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## DIPLOMARBEIT

# Thermoelectric properties of novel clathrates Ba<sub>8</sub>T<sub>x</sub>T'<sub>y</sub>Ge<sub>46-x-y</sub> (T=Cu,Si,Pd; T'=Zn) and Ba<sub>8</sub>Ag<sub>z</sub>Ge<sub>46-z</sub> (z=2, 3, 4, 5)

ausgeführt am Institut für Festkörperphysik zum Zwecke der Erlangung des akademischen Grades eines Diplomingenieurs der technischen Physik unter der Leitung von

Ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Ernst Bauer

eingereicht an der Technischen Universität Wien Fakultät für Physik

von

#### **Ingeborg Bednar**

Matrikelnummer: 0125485 Mühlstraße 43 2123 Wolfpassing

Wolfpassing, im Oktober 2009

## Abstract und Kurzfassung

## Abstract

In the present diploma thesis the thermoelectric properties of cubic type I Ba-Ge-based clathrates are studied, where Ge in  $Ba_8Ge_{43}\Box_3$  ( $\Box$  is a vacancy) is substituted by

```
\begin{array}{rcl} Ag & \rightarrow & Ba_8Ag_xGe_{46-x}\;x=2,\;3,\;4,\;5\\ Pd\;\&\;Zn & \rightarrow & Ba_8Pd_xZn_yGe_{46-x-y}\\ Cu\;\&\;Zn & \rightarrow & Ba_8Cu_xZn_yGe_{46-x-y}\\ Si\;\&\;Zn & \rightarrow & Ba_8Si_xZn_yGe_{46-x-y}. \end{array}
```

The specific compositions discussed in this diploma thesis are summarised in the Table on page iii. The synthesis of these materials as well as the structural investigations were conducted by Navida Nasir and Isolde Zeiringer at the Institute of Physical Chemistry, University of Vienna.

The structural investigations in all cases confirmed cubic primitive symmetry consistent with the space group type  $Pm\bar{3}n$  of a typical type I clathrate structure with lattice parameters ranging from  $a \approx 1.05$  nm to  $a \approx 1.08$  nm. Thermoelectric properties (electrical resistivity, thermal conductivity and Seebeck coefficient) were measured in a broad temperature range from 4.2 to about 800 K, demonstrating that substitution allows fine tuning of the charge carrier density, shifting the materials into the proximity of a metal-to-insulator transition. This is evidenced from giant thermopower reaching values of about  $400\mu$ V/K in the case of Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> at temperatures well below room temperature ( $T_{max}^S \approx 150$  K).

## Kurzfassung

In der vorliegenden Diplomarbeit wurden die thermoelektrischen Eigenschaften von auf Ba-Ge-basierenden kubischen Clathraten des Typs I untersucht. Ge wurde in  $Ba_8Ge_{43}\Box_3$  ( $\Box$  bedeutet eine Lücke im Kristallgitter) durch Ag sowie jeweils durch die beiden Elemente Pd und Zn, Cu und Zn und Si and Zn ersetzt

$$\begin{array}{rcl} \mathsf{Ag} & \to & \mathsf{Ba}_8\mathsf{Ag}_x\mathsf{Ge}_{46-x}\;x=2,\;3,\;4,\;5\\ \mathsf{Pd}\;\&\;\mathsf{Zn} & \to & \mathsf{Ba}_8\mathsf{Pd}_x\mathsf{Zn}_y\mathsf{Ge}_{46-x-y}\\ \mathsf{Cu}\;\&\;\mathsf{Zn} & \to & \mathsf{Ba}_8\mathsf{Cu}_x\mathsf{Zn}_y\mathsf{Ge}_{46-x-y}\\ \mathsf{Si}\;\&\;\mathsf{Zn} & \to & \mathsf{Ba}_8\mathsf{Si}_x\mathsf{Zn}_y\mathsf{Ge}_{46-x-y}. \end{array}$$

Die in dieser Diplomarbeit behandelten Zusammensetzungen werden in Tabelle auf Seite iii aufgelistet. Die Herstellung dieser Materialien sowie die Strukturuntersuchungen erfolgten am Institut für Physikalische Chemie der Universität Wien durch Navida Nasir und Isolde Zeiringer.

Die Strukturuntersuchungen aller Zusammensetzungen ergaben eine einfache kubische Struktur mit der Raumgruppe Pm3n, welche für Typ I Clathrate charakteristisch ist. Die Gitterparameter variieren von  $a \approx 1.05$  nm bis  $a \approx 1.08$  nm. Die thermoelektrischen Eigenschaften (elektrischer Widerstand, thermische Leitfähigkeit und Seebeck Koeffizient) wurden über einen weiten Temperaturbereich (von 4.2 bis 800 K) gemessen. Die Ergebnisse belegen, dass Substituierung von Ge eine Feinabstimmung der Ladungsträgerdichte und damit eine Verschiebung der Materialeigenschaften in die Nähe eines Metall-Isolator Überganges erlaubt. Offensichtlich wird diese Grenze für Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> erreicht, sodass sie einen außerordentlich großen Seebeck-Koeffizienten von etwa  $400\mu$ V/K bei  $T_{max}^S \approx 150$  K aufweist.

Table: Investigated compostions / nominal composition	Untersuchte Zusammensetzungen accepted composition
Nominalzusammensetzung	Akzeptierte Zusammensetzung
$Ba_8Pd_{2.4}Zn_{3.3}Ge_{40.3}$	$Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$
$Ba_8Cu_{5.2}Zn_{0.8}Ge_{40}$	$Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$
$Ba_8Zn_8Ge_{10}Si_{28}$	$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$
$Ba_8Zn_8Ge_{19}Si_{19}$	$Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$
$Ba_8Zn_8Ge_{19}Si_{19}$	$Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$
$Ba_8Zn_8Ge_{28}Si_{10}$	$Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$
$Ba_8Ag_2Ge_{44}$	not finalised yet / noch nicht bekannt
$Ba_8Ag_3Ge_{43}$	not finalised yet / noch nicht bekannt
$Ba_8Ag_4Ge_{42}$	not finalised yet / noch nicht bekannt
$Ba_8Ag_5Ge_{41}$	not finalised yet / noch nicht bekannt

## thanks to ...

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To Karl Parbus, my amazing grandfather who demonstrated "Where there's a will, there's a way".

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## 1. Introduction

#### What are clathrates?

Clathrates are crystalline materials with an internal cage structure (see Fig. 1.1). *Clathrate* (from Latin *clatratus* = encaged): an inclusion complex in which (neutral) molecules of one substance are completely enclosed in cavities formed by the crystal lattice, or are present in large molecules of another substance, i.e., the crystal accommodates in foreign molecules during growth, which cannot escape until the crystal is decomposed. In other words, the free aperture of the faces of the polyhedral void is too small to let the enclosed guests species pass. (cit. from [29])



Figure 1.1.: Typical structure of type I clathrates - with cubic unit cell

#### Why "novel" clathrates?

The novelty of the investigated compositions in this thesis is that the frameworks atoms Germanium are substituted by both Cu **and** Zn, Pd **and** Zn as well as Si **and** Zn. On the

#### 1. Introduction

other hand, there are no publications known - to the best of our knowledge - discussing  $Ba_8Ge_{46-x}$ -based clathrates where Ge atoms (and frameworks) are substituted by Ag.

#### Why investing clathrates?

In this thesis type I clathrates containing transition metal elements are discussed  $(Ba_8TM_xGe_{46-x}, TM=transition metal)$ . The implementation of transition metals is promising, regarding the type and concentration of charge carriers as well as a modification of the electronic density of states at the Fermi energy. Cage forming clathrates provide an almost ideal starting point to satisfy the requirements of the PGEC (phonon glass, electron crystal) concept of G. Slack. (For further details see [29])

#### What is the usefulness of thermoelectricity?

Thermoelectricity is the possibility of metals and intermetallic compounds to convert a temperature gradient (via the Seebeck-effect) in an electrical potential gradient. With closing an electric circuit, electrical current is flowing and electrical power is generated. Also the other way around is possible, absorbing heat at one side and refrigerating at the other side can be activated with an electric current passing through the thermoelectric generator. Thermoelectric materials (as the investigated materials are) are used as principal elements in thermoelectric generators. Thermoelectric generators can be used for converting (high-temperature) solar energy, waste heat of industrial processes, waste heat in the car as well as from chimneys. The dimensions of thermoelectric generators vary with the purpose. Today this technology is rapidly developing. [29]

#### What are thermoelectric properties?

Thermoelectric properties are the electric resistivity  $\rho \ [\mu\Omega cm]$ , the thermal conductivity  $\lambda \ [\frac{mW}{cmK}]$ , the Seebeck coefficient (also: thermopower)  $S \ [\mu V/K]$  as well as Hall coefficient  $R_H \ [Kcm^3c^{-1}]$ .<sup>1</sup> [29]

#### What is the thermoelectric performance?

The thermoelectric performance (figure of merit) links the Seebeck coefficient S, thermal conductivity  $\lambda$  and electric resistivity  $\rho$  in a simple manner by  $\frac{S^2}{\lambda\rho}$ . Consequently, while searching for materials with large S-values,  $\lambda$  and  $\rho$  should be as small as possible.

<sup>&</sup>lt;sup>1</sup>c...atomic concentration of an alloy component

Nature, however, does not favor such a combination, since a large thermopower requires usually materials with low charge carrier concentration. In the simplest model, the electronic structure of clathrates can be understood in terms of the Zintl concept: Binary  $Ba_8Ge_{43}\Box_3$  with three framework defects can be formulated as  $[Ba^{+2}]_8[Ge^0]_{43}[\Box^{-4}]_3$  yielding an electron surcharge of 4 electrons per formula unit. This simple concept was proven successful in previous substitution and doping studies carried out on binary  $Ba_8Ge_{43}\Box_3$  [9, 10, 12, 20, 21, 22, 23]. Substitution and doping turned out as a fruitful and promising tool to arrange the charge carrier concentration of clathrates in an optimal manner to tailor the highest possible thermoelectric performance. (cit. from [4])

The aim of the present work is a study of transport properties on type I clathrates  $Ba_8Ge_{43}\Box_3$  where the charge carrier density is fine-tuned by substituting Ge by both Cu and Zn, Pd and Zn, Si and Zn as well as Ag. In each case, the substitution causes the vacancies to become occupied [4].

## 2. Theoretical Aspects

## 2.1. Transport Phenomena

<sup>1</sup> In physics, chemistry, biology and engineering, transport phenomena are mechanism by which particles or quantities move from one place to another. This movement requires a "motive force". In solid-state physics transport phenomena of interest are:

transport phenomenon	driving force
electrical resistivity	external field (electrical)
thermal conductivity	temperature gradient
Seebeck coefficient	temperature gradient
magnetoresistance	external field (electrical + magnetic)
Hall coefficient	external field (electrical + magnetic)

For theoretical explanation of the electrical resistivity  $\rho$ , the thermal conductivity  $\lambda$  and the thermopower (Seebeck coefficient) S (which are the transport coefficients appearing in this thesis) the linearised Boltzmann equation 2.1 has to be derived.

$$\left(\frac{\partial}{\partial t} + \dot{\vec{r}} \cdot \nabla_r + \ddot{\vec{r}} \cdot \nabla_{\dot{\vec{r}}}\right) f(\nu, \vec{r}, t) = \left(\frac{\partial f(\nu, \vec{r}, t)}{\partial t}\right)_{coll}$$
(2.1)

The bracket term with subscript *coll* (meaning collision term) represents scattering processes which can be equalized with a field term (external fields and temperature gradients are the driving forces) because of the assumption of a steady state  $\left(\frac{df}{dt} = 0\right)$ . The function  $f(\nu, \vec{r}, t)$  is the probability distribution function of a conduction electron, depending on its position vector  $\vec{r}$  and wave vector  $\vec{k}$ ; the quantum number  $\nu$  includes the wave vector, the band index and the spin direction.

