



universität
wien

DIPLOMARBEIT

First-principles model study
of clathrates as thermoelectric materials

Elisabeth Durstberger

angestrebter akademischer Grad

Magistra der Naturwissenschaften (Mag.rer.nat)

Wien, März 2014

Studienkennzahl lt. Studienblatt: A 190 423 406

Studienrichtung lt. Studienblatt: Lehramtsstudium UF Chemie und Mathematik

Betreuer: Ao Univ.-Prof. Dr. Raimund Podlucky

Man muss das Unmögliche versuchen,
um das Mögliche zu erreichen.

Hermann Hesse

Abstract

Thermoelectrical materials are of special technological and ecological interest because their ability to convert waste heat directly into electric power. There are large efforts to optimize the thermoelectric properties in terms of the figure-of-merit for existing materials and to search for new promising materials. A class of such materials are the so-called clathrates, for which experimental as well as theoretical investigations are made in order to fabricate new compounds and/or to increase the figure of merit by finding a proper combinations of elements.

In the last decade, methods based on density functional theory (DFT) became very powerful tools for theoretically predicting materials properties and analyzing them by describing the bonding and related properties based purely on the solution of Schrödinger's equation without the need of any empirical parameters. The goal and perspective of the present work is now to apply the DFT package VASP (Vienna Ab initio Simulation Package [21]) for studying the electronic and binding properties of relevant clathrate model systems consisting of the group 3A, elements Al, Ga, In, the group 4A elements Si, Ge, Sn and the group 5A elements P, As, Sb. Their ground state crystal structure as well as the X_{46} clathrate structure is studied. For Ge also the Ge_{34} clathrate structure is investigated.

The important property for a thermoelectric material is, that the Fermi energy falls into or close to a gap, because then the so-called Seebeck coefficient, which relates the temperature gradient to the gradient of the electric field, may become large favouring a large figure-of-merit. For the bare clathrate backbones of group 4A elements X_{46} ($X=Si, Ge, In$) with their 4 valence electrons this is indeed the case. For the other groups elements having either one valence electron less (group 3A) or one more (group 5A) the Fermi energy is either below or above the characteristic gap of this clathrate structure.

Finally, an artificial compound $Ba_8In_{16}Ge_{30}$ is designed, which turns out to have the correct properties for a thermoelectric material: Ba atoms are inserted into the large voids of the clathrate structure, which should act as so-called filler atoms reducing the thermal transport. Because Ba adds 16

electrons to the valence electrons of the clathrate backbone 16 Ge atoms of the Ge_{46} backbone are replaced by 16 In atoms of group 3A, which in total gives the same number of valence electrons as Ge_{46} , which has a gap at the Fermi energy. By analysing the electronic properties of structures we can design new materials for thermoelectric applications and so the results of such first principle model studies are very important.

Zusammenfassung

Thermoelektrische Materialien sind von besonderem technologischen und ökologischen Interesse, weil sie Wärme direkt in Strom umwandeln. Es gibt viele Studien, um sowohl die thermoelektrischen Eigenschaften (Figure-of-Merit) für vorhandene Materialien zu optimieren als auch nach neuen viel versprechenden Materialien zu suchen. In diesem Zusammenhang ist eine Materialklasse, die sogenannten Clathrate, von großer Bedeutung.

Durch theoretische und experimentelle Studien versucht man neue Zusammensetzungen von Elementen zu finden, aber auch durch Optimierung von Elementkombinationen die Figure of Merit zu erhöhen.

Methoden basierend auf der Dichtefunktionaltheorie wurden in den letzten 10 Jahren immer wichtiger, um Eigenschaften von Verbindungen vorherzusagen oder sie zu analysieren. Die Analyse erfolgt durch Beschreibung der Bindungen und Lösen der Schrödinger Gleichung ohne Zuhilfenahme von empirischen Parametern. Das Ziel der vorliegenden Arbeit ist den Pseudo-Potentialcode VASP (Vienna-Ab-Initio-Simulation-Package) auf Clathrate anzuwenden, um sowohl die elektronischen Eigenschaften als auch die Bindungseigenschaften zu studieren. Die dafür herangezogenen Clathrate bestehen aus Elementen der 3. Hauptgruppe (Al, Ga, In), der 4. Hauptgruppe (Si, Ge, Sn) und der 5. Hauptgruppe (P, As, Sb). Die Grundzustandsstruktur aber auch die Clathratstruktur X_{46} wird diskutiert. Für Ge wird auch die Typ II Clathratstruktur Ge_{34} untersucht.

Eine Verbindung ist erst dann als thermoelektrisches Material interessant, wenn die Fermienergie in einer Bandlücke oder sehr nahe bei einer Bandlücke liegt. Das hat dann zur Folge, dass der Seebeckkoeffizient S sehr groß wird und somit auch die Figure of Merit, da hier S quadratisch eingeht. Bei den Clathratstrukturen der Elemente der 4. Hauptgruppe X_{46} ($X=Si, Ge, In$) mit 4 Valenzelektronen liegt die Fermienergie direkt in einer Bandlücke. Für die Elemente der 3. Hauptgruppe, die ein Valenzelektron weniger haben, liegt die Fermienergie unter der charakteristischen Bandlücke. Bei Elementen der 5. Hauptgruppe mit einem Valenzelektron mehr liegt sie darüber.

Den Abschluss der Arbeit bildet die konstruierte Verbindung $Ba_8In_{16}Ge_{30}$,

die die Eigenschaften für ein thermoelektrisches Material erfüllt. Ba-Atome, als sogenannte Füller-Atome bezeichnet, werden in die Lücken der Clathratstruktur eingebaut, um die thermische Leitfähigkeit zu reduzieren. Ba steuert 16 Elektronen zur Gesamtzahl der Valenzelektronen der ursprünglichen Clathratstruktur bei, somit müssen 16 Elektronen der Ge_{46} -Struktur durch 16 In-Atome (3. Hauptgruppe) ersetzt werden. Schlussendlich bleibt die Anzahl der Valenzelektronen gleich wie bei der Ge_{46} -Clathratstruktur, bei der die Fermienergie in einer Bandlücke zu liegen kommt. Durch Grundzustandsuntersuchungen werden die elektronischen Strukturen untersucht und es ist möglich neue thermoelektrische Materialien zu entwickeln.

Contents

1	Introduction and Motivation	12
2	Thermoelectricity	15
2.1	Seebeck effect	15
2.2	Figure-of-merit	16
2.3	Peltier effect	17
2.4	Thomson effect	18
2.5	Kelvin Relations	18
3	Theoretical background and computational aspects	19
3.1	DFT	19
3.1.1	Local Density Approximation	21
3.1.2	Generalized Gradient Approximation	22
3.2	VASP	22
4	Results and Discussion	24
4.1	DFT output	24
4.1.1	Total energy	24
4.1.2	Density of States	25
4.2	Clathrates	26
4.3	Aluminium	30
4.3.1	Aluminium (Al)	30
4.3.2	DFT results	31
4.4	Gallium	32
4.4.1	Gallium (Ga)	32

Contents

4.4.2	DFT results	33
4.5	Indium	35
4.5.1	Indium (In)	35
4.5.2	DFT results	35
4.6	Silicon	37
4.6.1	Silicon (Si)	37
4.6.2	DFT results	38
4.7	Germanium	40
4.7.1	Germanium (Ge)	40
4.7.2	DFT results	41
4.8	Tin	45
4.8.1	Tin (Sn)	45
4.8.2	DFT results	45
4.9	Phosphorus	47
4.9.1	Phosphorus (P)	47
4.9.2	DFT results	48
4.10	Arsenic	50
4.10.1	Arsenic (As)	50
4.10.2	DFT results	51
4.11	Antimony	53
4.11.1	Antimony (Sb)	53
4.11.2	DFT results	54
4.12	Clathrate $\text{Ba}_8\text{In}_{16}\text{Ge}_{30}$	56
4.12.1	General remarks	56
4.12.2	DFT results	57
5	Summary	60
6	Appendix	62
6.1	INCAR-file	62
6.2	POSCAR-file	63
	Bibiliography	64

List of Figures

2.1	Thermocouple	16
4.1	Structural units of type-I clathrates	28
4.2	Structure of type I clathrates	28
4.3	Structure of type II clathrates	29
4.4	Total and local partial density of states for clathrate type I Al ₄₆	32
4.5	Density of states per atom of Al in the fcc structure.	32
4.6	Total and local partial density of states clathrate type I Ga ₄₆	34
4.7	Total and local partial density of states per atom of Ga in the orthorhombic ground state structure.	34
4.8	Total and local partial density of states for clathrate type I In ₄₆	36
4.9	Total and local partial density of states per atom of In in its ground state tetragonal structure	37
4.10	Total and local partial density of states for clathrate type I Si ₄₆	39
4.11	Total and local partial density of states per atom of Si in the diamond structure	40
4.12	Total and local partial density of states clathrate type I Ge ₄₆	42
4.13	Total and local partial density of states for clathrate type II Ge ₃₄	43
4.14	Total and local partial density of states per atom of Ge in the diamond structure	44
4.15	Total and local partial density of states for clathrate type I Sn ₄₆	46
4.16	Density of states of Sn in the cubic diamond structure	47
4.17	Total and local partial density of states for clathrate type I P ₄₆	49

List of Figures

4.18	Total and local partial density of states per atom of P in the bcc structure	49
4.19	Total and local partial density of states for clathrate type I As_{46}	52
4.20	Total and local partial density of states of per atom arsenic in the triclinic ground state structure	52
4.21	Total and local partial density of states for clathrate type I $\text{Sb}_{46}a$	54
4.22	Total and local partial density of states per atom of Sb in the hexagonal rhomboedric ground state structure	55
4.23	Density of states of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$	58
4.24	Total DOSes for the compound $\text{Ba}_8\text{In}_{16}\text{Ge}_{30}$ in comparison to DOSes for the separated sublattices.	59

Introduction and Motivation

Thermoelectric materials are of particular interest for technological and ecological issues. The effect of thermoelectricity consists of producing electric energy directly by a temperature gradient in a material. No mechanical generators or transport of gas (e.g. steam) is needed for generating the electric energy.

In the early 19th century Thomas Seebeck and Jean Peltier, discovered thermoelectric phenomena. Seebeck first found that if a temperature gradient is created across the junctions of two suitable conductors, electrical current flows. Peltier then discovered that passing current through two suitable electrical conductors, causes heat to be either emitted or absorbed at the junction of the materials. However, it was only after the mid of the 20th century due to advancements in semiconductor technology, that practical applications for thermoelectric devices became possible. Modern techniques allow the production of thermoelectric modules efficiently working as solid state heat pumps for both cooling and heating. Because of environmental reasons (i.e. electric energy can be produced from waste gases) thermoelectric generators are very much in demand nowadays, in particular in the car industry.

The efficiency of the thermoelectric effect depends very strongly on the physical properties of the materials in contact. Therefore this topic is of great interest in materials sciences in which first-principles calculations based on density functional theory become more and more important. Without the need of empirical parameters materials properties can be predicted in a reliable way, provided the systems under study can be modelled by single crystals.

The basic motivation of this work is to calculate the electronic properties of model systems (clathrates) by using a density function theory concept. The efficiency of thermoelectric devices is determined by the dimensionless figure-of-merit ZT [1].

$$ZT = \frac{T\sigma S^2}{\kappa} \quad (1.1)$$

where T is the temperature, S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. The higher ZT the better the material is suited for thermoelectrical applications. According to equation (1.1) the thermoelectric performance of a material depends on the Seebeck coefficient S to the squared, the electric conductivity σ and the thermal conductivity κ . The coefficients S and σ are both transport properties of electrons, whereas κ is usually decomposed as $\kappa = \kappa_{el} + \kappa_{ph}$ referring to the electronic and phononic contributions.

Basically, there are two concepts for increasing ZT , namely a large Seebeck coefficient S and a large electrical conductivity σ . Increasing S is more important because it enters the figure-of-merit as S^2 . A large σ is much less desirable because it is detrimental for the Seebeck coefficient and also it is usually coupled to a large κ_{el} thereby enlarging the total κ and reducing ZT . A second strategy is to reduce κ by influencing the vibrational properties in a suitable way. For clathrate, an obvious choice would be to fill in loosely bound atoms in the large voids of the crystal structure. These atoms are called "rattlers". This aspect is not considered in this work where we focus on the electronic structure.

The first-principles calculation delivers the total energy of a system with given distribution of atoms as well as the electronic spectrum, i.e. the eigenvalues of the Schrödinger equation or Schrödinger-like equation as it occurs in the Kohn-Sham formulation of density functional theory. The electronic spectrum of a solid is often represented by the density of states showing the number of states within an (infinitely) small energy interval. These two theoretical properties, the total energy and the density of states (DOS), are the main objects of this work.

