

DIPLOMA THESIS

Thermoelectric properties of novel Cu₃Au-structure-type intermetallic compounds and alloys

under supervision of

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Vienna, December 18, 2024



Abstract

This diploma thesis investigates thermoelectric properties of novel Cu₃Au-structuretype intermetallic compounds and alloys, to demonstrate the enhanced thermoelectric performance of metallic systems due to *s*-*d* scattering of conduction electrons on narrow features in the electronic density of states near to the Fermi energy. Such narrow features originate from unfilled *d*-shells (e.g. Ni-3*d* states) of transition metal elements. High Seebeck coefficients can be achieved by combining mobile *s*-electrons and immobile *d*-electrons. Thus, a dramatically enhanced thermoelectric performance results. Besides, intermetallics generally exhibit much better mechanical properties and stability, when compared to classical thermoelectrics like Bi_2Te_3 . In this diploma thesis, the following intermetallics have been characterized:

- Ni_{3.05}Sb_xSi_{0.95-x}
- Pd₃Sn_{0.95}In_{0.05}
 Ni_{3.05-x}Cu_xSi_{0.95}
 - $Pt_3Sn_{0.95}Sb_{0.05}$
- Ni_{3-x}Cu_xGe • Ni_{2.95}Ag_{0.05}Ge
- Ni_{3-x}Cu_xAl

Ingots of about 2.5 g were prepared by induction melting and annealed for seven days at 973 K to achieve homogeneous samples.

The crystal structure and lattice parameters were examined and confirmed using X-ray diffraction, which was also applied to check the amount of impurity phases. The temperature-dependent resistivity, $\rho(T)$, and Seebeck coefficient, S(T), were measured across a wide temperature range from 4 K to 873 K, enabling the calculation of the temperature-dependent power factor, $PF(T) = \frac{S^2(T)}{\rho(T)}$.

The alloy Ni_{2.9}Cu_{0.1}Ge emerged as the most promising material, exhibiting complete solubility from x = 0.0 to x = 0.1, the Cu₃Au crystal structure, and an exceptionally high power factor of $PF = 8.5 \text{ mW}/(\text{m} \cdot \text{K}^2)$ at room temperature. This result was closely followed by Ni_{2.95}Cu_{0.05}Ge, with $PF = 8.3 \text{ mW}/(\text{m} \cdot \text{K}^2)$.

When compared to the widely studied thermoelectric material Bi_2Te_3 , which has a room-temperature power factor of $PF \approx 4 \text{ mW}/(\text{m} \cdot \text{K}^2)$, $Ni_{2.9}Cu_{0.1}Ge$ exhibits an almost $\approx 50\%$ higher power factor.



Zusammenfassung

In dieser Diplomarbeit werden die thermoelektrischen Eigenschaften neuartiger intermetallischer Systeme mit Cu₃Au-Struktur untersucht, um die verbesserte thermoelektrische Leistungsfähige von metallischen Systemen aufgrund der s-d-Streuung von Leitungselektronen an schmalen Strukturen in der elektronischen Zustandsdichte nahe der Fermi-Energie zu demonstrieren. Solche schmalen Strukturen entstehen durch ungefüllte d-Schalen (z. B. Ni-3d-Zustände) von Übergangsmetallelementen. Durch die Kombination von beweglichen s-Elektronen und unbeweglichen d-Elektronen können hohe Seebeck-Koeffizienten erreicht werden. Dadurch ergibt sich eine drastisch verbesserte thermoelektrische Leistungsfähigkeit. Darüber hinaus weisen intermetallische Verbindungen im Vergleich zu klassischen Thermoelektrika wie Bi₂Te₃ im Allgemeinen viel bessere mechanische Eigenschaften sowie Stabilität auf. In dieser Diplomarbeit wurden die folgenden intermetallischen Verbindungen charakterisiert:

• $Ni_{3.05}Sb_xSi_{0.95-x}$

• Pd₃Sn_{0.95}In_{0.05}

- Ni_{3.05-x}Cu_xSi_{0.95} • Pt₃Sn_{0.95}Sb_{0.05}
- Ni_{3-x}Cu_xGe • Ni_{2 95}Ag_{0 05}Ge
- Ni_{3-x}Cu_xAl

Die Proben, mit jeweils 2,5 g, wurden durch Induktionsschmelzen hergestellt und anschließend sieben Tage bei 973 K getempert, um eine homogene Materialzusammensetzung sicherzustellen.

Die Kristallstruktur und Gitterparameter wurden mittels Röntgendiffraktion analysiert und bestimmt, einschließlich der Menge von möglichen Verunreinigungsphasen. Zusätzlich wurden der temperaturabhängige elektrische Widerstand $\rho(T)$ sowie der Seebeck-Koeffizient S(T) im Temperaturbereich von 4 K bis 873 K gemessen, um den temperaturabhängigen Powerfaktor $PF(T) = \frac{S^2(T)}{\rho(T)}$ zu bestimmen.

Unter den untersuchten Legierungen zeigte sich Ni_{2.9}Cu_{0.1}Ge als die vielversprechendste, da sie eine vollständige Löslichkeit, eine homogene Cu₃Au-Kristallstruktur und einen außergewöhnlich hohen Powerfaktor von PF = 8.5 $mW/(m \cdot K^2)$ bei Raumtemperatur aufwies. Direkt dahinter folgt Ni_{2.95}Cu_{0.05}Ge mit einem Powerfaktor von $PF = 8.3 \text{ mW}/(\text{m} \cdot \text{K}^2)$.

Das etablierte thermoelektrische Material Bi₂Te₃ erreicht bei Raumtemperatur lediglich einen Powerfaktor von $PF = 4 \text{ mW}/(\text{m} \cdot \text{K}^2)$. Damit übertrifft Ni_{2.9}Cu_{0.1}Ge diesen Wert um $\approx 50\%$ und positioniert es als äußerst vielversprechenden Kandidaten für thermoelektrische Anwendungen und unterstreicht das erhebliche Potenzial für die kommerzielle Nutzung.

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1 Introduction

This diploma thesis explores the thermoelectric properties of metallic alloys. Thermoelectric materials can generate an electric potential difference U (measured in volt, 1 V), from a temperature difference ΔT (measured in kelvins, 1 K), or vice versa. These properties cause numerous industrial applications, including microchip cooling, heat pump operation, thermoelectric generators that convert waste heat into electrical energy, and other uses relevant to the global challenge of climate change, rare resources, and energy crisis.[1]

This year (2024) the European Union's Copernicus Climate Change Service declared Sunday July 22^{nd} as the hottest day on record.[2] Consequently the UN Secretary-General released a statement highlighting the severe and rising impacts of global heatwaves, with record-breaking temperatures that endanger billions and deepen inequalities. There is an urgent need for action to protect vulnerable populations, particularly urban poor, children, and workers, by expanding low-carbon cooling solutions, and heat health warnings. The crisis underscores the need for innovations in sustainable materials and technologies to improve resilience against extreme heat. Major emitters and G20 nations are called to accelerate the transition from fossil fuels, shift subsidies toward renewable energy, and commit to actions aligned with limiting global warming to 1.5 K.[2]

The message is clear: unified, immediate action and advancements in climateresilient materials are crucial in combating the climate crisis.

Thermoelectric materials are potentially helpful in this respect; they are studied across condensed matter physics, materials science, engineering, and solid-state chemistry.

The fundamental phenomenon, underlying thermoelectric energy conversion in matter, is the Seebeck effect, discovered by the German physicist Thomas Johann Seebeck in 1821.[3] He found that when holding a compass needle close to an electric circuit, made of two different metals, the needle was deflected if one of the junctions had a higher temperature. In Seebeck measurements, the Seebeck coefficient S (in 1 V/K) is obtained. A temperature gradient ∇T is applied across a sample, and the induced voltage U is recorded under open-circuit conditions.[4]

$$S = \frac{\Delta U}{\Delta T} \tag{1.1}$$

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The performance of thermoelectric materials is quantified by the power factor PF (in 1 W/(m · K²)), it is proportional to the Seebeck coefficient and the electrical conductivity of a certain material, induced by a temperature gradient:[4]

$$PF = S^2 \cdot \sigma, \tag{1.2}$$

with the electrical conductivity σ (in units of $(\Omega \cdot m)^{-1}$). In thermoelectric transport theory, the thermoelectric efficiency is proportional to the figure of merit ZT, introduced by Edmund Altenkirch in the 20th century, which determines the maximum conversion ability of a thermoelectric material:[4]

$$ZT = \frac{S^2 \sigma}{\kappa_{Electron} + \kappa_{Phonon}} T.$$
 (1.3)

Here, $\kappa_{Electron}$ and κ_{Phonon} represent the electronic and phononic contributions to thermal conductivity, respectively. Assuming that mostly electrons contribute to thermal conductivity in metals, ZT can be simplified to: $ZT \approx \frac{S^2\sigma}{\kappa_{Electron}}T$.

The ratio of thermal conductivity κ to electrical conductivity σ is known as Lorenz number L in units of $1 \text{ W}\Omega/\text{K}^2$:

$$L \sim \frac{\kappa}{T\sigma}.\tag{1.4}$$

In kinetic gas theory, L has the value $L \approx 1.11 \times 10^{-8} \text{W}\Omega/\text{K}^2$. The Wiedemann-Franz law predicts that most metals have approximately the same value for this ratio, $L \sim 2.44 \times 10^{-8} \text{W}\Omega/\text{K}^2$. The discrepancy arises because the specific heat in metals is not $c_v = \frac{3}{2}k_B$ per electron, with the Boltzmann constant $k_B \sim 1.38 \cdot 10^{-23}$ J/K. This discrepancy is corrected by introducing Fermi statistics and the Pauli exclusion principle. Consequently, for metals, we find:

$$ZT = \frac{S^2}{L},\tag{1.5}$$

which indicates that ZT depends only on the Seebeck coefficient S. In Figure 1.1 the temperature dependent figure of merit ZT for common material classes can be found. At room temperature $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alongside with Bi_2Te_3 exhibit the highest ZT values, while at high temperatures SnSe dominates. It should be noted, however, that for practical thermoelectric applications, large average ZT values (between hot and cold sides) are much better suited, than large singular ZT values in a narrow temperature range.[3]

The reversed process of the Seebeck effect is called the Peltier effect, where running an electrical current through a material also transports heat. This effect is widely used in thermoelectric refrigeration devices to transfer heat from one object to another.[5]

Seebeck coefficients are temperature-dependent and, in the case of semiconductors, strongly dependent on doping with foreign atoms. Typical values for metals



Figure 1.1: Temperature dependent figure of merit ZT for various materials.[3]

range from 10^{-5} V/K to 10^{-6} V/K, whereas semiconductors can reach up to 10^{-3} V/K. This has driven historically increased research into semiconductor materials.

The maximum efficiency η_{max} of a thermoelectric device, involving the hot side T_H and the cold side T_C of the temperature gradient, is given by the power conversion efficiency of a thermoelectric device and determined by the material property Z,

$$\eta_{max} = \frac{T_H - T_C \sqrt{ZT + 1} - 1}{T_H (\sqrt{ZT + 1} + 1)},\tag{1.6}$$

as well as by the Carnot pre-factor.[6]

1.1 Thermoelectric materials and applications

As described in [7], thermoelectric devices utilize the Seebeck effect and the mobility of charge carriers in metals and semiconductors, which can transport charge and heat. These mobile charge carriers tend to move from the hot end to the cold end, resulting in a net accumulation of charge at the cold end and generating an electrostatic potential. Equilibrium is reached, when the driving diffusion balances the electrostatic repulsion, caused by the charge build-up. In thermoelectric devices (see Figure 1.2), multiple thermoelectric couples are connected. These couples consist of n-type (containing free electrons) and p-type (containing free holes) thermoelectric elements, wired electrically in series and thermally in parallel.

A thermoelectric generator harnesses heat flow across a temperature gradient to convert it into electrical power, which can drive an external load. The temperature difference generates a voltage via the Seebeck effect, while the heat flow drives the electric current in the context of voltage generated by the Seebeck effect, determining the power output. The maximum efficiency of a thermoelectric material, whether for power generation or cooling, is characterized by its figure of merit ZT, as defined in Equation 1.5. To maximize the ZT value of a material, the absolute value of the Seebeck coefficient S must be large, which is realized if there is only one type of charge carrier present, or else they cancel out the induced Seebeck voltages. Another possibility to increase the ZT value is through large electrical and low thermal conductivities.[7]



Figure 1.2: Thermoelectric module showing the direction of charge flow on both cooling and power generation.[7]

The effective mass m^* of a charge carrier is related to the inertial mass m_i and leads for $m^* > m_i$ to lower velocities for heavy carriers, resulting in smaller mobilities and, thus lower electrical conductivity. The correlation between the effective mass and the mobility depends on electronic structure, scattering mechanisms, and anisotropy. This results in a compromise of high mobility and low effective mass for the dominant charge carriers. Elements with small electronegative differences with narrow bands like ionic compounds frequently meet this condition.[7]

General requirements for thermoelectric materials, as defined in [8], is a high crystal symmetry, with gaps of the electronic bands near the Fermi level, or narrow d-like features.[9]

Good thermoelectric materials can also be found in materials with lower mobility and high effective mass polaron conductors, such as oxides and chalcogenides or high mobility and low effective mass semiconductors like SiGe an GaAs. The lowest thermal conductivities are found in glasses, where heat flows in terms of a random walk through a lattice. Amorphous materials have broad bands and increased electron scattering, leading to lower mobility and therefore are generally less suitable for thermoelectric materials because of their lack of the well-needed electron-crystal properties.[7]

Crystalline semiconductors have shown the best thermoelectric performance, concluding that optimal materials have phonon-glass, electron-crystal-like structures, as introduced by [8]. There are recent studies [7] on materials with ZT > 1 that resemble a phonon glass with an electron crystal structure and re-optimized carrier concentration. Another possibility is to use complex crystal structures.[7]

Enhancement of the thermoelectric efficiency and getting a large Seebeck coefficient S can be band tightening with increasing quantum confinement of the charge carriers or decreasing dimensionality from 3D towards 1D. It is also possible to increase the ZT value by creating heterostructures that nearly decouple the Seebeck coefficient and electrical conductivity by electron filtering.[7]

Other strategies rely on reducing the lattice thermal conductivity, involving the scattering of phonons within the unit cell by creating rattling structures or point defects, like interstitials, vacancies, or alloying.

Scattering phonons at interfaces is realized in composites for various length scales; thin films are also realizable. The exploitation of involving atomic disorder, to reduce the lattice thermal conductivity, has a long history and is being continued with alloying binary tellurides such as Bi_2Te_3 , Sb_2Te , PbTe and GeTe.[7]

One of the most researched thermoelectric material, mentioned in [10], is Bismuth-Telluride, Bi_2Te_3 , with a comparable high power factor PF of 4-5mW/ (m · K²) and $ZT \sim 1.0$ near room temperature, making it ideal for cooling devices and low-temperature power generation. Bismuth-Telluride has a rhombohedral crystal structure, characterized by layered planes of bismuth and tellurium atoms, contributing to its low thermal conductivity by effectively scattering phonons.[10]

Lead-Telluride PbTe, with its cubic rock-salt crystal structure, where lead and tellurium atoms alternate in a tightly packed arrangement, exhibits also a high power factor with $PF \sim 4-6 \text{ mW}/(\text{m} \cdot \text{K}^2)$ at high temperatures, $T \sim 700 \text{ K}.[10]$ That makes it well-suited for applications in automotive exhaust heat recovery and aerospace industries.

Clathrates are known for their low thermal conductivity, primarily due to strong phonon scattering. In these materials, phonon scattering occurs because of weakly bound electropositive elements within cage-like structures.[7] Skutterudites, which naturally occur as CoAs₃ in the Skutterud region of Norway, possess a bodycentered cubic crystal structure.[11] Similar to clathrates, skutterudites exhibit low thermal conductivity by creating void spaces through corner-sharing octahedra. These voids can be filled with "rattling" atoms that disrupt phonon transport. The highest ZT value was reported as $ZT \sim 2.2$ at 883 K [11], for commercial (Sm,Mm)_{0.15}Co₄Sb₁₂ powder, achieved after densification via high-pressure torsion.[11] [7] [12]

A material class that is one of the topics in the research on thermoelectric materials is constituted by full and half-Heusler compounds, discovered in 1901 by Fritz Heusler and others.[13] Heusler systems are ternary intermetallics and semiconductors, with more than 1000 members and compositions, involving research topics like novel magnetic properties, thermoelectrics, skyrmions, spintronics applications, unconventional superconductivity, topological properties, and martensitic phase transitions.