The behaviour of electrons in solids is described by the Fermi-Dirac distribution func-

<sup>&</sup>lt;sup>1</sup>References: [5, 3, 16, 17, 28, 26, 29, 1, 32, 34]

tion:

$$f_0(E_\nu) = \frac{1}{e^{\frac{E_\nu - \mu}{k_B T}} + 1}$$
(2.2)

where  $k_B = 1.38 \times 10^{-23} J/K$  is the Boltzmann constant,  $\mu$  is the chemical potential which equals at T = 0 the Fermi-energy  $E_F$ . For free electrons  $E_F$  (energy of the highest occupied state of the ground state) reads

$$\mu(T=0) = E_F = \frac{h^2}{2m_e} \left(\frac{3n\pi^2}{V}\right)^{2/3}.$$
(2.3)

Only electrons in the proximity of the Fermi-energy are able to move and therefore to transport energy (mass, charge). This movement is limited by scattering events like scattering on impurities, imperfections of the lattice, phonons, other electrons and because of magnetic moments. To solve the Boltzmann equation (2.1) the collision term is substituted by a term which describes the collision events with a relaxation time  $\tau_{\nu}(\vec{r}, \vec{v})$ :

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f - f_0(E_\nu)}{\tau_\nu} \tag{2.4}$$

 $f_0(E)$  is the Fermi-Dirac distribution function. Particles move freely within a characteristic time  $\tau$  before being scattered. The relaxation of the distribution function to equilibrium is

$$\frac{\partial (f - f_0(E_{\nu}))}{\partial t} = -\frac{f - f_0(E_{\nu})}{\tau_{\nu}}$$
(2.5)

and the solution of this equation reveals an exponential dependence:

$$(f - f_0(E_\nu))_t = (f - f_0(E_\nu))_{t=0} \exp\left\{-\frac{t}{\tau_\nu}\right\}.$$
 (2.6)

Every individual scattering mechanism can be described by a distinct relaxation time  $\tau_i$ . Matthiessen's rule assumes that the scattering mechanisms are independent and so they can be added together:

$$\tau^{-1} = \sum \frac{1}{\tau_i}.$$
 (2.7)

Provided that in a parabolic conduction band only one type of charge carriers is responsible for transport phenomena it is possible to deduce the transport coefficients from the linearised Boltzmann equation (Eqn. 2.1) with applying the transport integrals,

$$K_n = -\frac{1}{(2\pi)^3} \int \tau_\nu \vec{v_\nu} \cdot \vec{v_\nu} (E_\nu - \mu)^n \left( -\frac{\partial f_0(E_\nu)}{\partial E_\nu} \right) d^3k$$
(2.8)

with  $\gamma=\vec{k},\vec{r}$ 

The electrical current density

$$\vec{j} = e^2 K_0 \vec{E} - \frac{e}{T} K_1 \vec{\nabla} T \tag{2.9}$$

compared with Ohm´s law  $\vec{j}=\sigma\vec{E}$  leads to the electric conductivity

$$\sigma = \frac{1}{\rho} = e^2 K_0, \qquad (2.10)$$

with the requirements of  $\vec{E} \neq 0$ ,  $\vec{T} = 0$  and  $\vec{B} = 0$ .

Comparing the density of heat flow

$$\vec{q} = eK_1 \frac{K_1}{eTK_0} - \frac{1}{T} K_2 \vec{\nabla} T$$
 (2.11)

with the definition

$$\vec{q} = -\lambda \vec{\nabla} T \tag{2.12}$$

the thermal conductivity results to

$$\lambda = \frac{1}{T} \left[ K_2 - \frac{K_1^2}{K_0} \right],$$
(2.13)

with the requirements of  $\vec{j}=0, \ \vec{T}\neq 0$  and  $\vec{B}=0.$ 

With  $\vec{j} = 0$ ,  $\vec{T} \not\models 0$  and  $\vec{B} = 0$  follows with the electrical current density

$$\vec{j} = e^2 K_0 \vec{E} - \frac{e}{T} K_1 \vec{\nabla} T = 0$$
(2.14)

and the definition

$$\vec{E} = S\vec{\nabla}T \tag{2.15}$$

for the electrical field intensity

$$\vec{E} = \frac{1}{eT} \frac{K_1}{K_0} \vec{\nabla} T.$$
(2.16)

Comparison with the definition leads to

$$S = \frac{1}{eT} \frac{K_1}{K_0}.$$
 (2.17)

symbol	meaning	
$\vec{k}$	wave vector	
$\vec{r}$	position vector	
$ec{v}_\gamma$	velocity of the electron at the $\gamma$ state	
$ec{E}$	electrical field	
$\sigma$	electrical conductivity	
ρ	electrical resistivity	
S	Seebeck coefficient	
$\lambda$	thermal conductivity	
$\lambda_e$	electronic contribution to $\lambda$	
e	electronic charge	
T	temperature	
$\mu$	chemical potential	
$K_n$	transport integrals	
$m_e^* = \left(\frac{1}{\hbar^2} \frac{d^2 E}{dk^2}\right)$	effective mass	
N(E)	electronic density of states	
$ au_e$	relaxation time for electron-scattering process	

Electrical Resistivity  $\rho [\mu \Omega cm]$ , thermal conductivity  $\lambda [mWcm^{-1}K^{-1}]$  and Seebeck coefficient  $S [\mu V K^{-1}]$  are necessary to describe the electronic and thermal transport an thus the thermoelectric performance of a distinct material in terms of the figure of merit. Each material has its own characteristics and already small variations in composition or manufacturing can change/shift physical properties; so it is possible to obtain unexpected results of specifically designed materials.

To investigate the materials manufactured for this project, the electrical resistivity, the thermal conductivity and the Seebeck coefficient were measured in a broad temperature range ( $\sim 4$  K to  $\sim 800$  K).

### 2.1.1. Electrical Resistivity

 $^2$  The characteristics of the electrical resistivity as a function of temperature defines the nature of a material. The electrical resistivity of metals increases with rising tempera-

<sup>&</sup>lt;sup>2</sup>References: [5, 21, 11, 3, 28, 33]

ture; it decreases for semiconductors [33]. Also superconductors can be identified easily. The scattering of electrons limits the mean free path and thus determines the absolute resistivity. The relaxation time  $\tau_i$ , describing the average time between two scattering events, links the electron velocity and the mean free path. Using Matthiessens rule, Eqn. 2.7, simple metals are described by

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{ph}},\tag{2.18}$$

where  $\tau_0$  is the time between two scattering events of electrons and imperfections and  $\tau_{ph}$  accounts for scattering between electrons and phonons. The Drude formula provides a relation between electrical resistivity and the total relaxation time  $\tau$ :

$$\rho = \frac{m_e}{ne^2\tau} \tag{2.19}$$

with  $m_e$  the electron mass, n the electron density and |e| the electron charge. In Eqn. 2.19 the relaxation time is the only variable, so it is obvious that this is the parameter responsible for the magnitude and temperature dependence of  $\rho(T)$ . A modified version of Eqn. 2.19 takes into account an effective mass of the charge carriers instead of the free electron mass.

According to Matthiessen's rule the temperature dependent electrical resistivity of simple metals follows than from

$$\rho(T) = \rho_0 + \rho_{ph}(T).$$
(2.20)

 $\rho_0$  is the residual resistivity resulting from scattering on static imperfections, such as impurities, which is usually temperature independent.  $\rho_{ph}(T)$  accounts for scattering on phonons - which is temperature dependent. The former term can be determined by measurements at temperatures near to absolute zero, the latter can also be calculated by theoretical concepts such as the Bloch-Grüneisen formula, which is derived from the linearised Boltzmann equation (Eqn. 2.1).

$$\rho_{ph} = \mathcal{R} \left(\frac{T}{\theta_D}\right)^5 \int_0^{\frac{\theta_D}{T}} \frac{z^5}{(e^z - 1)(1 - e^{-z})}$$
(2.21)

 $\mathcal{R}$  (which is temperature independent) describes the strength of interaction between the conduction electrons and the thermally excited phonons. For low temperatures  $\rho_{ph}(T)$  is

proportional to  $T^5$ 

$$\rho_{ph} \approx \frac{\mathcal{R}}{\theta_D} \left(\frac{T}{\theta_D}\right)^5 \dots \text{ for } T \ll \theta_D,$$
(2.22)

whereas for higher temperatures simple metals display an almost linear temperature dependence

$$\rho_{ph} \approx \frac{\mathcal{R}}{4} T... \text{ for } T \gg \theta_D.$$
(2.23)

The parameters  $\theta_D$  and  $\mathcal{R}$  are derived via fitting the actual experimental data.

To explain the behaviour of more complicated metals, like materials near a metal-toinsulator transition, a model regarding the temperature dependent electrical resistivity was developed by Stefan Berger [5, 21], combining the Bloch-Grüneisen law with a temperature dependent charge carrier density n(T) (also called 'two-band model').

$$\rho(T) = \frac{\rho_0 n_0 + \rho_{ph}}{n(T)}$$
(2.24)

The charge carrier density is calculated employing statistical mechanics, taking into account the Fermi-Dirac distribution function and using a density of states such as it is sketched in Fig. 2.1. The variation of the width and the location (regarding to the Fermi-



Figure 2.1.: Gap in the electronic density of states near to Fermi-energy

energy  $E_F$ ) of the band gap  $E_g$  explains the different behaviour of materials. Basically, a gap well above the Fermi-energy is consistent with a metal-like behaviour of the electrical resistivity. For semiconductors, small gaps in narrow distance to  $E_F$  are explaining the behaviour of decreasing resistivity with rising temperature. At higher temperatures, electrons cross the band gap into a largely unoccupied band, thus, finding a new amount of

#### 2. Theoretical Aspects

free states. The charge carrier density increases and therefore the resistivity decreases.

With varying the location of the energy gap according to the Fermi-energy and its gap width a further description is possible and metallic-like resistivity features may be followed by semiconducting temperature dependences of the electrical resistivity in a single piece of material. A material with a behaviour near a metal-to-insulator transition meaning a high resistivity even at low temperatures is described by a gap slightly above the Fermi-energy.

A further development of the discussed model gives the implementation of the Mott-Jones term  $AT^3$  [11] where the dependence of scattering processes on narrow features of the DOS in the proximity of  $E_F$  is taken into account<sup>3</sup>:

$$\rho(T) = \frac{\rho_0 n_0 + \rho_{ph}}{n(T)} + \frac{AT^3}{n(T)}.$$
(2.25)

Another model was developed by Matthias Ikeda [13], using also the formula as it is derived from Fig. 2.1, introducing a rectangular band into the gaps as shown in Fig. 2.2.



Figure 2.2.: Three-band model - sketch

### 2.1.2. Thermal Conductivity

<sup>4</sup> The total thermal conductivity can be written as a sum of two parts: the lattice thermal conductivity  $\lambda_{ph}$  (index *ph* for phonons) and the electronic contribution to thermal conductivity  $\lambda_e$ :

$$\lambda = \lambda_{ph} + \lambda_e \tag{2.26}$$

<sup>&</sup>lt;sup>3</sup>Idea from Leonid Salamakha, private conversation on October 13, 2009

<sup>&</sup>lt;sup>4</sup>References: [8, 7, 22, 28, 32, 24]

#### **Electronic Contribution to Thermal Conductivity**

Employing the Wiedemann-Franz law the electronic thermal conductivity can be calculated from the electrical resistivity via

$$\lambda_e = \frac{L_0 T}{\rho},\tag{2.27}$$

with the Lorenz number  $L_0 = 2.45 \cdot 10^{-8} \frac{W\Omega}{K^2}$ . Although this model is valid in extended temperature ranges only for free electron systems, it is widely used even for complex materials such as skutterudites or clathrates. (cit. from [22])

#### Lattice Contribution to Thermal Conductivity

 $\lambda_{ph}$  follows from the kinetic gas theory from  $\lambda = \frac{1}{3}c_v vl$  with  $c_v$  as the heat capacity of the system, v is the particle velocity and I the mean free path. According to [7, 8]  $\lambda_{ph}$  is given by

$$\lambda_{ph} = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \left[\frac{\tau_c x^4 e^x}{(e^x - 1)^2} + \frac{I_1}{I_2}\right] dx,$$
(2.28)

with the velocity of sound

$$v_s = \frac{k_B \theta_D}{\hbar (6\pi^2 n)^{1/3}}$$

and  $x = \hbar \omega / k_B T$ , as well as

$$I_1 = \int_0^{\theta_D} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{(e^x - 1)^2} dx$$
(2.29)

$$I_2 = \int_0^{\theta_D} \frac{1}{\tau_N} (1 - \frac{\tau_c}{\tau_N}) \frac{x^4 e^x}{(e^x - 1)^2} dx,$$
(2.30)

where n is the number of atoms per unit volume and  $\omega$  the phonon frequency.  $\tau_c^{-1}$  means the sum of reciprocal relaxation times:

$$\tau_c^{-1} = \tau_N^{-1} + \tau_U^{-1} + \tau_D^{-1} + \tau_B^{-1} + \tau_E^{-1}, \qquad (2.31)$$

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$$\tau_N^{-1} = B_N T^3 \omega^2$$
  

$$\tau_U^{-1} = B_U T^3 \omega^2$$
  

$$\tau_D^{-1} = A \omega^4$$
  

$$\tau_B^{-1} = \frac{v_s}{L}$$
  

$$\tau_E^{-1} = B_E \omega$$

with the following abbreviations

symbol	meaning
N	normal three phonon scattering
U	umklapp processes
D	point defect / impurity scattering
В	boundary scattering
E	scattering of phonons by electrons
$B_N$	a temperature independent factor
$B_U$	a material constant, containing $e^{rac{- heta_D}{aT}}$ - characteristic of the vibrational spectrum
L	some length characteristic of the material

In Chapter 4.2 the term  $\frac{I_1}{I_2}$  in Eqn. 2.28 is omitted. Such an approach is justified if the impurity level is significant and all phonon branches are scattered by resistive processes. This means that the relaxation time of normal processes is much larger than that of the other scattering processes  $\tau_N \gg \tau_{U,B,E}$ . The first integral in Eqn. 2.28 therefore predominates; the second term  $(\frac{I_1}{I_2})$  can be ignored. Since the experimental data (see Chapter 4.1) show quite large resistivity values (as usual for clathrates) this simplification (Eqn. 2.32) is appropriate.

$$\lambda_{ph} = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \frac{\tau_c x^4 e^x}{(e^x - 1)^2} dx$$
(2.32)

To account for radiation losses, an additional  $T^3$  term to Eqn. 2.32 is used in the least-squares fits in Chapter 4.2.

