Tl$_9$BiTe$_6$

A New Thermoelectric Material with Record Efficiencies

Result of a Systematic Material Screening Program

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Tl₉BiTe₆ – ein neues thermoelektrisches Material mit Rekord-Wirkungsgraden

Da thermoelektrische Bauelemente aufgrund ihrer elektronischen Funktionsweise verschiedene inhärente Vorteile gegenüber Kompressor-Kühlnern und konventionellen Generatoren besitzen, werden sie sowohl zur Kühlung als auch zur Energieerzeugung eingesetzt. Allerdings ist der Einsatz thermoelektrischer Bauelemente aufgrund ihrer niedrigeren Wirkungsgrade im Vergleich zur konventionellen Technik auf Nischenanwendungen beschränkt. Ziel dieser Arbeit ist es daher, nach neuen hocheffektiven thermoelektrischen Materialien zu suchen, um die Effizienz der aktuellen thermoelektrischen Bauelemente zu steigern. Die Effizienz eines Bauelementes hängt über die Gütezahl \( Z = S^2/(\rho \kappa) \) von den Transporteigenschaften des Materials ab, wobei \( S \) die Thermokraft, \( \rho \) der spezifische elektrische Widerstand und \( \kappa \) die thermische Leitfähigkeit ist. Die Gütezahl läßt sich in den sogenannten ‘power factor’ \( S^2/\rho \), der allein durch die elektronischen Transporteigenschaften bestimmt ist, und die thermische Leitfähigkeit, in die zusätzlich noch die Gittereigenschaften des Materials einfließen, aufspalten.

Mehrere Materialklassen, die vielversprechend für thermoelektrische Anwendungen sind, wurden auf Verbindungen untersucht, die das Potential haben, die gegenwärtig besten Materialien zu übertreffen. In diesem Rahmen wurden verschiedene Klatthrate, Oxyd-Pyrochlore, niedrigdimensionale Kristallstrukturen, insbesondere Schichtstrukturen, Chalkogenide mit kleiner Bandlücke und das Legierungssystem SmSe/TmSe mit intermediären Valenzzuständen untersucht. Unter diesen Materialien wurde das ternäre Chalcogenid Tl₉BiTe₆ mit einem ‘power factor’ von 0.46 mW/(mK²) als die aussichtsreichste Verbindung identifiziert und für die weitere Untersuchung und Optimierung ausgewählt.

Da Tl₉BiTe₆ zu einer Gruppe sieben eng miteinander verwandter Verbindungen gehört, die vom binären Tl₅Te₃ abgeleitet sind, wurden auch die anderen Materialien dieser Gruppe synthetisiert und bezüglich ihrer thermoelektrischen Güte mit Tl₉BiTe₆ verglichen. Alle Verbindungen dieser Gruppe schmelzen kongruent und können durch einfaches Zusammenschmelzen der Elemente in evakuierten Quarzampullen hergestellt werden. Die Messungen der einzelnen Verbindungen zeigen jedoch, daß wahrscheinlich kein anderes Mitglied Tl₅Te₃-Gruppe die thermoelektrischen Eigenschaften von Tl₉BiTe₆ übertreffen wird. Allerdings bietet diese große Gruppe von vollkommen miscbaren Materialien viele Möglichkeiten zur weiteren Optimierung von Tl₉BiTe₆.

Im Vergleich zum ursprünglich synthetisierten Material, konnte der ‘power factor’ von Tl₉BiTe₆ durch Vorreinigen der Elemente und anschließendem Zonenreinigen des synthetisierten Materials um mehr als 100% auf 1.0 mW/(mK²) gesteigert werden. Um diese deutliche Verbesserung zu verstehen, wurden die elektrischen Trans-
porteigenschaften mit Hilfe von Widerstands-, Hall- und Thermokraft-Messungen untersucht. Es zeigt sich, daß die Steigerung des ‘power factors’ aus der Verdoppelung der Ladungsträgerbeweglichkeiten resultiert, die durch die größere Reinheit und bessere strukturelle Qualität des Materials bedingt ist. Bei Raumtemperatur bleibt der ‘power factor’ von Tl₉BiTe₆ jedoch immer noch um einen Faktor vier hinter dem von optimierten Bi₂₋ₓSbxTe₃₋ₓSeₓ-Legierungen (~ 4 mW/(mK²)) zurück, die das Standardmaterial für thermoelektrische Anwendungen in diesem Temperaturbereich sind.

Da die thermische Leitfähigkeit von Tl₉BiTe₆ extrem niedrig ist, sind konventionelle stationäre Meßmethoden, bei denen ein Temperaturgradient über eine stabförmige Probe gemessen wird, aufgrund von Strahlungsverlusten auf Temperaturen von unter 150 K begrenzt. Daher wurde ein neuer Meßstand aufgebaut, mit dem Wärmeleitfähigkeiten mittels der 3ω-Methode auch bei höheren Temperaturen gemessen werden können. Die Wärmeleitfähigkeit von Tl₉BiTe₆ bei Raumtemperatur (0.49 W/(mK)) beträgt nur ein Viertel derjenigen von reinem Bi₂Te₃ (1.9 W/(mK)) und ist dreimal niedriger als die von optimierten Bi₂₋ₓSbxTe₃₋ₓSeₓ-Legierungen (1.38 W/(mK)), in denen die Wärmeleitfähigkeit aufgrund der Massenfluktuationen reduziert ist. Dadurch ist die thermoelektrische Gütezahl von Tl₉BiTe₆ bei Raumtemperatur ebenso groß wie die von reinem Bi₂Te₃ (ZT = 0.65), jedoch immer noch kleiner als die von optimiertem Bi₂₋ₓSbxTe₃₋ₓSeₓ (ZT ~ 1). Aufgrund der größeren Bandlücke – über 0.4 eV im Vergleich zu ~ 0.15 eV in Bi₂₋ₓSbxTe₃₋ₓSeₓ – liegt der optimale Wirkungsgrad von Tl₉BiTe₆ allerdings bei höheren Temperaturen. Oberhalb von 430 K steigt die thermoelektrische Gütezahl von Tl₉BiTe₆ auf Werte über 1 und ist damit größer als die optimierter Bi₂₋ₓSbxTe₃₋ₓSeₓ-Legierungen. Bei Temperaturen um 500 K übertrifft Tl₉BiTe₆, mit einer Gütezahl von ZT ~ 1.2, deutlich die thermoelektrischen Wirkungsgrade sowohl von Bi₂₋ₓSbxTe₃₋ₓSeₓ-Legierungen als auch von (GeTe)₅₅(AgSbTe2)₁₅ Verbindungen (eines der besten Materialien für Hochtemperaturanwendungen), die beide nur ein ZT von ungefähr 0.8 aufweisen. Daher schließt Tl₉BiTe₆ die Lücke, die zur Zeit zwischen hocheffizienten thermoelektrischen Materialien für Raumtemperatur- und Hochtemperatur-Anwendungen besteht.

Während der ‘power factor’ von Tl₉BiTe₆ nicht mit denen der besten thermoelektrischen Materialien konkurrieren kann, erweist sich die extrem niedrige thermische Leitfähigkeit als die Schlüsselleigenschaft, die zu den außergewöhnlich guten thermoelektrischen Eigenschaften des Materials führt. Daher wurden die Gittereigenschaften von Tl₉BiTe₆ durch Messungen der Wärmekapazität, Raman-Streuung und Neutronen-Streuung detaillierter untersucht. Die Ergebnisse legen nahe, daß die thermische Leitfähigkeit nicht durch sogenannte ‘rattling atoms’ (engl. to rattle: klappern) bestimmt ist, wie es in vielen momentan untersuchten Verbindungen, z.B. Klahtraten und Skutteruditen, der Fall ist. Stattdessen läßt sich die niedrige Wärmeleitfähigkeit in einem “klassischen” Model auf die schwachen Bindungen, die hohen Atomgewichte und einen intrinsisch ungeordneten Gitterplatz zurückführen.
Abstract

Thermoelectric devices are used for refrigeration as well as for power generation, since they possess several inherent advantages compared to compressor refrigerators and conventional power generators. However, due to their lower efficiency compared to conventional devices, the use of thermoelectric devices is currently limited to niche applications. The objective of this work has been to search for new highly efficient thermoelectric materials to improve the efficiency of current devices. The efficiency of a thermoelectric device depends on the transport properties of the material through the figure of merit $Z = S^2/(\rho \kappa)$, where $S$ is the thermopower, $\rho$ the electrical resistivity, and $\kappa$ the thermal conductivity. The figure of merit can be divided into the so-called power factor $S^2/\rho$, which is completely determined by the electronic transport properties, and the thermal conductivity $\kappa$, which is determined by the lattice properties as well.

Several classes of materials, identified as promising for thermoelectric applications, have been investigated in order to discover a new material with the potential to exceed the current state of the art materials. Various clathrates, oxide pyrochlores, low-dimensional – especially layered – crystal structures, small-band-gap chalcogenides, and the intermediate valence system SmSe/TmSe have been studied. Among these materials the ternary chalcogenide Tl$_9$BiTe$_6$, with a power factor of 0.46 mW/(mK$^2$) at 300 K, has been identified as the most promising compound and has therefore been chosen for further investigation and optimization.

Since Tl$_9$BiTe$_6$ belongs to a larger group of seven closely related compounds, which are derived from the binary Tl$_5$Te$_3$, these materials have been synthesized as well and have been compared to Tl$_9$BiTe$_6$. All materials of this group melt congruently and are obtained by direct synthesis of the elements in evacuated quartz ampoules. No compound of the Tl$_5$Te$_3$-group has been found to likely surpass the thermoelectric properties of Tl$_9$BiTe$_6$. However, since all members of the Tl$_5$Te$_3$-group are completely miscible, this system offers a wide phase space for further optimization of Tl$_9$BiTe$_6$.

Compared to the initially synthesized material, the power factor of Tl$_9$BiTe$_6$ could been more than doubled to 1.0 mW/(mK$^2$) at 300 K by the synthesis from pre-purified elements and subsequent zone refining of the material. To understand this drastic improvement, the electrical transport properties have been analyzed by resistivity, Hall and thermopower measurements. It is found that the increase of the power factor is due to a more than twofold enhancement of the charge carrier mobility, which
results from the higher purity and the improved structural quality of the zone refined material. However, at room temperature the power factor of Tl$_9$BiTe$_6$ still falls behind by a factor of four compared to optimized Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$-alloys ($\sim$ 4 mW/(m K$^2$)), which are the state of the art thermoelectric materials in this temperature range.

Since the thermal conductivity of Tl$_9$BiTe$_6$ is extremely low, conventional thermal conductivity measurements using the longitudinal steady state method are limited to low temperatures (< 150 K) due to radiation losses. Therefore, a new setup has been built using the 3$\omega$-technique as an additional method to measure thermal conductivities at higher temperatures. At room temperature the thermal conductivity of Tl$_9$BiTe$_6$ (0.49 W/(m K)) is only a fourth of that of pure Bi$_2$Te$_3$ (1.9 W/(m K)) and three times lower than that of optimized Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$-alloys (1.38 W/(m K)), where the thermal conductivity has been reduced due to mass fluctuation effects.

Thereby, at room temperature the thermoelectric performance of Tl$_9$BiTe$_6$ is equal to that of pure Bi$_2$Te$_3$ ($ZT = 0.65$) but still weaker than that of Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$ ($ZT \sim 1$). However, due to the larger band gap of Tl$_9$BiTe$_6$, greater than 0.4 eV as compared to $\sim$ 0.15 eV in Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$, the optimum performance of Tl$_9$BiTe$_6$ is at higher temperatures. Above 430 K the thermoelectric figure of merit of Tl$_9$BiTe$_6$ is greater than 1 and it outperforms optimized Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$-alloys. Around 500 K Tl$_9$BiTe$_6$, with $ZT \sim 1.2$, significantly exceeds the thermoelectric efficiency of optimized Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$-alloys and (GeTe)$_{85}$(AgSbTe$_2$)$_{15}$ alloys (a state of the art high temperature material), both with $ZT \sim 0.8$. Thus Tl$_9$BiTe$_6$ is filling the performance gap, existing between room temperature and high temperature thermoelectric materials.

While the power factor of Tl$_9$BiTe$_6$ is quite low compared to the current state of the art thermoelectric materials, the extremely low thermal conductivity turns out to be the key property of Tl$_9$BiTe$_6$ which leads to the exceptional thermoelectric performance. Therefore, its lattice properties have been studied in greater detail using heat capacity, light scattering and neutron scattering measurements. The data strongly suggest that the thermal conductivity is not determined by “rattling” atoms, as it is the case in many of the currently studied low thermal conductivity compounds, i.e clathrates and filled skutterudites, but has to be understood in a “classical” model as a result of weak bonds, heavy atoms, and an intrinsic disorder on one of the crystal sites.
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CHAPTER 1

Introduction

Progress in materials science often leads to the replacement of conventional technology by solid state devices based on new materials. The most prominent example is the invention of the transistor in 1947, which replaced the vacuum tube and is now present in almost every aspect of all day life. Another example are the blue (and white) light emitting diodes based on GaN, which may soon replace the light bulb, invented more than 100 years ago. Since fossil fuels are limited, solar cells are expected to be one of the key suppliers of energy in a few decades.

Apart from signal amplification, light emission and energy conversion also cooling can be obtained from solid-state devices. The cross-effects of thermal and electric fields and currents are called thermoelectric effects and have been studied by T. J. Seebeck, J. C. A. Peltier and W. Thomson in the first half of the nineteenth century. Consequently, it is known for more than 150 years that refrigeration and energy conversion from heat to electric energy can be achieved with solid state devices. The efficiency of thermoelectric coolers and power generators depends on the dimensionless thermoelectric figure of merit $ZT := S^2T/(\rho\kappa)$, where $S$ is the thermopower (also called Seebeck coefficient), $\rho$ the electrical resistivity, $\kappa$ the thermal conductivity, and $T$ is the temperature. In this definition a high $ZT$ corresponds to a high thermoelectric efficiency.

However, it turns out that the thermoelectric effects in metals or insulators result in very low figures of merit. Therefore, for more than 100 years not much attention was paid to the field of thermoelectricity. As the progress of material science led to materials of higher and higher purity, semiconductors were established as a third class of materials with intermediate properties. After it was discovered by Abram Ioffe that doped semiconductors have a great potential as thermoelectric compounds, a broad and intensive search was carried out to identify high efficiency materials from about 1940 to 1965. However, the compounds discovered then exhibit efficiencies lower by a factor of 3 to 5 compared to today’s standard systems, i.e. the steam turbine and compressor-based refrigerators.
After decades of standstill in research on thermoelectric materials, the field experienced a rebirth in the 1990s for several reasons. New compounds with large unit cells and complex structures have been synthesized, but not yet been studied regarding their thermoelectric properties. New mechanisms have been found, which enhance the thermoelectric properties of materials. New demands for solid-state cooling are created by the recent progress in microelectronics and communication technology. Although thermoelectric devices are still less effective than their conventional counterparts, they have several inherent advantages, which make them the system of choice in several applications (see Fig. 1).

- In contrast to compressor-based coolers or steam turbines, thermoelectric devices work completely electronically and contain no moving parts. Therefore, they are extremely reliable and well suited for remote applications, where repair is costly or impossible. Several deep space probes, which are too far from the sun to obtain sufficient power from solar cells, are powered by thermoelectric generators and no failure has been reported over millions of hours of operation.

- Thermoelectric devices are very small and lightweight. Therefore, they are employed in portable systems. A common product are beverage coolers, which can be powered by the battery of a car.

- For applications in microelectronics or communication technology the *scalability* of thermoelectric devices is the key feature. The large power densities in micro-processors, i.e. approximately 10 W/cm² in an Intel Pentium processor, require additional cooling to avoid performance losses. In communications technology, wavelength dependent multiplexing makes it important to stabilize the temperature of the lasers to minimize wavelength fluctuations. In these applications the cooling of small areas is needed and the use of a compressor and a liquid refrigerant is impracticable.

Further applications of thermoelectric devices are waste heat recovery, e.g. in a motor of a car and the temperature control of various types of detectors. Recently, the Seiko corporation has presented a wrist watch powered by the heat of the human body, which is converted into electrical energy by an array of very small thermoelectric generators. A possible future application is superconducting electronics, where cooling below the transition temperature could be obtained by thermoelectric devices.

Since the applications for thermoelectric generators and coolers are numerous, there is a strong need for new thermoelectric materials with higher efficiency. The focus of this work is to identify, to understand and to optimize such materials, regarding their thermoelectric properties.

In the following chapter a short theoretical introduction is given and “guidelines” for a systematic search of high efficiency thermoelectric materials are derived. Subsequently,
the state of the art of thermoelectric materials is discussed in order to illustrate the “guidelines” and to establish a benchmark to which the new materials have to be compared. Hereafter, the techniques to measure the key properties of thermoelectric materials – the thermopower $S$, the electrical resistivity $\rho$, and the thermal conductivity $\kappa$ – are discussed. In order to find a new high-efficiency thermoelectric material, a large number of compounds is surveyed. Since Tl$_2$BiTe$_6$ is identified as a promising thermoelectric material, its properties and those of several related compounds are studied. Furthermore, different crystal growth techniques have been applied to optimize the thermoelectric properties. Due to the extremely low thermal conductivity of the studied compounds, a more detailed analysis of their lattice properties is presented. Finally, the results of this work are summarized and compared to the benchmarks set by the current state of the art materials.

Figure 1.1. Schematic drawings of a thermoelectric generator (top) and cooler (bottom) and examples for applications as mentioned in the text.
CHAPTER 2

Guidelines for the Search of New Thermoelectric Materials

Thermoelectric devices can be used for refrigeration as well as for power generation. The efficiency of a thermoelectric device depends on three material properties, i.e., the thermopower $S$, the electrical conductivity $\sigma$, which is inverse to the electrical resistivity $\rho$, and the thermal conductivity $\kappa$. The dependence on these properties is described by the material thermoelectric figure of merit

$$Z = \frac{S^2 \sigma}{\kappa} \quad [Z] = 1/K$$

(2.1)

where a high $Z$ corresponds to a high efficiency. The actual value depends on the dimensionless figure of merit $ZT$ and the ratio of the temperatures at the hot and the cold end of the generator or refrigerator, respectively. The thermoelectric efficiency $\eta_{\text{TE}}$ reaches its theoretical maximum for $ZT \to \infty$, which corresponds to the efficiency $\eta_{\text{Carnot}}$ of the Carnot process. We obtain

$$\eta_{\text{TE}} = \frac{\eta_{\text{Carnot}} \sqrt{1 + ZT} - \frac{T_H}{T_C}}{\sqrt{1 + ZT} + 1} \quad \text{for refrigeration and}$$

(2.2)

$$\eta_{\text{TE}} = \frac{\eta_{\text{Carnot}} \sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \quad \text{for power generation,}$$

(2.3)

\(^1\text{Both, } ZT \text{ (dimensionless) and } Z \text{ (with dimension } 1/\text{K}) \text{ are usually denoted as “thermoelectric figure of merit”. To avoid confusion, } Z \text{ and } ZT \text{ are distinguished as the “material figure of merit” and the “dimensionless figure of merit”, respectively.}\)
where \( T_H \) and \( T_C \) are the temperatures at the hot end and the cold end of the thermoelectric device, respectively. The correlation between the dimensionless figure of merit and the efficiency of the thermoelectric device is shown in Fig. 2.1. The two examples are a typical household refrigerator and a power generator using low temperature waste heat as it might be recovered from a motor in a car.

To establish guidelines for the search of good thermoelectric materials the dependence of \( ZT \) on more fundamental material parameters as for example the energy gap, the carrier concentration and the mobility has to be examined. Yet, to make the guidelines practically useful for the search of good thermoelectric materials these parameters have to be related to properties like the crystal structure, constituting elements, melting point, etc. which are readily accessible for almost any known material. In the following sections theories to predict the thermoelectric performance of materials will be presented.

### 2.1 TRANSPORT THEORY

The electrical properties of thermoelectric materials will be discussed based on the Boltzmann equation in the relaxation time approximation. Though this approach includes some fundamental approximations it captures the fundamental properties correctly and due to its simplicity it allows some insight into the microscopic processes.

The influences of electric fields and temperature gradients on the distribution function of the charge carriers \( f(\mathbf{k}, \mathbf{r}, t) \) determine the thermoelectric effects. In this section it is supposed that the charge carriers are of single type - electrons or holes - and that they are contained in a single parabolic energy band. Furthermore, it will be assumed that the surfaces of constant energy in phase space are spherical. In this case the wave
vector $\mathbf{k}$ in the distribution function can be eliminated in favor of the energy $E$. The number of electrons per unit volume in a given range of energy is $f(E)g(E)\,dE$ where

$$g(E) = \frac{4\pi(2m^*)^{3/2}E^{1/2}}{\hbar^3}$$

(2.4)

is the density of states for carriers with the effective mass $m^*$ under the given assumptions. The electric current density $\mathbf{j}$ and the heat current density $\mathbf{w}$ are

$$\mathbf{j} = \mp e \int_E S(E) \mathbf{v}(\mathbf{k})f(E)g(E)\frac{dA}{4\pi v} \, dE$$

(2.5)

$$\mathbf{w} = \int_E S(E) \mathbf{v}(\mathbf{k})(E - E_v)\, f(E)\frac{dA}{4\pi v} \, dE$$

(2.6)

where $\mathbf{v}$ is the velocity of the charge carriers and $S(E)$ a surface of constant energy in the $\mathbf{k}$-space. Since the thermal velocity greatly exceeds the drift velocity and is uniform in all directions the average velocity along one axis is

$$v^2 = \frac{2E}{3m^*}.$$

(2.7)

If the electric field and the temperature gradient lie along the $z$-axis and using the relaxation time approximation the distribution function is described by the Boltzmann equation of the form

$$\frac{f(E) - f_0(E)}{\tau} = v \frac{\partial f_0}{\partial E} \left( \frac{\partial E_v}{\partial z} + \frac{E - E_v}{T} \frac{\partial T}{\partial z} \right)$$

(2.8)

where $f_0(E - E_v) = \left[ \exp \left( (E - E_v)/k_B T \right) + 1 \right]^{-1}$ is the unperturbed distribution function in the absence of fields and $\tau$ is the relaxation time. If the energy dependence of the relaxation time can be expressed as a power law of the form $\tau = \tau_0 E^r$ then the transport parameters are determined by combination of Eqs. 2.4 through 2.8:

$$S = \left( \frac{\partial E_v}{\partial z} \right)_{j=0} = \frac{1}{eT} \left( E_v - \frac{K_1}{K_0} \right)$$

(2.9)

$$\sigma = \left( \frac{j}{\frac{1}{e} \frac{\partial E_v}{\partial z}} \right)_{\Delta T=0} = e^2 K_0$$

(2.10)

$$\kappa_{el} = \left( \frac{w}{\frac{1}{T} \frac{\partial T}{\partial z}} \right)_{j=0} = \frac{1}{T} \left( K_2 - \frac{K_1^2}{K_0} \right)$$

(2.11)

with the integral functions

$$K_i := \frac{8\pi}{3k_B T} \left( \frac{2}{\hbar^2} \right)^{3/2} (m^*)^{1/2} \tau_0 \left( i + r + \frac{3}{2} \right) \int_0^{\infty} E^{i+r+1/2} f_0(E) \, dE.$$ 

(2.12)
In summary, the transport parameters that appear in the figure of merit $ZT$, other than the lattice thermal conductivity, have been expressed as functions of a band parameter (the effective mass $m^*$), a scattering parameter (the relaxation time $\tau_0 E_r$), and the Fermi energy $E_r$.

Applying the definition of the integrals $K_i$ to Eq. 2.9 yields a more operable form for the thermopower

$$S = \frac{k_B}{\varepsilon} \left( \varepsilon - \frac{r + 5/2}{r + 3/2} \cdot \frac{F_{r+3/2}(\varepsilon)}{F_{r+1/2}(\varepsilon)} \right)$$

where $\varepsilon = E_r/(k_n T)$ is the reduced Fermi energy and $F_i$ are the Fermi integrals defined as

$$F_i(\varepsilon) = \int_{0}^{\infty} x^i f_0(x - \varepsilon) \, dx.$$  \hspace{1cm} (2.14)

In the cases of a nondegenerate semiconductor ($-\varepsilon \leq 4$) and a metal ($\varepsilon \gg 1$) very good approximations for the Fermi integrals are found and the thermopower can be calculated analytically. Whereas for a degenerate semiconductor the thermopower has to be computed numerically.

It is found that for given $m^*$ and $r$ the highest $ZT$ is obtained for weakly degenerate ($\varepsilon \approx 0$) semiconductors. This corresponds to carrier concentrations in the range of $10^{19}$ cm$^{-3}$ to $10^{20}$ cm$^{-3}$. For a fixed Fermi energy $E_r$ and with a given scattering parameter $r$ the figure of merit only depends on the material parameter

$$\beta = \mu \frac{(m^*)^{3/2}}{\kappa_{\text{lat}}}$$  \hspace{1cm} (2.15)

where a high $\beta$ corresponds to a high $ZT$ [Ioffe57]. Therefore, a material that has high mass and high mobility carriers and at the same time a low lattice thermal conductivity is promising for thermoelectric applications.

Attention has to be paid to the fact that $\mu$ is not independent of the effective mass $m^*$. Thus the statement that high effective masses are favorable for thermoelectric materials is not quite correct. Rather, the dependence of $\beta$ on $m^*$ itself depends on the scattering parameter $r$. The following cases are discussed by [Wood88]

1. Neutral impurity scattering: $\mu \propto (m^*)^{+1} \quad \Rightarrow \ Z \text{ increases as } m^* \text{ increases.}$

2. Ionized impurity scattering: $\mu \propto (m^*)^{-1/2} \quad \Rightarrow \ Z \text{ increases as } m^* \text{ increases.}$

3. Acoustic mode scattering: $\mu \propto (m^*)^{-5/2} \quad \Rightarrow \ Z \text{ decreases as } m^* \text{ increases.}$

4. Polar optical mode scattering: $\mu \propto (m^*)^{-3/2} \quad \Rightarrow \ Z \text{ independent of } m^*.$

The scattering mechanisms are sorted in ascending order by the temperatures at which they are usually most pronounced.
2.2 Multivalley band structures

As seen in the previous section the influence of the effective carrier mass \( m^* \) on the figure of merit is not trivial. The following more detailed discussion will reveal further guidelines for the search of good thermoelectric materials. In several semiconductors the assumption of a single spherical band is oversimplified. The conduction and valence band structures may possess several equivalent extrema. Furthermore, in the case of an anisotropic crystal structure the surfaces of equal energy near the extrema are not spheres but ellipsoids described by

\[
E(\vec{k}) = \frac{\hbar^2}{2} \left( \frac{k_1^2}{m_1} + \frac{k_2^2}{m_2} + \frac{k_3^2}{m_3} \right)
\]

(2.16)

where the suffixes 1, 2, and 3 refer to the components along the principal directions of the ellipsoids. In this case two types of effective masses have to be distinguished. The first is the conductivity or inertial effective mass \( m_c^* \) which describes the moment of inertia the charge carriers exhibit in an electrical field. It is given by

\[
(m_c^*)^{-1} = \frac{1}{3} \left( m_1^{-1} + m_2^{-1} + m_3^{-1} \right).
\]

(2.17)

The second is the density-of-states effective mass which enters the expression for the carrier concentration. For a number \( N_V \) of equivalent valleys the carrier concentration is increased by the factor \( N_V \) when the Fermi energy is kept constant. Thus for the density-of-states effective mass we obtain

\[
m_d^* = N_V^{2/3}(m_1 m_2 m_3)^{1/3}.
\]

(2.18)

The inertial effective mass is a “bad” mass because a higher \( m_c^* \) lowers the mobility. The density-of-states effective mass is a “good” mass because a higher \( m_d^* \) increases the carrier concentration and thus the electrical conductivity without effecting the thermopower. There are two strategies to obtain a high ratio of \( m_c^*/m_d^* \).

