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Grundlagen-Untersuchungen des Seebeck
Koeffizienten der Clathrate $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$

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DIPLOMA THESIS

First-principles studies of the Seebeck coefficient
of the clathrate compounds $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$

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Abstract

Thermoelectric materials are of importance because of the prospect of a less environmentally damaging way of producing electrical energy. The search for effective thermoelectric materials became an intensive field in materials research. Promising thermoelectric materials are clathrate compounds with their typical cage forming crystal structure.

In this work, theoretical studies based on density functional theory are performed. The present work was motivated by the experimental work of Prof. Peter Rogl of the Institute of Physical Chemistry (Univ. Vienna), in whose group Ba-Zn-Ge clathrates—amongst many other related materials—were investigated. The main focus of the present diploma work is the calculation of components of the thermoelectric or Seebeck tensor based on the electronic structure as derived from density functional calculations. In particular $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ and related compounds and dopings such as $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$, $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ and $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ are studied in detail. During the search for optimised Seebeck coefficients the effects of doping—generally resulting in $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ compounds which are based on the rigid-band model for the electronic structure—are investigated. The main finding is that the most promising candidate as a technologically interesting material is the doped clathrate $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ which has a gap in the electronic structure. The doping was done by adding fractionally occupied electronic states to the system. The highest absolute value of a Seebeck coefficient is predicted for $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ with a doping of 0.01 electrons: at 200 K there is a minimum for the z-component of the Seebeck tensor of $-225 \mu\text{V K}^{-1}$. Doping by 0.1 electrons shifts the minimum to a higher temperature of 400 K, but its value of $-150 \mu\text{V K}^{-1}$ is less deep than for the 0.01 doping, because the Fermi energy is further away from the gap.

The self-consistent electronic structure was calculated by applying the Vienna Ab-initio Simulation Package (VASP). For that, the structural parameters of the compounds were fully relaxed. Taking

the relaxed structure as input the energy bands were calculated on a very fine grid in $\vec{k}$ space. The calculation of the Seebeck coefficients utilising the electronic structure of the materials—as derived by VASP—was done with the programme package BoltzTraP, which is based on Boltzmann’s transport theory. It had to be modified and adapted for the present purpose. The influence and effect of some inherent numerical parameters are also investigated and analysed. It turned out that BoltzTraP has numerical problems calculating the components of the Seebeck tensor at low temperature when there is a gap in the electronic structure. In case of metallic systems the numerical convergency is, however, very good and reliable.

Zusammenfassung

Thermoelektrische Materialien gewinnen immer mehr an Bedeutung auf Grund ihrer Eigenschaft, umweltfreundlich Strom zu produzieren. Deswegen wurde die Erforschung vielversprechender thermoelektrischer Materialien auch ein wichtiges Gebiet in den Materialwissenschaften. Besonders Erfolg versprechende thermoelektrische Materialien sind Clathrat-Verbindungen, die sich durch ihre Käfigstruktur charakterisieren.

In dieser Arbeit werden theoretische Studien basierend auf der Dichtefunktionaltheorie präsentiert. Inspiriert wurde diese Abhandlung durch experimentelle Forschungen von Professor Rogl vom Institut für Physikalische Chemie (Universität Wien), in dessen Arbeitsgruppe Ba-Zn-Ge Clathrate—unter diversen anderen Verbindungen—untersucht werden. Das Hauptaugenmerk dieser Diplomarbeit liegt in der Berechnung der Elemente des thermoelektrischen bzw. Seebeck Tensors. Diese Berechnungen beruhen auf der elektronischen Struktur, die aus Dichtefunktional-Berechnungen erhalten wird. Besondere Beachtung finden $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ und ähnliche, strukturverwandte Verbindungen und Dotierungen wie $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$, $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ und $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$. Bei der Suche nach den optimierten Seebeckkoeffizienten werden die Auswirkungen des Dotierens untersucht—welche in $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ Derivaten resultieren, berechnet durch die Rigid-Band Theory für elektronische Strukturen. Der vielversprechendste Kandidat für technische Einsätze ist das dotierte Clathrat $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$, da eine Lücke in der elektronischen Struktur existiert. Dotiert wurde durch das Zugeben von teilweise besetzten elektronischen Zuständen zum System. Der Maximalwert des Seebeckkoeffizienten wird für $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ mit einer Dotierung von 0,01 Elektronen vorhergesagt: Bei 200 K ist ein Minimum der z-Komponente des Seebecktensors mit $-225 \mu\text{V K}^{-1}$ feststellbar. Wird die Dotierung auf 0,1 Elektronen erhöht, verschiebt sich das Minimum auf 400 K, jedoch ist ein Wert von nur $-150 \mu\text{V K}^{-1}$ findbar. Dies ist erklärbar durch die größere Entfernung der Fermienergie von der Bandlücke.

Die selbstkonsistente elektronische Struktur wurde mittels des Vienna Ab-initio Simulation Package (VASP) berechnet. Die Strukturparameter der Verbindungen wurden vollständig relaxiert. Diese relaxierten Strukturen bildeten die Grundlage für die Berechnung der Energiebänder mit einem sehr fein gewählten Gitter im $\vec{k}$ -Raum. Berechnungen des Seebeck Koeffizienten, basierend auf der elektronischen Struktur des jeweiligen Materials, wurden mittels des BoltzTraP Programmes vollzogen, das auf der Boltzmann Transport Theorie beruht. BoltzTraP wurde für diese Berechnungen angepasst. Der Einfluss und die Auswirkung mancher numerischen Parameter wurden untersucht und analysiert. Es stellte sich heraus, dass in BoltzTraP numerische Probleme bei der Berechnung des Seebecktensors für niedrige Temperaturen vorhanden sind, wenn eine Bandlücke in der elektronischen Struktur besteht. Bei metallischen Verbindungen jedoch ist die numerische Konvergenz sehr gut und zuverlässig.

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1 Introduction

Today, environmentally less damaging energy generation is very important in all fields of everyday life and—also—in the technology of materials [13]. Thermoelectric effects have been discovered as early as the beginning of the 19th century but for a long time their potential has not been exploited due to the difficulty of fabricating suitable materials. Beginning in the 1950ies first thermoelements with a useful figure-of-merit have been discovered, namely materials based on BiTe and SiGe. Nowadays—because of the energy conserving aspect—the search for effective thermoelectric materials became an intensive field in materials research. Promising thermoelectric materials are clathrate compounds with their typical cage forming crystal structure. In this work, theoretical studies based on density functional theory are performed. Due to its flexibility and reliability (as has been proven for many cases) concepts and techniques based on density functional theory became a very powerful tool in materials science assisting the experiment and predicting new materials. The present work was motivated by the experimental work of Prof. Peter Rogl of the Institute of Physical Chemistry (Univ. Vienna), in whose group Ba-Zn-Ge clathrates—amongst many other related materials—were investigated (but not published yet). The main focus of the present diploma work is the first-principles derivation of components of the thermoelectric or Seebeck tensor for Ba-Zn-Ge clathrate compounds for scientific as well as for technological reasons. The figure-of-merit, which is the technologically important factor, is proportional to the square of the symmetrically averaged Seebeck coefficient. Therefore, one of the most promising routes for improving the figure-of-merit is the search for materials with large Seebeck coefficients. With this prospect in mind, $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ and related compounds such as $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$, $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ and $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ are studied in detail. Searching for optimised Seebeck coefficients also doped $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ compounds are investigated. For this purpose the so-called rigid band concept for the electronic structure has to be applied in order to deal with the partial site occupations of these materials. The self-consistent electronic structure was calculated by applying the Vienna

Ab-initio Simulation Package (VASP). The determination of the Seebeck coefficients based on the electronic structure of the investigated materials was done with the programme package BoltzTraP which had to be modified for the present purpose. The theoretical background of BoltzTraP is Boltzmann's transport theory.

2 Thermoelectricity and related properties

In the year 1821 the physicist Thomas Johann Seebeck [28] discovered that a specific material, a so called thermoelement, generates an electric current, when a difference in temperature was present. The reverse effect was found in 1834 by Jean Peltier [14], that thermoelements change temperature by applying an electric current. Finally William Thomson [27], 1st Baron of Kelvin, predicted 1851 that any current-transporting conductor absorbs or emits heat, if there is a temperature difference present within it. The exceptions—not known at this time—are superconductors which were detected by Kamerlingh Onnes [15] in 1911.

2.1 Thermoelements and their properties [26]

2.1.1 Thermoelement

A thermoelement consists of two different metals which are connected via a weld seam. If a temperature gradient between weld seam and the measuring point is present, a voltage proportional to the temperature difference is detectable. This voltage is rather low, somewhere in the range of μV . To increase the power output several thermoelements can be interconnected and thereby form a thermoelectrical generator. These generators can now either work for power generation (as used in space probes and in exploiting waste heat of combustion engines—making use of the Seebeck effect) or for thermal cooling (refrigeration and internal CPU-cooling—according to the Peltier effect). In thermoelectrical generators most commonly the alloys are Bi_2Te_3 , PbTe , SiGe , BiSb oder FeSi_2 , because of their relatively high degree of efficiency (3 to 8%). To increase their efficiency those materials are doped by proper elements resulting in n- and p-doped alloys.

Materials are doped by introducing foreign atoms. In the example of silicon a p-doped semiconductor is achieved by adding trivalent aluminium. Aluminium, having one electron less than silicon, generates an electronic

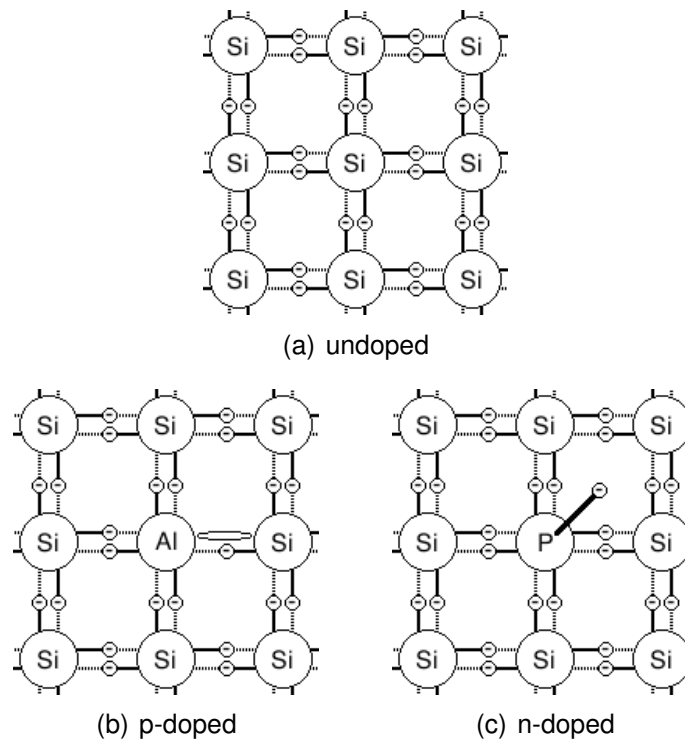


Figure 1: Different kinds of doping in Silicon: a. undoped Silicon, b. p-doped Silicon—doped with Aluminium (holes as charge carriers), c. n-doped Silicon—doped with Phosphorus (electron as charge carriers).

hole in the Silicon crystal. Electrons near the aluminium atom tend to fill the electron hole which thereby migrates through the crystal if a voltage is applied. Thus near the respective aluminium atom a stationary negative charge forms. If instead of aluminium phosphorus—which has five valence electrons—is used, an n-doped semiconductor is created. Phosphorus has five valence electrons of which one is not participating in the Si-P bonds and thus is freely to be moved in the crystal. Because of the transport of the electron a positive stationary charge is built at the respective phosphorus atom.

2.1.2 Seebeck Effect

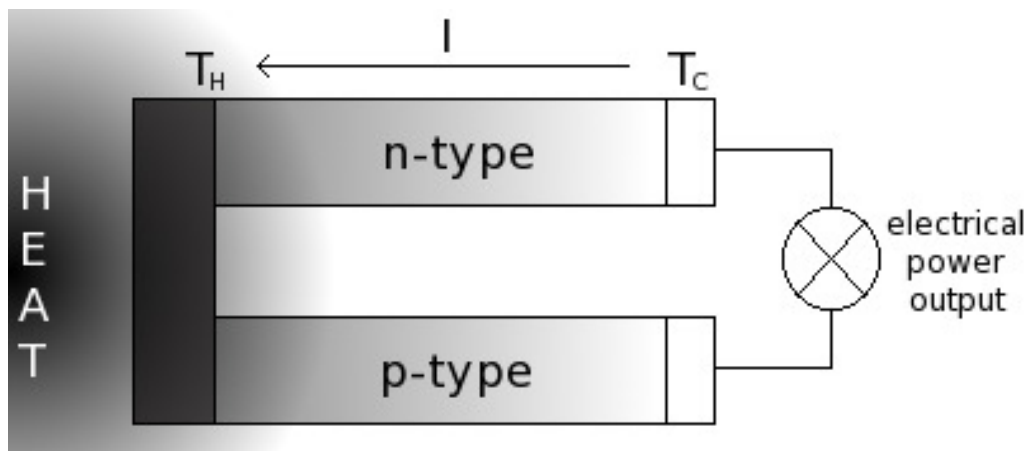


Figure 2: As the thermoelectric element is heated electrons start to travel from the hot section (T_H) to the cooler section (T_C) and thus generate an electrical current.

The Seebeck effect characterises the generation of electric current by heating a thermoelement. The weld seam of the thermoelement is at a higher temperature than the measuring points. So by means of thermal excitation charge carriers start to diffuse. They diffuse from the hotter to the cooler section of the thermoelement. The generated voltage is proportional to the temperature difference multiplied with the Seebeck coefficient (see equation (1)) (for small temperature differences).

$$U = \frac{\alpha}{\Delta T} \quad (1)$$

U ... voltage

α ... Seebeck coefficient

ΔT ... temperature difference

2.1.3 Peltier Effect

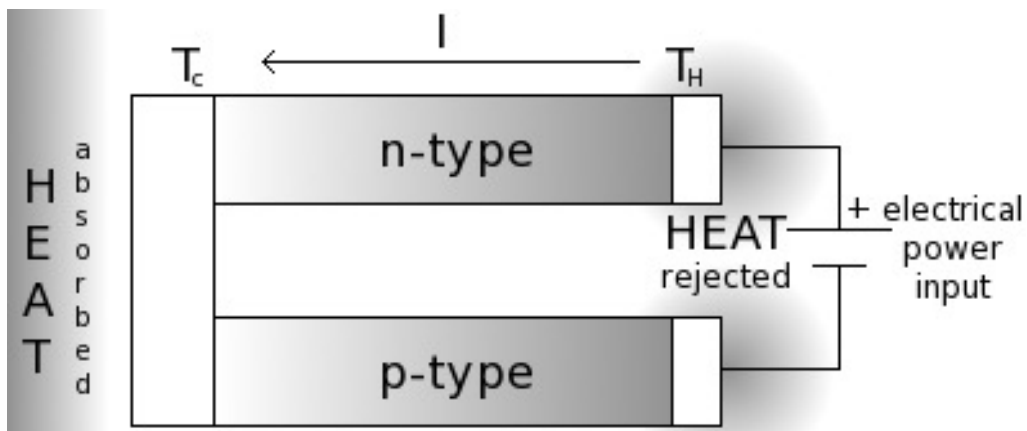


Figure 3: When voltage is applied to a thermoelectric element one part of it starts generating heat while the other side absorbs it.

The Peltier effect describes the reverted process of the Seebeck effect. An external power source is applied to the thermoelement. One part of the thermoelement starts to yield heat while the other absorbs it. The Peltier coefficient is defined by equation (2).

$$\pi = \frac{I}{q} \quad (2)$$

π ... Peltier coefficient

I ... electrical current

q ... rate of cooling

2.1.4 Thomson Effect

The Thomson effect describes the heating or cooling of a conductor by a temperature gradient while current is flowing. It is defined by equation (3). Because it is not easily detectable historically it was the last found of the thermoelectric effects. Up to now there is no practical application.

$$\dot{Q} = \frac{J^2}{\sigma} - \mu J \frac{dT}{dx} \quad (3)$$

$\dot{Q}$... net heat per unit per second

J ... current density

σ ... electrical conductivity

μ ... Thomson coefficient

$\frac{dT}{dx}$... temperature gradient

2.1.5 Kelvin Relations

The above mentioned effects are connected via the Kelvin relations as derived from irreversible thermodynamics. Although not tested for all known thermoelectric materials it is assumed that those relations are valid for all.

$$\alpha_{ab} = \frac{\pi_{ab}}{T} \quad (4)$$

α_{ab} ... Seebeck coefficient of materials a & b

π_{ab} ... Peltier coefficient of materials a & b

T ... temperature

$$\frac{d\alpha_{ab}}{dT} = \frac{\mu_a - \mu_b}{T} \quad (5)$$

α_{ab} ... Seebeck coefficient of materials a & b

μ_a / μ_b ... Thomson coefficient of materials a / b

T ... temperature

2.2 Seebeck coefficient in crystalline solids [9]

In crystalline solids it is possible to specify the Seebeck coefficient by two contributions. The first contribution consists of the change of the entropy when the amount of charge carriers is increased. The second contribution is made up of the transported energy divided by the temperature. In brief, the Seebeck coefficient encompasses the presence of charge carriers and their motion.

$$\alpha = \alpha_{present} + \alpha_{motion} \quad (6)$$

α ... Seebeck coefficient

$\alpha_{present}$... partial Seebeck coefficient originating from the presence of charge carriers

α_{motion} ... partial Seebeck coefficient originating from charge carriers in motion

The easiest accessible method to derive the Seebeck coefficient is to consider the change of entropy upon adding another charge carrier to the lattice. The ideal situation would be N charge carriers dispersed on N states of an energy band. The distribution of those charge carriers among the N states results in the following entropy:

$$S = -Nk[c \ln(c) + (1 - c) \ln(1 - c)] \quad (7)$$

S ... entropy

N ... number of states

k ... Boltzmann constant

$c \dots \frac{n}{N} \dots$ carrier concentration

n ... number of charge carriers

2.2.1 Noninteracting charge carriers

If a single charge carrier is added the Seebeck coefficient might be expressed by:

$$q\alpha = \frac{\partial S}{\partial n} = k \ln \left(\frac{1-c}{c} \right) \quad (8)$$

q ... carrier's charge
 α ... Seebeck coefficient
 S ... entropy
 n ... number of charge carriers
 k ... Boltzmann constant
 c ... $\frac{n}{N}$... carrier concentration

Equation 8 can be expressed in terms of the chemical potential, the electronic energy band and the thermal energy from equations 9 to 10.

$$c = e^{-\frac{E-\mu}{kT}} + 1 \quad (9)$$

c ... carrier concentration
 E ... energy of the electronic energy band
 k ... Boltzmann constant
 T ... temperature
 μ ... chemical potential

$$\alpha = \frac{k(E-\mu)}{qkT} \quad (10)$$

α ... Seebeck coefficient
 E ... energy of the electronic energy band
 q ... carrier's charge
 k ... Boltzmann constant
 T ... temperature
 μ ... chemical potential

2.2.2 Electron-electron interactions

Up to now the spin of the electrons has been neglected. Each electronic state—if not spin-polarised—is occupied by two electrons with opposite spins. This fact doubles the possible states available to each individual carrier if no spin-dependent interaction of it is regarded. Therefore, equation 8 has to be transformed into:

$$\alpha = \frac{k}{q} \ln \left(\frac{2-c}{c} \right) \quad (11)$$

α ... Seebeck coefficient

k ... Boltzmann constant

q ... charge carrier's charge

c ... number of carriers per orbital state

The charge carrier has one of the two spins, and thus the equation changes to:

$$\alpha = \frac{k}{q} \ln \left(\frac{2(1-c)}{c} \right) \quad (12)$$

α ... Seebeck coefficient

k ... Boltzmann constant

q ... charge carrier's charge

c ... number of carriers per orbital state

2.2.3 Electron-phonon interactions

The electron-phonon interactions describe the dependency of the electronic states on the vibrational states of the atoms in the crystal. This goes beyond the Born-Oppenheimer approximation which assumes that the electrons move infinitely fast when the positions of the nuclei are changing. Electron-phonon coupling is the mechanism for the superconducting properties of conventional superconductors but in general it might occur in any transport properties related to movements of electrons and atoms in a solid, for example in the electric and thermal conductivity. It is very demanding for first principles calculations.

2.3 Figure-of-merit [26]

To make the effects of chapters 2.1.2, 2.1.3 and 2.1.4 comparable and to express them by some technologically useful quantity, the efficiency or the figure-of-merit Z_c is introduced as it will be elaborated in the following.

Thermoelectric converters, being heat engines, have to obey—like all heat engines—the laws of thermodynamics. The efficiency of such converters—assuming they are indeed ideal generators (without heat loss)—is given by the ratio of electrical power generated to the absorbed heat at the hot junction (see equation 13).

$$\phi = \frac{\text{energy supplied to the load}}{\text{heat energy absorbed at hot junction}} \quad (13)$$

ϕ ... efficiency of generator

With the assumption that electrical and thermal conductivities and Seebeck coefficients of the materials a and b are constant within the arms of the thermoelectric generator and that the contact resistances of the junctions of the arms are negligible in comparison to the sum of resistances predominant in the arms, the following relation can be formed:

$$\phi = \frac{I^2 R}{\alpha_{a,b} I T_H} \quad (14)$$

ϕ ... efficiency of generator

I ... electrical current

R ... electrical resistance

$\alpha_{a,b}$... relative Seebeck coefficient

T_H ... temperature of hot junction

The quantity $\alpha_{a,b} I T_H$ is transformed to

$$\phi = \frac{I^2 R}{\lambda' (T_H - T_C) - \frac{1}{2} I^2 R} \quad (15)$$

ϕ ... efficiency of generator
 I ... electrical current
 R ... electrical resistance
 λ' ... thermal conductance of a and b
 T_H ... temperature of hot junction
 T_C ... temperature of cold junction

Since λ' and α are temperature dependent they have to be taken into account in the calculation by suitable averages in the temperature range in question. By that the maximum power output or power factor can be described as:

$$\phi_p = \frac{T_H - T_C}{\frac{3T_H}{2} + \frac{T_C}{2} + \frac{4}{Z_c}} \quad (16)$$

ϕ_p ... maximum power output of generator or power factor
 T_H ... temperature of hot junction
 T_C ... temperature of cold junction
 Z_c ... thermoelectric figure-of-merit of thermocouple

The maximum efficiency is formulated as follows:

$$\phi_{max} = \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1 + Z_c \bar{T}} - 1}{\sqrt{1 + Z_c \bar{T}} + \frac{T_C}{T_H}} \quad (17)$$

ϕ_{max} ... maximum efficiency of generator
 T_H ... temperature of hot junction
 T_C ... temperature of cold junction
 Z_c ... thermoelectric figure-of-merit of thermocouple
 $\bar{T} \dots \frac{T_H + T_C}{2}$

The general expression for the figure-of-merit is now:

$$Z_c = \frac{\alpha_{a,b}^2}{R\lambda'} \quad (18)$$

Z_c ... thermoelectric figure-of-merit of thermocouple

$\alpha_{a,b}$... relative Seebeck coefficient

R ... electrical resistance

λ' ... thermal conductivity of a and b

If the materials a and b are chosen to be in the state of minimum heat absorption, the equation changes to

$$Z_c = \frac{\alpha_{a,b}^2}{\left[\left(\frac{\lambda_a}{\sigma_a} \right)^{\frac{1}{2}} + \left(\frac{\lambda_b}{\sigma_b} \right)^{\frac{1}{2}} \right]^2} \quad (19)$$

Z_c ... thermoelectric figure-of-merit of thermocouple

$\alpha_{a,b}$... relative Seebeck coefficient

$\sigma_{a/b}$... electrical conductivity of a and b

$\lambda_{a/b}$... thermal conductivity of a and b

Usually the materials of the two arms of the generator are of the same material and have the materials parameters. If that is the case the figure-of-merit for a specific material can be derived:

$$Z = \frac{\alpha^2 \sigma}{\lambda} \quad (20)$$

Z ... material specific figure-of-merit

α ... Seebeck coefficient

σ ... electrical conductivity

λ ... thermal conductivity

Since the equations as given above are derived within the assumption that the thermoelectric parameters are temperature independent some more or less minor flaws occur. Nevertheless, the figure-of-merit as formulated in equation 20 usually agrees with the experimental data within 10%.