#### 2.1.3. Thermopower

<sup>5</sup> The thermopower of a material, represented by its Seebeck coefficient, is a consequence of the movement of the charge carriers due to a temperature gradient. (cit. from [28]) If a temperature gradient is exposed to a conducting solid, electrical charge carriers are moving - this effect is called thermodiffusion. The thermodiffusion causes a temperature-dependent and therefore position-dependent velocity distribution of charge carriers. (literal interpretation from [27])

In the presence of a temperature gradient along a conductor the thermodiffusion of charge carriers causes diffusion electricity, therefore an electric field is generated which involves a drift current.

With a voltmeter the difference between the electrochemical potentials  $\varphi_{e-ch}$  of the exits is measured (see Fig. 2.3), the resulting voltage follows as integral within the integration limits a and b

$$U = \int_{a}^{b} \vec{ds} \cdot \vec{\nabla} \varphi_{e-ch}.$$
 (2.33)

No contribution from the junctions occurs, because the electrochemical potential is continuous at the connection of two metals and the temperature is constant. The thermoelectric potential is expressed by

$$U = -\int_{a}^{b} SdT = -\int_{a}^{b} S\vec{\nabla}T \cdot \vec{ds}$$
(2.34)

If the Seebeck coefficients are temperature independent, Eqn. 2.34 reduces to

$$U = (S_A - S_B)(T_1 - T_2).$$
(2.35)

Comparing the integrands of the path integrals leads to

$$-\vec{\nabla}\varphi_{e-ch} = S \cdot \vec{\nabla}T. \tag{2.36}$$

Eqn. 2.36, the local form for thermoelectric voltages, results from the thermodiffusion of the conduction electrons which is valid for both, metals and semiconductors.

The test setup for thermopower consists of two conductors (A and B) with different

<sup>&</sup>lt;sup>5</sup>References: [3, 28, 27, 14, 6, 2, 31]



Figure 2.3.: Thermoelectric circuit - test setup for thermopower

temperatures  $T_1$  and  $T_2$  at the soldering points (see Fig. 2.3)

$$U = (S_A - S_B)(T_1 - T_2).$$
 (2.37)

$$U = -\int_{a}^{b} SdT = -\int_{a}^{b} S\vec{\nabla}T \cdot \vec{ds}$$
(2.38)

If  $T_1 \neq T_2$  an open-circuit voltage  $\Delta V$  is generated; if the circuit is closed, a thermoelectric circular current is flowing. Since the Ohmic current is proportional to a potential difference and the thermodiffusion current is proportional to a temperature difference, a proportionality between potential and temperature difference results, which corresponds to Eqn. 2.35 [...] Here  $S_A$  and  $S_B$  denote the Seebeck coefficient (thermoelectric power) of conductor A and B. [...] If a temperature dependence of S is taken into account, Eqn. 2.35 for the thermoelectric potential needs to be replaced by a path integral (Eqn. 2.38), taken along the pieces of metal between the exits a and b of the voltmeter in the circuit shown in Fig. 2.3. (cit. from [14]) Expression of the Seebeck coefficient in terms of the Peltier-heat II leads to

$$\Pi = T \cdot S = \frac{\sum_{i} h_i v_i(x)}{e \sum_{i} v_i(x)},\tag{2.39}$$

where the velocity  $v_i(x)$  of the  $i^{th}$  electron occurs. Assuming the thermal heat is the difference between the discrete electron energies  $E_i$  to  $E_F$ , the Fermi-energy,  $h_i = E_i - E_F$ , results to

$$S = \frac{1}{eT} \frac{\sum_{i} (E_i - E_F) v_i(x)}{\sum_{i} v_i(x)} = \frac{1}{eT} \frac{\sum_{i} (E_i - E_F) j_i(x)}{\sum_{i} j_i(x)}.$$
 (2.40)

Association of the electrical current  $j_i = e \cdot v_i$  with electrons having energies between E

and E + dE leads to

$$S = \frac{1}{eT} \frac{\int (E_i - E_F) j_x(E) dE}{\int j_x dE},$$
(2.41)

with the current density in x-direction  $j_x = \sum_i ev_i(x)$  (belonging to an electric field applied in positive x-direction  $\epsilon_x$ ). The charge current density in the scope of the linearised Boltzmann equation 2.1 is expressed as

$$j_x = -\epsilon_x \int \sigma_x(E) \frac{df_0}{dE} dE$$
(2.42)

with the partial electrical conductivity  $\sigma_x$  with integration over constant energies E in the  $\vec{k}$  space:

$$\sigma_x = \frac{e^2}{4\pi^3\hbar} \int \tau \frac{v_x^2}{v} dS.$$
(2.43)

So a general expression for the thermopower (of isotropic materials) can be written as

$$S = \frac{1}{eT} \frac{\int_0^\infty \sigma_x (E - E_F) \frac{df_0}{dE} dE}{\int_0^\infty \frac{df_0}{dE} dE}.$$
(2.44)

With further assumptions  $(df_0/dE)$  has noticeable values only in the range  $k_BT$  above  $E_F$ ,  $E = E_F$  and only elastic scattering are taken into account) the thermopower reads

$$S = \frac{\pi^2}{3} \frac{k_B}{e} k_B T \frac{\partial \ln \sigma(E)}{\partial E}.$$
(2.45)

The thermopower can be split to several contributions: Due to the fact that the drag

$$S = S_e + S_q + S_m. ag{2.46}$$

symbol	meaning
$S_e$	diffusion term, temperature gradient causes electron movement
$S_g$	phonon drag term, phonons causes electron drag
$S_m$	magnon drag term, magnons causes electron drag

terms are second order effects they are often ignored. The diffusion term  $S_e$  is dominated by scattering events of the conduction electrons while moving along the temperature gradient in the material. With the Kohler rule, the different contributions

$$S_e \cdot W_e = S_{e,0} \cdot W_{e,0} + S_{e,ph} \cdot W_{e,ph} + S_{e,mag} \cdot W_{e,mag}$$
(2.47)

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can be taken into account with  $W_e$  representing the thermal resistivity for electrons. A first order approximation, the Nordheim-Gorter rule, employs the Wiedemann-Franz law (see Chapter 2.1.2), thus,

$$S_{e} \cdot \rho_{e} = S_{e,0} \cdot \rho_{e,0} + S_{e,ph} \cdot \rho_{e,ph} + S_{e,mag} \cdot \rho_{e,mag}.$$
(2.48)
$$\underbrace{\text{symbol}}_{\text{index } e, 0} \qquad \text{electron-impurity scatter}_{\text{index } e, ph} \qquad \text{electron-phonon scatter}_{\text{index } e, mag}$$

From

$$S = \frac{\pi^2 k_B^2 T}{3e} \left[ \frac{\partial \ln \sigma(E)}{\partial E} \right]_{E_F}$$
(2.49)

where  $\sigma$  is the electrical conductivity, the application of the free electron gas model for simple metals yields:

$$S(T > \theta_D) = \frac{\pi^2 k_B^2 T}{eE_F}$$
(2.50)

$$S(T \ll \theta_D) = \frac{\pi^2 k_B^2 T}{3eE_F} = \frac{1}{3} \times S(T > \theta_D).$$
 (2.51)

For free electrons, the Fermi energy is interrelated with the charge carrier density n by

$$E_F = \frac{h^2}{2m} \left(\frac{3}{8\pi} \cdot n\right)^{2/3}.$$
 (2.52)

and n = N/V as the charge carrier density in the Fermi-Gas model.

With  $\sigma = \frac{1}{\rho}$  and the Drude-formula (Eqn. 2.19) the following relation results:

$$\sigma \propto n$$
 (2.53)

with n, the charge carrier density. According to Eqn. 2.49

$$S \propto \frac{\partial \ln \sigma(E)}{\partial E}$$
 (2.54)

results. Within the free electron gas model, the number of occupied states is equal to the number of electrons, so

$$\sigma \propto N(E)|_{E=E_F} \tag{2.55}$$

leads to

$$S \propto \frac{1}{N(E)} \frac{\partial N(E)}{\partial E}|_{E=E_F},$$
(2.56)

with N(E) as the density of states.

#### 2.1.4. Figure of Merit

<sup>6</sup> To characterize a material owing its thermoelectric performance, the figure of merit is used. In the previous chapters a dependence of the thermoelectric properties constituting the thermoelectric performance was already discussed. Generally, the figure of merit is expressed as

$$Z = \frac{S^2}{\rho\lambda} \left[\frac{1}{K}\right].$$
 (2.57)

To get a dimensionless figure, the figure of merit is often multiplied by T.

$$ZT = \frac{S^2 \cdot T}{\rho \lambda} \ [1] \tag{2.58}$$

To obtain a high figure of merit, the material should exhibit a large Seebeck coefficient and small electrical resistivity as well as small thermal conductivity. Materials usually do not provide such a combination - compare Eqn. 2.48. With a small electrical resistivity also the thermopower will be small.

A high Seebeck coefficient provides a large potential difference between two junctions, if the thermal conductivity is high, the temperature gradient will decrease and therefore the potential difference between the two junctions will decrease. Additional, a high electrical resistivity is causing Joule heating and a decrease of voltage output caused by the high internal resistance occurs.

Creating materials with a high figure of merit for a required temperature range is an aim of contemporary research.

## 2.2. Specific heat

<sup>7</sup> Specific heat, describing the ability to absorb heat, belongs to the fundamental characteristics of solids. A variety of thermodynamic variables can then be calculated employing

<sup>&</sup>lt;sup>6</sup>References: [29]

<sup>&</sup>lt;sup>7</sup>References: [18, 25, 6, 19, 22]

the specific heat. The heat capacity follows from

$$C = \frac{Q}{\Delta T},\tag{2.59}$$

with  $\Delta T \rightarrow 0$ .

$$c = \frac{1}{mol} \lim_{\Delta T \to 0} \frac{Q}{\Delta T}$$
(2.60)

The specific heat can be defined as the molar heat capacity at constant volume

$$c_V = \left(\frac{(\partial'Q)}{\partial T}\right)_V = \left(\frac{(\partial U)}{\partial T}\right)_V$$
(2.61)

or as the molar heat capacity at constant pressure

$$c_P = \left(\frac{(\partial'Q)}{\partial T}\right)_P = \left(\frac{\partial(U+pV)}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P, \qquad (2.62)$$

with  $\partial'Q$  an infinitesimal heat transfer, U, the total energy and H = U + pV, the enthalpy. The entropy S as well as the free energy F can be derived within the temperature dependent specific heat.

$$S(T) = \int_0^T \frac{c_V(T')}{T'} dT'$$
 (2.63)

$$F(T) = \int_0^T \int_0^{T'} \frac{c_V(T'')}{T''} dT'' dT'$$
(2.64)

Experimental measurements are usually restricted to the determination of  $c_P$ . The difference of  $c_P$  and  $c_V$  is negligible for solids; at low temperatures it tends to zero.

$$c_P - c_V = \frac{T v \alpha^2}{\kappa_T},\tag{2.65}$$

with v, the molar volume,  $\alpha = (\frac{1}{V})(\frac{\partial V}{\partial T})_P$ , the thermal expansion coefficient and  $\kappa = -(\frac{1}{V})(\frac{\partial V}{\partial P})_T$ , the isothermal compressibility. The most principal contributions to the specific heat of simple metals are thermal excitations of the conduction-electrons and the contributions of the lattice vibrations (phonons)

$$c = c_{el} + c_{ph}.\tag{2.66}$$

#### 2.2.1. Lattice contribution to specific heat

The following discussion is based on the harmonic approximation where the 3N vibration modes of a solid (consisting of N atoms) are represented by a set of 3N linear harmonic oscillators with frequencies  $\nu_i$  (i = 1, ..., 3N).

Generally, the phonon contribution to specific heat is

$$C_{ph}(T) = R \int_{0}^{\infty} F(\omega) \frac{4 \cdot \left(\frac{\omega}{2k_{B}T}\right)}{exp\left\{\frac{\omega}{k_{B}T}\right\} + exp\left\{-\frac{\omega}{k_{B}T}\right\} - 2} d\omega = R \int_{0}^{\infty} F(\omega) \frac{\left(\frac{\omega}{2k_{B}T}\right)}{\sinh^{2}\left(\frac{\omega}{2k_{B}T}\right)} d\omega,$$
(2.67)

with  $F(\omega)$  as the energy dependent phonon density of states.