The first is searching for materials with highly anisotropic carrier pockets. When the effective mass in one direction becomes much smaller than along the other two (i.e. \( m_1 \ll m_2 \sim m_3 \)) the reduction of \( m_c^* \) is more pronounced than that of \( m_d^* \). In the case of \( m_1 = \frac{1}{10} m_2 = \frac{1}{10} m_3 \) the ratio \( m_c^*/m_d^* \) is increased by a factor of approximately 2.

On the other hand, a large number \( N_V \) of equivalent valleys is also favorable because it increases \( m_d^* \) while it has no effect on \( m_c^* \). The maximum value of \( N_V \) is limited by the crystalline symmetry [DiSalvo99]. In cubic space groups it can be as high as 48, followed by values of 24 in hexagonal groups, 16 in tetragonal, 8 in orthorhombic, and 4 or less in the remaining groups. A drawback of multivalley band structures is that additional intervalley scattering decreases the mobility and therefore reduces the positive effect [Rowe85]. The magnitude of the additional scattering depends on several material properties and is not trivial to calculate [Herring55].
As it will be discussed in chapter 3, the currently used thermoelectric materials suggest that the second approach is the more promising one. Yet, Bi$_2$Te$_3$ the most successful thermoelectric material up to date combines both, high crystal symmetry and anisotropy.

### 2.3 Energy Gap

So far this discussion has only dealt with semiconductors with one type of charge carriers, electrons or holes. At temperatures, where the thermal energy becomes comparable to the width of the energy gap $E_g \approx k_B T$, electron-hole pairs are excited across the gap. Although, as discussed in section 2.1, an optimized thermoelectric material is heavily doped, the presence of minority carriers has a significant effect on the thermoelectric properties. In the case of bipolar conduction the thermopower is

$$ S = \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p} \quad \text{(2.19)} $$

where the indices $n$ and $p$ denote electrons and holes, respectively. Since the contributions $S_n$ and $S_p$ are of opposite sign bipolar conduction reduces the overall thermopower. Furthermore, the electronic contribution to the thermal conductivity is enhanced by a “bipolar term”. This results from diffusion of electron-hole pairs from the hot end to the cold end, where the excitation energy is released by recombination.

To minimize bipolar effects the energy gap has to be considerably larger than the thermal energy at the operating temperature $T_{op}$. The lower bound of the energy gap has been calculated by classical statistics ($E_g = 6k_B T_{op}$, [Chasmar59]) and by Fermi-Dirac-statistics ($E_g = 10k_B T_{op}$, [Mahan89]). It is a general trend that with increasing energy gap the lattice thermal conductivity increases and the mobility decreases. Thus the optimal energy gap is

$$ 6k_B T_{op} \lesssim E_g \lesssim 10k_B T_{op}. \quad \text{(2.20)} $$

### 2.4 Lattice Thermal Conductivity – Classical

The lattice thermal conductivity – as opposed to the thermopower, the resistivity, and the electronic thermal conductivity – is the only measure entering the figure of merit which does not relate to the electronic properties. A low lattice thermal conductivity is essential for a good thermoelectric material. Furthermore, while the electronic properties can be optimized by doping the possibilities to reduce $\kappa_{lat}$ in a
given material are rather limited. To establish practically useful guidelines for the
search of promising new materials for thermoelectric applications an estimation of the
thermal conductivity based on easily accessible material parameters is needed.

A theory to estimate the thermal conductivity from crystallographic data has been
developed by [Slack79]. Slack points out that the group velocity of optical phonons
is usually very low compared to that of acoustic phonons. Consequently, it can be
assumed the largest contribution to the lattice thermal conductivity comes from the
latter. Under this assumption the thermal conductivity is

\[
\kappa_{at} \propto \frac{1}{M} \Theta_D^3 \delta N_{at}^{-2/3} T^{-1} \gamma^{-2}
\]  

(2.21)

where \( M \) is the average atomic mass, \( \Theta_D \) is the Debye temperature, and \( \gamma \) is the
Grüneisen constant. The quantity \( \delta = \sqrt[3]{V_c/N_{at}} \), where \( V_c \) is the unit cell volume
and \( N_{at} \) is the number of atoms per cell, is a measure of the average atomic distance
in the structure. If the Debye temperature is not known it can be estimated with
Lindemann’s formula [Ziman60]

\[
\Theta_D \approx 120 \frac{T_m}{M}^{1/2} \rho_m^{1/3} T_m^{1/2} \frac{1}{M} \delta
\]  

(2.22)

where \( T_m \) is the melting point and \( \rho_m \) the mass density in g/cm\(^3\). Applying this to
Eq. 2.21 yields

\[
\kappa \propto \frac{1}{M} \delta^4 T_m^{-3/2} \rho_m^{-2/3} \gamma^{-2}.
\]  

(2.23)

According to Eq. 2.23 we can expect a material to exhibit a low thermal conductivity
if it has a low melting temperature, a large average mass of its constituent atoms, a
large number of atoms in the unit cell, and large atomic distances.

For a given material the thermal conductivity of the lattice can be reduced by forming
mixed crystals or alloy systems. While this has been very successful for some material
systems, there are limitations for others which are discussed in section 2.6. Another
approach is to reduce the thermal conductivity by producing materials from pressed
powders. The thereby induced crystal defects act as scatterers for the heat conducting
phonons and decrease the thermal conductivity. Nevertheless, the scattering of charge
carriers will also be enhanced and it depends on the balance of these two effects in
which way the figure of merit will be altered.

A good estimate for the further potential of reducing the thermal conductivity is the
so called “minimum thermal conductivity” [Slack79, Cahill92]

\[
\kappa_{\text{min}} = 3 \left( \frac{\pi}{6} \right)^{1/3} k_B \delta^{-2} \nu \left( \frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} \, dx
\]  

(2.24)
where a unique velocity \( v \) is assumed for transverse and longitudinal sound modes. If the velocity of sound is not known it can be estimated using the Debye model

\[
v \simeq \frac{k_B \Theta_D}{\hbar} \left(6\pi^2 \delta^{-3}\right)^{-1/3}.
\]

The minimum thermal conductivity is the thermal conductivity expected for a completely disordered material. It is calculated with the assumption that the minimum life time for a defined lattice vibrational mode is half the period of the vibration \( \tau_{\text{min}} = \pi/\omega \) [Cahill92].

Comparing the actual lattice thermal conductivity to this minimum value gives a measure on how much the figure of merit can be optimized by further reduction of the lattice thermal conductivity.

### 2.5 Lattice Thermal Conductivity – “Rattlers”

As it has been pointed out already, the low energy acoustic phonons carry most of the heat due to their high group velocities. Thus, a mechanism which leads to enhanced scattering of these low energy phonons, can greatly reduce the thermal conductivity. The frequencies of these phonons are typically about \( 10^{12} \text{ s}^{-1} \). It is found that this corresponds very well to the frequencies of loosely bound atoms in open crystal structures, for example in clathrates [Jianjun00] and filled skutterudites [Sales96, Sales97]. The “rattling” motion of these atoms produces strong resonant scattering of the phonons with the same frequency.

A simple model has been developed to predict the thermal conductivity of these structures only from room temperature x-ray diffraction data. From the analysis of the diffraction pattern not only the crystal structure but also the atomic displacement parameters (ADPs) are obtained which describe the static and thermal dislocation of the atoms from the assumed equilibrium positions in the crystal. For a particle in a harmonic potential, \( V(u) = f u^2/2 \), the Boltzmann distribution of the displacements \( u \) over the energy levels of a quantized harmonic oscillator in three dimensions leads to the second moment

\[
\langle u^2 \rangle = \frac{\hbar}{8\pi^2 m \nu} \coth \left( \frac{\hbar \nu}{2k_B T} \right)
\]

where \( \nu \) is the frequency and \( m \) is the mass of the oscillator. In the limits of very low and very high temperatures this results in

\[
\langle u^2 \rangle_0 = \frac{\hbar}{8\pi^2 m \nu} \quad (k_B T \ll \hbar \nu) \quad \text{and} \quad \langle u^2 \rangle_{\text{HT}} = \frac{k_B T}{4\pi^2 m \nu^2} \quad (k_B T \gg \hbar \nu),
\]

(2.27)
which are the zero point motion and the classical result, respectively. Considering
a set of oscillators with variable masses and frequencies and assuming that the mean
frequency of the oscillators corresponds to the Debye frequency, the Debye temperature
can be estimated from the ADPs by

$$\Theta_D^2 = \frac{3T\hbar^2}{4\pi^2 \overline{m} k_B \langle u^2 \rangle}$$

(2.28)

where $\overline{m}$ is the average mass of the atoms, where the "rattling" atoms are not included.
The Einstein frequency of the "rattlers" is obtained from the classical limit in Eq. 2.27
in a straightforward fashion. If the "rattling" is in the frequency range of the low
energy acoustic phonons it is assumed that the mean free path of the phonons is $d_{rat}$,
the distance between the "rattlers". Taking the simple formula from kinetic gas theory
and using the sound velocity $v$ from the Debye model,

$$\kappa_{rmt} = \frac{1}{3} Cv d_{rat}$$

(2.29)

is obtained, where $C$ is the heat capacity per unit volume. Even though these are
very crude approximations [Sales99] has shown for several compounds that the error
in the estimates is usually less than 20%. Nevertheless, it has to be kept in mind
that these computations are very sensible to errors in the ADPs, which can arise from
inaccuracies in the structure analysis as well as from static disorder in the structure.
Since the ADPs are usually only available for one temperature, static and dynamic
disorder cannot be distinguished.

### 2.6 Electronegativities

A piece of information that is available for every compound of known composition
are the Pauling electronegativities of the constituting elements. As pointed out by
[Slack95] the average of the electronegativity differences over all the bonds in the
structure $\overline{\Delta X}$ is a good indicator for the electrical quality of a thermoelectric material.
For example, in Bi$_2$Te$_3$ 80% of the bonds are Bi-Te bonds while 20% are Te-Te bonds.
Therefore, $\overline{\Delta X}$ of Bi$_2$Te$_3$ is calculated by

$$\overline{\Delta X} = \frac{4}{5} [X(Bi) - X(Te)] + \frac{1}{5} [X(Te) - X(Te)].$$

With $X(Bi) - X(Te) = 0.4$ and obviously $X(TE) - X(TE) = 0$ this results in an
average electronegativity difference of $\overline{\Delta X} = 0.3$ for Bi$_2$Te$_3$. For a large number of
compounds it is shown by [Slack95] that $\overline{\Delta X}$ is correlated with the weighted mobility
defined as $U := \mu m^3/2$. This is equivalent to $\beta \kappa_{rmt}$ and therefore a good measure
for electrical quality of a thermoelectric material (see section 2.1). The weighted
mobility decreases with increasing average electronegativity difference. Given a very
low thermal conductivity [Slack95] estimates that for $ZT = 1$ the weighted mobility has to be $U \geq 150 \text{ cm}^2/\text{Vs}$ which requires $|\Delta X| \leq 1$, while for $ZT = 2$ the limits are expected to be $U \geq 300 \text{ cm}^2/\text{Vs}$ and $|\Delta X| \leq 0.8$. For $ZT = 4$ it would be required that $|\Delta X| \leq 0.5$.

These considerations shed new light on the formation of mixed crystals to reduce the thermal conductivity. [Slack95] shows empirically that the reduction of the thermal conductivity only outweighs the decrease in mobility if the difference of the electronegativities of two elements mixed on one site of a crystal is $|\Delta X| \leq 0.05$.

2.7 Lower bound of the thermopower

In contrast to the thermal conductivity which consists of an electronic and a lattice contribution $\kappa = \kappa_{el} + \kappa_{lat}$ the thermopower $S$ and the electrical conductivity $\sigma$ are pure electronic properties. Therefore, a combination of the latter $S^2\sigma$, called power factor, is commonly used to evaluate the prospects of a thermoelectric material. In some materials a high power factor is obtained as a combination of a very high conductivity with a rather low thermopower. Even under the assumption of $\kappa_{lat} = 0$ these materials can be ruled out as being useful for thermoelectric applications. Assuming that for a highly conducting material the electronic contribution to the thermal conductivity is $\kappa_{el} = L_0 \sigma T$ where $L_0$ equals $2.45 \cdot 10^{-8} \text{W}\Omega^{-1}K^{-2}$, the Lorentz number for metals, the figure of merit is limited by

$$ ZT \leq \frac{S^2}{L_0} = \left( \frac{S}{157 \mu V K^{-1}} \right)^2 $$

where the equal sign corresponds to $\kappa_{lat} = 0$.

2.8 Summarized Results

At this point the results of this chapter are summarized in a table which can be regarded as a “cookbook” for thermoelectric materials. The properties are marked with “↑” if their values should be high and with “↓” if they should be low in order to obtain a good thermoelectric material.
### Table 2.1

"Cookbook" for thermoelectric materials.

<table>
<thead>
<tr>
<th>Property</th>
<th>depends on</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_D \downarrow$</td>
<td>$T_m \downarrow \overline{M} \uparrow \delta \uparrow$</td>
</tr>
<tr>
<td>$\Theta_D \downarrow$</td>
<td>$\overline{M} \uparrow \langle u^2 \rangle \uparrow$</td>
</tr>
<tr>
<td>$\kappa_{\text{sat}} \downarrow$</td>
<td>$\Theta_D \downarrow \overline{M} \uparrow \delta \uparrow \ n \uparrow \ \gamma \uparrow$</td>
</tr>
<tr>
<td>$\kappa_{\text{sat}} \downarrow$</td>
<td>$\Theta_D \downarrow \ d_{\text{rat}} \downarrow$</td>
</tr>
<tr>
<td>$m^*_d \uparrow$</td>
<td>symmetry $\uparrow$ anisotropy $\uparrow$</td>
</tr>
<tr>
<td>$\mu \uparrow$</td>
<td>$</td>
</tr>
<tr>
<td>$S^2 \sigma \uparrow$</td>
<td>$\mu (m^*_d)^{3/2} \uparrow$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$</td>
</tr>
<tr>
<td>$T_{\text{op}}$</td>
<td>$\frac{E_g}{10\kappa_B} \leq T_{\text{op}} \leq \frac{E_g}{6\kappa_B}$</td>
</tr>
</tbody>
</table>

where

- $\Theta_D$ is the Debye temperature
- $T_m$ is the melting point
- $\overline{M}$ is the average atomic mass
- $\delta$ is the average atomic distance
- $\langle u^2 \rangle$ is the atomic displacement parameter
- $\kappa_{\text{sat}}$ is the lattice thermal conductivity
- $d_{\text{rat}}$ is the distance between "rattlers"
- $\gamma$ is the Grüneisen parameter
- $m^*_d$ is the density of states effective mass
- $\mu$ is the mobility
- $|\Delta X|$ is the average electronegativity difference
- $S^2 \sigma$ is the power factor
- $E_g$ is the energy gap
- $T_{\text{op}}$ is the operating temperature
CHAPTER

3

State of the Art
Thermoelectric Materials

In this chapter the current state of the art thermoelectric materials will be discussed in some detail. This shall give a flavor for the applicability of the “Cookbook” presented in the previous chapter. Furthermore, these data set the standard to which the thermoelectric performance of the materials presented in this work have to be compared.

3.1 BISMUTH TELLURIDE AND ITS ALLOYS

Since Bi$_2$Te$_3$ is the best thermoelectric material at room temperature, it is also the most widely used and most intensely researched. Bi$_2$Te$_3$ and its isomorphic compounds Sb$_2$Te$_3$ and Bi$_2$Se$_3$ crystallize in the trigonal system (space group R$\bar{3}$m) with a rhombohedral unit cell$^1$. In order to emphasize the layered structure, which is a distinct characteristic of these crystals, a transformation into the hexagonal system is frequently carried out. The lattice consists of a sequence of atomic layers Te(1)$\sim$Te(1)-Bi-$\sim$Te(2)-Bi-$\sim$Te(1)$\sim$Te(1), such that after each five layers the stacking sequence is repeated, with three stacks forming the hexagonal unit cell. While the bonding between Te(2) and Bi is completely covalent, there is one electron transferred from the Te(1) to the Bi resulting in a mixed covalent-ionic bonding. The bonding between the Te(1) is a weak, van der Waals type bond which makes the crystals easy

$^1$Sb$_2$Se$_3$ which is also strongly related to Bi$_2$Te$_3$ crystallizes in the orthorhombic space group Pnma.
Table 3.1
TRANSPORT PROPERTIES AND RESULTING FIGURE OF MERIT OF Bi$_2$Te$_3$ AT 300 K [GOLDSMID64].

<table>
<thead>
<tr>
<th>Transport property</th>
<th>n-type</th>
<th>p-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermopower [µV/K]</td>
<td>-205</td>
<td>185</td>
</tr>
<tr>
<td>resistivity [mΩ cm]</td>
<td>0.97</td>
<td>1.03</td>
</tr>
<tr>
<td>total thermal conductivity [W/(mK)]</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>figure of merit ZT</td>
<td>0.68</td>
<td>0.52</td>
</tr>
</tbody>
</table>

To cleave along these planes. The highly anisotropic crystal structure gives rise to anisotropy in the electrical and thermal conductivity. Because the ratio of electrical to thermal conductivity is lower parallel to the c-axis than perpendicular to it and the thermopower is nearly isotropic, transport in the a, b-plane results in a higher figure of merit.

As already discussed in chapter 2, the low average electronegativity difference of |ΔX| = 0.3 gives rise to high mobilities, 1200 cm$^2$/Vs and 510 cm$^2$/Vs for electrons and holes at 295 K, respectively [GOLDSMID64]. The hexagonal symmetry in combination with the strong anisotropy gives rise to a band structure that suits thermoelectric applications extremely well. In the valence band as well as in the conduction band six equivalent valleys are found. In both bands the effective mass is very low along one of the principal axes of the valleys (valence band: $m^* \approx \frac{1}{20}m_e$, conduction band: $m^* \approx \frac{1}{40}m_e$) while reasonably high ($m^* \approx \frac{1}{4}m_e$) along the other directions. Thus, there is, at the same time, a high density of states effective mass and a low inertial effective mass. Consequently, Bi$_2$Te$_3$ exhibits a very high power factor.

The Debye temperature of Bi$_2$Te$_3$, $\Theta_D = 155$ K [SHOEMAKE69] is quite low. In combination with the high masses of the atoms, and the weak bonds, Bi$_2$Te$_3$ has all the prerequisites for a low lattice thermal conductivity. At room temperature the lattice thermal conductivities are 1.5 W/(m K) and 0.7 W/(m K) perpendicular and parallel to the c-axis, respectively. According to the energy gap of 0.16 eV Bi$_2$Te$_3$ is expected to be useful at temperatures from 200 K to 300 K. The transport properties of optimally doped material at 300 K are summarized Tab. 3.1.

Compared to Bi$_2$Te$_3$ the related compounds Bi$_2$Se$_3$, Sb$_2$Te$_3$, and Sb$_2$Se$_3$ have higher energy gaps of 0.28 eV, 0.30 eV, and 1.2 eV, respectively. Therefore alloying amongst these materials not only reduces the thermal conductivity but also allows to adjust the energy gap to make the material suitable for higher temperature applications. A vast number of alloy compositions has been studied for this system. The figure of
merit for the “best” materials is shown in Fig. 3.1. The low temperature and the high temperature data are taken from [Yim72] and [Wright70], respectively.

3.2 Bismuth-Antimony Alloys

Bismuth is a semimetal with a band overlap of 38 meV. In analogy to bismuth telluride, bismuth and antimony crystallize in the space group $R\bar{3}m$. An energy gap is formed upon alloying of the two metals when the concentration of antimony lies between 5 and 40 mole-%. At a concentration of 12 mole-% the gap reaches its maximum value of 14 meV [Goldsmid70]. Alloying is beneficial from the point of view of thermoelectric cooling for two reasons. The increase of the energy gap reduces the bipolar effects and hence allows for higher thermopowers. Additionally, the thermal conductivity is reduced due to alloy disorder scattering of the phonons, i.e. at 80 K the lattice thermal conductivity along the basal planes is reduced from 11 W/(mK) to 2.9 W/(mK) upon adding 6% antimony to bismuth [Erl62]. A further improvement of the figure of merit can be achieved by the application of a transverse magnetic field [Wolfe62]. The largest enhancement is produced with the magnetic field parallel to a bisectrix axis and the primary flow along the trigonal axis.

The thermoelectric performance of Bi$_{88}$Sb$_{12}$ with and without a magnetic field is shown in Fig. 3.2. At temperatures above 150 K fields of 1 T and more are needed to reach the maximum figure of merit. Since such strong magnetic fields cannot be provided in standard applications Bi$_{88}$Sb$_{12}$ cannot be regarded as useful for room temperature applications.
3.3 Lead Telluride

Lead telluride crystallizes in the NaCl structure (space group $Fm\overline{3}m$). It has a direct energy gap of 0.3 eV at 300 K [Preier79] with four equivalent valleys for both the valence and the conduction band. The mobilities of the electrons and holes at 295 K – 1620 cm$^2$/Vs and 750 cm$^2$/Vs, respectively [Allgaier58] – are higher than those in Bi$_2$Te$_3$. However, since the density-of-states effective masses of the carriers are lower in PbTe the optimally doped compound has a smaller power factor than Bi$_2$Te$_3$. Furthermore, the lattice thermal conductivity of lead telluride is about 2 W/(mK), which is slightly higher than that of bismuth telluride. However, at higher temperatures PbTe shows up to advantage compared to Bi$_2$Te$_3$ since bipolar conduction is suppressed due to its larger energy gap. It is stated that the performance can be improved by alloying PbTe with 25% SnTe [Rosi61] or 50% PbSe [Wright70] to reduce the thermal conductivity. However, the improvement is shown at 300 K while the operating temperature of PbTe-devices is between 450 K and 750 K. As pointed out by [Heikes61] the effect of alloy scattering becomes less pronounced with elevated temperatures and measurements in the operating temperature range have shown that alloys do not perform better than pure PbTe. The figure of merit of PbTe as a function of temperature is shown in Fig. 3.3 for $p$-type material [Rowe95] and $n$-type material [Jones98]. The data points for the latter do not represent one sample but the maximum $ZT$ achieved at the given temperatures.
3.4 The (AgSbTe$_2$)$_{1-x}$ (GeTe)$_x$ System

The two compounds AgSbTe$_2$ and GeTe, which form the alloy system discussed in this section, crystallize with different structures. While silver antimony telluride has the rocksalt structure, germanium telluride crystallizes with trigonal symmetry (space group $R3m$). Solid solutions between these compounds can be formed over the entire concentration range. In abbreviation the solid solutions are named TAGS-$x$, where the first are just the letters of the elements and $x$ is the percentage of GeTe. For increasing GeTe content a monotonic increase of the thermopower, the electrical resistivity, and the thermal conductivity is observed [Rosié60]. However, in the concentration range of 75% to 90% GeTe the system shows a room temperature phase transition from a rhombohedral (89.2°) to the rocksalt structure with very pronounced effects on the figure of merit. The thermopower and the electrical conductivity are slightly increased but more importantly there are two minima in the thermal conductivity at 80% and 85% GeTe concentration which are shown in Fig. 3.4(a).

Of these two compositions TAGS-85 turns out to be the better thermoelectric material. It is always obtained as $p$-type material and it is almost not amenable to doping [Skrabek74]. Due to its superior thermoelectric properties it is used as a replacement for PbTe in the $p$-type leg. Because of a second phase transition at 789 K and increasingly rapid sublimation the upper limit on the operating temperature of TAGS-85 is 780 K. The figure of merit up to this temperature is shown in Fig. 3.4(b) [Skrabek95].

The lattice distortion and the resulting minima in the thermal conductivity are a unique feature of the TAGS system. Unfortunately, such behaviour is rare and not predictable and can therefore not be used as a guidepost towards high $ZT$ materials.
Figure 3.4. (a) The total thermal conductivity of various TAGS compositions at selected temperatures. (b) The figure of merit $ZT$ of TAGS-85 as function of temperature compared to $p$-type PbTe.

## 3.5 Silicon-Germanium Solid Solutions

For thermoelectric applications at very high temperatures solid solutions of silicon and germanium are used. From the electrical point of view silicon is a very good thermoelectric material. Its conduction band has six equivalent minima along the [100]-axes of the Brillouin zone [Madelung90]. Because Si and Ge are elementary semiconductors with completely covalent bonds, the charge carriers exhibit very high mobilities compared to compound semiconductors. The thermopower of heavily doped $n$-type silicon was studied by [Brinson70]. At 300 K arsenic doped Si with a carrier concentration of $5.6 \cdot 10^{19}$ cm$^3$ has a thermopower of 280 $\mu$V/K. The dependence of the mobility on doping is well studied in Si [Madelung90] and for the given carrier concentration a value of 97 cm$^2$/Vs is found. Thus, the electrical conductivity is 870 (\Omega\text{cm})$^{-1}$ and the power factor is 6.8 mW/(mK$^2$), 70% higher than that of optimized Bi$_2$Te$_3$ based alloys. Unfortunately, the thermal conductivity of Si is extremely high (156 W/(mK)). As it is seen in Fig. 3.5(a) can be drastically lowered by alloying Si with Ge [Wood88] while the effect on the electron mobility is less pronounced [Madelung90]. Because the figure of merit depends on the ratio $\mu/\kappa_{\text{lat}}$ this leads to an increase in $ZT$. Nevertheless, the thermal conductivity remains too high for Si-Ge solid solutions to compete with Bi$_2$Te$_3$ at room temperature. Yet for high temperature applications Si$_{70}$Ge$_{30}$ is the material of choice because of its chemical stability and its large band gap of 0.95 eV.
Figure 3.5.  (a) The electron mobility and the thermal conductivity as function of composition in the Si-Ge system.  (b) The figure of merit of $n$-type and $p$-type Si$_{70}$Ge$_{30}$ vs. temperature.