3 Thermoelectric materials and their fabrication [26]

To achieve an as high as possible value of the figure-of-merit certain materials have to be fabricated and optimised. In the following, a short overview of the necessary prerequisites is given.

To classify the type of materials often the electrical conductivity is used. Metals have a rather high conductivity whereas pure undoped insulators and semiconductors have none because of the gap between valence and conduction bands. Since the electrical conductivity corresponds to the charge carrier concentration one can state that all three parameters of the figure-of-merit are functions of the charge carrier concentration. So the electrical conductivity rises when the amount of charge carriers grows, and in contrast the Seebeck coefficient declines [26]. Electronic conductivity and the thermal conductivity are related to each other which for simple metals is expressed by the Wiedemann-Franz law.

$$\frac{\lambda}{\sigma} = LT \quad (21)$$

λ ... thermal conductivity
 σ ... electrical conductivity
 L ... Lorenz number
 T ... temperature

However, the simple relation as described by the Wiedemann-Franz law is—as expected—a rather crude approximation. A first principles description of the thermal conductivity is at present restricted on vibrational contributions and even then it is very demanding. Recently, a variety of papers have been published along this direction. And to top the list of problems, one has to be aware that in general electron-phonon coupling also needs to be taken into account for a general description of the thermal as well as electric conductivity. Anyway, it can be stated that thermal conductivity also depends on the charge carrier concentration.

According to these observations, the material scientist tries now to fabricate the material and optimise its properties to get a high figure-of-merit Z . At present, the best suited materials for thermoelectric applications are doped semiconductors and insulators. In general, it is searched for materials which have an electronic gap near the Fermi energy, as it is the case for suitable clathrates, as they will be discussed later on.

It should be noted that the Z depends on temperature. Consequently, a more convenient materials parameter is ZT including the temperature (in K). It is established practice now to classify materials by this quantity. Good thermoelectric materials (i.e. of interest for technological applications) have values $ZT \geq 1.5$.

Basically, one can follow several routes for maximising ZT , according to equation 20: increasing the Seebeck coefficient, increasing the electrical conductivity or decreasing the thermal conductivity. Of course, all suitable combinations are also of interest. Most of the present efforts consist in increasing the Seebeck coefficient and decreasing thermal conductivity. In technological practice three types of thermoelectrics are classified, each operating in a different range of temperatures for which some typical examples are discussed here. The alloys working at the low temperatures consist of different combinations of bismuth and antimony, tellurium and selenium. Those materials work best at around 450 K. For applications at medium temperatures of about 850 K lead tellurides are used. At high temperature up to 1300 K thermoelectrics made up by silicon-germanium alloys are employed. As it is obvious from the discussion about the temperature ranges, the thermodynamical stability plays also an important role for the fabrication of a suitable thermoelectric material. Therefore, density functional calculations are very helpful, because they do not only provide the electronic structure but also total energies, from which formation energies and enthalpies are derived.

The materials mentioned above are just some typical examples, because since their discovery the research undertaken for optimised thermoelectric materials has been increased tremendously. Nowadays a large range of technological materials are available. There are two main branches of research at the moment. The first deals with so called “phonon glass-electronic crystals”. The theory behind those materials is a crystal structure which contains atoms or even molecules that are weakly bound within a cage of strongly bound atoms. It is assumed that those weakly bound atoms respectively molecules start to rattle in their cage if heated and thus have a heat conductance like glass. They consume most of the kinetic energy provided by their heated environment. Because of their weak bonding to the cage the heat is not transported very well. A well-studied and well-known class of such materials are skutterudites and clathrates. The other main branch of research deals with nano-structured materials—such as superlattices (3D), quantum wells (2D), quantum wires (1D) and quantum dots (nearly 0D). The expected effect to improve ZT is based on strong phonon scattering and thus an increase in lattice thermal conduction. The most promising nano-structured materials are the quantum wires because of their electronic properties and the easier fabrication.

But not only new materials are being searched for but also the properties of known thermoelectrics are being optimised according to the power factor as given in equation 16. Industrially of high importance are materials which are not harmful for the environment and—probably the most important factor—are cheap in production.

4 Computational machinery

4.1 Density Functional Theory [31]

$$\hat{H}\Psi = E\Psi \quad (22)$$

Ψ ... wave function
 $\hat{H}$... Hamilton operator ($\hat{H} = \frac{\hbar^2}{2m} \frac{\partial}{\partial \vec{r}^2} + V(\vec{r})$)
 E ... eigenvalues of the wave function

Density Functional Theory (DFT) is an approach to solve the many-body Schrödinger equation (see equation 22) in its time-independent formulation for stationary systems. This is the basis for studying the ground state of atoms, molecules and larger systems, such as solids.

Because of its applicability and useful numerical adaptations DFT is by far the most widely applied first-principles method. By that one understands methods, which do not require any empirical parameter and are therefore free from any experimental constraints. If such first-principles methods are reliable then their results are on the same footing as experiment. In fact, in many modern research works DFT and experiment work deeply together to resolve properties of more or less complex materials, such as the atomic structure of surfaces. The application in the present diploma work is also an example: the first-principles study of thermoelectric properties.

Of course, a price has to be paid. For a full-glory application the number of atoms, which can be treated by first-principles, is comparatively small, being in the range of a few hundreds per unit cell. However, compared to the situation maybe 20 years back this is a large number, and clever concepts exist to carry DFT accuracy to millions of atoms. Another price consists in the high computational costs and there is an ever increasing demand on computer power and resources. The backbone of DFT are the two Hohenberg-Kohn theorems [12, 21] imposing that the ground state of a system should be a functional of the electron density

of the ground state. Or in less mathematical words: the ground state density determines all properties and all operators and quantities entering the many-body Schrödinger equation, a rather striking proposition. As it turned out, this very strict unique dependence of everything on the electron density n cannot be carried through in its full mathematical strictness. Nevertheless, based on very fundamental studies DFT can be maintained in some softer version. In this work, only the most basic concepts are discussed. For reasons of simplicity atomic units were used in which the mass of the electron, its charge and Planck's constant are defined to be 1. Then, the energies are given in atomic units or so-called Hartrees.

Now, equation 23 is considered with all the quantities being functionals (i.e. like with functions there is a unique relationship between argument and function).

$$E[n] = F[n] + \int V_{ext}(\vec{r})n(\vec{r})d\vec{r} \quad (23)$$

$E[n]$... ground state total energy
 $F[n]$... kinetic energy and electron-electron interaction
 $V_{ext}(\vec{r})$... external potential
 $n(\vec{r})$... electron density

Note the elegant formulation: all the electronic properties are contained in the functional $F[n]$, whereas external influences, such as enforced by the nuclei of the atoms involved, are separated. The consequence is, that whenever approximations have to be made to the electron-electron interactions (and they have to be made for the so-called exchange-correlation interactions) they are universal, i.e. independent of V_{ext} , independent on the actual system under consideration. Only how $F[n]$ depends on n matters. Hohenberg and Kohn derived an equation involving the quantities on the right side of equation 23 and a chemical potential, which—although it looks very elegant—is impractical to be solved. In fact, applying DFT, nobody utilises the original formulation of Hohenberg and Kohn.

What is done for practical purposes is to go a small step back to a wave-function-like formulation of the quantum system under consideration, namely in terms of orbitals, i.e. single independent particle objects. The deep fundamental concept behind is the mapping of the fully interacting quantum many-body system—as described by the Schrödinger equation and recast by Hohenberg and Kohn—onto an artificial set of noninteracting quasiparticles. The connection between both worlds is the ground state density and the ground state total energy, then we have true DFT again.

This mapping was invented by Kohn and Sham resulting into their famous equation 24 (the so-called Kohn-Sham equations) which practically everyone in the DFT world uses in some or the other way.

$$\left(-\frac{\nabla^2}{2} + v_{eff} \right) \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \quad (24)$$

v_{eff} ... effective potential
 $\phi_i(\vec{r})$... Kohn-Sham orbital
 ε_i ... eigenvalue

with the definition

$$v_{eff} = v + v_H + v_{XC} \quad (25)$$

v_{eff} ... effective potential
 v ... external potential
 v_H ... Hartree potential
 v_{XC} ... exchange and correlation potential

$$v_{XC} = \int \frac{\delta E_{XC}(n)}{\delta n(\vec{r})} \quad (26)$$

v_{XC} ... exchange and correlation potential
 $E_{XC}(n)$... exchange and correlation energy
 $n(\vec{r})$... electron density

The Kohn-Sham equation (see equation 24) is a Schrödinger-like equation for solving the orbitals. All the many-body difficulties are packed into

V_{XC} , the exchange and correlation potential. This potential looks local, i.e. only dependent on $\vec{r}$, the argument of orbital $\phi_i(\vec{r})$. It must however contain the quantum mechanical influence of all the other orbitals and that is the crux for approximating this potential, which cannot be formulated in any exact way. Most importantly the only but decisive role of the Kohn-Sham orbitals is to build up the ground state density—the central quantity in DFT,

$$n(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2 \quad (27)$$

$n(r)$... function of electron density

$\phi_{i(r)}$... atomic orbitals

N ... sum over occupied orbitals

By construction, the Kohn-Sham [17] equations have to be solved self-consistently: the functionals entering the Hamilton operator depend on the density, which has to be constructed by the Kohn-Sham orbitals being solutions of the Kohn-Sham equation. The total energy of the ground state $E[n]$ being a functional of the ground state density as required by Hohenberg and Kohn, is now formulated explicitly in terms known from the Kohn-Sham equation,

$$\begin{aligned} & \overbrace{\sum_i^N \int \phi_i^*(\vec{r}) \left(-\frac{1}{2}\Delta_i\right) \phi_i(\vec{r}) d\vec{r}}^{\text{Kinetic energy}} + \overbrace{\int V_{ext}(\vec{r}) n(\vec{r}) d\vec{r}}^{\text{Nucleus-electron interaction}} + \\ & \overbrace{\iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}'}^{\text{Electron-electron interaction}} + \overbrace{E_{XC}[n]}^{\text{Exchange correlation}} = E[n] \quad (28) \end{aligned}$$

$\phi(\vec{r})$... one-electron wave-function

Δ ... Laplace operator (∇^2)

$V_{ext}(\vec{r})$... external potential generated by nuclei

$n(\vec{r})$... electron density

$E_{XC}[n]$... exchange and correlation potential

$E[n]$... ground state energy functional

A short remark: for deriving the complete total energy of the system the nuclei-nuclei Coulomb repulsions have to be added to the electronic total energy of equation 28. This term is separated due to the Born-Oppenheimer approximation. Since the exact form of the exchange correlation functional $E_{XC}[n]$ is and cannot be known, it has to be approximated. The simplest approach consists in considering a uniform electron gas and formulating the approximation in equation 29.

$$E_{XC}[n] = \int \epsilon_{XC}[n(\vec{r})]n(\vec{r})d\vec{r} \quad (29)$$

$E_{XC}[n]$... exchange and correlation potential
 $\epsilon_{XC}[n(\vec{r})]$... exchange correlation of a uniform electron gas
 $n(\vec{r})$... electron density

A very crucial step for the usefulness of DFT and Kohn-Sham equations is the approximation of the exchange-correlation potential and its functional derivative. Historically the first and—with regards to its simplicity—astonishingly successful approximation was the **local density approximation** (LDA) based on the homogenous electron gas, as described above [7].

LDA gives reasonable results for crystalline solids. However, it is based on the assumption that the density does not vary too strongly in space, whatever that means. The consequence is that in situations, where density deviates strongly from a constant, the failure of LDA becomes more drastic. Such systems are e.g. atoms, molecules, surfaces and solids with localised states, such as 3d states. For these problems an improvement was suggested including information about the local change of the density in terms of the gradient. This modification resulted in the **generalized gradient approximation** (GGA). Both approximations, LDA and GGA are computationally very convenient because their computing time is negligible [22]. In fact, GGA significantly improves the results for solid systems with 3d transition metal elements concerning the equilibrium volume and magnetic moment as well as phase stabilities. Also adsorption energies are often improved by about 50%.

Numerical concepts to practically solve the Kohn-Sham equations are numerous. Two methods are widely used: the so-called linear methods developed by O. K. Andersen [3] (which originated in the augmented plane wave method and the Korringa-Kohn-Rostocker methods [20]), and methods including pseudo-potentials (being both norm-conserving and ab-initio) developed by Hamann, Schlüter, and Chiang [16]. Linearised methods became very powerful tools for solving the Kohn-Sham equations from scratch by treating all electronic states and general potentials. Concerning computational power the so-called pseudo-potential methods are leading because they use plane waves as basis functions for the orbitals and most of the numerical work is done by fast Fourier transforms. Plane waves are the natural choice because they automatically obey Bloch's condition for wave functions of a translational invariant system, as represented by the potential of atoms in a single-crystalline solid. The concept of unit cells in real and reciprocal space leads to the natural expansion of the plane waves in terms of reciprocal lattice vectors. The disadvantage of pseudo-potential methods is that pseudo-potentials have to be constructed which is an art in itself. But thanks to the developments in the last 30 years it is now possible to treat any type of electronic states (also localised ones) by pseudo-potentials.

The concepts and history of pseudo-potentials range starting from native potentials, proceeding by norm-conserving ones, and finally after the development of ultra-soft pseudo-potentials to the projector augmented wave construction [6]. It is now possible to calculate systems consisting of first-row, second-row, even transition and rare earth elements in a reliable way provided that the approximation to the exchange-correlation functional is reliable—but this is another kind of error. One of the most successful and worldwide applied pseudo-potential codes is the Vienna-Ab-initio-Simulation-Package (VASP), as developed by Georg Kresse and co-workers from the Department of Computational Materials Physics at the University of Vienna [11, 23, 30].

Using plane waves as basis sets and expanding in terms of reciprocal lattice vectors the Kohn-Sham orbitals of the plane wave expansion can be formulated as

$$\phi_i(\vec{r}) = e^{i\vec{k}\vec{r}} \sum_G c_{i,G} e^{i\vec{G}\vec{r}} = \sum_G c_{i,k+G} e^{i(\vec{k}+\vec{G})\vec{r}} \quad (30)$$

$\phi_i(\vec{r})$... basis set
 $\vec{k}$... wave vector
 G ... reciprocal lattice vector
 i ... band index
 $c_{i,G}$... expansion coefficient

If this basis set is substituted into the Kohn-Sham equations and the minimisation of energy is required the following Schrödinger-like equation—involving now the Hamiltonian in terms of matrix elements—is derived:

$$\sum_{\vec{G}'} \{H_{\vec{k}+\vec{G},\vec{k}+\vec{G}'}\} c_{i,\vec{k}+\vec{G}'} = \epsilon_i c_{i,\vec{k}+\vec{G}}$$

$$H_{\vec{k}+\vec{G},\vec{k}+\vec{G}'} = |\vec{k}+\vec{G}|^2 \delta_{\vec{G}\vec{G}'} + V_{n\,elec}(\vec{G}-\vec{G}') + V_{elec}(\vec{G}-\vec{G}') + V_{XC}(\vec{G}-\vec{G}') \quad (31)$$

H ... Hamiltonian matrix
 $\vec{k}$... wave vector
 $\vec{G}$... reciprocal lattice vector
 i ... band index
 c_i ... eigenvector component
 ϵ_i ... eigenvalue
 δ ... Kronecker-delta
 $V_{n\,elec}$... electron nucleus interaction potential
 V_{elec} ... electron electron interaction potential
 V_{XC} ... exchange correlation potential

with the classical Coulomb repulsion energy enforced by the electron density n ,

$$V_{elec} = - \int \frac{n(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r} \quad (32)$$

V_{elec} ... electron electron interaction potential
 $n(\vec{r})$... electron density

It is noteworthy that in this form the various potentials and the kinetic energy in equation 31 are represented by their Fourier transforms. Each set of self-consistent solution of the Kohn-Sham equation for the given arrangement of atoms provide the total energy and the underlying electronic structure. The electronic structure, i.e. the distribution of Kohn-Sham eigenvalues for each $\vec{k}$ and band i , provides the ingredients for the calculations of transport properties, which are described in the following subsection.

4.2 Boltzmann transport theory [19, 35, 2]

In this diploma work the transport properties such as Seebeck coefficient and resistivity are calculated by means of Boltzmann's theory. It is described for a single-crystalline environment involving a real space unit cell and a Brillouin zone, and related quantities. This general theory takes all scattering effects into account, namely electron-electron, phonon-phonon, and electron-phonon scattering but in the present work only the pure electronic part of Boltzmann's theory is involved. The other terms, in particular, the electron-phonon scattering is very hard to model in a first-principles way. Only very recently studies were published focussing on phonon-phonon interactions. The electron-phonon term is the most complex one. The simplest approximation most often does not even depend on the scattering operator. By that it is possible to express the local distribution of electrons at a given point $\vec{r}$ with both a magnetic ($\vec{B}$) and an electric ($\vec{E}$) field as well as a thermal gradient (∇T) present in a steady state system:

$$F(k, r) = f[T - \mathbf{v}(\vec{k})\tau \cdot \nabla T; \varepsilon(\vec{k} - \vec{F}_{ext}\tau/\hbar)] \quad (33)$$

$F(k, r)$ distribution of electrons
 f ... Fermi-Dirac function
 T ... temperature
 $\varepsilon(\vec{k})$... energy of an electron with quantum numbers $(\vec{k}[n, \sigma])$
 n ... band index
 σ ... spin
 $\mathbf{v}(\vec{k})$... group velocity of an electron with quantum numbers $(\vec{k}[n, \sigma])$
 τ ... relaxation time
 ∇T ... thermal gradient
 $\hbar$... reduced Planck constant $\hbar = h/2\pi$

$$f(T, \varepsilon) = \left[e^{\frac{\varepsilon - \mu}{k_B T}} + 1 \right]^{-1} \quad (34)$$

f ... Fermi-Dirac function
 μ ... chemical potential
 ε ... energy of an electron
 k_B ... Boltzmann constant
 T ... temperature

$$\vec{F}_{ext} = -q\vec{E} - q\mathbf{v}(\vec{k} + q\vec{E}\tau/\hbar) \times \vec{B} \quad (35)$$

$q \dots$ charge of charge carrier

$\vec{E} \dots$ electric field

$\mathbf{v}(\vec{k}) \dots$ group velocity of an electron with quantum numbers $(\vec{k}[n, \sigma])$

$\tau \dots$ relaxation time

$\hbar \dots$ reduced Planck constant $\hbar = h/2\pi$

$\vec{B} \dots$ magnetic field

Since the relaxation time τ is the only free parameter it may be defined in order to give the maximum current of the distinct scattering operator. Therefore, if the only scattering type is the electron-phonon scattering type, then applying the variational principle one obtains the following equation:

$$\frac{\hbar}{\tau_{ep}} = 4\pi k_B T \int_0^{\Omega_{max}} \frac{d\Omega}{\Omega} \alpha_{tr}^2 F(\Omega) \left(\frac{\frac{\hbar\Omega}{2k_B T}}{\sinh(\frac{\hbar\Omega}{2k_B T})} \right)^2 \quad (36)$$

$\hbar \dots$ reduced Planck constant $\hbar = h/2\pi$

$\tau_{ep} \dots$ relaxation time of electron-phonon scattering

$k_B \dots$ Boltzmann constant

$T \dots$ temperature

$\Omega \dots$ angular frequency

$\alpha_{tr}^2 F \approx \alpha^2 F \dots$ electron-phonon scattering function

The factor $\alpha^2 F(\Omega)$ is the electron-phonon scattering function as utilised in the Eliashberg theory. Equation 33 can then be analysed in the following way: the amount of electrons located in point $\vec{r}$ with the state $\vec{k}$ is the same as one could find at equilibrium situation except for the drift upstream. This local difference of $\mathbf{v}_{\vec{k}}\tau$ implies a temperature difference of $-\mathbf{v}_{\vec{k}}\tau\nabla T$ as well as a smaller momentum of $\hbar\vec{k} - F_{ext}\tau$. Then, $F_{ext}\tau$ describes the amount of acceleration gained since the last collision. Using equations 33 to 36 the electrical current may be expressed by the relation

$$j_\alpha = \sigma_{\alpha\beta} \vec{E}_\beta + \sigma_{\alpha\beta\gamma} \vec{E}_\beta \vec{B}_\gamma + v_{\alpha\beta} \nabla_\beta T + \dots = - \left(\frac{q}{\Omega_0} \right) \sum_{\vec{k}} v_\alpha(\vec{k}) F(\vec{k}) \quad (37)$$

j_α ... electrical current
 σ ... conductivity tensors
 $\vec{E}$... electric field
 $\vec{B}$... magnetic field
 $v_{\alpha\beta}$... thermal conductivity
 ∇T ... thermal gradient
 Ω_0 ... normalisation volume
 q ... charge of charge carrier
 v_α ... group velocity
 $\vec{k}$... wave vector
 $F(k)$ distribution of electron momenta

considering

$$v_\alpha(\vec{k}) = \hbar^{-1} \frac{\partial \varepsilon(\vec{k})}{\partial k_\alpha} \quad (38)$$

v_α ... group velocity
 $\hbar$... reduced Planck constant $\hbar = h/2\pi$
 $\varepsilon(\vec{k})$... energy of an electron with quantum numbers $(\vec{k}[n, \sigma])$
 $\vec{k}$... wave vector

Thus it is possible to explicitly express the approximate formulas of the various transport coefficients:

$$\sigma_{\alpha\beta} = \left(\frac{q^2 \tau}{\Omega_0} \right) \sum_{\vec{k}} v_\alpha(\vec{k}) v_\beta(\vec{k}) \left[- \frac{\partial f}{\partial \varepsilon(\vec{k})} \right] \quad (39)$$

σ ... conductivity tensor
 q ... carrier's charge
 τ ... relaxation time
 Ω_0 ... normalisation volume
 v_α ... group velocity
 f ... Fermi-Dirac function
 $\varepsilon(\vec{k})$... energy of electron with quantum numbers $(\vec{k}[n, \sigma])$

$$\sigma_{\alpha\beta\gamma} = - \left(\frac{q^3 \tau^2}{\hbar \Omega_0} \right) \sum_{\vec{k}} v_{\alpha}(\vec{k}) \{ [\mathbf{v}(\vec{k}) \times \nabla(\vec{k})]_{\gamma} v_{\beta}(\vec{k}) \} \times \left[- \frac{\partial f}{\partial \varepsilon(\vec{k})} \right] \quad (40)$$

σ ... conductivity tensor
 q ... charge carrier's charge
 τ ... relaxation time
 Ω_0 ... normalisation volume
 $\hbar$... reduced Planck constant $\hbar = h/2\pi$
 v_{α} ... group velocity
 $\mathbf{v}(\vec{k})$... group velocity of an electron with quantum numbers $(\vec{k}[n, \sigma])$
 f ... Fermi-Dirac function
 $\varepsilon(\vec{k})$... energy of an electron with quantum numbers $(\vec{k}[n, \sigma])$

$$\nu_{\alpha\beta} = \left(\frac{q\tau}{\Omega_0 T} \right) \sum_{\vec{k}} v_{\alpha}(\vec{k}) v_{\beta}(\vec{k}) [\varepsilon(\vec{k}) - \mu] \left[- \frac{\partial f}{\partial \varepsilon(\vec{k})} \right] \quad (41)$$

ν ... thermal conductivity
 q ... charge carrier's charge
 τ ... relaxation time
 Ω_0 ... normalisation volume
 T ... temperature
 v_{α} ... group velocity
 μ ... chemical potential
 f ... Fermi-Dirac function
 $\varepsilon(\vec{k})$... energy of an electron with quantum numbers $(\vec{k}[n, \sigma])$

In a single-crystalline solid these expressions are anisotropic, which originates in the anisotropy of the Fermi surface geometry. That means, that the corresponding materials properties are expressed by tensors. $\nu_{\alpha\beta}$ is of the same symmetry as $\sigma_{\alpha\beta}$ —which has $\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz} \neq 0$ —while $\sigma_{\alpha\beta\gamma}$ is equal 0 unless all three indices are different. The remaining independent elements are σ_{xyz} , σ_{yxz} , σ_{zxy} —with the Onsager relation requiring $\sigma_{xyz} = -\sigma_{yxz}$, ...