A simple approximation for a free electron gas at low temperatures the Mott

relation for the Seebeck coefficient is

$$S = -\frac{\pi^2 k_B^2 T}{3 |e|} \left\{ \frac{1}{N(E)} \frac{dN(E)}{dE} \right\}_{E=\mu} \quad (1.2)$$

There, S and the density of states $N(E = \mu)$ enter, in which N is taken for the Fermi energy E_F at $T = 0$ or for the corresponding chemical potential of the electrons at $T > 0$. Even at larger T 's μ does not differ significantly from E_F . The formulation of S in a rigorous manner involves more complicated quantities of the electronic structure, as discussed later on.

Maximizing the Seebeck coefficient needs a large first derivative of the DOS and a small value of the DOS at the Fermi level. This can be achieved by placing E_F close to a band gap, at which $N(E_F)$ is obviously small but the DOS rises strongly (i.e. the derivative is large). Because of this reason doped semiconductors are considered to be ideal. Other systems with a gap, however, might be similarly suited with respect to the DOS but might offer additional optimization features. This may be the case for clathrates, because they offer a gap and the filling in of "rattlers". The main aspect of this work is to study the electronic features in terms of the DOS of typical backbones of a clathrate compound in order to understand the formation of the gap and how it is preserved by doping.

Thermoelectricity

There are several effects which are attributed to thermoelectricity. In the Seebeck effect a temperature difference leads to an electric current. The reverse effect is called Peltier effect: a voltage difference is applied over a thermocouple so that electric current is running through and heat flow occurs across the thermocouple. The connection between these two effects was later discovered by Thomson, Lord Kelvin, 1851: the Thomson effect describes the heating or cooling of a conductor having both a current and a temperature gradient [1] [2].

2.1 Seebeck effect

Thomas Seebeck found this effect in 1821 when he noticed that a compass needle was deflected by a metal to which a temperature difference is applied. He had two metal rods which were connected at both ends. If the contacts had different temperatures, a magnetic field was created. The effect occurs when a temperature gradient is applied over a thermocouple and by that generates a voltage difference. Such a device acts as an electric generator where the voltage difference leads to a charge flow of electrons.

The thermoelectric efficiency of a material is quantified by the figure-of-merit ZT ,

$$ZT = \frac{T\sigma S^2}{\kappa}. \quad (2.1)$$

which contains the three physical quantities,

- Seebeck coefficient (S)

2.2. Figure-of-merit

- electrical conductivity (σ)
- thermal conductivity (κ)

The Seebeck coefficient contains information on how many volts per degree temperature difference are generated. The electrical conductivity determines how well a material conducts electricity, and the thermal conductivity is a measure of how well heat is conducted. The first two quantities need to be as large as possible, while the last one needs to be small for maximizing ZT . The problem, which is intrinsic to the material, is that all three quantities are related, and cannot be optimised independently.

Fig. 2.1 shows a typical thermocouple. It consists of two dissimilar conductors 1 and 2 which are connected to each other at points a and b . If the junction points a and b are maintained at different temperatures T_1 and T_2 and $T_1 > T_2$ an electromotive force is developed between c and d [1].

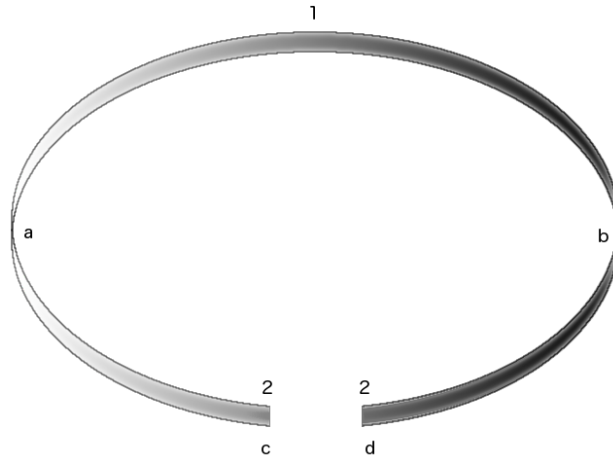


Figure 2.1: Illustration of a typical thermocouple

2.2 Figure-of-merit

The conversion efficiency ZT of thermoelectric materials is defined by the dimensionless thermoelectric figure-of-merit,

2.3. Peltier effect

$$ZT = \frac{T\sigma S^2}{\kappa} \quad (2.2)$$

with S the Seebeck coefficient, T the temperature, κ the thermal conductivity and σ the electrical conductivity.

The thermal conductivity has two contributing parts, the heat transport by electrons (κ_e) and the heat transport by lattice vibrations (κ_l). For a rough estimate for simple metals the thermal conductivity of electrons is related to the electrical conductivity (σ) by the Wiedemann-Franz law,

$$\kappa_e = L\sigma T \quad (2.3)$$

with the Lorenz number L . Increasing the electrical conductivity results in increased electrical thermal conductivity [3] [4]. With increasing charge carrier concentration it follows that the electronic part of thermal conductivity κ_e is increasing. This leads to an increasing thermal conductivity (κ). But when the electrical conductivity σ is increasing the Seebeck coefficient S is decreasing. Since increased thermal conductivity lowers the figure-of-merit while the electrical conductivity increases it, a balance between the properties has to be found while optimising the figure-of-merit [1] [4]. A large conductivity is the typical material quality for a metal, a large Seebeck coefficient indicates more a semiconductor-like material. Therefore, a compromise is necessary for optimising the thermoelectrical performance. The best thermoelectrical materials are consequently weakly degenerated semiconductors with a great band gap. Until now the best figure of merits are typically around the value of 1 for the best materials [4].

2.3 Peltier effect

In 1834 Jean Peltier discovered that a temperature difference induces a voltage gradient. The Peltier effect is the inverse phenomenon of the Seebeck effect. It occurs when an external electric power is applied on the thermocouple and heat is pumped from one side to another. This is the effect used

2.4. Thomson effect

for refrigeration. The Peltier coefficient π describes the correlation between the heat rate q transported over the thermocouple and the applied current I [1]

$$\pi = \frac{q}{I} \quad (2.4)$$

An interesting point on the Peltier effect is that the direction of heat transfer is controlled by the polarity of the electric current. Reversing the polarity of current will change the direction of heat transfer.

2.4 Thomson effect

The Thomson effect was observed in 1851 by William Thomson, 1st Baron Kelvin. It deals with the effect that all current-carrying conductors, except for superconductors, with a temperature difference between two points either absorb or emit heat. The Thomson effect is described by the equation [1]

$$q = \beta I \Delta T \quad (2.5)$$

in which β is the Thomson coefficient, q the heat per unit area, I the flow of current flow and ΔT the temperature gradient.

2.5 Kelvin Relations

The three thermoelectric effects are connected by the Kelvin relations. Irreversible thermodynamics is used to deduce this connection. Many thermoelectric materials have been tested and so it is assumed that these relations are true for all. The Kelvin relations are given by

$$S_{ab} = \frac{\pi_{ab}}{T} \quad (2.6)$$

in which S_{ab} is the Seebeck coefficient of the thermocouple, T the temperature and π_{ab} the Peltier coefficient of the thermocouple.

Theoretical background and computational aspects

3.1 Density Functional Theory

At present, the density functional theory (DFT) is the most successful approach to compute the electronic structure of solid matter from first-principles: no empirical parameters are needed for solving the Schrödinger equation of the interacting electronic system. In its original formulation, DFT provides the ground state properties of a system and in particular the total energy. The key quantity is the ground state total energy as a functional of the ground state electron density. DFT computational codes are used for investigating the structural, magnetic and electronic properties of molecules, materials and defects.

The goal of most approaches in solid state physics and quantum chemistry is the solution of the time-independent, non-relativistic Schrödinger equation. In its non-relativistic form it is an eigenvalue equation of the form

$$\hat{H}\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) = E_i\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) \quad (3.1)$$

There $\hat{H}$ is the Hamiltonian operator for a system with M nuclei and N electrons, with their respective coordinates $\mathbf{r}_i$ and $\mathbf{R}_j$, Ψ_i is the wave function of the system, i.e. the eigenfunction of state i to the energy eigenvalue E_i . The lowest energy eigenvalue E_0 denotes the ground state energy of the system. When the Born-Oppenheimer approximation is assumed – which usually is – then the electronic and the nuclear motion can be separated. The original

3.1. DFT

formulation of DFT searching for the ground state total energy by Hohenberg and Kohn [6] was modified by Kohn and Sham [7] one year later. This reformulation introduces a fictitious non-interacting system of quasiparticles, and the key-role of the respective orbitals is to build up correctly the true ground state density. In the Hamiltonian the respective potentials are functional derivatives of energy functionals, which appear already in the original DFT of Hohenberg and Kohn.

To determine the electronic density, N electronic Kohn-Sham orbitals φ_i , which are solutions of the Kohn-Sham equations, have to be calculated self-consistently via the Kohn-Sham equation,

$$\left(-\frac{\nabla^2}{2} + v_{\text{eff}}\right)\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}) \quad (3.2)$$

In this equation v_{eff} represents the effective potential, and ε_i the eigenvalues corresponding to the state i with orbital φ_i .

The ground state density is constructed by

$$\rho(\mathbf{r}) = \sum_1^N |\varphi_i(\mathbf{r})|^2 \quad (3.3)$$

summing over all N occupied states. The effective potential depends on the density

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + v_{\text{XC}}(\mathbf{r}) \quad (3.4)$$

The first term v_{ext} is the external potential which describes the attraction of the electrons by the atomic nuclei. The second term describes the electrostatic Coulomb interaction of the electron density with itself. The third term, the so-called exchange correlation potential contains all information on the quantum interactions, which are not described by the first terms. Such a typical interaction would be the exchange interaction, which provides the Pauli principle of Fermi-Dirac particles.

The effective potential as an input of the Kohn-Sham equations depends on the density which is constructed by the output of the Kohn-Sham equations, the orbitals φ_i . Thus the Kohn-Sham equations have to be solved iteratively in

a selfconsistent manner. Up to now, the Kohn-Sham equations provide exact solutions of the many-body Schrödinger equation in terms of the ground state density and the ground state total energy.

The fundamental problem for actual calculations is that the function form of $v_{\text{exc}}[n]$ is not known for a real system. Here approximations have to be introduced. The most common approximations of v_{exc} are based on the interacting homogenous electron gas, which works astonishingly well having in mind that the electron density of a real system does not look like the density of a homogenous electron gas, which would be constant. The concept of these approximations is that at each point in space r the value of the full ground state density is taken and for that value the exchange correlation energy and – potential is derived within the homogenous electron gas assumption. Because of this local concept these approximations are called local approximations. There are basically two forms of them with a variety of parametrisations.

3.1.1 Local Density Approximation

In the local density approximation (LDA), the exchange-correlation energy of an electronic system is constructed by assuming that the exchange-correlation energy per electron at a point in the electron gas, is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same electron density at the point. Within LDA, the exchange-correlation energy is given by [7]

$$E_{\text{xc}}^{\text{LDA}}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{\text{xc}}^{\text{LDA}}[\rho(\mathbf{r})] \quad (3.5)$$

where $\epsilon_{\text{xc}}^{\text{LDA}}$ is the exchange-correlation energy per electron for a homogeneous gas of interacting electrons. Although this approximation is extremely simple, it is surprisingly accurate and very fast in the calculation. It becomes worse and fails badly when the deviations of the real density from a constant density increase, which occurs for localized states such as 3d-states of transition elements. For such systems LDA tends to overestimate the bonding

3.2. VASP

leading to too small equilibrium volume and too large formation/cohesion energies. For these reasons the addition of corrections due to the gradient of the density have been suggested, which gives information about the local change of the density as well as of the density itself [16]. Such approximations are called semi-local.

3.1.2 Generalized Gradient Approximation

The generalized gradient approximation (GGA) was already proposed by Kohn and Sham in their original paper [7] and advanced by Herman et al [8]. The exchange correlation energy is

$$E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int d^3r \rho(\mathbf{r}) \epsilon_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|) \quad (3.6)$$

For GGA there exist a variety of parametrizations. One of them is described in the work of of Perdew, Burke and Ernzerhof (PBE) [9], which will be used for the calculations in this diploma thesis. Most of the overbinding effects occuring for 3d-metals and related compounds can be cured.

3.2 VASP

For the actual DFT calculations of a periodic solid system the Vienna Ab initio Simulation Package of G. Kresse [10–13] and his group is used. This DFT package is one of the most applied DFT codes around the world. It is a so-called pseudopotential method, in which the atoms are replaced by pseudoatoms in such a way, that the shape of the wave functions in the bonding region is described properly. Plane-waves are taken for describing the valence state wavefunctions, which makes the pseudopotential method a very powerful computational method. It is important that the pseudopotentials of the pseudoatoms are modelled within the projector augmented wave concept [22] in order to be able to treat also localised states and charge transfer systems. The output of VASP is – apart from many postprocessing data – the full glory of a total energy electronic structure method. The most basic

3.2. VASP

ones are used in the present diploma work.

