Structural Analysis of Phase-Change Materials using X-Ray Absorption Measurements

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Abstract

Phase-change materials belong to a group of materials, that are suitable for optical and electronic data storage applications due to their unusual combination of properties. Within very short time, phase-change materials can reversibly be switched between a disordered, amorphous and an ordered, crystalline phase, and both the crystallization and the amorphization can be induced with laser pulses or electrical pulses. Because of the high optical and/or electrical contrast between both phases, using laser radiation or electrical pulses also the state of the material can reliably be detected. The knowledge of the structure of the amorphous and crystalline phases, which are relevant for data storage devices, is important to understand the origin of the high contrast and to be able to link the stoichiometry of the material with its physical properties. Therefore, in this study the structure of different phase-change materials is investigated by means of extended x-ray absorption fine structure (EXAFS) measurements.

After a short introduction to phase-change materials, the theory of x-ray absorption measurements is discussed and the methods, that are used to analyse the EXAFS spectra, are explained. Subsequent, the experimental equipment to prepare and characterize the samples is presented. Within the scope of this thesis, the structure of the crystalline and the amorphous phase of three alloys, GeTe, Ge₈Sb₂Te₁₁ and Ge₁Sb₂Te₄, is studied. These materials lie along the pseudo-binary line, which ranges from GeTe to Sb₂Te₃. After the detailed description of the analysis of the EXAFS spectra and the results, the structures of the investigated materials are compared and discussed.

The different local order in the amorphous and the crystalline phase, which is already apparent in the EXAFS spectra, is characteristic for phase-change materials. In the Fourier transformed display of the EXAFS spectra in real space, not only the amplitudes but also the peak positions differ in both phases. The analysis of the EXAFS spectra yields, that in the studied materials the bond lengths are shorter in the amorphous phase as compared to the crystalline phase. Investigating the crystalline phase of the phase-change materials it can be seen, that the temperature has an exceptionally large influence on the EXAFS spectra. The information content increases significantly, if the recording temperature is lowered to 10 K, and the spectra contain information on interatomic distances up to approximately 6 Å (compared to ≈3 Å at room temperature). The large impact of the temperature can be associated with the large static disorder in the crystalline phase. Although at 10 K contributions from thermal oscillations on the EXAFS Debye-Waller factor can be neglected, these factors are large for the crystalline phase, even larger than for the
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amorphous phase. The results of the Reverse Monte Carlo simulations provide the same information: the pair correlation functions for the crystalline configurations have much broader peaks than for the respective amorphous configurations. This means, that in contrast to common semiconductors, like e.g. Ge, the local order in the investigated phase-change materials is smaller in the crystalline phase than in the amorphous phase, even though no long range, periodic order exists in the amorphous phase.
Kurzfassung

Übersetzung des englischen Originaltitels: Strukturanalyse von Phasenwechselmaterialien mit Hilfe von Röntgenabsorptionsmessungen


Nach einer kurzen Einführung in Phasenwechselmaterialien wird die Theorie von Röntgenabsorptionsmessungen diskutiert und die Methoden, mit denen die EXAFS-Spektren ausgewertet werden, werden erläutert. Im Anschluss werden die experimentellen Anlagen vorgestellt, die zur Probenpräparation und zur Probencharakterisierung verwendet werden. Im Rahmen dieser Arbeit wird die Struktur der kristallinen und amorphen Phase von drei Legierungen, GeTe, Ge₈Sb₂Te₁₁ und Ge₁Sb₂Te₄, studiert. Diese Materialien liegen entlang der pseudobinären Linie, die von GeTe bis Sb₂Te₃ reicht. Nachdem die Auswertung der EXAFS-Spektren und die Ergebnisse detailliert beschrieben sind, werden abschließend die Strukturen dieser Materialien verglichen und diskutiert.

Charakteristisch für Phasenwechselmaterialien ist die unterschiedliche lokale Ordnung in der amorphen und der kristallinen Phase, die bereits in den EXAFS-Spektren sichtbar ist. In der fouriertransformierten Darstellung der EXAFS-Spektren im Realraum unterscheiden sich nicht nur die Amplituden der Peaks in beiden Phasen sondern auch die Peakpositionen. Die Auswertung der EXAFS-Spektren zeigt, dass in den untersuchten Materialien die Bindungslängen in der amorphen Phase kürzer sind als in der kristallinen Phase. Bei der Untersuchung der Kristallstruktur von Phasenwechselmaterialien stellt sich heraus, dass die Temperatur einen
ungewöhnlich großen Einfluss auf die EXAFS-Spektren hat. Der Informationsgehalt steigt signifikant an, wenn die Messtemperatur auf 10 K verringert wird, und die Spektren enthalten Informationen über interatomare Abstände bis ca. 6 Å (im Vergleich zu ≈3 Å bei Raumtemperatur). Dieser große Temperatureinfluss hängt mit der hohen statischen Unordnung in der kristallinen Phase zusammen. Obwohl bei einer Temperatur von 10 K der thermische Einfluss auf den EXAFS-Debye-Waller Faktor vernachlässigt werden kann, sind diese Faktoren für die kristalline Phase sehr groß und sogar größer als für die amorphe Phase. Die Ergebnisse der Reverse Monte Carlo Simulationen liefern dasselbe Bild: die Paarverteilungsfunktionen der kristallinen Konfigurationen zeigen deutlich breiter Peaks als die der zugehörigen amorphen Konfigurationen. Dies bedeutet, dass im Gegensatz zu gewöhnlichen Halbleitern wie z.B. Ge, die lokale Ordnung in den untersuchten Phasenwechselmaterialien in der kristallinen Phase geringer ist als in der amorpben Phase, obwohl keine langreichweitige, periodische Ordnung in der amorphen Phase existiert.
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1 Introduction

Nowadays, the possibility to store data is so omnipresent that it is hard to believe that only 20 years ago computer based technologies were almost irrelevant in everyday life of most people. Although, today it is common to use mobile phones, MP3 players, digital cameras and laptops nearly constantly, the mass usage of these applications started only in the early 90s. Ever since, the increase in storage density as well as the price decline for a storage unit has been phenomenal. Furthermore, the memories have become faster and smaller. Devices based on computer technologies (e.g., digital photo cameras) have become affordable by a majority of the people. Together with the increasing availability of data storage and thus, the increasing applications in old and new devices, also the requirements on memories have become more demanding. A variety of storage principles is used to fulfil the needs in all possible applications (e.g., CD, DVD, BD, DRAM, SRAM, Flash-SSD). However, the research for new storage concepts with even higher data densities, faster programming speeds, higher cyclabilities, lower power consumptions and operation voltage is ongoing. Storage applications based on so-called phase-change technology are found to be most promising for next generations memories [1–3].

In this thesis, the structure of the phases of different phase-change materials, which are relevant for data storage applications, is investigated. In this introductory chapter, first the basic principles of phase-change materials are outlined and then the aim and the structure of this thesis are discussed.

1.1 Phase-Change Materials

To store information in current memory applications, two well-defined states are needed that build the smallest possible storage capacity of 1 bit. In phase-change materials the variables 0 and 1 are represented by two different states of the same material: an amorphous and a crystalline state. The optical and electrical properties of both phases differ largely, such that the state of the material can be faultlessly determined either by measuring the reflectivity or the conductivity. Moreover, it is possible to alter the state of a storage material using a laser or an electrical pulse. That means that data can be easily stored and also erased by amorphizing and recrystallizing a defined spot. The basic principle of data storage based on phase-change materials is presented in Figure 1.1.

The crystalline phase of phase-change materials is characterized by a high optical reflectivity and a high conductivity. To change the state of the material, either laser or
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crystalline phase
• high reflectivity
• high conductivity

amorphous phase
• low reflectivity
• low conductivity

crystallization
long, low laser or current pulse

crystalline phase

amorphization
short, high laser or current pulse

Figure 1.1: In memory applications based on phase-change materials the possibility to reversibly switch the material between a periodic crystalline and a disordered amorphous phase is used to store information. To amorphize a crystalline bit, the material is locally heated above the melting temperature $T_M$. Due to the high cooling rates, the molten bit is quenched into the amorphous phase after the laser or electrical pulse is turned off. The recrystallization of the bit is accomplished with a pulse of intermediate power, that increases the temperature locally above the crystallization temperature $T_C$ and thereby allowing the atoms to form a crystalline lattice.
1.1. Phase-Change Materials

electrical pulses are used to locally melt the material. A short, intense pulse provides the necessary power to increase the temperature above the melting point $T_M$ of the material. Only a small fraction of the material in a confined region is melted and the temperature gradient between this molten bit and the surrounding crystalline material is immense. The cooling rates, after the pulse has been turned off, can be higher than $10^9 \text{K/s}$ [1]. If the solidification happens fast enough, crystallization of the material is prevented and the material is quenched in a disordered amorphous phase. Due to the large optical and electrical contrast between the crystalline and the amorphous phase, the areas where the material has been amorphized can easily be detected with low-power laser or electrical pulses. To crystallize the amorphous phase, i.e. to erase the written bit, the material is heated above the crystallization temperature $T_C$. Thereby, the mobility of the atoms is increased, such that they can arrange on the energetically favourable crystalline lattice. The crystallization is the slowest part in the storage cycle [1, 4] and thus, the applied pulse has a long duration but also a low intensity, in order to not increase the temperature above $T_M$.

The high contrast between an amorphous and a crystalline phase and the possibility to switch between both states using electrical pulses has first been discovered by Ovshinsky in 1968 in several semiconductors [5]. These two characteristics might be seen as the most important prerequisite for a material to be called a phase-change material. But for the use in memory applications more demands need to be fulfilled [1]. The data retention and the chemical stability have to be high, that means the once written amorphous bits should maintain their structure (i.e. their information) for a decade. Furthermore, to be able to run many recording cycles, the composition has to be stable over more than $10^9$ phase transitions ($10^{11}$ cycles have been demonstrated [6]) and, in addition, the crystallization speed should be high to allow fast data processing. In 1987, a group of materials has been found by Yamada et al. that meet all requirements [7]. In particular, it has been shown that a laser pulse of a pulse length smaller than 50 ns is sufficient to crystallize materials along the tie-line between GeTe and Sb$_2$Te$_3$, namely Ge$_1$Sb$_2$Te$_4$, Ge$_2$Sb$_2$Te$_5$ and Ge$_1$Sb$_4$Te$_7$ (see Figure 1.2). These fast crystallization times have been ascribed to the crystallization into a meta-stable crystalline phase with cubic, rocksalt-like symmetry (space group $Fm\bar{3}m$). Thereby, the Te atoms build one fcc sublattice, while the second is occupied by germanium, antimony and vacancies [7]. This structure is considerably different from the stable phase of this materials, which has a hexagonal symmetry (space group $P\bar{3}m$ or $R\bar{3}m$) with a complex layer-stacking.

Meanwhile, apart from ternary GeSbTe alloys other phase-change materials have been identified. Moreover, phase-change materials are already successfully employed in commercially available devices (e.g. CD-RW, DVD-RAM and Blu-ray Disc) and first prototypes of electronic phase-change memories (PCRAM) exist. Nonetheless, the scientific interest in this material class is unbroken. Questions that directly influence the application in storage devices (such as switching speed [4]) are tackled as well as questions on the precise atomic configuration and bonding mechanism in the amorphous, liquid and crystalline state. In recent years, substantial progress
1. Introduction

Figure 1.2: The ternary GeSbTe phase diagram shows the phase-change materials which are investigated in this thesis: GeTe, Ge$_1$Sb$_2$Te$_4$ and Ge$_8$Sb$_2$Te$_{11}$. has been made to understand the origin of the high optical and electrical contrast between the amorphous and the meta-stable crystalline phase. Resonant bonding in the crystalline phase has been shown to be responsible for the high electronic polarizability [8, 9]. The understanding of the bonding characteristics was used to draw a map, which locates all known phase-change materials in a particular region [10]. It has been shown, that the bonds in materials, which qualify as phase-change materials, must not be too ionic and the hybridization between the valence s- and p-electron states must not be too large [10]. The ultimate goal of all these investigations is to identify the relationship between stoichiometry, structure and physical properties in order to be able to easily tailor suitable phase-change materials for all possible data storage applications.

1.2 Aim and Structure of this Thesis

The aim of this study is to gain insight into the structure of the amorphous and crystalline state of phase-change materials along the GeTe-Sb$_2$Te$_3$ pseudo-binary line. The knowledge of the atomic arrangements in both phases is necessary to determine structural similarities and differences between both phases, which lead to the large optical and electrical contrasts. The analysis of three different alloys, GeTe, Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$, will enable us to discuss the structural changes along the pseudo-binary line and identify structural characteristics of phase-change materials. In order to accomplish these goals, extended x-ray absorption fine structure (EXAFS) measurements are performed with the highest possible accuracy. To analyse the EXAFS spectra and exploit the full information content, two different complementary approaches are used: a standard EXAFS analysis, which is based on least squares refinements of only few scattering paths and Reverse Monte Carlo (RMC) simulations,
which yield a three-dimensional configuration of several hundred atomic sites in agreement with the experimental data.

The theory of x-ray absorption and the analysis of the extended x-ray absorption measurements is discussed in Chapter 2. Subsequently, the instruments and methods used to prepare the samples and perform the EXAFS measurements are described in Chapter 3. The analysis of the crystalline and the amorphous phase of GeTe and Ge$_1$Sb$_2$Te$_4$ is presented in Chapter 4 and Chapter 5. In Chapter 6 the findings of the analyses of the three phase-change materials are compared and the similarities and changes are discussed, before the presented results are summarized and concluded in Chapter 7. The analysis of the EXAFS spectra of Ge$_8$Sb$_2$Te$_{11}$ is summarized in Appendix A and Appendix B contains the normalized absorption spectra of GeTe, Ge$_1$Sb$_2$Te$_4$ and Ge$_8$Sb$_2$Te$_{11}$. 
2 Extended X-Ray Absorption Fine Structure

X-ray absorption measurements are very well suited to study and compare the structures of the amorphous and crystalline states of phase-change materials, since this method is independent of the phase of the examined material. Amorphous, crystalline and even liquid states can be measured and studied using the same techniques. Hence, similarities and differences between different phases become apparent already prior to the detailed analysis.

The principles of x-ray absorption and the x-ray absorption fine structure (EXAFS) are discussed in Section 2.1. In Section 2.2 the basics of Fourier transformations are outlined, since they are an important tool to isolate the fine structure oscillations (Section 2.3). Two different approaches are used to analyse the EXAFS measurements. The standard analysis using selected scattering paths to fit the experimental data is presented in Section 2.4 and in Section 2.5 the EXAFS analysis based on Reverse Monte Carlo (RMC) simulations are described.

2.1 Principles of EXAFS

Electromagnetic waves with wavelengths ranging from 0.01 Å to 100 Å are called x-rays. Through a photoelectric process the x-rays can be absorbed by all matter. Thereby the energy of the x-ray photon is used to excite a core-electron and the atom is left in an excited state with an empty electron orbital (a core hole). The excited electron is called photo-electron and the kinetic energy of this electron $E_{\text{kin}}$ equals the difference of the energy from the photon $\hbar \omega$ and the binding energy of the electron $E_i$ ($E_{\text{kin}} = \hbar \omega - E_i$). The probability that an x-ray photon is absorbed by the radiated material is given by the absorption coefficient $\mu$ and it can be observed that $\mu$ increases strongly when the x-ray energies equal the bonding energies $E_i$ of a core-electron of an element in the investigated material (see Figure 2.1). These step-like features in an absorption spectrum are called absorption edges.

X-ray absorption spectra measured at condensed matter show oscillations just above the absorption edge (see Figure 2.1). These oscillations are called x-ray absorption fine structure and result from the fact that in condensed matter all atoms are embedded in a defined structure with neighbouring atoms at specified distances. The absorption spectra contain information on the structure of the investigated material. The information content depends on the x-ray energy with respect to the
2. Extended X-Ray Absorption Fine Structure

Figure 2.1: Absorption spectrum of amorphous Ge₁Sb₂Te₄ measured at the germanium K edge. The part of the spectrum approximately ±50 eV around the absorption edge (XANES) provides information on the oxidation state of the absorber and the binding geometry. The EXAFS begins approximately 50 eV above the absorption edge and contains structural information like neighbour distances and coordination numbers.

The binding energy of the electron $E_i$ and thus the spectrum can be divided into two parts: the x-ray absorption near edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS).

The near edge structure extends up to 50 eV above the absorption edge. In this energy region the core electron is excited to an unoccupied bound state, so that the shape of the absorption edge depends on the density of states closely above the Fermi level. Therefore, the oxidation state and binding geometry affect the XANES part of the spectrum. The region from 50 eV-1000 eV above an absorption edge is called extended x-ray absorption fine structure. This part of the spectrum contains information on the types and number of neighbour atoms to the absorbing atom. In the following only EXAFS will be discussed, as this work focuses on the analyses of EXAFS measurements. After the discussion of the x-ray absorption of isolated atoms, the changes in the absorption coefficient due to neighbouring atoms of the absorbing atom in condensed matter are presented. Finally, the most important terms of the standard EXAFS equation are discussed.
Figure 2.2: Absorption spectra of several elements (values from Ref. 11). In addition to the strong energy dependence sharp, step-like features at element specific energies can be observed. The energies of the absorption edges correspond to the binding energies of the core-electrons, that are excited.

### 2.1.1 X-Ray Absorption by Isolated Atoms

When an x-ray beam penetrates a material, the intensity decreases due to the absorption of x-ray photons. This attenuation is described by the Lambert-Beer law:

\[
I_2(E) = I_1(E)e^{-\mu(E)d}.
\]

(2.1)

The intensities \(I_1\) and \(I_2\) are measured before and after the absorber with thickness \(d\) and linear absorption coefficient \(\mu\). Figure 2.2 shows the absorption spectra of different elements. As already mentioned, the sudden increase in absorption at the absorption edges results from the atomic photoelectric process. The x-ray energy \(\hbar \omega\) at an absorption edge is sufficient to excite a core-electron to a free unbound state. This means that at every absorption edge a new absorption channel is opened and \(\mu\) increases drastically. The position of the absorption edges is unique for every absorbing element, which makes EXAFS an element specific method.

The absorption edges are labelled with respect to the state of the core-electron according to the Bohr model with the letters \(K, L, M\) and \(N\). As the binding energies of the electrons in an atom do not only depend on the principal quantum number
but also on the orbital angular momentum \( l \) and the total angular momentum \( j = l + s \) with spin quantum number \( s \), the absorption edges are further indexed, e.g. \( L_\text{I}, L_\text{II} \) and \( L_\text{III} \) refer to excitations of \( 2s, 2p_{1/2} \) and \( 2p_{3/2} \) electrons respectively.

In addition to the step-like absorption edges, in Figure 2.2 it can be seen that the absorption coefficient \( \mu \) generally decreases with increasing x-ray energy. To understand this decrease, the absorption process has to be considered in more detail. Energy can be removed from the incoming x-ray beam only by absorbing photons that means that energy is removed in quanta \( \hbar \omega \). The absorbed energy per second \( \frac{du}{dt} \) is:

\[
\frac{du}{dt} = -\hbar \omega N_{\text{at}} W. \tag{2.2}
\]

The number density of atoms \( N_{\text{at}} \) depends on the mass density \( \rho \), the atomic mass \( A \) and Avogadro’s number \( N_a \): \( N_{\text{at}} = \rho N_a / A \). The transition rate \( W \), i.e. the probability of a transition to occur per unit time, can be calculated according to Fermi’s golden rule by \[12\]

\[
W = \frac{2\pi}{\hbar} \sum_f |\langle f | H_1 | i \rangle|^2 \delta (E_f - E_i - \hbar \omega). \tag{2.3}
\]

The initial state \( |i\rangle \) with energy \( E_i \) is assumed to be a \( K \) shell \( s \) state in the following. The final state \( |f\rangle \) with energy \( E_f \) is the final unoccupied state of the photo-electron, which has to be of \( p \) symmetry according to the dipole selection rules. If the incoming electromagnetic wave with frequency \( \omega \) has its electric field \( E_0 \) polarized along the \( z \) direction and the dipole approximation is assumed, the perturbation \( H_1 \) that causes absorption can be written as:

\[
H_1 = \frac{1}{2} e_0 E_0 z e^{-i\omega t}. \tag{2.4}
\]

The dipole approximation is valid if the electric field of the electromagnetic wave can be considered constant over the dimension \( a \) of the \( K \) shell of the absorbing atom \[12\]. This is true if \( (a/\lambda)^2 \ll 1 \[13\], with \( \lambda \) being the wavelength of the photon. For example, for the copper K edge \( (a/\lambda)^2 \approx 0.01 \) and hence the approximation is justified. Using this approximation the transition rate can be written as:

\[
W = \frac{\pi}{2\hbar} e_0^2 E_0^2 \sum_f |\langle f | z | i \rangle|^2 \delta (E_f - E_i - \hbar \omega). \tag{2.5}
\]

Inserting Eq. 2.5 in Eq. 2.2 with the energy density \( u = E_0^2 / 8\pi \[13\] yields:

\[
\frac{du}{dt} = -4\pi^2 \omega e_0^2 N_{\text{at}} u \sum_f |\langle f | z | i \rangle|^2 \delta (E_f - E_i - \hbar \omega). \tag{2.6}
\]

The attenuation of the energy density \( u \) due to absorption is
2.1. Principles of EXAFS

\[
\frac{du}{dx} = -\mu_0 u, \quad (2.7)
\]

and

\[
\frac{du}{dt} = \frac{dx}{dt} \cdot \frac{du}{dx} = c \cdot \frac{du}{dx} = -c\mu_0 u, \quad (2.9)
\]

as the electromagnetic wave travels with light velocity \(\frac{dx}{dt} = c\).

Using Equation 2.8 and Equation 2.6 the following expression for the linear absorption coefficient is obtained:

\[
\mu_0 = \frac{4\pi^2 \omega_0^2}{c} N a \sum_f \left| \langle f | z | i \rangle \right|^2 \delta \left( E_f - E_i - \hbar \omega \right). \quad (2.11)
\]

To understand the decrease in the absorption coefficient with increasing energy \(\hbar \omega\), these expression has to be further analysed (see Ref. 14). If it assumed that the initial state \(|i\rangle\) is a 1s core state and the final state can be approximated by a plane wave with kinetic energy \(E_{kin} = \hbar \omega - E_i\) due to the small atom approximation, the linear absorption coefficient \(\mu\) is proportional to the energy of the x-rays by \(E^{-7/2}\) and the atomic number by \(Z^5\). Although these energy dependence explains the strong dependence of the absorption coefficient on both parameters and the observed decrease in absorption with increasing x-ray energy \(E\) (Fig. 2.2), it should be mentioned that a more detailed analyses, considering also those factors, which have been neglected for simplicity here (e.g. the screening of the nuclear charge by the other electrons or the Coulomb interaction of the photo-electron by the ionized absorber atom) yield a different dependence on both parameters. Taking these effects into account, it can be shown that the absorption coefficient \(\mu\) is proportional to \(Z^4\) and \(E^{-3}\) [14].

2.1.2 X-Ray Absorption in Condensed Matter

Until now the absorption spectrum of isolated atoms has been discussed. The absorption coefficient \(\mu\) changes for absorber atoms embedded in condensed matter as can be seen in figure 2.1, where the absorption coefficient of amorphous Ge\(_3\)Sb\(_2\)Te\(_4\) is plotted versus energy close to the germanium \(K\) edge. In addition to the two characteristics already observed in the absorption coefficient \(\mu_0\) of isolated atoms, oscillations appear in the spectrum just above the absorption edge. The origin of these oscillations \(\chi(E)\) will be discussed in more detail in the following.

In the derivation of Equation 2.11 it has only been assumed that the final state \(|f\rangle\) can be approximated by a plane wave. Therefore, Equation 2.11 in principle also
describes the linear absorption coefficient of condensed matter, but the differences for isolated atoms and atoms in condensed matters have to be discussed. The initial state \( |i⟩ \) is assumed to be a K shell s-state and this state barely depends on the environment of the absorbing atom. It is only the final state \( |f⟩ \) that is modified due to the presence of neighbouring atoms as compared to isolated atoms. When the absorber is embedded in condensed matter, the final state \( |f⟩ \) can be written like

\[
|f⟩ = |f_0 + ∆f⟩, \tag{2.12}
\]

where \( |f_0⟩ \) is an outgoing spherical wave (or the final state in absorption by isolated atoms) and \( |∆f⟩ \) accounts for the changes due to the neighbouring atoms.

The absorption coefficient \( µ \) is proportional to the squared modulus of the matrix elements \( \langle f | H_1 | i⟩ \) (cf. Equation 2.5):

\[
µ ∝ |\langle f_0 + ∆f | H_1 | i⟩|^2 \tag{2.13}
\]

\[
≅ |\langle f_0 | H_1 | i⟩|^2 + \{ ∆f | H_1 | i⟩^* \langle f_0 | H_1 | i⟩ + c.c. \} \tag{2.14}
\]

\[
= |\langle f_0 | H_1 | i⟩|^2 \left( 1 + \left\{ \frac{⟨∆f | H_1 | i⟩⟨f_0 | H_1 | i⟩^*}{|f_0 | H_1 | i⟩^2} + c.c. \right\} \right) \tag{2.15}
\]

where c.c. is the complex conjugate of the previous expression. The first term \( |⟨f_0 | H_1 | i⟩|^2 \) is proportional to the absorption coefficient of the free absorber \( µ_0 \) (Eq. 2.11) and the second term, which is proportional to \( ⟨∆f | H_1 | i⟩ \), refers to the EXAFS oscillations \( χ(E) \). The term \( |⟨∆f | H_1 | i⟩|^2 \) can be neglected as \( µ − µ_0 \ll µ \).

Thus the absorption coefficient \( µ \) of an absorber in condensed matter can be written as

\[
µ(E) = µ_0(E)(1 + χ(E)), \tag{2.16}
\]

where \( χ(E) \) is the x-ray absorption fine structure.

This fine structure results from the modification of the final state \( |f⟩ \) due to the neighbouring atoms. The modification of the final state can be depicted through elastic scattering of the emitted photo-electron by the neighbouring atoms (Fig. 2.3). The emitted photo-electron can be described by a spherical wave, which propagates freely through the material. This photo-electron is scattered by the neighbouring atoms and both waves, the outgoing wave and the backscattered wave, interfere with each other. These interferences affect the probability to absorb a photon and, therefore, the absorption coefficient \( µ \) oscillates around the absorption coefficient of an isolated atom \( µ_0 \). In the extreme of destructive interference, when the outgoing and the backscattered wave are completely out of phase, they will cancel each other, which means that no free unoccupied state exists in which the core-electron could be excited to. Thus absorption is unlikely to occur and the EXAFS oscillations will have a minimum. As the energy of the incoming x-ray beam increases, the wavelength of the photo-electron decreases \( λ ∝ (E_{\text{photon}} − E_i)^{-1/2} \). Because the average distance to
2.1. Principles of EXAFS

The probability to absorb an x-ray photon depends on the final state of the photo-electron. The emitted photo-electron is backscattered from the atoms, which surround the absorber. The final state of the photo-electron depends on the photon energy and the atomic arrangement around the absorbing atom, as those change the phase of the emitted and backscattered waves. Constructive interference of both waves causes a maximum in the absorption coefficient, while destructive interference a minimum.

As previously mentioned, the scattering of the outgoing electron-wave from the neighbouring atoms affects the amplitude of the photo-electron (see Fig. 2.3), which eventually results in the oscillation of the linear absorption coefficient with changing x-ray energy. From this qualitative picture an expression to calculate the EXAFS can be deduced. Conventionally, the EXAFS oscillations are often defined with respect to the photo-electron wave number $k$:

2.1.3 The EXAFS Equation

In the following a derivation of the EXAFS equation will be presented. Thereby we focus on a qualitative description of the different terms affecting the fine structure. A more formal derivation of the EXAFS formula based on a further analysis of Eq. 2.11 with $|f⟩ = |f_0 + Δf⟩$ can be found for example in Ref. 13 and 15.

Figure 2.3: Origin of the x-ray absorption fine structure. The probability to absorb an x-ray photon depends on the final state of the photo-electron. The emitted photo-electron is backscattered from the atoms, which surround the absorber. The final state of the photo-electron depends on the photon energy and the atomic arrangement around the absorbing atom, as those change the phase of the emitted and backscattered waves. Constructive interference of both waves causes a maximum in the absorption coefficient, while destructive interference a minimum.

The neighbouring atoms does not change, the phase shift of the two waves varies continuously until both waves are completely in phase, causing a maximum in the EXAFS oscillations. Therefore, the EXAFS oscillations depend on the distances $R$ to the neighbouring atoms, but they also contain information on the number of neighbours $N_j$ and type of the neighbouring atoms.
\[ k = \sqrt{\frac{2m_e}{\hbar^2}} (\hbar \omega - E_i), \]  

(2.17)

where \( E_i \) is the binding energy of the core-electron that is excited and \( E = \hbar \omega \) is the energy of the absorbed x-ray photon.