Consequently, the Hall tensor also has three independent elements:

$$R_{xyz}^H \equiv \frac{\vec{E}_y}{j_x \vec{B}_z} = \frac{\sigma_{xyz}}{\sigma_{xx} \sigma_{yy}} \quad (42)$$

$R_{xyz}^H \dots$ Hall coefficient tensor
 $\vec{E} \dots$ electric field
 $\vec{B} \dots$ magnetic field
 $\sigma \dots$ conductivity tensor
 $j \dots$ electrical current

R_{yzx}^H and R_{zxy}^H are calculable with the cyclic permutation of the coordinates. For the thermoelectric tensor $j = 0$ is defined. This has the effect that the thermal gradient creates an $\vec{E}$ field.

$$S_{\alpha\beta} = \vec{E}_\alpha (\nabla_\beta T)^{-1} = -(\sigma^{-1})_{\alpha\gamma} v_{\gamma\beta} \quad (43)$$

$S_{\alpha\beta} \dots$ Seebeck coefficient tensor
 $\vec{E} \dots$ electric field
 $\nabla T \dots$ thermal gradient
 $v \dots$ thermal conductivity

The number of different matrix elements depends on the symmetry of the crystal structure. Considering this, the Seebeck tensor $S_{\alpha\beta}$ has 9 different non-zero elements for a triclinic lattice, 5 for a monoclinic, 3 for an orthorhombic, one for a cubic and 3 or 2 (depending on the classes) for trigonal, tetragonal and hexagonal lattices.

4.3 The machinery for electronic structures: VASP [18]

One of the most successful and worldwide applied pseudo-potential codes is the Vienna-Ab-initio-Simulation-Package (VASP), as developed by Georg Kresse and co-workers from the Department of Computational Materials Physics at the University of Vienna [11, 23, 30]. In its latest version it comprises many functionalities including ab-initio molecular dynamics. The code uses pseudo-potentials constructed by the projector augmented wave method [6].

Modifications of VASP

For the present work, the VASP output had to be adapted in order to provide symmetry operations needed for the Seebeck calculations. Some lines of code had to be inserted in the subroutine symplib, after this line (nr. 839)

```
(837) ! Test was successful:
(838) IF (Test) THEN
(839) NR=NR+1
```

following lines of text were added:

```
open(11111,file="SYMMETRY")
NULL=0
write(11111, '(I2)') NROTK
do abc=1, NROTK
write(11111, '(3I2,x,F9.7)') GRP(1,1:3,abc), NULL
write(11111, '(3I2,x,F9.7)') GRP(2,1:3,abc), NULL
write(11111, '(3I2,x,F9.7)') GRP(3,1:3,abc), NULL
write(11111, '(I8)') abc
enddo
close(11111)
```

The above mentioned code is essential to obtain the symmetry operations from VASP. Strictly speaking an additional file called SYMMETRY is generated. This file contains the necessary symmetry operations for Seebeck coefficient calculations with BoltzTraP. These symmetry operations are given in a 3×4 matrix. For BoltzTraP calculations not only the symmetry operations are of importance but also the lattice vectors and positions of the atoms in the unit cell—information that can be found in the POSCAR file. Merging the POSCAR file with the SYMMETRY file will generate one file containing the essential structural information for BoltzTraP—the STRUCT file.

4.4 The machinery for thermoelectric properties: BoltzTraP [19]

The package BoltzTraP (**B**oltzman **T**ransport **P**roperties) utilises the semi-classical Boltzmann transport theory. In its original form it is written for the output of WIEN2k [5, 23] which is a full-potential linearised plane wave code. As it is quite common in natural sciences BoltzTraP was written in Fortran (Fortran 90).

BoltzTraP calculates the Seebeck coefficient tensor as well as the Hall tensors and the conductivity tensor. Because it uses only the electronic band-structure as input only the electron-electron interactions of Boltzmann's theory are taken into account. The relaxation time for this scattering event is a free parameter which has to be chosen in some physically reasonable way. This can be done, for example, by fitting to one experimental value of the resistivity (or reciprocal conductivity), as done in Reference [34].

4.4.1 Working procedure

After generating the input-files and starting BoltzTraP, it requires input data which are collected by several subroutines before the calculation starts. The set of band energies within the complete Brillouin zone are Fourier transformed by means of the so-called star functions which reflect the symmetry of the space group of the crystal.

$$\tilde{\varepsilon}_i(\vec{k}) = \sum_{\vec{R}} c_{\vec{R},i} S_{\vec{R}}(\vec{k}) \quad , \quad S_{\vec{R}}(\vec{k}) = \frac{1}{n} \sum_{\Lambda} e^{i\vec{k} \cdot \Lambda \vec{R}} \quad (44)$$

$\tilde{\varepsilon}_i(\vec{k}) \dots$ Fourier expanded band energies
 $\vec{R} \dots$ direct lattice vector
 $\vec{k} \dots$ wave vector
 $c_{\vec{R},i} \dots$ expansion coefficient
 $\Lambda \dots n$ point group rotations

There are more star functions used to generate the $\tilde{\varepsilon}_i$ than band energies, ε_i . The fit is then constrained in a way that $\tilde{\varepsilon}_i$ are equal to ε_i , the ad-

ditional freedom is utilised to minimise a roughness function. The roughness function is constructed in the way to have no oscillations between data points. Finally the following function is accepted:

$$\rho_{\vec{R}} = \left(1 - C_1 \left(\frac{|\vec{R}|}{|\vec{R}_{min}|} \right)^2 \right)^2 + C_2 \left(\frac{|\vec{R}|}{|\vec{R}_{min}|} \right)^6 \quad (45)$$

$\rho_{\vec{R}} \dots$ roughness function
 $\vec{R} \dots$ direct lattice vector
 $\vec{R}_{min} \dots$ smallest non-zero lattice vector
 $C_1, C_2 \dots$ parameters

The values of C_1 and C_2 have been fixed to $3/4$ —since these values turned out to yield good results. It must be ascertained that $\tilde{\varepsilon}_i$ matches the calculated band energies as well as the roughness function is minimised. To satisfy these conditions the number of plane waves must be greater than the number of the band energies. The ratio of the numbers of plane waves to band energies is controlled by the parameter `lpfac`. The expansion coefficient, $c_{\vec{R},i}$, is then given by following equation:

$$c_{\vec{R},i} = \begin{cases} \varepsilon_i(\vec{k}_N) - \sum_{\vec{R} \neq 0} \frac{1}{n_{\vec{R}}} c_{\vec{R},i} e^{i\vec{k} \cdot \vec{R}} & \vec{R} = 0 \\ \rho_{\vec{R}}^{-1} \sum_{\vec{k} \neq \vec{k}_N} \lambda_{\vec{k}} [S_{\vec{R},i}^* - S_{0,i}^*] & \vec{R} \neq 0 \end{cases} \quad (46)$$

$c_{\vec{R},i} \dots$ expansion coefficient
 $\varepsilon_i(\vec{k}_N) \dots$ band energy
 $\vec{k} \dots$ wave vector
 $n_{\vec{R}} \dots$ point group operations of direct lattice vector
 $\rho_{\vec{R}} \dots$ roughness function
 $\vec{R} \dots$ direct lattice vector
 $S_{\vec{R}} \dots$ see equation 44
 $\lambda \dots$ see equation 47

By solving the following equation the parameters $\lambda_{\vec{R}}$ are obtained:

$$\Delta \varepsilon_i(\vec{k}) = \varepsilon_i(\vec{k}) - \varepsilon_i(\vec{k}_N) = \sum_{\vec{k}' \neq \vec{k}_N} H_{\vec{k}\vec{k}'} \lambda_{\vec{R}}^i \quad (47)$$

$\varepsilon \dots$ band energy
 $H_{\vec{k}\vec{k}'} \dots$ see equation 48

whereby

$$H_{\vec{k}\vec{k}'} = \sum_{\vec{R} \neq 0} \frac{[S_{\vec{R}}(\vec{k}) - S_{\vec{R}}(\vec{k}_N)][S_{\vec{R}}^*(\vec{k}') - S_{\vec{R}}^*(\vec{k}_N)]}{\rho_{\vec{R}}} \quad (48)$$

$\vec{R} \dots$ direct lattice vector

$S_{\vec{R}} \dots$ see equation 44

$\rho_{\vec{R}} \dots$ roughness function

4.4.2 Input parameters and output files

BoltzTraP has one specific file for its input (called INPUT). This file allows the setting of various options:

```
&general_input
neigen          =          1,
ispin           =          1,
lsorbit         =         "F"
eferm           =    1234567,
deltae          =    0.000001,
ecut            =         0.25,
nval            =          12,
lpfac           =          5,
tmax            =        1000,
deltat          =          1,
dosmethod       =    "TETRA",
seebtemp        =         "F",
doping          =         0.0
/
&band_control
dos_old         =         "F",
band_shift      =         0.0,
band_ref        =         0.0
/
&dos_control
analy_dos       =          0,
energy0         =          0
```

The parameters usually remain constant with the exception of `neigen` (number of EIGENVAL-files produced by VASP), `eferm` (the Fermi-En-

ergy as obtained by VASP), `nval` (number of valence electrons of the specific compounds), `lpfac` (parameter for obtaining an overview of the capabilities of the programme—see chapter 5.4.5) and `doping` (to give a specific doping—if wanted; also see chapter 5.4.5). For further information on the input parameter it is referred to the User’s Guide for programme SEEBECK [33].

The following files are written out by SEEBECK:

- OUTPUT
- `dos`
- `chemipot`
- `elecond`
- `seebtrace`
- `tmp`

The most important files for the current work are `dos` and `tmp`. These files contain the density of states calculated by BoltzTraP (`dos` file) as well as the Seebeck coefficient (`tmp` file). For further information on the output files please refer to the User’s Guide for SEEBECK [33].

5 Results and Discussion

5.1 Elemental solids

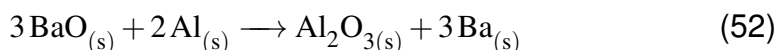
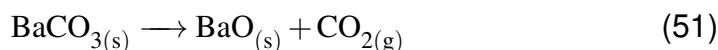
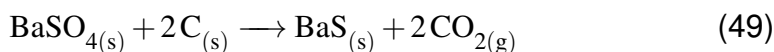
Before dealing with the clathrate compounds consisting of the elements Ba, Zn, and Ge the elemental solids in their ground state structures are discussed. For germanium, in addition to the diamond ground state structure the cage forming Ge_{46} structure was studied because it forms the structural backbone for the $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ clathrates which are the scope of this work. Furthermore and very important for the thermoelectric properties the electronic structure of Ge_{46} has a large gap which is very important for the thermoelectric properties of the clathrate compounds. For all the calculations the local density approximation is applied. The results for the density of states (DOS) shown below are obtained for the optimised lattice parameters at which the total energy is a minimum.

The calculations for the DOS have been conducted with VASP. To get the energetically stable configuration of the cell the first calculations are done with no special parameters (LREAL=Auto, ALGO=Fast, PREC=High). For this calculations the lattice constant was variegated. The potentials used for each calculation were LDA potentials.

5.1.1 Barium [32]

Barium belongs to the alkaline earth metals (II main group of the periodic table). Barium is in comparison to zinc and germanium the most common element of the geosphere (4×10^{-2} per cent by weight). For the human physiology Ba^{2+} is nonessential but toxic (maximum allowable concentration: 0.5 mg dust/m^3) and may cause muscular cramps and cardiac irregularities.

Barium most usually is manufactured by aluminothermic reduction of its oxides with aluminium at high temperatures—for this the basic material is barite, BaSO_4 (see equations (49) to (52)).



_(s)...solid, _(l)...liquid, _(g)...gaseous

As all alkaline earth metals solid barium is a light metal and it has higher density, melting point, boiling point, sublimation enthalpy and hardness in comparison to alkaline metals. Barium crystallises in the body-centred cubic structure and its colour normally is silver-white, whereas as a high-purity metal the colour changes to golden-yellow. Its melting point is at 710°C , its boiling point at 1537°C . The density of barium is 3.65 g/cm^3 .

Most commonly barium is used in compounds. Its usage reaches from fireworks to contrast media. Even in drilling industry barium (as barium sulphate) is used as a weighting agent.

In Figure 4 the DOS of barium in its body-centred cubic configuration is depicted. To calculate the DOS the INCAR-file of VASP was modified (see Appendix). The electronic configuration of the potential used was $5s^25p^66s^2$. The number of K-Points used for the calculation was a mesh of $11 \times 11 \times 11$. After applying symmetry operations 56 irreducible K-Points remain. The calculated equilibrium lattice parameter is $a=4.77$ Å—in comparison to values given in literature $a=5.02$ Å [4]. This discrepancy is within expectation. In the upper right corner the DOS around the Fermi energy level is pictured.

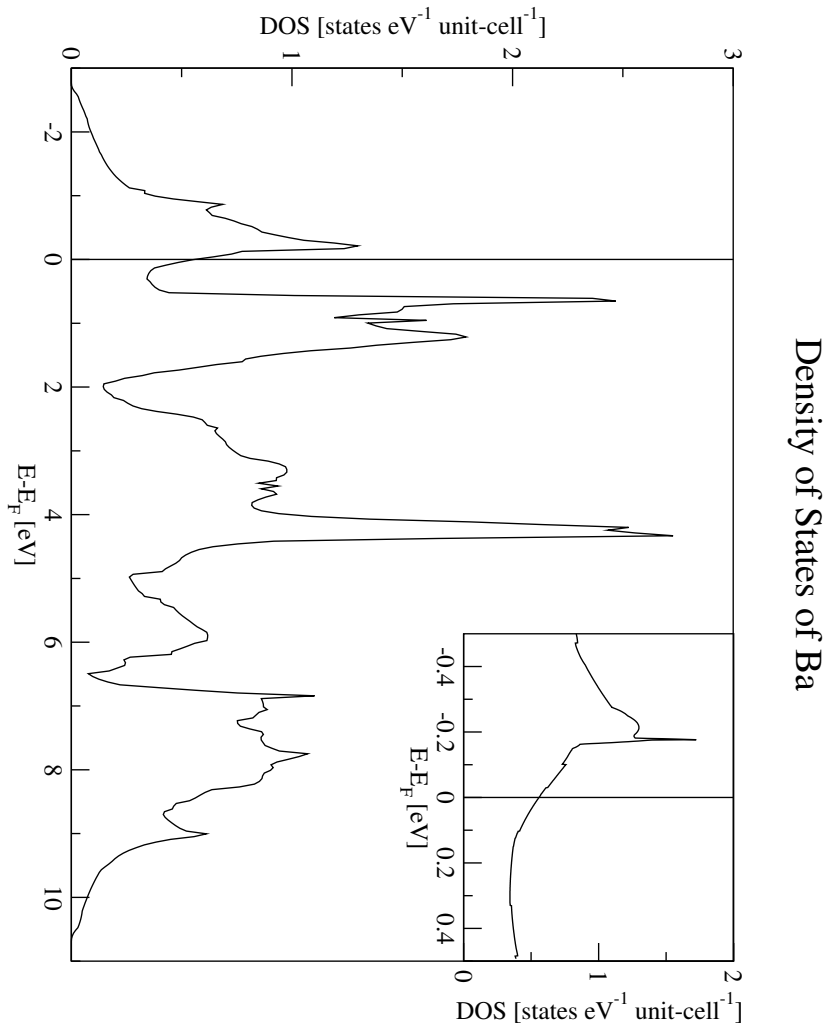
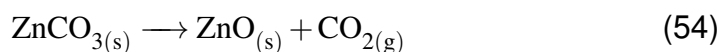
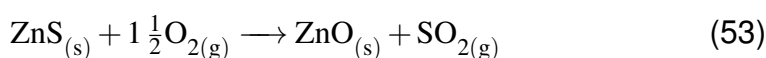


Figure 4: Density of states of bcc barium. The energy range around Fermi energy ($E=0$) is shown enlarged in the inset, see upper right corner.

5.1.2 Zinc [32]

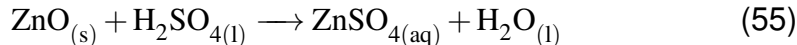
Zinc belongs to subgroup II (respectively group 12 elements) of the periodic table. Zinc accounts for approximately 7×10^{-3} per cent by weight of the geosphere. In average the human body contains 40 mg zinc per kg and is an important integral part in more than 200 enzymes.

Technical production of zinc is done in two ways - watery and aridly. 40% of the global production of zinc are accomplished via electrolysis of zinc sulphate solutions, 60% via reduction of zinc with coal.



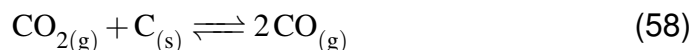
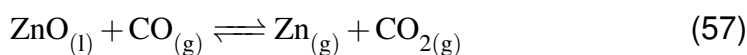
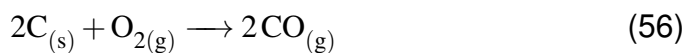
(s) ...solid, (l) ...liquid, (g) ...gaseous

To generate the zinc sulphate solution for the electrolytic method zinc oxide is treated with sulphuric acid.



(s) ...solid, (l) ...liquid, (g) ...gaseous

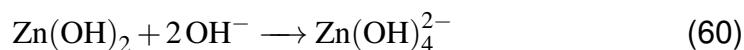
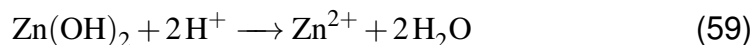
In the arid method zinc oxide is mixed with ground coal and deoxidised. As can be seen equations (57) and (58) show a chemical equilibrium. This equilibrium is call "Boudouard-equilibrium". It needs to be noted that with the watery method purer zinc can be generated, when Mercury is used as cathode material.



(s) ...solid, (l) ...liquid, (g) ...gaseous

Metallic zinc has a bluish-silver shiny surface. It crystallises in close-packed hexagonal geometry yet the axis orthogonal to the layers is stretched. At room temperature zinc is rather brittle but if heated to 100 to 150 °C, it turns flexible and metal sheets and wires can be formed. It has to be noted that zinc grows brittle again above 200 °C. The melting point of zinc is at 419.6 °C, its boiling point at 908.5 °C. The density of zinc is 7.14 g/cm³.

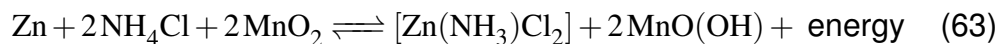
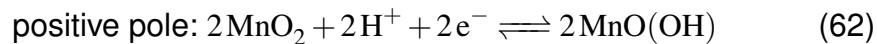
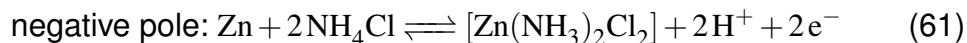
In difference to barium zinc is a more noble metal—as can be deduced by its higher first ionisation potential and more positive standard electrode potential, which is -0.7626 V (adverting to Zn^{2+}). If exposed to air a transparent oxide respectively carbonate layer protects the zinc from reaction. Since zinc reacts with acids to generate hydrogen it is used in Kipp's apparatus—an apparatus designed to generate small volumes of gases. As in air zinc is also stable in water by forming a protecting hydroxide layer of low solubility. If on the other hand the solution is acidic the hydroxide layer may not form and the metal dissolves, the same is true for alkaline dilutions (see equations (59) and (60)).



Equation 59: Dissolving of zinc in acidic dilutions.

Equation 60: Dissolving of zinc in alkaline dilutions.

Zinc is quite commonly used in batteries. Galvanic elements with zinc-electrodes for anodes are globally dominant in small size batteries. There are several ways to construct batteries, and the most common are: Leclanché cell (1.5 V), Alkaline batterie (1.5 V), zinc-carbon batterie (1.5 V), Mercury batterie (1.35 V), Rechargeable Alkaline Manganese (RAM) batteries (1.42 V), zinc-air batteries (1.65 V) and zinc-bromine flow batterie (1.8 V).



The crystal structure of zinc is close-packed hexagonal. The INCAR-file of VASP was modified (see Appendix). The electronic configuration of the potential used was $3d^{10}3p^2$. A K-Points mesh of $11 \times 11 \times 11$ has been used, this K-Point mesh was reduced to 216 irreducible K-Points due to symmetry operations. The optimised structural parameters are $a=2.66 \text{ \AA}$ and $c/a=1.62 \text{ \AA}$ —the parameters from literature are corresponding: $a=2.66 \text{ \AA}$ and $c/a=1.86 \text{ \AA}$ [4].

In Figure 5 the DOS per atom for zinc in its hexagonal close-packed structure is shown. In this graph the peak at approximately -10 eV formed by the semicore 3d-states is most prominent. In this image it was cut off because the fine structure of the remaining Density Of States would otherwise not be discernible. For this reason the area around the Fermi energy level is enlarged in the upper right corner.