Results and Discussion

4.1 DFT output

4.1.1 Total energy

The total energy of the ground state is calculated within the Kohn-Sham formulation equation (3.2) of the original DFT. This is done for a given distribution of atoms. The geometry, i.e., cell shape and atomic position, can be optimized by minimizing the atomic forces as well as the volume. Therefore, all results in the work refer to optimised geometry parameters, which makes theory independent from any empirical geometry input. The total energy of the electronic system is calculated according to

$$E_{\text{tot,el}} = \sum_i^N \varepsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} + E_{\text{xc}}[\rho] - \int v_{\text{xc}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (4.1)$$

summing over all N occupied states, correcting for the double counting of the Coulomb interaction, adding the exchange-correlation energy functional E_{xc} and finally subtracting the corresponding expression involving the exchange-correlation potential $v_{\text{xc}} = \delta E / \delta \rho$, which is the functional derivative of E_{xc} . For periodic boundary conditions the sum $\sum_i$ is replaced by the sum $\sum_{\mathbf{k},\nu}$ involving a vector of the first Brillouin zone $\mathbf{k}$ and the band index ν . So far the total energy of the electronic system has been derived. For the total energy of electrons and nuclei the Coulomb repulsion of the nuclei α with

4.1. DFT output

charges Z_α has to be added according to

$$E_{\text{tot}} = E_{\text{tot,el}} + \sum_{\alpha > \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \quad (4.2)$$

E_{tot} is now minimised for each geometry of nuclei according to the construction of the Kohn-Sham equation. Furthermore, E_{tot} can also be minimised with respect to the atomic distribution (i.e., positions and cell volumes) which includes the minimisation of forces acting on the atoms.

4.1.2 Density of States

The density of states describes the energy distribution of the Kohn-Sham equations according to relation (3.2). The distribution of energy levels around Fermi energy is of interest, which is expressed by the density of states (DOS) $n(E)$. The definition is straightforward: number of levels with precisely the energy E ,

$$n(E) = \sum_{i,\mathbf{k}} \delta(\varepsilon_{i,\mathbf{k}} - E) \quad (4.3)$$

We sum over all states labelled by the quantum numbers $i, \mathbf{k}$ according to the periodic boundary conditions. The δ -like function gives 1 if the argument is zero (i.e., $\varepsilon_{i,\mathbf{k}} = E$) and 0 otherwise. If we use a continuous $\mathbf{k}$ -space, then the $\mathbf{k}$ -sum is transformed into an integral,

$$n(E) = \frac{1}{\Omega_B} \sum_i \int d^3\mathbf{k} \delta(\varepsilon_{i,\mathbf{k}} - E) \quad (4.4)$$

Now, $\delta(\arg)$ is the true distribution "function": 0 if $\arg \neq 0$ and ∞ for $\arg = 0$. It is defined via the mathematical definition, $f(x_0) = \int_{-\infty}^{+\infty} f(x) \delta(x - x_0) dx$. The normalization volume Ω_B is the volume of the first Brillouin zone defined by the inverse of the volume of the unit cell Ω ,

$$\Omega_B = \frac{(2\pi)^3}{\Omega} \quad (4.5)$$

[14]

For analysing the DOS quite often the concept of the so-called local DOS is used: to each atom a sphere with a given radius is attributed and the local DOS is then derived by integrating over the atomic sphere. In this way the total DOS can be split into contributions originating from each atom. Furthermore, inside the atomic spheres all quantities such as the local DOS can be expanded into spherical harmonics thereby labelling the contributions with l-quantum number referring then to an s-, p- or d-like character. These DOS contributions are called partial DOSes. The local partial DOSes are helpful for understanding the atomic characteristics of states. The radii used are contained in the POSCAR of each atom as used by VASP. A typical POSCAR-file is given in the appendix.

For summing over occupied states the DOS has to be multiplied with the Fermi-Dirac distribution function

$$f(\varepsilon, T, \mu) = \frac{1}{e^{\frac{\varepsilon - \mu}{kT}} + 1} \quad (4.6)$$

The chemical potential μ at $T = 0$ corresponds to the Fermi energy E_F , which is then the energy of the highest occupied state. For semiconductors at finite temperatures the chemical potential must be in the gap in order to derive the correct number of occupied states.

4.2 Clathrates

Clathrates are typically (host) structures that contain voids which might be filled with guest atoms or even molecules. The first clathrate system was found in 1811 by Davy [17] and it was a hydrated clathrate system constructed of chlorine and water molecules. In 1935 Pauling clarified the atomic structure of these systems by X-ray diffraction. Also for elements of the semiconducting group 14 a clathrate structure was discovered.

There are two major groups of clathrates: type-I and type-II. Each type has a cubic unit cell, but the difference is that a) the point group symmetries are different and b) the number and size of the voids in the structure vary. Most of them are semiconductors with band gaps in their electronic structure.

4.2. Clathrates

Because of all these properties clathrates are promising candidates for thermoelectric materials. Nevertheless, it took quite some time until this point was noticed: in 1998 Nolas et al. [18] proposed clathrates as potential thermoelectric materials, and ever since many research groups got interested in detecting the best thermoelectric material. The aim of this work is to understand the electronic properties of some clathrate frameworks (i.e., filler-free) and in particular the placement of the Fermi energy and the occurrence of a band gap. This is important for the optimisation of the Seebeck coefficients, which is the most important contribution to the figure-of-merit.

Silicon and Germanium have often been studied and for these structures it was found in this work that the electronic gap in the clathrate structure is substantial larger than in the diamond ground state structure. Further related elemental systems will be studied, and finally the filled system $\text{Ba}_8\text{In}_{16}\text{Ge}_{30}$ is investigated.

Type I clathrates X_{46} have a simple cubic lattice with 46 atoms per unit cell and belong to the space group $\text{Pm}\bar{3}\text{n}$. Type II clathrates X_{34} are based on a face-centered cubic lattice with 34 atoms in the primitive cell (or 136 atoms in the conventional cell) and belong to the space group $\text{Fd}\bar{3}\text{m}$. The coordinates for both clathrate types can be seen in table 4.1. The atoms in both clathrates are covalently bonded and form two different cage-like units. Type I clathrates (Fig. 4.2) form two pentagonal dodecahedra (20 atom-cages with 12 pentagons) and six tetrakaidecahedra (24 atom-cages with 12 pentagons and 2 hexagons), of which the centers are on 2a and 6d Wyckoff sites. The dodecahedra and the tetrakaidecahedra can be seen in Fig. 4.1. In the type-II clathrate structure (Fig. 4.3), there are also two types of cages, eight pentagonal dodecahedra and sixteen hexakaidecahedra (12 pentagons and 4 hexagons) in the conventional unit cell, of which the centers are on 8b and 16c Wyckoff sites.

4.2. Clathrates

Wyckoff positions	
type-I	type-II
6d	8a
16i	32e
24k	96g

Table 4.1: Structural parameters of type-I and type-II clathrates

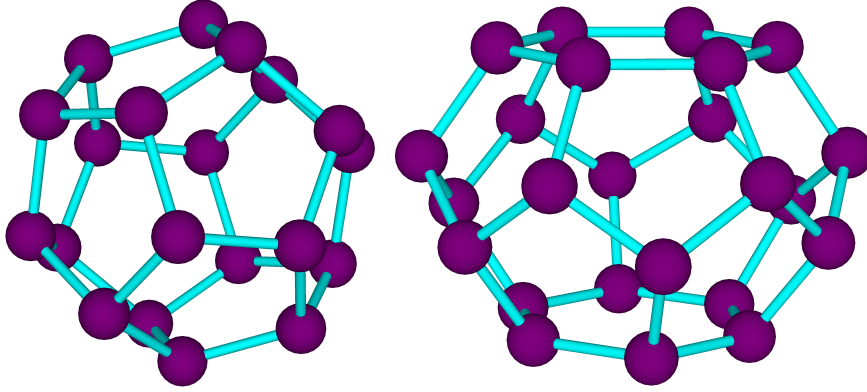


Figure 4.1: Structural units of type-I clathrates

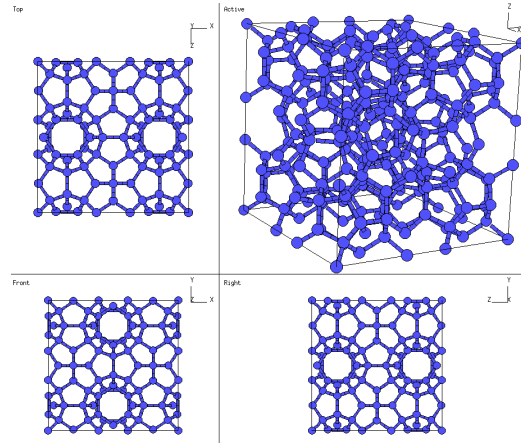


Figure 4.2: Structure of type I clathrates [19]

4.2. Clathrates

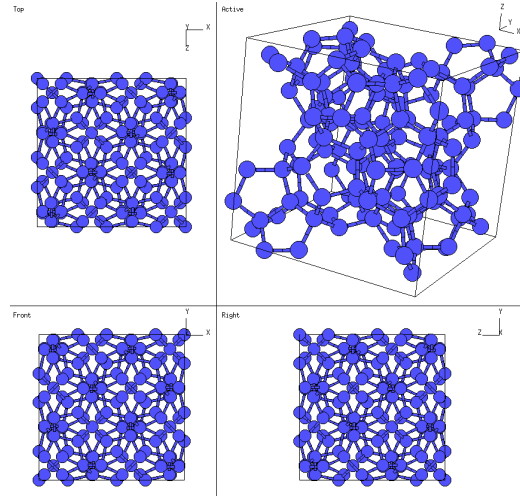


Figure 4.3: Structure of type II clathrates [20]

In the following a short overview of the elemental solids is given before the clathrate structures are discussed. Then type I clathrate structures (for Ge also type II clathrate structure), their ground state structure, their lattice parameters and their total energies per atom are given and the corresponding DOS are shown.

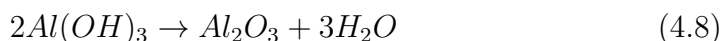
4.3 Aluminium

4.3.1 The element

Aluminum (Al) [26] is part of the 3rd main group, the boron group, in the periodic system. It is the third most frequent element in nature but because of its great oxygen affinity it only occurs in terms of oxidic compounds. One finds it predominantly as Al_2O_3 , which is known as Korund, and the hydride $\text{Al}(\text{OH})_3$. The technical representation of Al is made by electrolysis of aluminium in melted Kryolith. The mixture of aluminium oxide and aluminium hydroxide is melted and then $\text{Al}(\text{OH})_3$ is precipitated by sodium hydroxide solution (Bayer method).



Afterwards one filters $\text{Al}(\text{OH})_3$ and changes it to aluminium oxide which happens in trick tube furnaces or whirl layer stoves.



Then a glass river electrolysis (Hall-Heroult-process) is carried out. Because the melting point of aluminiumoxide is very high (2045°C) electrolysis of a mixture of aluminiumoxide and Kryolith (Na_3AlF_6) is performed.



Al is a silvery white light metal with a density of 2.699 g/cm^3 . It crystallizes in the cubic, thick packet, melts at 660.4°C and boils at 2330°C . Because it is very flexible, one can produce 0.004mm thin foils. Al has the tendency to oxidize itself to the trivalent Al and therefore it reacts with almost all nonmetals. Despite the affinity for oxygen, pure Al is stable at the air because it is covered with a firmly inherent oxide film. Al is dissolved by not oxidizing acids under hydrogen development. Elementary aluminum is one of the most important non-ferrous metals because of its outstanding qualities (low weight,

4.3. Aluminium

nonpoisonous, thermally and electrically well conducting, corrosion-resistant, not magnetic). It is therefore widely used in many different areas, such as extraction of metals according to the Thermit method, rust protection, production of bars and flagstones and much more.

4.3.2 DFT results

Al in the fcc ground state is a well-known metal with rather free-electron behaviour of the electronic structure. Clearly, the Fermi energy falls into a rather high value of the DOS as seen in figure 4.5. However, placing Al in the 46-atoms framework of the clathrate type I structure produces a DOS which is very similar to the DOSes of Si and Ge. On one hand Al_{46} is still metallic (see figure 4.4), because E_F falls into an energy region with a large DOS. The reason for that is that Al has 1 valence electron less than the semiconducting solids of Si and Ge. On the other hand, the typical clathrate type I gap still appears but now 1.5 eV above E_F . Energetically, the clathrate structure is much less stable by about 1 eV than the fcc ground state structure according to table 4.2.

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
Al_{46}	31.00	- 2.984	1.202
Al_{fcc}	15.82	- 4.186	0

Table 4.2: VASP results for the ground state and the clathrate structure of Al.