The outgoing photo-electron can be described by a spherical wave with wavenumber \( k \) and an amplitude which is proportional to \( r^{-1} \exp(ikr) \). The neighbouring atoms scatter the incoming wave into a new spherical wave and this wave is proportional to the amplitude of the incident wave and the backscattering amplitude \( F(k) \), which depends on the type of backscatterer (see Fig. 2.4). The backscattered wave emanates from \( R \) and not from the origin of the outgoing spherical wave. We are interested in the amplitude of the backscattered wave at the origin (at \( R = 0 \)), as the initial state \( |i\rangle \) is an \( s \)-state, which is non-zero only close to the origin and, therefore, the matrix element \( \langle \Delta f | H_1 | i \rangle \) will be unequal zero only close to the origin. The amplitude of the backscattered wave at the origin is proportional to \( F(k) \exp(i2kR)/R^2 \).

As the electron is not moving in a constant potential, a phase shift \( \delta(k) \) has to be added to this expression to account for the interaction of the electron with the varying potential of the absorber atom and of the backscattering atom. It must be distinguished between the phase shift of the absorbing atom \( \delta_a(k) \) and the backscattering atom \( \delta_b(k) \) (see Fig. 2.4). \( \delta(k) \) is the sum of both phase shifts, but the phase shift of the absorber atom \( \delta_a(k) \) has to be counted twice in this sum, hence, \( \delta(k) = 2\delta_a(k) - l\pi + \delta_b(k) \), where \( l = 1 \) for K edges according to the dipole selection rules. Thus we obtain for the EXAFS \( \chi(k) \)

\[
\chi(k) \propto F(k) \frac{\exp(2ikR+\delta(k)) + \text{c.c.}}{2R^2} 
= F(k) \frac{\sin(2kR + \delta(k))}{R^2}.
\]  

(2.18)  

(2.19)

In condensed matter the absorber atom has in general more than one next nearest neighbour and, therefore, Equation 2.18 must be summed over the scattering contribution of all neighbours. Atoms at the same radial distance and of the same element contribute to the same components of the EXAFS signal. This group of atoms is called a (coordination) shell. The coordination number of each shell is \( N_j \) and the sum in \( \chi(k) \) runs over all shells \( j \). The distance between the absorber and the backscatterers in one shell might not be identical due to structural disorder and moreover the atoms vibrate due to thermal excitations which also influences the distance between the absorber atom and the backscatterer. Thus the contributions from atoms in one shell will not be exactly in phase. If the disorder is small and has a Gaussian distribution around the average distance \( R \), the dephasing can be taken into account for by a factor \( \exp(-2k^2\sigma_j^2) \) and \( \sigma_j^2 = \left\langle \| \vec{r}_j \cdot (\vec{u}_j - \vec{u}_0) \|^2 \right\rangle \) is the mean
2.1. Principles of EXAFS

Figure 2.4: The dependency of important EXAFS parameters on the wavenumber $k$ is calculated with the program FEFF [16]. The backscattering amplitude $F(k)$ (a), the phase shift due to the backscatterer $\delta_b(k)$ (b) and the absorber $2\delta_a(k) - \pi$ (c) depend on the respective element (Ge, Sb, Te, Sn and Bi), which allows to discriminate in the later analyses the contributions from the different atoms. The electron mean free path (d) is similar for all elements.

The square average of the difference of displacements $(\vec{u}_j - \vec{u}_0)$ of the backscatterer $j$ and the absorber along the equilibrium bond direction $\vec{r}_j$. The term is often referred to as EXAFS Debye-Waller factor but it should be noticed that this factor is not equivalent to the Debye-Waller factor in x-ray diffraction $\sigma_{XRD}^2 = \langle (\vec{r}_j \cdot \vec{u}_j)^2 \rangle$, which is the mean square displacement. Usually the EXAFS Debye-Waller factor is smaller as compared to the XRD Debye-Waller factor as only the vibrations relative to the absorbing atom are taken into account for and for example long wavelength phonons will not contribute to the EXAFS Debye-Waller factor, since the two atoms (absorber and backscatterer) are too close to each other and the contribution to the difference $(\vec{u}_j - \vec{u}_0)$ is negligible.

The last effect, that has to be taken into account, is the lifetime $\tau_0$ of the excited photoelectron states, which depends on the time it takes until the core hole is filled by
another electron and on the lifetime of the photo-electron itself. Within the lifetime of the photo-electron state (e.g., $τ_0 = 2 \times 10^{-15}$ s for a Cu 1s electron [14]) the outgoing and the backscattered wave are coherent and thus both waves can interfere. This means that the number of shells contributing to the spectrum is limited by the fact that the outgoing and the backscattered wave must be coherent and, therefore, the finite lifetime of the photo-electron state damps the oscillations due to backscattering from neighbouring atoms at higher distances. Usually it is expected that shells, which are further apart than 10 Å from the absorber, are not visible in the spectrum. The damping factor equals $\exp\left(-2R_j/\lambda(k)\right)$ and $\lambda(k)$ is called the mean free path. As can be seen in figure 2.4 the mean free path depends only little on the element. So finally the following expression is obtained to describe the EXAFS oscillations $\chi(k)$

$$\chi(k) = \sum_j N_j S_0^2 F_j(k)e^{-2R_j/\lambda(k)}e^{-2k^2\sigma^2}\sin\left(2kR_j + δ_j(k)\right)/kR_j^2.$$  

(2.20)

The amplitude reduction term (or passive electron reduction factor) $S_0^2$ accounts for the relaxation of all other electrons in the absorber atom due to the creation of the core hole. Although $S_0^2$ is weakly energy dependent, it is usually approximated by a constant. The amplitude reduction term differs for different elements and the values range from $0.6 < S_0^2 < 1.0$ [17].

2.2 Fourier Transformations

"One of the earliest analyses of EXAFS [18] was based on the Fourier transform (FT) of the data expressed in momentum space" [15]. Although today’s analysis is based on a fitting procedure, in which a theoretical EXAFS spectrum is calculated using ab initio methods and afterwards refined (see Section 2.4), Fourier transformations still play an essential role in the analysis and interpretation of EXAFS data. Therefore the principles of Fourier transformations necessary to understand the analysis of EXAFS data are shortly discussed in the following. A detailed discussion of Fourier transformation can be found e.g. in Ref. 19.

Any periodic function $f(t)$ with period $T$ can be represented as a superposition of sine- and cosine-functions:

$$f(t) = \sum_{k=-\infty}^{+\infty} (A_k \cos ω_k t + B_k \sin ω_k t) = \sum_{k=-\infty}^{+\infty} C_k e^{iω_k t},$$

(2.21)

with $C_k = {A_k - iB_k \over 2}, \quad ω_k = {2πk \over T}$ and $k = 0, ±1, ±2\ldots$.  

(2.22)
The Fourier coefficients $C_k$ describe the amplitude of the corresponding sine- and cosine-waves and they can be calculated by integration of the function $f(t)$:

$$C_k = \frac{1}{T} \int_{-T/2}^{+T/2} f(t)e^{-i\omega_k t} dt \quad \text{for } k = 0, \pm 1, \pm 2 \ldots$$  \hspace{1cm} (2.24)

For an increasing period $T$, the angular frequency $\omega$ will get smaller. In the limit, when $T$ approaches infinity the summation over $k$ is replaced by an integral. And as the periodicity is no longer implicit, any function can be Fourier transformed using the following equations:

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(\omega)e^{i\omega t} d\omega,$$  \hspace{1cm} (2.25)

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(t)e^{-i\omega t} dt.$$  \hspace{1cm} (2.26)

The X-ray absorption fine structure is a function of energy $E$ or respectively wavenumber $k$ and their Fourier transform is therefore a function of space $R$. In contrast to the general definition (Equation 2.25) the Fourier transformation in the EXAFS analysis is defined such that the Fourier transform of a plane wave with frequency $2R_0$ is a delta function centred at $R_0$:

$$f(R) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-i2KR_0}e^{i2kR} dk$$  \hspace{1cm} (2.27)

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{i(2R-2R_0)k} dk$$  \hspace{1cm} (2.28)

$$= \delta(R - R_0).$$  \hspace{1cm} (2.29)

An electron wave, which emanates from the absorbing atom and is backscattered from a neighbouring atom at distance $R$, has a phase proportional to $2R$, because the wave travels from the absorbing atom to the backscattered atom at $R$ and back to the origin. The definition of the Fourier transform causes the peaks in the magnitude of the Fourier transform of an EXAFS spectrum to be related to the interatomic distances in the material investigated.

The integral in the definition of the Fourier transform ranges from $-\infty$ to $+\infty$, but the EXAFS is usually measured up to 1000 eV above the absorption edge and thus expressed in measures of the wavenumber the EXAFS ranges from $k = 3 \text{ Å}^{-1}$ up to
2. Extended X-Ray Absorption Fine Structure

Figure 2.5: Effect of a reduced data range on the Fourier transform. The data range of the fine structure $\chi(k)$ (left) that is Fourier transformed is marked with the dotted lines. The minimum $k$ value is the same for both transformations and only the maximum $k$ value is varied. On the right side the Fourier transformed spectra $|\chi(R)|$ are shown. It is obvious that the reduced data range causes a broadening of the peaks.

$k = 16 \, \text{Å}^{-1}$. The finite range causes extra characteristics in the Fourier transform of the $\chi(k)$.

First of all the finite data range is responsible for a broadening of the peaks in the Fourier transform. The smaller the $k$-range of the data is, the broader are the peaks in the Fourier transform. Therefore it is in principle desirable to use a $k$-range in the Fourier transform which is as large as possible. But as the oscillations are damped with higher wavenumbers $k$ (see Equation 2.20), the data range often cannot be extended beyond $k = 16 \, \text{Å}^{-1}$. In Figure 2.5 the effect of a shorter $k$-range on the magnitude of the Fourier transform is displayed. Due to the finite data range it can happen that two separated shells might not be resolved in the Fourier transform. In addition to the damping of the oscillations due to, for example, the EXAFS Debye-Waller factor, the signal-to-noise ratio usually decreases at higher wave numbers $k$. When choosing the appropriate $k$-range, this has to be taken into account since noise can cause high frequency oscillations (ripple effect) in the Fourier transform. Both influences, a large $k$-range to improve the spatial resolution and a high signal-to-noise ratio, have to be balanced in order to optimize the $k$-range used in the EXAFS analysis.

Second, due to the finite data range of $\chi(k)$ zeros have to be added to the data outside this range $\Delta k$ to create a dataset which ranges from $-\infty$ to $+\infty$ in order to perform the Fourier transformation. The resulting function is comparable to a step
function, where the steps are at the beginning and the end of the measured data. As the Fourier transform of a step function is unequal zero at all values for R, this causes characteristic oscillations in the Fourier transform (Fourier transform ripple). The effect is similar to the effect that noise has on the Fourier transform and is reduced when a window function is multiplied to the spectrum. A window function gradually increases the data from zero at the beginning and gradually decreases down to zero at the end of the data range $\Delta k$. Different types of windows can be used to process EXAFS data. In this work the Kaiser-Bessel function was applied.

Taking the discussed factors into account, the Fourier transform $\chi(R)$ of the fine structure $\chi(k)$ in the EXAFS analysis is defined by:

$$\chi(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k) w(k) e^{i2kR} dk,$$

with the window function $w(k)$. The $k$ range used in the transformation is given by $k_{\text{min}}$ and $k_{\text{max}}$. As can be seen, the fine structure $\chi(k)$ is weighted by a factor $k^n$ prior to the transformation and $n$ usually equals 1, 2 or 3. This is done to compensate for effects which diminish the amplitude with increasing $k$ such as the $1/k$ dependence of the fine structure and the characteristic behaviour of the backscattering amplitude function. The weighting factor $n$ should be chosen such that the amplitude of $k^n\chi(k)$ is constant over the $k$-range of data used in the transformation (see Figure 2.6) [13]. Since usually the noise increases at higher wavenumbers $k$, it also must be taken into account that a larger weighting factor $n$ amplifies the contribution from the higher $k$-values compared to the lower $k$-values and therefore it might be necessary to choose a small weighting factor when analysing data with a low signal-to-noise ratio.

In the analysis of EXAFS spectra, one possibility is to calculate theoretical spectra from model structures and fit these calculated spectra to the data while refining the structural parameters of interest (see Section 2.4). The fitting can be done either in $k$ space or in the Fourier transformed space, where both the imaginary and the real parts of the Fourier transform are used. The back Fourier transform of $\chi(R)$ is again a function of wavenumber $k$. To unambiguously distinguish between the spectrum $\chi(k)$ and the back Fourier transformed spectrum, the latter will be called $\chi(q)$, where $q$ is, as well as $k$, a measure of wavenumber in units Å$^{-1}$.

The back Fourier transform spectrum $\chi(q)$ can be used to investigate the influence of different shells on the absorption spectrum. This is done by changing the size and position of the window function in the spectrum $\chi(R)$ which is back Fourier transformed. Thereby the components of the original spectrum $\chi(k)$ that contribute to a certain $R$ range can be determined. Due to the back Fourier transformation of usually only parts of the spectrum $\chi(R)$, where the signal-to-noise ratio is large, the high frequency noise is removed from the data.

In many publications the magnitude of the Fourier transformed spectrum $|\chi(R)|$
Figure 2.6: Effect of k-weighting on the Fourier transform of $\chi(k)$. The absorption fine structure $\chi(k)$ multiplied by $k^n$ is plotted on the left hand side. The factor $n$ in the analysis is chosen such that amplitude of $k^n\chi(k)$ is constant. The influence of the different k-weightings on the Fourier transform can be seen on the right side. It seems that the resolution increases with increasing weighting factor $n$, since for $n = 3$ peaks can be distinguished that only appear as a shoulder in the Fourier transform, if the spectrum is weighted by $k$.

is shown, as in this display the peaks in $R$ are related to interatomic distances. Therefore differences in spectra from different materials or phases can easily been seen. $|\chi(R)|$ is often compared to a radial distribution function, but it is important to understand that some important differences exist.

First, the peak positions in $|\chi(R)|$ do not coincide with the distances between the absorbing atom and its neighbouring atoms. The phase shift $\delta(k)$ can be approximated by a function, which is linear in $k$: $\delta(k) \approx -\alpha_j k + \beta_j$, with the constants $\alpha_j > 0$ and $\beta_j$ [20]. Hence, the peaks in $|\chi(R)|$ appear at the position $R - \alpha_j$ and are phase shifted by 0.2 Å-0.3Å towards smaller distances. The actual phase shift depends on the identity of the absorbing atoms as well as the neighbouring atoms.

Second, the amplitude in a radial distribution function depends only on the coordination number $N$, while the amplitude of the peaks in $|\chi(R)|$ depends on many EXAFS variables like for example the EXAFS Debye-Waller-factor, the mean free path $\lambda(k)$ and the number of nearest neighbour. Also multiple scattering paths can play an important role and contribute to the amplitude in $|\chi(R)|$ (see Section 2.4 and Ref. 21).
2.3. Data Reduction

Although the magnitude of the Fourier transform contains easily accessible structural information (similar to a radial distribution function) it is indeed a complicated signal and one therefore must be careful when interpreting and comparing the magnitude of the Fourier transform $|\chi(R)|$ for different materials and compositions.

2.3 Data Reduction

The origin of the x-ray absorption fine structure is well understood and it is possible to model the fine structure using Equation 2.20. Since the EXAFS is defined as the oscillatory part of the absorption coefficient above an absorption edge, the fine structure $\chi(k)$ has to be extracted, before the desired structural information is obtained. The most important step in this data reduction is to subtract the step-like background from the data. Unfortunately the background function is unknown and it can also not be measured or calculated. Therefore an empirical method is used to determine this function. The necessary steps to extract $\chi(k)$ from the measured absorption spectrum $\mu(E)$ are discussed in the following.

2.3.1 Alignment and Energy Calibration

In this study at least two scans have been recorded at each absorption edge of the investigated material. This is done since already after a short time a complete spectrum is measured and one can easily decide whether the measurement conditions, such as energy range or sample position, need to be changed. This way, only a minimum amount of beamtime is lost, if the spectrum needs to be optimized by changing some parameters. Furthermore, by comparing two or more successive spectra, changes in the spectrum as a function of x-ray exposure time can easily be detected prior to the analysis. In order to increase the signal-to-noise ratio, multiple spectra can be merged. To do so, they need to be aligned to the same energy scale. To align the scans the energy scale of one scan relative to another can be shifted until both scans match. If all scans are aligned in this way, they can be merged into one spectrum and afterwards the energy of this spectrum is calibrated to an absolute energy scale.

The calibration of the absolute energy scale is especially important for XANES analysis, while in an EXAFS analysis a small misalignment of the energy could also be corrected for in the later analysis. But the discussed method avoids to oversee larger misalignments in the experiment which would induce errors in the results. It is common to measure the absorption of a pure material along with the sample as a reference. This is done since the edge energy of the reference spectrum corresponds to the tabulated edge energy (see Ref. 22) and can therefore be used to define the absolute energy scale. Another advantage is, that chemical information about the measured sample can be gained by comparing the edge energy of this material to the pure element. To calibrate the energy scale the edge energy $E_0$ of the reference
2. Extended X-Ray Absorption Fine Structure

Figure 2.7: Absorption spectrum measured at the Ge K edge. The pre-edge line and post-edge line (grey) are evaluated at the edge energy \( E_0 \). The difference between both line \( \Delta \mu_0(E_0) \) is used to normalize the absorption spectrum to an edge step equal to one.

The spectrum has to be defined. Since the absorption edge usually has a non-negligible width, the choice of the "edge energy" is a bit arbitrary and different definitions are used. In this study we refer to the maximum of the first peak of the first derivative of the EXAFS spectrum as edge energy. To calibrate the data, the energy scale of the reference spectrum is shifted in such a way that the maximum of the first peak of the first derivative coincides with the tabulated edge energy. The same energy shift is in the final calibration step also applied to the spectrum of the sample.

2.3.2 Normalization

In order to be able to compare measurements from different samples and spectra measured at different beamlines, the data have to be normalized. Differences in the height of the absorption edge in the spectra can result for example from a different concentration of the absorber element, sample thickness or detector settings. Therefore, the edge step is normalized to a height equal to one and the absorption in the pre-edge region \( (E < E_0) \) is set to zero (see Figure 2.7). This normalization is accomplished by fitting a line to the pre-edge region and extrapolate it over the whole data range (Figure 2.7). The pre-edge line is afterwards subtracted from the data. The post-edge region is fitted by a polynomial. The order of the polynomial can be controlled and ranges from 1 to 3 depending on the absorption spectrum. Both the pre-edge and the post-edge line are extrapolated and evaluated at the chosen edge energy \( E_0 \). The pre-edge subtracted data are divided by the difference of both lines \( \Delta \mu_0(E_0) \) at the edge energy \( E_0 \).
2.3. Data Reduction

Figure 2.8: Influence of the parameter $R_{bkg}$ on the Fourier transform $|\chi(R)|$. The magnitude of the Fourier transform $|\chi(R)|$ is shown for two different choices of $R_{bkg}$. All Fourier components, that are contributing to the spectrum in $R$ below $R_{bkg}$, are considered to be part of the background. The amplitude of the spectrum between 0-1 Å decreases significantly, when $R_{bkg} = 1.21$ (blue) is used to determine the background function instead of $R_{bkg} = 0$ (black).

2.3.3 Background Subtraction

As mentioned above the EXAFS is only the oscillatory part of the absorption spectrum above the absorption edge. The relation between $\chi(E)$ and $\mu_0(E)$ is:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}.$$

$\Delta\mu_0(E_0)$ is the step height, which was set to 1 in the normalization procedure. The term $\mu_0(E)$ is called the background function and is the absorption of an isolated atom with the same electronic configurations as the bound atoms in the sample. As $\mu_0(E)$ is not known and cannot be measured it must be extracted from the absorption measurement itself. One way to determine the background function is to fit splines connected with knots. A spline is a polynomial which might be of linear, quadratic or cubic order. Different ways exists to place the knots through the EXAFS oscillations. While in early approaches the knots have been placed manually to
2. Extended X-Ray Absorption Fine Structure

optimize the background function, in this work the AUTOBK approach (embedded in the program ATHENA [23]) is used to determine the background function [24]. In this approach the knots are evenly spaced in photoelectron wave number. The number of cubic splines determines the maximum frequency component that is allowed in the background function. The number of cubic splines is given by

\[
\text{number of cubic splines} = \frac{2R_{bkg} \Delta k}{\pi}.
\]

That is, the number of splines depends on the data range \(\Delta k\) and the number \(R_{bkg}\). All Fourier components contributing to the part of the spectrum in real space \(R\) below \(R_{bkg}\) are considered to be part of the background. As oscillations with long wavelengths contribute to the low \(r\) regions, the longest wavelength, which is actually part of the structural information, results from the atoms in the first coordination shell around the absorber. The number \(R_{bkg}\) has to be selected carefully and is usually chosen to be about one half of the nearest neighbour distance. The parameter is chosen well if the intensity of the first peak keeps constant and at the same time the amplitudes of the peaks at shorter radial distances are minimized (Figure 2.8). The normalized absorption spectra of the all materials analysed in this study are plotted together with the respective background function in Appendix B.

2.4 Data Analysis

In this section a standard EXAFS analysis is discussed, which is based on the least-squares refinement of scattering paths to model the experimental data. To accomplish this, the program ARTEMIS has been used, which is based on the IFEFFIT algorithm [23, 25]. A detailed description of the standard EXAFS analysis can be found in Ref. 26 and Ref. 13.

EXAFS spectra contain information on the local structure of the investigated material. From the fine structure oscillations the distances to the neighbouring atoms \(R_j\) (usually within max. 6-8 Å), the number of nearest neighbours \(N_j\), the type of atoms in the different coordination shells and the mean square displacements \(\sigma_j^2\) of the atomic distances can be determined. To receive these desired informations the backscattering amplitude \(F(k)\), the phase shifts \(\delta(k)\) and the mean free path of the electrons \(\lambda(k)\) for all elements in the investigated material must be known (see Eq. 2.20). These parameters can be calculated using the program FEFF, which computes x-ray absorption spectra based on ab initio self-consistent multiple scattering calculations [16].

In the derivation of Eq. 2.20 only single scattering events have been taken into account, i.e. scattering events where the neighbouring atoms directly scatters the wave back to the absorbing atom. Generally, the wave can be scattered onto one or more other atoms before it is scattered back to the absorber atom (see Figure 2.9). This multiple scattering is important for an accurate analyses of the EXAFS (and
2.4. Data Analysis

(a) single scattering path  
(b) double scattering path  
(c) triple scattering path

Figure 2.9: Schematic of the symmetry of different scattering paths. The multiple scattering paths are most important when the scattering angle at the middle atom is close to 180°.

...
summarized in the so-called path file, which is useful to select the scattering paths which are included in the fit of the EXAFS data. In Table 4.1 the path list calculated for crystalline GeTe is shown.

To perform the least-square fitting and refine the structural parameters of the scattering paths the program ARTEMIS has been used [23]. For every path, which is selected and included in the fit at least four parameters have to be defined: the change in the effective path length \( \Delta R \), the mean square displacement factor \( \sigma^2 \), the amplitude \( N S_0^2 \) and the energy shift \( \Delta E_0 \). The change in path length \( \Delta R \) is defined with respect to only half the total path length (the effective path length), since for single scattering paths the distance between the absorber and the back scatterer equals half the path length. The energy shift \( \Delta E_0 \) accounts for any misalignment of the energy scale in the FEFF calculation with respect to the data. This misalignment is possible for example due to the muffin-tin approximation, which is used to calculate the potential of the atoms [16]. The amplitude reduction term \( S_0^2 \) and the path degeneracy \( N \) are correlated 100% (see Eq. 2.20) and might therefore be considered as one parameter, if only one absorption edge is refined. By a simultaneous refinement of several spectra measured at different absorption edges this correlation is decreased, as the reduction term \( S_0^2 \) applies for all path of one absorption edge, while the coordination number \( N \) depends on only one scattering path, which might instead be relevant at two (or more) absorption edges.

Usually at least the above mentioned parameters are varied during the fit. Although this parameters are not necessarily independent of each other for different scattering paths, the number of refined parameters grows rapidly with the number of scattering paths, that is included in the fit. The number \( N_{\text{idp}} \) of parameters that can reliably be determined in a fit is limited by the data range \( \Delta k \) and \( \Delta R \) according to the Nyquist theorem [28]:

\[
N_{\text{idp}} = \frac{2\Delta k \Delta R}{\pi} + 2. \tag{2.31}
\]

\( N_{\text{idp}} \) gives an estimate of the maximum number of independent parameters. If many different paths have to be taken into account to simulate the measured EXAFS spectrum, the number of parameters to be refined in the fit can easily exceed the number of independent parameters. Therefore it is useful to define functions that correlate parameters with each other to decrease the number of refined parameters [29]. For example in the refinement of a crystal, the distances from the absorber to the neighbouring atoms depend on the crystalline structure. Therefore it is sometimes possible to parametrize the length of the scattering paths with respect to the lattice parameters and only the latter are refined.

The least-squares refinements performed in ARTEMIS aim at minimizing the function \( \chi^2 \), which depends on the number of independent points \( N_{\text{idp}} \) and the uncertainty in the measurement \( \epsilon \):
2.5 RMC Simulations

\[ \chi^2 = \frac{N_{idp}}{N\epsilon^2} \sum_{i=1}^{N} \left\{ [\text{Re}(f_i)]^2 + [\text{Im}(f_i)]^2 \right\}. \]  

(2.32)

The sum in \( \chi^2 \) runs over \( N \), the number of evaluation points. This number depends on the fitting space, as EXAFS data can be fitted either in \( k \)-space or after a Fourier transformation in real space \( R \). For a fit in \( R \) the number of evaluation points \( N = 2(R_{\text{max}} - R_{\text{min}})/\delta R \) and in \( k \)-space \( N = 2(k_{\text{max}} - k_{\text{min}})/\delta k \). Here \( \delta R \) and \( \delta k \) are the grid spacings in \( R \) and \( k \)-space and \( k_{\text{max}} \) and \( k_{\text{min}} \) (respectively \( R_{\text{max}} \) and \( R_{\text{min}} \)) are the limits of the chosen fitting range. The function \( f_i \) is the function that has to be minimized in the fit and also depends on the fitting space. For fitting in \( k \)-space the function to minimize is

\[ f(k_i) = \chi_{\text{data}}(k_i) - \chi_{\text{model}}(k_i), \quad k_{\text{min}} \leq k_i \leq k_{\text{min}}. \]  

(2.33)

To determine the goodness of the fit two different parameters are used. The first parameter is \( \chi^2_{\nu} = \chi^2/(N_{idp} - N_{\text{variys}}) \), where \( N_{\text{variys}} \) is the number of parameters that are varied during the fit. Usually a good fit should yield a \( \chi^2_{\nu} \) of approximately 1, but in an EXAFS analysis \( \chi^2_{\nu} \) tends to be much larger (\( \chi^2_{\nu} \approx 10 - 100 \) [30]), which means that the difference between the data and the fit is much larger than the measurement uncertainty in the data \( \epsilon \). This is most likely due to the fact that the measurement uncertainty is underestimated. The second statistical parameter to determine the fit quality is called \( R \)-factor and does not depend on the number of independent points \( N_{idp} \) or the measurement uncertainty \( \epsilon \)

\[ R = \frac{\sum_{i=1}^{N} \left\{ [\text{Re}(\chi_{\text{data}})]^2 + [\text{Im}(\chi_{\text{data}})]^2 \right\}}{\sum_{i=1}^{N} \left\{ [\text{Re}(\chi_{\text{model}})]^2 + [\text{Im}(\chi_{\text{model}})]^2 \right\}}. \]  

(2.34)

It is usually considered that fits, that yield an \( R \)-factor between 0.02 and 0.05, are acceptable, although there might be a mismatch between the fit and the data. Typically, \( R \)-factors below 0.02 indicate a good fit [31]

2.5 RMC Simulations

In addition to the standard EXAFS analysis, discussed in the previous section, we also perform Reverse Monte Carlo (RMC) simulations to analyse the EXAFS data. RMC modelling can be used to create a three dimensional particle configuration based on a set of experimental data. It has first been used to model the structure of liquids and glasses using the structure factor \( S(Q) \) or the pair distribution function \( g(r) \) resulting from neutron and x-ray diffraction experiments as input [32]. In the last years RMC simulations have also been applied to a variety of experimental data including neutron diffraction, x-ray diffraction (including anomalous scattering),
2. Extended X-Ray Absorption Fine Structure

electron diffraction and extended x-ray absorption fine structure \[33\]\[34\]. Moreover, the method has not only been utilized to study liquids and amorphous materials but also crystalline and magnetic structures \[35\]. The main principles of RMC simulations of EXAFS data will be outlined in the following. A detailed introduction to Reverse Monte Carlo modelling can be found in Ref. 36.

The aim of RMC simulations is to obtain a three dimensional configuration of atoms which is consistent with the set of experimental data. This consistency is achieved by the following algorithm. The description has been condensed for a better clarity and some parameters are afterwards discussed.

1. An RMC simulation starts with the generation of the initial configuration. N points (representing the atoms and will be referred to as atoms in the following) are placed in a cell with orthorhombic symmetry and periodic boundary conditions. The distribution of the atoms in this initial cell can have any symmetry, e.g. it can reflect a crystalline structure but it is also possible to place the atoms at random. The only constraint is that atomic number density and chemical composition must coincide with the experimental values of the structure that is simulated.