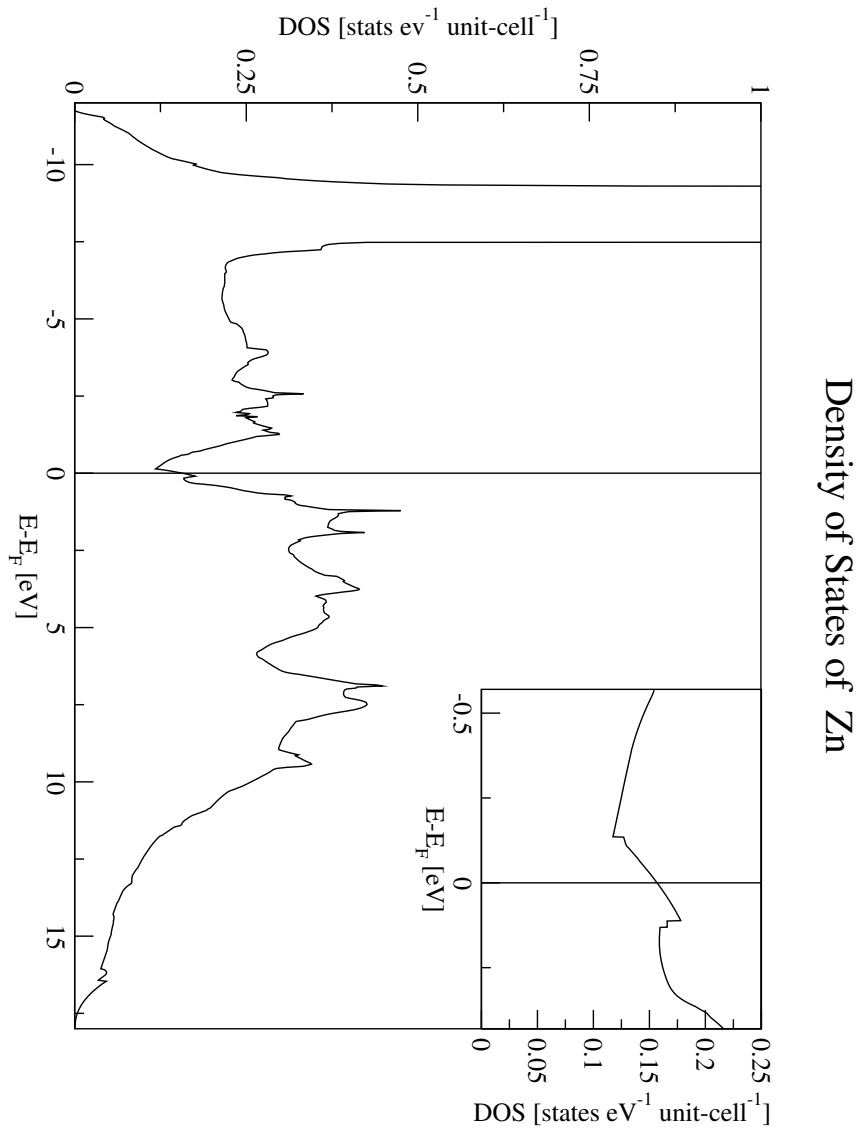
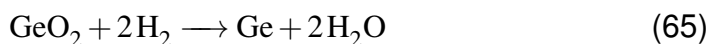
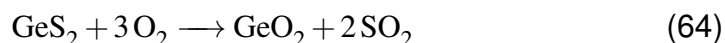


Figure 5: Density of States of hcp zinc per atom. The region the Fermi level is enlarged in the inset, see upper right corner.

5.1.3 Germanium [32]

Germanium belongs to the carbon group (main group IV of the periodic table). Germanium accounts for approximately 1.4×10^{-4} per cent by weight of earths geosphere. For humans germanium is non essential, as for other species only certain plants accumulate germanium.

In nature germanium appears most often in form of sulphides, e. g. as Argyrodite ($\text{Ag}_8\text{GeS}_6 = "4 \text{Ag}_2\text{S} \cdot \text{GeS}_2"$) and Germanite ($\text{Cu}_6\text{FeGe}_2\text{S}_8 = "3 \text{Cu}_2\text{S} \cdot \text{FeS} \cdot 2 \text{GeS}_2"$). Elemental germanium is gained from stack gas obtained by zinc ore processing or oxidation of GeS_2 . For enrichment GeO_2 fine dust is dissolved in sulphuric acid and after adding of sodium hydroxide until pH 5 is reached GeO_2 and ZnO precipitate. After this procedure the germanium has a concentration of up to 10%. Germanium then is separated from zinc by adding hydrochloric acid and distilling GeCl_4 (boiling point of GeCl_4 : 83.1 °C, boiling point of ZnCl_2 : 756 °C). After repeated distillation GeCl_4 is hydrolysed (GeO_2) and reduced to elemental germanium by hydrogen. To obtain high purity germanium is processed in the floating-zone melting technique.



Semi-metallic germanium (α -germanium) is greyish-white (having a metallic luster), crystallises in cubic diamond structure. The melting point is 937.4 °C, the boiling point 2830 °C. In its α -configuration germanium conducts like silicon because it is also a semiconductor. The density of α -germanium is 5.323 g/cm³. If exposed to high pressures (in order of 120 000 bar and higher) germanium converts from α -phase to the β -phase, which crystallises in a tetragonal structure and is metallic. Noticeable is the slightly higher density of the germanium β -phase in comparison to the α -phase: 5.88 g/cm³. Besides the α - and β -phases under certain temperature and pressure conditions the metastable modifications γ -

and δ -germanium are formed. It is possible to obtain amorphous germanium if molten germanium is hardened by quenching. Pure amorphous germanium is highly unstable and tends to transform explosively into crystalline germanium by generating intense heat. The expansion of germanium when solidifying from the molten state (the same phenomenon occurs with e. g. water, bismuth) is a fact worth mentioning (since only a very few substances do).

At room temperature germanium undergoes no reactions with air, if warmed up to red heat it will react with oxygen by generating white smoke. In non-oxidising acids (e.g. hydrochloric acid, diluted sulphuric acid) germanium is insoluble, but in oxidising acids (e.g. concentrated sulphuric acid, nitric acid) it reacts and forms dioxides. The standard potential of germanium is -0.036 V ($\text{Ge} \rightarrow \text{Ge}^{4+}$).

The main uses of germanium is or was in transistor-technology, optical instruments, special metal alloys, superconductors, stain gauges and luminophores.

The ground state structure of germanium under normal conditions is a cubic diamond structure. Again the INCAR-file of VASP has been modified (see Appendix). The potential in use for the electronic structure includes the $3d^{10}4s^24p^2$ electrons. The K-Points mesh in use was $11 \times 11 \times 11$ and after the symmetry operations were performed 56 irreducible K-Points remained. The minimum energy structural parameter is $a=5.64\text{ \AA}$ —being quite in agreement to literature $a=5.64\text{ \AA}$ [4].

In Figure 6 the DOS per atom is depicted. It can be seen that in the area from -13 to 13 two gaps are present. The one at Fermi energy is of importance for germanium being a semiconductor. The width of this gap is 0.07 eV . The gap at Fermi energy is far too small as compared to experiment, which is a well-known shortcoming of standard DFT calculation. Because the essential gap is hardly visible in the large graph

the section around the gap can be seen enlarged in the inset in the upper right corner—for this enlargement the energy minimum and energy maximum for the calculation were set to $E_{\text{MIN}}=2.4$ and $E_{\text{MAX}}=3.4$.

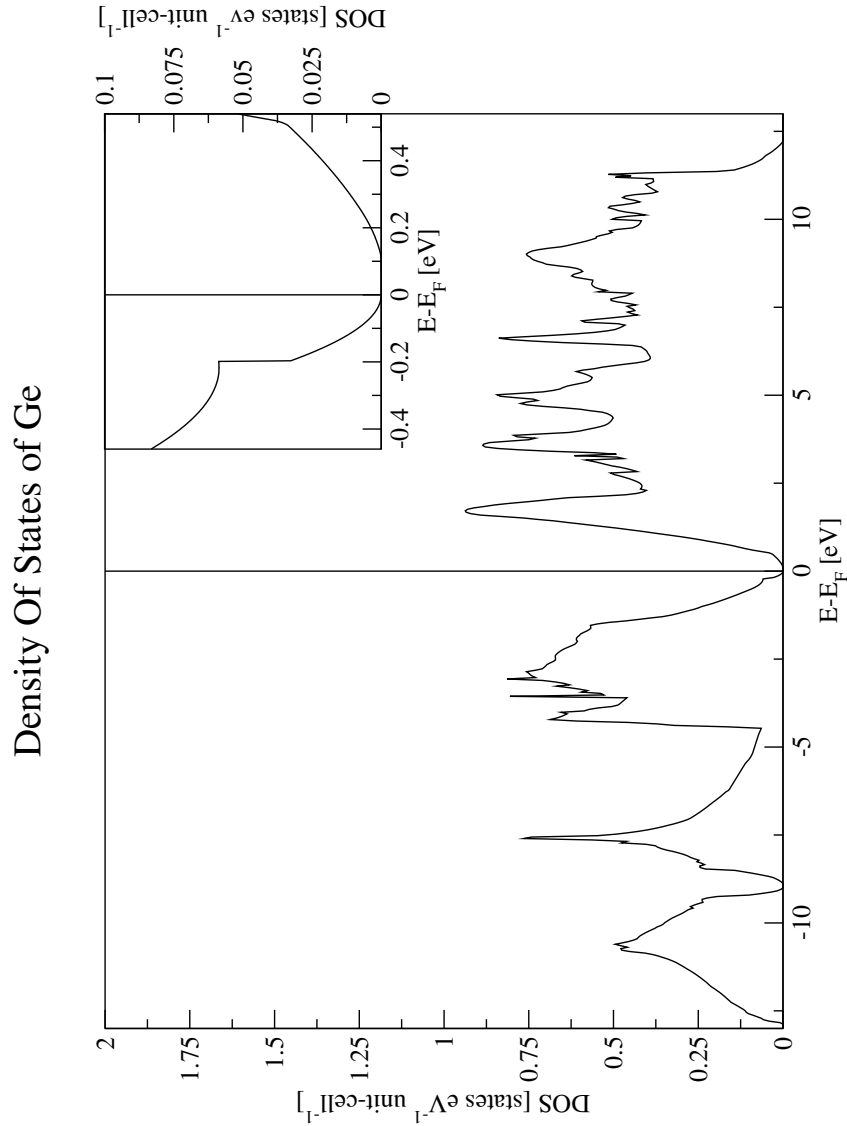


Figure 6: Density of states per atom of germanium in the diamond structure. The area around the gap is shown enlarged in the inset, see upper right corner.

For germanium, in addition to the diamond ground state structure the cage forming Ge_{46} structure is of interest because it forms the structural backbone for the $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ clathrates which are the scope of this work. The cage structure is the same for it occurs in the clathrates, see e.g. Ref. [1]. In the DOS the most important feature is the formation of a sizeable gap of 1.24 eV at Fermi energy (see Figure 7), which is substantially larger than the one for germanium in its ground state structure. This gap has been found using a K-Point mesh of $11 \times 11 \times 11$ which are reduced by the symmetry operations to 56 irreducible K-Points. The remaining settings are identical to the germanium in diamond structure except the ICHARG-flag has been set to ICHARG=1.

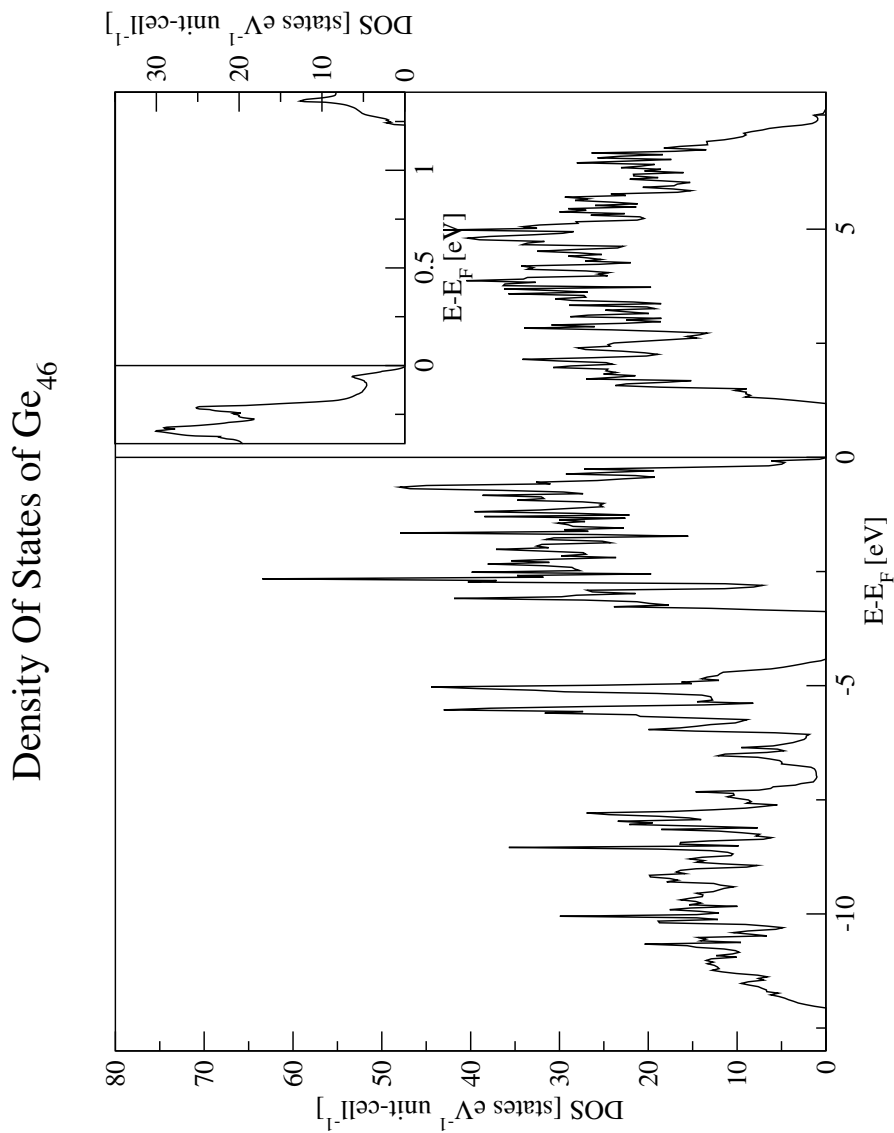


Figure 7: Density of states per atom of Ge_{46} with the clathrate cage structure. The area around the gap can is enlarged in the inset, see upper right corner.

5.2 Clathrates [25, 24]

Clathrates (lat. clatratus 3 = grated [29]) are inorganic—in the majority of cases even inter-metallic—compounds and became famous because of their thermoelectric properties. As the name suggests, the atoms are arranged tetrahedrally and by that form a periodic network of cages in which guest atoms are enclosed. The first clathrates described were “clathrate hydrates” with the structure $8 M_a \cdot 16 M_b \cdot [136 H_2O]$ which are stable only at very low temperatures and rather high pressures. Later on the name clathrates was then given also to inter-metallic compounds with a similar structure. Nowadays, clathrates are distinguished by 9 groups:

Type	Ideal formula	Structure
I	$6 X \cdot 2 Y \cdot 46 T$	$Pm\bar{3}n$
II	$8 X \cdot 16 Y \cdot 136 T$	$Fd\bar{3}m$
III	$20 X \cdot 10 Y \cdot 172 T$	$P4_2/mnm$
IV	$8 X \cdot 6 Y \cdot 80 T$	$P6/mmm$
V	$4 X \cdot 8 Y \cdot 68 T$	$P6_3/mmc$
VI	$16 X \cdot 156 T$	$I\bar{4}3d$
VII	$2 X \cdot 12 T$	$Im\bar{3}m$
VIII	$8 Y \cdot 46 T$	$Im\bar{3}m$
IX	$16 Y \cdot 8 X \cdot 100 T$	$P4_132$

Table 1: The 9 different types of clathrates. Not all them are inter-metallic compounds [25].

5.3 Clathrates $Ba_8Zn_xGe_{46-x-y}\square_y$

In general, studies of thermoelectric properties in terms of Seebeck coefficients revealed that very few material classes exhibit reasonable performance. Promising candidates are clathrate, zeolite, skutterudite and clathrasil compounds which are of recent research interest. In this work, we are interested in the clathrate type I compound $Ba_8Zn_6Ge_{40}$ and its closely related derivatives $Ba_8Zn_6Ge_{39}$, $Ba_8Zn_7Ge_{39}$ and $Ba_8Zn_8Ge_{38}$ because they show a promising Seebeck effect. The typical structural elements are pentagonal dodecahedra (12 faced body with of 20 atoms,

see Figure 8.a), and tetrakaidecahedra (14 faced body of 36 atoms, see Figure 8.b).

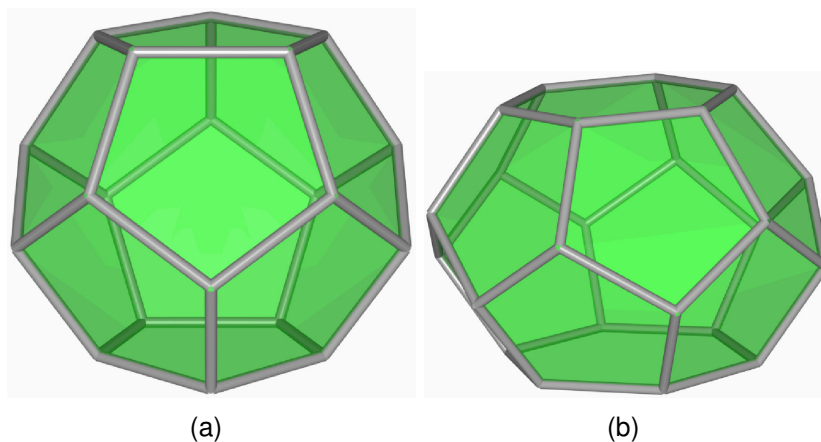


Figure 8: a. Pentagonal dodecahedron; b. Hexagonal truncated trapezohedron (Tetrakaidecahedron)

In the crystal these structural elements form a structure as shown by Figure 9. In each polyhedron a Ba-atom is located.

The crystal structure of $Ba_8Zn_6Ge_{40}$ has the point group symmetry O_h (with its 48 symmetry operations), while its compositional derivatives have a reduced symmetry. It should be noted here, that the crystal structure of the experimental samples even with stoichiometries deviating from $Ba_8Zn_6Ge_{40}$ were measured to be of high symmetry. This means that some averaged occupation at certain lattice sites have taken place. This is due to the fabrication of the samples at high temperatures and the freezing in of the high-temperature structure for the actual measurements. The symmetry of the compounds $Ba_8Zn_6Ge_{39}$ and $Ba_8Zn_7Ge_{39}$ is of point group C_3 (3 symmetry operations), and of $Ba_8Zn_8Ge_{38}$ of point group C_2 (2 symmetry operations). In the present study for the respective compounds, vacancies are all placed at 16i site. The reason is, that DFT calculations have shown that this site is energetically preferred, as also supported by experiment. Because the symmetry is different for the discussed cases, this is also the case for their physical properties, and

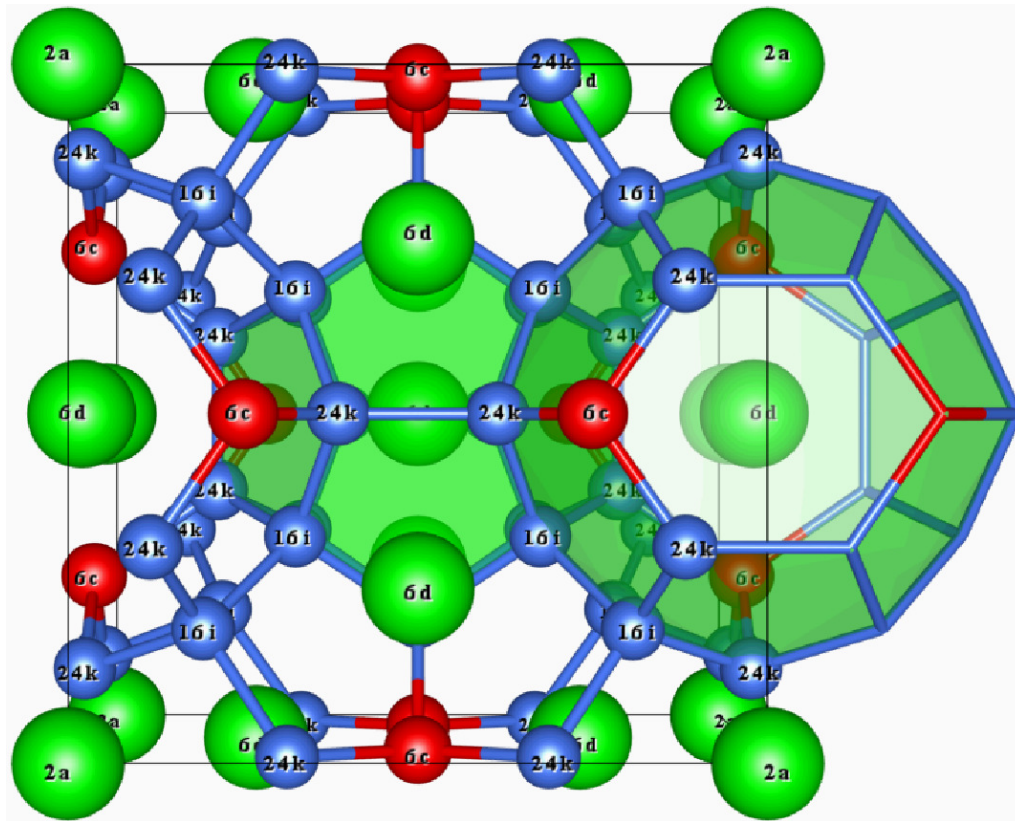


Figure 9: General crystal structure of a type I clathrate—in the present case site 2a & 6d is occupied by Ba, site 6c by Zn, and finally sites 16i and 24k by Ge ; Ba—green, Zn—red, Ge—blue.

in particular for the electronic structure which is needed for deriving the Seebeck coefficients and the conductivity.

All results presented and discussed later were derived from VASP calculations in which all structural parameters including unit cell shape, lattice parameters and atomic positions were fully relaxed.

5.4 Results

5.4.1 General remarks

It is speculated that for some of the Ba-based clathrate compounds the Seebeck coefficient is high because of the heavy and loosely bound barium atoms which absorb thermal energy and thus hinder the transport of thermal energy. (This was elaborated in subsection 2.2 in which it was argued that a good thermal conductivity is disadvantageous due to its effects on the figure-of-merit, ZT). This is knowledge and the dependency of ZT on S^2 makes it desirable to achieve large Seebeck coefficients. As shown in Figures 8.a, 8.b and 9 barium is enclosed in either a cage made of zinc atoms (Ba at the 2a position) or a cage made of zinc and germanium atoms (Ba at the 6d position).

The Seebeck coefficients for the above mentioned Ba-Zn-Ge composites were calculated making use of the modified programme package BoltzTraP. The investigated derivated structures aside from $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$, $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$ and $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ are several dopings of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$. Compounds with fractional occupation were treated by the so-called rigid band model to get a clearer view on the comportment of the Seebeck effect of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$. The rigid band model postulates that the electronic structure does not change when electrons are added or removed, and only the Fermi energy is adjusted accordingly.

The doped materials are either electron doped (electrons added) or electron hole (electrons removed) doped, according to the nomenclature for semiconductors. And the dopings have been accomplished by adding or removing zinc respectively germanium. The amount of doping is calculated from the number of valence electrons as follows: barium provides 2 valence electrons to the system, for zinc—like barium—one may count 2 valence electrons (its d-shell is considered not to contribute), and finally germanium has 4 valence states. Based on this classification for $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ one counts 188 valence electrons in total, for $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$

there are 186 valence electrons, for $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ 184 valence electrons and finally for $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ 184 valence electrons. By that, the compounds differ in the number of charge carriers, which decreases from $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ by 2 electrons to $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$ and by another 2 electrons to $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ and $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ (see Figure 10).

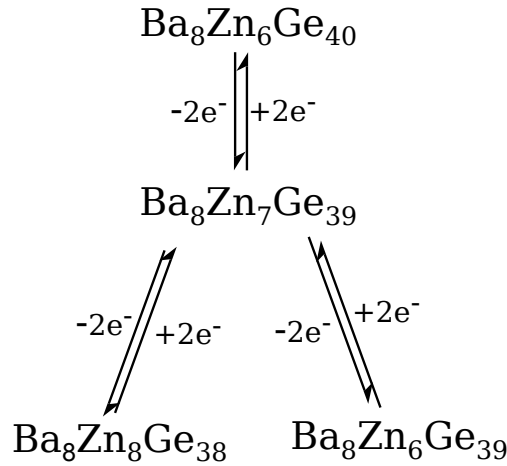


Figure 10: Diagram of charge relations between the $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$, $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$, $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ and $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ compounds.