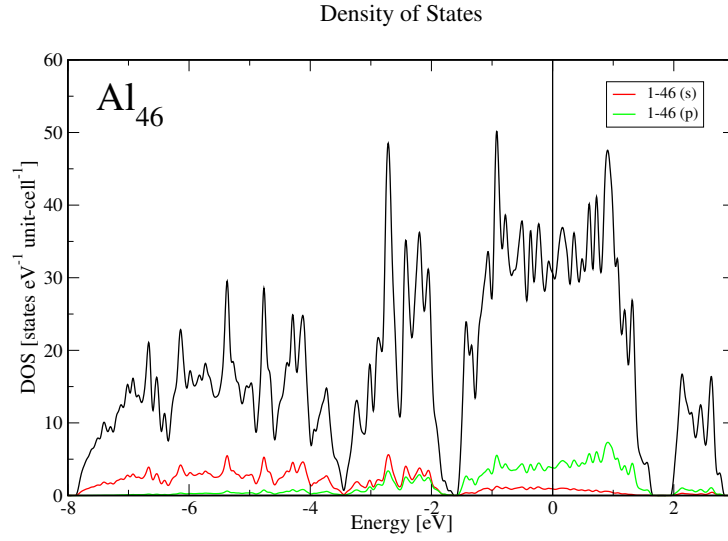


Figure 4.4: Total and local partial density of states for clathrate type I Al_{46}

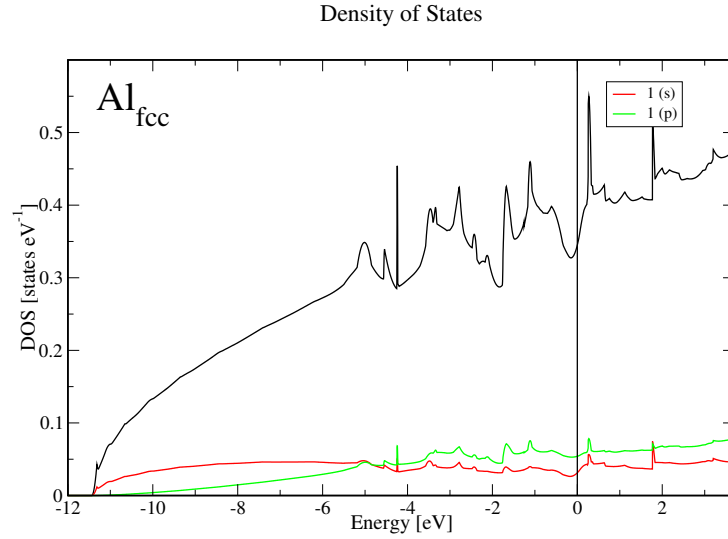


Figure 4.5: Density of states per atom of Al in the fcc structure.

4.4 Gallium

4.4.1 The element

Gallium (Ga) [26] is a rare metal, which was discovered in 1875. In the periodic table it is in the 4th period and the 3rd main (boron group). In

4.4. Gallium

nature Ga is found always connected to zinc (zinc blende), germanium (Germanit) or aluminum (Bauxite). The representation is carried out mainly as a by-product of the production of Zinc. Ultra-pure Ga for semiconductors can be produced by vacuum distillation, by anodic dissolving and cationic re-deposition or by the zone melting method.

Ga is a single silvery white, hard and brittle element, which melts just above the room temperature at 29.78°C and boils at 2403°C. It is counted as one of the semi-metals despite its high electrical conductivity.

At low pressure Ga has 4 possible modifications, namely α , β , γ und δ , and also 3 high pressure modifications. α -Ga crystallizes in the orthorhombic crystall structure and is the most stable modification.

β -Ga crystallizes in the monoklin, γ -Ga in the orthorhombic and δ -Ga in the rhomboedric crystall structure. Ga is stable at dry air and burns in pure oxygen and under high pressure with a bright flame. It dissolves in acids and bases. In water it is insoluble because of an indelible protective covering ($\text{Ga}(\text{OH})_3$). Ga is used predominantly in semiconductor technology. Different gallium compounds are also used, primarily gallium arsenide (GaAs) which is needed for solar cells and light-emitting diodes. Gallium is liquid in a very big temperature range and also because of its low steam pressure it is used for thermometers.

4.4.2 DFT results

Similar to In – as discussed later – Ga has 1 valence electron less than Ge and therefore E_F has been shifted to lower energy and falls into the p-like feature of the DOS as shown in figure 4.6. Interestingly, observing the DOS for the rather complex ground state structure E_F falls very close to a minimum of the DOS indicating electronic stabilisation of the structure. Table 4.3 indicates that the stability of Ga_{46} is also rather unfavourable being less stable by about 1 eV than the ground state structure.

4.4. Gallium

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
Ga_{46}	27.81	- 2.578	0.994
$\text{Ga}_{\text{orthorhombic}}$	18.39	- 3.572	0

Table 4.3: VASP results for the ground state and the clathrate structure type I of Ga.

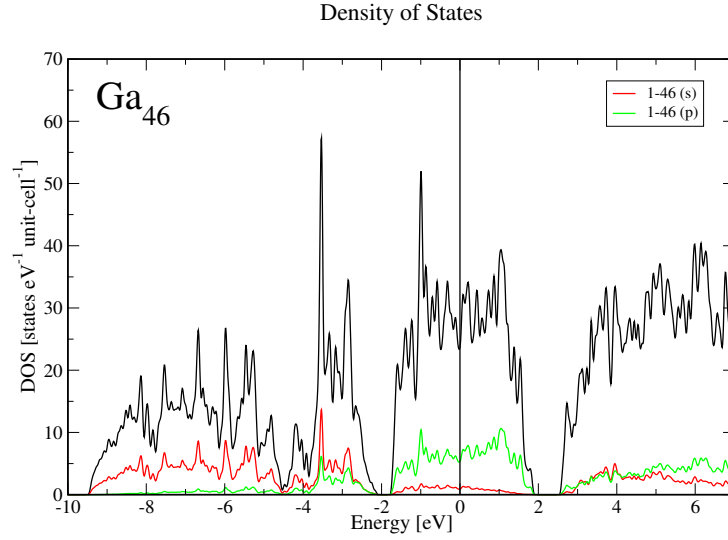


Figure 4.6: Total and local partial density of states clathrate type I Ga_{46}

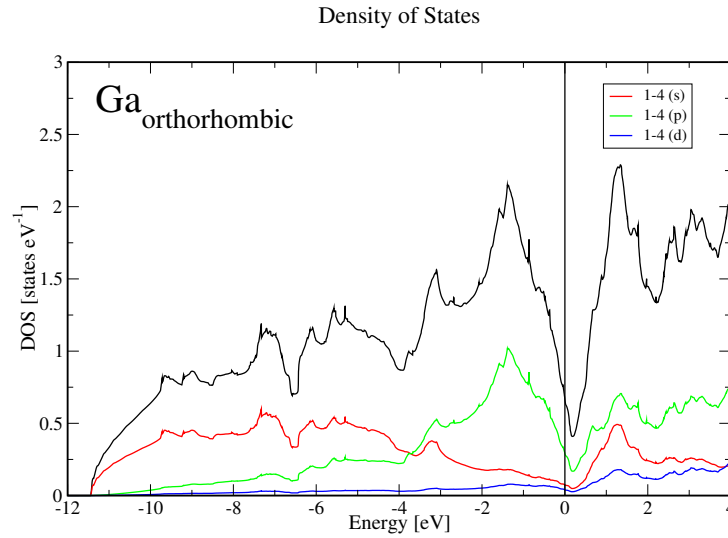


Figure 4.7: Total and local partial density of states per atom of Ga in the orthorhombic ground state structure.

4.5 Indium

4.5.1 The element

Indium (In) [26], which was discovered in 1863, is a very rare element whose share in the continental earth's crust is only 0.05 ppm. It is thus similarly frequent as silver and mercury. In is mainly found in zinc ores, particularly in the Sphalerit. It is won almost exclusively as a by-product at the production of zinc or lead. The production of pure In is carried out electrolytically. By zone melting or repeated electrolysis one gets purer In.

In is a silverly, white heavy metal with a low melting point of 156.1°C. The boiling-point is 2070°C and the density 7.31 g/cm³. The toxic metal has a high ductility and a low hardness. It is therefore possible to cut In like sodium with a knife. At regular conditions only one crystalline modification is known, which crystallizes in the tetragonal crystalsystem in the space group of I4/mmm.

In high pressure experiments a further modification was discovered which is stable above 45 GPa and crystallizes in the orthorhombic crystallization system (space group Dmmm). The chemical qualities resemble those of the group neighbours. In air it is stable at room temperature because of the oxide film which protects the metal from wider oxidation by passivation. At higher temperatures In deflagrates to Indium(III)-oxide In₂O₃. In is attacked by nitric acid or sulfuric acid and isn't soluble in hot water, bases and most organic acids. Although versatile, the use of In is limited due to rareness and high price.

4.5.2 DFT results

Compared to ground state Ge the ground state of In with its tetragonal structure is electronically different: In is a metal as can be seen in the DOS of the ground state structure in figure 4.9) because In has 1 valence electron less than Ge. Therefore, with respect to Ge the Fermi energy has to be shifted to lower energies and therefore for In₄₆ it falls into the p-like region

4.5. Indium

of the DOS below the gap as in figure 4.8, as discussed later for Ge. With respect to stability, the type I clathrate (and even more so for type II) is significantly less stable than the ground state structure by more than 0.8 eV per atom (see Table 4.4).

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
In_{46}	43.4	- 2.342	0.848
$\text{In}_{\text{tetragonal}}$	24.62	- 3.190	0

Table 4.4: VASP results for the ground state and the clathrate structure of In

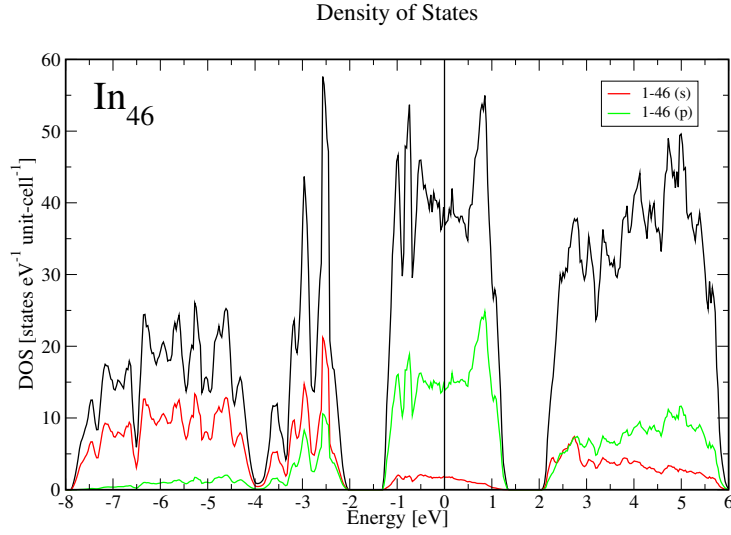


Figure 4.8: Total and local partial density of states for clathrate type I In_{46}

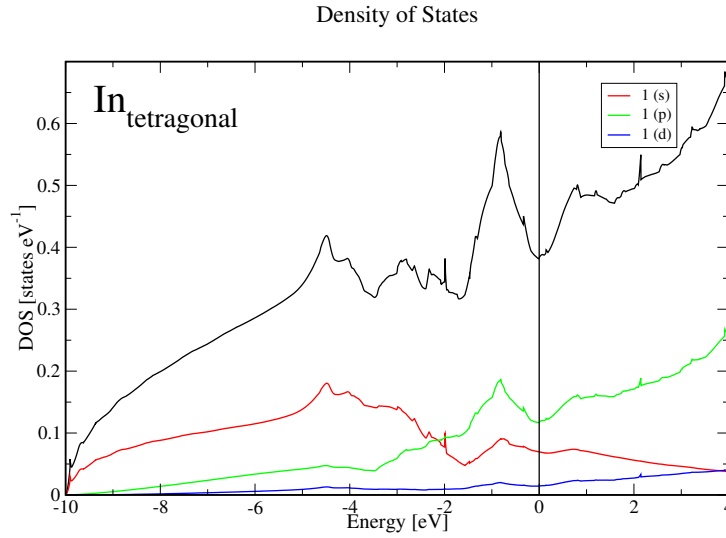


Figure 4.9: Total and local partial density of states per atom of In in its ground state tetragonal structure

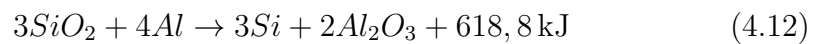
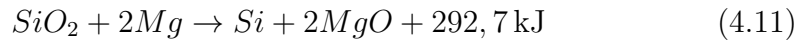
4.6 Silicon

4.6.1 The element

Silicon (Si) [26] is the most common element after oxygen and to be more precise, more than a quarter of the earth bark is from Si. Si is in the carbon group (4th main) and 3rd period of the periodic system. Because of its great oxygen affinity one never finds Si elementarily, only bound in the form of salts. Technically Si can be produced by reduction of quartz in compact pieces with coal at high temperatures (approx. 2000°C).