2. The fine structure \(\chi_{\text{old}}(k)\) for the initial configuration and their weighted difference \(\chi^2_{\text{old}}\) with respect to the experimental fine structure \(\chi_{\text{exp}}(k)\) is calculated.

3. To create a new configuration one particle in the cell is moved at random and the respective fine structure \(\chi_{\text{new}}(k)\) is determined.

4. The weighted difference for the new configuration \(\chi^2_{\text{new}}\) is calculated and compared to the difference of the former configuration \(\chi^2_{\text{old}}\). If \(\chi^2_{\text{new}} < \chi^2_{\text{old}}\) the so-called move is accepted and the new configuration becomes the old configuration. If \(\chi^2_{\text{new}} > \chi^2_{\text{old}}\) the move is accepted with probability \(\exp \left( -\frac{1}{T_{\text{RMC}}} (\chi^2_{\text{new}} - \chi^2_{\text{old}}) \right)\) or else it is rejected.

5. The new configuration (if accepted) becomes the old configuration in the following.

6. Repeat from step 3 until \(\chi^2\) reaches an equilibrium value, about which it oscillates.

The program that has been used in this study was written by Dr. C. Bichara. The outlined basic algorithm has been extended to suit the existing assignments and the additional program features will be described.

Since in this study EXAFS data are analysed, the fine structure \(\chi(k)\) is fitted but in principle any set or sets of data, that can be directly related to the structure, can be modelled by RMC simulations. We have measured absorption spectra of all elements in the sample and hence, for every alloy, that is discussed in this thesis, at least two
data sets exist, which are modelled simultaneously. The parameter that is minimized
in the simulation is $\chi^2$, which is defined as

$$\chi^2 = \sum_{j=1}^{N_{\text{datasets}}} \left( \sum_{k=k_{\text{min}}}^{k_{\text{max}}} \frac{[\chi_{\text{exp}}(k) - \chi_{\text{calc}}(k)]^2}{\sigma_j^2} \right),$$

(2.35)

where $\chi_{\text{calc}}(k)$ is either $\chi_{\text{old}}(k)$ or $\chi_{\text{new}}(k)$. The first sum runs over all data sets, that
means all measured absorption spectra for the analysed material. The second sum
ranges from $k_{\text{min}}$, which is usually around $3 \text{ Å}^{-1}$ to exclude the near edge region
of the spectra, to $k_{\text{max}}$, which depends on the measured data range. To be able
to compare $\chi_{\text{calc}}$ with $\chi_{\text{exp}}$ a grid with a step width of $0.05 \text{ Å}^{-1}$ is used. $\sigma_j$ is the
standard deviation estimated on $\chi(k)$.

As mentioned, during the RMC simulation the function $\chi^2$ is minimized. Never-
theless, a move that increases $\chi^2$ as compared to the configuration before, is accepted
with the probability $\exp\left[-\frac{1}{T_{\text{RMC}}} (\chi^2_{\text{new}} - \chi^2_{\text{old}})\right]$. This is done so that the result is in
principle independent of the starting configuration. The parameter $T_{\text{RMC}}$ is stated in
the beginning of the simulation. It is called temperature following the Metropolis
Monte Carlo (MMC) method of which RMC is a variation [37]. The function to
be minimized in MMC is the total potential energy $U$ and if the change in energy
$\Delta U = U_{\text{new}} - U_{\text{old}}$ increases for the new configuration ($\Delta U > 0$) a move is accepted
with the probability $\exp\left(-\frac{\Delta U}{k_B T}\right)$, where $k_B$ is the Boltzmann constant and $T$ the
temperature.

In order to enforce convergence of the simulation the temperature $T_{\text{RMC}}$ is reduced
during the simulations. To control the reduction of the temperature the RMC code is
organized in two loops. The so-called inner loop consists in principle of the above
discussed steps 3-6, but with one additional feature that will be explained. The
outer loop contains a specified number of inner loops and after each outer loop the
factor $T_{\text{RMC}}$ is reduced to enforce convergence. The factor $T_{\text{RMC}}$ must not be chosen
too small, because otherwise the temperature $T_{\text{RMC}}$ will drop too quickly and the
rejection rate of new configurations will be too high. As a consequence the sampling
of different configurations will be too low and the result might not be independent
from the initial configuration.

The mentioned additional feature in the inner loop is the possibility to swap the
position of any two atoms (a vacancy is treated as an atom regarding the swaps). The
atoms that interchange positions are selected randomly. Also after the atom swap $\chi^2$
is calculated for the new configuration and the same argument as used for the moves
of the atoms is applied to accept/reject the swap. Whether the inner loop starts with
the movement of an atom or with an interchange is chosen in a random manner. The
number of swaps per inner loop is, like the number of moves, stated in the input file
of the RMC simulations. This feature to interchange atoms was included in the code,
since it enhances the independence of the final from the initial configuration.
2. Extended X-Ray Absorption Fine Structure

In principle it is possible to perform an RMC simulation using only the experimental data to determine the three dim. configuration. While of course one strong constraint already applied is the atomic number density that is needed to create the initial configuration. Additional constraints can be applied easily during the RMC run. In this study one constraint has been applied in all simulation. The atoms have not been allowed to move an unlimited distance from the starting position, but the maximal distance was restricted by a sphere centred around the initial position. The radius of the spheres varied for the different alloys and phases investigated. It was always larger when analysing an amorphous phase as compared to a crystalline phase. Moreover, in many fits the minimal distance between two atoms has also been constrained. It is physically reasonable that the center of two atoms cannot come closer than the sum of the covalent radii of both atoms. Therefore, the minimal distances between the points have been constrained in many fits to the sum of covalent radii of the atoms, which the points are representing. When starting from a crystalline phase this constraint is not always needed.

In the description of the RMC algorithm one step, which is needed to simulate EXAFS data, was left out for simplicity. The function that is fitted is the fine structure $\chi(k)$, which can be calculated using Equation 2.20. Thus for the calculation the standard EXAFS parameters, i.e. amplitude reduction factor $S_0^2$, phase shifts ($\delta_b(k)$ and $\delta_a(k)$) and the electron mean free path $\lambda(k)$, are needed. Those parameters are calculated using FEFF8.4 [16]. Thereby we limit ourself to single scattering paths, thus we use a two-body approximation [38]. For any atom in the configuration the single scattering paths until a defined effective path length (usually $R_{\text{eff}} \approx 6-7$ Å) are calculated and stored. The path informations include the fine structure $\chi_j(k)$ and all standard EXAFS parameters for each path. In the end, these contributions are averaged over all atoms in the configuration for every element separately and stored in different files, which are needed for the RMC simulations. During the simulations, when the new $\chi(k)$ is calculated, the needed EXAFS parameters can be read from these input files.
3 Experimental Details

In this chapter, the set-ups and methods are described, which have been used to prepare and characterize the samples.

3.1 Sample Preparation

For many phase-change materials the phases, which are relevant for data storage applications, are meta-stable not only in the amorphous but also in the crystalline state. To obtain materials in the desired meta-stable phases, all samples are prepared using DC magnetron sputtering. A schematic drawing of the sputter chamber and the sputter process is shown in Figure 3.1.

After the evacuation of the sputter chamber ($P \approx 10^{-6}$ mbar), the chamber is filled with argon as process gas. Due to the applied voltage, Ar-ions are accelerated onto the negative-charged target, from which atoms and electrons are expelled due to the collision with the ions. The atoms precipitate on any surface in the chamber, also on the substrates which are placed just above the sputter target. Thereby the substrates are rotated to improve the uniformity of the developing layers. The expelled electrons are accelerated away from the target and through collisions they ionize more argon atoms on their way. The sputter rate and thus the speed of the layer growth depends on the number of argon ions, that exist above the target. To increase the number of Ar ions, a magnet is placed underneath the target, which forces the electrons on circular paths above the target. Due to the longer path length, the number of collisions between the electrons and the Ar atoms is enhanced and therefore the number of argon ions above the target increases. Thus the magnet underneath the target increases the sputter rate and also stabilizes the plasma.

In the context of this work, films with thicknesses from one to two micrometers have been sputtered on Si-substrates which had been coated by PMMA. To remove this film from the substrate, the PMMA has been dissolved in acetone. The resulting flakes are ground to a fine powder. Another procedure has been to sputter films on stainless steel, afterwards scrape off the material with a spatula and finally ground the material to a fine powder.

After sputtering, all films have been in the amorphous state, as has been affirmed by XRD measurements. The amorphous powder has been annealed in an oven under argon atmosphere to crystallize the materials in the desired (meta-stable) crystalline phases. The annealing temperatures of the different samples are stated in Table 3.1. XRD measurements have confirmed that the samples have crystallized in the desired
3. Experimental Details

Figure 3.1: Sketch of a magnetron sputter process (taken from D. Krebs [39]). Due to the applied high voltage, the ions in the plasma are accelerated onto the target. The expelled target atoms precipitate on the substrates.

crystalline states (NaCl-like phase for Ge$_1$Sb$_2$Te$_4$ and Ge$_8$Sb$_2$Te$_{11}$ and rhombohedral phase for GeTe).

Finally, for the EXAFS measurements, the fine powder of the materials has been mixed with cellulose and pressed to pellets. Thereby, the amount of material in a pellet was specified to optimize the signal-to-noise ratio and yield a reasonable edge step. Usually the signal-to-noise ratio is good, when the absorption $\mu \cdot d$ in a sample with absorption coefficient $\mu$ and thickness $d$ is approximately $\mu \cdot d = 2 - 3$ [26]. The absorption is defined according to Equation 2.1 by $\mu \cdot d = \ln \frac{I_2}{I_1}$ and can be calculated from $\mu = \rho \mu_m$, where $\rho$ is the density, $\mu_m$ is the mass absorption coefficient and $d$ is the sample thickness. Values of the mass absorption coefficients for the different elements can be found in Ref. 40. The mass absorption coefficient $\mu_m$ of an alloy is the weighted sum of the absorption coefficients of the elements $\mu_{m_i}$: $\mu_m = \sum_i f_i \mu_{m_i}$, where $f_i$ is the mass fraction of element $i$. Since the absorption changes with energy, different pellets have to be prepared for the measurements at different absorption edges. In Table 3.2 the amount of the material needed to prepare a pellet with a diameter of $S = 13$mm$^2$ and to obtain an absorption of $\mu \cdot d = 2.5$ is given for all
3.2. Beamline CEMO at Hasylab

Table 3.1: Parameters for the crystallization of the phase-change materials. The temperature, at which the materials have been crystallized, and the duration of the annealing process is stated.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$_1$Sb$_2$Te$_4$</td>
<td>105°C</td>
<td>60 h</td>
</tr>
<tr>
<td>GeTe</td>
<td>235°C</td>
<td>0.5 h</td>
</tr>
<tr>
<td>Ge$_8$Sb$<em>2$Te$</em>{11}$</td>
<td>185°C</td>
<td>1 h</td>
</tr>
</tbody>
</table>

Table 3.2: Preparation of the EXAFS samples. For every material investigated and every measured absorption edge, the amount of material needed to prepare a pellet with a diameter of $S = 13\text{mm}^2$ and to obtain an absorption of $\mu \cdot d = 2.5$ is stated and in addition the corresponding sample thickness $d$ for the crystalline phase is given.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ge edge</th>
<th>Sb edge</th>
<th>Te edge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m (mg)</td>
<td>d (µm)</td>
<td></td>
</tr>
<tr>
<td>Ge$_1$Sb$_2$Te$_4$</td>
<td>27</td>
<td>33</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>113</td>
<td>96</td>
</tr>
<tr>
<td>Ge$_8$Sb$<em>2$Te$</em>{11}$</td>
<td>24</td>
<td>30</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>109</td>
<td>131</td>
<td>137</td>
</tr>
<tr>
<td>GeTe</td>
<td>23</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>154</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

measured absorption edges. In addition, the corresponding sample thickness $d$ is stated.

3.2 Beamline CEMO at Hasylab

All EXAFS measurements have been performed at the experimental station CEMO [41–43] at the storage ring DORIS III of HASYLAB (Hamburger Synchrotronstrahlungslabor). The synchrotron radiation used at beamline CEMO is produced by a bending magnet. To select specific energies from the white beam, two different monochromators are available at the station, which allow to measure with x-ray energies ranging from 2.3 keV to 43.4 keV. Thus EXAFS measurements at the K absorption edges of Ge (11103 eV), Sb (30491 eV) and Te (31814 eV) can be carried out. A sketch of the beamline set-up is shown in Figure 3.2 and the function and alignment of the different components is explained in the following.
3. Experimental Details

The x-ray beam profile and size is determined by two pairs of slits before and after the monochromator. Moreover, the slits block unwanted x-rays, e.g. x-rays with too high angular divergence. The window, which is left open by the entrance slits, has a height of 1.1-1.4 mm and a width of 10 mm. The position of the exit slits, which are placed after the monochromator, can be adjusted for every measurement in such a way, that the beam hits the sample at the desired position and with the ideal size. For example the beam should never be larger than the sample in any direction, in order to reduce noise in the measurement. The opening of the exit slits has a height, which varies in the different measurements from 1 mm to 2 mm, and a width in the range of 6-12 mm. Usually the slit system is evacuated to reduce absorption.

The monochromator is used to select the desired energy of the white synchrotron beam. At beamline CEMO, a double crystal fixed-exit monochromator is used, which is placed 19 m from the bending magnet source. Two sets of monochromator crystals are available at the experimental station. The Si(111) crystal pair enables measurements with x-ray energies from 2.3 keV to 22.3 keV and the Si(311) crystal pair from 4.4 keV to 43.4 keV. The energy of the x-rays that passes the monochromator is varied by rotating the monochromator in the white beam. Only the x-rays that satisfy Bragg's law $n \lambda = 2d \sin \theta$ (with wavelength $\lambda$, spacing between the lattice planes $d$, diffraction angle $\theta$ and the order of diffraction $n$) are diffracted and thus pass the monochromator.

According to Bragg's law, not only x-rays with one wavelength are diffracted by a crystal but also the so-called higher harmonics with $n > 1$ are present in the diffracted beam. It is important to reduce the contributions of the higher harmonics in the x-ray beam, since these will affect the EXAFS measurement. Therefore such monochromator crystals (Si(111) and (311)) are used, which do not diffract the second harmonic ($n = 2$), because the intensity of the second harmonic is usually larger than the higher harmonics ($n > 2$). Moreover, to minimize the harmonics with $n > 2$, one takes advantage of the fact, that the beam profiles of the diffracted harmonics are different [13]. The beam profile of diffracted x-rays with fundamental energy $E$ is broader than the profiles of x-rays with higher energies $nE$. Therefore, the second monochromator is slightly detuned, that means that the angle of the second crystal differs slightly from the angle of the first monochromator crystal. This detuning decreases also the total intensity of the diffracted beam, but the drop of the contribution of the higher harmonics is significantly larger. Usually, the monochromator has been detuned such that the intensity of resulting beam was decreased to 60-70 % of its maximum value.

The intensity of the x-rays is measured in ionization chambers to calculate the absorption in the sample (and the reference) according to Lambert-Beer’s law (Eq. 2.1). The three ionization chambers have a length of 10 cm and can be filled with different inert gases ($N_2$, Ar, Kr) with a pressure from 100 mbar till 1000 mbar. The gases and the pressure in the ionization chambers depend on the energy of the absorption edge, at which the measurement is performed. The ionization chambers are filled such that the absorption level in the first ionization chamber is 10 %, in the second 50 %
and the third 90% of the incident beam. Thereby, it is assured that the absorption level in every chamber is high enough to yield a meaningful result and yet enough intensity reaches even the reference sample. The current in the ionization chamber is measured with Keithley 428 nanoAmpere meters.

At beamline CEMO, two different cryostats are available, covering a temperature range from approximately 5 K to room temperature. Most of the measurements have been performed using the liquid He flow cryostat, while for the measurements at 80 K it was sometimes necessary to use the liquid nitrogen cryostat.

Between the ionization chambers vacuum sample crosses are installed, to evacuate the sample and the reference sample chamber. The vacuum reaches $10^{-6}$ mbar. The evacuation of the chambers is necessary when measuring at low temperatures. In addition, the evacuation minimizes unwanted absorption along the beam path.
3. Experimental Details

Figure 3.2: Sketch of the EXAFS set-up. The size of the x-ray beam on the sample is determined by the different slits and the energy of the x-ray beam is chosen with the monochromator. The intensity of the beam is measured in the ionization chambers $I_1$, $I_2$ and $I_3$ before and behind the sample and behind the reference sample in order to calculate the absorption in the sample and the reference sample.

Figure 3.3: Picture of the beamline (taken from [44]). The monochromatic synchrotron beam enters the beamline from the left side. The beam runs through the evacuated sample crosses and the intensity is measured in the ionization chambers. The sample is mounted on the He cryostat, while the reference is kept a room temperature.
4 GeTe

The compound GeTe is due to the fast switching behaviour a promising candidate for future data storage applications based on phase-change materials, as has been shown recently by Bruns et al. [4]. Moreover, GeTe is a parent structure of the ternary Ge-Sb-Te alloys along the pseudo-binary line. Therefore, the detailed knowledge of the structure of the amorphous and the crystalline phase is important to understand the fundamental structural characteristics of phase-change materials. In addition, since GeTe is a binary compound, it is to be expected that the analysis is less challenging than the analysis of the ternary compounds, and thus a good starting point for the analysis presented in this thesis.

The measured absorption spectra are all treated using the AUTOBK approach, as described in Section 2.4, to determine the background and isolate the x-ray absorption fine structure oscillations [24]. The normalized absorption spectra measured at the Ge and Te absorption K edges of crystalline and amorphous GeTe at 10 K are shown in Figure B.1 together with the background function \( \mu_0(E) \). The signal-to-noise ratio of the data, measured at 10 K, is excellent. The fine structure oscillations are still significant and with a low level of noise even 1 keV above the absorption edges and it was therefore possible to increase the measurement range up to 1.5 keV above the absorption edge for the measurement of the crystalline phase.

In Figure 4.1 two EXAFS spectra measured at the Ge edge at 300 K and 10 K are compared. The increased signal-to-noise ratio and the higher information content at lower temperature is clearly visible. In the spectrum recorded at 10 K the amplitude is considerably higher and the signal-to-noise ratio is better as compared to the spectrum measured at room temperature. In addition, in the spectrum recorded at 10 K contributions from scattering atoms at distances up to 9 Å are visible, while in the other spectrum only peaks corresponding to the first coordination shell exist. The excellent quality of the data is an important prerequisite for the precise determination of the atomic structure of GeTe in the amorphous and the crystalline phase. The comparison of the EXAFS spectra of the crystalline and the amorphous phase (Section 4.1) is followed by the detailed analysis of both phases (Section 4.2 and 4.3). Finally, the results are summarized and discussed in Section 4.4.
4. GeTe

Figure 4.1: EXAFS data of GeTe in the crystalline phase at 10 K (blue) and 300 K (red) measured at the absorption K edge of germanium. The EXAFS is plotted in k-space (left side) and after a Fourier transformation in real space (right side). It is obvious that the information content is much higher with lower temperature; the oscillations in k-space have a higher amplitude and extend over a longer k-range. The signal-to-noise ratio increases with decreasing temperature. In R-space the temperature effect becomes even more evident. Contributions from atoms at distances up to 9 Å are visible in the EXAFS spectrum recorded at 10 K.

4.1 Comparison of the Amorphous and Crystalline Phase

One of the big advantages of EXAFS over other analysis techniques is that the absorption spectra of the amorphous and the crystalline phase can be easily compared. Therefore prior to the detailed analysis of the crystalline and the amorphous phase, the differences between both phases will be discussed with the help of the Fourier Transforms $|\chi(R)|$ of the fine structure oscillations $\chi(k)$, which are plotted in Fig. 4.2.

The most striking difference is that the magnitude of the Fourier transform $|\chi(R)|$ of the crystalline phase exhibits several peaks in the range between 2 Å and 9 Å, while for the amorphous phase well distinguishable peaks only appear up to a radial distance of 3 Å. As mentioned earlier (Section 2.4), the peaks in the Fourier transform result from the neighbouring atoms in the different coordination shells. Due to the lack of periodicity in the amorphous phase the distances $R_j$ of the coordination shells $j > 1$ to the absorber are ill defined and this large static disorder is responsible for the large amplitude reduction of the contributions of the higher coordination shells. Therefore in most absorption spectra of amorphous materials only contribution of
4.1. Comparison of the Amorphous and Crystalline Phase

Figure 4.2: Absorption spectra of GeTe in the amorphous (red) and the crystalline phase (black) measured at 10 K. Noticeable are the differences between both phases, such as the differences in amplitude and peak positions, which indicate a different local order in both phases.

Moreover it can be seen that, at both absorption edges, the peak with highest amplitude in the amorphous phase is shifted towards smaller distances as compared to the highest peak in the crystalline phase. Although, due to the phase shift the actual distances cannot be determined from Fig. 4.2, it can be concluded that the bond distances are shorter in the amorphous phase than in the crystalline phase.

Another dominant feature seen in Fig. 4.2 is the change in amplitude from the crystalline to the amorphous phase, especially at the Te edge, where the amplitude of the first peak of the crystalline phase is approximately twice as large of the peak of the amorphous phase. Several parameters influence the amplitude (e.g., amplitude reduction factor $S_0^2$, mean-square displacement factor $\sigma^2$, coordination numbers $N$), but this large change in amplitude can only be explained by a change in local order, probably accompanied by a change of coordination numbers upon crystallization.

It is thus apparent that the local order differs largely in amorphous and crystalline GeTe, since the peaks in $|\chi(R)|$ are located at different radial distances and also the amplitude of the peaks is different. One would expect that the EXAFS spectrum of the amorphous phase exhibits one peak which is located at the same position as the first peak of the crystalline phase of the same material, since usually the bond length to the nearest neighbours is the same in both phases [45]. For common semiconductors, like Ge or Si, it is known that the number of nearest neighbours is equal in the crystalline and amorphous phase and therefore it is observed that
the amplitude in the EXAFS spectrum is comparable or maybe a little lower in the amorphous phase due to the higher disorder as compared to the crystalline phase. The large change in local order from the crystalline to the amorphous phase is one important characteristic of phase-change materials.

Besides the already discussed differences in the absorption spectra of both phases, other observations can be made, too. At the Te edge, it seems that small peaks exist at approximately the same positions that the peaks of the second and fourth coordination shells appear in the spectrum of the crystalline phase. In the crystalline phase the peaks result from TeTe distances and since no peaks at higher distances are visible in the amorphous phase at the Ge edge and it is known that Te chains even persist in the liquid phase of pure tellurium [46], the peaks in the amorphous phase probably also result from TeTe distances. Although, usually only one peak is visible in an amorphous spectrum, the existence of more peaks at higher distances does not necessarily mean that the sample has been crystalline or partially crystalline.

Already by this comparison of the EXAFS spectra of the crystalline and amorphous state, significant differences between both states have been found. In the following, a detailed structural analysis of the crystalline and the amorphous phase is presented, which will certify and complement this first visual examination.

4.2 Crystalline Phase

At room temperature crystalline GeTe forms in a rhombohedral phase (α-phase), while at temperatures higher than 420 °C it transforms to a cubic crystal (β-phase) [47]. The rhombohedral α-phase is relevant for data storage applications, and therefore this phase is investigated. Two approaches are used to analyse the EXAFS data measured at 10 K and the results of both methods are presented, compared and discussed in the following.

4.2.1 Least Squares Refinement

In order to extract the structural information about the crystalline phase of GeTe from the x-ray absorption spectra measured at both the Te and Ge K edges, the theoretical standards, i.e. the backscattering amplitudes and phase shifts, have to be calculated for a crystal structure that should resemble the investigated structure as closely as possible (see Section 2.4). Therefore, the result of an XRD study of crystalline GeTe [48] is used to create the starting model, for which the theoretical standards are calculated. The space group of the α-phase of GeTe is $R\overline{3}m$ and in this work the rhombohedral settings (the space group can also be described in a hexagonal setting) are used to describe this crystal structure (see Figure 4.3). In the rhombohedral setting the resemblance with the cubic rocksalt structure ($a_{\text{cubic}} = 60^\circ$ and displacement parameter $x = 0.5$) is obvious. Like in the rocksalt structure the crystalline phase is composed of two sublattices, one occupied by Te and the
4.2. Crystalline Phase

<table>
<thead>
<tr>
<th>GeTe</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>crystal symmetry</td>
<td>R3m</td>
</tr>
<tr>
<td>lattice constant ( a )</td>
<td>4.281 Å</td>
</tr>
<tr>
<td>lattice angle ( \alpha )</td>
<td>58.358 °</td>
</tr>
<tr>
<td>displacement parameter ( x )</td>
<td>0.521</td>
</tr>
</tbody>
</table>

Figure 4.3: Rhombohedral structure of GeTe at room temperature. The unit cell of the rhombohedral crystal is marked with red lines, while the black lines symbolise a bond. The lattice parameters result from XRD measurements by Nonaka et al. [48] and are used to create the starting model in the refinement. The resemblance of the rhombohedral phase with the cubic rocksalt phase can be seen.

second by Ge. In contrast to the cubic rocksalt structure the GeTe lattice is stretched along the \([111]\) direction, with the result that the bond angle \( \alpha \) is less than 60° in crystalline GeTe. In addition, the two sublattices are located at \((0, 0, 0)\) and \((x, x, x)\) with \(x = 0.521\), thus the 6 bond distances to the nearest neighbours split in 3 shorter and 3 longer bonds in GeTe.

For the rhombohedral structure, the scattering paths are calculated using the program FEFF6 [21] for both the Ge and the Te absorption edge. Thereby, only atoms within a distance of 9 Å are taken into account to reduce the number of possible paths. This limitation is valid, since usually the signals from atoms within a sphere with radius 6-7 Å are dominant in the spectrum. In addition, the number of multiple scattering paths is reduced by the fact that only those paths are considered, which contribute significantly to the analysed data range \( \Delta R \). A list containing the first scattering paths of the FEFF calculation with germanium as central atom is given in Table 4.1. Aside from the amplitude of every path with respect to the strongest scattering path, the degeneracy, the effective path length and the scattering geometry are noted. This path list is helpful to decide which paths should be implemented in the fit. It can be seen that both single scattering paths and multiple scattering paths are described. The symbol [+\(]\) denotes the absorbing atom and all atoms that scatter the photoelectron and thereby affect the respected scattering path are noted.

Once a path has been selected and is included to model the experimental spectrum, there are five EXAFS parameters \((N, S_0^2, \Delta E, \Delta R, \sigma^2)\) that have to be defined for each path (see Section 2.4). It can be seen from Table 4.1 that 24 different scattering paths exist within a radial distance of approximately 6 Å that could be included in the fit. Thus the number of variables \((5 \times 24)\) would exceed the number of independent points if all parameters were allowed to vary independently (see
Table 4.1: Path list for the FEFF calculation on $\alpha$-GeTe at the Ge edge. The effective path length $R_{\text{eff}}$ equals half the scattering length of the given path, which for a single scattering path is equivalent to the distance to the scattering atom. The amplitude of the most important path is set to 100 % and the amplitudes of the others paths are given with respect to the strongest. The symbol [+] in the scattering paths denotes the absorbing atom, which is Ge for this calculation. The scattering atoms Te$_x$ (Ge$_x$) are sorted according to their distance to the absorber atom. Single scattering paths are marked blue while grey indicates the multiple scattering paths, that are included in Fit 3.