The most common crystal structure in the Heusler family is cubic, where full Heusler compounds X₂YZ crystallize in the cubic L21 structure, inhabiting four interpenetrating face-centered-cubic (fcc) sublattices. Full Heuslers have power factors up to 10 mW/ (m · K²).[9] Half-Heusler compounds are XYZ compounds, that are attractive for thermoelectric applications due to their large power factors, thermal and mechanical stability, and the use of inexpensive and earth-abundant elements. Alternative structural variations are characterized by structural distortions, variations in atomic site ordering, or variations in atomic layer stacking.[13] Half-Heusler of n- and p-type, reach maximum values of up to ZT = 1.5 around 800 K for the n-type compound $Zr_{0.5}Hf_{0.5})_{0.5}Ti_{0.5}NiSn_{0.994}Sb_{0.06}$ and the p-type compound Ta_{0.74}V_{0.1}Ta_{0.16}FeSb. The best p-type half-Heusler materials are based on FeNbSb, exhibiting a very high power factor of up to PF = 10.6 mW/ (m · K²).[14]

Thallium-based thermoelectric materials like Ag_9TITe_5 and Tl_9BiTe_6 have thermal conductivity as low as $0.23 \text{ W}(\text{m}\cdot\text{K})^{-1}$ at room temperature [7], that is a result of the extremely soft thallium bonding and its low elastic modulus. Zn_4Sb_3 has a high ZT value resulting from a low glass-like thermal conductivity, where 20% of the Zn atoms are on three crystallographically distinct interstitial sites. The Zn diffusion rates are similar to superionic conductors and are accompanied by local lattice distortions. An analysis of X-ray and neutron diffraction data shows disorder at multiple length scales.[7] Nanostructured materials like Graphene and Carbon Nanotubes [15] are also being explored at new frontiers in thermoelectric research. These materials present cutting-edge research opportunities to improve thermoelectric efficiency across various applications, with the ongoing challenge of enhancing their ZT values while maintaining high power factors.

This thesis focuses on a different Ansatz, i.e., considering metallic-like systems, exhibiting narrow *d*-band-like structures in the electronic density of states D(E) near the Fermi energy. The stoichiometric compound Ni₃Ge, taken as the source material, has demonstrated in previous studies a high thermoelectric power factor of $PF = 7.2 \text{ mW}/(\text{m} \cdot \text{K}^2)$.[9] This is believed to result from the energy-dependent scattering of charge carriers at states formed by 3*d* electrons near the Fermi energy.

The crystal structure of Ni₃Ge is shown in Figure 1.3; the red spheres represent Ge and the blue spheres represent Ni. It exhibits a face-centered cubic crystal structure with Wyckoff positions of Ge: 1a(0,0,0) and Ni: 3c(1/2,0,1/2), spacegroup 221. The black lines indicate the unit cell and the gray lines mimic the bonds.

To further investigate this material and increase the power factor, a series of quasibinary alloys have been synthesized by altering the electron count in the compound. Their structural and thermoelectric properties are experimentally evaluated and analyzed using phenomenological solid-state physics models.





The crystal structure of Ni₃Ge is a face-centered cubic. The red spheres represent Ge and the blue spheres represent Ni. Wyckoff positions of Ge: 1a(0,0,0) and Ni: 3c(1/2,0,1/2), spacegroup: 221 The black lines represent the unit cell, while the gray lines depict the bonds. Image is created by PowderCell 2.4



2 Theoretical Aspects

Historians suggest that humans began using metals like copper Cu around 8000 BC [5], and since then, these materials have found countless applications. In 1896, J. J. Thomson discovered the electron e^- , referred to as "corpuscles of charge" that can be extracted from metals. In 1900, Paul Drude used Boltzmann's kinetic theory of gases to describe the motion of electrons in metals, providing an understanding of metallic conduction. For electrons in an electric field **E**, represented by a vector field, the electric current vector \mathbf{j}_e is defined via [5][16]

$$\mathbf{j}_e = \sigma \mathbf{E}.\tag{2.1}$$

The electric conductivity σ ,

$$\sigma = \frac{e^2 \tau \cdot n}{m},\tag{2.2}$$

in $(\Omega \cdot m)^{-1}$, can be derived from the equation of motion $m\mathbf{v} = -e\tau \mathbf{E}$ in steady state with constant momentum.[5] The conductivity σ ("Drude formula") in Equation 2.2 depends on the number of charge carriers n, the magnitude of their charge e, the mass of the carriers m and the relaxation time τ . Metals have an almost fixed carrier concentration, and, in general, a temperature and energy-dependent relaxation time τ . In semiconductors, the carrier concentration is very sensitive to temperature. In general, n increases due to thermal excitations of charge carriers from the valence band across the energy gap into the conduction band. Doping semiconductors with foreign atoms can have an impact on n as well.[16]

Drude subsequently calculated the thermal conductivity κ (in Watts per meter-Kelvin, W/m·K, detailed expression in standard textbooks) due to mobile electrons, which is defined by the heat current \mathbf{j}_q as well as by a temperature gradient ∇T :[5]

$$\mathbf{j}_a = \kappa \cdot \nabla T. \tag{2.3}$$

Electrons that do not interact with each other, with the background crystal lattice, impurities, or anything else, are called "free". The probability that an eigenstate of energy E being occupied is given by the Fermi factor $n_F(\beta(E-\mu))$:[5]

$$n_F(\beta(E-\mu)) = \frac{1}{\exp(\beta(E-\mu)) + 1}$$
(2.4)

with the chemical potential μ and $\beta = k_B T$. This distribution has a step at the chemical potential at T = 0 K and for finite T smears over a range of energies of

width $k_B T$. The Fermi energy E_F is the chemical potential at T = 0. The Fermi temperature $T_F = E_F/k_B$ and the Fermi wavevector k_F is defined via

$$E_F = \frac{\hbar^2 k_F^2}{2m}.\tag{2.5}$$

In a continuum system, the Fermi energy is the energy of the uppermost occupied electron state.[16][5]

According to [16], electrons in an isolated atom move only under the influence of the atomic nucleus's force field. Electrons in solids, however, are affected by the nuclei of neighboring atoms and all other nuclei within the solid. Quantum mechanics suggests that each electron can directly or via tunneling, interact with all other atoms in the solid. At high atomic energy levels, the electron can tunnel freely in the solid and further, in the uppermost levels, where energies exceed potential barriers, move without tunneling.

A crystal, with certain edge lengths, possesses N electron states, consisting of the original electron states of the free atom. Pauli's principle allows for two electrons per state (spin \uparrow and spin \downarrow). In solids, each energy level of the free atom broadens into bands. Except for ionisation, the electrons are confined within the solid.[16]

2.1 Scattering Processes: Interactions, Mechanisms and Implications

Essential insights into the structure of atomic nuclei, and atomic shells, along with interactions originate from studies of scattering processes. When two particles collide with each other, they change their momentum \mathbf{p} and kinetic energy E_{kin} in the interaction region. Based on the laws of energy and momentum conservation, predictions about the post-scattering direction of the momentum \mathbf{p}' and pre-scattering momentum \mathbf{p} , can be made. The total energy of the scattering partners is conserved and is converted into other forms of energy, such as heat or potential energy E_{pot} . In non-relativistic mechanics this can be expressed by the energy law:[17]

$$\frac{p_1'^2}{2m_1'} + \frac{p_2'^2}{2m_2'} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + U.$$
(2.6)

- U = 0: Kinetic energy is conserved in *elastic scattering*, shared between the interacting particles.
- U < 0: Kinetic energy decreases in *inelastic scattering*, with some energy converted to thermal energy.
- U > 0: Kinetic energy increases in *superelastic scattering*, because at least one interaction partner had thermal energy before.

As discussed in [18], the scattering cross sections correspond in quantum mechanics to transitions between states. Non-relativistic transition rates Γ_{fi} are described by Fermi's golden rule

$$\Gamma_{fi} = 2\pi |T_{fi}|^2 D(E_i), \qquad (2.7)$$

which is not a trivial derivation. The transition rate Γ_{fi} from an initial state $|i\rangle$ to a final state $|f\rangle$, includes the density of states $D(E_i)$ (will be detailed in the following pages) and the transition matrix element T_{fi} , which results from the Hamiltonian that causes the transition H', in the limit where the perturbation is weak.[18]

$$T_{fi} = \langle f|H'|i\rangle + \sum_{j \neq i} \frac{\langle f|H'|j\rangle \langle j|H'|i\rangle}{E_i - E_j} + \dots$$
(2.8)

The outcome of a single scattering process, as described in [16], depends on the probability of an electron transitioning from a given state to an empty final state. The Boltzmann equation can determine the effects of the individual scattering events of transport properties. There, the state of the electron population is represented by the Fermi-Dirac distribution function. An electron that is scattered by a scattering center, like an impurity or a lattice defect, where on average its energy and momentum are randomized during the process, exhibits a relaxation time to equilibrium that is equivalent to the time between those scattering processes.[16]

Boltzmann's equation can be applied to describe transport properties. Here, a brief outline of the Boltzmann transport equation is provided; for a detailed treatment, see additional literature (e.g., [19][20]). It accounts for the interplay of external driving forces, diffusion, and dissipative effects from scattering processes:[19]

$$\frac{\partial f(\mathbf{r}, \mathbf{k}, t)}{\partial t} = -\mathbf{v} \cdot \nabla_{\mathbf{r}} f - \frac{e}{\hbar} \left(\mathbf{E} + \mathbf{v} \times \mathbf{B} \right) \cdot \nabla_{\mathbf{k}} f + \left(\frac{\partial f(\mathbf{r}, \mathbf{k}, t)}{\partial t} \right)_{\text{scatter}}.$$
 (2.9)

 $\frac{\partial f}{\partial t}$ corresponds to a local, direct dependence of the non-equilibrium distribution concerning time. The function f describes the deviation from the Fermi-Dirac distribution function f_0 , relaxing over a characteristic time τ_e , i.e. $f = f_0 + f_1$ with f_1 being rather small.

$$\left(\frac{df(E)}{dt}\right)_{scatter} = -\frac{f(E) - f_0(E)}{\tau_e}.$$
(2.10)

 $\mathbf{v} \cdot \nabla_{\mathbf{r}} f$ is a spatially dependent distribution function resembling a diffusion term, describing transport characteristics based on local temperatures and charge carrier concentration. The forces acting on the particle are described by

 $\frac{e}{\hbar} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} f$. In a stationary state, the concentration of charge carriers in a specific volume does not change, therefore it can be simplified to:[19]

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{diffusion}} + \left(\frac{\partial f}{\partial t}\right)_{\text{force}} + \left(\frac{\partial f}{\partial t}\right)_{\text{scatter}} = 0.$$
(2.11)

For a reciprocal vector scattered near the Brillouin zone boundary, as described in [5], a gap opens, and states with energies higher than the zone boundary intersection point, are pushed up in energy. Conversely, electrons with slightly lower energies than the zone boundary intersection point are pushed down in energy. In the nearly free electron model, the gaps are proportional to the periodic potential $|V_{\mathbf{G}}|$, with the reciprocal lattice vector

$$\mathbf{G} = \mathbf{k} - \mathbf{k}'.\tag{2.12}$$

The crystal momentum can be described via a periodic potential; therefore, the nearly free electrons can be represented by plane waves. This fact was confirmed by Felix Bloch in 1928 and described first by the mathematician Gaston Floquet in 1883.[5] An electron in a periodic potential has eigenstates of the form $\Psi^{\alpha}_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u^{\alpha}_{\mathbf{k}}(\mathbf{r})$ [16][19], with $u^{\alpha}_{\mathbf{k}}(\mathbf{r})$ being periodic in the unit cell and \mathbf{k} being the crystal momentum, both can be chosen within the first Brillouin zone. By solving, for example, the tight-binding Schrödinger equation for electron waves, the energy bands are obtained, containing eigenstates and gaps between bands.[5]

Figure 2.1 schematically visualizes the position of the Fermi energy E_F and the occupation of different bands for insulators and metallic conductors. Orange represents filled states, while yellow indicates empty states. Additionally, in semi-metals, the bands overlap, and E_F lies within a partially filled band. The highest occupied band is referred to as the valence band, while the lowest unoccupied band is known as the conduction band.[19]



Figure 2.1: Position of the Fermi level in the band scheme for insulators, metals, and semi-metals.

In a periodic potential, scattering centers cause a coherent diffraction pattern and are summed up in dispersion curves or band structure of the crystal. A perfect periodic potential, realized theoretically by an ideal crystal at absolute zero, does not exhibit electrical resistivity. This, along with the Bloch theorem, gives the reason for the low resistivity of very pure metals at low temperatures.[16]

As elaborated in reference [16], energy gaps or discontinuities, where the electron can not propagate in the lattice, occur at values of a k-vector, satisfying the Bragg reflection condition:[21]

$$2D \cdot \sin\left(\frac{\theta}{2}\right) = n \cdot \lambda. \tag{2.13}$$

D is the grating constant, θ the angle between incident and diffracted waves,



Figure 2.2: Schematic representation of Bragg diffraction.

and *n* the diffraction order. A schematic image is shown in Figure 2.2. Bragg diffraction in reciprocal space is realized by the diffraction vector (Equation 2.12) with the wave number vector **k** of the incident wave and **k'** of the diffracted wave. The wavelength λ of the radiation and the wave number vector **k** are related by $|\mathbf{k}| = 2\pi/\lambda$. Diffraction at periodic structures resembles elastic scattering at many individual atoms at location **r**. The relationship between the scattering amplitude \mathbf{E}_s and the incident amplitude \mathbf{E}_0 leads to the differential scattering cross section $\frac{d\sigma}{d\Omega}$. For example, for unpolarized X-rays, the \mathbf{E}_0 vector is on average evenly distributed in the x - y-plane of e.g. a powder sample and the averaging over all polarizations of the electric field, resulting in the differential scattering cross-section

$$\frac{d\sigma}{d\Omega} = r^2 \left(\frac{\mathbf{E}_s}{\mathbf{E}_0}\right)^2 = \frac{e^4}{c^4 \cdot m_e^2} \left(\frac{1 + \cos^2(\Theta)}{2}\right). \tag{2.14}$$

Semi-classically, the scattering atom consists of a positive nucleus, which hardly contributes to the scattered radiation due to its large mass and an electronic charge cloud. If the charge cloud of electrons is forced to vibrate without being hindered by atomic binding forces, the scattered waves from different parts of the electron shell overlap. When the electron shell absorbs an X-ray beam, inelastic scattering and energy loss occur.[21]

As outlined in [8], the electron-scattering process depends on the concentration of charge carriers and the mean free path between collisions, limited by scattering due to local distortions of the electronic potential.

In a perfect crystal, charge carriers are scattered only by thermal vibrations of the lattice. Acoustic modes and optical modes of the lattice vibrations distort the periodic potential. Electrons and holes located in different points in the Brillouin zone, experience changes in the wave function due to their interaction with these vibrations. Imperfect or impure crystals, experience other scattering processes, where impurity atoms act as scattering centers. For solid solutions, experimentally produced and measured in this work, alloy scattering needs to be added. Those materials, in addition, contain a substantial portion of *d*-elements, also called transition metal elements (e.g. Ni, Fe, Co, ...).[8]

As discussed in Reference [16], transition metals are generally divided into three groups, that have an incomplete 3d, 4d, or 5d-shell. In a solid, the *d*-shells expand to *d*-bands, forming a narrow energy band, compared to an *s*-band, due to a strong localisation of *d*-electrons and thus a reduced overlap of the *d*-electron-states of neighboring atoms. The properties of *d*-band electrons are inbetween the *s*-electron-states and very narrow levels of *f*-electrons e.g. in rare earth elements.[16]



Figure 2.3: Visualization of the schematic s- and d-band density of states D(E) (a) and calculated D(E) from [22] (b).