One uses Mg or Al as a reducing agent in the laboratory.

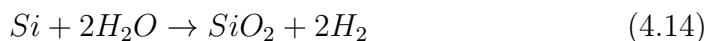


4.6. Silicon

Purest Si one can get by a thermal reduction of Silicochloroform HSiCl_3 with hydrogen at 1000°C or by pyrolysis of purest Silan SiH_4 . The pure crystallized Si (α -Si) forms dark gray, non-transparent, strongly shiny, hard brittle octahedra with a density of 2.328 g/cm^3 which melts at 1414°C and boils at 2477°C . The crystal structure is a cubic diamond lattice. There are also high pressure modifications of Si. Si converts into tetragonal β -Si above a pressure of 130 kbar. At decompression it changes into γ -Si, when heating up it turns either into α -Si or into a mega-stable cubic δ -Si with hexagonal diamond structure. In air Si burns under release of relatively much energy (911.6 kJ) into the dioxide.



In contact with water it also converts by an exothermic reaction to dioxide.



Si is despite of its strongly negative potential insoluble in nearly all acids. The reason for this is SiO_2 which prevents the attack of the acid. Technologically Si is used as an alloying component of cast alloys as well as a basic material for chemical compounds (silicones). The application fields for highly purified Si are permanently growing. For example it is used for electronics as a semiconductor element and in solar cells.

4.6.2 DFT results

For Si the diamond ground state structure and the clathrate type I structure Si_{46} were calculated. Its electronic properties are much less promising for thermoelectric applications as discussed for Ge. One expects that the features which have been discussed for Ge_{46} are very similar, as it is indeed the case, shown by figure 4.10. All the gaps are there and even the size of the main gap is comparable to Ge_{46} . The gap at about -4 eV , however, is much smaller due to the more localized 3s- and 3p orbitals of Si. This is also expressed by the equilibrium lattice parameters table 4.5 which is about 4% smaller than

4.6. Silicon

for Ge. However, according to table 4.5 Si_{46} is significantly less stable than Ge_{46} when compared to the respective ground states.

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
Si_{46}	23.15	- 5.362	0.482
$\text{Si}_{\text{diamond}}$	19.50	- 5.844	0

Table 4.5: VASP results for the ground state structure and the clathrate structure I of Si.

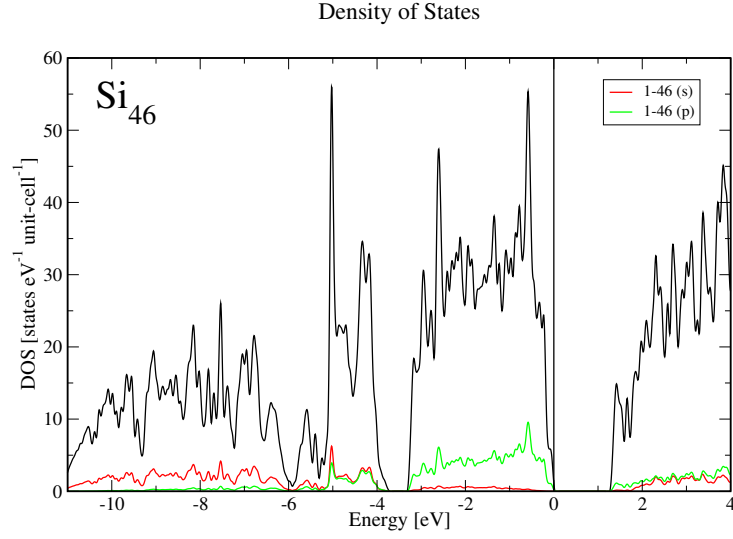


Figure 4.10: Total and local partial density of states for clathrate type I Si_{46}

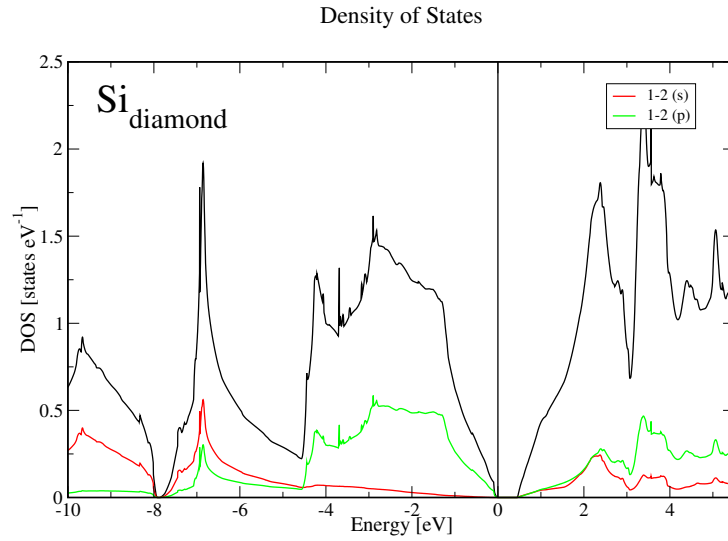


Figure 4.11: Total and local partial density of states per atom of Si in the diamond structure

4.7 Germanium

4.7.1 The element

In the periodic table of the elements Germanium (Ge) [26] is in the 4th period as well as the 4th main (group 14) or carbon group. Ge is rather common but occurs only in very small concentrations. It accounts for approximately 1.4×10^{-4} per cent by weight of the earth's geosphere. Ge was discovered in 1886. It is a semiconductor with greyish-white crystals in the cubic diamond structure and a small band gap of 0.67 eV (α -Ge). Its melting point is 937.4° C and the boiling temperature 2830° C. The density of α -Ge is 5.323 g/cm³. There is also β -Ge, which one gets from α -Ge at high pressure. The β -phase crystallises in a tetragonal structure and is metallic. Beside this there are two more metastable modifications, namely γ - and δ -Ge, which occur under certain temperature and pressure conditions. The resistance at room temperature of α -Ge is comparable to Si in the diamond structure, which has a larger gap of 1.1 eV. Ge occurs mainly in form of sulphides, such as Argyrodite ($\text{Ag}_8\text{GeS}_6 = 4 \text{ Ag}_2\text{S} \cdot \text{GeS}_2$) and Germanite ($\text{Cu}_6\text{FeGe}_2\text{S}_8 = 3$

4.7. Germanium

$\text{Cu}_2\text{S} \cdot 2 \text{GeS}_2$). In addition one can find Ge in many other materials like carbon or zinc ore but only with rather low concentrations. Ge is insoluble in not-oxidising acids and is converted to the dioxide by oxidising acids. At room temperature it is consistent but when it is heated up until it glows it burns and forms GeO_2 . The main uses of Ge are in transistor technology, metal alloys, superconductors and optical instruments.

4.7.2 DFT results

The results of the VASP calculations are presented in Table 4.6 and Figs. 4.12, 4.13, 4.14 summarising the results for the diamond ground state structure and the clathrate structures of type I (Ge_{46}) and type II (Ge_{34}).

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
Ge_{46}	26.90	- 4.590	0.020
Ge_{34}	27.37	- 4.597	0.013
$\text{Ge}_{\text{diamond}}$	23.92	-4.610	0

Table 4.6: Volume per atom and the total energies per atom as calculated by VASP. The last column shows the energy difference per atom with respect to the ground state diamond structure.

Table 4.6 shows the volume per atom and the total energies per atom in the ground state structure as well as in the clathrate structure type I and type II. In accordance with nature the most stable structure is the diamond structure with a lattice constant of 5.646 $\text{\AA}$. Very interestingly, concerning the energy difference the clathrate structure type I is rather close to the ground state, it is less stable by only 0.020 eV per atom, which is about 2 kJ per mol.

The DOS of Ge_{46} (Fig.4.12) shows two gaps, whereby the gap at Fermi energy is the important one for the electron transport properties. Clearly, the lower lying gap separates two distinctly different regions as indicated by the local DOS. In the energy region between -12 and - 4eV most of the states have 4s-like character. Above the gap of about 1.5 eV in the region of -3 to 0 eV the states have mostly 4p-like character. In the conduction band, which is split off by more than 1 eV from the valence band edge, the states are of mixed s-

4.7. Germanium

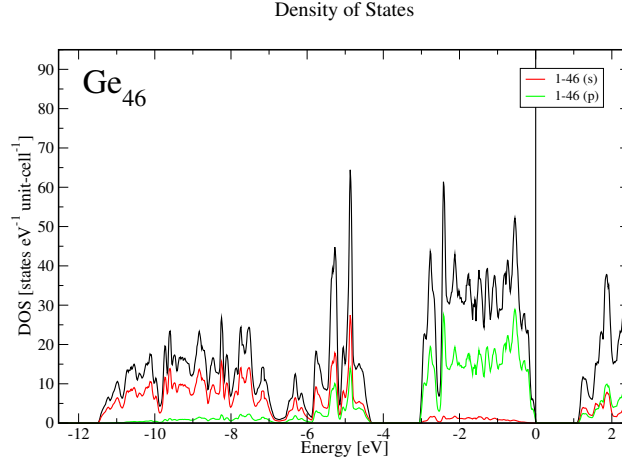


Figure 4.12: Total and local partial density of states clathrate type I Ge_{46} . The energy is plotted relative to the Fermi energy. The black vertical line marks the Fermi energy E_F .

and p-character. The rather large gap of the Ge_{34} structure is more surprising because according to all standard DFT calculations the gap for the diamond structure is zero (or even slightly negative) in contrast to the experimental gap of 0.67 eV. This failure is usually attributed to a shortcoming of standard DFT applications, which might be corrected by post-DFT developments. Therefore it is very important to notice, that the clathrate Ge_{34} is close to stability and has a large gap. The occurrence of a gap is very important for optimising the Seebeck coefficient according to equation (1.2) estimating S at low temperatures: if Fermi energy is close to the gap then the DOS at E_F is small but its energy derivative is large. Therefore, experimentally one seeks for backbone clathrate structure such as Ge_{46} with large gaps. A suitable clathrate compound is then fabricated (if it is thermodynamically stable) by filling the voids with rattlers, which adds electrons to the system shifting the Fermi energy away from the gap. This shift can be compensated by replacing Ge with atoms with a smaller number of free-electron like valence electrons, which are typically late transition elements such as Ag, Cu and even Zn. Of course, the hope is (and it is often justified) that the original gap of the pure backbone is not totally destroyed by changing the chemical composition. In this case, DFT calculations are of enormous importance because they predict

4.7. Germanium

the electronic structure without the need of any empirical information, which does not exist anyway for not-yet existing compounds.

One further important point is to notice, that the total number of occupied valence states is $46 \times 4 = 194$ because of the $4s^2 4p^2$ valence state configuration of Ge. Therefore, in the clathrate type I structure 184 valence states are needed for placing the Fermi energy at the gap. Any change of this number will shift E_F away from the gap.