Calculations for some of the mentioned materials have been done via VASP for the electronic band structures and densities of states. In each of these calculations, the crystal structure in terms of cell shape, lattice parameters and atomic positions was fully relaxed. Then, the electronic structure in terms of sets of Kohn-Sham energy levels for each $\vec{k}$ -point was taken as input for BoltzTraP. Actual VASP calculations were only made for $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$, $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$, $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ and $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$. All other cases of dopings (as described above) were treated within the rigid band model.

For small changes of composition (in the order of tenth of an electron) the rigid band calculations may be assumed to be accurate, depending on the requirement, that the electronic structure near Fermi energy is not

changed upon doping. In principles this has to be checked, as done in the work of Zeiringer et al. [34].

It is believed and it can be argued (at least for low temperatures) that for favourable Seebeck coefficients the Fermi energy is in or close to a band gap. For compounds of type $\text{Ba}_8\text{M}_x\text{Ge}_{46-x}$ this was proposed theoretically and proved experimentally and theoretically. As M (M being the dopant) replaces Ge, $4 \cdot x$ electrons are removed while $n \cdot x$ electrons are added (with n being the valency of the dopant). The Ba_8 atoms always provide 16 electrons. On the basis of this considerations a critical concentration for the Fermi energy falling in the gap was formulated [34]:

$$x_{\text{gap}} = \frac{16}{4 - n} \quad (66)$$

x_{gap} ... amount of substituted atoms
 n ... valency of substituted atoms

This is based on the fact (see results above in chapter 5.1.3), that the electronic structure of the pure Ge_{46} has a large gap of 1.46 eV which is maintained but strongly reduced upon filling the crystal structure with Ba and M atoms. When one considers that Zn provides 2 valence electrons the expression for x_{gap} changes to

$$x_{\text{gap}} = \frac{16}{4 - 2} = \frac{16}{2} = 8 \quad (67)$$

It turned out that the claimed relation holds for a variety of related compounds as proven by experiment and calculations, e.g. for compounds with metal atoms such Ag, Au, Cu, Ga, and so on.

When applying the rigid band model the chemical potential (corresponding to the Fermi energy at $T = 0\text{K}$) is derived by

$$N = \int_{-\infty}^{\infty} N(E) f(T, \mu) dE \quad (68)$$

$N = N_0 + \Delta n$... total number of valence electrons
 N_0 total number of valence electrons of reference structure
 Δn ... amount of electron or hole doping
 N_0 ... number of valence electrons of reference compound
 $F(T, \mu)$... temperature-dependent Fermi-Dirac distribution
 $N(E)$... DOS of reference compound

The doping in terms of adding or removing electronic charge can be translated into chemical doping, taking proper account of the number of valance states. For example, considering $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ as a reference and adding 0.01 electrons the chemical composition might be changed to $\text{Ba}_8\text{Zn}_{7.995}\text{Ge}_{38.005}$. This doping/composition relationship is not unique in one direction. If, however, the experimental composition is given then the corresponding number of valence electrons can be derived. It should be noted that there is a considerable experimental uncertainty for determining the correct composition of a sample. According to P. Rogl, variations of 0.1 of an atomic fraction are easily possible. This might look like a small number, but when it is translated into the corresponding number of valence electrons, then Δn might vary as much as by 0.4. As a consequence, the Fermi energy is shifted and the calculated transport properties may vary rather significantly too. The coefficients of the Seebeck tensors as calculated from the electronic structure can be formulated in a compact manner by

$$S(T, \mu) = \frac{K_1}{eTK_0} \quad (69)$$

$S(T, \mu)$... Seebeck coefficient
 K_n ... transport Integrals
 T ... temperature

using the definition

$$K_n = \frac{1}{4\pi^3} \frac{\tau}{\hbar} \sum_{i,\vec{k}} \vec{v}(i,\vec{k}) \vec{v}(i,\vec{k}) (E(i,\vec{k}) - \mu)^n \left(-\frac{\partial f_\mu(T, E(i,\vec{k}))}{\partial E} \right) \quad (70)$$

$E(i,\vec{k})$... Kohn-Sham energies of DFT calculation

$\vec{k}$... vector in Brillouin zone

i ... band index

K_n ... transport Integrals

$\vec{v}(i,\vec{k})$... electron velocity

μ ... chemical potential

τ ... relaxation time

$\hbar$... reduced Planck constant $\hbar = h/2\pi$

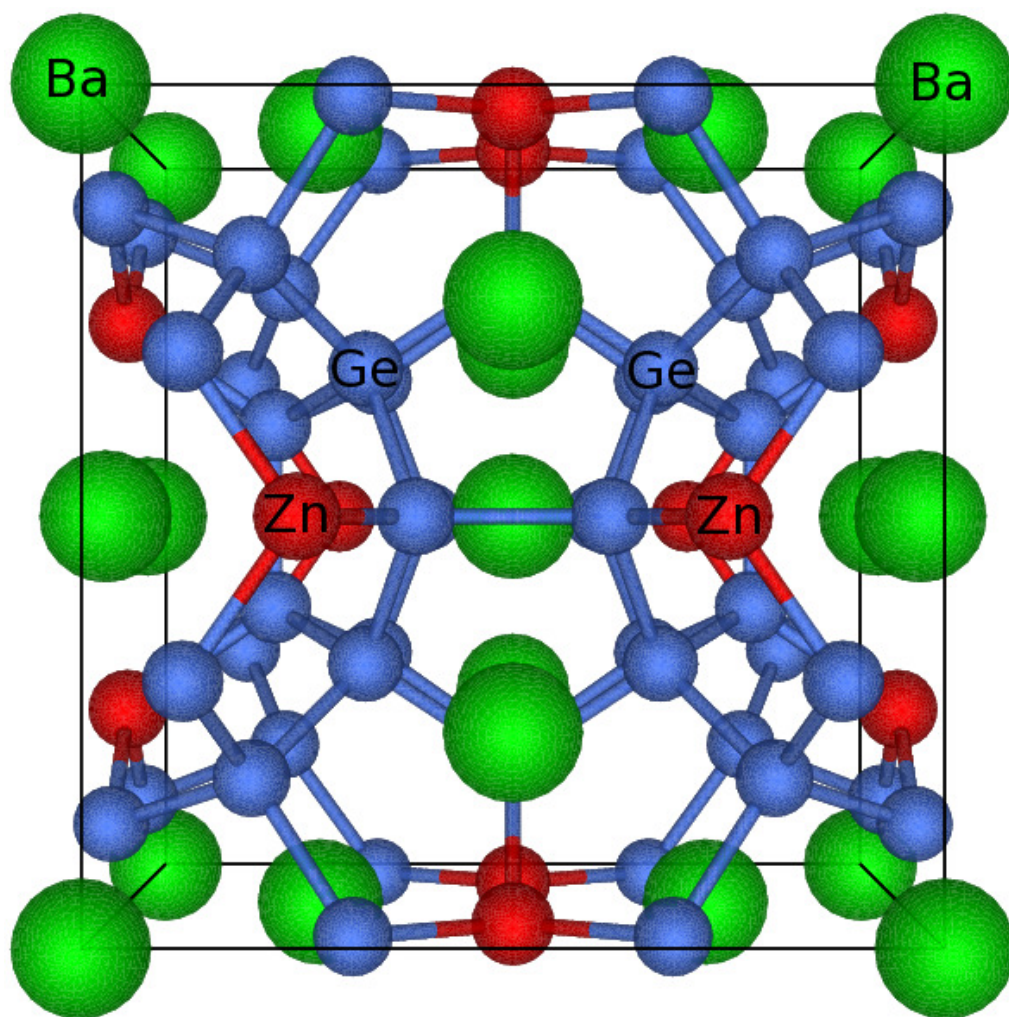
5.4.2 $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ 

Figure 11: Crystal Structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$: barium atoms—green, zinc atoms—red, germanium atoms—blue.

The crystal structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ is cubic. In Schoenflies notation the point group symmetry is O_h , in Hermann-Mauguin notation the corresponding space group is $\text{Pm}\bar{3}\text{n}$. It can be seen from Figure 11 that the centre of the unit cell is formed by the pentagonal dodecahedron. Grouped around this pentagonal dodecahedron are twelve hexagonal truncated trapezohedra. Per unit cell there are only six hexagonal trun-

cated trapezohedra and two pentagonal dodecahedra.

Because of the full cubic symmetry the Seebeck tensor is diagonal and all its elements are equal. Therefore, only one component needs to be calculated and is presented. In the low temperature range the absolute values of the Seebeck coefficient is rather small according to Figure 14. It can be seen that it increases from zero to nearly $1 \mu V K^{-1}$ only to drop to $-9 \mu V K^{-1}$ in the normal temperature region and up to 900 it reaches the value $-11 \mu V K^{-1}$. However, these values are all rather small and one can expect that the figure-of-merit or rather ZT will be also small, because there the square of the Seebeck coefficient enters, according to Equation (20).

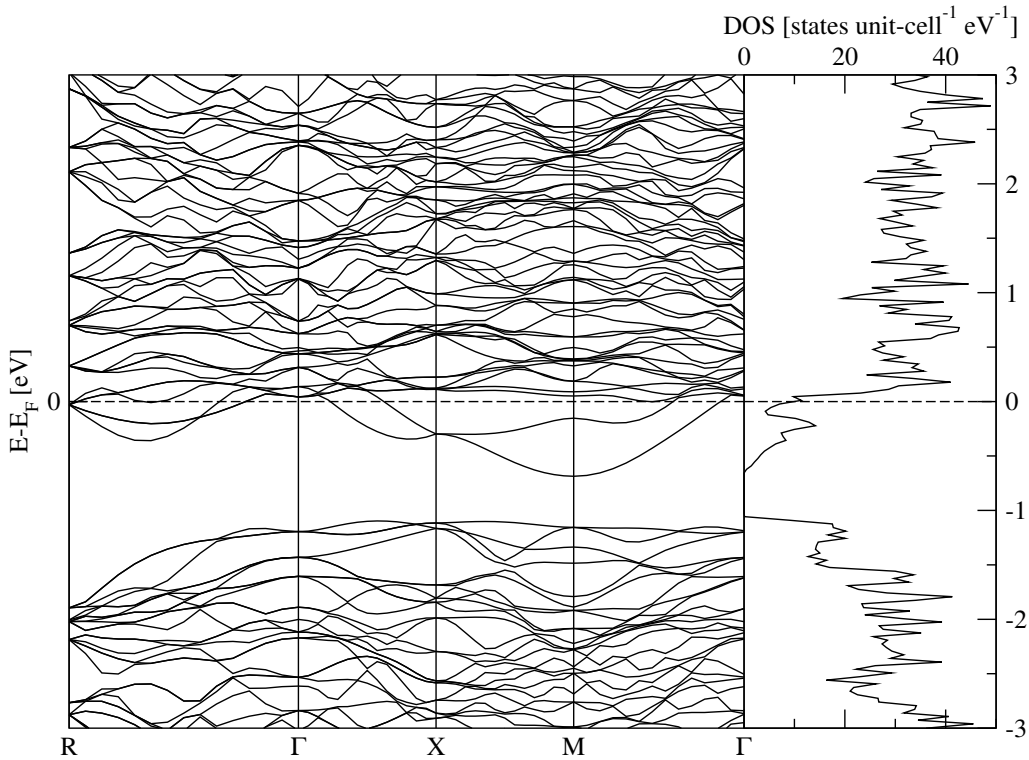


Figure 12: Band structure and density of states of the clathrate type I compound $Ba_8Zn_6Ge_{40}$.

The density of states (DOS) and the band structure is shown in Figure 12. The DOS as well as the band structure is well within agreement of published data [10]. The discrepancy between the DOS as directly derived from VASP in Figure 12 and the one derived from BoltzTraP in Figure 13 is due to the much larger $\vec{k}$ -point set used in the BoltzTraP application. For the VASP DOS a 5x5x5 mesh was constructed, whereas for BoltzTraP a much finer 11x11x11 mesh was utilised. The reason is, that BoltzTraP needs a very fine mesh, because electron velocities are needed which are defined as derivatives of the band structure along $\vec{k}$. The gap in the DOS, however, remains quite unchanged.

Density Of States of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$

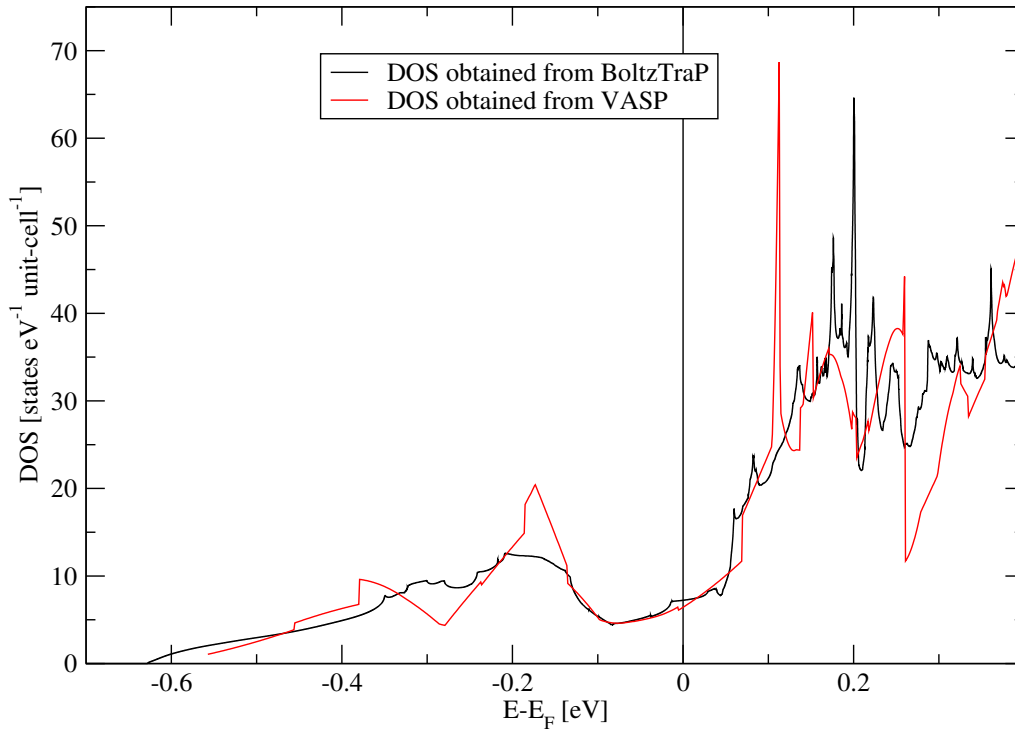


Figure 13: Density Of States of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$. BoltzTraP result: black curve; VASP result: red curve. Fermi energy at $E=0$ eV

Figure 13 reveals the DOS of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ showing the results as obtained directly from VASP and obtained from BoltzTraP. As discussed

above, BoltzTraP utilises a much finer grid in $\vec{k}$ space, consequently BoltzTraP resolves finer and more detailed features of the DOS.

From Figure 13 it can be seen that there is no band gap near Fermi energy, which might be one reason that the Seebeck coefficient (i.e. its absolute value) is rather small. The gap appears -0.6 eV below Fermi energy. In fact, if performing BoltzTraP for hole doping (i.e. reducing the number of filled states by shifting the Fermi energy to smaller values within the rigid band model) it appeared that the Seebeck coefficients becomes more favourable (i.e. its absolute values are increasing).

Seebeck Coefficient of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$

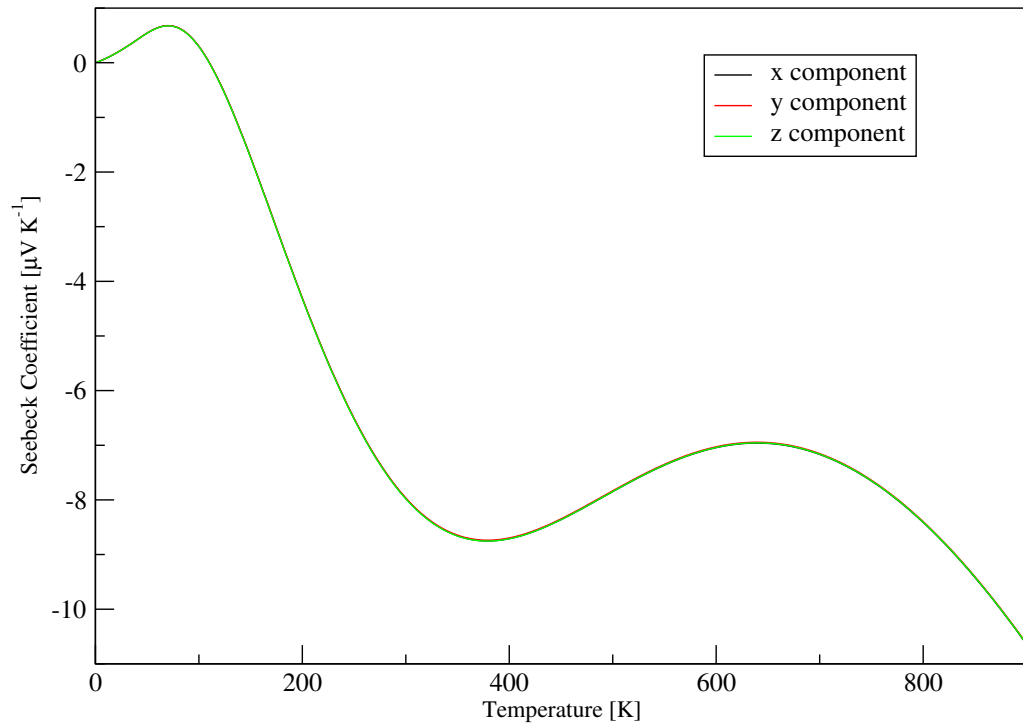


Figure 14: Seebeck coefficient of cubic $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ vs. temperature.

5.4.3 $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$

As mentioned above, reducing the number of valence electrons is desirable for shifting Fermi energy in direction to the gap. In the present case this was done by removing one germanium atom from the lattice of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ by creating a vacancy in the corresponding germanium sublattice, according to Figure 15. This change in composition corresponds to a removal of 4 valence states from the system.

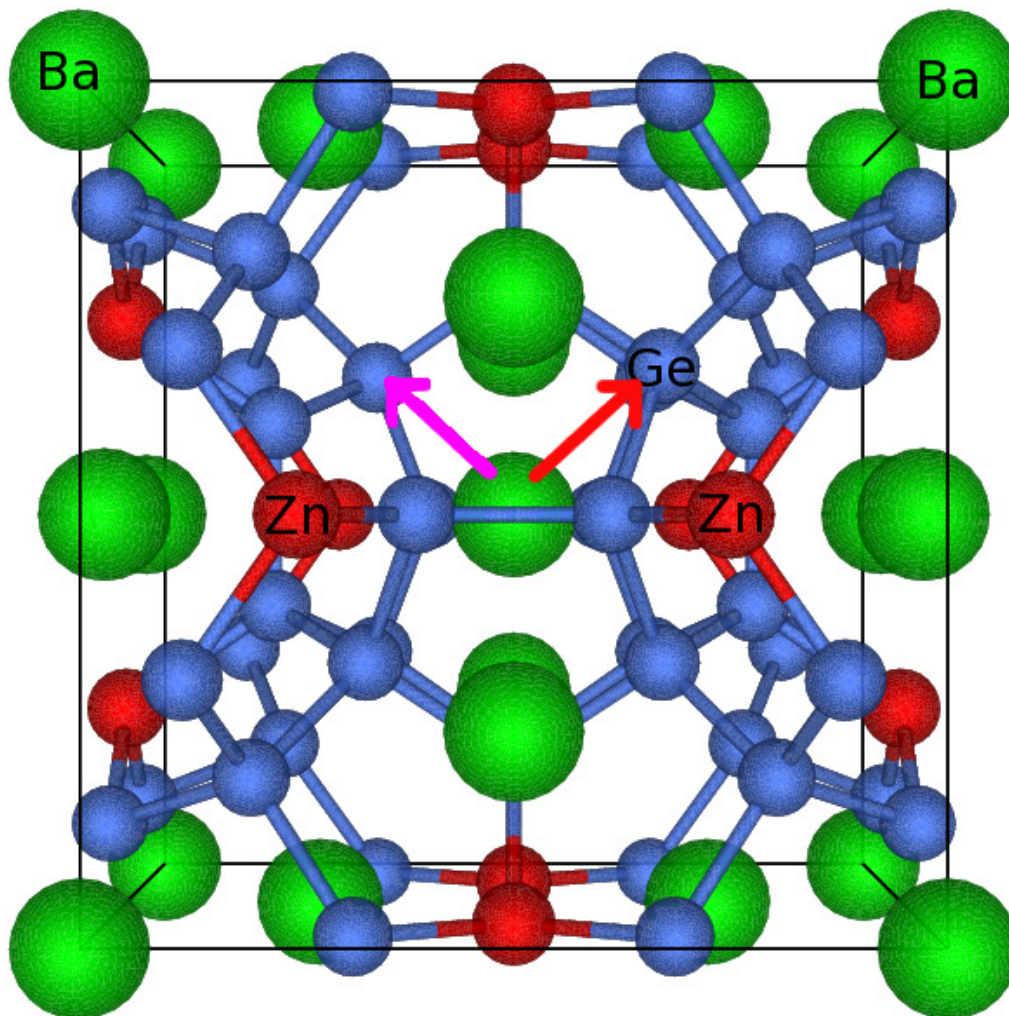


Figure 15: Crystal structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$: barium atoms—green, zinc atoms—red, germanium atoms—blue, the magenta arrow points at the vacancy.

By removing one germanium atom the original symmetry of the fully stoichiometric reference compound $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ is destroyed and severely reduced to space group C_3 . This has the immediate consequence that VASP calculations become significantly more expensive, because the number of inequivalent $\vec{k}$ -points is much larger now. As discussed above, the experimental samples usually maintain cubic symmetry, even after the perfect stoichiometry is changed. This is because of the sample preparation at elevated temperatures. In order to mimic the experimental conditions VASP calculations for $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ were also made for a cubic unit cell and the atomic positions were kept fixed as obtained for $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$.

