FIRST-PRINCIPLES STUDY OF PbTe:
FROM EXOTIC SUPERCONDUCTIVITY TO
EMERGENT FERROELECTRICITY

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by
BORIS GIUSEPPE SANGIORGIO
MSc ETH Physics, ETH Zurich
born on 09.09.1987
citizen of
Castel S. Pietro (TI)

accepted on the recommendation of
Prof. Dr. Nicola A. Spaldin, examiner
Prof. Dr. Manfred Fiebig, co-examiner
Prof. Dr. Manfred Sigrist, co-examiner

2017
Boris Giuseppe Sangiorgio

First-principles study of PbTe: from exotic superconductivity to emergent ferroelectricity

Diss. ETH No. 24624

Digital Object Identifier doi: 10.3929/ethz-b-000199348
E-mail boris.sangiorgio@alumni.ethz.ch

© 2017 by Boris Giuseppe Sangiorgio

This work is licensed under the Creative Commons Attribution 4.0 International License. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.
A b s t r a c t

Lead telluride (PbTe) is a rocksalt structure narrow-gap semiconductor. It is interesting because it sits on the edge of both structural and electronic instabilities: it is known to be an incipient ferroelectric, which undergoes a ferroelectric transition upon doping with Ge or Sn, it can be made topologically non-trivial with Sn doping, and superconductivity arises with Tl doping. The closeness to a ferroelectric transition is regarded as the origin of the high thermoelectric performance of PbTe, making it one of the most used thermoelectric materials in the mid-temperature range (500 – 900 K).

Recent neutron total scattering and inelastic neutron scattering experiments questioned whether the rocksalt structure occurs at a local level. These experiments were interpreted to show a local symmetry breaking of the cubic symmetry on heating that manifests as a lead off-centering and the appearance of an additional phonon mode. The corresponding phenomenon was called *emphanisis*, the appearance of something out of nothing.

Thallium doping of PbTe causes interesting behaviors. At high temperatures it boosts its thermoelectric performance, while at low temperatures it is the only known dopant causing superconductivity in PbTe. Recent measurements reported an intriguing upturn of the resistivity as a function of temperature with the formation of a minimum in resistivity. The usual mechanism linked to such an upturn, the Kondo effect, was ruled out by the lack of magnetic impurities. Based on the proposed valence-skipping nature of Tl, the *charge Kondo effect* was proposed as the underlying mechanism of both superconductivity and upturn in resistivity.

To gain a better understanding of the underlying physics and to settle an ongoing controversy regarding the nature of the off-centering I present a detailed analysis of the structural and electronic properties of (doped) PbTe from first-principles calculations. My ab-initio molecular dynamics (MD) simulations analyzed together with single-crystal diffuse scattering experiments indeed prove that the cubic symmetry is locally broken. However, lead atoms are not off-centered in the strict meaning of the word. Instead, the symmetry breaking originates from dynamically fluctuating correlated dipoles along the ⟨100⟩ directions.

We identify the underlying mechanism to be a strong coupling between acoustic and optic phonons. We link this dynamic stereochemical activity of the lead lone pair with the good thermoelectric performance.

Looking for a way of performing larger simulations to understand the dynamics of these correlated dipoles I fit a Tersoff potential to the ab-initio MD. However, it fails to capture the peculiar local structure; the search for a good classical potential for PbTe is still open.
Regarding doped PbTe my calculations focus on understanding the Fermi surface with Na and Tl doping. I show that the rigid-band approximation on the density functional theory (DFT) band structure is able to describe the evolution of the Fermi surface with Na doping in good agreement with quantum oscillations experiments. On the other hand, Tl doping introduces an impurity band at the Fermi level making the situation more complex. Using the band unfolding technique I question its contribution to the Fermi surface, but larger supercells are needed to reasonably take into account disorder effects.
Riassunto

Il tellururo di piombo (PbTe) è un semiconduttore a piccola banda proibita che cristallizza nella struttura tipo cloruro di sodio. È un materiale interessante perché si trova al confine con instabilità sia strutturali che elettroniche: è noto per essere un ferroelettrico incipiente che subisce una transizione di fase ferroelettrica mediante drogaggio con Ge o Sn, diventa un isolante topologico mediante drogaggio con Sn e superconduttivo mediante drogaggio con Tl. La vicinanza ad una transizione di fase ferroelettrica è considerata l’origine dell’alto rendimento termoelettrico del PbTe, che lo fa uno dei materiali termoelettrici più usati a temperature medio-alte (500 – 900 K).

Esperimenti recenti di diffrazione neutronica totale e anelastica hanno messo in dubbio la struttura tipo cloruro di sodio a livello locale. Questi esperimenti sono stati interpretati con una rottura locale della simmetria cubica all’aumentare della temperatura che si manifesta come un decentramento (off-centering) degli atomi di piombo dalle posizioni ad alta simmetria e dall’apparizione di un fonone supplementare. Il fenomeno corrispondente è stato chiamato enfanisi, l’apparizione di qualcosa dal niente.

Il drogaggio del PbTe mediante Tl porta a proprietà interessanti. Ad alte temperature incrementa il suo rendimento termoelettrico, mentre a basse temperature è l’unico drogante conosciuto che causa superconduttività nel PbTe. Recenti misurazioni della resistività elettrica hanno riportato una crescita interessante in funzione della temperatura e, in parallelo, si è osservato un minimo nella resistività. Il meccanismo abitualmente collegato a quest’andamento, l’effetto Kondo, è stato escluso da data la mancanza di impurità magnetiche. Basandosi sull’idea che gli atomi di Tl presentino un salto di valenza (valence skipping), l’effetto Kondo “di carica” (charge Kondo effect) è stato proposto come il meccanismo alla base sia della superconduttività che del minimo della resistività.

In questa tesi presento un’analisi dettagliata delle proprietà strutturali ed elettroniche del PbTe (drogato e non) con calcoli ab-initio al fine di ottenere una comprensione migliore del composto e risolvere la disputa sulla natura del decentramento locale degli atomi di piombo. Le mie simulazioni di dinamica molecolare (MD) ab-initio analizzate insieme a esperimenti di diffrazione diffusiva monocristallina confermano che la simmetria cubica è localmente violata. Tuttavia, gli atomi di piombo non mostrano decentramenti nello stretto senso del termine. La rottura di simmetria è in effetti causata da doppietti elettrici correlati, che fluttuano dinamicamente lungo le direzioni cristalografiiche (100).

Grazie a questa analisi, siamo in grado di identificare il meccanismo di fondo in un accoppiamento dei fononi acustici ed ottici. Inoltre troviamo un collegamento tra la dinamicità dell’attività stereochemica del doppietto elettronico spaiato degli
atomi di piombo ed il buon rendimento termoelettrico del PbTe.

Col fine di eseguire simulazioni a più larga scala, in modo da comprendere la
dinamica di questi dipoli correlati, ho fittato un potenziale Tersoff a partire dalle
traiettorie di dinamica molecolare ab-initio. Purtroppo il potenziale risultante
non è in grado di riprodurre la caratteristica struttura locale; la ricerca di un buon
potenziale classico per il PbTe è pertanto ancora in corso.

Riguardo al PbTe drogato, i miei calcoli si concentranosulla caratterizzazione
della superficie di Fermi mediante drogaggio con Na e Tl. Dimostro che l’appo-
rossimazione di bande rigide (rigid-band approximation) sulla struttura a bande
ottenuta con la teoria del funzionale della densità (DFT) nel caso di drogaggio
con Na è in grado di descrivere l’evoluzione della superficie di Fermi in buon
accordo con esperimenti sulle oscillazioni di Shubnikov-de Haas. Al contrario,
il drogaggio con Tl introduce una banda di impurità al livello di Fermi e la situa-
tione è più complicata. Usando la tecnica del “band unfolding”, ne contesto il
contributo alla superficie di Fermi. Tuttavia supercelle più grandi sono necessarie
per tenere in considerazione effetti di disordine.
ACKNOWLEDGMENTS

This thesis would not have been possible without interaction with, and the help of, several people. First of all I would like to thank Prof. Nicola Spaldin for giving me the opportunity to work on this interesting project. I greatly appreciated your warm welcome in your research group. Your scientific guidance and supervision have always been amazing. I have come to admire your scientific intuition and hope to have gained some of your deep understanding of chemical and physical processes.

A big thanks to Dr. Michael Fechner for guiding me through my first steps in DFT and shaping my knowledge of first-principles computations. I really appreciated your patience and help in explaining to me how to run DFT computations and the physical concepts at the basis of my research project. I also truly enjoyed the deep scientific (and non!) discussions with you and our common officemate Natalya Fedorova and, more recently, Dr. Walter Tarantino. It has always been a pleasure coming to the office and meeting you all every day.

I would like to thank Prof. Claude Ederer, Prof. Ulrich Aschauer, Dr. Andrea Scaramucci and Dr. Awadhesh Narayan for being always available for advice and help.

A big thanks to all the (current and former) members of the Materials Theory group for being such wonderful colleagues and most importantly friends: Alexander E., Alexander H., Andrea, Awadhesh, Bastien, Carina, Chiara, Claude, Dominik, Florian, Frank, Gabriele, Gerhard, Jaime, Krzysztof, Madhura, Mani, Maribel, Maryam, Martin, Michael, Natalya, Quintin, Roisin, Sandra, Sinead, Sophie, Uday, Uli, Walter, and Yaël. It has been a pleasure and honor to run so many “SOLA” with the Schrödinger’s Kittens.

Thank you also to Dr. Federico Zipoli for being always available to dispense advice on MD and for reading the manuscript. I really enjoyed our collaboration.

A big thanks to Dr. Paula Giraldo-Gallo and Prof. Ian Fisher for the fruitful collaboration and for welcoming me in Stanford. I really enjoyed our thought-provoking discussions and my stay in Stanford.

A big thanks to Dr. Thomas Weber. Our collaboration and your knowledge of total scattering experiments were instrumental to the successful completion of my research.

I would like to express my gratitude to Prof. Joost VandeVondele for his advice and help in molecular dynamics and in the use of the CP2K code.

I am deeply obliged to Susanne for her availability and support in any administrative matter. You simplified a lot my PhD life.

A big thanks to Chiara and Walter who helped me in the challenging task of translating the abstract into Italian.
Last but not least, a very big thanks to all my friends and family, who always believed in me and supported me throughout my studies. Without you I would not have succeeded.
CONTENTS

ABSTRACT iii

RIASSUNTO v

ACKNOWLEDGMENTS vii

1 INTRODUCTION 1
   1.1 Structural properties of PbTe 4
   1.2 Thermoelectricity in PbTe 10
   1.3 Tl-doped PbTe at low temperatures 14
   1.4 Performed research 21
       1.4.1 Structure of the thesis 22

2 THEORY & METHODS 23
   2.1 Density functional theory 23
       2.1.1 Approximations to the exchange-correlation energy 26
   2.2 Molecular dynamics 29
       2.2.1 Thermodynamic averages and different ensembles 30
   2.3 Unfolding of band structures 34
   2.4 Quantum oscillations formalism 37
   2.5 Pair distribution function technique 37

3 FUNDAMENTAL PROPERTIES OF PbTe 41
   3.1 Computational details 41
   3.2 Structural properties 42
   3.3 Electronic properties 44
   3.4 Volume dependence of relevant quantities 48
       3.4.1 Volume dependence of phonon modes 48
       3.4.2 Volume dependence of the band gap 49
   3.5 Conclusions 50

4 POLAR FLUCTUATIONS IN PbTe 53
   4.1 Computational details 53
   4.2 T = 0 K structural properties 54
   4.3 T = 0 K energetics of off-centering 55
   4.4 Review of previous MD studies 56
   4.5 Paper 59
   4.6 Additional material 85
   4.7 Comments on the presented MD simulations 87
4.8 Conclusions & Outlook 89

5 Effective potentials for PbTe 91
5.1 Computational details 92
5.2 Validation of Coulomb-Buckingham potential for PbTe 92
  5.2.1 $T = 0$ K properties 94
  5.2.2 Finite temperature properties 95
5.3 Construction and validation of a Tersoff potential 100
  5.3.1 Introduction into Tersoff potentials 100
  5.3.2 Method for constructing a Tersoff potential 104
  5.3.3 Validation of Tersoff potential 106
5.4 Comparison between Buckingham and Tersoff potentials 114
5.5 Conclusions & Outlook 114

6 Hole doping in PbTe 117
6.1 Computational details 118
6.2 Substitutional doping with supercells 118
  6.2.1 Structural relaxations in the small supercell 119
  6.2.2 Comparison of different configurations of the big supercell 122
  6.2.3 Electronic structure with supercells 125
  6.2.4 Unfolded bands with Na and Tl impurities 128
6.3 Fermi surface evolution 134
  6.3.1 Paper 137
  6.3.2 Characterization of $\Sigma$ pockets 157
  6.3.3 Comparison with experiments 159
6.4 Conclusions & Outlook 162

7 Conclusions & Outlook 163

Appendices 165
A Computation of DHVA frequencies 165
B Analysis of molecular dynamics simulations 165
  B.1 Pair distribution function 166
  B.2 Phonon-related properties 167
C Determination of cross-sectional areas of an ellipsoid 169
D Characterization of the L- and $\Sigma$-pockets 170

List of Publications 175

Bibliography 177
ACRONYMS

ADP  atomic displacement parameter
AM05  Armiento-Mattson-2005
ARPES  angle-resolved photoemission spectroscopy
BCS  Bardeen-Cooper-Schrieffer
CPA  coherent potential approximation
CSV R  canonical sampling through velocity rescaling
DFT  density functional theory
DHVA  de Haas–van Alphen
DMFT  dynamical mean field theory
DOS  density of states
EBS  effective band structure
ELF  electron localization function
EXAFS  extended x-ray absorption fine structure
FFT  Fast Fourier Transform
GGA  generalized gradient approximation
GLE  generalized Langevin equation
GPW  Gaussian and plane wave
GTH  Gödecker-Teter-Hutter
IFC  interatomic force constant
INS  inelastic neutron scattering
JT  Jahn-Teller
LA  longitudinal acoustic
LDA  local density approximation
<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LO</td>
<td>longitudinal optic</td>
</tr>
<tr>
<td>MD</td>
<td>molecular dynamics</td>
</tr>
<tr>
<td>PAW</td>
<td>projector augmented wave</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
</tr>
<tr>
<td>PBEsol</td>
<td>PBE revised for solids</td>
</tr>
<tr>
<td>PC</td>
<td>primitive cell</td>
</tr>
<tr>
<td>PDF</td>
<td>pair distribution function</td>
</tr>
<tr>
<td>PW91</td>
<td>Perdew-Wang-1991</td>
</tr>
<tr>
<td>RDF</td>
<td>radial distribution function</td>
</tr>
<tr>
<td>revPBE</td>
<td>revised PBE</td>
</tr>
<tr>
<td>SC</td>
<td>supercell</td>
</tr>
<tr>
<td>TA</td>
<td>transverse acoustic</td>
</tr>
<tr>
<td>TO</td>
<td>transverse optic</td>
</tr>
<tr>
<td>VCA</td>
<td>virtual crystal approximation</td>
</tr>
<tr>
<td>VSEPR</td>
<td>valence shell electron pair repulsion</td>
</tr>
</tbody>
</table>
Introduction

IV-VI binary chalcogenides AX, A = Ge, Sn, Pb and X = S, Se, Te, have a broad range of applications in infrared and laser technologies, as thermoelectric materials, and for memory storage applications. They are also interesting in fundamental research, for example in the ferroelectric, topological insulator or superconductivity fields of study. In the following I introduce this class of materials concentrating on lead telluride (PbTe).

The IV-VI chalcogenides belong to the class of narrow-gap semiconductors, the band gap being of the order of $10^{-1}$ eV making them suitable for infrared lasers (see, e.g., Refs. [1–4]) and detectors (see, e.g., Refs. [2, 5, 6]). One of the great advantages of these compounds is that the band gap can be tuned by changing the composition. For example, in lead tin telluride, Pb$_{1-x}$Sn$_x$Te, the band gap can be tuned between 0 and 0.3 eV, because by alloying Sn the band gap first decreases, closes, and then reopens again [1, 7]. Furthermore, also pressure, strain and temperature can be additionally used to change the band gap [8–11]. The band gap evolution in this case is actually a consequence of the different topology of the end compounds in the alloy: PbTe is a normal insulator, while SnTe is a crystalline topological insulator [7, 12–14]. The only way to go from one topologically trivial to a non-trivial state is through a metallic state so that the character of the valence and conduction bands is inverted $^1$ [1, 7–9, 12, 13, 18].

Lone pairs

A lone pair (called also non-bonded pair or inert electron pair) is a pair of electrons in the valence shell of a single atom that does not participate in conventional covalent bond formation. When a lone pair affects the geometry and shape of a compound it is said to be stereochemically active. This concept is used, for example, in valence shell electron pair repulsion (VSEPR) theory to explain the shapes of molecules. The lone pair distributes itself in such a way to minimize electrostatic repulsion, causing ammonia to be non-planar, and the bonding angle in water to be smaller than the ideal tetrahedral angle. The lone pairs on nitrogen and oxygen occupy space and repel the bonding hydrogen atoms (see Fig. 1.1).

$^1$ Actually, one could circumvent the metallic state by finding a tunable parameter that breaks the symmetry that protects the metallic surface states in the non-trivial topological state [15–18].
Other systems displaying a lone pair are, e.g., compounds of Tl\(^+\), Ge\(^{2+}\), Pb\(^{2+}\) and Bi\(^{3+}\). Their valence configuration \(d^{10}s^2p^0\) results in the formal occupation of the metal \(s\) orbitals with empty \(p\) orbitals. The stereochemical activity of the lone pairs in such compounds is the driving force for ferroelectric distortions, e.g., in GeTe and SnTe.

The original theory explaining the stereochemical expression of the lone-pair is attributed to Orgel [20, 21]. In his model the stereochemistry of the lone pair originates from the on-site mixing of non-bonding cation \(s\) and \(p\) orbitals. Since \(s\) and \(p\) orbitals have different parity this on-site mixing can happen only on sites lacking inversion symmetry, and therefore couples to a symmetry-lowering structural distortion, e.g. in GeTe and PbO. Figure 1.2 shows a pictorial representation of stereochemical active lone pairs in GeTe. The figure shows the cubic \((100)\) plane with Te atoms at the four corners and Ge at the center. Panel (a) shows the inactive Ge lone pair as a spherically symmetric electron localization function (ELF) (yellow circle), while (b) shows the anisotropic lone pair forming on the opposite side of the Ge displacement.

However, the original model is unsatisfactory in explaining why certain materials distort (e.g. GeTe, SnTe, PbO) and others do not (e.g. PbTe, PbS) [22]. Moreover, DFT calculations have shown that the \(s^2\) electrons in the undistorted structure are not chemically inert [23–27]. They interact
strongly with the anion $p$ electrons producing bonding and anti-bonding states appearing at the bottom and top of the valence band, respectively.

Figure 1.3: Sketch of the energy levels of binary Pb compounds. Adapted figure from [A. Walsh et al., Chem. Soc. Rev. 40, 4455 (2011)] with permission of The Royal Society of Chemistry.