3.6 OTHER MATERIALS

Besides the established thermoelectric materials, which have been discussed in the previous sections, there are a few others, which exhibit a figure of merit $ZT \approx 1$ but are currently not employed in thermoelectric devices for different reasons. These materials are

- Very recently, $CsBi_4Te_6$ has been identified as high-performance material with a maximum figure of merit of $ZT = 0.8$ at 225 K [Chung00], while Bi$_2$Te$_3$-alloys only exhibit a figure of merit of approximately 0.6 at this temperature. The research on this material and its optimization are still in progress and presumably the next years will show, whether it is going to be established as material for low-temperature devices.

- The filled skutterudites are a class of materials, that exhibits large voids in the crystal structure, which can be filled by “rattling” guest atoms. Therefore, these compounds typically exhibit low thermal conductivities ($\sim 1.5$ W/(mK)). While high figures of merit in $p$-type skutterudites are known for some years, $ZT = 1.07$ at 730 K for Ce$_{0.5}$Fe$_3$CoSb$_{12}$ [Sales97], a high efficiency $n$-type compound, $ZT = 1.1$ at 830 K for Ba$_{0.3}$Co$_4$Sb$_{12}$, has been reported only very recently [Chen00].

- Ag$_2$Se exhibits very good thermoelectric properties [Ramazanzade81] at 300 K, but it is not thermoelectrically applicable due to its high ionic conductivity [Korte98].

- $\beta$-Zn$_4$Sb$_3$ exhibits almost the same thermoelectric performance as the AgSbTe$_2$-GeTe alloys [Caillat97]. However, its application as a high temperature ther-
Figure 3.6. The figure of merit of the currently best materials employed in thermoelectric devices up to 1000 K. The thermomagnetic effects in Bi-Sb have not been regarded.

...moelectric material is limited, since the \( \beta \)-phase is only stable from 263 K to 765 K [Koyanagi97]. Therefore, it is not likely to replace the already established TAGS-85.

3.7 SUMMARY – LIMIT TO \( ZT \)?

In this chapter the thermoelectric properties of the current state of the art thermoelectric materials Bi-Sb, Bi\(_2\)Te\(_3\), TAGS-85, PbTe, and Si-Ge have been discussed. Further materials, which are the best at a certain temperature or exhibit \( ZT \gtrsim 1 \), are CsBi\(_4\)Te\(_6\), Ag\(_2\)Se, Zn\(_4\)Sb\(_3\), and filled skutterudites. The thermoelectric performance as function of operating temperature of the materials, discussed in detail, is shown in Fig. 3.6. Only very few materials have been identified, which exhibit a figure of merit \( ZT > 1 \), and up to date no material has been found with \( ZT \approx 2 \).

There is an ongoing discussion, whether there is a theoretical limit to \( ZT \) [Min00]. However, no exact proof can be provided for any limit of \( ZT \), since it would require the calculation of the thermopower, the electrical resistivity and the thermal conductivity of an indefinite number of known (and unknown) materials. Therefore, the discussion mainly relies on conclusions drawn from experimental data, e.g. combining the best properties of different materials, or calculations based on simplified models (single parabolic band, relaxation-time approximation, etc.) and estimates about the thermal conductivity. The most recent estimate [Min00], suggests a temperature dependent
limit of $ZT$, which is $ZT \lesssim 1.5$ at lowest temperatures and $ZT \lesssim 4$ at 1000 K, and a linear behaviour in between. The calculated limit for $ZT$ at 300 K is between 2 and 2.5. Thus, even if there is a limit to $ZT$, it would still allow a 100% improvement of the current state of the art thermoelectric materials. This would definitely greatly enhance the range of application for thermoelectric devices.
CHAPTER 4

Measurement of Thermoelectric Properties

To determine the thermoelectric figure of merit $ZT$ accurate measurements of the thermopower $S$, the electrical resistivity $\rho$, and the thermal conductivity $\kappa$ are needed. To obtain further understanding of the material properties additional measurements have been carried out, i.e. heat capacity measurements, Hall measurements, Raman scattering and elastic as well as inelastic neutron scattering experiments.

The following sections focus on the measurement of three properties ($S$, $\rho$, and $\kappa$) which are necessary to determine the figure of merit $ZT$.

4.1 Electrical Resistivity and Hall Effect

The electrical resistivity and Hall effect have been measured in a commercial device, Physical Properties Measurement System (PPMS) by Quantum Design. It allows measurements at temperatures from 1.8 K to around 350 K in magnetic fields up to 9 T. With a built-in bridge resistances from about 4 $\mu\Omega$ to approximately 5 M$\Omega$ can be measured. The bridge can operate in either an AC (7.5 Hz square wave) or DC drive mode. For resistivity measurements on thermoelectric materials the AC mode is preferable. A sample of a good thermoelectric material can be regarded as a single leg of a Peltier cooler. Therefore a direct current will establish a temperature gradient across the sample which obviously will result in a Seebeck voltage. This additional voltage will influence the resistivity measurement. Compared to electrical
Figure 4.1. Sample geometry. The contacts $V_1$ and $V_2$ are used for resistivity measurements while the Hall voltage is measured between $V_3$ and $V_4$.

processes the temperature gradient establishes rather slowly, because it is limited by the sample’s thermal diffusivity. Consequently, an alternating current with a 7.5 Hz frequency minimizes this effect.

The electrical measurements were carried out on bar shaped samples in a 4-point-geometry, as shown in Fig. 4.1. The accuracy of the resistivity measurement is mainly determined by the measurement of the sample geometry. Typical errors are ±0.02 mm for the width and thickness of the sample and ±0.1 mm for the contact distance. With a typical sample size of $0.5 \times 0.5 \times 3 \text{ mm}^3$ this results in an uncertainty of less than 5%. To obtain ohmic contacts on $p$-type material gold pads of approximately 200 Å thickness were evaporated onto the samples at the sites of the contacts, while for $n$-type material such a step proved not necessary. The wire leads were glued to the sample with silver epoxy (Epothek H20E).

The Hall measurements are carried out analogously to the resistivity measurements

$$R_{\text{app}} = \frac{V_H}{T} = \frac{R_H B}{d} + V_{\text{off}}$$

where $R_{\text{app}}$ is the apparent resistance as measured with the PPMS, $V_H$ is the Hall voltage, $R_H$ the Hall coefficient $B$ the magnetic field and $V_{\text{off}}$ the voltage at zero field. To determine $R_H$ the apparent resistance $R_{\text{app}}$ has been measured as function of the magnetic field from -1 T and 1 T. From the slope of the linear fit the Hall coefficient is calculated, using

$$R_H = \frac{\delta R_{\text{app}}}{\delta B}d$$

### 4.2 Thermopower Measurements

Two rather similar experiments have been used to measure the thermopower as a function of temperature. The first one is a commercial apparatus provided by MMR Technologies, which compares the thermal voltage across the sample to a thermocouple grade constantan standard. Although the idea behind the setup is reasonable, the
electronics built into the setup are quite unstable and noisy and since only the temperature and the calculated thermopower are recorded, the measurements are rather unreliable. Therefore a new sample holder, as shown in Fig. 4.2, was designed to be used in the PPMS. Intrinsic silicon was chosen as the base material because, due to its high thermal conductivity, temperature gradients in the holder are avoided. The sample and the Pt leads are mounted to the holder with silver paint. The electrical contact resistance between the leads and the sample is typically 50 Ω. The heater and the thermocouple are bond to the holder with epoxy glue. In this way, the sample can be easily washed off with acetone after a measurement, while the rest of the holder remains intact. The heated part of the sample holder is not mounted to the glass plate. Therefore, it is possible to measure samples of different length. Furthermore, stresses due to the different thermal expansion coefficients of the various materials are avoided by this design. The measurement is controlled by a program which adjusts the power dissipated over the heater so that each data point is taken at temperature differences of 0.5 K and 1 K. The thermopower is calculated with regard to the voltages over the sample and the thermocouple at zero power at the heater.

Since the thermocouple is not mounted to the sample but to the holder this measurement corresponds to a 2-point geometry in electrical measurements. A thermal contact resistance between the holder and the sample leads to an overestimation of the temperature gradient across the sample. Due to this error the measured thermopower tends to be too low. The setup was calibrated by measuring thermocouple wires with known thermopowers to determine the significance of these considerations. The measured thermopowers of thermocouple grade constantan and chromel agreed with the specifications of the vendor. It can be concluded that the presented design is feasible for accurate thermopower measurements.
Figure 4.3. Longitudinal steady state method for thermal conductivity measurements. The arrows indicate the different paths of heat flow.

4.3 THERMAL CONDUCTIVITY

4.3.1 LONGITUDINAL STEADY STATE METHOD

In this work two methods have been used to measure thermal conductivities. The classical method is the longitudinal steady state method, which is the thermal analog to the 4-point electrical conductivity measurement. The schematics of the measurement are shown in Fig. 4.3. The arrows represent the directions of heat flow, which have to be considered.

Ideally, the only considerable heat flow occurs through the sample into the heat sink. Then, the thermal conductivity $\kappa$ can be calculated as

$$\kappa = \frac{\dot{Q}}{\Delta T \frac{d}{wt}}$$

where $\dot{Q}$ is the power generated by the heater, $\Delta T$ is the temperature difference between the two contacts of the differential thermocouple and $w$, $t$ and $d$ are the sample dimensions in analogy to the electrical 4-point measurement. The heat flow through the leads to the heater can be kept small by using long and thin manganine wires. For the same reason, the thermocouples have been fabricated from very thin ($50 \mu m$) chromel and constantan wires. In both cases, different wire lengths have not resulted in any measurable effect. Therefore, it can be concluded that heat losses through the wires are negligible. The long manganine wires have a fairly high resistance of approximately 30 $\Omega$. To avoid heat losses by joule heating in the wires a heater with a much higher resistance of 10 $k\Omega$ was used. Heat loss due to convection was ruled out by providing a vacuum better than $10^{-5}$ Torr during the measurement.

The only heat loss mechanism left is heat radiation. For a sample with a temperature gradient $\Delta T$ in an environment with a temperature $T$ and under the condition
$\Delta T \ll T$ the radiative heat loss per unit area is

$$\dot{Q}_{\text{rad}} \simeq \epsilon \sigma_{\text{SN}} T^3 \Delta T$$

where $\epsilon$ is the emissivity of the sample and $\sigma_{\text{SN}}$ is the Stefan-Boltzmann constant. Since $\dot{Q}_{\text{rad}}$ is linear in $\Delta T$ as well as the heat flow through the sample these effects cannot be separated by applying different temperature gradients. Due to the $T^3$-dependence radiation losses can be neglected at temperatures below 150 K even for very low thermal conductivity samples. At higher temperatures the effect of radiation losses might become very pronounced. Fig. 4.4 shows the thermal conductivity of fused quartz as determined with the longitudinal steady state method and the $3\omega$-method [Cahill90] compared to the reference data of the National Bureau of Standards [Powell66].

### 4.3.2 3$\omega$-TECHNIQUE

As seen in Fig. 4.4 the $3\omega$-technique is much less susceptible to radiation heat losses than the longitudinal steady state method. Therefore, this method has been established to obtain reliable thermal conductivity data at temperatures above 150 K.

The $3\omega$-technique can be used to measure the thermal conductivity of thin films and bulk materials from fairly low temperatures ($\approx 50$ K) to very high temperatures up to 1000 K and more [Cahill90]. The $3\omega$-method uses a radial heat flow from a metal line, which is evaporated onto the sample, and is used both as a heater and a thermometer. A periodic current $I(t) = I_0 \sin(\omega t)$ is applied to the line, which results in a periodic power dissipation $P(t) = RI^2$ and a heating of the metal line with the doubled frequency $2\omega$. Since the resistance $R$ of the metal line is in good approximation linear in temperature, it acts as a thermometer to measure the periodic heating.
The resistance changes with \( R(t) = R_0 - \Delta R \cos(\omega t) \). The periodic current applied to the periodically changing resistance results in a voltage across the line of the form \( V = V_0 \sin(\omega t) - V_3 \sin(3\omega t) \). The thermal conductivity of the material is determined by the dependence of \( V_3 \) on \( \ln(\omega) \). The complete theoretical treatment of this method is given in Appendix A.

In principle, the implementation of a 3\( \omega \)-measurement system is rather straightforward. Nevertheless, there are several difficulties in the details of the experiment. Therefore, the sample preparation and the implementation of the measurement will be discussed in the following sections.

**Sample Preparation**

As seen in Appendix A two geometrical requirements concerning the size of the sample and the metal line have to be fulfilled. Since the treatment of the problem assumes an "infinite" half-cylindrical sample, the width \( w \) and the thickness \( t \) of the sample, as shown in Fig. 4.5(a) have to be much larger than the thermal penetration depth \( \Lambda \). On the other hand, the width \( b \) of line is considered to be infinitely small. Therefore it has to be much larger than the line width. Summarized, the constraints are \( b \ll \Lambda \ll w, t \). Therefore, the width of the metal line should be orders of magnitude smaller than the typical sample dimensions. Fortunately, a study of the influence of the finite width of the metal line and the limited sample thickness [Jacquot99] shows that the conditions are less stringent. Comparing measurements with a 20 \( \mu \)m line on a Kapton foil of 130 \( \mu \)m thickness with finite element simulations [Jacquot99] find that the constraints are much less tight

\[
\frac{1}{3} b \leq \Lambda \leq \frac{1}{2} t.
\]

The thermal wavelength has to be less than half the thickness of the sample. It may even be smaller than the width of the metal line and Eq. A.17 will still be valid. Another kind of edge effect has to be considered because of the finite length of the line. Since no heat is generated beyond the ends of the line, there is considerable heat flow along the line axis in the outer parts. Only far enough away from the ends of the line, presumably several thermal wavelengths, the heat flow will be completely radial. Therefore, the whole line has to be considerable longer than the distance of the inner contacts. These considerations determine the design of the shadow mask shown in Fig. 4.5(b).

The line width of the mask was limited by the manufacturer but it is suitable for the standard samples with a thickness of approximately 3 mm. Molybdenum is used as mask material because it can easily be cleaned by etching.

In contrast to the longitudinal steady state method, which requires precisely shaped samples, only one polished surface on an otherwise arbitrarily shaped sample is re-
Figure 4.5. (a) Schematic drawing of the geometry of a $3\omega$-measurement. The measure $\lambda$ is denoted as thermal wavelength or, more precisely, thermal penetration depth. (b) The design of the molybdenum shadow mask for the metal line.

required for the $3\omega$-technique. This surface of the sample must be smooth enough, so that the narrow metal line is continuous. With five steps of polishing (2 papers, 3 pastes, each step about 2 minutes) a near mirror finish can be easily obtained on the studied materials.

For $3\omega$-measurements on insulators the silver line can be directly evaporated onto the sample. In order to avoid the electrical shortcut of the line by conducting samples an insulating layer between the material and the line is needed. Since the $3\omega$-voltage is three orders of magnitude smaller than the $1\omega$-voltage the measurement is very sensitive to influences on the fundamental frequency, which generate additional harmonics. Therefore the resistance between the line and the sample has to be at least five or six orders of magnitude larger than that of the line. For a typical line resistance of 20 $\Omega$ this requires an insulation of 2 M$\Omega$ to 20 M$\Omega$. Furthermore the heat from the silver line should not diffuse out in the insulating layer. Therefore the thickness of the layer should be much smaller than the width of the line. Given the line width of 45 $\mu$m this corresponds to a thickness of the order of 5 $\mu$m. A third requirement is that the layer is mechanically stable over temperatures from 5 K to 350 K.

Different layer materials (MgF$_2$, Si$_3$N$_4$, varnish, spin-on resists, etc.) and deposition techniques (thermal evaporation, PECVD, spray coating, and spin coating) have been studied. The only layer that provides a sufficient resistance over a thickness of a few $\mu$m and that does not form cracks over the entire temperature range is a spin-on glass resin provided by Techneglas (Techneglas 150F). It has a specified resistivity of $10^{14}$ $\Omega$ cm and a thermal expansion coefficient of $13 \cdot 10^{-5}$ K$^{-1}$. With layer thicknesses around 3 $\mu$m resistances of more than 20 M$\Omega$ are achieved.

Different materials for mounting the sample to the heat sink have been tested. Since the measurements are carried out under vacuum no liquids or pastes can be used
because gas inclusions between the sample and the holder, which are inevitable, will result in large bubbles when the pressure is lowered. This reduces the contact area between sample and heat sink and thereby deteriorates the thermal contact. On the other hand, mounting the sample with materials which form a non-flexible bond, i.e. epoxy or silver paint, leads to thermal stresses. Below certain temperatures this will always result in cracking of either the bond or the sample. The contact problems have been overcome using a flexible material, HI-FLOW™ 200-G ¹, which is used as thermal interface material for computer processors. It forms a bond with low thermal impedance and enough flexibility to avoid thermal cracking.

**Measurement implementation**

![Diagram](image)

Figure 4.7. Setup of the 3ω-measurement.

The setup of the 3ω-experiment is shown in Fig. 4.7. The heart of the measurement setup is an SR830 lock-in amplifier. Via the “Sine Out”-Channel it can provide a

¹Provided by: The Bergquist Company, 5300 Edina Industrial Blvd., Minneapolis, MN, USA.
sinusoidal voltage with amplitudes from 4 mV to 5 V and frequencies from 10 mHz to 102 kHz with an output impedance of 50 Ω. Since this is comparable to the resistance of the wire, the “Sine Out” cannot be regarded as current source. Therefore, the “Sine Out”-signal is used as input for a Valhalla 2500 Current Calibrator. It transforms the sinusoidal voltage input into a corresponding current. The range of output currents is 2 µA to 2 A with an accuracy of 0.05% and a frequency response of 10 kHz. No harmonics of the reference frequency can be found in the output current. The current source is connected with the current contacts, \( I_1 \) and \( I_2 \), of the silver line on the thermal conductivity sample (see Fig. 4.5(b)). The two voltage pads, \( V_1 \) and \( V_2 \), are connected with the “Signal Input” of the lock-in amplifier. The amplitudes of the 1\( \omega \)- and the 3\( \omega \)-signals are measured successively. As shown in Appendix A the thermal conductivity of the sample is calculated from the following equation

\[
\kappa = \frac{R I_0^2 d \ln(\omega) dR}{4\pi l dV_3\omega dT}.
\]

(4.1)

The current \( I_0 \) is known because it is provided by the current calibrator. The resistance of the line \( R \) is calculated from the 1\( \omega \)-voltage and \( I_0 \). The slope of the resistance \( \frac{dR}{dT} \) is obtained by a linear fit to the resistance data. The length of the line \( l = 2 \text{ mm} \) is determined by the design of the mask. The 3\( \omega \)-voltage \( V_3\omega \) is measured at five different frequencies and the derivative \( \frac{dV_3\omega}{d\ln(\omega)} \) is determined by a linear fit to \( V_3\omega \) versus \( \ln(\omega) \).

To discuss the right settings for the lock-in amplifier would be beyond the scope of this section. Therefore, the settings used for the measurements are just summarized in Table 4.1. The time constant is adjusted by the measurement control software and is always larger than 10 periods of the 1\( \omega \)-signal.

### Table 4.1

**The settings of the SR830 lock-in amplifier during the 3\( \omega \) measurements.**

<table>
<thead>
<tr>
<th>Option</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal Input Configuration</td>
<td>A-B</td>
</tr>
<tr>
<td>Input coupling</td>
<td>DC</td>
</tr>
<tr>
<td>Shield Ground Configuration</td>
<td>Float</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>1 V</td>
</tr>
<tr>
<td>Reserve Mode</td>
<td>High Reserve</td>
</tr>
<tr>
<td>Low Pass Filter Slope</td>
<td>24 db/oct</td>
</tr>
<tr>
<td>Filter Settings</td>
<td>None</td>
</tr>
<tr>
<td>Time Constant</td>
<td>(computer controlled)</td>
</tr>
</tbody>
</table>
CHAPTER 5

Survey of explored Materials

In order to find a promising thermoelectric material a broad search has been carried out. Several materials have been chosen for this study following the rules of the "cookbook" presented in chapter 2. The results of this survey are summarized in this chapter. The initial state of knowledge about the various compounds differed a lot. In some cases only the crystal structure has been published and no information regarding the transport properties was available. For several others only a resistivity value at room temperature has been given, sometimes determined by two point measurements. In a few instances the materials have already been studied regarding their thermoelectric properties but it was questionable whether the results represented the full potential of the investigated material.

Fundamentally, a material promising for thermoelectric applications at not too high temperatures can be described as a small energy gap, high mobility semiconductor with low thermal conductivity. A question that has been left open so far is how to identify a semiconductor just by crystallographic information. In several occasions semiconducting compounds can be identified by the rule of Grimm-Sommerfeld

$$\frac{\sum_i n_i v_i}{\sum_i n_i} = 4$$  \hspace{1cm} (5.1)

where $n_i$ is the number of atoms of type $i$ in the formula unit and $v_i$ the number of its valence electrons. Originally, this rule has been deduced for compounds with tetrahedral bonds only but it seems to be applicable for several other materials as well. Nevertheless, there are many non-tetrahedral cases where the rule of Grimm-Sommerfeld fails to predict the semiconduction properties. Furthermore, for transition metals the number of valence electrons is not well defined. A more detailed analysis,
which also takes account of the crystal structure, leads to the rule of Mooser-Pearson

\[
\frac{n_v - b_c + b_a}{n_a} = 8
\]  

(5.2)

where \( n_v \) is the number of valence electrons per unit cell, \( b_c \) and \( b_a \) the number of cation-cation and anion-anion bonds, respectively, and \( n_a \) the number of the most electronegative anions. This rule is not applicable if \( d \)-electrons are involved in the bonds. Furthermore, for complicated crystal structures the assignment of bonds is rather ill-defined and thus the determination of \( b_c \) and \( b_a \) difficult. Consequently, these rules should be perceived not as stringent laws but as good indicators for semiconducting compounds.

Compound semiconductors can be classified with regard to their most electronegative anions. Compounds with group V, group VI, and group VII elements are referred to as pnictides, chalcogenides, and halides, respectively. It turns out that the large electronegativity differences in the halides result in low mobilities, whereas pnictides based on Bi are usually metallic. Therefore, most of the investigated compounds are chalcogenides, where the tellurides are prevailing because Te has the largest mass and the smallest electronegativity. Additionally, also clathrates and pyrochlores have been studied.

It has to be pointed out that in order to investigate a large number of materials in a reasonable period of time, the single experiments are aimed at estimating the thermoelectric prospects of the different materials rather than understanding their physical properties. Therefore, for each material a short motivation for studying its properties and a brief, descriptive presentation of the results is given.

Clathrates

Originally, the germanium type I clathrates have been identified as promising thermoelectric compounds by G. A. Slack [Slack97, Slack95]. They are a model system for enhanced phonon scattering by “rattling” atoms and over the last years they have attained a lot of attention (see [Iversen00] and references therein). The germanium type I clathrates have the stoichiometry, \( X_8E_{46} \), where \( X \) is an alkali or alkaline-earth metal and \( E \) represents a group IV element. Their cubic crystal lattice has the space group \( Pm3n \) and consists of tetrahedral networks with periodic voids, so called “cages”, of 20 and 24 coordinated \( E \) polyhedra in a 3:1 ratio. These compounds belong to the crypto-clathrates in the sense that the cage like structure only exists in the presence of the additional, so called “guest”, atoms. In order to obtain semiconducting compounds the additional electrons from the guest atoms are balanced by substituting 16 Ge atoms by Ga. The highest figure of merit in clathrates up to date has been found for \( Sr_8Ga_{16}Ge_{30} \) with \( ZT=0.25 \) at 300 K [Nolas98]. Since this is a very promising re-
Table 5.1
The thermopower and resistivity of several clathrates. The values marked by * are from [Nolas98].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S(300K)$ μV/K</th>
<th>$\rho(300K)$ Ωcm</th>
<th>$S^2_\sigma$ W/(mK²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr₈Ga₁₆Ge₃₀</td>
<td>-63</td>
<td>6.5 \cdot 10⁻¹</td>
<td>6.1 \cdot 10⁻¹</td>
</tr>
<tr>
<td>Sr₈Ga₁₆Ge₃₀*</td>
<td>-125</td>
<td>0.002</td>
<td>7.9 \cdot 10⁻¹</td>
</tr>
<tr>
<td>Sr₈Ga₁₆Ge₃₀*</td>
<td>-155</td>
<td>0.0027</td>
<td>8.9 \cdot 10⁻¹</td>
</tr>
<tr>
<td>Sr₈Ga₁₆Ge₃₀*</td>
<td>-320</td>
<td>0.013</td>
<td>7.8 \cdot 10⁻¹</td>
</tr>
<tr>
<td>Ba₈Ga₁₆Ge₃₀</td>
<td>-92</td>
<td>0.0018</td>
<td>4.7 \cdot 10⁻¹</td>
</tr>
<tr>
<td>Sr₈Ga₁₆Si₃₀</td>
<td>-23</td>
<td>4.3 \cdot 10⁻¹</td>
<td>1.2 \cdot 10⁻¹</td>
</tr>
<tr>
<td>Ba₈Zn₈Ge₃₈</td>
<td>-25</td>
<td>9.1 \cdot 10⁻¹</td>
<td>6.9 \cdot 10⁻⁵</td>
</tr>
<tr>
<td>Ba₈Ag₆Ge₄₀</td>
<td>16</td>
<td>0.0039</td>
<td>6.6 \cdot 10⁻⁶</td>
</tr>
<tr>
<td>Ba₈Au₆Ge₄₀</td>
<td>102</td>
<td>0.002</td>
<td>5.2 \cdot 10⁻¹</td>
</tr>
<tr>
<td>Ba₈Ga₁₆Sn₅₂</td>
<td>-9.8</td>
<td>1.7 \cdot 10⁻¹</td>
<td>5.7 \cdot 10⁻⁵</td>
</tr>
</tbody>
</table>

As a result, we have studied several related compounds. The electrical properties are shown in Tab. 5.1, including the results of [Nolas98] which are marked by an asterisk.

Due to the high oxygen affinity of the alkaline-earth metals the synthesis of these compounds cannot be carried out in quartz ampoules. Instead, Ta is chosen as container material for the reaction process. Stoichiometric amounts of the elements are filled into a Ta tube, which is folded at the ends. Thereby a seal is provided which prevents the loss of the alkaline-earths due to evaporation during the reaction. The Ta tube is mounted between two electrodes in a vacuum chamber and can be heated with currents up to 200 A. Thereby temperatures of more than 2000°C can be achieved. In order to homogenize the reaction product the Ta tube is turned over and the material remelted two or three times.