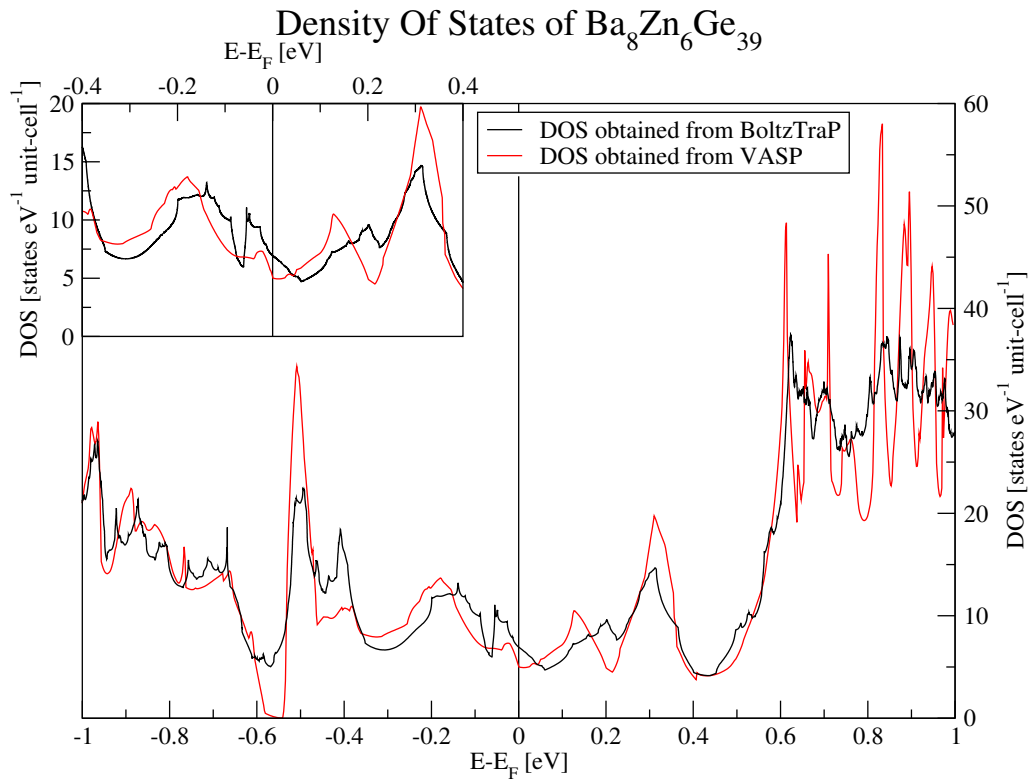


Figure 16: Density Of States of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ with a germanium vacancy. Structural parameters such as cell shape, lattice parameters and atomic positions are fully relaxed.

As can be seen from Figure 16 the DOS becomes significantly changed when compared to the DOS of the stoichiometric compound, and there is no gap to be found anymore. The VASP DOS shows a gap far below Fermi energy, which however disappears in the much finer resolved DOS achieved by BoltzTraP. Nevertheless, the Seebeck coefficient improved significantly in comparison to $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$, as can be seen in Figure 17. It is rather remarkable, that the Seebeck tensor shows the symmetry of the full cubic lattice, i.e. 3 components are different from zero and they are all equal, although symmetry is now reduced. This might be due to the electronic states which contribute to the Seebeck coefficient, which remain rather unimpressed by the vacancy.

Seebeck Coefficient of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$

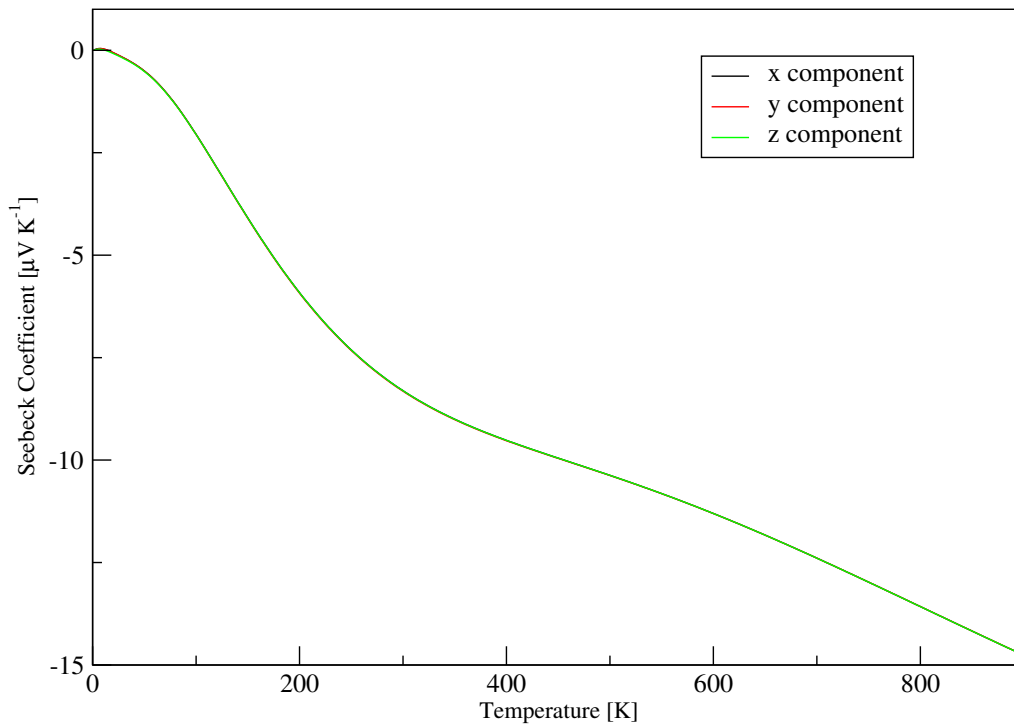


Figure 17: Seebeck coefficient of the vacancy structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$.

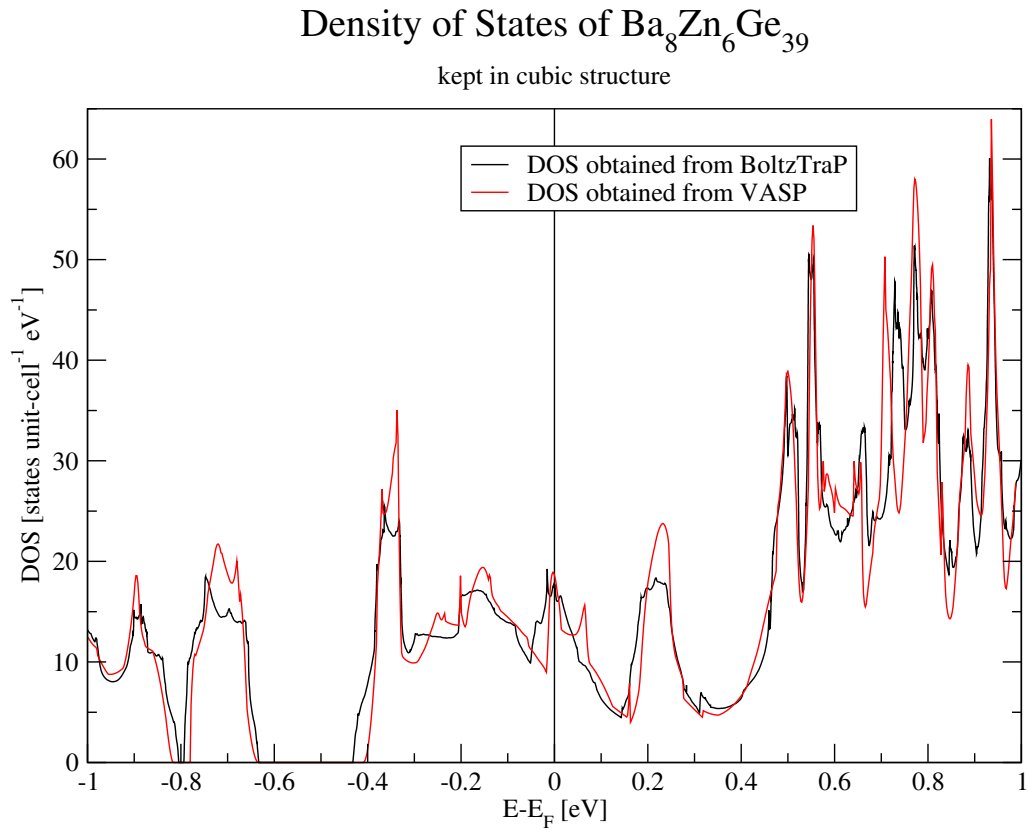


Figure 18: Density Of States of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ with frozen cubic structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$.

Keeping the cubic structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ frozen for the calculation of the electronic structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ the DOS in Figure 18 reveals some significant changes when compared to the fully relaxed case: the most striking feature is that there is now a gap of approximately 0.2 eV from approximately -0.6 eV to -0.4 eV below Fermi energy.

Figure 19 shows the Seebeck coefficient of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ in the frozen cubic structure. In comparison to the fully relaxed case, there are some significant changes. In particular, for the frozen structure there appears now a deep minimum just below 200K which is smeared out for the fully relaxed case. The overall qualitative behaviour as a function of temperature remains rather similar, and also the highest absolute values in the given temperature range are about the same. Interestingly, again the

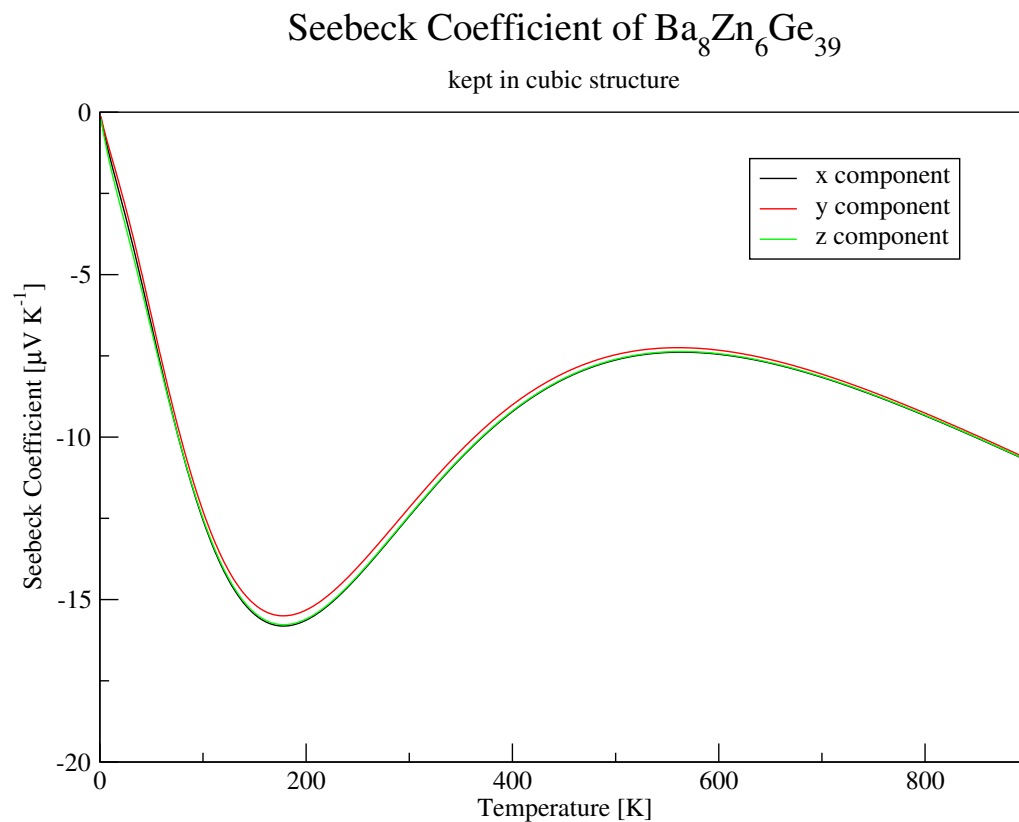


Figure 19: Seebeck coefficient of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ with frozen cubic structure.

Seebeck tensor seems to be of cubic symmetry, although the crystal structure has also reduced symmetry due to the vacancy.

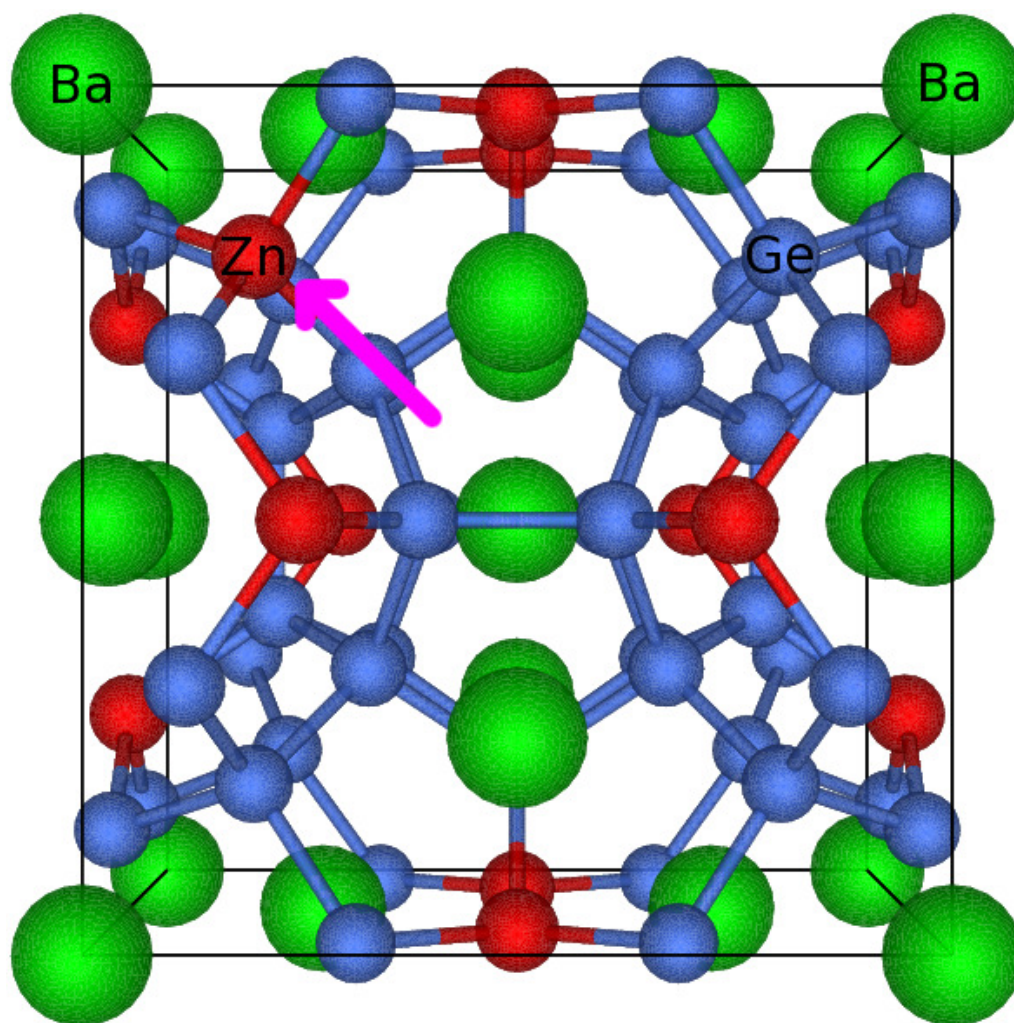
5.4.4 $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$ 

Figure 20: Crystal structure of $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$: barium atom—green, zinc atom—red, germanium atom—blue, the magenta arrow points at the zinc atom in the germanium sub-lattice.

The change of the crystal structure in comparison to the reference compound $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ results in a symmetry change equal to the change for the vacancy structure, as discussed just above, resulting in the same group symmetry of C_3 . Though the polyhedral symmetry was destroyed in the crystal structure of $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ it remains intact for $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$.

Density Of States of $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$

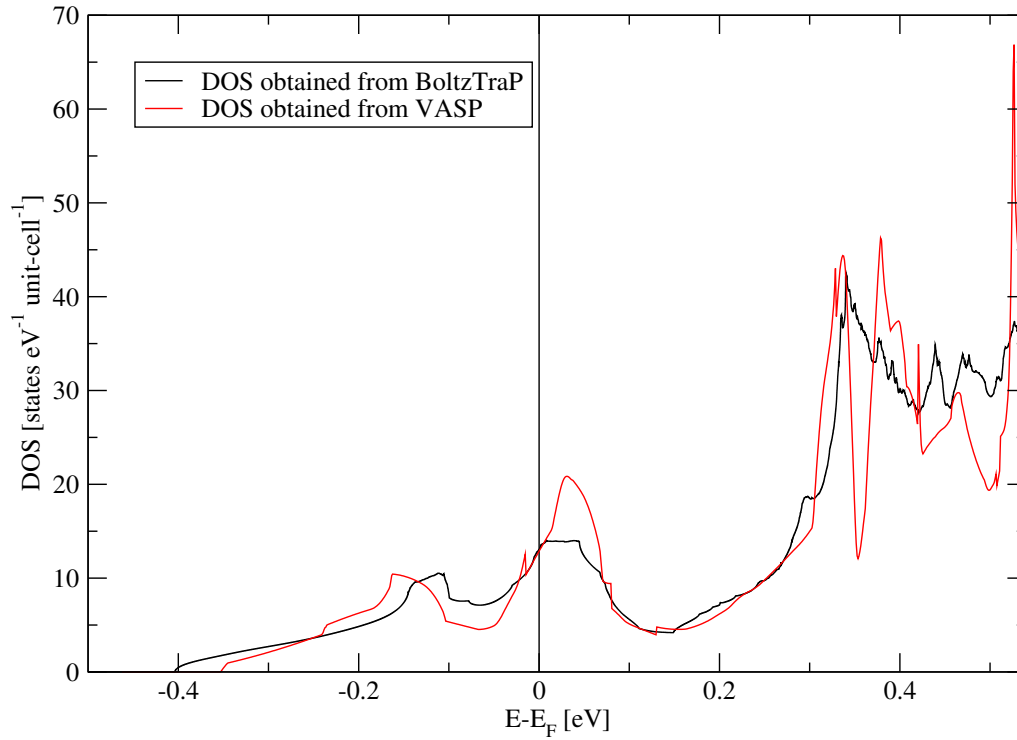


Figure 21: Density Of States of $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$.

Inspecting the DOS in Figure 21 one finds the Fermi energy still is not located close to the band gap appearing -0.4 eV below Fermi energy, although 2 valence electrons are lost when compared to $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$. Nevertheless, according to Figure 22 the absolute value of the Seebeck coefficient has increased considerably, its maximum being about twice as large as the one for the vacancy structure. This might be due to the fact that the Fermi energy now falls into the descending flank of a peak in the DOS: the Seebeck coefficient—at least at low temperatures—is proportional to the derivative of the DOS at Fermi energy.

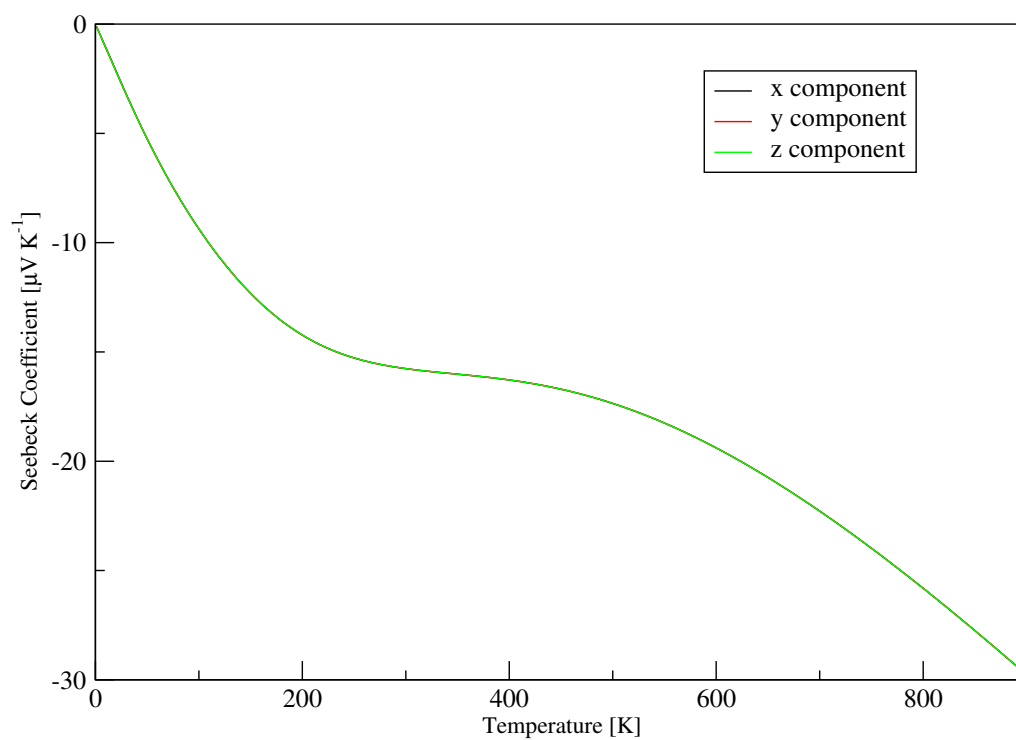
Seebeck Coefficient of $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$ 

Figure 22: Seebeck coefficient of the compound $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$ vs. temperature.

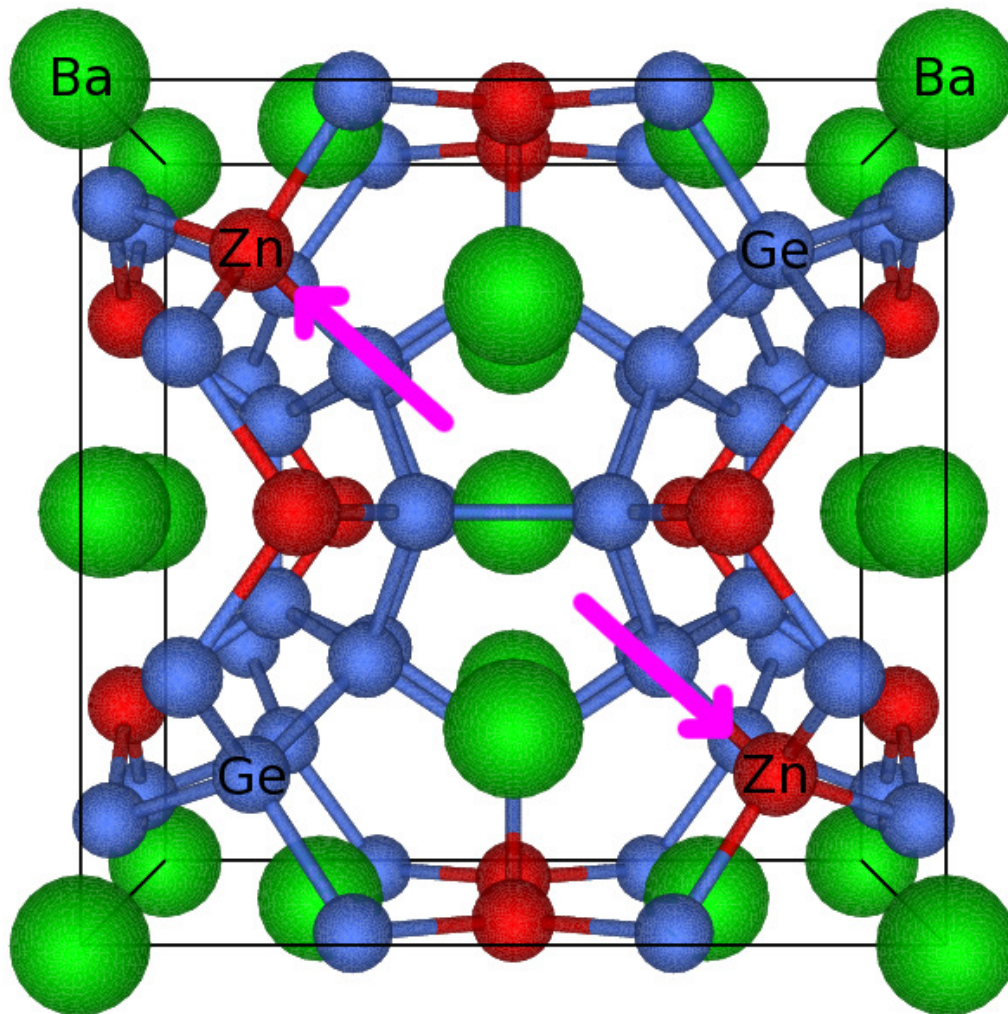
5.4.5 $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ 

Figure 23: Crystal structure of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$: Barium atoms—green, Zinc atoms—red, Germanium atoms—blue, the magenta arrows point at the two Zinc positions in the Germanium sublattice.

