

Design Rules, Local Structure and Lattice-Dynamics of Phase-Change Materials for Data Storage Applications

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Abstract

Our modern information society is characterized by a steadily increasing demand for powerful data storage devices, which calls for the development of innovative storage concepts. Consequently, memories based on phase-change materials have attracted considerable interest in recent years. These materials can reversibly be switched between an amorphous and a crystalline state. Since both phases exhibit significantly different physical properties, in particular reflectivity and conductivity, they enable optical and electrical storage applications. However, the properties of the employed phase-change material limit the performance of such devices. By now, only few suitable materials have been identified by empirical means. Therefore, the present work aims at developing a theoretical understanding of the material physics of phase-change materials. It is divided into four parts. First, the current state of research is reviewed, which motivates the research questions that this work is concerned with.

In the second part, resonant bonding in the crystalline state is identified as a generic property of phase-change materials based on experimental results on optical properties and crystal structure. It causes the contrast between the phases that is employed in phase-change applications. The resonance is endangered, however, by Peierls-like atomic distortions that shift atoms out of the symmetry-positions of the crystal. By means of density functional theory-calculations, it is shown that in phase-change materials the resonance character is weakened by these distortions, but prevails. Subsequently, this newly gained understanding is employed to develop a design-scheme for suitable materials in form of a map. The coordinates of a material, which reflect the ionicity and tendency towards hybridization of the bonding, enable the identification of materials that are characterized by resonant bonding. The map successfully locates suitable materials in a confined region.

This design-principle, its predictions, but also the limits of its validity are investigated in the third part. Therefore, density functional theory-calculations are performed on a wide range of materials in order to study and to quantify the structure and the bonding. The results support the principal validity of the map and its predictions regarding property trends. Yet, the calculations also reveal some effects that are not incorporated in the simple map-scheme.

Among these are variations in the distortion patterns in the non-binary phase-change materials which are traced back to the local structure in the fourth part of this thesis. Moreover, the volume- or pressure-dependence, respectively, of the structure and the bonding is calculated and discussed. Finally, the potential energy surface is investigated to gain insight not only into the static distortions, but also into the lattice-dynamics.

Kurzfassung

Übersetzung des englischen Originaltitels: Designregeln, lokale Struktur und Gitterdynamik von Phasenwechselmaterialien für Datenspeicheranwendungen

Der stetig steigende Bedarf unserer modernen Informationsgesellschaft an leistungsfähigen Datenspeichern erfordert die Entwicklung innovativer Speicherkonzepte. Daher haben sich neuartige Speicher auf der Grundlage von Phasenwechselmaterialien in den Fokus der Forschung geschoben. Diese Materialien können lokal innerhalb kürzester Zeit reversibel zwischen einer amorphen und einer kristallinen Phase umgeschaltet werden. Somit lassen sich verschiedene Zustände unterscheiden, da beide Phasen stark voneinander abweichende physikalische Eigenschaften aufweisen. Insbesondere Reflektivität und elektrische Leitfähigkeit sind hier zu nennen, wodurch Anwendungen in optischen und elektrischen Speichern möglich werden. Allerdings limitieren die Eigenschaften des jeweils eingesetzten Phasenwechselmaterials die Leistungsfähigkeit solcher Speicher. Nur wenige geeignete Materialien sind bisher empirisch identifiziert worden. Die vorliegende Arbeit befasst sich daher mit dem Verständnis der einzigartigen Materialphysik von Phasenwechselmaterialien. Sie gliedert sich dabei in vier Teile. Im ersten Teil wird eine Zusammenfassung des bisherigen Stands der Forschung präsentiert. Hieraus ergeben sich die wesentlichen Fragestellungen der Materialentwicklung, die in dieser Arbeit behandelt werden.

Im zweiten Teil wird auf der Grundlage von experimentellen Resultaten zur Struktur und zu den optischen Eigenschaften das Auftreten von resonanten Bindungen in der kristallinen Phase als charakteristisches Merkmal dieser Materialfamilie identifiziert, welches für den ausgenutzten Kontrast zwischen den Phasen verantwortlich ist. Resonante Bindungen stehen jedoch in Konkurrenz zu Peierls-artigen Verzerrungen, welche die Atome aus den Symmetriepositionen der Kristallstruktur auslenken. Auf der Grundlage von rechnergestützten Dichtefunktionaltheorie-Rechnungen (DFT) zeigt sich jedoch, dass bei Phasenwechselmaterialien die charakteristischen Eigenschaften von Resonanzbindungen dadurch nicht vollständig aufgehoben werden. Aus diesem Verständnis wird eine Designregel in Form einer Karte entwickelt. Aus den Koordinaten, welche für die Ionizität der Bindung und die Wahrscheinlichkeit von Hybridisierung stehen,

ergibt sich dabei die zu erwartende Ausprägung von Resonanzeigenschaften eines Materials. Die Karte lokalisiert die bis dato identifizierten Phasenwechselmaterialien erfolgreich in einem eng begrenzten Bereich.

Im dritten Teil werden diese Karte, ihre Aussagen und die Grenzen Ihrer Gültigkeit mittels DFT-Rechnungen beleuchtet. Dazu werden mehrere Materialien hinsichtlich ihrer Struktur und der Eigenschaften ihrer Bindungen untersucht. Die Ergebnisse bestätigen dabei die grundsätzliche Gültigkeit der Karte sowie ihrer Vorhersagen in Bezug auf Trends in den Materialeigenschaften. Es zeigen sich jedoch auch Effekte, die in einer Karte nicht berücksichtigt werden können. Darunter fallen Variationen in den atomaren Verzerrungen der mehrkomponentigen Materialien, welche im vierten Teil auf die lokale Struktur zurückgeführt werden. Darüber hinaus wird der Einfluss von Volumen- bzw. Druckänderungen auf die Struktur und die Bindungen berechnet und diskutiert. Die vorliegende Arbeit schließt mit der Untersuchung der atomaren Potentiallandschaft, welche über die statischen Verzerrungen hinaus Einblicke in die Gitterdynamik gibt.

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1. Introduction

Throughout the history of mankind, the ability to store, share and combine information has been key to its evolution. We may only guess what course history would have taken if apparently simple inventions such as pen, paper and letterpress but also the modern wonder of computers would not be omnipresent, but existed only in the minds of gifted science-fiction authors. This emphasizes the importance of the research on data storage and processing. We may only approach the limits of our cultural advancement if we succeed in providing ultimate memories that combine availability with speed and reliability.

A particular promising approach for such data storage devices is based on the fast reversible switching of so-called *phase-change materials* between an amorphous and a crystalline state. Both phases are characterized by very different material properties, thus providing the contrast required to distinguish between set and unset bits. Phase-change recording was initiated in the 1960s by S. Ovshinsky [1]. It is the state-of-the-art technique for rewritable optical storage since the market introduction of the CD-RW in 1996, and continues to hold this position up to now in the form of the rewritable implementation of the Blu-ray disc format (i. e., BD-RE). It is also among the most promising candidates to succeed Flash memory as *PCRAM* (Phase-Change Random Access memory), with the potential to fulfill its duties at a speed currently reached by the volatile DRAM [2–4]. A wide scope of aspects in material science is involved in understanding phase-change materials. This founds the significant scientific interest in these materials that has led to hundreds of publications. Ultimately, an in-depth understanding of the few known successful phase-change materials is commonly thought to lead to design-rules for optimal materials, which is one of the driving forces of the field. The present thesis aims at supporting these efforts. To motivate what the main challenges are and how they are tackled in this work, first a brief introduction into the basics of phase-change recording shall be given.

The principle of operation of phase-change based devices is illustrated in [Fig. 1.1](#). A phase-change material is switched between the crystalline and amorphous state by providing a precisely controlled amount of heat. Currently, either laser pulses or electrical pulses are employed as heat sources. Starting from a crystalline bit, the temperature needs to be elevated

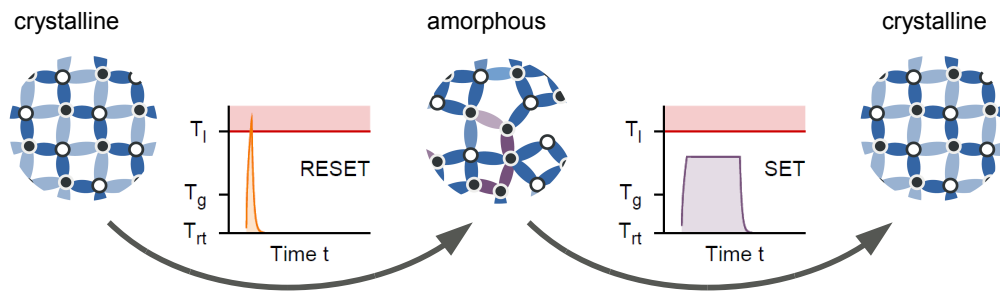


Figure 1.1: The operation principle of phase-change devices is based on the reversible switching between the crystalline and amorphous state. Amorphization (also called RESET-operation) of a bit proceeds via melt-quenching, employing short current or laser pulses as heat sources. Here, a huge temperature difference between the confined melt and the surrounding material leads to extremely high cooling rates. Thus, the disorder of the liquid is frozen in. Crystallization (SET-operation) requires annealing of an amorphous bit at a temperature below the melting temperature for the atoms to adopt the energetically favorable crystalline order.

above the liquidus temperature T_l using a short, high intensity (high current) pulse. Since only a spatially confined region is heated up, a huge temperature gradient between the molten bit and the surrounding material is obtained, leading to high cooling rates of about 10^{10} K/s. If the melt cools fast enough, crystallization is bypassed and a melt-quenched amorphous bit is formed once the temperature falls below a critical temperature, the glass transition temperature T_g . In this temperature regime, the atomic mobility is so small that crystallization, though energetically favorable, is kinetically hindered. To switch from the amorphous back to the crystalline state, the temperature of the bit needs to be elevated for a sufficiently long period of time to a temperature where the atomic mobilities are high enough for crystallization to occur. Hence, the sample has to be heated significantly above the glass transition temperature. To read out whether a bit is amorphous or crystalline, low intensity (low current) pulses are employed to distinguish between low and high reflectivity (conductivity). Noteworthy are the timescales of phase-change recording; crystallization is typically the slowest process involved. Nevertheless, under optimal conditions it may proceed in a matter of nanoseconds. At ambient conditions, however, crystallization of an amorphous bit must not take place within many years to ensure data retention. This means that the crystallization rate of phase-change materials

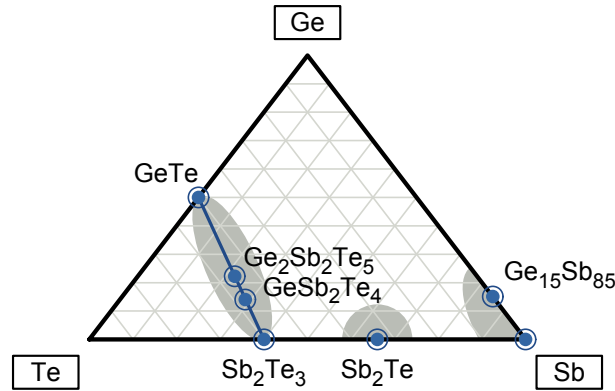


Figure 1.2.: Most phase-change materials are found within the ternary Ge:Sb:Te-phase diagram. In particular, the pseudo-binary line between GeTe and Sb_2Te_3 stands out as it hosts the most prominent phase-change materials composed as $(\text{GeTe})_m(\text{Sb}_2\text{Te}_3)_n$, with m and n being integer numbers.

must increase by up to twenty orders of magnitude while the temperature is elevated by only a few hundred Kelvin.

The task for material researchers that is to be accomplished is to find out which materials are suitable for application. This is a challenging quest, since the requirements regarding kinetics are not the only ones phase-change materials have to meet; the most important demands for materials that enable the application in storage applications are compiled in [Tab. 1.1](#). Further requirements may occur in the context of a particular type of application. For instance, a small density change upon crystallization may be desirable to improve the cyclability of a memory cell.

Besides unique kinetics, optical and/or electrical contrast is of utmost importance for phase-change materials. In order to distinguish between the phases, their material properties, namely resistivity and conductivity, must differ significantly. At first sight, this seems to require also a significant difference in local structure. But then the question arises, why the phase transition is so fast. If, however, the local structure is not so different, how can the tremendous differences in properties between phases occur? Clearly, this class of material exhibits unique features, which are absent in 'ordinary' semiconductors such as silicon or the III-V-materials.

Table 1.1.: Numerous material requirements for phase-change materials follow from the desired use in data storage applications. This table compiles the most important, partially conflicting demands. Thus, the task material research is confronted with is to find materials that suit these needs. These aspects will be further discussed in [Chapter 2](#).

Application Requirement	Material Requirement
Distinguishable logical states	ability to switch between phases that exhibit significantly different optical/electrical properties
Fast data transfer rates	rapid crystallization at elevated temperatures
Stability	no crystallization at ambient temperatures
Scalability/Data density	simple compositions, insensitivity to composition variations, functionality retained in small volumes with large interfaces
Cyclability	No irreversible modifications due to the switching process itself (e.g., electromigration), intrinsic change of the material over time (e.g., relaxation) or interaction with the environment (e.g., chemical reaction)
Operability of PCRAM at low voltages	Nonlinear electrical behavior in the amorphous state and reasonably high resistivity in the crystalline state
Easy to fabricate	production compatible with established processes and compliant with environmental legislation

Though there exist certain materials that have empirically been confirmed to meet the aforesaid requirements, it is not clear whether these are really the best materials. Most of the material families already identified can be found in the ternary Ge:Sb:Te-phase diagram shown in Fig. 1.2. On the pseudo-binary line connecting GeTe and Sb_2Te_3 , the most prominent materials such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are located [5, 6]. Besides Sb_2Te_3 , also Sb_2Te offers suitable properties when combined with fractions of silver and indium, for instance, yielding the widely employed AgInSbTe (abbrev. AIST) [7]. Finally, another material family that has attracted considerable interest in the last years is found here, namely modifications of antimony such as $\text{Ge}_{15}\text{Sb}_{85}$ [8, 9]. It stands out since it does not contain a chalcogen component, despite the fact that this was commonly assumed to be a requirement. It can be understood as 'doped' antimony¹. The question to be answered is *why* the materials in the ternary Ge:Sb:Te-phase diagram work as phase-change materials. What distinguishes these materials from others? How do their properties relate to their composition? Furthermore, the question arises whether materials, that are composed of other elements, could work as well.

Goals and Structure of this Work

The present thesis is divided into four main chapters. The aim of Chapter 2 is to give an overview of the current state of understanding of phase-change materials. It provides a review of this class of materials and highlights the most pressing research topics in this field. It motivates the main challenge that this thesis is concerned with: *What characterizes phase-change materials and how can suitable materials be designed?*

Thus, in the subsequent Chapter 3, we will focus on the identification of a common signature of phase-change materials, *resonant bonding*, and exploit this finding to develop a universal design scheme, *a map for phase-change materials*. Furthermore, systematics in material trends, that relate to this map, are discussed in this chapter.

Due to the fact that the theoretical concepts behind the map are rather simple, it is desirable to test these by using a more accurate though also much more costly method, that is density functional theory-calculations. Chapter 4 presents the results on a wide range of materials that span the area of the map where phase-change materials are located. Furthermore, trends in the material properties are discussed and compared to the expectations derived from the map.

¹Doping in the field of phase-change materials refers to much larger concentrations (typically on the order of some percent) than in usual semiconductors such as silicon.

[Chapter 5](#) illuminates the local structure of phase-change materials and relates it to the dynamical properties of these alloys. Based on these results, interesting crosslinks can be drawn that relate this class of materials to others such as ferroelectrics and thermoelectrics.

At the end of this thesis, the main results are summarized in [Chapter 6](#), and an outlook on future research is provided.

The methods used in this work, density functional theory and its extension, density functional perturbation theory, are introduced in [Appendix A](#). In particular, important parameters that enter the simulations are discussed here. The theoretical concepts of lattice-dynamics and related properties (i. e., dynamic charges, dielectric properties and phonons) as well as static charges and electron localization are presented in [Appendix B](#). The reader may refer to these two appendices depending on his or her previous knowledge. Further supplementary material is compiled in [Appendices C, D and E](#).

2. Phase-Change Memories: Material Aspects of a Future Technology

In order to gain a thorough understanding of phase-change materials, many aspects need to be considered. First, it is necessary to learn about the phases involved in phase-change recording, that is liquid phase, amorphous phase and crystalline phase. Which structures do these phases exhibit? Ideally, insight into material properties that are relevant for applications (i. e., the functional behavior) can then be gained based on the knowledge of the bonding that is associated with these structures. What sounds so simple, is in fact a very challenging task since none of the employed phases represents equilibrium-conditions, either inherently (amorphous phase) or due to the fast switching. Thus, since the phases are not unique (i. e., depend on the preparation conditions), their characterization is hampered. In addition, high temperatures, which are necessary for melting and the transition to the crystalline phase, as well as the lack of periodicity lead to further complications. But even if these obstacles are overcome and the temperature-dependent material properties are obtained, further challenges arise; how does the transition between the phases proceed? What energy barriers separate the phases? Of course, all these questions need to be answered not only for one particular material, but also an understanding of the composition-dependence needs to be developed in order to enable the design of phase-change materials that best suit the needs of a particular application.

It is the aim of this chapter to briefly review the current state of research on phase-change materials, to highlight interesting research topics and to present results that will be of importance in later chapters. Therefore, one switching cycle, that is from crystalline over the liquid to the amorphous state, and back again to the crystalline state, is discussed. At the end, current and future applications that employ phase-change materials, and the respective research topics are presented.

After a basic introduction into the phase-change cycle has been given already in [Chapter 1](#), a more detailed view shall be presented here. Therefore, [Fig. 2.1](#) shows the phase transitions in terms of a time-temperature-transformation diagram. As this figure describes, the principle of

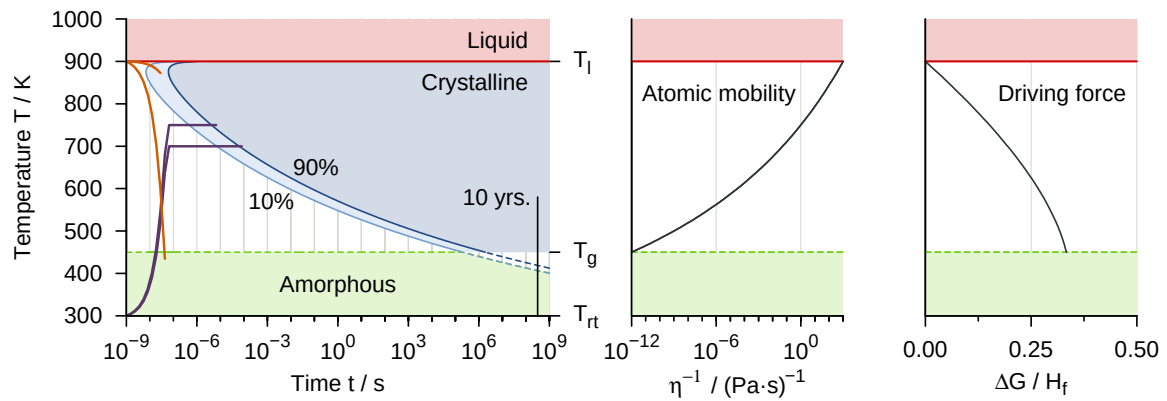


Figure 2.1.: The graph on the left schematically shows the transformation of a fixed volume of a phase-change material depending on the time spent at a certain temperature. The crystallization of 10 (90) percent of the material is indicated by the thin (thick) blue lines/areas. As one cools the melt below the liquidus temperature T_l (typically around 900 K), the atomic mobility, related to the reciprocal viscosity shown in the middle, is very large. However, since the driving force for crystallization, that is the difference in Gibbs free energy between (undercooled) liquid and crystal, visualized on the right in units of the heat of fusion H_f , is small, crystallization does not take place immediately. It may thus be bypassed, if the melt is quenched sufficiently fast. This is visualized by two constant rate-quenching processes starting at T_l , the slower of which leads to partial crystallization. Typically, quenching rates of 10^{10} K/s are required. At low temperatures, the driving force becomes larger, but the vanishing atomic mobility kinetically hinders crystallization. Eventually, as the glass transition temperature T_g (typically ranging around half T_l) is passed, an amorphous bit is formed. While ideally it is long-time stable against crystallization at ambient conditions, it crystallizes in fractions of seconds if the temperature is elevated and kept for a sufficiently long time. Two annealing processes starting at room temperature T_{rt} are indicated. Obviously, crystallization time and temperature are mutually dependent.

phase-change materials relies on a peculiar interplay of the temperature-dependent atomic mobility (macroscopically observed as the reciprocal of the viscosity η) and Gibbs free energy G . The difference in G between the phases is the driving force for phase transitions; in equilibrium, the phase that minimizes G is adopted, but on small timescales, the finite atomic mobility kinetically hinders the establishment of equilibrium conditions. This enables the preparation of glassy bits by 'freezing' a configuration of the undercooled liquid. Small atomic mobilities at ambient temperatures are also a key requirement for the stability of an amorphous bit. The mobilities, on the contrary, must not be small at elevated temperatures to enable fast crystallization. How can these conflicting demands be met by phase-change materials? What distinguishes the amorphous and the crystalline phase, and causes the pronounced property

contrast? We start our survey with the crystalline phase. Throughout this chapter, we will focus on studies of prototype-materials from the Ge:Sb:Te-system.

2.1. The Crystalline Phase

As was mentioned in the beginning, the lack of uniqueness concerns *all* phases, including the crystalline. In small volumes or thin films, as well as on short timescales, phase-change materials typically behave different from what is observed on bulk samples. Many of these materials transform into a metastable crystalline phase upon heating that is also the relevant phase in applications. Consequently, only samples that have been crystallized in actual devices can unambiguously reflect the absence of equilibrium-conditions. However, since only tiny amounts of material can be prepared by laser-switching, for instance, most characterization techniques would be rendered unfeasible. So instead of laser- or current pulse-crystallized bits, oven-annealed thin-film samples are typically investigated. As technological films are usually prepared by sputter deposition, this is commonly also the method of choice for film-preparation in this field. Thus, experimental characterization of the crystalline phase of phase-change materials is typically limited to powder or polycrystalline films rather than bulk samples prepared from the melt, so experiments that rely on resolving the Brillouin-zone (i. e., require well-oriented crystals) are rendered unfeasible. Attempts to deposit epitaxial thin film samples of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ on GaSb-substrates to overcome this limitation have successfully been conducted [10], yet the comparability to the properties of sputter-deposited thin films and crystalline bits, in particular, needs to be critically reviewed. We will re-encounter this issue in [Section 5.2](#).

Thin-film samples of phase-change materials also exhibit a metastable crystalline phase upon oven-annealing as revealed by irreversible heat release in differential scanning calorimetry experiments [11], and the measured properties reflect the behavior encountered in devices, which justifies this approach. We will see later that preparation of amorphous samples that resemble the structure obtained in devices is a much bigger issue. Nevertheless, the thermal history of a sample affects its properties, and for that reason has to be carefully considered [12, 13]. A positive aspect of the occurrence of non-equilibrium phases in devices is the fact that materials that are unstable at equilibrium conditions can be used, such as 'doped' materials and eutectics. Actually, the selection of eutectics was one of the first search rules for the empiric identification of phase-change materials due to the fact that the liquidus temperature is lowest at the eutectic composition. Typically, the glass transition temperature does not vary as much with composition as the liquidus temperature does. Materials that are easy to amorphize may thus

be obtained by reducing the temperature interval that has to be bypassed by quenching, that is by using eutectics. In addition, a low liquidus temperature reduces the power consumption. Nevertheless, an eutectic material melts congruently, but it does not form a homogeneous phase upon crystallization, at least not in equilibrium. Given the required temperature and time, decomposition is inevitable. That poses challenges for the stability and cyclability of a phase-change device [14]. The small timescales and spatial dimensions encountered in electrical devices, however, generally lead to operation conditions where equilibrium is not obtained. Thus, alloys such as $\text{Ge}_{15}\text{Sb}_{85}$ are applicable as phase-change materials, which considerably widens the compositional space. Yet, the characterization of oven-annealed thin-film samples of such materials is prone to lead to deviations from the behavior encountered in applications. This is one of the reasons why theoretical methods (density functional theory, molecular dynamics simulations) have been established as an important pillar of material studies. Such calculations provide unrivaled control of environmental and structural parameters.

We now turn to the typical crystal structures of phase-change materials, focusing on the prototype Ge:Sb:Te-materials. The two limiting cases of the pseudobinary line, GeTe and Sb_2Te_3 , are well suited to discuss typical structural features as demonstrated by Da Silva et al. [15, and references therein], see also Fig. 2.2. Let us first consider GeTe. It exhibits a structure that closely resembles the rocksalt-structure, with Ge occupying the cation, and Te the anion sublattice. At temperatures below approximately 700 K, two kinds of distortions deform this lattice. First, there is a displacement of the atomic positions along the $[1\ 1\ 1]$ -direction. This reduces the number of bonds from six to three short (and three weakened, long) ones. This is in line with the Peierls-model of distortions for a system with an average number of p-electrons of three; we will come back to this model in Section 3.3. As a secondary effect, the shift of the atomic positions leads to a small decrease of the cell angle. Altogether, a rhombohedral rather than a cubic cell is obtained ([16] and references therein). Above around 700 K, a second order phase transition lifts the distortion.

Also the structure of Sb_2Te_3 can be understood in terms of a distorted rocksalt-like atomic arrangement. Again, there is an atomic alternation as antimony has only tellurium neighbors in an octahedral environment. However, since there is an excess of Te-atoms, these would need to be arranged in adjacent sites. Instead, well separated layers exhibiting an internal sequence 'Te-Sb-Te-Sb-Te' form, with interlayer bonding being ascribed to Van der Waals-interaction. The spatial separation may be explained by electrostatic repulsion of the anionic Te-atoms. For the further discussion, it will be instructive to view the space between two layers as lattice sites that are occupied by intrinsic vacancies. The internal layer periodicity depends on the Sb to Te-ratio as investigated by x-ray diffraction [17].

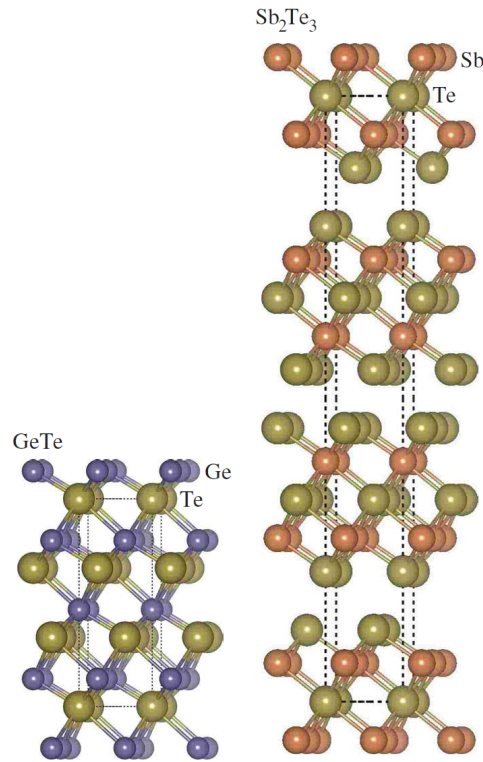


Figure 2.2.: This figure shows the crystal structures of GeTe and Sb_2Te_3 as explained in the text. Phase-change materials inherit the principal structural features of these two border cases. Yet, the situation is more complex for the Ge:Sb:Te -materials, for instance, since they typically exhibit disorder of the cationic sublattice that is occupied by germanium and antimony atoms as well as intrinsic vacancies. From ref. 15.

The Ge:Sb:Te -compounds inherit the aforementioned structure ingredients. In the metastable crystalline phase, they exhibit a rocksalt-like structure with tellurium occupying the anion sublattice. The other, cation sublattice is occupied by germanium, antimony and intrinsic vacancies. Thus, there is atomic alternation and a principal octahedral coordination. The atomic positions exhibit (Peierls-)distortions from the high-symmetry-positions. For compositions close to GeTe , also a rhombohedral distortion of the unit cell is observed [18]. In the following, we shall be concerned with the three structural aspects of sublattice occupation, occurrence of intrinsic vacancies and atomic distortions in more detail.

The occupation of the cation sublattice depends on the thermal history. After (fast) crystallization, typically a random one is obtained (as will be shown below). Density functional theory

calculations have been performed in order to find out whether there is an energetically preferred occupation [15, 19, 20]. The principal finding is that certain layer-sequences are favored, with the layers being orientated normal to the $[1\ 1\ 1]$ -direction. The layer sequence is typically similar to what is found for Sb_2Te_3 ; the germanium-incorporation leads in most cases to the formation of additional 'Te-Ge-Te' sequences within the layer. The initially randomly dispersed vacancies form the vacant space between two layer-stacks. For $\text{Ge}_1\text{Sb}_2\text{Te}_4$, for instance, Da Silva et al. [15] obtain a 'Te-Sb-Te-Ge-Te-Sb-Te'-sequence. Though, an intermixing of Ge and Sb seems energetically not very different and has in fact been obtained for $\text{Ge}_2\text{Sb}_2\text{Te}_5$, where rather than a 'Te-Sb-Te-Ge-Te-Ge-Te-Sb-Te'- a mixed 'Te-Ge/Sb-Te-Ge/Sb-Te-Ge/Sb-Te-Ge/Sb-Te'-sequence is found. It has been argued to arise from a preference of Te-atoms to be surrounded by three Ge and Sb atoms. Without the intermixing, the central Te-layer would be neighbored only by Ge-atoms. Yet, the same authors state that the theoretically most favorable structure is likely not obtained in experiments given the mismatch between optical properties calculated for those structures and measured ones [21]. Very similar layer-sequences are obtained for the stable, hexagonal phases as shown by Kooi and De Hosson [22]. Thus, it is reasonable to assume that the disordered metastable phase exhibits a tendency towards the same stacking sequence by atomic diffusion that is kinetically hampered [23].

Considerable attention has been devoted to the investigation of the large concentration of intrinsic vacancies. Though not limited to phase-change materials, this is a rather unusual crystal feature. It is only noted in the case of insufficient ordering as otherwise the intrinsic vacancies would just form the unsuspecting space between the layers. It has been argued to arise to balance the number of p-electrons per lattice site, $N_p^\square$. The respective count given n_i atoms per formula unit reads

$$N_p^\square = \frac{2n_{\text{Ge}} + 3n_{\text{Sb}} + 4n_{\text{Te}}}{n_{\text{Ge}} + n_{\text{Sb}} + n_{\text{Te}} + n_V} . \quad [2.1]$$

Those compositions along the $\text{GeTe}-\text{Sb}_2\text{Te}_3$ pseudobinary line that form stable phases correspond to a number of three with $n_V = n_{\text{Te}} - (n_{\text{Ge}} + n_{\text{Sb}})$ (i. e., by balancing the mismatch between the number of anions and cations by intrinsic vacancies). For purely structural considerations, this is the concentration of vacancies required to establish the aforementioned layers of intrinsic vacancies. Density functional theory studies have been conducted in order to further investigate the role of intrinsic vacancies. By artificially filling intrinsic vacancy-sites in a randomly occupied cell representing GeSb_2Te_4 with germanium (from a chemical reservoir of elemental germanium), Wuttig et al. [24] found that $\text{Ge}_{1.5}\text{Sb}_2\text{Te}_4$ represents a minimum with respect to energy. They argued that though the electronic states occupied due to the Ge-excess are antibonding, the increase in the number of bonds counteracts and results in an energetic

minimum. Since $\text{Ge}_{1.5}\text{Sb}_2\text{Te}_4$, however, is not observed as a stable phase when cooling a melt, the random occupation might thus affect the stability of a composition. It is important not to confuse intrinsic vacancies, that are electronically inactive, with vacant defect sites. Those play an important role in electrical conductivity and will be addressed in [Section 3.5.3](#) and in the outlook on page 149.

Finally, we shall be concerned with the atomic distortions. While their presence is anticipated from the model of Peierls-distortions ([Section 3.3](#)), their experimental confirmation and magnitude shall be presented here. The simplest approach is to compare the lattice constant of the rocksalt-type structures with the actual bond lengths. These may for instance be obtained from EXAFS measurements [25] or pulsed neutron diffraction data [26]. A split of the six hypothetically equal Ge-Te and Sb-Te bonds (recalling the principal octahedral coordination and atomic alternation) is observed, with distortions ranging around $0.2\text{\AA}$ per atom. Further quantifications have been given by means of computer simulations by various authors [27–30].

In the present thesis, these four fingerprints of the structure (octahedral-like structures with atomic alternation, Peierls-like distortions, intrinsic vacancies and sublattice occupation), their composition-dependence, the impact on the bonding and thus their relevance for the success of phase-change materials are investigated. In addition, their relation to further material properties is discussed. While historically the amorphous phase has been in the focus of material research as it was considered to be the key to phase-change materials, the results in the following chapters emphasize that it is actually a unique bonding situation in the crystalline phase that dominates the functional behavior. Off course, this does not mean that it would be futile to study the amorphous phase; the non-periodic state is characterized by interesting electrical effects that we will turn to later in this chapter. For the understanding of the phase transition kinetics, knowledge about the structure and the energetics of the amorphous phase is indispensable. Thus, the next stop along the phase-change-cycle is the transition from the crystalline to the amorphous phase.

2.2. From the Crystalline to the Amorphous Phase

Let us assume that we start with a crystalline bit, that is ought to be amorphized. According to [Fig. 2.1](#), its temperature needs to be quickly raised above the liquidus temperature T_l in order to melt it. After switching off the heat source, a glassy bit may be formed if quenching proceeds fast enough. This depends on the temperature gradient with respect to the surrounding of the

bit, and thereby the thermal properties of the material itself as well as those of the adjacent materials. How can the glass formation be modeled?

2.2.1. Glass Formation

As a melt is quenched, it becomes increasingly rigid. Once a critical temperature, the glass transition temperature T_g , is passed and given that crystallization has been avoided, the atomic mobilities D become too small for structural rearrangements as required by equilibrium. Thus, the undercooled liquid is 'frozen' in its current structural configuration. The glass transition temperature is commonly defined as the temperature, at which the viscosity equals $1 \cdot 10^{12}$ Pa.s. As mentioned in the beginning, the microscopic atomic mobilities of a liquid can be inversely related to the macroscopic viscosity η via the Stokes-Einstein relation,

$$D(T) \propto T/\eta(T) . \quad [2.2]$$

The resulting glass is out of thermal equilibrium. Thus, a glass is always subject to 'aging' effects, evidencing the relaxation towards equilibrium conditions. Only the timescale of the relaxation may be controlled by temperature.

To assess the ease of glass formation, it is instructive to note that the shape of the area in Fig. 2.1 that refers to crystallization is strongly affected by the temperature-dependence of the viscosity as we will address in detail in Section 2.4. Whether a glass may be formed at small cooling rates (*easy glass former*) or whether this may only be facilitated via rapid quenching (*marginal or bad glass former*) as in the case of phase-change materials, can thus be linked to the viscosity. Equivalently, it also relates to the speed of crystallization. The temperature-dependence of η varies among materials as is shown in Fig. 2.3. If it is Arrhenius-like, a liquid is called *strong*. However, many materials exhibit a behavior empirically described by the Tamann-Vogel-Fulcher ansatz

$$\eta(T) = \eta_0 \cdot \exp(A/(T - T_0)) , \quad [2.3]$$

with η_0 , A and T_0 being constants. Such liquids are referred to as *fragile*. As a measure of the deviation from Arrhenius-behavior, the fragility m is introduced as a steepness-index at T_g via

$$m = \left. \frac{\partial(\log_{10} \eta)}{\partial(T_g/T)} \right|_{T=T_g} . \quad [2.4]$$

A detailed review of these aspects has been given by Angell et al. [31]. Crystallization upon cooling of a strong (undercooled) melt is more likely bypassed even at moderate cooling rates

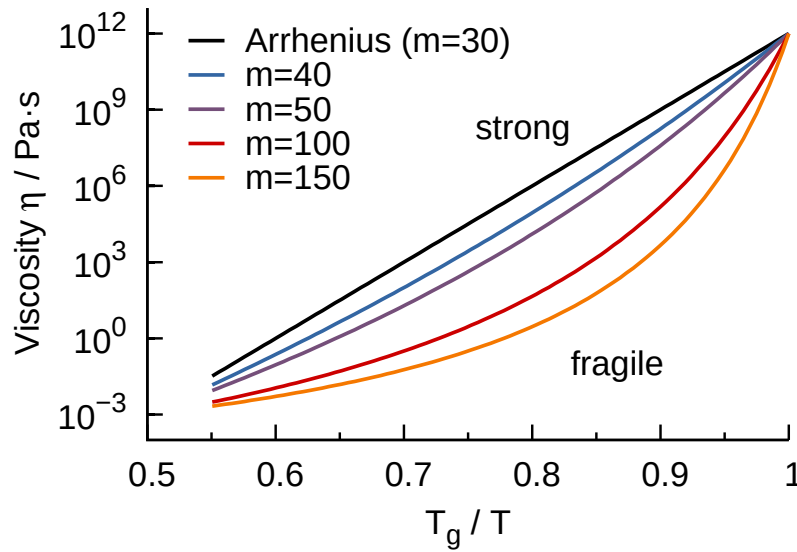


Figure 2.3.: The viscosity of a liquid typically depends exponentially on temperature. If the dependence is Arrhenius-like, it is called a strong liquid. If the dependence at T_g is steeper, the liquid is referred to as fragile. The deviation from Arrhenius-behavior is indicated by the steepness at T_g , the fragility m .

as compared to the case where the melt is a fragile liquid. So a link between fragility and the ease of glass formation can be drawn. For phase-change applications, a rather fragile liquid appears favorable since the crystallization speed would increase with temperature (above T_g) more rapidly. However, the selection of a material with a fragile liquid over one with a strong liquid is, of course, only reasonable if not only the normalized temperature-dependence, but also the absolute values of T_g and the atomic mobility at elevated temperatures are suitable for operation.

The term 'glass' is originally reserved for amorphous solids that are formed by melt-quenching. As will be discussed later, materials may also be amorphous due to certain fabrication conditions or the application of pressure. Generally, the initial configuration might be quite different from that of a melt-quenched sample, possibly also resulting in different properties as these two are compared.

Glass transition temperatures can experimentally be assessed via differential scanning calorimetry since the transition from the glass to an undercooled liquid appears as an endothermic step. Such measurements have shown that for phase-change materials, T_g adopts

values of about 450 K, ranging around half the liquidus temperatures [32]. Empirically, this ratio between T_g and T_l characterizes phase-change materials as marginal glass formers. The glass transition is easily obscured by crystallization, and is for practical reasons often estimated to be equal to the crystallization temperature T_c obtained upon heating with a moderate heating rate.

2.2.2. Glass Rigidity and Bond Constraint Theory

In order to design a phase-change material, it is desirable to have a theory that connects stoichiometry with structure, but also with glass forming ability. Thus, the concept of *bond constraint theory* will be briefly explained. This theory is an approach to characterize the rigidity of an amorphous covalent network, based on the (mean) atomic coordination. In order to fix an object at a given place, three constraints are required. If more are present, the loss of one does not generally lead to the release of this fixation. Less constraints, on the other hand, leave open degrees of freedom, giving room to limited movement (i. e., so-called floppy modes). It is hence reasonable to classify covalent networks such as glasses according to the number of constraints per atom, n_c . An *ideal* glass has a value of three, whereas *floppy* glasses have less and *stressed rigid* glasses more constraints per atom. Moreover, bond constraint theory also provides a link between n_c and the experimentally accessible coordination number, r . Given that in a covalent network the number of bond-stretching constraints equals half the number of bonds and the respective number of bond-bending constraints sums up to $2r - 3$, then the total relationship as proposed by Phillips [33] reads

$$n_c(r) = \frac{5}{2}r - 3 \Leftrightarrow r = \frac{2}{5}(n_c + 3) . \quad [2.5]$$

This implies that in an ideal glass, $n_c = 3$, the average coordination should take the value 2.4. Vice versa, since the average coordination is often characteristic for an atomic species, changing the stoichiometry of a glass allows to modify r and thereby to affect the rigidity of the glass. In this context, it is worth noting the so-called $8 - N$ -rule; with N being the number of valence electrons of an atom, this rule states that generally, the coordination in a covalent environment is equal to $8 - N$. For instance, germanium with its two s- and two p-valence electrons is expected to be four-fold coordinated, while antimony would accordingly adopt a three-fold and tellurium a two-fold coordination. The $8 - N$ -rule successfully explains and predicts the atomic coordination for a wide range of materials composed of elements from the groups V, VI and VII [34]. But as one goes down in germanium's row of the periodic table, the limits of the

8 – N -rule become obvious; elemental lead is not tetrahedrally, but octahedrally coordinated, owing to the fact that due to relativistic effects hybridization becomes unfavorable [35].

To be precise, it has been found that mostly rather than a unique point a so-called intermediate phase exists that separates floppy and stressed rigid glasses. Thus, instead of one there are two rigidity transitions upon variation of r as evidenced by experiments for chalcogenide glasses, with the intermediate phase marking a range of *isostatic* rigidity [36]. Interestingly, a link between rigidity of the glass and the temperature-dependence of the viscosity of the liquid has been discussed. In ref. Micoulaut [37], it has been claimed that both floppy and stressed rigid glasses exhibit fragile liquids, whereas intermediate glasses should exhibit strong liquids.

The complexity of the connections between rigidity, fragility, glass transition and the bond characteristics of a specific material sounds a note of caution when it comes to simplifications. Nevertheless, an intuitive approach to the link between ease of glass formation and glass rigidity shall be provided. The degrees of freedom that are present in a floppy glass (and the ease of thermal excitation of 'floppy modes') are favorable for crystallization, so glass forming ability fades as r tends to small numbers, and T_g decreases. As r increases – coming from the intermediate/ideal glass – T_g should – to a first approximation – become larger, since more thermal energy is required for structural rearrangements as more bonds are formed. Yet, the increase of the number of bonds can be overcompensated by a weakening of the bond strengths, giving rise to a non-monotonous behavior of $T_g(r)$. In addition, the increasing number of bonds becomes hard to form without what is called *bond mismatch*; the bond lengths deviate from the energetic optimum, which increases the energy of the glassy state and thereby also the driving force for crystallization. Consequently, the glass forming ability fades towards the stressed rigid regime [37].

Easy glass formation is thus expected only for ideal/intermediate glasses, that appear to be unfavorable for fast-crystallizing phase-change materials as argued before. Indeed, typical phase-change materials yield, according to the 8 – N -rule, numbers of r between 2.6 and 3.2, locating them in the transition region towards stressed rigid glasses and at the same time should lead to a higher fragility of the liquid. Thus, the application of bond constraint theory provides simple means of *a priori* material selection. However, as mentioned before, the determination of r from simple rules such as the 8 – N -rule can be insufficient. Hence, reliable coordination numbers may only be determined experimentally or by simulation. In both cases, determination of r via integration of a pair distribution function (i. e., counting of bonds based only on atomic distances) requires the selection of a cut-off-radius, which leads to ambiguous results as we will see for the amorphous phase. A successful example of experimental

confirmation of the predictions of bond constraint theory is given by Jovari et al. [38]. Here, $\text{Ge}_{15}\text{Te}_{85}$ was shown by Reverse Monte Carlo analysis of both neutron and x-ray diffraction data to have an average coordination number slightly above 2.4, in line with the expectation according to the $8 - N$ -rule and its easy glass formation ability. Improving the counting of constraints to determine $n_c(r)$ based on r 's derived from EXAFS-data was proposed, but led to the controversial result that $\text{Ge}_2\text{Sb}_2\text{Te}_5$ were also an easy glass former [39], in contradiction to its fast crystallization behavior. The prospects of the conceptual framework of bond constraint theory and rigidity for the study and the design of phase-change materials have recently been further discussed by Micoulaut et al. [40].

Due to the importance of T_g for data retention, a large body of work on phase-change materials is concerned with means of material modifications to increase the value of T_g . In general, a host phase-change material such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ or antimony is chosen for its optical and electrical properties in the amorphous and crystalline phase. Then, the impact of the addition of other elements is investigated. Theoretically, means of (semi-empiric) prediction of T_g have been proposed. For tellurium-based materials for instance, the application of the (modified) Gibbs-DiMarzio equation has been demonstrated to yield a trend for fixed concentrations of Te-content [41]. This approach was originally proposed for chain-like structures such as polymers. It may hence be expected to work only for chalcogenide-rich materials, that retain the chain-like structure of elemental tellurium and selenium, but is not generally applicable to phase-change materials. A more universal model was proposed by Lankhorst [42] (see also ref. 43), that empirically relates T_g to the enthalpy of atomization of an amorphous network. The latter is calculated from the bond enthalpies of all bonds present in the system. It has been successfully applied to resolve the impact of Al- and Cu-doping on the glass transition temperature in Ge:Sb and Sb:Te as has been confirmed by experiment [44]. A complimentary study on Al-doping of Ge:Te was conducted by Katsuyama and Matsumara [45]. Here, it was also shown that a material composed only of Ge:Sb:Te forms a glass only in a relatively small compositional region close to $\text{Ge}_{15}\text{Te}_{85}$ upon liquid N_2 -quenching.

In the framework of bond constraint theory, the observed increase of T_g via the addition of so-called network forming elements, for instance from group IV, to a host phase-change material can be understood by the resulting increase of the average coordination number r . One important aspect not included in bond constraint theory, is the fact that not only the number of bonds, but also the bond energies need to be taken into consideration. Thus, the dependence of T_g on r via stoichiometry variation may deviate from a monotonous increase. That explains the success of the Lankhorst-model since it incorporates both bond numbers and bond energies. This, however, is facilitated at the expense of simplicity as for the bond

energies the atoms participating in each bond need to be explicitly known. Hence, structural information on phase-change materials in the amorphous phase is required. Before we turn to the amorphous phase, another way of amorphizing certain phase-change materials needs to be mentioned.

2.2.3. Pressure-Induced Amorphization

An alternative route to amorphization of Ge:Sb:Te-based phase-change materials has been identified as the application of hydrostatic pressure. Though the necessary pressures are not immediately relevant for applications, respective measurements provide interesting information on the crystalline structure and the phase transition.

For pressures up to about 10 GPa, a decrease of the splitting of Ge-Te bond lengths, that is the strength of atomic distortion, is observed, but the crystallinity is maintained [46]. Kolobov et al. [47] found by x-ray diffraction and absorption fine structure measurements that for the metastable crystalline phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, lattice periodicity ceased in the pressure interval between 10 and 20 GPa. A similar result was subsequently obtained for $\text{Ge}_1\text{Sb}_2\text{Te}_4$ [48]. However, the amorphization pressure is smaller, which is correlated to the fact that the concentration of intrinsic vacancies is higher in $\text{Ge}_1\text{Sb}_2\text{Te}_4$ (12.5%) than in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (10%). In favor of this explanation is the fact that pressure-induced amorphization is only obtained for the metastable crystalline phase in which intrinsic vacancies are randomly distributed. The stable crystalline phase does not show this effect. Further investigation of the temperature-dependence by Krbal et al. [49] does not show an influence up to 145 °C. The amorphization is irreversible upon decompression below 110 °C. The transition from the metastable to the stable phase upon annealing is hindered by pressures exceeding 5 GPa.

Thus, it becomes clear that pressure-induced amorphization depends on the initial structure, and that pressure affects the atomic diffusivity that is necessary for the transition to the stable phase. This is underlined by the study of Krbal et al. [50]. Here, both stable and metastable phase have been exposed to high pressures. The metastable phase was first amorphized, and crystallized again to a bcc-phase above 33 GPa. The stable phase also exhibited a transition to a bcc-phase, but with an important difference; only the bcc-phase formed from the stable phase reverted to the initial phase upon decompression.

While the pressure-induced amorphization was initially argued to mainly involve switching of germanium to tetrahedral positions similar to the so-called umbrella-flip model that will

be addressed later in this chapter, a different explanation was proposed based on a molecular dynamics simulation of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ under pressure. Caravati et al. [51] found that while the fraction of tetrahedral germanium increases with pressure, the absolute value remains small. The mechanism of amorphization was investigated and shown to indeed involve the presence of vacancies; Te-atoms move towards the vacant sites, giving rise to homopolar Ge/Sb bonds in squared rings rotated by 45° with respect to the crystalline axis.

2.3. The Amorphous Phase

Now that we have reached the second of the two phases, its structure shall be presented. Moreover, further details on currently very active fields of research are presented in this section: the electronic structure, threshold switching and the low conductivity drift.

2.3.1. Atomic structure

Since amorphization via melt-quenching relies on a rapid decrease of atomic mobilities, it can be expected that the glass inherits structural features of the liquid. So our first step in the presentation of the amorphous phase shall be structural investigations of the liquid phase. The general result of these studies is that materials successfully employed as phase-change materials are characterized by an octahedral bonding geometry of the atoms, with bond angles ranging around 90 degrees, just as in the crystalline phase. Other materials deviate from this scheme, exhibiting tetrahedral sites with angles in the range of 109.5° as expected for sp^3 -hybridization. Steimer et al. [52] have performed neutron diffraction experiments on a wide range of materials, and found that only phase-change materials exhibited octahedral liquids. Moreover, the average number of valence electrons per atom, $\overline{N}$, was identified as an order parameter, with the octahedral-to-tetrahedral transition occurring at a threshold of about $\overline{N} = 4.25$. Micoulaut et al. [53] noted that also isoelectronic exchange impacts the occurrence of tetrahedral coordination as they changed stoichiometry from SnSe_2 to GeSe_2 [54]. Furthermore, an alternation between atomic species (e. g., ABAB) is observed in phase-change materials, resembling features of the crystalline structures [29]. In summary, these structural fingerprints of phase-change materials are among their key characteristics, and the identification of octahedral or tetrahedral bonding geometries a recurring motif in literature. The reason why the occurrence of octahedral geometries is of interest is the fact that it is rather unexpected according to the $8 - N$ -rule. For germanium, sp^3 -hybridization

may be regarded as the energetically most favorable electronic structure to achieve a four-fold coordination, and unsurprisingly is adopted in elemental germanium. The presence of non-tetrahedrally coordinated germanium in phase-change materials thus is remarkable and clearly caused by its bonding environment.

The structure of the vitrified, amorphous phases of phase-change materials has been a hotly debated topic among phase-change researchers. Conflicting results have been obtained by various groups utilizing different techniques, and the problem, to what extent the experimental results depend on the sample preparation and thermal history, remains unclear as of this writing. In many studies, the use of as deposited-amorphous samples is necessary to yield the required, large amount of amorphous material. Yet, the kinetics of as deposited-amorphous and melt-quenched amorphous phase differ significantly, which must have its origin in structural differences [55].

The atomic structure has been studied primarily by means of x-ray techniques that are sensitive to local atomic environments, e.g., extended x-ray absorption fine structure (EXAFS) measurements, neutron diffraction and molecular dynamics-simulations. With the amorphous phase of phase-change materials generally representing a covalently bonded network, the aim is to reveal the coordination number and the bonding geometry of each atomic species, respectively. This allows to assess the amorphous phase in terms of the previously introduced concepts and aids the understanding of the transition kinetics on an atomistic level.

X-ray reflectometry measurements by Njoroge et al. [56] show that there is a significant decrease of the density upon amorphization. In turn, this leads to plastic deformation or significant strains upon crystallization [57].

From EXAFS measurements on GeTe and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [58], it was found that chemical ordering takes place in the amorphous phase, leaving Te-atoms with germanium (and antimony) neighbors. The Ge-Te bond length was determined to be around 2.6 Å and the coordination number of Ge was derived as four. Since the bonds could not be angular resolved, tetrahedrally coordinated germanium due to sp^3 -hybridization in GeTe_4 -configuration was assumed. The same result was later reported based on EXAFS- and XANES- (x-ray absorption near-edge spectroscopy) measurements [25]. Further experimental support of this model was provided by x-ray fluorescence holography [59], Raman scattering studies [60, 61] and density-functional theory calculations [62].

More detailed structural investigations have focused on resolving limitations of the x-ray-based studies. The combination with neutron diffraction data yields better contrast between

Sb- and Te-atoms, that can hardly be distinguished by x-rays alone. The use of Reverse Monte Carlo method to simultaneously fit all data sets enables the simulation of the amorphous structure in large models, that allow for more than just a few local motifs and can statistically be evaluated. Employing this approach for as deposited-amorphous samples of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeSb_2Te_4 [63, 64], chemical ordering was confirmed. In particular, homopolar Te-Te- and Sb-Sb-bonds were ruled out, while a significant portion of Ge-Sb and Ge-Ge bonds was reported. Those were referred to as 'wrong bonds' as they were not included in the original model. Coordination numbers were found to closely match the $8 - N$ -rule. A predominance of the suggested GeTe_4 -tetrahedra was not obtained, leading the authors to reject approximations of the structure of the amorphous phase using simple local motifs. However, while the bond angle distribution Te-Sb-Te showed a preferentially octahedral environment, the bond angle distribution Te-Ge-Te indicated a mostly tetrahedral environment.

The latter finding is in contrast to the expectation we infer from studies on the liquid phase, that indicate a octahedral structure also for germanium [65], but also to the results of another study of the solid amorphous phase. Kohara et al. [66] performed Reverse Monte Carlo-simulations with synchrotron-radiation x-ray diffraction data for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe. For the former, bond angles around 90 degrees and no homopolar bonds were obtained. Only for GeTe, both the presence of homopolar Ge-Ge-bonds and a deviation in bond angles from 90 degrees coincided. Noteworthy is the analysis of the material topology in terms of *ring statistics*. A ring is defined 'as the shortest closed path through nearest-neighbor atoms with each bond passed only once' [67]. A predominance of even-numbered rings was found in $\text{Ge}_2\text{Sb}_2\text{Te}_5$. This finding is linked to chemical ordering, with an alternation of A (Ge/Sb) and B (Te) atoms in each ring. GeTe, however, exhibited an even distribution of even- and odd-numbered rings in line with the occurrence of homopolar Ge-Ge-bonds.

Due to the obvious differences between structure models derived from experiments alone, various large-scale molecular-dynamics simulations have been performed in recent years, enabling an unprecedented and detailed insight into structure and properties of the amorphous phase of phase-change materials. Materials investigated span the pseudobinary line $(\text{GeTe})_m(\text{Sb}_2\text{Te}_3)_n$ from GeTe [68, 69] over $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ [70] and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [29, 30, 68, 71–74] to Sb_2Te_3 [75].

The general result of these studies is a confirmation of chemical ordering, leading to the occurrence of 4-rings with pronounced AB-alternation. Nevertheless, also a significant number of homopolar bonds as well as Ge-Sb bonds is obtained. Calculated bond-angle-distributions range primarily around 90 degrees. Average coordination numbers suffer from both the ambi-

guity in selecting a cut-off distance as mentioned before, but also average over atoms in different environments. Yet, they tend to be larger than $8 - N$ but smaller than six. Thus, the amorphous structure contains *defective octahedral* sites. In particular, germanium is found to coexist in both defective octahedral and tetrahedral environments, the latter comprising typically one third of the Ge-atoms in $\text{Ge}_2\text{Sb}_2\text{Te}_5$, that at the same time tend to be involved in homopolar (or Ge-Sb) bonds. Along the pseudobinary line, the concentration of tetrahedrally coordinated germanium increases towards GeTe, in line with the results inferred by Kohara et al. [66]. The AB-alternation between Ge with its two p-electrons and Te with four p-electrons, yielding an average of three upon covalent electron sharing, results in the preferentially octahedral rather than tetrahedral sp^3 -like coordination of germanium. Hence, the correlation between the occurrence of tetrahedrally coordinated germanium and deviations from the strict alternation (i. e., homopolar and Ge-Sb-bonds) can be understood in this simple model [74]. One further aspect is the presence of cavities in the amorphous network, that occupy an increasing amount of space as the antimony-concentration is increased. They may thus be regarded as precursors of the intrinsic vacancies found in the crystalline phases.

By constraining the models according to experimental input, the level of agreement between simulation [29, 68] and experiments, namely x-ray photoelectron spectroscopy [76] and high energy x-ray diffraction data [66] could be improved, though the qualitative results on the structure presented before remained the same [73].

It is observed that coordination numbers - despite the ambiguity in defining them - tend to be larger than those derived from the $8 - N$ -rule. A recent approach to define bonds based on a threshold for the localization of charges (measured by the electron localization function) rather than a threshold distance has been proposed by Xu et al. [74]. While the coordination of Te was found to be larger than two, Sb exhibited dominant threefold-coordination. Germanium was obtained in both fourfold-coordinated environments, related to sp^3 -hybridization, and right-angled but only threefold-coordinated structures. Hence, while the coexistence of germanium in tetrahedral and octahedral sites is confirmed, the coordination numbers deviate from both previous reports and the $8 - N$ -rule (if applied per species). They all tend to be close to three, the number inferred from the $8 - N$ -rule upon averaging all species. This method of defining coordination numbers promises to be more precise in obtaining real bond numbers, though again ambiguity in defining a localization threshold remains. In order to link the results on coordination numbers to bond constraint theory, we may conclude that the variance in the published results prevents a unique comparison to the prediction of the $8 - N$ -rule. Nevertheless, as there is a tendency towards higher numbers, phase-change materials are seemingly even more stressed rigid than expected by the $8 - N$ -rule.

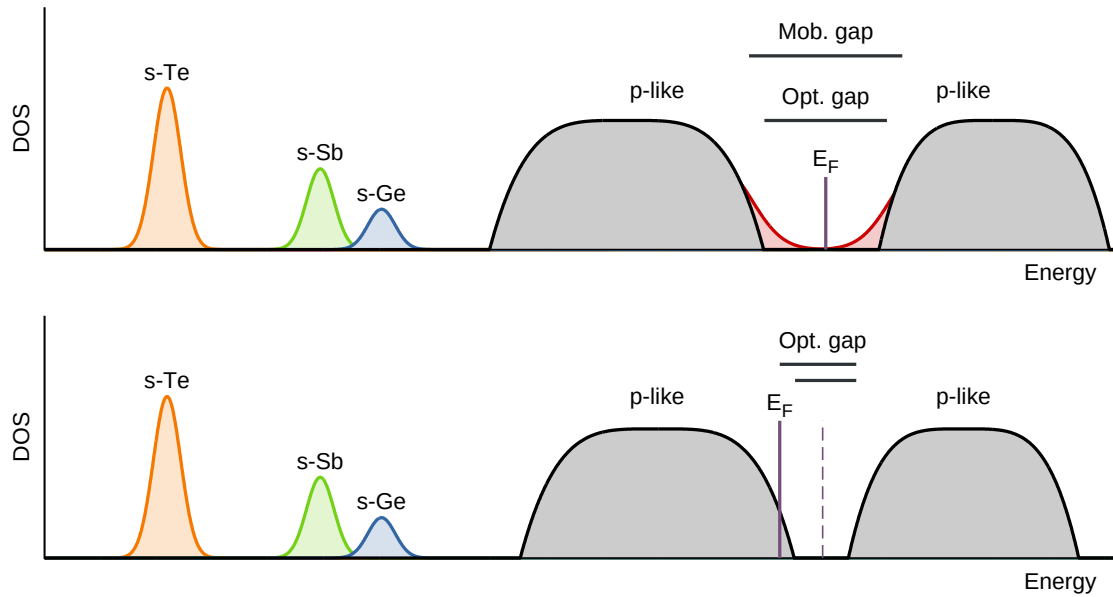


Figure 2.4.: The schematic electronic densities of states of Ge:Sb:Te-materials in the amorphous (top) and crystalline (bottom) phase are compared. The s-states of the atoms are well separated below the p-like states. The latter are broadened and overlap. The optical gap of the amorphous phase is larger than in the crystalline state. Localized states (red) due to band tails (or defects) are found within the mobility gap. The Fermi level is pinned within the optical gap. In the crystalline state, the Fermi level is typically shifted towards or even into the valence band due to the formation of defects. Then, the optical gap exceeds the electronic gap due to the Burstein-Moss-effect.

It has to be recalled that there is no unique amorphous phase, which affects the validity of comparisons between studies on amorphous solids. The extremely rapidly melt-quenched amorphous molecular dynamics-models differ in the concentration of tetrahedrally coordinated germanium, for instance, from as-deposited amorphous samples used for experiments. Also, preparation conditions and structural relaxation are likely to affect such features. Consequently, the uncertainties about the amorphous structure sustain when it comes to the modeling of material properties as the next section shows.

2.3.2. Electronic Structure

The electronic structure of the amorphous phase and the resulting electrical properties are scientifically rich topics that are very important for upcoming electrical applications of phase-change materials. Therefore, we shall take a closer look at these aspects. The electronic density

of states of various Ge:Sb:Te-materials has been investigated experimentally by means of photoemission spectroscopy [76, 77]. The electronic configuration of the constituting atoms is generally such that each atom contributes two s-electrons, that form peaks well below the Fermi level. At around the Fermi level, a broad distribution of the p-like states is obtained, that is split into an occupied and an unoccupied range, separated by a gap. The narrow distribution of the s-like states (i. e., little interaction of the s-states) and the broad superposition of p-like states hints at principal p-bonding in these materials in both phases, that yield very similar results.

The experimental results are well in line with the molecular dynamics simulations presented before, that also yield electronic densities of states of the model systems, though only for those electrons that have explicitly been taken into account (i. e., no core states). The overall similarity in the electronic density of states hints at the general structural similarity between the crystalline and amorphous phase. However, the position of the Fermi-level and the states around it differ significantly, as is visualized in a simplified manner in Fig. 2.4. These states dominate the electrical behavior.

Consequently, the position of the Fermi-level and the presence of defect states within the optical (or the mobility) gap in the amorphous phase have been intensely addressed throughout the course of phase-change material research. Consistently, the Fermi-level is found midgap for the amorphous phase, with sources of evidence involving the aforementioned photoemission spectroscopy and molecular dynamics simulations, surface investigations via scanning tunneling microscopy [78] as well as optical and electrical measurements addressed below. Therefore, a microscopic picture explaining the pinning of the Fermi level is desirable, that can moreover also be related to aspects of electrical conductivity. For chalcogenides, the model of valence alternation pairs (VAP) was proposed (see [79] and references therein). Here, the deviation from two-fold-coordination of chalcogen-atoms 'C', namely threefold-coordination that is unstable against the reaction $2C_3^0 \rightarrow C_3^+ + C_1^-$, creates a pair of acceptor-like and donor-like states, which thus pin the Fermi-level near midgap. Though attempts to apply this scheme to phase-change materials have been performed [80, 81], the presence of VAPs in phase-change materials has been questioned by various authors. Robertson et al. [82] noted that *mean* coordination numbers exceeding two, as shown for phase-change materials, rule out the occurrence of VAPs. MD-simulations by Caravati et al. [30] could neither obtain tellurium-chains nor precursors of the required structures in $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Furthermore, the absence of VAPs was concluded based on the absence of highly charged sites. Midgap-states were obtained only upon fast-quenching, localized at Sb-Te-chains [30].

Experimentally, electron spin resonance (ESR) measurements can illuminate the electronic state of defects. Singly-charged defects with non-zero spin exhibit microwave absorption upon the application of a magnetic field. However, unlike for conventional chalcogen-containing glasses such as As_2Se_3 , no signal for amorphous GeTe and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is found (unless upon significant oxygen incorporation). That leaves the absence of defects, or doubly charged defects as possible explanations. The latter would be indicative of 'negative U'-behavior, that is an overcompensation of Coulomb repulsion of the two carriers by the energy gain by distortion around the defect site [83].

To conclude, phase-change materials deviate from typical chalcogen glasses in their defect properties (VAPs, ESR) owing to the atomic alternation and the resulting overcoordination. No unique defect model for amorphous phase-change materials can be inferred from the literature. In contrast, the absence of characteristic states within the gap such as VAPs is advocated. In that case, one might only distinguish between two kinds of states in amorphous phase-change materials; states at the gap edges exhibit localization, whereas states within the valence (conduction) bands are extended. The two are separated by the so-called mobility edges. This model is of great importance for attempts to relate generic effects in the electrical conductivity to generic electronic (defect) properties.

2.3.3. Electrical Properties

One of the most active areas of research on phase-change materials is the electrical conduction. The motivation is sparked by the need to precisely control this material property in devices. Unlike optical properties, the electrical conductivity is very sensitive to all kinds of intrinsic and extrinsic parameters. It may therefore also serve as a probe of the material physics, though the results are hard to interpret given the variety of (possible) effects that have to be considered.

As a basic result of frequently conducted thin film resistance measurements, the electrical conductivity for small electric fields exhibits a thermally activated transport behavior (at around room temperature),

$$\sigma(T) = \sigma_0 \exp(-E_A^{\text{cond.}}/kT), \quad [2.6]$$

with an activation energy of approximately half the measured optical gap, $E_A^{\text{cond.}} \approx 1/2 E_G^{\text{opt}}$. The exponential temperature-dependence, that might appear as a challenge for applications, does in fact not play a role; the contrast to the crystalline phase remains some orders of magnitude at all temperatures, and is thus always sufficient to distinguish between the two states. Also, as will be discussed below, switching is not facilitated in the low field-regime.

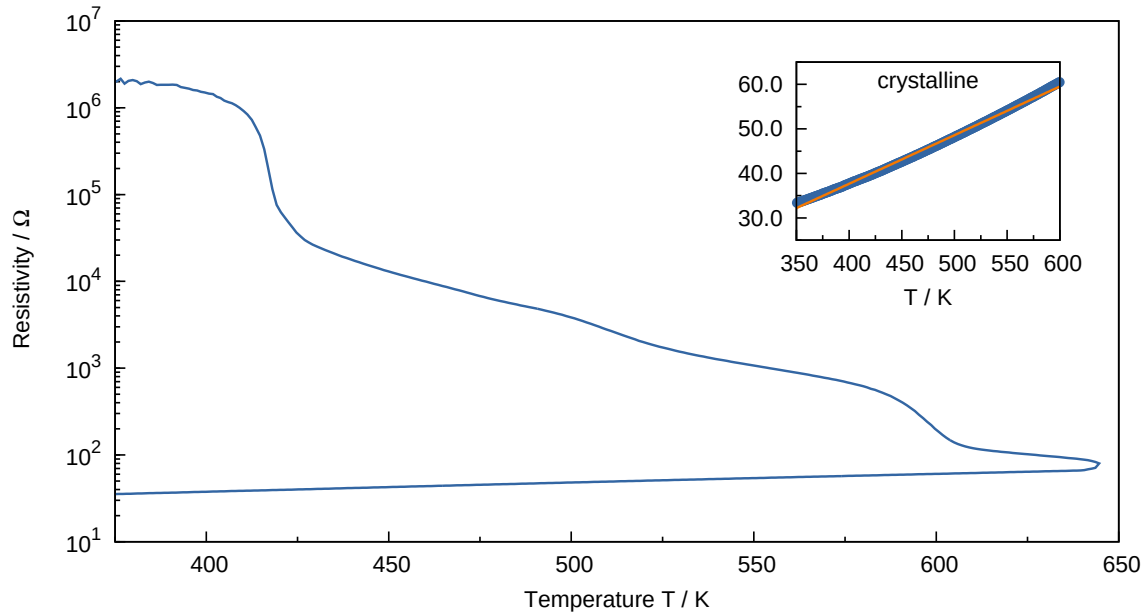


Figure 2.5.: Shown are the phase transitions of a sample of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ measured by the Van der Pauw-method. Crystallization occurs at around 420 K and leads to a significant drop in resistivity. A second irreversible, solid-solid transition is observed at about 600 K, which is identified as the transition from the metastable rocksalt- to the stable hexagonal phase. The charge transport in the amorphous phase is reasonably well described as thermally activated, while the crystalline phase obtained here exhibits a metal-like temperature-dependence (inset), as the linear fit (orange line) proofs. (Data from M. Woda.)

Another fingerprint of the charge carriers and the mechanism of their transport is provided by Hall- and Seebeck-measurements. From these measurements, the majority species of charge carrier (i. e., holes or electrons) can usually be deduced. However, respective measurements on Sb_2Te_3 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ by Baily and Emin [84], Baily et al. [85] between 200 and 300 K yield opposite signs for both techniques. The Seebeck coefficient is large and indicates p-type conductivity. The Hall mobility is very low and anomalously signed (n-type). This is interpreted as indication of conduction via hopping of small polarons (i. e., localized charges that trap themselves by distorting the surrounding atoms). Ielmini and Zhang [86] argue that trap-limited transport is observed in phase-change materials. Such traps can be any kind of localized states close to the extended states, arising for instance as band tails. In this picture, charge transport takes place within extended states, but the mobility is significantly reduced since carriers are easily captured by unoccupied traps. The physical model for this mechanism is Poole-Frenkel conduction.

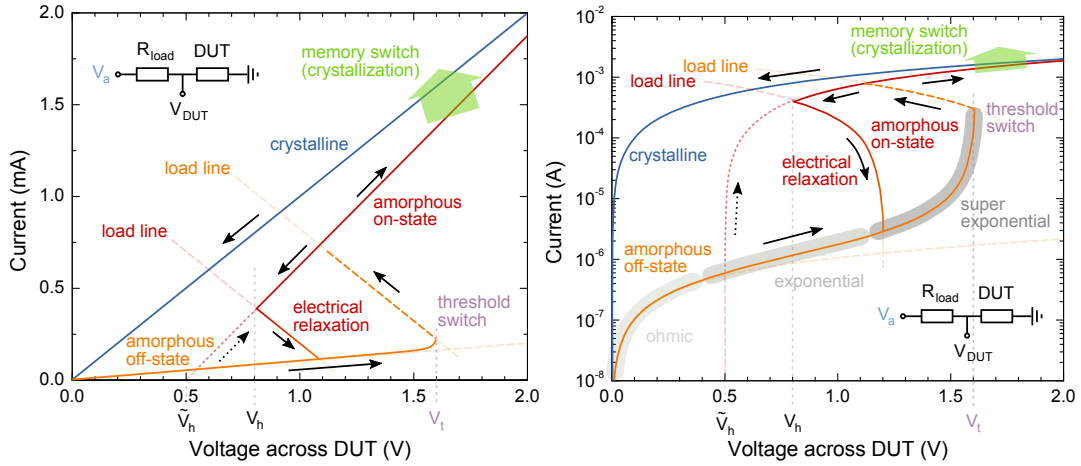


Figure 2.6.: The current-voltage characteristics of phase-change materials (device under test, DUT), shown schematically in both linear (left) and logarithmic scaling (right), exhibit an interesting effect called threshold switching. For small electric fields the curves of the low resistive, crystalline and the high resistive, amorphous phase differ significantly. However, the situation changes if a critical voltage (corresponding to a field strength of some ten V/ μm) is exceeded. The amorphous phase suddenly becomes much more conductive, switching to the so-called ON-state as opposed to the OFF-state. This effect, called threshold switching, enables sufficient joule heating for crystallization (memory switching) at moderate voltages. Further aspects of threshold switching marked in the graphs are discussed in the text. From ref. 87.

The litmus test of all models describing charge transport in amorphous phase-change materials is whether they can account for the behavior at elevated field strength; the electrical conductivity of amorphous phase-change materials exhibits a pronounced dependence on the strength of the applied electric field as shown in Fig. 2.6. Two states can be discerned, the amorphous OFF- and ON-states. Until a critical field is reached, the threshold field E_t (or threshold voltage V_t), the system remains in the OFF-state. Here, the conductivity remains small, and follows first a linear, then an exponential and finally super-exponential behavior. When the field exceeds the threshold value, the conductivity largely increases. In this ON-state, the conductivity shows a linear dependence. From a technical point of view, this behavior is very desirable since crystallization of an amorphous bit is facilitated via Joule-heating. Without the *threshold switching*, large voltages would need to be applied in order to drive a sufficiently large current for heating and thus crystallization to occur. Furthermore, threshold switching can be exploited for selector devices in electrical memories, cf. Section 2.5.2. Threshold switching is to be distinguished from *memory switching* that refers to crystallization, whereas

threshold switching is a phenomenon specific to the amorphous phase and does not involve a phase transition.

Experimentally, only applied voltages rather than fields can be measured, so studies on the threshold fields employing electric testers have concentrated on the determination of voltages. If the geometry of the amorphous volume is known as in the as-deposited amorphous phase, the material-dependent field can be calculated from the voltage. It is typically about some ten V/ μm ([79] and references therein, [88, 89]). This enables threshold switching and thereby the operation of phase-change devices at voltages as small as about 1 V for phase-change cells with a distance between the electrical contacts of about 100 nm.

The discovery of threshold switching for data storage devices dates back to the pioneering work by Ovshinsky [1], and many models have been proposed to account for it ever since. Sophisticated experiments have been designed to probe various aspects of threshold switching. Three of the key characteristics shall be summarized.

1. Threshold switching occurs upon reaching the critical field strength only after a delay time.
2. After the threshold switch, the ON-state is retained unless the field strength drops below a holding field strength E_h .
3. Shortly after the ON-to-OFF transition, an electric field E with $E_h < E < E_t$ is sufficient to recover the ON-state.

Most authors suppose that threshold switching is an electronic (rather than a thermal or structural) effect. Emin [90] concludes that at elevated fields, the density of small polarons becomes larger. Thus, due to their proximity, lattice deformation becomes unfeasible once the threshold field is reached. Therefore, carriers may not localize anymore and the material becomes highly conductive. In the picture of Ielmini and Zhang [91], Ielmini [92] (and references therein), that is Poole-Frenkel conduction, the electric field increases the probability of a carrier that occupies one trap to get to another one nearby. At low fields, this requires extended states. At the threshold field, also direct tunneling becomes possible, leading to the conductivity increase. Another model presumes that threshold switching stems from a field- and carrier density-dependent generation mechanism, thus providing a positive feedback once a critical field is attained. At low fields, however, recombination counterbalances the generation [79, 93, 94]. There are various possible microscopic models that could account for this phenomenological effect such as impact ionization [95].

An alternative to the electronic models of threshold switching is provided by field-induced nucleation [96]. It is argued that at the threshold field, a crystalline filament forms in the amorphous volume, connecting the electrodes. The origin of this effect is ascribed to a field-dependence of the free energy of the system (see also [Section 3.5.2](#)).

A more detailed comparison between these models (and others not presented here) is beyond the scope of this review. The interested reader is referred to the recent, extensive assessment of threshold switching models in the PhD-thesis of Krebs [87].

An issue important for so-called *multi-level storage* is the drift of the amorphous resistivity with time. Multi-level storage aims at increasing storage density by differentiating more than two logical states per cell. This is done by varying the volume of the amorphized part of the cell. However, one finds that the resistivity of an (partially) amorphous cell steadily increases with time. Multi-level storage is only feasible, if this drift is confined to a small resistivity interval associated with one logical state. The increase obeys a power law dependence on time. The process is temperature-activated, it can be accelerated by raising the temperature.

Since progressing crystallization is expected to lead to a drop in resistivity (as the crystalline phase is more conductive), a different mechanism must be responsible. Moreover, since also threshold voltages tend to drift in the same fashion, a common origin of both effects is anticipated. There are multiple candidates to explain the resistance drift effect. At any rate, it is desirable to identify an atomistic model for the structural rearrangement, that obviously occurs in this non-equilibrium phase, and to understand its impact on the material properties that surface in the observed drift. Yet, this topic is still up to debate. Most authors consider a general time and temperature-dependence of the parameters entering [Eq. 2.6](#), in particular of the activation energy [97].

On the one hand, a change in the size of the gap due to stress relief has been discussed. In this universal model, the density difference between amorphous and crystalline state leads to hydrostatic pressure that is exerted on the amorphous volume after quenching. This causes the gap and thus the activation energy to decrease. The recovery of the gap then leads to the observed drift [80]. This model has been further advocated by Karpov et al. [98]. On the other hand, models involving a change in the occurrence of particular electronic states have been proposed. More specifically, the presence of VAPs and an increase in their number, resulting in an increasing resistivity, have been suggested [80, 81]. This, however, is to be contrasted with the unsuccessful search for VAPs in phase-change materials as was discussed in [Section 2.3.2](#). Another model (see ref. 99 and references therein) also aims at localized states at the gap edges, that might arise as tails; charge transport via hopping involving these states is hampered, if

the respective density of states decreases. If the states vanish due to structural relaxation, a decrease in the hopping-conductivity results in a resistance drift. In addition, the position of the Fermi-level may be expected to move towards the middle of the gap, if it had previously been pulled towards one edge by these states.

2.4. Crystallization of an Amorphous Bit

After the discussion of the properties of both the crystalline and the amorphous phase, as well as the process of amorphization in the preceding sections, only the process of crystallization remains to return to the initial point of the phase-change cycle. Commonly, this phase transition is modeled along the lines of the classical theory of crystallization.