A sample of Sr₈Ga₁₆Ge₃₀, which has been prepared in the described fashion, exhibits a smaller thermopower than reported in [Nolas98] but due to the lower resistivity the power factor is comparable. From these four samples a maximum power factor of about 1.2 mW/(mK²) for a sample with 6 to 10 mΩ cm can be estimated by a simple interpolation of the electrical properties. This would result in a maximum $ZT$ of about 0.4 at 300 K.

Upon substituting Sr with Ba the electrical properties remain almost unchanged. This supports the idea that the electrical properties are only governed by the cage-like frame work. Therefore, in order to improve the electrical properties the chemistry of the frame work has been varied in different ways. The Ge atoms in the frame work
Table 5.2
THE THERMOPOWER AND RESISTIVITY OF SOME PYROCHLORES.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( S(300\text{K}) ) ( \mu \text{V/K} )</th>
<th>( \rho(300\text{K}) ) ( \Omega\text{cm} )</th>
<th>( S^2/\rho ) ( \text{W/(mK}^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Nd}_2\text{Ru}_2\text{O}_7 )</td>
<td>265</td>
<td>1.93</td>
<td>3.64 ( \times ) 10(^{-6} )</td>
</tr>
<tr>
<td>( \text{Nd}_2\text{Mo}_2\text{O}_7 )</td>
<td>-9</td>
<td>0.327</td>
<td>2.48 ( \times ) 10(^{-8} )</td>
</tr>
<tr>
<td>( \text{Bi}_2\text{Ir}_2\text{O}_7 )</td>
<td>-6</td>
<td>4 ( \times ) 10(^{-4} )</td>
<td>9 ( \times ) 10(^{-6} )</td>
</tr>
</tbody>
</table>

can be substituted by Si but this results in a decreased power factor. In analogy to substituting 16 Ga, which can accommodate 1 electron each, the substitution of 8 Zn should result in a semiconducting compound as well. The sample of \( \text{Ba}_8\text{Zn}_8\text{Ge}_98 \) exhibits resistivity which increases linearly with temperature and a resistivity ratio \( \rho(300\text{K})/\rho(5\text{K}) \) of less than two. Thus it can be speculated that it is a highly doped semiconductor. The low powerfactor suggests that even upon optimization this will not be a promising compound. The two compounds, \( \text{Ba}_8\text{Ag}_6\text{Ge}_{40} \) and \( \text{Ba}_8\text{Au}_6\text{Ge}_{40} \), cannot be discussed by plain valence counting. Furthermore, among the investigated compounds they are the only ones which exhibit a \( p \)-type thermopower. Thus, this kind of substitution overcompensates the donation of electrons by the alkaline-earth atoms in contrast to the other compounds where the compensation seems to be incomplete. The Au-compound has a power factor comparable to that of the best \( n \)-type clathrates. Since for thermoelectric coolers and generators both \( p \)-type and \( n \)-type legs are needed this material is an interesting complement to the \( n \)-type compounds.

Finally, some clathrates with slightly different cage-like structures have been investigated. The tin-based clathrate \( \text{Ba}_8\text{Ga}_{16}\text{Sn}_{32} \) could not be obtained as a pure phase, resulting in quite poor performance, and the compound \( \text{Ba}_6\text{In}_4\text{Ge}_{21} \) turns out to be unstable in air. Also the compound \( \text{Ba}_8\text{Al}_{16}\text{Ge}_{30} \), where the electrons should be accommodated by Al instead of Ga decomposes quickly under ambient conditions. Since no compound proved to be more promising than \( \text{Sr}_8\text{Ga}_{16}\text{Ge}_{30} \), which has been estimated to have a maximum \( ZT \) of less than 0.4, no further investigation of clathrates has been carried out. Retrospectively, this seems to be the correct choice, because no further progress on clathrates has been reported since [Nolas98].

**Oxide Pyrochlores**

As shown in Fig. 5.1 the lattice thermal conductivity of the oxide pyrochlore \( \text{Bi}_2\text{Ir}_2\text{O}_7 \) is only 2 \( \text{W/(mK)} \) at 300 K. Therefore, the electrical properties of this and two further compounds have been studied.

It turns out that the electrical properties of these compounds are not favourable
Figure 5.1. Thermal conductivity of Bi$_2$Ir$_2$O$_7$ versus temperature as measured with the longitudinal steady state method. The electronic contribution to the thermal conductivity has been calculated by the Wiedemann-Franz law. The increase above 300 K is presumably due to radiation heat losses.

for thermoelectric applications. The only reasonable thermopower is obtained in Nd$_2$Ru$_2$O$_7$ but the resistivity of this compound is three orders of magnitude too high. The thermopowers of the other two compounds are definitely too small. Since for oxides no high carrier mobilities are expected the high conductivity of Bi$_2$Ir$_2$O$_7$ indicates a high carrier concentration, which may be due to oxygen deficiency. A large group of more than 50 analogous oxide pyrochlores is listed in [Subramanian83] but despite the low thermal conductivity these compounds do not seem to be promising.

SmSe/TmSe Solid Solutions

Intermediate valence (IV) is an interesting, but rare property of some compounds containing rare earths, i.e. Ce, Sm, Eu, Tm or Yb. As the name implies, IV systems behave as if the rare earth atom is in a fractional valence state. The IV state produces anomalies in several physical properties, and – most importantly – an unusually high thermopower is often found in IV materials [Jaccard82]. Several rare earth monochalcogenides exhibit a pressure-induced valence transition at moderately low pressures and different behaviours, i.e. continuous vs. abrupt transition modes and transitions with and without structural changes, have been observed [Chatterjee72]. Instead of applying external pressure to induce the valence transition, the pressure can also be induced internally by the substitution of smaller atoms. A very promising system is SmSe because it exhibits a continuous transition, which allows IV behaviour over a certain pressure range, at very low pressures around 50 kbar.

In this study the chemical pressure is applied by alloying SmSe (NaCl-structure, 6.202 Å) with the isomorphous but smaller TmSe (5.688 Å). The expected electronic collapse from Sm$^{2+}$ to Sm$^{3+}$ should be easily observable as pronounced decrease in the
Figure 5.2. The lattice constant of Sm$_x$Tm$_{1-x}$Se alloys (full line and squares) as function of composition. The dotted line represents “Vegard’s Law” [Vegard21]. The dashed line represents the expected behaviour, where the size of the valence instability effect described in the text and the composition at which it occurs are chosen arbitrarily.

Figure 5.3. The thermopower of the alloys Sm$_x$Tm$_{1-x}$Se (x = 0.1, 0.2, …, 0.9). The most negative thermopower at 300 K corresponds to x=0.9 and it monotonically decreases towards x=0.1, where only x=0.2 and x=0.3 are in reversed order.

lattice constant at the transition. For different Sm/Tm ratios the lattice constant has been determined by powder x-ray diffraction, see Fig. 5.2. The observed change in the lattice constant, shown as squares, clearly deviates from the expected behaviour, indicated by the dashed line. The dotted line, representing “Vegard’s Law” [Vegard21], marks the change that would take place if just rigid spheres of Sm$^{2+}$ were replaced by rigid Tm$^{2+}$. Since all observed lattice constants are above this line the presence of a Sm$^{3+}$ valence state can be ruled out. A possible explanation for increased lattice constants is a kind of “negative pressure” experienced by the thulium atoms in the oversized environment of SmSe. The thermopowers of several alloys are shown in Fig. 5.3. A negative thermopower is observed in all alloys, which is decreasing constantly with decreasing Sm content. The monotone and rather smooth transition from $S = -132 \, \mu V/K$ (Sm$_{0.9}$Tm$_{0.1}$Se) to $S = -8 \, \mu V/K$ (Sm$_{0.1}$Tm$_{0.9}$Se) shows that no
Table 5.3

**Electrical properties of SmSe related compounds.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S(300\text{K})$ $\mu\text{V/K}$</th>
<th>$\rho(300\text{K})$ $\text{m\Omega cm}$</th>
<th>$s^2\sigma$ $\text{W/(mK}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$<em>{0.9}$Tm$</em>{0.1}$Se</td>
<td>-132</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm$<em>{0.8}$Tm$</em>{0.2}$Se</td>
<td>-98</td>
<td>0.0021</td>
<td>8.17 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>Sm$<em>{0.7}$Tm$</em>{0.3}$Se</td>
<td>-65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm$<em>{0.6}$Tm$</em>{0.4}$Se</td>
<td>-38</td>
<td>7.1 $\cdot 10^{-4}$</td>
<td>5.95 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>Sm$<em>{0.5}$Tm$</em>{0.5}$Se</td>
<td>-24</td>
<td>5.9 $\cdot 10^{-4}$</td>
<td>2.45 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>Sm$<em>{0.4}$Tm$</em>{0.6}$Se</td>
<td>-22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm$<em>{0.3}$Tm$</em>{0.7}$Se</td>
<td>-16</td>
<td>2.7 $\cdot 10^{-4}$</td>
<td>1.34 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>Sm$<em>{0.2}$Tm$</em>{0.8}$Se</td>
<td>-19</td>
<td>2.9</td>
<td>1.67 $\cdot 10^{-8}$</td>
</tr>
<tr>
<td>Sm$<em>{0.1}$Tm$</em>{0.9}$Se</td>
<td>-7.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SmSe</td>
<td>-71</td>
<td>528</td>
<td>9.55 $\cdot 10^{-10}$</td>
</tr>
<tr>
<td>SmSe$<em>{0.997}$Sb$</em>{0.003}$</td>
<td>230</td>
<td>257</td>
<td>2.06 $\cdot 10^{-8}$</td>
</tr>
<tr>
<td>Sm$<em>{0.99}$Gd$</em>{0.01}$Se</td>
<td>-116</td>
<td>540</td>
<td>2.49 $\cdot 10^{-9}$</td>
</tr>
<tr>
<td>Sm$_{0.98}$</td>
<td>-214</td>
<td>54</td>
<td>8.48 $\cdot 10^{-8}$</td>
</tr>
<tr>
<td>Sm$<em>{0.9}$Tm$</em>{0.1}$S</td>
<td>-82</td>
<td>5.1</td>
<td>1.32 $\cdot 10^{-7}$</td>
</tr>
</tbody>
</table>

significant improvement of the thermoelectric properties due to intermediate valence effects is obtained in the alloy system.

The materials are sensitive to humidity and tarnish quickly under ambient conditions. It is therefore difficult to obtain ohmic contacts for resistivity measurements so that measurements have not been carried out on all the compounds. The resistivity values and the thermopowers are given in Tab. 5.3.

From the data it appears that the effect of adding Tm corresponds to doping rather than to applying chemical pressure. Since the power factor of Sm$_{0.8}$Tm$_{0.2}$Se is on the order of that of Bi$_2$Te$_3$, it seemed promising to study further dopants for SmSe and also the related SmS. However, as shown in the lower part of Tab. 5.3 the pure SmSe as well as the Gd-doped and the Sb-doped material and the two SmS samples exhibit resistivities in excess of 1 Ω. Since the material seems to be not amenable to doping and considering its sensitivity to humidity no further investigations have been carried out.
CHALCOCENIDES

The room temperature thermopower and resistivity of the investigated chalcogenides and their calculated power factors are shown in Tab. 5.4. For some samples either the thermopower or the resistivity data are missing. These materials exhibited either only limited stability in air or the measurement of a high resistivity or a very low thermopower already disproved their thermoelectric usefulness.

The chalcopyrites are tetrahedrally bonded chalcogenides with stoichiometry ABQ₂ (Q= Se, Te). Several of these compounds have been studied regarding their thermoelectric properties [Zhuze58]. One of the most promising of the investigated compounds is CuSbSe₂ with a thermopower of 400 μV/K and a resistivity of 250 mΩcm at room temperature. The compound melts congruently and ingots of CuSbSe₂ are easily obtained by melting stoichiometric amounts of the elements in an evacuated quartz ampoule. The as grown sample exhibited a considerably higher thermopower of 549 μV/K at room temperature. In combination with the measured resistivity of 3.75 Ωcm the power factor is lower than that of the previously reported material. Upon doping with tin the resistivity is lowered to 490 mΩcm in CuSb₀.₉₈Sn₀.₀₂Se₂. Yet, also the thermopower is considerably decreased and with a value of 408 μV/K it is already equal to that of the reported material. Thus no progress has been achieved. The attempt to achieve a negative thermopower by doping with Zn on the Cu-site resulted in a material with very high resistivity, presumably due to compensation effects.

The three materials, Pb₂GeTe₄, GeBi₂Te₄, and HgIn₂Te₄, can be understood as alloys of the binary semiconductors PbTe/GeTe, GeTe/Bi₂Te₃ and HgTe/In₂Te₃. The power factor of GeBi₂Te₄ is rather high but its thermopower is well below the “critical” value of 157 μV/K. Moreover, a study on single crystals of GeBi₂Te₄ [Tichy79] did also not reveal promising properties.

The crystal structure of Re₅Te₁₅ has been resolved by [Klaiber83]. It has a quite open cluster structure where the rhenium atoms have an almost “cage”-like coordination of 5 Te and 4 Re. This structure is promising for a low thermal conductivity. Furthermore, [Klaiber83] report a high positive thermopower of 490 μV/K at room temperature but the high resistivity of 100 Ωcm prevents it from being a useful material. Thus, it has been tried to incorporate different types of dopands on the Re- as well as on the Te-sites. A pronounced improvement was achieved by substituting Sb for Te, lowering the resistivity by three orders of magnitude to 0.82 Ωcm while the thermopower stays as high as 347 μV/K. Despite this improvements the power factor still falls short by more than two orders of magnitude compared to Bi₂Te₃. Simultaneously, another group has tried to optimize the properties of Re₅Te₁₅ by doping with Ga, In, and Ag [DalaFave98] and substituting Se for Te [DalaFave98b], yet not obtaining any improvements at all.

Since anisotropy may lead to a high ratio of $m_3^*/m_c^*$ several layered compounds have
<table>
<thead>
<tr>
<th>Compound</th>
<th>$s(300\text{K})$ $\mu\text{V/K}$</th>
<th>$\rho(300\text{K})$ $\mu\Omega\text{cm}$</th>
<th>$s^2\sigma$ $\text{W/(mK}^2\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CuSbSe$_2$ doping</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuSbSe$_2$</td>
<td>549</td>
<td>3.75</td>
<td>$8.04 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>CuSb$<em>{0.98}$Sn$</em>{0.02}$Se$_2$</td>
<td>408</td>
<td>0.49</td>
<td>$3.4 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>Cu$<em>{0.98}$Zn$</em>{0.02}$SbSe$_2$</td>
<td>378</td>
<td>20.6</td>
<td>$6.94 \cdot 10^{-7}$</td>
</tr>
<tr>
<td><strong>Pseudobinaries</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb$_3$GeTe$_4$</td>
<td>146</td>
<td>0.017</td>
<td>$1.25 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>GeBi$_2$Te$_4$</td>
<td>106</td>
<td>0.0016</td>
<td>$7.02 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>HgIn$_2$Te$_4$</td>
<td>384</td>
<td>55</td>
<td>$2.68 \cdot 10^{-7}$</td>
</tr>
<tr>
<td><strong>Re$_2$Te$_5$ doping</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re$<em>2$Te$</em>{4.95}$Sb$_{0.05}$</td>
<td>347</td>
<td>0.82</td>
<td>$1.47 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>Re$<em>2$Te$</em>{4.95}$Bi$_{0.05}$</td>
<td>–</td>
<td>19</td>
<td>–</td>
</tr>
<tr>
<td>Re$<em>{1.98}$W$</em>{0.02}$Te$_5$</td>
<td>–</td>
<td>11</td>
<td>–</td>
</tr>
<tr>
<td>Re$<em>{1.96}$Os$</em>{0.04}$Te$_5$</td>
<td>–</td>
<td>119</td>
<td>–</td>
</tr>
<tr>
<td><strong>Layered compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta$_2$NiS$_5$</td>
<td>-1</td>
<td>0.032</td>
<td>$3.13 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>Ta$_2$NiSe$_5$</td>
<td>19</td>
<td>0.018</td>
<td>$1.96 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>Ta$_2$PdSe$_6$</td>
<td>-21</td>
<td>$9.7 \cdot 10^{-4}$</td>
<td>$4.55 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>TlBiS$_2$</td>
<td>-49</td>
<td>0.0015</td>
<td>$1.6 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>TlCuZrSe$_3$</td>
<td>420</td>
<td>1.9</td>
<td>$9.28 \cdot 10^{-6}$</td>
</tr>
<tr>
<td><strong>Miscellaneous Chalcogenides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$_2$SnS$_3$</td>
<td>94</td>
<td>0.053</td>
<td>$1.67 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>CrSbSe$_3$</td>
<td>–</td>
<td>$1.8 \cdot 10^4$</td>
<td>–</td>
</tr>
<tr>
<td>Sn$_4$Bi$_2$Se$_7$</td>
<td>-71</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CuTh$_2$Te$_6$</td>
<td>25</td>
<td>1.5</td>
<td>$4.17 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>Fe$_3$As$_2$Te$_6$</td>
<td>79</td>
<td>6.2</td>
<td>$1.01 \cdot 10^{-7}$</td>
</tr>
<tr>
<td>Co$_3$As$_2$Te$_6$</td>
<td>-26</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tl$_9$BiTe$_6$</td>
<td>162</td>
<td>$6.2 \cdot 10^{-3}$</td>
<td>$4.2^{-4}$</td>
</tr>
<tr>
<td>Ag$<em>{7.96}$Cd$</em>{0.04}$Ge$<em>{0.95}$As$</em>{0.005}$Te$_6$</td>
<td>-341</td>
<td>7.2</td>
<td>$1.62 \cdot 10^{-6}$</td>
</tr>
</tbody>
</table>
been investigated, with the results shown in Tab. 5.4. Ideally, as pointed out in Chapter 2, the anisotropy is accompanied by a crystal structure with high symmetry. The compounds Ta$_2$NiS$_5$ and Ta$_2$NiSe$_5$ are orthorhombic and monoclinic, respectively, but the latter shows just a slight distortion ($\beta = 90.53^\circ$) from the orthorhombic cell [Sunshine85]. The value of -1 $\mu$V/K at 300 K represents a minimum in the thermopower of Ta$_2$NiS$_5$ but even over the entire temperature range it does not exceed -10 $\mu$V/K. Also the thermopower of Ta$_2$NiSe$_5$ is about one order of magnitude smaller than necessary for thermoelectric applications. The material in this group with the highest symmetry, the hexagonal TlBiS$_2$ [Oezer96], also exhibits the highest power factor. However, still it seems too low to regard the material as promising. The remaining two materials, Ta$_2$PdSe$_6$ [Keszler85] and TlCuZrSe$_3$ [Klepp96] have a monoclinic and orthorhombic unit cell, respectively.

The last group, presented in Tab. 5.4, represents a set of generic chalcogenides which can be expected to be narrow-gap semiconductors. While most of the compounds from this group are definitely not useful for thermoelectric applications, the compound Tl$_9$BiTe$_6$ seems to be the most promising of all chalcogenides. The prepared material has a thermopower of 162 $\mu$V/K and a resistivity of 6.2 m$\Omega$ cm at 300 K which gives a power factor of 0.42 mW/(mK$^2$). Furthermore, it is reported that Tl$_9$BiTe$_6$ has a low thermal conductivity of less than 1 W/(mK). Thus, in the following the properties of Tl$_9$BiTe$_6$ and several related compounds will be discussed.

RESULTS

Several different approaches to find promising thermoelectric materials have been presented. Only very few of the investigated materials have a power factor which is on the same order of magnitude as Bi$_2$Te$_3$. The highest power factor, 0.8 mW/(mK$^2$), has been found in Sm$_{0.8}$Tm$_{0.2}$Se. However, this compound is not stable in air and is therefore not useful for thermoelectric applications.

The most promising compound found in this survey is Tl$_9$BiTe$_6$. Thus, in the following chapters its properties and those of several related compounds will be discussed.
CHAPTER 6

The Tl$_5$Te$_3$-Group

Tl$_5$Te$_3$ and the ternary compounds Tl$_9$BiTe$_6$, Tl$_9$BiSe$_6$, Tl$_9$SbTe$_6$, Tl$_9$SbSe$_6$, Tl$_8$Pb$_2$Te$_6$, Tl$_8$Pb$_2$Se$_6$, and Tl$_8$Sn$_2$Te$_6$ are known for a long time [Bhan70, Berg70]. In the first part of this chapter the general properties - i.e. crystal structure, phase diagrams, some transport properties, etc. - of these materials and their relationship to each other are discussed. In the second part, a first evaluation of these materials is presented. From this evaluation the further strategy to explore this material group is derived.

6.1 CRYSTAL STRUCTURE

There is some disagreement about the crystal structure of Tl$_5$Te$_3$. Electron diffraction measurements [Man71] suggest that Tl$_5$Te$_3$ crystallizes in space group $I\bar{4}$, whereas [Toure90] determine space group $I4/m$ from powder x-ray diffraction. Single crystal diffraction data [Bhan70, Schewe89] lead to space group $I4/mcm$ with the $B_5C_{r_5}$-type structure. The single crystal data seems to be the most reliable one, especially considering that it is commonly agreed that all ternary derivatives also crystallize in the same space group [Villars91].

The unit cell of these compounds consists of 32 atoms which are arranged on four different sites as shown in Fig. 6.1. The ternary compounds can be divided into two subgroups depending on the occupation of the 4c site. In the compounds with 8-2-6 stoichiometry, Tl$_8$Pb$_2$Te$_6$, Tl$_8$Pb$_2$Se$_6$, and Tl$_8$Sn$_2$Te$_6$, the 4c site is completely occupied by Pb or Sn. Whereas in the 9-1-6 compounds the site is equally occupied by Tl and the additional Bi or Sb.
Figure 6.1. The tetragonal unit cell of Tl$_5$Te$_3$ as seen perpendicular to the c-axis. The four different crystal sites and their coordination polyhedra are shown. The tellurium atoms are depicted in dark gray with the coordination for the 4a site and the 8h site shown in the lower right and on top, respectively. The thallium atoms are shown in white on the 16f site, coordination as in the lower left, and in light gray on the 4c site, where they are octahedrally coordinated (center). In the ternary compounds the additional atoms are substituted on the 4c site.

6.2 THERMODYNAMIC PROPERTIES

The ternary compounds of this group of materials can be derived from pseudo-binary phase diagrams. The compound Tl$_9$BiTe$_6$ for example can be understood as a mixture of 9×Tl$_2$Te with 1×Bi$_2$Te$_3$. In the same fashion, the other three 9-1-6 compounds are formed by mixing Tl$_2$Te and Tl$_2$Se with Bi$_2$Se$_3$, Sb$_2$Te$_3$ and Sb$_2$Se$_3$, respectively. The 8-2-6 compounds consist of 2 parts Tl$_2$Te or Tl$_2$Se and 1 part PbTe, PbSe or SnTe, respectively. The compound Tl$_8$Sn$_2$Se$_6$ does not seem to exist. In a study on the ternary phase diagram Tl-Sn-Se [Houenou81] the ternary compounds Tl$_2$SnSe$_3$, Tl$_3$SnSe$_4$ and Tl$_4$SnSe$_4$ are reported but there is no evidence for Tl$_8$Sn$_2$Se$_6$.

As shown in Fig. 6.2, taken from [Barchii88], there is a certain width of formation for Tl$_9$BiSe$_6$ and Tl$_9$BiTe$_6$. The maximum extent of the homogeneity region is 3.8 mole-% for Tl$_9$BiSe$_6$ and 2.5 mole-% for Tl$_9$BiTe$_6$, respectively. In certain cases the existence
of such a homogeneity range is of concern for obtaining homogeneous stoichiometric samples from a slow melting process. Fortunately, in both cases the highest melting temperature is found close to the exact 9-1-6 stoichiometry. In the case of Tl$_9$BiTe$_6$ the results of the X-ray phase analysis and the microhardness measurement are slightly inconsistent. In contrast to the maximum melting point the peak in the microhardness is shifted away from the stoichiometric composition towards Bi$_2$Te$_3$.

For some of the cases the miscibility among the different compounds of the Tl$_5$Te$_3$ group has been studied. [Babanly79] report that the system Tl$_5$Te$_3$-Tl$_8$Sn$_2$Te$_6$-Tl$_8$Pb$_2$Te$_6$ is completely miscible. Likewise, the system Tl$_8$Pb$_2$Se$_6$-Tl$_8$Pb$_2$Te$_6$ is found to be completely miscible by [Latypov88].

6.3 KNOWN THERMOELECTRIC PROPERTIES

Literature published on the thermoelectric properties of Tl$_5$Te$_3$ and its related compounds is quite sparse. [Latypov88] report thermopower and electrical resistivity data of Tl$_8$Pb$_2$Se$_6$-Tl$_8$Pb$_2$Te$_6$ solid solutions. There is no temperature given at which the measurements are carried out but very likely it is room temperature data. The thermopowers and resistivities are $-50 \mu$V/K and 2 m$\Omega$ cm for Tl$_8$Pb$_2$Te$_6$ and $+15 \mu$V/K and 9 m$\Omega$ cm for Tl$_8$Pb$_2$Se$_6$, respectively. The solid solution system has a maximum in the thermopower (80 $\mu$V/K) at the composition Tl$_4$Pb(Te$_{70}$Se$_{30}$)$_3$, which is accompanied by a maximum in the resistivity (2 $\Omega$ cm) as well.
A study about the thermoelectric properties of Tl\textsubscript{5}BiTe\textsubscript{6} has been carried out by [Pradel82]. They report a resistivity of 1.5 mΩ\textpercm and a thermopower of 62 μV/K for material with a carrier concentration of 5.6 \times 10^{21} \text{cm}^{-3} at 300 K. The thermal conductivity, measured from 150 K to 400 K, is rising monotonically with temperature. This leads to the assumption that the data are dominated by radiation losses and the true thermal conductivity at 300 K is even lower than the reported 0.7 W/(mK). Using these values a figure of merit of \( ZT = 0.1 \) at 300 K is calculated. Finally, [Pradel82] state that the highest figure of merit that may be expected for optimized Tl\textsubscript{5}BiTe\textsubscript{6} is \( ZT_{\text{max}} = 0.35 \) based on the theory presented by [Goldsmid64].

Electrical resistivity data of Tl\textsubscript{5}Pb\textsubscript{2}Te\textsubscript{6}, Tl\textsubscript{5}Sn\textsubscript{2}Te\textsubscript{6}, and Tl\textsubscript{5}Te\textsubscript{3} are reported by [Chami83]. Both ternary materials show metallic behaviour with resistivities of 0.75 mΩ\textpercm for Tl\textsubscript{5}Pb\textsubscript{2}Te\textsubscript{6} and 0.87 mΩ\textpercm for Tl\textsubscript{5}Sn\textsubscript{2}Te\textsubscript{6} at 300 K. The binary compound Tl\textsubscript{5}Te\textsubscript{3} has a lower resistivity of 0.21 mΩ\textpercm. The authors conclude that these compounds are semimetals or degenerate semiconductors.