 $F(\omega)$  can be approximated, the Debye model sets for acoustic phonons  $F(\omega) \sim \omega^2$  to an upper frequency limit of  $\omega_D$ , respectively a characteristic temperature  $\Theta_D = \hbar \omega_D / k_B$ . The Einstein model for optical phonons sets the density of states to  $F(\omega) \sim \delta(\omega - \omega_E)$ , with the characteristic temperature of  $\Theta_E = \hbar \omega_E / k_B$ . For low temperatures the Debye model provides a  $T^3$ -dependence while the Einstein model provides an exponential dependence of temperature to the specific heat. At high temperatures both models deliver the Dulong-Petit value of 3R. (literal interpretation from [19])

#### 2.2.2. Contribution of the conduction electrons to specific heat

The heat capacity of the conduction electrons is determined similar to the lattice contribution to specific heat but for electrons the Fermi-Dirac distribution function f(E,T) has to be used instead of the Bose-Einstein distribution function. The density of states  $N(E_F)$ is proportional to  $\sqrt{E}$  within the free electron gas model (non-interacting electron-gas). The relation for specific heat of electrons and temperature is

$$c_V^e = \gamma T (1 + bT^2) \tag{2.68}$$

with

$$\gamma = \frac{\pi^2 k_B^2}{3} N(E_F) \tag{2.69}$$

where  $bT^2$  is a term for high-temperature correction, *b* depends on the shape of the density of states. To include band effects or electron-phonon interactions, further corrections are necessary. (literal interpretation from [19])

## 3. Experimental Design

<sup>1</sup> A series of type I clathrates ( $Ba_8Zn_xGe_{46-x-y}Si_y$ , x = 8, y = 10, 19, 28;  $Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$  and  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$ ) was prepared with a weight of 2-4 grams from elemental ingots (Ba 99.9, Zn, Cu, Pd 99.99, Ge and Si 99.999 mass.%) by reaction in vacuum-sealed quartz tubes at  $T = 800^{\circ}C$  for 4 days followed by quenching in cold water. The reaction products were pulverized<sup>2</sup> and compacted in cylinders with diameter 10 mm and height 6 mm by hot pressing. Samples were analysed by x-ray powder diffraction and electron probe micro analysis (EPMA). (cit. from [4])

Another series of type I clathrates,  $Ba_8Ag_zGe_{46-z}$  (z=2, 3, 4, 5), was prepared with a weight of 1.5 g/sample from elemental ingots (Ba and Ag 99.9, Ge 99.999 mass.%) by arc melting followed by annealing at  $T = 800^{\circ}$  C for 5 days and quenching in cold water. The alloys were powderized by ball milling and then compacted in cylinders with a volume of 1 cm<sup>3</sup> ( $\approx$  6 g) by hot pressing. Afterwards the samples were annealed at  $T = 800^{\circ}$ C again for 3 days.

The samples were cut into parallelepipeds with approximate dimensions  $1.5 \times 1.5 \times 6.5$  mm and cylinders with a diameter of 6 mm and a height of  $\sim 0.9$  mm with diamond and wire saw as well as with an ultrasonic driller.

To physically characterize the samples, the temperature dependent resistivity, thermal conductivity and Seebeck coefficient were investigated.

### 3.1. Electrical Resistivity

The temperature dependent resistivity was measured in a standard technique above room temperature employing a four-terminal DC measurement system. Below room temperature both a DC technique and also an AC bridge was used. (cit. from [4]) The samples analysed are bar-shaped with a length of about 5-8 mm and a cross section of ca. 1-2 mm $\times$ 1.5 mm.

<sup>&</sup>lt;sup>1</sup>References: [4, 17, 28]

 $<sup>^2\</sup>text{all}$  samples were hand milled except  $\text{Ba}_8\text{Zn}_{7.4}\text{Ge}_{19.8}\text{Si}_{18.8}$  which is ball milled

#### **3.1.1.** $\rho$ below room temperature

The temperature dependent electrical resistivity below room temperature was obtained with a home-made standard four-terminal AC and DC measuring technique. The principle is shown in Fig. 3.1.



Figure 3.1.: Principle of the standard four-terminal DC technique to measure electrical resistivity; the grey bar illustrates the sample

The four point technique is realised by four gold needles which are pressed to the sample by springs or for small samples by adhesive bonding of wires. Via the outer contacts the current is applied, at the inner contacts the voltage is measured - the resulting resistivity is calculated by Ohm´s law

$$R = \frac{U}{I} \left[ \frac{V}{A} = \Omega \right]$$
(3.1)

$$R = \rho \frac{l}{A} \left[ \Omega m \cdot \frac{m}{m^2} = \Omega \right].$$
(3.2)

A is the cross section and l the length along the voltage drops - the specific resistivity is obtained by

$$\rho = \frac{U}{I} \cdot \frac{A}{l} \left[ \frac{V}{A} \cdot \frac{m^2}{m} = \Omega m \right].$$
(3.3)

In the DC-mode the current direction is switched back and forth at every measured point to avoid errors in the measurement because of any thermo voltages. To measure the temperature in the DC-mode a AuFe0.07% / Chromel thermocouple was used; the

reference temperature was obtained by using a thermos bottle with sludge. The ACequipment uses resistive sensors of Ge (T<30K) and Pt (T>30K) for the temperature measurement and an AC resistance bridge 370 by LakeShore with an additional low resistance scanner (Model 3716L). After the cool down with liquid <sup>4</sup>He in a cryostat the temperature dependent electrical resistivity is automatically measured by a PC while the reheating. (For further details see [28].)

#### **3.1.2.** $\rho$ above room temperature

The temperature dependent electrical resistivity above room temperature was taken employing a ZEM3 Unit (Ulvac, Japan) which also uses the four point technique. The sample, which is bar-shaped (as mentioned before), is fixed vertically between two brackets which provide the contacts for the current. To measure the voltage, two horizontally probes are pressed on the sample using a micrometer. After entering the needed parameters the measuring process is computer-operated.

## 3.2. Thermal Conductivity

#### **3.2.1.** $\lambda$ below room temperature

Thermal conductivity below room temperature was obtained by a steady state heat flow method on rectangular shaped samples with a typical cross section of  $1-2 \text{ mm}^2$  and a length of about 7 mm. (cit. from [4]) The principle is facing reality in Fig. 3.2 vs. Fig. 3.3.

The test setup as it is shown in Fig. 3.3 is enclosed by two radiation shields and a final cylindrical cover and evacuated. The block where the bottom of the sample is fixed and so in thermal contact with the heat sink is cooled by a flow of <sup>4</sup>He. The flow of He is automatically regulated but can be overruled by hand. After stabilising at a certain temperature the sample is heated from the top using a strain gauge (called heater in Fig. 3.2). At the bottom the sample is still on the set-temperature. After reaching a constant heat flux (which is detected by two thermocouples along the sample and a third one at the heat sink providing a reference), the thermal conductivity is obtained by the average of three measurements. The measured data are attached to a middle temperature  $T_m$  calculated by

$$T_m = T_0 + \Delta T_B + \frac{\Delta T_S}{2}.$$
(3.4)



Figure 3.2.: The principle of measuring thermal conductivity



Figure 3.3.: The reality of measuring thermal conductivity

symbol	meaning
$T_0$	temperature of the heat sink
$\Delta T_B$	temperature difference between heat sink and lower thermocouple
$\Delta T_S$	temperature difference between the thermocouples alongside the sample

The thermal conductivity  $\lambda$  can be derived from the Fourier law

$$\vec{q} = -\lambda \nabla T = \frac{1}{A} \frac{dQ}{dt} = \frac{1}{A} \dot{Q}$$
(3.5)

symbol	meaning
$\nabla T$	temperature gradient
$\lambda$	thermal conductivity
$\vec{q}$	heat flux density
A	cross section
Q	amount of heat which can be transported
$\Delta T$	temperature difference

with an approximation of  $\nabla T$  by

$$\nabla T = \frac{dT}{dl} \approx \frac{T_2 - T_1}{l} = \frac{\Delta T}{l},$$
(3.6)

while l is the distance between the copper wires spooled around the sample to function as thermal contact and to clamp the thermocouples - see Fig. 3.3. With the modulus

#### 3. Experimental Design

of  $\vec{q}$ :  $(|\vec{q}| = \lambda |\nabla T|)$  the thermal conductivity reads

$$\lambda = \frac{l}{A} \frac{\dot{Q}}{\Delta T} \left[ \frac{mW}{cmK} \right]. \tag{3.7}$$

This measuring process includes errors of heat losses at elevated temperatures. To calculate this radiation losses a black body radiation is assumed. With the Stefan-Boltzmann equation the heat loss can be calculated:

$$Q = \epsilon \sigma_{SB} A \left( T_S^4 - T_0^4 \right). \tag{3.8}$$

symbol	meaning
$T_S$	sample temperature
$T_0$	temperature of the heat sink and surrounding radiation shield
A	sample surface
$\sigma_{SB}$	Stefan-Boltzmann constant: $\sigma_{SB} = 5.7 \times 10^{-8} \left[ \frac{W}{m^2 K^4} \right]$
$\epsilon$	emissivity $0 \le \epsilon \le 1$

It follows that

$$Q_{rad} = 2\epsilon \sigma_{SB} A T_S^3 \bigtriangleup T_S = a T_S^4. \tag{3.9}$$

Because of  $\lambda \propto \frac{\dot{Q}}{\Delta T}$  (see eqn. (3.7)) the heat loss due to radiation has a  $T^3$ -dependence. (For further details see [28].)

#### **3.2.2.** $\lambda$ above room temperature

Thermal conductivity above room temperature was obtained by a flash method (Flashline3000, Anter, USA) while NIST stainless steel served as reference material. To be measured with the Flashline the samples have to be cylindrical shaped with a diameter of d = 6 mm and a thickness of  $\sim 1$  mm. The equipment provides two parts: one part to measure consecutively four samples from room temperature up to 1000°C and the second part to measure one sample from -100°C to 200°C - the cooling is maintained by using liquid nitrogen. Also this equipment is computer-operated.

## 3.3. Thermopower

The Seebeck coefficient below room temperature was derived from an (home-made) AClike heating technique of the samples, using Ni/Cr-Ni as electrodes. The high temperature data were taken employing a ZEM3 Unit (Ulvac, Japan). (cit. from [4])

The analysed samples are bar-shaped with a length of about 5-8 mm and a cross section of ca. 1-2 mm $\times$ 1.5 mm.

### 3.3.1. S below room temperature

The AC-like heating technique to measure the Seebeck coefficient mentioned before works as follows: The specimen holder consists of two blocks with strain gauges glued on top with superglue (see fig. 3.4). The bar shaped sample was fixed to this blocks with an ethanol soluble glue so that the strain gauges have contact near top and bottom of the sample. A temperature gradient can be obtained in two directions (AC-like heating technique). On the sample - localised between the strain gauges - the two thermocouples are fixed with silver conductive paste to measure the voltages caused by the temperature gradients (in both directions), the results are averaged.



Figure 3.4.: Device for Seebeck-measurements

The assembly is encased in a vacuum-sealed measuring chamber, which was inserted in a  ${}^{4}$ He bath cryostat. The measuring process is computerised. (For further details see

[28, 17].)

### 3.3.2. S above room temperature

The temperature dependent thermopower above room temperature was obtained by a ZEM3 Unit (Ulvac, Japan) which is using the four probe point technique. The sample which is bar-shaped as mentioned before is fixed vertically between two brackets which provide the temperature gradient. To measure the voltage, two horizontally probes are pressed on the sample using a micrometer. After entering the needed parameters the measuring process is computer-operated.

## 3.4. Specific heat

### **3.4.1.** c<sub>P</sub> below room temperature

<sup>3</sup> The specific heat measurement in the temperature range between 3 K and 100 K was taken in an automated calorimeter using a quasi adiabatic step heating technique. The sample holder consists of a sapphire plate with a strain gauge acting as pulse heater and a *Cernox* temperature sensor and is fixed by nylon wires. This assembly is surrounded by a radiation shield. Samples, plain polished at the bottom, with a weight of 2 - 3 g are glued to the sapphire plate with Apiezon grease to establish thermal contact. Further details of this experimental setup provides the diploma thesis (1991) and thesis (1995) of G. Schaudy, TU Vienna and the diploma thesis of H. Michor, TU Vienna, 1993.

### 3.4.2. $c_P$ above room temperature

The experimental data of specific heat above room temperature was received simultaneously while thermal conductivity measurements by a flash method (Flashline3000, Anter, USA). For determination of the specific heat the temperature dependent density of the investigated material is needed. The density at room temperature was measured and linear approximated to higher and lower temperatures. NIST stainless steel served as reference material. To be measured with the Flashline the samples have to be cylindrical shaped with a diameter of d = 6 mm and a thickness of  $\sim 1$  mm. The equipment provides two parts: one part to measure simultaneously four samples from room temperature up

<sup>&</sup>lt;sup>3</sup>References: [5]

to 1000°C and the second part to measure one sample from -100°C to 200°C - the cooling is maintained by using liquid nitrogen, the equipment is computer-operated.