To overcome these problems a revised lone pair model was proposed [22] in which the interaction with the anion $p$ states is of primary importance. In particular, the stereochemical activity is strongly influenced by the relative energies of the cation $s$ and anion $p$ states. The revised model relies on two processes (see Fig. 1.3):

1. a strong interaction between cation $s$ and anion $p$ states resulting in an anti-bonding state with considerable cation $s$ character at the top of the upper valence band;

2. a distortion of the lattice to allow for an hybridization of the empty cation $p$ states with the previous anti-bonding state; this results in the asymmetric lone pair shown in Fig. 1.2(b).

Note that the arguments can be rationalized in the second-order Jahn-Teller instability (see ferroelectrics text box on page 5). Figure 1.3 exemplifies the revised model for Pb binary compounds and indicates why not all of them have a distorted ground state. If the energy of the anion $p$ states is too high the anti-bonding state from process 1 does not have enough cation $s$ character for a successful subsequent on-site mixing with $p$ states. Thus, the relative energies of the cation $s$ and anion $p$ states are very important because they determine how much cation $s$ character lies close to the Fermi energy.

Many IV-VI compounds also display interesting structural properties. For example chalcogen alloys (as Ge$_2$Sb$_2$Te$_5$) and the binary GeTe are considered promising phase change materials for memory storage applications [28]. Upon
heating and cooling they undergo a fast and reversible interconversion between the crystalline and the amorphous phases. The different electrical and optical properties of the two phases can then be used to store data.

The adopted structure in binary systems is in all cases either rocksalt or a distorted rocksalt structure; germanium and tin sulfide and selenide form layered structures with four-coordinated cations, germanium and tin telluride a polar rhombohedral structure, and lead chalcogenides the rocksalt structure. However, it is not obvious why some of them are distorted and some not. Waghmare et al. [27] and Walsh and Watson [29–31] proved that it is the stereochemical activity of the cation lone pair that determines whether a compound distorts or not [for an introduction into the concept of lone pairs see the corresponding text box on page 1]. Furthermore, using the same concept Waghmare et al. [27] showed that the rocksalt structure gets increasingly stable for each of the three carbon-group cations when going down in the chalcogen group on the periodic table ($S \rightarrow Se \rightarrow Te$).

### 1.1 Structural properties of PbTe

Relevant for this work is in particular the trend for the binary tellurides: both GeTe and SnTe adopt a ferroelectric rhombohedral structure, while PbTe does not distort. This is the first indication that lead telluride is close to a ferroelectric transition [for an introduction into the concept of ferroelectrics see the corresponding text box on page 5]. In fact, Alperin et al. [32] showed that PbTe is in a paraelectric phase, with similar characteristics to the corresponding phase in GeTe and SnTe. Specifically, the transverse optic (TO) mode at $\Gamma$ was measured with inelastic neutron scattering (INS) at different temperatures [32, 33]; the temperature evolution matched the softening described by the soft-mode theory of ferroelectrics (see Eq. 1.1). This means that by decreasing the temperature lead telluride gets closer and closer to a ferroelectric transition, but it does not reach the ferroelectric state because the TO mode does not soften completely; Alperin et al. [32] extrapolated a Curie temperature of $-135$ K. This is usually called incipient ferroelectricity.

Further evidence for the vicinity to a ferroelectric transition is obtained through the Born effective charges, which were calculated with DFT in Ref. [27] [for an introduction into the concept of Born effective charges see the corresponding text box on page 8]. The authors found anomalously large Born effective charges, $+6.16$ instead of the nominal $+2$, indicative of the large polarizability of lead telluride.

Recent INS experiments reported a strong anharmonic coupling between the TO and the longitudinal acoustic (LA) modes [34]. This leads to an avoided crossing in the phonon dispersions and affects the heat-carrying longitudinal acoustic phonons. The authors speculated that this mechanism is responsible for the low thermal conductivity and, thus, partly explains the good thermoelectric properties.
of lead telluride [for an introduction into thermoelectrics see the corresponding text box on page 11].

In 2010, neutron total scattering experiments [35] analyzed with the pair distribution function (PDF) technique in real space provided some indications that the lead lone pair is actually stereochemically active also in lead telluride and lead sulfide [for an introduction into the PDF technique refer to section 2.5]. Since this study is the main motivation for one of the projects presented in this thesis I will describe it, and also the subsequent related studies, in detail. It was found that the PDF analysis delivers anomalous features with temperature: the peaks broaden “unusually” and develop non-gaussian and structured features. For example, the nearest-neighbor peak displays increasing asymmetry and the appearance of a shoulder on the high-$r$ side. The subsequent refining led to the conclusion that lead atoms are locally off-centered starting from a temperature of $100 - 200$ K, while the average structure still remains rocksalt; for example, at 300 K the obtained displacement is 0.2 Å. This is also supported by the reported anomalous temperature evolution of the atomic displacement parameters (ADPs): at the same temperature where lead off-centering is first reported, the ADPs show a kink, which is an indication of possible disorder (off-centering). In fact, in a system showing normal behavior (no disorder, off-centering, or similar) a linear extrapolation of the high-temperature ADPs crosses the origin at zero Kelvin.

**Ferroelectrics**

Ferroelectric materials are insulating systems that exhibit two or more equivalent states with non-zero electric polarization in zero applied electric field. Important to characterize a material as a ferroelectric is the possibility of switching between these states with an electric field. [For a thorough introduction to ferroelectrics see the excellent book *Physics of Ferroelectrics: A Modern Perspective* [36]]

The spontaneous polarization is produced by the atomic positions in the crystal structure. A polar structure, i.e. a structure lacking a center of inversion, is a necessary condition. However, not every polar material is ferroelectric, because the polarization has additionally to be switchable.

Ferroelectrics can be found, among others, in the family of perovskite oxides, with BaTiO$_3$ as a prototypical example, as well as in the IV-VI semiconductors, e.g. GeTe. Applications of ferroelectrics comprise piezo- and pyroelectric devices (piezo- and pyroelectricity are necessary conditions for ferroelectricity), memories, and cooling devices. A current hot topic in research is to combine multiple ferroic orders in the same material that possibly couple together [37], which would open the road to more energy efficient memory devices. Such materials are called multiferroics.

Usually, the ferroelectric state is the result of a symmetry-breaking distortion of a higher symmetry (reference) structure. Above the Curie tempera-
ture, $T_c$, ferroelectrics undergo a phase transition to a non-polar paraelectric phase.

Figure 1.4: Free energy as a function of the Ge-Te distance along ⟨111⟩, $d$. The blue line shows the double-well shape obtained in the high-symmetry rocksalt structure with DFT. The magenta dashed line sketches the energetics in the paraelectric phase above $T_c$, while the vertical dashed black line indicates the equilibrium distance in the paraelectric structure. The inset shows the rhombohedral (primitive) cell of the rocksalt structure with the Ge-Te distance $d$ indicated by a light-blue arrow. Note that the Ge-Te distance $d$ plays the role of the order parameter, since it is related to the polarization.

The phase transition can be phenomenologically described by the soft-mode theory of ferroelectrics [38], which builds on the Landau theory of second-order transitions; in this case the order parameter is the electric polarization and at the phase transition the electric susceptibility diverges. The central idea is that at the phase transition a polar phonon has a vanishing frequency, i.e. atomic displacements along its eigenvectors do not cost any energy. This is also the signature of a ferroelectric instability in computations; in the high-symmetry structure the zone-center optical phonons have imaginary frequencies. Experimentally, in ferroelectrics the temperature dependence of polar phonons show a hardening (increasing frequencies) away from $T_c$, both in the ferroelectric and paraelectric phase. The soft-mode theory of ferroelectricity predicts that the transverse optic (TO) mode at $\Gamma$ behaves as

$$\omega_{\text{TO}} \propto (T - T_c)^{1/2}. \quad (1.1)$$

I now discuss the aforementioned mechanism for the case of GeTe, probably the simplest ferroelectric material. It was also one of the first ferro-
1.1 Structural properties of PbTe

Electrics studied with first-principles calculations [39]. At high temperatures GeTe crystallizes in the rocksalt structure and at 670 K [40] it undergoes a phase transition to a ferroelectric state. The observed low-temperature structure can be obtained in a two-step distortion: (i) the two fcc sublattices displace in opposite directions along the ⟨111⟩ direction, and (ii) the lattice experiences a rhombohedral shear along ⟨111⟩ diminishing the rhombohedral angle from 60° to 58.36° [41].

Figure 1.4 shows the energetics of the ferroelectric distortion for GeTe. In the paraelectric phase the energy landscape is described by a single-well potential (magenta dashed line). When the temperature is lowered the curvature decreases and at $T_c$ it vanishes. By further temperature lowering the system can eventually distort into one of the energy-equivalent minima (blue line).

A microscopic mechanism describing polar distortions is the pseudo (or second-order) Jahn-Teller (JT) effect [42–45]. This effect deals with systems with non-degenerate ground states, so that the first-order JT effect does not play any role. We consider a collection of nuclei and electrons in a reference (high-symmetry) configuration. If we distort the system we can write the energy as a function of the coordinate of the distortion, $Q$,

$$E(Q) = E(0) + \langle \psi_0 | \frac{\delta H}{\delta Q} | \psi_0 \rangle Q + \frac{\langle \psi_0 | \frac{\delta^2 H}{\delta Q^2} | \psi_0 \rangle Q^2}{2} - \sum_{k \neq 0} \frac{\langle \psi_0 | \frac{\delta H}{\delta Q} | \psi_k \rangle}{E_k - E(0)} Q^2,$$

up to second order in perturbation theory. The linear term in $Q$ is zero for a centrosymmetric reference structure (it corresponds to the JT term). Of the second-order terms, the first is always positive [45], while the second is always negative (if it is nonzero). The first term describes the increase in energy caused by the distortion when there is no electronic redistribution; the second term describes the mixing between the ground state and the excited electronic states due to the distortion and is related to the formation of new chemical bonds in the low-symmetry structure.

For the second term to dominate and produce a distortion two criteria must be fulfilled: first, the matrix element has to be nonzero, which for a centrosymmetric ground state and a non-centrosymmetric distortion means that the (lowest-lying) excited states have to be non-centrosymmetric. Second, the denominator has to be small, meaning that low-lying excited states have to be available. This occurs when the band gap is not too large.

The anomalous behavior was brought onto a firmer ground by INS experiments [33] performed in the same research group. Their analysis revealed a local symmetry breaking linked to the appearance of an additional phonon branch above 100 K; the TO mode at $\Gamma$ splits with increasing temperatures. The off-centering was also observed in the paraelectric phase of SnTe [46]. The observation of symmetry lowering on heating was termed *emphanisis*, from the greek meaning...
the appearance of something out of nothing, in this case the emergence of local electric dipoles from a centrosymmetric ground state.

This exciting observation triggered a lot of research to understand the phenomenon. At the start of my work the situation was highly controversial; several studies, both theoretical and experimental, tried to reproduce the anomalous findings but with contradicting conclusions; some related them just to large anharmonic effects and some reported an off-centering. The controversy is partly originating from the fact that Božin et al. [35] did not specify exactly what they meant under off-centering. Many follow-up studies interpreted this concept differently, with the majority of them as lead atoms being (statically) displaced from the high-symmetry rocksalt positions and oscillating around this off-centered position. My work helps settle this dispute by clarifying precisely the nature of the “off-centering”. Through our collaboration with Božin et al. we came to the conclusion that a good definition of off-centering relates the position of the lead atoms to the local environment. That is, the off-centering measures the deviations from, e.g., the center of gravity of the coordination polyhedron (see paper in section 4.5).

**Born effective charges**

Born effective charges are a useful concept for discussing ferroelectric polarization [36, 47]. In an ionic system the polarization resulting from the displacement of an ion can be computed by multiplying its nominal charge with the displacement. However, in covalent systems this is not the case, because one has to consider also the electronic contributions to the polarization. One way to think of it is to assign effective charges to the ions to compensate for the electronic part; these are formalized in the Born effective charge tensor, $Z^*_{i\alpha\beta}$, defined as the first derivative of polarization with respect to atomic displacement or as the derivative of the electric force with respect to the electric field

$$Z^*_{i\alpha\beta} = \frac{\Omega}{e} \left. \frac{\partial P_\alpha}{\partial u_{i\beta}} \right|_{E=0} = \left. \frac{1}{e} \frac{\partial F_{i\alpha}}{\partial E_{\beta}} \right|_{u=0},$$

(1.3)

where $i$ indicates the ion, $\Omega$ is the unit cell volume, and $F$ the force acting on a given ion from the electric field $E$. Usually, in ferroelectrics Born effective charges are much larger than the nominal charges, for example in GeTe they are 10.8 instead of the nominal 2 [27]. Large Born effective charges mean that the force acting on an ion caused by the electric field is large, even if the field is small; a polarized ground state is, thus, favored.

The first study to address the off-centering question was an ab-initio molecular dynamics (MD) study performed by Zhang et al. [48] in 2011. The authors claimed to reproduce all PDF-related properties but did not find any off-centering.
Instead, they reported *abnormally large-amplitude thermal vibrations*, i.e. large anharmonic effects. However, a subsequent ab-initio MD work by Kim and Kaviany [49] in 2012 reported the full reproduction of all PDF-related properties accompanied by lead off-centering.

On the experimental side, the first additional studies followed a year later. In 2013 two contradicting works were published; the first [50], reported possibly even larger lead off-centering (0.3 Å at 300 K) by synchrotron powder x-ray diffraction data analyzed with the maximum entropy method. The second [51], found no evidence for lead off-centering from extended x-ray absorption fine structure (EXAFS) measurements and stated that the suggested displacements are inconsistent with their data.

2014 was a very productive year with several papers dealing with this controversy. New techniques were used, including classical molecular dynamics with potentials fit from first-principles. Chen et al. [52] used a novel slave-mode expansion of the potential energy to perform classical molecular dynamics with an 8000-atom supercell. The authors were able to reproduce the splitting of the zone-center optical mode observed in Ref. [33], but attributed it to anharmonic effects, or more precisely to competing third and fourth order anharmonicities. They claimed to reproduce the PDF asymmetry but did not find any deviation from the rocksalt high-symmetry positions.

A further classical MD study was performed by Shiga et al. [53], but this time with a non-empirical force field based on accurate anharmonic interatomic force constants (IFCs) computed from first-principles. The authors reproduced the splitting of the TO mode at Γ and attributed it to anharmonic effects, or more precisely, to unusually large cubic IFCs along the ⟨100⟩ direction.

Interestingly, also studies [54,55] combining several techniques, such as single-crystal and powder neutron diffraction, and inelastic neutron scattering and (ab-initio) MD, were published. The authors claimed to reproduce the asymmetry of the PDF peaks, but did not find any off-centering. Furthermore, with the help of ab-initio MD, they suggested that the splitting of the zone-center mode can be attributed to a sharp resonance in the phonon self energy caused by the nesting of phonon dispersions that combines with the anharmonicity to produce the large splitting.

Also in 2014 Knight [56] published a puzzling high-resolution neutron powder diffraction study. The author did not focus on the local properties, but rather performed a usual Rietveld refinement based on Bragg scattering. He found no anomalous temperature evolution of the ADPs and attributed the earlier report [35] to inaccurate thermometry, i.e. samples being at a significantly lower temperature than the target temperature above room temperature. This would remove a strong supporting point for an off-centering; only the asymmetric and structured PDF peaks remain suggesting a more complex local structure.

Finally, in 2016 Christensen et al. [57] performed a powder x-ray diffraction study that included the effects of Pb vacancies and microstrain in the Rietveld and maximum entropy method modeling. They reported a local breaking of
the cubic symmetry consistent with a static off-centering of at most 0.2 Å at 100 K. Furthermore, they commented on the possibility of sample dependence as a source of the inconsistent measurements.

To shed more light into this mysterious effect, Thomas Weber also at ETH Zurich performed single-crystal x-ray scattering experiments and analyzed the diffuse scattering with the PDF. The refined atomic pair correlations show a peculiar decay with distance that points to a dimerization of neighboring atoms along the ⟨100⟩ direction. We started a collaboration with the goal of reproducing his observations using ab-initio MD, the output of which can then be further analyzed in terms of higher-order correlations and their impact on the local bond structure. The resulting experimental and theoretical characterization of the local structure of PbTe is presented in the paper in section 4.5.

Similar behavior has also been found in different classes of materials. In La$_{1-x}$Ca$_x$MnO$_3$ atomic PDF analysis of neutron diffraction data [58, 59] reported Jahn-Teller distortions in the high-temperature insulating phase that are not present in the low-temperature metallic phase, even if the average crystal structure is the same. In KNi$_2$Si$_2$ x-ray diffraction and neutron scattering data were interpreted by Neilson et al. [60] as an emergence on warming of local Ni displacements accompanied by differences in the electron density at the Ni sites, suggesting a fluctuating charge density wave. In CsSnBr$_3$ the PDF analysis of x-ray diffraction data performed by Fabini et al. [61] showed a dynamic off-centering of Sn$^{2+}$ on warming, while again the average perovskite structure is not affected. Interestingly, the PDF peaks are increasingly asymmetric but not as structured as in Ref. [35] for PbTe, as the shoulder on the high-τ side is missing. Finally, the same observation was made in hybrid tin and lead halide perovskites from a PDF analysis of x-ray diffraction data [62].

1.2 Thermoelectricity in PbTe

As mentioned before lead telluride is known to be very anharmonic [34, 48, 63]. The large coupling between optical and acoustic phonons has been interpreted as being favorable for thermoelectric properties [for an introduction into thermoelectrics see the corresponding text box on page 11]. In fact, since acoustic phonons are the primary heat carriers in the system, scattering processes involving them reduce the lattice thermal conductivity. In the literature this is one of the major research interests in the search for better thermoelectrics, together with larger Seebeck coefficients, while the electronic thermal conductivity can usually not be optimized because of its direct link to the electric conductivity.

Correspondingly, the stereochemical activity of lone pairs is also known to be beneficial for thermoelectricity [64–68]. By softening the optical modes it introduces anharmonicities and strong phonon-phonon coupling that decrease the lattice thermal conductivity. Moreover, it is predicted that lone-pair activity opens the band gap and, thus, bipolar effects are suppressed [65]. Interestingly,
optical measurements of the lead chalcogenides have shown a monotonic increase in band gap with temperature [10].

The band structure close to the Fermi energy (see Fig. 3.4) suggests an additional mechanism to increase the thermoelectric performance. In addition to the valence band maximum at $L$ another pocket is located along the $\Sigma$ line with a slightly smaller energy. If the band offset ($E_o$ in Fig. 3.4), i.e. the difference in energy between the $L$ and $\Sigma$ pockets, is decreased, which is called band convergence, the valley degeneracy increases from 4 ($L$ pockets) to an effective band degeneracy of $16 = 4 + 12$, such that the power factor $\alpha^2\sigma$ is increased [65, 67–70]. In fact, spectroscopic measurements [11] suggested a band convergence at about 700 – 800 K.