Figure 2.3 (a) schematically illustrates the s- and d-band structures of ferromagnetic Nickel (Ni), a 3d transition metal with 8 electrons in the d-shell (see Figure 3.1(a) for reference) of an isolated Ni atom. The density of states (DOS) for the s-band (blue line) follows the Sommerfeld model, given by $D(E) \propto \sqrt{E}$.[23]

In contrast, the DOS for the d-band (red line) is modeled frequently by a Lorentzian: [24][4]

$$D(E) \sim \frac{A}{1 + \frac{E - E_0^2}{\gamma}}$$
 (2.15)

A represents the peak amplitude, E_0 the resonance energy (center of the peak), and γ the peak width, commonly referred to as the half-width at half-maximum. The vertical black dashed line represents the Fermi energy of Ni, E_F at 13 eV. The calculated band structure of Ni (from [22]) is presented in Figure 2.3 (b).

In the 3d series from Sc to Ni, the *d*-band is progressively filled with electrons, causing the Fermi energy to shift from the bottom to the top of the *d*-band, while in Cu the d-level is full and lie below the Fermi energy. The different arrangements of the *d*-shell influence the crystalline potential and affect the electronic and magnetic properties of a material dependent on the density of states at the Fermi energy. A special feature of transition metals is that *s*-electrons can be scattered by supporting phonons into unoccupied states in the *d*-band, where the scattering probability is proportional to the total density of final states. This high density of final states leads to distinct resistivity features, as conduction electrons have a higher likelihood of scattering.[16]

Transition elements exhibit electronic bands that correspond to the ns and (n-1)d states of the free atom, where n is the principal quantum number of the outermost s electron [25](n = 4 for nickel and n = 5 for palladium). The energy required to scatter an electron from the s state to the d state is small, and the energy of an electron in the (n-1)d state is nearly the same as in the ns state. In our discussion of transition metals, the essential assumption is that the interaction energy between the d shells of neighboring atoms is small due to the limited overlap of their wave functions.

The s electrons are responsible for nearly all cohesion and binding in the solid. They change with temperature, by a small quantity, of the order of $k_BT/(binding energy per atom)$. Positive holes in the d band can contribute to conductivity and move freely through the lattice. However, due to reduced mobility, they take significantly longer to transition from one atom to the next, compared to s-electrons, making their contribution to conductivity relatively small. The density of states D(E) is large in the d band, allowing electrons to jump more frequently from the s to the d band than from one s state to another. Therefore the time of relaxation and thus of the mean free path is shorter and the conductivity smaller.[25]

2.2 Electrical Resistivity Models

Transport phenomena involve the movement of particles or heat driven by external forces or fields. When electric or magnetic fields interact with a temperature gradient in a material, a variety of transport coefficients arise. These coefficients can be analyzed using the temperature-dependent linearised Boltzmann equation, a semiclassical approach that relates a field-driven term to a scattering term. This model captures the dynamic equilibrium between the driving forces and the scattering interactions of charge or conduction carriers.[20]

The simplest expression for electrical resistivity ρ is given by the Drude formula

$$\rho = \frac{m}{ne^2\tau},\tag{2.16}$$

that is reciprocal to electrical conductivity σ (compare with Equation 2.2).[20]

The relaxation time τ for simple metals corresponds to the time it takes to traverse an electron over a certain mean free path l between successive scattering events, determined mainly by:

- scattering processes of conduction electrons on static lattice imperfections like impurity atoms, grain boundaries,...
- scattering of the conduction electrons on thermally excited lattice vibrations (phonons)

If both processes are considered to be independent from each other, Matthiesens's rule can be applied; τ follows then from

$$\frac{1}{\tau} = \sum \frac{1}{\tau_i} = \frac{1}{\tau_0} + \frac{1}{\tau_{ph}}.$$
(2.17)

 τ is responsible for both the magnitude and the temperature dependence of the electrical resistivity $\rho(T)$, in simple metals given by

$$\rho(T) = \rho_0 + \rho_{ph}(T). \tag{2.18}$$

The linearised Boltzmann equation, in terms of variational type calculations, due to the electron-phonon interaction leads to the Bloch-Grüneisen equation

$$\rho_{ph} = c_2 \Theta_D \left(\frac{T}{\Theta_D}\right)^5 \int_0^{\frac{\Theta_D}{T}} \frac{z^5 dz}{(\exp(z) - 1)(1 - \exp(-z))}.$$
 (2.19)

 c_2 is the temperature independent interaction strength of the conduction electrons with thermally excited phonons. The following approximations are involved:

- variation type calculation to lowest order
- lattice vibrations with a sound velocity v_s are described by the Debye model

- no Umklapp processes are considered
- coupling of electrons with longitudinal phonons only
- spherical Fermi-surface
- the first Brillouin zone is approximated by a Debye-sphere with radius q_D

If temperatures are much smaller or larger, then the Debye-temperature Θ_D , the Debye-integrals can be expanded, resulting in:[20]

- $z \ll 1...T \gg \Theta_D$, high temperatures: $\rho_{ph}(T) \approx \frac{c_2}{4}T$
- $z \gg 1...T \ll \Theta_D$, low temperatures: $\rho_{ph}(T) \approx \frac{124.4 \cdot c_2}{\Theta_D} \left(\frac{T}{\Theta_D}\right)^5$

2.2.1 Deviation from linear temperature dependence

At high temperatures, from room temperature and beyond, the resistivities of *d*elements Pd and Pt deviate from the linear temperature dependence as expected from Equation 2.19.[16] As stated in [26], for certain metals, when the temperature is above the Debye characteristic temperature Θ , the ideal resistivity due to electron-phonon interaction follows from the Bloch-Grüneisen equation, i.e., $\rho_{ph} = KT/\Theta^2$ for high temperatures, where K is a constant. For transition metals in groups IV and VI, ρ increases more rapidly than linearly with temperature, while for those in groups III and V, ρ increases more slowly than linearly. Due to the linear lattice thermal expansion coefficient α in metals, the Debye temperature Θ of a metal should decrease with increasing temperature, with the Debye temperature Θ_0 at T = 0 K and the Grüneisen constant γ , following

$$\frac{1}{\Theta^2} = \frac{1}{\Theta_0^2} 1 + 6\alpha\gamma T. \tag{2.20}$$

Another mechanism for deviations of the linear temperature dependence can be explained by s(p)-d scattering to unoccupied d states under the influence of lattice vibrations. This is proportional to the density of states D(E) and its derivatives, concerning the electron energy E in the d band at Fermi energy E_F .[26]

Since the Fermi temperature of *d*-holes in Ni, Pd and Pt is low $(T_F \sim 4500 \text{ K})$, the contribution of T must be taken into account by higher order terms of $\left(\frac{T}{T_F}\right)$. Since the quantity $\frac{df_0}{dE}$ (compare Equation 2.10) can not be treated as a δ -function anymore, it leads to the additional term $(1 - AT^2)$.[16]

Based on equation 2.20, the ideal resistivity ρ_i for $T > \Theta$ follows then from:[26]

$$\rho_i = \frac{K}{\Theta_0^2} T (1 + 6\alpha \gamma T) (1 - AT^2).$$
(2.21)

the parameter A is calculated as [16][26]

$$A = \frac{1}{6} (\pi k_B)^2 \left[3 \left(\frac{1}{D(E)} \frac{dD(E)}{dE} \right)^2 - \frac{1}{D(E)} \frac{d^2 D(E)}{dE^2} \right]_{E_F}.$$
 (2.22)

The magnitude and sign of A depends on the individual shape of the density of states in a specific metal and has for example in parabolic bands, the form $A = \frac{1}{6} \frac{\pi^2}{T_F^2} . [16]$

These relations determine that transition metals with Fermi energy E_F close to a maximum position of the density of states D(E) exhibit a positive value of A and thereby a negative deviation. If the Fermi energy E_F is close to a minimum of the density of states D(E), the resistivity $\rho(T)$ deviates positively.[26] The trajectory of D(E) influences the resistivity and has to be considered in a range of k_BT around the Fermi level. Analyzing the temperature dependent electrical resistivity of delement based materials the Bloch-Grüneisen equation can be used, together with the T^3 term of Equation 2.21, i.e.,

$$\rho(T) = \rho_0 + \rho_{BG} + A \cdot T^3. \tag{2.23}$$

The term $A \cdot T^3$ in Equation 2.23 is known in literature as Mott-Jones term.[20]

2.2.2 Hopping Conductivity

Several families of metallic solids exhibit upon decreasing temperature an increasing resistivity $\rho(T)$. Many of them can be accounted for in terms of hopping conductivity, $\sigma_{hc}(T)$, derived by Sir Nevill Francis Mott [27]

$$\sigma_{hc}(T) = \sigma_0 \cdot \exp\left(\frac{-A}{T}\right)^{\frac{1}{4}}.$$
(2.24)

 σ_0 is a material constant and A resembles a characteristic temperature of the system. This phenomenon describes the electrical transport at low temperatures, where the material is characterized by substantial disorder. The width of the hopping conductivity regime is in general related to the amount of atomic disorder in the unit cell. In such a scenario, the wave function of charge carrying electrons is spatially confined in a very small region of the whole crystal. This results in the inability of the electrons to diffuse at T = 0 and thereby being in an almost insulating state, while electrons for T > 0 diffuse only by thermal activation due to phonons. The temperature-independent background contribution is minded by using $\rho(T) = \rho_0 + \rho(T)_{hc}$, with ρ_0 being the residual resistivity and $\rho(T)_{hc} = 1/\sigma_{hc}$. Hopping conductivity can be visualized by plotting σ on a logarithmic scale versus $T^{\frac{-1}{4}}$, revealing a linear trajectory, if Equation 2.3 is fulfilled for the material considered.[27]

2.2.3 Kondo Effect

In the early 1930-ties, Netherland physicists observed upon cooling of some simple metals an unexpected increase of the respective electrical resistivity $\rho(T)$ as the temperature moved towards zero. Overall, a local minimum in $\rho(T)$ at finite temperatures is formed; below this minimum, $\rho(T)$ starts to increase logarithmically, i.e. $\rho \propto -\ln(T/T_0)$, with T_0 being a characteristic temperature.[28] For $T \to 0$, however, $\rho(T)$ tends towards a constant value (i.e., the unitarity limit).

Within a couple of years, these scientists figured out that those simple metals (e.g., Cu) were polluted by statistically distributed diluted magnetic impurities like Mn, Fe or Co. Only those samples exhibited the logarithmic resistivity features, while pure simple metals arrived at the expected residual resistivity. Several properties could be identified subsequently:[28]

- The low temperature resistivity anomalies result from magnetic impurities.
- The depth of the resistivity minimum $(\Delta \rho = \rho(T = 0) \rho_{min})$ turned out to be proportional to the impurity concentration.
- The absolute minimum resistivity value ρ_{min} is also proportional to the impurity concentration; thus $\Delta \rho / \rho_{min}$ is concentration independent.
- The temperature of the resistivity minimum is almost independent on the impurity concentration.

These observations indicate that this phenomenon is not due to interactions between magnetic moments of the 3d elements. Rather, these moments appear to be locally isolated from each other.

It took more than 30 years before J. Kondo in 1964 was able to describe these observations for the first time, based on a perturbation-type calculation of the so-called Heisenberg Hamiltonian, i.e,[28]

$$H = -2J\vec{s}\vec{S}.\tag{2.25}$$

J is the exchange integral and can be treated simply as a constant. Kondo found that by considering not only first-order, but also second-order scattering processes, the scattering of the conduction electron with spin \vec{s} by magnetic impurities with spin \vec{S} becomes temperature dependent. In particular if J is negative, the resistance due to this scattering falls logarithmically as the temperature rises.

In a microscopic picture, this scattering involves an intermediate state with a spin-flip process and thus a spin singlet state is formed, i.e., both \vec{s} and \vec{S} are arranged anti-parallel. As a consequence, the magnetic moment of this quasi-particle becomes zero, i.e., the system becomes non-magnetic below a characteristic temperature T_{Kondo} . Due to this modification from magnetic to non-magnetic, the system gains energy of the order of $k_B T_{\text{Kondo}}$.[28] This non-magnetic singlet state is separated by an energy $k_B T_{\text{Kondo}}$ from the magnetic triplet state, i.e., both spins are parallel. The interaction process is known as the *Kondo effect*.

The origin of the Kondo effect is therefore an energy gain of the order of $k_B T_{\text{Kondo}}$ owing to the formation of a non-magnetic ground state. The Kondo effect not only influences the temperature dependent electrical resistivity, but also many other physical quantities and causes e.g., a crossover of the magnetic susceptibility from Curie - Weiss behavior at high temperatures to Pauli susceptibility at low temperatures. Note, the crossover temperature corresponds to T_{Kondo} . The Kondo temperature itself does not mark any physical phase transition of first or second order; it characterizes just a change of the regime (e.g., from magnetic to non-magnetic).[28]

2.3 Landauer's theory

Landauer's theory provides a unified framework for describing electronic and thermal transport in ordered and disordered metals. It accounts for various scattering processes, including electron interactions with grain boundaries, point defects, phonons, and other mechanisms in both crystalline and amorphous materials.

Temperature gradients induce gradients in the particle distribution function, driving the transportation of particles. The electronic transport induced by electric fields under isothermal conditions results in a gradient in the electron chemical potential $\nabla \mu = q \nabla U$ and induces a gradient in the electron occupation statistics. Consequently, high energy states near one contact result in a higher occupation than those near low energy states. This difference in electron occupation is the driving force to transfer electrons from one contact to another.[4]

Using Landauer's approach for an infinitesimal slice of bulk material, the current density J can be calculated, incorporating electrical conductivity σ , the Seebeck coefficient S, and contributions to thermal conductivity from both electrons and vibrational quanta.

Here, Landauer's theory for bulk materials can be applied, as it relates the current density J to the gradient in occupation ∇f induced by a gradient in chemical potential or temperature.[4]

$$J = -q \int_{-\infty}^{\infty} G(E) \nabla f dE \qquad (2.26)$$

G(E) represents an energy-dependent transport function, which is a combination of transport channels T(E) and their associated transition probabilities M(E). For crystalline materials, G(E) (see Figure 2.4) can be obtained from the band structure and scattering theory. The collective motion of all the particles at a given energy has to be taken into consideration. This is provided by the band structure, where all electrons or phonons are organized by energy in the reciprocal



Figure 2.4: Sommerfeld model of the average squared velocity $\langle v(E)^2 \rangle \sim E$, average of each particle scattering after a characteristic relaxation time $\tau(E) \sim E^{-1/2}$ and the density of states $D(E) \sim \sqrt{E}$ (compare equation 2.33)

space. Slopes of the band structure correspond to the group velocity $v_g = \partial E / \partial k$, with which each particle travels along the transport direction. With the average squared velocity $\langle v(E)^2 \rangle$ of the particles at a given energy, their collective transport with the density of states D(E) and the average of each particle scattering after a characteristic relaxation time $\tau(E)$, the energy-dependent transport function forms as [4]

$$G(E) = \langle v(E)^2 \rangle \tau(E) D(E).$$
(2.27)

The density of states D(E), as discussed in [23], represents the number of states within a given energy interval. It can be derived from the Sommerfeld model, which combines the Pauli exclusion principle with Fermi-Dirac statistics to describe the velocity distribution of free electrons. The macroscopic spatial volume $V = L^3$ of the crystal sample is assumed to contain a periodic lattice and is approximated by a three-dimensional potential well with an infinitely high energy threshold at all borders, in which the electron gas is confined. To determine possible energy levels, the Hamiltonian operator

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{2.28}$$

is constructed for an electron in the box potential $V(\mathbf{r})$ where V_0 is constant for $0 \le x, y, z \le L$ and $V = \infty$ otherwise. This energy operator H forms the Schrödinger equation in the eigenvalue equation $H\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$. Electrons in a vacuum, without boundary conditions, are represented by plane waves $\Psi(\mathbf{r}) = a \cdot \exp(i\mathbf{kr})$, yielding the energy eigenvalues and the dispersion relation

$$E = \hbar\omega = \frac{\hbar^2 k^2}{2m}.$$
(2.29)