## 4. Measurement Results and Analyses

The measured data were obtained by the measurement equipments described in chapter 3. The materials can be classified in two series: first the Pd, Cu, Si - Zn series (row 1-6 in table 4.1) and the Ag-series (row 7-10 in table 4.1). Consequently mentioning the Si - Zn series the  $Ba_8Zn_xGe_{46-x-y}Si_y$  series is meant (row 3-6 in table 4.1). The atoms per unit cell, the lattice parameter a and the resulting atoms per unit cell N are indicated in table 4.1 The lattice parameters of the Ag-series increase with the amount of Ag in the

composition	N [1]	lattice parameter [nm]
$Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$	54	1.07664
$Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$	54	1.06994
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	54	1.05278
$Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$	54	1.06086
$Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$	54	1.06026
Ba <sub>8</sub> Zn <sub>7.6</sub> Ge <sub>29.3</sub> Si <sub>9.1</sub>	54	1.06833
Ba <sub>8</sub> Ag <sub>2</sub> Ge <sub>44</sub>	54	1.0742
$Ba_8Ag_3Ge_{43}$	54	1.078
$Ba_8Ag_4Ge_{42}$	54	1.0814
$Ba_8Ag_5Ge_{41}$	54	1.0842

Table 4.1.: Atoms per unit cell, N and lattice parameter of all compounds

composition. To keep the survey of the measured data, first the results of the Pd, Cu, Si - Zn series will be shown, then the results of the Ag-series.


Figure 4.1.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>T<sub>x</sub>T'<sub>y</sub>Ge<sub>46-x-y</sub> for various values of x and y - Overview.

#### 4.1. Resistivity

# 4.1.1. Temperature dependent electrical resistivity of Ba<sub>8</sub>T<sub>x</sub>T'<sub>y</sub>Ge<sub>46-x-y</sub>

Fig. 4.1 summarizes the temperature dependence of the electrical resistivity of the Pd, Cu, Si - Zn series. Obviously two compounds are semiconductors:  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$ and  $Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$ . To achieve a closer look to the remaining four compounds in Fig. 4.2 the two semiconductors are omitted. A further very interesting point is the diverse behaviour of the slightly different compositions  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  and  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$ . The difference resulted from the preparation (as it is pointed out in Fig. 4.3), where one material was ball milled and the other one hand milled.

To describe the experimental data (see overview in Fig. 4.1 and Fig. 4.2) theoretically, the Bloch-Grüneisen model (Eqn. 2.21), the two-band model (Eqn. 2.1), the two-band model with Mott-Jones term (Eqn. 2.25) and the three-band model (for semiconductors respectively for metals) are applied with least-squares fits to the measurement results of



Figure 4.2.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>T<sub>x</sub>T'<sub>y</sub>Ge<sub>46-x-y</sub> for various values of x and y - without semiconductors.



Figure 4.3.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> which is ball milled and Ba<sub>8</sub>Zn<sub>7.2</sub>Ge<sub>19.9</sub>Si<sub>18.9</sub> which is hand milled.



Figure 4.4.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> and Ba<sub>8</sub>Zn<sub>7.2</sub>Ge<sub>19.9</sub>Si<sub>18.9</sub> below room temperature. The solid lines are the fits of the modified Bloch-Grüneisen formula. The inset displays the energy dependent electronic density of states as explained in the text.

the compositions of the Pd, Cu, Si - Zn series.

To explain the different behaviour of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  (semiconductor-like behaviour) and  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  (metal-like behaviour) as it is shown in Fig. 4.3 the Bloch-Grüneisen formula with a temperature dependent charge carrier concentration n(T) (two-band model) was used to fit the results below room temperature - see Fig. 4.4. The solid curves in Fig. 4.4 represent modified Bloch-Grüneisen (two-band model) fits. Also two sketches are drawn in the picture showing qualitatively the density of states with respect to energy for both compositions. If the density of states  $N_0(E)$  is relatively low (as it is appropriate for  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$ ) the general resistivity is higher - especially in comparison with the resistivity of  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  where a larger density of states would provide an explanation for the generally smaller resistivity.

Both the position and the width of the band gap differs for the two materials. A small gap with a larger  $E_1$  (describing the position of the gap) as it is shown for Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> n(T) implies semiconducting-like behaviour. For



Figure 4.5.: Temperature dependent resistivity  $\rho$  of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$ . The filled black circles represent the experimental data. The pale solid and dash-dot lines represent the fits as explained in the text.





 $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  the modified Bloch-Grüneisen model results in an extremely large gap located slightly above the Fermi Energy  $E_F$ . This evidences the proximity of these materials to a metal-to-insulator transition.

Further investigations on the temperature dependent electrical resistivity of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  and  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  with regard also to higher temperatures up to 800 K are displayed in Fig. 4.5 and in Fig. 4.6. For both compositions the two-band model with the Mott-Jones term is the best choice, although in the case of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  the two-band model even with the Mott-Jones term describes the experimental data only rawly.

Both  $Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$  and  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$  exhibit high resistivities at low temperatures.

With decreasing temperatures the resistivity of Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> is rising, between  $\sim 300$  and  $\sim 550$  K the dependence of resistivity to temperature is almost linear, beyond that, the resistivity is again decreasing with rising temperature.  $\rho(T)$  appears like applying two semiconductors in a raw being a the motivation for applying the three-band model



Figure 4.7.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub>, the filled black circles represent the experimental data. The three pale solid, dash-dot and dashed lines represent the fits as explained in the text.



Figure 4.8.: Experimental data of the temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub>.

(see Fig. 4.7). The decrease from  $\sim 550$  K is not explained by both theoretical models used, but, like for the Zn-Si series, the two-band model is describing the semiconducting-like behaviour with unusual characteristics best.

 $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$  exhibits semi-conducting behaviour with very high values of the electrical resistivity but unfortunately, fitting of the experimental data of  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$  was not possible.

 $Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$  exhibits a metal-like behaviour, at very low temperatures the resistivity is rising with decreasing temperature, which is described by both two-band models, as it is shown in Fig. 4.9.

Also  $Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$  behaves metal-like up to 300 K, then saturation is followed by a slight decrease; finally, there is a  $\rho(T)$  rise again, starting at  $\sim 500$  K, which seems like applying two metals in a raw. Therefore, the three-band model was taken to fit the data (see Fig. 4.10). Surprisingly the model for semiconductors fits (until room temperature) better than the one for metals (see Fig. 4.10). The best qualitatively description of the behaviour of $\rho(T)$  provides the two-band model. The model represents the saturation



Figure 4.9.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Zn<sub>7.6</sub>Ge<sub>29.3</sub>Si<sub>9.1</sub>. The filled black circles represent the experimental data. The three pale solid, dash-dot and dashed lines represent fits as explained in the text.





and the rise starting at  $\sim 500$  K, but not the slight decrease of  $\rho(T)$  from  $\sim 350$  to  $\sim 550$  K, which leads to the association that this model is slightly too simple to explain this behaviour properly.

#### 4.1.2. Temperature dependent electrical resistivity of Ba<sub>8</sub>Ag<sub>x</sub>Ge<sub>46-x</sub>

In Fig. 4.11 the experimental results of the electrical resistivity of the Ag - based - series are plotted. All of the compositions showing a metal-like behaviour. From  $\sim 4.2$  K to  $\sim 20$  K a small decrease of resistivity is observed. With an increasing amount of Ag the resulting minimum in  $\rho(T)$  becomes more distinct.

All compositions of the Ag-series exhibit a maximum at high temperatures: For  $Ba_8Ag_3Ge_{43}$  at ~ 708 K the resistivity is  $\rho \sim 1935 \ \mu\Omega$ cm, for  $Ba_8Ag_4Ge_{42}$  at ~ 708 K with  $\rho \sim 2418 \ \mu\Omega$ cm and for  $Ba_8Ag_5Ge_{41}$  at ~ 609 K with  $\rho \sim 4162 \ \mu\Omega$ cm.

A theoretically description of the experimental data (see overview in Fig. 4.11) is done



Figure 4.11.: The temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Ag<sub>x</sub>Ge<sub>46-x</sub>, for various values of x

with applying the Bloch-Grüneisen model (Eqn. 2.21), the two-band model (Eqn. 2.1) and the two-band model with a Mott-Jones term (Eqn. 2.25) with least-squares fits to the experimental data of all the compositions of the Ag-series.

Because the resistivity of the Ag-series builds a maximum at higher temperatures (see Fig. 4.11), this leads to the idea of superposing the metal-like behaviour with a semiconducting behaviour at higher temperatures. Such a superposing would mean at least three bands for a simple theoretical model where at low temperatures a semiconducting like behaviour and at medium temperatures metal behaviour occurs. Upon a certain temperature a crossing of the second gap is possible which leads to semiconducting like behaviour at high temperatures. The band gap as well as the dimensions of the bands change with the amount of Ag (compare Fig. 4.11).

For  $Ba_8Ag_2Ge_{44}$ , a metal-like material, the low temperature behaviour and applied models are displayed in Fig. 4.13, where a rise in resistivity at decreasing temperature also results from the two-band models but the experimental data are not behaving exactly this way. Globally, over the temperature range of 4.2 K to 300 K the data are described best by the two-band model with the Mott-Jones term.



Figure 4.12.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Ag<sub>2</sub>Ge<sub>44</sub>, the filled black circles represent the experimental data. The three pale solid, dash-dot and dashed lines represent the fits as explained in the text



Figure 4.14.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub>, the filled black circles represent the experimental data. The three pale solid, dash-dot and dashed lines represent the fits as explained in the text



Figure 4.13.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Ag<sub>2</sub>Ge<sub>44</sub> up to 100 K for comparison of the different fits at low temperatures



Figure 4.15.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub> up to 100 K for comparison of the different fits at low temperatures



Figure 4.16.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub>, the filled black circles represent the experimental data. The three pale solid, dash-dot and dashed lines represent the fits as explained in the text





The high temperature maximum of the resistivity of  $Ba_8Ag_3Ge_{43}$  is described rawly by the two-band model with the Mott-Jones term, also at low temperatures this model is the best choice (see Fig. 4.14 and Fig. 4.15).

With higher amount of Ag the description of  $\rho(T)$  with the two band model with the Mott-Jones term becomes better (compare Fig. 4.16, Fig. 4.17, Fig. 4.18 and Fig. 4.19).

Looking like an error in measurement at a first glance, the whole Ag-series display an increase of resistivity strongly localized at 27 to 30 K (see Fig. 4.13, Fig. 4.15, Fig. 4.17 and Fig. 4.19). With increasing amount of Ag this characteristics becomes worse observable maybe because of the general rise of overall values of the resistivity. Such a discontinuity exhibits the complexity of the band structure.



Figure 4.18.: Temperature dependent resistivity  $\rho$  of Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub>. The filled black circles represent the experimental data. The three pale solid, dash-dot and dashed lines represent the fits as explained in the text





## 4.2. Thermal Conductivity

# 4.2.1. Temperature dependent thermal conductivity of $Ba_8T_xT'_yGe_{46-x-y}$

In Fig. 4.20 the data of temperature dependent thermal conductivity taken at low temperatures (4.2 K - room temperature) for all compositions of the Pd, Cu, Si - Zn series are compared. In Fig. 4.20 two different types of low temperature features are evident:  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$  exhibits a maximum at low temperatures, which is a signature of reduced phonon scattering on point defects and grain boundaries, while  $Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$  does not show such a maximum. The temperature dependent thermal conductivities of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  and  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  are dissimilar as the former shows no peak at low temperatures while the latter does.

The overall values of  $\lambda(T)$  as shown in Fig. 4.20 are rather small, which is expectable for cage forming compounds filled by loosely bound electro-positive elements. According



Figure 4.20.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>T<sub>x</sub>T'<sub>y</sub>Ge<sub>46-x-y</sub> below room temperature for various values of x and y.

to the Wiedemann-Franz law (Eqn. 2.27) the electronic contribution to thermal conductivity is small for materials with high resistivity - consequently the phonon scattering on electrons is noticeably reduced. Further inspection of the experimental data is done by fitting the lattice contribution to the low temperature thermal conductivity ( $\lambda_{ph}$ ) by the Callaway-model (see Chapter 2.1.2).

As already mentioned, the low temperature thermal conductivity measurement of  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$  shows a maximum at  $\sim 14$  K which is a signature of reduced phonon scattering on point defects and grain boundaries while  $Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$  does not exhibit such a maximum. The disorder owing to the twofold substitution of Ge by Pd and Zn appears to be quite efficient in scattering phonons compared to the case of Cu and Zn. At a first glance, this might result from a combination of the heavy mass element Pd and the substantial mass difference of Pd and Zn, which is significantly larger than that of Cu and Zn.

It is not possible to explain the behaviour of  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$  completely employing the Callaway model as it is displayed in Fig. 4.21. The sharpness of the maximum



Figure 4.21.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40</sub> (filled black circles - nearly covered by the green filled circles, representing  $\lambda_{ph}$ + radiation losses); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.