### Thermoelectrics

The thermoelectric effects describe the direct conversion of temperature gradients into electric voltages and vice versa. [For a thorough introduction to thermoelectricity see the excellent book *Introduction to Thermoelectricity* [71]]. The first effect to be discovered was the Seebeck effect, i.e. the conversion of heat into electricity in a thermocouple, a device consisting of two different conductors at different temperatures forming a junction. The inverse effect, i.e. the generation or removal of heat at the junction of a thermocouple when a current is flowing, is called the Peltier effect. Finally, the Thomson effect describes the heating or cooling of a homogeneous conductor when both an electric current and a temperature gradient are present.

In principle, a thermocouple can be used either to generate electricity from heat, or as a heat pump or refrigerator. However, they are usually quite inefficient because the reversible thermoelectric effects are always accompanied by the irreversible Joule heating and thermal conduction. The first thermoelectric devices were built in the 1940s with an efficiency of 5 – 6%. Since the 1970s they have been widely used by the National Aeronautics and Space Administration (NASA), as well as by the Soviet Union, to power their spacecrafts (for example the Viking and Voyager space probes, or the Apollo Lunar Surface Experiments Package left on the Moon by the Apollo missions). The recently launched Mars rover Curiosity has a radioisotope thermoelectric generator made out of lead telluride.

Even though the efficiency has more than doubled since the first applications, thermoelectric devices are still used only in niche technologies. However, the quest for more energy efficient systems and for reducing energy (heat) waste has triggered a lot of research in the thermoelectrics field.

Figure 1.5 sketches a thermoelectric device. In practice, several of these units would be connected together to deliver a reasonably large effect. The
performance of such a device is measured by the figure of merit $Z$ for a pair of materials defined as

$$Z = \frac{(\alpha_p - \alpha_n)^2}{\left[\sqrt{\kappa_p \rho_p} + \sqrt{\kappa_n \rho_n}\right]^2},$$

(1.4)

where $\alpha = V/\Delta T$ is the Seebeck coefficient (i.e. the ratio between the voltage and the temperature difference), $\kappa$ the thermal conductivity, and $\rho$ the electrical resistivity. The indices $p$ and $n$ refer to the two different (doped) materials. The figure of merit can be used to determine the conversion efficiency $\eta$ of a thermocouple as

$$\eta = \eta_c \frac{\sqrt{1 + ZT_{av}} - 1}{\sqrt{1 + ZT_{av} + T/(T + \Delta T)}},$$

(1.5)

where $\eta_c$ is the Carnot efficiency, and $T_{av}$ is the average temperature. Note that this formula is not always reliable because it assumes temperature-independent $\alpha$, $\rho$, and $\kappa$ [72].

![Figure 1.5: Sketch of a thermocouple, a device consisting of two different conductors (in green) at different temperatures forming a junction. Usually, p- and n-doped semiconductors are used. The mode of operation sketched is a refrigerator or a heat pump.](image)

For research purposes one usually does not investigate a pair of materials at the same time. Therefore, the figure of merit $z = \alpha^2/\kappa \rho$ of a single material is usually used, or its dimensionless variant $zT$. Note that $z$ can, in general, not be used to compute the figure of merit $Z$ of a thermocouple. However, in many cases $Z$ is approximately the average of $z_p$ and $z_n$.

In the search for better performing thermoelectric materials several strategies are followed nowadays, including band engineering (multiple valley bands, resonant states, suppression of bipolar effects,\ldots) and multiple length-scale hierarchical structuring (point defects, dislocations, elastic strain, nanoscale precipitates,\ldots) [64–68, 70, 73–86]. Here, I describe briefly the general principles without going into details. The figure of
merit $z$ is a good starting point to extract the key properties influencing the performance:

1. the electric conductivity should be high
   - small band effective masses
   - optimal carrier concentration
   - weak scattering of carriers
2. the thermal conductivity should be low
   - multiscale phonon scattering
   - large band gap, such that bipolar conduction is suppressed
3. the Seebeck coefficient should be high
   - strongly varying density of states (DOS) at the Fermi energy, e.g. with resonant levels
   - band flattening
   - band convergence
   - large band gap, such that bipolar conduction is suppressed

Unfortunately, many of the strategies to improve one property are bad for another one, e.g. disorder in the system increases scattering and thus decreases the thermal conductivity, but at the same time also the electric conductivity. Heterostructures, in which the interfaces scatter the phonons but not the electrons, help circumvent this problem \[76, 87\].

Thus, high-performance thermoelectrics stem from a very delicate balance between these “incompatible” features. Only in the last decades, materials with a figure of merit $zT \gtrsim 1$ have been reported, e.g. chalcogenides, pnictides, intermetallics, bismuth-chalcogenide-based systems, and organic materials \[66, 87, 88\] among others, with the current record held by, to my knowledge, single crystals of SnSe with a $zT = 2.6 \pm 0.3$ at 923 K \[89\]. Note that it is believed that for large-scale applications to be economic, a $zT \sim 3$ is required.

Another strategy followed to improve thermoelectric properties consists of doping or alloying PbTe with other compounds. The desired effects range from an increase in the band gap (to suppress bipolar conduction), microstructuring (to lower the thermal conductivity), band convergence (to increase the conductivity and the Seebeck coefficient), and the introduction of resonant levels (to increase the Seebeck coefficient). An example combining several of the previous features is PbTe-SrTe(4 mol\%) doped with 2 mol\% Na with a $zT = 2.2$ at 915 K \[90\], which is, to my knowledge, the highest reported $zT$ value in PbTe-based compounds so far.
Considering simpler compounds, Na- and Tl-doped PbTe were shown to have a high thermoelectric performance, \( zT \sim 1.5 - 2 \) at 600 – 900 K [66, 69, 91]. Na leads to band degeneracy near the Fermi level by tuning the carrier concentration and can introduce point defects and precipitates to lower the thermal conductivity [92], while in Tl-doped PbTe an additional effect comes into play, a resonant level [77, 91, 93, 94]. Mahan and Sofo [74] showed that the optimal \( zT \) from an impurity state is obtained by a delta function located \( 2.4k_BT \) above or below the Fermi energy, a situation which is clearly not realizable in nature. Furthermore, they showed that a background DOS (the DOS created by atoms other than those producing the delta peak) is very detrimental for the thermoelectric performance. However, such a background is needed to control the position of the delta peak. Current research focuses on ways of distorting and increasing the DOS near the Fermi level as a way of increasing the power factor \( \alpha^2\sigma \).

Going back to Tl-doped PbTe, Heremans et al. [91] proposed that Tl introduces a resonant level, also called a virtual bound state, slightly below the Fermi energy. The authors showed that a couple of percent of Tl doping are able to bring the figure of merit close to \( zT = 2 \).

1.3 Tl-doped PbTe at low temperatures

To be correct, the previous statement about the resonant level created by thallium doping in PbTe is still under debate; in total three different mechanisms [95] have been proposed to describe thallium impurities in PbTe: (i) the previously mentioned “impurity level” model [96], in which the thallium impurities hybridize with the Te \( p \) electrons and form a localized impurity state that overlaps with the valence band; (ii) the “auto-compensation” model, in which two impurity atoms dissociate into singly positively and singly negatively charged states \((2\text{Tl}^0 \rightarrow \text{Tl}^+ + \text{Tl}^-)\) [97]; (iii) the “mixed-valence” model, in which the impurity acts as a negative-\(U\) center, and the doubly-charged state is unstable and dissociates into singly and triply positively charged states \((2\text{Tl}^{2+} \rightarrow \text{Tl}^+ + \text{Tl}^{3+})\) [98, 99].

I now spend some time in motivating and explaining the third mechanism, because it was the main motivation for one of the projects presented in this thesis. Resistivity measurements in Tl-doped PbTe \((\text{Pb}_{1-x}\text{Tl}_x\text{Te})\), have revealed a low-temperature anomaly in the temperature dependence [98, 100]; the resistivity passes through a minimum that depends on the thallium content. This behavior is normally observed in metals with magnetic impurities, where the conduction electrons are scattered by the impurities – this is the so-called Kondo effect [for an introduction into the Kondo effect see the corresponding text box on page 15].

\footnote{A resonant level can be thought as a bound level with an energy that coincides with an extended state. In this way, they resonate and build up two extended states with slightly different energies. These in turn resonate with other extended states, and so on. Thus, the resonant level acquires a certain width.}
However, magnetic measurements did not reveal any localized magnetic moment in the samples. Interestingly, above a critical concentration $x^* \approx 0.3\%$ superconductivity emerges with critical temperatures on the order of Kelvins. This is surprisingly high, if compared with other systems with similar carrier concentrations ($\sim 10^{20}$ holes/cm$^3$), or other dopants in PbTe.

A suggested explanation [94, 98, 99] for both effects, upturn in resistivity and superconductivity, is based on the negative-$U$ Anderson model. The basic idea is that the thallium ions skip valences, meaning that Tl$^+$ ($6s^2p^0$) and Tl$^{3+}$ ($6s^0p^0$) are by several eVs more stable than Tl$^{2+}$ ($6s^1p^0$). This defines negative-$U$ behavior, because if a pair of such atoms would have the “forbidden” configuration, they would split with one atom donating one electron to the other. In this way the usual positive (repulsive) $U$ energy has been replaced by a negative (attractive) $U$.

Considering the electronic configuration of the different valence states it is easy to argue that Tl$^{2+}$ is energetically unfavorable; the other two states have closed shells. However, it is not clear if this situation applies also to every compound where the forbidden state should occur, e.g. in TlTe where Tl is expected to enter as Tl$^{2+}$. Both in experiments and theory it is still under debate whether thallium charge disproportionates in doped lead telluride [95, 101–106]. In this respect Harrison [103] performed an interesting theoretical study. The author concluded that the only mechanism creating negative-$U$ behavior in metals originates from lattice relaxations in compounds with large dielectric constants; such dielectric constants can be found in the compounds of the Tl row (e.g. PbTe). In other words, negative-$U$ behavior (charge disproportionation) is intimately linked to bond disproportionation. For Tl-doped PbTe this means that Tl$^+$ states correspond to larger nearest-neighbor octahedra (longer Tl-Te bonds), while Tl$^{3+}$ states correspond to smaller nearest-neighbor octahedra (smaller Tl-Te bonds). This situation is reminiscent of rare-earth nickelates RNiO$_3$ [107, 108] (where $R$ represents the rare-earth element) in their low-temperature insulating phase where two types of NiO$_6$ octahedra exist; half of them are compressed and the other half are expanded corresponding to Ni$^{4+}$ and Ni$^{2+}$, respectively.

### Kondo effect

The resistivity in metals is governed by different scattering mechanisms that provide different temperature dependences. For example, electron-electron scattering gives rise to a characteristic $T^2$ behavior; electron-phonon scattering provides a $T^5$ behavior for temperatures much smaller than the Debye temperature ($T \ll \Theta$) and a linear dependence for $T \gg \Theta$. However, in 1934 de Haas et al. [109] reported an upturn in resistivity (i.e. a resistance minimum at finite temperatures) in gold. The explanation followed only thirty years later from Kondo [110]. The underlying effect that took his name describes the scattering of conduction electrons on magnetic impurities in...
metals. For a thorough introduction into the Kondo effect see the excellent book *The Kondo Problem to Heavy Fermions* [111].

The Kondo Hamiltonian describing the coupling between the local spin impurities $S_i$ at $R_i$ and the quasiparticle spin $s$ has an exchange form

$$\hat{H}_K = J \sum_i \hat{S}_i \cdot \hat{s}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{R}_i).$$  \hspace{1cm} (1.6)

By second-order perturbation theory it can be seen that the resistivity acquires an additional logarithmic term such that the total resistivity may take the form (see Fig. 1.6)

$$\rho = a T^5 + \rho_0 - c \ln k_B T / d,$$  \hspace{1cm} (1.7)

where the first term is the phonon contribution, the second the temperature-independent contribution from the impurity scattering (residual resistivity), and the third the contribution from the spin scattering with the local (impurity) moment.

![Figure 1.6: Sketch of the resistivity for a metal with magnetic impurities described by Eq. (1.7). The green line indicates the phonon contribution with the residual resistivity $\rho_0$, the red line the logarithmic (Kondo) term, and the blue line the total resistivity.](image)

Note that the logarithmic term not only leads to a resistivity minimum, but also to a divergence for $T \to 0$. The resistivity behavior for temperatures much smaller than the so-called Kondo temperature, $T_K$, can not be derived by simple perturbation theory; this is called the Kondo problem. The Kondo temperature describes the energy scale at which the magnetic impurities are fully screened by the conduction electrons.

In any case, the negative-$U$ Anderson model would be able to explain both the upturn in resistivity and the superconductivity: already Schrieffer and Wolff [112]
showed that the negative-\(U\) Hamiltonian can be rewritten in the same form as the Kondo Hamiltonian, and the coherent fluctuations inherent of the model, which involve tunneling of pairs of electrons between the two impurity sites \(\text{Tl}^+\) and \(\text{Tl}^{3+}\), provide a pairing mechanism for superconductivity [98, 99].

I now present a more detailed discussion of the proposed model [93, 94, 99]. An isolated Tl impurity (valence skipper), in a PbTe crystal is described by the Hamiltonian

\[
H = H_{\text{band}} + H_{\text{imp}} + H_{\text{hyb}},
\]

where

\[
H_{\text{band}} = \sum_{k\sigma} (\epsilon_k - \mu) c_{k\sigma}^\dagger c_{k\sigma},
\]

\[
H_{\text{imp}} = (\epsilon_0 - \mu) \sum_{\sigma} n_{s,\sigma} + Un_{s\uparrow}n_{s\downarrow},
\]

\[
H_{\text{hyb}} = V \sum_{i\sigma} (s_{i\sigma}^\dagger c_{i\sigma} + c_{i\sigma}^\dagger s_{i\sigma}).
\]

\(c_{k\sigma}^\dagger\) creates an electron with spin \(\sigma\) in the valence \(p\) band with energy \(\epsilon_k\).

\(n_{s,\sigma} = s_{\sigma}^\dagger s_{\sigma}\) is the occupation of a spin \(\sigma\) electron in the Tl 6s shell with energy \(\epsilon_0\), \(\mu\) is the chemical potential, and \(U < 0\).

The energy difference between the two Tl states is (for \(\text{Tl}^+\), \(n_{s\uparrow} = n_{s\downarrow} = 1\); for \(\text{Tl}^{3+}\), \(n_{s,\sigma} = 0\))

\[
\delta E = E(\text{Tl}^{3+}) - E(\text{Tl}^+) = -[2(\epsilon_0 - \mu) + U],
\]

i.e. \(\delta E = 0\) if the chemical potential is \(\mu^* = \epsilon_0 + U/2\). Charge neutrality implies that the concentration of holes in the valence band, \(n_0\), donated by thallium doping is

\[
n_0 = x(n_s - 1),
\]

where \(n_s = \sum_{\sigma} \langle n_{s,\sigma} \rangle\) is the average number of \(s\) electrons. For an acceptor (\(\text{Tl}^+\)) \(n_0 > 0\), whereas for a donor (\(\text{Tl}^{3+}\)) \(n_0 < 0\). Eq. (1.11) has to be satisfied for a given \(x\) (and temperature \(T\)) by adjusting the chemical potential \(\mu\).

Let us first see what happens when we increase the thallium concentration \(x\) starting from pristine PbTe in the atomic limit \(V = 0\) (i.e. \(H_{\text{hyb}} = 0\)). In pure PbTe the chemical potential is between the valence and the conduction bands. Experiments [98, 100, 113, 114] predict an acceptor behavior of thallium impurities for small concentrations, i.e. \(\delta E > 0\), and the chemical potential \(\mu > \mu^*\). For increasing Tl concentrations there are no holes in the Tl \(s\) levels (\(n_s = 2\)) and all holes are in the valence \(p\) band. This means that \(n_0 = x\) grows linearly with Tl concentration and the chemical potential shifts downward in the valence band.

At a critical concentration \(x^*\) the chemical potential reaches the critical value \(\mu = \mu^*\). Any further impurity would lower the chemical potential below \(\mu^*\) and
\[ \delta E < 0, \text{ meaning that } Tl^{3+} \text{ would be more stable. Instead of decreasing the chemical potential additional impurities will equally split between } Tl^{+} \text{ and } Tl^{3+} \text{ in a self-compensating manner. Additional impurities can not lower the chemical potential below } \mu^* \text{ because the required conversion of all impurities to } Tl^{3+} \text{ would add electrons to the valence band, which would increase the chemical potential. No new holes will be added in the valence band and the chemical potential will be pinned at } \mu^*. Tl^{+} \text{ and } Tl^{3+} \text{ are degenerate and coexist.} \]

If we now include the hybridization term \( H_{hyb} \), quantum fluctuations between the two Tl states, \( Tl^{+} \) and \( Tl^{3+} \), become important and lead to a charge Kondo effect \([99, 115]\). To see this in the limit of large \(|U|/V\) one can perform a Schrieffer-Wolff transformation \([112]\) by defining the Nambu spinor \( \hat{c}_i = (c_{i\downarrow}, c_{i\uparrow}^\dagger) \) and the isospin \( t_i = \hat{c}_i^\dagger \tau \hat{c}_i / 2 \) (\( \tau \) is the vector of Pauli matrices) \([99, 115]\). The same can be done for the Tl s-electron operators by defining \( \hat{s}_i = (s_{i\downarrow}, s_{i\uparrow}^\dagger) \) and the isospin \( T_i = \hat{s}_i^\dagger \tau \hat{s}_i / 2 \) [the different isospin states correspond to double or zero occupancy of the s shell]. For \( \delta E = 0 \) the hybridization term can be rewritten as

\[
H_{hyb} = J \sum_i T_i \cdot t_i, \tag{1.12}
\]

with \( J = 8V^2/|U| \). This expression has the same form as the Kondo Hamiltonian in Eq. (1.6) and causes a logarithmic upturn in the resistivity. This has been checked by renormalization group computations by Costi and Zlatić \([93, 94]\), which also reproduced the predicted \([99]\) and experimentally observed \([113, 114]\) behavior for the hole concentration \( n_0 \), i.e. a linear increase for small Tl concentrations and a pinning for \( x > x^* \). Furthermore, Dzero and Schmalian \([99]\) showed that the previous model is indeed capable of generating a superconducting state with \( T_c \approx T_K \) for \( x > x^* \) [the Kondo temperature extracted from resistivity measurements in Pb\(_{1-x}\)Tl\(_x\)Te, \( T_K = 6 \) K, is of the same order as \( T_c \sim 1 \) K \([98]\)].

As appealing as this model might be it is not yet completely accepted in the research community. Several studies followed the first proposal and tried to characterize the superconducting state in view of the charge Kondo effect.

Matsushita et al. \([114]\) measured the superconducting parameters for Tl concentrations up to \( x = 1.4 \% \). The authors performed Hall-effect, heat capacity, and resistivity measurements. Remarkably, the critical temperature increases by two orders of magnitude from 15 mK (\( x \sim 0.3 \% \)) to 1.5 K (\( x \sim 1.5 \% \)), while at the same time the hole concentration measured by Hall experiments reaches saturation and varies by less than a factor of 2. The authors concluded that Tl-doped PbTe is a type II, weak-coupled BCS superconductor in the dirty limit. They did not find any disagreement with a charge Kondo picture but put some limits on its validity. In particular, they observed a relatively small enhancement of the electronic contribution to the heat capacity, meaning that only a small fraction (a few percent) of Tl participates in the Kondo physics, if the charge Kondo effect is appropriate. This can be understood with a distribution of \( \mu^* \) values, such that only the subset of Tl impurities having a chemical potential in this range has degenerate valence states. In addition, the Hall number continues to rise even for
$x > x^*$, meaning that it is not pinned at one value, but its increase is only slowed down with increasing concentrations.