Positive and negative **k** values result in linearly independent solutions, and the wave is normalizable for k = 0. Therefore, the possible states occupy the entire **k** space, represented as a grid of points with a spacing of $2\pi/L$, resulting in the reciprocal volume per state

$$V_k = \left(\frac{2\pi}{L}\right)^3. \tag{2.30}$$

The total number of states $N = V_{shell}/V_k$ within the interval k and k + dk, in a spherical shell with radius k and wall thickness dk, has the volume $V_{shell} = 4\pi k^2 dk$ in reciprocal space. Considering the two spin states \uparrow and \downarrow , the electron density of states gives the relation

$$dN = D(k)dk = 2 \cdot dN = 2 \cdot \frac{Vk^2dk}{2\pi^2}.$$
 (2.31)

For a material with N electrons, each occupying only one state, these electrons can fill the states at T = 0 K up to a maximum wave vector k_F , yielding:

$$N = \int_0^{k_F} D(k)dk = \frac{Vk_F^3}{3\pi^2}$$
(2.32)

Finally, the density of states D(E) as a function of energy, with the total electron density n = N/V, provides:[23]

$$D(E) = \frac{dn}{dE} = \frac{(2m)^{\frac{3}{2}}}{2\pi^2 \hbar^3} \sqrt{E}$$
(2.33)

To relate the spatial gradient of the occupation statistics $\nabla f = \partial f / \partial x$ to the spatial gradient of the electron chemical potential $\nabla \mu = \partial \mu / \partial x$, the current density induced by an applied voltage can be determined via [4]

$$\nabla f = \frac{\partial f}{\partial \mu} \frac{\partial \mu}{\partial x} \tag{2.34}$$

This, along with the Fermi factor $n_F(\beta(E-\mu))$ (see Equation 2.4), leads to the relation

$$\nabla f = -\frac{\partial f}{\partial E} \cdot \nabla \mu, \qquad (2.35)$$

resulting in a general current density equation that describes, how a material responds to an applied voltage:

$$J_{\nabla U} = -q^2 \nabla U \int_{-\infty}^{\infty} G(E) \frac{-\partial f}{\partial E} dE.$$
(2.36)

From Ohm's law (2.1) $\mathbf{j}_e = \sigma \mathbf{E} = -\sigma \nabla U$, one of the main properties that is of interest, the electric conductivity σ can be derived.

$$\sigma = q^2 \int_{-\infty}^{\infty} G(E) \frac{-\partial f}{\partial E} dE$$
(2.37)

This quantity is always positive, and the electron distribution function $(-\partial f/\partial E)$ determines the type of carriers involved in the transport process. When a temperature gradient is applied to a sample, it induces a gradient in the carrier occupation statistics. As the temperature increases, the carrier distribution function broadens around the electron chemical potential. Regions with higher temperatures have more electrons in high-energy states and fewer in low-energy states.[4]

According to the second law of thermodynamics, heat flows spontaneously from hotter to colder regions, driving high-energy electrons from hot to cold areas and low-energy electrons from cold to hot areas. The relation between the spatial gradient of the occupation statistics ∇f and the spatial gradient of the temperature ∇T is given by

$$\nabla f = \frac{\partial f}{\partial T} \cdot \nabla T = \frac{E - \mu}{T} \left(-\frac{\partial f}{\partial E} \right) \cdot \nabla T.$$
(2.38)

With these results, the Landauer solution for the current density induced from a temperature gradient is:

$$J_{\nabla T} = -q\nabla T \int_{-\infty}^{\infty} G(E) \left(\frac{E-\mu}{T}\right) \frac{-\partial f}{\partial E} dE.$$
(2.39)

The relation of the heat current \mathbf{j}_q (Equation 2.3) can be used to determine κ within the Landauer theory as:[4]

$$\kappa = q \int_{-\infty}^{\infty} G(E) \left(\frac{E-\mu}{T}\right) \frac{-\partial f}{\partial E} dE.$$
(2.40)

This is analogous to an Onsager coefficient that determines the current response from a temperature gradient. The current densities induced by temperature and voltage gradients are additive in the linear regime and are called the diffusion and drift currents,

$$J = J_{\nabla U} + J_{\nabla T} = -\sigma \cdot \nabla U - \kappa \cdot \nabla T.$$
(2.41)

The Seebeck effect in Landauer's theory, describes the generation of a voltage gradient ∇U by a temperature gradient ∇T in a material, with a net current density J = 0. The Seebeck coefficient S (Equation 1.1) is defined by a temperature gradient ∇T across a sample and the measurement of the induced voltage in an open-circuit condition. This is formally realized by the ratio of the voltage difference ΔU and the temperature difference ΔT :[4]

$$S = -\frac{d \cdot \Delta U}{d \cdot \Delta T} = \frac{\kappa}{\sigma} = \frac{\int_{-\infty}^{\infty} G(E) \left(E - \mu\right) \frac{-\partial f}{\partial E} dE}{q \cdot T \int_{-\infty}^{\infty} G(E) \frac{-\partial f}{\partial E} dE}.$$
(2.42)

0.0

Since σ and κ determine the material's response to a voltage gradient ∇U and a temperature gradient ∇T , the Seebeck coefficient S would have its largest value

if $\sigma = 0$. However, it is not feasible for a material to respond to a temperature gradient ∇T but not to a voltage gradient ∇U .

To classify the thermoelectric performance, a power factor PF (Equation 1.2) is introduced, which is proportional to the electrical conductivity and the Seebeck coefficient S^2 . With Equation 2.42, the power factor can be expressed as:[4]

$$PF = S^{2}\sigma = \frac{\left[\int_{-\infty}^{\infty} G(E) \left(E - \mu\right) \frac{-\partial f}{\partial E} dE\right]^{2}}{q \cdot T^{2} \int_{-\infty}^{\infty} G(E) \frac{-\partial f}{\partial E} dE}.$$
(2.43)

3 Auricuprid and Ni₃Ge

Cu and Au form, among others, the intermetallic compound Cu_3Au , which mostly occurs naturally with 40 % Au. It exhibits a face-centered-cubic crystal structure with Au atoms at the edges of the cube and Cu in the faces (compare also with Figure 1.3). In addition, it is harder than pure gold with a distinct red coloration. Known occurrences originate from hydrothermal veins and are poor in sulfur.[29]

The face-centered-cubic structure of Cu₃Au can be visualized as four interpenetrating simple cubic sublattices. Close to the structural ordering temperature $T \sim 663$ K, the gold atoms segregate onto one of the sublattices, showing shortrange order.[30]

The stoichiometric compound Ni₃Ge is an intermetallic compound, that is formed from the elements Ni and Ge. Ni₃Ge is a reference material in academic and industrial research due to its exceptional electronic, thermal, and mechanical properties. It has the fcc crystal structure (see Figure 1.3), which leads to its thermal and mechanical stability and is useful for applications under extreme conditions. The thermoelectric PF in the temperature range T = 500 K and T = 650 K is well above 7 mW/ (m · K²) [9] and therefore serving as a reliable benchmark for researching thermoelectric properties. Additionally, it is used to form low-resistivity contacts between metal and semiconductor components in integrated circuits.[9]

Both elements Ni and Ge are chemical elements in the fourth row of the periodic table of chemical elements. Doping or introducing foreign elements into Ni₃Ge through isoelectronic or non-isoelectronic substitution, maintains either a constant electron count or allow tuning of electronic properties, e.g., by shifting the Fermi energy (E_F) . This can potentially enhance the power factor PF (see Equation 1.2).

Figure 3.1 shows the relevant section of the periodic table, highlighting the elements involved in this study. In Figure 3.1 (a) the focus is on the electron configuration of chemical elements, where the rows represent the electron shells; the number represents the number of electrons in it. Figure 3.1 (b) displays the density of states (states/eV/atom) versus $E - E_F$ in units of eV, with the dashed line as Fermi energy (Equation 2.5).[22]

Research on cubic fcc Ni_xAu_{1-x} alloys in [22], with power factors $PF > 30 \text{ mW}/(\text{m} \cdot \text{K}^2)$, exceeding dramatically those of any other known bulk material from room temperature and above, has inspired the choice of compounds and alloys in this Diploma thesis. Outstanding properties are expected from a strongly

energy-dependent scattering rate τ , that is originating from a steep gradient of the electronic density of states from Ni d states around E_F . Similar DOS features can be found in several other 3d, 4d and 5d elements. The mobility remains high for conduction electrons above E_F , but s-type charge carriers are scattered into more localized unoccupied Ni d states near E_F .



Figure 3.1: Detailed periodic tables with electron configuration (a) density of states [22] (b).

- Nickel (Ni), is a hard, ductile transition metal with 28 electrons and has a 3d orbital along with a face-centered cubic (FCC) crystal structure. Its electron configuration is [Ar] $3d^84s^2$, and it belongs to the d-block of the periodic table.
- Germanium (Ge) is a hard and brittle metalloid with 32 electrons featuring a diamond crystal structure. It has an electron configuration of [Ar] $3d^{10}4s^24p^2$, including a 4p orbital.
- Silicon (Si) is a hard, brittle metalloid with 14 electrons and protons, crystallizing in a diamond cubic structure. Its electron configuration is [Ne] $3s^23p^2$, featuring a complete neon core.

- Antimony (Sb) is a brittle metalloid with 51 electrons and protons, crystallizing in a rhombohedral structure, with an electron configuration of [Kr] $4d^{10}5s^25p^3$ and a full krypton core.
- Copper (Cu) is a soft, malleable, and ductile transition metal with 29 electrons and protons. It has an FCC structure and an electron configuration of [Ar] $3d^{10}4s^1$.
- Silver (Ag) is a soft transition metal with 47 electrons and protons, also crystallizing in an FCC structure, with an electron configuration of [Kr] $4d^{10}5s^1$.
- Tin (Sn), is an element in the 4th main group has 50 electrons and protons. It crystallizes in a body-centered tetragonal (BCT) structure and has the electron configuration [Kr] $4d^{10}5s^25p^2$.
- Palladium (Pd) is in the main group a 5d transition metal with 46 electrons and protons, crystallizing in an FCC structure, with an electron configuration of [Kr] $4d^{10}$.
- Platinum (Pt), a soft transition metal is in the main group a 6d and has 78 electrons and protons, crystallizing in a BCT structure. Its electron configuration is [Xe] $4f^{14}5d^96s^1$.
- Indium (In), one of the softest metals, has 49 electrons and protons, with a BCT structure and an electron configuration of [Kr] $4d^{10}5s^25p^1$.
- Aluminium (Al) is a soft, ductile metal with 13 electrons and protons, crystallizing in an FCC structure. Its electron configuration is [Ne] $3s^23p^1$, featuring a complete neon core.


4 Experimental Results and Discussion

This experimental section summarizes all experimental studies and analyses obtained for several Cu_3Au -crystal structure-based binary materials, beginning with a detailed description of the experimental setup.

Concerning the thermoelectric properties of Cu₃Au-crystal structure-like systems discussed in Chapter 3, efforts were made to surpass the previously achieved power factors of $PF > 5 \text{ mW}/(\text{m} \cdot \text{K}^2)$, at the same time, to find thermoelectric materials that are affordable.

Therefore, element combinations were selected from transition metals with incomplete d-shells, forming binary compounds with metals or semi-metals. In these compounds, the transition metal elements and metals or semi-metals were alternately substituted with transition metals possessing complete d-shells.

Additionally, materials involving a ternary composition were conducted, guided by the mentioned considerations.

The samples include:

- Ni_{3.05}Si_{0.95}
- Ni_{3.05}Si_{0.9}Sb_{0.05}
- Ni_{3.05}Si_{0.85}Sb_{0.1}
- Ni_{3.0}Cu_{0.05}Si_{0.95}

• Ni_{2.9}Cu_{0.15}Si_{0.95}

- $Ni_{2.95}Cu_{0.1}Si_{0.95}$
- $Ni_{2.95}Cu_{0.05}Ge$
- $Ni_{2.9}Cu_{0.1}Ge$
- Ni_{2.95}Ag_{0.05}Ge
- Pd₃Sn_{0.95}In_{0.05}
- Pt₃Sn_{0.95}Sb_{0.05}

- Ni₂CuAl
- $Ni_{2.2}Cu_{0.8}Al$
- $Ni_{2.4}Cu_{0.6}Al$
- $Ni_{2.6}Cu_{0.4}Al$
- $Ni_{2.8}Cu_{0.2}Al$

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4.1 Experimental Setup

4.1.1 Synthesis and Characterization Measurements

The samples listed in the introduction of Chapter 4 were carefully prepared, with each 2.5 g, from the respective pure elements (Cu: 99.98%; Ni, Al, Sb, Ag, Pt, Pd: 99.99%; Sn: 99.998%). During this process, larger pieces were extracted from the raw element blocks, and dust or small fragments were avoided to minimize mass loss in the final product.

Mass measurements were conducted using a Sartorius scale (Serial No: ME235S-OCE 22707453), calibrated in July 2024. The masses of each element for the stoichiometric compounds are listed in Table 6.1 (measured in grams).



Figure 4.1: Schematic of a frequency induction furnace consisting of a water-cooled copper crucible enclosed by a quartz glass cylinder surrounded by a copper coil.

The experimental setup of the high-frequency induction furnace (see Figure 4.1) includes a water-cooled copper crucible enclosed by a quartz glass cylinder and surrounded by a copper coil, powered by a high-frequency generator. The melting process of the pure elements into alloys was performed several times under an argon 5.0 atmosphere inside the quartz glass cylinder, utilizing Faraday induction voltage

$$U_{induction} = -\frac{d}{dt} \int \boldsymbol{B} \cdot d\boldsymbol{A}$$
(4.1)

derived from the Maxwell equation $\nabla \times E = -\frac{dB}{dt}$, where **B** is the magnetic flux density (measured in tesla, T) and **A** is the copper coil area. The induced voltage generates a current in the metallic samples, producing irreversible Joule heat $P = I^2 \cdot R$ (measured in watt, W). Joule heating arises from an exchange of energy between electrons and the lattice, indicating the inelastic nature of the scattering process.[6][16]

All alloy samples were subjected to heat treatment, performed with a Naber industrial furnace (Model N7) in quartz glass cylinders, separated by glass wool. This procedure ensures a homogeneous distribution of elements within the ingots. The post-tempering masses are also listed in Table 6.1.

Basic structural characterization of the crystal is performed at room temperature by using X-ray diffraction (XRD) with a Panalytical AERIS DY992 diffractometer (Type: 9430 070 99991, Serial No.: 810–00519253). It has a peak position accuracy of 2 Θ , well below ± 0.02 2 Θ . For this analysis, parts of the samples were ground into a fine powder. With this method the diffraction condition $\mathbf{k} - \mathbf{k}' = G_{hkl}$ with $|\mathbf{k}| = \frac{2\pi}{\lambda}$ can be fulfilled by varying the direction between the incident (\mathbf{k}) and diffracted (\mathbf{k}') beam (compare with Chapter 2.1). The $\Theta - 2\Theta$ scan ensures that the detector is always at the same angle to the sample as the incident beam. This makes the diffractometer arrangement particularly suitable for diffraction intensity measurements with electronic counters, because there is an increase in intensity in weakly diverging X-rays with a certain spectral width. Small twists in the sample can cause different wavelength components of the beam to be diffracted to the same point in the focusing circle. The present measurement is based on a Cu-based X-ray tube, with a wavelength $\lambda \sim 0.124$ nm of the radiation, utilizing Bragg diffraction (compare Equation 2.13).

The XRD results of the crystalline powder samples are analyzed using the program PowderCell 2.4. Initially, the free parameters are minimized, typically reduced to only the lattice parameter. The fitting process employs Rietveld refinements, where the Bragg peaks are modeled using pseudo-Voigt functions, $I(\Delta\Theta)$. These functions approximate the Voigt profile by replacing the convolution with a linear combination of Gaussian and Lorentzian curves. This approach enables the fitting of X-ray diffraction profiles through a least-squares method, refining a theoretical line profile to match the measured data.

$$I(\Delta\Theta) = \begin{cases} I_{hkl} \cdot e^{-b \cdot \Delta\Theta^2}, & \text{for } \Delta\Theta^2 \leq \frac{\ln 2}{b} \\ \frac{0.5 \cdot I_{hkl}}{1 + b \cdot \Delta\Theta^2}, & \text{for } \Delta\Theta^2 \geq \frac{\ln 2}{b} \end{cases}$$
(4.2)

The line intensities, I_{hkl} , are connected to the full width at half maximum (FWHM) through the relation $b = \frac{2.772}{\text{FWHM}^2}$, where FWHM $= U \cdot \tan^2 \Theta + V \cdot \tan \Theta + W$; with U, V, and W as fitting parameters. The fitting process also includes the following parameters:

- Debye-Waller factor: Describes an overall temperature-dependent factor accounting for atomic vibrations within the unit cell.
- Scale Factor: Determines the relative proportion of the phase within a mixture, affecting the overall intensity.
- Zero-Shift: Accounts for potential detector calibration errors, which are independent of the Bragg angle.
- Displacement: Corrects for misalignment of the sample, ensuring it is accurately centered in the diffractometer circle.