Figure 4.22.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.



Figure 4.23.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Zn<sub>7.2</sub>Ge<sub>19.9</sub>Si<sub>18.9</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.

observed cannot be reached within this model. At temperatures above  $\sim 150$  K it seems that failures of the measurement, specifically the radiation losses, are not behaving as predicted by the model described in Eqn. 2.28. The fit-parameter describing the slope at higher temperatures (above 150 K) was fixed to a value such that the model-curve is parallel to the measured values. This was necessary to obtain reasonable results after subtracting the radiation loss contribution (solid curve  $\propto T^3$ ).

The Callaway model describes the  $\lambda_{ph}$  curve of Ba<sub>8</sub>Pd<sub>2.4</sub>Zn<sub>3.3</sub>Ge<sub>40.3</sub> Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> well at temperatures below 150 K. Above this temperature a proper description of the measured data is not possible. Like for Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> a compromise was selected such that the model curves shapes parallel to  $\lambda_{ph}$ .

The measurement results of the thermal conductivity of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  (Fig. 4.24) and  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  (Fig. 4.23) are nearly as different as the measurement results of  $Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$  and  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$ . Similar to



Figure 4.24.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.

 $Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$ ,  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  exhibits (almost) no maximum at low temperatures while  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  does - like  $Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$ . The maximum at ~ 13 K has not the same sharpness - but is comparable. An argument about heavier elements in the cage cannot be taken into account at first sight.

With the fact that a larger molecular mass, in general, favours decreasing overall values of thermal conductivity (see [22]) and the comparison of the results of  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  and  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  with results from [21], where a suppression of the  $\lambda(T)$  maximum at low temperatures is attributed to the occurrence of vacancies, owning to a decreasing amount of Zn in  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  and  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  with results from [21], where a suppression of the behaviour at low temperatures of  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  and  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  can be found. Because Ge is substituted by both Zn and Si, in  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  and  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$ , both contributions to the molecular mass have to be taken into account. The molecular mass of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  is slightly higher than the molecular mass of  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  which explains, in a first approximation, the slightly smaller overall values of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  (Fig. 4.20).

Another effect provides a better explanation for the suppression of the  $\lambda(T)$  maximum in Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub>, than the slightly different amount of Zn in the two similar compositions.

Generally, smaller particles of the alloy can cause smaller grain sizes in the prepared material which is responsible for different mechanical as well as for thermoelectric properties. The two compositions are characterised by differences in preparation - Ba<sub>8</sub>Zn<sub>7.2</sub>Ge<sub>19.9</sub>Si<sub>18.9</sub> was hand milled, while Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> was ball milled before melting. With ball milling, particles with grain size in the  $\mu$ m-scale can be reached; hand milling usually causes larger particles than ball milling. In Ref. [22] the initial rise of  $\lambda_{ph}(T)$  is referred to boundary and point defect (defects comprise also vacancies) scattering; it becomes large when both quantities are small. If the strength of umklapp scattering increases,  $\lambda_{ph}$  starts to strongly decrease, thereby forming a maximum at lower temperatures. (cit. from [22]) Smaller grain sizes provide more scattering on boundaries, therefore a suppression of the maximum at low temperatures for Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> - which is ball milled - can be explained.

The Callaway model describes the thermal conductivity of  $Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$  (Fig. 4.25) and  $Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$  (Fig. 4.26) reasonably well from 4.2 K to ~100 K. In the



Figure 4.25.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Zn<sub>7.3</sub>Ge<sub>10.6</sub>Si<sub>28.1</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.



Figure 4.26.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Zn<sub>7.6</sub>Ge<sub>29.3</sub>Si<sub>9.1</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.



Figure 4.27.: Temperature dependent thermal conductivity  $\lambda$  within the temperature range of  $\sim 4$  to  $\sim 800$  K of  $\mathsf{Ba_8T_xT'_yGe_{46-x-y}}$  for various values of x and y.

temperature region above ~100 K the model reveals a different radiation loss compared to the experimental data. While comparing the results of  $Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$  (Fig. 4.25) and  $Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$ , it is obvious that  $Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$  - which is the one with the considerable higher molecular weight - shows smaller overall values of the thermal conductivity. But comparing the whole Zn-Si-series the described effect of the different molecular masses on the overall values of the thermal conductivity is not confirmed. Rather, scattering on various static imperfections seem to be predominant.

Also high temperature experimental data of  $\lambda(T)$  were determined. In Fig. 4.27  $\lambda(T)$  above room temperature, obtained by the flash method (see Chapter 3), is compared with the radiation-corrected data of  $\lambda(T)$ , determined with the low temperature equipment.

In principle the Flash data fits good with the low temperature experimental data as shown in Fig. 4.27. A detailed view is shown in Fig. 4.28. It displays the overlap at  $\sim 170-290$  K between the low temperature experimental data (from  $\sim 4$  to  $\sim 300$  K) with the data obtained with the Flash method. Additionally, a comparison is possible between the results obtained from the two units of Flashline3000. For Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> the



Figure 4.28.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>T<sub>x</sub>T'<sub>y</sub>Ge<sub>46-x-y</sub> for various values of x and y at the temperature range from  $\sim 150$  to  $\sim 800$  K.

data displays a step from  $\sim 15$  mW/cmK at $\sim 470$  K to  $\sim 24$  mW/cmK at $\sim 570$  K. Because already minor differences in preparation, as for example the constancy in graphite layering, can provoke very different measurement results. This step is not seen as a significantly change of thermal conductivity rather as a random error.

# 4.2.2. Temperature dependent thermal conductivity of $Ba_8Ag_xGe_{46-x}$

In Fig. 4.29 the temperature dependent thermal conductivity  $\lambda$  of all compositions of the Ag-series at low temperatures (4.2 K to ~ 300 K) is illustrated. The overall values of  $\lambda(T)$  of Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> and Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> are similar, Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub> exhibits a generally larger thermal conductivity.

Cage forming compounds usually exhibit small overall values of thermal conductivity, the overview in Fig. 4.29 confirms this also for the Ag-series. According to the



Figure 4.29.: The temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Ag<sub>x</sub>Ge<sub>46-x</sub> below room temperature for various values of x.

Wiedemann-Franz law (Eqn. 2.27) the electronic contribution to thermal conductivity is more significant for materials with lower resistivity (compare with Chapter 4.2.1)- consequently the phonon scattering on electrons may become important. Again fitting the lattice thermal conductivity ( $\lambda_{ph}$ ) with the Callaway-model (see Chapter 2.1.2) was done for further investigation.

In Fig. 4.30 the model fits  $\lambda_{ph}(T)$  reasonably well up to ~ 100 K. Above this temperature, experimental  $\lambda(T)$  data do not follow strictly the expected power law proposed by Eqn. 2.28.

The initial rise of  $\lambda_{ph}(T)$  of Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> at low temperatures is not well described by Eqn. 2.28 (see Fig. 4.31), but it fits well from  $\sim 37$  K to  $\sim 100$  K.

Also for Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> the model is not able to describe the initial rise starting at  $\sim 4.2$  K as it is displayed in Fig. 4.32, but it fits the lattice contribution to the thermal conductivity well from  $\sim 20$  K until  $\sim 130$  K.

With decreasing amount of Ag the overall values of the temperature dependent thermal



Figure 4.30.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.



Figure 4.31.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.



Figure 4.32.: Temperature dependent thermal conductivity  $\lambda$  of Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> (filled black circles); the lattice contribution  $\lambda_{ph}$  and the electronic part  $\lambda_e$  are shown as yellow filled triangles and grey solid line, respectively; the pink solid line is a least squares fit as explained in the text.



Figure 4.33.: Temperature dependent thermal conductivity  $\lambda$  within the temperature range of  $\sim 4$  to  $\sim 470$  K of Ba<sub>8</sub>Ag<sub>x</sub>Ge<sub>46-x</sub> for various values of x.

conductivity are rising (see Fig. 4.29).

The high temperature experimental data of  $\lambda(T)$  as determined by the flash method, is compared with the radiation-corrected data of low temperature  $\lambda(T)$  (see Fig. 4.33). The low temperature data of Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> and Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> achieve only 70 % and 63%, respectively, of the values obtained with the Flashline equipment, but the low and high temperature experimental data of Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub> fits well as it is displayed in Fig. 4.33.

A deviation in values of experimental data usually is explained with geometric irregularity, but such a large difference can not result only from a shift of the soldered wires (compare Chapter 3, Fig. 3.3) while fixing the sample to the low temperature device, moreover this would have been noticed. Giving a reason for this relative error is not possible without further investigations which had to be omitted due to time constraints.



Figure 4.34.: Temperature dependent Seebeck coefficient S of  $Ba_8Zn_xGe_{46-x-y}Si_y$  with various values of x and y

### 4.3. Thermopower

#### 4.3.1. Temperature dependent thermopower of $Ba_8T_xT'_yGe_{46-x-y}$

The temperature dependent Seebeck coefficients of the Ba<sub>8</sub>Zn<sub>x</sub>Ge<sub>46-x-y</sub>Si<sub>y</sub> series behave linearly and exhibit negative thermopower values (see Fig. 4.34). S(T) of Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> and Ba<sub>8</sub>Zn<sub>7.2</sub>Ge<sub>19.9</sub>Si<sub>18.9</sub>, although the similar composition is obvious<sup>1</sup>, is very different for these two compositions. While Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> @  $T \simeq 763$  K has a Seebeck coefficient of  $S \simeq -109 \ \mu\text{V/K}$  the thermopower of Ba<sub>8</sub>Zn<sub>7.2</sub>Ge<sub>19.9</sub>Si<sub>18.9</sub> @  $T \simeq 765$  K is  $S \simeq -189 \ \mu\text{V/K}$ .

On the other hand, the thermopower of  $Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$  and  $Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$  is almost similar with  $S(T \simeq 765 \text{ K}) \simeq -160 \mu \text{V/K}$  although the different composition would not lead to such an expectation.

 $<sup>^1</sup> remember$  the different preparation method,  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  is ball milled,  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$  is hand milled



Figure 4.35.: Temperature dependent Seebeck coefficient S of  $\mathsf{Ba}_8\mathsf{Cu}_{5.2}\mathsf{Zn}_{0.8}\mathsf{Ge}_{40.0}$  and  $\mathsf{Ba}_8\mathsf{Pd}_{2.3}\mathsf{Zn}_{3.6}\mathsf{Ge}_{40.1}$ 

The temperature dependent thermopower of Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> and Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> (both semiconductors - see Fig. 4.1) is more complex than that of the Si - Zn series (see Fig. 4.35). S(T) of Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> varies from  $-2.38 \ \mu\text{V/K} @ T = 5 \ \text{K}$  via 386  $\ \mu\text{V/K} @ T \simeq 146 \ \text{K}$  and  $\simeq -121 \ \mu\text{V/K} @ \simeq 501 \ \text{K}$  to  $\simeq 12.8 \ \mu\text{V/K} @ \simeq 764 \ \text{K}$  - compare Fig. 4.35. The thermopower of Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> shows a sharp rise until  $T = 24 \ \text{K}$  with  $S = 123 \ \mu\text{V/K}$  followed by a smooth increase up to  $T \simeq 418 \ \text{K}$  where S reaches  $\simeq 198 \ \mu\text{V/K}$ .

S(T) of Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> and Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> does not exhibit a linear temperature dependence. The thermopower, however, as it is expressed in Eqn. 2.56, can be written as a function of the density of states N(E) and the derivative of density of states with respect to the energy. A change from positive to negative values of thermopower can occur when the slope of  $\frac{\partial N(E)}{\partial E}$  changes from positive to negative with rising temperature / energy as it is shown in Fig. 4.36 and Fig. 4.37.

The thermopower of Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> between  $\sim 15$  K and 146 K is positive and increasing, that is followed by the consideration of meeting a positive slope of  $\frac{\partial N(E)}{\partial E}$  as it is sketched in Fig. 4.36. Negative values of S(T) are referred to a negative slope of



Figure 4.36.: example for a derivative of density of states at low temperatures





 $\frac{\partial N(E)}{\partial E}$  as shown in Fig. 4.37.

The behaviour of S(T) of Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> can be explained with a variation of the positive slope of density of states with temperature as S(T) is positive all over the temperature range observed.