The “spin” Kondo effect is known to lead to an anomalously large and temperature-dependent Seebeck coefficient. It is thought that the same applies also for the “charge” Kondo effect [99]. Matusiak et al. [116] measured the Seebeck coefficient and found clear evidence for a Kondo effect. However, the extracted Kondo temperature is a factor of 10 larger than that extracted from resistivity measurements [98]; $T_K = 45 – 75$ K instead of $T_K \sim 6$ K. With this higher Kondo temperature the subset of thallium impurities contributing to the charge Kondo effect would be increased to $\sim 10\%$. Moreover, the authors suggested that for low concentrations $x < 0.3\%$ only the $L$ band contributes to the electronic transport, while for larger concentrations the $\Sigma$ band dominates.

Trying to find a correlation between chemical potential pinning, superconductivity, and the Kondo-type resistance upturn, Erickson et al. [117] studied these properties in Pb$_{0.99-y}$Tl$_{0.01}$In$_y$Te. Indium impurities in PbTe (Pb$_{1-y}$In$_y$Te) are also proposed to charge disproportionate; in this case, however, the effect is thought to be static and not dynamically fluctuating (see Ref. [117] and references therein). In fact, superconductivity is not observed. The authors found a clear correlation between those properties: for small concentrations of In, $y < 1\%$, the Hall number does not vary, consistent with a pinning of the Fermi level; for larger In concentrations the residual resistivity drops significantly and the upturn in resistivity disappears; simultaneously the density of states at the Fermi energy is substantially reduced and the superconductivity disappears.

In spite of these many studies, the peculiar properties observed in Tl-doped PbTe are not understood and, in principle, more mundane explanations may be possible. In particular, experiments could not rule out the possibility of a narrow impurity band with a large density of states at the Fermi energy. However, some factors point to the more exciting charge Kondo mechanism: (i) the low-temperature upturn in resistivity follows a behavior characteristic of the Kondo effect, but without magnetic impurities; (ii) the concentration at which the Hall number slows down its increase is remarkably close to the concentration at which the onset of superconductivity is observed; (iii) thallium is the only known dopant that causes superconductivity in PbTe.

To shed more light into this exciting material Paula Giraldo-Gallo and Ian R. Fisher at Stanford University measured the Fermi surface of Tl- and Na-doped PbTe with quantum oscillation experiments [for an introduction into quantum oscillation experiments see Appendix A in the paper in section 6.3.1]. Na doping was chosen to have a comparison with a dopant that does not cause superconductivity and because it is better understood. For this task we started a collaboration, where my contribution was to help to analyze the angular evolution of the de Haas–van Alphen (DHVA) frequencies by computing them from DFT, and, at the same time, to study the general properties of the two systems in DFT, in particular to try to establish whether thallium impurities charge disproportionate.
The resulting experimental and theoretical characterization of Na-doped PbTe is presented in the paper in section 6.3.1. Here, I present a short review of Paula Giraldo-Gallo’s experimental work [118] (see Fig. 1.7 for a summary of the experimental results). The Fermi surface of Na-doped PbTe can be described well by only ellipsoidal pockets located at the $L$ points for all concentrations studied ($x \leq 0.62\%$); only at the largest concentration can deviations from ellipsoidal pockets be observed. Thus, in this concentration range the material is single band and the $\Sigma$ pockets do not contribute to the Fermi surface. Furthermore, Na is found to act as an acceptor by donating one hole to the valence band per impurity atom.

The situation for Tl-doped PbTe is more difficult to assess; the amplitude of quantum oscillations is drastically reduced because of the increased scattering with respect to Na-doped PbTe (for example the residual resistivity in Tl samples is much higher than in Na samples for the same carrier densities). For thallium

Figure 1.7: Sketch of the experimental results obtained by Giraldo-Gallo [118] with quantum oscillation experiments. Reprinted figure with permission from Ref. [118] (page 152).
concentrations smaller than \( x^* = 0.3\% \) the evolution of the Fermi surface is identical with Na-doped PbTe; each thallium atom donates one hole to the valence band. However, for larger concentrations the Fermi energy increases much more slowly than for Na-doped PbTe, meaning that the number of holes donated to the valence band is less than one per impurity. Moreover, the \( L \)-pockets’ cross-sectional areas saturate, while at the same time the Hall number continues to increase, even if at a smaller rate. This means that the carrier concentration grows faster than the size of the \( L \) pockets. Since no indications of a contribution from the \( \Sigma \) pockets was found, Giraldo-Gallo concluded that the additional carriers measured in the Hall experiments could not be associated with a coherent band, but were consistent with the presence of thallium states in the valence band, i.e. the resonant states discussed before.

However, angle-resolved photoemission spectroscopy (ARPES) measurements at \( x = 0.5\% \) \cite{119} did not find any indication of impurity states. The authors commented that possible localized states should have been resolved even if the cross section for Tl electrons was relatively small. Interestingly, they found that the Te \( p \) bands are affected by and dependent on doping, meaning that the rigid-band approximation is not valid.

Anyway, quantum oscillation experiments are not able to distinguish the origin of the superconductivity, and as such it is not clear how much of the enhanced critical temperature is originating from the increased density of states (from the impurity states), and how much is due to correlation effects from the charge Kondo model.

\subsection*{1.4 Performed research}

In view of the interesting and controversial understanding of lead telluride I present in this thesis a detailed ab-initio study of its structural and electronic properties. I performed \( T = 0 \) K DFT calculations and (ab-initio) MD to investigate the local structure of lead telluride and the role of Na and Tl impurities on the electronic degrees of freedom. My research can be split into two categories:

\begin{enumerate}
  \item Local structure at “high” temperatures
    \begin{enumerate}
      \item Central question: \textit{Are the reported features \cite{33, 35} a consequence of large anharmonic vibrations or of local structural distortions?}
      \begin{itemize}
        \item Analyze and understand the alleged lead off-centering
        \item Study the mechanisms behind the reported broadening and asymmetry of the PDF peaks
        \item Find a physical picture as consistent as possible with the contradicting reports
      \end{itemize}
    \end{enumerate}
    I am confident that my work helps to settle the off-centering controversy.
\end{enumerate}
2. Doped PbTe at low temperatures

Understand the similarities and differences between Na and Tl impurities in PbTe in view of the alleged charge Kondo effect

- Understand the structural and electronic effects of the two types of impurities
- Study the charge disproportionation nature of thallium impurities
- Compute the evolution of the Fermi surface and compare with quantum oscillation experiments

An indirect outcome of this study is an evaluation of the usefulness of DFT for the comparison with experiments measuring detailed structural and electronic properties.

1.4.1 Structure of the thesis

The remainder of this thesis is structured as follows: in the next chapter I present an overview of the methods used and of the required concepts. Afterwards, I discuss the basic structural and electronic properties of lead telluride with an evaluation of the different exchange-correlation functionals implemented in the VASP package [120–123]. I find that the best overall agreement with experiments is obtained with the PBEsol [124] functional.

Next, I present my ab-initio molecular dynamics simulations for the study of the off-centering issue. I find good agreement with the single-crystal diffuse scattering experiments of Thomas Weber. While the lead atoms sit at the center of their nearest-neighbor octahedra, we find a local symmetry breaking of the cubic symmetry caused by correlated dipole regions in the material. We discuss a possible link with the known high thermoelectric properties.

Afterwards, I present our search for an effective potential for lead telluride. Our strategy was to fit an interatomic potential to perform classical MD with larger supercells and longer simulation times to improve our understanding of the correlated dipole regions. Unfortunately, we failed to reproduce the local structure and our search for a better potential continues.

Finally, I discuss the role of Na and Tl impurities in lead telluride. Na is found to not affect much the electronic properties and a simple rigid band approximation is enough to describe the material well. On the other hand, Tl impurities give rise to an impurity band at the Fermi level, but its role on the evolution of the Fermi surface could not be clearly determined. Furthermore, my calculations did not provide any indication for a thallium charge disproportionation.
In this chapter I summarize the computational methods and the theoretical concepts needed for the understanding of this thesis.

Advances in computer hardware now allow the description of many-body systems using complex and computationally demanding methods. Nowadays, first-principles methods are routinely used not only for the description and understanding of physical, chemical and biological processes, but also for the prediction and design of new materials with the desired properties.

Also on the experimental front more accurate techniques for the study of the electronic and structural properties are being developed and become ever more accurate. Worth mentioning, among others, are techniques to measure the electronic and phonon spectrum of solid-state systems and to characterize the local structural properties.

I first introduce density functional theory (DFT), one of the most widely used and successful computational techniques in the materials and chemical sciences; this is a \( T = 0 \) K theory and the electrons are treated on the mean-field level. Next, I discuss (ab-initio) molecular dynamics (MD), which allows study of the evolution of many-body systems at finite temperatures. Afterwards, I discuss the unfolding of the electronic properties computed in a supercell, such that a comparison with experiments is more straightforward. Finally, I present the pair distribution function (PDF) technique, which is a powerful method for the analysis of total scattering experiments and allows the characterization of local properties in solid-state systems.

### 2.1 Density functional theory

With the advent of more powerful computers the possibility of computing and predicting material properties from first-principles (widely used is also the Latin term ab-initio), i.e. without any experimental input parameter, has gained popularity. One of the most versatile and widely used methods for solving the many-body interacting Schrödinger equation for a collection of interacting nuclei and electrons is density functional theory (DFT). Through a series of mathematical steps the many-body interacting problem is converted to a single-particle problem where the central quantity is the electronic density. For a thorough introduction into the theory behind DFT see the excellent reviews in Refs. [125–127].

The starting point is the Hamiltonian for \( N_n \) nuclei and \( N_e \) electrons

\[
\mathcal{H} = \hat{T}_n(\mathbf{R}) + \hat{V}_{nn}(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{en}(\mathbf{R}, \mathbf{r})
\]  

(2.1)
describing interacting electrons at positions $\mathbf{r} = \{\mathbf{r}_1, \ldots, \mathbf{r}_{Ne}\}$ and nuclei at positions $\mathbf{R} = \{\mathbf{R}_1, \ldots, \mathbf{R}_{Nn}\}$. The different terms are

$\hat{T}_n(\mathbf{R})$Kinetic energy of the nuclei

$$\hat{T}_n(\mathbf{R}) = -\frac{\hbar^2}{2} \sum_I \frac{\nabla^2_I}{M_I},$$

$\hat{V}_{nn}(\mathbf{R})$Coulomb interaction between nuclei

$$\hat{V}_{nn}(\mathbf{R}) = \frac{1}{2} \sum_{I \neq J} \frac{e^2 Z_I Z_J}{4\pi \varepsilon_0 |\mathbf{R}_I - \mathbf{R}_J|},$$

$\hat{T}_e(\mathbf{r})$Kinetic energy of the electrons

$$\hat{T}_e(\mathbf{r}) = -\frac{\hbar^2}{2m_e} \sum_i \nabla^2_i,$$

$\hat{V}_{ee}(\mathbf{r})$Coulomb interaction between electrons

$$\hat{V}_{ee}(\mathbf{r}) = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|},$$

$\hat{V}_{en}(\mathbf{R}, \mathbf{r})$Coulomb interaction between electrons and nuclei

$$\hat{V}_{en}(\mathbf{R}, \mathbf{r}) = -\sum_{I,J} \frac{e^2 Z_I}{4\pi \varepsilon_0 |\mathbf{R}_I - \mathbf{r}_J|}.$$

The many-body wavefunction $\Psi(\mathbf{R}, \mathbf{r})$ describing the system is the solution of the many-body Schrödinger equation

$$\hat{H}\Psi(\mathbf{R}, \mathbf{r}) = E\Psi(\mathbf{R}, \mathbf{r}).$$ (2.2)

The motion of the much heavier nuclei can be decoupled from the electronic motion – the Born-Oppenheimer approximation [128] – leaving the electronic problem

$$\hat{H}_e\psi(\mathbf{R}) := [\hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}] \psi(\mathbf{R}) = E_e \psi(\mathbf{R}).$$ (2.3)

The electronic properties depend now on the positions of the nuclei $\mathbf{R}$ and we are left with a $N_e$-electron problem. We will drop from now on the subscripts $\mathbf{R}$, which make explicit the dependence on the nuclei coordinates, and $e$, which states that we are dealing only with the electronic problem. It will be useful for later to rewrite the Coulomb interaction between nuclei and electrons, $\hat{V}_{en}(\mathbf{r})$, in
terms of the “external” potential of the nuclei (which are fixed in space) on the electrons

$$\hat{V}_{en}(\mathbf{r}) = \sum_i \hat{V}_{\text{ext}}(\mathbf{r}_i), \quad \text{with} \quad \hat{V}_{\text{ext}}(\mathbf{r}_i) = -\sum_j \frac{e^2}{4\pi\varepsilon_0 |\mathbf{R}_j - \mathbf{r}_i|}.$$

The ground-state energy $E_0$ is then computed using the variational principle by minimizing the energy functional over all allowed $N$-electron wave functions

$$E_0 = \min_{\psi} E[\psi] = \min_{\psi} \frac{\langle \psi | \hat{H}_e | \psi \rangle}{\langle \psi | \psi \rangle}.$$  

(2.5)

A great simplification, but still exact, was introduced by the Hohenberg-Kohn theorems [129] that put the electronic density as the central variable. The theorems state that the total energy is a unique functional of the density and the (exact) ground-state density minimizes the total-energy functional. In other words, every observable can be computed by the knowledge of the density alone and the ground state can be determined by finding the density that yields the lowest energy.

However, this is not enough for an efficient calculation of electronic properties. One way to proceed is the exact Kohn-Sham ansatz [130] that relies on a map linking the full interacting system with the real potential to a non-interacting system, having the same density $\rho$, with an effective Kohn-Sham single-particle potential $V_{KS}(\mathbf{r})$. Given that it is a non-interacting problem, the computation is greatly simplified and the equations decouple. The Kohn-Sham potential, in turn, includes the external potential and the electron-electron interactions. It can be decomposed into three terms

$$V_{KS}[\rho(\mathbf{r}), \mathbf{r}] = V_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{XC}[\rho],$$

(2.6)

with the external potential $V_{\text{ext}}$ describing the interaction with the nuclei (and applied external fields), the Hartree potential $V_H$ describing the classical Coulomb interaction between electrons, and what remains is by definition the exchange-correlation potential $V_{XC}$. The latter includes all the effects of the many-body character of the true electron system.

The total (Kohn-Sham) energy is then given by

$$E_{KS}[\rho] = T_s[\rho] + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{XC}[\rho].$$

(2.7)

Here, $T_s[\rho]$ represents the kinetic-energy functional of the non-interacting system; the kinetic-energy contributions of the interacting system have been moved into the exchange-correlation functional $E_{XC}[\rho]$. 
A density functional calculation then usually involves solution of the set of Kohn-Sham equations, i.e. the Schrödinger equations for the single-particle non-interacting wavefunctions $\phi_i$,

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{KS}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

that can be solved self-consistently to minimize the total energy

$$\sum_i^{occ} \epsilon_i = T_s[\rho] + \int \rho(\mathbf{r})V_{KS}(\mathbf{r}) \, d\mathbf{r},$$

as shown in Fig. 2.1.

A word of caution about the meaning of Kohn-Sham orbitals and eigenvalues. In the Kohn-Sham theory they are introduced as artificial objects, namely as eigenfunctions and eigenvalues of an auxiliary one-particle problem whose density corresponds to the correct one. Strictly speaking they do not in general have any physical meaning and have only a semiquantitative resemblance to the exact solutions \[127,131\]. The number and symmetry of the Kohn-Sham orbitals are generally correct for the occupied orbitals and their eigenvalues are usually a reasonable approximation of the exact energy levels. Note that the energy of the highest occupied Kohn-Sham orbital (HOMO) is the only eigenvalue with a physical meaning: it can be shown that with the exact exchange-correlation functional its energy equals the first ionization potential \[132–134\]. In practice, even the HOMO energy differs from the experimental value. Nonetheless, the (Kohn-Sham) band structure of solid systems computed with DFT is usually a good approximation to the experimental data obtained with photoemission experiments. Note that, however, the use of DFT for such calculations means that it is not anymore a many-body theory but a mean-field theory, though one with a quite sophisticated mean field $V_{KS}$ \[127\].

2.1.1 Approximations to the exchange-correlation energy

If the exact form of the exchange-correlation functional were known, the Kohn-Sham ansatz would give the exact ground-state density and energy. Unfortunately, this is not the case and approximations have to be made. In general, the exchange-correlation potential depends on the density and all its derivatives

$$V_{XC}[\rho]|_r = V_{XC}[\rho, \nabla \rho, \nabla^2 \rho, \ldots]|_r .$$

In the following I review some commonly used approximations for the exchange-correlation potential.
2.1 Density functional theory

Initial guess for the density $\rho(r)$

Construct the effective potential
$$V_{KS}[\rho(r), r] = V_{\text{ext}}(r) + V_{H}[\rho] + V_{\text{XC}}[\rho]$$

Solve the Kohn-Sham equations
$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{KS}(r)\right] \phi_i(r) = \varepsilon_i \phi_i(r)$$

Compute the density and the total energy
$$\rho(r) = \sum_{i=1}^{\text{occ}} |\phi_i(r)|^2 \rightarrow E_{KS}[\rho] = \ldots$$

Converged?

Yes

Output quantities
$\rho_0(r), E_{KS}[\rho_0(r)] \rightarrow$ forces, eigenvalues, \ldots

No

Figure 2.1: Typical self-consistent workflow for a DFT computation.
**Local density approximation (LDA)**  In the local density approximation (LDA), $V_{XC}$ is assumed to be a local functional of the density, meaning that it depends only on the density but not on its derivatives,

$$E_{xc}^{\text{LDA}}[\rho(r)] = \int f(\rho(r)) \, dr,$$

where $f(\rho)$ is some function of the density $\rho$ determined by considering a uniform electron gas with density $\rho(r)$. The kinetic and exchange energy can be evaluated using the Kohn-Sham wavefunctions, whereas the correlation energy is usually parametrized from Quantum Monte Carlo simulations. LDA is exact for the interacting homogeneous electron gas.

LDA is known to underestimate the exchange-correlation energy by about 7\% and bond-lengths by about 1 − 2\% [125]. One of the most infamous failures of LDA is the prediction of a non-magnetic ground state for iron due to its prediction of the incorrect structure.

**Generalized gradient approximation (GGA)**  An improvement can be achieved by the generalized gradient approximations (GGAs) which are semi-local functionals, in which a dependence on the gradient of the density is also considered

$$E_{xc}^{\text{GGA}}[\rho(r), \nabla \rho(r)] = \int f(\rho(r), \nabla \rho(r)) \, dr.$$

Nowadays there are various GGAs that usually improve bonding properties (length, angles and energies), such as Perdew-Burke-Ernzerhof (PBE) [135] and PBE revised for solids (PBEsol) [124].