### 6.3.1 Valence states of Tl in Tl\textsubscript{5}Te\textsubscript{3}

As already pointed out, the ternary members of the Tl\textsubscript{5}Te\textsubscript{3} group can be understood as pseudobinary alloys of Tl\textsubscript{2}Te and Tl\textsubscript{2}Se with the known thermoelectric materials Bi\textsubscript{2}Te\textsubscript{3} and PbTe and their related compounds. Nevertheless, all the ternaries have the same crystal structure as Tl\textsubscript{5}Te\textsubscript{3} and are not related to the other binaries. So it is more intuitive to understand this group as being formed by substitutions in Tl\textsubscript{5}Te\textsubscript{3} rather than by alloying of other binaries.

The substitution approach is supported by a simple valence count model. Considering the rather high resistivity of Tl\textsubscript{5}Te\textsubscript{3} single crystals (200 μΩ\textpercm at 300 K) [Chami83] speculate that it is a semimetallic compound. As it is seen from the coordination polyhedra in Fig. 6.1, there are no Te-Te bonds in the structure since the nearest neighbours of the Te-atoms are exclusively Tl-atoms. Under the assumption that the tellurium atoms are in the valence state Te\textsuperscript{2}\textsuperscript{−}, the five thallium atoms have to provide 6 electrons to obtain completely filled bands. The electron configuration of thallium, \([Xe]4f^{14}5d^{10}6s^{2}6p^{1}\), allows the two valence states, Tl\textsuperscript{1+} and Tl\textsuperscript{3+}. In order to obtain the right number of electrons, the formula unit has to be expanded to Tl\textsubscript{9}+Tl\textsubscript{3}+Te\textsubscript{6}. A rather short bond distance between the Te atoms on the 8\(\bar{h}\) site and the Tl on the 16\(l\) site suggests that quasimolecular Tl\textsubscript{2}Te units are formed inside the crystal [Schewe89]. Therefore, the expected valence state on the 16\(l\) site is Tl\textsuperscript{1+}. Provided that Tl\textsubscript{5}Te\textsubscript{3} is a semimetal then the 4\(c\) site has to be equally occupied by Tl\textsuperscript{1+} and Tl\textsuperscript{3+}.

Even though, it seems farfetched to develop this valence model just on the grounds of resistivity data it gives a very good description of the ternary compounds in the Tl\textsubscript{5}Te\textsubscript{3} group. The compounds with 9-1-6 stoichiometry are obtained by substituting
the Tl$^{3+}$ with the trivalent elements Bi and Sb. On the other hand, since the 4c site is originally equally occupied by Tl$^{1+}$ and Tl$^{3+}$ it can be understood as a site with an average valence of 2+. From this the 8-2-6 compounds are obtained by substituting the complete site with Pb$^{2+}$ or Sn$^{2+}$. Apart from Tl$_8$Sn$_2$Te$_6$, for all ternary compounds the corresponding selenides exist as well. The structure of this group is visualized in Fig. 6.3.

6.4 Evaluation

The large number of compounds in this family and their complete miscibility offer a lot of possibilities to find and optimize good thermoelectric materials. On the other hand, it is necessary to get an overview and to find a starting point. Thus in the first evaluation step all seven ternary compounds of this family were synthesized and characterized. In this step it is not necessary to aim at a high quality material but to assure similar quality levels for each sample. Even then the comparison based on these samples is somewhat inaccurate because the effect of impurities may vary in the different materials. Nevertheless, the results of these experiments will serve as a guidepost for further explorations. Since most thermoelectric applications operate at room temperature and a point of reference is needed to compare the different materials, 300 K is chosen as reference temperature. For the sake of legibility, in some cases this temperature is not explicitly specified. Therefore, it is emphasized, that property data, that are not assigned to a specific temperature, refer to 300 K.
(a) During the “standard” sealing the reagents are exposed to air during the formation of the constriction.

(b) By using an inner ampoule the exposure to air can be avoided.

Figure 6.4. The sealing processes for quartz ampoules.

6.4.1 Material synthesis

As mentioned above, all compounds melt congruently and none of the used elements reacts with quartz. Therefore, the material is prepared by reacting stoichiometric compositions of the elements in fused quartz ampoules. The purities of the elements are 5N and better based on metals impurities. However, the thallium, which is provided by Alfa Aesar, has a black, heavily oxidized surface. This surface layer is removed and only the shiny gray metal from the interior is used. Since thallium oxidizes quickly in air this preparation step as well as filling the elements into the ampoules is carried out in an argon glove box.

To avoid oxidation during the reaction process the ampoules have to be sealed under vacuum. Ampoules with inner diameters of more than a few millimeters usually cannot be evacuated and sealed in a one-step process. In this case the ampoule will implode at the hottest and therefore softest spot. Consequently, a constriction with an inner diameter of only 1 to 2 mm has to be formed under ambient pressure before the ampoule is sealed. During this process, which takes a few minutes, the unreacted elements are exposed to air and the surface of the thallium pieces slightly tarnishes due to oxidation. After the constriction is formed the ampoule is evacuated and sealed off. To circumvent this unwanted contamination with oxygen, a different sealing process has been used after the first set of samples. A slightly constricted ampoule is filled with the elements in the argon glove box. A second ampoule which fits tightly into the first one sits on top of this constriction. In this case, the ampoule can be evacuated immediately after it is transferred out of the argon box and it is sealed by “welding” it to the inner ampoule. The two processes are compared in Fig. 6.4.

After sealing, the ampoules are heated to 650°C for several hours. Once the material
Figure 6.5. X-ray powder diffraction pattern of $\text{Tl}_9\text{BiTe}_6$. The measured pattern is shown above the x-axis while the calculated pattern for space group $I4/mcm$ is represented as mirror image below.

Figure 6.6. Thermopowers of the 9-1-6 compounds as function of temperature from 80 K to 560 K.

has reacted, the ternary compound is rather stable in air. A typical X-ray powder diffraction pattern as taken with Cu-K$_\alpha$ radiation is shown in Fig. 6.5. There is very good agreement between the measured and the calculated pattern and no additional peaks are found. This shows that the material is phase pure within a few percent. Furthermore, the lower symmetry space groups $I4$ and $I4/m$ can be ruled out because they would imply additional peaks at detector angles between 20 and 25 degrees.

6.4.2 Properties of the 9-1-6 Compounds

The thermopowers of the 9-1-6 compounds as a function of temperature are shown in Fig. 6.6. For three of the compounds, $\text{Tl}_9\text{BiTe}_6$, $\text{Tl}_9\text{SbTe}_6$, and $\text{Tl}_9\text{SbSe}_6$, the thermopower rises monotonically, almost linearly, with temperature. This behaviour is expected for metals or extrinsic semiconductors. The thermopower of metals are usu-
ally only a small fraction of $k_B/e$, which is 86 $\mu$V/K. Since the thermopowers at 300 K are 90 $\mu$V/K, 138 $\mu$V/K, and 185 $\mu$V/K for Tl$_9$SbTe$_6$, Tl$_9$SbSe$_6$, and Tl$_9$BiTe$_6$, respectively, they have to be regarded as extrinsic semiconductors or possibly semimetals. The thermopower of Tl$_9$BiSe$_6$ is almost constant with values slightly above 300 $\mu$V/K over the entire temperature range. The sudden dip below 150 K and the scattering at high temperatures reflect problems in the electronics of the MMR measurement device. While the thermopower of Tl$_9$SbTe$_6$ seems to be too low for a good thermoelectric material, the thermopowers of the other three compounds are quite notable.

In order to determine the power factor $S^2/\rho$ the electrical resistivity of these compounds has been measured as a function of temperature from 5 K up to 350 K. The different temperature dependences are compared in Fig. 6.7(a). Three different trends can be distinguished. The two telluride compounds, Tl$_9$BiTe$_6$ and Tl$_9$SbTe$_6$, exhibit an “extrinsic” behaviour, i.e. a monotonic increase of resistivity with temperature. In contrast, Tl$_9$BiSe$_6$ clearly shows an activated behaviour. The third case is Tl$_9$SbSe$_6$, where the resistivity shows almost no temperature dependence.

When the resistivity of Tl$_9$BiSe$_6$ is plotted logarithmically versus the reciprocal temperature, as shown in Fig. 6.7(b), the activation energies can be determined. Two different temperature regions can be distinguished. At temperatures below 40 K an activation energy of 13 meV is found. In the higher temperature region up to 340 K the activation energy is 50 meV. It is noteworthy that up to date no semiconducting behaviour has been reported for compounds of the Tl$_5$Te$_3$-group. Bearing in mind the thermopower data it can be ruled out that the activated behaviour corresponds to excitation over the energy gap. [Goldsmid99] showed that the energy gap can be
estimated from the maximum value of the thermopower $S_{\text{max}}$ and the temperature $T_{\text{max}}$ at which it occurs

$$E_g = 2eS_{\text{max}}T_{\text{max}}.$$  \hfill (6.1)

Above $T_{\text{max}}$ the thermopower starts to decrease due to bipolar conduction. Since $T_{\text{max}}$ is not reached at 560 K a lower bound of the energy gap can be estimated. With the thermopower of 350 $\mu$V/K at this temperature a lower bound of $E_g \geq 0.4$ eV is calculated. The resistivity of Tl$_9$BiSe$_6$ is 48 m$\Omega$ cm. In combination with the thermopower of 312 $\mu$V/K this results in a power factor of 0.2 mW/(m K$^2$) compared to 4 mW/(m K$^2$) for optimized Bi$_2$Te$_3$ alloys.

The almost flat temperature dependence of the resistivity of Tl$_9$SbSe$_6$ indicates that it is “extrinsic” material with a temperature independent scattering mechanism. Furthermore, compared to the other two samples with an “extrinsic” temperature dependence of the thermopower Tl$_9$SbSe$_6$ has a fairly high resistivity. A possible explanation for such a behaviour is very strong scattering due to impurities or other defects which outranges phonon scattering over the entire temperature range. Therefore, another sample of Tl$_9$SbSe$_6$ has been prepared using the “double-ampoule” sealing process, shown in Fig. 6.4(b). The two results are compared in Fig. 6.8. The properties of the first sample are shown as open symbols while the full symbols represent the second sample. The resistivity is increased by a factor of 4 but the temperature dependence is almost identical. Both samples exhibit shallow minima in the resistivity around 40 K and 300 K and a broad maximum around 200 K with an overall change of less than 25%. Compared to the previous sample, the thermopower is increased from 138 $\mu$V/K to 215 $\mu$V/K. Even though the properties of the samples differ appreciably regarding their absolute values, their temperature dependences are very similar. Therefore, it can be assumed that to a certain extent that this behaviour is ”intrinsic” to Tl$_9$SbSe$_6$. The power factors of the two samples are 0.12 mW/(m K$^2$) and 0.07 mW/(m K$^2$) for
the “old” and the “new” sample, respectively, which is only half of that of Tl$_9$BiSe$_6$. Consequently, this material has not been studied further.

The resistivities of the 9-1-6 tellurides, shown in Fig. 6.9, increase monotonically with temperature by a factor of 10 from 0.7 mΩ cm and 0.2 mΩ cm at 10 K to 7.4 mΩ cm and 2.2 mΩ cm at 300 K for Tl$_9$BiTe$_6$ and Tl$_9$SbTe$_6$, respectively. For a degenerate semiconductor with $E_F \approx k_B T$ and a temperature independent carrier concentration the temperature dependence of resistivity is determined by the dominant scattering process. In Fig. 6.9 the resistivity data is compared to a $T^{3/2}$ curve. The good agreement indicates that acoustic phonon scattering is dominant over a wide temperature range.

Hall measurements have been carried out to determine the carrier concentration of Tl$_9$BiTe$_6$ as function of temperature. In accordance with the positive thermopower, the Hall measurements show that holes are the dominant carriers. The hole concentration is calculated from the Hall coefficient $R_H$ by

$$ p = \frac{r_H}{eR_H} \approx \frac{1}{eR_H} $$

with the assumption that only one type of carriers is present. The Hall factor $r_H$ depends on the scattering parameter $r$ and it is given by

$$ r_H = \frac{3\sqrt{\pi} \ (2r + 3/2)!}{4 \ [(r + 3/2)!]^2}. $$

For neutral impurity scattering ($r = 0$) the Hall number is exactly 1, while for acoustic phonon scattering where $r = -\frac{1}{2}$ it is $r_H = 3\pi/8 \approx 1.18$. The carrier concentration and the mobility calculated using $\sigma = ne\mu$ are shown in Fig. 6.10. It is seen from the mobility data (Fig. 6.10(b)) that the dominant scattering mechanism changes with temperature. While the almost constant mobility at low temperatures indicates the prevalence of neutral impurity scattering, acoustic phonons are dominant at higher

![Graph showing electrical resistivity of Tl$_9$BiTe$_6$ and Tl$_9$SbTe$_6$ as function of temperature.](image)
temperatures as suggested by the $T^{-3/2}$-dependence. Since the Hall factor depends on the scattering parameter (see Eq. 6.3) it becomes temperature dependent as result of the changing scattering parameter. The average Hall factor is calculated weighing the contribution of neutral impurity scattering and acoustic phonon scattering by their inverse mobilities $\mu_n^{-1}$ and $\mu_a^{-1}$, respectively

$$r_{H,av} = \frac{\mu_n^{-1} \cdot 1 + \mu_a^{-1} \cdot 1.18}{\mu_n^{-1} + \mu_a^{-1}}, \quad (6.4)$$

where $\mu_n = \text{const}$ and $\mu_a \propto T^{-3/2}$.

The following procedure has been applied to calculate the hole concentration $p$, the mobility $\mu$, and the average Hall factor $r_{H,av}$ in a self-consistent way. First, $p$ is calculated assuming $r_H = 1$ and the mobility is calculated from the resistivity data by $\rho = 1/(ne\mu)$. A function of the form

$$\frac{1}{\mu_{\text{tot}}} = \frac{1}{\mu_n} + \frac{1}{\mu_a} \quad (6.5)$$

is applied to fit the mobility. The average Hall factor is calculated by using the results of Eq. 6.5 in Eq. 6.4. Now, the first step is repeated, but the hole concentration is calculated from $r_{H,av}$ instead of $r_H = 1$. In subsequent repetitions the values of $p$, $\mu$, and $r_{H,av}$ converge quickly. It turns out that two cycles are sufficient to approximate the self-consistent values within less than 1%. The results of this calculations are the data shown in Fig. 6.10. There is very good agreement between the fit and the data. At low temperatures, the mobility is limited to approximately 250 cm$^2/(Vs)$ due to neutral impurity scattering.
Figure 6.11. The resistivity (a) and the thermopower (b) of the 8-2-6 compounds as function of temperature.

Since the purpose of this section is the evaluation of the different materials the power factors of the two tellurides are calculated. The values are 0.46 mW/(m K²) and 0.37 mW/(m K²) for Tl₉BiTe₆ and Tl₉SbTe₆ respectively. In comparison to the selenides the tellurides seem to be more useful as thermoelectric materials.

6.4.3 Properties of the 8-2-6 Compounds

Since Tl₈Sn₂Se₆ does not exist, there are only three 8-2-6 compounds. Their resistivities, shown in Fig. 6.11(a), resemble that of the 9-1-6 tellurides. However, the resistivity ratios \( \rho(300 K) / \rho(10 K) \) are only about 4 for the tellurides and approximately 2 for the selenide, compared to \( \rho(300 K) / \rho(10 K) > 10 \) for the 9-1-6 tellurides. The thermopowers of the 8-2-6 compounds, shown in Fig. 6.11(b), are moderate compared to the 9-1-6 sub-group. The thermopower of Tl₈Sn₂Te₆ is almost zero up to 150 K and shows a rather steep increase to higher temperatures. Among the 8-2-6 it exhibits the highest thermopower at 300 K \( (S = 95 \, \mu V/K) \). At 560 K its thermopower is as high as 290 \( \mu V/K \). The thermopowers of Tl₈Pb₂Te₆ and Tl₈Pb₂Se₆ are 80 \( \mu V/K \) and 63 \( \mu V/K \), respectively, and exhibit a quite similar, almost linear temperature dependence.

Due to the moderate thermopowers the power factors of Tl₈Sn₂Te₆ and Tl₈Pb₂Se₆ are quite low, 0.17 mW/(m K²) and 0.13 mW/(m K²), respectively. However, because of its low resistivity the power factor of Tl₈Pb₂Te₆ (0.4 mW/(m K²)) is comparable to that of Tl₉BiTe₆.
Figure 6.12. $\log(S)$-$\log(\sigma)$-plot for the ternary members of the Tl$_5$Te$_3$-group. The dashed lines are lines of equal power factor. From the lower left to the upper right the lines correspond to values of 0.1 mW/(mK$^2$), 0.3 mW/(mK$^2$), and 1 mW/(mK$^2$). The full line represents a thermopower of 157 $\mu$V/K, the theoretical minimum thermopower needed to achieve a $ZT$ of one.

6.5 EVALUATION AND FURTHER STRATEGY

The results of the previous section are summarized in Fig. 6.12 where $\log(S)$ is plotted against $\log(\sigma)$. As seen from this plot, Tl$_9$BiTe$_6$ is the most promising material for thermoelectric applications among the Tl$_5$Te$_3$-group compounds, since it exhibits the highest power factor and its thermopower is well above the minimum value of 157 $\mu$V/K, required for $ZT = 1$. The power factors of Tl$_9$SbTe$_6$ and Tl$_8$Pb$_2$Te$_6$ are comparable to that of Tl$_9$BiTe$_6$ but in order for them to be thermoelectrically useful materials, their power factors have to be increased by a factor of 2. Although the power factor of Tl$_9$BiSe$_6$ is considerably lower than those of the compounds mentioned above, it is interesting due to its high thermopower and its clearly semiconducting behaviour. Because of their much lower power factors, the compounds Tl$_9$SbSe$_6$, Tl$_8$Sn$_2$Te$_6$, and Tl$_8$Pb$_2$Se$_6$ are not considered for further optimization experiments.

As mentioned above, due to its composition and its structural properties Tl$_9$BiTe$_6$ is expected to exhibit a very low thermal conductivity. Since the $3\omega$-method to measure the thermal conductivity has not been established during the early stages of this study, no accurate measurements could be carried out. However, using the data from later samples (see Chapter 9), the thermal conductivity can be estimated with the help of the Wiedemann-Franz-Law. Since the higher quality samples have less lattice defects, this calculation presumably results in an overestimation of the thermal conductivity. Therefore, the figure of merit $ZT$ will be underestimated. It turns out, that in Tl$_9$BiTe$_6$ generally charge carrier scattering is dominated by acoustic phonons ($r = -\frac{1}{2}$) and
that the Fermi level is close to the valence band edge \( E_F \approx 0 \). In this case, a Lorenz number of \( L = 2 \cdot 10^{-8} \text{ W} \Omega /\text{K}^2 \) is calculated, compared to \( L = 2.45 \cdot 10^{-8} \text{ W} \Omega /\text{K}^2 \) for metals and \( L = 1.48 \cdot 10^{-8} \text{ W} \Omega /\text{K}^2 \) for an intrinsic nondegenerate semiconductor with \( r = -\frac{1}{2} \). This results in a lattice thermal conductivity of 0.39 \text{ W/(m K)} for Tl\(_3\)BiTe\(_6\) (see chapter 9). For the sample of Tl\(_3\)BiTe\(_6\) presented in this chapter, the resistivity of 7.4 m\( \Omega \) cm results in an electronic contribution to the thermal conductivity of \( \kappa_{el} = 0.08 \text{ W/(m K)} \) and a total thermal conductivity of 0.47 \text{ W/(m K)} is obtained. Along with the power factor of 0.46 mW/(m K\(^2\)) the figure of merit is calculated to \( ZT = 0.29 \). Compared to the figure of merit of optimized pure \( p \)-type Bi\(_2\)Te\(_3\), which is \( ZT = 0.54 \), this is already more than half as good.
CHAPTER 7

The Alloy System
Tl$_9$BiTe$_6$/Tl$_9$BiSe$_6$

Since Tl$_9$BiTe$_6$ and Tl$_9$BiSe$_6$ belong to the most promising compounds in the Tl$_5$Te$_3$-group, the effects of alloying these two materials have been studied. The success of this approach depends on the trends of the thermopower and the resistivity of the quasitermary compounds. Since the thermopower of Tl$_9$BiTe$_6$ (0.46 mW/(mK$^2$)) outranges that of Tl$_9$BiSe$_6$ (0.2 mW/(mK$^2$)) by more than a factor of two, enhancements are more likely to be found in compounds with a high Te/Se ratio.

7.1 Sample Preparation

The example of Tl$_9$SbTe$_6$ in chapter 6 has shown that the properties of the Tl$_5$Te$_3$-compounds depend considerably on the route of synthesis. In order to rule out the synthesis process as an influence on the thermoelectric properties “master” compounds of Tl$_9$BiTe$_6$ and Tl$_9$BiSe$_6$ have been produced. The alloys are formed by remelting corresponding mixtures of the two master compounds. Since the ternary compounds are stable in air this process is much less critical than the initial synthesis. Furthermore, the stoichiometries are locked to those of the master compounds which avoids changing properties due to small fluctuations in the exact composition of the samples.

Bismuth, as most metals, forms a protective oxide coating when exposed to air. Therefore the surface of the Bi-pellets which are stored under ambient conditions exhibit a pinkish tinge. This corresponds to a thin coating of Bi$_2$O$_3$ [Lide95]. In order to reduce the influence of unwanted impurities and to get more insight into the intrinsic properties of the materials an additional cleaning step was introduced to remove the surface oxide from the bismuth pellets. There are two alternative processes to remove the oxides. The “chemical” procedure is to etch Bi in diluted HCl. During the etch
the oxide is completely removed and Bi exhibits a lustrous, silvery surface. However, it re-oxidizes quickly when the material is rinsed off with water and dried. The second cleaning process takes advantage of the fact that metallic oxides adhere much better to silicon oxide than the pure metals. The material to be cleaned is filled into a quartz ampoule and a thin, elongated constriction, comparable to that Fig. 6.4, is formed. The ampoule is sealed off under vacuum further away from the material, leaving two “chambers” separated by the constriction. Then the ampoule is placed in a horizontal tube furnace and heated until the metal in the filled chamber is molten. By tilting the furnace the metal is forced to run through the constriction into the empty chamber. Since the oxides adhere well to the ampoule they get caught at the constriction and only oxide free metal is found in the second chamber. The effect of purification for lead, bismuth, and thallium is evident in Fig. 7.1. In the case of thallium the “dirty” chamber is completely covered with a yellowish coating. Most probably this is thallium hydroxide which has formed due to the atmospheric humidity.

Though the effects of purification become very clear in this process further improvement was needed for lead and thallium. These two metals wet quartz very well and the solidified material adheres strongly to the ampoule after the process. In order to avoid this, the chamber for the purified material was coated with a thin layer of pyrolytic carbon. This is done by wetting the ampoule with isopropanol and then heating it slowly to the point where the alcohol decomposes. By repeating this process a few times a continuous coating is formed which does not adhere to either of the metals.

After the solidification of the purified material the closed ampoules are transferred into the argon glove box. The ampoules are broken using a vice and the material is ready for the synthesis. The same cleaning procedure has been applied to tellurium
7.2 Properties of the Pure Ternary Compounds

Figure 7.2. The thermopower (triangles, left axis) and the resistivity (squares, right axis) of Tl₀BiTe₆ synthesized from the purified elements.

Figure 7.3. (a) The carrier concentration is almost independent of temperature. (b) The mobility of Tl₀BiTe₆ and the contributions of neutral impurity and acoustic phonon scattering. At 300 K the mobility is 39 cm²/(Vs), while at low temperatures it is limited by neutral impurity scattering (μₙ ≈ 450 cm²/(Vs)).

and selenium as well but no residues have been found.

7.2 Properties of the Pure Ternary Compounds

Before the effects of alloying are being discussed the properties of the two master compounds are presented to demonstrate the impact of the element purification process. The resistivity and the thermopower of the Tl₀BiTe₆-master are shown in Fig. 7.2. At low temperatures (T ≤ 20 K) the resistivity has a constant value of approximately 0.5 mΩcm which results from neutral impurity scattering. At higher temperatures the resistivity increases with Tₓ, where x is approximately 1.5, indicating that acous-
tic phonon scattering is the dominant process. The purification process results in a higher thermopower, 205 $\mu$V/K as compared to 185 $\mu$V/K, and a decreased resistivity of 5.5 m$\Omega$ cm (7.4 m$\Omega$ cm) at 300 K. Thereby the power factor increases by more than 60% to 0.76 mW/(mK$^2$). From the resistivity the total thermal conductivity is estimated to 0.50 W/(mK) resulting in a calculated figure of merit of 0.46.

The Hall measurements have been analyzed as discussed in chapter 6. The results, shown in Fig. 7.3, reveal that the number of carriers has been reduced by about 15% from 3.3 -$10^{19}$ cm$^{-3}$ (see previous chapter) to 2.8 -$10^{19}$ cm$^{-3}$ at 300 K, which explains the increase in the thermopower. The increase in $\mu_n$ from 250 cm$^2$/Vs to 450 cm$^2$/Vs compared to the initially prepared sample (Figs. 6.10(b) and 7.3(b)) indicates that the number of neutral impurities has been decreased by almost 50%. Also the mobility at 300 K has been significantly increased from 25 cm$^2$/Vs to 39 cm$^2$/Vs. Apart from any progress, which might be achieved in the alloy system, this improvement represents an important step towards a useful thermoelectric material.

The effect of the purification process on the properties of Tl$_9$BiSe$_6$ is even more pronounced. The resistivity, shown in Fig. 7.4(a), exhibits the characteristic temperature dependence of a semiconductor with various regimes in different temperature ranges. The positive thermopower indicates that holes are the dominating charge carriers. At temperatures below 180 K the resistivity decreases with temperature due to the activation of the acceptors. From 180 K to 280 K, where all acceptors are ionized and no excitation over the energy gap takes place, the resistivity is almost independent of temperature. The hole concentration in this temperature range is approximately 7 -$10^{15}$ cm$^{-3}$, as seen in Fig. 7.4(b). Above 280 K a second activation process is observed. In the same temperature range the slope of the thermopower falls off rapidly and it seems to have a maximum of 750 $\mu$V/K at 350 K. This indicates that Tl$_9$BiSe$_6$
becomes intrinsic above 280 K, and the opposite thermopowers of the electrons and the holes start to cancel out each other. Assuming that the maximum in the thermopower is seen at 350 K the energy gap is estimated to be $E_g \approx 0.5$ eV.

The mobility of the holes has a constant value of about $1.3 \, \text{cm}^2/(\text{Vs})$ from 150 K to 340 K, and the fluctuations are artifacts from the noise of the Hall measurements. Due to the low, temperature independent value of the mobility it is assumed that there is very strong scattering by neutral impurities. Therefore, it is likely that the low carrier concentration is at least partly due to compensation effects. In consideration of the scattering parameter of $r = 0$, an energy gap of 0.4 eV is calculated from the high temperature decrease of the resistivity. This corresponds well to the value of 0.5 eV, estimated from the thermopower data.