#### 4.3.2. Temperature dependent thermopower of Ba<sub>8</sub>Ag<sub>x</sub>Ge<sub>46-x</sub>

The experimental results of the temperature dependent thermopower S of the Ag series exhibit an interesting behaviour. S(T) behaves almost linearly before reaching a minimum at high temperatures. The minimum varies both in position and magnitude from  $S \sim -108 \ \mu\text{V/K}$  at  $T \sim 758 \ \text{K}$  for Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub> via  $S \sim -129 \ \mu\text{V/K}$  at  $T \sim 758 \ \text{K}$  for Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> to  $S \sim -163 \ \mu\text{V/K}$  at  $T \sim 609 \ \text{K}$  for Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> as it is illustrated in Fig. 4.38. As the thermopower above room temperature had been measured simultaneously with the resistivity (see chapter 3) the extrema deduced are compared in Table 4.2.

composition	T of maximal resistivity [K]	T of minimal thermopower [K]
$Ba_8Ag_3Ge_{43}$	$\sim 708$	$\sim 758$
$Ba_8Ag_4Ge_{42}$	$\sim 708$	$\sim 758$
$Ba_8Ag_5Ge_{41}$	$\sim 609$	$\sim 609$

Table 4.2.: Comparison of occurring extrema in temperature dependent Seebeck and resistivity measurements above room temperature



Figure 4.38.: Temperature dependent thermopower of  $\mathsf{Ba}_8\mathsf{Ag}_x\mathsf{Ge}_{46\text{-}x}$  with various values of x

It is noticeable that the extrema of Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub> and Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> are located virtually at the same temperatures, but the temperatures of thermopower and resistivity extrema differ from each other by  $\Delta T = 50$  K. For Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> both extrema occur at ~ 610 K.

According to Eqn. 2.56, where S is related to the derivative of density of states with respect to the energy, the temperature dependent thermopower of  $Ba_8Ag_xGe_{46-x}$  can be explained with a change of this derivative. As S(T) is negative for the whole Ag - series, the derivative  $\frac{\partial N(E)}{\partial E}$  is negative, but varies with temperature - therefore changes in the temperature dependence of S occur.



Figure 4.39.: Temperature dependent figure of merit ZT of  $Ba_8T_xT'_yGe_{46-x-y}$  for various values of x and y

# 4.4. Figure of Merit

#### 4.4.1. Temperature dependent Figure of Merit of $Ba_8T_xT'_yGe_{46-x-y}$

The figure of merit is calculated according to Eqn. 2.58 with *DATAP*, Version 3.0, (c) H. Müller, TU Vienna, November 21, 1991, a program which allows mathematical operations with experimental data. The data have to be arranged in columns, the x-data in the first, the y-data in the second column then it is (among other things) possible to execute mathematical operations like  $+, -, *, \div$  with two different files, even if the x-data are not conform. To calculate the figure of merit, the radiation corrected values of low temperature thermal conductivity were used.

Although Ba<sub>8</sub>Cu<sub>5.2</sub>Zn<sub>0.8</sub>Ge<sub>40.0</sub> exhibits promising huge thermopower values (compare Fig. 4.35), the figure of merit reaches a maximum  $ZT \sim 8.9 \cdot 10^{-3}$  at  $\sim 530$  K. The interesting shape with three minima result from the thermopower values crossing the x-axis. The largest thermopower values obtained within the Pd, Cu, Si - Zn series show Ba<sub>8</sub>Pd<sub>2.3</sub>Zn<sub>3.6</sub>Ge<sub>40.1</sub> with  $ZT \sim 0.15$  at 467 K, Ba<sub>8</sub>Zn<sub>7.2</sub>Ge<sub>19.9</sub>Si<sub>18.9</sub> with  $ZT \sim 0.27$ 



Figure 4.40.: Temperature dependent figure of merit ZT of  ${\rm Ba_8Ag_xGe_{46-x}}$  for various values of x

at ~ 764 K and Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub> with  $ZT \sim 0.4$  at ~ 765 K. Comparing these values with other type I clathrates [20, 21, 22, 23], where the maximal figure of merit is predicted for Ba<sub>8</sub>Zn<sub>7.7</sub>Ge<sub>38.3</sub> with ZT = 0.42 at 700 K, the maximal figure of merit based to experimental data is ZT = 0.15 at 600 K for Ba<sub>8</sub>Pt<sub>2.7</sub>Ge<sub>41.8</sub> $\Box_{1.5}$ . ZT does not reach the predicted values of ZT = 1.7 @ 800 K (see NoIas, in [30]) for optimised compositions by far.

#### 4.4.2. Temperature dependent Figure of Merit of Ba<sub>8</sub>Ag<sub>x</sub>Ge<sub>46-x</sub>

The two compositions Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> and Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> display an unsteadiness around room temperature (see Fig. 4.40) which results from a deviation in experimental data obtained with different devices, as discussed in Chapter 4.2.2. These two compounds exhibit ZT(463 K) = 0.11 for Ba<sub>8</sub>Ag<sub>4</sub>Ge<sub>42</sub> and ZT(462 K) = 0.14 for Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub>.

The same is it for Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub>, the maximum figure of merit reaches  $ZT \sim 0.05$  at  $\sim 463$  K, as it is shown in Fig. 4.40. As already mentioned, Nolas predicts in [30] a figure of merit of ZT = 1.7 @ 800 K for optimized compositions.



Figure 4.41.: Temperature dependent specific heat of  $Ba_8Ag_xGe_{46-x}$ , plotted as  $c_P\left[\frac{J}{kgK}\right]$ vs T[K]

 $Ba_8Ag_2Ge_{44}$  exhibits the smallest electrical resistivity of the Ag-series, further investigation on this composition had, unfortunately, to be omitted within this diploma thesis due to time constraints but a significantly higher figure of merit is not to expect.

# 4.5. Specific heat

# 4.5.1. Temperature dependent specific heat of $Ba_8T_xT'_yGe_{46-x-y}$

Fig. 4.44 displays the high temperature specific heat of the Ag-series, determined with the Flash method.



Figure 4.42.: Temperature dependent specific heat  $c_P$  of  ${\rm Ba_8Ag_3Ge_{43}},$  plotted as  $c_P/T$  vs T

#### 4.5.2. Temperature dependent specific heat of Ba<sub>8</sub>Ag<sub>x</sub>Ge<sub>46-x</sub>

Specific heat at low temperatures was investigated only for  $Ba_8Ag_3Ge_{43}$ , the results are displayed in Fig. 4.5.2, the analyse in Fig. 4.5.2.

Significant deviations from the simple Debye model indicate a rather complicated phonon spectrum for this family of clathrates. The spectrum is supposed to be composed of background vibrations originating from the cage like structure - represented by a Debye spectrum - and, additionally, from the rattling modes of the loosely bound electropositive Ba atoms. (cit. from [22]) The model used in Fig. 4.5.2 was developed by Junod et al. [15]. Besides a background composed by a Debye spectrum, two Einstein modes are used to describe the behaviour of the phonon part of specific heat. The frequencies  $\omega_{E1} = 50$  K and  $\omega_{E2} = 81$  K are derived from the least-squares fit together with respective widths of  $\omega_{E1} \approx 4.4$  K and  $\omega_{E2} \approx 3.6$  K. The cut of frequency is 213.6 K. In comparison with the Debye temperature derived from the Callaway model (see A.2.1) - for Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub>  $\theta_D^{Callaway} = 53$  K - this result is more realistic.



Figure 4.43.: Temperature dependent specific heat  $c_P$  of Ba<sub>8</sub>Ag<sub>3</sub>Ge<sub>43</sub>, plotted as  $(c_P - \gamma T)/T^3$  vs  $\ln T$ . The dashed line is a least-squares fit of the experimental data using the model described in the text with two Einstein-like modes ( $\omega_{E1} = 50$  K and  $\omega_{E2} = 81$  K). The narrow, red solid line is the simple Debye function with  $\theta_D^{LT} = 260$  K. The broad, blue line (referring to the right axis) sketch the phonon spectral function F( $\omega$ ) plotted as  $\omega/4.93$  vs  $(5/4)R\pi^4\omega^{-2}2F(\omega)$  for which  $\omega$  is given in Kelvin.



Figure 4.44.: Temperature dependent specific heat of  $Ba_8Ag_xGe_{46-x}$ , plotted as  $c_P\left[\frac{J}{kgK}\right]$  vs T[K]

Fig. 4.44 displays the high temperature specific heat of the Ag-series, determined with the Flash method.

# 5. Conclusion

Intermetallic type I clathrates are ideally suited to match those condition required by G. Slack's concept of a phonon glass and an electron crystal to generate an optimum thermoelectric output. Thus Ba-Ge based type I clathrates have been prepared and studied with respect to their thermoelectric properties.

Substitutions and various routes of synthesis allow to fine-tune the electronic structure of these materials such that extremely high values of the Seebeck effect are obtained as a signature of the closeness to a metal-to-insulator transition. Such an electronic state can even provoke a temperature driven change from hole to electron dominated electronic transport when proceeding from very low to very high temperatures.

Similarity in composition of materials does not definitely imply a similarity in measurement results (compare the results of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  and  $Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$ ) as shown in Chapter 4.

The thermoelectric performance, as it is expressed by the figure of merit reaches ZT = 0.42 at T = 765 K for Ba<sub>8</sub>Zn<sub>7.4</sub>Ge<sub>19.8</sub>Si<sub>18.8</sub>, while Ba<sub>8</sub>Ag<sub>5</sub>Ge<sub>41</sub> approaches ZT = 0.14 at T = 462 K.
# A. Fitting procedure of the transport properties

<sup>1</sup> Theoretical models were adjusted to the experimental data of temperature dependent electrical resistivity and thermal conductivity with least squares fits, as described in Chapter 2 and displayed in Chapter 4. With *TableCurve 2D Version 5.01* so called *user defined functions (\*.udf)* can be programmed which include the possibility to limit the fit parameter between two values.

# A.1. Electrical Resistivity

The experimental data of the electrical resistivity  $\rho(T)$  in units of  $[\mu\Omega cm]$  were fitted over the whole temperature range available - mostly 4 K to 800 K.

### A.1.1. Bloch-Grüneisen

The temperature dependent resistivity follows from Matthiessen's rule to

$$\rho(T) = \rho_0 + \rho_{ph}(T) \tag{A.1}$$

with the Bloch-Grüneisen formula<sup>2</sup>

$$\rho_{ph} = \mathcal{R} \left(\frac{T}{\theta_D}\right)^5 \int_0^{\frac{\theta_D}{T}} \frac{z^5}{(e^z - 1)(1 - e^{-z})}.$$
 (A.2)

<sup>&</sup>lt;sup>1</sup>References: [17, 13, 28, 5]

<sup>&</sup>lt;sup>2</sup>The user defined function differs from Eqn. A.2 with a factor 4, this does not influence the result because  $\mathcal{R}$  is a fit parameter.

### User defined function corresponding to Eqn. A.1

#F1=\$^5/(EXP(-\$)+EXP(\$)-2)
#F2=#A2/X
Y=#A0+4\*#A1\*QIN(1,0.01,#F2,12)/#F2^5

### Variables and Fit parameters for the Bloch-Grüneisen model

- \$ ... dummy variable of integration
- #F1 ... integrand of Bloch-Grüneisen formula
- **#F2** ...  $\frac{\theta_D}{T}$
- x ... temperature
- Y ... resistivity  $\rho(T)$  [ $\mu\Omega cm$ ] according to Eqn. A.1
- #A0 ... residual resistivity  $\rho_0 \ [\mu \Omega cm]$
- #A1 ... electron-phonon interaction constant  $\mathcal{R}$  [ $\mu\Omega$ cm/K]
- **#A2** ... Debye temperature  $\theta_D$  [K]

Table A.1.:	Fit	parameter	Bloch-	Grüneisen	Fit

composition	#A0	#A1	#A2
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	10300	1987	237.9
$Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$	709	542.6	493.3
Ba <sub>8</sub> Zn <sub>7.6</sub> Ge <sub>29.3</sub> Si <sub>9.1</sub>	2697	399	216.7
$Ba_8Ag_2Ge_{44}$	325.6	202.7	224.9
$Ba_8Ag_3Ge_{43}$	557.5	559.8	353.8
$Ba_8Ag_4Ge_{42}$	893.9	1274.5	554.5
$Ba_8Ag_5Ge_{41}$	1786.3	1719.9	553.9

# A.1.2. Two-band model

An advancement of the Bloch-Grüneisen law is to apply a temperature dependent charge carrier density n(T), so that

$$\rho(T) = \frac{\rho_0 n_0 + \rho_{ph}}{n(T)}$$
(A.3)

using the Bloch-Grüneisen formula (Eqn. A.2) for  $\rho_{ph}$ .