In this work I mostly use the previous two types of functionals.

**Meta-GGA**  In addition to a dependence on the density and on its gradient meta-GGAs include also a dependence on the Kohn-Sham kinetic energy density\(^1\), $\tau(r)$,

$$\tau(r) = \frac{\hbar^2}{2m} \sum_i |\nabla \phi_i|^2,$$

such that

$$E_{xc}^{\text{meta-GGA}}[\rho(r), \nabla \rho(r), \tau(r)] = \int f(\rho(r), \nabla \rho(r), \tau(r)) \, dr.$$

They are thought to improve the description of the band gap and first results are promising, but more systematic comparisons have yet to be done. Examples include Tao-Perdew-Staroverov-Scuseria (TPSS) [136], Made Simple (MS) [137, 138], and Strongly Constrained and Appropriately Normed Semilocal (SCAN) density functional [139].

\(^1\) In their original form meta-GGAs depended on the Laplacian of the density, but nowadays meta-GGAs are considered to be all functionals that depend on the Kohn-Sham kinetic energy density.
Hybrids

Hybrid functionals combine a fraction of exact exchange from Hartree-Fock with the DFT exchange functional. They have proved to be very successful for the description of the thermochemistry of molecular systems, e.g. for the computation of atomization energies or heats of formation, and for the description of band gaps, ionization potentials, and surface energies in semiconductors and insulators. The biggest drawback is the increased computational cost because exact exchange is non-local. Examples include PBE0 [140] and Becke, three-parameter, Lee-Yang-Parr (B3LYP) [141, 142].

2.2 Molecular dynamics

Molecular dynamics (MD) is one of the standard methods to study the evolution of a many-body system at finite temperatures. For a detailed review of the method and approximations involved see the excellent Refs. [143–146].

In the traditional scheme, the motion of the particles (for example atoms) is modeled using the laws of classical mechanics. This approach is justified as long as the quantum effects are negligible. Under this assumption, MD consists of the numerical integration of the (classical) Euler-Lagrange equations for a system of \( N \) particles derived from the following Lagrangian

\[
\mathcal{L} = \sum_{I=1}^{N} \frac{M_I}{2} \dot{R}_I^2 - U(\mathbf{R}_1, \ldots, \mathbf{R}_N),
\]  

(2.10)

where \( U \) is the potential energy of the system, which is assumed to be a function of the positions \( \{\mathbf{R}_I\}, I = 1, \ldots, N \) only. Particles are described by their positions \( \mathbf{R}_I \) and velocities \( \dot{\mathbf{R}}_I \). The Newton equation can be derived from the associated Euler-Lagrange equation

\[
\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad \iff \quad M_I \ddot{\mathbf{R}}_I = -\frac{\partial U}{\partial \mathbf{R}_I} = \mathbf{F}_I
\]  

(2.11)

The potential energy function \( U \) contains the information of how the atoms interact. Depending on the methods used to define the potential energy function \( U \), it is possible to distinguish the following categories: empirical or classical potentials, semi-empirical potentials, and first-principles methods.

First-principles methods use quantum-mechanical formulae to calculate the potential energy of the system of atoms. Although various approximations may be used, these methods are based on theoretical considerations and not on empirical fitting. In this way, they allow a high accuracy in the description of the total energy of different systems. However, this comes at the cost of the system sizes and time scales that can be studied.

In the present work I carry out so-called Born-Oppenheimer molecular dynamics simulations. The nuclear degrees of freedom are propagated using ionic forces that are calculated at each iteration under the adiabatic approximation, assuming that the electrons are always on the ground state. Other possibilities exist, such
as Ehrenfest MD [147, 148], where the electronic subsystem can evolve on any
adiabatic electronic state (not only on the ground-state as in Born-Oppenheimer
MD), or the Car-Parrinello method [149], which explicitly introduces the elec-
tronic degrees of freedom as fictitious dynamical variables, resulting in coupled
equations of motion for both ions and electrons.

Within Born-Oppenheimer MD the static electronic problem is solved at each
time step (using, e.g., DFT) with fixed nuclei coordinates $\mathbf{R}_I$. The resulting energy
is then inserted into the nuclear equations. In our case, the nuclei are modeled
using classical mechanics. This is a reasonable approximation as long as light
atoms or vibrations with frequencies of the order or greater than the temperature
of interest are not involved. Thus, the potential energy $U$ in Eq. (2.10) is the total
energy calculated with any first-principles method, e.g. DFT or Hartree-Fock.
The resulting equations of motion are

$$M_I \ddot{\mathbf{R}}_I = - \nabla_I \min_{\psi_0} \{ \langle \psi_0 | \mathcal{H}_e | \psi_0 \rangle \}$$

$$\mathcal{H}_e \psi_0 = E_0 \psi_0,$$

(2.12)

where $\mathcal{H}_e$ is the electronic Hamiltonian (see Eq. (2.3) for the DFT formalism),
and $\psi_0$ and $E_0$ are the ground-state wave function and energy, respectively. The
second equation in Eq. (2.12) can be solved using any first-principles method; in
this work I use DFT.

2.2.1 Thermodynamic averages and different ensembles

Under the ergodic hypothesis, the time evolution given by Eqs. (2.11) and (2.12)
corresponds to a microcanonical (NVE) ensemble in statistical physics [NVE
means that the external thermodynamic control variables, i.e. the number
of particles $N$, the volume $V$, and the total energy $E$, are constant]. In this sense
MD allows the computation of thermodynamic properties of the systems under
investigation. In some cases, however, it is desirable to study a system using other
control variables such as the temperature or pressure. In statistical physics this
is accomplished with a Laplace transform of the partition function in which the
conjugate extensive and intensive variables are exchanged [in thermodynamics
this corresponds to a Legendre transform of the thermodynamic potential]. In this
way other ensembles can be generated that are equivalent to the microcanonical
ensemble in the thermodynamic limit. For example, by exchanging energy with
temperature we obtain the canonical (NVT) ensemble, volume with pressure and
energy with temperature the isothermal-isobaric (NpT) ensemble, and particle
number with chemical potential and energy with temperature the grand-canonical
($\mu$VT) ensemble, respectively. For a nice overview of the different ensembles
and the related fluctuations in the control parameters see Ref. [150].

In MD, different ensembles can be simulated with the help of additional degrees
of freedom that ensure the recovery of the distribution function of the sought-
after ensemble. The idea is to couple the system of interest to a (infinitely) large
reservoir with a sufficiently weak coupling to obtain thermodynamic equilibrium. For example, the control of temperature is achieved using a thermostat, the control of pressure using a barostat.

In the literature one can find many different approaches to achieving different thermodynamic ensembles. They can be categorized in two main classes: (i) the stochastic approach, i.e. combining MD with certain Monte Carlo moves, and (ii) the extended-system approach, i.e. adding dynamical variables (and their velocities) to the Lagrangian such that the dynamics of the (sub)system of interest occurs in the desired ensemble.

**Thermostats**

A thermostat provides a way to modify the microcanonical dynamics to obtain a constant-temperature ensemble. For a complete review of the most-used thermostats see the nice work by Hünenberger [150]. The main reasons to enforce a desired temperature are the reproduction of experimental conditions and the study of temperature-dependent processes/quantities.

The first thing that is needed to define a thermostat is a definition for the instantaneous temperature $T$. This is usually done through the equipartition theorem applied to the instantaneous kinetic energy $K$

$$\mathcal{K} = N_{\text{dof}} \frac{k_B T}{2},$$

with $k_B$ the Boltzmann constant, and $N_{\text{dof}}$ the number of degrees of freedom; for a system of $N$ particles under periodic boundary conditions $N_{\text{dof}} = 3N - 3$ (the rigid-body translational degrees of freedom are subtracted out).

In this work I use the generalized-Langevin-equation (GLE) and the canonical-sampling-through-velocity-rescaling (CSVR) thermostats.

**Generalized Langevin equation thermostats**

The GLE thermostats [151–153] are based on a generalization of the Langevin equation to colored (correlated) noise. The Langevin dynamics is described by the following equation

$$M_I \ddot{\mathbf{r}}_I = \mathbf{F}_I - M_I \gamma_I \dot{\mathbf{r}}_I + \mathbf{W}_I,$$

where $\gamma_I$ is an atomic friction coefficient and $\mathbf{W}_I$ a stochastic force with zero mean and intensity given by

$$\langle W_{I \mu}(t) W_{J \nu}(t') \rangle = 2M_I \gamma_I k_B T_0 \delta_{IJ} \delta_{\mu\nu} \delta(t - t').$$

Physically, this corresponds to collisions with light particles forming an ideal gas at the desired temperature $T_0$. The coupling with the heat bath is determined by the friction coefficient $\gamma_I$. The equations of motion of the GLE thermostats are linear so that it is possible to easily tune the coupling of the thermostat with the different degrees of freedom to minimize the correlation time for the sampling potential or the total energy. This results in a more efficient sampling of the canonical
ensemble without any a priori knowledge of the system of interest: equilibrium can be reached much faster than with Nosé-Hoover chains. Furthermore, the implementation is simple and robust. On the other hand, depending on the specific GLE used, the dynamics can be disturbed such that dynamical properties cannot be computed.

In this work I use the optimal sampling GLE thermostat\(^2\). This particular implementation of GLE allows a coupling between the system and the heat bath over a range of frequencies that can be appropriately tuned; it can be chosen to cover the whole vibrational spectrum or to leave out some frequencies that do not have to be excited. Importantly, all vibrational modes can behave as critically damped\(^3\), meaning that equilibrium can be reached as fast as possible.

**Canonical-sampling through velocity rescaling** As the name tells, the CSVR approach\([154]\) is a modification of the velocity rescaling algorithm: instead of rescaling the atomic velocities every certain number of steps, the target temperature is chosen with a stochastic procedure to sample the canonical ensemble. It resembles the Berendsen thermostat, with the auxiliary dynamics described by

\[
d\mathcal{K} = (K_0 - \mathcal{K}) \frac{dr}{\tau} + 2 \sqrt{\frac{\mathcal{K} K_0}{N_{dof}}} \frac{dW}{\sqrt{\tau}},
\]

where \(W\) is the stochastic term and \(K_0\) the desired kinetic energy. Without the stochastic term, the Berendsen thermostat is obtained back. It can be shown that the CSVR thermostat samples the proper canonical ensemble, and that it has only marginal effects on the dynamics allowing, in principle, the computation of dynamical properties directly. Furthermore, a constant quantity can be defined.

**Barostats**

Similar to a thermostat, a barostat is a tool to modify the microcanonical dynamics but in this case to obtain a constant-pressure ensemble. The main reasons for pressure control are to match experimental conditions and to study pressure-dependent processes. The instantaneous pressure (or stress) tensor \(\Pi\) is usually computed using the virial equation

\[
\Pi = \frac{1}{V} \left( \sum_I M_I \dot{R}_I \dot{R}_I^T + \sum_I R_I \cdot \dot{F}_I^T \right).
\]

In this work I use the Berendsen and the Martyna barostats.

---

\(^2\) One can find, among others, ready-to-use GLE parameters for various simulations, sample code to include GLE in the MD code, and tools for fitting the GLE matrices on the website [http://gle4md.org/](http://gle4md.org/)

\(^3\) A critically damped harmonic oscillator returns back to the equilibrium position as fast as possible.
**Berendsen barostat**  The coupling with the constant-pressure bath is described by a first-order differential equation for the instantaneous pressure [155]

\[ \dot{\Pi}(t) = \tau_B^{-1} [\Pi_0 - \Pi(t)] , \]

where \( \tau_B \) describes the pressure relaxation time and \( \Pi_0 \) is the desired pressure. The pressure change is accomplished through coordinate and volume scaling. It can be shown that the volume fluctuations are not correctly captured with this method. Thus, the isothermal compressibility cannot be determined, but the thermal expansion can be correctly described (as it depends only on averages and not on fluctuations).

**Extended Lagrangian methods**  The first control of pressure through the addition of auxiliary variables to the Lagrangian was done by Andersen [156]. His extended Lagrangian formalism can describe a time-dependent volume under an external isotropic stress. The extension to time-dependent shapes and anisotropic stress was accomplished by Parrinello and Rahman [157–159]. The Lagrangian of the Parrinello-Rahman barostat for an external isotropic pressure \( p \) is given by

\[ \mathcal{L} = \frac{1}{2} \sum_I M_I \dot{S}_I^T G S_I - U + \frac{W}{2} \text{tr}(\ddot{h}^T \dot{h}) - pV, \]

where \( \dot{R}_I = \dot{h} S_I \) with \( h = \{a, b, c\} \) the matrix of cell vectors, \( G = h^T h \) is the metric tensor, and \( W \) is the fictitious mass parameter. The choice of the mass \( W \) does not influence the equilibrium properties of the system. Nonetheless, it affects the dynamics of the system, in particular, the timescale of the fluctuation of the box is determined by \( W \). Andersen proposed to choose a mass value \( W \) such that the vibrational motion of the atoms and the timescale of vibration of the cell are separated. A further improvement of the Parrinello-Rahman barostat with the elimination of some inconsistencies was accomplished by Martyna et al. [160]. The Martyna barostat (with some variations) is probably the most used extended-Lagrangian barostat in MD codes. It can be shown that these barostats sample the proper isobaric-isenthalpic (\( NpH \)) ensemble.

As a last thing, I comment on the combination of thermostats and barostats that I use in this work. The GLE thermostat cannot be used in conjunction with a barostat in CP2K [161]. Thus, for \( NpT \) MD simulations I chose the CSVR thermostat, while for \( NVT \) simulations I used the GLE thermostat.

Concerning the barostat, in CP2K only the Martyna barostat is provided; in LAMMPS [162] the CSVR and GLE thermostats can only be used in conjunction with the Berendsen barostat and the Martyna barostat only with Nosé-Hoover chains.
2.3 Unfolding of band structures

For a perfectly periodic system the band structure can be computed using any choice of unit cell. To minimize the computational cost the primitive cell is usually preferred. If, on the other hand, a larger supercell is used the resulting bands can still be exactly unfolded onto the primitive-cell description. However, for alloys and systems with random impurities some problems arise. In particular, a description using the wave vector $k$ is in principle meaningless, since the periodicity is lost. Nonetheless, many experimental properties of doped systems are still described using the primitive cell of the undoped system with a band-structure language. This relies on linking the measured properties with a translationally invariant model to build an effective band structure (EBS).

From the theoretical point of view alloys and systems with impurities are tackled primarily in two different ways. Firstly, by using effective medium approaches, like the virtual crystal approximation (VCA) or the coherent potential approximation (CPA). In this way we automatically obtain properties in the band-structure language of the primitive-cell description. Secondly, by using supercells and the explicit insertion/substitution of impurity atoms. The question then arises how to compare these calculations with experiments, or in other terms, how to build an EBS. Since the increase in computational power of recent years made possible the computation of big supercells, this question has prompted a lot of interest and research and many studies were published tackling the problem from different points of view [163–176]. Here, I will follow the procedure presented in Refs. [163, 168, 169, 175, 176]. The idea is to calculate the eigenstates of the supercell and determine the amount of character linked to a Bloch state of the primitive cell with wave vector $\mathbf{k}$ through the computation of a spectral function. This method has been shown to match angle-resolved photoemission spectroscopy (ARPES) spectra in the case of weak-symmetry breaking disorder [167, 170].

A supercell (SC) is usually understood as the stacking of primitive building blocks, or primitive cells (PCs), along some spatial directions. In the following all quantities related to the SC (PC) will be written in capital (small) symbols. The SC unit cell vectors $\mathbf{A}_i$ are related to the PC cell vectors $\mathbf{a}_i$ by the matrix $M$ through $\mathbf{A}_i = \sum_j M_{ij} \mathbf{a}_j$. We will consider only commensurate SCs, meaning that the elements $M_{ij}$ are integer numbers. The volumes of the SC, $V_{SC}$, and PC, $v_{PC}$, are related by $V_{SC} = \det M \cdot v_{PC}$.

In the same way, the reciprocal unit cell vectors of the SC, $\mathbf{B}_i$, are related to those of the PC, $\mathbf{b}_i$, through $\mathbf{B}_i = \sum_j (M^{-1})_{ij} \mathbf{b}_j$, and the volumes of the primitive Brillouin zone (pBZ), $v_{pBZ}$, and the supercell Brillouin zone (SBZ), $v_{SBZ}$, through $V_{SBZ} = v_{pBZ}/\det M$. The reciprocal lattice vectors $g_n$ of the primitive Brillouin zone form a subset of the reciprocal lattice vectors $G_n$, $\{g_n\} \subset \{G_n\}$.

The folding and unfolding of wave vectors depends only on the geometry and symmetry relations between the primitive and the supercell Brillouin zone. A wave vector $\mathbf{k}$ in the primitive Brillouin zone is said to fold into a wave vector $\mathbf{K}$
in the supercell Brillouin zone, if there exists a SC reciprocal lattice vector $\vec{G}_0$ with

$$\vec{K} = \vec{k} - \vec{G}_0. \tag{2.14}$$

A wave vector $\vec{K}$ in the supercell Brillouin zone is said to unfold into wave vectors $\vec{k}_i$ in the primitive Brillouin zone, if

$$\vec{k}_i = \vec{K} + \vec{G}_i \quad i = 1, \ldots, N_K. \tag{2.15}$$

where $N_K = \det M$. At first sight, Eqs. 2.14 and 2.15 seem to be equivalent, but they are not. While in the folding (Eq. 2.14) $\vec{K}$ and $\vec{G}_0$ are unique, in the unfolding (Eq. 2.15) there are $N_K$ vectors $\vec{k}_i$ related to $\vec{K}$. Figure 2.2 presents a sketch of the unfolding procedure for a fictitious two-dimensional case.

![Figure 2.2: Sketch of a two-dimensional band unfolding process for (a) the periodic system AB and (b) for an alloy $A_{1-x}B_xC$. (c) and (d) show the connection between the supercell (SC) and the primitive cell (PC) representations in (c) direct space and (d) reciprocal space. In (d) $\vec{k}_C$ and $\vec{K}_C$ are wave vectors equivalent to $\vec{k}$ and $\vec{K}$ by a symmetry operation C of both the primitive Brillouin zone and the supercell Brillouin zone. Reprinted figure with permission from [V. Popescu and A. Zunger, Phys. Rev. B 85, 085201 (2012)] Copyright (2012) by the American Physical Society.]