### 7.3 The Effects of Alloyning

The lattice constants of solid solutions of Tl$_9$Bi(Te$_{1-x}$Se$_x$)$_6$ with several different compositions ($x=0, 0.1, 0.2, 0.5, 0.7, 0.8,$ and 1) have been determined by powder x-ray diffraction. The dependence of the lattice constants $a$ and $c$ on the stoichiometry $x$ is shown in Fig. 7.5. According to a “law” proposed by [Vegard21] the lattice spacing of solid solutions should vary linearly between the lattice spacing of the endmembers. The lattice constants found in the solid solution system of Tl$_9$BiTe$_6$ and Tl$_9$BiSe$_6$ clearly deviate from this “law”. The lattice constant $c$ of Tl$_9$BiTe$_6$ and Tl$_9$BiSe$_6$ are 13.06 Å and 12.69 Å, respectively. Over a concentration range from 100% Te to 50% Te $c$ does not change within the resolution of the x-ray diffraction measurements. At a ratio Te/Se of 30/70 the lattice constant $c$ has decreased by only 0.04 Å. From there it
Figure 7.6. (a) Structure of Tl$_9$BiTe$_6$ and Tl$_9$BiSe$_6$ as seen along the c-axis. The bonds between the chalcogenide atoms and the metal atoms on the 4c site are shown as sticks. Tl: light, Q: medium, (Tl, Bi): dark. (b) Crystal structure as seen perpendicular to the c-axis. The (Tl,Bi)O$_6$ units are shown as octahedra. Tl: light, Q: dark. The (Tl,Bi) site is in the center of the octahedra.

falls off linearly towards 12.69 Å (Tl$_9$BiSe$_6$). The entire change in the lattice constant takes place over 30% of the substitution range. For the lattice constant a the picture is similar but less dramatic. Starting from Tl$_9$BiSe$_6$ no change in a is observed up to a substitution of 20% Te. From there the lattice constant increases linearly towards 8.859 Å (Tl$_9$BiTe$_6$).

A closer look at the crystal structure and the bonds offers an explanation for this peculiarity. The Tl and Bi atoms on the 4c site have 6 nearest neighbors (Te) which form octahedra. Four of the Te-atoms, which are on the 8h site, share the a, b-plane with the central Tl or Bi atom. The coordination in the a, b-plane is shown in Fig. 7.6(a). For clarity reasons a ball and stick representation has been preferred to polyhedra. The third axis of the octahedra is parallel to the c-axis. These corners correspond to the 4a site. Fig. 7.6(b) shows that the (Tl,Bi)O$_6$ units form chains along the c-axis. In the a, b-plane a corner sharing network is formed. It is now comprehensible that the lattice constant c is mainly determined by the atoms on the 4a site while the lattice constant a is determined by the 8h site. Assuming that Te shows a greater affinity towards the 4a site than Se, then the latter will start to occupy the 8h site upon Se substitution in Tl$_9$BiTe$_6$. In a first order approximation the lattice constant a can be expected to decrease while c remains constant. By substituting two thirds of the Te atoms with Se the 8h site will be completely occupied by Se while the 4a site remains occupied by Te. This results in an intermediate, ordered compound with the
formula unit Tl₉Bi₄Se₁₂Te₂. By further increasing the Se/Te ratio also the Te on the 4a site will be replaced by Se. The lattice constant c will shrink to 12.69Å for pure Tl₉BiSe₆. From this model we expect c to be constant from 100% Te (pure Tl₉BiTe₆) down to a fraction of only 33% Te and then decrease linearly. On the other hand the lattice constant a is expected to be constant from pure Tl₉BiSe₆ to 33% Te and then increase linearly. Experimentally the critical concentrations for changes in the lattice constants are 23% Te for a and 32% for c. This is in very good agreement with the model, especially considering that 50% of the atoms in the structure – the Tl on the 16l site – have been omitted from the discussion.

Though the discovery of an ordered compound in the Tl₉Bi(Te₁₋ₓSeₓ)₆ alloy system is very interesting, the original motivation is the optimization of the thermoelectric properties. The thermopower and the resistivity of the pure ternary compounds and some intermediates (x= 0.05, 0.08, 0.2, 0.5) are shown in Fig. 7.7. The thermopower changes linearly from Tl₉BiTe₆ to Tl₉BiSe₆. In contrast to the thermopower, which changes only by a factor of 4, the resistivity increases by almost five orders of magnitude. Further insight into the variation of the thermopower with stoichiometry can be obtained using Eq. 2.13 from chapter 2. The two parameters which determine the thermopower are the reduced Fermi energy ε and the scattering parameter r. Since at 300 K acoustic phonon scattering is dominant the scattering parameter equals −1/2. From the thermopower of 205 μV/K and Eq. 2.13 the Fermi energy is found to be almost exactly at the conduction band edge (E_F ≈ 0 meV). When the Fermi energy
increases it starts to shift into the band gap and the thermopower increases. From the thermopower of Tl\textsubscript{9}BiSe\textsubscript{6}, \( S = 755 \ \mu\text{V/K} \) a Fermi energy of \( E_F = 175 \ \text{meV} \) is calculated. Actually, to be consistent with the Hall measurements it would have to be taken into account that neutral impurity scattering (\( r = 0 \)) is dominant in Tl\textsubscript{9}BiSe\textsubscript{6}. However, this has only little effect on the determined Fermi level, where \( E_F = 165 \ \text{meV} \) is obtained instead of \( E_F = 175 \ \text{meV} \). Since this is just a qualitative description rather than a quantitative analysis and the variation of the scattering parameter seems to have only little effect, a scattering parameter of \( r = -1/2 \) is assumed for Tl\textsubscript{9}BiSe\textsubscript{6} as well as all intermediate compounds. It is seen in Fig. 7.7(a) that the change in thermopower can be described very well assuming that the Fermi energy shifts linearly into the energy gap as the stoichiometry is changed.

The carrier concentration of a degenerate semiconductor is given by

\[
n = 2 \left( \frac{m^* k_B T}{2 \pi \hbar^2} \right)^{3/2} F_{1/2}(\varepsilon). \tag{7.1}
\]

With the given Fermi energies and assuming an effective mass of \( m^* = m_e \), the carrier concentrations calculated for Tl\textsubscript{9}BiTe\textsubscript{6} and Tl\textsubscript{9}BiSe\textsubscript{6} are \( 3.1 \cdot 10^{18} \ \text{cm}^{-3} \) and \( 4.7 \cdot 10^{15} \ \text{cm}^{-3} \), respectively. This corresponds to a relative change of 2.8 orders of magnitude, i.e. a factor of \( 660 \simeq 10^{28} \), whereas the change observed from the Hall measurements is 3.1 orders of magnitude. In Fig. 7.7(b) the increase in resistivity is split up into the decrease in the carrier concentration, shown by the straight line, and the decrease in the mobility which is indicated by the arrow. The difference between the upper curve and the straight line indicates the decrease in mobility in the alloys.

To obtain the absolute values of the carrier concentration of \( 2.8 \cdot 10^{19} \ \text{cm}^{-3} \) and \( 2.3 \cdot 10^{16} \ \text{cm}^{-3} \) as determined from the Hall measurements for Tl\textsubscript{9}BiTe\textsubscript{6} and Tl\textsubscript{9}BiSe\textsubscript{6} the density-of-states effective mass would have to be \( m^* = 4.5 m_e \) and \( m^* = 3.0 m_e \), respectively. Even considering the effects of a multi-valley band structure such high values seem quite unlikely. It is therefore restated that this model assumes a single parabolic band and it cannot be expected to give quantitatively correct results. Nevertheless, the trends for the thermopower and the resistivity are captured quite closely and the concept of the shift of the Fermi energy with composition appears reasonable.

It is seen in Fig. 7.3 that there is no intermediate maximum of the power factor but a monotonic decrease from Tl\textsubscript{9}BiTe\textsubscript{6} to Tl\textsubscript{9}BiSe\textsubscript{6}. Since the decline is very sharp at low Se-concentration it cannot be expected that even an imaginable decrease in the thermal conductivity could improve the figure of merit compared to pure Tl\textsubscript{9}BiTe\textsubscript{6}. It has to be concluded that no enhanced thermoelectric properties can be achieved by forming solid solutions of Tl\textsubscript{9}BiTe\textsubscript{6} and Tl\textsubscript{9}BiSe\textsubscript{6}. Nevertheless, the opportunity to control the Fermi energy by adjusting the Te/Se ratio might prove to be useful for the optimization of other materials of the Tl\textsubscript{5}Te\textsubscript{3}-group.
7.4 Doping of \( \text{Tl}_9 \text{BiSe}_6 \)

The very high thermopower of \( \text{Tl}_9 \text{BiSe}_6 \) makes it tempting to explore its susceptibility to doping. As a by-product of this study, two additional samples of \( \text{Tl}_9 \text{BiSe}_6 \) have been doped with Bi and Se. The sample shown in Fig. 7.4 has been doped with additional Se with the stoichiometry \( \text{Tl}_9 \text{BiSe}_{6.16} \). The resistivity has been reduced from 260 \( \Omega \) cm to 5.9 \( \Omega \) cm at 300 K but the thermopower has also been lowered to 180 \( \mu V/K \). Since the thermopower is lower than in pure \( \text{Tl}_9 \text{BiTe}_6 \) and the resistivity is higher, Se-doping does not appear to be promising.

While Se is expected to be an acceptor in \( \text{Tl}_9 \text{BiSe}_6 \), doping with Bi should act as a donor. Since all samples to date exhibited \( p \)-type thermopowers the proof that \( n \)-type materials can be obtained in the \( \text{Tl}_5 \text{Te}_3 \)-group is as important as further optimization of the thermoelectric properties. The thermopower and the resistivity are shown in Fig. 7.10 as a function of temperature and inverse temperature, respectively. From the resistivity of the Bi-doped sample an activation energy of 45 meV can be determined.

![Diagram](image-url)

Figure 7.8. The power factor of \( \text{Tl}_9 \text{Bi(Te}_{1-x} \text{Se}_x)_6 \) solid solutions with \( x \leq 0.5 \). For higher Se-concentrations the power factor is approximately zero.

![Diagram](image-url)

Figure 7.9. The resistivity and the thermopower of Se-doped \( \text{Tl}_9 \text{BiSe}_6 \) as functions of temperature.
Figure 7.10. (a) The resistivity of Bi-doped Tl₉BiSe₆ versus inverse temperature. From 200 K to 300 K an activated behaviour is observed with an activation energy of 45 meV. (b) The thermopower as function of temperature. Upon doping with 1% Bi the Tl₉BiSe₆ the thermopower is inverted to n-type behaviour.

Since the negative thermopower indicates that the charge carriers originate from the donors this energy presumably corresponds to the impurity level of Bi in Tl₉BiSe₆. The somewhat irregular behaviour of the thermopower, especially the fall-off to zero at 200 K, indicates that the sample is not doped homogeneously. Certainly, this sample does not represent the full potential of n-type material.

In summary, the great potential of optimizing the thermoelectric properties of Tl₉BiTe₆ by purification of the material has been shown. Furthermore, the solid solutions of Tl₉BiTe₆ and Tl₉BiSe₆ have been studied and a plausible model for the properties of the intermediate compounds has been presented. From x-ray data it is concluded that an ordered intermediate compound exists with the stoichiometry Tl₉BiTe₂Se₄. Finally, a brief exploration of doping effects has proved that n-type material, which is necessary to build a complete thermoelectric device, can be obtained from Tl₉Te₃-group members. At this point both routes, further purification of the material and more systematic doping studies seem promising. To keep things in order it has been decided to research the possibilities of improving the “purity” of Tl₉BiTe₆ which may result in an intrinsic semiconducting compound. Subsequently, the effects of doping can be studied on the optimized material.
CHAPTER 8

Growth Techniques

In the previous chapter it has been shown that improvements in the quality of the material drastically enhance the thermoelectric properties of Tl$_9$BiTe$_6$. The additional cleaning of the elements prior to the synthesis has proven to remove most of the oxides and hydroxides. For further improvement of the thermoelectric properties and to explore the anisotropy of the Tl$_5$Te$_3$-group materials, different crystal growth techniques have been applied to obtain single crystalline material.

8.1 Flux Growth

Flux growth, or solution growth, is a common technique for the growth of single crystals [Landise70]. For this growth technique a solvent is required, which exhibits negligible solubility in the crystals to be grown, while it can solve a considerable concentration of the crystal material in its liquid phase. Ideally, the solvent is a single element and constituent of the grown material. In the case of Tl$_9$BiTe$_6$, it is therefore close at hand to use Te as the solvent. Considering that the compounds Tl$_9$BiTe$_6$ and Tl$_5$Te$_3$ (≡Tl$_9$PbTe$_6$) are very similar, the binary phase diagram of Tl and Te, shown in Fig. 8.1(a), is used to discuss the flux growth process.

About 10% additional Te is added to Tl$_9$BiTe$_6$, which has been synthesized from the purified elements, resulting in the stoichiometry indicated by the dashed vertical line in the phase diagram. The material is sealed in an evacuated quartz ampoule and heated to 650°C for several hours to obtain a homogeneous solution. When the ampoule is cooled down it contains a unsaturated solution of Tl$_9$BiTe$_6$ in Te until the saturation line (liquidus), indicated by the arrow, is reached. Below this line the solution becomes supersaturated. Therefore, Tl$_9$BiTe$_6$ is deposited on the walls of the ampoule or spontaneously nucleates in the solution. Since the solubility decreases with lowering temperature, additional Tl$_9$BiTe$_6$ crystallizes from the solution. When the temperature is reduced slowly, the growth of existing crystals predominates further
nucleation and macroscopic single crystals can be obtained.

To separate the crystals from the solvent, the growth process is stopped at a certain temperature and the remaining liquid is decanted. It turns out that nucleation takes place at the walls of the ampoule resulting in several coalescing crystals, which exhibit a platelike structure. Unfortunately, the crystals cannot be separated from each other. Thus only small single-crystalline pieces have been obtained. The surface of the crystal plates is perpendicular to the c-axis, which indicates that the a,b-plane is the preferred growth direction. The experiment has been repeated several times with different concentrations and decanting temperatures but no free-standing single crystals have been obtained. Therefore, only thermopower measurements, shown in Fig. 8.1(b), have been carried out on a small single-crystalline piece. The low thermopower of 130 μV/K at 300 K suggests that there is considerable doping due to considerable solubility of Te in Tl₉BiTe₆. Since this is an intrinsic problem of this technique, no further flux growth experiments have been carried out.

8.2 Physical Vapor Transport

The use of an additional solvent is not necessary for crystal growth by physical vapor transport. To grow crystals by this technique polycrystalline pieces of Tl₉BiTe₆ are placed in an evacuated quartz ampoule, which is then heated in a temperature gra-
8.3 Bridgman-Stockbarger Method

While the uncontrolled freezing of a melt generally results in a fine grained polycrystalline matrix, larger crystallites or even single crystals can be obtained when the melt is cooled slowly in a temperature gradient. Generally, in the Bridgman-Stockbarger method the material to be crystallized is contained in a cylindrical crucible, which is lowered through a temperature gradient. In some cases the crucible is held stationary while the furnace is cooled, maintaining the temperature gradient. This technique is called gradient freezing. In both cases an isotherm, normal to the axis of the crucible, is moving through the crucible slowly enough that the melt interface can follow it. Initially the whole content of the crucible is molten and the first nucleation will be

Figure 8.2. Vapor transport grown single crystals of Tl$_3$Bi$_9$Te$_6$. The larger crystals have a typical length of approximately 100 $\mu$m.

dient. The material sublimes at the hot end and condenses at the cold end of the ampoule. The transport rate depends on the difference in the vapor pressure at both temperatures, the type of transport process (i.e. convection vs. diffusion) and the kinetics of the surface reaction. The slowest of these processes determines the growth rate. The size of the crystals depends on the transport rate, the growth time and the number of nucleated crystals. In order to condense the transported material as crystals rather than as liquid droplets, the temperature is kept slightly below 540°C, the melting point of Tl$_3$Bi$_9$Te$_6$. Unfortunately, at this temperature the vapor pressure is quite low, resulting in a small amount of transported material and therefore very small (100$\mu$m $\times$ 100$\mu$m, see Fig. 8.2) single crystals. A common technique to increase the rate of transport is to introduce a transport agent to the system, which acts as a volatizing agent. However, the flux growth experiments have shown that Tl$_3$Bi$_9$Te$_6$ accepts considerable amounts of additional Te, which results in unintentional doping of the crystals. Therefore, no experiments using additional transport agents have been carried out.
several crystallites at the bottom tip of the crucible where the temperature is lowest. In order to obtain a single crystal, despite the initial nucleation of several crystallites, various tip designs are employed to cause one of the crystallites to dominate the interface [Laudise70].

In the current experiment quartz is used as the crucible material because it has already proven unreactive with the Tl$_5$Te$_3$-compounds and it can be formed into the desired shape. The most common designs are a conical tip and a capillary tip. In either case only a small volume of the melt is supercooled before the nucleation and the probability is increased that a suitably oriented crystallite can dominate the growth. In the present experiment the conical design is preferred because the surface tension of the material prevents the melt from filling the small capillaries.

A schematic drawing of the furnace used for the crystal growth is shown in Fig. 8.3(a). Initially, the whole quartz crucible is located in the upper zone, which is heated above the melting point of the compound to be grown. During the growth the crucible is lowered with a speed of 4 mm/h into the lower zone, where the material solidifies. The temperature gradient between the two zones has to be steep enough to ensure that the initial nucleation occurs before large parts of the melt are supercooled. Otherwise, the crystallization through the supercooled melt is very rapid and results in small-grain polycrystalline material. However, a too large temperature gradient results in thermal stresses and cracking of the solidified material.

In the previous considerations of the nucleation and growth processes it was assumed that the grown material exhibits a higher thermal conductivity than the crucible. In this case, after the initial nucleation the coolest interface, where the growth takes place, is that between the material and the melt and the growth front develops as shown in Fig. 8.3(b). However, in the opposite case, when the material acts as a very good thermal insulator, the walls of the crucible above the solidified material are cooler than its interface to the melt. Therefore, the material nucleates at the walls of the crucible throughout the process and grows from there to the interior (Fig. 8.3(b), bottom). Unfortunately, it turns out that the very low thermal conductivity of the Tl$_5$Te$_3$-compounds leads to the latter type of freezing process, preventing the growth of single crystals with this method.

Nevertheless, the directional freezing process resulted in slightly enhanced thermoelectric properties (see Fig. 8.4). The thermopower has increased considerably from 205 $\mu$V/K to 233 $\mu$V/K at 300 K. However, most of the increase in the thermopower is counterbalanced by the increased resistivity. The figure of merit, calculated from the electrical properties and the lattice thermal conductivity, is $ZT = 0.49$. Despite the preceding purification of the elements, there are still impurity phases found on the surface of the grown material. This suggests that the slight improvement of the electrical properties is due to the removal of the impurities from the material. Therefore,
Figure 8.3. (a) The furnace used for the Bridgman-Stockbarger method. Two heating coils are used to control the absolute temperature and the gradient. The solid and the liquid material are indicated by dark gray and light gray filling, respectively. (b) Top: The solidification of the material as it takes place in the Bridgman-Stockbarger method when the thermal conductivity of the grown material exceeds that of the crucible. Bottom: If the material exhibits a lower thermal conductivity new nuclei are formed on the wall throughout the process and single crystal growth is inhibited.

another growth technique, which is known to have a pronounced purification effect, has been employed.

8.4 Zone Melting

Although zone melting may be used as single crystal growth technique, it is mainly applied as purification technique [Laudise70]. Therefore, it is also named “zone refining”. In this technique a small, hot zone of melt, typically approximately 1 cm long, is travelled through the material. The impurities, which solidify at lower or higher temperatures, are moved in or against the direction of the moving zone, respectively. The process can be repeated several times resulting in an enrichment of the impurities at both ends and high purity material between them. Zone refining often results in
Figure 8.4. The resistivity (a) and thermopower (b) of Tl$_9$BiTe$_6$ grown with the Bridgman-Stockbarger method. At 300 K, the values of 7.0 m$\Omega$ cm and 233 $\mu$V/K result in a power factor of 0.78 mW/(m K$^2$).

the growth of single crystals.

Zone melting techniques can be employed in several different configurations, i.e. horizontal versus vertical and crucible versus crucible-less techniques. Due to the volatility of tellurium a closed quartz ampoule is used as a crucible to hold the material. A horizontal arrangement is preferred to a vertical configuration for two reasons. First, in order to control the size of the molten zone the setup has to allow visual observation of the zone. It turns out that the interfaces solid-quartz and liquid-quartz are very difficult to distinguish in the vertical configuration, while in the horizontal geometry the liquid zone is easy to recognize. The second reason is that the surface of the melt seems to play an important role in the refining process. There is a small, but perceivable amount of impurities floating on top of the melt. Presumably, these are oxides, which have a higher melting point and a lower mass density than the melt. Due to convection in the melt, these impurities travel on top of the liquid phase to the back end of the material. The design of the zone refining furnace, which has been built, is shown in Fig. 8.5.

The length of the zone and the temperature gradient at both sides are controlled by the inner and the outer heater, respectively. An abrupt temperature gradient between the inner and the outer zone, enables accurate control of the length of the zone. Furthermore, the temperature gradient reduces diffusion of impurities in the crystallized solid. Therefore, to obtain the most pronounced purification effect, the temperature of the outer zone is to be kept low. However, a steep temperature gradient also introduces thermal stresses into the material, causing cracks during the growth. Heating of the outer zone reduces the thermal stresses but also the efficiency of the refining process. For the growth of Tl$_9$BiTe$_6$ a temperature of 400$^\circ$C is chosen for the
8.4. ZONE MELTING

Figure 8.5. Design of the zone refining furnace for further purification of Tl₂Te₃-group thermoelectric materials. The furnace has an inner and an outer heater coiled around two quartz tubes to control the length of the molten zone and the temperature gradient, respectively. During the process phases with a high (low) melting point will be moved towards the front (back) end.

![Diagram of zone refining furnace](image)

Figure 8.6. A sample of Tl₉BiTe₆ obtained from zone refining. The overall sample length is approximately 9 cm. At the left, the back end of the sample, 1.5 cm exhibit a dark surface indicating the accumulation of impurities.

outer zone, while the inner zone is above the melting point of 540°C. The ampoule is moved through the hot zone with a speed of 4.5 mm/h for three subsequent passes.

A sample obtained from the described process is shown in Fig. 8.6, where the right end corresponds to the front end in analogy to Fig. 8.5. While for the most part the sample exhibits a shiny surface, the dark surface at the back end (left) reflects the accumulation of impurities.

The thermoelectric properties of the material are measured on samples cut from the middle of the zone melted ingots. The resistivity and the thermopower of zone refined Tl₉BiTe₆ are shown in Fig. 8.7. Compared to the Bridgman-Stockbarger-grown sample the thermopower has increased by 30 μV/K to 261 μV/K at 300 K while the resistivity has been slightly reduced. Consequently, the power factor has been increased from 0.78 mW/(m K²) to 1.02 mW/(m K²).

The Hall measurements, shown in Fig. 8.8, reveal that the contribution of neutral impurity scattering has again been decreased drastically, since the mobility limit due to neutral impurity scattering increased from 450 cm²/(Vs) to 840 cm²/(Vs). At
Figure 8.7. The resistivity (a) and the thermopower (b) of zone refined Tl$_9$BiTe$_6$ as function of temperature. Due to the refining the thermopower is as high as 261 $\mu$V/K while the resistivity of 6.7 m$\Omega$cm is comparable to that of the previous samples (values at 300 K).

Figure 8.8. (a) The hole concentration of zone refined Tl$_9$BiTe$_6$ is almost constant over the entire temperature range. (b) The mobility of Tl$_9$BiTe$_6$ and the contributions of neutral impurity and acoustic phonon scattering. At 300 K the mobility is 62 cm$^2$/Vs, while at low temperatures it is limited by neutral impurity scattering ($\mu_n \approx$ 840 cm$^2$/Vs).

higher temperatures the mobility is almost completely dominated by acoustic phonon scattering. Using a scattering parameter of $r = -1/2$ and the thermopowers and the hole concentrations determined from the experiments, the Fermi level and the the density-of-states effective mass of the holes can be calculated from Eq. 2.13 and Eq. 7.1, respectively. However, the values obtained for 300 K ($E_F = 22$ meV, $m_d = 1.55 m_e$) and 340 K ($E_F = 37$ meV, $m_d^* = 1.75 m_e$) differ significantly considering the small relative temperature change. Therefore, the assumption of transport in a single parabolic band seems be unjustified.

The thermal conductivity of zone refined Tl$_9$BiTe$_6$ has been measured with the 3$\omega$-
Figure 8.9. (a) The total thermal conductivity $\kappa_{\text{tot}}$ as measured by the longitudinal steady state method and the 3\(\omega\)-technique, and its electronic ($\kappa_{\text{el}}$) and lattice contribution ($\kappa_{\text{lat}}$) calculated from the Wiedemann-Franz-Law. (b) The power factor (left) and the thermoelectric figure of merit (right) of zone melt grown Tl$_9$BiTe$_6$ as function of temperature up to 340 K.

The 3\(\omega\)-technique and the longitudinal steady-state method. While the latter is limited to temperatures below 150 K for such low thermal conductivities, the 3\(\omega\)-technique can only be applied at temperatures where the resistivity of the line heater is sufficiently linear with temperature, i.e. above approximately 60 K. The data obtained from the two methods are shown in Fig. 8.9(a). From 80 K to 140 K, where the temperature ranges of the two methods overlap, the absolute agreement is excellent. The small, uniform difference of approximately 5% can be ascribed to uncertainties in the geometry of the steady state method. Since the extremely low thermal conductivity is the key property of Tl$_9$BiTe$_6$, the lattice properties are discussed in the following chapter in greater detail.

In Fig. 8.9(b) the power factor and the figure of merit of the zone refined Tl$_9$BiTe$_6$ are shown as function of temperature. The power factor rises linearly with temperature below 220 K, where it reaches a value of 1 mW/(m K$^2$). In the temperature range from 220 K to 340 K it remains constant at that value within less than 5%. On the contrary, the thermoelectric figure of merit $ZT$ exhibits a monotone increase over the entire temperature range. At 300 K pure Tl$_9$BiTe$_6$ has a figure of merit of $ZT = 0.63$ and thereby outperforms pure $p$-type Bi$_2$Te$_3$ by more than 10%. At 340 K the figure of merit increases to $ZT = 0.77$.