This process ensures precise modeling of diffraction patterns, enabling accurate structural characterization.(more details in PowderCell 2.4 instruction manual)

4.1.2 Transport Properties Measurements

For the measurement of the Seebeck coefficient S and the electric resistivity ρ of each sample, a power conversion efficiency measuring instrument (LOT.No.: 071082010, MFG.No.: ZA07-9609, Model: ZEM-3 (M10L)) from the company ULVAC-RIKO, INC is being utilized.

The procedure involved shaping the samples into rectangular rods using a diamond cup wheel (M1D08) on an Accutom-100 device from Struers GmbH. (Type: 06176127 and Serial No: 61710013).

The sample is clamped between the electrodes and in contact with probes A and B. Measurement of voltage ΔU and the temperature difference ΔT between probe A and probe B (see Figure 4.2) provides the relation of the Seebeck coefficient S

$$S = \frac{\Delta U}{T_B - T_A}.\tag{4.3}$$

Temperature and electromotive force are measured using probe A and probe B,



Figure 4.2: Conceptual diagram illustrating the measurement of the Seebeck coefficient S, where the sample is clamped between a hot and cold end and probes A and B measure the voltage ΔU .

where the measured temperature T_{measured} is

$$T_{\text{measured}} = \frac{T_A + T_B}{2}.$$
(4.4)

The sample resistivity $\rho = 1/\sigma$ is determined by measuring the current *I*, set with the constant current power supply and the voltage ΔU between wires *A* and *B*, where $R = \Delta U/I$. The uniform known cross-sectional area A_{cross} of each sample shape (see Table 6.2) and the distance d_{AB} between probe *A* and *B*, is needed to obtain the resistivity value [16]

$$R = R_{\text{Sample}} \cdot \frac{A_{\text{cross}}}{d_{AB}}.$$
(4.5)



Figure 4.3: Conceptual diagram for the measurement of the resistivity ρ where the sample is clamped between contacts that supply current and wires A and B measure the voltage ΔU from room temperature to 873 K.

The temperature-dependent resistivity $\rho(T)$ from 4 K to room temperature was measured using the 4-point method. Gold Au wires were attached to a rod-shaped sample using spot welding. A Schmidt Instruments power supply (UIP 1000 digital, Serial No.: 3/08) and a Zeiss microscope (Stemi 2000-C, Serial No.: 038-18835) ensured precise spot welding. The sample is glued to a circuit board, and the gold wires are soldered. The circuit boards are installed on the sample holder and a shield is placed above to block radiation heat. The sample holder is then placed in a bath cryostat filled with liquid ⁴He, cooling it to 4 K. The bath cryostat then warms up by heat exchange with ambient temperature and the measurement data are collected while slowly drifting to room temperature. The four-point probe method (see Figure 4.3) utilizes a fixed current I that passes through the outer wires and measures the voltage ΔU between the inner ones.

The elements and inventory used were provided by the working group at the Institute of Solid State Physics, TU Wien.

4.2 Optimization of off-stoichiometric $Ni_{3.05}Si_{0.95}$

This chapter presents the measurement and analyses data for off-stoichiometric compounds $Ni_{3.05}Sb_xSi_{0.95-x}$ and $Ni_{3.05-x}Cu_xSi_{0.95}$. Since Ni_3Ge exhibits excellent thermoelectric properties, there is a search for materials that are equally good in performance and more cost-efficient. For these reasons, Ge was exchanged for Si, also known for its conductive nature and affordability.

The compound Ni₃Si is indicated by the orange vertical line in the phase diagram shown in Figure 4.4, appears to be rather unstable and hard to obtain in single phase condition; thus giving the reason for the choice of off-stoichiometric compound Ni_{3.05}Si_{0.95}. The solidus and liquidus lines of Ni-Si exhibit several minima, indicating eutectic phases. In addition, there are 3 congruently melting phases. The solidstate equilibrium of Ni_{3.05}Si_{0.95}, is found next to the β_1 phase (green area), with a peritectoid formation at 1035 °C, as confirmed by optical, X-ray and differential thermal analyze (DTA) techniques.[31]

In this diploma work, $Ni_{3.05}Si_{0.95}$ was substituted on the Si side with Sb and on the Ni side with Cu, to modify the electronic band structure. Antimony being a



Figure 4.4: NiSi phase diagram with the orange vertical line marking Ni_3Si next to the solid-state of $Ni_{3.05}Si_{0.95}$ in the green area.[31]

metalloid, has a higher electron count and is used here to add electrons to increase the Fermi energy and probably raise the electrical conductivity and the Seebeck coefficient. Copper is also chosen for its metallic nature and high carrier mobility, intended to enhance the thermoelectric power factor.

4.2.1 Synthesis and Characterization

Two samples from the series $Ni_{3.05}Sb_xSi_{0.95-x}$ (x = 0.05 and x = 0.1), each weighing 2.5 g, were prepared by high-frequency induction melting (see Figure 4.1 in Chapter 4.1), with all elements fused simultaneously and inverted five times during each melting process. Similarly, three samples of $Ni_{3.05-x}Cu_xSi_{0.95}$ (x = 0.05, 0.1, and 0.15), each weighing 2.5 g, were synthesised using the high-frequency furnace method. All ingots were subjected to heat treatment, which was accomplished by tempering at 973 K for seven consecutive days.

In Figure 4.5, the X-ray diffraction patterns of each sample set, is presented normalized to the maximum intensity and shifted with increasing x by an offset of 10 % to obtain a better perspective. The red vertical lines mark the Miller indices, corresponding to the diffraction peaks of the crystal planes in the cubic Cu₃Au structure. Obviously, all samples substituted with Sb or Cu exhibit intensities corresponding to the Cu₃Au-type structure.



Figure 4.5: Normalized X-ray diffraction pattern for each sample of Ni_{3.05}Sb_xSi_{0.95-x} (a) and Ni_{3.05-x}Cu_xSi_{0.95} (b) shifted with increasing x by an offset of 10 %.

The X-ray diffraction patterns of Ni_{3.05}Sb_xSi_{0.95-x} (see Figure 4.5 (a)) confirm good solubility for x = 0.05, but already for x = 0.1 impurities appear between $2\Theta = 26^{\circ}$ and $2\Theta = 28^{\circ}$ and around the main peak at $2\Theta = 45^{\circ}$, indicating additional



Figure 4.6: Lattice parameter of $Ni_{3.05-x}Cu_xSi_{0.95}$ and $Ni_{3.05}Sb_xSi_{0.95-x}$ starting with $Ni_{3.05}Si_{0.95}$.

secondary phases in the sample. In contrast, $Ni_{3.05-x}Cu_xSi_{0.95}$ (see Figure 4.5 (b)) remains impurity-free up to x = 0.1, foreign phases emerge for x = 0.15 at $2\Theta = 43.9^{\circ}$, $2\Theta = 45.9^{\circ}$ and $2\Theta = 47.2^{\circ}$, along with an intensity shift in the range from $2\Theta = 20^{\circ}$ to $2\Theta = 39^{\circ}$.

The lattice parameters of the respective alloys, listed in Table 6.3, are determined via Rietveld refinement of the XRD patterns. The behavior of the lattice parameter of Ni_{3.05}Si_{0.95} is visualized in Figure 4.6, beginning with Ni_{3.05}Si_{0.95}, with the atomic radius of Ni being $1.24 \cdot 10^{-10}$ m and Si $1.11 \cdot 10^{-10}$ m. The contribution in steps of $\Delta x = 0.05$ from Sb, with an atomic radius of $1.40 \cdot 10^{-10}$ m, leads to a higher value of the lattice parameters of the samples, than those of Cu with an atomic radius of $1.28 \cdot 10^{-10}$ m. The gradient from light to dark color symbolizes increasing substitution. The Rietveld refinement results for the individual samples are presented in Figure 4.7. The initial fit parameters were derived from a face-centered cubic crystal structure, with Si positioned at 1a(0,0,0) and Ni at 3c(0,1/2,1/2), within the space group 221. Subsequently, Cu was incorporated proportionally at the 3c(0,1/2,1/2) position, while Sb was added at 1a(0,0,0).

The detailed examination reveals that for all samples the intensity count of the chosen fit function is higher in height and smaller in width of the main intensity peak, representing the crystal plane (111), than the measured pattern, alongside the (200) plane. The height of the peaks for planes (100), (110), and (220) is lower.

This observation can likely be attributed to the preferred orientation of grains within the material, which may have resulted from the mechanical stresses introduced during the grinding process of the ductile samples. The grinding process can cause plastic deformation, aligning the grains in specific orientations, which can affect the material's microstructure and influence its properties, such as anisotropy in thermal or electrical conductivity.



Figure 4.7: Normalized X-ray diffraction pattern for $Ni_{3.05}Si_{0.95}$ (a), $Ni_{3.05}Sb_xSi_{0.95-x}$ (c,e) and $Ni_{3.05-x}Cu_xSi_{0.95}$ (b,d,f) including the difference (red) between sample (blue) and fit function (black).

4.2.2 Transport Properties

A comparison of the source material Ni₃Ge with Ni_{3.05}Si_{0.95} is given in Figure 4.8, focusing on the temperature-dependent resistivity $\rho(T)$ (a) and the Seebeck coefficient S(T) (b).



Figure 4.8: Temperature-dependent resistivity $\rho(T)$ (a) and Seebeck coefficient S(T) (b) of Ni_{3.05}Si_{0.95} compared to Ni₃Ge. The solid and the dashed lines in (a) represent least squares fits according to Equations 2.21 and 2.23.

To qualitatively and quantitatively account for the temperature-dependent electrical resistivity, the Bloch-Grüneisen model (Equation 2.19), is considered. This model takes into account the interaction of electrons with thermally excited phonons, yielding a T^5 behavior at low temperatures and a *T*-linear behavior at high temperatures. A Mott-Jones term $A \cdot T^3$, as discussed in Chapter 2.2, is added to include the phonon-assisted scattering process of *s*-electrons into *d*-states of Ni/ Cu near to the Fermi energy. The solid and dashed lines in Figure 4.8 (a) represent least squares fits of the combined Ansatz as discussed above. Relevant equations are Eqn. 2.21 (solid line) and Eqn. 2.23 (dashed line). Fit parameters are summarized in Tables 6.7 and 6.8).

Excellent agreement is derived between the experimental data and the model utilized. In both cases, deviations from linearity of $\rho(T)$ are found. The analyses revealed, through the parameter A (discussed in Chapter 2.2.1), that for Ni₃Ge the Fermi energy E_F is near a minimum position of the density of states D(E); while in Ni_{3.05}Si_{0.95}, E_F is close to a maximum position of D(E) (compare with Table 6.7). Both models align well with each other and the measured data. Additionally, Ni_{3.05}Si_{0.95} exhibits a significantly higher $\rho(T)$ and a lower S(T) (Figure 4.8 (b)) compared to Ni₃Ge.

Figure 4.9 visualizes the measured temperature-dependent resistivity $\rho(T)$, the Seebeck coefficient S(T) and power factor PF(T) for Ni_{3.05}Sb_xSi_{0.95-x} and Ni_{3.05-x}Cu_xSi_{0.95} alloys.

The temperature-dependent resistivity $\rho(T)$ (see Figure 4.9 (a)), from room temperature to 873 K, of the Ni_{3.05}Sb_xSi_{0.95-x} alloys increases with higher Sb content, x = 0.05 and x = 0.1, while the Seebeck coefficient S(T) (see Figure 4.9 (b)) decreases with increasing substitution. This trend results in a decreasing power factor PF(T) (see Figure 4.9 (e)) of Ni_{3.05}Sb_xSi_{0.95-x}, with an increasing amount of Sb. The highest PF(T) is reached for Ni_{3.05}Si_{0.95} with 3.83 mW/ (m · K²) at $T \sim 600$ K, which is close to the values of PbTe, with 4 - 6 mW/ (m · K²) at $T \sim 700$ K [10].

In Figure 4.9 (c) the temperature-dependent electrical resistivity $\rho(T)$ is shown for the sample series Ni_{3.05-x}Cu_xSi_{0.95} for x = 0, 0.05, 0.1, 0.15. Initially an increase of the resistivity $\rho(T)$ is observed, but it returns to near-original $\rho(T)$ levels of Ni_{3.05}Si_{0.95} for x = 0.1 and x = 0.15. The Seebeck coefficient S(T), see Figure 4.9 (d) is similar for x = 0.05 and x = 0, but increases for x = 0.1. The sample with x = 0.15 is similar at room temperature to the one with x = 0.1, but changes its behavior with increasing temperature to x = 0 and x = 0.05. Overall, the Seebeck effect is negative, referring to electrons as principal charge carriers. The sample with x = 0.1 has a power factor at high-temperatures, similar to PbTe, exhibiting $PF = 4.78 \text{ mW}/(\text{m} \cdot \text{K}^2)$ at $T \sim 520 \text{ K}$ (Figure 4.9 (f)).

As already demonstrated for experimental data of Figure 4.8 (a), Equations 2.21 and 2.23 were used to account for the temperature-dependent resistivities of Figure 4.9. Results of least squares fits are shown again by solid and dotted lines. The fit parameters are provided in Table 6.7. All samples, except for Ni_{2.95}Cu_{0.1}Si_{0.95}, exhibit a positive parameter A and therefore a negative deviation from linearity, suggesting that the Fermi energy, E_F , is near a maximum in the density of states, D(E). The positive deviation, observed in Ni_{2.95}Cu_{0.1}Si_{0.95} indicates that E_F is near a minimum in D(E).

In both sample series, $Ni_{3.05}Sb_xSi_{0.95-x}$ and $Ni_{3.05-x}Cu_xSi_{0.95}$, the increasing resistivity $\rho(T)$ for increasing x values, is likely resulting from disorder due to alloying and impurity phases, constituting defects in the periodic crystal lattice (compare Figure 4.7), thus reducing the electrical and thermal conductivity.

Since doping of $Ni_{3.05}Si_{0.95}$ has not led to considerably better thermoelectric properties, this series can be closed for now.



Figure 4.9: Temperature-dependent resistivity $\rho(T)$ (a,c). Solid and dashed lines are showcasing fits according to Equations 2.21 and 2.23. Temperature-dependent Seebeck coefficient S(T) (b,d) and power factor PF(T) (e,f) for each sample of Ni_{3.05}Sb_xSi_{0.95-x} and Ni_{3.05-x}Cu_xSi_{0.95} from room temperature to 873 K.

4.3 Physical Properties of substituted Ni₃Ge

This chapter discusses the measurement $(0 \le x \le 0.1)$ and data evaluation of pseudo-binary intermetallics Ni_{3-x}Cu_xGe and Ni_{2.95}Ag_{0.05}Ge. Using copper as a dopant for its metallic properties and high carrier mobility, along with the introduction of silver in a new experiment, is expected to enhance electrical conductivity by utilizing silver's exceptional carrier mobility. According to the phase diagram shown in Figure 4.10, the β Ni₃Ge phase (green area) melts almost congruently at 1132 °C and exhibits phase width of about3%.[32]



Figure 4.10: NiGe phase diagram showcasing the solid state phase of Ni_3Ge in the green area.[32]

4.3.1 Synthesis and Characterization

When preparing Ni_{2.95}Ag_{0.05}Ge, Ag is pre-reacted with Ge by high-frequency melting, before the final product is synthesized. Similarly, for the two Ni_{3-x}Cu_xGe samples (x = 0.05 and x = 0.1), Cu was pre-reacted with Ge in the same manner to achieve homogeneous ingots.