When solving the many-body Schrödinger equation for a periodic system in the PC (SC) one obtains the eigenstates $|\vec{k}n \rangle$ ($|\vec{K}m \rangle$) [$n, m$ are the band indices] and the dispersion relations $E(\vec{k})$ ($E(\vec{K})$). Any SC eigenstate can be expressed as a linear combination of the PC eigenstates with wavevectors obeying the folding/unfolding relations. Formally, the folding of states can be written as

$$|\vec{K}n \rangle = \sum_{i=1}^{N_K} \sum_m F(\vec{k}_i, m; \vec{K}, n) |\vec{k}_i m \rangle. \tag{2.16}$$

Unfolding of states then means either determining the PC eigenstates $|\vec{k}n \rangle$ and the expansion coefficients $F(\vec{k}_i, m; \vec{K}, n)$ or the band dispersion $E(\vec{k})$ from the more complicated $E(\vec{K})$. The final step for the determination of the EBS is the computation of the spectral weight $P_{\vec{k}_n}(\vec{k}_i)$ and the spectral function $A(\vec{k}_i, E)$. 
The former represents the probability that the set of $|\vec{k},m\rangle$ states contributes to the SC state $|\vec{K}n\rangle$, or equivalently the amount of Bloch character $\vec{k}_i$ (with PC-periodicity) contained in $|\vec{K}n\rangle$ at the same energy $E_n = E_m$.

$$P_{\vec{K}n}(\vec{k}_i) = \sum_m \left|\langle \vec{K}n|\vec{k},m\rangle\right|^2.$$ (2.17)

In the case of a perfect SC (without defects and disorder) the spectral weight would be equal to the degeneracy $g_m(\vec{k}_i)$ of the PC state $|\vec{k}_i,m\rangle$ at $E_m$, $P_{\vec{K}n}(\vec{k}_i) = g_m(\vec{k}_i)\delta(E_m - E_n)$. The spectral function is then a continuous function of the energy defined as

$$A(\vec{k}_i, E) = \sum_n P_{\vec{K}n}(\vec{k}_i)\delta(E_n - E).$$ (2.18)

Finally, the EBS can be determined using the cumulative probability function, $dS(\vec{k}_i, E) = A(\vec{k}_i, E)\,dE$, where $dS(\vec{k}_i, E)$ represents the number of bands crossing the energy interval $(E, E + dE)$ at wavevector $\vec{k}_i$. We can assign a weight $\delta N$ to each point $(\vec{k}_i, E_n)$ as

$$\delta N(\vec{k}_i, E_n) := \int_{E_n-\delta E/2}^{E_n+\delta E/2} dS(\vec{k}_i, E) = \sum_m P_{\vec{K}m}(\vec{k}_i) \int_{E_n-\delta E/2}^{E_n+\delta E/2} \delta(E_m(\vec{K}) - E)\,dE,$$ (2.19)

and then plot the EBS as a density plot.

Equation 2.18 seems to suggest that knowledge of the PC states $|\vec{k}_i,m\rangle$ is needed to actually unfold the band structure. Ref. [170] formally showed that this is not the case. In fact, using a plane wave expansion for the SC states

$$|\vec{K}n\rangle = \left(\sum_\vec{G} C_{\vec{K}n}(\vec{G})e^{i\vec{G}\cdot\vec{r}}\right)e^{i\vec{K}\cdot\vec{r}},$$ (2.20)

the spectral weight can be expressed as

$$P_{\vec{K}n}(\vec{k}_i) = \sum_\vec{g} \left|C_{\vec{K}n}(\vec{g} + \vec{k}_i - \vec{K})\right|^2 = \sum_\vec{g} \left|C_{\vec{K}n}(\vec{g} + \vec{G}_i)\right|^2.$$ (2.21)

**What about experiments?** An effective way to measure the band structure is by photoemission experiment, such as ARPES, which is now routinely used to this effect. Roughly speaking, ARPES measures the spectral function of the valence electrons (related to the density of states) corrected by the matrix element describing the transition from the initial to the final state. In this sense, the EBS derived before can be directly compared to this kind of experiments. Now, the same question that we tried to answer in the previous section can be asked also for experimental measurements, namely how to best and most easily interpret photoemission spectra for disordered and doped systems. The outcome
of these experiments is usually a map of energy and momentum of the electrons in the solid. For an undoped system this could be directly interpreted in a band-structure language by taking into account the translational symmetry with respect to the primitive cell: the momenta would be translated into the primitive Brillouin zone and the band dispersions are obtained. In disordered systems, the same approximations described above are applied; a reference cell is assumed, usually the primitive cell of the pristine system, and the band dispersions are derived by translating all momenta into the corresponding Brillouin zone. In the same way as before, this procedure can break down if the influence of the impurities and/or disorder is too large.

Additional limiting factors for the detection of impurity bands are experimental resolution and the intensity of the signal. The former can be overcome if the resolution is smaller than the bandwidth of the localized states; the latter requires some way of filtering out the stronger signal from the coherent electronic bands in the material.

For the determination of the Fermi surface the state of the art technique is the measurement of (bulk) quantum oscillations, although the precision of ARPES is starting to reach the same level [177, 178]. In principle, quantum-oscillation experiments suffer from the same conceptual limitations regarding the interpretation in reciprocal space, accentuated by the fact that to measure the oscillations one needs the electrons to make at least an entire orbit around the Fermi surface (in the semi-classical picture). This is a problem because in many cases impurity bands correspond to heavy effective masses (the bands are quite flat), meaning that the electrons’ mean free path may not be large enough to produce a detectable signal.

2.4 Quantum oscillations formalism

For a brief introduction into quantum oscillations see Appendix A in section 6.3.1. An excellent and thorough treatment of this field can be found in the book Magnetic Oscillations in Metals [179].

2.5 Pair distribution function technique

The determination of the structure of solid-state systems is usually accomplished with x-rays and neutron diffraction techniques⁴. For a long time diffraction experiments were analyzed in reciprocal space using the Bragg technique. In the Bragg analysis only the position and intensity of the Bragg peaks enter the refinement procedure, while the rest, i.e. the diffuse scattering, is discarded. In this way the structural modeling is incomplete because it lacks the possibility to describe disordered systems. Only the average structure can be determined, because the

⁴ For biological applications, e.g. the determination of proteins’ structure, nuclear magnetic resonance (NMR) is also widely used.
Bragg technique implies space and time averages over all unit cells [180]. The information about the local structure and its deviations from the average structure are contained in the diffuse scattering. For a long time the latter was neglected because powerful and general methods for its analysis were missing.

A breakthrough happened in the 1990s with the development of the pair distribution function (PDF) technique for powder diffraction [181]. The PDF is a so-called total-scattering technique [182, 183], meaning that the Bragg and diffuse scattering are treated on an equal footing so that information about the local structure can be extracted. The analysis of the data is done with a Fourier transform of the powder diffraction pattern in real space. Meanwhile, the PDF was extended to the analysis of single-crystal diffraction [184]. If the full single-crystal diffraction pattern is used we obtain the 3D-PDF; if only the diffuse part is used the 3D-ΔPDF, which shows only the deviations from the average structure.

The PDF and related local-sensitive techniques are nowadays routinely used for the characterization of crystalline and quasi-crystalline systems. They are of fundamental importance to describe the local environment and have provided new insights in many materials. For example, in GeTe extended x-ray absorption fine structure (EXAFS) spectroscopy questioned the displacive nature of the ferroelectric transition [185]. The authors found that the local distortions associated with the ferroelectric state do not essentially change with temperature, even in the paraelectric phase. Or, in LaMnO$_3$ powder PDF reported disordered Jahn-Teller distorted MnO$_6$ octahedra (with four shorter and two longer bonds) in the high-temperature orthorhombic phase, while Bragg scattering predicts regular octahedra (with six equal bonds) [186].

I now present a short introduction into the PDF formalism. For a thorough treatment refer to the excellent book *Underneath the Bragg peaks: structural analysis of complex materials* [182]. The central quantity of the total-scattering technique is the total scattering structure function $S(Q)$ ($Q$ is the diffraction vector, i.e. the momentum transfer of the scattering particle), that is, the normalized, measured scattering intensity from a sample. Its Fourier transform yields the 3D-PDF, $G(r)$, via the following manipulations:

\[
G(r) := \rho_0 [g(r) - 1] = \frac{1}{8\pi^3} \int [S(Q) - 1] e^{-iQr} \, dQ, \quad (2.22)
\]

where $\rho_0$ is the atomic number density, and $g(r)$ is the 3D correlation function

\[
g(r) = \frac{1}{\rho_0^2 V} \int \rho(r')\rho(r + r') \, dr', \quad (2.23)
\]

with $V$ the volume of the sample, and $\rho(r)$ the single-atom density function. If the scattering is isotropic, we can take a spherical average and get an expression that depends only on the distance, $r$,

\[
G(r) := 4\pi r \rho_0 (g(r) - 1) = \frac{2}{\pi} \int_0^\infty Q \left[ S(Q) - 1 \right] \sin(Qr) \, dQ. \quad (2.24)
\]
$G$ is called the reduced pair distribution function. A related function is the radial distribution function (RDF)

$$R(r) = 4\pi r^2 \rho_0 g(r).$$  \hfill (2.25)

These three different functions ($g(r)$, $G(r)$, and $R(r)$) have different asymptotic behaviors and advantages:

$g(r)$ the pair distribution function is normalized so that $\lim_{r \to \infty} g(r) = 1$, and $\lim_{r \to 0} g(r) = 0$. It is closely related to the pair density function $\rho(r) = \rho_0 g(r)$: for any atom it is proportional to the probability of finding another atom at a distance $r$ apart. The advantage of the $g(r)$ function is that it emphasizes the low-$r$ short-range order.

$G(r)$ the reduced pair distribution function oscillates around zero for large $r$ and at small $r$ it is a straight line $-4\pi \rho_0 r$, with slope proportional to the atomic number density. One of the advantages of this function is that it is directly obtained from the Fourier transform of the experimental data, and so no assumption on $\rho_0$ has to be made. Furthermore, the random uncertainties in the data are constant with $r$.

$R(r)$ the radial distribution function has the useful property that $R(r) \, dr$ gives the number of neighbors in a spherical shell of thickness $dr$ at a distance $r$ from an atom. Thus, the coordination number is just the integral over the peak of the coordination shell in question. Another useful property is that the shape of the peaks reflects the underlying pair-probability distribution, so that in the harmonic approximation the peaks have a Gaussian shape. It can be easily extracted from MD simulations (see Appendix B.1).

In general, the PDF analysis is a powerful method that can extend conventional Rietveld refinement to obtain information about short-range atomic correlations. Moreover, structural information can be extracted without the need of a structural model:

1. the position of the peaks directly indicates an interatomic distance in the solid. Even for disordered systems (e.g. liquids), the RDF indicates the smallest neighbor distance, because there is no intensity for lower distances;

2. the number of neighbors can be determined by integrating the RDF;

3. the width and shape of the peaks contain information about the real atomic probability distribution: for example, thermal motion of the atoms or static disorder cause the PDF peaks to broaden, and non-Gaussian shapes may suggest anharmonic effects or local distortions.
Fundamental properties of PbTe

In this chapter I present the calculated structural and electronic properties of PbTe. In addition, I take the opportunity to compare the results obtained using the different functionals available in VASP with experimental data for PbTe to determine the overall best performing. Since Pb is a heavy element, spin-orbit coupling is expected to be important. Therefore, I present results with spin-orbit coupling included in the Hamiltonian and not. The chosen functionals are: local density approximation (LDA) [187], Perdew-Wang-1991 (PW91) [188, 189], Perdew-Burke-ERNzerhof (PBE) [135], revised PBE (revPBE) [190], Armiento-Mattson-2005 (AM05) [191, 192], and PBE revised for solids (PBEsol) [124]. I chose to compare only “standard” functionals, i.e. local density approximation (LDA) and generalized gradient approximations (GGAs), because the functionals such as hybrids and meta-GGAs would be too time-consuming for the supercell and molecular dynamics calculations needed for this work.

The chapter is rather technical and is structured as follows: I will start by showing structural data (lattice constant, bulk modulus, and phonons), and afterwards electronic properties (band gap, band offset, and band effective masses). Finally, I will present the volume dependence of two quantities that are particularly relevant for this study, the phonons and the electronic band gap.

3.1 Computational details

The computations shown in this chapter were done using the projector augmented wave (PAW) implementation [193, 194] of DFT of the VASP package [120–123]. I used the LDA [187], PW91 [188, 189], PBE [135], revPBE [190], AM05 [191, 192], and PBEsol [124] exchange-correlation functionals, an energy cutoff of 600 eV, and valence electron configurations $5d^{10}6s^26p^2$ for lead, and $5s^25p^4$ for tellurium. A Γ-centered $20 \times 20 \times 20$ $k$-point grid for the primitive 2-atoms unit cell was used and the effect of spin-orbit coupling was studied. The phonon properties were computed using the supercell approach with the finite-displacement method as implemented in the Phonopy package [195].
3.2 Structural properties

To determine the equilibrium volume I fitted an equation of state to the internal energy $E(V)$ using the parametrization of Birch and Murnaghan [196]

$$E(V) = E(V_0) + \frac{9B_0V_0}{16}\left[\frac{V_0}{V}\right]^{2/3} - 1 \right]^2 \times$$

$$\times \left\{B'_0 \left(\frac{V_0}{V}\right)^{2/3} - 1 \right\} + 6 - 4 \left(\frac{V_0}{V}\right)^{2/3} \right\}, \quad (3.1)$$

where $V_0$ is the equilibrium volume, $B_0$ the bulk modulus

$$B_0(p, T) = -V \left. \frac{\partial p}{\partial V} \right|_T, \quad (3.2)$$

and $B'_0$ the pressure derivative of the bulk modulus. Figure 3.1(a) shows the obtained lattice constants. All functionals perform well – the obtained values are within a few % of the experimental value 6.43 Å [35] (horizontal dashed line) – and spin-orbit coupling has a negligible effect. The usual underestimation by the LDA and overcorrection by the GGAs is also observable. The best agreement with experiment is obtained by PBEsol.

Panel (b) shows the obtained values for the bulk modulus $B_0$. The values show a larger scattering, but still all functionals produce values in the same order
as the experimental value (horizontal dashed line). Spin-orbit coupling is seen to not have a large impact, but it consistently gives smaller values with respect to results when spin-orbit coupling is not included, indicating that spin-orbit coupling increases the compressibility. The best agreement is obtained by PW91 and PBE. Note, however, that the experimental value was measured at 300 K and is likely smaller than the 0 K value.

Next I discuss the $T = 0$ K stability of the rocksalt structure. When questioning structural stability, the computation of the phonon spectrum allows one to assess whether a given structure corresponds to a (global or local) minimum of the energy surface. Phonon frequencies are computed as the square root of the eigenvalues of the dynamical matrix, which is the mass-weighted version of the force-constant matrix, the Hessian (the matrix of second-derivatives) of the potential energy. If imaginary modes (phonon modes with imaginary frequencies) are found, the structure is unstable: by displacing the atoms according to the corresponding eigenmodes the energy can be lowered\(^1\).

Figure 3.2 shows the phonon band structure for PbTe in the rocksalt structure computed using the PBEsol functional without including spin-orbit coupling\(^2\). The non-analytic term correction to the dynamical matrix [198–201] that arises in the long-wavelength limit was included. In semiconductors, because of the long-range Coulomb interactions, the longitudinal optic (LO) modes for $q \to 0$ are accompanied by macroscopic electric fields, which have to be treated with care because their potentials are not lattice-periodic. In this situation, it can

---

\(^1\) In fact, it is well-known that solely positive eigenvalues of the Hessian are required to be in a minimum.

\(^2\) This is done because the computation of the Born-effective charges does not always converge and is highly dependent on the chosen volume when spin-orbit coupling is included.
be shown that the dynamical matrix can be decomposed into an analytic and a non-analytic term. The latter is found to depend on the Born effective charges and on the high-frequency (electronic) dielectric tensor. This gives rise to the LO-TO splitting and the Lyddane-Sachs-Teller relation [202].

The first thing to notice in Fig. 3.2 is the presence of solely real frequencies – a proof of the stability of the structure, and consistent with experiments. Secondly, the LO-TO splitting at $\Gamma$ amounts to 2 THz. This is much smaller than 20 THz in ferroelectric perovskites, even though I find large Born effective charges of about 6 (instead of nominal 2). The reason is a (large) high-frequency dielectric constant of about 30 that results in a screening of the long-range interactions [27].

Finally, we can observe the closeness to a ferroelectric instability; the transverse optic (TO) mode at $\Gamma$ with a frequency of 1.4 THz is very soft\(^3\), but still harder than in experiments, where the reported value is 0.7 THz [33]. Furthermore, I will show in section 3.4 that a small volume change can soften this mode completely giving a ferroelectric ground state. The strong dependence of the TO mode on volume shown in Fig. 3.7 is the signature of a coupling between acoustic and optic modes [63]. This coupling manifests in DFT studies as the crossing between longitudinal acoustic (LA) and transverse optic (TO) modes along the $\Delta$ ($\Gamma$ – $X$) line [63, 203–207]. However, experimentally no crossing is found; instead the strong anharmonic coupling between LA and TO results in an avoided crossing of the modes [34].

Figure 3.3 compares the TO frequencies computed with the different functionals, where imaginary frequencies – unstable modes – are represented as negative values. One can see that spin-orbit coupling causes a softening of the TO modes, making them become unstable in many cases – only LDA and PBEsol predict the correct ground state (rocksalt) at the equilibrium volume. On the other hand, at the experimental volume all functionals confirm the stability of the rocksalt structure. In any case, the soft frequencies are consistent with the known incipient ferroelectricity.

Finally, Table 3.1 presents an overview of all computed structural properties.

### 3.3 Electronic properties

Next, I discuss the electronic properties and start by showing the electronic band structure close to the Fermi energy. Figure 3.4 shows the band dispersions computed with PBEsol without the inclusion of spin-orbit coupling\(^4\). A direct gap is observed at the $L$ point, and a second valence band maximum occurs along the $\Sigma$ ($\Gamma$ – $K$) high-symmetry line. Relevant quantities are indicated in the figure: the direct band gap $E_g$ at $L$, the band offset $E_o$ between the valence band maximum and the secondary pocket along the $\Sigma$ line, and the effective masses

---

\(^3\) If spin-orbit coupling were included, its frequency would be even smaller, about 0.9 THz (see Table 3.1).

\(^4\) This is done only for visualization reasons; if spin-orbit coupling were included, the band gap and band offset would be very small, making it more difficult to visualize them.
Figure 3.3: TO frequencies at the equilibrium volume (a) and at the experimental volume (b) calculated using the functionals shown along the horizontal axis. Open bars represent results when spin-orbit coupling was not included, filled bars with spin-orbit coupling. The horizontal dashed line indicates the experimental value 0.7 THz [33]. Spin-orbit coupling has a huge impact on the stability of the structure – only LDA and PBEsol predict the correct ground state at the equilibrium volume, while at the experimental volume all functionals produce stable TO modes.