From Fig. 8.9(b) it is clear that the optimum operating temperature of Tl$_9$BiTe$_6$ is above 340 K, which is the high temperature measurement limit of the PPMS cryostat. Therefore, the temperature range of the resistivity, the thermopower and the thermal conductivity measurements have been extended to higher temperatures.

The high temperature measurements are carried out inside a quartz tube in a tube
Figure 8.10. (a) The thermopower and the resistivity of zone refined Tl$_5$Bi$_5$Te$_8$ as function of temperature up to 500 K. (b) The power factor $S^2\sigma$, calculated from (a), and the thermal conductivity $\kappa$. Squares and triangles indicate the low temperature and high temperature measurements, respectively. For all three measurements the offset between the two data sets is less than 5%.

furnace. One end of the glass tube is connected to a rotary vane pump, while a flange with electrical feedthroughs seals the other end, so that the measurements can be carried out in vacuum, which is especially necessary for the thermal conductivity measurements. A platform has been designed, which is employed as the sample holder for the measurements of the different thermoelectric properties. Since the thermocouple, which controls the temperature of the furnace, is in appreciable distance to the sample holder, its temperature is measured with an additional resistive thermal device. The thermopower and the electrical resistivity have been measured up to 500 K. The temperature range for thermal conductivity measurements is limited, because the insulating glass resin layer starts to delaminate at high temperatures. Therefore, the thermal conductivity data is limited to 440 K.

The results of the measurements are shown in Fig. 8.10. The thermopower, the resistivity, and the thermal conductivity basically continue their low temperature trends. The open triangles in Fig. 8.10(b) represent an extrapolation based on a fit to the lattice thermal conductivity, which will be discussed in the next chapter. The extrapolation from 340 K to 500 K was carried out before the high temperature measurements. The very good agreement with the data measured up to 440 K illustrates its predictive power. Furthermore, neither the resistivity nor the thermopower exhibit abrupt changes above 440 K. Therefore, the extrapolation of the thermal conductivity to 500 K is expected to be accurate within a few percent.
Figure 8.11. The dimensionless thermoelectric figure of merit $ZT$ (squares) of zone refined Tl$_3$BiTe$_6$ as function of temperature up to 500 K. Separating the factor $T$ leads to the figure of merit $Z$ (triangles) with the unit 1/K, which exhibits a maximum of $2.5 \cdot 10^{-3}$ K$^{-1}$ at 430 K. Due to the factor of $T$, $ZT$ is still increasing at 500 K, where it reaches 1.2.

The thermoelectric figure of merit $ZT$ of zone refined Tl$_3$BiTe$_6$ is shown in Fig. 8.11. The material figure of merit $Z$ exhibits a broad maximum at 430 K with a value of $2.5 \cdot 10^{-3}$ K$^{-1}$. However, due to the increasing temperature the dimensionless figure of merit $ZT$ and therefore also the thermoelectric performance are still increasing above 430 K. The highest value determined so far is $ZT = 1.2$ at 500 K.

From the thermopower of 399 $\mu$V/K at 500 K and the fact, that it exhibits no maximum up to this temperature, the energy gap, which prevents the onset of bipolar conduction, is estimated to be at least 0.4 eV. Due to this high energy gap, the optimal operating temperature of Tl$_3$BiTe$_6$, is expected to be above 800 K. Since the melting point of Tl$_3$BiTe$_6$ is only 813 K it will be the limiting factor at high temperatures.

The improvement of the thermoelectric properties with the progress of the material preparation is illustrated in Fig. 8.12. The thermopower, which is a good measure for the relative purity of the material, is constantly increased from 185 $\mu$V/K from the initially prepared sample to 261 $\mu$V/K for the zone refined material. Originally, Tl$_3$BiTe$_6$ has been reported to have a thermopower of 62 $\mu$V/K [Pradel82].
Figure 8.12. The thermopower of different Tl₉BiTe₆-samples plotted as ‘function’ of the preparation method.

The great thermoelectric performance of Tl₉BiTe₆ is mainly due to its very low thermal conductivity. Considering only the electrical properties, i.e. the power factor, Tl₉BiTe₆ falls behind pure Bi₂Te₃ by a factor of more than three. Nevertheless, since the thermal conductivity is lower by almost a factor of four, Tl₉BiTe₆ outperforms Bi₂Te₃ at room temperature. The extremely low thermal conductivity is the outstanding property of Tl₉BiTe₆ and it is discussed in more detail in the following chapter.
CHAPTER 9

Lattice Properties

As has been pointed out in chapter 8, the high figure of merit of Tl$_9$BiTe$_6$ is primarily due to the very low thermal conductivity of this compound. Therefore, understanding the lattice properties of Tl$_9$BiTe$_6$ is not of purely scientific interest but may also serve as a guideline to further optimization steps. Several methods can be applied to study the lattice properties of solid state materials. In this chapter, data obtained from heat capacity measurements, Raman scattering, and elastic as well as inelastic neutron scattering are presented. Naturally, the data obtained from the different methods are related to each other and have to be analyzed with regard to each other to obtain the best possible insight into the lattice properties. However, for the clarity of presentation the different measurements are discussed in sections of their own.

9.1 Heat Capacity

The measurement of the heat capacity provides information about the lattice, the electronic and also the magnetic properties. It probes the density of states and the energy levels of the different contributions. In this chapter the analysis of the heat capacity data is focused on the contribution of the lattice properties.

Essentially, there are two different methods to measure the heat capacity of a solid: a static method, where the sample is thermally insulated and heated with a known amount of energy $\Delta Q$. The temperature rise $\Delta T$ of the sample is measured and the heat capacity is calculated as the fraction $\frac{\Delta Q}{\Delta T}$. However, since the sample has to be mounted to a sample holder in some way, perfect thermal insulation cannot be achieved, even in a very good vacuum and at low temperatures, where radiation losses can be neglected. In order to keep the losses small, the heating pulse has to be kept short. However, in any case a certain amount of time is needed for the sample to get into thermal equilibrium, before its temperature can be measured. Since heat already “leaks out” during this time, the initial temperature increase can only be determined
by extrapolation.

In a dynamic setup, a controlled heat loss actually serves to measure the heat capacity. In the current experiment, the sample is mounted onto a small platform, which is attached to the heat sink by thin wires of known thermal conductivity. After a short heating pulse, which increases the sample temperature by $\Delta T$, the sample cools again to the ambient temperature. The time constant of the heat loss is determined by the thermal conductivity of the wires, the heat capacity of the platform (both of which are known) and the heat capacity of the sample. The time constant and consequently the heat capacity are calculated by fitting the measured temperature of the platform versus time to an exponential decay function. Since the inevitable heat loss is made part of the measurement, generally dynamic measurements of the heat capacity are more accurate than static ones.

In the Debye approximation a crystal is modeled as a continuous solid. The lattice structure is only regarded in so far, that the number of phonon modes is limited to $3N$, where $N$ is the number of atoms in the crystal. The approximation results in a constant, i.e. frequency independent, sound velocity $v$ and a phonon density of states

$$z(\omega) = \frac{9N}{\omega_D^3} \omega^2,$$

where $\omega_D$ is the cut-off or so called Debye frequency. The Debye model provides a good description of the heat capacity in the limits of very low ($T \ll \Theta_D$) and high ($T \gg \Theta_D$) temperatures, where the Debye temperature is defined by $k_B \Theta_D := \hbar \omega_D$. Experimentally it is found that the upper limit is usually less stringent, i.e. the Debye model is valid as $T \gtrsim \Theta_D$ (see Fig. 9.1(a)). At very low temperatures, only phonons with wavelengths very long compared to the unit cell dimensions are excited. Therefore, the continuum approximation is justified and the predictions of the Debye model accurate. At high temperatures, where all phonons are excited, the heat capacity only depends on the total number of energy states, which is $3N$, and not on the specific form of $z(\omega)$. Thus, in the high temperature limit the heat capacity of solids is generally $3R$, where $R = 8.314$ J/(mole K) is the universal gas constant. The high temperature value is independent of any material properties and therefore of not much analytical value. However, more insight into the energy levels and the density of states of the different excitations (electronic, magnetic, lattice) is obtained by analyzing the heat capacity at lower temperatures. The lattice heat capacity at $T \ll \Theta_D$ is

$$C_{lat} = \frac{12\pi^4}{5} \frac{T}{\Theta_D} R \left( \frac{T}{\Theta_D} \right)^3.$$  

Since Tl$_9$BiTe$_6$ has to be regarded as being "metallic" in the sense that it exhibits a finite resistivity at very low temperatures, the electronic contribution to the heat capacity has to be taken into account as well. In the case of a metal the specific heat
of the electron gas is

\[ C_{el} = \frac{\pi^2}{3} k_B^2 T g(E_F) , \]  

(9.3)

where \( g(E_F) \) is the electronic density of states at the Fermi level. The total heat capacity is the sum of Eqs. 9.2 and 9.3 and depends on temperature as \( C_{\text{tot}}(T) = aT + bT^3 \), where the linear and the cubic term are contributed from \( C_{el} \) and \( C_{\text{lat}} \), respectively. The two contributions are usually separated by plotting \( C_{\text{tot}}/T \) versus \( T^2 \), which results in a linear function. The electronic density of states at the Fermi level \( g(E_F) \) at \( T \approx 0 \) K is determined from \( a \), the intercept of the curve with the \( C_{\text{tot}}/T \)-axis, by extrapolating \( C_{\text{tot}}/T \) linearly to \( T^2 = 0 \). The Debye temperature is obtained from \( c \), which is the slope of \( C_{\text{tot}}/T \) versus \( T^2 \).

The plot of \( C/T \) of Tl₂BiTe₆ as function of \( T^2 \) for temperatures from 1.9 K to 3 K is shown in Fig. 9.1(b). However, it is evident that \( C/T \) does not exhibit a linear dependence on \( T^2 \) in this temperature range. Furthermore, a fit to the lowest temperature points would result in a negative \( g(E_F) \). Therefore, it can be concluded that the low temperature approximations are not valid above 2 K. Consequently, data at lower temperatures are required for further analysis.

While the Debye model generally describes the heat capacity accurately in the limits of low and high temperatures, the results at intermediate temperatures deviate considerably from the measurements. However, a graphic representation has been introduced by [Chambers61], to obtain a more detailed picture of the phonon density of states from heat capacity data than by the Debye approximation. It is shown that certain functionals of the phonon heat capacity take the form of convolutions of the phonon
Figure 9.2. Two Einstein peaks in the phonon density of states at $\omega = 3 \cdot 10^{12}$ s$^{-1}$ and $\omega = 3 \cdot 10^{13}$ s$^{-1}$ and their corresponding responses in the heat capacity. For the given functional the shape of the response is independent of the Einstein frequency.

spectrum [Junod83]. For example, the response of $C_{\text{lat}}/T^3$ to a $\delta$-function (Einstein peak) in the phonon density of states is a bell-shaped curve on a logarithmic temperature scale with a halfwidth of about 0.49 (see Fig. 9.2). Particularly, $5\pi^4 C_{\text{lat}} T^{-3}$ is an image of the spectrum $\omega^{-2} z(\omega)$ for $\omega = 4.928 T$, where $\omega$ is expressed in degrees Kelvin [Junod83].

The heat capacity data of Tl$_6$BiTe$_6$ is plotted as $c/T^3$ versus $\log(T/1K)$ in Fig. 9.3(a). To obtain a more detailed picture of the phonon spectrum, instead of $z(\omega)/\omega^2 = \text{const}$ as in the Debye approximation, a phonon density of states is assumed, where $z(\omega)/\omega^2$ is a step function with equidistant steps in $\ln(\omega)$. Due to the width of the single contributions, the smallest step width for which the amplitudes of the single steps can be resolved from the heat capacity data, is $\Delta(\log(\omega/4.93 K)) = 0.2$. Since the low temperature limit of the heat capacity measurement is 1.9 K a constant $z(\omega)/\omega^2$ is assumed for $\log(\omega/4.93 K) \leq 0.4$. The amplitudes of the steps above $\log(\omega/4.93 K) = 1.6$ are found to be approximately zero. Therefore, they are disregarded and $z(\omega)/\omega^2 \equiv 0$ is assumed in this frequency range. The result is a fit function with 7 free parameters corresponding to the amplitudes of the steps. The purpose of this procedure is not to obtain a good description of the heat capacity as a function of temperature, but to obtain a better resolved image of the phonon spectrum than from the Debye model. Therefore, the number of fit parameters is to be chosen as large as possible, but avoiding too strong correlation between the amplitudes of the single steps. The step function and the contribution of the single steps to the heat capacity are shown in Fig. 9.3(a). The phonon density of states $z(\omega)$ is obtained by multiplying the obtained step function by $\omega^2$.

In Fig. 9.3(b) the result is compared to the phonon density of states obtained from the Debye model. The high energy limits of the phonon energies agree rather well. How-
Figure 9.3. (a) $C/T^3$ of Tl$_9$BiTe$_6$ as function of logarithmic temperature (squares). It resembles the density of states step function $z(\omega)/\omega^2$ plotted versus $\log(\hbar\omega/k_B/4.93 \text{ K})$. The lower curves are the contributions of the single steps. The line through the heat capacity data is the sum of the single contributions. (b) Phonon density of states $z(\omega)$ obtained from the step function (solid line) and from the Debye model (dashed line, divided by 2). The vertical strokes indicate the width of the steps.

However, the extended model shows a greatly enhanced phonon density of states at energies between approximately 1.7 meV and 4.2 meV. The lower energy corresponds to a temperature of 20 K, which results in a response in the heat capacity at 20 K/4.93 $\approx$ 4 K. Due to the width of the response function, this additional density of states is seen in the heat capacity data even at the lowest temperatures. This explains why the low temperature data do not agree with the Debye model. The saw tooth form of the phonon density of states is due to the initial choice of the function for $z(\omega)/\omega^2$ and the peaks at 6.6 meV and 10.4 meV have to be considered as artifacts. However, while these two peaks result from single steps in $z(\omega)/\omega^2$, the lowest energy peak at 4.2 meV is a result of 2 steps. Although, the heat capacity data do not allow to resolve the shape or the exact amplitude of this peak, it clearly indicates a strong phonon mode in this energy range.

9.2 Neutron Scattering

Elastic and inelastic neutron scattering measurements$^1$ have been carried out to analyze the phonon density of states and the thermal motion of the different atomic species in Tl$_9$BiTe$_6$.

$^1$The measurements have been carried out with Craig Brown at the NIST (National Institute of Standards and Technologies) in Gaithersburg, MD, USA.
9.2.1 Inelastic Neutron Scattering

A schematic drawing of the time-of-flight measurement is shown in Fig. 9.4. A pulsed beam of cold neutrons is scattered from the powdered material under different angles $2\theta$. The elastic scattering events are described by

$$k_s = k_i + K \quad \text{and} \quad \hbar \omega_s = \hbar \omega_i,$$

where $\omega$ is the frequency and $k$ is the wave vector of the neutrons and $K$ is a reciprocal lattice vector. The indices $i$ and $s$ refer to the incident and scattered neutrons, respectively. Inelastic neutron scattering involves the additional excitation and absorption of phonons. In the case of one-phonon scattering

$$k_s = k_i \pm q + K \quad \text{and} \quad \hbar \omega_s = \hbar \omega_i \pm \hbar \omega_{ph},$$

where $q$ is the wave vector of the phonon and "+" and "-" correspond to the absorption and excitation of a phonon, respectively. Since the measurement is carried out on powdered material, there is no information about $K$. Thus the wave vector of the scattering phonon $q$ cannot be determined. Nevertheless, since the velocity of the neutrons is determined by $E = \frac{1}{2} m_n v^2$, where $m_n$ is the mass of the neutrons and $v$ their velocity, it is changed when the neutron transfers energy from or to a phonon in a scattering event. Consequently, the energy of the involved phonon can be determined by the time it takes the neutron to travel from the sample to the detector. The phonon spectrum is determined from the time resolved measurement of the scattered neutron pulse. However, while one-phonon scattering processes give an image of the phonon spectrum, multi-phonon processes contribute a smooth background. In the data analysis, the expected multi-phonon background is subtracted from the data.
The phonon spectrum of Tl₁₀BiTe₆ measured at 300 K is shown in Fig. 9.5(a). There are a few distinct peaks in the density of states at phonon energies below 15 meV and two broad maxima at approximately 20 meV and 35 meV. According to the Debye model, at very low energies the density of states is proportional to \( E^2 \). As seen in the inset in Fig. 9.5(a) this behaviour is in fact observed for energies below 1.6 meV. From the factor of proportionality, determined by a fit to the data, a Debye temperature of 124 K is derived. Because of the inaccuracies of the Debye model the Debye temperature itself is temperature dependent. Consequently, the Debye temperature determined from neutron scattering, which corresponds to \( \Theta_D(0 \text{ K}) \), is not in contradiction to the Debye temperature of 107 K from the heat capacity measurements, which corresponds to the Debye temperature at an intermediate temperature between 0 K and 300 K.

The phonon spectrum below 15 meV is shown in Fig. 9.5(b) and compared to the spectra obtained from the heat capacity measurements. The spectrum obtained from the step function approach described in section 9.1 agrees quite well with the neutron data. Especially, the finding of a low energy peak between 1.7 meV and 4.2 meV in the phonon density of states is confirmed by the neutron data, where the lowest energy peak is found at 3.2 meV. However, it is obvious that with the given step width no further details of the phonon spectrum can be resolved. Only extremely accurate heat capacity measurements would allow to obtain more detailed information about the phonon spectrum.

The sound velocity \( v_s \) can be estimated from the Debye temperature and the number density of atoms \( n_{at} = N_{at}/V_c \), where \( N_{at} \) is the number of atoms per unit cell with
volume $V_c$. From
\[ v_s = \frac{k \Theta_D}{h} \left( \frac{V}{6 \pi^2 N_{at}} \right)^{1/3} \]  
(9.6)
a sound velocity of $v_s = 1300$ m/s is calculated for Tl$_3$BiTe$_6$. From this and the Debye temperature the “minimum thermal conductivity” is calculated by (see discussion in section 2.4)
\[ \kappa_{\text{min}} = \left( \frac{\pi}{6} \right)^{1/3} k_B \delta^{-2} v \left( \frac{T}{\Theta_D} \right)^2 \int_0^\infty \frac{x^3 e^x}{(e^x - 1)^2} \, dx \]  
(9.7)
and compared to the measured thermal conductivity. The difference between the two is a measure of how close the lattice properties are to the limit of a completely disordered solid, which would be the ideal for a thermoelectric material regarding the contribution of $\kappa_{\text{sat}}$ to the figure of merit. The lattice thermal conductivity of Tl$_3$BiTe$_6$, as calculated from the measurement using the Wiedemann-Franz law, is compared to the calculated minimum thermal conductivity in Fig. 9.6(a). At low temperatures, below 50 K, the lattice thermal conductivity is about one order of magnitude higher than the calculated minimum value. However, at 300 K the lattice contribution (0.39 W/(m K)) is only approximately twice the expected minimum of 0.17 W/(m K). For Bi$_2$Te$_3$ at 300 K, a ratio $\kappa_{\text{sat}}/\kappa_{\text{min}} = 5$ is obtained from the lattice contribution of 1.5 W/(m K) and a calculated minimum thermal conductivity of 0.28 W/(m K), indicating that the lattice properties of Tl$_3$BiTe$_6$ are much more suitable for thermoelectric applications.

A fit to the thermal conductivity of the lattice is shown in Fig. 9.6(a). In most crystalline solids at low temperatures phonon scattering is dominated by crystal imperfec-
tions (grain boundaries, impurities, etc.), while at higher temperatures phonon-phonon scattering is the prevailing mechanism. Above the Debye temperature phonon-phonon scattering generally results in $\kappa_{\text{lat}} \propto T^{-x}$, with $x$ between 1 and 2 depending on the importance of scattering processes produced by cubic ($x = 1$) and quartic ($x = 2$) anharmonic terms in the ionic interaction energy [Ashcroft76]. However, as discussed in chapter 2, $\kappa_{\text{lat}} \geq \kappa_{\text{min}}$ based on the assumption that the minimum life time for a defined phonon mode is half the period of the vibration: $\tau_{\text{min}} = \pi / \omega$. Therefore, as the lattice thermal conductivity is approaching its minimum value it is more accurately described by $\kappa_{\text{lat}} = AT^{-x} + \kappa_{\text{min}}$. As seen in Fig. 9.6(a), a fit based on this model with the parameters $x = 0.93 \pm 0.01$ and $\kappa_{\text{min}} = 0.21 \pm 0.05$ W/(m K) describes the data very well from 20 K to 340 K.

In Fig. 9.6(b) the lattice thermal conductivity of Tl$_9$BiTe$_6$ is compared to those of Tl$_9$BiSe$_6$ and Tl$_8$Pb$_2$Te$_6$. The temperature dependence of $\kappa_{\text{lat}}$ of Tl$_9$BiSe$_6$ is only slightly weaker than that of Tl$_9$BiTe$_6$ and the absolute values of the conductivities coincide within 10% above 100 K. On the other hand, the Tl$_8$Pb$_2$Te$_6$-sample exhibits a different behaviour of the thermal conductivity. The broad maximum between 100 K and 150 K with a value of only 1 W/(m K) indicates that the crystalline quality of the sample is lower than that of the other two samples. However, at 300 K the thermal conductivity of Tl$_8$Pb$_2$Te$_6$ (0.72 W/(m K)) is approximately twice as high as those of Tl$_9$BiTe$_6$ and Tl$_9$BiSe$_6$. This suggests, that the additional disorder on the 4c-site of the 9-1-6 compounds as compared to the 8-2-6 compounds (see chapter 6) plays an important role for the very low thermal conductivity of Tl$_9$BiTe$_6$. Further reduction of the thermal conductivity may be expected by increasing the disorder on the 4c-site forming alloys with the composition Tl$_9$Bi$_{1-x}$Sb$_x$Te$_6$.

### 9.2.2 NEUTRON DIFFRACTION

Neutron diffraction measurements have been carried out on Tl$_9$BiTe$_6$ at temperatures from 1.5 K to 300 K. From the diffractograms the lattice constants and the atomic displacement parameters are determined using Rietveld analysis (PROFIL Version 5.17). The atom positions are fixed as published in [Villars91]. The lattice parameters $a$ and $c$ as function of temperature are shown in Fig. 9.7. The linear thermal expansion coefficient $\alpha = 1/l(dl/dT)$ is approximated by

$$\alpha = \frac{1}{l(T_{i+1}) + l(T_i)/2} \frac{l(T_{i+1}) - l(T_i)}{T_{i+1} - T_i}.$$ 

Above 200 K the thermal expansion coefficients are approximately constant, with values of $\alpha_a = 23 \cdot 10^{-6}$ and $\alpha_c = 33 \cdot 10^{-6}$. The anisotropic thermal expansion is likely to be responsible for the observed tendency of polycrystalline material to crack in thermal gradients as observed in the crystal growth experiments. This might limit the
thermal gradients, which can be applied in thermoelectric devices of polycrystalline material.

The atomic displacement parameters (ADPs) of the four different crystal sites in Tl₉BiTe₈ versus temperature are shown in Fig. 9.8. As discussed in chapter 2, in a first approximation the atoms can be regarded as quantized harmonic oscillators of which the displacement is described by Eq. 2.26. The displacement parameters measured at low temperatures are usually larger than the expected zero point motion. On the one hand, this is due to static disorder in the crystal, e.g. incomplete occupation of a crystal site, substitutional effects between different crystal sites or a form of the potential with minima for different atom positions [Sales98]. On the other hand, inaccuracies in the structure determination lead to increased ADPs, which “smear out” the atom and thereby reduce the calculated errors of the structure determination. Therefore, Eq. 2.26 is extended by a term \( \langle u^2 \rangle_{\text{offset}} \), which describes the additional displacement at zero temperature due to the reasons discussed above. However, in some cases also negative \( \langle u^2 \rangle_{\text{offset}} \) have been obtained. Possible reasons are inaccuracies in the Rietveld analysis and the harmonic oscillator model, from which the zero point motion has been calculated using the oscillator frequency from the fit. The fits to the ADP data have been carried out using the function

\[
\langle u^2 \rangle = \frac{h}{8\pi^2 m \nu} \coth \left( \frac{h \nu}{2k_B T} \right) + \langle u^2 \rangle_{\text{offset}},
\]

with \( \langle u^2 \rangle_{\text{offset}} \) and \( \nu \), the oscillator frequency, as the fit parameters. For all crystal sites the zero point motion (\( \langle u^2 \rangle_0 = h/(8\pi^2 m \nu) \)) of both components, 11 and 33, obtained from the fitted frequency is approximately \( 2.5 \times 10^{-3} \text{ Å}^2 \) (±20%). The difference between the low temperature value of the fit and the zero point motion corresponds to \( \langle u^2 \rangle_{\text{offset}} \).

The Rietveld analysis seems to give reliable values for the ADPs of the atoms Te2, Tl,
Figure 9.8. (a)–(d) Temperature dependence of the anisotropic atomic displacement parameters of the four different crystal sites as determined from neutron scattering and Rietveld analysis. The model with two parameters, $\nu$ and $\langle u^2 \rangle_{\text{offset}}$, to fit the data (lines) is described in the text. (e) Summarizing representation of the results of (a)–(d) showing the errors in the fit parameters.
and Bi/Tl, which can be fitted using Eq. 9.8 with relatively small \( \langle u^2 \rangle_{\text{offset}} \). However, the data obtained for Te1, see Fig. 9.8(a), exhibits much larger uncertainties, especially in the 33-component. Furthermore, the zero point offset is more than twice as high as in the other cases. At 50 K and 100 K correlation of the 11 and the 33 component in the Rietveld analysis becomes observable, such that \( U_{11} \) becomes overestimated, while in turn \( U_{33} \) gets underestimated. The correlation effect is also visible in Fig. 9.8(e), where the large uncertainties in \( \nu \) and \( \langle u^2 \rangle_{\text{offset}} \) seem to be carried over from the 33-component to the 11-component. It cannot be resolved, whether these increased ADPs are due to disorder on the 4a-site or an inaccurate atom position for the Te1.

The rattling motion of loosely bound atoms in a crystal, which can reduce the thermal conductivity considerably, is revealed by large ADPs. As seen in Fig. 9.8(a)–(d) the Tl atoms on the 16l-site exhibit the highest ADPs. (Due to the uncertainties discussed above, the \( U_{33} \) of Te1 is disregarded.) If the oscillation of the Tl atoms corresponds to a rattling motion independent of the other atoms in the crystal, then an Einstein peak will appear in the phonon spectrum at the rattling frequency. The frequencies obtained from the fits are \( 9.4 \times 10^{11} \) s\(^{-1} \) and \( 1.03 \times 10^{12} \) s\(^{-1} \) for \( U_{11} \) and \( U_{33} \), respectively. The corresponding energies are 3.9 meV and 4.3 meV. As mentioned above, the lowest energy peak in the phonon spectrum is centered at 3.2 meV, which is significantly lower and therefore cannot be related to a rattling of the Tl atoms. A comparison between the frequencies determined from the oscillator model and the phonon spectrum is shown in Fig. 9.9. The range of energies of the oscillators corresponds to the high density of states energy region of the phonon spectrum. Nevertheless, the peaks in the phonon spectrum do not seem to correlate to the oscillation frequencies determined for the single atoms. Therefore, it is concluded that there are no distinct “rattlers”,

![Phonon Spectrum](image-url)

**Figure 9.9.** The phonon spectrum (squares) and the energies of the atomic oscillations determined from the ADP-data, if the atoms are regarded as independent harmonic oscillators.
which are responsible for the low thermal conductivity of Tl$_9$BiTe$_6$.