<table>
<thead>
<tr>
<th>degeneracy</th>
<th>$R_{\text{eff}}$(Å)</th>
<th>amplitude (%)</th>
<th>scattering path</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>2.863</td>
<td>100 [+] → Te$_1$ → [+]</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>3.127</td>
<td>81.37 [+] → Te$_2$ → [+]</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>4.174</td>
<td>49.30 [+] → Ge$_1$ → [+]</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>4.281</td>
<td>46.06 [+] → Ge$_2$ → [+]</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>4.950</td>
<td>9.00 [+] → Ge$_1$ → Te$_1$ → [+]</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>5.062</td>
<td>22.61 [+] → Te$_3$ → [+]</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>5.084</td>
<td>7.44 [+] → Te$_4$ → [+]</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>5.136</td>
<td>5.78 [+] → Te$_2$ → Te$_1$ → [+]</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>5.136</td>
<td>7.29 [+] → Ge$_2$ → Te$_1$ → [+]</td>
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<tr>
<td>10</td>
<td>12</td>
<td>5.136</td>
<td>7.44 [+] → Ge$_2$ → Te$_2$ → [+]</td>
</tr>
<tr>
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<td>12</td>
<td>5.214</td>
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<td>3</td>
<td>5.215</td>
<td>20.71 [+] → Te$_5$ → [+]</td>
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<td>14</td>
<td>3</td>
<td>5.727</td>
<td>3.60 [+] → Te$_1$ → [+] → Te$_1$ → [+]</td>
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<td>15</td>
<td>6</td>
<td>5.979</td>
<td>17.98 [+] → Ge$_3$ → [+]</td>
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<td>6</td>
<td>5.985</td>
<td>16.34 [+] → Te$_1$ → Te$_2$ → [+]</td>
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<td>6</td>
<td>5.985</td>
<td>32.02 [+] → Ge$_3$ → Te$_1$ → [+]</td>
</tr>
<tr>
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<td>6</td>
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<td>31.69 [+] → Ge$_3$ → Te$_2$ → [+]</td>
</tr>
<tr>
<td>19</td>
<td>6</td>
<td>5.990</td>
<td>22.96 [+] → Te$_1$ → [+] → Te$_2$ → [+]</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>5.990</td>
<td>10.01 [+] → Te$_1$ → Ge$_3$ → Te$_1$ → [+]</td>
</tr>
<tr>
<td>21</td>
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<td>20.01 [+] → Te$_1$ → Ge$_3$ → Te$_1$ → [+]</td>
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<td>22</td>
<td>3</td>
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<td>29.42 [+] → Te$_2$ → Ge$_3$ → Te$_2$ → [+]</td>
</tr>
<tr>
<td>24</td>
<td>12</td>
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<td>5.38 [+] → Te$_3$ → Te$_1$ → [+]</td>
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<tr>
<td>25</td>
<td>12</td>
<td>6.050</td>
<td>4.01 [+] → Te$_3$ → Ge$_1$ → [+]</td>
</tr>
</tbody>
</table>
4.2. Crystalline Phase

Table 4.2: Parametrization of the atomic distances in α-GeTe with respect to the lattice parameters.

\[
\begin{align*}
  d_{Te_1} &= a\sqrt{3x^2 - 4x + 2 + \cos\alpha(6x^2 - 8x + 2)} \\
  d_{Te_2} &= a\sqrt{3x^2 - 2x + 1 + \cos\alpha(6x^2 - 4x)} \\
  d_{Ge_1} &= a\sqrt{2 - 2\cos\alpha} \\
  d_{Ge_2} &= a \\
  d_{Te_3} &= a\sqrt{3x^2 - 4x + 4 + \cos\alpha(6x^2 - 8x)} \\
  d_{Te_4} &= a\sqrt{(x - 1)^2(3 + 6\cos\alpha)} \\
  d_{Te_5} &= a\sqrt{3x^2 - 2x + 3 - \cos\alpha(-6x^2 + 4x + 2)} \\
  d_{Te_6} &= ax\sqrt{3 + 6\cos\alpha} \\
  d_{Ge_3} &= a\sqrt{3 - 2\cos\alpha}
\end{align*}
\]

Section 2.4). Therefore, constraints must be applied to decrease the number of parameters that are varied during the fit.

When analysing a crystalline structure, the variation of the path lengths \(R_j\) can be constrained by the crystal symmetry. In a crystal, the position of all atoms can be expressed in terms of the lattice parameters, that are lattice constant, lattice angle and displacement factor. Including these parametrization in the fit, instead of refining independently the path length for every path, only the three lattice parameters have to be refined. The effective path lengths as a function of the lattice parameters are described in Table 4.2 for the first single scattering paths up to a distance of about 6 Å. A second step to significantly decrease the number of variables is to fit the absorption spectra measured at the germanium and tellurium K edge simultaneously. For example, the \(\sigma^2\) for a given GeTe distance has the same value regardless of which atom is the central atom. Thus during the fit, the parameters of the respective scattering paths are linked and the number of \(\sigma^2\) parameters is almost cut in half.

Using the above mentioned approach, it is possible to include a large number of paths in the fit, since all fits in the crystal can be expressed in terms of the three lattice parameters. To test the model, it is useful to start the refinement using as few parameters as possible. In order to be able to determine the three lattice parameters all paths up to a radial distance of 4.3 Å are included in the first fit. This means that two GeTe distances and two GeGe and TeTe distances are refined, and for every path an independent mean-square displacement factor \(\sigma^2\) is used. As already mentioned, the fit is performed simultaneously at both edges and the data are fitted in the Fourier transformed \(q\)-space to limit the refinement to the first two coordination shells at both edges. One amplitude reduction term \(S_0^2\) and one \(\Delta E\) is fitted for each edge, and the number of neighbours \(N\) is constrained by the degeneracy values based on the rhombohedral crystal structure. The results of all fitted parameters are summarized in Table 4.3 (Fit 1) and a comparison of the fit to the data is shown in Figure 4.4.

The agreement between the fit and the data is already convincing (R-factor: 0.025),
Figure 4.4: Results of Fit 1 of the co-refinement of Ge and Te K edges for crystalline GeTe assuming an ideal rhombohedral symmetry without vacancies and GeGe bonds. The data are shown in black and the fit in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.
4.2. Crystalline Phase

but it can also be seen that at the germanium edge the fit is not as good as at the
tellurium edge. In the display in real space, it can be seen that one feature of the
data is not at all reproduced by the fit at the Ge edge. The shoulder at approximately
\( R = 2.2 \, \text{Å} \), which is not fitted by the used model, appears as a well separated peak,
if the data are plotted with different \( k \)-weightings (\( n=1 \) or \( 2 \), not shown here). It
must be noted that no additional peak appears at the tellurium edge. Since the
backscattering amplitude at high \( k \) values increases with increasing atomic number
\( Z \) (see Figure 2.4) and a higher weighting factor emphasizes the part of the spectrum
with higher \( k \) values, this indicates that the additional feature at the Ge K edge
results from a backscattering atom with lower atomic number than tellurium, which
occupies the first shell of germanium in rhombohedral GeTe. Because the sample
contains only germanium and tellurium, it can be concluded that the additional
feature at the germanium absorption edge results from GeGe distances and this is
tested by performing a second fit (Fit 2, Figure 4.5).

In the rhombohedral \( \alpha \)-phase of the compound GeTe no GeGe bonds exists, thus
the GeGe bonds can only be modelled, if it is assumed that a second phase is present
in the sample. Since both in the amorphous and crystalline phase germanium is
fourfold (tetrahedrally) coordinated, it is assumed the second phase is tetrahedrally
coordinated germanium with a GeGe bond length of 2.45 Å. During the fit, the bond
length is refined, while the number of GeGe neighbours is kept constant, so that the
fraction of Ge atoms that forms GeGe bonds is always fourfold coordinated. Further-
more, it is assumed that the amplitude factor \( S_0^2 \) of an absorbing germanium atom is
independent of the surrounding atoms, thus for both phases, the rhombohedral GeTe
phase and the additional GeGe bonds, the same amplitude factor is refined. To take
into account that the measured signal is a superposition of the signal of germanium
atoms in two different local environments, the amplitude of the GeGe distance is
multiplied by an additional factor \( c \) (\( 0 \leq c \leq 1 \)). In addition, at the Ge edge, the
amplitude of all paths to model the rhombohedral structure are multiplied by \( (1-c) \),
so that the sum of both phases adds up to 100%. Furthermore, it must be taken
into account that the assumption of GeGe bonds implies that vacancies exist on the
germanium sublattice, because we have to maintain the stoichiometry of the sample.
The second option, that a fraction of Te atoms occupies atom sites of the germanium
sublattice, can be ruled out, as no indication for TeTe bonds can be found. Therefore,
in the model of the Te edge the amplitude of all paths containing one germanium
atom is multiplied by a factor \( (1-c) \). These vacancies have also to be taken into
account at the Ge edge. Hence, the amplitude of all scattering paths, that contain one
germanium atom besides the central atom are multiplied by \( (1-c)^2 \) (except for the
GeGe path). Thus for example at the Ge edge the amplitude of path 3 and 4 (see
Table 4.1) is multiplied by \( (1-c)^2 \), while the amplitude of path 1 and 2 by \( (1-c) \).

The results of the best fit using the model described above are summarized in
Table 4.3. Comparing the models used in Fit 1 with Fit 2 it can be seen that the
\( R \) factor calculated for the germanium edge decreases significantly from 0.038
(Fit 1) to 0.008 (Fit 2). Moreover, it is noticeable that the lattice parameters of the
Figure 4.5: Results of Fit 2 of the co-refinement of Ge and Te K edges for crystalline GeTe assuming a rhombohedral symmetry. In contrast to Fit 1, this fit contains vacancies and additional GeGe bonds. The data are shown in black and the fit in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.
rhombohedral phase stay almost constant and the change in the other parameters is small. As the second phase is introduced to account for a feature in the spectrum, that could not be modelled using only a rhombohedral structure, this behaviour is to be expected. Therefore, the good agreement between the fit to the data, which can also be observed visually in Figure 4.5, and the fact, that there are no significant changes in parameters affirms the assumption that GeGe bonds with a distance of 2.45 Å exist in the investigated sample of GeTe.

Having found a structural model to fit the first coordination shells of the absorption spectra measured on crystalline GeTe, in the final fit (Fit 3) the fitted data range is extended from 1.87 Å to 6.44 Å (1.95-6.70 Å) at the Ge edge (Te edge) to include more scattering paths in the fit. In particular, multiple scattering paths are important in this data range and need to be considered. From the paths list (Table 4.1) it can be seen that the relative amplitude of some multiple scattering paths even exceed the amplitude of single scattering paths at almost the same distance, e.g. compare path 15 (single scattering, amplitude 17.98 %) with path 18 (multiple scattering, amplitude 31.69 %). A refinement without taking multiple scattering paths into account yields a total R factor of 0.25, which indicates that the spectra are not sufficiently modeled by the fit, and multiple scattering paths cannot be neglected in the fit.

It is obvious that the effective path length of the multiple scattering paths depends strongly on the path length of the single scattering paths (see Figure 2.9). Therefore, regarding the path lengths no additional parameters have to be refined. To allow the effective path length of a multiple scattering path to vary according to the change of the lattice parameters during the fit, the change in path length ΔR of the single scattering paths contributing to the multiple scattering paths are summed. For example, the change in length of path 1 (Table 4.1) is ΔR₁ and ΔR₂ for path 2. Path 20 from the path list is a multiple scattering path and, since the outgoing photoelectron is scattered from Te₁ to Te₂ and back to the absorbing atom, the change in path length is ΔR₂₀ = ΔR₁ + ΔR₂. In an analogous manner the multiple scattering paths, that turned out to have a significant influence on the fit, are included in the model.

The mean-square displacement factors of the multiple scattering paths are refined and for the multiple scattering paths that are included in the fit two more displacement factors σ² are used. Since the effective path length of some multiple scattering paths are the same (e.g. path 16, 17 and 18), in the refinement the same mean-square displacement factor is assigned to all paths with the same effective path length. Already from the path list it can be seen that the relative amplitude of some multiple scattering paths are small. The impact of these paths has been tested. But, although, the number of free parameters was enlarged by the inclusion, the fit quality did not improve significantly and, therefore, only the multiple scattering paths underlined grey in Table 4.3 are used in the fit. All single scattering paths until a radial distance of R = 6.9287 Å are included in Fit 3.

The fit compared to the data is plotted in Figure 4.6 and the parameters of Fit 3 are summarized in Table 4.3. The agreement between the data and the fit is good,
although the R factor is higher as compared to Fit 2. This is an effect of the enlarged data range used in Fit 3. Comparing the results of all three fits, the change in the lattice parameters, bond length $a$ and bond angle $\alpha$, are most distinct. This is due to the fact that while in Fit 1 and Fit 2 only 4 paths are taken into account to model the rhombohedral phase (plus one GeGe path in Fit 2) in Fit 3 21 paths are taken into account at the Ge edge and 20 paths at the Te edge, while in all fits only three parameters are used to model all path lengths. Due to the local order and the periodicity of the rhombohedral phase of GeTe it is possible to include a large number of different scattering paths and fit the data in $R$ space up to approximately 6.5 Å, and only refine the lattice parameters.

Also in the model of this final fit GeGe bonds are included. The path length and the mean-square displacement factor are refined during the fit. Also the fraction of Ge atoms that forms the GeGe bonds (this is identical to the vacancy concentration at the Ge sublattice) is determined. The GeGe bond length is found to be 2.45 Å, which agrees very well with the bond distance in pure germanium [45]. Since the sample has been crystallized at 235 °C, but the crystallization temperature of germanium is 250 °C [49] and no Bragg peaks related to a germanium crystal have been visible in the XRD measurements, it must be concluded that the germanium clusters in the sample are amorphous. The refined mean-square displacement factor of the respective GeGe bond is surprisingly small, while the statistical error is large. Also the error on the vacancy concentration is relatively large as compared to other parameters, which are also mainly influenced by the amplitude of the EXAFS spectrum. One possible explanation is the fact, that the vacancy concentration and the mean-square displacement factor are highly correlated. The vacancy concentration would increase if the mean-square displacement factor of the GeGe bond was larger. This high correlation makes the interpretation of the values of both parameters difficult. This means that while we have evidence that GeGe bonds exist in our sample and that vacancies exist on the germanium sublattice, the vacancy concentration cannot be determined more precisely than $5\pm4\%$ on the germanium sublattice.

Summarizing the result of the least-squares refinement, it has been shown that the EXAFS data measured at Te K edge can be fitted with a model based on a rhombohedral crystal structure. The local order and the periodicity is high and therefore many scattering paths can be included in the fit, while only three lattice constants are refined. Moreover, multiple scattering plays an important role in the absorption spectrum at higher coordination shells and cannot be neglected. In contrast, at the Ge K edge the rhombohedral model is not sufficient to explain all features in the spectrum and it has been found that the additional peak (shoulder) can be explained if it is assumed that amorphous Ge clusters exist in the sample.

In the following, the results of the Reverse Monte Carlo simulation of the GeTe EXAFS data measured at 10 K are discussed.
Figure 4.6: Final result of the co-refinement of Ge and Te K edges for crystalline GeTe assuming a rhombohedral symmetry with vacancies and in addition GeGe bonds (Fit 3). As compared to Fit 2 the data range in this fit was enlarged and thus more scattering paths are included in the fit. The data are shown in black and the fit in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.
Table 4.3: Summary of the fitting parameters used in the different fits of crystalline GeTe. The Fits are presented in Figure 4.4, 4.5 and 4.6. In Fit 1 an ideal rhombohedral crystal has been used to model the EXAFS spectrum, while in Fit 2 we additionally allowed for GeGe bonds. For Fit 2 and Fit 3 the same model has been used, but the data range, that has been fitted, has been expanded in Fit 3 as compared to Fit 2.

<table>
<thead>
<tr>
<th></th>
<th>Fit 1</th>
<th>Fit 2</th>
<th>Fit 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R-factors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>0.025</td>
<td>0.017</td>
<td>0.043</td>
</tr>
<tr>
<td>Ge edge</td>
<td>0.038</td>
<td>0.008</td>
<td>0.031</td>
</tr>
<tr>
<td>Te edge</td>
<td>0.016</td>
<td>0.018</td>
<td>0.024</td>
</tr>
<tr>
<td>$S_0^2$(Ge)</td>
<td>0.65 ± 0.05</td>
<td>0.68 ± 0.05</td>
<td>0.67 ± 0.06</td>
</tr>
<tr>
<td>$S_0^2$(Te)</td>
<td>0.83 ± 0.06</td>
<td>0.87 ± 0.06</td>
<td>0.86 ± 0.08</td>
</tr>
<tr>
<td>$\Delta E_0$(Ge) (eV)</td>
<td>5.9 ± 0.8</td>
<td>6.3 ± 0.7</td>
<td>5.8 ± 0.6</td>
</tr>
<tr>
<td>$\Delta E_0$(Te) (eV)</td>
<td>5.8 ± 0.7</td>
<td>6.0 ± 0.6</td>
<td>6.7 ± 0.7</td>
</tr>
<tr>
<td><strong>lattice parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>4.267 ± 0.006</td>
<td>4.268 ± 0.005</td>
<td>4.277 ± 0.005</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>58.38 ± 0.11</td>
<td>58.39 ± 0.09</td>
<td>58.30 ± 0.08</td>
</tr>
<tr>
<td>x</td>
<td>0.528 ± 0.001</td>
<td>0.528 ± 0.001</td>
<td>0.528 ± 0.001</td>
</tr>
<tr>
<td><strong>displacement factors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma^2$ (10^{-3}Å²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeTe$_{short}$</td>
<td>3.2 ± 0.2</td>
<td>3.1 ± 0.3</td>
<td>3.1 ± 0.3</td>
</tr>
<tr>
<td>GeTe$_{long}$</td>
<td>5.0 ± 0.4</td>
<td>4.9 ± 0.4</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>GeGe$_{short}$</td>
<td>7.0 ± 1.0</td>
<td>6.5 ± 0.9</td>
<td>5.6 ± 1.0</td>
</tr>
<tr>
<td>GeGe$_{long}$</td>
<td>6.7 ± 1.0</td>
<td>6.2 ± 0.9</td>
<td>6.0 ± 1.1</td>
</tr>
<tr>
<td>TeTe$_{short}$</td>
<td>4.2 ± 0.8</td>
<td>4.5 ± 0.7</td>
<td>4.0 ± 0.8</td>
</tr>
<tr>
<td>TeTe$_{long}$</td>
<td>5.2 ± 1.1</td>
<td>5.5 ± 1.0</td>
<td>4.9 ± 1.1</td>
</tr>
<tr>
<td>GeTe$_{3,shell}$</td>
<td></td>
<td>6.0 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>GeGe$_{4,shell}$</td>
<td></td>
<td>2.3 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>TeTe$_{4,shell}$</td>
<td></td>
<td>2.9 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>Mult.Scatt1</td>
<td></td>
<td>3.2 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Mult.Scatt2</td>
<td></td>
<td>4.1 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>GeGe-bonds (Å)</td>
<td>2.45 ± 0.01</td>
<td>2.45 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>$\sigma^2$ (10^{-3}Å²)</td>
<td>0.7 ± 1.4</td>
<td>0.4 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>vacancy conc. (%)</td>
<td>7 ± 3</td>
<td>6 ± 4</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.4: Lattice parameters of the rhombohedral and the hexagonal setting of the GeTe α-phase.

<table>
<thead>
<tr>
<th></th>
<th>Rhombohedral</th>
<th>Hexagonal</th>
</tr>
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<tbody>
<tr>
<td>lattice constants</td>
<td>(a_r) 4.277 Å</td>
<td>(a_h) 4.16 Å</td>
</tr>
<tr>
<td></td>
<td>c 10.59 Å</td>
<td></td>
</tr>
<tr>
<td>bond angle</td>
<td>(\alpha) 58.29°</td>
<td></td>
</tr>
<tr>
<td>displacement</td>
<td>x 0.528</td>
<td>u 0.236</td>
</tr>
</tbody>
</table>

4.2.2 RMC Simulations

Reverse Monte Carlo (RMC) simulations have been beneficial for investigations of disorder also in crystalline materials [50]. Moreover, using RMC simulation to model EXAFS spectra, we have convincingly shown that phase separation occurs in Ge\(_{15}\)Sb\(_{85}\) upon crystallization at 250°C [51]. In the previous section, it has been found that also in crystalline GeTe a phase separation occurs, since GeGe bonds with a bond length of 2.45 Å exist in the material, which result from germanium clusters. Therefore the EXAFS data of crystalline GeTe are also investigated using RMC simulations, to gain further insight into the structure. In this simulations, apart from the experimental data additional information (e.g., densities and minimal neighbour distances) is used to constrain the fitted configuration, thus we expect to learn more on the origin of the existing GeGe bonds at 2.45 Å and obtain the vacancy concentration and the fraction of atoms in Ge clusters with a higher precision.

To create the initial configuration the crystal parameters obtained from the least squares refinement of the previous section are used. In order to create the starting configuration the hexagonal setting of the crystalline structure is used to describe the structure. While the rhombohedral cell is the elementary cell of the structure, the hexagonal cell contains three times the volume of the rhombohedral cell and thus contains 3 Ge and 3 Te atoms. The cell parameters of both the rhombohedral and the hexagonal setting are listed in Table 4.4. According to the crystal symmetry, lattice points are placed in an orthorhombic box, with cell dimension [24.97 28.83 21.18] and periodic boundary conditions are applied. This cell contains 576 atomic sites. While these number is small, considering that the configuration in RMC modelling often contains some thousands of atoms, the box size is large enough to image the possible disorder and identify important features. Moreover, the sampling time critically depends on the number of atoms, thus it seems wise to start the simulation on a rather small box.

Several simulations are run and various possible constraints are varied to check their influence on the resulting configuration and improve the agreement between the simulations and the experimental data. Thereby the following observation are made:

- The atoms are moved at random during the RMC simulations. To assure that
the final calculation represents indeed a crystalline structure, the movement of the atoms is restricted to vary within a sphere of a specified radius. Different radii for germanium and tellurium atoms can be chosen. The dependence of the final results on the sphere radii is large. The best fit is obtained using a sphere radius of 0.2 Å for Te and 0.4 Å for Ge atoms. Larger sphere radii will not improve the fit quality. As can be seen from Figure 4.2, scattering paths up to an effective path length of at least 6 Å contribute significantly to the spectra. If the spheres are chosen to be too large, the medium and long range order is not maintained and, therefore, the agreement between the calculated and experimental fine structure is reduced.

• Before executing the FEFF calculations to determine the EXAFS parameters (see Section 2.5), the maximum radial distance from the scattering atom to the absorber atom has to be stated. All atoms within this distances are counted as neighbours and only for those atoms the scattering paths are calculated. Due to the just mentioned significant contributions of higher coordination shells, it is important that this cut-off distance is chosen to be around 9 Å in the analysis.

• Usually, it can be assumed that the agreement in the fit is better the more degrees of freedom the system has. The distribution of the elements on the two sublattices is a strong constraint. Therefore, one would suspect that the permission to swap atoms will increase the fit quality. While this is in principle true, the improvement are just minimal and must be considered insignificant, which suggests that no intermixing (or very little) exists between both sublattices.

• The parameter that has the strongest influence on the result of the simulation is the number of vacancies that is implemented in the starting configuration. The previous analysis using ARTEMIS [23] revealed that GeGe bonds and vacancies on the Ge sublattice are present in the sample. Therefore, the influence of these parameters is also tested using RMC simulations. To test the influence of germanium vacancies, some germanium atoms are removed from the starting configuration. Of course, this leads to the situation, that in the starting configuration more Te atoms exist than Ge atoms. But in a RMC simulation it is necessary that the configuration resembles the same composition as the material, that is simulated. Hence, we need to have 50 % Te atoms and 50 % Ge atoms in the starting configuration. While it is common to speak of atoms in the sampled configuration, in principle the three dim. configuration is an specified arrangement of points. Those points are assigned to different elements and the dimension of the real atoms can be considered by constraints which state the minimal distances between two atomic sites. Therefore, to conserve the correct composition of GeTe while introducing vacancies on the Ge sublattice, the label of some atomic sites representing Te atoms is changed to Ge atoms. This means that in addition to the vacancies,
we introduce at the same time germanium antisites on the Te sublattice. As mentioned above, changing the vacancy concentration has the major influence of all constraints on the fit quality.

From these considerations the constraints to obtain the best possible fit are singled out and the result of these fit is presented in the following. The best agreement between the calculated and the experimental data is achieved, when a vacancy concentration of 15% vacancies on the germanium sublattice is applied, thus a total vacancy concentration of 7.5%.

The starting configuration of the RMC simulation is shown in Figure 4.7 together with the partial radial distribution functions calculated from this configuration. The vacancies can be observed in the image of the starting configuration and the GeGe distances are visible in the GeGe partial pair correlation function. In an ideal rhombohedral GeTe structure no GeGe bonds would be present at 2.81 Å and 3.16 Å. From the partial pair correlation function, the differences and similarities of the rhombohedral structure, which can also be seen as a distorted cubic structure, with the cubic rocksalt structure can be seen. While atoms in the cubic rocksalt phase have six nearest neighbours in the first coordination shell, in the rhombohedral cell the one bond length splits up and atoms are 3+3 coordinated. Similarly, the atoms in the second coordination shell (just above 4 Å) and most higher coordination shells split up and form several distances in the rhombohedral phase as compared to a cubic rocksalt phase.

The best RMC fit starting from the discussed initial configuration is plotted in Figure 4.8 and the resulting configuration together with the final partial pair correlation functions are plotted in Figure 4.9. Although, the agreement between the fit and the data (see Figure 4.8) seems to be quite good, the $\chi^2$ is still high ($\chi^2 = 1295$). It has not been possible to reduce the $\chi^2$ beyond this value, which indicates that the final configuration does not image all relevant features in the crystalline structure of GeTe. The GeGe partial pair distribution function provides first information on the missing features. In the last section, it has been shown that GeGe bonds exist in the investigated material. These bonds are not reproduced during the RMC simulation. Further insight into the differences between the fit and the data can be gained by comparing the Fourier transform of the fit and the data at both edges (see Figure 4.10). As can be seen, the essential features are modelled by the fit, while at the same time the partially large deviations are also apparent. First of all, as already mentioned, no GeGe bonds with a distance of 2.45 Å exist in the simulated configuration. Therefore, at the Ge edge the first peak in the Fourier transform $|\chi(R)|$ is not fitted. Second, it is apparent that especially at higher radial distances (>5 Å) the amplitude of the data and the fit differs significantly. This is possibly due to limitation of the two-body approximation (see Section 2.5). Already in the analysis based on the modelling of path parameters in the previous section, it has been mentioned that it is important to include multiple scattering paths in the fitting model to obtain good agreement between the fit of the data. Therefore, the
4. GeTe

(a) Starting configuration.

(b) Partial pair correlation functions.

Figure 4.7: Starting configuration and calculated partial pair correlation functions $g_i(R)$ of the RMC simulations of crystalline GeTe. In the image of the starting configuration the Te atoms are marked orange and the germanium atoms are coloured blue. The partial pair correlation function representing the GeGe correlations are marked blue, GeTe correlations are coloured bright orange and TeTe correlations dark orang. Moreover, the TeTe pair correlation function is shifted along the y-axes for clarity.
4.2. Crystalline Phase

![Graph showing RMC simulations of crystalline GeTe](image)

Figure 4.8: Final result of the RMC simulations of crystalline GeTe at the germanium K edge (blue) and the tellurium K edge (orange). The data are shown in circles and the best fits as lines.

approximation to only consider single scattering paths (two-body approximation) is not valid, when analysing the crystalline structure of GeTe.

The fact, that the feature in the data due to the GeGe bonds is not represented in the fit, has already been mentioned. In contrast, when analysing the crystalline structure of Ge$_{15}$Sb$_{85}$ [51] it has been shown that phase separation occurs. Since the GeGe bonds in the material can only be explained with the existence of Ge clusters, we also have a phase separation in crystalline GeTe. One reason while it has been possible to model the phase separation in the case of Ge$_{15}$Sb$_{85}$ and not in the current, might be that in GeTe only a small fraction of Ge atoms is phase separated. Furthermore, it has been found, that to maintain the periodicity and the resulting strong scattering contributions from atoms in higher coordination shells in GeTe, that the atoms must not be allowed to move far away from the ideal lattice positions. Since most atoms are 3+3 coordinated in the rhombohedral phase, while it must be expected that Ge in Ge clusters is tetrahedrally coordinated, the Ge atoms would have to move further away from the starting positions than allowed by this constraint. It is not possible to give the system as much degrees of freedom to model the Ge clusters and at the same time conserve the periodicity. Therefore, it must be concluded that it is not possible to obtain a better fit using the present RMC
4. GeTe

(a) Final configuration.

(b) Partial pair correlation functions calculated from the final configuration.

Figure 4.9: Final configuration and calculated partial pair correlation functions $g_i(R)$ of the RMC simulations of crystalline GeTe. In the image of the final configuration the Te atoms are marked orange and the germanium atoms are coloured blue. The partial pair correlation function representing the GeGe correlations are marked blue, GeTe correlations are coloured bright orange and TeTe correlations dark orang. Moreover, the TeTe pair correlation function is shifted along the y-axes for clarity.
4.2. Crystalline Phase

code. Since the two mentioned obstacles cannot be overcome, neither can the GeGe bonds at 2.45 Å be modelled, since otherwise the medium and long range order in the configuration will be lost, nor can the important multiple scattering paths be included in the fit.
Figure 4.10: Fourier transform $|\chi(R)|$ of the fine structure oscillations $\chi(k)$ calculated from the final configuration of the RMC simulations (red) in comparison to the spectrum measured from crystalline GeTe (black). The large misfits especially at larger distances $R$ between the fit and the data are apparent and result probably mainly from the two-body approximation in the analysis.
4.2.3 Summary

In the last two section, the analysis of crystalline GeTe in the rhombohedral phase using two different approaches has been presented. Although, it has to be concluded that it is not possible to obtain a good fit using the present RMC algorithm to model this structure, still from both approaches the same conclusions can be drawn.

The rhombohedral symmetry of the crystalline structure has been confirmed using both approaches. One sublattice is occupied by germanium and the second by tellurium atoms. Despite the fact that vacancies exists on the germanium sublattice and at the same time germanium cluster are present in the material, the order (local, medium and long range order) in the material is high. This is possibly also one reason that the multiple scattering paths play an important role in the analysis and the two-body approximation made in the RMC code is not valid. The lattice parameters of the crystalline structure have been determined ($a = 4.28 \pm 0.01 \text{ Å}$, $\alpha = 58.30 \pm 0.08^\circ$ and $x = 0.528 \pm 0.001$) and the two GeTe bond lengths to the closest neighbors are 2.81 Å and 3.16 Å. It has been proven that vacancies are present in crystalline GeTe. But it is not possible to determine the vacancy concentration with a high precision from the EXAFS data, although the data have an excellent quality and a very high signal-to-noise ratio even at high $k$-values due to the low recording temperature of 10 K. The least-squares analysis resulted in a vacancy concentration of 5±4 % and the best fit using RMC simulations yielded a vacancy concentration of 15 %.