Table 3.1: Calculated structural properties when spin-orbit coupling is included. $a_0$ is the lattice constant, $B_0$ the bulk modulus, $B'_0$ the pressure derivative of the bulk modulus, TO and TO’ the $\Gamma$-point-frequency of the transverse optic mode at the equilibrium and experimental volume, respectively.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>AM05</th>
<th>PBE</th>
<th>PBEsol</th>
<th>PW91</th>
<th>revPBE</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$ [GPa]</td>
<td>47.63</td>
<td>40.64</td>
<td>37.22</td>
<td>43.71</td>
<td>37.94</td>
<td>32.57</td>
<td>38.39 [197]</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>4.65</td>
<td>4.65</td>
<td>4.56</td>
<td>4.61</td>
<td>4.56</td>
<td>4.56</td>
<td>–</td>
</tr>
<tr>
<td>TO [THz]</td>
<td>1.10</td>
<td>–0.17</td>
<td>–0.71</td>
<td>0.91</td>
<td>–0.66</td>
<td>–1.15</td>
<td>0.7 [33]</td>
</tr>
<tr>
<td>TO’ [THz]</td>
<td>0.57</td>
<td>0.75</td>
<td>1.21</td>
<td>0.97</td>
<td>1.26</td>
<td>1.27</td>
<td>0.7 [33]</td>
</tr>
</tbody>
</table>
Figure 3.4: Computed band structure (left) and density of states (DOS) (right) close to the Fermi energy, $E_F$, with PBEsol and without including spin-orbit coupling. A direct gap is observed at the $L$ point, and a second valence band maximum occurs along the $\Sigma$ ($\Gamma - K$) high-symmetry line. The band gap $E_g$, the band offset $E_0$ and the effective masses $m^*$ at $L$ are indicated.

at $L$. The density of states (DOS) shows that the highest lying valence bands have a predominant Te $p$ character, but just below $E_F$ Pb $s$ character can also be observed, which is consistent with the revised lone-pair model (see text box on page 1). On the other hand, the conduction bands have predominantly Pb $p$ character.

Figure 3.5 compares the band gaps and offsets obtained with the different functionals. Spin-orbit coupling decreases the gap’s size considerably, bringing it into better agreement with experiments. All functionals produce a semiconducting ground state, but in the majority of the cases the gap is underestimated. LDA and revPBE are the best functionals here.

All functionals consistently underestimate the band offset, and spin-orbit coupling is seen not to play a big role, except in the case of LDA; there the offset becomes negative, meaning that the valence band maximum moves to the $\Sigma$ line and the band gap is indirect.

Figure 3.6 presents the effective masses of the highest valence band at the $L$ point. For the highest valence band the surfaces of constant energy can be described by a prolate ellipsoid elongated along the $\langle 111 \rangle$ direction centered at $L$ [197]. Except again for LDA, all functionals describe quite well the curvature of the highest valence band at the $L$ point when spin-orbit coupling is included. Within LDA the longitudinal curvature even becomes positive, pointing to large distortions close to the valence band maximum (this is related to the issue of band inversion, see section 3.4.2).

Finally, Table 3.2 presents an overview of all computed electronic properties.
3.3 Electronic properties

Figure 3.5: Direct band gaps at \( L \) (a) and band offsets (b) computed at the equilibrium volume using the functionals shown along the horizontal axis. Open bars represent results when spin-orbit coupling was not included, filled bars with spin-orbit coupling. The horizontal dashed lines indicate the experimental values [197]. Spin-orbit coupling decreases the band gap considerably, while it does not affect much the offsets, except for LDA, where a negative value is obtained as the band gap becomes indirect (the valence band maximum is moved to the \( \Sigma \) line).

Figure 3.6: Effective masses at the valence band maximum, (a) \( m^*_{\parallel} \) longitudinal along [111] and (b) \( m^*_{\perp} \) transverse, calculated using the functionals shown along the horizontal axis. Open bars represent results when spin-orbit coupling was not included, filled bars with spin-orbit coupling. The horizontal dashed lines indicate the experimental values [197].
Table 3.2: Calculated electronic properties when spin-orbit coupling is included. \( E_g \) is the direct gap at \( L \), \( E_o \) the band offset between valence band maximum and secondary pocket along \( \Sigma \), \( m_\parallel^* \) the longitudinal effective mass at the valence band maximum, and \( m_\perp^* \) the transverse effective mass.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>AM05</th>
<th>PBE</th>
<th>PBEsol</th>
<th>PW91</th>
<th>revPBE</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_g ) [eV]</td>
<td>0.19</td>
<td>0.02</td>
<td>0.10</td>
<td>0.07</td>
<td>0.08</td>
<td>0.21</td>
<td>0.19</td>
</tr>
<tr>
<td>( E_o ) [eV]</td>
<td>−0.02</td>
<td>0.12</td>
<td>0.11</td>
<td>0.07</td>
<td>0.11</td>
<td>0.09</td>
<td>0.17</td>
</tr>
<tr>
<td>( m_\parallel^* ) ([m_e])</td>
<td>1.69</td>
<td>−0.05</td>
<td>−0.23</td>
<td>−0.32</td>
<td>−0.18</td>
<td>−0.44</td>
<td>−0.31</td>
</tr>
<tr>
<td>( m_\perp^* ) ([m_e])</td>
<td>−0.057</td>
<td>−0.004</td>
<td>−0.016</td>
<td>−0.015</td>
<td>−0.013</td>
<td>−0.034</td>
<td>−0.022</td>
</tr>
</tbody>
</table>

### 3.4 Volume Dependence of Relevant Quantities

After having considered the functional dependence of the DFT-extracted properties, I now discuss the volume dependence of two quantities that are particularly relevant for this work, the phonons and the band gap. In fact, Refs. [63, 204, 206, 208] already reported a high sensitivity of the results of first-principles calculations to the unit-cell volume. In Appendix C in the paper [209] presented in section 6.3.1 I present the volume dependence of other electronic properties relevant for an estimation of the usefulness of DFT calculations for the prediction of de Haas–van Alphen (DHVA) frequencies and cyclotron masses. We find that the evolution with doping of quantum-oscillation properties is not affected significantly by volume, at least in the range of volume changes found experimentally.

#### 3.4.1 Volume Dependence of Phonon Modes

Figure 3.7 shows the volume dependence of the phonon modes at the \( \Gamma \) and \( X \) points computed with the PBEsol functional and spin-orbit coupling. We can see that the optical phonon frequencies depend strongly on the volume, in particular for lattice constants close to the equilibrium volume; Ref. [63] linked this sensitivity to a strong coupling between optical and acoustic modes, since acoustic modes correspond to compressive waves. Note, however, that the trend stands in contrast to experiments, for which the softening of TO(\( \Gamma \)) happens on cooling, i.e. with reduction in volume. Our failure to reproduce the volume dependence means that the quasi-harmonic approximation is not able to reproduce the TO(\( \Gamma \)) temperature dependence. Other anharmonic effects are clearly required to renormalize the phonon frequencies in the correct way.

We can observe also two phase transitions: (i) with expansion the optical phonons at \( \Gamma \) soften completely at a lattice constant of about 6.5 Å (or at a pressure of about −1 GPa) pointing to a ferroelectric-like transition. This shows
3.4 Volume dependence of relevant quantities

Figure 3.7: Volume dependence of phonon modes at the $\Gamma$ and $X$ points. The vertical dashed line represents the equilibrium volume. LO-TO splitting was not taken into account again the closeness to a ferroelectric instability (incipient ferroelectricity) of PbTe. Note that this is the same volume at which the band gap closes (see Fig. 3.8(a)); while this might be a coincidence, it is also consistent with arguments based on the second-order Jahn-Teller effect (see Eq. (1.2)). (ii) Upon compression the transverse acoustic (TA) modes soften and become unstable at a lattice constant of about 6.0 Å, corresponding to a pressure of about 12 GPa. Refs. [204, 208] showed that this corresponds to the high-pressure transition to an eight-fold coordinated CsCl structure, which occurs experimentally at about 13 – 16 GPa [210, 211].

3.4.2 Volume dependence of the band gap

Figure 3.8(a) shows the volume dependence of the band gap computed with the PBEsol functional and spin-orbit coupling. As you can see, at a critical lattice constant of about 6.5 Å the band gap closes. Barone et al. [8] showed that the closure is related to a band inversion, meaning that the character of the valence and conduction band close to the $L$ point are exchanged: in fact, panel (b) shows how close to the $L$ point the valence band acquires Pb $p$ character and the conduction band becomes Te $p$-like. This in turn is the signature of a topological phase transition (Barone et al. [8] additionally computed the Chern number to prove this) driven by a strongly asymmetric $sp$ hybridization and large spin-orbit coupling – under pressure PbTe is topologically non-trivial (as is the case for SnTe at standard conditions [12, 13]).

Returning to the volume dependence of the band gap, one can see that at both the experimental and equilibrium volumes PBEsol predicts the wrong topological state. Computations with LDA and PBE result in the same picture at the
Fundamental properties of PbTe

Figure 3.8: (a) Evolution of band gap, $E_g$, with lattice constant $a$ using PBEsol; spin-orbit coupling was included. The gray region represents the volumes corresponding to a band inversion in my calculations. The green dashed line shows the experimental and equilibrium volume. (b) Character of the bands close to the Fermi energy, $E_F$, computed with PBEsol at the equilibrium volume.

Experimental volume, while at the equilibrium volume PBE predicts the correct topological state. Since in this work I am interested only in the dispersion of the bands below the Fermi energy, and the curvature is well described by PBEsol (see discussion about effective masses in section 3.3), the band inversion is not expected to influence the results.

3.5 Conclusions

The previous considerations show that an accurate description of PbTe within DFT is not easy. I obtained a large variability of the results with respect to the functional and the lattice constant used in the calculations. This sensitivity to the computational settings is related to the closeness of PbTe to structural (incipient ferroelectricity [35]), topological [8, 9] and electronic (superconductivity [98, 99, 114]) phase transitions.

Most of the electronic properties are not captured very well, allowing in principle only qualitative predictions. Furthermore, many functionals do not predict the correct structural ground state at the equilibrium volume. A discussion could be started now, regarding whether comparisons with experiments should be done at the equilibrium or experimental volume. I think it is preferable to perform DFT computations, if possible, in a stress-free state at the equilibrium volume as well as in a stable structure. This leaves only LDA and PBEsol as possible candidates for the choice of a functional. LDA can be discarded because important electronic properties are badly captured, for example the curvature along the longitudinal
direction has the wrong sign. Therefore, in agreement with Ref. [212], I conclude that the best functional for calculating the properties of PbTe is PBEsol.
Polar fluctuations in PbTe

In this chapter I present my work on modeling and characterization of the local structure of lead telluride. The driving force behind this work is the ongoing controversy launched by the report of a lead off-centering on heating [33, 35]. The exciting discovery of a (local) symmetry breaking on heating obviously triggered a lot of research. However, the lack of a specific definition of off-centering in the original report led to confusion in the research community. Our work in collaboration with Thomas Weber, specifically our understanding of the local structure gained with ab-initio MD simulations and single-crystal diffuse scattering experiments, has resolved the controversy and shown that it was more a consequence of the different interpretation of the term off-centering than of fundamental physics.

The chapter is structured as follows: I start by discussing $T = 0 \text{ K}$ properties computed by CP2K as a way of validating the PBEsol functional with respect to the VASP computations showed in chapter 3. I then continue by looking for indications of a possible off-centering at finite temperatures with standard DFT calculations. Next, I will critically discuss the previous MD studies that tackled the off-centering issue. Afterwards, I will present our understanding of the local structure and how, we hope, resolves the controversy. To this end I attach a paper [213] written in collaboration with Thomas Weber, Emil Božin and Simon Billinge. There, we present a combined ab-initio MD and single-crystal diffuse scattering study of PbTe. Next, I will present some additional material not included in the paper that is useful to assess the incipient ferroelectricity and the asymmetry of the PDF peaks. Finally, I will critically discuss the validity and limitations of the presented MD simulations.

4.1 Computational details

The calculations shown in this chapter were performed using the CP2K code [161] with the hybrid Gaussian and plane wave (GPW) scheme [214, 215]. Gamma-point only calculations with a plane wave cutoff of 500 Ry were performed. The PBEsol [124] exchange-correlation functional and Gödecker-Teter-Hutter (GTH) pseudopotentials [216, 217] were used. We used valence electron configurations $6s^26p^2$ for lead, and $5s^25p^4$ for tellurium. Spin-orbit coupling was not included. Calculations were performed with a $3 \times 3 \times 3$ supercell of the conventional (cubic)
Polar fluctuations in PbTe cell (216 atoms) at temperatures between 50 K and 500 K in steps of 50 K. Long simulations (150 ps) in the isothermal-isobaric (NpT) ensemble using the thermostat developed by Bussi et al. [154] were performed, followed by 150 ps production runs in the microcanonical (NVE) ensemble. The timestep used was 2 fs. To check for finite-size effects, one run with a $6 \times 6 \times 6$ supercell (1728 atoms) was performed at 300 K with a reduced simulation time of $60 + 80$ ps; this run was also used to analyze in details the local structure.

The analysis of the MD simulations was performed with a self-written C++ code that uses OpenMP [218] and the Armadillo linear algebra library [219]. The principal reasons for the latter library are its syntax similar to MATLAB® and its speed, which is accomplished by advanced template techniques and the possibility to link high-speed libraries for matrix operations, like BLAS and LAPACK [220] or Intel® Math Kernel Library (MKL). The Fast Fourier Transform (FFT) is performed either by linking FFTW3 [221] or a high-speed replacement, like Intel MKL. The methods used to compute the pair distribution function (PDF) and the phonon spectrum are presented in Appendix B.

4.2 $T = 0$ K structural properties

I start by comparing the structural properties obtained with CP2K with those from VASP. For a fair comparison the same computational settings were used for both software: a $3 \times 3 \times 3$ supercell, only the $\Gamma$ point, and spin-orbit coupling was not included. The phonon properties were computed using the supercell approach with the finite-displacement method as implemented in the Phonopy package [195]. This section has to be thought as a validation of the GTH pseudopotentials and the PBEsol functional in CP2K for the determination of structural properties of PbTe.

Table 4.1 presents the computed structural properties. We observe a very

<table>
<thead>
<tr>
<th></th>
<th>CP2K</th>
<th>VASP</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ [Å]</td>
<td>6.51</td>
<td>6.44</td>
<td>6.43$^{35}$</td>
</tr>
<tr>
<td>$B_0$ [GPa]</td>
<td>42.49</td>
<td>44.86</td>
<td>38.39$^{197}$</td>
</tr>
<tr>
<td>$B_0'$</td>
<td>4.55</td>
<td>4.57</td>
<td>–</td>
</tr>
<tr>
<td>TO [THz]</td>
<td>1.4</td>
<td>1.6</td>
<td>0.7$^{33}$</td>
</tr>
</tbody>
</table>

good agreement between CP2K and VASP, even though the lattice constant is slightly larger with CP2K and the TO frequency is a bit smaller. Figure 4.1 shows
a comparison of the phonon band structure between CP2K (green) and VASP (dashed blue). The agreement is very good; the largest difference is the softer TO mode at \( \Gamma \) with CP2K, but this is welcome since it makes it closer to the experimental value of 0.7 THz \[33\]. This figure is different from Fig. 3.2 as the LO-TO splitting was not incorporated and the Brillouin zone was sampled only at the \( \Gamma \) point.

**\( k \)-point convergence** To check for \( k \)-point convergence in CP2K I computed the phonon band structure using also a \( 6 \times 6 \times 6 \) supercell. The overall dispersions are not changed much, but the TO frequency is lowered to 1.2 THz. This shows that the \( 3 \times 3 \times 3 \) supercell is not completely converged with respect to \( k \)-points, but the variations should not influence the outcome of my results\(^1\). In fact, I performed a MD simulation also with the larger supercell, and I did not find any qualitative effect (see section 4.5). On the other hand, using the larger supercell for all different runs would have meant a very large computational cost that I did not have at my disposal.

### 4.3 \( T = 0 \text{ K} \) energetics of off-centering

Next, I show what standard DFT, which is a \( T = 0 \text{ K} \) theory, tells us about the tendency for structural distortions at finite temperatures. In Fig. 4.2 I show computations of the total energy as a function of a “ferroelectric” distortion along different high-symmetry directions, \( \langle 100 \rangle \) (blue), \( \langle 110 \rangle \) (dashed green), and \( \langle 111 \rangle \) (dotted red). We are looking for secondary (meta-stable) minima

\(^1\) Note that \( 3 \times 3 \times 3 \) is also the supercell size mostly used in the literature.
Figure 4.2: Calculated energy dependence for a ferroelectric distortion along different directions, ⟨100⟩ (blue), ⟨110⟩ (dashed green), and ⟨111⟩ (dotted red). Pb atoms were cooperatively moved in the specified direction. The inset shows a zoom for small displacements.

that indicate distorted structures that could be reached with thermal fluctuations. We observe a monotonic increase of the energy for all considered directions; the ⟨100⟩ direction is the hardest, a consequence of the repulsion from the nearest-neighbor atoms. While the peculiar curve for the ⟨110⟩ direction is a consequence of periodic boundary conditions (the structures for zero and 4.5 Å distortions are equivalent), a second minimum is obtained along ⟨111⟩. However, the corresponding displacements and energies involved are by far too large to allow a thermal activation; the obtained structure corresponds to the zincblende structure.

While a cooperative distortion, which is accompanied by a global symmetry lowering, does not correspond to the proposed (uncorrelated) local off-centering [35], it can provide upper bounds for the tendency to distort. I also computed the energy when only one Pb atom is displaced (and the others are kept fixed in the supercell) and the energy increased monotonically without any indication of a meta-stable state (not shown).

To take into account temperature effects I next present my Born-Oppenheimer MD simulations. A big advantage of MD is that anharmonic effects are automatically taken into account. This, however, comes with a big downside, namely the computational cost.

4.4 Review of previous MD studies

Before discussing in details my MD simulations, I review previously published MD studies that tried to reproduce and explain the reported emphanitic behav-
ior [33, 35] with the related Pb off-centering and the splitting of the zone-center optical mode. [Other MD studies on PbTe were published in the last years, but they focused on the thermoelectric properties. These are not commented on in this section.] I focus especially on the computational settings and the techniques used. Since in the original Science paper [35] it was not stated clearly what was meant by off-centering, the subsequent studies (both experimental and theoretical) interpreted the concept differently. Note that it is not easy to compare the published studies because in some cases important computational settings were not mentioned in the manuscripts. Anyway, none of the works compared the obtained PDFs with the original data by plotting them on top of each other. I think this would be the easiest way to start a comparison and determine whether the experiments are reproduced.

The first (ab-initio) MD study after the publication of the off-centering report was performed by Zhang et al. [48]. The authors used the VASP package with a $3 \times 3 \times 3$ cubic supercell and simulated for $8 + 12$ ps [8 ps for equilibration and 12 ps for the production run] with a timestep of 2 fs; the exchange-correlation functional, the $k$-points grid and whether spin-orbit coupling was included were not specified. Also not very clear is the simulated ensemble; some points in the text hint to a canonical ensemble with a Nosé thermostat. Zhang et al. computed the PDF at six temperatures between 50 and 500 K and claimed to reproduce the broadening and asymmetry of the nearest-neighbor peak; however, their PDFs do not show any shoulder on the high-$r$ side of the first peak. They computed the off-centering as the average displacement from the high-symmetry rocksalt positions and found that they were negligibly small. Thus, they concluded that Pb is not off-centered and that the reported features are the consequence of large thermal vibrations, i.e. large anharmonic effects, caused by the vicinity to the ferroelectric instability.