### User defined function corresponding to Eqn. A.3

```
#F7=1.381*10^(-23)
#F1=$^5/(EXP($)-1)/(1-EXP(-$))
#F2=4*#A*(X/#F)^5*AI(1,1E-10,#F/X)
#F3=#F7*(-#B+X*LN(2)-X*LN(1+EXP(#G/X))+X*LN(1+EXP((#G+#B)/X)))
#F4=#D*SQRT(#F3*X*F7*LN(2))+#C
Y=(#C*#E/#F4)+(#F2)/#F4
```

### Variables and Fit parameters for the two-band model

\$	 dummy variable of integration
#F7	 Boltzmann's constant $k_B$
#F1	 integrand of Bloch-Grüneisen formula
#F2	 Bloch-Grüneisen formula
#F3	 number of electrons per density of states $rac{n_e(T)}{N(T)}$
#F4	 total charge carrier density $n(T)$
Х	 temperature
Y	 resistivity $ ho(T) \; [\mu \Omega cm]$ according to Eqn. A.3
# A	 electron-phonon interaction constant $\mathcal{R} \; [\mu \Omega cm/K]$
#B	 energy gap $E_g$ [K]
#C	 residual charge carrier density $n_0$
#D	 density of states $N(E) [1/J]$
#E	 residual resistivity $ ho_0 \ [\mu\Omega cm]$
#F	 Debye temperature $\theta_D$ [K]
#G	 energy difference between $E_F$ and the lower band edge $(E - E_F)$ [K]

Table	A.2.:	Fit	parameter	2-band	model

composition	#A	#B	#C	#D	#E	#F	#G
$Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$	9900	159	0.00625	3.5e+22	1.6e+08	1.6e+15	8.56e-08
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	790.2	17470	1.306	6.9e+17	10300	118.60	1.40e-05
$Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$	4965	36150	0.0663	1.6e+22	3665	6915	3.53e-05
$Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$	590	32470	1.786	6.9e+17	708	357	1.25e-05
Ba <sub>8</sub> Zn <sub>7.6</sub> Ge <sub>29.3</sub> Si <sub>9.1</sub>	418	3615	0.625	7.5e+21	2698	170	10e-05
$Ba_8Ag_2Ge_{44}$	291	6665	1.51	7.9e+19	325	215	0.07908
$Ba_8Ag_3Ge_{43}$	591	19660	1.511	5.2e+20	560	248	0.0789
$Ba_8Ag_4Ge_{42}$	590	32470	1.295	9.7e+19	888	225	0.1248
$Ba_8Ag_5Ge_{41}$	590	32470	1.323	9.7e+19	1766	218	0.1248 67

# A.1.3. Two-band model with Mott-Jones term

A further development of the Bloch-Grüneisen law with temperature dependent charge carrier density n(T) is to add a term  $\propto T^3$ 

$$\rho(T) = \frac{\rho_0 n_0 + \rho_{ph}}{n(T)} + \frac{AT^3}{n(T)}$$
(A.4)

while using the Bloch-Grüneisen formula (Eqn. A.2) for  $\rho_{ph}$ .

### User defined function corresponding to Eqn. A.4

```
#F7=1.381*10^(-23)
#F1=$^5/(EXP($)-1)/(1-EXP(-$))
#F2=4*#A*(X/#F)^5*AI(1,1E-10,#F/X)
#F3=#F7*(-#B+X*LN(2)-X*LN(1+EXP(#G/X))+X*LN(1+EXP((#G+#B)/X)))
#F4=#D*SQRT(#F3*X*F7*LN(2))+#C
Y=(#C*#E/#F4)+(#F2)/#F4+#H*X^3/#F4
```

# Variables and Fit parameters for the two band model with Mott-Jones term - additional to the two-band model

- Y ... resistivity  $\rho(T)$  according to Eqn. A.4
- **#H** ... Mott-Jones prefactor A

composition	#A	#B	#C	#D	#E	#F
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	1004	1949	1.055	1.4e+21	10308	216
$Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$	6.014	43684	0.2438	3.4e+22	3686	240
$Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$	117	27998	0.4581	6.9e+21	709	286
$Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$	176	13170	0.4511	4.5e+21	2703	196
$Ba_8Ag_2Ge_{44}$	86.6	15170	0.4488	4.5e+21	326	206
$Ba_8Ag_3Ge_{43}$	103	7264	0.4457	5e+21	560	180
$Ba_8Ag_4Ge_{42}$	132	8294	0.4149	5.6e+21	892	198
$Ba_8Ag_5Ge_{41}$	245	6941	0.4353	6.6e+21	1776	324
composition	#G	#H				
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	7.96e-07	1.348e-04				
$Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$	1.9e-04	4.34e-07				
$Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$	5.37e-05	3.56e-07				
$Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$	3.543e-05	4.62e-06				
$Ba_8Ag_2Ge_{44}$	2.866e-04	1e-07				
$Ba_8Ag_3Ge_{43}$	1.99191e-04	1.76e-06				
$Ba_8Ag_4Ge_{42}$	3.24e-11	1.31e-06				
$Ba_8Ag_5Ge_{41}$	1.89e-10	5.25e-06				

Table A.3.: Fit parameter 2-ba	nd model with Mott-Jones
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# A.1.4. Three-band model

This is another model using also the formula as it is plotted in Eqn. A.3 but with a much more complicated relation for the charge carrier density n(T).

### User defined function corresponding to Eqn. A.3 with another n(T) for metals

K=8.617343*10 <sup>-5</sup>	BOLTZMANNKONSTANTE
	'[J/K]
#F1=\$^5/(EXP(\$)-1)/(1-EXP(-\$))	'INTEGRAND
#F2=4*#A*(X/#F)^5*AI(1,1E-10,#F/X)	'BLOCH-GRÜNEISEN
#F3=K*((#I/20-1)*#H+X*LN(2)+X*LN(1+EXP((#B+#H)/(X)))	'ELEKTRONENZAHL/DOS
-X*LN(1+EXP((#B)/(X)))+#I*X*LN(1+EXP((#B+#G)/(X)))	,
-#I*X*LN(1+EXP((#B+#G+1/20*#H)/(X))))	,
#F4=K*X*LN(2)	'LÖCHERZAHL/DOS
#F5=#D*SQRT(#F3*#F4)+#C	'LADUNGSTRÄGERZAHL
Y=(#C*#E/#F5)+(#F2)/#F5	'WIDERSTAND

User defined function corresponding to Eqn. A.3 with another n(T) for semiconductors

K=8.61/343*10 <sup>-5</sup>	BOLIZMANNKONSTANTE
	'[J/K]
#F1=\$^5/(EXP(\$)-1)/(1-EXP(-\$))	'INTEGRAND
#F2=4*#A*(X/#F)^5*AI(1,1E-10,#F/X)	'BLOCH-GRÜNEISEN
#F3=K*(#B*1/20*#H+#G/2-#H+X*LN(1+EXP((#H-#G/2)/(X)))	'ELEKTRONENZAHL/DOS
+#B*X*LN(1+EXP((#G/2)/(X)))	,
-#B*X*LN(1+EXP((#G/2+1/20*#H)/(X))))	,
#F4=K*X*LN(1+EXP((-#G/2)/(X)))	'LÖCHERZAHL/DOS
#F5=#D*SQRT(#F3*#F4)+#C	'LADUNGSTRÄGERZAHL
Y=(#C*#E/#F5)+(#F2)/#F5	'WIDERSTAND

### Variables and Fit parameters for the three-band model

- \$ . . . dummy variable of integration integrand of Bloch-Grüneisen formula #F1 . . . #F2 Bloch-Grüneisen formula . . . number of electrons per density of states  $\frac{n_e(T)}{N(T)}$ number of holes per density of states  $\frac{n(T)-n_e(T)}{N(T)}$ #F3 . . . #F4 ... #F5 . . . number of charge carriers n(T)temperature Х . . . ... resistivity  $\rho(T)$  [ $\mu\Omega cm$ ] according to Eqn. A.3 Y ... electron-phonon interaction constant  $\mathcal{R} \left[ \mu \Omega \text{cm} / \text{K} \right]$ # A ... lower band edge  $E_1$  [K] #B ... residual charge carrier density  $n_0$ #C #D ... density of states N(E) [1/J] ... residual resistivity  $\rho_0 \left[ \mu \Omega \text{cm} \right]$ #E ... Debye temperature  $\theta_D$  [K] #F
- **#G** ... first gap width  $E_{g1}$  [K]
- #H ... second gap width  $E_{g2}$  [K]
- **#I** ... factor for density of states of the impurity band

Table A.4.: Fit parameter 3-band model, parameter #I for metal-UDF

composition	#A	#B	#C	#D	#E	#F
$Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$	0.1	0.9598	2.893e-05	16.52	1.4e+08	250
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	1466	1.153e-05	0.4969	166	10350	323
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	17600	2000	27.87	81.28	10320	117
composition	#G	#H	#I			
$Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$	169	99770	-			
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	0.069	4892.0	-			
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	450	2288	2.519			

# A.2. Lattice Contribution to Thermal Conductivity

# A.2.1. Callaway-model

The lattice contribution  $\lambda_{ph}$  to the thermal conductivity with radiation loss (term  $F \cdot T^3$ ) is given by

$$\lambda_{ph} = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \left[\frac{\tau_c x^4 e^x}{(e^x - 1)^2}\right] dx + F \cdot T^3.$$
(A.5)

### User defined function corresponding to Eqn. A.5

```
F = 1640516349
F1=#A*$^4*X^4
(*POINT DEFECT SCATTERING*)
F2=#B*$^2*X^3*EXP(-#E/(3*X))
F3=#C
F3=#C
F4=#D*X*$
F4=#D*X*$
F5=1/(F1+F2+F3+F4)
F9= ($^4*EXP($)/(EXP($) - 1)^2)*F5
Y=(F*X^3/#E)*AI(9, 0, (#E/X))+#F*X^3
```

#### Variables and Fit parameters for the Callaway model

- \$ ... dummy variable of integration
- F ... prefactor to integral [mW/cmK] according to Eqn. A.6
- F1 ... point defect scattering  $au_D^{-1}$
- F2 ... umklapp processes  $au_U^{-1}$
- F3 ... boundary scattering  $\tau_B^{-1}$
- F4 ... scattering of phonons by electrons  $\tau_E^{-1}$
- F5 ... sum of reciprocal relaxation times  $au^{-1}$
- F9 ... integrand of Callaway equation according to Enq. A.5
- Y ... thermal conductivity  $\lambda_{ph}$  according to Eqn. A.3 + radiation losses
- #A ... parameter for scattering processes on defects  $[K^{-4}s^{-1}]$
- **#B** ... parameter for umklapp-processes  $[K^{-3}s^{-1}]$
- #C ... parameter for scattering on boundaries  $[s^{-1}]$
- #D ... parameter for scattering of phonons by electrons  $[K^{-1}s^{-1}]$
- **#E** ... Debye temperature  $\theta_D$  [K]
- **#F** ... parameter for correction of radiation losses

Calculation of the prefactor to the Callaway-fit:

$$F = K \cdot \left(\frac{N}{V}\right)^{(1/3)} \cdot 10 \tag{A.6}$$

with K = 0.046729, a factor using Callaway and Debye.

Table A.5.: Atoms per unit cell, lattice parameter and prefactor to the integral in the Callaway model - for all compounds

composition	N [1]	lattice parameter [nm]	prefactor Callaway [mW/cmK]
$Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$	54	1.07664	1640516349
$Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$	54	1.06994	1650789317
Ba <sub>8</sub> Zn <sub>7.3</sub> Ge <sub>10.6</sub> Si <sub>28.1</sub>	54	1.05278	1677696691
Ba <sub>8</sub> Zn <sub>7.4</sub> Ge <sub>19.8</sub> Si <sub>18.8</sub>	54	1.06086	1664918578
Ba <sub>8</sub> Zn <sub>7.2</sub> Ge <sub>19.9</sub> Si <sub>18.9</sub>	54	1.06026	1665860753
$Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$	54	1.06833	1653277098
$Ba_8Ag_2Ge_{44}$	54	1.0742	1644242713
$Ba_8Ag_3Ge_{43}$	54	1.078	1638446681
$Ba_8Ag_4Ge_{42}$	54	1.0814	1633295286
$Ba_8Ag_5Ge_{41}$	54	1.0842	1629077220

Table A.6.: Fit parameter Callaway model

composition	#A	#B	#C	#D	#E	#F
$Ba_8Pd_{2.3}Zn_{3.6}Ge_{40.1}$	735	628	3.9e+07	3.3e+09	54.54	8.598e-07
$Ba_8Cu_{5.2}Zn_{0.8}Ge_{40.0}$	519	266100	6.972e+09	51000	24.73	8.997e-07
$Ba_8Zn_{7.3}Ge_{10.6}Si_{28.1}$	4222	150500	2.8e+10	1.4e+08	40	6.792e-07
Ba <sub>8</sub> Zn <sub>7.4</sub> Ge <sub>19.8</sub> Si <sub>18.8</sub>	8370	318500	1.1e+09	1.7e+08	296	8.5e-07
$Ba_8Zn_{7.2}Ge_{19.9}Si_{18.9}$	62566	629919	2.4e+09	1.2e+07	51	7.4e-07
$Ba_8Zn_{7.6}Ge_{29.3}Si_{9.1}$	4016	457900	3e+08	9.6e+08	28.98	6.262e-07
$Ba_8Ag_3Ge_{43}$	36700	332100	4.5e+09	3.9e+08	53	6.699e-07
$Ba_8Ag_4Ge_{42}$	19950	701600	3.7e+10	9.1e+08	71	7.73e-07
$Ba_8Ag_5Ge_{41}$	4000	488300	7.9e+10	5e+07	50	7.057e-07

Debye temperatures below 200 K are not realistic, therefore the validity of the Callaway model is to scrutinize, particularly due to the fact that the Callaway-fit of  $Ba_8Zn_{7.4}Ge_{19.8}Si_{18.8}$  (the only (!) composition investigated in this diploma thesis which was ball milled while preparation) results in a realistic Debye temperature above 200 K.

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