In Figure 4.11 (a), the X-ray diffraction data of $Ni_{3-x}Cu_xGe$ can be found, normalized to the maximum intensity and shifted against each other with increasing xby an offset of 10 %. Likewise, Figure 4.11 (b) shows the X-ray diffraction data of $Ni_{2.95}Ag_{0.05}Ge$ for the core and the surface of the sample, in comparison to Ni_3Ge . Figure 4.11 (b) clearly reveals that the sample's surface area contains secondary phases, while the core exhibits a more homogeneous structure.

X-ray diffraction plots include Miller indices indicated by red vertical lines, at the reflection peaks of the preferred crystal planes of the Cu_3Au structure. For $Ni_{3-x}Cu_xGe$ all intensities fit the theoretically expected Bragg peaks, except for the (210) and (211) peaks that are completely missing in the experiment. The XRD results of $Ni_{2.95}Ag_{0.05}Ge$ for the core align with the Bragg peaks of the Cu_3Au structure, except for the absence of the (211) peak; several impurity peaks, however, are present.

The results from the Rietveld refinement for each sample are shown in Figure 4.11 (c,d,e). The obtained fit functions based on a face-centered-cubic-crystal structure, were calculated using Wyckoff positions; Ge at 1a(0,0,0) and Ni sharing the 3c(0,1/2,1/2) position proportional with one of {Cu,Ag}, within space group 221.

This reveals that for $Ni_{3-x}Cu_xGe$ the chosen fit function has a larger height that is smaller in width for the (111) peak. The (100) and (110) planes exhibit higher intensities, while the (220), (311), and (222) planes show lower peak intensities, as determined by the XRD results (Figure 4.11 (c) and (d)).

The Rietveld refinement for the Ni_{2.95}Ag_{0.05}Ge core in Figure 4.11 (e) shows the compliance with the cubic Cu₃Au crystal structure, but also foreign phases are found around the main peak. The fit function has a larger intensity at the (200) plane and is smaller for the intensity peaks of planes (220), (311), and (222). Like in chapter 4.2, this observation is likely due to the preferred orientation of grains and might originate from the grinding process of the ductile samples.



(e) Ni_{2.95}Ag_{0.05}Ge core

Figure 4.11: Normalized X-ray diffraction pattern for each sample of Ni_{3-x}Cu_xGe (a), Ni_{2.95}Ag_{0.05}Ge surface vs core of the sample (b) with offset= 10, Ni_{2.95}Cu_{0.05}Ge (c), Ni_{2.9}Cu_{0.1}Ge (d) and Ni_{2.95}Ag_{0.05}Ge core (e) including the difference (red) between sample (blue) and fit function (black).

The lattice parameters, determined through Rietveld refinement, are listed in Table 6.3. Its behavior relative to the stoichiometric components is illustrated in Figure 4.12. Both the substitution of Ni by Cu and Ag in $Ni_{3-x}Cu_xGe$ and $Ni_{2.95}Ag_{0.05}Ge$ causes an increase of the lattice parameters.

Empirically this can be attributed to the larger atom radii of Ag ($a_{Ag} = 1.44 \cdot 10^{-10}$ m) and Cu ($a_{Cu} = 1.28 \cdot 10^{-10}$ m) compared to Ni, with $a_{Ni} = 1.24 \cdot 10^{-10}$ m. In addition $a_{Ag} > a_{Cu}$ explains the larger lattice parameter of the Ag based alloy compared to the Cu based materials. The gradient from light to dark color symbolizes increasing dopant concentrations.



Figure 4.12: Lattice parameter of Ni_{3-x}Cu_xGe and Ni_{2.95}Ag_{0.05}Ge

4.3.2 Transport Properties

Figure 4.13 presents the measured temperature-dependent resistivity $\rho(T)$, the Seebeck coefficient S(T) and the power factor PF(T) for Ni_{3-x}Cu_xGe and Ni_{2.95}Ag_{0.05}Ge. The pure stoichiometric compound Ni₃Ge is added in all plots by blue circles.

The substitution of Ni by Cu (see Figure 4.13 (a)) results in a higher resistivity $\rho(T)$ that is also increasing with increasing temperature from 4 K to 873 K, indicating a metallic behavior.

Figure 4.13 (c) compares the measured resistivity $\rho(T)$ of Ni₃Ge with both Cu and Ag (5%). Overall the lowest $\rho(T)$ values are found for the Ag-based alloy. The empty symbols in Figure 4.13 indicate the measurement data upon cooling to room temperature.

The resistivity data of Figures 4.13 (c) and 4.14 (a) were again accounted for by a combination of the Bloch-Grüneisen formula with a Mott-Jones term $A \cdot T^3$, according to Equations 2.21 and 2.23 and plotted by solid and dashed lines. The fit parameters are presented in Tables 6.7 and 6.8. Using the more simple Ansatz of Equation 2.21 demonstrates substantial *s*-*d* scattering accounted for by the Mott-Jones term and revealing fine agreement. This scattering causes a negative deviation from a linear $\rho(T)$ dependence in substitued Ni_{3-x}Cu_xGe (x = 0.05, 0.1) Ni_{2.95}Ag_{0.05}Ge, suggesting that E_F is near a maximum in D(E) (solid lines in Figure 4.13 (c)).

The Seebeck coefficient S(T) for each alloy of Ni_{3-x}Cu_xGe is shown in Figure 4.13 (b), revealing increasing |S(T)| values for increasing substitution with Cu at room temperature, compared to Ni₃Ge, as well as a smooth temperature variation. Figure 4.13 (d) presents Seebeck coefficients S(T) of Ni_{2.95}{Cu,Ag}_{0.05}Ge, with an obvious decrease of S(T) upon Ag substitution. Both alloy series Ni_{3-x}Cu_xGe and Ni_{2.95}Ag_{0.05}Ge, exhibit negative S(T) values. Considering Mott's formula, it implies that electrons are the dominant charge carriers (compare [22]).

The temperature-dependent power factor PF(T) is calculated according to Equation 1.2, combining the measured temperature-dependent resistivity $\rho(T)$ and Seebeck coefficient S(T) as shown in Figure 4.13 (e,f), for each sample of Ni_{3-x}Cu_xGe and Ni_{2.95}Ag_{0.05}Ge respectively. It is clearly visible that Ni_{2.9}Cu_{0.1}Ge has the highest power factor with $PF = 8.5 \text{ mW}/(\text{m} \cdot \text{K}^2)$ at room temperature, which is 18 % larger than PF of undoped Ni₃Ge ($PF = 7.2 \text{ mW}/(\text{m} \cdot \text{K}^2)$). The second best result is revealed for Ni_{2.95}Cu_{0.05}Ge with a power factor $PF = 8.3 \text{ mW}/(\text{m} \cdot \text{K}^2)$ at room temperature.

The uncommon increase of the resistivity $\rho(T)$ of Ni_{2.9}Cu_{0.1}Ge with decreasing temperature prompted further exploration (see Figure 4.14 (b)). Instead of the expected monotonous decrease of $\rho(T)$ towards a residual resistance, or onset of superconductivity below a critical temperature T_{critical} , there are distinct differences



Figure 4.13: Temperature-dependent resistivity $\rho(T)$ (a) for each sample of Ni_{3-x}Cu_xGe from 4 K to 873 K. Seebeck coefficient S(T) for each sample of Ni_{3-x}Cu_xGe (b) and Ni_{2.95}{Cu,Ag}_{0.05}Ge(d) from room temperature to 873 K. Temperature-dependent resistivity $\rho(T)$ for Ni_{2.95}{Cu,Ag}_{0.05}Ge (c), with solid and dashed lines are fits according to Equations 2.21 and 2.23. Alongside with the power factor PF(T) for Ni_{3-x}Cu_xGe (e) and Ni_{2.95}{Cu,Ag}_{0.05}Ge in comparison to Ni₃Ge (f).

to all other samples within this thesis. The measured resistivity $\rho(T)$ was examined in the range 7-30 K in terms of the Kondo effect, revealing $\rho(T) = \rho_0 - a \ln(T/T_0)$, $\rho_0 = 32.53 \ \mu\Omega$ cm and $a = 0.68 \ \mu\Omega$ cm. The fit function is shown as a black line in Figure 4.14 (d) (see Chapter 2.2.3).[33] Besides the Kondo effect, increasing electrical resistivity with decreasing temperatures can result from localizing charge carriers. In such a scenario $\rho(T)$ can be examined in terms of hopping conductivity. In Figure 4.14 (c) and (d) data are plotted on a $T^{1/4}$ and $T^{1/2}$ scale. The former corresponds to the classical model of Mott for hopping conductivity (Equation 2.24[27]). The fit function (red line) for $T^{1/4}$ coincides with 99.4 % to the experimental data in (c) and $T^{1/2}$ with 98.63 % (d) in a narrow temperature range; thus, supporting hopping conductivity, too (discussed in Chapter 2.2.2). Even though σ_{hc} is related to the amount of disorder in the unit cell, the present samples, are not influenced by the magnetic state, as the magnetoresistance is below 1 % for T > 0.5 K and magnetic fields up to 12 T.[27] The comparison of all resistivity models reveals that the low-temperature behavior is best described by hopping conductivity σ_{hc} with the famous $T^{1/4}$ dependence, as it aligns most closely with Equation 2.24 over a broader temperature range compared to other models.

The temperature-dependent resistivity of Ni_{2.95}Cu_{0.05}Ge and Ni_{2.9}Cu_{0.1}Ge from 4 K to 70 K is shown in Figure 4.14 (e). Both alloys exhibit distinct low-temperature features. While the latter is characterized by an increase of $\rho(T)$ upon lowering the temperature, the former shows an unusual T^3 behavior, which is demonstrated by plotting data versus T^3 as x-axis (compare Chapter 2.2). To emphasize this temperature dependence once more, data are plotted on a standard T^5 scale as well (Figure 4.14 (f)). Fit functions, represented by solid lines, correspond to $a + bT^3$ and $a + bT^5$ for Ni_{3-x}Cu_xGe, respectively, confirming that the $\rho(T)$ behavior of the samples aligns with the Bloch-Wilson limit, being characteristic for transition metals.[34] The numerical values of the fit parameters a and b are listed in Table 6.5 (compare with Chapter 2.1).

The impressive PF results of the Cu substituted sample series imply further interesting compositional possibilities to be researched.





Temperature-dependent resistivity $\rho(T)$ for each sample of Ni_{3-x}Cu_xGe (a). Solid and dashed lines are fits according to Equations 2.21 and 2.23. The Kondo effect with fit function plotted by a solid black line (b). Comparison of the measured

resistivity $\rho(T)$ applied on the $\ln(\frac{1}{\rho(T)})$, with the fit function (solid line) for temperature-dependent hopping conductivity for $T^{1/4}$ (c) and for $T^{1/2}$ (d) in Ni_{2.9}Cu_{0.1}Ge. Temperature-dependent resistivity $\rho(T^3)$ (e) and $\rho(T^5)$ (f) including corresponding fit function presented by solid lines, for each sample of Ni_{3-x}Cu_xGe.

4.4 Physical Properties of doped Pd₃Sn and Pt₃Sn

This chapter focuses on the $Pd_3Sn_{0.95}In_{0.05}$ and $Pt_3Sn_{0.95}Sb_{0.05}$ alloys. The transition metals Pd and Pt, with their incomplete 4d and 5d shells, respectively, were chosen to examine the significant influence of their intrinsic differences on the density of states at the Fermi energy, and consequently, the thermoelectric performance of these materials. X-ray diffraction, electrical resistivity, and Seebeck measurements on these materials are presented, using analyses discussed in Chapter 2.

As presented in Figure 4.15 [35] and 4.16 [36] the phase diagrams of Pd-Sn and Pt-Sn, reveal in both cases several binary compounds as well as eutectic phases. It is interesting to note that in the case of Pd-Sn, the binaries exhibit a certain solubility range, while in the case of Pt-Sn all binaries appear to be line compounds. In both cases, TM_3Sn are formed (TM=Pd, Pt). Figure 3.1 shows that the



Figure 4.15: PdSn phase diagram with the orange vertical line displaying Pd_3Sn within the solid-state phase of Pd_3Sn (green area).[35]

number of electron shells increases by one from Ni (3d) to Pd (4d) and again from Pd to Pt (5d), meanwhile the number of electron shells also increases by one from Ge to Sn. To tune the electronic structure, Pd₃Sn_{0.95} was doped with In and Pt₃Sn_{0.95} with Sb, which has 2 more electrons in its outermost shell than In. Binary intermetallics with Pd and Pt can enhance the thermoelectric properties by introducing heavier atoms, which might reduce lattice thermal conductivity and, additionally, shift the Fermi energy favorably. Moreover, spin fluctuations in many Pd-based components and alloys can also positively influence thermoelectric properties. Sn and In are softer main group metals with low electronegativity. They



Figure 4.16: PtSn phase diagram with the orange vertical line showing the solid state of $Pt_3Sn.[36]$

could decrease the thermal conductivity by altering the band structure, improving the Seebeck coefficient, and increasing the electrical conductivity. In most cases, however, the respective electronic structure of the various systems can be quite different from a simple superposition of its constituting elements.

4.4.1 Synthesis and Characterization

Samples $Pd_3Sn_{0.95}In_{0.05}$ and $Pt_3Sn_{0.95}Sb_{0.05}$ were melted in separate quartz glass cylinders, where the weighed elements were pre-melted together at 1000 K for 24 hours due to the low melting point of In (429 K). Following this step, the fusion process was completed in a high-frequency furnace as usual.

The X-ray diffraction patterns of $Pd_3Sn_{0.95}In_{0.05}$ and $Pt_3Sn_{0.95}Sb_{0.05}$ can be found in Figure 4.17 (a), normalized to the maximum intensity, with an offset of 10 %. Red vertical lines indicate the Miller indices of the Cu₃Au structure at the peaks of the respective Bragg reflections, emphasizing the similarities with the measured data. Furthermore the intensities of $Pt_3Sn_{0.95}Sb_{0.05}$ coincide perfectly with prototypic Cu₃Au. Nevertheless, several additional peaks are present off Bragg positions, indicating foreign phases. $Pd_3Sn_{0.95}In_{0.05}$ exhibits intensities at the same reflection peaks (111), (200), (220), (311) and (222) as Cu₃Au, while the intensities (100), (110), (210) and (211) are not complying. Additionally, the sample $Pd_3Sn_{0.95}In_{0.05}$ shows a macroscopic visible distinction of coloration about 1 mm from the surface



Figure 4.17: Normalized X-ray diffraction pattern for $Pd_3Sn_{0.95}In_{0.05}$ and $Pt_3Sn_{0.95}Sb_{0.05}$ (a) and $Pd_3Sn_{0.95}In_{0.05}$ core vs surface (b) with offset= 10 %.

and the core, Figure 4.17 (b). This leads to the conclusion that the elements have not bonded homogeneously throughout the entire sample and thus impurity phases have been formed locally.

Using the face-centered-cubic crystal structure, the fit functions were derived based on Wyckoff positions: Pd/Pt fixed at 1a(0,0,0) and Sn occupying the 3c(0,1/2,1/2) site, proportionally aligned with its substitutive elements {In, Sb} and space group 221.

Individual Rietveld refinements for measured patterns are shown in Figure 4.18, revealing in Figure 4.18 (a) that the fit function of $Pd_3Sn_{0.95}In_{0.05}$ is larger in height and smaller in width for the crystal plane (111), while the height of the reflection peaks for the planes (100), (110), (200), (220) and (311) are larger. For the sample $Pt_3Sn_{0.95}Sb_{0.05}$ the Rietveld refinement is shown in Figure 4.18 (b) where the highest peak, (111), is described more accurately by the fit compared to the one of $Pd_3Sn_{0.95}In_{0.05}$. But the intensities of the planes (100) and (110) are again larger for the fit function and smaller for (220), (311) and (222). Given the appropriateness of the respective fit-function, this would again refer to a preferred orientation of grains. Figure 4.19 summarizes the lattice parameters derived from the respective Rietveld refinements (compare also Table 6.3). Starting with Ni₃Ge, which has a lattice parameter of 3.574 Å, the lattice parameter for the Pd and Pt based alloys are significantly larger compared to Ni₃Ge due to increased atomic radii of Pd, Pt, Sn,In and Sb. The gradient from light to dark colors represents an increasing number of substituents, with dotted lines that serve as guides for the eyes.