In contrast to many ternary phase-change material like e.g. Ge$_1$Sb$_2$Te$_4$, the rhombohedral phase is known and studied already in 1969 [52]. Meanwhile, the material has been studied using different approaches [53–55] and especially in the last years, since the application of GeTe in memory applications is discussed the number of studies has increased [10, 47, 48, 56–60]. Different experimental methods (including neutron diffraction, XRD and EXAFS measurements) as well as theoretical methods have been used to study the crystalline structure. The results of the present studies, where the lattice parameters have been reported, are summarized in Table 4.5. The lattice constants found in the different studies range from 4.21 Å to 4.40 Å, with bond angles from 57.51° to 58.59° and displacement factors from 0.521 to 0.532 and agree very well with the present results. The results from the studies based on theoretical approaches (DFT calculation) differ more from the experimental studies, which can probably be attributed to the use of approximation of the atomic potentials, which are know to either underestimate or overestimate the real distances.

In three publications the existence of germanium vacancies is discussed. One study is based on EXAFS data recorded at room temperature [57]. It is stated that 12 % GeGe bonds are present in the sample. In a second study XRD data are analyzed and a vacancy concentration of 2 % is found [60]. One reason for these deviations of the vacancy concentration can be found by Edwards et al. [58]. It is shown using DFT calculations that the number of germanium vacancies depends on the crystallization temperature.

For the first time in this study EXAFS data recorded at 10 K have been presented
Table 4.5: Results of the crystal structure of GeTe. The lattice constant \( a \), the lattice angle \( \alpha \) and the distortion parameter \( x \) from recent studies of the crystalline phase are compared.

<table>
<thead>
<tr>
<th>method</th>
<th>T (K)</th>
<th>( a ) (Å)</th>
<th>( \alpha ) (°)</th>
<th>( x )</th>
</tr>
</thead>
<tbody>
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<td>present study</td>
<td>EXAFS</td>
<td>10</td>
<td>4.277</td>
<td>58.29</td>
</tr>
<tr>
<td>Nonaka et al. [48]</td>
<td>XRD</td>
<td>4.281</td>
<td>58.358</td>
<td>0.521</td>
</tr>
<tr>
<td>Edwards et al. [58]</td>
<td>DFT</td>
<td>0</td>
<td>4.21</td>
<td>58.59</td>
</tr>
<tr>
<td>Matsunaga et al. [60]</td>
<td>XRD</td>
<td>9.7</td>
<td>4.276</td>
<td>57.879</td>
</tr>
<tr>
<td>Da Silva et al. [59]</td>
<td>DFT</td>
<td>0</td>
<td>4.38</td>
<td>57.69</td>
</tr>
<tr>
<td>Lencer et al. [10]</td>
<td>DFT</td>
<td>0</td>
<td>4.40</td>
<td>57.51</td>
</tr>
</tbody>
</table>

and analysed. The determined lattice parameters are comparable to the results of previous studies. Although the data quality is excellent, the precision of the determination of the vacancy concentration is low. This must be mainly attributed to the chosen experimental technique (EXAFS). Nevertheless, the data and the analysis fortify that GeGe bonds, that means a second phase in addition to \( \alpha \)-GeTe, and germanium vacancies exists in the sample. Thus intrinsic vacancies are also present in crystalline GeTe.
4.3 Amorphous Phase

The differences in the local order of the amorphous and the crystalline phase have already been discussed in Section 4.1. In order to quantify these differences in Section 4.4, the EXAFS spectra of the amorphous phase of GeTe have to be analysed. Therefore, at first the program ARTMIS \[23\] is used to model the short range order based on the most important scattering paths and thereafter RMC simulations are performed, which will result in a three dimensional configuration in agreement with the experimental data.

4.3.1 Least Squares Refinement

Uncommon for the x-ray absorption fine structure of an amorphous material, the measured EXAFS spectrum with Te as absorbing element, contains not only information on the first coordination shell, but also peaks at higher distances \(R\) are visible in the Fourier transform \(|\chi(k)|\). In the analysis, we focus on the local order in GeTe and therefore we confine the part of the spectrum that is fitted to a distance of 3.084 Å at the Ge edge and 3.197 Å at the Te edge. These distances coincide with the positions of lowest amplitude just after the first peaks. This means that we limit the analysis to radial distances of approximately 3.2-3.3 Å. The differences between the numbers arise since the phase shift is not yet accounted for in Figure 4.2 and therefore the real distances are 0.2-0.3 Å longer than the position of the minimum in the spectra.

In principal three bond pairs might exist in amorphous GeTe: GeTe, GeGe and TeTe bonds. The existence of these bonds can be verified in the analysis and the bond distances must be determined. To do so, starting from a model based only on one scattering path, step by step more scattering paths are included. The results are plotted in Figure 4.11 for the germanium and the tellurium edge. The different fits are discussed in the following and the results are summarized in Table 4.7.

In the first fit (Fit 1), the model consists only of one GeTe scattering path. It is obvious that just this one path is not sufficient to model the measured absorption spectra. At the Ge absorption edge, the peak in the measured spectra is asymmetric towards smaller distances, which might be due to an asymmetric bond distribution or a second bond pair, with a smaller bond distance then the GeTe bonds. At the Te absorption edge the misfit between the fit and the data is even more obvious since the amplitude is largely overestimated by the fit. A second bond distance at the Ge edge could be a possible explanation. If GeGe bonds exist in the sample, the measured amplitude of the fit at the germanium edge is a result of GeTe and GeGe bonds. Therefore the amplitude might be higher than if only GeTe bonds are present. In Fit 1 only GeTe bonds are accounted for, and in the refinement a balance has to be found between the higher amplitude at the Ge edge, due to existing (but not fitted) GeGe bonds, and the lower amplitude at the Te edge, which results in the overestimation of the amplitude at the Te edge.

Therefore, in Fit 2 in addition to the GeTe bonds, GeGe bonds are added to the
model. It is obvious that the additional bond pair increases the agreement between the fit and the data considerably. From a visual inspection of the data, the largest peak in both spectra is excellently fitted, while only the smaller peaks at larger radial distances are not yet described by the fit. The R factors also decrease significantly from Fit 1 to Fit 2 but it can also be seen that the R factor is larger by almost a factor 3 for the Te edge compared to the Ge edge. Possible explanations for this difference are that either bond pairs (TeTe bonds) are not yet considered or that neighbouring atoms with larger radial distances to the absorber atoms are not yet included. Since also at the Ge edge it can be seen that one peak is not yet modelled, in Fit 3 a second, larger GeTe distance is refined while in Fit 4 an additional TeTe bond pair is fitted.

Adding a second GeTe bond pair (Fit 3) with longer radial distance than the first GeTe bond results in an almost perfect fit of the Ge edge. Instead, when adding a TeTe bond pair (Fit 4) the fit at the Ge edge does not change compared to Fit 2, where only one GeTe and one GeGe distances is utilized. For the Te edge the third distance (no matter whether GeTe or TeTe) improves the fit considerably, but this improvement is larger for Fit 4 (see also Table 4.7).
Thus from Fit 3 and 4 it can be learned that more than two different bond distances are needed to fit the experimental data, although the agreement between the fits and the data has not yet been sufficient. If further scattering paths are added to the model used in Fit 2, GeGe and TeTe pairs offer the largest degree of freedom, since they only depend on one absorption edge, respectively. This model has been tested in Fit 5. Thus, in this fit GeTe, TeTe and two GeGe scattering paths are used to model the spectra. While again at the Ge edge this fit is very convincing, the R factor for the Te edge indicates, that these model is even worse than the models used in Fit 3 and Fit 4.

The best fit so far has been Fit 3, where two different GeTe distances and one GeGe distance are refined. The result is already very good at the Ge edge, while it needs improvements at the Te edge as indicated by the larger R factor. Therefore in the last model, a TeTe bond pair was additionally refined. This last fit models both spectra (at the Ge edge and the Te edge) reasonable well. Although we refine 4 different, independent bond length the number of refined parameters (14 in total) is still below the number of independent points according to the Nyquist theorem ($N_{idp} = 28$).

In Table 4.7 the results of the structural parameters are listed for every fit. In addition to the bond length, the number of bonds $N$ and the mean square displacement $\sigma^2$ have been refined for every bond pair. Since in the amorphous phase the number of neighbours, or better the degeneracy of a scattering path is not defined by any symmetry (like in the crystal), it is nearly impossible to fit the degeneracy $N$ and the amplitude reduction factor $S_0^2$, since both parameters are 100% correlated (see Equation 2.20). Therefore we used in all refinements the amplitude reduction factors that have been obtained in the analysis of the crystalline phase. EXAFS is known to find the radial distances with a high accuracy, but due to correlations of parameters and difficulties to unambiguously define the background the amplitude, and thus the coordination numbers, are less well defined. This can also be seen in this analysis, since the error bars on the numbers of neighbours are in some cases more than 50% of the parameter. But at the same time it can be seen that the coordination number $N$ especially of the first GeTe and GeGe bonds is nearly unaffected by adding further bonds. At last, it should be noted, that the mean square displacements of the TeTe and the second GeTe bond is larger that the mean square displacements for the two shortest distances. Thus, these distances are less well defined and have a broader distribution.

If we calculate the number of neighbours, and assume that all distances that have been fitted are indeed bonded to the respective absorber atom, we receive the following coordination numbers:

$$N_{Ge} : \quad 3 \pm 1$$
$$N_{Te} : \quad 1.7 \pm 1$$

The magnitude of the error bars hampers an in depth interpretation of these values. A detailed discussion of the coordination numbers follows in Section 4.3.3.
### Table 4.6: Summary of the fitting models of amorphous GeTe. The fits are presented in Figure 4.11.

<table>
<thead>
<tr>
<th></th>
<th>R factors</th>
<th>bond pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total Ge edge Te edge</td>
<td>GeTe GeGe GeTe₂ TeTe GeGe₂</td>
</tr>
<tr>
<td>Fit 1</td>
<td>0.271     0.155 0.437</td>
<td>x</td>
</tr>
<tr>
<td>Fit 2</td>
<td>0.066     0.023 0.074</td>
<td>x x</td>
</tr>
<tr>
<td>Fit 3</td>
<td>0.019     0.005 0.023</td>
<td>x x x</td>
</tr>
<tr>
<td>Fit 4</td>
<td>0.028     0.022 0.018</td>
<td>x x x</td>
</tr>
<tr>
<td>Fit 5</td>
<td>0.029     0.006 0.042</td>
<td>x x x x</td>
</tr>
<tr>
<td>Fit 6</td>
<td>0.010     0.005 0.012</td>
<td>x x x x</td>
</tr>
</tbody>
</table>

Until now, the analysis has been restricted to only parts of the spectra at both absorption edges. Especially at the Te edge it is important to include the whole spectrum in the analysis, since at this edge atoms until a distance of approximately 6 Å from the absorbing atom contribute to the spectrum. In contrast to the crystalline phase, the radial distances in the amorphous state are not restrained by the crystal symmetry. Thus each additional scattering path increases the number of varied parameters. To exploit the whole data range without facing problems due to an increasing number of varied parameters, RMC simulation have been performed and the results are presented in the next section.
### Table 4.7: Summary of the fitting results used in the different fits of amorphous GeTe.
The fits are presented in Figure 4.11.

<table>
<thead>
<tr>
<th>Fit</th>
<th>R (Å)</th>
<th>GeTe</th>
<th>GeGe</th>
<th>GeTe₂</th>
<th>TeTe</th>
<th>GeGe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.57 ± 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9 ± 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.7 ± 0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.59 ± 0.01</td>
<td>2.46 ± 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.2 ± 0.3</td>
<td>1.6 ± 0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5 ± 0.8</td>
<td>3.4 ± 2.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.61 ± 0.01</td>
<td>2.48 ± 0.01</td>
<td>2.79 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4 ± 0.3</td>
<td>1.7 ± 0.3</td>
<td>1.0 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.9 ± 0.9</td>
<td>3.4 ± 0.9</td>
<td>5.5 ± 2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.59 ± 0.01</td>
<td>2.46 ± 0.02</td>
<td></td>
<td></td>
<td>2.92 ± 0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.3 ± 0.3</td>
<td>1.5 ± 0.5</td>
<td></td>
<td>0.9 ± 0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6 ± 0.8</td>
<td>3.3 ± 1.9</td>
<td></td>
<td>7.6 ± 4.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.60 ± 0.01</td>
<td>2.47 ± 0.01</td>
<td></td>
<td>2.92 ± 0.02</td>
<td>2.97 ± 0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4 ± 0.2</td>
<td>1.6 ± 0.3</td>
<td></td>
<td>0.8 ± 0.4</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0 ± 0.6</td>
<td>3.4 ± 0.0</td>
<td></td>
<td>6.6 ± 2.8</td>
<td>3.4</td>
</tr>
<tr>
<td>6</td>
<td>2.61 ± 0.01</td>
<td>2.47 ± 0.07</td>
<td>2.78 ± 0.02</td>
<td>3.00 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4 ± 0.3</td>
<td>1.7 ± 0.3</td>
<td>0.9 ± 0.4</td>
<td>0.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8 ± 0.9</td>
<td>3.2 ± 0.8</td>
<td>5.0 ± 3.2</td>
<td>6.3 ± 5.4</td>
<td></td>
</tr>
</tbody>
</table>
4.3.2 RMC Simulations

To analyse the amorphous structure with RMC simulations, it turns out to be important that the initial structure has no long or medium range order. First simulations starting from a strongly distorted crystalline structure, resulted in a final configuration where lattice planes could still be identified. Thus efforts have to be made to create an amorphous configuration. To do so, a crystalline structure with rhombohedral symmetry is build, but the lattice constants are chosen such, that the structure has the density of amorphous GeTe (0.0335 atoms/Å³ [61]). The first configuration contains 864 atomic sites and has a $R\bar{3}m$ symmetry, with lattice constants (hexagonal setting): $a = 4.331$ Å and $c = 11.023$ Å. During the simulation, the atoms are allowed to move at random from their ideal lattice points within a sphere of radius 5 Å. The resulting configuration is plotted in Figure 4.12(a). The calculated partial pair correlation functions (Figure 4.12(b)) reveal that these configuration is completely disordered but also not physically reasonable. Bond distances beyond 2 Å, as existent in the configuration, are very unrealistic. In addition, these short distances cause a problem when calculating the EXAFS parameters with the program FEFF [16]. For every atom in the configuration the EXAFS signal is calculated and all neighbouring atoms within a specified radius are considered. We discovered that whenever two atoms are too close to each other, hence, the effective path length of the scattering path is $\approx 1-1.5$ Å, only this path is considered in the calculation and all longer possible scattering paths are neglected. One explanation is that the amplitudes of the scattering paths with such small effective path lengths are extremely large as compared to the amplitudes of the scattering paths with longer path lengths, which will, therefore, be neglected. Due to the fact that for some atoms only the unrealistic short scattering paths are taken into account to calculate the EXAFS signal, the determination of the EXAFS parameters will not be reliable.

To overcome this problem, a short RMC simulation is performed, to create a disordered configuration with physical reasonable atomic distances. The minimal distances between the atoms are constrained to achieve this goal. After few simulation steps the simulation is ended although convergence between the fit and the data has not been reached, but usually the movements are largest the first few loops. The resulting configuration and the partial pair correlation functions are plotted in Figure 4.13. As can be seen, in the new configuration the minimal bond distances are already larger than 1 Å, but the problem of too short atomic distances is not yet fully overcome. Therefore this step is repeated. The EXAFS parameters are calculated for the new configuration, and used in a simulation, which runs until convergence is reached. The resulting configuration is used as the starting configuration for the further analysis. To fit the EXAFS data, several RMC simulation are run to test the influence of the different constraints. Since the atoms are allowed to move within sphere with radii from 2-4 Å, minimal distances have to be applied to obtain a physical reasonable result. These minimal distances are constraint to about the sum of the covalent radii of the elements (GeGe: 2.35 Å, GeTe: 2.50 Å, TeTe: 2.70 Å) [62].
4.3. Amorphous Phase

(a) First configuration.

(b) Partial pair correlation functions.

Figure 4.12: First configuration and calculated partial pair correlation functions $g_i(R)$ of the RMC simulations of amorphous GeTe. In the image of the configuration the tellurium atoms are marked orange, while germanium atoms are coloured blue. The partial pair correlation function representing the GeGe correlations are marked blue, GeTe correlations are coloured bright orange and TeTe correlations dark orange. Moreover, the GeTe correlation function is shifted along the y-axes for clarity.
4. GeTe

(a) Starting configuration.

(b) Partial pair correlation functions.

Figure 4.13: Starting configuration and calculated partial pair correlation functions $g_i(R)$ of the RMC simulations of amorphous GeTe. In the image of the configuration the tellurium atoms are marked orange, while germanium atoms are coloured blue. The partial pair correlation function representing the GeGe correlations are marked blue, GeTe correlations are coloured bright orange and TeTe correlations dark orange. Moreover, the TeTe correlation function is shifted along the y-axes for clarity.
4.3. Amorphous Phase

In addition, the atoms are allowed to interchange positions during the simulation. The final configuration is presented in Figure 4.14. The agreement between the data and the fit is quite high (Figure 4.15) and $\chi^2$ for the presented configuration is $\chi^2 = 54$.

From the partial pair correlation function it can be seen that besides GeTe bond at 2.59 Å, GeGe bonds with different bond lengths are present in the configuration. The highest amplitude has the peak at a radial distance of 2.45 Å. The TeTe partial pair correlation function shows no clear separated peaks, so it is difficult to tell whether TeTe bonds exist in the material.

In addition to the bond lengths, we are interested in the coordination numbers in amorphous GeTe. The number of atoms within a specified distance between ($R_{\text{min}}$ and $R_{\text{max}}$) can be calculated from the partial pair distribution function. For example the number of atoms $Y$ around atom $X$ are calculated by integrating the partial pair correlation function $g_{xy}(r)$:

$$N_{XY} = 4\pi N_Y \frac{V}{V} \int_{R_{\text{min}}}^{R_{\text{max}}} r^2 g_{xy}(r) dr. \quad (4.1)$$

$N_Y$ equals the number of atoms from element $Y$ in the investigated volume $V$. The number of atoms plotted against the radial distance is shown in Figure 4.16. The blue line (GeGe) shows the distribution of germanium atoms around a central Ge atom. A plateau in this function means that no atoms can be found in this range. The integration of the pair correlation functions yields all atoms within the chosen range. Thus Figure 4.16 contains no information, which atoms are actually bonded to the absorbing atoms. To calculate the coordination numbers, additional criterion have to be defined to select the bonded atoms and calculate the coordination numbers. Two different common approaches are used in the following to determine the coordination numbers.

The first method takes advantage of the fact that atoms are bonded to their neighbours within certain distances. The GeTe and GeGe pair correlations functions Fig. 4.14(b) have distinct peaks until a distance of 3.1 Å for GeGe pairs and 2.7 Å for GeTe pairs. If we assume that the existence of well separated peaks in the correlation function indicates a bond, the following coordination numbers are obtained:

$$N_{\text{GeGe}} > 2.4 \quad N_{\text{GeTe}} > 1.0$$

Since in the TeTe correlation function no distinct peaks exist, according to the chosen criterion no TeTe bonds exist. This means that the germanium atoms have an average coordination number of 3.4, tellurium a coordination number of 1 and the average total coordination number is 2.2. According to this values, the coordination number
4. GeTe

(a) Final configuration.

(b) Partial pair correlation functions.

Figure 4.14: Final configuration and calculated partial pair correlation functions \( g_{ij}(R) \) of the RMC simulations of amorphous GeTe. In the image of the configuration the tellurium atoms are marked orange, while germanium atoms are coloured blue. The partial pair correlation function representing the GeGe correlations are marked blue, GeTe correlations are coloured bright orange and TeTe correlations dark orange. Moreover, the GeTe and TeTe correlation functions are shifted along the y-axes for clarity. The bond lengths of the refined scattering paths using the program ARTEMIS are marked black.
4.3. Amorphous Phase

Figure 4.15: Results of the RMC simulations for amorphous GeTe at the germanium K edge (blue) and tellurium K edge (orange). The data are shown as circles and the best fits as lines.

For Te is only half the value that is expected from the $8 - N$ rule [63], where $N$ equals the number of valence ($s$ and $p$) electrons. But although no peaks exist in the TeTe correlation function, it can be seen from Figure 4.14(b) and Figure 4.16 that TeTe pairs exist with a distance of less than 3 Å, thus it is reasonable to assume that those atomic pairs are actually forming bond pairs. Hence, another criterion has to be chosen to define the number of coordinated atoms in amorphous GeTe. Another common method to determine coordination numbers with the help of pair correlation functions is to calculate the number of all atoms within a sphere of radius $R_{cut}$ and this radius is determined by the first minimum in the total pair correlation function, which is plotted in Figure 4.17 together with the neighbour distribution. It can be seen that it is difficult to unambiguously define the position for the cut-off radius $R_{cut}$. The first minimum could be defined to be at 2.75 Å. This cut-off distance corresponds to the following coordination numbers:

$$N_{\text{GeGe}} > 1.4$$
$$N_{\text{GeTe}} > 1.0$$
$$N_{\text{TeTe}} > 0.1$$

Thus the average coordination of Ge is 2.4, of Te 1.1 and the total average coordination
Figure 4.16: Partial neighbour distribution functions of amorphous GeTe. The number of atoms is calculated from the partial pair correlation functions presented in Figure 4.14.

number is 1.8.

The values, obtained using the different criterion to define a bond, differ significantly from each other. This shows the arbitrariness of the criteria to define, which atoms are actually bonded to the absorbing atom. Calculations of the electron localization functions using DFT methods, could identify the bonded atoms and help to unambiguously define the coordination numbers. Meanwhile it is only possible to say that the coordination numbers are smaller than the values predicted by the $8-N$ rule [63]. This rule proposes a coordination of 4 for the Ge atoms and 2 for the Te atoms, which results in an average coordination of 3.

In the beginning of this chapter, it has been discussed that the EXAFS spectrum measured at the Te edge shows peaks in the Fourier transform $|\chi(R)|$ up to a radial distance of 6 Å even in the amorphous phase. It can be excluded that crystalline grains are responsible for this peaks. The amorphous phase of the as deposited sample was confirmed by XRD measurements. And the sample have been prepared in such a way that a crystallization is highly improbable. Shimada et al. [54] have found that even a pressure of 120 kbar at a temperature of 100 °C applied for 15 h is not sufficient to crystallize the sample. In contrast, the preparation of the pellets involves a pressure of less than <5 kbar applied at room temperature for few minutes:
4.3. Amorphous Phase

Figure 4.17: The total pair correlation function of GeTe (black) is plotted together with the neighbour distribution function. The first minimum is identified to be at 2.75 Å. Thus, GeTe has an average coordination number of 1.8.

A partly crystallization of the sample can, therefore, be excluded. Thus, the peaks visible in the Fourier transform of the spectra measured at the Te edge are related to medium range order TeTe correlations. In the TeTe partial pair correlation function this peaks are almost not present. This can be explained by the characteristics of RMC simulations to yield a solution with a large amount of disorder.
Table 4.8: Comparison of the results of the analysis of the amorphous phase of GeTe using least-square refinements (EXAFS) and RMC simulations.

<table>
<thead>
<tr>
<th></th>
<th>EXAFS</th>
<th></th>
<th></th>
<th>RMC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R$ (Å)</td>
<td>$N$</td>
<td>$R$ (Å)</td>
<td>$N$</td>
</tr>
<tr>
<td>GeTe</td>
<td>2.61(1)</td>
<td>1.4(3)</td>
<td>2.60</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>2.78(7)</td>
<td>0.9(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeGe</td>
<td>2.47(2)</td>
<td>1.7(3)</td>
<td>2.45</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>2.56</td>
<td>0.4</td>
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<td>2.81</td>
<td>0.3</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2.97</td>
<td>0.7</td>
</tr>
<tr>
<td>TeTe</td>
<td>3.00(4)</td>
<td>0.3(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.3 Summary

Least-squares refinements and RMC simulations have been used to analyse the EXAFS spectra measured of amorphous GeTe. In the least-squares refinement a small number of scattering paths is used to model the spectra, and the result provides information on the smallest amount of bond pairs that is needed to model the fine structure. In contrast, RMC simulations yield a three dimensional structure with as much disorder as is in agreement with the data and the applied constraints. But, despite the significant different approaches, both methods provide similar features, which dominate the local order in amorphous GeTe, although differences exist, too (see also Table 4.8).

In Figure 4.14(b) the effective path lengths of the scattering paths refined in Fit 6 are plotted together with the partial pair correlation functions calculated from the final configuration. In Section 4.3.1 it has been shown that the most dominant peak in the Fourier transformed spectra $|\chi(R)|$ can be fitted with two different scattering paths (GeGe: 2.47 Å, GeTe 2.61 Å). The effective bond lengths of these two paths, a GeTe and a GeGe path, match very well with the peaks with largest amplitude in the respective pair correlation functions. Hence, both analysing techniques provide agreement in the bond lengths of the dominant GeTe and GeGe bond pairs in amorphous GeTe. Moreover, it has been shown using least-square refinements, that the smaller features at higher radial distances in the EXAFS spectra can be modelled if further scattering paths are added to the fit model. And also in the partial pair correlation functions, especially for GeGe, several well separated peaks, representing distinct bond length, can be observed.

In the final Fit 6, in addition to GeTe and GeGe paths, one TeTe scattering path has been refined. The resulting mean square displacement factor $\sigma^2$ for this path is large as compared to the other displacement factors. In addition, the TeTe partial pair correlation function shows several peaks within a radial distance of 3.5 Å. But
4.3. Amorphous Phase

Table 4.9: Comparison of previous EXAFS studies of amorphous GeTe. The EXAFS spectra have all been recorded at room temperature. Kolobov et al. [64] have reported that they find a GeGe bond, but the bond length has not been stated.

<table>
<thead>
<tr>
<th></th>
<th>Maeda [65]</th>
<th>Hirota [66]</th>
<th>Kolobov [64]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeTe R (Å)</td>
<td>2.65</td>
<td>2.59</td>
<td>2.60</td>
</tr>
<tr>
<td>N</td>
<td>2.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>GeGe R (Å)</td>
<td>2.48</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

this peaks have a small amplitude and are rather broad as compared to the peaks in the GeGe and GeTe pair correlation functions. It can be argued that the large mean square displacement factor $\sigma^2$ of TeTe results from the least-square refinement using ARTEMIS relates to the broad distribution in the TeTe partial pair correlation function.

The most obvious difference between the results of the two techniques is, that the second refined GeTe scattering path obviously finds no equivalent in the GeTe pair correlation function. While in the pair correlation function no GeTe peaks exist around this radial distance, both the TeTe as well as the GeGe pair correlation function exhibit peaks in this range. It might be that the GeTe paths improves the agreement between fit and data, but account for the GeGe and TeTe scattering paths, which exist in the amorphous structure but are not modelled by the fit. Since it is not possible to include further GeGe or TeTe bond in the fit, this assumption cannot be justified.

The discussion of the number of neighbours or bonds is difficult. On the one side, the error bars for the coordination numbers refined in the least-squares analysis are so large, that it even cannot be judged if the $8-N$ rule is fulfilled, and on the other hand it has been shown that it is without further information not possible to determine unambiguously the coordination number from the pair correlation function.

Previous analyses of EXAFS data [64–66] measured at room temperature differ in some points from the present results (see Table 4.9). Probably due to the higher temperature only the largest peak is visible in the Fourier transformed spectra in [65, 66], and thus Maeda et al. [65] detected only two different bond length. The GeGe bond with a length of 2.48 Å and a coordination number of 1.2 and a GeTe bond with coordination number 2.5 and a bond length of 2.65 Å. Hirota et al. [66] measured the EXAFS only at the tellurium edge and found only GeTe bonds with a bond length of 2.59 Å. The bond length determined in these two studies are in very good agreement with the recent results.

Kolobov et al. [64] report that they have found GeTe and GeGe bonds, but only the bond length of GeTe (2.60 Å) is reported. It is argued that the determined coordination numbers, $3.3 \pm 0.3$ for germanium and $2.2 \pm 0.2$, suggest that it is more
likely that Ge is fourfold coordinated and Te is twofold coordinated, than that both elements are 3-fold coordinated. It should be noted that the stated error bars in the study by Kolobov et al. are lower than the error bars in our analysis, although our EXAFS data have been recorded at 10 K, which has been shown to increase the data quality significantly.

Using DFT calculations to investigate GeTe Akola et al. [67] have found a medium range order in amorphous GeTe and the radial distribution function show pronounced maxima at approximately 4 Å and 6 Å. These values agree very well with the position of the peaks in the Fourier transform $|\chi(R)|$, if it is taken into account that the peaks in Figure 4.2 are phase shifted. Also Kohara et al. [68] found those medium range correlations with similar peak positions using RMC simulations based on XRD measurements, but the origin of these peaks is not discussed.

In comparison to previous EXAFS studies, decreasing the recording temperature down to 10 K enhanced the information content in the data significantly. Not only have we been able to show, that besides a GeTe and a GeGe bond, further bond distances exist in amorphous GeTe, we also see a medium range coordination in the spectrum measured at the Te edge, which has been attributed to TeTe distances and coincide with previous DFT calculations [67].
4.4 Conclusion

Already from the visual inspection of the data, changes in the local order in both phases have been apparent (see Section 4.1) and the detailed analysis of the local order in the amorphous and crystalline phase of GeTe supports these first observations.