2.4.1. Classical Theory of Crystallization

Within this theoretical framework, two mechanisms of crystallization are discernible, nucleation and growth. Nucleation is the process of forming a crystalline nucleus within an amorphous matrix. By growth, the progression of the phase front separating amorphous and crystalline regions is referred to. The driving force for crystallization is the free energy gain. Since an energy barrier separates amorphous and crystalline structures, sufficient thermal energy has to be provided to enable the system to overcome it. Nucleation is typically modeled in a continuum-approximation, neglecting the discrete atomic structure. Then, the formation of a crystalline nucleus involves the formation of an continuous interface. We shall briefly review the modeling of nucleus formation and growth. Detailed information may for instance be obtained from the PhD-thesis of Salinga [100, and references therein].

It is found that the difference in free energy $\Delta G(r)$ for a spherical crystalline cluster of radius r within a liquid (undercooled melt) is

$$\begin{aligned}\Delta G(r) &= V(r) \cdot \Delta G_V + A(r) \cdot \sigma \\ &= \frac{4}{3}\pi r^3 \cdot \Delta G_V + 4\pi r^2 \cdot \sigma ,\end{aligned}\tag{2.7}$$

with V and A being volume and surface of the nucleus, ΔG_V the difference in G between the two phases per unit volume and σ the interfacial energy per unit surface. At the critical radius,

$$r_c = \frac{2\sigma}{|\Delta G_V|} ,\tag{2.8}$$

$\Delta G(r)$ exhibits a maximum. So only nuclei of a sufficient initial size greater than r_c gain energy by growth. Below this critical size, their dissolution is energetically preferred as it removes the interface. According to Becker and Döring, a steady-state distribution of subcritical clusters is formed after an incubation time τ . Recently, Lee et al. [101] proposed fluctuation transmission electron microscopy to experimentally study the evolution of such subcritical nuclei in thin films (here AIST) upon laser irradiation. From the steady-state distribution, a steady-state nucleation rate I_{ss} given by

$$I_{ss} \propto \eta(T)^{-1} \exp\left(-\frac{\Delta G(r_c)}{k_B T}\right) = \eta(T)^{-1} \exp\left(-\frac{16\pi}{3k_B T} \frac{\sigma^3}{(\Delta G_V)^2} \cdot f(\theta)\right) \quad [2.9]$$

is derived. For the moment, we shall neglect the factor $f(\theta)$, thus setting it to unity. Once postcritical crystalline nuclei have been formed, their speed of growth for sizes $r \gg r_c$ is derived in the framework of classical crystallization theory as

$$u(T) = \frac{\partial r}{\partial t} \propto \frac{T}{\eta(T)} \left[1 - \exp\left(-\frac{\Delta G(T)}{k_B T}\right)\right]. \quad [2.10]$$

The temperatures at which nucleation and growth exhibit their respective peak values are not the same, and also one process might generally be more dominant than the other. Hence, nucleation-dominated and growth-dominated crystallization have been observed in the rather large volumes encountered in optical recording, leading to a sub-classification of phase-change materials. In the case of nucleation-dominated crystallization, the time it takes to crystallize an amorphous bit does not depend on its volume to a first approximation. Growth-dominated materials, on the contrary, do exhibit a volume dependence; the smaller the volume, the quicker it is completely crystallized [102]. In general, the sub-classification becomes less helpful for small volumes, where geometry and interfaces play a more important role, increasing the contribution of crystal growth to the transformation.

From this, it is clear that an appropriate description of crystallization kinetics of a phase-change material needs to consider and distinguish between both processes, that – though one might dominate the other – are always simultaneously present. The widely employed Kissinger-analysis does not separate the two and should for this reason be critically reviewed [100].

One can distinguish between three temperature regimes relevant for research on the crystallization kinetics. The first regime is located at around the glass transition temperature. In this temperature interval, crystallization is ought to proceed very slowly. For data retention, a ten years at 80° C-requirement on the stability of a logical state is typically envisaged. Experimentally, the slow crystallization enables the direct observation of nucleation and growth. This has

been demonstrated using high-resolution transmission electron microscopy during annealing of Ge:Sb:Te-films [103, 104]. An alternative approach is the use of atomic force microscopy on isothermally annealed samples [105]. This way, growth velocities of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, Ge_4SbTe_5 and AIST were obtained, they obey an exponential temperature dependence. From this knowledge, data retention at given temperatures may be assessed.

A second temperature regime of interest is situated at around the liquidus temperature. The small driving force for crystallization enables to study the undercooling of droplets employing differential thermal analysis. Here, the maximum undercooling is determined, that is the difference between liquidus temperature and the temperature at which crystallization occurs upon the application of a constant cooling rate. Combined with measurements of the heat of fusion, limits for the interfacial energy σ and the steady-state nucleation rate I_{ss} are derived. From their results, Kalb et al. [106] concluded that steady-state nucleation rates were larger for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and Ge_4SbTe_5 than for $\text{Ge}_{12}\text{Sb}_{88}$ and AIST. This explains why the latter materials belong to the class of growth-dominated materials, whereas the former are nucleation-dominated. The main difference between the two groups was identified in the heat of fusion normalized to the liquidus temperature; the nucleation-dominated materials exhibit smaller values.

The experimentally most challenging yet technologically relevant temperature regime is of course located somewhere between liquidus and glass transition temperature, where crystallization proceeds the fastest. Insight into material characteristics may here be gained by two approaches. On the one hand, materials may just be tested under operation conditions. Either embedded in production-type samples or using specialized equipment to spatially and or temporally resolve the phase transition, the performance of a material and the suitability of the device geometry may directly be investigated. In particular, the minimum crystallization time is assessed this way. Figure 2.7 shows an example of such an optic tester measurement in terms of a power-time-effect diagram. By the variation of pulse length and intensity, different degrees of change in optical reflectivity are obtained. We will be concerned with such experiments for electronic memories in the final section.

On the other hand, information on the physical processes that lead to crystallization can be reconstructed also from the morphology of a crystallized bit [108–110]. In particular transmission electron microscopy as presented by Friedrich et al. [107] – shown in Fig. 2.8 – yield detailed insight into the distribution and shape of crystallites, from which the distribution of nuclei and their growth may be inferred.

So far, we have only considered homogeneous phases. However, the activation energies can be affected by introducing heterogeneities. This is incorporated into the framework of

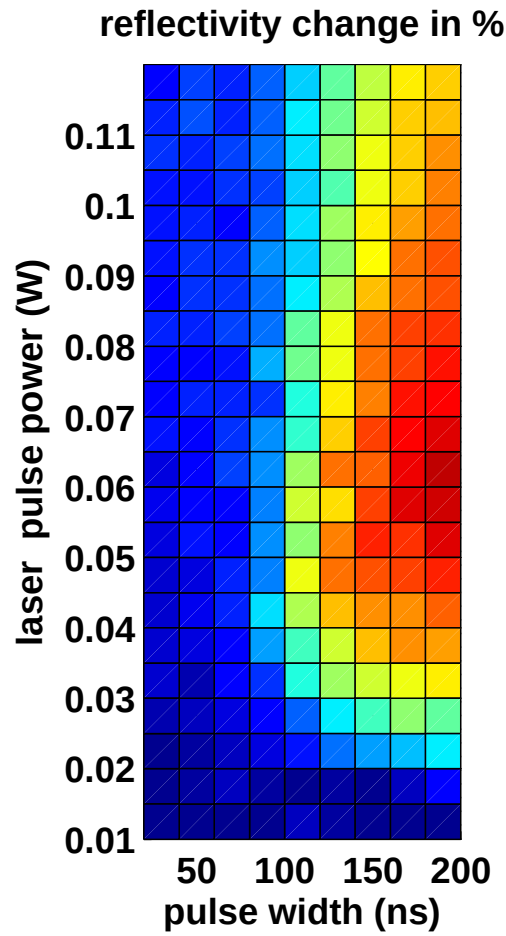


Figure 2.7.: Power-Time-Effect diagram for optical characterization of the crystallization behavior of an as-deposited amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -film deposited on silicon. A laser pulse power of about 50 mW applied for only 150 ns leads to crystallization of the illuminated spot as evidenced by the pronounced change in reflectivity. From ref. 100.

crystallization theory by a factor $f(\theta)$, with θ being the wetting angle. Impurities and interfaces can catalyze nucleation, but also, they can hinder growth. If heterogeneous sites play a dominant role, crystallization shifts from being triggered in the whole volume of the material to the vicinity of these heterogeneous sites. Interfaces are almost inevitable in phase-change recording. In nano-scaled electrical devices, their presence near the active material cannot be avoided. But also homogeneous films of phase-change materials, as employed for optical recording, are strongly affected by interfaces despite their spatial extension. In fact, the choice of the dielectric capping material in optical discs [111, 112] or electrode material in electrical memory cells [113] have been shown to significantly influence the crystallization behavior. The latter

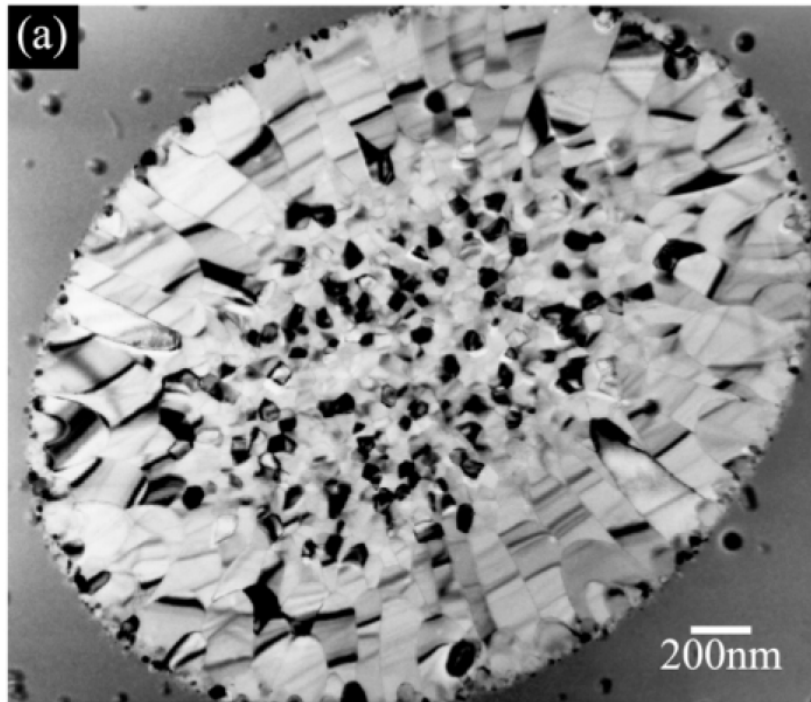


Figure 2.8.: Transmission electron micrograph of a laser-crystallized spot in an as deposited-amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -film. From ref. 107.

work highlights the importance of such considerations in particular for thin films; below a thickness of about 5 nm, crystallization temperatures are dominated by the choice of the interface material.

But not only the materials adjacent to the phase-change material play a role; by amorphization of a bit, a crystalline rim is created since the temperature gradient and thus the cooling rate becomes too small for amorphization at a certain distance from the center of the laser spot or conductive filament, respectively. Hence, the process of growth is typically decisive in electronic phase-change memories, also because no incubation time as for nucleation is involved.

Finally, the actual configuration of the amorphous phase itself has a pronounced impact on the crystallization properties. Particular structural features of an as-deposited amorphous phase, that are not present in a melt-quenched amorphous phase, might vanish for good after the first crystallization, and thus be irrelevant for applications that involve countless numbers of cycles. Various authors have noted that the first crystallization of an as deposited amorphous phase may be very different from re-crystallization of a melt-quenched phase [109, 114–116].

Thus, it becomes clear that one has to be very cautious about the exact experimental conditions and the comparability of experiments that state, for instance, crystallization temperatures.

As mentioned already in [Section 2.2.2](#), tuning the crystallization kinetics by 'doping' (stoichiometry variation) is routinely investigated in the field of phase-change materials. The interested reader is referred to the article of Zhou [117], who reviews the effect of addition of nitrogen or oxygen, for instance, on the crystallization behavior. Notably, two scenarios may be discerned; a nucleation-dominated material may crystallize faster if doped with a certain element. However, the same dopant may impede growth in a growth-dominated material.

So far, we have employed the continuum approximation, neglecting the discrete atomic structure. The energy barrier separating the phases has not been linked to the composition or the microscopic structure. Thus, it is desirable to improve the understanding of the crystallization kinetics by developing and testing atomistic models of the phase transition.

2.4.2. The Umbrella-flip Model

A remarkable, now obsolete model for Ge:Sb:Te-systems was given by Kolobov et al. [25], the so-called umbrella-flip model. It stated that the main structural rearrangement taking place upon crystallization is a flip of germanium from tetrahedral to octahedral sites. Since this model not only gave an intuitive explanation of why the phase transition proceeds so fast, yet involved a change in bonding significant enough to account for the contrast observed, it attracted much attention. A lot of successive studies attempted to test this model.

The extensive theoretical simulations and experimental studies in recent years that have been addressed in [Section 2.3.1](#) show that while tetrahedrally coordinated germanium-atoms are indeed present in the amorphous phase, they represent only a minority, making up only roughly one third of all germanium atoms. Also, they typically involve homopolar Ge-Ge or Ge-Sb bonds ('wrong bonds') rather than only Ge-Te bonds as stated by the umbrella-flip model. Preparation conditions may have significant influence on the concentration of tetrahedral germanium. As for phase-change devices the performance after thousands of switches is of importance, the results obtained from melt-quenched samples appear to be most relevant. Another issue is that this model implicitly requires a certain atomic order or distortion pattern. Otherwise, the coordination of germanium would exceed four upon flipping from the octahedral site [118].

To conclude, the umbrella-flip model turned out not to be a realistic model of the phase transition. Though tetrahedral germanium is indeed present in the amorphous phase, it is not a universal motif. Moreover, this model does not apply to phase-change materials that do not contain germanium.

2.4.3. Evolution of Ring Statistics during the Phase Transition

Though a simple local structural scheme like the umbrella-flip model is appealing, it is unlikely that such a model realistically or universally accounts for the phase transition in phase-change materials. Thus, we might turn to a more statistical, qualitative evaluation of the structural differences. Based on the current state of structure assessments (cf. [Section 2.3.1](#) and [Section 2.1](#)), it is noted that both phases share structural features such as AB-alternation and preferentially octahedral coordination. To a first approximation, the amorphous phase represents a distorted copy of the crystalline phase, but with a lack of mid-range order [66, 68]. This observation is of great importance for the occurrence of contrast between the phases, as we will see in [Chapter 3](#), but also for the kinetics; similar to the line of reasoning in the umbrella-flip model, one might suspect that the rapidness of crystallization stems from the fact that only a small change in structure is required. In fact, the presence of a *metastable* crystalline phase, that only successively orders to eventually transform into the stable phase, shows how little 'medium-ranged' diffusion takes place upon crystallization. The erasure of 'wrong bonds' and the tetrahedral portion of Ge-atoms appears to be the most significant rearrangement, and likely impedes fast crystallization. Nevertheless, apparent structural similarities are not sufficient to assess the kinetics, since also knowledge about the energy barrier along the reaction path is of crucial importance.

The evolution of the amorphous phase upon crystallization can best be described in terms of the ring statistics. As explained before, four-membered rings with ABAB-alternation, resembling the crystalline structure, are obtained in the amorphous phase. Hegedus and Elliott [72] performed molecular dynamics simulations on $\text{Ge}_2\text{Sb}_2\text{Te}_5$, simulating a whole phase change cycle, that is melt-quenching and subsequent re-crystallization. From this, the time-resolved evolution of wrong bonds and near-regular four-fold rings (i. e., near-planar, near-rectangular four-fold rings) was obtained. Indeed, crystallization leads to a decrease in the concentration of wrong bonds. Simultaneously, the concentration in the number of the near-regular four-fold rings increases. In summary, a concise view on the phase transition in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is presented.

The procedure might be applied to other materials to gain further insight into the process of crystallization at an atomistic level.

2.5. Applications employing Phase-Change Materials

The aim of the last part of the present chapter is to give an overview over the various applications that employ phase-change materials, and an outlook on their future development.

2.5.1. Optical Storage

Presently, optical data storage devices represent the most common application of phase-change based recording. With the introduction of blue laser light and maximization of the numerical aperture, the race for higher resolution and hence the development of this field may at first seem exhausted. Room for increasing storage capacity would be left only by increasing the number of data layers per disk. At present, a 100 GB disk employing three data layers marks the upper limit for such data storage devices, paving the way to the fourth generation of commercial optical phase-change based media [119]. However, another way of increasing capacity has been found in the course of phase-change research, that is near-field recording. The so-called Super-RENS effect (super-resolution near-field structure) refers to the observation that structures smaller than the diffraction limit can be fabricated by combining phase-change films with an additional thin layer in optical near-field range [120]. In other words, the part of the optical system that needs to be located very close to the phase-change film to enable near-field recording is incorporated into the disk structure itself. The extra layer typically functions as a dynamic aperture, which should at the same time be small and highly transmissive (aperture-type Super-RENS). Materials successfully employed for these mask layers typically comprise materials related to phase-change materials such as antimony [120, 121], Sb_2Te_3 [122] and PbTe [123] or even phase-change materials themselves [124].

Phenomenologically, it is clear that the laser illumination – or more precisely its intensity profile – must cause an optical inhomogeneity in the mask layer. The effect of super-resolution may be achieved by various types of interaction between matter and light. No consensus on the exact origin of the Super-RENS-effect using the aforementioned materials has been reached yet. Mostly, a predominantly thermal effect is considered. Laser irradiation leads to heating of the resolution-enhancing layer. Since the optical properties of the mask layer

material are temperature-dependent (thermoreflectance) an aperture is created [125]. If even melting occurs at the center of the laser spot (given sufficient laser power), the locally confined change in optical properties is even more pronounced. As a mean to gain information on structure and temperature of the respective portion of the mask layer, Raman scattering has been proposed [126]. Li et al. [127] suggested thermal expansion and the consequent change in light transmission as a possible origin for super-resolution effect. Tominaga et al. [128] argued that Super-RENS might stem from ferroelectric catastrophe in the mask materials. Other authors consider a predominance of electronic effects such as saturable absorption due to band filling by free carriers [124, 129]. Liu and Wei [130] state that the optical non-linear absorption characteristics (here AIST) lead to recording beyond the diffraction limit. Thus, given the variety of proposed explanations, the field of phase-change based near-field recording remains an active research area.

2.5.2. Electronic Storage

When phase-change materials were introduced in 1968 by Ovshinsky [1], electronic memories were among their first suggested applications. Nevertheless, only now that the discovery of fast-switching phase-change materials meets the ability to create nano-scaled structures, it is possible to create competitive, non-volatile phase-change based electronic memories: *phase-change random access memory*, usually abbreviated *PRAM* or *PCRAM*. As can be seen from the PTE-diagram shown in Fig. 2.9, operation can be facilitated on the timescale of few nanoseconds which is orders of magnitude faster than Flash.

Two principle designs of PCRAM cells have been proposed, line-cells and vertical structures, cf. Fig. 2.10. A line-cell is simply a lateral line of a phase-change material that connects two electrodes. Given the occupied area, its use is mainly limited to research projects – favoring the possibility to access the cell from the top – rather than actual memories. Though, some applications may exploit the ease of fabrication and low power consumption of these cells [88]. The other type is a stack of layers, where a thin volume of phase-change is on top of a highly resistive heater element. Here, a portion of the phase-change volume that is close to the heater, that typically features a reduced diameter to increase the current density, is switched between the phases. Recently, an improved version of a PCRAM-cell has been realized that comfortably integrates the cell selector into the cell design [131]. By the use of an Ovonic threshold-switch (OTS) rather than a transistor, a selector with no more than the same spatial footprint as the memory cell itself (i. e., $4F^2$, F being the feature size) is possible. The OTS is just a thin layer

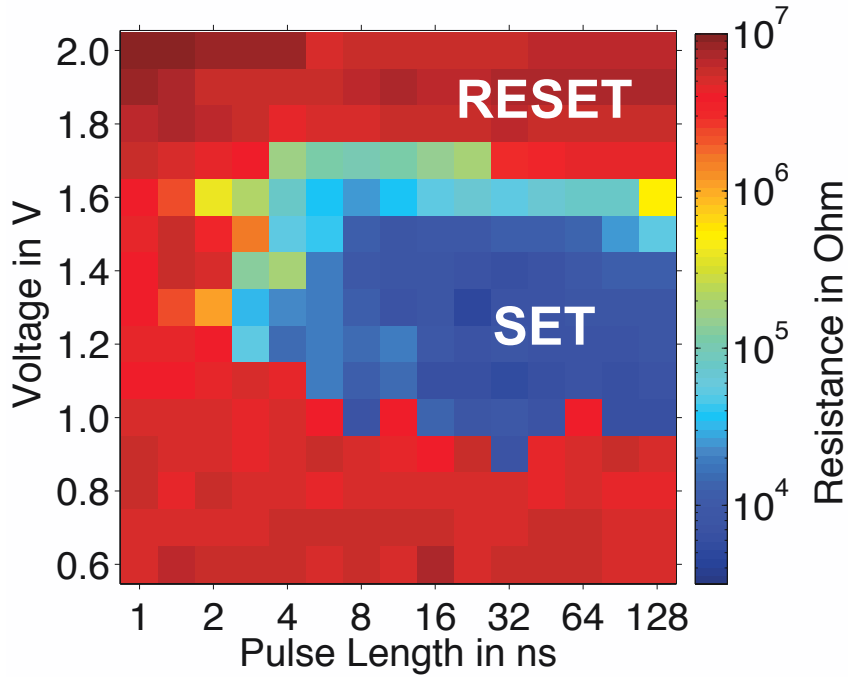


Figure 2.9.: Characterization of a PCRAM-device employing GeTe as the active material using an electric tester (from ref. 102). The visualization adopts the style of the corresponding Power-Time-Effect diagrams from optical experiments using a static tester, cf. Figure 2.7. Here, crystallization, the time-limiting process involved in phase-change recording, can be triggered by applying pulses as short as only about 5 ns.

of a material that exhibits threshold-switching. If the voltage drop over the OTS (due to the voltage applied between word- and bit-line) exceeds the threshold field, the memory cell that is in series with the OTS is selected. The simple design may also allow the stacking of layers of PCRAM-cells, increasing the storage density by making use of the third dimension.

PCRAM makes extensive use of the threshold switching effect presented in Section 2.3.3. In order to supply sufficient Joule heating power $P_J = U \cdot I = U^2/R(U)$ to quickly raise the temperature to levels high enough for crystallization to occur on a small timescale (cf. Fig. 2.6), very high voltages would be required, if threshold switching would not occur. Thus, it allows to avoid voltage upconversion and the problems linked with high voltages in nano-scaled electronics.

Among the criteria for a memory technique to be promising, scalability is a key requirement. It should be possible to exploit the steady improvement in reducing feature sizes in mass production to enable increasing data densities. Lack of scalability is one of the reasons

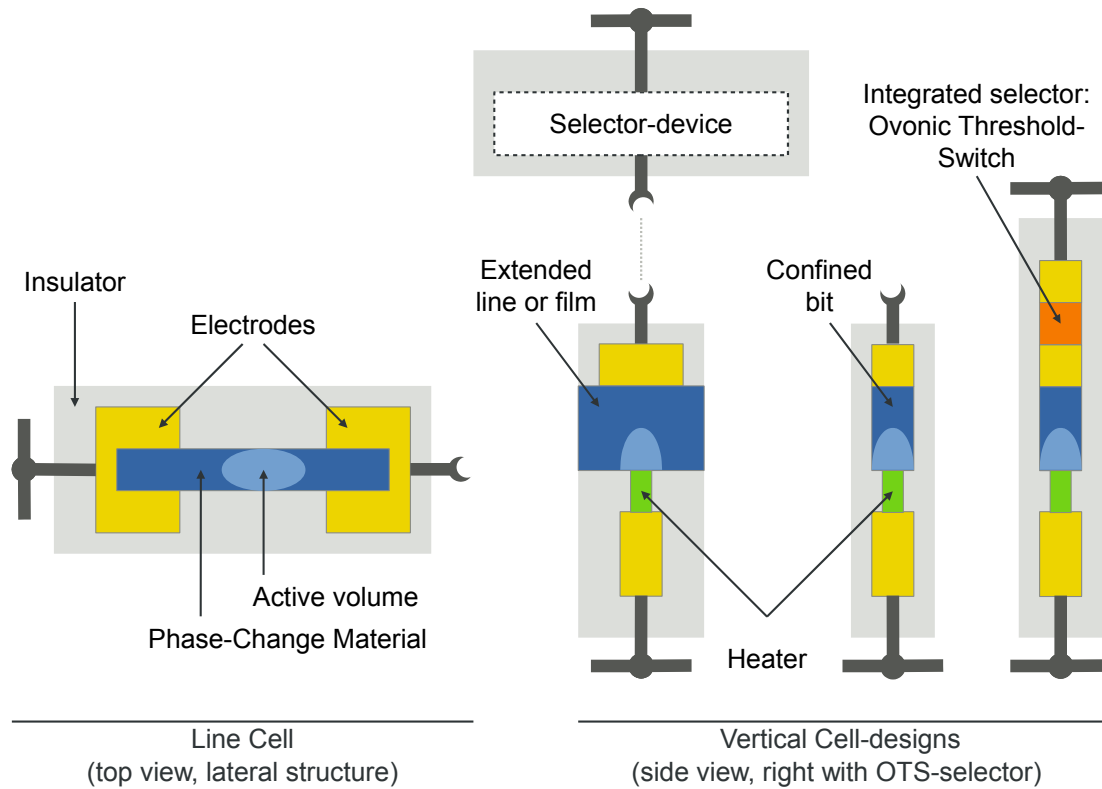


Figure 2.10.: Shown is a comparison of typical designs of phase-change cells. While the lateral design is of particular interest to researchers, the vertical structures have a smaller lateral size and are thus favorable to achieve high storage densities. Here, one may distinguish between two sub-types with extended or confined volumes of a phase-change material. The former employ a thin layer (or line) of a phase-change material, while the latter involve pores in which the active volume more closely matches the actual volume of the material. Though this allows for a better control of the thermal environment of the cell, it also necessitates advanced production techniques that allow for high aspect ratios. Since the cells typically require also some selector devices, their actual spatial footprint is unfavorably enlarged. Thus, the concept shown on the very right is promising, where the selector is integrated into the cell design, not requiring any additional lateral space. It may consist of a material that exhibits threshold-switching and does not change its characteristics – for instance due to crystallization – throughout operation.

why alternatives to Flash memory are actively pursued. Two factors may be discerned when scalability is addressed. On the one hand, the phase-change material must retain its properties despite reduction of its volume. On the other hand, the space taken up by dielectrics and the electronics necessary to address and control the memory cell must also be taken into account. Nano-scaling is particularly advantageous to phase-change memory, since both energy consumption and crystallization time decrease upon volume reduction. The latter stems from the fact that for small memory cells, crystallization dominantly takes place via growth. The impact of nano-scaling on the material and device characteristics has recently been summarized in detail in the work of Raoux et al. [3]. Other aspects that we may subsume under scalability are the aforementioned prospect of stackability as well as multi-level storage via control of the amorphized volume fraction as introduced before.

So far, the advantages of PCRAM over competing memory technologies have been given in terms of its non-volatility, speed and attainable storage density. Another aspect, however, is cyclability (i. e., the number of possible write-cycles). The two main wear processes identified so far are electromigration and void formation. It is found that for cells based on Ge:Sb:Te-materials, the spatial distribution of the elements changes upon set and reset operations. In particular, antimony accumulates at the cathode, pushing germanium aside. Thus, the composition in the active volume and thereby the cell properties change. Operation at reversed polarity, though, can 'repair' such a cell [132]. The density change upon crystallization and atomic mobility may also hamper the electrical contact via void formation [133]. In addition, degradation of the electrodes (e. g., diffusion into the phase-change material) and phase segregation in the case of non-stoichiometric materials may also be regarded as limiting factors. Nevertheless, though the exact number of possible cycles depends on a variety of factors, it is generally expected to exceed the corresponding value of Flash by some orders of magnitude.

2.5.3. Other Applications

Beyond the commercialized optical and electrical memories introduced before, a variety of possible future uses and research opportunities for phase-change materials have been investigated. The concept of probe-based storage sees the use of an array of conductive AFM-tips to parallelly switch bits of a phase-change layer [134]. It combines high resolution (i. e., storage density) with 'simple' media. No costly production of the storage medium itself as it is the case for PCRAM is required. The interest in one-dimensional systems has been adopted by few

phase-change researchers that have successfully synthesized and characterized phase-change nanowires for data storage [135–141].

Other authors seek to combine the reversible amorphous-to-crystalline transition with other material properties or device characteristics, that enable additional degrees of freedom to store or access data; Pandian et al. [142; 143], for example, investigate the possibility of polarity-dependent resistance switching. By employing Sb-excess $\text{Ge}_2\text{Sb}_2\text{Te}_5$ in electrical cells, additional conductive Sb-filaments can be formed or broken. Thus, there is a second mechanism to set the resistivity of a cell. Song et al. [144] incorporated iron into phase-change materials. This way, ferromagnetic, so-called *phase-change magnetic materials* could be obtained. For sufficiently small Fe-concentrations, it was possible to control the magnetization by switching between the phases. This observation was attributed to the difference in carrier concentration between both phases, since the carriers were supposed to provide indirect interaction between Fe-precipitates.

Finally, the fact that the resistivity of a phase-change cell depends on its history (i. e., more than just two logical states can be represented by one cell, multi-level storage) has led to the proposal of using such devices to emulate the behavior of synapses, paving the way for cognitive information processing [145]. In that sense, phase-change based data storage does not only hold the potential to serve as a fast and reliable, universal non-volatile memory. Moreover, this technology could also revolutionize the way we process data.

3. Resonant Bonding and the Design of Phase-Change Materials

In the preceding chapter, the research on phase-change materials in the last decades has extensively been outlined. Fascinating and promising as these materials and their (possible) applications are, a profound understanding of the material physics is desired. Since the properties of the employed phase-change material define the boundaries for any device characteristics such as contrast, speed and scalability, it is of utmost importance to make sure that the most suitable materials are identified. Though detailed information is available for certain prototype materials such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$, it is not clear whether there are more suitable materials that just have not yet been revealed by the extensive trial-and-error studies, or whether material optimization may only proceed via modifications (e. g., doping) of already known materials.

The work presented in this chapter aims at overcoming this situation. As a first step, identification of those properties that are both important and generic to phase-change materials is required. If we succeed in discovering what makes a material suitable for phase-change application and where this property stems from, we may be able to employ this knowledge to design superior materials.

3.1. Generic Optical Properties of Phase-Change Materials

To work out the characteristics, optical experiments on numerous known phase-change materials but also non-phase-change materials were performed. The following section gives a brief summary of these results, while more detailed information may be found in ref. 146 and the PhD-thesis of Kremers [147].

In this study, thin films of the investigated materials were sputter-deposited onto gold-coated glass substrates. They were subsequently characterized by means of *spectroscopic ellipsometry*

and *Fourier transform infrared spectroscopy (FTIR)* in reflection mode. By the combination of these two measurement techniques, the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ could be determined in the energy range from about 0.025 eV to 3 eV. Thus, not only the behavior at the wavelengths of application in rewritable discs was obtained (i. e., CD: 1.59 eV, DVD: 1.91 eV, Blu-Ray: 3.06 eV), but also in the infrared. In particular, this illuminates the energy range at and below the optical gap. All phases, that is as-deposited amorphous, metastable cubic (where applicable) and the stable phase, could be investigated thanks to oven-annealing (for 30 minutes at temperatures about 20 K above the respective transition temperatures in Ar-atmosphere). The atomic structures and densities were monitored simultaneously by means of *x-ray diffraction (XRD)* and *reflectometry (XRR)* measurements.

The resulting spectra were fitted employing a model dielectric function composed as

$$\epsilon(\omega) = \epsilon_{\text{TL}}(\omega) + \epsilon_{\text{const.}} + \epsilon_{\text{Drude}}(\omega) . \quad [3.1]$$

Here, $\epsilon_{\text{TL}}(\omega)$ denotes the dielectric response of the valence- to conduction-band interband transition, which is modeled in terms of a Tauc-Lorentz oscillator [see 147, p. 37ff.]. The dielectric contribution of all other, energetically higher-lying transitions are incorporated by means of a constant, $\epsilon_{\text{const.}}$. For the crystalline phase-change materials, also free carriers were found to contribute to the polarization. They were taken into account by means of a Drude-type response $\epsilon_{\text{Drude}}(\omega)$ [see 147, p. 41ff.]. From this analysis, the dielectric functions of a wide number of materials have been obtained. Here, we shall not be concerned with the results on the Drude-type contribution that is due to defect-induced shifting of the Fermi-level (see Section 3.5). Assuming that the free carrier-contribution does not influence the other dielectric contributions (i. e., the Moss-Burstein effect, that results if the Fermi-level shifts into the valence bands, can be neglected), we shall solely focus on the interband transition.

There are some striking features of the interband transition observed for phase-change materials that are absent in non-phase-change materials. Two instructive examples are shown in Fig. 3.1. If one compares the (as-deposited) amorphous phase with the crystalline phase, there is hardly any difference for non-phase-change materials. For phase-change materials, however, one observes two changes upon crystallization. First, the optical gap G becomes smaller. The decrease amounts to at least 20%. Second, the optical dielectric constant, ϵ^∞ , (i. e., the limit of the real part of the dielectric function for small energies, but above the phonons, cf. Fig. B.2.) is largely enhanced. The increase exceeds 100% for all phase-change materials investigated. How can we understand these changes?

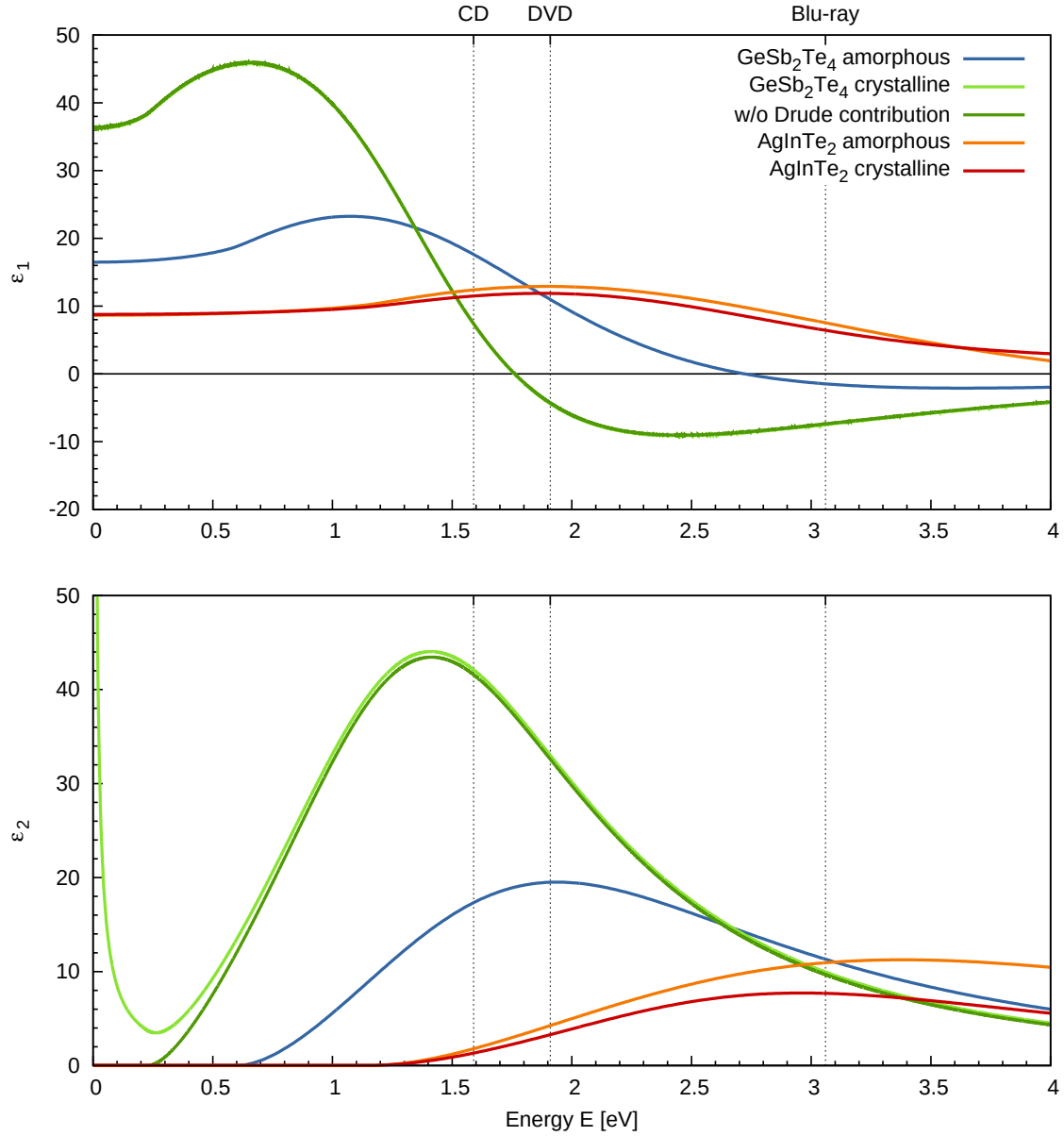


Figure 3.1.: This figure shows the dielectric functions determined for GeSb_2Te_4 , that represents phase-change materials, and AgInTe_2 , that represents non-phase-change materials (despite the fact that it is a chalcogenide). Only for the phase-change materials, remarkable changes upon crystallization are observed; there is a significant decrease of the optical gap accompanied by a pronounced increase of the low-frequency limit of ϵ_1 , that is the optical dielectric constant ϵ^∞ (cf. Fig. B.2).

To supplement the discussion, it is instructive to study the dielectric model of the interband absorption in more detail. Instead of the Tauc-Lorentz oscillator, that was used to fit the data, we shall study a simple Lorentz-oscillator (or Gauss-oscillator), $\epsilon_L(\omega)$. This simplifies the math but retains the physics. The real part of this oscillator reads

$$\epsilon_{L,1}(\omega) \propto S^2 \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} . \quad [3.2]$$

Here, ω_0 represents the position, γ the dampening and S the strength of the oscillator. Its behavior is illustrated in Fig. 3.2. The low-frequency limit of this oscillator is given by

$$\epsilon_L^\infty = \lim_{\omega \rightarrow 0} \epsilon_{L,1}(\omega) \propto \frac{S^2}{\omega_0^2} . \quad [3.3]$$

From this, we see that the increase in ϵ^∞ observed for the phase-change materials is in line with the decrease of the gap that is directly linked to the position of the oscillator. However, if we put in the numbers obtained for GeTe, for example, we see that this effect alone is not sufficient to explain the polarizability enhancement. If we assume $\epsilon_{\text{const.}}$ to be unity, then the relative change in ϵ^∞ is approximately

$$\frac{\epsilon_{\text{cry.}}^\infty - \epsilon_{\text{const.}}}{\epsilon_{\text{amo.}}^\infty - \epsilon_{\text{const.}}} \approx \frac{32}{12} = 2.67 . \quad [3.4]$$

At the same time, the position of the oscillator shifts from $\omega_{\text{amo.},0} \approx 2.0 \text{ eV}$ to $\omega_{\text{cry.},0} \approx 1.5 \text{ eV}$. The squared ratio amounts to 1.78. Yet, this is not enough to account for the total change in the dielectric constant:

$$\frac{\epsilon_{\text{cry.}}^\infty - \epsilon_{\text{const.}}}{\epsilon_{\text{amo.}}^\infty - \epsilon_{\text{const.}}} = \frac{\omega_{\text{cry.},0}^2}{\omega_{\text{amo.},0}^2} \frac{S_{\text{amo.}}^2}{S_{\text{cry.}}^2} \Rightarrow \frac{S_{\text{cry.}}}{S_{\text{amo.}}} = \sqrt{\frac{2.67}{1.78}} = 1.22 . \quad [3.5]$$

Hence, also the oscillator strength increases considerably ($\sim 20\%$) upon crystallization.

We can further resolve the physics behind the polarizability enhancement by mapping the oscillator model used for fitting to the underlying quantum mechanical model of interband transitions as provided by *Fermi's Golden Rule*. To briefly summarize the latter, the transition rate $\Gamma_{i \rightarrow f}$ from an initial electronic state $|i\rangle$ to a final state $|f\rangle$ due to the interaction with a photon $\hbar\omega$ is given by

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} \left[|\langle f | \hat{V} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) - |\langle i | \hat{V} | f \rangle|^2 \delta(E_f - E_i + \hbar\omega) \right] , \quad [3.6]$$

where $\hat{V}$ is the operator of the interaction and E_x the energy of state x . The leading term corresponds to absorption, the second to stimulated emission. In a solid, there is a multitude

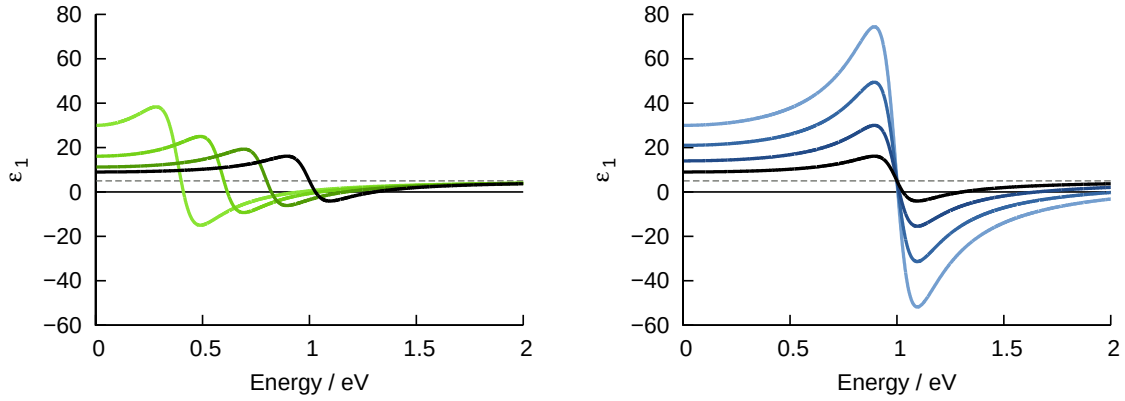


Figure 3.2.: Shown here is the real part of the dielectric function of a Lorentz-oscillator. On the left-hand side, the position of the oscillator is varied while all other parameters are fixed. On the right-hand side, only the oscillator strength is varied. Both a decrease in the size of the gap as well as an increase in the oscillator strength lead to a rapid increase in ϵ^∞ .

of pairs of initial and final states that satisfy the energy conservation requirement. The number of possible transitions given a photon $\hbar\omega$ is measured by the *joint density of states* $g(\hbar\omega)$. The probability of each of these transitions is given by the matrix elements $\langle f|\hat{V}|i\rangle$. Thus, S in the oscillator picture corresponds to the amplitude of the transition matrix elements. The oscillator position and its width (damping) match the distribution of $g(\hbar\omega)$ (weighted by the transition matrix elements). The optical properties of GeTe in terms of Fermi's Golden Rule, that is $g(\hbar\omega)$ and the transition matrix elements, have been obtained from density functional theory-calculations by Welnic et al. [148]. Indeed, as we have already derived from the simple oscillator model, it was found that the optical contrast stems not only from a red-shift of the dominant first peak in the joint density of states (i. e., band gap decrease), but also the increase of the amplitude of the transition matrix elements. Thus, GeTe works as a phase-change material in terms of optical contrast due to these pronounced changes that are absent in other materials.

Based on the results of the optical experiments (i. e., all phase-change materials generically exhibit the behavior just discussed for GeTe), we may now invert this last statement. In order to be a suitable phase-change material for optical applications, a material needs to exhibit a pronounced decrease of its gap and a concurrent increase of the interband transition probability upon crystallization. But what do these changes stem from?

One possible origin could be the density contrast. While the principal bonding would be the same in both phases, the polarizability in the crystalline state would increase due to the increase of the density of polarizable elements (simple Clausius-Mossotti model). The latter

may be the atoms themselves or their bonds. But such an approach has been shown to fail [see 146, p. 84ff.]; given atomic polarizabilities fitted to the amorphous phase, the experimentally determined density change upon crystallization does not lead to an increase in the calculated values of ϵ^∞ by as much as is measured. Consequently, the density contrast itself is not the necessary ingredient for phase-change materials. Instead, a change in the bonding must occur during the phase transition. But what kind of bonding could be present in the crystalline state that leads to extraordinary high polarizabilities? As we shall see in the next section, it is the occurrence of *resonant bonding* that causes this unique feature of phase-change materials.

3.2. Resonant Bonding

Resonant bonding is a component of *valence bond theory* and represents a special case of covalent bonding [149]. According to valence bond theory, a covalent bond between two atoms is formed by the overlap of atomic orbitals that contain one unpaired electron each. Depending on the relative phase of the orbitals, the overlap of the wavefunctions either leads to an accumulation (bonding state) or a reduction (antibonding state) of electrons in the bond region between the nuclei. The bond is denoted ' σ ' if the orbitals point towards each other and ' π ' in the case of parallel orbitals.

In some cases, the number of electrons is insufficient to saturate all bonds that a system forms. This is a well-known phenomenon in chemistry, popular examples being ozone, nitrogen dioxide and benzene. In the latter case, C_6H_6 , the six carbon atoms exhibit sp^2 -hybridization. Each C-atom forms two σ -bonds to neighboring C-atoms and one σ -bond to hydrogen. The bond angles amount to 120° , thus resulting in a ring-structure. The non-hybridized p_z -orbitals are oriented normal to the molecule plane. Their overlap promotes π -bonding. According to the *octet rule*, each C-atom forms four covalent bonds in order to have eight electrons in its surrounding. If one counts the number of valence electrons per C-atom, four, and compares this to the number of σ -bonds, three, we see that there is one electron left for π -bonding. But two electrons would be required to form saturated π -bonds with *both* neighboring C-atoms. Thus, only one double bond ($\sigma + \pi$) per C-atom to either one of its carbon neighbors can be formed. In result, two possible structures result from the requirement of bonds to be saturated, that are energetically equivalent. Hence, these so-called *contributing structures* are in *resonance*. What is obtained experimentally is that unsaturated bonds are formed to both neighbors as a superposition of the contributing structures. As a consequence, the π -electrons are delocalized on the ring. This bonding situation is called resonance bonding [149].

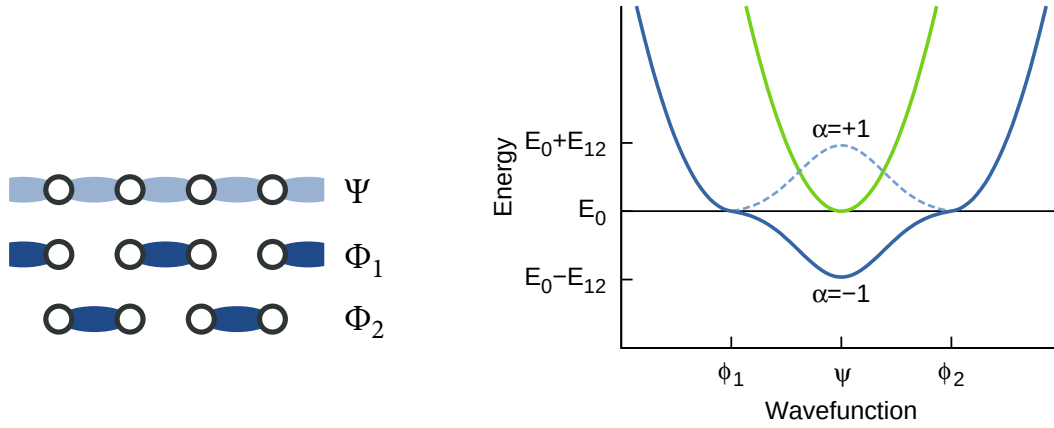


Figure 3.3.: The essence of resonant bonding can be visualized using a simple linear chain of equal atoms (left-hand side). The strength of the shading of the covalent bonds symbolizes their saturation. The electronic wavefunction of the undistorted system Ψ (top) can be expanded in a basis consisting only of saturated bond configurations ϕ_i . The latter are energetically equal due to symmetry, that is 'in resonance'. Consequently, the situation drawn at the top corresponds to an easily disturbed superposition of these states. The sensitivity of the resonant configuration becomes clear if one thinks about the energy associated with changes in the wavefunction due to external perturbations (schematically, right-hand side). For a system that exhibits resonance bonding (blue), there is a shallow minimum around the ground state configuration ($\alpha = -1$). Thus, the resistance of the electronic configuration to perturbations is reduced as compared to a non-resonant system, that is characterized by a steep minimum (green).

To elaborate the importance of this feature for phase-change materials, we shall discuss it in more detail. We employ the model of an infinitely extended, linear chain of equal atoms [150]. The situation is visualized in Fig. 3.3. Given that a suitable basis to expand the electronic wavefunction Ψ consists of saturated bond configurations ϕ_i , then for a linear chain it can be expanded as

$$\Psi = \frac{1}{\sqrt{1 + \alpha^2}} (\phi_1 + \alpha\phi_2) , \quad [3.7]$$

with α being the mixing coefficient. All contributing structures ϕ_i are energetically equivalent due to symmetry,

$$\langle \phi_1 | H | \phi_1 \rangle = \langle \phi_2 | H | \phi_2 \rangle = E_0 , \quad [3.8]$$

that is in resonance. In the ground state, $\alpha = -1$, the total energy is lowered by the resonance energy E_{12} ,

$$E = E_0 - E_{12} \text{ where } E_{12} = \langle \phi_1 | H | \phi_2 \rangle . \quad [3.9]$$

It has been argued in ref. 150 that resonant bonding leads to a pronounced coupling of the electronic configuration to perturbations via changes in α^1 . The competing energies are the resonance energy on the one hand and the energy gain by adoption of the electronic configuration to the perturbation on the other. As opposed to an electronic structure that occurs as a 'unique minimum' in Hilbert space, a resonance structure may be expected to be very sensitive to perturbations as is visualized on the right-hand side of Fig. 3.3.

Given an atomic displacement (phonon) in favor of one contributing structure over the other (such as shown in a different context in Fig. 3.5), the resonance is lifted. The resulting charge redistribution, that is the electron transfer from the elongated, weakened bond to the shortened bond, leads to a polarization. The derivative of the polarization with respect to atomic displacements is measured by the *Born effective charge* Z^* (see Section B.1.2 for details). Also in the case of an external electric field, the charge may easily be redistributed to create a polarization that screens the external field. This is measured by the *optical dielectric constant* ϵ^∞ (see Section B.3 for details). In result, anomalously large values of Born effective charges and (optical) dielectric constants prevail in resonantly bonded materials [35, 150, and references therein].

Thus, resonance bonding in the crystalline state yields the properties that are desired for phase-change materials. If we combine this conclusion with the finding that suitable phase-change materials indeed exhibit both approximately six-fold coordinated structures, but with insufficient numbers of electrons to saturate all bonds (see Tab. 3.1), and the fingerprint-effects of resonance bonding, such as large values of ϵ^∞ as experimentally obtained, the presence of resonant bonding in the crystalline state in these materials is evident. One may conclude that unknowingly, the trial-and-error-search for suitable phase-change materials in the past has in fact been a search for materials that exhibit resonant bonding. This conclusion will find further support by the results of Section 3.4.2.

From these results, several questions arise immediately that will be addressed in the course of this work. *Can we find a recipe for how materials that exhibit resonant bonding can be a priori*

¹Note that in this reference from the 70s, the polarization upon atomic displacements was calculated from the charge distribution within a certain unit cell. The correct way of calculating polarizations in periodic solids, however, has only been presented in 1993 in the seminal work of King-Smith and Vanderbilt [151]. In the so-called *Modern Theory of Polarization*, the polarization needs to be obtained in terms of a geometric phase (*Berry phase*) from the adiabatic polarization currents that occur upon displacing the atoms. Such calculations require the explicit knowledge of the Bloch wavefunctions and their derivatives with respect to their wavevectors $\underline{k}$. For a linear chain, such calculations are discussed in ref. 152.

Table 3.1.: This table compiles valence electron numbers in prototype phase-change materials per atom and – taking intrinsic vacancies in chemically disordered metastable cubic phases or vacancy layers in the ordered phases, respectively, into account – per site. In a six-fold coordinated structure, one p-electron per atom must be present for each bond to be saturated. But here, the number of electrons per atom is too small to saturate all bonds per atom. Approximately, only half the number of electrons required is present (highlighted).

	s+p-electrons		p-electrons		bonds per atom	
	per atom	per site	per atom	per site	without vac.	with vac.
Sb	5	←	3	←	6	6
GeTe	5	←	3	←	6	6
Ge ₂ Sb ₂ Te ₅	5.33	4.80	3.33	3	6	5.33
Ge ₁ Sb ₂ Te ₄	5.43	4.75	3.43	3	6	5.14
Sb ₂ Te ₃	5.60	4.67	3.60	3	6	4.80

identified? What further consequences stem from the occurrence of resonant bonding? Before we may turn to these important considerations, we have to address an important issue that has been left out of the discussion so far. The crystalline phases only approximately exhibit octahedral coordination. In fact, slight local atomic distortions lead to a split into short and long bonds (cf. [Section 2.1](#)). What causes this effect and how does it influence the resonance characteristics?

3.3. Impact of Static Atomic Distortions

Static local atomic distortions counteract the resonance. A static atomic displacement favors certain contributing structures over others and thus, shifts them out of resonance. The stronger the distortion, the less pronounced are the resonance effects as discussed in [Fig. 3.4](#). But what mechanism causes such local distortions? As was briefly mentioned in [Section 2.1](#), Peierls-like distortions are responsible. Therefore, we shall briefly review this model [[153](#)].

To simplify, we again assume a one-dimension chain of equally spaced atoms with a simple parabolic band structure as shown in [Fig. 3.5](#). Depending on the number of electrons per unit

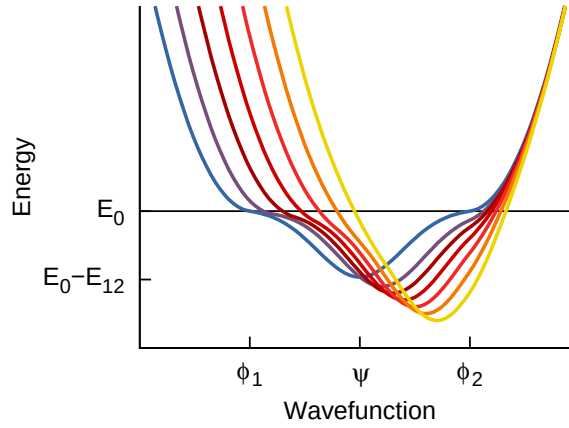


Figure 3.4.: Schematically, an increasing static distortion shifts the energies of the contributing structures out of resonance. Here, a distortion that favors the ϕ_2 -configuration is considered. The ϕ_1 -configuration does not represent a favorable electronic configuration anymore. The minimum shifts and becomes sharper, the electrons are more tightly bonded. In consequence, external perturbations have less effect on the electronic system as rearrangements of the electronic structure become more expensive energy-wise. Thus, the fingerprint-effects of resonance bonding are diminished by increasing distortions.

cell or equivalently, the position of the Fermi wavevector k_F , this chain is unstable against a periodic distortion. Given k_F is located within the Brillouin zone,

$$k_F = \gamma \cdot \frac{G}{2}, \quad \gamma < 1, \quad [3.10]$$

a distortion that introduces a Fourier component of the potential at this wavevector, V_{k_F} , leads to the opening of a gap of size $2|V_{k_F}|$ and thus a decrease of the energy of the occupied states. The Brillouin zone shrinks according to the periodicity of the distortion pattern. With this model, we can understand the coordination of many materials such as elemental antimony, if we assume that each dimension may be treated separately. Then, we have three p-valence electrons per atom out of a maximum of six, one per dimension, which yields $\gamma = 1/2$. Thus, the initially equally long bonds in one dimension (assuming a octahedral structure) split into a short and a long bond. So in three dimensions, we see that elemental antimony results as having three short bonds (in line with the $8 - N$ -rule). The same line of reasoning can be employed for elemental tellurium, yielding two short and four long bonds per atom and reproducing the experimentally obtained zig-zag chain-structure. Yet, there is one degree of freedom per dimension, the relative phase of the distortion, that we could not infer from the preceding arguments [154]. Peierls-like distortions can also prevail in non-crystalline systems.

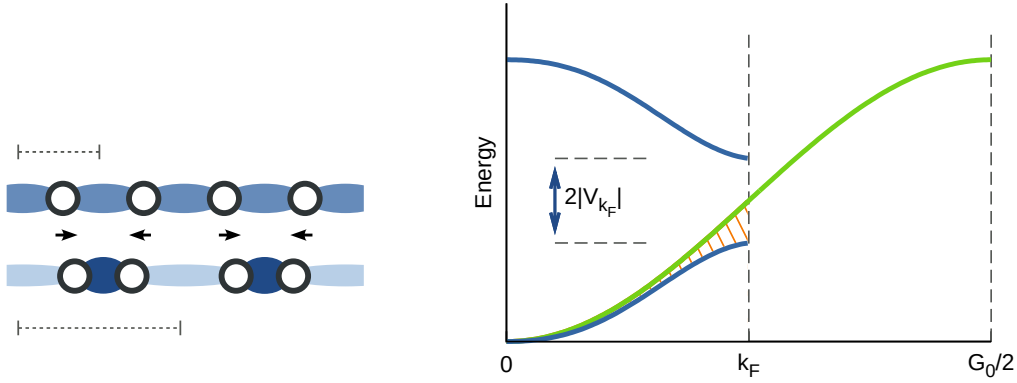


Figure 3.5.: Shown is the model of Peierls-distortions for a one-dimensional chain with a half-filled band. By a (periodic) distortion, the size of the Brillouin zone is reduced and a potential component is introduced. This leads to an opening of a gap and concurrently a decrease in energy for the occupied states (hatched) that is the driving force behind these distortions.

The conceptual translation from a periodic to a local picture can be given by local hybridization of the atoms, thus maximizing the degree of saturation of a few short covalent bonds at the expense of less saturated long bonds. We will study the latter view in more detail in [Section 3.4](#). To summarize, a material that is ought to exhibit strong resonance effects must concurrently exhibit only small distortions. According to the Peierls-model, this is the case if the potential component V_{k_F} is small, or equivalently, if the local hybridization of the atoms is unfavorable.

In order to transpose the discussion from a qualitative to a quantitative level, density functional theory-calculations (see [Appendix A](#) and [Appendix B](#) for an introduction to the method and the physics) on the prototype material GeTe have been performed (published in ref. [16](#)). This material was chosen since it shows resonance effects (large ϵ^∞) and allows to easily vary the level of distortion. At low temperatures, GeTe exhibits a rhombohedral structure (lattice constant a , lattice angle α) with two atoms in the primitive unit cell, see [Fig. 3.6](#). The atomic positions are close to those of sodium chloride, that is $(0, 0, 0)$ and (x, x, x) in reduced coordinates, where $x \approx 0.5$. The aim of the calculations is to monitor the properties affected by the resonance, Z^* and ϵ^∞ , while the system is stepwise distorted from a perfect rocksalt- to the distorted equilibrium-structure. Of course, such an investigation is only feasible theoretically since the distortion parameters are not accessible experimentally. The present results have been obtained through the use of the ABINIT code, a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (<http://www.abinit.org>) [[155–161](#)]. For the calculations, the GGA-PBE exchange- and cor-

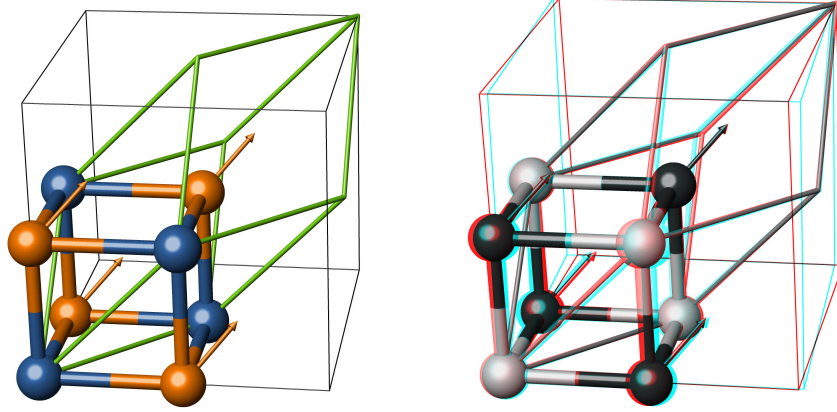
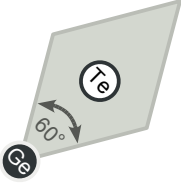
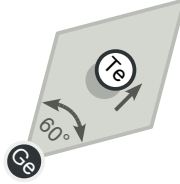
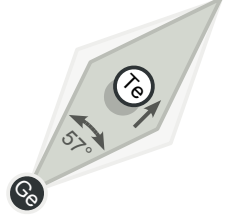


Figure 3.6.: Comparison of the conventional rocksalt-cell, which contains eight atoms, and the primitive unit cell, which contains only the two atoms at (0,0,0) and (0.5,0.5,0.5). The 3D-plot is best viewed online with red-cyan-glasses.

relation functional [162] has been used. The employed pseudopotentials were created by Welnic [163]. A cut-off energy of 20 Ha = 544 eV and a $14 \times 14 \times 14$ - k -point grid have been employed to ensure converged results. Relaxations have been performed such that the remaining forces do not exceed 1×10^{-8} Hartree/Bohr = 5.1×10^{-7} eV/Å and, in case of cell relaxations, stresses remain below 1×10^{-10} Hartree/Bohr³ = 2.95×10^{-6} GPa.

The results of these calculations are compiled in Tab. 3.2. In the undistorted cubic case, where all bonds are equal and only half-saturated, extraordinary high, isotropic values of Z^* and ϵ^∞ are obtained. The atomic distortion, that is the shift along the $[1\ 1\ 1]$ -direction, leads to a split into three short (r_1) and three long bonds (r_2). The energy gain amounts to up to about 17 meV per atom. Expectedly, the monitored tensors exhibit a pronounced reaction to the structural changes. All entries are drastically lowered upon the distortion. Furthermore, the atomic displacement leads to anisotropy so that the entries for the z -direction ($[1\ 1\ 1]$) differ from the others. From our previous discussion, we can easily understand these effects. The split into three short, more saturated and three long, less saturated bonds due to the Peierls-type distortion shifts the corresponding contributing structures out of resonance. Now, the electrons are more tightly bound in the three short bonds. Consequently, they are less polarizable, and in particular the $\epsilon_{3,3}^\infty$ entries become smaller. Equivalently, especially the $Z_{3,3}^*$ are reduced as less charge is removed from the short bond and hence less change in polarization is obtained upon atomic vibrations.

Table 3.2.: The results of the density functional theory-calculations on the impact of distortions on the properties of GeTe are compiled here. On the distortion from a symmetric rocksalt-structure towards the experimentally observed distorted phase, signature quantities of resonant bonding (last two rows) are significantly decreased, but remain anomalously large. Note that all tensors are symmetric and have thus been diagonalized.

	Structures (from left to right)			
	relaxed undistorted cubic	distorted cubic	relaxed distorted cubic	relaxed rhombohedral
				
a [Å]	4.26	←	4.29	4.40
α [deg]	60.0	←	←	57.51
x	0.5	0.524	0.527	0.532
r_1 [Å]	3.01	2.87	2.88	2.85
r_2 [Å]	–	3.16	3.20	3.28
r_2/r_1	1.00	1.10	1.11	1.15
ΔE [meV/atom]	0	–10.0	–11.6	–17.2
Z^* [e]	$\pm \begin{pmatrix} 9.0 & 0.0 & 0.0 \\ 0.0 & 9.0 & 0.0 \\ 0.0 & 0.0 & 9.0 \end{pmatrix}$	$\pm \begin{pmatrix} 6.7 & 0.0 & 0.0 \\ 0.0 & 6.7 & 0.0 \\ 0.0 & 0.0 & 4.3 \end{pmatrix}$	$\pm \begin{pmatrix} 6.4 & 0.0 & 0.0 \\ 0.0 & 6.4 & 0.0 \\ 0.0 & 0.0 & 4.0 \end{pmatrix}$	$\pm \begin{pmatrix} 5.2 & 0.0 & 0.0 \\ 0.0 & 5.2 & 0.0 \\ 0.0 & 0.0 & 3.0 \end{pmatrix}$
ϵ^∞	$\begin{pmatrix} 74.7 & 0.0 & 0.0 \\ 0.0 & 74.7 & 0.0 \\ 0.0 & 0.0 & 74.7 \end{pmatrix}$	$\begin{pmatrix} 53.1 & 0.0 & 0.0 \\ 0.0 & 53.1 & 0.0 \\ 0.0 & 0.0 & 45.9 \end{pmatrix}$	$\begin{pmatrix} 49.2 & 0.0 & 0.0 \\ 0.0 & 49.2 & 0.0 \\ 0.0 & 0.0 & 40.8 \end{pmatrix}$	$\begin{pmatrix} 40.9 & 0.0 & 0.0 \\ 0.0 & 40.9 & 0.0 \\ 0.0 & 0.0 & 34.3 \end{pmatrix}$

Beyond this qualitative result, the numbers show that for GeTe, the resonance effects are not completely removed by the distortion. Instead, Z^* and ϵ^∞ remain anomalously large despite the fact that in equilibrium the short and long bond lengths differ by as much as 0.4 Å. The spatially averaged value of ϵ^∞ , 38.7, agrees well with the experimental result of 33.2 on the polycrystalline thin-film sample (Section 3.1 or ref. 146, respectively).

The occurrence of resonant bonding is not immediately visible just from inspecting the electronic density of states, but as a pronounced response of the system to perturbations. Nevertheless, the distortions also have an impact on the band structure. As we have seen in the simple model of the Peierls-distortion, the stronger the distortion of the resonant system, the larger the gap gets. To study these aspects for GeTe, the calculated (projected) electronic densities of state (DOS) and the corresponding band structures are shown in Fig. 3.7 and Fig. 3.8. These results show that – in agreement with the experimental observation – GeTe is a narrow gap semiconductor². The projected DOS shows that the s-like states of germanium and tellurium are relatively sharp and separated from the p-like states. The latter are broadly located around the Fermi-level. Hence, the system is dominantly p-bonded, which results in unsaturated bonds as we have discussed in Tab. 3.1. Upon the distortion, states are moved away from the original gap³, in line with the Peierls-model. Those shifts can be associated with changes at around the L-point (0.5, 0, 0). In summary, we find that resonant bonding is endangered by Peierls-like local distortions. These distortions lead to an increase of the gap and a decrease of the signature-effects of resonance bonding.

Now we are also in the position to understand why resonance effects are limited to the crystalline phase. To a first approximation, the amorphous phase differs from the crystalline phase by two effects (see Section 2.3). On the one hand, it features a fraction of atoms in different local environments, where saturated covalent bonds are formed (e. g., tetrahedrally-coordinated germanium). On the other hand, those regions that resemble the crystalline structure, that is where atoms are involved in ABAB-rings, do not feature the required structural medium-range order. The strong, varying distortions of the atoms from octahedral coordination open the gap and diminish the resonance effects. This is confirmed by the work of Welnic et al. [148], which we have addressed before, and recently by Huang and Robertson [164]. They argue that structures that support resonant bonding, in particular the crystalline structure of phase-change materials, lead to small gaps and large transition matrix elements $|\langle f|\hat{V}|i\rangle|^2$,

²Though, gaps are systematically underestimated in density functional theory-calculations.

³Note that a gap exists even in the undistorted case due to the ionic contribution to the bonding.

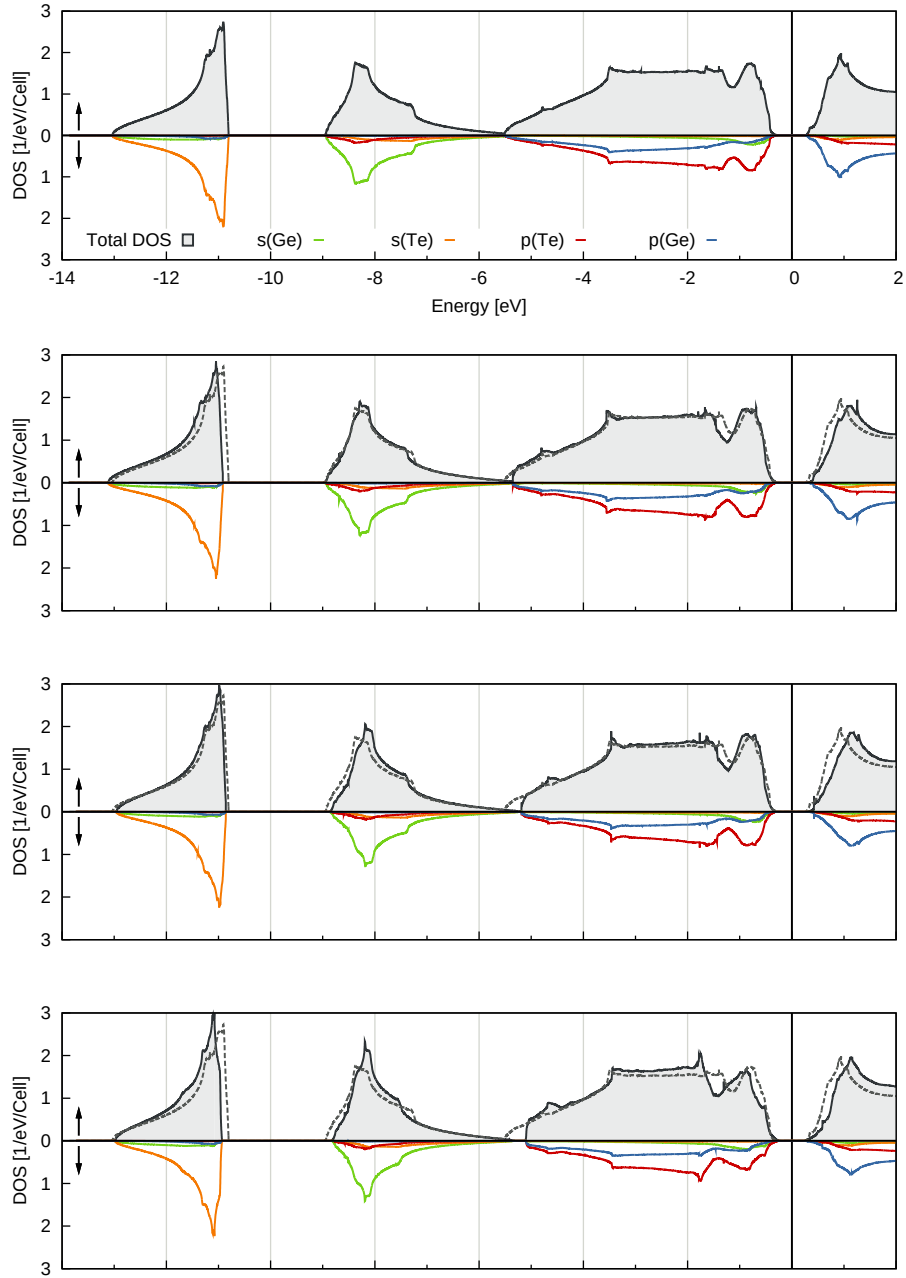


Figure 3.7.: Here, the (projected) electronic density of states (DOS) of GeTe for each of the four levels of distortion considered in Tab. 3.2 (top to bottom) are plotted. The dashed lines indicate the total DOS of the undistorted case. The distortion reduces the number of states at the gap. The respective bandstructures are shown in Fig. 3.8.

while other structures (orthorhombic GeS-type structure, spinel, ...), in particular those that resemble the amorphous case, do not. Both references employ geometric arguments to explain the enhancement of the transition matrix elements in the structures that are close to resonance. To a first approximation, large values of $|\langle f|\hat{V}|i\rangle|^2$ require significant overlap of the states, that is $|\langle f|i\rangle|^2$. In octahedrally coordinated resonance structures, the p-orbitals are aligned, which causes large overlap integrals. In the other structures, in particular distorted ones, the misalignment of the p-orbitals reduces the overlap and thus the transition matrix elements.

To summarize, it has been shown that resonant bonding, a peculiar type of covalent bonding, prevails in crystalline phase-change materials. Consequently, the crystalline phase exhibits some unique properties. Narrow optical gaps and large transition matrix elements (or oscillator strengths) occur concurrently with extraordinary large optical dielectric constants and values of Born effective charges. Thus, it is the crystalline phase that is key to (at least) the optical contrast of phase-change materials. Now that we have unraveled these aspects, we may employ this insight to design phase-change materials.

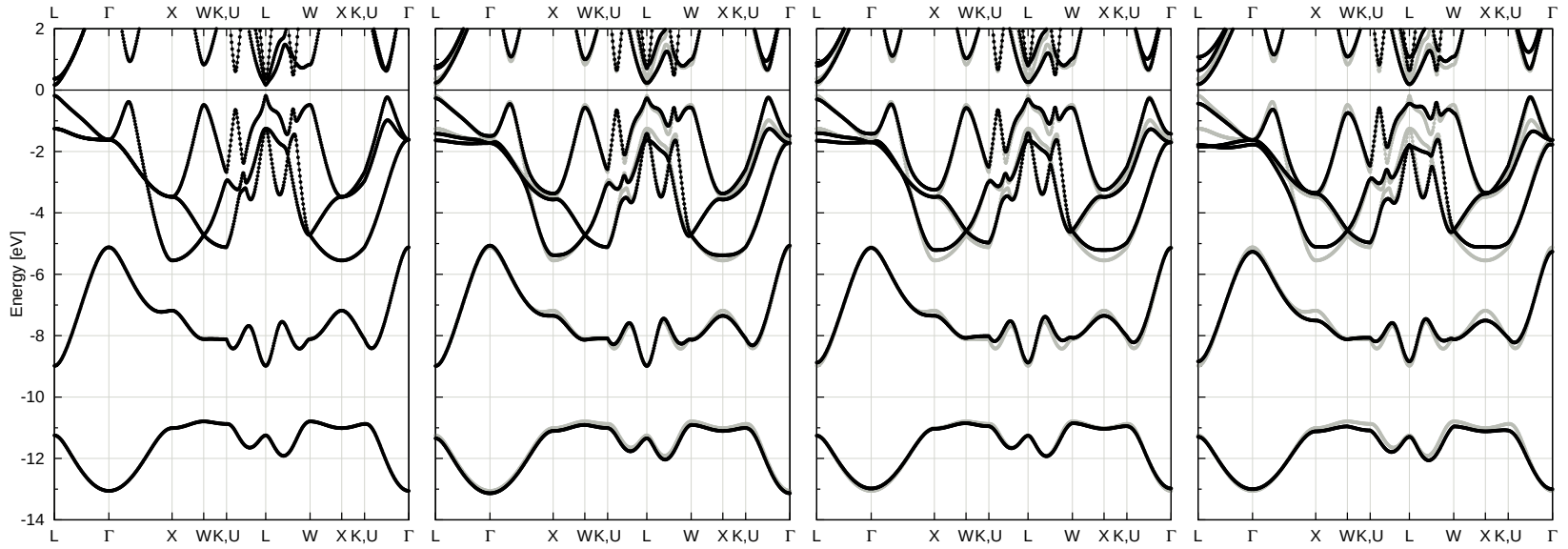


Figure 3.8.: These viewgraphs show the band structure of GeTe as the level of distortion is increased from left to right, cf. [Tab. 3.2](#). The shaded lines correspond to the undistorted cubic case. The respective densities of states are shown in [Fig. 3.7](#). The paths through reciprocal space are (in reduced coordinates): $(1/2, 0, 0)$ (L) $\rightarrow$ $(0, 0, 0)$ (Γ) $\rightarrow$ $(0, 1/2, 1/2)$ (X) $\rightarrow$ $(1/4, 1/2, 3/4)$ (W) $\rightarrow$ $(3/8, 3/8, 3/4)$ (K,U) $\rightarrow$ $(1/2, 0, 0)$ (L) $\rightarrow$ $(1/4, 1/2, 3/4)$ (W) $\rightarrow$ $(1/2, 1/2, 1)$ (X) $\rightarrow$ $(3/8, 3/8, 3/4)$ (K,U) $\rightarrow$ $(0, 0, 0)$ (Γ)

3.4. A Map for Phase-Change Materials

After we have identified the occurrence of resonant bonding as a generic feature of and key requirement for phase-change materials in the preceding sections, naturally the question arises: what materials exhibit resonant bonding? Parts of the answer are immediately clear; just by counting the average number of valence electrons per atom, it is clear that for materials with on average three p-electrons per atom, six-fold coordinated structures would lead to unsaturated covalent bonds and hence, resonance conditions. Generally, materials with on average less electrons may favor sp^3 -hybridization, leading to less, but saturated bonds, while materials with more electrons might as well encounter resonance conditions. This is in line with the work of Luo and Wuttig [165], where a critical value of the average valence electron number of about 4.1 was identified; tellurides with less electrons were found to adopt tetrahedral-like structures (chalcopyrite), while materials with more electrons formed octahedral-like structures (rocksalt). Yet, this still leaves us with countless possible material systems and no clear search scheme. What defines boundaries for materials that adopt covalent, octahedral structures that are close to resonance conditions? In other words: *What materials exhibit resonant bonding with little distortions?* This section will be concerned with finding an answer (published in ref. 16). Valuable input comes from work done in the 1960s to 1980s on so-called structure maps.