9.3 Raman Scattering

Complementary to neutron scattering, the phonon spectrum can also be probed by light scattering. The process is referred to as Raman scattering, when the emitted or absorbed phonon is optical, and Brillouin scattering, when the phonon is acoustic. In this chapter only Raman scattering data is discussed.

Due to their different dispersion relation, photons with typical thermal energies ($\sim 1$ meV to $\sim 100$ meV) usually have wave vectors of less than $10^4$ cm$^{-1}$, which is very small compared to typical Brillouin zone dimensions, which are of order $10^8$ cm$^{-1}$. Therefore, one-phonon scattering processes only provide information about the immediate neighborhood of the center of the Brillouin zone. However, in two-phonon processes, provided that the photon is scattered by two phonons with opposite wave vector $\mathbf{q}$ and $-\mathbf{q}$, the conservation laws reduce to

$$\hbar \omega_s = \hbar \omega_i \pm 2 \hbar \omega_{ph}(\mathbf{k}) \quad \text{and} \quad n\mathbf{k}_s = n\mathbf{k}_i + \mathbf{K},$$

(9.9)

where the annotation is analogous to the case of neutron scattering and the lower sign refers to phonon excitation (known as Stokes component) and the upper sign refers to phonon absorption (anti-Stokes component). The photon wave vectors inside a crystal differ from their free space values by a factor of the index of refraction of the material $n$. Since the momenta of the two phonons cancel out and the conservation laws independent of the phonon wave vector $\mathbf{q}$, two-phonon processes allow to probe the whole Brillouin zone by Raman scattering.

The spectrum shown in Fig. 9.10(a) is obtained from the Stokes component of Raman measurements on Tl$_9$BiTe$_6$ at a temperature of 5 K. The spectrum has been recorded from 50 cm$^{-1}$ to 700 cm$^{-1}$. A sharp peak in the response is seen at approximately 100 cm$^{-1}$, while the second peak, at about 200 cm$^{-1}$, is weaker by two orders of magnitude. The inset shows a high resolution measurement of the first peak. Two peaks becomes clearly distinguishable, which are centered at 99.4 cm$^{-1}$ and 103.0 cm$^{-1}$ and which are referred to as $A$ and $B$, respectively.

The response around 100 cm$^{-1}$ is measured at temperatures of 5 K, 50 K, 100 K, 200 K, and 300 K. For the sake of clarity only the data at three temperatures are shown in Fig. 9.10(b). A broadening of the peaks and a shift to lower energies are observed as a result of increasing temperature.

The normalized spectral lineshape contributed by the phonon lifetime $\tau_\mathbf{q}$ is a Lorentzian [Cardona83]

$$S(k_s, q) = \frac{\Gamma_\mathbf{q}}{\pi ((k_s - k_i + q)^2 + \Gamma_\mathbf{q}^2)},$$

(9.10)
where the width $\Gamma_q = \tau_q^{-1}/2\pi c$ is a measure of the inverse lifetime of the phonons and $c$ is the speed of light. The high resolution data is fitted to the sum of two Lorentzians and the fit parameters, position and width, are shown in Figs. 9.11(a) and 9.11(b), respectively.

The observed shift to lower phonon energies with increasing temperature can be understood from a “quasiharmonic” oscillator model described in [Postmus68]. The only anharmonic effect regarded in this model is the thermal expansion of the crystal lattice. This affects the frequencies of the harmonic oscillators through the harmonic force constant, which changes with volume. The volume dependence of $\nu_j(\mathbf{q})$, the phonon frequency of the $j$th branch at point $\mathbf{q}$ in the first Brillouin zone, is described by the Grüneisen parameter

$$\gamma_j(\mathbf{q}) := -\frac{d\ln \nu_j(\mathbf{q})}{d\ln V}.$$  

As a result of the definition of $\gamma$ the temperature dependence of the phonon frequencies in the Grüneisen approximation is

$$\nu_c(T) = \nu(0) \exp \left( -3\gamma \int_0^T \alpha \, dT \right). \quad \text{(9.11)}$$

Using the thermal expansion coefficient $\alpha$ determined from neutron diffraction (see Fig. 9.7), Eq. 9.11 can be applied to determine the Grüneisen parameter of the phonon modes. The two modes exhibit different Grüneisen parameters of $2.3 \pm 0.2$ and $1.9 \pm 0.2$ for mode $A$ and $B$, respectively. Although there is good agreement of the data and
Figure 9.11. The position (a) and the width $\Gamma_q$ (b) of the Lorentzians fitted to the high resolution Raman data. The full squares and the open squares correspond to the peak $A$ and $B$, respectively. The shift to lower wave vectors with increasing temperature is fitted to a model described in the text.

the fit in Fig. 9.11(a), one has to bear in mind that no contribution of the anharmonic terms of the atomic potential other than the thermal expansion has been taken into account.

Since the peaks overlap significantly, particularly at higher temperatures, the uncertainties in the determination of the peak width are much larger than in the peak position. Especially, the cross-over of the peak width between 100 K and 200 K is an artifact due to the large peak overlap. Therefore, instead of any more detailed analysis, only the order of magnitude of the phonon lifetime is estimated. The inverse life time of the phonons is calculated from the peak width $\Gamma_q$ by

$$\tau_{ph}^{-1} = 2\pi c \Gamma_q.$$  \hspace{1cm} (9.12)

In average the peak widths are of the order $\Gamma_q \approx 3 \text{ cm}^{-1}$, which results in $\tau_{ph}^{-1} \approx 5 \cdot 10^{11} \text{ s}^{-1}$. Compared to the typical phonon frequencies in Tl$_3$BiTe$_6$ of some $10^{12}$ s$^{-1}$, this means that the lifetime of the phonons is only a few times the period of their vibration. This corresponds to the finding that the thermal conductivity is close to its minimum value.

Comparing the energy of the strong Raman mode at 100 cm$^{-1}$ to the phonon spectrum obtained from inelastic neutron scattering strongly suggests that the observed Raman mode results from two-phonon scattering. One-phonon scattering would relate the wave vector of 100 cm$^{-1}$ to a phonon energy of approximately 12 meV. As seen in Fig. 9.5(b), this does not correspond to any phonon mode observed in inelastic neutron scattering. However, a two-phonon scattering process results in an observed energy shift, which is twice the energy of the phonon mode. In this case, the phonon energy
would only amount to approximately 6 meV. In Fig. 9.12 the Raman responses at 100 K and 300 K are compared to the inelastic neutron spectra measured at the same temperatures. Although the Raman peaks are shifted to slightly higher energies, they correspond reasonably well to the peak in neutron data, which is centered at 5.80 meV and 5.63 meV at 100 K and 300 K, respectively. Furthermore, the observed energy shift of 0.17 meV in the neutron data agrees well with the shifts of 0.23 meV and 0.18 meV of the peaks A and B, respectively. All other phonon modes observed with inelastic neutron scattering exhibit no significant energy shift from 100 K to 300 K.

In summary, the lattice properties of Tl\textsubscript{9}Bi\textsubscript{7}Te\textsubscript{6} have been studied by heat capacity, neutron scattering and light scattering experiments, to understand the very low thermal conductivity of this compound. Two different mechanisms have been discussed in sections 2.4 and 2.5, which result in low thermal conductivities. Although there is a peak in the phonon density of states at very low energy (3.2 meV, \( \nu = 8 \cdot 10^{11} \) s\(^{-1} \)), which is similar to those observed for typical rattling compounds as clathrates and filled skutterudites [Tritt98], the oscillation frequencies of the atoms suggest that this peak is not that of a rattling mode of a single atom but rather a low energy collective mode (see Fig. 9.9). Therefore, the rattling model seems not applicable to Tl\textsubscript{9}Bi\textsubscript{7}Te\textsubscript{6}. However, in the “classical” theory of [Slack79] the low thermal conductivity becomes understandable. The low Debye temperature and the large atomic displacement parameters indicate that the bonds of the atoms in the crystal are weak. Furthermore, because of the large unit cell of 32 atoms the contribution of the acoustic phonons to the thermal conductivity is small. Finally, Tl\textsubscript{9}Bi\textsubscript{7}Te\textsubscript{6} exhibits an intrinsic disorder on the 4c crystal site, which plays an important role for the low thermal conductivity (see Fig. 9.6(b)). While further studies are necessary to understand the details of the lattice properties, e.g. the origin of the low energy peak and the splitting of the Raman mode, the general picture of the lattice properties has been obtained from the measurements presented in this chapter.
CHAPTER 10

Conclusions

The number of materials (elements, binaries, ternaries, etc.), which could be examined regarding their thermoelectric applicability, is almost unlimited. The “Pearson’s Handbook of Crystallographic Data” in its latest edition [Villars97] lists more than 27000 different compounds and further new compounds are reported at a high rate. Therefore, guidelines have been established to identify materials, which are likely to exhibit a high thermoelectric figure of merit.

The objective of this work has been to study a large number of compounds selected according to these guidelines and to identify the ones, which are most promising for thermoelectric applications. In a survey of promising thermoelectric materials, approximately 50 different compounds and solid solutions have been examined. Thereby the following approaches to find a new high-efficiency thermoelectric materials have been taken.

- A number of new clathrate compounds have been studied. This class of materials, especially the germanium type I clathrates had been identified as promising thermoelectric compounds due to their non-typical, very low thermal conductivity [Slack97]. In this work, the chemistry of the germanium cage sublattice has been changed in various ways in order to improve the electrical properties. Most of the currently studied clathrate compounds exhibit $n$-type thermopowers [Uher98], while a complementary $p$-type compound has been missing. In this study, we have identified the clathrate $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$ as a $p$-type material, which exhibits a power factor comparable to that of the best known $n$-type clathrate compound.

- The compound SmSe exhibits a continuous valence transition of the Sm-atoms at low pressures [Chatterjee72]. Since intermediate valence states in $4f$-electron systems are often found to produce unusually high thermopowers [Jacqard82], it has been tried in this work to apply pressure chemically by forming alloys with
TmSe. However, no significant improvement of the thermoelectric properties due to intermediate valence behaviour has been observed in the alloy system.

- A large number of chalcogenides, which have been expected to be small band gap semiconductors, has been studied including some layered materials. In this group Tl$_9$BiTe$_6$ has been identified as promising material to obtain a high thermoelectric figure of merit.

Of all studied materials in the different subsets Tl$_9$BiTe$_6$ has been expected to exhibit the most potential regarding its thermoelectric properties. Therefore, it has been chosen for further study and optimization.

Since Tl$_9$BiTe$_6$ belongs to a group of seven ternary materials, which are chemically very similar to Tl$_9$BiTe$_5$ and are derived from the binary Tl$_5$Te$_3$, the materials of this group have been analyzed regarding their thermoelectric properties. However, none of the other compounds in the Tl$_5$Te$_3$-group seems to exceed the thermoelectric properties of Tl$_9$BiTe$_6$. Nevertheless, the miscibility of all compounds in the group allows the formation of several different solid solution systems to optimize the thermoelectric properties.

Different purification and growth techniques have been applied to optimize the thermoelectric properties of Tl$_9$BiTe$_6$. Thereby, the thermopower has been improved from 185 $\mu$V/K of the initially prepared material to 261 $\mu$V/K in zone refined ingots from pre-purified material. Compared to the previous reports about Tl$_9$BiTe$_6$ (62 $\mu$V/K, [Pradel82]) already the initial sample represents high quality material. The progress in material preparation has also led to an increase of the power factor by more than a factor of 2.

The very low thermal conductivities of the Tl$_5$Te$_3$-compounds cannot be determined accurately by measurements with the standard longitudinal steady-state method. Therefore the $3\omega$-technique has been chosen as an alternative method and a new thermal conductivity measurement setup has been built. Low temperature measurements have been carried out in a cryostat, which is limited to temperatures below 340 K. However, since the thermoelectric performance of Tl$_9$BiTe$_6$ peaks at higher temperatures, a furnace measurement station has been built.

While the electrical properties, $S$ and $\rho$, are very good but not outstanding compared to the current state of the art materials, the extremely low thermal conductivity turns out to be the key property of Tl$_9$BiTe$_6$. Therefore, its lattice properties have been studied in greater detail using heat capacity, light scattering and neutron scattering measurements. It has been shown, that the very low thermal conductivity, is due to the soft bonds in Tl$_9$BiTe$_6$. Especially, the Tl-atoms on the 16l-site, which amount to 50% of the atoms in the structure, are very weakly bound, as indicated by the large atomic displacement parameters. Furthermore, it has been demonstrated, that
the thermal conductivity is not determined by “rattling” atoms in the structure, but has to be understood in a “classical” model. However, for a detailed study of the phonon dispersion relations, large single crystals are required, which are currently not available.

In summary, among a large number of possibly promising thermoelectric materials, Tl$_9$BiTe$_6$ has been identified as having the potential to be a high efficiency thermoelectric material. High quality material has been synthesized and a figure of merit of $ZT = 1.17$ at 500 K has been achieved. Compared to the current state of the art materials (see Fig. 10.1), Tl$_9$BiTe$_6$ has been proven to be the best $p$-type compound at temperatures from 430 K to 500 K and prospects are that this holds for temperatures above 600 K. At 480 K, where TAGS-85 starts to exceed $p$-type Bi$_2$Te$_3$, the thermoelectric figure of merit of Tl$_9$BiTe$_6$ surpasses the current state of the art materials by more than 40%.

In the approximately 5 decades of thermoelectric research only a handful of thermoelectric materials with a figure of merit of $ZT \gtrsim 1$ has been found (see chapter 3). Therefore, the finding of Tl$_9$BiTe$_6$ as new material in this class and the fact that it significantly exceeds all known $p$-type materials at temperatures around 500 K is truly exciting.
Outlook

Even though Tl$_9$BiTe$_6$ is already among the very best thermoelectric materials, there are still prospects for further improvements of its performance. This study has concentrated on optimizing the thermoelectric performance by improving the purity of the material. Further optimization will include doping studies – with one focus on obtaining a high-efficiency n-type compound – and the research of the alloy system Tl$_9$Bi$_{1-x}$Sb$_x$Te$_6$, which is expected to exhibit even lower thermal conductivities than the pure compound. Finally, the growth of single crystals will be further pursued to explore the anisotropy of the transport parameters in Tl$_9$BiTe$_6$.

While the great thermoelectric performance of Tl$_9$BiTe$_6$ has been proven unambiguously in the laboratory, there are still some open questions regarding its applicability in actual thermoelectric devices. One issue are the brittleness and the anisotropy of the thermal expansion, which may limit the application of polycrystalline material. Furthermore, the long-term stability of the material in thermal gradients and electrical fields at elevated temperatures have to be tested. Finally, thallium is a heavy metal and forms toxic oxides. Therefore, in “every-day” applications precautions have to be taken, for instance by encapsulation and/or recycling of the material. Although these are important issues, they rather belong to the field of device engineering and are beyond the scope of this work.
Temperature Oscillations in the $3\omega$ measurement

In the literature on the $3\omega$ technique no complete, consistent and error free derivation of the formula to calculate the thermal conductivity from the frequency dependence of the $3\omega$-Voltage $V_{3\omega}$ is found. The first part of the presented derivation is mainly based on the Carslaw’s and Jaeger’s [Carslaw59] treatment of “The flow of Heat in an Infinite Circular Cylinder”. The application of the solution to the $3\omega$-technique follows the treatment in [Cahill90].

We now consider an infinite half cylinder of a homogeneous, isotropic solid whose axis coincides with the $z$-axis of the cylindrical coordinate system. The thermal conductivity $\kappa$ shall be constant within the temperature changes $\Delta T$. Apart from phase transitions this is true for all solids when $\Delta T \ll T$. In this case the flow of heat is described by:

$$\left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \cdot \kappa = \rho C \frac{\partial T}{\partial t} \quad \text{(A.1)}$$

where $\rho$ is the density of the solid and $C$ its specific heat. This equation can be simplified to

$$\nabla^2 T - \frac{1}{D} \frac{\partial T}{\partial t} = 0 \quad \text{(A.2)}$$

where $D = \kappa/\rho C$ is the thermal diffusivity.

In cylindrical coordinates the Laplace operator becomes

$$\nabla^2 T = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2}. \quad \text{(A.3)}$$
Because of the symmetries of an infinite half cylinder there is no temperature gradient along \( z \) or \( \Theta \). The latter is not true at the surface of the half cylinder. But with adiabatic boundary conditions there is no heat flow perpendicular to the surface. Thus Eq. A.3 simplifies to

\[
T'' + \frac{1}{r} T' - \frac{1}{D} \frac{\partial T}{\partial t} = 0
\]  
(A.4)

where the annotation was changed (\( \partial / \partial r \equiv ' \)). Now we seek periodical solutions of the form \( T = T_0 + \Delta T \exp(i2\omega t) \). Then Eq. A.4 becomes

\[
T'' + \frac{1}{r} T' - \frac{i2\omega}{D} \Delta T = 0.
\]  
(A.5)

The constant temperature \( T_0 \) has no effect on the derivatives: \( T' \to (\Delta T)' \) and \( T'' \to (\Delta T)'' \). With the substitution \( \tilde{r} = \sqrt{i2\omega/D} r \) we obtain

\[
\tilde{r}^2 (\Delta T)'' + \tilde{r} (\Delta T)' - (\tilde{r}^2 + 0) \Delta T = 0
\]  
(A.6)

which is the modified Bessel differential equation. The general solution to Eq. A.6 is

\[
(\Delta T)(\tilde{r}) = A \cdot I_0(\tilde{r}) + B \cdot K_0(\tilde{r})
\]  
(A.7)

where \( I_0 \) and \( K_0 \) are the modified Bessel functions [Bronstein99]. Since \( I_0(\tilde{r}) \to \infty \) as \( r \to \infty \) we must have \( A = 0 \). Now we resubstitute \( r \) for \( \tilde{r} \) and obtain

\[
\Delta T(r) = B \cdot K_0 \left( \sqrt{\frac{i2\omega}{D}} r \right).
\]  
(A.8)

Since the heater line in the 3\( \omega \)-experiment is of finite width \( w \) this solution can only be applied where \( r \gg w \). The characteristic length \( \sqrt{D/2\omega} \) is referred to as "thermal wavelength". In the limit of \( \sqrt{D/2\omega} \gg r \) the modified Bessel function can be approximated as

\[
K_0 \left( \sqrt{\frac{i2\omega}{D}} r \right) = -\frac{1}{2} \ln(2\omega) + \frac{1}{2} \ln \left( \frac{D}{r^2} \right) + \ln 2 - C_E - \frac{i\pi}{4}
\]  
(A.9)

where \( C_E \simeq 0.5772 \) is Euler’s constant. In the experiment a wire of length \( l \) is heated with a power \( P \). The heating power per unit length \( P/l \) results in a radial heat flow \( \kappa \cdot \frac{\partial}{\partial r} \Delta T \). From this we obtain that \( B = P/l\pi \kappa \) and thus

\[
\Delta T(r) = \frac{P}{l\pi \kappa} \left( -\frac{1}{2} \ln(2\omega) + \frac{1}{2} \ln \left( \frac{D}{r^2} \right) + \ln 2 - C_E - \frac{i\pi}{4} \right).
\]  
(A.10)

To determine \( \kappa \) from Eq. A.10 we have to measure \( \Delta T \). Therefore, it will be shown in the following that the wire not only acts as heater but can be used as thermometer as
well. Above low temperatures, typically 50 K, the resistance of the metal heater lines show a linear temperature dependence

\[ R = R_0 + \frac{dR}{dT} \Delta T. \]  

(\ref{eq:linear_temperature_dependence})

For a small periodic current \( I = I_0 \sin(\omega t) \) the power dissipated in the line can be calculated neglecting the temperature dependence of the resistance:

\[ P = RI^2 = \frac{1}{2} P_0 - \frac{1}{2} P_0 \cos(2\omega t) \]  

(\ref{eq:power_dissipation})

where \( P_0 = R_0 I_0^2 \). The dissipated power results in heating of the metal line and hence in the same time dependence of the resistance

\[ R = R_0 - \Delta R \cos(2\omega t) \]  

(\ref{eq:resistance_temperaturedependence})

where \( \Delta R \) depends on several parameters of the experiment, i.e. the power, the frequency, the thermal contact between line and sample etc.. The voltage along the metal line is then

\[ V = RI = R_0 I_0 \sin(\omega t) - V_{3\omega} \sin(3\omega t) \]  

(\ref{eq:voltage})

where \( V_{3\omega} := \frac{1}{2} \Delta R I_0 \) is the \( 3\omega \)-voltage. When \( V_{3\omega} \) is measured the temperature difference \( \Delta T \) can be calculated

\[ \Delta T = 2 \frac{dT}{dT} \frac{V_{3\omega}}{I_0}. \]  

(\ref{eq:temperature_difference})

Using this result in Eq. \ref{eq:kappa_equation} and we obtain the following equation for the thermal conductivity

\[ \kappa = \frac{RI_0^3}{2\pi l V_{3\omega}} \frac{dR}{dT} \left( -\frac{1}{2} \ln(2\omega) + \frac{1}{2} \ln \left( \frac{D}{\tau^2} \right) + \ln 2 - C_E - \frac{i\pi}{4} \right). \]  

(\ref{eq:kappa})

Now, either the real or the imaginary part of the temperature oscillations \( \Delta T \) can be used to determine the thermal conductivity. The imaginary part (the out-of-phase oscillations) gives the thermal conductivity directly, but it is found experimentally that the slope of the real part (the in-phase oscillations) versus \( \ln(\omega) \) is a more reliable measure. In addition the latter is insensitive to a boundary resistance which only would produce a frequency independent correction to Eq. \ref{eq:kappa_equation}. Therefore \( \kappa \) is determined from the slope \( dV_{3\omega}/d\ln \omega \) by

\[ \kappa = \frac{RI_0^3}{4\pi l} \frac{d\ln(\omega)}{dV_{3\omega}} \frac{dR}{dT}. \]  

(\ref{eq:kappa_slope})
APPENDIX

B

Symbols

\( \alpha \)  
linear thermal expansion coefficient

B  
magnetic flux density

\( \beta \)  
thermoelectric material parameter

C  
heat capacity

\( C_E \)  
Euler's constant

\( \gamma \)  
Grüneisen parameter

D  
thermal diffusivity

d_{rat}  
distance between rattling atoms

\( \delta \)  
average atomic distance in a crystal

e  
electron charge

E  
energy

\( E_a \)  
activation energy

\( E_F \)  
Fermi energy

\( E_g \)  
energy gap

\( \varepsilon \)  
reduced Fermi energy

\( \eta \)  
efficiency

f  
distribution function of the charge carriers

\( F_i \)  
Fermi integral

g  
density of state function of the electrons

h  
Planck constant

\( \hbar \)  
h/2\( \pi \)

I  
electric current

j  
electric current density

k  
wave vector, electrons and neutrons

\( k_B \)  
Boltzmann constant

\( \kappa, \kappa_{\text{tot}} \)  
thermal conductivity (total)

\( \kappa_{\text{el}} \)  
thermal conductivity (electronic contribution)

\( \kappa_{\text{lat}} \)  
thermal conductivity (lattice contribution)

\( \kappa_{\text{min}} \)  
theoretical minimum of thermal conductivity
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>l</td>
<td>length</td>
</tr>
<tr>
<td>L</td>
<td>Lorentz number</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>thermal penetration depth</td>
</tr>
<tr>
<td>m</td>
<td>mass</td>
</tr>
<tr>
<td>$\bar{M}$</td>
<td>average atomic mass</td>
</tr>
<tr>
<td>$m^*$</td>
<td>effective mass of a charge carrier</td>
</tr>
<tr>
<td>$m^*_e$</td>
<td>inertial effective mass</td>
</tr>
<tr>
<td>$m^*_d$</td>
<td>density of states effective mass</td>
</tr>
<tr>
<td>$\mu$</td>
<td>mobility</td>
</tr>
<tr>
<td>n</td>
<td>electron concentration</td>
</tr>
<tr>
<td>$N_{at}$</td>
<td>number of atoms per unit cell</td>
</tr>
<tr>
<td>$N_V$</td>
<td>number of equivalent valleys in the band structure</td>
</tr>
<tr>
<td>$\nu$</td>
<td>frequency</td>
</tr>
<tr>
<td>p</td>
<td>hole concentration</td>
</tr>
<tr>
<td>P</td>
<td>power</td>
</tr>
<tr>
<td>$\mathbf{q}$</td>
<td>phonon wave vector</td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>heat flow</td>
</tr>
<tr>
<td>R</td>
<td>molar gas constant or resistance</td>
</tr>
<tr>
<td>r</td>
<td>scattering parameter</td>
</tr>
<tr>
<td>$R_H$</td>
<td>Hall coefficient</td>
</tr>
<tr>
<td>$r_H$</td>
<td>Hall factor</td>
</tr>
<tr>
<td>$\rho$</td>
<td>electrical resistivity</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>mass density</td>
</tr>
<tr>
<td>S</td>
<td>thermopower</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>electrical conductivity</td>
</tr>
<tr>
<td>$\sigma_{\text{SB}}$</td>
<td>Stefan-Boltzmann constant</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>melting point</td>
</tr>
<tr>
<td>$\tau$</td>
<td>relaxation time</td>
</tr>
<tr>
<td>$\Theta_D$</td>
<td>Debye temperature</td>
</tr>
<tr>
<td>$U$</td>
<td>weighted mobility or atomic displacement parameter</td>
</tr>
<tr>
<td>$v$</td>
<td>electron velocity or sound velocity</td>
</tr>
<tr>
<td>V</td>
<td>electric potential</td>
</tr>
<tr>
<td>$V_{3\omega}$</td>
<td>third harmonic in the electric potential</td>
</tr>
<tr>
<td>$V_c$</td>
<td>volume of the unit cell</td>
</tr>
<tr>
<td>w</td>
<td>heat current density</td>
</tr>
<tr>
<td>X(element)</td>
<td>electronegativity of an element</td>
</tr>
<tr>
<td>z</td>
<td>density of state function of the phonons</td>
</tr>
<tr>
<td>Z</td>
<td>material thermoelectric figure of merit</td>
</tr>
<tr>
<td>ZT</td>
<td>(dimensionless) thermoelectric figure of merit</td>
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</tbody>
</table>
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