Figure 4.18: Normalized X-ray diffraction pattern for $Pd_3Sn_{0.95}In_{0.05}$ (a) and $Pt_3Sn_{0.95}Sb_{0.05}$ (b) with difference (red) between sample (blue) and fit function (black).



Figure 4.19: Lattice parameter of Ni₃Ge, Ni₃Sn, Pd₃Sn_{0.95}In_{0.05}, Pt₃Sn_{0.95}Sb_{0.05}, Pd₃Sn and Pt₃Sn.

4.4.2 Transport Properties

The temperature-dependent resistivities $\rho(T)$ of Pd₃Sn_{0.95}In_{0.05}, Pt₃Sn_{0.95}Sb_{0.05} and Ni₃Ge are shown in Figure 4.20 (a) from 4 K to 873 K. In all cases, $\rho(T)$ of the samples, behaves almost linearly from room temperature to 873 K, corresponding to metals, while exhibiting a much stronger curvature from T = 45 K to T = 300 K. $\rho(T)$ from room temperature to 873 K, is described using Equations 2.21 (solid lines) and 2.23 (dashed lines) (see Tables 6.7 and 6.8 for the corresponding fit parameters). The fitted relationships are illustrated in Figure 4.20(b). This analysis reveals contributions from the T^3 term, indicative of *s*-*d* scattering, being characteristic for transition metals.

Furthermore, the parameter A is positive for $Pd_3Sn_{0.95}In_{0.05}$, implying a negative deviation from linearity of $\rho(T)$ and that the Fermi energy E_F is near a maximum in the density of states D(E). On the other hand, $Pt_3Sn_{0.95}Sb_{0.05}$ exhibits a positive deviation from linearity, suggesting that the actual E_F is near a minimum in D(E). Due to substitution-induced disorder, the residual resistivity increases for the Pd and Pt-based samples, in comparison to Ni₃Ge.

In Fig 4.20 (c,d), low temperature resistivity data of $Pd_3Sn_{0.95}In_{0.05}$ and $Pt_3Sn_{0.95}Sb_{0.05}$, in order to reveal the impact of *s*-*d* scattering on the temperaturedependent resistivity of these samples. In the range of 4 K to 45 K, the fit functions $a + b \cdot T^3$ (Figure 4.20 (c)) and $a + b \cdot T^5$ (Figure 4.20 (d)) are visualized by solid lines. The corresponding values of *a* and *b* are provided in Tables 6.5 and 6.6. The distinguished agreement with the T^3 dependence refers to the presence of substantial *s*-*d* scattering. Thus, simple electron-phonon scattering as expressed by the standard Bloch-Grüneisen formula is less important.

The temperature-dependent Seebeck coefficient S(T) and power factor PF(T) for $Pd_3Sn_{0.95}In_{0.05}$, $Pt_3Sn_{0.95}Sb_{0.05}$ in comparison to Ni_3Ge can be found in Figure 4.20, with S(T) in (e) and PF(T) in (f). Due to the relatively low values of the Seebeck coefficient S(T), the power factor PF(T) is also low, compared to Ni_3Ge ; but PF of $Pt_3Sn_{0.95}Sb_{0.05}$ is still larger than that of $Pd_3Sn_{0.95}In_{0.05}$. While both Ni_3Ge and $Pt_3Sn_{0.95}Sb_{0.05}$ exhibit negative S(T) values, $Pd_3Sn_{0.95}In_{0.05}$ shows positive Seebeck data. Following Mott's model [22] for the description of the thermopower, i.e., $S(T) \propto -\frac{1}{D(E)} \cdot \frac{\partial D(E)}{\partial E}|_{E=E_F}$, the latter is expected to exhibit a negative slope of D(E) at $E = E_F$, and the former a positive one. Considering semiconductors, this would correspond to holes as dominating charge carriers for $Pt_3Sn_{0.95}Sb_{0.05}$, but electrons for the remaining samples.





Temperature-dependent resistivity $\rho(T)$ from 4 K to 873 K (a). Solid and dashed lines are fits according to Equations 2.21 and 2.23 from room temperature to 873 K (b). $\rho(T^3)$ (c) and $\rho(T^5)$ (d) with fit functions presented by solid lines from 4 K to 45 K. Temperature-dependent Seebeck coefficient S(T) (e) and power factor PF(T) (f) for the compounds Pd₃Sn_{0.95}In_{0.05}, Pt₃Sn_{0.95}Sb_{0.05} and Ni₃Ge from room temperature to 873 K.

4.5 Physical Properties of Ni_{3-x}Cu_xAl

This chapter investigates quasi-binary $Ni_{3-x}Cu_xAl$ alloys, by varying the ratio of Ni and Cu in small steps of $\Delta x = 0.2$. This approach allows for precise tracking of how changes in electron count affect electronic properties, and thereby thermoelectric behavior. Nickel, a 3*d* transition metal with high electron mobility, can modify the magnetic state due to an unfilled *d*-shell, while copper, known for its excellent electrical conductivity, can increase overall conductivity. Aluminum, with its low density, contributes to structural integrity. By systematically varying the Ni/Cu ratio, the alloy can be optimized to shift the Fermi energy, improving the power factor and making $Ni_{3-x}Cu_xAl$ an interesting alloy for thermoelectric applications near room temperature. Figure 4.21, shows the NiAl phase diagram [37], with



Figure 4.21: NiAl phase diagram with the orange vertical line indicating the solid state of $Ni_3Al.[37]$

the orange vertical line marking the Ni₃Al phase, indicating some solubility of Ni₃Al. The solidus and liquidus lines in the phase diagram show two distinct minima, indicating the presence of eutectic points. At this eutectic composition and temperature, two phases coexist in equilibrium, allowing the material to transition directly from solid to liquid. This behavior is characteristic of eutectic systems, where the solidus and liquidus converge, defining the locally lowest temperature at which the mixture melts completely. The ternary phase diagram of NiCuAl [38] for the isothermal section at 1073 K, is presented in Figure 4.22. The five quasi-binary

alloys prepared in this diploma work, from left to right Ni₂CuAl, Ni_{2.2}Cu_{0.8}Al, Ni_{2.4}Cu_{0.6}Al, Ni_{2.6}Cu_{0.4}Al and Ni_{2.8}Cu_{0.2}Al are marked with red points, within the possible Ni₃Al phase (green area). It also includes five intermediate phases NiAl₃ (Fe₃C-type, orthorhombic), Ni₂Al₃ (D₅₁₃-type, hexagonal), NiAl (CsCl-type, cubic), Ni₅Al₃ (Ga₃Pt₅-type, orthorhombic), and Ni₃Al (AuCu₃-type, cubic) [38].



Figure 4.22: NiCuAl isothermal section at 1073 K.[38]

4.5.1 Synthesis and Characterization

For the stoichiometric alloys $Ni_{3-x}Cu_xAl$, five 2.5 g samples were prepared by synthesizing weighed amounts of Cu and Al via high-frequency induction melting, followed by complementing the resulting ingots with Ni. Each sample underwent identical heat treatment, tempered at 973 K for one week, consistent with the procedures applied throughout this study.

Due to the high density of Ni and the increasing amount in the samples, it was not possible to produce crystalline powder from the samples. Instead, bulk materials were examined by using XRD. In Figure 4.24 (a), the diffraction data of each sample is normalized to the maximum intensity and shifted against each other with increasing x by an offset of 10 %, to obtain better visibility. The red vertical lines indicate the Miller indices at the peaks of the respective crystal planes of the Cu₃Au structure. All samples studied in this chapter show X-ray intensities at all those crystal planes.

The X-ray diffraction patterns for each sample of $Ni_{3-x}Cu_xAl$ (see Figure 4.24 (a)) reveal phase purity for x = 1 and x = 0.2, but show second phases in all other samples. The individual Rietveld refinement results are shown in Figure 4.24 (b), (c), (d), (e), (f). The fit functions reveal for a face-centered cubic crystal, a good agreement with Al at 1a(0,0,0); Ni gradually vacates the 3c(0,1/2,1/2) site, allowing the stepwise incorporation of Cu. Lattice parameters determined through



Figure 4.23: Lattice parameter of Ni_{3-x}Cu_xAl with decreasing $\Delta x = 0.2$.

these fits are listed in Table 6.3. The relationship between lattice constants and the stoichiometric composition is depicted in Figure 4.23. Starting from Ni_2CuAl

and increasing $\Delta x = 0.2$ up to the final composition Ni₃Al, a decreasing lattice parameter is observed at 300 K, corresponding to the reduction in Cu content. Considering the atomic radii of Ni $(1.24 \cdot 10^{-10} \text{ m})$, Al $(1.43 \cdot 10^{-10} \text{ m})$, and Cu $(1.28 \cdot 10^{-10} \text{ m})$, the smooth trend for Cu substitutions by Ni can be attributed to the smaller atomic radius of Ni. The dotted lines in the figure serve as visual guides.

The fitting process reveals that employing the chosen set of parameters, the fit function for the pattern Ni₂CuAl is larger than the measured height and smaller in width for the (111) plane. The X-ray data of crystal planes (200), (220) alongside the (311) plane are overestimated by the fit function, while the peaks for planes (100) and (110) are underestimated (see Figure 4.24 (b)).

For x = 0.8 (see Figure 4.24 (c)) the predicted peak for the (100) plane by the fit function at $2\Theta = 24.8^{\circ}$ is larger, but the measurement data show instead an impurity at $2\Theta = 26.6^{\circ}$, additionally to a foreign phase peak at $2\Theta = 20.8^{\circ}$. The main intensity peak for the (111) plane, is smaller in height and larger in width, while the peaks for the (110) and (311) planes are larger and the intensity of the (200) plane is smaller.

Figure 4.24 (d) presents the Rietveld refinement for x = 0.6, where the fit function underestimates the measured data and the difference between both is visualized and shifted with an offset -25 %. Slightly above the (111) peak an impurity phase is present. A slight overestimation of the intensities for the planes (210), (211) and a comparably big overestimation of the intensity from the (222) of the fit function is also clear in Figure 4.24 (d).

The results for the alloy Ni_{2.6}Cu_{0.4}Al are shown in 4.24 (e). Again, the (311) Bragg peak is underestimated. As an exception to all other Ni_{3-x}Cu_xAl compounds, the (200) plane shows in the XRD data a much higher intensity than the (111) plane. Additionally, the x = 0.4 substitution leads to a slight overestimation by the fit function of the intensity of the (200) plane and a big overestimation by the fit function of the intensity of the (222) plane, which is probably a result of the more preferred (311) plane.

A good correspondence between data and the Rietveld refinement is found for x = 0.2 (Figure 4.24 (f)) confirming the Cu₃Au structure. Slight overestimations of the intensities for the planes (100), (110), (111), (210), (211), and (220) of the fit curves can be observed, which are even more subtle for (311) and (222). The intensity of the (200) plane is in all substitutions $x \neq 0$ underestimated. Thus, this plane is a more dominant crystal plane than statistically expected.



Figure 4.24: Normalized X-ray diffraction pattern for Ni_{3-x}Cu_xAl with offset 10 % with increasing x (a) x=1 (b) x=0.8 (c) x=0.6 (d) x=0.4 (e) x=0.2 (f) including the difference (red) between sample (blue) and fit function (black).

4.5.2 Transport Properties

The temperature-dependent resistivity, $\rho(T)$, of Ni_{3-x}Cu_xAl (Figure 4.25(a)) displays a nearly linear trend from room temperature to 873 K, characteristic of metallic behavior. The highest overall resistivity values are observed for a doping level of x = 0.6. In contrast, the resistivities for x = 0.8 and x = 0.4 are nearly identical. While Ni₃Al exhibits the lowest $\rho(T)$ values at room temperature, substitution with x = 0.2 Cu results in lower resistivity above ~ 500 K.

Solid and dashed lines in Figure 4.25(a) are results of least squares fits according to Equations 2.21 and 2.23. Both model equations reveal for temperatures $T > \Theta_D$ a linear resistivity due to electron phonon interaction and additionally, an $A \cdot T^3$ term (Mott-Jones term, Chapter 2.2.1) owing to phonon assisted *s*-*d* scattering. The latter is responsible for the well known resistivity deviation from linearity, generally found in transition metal element based materials. As already discussed in previous chapters, the sign of *A* determines, whether there is a super or supralinear $\rho(T)$ dependence.

All samples, except Ni_{2.8}Cu_{0.2}Al, exhibit a negative fit parameter A, suggesting the Fermi energy E_F is near a maximum in the density of states D(E). In contrast, Ni_{2.8}Cu_{0.2}Al exhibits a negative deviation, indicating E_F is near a minimum in D(E). The corresponding fit parameters are listed in Table 6.7.

The Seebeck coefficient S(T) (see Figure 4.25 (b)), exhibits both positive and negative values. The positive values are found for the Ni-rich samples, indicating classically hole-like carriers. In a more sophisticated picture, the logarithmic derivation of the energy-dependent density of states at $E = E_F$ becomes negative. Increasing Cu drives the Seebeck effect negative, resulting in electrons being the dominant carriers or more accurate, $\frac{1}{D(E)} \frac{\partial D(E)}{\partial E} |_{E=E_F} < 0$. For x = 0.8, S(T) reaches the highest value and decreases with decreasing x. Overall, the |S(T)| values are relatively small.

Figure 4.25 (c) shows the temperature-dependent power factor PF(T) of Ni_{3-x}Cu_xAl. Overall, PF is very low from room temperature to 873 K. Ni₃Al exhibits the highest PF(T) at room temperature. With decreasing x = 0.6 to x = 0.2 the value of PF(T) is decreasing and does not support further investigation of these compositions.



Figure 4.25: Temperature-dependent resistivity $\rho(T)$ of Ni_{3-x}Cu_xAl(a) illustrated by various symbols. The solid and dashed lines are fits according to Equations 2.21 and 2.23. The Seebeck coefficient S(T) (b) and power factor PF(T) (c) for each sample marked by various symbols from room temperature to 873 K.

5 Conclusion and Outlook

This diploma thesis, as discussed in the preceding chapters, focused on the thermoelectric properties and performance of intermetallic compounds based on metals with incomplete d shells. As was pointed out recently in a seminal paper[9], metals, due to narrow features near the Fermi energy, can exhibit very large values of the Seebeck coefficient, which are even comparable to the much better-known and studied thermoelectric materials based on semiconductors. The flat bands in the electronic structure of d-elements, which give rise to the narrow density of states features, are key elements concerning the enhancement of the Seebeck effect and thus of the thermoelectric power factor. Microscopically, this enhancement is based on a strong energy dependence of the relaxation time due to phonon-assisted scattering of conduction electrons, involving these narrow 3d states.

In terms of an extension of this novel direction in the field of thermoelectricity, several alloys based on transition metals, such as Ni, Cu, Pd or Pt and main group elements such as Ge or Si were prepared by high frequency melting of appropriate amounts of pure elements under a protective argon atmosphere. The latter were examined using X-ray diffraction, where foreign phases and respective lattice parameters were evaluated. To obtain information regarding thermoelectricity, the temperature dependent electrical resistivity as well as the Seebeck coefficient were obtained experimentally in a wide range of temperatures.

Selected experimental data were analyzed in terms of solid state physics models to get information on relevant microscopic parameters (e.g., localisation, electronphonon or Kondo interaction, etc.), determining ground state properties as well as the thermoelectric performance of such *d*-electron based materials. As an example, the lattice parameter dependent resistivity of all samples prepared in this diploma thesis is sketched in Figure 5.1 (see also Table 6.3).

The increased power factor for increasing x in Ni_{3-x}Cu_xGe is a reliable cornerstone for further exploration of metals being well suited for thermoelectric applications.