3.4.1. The Concept of Structure Maps

In the middle of the last century, the field of solid-state physics grew rapidly thanks to various cumulating developments. On the one hand, the theoretical understanding of matter on the basis of quantum theory prospered tremendously. Even listing the achievements would go far beyond the scope of this thesis. On the other hand, more and more material systems could be characterized, thus creating a rich database that enabled the search for compositional trends. This inspired researchers to develop classification schemes for materials. The aim was to assess the bonding and resulting physical properties of materials, preferentially based only on the knowledge of the atomic composition.

A first step in this direction was the structure map proposed by Phillips and Van Vechten [166–170]. For the family of semiconducting/insulating $A^N B^{8-N}$ -materials, that is materials with four valence electrons per atom, it is shown in Fig. 3.9. The map is spanned by two coordinates,

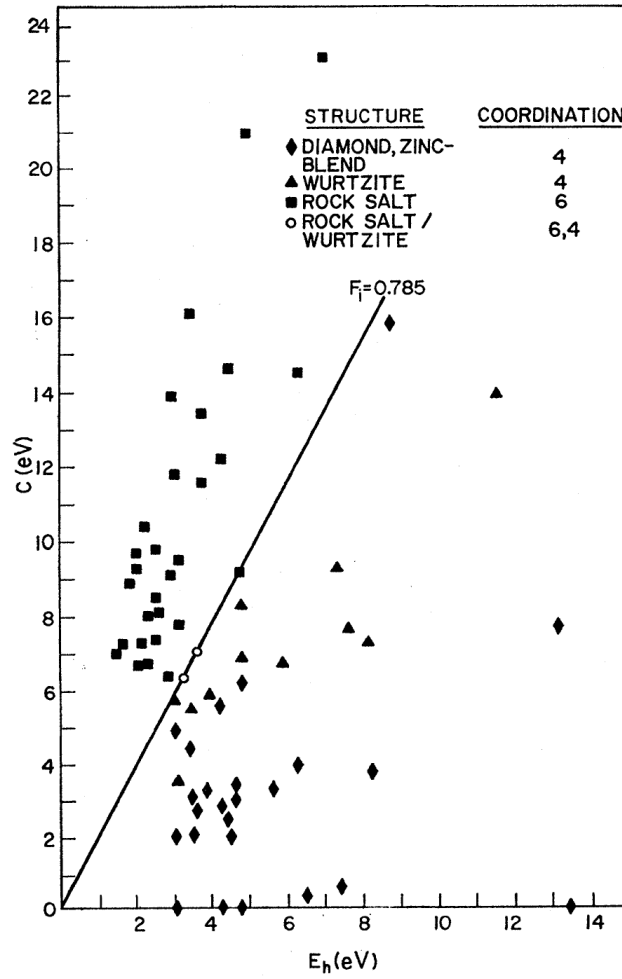


Figure 3.9.: Shown here is the map of Phillips and Van Vechten for $A^N B^{8-N}$ -materials. A critical ionicity indicated by a line separates four-fold-coordinated and six-fold-coordinated structures. From ref. 166.

C and E_h . These coordinates are supposed to represent an ionic and a covalent contribution to the gap, respectively. Thus, in this model the optical gap G results as

$$G = \sqrt{C^2 + E_h^2} . \quad [3.11]$$

The remarkable result is the fact that by virtue of these two coordinates, materials with different crystal structures can be distinguished. The map in Fig. 3.9 clearly separates between materials with six-fold and four-fold coordinated structures. The two regions are separated by a critical value of the ionicity of the bonding, that is the ratio

$$F_{\text{ion.}} = C^2 / G^2 . \quad [3.12]$$

This threshold amounts to ~ 0.785 . Hence, one can apply this map to empirically predict the properties of a material. If the coordinates of a material locate it in a region where six-fold coordination occurs, it is very likely that also this new material will exhibit such a structure. Clearly, such a scheme could be very helpful for the design of phase-change materials. The present scheme, however, has some disadvantages. First, it works only for materials with on average less electrons per atom, four, than we have in phase-change materials, about five. Second, the determination of the coordinates relies on spectroscopic input, that is a measurement of the gap, as well as some approximations (that will not be further discussed here). Thus, it is not '*a priori*'. To conclude, a structure map for phase-change materials would be very desirable, but the coordinates of Phillips and Van Vechten do not suit our case. Nevertheless, further developments can be found in literature that will help us to obtain such a scheme for our materials.

The scheme that shall be presented is based on the work of Simons and Bloch [172] and St.John and Bloch [171]. These authors have developed so-called *Pauli-force model potentials* for a wide range of atoms. From these, the radial maxima of the valence eigenfunctions, that is orbital radii r_s and r_p for s- and p-orbital, respectively, have been obtained. The most important contribution of these authors, though, is the study of 'structure factors'. They showed that certain combinations of these radii yield information classically interpreted as electronegativity and the promotion energy for s-p-hybridization. Hence, such functions of the radii hold the potential to serve as coordinates of structure maps. The corresponding results of these authors are shown in Fig. 3.10. The coordinates for elements (top) and $A^N B^{8-N}$ -materials (bottom), expressed in terms of r_l or $X_l \equiv 1/r_l$, clearly separate regions of different structures. This result has two important implications. On the one hand, the coordinates are based solely on the orbital radii. Thus, a classification scheme based on such coordinates is '*a priori*'. On the other hand, the success in distinguishing $A^N B^{8-N}$ -materials *and* elements indicates that similar coordinates can be constructed to apply this scheme not only to materials with on the average four valence electrons. Indeed, successful translations to families composed as $A^N B^{P-N}$, $P = 2 \dots 6$ have been given in the past [see 173, and references therein]. Most interesting for us is the work by Littlewood [154, 174, 175], who has studied the case for $P = 10$ (i. e., materials with on average five valence electrons).

In the spirit of the orbital radii models developed by Simons, St.John and Bloch, the map developed by Littlewood is spanned by two radii-based coordinates. They are defined as

$$r_{\pi}^{-1} = \left[(r_p^A - r_s^A) + (r_p^B - r_s^B) \right]^{-1}, \quad [3.13]$$

$$r_{\sigma}' = r_p^A - r_p^B. \quad [3.14]$$

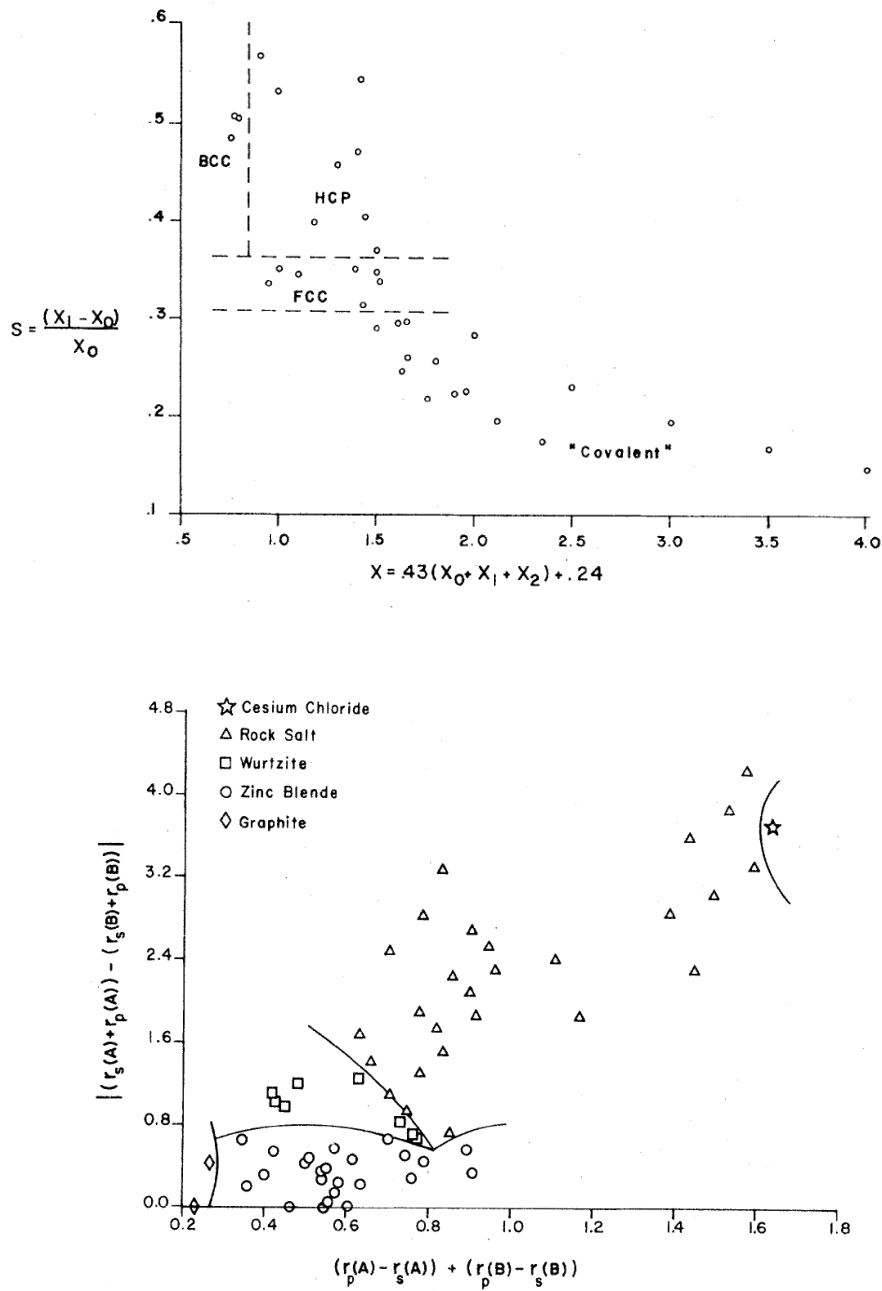


Figure 3.10.: In the top graph, elements are plotted in a map, proving that certain functions of the orbital radii, that serve as coordinates, allow the separation of structures. The bottom graph transfers this approach to $A^N B^{8-N}$ -materials. Again, different structures are clearly separated into different regions of this map. Thus, orbital radii allow for a priori material characterization. From ref. [171](#).

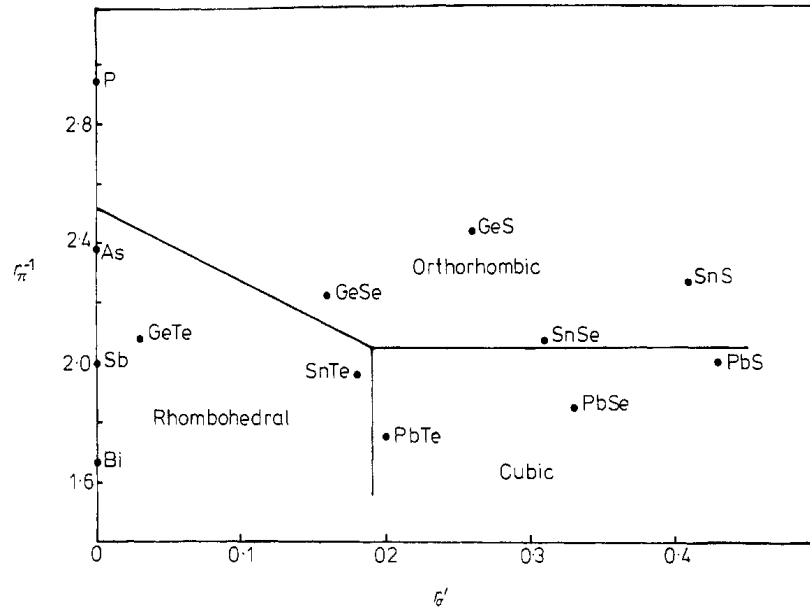


Figure 3.11.: Here, the map for $A^N B^{10-N}$ -materials by Littlewood is shown. The coordinates separate cubic, rhombohedral and orthorhombic structures. The rhombohedral-to-cubic transition follows from increasing ionicity, the transition to orthorhombic structures from the preference of saturated covalent bonding. From ref. 174.

The radii employed are obtained from ref. 173, they are compiled in [Appendix C](#). Before we can understand these coordinate definitions, we may first inspect the resulting map that is shown in [Fig. 3.11](#). Three distinct regions result from this treatment. For small values of r_{π}^{-1} , either cubic or rhombohedral structures are obtained. The transition between the latter two occurs at a critical value of $r'_{\sigma} \approx 0.2$. For high values of r_{π}^{-1} , only orthorhombic structures result. All three structures can be viewed as modifications of rocksalt-structures; there are no distortions in the cubic systems, A- and B-atoms populate the two sublattices and every atom has six equal bonds. In the rhombohedral structures, there is a small atomic displacement in the $[111]$ -direction and a concurrent decrease of the lattice angle. The bonds split into three short and three long ones ('back bonds'), see the discussion of the structure of GeTe in [Section 3.3](#). The orthorhombic structures also have three short bonds per atom, yet the medium-range order is significantly different; it is most instructive to study the differences by inspecting the bond distribution ([Fig. 3.12](#)). To simplify, the orthorhombic structures maximize the strength (saturation) of the short bonds at the expense of the long bonds, and are characterized by a 'loss of order' in the higher shells [164, 174, 176].

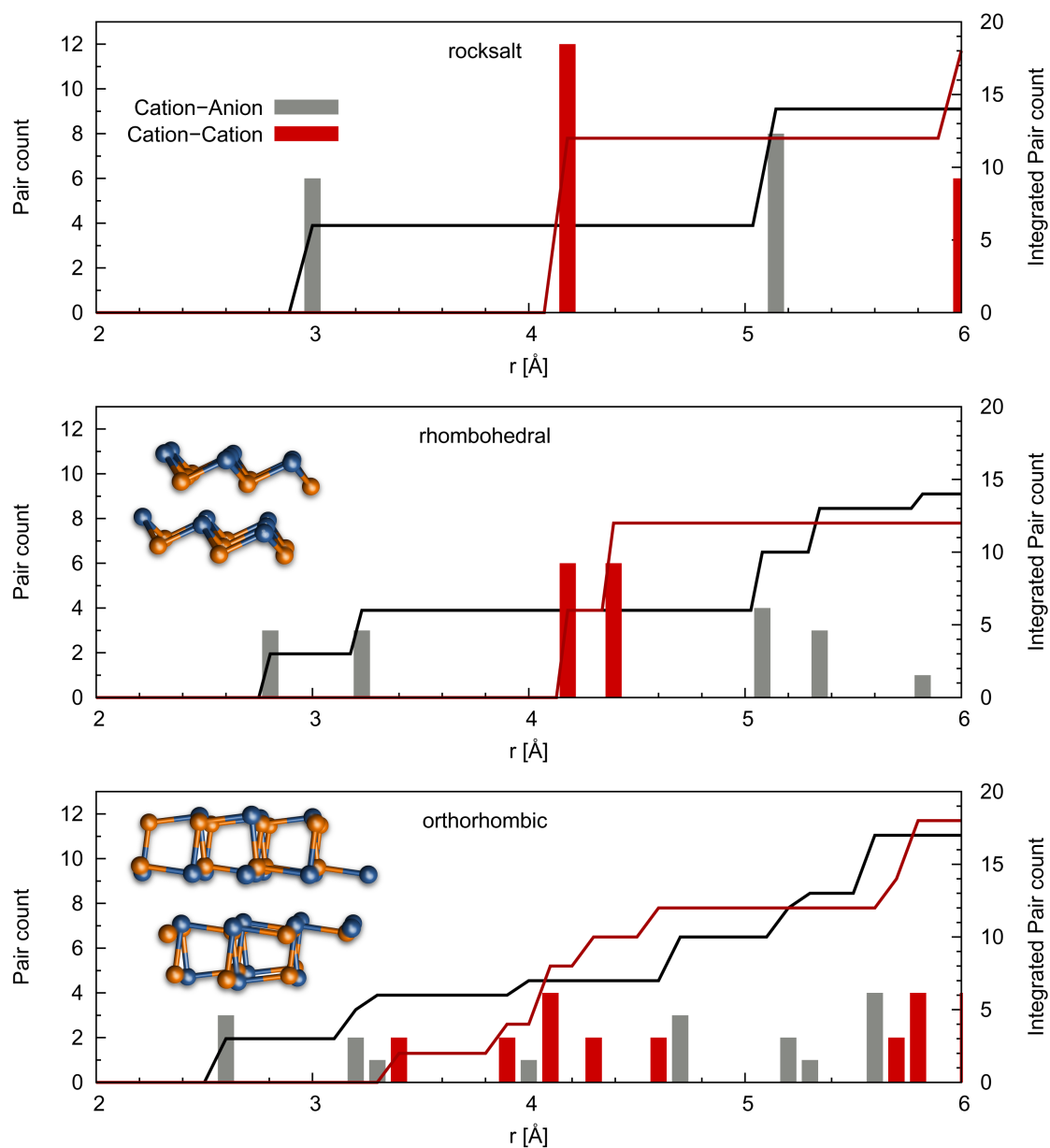


Figure 3.12.: The differences between the three structure-types in Fig. 3.11 are easily revealed by the distribution of the bond lengths. From top to bottom, a simple rocksalt-structure, a rhombohedral (GeTe) and an orthorhombic structure (SnS, data from ref. 177) are shown. The number of bonds per atom are indicated on the left axis, their sum is given on the right axis. The nearest-neighbor peak splits into two upon a rhombohedral and into three upon the orthorhombic distortion. Interestingly, the amplitude of the splitting, which is related to the increase in strength/saturation of the short bond, increases from top to bottom. In addition, the higher shells exhibit increasing 'disorder' from top to bottom. The structure plots visualize the characteristic layer-structure of the distorted systems.

Interestingly, the non-cubic structures become unstable at high temperatures, that is the distortions prevail only at low temperatures. In GeTe, the distortion is lifted at around 670 K, in SnTe the transition is even as low as 75 K. At elevated temperatures, the orthorhombic systems GeS and GeSe as well as SnS and SnSe are known to exhibit the tendency to transform to the rocksalt structure (i. e., 924 K for GeSe) or the 'intermediate' TII-structure (i. e., 878 K and 807 K for SnS and SnSe, respectively), only GeS melts before the transition occurs. At the same time, anomalies in the thermal expansion are observed below the transition regime [176]. We will focus on these aspects in more detail in [Section 3.5.1](#) and [Section 5.4](#).

At this point, we want to understand why the above coordinates facilitate the separation between the three structures. The coordinate r'_σ can be viewed as a measure of ionicity. As shown in ref. 173, it scales almost linearly with Pauling's electronegativity differences. The underlying concept is to measure the size difference of the atoms. The more similar the atoms are, the smaller the charge transfer and thus, the ionic contribution to the bonding. As is well-known, ionic systems favor highly symmetric structures (e. g., NaCl, CsCl) due to the electrostatic interaction between the ions. Consequently, distortions are rendered energetically unfavorable above a critical value of r'_σ . This explains the separation between rhombohedral and cubic systems. Indeed, upon closer inspection it is observed that the rhombohedral distortion increases as r'_σ tends towards zero.

Also the other coordinate, r_π , can be given a physical interpretation. By its definition, it is a measure of the average difference between s- and p-orbital radii and thereby serves as a measure of the energetic splitting between s- and p-levels. To understand this finding, we have to remind ourselves of how hybridization works. By the superposition of (at least) s- and p-states, the energy of the newly formed hybrid orbital is reduced as compared to that of the initial p-orbital. However, the s-electron has to be promoted to this level. The higher the promotion energy, that is the larger the splitting between s- and p-level, the less energy is gained by hybridization. Therefore, the coordinate r_π serves as a measure of 'covalency' or 'tendency towards hybridization'⁴. In order to have high numbers in the case of more pronounced hybridization, we employ the reciprocal, r_π^{-1} . The higher this value, the more likely is s-p-hybridization. Now we may also understand the cubic-to-orthorhombic-transition. The smaller the s-p-splitting, the more energy can be gained by hybridization. Mixing of s- and p-states, though, leads to deviations from octahedral coordination (compare the geometries obtained from sp²- or sp³-hybridization). Hence, upon going upwards in the map, (orthorhombic)

⁴For brevity, the coordinate r_π^{-1} will be called 'hybridization' in the following.

distortions are obtained once the energy gain by forming more saturated, covalent bonds outweighs the ionic forces that counteract deviations from a symmetric arrangement.

In summary, the coordinates by Littlewood enable a structure map for materials with on average five valence electrons (three p-electrons) per atom and equal numbers of anions and cations. The coordinates reflect the bonding properties; r_{π}^{-1} measures the tendency towards s-p-hybridization and r'_{σ} measures the ionicity of the bonding. This scheme works surprisingly well, although it relies only on properties of the free atoms. How can these coordinates be employed to study or even design phase-change materials?

3.4.2. Application to Phase-Change Materials

Littlewood's coordinates cannot be immediately applied to arbitrary phase-change materials for three reasons; first, the average number of p-electrons per atom is typically slightly larger than three, cf. [Tab. 3.1](#). Second, phase-change materials are typically composed of more than two atomic species. Third, the number of cations is occasionally different from the number of anions. Why do these three aspects present obstacles, and how can they be dealt with?

Regarding the first issue, two different routes can be taken. As we have seen in [Section 2.1](#), phase-change materials typically form large concentrations of intrinsic vacancies. In result, a consistent number of three p-electrons *per lattice site*, $N_p^{\square} = 3$, is obtained. Thus, it appears reasonable to treat them in one map. Alternatively, one map for each number of electrons or a three-dimensional map employing the electron count as a third coordinate would need to be established [178–180].

Regarding the second issue, we adopt an averaging procedure. By averaging cationic and anionic species, respectively, materials can be treated as effective AB-materials. Though, this is meaningful only if the atoms are not too different (i. e., this rules out extreme combinations such as C ($r_s = 0.38$, $r_p = 0.47$) and Bi ($r_s = 0.72$, $r_p = 1.02$)). Here, we also accept slight deviations from equal numbers of anions and cations, which includes most phase-change materials. This approach is further motivated by the fact that the difference between the number of anions and cations is typically compensated in these materials by the formation of intrinsic vacancies.

Finally, for materials with effective compositions that deviate from the 'effective AB'-scheme, for instance those close to A_2B or A_2B_3 , the use of a separate map appears necessary; although the physical motivation behind the coordinates is unaffected by the stoichiometry and successful separation between structures is likely to persist, additional structures and different numerical

ranges prevent the use of *one* universal map [178–182]. The validity limits of the outlined procedure will be put to the test by means of density functional theory-calculations in Chapter 4.

The generalized coordinates now read:

$$r'_\sigma = \underbrace{\left(\frac{\sum_i n_i r_{p,i}}{\sum_i n_i} \right)}_{\text{Anions}} - \underbrace{\left(\frac{\sum_j n_j r_{p,j}}{\sum_j n_j} \right)}_{\text{Cations}}, \quad [3.15]$$

$$r_\pi^{-1} = \left[\underbrace{\left(\frac{\sum_i n_i (r_{p,i} - r_{s,i})}{\sum_i n_i} \right)}_{\text{Anions}} + \underbrace{\left(\frac{\sum_j n_j (r_{p,j} - r_{s,j})}{\sum_j n_j} \right)}_{\text{Cations}} \right]^{-1}. \quad [3.16]$$

The sums run over the anions and cations, respectively. n_i denotes the concentration of species i , while $r_{p,i}$ and $r_{s,i}$ refer to the corresponding radii of p- and s-orbital, respectively. The coordinates of a wide number of materials composed of elements from group IV, V and VI as A^V , $A^{IV}B^{VI}$, $A^{IV}_2B^V_2C^{VI}_5$, $A^{IV}_1B^V_2C^{VI}_4$ and $A^{IV}_1B^V_4C^{VI}_7$ have been calculated. Appendix C provides a table of the results. In addition, the locations of empirically identified phase-change materials have been calculated. The resulting map is shown in Fig. 3.13. One observes a split into 'bands' of tellurides, selenides, sulfides and oxides. Most importantly, all phase-change materials (indicated by green circles) are located in a small region of the map in proximity of the prototype materials antimony ($r'_\sigma = 0$, $r_\pi^{-1} = 2.00$) and GeTe ($r'_\sigma = 0.03$, $r_\pi^{-1} = 2.08$). A magnification of this region is presented in Fig. 3.14. Only here, the tendency towards hybridization is small enough to prevent strong distortions. At the same time, the ionic component, that comes at the expense of covalent bonds, is small. Hence, this is the region where significant resonance effects prevail and thus, where phase-change materials can be found. For this reason, the map provides the desired *a priori*-design scheme for phase-change materials. The coordinates of a material can easily be calculated according to Eq. 3.15 and Eq. 3.16. If the material is located in the right region, it is very likely that this material will also be characterized by resonance effects and thus provides the required contrast.

To pin down the spatial extension of the region that holds phase-change materials, further experimental and theoretical material characterization (following the measurement routine presented in ref. 146, for instance) is required. In particular, unsuccessful materials, which are hardly reported in literature, would provide important information. To assist such efforts, the ratio

$$\zeta = \frac{\epsilon_\infty^{\text{cry}}}{\epsilon_\infty^{\text{amo}}} - 1 \quad [3.17]$$

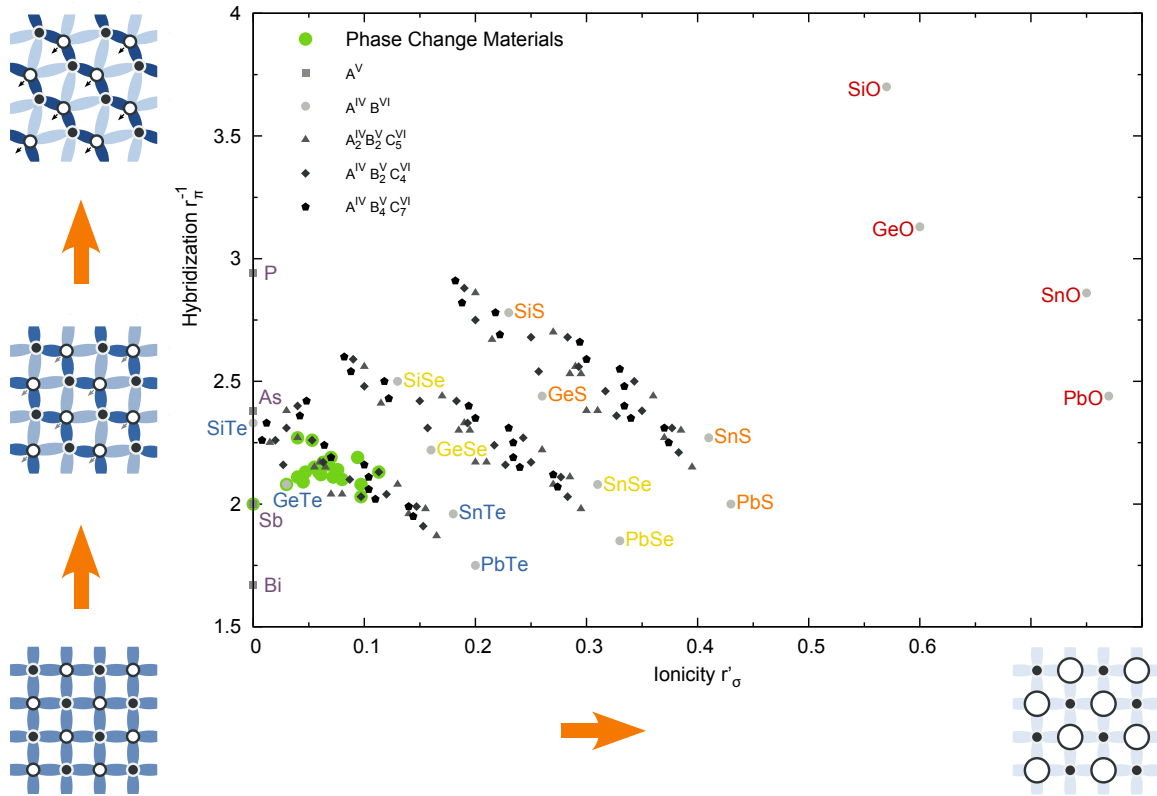


Figure 3.13.: Shown is the empiric map for materials with about three p -electrons per lattice site and approximately even numbers of anions and cations. The axes that span the map are the tendency towards hybridization, r_{π}^{-1} , and the ionicity, r'_{σ} , both defined in the text. The coordinates of a large number of materials have been calculated (see [Chapter C](#) for a table of materials that for clarity cannot be labeled here). Phase-change materials (indicated by green circles) are located within a small region of the map that is prone to the occurrence of resonant bonding. The graphs on the outside illustrate the weakening of resonance effects as one leaves this region due to the formation of less, more saturated covalent bonds via distortions or due to charge localization at the ions due to increasing ionicity.

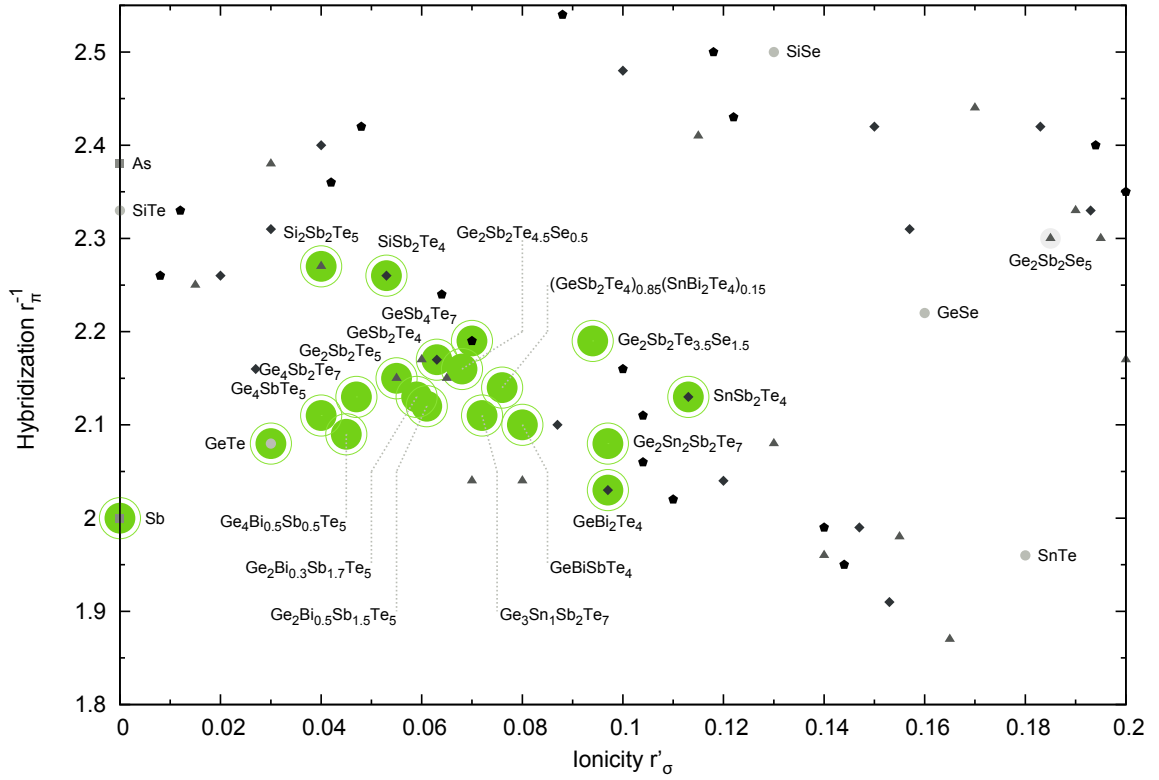


Figure 3.14.: This figure shows a magnification of the region of the map presented in Fig. 3.13 where phase-change materials are located.

can serve as an indicator of the occurrence of resonance bonding. For large values, a change in bonding upon crystallization towards resonant bonding is very likely. Similarly, the ratio of the optical gaps, $\gamma = G^{\text{amo}}/G^{\text{cry}}$, or the bond lengths, r_2/r_1 , could yield further insight into trends on the map.

As an experimental test of the present scheme, a new sample of SiSb_2Te_4 ($r'_\sigma = 0.05$, $r_\pi^{-1} = 2.26$) was prepared by M. Klein and analyzed by S. Kremers in analogy to the procedure in Section 3.1. The resulting dielectric function is compared to that of GeSb_2Te_4 ($r'_\sigma = 0.06$, $r_\pi^{-1} = 2.17$) in Fig. 3.15. Clearly, the resonance effects that are unequivocally present in GeSb_2Te_4 are greatly reduced upon going upwards in the map by the substitution of silicon for germanium. While ζ amounts to 1.2 for GeSb_2Te_4 (and 1.5 in GeTe), it drops to 0.4 in the case of SiSb_2Te_4 . This confirms our expectation from the map that an increase in r_π^{-1} leads away from resonance.

Careful application of the map concept is advised. The stability of a composition against phase separation cannot be inferred from a map. In that sense, each material is hypothetical

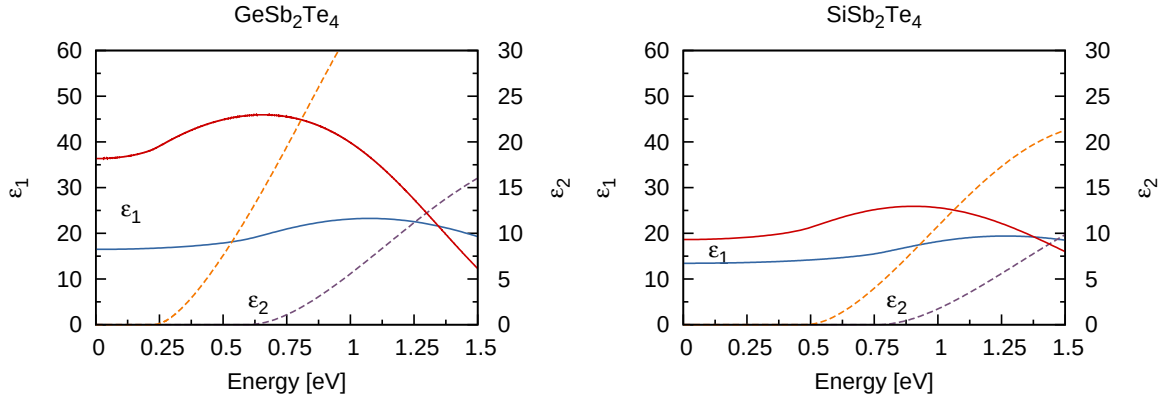


Figure 3.15.: Upon substituting Si for Ge in GeSb_2Te_4 the optical contrast between crystalline (red/orange) and amorphous phase (blue/purple) is greatly reduced since resonance effects are diminished.

prior to experimental realization, though the rapid transition in phase-change based devices enables the use of off-stoichiometric compositions to some extent. As mentioned before, it is meaningless to put materials with an average number of p-electrons of two or four, or pronounced deviations in composition from an equal amount of anions and cations onto the same plane. Yet, the development of projection schemes or new maps for materials with different electron numbers and compositions (e. g., A_2B) could be subject of future research. Elements with d-states close to the Fermi-level are not incorporated in the present scheme. To measure the position of d-states relative to s- and p-states, an additional coordinate/dimension would be required. Further information on the development of structure maps may for instance be obtained from the work of Pettifor [183].

To summarize, a first, simple design-scheme has been developed in the present section that enables the *a priori*-characterization of material candidates. It locates suitable materials in a limited region of a map that is characterized by the occurrence of bonding conditions close to resonance. Hence, to this point a consistent framework has been obtained that facilitates an understanding of the unique property contrast of phase-change materials *and* a recipe for how suitable materials can be found. Along these line, it becomes possible to model further material properties that are affected by the bonding properties. This shall be accomplished in the next section.

3.5. Consequences of Resonant Bonding and Trends on the Map

The occurrence of resonant bonding and its resulting fingerprint-effects in the crystalline phase have consequences for the material beyond the optical contrast that is employed in phase-change materials. In this section, various material properties that are affected by the 'softness' of the electronic system and Peierls-like distortions shall be discussed. It is also the foundation of more quantitative investigations that will be covered in the following chapters.

3.5.1. Lattice-Dynamics and Anharmonicity

The most obvious link can be established to the lattice-dynamics. As is discussed in more detail in [Section A.5](#), the potential energy that the nuclei sense is composed of two components. On the one hand, there is the Coulomb-interaction between the nuclei. On the other hand, there is the energy of the electronic system that adiabatically adopts to the momentary configuration of the nuclei. By virtue of resonant bonding, in particular the aspects illustrated in [Fig. 3.3](#) and [Fig. 3.4](#), only small changes in the total electronic energy are expected upon atomic displacements. For that reason, small force constants and thus low phonon frequencies (and elastic constants) are expected. Though, due to Peierls-like distortions, the potential energy surface takes a peculiar shape as is illustrated in the top row of [Fig. 3.16](#). Rather than a simple, approximately harmonic situation, either a flat basin or, if the energy gain by Peierls-like distortions is more pronounced, a complex surface with multiple minima is obtained. The consequences for the lattice-dynamics are shown in the second and third row of the same figure. The lowest energy levels in the intermediate case of small distortions are spatially very extended. Thus, large amplitudes of the atomic vibrations result even at small temperatures. If, however, the resonance energy is so large that it suppresses the 'flexibility' of the system or if the distortions are very pronounced, an approximately harmonic behavior is recovered (at low temperatures).

The Debye-Waller-factor B^{DW} for an atom α serves as a measure of these amplitudes. It is defined as [\[30\]](#)

$$B_{\alpha}^{\text{DW}} = \frac{8\pi^2}{3} \langle u_{\alpha}^2 \rangle, \quad [3.18]$$

where the average square displacements follow within the harmonic approximation as

$$\langle u_{\alpha}^2 \rangle = \sum_i \frac{\hbar}{\omega_i M_i} |\underline{e}(i, \alpha)|^2 \left[n(\omega_i, T) + \frac{1}{2} \right]. \quad [3.19]$$

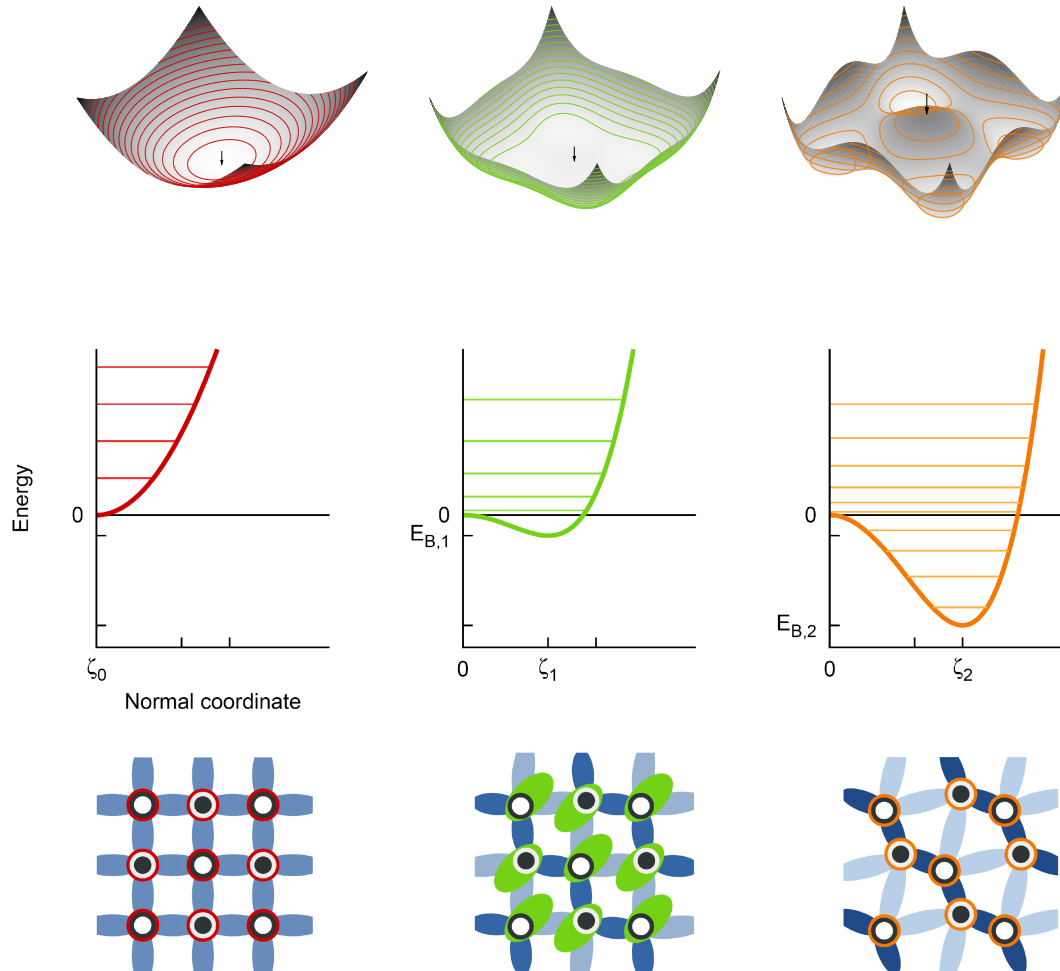


Figure 3.16.: The competition between resonance bonding and Peierls-like distortions leads to a peculiar shape of the potential energy surface of phase-change materials. From left to right, the transition from an undistorted to a strongly distorted system is visualized. The top row illustrates the potential energy surfaces. In the middle row, cuts trough this surface are shown. Here, the horizontal lines mark energy levels of atomic vibrations. For low temperatures, that is when only the lowest levels are populated, large amplitudes of atomic displacements follow from the intermediate, anharmonic shape shown in the middle. This is further illustrated by the sketches in the bottom row. The shaded ares indicate the spatial extension of atomic movements due to the respective potentials.

Here, i runs over all phonon modes of frequency ω_i . The displacement of atom α due to mode i is given by the respective component of the eigenvector $\underline{e}(i, \alpha)$. In the harmonic approximation, a temperature-dependence is introduced only via the Bose-statistics $n(\omega_i, T)$, see Eq. B.29. For elevated temperatures, the T-dependence would then be linear. The discussed anharmonicity, on the contrary, would lead to a super-linear increase once the temperature is increased sufficiently high to 'probe' the anharmonic portion of the potential energy surface. So what behavior do phase-change materials exhibit? Debye-Waller factors have been obtained by means of density functional-theory calculations by Caravati et al. [30] for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (limited to the harmonic approximation!) and x-ray diffraction measurements by Matsunaga and Yamada [184]. In the latter work, a series of compositions, that is GeSb_2Te_4 , GeSbBiTe_4 and GeBi_2Te_4 , was studied. The materials are also plotted in Fig. 3.14. Indeed, a super-linear increase at elevated temperatures is observed, which is the more pronounced the higher the Bi-content or equivalently, the further the material coordinates are shifted to the lower right of the map. Hence, we find the above qualitative picture confirmed in these experiments. In addition, the composition-dependence shows that the shape of the potential energy surface varies along the coordinates of the map. This topic is further addressed in Chapter 5.

The anharmonicity of the potential has further consequences for material properties. On the one hand, anharmonicity leads to thermal expansion. On the other hand, anharmonic interaction limits the lifetime of phonons and thus reduces the thermal conductivity. Both properties are of immediate importance for phase-change materials. The latter shall be discussed in some more detail.

Employing time-domain thermorefectance measurements, Lyeo et al. [185] have investigated the thermal conductivities of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ in all phases. In the metastable crystalline phase, those are very low, taking values on the order of $1 \text{ W m}^{-1} \text{ K}^{-1}$ (similar to window glass). Amorphous and metastable cubic phase differ by a factor of only about two. In both cases, the electronic contribution was found to be negligible. Differences were obtained between rapidly laser-crystallized and slowly oven-annealed samples. The former exhibited a smaller conductivity, ascribed to disorder. This is in line with the expectation of progressing ordering of the cationic site discussed in Section 2.1. Measurements of the thermal properties of phase-change materials have also been performed using the 3ω -method, yielding information on the behavior of the material itself but also at interfaces [186]. Further measurements are reported by Giraud et al. [187], Kuwahara et al. [188; 189], Risk et al. [190]. To summarize, the observed behavior of small thermal conductivities is generic and indicative of the importance of the anharmonicity. This emphasizes a relation to another interesting material family; phase-change materials are very similar to thermoelectric materials. Bi_2Te_3 and PbTe , for example, are well established

thermoelectrics, differing from Sb_2Te_3 and GeTe only by isoelectronic exchange. The figure of merit of thermoelectrics, Z , is defined as

$$Z = \frac{\sigma S^2}{\kappa}, \quad [3.20]$$

where σ is the electrical and κ the thermal conductivity, S is the Seebeck coefficient. A suitable material is characterized by a high electrical conductivity as well as small thermal conductivity. Regarding the electronic contribution, both are coupled by the Wiedemann-Franz law, so only the phonon-contribution to the thermal conductivity can independently be tuned. While attempts to pattern or stack materials in a way that additional phonon-scattering takes place (i. e., to enlarge the figure of merit by an extrinsic effect) it is desirable to have a material that intrinsically exhibits small phonon lifetimes. Anharmonicity as in the present case may serve as such an intrinsic mechanism that is suitable to limit the lattice contribution to the thermal transport, a fact also noted by Rhyee et al. [191]. Anharmonicity is expected to be more pronounced in materials further down in the map as we have seen before, so it is little surprise that PbTe , for instance, exhibits the suitable properties. The map concept may thus be helpful also for thermoelectric materials.

3.5.2. Phase Transition Kinetics

Resonant bonding, its signature-effects, the competition with Peierls-like distortions and the relation to the map presented so far are limited to the crystalline phase. Despite this, some possible links to the phase transition kinetics can be drawn. Nevertheless, since an understanding of the crystallization kinetics requires knowledge of not only one but both phases as well as the transition path, the following arguments do not aim at modeling the phase transition, but to make certain trends plausible. This might be helpful for future research on the transition.

A simple argument can be derived from the inspection of the energy landscape, illustrated in Fig. 3.17. Both amorphous and crystalline phase correspond to two regions of the energy landscape. The crystalline minimum is typically unique and sharp, whereas 'the' glassy phase comprises many configurations. The crystallization probability depends on the energy barrier that separates the phases, but also on the number of possible transition paths. The more the region that corresponds to crystallization is extended, the more probable is crystallization. In other words, the more blurry the 'right' crystalline atomic order is, the more likely is it that the atomic movement in the amorphous phase puts the atoms in 'right' positions (also

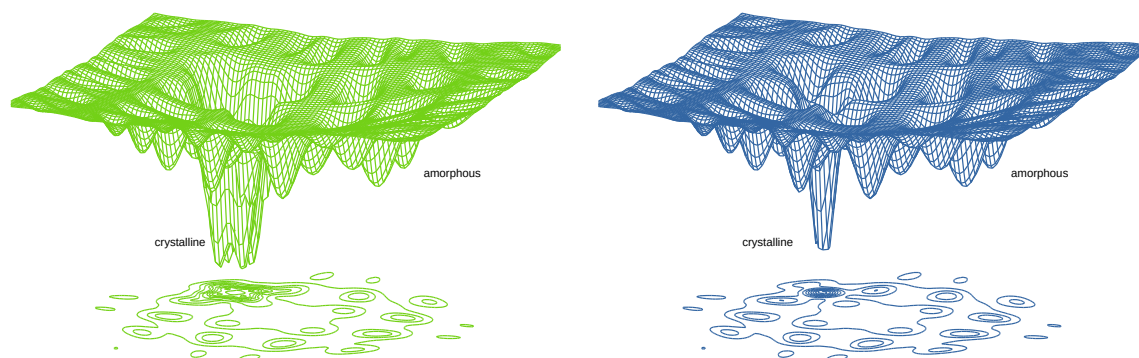


Figure 3.17: Schematically shown is a simplified energy landscape of a material with (left) and without (right) resonant bonding (but some Peierls-like distortions). Though the energy barrier, that separates an amorphous from the crystalline phase, has to be overcome in both cases, crystallization is more likely to occur if the region corresponding to the crystalline phase is further extended. This is due to the increase in possible transition paths.

noted in the work of Matsunaga and Yamada [184]). One may thus speculate that the unique energy landscape that follows from the competition between resonant bonding and Peierls-like distortions supports fast kinetics.

The relation to the map coordinates deserves some further words. A variation in the crystallization kinetics due to the shape of the energy landscape in the region which corresponds to the crystalline phase should be reflected by a corresponding variation of measurable quantities along the coordinates of the map. Indeed, such a trend is visible in the reported values of crystallization temperatures T_c . As a word of caution, such temperatures are ill-defined since they depend on the timescale of the experiment and environmental conditions. Nevertheless, within these uncertainties the results of 'similar' experiments may still be compared. Whereas for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ the crystallization temperature amounts to about 150°C , it slightly increases on the substitution of silicon [192]. However, it decreases on substituting Sn for Ge or Bi for Sb, for example, in the case of $\text{Ge}_2\text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_5$, where it drops to approximately 136°C [193]. Equivalently, starting from GeSb_2Te_4 ($T_c = 131^\circ\text{C}$ [6]), it was found that both $T_c(\text{GeBi}_2\text{Te}_4)$ and $T_c(\text{SnSb}_2\text{Te}_4)$ are as low as approximately 70°C (unpublished data from M. Austgen). For $\text{Ge}_{4-x}\text{Sn}_x\text{Sb}_2\text{Te}_7$, a linear decrease in T_c was observed from 195°C to 165°C on increasing x from 0 to 2.34, alongside a significant decrease of crystallization time [194]. In summary, we see a trend in crystallization temperatures as well as some evidence for a similar trend in crystallization time along the band of tellurium-based alloys shown in Fig. 3.14.

On the level of bond constraint theory, another approach can be obtained for why these trends on the map could arise. By virtue of bond constraint theory, glass rigidity and glass forming ability are related to the average coordination number r (see Section 2.2.2). The higher the coordination number becomes, the worse the glass forming ability gets. Since the position on the map relates to the deviation from six-fold coordination and thus the average coordination number, a trend appears likely. Indeed, the observed decrease in T_c matches this pattern; moving to the lower right of the map, r is expected to increase and indeed, T_c decreases as shown above. Moreover, even the elements in the theory of Lankhorst [42], that go beyond bond constraint theory by also taking into account bond energies, could be linked to the map if the two coordinates comprise also information on the bond strengths. Interestingly, a link between the map coordinates and the heat of formation, H_f , in terms of a polynomial $H_f(r'_\sigma, r_\pi^{-1})$ has been discussed in the work of Chelikowsky and Phillips [173, and references therein]. In summary, further research is motivated to investigate trends on the map and to check for the existence of a mapping of hybridization and ionicity coordinates to average coordination numbers and bond energies.

To conclude this section, a last possible relation between kinetics and resonant bonding shall be presented. In devices, the phase transition occurs in the presence of external electric fields E that induce a polarization P . This, however, leads to a shift in the Gibbs free energy G ⁵:

$$G(E) \approx G(0) - PE = G(0) - \chi E^2 = G(0) - (\epsilon - 1)E^2. \quad [3.21]$$

Due to the occurrence of resonance effects in the crystalline phase, ϵ and hence also the energy shift is larger in the crystalline than in the amorphous phase. In result, the driving force for crystallization, ΔG (< 0), is enhanced:

$$\Delta G(E) = G_{\text{cry.}}(E) - G_{\text{amo.}}(E) \approx \Delta G(0) + (\epsilon_{\text{amo.}} - \epsilon_{\text{cry.}})E^2. \quad [3.22]$$

As an example, a difference in ϵ by about twenty (a typical difference in ϵ^∞) and a field-strength of $10 \text{ V}/\mu\text{m}$ (a typical threshold-switching field-strength) leads to a relative shift of $2 \times 10^4 \text{ J}/\text{m}^3$ or roughly $3 \mu\text{eV}/\text{atom}$. Yet, typical transition energies are on the order of $3 \times 10^4 \mu\text{eV}/\text{atom}$ [11]. Comparing these numbers, it appears unlikely that this mechanism influences the crystallization kinetics significantly. Though, so far we only know the dielectric constant above the phonons, that is ϵ^∞ . But crystalline GeTe, for instance, is known to be a ferroelectric. Here, the low frequency-limit of ϵ shows a strong dependence on temperature and can take large values of up to several thousands close to the Curie-temperature (see for instance

⁵I would like to acknowledge an interesting discussion with M. Salinga on this topic.

ref. [95]). In such a regime, the present effect becomes much more significant. Thus, electrical switching, which takes place at electric field frequencies far below the phonon range, motivates the investigation of ϵ at low frequencies and ferroelectric properties of phase-change materials. Also since Peierls-like distortions, the origin of ferroelectricity in GeTe, are a common feature of phase-change materials, this aspects deserves further study (see Chapter 5).

A related model is the nucleation switching-model by Karpov et al. [96]. Here, however, the crystalline phase is treated as a metal. Hence, no field penetrates crystalline volumes. Then, the formation of a conducting crystalline nucleus within an insulating amorphous film that is embedded between two electrodes significantly changes the surrounding local electric field. This, in turn, changes the free energy of the system (depending on the geometry of the nucleus). In that sense, a field-dependence of the free energy is incorporated in that model.

3.5.3. Electrical Conductivity

Electrical conductivity in phase-change materials becomes increasingly important as the focus shifts from optical to electrical applications. Nevertheless, the materials employed in PCRAM-prototypes are still the same as those developed for optical applications. Why is this so? On the one hand, the requirement of fast phase transition kinetics urges the use of these materials. On the other hand, they do not only exhibit optical contrast, but also electrical contrast. In $\text{Ge}_2\text{Sb}_2\text{Te}_5$, for instance, the specific electrical conductivity at room temperature changes upon crystallization from $\sim 4 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$ to $\sim 1.5 \times 10^3 \Omega^{-1}\text{cm}^{-1}$, that is by six orders of magnitude [107]. Further analysis shows that the concentration of charge carriers in the crystalline phase is particularly high, reaching values on the order of $\sim 1 \times 10^{20} \text{cm}^{-3}$. This, however, is not a consequence of the small gap, but induced by a pronounced shift of the Fermi-level towards or even into the valence bands.

The Fermi-level shift has been attributed to the occurrence of defects. The case has been extensively studied for GeTe by Edwards et al. [196]. The calculation of the energy of formation of various defect types and charge states showed that Ge-vacancies, in particular, are easily formed, requiring little thermal energy (independently of the chemical reservoir considered). Depending on the position of the Fermi-level, these defects are (negatively) charged or neutral. With increasing temperature, there is an increasing number of these defects. Concurrently, the Fermi-level is dragged towards the valence band. Though a finite, temperature-dependent concentration is expected in thermal equilibrium, the number might not vary with temperature on short timescales as predicted due to kinetics. If the expelled germanium aggregates at grain

boundaries, for example, its diffusion back into the grain upon cooling appears unlikely. The presence of significant amounts of vacancies in the germanium-sublattice has been confirmed by EXAFS [197] and x-ray diffraction [18]. The same mechanism of defect formation – vacancies on the cation sublattice – is commonly anticipated to hold for other phase-change materials [30, 196]. A comparable defect study for Ge:Sb:Te-materials, however, is pending. A systematic variation of the composition (with – hypothetically – no defects), that is excess or deficiency of the individual atomic species, also yields a strong effect on the position of the Fermi-level as shown in density functional theory-calculations [24, 30].

Same as with other properties before, also here possible connections between the map and electrical conductivity σ shall be discussed. The latter can be decomposed (for simplicity assuming only one type of carrier) as

$$\sigma = qn\mu , \quad [3.23]$$

where q is the charge, n the carrier concentration and μ the mobility. The value of μ comprises the effective carrier mass m^* . One may speculate that concurrently to increases in the size of the gap, the effective mass increases, thus reducing the value of μ . The 'intrinsic' carrier concentration, on the other hand, is linked to the size of the optical gap, which increases with both increasing ionicity and increasing distortions. Thus, a correlation to the coordinates is immediately obvious. But the predominant contribution to n stems from the 'extrinsic' Fermi-level shift. Consequently, possible trends in n need to relate to the defect formation energies. Here, two options are discernible. On the one hand, the enhanced screening due to large values of ϵ affects the formation energies given that the defects behave like in a simple hydrogen-model. On the other hand, a systematic variation in the heat of formation could provide a link. Since the formation of defects (vacancies) requires the exchange of atoms with chemical reservoirs, defect formation is the more likely, the 'cheaper' it becomes to expel atoms. In turn, the more defects are formed, the more pronounced is the Fermi-level shift. Here, the link to heat of formations mentioned before may yield a systematic trend. In summary, further research on the defect formation energies in phase-change materials is motivated (see outlook on p. 149). Yet, it has to be acknowledged that electrical conductivity is very sensitive to all kinds of intrinsic and extrinsic parameters. For instance, chemical/structural disorder has been proposed as a decisive factor for the scattering of electrons and thus the electrical conductivity (mobility)⁶.

⁶Personal communication with M. Wuttig, publication in preparation as of this writing.

3.6. Conclusions

Resonance effects are a generic fingerprint of crystalline phase-change materials and the corner stone of the optical contrast employed in phase-change devices. But resonant bonding is endangered by static Peierls-like distortions that lift the resonance. Nevertheless, for small distortions resonance effects are weakened but prevail. Density functional perturbation theory-calculations on the prototype material GeTe prove that while the Peierls-like distortion and the subsequent cell distortion significantly reduce the values of the signature-quantities of resonant bonding (Born effective charges and the optical dielectric constant), they remain anomalously large. Therefore, it is proposed that the search for phase-change materials may be directed to those materials that exhibit resonant bonding and only a limited degree of distortions. In fact, the presently known, empirically identified phase-change materials match this pattern. This is indicative for further links between resonant bonding and material properties.

Based on the work on empiric structure maps by Littlewood, a simple *a priori* design-scheme for phase-change materials is developed. Two coordinates characterize the bonding; r'_σ represents the ionicity and r_π^{-1} measures the tendency towards s-p-hybridization. These coordinates span a map where phase-change materials are located in a confined region, for which conditions close to resonance are expected. This way, suitable materials can be identified prior to characterization and trends in the material properties can be predicted.

The competition between resonance bonding and Peierls-like distortions, that is reflected by the location on the map, leads to peculiar shapes of the potential energy surface. The anharmonicity causes significant amplitudes of the atomic vibrations. It limits phonon lifetimes and thus, contributes to small thermal conductivities that highlight the relationship of phase-change materials to thermoelectric materials. Furthermore, a selection of (possible) correlations between the presented framework for the modeling of phase-change materials and important material properties has been presented, motivating further research.

4. Study of the Map by Density Functional Theory Calculations

The design-scheme that has been developed in the preceding chapter (i. e., the map) has the advantage of extreme simplicity. It is a formal instrument to predict material properties while its application is just a matter of seconds. But simplicity comes at the expense of precision. Since the coordinates are calculated based only on properties of the constituting atoms, the question is to what extent the actual bonding leads to deviations from the expected behavior. This question motivates the investigation of a wide range of materials situated on the map by experimental and theoretical means. Given the successful application of density functional theory-calculations in [Chapter 3](#), it is clear that this theoretical method provides a powerful approach to dissect material properties. Moreover, such calculations not only allow the precise control of all relevant parameters – one of the main challenges the experimentalists have to face – but also enable the investigation at conditions that may only barely (not to say impossibly) be prepared experimentally.

Therefore, the present chapter aims at evaluating the validity of the map by density functional theory-calculations. It provides insight into the key question: *How well does the map predict material properties?* Moreover, given the generally high quality of density functional theory-results, not only the qualitative results are of interest, thus: *What are the quantitative results of the theoretical study?* The first step shall be the presentation of what materials have been investigated and how their crystalline phases have been modeled.

4.1. Material Selection and Method

[Figure 4.1](#) shows the region of the map where phase-change materials are located. To answer the above research questions, materials need to be identified that both span the most interesting region of the map and at the same time are suitable for density functional theory-calculations

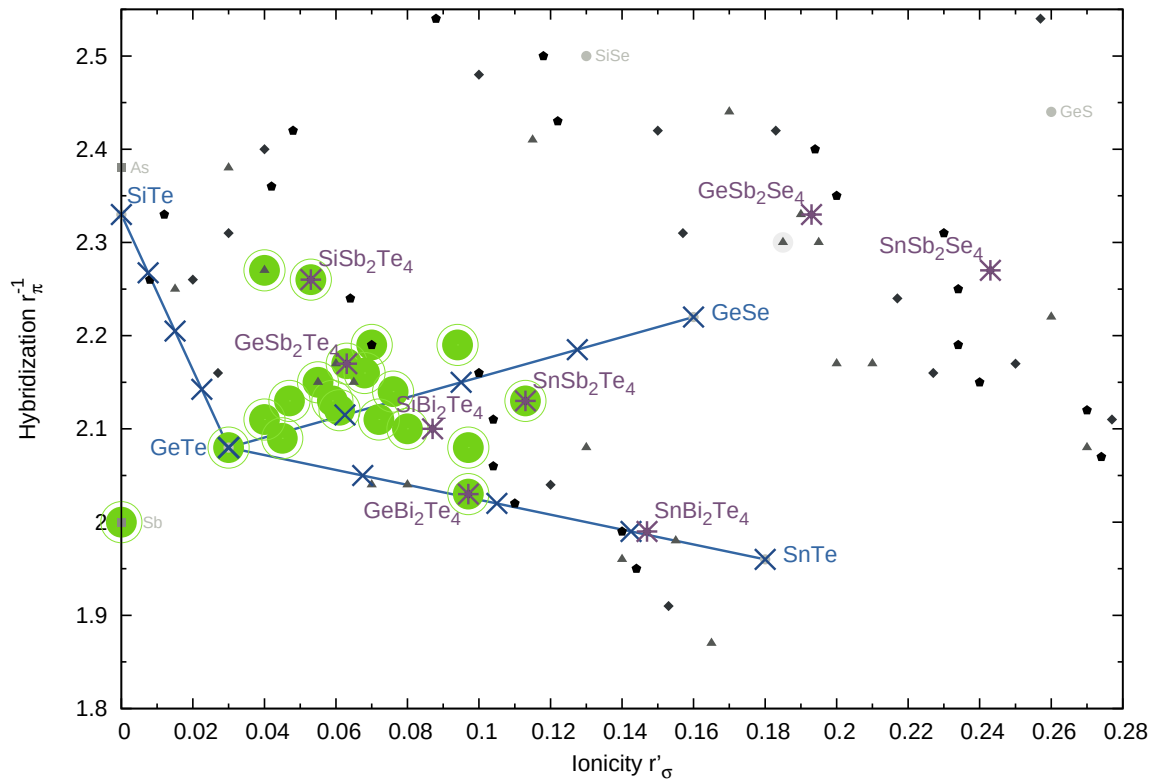


Figure 4.1.: Two classes of materials are considered for the density functional theory-calculations. On the one hand, the binary materials GeTe, SiTe and SnTe as well as intermediate compositions with only partial substitution of silicon, tin and selenium for germanium and tellurium are taken into account (blue crosses). On the other hand, $A_1B_2C_4$ -type materials (purple double-crosses) are investigated. This way, a large number of materials, that are located in the empirically identified region of the map where phase-change properties prevail, are tested.

(i. e., can be represented with small numbers of atoms per unit cell). Hence, two routes have been taken. On the one hand, binary materials are considered. Starting at GeTe, the influence of isoelectronic substitution of selenium for tellurium as well as silicon or tin for germanium is investigated. Furthermore, intermediate steps representing partial substitutions are realized. These materials will be referred to as *AB-systems* in the following. On the other hand, various materials composed as $A^{IV}_1B^V_2C^{VI}_4$ (with one vacancy 'V' per formula unit) are taken into account, exploring in addition to the other isoelectronic exchanges also the effect of bismuth substitution for antimony. Pure antimony and germanium-doped antimony have previously been investigated in the diploma thesis of Zalden [198] (advised within the framework of the present thesis).

4.1.1. Crystalline Models

All systems are treated in (hypothetical) distorted rocksalt-type structures. For the AB-systems, the primitive rhombohedral unit cell with two atoms introduced in Section 3.3 (see Fig. 3.6) has been employed. Yet, the cell angle has been fixed to 60° , that is the cubic case. For the AB_2C_4 -systems, two different models have been set up. On the one hand, cubic unit cells with 64 lattice sites of which 56 are populated with atoms have been used. The respective cell for $GeSb_2Te_4$ is shown in Fig. 4.2. All other AB_2C_4 -systems have been derived from this model by isoelectronic exchange. The cation sublattice is randomly occupied, though certain unfavorable motifs, such as vacancy clustering or chains of vacancies (e. g., Te-V-Te-V) have been avoided (based on unpublished results in the course of preparing ref. 24 and private communication with D. Lüsebrink). These models will be referred to as *56-cells* in the following. On the other hand, in addition to these large models, that are computationally very demanding, a set of smaller models has been employed. They resemble a $2 \times 2 \times 2$ -supercell of the primitive unit cell of the binary compounds, offering 16 lattice sites of which 14 are populated with atoms as can be seen in Fig. 4.3. The structural features of these cells will be discussed thoroughly in Chapter 5. For now, we acknowledge that these so called *14-cell*-models provide a compromise between computational demand and representation of structural features. In some cases, results on these cells are shown in the present chapter, though the main focus is on the 56-cells. Thus, if not stated otherwise, results on AB_2C_4 -systems refer to the large models.

4.1.2. Technical Details of the Calculations

The method of density functional theory-calculations is introduced in Appendix A. The employed code is again ABINIT [155–161]. For all systems investigated, Troullier-Martins-type pseudopotentials [199, 200] for the valence s- and p-electrons employing the GGA-PBE exchange- and correlation-functional [162] have been used ¹. They have been retrieved from the ABINIT website (<http://www.abinit.org>). For the AB-systems, these pseudopotentials have been mixed to obtain intermediate compositions, a procedure known as *Virtual Crystal Approximation* (VCA). For the sampling of the Brillouin zone, a $10 \times 10 \times 10$ $\underline{k}$ -point grid shifted by (0.5 0.5 0.5) has been employed. For the AB_2C_4 -systems in the 56-cell, an equivalently shifted $4 \times 4 \times 4$ -grid has been used. The respective calculations in the 14-cell have been carried out with a grid consisting of four $2 \times 2 \times 2$ -grids shifted by (0.5, 0.5, 0.5), (0.5, 0.0, 0.0), (0.0, 0.5, 0.0)

¹Note that in the previous chapter, different pseudopotentials were used for GeTe. Thus, the results differ slightly.

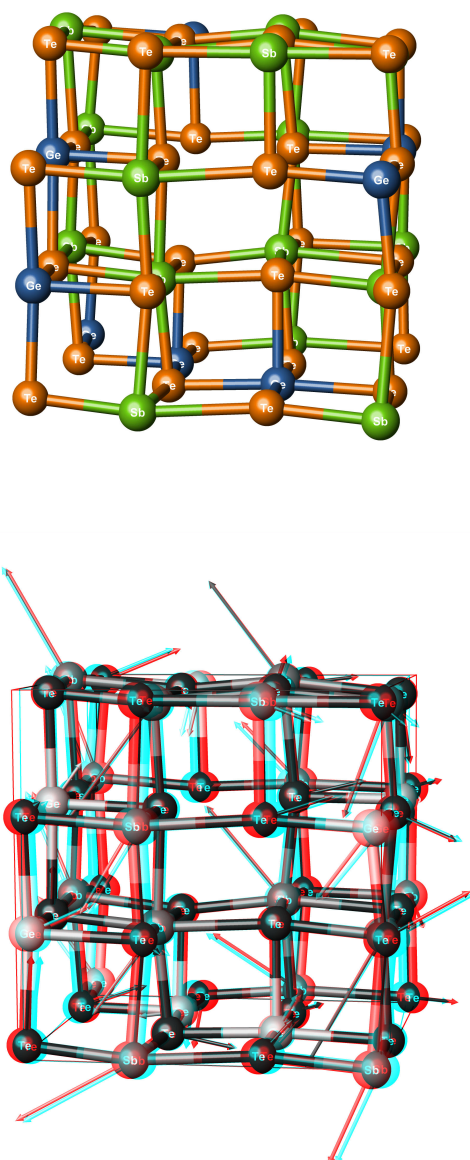


Figure 4.2.: Structure of the 56-cells (shown: GeSb_2Te_4). The vectors indicate the distortion from the rocksalt positions. The 3D-plot is best viewed online with red-cyan-glasses.

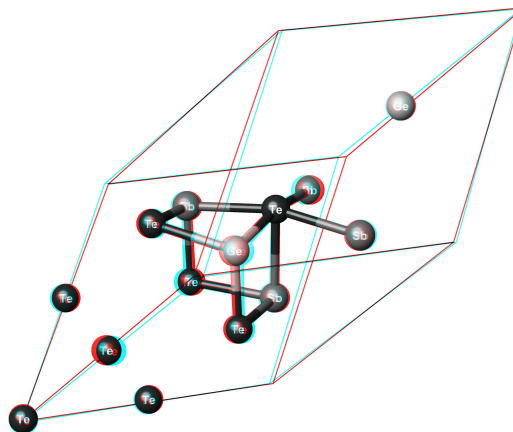
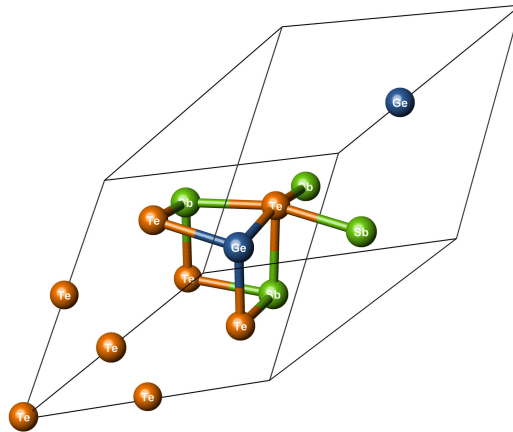


Figure 4.3.: Structure of the 14-cells (shown: GeSb_2Te_4). The 3D-plot is best viewed online with red-cyan-glasses.

and (0.0, 0.0, 0.5). The cutoff-energy E_{cut} has been 20.0 Hartree = 544 eV for the AB-systems and has exceeded 16 Hartree = 435 eV for the AB₂C₄-systems. In the latter case, the effective cutoff-energy is slightly larger than the specified value due to an additional margin imposed by ABINIT in the case of automatic relaxations ². Thus, the effective cutoff-energy amounts to 16 Hartree times 1.1 (56-cell) or 1.44 (14-cell), respectively. To maintain consistency, the parameters that have an impact on the convergence have been kept fixed throughout the further calculations. Structural optimizations were carried out 'by hand' in the case of AB-systems; here, the cubic lattice constant and the displacement of the atoms have been varied manually and fitted as will be explained in the text. For the other systems, also automatic relaxations have been run such that for the AB₂C₄-systems in the 14-cell the remaining forces do not exceed 6×10^{-8} Hartree/Bohr = 3.1×10^{-6} eV/Å and, in case of cell relaxations, stresses remain below 2×10^{-5} Hartree/Bohr³ = 6×10^{-1} GPa. Due to the immense computational expense, not all relaxations for the AB₂C₄-systems in the 56-cell could be brought to this level. The 'worst' values remain below 1×10^{-5} Hartree/Bohr = 5.1×10^{-4} eV/Å for the forces and 4×10^{-5} Hartree/Bohr³ = 1.2×10^0 GPa for stresses. Nevertheless, these relaxation parameters yield converged results as has been checked. The drawback is, however, that future phonon- or linear response-calculations on the 56-cell systems require further relaxation.

4.2. Results and Discussion

The presentation of the results of the calculations is subdivided into several sections. The first aspect to be discussed is the structure, in particular the quantification of the average atomic distortions. Further sections illuminate the actual bonding (i. e., ionic and covalent contribution) and the distribution of electronic states. Furthermore, parts of [Chapter 5](#) are devoted to the local structure as well as the lattice-dynamics of these materials.

4.2.1. Structure and Distortions

For the AB-systems, the equilibrium volume without distortions (i. e., $\alpha = 60.0^\circ$, $x = 0.5$) has been determined by fitting the Murnaghan-function (see [Appendix A.5](#)) to the total energies obtained for various fixed lattice constants a . These data points and the corresponding fits are

²Parameters used were $\text{ecutsm}=0.5$, $\text{dilatmx}=1.05$ (56-cell) or $\text{dilatmx}=1.20$ (14-cell), respectively

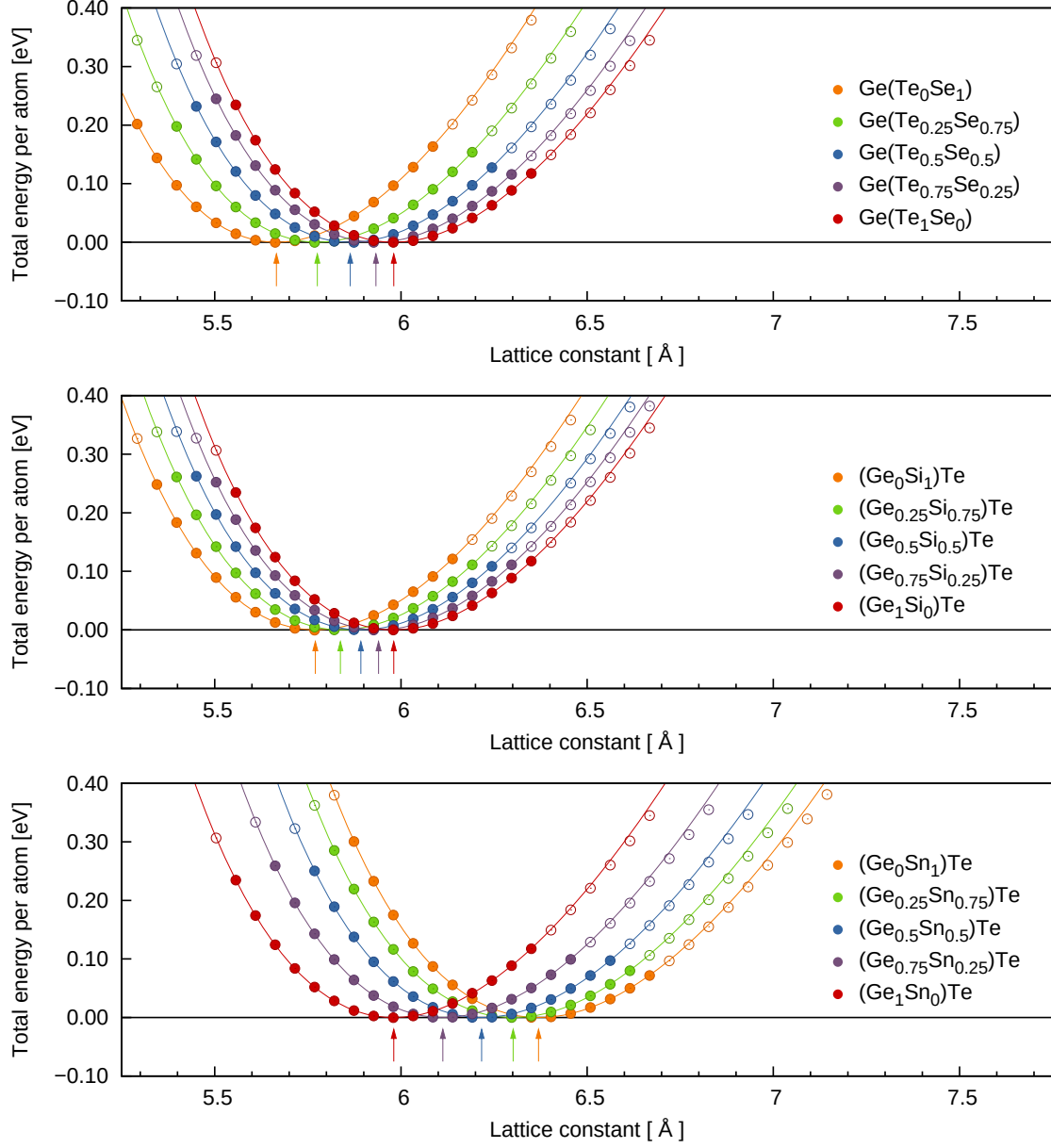


Figure 4.4.: Results of the Murnaghan-fits for $(\text{Ge}_x\text{Sn}_{1-x})\text{Te}$, $(\text{Ge}_x\text{Si}_{1-x})\text{Te}$ and $\text{Ge}(\text{Te}_x\text{Se}_{1-x})$. Only the filled circles have been taken into account for the Murnaghan fits. The arrows at the bottom indicate the positions of the minima.