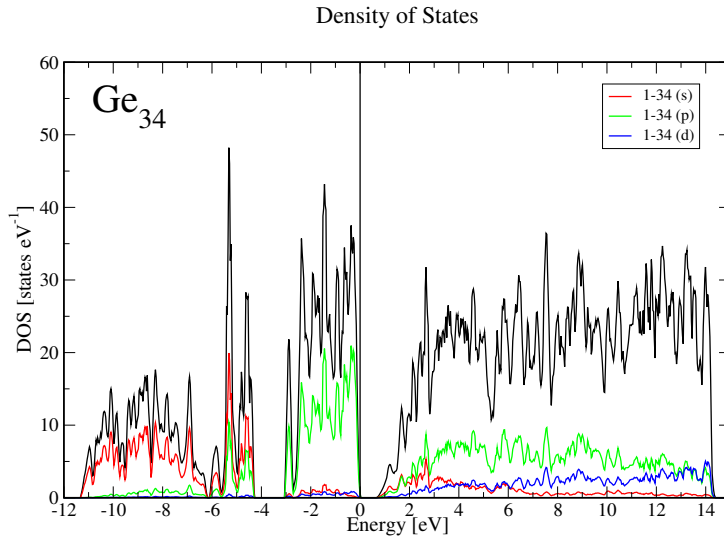


Figure 4.13: Total and local partial density of states for clathrate type II Ge_{34}

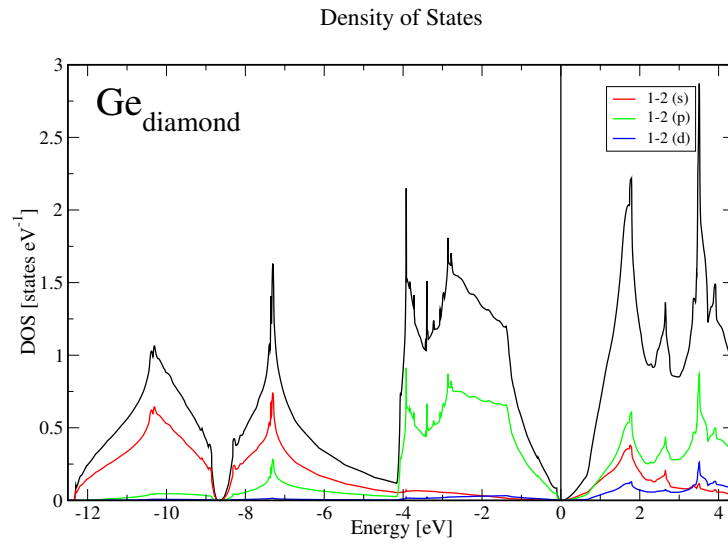
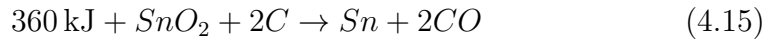


Figure 4.14: Total and local partial density of states per atom of Ge in the diamond structure

4.8 Tin

4.8.1 The element

Tin [26] is in the periodic system in the 5th period and in the 4th main or carbon group. It is available in the continental earth's crust with a share of 2.3 ppm. Pure tin happens only rare, one finds it in the form of oxides or sulfides mostly. The most important tin ore is the "tin stone" SnO_2 but also "tin gravel" is found ($Cu_2FeSnS_4 = Cu_2S \cdot FeS \cdot SnS_2$). To produce tin from tinstone, this is freed from pollutions (S, As) and reduced after that into stoves with coke by roasting first.



This tin is still polluted strongly with iron and so it is heated up about its melting point and divided off. Recycling tin is made by electrolysis. Sn is a silvery white, strongly shiny metal with a melting point at 231.91°C and a boiling point at 2687°C . It has a low degree of hardness, however, it is exceptionally flexible thus one can produce very thin sheets out of it. If Sn is bent, then one is aware of the typical "tin screaming" which arises from the friction of the crystals to each other.

There are 2 different modifications of tin, the α -Sn and the β -Sn. The α -Sn is a gray powder which crystallizes in the cubic diamond lattice. In the β -Sn every tin atom is surrounded octahedrally by six other Sn atoms and. Sn is resistant to air and water under regular conditions, however, it is attacked by strong acids under formation of Sn(II)- and strong bases under formation of Sn(IV)-compounds. Today Sn alloys are widely used whereas only needed sometimes. The best known alloy is bronze (Cu and Sn). Because of its resistance, Sn is also used to cover other metals.

4.8.2 DFT results

Sn has the same number of valence electrons as Ge and therefore one expects some common features in the DOS. This is not the case for the cubic ground

4.8. Tin

state structure for which E_F does not fall into a gap, and therefore Sn in its ground state is metallic. However, The DOS feature for the clathrate Sn_{46} (see figure 4.15) are comparable to the Ge case. In particular, for the type I clathrate the typical distinct blocks of the DOS are seen, and a gap of size occurs in the clathrate structure. The structure therefore is responsible to convert the metallic Sn into a semiconductor. Concerning the energetical stability in table 4.7 Sn_{46} is less stable by 0.46 eV than the ground state, which is significantly different from Ge, for which the clathrate type I structure is energetically rather close to the ground state.

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
Sn_{46}	41.38	- 3.982	0.459
$\text{Sn}_{\text{cubic diamond}}$	26.21	- 4.441	0

Table 4.7: VASP results for the diamond ground state structure and the clathrate structure of Sn

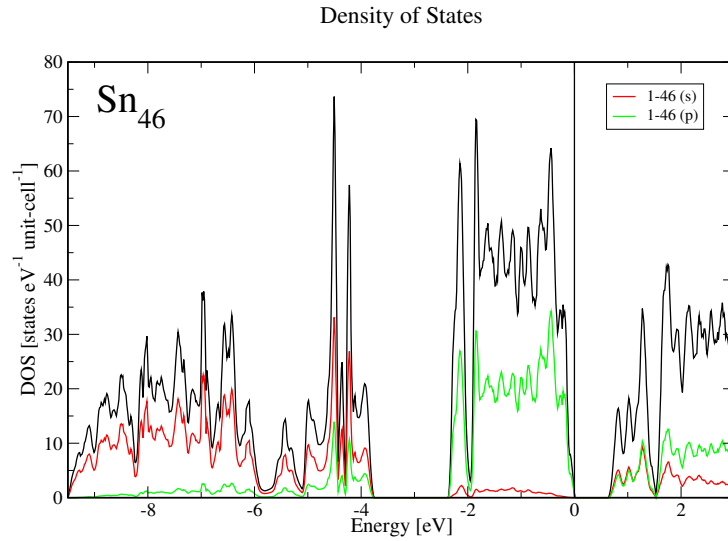


Figure 4.15: Total and local partial density of states for clathrate type I Sn_{46}

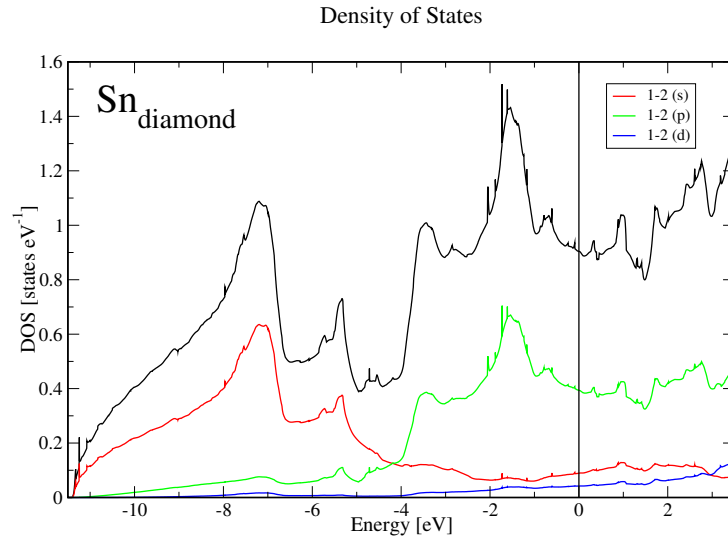
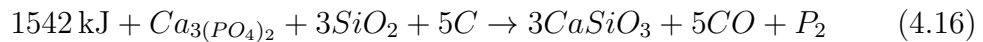


Figure 4.16: Density of states of Sn in the cubic diamond structure

4.9 Phosphorus

4.9.1 The element

Phosphorus [26] is in the periodic system of the elements in the nitrogen group. Pure P does not exist in nature but only in the form of derivatives of the phosphoric acid. The white phosphorus P_4 is produced by putting Apatit ($Ca_5(PO_4)_3$) with coke and gravel in an electrical arc stove at 1400-1500°C.



By heating up to 200-400°C white P is transformed into red P.

P occurs in several crystalline modifications as white, violet, fibrous red and black P. The cubic white P serves as basic material for the representation of all modifications. At room temperature it is waxy and without colour. It melts at 44.25°C and boils at 280.5°C.

The orthorhombic black P is built up from layers over each other. It is

4.9. Phosphorus

therefore also scaly like graphite. Heating up white P over 550°C for a longer time produces violet P. The violet P also is based on layer bars which have a very complicated construction. White P is extremely reactive. It ignites itself at room temperature and in air. White P burns with a yellowish-white, brightly shining flame and strong heat generation to phosphoruspentoxide (P_4O_{10}).



Because of the spontaneous ignitability one may cut white P only under water. By the strong oxygen affinity white P is also a good and strong reducing agent. More than 90 per cent of the elementary P is burned to P_4O_{10} and is used for the production of phosphoric acid, Pentanatriumtriphosphat ($Na_3P_3O_{10}$) and for fertilizer. P is applied also by the matchstick production.

4.9.2 DFT results

P has 1 valence electron more than the semiconducting elements SI and Ge. Consequently, E_F for the clathrate type I structure falls above the main gap as shown in figure 4.17. Nevertheless, the main gap still exists and occurs now 3 eV below the Fermi energy.

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
P_{46}	18.0	- 4.867	0.187
P_{bcc}	23.85	- 4.680	0

Table 4.8: VASP results for the ground state and the clathrate I structure of P

4.9. Phosphorus

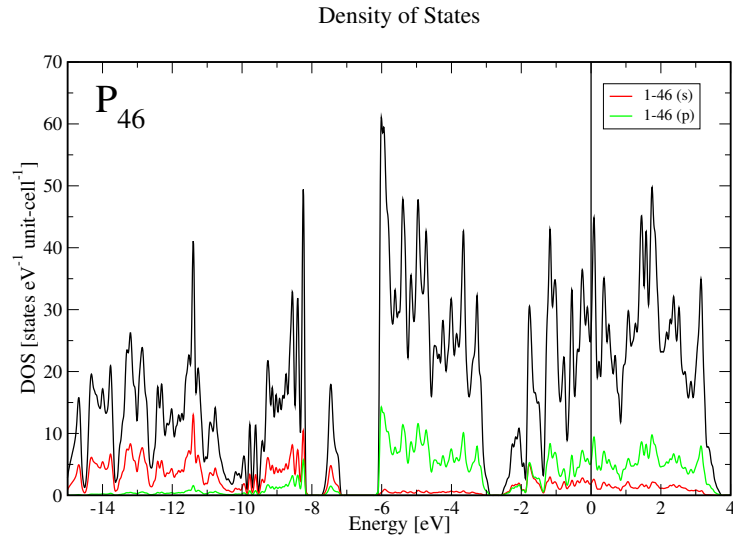


Figure 4.17: Total and local partial density of states for clathrate type I P₄₆

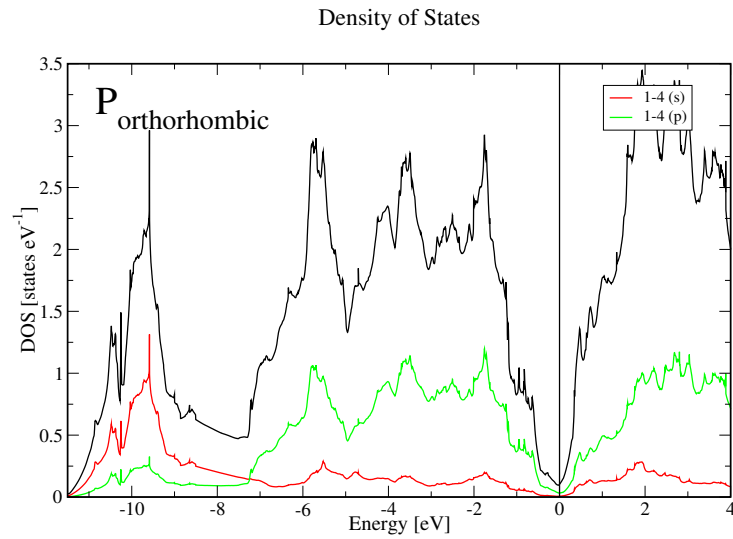


Figure 4.18: Total and local partial density of states per atom of P in the bcc structure

4.10 Arsenic

4.10.1 The element

Arsenic [26] is in the 5th main, the nitrogen group, in the periodic system of the elements. Seldomly it occurs pure, mostly in the form of its sulfides. As belongs to the semi-metals because it shows metallic and not metallic qualities depending on the modification. As appears in little concentrations up to 10 ppm everywhere in the ground. It is formed in larger quantities as by-product at the extraction of copper and lead. Technically it is produced by heating up Arsenkies (FeAsS) or Arsenikalkies (FeAs_2) by a thermal diminution of arsenic(III)-oxide with coke or iron under air degree.



For the extraction of As in semiconductor thechnology highly purified As is needed. Either it is sublimed out of solutions in liquid lead or melted As is used to crystallise out at high temperatures. As occurs in different modifications namely as gray, yellow, black and brown arsenic. The stablest form is gray or metallic arsenic with a density of 5.72 g/cm^3 . The crystals are shiny steel-graily, metallically and conduct the electric current. Yellow As which consists of tetrahedral As_4 -molecules forms if one cools arsenic steam down fast. Amorphous black arsenic arises from cooling of arsenic steam at $100\text{-}200^\circ\text{C}$. Black As consists of element forms which are brittle. They don't conduct the electric current and convert themselves into gray arsenic above of 270°C . Crystalline As does not change at room temperatures. When heating it up it burns with a bluish flame to As_2O_3 and As_2O_5 . As dissolves not in oxidizing acids due to his position in the voltage series. One uses As as an alloying component because it is able to harden other metals like tin or lead considerably. As connections also serve as pesticide, as fungicides, as wood preservative and as decolorizing means in the glass production. As

connections are very toxic, though and the use is therefore very controversial.