Figure 5.1: Resistivity ρ at room temperature versus increasing lattice constant.
6 Data Tables

sample	mass [g]	mass [g]	mass [g]	tempered [g]	deviation [%
Ni _{3.05} Si _{0.95}	Ni: 2.17571	Si: 0.32430	-	2.50017	100.01
$Ni_{3.0}Cu_{0.05}Si_{0.95}$	Ni: 2.13750	Si: 0.32395	Cu: 0.03858	2.49949	99.98
$Ni_{2.95}Cu_{0.1}Si_{0.95}$	Ni: 2.09945	Si: 0.32358	Cu: 0.07700	2.49974	99.99
$Ni_{2.9}Cu_{0.15}Si_{0.95}$	Ni: 2.06144	Si: 0.32319	Cu: 0.11547	2.49995	99.99
$Ni_{3.05}Si_{0.9}Sb_{0.05}$	Ni: 2.12722	Si: 0.30037	Sb: 0.07230	2.49206	99.69
$Ni_{3.05}Si_{0.85}Sb_{0.1}$	Ni: 2.08091	Si: 0.27757	Sb: 0.14149	2.49864	99.95
$Ni_{2.95}Cu_{0.05}Ge$	Ni: 1.73870	Ge: 0.72938	Cu: 0.03188	2.49811	99.93
$Ni_{2.9}Cu_{0.1}Ge$	Ni: 1.70756	Ge: 0.72866	Cu: 0.06388	2.49871	99.94
$Ni_{2.95}Ag_{0.05}Ge$	Ni: 1.72350	Ag: 0.05360	Ge: 0.72296	2.48380	99.35
$\mathrm{Pd}_{3}\mathrm{Sn}_{0.95}\mathrm{In}_{0.05}$	Pd: 1.82310	Sn: 0.64403	In: 0.03280	2.53189	101.28
$Pt_3Sn_{0.95}Sb_{0.05}$	Pt: 2.05920	Sn: 0.41819	Sb: 0.02267	2.47709	99.08
Ni_2CuAl	Ni: 1.41147	Al: 0.32439	Cu: 0.76409	2.49985	99.99
$Ni_{2.2}Cu_{0.8}Al$	Ni: 1.55987	Al: 0.32605	Cu: 0.61415	2.47382	98.95
$Ni_{2.4}Cu_{0.6}Al$	Ni: 1.70970	Al: 0.32751	Cu: 0.46281	2.49374	99.75
$Ni_{2.6}Cu_{0.4}Al$	Ni: 1.86109	Al: 0.32904	Cu: 0.31008	2.49663	99.86
$Ni_{2.8}Cu_{0.2}Al$	Ni: 2.01372	Al: 0.33067	Cu: 0.15575	2.49707	99.88

Table 6.1: Weighted masses before the melting process and after tempering for each sample including the deviation.

sample	width [mm]	depth [mm]
Ni _{3.05} Si _{0.95}	1.61	2.2
$Ni_{3.0}Cu_{0.05}Si_{0.95}$	1.62	1.42
$Ni_{2.95}Cu_{0.1}Si_{0.95}$	2.1	1.78
$Ni_{2.9}Cu_{0.15}Si_{0.95}$	1.59	1.48
$Ni_{3.05}Si_{0.9}Sb_{0.05}$	2.38	2.08
$Ni_{3.05}Si_{0.85}Sb_{0.1}$	1.27	1.7
$Ni_{2.95}Cu_{0.05}Ge$	2.25	2.06
$Ni_{2.9}Cu_{0.1}Ge$	1.61	1.2
$Ni_{2.95}Ag_{0.05}Ge$	1.51	1.76
$Pd_{3}Sn_{0.95}In_{0.05}$	1.34	0.71
$Pt_3Sn_{0.95}Sb_{0.05}$	1.97	1.55
Ni_2CuAl	2.09	2.25
$Ni_{2.2}Cu_{0.8}Al$	1.62	1.52
$Ni_{2.4}Cu_{0.6}Al$	1.73	1.89
$Ni_{2.6}Cu_{0.4}Al$	1.92	1.54
Ni _{2.8} Cu _{0.2} Al	1.42	1.45

Table 6.2: Sample dimensions.

sample	maximum intensity [Counts]	lattice parameter [Å]
Ni _{3.05} Si _{0.95}	35412	3.511
$Ni_{3.0}Cu_{0.05}Si_{0.95}$	114751	3.512
$Ni_{2.95}Cu_{0.1}Si_{0.95}$	112055	3.514
$Ni_{2.9}Cu_{0.15}Si_{0.95}$	55411	3.516
$Ni_{3.05}Sb_{0.05}Si_{0.9}$	145065	3.515
$Ni_{3.05}Sb_{0.1}Si_{0.85}$	99404	3.517
Ni ₃ Ge	105763	3.574
$Ni_{2.95}Cu_{0.05}Ge$	333774	3.577
$Ni_{2.9}Cu_{0.1}Ge$	295252	3.578
$Ni_{2.95}Ag_{0.05}Ge$	135939	3.579
$\mathrm{Pd}_{3}\mathrm{Sn}_{0.95}\mathrm{In}_{0.05}$	34662	3.971
$\mathrm{Pt}_{3}\mathrm{Sn}_{0.95}\mathrm{Sb}_{0.05}$	41946	3.978
Ni_2CuAl	82490	3.590
$Ni_{2.2}Cu_{0.8}Al$	106965	3.588
$Ni_{2.4}Cu_{0.6}Al$	32439	3.585
$Ni_{2.6}Cu_{0.4}Al$	31494	3.582
$\rm Ni_{2.8}Cu_{0.2}Al$	54780	3.579

Table 6.3: Measured intensity and lattice parameters for spacegroup: 221.

sample	a	b	accuracy $[\%]$
$\overline{\text{Ni}_{2.9}\text{Cu}_{0.1}\text{Ge for }T^{-\frac{1}{2}}}$	-3.3823064	-0.15745885	98.6
$Ni_{2.9}Cu_{0.1}Ge \text{ for } T^{-\frac{1}{4}}$	-3.3323387	-0.17953206	99.4

Table 6.4: fit parameters $\rho(T) = a + b * T^{-\frac{1}{2}}$ and $\rho(T) = a + b * T^{-\frac{1}{4}}$ for hopping conductivity.

sample	a	b	range [K]	accuracy [%]
Ni ₃ Ge	1.89	$2.705 \cdot 10^{-5}$	0-40	99.6
$Ni_{2.95}Cu_{0.05}Ge$	21.888992	$2.5227965 \cdot 10^{-5}$	0-50	99.7
$Ni_{2.9}Cu_{0.1}Ge$	30.158329	$1.174301 \cdot 10^{-5}$	30-70	99.8
$\mathrm{Pd}_{3}\mathrm{Sn}_{0.95}\mathrm{In}_{0.05}$	5.5348441	$5.0564499 \cdot 10^{-5}$	0-30	97.2
$\mathrm{Pt}_{3}\mathrm{Sn}_{0.95}\mathrm{Sb}_{0.05}$	4.4643949	$3.4996547 \cdot 10^{-4}$	0-20	99.7

Table 6.5: Fit parameters for $\rho(T) = a + b * T^3$.

		-	[= -1	r~1
sample	a	b	range [K]	accuracy [%]
Ni ₃ Ge	30.789972	$2.3025822 \cdot 10^{-9}$	30-70	96.2
$Ni_{2.95}Cu_{0.05}Ge$	22.40114	$8.8721633 \cdot 10^{-9}$	0-50	94.9
$Ni_{2.9}Cu_{0.1}Ge$	30.427054	$3.9458269 \cdot 10^{-9}$	30-55	98.0
$\mathrm{Pd}_{3}\mathrm{Sn}_{0.95}\mathrm{In}_{0.05}$	5.6064927	$7.9026421 \cdot 10^{-8}$	0-25	92.6
$\mathrm{Pt}_{3}\mathrm{Sn}_{0.95}\mathrm{Sb}_{0.05}$	4.622	$1.2645824 \cdot 10^{-6}$	0-18	94.6

Table 6.6: Fit parameters for $\rho(T) = a + b * T^5$.

sample	a	В	А	С	accuracy [%]
Ni _{3.05} Si _{0.95}	0.18410361	$-4.5927527 \cdot 10^{-4}$	$3.995272 \cdot 10^{-8}$	15.218725	99.8
$Ni_{3.0}Cu_{0.05}Si_{0.95}$	0.16222593	$-4.7010784 \cdot 10^{-4}$	$5.0845438 \cdot 10^{-8}$	35.963743	99.6
$Ni_{2.95}Cu_{0.1}Si_{0.95}$	0.091224186	$-3.2677264 \cdot 10^{-4}$	$-2.2068045 \cdot 10^{-7}$	43.018246	99.5
$Ni_{2.9}Cu_{0.15}Si_{0.95}$	0.12011669	$-3.3876358 \cdot 10^{-4}$	$1.0773221 \cdot 10^{-8}$	36.651463	99.6
$Ni_{3.05}Si_{0.9}Sb_{0.05}$	0.15133995	$-4.651541 \cdot 10^{-4}$	$3.19121 \cdot 10^{-8}$	37.005666	99.5
$Ni_{3.05}Si_{0.85}Sb_{0.1}$	0.25045414	$-5.0791745 \cdot 10^{-4}$	$1.3055212 \cdot 10^{-7}$	31.382044	99.4
Ni_3Ge	0.12230165	$-3.3417085 \cdot 10^{-4}$	$-1.53916 \cdot 10^{-7}$	15.232428	99.9
$Ni_{2.95}Cu_{0.05}Ge$	0.093888639	$-8.8754102 \cdot 10^{-5}$	$-2.120908 \cdot 10^{-7}$	32.163929	99.9
$Ni_{2.9}Cu_{0.1}Ge$	0.094647128	$-1.3112619 \cdot 10^{-4}$	$-2.3433118 \cdot 10^{-7}$	30.644853	99.9
$Ni_{2.95}Ag_{0.05}Ge$	0.092379754	$-2.7021951 \cdot 10^{-4}$	$-2.495685 \cdot 10^{-7}$	18.087951	99.2
$\mathrm{Pd}_{3}\mathrm{Sn}_{0.95}\mathrm{In}_{0.05}$	0.045376193	$-1.7628985 \cdot 10^{-4}$	$1.9781653 \cdot 10^{-8}$	9.7751076	99.9
$\mathrm{Pt}_{3}\mathrm{Sn}_{0.95}\mathrm{Sb}_{0.05}$	0.17000771	$-3.6664129 \cdot 10^{-4}$	$-1.2260729 \cdot 10^{-7}$	53.686417	99.9
Ni_2CuAl	0.039337102	$-2.238345 \cdot 10^{-4}$	$-2.6806999 \cdot 10^{-7}$	29.335928	99.7
$Ni_{2.2}Cu_{0.8}Al$	0.035132958	$-2.3370635 \cdot 10^{-4}$	$-3.1677167 \cdot 10^{-7}$	40.603456	99.2
$Ni_{2.4}Cu_{0.6}Al$	0.051892347	$-3.3255094 \cdot 10^{-4}$	$-1.275436 \cdot 10^{-7}$	38.002391	99.6
$Ni_{2.6}Cu_{0.4}Al$	0.042835869	$-2.7593393 \cdot 10^{-4}$	$-9.9905987 \cdot 10^{-8}$	38.974587	99.9
$Ni_{2.8}Cu_{0.2}Al$	0.044142942	$-3.1211956 \cdot 10^{-4}$	$6.3348136 \cdot 10^{-8}$	27.326755	99.8
Ni ₃ Al	0.067876981	$-2.58644 \cdot 10^{-4}$	$-1.3460031 \cdot 10^{-7}$	13.995356	99.9

Table 6.7: high temperature fit $\rho(T) = aT(1+BT)(1-AT^2) + C$.

sample	А	В	С	D	accuracy [%]
Ni _{3.05} Si _{0.95}	37.727427	83.806291	708.85548	$4.3401536 \cdot 10^{-8}$	99.7
$Ni_{3.0}Cu_{0.05}Si_{0.95}$	55.459164	70.650918	684.74099	$3.9737933 \cdot 10^{-8}$	99.5
$Ni_{2.95}Cu_{0.1}Si_{0.95}$	52.375418	44.639225	655.86347	$5.8145383 \cdot 10^{-10}$	99.5
$Ni_{2.9}Cu_{0.15}Si_{0.95}$	49.212431	55.353397	640.12175	$1.9031768 \cdot 10^{-8}$	99.6
$Ni_{3.05}Si_{0.9}Sb_{0.05}$	54.85447	65.499798	673.50238	$3.5393255 \cdot 10^{-8}$	99.4
$Ni_{3.05}Si_{0.85}Sb_{0.1}$	63.766594	108.40346	722.60501	$7.4130969 \cdot 10^{-8}$	99.2
Ni ₃ Ge high	28.047502	59.77667	662.07323	$6.5796371 \cdot 10^{-9}$	99.9
Ni_3Ge	3.8228682	29.88819	203.20282	$5.4691946 \cdot 10^{-8}$	99.4
Ni_3Ge low	2.1287065	58.216618	305.01315	$2.9202744 \cdot 10^{-7}$	99.9
Ni _{2.95} Cu _{0.05} Ge high	40.564843	50.786792	633.61744	$-1.7402535 \cdot 10^{-8}$	99.9
$Ni_{2.95}Cu_{0.05}Ge$	24.311005	17.441888	151.01676	$1.0753655 \cdot 10^{-8}$	99.7
$Ni_{2.95}Cu_{0.05}Ge$ low	21.910797	37.090752	227.49454	$3.9125351 \cdot 10^{-7}$	99.9
Ni _{2.9} Cu _{0.1} Ge high	36.089356	37.56961	453.52585	$-1.4445818 \cdot 10^{-8}$	99.9
$Ni_{2.9}Cu_{0.1}Ge$	31.207249	18.152143	197.74403	$-8.1322332 \cdot 10^{-9}$	99.9
$Ni_{2.9}Cu_{0.1}Ge$ low	30.506294	29.712499	265.25845	$1.1673021 \cdot 10^{-7}$	99.9
$Ni_{2.95}Ag_{0.05}Ge$	28.995121	43.972693	638.99714	$-6.3150186 \cdot 10^{-9}$	99.7
$Pd_3Sn_{0.95}In_{0.05}$ high	12.520238	16.790352	438.53896	$4.0590173 \cdot 10^{-9}$	99.9
$\mathrm{Pd}_{3}\mathrm{Sn}_{0.95}\mathrm{In}_{0.05}$	14.460218	24.16822	673.04919	$2.8853414 \cdot 10^{-9}$	99.9
$Pd_{3}Sn_{0.95}In_{0.05}$ low	5.6566507	5.1311429	76.434791	$1.3322873 \cdot 10^{-7}$	99.9
$Pt_3Sn_{0.95}Sb_{0.05}$ high	71.486451	79.210579	647.93438	$1.6469615 \cdot 10^{-8}$	99.9
$Pt_{3}Sn_{0.95}Sb_{0.05}$ low	4.94382663	46.593356	121.26698	$7.9187777 \cdot 10^{-7}$	99.9
Ni ₂ CuAl	33.514489	21.551124	698.17511	$-4.7220776 \cdot 10^{-9}$	99.7
$Ni_{2.2}Cu_{0.8}Al$	44.084363	18.541965	665.17451	$-4.9537884 \cdot 10^{-9}$	99.2
$Ni_{2.4}Cu_{0.6}Al$	43.292643	24.613102	643.04735	$3.6610047 \cdot 10^{-9}$	99.6
$Ni_{2.6}Cu_{0.4}Al$	44.209111	24.61005	775.96144	$1.7839987 \cdot 10^{-9}$	99.9
$Ni_{2.8}Cu_{0.2}Al$	32.110384	21.36923	668.00627	$7.774559 \cdot 10^{-9}$	99.8
Ni ₃ Al	21.196683	35.597946	685.74958	$5.9928876 \cdot 10^{-10}$	99.9

Table 6.8: temperature fit $\rho(T) = \rho_0 + \rho_{ph} + \rho_{MJ} = A + 4B \int_{0.01}^{C/T} z^5 / (\exp(-z) - \exp(z) - 2) - DT^3$.



Acknowledgements

First and foremost, I wish to express my heartfelt gratitude to Univ. Prof. Dipl.-Ing. Dr.techn. Ernst Bauer for granting me the opportunity to work on this fascinating topic and for guiding me to explore physics, mathematics, and the universe from various perspectives - and ultimately, myself.
I am also deeply grateful to the scientists, researchers, explorers,

thinkers, and dreamers of the past and present, upon whose shoulders we all stand.



Figure 6.1: Illustration of young Thomas Johann Seebeck created by DALL-E.

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