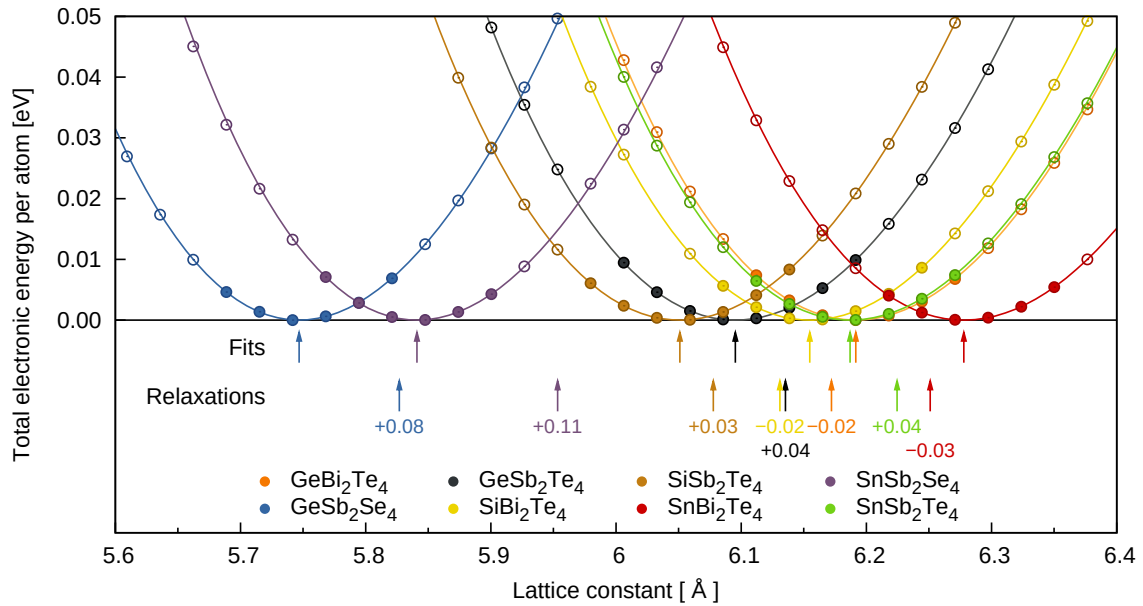


Figure 4.5.: Results of the Murnaghan-fits for the AB_2C_4 -systems. Only the filled circles have been taken into account for the Murnaghan-fits (where the Murnaghan-function is a valid approximation). The arrows at the bottom indicate the positions of the minima derived from the Murnaghan-fits for the undistorted rocksalt-structures (upper row) and the results of the full relaxations (including atomic displacements, lower row). The numbers indicate the differences. For the selenium-systems, the relaxation leads to significant volume expansion, while the change is less pronounced for the tellurium-containing systems. For the systems with bismuth, even a slight compression is obtained.

shown in Fig. 4.4³. Put simply, the position of the minimum yields the lattice constant, while the curvature determines the bulk modulus B . Both selenium and silicon substitution lead to a decrease of a , while tin substitution leads to an increase.

For the AB_2C_4 -systems, the same procedure has been applied as can be seen in Fig. 4.5⁴, assuming undistorted rocksalt-structures. Relaxation of the atomic positions for each volume, though, is presently impossible for the large systems due to the excessive computational demand. Thus, bulk moduli B obtained from these Murnaghan-fits refer to undistorted rocksalt-systems for both AB- and AB_2C_4 -systems. The lattice constants that have been obtained from the full relaxations (i. e., including atomic relaxations) of the AB_2C_4 -systems are also indicated in

³In the primitive unit cell, the length of the basis vectors is $2^{-1/2}$ times the printed lattice constant, which is the edge length in the conventional unit cell.

⁴Note that the edge length of the 56-atom unit cells is twice the printed lattice constant.

Table 4.1.: This table compiles the structural results for the AB-systems, that is lattice constants a , bulk moduli B and x , the reduced coordinate of the second sublattice. The materials are sorted by the respective substitute and the value of the hybridization coordinate r_{π}^{-1} .

Material	r'_{σ}	r_{π}^{-1}	a [Å]	B [GPa]	x_0
			(undist.)	(undist.)	
GeTe	0.0300	2.0800	5.98	48.8	0.5229
(Ge _{0.75} Si _{0.25}) Te ₁	0.0225	2.1425	5.94	49.5	0.5231
(Ge _{0.5} Si _{0.5}) Te ₁	0.0150	2.2050	5.89	50.2	0.5232
(Ge _{0.25} Si _{0.75}) Te ₁	0.0075	2.2675	5.84	51.3	0.5228
(Ge ₀ Si ₁) Te ₁	0.0000	2.3300	5.77	52.8	0.5215
(Ge ₀ Sn ₁) Te ₁	0.1800	1.9600	6.37	41.6	0.5036
(Ge _{0.25} Sn _{0.75}) Te ₁	0.1425	1.9900	6.30	42.8	0.5088
(Ge _{0.5} Sn _{0.5}) Te ₁	0.1050	2.0200	6.22	44.2	0.5140
(Ge _{0.75} Sn _{0.25}) Te ₁	0.0675	2.0500	6.11	46.3	0.5187
Ge ₁ (Te _{0.75} Se _{0.25})	0.0625	2.1150	5.93	49.9	0.5231
Ge ₁ (Te _{0.5} Se _{0.5})	0.0950	2.1500	5.86	51.7	0.5232
Ge ₁ (Te _{0.25} Se _{0.75})	0.1275	2.1850	5.78	54.2	0.5233
Ge ₁ (Te ₀ Se ₁)	0.1600	2.2200	5.67	57.7	0.5236

Fig. 4.5 as a second row of arrows. Obviously, the atomic distortions lead to a significant volume expansion for the selenium-systems. For the tellurium-systems, the change is smaller, and even reversed for the bismuth-containing materials, where the lattice constant slightly decreases. All structural results are compiled in Tab. 4.1 and Tab. 4.2 alongside the map-coordinates. We will turn to the discussion of trends at the end of this section.

The distortions of the AB-systems have been studied by isochoric displacement of the two sublattices, that is by varying x while a has been fixed to the equilibrium value. The results are shown in Fig. 4.6. Due to symmetry, only one branch (positive displacements, $0.5 \leq x$) needs to be presented. In line with the arguments given in Section 3.3 and Section 3.5.1, double well-shaped energy surfaces are found for these systems (the shown branch represents one of the symmetric wells). The undistorted rocksalt-structures ($x = 0.5$) represent local maxima (due to symmetry), for which certain Peierls-like displacements ($x_0 \geq 0.5$) lead to a lowering

Table 4.2.: Similar to [Tab. 4.1](#), this table compiles the structural results for the AB_2C_4 -systems. Here, the distortion is measured by w , that is the width of the first peak in the pair histogram (cf. [Appendix D](#)). The materials are sorted by their value of the hybridization coordinate r_π^{-1} .

Material	r'_σ	r_π^{-1}	a [Å]		B [GPa]		w [Å]	w/a
			(14-cell, dist.)	(undist.)	(dist.)	(undist.)		
SnBi ₂ Te ₄	0.147	1.99	6.30	6.28	6.25	43.1	0.189	0.030
GeBi ₂ Te ₄	0.097	2.03	6.22	6.19	6.17	45.2	0.284	0.046
SiBi ₂ Te ₄	0.087	2.10	6.19	6.15	6.13	45.9	0.366	0.060
SnSb ₂ Te ₄	0.113	2.13	6.24	6.19	6.22	44.5	0.320	0.051
GeSb ₂ Te ₄	0.063	2.17	6.14	6.10	6.14	46.3	0.370	0.060
SiSb ₂ Te ₄	0.053	2.26	6.09	6.05	6.08	47.3	0.335	0.055
SnSb ₂ Se ₄	0.243	2.27	5.95	5.84	5.95	54.0	0.546	0.092
GeSb ₂ Se ₄	0.193	2.33	5.83	5.75	5.83	57.1	0.489	0.084

of the total energy. By the displacement in the $[1\ 1\ 1]$ -direction, the six bond lengths split into three short and three long ones. Here, we are only interested in the respective values of x_0 that represent the lowest energies⁵. These minima are indicated in the figure and also listed in [Tab. 4.1](#). Clearly, one observes a depression of the distortion as tin is substituted for germanium, while the other two substitutions hardly affect the reduced coordinate. Yet, the electronic structure changes for the latter two substitutes as the absolute bond lengths of the short bonds become smaller due to the decrease of the lattice constants.

For the AB_2C_4 -systems, the distortions do not follow a simple pattern as in the binaries. Hence, a quantification of the level of distortion requires the inspection of either the bond lengths of the individual atoms or – more universal yet not atom-resolved – the pair histograms. The two approaches are presented for GeSb₂Te₄ in [Fig. 4.7](#) and [Fig. 4.8](#). The respective figures for the remaining materials are compiled in [Appendix D](#). In the former figure, it can be seen that the atoms do not behave in a homogeneous manner, but exhibit very different local behaviors. Rather than a simple 3+3-split of the bond lengths as in the binary systems, one finds various local motifs, that can be subdivided into groups with approximately 1+4+1-, 2+2+2- and 3+3-splits of the bonds. These splits occur if in a rocksalt-structure, an atom is displaced in the

⁵The discussion of the energy landscape and its consequences for the lattice-dynamics is postponed to [Chapter 5](#).

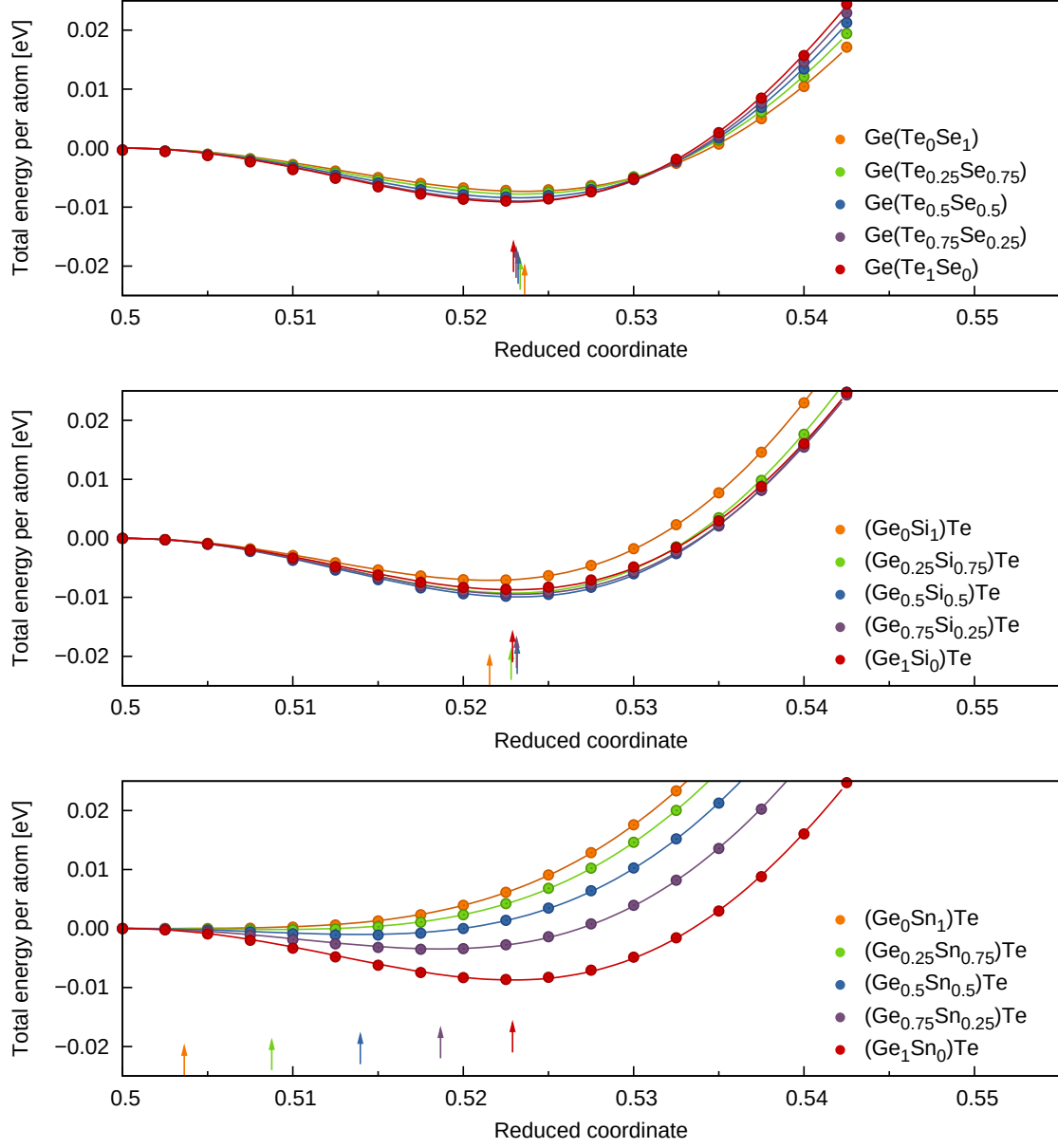


Figure 4.6.: Shown here is the variation of the total energy of the AB-systems upon displacing the two sublattices, that is by the variation of x . The curves have been fitted by polynomials $f(x) = ax^2 + bx^4 + cx^6$ that represent the shape of the curves extremely well. The arrows indicate the positions of the minima of the fitted curves.

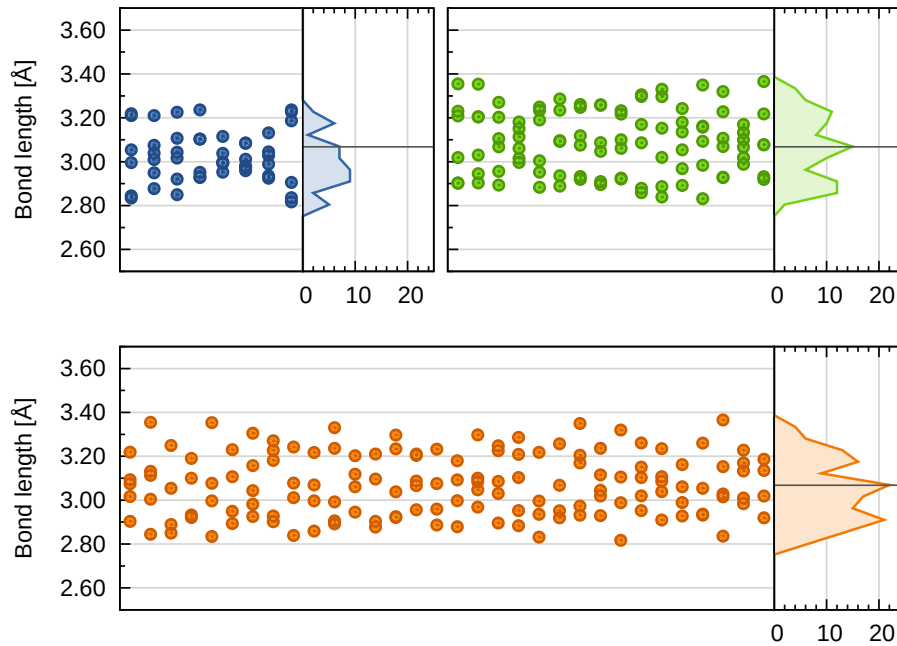


Figure 4.7.: In this figure, the six shortest atomic distances for each atom in GeSb_2Te_4 (Ge: blue, Sb: green, Te: orange) are presented. For tellurium, less distances are plotted due to vacancies. The horizontal line indicates the position expected for an undistorted rocksalt structure with the same lattice constant a , that is $a/2$.

$[100]$ -, $[110]$ - or $[111]$ -direction, respectively. The reason for these different local structures will be unraveled in Chapter 5. The overall-behavior, that is the species-dependent distribution of the bond lengths, is given in the same figure. To enable a comparison, the results for all AB_2C_4 -systems are compiled in Fig. 4.9 side by side. This figure shows that from left to right, that is with increasing value of the hybridization-coordinate r_π^{-1} , the bond distribution in the second (B-C) and third row (C-A/B) becomes increasingly broader, that is the distortion increases. Also, it can be seen that the cations A and B behave very similar in SnBi_2Te_4 and GeSb_2Se_4 , for instance, while significant differences are obtained for systems where the cations are very different in size; SiBi_2Te_4 but also SiSb_2Te_4 and GeBi_2Te_4 exhibit on average shorter bonds for the small A-species. For the other systems, the distributions are centered around the value expected for undistorted rocksalt-systems. The bond-distributions for species C shown in the bottom row of the same figure resemble the sum of the bonds of species A and B since only A-C and B-C bonds exist.

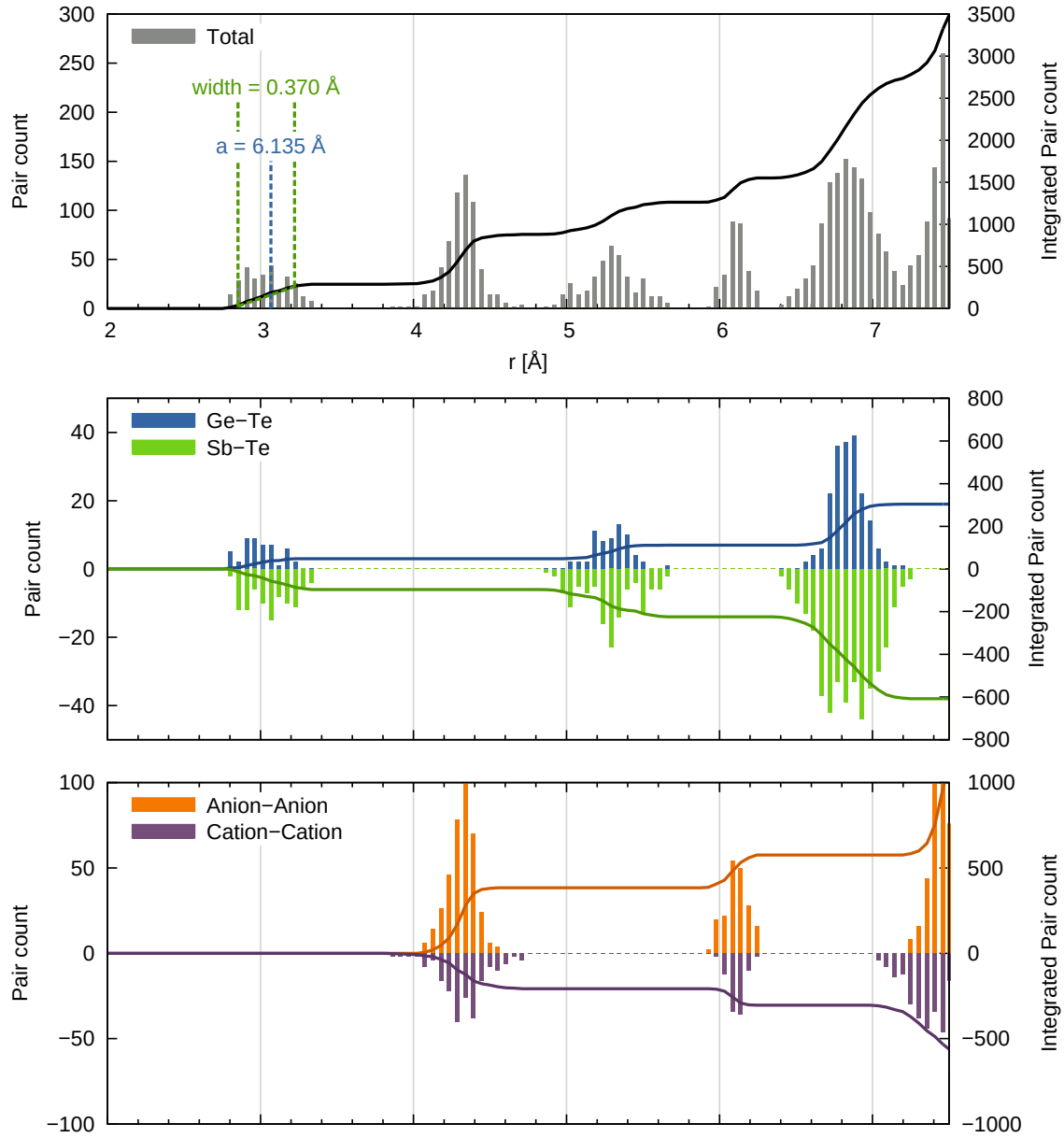


Figure 4.8.: Pair histogram for GeSb_2Te_4 . Indicated are the width w of the first anion-cation-peak (see [Appendix D](#) for details) as well as the position expected for an undistorted rocksalt structure with the same lattice constant a , that is $a/2$.

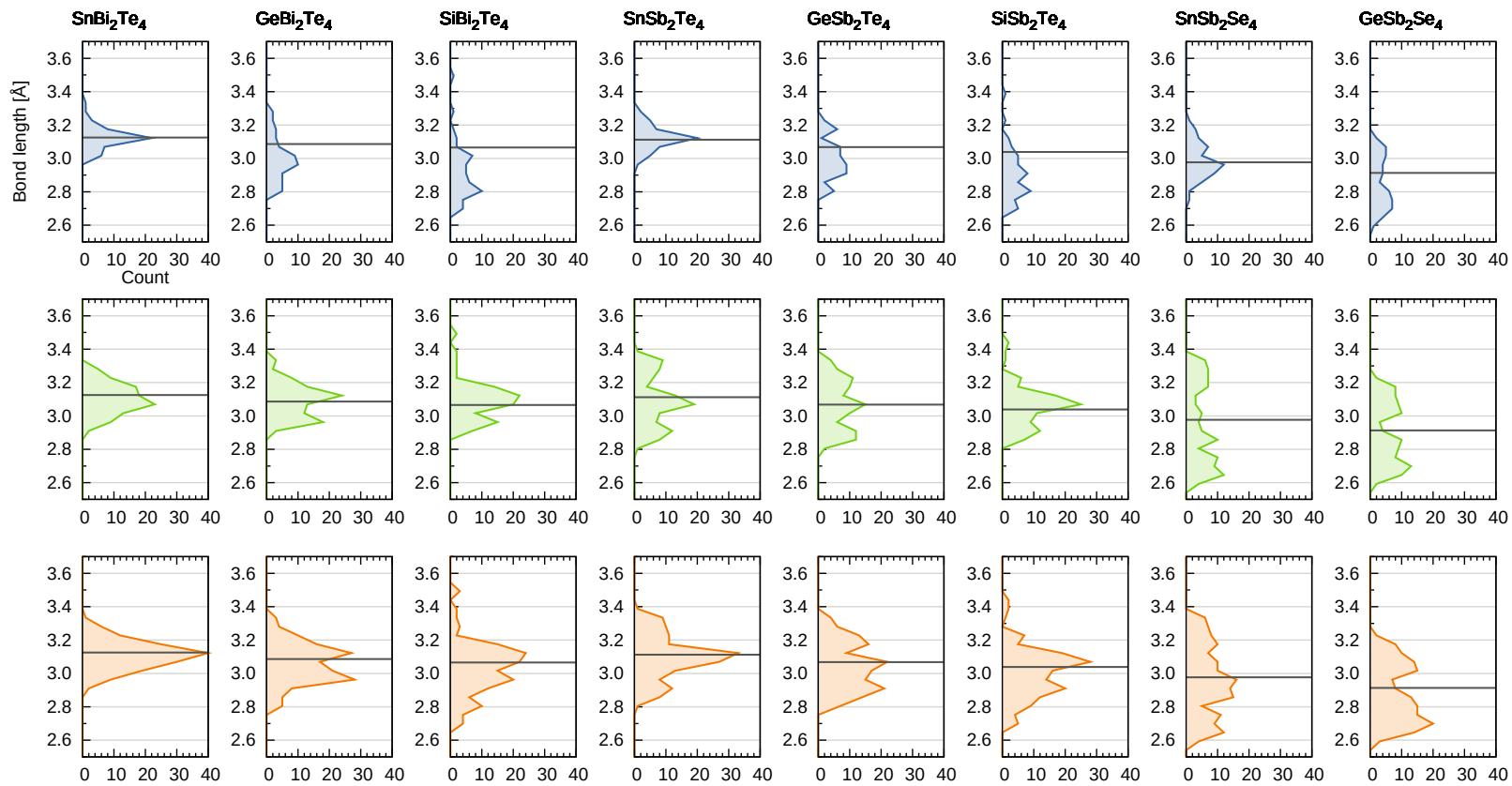


Figure 4.9.: Comparison of the summed six nearest-neighbor-distances in the AB_2C_4 -systems at equilibrium (top/blue: A, middle/green: B, bottom/orange: C) as discussed in the text. The horizontal line indicates the bond length expected for an undistorted rocksalt-structure. The structures are analyzed in more detail in [Appendix D](#) as well as [Fig. 4.7](#) and [Fig. 4.8](#).

Due to the variation in distortions of the two cationic species, no simple behavior such as two distinct peaks due to 3+3-splitting as in the binary systems is obtained. To quantify the average distortion, the width w of the first peak in the pair histograms (Fig. 4.8 and Appendix D), which is located at around half the lattice constant and comprises both A-C and B-C-bonds, has been evaluated (neglecting outliers, see page D-39 of Appendix D for technical details). The results for w and the relative displacement w/a are given in Tab. 4.2.

Now that we have compiled all the information about the structures and distortions, we can turn to the identification of trends. Therefore, the data in Tab. 4.1 and Tab. 4.2 are plotted for both AB- and AB₂C₄-systems side by side on top of the map (Fig. 4.1) in Fig. 4.10. In the AB-systems, the substitution of tin for germanium leads to an increase in the lattice constant, while the other two substitution routes lead to a decrease. Likewise, the lattice constant of the AB₂C₄-systems tends to increase towards the lower right part of the map, reflecting the size increase of the constituting atoms. The bulk moduli (of the undistorted structures) decrease towards the lower part of the map. Thus, since $B = -Vdp/dV$, the materials become less resistant to compression/expansion which might be relevant for applications in terms of wear mechanisms due to density changes, and at interfaces. Only SnSb₂Te₄ stands out since its bulk modulus is too small to fit the trend, an issue that is addressed in the next section. Finally, also the measures of distortions show a trend along the coordinates of the map. In line with the expectation, the distortion decreases towards the lower right (Littlewood: 'cubic') region of the map and increases towards the upper right (Littlewood: 'orthorhombic'). Interestingly, the distortion remains almost constant/decreases very slightly towards the upper left edge. This might reflect the diagonal rhombohedral/orthorhombic-border in Littlewood's original map (Fig. 3.11).

In summary, the behavior expected from the map is largely reproduced by the *average* structure properties of all systems investigated. Hence, the validity of the map as a quick instrument for *a priori*-material assessment is verified. There are, however, also variations between the cationic species in the case of significant size mismatches and – less pronounced – between atoms of the same species due to different local environments (as covered in Chapter 5). The former finding may be considered in the interpretation of map coordinates; if size mismatches occur, the smaller species may be expected to be distorted more than the average, thus reducing the resonance effects more than expected. In result, simple compositions without 'small' species appear more favorable for phase-change materials to increase the resonance character and thereby the contrast. Yet, in terms of crystallization temperatures (data retention), the addition of small portions of network-forming elements such as silicon or germanium has proven advantageous as evidenced by the material Ge₁₅Sb₈₅, for instance. The aim of further

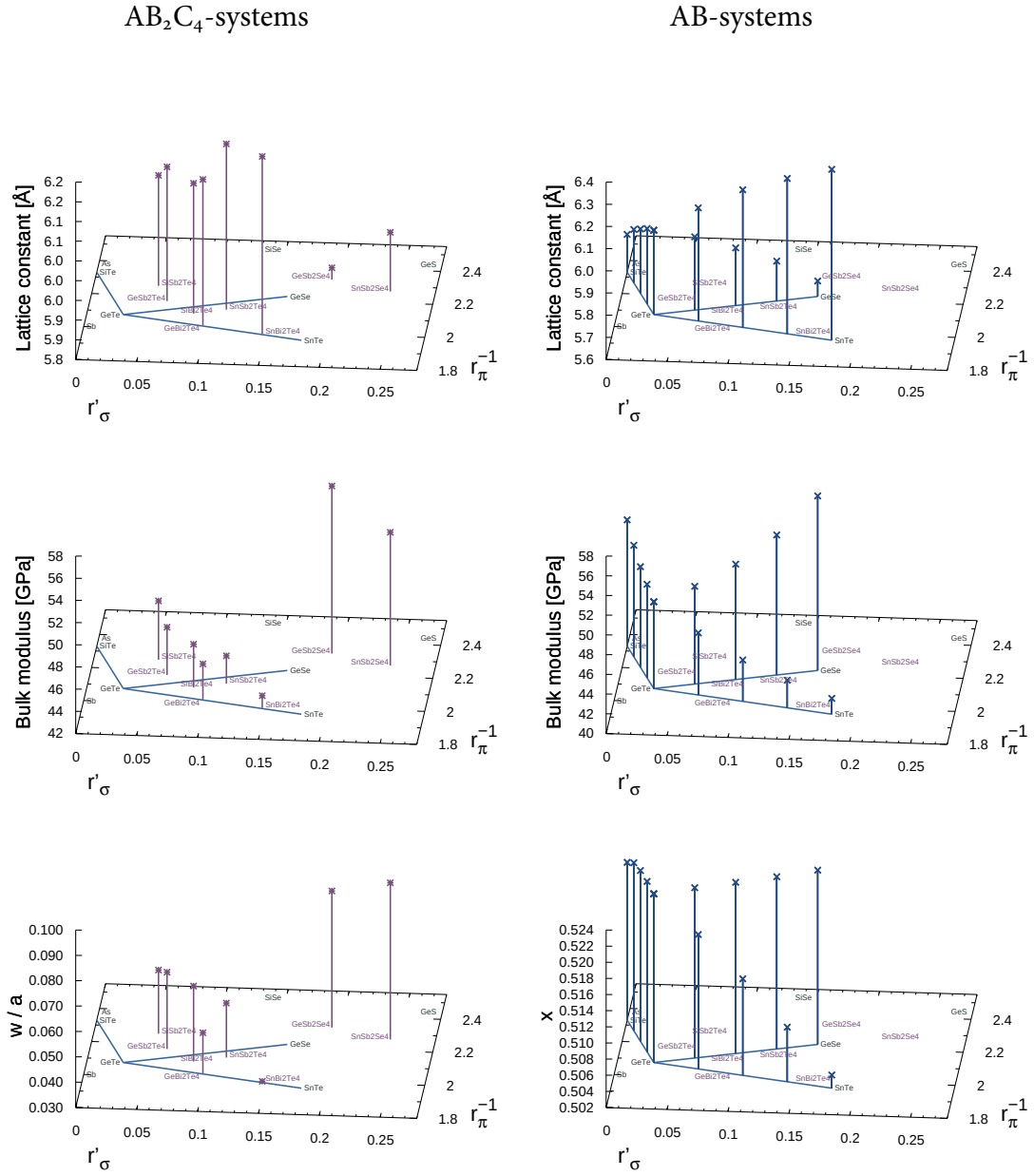


Figure 4.10.: These figures show the correlation between the structural data in Tab. 4.1 and Tab. 4.2 and the map coordinates (cf. Fig. 4.1). The results for the AB_2C_4 -systems (purple) are shown on the left-hand side, those for the AB-systems (blue) on the right-hand side. From top to bottom, the lattice constants a (relaxation-results including distortions for the AB_2C_4 -materials), the bulk moduli B of the undistorted systems and the relative measures of the level of distortion (w/a for the AB_2C_4 -systems, x_0 for the AB-systems) are presented.

experimental research could be whether size differences also have a negative impact on the miscibility and thereby the phase stability.

The next step in the study of the map shall be the comparison between the properties that the map coordinates stand for and corresponding quantities obtained from the density functional theory-calculations.

4.2.2. Analysis of the Bonding

To gain further insight into the bonding in the materials, the aim of this section is to quantify the ionic and covalent contribution at the level of density functional theory-calculations. This way, the validity of the interpretation of the map coordinates shall be assessed.

Ionicity

To quantify the ionic contribution to the bonding, the Bader charge analysis introduced in [Appendix B.1.1](#) has been performed. For each atom, this procedure yields a Bader charge, which deviates from the nominal atomic charge. The respective charge differences serve as a measure of ionicity. For the 56-cell of GeSb_2Te_4 , the results are shown in [Fig. 4.11](#). The respective results for the other 56-cell systems are compiled in [Appendix D](#). First of all, one observes that in line with our expectation, the species A and B in the AB_2C_4 -Systems are cationic since the difference between Bader charge and nominal charge is negative. Charge is transferred from them to the anions, that is atoms of species C. Each species shows a narrow distribution of charges, which is related to the local structure as will be discussed in [Chapter 5](#). The two cationic species show different average levels of charge transfer.

The results of the Bader charge analyzes for all systems are compiled in [Fig. 4.12](#). For every AB_2C_4 -material, the charges of the individual atoms of each species are plotted on top of each other as open (14-cell) or filled circles (56-cell). The dashed lines connect the mean values of the latter. Due to charge conservation, the mean anionic charge (dashed orange line) denotes at the same time also the average ionicity of the bonding. For the AB_2C_4 -systems, the variation between the cationic species is resolved as they are treated as separate atoms in the calculations, while this is not the case for the intermediate compositions of the AB-systems. As here the cations are represented by mixed pseudopotentials due to the use of the virtual crystal approximation, only an average value results. Thus, for all AB-systems, the cationic

charge is equal to the negative of the shown anionic charge. One could wonder whether the use of the undistorted rocksalt-cells for the AB-systems is justified as the distortions might have an impact on the Bader charges. However, as will be shown in [Chapter 5](#), the distortions (and also the volume) have only a small influence on the Bader charges. Between the distorted and undistorted charges calculated for the 14-cell of GeSb_2Te_4 , the maximal deviation is as small as $0.06e$.

The comparison between the trends in the *average* ionicity of the bonding derived from the expensive calculations and the simple ionicity coordinate of the map, r'_σ , shows very good agreement. With the exception of SnSb_2Te_4 , both quantities lead to the same sequence of materials. The dashed orange line, representing the average ionicity, and the black line, denoting the calculated values of r'_σ , are almost parallel. Hence, the validity of the simple ionicity coordinate r'_σ is confirmed by these calculations. This is further visualized in [Fig. 4.13](#). It is interesting to note that also the bulk modulus of SnSb_2Te_4 exhibits a deviation from the sequence implied by the map. It is reasonable to assume that both quantities are related, because the bulk modulus includes a component that reflects the change in the electrostatic interaction between the ions upon variation of the volume (distance). Thus, it is immediately clear that a decrease in the ionicity should be reflected by a decrease of the bulk modulus.

A closer look at differences between the two cationic species in the AB_2C_4 -systems reveals some variations. SnSb_2Te_4 again stands out since here, the charge transfer for species B is smaller than it is for species A, while in all other cases the situation is reversed. Furthermore, the comparison shows that the charge differences of the cations are most similar in the case of SnBi_2Te_4 and SnSb_2Se_4 , while the difference is most pronounced in SiBi_2Te_4 , GeBi_2Te_4 and

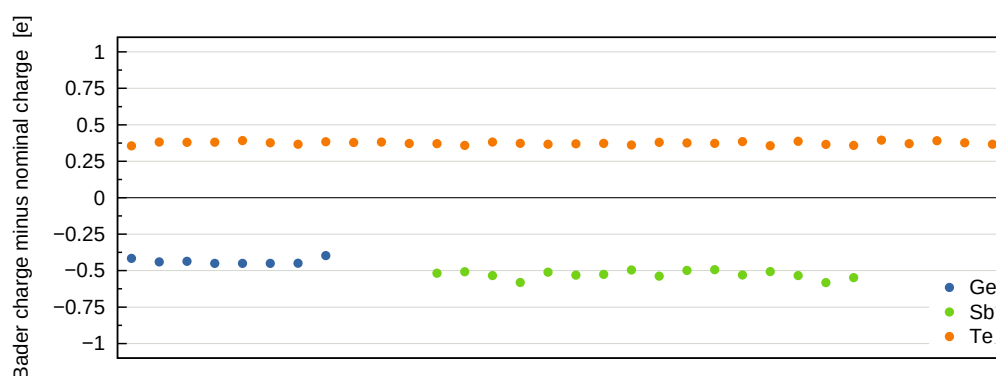


Figure 4.11: Bader charges in GeSb_2Te_4 . The sequence of atoms is the same as in [Fig. 4.7](#).

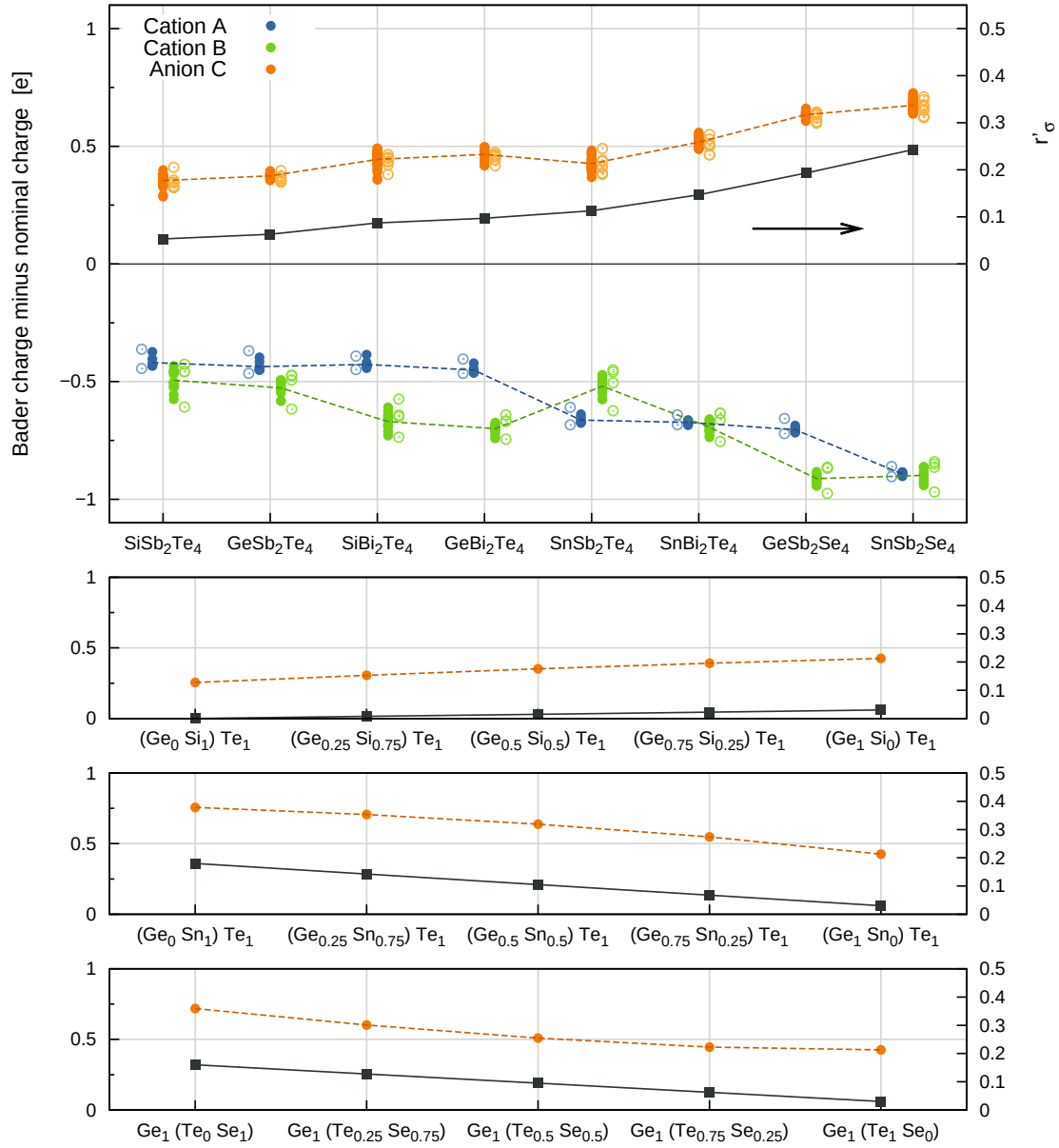


Figure 4.12.: Results of the Bader charge analysis for the AB_2C_4 -systems (top) and the AB -systems (bottom three). In the top graph, filled symbols denote the results for the 56-cells, open symbols the results for the 14-cells. To improve the readability, the symbols denoting the cations A and B, as well as open and filled symbols are slightly shifted. The dashed lines connect the mean values for the 56-cells. The 14-cell-results coincide with the extrema of the distribution in the 56-cell. For the AB -systems, only the anionic charges are shown since the cationic charges are the same save for a reversed sign (due to the use of the VCA and charge conservation). The trends in the Bader charge as a measure of ionicity is very well reproduced by the values of r'_σ (black dots/lines, right axis); with the exception of $SnSb_2Te_4$, all systems are lined up in the same sequence.

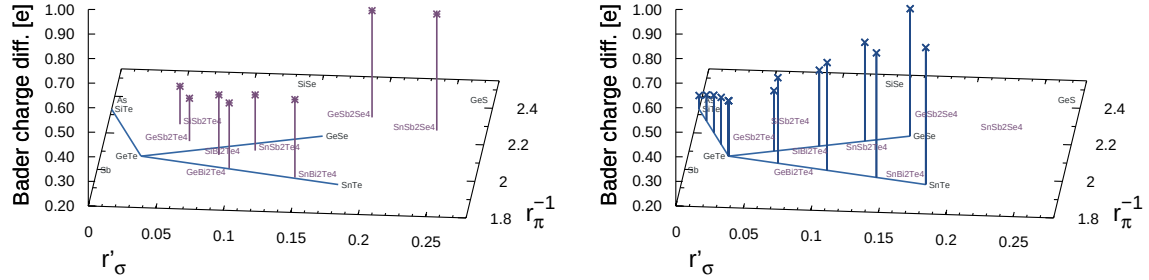


Figure 4.13.: The average difference between Bader charge and nominal charge plotted versus the map coordinates (cf. Fig. 4.1) shows the validity of the ionicity coordinate r'_σ : the differences increase as r'_σ increases.

GeSb_2Se_4 . Thus, the averaging of the cations for the calculation of r'_σ appears to be most valid for the former.

Covalency

To investigate the covalent bonds of the systems, the *electron localization function* (ELF) introduced in Appendix B.2 has been calculated for the AB_2C_4 -systems in the 56-cell⁶. The focus has been set on the variation of the ELF along the bonds, that is along the six shortest distances between each cation and its surrounding anions. Figure 4.14 shows the respective results for the instructive cases of SnBi_2Te_4 and GeSb_2Se_4 (the remaining materials are shown in Fig. D.22 in Appendix D). Here, results on simple models from some showcase material families found in the Bachelor thesis of Czaja [201] (advised within the framework of the present thesis) provide a guide for the interpretation. If there is no bond, the ELF drops to zero unless there is charge delocalization as in aluminum, where the valence charge is not contained within directed bonds but smeared over the crystal volume. The ELF remains constant in the interatomic region, adopting values slightly above $\frac{1}{2}$, the value of a homogeneous electron gas, and no shell-structure is seen. In contrast to this, only the localized valence shell of the anion is obtained for ionic systems (NaCl, CsCl). For classical semiconductors (Si and Ge from group IV, GaAs and

⁶The AB-systems have not been regarded for the analysis of the covalency since they were treated only in the undistorted structures.

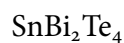
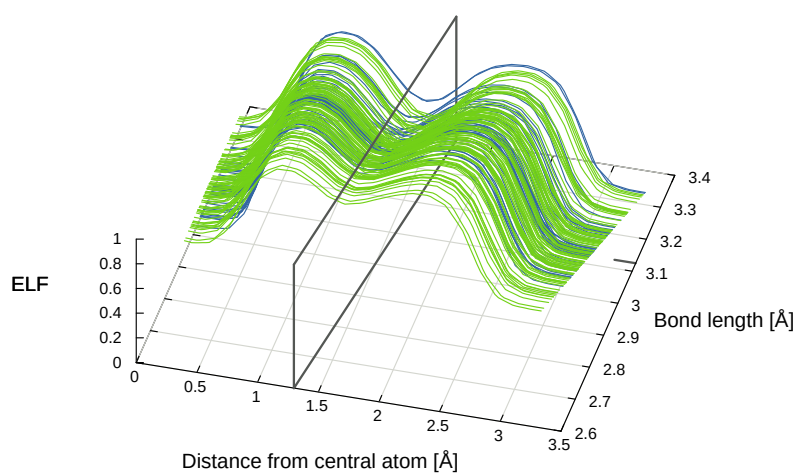
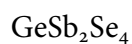
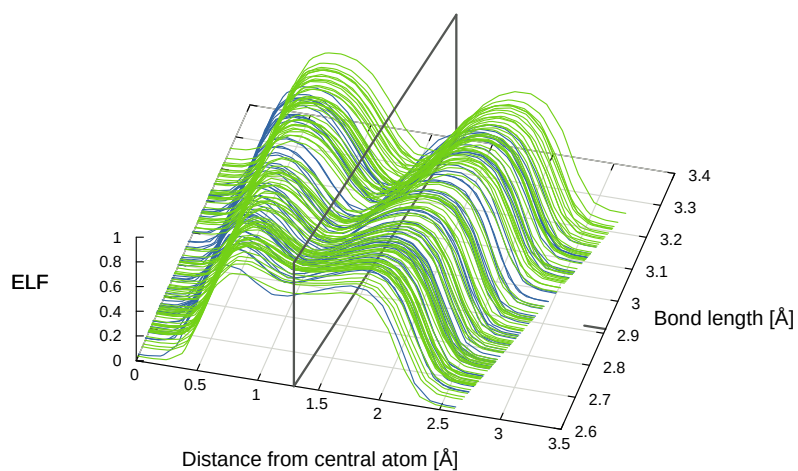


Figure 4.14.: Shown here is the electron localization function along the bonds for species A (blue) and B (green) in the AB_2C_4 -materials SnBi_2Te_4 and GeSb_2Se_4 . The thick mark on the right axis marks the unique bond-length expected for an undistorted rocksalt-structure, that is half the lattice constant. The frame shows where the bonds middles are. The more the bond lengths are split, the more the minimum value of the ELF in the middle varies; the shortened bonds are strengthened and show an increase of the ELF, while the elongated ones are weakened, their ELF minimum is decreased.

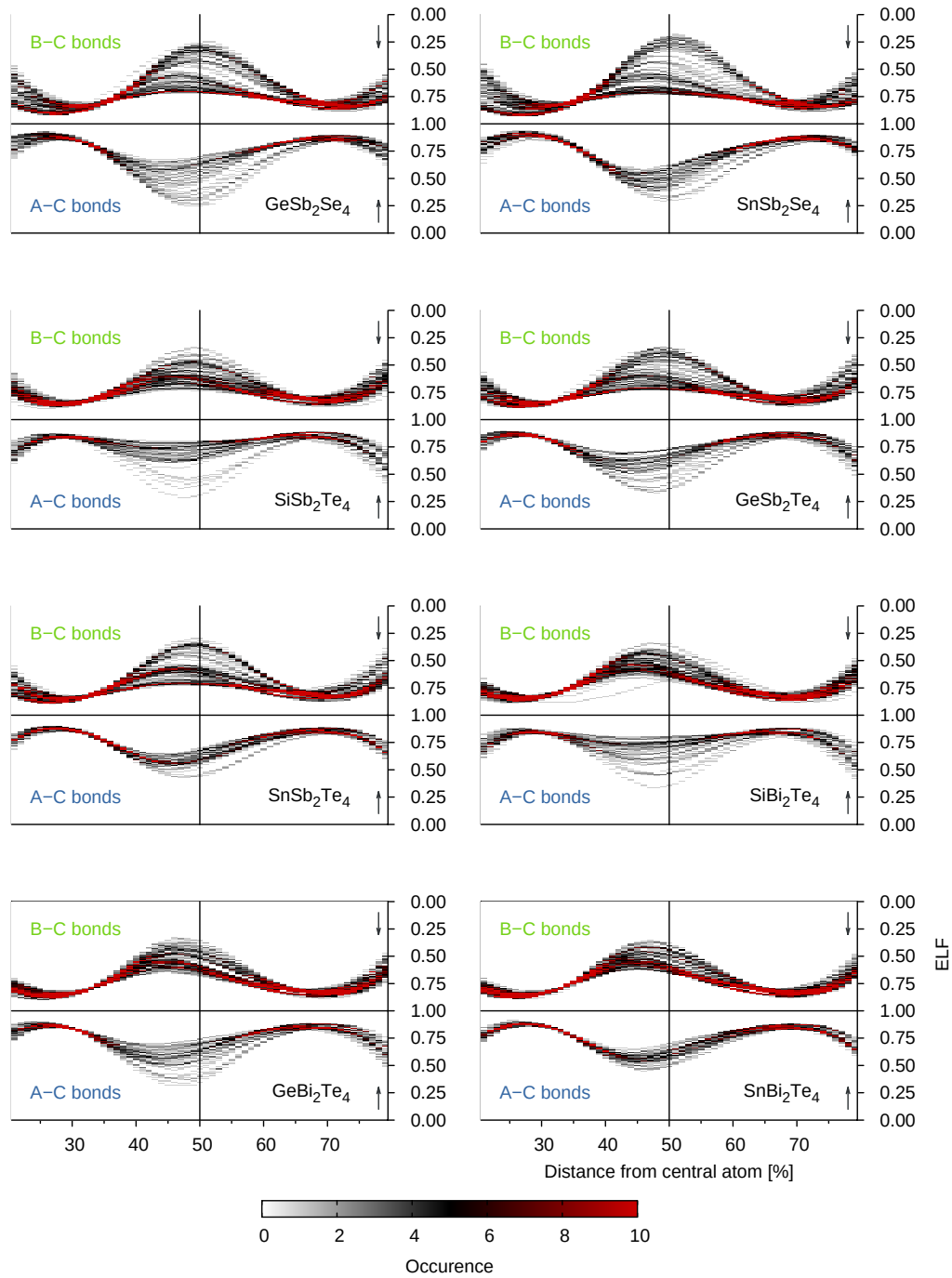


Figure 4.15.: Occurrence maps of the ELF results (Fig. 4.14 and Fig. D.22) for A-C and B-C bonds in the AB_2C_4 -systems (56-cell). Note that to improve the visual comparison between both types of bonds, the y-axis (ELF) is mirrored for the B-C bonds. From top to bottom, the distribution at the center of the bond becomes narrower, and the maximal value of the minimum decreases.

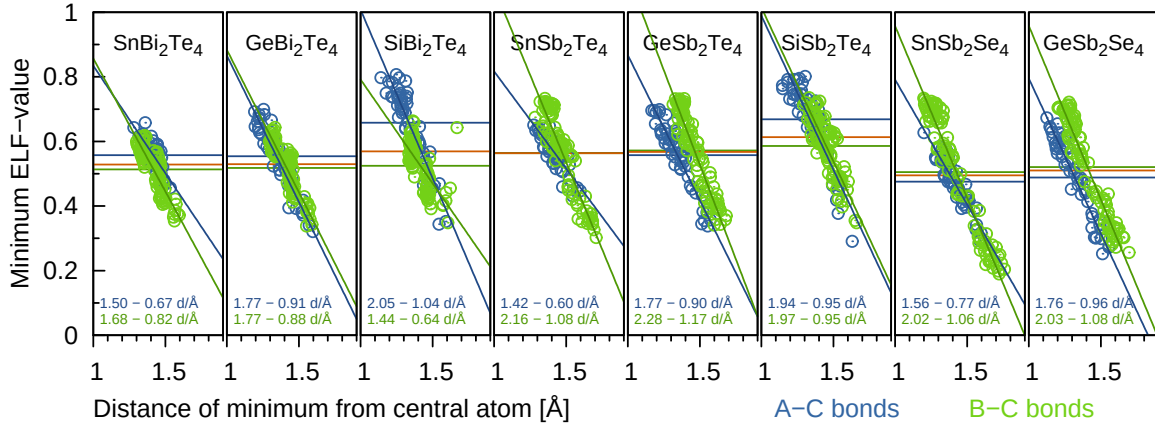


Figure 4.16.: Compiled here are the minimum values of the ELF versus their absolute positions for all bonds shown in Fig. 4.15. The horizontal lines indicate the mean value for A-C (blue) and B-C bonds (green) as well as the total mean (orange). Since the observed behavior is linear, simple fits have been performed; the resulting parameters are noted at the bottom. The width of the distribution approximately increases for the B-C bonds from left to right, that is with increasing value of the hybridization coordinate r_{π}^{-1} . The maximum value also increases slightly from left to right, saturating at about 0.7. The A-C bonds exhibit a similar behavior, yet for the systems where species A is significantly smaller than the others, in particular the silicon-containing materials, the A-C-bonds are shorter and much more saturated (i. e., the value of the ELF approaches unity). For the selenides, the mean drops as here, the back-bonds are significantly less saturated. No trend is seen in the linear fits.

InSb as representatives of III-V-semiconductors), the ELF exhibits a plateau along the bonds. Its value exceeds 0.8, which is close to the maximum of perfect localization (unity). Moreover, the amplitude of this plateau indicates the strength of the covalency; it decreases from silicon to germanium (see also ref. 202) and from GaAs to InSb. This is remarkable as it reflects the trends expected from a map for the average valence-IV materials; in Littlewood's coordinates, the ionicity r'_{σ} is about the same for GaAs (0.21) and InSb (0.20), and zero for silicon and germanium. The hybridization, r_{π}^{-1} , drops from 2.17 (Si) over 1.79 (Ge) and 1.70 (GaAs) to 1.47 (InSb). This decrease is reflected by the decrease of the plateau value, which drops by about 0.05 from silicon to germanium, and similarly from GaAs to InSb. This underlines the potential value of the ELF to quantify trends in the covalency, in particular for the present set of materials.

Coming back to the present results, we observe 'M'-shaped curves in Fig. 4.14, that approach zero at the positions of the nuclei at the ends of the lines. This is due to the fact that the valence

charge avoids the core electrons. Thus, the ELF vanishes here as the valence charge density approaches zero. The two visible maxima are related to the valence shells of the atoms. They can be associated with the s-electrons, that are only weakly involved in the bonding as is evidenced by the electronic structure; the respective states in the density of states are rather sharp as will be shown in the next section. Most important for us, though, is the behavior at around the center of the bonds, which is related to the covalent p-type bonding. Clearly, the longer the bond is, the lower the minimum halfway along the bond becomes. At the bond length that would be obtained for undistorted rocksalt-structures (marked in the figures by a line), the ELF exhibits a medium value. This is in line with the qualitative picture of an increase of the bond strength for the short bonds at the expense of the elongated bonds due to Peierls-like distortions. Since these figures show the overall bond length-dependent behavior, but hardly allow to distinguish between A-C and B-C bonds or to extract absolute values, the central portion of the same data is plotted in Fig. 4.15 as 'heat maps' (also for the remaining materials, sorted from top left to bottom right by the value of r_{π}^{-1}). For better readability, the coordinate along the bond (x-axis) is shown in percent rather than absolute numbers, and the y-axis is mirrored for the B-C bonds. For most bonds, the minima are slightly shifted towards the cations (up to 5%). Also, there is a principle trend of decreasing distribution widths from the top left to the bottom right for the B-C bonds. Figure 4.16 shows the absolute positions and values of the minima of the ELF. The minima show a fairly linear dependence on their position, which in turn depends on the bond length as Fig. 4.14 implies. Yet, no compositional trend in the parameters of the linear fits is observed. The results are closely linked to the structural results shown in Fig. 4.9. Same as there, a clear trend is observed for the B-C bonds; the higher the hybridization coordinate r_{π}^{-1} (left to right), the broader the distribution gets. For the A-C bonds, however, the behavior depends on the size of the A-atoms. The smaller they are as compared to the average value, the more the A-C bonds are distorted which results in an elevation of their minimal ELF-values.

In summary, the analysis of ELF largely confirms the trends on the map already discussed for the distortions. Small values of r_{π}^{-1} lead to less distortions and thus, more homogeneous but weaker covalent p-type bonds, that is more delocalized electrons as expected for an increase in the resonance character. Deviations from the average trend in distortion magnitude again stem from small sizes of the cations of species A; they exhibit stronger distortions than the other species.

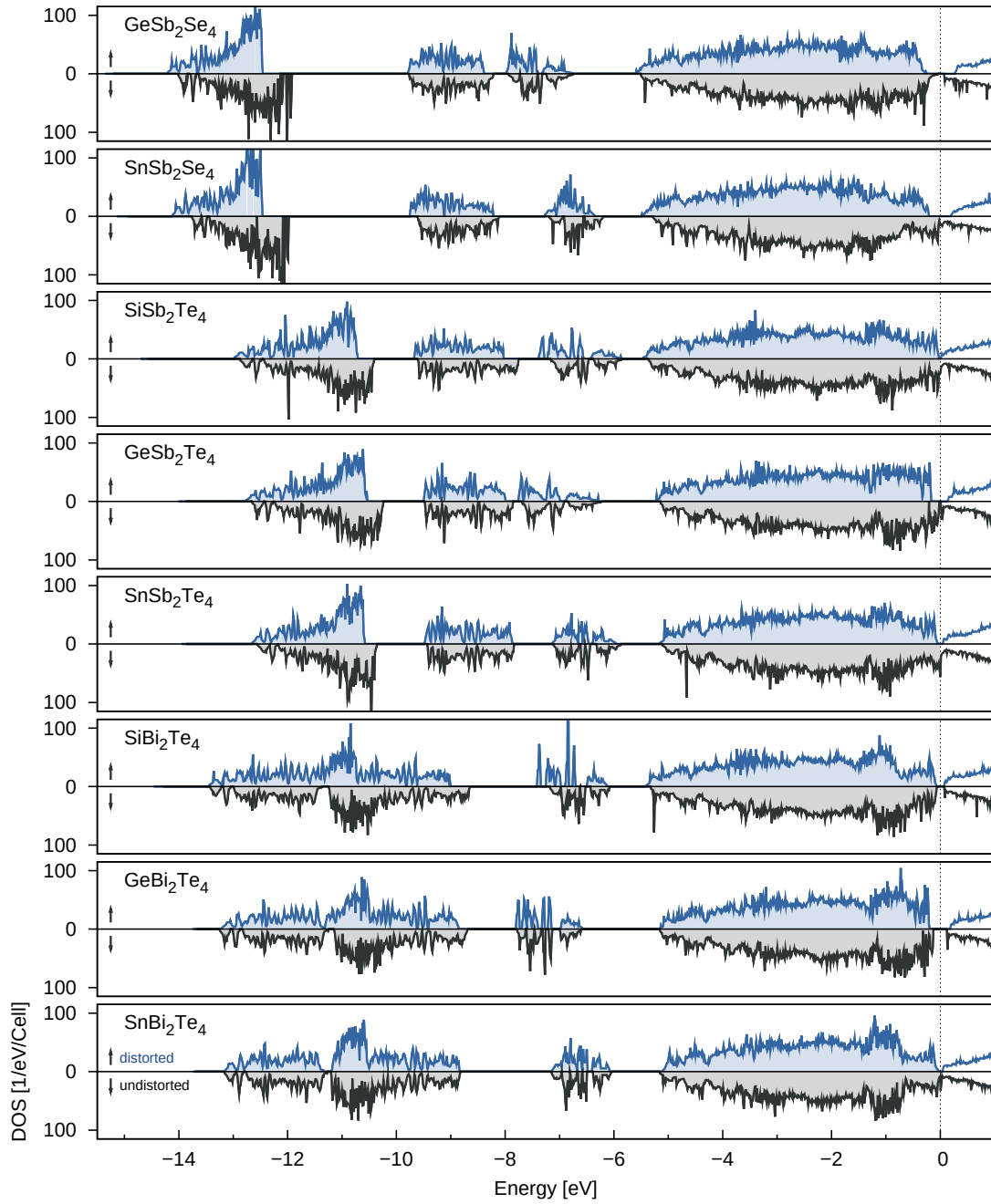


Figure 4.17.: This figure compares the electronic densities of states for the AB_2C_4 -systems (56-cells) for the fully relaxed structures (blue, pointing upwards) and the undistorted rocksalt-structures with equal lattice constant (gray, pointing downwards). The shaded area is occupied by electrons. The dashed line at $E = 0$ indicates the Fermi-level. The distortion leads to an opening of the electronic gap or increases it, if it already exists in the undistorted case, respectively.

4.2.3. Electronic States

The electronic densities of states of the AB_2C_4 -systems (56-cell) have been calculated for both the fully relaxed and the undistorted case (at the same lattice constant). The results are shown in Fig. 4.17. First, the relaxed cases shall be discussed. The shaded, occupied states have been further analyzed qualitatively by projection onto atomic orbitals (for simplicity using the qualitatively equivalent results from the 14-cells, not shown). From this procedure, it is clear that the states below -6 eV have s-character. For $GeSb_2Se_4$, for instance, the sharp peak at around -13 eV represents s-like states of species C (selenium). Towards the Fermi-level, first the s-states of species B (antimony) at -9 eV, then the respective states for species A at around -7 eV are found. The sequence of the s-like states (C-B-A) is the same for all materials except for those that contain bismuth. Here, the s-like states of the heavy species B (bismuth) coincide energetically with those of species C (tellurium) and lead to the observed energetic splitting. Only the higher peak at around -11 eV is associated solely with tellurium and stems from C-V and C-A (i. e., non-C-B) environments. In the range of -6 eV up to the Fermi level, the broadly distributed states are p-like, in line with the assumed p-type bonding. Though all species contribute to the density of states in this region, one notices that the weights of the individual contributions are located at different positions. Species B mostly contributes the energetically lowest, species A the intermediate and species C the highest states.

It is tempting to compare the distances between s- and p-like states to the differences in s- and p-radii, that is the hybridization coordinate r_π^{-1} . However, since the calculations necessarily comprise the effects of the bonding on these states, that is spreading and down-shifting (cf. results on simple tight-binding models), this is not feasible unambiguously. For instance, it is not clear what unique position the p-like states should be associated with given their extension over several eV.

Each of the materials (56-cell) exhibits a band gap in the calculations. Yet, density functional theory is well-known to systematically, sometimes severely underestimate gaps, occasionally even yielding metallic instead of semiconducting behavior. Indeed, if we compare the experimental result on $GeSb_2Te_4$ and $SiSb_2Te_4$ in Chapter 3 to the present calculations, it is obvious that the size of the gaps cannot be trusted. In the experiment, the gap opens upon silicon substitution, while here, the gap almost vanishes. Hence, the absolute values of the gaps are not evaluated. However, we can compare the *difference* between the distorted and the undistorted case, as both are equally affected by this weakness of density functional theory. Clearly, the distortion leads to an opening (or increase) of the gap, in line with the Peierls-model (see Section 3.3). Materials with small distortions, such as $SnBi_2Te_4$ and $GeBi_2Te_4$, exhibit small

changes of their electronic states, while significant changes can be seen in the selenium-systems. Interestingly, especially the s-like states of selenium are lowered by the distortion, which is indicative for their involvement in the bonding.

4.3. Conclusions

A large number of materials, that are located in the region of the map that contains phase-change materials, have been studied by means of density functional theory-calculations. The simulation results largely verify the validity of the map as a design-scheme. The ionicity coordinate r'_σ is very well reflected by the Bader charges. No simple translation of the hybridization coordinate r_π^{-1} can be derived from the calculations, yet the level of distortion varies along the map as expected, thus confirming the role of this second coordinate. At the same time, the ELF as a tool to quantify the covalent bonding reflects the qualitative expectations. The stronger the distortions from octahedral rocksalt-positions, the more electrons are localized in fewer, shorter and stronger bonds at the expense of the elongated ones. Materials with less distortions exhibit more homogeneous bonds where electrons are less localized, in line with the expectation of an increase in the resonance character. The well-known gap-problem prevents the analysis of variations of the electronic gap along the map coordinates.

Deviations between calculation results and expectations from the map mainly arise if the cations (anions), which are averaged for the calculation of r'_σ and r_π^{-1} , are very different in size, or to be more precise, if there is a species that is significantly smaller than the average. Such elements show stronger distortions and thus weaken the resonance character more than expected. Hence, one needs to be aware of such effects in the application of the map.

Based on the results of the present chapter, further studies are motivated; principal limitations of density functional theory-calculations call for either experimental studies or calculations that compensate for the band-gap issue (such as GW-methods). Furthermore, the variations in the local structure are of interest; unlike in the simple binaries, there is an interesting variation in the behavior of atoms of the same species, which is to be investigated in the next chapter. Also the impact of the distortions on the lattice dynamics will be subject to the studies presented on the following pages.

5. Local Atomic Structure and Lattice-Dynamics

In the preceding two chapters, a simple design-scheme in form of a map has been developed. Furthermore, its validity has been investigated by means of density functional theory-calculations. This map correctly describes the principal material behavior, nevertheless, the local atomic distortions deserve a closer look. Several key questions arise in this context, in particular: *What do the local atomic distortions in phase-change materials look like? What parameters govern the shape of the local atomic distortion patterns?* Moreover, a more complete understanding does not only require the assessment of the static distortions a material system ends in, but also a more profound modeling of the overall shape of the potential the atoms experience: *What does the energy landscape look like? How are the lattice-dynamics and related material properties affected?* It is the aim of this chapter to illuminate these aspects of phase-change materials and to relate them to other material classes such as ferroelectrics and thermoelectrics.

5.1. Volume-Dependent Distortion Patterns

For the study of distortion patterns, it is advantageous to do this volume-resolved. One of the reasons is fairly simple; as we will see, distortions increase as the volume increases, and thus, patterns become clearer. Moreover, information on the volume- (or pressure-) dependence is also of interest since it yields additional information on the bonding. As a starting point, GeTe shall again serve as a simple prototype material to study the principal effects, before we turn to the more complicated case of the ternary compound GeSb_2Te_4 .

The basic structure of GeTe at around the equilibrium – Peierls-like distortions lead to a relative displacement of the sublattices in the $[1\ 1\ 1]$ -direction and thus, a 3+3-split of the bonds – has been presented in the preceding chapters. To resolve the volume-dependence, density functional theory-calculations on the same model as presented in [Chapter 3](#) have

been performed¹. The results are presented in Fig. 5.1. Below a critical volume of about $47 \text{ \AA}^3$, which corresponds to a pressure of $\sim 10 \text{ GPa}$, the Peierls-like distortions disappear. The most simple explanation is that the space required for atomic distortions vanishes upon compression. However, the atomic distance at the bifurcation point, where the split into short and long bonds occurs, amounts to $\sim 2.85 \text{ \AA}$ and thus is larger than the sum of the covalent radii ($1.22 + 1.37 = 2.59 \text{ \AA}$ [203]). Even if the typical error of the GGA-PBE exchange correlation functional ($\sim 2\%$) is considered, the bifurcation point is located at a distance that is too high to be in line with a pure geometrical argument. Hence, it appears likely that it is not just the geometry, but characteristics of the bonding that rule the position of the bifurcation point. Possible explanations for a shift to higher distances comprise the ionicity or an increasing metalization/delocalization of electrons out of directed bonds, which reduces the energy gain by distortions.

Above the critical volume, the displacement coordinate x_0 increases above 0.5 in a root-like fashion and concurrently, the cell angle α decreases (if allowed in the relaxation, filled symbols). It is interesting to note the shape of the volume-dependence of the bond lengths; the short bond-length exhibits a hook-shaped dependence. After the bifurcation, it decreases in a very limited region, while it steadily increases for most volumes, in particular at around the equilibrium volume. This slight increase can probably be linked to a result of Section 5.3, which is an equally slight increase in charge transfer/ionicity (leading to repulsion). However, the increase is only small. The length of the long bonds, on the contrary, increases significantly. So the structure adapts to volume expansion by displacing the sublattices such that the short bond length remains approximately constant.

The Murnaghan-fits for the undistorted rocksalt-structure (red) and the fully relaxed structure (blue) show that just as for the AB_2C_4 -tellurides in Section 4.2.1, the relaxation leads to volume expansion. Furthermore, the additional free parameters x_0 and α lead to a decrease of the curvature; while the bulk modulus amounts to 49 GPa for the undistorted case, it drops to 36 GPa for the fully relaxed structure.

In summary, the study of GeTe indicates that Peierls-distortions decrease with decreasing volume and eventually vanish at around 10 GPa . Both long and short bonds increase as the

¹Here, the effective cut-off energy is significantly larger due to the use of the ABINIT-parameter `dilatmx=2.0`. Hence, the cut-off energy effectively amounts to $4 \times 20 \text{ Hartree} = 2177 \text{ eV}$ throughout these calculations. A smearing of $T_{\text{smear}} = 0.001 \text{ Hartree} = 316 \text{ K}$ in combination with the unchanged $14 \times 14 \times 14$ - k -point grid ensures reliable results also in the case of vanishing gaps.

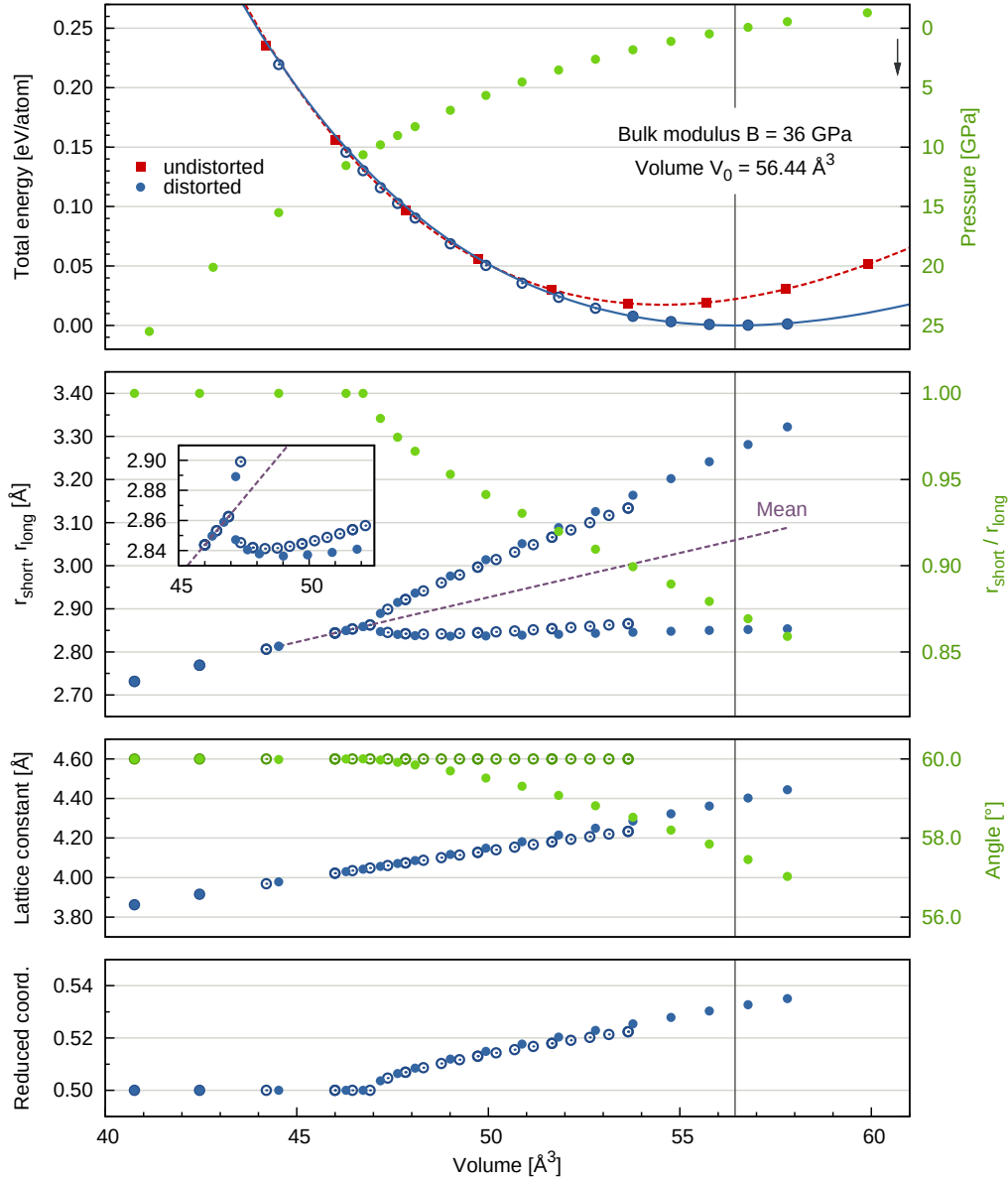


Figure 5.1.: This figure compiles data on the volume-dependence of the structure of GeTe. The top figure shows the dependence of the total energy on the volume for the fully relaxed (blue) and the undistorted rocksalt-structure (red). For the former, the results of the Murnaghan-fit (filled symbols denote the considered data points) as well as the pressure (axis reversed, green) are also indicated. The remaining three graphs illuminate the volume-dependent bond lengths as well as lattice geometry (a , α) and distortion (x). Here, open symbols refer to cubic cells ($\alpha = 60^\circ$), filled symbols to rhombohedrally distorted cells. The Peierls-like distortion occurs at a critical unit cell volume (pressure) of about $47 \text{ \AA}^3$ (10 GPa). Notably, the inset shows that the short bond length has a hook-shaped volume-dependence.

volume is expanded, yet the distortion minimizes the change for the short bond, which remains almost constant. The qualitative result is unaffected by whether the cell angle is allowed to decrease from the cubic value of 60° or not.

Next, the behavior of the ternary material GeSb_2Te_4 shall be investigated analogously. Both a 56-cell and a 14-cell model are taken into account². For the computationally expensive 56-cell, relaxations for four volumes could be performed, while the smaller model allowed for calculations with a significantly larger range and resolution of volumes. Yet, for this model the convergence with respect to the k -point-grid becomes worse as the volume is compressed. The convergence of the total energy, however, remains within a 10 meV/atom-frame down to $a = 5.6 \text{ \AA}$. This is sufficient for the mostly qualitative analysis we are looking into. The cell angle has been fixed to the cubic value (see Section 5.2). Thus, the cell volume depends only on the lattice constant.

The results of the Murnaghan-fits are shown in Fig. 5.2. Again, the comparison between undistorted (red) and distorted case (blue) shows that both a volume expansion and a decrease of the bulk modulus result from the atomic distortions. Both the 56-cell and the 14-cell model lead to very similar results, and agree qualitatively with the case of GeTe. Though, the bulk moduli are rather small. For the 14-cell, it drops from 45 GPa to 20 GPa if atomic distortions are allowed. For the 56-cell, it is even smaller (15 GPa). These values are smaller than experimentally reported ones (ref. 48: $41 \pm 2 \text{ GPa}$), probably due to the characteristics of the exchange- and correlation functional.

The most striking result is that unlike in the case of GeTe, relaxed and unrelaxed curves do not coincide for small volumes. Instead, the blue data points even increasingly depart from the red curve. Since atomic relaxations are the only difference between the blue and the red curve, this means that in contrast to GeTe the distortions do not vanish. The effect of the compression on the structure is shown in Fig. 5.3. Starting from the largest volume, the decreasing width of the first peak clearly signals a decrease of the level of distortion. However, the width of the peak remains finite, while a perfect rocksalt-structure would yield a unique bond length. Moreover, below a critical lattice constant of $5.5 \text{ \AA}$ ($\sim 24 \text{ GPa}$), a significant structural change occurs. Rather than exclusively cation-anion (Ge-Te and Sb-Te) bonds, now also homopolar bonds

²Using the same pseudopotentials for germanium and tellurium as for GeTe. These two as well as the employed antimony-pseudopotential have been created and discussed by Welnic [163]. Therefore, the results differ slightly from those in Chapter 4, where the pseudopotentials from the ABINIT-website have been employed. The convergence parameters are the same as in Chapter 4.