Evaluating the EXAFS data of the crystalline phase of GeTe, the lattice parameters of the crystal with rhombohedral symmetry (space group $R\bar{3}m$) have been determined. The lattice constant of crystalline GeTe at 10 K is $a = 4.277 \pm 0.005$ Å and the bond angle equals $\alpha = 58.30 \pm 0.08^\circ$. The two sublattices are located at $(000)$ and $(xxx)$ with $x = 0.528 \pm 0.001$. From these parameters the distances to the neighbouring atoms can be calculated (see Table 4.2). According to the crystal symmetry, the atoms in crystalline GeTe are 3+3 coordinated and the bond lengths are 2.82 Å and 3.17 Å. Moreover, it has been shown that a fraction (6±4%) of lattice sites on the germanium sublattice are empty (germanium vacancies) and that germanium cluster exists. In these clusters the atoms are fourfold coordinated with a bond length of 2.45 ± 0.02 Å.

In the amorphous phase GeTe and GeGe bond pairs have been found to dominate the local order, while only a small number of TeTe bonds exist. The peak with the highest amplitude in the GeTe pair correlation function corresponds to a bond length of 2.61 Å. Hence, this bond distance is about 0.2 Å shorter than the shorter bond length in crystalline GeTe. The shortening of the GeTe bond length upon amorphization is in agreement with results reported in Ref. 65 and 64. The length of the GeGe scattering path refined in the least-square refinement analysis is 2.47±0.07 Å. In contrast to the GeTe bond length, this bond length, thus, agrees very well with the GeGe bond length in crystalline GeTe. Although in an ideal rhombohedral GeTe crystal, no GeGe bonds exists, since the elements occupy different sublattices, it has been shown that a small fraction of GeGe bonds are necessary to fit the EXAFS spectrum measured at the Ge edge. Edwards et al. have reported, that germanium vacancies in GeTe have a low formation energy and hence are easily been formed [58]. This finding together with the presence of GeGe bonds in crystalline GeTe leads to the assumption that a fraction of germanium atoms segregates from the GeTe crystal forming amorphous Ge clusters.

Aside from the peak positions also the amplitudes in the EXAFS spectra vary significantly upon crystallization. These changes are much more pronounced at the Te edge as compared to the Ge edge. The difficulties to precisely determine the coordination numbers in the amorphous phase have been discussed, but, nonetheless, these amplitude changes can mainly be related to a change in coordination numbers. Strong influences of other parameters (see Section 2.1) on the amplitude can be ruled out, since the parameters have similar values for both phases in GeTe. For example, the mean square displacement factors $\sigma^2$ are comparable for both phases, which indicates a similar disorder on the local scale. The coordination numbers of Ge and Te in the amorphous phase of GeTe are considerably smaller than in crystalline GeTe. While in the crystalline state the atoms are 6-fold coordinated, the different approaches to analyse the EXAFS data yield coordination numbers for Te from 1.0
to 2.6 and for Ge the numbers range from 2.4 to 4. The large spread of the values obtained with different methods shows the imprecision of EXAFS measurements towards the determination of coordination numbers. But all approaches constantly yield, that the number of GeGe bonds per germanium atom is always higher than the number of GeTe bonds.

Hence, we have been able to show that the short range order changes significantly upon amorphization. In the amorphous phase the bond length is shorter, the coordination numbers changes upon amorphization and a significant number of GeGe bonds exists in the amorphous phase. Moreover, it has been discussed that medium range order TeTe correlation exist (up to 6 Å) in amorphous GeTe. This result is in line with the outcome of a DFT study by Akola and Jones [67].

Finally, the questions arises, how the analysis of the local structure of the amorphous and crystalline phase can help to improve the understanding of phase-change materials? One characteristic of phase-change materials is the large optical contrast between the two phases, which necessarily must have its origin in either a different structure or a different bonding in both phases. The increase in the dielectric constant $\epsilon_\infty$ upon crystallization can be as large as 200% upon crystallization [8]. At first, it has been discussed that these difference result from a change in the coordination numbers, more precise a change from octahedral to tetrahedral coordiantion of the Ge atoms, upon amorphization [64]. These structural changes affect the density of states (DOS) and thus result in different optical properties. However, it has been found that the changes in the DOS between both phases are not large enough to account for the observed contrasts [69, 70]. Thus the change in coordination cannot be the only reason for large optical and electrical contrast between both phases.

Shportko et al [8] found out that resonant bonding in the crystalline phase is responsible for the large optical contrast. It has been argued that, since no medium range order exist in the amorphous phase, resonant bonding cannot persist in this phase. Recently, Huang et al. [9] have found that the existence of resonant bonding depends on a linear alignment of the $p$-orbitals in addition to the existence of medium and long range order.

It the present study, it has been shown that medium range correlations are present in amorphous GeTe. But nonetheless, the observed dielectric constant $\epsilon_\infty$ of amorphous GeTe [8] indicates that resonant bonding does not exist in this phase. Since EXAFS spectra of the amorphous phase do not allow for an analysis of the bond angle distribution, and in addition these correlations have not been completely reproduced by the RMC simulations, we can only assume, that though medium range correlation of the Te atoms are present, the $p$-orbitals in the amorphous phase are not linearly aligned.
The interest in phase-change materials along the GeTe-Sb$_2$Te$_3$ pseudo-binary line has been immense, since it has been shown by Yamada et al. that these materials show fast switching upon laser irradiation [7]. X-ray diffraction measurements revealed that upon laser irradiation these materials crystallize in a cubic rocksalt structure [1, 71]. The anion sites of the lattice are occupied by tellurium and the cation sites by antimony and germanium. First EXAFS measurements on Ge$_2$Sb$_2$Te$_5$ at room temperature [72] showed that, unlike in common semiconductors like Ge, the local order of the Ge atoms changes upon amorphization from an octahedral to a tetrahedral coordination and it has been argued that these changes are responsible for the last contrast between both phases. These studies have motivated a number of further investigations, which mainly focused on the atomic arrangement in the amorphous phase [67, 68, 73–75]. In the present study we investigate the local order in amorphous and crystalline Ge$_1$Sb$_2$Te$_4$ since in a recent investigation by Shportko et al. [8] it has been shown that it is the structure of the crystalline phase rather than the amorphous phase, which is important to understand the large differences of the optical properties between both phases.

To investigate the structure of Ge$_1$Sb$_2$Te$_4$, absorption spectra have been measured at 10 K, since similar to GeTe the influence of the temperature on the EXAFS data is unusually large. This temperature effect on the fine structure oscillations especially of the crystalline phase can be seen in Figure 5.1. Since the thermally induced vibrations are minimized by lowering the temperature, the amplitude of the oscillations especially at higher k-values increases with lower temperature and the signal-to-noise ratio improves. Therefore, a longer k-range can be used in the analysis of data measured at 10 K, which leads to a higher resolution in real space. Moreover, in the spectra recorded at 10 K, as compared to the spectra measured at higher temperatures, additional maxima with small amplitude can be distinguished at high k-values. These maxima results from high frequency oscillations, which are only visible in the spectra due to the damping of thermal oscillations of the atoms as a result of the low temperature. The larger the distance from the absorber to the backscattering atom is, the higher is the frequency of the oscillation in k-space in the fine structure. Thus, in addition to the improved data quality also the information content is increased significantly by lowering the temperature. This can also be seen in the Fourier transform $|\chi(R)|$ of the spectra (Figure 5.1). While in the spectra recorded at room temperature only atoms in the first coordination shell contribute to the EXAFS signal, in the spectra measured at 10 K distinct peaks are visible until approximately 6 Å. The higher information content will also improve the
Figure 5.1: EXAFS data of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ in the crystalline phase at 10 K (blue), 80 K (green) and 300 K (red) measured at the absorption K edge of tellurium. The EXAFS is plotted in k-space (left side) and after a Fourier transformation in real space (right side). It is obvious that the information content is much higher with lower temperatures; the oscillations in k-space get more pronounced and extend over a longer k-range. The signal-to-noise ratio increases with decreasing temperature, and additional maxima, resulting from high frequency contributions of higher coordination shells, can be distinguished at 10 K at high k-values. In real space the temperature effect becomes even more evident. Contributions even from the fourth coordination shell (6 Å) are visible in the EXAFS spectrum recorded at 10 K.

accuracy that can be reached in the data analysis. Therefore, EXAFS spectra at all three absorption edges have been measured at 10 K for both the amorphous and the crystalline phase. The fine structure oscillations have been isolated using the AUTOBK approach (see Section 2.4) and the normalized absorption spectra are plotted together with the determined background in Figure B.2 and Figure B.3 (see Appendix B).

5.1 Comparison of the Amorphous and Crystalline Phase

One of the most interesting aspects in the analysis of EXAFS data of phase-change materials are the similarities and differences between the crystalline and the amorphous phase, which are relevant in data storage applications. Therefore, prior to the detailed analysis of the crystalline (Section 5.2) and the amorphous phase
5.1. Comparison of the Amorphous and Crystalline Phase

Figure 5.2: Absorption spectra of Ge$_1$Sb$_2$Te$_4$ in the amorphous (red) and the crystalline phase (black) measured at 10 K. Noticeable are the differences between both phases, such as the differences in amplitude and peak positions, which indicate a different local order in both phases.

(Section 5.3), the differences in both phases are discussed on the basis of their Fourier transforms $|\chi(R)|$ (see Figure 5.2).

The differences between the spectra of the two phases are evident at first sight. Due to the lack of medium and long range order in the amorphous phase, only contributions of the first coordination shell, until approx. 3 Å, are visible in the Fourier transform, while especially at the Te edge peaks until approx. 6 Å can be seen. It is interesting to note that the peaks corresponding to the higher coordination shells are clearly visible at the Te edge, while at the Ge and Sb edge, the peaks of the higher shells can barely be observed.

Contrary to the expectations and results of ordinary semiconductors is the large difference in amplitude between the spectra of both phases. In common semiconductors like Ge or Si [45, 49], it can be observed that the peaks in the spectra of the amorphous phase are a little bit lower in amplitude and possibly broader due to the higher disorder in the amorphous phase as compared to the crystalline phase. But it is expected that the peak positions are similar and also the amplitudes of the peaks are at least comparable in the spectra of both phases. In contrast, for amorphous and crystalline Ge$_1$Sb$_2$Te$_4$ the amplitude of the largest peak is significantly higher in the amorphous phase than in the crystalline phase. In addition, the peak is shifted towards smaller distances in the amorphous phase as compared to the crystalline phase, which is most obvious at the germanium edge. From these observations, i.e., the change in peak position and amplitude, it must be concluded that the local order in amorphous Ge$_1$Sb$_2$Te$_4$ differs significantly from the local order in crystalline Ge$_1$Sb$_2$Te$_4$. After the analysis of the structure of both phases we will be able to quantify these findings and specify the differences in local order between both phases (Section 5.4).
Figure 5.3: The cubic rocksalt structure of Ge$_1$Sb$_2$Te$_4$. One sublattice is occupied by tellurium atoms (orange) and the second sublattice by germanium (blue), antimony (green) and vacancies (white). Due to the limited dimensions of the cell, the stoichiometry and the arrangement of Ge, Sb and vacancies is not represented correctly in the model.

5.2 Crystalline Phase

While in the stable phase Ge$_1$Sb$_2$Te$_4$ forms in a hexagonal crystal structure ($R\overline{3}m$), in the meta-stable crystalline phase Ge$_1$Sb$_2$Te$_4$ has a cubic symmetry ($Fm\overline{3}m$) [71]. This rocksalt like structure is formed in data storage applications when the amorphous material is crystallized by laser or electrical pulses. Therefore, in this section the meta-stable crystalline structure of Ge$_1$Sb$_2$Te$_4$ is investigated.

5.2.1 Least Squares Refinement

The crystal symmetry and lattice parameters of the crystalline phase of Ge$_1$Sb$_2$Te$_4$ are known from XRD measurements [71, 76]. One sublattice is occupied by tellurium atoms and the second sublattice by germanium and antimony atoms and vacancies according to the stoichiometry (see Figure 5.3). The lattice constant has been determined to be 6.036 Å [76] and this value has been used to calculate the different scattering paths using FEFF6 [21]. Thereby, only atoms within a distance of 8 Å have been considered in order to limit the number of scattering paths. Since significant contribution of atoms can only be seen until a distance of approximately 6 Å in the Fourier transform, this restriction is justified.

The FEFF calculation has been performed for every absorption edge separately.
5.2. Crystalline Phase

using the same structure model. Thereby, it has to be taken into account that the second sublattice is assumed to be randomly occupied by Ge, Sb and vacancies. While every germanium and antimony atom is octahedrally coordinated by 6 Te atoms (see Figure 5.3), the Te atoms are in average surrounded by 3 Sb atoms and 1.5 Ge atoms. In the first coordination of Te in average 1.5 lattice sites are unoccupied. The second coordination shell of an absorbing Te atoms contains only tellurium, while for a germanium (or antimony) atom the second shell is occupied by germanium, antimony and vacancies. The large chemical disorder on the second shell of Ge is also one reason for the fact that no peak is visible at the germanium or antimony edge, that corresponds to this shell. In contrast, the peak representing the TeTe distances at approximately 4.2 Å at the Te edge has a high amplitude.

In the beginning, we restricted the analysis to the first coordination shell at the germanium and the antimony edge. Because it is difficult to differentiate between the first and the second coordination shell at the Te edge the second shell has been included in the fit.

As mentioned, the cation sites in the crystal are occupied by Ge, Sb and vacancies. To take this random occupation of the second sublattice into account, different FEFF calculations are run on crystals with ideal rocksalt symmetry. Thereby, always one sublattice is occupied by tellurium atoms and the second sublattice is either completely occupied by antimony or germanium. Thus, calculations are performed on two different crystals (GeTe and SbTe), such that we obtain two different list of scattering paths with either TeSb and TeTe scattering paths or TeGe and TeTe scattering paths. Using both path lists in the fit, it is possible to model a crystal with any desired stoichiometry. Since the scattering paths have been calculated for ideal cubic crystals, the degeneracies of the shortest scattering path (GeTe and SbTe) equals six in all path lists independent of the absorber atom. To account for the correct stoichiometry, the degeneracies of the paths with Te as central atom have to be changed, such that the tellurium atoms have only 3 Sb neighbours, 1.5 Ge neighbours and 1.5 neighbouring lattice site are unoccupied.

Based on the known rocksalt symmetry of Ge$_4$Sb$_2$Te$_4$, in the first fitting attempts, the following scattering paths have been taken into account to model the EXAFS spectrum of the Te edge: one TeGe scattering path with an effective length of $R_{\text{TeGe}} = 3.018$ Å and a degeneracy of 1.5, one TeSb scattering path with an effective path length of $R_{\text{TeSb}} = 3.018$ Å and a degeneracy of 3, and one TeTe scattering path with degeneracy 12 and an effective path length of $R_{\text{TeTe}} = 4.27$ Å. The fit is performed simultaneously on all three absorption edges. While the path lengths of the scattering paths (e.g., GeTe) have to be identical at the Te and Ge (Sb) absorption edge, the degeneracies are different, such that Ge (Sb) is surrounded by six Te atoms. For every path the path length and a mean-square displacement factor $\sigma^2$ is varied independently and, in addition, for every edge one amplitude reduction factor $S_0^2$ and one $\Delta E_0$ is fitted. The results of this first fit (Fit 1) are summarized in Table 5.1 and the fit is plotted together with the data in Figure 5.4. As can be seen, it is not possible to obtain a reasonable fit based on this constraints. The agreement between the fit and the data
Figure 5.4: Results of Fit 1 of the co-refinement of Ge, Sb and Te K edges of crystalline Ge$_1$Sb$_2$Te$_4$. In this fit the first coordination shell is fitted with one GeTe and one SbTe bond. The data are shown in black and the fit in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.
is not sufficient and, in addition, the refined parameters have partially unrealistic values. This unambiguously proves, that the crystalline structure of Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4} is distorted on a local scale, although the XRD measurements reveal the cubic fcc periodicity of the crystal.

The comparison of Fit 1 to the data (Figure 5.4) reveals, that at the germanium and the antimony absorption edge the peaks with highest amplitude are well described by the fit, while in both spectra a second peak with smaller amplitude is visible, which is not fitted. Therefore, in the next Fit (Fit 2) the fitting model is changed such that a second GeTe and a second SbTe distance is refined. This means, that if we imagine a fixed octahedron with Te atoms at the edges and a germanium atom in the center, this means that the germanium atom is allowed to change the position away from the center, thereby, forming 6 shorter and longer GeTe bonds. Depending on the direction of the distortion (and of course on the distortion of the Te atoms) the fraction of shorter to longer bond varies, while the sum of all GeTe distances is constant. This model is also applied in the fit. The number of GeTe bonds in the first coordination shell is kept constant at 6, and the fraction of shorter and longer bonds is varied. The number of TeGe bonds is always \( \frac{1}{4} \) of the number of GeTe bonds. This constraint results from the stoichiometry of Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4}. In addition, a second TeTe distance is fitted and the fraction of shorter to longer distances is varied, while the sum of TeTe scattering paths is constraint to equal 12. As can be seen in Figure 5.5 these distortions due to the additional distances significantly improve the fit. The refined parameters are noted in Table 5.1.

In Fit 3 a third GeTe distance and a third SbTe distance is refined. The result is plotted in Figure 5.6 and summarized in Table 5.2. As indicated by the R factors the agreement between the fit and the data is higher for Fit 3 than for Fit 2. But at the same time the error bars of some parameters increase significantly by adding the third GeTe and SbTe distance. This is an indication that the number of refined parameters gets critically high, although it is still only half the number predicted by the Nyquist theorem. Despite the large error bars, the results are reasonable.

In Fit 2 only two GeTe and two SbTe distances are used to fit the first coordination shell. It can be seen that the mean square displacement factor \( \sigma^2 \) of the longer band is extremely large, especially if it is taken into account that the measurement has been performed at 10 K. Comparing the results of Fit 3 to the results of Fit 2 it can be seen that, when a third distance is allowed, the longer bond in Fit 2 splits up and two different bond are formed in Fit 3, one with a shorter and the other with a longer bond length. At the same time the mean square displacement factor \( \sigma^2 \), which is the same for both distances, decreases. Although these factors are still large, they are now comparable to the mean square displacement factors \( \sigma^2 \) of the shortest GeTe and SbTe bonds. The parameters of the first bond length (GeTe and SbTe) are nearly unaffected by the third bond length introduced in Fit 3. Thus, it must be concluded that the model with three different GeTe and SbTe bond length in the first coordination shell describes the local order in crystalline Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4} better than the model used in Fit 2.
Figure 5.5: Results of Fit 2 of the co-refinement of Ge, Sb and Te K edges of crystalline Ge$_1$Sb$_2$Te$_4$. In this fit the first coordination shell is fitted with two GeTe and two SbTe bonds. The data are shown in black and the fit in red. The vertical lines in |χ(R)| indicate the range that was Fourier transformed to χ(q) and then fitted.
5.2. Crystalline Phase

![Graphs showing results of Fit 3 of the co-refinement of Ge, Sb and Te K edges of crystalline Ge$_4$Sb$_2$Te$_4$. In this fit the first coordination shell is fitted with three GeTe and three SbTe bond. The data are shown in black and the fits in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.](image)

Figure 5.6: Results of Fit 3 of the co-refinement of Ge, Sb and Te K edges of crystalline Ge$_4$Sb$_2$Te$_4$. In this fit the first coordination shell is fitted with three GeTe and three SbTe bond. The data are shown in black and the fits in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.
Table 5.1: Summary of the fitting results of crystalline $\text{Ge}_1\text{Sb}_2\text{Te}_4$. The results of the refined path parameters for the different fits are presented in Table 5.2. The Fits are shown in Figure 5.4, 5.5 and 5.6.

<table>
<thead>
<tr>
<th>R-factors</th>
<th>Fit 1</th>
<th>Fit 2</th>
<th>Fit 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>total</td>
<td>0.130</td>
<td>0.016</td>
<td>0.012</td>
</tr>
<tr>
<td>Ge edge</td>
<td>0.095</td>
<td>0.008</td>
<td>0.006</td>
</tr>
<tr>
<td>Sb edge</td>
<td>0.090</td>
<td>0.012</td>
<td>0.011</td>
</tr>
<tr>
<td>Te edge</td>
<td>0.139</td>
<td>0.027</td>
<td>0.021</td>
</tr>
<tr>
<td>$S^2_0$(Ge)</td>
<td>0.32 ± 0.04</td>
<td>0.77 ± 0.04</td>
<td>0.72 ± 0.04</td>
</tr>
<tr>
<td>$S^2_0$(Sb)</td>
<td>0.33 ± 0.12</td>
<td>0.88 ± 0.10</td>
<td>0.81 ± 0.09</td>
</tr>
<tr>
<td>$S^2_0$(Te)</td>
<td>0.28 ± 0.11</td>
<td>0.76 ± 0.09</td>
<td>0.70 ± 0.08</td>
</tr>
<tr>
<td>$\Delta E_0$(Ge) (eV)</td>
<td>0.7 ± 0.9</td>
<td>5.1 ± 0.4</td>
<td>4.9 ± 0.4</td>
</tr>
<tr>
<td>$\Delta E_0$(Sb) (eV)</td>
<td>6.7 ± 2.7</td>
<td>10.0 ± 0.8</td>
<td>10.1 ± 0.8</td>
</tr>
<tr>
<td>$\Delta E_0$(Te) (eV)</td>
<td>6.1 ± 3.3</td>
<td>6.9 ± 1.0</td>
<td>7.1 ± 0.9</td>
</tr>
</tbody>
</table>

It can also be observed that the error bars increase in Fit 3 as compared to Fit 2, for example the error bars of the displacement parameters $\sigma^2$, of the number of neighbours $N$, but also of the bond distances, especially of the intermediate GeTe and SbTe bonds. This increase indicates, that in this data range it is not possible to enhance the amount of disorder further by refining more GeTe or SbTe distances. The number of refined parameters in the final Fit 3 is already critically high. One solution would be to increase the fitted data range and, thereby, increase the number of independent points $N_{idp}$. But, although, at the Te edge contribution from higher shells can easily be seen, it is hardly possible to include the whole EXAFS spectrum in the fitting model. Since $\text{Ge}_1\text{Sb}_2\text{Te}_4$ is a ternary compound and the structural disorder, as shown for the first shell, is large, the number of paths, which are needed to fit the higher coordination shells, would easily exceed the number of free parameters. To exploit all structural information in these spectra a second approach, Reverse Monte Carlo (RMC) modelling, is used and the results are presented in the following section.
5.2. Crystalline Phase

Table 5.2: Summary of the path parameters refined in the fits of crystalline Ge$_1$Sb$_2$Te$_4$. The number of GeTe and SbTe pairs is given for the Ge and Sb atoms. The number of TeGe bonds is $\frac{1}{4}$ of the number GeTe bonds plus $\frac{1}{2}$ of the SbTe bonds. No error bars are indicated, when a parameter has not been fitted but calculated due to existing constraints. The Fits are shown in Figure 5.4, 5.5 and 5.6. Further refined parameters are presented in Table 5.1.

<table>
<thead>
<tr>
<th></th>
<th>Fit 1</th>
<th>Fit 2</th>
<th>Fit 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeTe</td>
<td>R (Å) 2.83 ± 0.01</td>
<td>R (Å) 2.85 ± 0.01</td>
<td>R (Å) 2.85 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 5.9 ± 0.8</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 6.0 ± 0.4</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 5.3 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>N 6</td>
<td>N 2.8 ± 0.3</td>
<td>N 2.8 ± 1.3</td>
</tr>
<tr>
<td>SbTe</td>
<td>R (Å) 2.92 ± 0.02</td>
<td>R (Å) 2.93 ± 0.01</td>
<td>R (Å) 2.92 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 4.3 ± 1.6</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 5.4 ± 0.7</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 4.2 ± 3.1</td>
</tr>
<tr>
<td></td>
<td>N 6</td>
<td>N 3.1 ± 0.5</td>
<td>N 2.8 ± 2.3</td>
</tr>
<tr>
<td>GeTe</td>
<td>R (Å) 3.09 ± 0.01</td>
<td>R (Å) 2.86 ± 0.03</td>
<td>R (Å) 2.85 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 13.2 ± 1.8</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 6.4 ± 4.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N 6</td>
<td>N 3.2 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>SbTe</td>
<td>R (Å) 3.16 ± 0.01</td>
<td>R (Å) 2.97 ± 0.02</td>
<td>R (Å) 2.93 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 9.8 ± 2.4</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 4.5 ± 5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N 2.9</td>
<td>N 1.5 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>GeTe</td>
<td>R (Å) 3.14 ± 0.05</td>
<td>R (Å) 3.10 ± 0.10</td>
<td>R (Å) 3.08 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 6.4 ± 4.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N 1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbTe</td>
<td>R (Å) 3.20 ± 0.06</td>
<td>R (Å) 3.18 ± 0.08</td>
<td>R (Å) 3.16 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 4.5 ± 5.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N 1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TeTe</td>
<td>R (Å) 4.26 ± 0.06</td>
<td>R (Å) 4.30 ± 0.2</td>
<td>R (Å) 4.30 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 16.6 ± 6.1</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 12.0 ± 1.9</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 11.2 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>N 12</td>
<td>N 8.2 ± 0.4</td>
<td>N 8.0 ± 0.4</td>
</tr>
<tr>
<td>TeTe</td>
<td>R (Å) 4.13 ± 0.3</td>
<td>R (Å) 4.14 ± 0.03</td>
<td>R (Å) 4.14 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 12.0 ± 1.9</td>
<td>$\sigma^2$ (10$^{-3}$Å$^2$) 11.2 ± 1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N 3.8</td>
<td>N 4.0</td>
<td></td>
</tr>
</tbody>
</table>
5.2.2 RMC Simulations

The analysis of the crystalline phase of Ge$_1$Sb$_2$Te$_4$ has shown that despite the fact that the material has a cubic periodicity the crystal is distorted on a local scale. To further investigate this disorder and to be able to take advantage of the full information content in our measurements RMC simulations are performed. The RMC simulations to model the structure of Ge$_1$Sb$_2$Te$_4$ have all been performed by Dr. Christophe Bichara.

The start configuration of the first simulations is a rocksalt cubic structure with an atomic density of 0.0318 Å$^{-3}$. The size of the start configuration is varied (up to 8000 lattice sites), but the cubic box always contained 50% Te, 25% Sb, 12.5% Ge and 12.5% sit are unoccupied according to the stoichiometry. In addition, one fcc sublattice is completely occupied by Te atoms and the second sublattice is randomly occupied by Sb, Ge and vacancies. Periodic boundary conditions are applied. To model the measured EXAFS data and to obtain a reasonable result, beside the density further constraints are applied, e.g. to limit the distances between two atoms.

The influence of several constraints is tested and plenty simulations are run, but the first results have always shown that the system favours (in the crystal unlikely) short (and long) GeTe bonds. In the Fourier transform $|\chi(R)|$ (Figure 5.2) of the measured absorption fine structure, it can be seen, that even in the range of (1-2) Å the amplitude at the Ge edge is unequal zero. The peaks in this range compared to the overall amplitude in the spectra are high. These peaks result from low frequency components (in $k$) in the spectra and contain no structural information. Through the background subtraction it is tried to minimize these Fourier components, but for this material the contribution are obviously still significant. In the RMC modelling the fine structure is calculated for the configuration, which represents the structure, and the measured fine structure $\chi(k)$ is fitted. Thus the observed tendency to form unreasonable small atomic distances probably results from this low frequency components in $\chi(k)$. Therefore we used window functions at all three absorption edges to Fourier filter the data and get rid of the contribution in the range of (1-2) Å. The spectra that are fitted are thus the Fourier filtered spectra $\chi(q)$ at all three absorption edges. The window functions select the range in real space that is back-Fourier transformed and ranges from 1.84-7.13 Å at the Ge edge, 1.95-6.49 Å at the Sb edge and 1.50-8.06 Å at the Te edge. Once the Fourier filtered data have been used in the simulations, the unreasonable small distance have not been favoured any more.

Further simulations have been performed, and the constraints that are important to fit the data, are identified. During the simulations the position of the atom is varied within spheres of different radii and, in addition, the atoms are allowed to interchange positions. The movement of the atoms is limited to conserve the medium and long range order in the configuration. Therefore, no further constraints to confine the minimal distances have to be applied. Performing several simulations, the following observations can be made:
5.2. Crystalline Phase

- If larger configurations (>2000 atomic sites) are used in the simulation an alignment of the vacancies on their sublattice along the [100] and the [110] directions can be observed. If the box size is too small this ordering is not observable. But for small configurations the swaps of atoms and vacancies is in general less favourable than for the larger boxes, which probably also prevents the ordering. It must be expected that the interchange of atoms and vacancies rapidly increases $\chi^2$, so probably the change in $\chi^2$ is too large for the smaller boxes, so that the rejection rate is too high.

- The simulation, which are in good agreement with the data, have a large fraction of Ge atoms as next nearest neighbours to Ge atoms.