4.10.2 DFT results

As has 1 valence electron more than Si and Ge which in the solid ground state are semiconductors. Therefore, the Fermi energy of As is above the main gap as seen in the DOS of Ge and Si in the diamond structure. For As, this gap even disappears only the characteristic second gap separating the s-like and p-like states can be seen (see figure 4.19) and it is even significantly larger than for Si and Ge. According to table 4.9 the clathrate type I structure is less stable by about 0.4 eV which is much closer to the ground state energy than it is for Sb_{46} with the same number of valence electrons. From the DOS of the ground state structure in figure 4.20 it can be observed that the Fermi energy falls into a deep minimum of the DOS, which is a typical stabilisation behaviour of systems with rather delocalised (or free-electron-like) valence states.

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
As_{46}	29.09	- 4.286	0.390
$\text{As}_{\text{triclinic}}$	22.81	- 4.676	0

Table 4.9: VASP results for the ground state and the clathrate structure type I of As_{46}

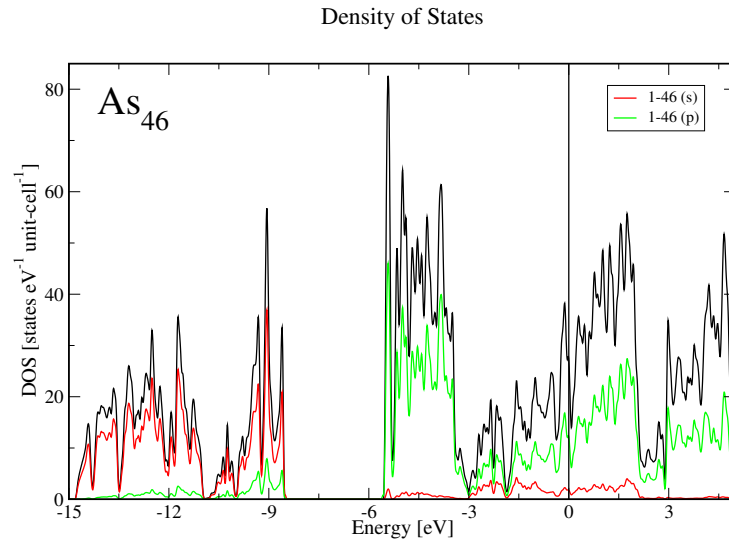


Figure 4.19: Total and local partial density of states for clathrate type I As_{46}

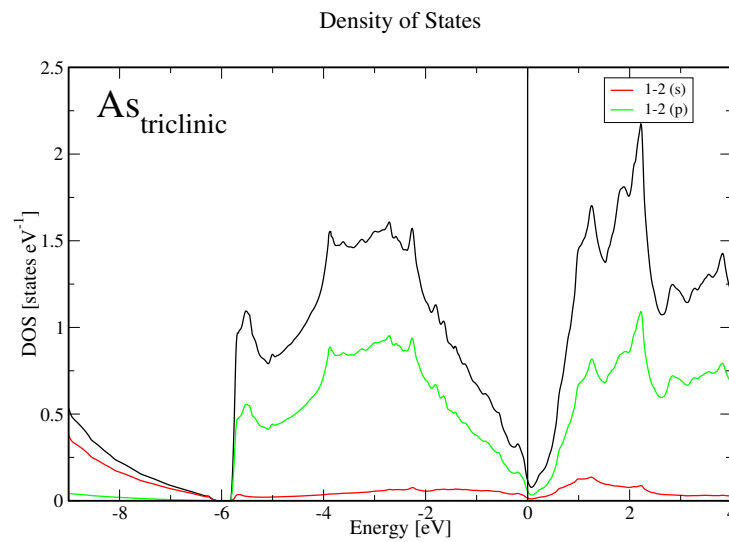
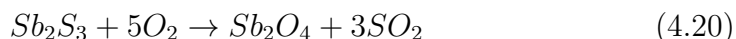


Figure 4.20: Total and local partial density of states of per atom arsenic in the triclinic ground state structure

4.11 Antimony

4.11.1 The element

Antimony [26] is in the nitrogen group in the periodic system of the elements (5th period). It is a seldom element and one finds it predominantly as a sulphide mineral Stibnit Sb_2S_3 . Mostly it occurs in isomorphic mixture with arsenic (Allemenit). Metallic Sb is won technically after several procedures from antimony shine (Stibnit). A procedure is based on the reduction with carbon.



Another possibility exists in carrying out the reduction with iron.



Sb can appear in three different modifications and metallic, grey Sb is the most continual one. If Sb steam is deterred the black amorphous Sb originates, this can be transferred in metallic Sb by heating it up. Under normal conditions antimony crystallises in the hexagonal rhombic crystal structure with the space group $R\bar{3}m$. There exist also high pressure modifications of Sb: On the one hand a form with a primitive, cubic structure and on the other hand a form with the hexagonal, thick atom packet.

Sb which can be pulverized very easily is a silverly whitely, shiny and very brittle metal. In air crystalline Sb does not react. When heating up it burns with a bluish, white flame to Sb_2O_3 . Due to the position in the voltage series, Sb does not dissolve in non-oxidizing acids (like hydrochloric acid or thinned sulfuric acid). Sb dissolves in oxidizing acids (nitric acid or sulfuric acid) under formation of antimony acid. The largest part of the produced Sb is processed to alloyings since it has the quality to harden soft metals like tin or lead. But it is also used for the production of semiconductors.

4.11.2 DFT results

According to table 4.10 again – as in In – the clathrate structures are much less stable than the hexagonal ground state structure. The DOS for Sb_{46} in figure 4.21 still shows some common basic features with Ge_{46} : for Sb_{46} the second lower lying gap between occupied states of Ge_{46} is even larger, and it separates p-like states (above the gap) from s-like states (below the gap). Because Sb has 1 valence electron more than Ge E_F has been shifted towards higher energies making Sb_{46} metallic. Very importantly, the main gap of Ge_{46} disappeared due to the more delocalized nature of the Sb valence states.

structure	volume per atom [$\text{\AA}^3$]	E_0 [eV/atom]	$E_{ref} - E_0$ [eV/atom]
Sb_{46}	47.04	- 3.760	1.033
$\text{Sb}_{\text{hex. rhomb.}}$	29.53	- 4,793	0

Table 4.10: VASP results for the ground state structure and the clathrate structure of Sb.

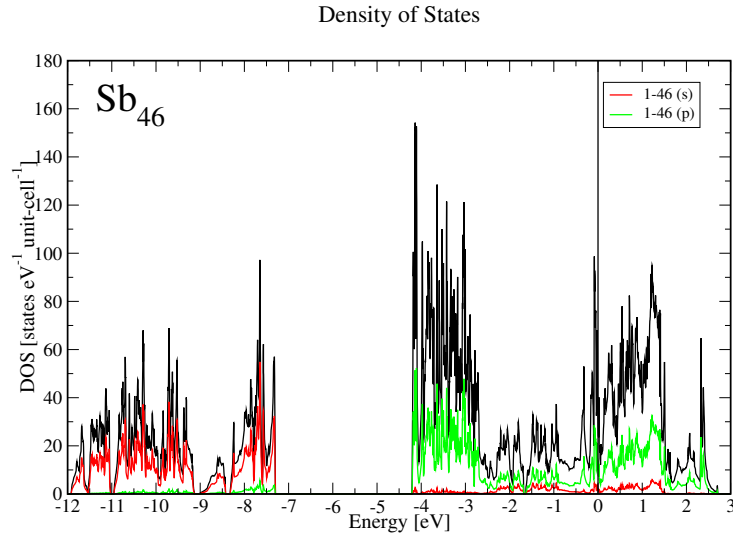


Figure 4.21: Total and local partial density of states for clathrate type I Sb_{46a}

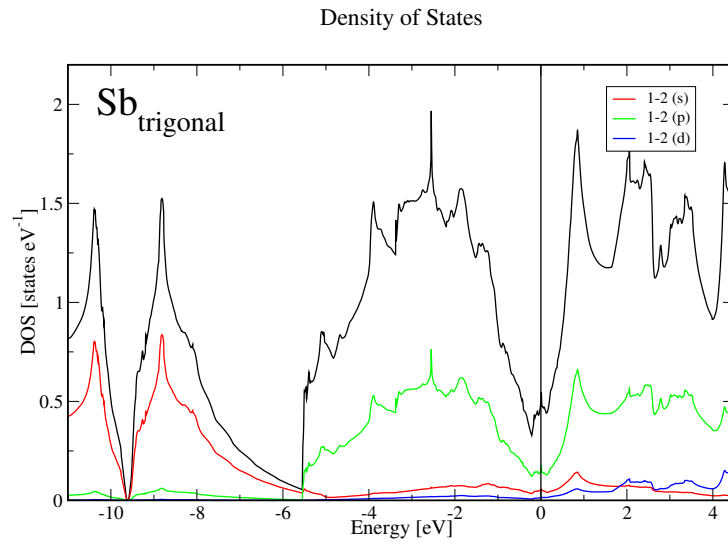


Figure 4.22: Total and local partial density of states per atom of Sb in the hexagonal rhomboedric ground state structure

4.12 Clathrate $\text{Ba}_8\text{In}_{16}\text{Ge}_{30}$

4.12.1 General remarks

As demonstrated above by the calculated results the clathrate type I structure of most of the studied elements produces a gap, which for the semiconducting elemental solids of Si, Ge and Sn is the main gap separating valence states from conducting states. Therefore, a simple counting rule of valence electrons might provide a reasonable estimate how to design a thermoelectric material with filled voids.

Inorganic clathrate structures are very interesting for thermoelectric materials because of the high ZT values, arising from good electronic mobility and low lattice thermal conductivity. Additionally, the complexity of their unit cells allows for the tuning of the bulk materials properties by doping elements and/or through subtle synthetic adjustments. [27] [28]

Compounds crystallizing in the clathrate structure types (referred to as type-I, -II, -III, and so on) have the general form of a covalently bonded framework of polyhedra in which an atom is encapsulated. The covalently bonded framework promotes high electron mobility, leading to reasonable values of electrical conductivity, while the encapsulated atoms vibrate at a frequency that contributes to the scattering of phonons, which lowers the material's thermal conductivity. There exists a rich literature on thermoelectric properties of ternary type-I clathrates with the general formula $(2)_8(13)_x(14)_{46-x}$, where the numbers in parentheses indicate the appropriate group from the Periodic Table and the subscripts indicate stoichiometry [29].

One knows that the electronic structure of the filler-free clathrates does not change when electrons are added or removed, but, and that is important, the Fermi energy is adapted accordingly. With a simple electron counting procedure one can calculate the composition of clathrates, where the Fermi energy is among the gap. Zeiringer et al. [30] formulated a critical concentration for the Fermi energy falling in the gap for compounds of type $\text{Ba}_8\text{M}_x\text{Ge}_{46-x}$:

$$x_{gap} = \frac{16}{4 - n} \quad (4.23)$$

in which x_{gap} is the stoichiometry of $\text{Ba}_8\text{M}_x\text{Ge}_{46-x}$ with the substitution element M and n its valency.

This was proposed theoretically and proved experimentally and theoretically. When M replaces Ge in $\text{Ba}_8\text{M}_x\text{Ge}_{46-x}$, $4x$ electrons are lost but nx states (where n is the valency of the dopant) are gained, whereas Ba_8 contributes 16 electrons. For $\text{M} = \text{Ga}$ the value of $x_{gap} = 16$ is derived. [30]

The doping of the calculated system in this thesis has been accomplished by adding or removing gallium respectively germanium. The number of the valence electrons which affect the doping is calculated in the following. Barium provides 2 electrons for the system, for gallium 3 electrons are counted and at last germanium has 4 valence states. That means in the system of $\text{Ba}_8\text{M}_x\text{Ge}_{46-x}$ there are 184 valence electrons.

4.12.2 DFT results

In order to study the effect of the hybridization of Ge, In and Ba the following calculations were made: the full structure was taken and the corresponding atoms (Ba and Ge) were removed and electronically selfconsistent calculations were made. No structural relaxation was allowed for this In_{16} sublattice study. Similar calculations were made for the Ba_8 and Ge_{30} sublattice. One further aspect has to be considered when overlapping the DOSes (i.e. electronic spectrum) for the sublattices, namely how the energy scales are adjusted. Clearly, the Fermi energy refers to different electron numbers in all different cases and therefore just adding the DOS as they come out from VASP has no meaning. However, there is a cure for that because for each of atoms, Ba, In, and Ge, there are deep lying semi-core states in the potentials. These states are strongly localized and can use as fingerprint for each of the elements. In the DOSes of the compound these localized peaks can be identified and then the DOSes of the sublattice studies are shifted accordingly. By this procedure the DOS in figure 4.23 were constructed. There, in the shown energy range no contribution of Ba_8 are seen because they are higher up in energy. This can also be suspected from figure 4.24 in which the first peak of the Ba DOS is about 3 eV above Fermi energy. Figure 4.23 shows that In_{16}

4.12. Clathrate $\text{Ba}_8\text{In}_{16}\text{Ge}_{30}$

and Ge_{30} both have gaps at the Fermi energy, the one for In is significantly larger than for Ge_{30} . There are narrow and spiky features in both sublattice DOSes because of the missing neighbours of the full structure. Allowing now for the hybridization of all the sublattices (however Ba does not count below Fermi energy) broadens significantly the DOS features and closes the gap at Fermi energy, which is less favourable for a large Seebeck coefficient. Nevertheless, for the full compound the DOS at Fermi energy rises sharply which -as discussed above- is favourable for a good Seebeck coefficient.