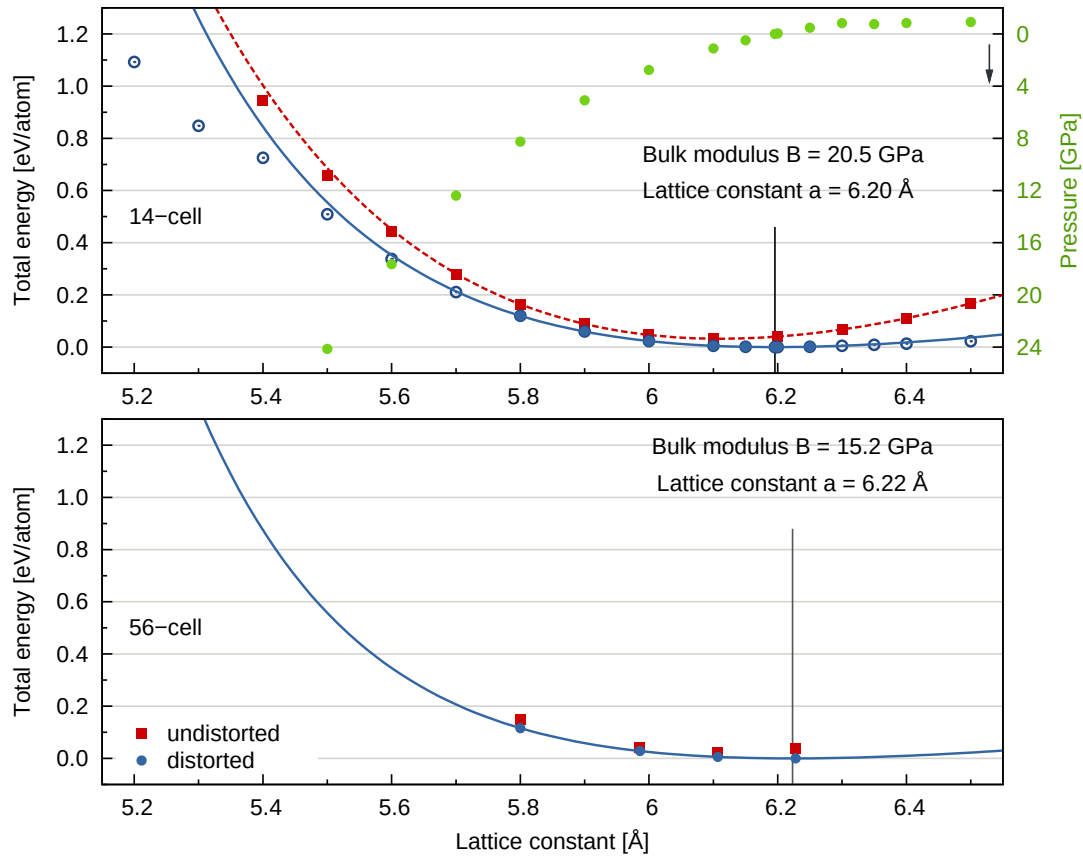


Figure 5.2.: This figure compares the volume-dependence of the total energy of the 14-cell (top) and the 56-cell model (bottom) of GeSb_2Te_4 . Since here the volume is only a function of the lattice constant, the lattice constant for the conventional unit cell is employed as x-axis. The figures compare the distorted (relaxed atomic positions) and undistorted (unrelaxed rocksalt-positions) structure. The behavior upon compression clearly deviates from the one observed in GeTe in Fig. 5.1; the distorted and undistorted curves do not coincide.

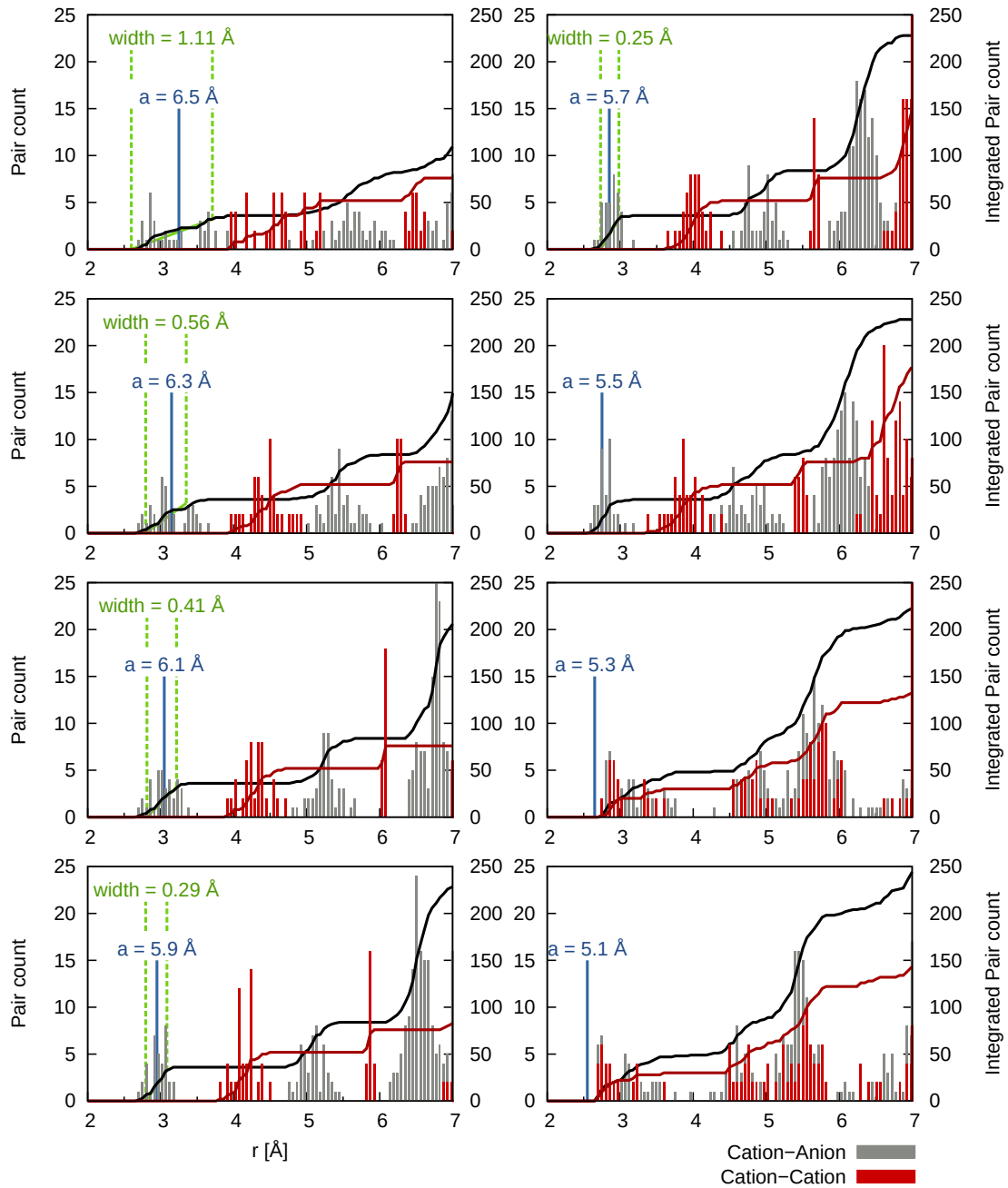


Figure 5.3.: The volume-dependent pair histograms for GeSb_2Te_4 in the 14-cell reveal two interesting features. On the one hand, a decrease of the width of the first peak with decreasing volume is observed, in line with a reduction of the level of Peierls-like distortion. On the other hand, a dramatic change of the structure occurs below $5.5 \text{ \AA}$; as can be seen from the intermixing of the peaks of the cation-anion and the cation-cation histograms, the cations start to be involved in bonds to each other.

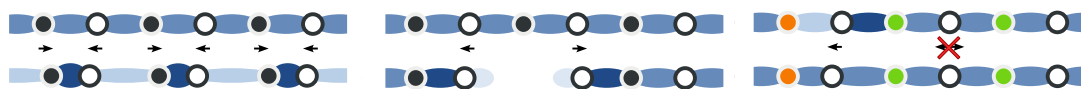


Figure 5.4.: From left to right, three principle mechanisms of atomic distortions are shown schematically. The figure on the left hand-side shows the familiar Peierls-like distortions. For the AB_2C_4 -systems, two additional mechanisms occur. The graph in the middle indicates the impact of intrinsic vacancies, from which the adjacent ions are displaced for electrostatic reasons (indicated by arrows). Finally, the figure on the right hand-side illustrates the effect of symmetry-breaking due to chemical disorder on one sublattice. An anion with equivalent neighbors on each side (both green) will not be affected by this effect. If the neighbors are different (green and orange), however, a force results both due to electrostatic reasons, if the charge transfer is different, but also because of the covalent bonds; most likely, the two bonds to different species are not in resonance if their lengths are equal.

and bonds between the cations form. This is in line with previous reports on pressure-induced amorphization as presented in [Section 2.2.3](#). Our main concern here, however, is to find out *how* and *why* the distortions in the rocksalt-like structure differ from those in GeTe, and why they do not vanish upon compression.

In the case of GeTe, the undistorted structure represents a local extremum in the potential energy surface (or 'energy landscape') as seen in [Fig. 4.6](#). For the AB_2C_4 -systems, on the contrary, this is generally not the case. Here, the undistorted structure is not a local maximum. In the calculations this is revealed as forces act on the atoms. The origin of this difference between AB- and AB_2C_4 -materials lies within the sublattice occupation; in the binary material, the crystal is symmetric about every site, while the chemical disorder in the AB_2C_4 -systems breaks this symmetry. To aid this argument, take a look at [Fig. 5.4](#). As is described in the caption, the step from binary to ternary systems with intrinsic vacancies brings about additional forces. This has important consequences; the structure in which the resonance is maximized is no longer the undistorted rocksalt-structure. Hence, it does not coincide anymore with the structure in which also the enhancement of the transition matrix elements, that has been argued to arise for geometric reasons (alignment of p-orbitals, see [Section 3.3](#)), is maximized. Consequently, the resonance character should be more pronounced in binary materials than in equivalent ternary materials as only the former can maximize the resonance of the bonds and transition matrix elements simultaneously. Yet, we cannot exclude that the inevitable Peierls-like distortions will reverse the situation.

To summarize what we have found to this point, the AB_2C_4 -materials are very similar to the binary materials in their average behavior. Both show Peierls-like distortions that are diminished by compression of the volume. But in the ternary materials, additional forces due to intrinsic vacancies and chemical disorder lead to distortions from rocksalt-positions. Hence, we now understand why the distortion is not completely removed in $SnBi_2Te_4$, for instance, where the first peak in the pair histogram exhibits a finite width although this material lies far in the 'cubic' region of the map (see Fig. D.15). Also, these considerations provide us with a hint on why the distortions in the AB_2C_4 -materials do not follow a simple pattern; we have to take into account the local environment of the individual atoms. For the remainder of this section, we will therefore be concerned with identifying correlations between the local distortion pattern of an atom and its surrounding.

Before, though, the question needs to be addressed how strong the 'new' distortion mechanisms are compared to the Peierls-mechanism that we have discussed so far. Since all mechanisms act necessarily simultaneously, we cannot decompose the observed distortion into individual contributions. However, it can be expected that the distortion for electrostatic reasons is particularly large in $SnBi_2Te_4$ due to its high ionicity. Nevertheless, here the width of the bond length-distribution is narrowest. Also the other mechanism, that restores the resonance of covalent bonds, can be expected to play only a limited role; the inequality of bonds of equal length in the case of different neighbors would facilitate a strengthening of fewer than six bonds at the expense of the others *without* displacement from the rocksalt position. So rather than increasing the amplitude of local distortions, this mechanism should decrease it. Yet, we see the expected broadening of the bond distributions along the coordinates of the map. In summary, these additional distortion mechanisms appear to have an impact on the distortion patterns, but little effect on the strength of the distortion, which is dominated by the Peierls-mechanism.

Finally turning to the investigation of distortion patterns, we have to take a look at the atom-resolved bond length distribution. For the 56-model of $GeSb_2Te_4$, it is shown in Fig. 5.5 for the largest calculated volume, $a = 6.228 \text{ \AA}$, where the patterns are clearest. The results for the remaining three volumes are compiled in Appendix E. They imply that the basic pattern is mostly independent of the volume. In the present figure, three-digit numbers are given for each cation, that describe the local environment. The first shell contains only tellurium atoms, so the variation must result from the cation sublattice occupation in the higher shells (second or fourth shell). Hence, these number give the count of germanium-atoms, antimony-atoms and intrinsic vacancies in the fourth shell which contains the sites behind the neighboring tellurium atoms (following the Cartesian directions, at a distance of around a). A clear correlation is

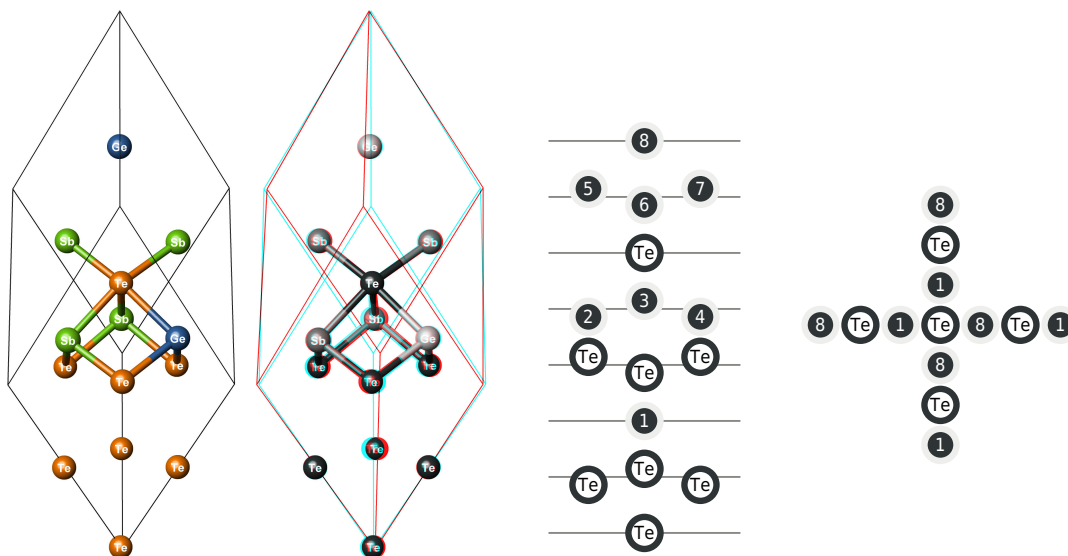


Figure 5.6.: The two plots on the left show the sublattice occupation of the 14-cell model. The third figure introduces a numbering-scheme for the lattice sites. Germanium occupies the sites 4 and 8, antimony 2, 3, 5 and 7, and intrinsic vacancies are located at the sites 1 and 6. The figure on the right visualizes that along all Cartesian directions, there is always an alternation of two of the lattice sites, respectively. Consequently, the fourth shell-occupation is isotropic in the 14-cell model, while it can be anisotropic in the 56-cell.

The characteristic numbers in Fig. 5.5 are all even. This is due to the fact that the 56-cell, which is a $2 \times 2 \times 2$ -supercell built from the conventional NaCl-cell, has four lattice sites in each Cartesian direction (x , y and z). Thus, due to the periodic boundary conditions, the cation in the fourth shell is the same in both positive and negative directions. The respective cation can be different in each of the three Cartesian directions, though. Hence, the 56-cell is the smallest cell that contains a quarter of the important fourth shell within its dimensions, which enables the investigation of the impact of its occupation *and* allows for it to be *anisotropic*. In contrast, in a conventional cell with only eight lattice sites, the cation in the fourth shell would be a periodic image of the cation itself. In a larger, $3 \times 3 \times 3$ -supercell, also the effect of unequal cation sublattice occupants in positive and negative direction could be studied, but such a cell is presently beyond the computational possibilities.

Now that we have identified that the representation of different fourth shell-occupations is a necessity for cells that are ought to represent the structure fair enough for distortion patterns

to be studied, the question is whether the 14-cell is a suitable model. Therefore, its structural features are presented in Fig. 5.6. As is shown, this small cell allows to study the impact of the fourth-shell occupation just as the 56-cell, but here, this shell is *isotropic*. The atomic alternations along the Cartesian directions, that result from the chosen cell setup, are compiled in Tab. 5.1. This cell contains most of the possible alternations, but not the less probable ones such as 'V-Te-V-Te' (as mentioned before, this is energetically very unfavorable) or 'Ge-Te-Ge-Te'. Consequently, this cell allows no more and no less than the study of extrema of the structure.

Table 5.1.: Local environment of each of the cations in the 14-cell. Along the Cartesian directions, there is an alternation between the marked cations. For instance, the first row states that there is an alternation between Ge1 and a vacancy (Ge1-Te-V-Te-Ge1 ...). Each of the 2nd-shell sites is seen twice by the central atom.

Central atom	2nd shell (12 atoms)	4th shell (6 atoms)
Ge1	Ge2, Sb1, Sb2, Sb3, Sb4, V	V
Ge2	Ge1, Sb2, Sb3, Sb4, V, V	Sb1
Sb1	Ge1, Sb2, Sb3, Sb4, V, V	Ge2
Sb2	Ge1, Ge2, Sb1, Sb3, V, V	Sb4
Sb3	Ge1, Ge2, Sb1, Sb2, Sb4, V	V
Sb4	Ge1, Ge2, Sb1, Sb3, V, V	Sb2

The variation of the six bonds of each atom in the 14-cell is presented in Fig. 5.7. Notably, the atoms exhibit different local structures; above around 6 Å, Ge1 and Sb3 show significantly less splitting than the other cations. Here, the distortion is 2+2+2-like for Ge1 and 1+4+1-like for Sb3, while it is more or less 3+3-like for the remaining cations. Below 6 Å, the distortion increases for Ge1 and Sb3 while it clearly decreases for the other cations. Furthermore, for these two atoms the average bond length is smaller than $a/2$ above the critical value, and larger below, while the remaining cations split symmetrically around this value.

It is little surprising that Ge1 and Sb3 stand out; these two atoms have intrinsic vacancies in the fourth shell, while this is not the case for the remaining cations. The fact that the latter are rather similar despite the differences in the occupation of the 2nd and 4th shell emphasizes that intrinsic vacancies in the fourth shell are most important for the distortion pattern. Compared to the results on the anisotropic 56-cell, where many of the cations have at least two vacancies in the fourth shell, the isotropic 14-cell model shows a pronounced preference of 3+3-type splittings, as all cations have either six or no vacancies in the fourth shell. It is interesting to note

that unlike in GeTe, the short bond lengths seem to slightly decrease rather than to increase upon expansion. Though, the change is very small in both cases, showing that stabilizing the short bond lengths is a driving force for the distortions in both binary and ternary materials.

Summarizing the present section, we have obtained some important results on the distortion patterns and their volume-dependence in phase-change materials. First of all, we have found that generally, compression decreases the level of Peierls-like distortions, which should yield an increase of the resonance character. Though, they only vanish in the binary systems, while the AB_2C_4 -systems exhibit a more peculiar behavior owing to the presence of intrinsic vacancies and chemical disorder due to random sublattice occupation. Consequently, the level of distortion is always finite in the pressure-range studied. The atomic distortion patterns are sensitive to the local environment, in particular to the occupation of the fourth shell. The presence of intrinsic vacancies in this shell leads to deviations from displacements in the $[1\ 1\ 1]$ -direction, while in the intrinsic vacancy-free binaries only these displacements are present. Thermally induced ordering of the cation sublattice, in particular the formation of a vacancy layer (see [Section 2.1](#)), must thus be expected to have a significant influence on the local distortion patterns.

Based on these results, it is interesting to analyze the bonding in more detail, that is to quantify ionicity and covalency, and to relate them to the local distortion pattern. Before, however, we shall be concerned with one apparent difference between binaries and ternaries that has not been addressed yet; why is there a rhombohedral distortion in GeTe, but none in GeSb_2Te_4 ?

5.2. Rhombohedral Distortion of the Unit Cell?

The 14-cell model of GeSb_2Te_4 resembles a supercell of the primitive rhombohedral unit cell of GeTe. Thus, it allows to investigate the energetics of a rhombohedral distortion of the cell angle α . To do so, full relaxations for various fixed angles have been performed. The results are presented in [Fig. 5.8](#). In these calculations, it has been found that the relaxation is not unique, but depending on the initial structure, two different minima are obtained. These two structures favor different cell angles. As is indicated by the auxiliary lines, one favors a rhombohedral distortion just like GeTe, whereas the other does not. At around the cubic angle ($\alpha = 60^\circ$), both curves intersect. The calculated energy difference between the cubic and the rhombohedral case, though, is very small, amounting to only about 6 meV/atom. Despite the

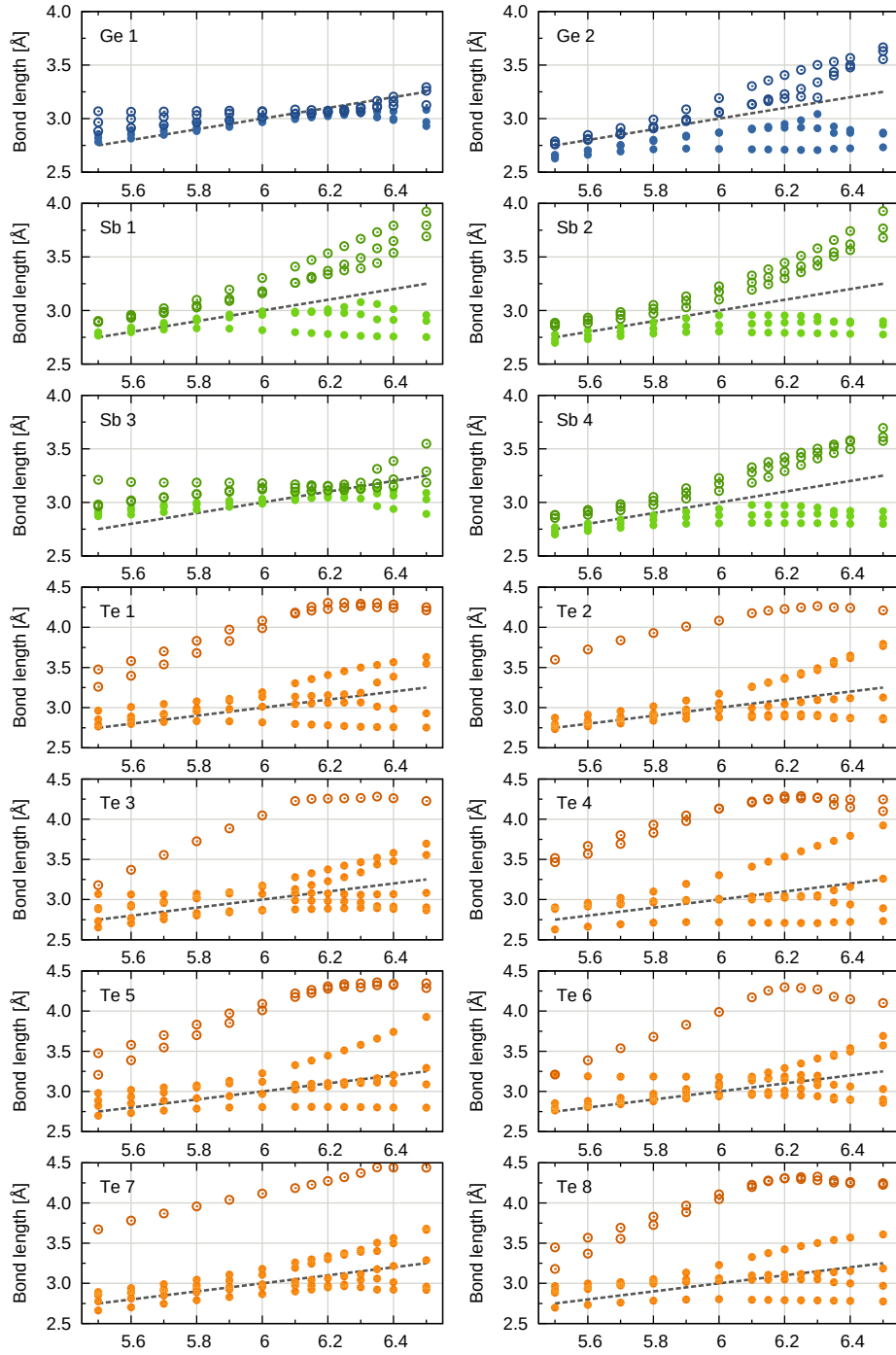


Figure 5.7: Shown is the variation in the six shortest nearest neighbor-distances of all atoms in the 14-cell representing GeSb_2Te_4 upon variation of the lattice constant a . For reference, the gray dashed line indicates the bond length expected for undistorted rocksalt-structures ($a/2$). The results are discussed in the text.

different behavior of both structures, the bond lengths (not shown) appear similar and provide no hints at the origin of this effect.

To resolve the difference between the two relaxations, we have to remind ourselves of why a rhombohedral distortion occurs in GeTe. In this simple binary material, a collective, relative displacement of the two sublattices in one $[1\ 1\ 1]$ -direction characterizes the equilibrium structure at low temperatures. The cell stretches along this direction (and squeezes). If, however, the displacement would not be collective, but random (i. e., every atom of one sublattice would be displaced in one of the equivalent $[1\ 1\ 1]$ -directions randomly) such a cell distortion would be forbidden by symmetry. Transferring these arguments to the present case, a rhombohedral distortion of the unit cell could be linked to an *average* $[1\ 1\ 1]$ -type relative displacement of the sublattices. Indeed, the calculation of GeTe-like mean reduced coordinates for the two sublattices, with the coordinate of the tellurium-sublattice set to zero, yields different results for the two relaxed structures. Take for instance the case of $\alpha = 59.5^\circ$, where data for both structures exists. The projection of the mean reduced coordinates of the cation sublattice onto the $[1\ 1\ 1]$ -axis amounts to $x = 0.583$ for the energetically most favorable structure. In contrast, the same procedure for the less favorable structure results in a value of only $x = 0.539$. Hence, the structure that favors a rhombohedral distortion of the cell angle indeed exhibits a more pronounced mean distortion in the $[1\ 1\ 1]$ -direction than the other³.

By the time of these calculations, no experimental confirmation of a rhombohedral distortion of the metastable phase was reported. Consequently, all calculations employing 14-cell models have been performed using the energetically most favorable structure for a fixed angle of $\alpha = 60^\circ$ (cubic case). Only very recently, a rhombohedral distortion of the metastable phase was obtained for epitaxially grown samples of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ by Shayduk et al. [204]. The deviation from the cubic angle there, though, is much smaller than the one in the above calculations (below one degree). In summary, it can be concluded that either this group is the first to investigate the structure with the resolution required to obtain this angular deviation, or their sample preparation leads to a local structure that differs from previous experiments and thus favors a rhombohedral distortion. The presented calculations show what this peculiarity about the local structure needs to be: a preference of local distortions in a common $[1\ 1\ 1]$ direction. The fact that the calculated angle deviates more from 60° than the one found experimentally

³Note that we have not included the vacancies in above calculations of the mean of the position of the cation sublattice. If their reduced coordinates are assumed to be unaffected by the atomic distortion, the numbers read $x = 0.524$ and $x = 0.513$, respectively, consistent with the above conclusion.

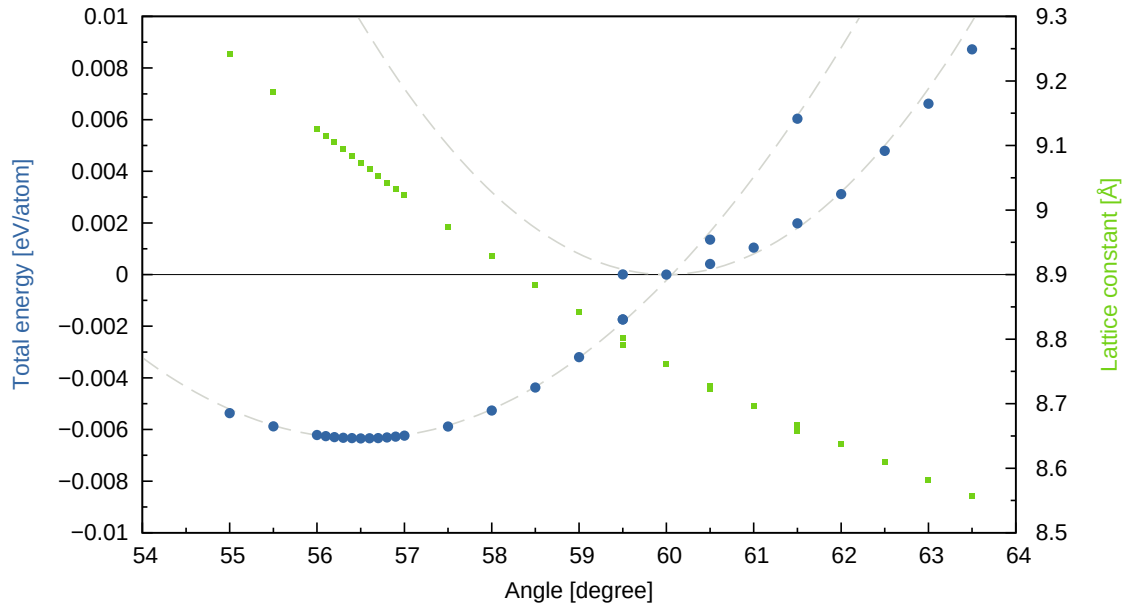


Figure 5.8.: Upon variation of the cell angle of the 14-cell model representing GeSb_2Te_4 from the cubic value of 60° , a peculiar behavior is obtained. As indicated by the gray auxiliary lines, there are two possible local structures, one of which yields a minimum at the cubic lattice angle, while the other favors a rhombohedral distortion of the cell just as in the case of GeTe .

indicates that – in line with the results of the structural investigation presented in the preceding section – the 14-cell over-represents distortions in the $[1\ 1\ 1]$ -direction (or equivalently, 3+3-like splits). As the local distortion is correlated to the distribution of the intrinsic vacancies in the calculations, a peculiar distribution of these in the epitaxially grown samples is implied by the occurrence of a rhombohedral distortion of the cell.

Another interesting facet of this finding concerns the aspect of ferroelectricity. Due to the displacement of the sublattices, GeTe is a ferroelectric material with a remnant polarization $\underline{P}$. Would the distortions be randomly orientated, the macroscopic polarization would vanish in the same way as the rhombohedral distortion of the cell angle. If, however, such a distortion is obtained for samples of GeSb_2Te_4 or $\text{Ge}_2\text{Sb}_2\text{Te}_5$, it is reasonable to assume that they also exhibit a remnant macroscopic polarization. This calls for future studies, both experimentally (measure $\underline{P}$ versus α) and theoretically (Berry phase-calculations of the polarization [151]).

5.3. Impact of Volume-Variations on the Bonding and the Electronic States

Variations of the volume affect the distortion, as we have seen before, and must thus be expected to affect the bonding and the electronic states. To investigate these effects, this section presents the volume-dependence of the ionicity, the covalency of the bonds and the electronic states, adopting the procedure introduced in [Section 4.2.2](#).

For the ionicity, the Bader charges of GeSb_2Te_4 in the 14-cell have been calculated for a wide range of volumes⁴. The results are shown in [Fig. 5.9](#). First of all, if one compares the total ionicity at the equilibrium volume (represented by the mean charge difference of the anions, orange) between the distorted and the undistorted case (open blocks), little difference is observed. Hence, we can conclude that the charge transfer is mostly unaffected by the distortion. This is further supported by the observation that also the volume has only a small effect; though the distortion changes significantly upon variation of V , the Bader charges decrease only slightly upon compression. The weak dependence can be associated with an increasing metalization of the material. Only below about 5.5 Å, a sudden drop of the ionicity is observed. It occurs concurrently with the major structural change away from the rocksalt-like coordination, that we have seen before in [Fig. 5.3](#). Thus, the drop is due to the formation of atomic neighborhoods other than Ge-Te and Sb-Te, in particular the occurrence of homopolar bonds, which leads to less charge transfer.

If not only the average behavior is considered, but also the variation among the cations, a notable observation can be made. The two atoms Ge1 and Sb3, that we have previously identified as the least distorted atoms with intrinsic vacancies in their fourth shell, exhibit the highest differences between their nominal and the Bader charge. This result remains in the undistorted case. Thus, it can be concluded that the variation in charge among the cations depends on the local environment rather than the distortion; put simply, if a tellurium atom has less atoms around it to attract charge from due to intrinsic vacancies, it attracts the more from the remaining atoms. In addition, this increases the electrostatic interaction between positively charged anion (Te) and negatively charged cation (Ge, Sb), which has its share in decreasing the distortion for these cations. Since Ge1 and Sb3 have intrinsic vacancies in their fourth shell in all three directions rather than only a few as atoms in the 56-cell, they represent

⁴Here, the 14-cell is most suitable since it allows to study a wide range of volumes while the resulting charges very well reproduce the width of the distribution that would result for the respective 56-cell as was shown in [Fig. 4.12](#).

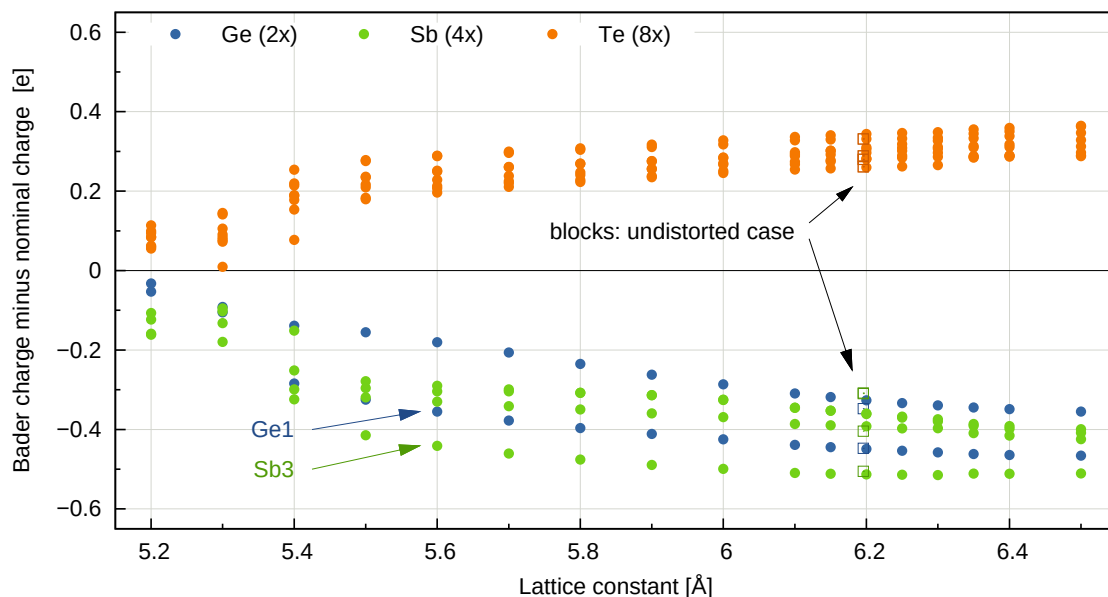


Figure 5.9.: The Bader charges show a weak volume dependence as long as no major structural change occurs; the charge differences increase with increasing volume for lattice constants above 5.5 Å. On the contrary, they drop rapidly below this value as bonds different from the rocksalt-like A-C- and B-C-type are formed (as seen in Fig. 5.3). Again, Ge1 and Sb3 stand out since they exhibit the largest charge differences. The most pronounced dependency is found for Ge2. The differences obtained for an undistorted rocksalt-structure are shown as open blocks for comparison. The distortion has little effect on the total ionicity and only slightly affects the cationic charges.

extrema; their charge differences are the largest. Contrariwise, the remaining cations are more distorted than the average atom in the 56-cell as they have no intrinsic vacancies in the fourth shell. Thus, they represent the opposite extrema.

To investigate the behavior of the covalent bonds, we turn again to the variation of the electron localization function (ELF) at around the center of the bonds (cf. Section 4.2.2). Figure 5.10 shows the case for the 56-cell of GeSb_2Te_4 ⁵. Clearly, decreasing the volume and thereby the level of distortion leads to more homogeneous bonds that differ less in their strengths. This is further resolved in Fig. 5.11, which shows the minima of the ELF and their positions. Upon compression (from right to left), the maximum value decreases and the distribution becomes much more narrow. This unambiguously proves that the decrease of the level of distortion

⁵For the study of the covalency and also the electronic states, the 56-cell instead of the 14-cell is discussed here to highlight the 'average' behavior rather than the extrema.

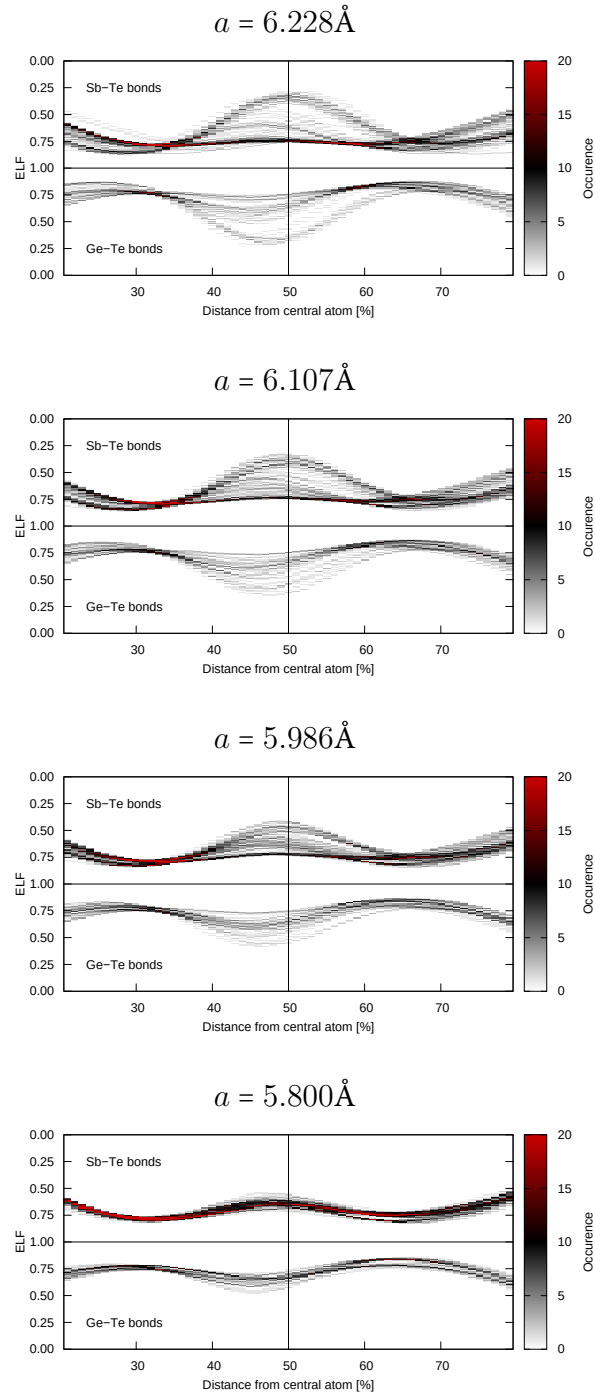


Figure 5.10.: Here, the electron localization function along the Ge-Te and Sb-Te bonds in GeSb_2Te_4 (56-cell) is presented (cf. Section 4.2.2). As the level of distortion decreases, the bonds become more homogeneous.

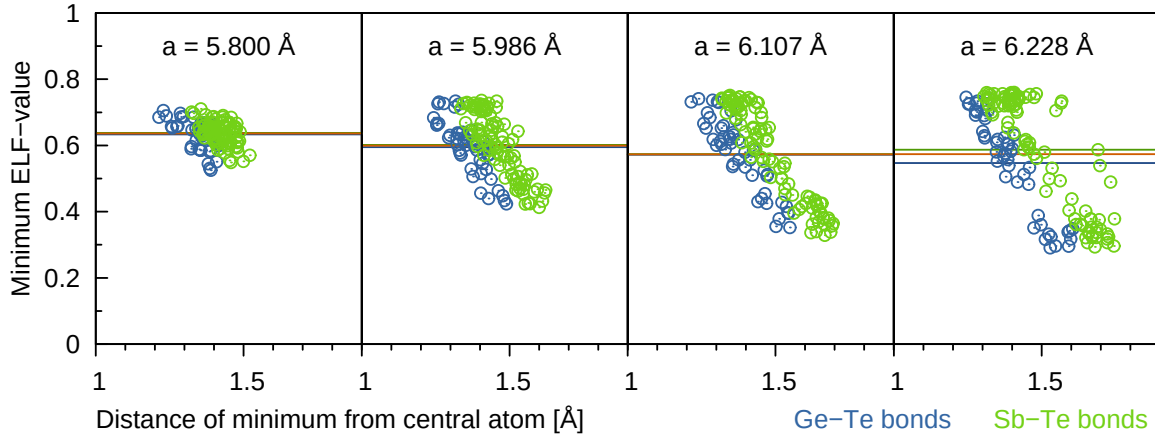


Figure 5.11.: The minimum values of the ELF of all bonds shown in Fig. 5.10 confirms that the bonds become increasingly more homogeneous as the volume and thereby the distortion is decreased. Interestingly, the average value (horizontal line) increases slightly from right to left, while the maximum value decreases. This proves the increasing resonance character of the bonding; the back bonds become important, thus increasing the average value, while the covalency of the strong bonds decreases in favor of delocalization.

significantly strengthens the long back-bonds at the expense of the strong short bonds. This leads to an increase of the average value of the ELF minimum; the localization of charge in the long bonds increases much more than the localization in the strong bonds decreases. This emphasizes how delicate resonance conditions in materials are; distortions that are adopted as they slightly strengthen/maintain a limited number of bonds (in line with the $8 - N$ -rule) considerably weaken the remaining bonds and thus lift the resonance conditions.

Finally, we turn to the volume-dependence of the electronic density of states. The compression increases the overlap between adjacent atoms and thus, the peaks become broader. This also affects the s-like states (below $\sim -6 \text{ eV}$), which are at the same time slightly shifting. The increasing delocalization of the s-electrons is also seen in Fig. 5.10, where the maxima (rather than the minima discussed so far), that are associated with the s-shell, decrease slightly. Yet, the bonding remains dominated by the p-like states at around the Fermi-level. As expected for a Peierls-like distortion, the gap decreases and eventually vanishes (in the present model at around $a = 6 \text{ Å}$). Again, the well-known weakness of density functional theory-calculations prevents further analysis of the absolute size of the gap.

To summarize, the variation of the volume and thereby the level of distortion affects the bonding expectedly; the stronger the distortion, the more the short bonds are strengthened

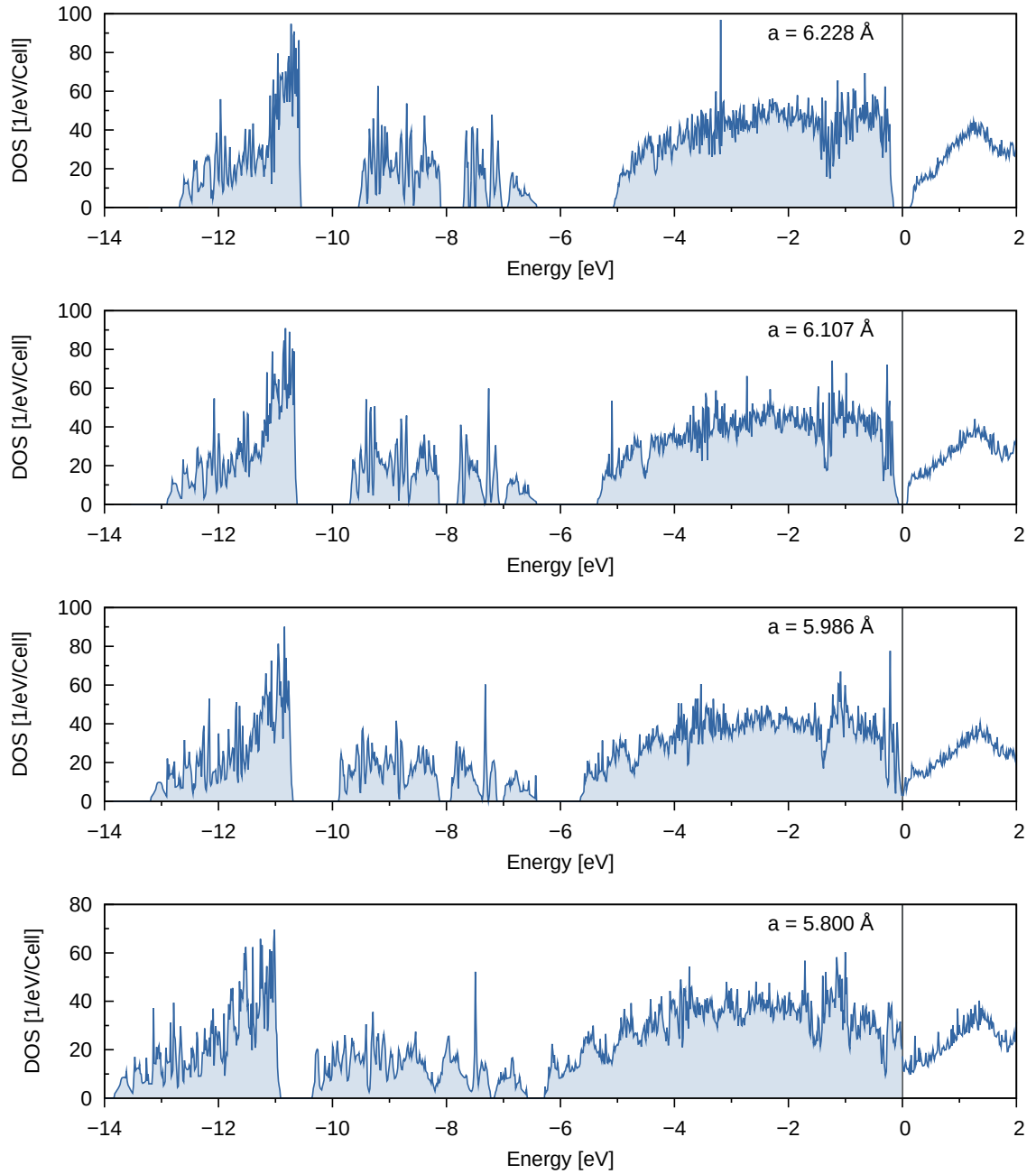


Figure 5.12.: The suppression of the Peierls-like distortion in GeSb₂Te₄ (56-cell) upon volume compression is reflected by the electronic density of states: the gap decreases and eventually vanishes.

at the expense of the long ones. Though, the change is significantly more pronounced for the weakened bonds. Furthermore, compression leads to delocalization/metalization. The ionic contribution shows little dependence on volume or distortion. The variation among the cations in both ionicity and local distortion can be traced back to the local atomic neighborhood. The presence of intrinsic vacancies in the fourth shell increases the charge transfer and decreases the local distortion amplitude.

5.4. Energy-Landscape and Lattice-Dynamics

At the end of this chapter, we turn to the last of the research questions that this work is concerned with. While so far we have studied the *static* structure and its relationship to the bonding, both volume- and composition-resolved for simple binaries and the more complex ternary materials, we finally want to learn more about the *dynamics* of the structure. Why is this topic of interest? Recalling that phase-change devices operate at temperatures in excess of 300 K, in particular during SET- and RESET-operations, it is clear that thermal excitation of atomic vibrations is relevant for applications. Moreover, as already discussed in [Section 3.5.1](#), the competition between resonant bonding and Peierls-like distortions must be expected to lead to peculiar shapes of the potential energy surfaces, giving rise to anharmonicity. But how pronounced is this anharmonicity? How does it vary with pressure and stoichiometry? And what are the differences between the AB- and AB₂C₄-materials?

Let us again begin with the binary prototype GeTe. If its equilibrium structure were the undistorted rocksalt-structure, it would suffice to calculate its phonons. This would provide us with the curvature of the total energy around this minimum and thus, with a simple way to determine the vibrational properties within the harmonic approximation. However, the competition between resonant bonding and Peierls-like distortions drastically changes the case; the undistorted rocksalt-structure does represent an extremum of the energy surface where all forces vanish, but it is a maximum, and the forces vanish only due to symmetry. As was shown in the diploma-thesis of the present author [205], the calculation of phonons of the undistorted structure is possible, but since it is a maximum rather than a minimum, the phonon frequencies become imaginary (since $\omega^2 < 0$, 'soft modes'). Along each eigendisplacement-coordinate, the total energy exhibits a double-well-shaped behavior. This is schematically visualized on the left-hand side of [Fig. 5.13](#). It turned out that the position of the minimum of this energy surface (keeping the unit cell fixed) is very close to the sum of those displacements that mark the minima of the individual soft modes, so the distortions along the three Cartesian directions,

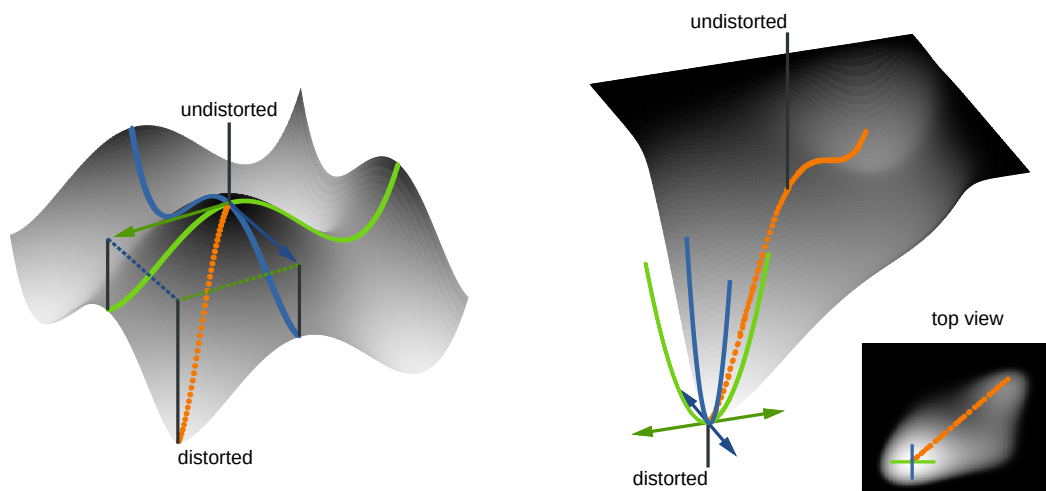


Figure 5.13.: Compared are the two approaches to the characterization of the energy landscape for AB-materials (left) and AB₂C₄-materials (right). For the binary materials, the undistorted structure represents a maximum. Analysis of the soft modes (blue, green) at this point yields the characteristic double-well curves. The superposition of the soft modes leads very close to the distorted equilibrium structure. Sampling of the total energy along the distortion coordinate (orange) thus yields insight into the overall shape of the potential energy surface. For the AB₂C₄-systems, the soft-mode analysis is not feasible as the undistorted structure is not force-free. Instead, sampling of the phonon modes around the distorted structure (blue, green) as well as along the distortion coordinate (orange) yield insight into deviations from harmonicity around the minimum and the occurrence of further wells.

that sum up to the characteristic $[1\ 1\ 1]$ -displacement, can fairly well be treated separately. Consequently, the relevant portion of the energy landscape around the rocksalt-structure is largely revealed just by sampling the total energy along the distortion coordinate x . The volume-dependence of the total energy along this coordinate is shown in Fig. 5.14. Clearly, the energy landscape becomes harmonic if the Peierls-like distortions are removed via pressure (cf. Section 5.1). Around the equilibrium, the position of the minimum and the energy gain by the distortion shift significantly. As was discussed in Section 3.5.1, a harmonic behavior is to be expected if the distortion is so favorable that typical temperatures are insufficient for the atoms to probe the anharmonicity of the potential energy surface. At positive pressures, the distorted rocksalt-structure even competes with the ZnS-type structure ($x = 0.75$). The results for the other AB-systems treated in this work (at their respective equilibrium volumes), that were shown in Fig. 4.6, indicate that stoichiometry variation is equivalent to volume-variation in the sense that it modifies the equilibrium-potential energy surface in a similar fashion

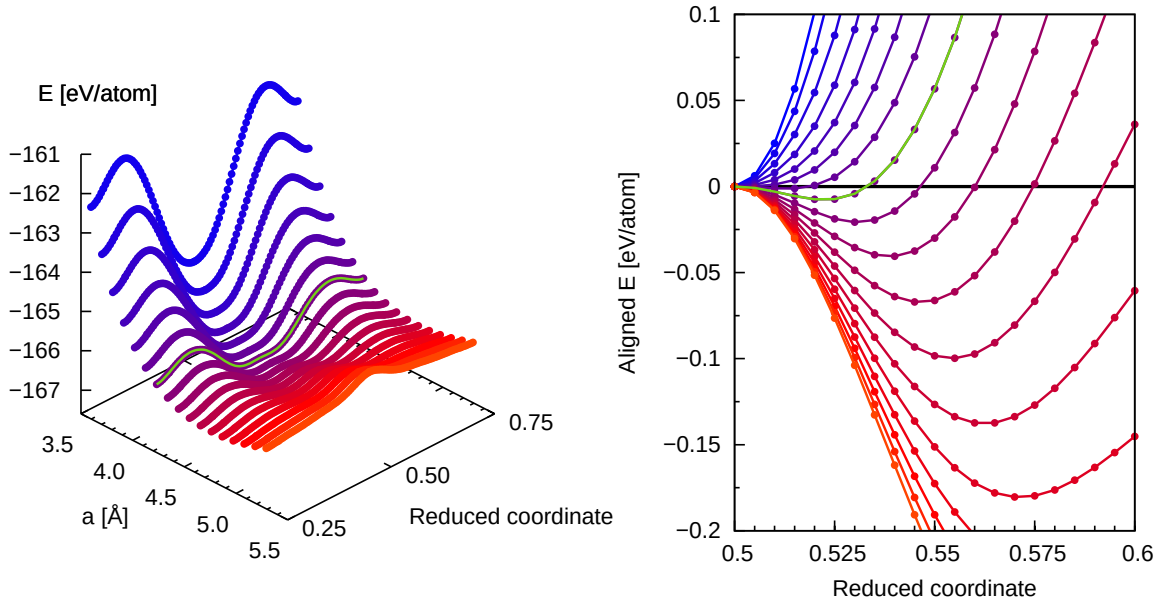


Figure 5.14.: For cubic GeTe ($\alpha = 60^\circ$), these figures show the total energy as the distortion x is varied for various fixed lattice constants (in terms of the lattice constant of the conventional unit cell, the range is 4.94 (blue) to 7.48 Å (red)). On the left-hand side, the total energies are non-aligned, while on the right-hand-side, the undistorted case ($x = 0.5$) is set to zero for all volumes. The green curve represents the minimum.

as compression. For example, SnTe with its shallow minimum close to $x = 0.5$ resembles compressed GeTe.

In the experiment, the energy gain by distortion is even larger than shown here since also the lattice relaxes (see Tab. 3.2, for simplicity the present approach is limited to the structures in the first and second column of this table). Nevertheless, the consequences of this peculiar shape of the energy landscape clearly surface in studies of the structure; the transition to the undistorted, rocksalt-like β -phase observed at around 670 K is a consequence of two effects. On the one hand, vibration levels are thermally populated that probe the potential energy surface outside of the 'wells'. On the other hand, the volume of the cell adapts to the temperature; since the Gibb free energy G , which contains a vibrational contribution, can be lowered by changing the potential energy surface so that G remains minimal also at elevated temperatures, the volume changes. Consequently, the amplitude of atomic motions becomes large and less confined, giving rise to large polarizabilities close to the transition temperature [195]. This is to be contrasted with the behavior expected from a harmonic system. The spatially averaged value of ϵ^0 calculated for GeTe in the fully relaxed structure (last column of Tab. 3.2), which relies on

the validity of the harmonic approximation, reads 81, while values up to several thousands are reported in ref. 195.

To summarize, the binary materials exhibit an unique energy landscape that is characteristic of the competition between resonant bonding and Peierls-like distortions. Both volume- and stoichiometry-variation have an impact on the relevance of the anharmonicity; the shallower the 'wells' relative to the thermal energy scale, the more important becomes the anharmonicity. The calculation of the total energy along the distortion coordinate is a suitable method to quantify the shape of the energy landscape.

Turning now to the AB_2C_4 -material $GeSb_2Te_4$, it is immediately clear that the energy landscape is much more complex. First of all, it has many more dimensions since more atoms need to be in the unit cell for it to be represented. In addition, the unit cell is not unique. Furthermore, due to symmetry breaking it is impossible to adopt the procedure of sampling the soft phonon modes that occur in the undistorted structure since the latter is not a force-free point of the potential energy surface⁶. Consequently, a different approach must be taken here, shown on the right-hand side of Fig. 5.13. On the one hand, the phonons can be calculated for the distorted structure. Then, sampling of the total energy along the eigendisplacements allows to check for deviations between calculated energy and the energy expected within the harmonic approximation. Those would be fingerprints of anharmonicity. On the other hand, sampling of the total energy along the distortion coordinate yields further insight; is the well around the minimum unique, or are there further wells as in the binaries? While the latter method could be applied to all models, the calculation of the phonons was limited to the 14-cell model for the reasons given in Section 4.1.2 (i. e., the computational demand). Note that neither Born effective charges nor values of ϵ (and thus, no non-analytical terms, see Section B.4.3) are considered here as the level of convergence of these quantities with respect to the k -point-grid calls for improvement. This part of the analysis needs to be postponed until calculations using the 56-cells, that exhibit a dense grid and also represent the average structure more accurately, become feasible. The same is true for respective calculations of the fingerprint-effects of resonant bonding for other compositions. The forces, however, are converged well enough for the present study of the energy landscape as has been checked.

⁶A conventional unit cell with only eight lattice sites, where the undistorted structure does represent a force-free saddle point (with 7 out of 21 modes being soft), was considered in the diploma thesis of the present author [205], but is an insufficient representation of the structure since the fourth shell of an atom contains only periodic images of itself. In addition, unfavorable tellurium-vacancy-chains form.

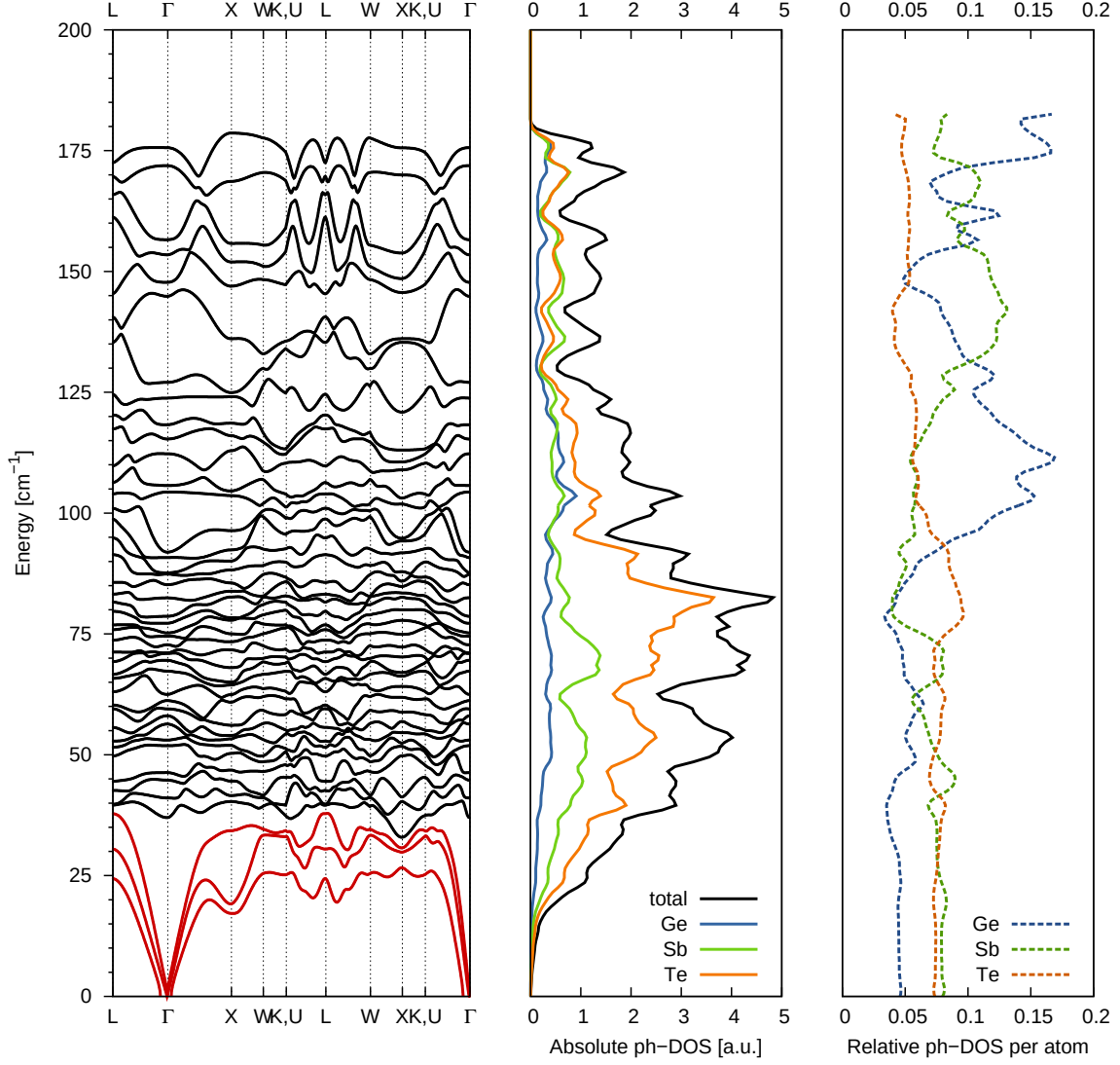


Figure 5.15.: This figure shows the phonon bands (left-hand side, reduced coordinates as defined in the caption of Fig. 3.8, acoustic modes in red) and the corresponding phonon-density of states for GeSb_2Te_4 in the 14-cell. The density of states is plotted both in terms of absolute values per species, $g_i(E)$ (middle), as well as relative to the total density, $g_i(E)/(g(E) \cdot N_i)$, N_i being the number of atoms of species i (right-hand side). The latter presentation shows that below 75 cm^{-1} , antimony and tellurium dominate. Above 100 cm^{-1} , the light germanium in particular and antimony alternately contribute the most per atom.

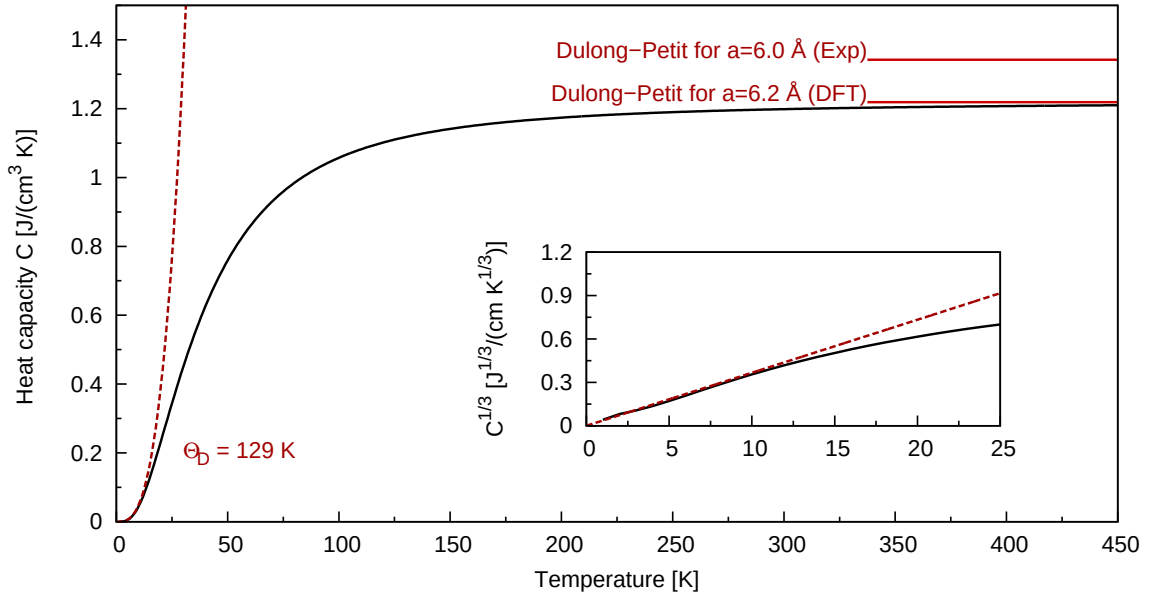


Figure 5.16.: The heat capacity of the lattice, that results in the harmonic approximation, is shown. For high temperatures, the Dulong-Petit limits of the heat capacity for both the experimental lattice constant and the one that represents equilibrium in the calculations is indicated. The inset shows the low temperature regime, where a cubic temperature-dependence is obtained. Taking into account the data up to 10 K as shown in the figure (dashed line), a Debye-temperature of $\Theta_D = 129$ K is obtained.

The resulting phonon dispersion (extrapolated from a homogeneous q -point-grid that satisfies the condition $\underline{k} + \underline{q} = \underline{k}$) and phonon-density of states are shown in Fig. 5.15. The energetic range spanned by the phonon modes, that reaches up to about 180 cm^{-1} , agrees with previous reports on the close relative $\text{Ge}_2\text{Sb}_2\text{Te}_5$. For this material, Raman-spectra [10, 25, 61] and vibrational densities of states based on molecular dynamics (MD) simulations [29, 30] have been reported. These reported Raman-spectra exhibit significant differences between each other in the distribution of their spectral weights. They are rather feature-less, though. Furthermore, the spectra are typically noisy because of the small intensity of the (anti-)Stokes-scattering peak for thin films, and can be obtained only above about 80 cm^{-1} due to the energetic proximity to the unshifted Rayleigh-scattering peak. The MD-simulations roughly agree with each other and imply that the phonon-DOS can be viewed as a superposition of broad overlapping peaks located at $\sim 100 \text{ cm}^{-1}$, $\sim 50 \text{ cm}^{-1}$ (about $\frac{3}{4}$ the height) and $\sim 150 \text{ cm}^{-1}$ (about $\frac{1}{2}$ the height). The fact that the 14-cell over-represents extrema of the structure leads to deviations; here, the peak that would need to be located at around 100 cm^{-1} is shifted down to about 75 cm^{-1} .

In summary, the lack of uniqueness of the metastable crystalline phase gives rise to notable variations in the vibrational fingerprint.

The isochore heat capacity, that results from the calculated phonon density of states, is presented in Fig. 5.16. A Debye-temperature of $\Theta_D = 129$ K is obtained upon fitting up to 10 K. Due to the use of the GGA-PBE XC-functional, this value must be expected to underestimate the experimental value. No measurement of the low-temperature regime is known to the author, though. Respective experiments in collaboration with R. Hermann from the IFF Jülich failed since only insufficient powder samples (small mass, bad internal heat coupling) could be prepared. Anharmonic effects should be most pronounced at high temperatures, so respective measurements of the heat capacity in the temperature regime above room-temperature are proposed.

The 42 Γ -point phonon-modes have been sampled for lattice constants from 5.8 Å to 6.4 Å (in steps of 0.2 Å). Clearly, these results are too voluminous to be shown here explicitly. Only one complete set of results is presented in Appendix E. Here, only examples shall be shown to elaborate the principal results. Figure 5.17 presents three exemplary calculations for GeSb_2Te_4 at equilibrium volume. Clear signs of anharmonicity are obtained. The energy range, at which the deviation between harmonic approximation and calculated energy occurs in these curves, is only an upper limit; anharmonic interaction of the phonon modes must be expected to yield an even 'softer' path that none of the modes coincides with. The results for the other volumes (not shown) indicate that the occurrence of deviations from the quadratic dependence of the total energy on atomic displacements is a volume-independent signature of GeSb_2Te_4 . This is in line with the aforementioned observation that distortions do not vanish in the AB_2C_4 -materials despite compression.

Next, the results of the sampling along the displacement coordinates shall be presented. From this analysis, we can infer information about the energy landscape of the unit cell (limited to the Γ -point) in terms of the effect of collective atomic displacements. We start with the volume-dependence in the case of GeSb_2Te_4 . The results for the 14-cell are shown in Fig. 5.18, those for the 56-cell (employing the same energy scales) in Fig. 5.19.

The 14-cell-results exhibit a double-well-shaped curve for large lattice constants, and a rather quadratic one for small values of a . The transition between the two types is continuous. Just as before, we see that compression first leads to a decrease of the distortion. To show this, the second and third graphs of this figure employ the distortion per atom in absolute values and

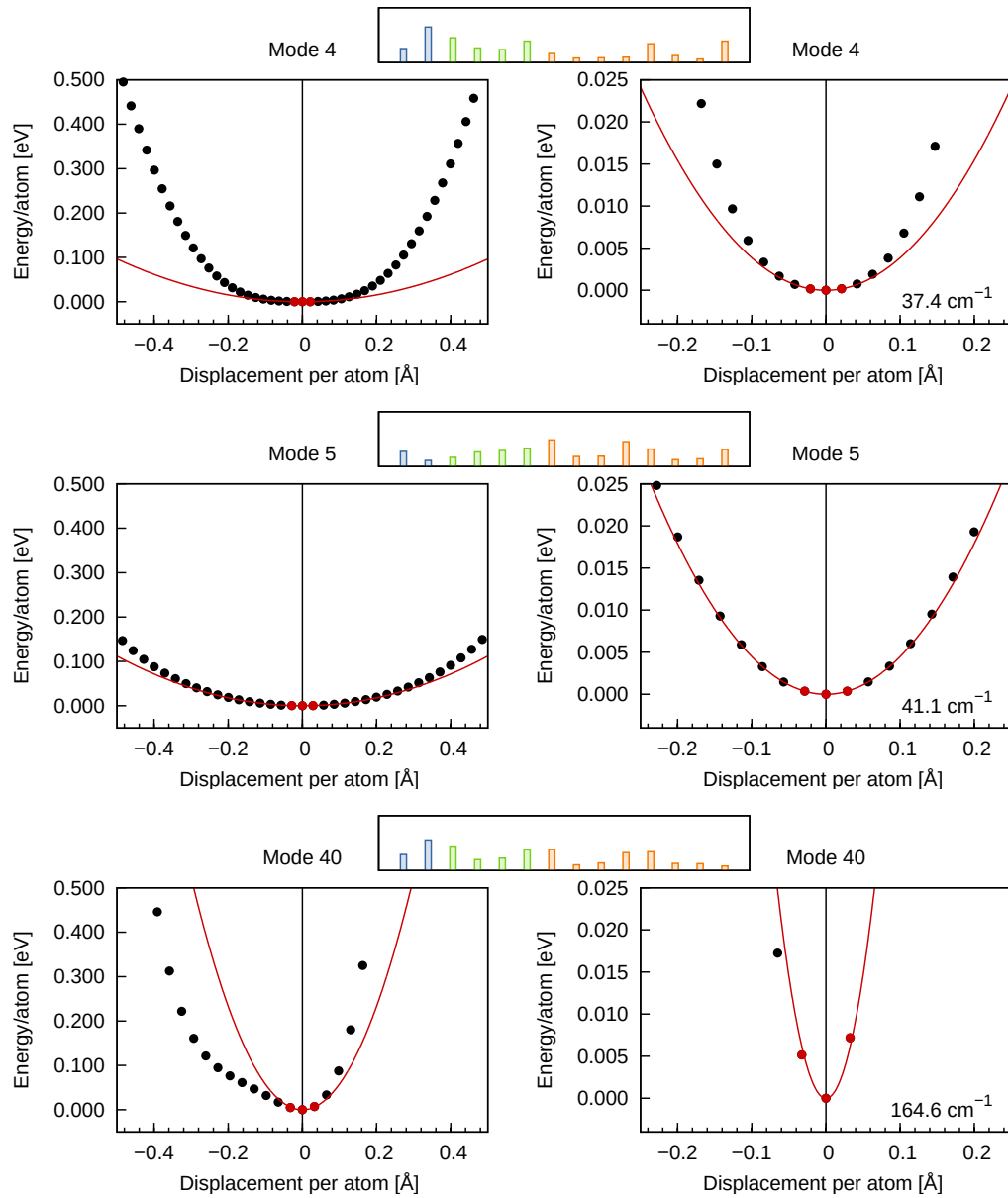


Figure 5.17: Shown is the total energy as a function of the eigendisplacement according to of the modes 4, 5 and 40 (out of 42). The contribution of the individual atoms is indicated by the small graphs; from left to right, the bars represent Ge1 and Ge2 (blue), Sb1 to Sb 4 (green) and the tellurium atoms. While some modes, such as mode 5 in the middle, do not exhibit any peculiarities, pronounced anharmonicity is obtained for others.

normalized to the lattice constant, respectively, as x-axis⁷. Between 6.2 Å and 5.8 Å, however, the case changes, and concurrently to the change in the shape of the curve, the position of the minimum starts to move away from the undistorted case again. Just as Fig. 5.3, this emphasizes that it is not the undistorted rocksalt case that compression leads to.

The difference in energy between the undistorted rocksalt-structure and the distorted structure, where the energy is minimal, is linked to the position of the minimum. If it is close to the undistorted case, the energy difference becomes small. In turn, the difference becomes large if also the distortion is large. In comparison to the curve that corresponds to cubic GeTe (only half of its symmetric curve is shown for clarity), we see that the height of this central energy barrier in GeTe is smaller than it is in GeSb₂Te₄ for any of the considered volumes. Furthermore, the second well located at negative values of the distortion coordinate is not symmetric to the first one. Upon compression, it even vanishes.

The results on the 56-cell resemble those on the 14-cell, in particular the shift of the minimum is recovered here. However, also some differences can be observed. First, the distortion per atom as well as the associated energy gain is generally smaller. Moreover, the second well at negative values of the distortion coordinate disappears.

In summary, we find that GeSb₂Te₄ shows a significant difference in its energy landscape as compared to the binary GeTe. It is not unique, but depends on the sublattice occupation. The closer the structure resembles the binary material (as in the 14-cell, where the average distortion patterns are more GeTe-like as shown before), the more similar the energy landscape looks, yet the undistorted structure is not a distinguished point and also the symmetry about this point is lost. The energy gain by distortion appears to be larger than in a comparable cubic GeTe at all volumes, indicating that a hypothetical, temperature-induced phase transition towards an undistorted structure would only occur at a higher temperature than in GeTe, and thus would be screened by the transition to the stable phase or even by melting. No indication of further favorable wells other than the one around the equilibrium structure is obtained. Though, the distortion coordinate might miss the minimum of the well at negative values (see the 'top view' in Fig. 5.13).

⁷The integral distortion is calculated from the difference between the distorted and undistorted coordinates as its norm, correcting for any translations during the relaxations by minimizing the norm with respect to a rigid, relative shift of the lattices; this way, it is ensured that this measure of distortions does not deviate from zero in the case of a simple translation.

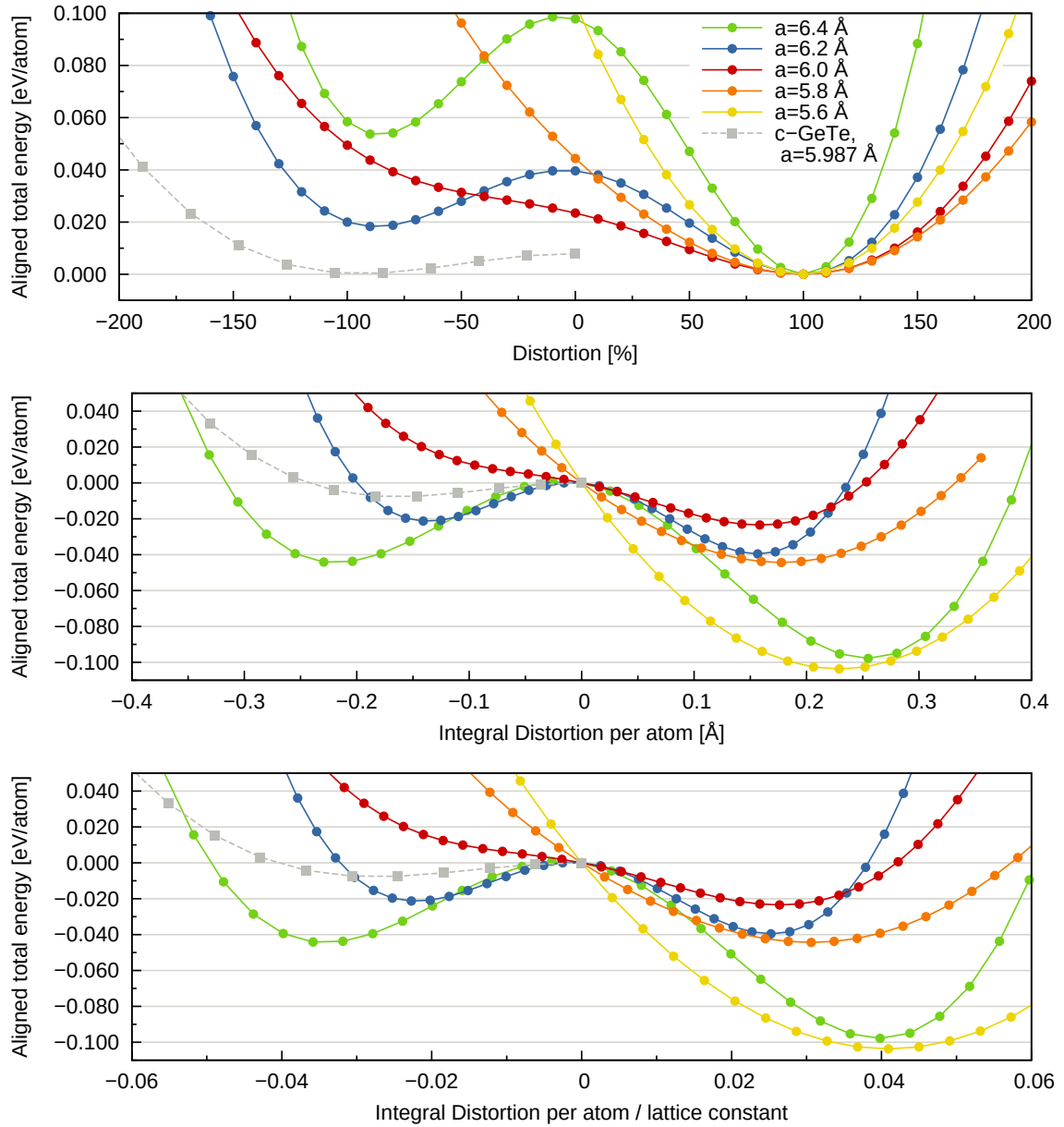


Figure 5.18.: Energy along distortion coordinate for GeSb_2Te_4 (14-cell) at various volumes.