- It has been noticed that the radii of the spheres, which the atoms are allowed to move in, are important parameters. The best results are obtained using different radii for the different elements. Tellurium atoms are constraint to move in spheres with radius $r = 0.15$ Å. The radii of antimony and germanium have to be larger to obtain a good fit. A radius of $r = 0.25$ Å has been used to limit the movement of the antimony atoms and $r = 0.35$ Å for germanium atoms.

Based on this observations several simulations are run with different starting configurations, in which the occupation of the second sublattice is not at random but following certain rules to increase for example the number of GeGe second neighbour pairs. The starting configuration of the best fit is plotted in Figure 5.7. In this final simulation the atoms are not allowed to swap positions, to preserve the ordering that was imposed on the starting configuration. The configuration contained 768 atomic sites and despite this rather small configuration the resulting $\chi^2$ is 256. The partial pair correlations functions are calculated and plotted together with the configuration in Figure 5.9. As can be seen, the change in bond distance as compared to the ideal rocksalt structure is high, especially for the GeTe distances. The distance of the ideal rocksalt structure splits up and form several distances in the range of 2.5-3.5 Å. Although the radii of the spheres are chosen rather large, taking into account that we model a crystalline structure, it can be seen that the distances spread over the complete range of allowed bond variations $\pm 0.5$ Å for the GeTe bonds ($\pm 0.4$ Å for SbTe bonds). The peak in the GeTe pair correlation function towards the high and low end of the GeTe distances can be attributed to the constraints and indicate that the system would like to form GeTe bonds with even larger distances.
5. $\text{Ge}_1\text{Sb}_2\text{Te}_4$

(a) Initial configuration.

(b) Partial pair correlation functions.

Figure 5.7: The starting configuration (top) of the final RMC fit of crystalline $\text{Ge}_1\text{Sb}_2\text{Te}_4$ is shown together with the calculated partial pair correlation functions $g_i(R)$ (bottom). In the configuration tellurium atoms are marked orange, antimony is green and germanium atoms are coloured blue.
Figure 5.8: Results of the RMC simulations of crystalline Ge$_1$Sb$_2$Te$_4$ at the germanium edge (blue), the antimony edge (green) and the tellurium edge (orange). The data are shown as circles and the fits as lines.
5. Ge$_1$Sb$_2$Te$_4$

(a) Final configuration.

(b) Partial pair correlation functions.

Figure 5.9: The final configuration (top) of the final RMC fit of crystalline Ge$_1$Sb$_2$Te$_4$ is shown together with the calculated partial pair correlation functions $g_i(R)$ (bottom). In the configuration tellurium atoms are marked orange, antimony is green and germanium atoms are coloured blue. The black bars in the partial pair correlation function mark the results of the least square refinement presented in the previous chapter.
5.2. Crystalline Phase

5.2.3 Summary

In the previous sections, the EXAFS data measured on Ge$_1$Sb$_2$Te$_4$ in the crystalline phase have been investigated with two different methods. It has been shown that the EXAFS spectra (limited to the first coordination shell) cannot be fitted, if the local order of an ideal rocksalt structure is assumed. At least two GeTe and SbTe distances are needed to fit the crystalline data. Even when the fit is performed with 3 GeTe and 3 SbTe bond lengths the mean square displacement factor, which account for thermal and static disorder in the structure, are large ($\sigma^2 > 0.005 \text{Å}^2$), regarding the fact the thermal vibrations should be negligible at 10 K.

With RMC simulation the full information content of the EXAFS data can be used to create a three dimensional configuration, which is in agreement with the experimental EXAFS data. RMC simulations are known to provide solutions with a large amount of disorder. But as can be seen in Figure 5.9 the medium and long range order of the crystalline phase is preserved in the final configuration due to the applied constraints. Moreover, in the partial pair distribution functions the large deviations of GeTe and SbTe bonds lengths from the ideal rocksalt bond lengths of 3.02 Å, which is already seen from the least square refinement, is highly visible. To compare the results of both approaches, the GeTe and SbTe bond lengths determined by the least square refinements have been marked in Figure 5.9. The results of both approaches are in fairly good agreement making the analysis quite reliable.

Indications for this observed large disorder can also be found in previous studies. Matsunaga et al. [71] have performed XRD measurements at room temperature on the meta-stable crystalline phase of Ge$_1$Sb$_2$Te$_4$ and proposed for the first time the crystal symmetry of the meta stable phase. The temperature factors refined in the Rietveld analysis are smaller for the Te atoms (B=1.4 Å$^2$) than for the Ge and Sb atoms (B=3.2 Å$^2$). Since the temperature factor (or Debye-Waller factor) is related to the deviations of the atoms from their ideal lattice positions, this means that the Ge and Sb atoms deviate more from their ideal lattice sites than Te atoms. This is in line with the results of the RMC simulations. In these simulations the movement of the Te atoms could be constrained to be within a sphere of 0.15 Å, while the sphere radius of the Ge (0.35 Å)and Sb atoms (0.25 Å) had to be larger to obtain a good fit.

If large configurations (>2000 atomic sites) have been used to simulate the crystalline phase of Ge$_1$Sb$_2$Te$_4$ and the atoms have been allowed to interchange positions on their sublattice, it has been observed that the vacancies align along the [1 0 0] and [1 1 0] direction. To further investigate this observation, several RMC simulations have been run, using variable starting configurations and different ordering had been imposed on those starting configurations (see also Fig. 5.7). To preserve the order, swaps have not been allowed in these simulations. Starting configurations where the vacancies were ordered along the specified directions and where a large fraction of GeGe pairs in the second coordination shell existed, have led to the highest convergence between the fit and the data as compared to configurations with different ordering. Da Silva et al. [59] used DFT calculations to identify the meta-stable phase
with lowest energy for Ge$_1$Sb$_2$Te$_4$. The total energy is minimized if the number of Te atoms surrounded by 3 Ge atoms and 3 Sb atoms is maximized and the vacancies occupy $\{111\}$ planes. It turns out that this structure has the same two motives that have been identified in the RMC simulations to be important to obtain a good fit. The structure suggested by Da Silva et al. has also been used as starting configuration in one of the simulations and yielded a $\chi^2$ comparable to the value of the fit presented in Figure 5.9. The ordering of the vacancies in planes, as found by Da Silva et al., has never been observed in the RMC simulations. This might be, of course, due to the fact, that RMC is known to find a solution with large disorder. But it should also be mentioned that the group of Da Silva found in a second publication (Park et al. [77]) evidence, that the real meta-stable crystalline phase differs from their predicted structure, with lowest energy. In Ref. 77 the optical properties of different GeSbTe phase-change materials have been studied using ellipsometry measurements and DFT calculations. It is shown, that measured dielectric functions and absorption coefficients show large differences between the meta-stable and the stable phase of Ge$_1$Sb$_2$Te$_4$, while from the previous DFT study of the crystalline structure of the stable and meta-stable phase [59] only small differences would be expected. On the basis of this difference, they conclude that the vacancy ordering is insufficient in the meta-stable phase of real materials as compared to the ideal ordered structures found in the DFT calculations and empty lattice planes do possibly not exist. And this might explain, why the predicted vacancy ordering in planes, which is energetic favourable, has not been observed in our analysis. Nonetheless, this is the first time that any ordering on the second sublattice of Ge$_1$Sb$_2$Te$_4$ in the meta stable phase has been detected based on experimental data. This observation has only been possible since by lowering the temperature down to 10 K the information content in the data has been increased significantly compared to measurements at room temperature.
5.3 Amorphous Phase

Already from the visual inspection of the Fourier transform of the EXAFS data (Figure 5.2), it can be seen that the local order in amorphous Ge$_1$Sb$_2$Te$_4$ is different from the local order in crystalline Ge$_1$Sb$_2$Te$_4$. To be able to quantify this statement, the EXAFS data of the amorphous phase measured at 10 K are analysed using the same methods as in the analysis of the crystalline phase.

5.3.1 Least Squares Refinement

In the crystalline phase of Ge$_1$Sb$_2$Te$_4$ only GeTe and SbTe bonds exists due to the ordering of the atoms on the two sublattices. Therefore, in the first attempt to fit the EXAFS data of the amorphous phase of Ge$_1$Sb$_2$Te$_4$ only GeTe and SbTe bonds are allowed. For every bond pair the path length $R$, the mean square displacement factor $\sigma^2$ and the number of bonds $N$ is refined and the three absorption edges are fitted simultaneously. Thus, it is assumed that the first coordination shell of germanium and antimony contains only Te atoms at distances $R_i$. Hence, tellurium has both germanium and antimony as neighbouring atoms. To ensure that the results are consistent at all three edge, the bond length and the mean square displacement factors of the bond pairs are restrained to be the same at the two absorption edges that are affected by the bond. The number of GeTe (SbTe) bonds is restrained differently at the Ge (Sb) and Te edge, to take into account the different concentration of both elements in the sample. If the Ge atoms are surrounded by $N$ Te atoms, this means due to the four times higher concentration of Te in the alloy, that Te has $\frac{N}{4}$ Ge neighbours.

The amplitude reduction factors are not refined in the fit. These values are taken from the analysis of the crystalline phase of Ge$_1$Sb$_2$Te$_4$, since the values are interchangeable for the two materials. In the analysis of an amorphous material, the determination $S_0^2$ and the number of bonds $N$ is not recommended, since both factor are highly correlated (see Equation 2.20). The correlation is 100 % if only one absorption edge is fitted, but it is reduced by the simultaneous fit of all three absorption edges, since $N$ and $S_0^2$ affect the three edges differently.

The results of the co-refinement are plotted in Figure 5.10. As can be seen the agreement between the fit and the EXAFS spectra of Ge$_1$Sb$_2$Te$_4$ in the amorphous phase is reasonable. One GeTe bond pair and one SbTe bond pair is sufficient to model the EXAFS spectra. The parameters refined in this fit are summarized in Table 5.3. The resulting distances of 2.61 Å for the GeTe and 2.84 Å for the SbTe bond are realistic, since the bond lengths are slightly larger than the sum of covalent radii of the elements (GeTe: 2.58 Å, SbTe: 2.76 Å [62]). It is noticeable that the least square displacement parameters are significantly smaller ($0.0035 \text{ Å}^2$ for GeTe) than the displacement factors that have been found in the refinement of crystalline phase ($\sigma^2 > 0.0053 \text{ Å}^2$) and this shall be discussed further in Section 5.4.

From the number of GeTe and SbTe bonds in the fit the coordination numbers in
Figure 5.10: Results of the co-refinement of Ge, Sb and Te K edges of amorphous Ge$_1$Sb$_2$Te$_4$. In this fit the first coordination shell is fitted with one GeTe and one SbTe bond. The data are shown in black and the fit in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.
5.3. Amorphous Phase

Table 5.3: Summary of the results of the fit of amorphous Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4}.

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<thead>
<tr>
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<th>Ge</th>
<th>Sb</th>
<th>Te</th>
<th>total</th>
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<tbody>
<tr>
<td>R factor</td>
<td>0.013</td>
<td>0.015</td>
<td>0.015</td>
<td>0.013</td>
</tr>
<tr>
<td>$S_0^2$</td>
<td>0.72</td>
<td>0.80</td>
<td>0.70</td>
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<tr>
<td>$\Delta E_0$ (eV)</td>
<td>4.1 ± 0.55</td>
<td>8.8 ± 1.1</td>
<td>5.4 ± 1.6</td>
<td></td>
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</tbody>
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<table>
<thead>
<tr>
<th></th>
<th>GeTe</th>
<th>SbTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (Å)</td>
<td>2.61 ± 0.01</td>
<td>2.84 ± 0.01</td>
</tr>
<tr>
<td>N</td>
<td>3.3 ± 0.3</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>$\sigma^2$ 10^{-3}Å\textsuperscript{2}</td>
<td>3.5 ± 0.4</td>
<td>3.7 ± 0.6</td>
</tr>
</tbody>
</table>

the material can be calculated. The coordination number of germanium is 3.3 ± 0.3 and of antimony 2.9 ± 0.4. Thus, the coordination number of tellurium is 2.3 ± 0.3. In agreement with the 8 – N-rule [63], it is expected that germanium is fourfold coordinated and Sb and Te have 3 and 2 neighbours respectively. Whereas the coordination number of Sb and Te agree well with this prediction, the coordination number of germanium deviate significantly from the predicted value. Therefore, it seems likely to test whether the inclusion of GeGe bonds in the fit model improves the fit and affects the coordination number of germanium.

Several further fits have been performed and all possible other bond pairs (e.g., GeGe or GeSb) were included in the fit. Due to the limited number of free parameters it is not possible to include all possible bond pairs in one fit and, therefore, one after the other bond pair has been included to the model in addition to the GeTe and SbTe distances, such that in every fit only three different bond pairs have been allowed. Additional bonds pairs, including GeGe, SbSb, TeTe, GeSb and second GeTe and SbTe bonds, have been tested. Except for the TeTe bonds, all fits yielded slightly better agreement between the fit and the data than the fit presented in Figure 5.10. But keeping in mind that the number of refined parameters is increased by 3 with respect to the fit presented in Figure 5.10, the improvements have been too small to be statistically relevant. Thus, it must be concluded that GeTe and SbTe bonds are most dominant in amorphous Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4}. Indications exist that further bonds exists in Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4}, but those bonds are not needed to successfully fit the absorption spectra. The factors that indicate further existing bond pairs are the small disagreement between the fit and the data, e.g. at the germanium edge the amplitude of the fit at the small pre-peak mismatches the amplitude of the data, together with the fact that the coordination number of germanium is smaller than expected from the 8 – N rule.

Further insight into the structure of amorphous can be gained by RMC simulations, which are presented in the following section.
5.3.2 RMC Simulations

The amorphous phase of Ge$_1$Sb$_2$Te$_4$ has been recently investigated by Raty et al. using ab initio molecular dynamics methods [78]. The resulting amorphous structure (containing 168 atoms) has been doubled in each x, y and z direction and is used as starting configuration for the RMC simulations. The resulting cubic box has an edge length of 35.64 Å and contains 1344 atoms, thus, the number density is 0.0298 Å$^{-3}$.

Starting from this amorphous structure (Figure 5.11) the atoms are allowed to move in spheres with radius 2 Å around the starting position and in order to sample the structure all atoms are allowed to swap positions. To avoid unrealistic small distances between any two atoms the minimal distance of every bond pair is restrained to the following distances: 2.45 Å for GeGe and GeTe pairs, 2.75 Å for GeSb, SbSb and SbTe pairs and 3.00 Å for TeTe pairs.

The result of the best fit, which yields a $\chi^2$ of 223, is plotted in Figure 5.12. The agreement between the fit and the data is excellent. For further interpretation of the resulting configuration the partial pair correlations functions are calculated and plotted in Figure 5.13. The black bars in Figure 5.13(b) indicate the bonds length determined by the fitting of the GeTe and SbTe scattering path in the previous section. The most obvious feature in the partial pair correlation function is the sharpness of the peaks corresponding to GeTe and SbTe bonds. This is rather unusual for an amorphous material but is in line with the fact that the mean square displacement factors $\sigma^2$, resulting from the fit of two scattering paths using ARTEMIS, are small.

Moreover, it can be seen that in agreement with the results from the previous section, the GeTe and SbTe bonds are most dominant in the structure. But it must also be noted that the GeGe bonds around 2.45 Å, that have been present in the starting structure, prevail in the final configuration. This means that a small fraction of homopolar bonds is in agreement with the experimental EXAFS data. It must be kept in mind that the partial pair correlation functions are all normalized to equal one at large distances. Since the concentration of germanium in Ge$_1$Sb$_2$Te$_4$ is four times smaller than the concentration of Te, this means that the fraction of GeGe bonds seems to be much more significant in Figure 5.13(b). The importance of the different bond pairs can be judged better from the calculated neighbour distributions which are plotted in Figure 5.14. It can clearly be seen that GeGe bonds play only a minor role in the bonding in amorphous Ge$_1$Sb$_2$Te$_4$ and GeTe and SbTe bonds dominate the bonding distances until at least 3.5 Å. The partial pair correlation functions for SbTe and SbSb seem rather similar, while in the result of the MD simulations [78] they exhibit clear differences. This might be due to the fact that Sb and Te can hardly be distinguished with x-ray radiation since their atomic numbers $Z$ differ by only one.

Similar to the analysis of amorphous GeTe the determination of coordination numbers if difficult (see also Table 5.4). The well defined peaks, that could be interpreted as bonds, range until a distance of approximately 3.5 Å for GeTe and 3 Å for SbTe, which would result in 4.3 Te neighbours around germanium and 2.2 Te

100
5.3. Amorphous Phase

(a) Initial configuration.

(b) Partial pair correlation functions.

Figure 5.11: The starting configuration (top) of the RMC fit of amorphous Ge$_1$Sb$_2$Te$_4$ is shown together with the calculated partial pair correlation functions $g_{ij}(R)$ (bottom). The configuration resulted from ab initio molecular dynamics simulations [78]. In the configuration tellurium atoms are marked orange, antimony is green and germanium atoms are coloured blue.
Figure 5.12: Results of the RMC simulations of amorphous Ge$_1$Sb$_2$Te$_4$ at the germanium (blue), antimony (green) and tellurium K edges (orange). The data are shown as circles and the best fits as lines.

Table 5.4: Coordination numbers in crystalline Ge$_1$Sb$_2$Te$_4$ on the basis of RMC simulations. Two methods are applied to determine the coordination numbers and yield contrary results. In the first approach sharp peaks in the pair distribution functions are interpreted as bonds (method 1) and the number of neighbours is calculated, while in the second method the first minimum in the total pair distribution function has been used as cut-off distance to define a bond (method 2).

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<tr>
<th></th>
<th>method 1</th>
<th>method 2</th>
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<tbody>
<tr>
<td>$N_{\text{Ge}}$</td>
<td>5.8</td>
<td>2.4</td>
</tr>
<tr>
<td>$N_{\text{Sb}}$</td>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>$N_{\text{Te}}$</td>
<td>2.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
5.3. Amorphous Phase

(a) Final configuration.

(b) Partial pair correlation functions.

Figure 5.13: The resulting configuration (top) of the final RMC fit of crystalline Ge$_1$Sb$_2$Te$_4$ is shown together with the calculated partial pair correlation functions $g_i(R)$ (bottom). The position of the bond lengths determined using the program ARTEMIS are marked with black bars. In the configuration tellurium atoms are marked orange, antimony is green and germanium atoms are coloured blue.
Figure 5.14: Partial neighbour distributions of amorphous Ge$_1$Sb$_2$Te$_4$. The number of atoms is calculated from the partial pair correlation functions presented in Figure 5.13.

Figure 5.15: Total pair correlation function of amorphous Ge$_1$Sb$_2$Te$_4$ obtained from the configuration of the RMC simulations.
atoms around antimony. These values can also be used as cut-off distances to calculate the total coordination numbers in Table 5.4. The position of the first minimum in the total pair correlation function (Figure 5.15) might be defined to be at 3.05 Å. Using this cut-off distance to calculate the coordination for the different elements yields a coordination number of 2.4 for Ge, 2.5 for Sb and 1.8 for Te. Thus, all atoms would be undercoordinated in the material with respect to the prediction of the $8 - N$ rule [63]. Both approaches to calculate the coordination numbers in amorphous Ge$_3$Sb$_2$Te$_4$ yield contrary results especially for the Ge edge: once, germanium is overcoordinated (5.8), while the other approach yields a coordination number of 2.4 for Ge, which implies an undercoordination. It seems to be impossible to define the actual number of bonds (and not distances) using the standard approaches. To be able to unequivocally define the number of bonds, DFT calculations of the electron localization function could help.
5.3.3 Summary

In the last two sections, the analysis of the amorphous phase of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ has been presented. The results obtained with the two different approaches yield a unified picture of the local order in amorphous $\text{Ge}_1\text{Sb}_2\text{Te}_4$. The structure is dominated by GeTe and SbTe bonds with a distance of 2.61 Å and 2.84 Å, respectively. The bond lengths determined in the refinement if only GeTe and SbTe scattering paths and the corresponding peaks in the partial pair correlation functions resulting from the RMC simulation agree very well. Moreover, it has been shown that bond distances are very well defined in the amorphous phase. The peaks in the pair correlation functions are noticeably sharp and the mean square displacement factors $\sigma^2$ of the GeTe and SbTe are small compared to the values obtained in the analysis of the crystalline phase.

It is not possible to compare the coordination numbers of the two different approaches, since it has been shown that without further calculations unique coordination numbers cannot be obtained from the result of the RMC simulations. The well separated peaks range until a radial distance of 4 Å and without additional information it cannot be judged which atoms actually form bonds and, thus, which atoms must be counted to calculate the coordination number. The refinement of the GeTe and SbTe scattering paths using ARTEMIS in Section 5.2.1 is unique and yields the following coordination numbers: $3.3\pm0.3$ (Ge), $2.9\pm0.4$ (Sb) and $2.3\pm0.3$ (Te). The existence of further bond pairs has not been excluded in the analysis, quite the contrary, some small features (and also the RMC simulations) indicate that further pairs exist. But the already high agreement between the fit based on two scattering path and the data made the inclusion of further bonds in the fitting model unnecessary. Moreover, when more scattering paths have been included in the fit, the changes in statistical values to judge the quality of the fit have been insignificant, if it is taken into account that the number of refined parameters was raised by 3 with any additional scattering path.

In comparison to previous studies [67, 68, 74, 75] of the amorphous phase of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ (and $\text{Ge}_2\text{Sb}_2\text{Te}_5$) both similarities and differences can be found (see Table 5.5). All studies have in common that the most dominant bond pairs in the local order are GeTe and SbTe bonds, while the number of these bonds and also number of further bond pairs vary from one to the other. The investigations have mainly been focussed on the analysis of the coordination symmetry namely octahedral or tetrahedral coordination. It has been found that in contrast to the results by Kolobov et al. [72] only a fraction of the Ge atoms is tetrahedrally coordinated. Therefore, it would be interesting to analyse the bond angle distribution of the configuration which results from the RMC simulations. But since EXAFS data of the amorphous phase contain only information on the first coordination shells, the method provides not enough information to reliably investigate the bond angle distributions in the present study. It might be speculated, whether the existence of GeTe bonds at 2.61Å (and GeGe bonds at 2.47Å) result from tetrahedrally bonded germanium, since the bond length is much smaller than the bond lengths found in the crystalline phase, in
Table 5.5: Comparison of the results of previous studies of the amorphous phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. As can be seen, the results disagree in the existing bond pairs, coordination numbers (N) and the fraction of germanium atoms, that is tetrahedrally coordinated (Ge-X$_4$). Nonetheless, all four studies show, that GeTe and SbTe bonds dominate the local structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and that only a fraction of Ge atoms is tetrahedrally coordinated.

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<tr>
<td>bond pairs</td>
<td>DFT</td>
<td>DFT</td>
<td>EXAFS</td>
<td>XRD</td>
</tr>
<tr>
<td>(N)</td>
<td>GeTe(3.6)</td>
<td>GeTe(3.28)</td>
<td>GeTe(2.45)</td>
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<td>SbTe(2.53)</td>
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<tr>
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</tr>
<tr>
<td></td>
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<td>GeSb(0.27)</td>
<td>GeSb(0.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SbSb(0.6)</td>
<td>SbSb(0.59)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TeTe(0.29)</td>
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</tr>
<tr>
<td>Ge-X$_4$</td>
<td>34 %</td>
<td>33 %</td>
<td>55 %</td>
<td></td>
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</table>

which the atoms are (distorted) octahedrally coordinated.

Jovari et al. have performed RMC simulations to model simultaneously experimental EXAFS, XRD and neutron diffraction data [74]. Thereby the high sensitivity of EXAFS measurement to distances are combined with the more accurate information on coordination numbers of the scattering techniques. But the resulting pair correlation functions do not show the sharp distances that can be seen in Figure 5.13(b). This can probably be attributed to the higher measurement temperatures. All measurement in the study by Jovari et al. have been performed at room temperature, while it has been shown in Section 5.1 that lowering of the temperature significantly increases the information content in the data, since the thermal oscillations of the atoms are damped.

It is the first time that absorption spectra recorded at 10 K of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ in the amorphous phase have been analysed, and the extremely well defined bonds in the amorphous phase have been detected. The amorphous phase of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ is highly ordered on the local scale, though no medium and long range order exists.
5.4 Conclusion

The data analysis using the ARTEMIS software and RMC simulations presented in the previous sections, support the results of the visual inspection of the data on the basis of the Fourier transformed spectra $\chi(R)$ (Figure 5.2). The observed peaks shift towards smaller distances in the spectra measured at the amorphous phase as compared to those of the crystalline phase can confidently be attributed to the existence of shorter GeTe and SbTe bonds in the amorphous phase. The results of the least squares fits of the dominant GeTe and SbTe bonds in both phases are collected in Table 5.6. The GeTe bond length detected using ARTEMIS is 2.85 Å in the crystalline phase and decreases to 2.61 Å in the amorphous. Also the SbTe bond length decreases significantly upon amorphization.

In addition to the peak shift, the rather unusual amplitude difference in the spectra of the amorphous and the crystalline phase has been mentioned. From the visual inspection, it cannot simply be deduced that due to this difference the coordination number in the amorphous phase must be higher than in the crystalline phase. Several parameters, not only the number of neighbours, influence the amplitude in an EXAFS spectra. It must not be forgotten that, e.g., the germanium atoms in crystalline GeTe must have in total 6 tellurium atoms occupying the first coordination shell, while in the amorphous phase only about half that number is found in the least square fit of the first peak. Nonetheless, the amplitude of the peak in the spectrum of the amorphous phase is higher than the peak in the crystalline spectrum.

Rather than to the change in coordination numbers, the changes in amplitude visible at all three absorption edges must be related to the higher disorder in the crystalline phase than in the amorphous phase. The GeTe and SbTe partial pair correlation functions of the amorphous configuration show several sharp peaks until a distance of at least 3.5 Å. In contrast, for the crystalline phase the first coordination shells of Ge and Sb (and hence Te) display a much broader distance distribution. This cannot be an artefact of the RMC simulations, since the atoms were allowed to change position within much larger spheres (2 Å) in the amorphous phase than in the crystalline phase (typically 0.3 Å). Moreover, also in the least square refinements the displacement factors $\sigma^2$ are higher in the crystalline phase than in the amorphous phase. The large disorder on a local scale in crystalline $\text{Ge}_1\text{Sb}_2\text{Te}_4$, despite the periodicity, makes this phase very exceptional.

Thus, after the analysis of the EXAFS data of $\text{Ge}_1\text{Sb}_2\text{Te}_4$, the question arises, what impact the finding has on the understanding of phase-change materials? The first model to explain the large optical contrast between the amorphous and the crystalline phase was suggested by Kolobov et al. [72]. The proposed "umbrella-flip" model relates this contrast to a change of the Ge atoms from an octahedral coordination in the crystal to a tetrahedral coordination in the amorphous phase. From this analysis this picture must be considered as much too simplified, since we observe considerable changes upon amorphization at all three absorption edges and not only around germanium.
Recently it has been shown by Shportko et al. [8] that resonant bonding in crystalline phase-change materials strongly enhances the optical dielectric constants. Since in the amorphous phase the dielectric constants match the expected values of covalent semiconductors, it is concluded that regarding the property contrast it is the crystalline phase which is unique. Thus, resonant bonding is identified as one characteristic of the crystalline state of phase-change materials. Resonant bonding can only occur in semiconductors with unsaturated covalent bonds and the bonded p orbitals have to be linearly aligned [9]. Therefore, the existence of distortions, for example Peierls like distortions [63], which leads to a higher localization of the electrons prevents resonant bonding. The analysis of the EXAFS data of Ge$_1$Sb$_2$Te$_4$ clearly show that the local distortions (up to 0.4 Å) are larger in the crystalline phase than in the amorphous phase. Nonetheless, resonant bonding is present in crystalline Ge$_1$Sb$_2$Te$_4$, since large dielectric constants are observed [8]. Thus, obviously the medium range order and the linear alignment of the p bonds (the prerequisite for resonant bonding [9]) prevail despite the large local distortions in crystalline Ge$_1$Sb$_2$Te$_4$. 

Table 5.6: Summary of the dominant GeTe and SbTe scattering paths in amorphous and crystalline Ge$_1$Sb$_2$Te$_4$.

<table>
<thead>
<tr>
<th></th>
<th>crystalline phase</th>
<th>amorphous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeTe R (Å)</td>
<td>2.85 ± 0.01</td>
<td>2.61 ± 0.01</td>
</tr>
<tr>
<td>$\sigma^2$ (10^{-3} Å$^2$)</td>
<td>5.3 ± 1.7</td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>N</td>
<td>2.8 ± 1.3</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td>SbTe R (Å)</td>
<td>2.92 ± 0.05</td>
<td>2.84 ± 0.01</td>
</tr>
<tr>
<td>$\sigma^2$ (10^{-3} Å$^2$)</td>
<td>4.2 ± 3.1</td>
<td>3.7 ± 0.6</td>
</tr>
<tr>
<td>N</td>
<td>2.8 ± 2.3</td>
<td>2.9 ± 0.4</td>
</tr>
</tbody>
</table>
6 Structural Changes along the Pseudo-Binary Line

The discovery of the fast switching properties of materials along the GeTe-Sb$_2$Te$_3$ pseudo-binary line has triggered tremendous scientific and technological interest in these alloys [7]. Although these materials are by now commonly used in data storage applications, the scientific interest is unchanged. In this thesis we have studied the structure of three materials along this pseudo-binary line and the local order in GeTe, Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$ are compared and discussed in the following.