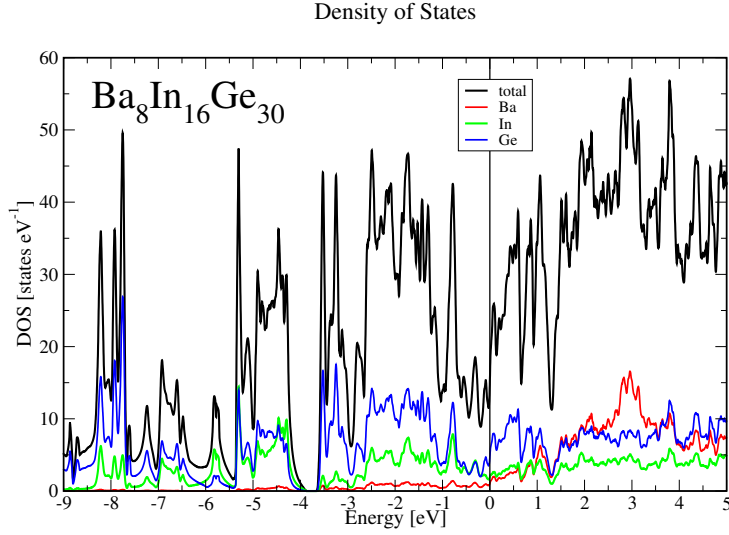


Figure 4.23: Density of states of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$

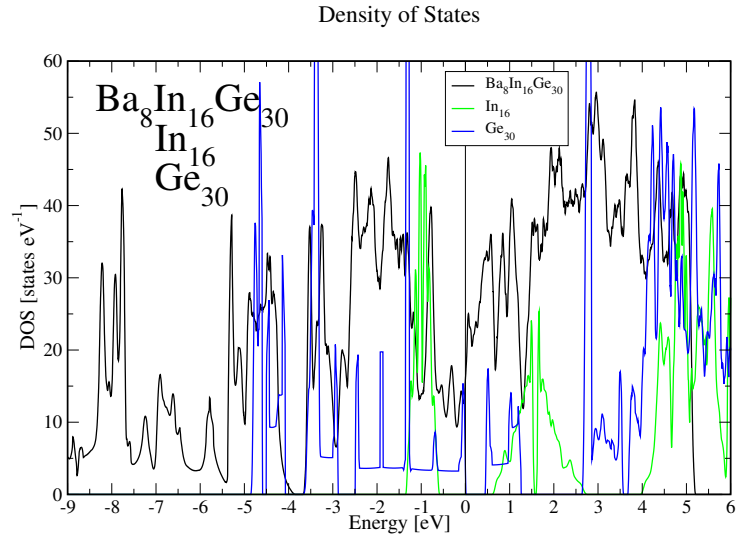


Figure 4.24: Total DOSes for the compound $\text{Ba}_8\text{In}_{16}\text{Ge}_{30}$ in comparison to DOSes for the separated sublattices. The energy scales of the sublattice DOSes is adjusted in such a way that the deep lying semi-core states of each of the sublattice DOSes agree with the corresponding peaks in the compound DOS. For the sublattice calculations the structure was kept fixed.

Summary

In this first-principles study based on density functional theory the electronic structure and energetics of material were investigated, which are of interest as thermoelectrics. A class of such materials are the so-called clathrates, for which experimental as well as theoretical efforts are undertaken in order to fabricate new compounds and/or to increase the figure-of-merit by finding a proper combinations of elements.

The goal and perspective of the present work was to apply the DFT package VASP (Vienna Ab initio Simulation Package [21]) for studying the electronic and binding properties of relevant clathrate model systems consisting of the group 3A elements (Al, Ga, In), the group 4A elements (Si, Ge, Sn), and the group 5A elements (P, As, Sb). Their ground state crystal structure as well as the X_{46} clathrate structure is studied. For Ge also the Ge_{34} clathrate structure is investigated.

Being of interest as a thermoelectric material it is important that the Fermi energy falls into or close to a gap, because then the so-called Seebeck coefficient, which relates the temperature gradient to a gradient of the electric field, may become large favouring a large figure-of-merit. For the bare clathrate backbones of group 4A elements X_{46} , $X=Si, Ge, In$ with their 4 valence electrons this is indeed the case. For the other groups elements having either one valence electron less (group 3A) or one more (group 5A) the Fermi energy is either below or above the characteristic gap of this clathrate structure.

Finally, an artificial compounds $BaIn_{16}Ge_{30}$ is designed, which should have the correct properties for a thermoelectric material: Ba atoms are inserted into the large voids of the clathrate structure, which should act as so-called

filler atoms reducing the thermal transport. Because Ba adds 16 electrons to the valence electrons of the clathrate backbone 16 Ge atoms of the Ge_{46} backbone are replaced by 16 In atoms of group 3A, which in total gives the same number of valence electrons as Ge_{46} , which has a gap at Fermi energy. A model study for the separated sublattices shows the strong influence of hybridization on the electronic structure, and in particular for the gap at Fermi energy. By that the technique of the present model study by combining rattlers and suitable group 3, 4, 5 elements may help to design improved thermoelectric materials.

Appendix

6.1 INCAR-file

An example for an INCAR-file used by VASP:

```
SYSTEM=Ge
LREAL=Auto
ALGO=Fast
PREC=High
IBRION=-1
ISIF=2
LORBIT=10
ISMear=-5
ICHARG=11
NEDOS=1000
EMIN=-4
EMAX=12
INCAR (END)
\end{}
```

6.2 POSCAR-file

The POSCAR file contains the positions of the ions.

For the diamond structure, the POSCAR-file contains the following lines:

cubic diamond	comment line
3.7	universal scaling factor
0.5 0.5 0.0	first Bravais lattice vector
0.0 0.5 0.5	second Bravais lattice vector
0.5 0.0 0.5	third Bravais lattice vector
2	number of atoms per unit cell
direct	direct or cartesian coordinates
0.0 0.0 0.0	positions
0.25 0.25 0.25	

Bibliography

- [1] Rowe, D.M., Thermoelectric Handbook Macro to Nano. 2005, Boca Raton: CRC Press.
- [2] Goldsmid, H.J., CRC Handbook of Thermoelectrics. 1995, CRC Press: Boca Raton. 3.
- [3] Kittel, C., Introduction to Solid State Physics. 2005: Wiley.
- [4] Snyder, G.J. and E.S. Toberer, Complex thermoelectric materials. Nature Materials, 2008. 7: p. 105-114. 4.
- [5] Rowe, D.M., CRC Handbook of Thermoelectrics. 1995, Boca Raton: CRC Press: Boca Raton. 5.
- [6] P. Hohenberg and W. Kohn, "Inhomogeneous Electron Gas", Phys. Rev. **136**, B864 (1964)
- [7] W. Kohn and L.J. Sham, Phys. Rev. **140**, A 1133 (1965)
- [8] Herman, Frank, V. Dyke, J. P., Ortenburger, and I. B., Phys. Rev. **22**, 807-811 (1969)
- [9] J. P. Perdew, K. Burke, M. Ernzerhof, "Generalized Gradient Approximation Made Simple", Phys. Rev. **77**, 3865 (1996)
- [10] Kresse G. and Hafner J., Phys. Rev. B **47**, 558 (1993)
- [11] Kresse G. and Hafner J., Phys. Rev. B **49**, 14251 (1994)
- [12] Kresse G. and Furthmüller J., Compt. Mater. Sci **6**, 15 (1996)

- [13] Kresse G. and Furthmüller J., Phys. Rev. B **54**, 11169 (1996)
- [14] R. Podloucky, Skriptum VO Chemische Bindung und Eigenschaften fester Materie, 2012
- [15] Matsubara, K. and M. Matsuura, Thermoelectric Handbook Macro to Nano. 2005, CRC Press: Boca Raton. 6.
- [16] F. W. Kutzler, G. S. Painter, Phys. Rev. B **45**, 3236 (1992)
- [17] Davy, H.: On a Combination of Oxymuriatic Gas and Oxygen Gas. Philosophical Transactions of the Royal Society of London, 101, 155-162, 1811
- [18] Nolas, G.S., et al., Semiconducting Ge clathrates: Promising candidates for thermoelectric applications. Applied Physics Letters **73**(2), p. 178-180 (1998)
- [19] web.archive.org/web/20070713192109/http://cst-www.nrl.navy.mil/lattice/struk.picts/Si34.s.png (12.2.2014)
- [20] web.archive.org/web/20070713192109/http://cst-www.nrl.navy.mil/lattice/struk.picts/Si46.s.png (12.2.2014)
- [21] G. Kresse, M. Marsman and J. Furthmüller. VASP the GUIDE. 23rd April 2009. URL: <http://cms.mpi.univie.ac.at/vasp/vasp.pdf>
- [22] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B **50**, 17953 (1994)
- [23] G. Kresse, J. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. **59** B 1758 (1999)
- [24] D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, Phys. Rev. **41** B 7892 (1990)
- [25] O. K. Andersen, Linear methods in band theory, Phys. Rev. **12** B 3060 (1975)

- [26] N. Wiberg, Lehrbuch der Anorganischen Chemie (German Edition), 102nd, Walter de Gruyter, 2007, ISBN: 9783110177701
- [27] Y. Mudryk, P. Rogl, C. Paul, S. Berger, E. Bauer, G. Hilscher, C. Godart, H. Noel, J. Phys.—Condens. Matter. **14** (34) 7991–8004 (2002)
- [28] M. Beekman, G.S. Nolas, J. Mater. Chem. 18 (8) (2008) 842–851.
- [29] John H. Roudebusha, Eric S. Toberer, Hakon Hopea, G. Jeffrey Snyderb, Susan M. Kauzlarich, Journal of Solid State Chemistry 184 (2011) 1176–1185
- [30] I. Zeiringer, MingXing Chen, I. Bednar, E. Royanian, E. Bauer, R. Podloucky, A. Grytsiv, P. Rogl, H. Effenberger, Acta Materialia 59 (2011) 2368–2384
- [31] Sachs, M., Solid State Theory, McGraw-Hill Book Company, 1963

Curriculum vitae

Personal Data

Name: Elisabeth Durstberger

Date of birth: 1.2.1985

Place of birth: Vöcklabruck

Nationality: Austria

Education

1991 - 1993 Volksschule in Roitham (OÖ)

1993 - 1995 Volksschule in Stadl-Paura (OÖ)

1995 - 2003 Realgymnasiums im Stift Lambach (OÖ) mit Schwerpunkt Darstellende Geometrie und Vertiefung in den Wahlpflichtfächern Informatik und Italienisch

Februar 2003 Fachbereichsarbeit in Musik zum Thema “ Die Cello-Solosuiten von Johann Sebastian Bach” unter der Betreuung von Mag. Ulrich Prack

Juni 2003 Matura

Oktober 2003 Beginn des Diplomstudiums Chemie

Oktober 2004 Beginn des Lehramtstudiums UF Chemie und UF Mathematik

2014 Abschluss des Lehramtstudiums UF Chemie und Mathematik

working experiences

Oktober 2006 - Februar 2013 Tutorium zu “Mathematik Übungen für Chemiker” bei Prof. Irene Schnöll-Bitai und bei Prof. Raimund Podlocky (jeweils im WS)

Oktober 2009 - Juli 2010 Tutorium zu “Schulversuche aus Anorganischer Chemie” bei Prof. Hans Flandorfer

September 2010 - Juni 2011 Unterrichtstätigkeit am BG/BRG Purkersdorf im Fach Chemie

September 2011 Beginn der Unterrichtstätigkeit am BG/BRG Purkersdorf - Standort Tullnerbach im Fach Chemie

September 2012 Volle Lehrverpflichtung in den Fächern Chemie und Mathematik im BG/BRG Purkersdorf - Standort Tullnerbach

Congresses

April 2010 Chemietage an der Montanuniversität Leoben

April 2011 Chemielehrerkongress an der Alpen-Adria Universität in Klagenfurt

April 2012 Chemietage an der Universität Wien

April 2013 Chemielehrerkongress am Francisco Josephinum Wieselburg