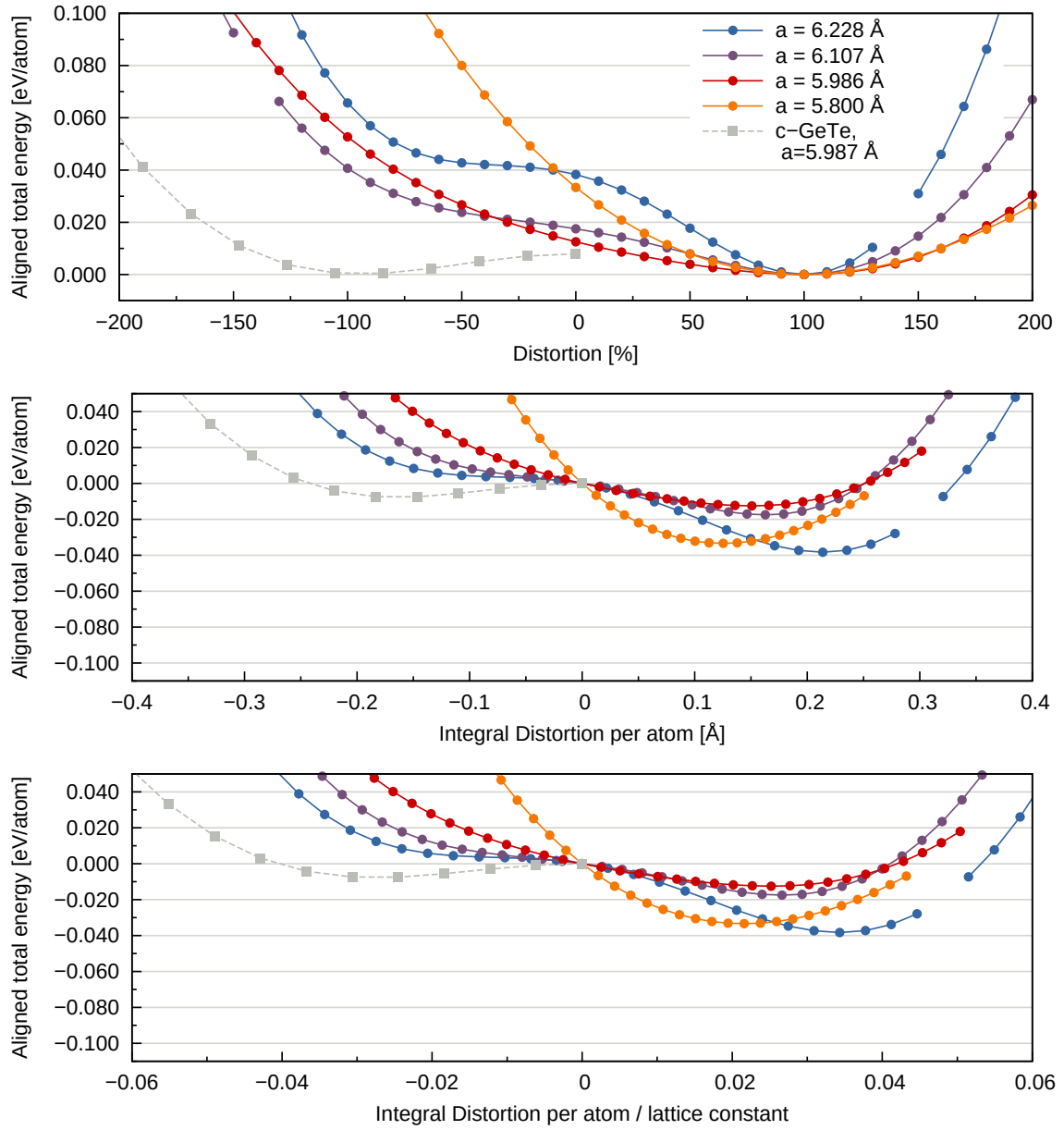


Figure 5.19.: Energy along distortion coordinate for GeSb_2Te_4 (56-cell) at various volumes.

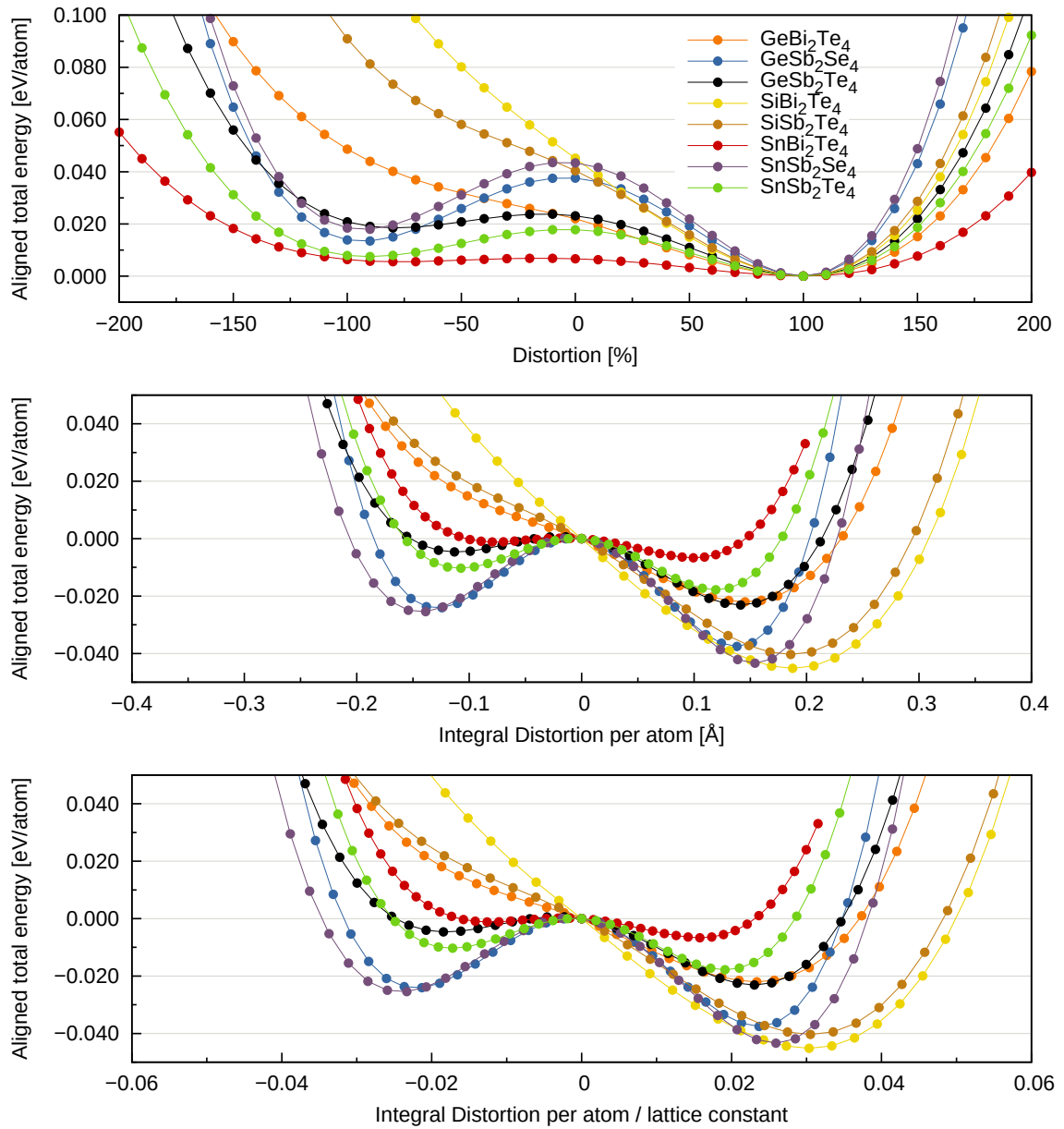


Figure 5.20.: Energy along distortion coordinate for AB_2C_4 -systems in the 14-cell.

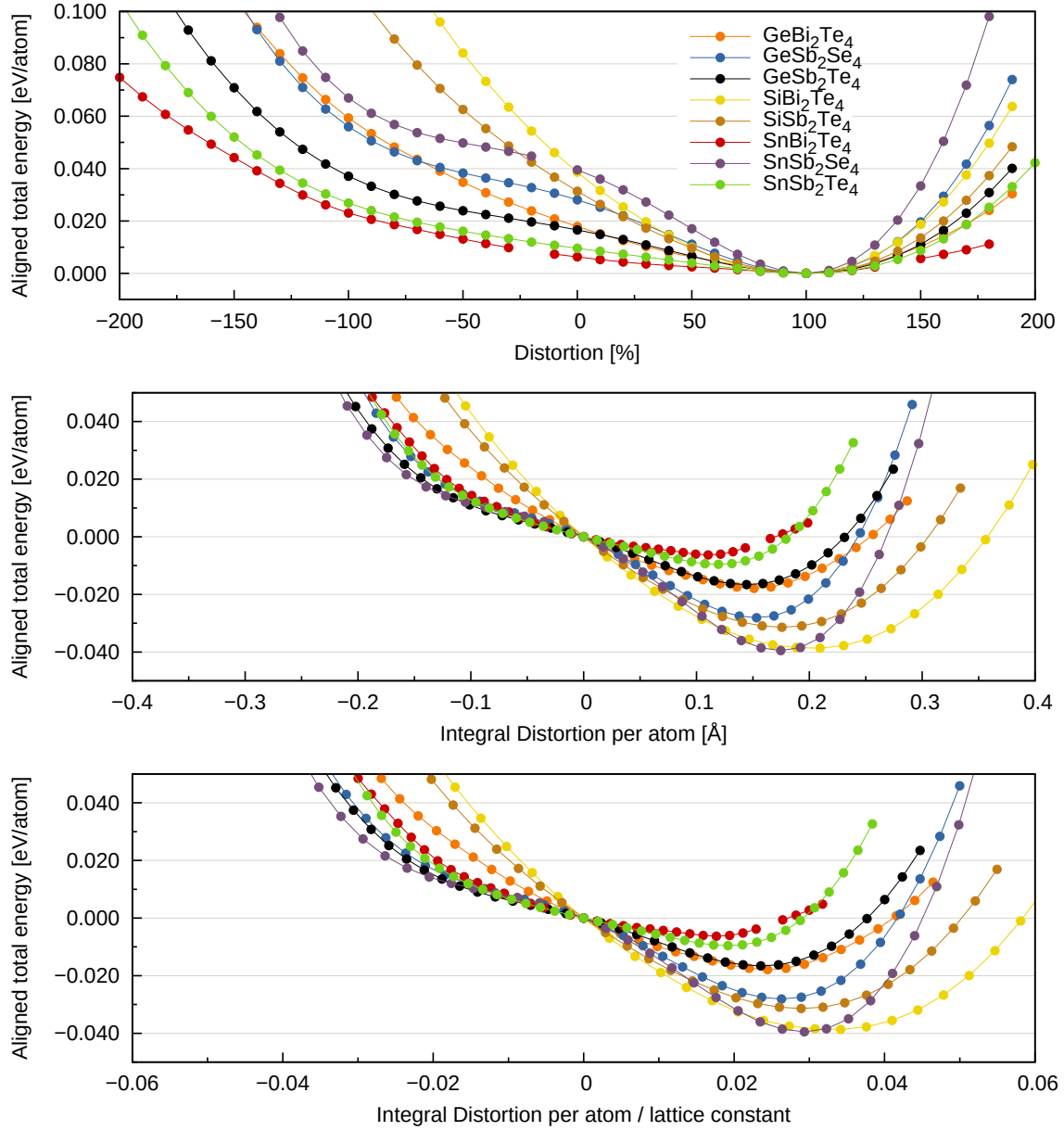


Figure 5.21.: Energy along distortion coordinate for AB_2C_4 -systems in the 56-cell.

The differences between the 14- and 56-cell models indicate that the vibrational behavior of individual atoms (rather than the collective behavior represented by the distortion coordinate, which affects all atoms simultaneously) may be very different. An atom with a certain occupation symmetry about its lattice site may have multiple favorable positions in its surrounding (much like rattler-atoms in thermoelectric materials, that are viewed as phonon-scatterers), or only a unique position about which it vibrates. This calls for further experimental studies of the dynamics using different samples of GeSb_2Te_4 that vary in their sublattice occupation. This could involve the epitaxial films addressed in [Section 5.2](#), but also sputtered films with different annealing temperatures (though to yield progressive ordering of the sublattice occupation, see [Section 2.1](#)).

The study of the total energy along the distortion coordinate for the various AB_2C_4 -systems (from [Chapter 4](#)) at their equilibrium lattice constants are shown in [Fig. 5.20](#) (14-cell) and [Fig. 5.21](#) (56-cell). The comparison between both 14- and 56-cell models yields the same results as for the case of GeSb_2Te_4 . Furthermore, the equivalence of stoichiometry- and volume-variation is evidenced by these plots; the least distorted system, SnBi_2Te_4 , exhibits the shallowest minimum and thus is prone to exhibit anharmonic effects. Indeed, the sampling of the phonon modes emphasize this conclusions. The results for two energetically low modes are shown in [Fig. 5.22](#) and highlight the inadequacy of the harmonic approximation to represent the energy landscape.

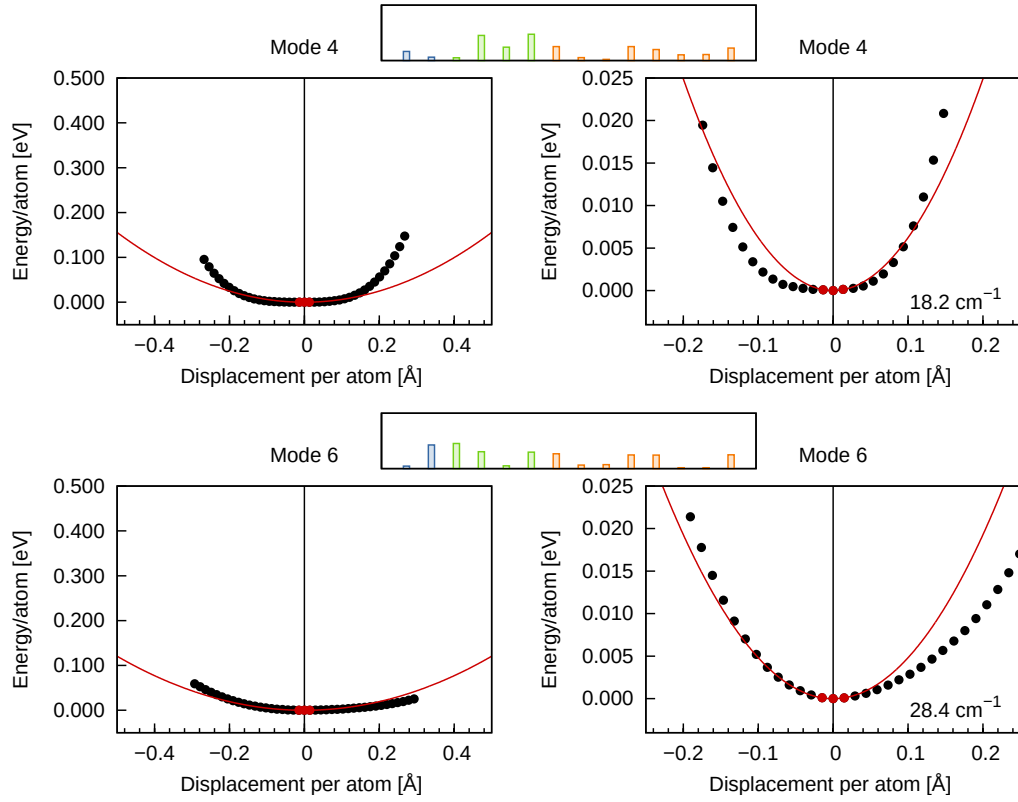


Figure 5.22.: The variation of the total energy along the lowest non-acoustic Γ -mode, mode 4 (top), and mode 6 in SnBi_2Te_4 (14-cell) emphasizes that anharmonicity must be expected to play an important role in this material.

5.5. Conclusions

The present chapter has revealed novel insight into the local structure and lattice-dynamics of phase-change materials. The volume-/pressure-dependent investigation of the structure and the bonding shows that stoichiometry-variation and pressure have similar effects. Though, only the composition is a viable way to tune the properties for a given application since it appears rather unlikely that despite phase transitions, a constant pressure of several GPa can be maintained in a PCRAM-cell, for instance. The distortion patterns of the individual atoms heavily correlate to the adjacent sublattice occupation, in particular to the occupation of the fourth shell. The occurrence of intrinsic vacancies is the driving force for deviations between the AB_2C_4 -materials and the AB-compounds. These differences manifest themselves in the rhombohedral distortion of the unit cell and the shape of the volume-dependent energy landscape. At around the equilibrium, the relative importance of anharmonicity as a consequence of the competition between resonant bonding and Peierls-like distortions is found to scale with the amplitude of the distortion. For both AB- and AB_2C_4 -materials, the larger the distortion, the larger the energy gain and thus, the less important the anharmonicity becomes. This confirms the map's validity in this regard as anticipated in [Section 3.5](#), since it correctly predicts the trends in the average distortion (see [Chapter 4](#)).

6. Summary and Outlook

At the end of this thesis, a brief summary of its contents and main results shall be provided. First, a review of the current state of research has been given in [Chapter 2](#). It turns out that the identification of optimal phase-change materials, that best suit the needs of the various desired applications, is one of the most important challenges in this field. So far, however, material research has proceeded mainly by trial-and error-studies, and only few systematic approaches to material design have been proposed.

Thus, in [Chapter 3](#) a framework for the discussion and understanding of the physical properties of phase-change materials has been developed; based on optical characterizations and structure investigations, the occurrence of resonant bonding in the crystalline phase is identified as the origin of the contrast between amorphous and crystalline phase that enables phase-change-based applications. Resonant bonding leads to small optical gaps, large optical dielectric constants and large Born effective charges. The competition between resonance of the bonds and Peierls-like atomic distortions has been studied by means of density functional theory-calculations. It turns out that although these distortions significantly decrease the fingerprint-effects of resonant bonding in the prototype-phase-change material GeTe, the dielectric constants and Born effective charges remain anomalously large.

Subsequently, this newly gained insight has been employed to develop a design-scheme for phase-change materials and thereby to replace the empirical approaches pursued so far; based on the work on structure maps in the 1960s to 1980s, in particular by Peter Littlewood, a map for phase-change materials is proposed. This map is spanned by two coordinates that represent the ionicity of the bonding (r'_σ) and the tendency towards hybridization (r_π^{-1}). The empirically identified phase-change materials, that are characterized by a pronounced resonance character (i. e., little ionicity and little distortions), are successfully located within a confined region of this map. Moreover, a wide range of implications of the map for material properties have been discussed. This calls for further experimental and theoretical studies of property trends that are predicted by the map. Consequently, [Chapter 4](#) presents the results of a density functional theory-based study of a wide range of materials that span the most interesting region of the map,

where phase-change materials are located. Two classes of materials have been considered, AB-materials (such as GeTe) and AB_2C_4 -materials (such as $GeSb_2Te_4$). The results on the structure but also the quantification of the bonding properties confirm the qualitative expectations of Chapter 3; the average distortion enlarges towards increasing values of r_π^{-1} , the behavior of the ionicity coordinate r'_σ is very well reproduced by the calculated Bader charges, and the covalent bonds react to distortions just as expected. Nevertheless, this study also reveals a limitation of the map; if one atomic species is significantly smaller than the remaining species, it typically exhibits stronger distortions. In particular those materials that contain silicon have been found to show this effect.

A further result of this study is the observation that while the average level of distortion is well in line with the prediction of the map, there is a significant variation among the cations in the AB_2C_4 -materials. Their distortion patterns vary greatly from the simple scheme that the binary materials display. These variations have been traced back to the sublattice occupation in the AB_2C_4 -materials in Chapter 5. In particular the presence of intrinsic vacancies in the fourth shell of a cation strongly affects its distortion pattern. The resulting variation in the displacement directions is also what causes the absence of a rhombohedral distortion in the ternary materials. Furthermore, the calculations discussed in this chapter reveal the volume- or pressure-dependence, respectively, of the structure and the bonding. Peierls-like distortions decrease upon compression and hence, the resonance character is strengthened. However, the distortion from the rocksalt-positions remains finite in the non-binary materials. Finally, the potential energy landscapes of phase-change materials have been studied to illuminate not only the static distortions, but also the lattice-dynamics in this material family. The results on the volume- and composition-dependent potential energy surface imply that the least distorted systems are prone to exhibit anharmonic effects.

Various future research opportunities have been outlined in the respective chapters. A particular follow-up project of this thesis is the investigation of defect formation in phase-change materials. Preliminary results for an uncharged germanium-vacancy are shown in Fig. 6.1. Defects are at the origin of the large carrier concentrations in the crystalline phases of these materials and thus of utmost importance for electrical applications (cf. Section 3.5.3). Despite this fact, the defect characteristics in materials other than simple binaries such as GeTe, in particular $GeSb_2Te_4$, as well as the stoichiometry-dependence of defect formation energies have not been studied so far. Hence, this project aims at revealing the defect properties of phase-change materials, taking into account the differences between atomic sites as obtained in the present work.

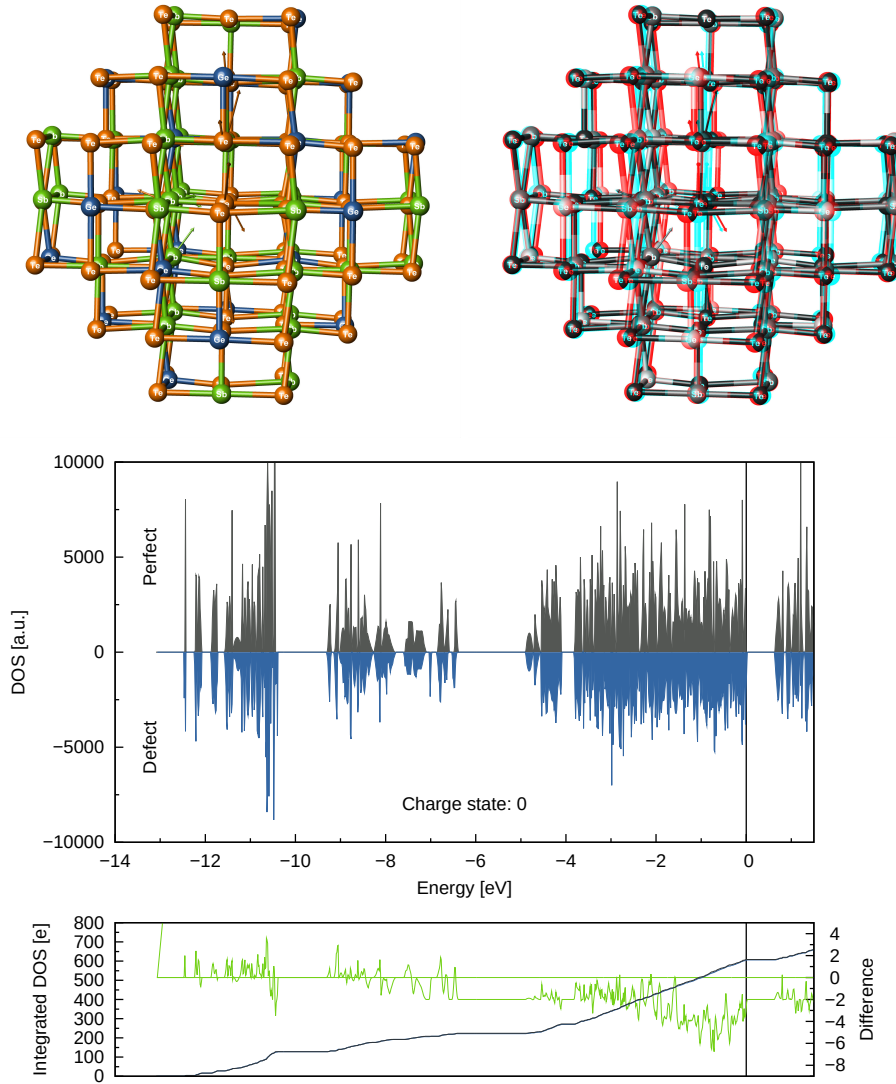


Figure 6.1: The top figure shows a spherical portion of a GeSb_2Te_4 -crystal that is centered around a single germanium-vacancy (Ge_1 from the 14-cell model). The arrows indicate the atomic relaxation around the defect site. The 3d-plot is best viewed online with red-cyan-glasses. The middle figure compares the electronic density of states of the defect-free (gray) and the defective system (blue). The Fermi-level of the defect-system is located at $E = 0$. The DOS of the perfect system is shifted accordingly. The difference (green) between the integrated DOS of the two systems (gray, blue) shown in the bottom figure reveals that the removal of the germanium atom, which contributes two s- and two p-electrons, does not reduce the total number of states up to the conduction band edge by four but only by two. This is due to the defect-induced appearance of former conduction band-states at the valence band-edge that gives rise to p-type conductivity.

Appendix A.

Density Functional Theory

For the present thesis, density functional theory is the method of choice for the investigation of the material physics of phase-change materials. This simulation method provides an accurate alternative to experimental studies and enables an unprecedented insight into the solid state of matter. The availability of computational resources, that has grown tremendously since the introduction of density functional theory in the 1960s, nowadays makes density functional theory-calculations a well-established method for material scientists. Thus, a basic introduction into density functional theory and its extension, density functional perturbation theory, shall be given in this chapter. The interested reader is referred to the book of Martin [206] that may serve as a starting point to immerse deeper into this exciting topic. Besides this reference, the following presentation is based on refs. 205, 207–210.

The aim of density functional theory is to provide an *ab initio*, quantum theoretical approach that enables the treatment of the Schrödinger equation for a molecule or solid. Generally, the time-independent many-body Hamiltonian reads

$$\hat{H} = \hat{T}_n + \hat{T}_{el} + \hat{V}_{n-n} + \hat{V}_{el-n} + \hat{V}_{el-el} . \quad [A.1]$$

Here, the kinetic energy of the nuclei and electrons are denoted as $\hat{T}_n$ and $\hat{T}_{el}$, respectively. In addition, three types of (Coulomb) interaction have to be considered, the nuclei-nuclei ($\hat{V}_{n-n}$), electron-nuclei ($\hat{V}_{el-n}$) and the electron-electron interaction ($\hat{V}_{el-el}$). However, the attempt to solve this Hamiltonian is doomed to fail even for small systems (i. e., systems that contain only a small number of nuclei, N_n , and electrons, N_{el}).

As a first step, the well-established *Born-Oppenheimer* (or *adiabatic*) *approximation* is applied; owing to the fact that the mass of any nuclei I , M_I , exceeds the electron mass, m_{el} , by some orders of magnitude, the kinetic energy contribution of the nuclei $\hat{T}_n$ may be neglected.

Thus, the set of positions of the nuclei, $\{\underline{R}_I\}$ with I running over all nuclei, are fixed in the following. Nevertheless, the lattice-dynamics are not out of reach of density functional theory, we shall be concerned with them in [Section B.4.1](#). The introduction of the Born-Oppenheimer approximation simplifies the situation as for the nuclei, only $\hat{V}_{n-n}$ remains to be obtained, which is rather simple given the fact that the atomic positions are now fixed. However, the rest of the Hamiltonian still remains too complex to be solved for any solid, even numerically. The task of finding an – at least approximative – solution has attracted very much attention throughout the last decades. In the following section, the famous achievements of Hohenberg and Kohn shall be presented.

A.1. The Hohenberg-Kohn Theorem

In 1964, Hohenberg and Kohn provided the foundations of density functional theory by obtaining a density-based approach to assess the above Hamiltonian ([Eq. A.1](#)). Their work contains two findings referred to as the *Hohenberg-Kohn Theorem* [\[207\]](#).

First, for a collection of electrons under the influence of an external potential $v(\underline{r})$, they proved that $v(\underline{r})$ is a unique functional of the electronic groundstate density, $n(\underline{r})$, that is $v(\underline{r}) = v[n(\underline{r})]$.

To understand the consequences of this finding, we shall remind ourselves of how the solution of the Schrödinger equation would usually proceed. From $v(\underline{r})$, which defines the Hamiltonian, the eigenfunctions Ψ would be derived. From these, the electronic density $n(\underline{r})$ could be determined. For the groundstate, the above theorem now turns this sequence into a circle. As $n(\underline{r})$ determines $v(\underline{r})$ and thereby the Hamiltonian, the full many-body groundstate becomes a unique functional of $n(\underline{r})$. Thus, any observable O may in principle be expressed as a functional of $n(\underline{r})$:

$$O = \langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi[v[n(\underline{r})]] | \hat{O} | \Psi[v[n(\underline{r})]] \rangle = O[n(\underline{r})] . \quad \text{[A.2]}$$

All information about the groundstate may therefore be derived from a three-dimensional scalar field, $n(\underline{r})$, which is a great simplification as compared to handling the many-body eigenfunctions Ψ .

The second part of the Hohenberg-Kohn theorem makes direct use of this finding. Since the energy represents an observable of the system, it may also be expressed as a functional of $n(\underline{r})$, that is $E[n(\underline{r})]$. The exact groundstate density minimizes this functional,

$$E_0 = \min_{n(\underline{r})} E[n(\underline{r})] = E[n_0(\underline{r})] . \quad [\text{A.3}]$$

Thus, by virtue of the Hohenberg-Kohn theorem, it is possible to obtain all information about the groundstate if only the groundstate density can be obtained. However, this requires an ansatz for the energy functional, which leads us to the second step in the development of density functional theory, the *Kohn-Sham equations* developed by Kohn and Sham in 1965 [208].

A.2. The Kohn-Sham Equations

What needs to be done to make use of the Hohenberg-Kohn theorem is to find an expression of the electronic energy, E_{el} , defined as

$$E_{\text{el}} = \langle \Psi | \hat{H}_{\text{el}} | \Psi \rangle , \quad [\text{A.4}]$$

in terms of a functional of the electronic density $n(\underline{r})$. As a prerequisite, let us first consider some properties of the latter that will help us to obtain the desired functional.

The electron density is calculated as the expectation value of the single-particle density operator $\hat{n}(\underline{r})$,

$$\hat{n}(\underline{r}) = e \sum_i^{N_{\text{el}}} \delta(\underline{r} - \underline{r}_i) , \quad [\text{A.5}]$$

where $\underline{r}_i$ denotes the spatial variable associated with the i -th electron. Thus, the electron density is

$$n(\underline{r}) = \langle \Psi | \hat{n}(\underline{r}) | \Psi \rangle \quad [\text{A.6}]$$

$$= e N_{\text{el}} \int |\Psi(\underline{r} \dots \underline{r}_{N_{\text{el}}})|^2 d\underline{r}_2 \dots d\underline{r}_{N_{\text{el}}} . \quad [\text{A.7}]$$

A second important quantity is the two-particle density $n^{(2)}(\underline{r}, \underline{r}')$, defined as

$$n^{(2)}(\underline{r}, \underline{r}') = e^2 \frac{N_{\text{el}}(N_{\text{el}} - 1)}{2} \int |\Psi(\underline{r}, \underline{r}' \dots \underline{r}_{N_{\text{el}}})|^2 d\underline{r}_3 \dots d\underline{r}_{N_{\text{el}}} . \quad [\text{A.8}]$$

While $n(\underline{r})$ basically gives the probability of finding an electron at $\underline{r}$, the two-particle density $n^{(2)}(\underline{r}, \underline{r}')$ represents the conditional probability of finding one electron at $\underline{r}$ given that a second

electron is at $\underline{r}'$. Finally, another important aspect of the charge density shall be noted here, that is charge conservation, requiring

$$\int n(\underline{r}) d\underline{r} = eN_{\text{el}} . \quad [\text{A.9}]$$

These three results – $n(\underline{r})$, $n^{(2)}(\underline{r}, \underline{r}')$ and charge conservation – will help us to derive a functional expression for the energy.

As a starting point, we shall explicitly write down the electronic part of the Hamiltonian, that can be written as¹:

$$\hat{H}_{\text{el}} = \hat{T}_{\text{el}} + \hat{V}_{\text{el-n}} + \hat{V}_{\text{el-el}} \quad [\text{A.10}]$$

$$= -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \sum_I \frac{Z_I}{|\underline{r}_i - \underline{R}_I|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|\underline{r}_i - \underline{r}_j|} . \quad [\text{A.11}]$$

To find the desired energy functional $E[n(\underline{r})]$, one needs to calculate the expectation value of the operators in Eq. A.10 one by one. After some calculus (not shown, see for instance ref. 210), one finds

$$E_{\text{el-n}} = \langle \Psi | \hat{V}_{\text{el-n}} | \Psi \rangle = \int n(\underline{r}) V_{\text{el-n}} d\underline{r} , \quad [\text{A.12}]$$

$$E_{\text{el-el}} = \langle \Psi | \hat{V}_{\text{el-el}} | \Psi \rangle = \frac{1}{2} \int \int \frac{n^{(2)}(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' . \quad [\text{A.13}]$$

So while we have accomplished our goal for $E_{\text{el-n}}$, we have not succeeded for $E_{\text{el-el}}$; our aim is an expression in terms of the single-particle density $n(\underline{r})$, not the two-particle density $n^{(2)}(\underline{r}, \underline{r}')$. But we can express $n^{(2)}(\underline{r}, \underline{r}')$ as

$$n^{(2)}(\underline{r}, \underline{r}') = n(\underline{r})n(\underline{r}') + \Delta n^{(2)}(\underline{r}, \underline{r}') , \quad [\text{A.14}]$$

that is as a product of uncorrelated one-particle densities plus a separate correction term that accounts for the correlation. Entering this, we obtain

$$E_{\text{el-el}} = \frac{1}{2} \int \int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + \Delta E_{\text{el-el}} , \quad [\text{A.15}]$$

which means that for the moment, we treat the electronic correlation separately as a yet to be specified term $\Delta E_{\text{el-el}}$ that we will be concerned with in Section A.3. The leading term resembles just the Hartree theory.

¹Note that without loss of generality, we will limit us to even numbers of spin-degenerate electrons. Incorporation of a spin variable may easily be accomplished, but is for simplicity omitted in the following.

What remains is the calculation of the expectation value of $\hat{T}_{\text{el}}$. But for the kinetic energy operator, it is not possible to write it down as a functional of $n(\underline{r})$ straight away. To go on, one of the key ideas of density functional theory comes into play, that is mapping of the many-body problem onto a single-particle problem. We note that we have basically done this already for the potential energy in the last step by separating the correlation term. For the kinetic energy, this means that in analogy we split it into a single-particle contribution, $T_{\text{s,el}}$, and a correction term, ΔT_{el} ,

$$T_{\text{el}} = T_{\text{s,el}} + \Delta T_{\text{el}} . \quad [\text{A.16}]$$

The single-particle kinetic energy operator acts on a new set of single-particle orbitals, so-called *Kohn-Sham Orbitals* $\varphi_h(\underline{r})$, that are assumed to yield the exact same electronic density as before via

$$n(\underline{r}) = 2e \sum_h^{N_{\text{el}}/2} |\varphi_h(\underline{r})|^2 . \quad [\text{A.17}]$$

In summary, the energy expression we have obtained so far reads

$$\begin{aligned} E_{\text{el}} = & - \frac{1}{2} \sum_h^{N_{\text{el}}} \int \varphi_h^*(\underline{r}) \nabla^2 \varphi_h(\underline{r}) d\underline{r} \\ & + \int n(\underline{r}) V_{\text{el-n}} d\underline{r} + \frac{1}{2} \int \int \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' \\ & + \underbrace{\Delta T_{\text{el}} + \Delta E_{\text{el-el}}}_{E_{\text{xc}}} . \end{aligned} \quad [\text{A.18}]$$

We still have to deal with the last term, E_{xc} . This term needs to account for the difference between the non-interacting particle-picture, that we have adopted, and the true interacting particle-picture. It comprises the impact of electronic correlation (Coulomb repulsion) and exchange (Pauli repulsion). We assume that it is possible to express this correction as a functional of $n(\underline{r})$, and will get back to this so-called *exchange-correlation functional* (or *XC-functional*) in the next section.

Under this assumption, Eq. A.18 represents the desired functional expression for the ground-state energy². We may now proceed by applying the variational principle to obtain the minimum

²Note that this is not quite true since the kinetic energy involves the Kohn-Sham orbitals rather than the density. Nevertheless, since there is a simple prescription for how to obtain the density from the orbitals, we have instead obtained a functional of the single-particle orbitals. The variation principle may still be applied as the 'right' Kohn-Sham orbitals, that yield the groundstate density $n_0(\underline{r})$, must simultaneously minimize the energy.

according to Hohenberg and Kohn. Though, we differentiate equivalently with respect to the Kohn-Sham orbitals $\varphi_h^*(\underline{r})$ rather than with respect to the density:

$$\frac{\delta E_{\text{el}}}{\delta \varphi_h^*(\underline{r})} = \frac{\delta T_{\text{s,el}}}{\delta \varphi_h^*(\underline{r})} + \left[\frac{\delta E_{\text{el-n}}}{\delta n(\underline{r})} + \frac{\delta E_{\text{el-el}}}{\delta n(\underline{r})} + \frac{\delta E_{\text{xc}}}{\delta n(\underline{r})} \right] \frac{\delta n(\underline{r})}{\delta \varphi_h^*(\underline{r})} \quad [\text{A.19}]$$

$$= -\frac{\hbar^2}{2m_e} \nabla^2 \varphi_h(\underline{r}) + \underbrace{\left[V_{\text{el-n}} + \underbrace{\int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}'}_{V_{\text{H}}} + \underbrace{\frac{\delta E_{\text{xc}}}{\delta n(\underline{r})}}_{V_{\text{xc}}} \right]}_{V_{\text{eff}}} \varphi_h(\underline{r}) . \quad [\text{A.20}]$$

Next, we incorporate the constraint of charge conservation by means of a Lagrange-multiplier μ and require the functional derivative to be stationary:

$$\frac{\delta E_{\text{el}}}{\delta \varphi_h^*(\underline{r})} + \frac{\delta}{\delta n(\underline{r})} \left[\mu \left(eN_{\text{el}} - \int n(\underline{r}) d\underline{r} \right) \right] \frac{\delta n(\underline{r})}{\delta \varphi_h^*(\underline{r})} = 0 \quad [\text{A.21}]$$

$$\frac{\delta E_{\text{el}}}{\delta \varphi_h^*(\underline{r})} + \mu \frac{\delta}{\delta n(\underline{r})} \left(eN_{\text{el}} - \int n(\underline{r}) d\underline{r} \right) \varphi_h(\underline{r}) = 0 \quad [\text{A.22}]$$

$$\frac{\delta E_{\text{el}}}{\delta \varphi_h^*(\underline{r})} - \mu \varphi_h(\underline{r}) = 0 . \quad [\text{A.23}]$$

Finally, by combining the last two results, we have derived the famous *Kohn-Sham equations*:

$$\underbrace{\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} \right]}_{H^{\text{KS}}} \varphi_h(\underline{r}) = \varepsilon_h \varphi_h(\underline{r}) . \quad [\text{A.24}]$$

These represent a set of single-particle Schrödinger equations, that can numerically be solved to obtain the Kohn-Sham orbitals, the groundstate density and the electronic energy. Though, the effective potential depends on the density and thus the orbitals. Therefore, the Kohn-Sham equations have to be solved self-consistently. The calculation is iteratively restarted with a trial density $n^{(k+1)}$ calculated from the eigensolutions of the k -th iteration. For the initial starting density, $n^{(0)}$, usually a normal distribution of the electrons around the atoms or the charge density of the free atoms is assumed. The iteration is discontinued when the electronic energy

$$E_{\text{el}} = 2 \sum_h^{N_{\text{el}}/2} \varepsilon_h - \underbrace{\left[\frac{1}{2} \int \int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + \int n(\underline{r}) \frac{\delta E_{\text{xc}}}{\delta n(\underline{r})} d\underline{r} - E_{\text{xc}}[n(\underline{r})] \right]}_{\text{double-counting correction}} \quad [\text{A.25}]$$

has converged within a given tolerance interval. Noteworthy, the electronic energy is not just the sum of the eigenvalues, but requires so-called double-counting correction. To get from the

electronic energy, E_{el} , to the total energy E , the nucleus-nucleus interaction is added, that is $E = E_{\text{el}} + E_{\text{n-n}}$ as discussed in Section A.5.

More generally, fractionally occupied and unoccupied orbitals may also be obtained. The present electrons are filled into the available orbitals according to Fermi-statistics, starting from the energetically lowest. This requires the introduction of occupation numbers $0 \leq c_h \leq 2$ (for the spin-degenerate case) of the Kohn-Sham orbitals. The generalization then reads

$$2 \sum_h^{N_{\text{el}}/2} \varepsilon_h \rightarrow \sum_h^{\infty} c_h \varepsilon_h . \quad [\text{A.26}]$$

Though the calculation of unoccupied orbitals is easily facilitated within density functional theory, the theory is only valid for the groundstate. Thus, it is limited to zero temperature and only holds for the occupied states. For instance, band gaps derived as energy difference between highest occupied and lowest unoccupied orbital are usually severely underestimated.

The non-interacting Kohn-Sham particles as well as the Kohn-Sham eigenvalues are not immediately physically meaningful. Nevertheless, in solid state physics the electronic system is typically treated as a non-interacting collection of particles. Therefore, the Kohn-Sham particle comes close to what is typically called an electron in classic solid state theory and yields a good description of bands and bonds.

To summarize, density functional theory allows to treat the Schrödinger equation of a solid for the groundstate. All observables may be calculated as functionals of the charge density that minimizes the energy. To obtain an energy functional, the many-body problem is mapped onto a single-particle picture. The resulting single-particle Schrödinger equations can be solved self-consistently. The results of density functional theory are exact, if an exact treatment of exchange and correlation effects can be facilitated. Therefore, the choice of the XC-functional is of crucial importance and shall be discussed in the next section.

A.3. Exchange and Correlation Functional

In this section, suitable approximations to the exchange and correlation term E_{XC} from Eq. A.18 will be discussed. One of the first ideas that is still very popular is to employ the so-called *Local Density Approximation (LDA)* [208]. In this approach, the electronic system is assumed to be close to the case of a homogeneous electron gas. Hence, the aim is to reduce the treatment of exchange and correlation in the real solid to that of a homogeneous electron gas. Thus, Kohn

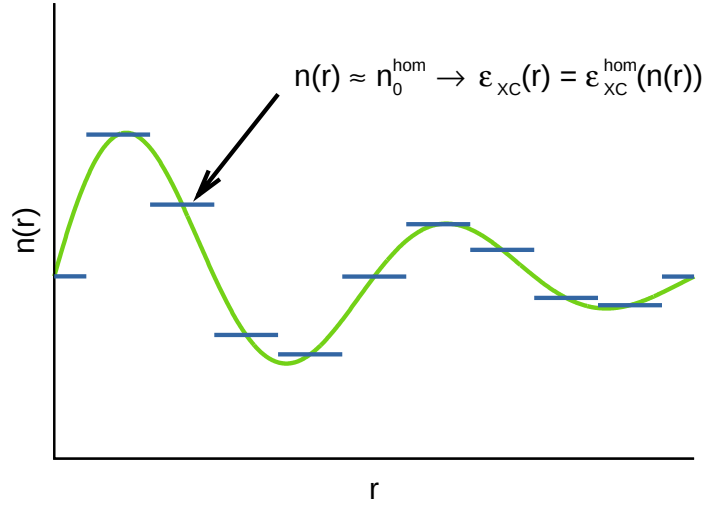


Figure A.1: In the Local Density Approximation (LDA), the exchange-correlation contribution of a material system is approximated by that of a homogeneous electron gas of the same local density.

and Sham proposed to replace the exchange-correlation energy density locally by that of a homogeneous electron gas of same density, see Fig. A.1. So the LDA-XC-functional may be expressed as

$$E_{XC}^{LDA}[n(\underline{r})] = \int n(\underline{r}) \epsilon_{XC}^{hom}(n(\underline{r})) d\underline{r}, \quad [A.27]$$

with $\epsilon_{XC}^{hom}(n(\underline{r}))$ being the XC-contribution of a homogeneous electron gas with density $n^{hom} = n(\underline{r})$. This way, one can exploit the fact that for the homogeneous electron gas, the exchange contribution ('X') can be expressed analytically as a function of n :

$$\epsilon_X^{hom}(n) = -\frac{3}{4}e^2 \left(\frac{3n}{\pi} \right)^{1/3}. \quad [A.28]$$

The missing correlation contribution ('C') may be obtained from Monte Carlo methods to great accuracy.

The LDA may be considered to work best for high, slowly-varying densities (i. e., metals) and to become worse the more inhomogeneous the electron density of the system becomes. Thus, the above approach can be improved by also taking into account the gradient of the density. This leads to the wide class of *Generalized Gradients Approximation* (GGA) functionals,

$$E_{XC}^{GGA}[n(\underline{r})] = \int f(n(\underline{r}), \nabla n(\underline{r})) d\underline{r}. \quad [A.29]$$

Various proposals for $f(n(\underline{r}), \nabla n(\underline{r}))$ are reported in literature. The functional used in this thesis, so called GGA-PBE, is the one given by Perdew, Burke and Enzerhof [162].

There are some systematic features of both LDA and GGA that should be briefly noted here. GGA is known to overestimate bond lengths, hence yielding softer systems than LDA which in turn often underestimates the bonds. Thus, experimental lattice constant are typically missed by about 2%.

A.4. Practical Aspects of DFT

In this section, the realization of density functional theory-calculations for crystalline solids is presented. Starting from the introduction of a suitable basis (plane waves) it shall be highlighted how the solution of the Kohn-Sham equations is obtained numerically and in particular, what approximations and parameters are important for the numerical treatment.

A.4.1. Plane Wave Basis

In principle, the solutions to the Kohn-Sham equations φ_h can be expanded in any complete basis set $\{\Phi_j\}$,

$$\varphi_h = \sum_j \alpha_{h,j} \Phi_j , \quad [\text{A.30}]$$

but for a crystalline solid, that is an infinitely extended periodic array of atoms, a basis set that reflects this periodicity is most suitable. Hence, this section shall be dedicated to the introduction of the plane wave basis.

A crystalline solid and its potential $v(\underline{r})$ are translational-invariant,

$$v(\underline{r}) = v(\underline{r} + \underline{R}) , \quad [\text{A.31}]$$

with $\underline{R}$ being a lattice vector. Thus, according to the Bloch-theorem, φ_h takes the form

$$\varphi_h(\underline{r}) \rightarrow \varphi_{\nu,\underline{k}}(\underline{r}) = u_{\nu,\underline{k}}(\underline{r}) e^{i\underline{k}\underline{r}} \quad \text{with} \quad u_{\nu,\underline{k}}(\underline{r}) = u_{\nu,\underline{k}}(\underline{r} + \underline{R}) . \quad [\text{A.32}]$$

The index h is replaced by the indices ν and $\underline{k}$, representing band index and wave vector, respectively. The band index is required to distinguish between different solutions for same values of $\underline{k}$. The lattice periodic function $u_{\nu,\underline{k}}(\underline{r})$ is to be expanded in plane waves. But because of the lattice periodicity, only those plane waves corresponding to reciprocal lattice vectors $\underline{G}$ contribute to this expansion,

$$u_{\nu,\underline{k}}(\underline{r}) = \sum_{\underline{G}} c_{\nu,\underline{k}}(\underline{G}) e^{i\underline{G}\underline{r}} . \quad [\text{A.33}]$$

So the plane wave ansatz reads

$$\varphi_{\nu,\underline{k}}(\underline{r}) = \sum_{\underline{G}} c_{\nu,\underline{k}}(\underline{G}) e^{i(\underline{k}+\underline{G})\underline{r}} = \sum_{\underline{q}} c_{\nu,\underline{q}} |\underline{q}\rangle . \quad [\text{A.34}]$$

In the last step, we have introduced $\underline{q} = \underline{k} + \underline{G}$ and $|\underline{q}\rangle = e^{i\underline{q}\underline{r}}$ to simplify the notation.

Accordingly, the Kohn-Sham-equations have to be reformulated in reciprocal space by calculating $\langle \underline{q}' | H^{\text{KS}} | \underline{q} \rangle$. The non-zero kinetic energy matrix elements become

$$\langle \underline{q}' | -\frac{\hbar^2}{2m} \nabla^2 | \underline{q} \rangle = \frac{\hbar^2}{2m} |\underline{q}|^2 \delta_{\underline{q},\underline{q}'} . \quad [\text{A.35}]$$

The expansion of the effective potential in plane waves yields

$$V_{\text{eff}}(\underline{r}) = \sum_{\underline{G}} V(\underline{G}) e^{i\underline{G}\underline{r}} . \quad [\text{A.36}]$$

Again, any other than components corresponding to reciprocal lattice vectors must vanish. The non-zero potential energy matrix elements become

$$\langle \underline{q}' | V_{\text{eff}}(\underline{r}) | \underline{q} \rangle = \sum_{\underline{G}} V(\underline{G}) \delta_{\underline{q}'-\underline{q},\underline{G}} . \quad [\text{A.37}]$$

With these results, we can finally obtain the reciprocal space representation of the Kohn-Sham equations. Therefore, Eq. A.34 is inserted into Eq. A.24, the result is multiplied from the left with $\varphi_{\nu,\underline{k}}^*(\underline{r})$. Employing our last results, we obtain after some calculus the set of equations

$$\sum_{\underline{G}'} \left[\frac{\hbar^2}{2m} |\underline{k} + \underline{G}'|^2 \delta_{\underline{G},\underline{G}'} + V_{\text{eff}}(\underline{G}' - \underline{G}) \right] c_{\nu,\underline{k}}(\underline{G}') = \epsilon_{\nu,\underline{k}} c_{\nu,\underline{k}}(\underline{G}) . \quad [\text{A.38}]$$

Just as before, these equations must be solved self-consistently, which may mathematically be reduced to matrix diagonalization. One typically exploits the fact that there is a separate equation for each $\underline{k}$ -point, which enables the parallelization of this calculation step by using multiple computer nodes simultaneously.

As the computational demand greatly depends on the size of the chosen basis set, that is how many plane waves are considered for the expansion, a cut-off energy E_{cut} is introduced in order to truncate it,

$$\frac{\hbar^2}{2m} |\underline{k} + \underline{G}|^2 \leq E_{\text{cut}} . \quad [\text{A.39}]$$

Only those plane waves obeying this condition are included. Physically, this limits the possibility of describing charge localization. As the choice of E_{cut} must not influence the results, its value

has to be determined in a convergence study so that the calculated quantities are not affected significantly.

Since density functional theory requires the frequent transformation between reciprocal and real space, an efficient algorithm needs to be applied. Thus, *Fast Fourier Transformation (FFT)* is the method of choice to facilitate the transformation, despite the fact that FFT acts on a cube-shaped grid, whereas the basis set of plane waves is confined to a sphere. Also, since $n(\underline{r})$ is calculated from the norm square of the wavefunction, the FFT-grid edge needs to be at least twice as long as the sphere diameter (the ratio being the so-called *boxcut*).

A.4.2. Discretization

In the above treatment, $\underline{k}$ is a continuous variable for the infinite periodic lattice and confined to the first Brillouin zone (BZ). Most properties of the system are expressed as integrals in reciprocal space. However, the desired numerical treatment calls for discretization of the reciprocal space. Thus, integrals in $\underline{k}$ -space are replaced by summations over a discrete set of $\underline{k}$ -points. Just as for the cut-off energy, one has to make sure that the considered grid of $\underline{k}$ -points is homogeneous and dense enough so that the calculated quantities are unaffected by its choice. However, the computational effort is proportional to the number of $\underline{k}$ -points. In particular, this calls for smart use of symmetries; calculations have to be run only for those $\underline{k}$ -points that lie in the *Irreducible Brillouin Zone (IBZ)*. Any other $\underline{k}$ -points of the grid can be reduced to $\underline{k}$ -points within the IBZ. Thus, a grid may be shifted to maximize this effect [211], that is to increase the number of symmetry-equivalent $\underline{k}$ -points without changing the $\underline{k}$ -point density. This is illustrated in Fig. A.2. Conclusively, the discretization of the calculation of a quantity F proceeds as

$$F = \frac{1}{\Omega} \int_{\text{BZ}} f(\nu, \underline{k}) d\underline{k} \rightarrow \frac{1}{N_{\underline{k}}} \sum_{\nu, \underline{k}}^{\text{BZ}} f(\nu, \underline{k}) = \sum_{\nu, \underline{k}}^{\text{IBZ}} w_{\nu, \underline{k}} f(\nu, \underline{k}) , \quad [\text{A.40}]$$

where Ω is Brillouin zone volume, $N_{\underline{k}}$ the number of $\underline{k}$ -points and $w_{\underline{k}}$ the weight (or multiplicity, 'how many $\underline{k}$ -points in the whole BZ are represented?') of a point in the IBZ.

Typically, only occupied states $\nu, \underline{k}$ below the Fermi energy, $\epsilon_{\nu, \underline{k}} < \epsilon_F$, play a role in the determination of F , so we have to incorporate this condition into the above formula, for instance

$$F = \sum_{\nu, \underline{k}}^{\text{IBZ}} w_{\nu, \underline{k}} f(\nu, \underline{k}) \theta(\epsilon_{\nu, \underline{k}} - \epsilon_F) . \quad [\text{A.41}]$$

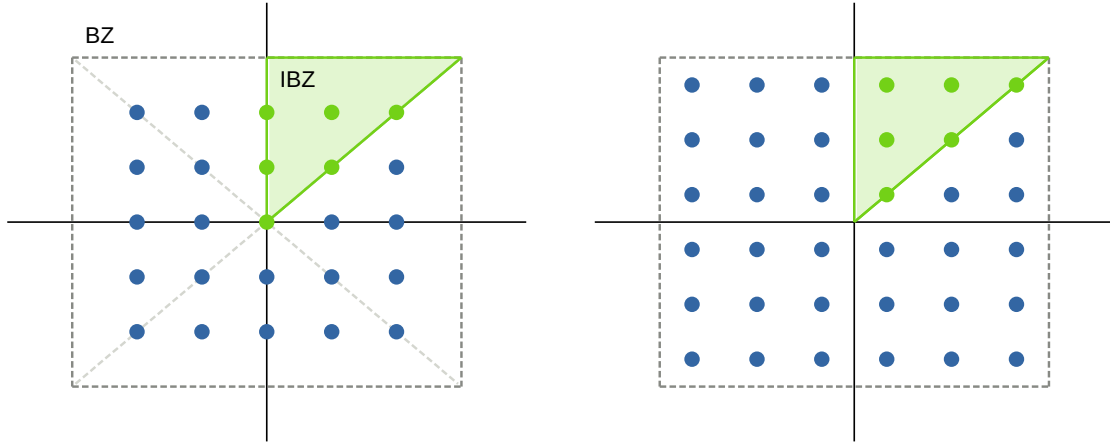


Figure A.2.: On the left-hand side an unshifted $\underline{k}$ -point-grid that is used to sample the first Brillouin Zone (BZ) is shown. Due to symmetry, it is sufficient to restrict calculations to those $\underline{k}$ -points that reside in an Irreducible Brillouin Zone (IBZ), which is highlighted. On the right-hand side, the grid has been shifted. Comparing the two cases in terms of the ratio of points within the IBZ, in both cases six, to the number of points in the entire Brillouin zone, 36 in the unshifted and 49 in the shifted case, it becomes immediately obvious that the use of a shifted grid is often favorable. Without increasing the computational effort it leads to a denser sampling of the Brillouin zone and hence to faster convergence.

The step-function $\theta(\epsilon_{\nu,\underline{k}} - \epsilon_F)$ is not an issue for semiconductors, where the density of states smoothly approaches zero below ϵ_F . For metals, however, the sharp step-function requires a dense grid of $\underline{k}$ -points to be resolved adequately. To cope with this situation, the step-like occupation function is usually replaced by a smoother function such as the Fermi distribution with a finite temperature, the so-called *smearing temperature* T_{smear} .

A.4.3. Pseudopotentials

A further simplification routinely employed in density functional theory-calculations is the use of pseudopotentials. What is the advantage? Neglecting screening effects, the electrostatic potential of an atomic core sensed by the electrons is of Z/r -kind. The core electrons are tightly bound in this potential and in comparison to the valence electrons they are very localized. In order to describe localization using plane waves, a very high cut-off energy E_{cut} is necessary. Often one does not benefit from treating all electrons with DFT, as the core electrons are not involved in bonding but behave just as in free atoms. If the core electrons can be left out,

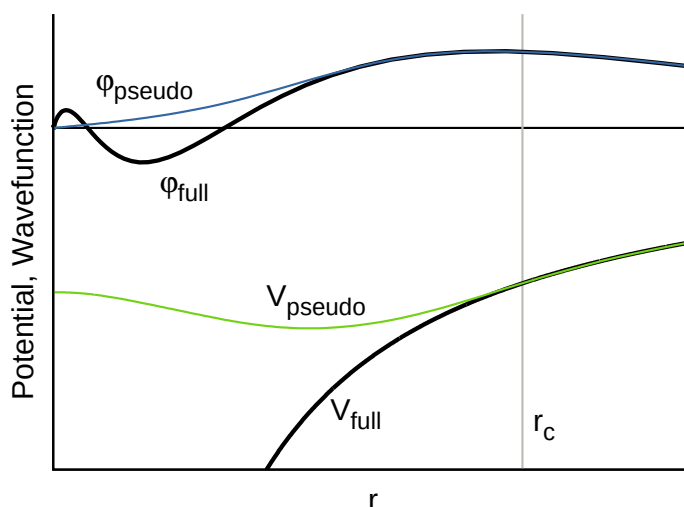


Figure A.3.: A comparison between a full $1/r$ -potential and an approximative pseudopotential as well as between the corresponding wavefunctions is presented. In the core region, the wavefunction in the case of the pseudopotential is nodeless and can be represented by a smaller set of plane waves, a small E_{cut} is sufficient. This vastly reduces the computational demands. Beyond the core region, both the full potential and the pseudopotential coincide and result in identical bonding properties.

however, the number of electrons to be treated and hence, the computational demand vastly decreases. Therefore, the atomic potentials are replaced by pseudopotentials that incorporate the impact of the core electrons on the potential for the valence electrons, cf. Fig. A.3. The core electrons are being 'frozen' (*Frozen Core Approximation*). This procedure yields 'softer' potentials for the valence electrons, since the core electrons partially screen the $1/r$ -potential. Softer potentials lead to smoother wavefunctions. Thus, not only the electron number but also the necessary size of the plane wave basis set and thereby the memory needs of calculations are significantly reduced thanks to the use of pseudopotentials.

The pseudopotentials are created under the constraints that

- real and pseudo eigenvalues agree,
- the wavefunctions coincide beyond a certain core radius r_{core} ,
- the norm is conserved (upon integration of the wavefunction from 0 to $r > r_{\text{core}}$) and
- the scattering properties are maintained.

To summarize, the numerical implementation of density functional theory-calculations for crystalline solids defines important constraints for practical applications. Most importantly, the number of electrons per unit cell must be small, even though only valence electrons are treated. Both the size of the plane wave basis set and the density of the $\underline{k}$ -point grid used to sample the Brillouin zone have a pronounced impact on the computational demand and need to be defined in a way that the calculated quantities are unaffected. In result, calculations are typically limited to less than about a hundred atoms. In the creation of pseudopotentials, 'hidden' parameters such as the choice of the core radius r_{core} enter the calculation, that can slightly affect the calculated properties such as the equilibrium volume.

A.5. The Born-Oppenheimer or Potential Energy Surface

Up to now, we have acquainted ourselves with the treatment of the electronic system in the adiabatic approximation. The positions of the nuclei only entered the effective potential as a set of parameters $\{\underline{R}_I\}$, while their kinetic energy was neglected. However, we now want to make a first step towards the energetics and dynamics of the whole system by treating the nucleus-nucleus interaction,

$$\hat{V}_{\text{n-n}} = \frac{1}{2} \sum_I^{N_n} \sum_{J \neq I}^{N_n} \frac{Z_I Z_J}{|\underline{R}_I - \underline{R}_J|} . \quad [\text{A.42}]$$

The actual calculation in the case of an infinitely extended, periodic solid proves complicated owing to the long-range interaction of the Coulomb potential. The most widely used method is the Ewald-summation. The key idea is to introduce an auxiliary, Gaussian charge distribution $c(\underline{r})$ around every atom to improve the treatment of the potential due to the nuclei charge distribution $\rho_n(\underline{r})$,

$$\begin{aligned} \rho_n(\underline{r}) &= \sum_I^{N_n} Z_I \delta(\underline{r} - \underline{R}_I) \\ &= \underbrace{\sum_I^{N_n} Z_I \delta(\underline{r} - \underline{R}_I) - \sum_I^{N_n} c(\underline{r} - \underline{R}_I)}_{\rho_n^{\text{sr}}(\underline{r})} + \underbrace{\sum_I^{N_n} c(\underline{r} - \underline{R}_I)}_{\rho_n^{\text{lr}}(\underline{r})} . \end{aligned} \quad [\text{A.43}]$$

The advantage of this procedure is that the first term, $\rho_n^{\text{sr}}(\underline{r})$, leads to a screened and thus short-ranged potential that now can reasonably well be treated in real space. The compensation charge, $\rho_n^{\text{lr}}(\underline{r})$, however, is a periodic, smooth charge distribution so that its potential can efficiently be calculated in reciprocal space. This way, the potential energy due to the nuclei,

E_{n-n} , may be obtained. Together with the electronic energy, E_{el} , the *Born-Oppenheimer Energy Surface* $E_{\text{BOS}}(\{\underline{R}_I\})$ (more universally also called *Potential Energy Surface*) is formed,

$$E_{\text{BOS}}(\{\underline{R}_I\}) = E_{\text{el}}(\{\underline{R}_I\}) + E_{n-n}(\{\underline{R}_I\}) , \quad [\text{A.44}]$$

which is considered to serve as an effective potential for the nuclei. Thus, the forces acting on the nuclei can be derived,

$$\begin{aligned} \underline{F}_J &= -\frac{dE_{\text{BOS}}(\{\underline{R}_I\})}{d\underline{R}_J} \\ &= -\frac{dE_{\text{el}}(\{\underline{R}_I\})}{d\underline{R}_J} - \frac{dE_{n-n}(\{\underline{R}_I\})}{d\underline{R}_J} . \end{aligned} \quad [\text{A.45}]$$

The actual calculation of the derivative of the electronic energy is feasible thanks to the *Hellmann-Feynman Theorem*. By virtue of this theorem, first-order derivatives of the electronic energy can easily be obtained. It shall briefly be derived here. Let λ be a continuous parameter, that (implicitly) affects Hamiltonian H_λ and eigenfunctions φ_λ . Then:

$$\begin{aligned} \frac{\partial}{\partial \lambda} E &= \frac{\partial}{\partial \lambda} \langle \varphi_\lambda | H_\lambda | \varphi_\lambda \rangle = \langle \varphi_\lambda | \frac{\partial}{\partial \lambda} H_\lambda | \varphi_\lambda \rangle + \\ &\quad \langle \frac{\partial}{\partial \lambda} \varphi_\lambda | H_\lambda | \varphi_\lambda \rangle + \langle \varphi_\lambda | H_\lambda | \frac{\partial}{\partial \lambda} \varphi_\lambda \rangle \\ &= \langle \varphi_\lambda | \frac{\partial}{\partial \lambda} H_\lambda | \varphi_\lambda \rangle + \\ &\quad \langle \frac{\partial}{\partial \lambda} \varphi_\lambda | E_\lambda | \varphi_\lambda \rangle + \langle \varphi_\lambda | E_\lambda | \frac{\partial}{\partial \lambda} \varphi_\lambda \rangle \\ &= \langle \varphi_\lambda | \frac{\partial}{\partial \lambda} H_\lambda | \varphi_\lambda \rangle + E_\lambda \left[\langle \frac{\partial}{\partial \lambda} \varphi_\lambda | \varphi_\lambda \rangle + \langle \varphi_\lambda | \frac{\partial}{\partial \lambda} \varphi_\lambda \rangle \right] \\ &= \langle \varphi_\lambda | \frac{\partial}{\partial \lambda} H_\lambda | \varphi_\lambda \rangle + E_\lambda \underbrace{\frac{\partial}{\partial \lambda} \langle \varphi_\lambda | \varphi_\lambda \rangle}_{=1} \\ &= \langle \varphi_\lambda | \frac{\partial}{\partial \lambda} H_\lambda | \varphi_\lambda \rangle . \end{aligned} \quad [\text{A.46}]$$

So the groundstate eigenfunctions resulting from a self-consistent calculation can be used to calculate the expectation value of first-order derivatives. In particular, the electronic force contributions result as

$$\frac{dE_{\text{el}}(\{\underline{R}_I\})}{d\underline{R}_J} = \frac{d}{d\underline{R}_I} \langle \varphi | H(\{\underline{R}_I\}) | \varphi \rangle = \langle \varphi | \frac{d}{d\underline{R}_J} H(\{\underline{R}_I\}) | \varphi \rangle . \quad [\text{A.47}]$$

Thus, DFT calculations allow not only for the simulation of the electronic system of a given arrangement of nuclei, but by minimizing the energy upon variation of atomic coordinates and/or cell shape, it is also possible to obtain the equilibrium structure. To facilitate the

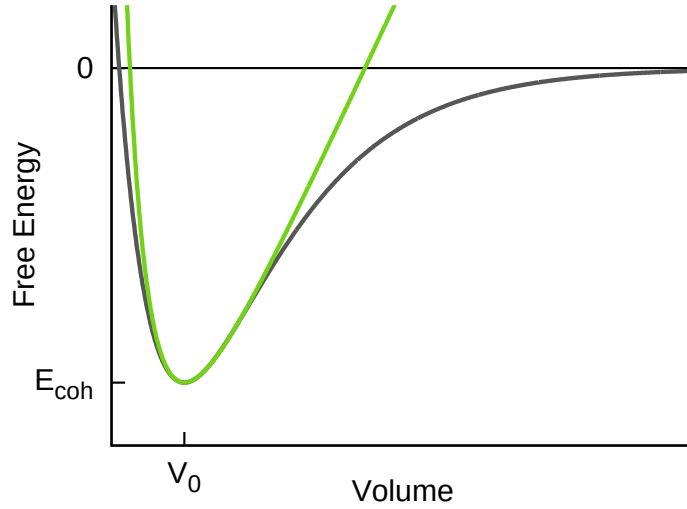


Figure A.4.: Shown in black is the free energy of a solid upon variation of its volume. Around the minimum, V_0 , the curve is approximated by the Murnaghan equation Eq. A.48 (green). For $V \rightarrow \infty$, the system decomposes into free atoms. The difference between $E(V_0)$ and $E(V \rightarrow \infty)$ is the cohesive energy E_{coh} .

search for a minimum in the Born-Oppenheimer energy surface, cell parameters and atomic coordinates are iteratively improved according to the calculated forces/stresses. Convergence is achieved when all forces or components of the stress tensor, respectively, fall below a tolerated limit. In this work the *Broyden-Fletcher-Goldfarb-Shanno algorithm* has been employed for structural relaxations.

The deliberate variation of atomic positions and the cell parameters can be very revealing since it yields insights into the properties of the solid state that are hardly accessible experimentally. For instance, it is rather simple to obtain the equation of state, that is the free energy as a function of the volume, from density functional theory-calculations. In the approach by Murnaghan, the equation of state reads

$$F(T, V) = F(T, V_0) + \frac{B_0(T)V}{B'_0(T)(B'_0(T) - 1)} \left[B'_0(T) \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{B'_0(T)} - 1 \right]. \quad [\text{A.48}]$$

Here F is the free energy, V the volume, T the temperature, B_0 the bulk modulus at zero pressure and B'_0 its derivative with respect to the pressure, evaluated at zero pressure and zero temperature. So by relaxing a system at various given volumes around the equilibrium it is possible to fit this equation (for $T = 0$). This is illustrated in Fig. A.4.

Finally, if not only the minimum of the Born-Oppenheimer energy surface is known but also its shape around the minimum, one may also access the dynamics of a system, that is its phonons. But before we can turn to the lattice-dynamics in [Appendix B](#), we shall first focus on the incorporation of small perturbations such as collective atomic displacements in density functional theory.

A.6. Perturbation Theory

Although DFT as introduced above is already a very powerful tool, it has been significantly extended to cover the response of a material to small external perturbations. Here the result of this effort, *Density Functional Perturbation Theory (DFPT)*, shall be briefly described [[160](#), [161](#), [212](#), [213](#)].

Small perturbations of the electronic system can be incorporated into the density functional framework as an additional contribution to the potential V_{eff} in a Taylor-like expansion,

$$V_{\text{eff}}(\lambda) = V_{\text{eff}}^{(0)} + \lambda V_{\text{eff}}^{(1)} + \lambda^2 V_{\text{eff}}^{(2)} + \dots \quad [\text{A.49}]$$

$$\Rightarrow H(\lambda) = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots, \quad [\text{A.50}]$$

where λ is a small parameter. The physical quantities χ that are affected by this perturbation – the energy, the wavefunction or the density – are expanded in the same way,

$$\chi(\lambda) = \chi^0 + \lambda \chi^{(1)} + \lambda^2 \chi^{(2)} + \dots \quad [\text{A.51}]$$

In all cases the expansion terms take the form

$$\chi^{(n)} = \frac{1}{n!} \left. \frac{\text{d}^n \chi}{\text{d} \lambda^n} \right|_{\lambda=0}, \quad [\text{A.52}]$$

where n denotes the order of the expansion. The great achievement of DFPT is the possibility to calculate these n -th order derivatives of the energy. Most physical quantities are derivatives of the energy, such as the dielectric susceptibility, elastic constants and the dynamical matrix as we will see in the following chapter. Hence, they can be calculated *ab initio* following the perturbation formalism.

As prerequisite, the unperturbed system ($\lambda = 0$) has to be calculated, yielding $\varphi_h^{(0)}$, $n^{(0)}$ and $\epsilon_h^{(0)}$. The expansions above are then explicitly inserted into the Schrödinger equation and sorted by orders of λ . For the first two orders a comparison yields

$$\epsilon_h^{(1)} = \langle \varphi_h^{(0)} | \frac{d}{d\lambda} H | \varphi_h^{(0)} \rangle = \langle \varphi_h^{(0)} | H^{(1)} | \varphi_h^{(0)} \rangle , \quad [\text{A.53}]$$

$$\epsilon_h^{(2)} = \frac{1}{2} \left(\langle \varphi_h^{(0)} | H^{(1)} | \varphi_h^{(1)} \rangle + \langle \varphi_h^{(1)} | H^{(1)} | \varphi_h^{(0)} \rangle \right) . \quad [\text{A.54}]$$

While the first order derivative only depends on the groundstate wavefunction – as we know already from the Hellmann-Feynman theorem – the second order requires the knowledge of the first order derivative of the wavefunction. For density functional theory calculations this means that the calculation of the *first order* derivative of the orbitals is sufficient to calculate quantities related to *second order* derivatives of the energy. Thus, density functional perturbation theory up to this order is often referred to as the *Linear Response Method*. But how can $\varphi_h^{(1)}$ be obtained?

From the above treatment (sorting by orders of λ), one may concurrently derive the *Sternheimer-equation*,

$$\left(H^{(0)} - \epsilon_h^{(0)} \right) | \varphi_h^{(1)} \rangle = - \left(H^{(1)} - \epsilon_h^{(1)} \right) | \varphi_h^{(0)} \rangle , \quad [\text{A.55}]$$

that provides a way to obtain the first-order derivatives of the orbitals, $\varphi_h^{(1)}$. For the non-degenerate case, one finds the well-known result

$$| \varphi_h^{(1)} \rangle = \sum_{j \neq h} | \varphi_j^{(0)} \rangle \frac{\langle \varphi_j^{(0)} | H^{(1)} | \varphi_h^{(0)} \rangle}{\epsilon_h^{(0)} - \epsilon_j^{(0)}} . \quad [\text{A.56}]$$

Also higher derivatives of order n can be obtained analogously, but in the present scheme the calculation of $\epsilon_h^{(n)}$ requires all wavefunctions up to $\varphi_h^{(n-1)}$. While the above result may give an idea of how perturbation theory works, the crucial task is to find an efficient way to numerically determine the desired energy derivatives from density functional theory-calculations. Moreover, also mixed derivatives need to be taken into account since most physical properties are not related to one perturbation alone. For instance, Born effective charges are – as we shall see in the next chapter – mixed energy derivatives with respect to an electric field and an atomic displacement.

The derivation of a suitable algorithm, that is implemented in ABINIT, has been developed by Gonze [160], Gonze and Lee [161]. Unfortunately, compiling the extensive derivation would go far beyond the scope of this chapter. Instead, we will limit us to a brief description of

the algorithm. Nevertheless, it is highly recommended to acquaint oneself with the details in these seminal papers. On the one hand, it is required to find a scheme that allows the determination of first-order derivatives of the wavefunctions. In the framework of Gonze [160], this is done by translating the problem to a variational problem for even orders of the expansion. Hence, this allows to exploit techniques developed for 'pure' density functional theory. On the other hand, it is necessary to derive formulas that yield mixed second order energy derivatives. Here, two approaches have been described by Gonze and Lee [161]. The first option is to employ a stationary expression for which the first order wavefunction-derivative with respect to each perturbation needs to be determined. The second option is to employ a non-stationary expression, for which the derivative with respect to only one perturbation is required. ('interchange theorem'). Thus, the latter kind of expression is more easily employed and indeed implemented in ABINIT, though in terms of the errors the first option would be more accurate. Further details shall be provided in the discussion of each quantity derived within this framework in the next chapter.

It is interesting to note that by virtue of the so-called $2n + 1$ -theorem [214], it is possible to obtain energy derivatives up to $(2n + 1)$ -th order from the knowledge of the n -th derivative of the wavefunction. To illustrate this, we assume that the correct wavefunction φ_h is known up to order n ,

$$\varphi_h = \varphi_h^{(n)} + O(\lambda^{(n+1)}) . \quad [\text{A.57}]$$

It naturally serves as a trial wavefunction φ_h^{trial} for the calculation of $\epsilon_h^{(n+1)}$. Due to the variational property of the energy functional, though, for a trial wavefunction undetermined up to order $O(\eta)$ it follows

$$\epsilon_h\{\varphi_h^{\text{trial}} + O(\eta)\} = \epsilon_h\{\varphi_h^{\text{trial}}\} + O(\eta^2) . \quad [\text{A.58}]$$

Thus, applying the substitution $\eta = \lambda^{n+1}$, one finds

$$\epsilon_h\{\varphi_h^{(n)} + O(\lambda^{(n+1)})\} = \epsilon_h\{\varphi_h^{(n)}\} + O(\lambda^{(2n+2)}) . \quad [\text{A.59}]$$

This means that the knowledge of $\varphi_h^{(n)}$ is sufficient to obtain ϵ_i up to order $2n + 1$. In particular, third order derivatives could as well be derived from $\varphi_h^{(1)}$.

In principle, rather than employing density functional perturbation theory one may also choose the *direct approach* to obtain (energy) derivatives. Here, the perturbation is explicitly introduced into the system (e. g., atomic displacements are taken into account by actually moving the atoms). The derivative may thus be approximated by the finite difference obtained from the calculations with and without the perturbation,

$$\frac{\partial E}{\partial \lambda} \approx \frac{E(\lambda) - E(0)}{\lambda} . \quad [\text{A.60}]$$

One of the drawbacks of the direct approach is the fact that incommensurate perturbations pose a serious challenge. For instance, phonons with arbitrary, non-zero wavevectors may require calculations with very large cells that easily exceed the available computational resources. Thus, density functional perturbation theory has become the most popular approach to obtain energy derivatives since implementations have become available in most of the popular codes.

Appendix B.

Solid State Properties from First Principles

In this chapter, we shall briefly review the lattice-dynamics of crystalline solids and immediately related properties, in particular effective charges as well as the dielectric function. Furthermore, it shall be highlighted how these quantities can be obtained by means of density functional perturbation theory-calculations. We begin with the investigation of charges in solids that reveal a wealth of information on the bonding and its sensitivity with respect to atomic displacements.

B.1. Static and Dynamic Charges

While free atoms have unambiguously defined electronic charges, bonding in molecules and solids leads to a charge redistribution. This raises the question what atom certain charge 'belongs to'. There are two approaches to associate charges with particular atoms, namely static (Bader, Mulliken, ...) and dynamic (Born, Callen, Szigeti, ...) definitions.