The Fourier transform $|\chi(R)|$ of the EXAFS spectra measured at the amorphous and crystalline phases are plotted in Figure 6.1. Thereby, it can be seen that for all materials large differences exist in the local order of the amorphous and the crystalline phase: upon amorphization the peaks shift towards smaller distances and a change in amplitude can be observed. If the change in amplitude is studied in detail, it can be seen that in GeTe the amplitudes are larger in the crystalline phase than in the amorphous phase, while in Ge$_1$Sb$_2$Te$_4$ the contrary can be observed. In the alloy Ge$_8$Sb$_2$Te$_{11}$, which lies in between GeTe and Ge$_1$Sb$_2$Te$_4$ on the pseudo-binary line, the amplitude increases upon amorphization at the Ge edge, but has similar heights at the Te and Sb edge. These changes can mainly be attributed to changes in the coordination numbers and the static disorder expressed through the mean square displacement factors $\sigma^2$.

If we focus on the crystalline phase, it can be seen that the amplitude in the absorption spectra decreases from GeTe to Ge$_1$Sb$_2$Te$_4$. The first coordination shell of germanium in all three materials consists of six tellurium atoms, and hence, it could be expected that the amplitude of the peaks corresponding to first shell are comparable at the Ge and Sb edge. Since differences in the amplitude from different backscattering elements can be excluded, the discrepancies in amplitude must be related to structural changes on the first coordination shell. The comparison of the bond distances shows, that in all materials at least two different GeTe bond length exist. The split in shorter and longer bond length is largest for GeTe (2.81 Å and 3.16 Å) and smallest for Ge$_1$Sb$_2$Te$_4$ (2.85 Å and 3.09 , if the first coordination shells is modelled with two distances only). Hence in terms of distortions, we could argue that the amplitude of the distortion is larger in GeTe as in Ge$_1$Sb$_2$Te$_4$, and since the vacancy concentration is considerably lower in GeTe, that the amplitude of the distortions depends on the vacancy concentration in the material. In contrast to a previous study on the basis of DFT calculations by Wuttig et al. [79], we find that a higher number of vacancies lowers the amplitude of the distortions. Although this
Figure 6.1: Comparison of the Fourier transforms $|\chi(R)|$ of GeTe (red), Ge$_8$Sb$_7$Te$_{11}$ (violet) and Ge$_1$Sb$_2$Te$_4$ (blue) in the crystalline and the amorphous state. The large differences in the spectra of the crystalline state of the different material, e.g., the change in amplitude, can be attributed to an increasing static disorder from GeTe to Ge$_1$Sb$_2$Te$_4$. The changes in the spectra of the amorphous phase from GeTe to Ge$_1$Sb$_2$Te$_4$ are mainly related to changes in coordination.
is interesting to note, it cannot help to explain the reduction of amplitude in the EXAFS spectra from GeTe to Ge$_1$Sb$_2$Te$_4$. But another parameter that influences the amplitude of the EXAFS spectra and depends on the structure in the material is the mean-square displacement factor $\sigma^2$. This factor usually accounts for thermal and static disorder in an EXAFS spectra and reduces the amplitude according to $\exp(-2k^2\sigma^2)$ (see Section 2.1.3). This displacement factors have been refined independently for the different bond lengths. Since all spectra have been recorded at 10 K an effect of the temperature on the spectra can be excluded and different displacement factors must result from an increase or decrease in static disorder. Taking into account that the spectra have been recorded at 10 K all displacement factors $\sigma^2$ are unusually large ($\sigma^2 > 3.1\times10^{-3}$ Å$^2$ compared to e.g., $\sigma^2 = 2.3\times10^{-3}$ Å$^2$ for crystalline Ge [80]). Moreover, the displacement factors for the GeTe bonds increase from GeTe to Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$. Thus, the width of bond distributions of the GeTe bonds increases, with increasing Sb$_2$Te$_3$ concentration in the alloy. This conclusion is also supported by the fact, that a third GeTe bonds improved the fit quality of crystalline Ge$_1$Sb$_2$Te$_4$, which has the highest static disorder of the investigated materials.

The same effect, a decrease of the amplitudes of the first coordination shell from GeTe to Ge$_1$Sb$_2$Te$_4$, can be observed at the tellurium edge and the antimony edge. At the Te edge this decrease in amplitude from GeTe to Ge$_1$Sb$_2$Te$_4$ is even more astonishing than at the Ge edge, since in addition to the larger static disorder further parameters influence the amplitude of the peaks of the first coordination shell. The cation sites in the investigated crystal are occupied by germanium, antimony and vacancies. With an increasing fraction of Sb$_2$Te$_3$ in the alloy, both the number of vacancies and the number of antimony atoms increase. In GeTe, the tellurium atoms are surrounded by germanium atoms (and a few vacancies), while in Ge$_1$Sb$_2$Te$_4$ 50% of the neighbouring atomic sites are occupied by antimony atoms. Since the backscattering amplitude of an element increases with its atomic number, the backscattering amplitude is higher for antimony than for germanium. Hence, an increase in amplitude could be expected with an increase of the antimony concentration. Since in contrast a decrease in the amplitude from GeTe to Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$ is observed, it seems that the influence of the increasing vacancy concentration and the increase in static disorder is the most dominant effect.

The increasing disorder in Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$ as compared to GeTe can also be observed at the higher coordination shells. The second coordination shell of tellurium contains 12 Te atoms, which are split in two different bonds length in a crystal with rhombohedral symmetry like GeTe. In an ideal cubic crystal the 12 Te atoms have the same distance from the absorber atom. At the Te edge, it can be seen that the amplitude of the peak corresponding to the second coordination shell around 4 Å is almost identical for Ge$_8$Sb$_2$Te$_{11}$ and GeTe but significantly smaller for Ge$_1$Sb$_2$Te$_4$. Also this observation can only be explained by the much larger static disorder in cubic Ge$_1$Sb$_2$Te$_4$. This is also fortified by the larger mean-square displacement factors $\sigma^2$ for the TeTe scattering paths in Ge$_1$Sb$_2$Te$_4$ (>0.011 Å$^2$) as
6. Structural Changes along the Pseudo-Binary Line

cmpared to Ge$_8$Sb$_2$Te$_{11}$ (0.008 Å$^2$) and GeTe (<0.005 Å$^2$). The same argument is valid to explain the amplitude differences at the higher coordination shell, but at the higher shells also multiple scattering has to be taken into account. At the germanium edge significant amplitude differences between GeTe and Ge$_8$Sb$_2$Te$_{11}$ can already be seen at the second coordination shell. This is related to the higher chemical disorder in Ge$_8$Sb$_2$Te$_{11}$ as compared to GeTe. While the second shell of an absorbing Ge atoms contains only Ge atoms (and vacancies) in crystalline GeTe, in the crystalline state of Ge$_8$Sb$_2$Te$_{11}$ also Sb atoms occupy the second coordination shell. It is the combination of the high static disorder and, in addition, the chemical disorder, which leads to a decrease of the amplitude due to negative interferences of the backscattered waves. This characteristic of EXAFS measurements is well known from amorphous materials, were usually only the first coordination shell can be seen in the Fourier transform |χ(R)|.

All these observations support the conclusion that the disorder increases along the pseudo-binary line from GeTe to Ge$_1$Sb$_2$Te$_4$. These structural changes can be related to different optical contrasts between the crystalline and the amorphous state. Resonant bonding in the crystalline state of phase-change materials has been found to be the reason for the significant (optical) contrast between the crystalline and the amorphous phase [8]. Here, the delocalization of the p-type electrons, that are involved in more bonds than can be saturated with the number of electrons present in the system, leads to high polarizibilities and hence large optical dielectric constants. Distortions (e.g., Peierls distortion [63]) cause localization of the electrons in less bonds and, thus, counteract the resonance character of the bonds. The change in the dielectric optical constant upon crystallization is 152% for GeTe, while in Ge$_1$Sb$_2$Te$_4$ the increase upon crystallization is only 118%. Thus, the changes in the optical contrast can be related to the increase in the disorder in the crystalline phase.

The analysis of the amorphous phase of GeTe, Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$ yields that the bond lengths, which have been determined by refining the scattering paths using the program ARTEMIS [23], agree very well in the different materials. The shortest bond is formed by two germanium atoms, and this GeGe bond has a length of 2.47±0.07 Å in amorphous GeTe and 2.48±0.01 Å in Ge$_8$Sb$_2$Te$_{11}$. GeTe bonds are present in all three materials and the bond length is 2.61±0.01 Å. The agreement found for the SbTe bond length in Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$ is as high as the previous mentioned bond lengths and is 2.83±0.01 Å in Ge$_8$Sb$_2$Te$_{11}$ and 2.84±0.01 Å in Ge$_1$Sb$_2$Te$_4$. But despite these analogy between the local order in the amorphous phase of the three materials, the measured EXAFS spectra also show a pronounced difference. At the tellurium edge, the peak with highest amplitude is shifted (approximately 0.2 Å towards larger distances in Ge$_1$Sb$_2$Te$_4$ as compared to Ge$_8$Sb$_2$Te$_{11}$ and GeTe, and this effect can also been observed at the Ge edge, although here the shift is much smaller. These differences cannot be attributed to different bond lengths, since we found that these are similar in all three amorphous materials. Therefore, the changes must result from different bond pairs and the respective coordination numbers, which depend on the stoichiometry of the investigated
material. While GeGe and GeTe bonds dominate the local coordination in GeTe, in Ge$_1$Sb$_2$Te$_4$ one GeTe and one SbTe scattering paths is sufficient to achieve a reasonable fit of the data. In Ge$_8$Sb$_2$Te$_{11}$, in addition to GeTe, SbTe and GeGe bond pairs, also a small fraction of GeSb bonds is detected. The large fraction of SbTe bonds in Ge$_1$Sb$_2$Te$_4$, which have a larger bond length than the GeTe bonds, is responsible for the peak shift in Ge$_1$Sb$_2$Te$_4$ as compared to GeTe and Ge$_8$Sb$_2$Te$_{11}$ at the Te edge.

In addition to the bond lengths, also the mean-square displacement factors $\sigma^2$ of the different bonds are similar in all three amorphous materials. This means that the static disorder is similar in all three materials. Further insight in the amorphous structures could be gained by comparing the coordination numbers in the three materials. But it is known that the coordination numbers determined solely from EXAFS measurements have a high uncertainty [81] and the difficulties to unambiguously determine the coordination numbers from the configuration, which results from the RMC simulations have already been discussed (Section 4.3.2 and Section 5.3.2). Therefore, we rather focus on the structural differences between the amorphous and the crystalline phase, which all three materials have in common.

The increase in local disorder and the resulting decrease in amplitude in the Fourier transforms $|\chi(R)|$ from GeTe to Ge$_8$Sb$_2$Te$_{11}$ and Ge$_1$Sb$_2$Te$_4$ has already been discussed. It has also been mentioned that the amplitude in the amorphous phase is unexpectedly higher than in the crystalline phase in Ge$_1$Sb$_2$Te$_4$ (and Ge$_8$Sb$_2$Te$_{11}$), while in GeTe it is the other way round. Despite this differences, in all three alloys the bond lengths shorten upon crystallization and, in addition, the mean-square displacement factors $\sigma^2$ are large in the crystalline phase, as compared to common semiconductors like Ge, but most important the mean-square displacement factors $\sigma^2$ are lower in the amorphous state than in the crystalline state. Thus, it must be concluded, that the local order is different in the amorphous and crystalline state of phase-change materials, and the local order is larger in the amorphous than in the crystalline state. The fact that the local disorder is larger in the crystalline phase, and, nonetheless, the medium range order and the periodicity are maintained, show the uniqueness of the metastable, crystalline state of these materials.
7 Summary and Conclusions

In memory applications based on phase-change materials, the large optical and electrical contrast between the amorphous and a crystalline state are utilised to store data. This study is motivated by the desire to understand the origin of the portfolio of properties, that makes these alloys unique, and technologically and scientifically interesting. Therefore, the structure of the amorphous and the crystalline state, that are relevant in storage applications, has been investigated on the basis of EXAFS experiments for GeTe, Ge₈Sb₂Te₁₁ and Ge₁Sb₂Te₄. Thereby it has been shown, that the temperature, at which the EXAFS spectra are recorded, has a huge influence on the quality of the EXAFS spectra. The information content increases significantly if the temperature is lowered to 10 K, and coordination shells, that cannot be observed even at 80 K, contribute to the spectrum. In the Fourier transformed spectra |χ(R)| of GeTe, peaks up to a radial distance of 6 Å can be distinguished.

This unusual large temperature influence on the EXAFS spectra is related to the large static disorder in these materials. Even when measuring at 10 K, where the thermal contributions due to atomic vibrations are supposedly negligible, the mean-square displacement parameters σ² for the crystalline phase are large. Moreover, they are smaller in the amorphous phase than in the crystalline phase. This is indeed unique, since usually it is expected that it is the amorphous phase, where the local order is less well-defined. The same conclusions can be drawn from the results of the RMC simulations of the EXAFS data of GeTe and Ge₁Sb₂Te₄. Although less constraints have been applied to model the experimental data, the partial pair correlation functions of the amorphous phases exhibit much sharper peaks than the correlation functions of the crystalline phases, while at the same time no medium and long range order is present in these states.

In addition to the change in static disorder upon amorphization, which can be deduced from the increase in the displacement factors σ², in all three alloys the bond lengths decrease upon amorphization. Thus, in combination with the decrease of the density [82] during this transition, this means that the local order changes significantly upon amorphization. Furthermore, the distance distributions are broader in the crystalline phase as compared to the amorphous phase. By using very accurate EXAFS measurements recorded at 10 K and by fitting the absorption spectra simultaneously at all absorption edges for GeTe, Ge₈Sb₂Te₁₁ and Ge₁Sb₂Te₄, we have been able to show that large differences in the local order of the amorphous and crystalline phase exist not only around germanium but also for antimony and tellurium. Moreover, the increase in disorder on the GeTe-Sb₂Te₃ pseudo-binary line from GeTe to Ge₁Sb₂Te₄ can be related to the decrease in the optical contrast upon
crystallization in Ge$_1$Sb$_2$Te$_4$ as compared to GeTe [8].

Since the disorder is large in the crystalline phase of Ge$_1$Sb$_2$Te$_4$, RMC simulations have been used to exploit the full information content in the data. This way, it has been possible to detect an ordering of the vacancies along lines in certain directions ([1 0 0] and [1 1 0], see Section 5.2.2), if large configurations are used (>2000 atomic sites). It is the first time that these vacancy ordering could be observed based on experimental data, but it is already known from DFT calculations that the distribution of vacancies, germanium and antimony atoms on the (1 1 1) planes is energetically favourable [59]. In a recent study by Siegrist et al., the influence of the annealing temperature on the electrical properties of different phase-change material along the GeTe-Sb$_2$Te$_3$ pseudo-binary line has been discussed [83]: depending on the crystallization temperature, the conductivity of the materials shows either metallic or insulating conductivity. This metal-insulator transition in Ge$_1$Sb$_2$Te$_4$ takes place at an annealing temperature of approximately 250 °C, hence, in the hexagonal phase of Ge$_1$Sb$_2$Te$_4$. This means that these changes are not related to the structural transition from the cubic to hexagonal phase. The changes in conductivity have been related to a different ordering in the crystal. Thus, it would be very interesting to perform EXAFS measurements on samples of Ge$_1$Sb$_2$Te$_4$, that have been annealed at different temperatures, to analyse the dependency of the local order on the crystallization temperature.
Appendix A

Ge$_8$Sb$_2$Te$_{11}$

The results of the analysis of the crystalline and the amorphous phase are discussed in this chapter.

The EXAFS measurements of Ge$_8$Sb$_2$Te$_{11}$ have been performed at 10 K. The result of the analysis of the crystalline phase is plotted in Figure A.1 and the refined parameters are summarized in Table A.2. In the analysis the first and second coordination shell have been fitted. The Te atoms occupy the anion sites in the lattice while the cations sites are shared by germanium, antimony and vacancies. Two GeTe and SbTe bond length are necessary to fit the first shell of the EXAFS spectra. Thereby, it has been possible to constrain the GeTe distances in such a way that the germanium atoms are allowed to move only along the (1 1 1) direction. Thus, the GeTe distances have been parametrized with respect to the lattice constant $a$ and a displacement parameter $x$:

$$
\text{GeTe}_1 = a\sqrt{6x^2 - 8x + 3}
$$

(A.1)

$$
\text{GeTe}_2 = a\sqrt{6x^2 - 4x + 1}.
$$

(A.2)

It is not possible to constrain the SbTe bonds in the same way. Even a fit with a different displacement parameter $x_2$ yields no satisfying agreement between the fit and the data. To model these bonds, two unconstrained SbTe distances have been fitted.

The scattering paths of the second coordination shell, i.e., TeTe, GeGe, SbSb and SbGe paths, also depend on the lattice constant $a$. In an ideal cubic crystal, all scattering paths in the second shell have the same path lengths. Due to the detected distortions of the atoms from the ideal lattice positions in the first coordination shell, also the path lengths of the second coordination shell vary. The TeTe scattering paths are constrained to equal the lattice constant $a$, but the GeGe, SbSb and GeSb path lengths are refined independently. In addition to the path length, for every bond pair a different mean-square displacement parameter $\sigma^2$ is refined.

The fitting of the crystalline phase of Ge$_8$Sb$_2$Te$_{11}$ is based on a cubic symmetry. This result conflicts with the result of a previous study by Matsunaga et al. [60]. They studied the laser crystallized phase of Ge$_8$Sb$_2$Te$_{11}$ using x-ray diffraction (XRD) measurements and found that, similar to GeTe, this alloy has a high-temperature cubic phase and a low temperature rhombohedral phase. These phases have been
observed at 823 K and 92 K, respectively. In a crystal with rhombohedral symmetry, according to the results by Matsunaga et al., the second coordination shell consists of two different scattering path and the path lengths differ by 0.09 Å. In contrast, in our analysis the second coordination shell can be fitted with only one TeTe distance. The corresponding peak in the measured spectrum does not even show an asymmetry towards larger distances, as has been observed in the spectra of crystalline GeTe. To explain these apparent differences, it could be argued that the difference in path lengths (assuming rhombohedral symmetry) is so small that only one peak with an increased peak width is visible in the spectrum. The larger peak width could result in an increased mean-square displacement factor and indeed, if the mean-square displacement factor of the TeTe scattering path of Ge₈Sb₂Te₁₁ (0.008 Å²) is compared with the displacement factors in GeTe (<0.005 Å²), this seems to be true. But on the other hand already the first coordination shell of the tellurium atom is more distorted in Ge₈Sb₂Te₁₁ than in GeTe, due to existence of antimony atoms in addition to germanium atoms and vacancies. Hence the larger mean-square displacement factor could also result from the higher disorder in Ge₈Sb₂Te₁₁ and it must not be forgotten that the mean-square displacement factors of the TeTe distances in Ge₁₁Sb₂Te₄, which has a cubic phase, are even larger than the factors in Ge₈Sb₂Te₁₁. Based on the EXAFS data only it cannot be unambiguously decided, whether the investigated material has a cubic or a rhombohedral symmetry. The XRD measurements by Matsunaga et al. [60] show that the crystalline phase at 92 K has no cubic symmetry. But since they studied laser-crystallized Ge₈Sb₂Te₁₁ and the measurements have been performed at a different temperature than the EXAFS measurements in this study, it is possible that the investigated structures deviate from each other. Hence, to be able to unambiguously determine the crystal symmetry of Ge₈Sb₂Te₁₁ at 10 K, one would need to perform XRD measurements at 10 K on our sample.

The result of the co-refinement of the EXAFS data of the amorphous phase of Ge₈Sb₂Te₁₁ is shown in Figure A.2. As can be seen the agreement between the fit and the data is excellent. In amorphous Ge₈Sb₂Te₁₁, in addition to GeTe bonds with bond lengths of 2.60 Å and 2.83 Å, GeGe bonds (2.48 Å) and GeSb bonds (2.68 Å) exist. For every bond pair a mean-square displacement factor \( \sigma^2 \) is fitted independently and also the number of bonds \( N \) is refined. The total coordination numbers can be calculated from the number of bonds. According to these numbers Ge has a coordination number of 5.5 ± 0.4, antimony of 3.9 ± 0.4 and tellurium of 2.6 ± 0.1. Compared to the numbers that are expected for covalent bonded material according to the \( 8-N \) rule [63], the coordination numbers indicate that the atoms are highly overcoordinated in amorphous Ge₈Sb₂Te₁₁. These results agree fairly well with a DFT study of Ge₈Sb₂Te₁₁ performed by Akola et al. [84] (see Table A.1). They found coordination numbers of 4.0 for Ge, 3.7 for Sb and 2.9 for Te. Only the coordination number of germanium deviates from our result and this can mainly be attributed to different partial coordination numbers of GeGe bonds. In the present analysis we found that a germanium atom is in average bonded to 2.1 germanium atoms, while
Table A.1: Comparison of results of the structure of the amorphous phase of Ge$_8$Sb$_2$Te$_{11}$. In this study the structure is investigated using EXAFS measurements, whereas Akola et al. [84] have performed DFT calculations.

<table>
<thead>
<tr>
<th></th>
<th>present study</th>
<th>Akola [84]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeTe</td>
<td>R (Å)</td>
<td>2.60(1)</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>3.0(1)</td>
</tr>
<tr>
<td>SbTe</td>
<td>R (Å)</td>
<td>2.83(1)</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>2.2(2)</td>
</tr>
<tr>
<td>GeGe</td>
<td>R (Å)</td>
<td>2.48(1)</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>2.1(2)</td>
</tr>
<tr>
<td>GeSb</td>
<td>R (Å)</td>
<td>2.68(1)</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.4(1)</td>
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<td></td>
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<td></td>
<td>N</td>
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</tr>
<tr>
<td>TeTe</td>
<td>R (Å)</td>
<td></td>
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<tr>
<td></td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>$N_{Ge}$</td>
<td></td>
<td>5.5(4)</td>
</tr>
<tr>
<td>$N_{Sb}$</td>
<td></td>
<td>3.9(4)</td>
</tr>
<tr>
<td>$N_{Te}$</td>
<td></td>
<td>2.6(1)</td>
</tr>
</tbody>
</table>

Akola et al. find 0.7 bonds. A further difference in both studies is, that Akola et al. found a small fraction of SbSb and TeTe bonds in their configuration. It has not been necessary to allow these bonds in the EXAFS analysis, since the fit quality has already been excellent with only the four mentioned bond pairs. This might be due to the fact, that it is hardly possible to distinguish between Sb and Te using x-ray, since their atomic numbers $Z$ differ only by one ($Z = 51$ and 52). The comparison of the bond lengths yield that the distances are larger in the DFT study by Akola et al. as compared to our values. This results from the approximation of the exchange correlation functionals used in the DFT calculations.

A comparison of the results of the analysis of the crystalline and the amorphous phase shows, that also in Ge$_8$Sb$_2$Te$_{11}$ the local order changes upon amorphization. The GeTe and SbTe bond lengths decrease and further bonds (GeGe and GeSb) form. The mean-square displacement factors of the bonds in the amorphous phase are smaller than the displacement factors of the bonds in the crystalline phase, which indicates that the bond distances are better defined and that the local order is higher in the amorphous phase than in the crystalline phase.
Figure A.1: Results of the co-refinement of the EXAFS spectra measured at the Ge, Sb and Te K edges of crystalline Ge$_8$Sb$_2$Te$_{11}$ at 10 K. The data are shown in black and the fit in red. The vertical lines in |χ(R)| indicate the range that was Fourier transformed to χ(q) and then fitted.
Figure A.2: Results of the co-refinement of the EXAFS spectra measured at the Ge, Sb and Te K edges of amorphous Ge$_8$Sb$_2$Te$_{11}$ at 10 K. The data are shown in black and the fit in red. The vertical lines in $|\chi(R)|$ indicate the range that was Fourier transformed to $\chi(q)$ and then fitted.
Table A.2: Summary of the results of the analysis of the crystalline and amorphous phase of Ge$_8$Sb$_2$Te$_{11}$. For all parameters that have been refined the statistical error is stated. If no error is indicated the corresponding parameter has not been refined, but the value has been kept constant.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Crystalline Phase</th>
<th>Amorphous Phase</th>
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<tbody>
<tr>
<td>R factor</td>
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<td>0.001</td>
</tr>
<tr>
<td>$S_0^2$(Ge)</td>
<td>0.56 ± 0.05</td>
<td>0.56</td>
</tr>
<tr>
<td>$S_0^2$(Sb)</td>
<td>0.77 ± 0.13</td>
<td>0.77</td>
</tr>
<tr>
<td>$S_0^2$(Te)</td>
<td>0.66 ± 0.04</td>
<td>0.66</td>
</tr>
<tr>
<td>$E_0$(Ge) (eV)</td>
<td>5.4 ± 0.5</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>$E_0$(Sb) (eV)</td>
<td>9.4 ± 1.1</td>
<td>6.8 ± 0.6</td>
</tr>
<tr>
<td>$E_0$(Te) (eV)</td>
<td>6.1 ± 0.3</td>
<td>4.2 ± 0.3</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.20 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>$x$</td>
<td>0.525 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>GeTe$_1$ R (Å)</td>
<td>2.83 ± 0.01</td>
<td>2.60 ± 0.01</td>
</tr>
<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>3.8 ± 0.4</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>N</td>
<td>3</td>
<td>3.0 ± 0.1</td>
</tr>
<tr>
<td>GeTe$_2$ R (Å)</td>
<td>3.12 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>8.8 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>SbTe$_1$ R (Å)</td>
<td>2.91 ± 0.01</td>
<td>2.83 ± 0.01</td>
</tr>
<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>4.7 ± 0.9</td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>N</td>
<td>3.2 ± 0.6</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>SbTe$_2$ R (Å)</td>
<td>3.17 ± 0.02</td>
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</tr>
<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>11.0 ± 3.7</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2.8 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>TeTe R (Å)</td>
<td>a=4.20 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>8.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>12</td>
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</tr>
<tr>
<td>GeGe R (Å)</td>
<td>4.24 ± 0.02</td>
<td>2.48 ± 0.01</td>
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<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>12.2 ± 1.4</td>
<td>4.4 ± 0.5</td>
</tr>
<tr>
<td>N</td>
<td>12*8/11</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>SbSb R (Å)</td>
<td>4.32 ± 0.10</td>
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<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>11.4 ± 9.0</td>
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</tr>
<tr>
<td>N</td>
<td>12*2/11</td>
<td></td>
</tr>
<tr>
<td>GeSb R (Å)</td>
<td>4.26 ± 0.03</td>
<td>2.68 ± 0.01</td>
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<tr>
<td>$\sigma^2$ (10$^{-3}$Å$^2$)</td>
<td>14.7 ± 3.6</td>
<td>3.8 ± 0.8</td>
</tr>
<tr>
<td>N</td>
<td>12*2/11</td>
<td>0.4 ± 0.1</td>
</tr>
</tbody>
</table>
Appendix B

Normalized Absorption Spectra

In this section the normalized absorption spectra of GeTe, Ge$_1$Sb$_2$Te$_4$ and Ge$_8$Sb$_2$Te$_{11}$ in the crystalline and the amorphous state measured at 10 K are shown. To determine the background functions and isolate the x-ray fine structure oscillations the AUTOBK approach implemented in the program ATHENA has been used [23, 24].
Appendix B. Normalized Absorption Spectra

Figure B.1: The absorption \( \mu(E) \) (black line) in GeTe has been measured at 10 K for the crystalline phase (a) and the amorphous phase (b) at the Te and the Ge K edges. The background function \( \mu_0(E) \) (red line) has been determined using the AUTOBK approach. In the insets the region near the absorption edge is shown.
Figure B.2: The absorption $\mu(E)$ (black line) in crystalline Ge$_1$Sb$_2$Te$_4$ has been measured at 10 K at the Te, Sb and the Ge K edges. The background function $\mu_0(E)$ (red line) has been determined using the AUTOBK approach. In the insets the region near the absorption edge is shown.
Appendix B. Normalized Absorption Spectra

Figure B.3: The absorption $\mu(E)$ (black line) in amorphous Ge$_1$Sb$_2$Te$_4$ has been measured at 10 K at the Te, Sb and the Ge K edges. The background function $\mu_0(E)$ (red line) has been determined using the AUTOBK approach. In the insets the region near the absorption edge is shown.
Figure B.4: The absorption $\mu(E)$ (black line) in crystalline Ge$_8$Sb$_2$Te$_{11}$ has been measured at 10 K at the Te, Sb and the Ge K edges. The background function $\mu_0(E)$ (red line) has been determined using the AUTOBK approach. In the insets the region near the absorption edge is shown.
Figure B.5: The absorption $\mu(E)$ (black line) in amorphous Ge$_8$Sb$_2$Te$_{11}$ has been measured at 10 K at the Te, Sb and the Ge K edges. The background function $\mu_0(E)$ (red line) has been determined using the AUTOBK approach. In the insets the region near the absorption edge is shown.
Bibliography


Bibliography


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