As discussed above, now the critical number of valence electrons is achieved and the Fermi energy falls into a small gap, according to Figure 24. Compared to the reference compound $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ 4 valence electrons are lost. As already mentioned, one might now expect that the Seebeck tensor is getting large, at least larger than it was the case for the

Density Of States of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$

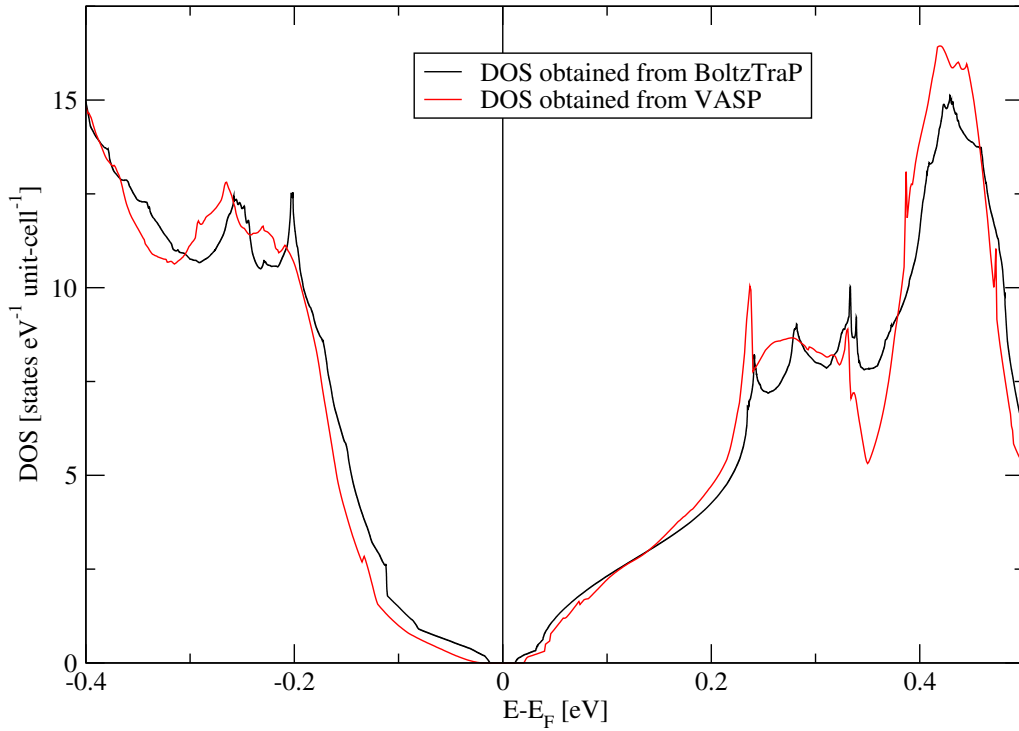


Figure 24: Density Of States of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$.

metallic systems as discussed above. This is in fact the case, as shown in Figure 25. First of all, we realise a significant splitting of the coefficients appearing already at rather low temperature. Obviously, this is the result of breaking the full cubic symmetry. Interestingly, in all other cases of compounds with reduced symmetry the splitting of the tensor components is rather negligible, presumably because the tensor components are much smaller than in the case of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$. The components show strong fluctuations at low temperatures reaching a maximum of $600 \mu\text{V K}^{-1}$ and a minimum of $-300 \mu\text{V K}^{-1}$ below 50K. However, such temperatures are not of practical importance, and it can be seen that at about room temperature only the y-component is still interestingly large, being about $100 \mu\text{V K}^{-1}$. The very large/small values of the Seebeck components at very low temperatures have—however—to be taken with care: according to extensive test calculations there is a strong dependence on one of the

parameters, $lpfac$, which determines the smoothness of the band structure interpolations. The $lpfac$ in fact is an expansion coefficient applied to the $\vec{k}$ -points (see chapter 4.4.1). Various calculations have been made with $lpfac=15, 45, 85, 95, 105$ and 115 . According to Figure 26 at temperatures below 50K the Seebeck coefficients strongly depend on this parameter, making the results rather not trustful. Clearly, some working on the code is necessary to overcome this problem which is due to the fact, that the Fermi energy falls now precisely into a gap. It has to do with the calculation of the temperature dependent chemical potential which needs numerical improvement. At temperatures above 50K all disparate curves more or less merge into one result for all the Seebeck components. Therefore the results can be considered to be trustful in the higher temperature range. It should be noted that in Figure 26 the largest value $lpfac=115$ was chosen for the calculation of the Seebeck coefficients.

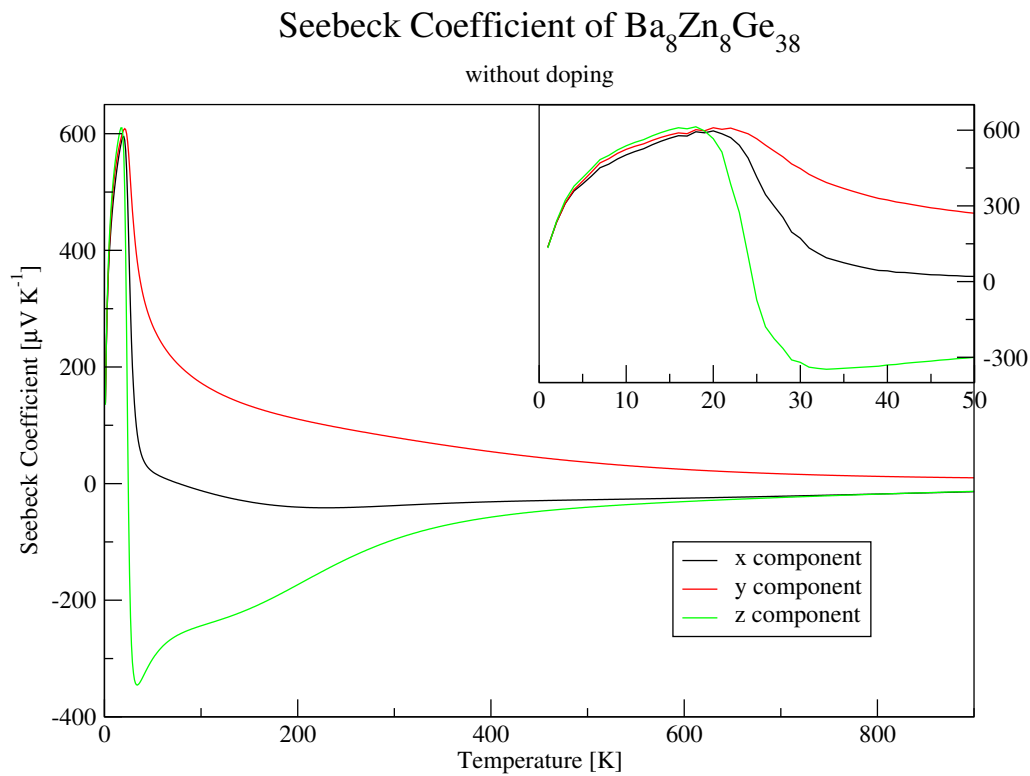


Figure 25: Seebeck coefficient of $Ba_8Zn_8Ge_{38}$ as calculated by BoltzTraP with $lpfac=115$ vs. temperature.

At higher temperatures of 400K a comparison can be made with the work of Christensen and Iversen [8] who published a Seebeck coefficient of $-175 \mu\text{V K}^{-1}$. In the present work, the 3 tensor components are -31.2 [x-component], 54.8 [y-component] and -57.6 [z-component]. Taking the arithmetic average amounts to $-11 \mu\text{V K}^{-1}$, being less negative by about one order of magnitude. Since—from a numerical point of view—the BoltzTraP calculations are trustful at this temperature the differences have to be attributed to some other reasons. One reason might be that we fully relaxed the structure in the present VASP calculation.

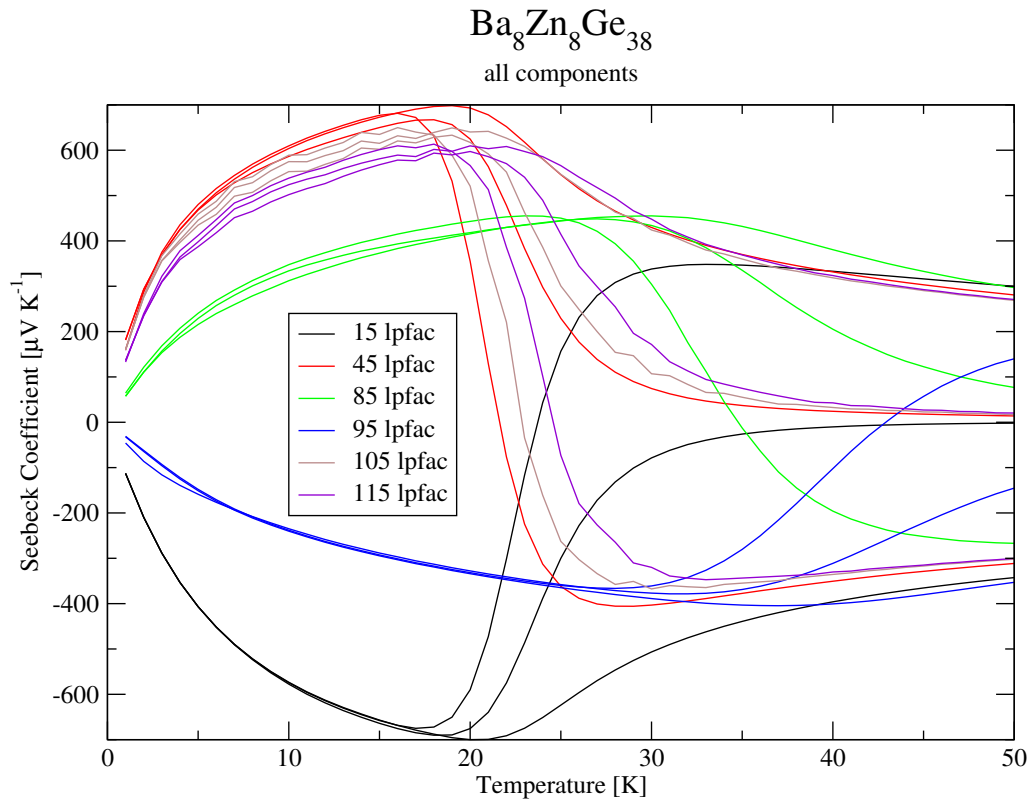


Figure 26: Low temperature Seebeck coefficients of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ all components varying the BoltzTraP parameter l_{pfac} (an expansion coefficient see chapter 4.4.1).

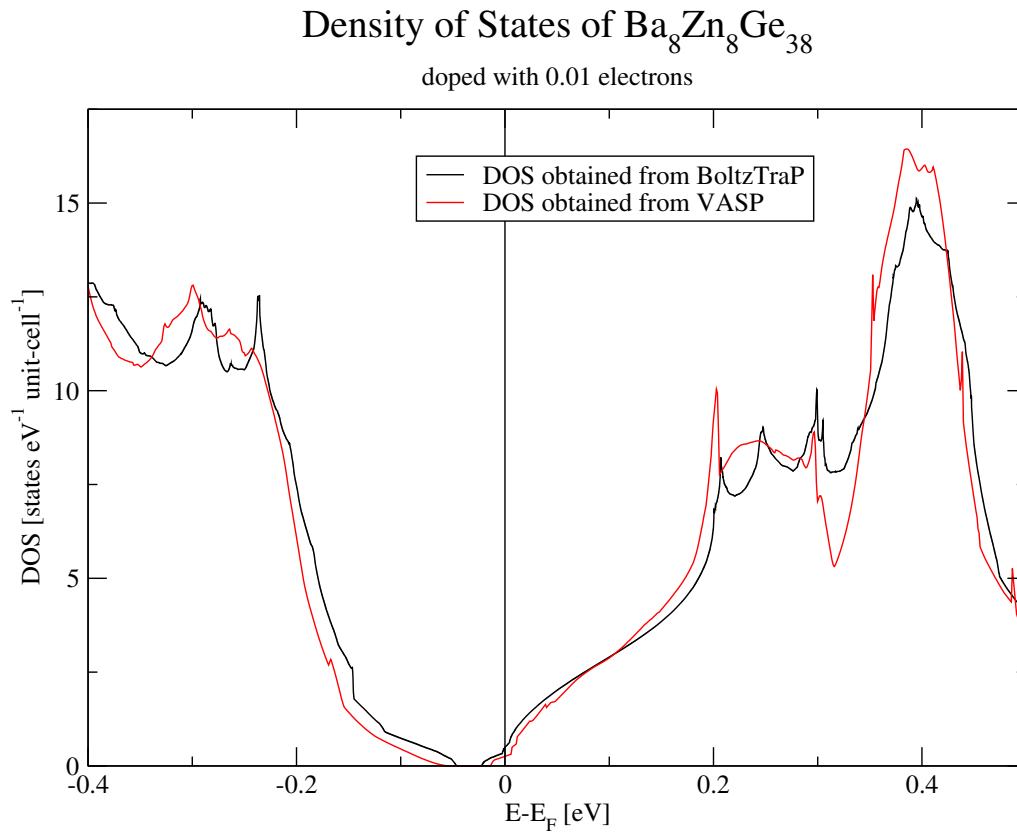


Figure 27: Density Of States of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ with 0.01 electrons doping.

As mentioned in the previous paragraphs for the semiconducting phase $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ the BoltzTraP programme in its present version seems to have some numerical problems at very low temperatures. This is an important finding of this diploma work and currently this problem is more deeply investigated in the group of R. Podloucky. However, at sufficiently high temperatures (which for $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ is only about 50K because of the small gap) the mentioned problem vanishes and the results become trustful. Another—physical—possibility is to dope the material by smaller or larger amounts of charge carriers. In this case, the Fermi energy is placed close to the valence band maximum or conduction band minimum. At sufficiently high temperatures the Seebeck coefficients as a function of temperature for the small gap case and the very weakly doped materials

should behave qualitatively similar. This is indeed the case as realised by comparing Figures 26 and 31. Physically, the material is not a semiconductor anymore because its conductivity must be metallic. In the latter figure the results for doping $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ by 0.01 electronic states are shown. As mentioned earlier, the effect of small doping is modelled within the rigid band concept, in which the DOS of the parent material remains unchanged but only the Fermi energy has to be adjusted accordingly to account for the changed number of valence states. In the present doping case, electronic states are added and the Fermi energy shifts to higher energies, as shown on Figure 27. It should be noted, that the energy zero of the DOS is usually placed at Fermi energy, which in the present case means that the DOS has to shift to lower energies with respect to the Fermi energy. Therefore, the gap is now below Fermi energy in Figure 27.

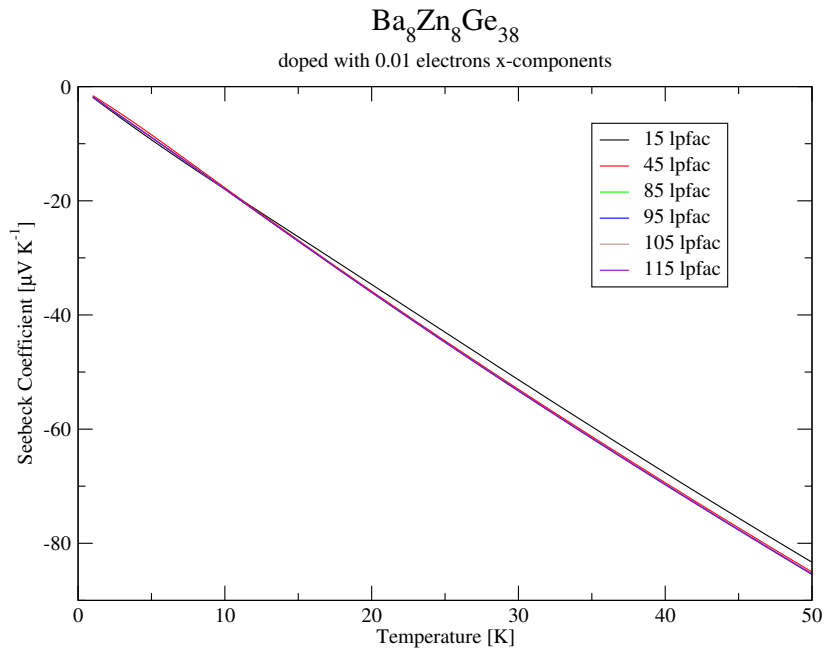


Figure 28: *x*-component of the low temperature Seebeck tensor of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 0.01 electrons.

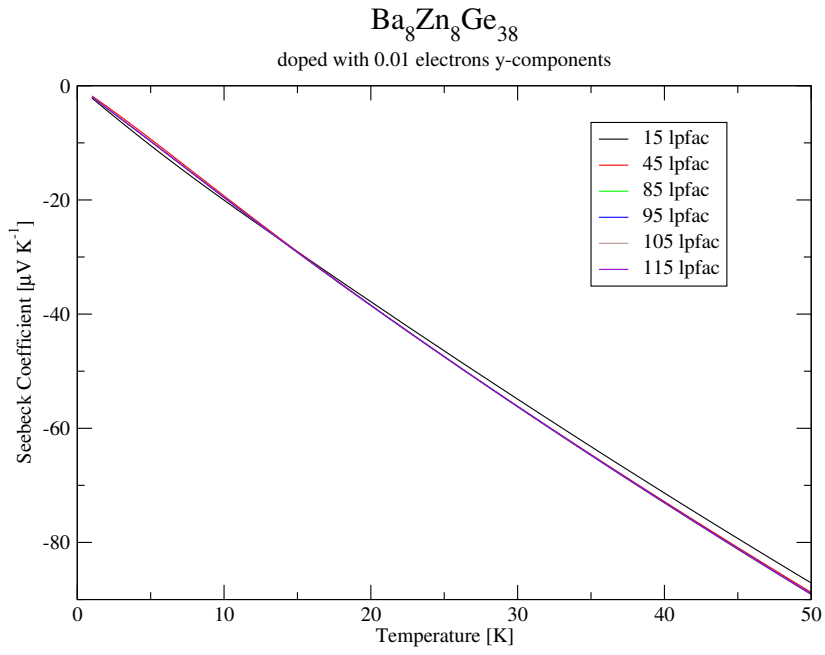


Figure 29: y-component of the low temperature Seebeck coefficients of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 0.01 electrons.

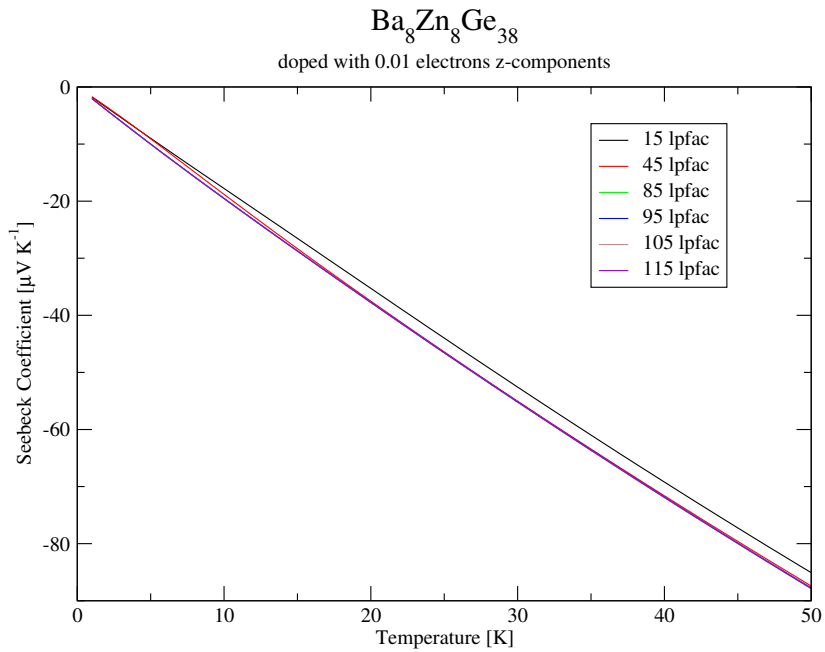


Figure 30: z-component of the low temperature Seebeck coefficients of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 0.01.

Now, in the doped case the numerical difficulties of BoltzTraP disappear, as illustrated by the Figures 28, 29 and 30 studying all three components of the Seebeck tensor as a function of the parameter l_{pfac} , as done for the gap case. Clearly, all lines coincide apart from the one for the lowest value of l_{pfac} , which points to a very satisfying numerical convergence. All these numerical tests indicate that l_{pfac} should be sufficiently large, being at least about 100, which makes the BoltzTrap calculations more costly but still feasible.

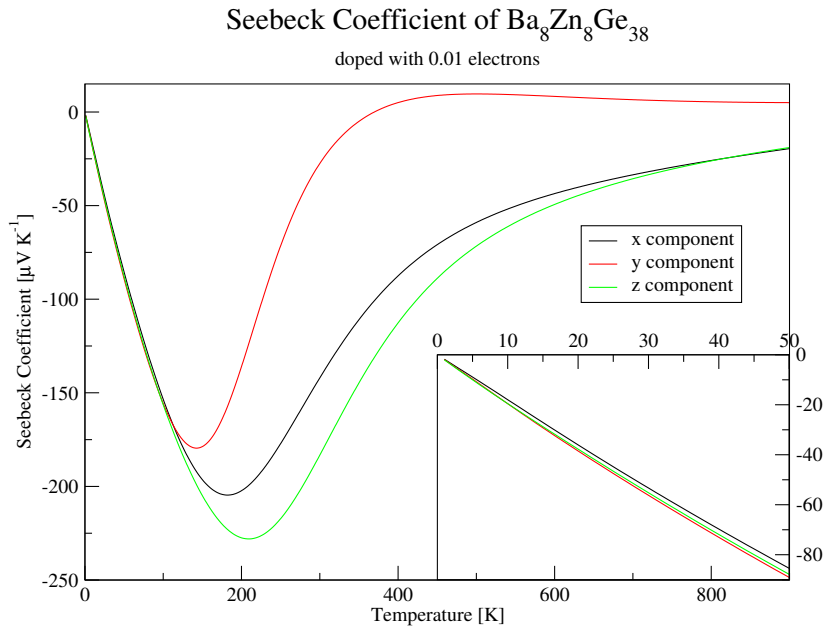


Figure 31: Seebeck coefficient of $Ba_8Zn_8Ge_{38}$ doped with 0.01 electrons calculated with $l_{pfac}=115$ as a function of temperature.

Inspecting Figure 31 showing the Seebeck coefficients up to 900 K a few significant features are noticeable: at low temperatures below 300 K there is no splitting and at higher temperatures the x- and the z-component behave similarly, coinciding at temperatures about 750K. The y-component is significantly split off from the other ones. A minimum value of $225 \mu V K^{-1}$ at 200 K for the z-component is derived, which makes the doped compound interesting for applications. (Of course, as discussed above other properties such as electric and thermal conductivity also play

a role in achieving an acceptable high ZT).