B.1.1. Bader Charge Analysis

The static charge definition by Bader [215] relies on the partitioning of the charge density $n(\underline{r})$ as obtained for instance by density functional theory-calculations. Especially for covalently bonded materials, such a definition suffers from arbitrariness – how can a certain region in space be attributed to one particular atom? The approach by Bader is based on analyzing the gradient vector field of the charge density, $\nabla n(\underline{r})$. If one follows the density gradient lines starting at some point $\underline{r}_0$, one usually ends at the site of one nucleus, since here, the (total) charge density exhibits a maximum. Thus, the starting point may be associated with the specific

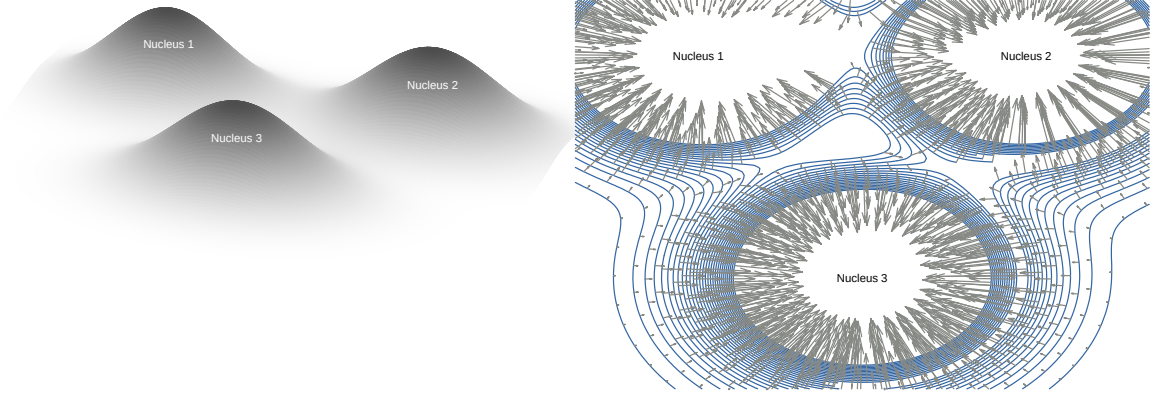


Figure B.1.: Shown on the left-hand side is a schematic, two-dimensional charge distribution $n(x, y)$. The right-hand side visualizes the contour lines (blue) as well as the gradients of this distribution, $\nabla n(x, y)$ (gray). Following the gradient lines, each point is either attributed to one of the nuclei or is part of the separating zero-flux lines.

nucleus that one ends at. This is shown in Fig. B.1. This way, each atom is attributed a certain so-called *Bader volume*. These volumina are separated by zero-flux surfaces, where

$$\nabla n(\underline{r}_s) \underline{s}(\underline{r}_s) = 0, \quad [\text{B.1}]$$

with $\underline{s}(\underline{r}_s)$ being the normal to this surface. Integrating the enclosed charge density yields the *Bader charge* of an atom, Z , that may serve as a measure of ionicity. Further analysis of the extrema of the charge density can be used to describe the bonding geometry. For instance, along a covalent bond a so-called *Bond Critical Point (BCP)* is found. At this saddle point, the charge density along the bond exhibits a minimum, but a maximum with respect to any direction normal to the bond axis.

B.1.2. Born Effective Charge

The arbitrariness of static charge definitions is absent in the treatment of dynamic charges. The following presentation is based on ref. 216. Definitions of dynamical charges rely on quantities affected by these, that can (at least in principle) be determined experimentally. Therefore, the change of the macroscopic polarization $\underline{P}$ induced by atomic displacements $\underline{X}$ is a reasonable

way to define effective charges Z^{*1} . Depending on the boundary conditions, there are different definitions, the most important ones are:

- *Transversal charge or Born effective charge* [217]

$$Z_{\alpha,\mu\nu}^{*(T)} = \Omega_0 \left. \frac{\partial P_\nu}{\partial X_{\alpha\mu}} \right|_{\underline{E}=0}, \quad [\text{B.2}]$$

- *Longitudinal charge or Callen charge* [218]

$$Z_{\alpha,\mu\nu}^{*(L)} = \Omega_0 \left. \frac{\partial P_\nu}{\partial X_{\alpha\mu}} \right|_{\underline{D}=0}, \quad [\text{B.3}]$$

- *Szigeti charge* [219]

$$Z_{\alpha,\mu\nu}^{*(S)} = \Omega_0 \left. \frac{\partial P_\nu}{\partial X_{\alpha\mu}} \right|_{\underline{E}_{\text{loc}}=0}. \quad [\text{B.4}]$$

The index α denotes an atom in the unit cell, the latter having the volume Ω_0 . The indices μ and ν run over the three linearly independent (Cartesian) directions. The different boundary conditions require either the *macroscopic* electric field $\underline{E}$, the *macroscopic* displacement field $\underline{D}$ or the *local* electric field at the atomic site $\underline{E}_{\text{loc}}$ to vanish. Longitudinal and transversal charges are connected by the optical dielectric tensor,

$$Z_{\alpha,\mu\nu}^{*(T)} = \sum_{\tau} \epsilon_{\nu\tau}^{\infty} Z_{\alpha,\mu\tau}^{*(L)}. \quad [\text{B.5}]$$

No universal relation to the Szigeti charge can be given as such relations depend on specific estimates of the non-observable local electric field for a given material. Though, in the case of an isotropic material one finds

$$Z_{\alpha}^{*(T)} = \frac{(\epsilon^{\infty} + 2)}{3} Z_{\alpha}^{*(S)}. \quad [\text{B.6}]$$

Because of charge neutrality, the Born effective charges must fulfill the *sum rule*

$$\sum_{\alpha} Z_{\alpha,\mu\nu}^{*(T)} = 0. \quad [\text{B.7}]$$

¹Note that the commonly employed notation ' Z^* ', that is also adopted in this thesis, does not denote the complex conjugate (effective charges are real numbers).

From here, we will be concerned only with Born effective charges, thus the index '(T)' will be omitted in the following.

The significance of static and dynamical charges can be understood by investigating a simple example: a diatomic molecule, consisting of atoms 'A' and 'B' with an interatomic distance u and dipole moment $p(u)$,

$$p(u) = Z(u)u . \quad [\text{B.8}]$$

The dynamical charge is defined as

$$Z^*(u) = \frac{\partial p(u)}{\partial u} \quad [\text{B.9}]$$

$$= \frac{\partial (Z(u)u)}{\partial u} \quad [\text{B.10}]$$

$$= Z(u) + u \frac{\partial Z(u)}{\partial u} . \quad [\text{B.11}]$$

So the dynamical charge is composed of the static charge and an additional dynamical contribution. The latter is the higher the more sensitive the charge distribution to changes in the atomic positions is. In general, dynamical charges can exceed not only the static charges, but also the nominal atomic charges. In the latter case, the amplitude of Z^* is termed anomalous.

For solids, the Born effective charge is the most interesting definition of a dynamical charge. As explained above, it indicates the strength of the coupling between small structural distortions and the charge distribution. Moreover, it determines the amount of LO-TO splitting for phonons at Γ as we shall see in [Section B.4.3](#). A high value can indicate a (ferroelectric) instability. It is therefore desirable to determine the Born effective charge tensor to investigate the connection between electronic properties, the bonding and the crystal structure.

According to [ref. 161](#), Born effective charges can be calculated *ab initio* using density functional perturbation theory. The present method is based on the identity

$$Z_{\alpha,\mu\nu}^{*(T)} = \Omega_0 \left. \frac{\partial P_\nu}{\partial X_{\alpha\mu}(\underline{q}=0)} \right|_{\underline{E}=0} = \frac{\partial F_{\alpha\nu}}{\partial E_\nu} , \quad [\text{B.12}]$$

and is calculated as

$$Z_{\alpha,\mu\nu}^{*(T)} = Z_\alpha \delta_{\mu\nu} + \Delta Z_{\alpha,\mu\nu} , \quad [\text{B.13}]$$

with the leading term denoting the ionic charge and the last term, $\Delta Z_{\alpha,\mu\nu}$, being the actual dynamic electronic contribution. The non-stationary implementation in ABINIT requires the calculation of the first-order derivatives of the wavefunction with respect to their wavevectors and to atomic displacements [see [161](#), section V. eq. 39 to 43]. The sum rule is likely to be broken

due to the discretization and the finite set of plane waves. It can be corrected by redistributing the excess charge among the atoms.

B.2. Electron Localization Function

Static Bader charges primarily provide a measure of ionicity and, if the critical points are evaluated, a description of the geometry of the bonding. However, the Bader analysis does not quantify the covalency. Thus, a measure of electron localization in covalent bonds is desired. The *electron localization function (ELF)* introduced by Becke and Edgecombe [220] serves this purpose. Using σ as a spin variable, it is defined as

$$\text{ELF} = [1 + (D_\sigma/D_\sigma^0)^2]^{-1}, \quad [\text{B.14}]$$

where the quantity D_σ reads

$$D_\sigma = \sum |\nabla \varphi_h|^2 - \frac{1}{4} \frac{(\nabla n_\sigma)^2}{n_\sigma} \quad [\text{B.15}]$$

and D_σ^0 is the respective expression for a homogeneous electron gas,

$$D_\sigma^0 = \frac{3}{5} (6\pi^2)^{2/3} n_\sigma^{5/3}. \quad [\text{B.16}]$$

By this definition, the ELF yields a relative measure of localization. Why is this so? As argued in ref. 220, the conditional probability of finding an electron of spin σ near a like-spin reference electron is the smaller the more localized the reference electron is. The quantity D_σ provides a measure of this conditional probability; the smaller D_σ , the smaller the pair probability and thus the more localized the reference electron. The ELF takes values between zero ($D_\sigma \rightarrow \infty$) and unity (perfect localization, $D_\sigma \rightarrow 0$). A value of $1/2$ denotes electron-gas like pair probability (i. e., $D_\sigma = D_\sigma^0$). The investigation of the ELF along a line connecting two atoms thus yields insight into the strength of the covalent bond between the atoms. For instance, Savin et al. [202] analyzed the ELF for a series of IV-crystals, that is silicon, germanium and tin. Here, the transition from strong covalent to more metallic bonding could be observed as a drop of the ELF-values in the bonding region. From a comparison between metallic (Al), ionic (NaCl, CsCl) and semiconducting system (tetrahedral: Si, Ge, GaAs, InSb; octahedral: GeTe, SnTe) in the Bachelor thesis of Czaja [201] (advised within the framework of this thesis), the significance of variations in the ELF in particular along the bonds could be confirmed.

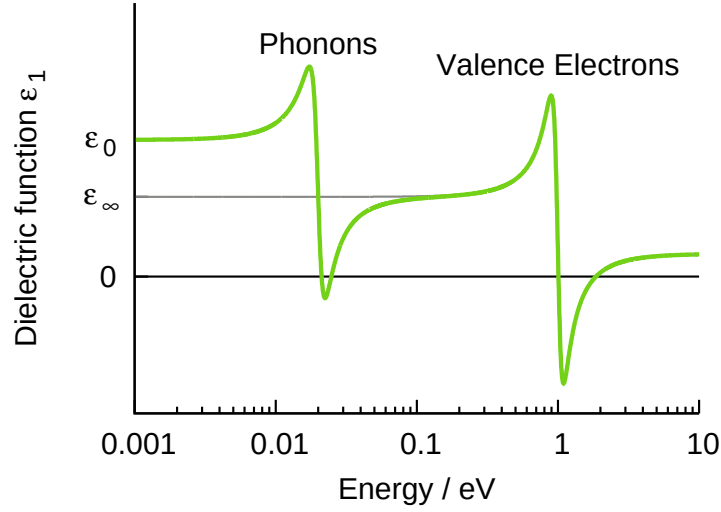


Figure B.2.: The real part of the dielectric function, $\epsilon_1(\omega)$, exhibits contributions due to transitions of the valence electrons (typically ~ 1 eV) and phonon contributions (~ 0.01 eV). The definitions of the optical dielectric constant ϵ^∞ and the static dielectric constant ϵ^0 are indicated.

B.3. Dielectric Tensor

An important property of a solid is its response to an external field and is described by the dielectric tensor $\epsilon_{\mu\nu}$. It relates the macroscopic displacement field $\underline{D}$ to the macroscopic electric field $\underline{E}$,

$$\underline{D} = \epsilon_0 \underline{E} + \underline{P} \approx \epsilon_0 \underline{E} + \epsilon_0 \underline{\chi} \underline{E} = \underline{\epsilon} \underline{E} \quad \Rightarrow \quad D_\mu = \sum_\nu \epsilon_{\mu\nu} E_\nu . \quad [\text{B.17}]$$

The polarization $\underline{P}$ is approximately linear in $\underline{E}$, with the susceptibility tensor $\underline{\chi}$ as proportionality factor. The dielectric tensor is related to it by $\underline{\epsilon} = \epsilon_0 (\underline{1} + \underline{\chi})$. It is a frequency-dependent property with two important regimes as shown in Fig. B.2. In the limit of high frequencies, that is immediately above the phonon regime but below any interband transitions, only the electronic system contributes to the polarization. The high frequency limit of the dielectric tensor is called optical dielectric tensor $\epsilon_{\mu\nu}^\infty$. For small frequencies, also the atomic system is able to respond and contributes to the polarization. The static limit is denoted $\epsilon_{\mu\nu}^0$.

The formula implemented in ABINIT within the density functional perturbation theory-framework to obtain the optical dielectric tensor reads [161]

$$\epsilon_{\mu\nu}^\infty = \delta_{\mu,\nu} - \frac{2}{\epsilon_0 \Omega_0} E_{\text{el}}^{E_\mu^* E_\nu} , \quad [\text{B.18}]$$

where $E_{\text{el}}^{E_\mu^* E_\nu}$ may be obtained in the non-stationary approach from the knowledge of the first-order derivatives of the wave functions with respect to an electric field and wave vectors [see 161, section IV, eq. 36 to 38].

The static dielectric tensor can be derived from the knowledge of the electronic contribution, $\epsilon_{\mu\nu}^\infty$, and – in the harmonic approximation – the phonons that will be treated in the next section. We will be concerned with the determination of the frequency dependent dielectric tensor, including the static limit, in Section B.4.2.

B.4. Lattice-Dynamics

The atomic potential landscape is of utmost importance for many material properties. First of all, its principal shape is of interest as it reveals structural instabilities that can be traced back to the bonding properties. Then, thermal excitation leads to movement of the atoms in this potential. Based on the knowledge of the vibrational degrees of freedom, it becomes possible to predict thermodynamic quantities such as the free energy of a solid, $F(T, V)$, and temperature-induced phase transitions. Hence, the theory of lattice-dynamics and their calculation with *ab initio*-methods is presented in this section.

B.4.1. Lattice-Dynamics in the Harmonic Approximation

As has been stated previously in Section A.5, the Born-Oppenheimer or Potential Energy Surface $E_{\text{BOS}}(\{\underline{R}_I\})$ can be regarded as an effective potential for the nuclei. Hence, it is possible to determine the lattice-dynamical properties by solving the Schrödinger equation

$$\underbrace{\left[-\sum_I^{N_n} \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \underline{R}_I^2} + E_{\text{BOS}}(\{\underline{R}_I\}) \right]}_{H_{\text{ph}}} \Theta(\{\underline{R}_I\}) = \varepsilon \Theta(\{\underline{R}_I\}), \quad [\text{B.19}]$$

where $\underline{R}_I$ is the coordinate and M_I the mass of nucleus I . In order to make this feasible analytically, the potential is expanded up to the second order around the equilibrium positions $\{\underline{R}_I^0\}$,

$$E_{\text{BOS}}(\{\underline{R}_I\}) \approx E_{\text{BOS}}(\{\underline{R}_I^0\}) + \frac{1}{2} \sum_{\alpha, \beta=1}^{N_n} \sum_{\mu, \nu=1}^3 \left(\frac{\partial^2 E_{\text{BOS}}(\{\underline{R}_I\})}{\partial R_{\alpha\mu} \partial R_{\beta\nu}} \right) \bigg|_{\{\underline{R}_I^0\}} X_{\alpha\mu} X_{\beta\nu} + \dots \quad [\text{B.20}]$$

The indices α, β run over the atoms, μ, ν over the Cartesian directions, and the atomic displacements are denoted X , defined as

$$\underline{R}_I = \underline{R}_I^0 + \underline{X}_I . \quad [\text{B.21}]$$

Derivatives with respect to $\underline{R}_I$ may simply be replaced by derivatives with respect to $\underline{X}_I$,

$$\frac{\partial^2}{\partial \underline{R}_I^2} \rightarrow \frac{\partial^2}{\partial \underline{X}_I^2} . \quad [\text{B.22}]$$

In this so called harmonic approximation, the first-order term vanishes in the equilibrium configuration (zero forces). Some phenomenological findings cannot be explained within this approximation, such as the thermal expansion or the finite heat conductivity due to Umklapp processes. With the *dynamical matrix* $\underline{D}$ being defined as

$$\begin{aligned} D_{\beta\nu}^{\alpha\mu} &= \frac{1}{\sqrt{M_\alpha M_\beta}} \left(\frac{\partial^2}{\partial R_{\alpha\mu} \partial R_{\beta\nu}} E_{\text{BOS}}(\{\underline{R}_I\}) \right) \Big|_{\{\underline{R}_I^0\}} \\ &= \frac{1}{\sqrt{M_\alpha M_\beta}} \left(\frac{\partial}{\partial R_{\beta\nu}} F_{\alpha\mu}(\{\underline{R}_I\}) \right) \Big|_{\{\underline{R}_I^0\}} , \end{aligned} \quad [\text{B.23}]$$

Equation B.19 reads in the harmonic approximation:

$$H_{\text{ph}} - E_{\text{BOS}}(\{\underline{R}_I^0\}) \approx - \sum_{\alpha=1}^{N_n} \sum_{\mu=1}^3 \frac{\hbar^2}{2M_\alpha} \frac{\partial^2}{\partial X_{\alpha\mu}^2} + \frac{1}{2} \sum_{\alpha,\beta=1}^{N_n} \sum_{\mu,\nu=1}^3 \sqrt{M_\alpha M_\beta} D_{\beta\nu}^{\alpha\mu} X_{\alpha\mu} X_{\beta\nu} . \quad [\text{B.24}]$$

This expression is almost the same as for a harmonic oscillator as known from quantum theory, but up to now all degrees of freedom are coupled. In order to apply the harmonic oscillator-formalism, they have to be decoupled. Obviously, the dynamical matrix is symmetric due to Newton's third law,

$$D_{\beta\nu}^{\alpha\mu} = D_{\alpha\nu}^{\beta\mu} , \quad [\text{B.25}]$$

so an unitarian transformation $\underline{U}$ exists that diagonalizes $\underline{D}$,

$$\underline{U}^{-1} \underline{D} \underline{U} = \delta_{\alpha,\beta} \delta_{\mu,\nu} \omega_{\alpha\mu} = \delta_{i,j} \omega_i^2 = \begin{pmatrix} \omega_1^2 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \omega_{3N_n}^2 \end{pmatrix} . \quad [\text{B.26}]$$

To simplify the notation, the indices have been combined ($\alpha\mu \rightarrow i, \beta\nu \rightarrow j$). The application of this transformation to the Hamiltonian H_{ph} results in

$$H_{\text{ph}} - E_{\text{BOS}}(\{\underline{R}_I^0\}) = \sum_{i=1}^{3N_n} \left(-\frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial \zeta_i^2} + \frac{1}{2} M_i \omega_i^2 \zeta_i^2 \right) . \quad [\text{B.27}]$$

As the transformation $\underline{U}$ also affects the basis, the *normal coordinates* ζ_i replace the original coordinates X_i . Equation B.27 is just a sum of Hamiltonians of decoupled harmonic oscillators. Hence, by comparison the energy eigenvalue is found to be

$$\varepsilon - E_{\text{BOS}}(\{\underline{R}_I^0\}) = \sum_{i=1}^{3N_n} \hbar \omega_i \left(n_i + \frac{1}{2} \right), \quad [\text{B.28}]$$

where n_i is the occupation number of mode i . The latter numbers depend on the temperature as phonons are thermally activated, and are given by the Bose-Einstein-distribution

$$n_i = \frac{1}{\exp(\hbar \omega_i / k_B T) - 1}. \quad [\text{B.29}]$$

Usually, in introductory solid state physics textbooks the classical Hamiltonian $H_{\text{ph}}^{\text{class}}$ corresponding to Eq. B.19 is solved instead of the quantum mechanical system in order to discuss the normal modes. Following this approach, we obtain (with the constant $E_{\text{BOS}}(\{\underline{R}_I^0\})$ omitted for simplicity):

$$H_{\text{ph}}^{\text{class}} = - \sum_{\alpha=1}^{N_n} \sum_{\mu=1}^3 \frac{M_{\alpha}}{2} \dot{X}_{\alpha\mu}^2 + \frac{1}{2} \sum_{\alpha,\beta=1}^{N_n} \sum_{\mu,\nu=1}^3 \sqrt{M_{\alpha} M_{\beta}} D_{\beta\nu}^{\alpha\mu} X_{\alpha\mu} X_{\beta\nu}. \quad [\text{B.30}]$$

The Euler-Lagrange differential equations or *equations of motion* to solve then read

$$M_{\alpha} \ddot{X}_{\alpha\mu} + \sum_{\beta=1}^{N_n} \sum_{\nu=1}^3 \sqrt{M_{\alpha} M_{\beta}} D_{\beta\nu}^{\alpha\mu} X_{\beta\nu} = 0. \quad [\text{B.31}]$$

Again, these are the coupled equations of motion for classical harmonic oscillators. For the time-dependence, a harmonic ansatz is made,

$$X_{\alpha\mu}(t) = \tilde{X}_{\alpha\mu} \cos(\omega t) \Rightarrow -\omega^2 M_{\alpha} \tilde{X}_{\alpha\mu} + \sum_{\beta=1}^{N_n} \sum_{\nu=1}^3 \sqrt{M_{\alpha} M_{\beta}} D_{\beta\nu}^{\alpha\mu} \tilde{X}_{\beta\nu} = 0. \quad [\text{B.32}]$$

For this system of linear equations to be solvable, the determinant has to vanish, eventually resulting in a calculation rule for the frequencies,

$$\det(\underline{D} - \omega^2 \underline{1}) \stackrel{!}{=} 0. \quad [\text{B.33}]$$

By now, we have treated a finite system, but a solid has an infinite number of atoms. However, by exploiting the lattice periodicity we can restrict the actual calculation to one unit cell (Brillouin zone). Therefore, we now limit the range of α and β to the s atoms in the unit cell and sum over all unit cells separately (indices τ, κ). The solutions of eq. B.31 are expanded in plane waves,

$$X_{\tau\alpha\nu} = \zeta_{\alpha\mu}(\underline{q}) e^{i(\underline{q}\underline{r}_{\tau} - \omega t)}, \quad [\text{B.34}]$$

where $\underline{r}_\tau$ points to the origin of cell τ , altogether resulting in

$$-\omega^2 M_\alpha \zeta_{\alpha\mu}(\underline{q}) + \sum_{\beta=1}^s \sum_{\nu=1}^3 \sqrt{M_\alpha M_\beta} \underbrace{\left(\sum_{\tau} D_{\kappa\beta\nu}^{\tau\alpha\mu} e^{iq(\underline{r}_\tau - \underline{r}_\kappa)} \right)}_{D_{\beta\nu}^{\alpha\mu}(\underline{q})} \zeta_{\beta\nu}(\underline{q}) = 0. \quad [\text{B.35}]$$

Implicitly, the definition of the reciprocal dynamical matrix $D_{\beta\nu}^{\alpha\mu}(\underline{q})$ is given, which is indeed independent of κ because of translation invariance,

$$D_{\kappa\beta\nu}^{\tau\alpha\mu} = D_{(\tau-\kappa)\beta\nu}^{\alpha\mu}. \quad [\text{B.36}]$$

As the sum depends only on differences between τ and κ and spans all unit cells, it is independent of the choice of κ . Again, the transformation into reciprocal space has vastly simplified the calculation. Finally, the energy eigenvalues are taken from the quantum theoretical calculation, but with respect to the Fourier transform they now read

$$\varepsilon - E_{\text{BOS}}(\{\underline{R}_I^0\}) = \sum_{\underline{q}} \sum_{i=1}^{3s} \hbar \omega_i(\underline{q}) \left(n_i(\underline{q}) + \frac{1}{2} \right). \quad [\text{B.37}]$$

Three $\underline{q}$ -dependent modes are obtained for every atom in the unit cell. Three of them correspond to translations in the limit of $\underline{q} \rightarrow 0$ and are hence called acoustic modes ('A'). While their frequencies vanish at the zone center ($=\Gamma$ -point), the slope of these modes determines the speed of sound. The remaining $(3s - 3)$ modes are referred to as optical modes ('O'). The latter name arises from the fact that the atoms vibrate against each other at $\underline{q} = 0$, giving rise to interactions with electro-magnetic waves. Further, the modes can be classified as transverse ('T') or longitudinal ('L') modes. For simple systems, this classification just depends on whether the displacements are perpendicular or parallel to a given wavevector $\underline{q}$. We will introduce a more general definition below. Before, we shall first turn to the dielectric response of the phonons.

B.4.2. Dielectric Contribution and Mode-Effective Charges

Now that we have obtained Born effective charges, the optical dielectric tensor as well as the phonons (in particular at the Γ -point), we are in a position to calculate the low-frequency dielectric tensor $\epsilon_{\mu\nu}(\omega)$ [see 161, section VIII, eq. 54 to 55]. It is composed of the electronic contribution plus the polarization due to the ionic response that can be taken into account as a series of harmonic oscillators,

$$\epsilon_{\mu\nu}(\omega) = \epsilon_{\mu\nu}^\infty + \frac{4\pi}{\Omega_0} \sum_i \frac{S_{i,\mu\nu}}{\omega_i^2 - \omega^2}. \quad [\text{B.38}]$$

Here, the index i runs over all $\underline{q} = 0$ -modes of frequencies ω_i . The measure of the contribution of each mode to the polarization is provided by the *mode-oscillator-strength tensors* $S_{i,\mu\nu}$, defined as

$$S_{i,\mu\nu} = \left(\sum_{\beta\tau} Z_{\beta,\mu\tau}^* \zeta_{i,\underline{q}=0}(\beta\tau) \right) \times \left(\sum_{\gamma\kappa} Z_{\gamma,\nu\kappa}^* \zeta_{i,\underline{q}=0}(\gamma\kappa) \right). \quad [\text{B.39}]$$

It is little surprise that the mode-oscillator strength tensors primarily result from the Born effective charges; the larger the dynamic charges are, the larger the change in polarization due to atomic displacements can get, with an approximately quadratic dependence (e. g., $\epsilon^0 - \epsilon^\infty \propto (Z^*)^2$ for a simple cubic material with only two atoms in the unit cell.).

It is important to note that the determination of $\epsilon_{\mu\nu}^0$ following this procedure is limited by the validity boundaries of the harmonic approximation.

We may use the last result as motivation to assign the individual Γ -modes so-called *mode-effective charges* $\underline{Z}_i^*$. To do so, we may just evaluate the contributions of all atoms involved in a particular mode i . In result, the components of the vector $\underline{Z}_i^*$ are given by

$$Z_{i,\mu}^* = \frac{\sum_{\alpha,\nu} Z_{\alpha,\mu\nu}^* \zeta_{i,\underline{q}=0}(\alpha\nu)}{\sqrt{\sum_{\alpha\nu} (\zeta_{i,\underline{q}=0}(\alpha\nu))^* \zeta_{i,\underline{q}=0}(\alpha\nu)}}, \quad [\text{B.40}]$$

where $\zeta_{i,\underline{q}=0}(\alpha\nu)$ is the eigendisplacement of atom α along ν for the i -th Γ -point mode [see 161, section VIII, eq. 52 to 53]. The mode-effective charge vectors allow for the promised generalized definition of TO- and LO-modes; only for directions of $\underline{q}$ along the direction of $\underline{Z}_i^*$ does mode i contribute to $\epsilon_{\mu\nu}(\omega)$. Thus, for a given direction in reciprocal space, $\hat{e}_{\underline{q}}$, a mode may be called longitudinal if its mode effective charge vector is parallel to $\hat{e}_{\underline{q}}$. If both are perpendicular, $\hat{e}_{\underline{q}} \underline{Z}_i^* = 0$, the mode is referred to as transversal. Moreover, the length of $\underline{Z}_i^*$ reveals how sensitive the charge distribution (or polarization) is with respect to the i -th mode.

The polarization that is induced by a longitudinal long-wavelength phonon has an impact on the interatomic forces. This leads to some subtleties in the treatment of phonons near the Γ -point that we shall turn to next.

B.4.3. Zone-Center Phonons and the LO-TO-Splitting

At long wavelengths (i. e., close to the Γ -point), a splitting of LO- and TO-modes is observed in many materials. The reason for this lies in the origin of the force constants that enter the dynamical matrix. To illustrate this, we may compare the planes of (charged) atoms in a crystal

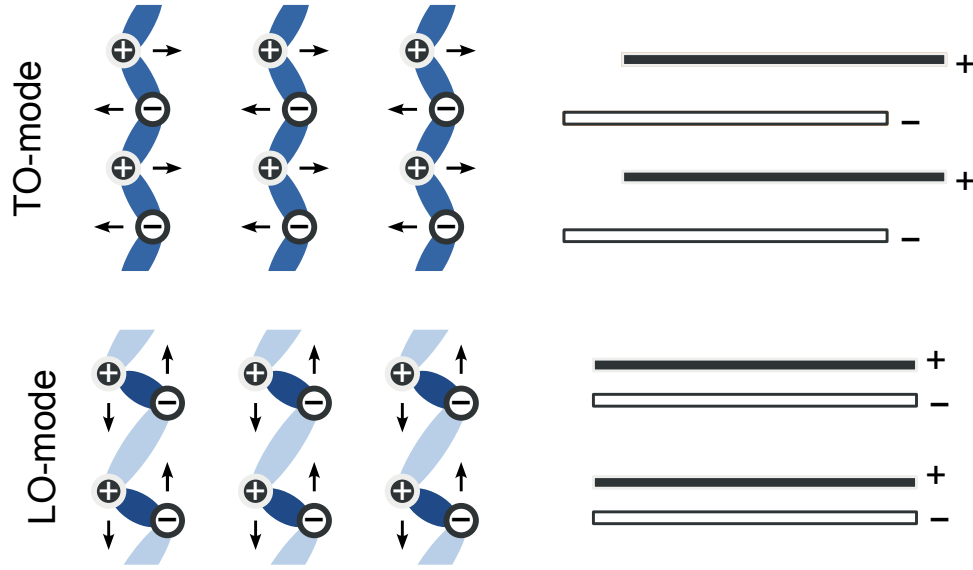


Figure B.3.: The origin of the LO-TO-splitting may be illustrated by the model of a parallel plate capacitor [221]. A long-wavelength phonon with $\underline{q}$ pointing towards the top of the page displaces the atoms. Each plane of atoms perpendicular to $\underline{q}$ may be replaced by a charged plate. The charge stems from the atomic Born effective charges, while the optical dielectric constant of the material screens the Coulomb-interaction between the plates. In the top row, a TO-mode causes the plates to slide pass each other. The LO-mode shown in the bottom row, however, changes the distance between the plates. Thus, an additional force arises for the LO-mode that increases its energy.

to the plates of a parallel plate capacitor as noted by Yu and Cardona [221], see Fig. B.3. If the plates slide pass each other (like in a TO-mode), the energy of the capacitor does not change. But if their distance is varied (LO-mode), the energy does change and an additional restoring force arises. Due to this force, the frequency of the LO mode is shifted to a higher energy. The amount of the split is determined by the magnitude of the charges and the dielectric tensor. The latter comes into play due to the screening of the charge. While this effect averages out for short wavelengths, it is important for long wavelengths and thus, it must be taken into consideration for the appropriate calculation of phonon modes near the Γ -point.

Mathematically, this effect is obtained if one explicitly writes down the individual contributions to the force constants in the dynamical matrix, $D_{\beta\nu}^{\alpha\mu}(\underline{q})$. First, we have contributions by the nuclei, that can be treated by the Ewald summation technique, cf. Section A.5. For the

electronic contribution, one finds that in the limit of long wavelengths, $\underline{q} \rightarrow 0$, the entries in the dynamical matrix split into two terms [see 161, section VIII.B, eq. 59 to 64],

$$D_{\beta\nu}^{\alpha\mu}(\underline{q} \rightarrow 0) = A_{\beta\nu}^{\alpha\mu}(\underline{q} = 0) + N_{\beta\nu}^{\alpha\mu}(\underline{q} \rightarrow 0) , \quad [\text{B.41}]$$

where the first term denotes an analytical contribution and the second, non-analytical and direction-depending term represents the effect of the polarization. The mathematical origin of this splitting is a divergence in the second-order derivative of the energy if $|\underline{q} + \underline{G}|$ vanishes [160, section V.C, eq. 60 and section VII.A]. The non-analytical term is given by

$$N_{\beta\nu}^{\alpha\mu}(\underline{q} \rightarrow 0) = \frac{4\pi}{\Omega_0} \frac{(\sum_{\tau} q_{\tau} Z_{\alpha,\tau\mu}^*)(\sum_{\kappa} q_{\kappa} Z_{\beta,\kappa\nu}^*)}{\sum_{\mu,\nu} q_{\mu} \epsilon_{\mu,\nu}^{\infty} q_{\nu}} . \quad [\text{B.42}]$$

As mentioned before, this formula shows that the optical dielectric constant along $\underline{q}$ screens the effect and reduces the extra-force, while large effective charges give rise to the splitting and shift the frequencies of LO-modes to higher values. If one assumes that – due to symmetry – the non-analytical contribution does not change the eigendisplacements despite its impact on the frequencies, one obtains

$$\omega_i^2(\underline{q} \rightarrow 0) - \omega_i^2(\underline{q} = 0) = \frac{1}{\epsilon_0 \Omega_0} \frac{\sum_{\mu\nu} q_{\mu} S_{i,\mu\nu} q_{\nu}}{\sum_{\mu\nu} q_{\mu} \epsilon_{\mu,\nu}^{\infty} q_{\nu}} , \quad [\text{B.43}]$$

where the last term describes the splitting of LO- and TO-modes. It is important to note that the addressed effect commonly referred to as LO-TO-splitting must not be mistaken for the sole origin of a splitting of frequencies near the Γ -point. Only if symmetry leads to a degeneracy of phonon frequencies at the Γ -point, as is typically the case in the examples treated analytically in textbooks, then this holds true, while in general, a split may already be caused by crystal anisotropy.

A well-known relation exists that connects the splitting with the dielectric tensor, the *Lyddane-Sachs-Teller (LST) relation*. In the simplest case of a cubic material with two atoms in the unit cell, it states

$$\frac{\omega_{\text{LO}}^2}{\omega_{\text{TO}}^2} = \frac{\epsilon^0}{\epsilon^{\infty}} . \quad [\text{B.44}]$$

In line with our previous considerations, the split derived from this familiar expression is the higher, the more the high- and low-frequency limits of the dielectric constant differ. The above treatment allows us to obtain the following generalization of the frequency-dependent LST-relation [see 161, section VIII.B, eq. 64]:

$$\frac{\sum_{\mu,\nu} q_{\mu} \epsilon_{\mu,\nu}(\omega) q_{\nu}}{\sum_{\mu,\nu} q_{\mu} \epsilon_{\mu,\nu}^{\infty} q_{\nu}} = \prod_i \frac{\omega_i^2(\underline{q} \rightarrow 0) - \omega^2}{\omega_i^2(\underline{q} = 0) - \omega^2} . \quad [\text{B.45}]$$

Note that our results are derived for an insulating solid. In a metal, no macroscopic fields and thus no polarization due to the nuclei may be obtained due to the screening of the free electrons. Therefore, the LO-TO-splitting vanishes in this case. But also in non-polar materials such as elemental solids, where the effective charges vanish, no splitting may occur.

B.4.4. Phonons from Linear Response Calculations

Phonons can be calculated from density functional perturbation theory, considering atomic displacements as small perturbations. With the implementation in ABINIT, the calculation of reciprocal dynamical matrices at $\underline{q}$ -values that comply with $\underline{k} + \underline{q} = \underline{k} + \underline{G}$, where $\underline{k}$ is an element of the grid used to sample the Brillouin zone, is directly feasible. For $\underline{q} = 0$, the calculations of the mixed second order derivatives of the energy with respect to these displacements may be performed without considering those terms that diverge (i. e., where $G = 0$). The elements required for the non-stationary expression [see 161, section III.A to C] are the derivatives of the wavefunctions with respect to all (symmetry-inequivalent) atomic displacements. The additional, non-analytical contribution has to be treated separately as described in the previous section, employing the knowledge of the optical dielectric tensor and the Born effective charges that need to be determined concurrently.

Appendix C.

Supplement to Chapter 3

This chapter first compiles the atomic orbital radii (in a.u.) from ref. 173 that are used to calculate the coordinates of the map developed in Chapter 3. The entries are sorted by columns (and rows) of the periodic table. Note that only a selection of elements was considered in this reference.

Furthermore, this chapter contains a table of the materials on the map, shown in Fig. 3.13 and Fig. 3.14, that for clarity could not be labeled. The entries are sorted by increasing values of r'_σ . As a reminder, the calculation of the coordinates requires averaging of cations and anions, respectively. To mark what species have been considered as cations and anions, they are separated by a vertical bar. For instance, $\text{SnBi}_2 | \text{Te}_4$ means that tin and bismuth are considered cations while tellurium is considered an anion.

Orbital Radii

Element	r_s	r_p	r_d
Li	0.93	1.88	5.99
Na	1.02	2.36	5.95
K	1.36	2.76	5.29
Rb	1.45	2.95	4.89
Cs	1.62	3.18	3.96
Be	0.63	0.93	3.00
Mg	0.86	1.43	2.92
Ca	1.22	1.87	1.52
Sr	1.36	2.09	1.74
Ba	1.55	2.34	1.71
Cu	0.43	1.61	5.89
Ag	0.45	1.66	5.90
Au	0.26	1.4	5.87
Zn	0.64	1.22	3.06
Cd	0.71	1.32	3.18
Hg	0.60	1.26	3.24
B	0.48	0.62	2.00
Al	0.74	1.08	1.92
Ga	0.66	1.04	2.15

In	0.76	1.17	2.31
Tl	0.69	1.16	2.41
C	0.38	0.47	1.50
Si	0.66	0.89	1.42
Ge	0.64	0.92	1.68
Sn	0.76	1.07	1.87
Pb	0.72	1.09	1.98
N	0.32	0.38	1.20
P	0.59	0.76	1.13
As	0.62	0.83	1.41
Sb	0.72	0.97	1.56
Bi	0.72	1.02	1.78
O	0.28	0.32	1.00
S	0.53	0.66	0.94
Se	0.59	0.76	1.21
Te	0.69	0.89	1.35
F	0.24	0.27	0.86
Cl	0.49	0.59	0.80

Map Coordinates

Material	r'_σ	r_π^{-1}
Bi	0.00	1.67
Sb	0.00	2.00
Si Te	0.00	2.33
As	0.00	2.38
PbAs ₄ Te ₇	0.01	2.26
SnAs ₄ Te ₇	0.01	2.33
Ge ₂ As ₂ Te ₅	0.02	2.25
SnAs ₂ Te ₄	0.02	2.26
Ge Te	0.03	2.08
PbAs ₂ Te ₄	0.03	2.16
GeAs ₂ Te ₄	0.03	2.31
Si ₂ As ₂ Te ₅	0.03	2.38
Si ₂ Sb ₂ Te ₅	0.04	2.27
GeAs ₄ Te ₇	0.04	2.36
SiAs ₂ Te ₄	0.04	2.40
SiSb ₂ Te ₄	0.05	2.26
SiAs ₄ Te ₇	0.05	2.42
Ge ₂ Sb ₂ Te ₅	0.06	2.15
Sn ₂ As ₂ Te ₅	0.06	2.17
GeSb ₂ Te ₄	0.06	2.17
SiSb ₄ Te ₇	0.06	2.24
Pb ₂ As ₂ Te ₅	0.07	2.04
Si ₂ Bi ₂ Te ₅	0.07	2.15
GeSb ₄ Te ₇	0.07	2.19
Ge ₂ Bi ₂ Te ₅	0.08	2.04
SiAs ₄ Se ₇	0.08	2.60
SiBi ₂ Te ₄	0.09	2.10

GeAs ₄ Se ₇	0.09	2.54
SiAs ₂ Se ₄	0.09	2.59
GeBi ₂ Te ₄	0.10	2.03
SiBi ₄ Te ₇	0.10	2.06
PbSb ₄ Te ₇	0.10	2.11
SnSb ₄ Te ₇	0.10	2.16
GeAs ₂ Se ₄	0.10	2.48
Si ₂ As ₂ Se ₅	0.10	2.56
GeBi ₄ Te ₇	0.11	2.02
SnSb ₂ Te ₄	0.11	2.13
PbSb ₂ Te ₄	0.12	2.04
Ge ₂ As ₂ Se ₅	0.12	2.41
PbAs ₄ Se ₇	0.12	2.43
SnAs ₄ Se ₇	0.12	2.50
Sn ₂ Sb ₂ Te ₅	0.13	2.08
Si Se	0.13	2.50
PbBi ₄ Te ₇	0.14	1.95
Pb ₂ Sb ₂ Te ₅	0.14	1.96
SnBi ₄ Te ₇	0.14	1.99
PbBi ₂ Te ₄	0.15	1.91
SnBi ₂ Te ₄	0.15	1.99
SnBi ₂ Se ₄	0.15	2.11
SnAs ₂ Se ₄	0.15	2.42
Sn ₂ Bi ₂ Te ₅	0.16	1.98
Ge Se	0.16	2.22
PbAs ₂ Se ₄	0.16	2.31
Pb ₂ Bi ₂ Te ₅	0.17	1.87
Si ₂ Sb ₂ Se ₅	0.17	2.44
Sn Te	0.18	1.96

SiSb ₂ Se ₄	0.18	2.42
SiAs ₄ S ₇	0.18	2.91
Ge ₂ Sb ₂ Se ₅	0.19	2.30
Sn ₂ As ₂ Se ₅	0.19	2.33
GeSb ₂ Se ₄	0.19	2.33
SiSb ₄ Se ₇	0.19	2.40
GeAs ₄ S ₇	0.19	2.82
SiAs ₂ S ₄	0.19	2.88
Pb Te	0.20	1.75
Pb ₂ As ₂ Se ₅	0.20	2.17
Si ₂ Bi ₂ Se ₅	0.20	2.30
GeSb ₄ Se ₇	0.20	2.35
GeAs ₂ S ₄	0.20	2.75
Si ₂ As ₂ S ₅	0.20	2.86
Ge ₂ Bi ₂ Se ₅	0.21	2.17
SiBi ₂ Se ₄	0.22	2.24
Ge ₂ As ₂ S ₅	0.22	2.67
PbAs ₄ S ₇	0.22	2.69
SnAs ₄ S ₇	0.22	2.78
GeBi ₂ Se ₄	0.23	2.16
SiBi ₄ Se ₇	0.23	2.19
PbSb ₄ Se ₇	0.23	2.25
SnSb ₄ Se ₇	0.23	2.31
Si S	0.23	2.78
GeBi ₄ Se ₇	0.24	2.15
SnSb ₂ Se ₄	0.24	2.27
PbSb ₂ Se ₄	0.25	2.17
SnAs ₂ S ₄	0.25	2.68
Sn ₂ Sb ₂ Se ₅	0.26	2.22

Ge S	0.26	2.44
PbAs ₂ S ₄	0.26	2.54
PbBi ₄ Se ₇	0.27	2.07
Pb ₂ Sb ₂ Se ₅	0.27	2.08
SnBi ₄ Se ₇	0.27	2.12
Si ₂ Sb ₂ S ₅	0.27	2.70
PbBi ₂ Se ₄	0.28	2.03
SiSb ₂ S ₄	0.28	2.68
Sn ₂ Bi ₂ Se ₅	0.29	2.11
Ge ₂ Sb ₂ S ₅	0.29	2.53
Sn ₂ As ₂ S ₅	0.29	2.56
GeSb ₂ S ₄	0.29	2.56
SiSb ₄ S ₇	0.29	2.66
Pb ₂ Bi ₂ Se ₅	0.30	1.98
Pb ₂ As ₂ S ₅	0.30	2.38
Si ₂ Bi ₂ S ₅	0.30	2.53
GeSb ₄ S ₇	0.30	2.59
Sn Se	0.31	2.08
Ge ₂ Bi ₂ S ₅	0.31	2.38
SiBi ₂ S ₄	0.32	2.46
Pb Se	0.33	1.85
GeBi ₂ S ₄	0.33	2.36
SiBi ₄ S ₇	0.33	2.40
PbSb ₄ S ₇	0.33	2.48
SnSb ₄ S ₇	0.33	2.55
GeBi ₄ S ₇	0.34	2.35
SnSb ₂ S ₄	0.34	2.50
PbSb ₂ S ₄	0.35	2.38
Sn ₂ Sb ₂ S ₅	0.36	2.44

PbBi ₄ S ₇	0.37	2.25
Pb ₂ Sb ₂ S ₅	0.37	2.27
SnBi ₄ S ₇	0.37	2.31
PbBi ₂ S ₄	0.38	2.21
SnBi ₂ S ₄	0.38	2.31
Sn ₂ Bi ₂ S ₅	0.39	2.30
Pb ₂ Bi ₂ S ₅	0.40	2.15
Sn S	0.41	2.27
Pb S	0.43	2.00

Appendix D.

Supplement to Chapter 4

This chapter provides supplementary material for [Chapter 4](#). It comprises the detailed structural analysis of the AB_2C_4 -systems in the 56-cells (except for $GeSb_2Te_4$ which is shown in [Chapter 4](#)) in terms of pair histograms and bond length distributions. Moreover, the Bader charges of all atoms are presented on the following pages. The sequence of materials reflects ascending values of r'_σ (ionicity coordinate).

For the histograms, the bin width was chosen to be $0.1 \text{ Bohr} = 0.0529177 \text{ \AA}$. The width of the first peak is evaluated as the extension of the region that contains at least 28 and no less than 260 of the first 288 pairs ($288 = 56 \times 6 - 8 \times 6$, the first term is the number of nearest neighbors, the second term corrects for the vacancies), that is at least 10% and no less than 90%. This way, a small number of outliers does not affect the calculated width. The unique bond length expected for a perfect rocksalt-lattice of equal lattice constant is also indicated for comparison.

The bond-length distributions show the six shortest distances to neighboring atoms for each atom. The advantage of this presentation is that it allows to check for varying local configurations. For instance, a split into 3+3 bonds indicates a $[1\ 1\ 1]$ -distortion, a 2+2+2-split is in line with a $[1\ 1\ 0]$ -distortion and a 1+4+1-configuration resembles a $[1\ 0\ 0]$ -displacement. This is further discussed in [Chapter 5](#). From left to right, the atoms are ordered by their number, that is the sequence in which they appear in the description of the structure in the ABINIT-input files. To enable a comparison, the order of the atoms is the same also for the Bader charges.

Finally, the ELF versus bond length-diagrams as shown in [Fig. 4.14](#) for $GeSb_2Se_4$ and $SnBi_2Te_4$ (56-cell) are plotted for the remaining materials on page D-54.

SiSb_2Te_4

Coordinates: $r'_\sigma = 0.053$, $r_\pi^{-1} = 2.26$

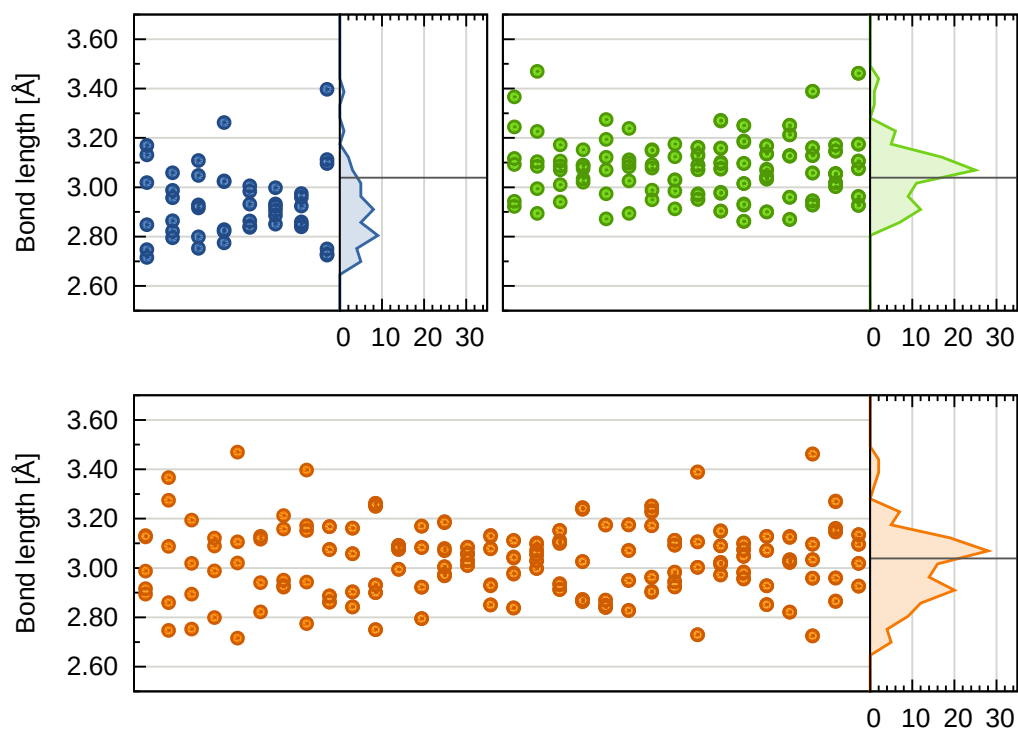


Figure D.1.: Six shortest atomic distances for SiSb_2Te_4 (Si: blue, Sb: green, Te: orange).

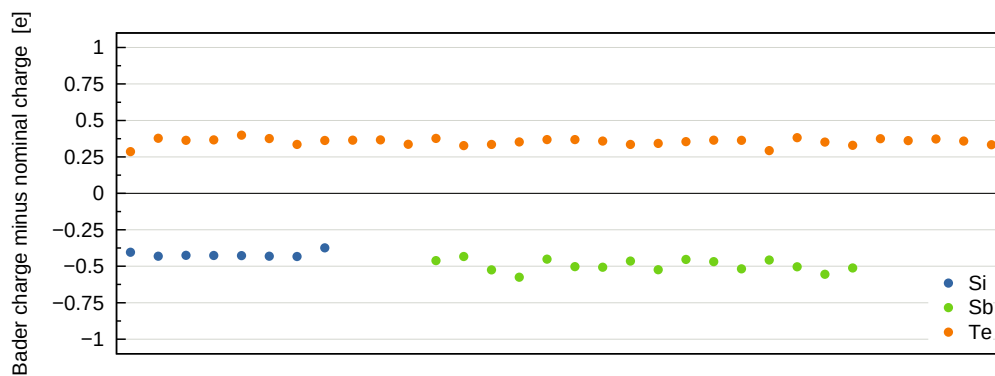


Figure D.2.: Bader charges in SiSb_2Te_4 .

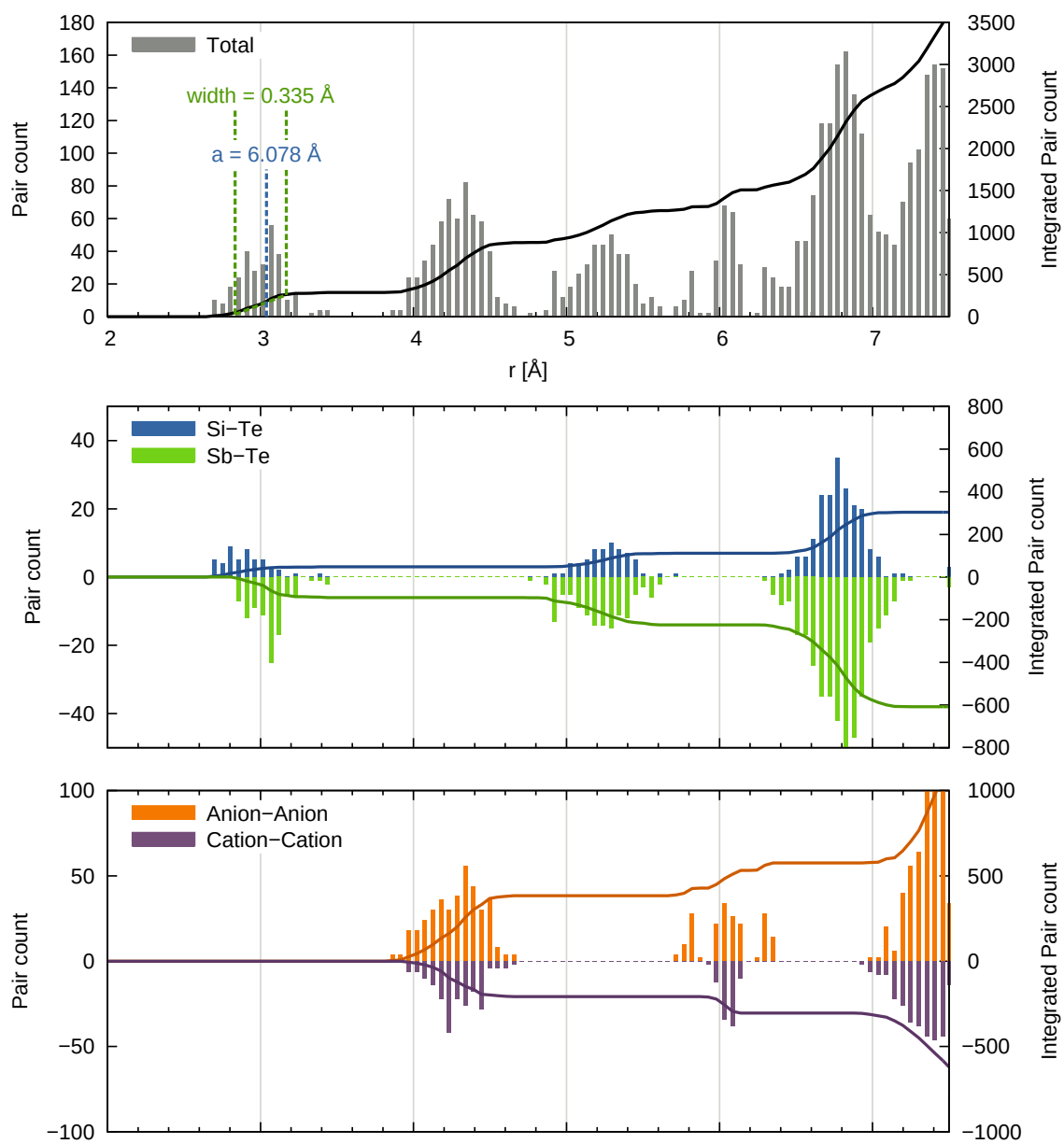


Figure D.3.: Pair histogram for SiSb_2Te_4 .

SiBi_2Te_4

Coordinates: $r'_\sigma = 0.087$, $r_\pi^{-1} = 2.10$

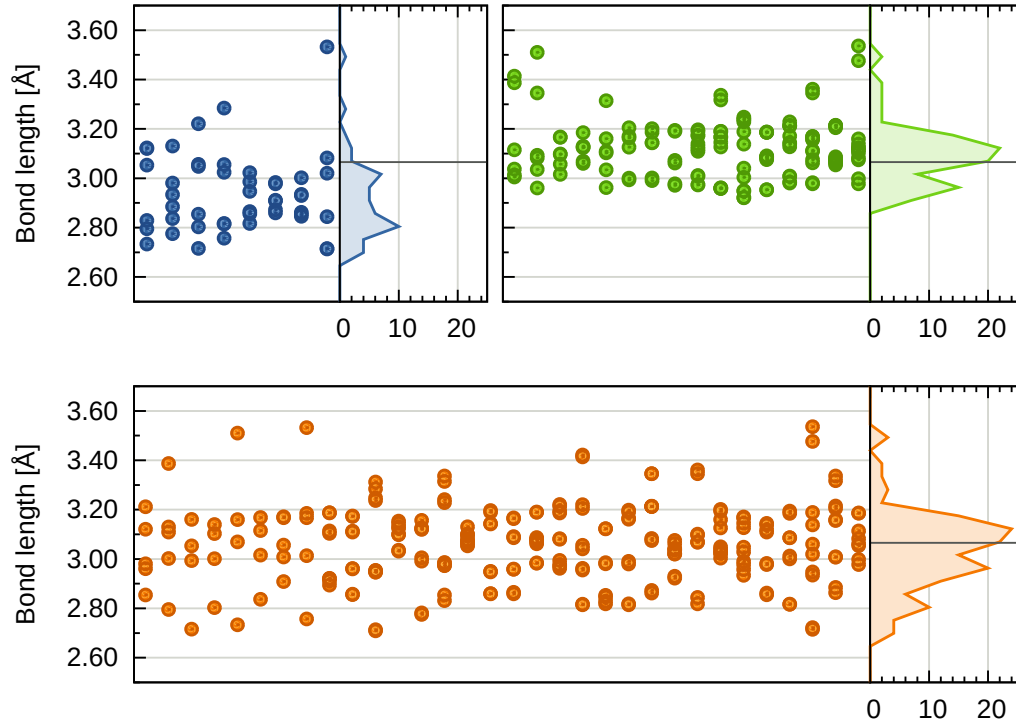


Figure D.4.: Six shortest atomic distances for SiBi_2Te_4 (Si: blue, Bi: green, Te: orange).

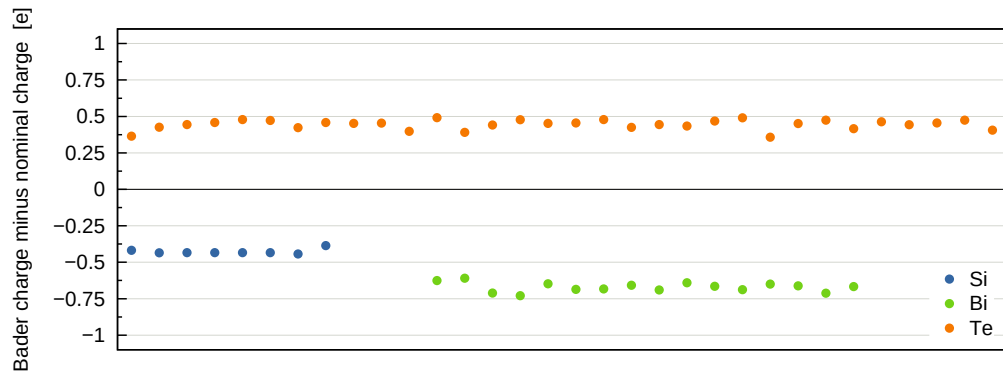


Figure D.5.: Bader charges in SiBi_2Te_4 .

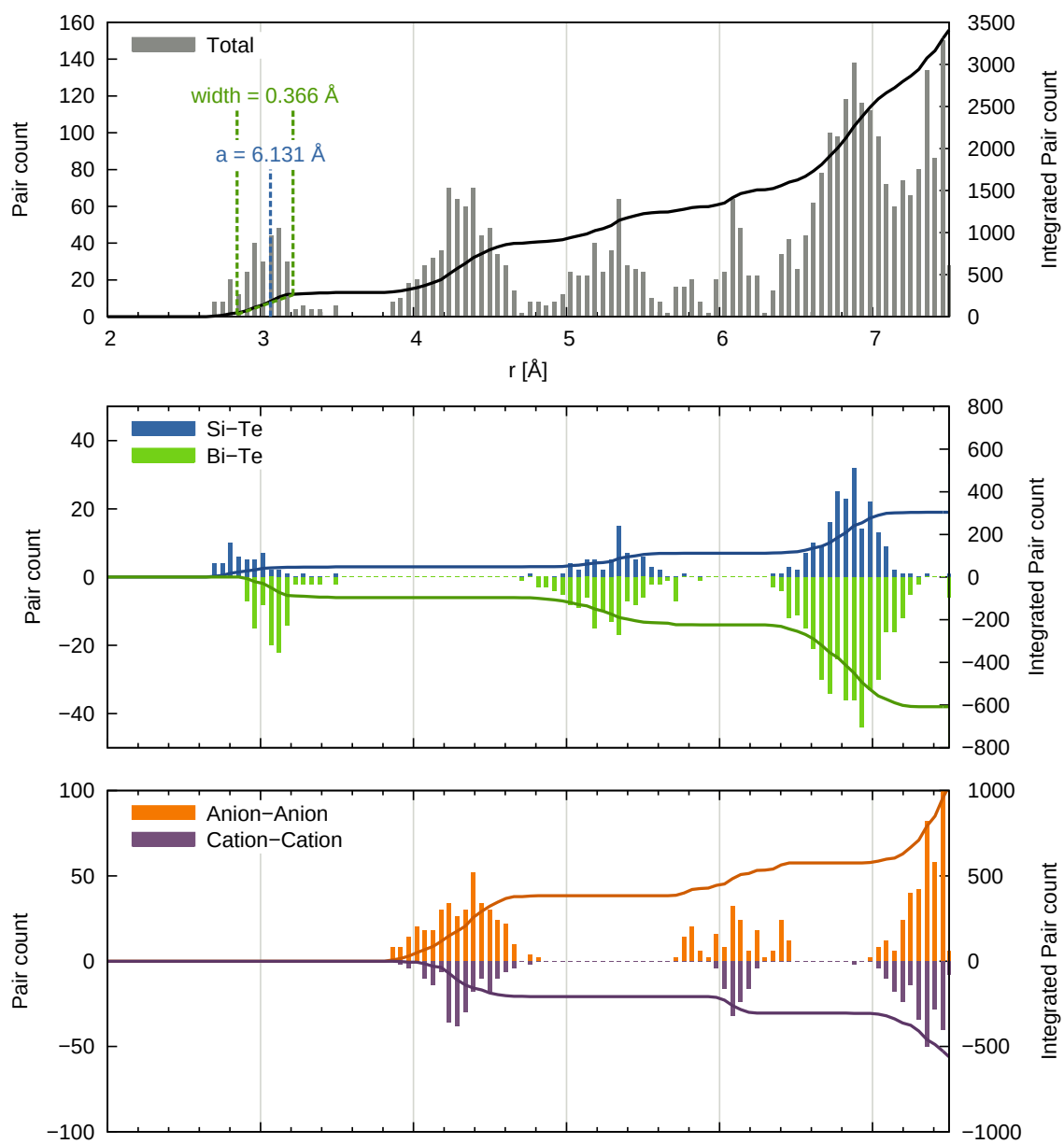


Figure D.6.: Pair histogram for SiBi_2Te_4 .

GeBi₂Te₄

Coordinates: $r'_\sigma = 0.097$, $r_\pi^{-1} = 2.03$

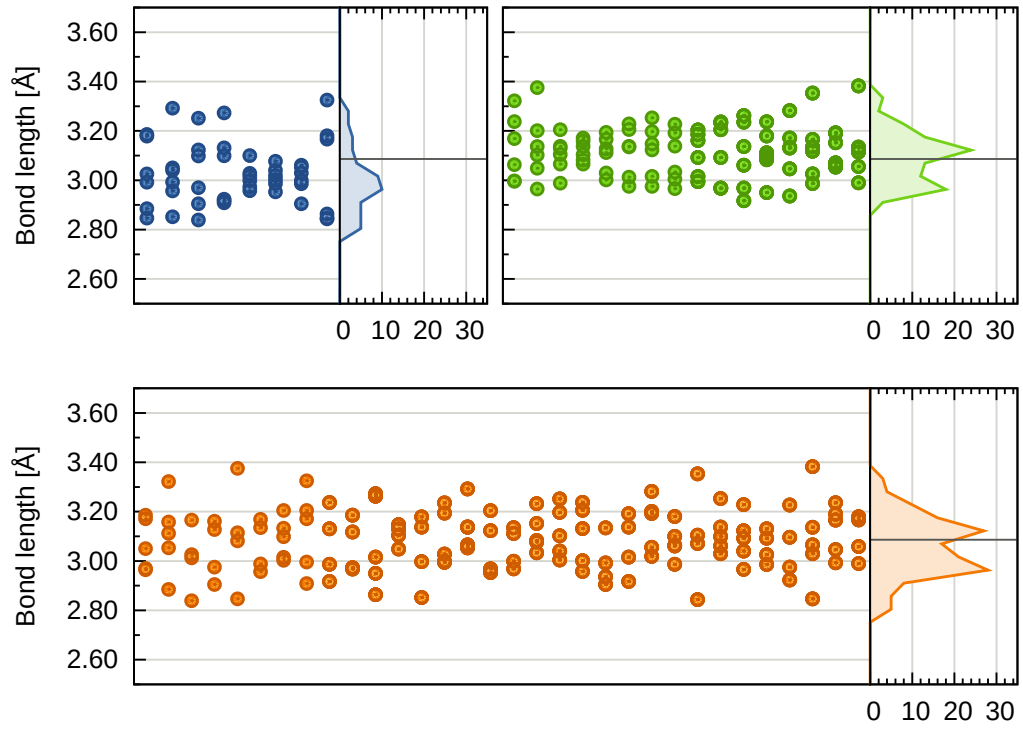


Figure D.7.: Six shortest atomic distances for GeBi₂Te₄ (Ge: blue, Bi: green, Te: orange).

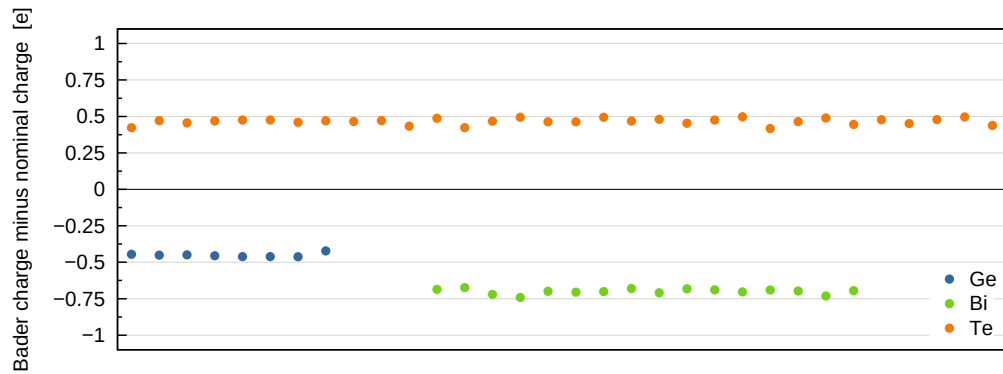


Figure D.8.: Bader charges in GeBi₂Te₄.

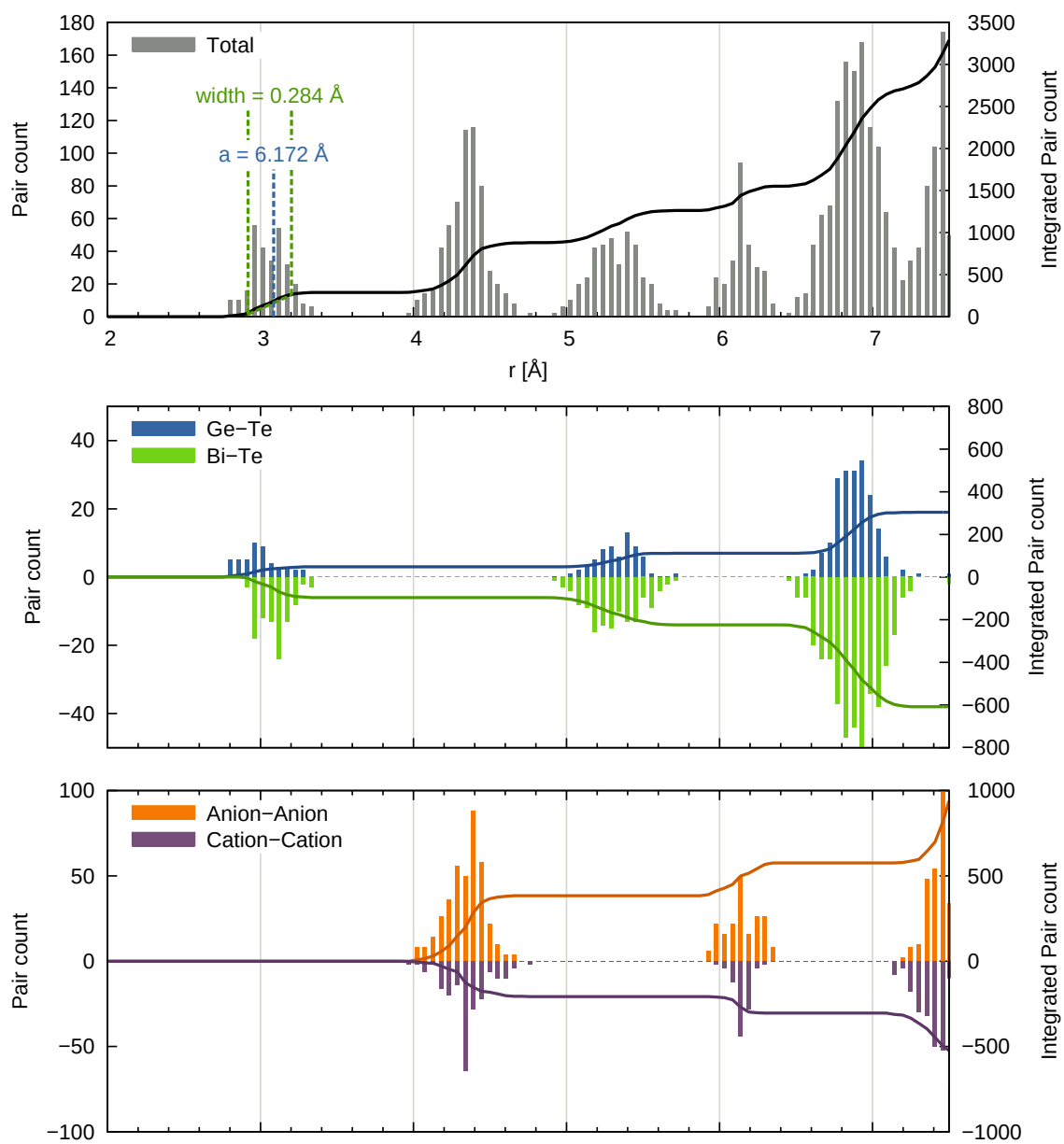


Figure D.9.: Pair histogram for GeBi_2Te_4 .

SnSb₂Te₄

Coordinates: $r'_\sigma = 0.113$, $r_\pi^{-1} = 2.13$

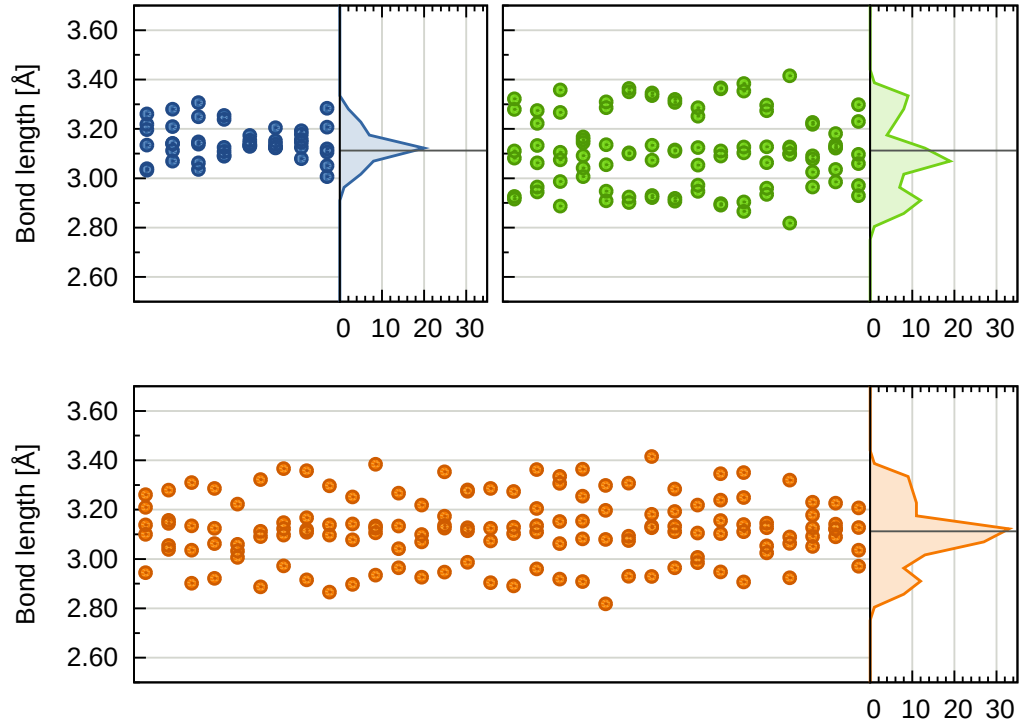


Figure D.10.: Six shortest atomic distances for SnSb₂Te₄ (Sn: blue, Sb: green, Te: orange).

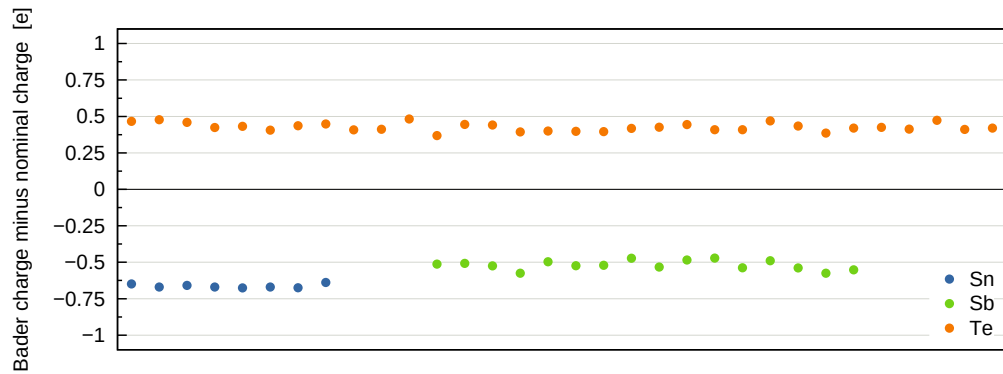


Figure D.11.: Bader charges in SnSb₂Te₄.

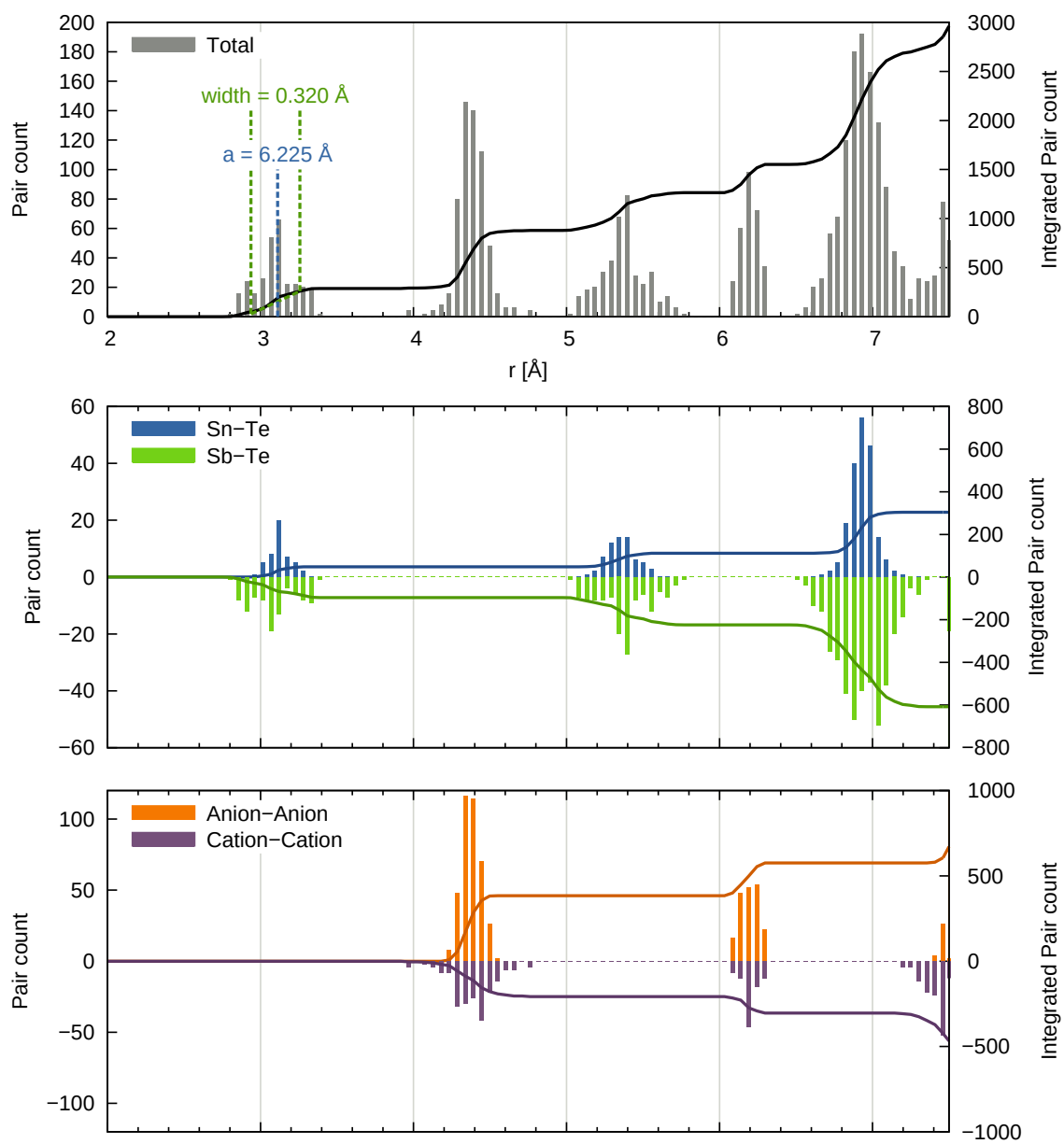


Figure D.12.: Pair histogram for SnSb_2Te_4 .