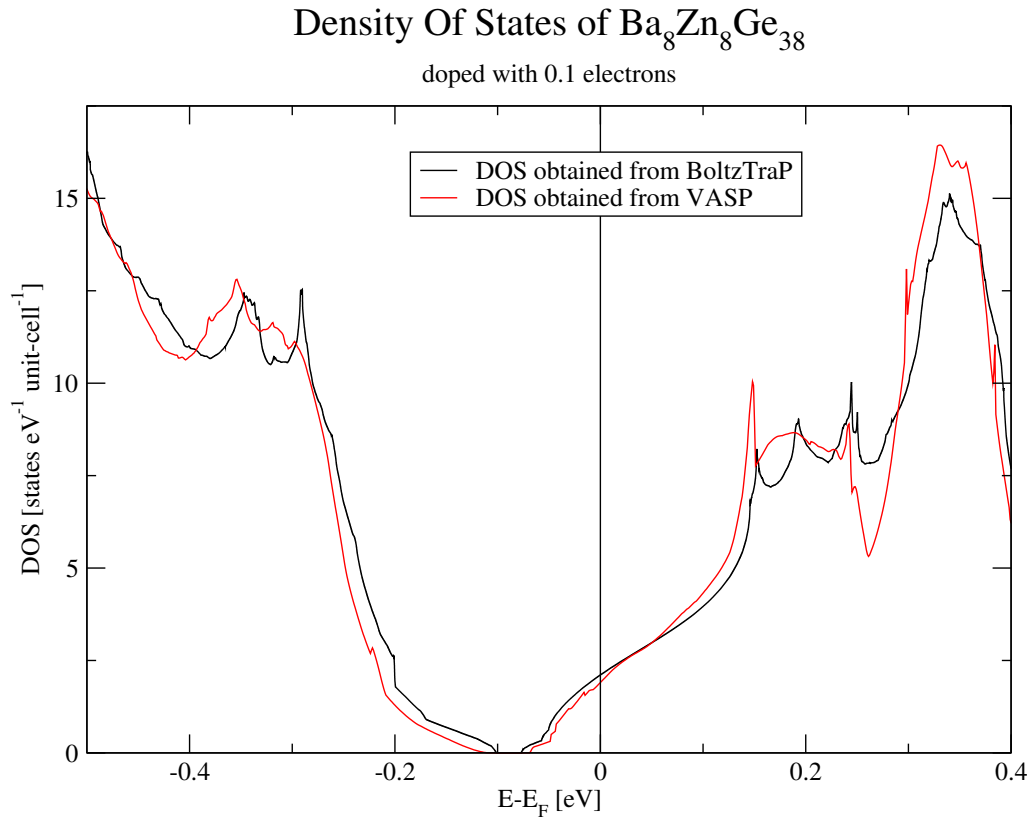


Figure 32: Density Of States of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ with 0.1 electrons doping.

Increasing the doping by adding 0.1 electron to the system the Fermi energy moves to even higher energies. Inspecting the DOS in Figure 32 one can perceive that the Fermi energy is now at a larger DOS with an upward slope. The Seebeck coefficients qualitatively behave similar compared to the small doping case but the minimum is shifted to higher temperatures of about 400 K and is less deep. The x-component having the lowest minimum value of $-150 \mu\text{V K}^{-1}$, and the z-component is nearly equal. Again, the y-component is significantly split off.

Studying once more the numerical convergency of BoltzTraP depending on the parameter `lpfac` it becomes obvious from Figures 33 to 35 that

recurrently the numerical convergency for $lpfac \geq 85$ is very satisfying.

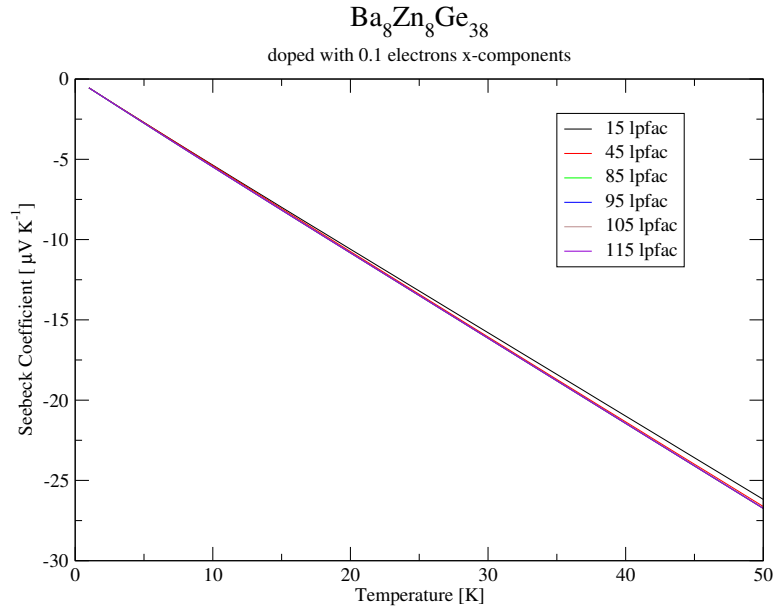


Figure 33: *x*-component of low temperature Seebeck tensor of $Ba_8Zn_8Ge_{38}$ doped with 0.1 electrons.

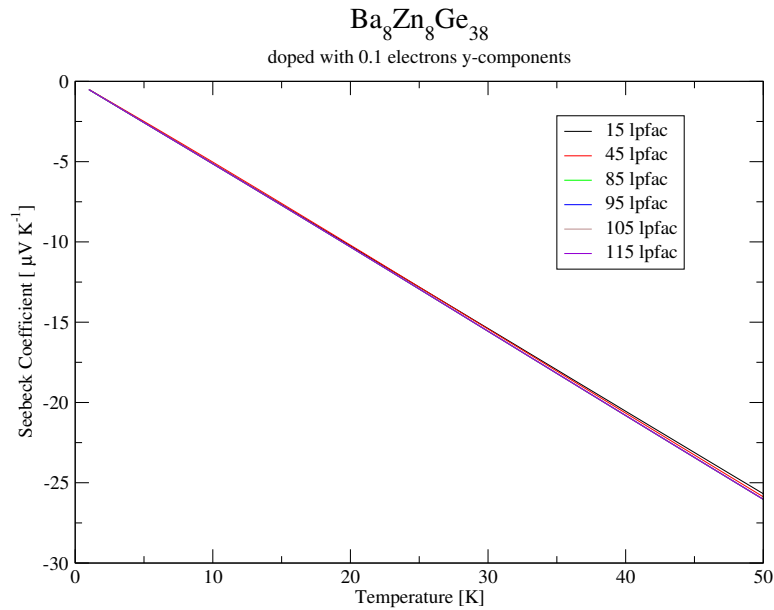


Figure 34: *y*-component of the low temperature Seebeck tensor of $Ba_8Zn_8Ge_{38}$ doped with 0.1 electrons.

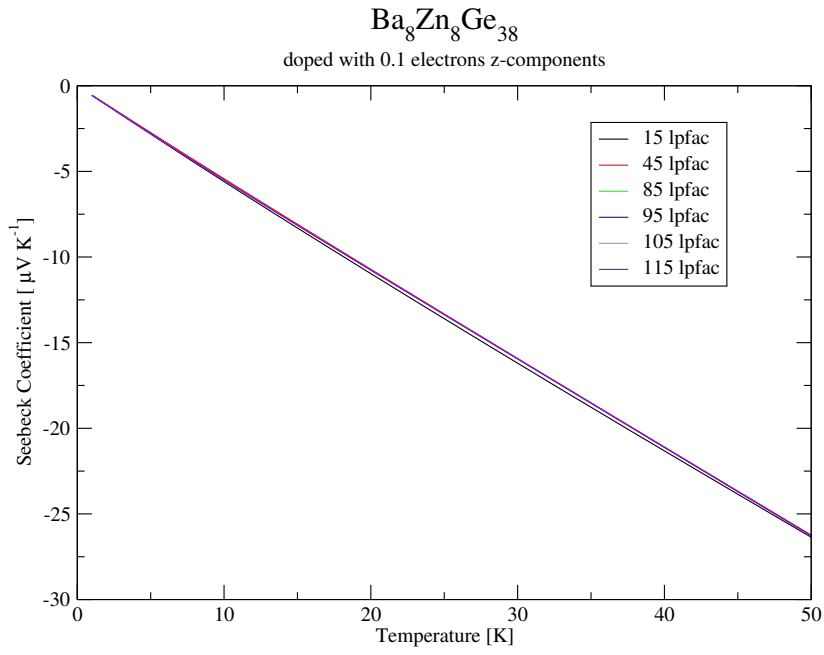


Figure 35: z-component of low temperature Seebeck tensor of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 0.1 electrons.

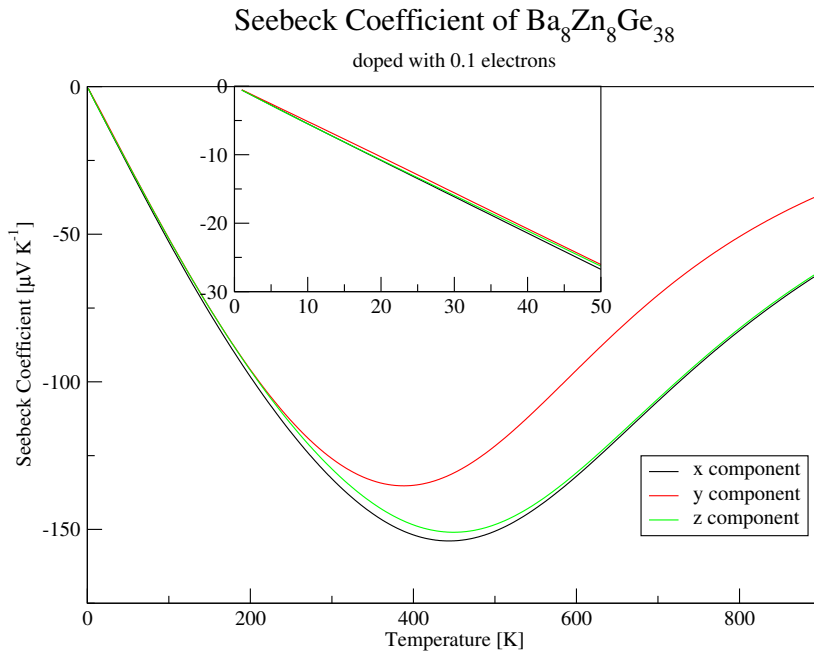


Figure 36: Seebeck coefficients of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 0.1 electrons calculated for $l_{pfac}=115$ vs. temperature.

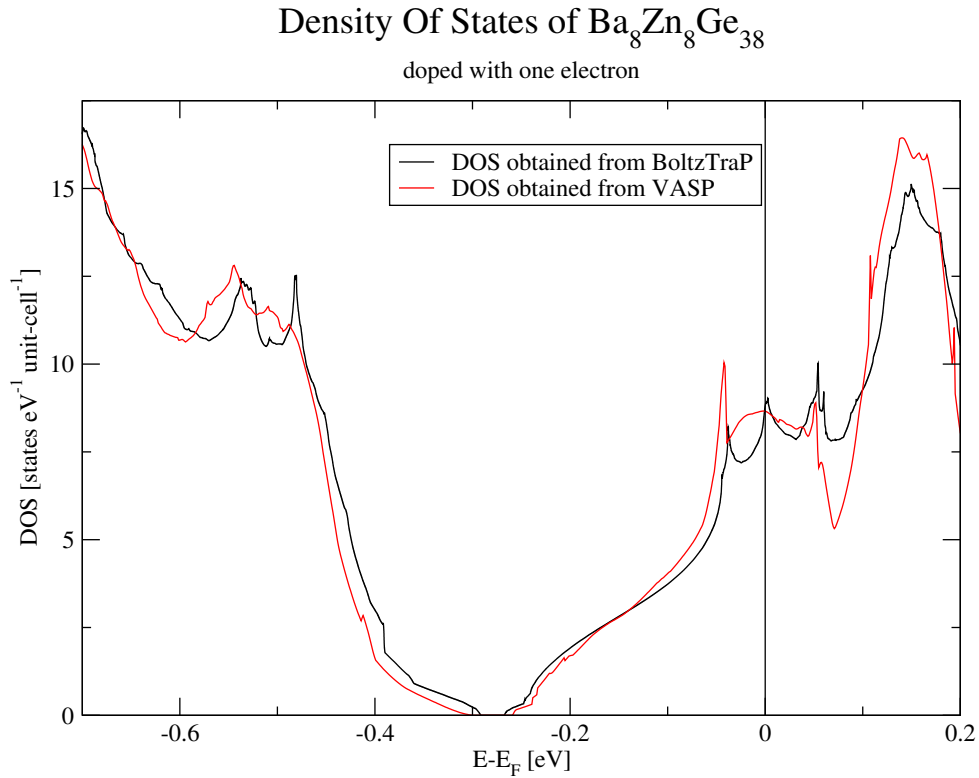


Figure 37: Density Of States of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ with 1 electron doping.

For studying the Seebeck coefficient for larger dopings $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ has been doped with 1 electron. Most striking is the change of the algebraic sign of the Seebeck coefficient. One might suggest a cleavage of the Seebeck coefficient at low temperature but examining the high temperature Seebeck coefficient it becomes obvious that a uniform Seebeck coefficient no longer forms (see Figure 41). It may be assumed that this change in composition exceeds the applicability of the rigid band method. But one ought not forget that one electron added to this compound—if translated into atomic composition—responds to a composition like $\text{Ba}_8\text{Zn}_{7.5}\text{Ge}_{38.5}$.

Concerning the numerical convergency of the Seebeck coefficient it is clearly visible that the `1pfac` parameter of BoltzTraP should be chosen well above 85 (see Figures 38 to 40).

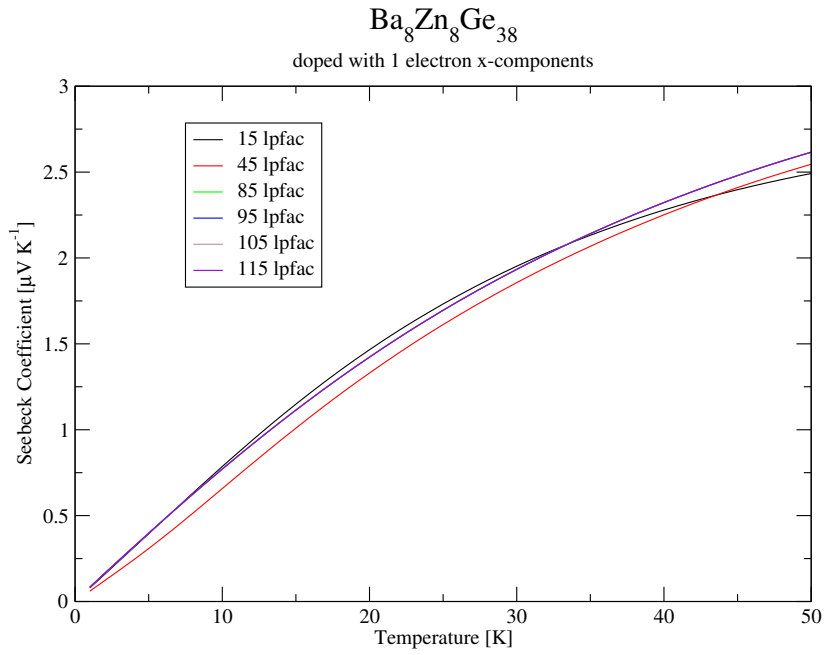


Figure 38: Low temperature Seebeck coefficients of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 1 electron only x-components.

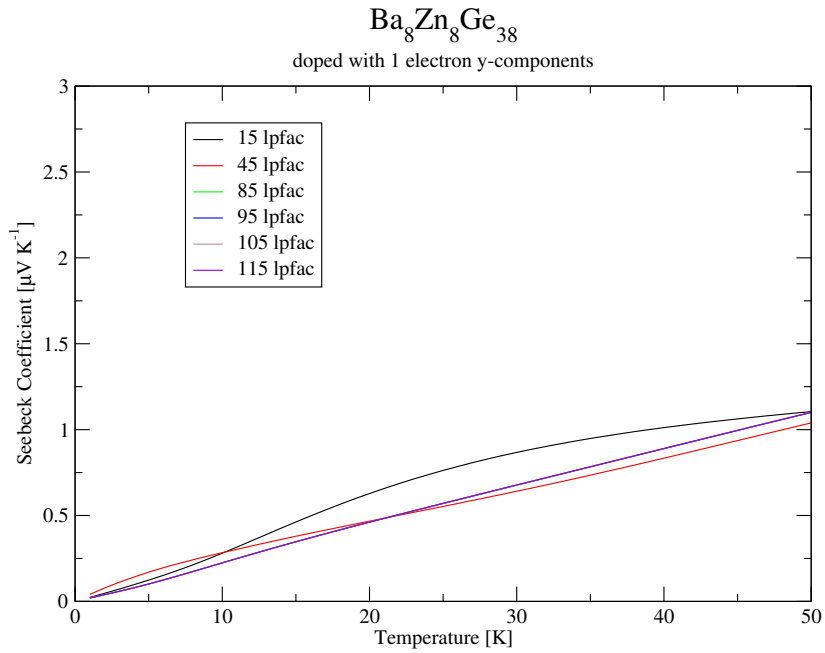


Figure 39: Low temperature Seebeck coefficients of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 1 electron only y-components.

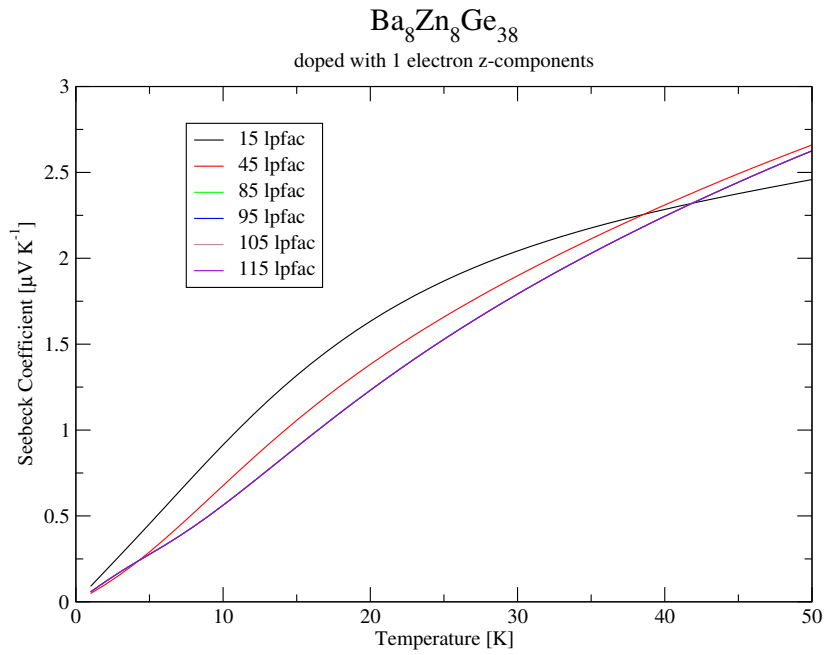


Figure 40: Low temperature Seebeck coefficients of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 1 electron only z-components.

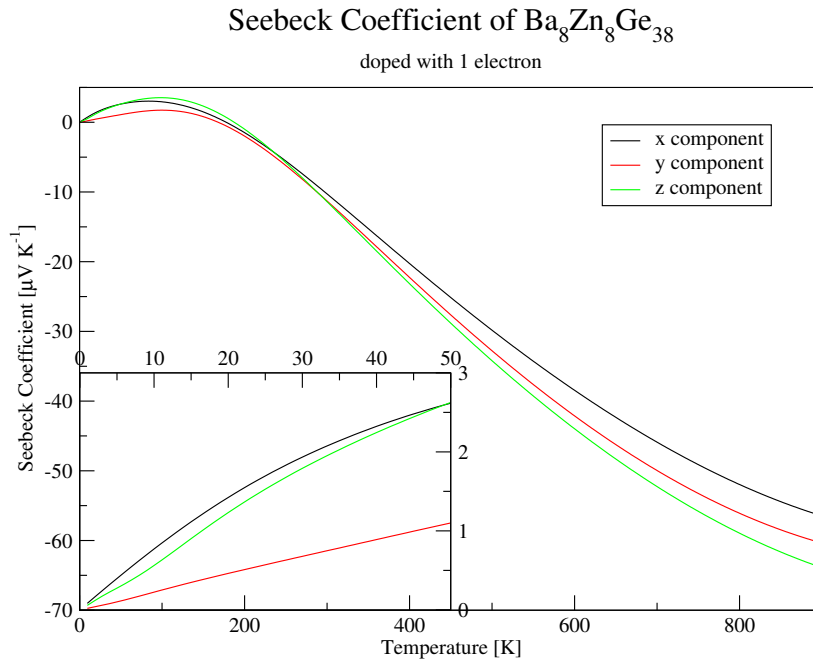


Figure 41: Seebeck coefficient of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ doped with 1 electrons calculated with 115 lpfac over a larger temperature scale (up to 900 K).

6 Conclusion

Thermoelectric materials are of importance because of the prospect of a less environmentally damaging way of producing electrical energy. The search for effective thermoelectric materials became an intensive field in materials research. Promising thermoelectric materials are clathrate compounds with their typical cage forming crystal structure.

The main motivation of the present thesis was to study important thermal materials properties of solid compounds, such as the Seebeck tensor and the conductivity tensor from first-principles, i.e. without the need of any empirical parameter. For these rather complex properties their dependence on the electronic structure of the material was investigated. This was done by making use of density functional theory as implemented in the very powerful VASP code. The electronic structure as calculated by VASP for the fully relaxed crystal structures served as input for the BoltzTraP code, which tackles transport properties within Boltzmann's transport theory. Because clathrates are very promising materials for large absolute values of Seebeck coefficients clathrate type I Ba-Zn-Ge clathrates were studied, particularly $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ and related compounds and dopings such as $\text{Ba}_8\text{Zn}_7\text{Ge}_{39}$, $\text{Ba}_8\text{Zn}_6\text{Ge}_{39}$ and $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ were investigated in detail. During the search for optimised Seebeck coefficients the effects of doping—generally resulting in $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ compounds which are based on the rigid-band model for the electronic structure—were considered. The main finding is that the most promising candidate as a technologically interesting material is the doped clathrate $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ which has a gap in the electronic structure. The doping was done by adding fractionally occupied electronic states to the system. The highest absolute value of a Seebeck coefficient is predicted for $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ with a doping of 0.01 electrons: at 200 K there is a minimum for the z-component of the Seebeck tensor of $-225 \mu\text{V K}^{-1}$. Doping by 0,1 electrons shifts the minimum to a higher temperature of 400 K, but its value of $-150 \mu\text{V K}^{-1}$ is less deep than for the 0.01 doping, because the

Fermi energy is further away from the gap.

The self-consistent electronic structure was calculated by applying the Vienna Ab-initio Simulation Package (VASP). For that, the structural parameters of the compounds were fully relaxed. Taking the relaxed structure as input the energy bands were calculated on a very fine grid in $\vec{k}$ space. The calculation of the Seebeck coefficients utilising the electronic structure of the materials as derived by VASP was done with the programme package BoltzTraP, which is based on Boltzmann's transport theory. It had to be modified and adapted for the present purpose. The influence and effect of some inherent numerical parameters are also investigated and analysed. It turned out that BoltzTraP has numerical problems calculating the components of the Seebeck tensor at low temperature when there is a gap in the electronic structure. In case of metallic systems the numerical convergency is, however, very good and reliable.

7 Appendix

An example for an INCAR-file used by VASP:

```
SYSTEM=Zn
LREAL=Auto
ALGO=Fast
PREC=High
IBRION=-1
ISIF=2
LORBIT=10
ISMEAR=-5
ICHARG=11
NEDOS=1000
EMIN=3.6
EMAX=4.6
INCAR (END)
```

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