SnBi₂Te₄

Coordinates: $r'_\sigma = 0.147$, $r_\pi^{-1} = 1.99$

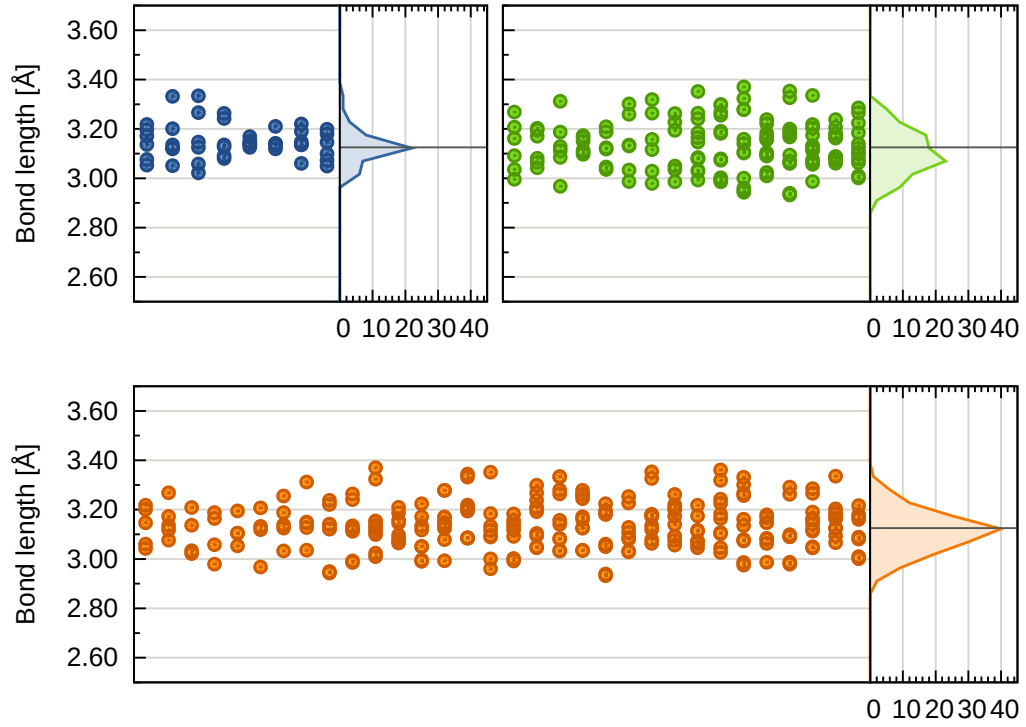


Figure D.13.: Six shortest atomic distances for SnBi₂Te₄ (Sn: blue, Bi: green, Te: orange).

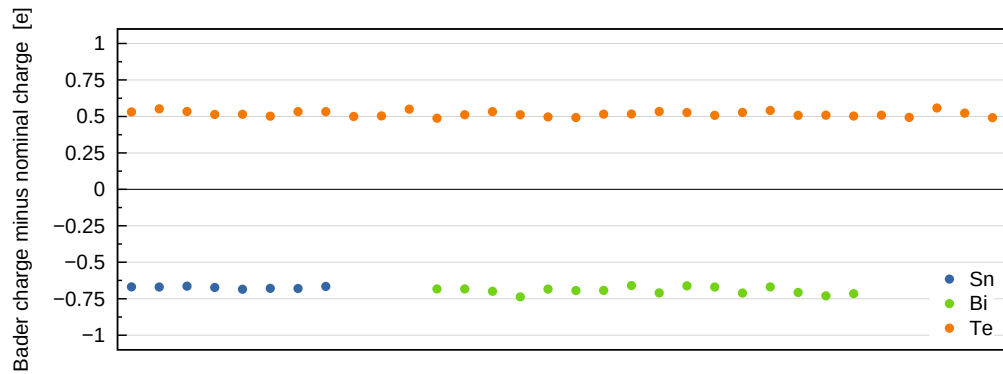


Figure D.14.: Bader charges in SnBi₂Te₄.

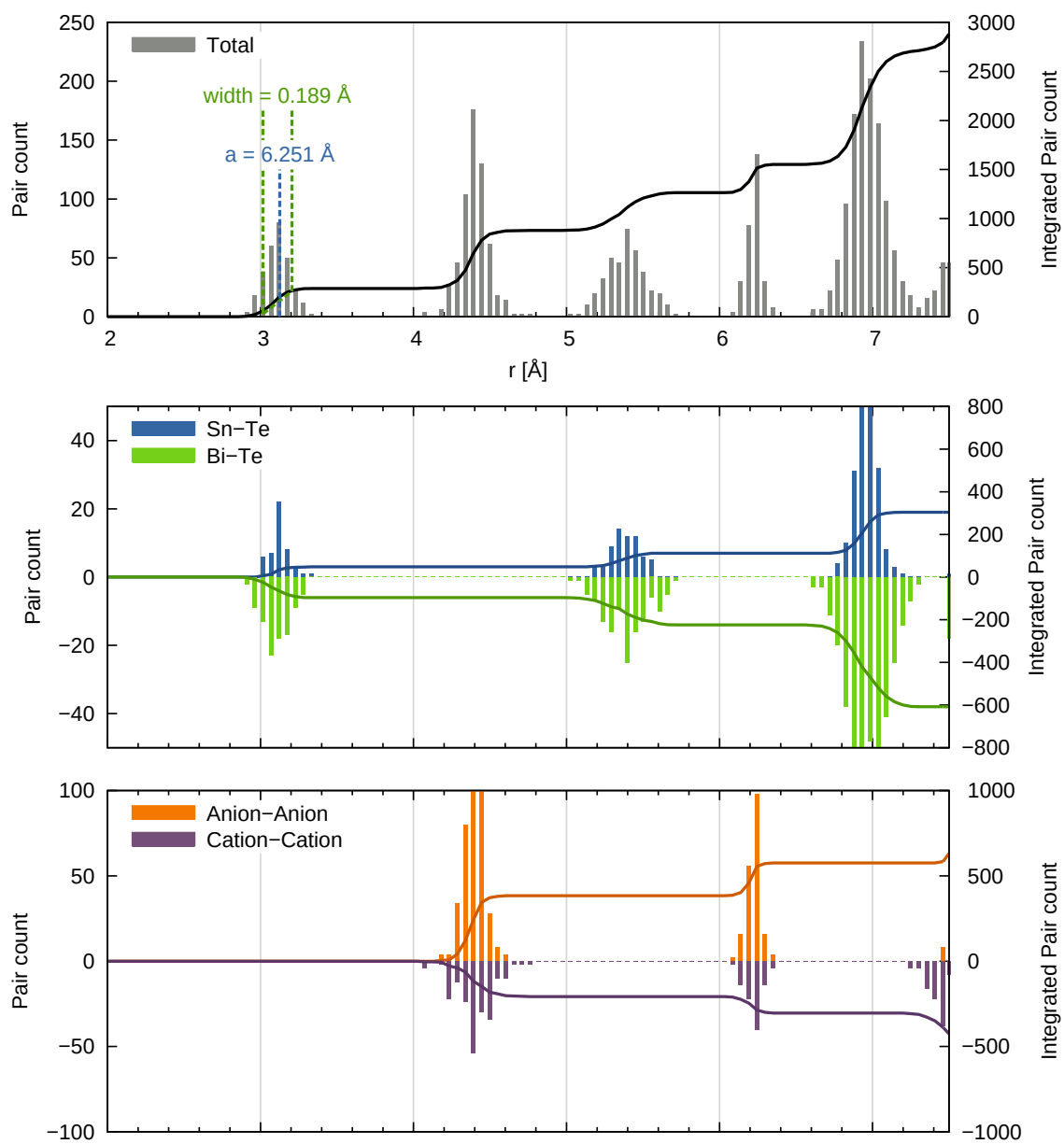


Figure D.15.: Pair histogram for SnBi_2Te_4 .

GeSb_2Se_4

Coordinates: $r'_\sigma = 0.193$, $r_\pi^{-1} = 2.33$

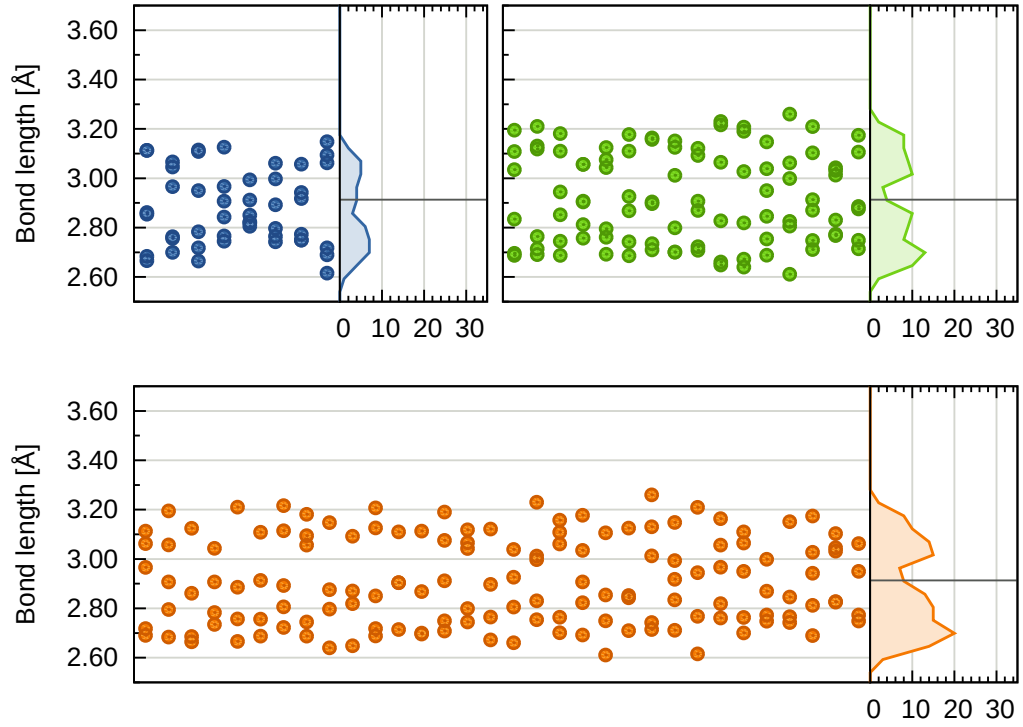


Figure D.16.: Six shortest atomic distances for GeSb_2Se_4 (Ge: blue, Sb: green, Se: orange).

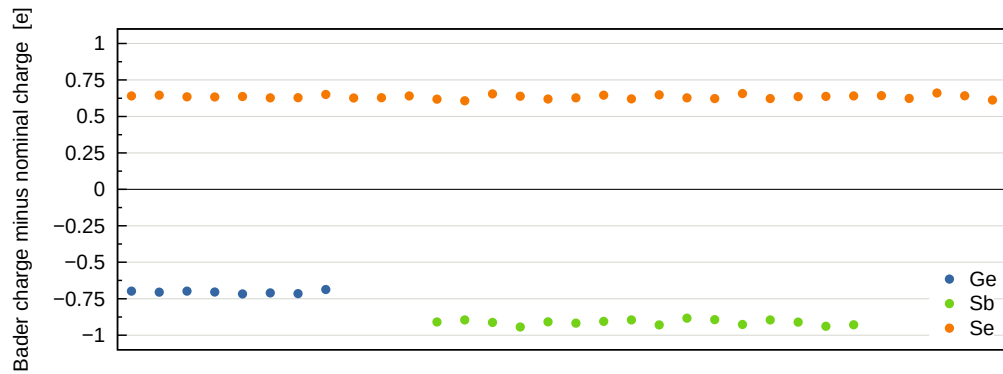


Figure D.17.: Bader charges in GeSb_2Se_4 .

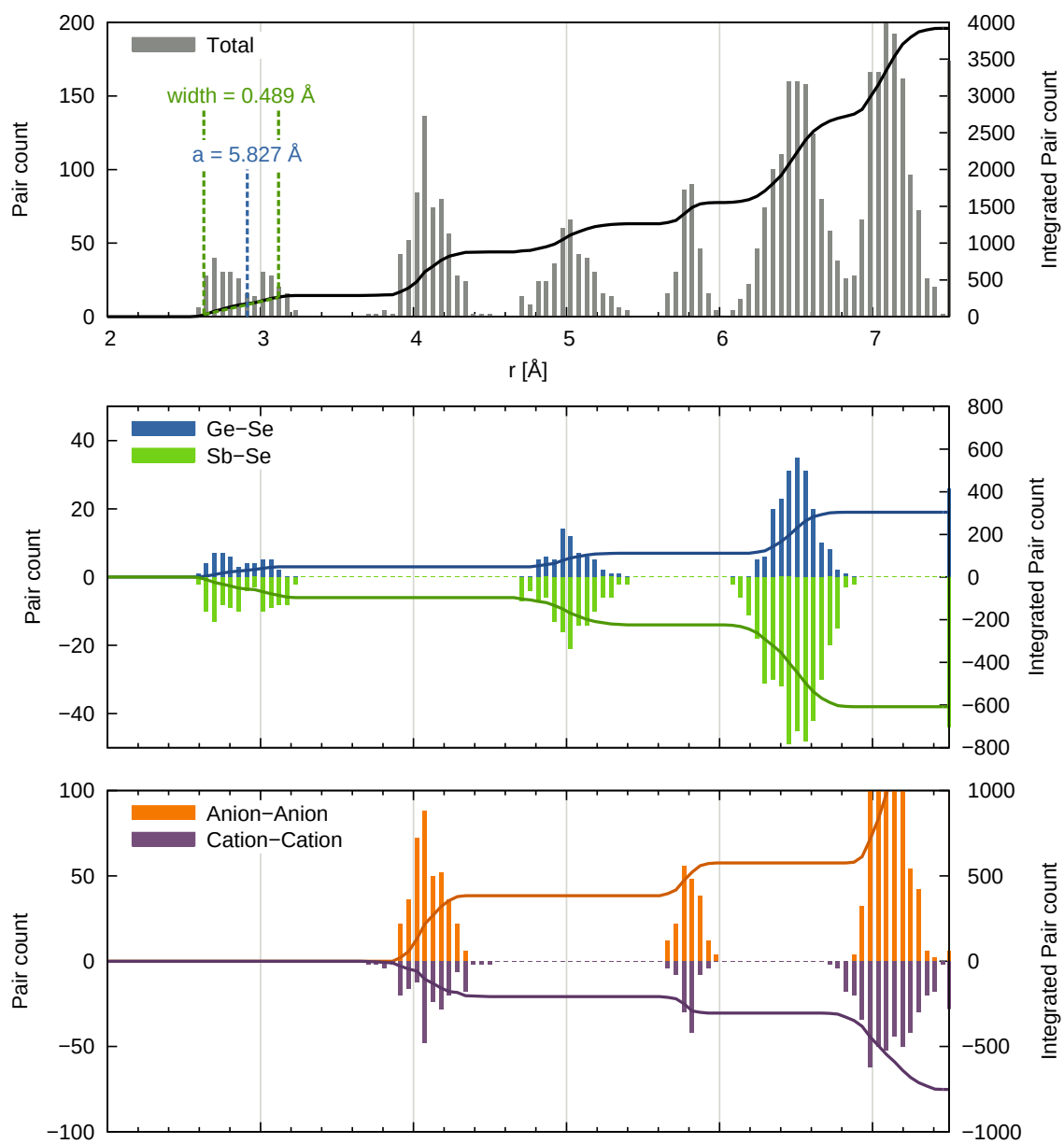


Figure D.18.: Pair histogram for GeSb_2Se_4 .

SnSb_2Se_4

Coordinates: $r'_\sigma = 0.243$, $r_\pi^{-1} = 2.27$

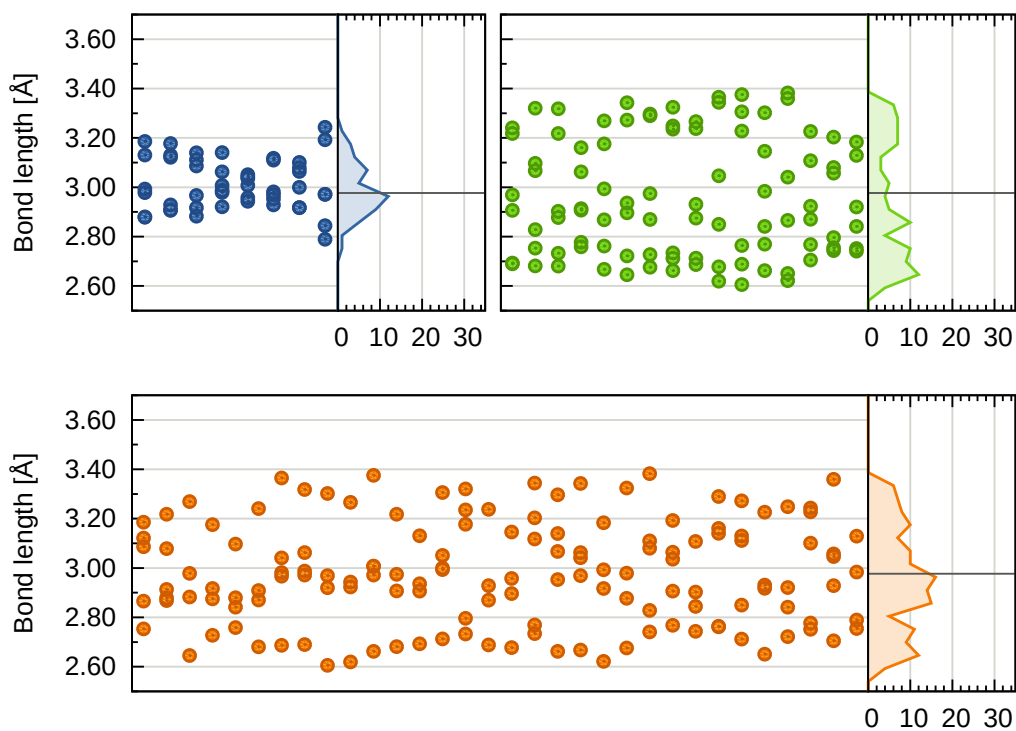


Figure D.19.: Six shortest atomic distances for SnSb_2Se_4 (Sn: blue, Sb: green, Se: orange).

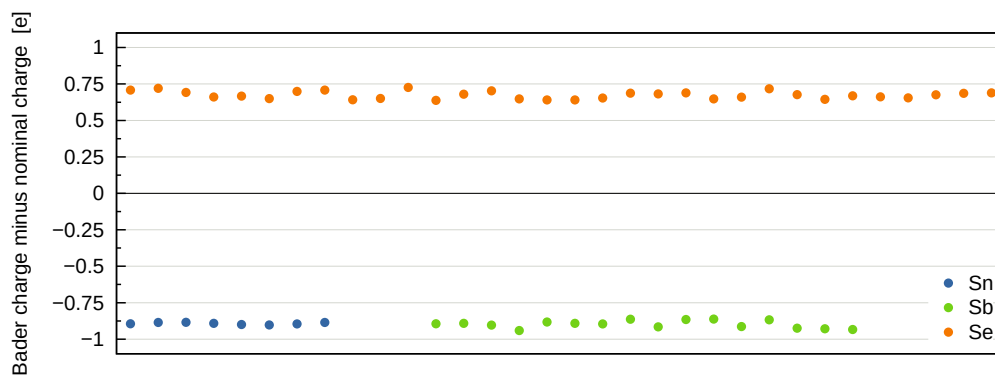


Figure D.20.: Bader charges in SnSb_2Se_4 .

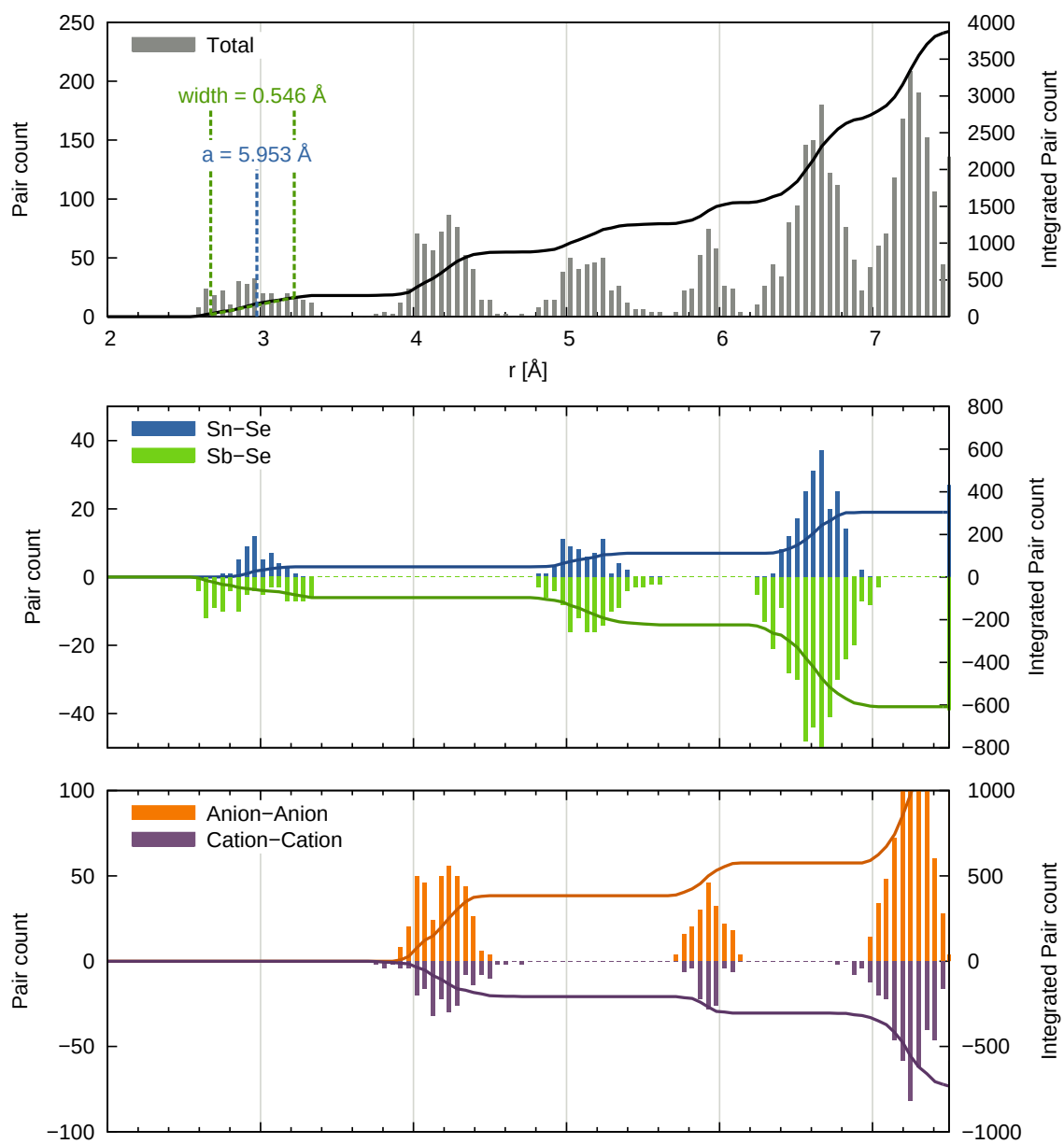


Figure D.21.: Pair histogram for SnSb_2Se_4 .

Electron Localization Function

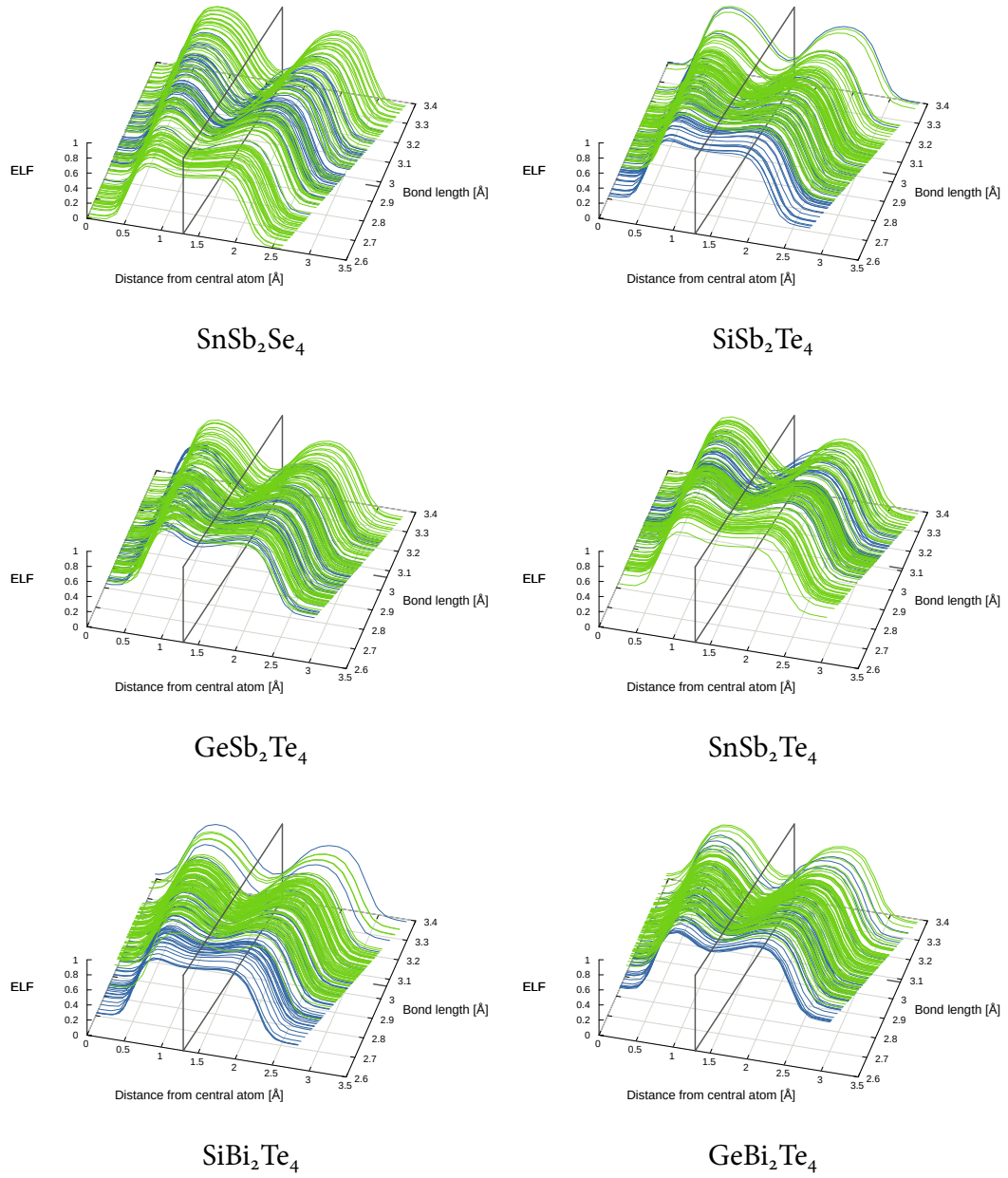


Figure D.22.: Same as Fig. 4.14 but for the remaining AB_2C_4 -materials.

Appendix E.

Supplement to Chapter 5

This appendix contains numerous figures in the context of [Chapter 5](#) that have been moved here to avoid interrupting the reading flow by a series of consecutive figures.

First, the atom-resolved bond-length distribution in GeSb_2Te_4 (56-cell) is shown as a function of the lattice constant in [Fig. E.1](#) and [Fig. E.2](#). These figures help to identify what impact pressure on the level of distortion and the distortion patterns has. Furthermore, the correlation between distortion pattern and the sublattice occupation is revealed.

Finally, the lengthy results of the sampling of the Γ -phonon modes for the 14-cell model of GeSb_2Te_4 at equilibrium volume are shown and discussed.

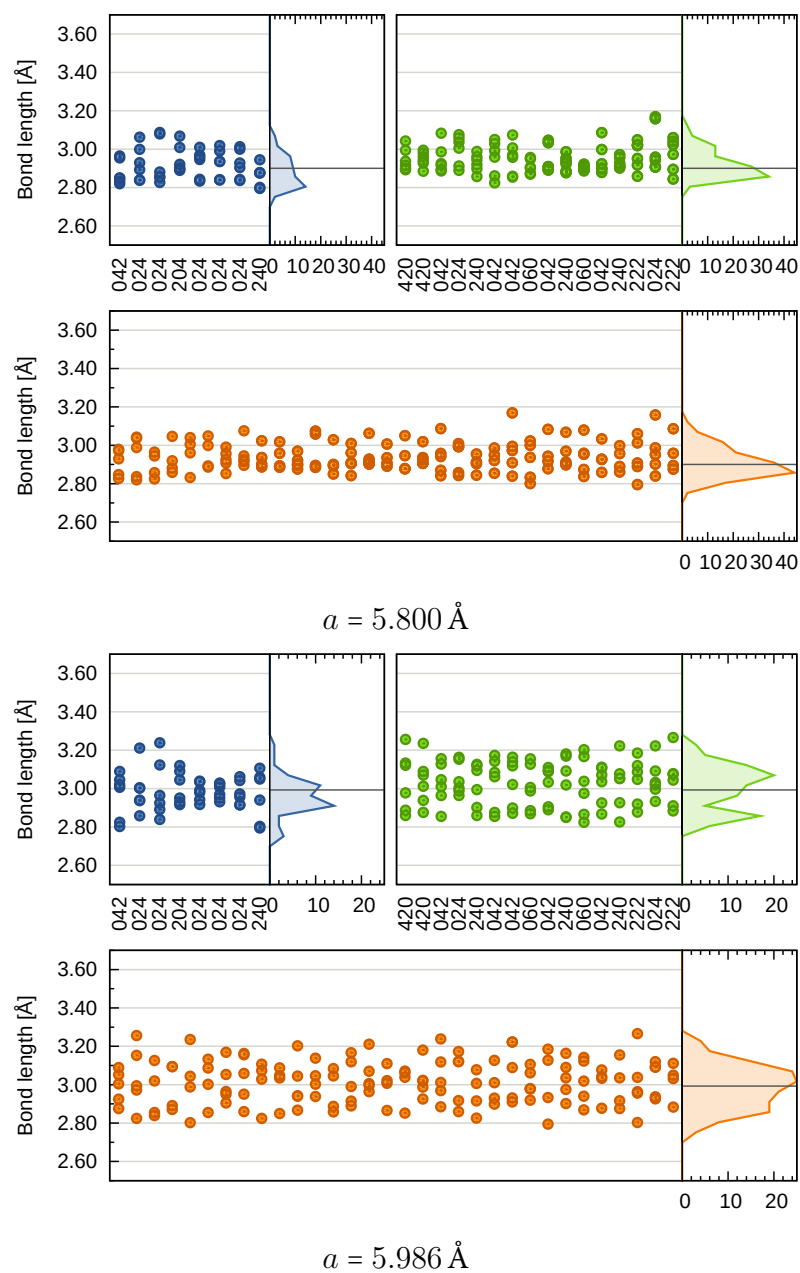


Figure E.1.: This figure and the following one, [Fig. E.2](#), show the distribution of bond lengths for germanium (blue), antimony (green) and tellurium (orange) for various volumes of the cell (56-cell), see also [Fig. 5.5](#). Horizontal lines indicate the respective unique bond lengths expected for undistorted rocksalt-structures. The smaller the volume, the smaller the distortions.

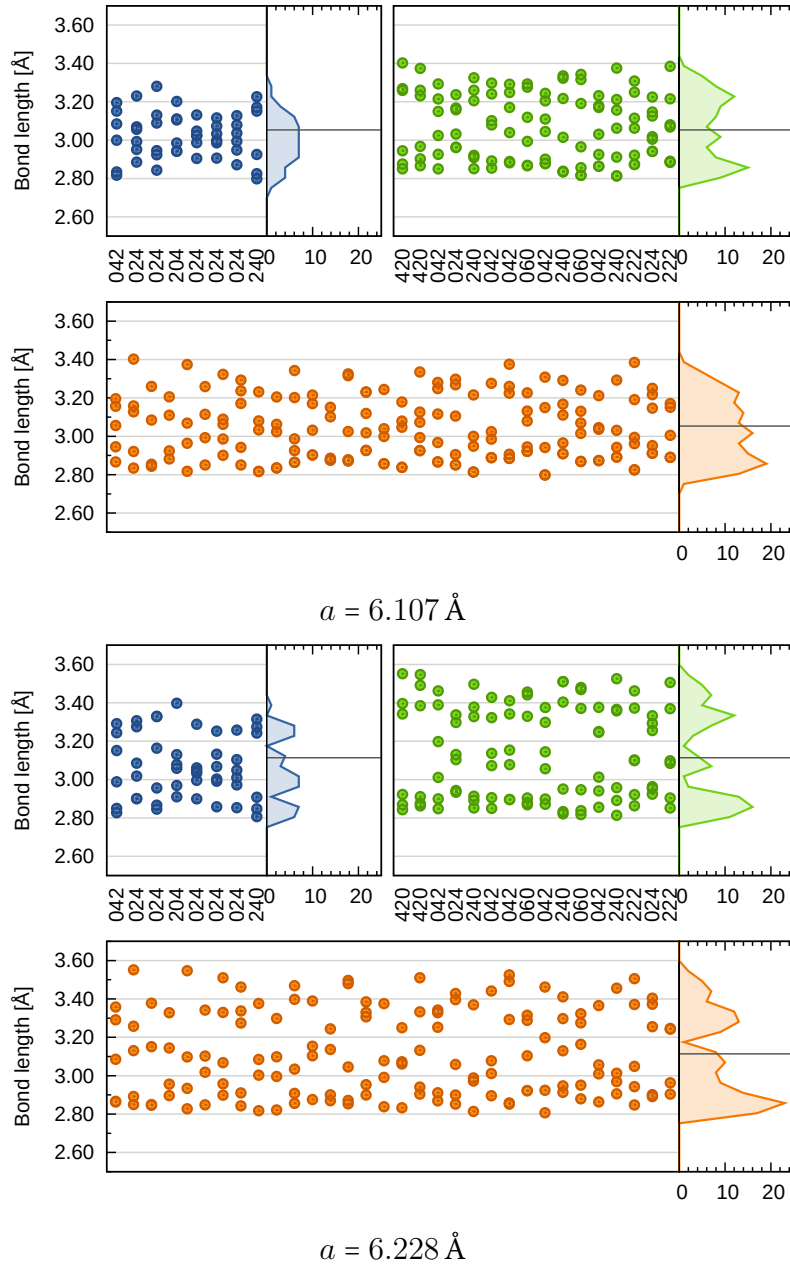


Figure E.2.: Continuation of Fig. E.1. The rotated three digit-numbers describe the local neighborhood. XYZ means there are X Ge-, Y Sb-atoms and Z vacancies in the fourth shell. Clearly, the occurrence of a 3+3+3-type split (corresponding to a $[1\ 1\ 1]$ -type distortion) is very likely if $Z = 0$. The local distortion pattern is mostly independent of the volume.

Sampling of Phonon Modes

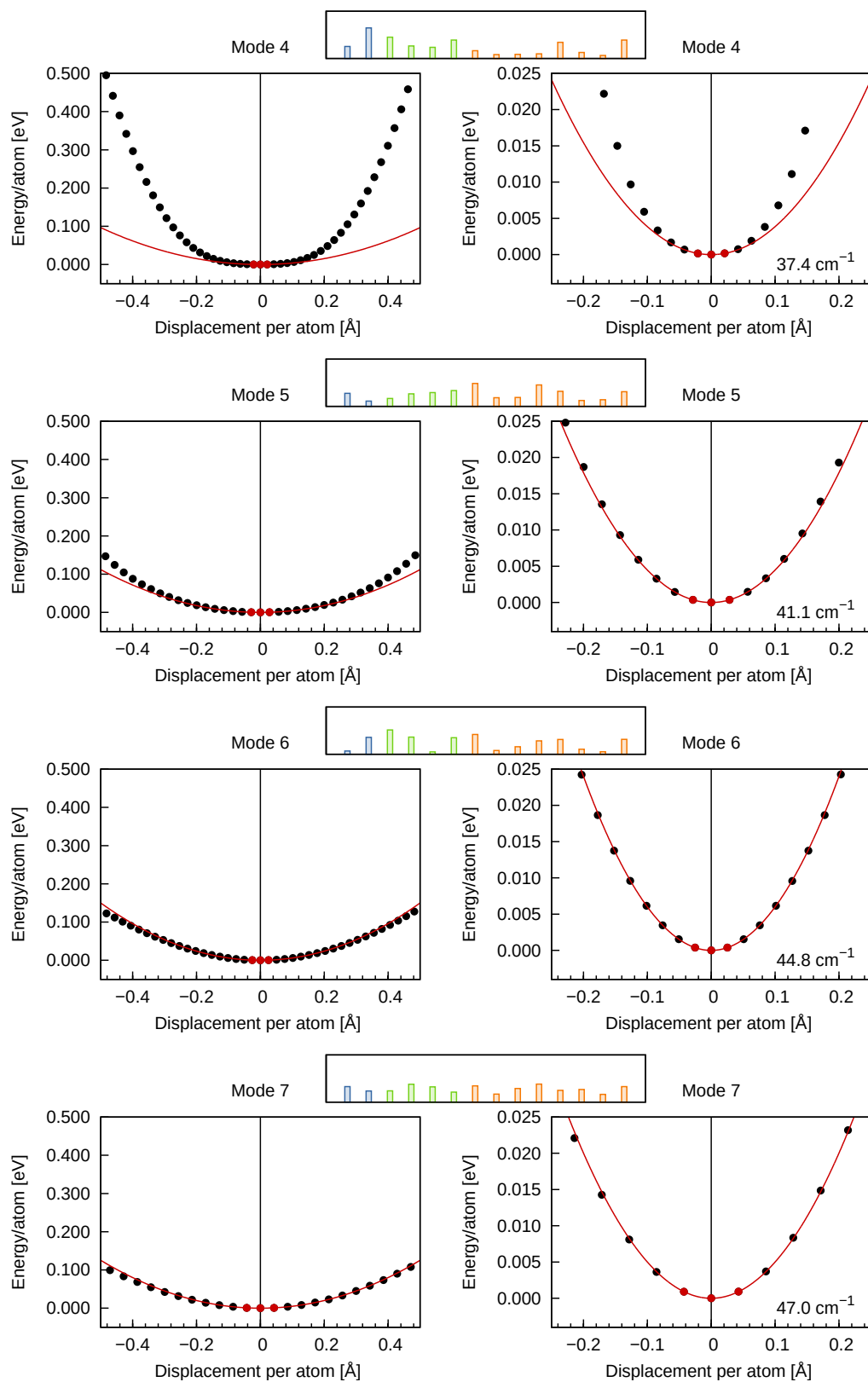
On the following pages, the 39 non-acoustic Γ -phonon modes calculated for GeSb_2Te_4 in the 14-cell (at equilibrium) are sampled (i. e., the total energy upon displacement of the atoms according to the eigendisplacements is determined). For each mode, three figures are shown; on the one hand, the sampling itself is presented in a wide (left) and a small range (right) around the minimum. In each figure, the results of the harmonic approximation are indicated as a red parabola. Deviations between the red curve and the calculated energy hint at anharmonicity. A third, small figure (middle) indicates the relative contribution of the 14 atoms to the respective eigendisplacement-coordinate. The first two blue bars correspond to Ge1 and Ge2, the four green ones to Sb1 to Sb4, and the orange bars to the tellurium atoms.

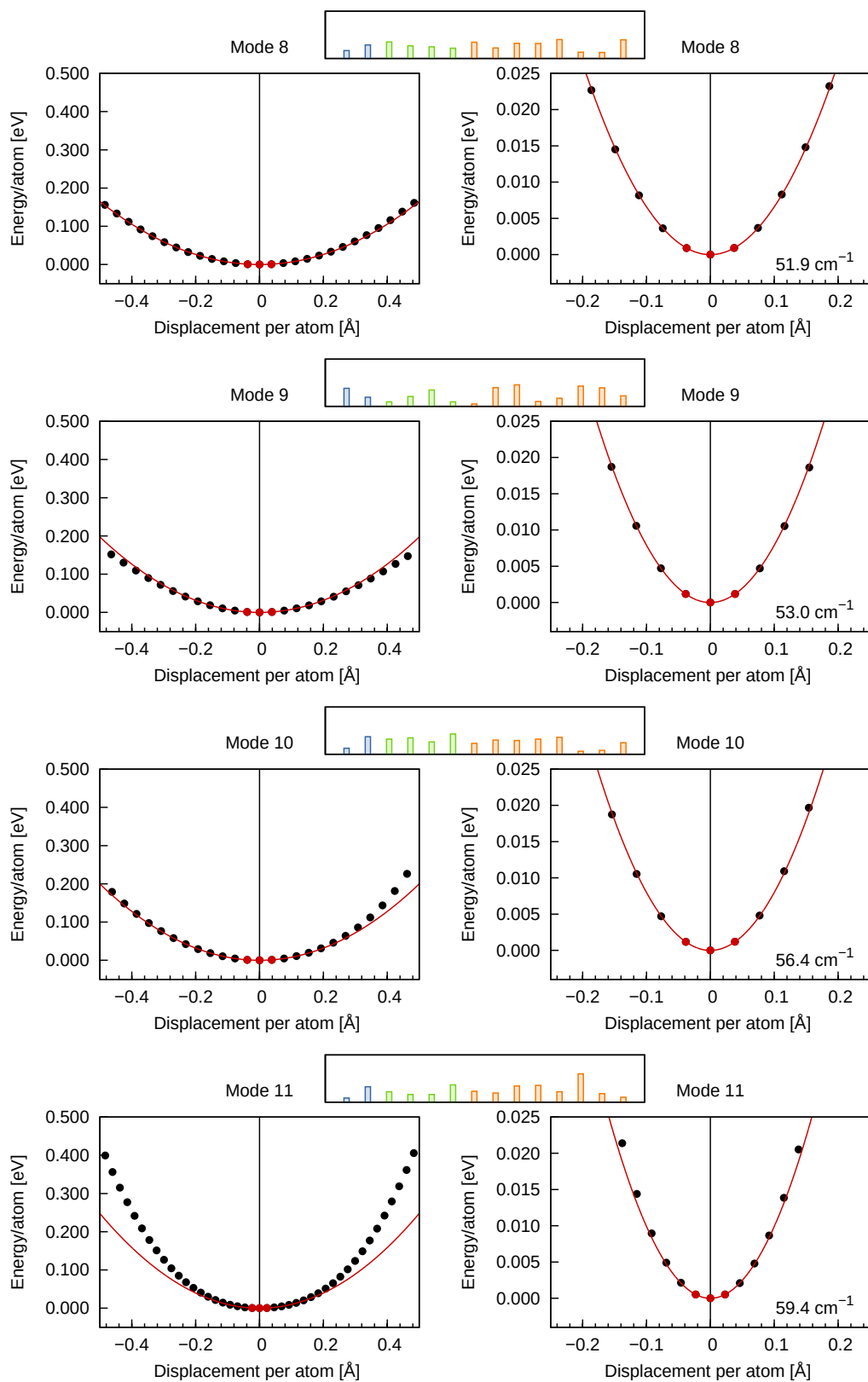
A notable deviation in the energy range up to a few meV per atom is observed for the lowest mode, mode 4. For other modes, significant deviations, in particular asymmetric softening in either positive or negative directions, are found at higher energies (e. g., mode 40). Hence, signs of anharmonicity are indeed obtained from the sampling of the phonon modes.

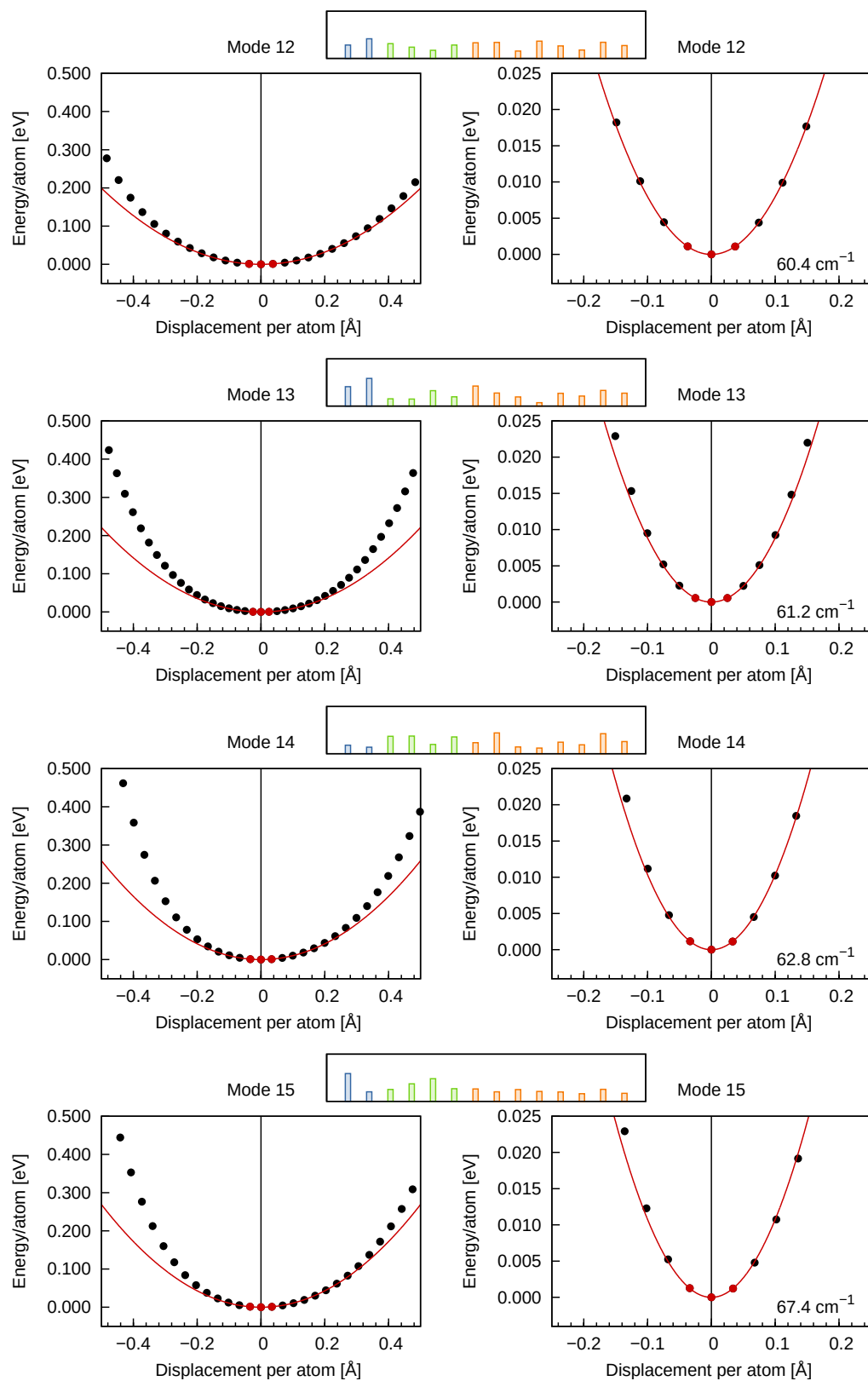
The distortion coordinate, that connects distorted and undistorted structure and may thus serve as a guess for a particular 'soft' direction in the energy landscape, can be expanded in the phonon-eigendisplacements. The expansion coefficients are given in [Tab. E.1](#). The non-vanishing coefficients of the acoustic modes indicate that the distortion coordinate contains a slight translation as an artifact of the relaxation. This is taken into account in the calculation of the amplitude of the distortion, see the footnote on p. 139. No unambiguous correlation between the value of the expansion coefficient and the validity of the harmonic approximation is visible upon inspection of the sampling curves; the modes 36 and 40, for example, show both a pronounced deviation from harmonicity and large coefficients. Also the signs correctly yield the direction in which the deviation occurs. However, no such correlation is obtained for mode 34, for instance. For mode 17, a large negative coefficient is obtained, but along this direction, the calculated total energy increases more than expected from the harmonic approximation. Hence, either the linear path represented by the distortion coordinate does not coincide with a (probably curved) path along which the energy landscape is particularly soft, or the anharmonic interaction of the modes prevents this simple approach.

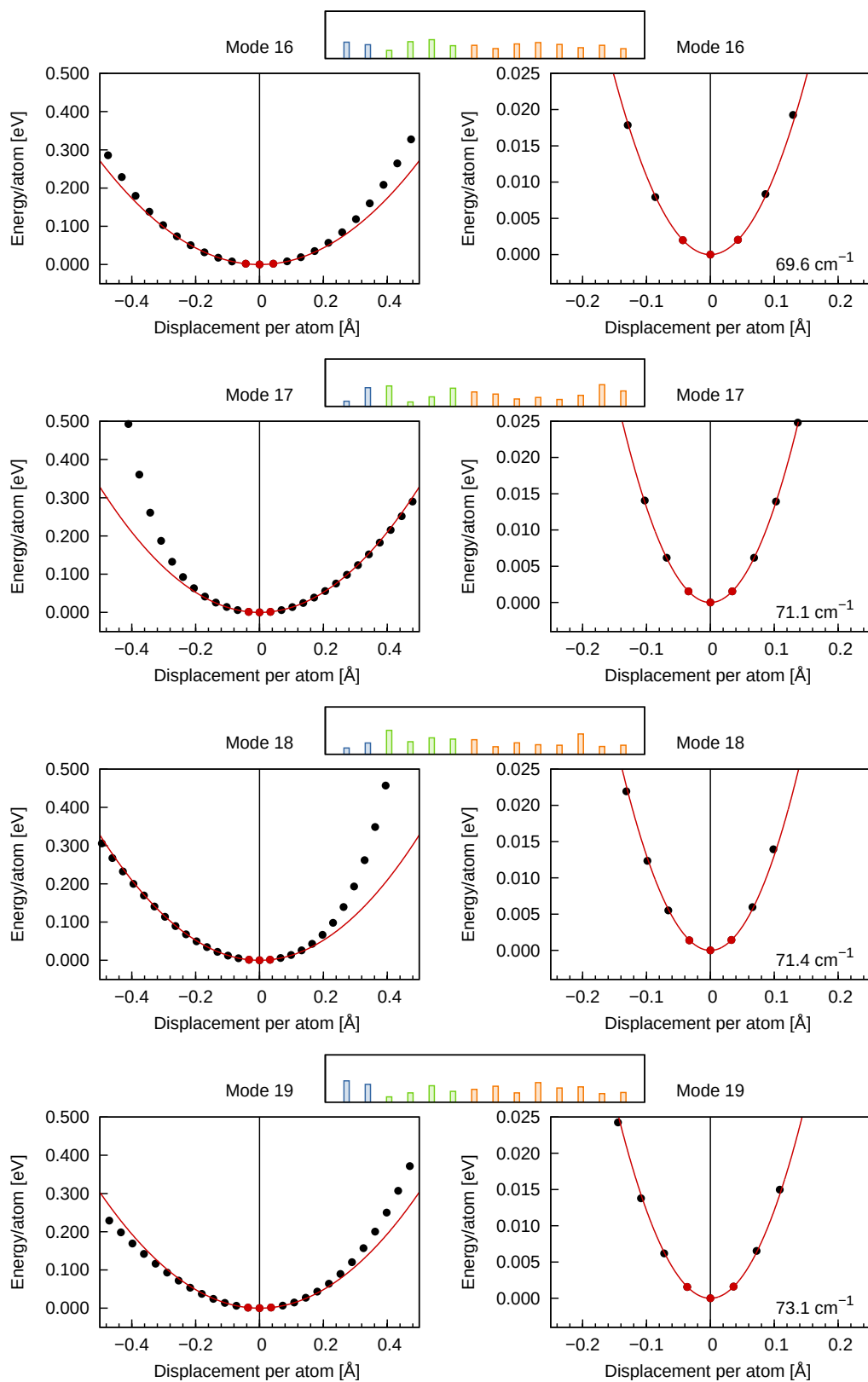
Table E.1. *The expansion of the distortion coordinate into phonon-eigendisplacements yields the expansion coefficients that are compiled in this table.*

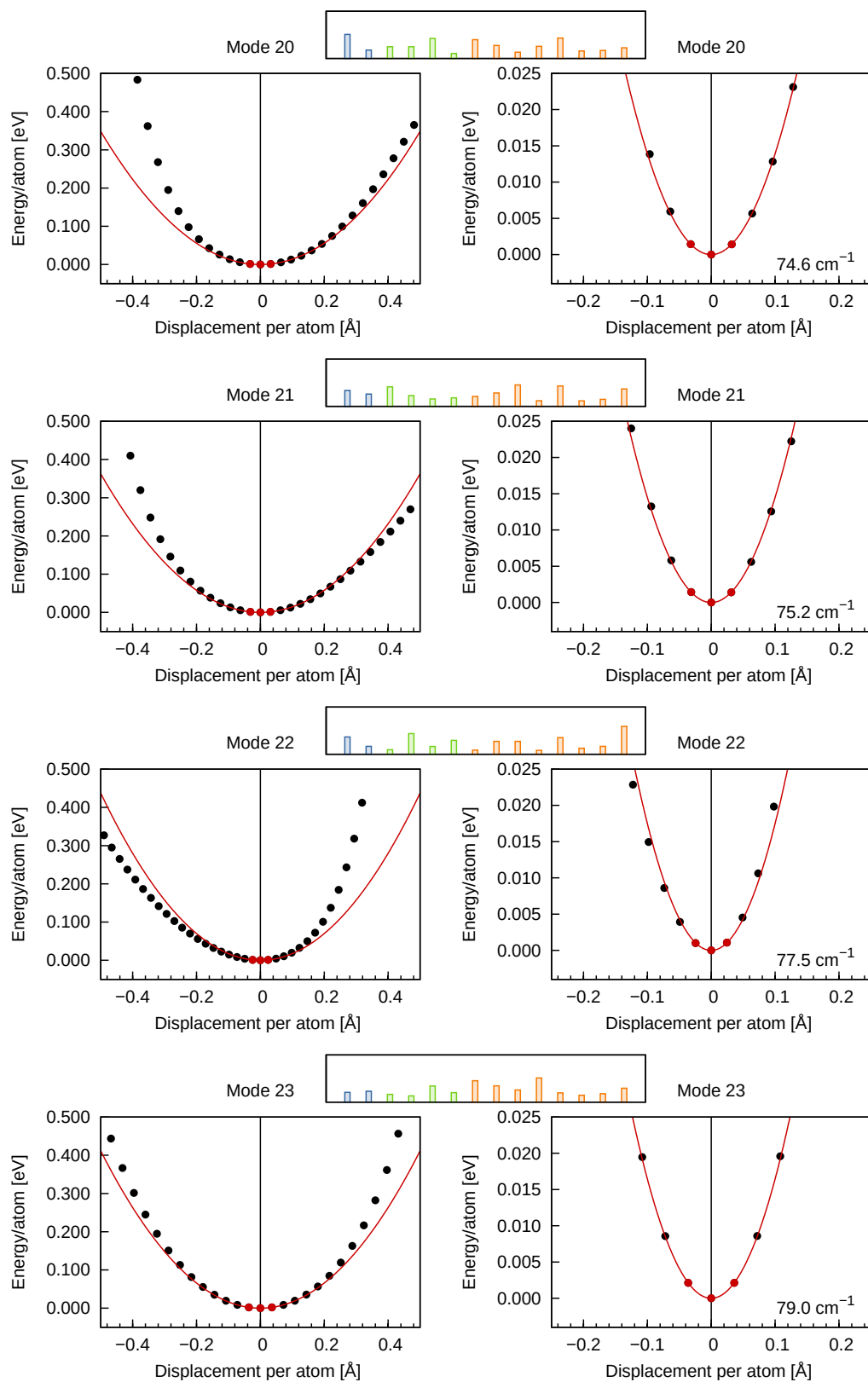
Mode	Exp. coefficient	Mode	Exp. coefficient
1	−0.70	22	37.55
2	7.57	23	−3.64
3	12.97	24	104.50
4	−23.53	25	24.52
5	30.46	26	−41.42
6	−23.10	27	35.46
7	−122.53	28	24.00
8	42.35	29	−42.80
9	29.64	30	−3.79
10	26.98	31	−21.99
11	16.04	32	53.45
12	−113.79	33	2.60
13	13.37	34	−219.23
14	−32.15	35	116.59
15	27.71	36	266.30
16	53.19	37	−91.22
17	−295.87	38	−43.97
18	−0.85	39	72.50
19	−153.70	40	−277.90
20	28.57	41	−76.81
21	−146.40	42	45.20

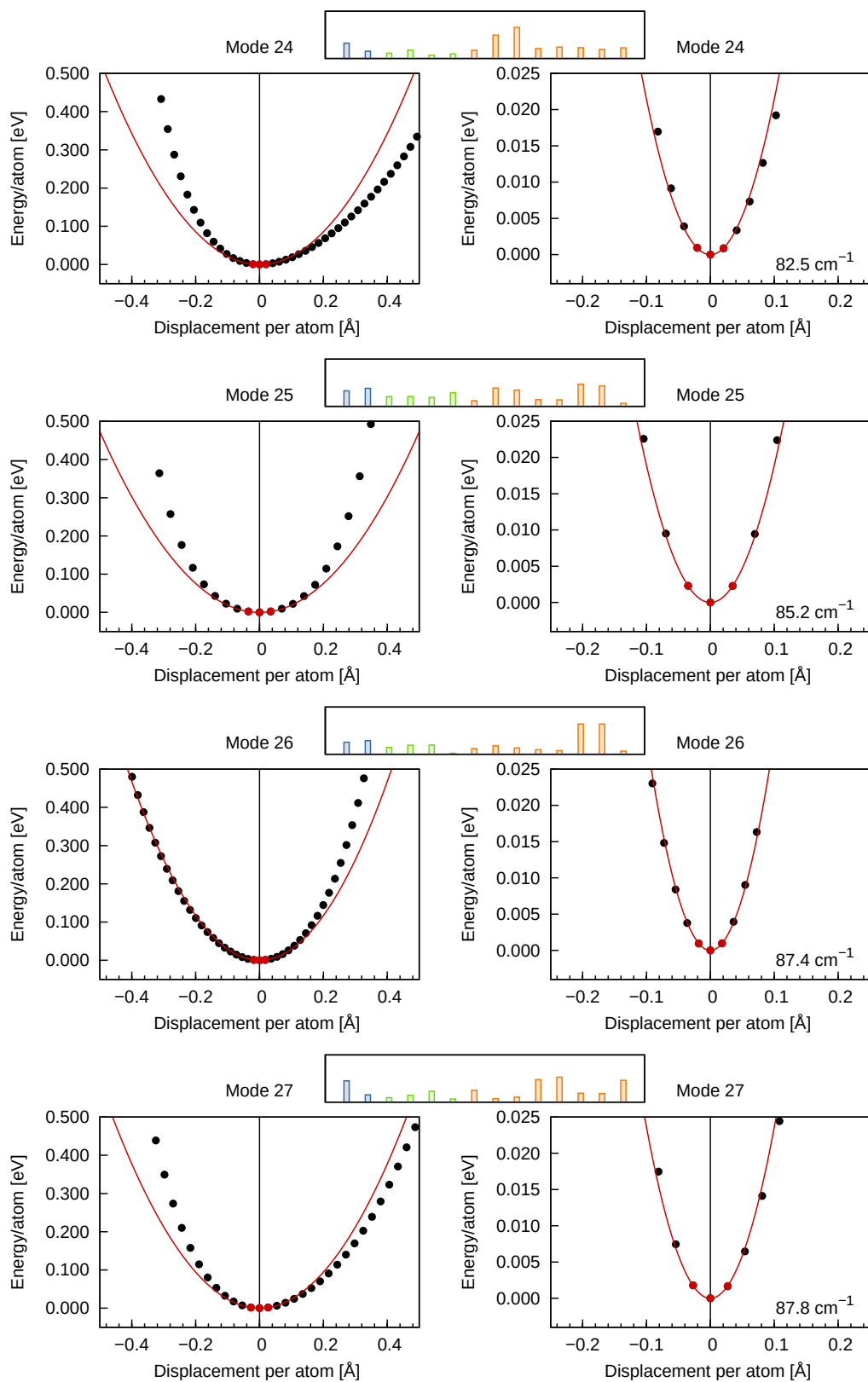


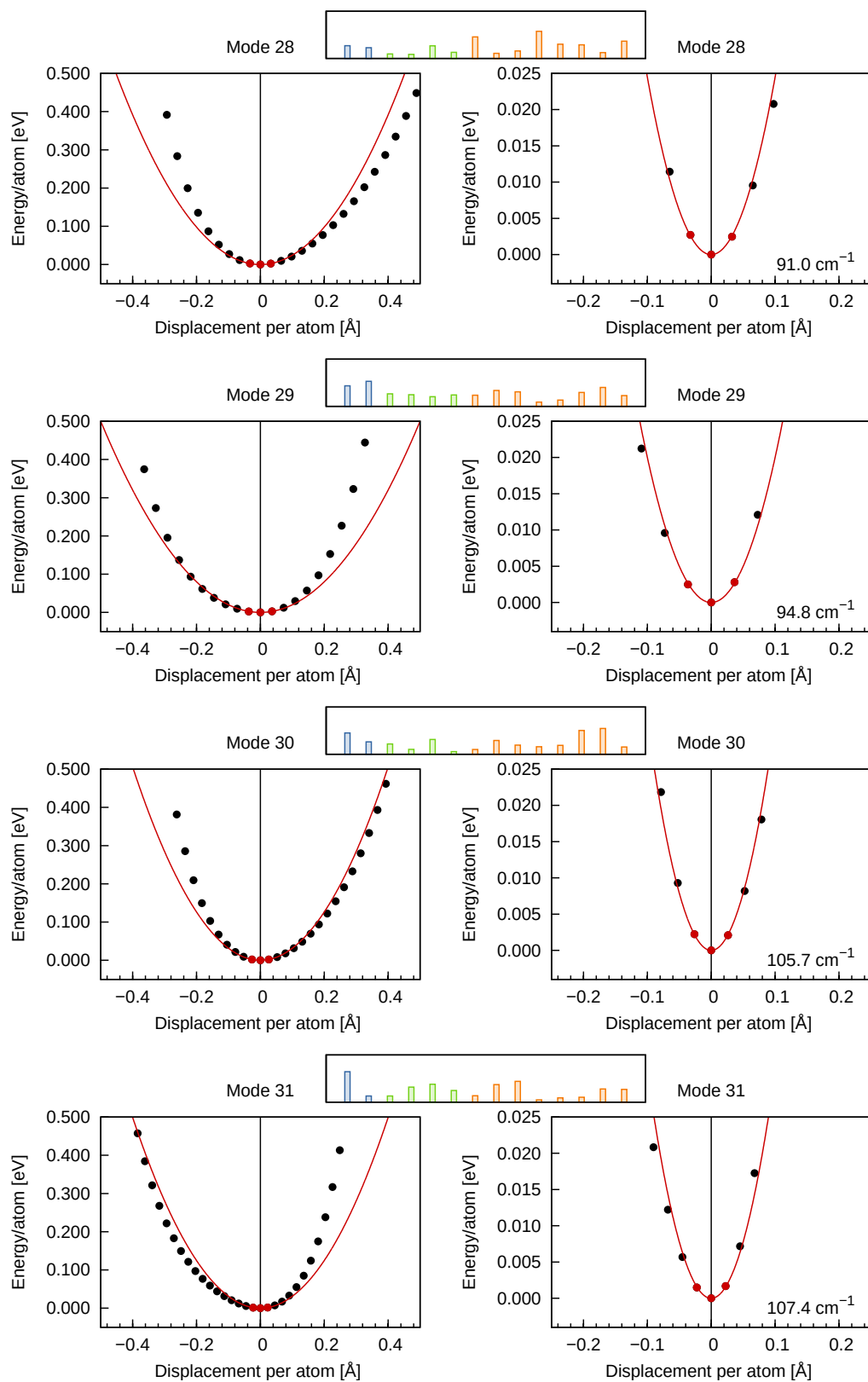


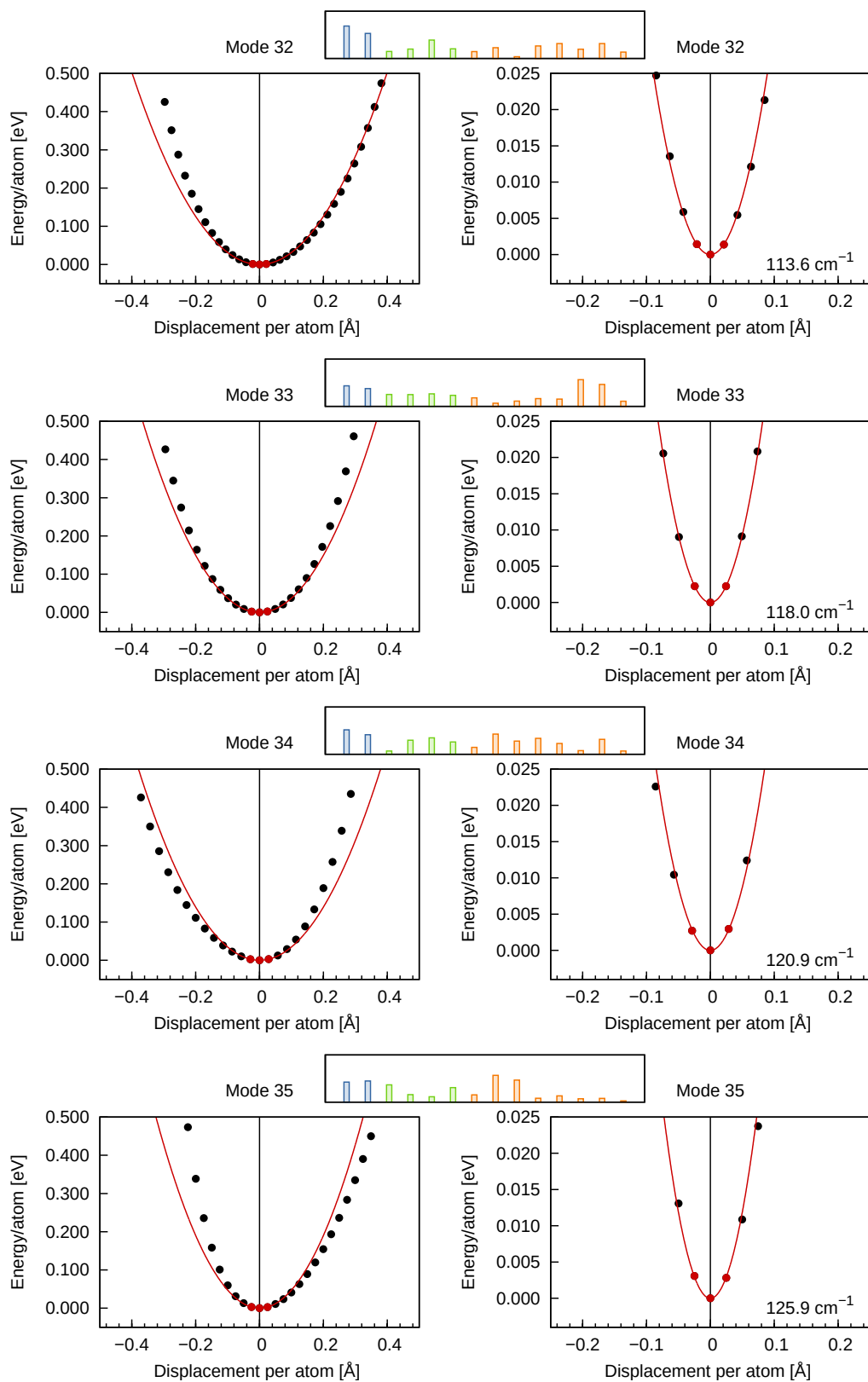


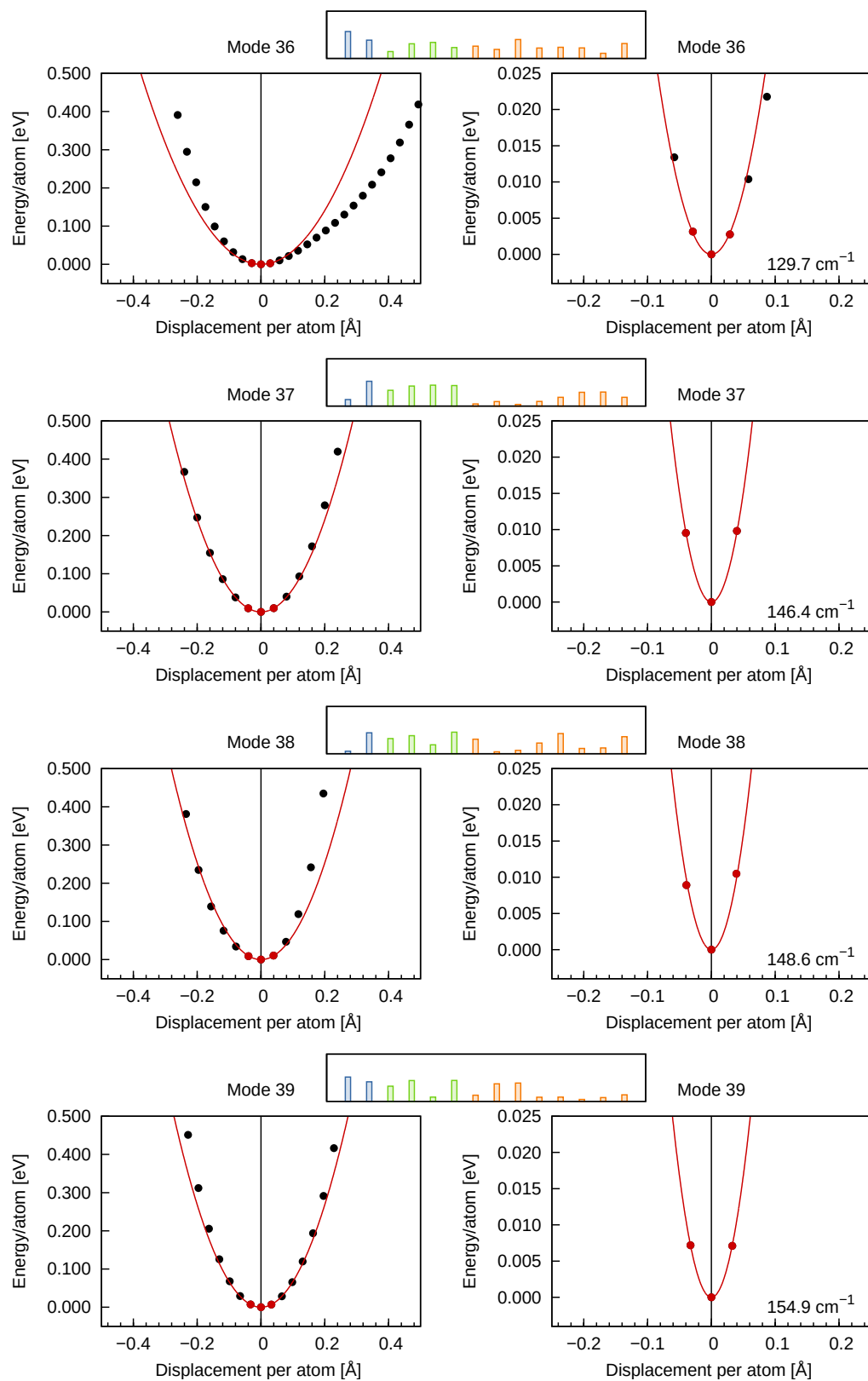


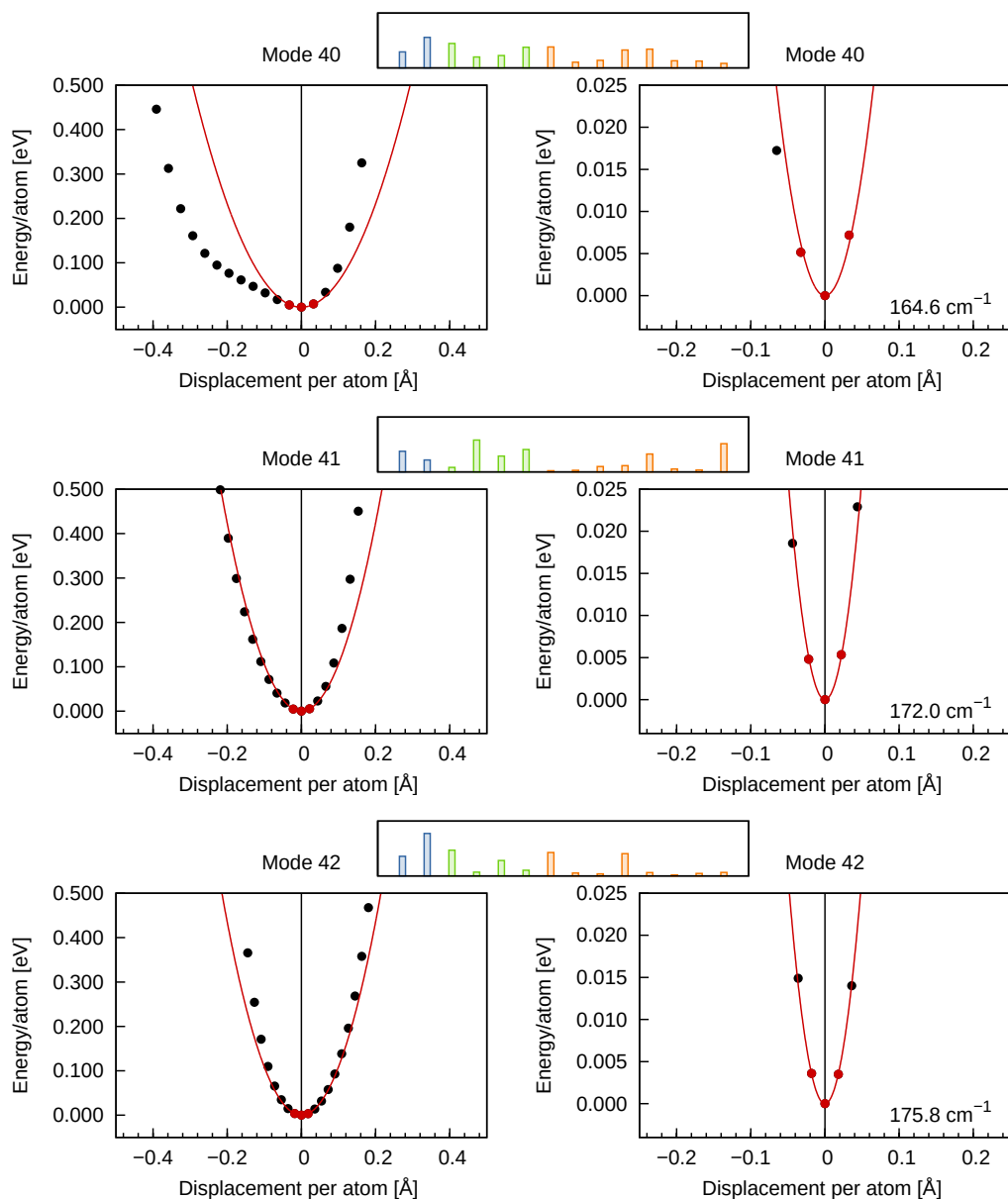












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Betreuung von Bachelor- und Diplomarbeiten

2010	Philippe Czaja (Bachelorarbeit: „Ab initio-Analyse elektronischer Materialeigenschaften“)
2007-2008	Peter Zalden (Diplomarbeit: „Combined experimental and theoretical study of structure and electronic properties of the chalcogenide-free phase-change material $\text{Ge}_x\text{Sb}_{100-x}$ “)

Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit selbstständig verfasst und nur die angegebenen Quellen und Hilfsmittel benutzt habe. Eine Anmeldung der Promotionsabsicht habe ich an keiner anderen Fakultät oder Hochschule beantragt.

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