The second ab-initio MD work was performed by Kim and Kaviany [49] and also used the VASP package, but with smaller supercells ($3 \times 3 \times 3$ primitive supercells and $2 \times 2 \times 2$ cubic supercells). Again it was not specified whether spin-orbit coupling was included and which exchange-correlation functional was chosen. The Brillouin zone was sampled at the $\Gamma$ point only. The $6 + 11$ ps simulations were performed in the canonical ensemble with a Nosé thermostat using a timestep of 0.2 + 1 fs; six temperatures between 300 and 800 K were simulated. Interestingly, the volume was changed according to the experimental thermal expansion. However, the size of the supercell leaves me with some doubts about the correctness of the work, because in my computations with such small supercells the phonons showed instabilities throughout the whole Brillouin zone. Nonetheless, Kim and Kaviany reported a full reproduction of the original PDFs and extracted an even larger Pb off-centering; however, they computed it as the root-mean-square displacement from the high-symmetry rocksalt positions, i.e. a quantity that has to be compared to the ADPs.

More recently, Chen et al. [52] performed classical MD with a novel slave-mode expansion of the DFT energies [222]. The expansion coefficients were
computed without the inclusion of spin-orbit coupling. The authors used a $10 \times 10 \times 10$ cubic supercell and simulated for 1000 ps in the microcanonical ensemble after having equilibrated for 50 ps at six temperatures between 13 and 580 K; the timestep was 5 fs. Interestingly, Chen et al. reproduced the splitting of the zone-center optical phonon on warming [33], but ascribed it to competing third- and fourth-order anharmonicities instead of to a local symmetry lowering. Moreover, they claimed to reproduce all PDF features of the original report [35]. Finally, they interpreted the off-centering as the mean displacements from the high-symmetry rocksalt positions and found that they were negligibly small.

A further classical MD study was performed by Shiga et al. [53] using a non-empirical force field based on accurate anharmonic interatomic force constants (IFCs)$^2$ computed from first-principles. The authors used a $4 \times 4 \times 4$ cubic supercell and simulated for 600 ps in the microcanonical ensemble after having equilibrated the system at nine temperatures between 50 and 250 K; the timestep was 2 fs. Interestingly, for each temperature ten MD simulations were ensemble-averaged. Shiga et al. were also able to reproduce the splitting of the zone-center optical phonon on warming, but ascribed it to unusually large cubic IFCs along the $\langle 100 \rangle$ direction. Furthermore, they claimed to reproduce all PDF features of the original report [35], even if the shoulder on the high-$r$ side of the first peak was not reproduced. The off-centering was again interpreted as the average displacement from the high-symmetry rocksalt positions and was found to be negligibly small.

The last work, at least to my knowledge, presenting an ab-initio MD study was performed by Li et al. [54] using VASP. The authors chose a $3 \times 3 \times 3$ cubic supercell, AM05 as the exchange-correlation functional, and the Brillouin zone was sampled at the $\Gamma$ point only; it is not specified whether spin-orbit coupling was included. The simulations were performed in the canonical ensemble with a Nosé thermostat for 20 ps after equilibration; three temperatures, 100, 300 and 600 K, were simulated and the timestep was 2 fs. The interatomic force constants needed for the computation of the phonon self-energy were obtained with the temperature-dependent effective potential (TDEP) method [223]. Li et al. were able to reproduce the splitting of the zone-center optical phonon on warming, but attributed it to a sharp resonance in the phonon self-energy caused by nesting of phonon dispersions that combines with the anharmonicity to produce the large splitting.

In summary, all MD studies reproduced some of the reported emphatic features [33, 35], such as the increased asymmetry of the PDF nearest-neighbor peak and the splitting of the TO phonon at $\Gamma$. On the other hand, the additional structure in the PDF peaks, e.g. the shoulders, and the non-Gaussian peaks at higher $r$-values have not yet been captured. The interpretations varies between off-centering and large anharmonic effects.

---

2 IFCs are defined as the Taylor expansion coefficients of the potential energy around the equilibrium configuration.
The following paper, Sangiorgio et al. [213], presents the study of the local structure of lead telluride both experimentally and theoretically. The paper is close to its final version and is intended to be submitted to Physical Review X. The work was done in collaboration with Thomas Weber also from ETH Zurich, Emil Božin from Brookhaven National Laboratory, and Simon Billinge from Columbia University; the last two being the lead authors of the original report [35] about off-centering. I performed and analyzed all MD simulations and first-principles calculations, wrote the corresponding sections, and was involved in the writing of the whole paper and in the interpretation of the results. The x-ray single-crystal diffuse scattering measurements and analysis was performed by Thomas Weber, the modeling of the PDF extracted from my MD trajectories with the PDFgui package [224] by Emil Božin and Simon Billinge, and the single-crystal samples were prepared by Christos Malliakas and Mercouri Kanatzidis.

In the paper we start by discussing the average structure as obtained from standard single-crystal structure refinement and ab-initio MD. As expected the average structure is rocksalt and the atomic positions are, on average, centered on the corresponding Wyckoff positions. The atomic displacement parameters (ADPs) compare well between theory and experiments and do not show any indication for a static off-centering.

We continue by characterizing the local structure using the 3D-ΔPDF, which is the Fourier transform in real space of the diffuse scattering intensity, and the MD trajectories. The quantities refined in the 3D-ΔPDF method are the displacement covariances

$$
\text{Cov}_{uvw,ij}^{mn} = \langle u_i^m u_j^n \rangle_{uvw},
$$

where $u_i^n$ is the $i$-th component of the displacement vector of atom $n$ from its average position in fractional units and $\langle \ldots \rangle_{uvw}$ indicates space and time averaging of the displacements of all atoms $m$ and $n$ that are $uvw$ unit cells apart. It is convenient to define the correlation matrices as the normalized covariance matrices

$$
\text{Cor}_{uvw,ij}^{mn} = \frac{\langle u_i^m u_j^n \rangle_{uvw}}{\sqrt{\beta_{aver,ii}^m \beta_{aver,jj}^n}}.
$$

that assume values between $-1$ and 1. $\beta_{aver}^n$ is the average ADP matrix of atom $n$.

We find that correlations are very strong for pairs separated by $\langle x00 \rangle$ interatomic vectors with strong longitudinal correlations. Interestingly, the decay with distance is not smooth but displays “steps”. We interpret these steps as a coupling between acoustic- and optic-like displacements giving rise to dynamically fluctuating electric dipoles.

Using my MD trajectories we go one step further and extract also higher-order correlations that indicate a local symmetry breaking with the formation of regions
in the material of correlated dipoles. We then interpret these correlated dipoles as the proposed *emphasis*, even if the lead atoms are not locally off-center on average, but rather centered in their coordination octahedra.

We also identify a possible misinterpretation of the current PDF modeling software PDFgui [224] as a source of the off-centering claim. Since this code cannot handle anharmonic effects, anharmonicity is introduced via discrete bond-length distributions and partial occupancies (so-called split models). Thus, if the final distribution is not multivalued, anharmonicity and off-centering cannot be distinguished.

Finally, we discuss the role of the correlated dipoles in the formation of asymmetric PDF peaks and for the thermoelectric performance.
Correlated local dipoles in PbTe

Boris Sangiorgio,1 Emil S. Bozin,2 Christos D. Malliakas,3 Michael Fechner,1 Arkadiy Simonov,1 Mercouri G. Kanatzidis,1 Simon J. L. Billinge,4,2 Nicola A. Spaldin,1 and Thomas Weber1

1Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland
2Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA
3Department of Chemistry, Northwestern University, Evanston, IL 60208, USA
4Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA

(Dated: December 8, 2017)

We present a combined single-crystal x-ray diffuse scattering and ab-initio molecular dynamics study of lead telluride, PbTe. Well-known for its thermoelectric and narrow-gap semiconducting properties, PbTe recently achieved further notoriety following the report of an unusual off-centering of the lead atoms, accompanied by a local symmetry breaking, on heating. This observation, which was named emphasis, ignited considerable controversy regarding the details of the underlying local structure and the appropriate interpretation of the total scattering experiments. In this study, we demonstrate close agreement between our diffuse scattering measurements and our calculations, which allows us to analyze features such as higher-order correlations that are accessible in the simulations but not experimentally. This allowed us to discover an unusual correlated local dipole formation extending over several unit cells with an associated local reduction of the cubic symmetry in both our x-ray diffuse scattering measurements and our molecular dynamics simulations. Importantly, when averaged spatially or temporally, the most probable positions for the ions are at the centers of their coordination polyhedra. Our results therefore clarify the nature of the local symmetry breaking, and reveal the source of the earlier controversy regarding the existence or absence of off-centering. Finally, we provide an interpretation of the behavior in terms of coupled soft optical and acoustic modes, which is linked also to the high thermoelectric performance of PbTe.

Lead telluride (PbTe) is a narrow-gap semiconductor widely used in electronic and thermoelectric devices. Although its transverse optical (TO) phonon is soft, indicative of proximity to a ferroelectric phase transition, measurements of its bulk structure show that it retains its high-symmetry paraelectric $Fm\overline{3}m$ rocksalt structure at all temperatures. In contrast to its apparently simple average structural behavior, a recent analysis of the local structure, based on pair distribution function (PDF) analysis of neutron powder diffraction data, suggested the emergence of considerable local non-Gaussian distortions: The PDF peaks of the local structure broadened strongly with increasing temperature, accompanied by an asymmetry and the development of non-Gaussian lineshapes with shoulders. The PDF could be explained with a model that included off-centering of lead atoms with respect to their high symmetry positions, in the manner of fluctuating local dipoles, caused by Pb–Te dimerization, on heating to temperatures higher than 100 K. The phenomenon was called emphasis.

The striking observation of an apparent local symmetry lowering on warming, in contrast to a conventional global symmetry-lowering phase transition that occurs on cooling, led to intense interest and many subsequent theoretical and experimental studies seeking to explain the behavior. A detailed understanding of the effect is still lacking, however, and indeed the existence of off-centering has even been questioned in some works. Significant anharmonicity was found in inelastic neutron scattering measurements, consistent with the non-Gaussian PDF peaks, and the appearance of an additional phonon branch above 100 K in Ref. 3 was interpreted in terms of a dynamic local symmetry breaking on warming. However, while all experiments indicate large amplitude dynamic and anharmonic excursions of the Pb ions away from their central positions, there remains controversy regarding whether the probability distribution of the Pb ions is peaked at the high symmetry positions or displaced away from it on average. An analysis of synchrotron powder x-ray diffraction data using the maximum entropy method was consistent with large Pb atomic probability density away from the average position in all the lead chalcogenides, with refined magnitudes of the Pb displacement in PbTe ($0.3 \AA$ at 300 K) comparable to but exceeding that found in the original report. Subsequent extended x-ray absorption fine structure (EXAFS) measurements reported that the Pb atomic probability distribution was peaked on average at the high symmetry position, albeit with large amplitude atomic displacement parameters (ADPs), and stated explicitly that the large displacements seen in diffraction measurements are inconsistent with the EXAFS data. A high-resolution neutron powder diffraction study found large increases in Pb ADPs on warming but did not reproduce the anomalies in their temperature dependence, attributing the earlier reports to errors in temperature calibration. Finally, a recent powder x-ray diffraction study that included the effects of Pb vacancies and microstrain in the Rietveld and maximum entropy method modeling was consistent with a local symmetry breaking from cubic static off-centering of 0.2 Å or less at 100 K. In addition, high concentrations of lead vacancies were found, pointing to sample dependence as a possible source of the inconsistencies between different measurements.

On the theory side, DFT calculations in the original report using the local density approximation (LDA) and the self consistent ab initio lattice dynamical (SCAILD) method indicated a softer potential for local Pb displacements with
increasing temperatures, counter to the usual hardening with increasing temperature of the free energy for a long-range ferroelectric transition. The first ab initio molecular dynamics (MD) study\textsuperscript{30} (using the generalized gradient PW91 functional in a 216-atom supercell within the VASP code) confirmed the soft and strongly anharmonic TO phonon but did not identify local dipole formation and concluded that the experimental results of Božin et al.\textsuperscript{2} could be attributed to abnormally large-amplitude thermal vibrations. The calculated PDFs missed key physics, however, since while they showed broad peaks and some asymmetric character in the nearest neighbor Pb-Te peak, they did not reproduce the highly-non-Gaussian lineshapes and anomalous shifts in peak centroid with temperature seen in the data\textsuperscript{2}. A subsequent ab initio MD study\textsuperscript{11}, (again using the VASP package but this time with 64-atom supercells), claimed to successfully reproduce the measured lattice dynamics, peak broadening with rising temperature, and non-Gaussian asymmetry and reported a larger lead off-centering than in the original experimental study. However, a comparison with the experimental data was not shown and the choice of exchange-correlation functional was not stated, making it difficult to compare with the study of Ref. 10. More recently, a novel slave-mode expansion method was used to calculate the finite-temperature dynamics of an 8000-atom supercell\textsuperscript{12}. This study reproduced the observed splitting of the phonon peak on warming\textsuperscript{13}, and used the language of competing third- and fourth-order anharmonicities – which tend to result in off-centerings – rather than a local symmetry lowering to interpret the result. Classical MD simulations of 512-atom supercells based on ab initio inter-atomic force constants (IFCs)\textsuperscript{13} also reproduced the phonon splitting and identified unusually large cubic IFCs along the \( \langle 100 \rangle \) direction as the source. In contrast, later studies\textsuperscript{14,15} combining ab initio MD simulations (using 512 atom supercells and the PBE functional in the VASP code) with single-crystal and powder neutron diffraction and inelastic neutron scattering suggested that a sharp resonance in the phonon self energy caused by nesting of phonon dispersions could combine with the anharmonicity to produce the large phonon splitting. Once again, however, while the simulated nearest-neighbor Pb-Te PDF peak showed increasing asymmetric character with temperature, the highly-non-Gaussian lineshapes and anomalous shifts in peak centroid were not captured.

Finally, we note that similar behaviors and the associated controversies have also been reported in other materials. In related group IV chalcogenides, Ref. 2 (supporting online material) already reported emergent local dipoles on warming in PbS, with the formation of shoulders on both sides of the PDF nearest neighbor peak, an interpretation supported in Ref. 5. More intriguingly, similar behavior has been reported in SnTe above its ferroelectric phase transition at low temperature\textsuperscript{16}, although again the temperature dependence has been disputed\textsuperscript{2}. The emergence of local displacements on warming is not exclusive to the group IV chalcogenides. In KNiSi\(_2\), the average crystallographic structure is the same at all temperatures, but analysis of the local structure has been interpreted as an emergence on warming of local Ni displacement accompanied by differences in the electron density at the Ni sites, suggesting a fluctuating charge density wave\textsuperscript{17}. In CsSnBr\(_3\) a dynamic off-centering of Sn\textsuperscript{2+} on warming has been reported, while again the average perovskite structure is not affected\textsuperscript{18}. Interestingly, in the latter case the PDF peaks showed similar asymmetries as in the earlier PbTe studies, but no clear shoulders. Finally, in La\(_{1-x}\)Ca\(_x\)MnO\(_3\) local Jahn-Teller distortions have been reported in the high-temperature insulating phase that are not present in the low-temperature metallic phase, even though the average crystal structure is the same\textsuperscript{19,20}.

In summary, some aspects of the originally reported emphatic behavior of PbTe\textsuperscript{3,11} are reproduced by all studies, notably the asymmetry of the PDF peaks and the splitting of the TO phonon. Other features, particularly the shoulders in the PDF peaks, remain elusive in the theoretical studies, thwarting a consistent interpretation of the behavior. In particular, two seemingly contradictory interpretations need to be reconciled in order to fully understand the underlying physics: The picture of local off-centering, which is based largely on diffraction data, compared with the picture of strong anharmonicity, which is based primarily on measurements of the dynamics.

Here we present the first single-crystal x-ray diffuse scattering study of the temperature dependence of the local structure of PbTe, which we interpret with the aid of new ab-initio molecular dynamics simulations. We start by discussing the average structure and find, as expected, that the rock-salt structure is retained at studied temperatures, with displacive disorder associated with positional fluctuations. Next, we study the local structure with an analysis of the diffuse scattering. We obtain a peculiar decay of the atomic pair correlations which we are able to explain with the aid of higher-order correlations extracted from our MD simulations: We identify spontaneous displacements of Pb ions relative to their Te neighbors, resulting in correlated local dipoles that propagate for several unit cells. This is consistent with the earlier description of emphatic behavior. We find, however, that in spite of these correlated displacements, the most probable position for each individual Pb ion is on average at the center of its coordinating Te polyhedron. However, our new finding that the local dipoles are correlated between unit cells resolves the apparent controversy by providing a picture that is consistent with both previously conflicting pictures: If at one instant in time, a Pb ion is displaced from the center of its coordination octahedron along \( \langle 100 \rangle \) say, the Pb ion in the neighboring unit cell in that direction is also displaced along \( \langle 100 \rangle \), and so on, over a correlation length of a few unit cells. The emergence of such fluctuating but correlated local dipoles on warming may then be considered as the definition of emphasis. The correlations between the dipoles fall off in distance and in time and are evident in diffraction experiments only in the diffuse scattering signal, and propagates to the PDF in a total scattering experiment, and the 3D-APDF measurements described here. From our calculations we identify a possible origin for the asymmetry of the PDF peaks as an alternation of short and long bonds, and establish a link between the correlated dipoles and the high thermo-
electric performance of PbTe.

I. AVERAGE STRUCTURE AND LATTICE DYNAMICS

We begin with an experimental and theoretical determination of the average atomic displacements as a function of temperature, focusing in particular on whether the atomic displacements are best approximated as single minimum harmonic or anharmonic oscillators or if the atoms occupy multi-minimum split positions. The experimental and computational details can be found in the Appendix. The refinement of the average crystal structure was done with the program SHELXL based on single crystal Bragg scattering. Atomic displacements were modeled in two approaches. First, Pb and Te were located at the highest symmetry Wyckoff positions 4a (0,0,0) and 4b (0.5, 0.5, 0.5), and any static or dynamic displacements away from the high-symmetry positions had to be captured by the harmonic atomic displacement parameters (ADPs) $U_{iso}^{Pb}$ and $U_{iso}^{Te}$. Second, the atomic displacements were described as a convolution of discrete split vectors, which shift the atoms away from the high-symmetry to lower symmetry Wyckoff positions, and harmonic displacement functions. We tested such a split-position model only for Pb because its average displacements are larger than those of Te and refined models with split vectors $(x00)$, $(xx0)$ and $(xxx)$. To avoid numerical correlations $U_{iso}^{Pb}$ and $U_{iso}^{Te}$ were constrained to the same values in each of the split model refinements. Consequently, each of our displacement models comprised two free structural parameters: $U_{iso}^{Pb}$ and $U_{iso}^{Te}$ in the harmonic model and a common $U_{iso}^{Pb/Te}$ plus a Pb split vector variable $x$ in the split models. The results of the refinements are summarized in Table I.

The refinements did not provide a unique answer for the best average displacement model, however surprisingly, the $(x00)$ split model, as was proposed by Božin et al. and Kastbjerg et al., gave the highest R-values in all cases. All other models have very similar reliability factors, but at high temperatures the $(x00)$ and $(xxx)$ split models seem to be slightly better than the harmonic model.

Figure 1 shows the probability density functions obtained within the various displacement models. The $(x00)$ split model represents the most anisotropic distribution function because it has the smallest number of split positions and needs to refine the largest Pb displacement per position to explain the non-thermal disorder, while the $(xx0)$ and $(xxx)$ split models appear more isotropic. It is important to note that even in the cases of the split models the convolution of the ADPs with the split vectors results in a probability distribution function that is similar to a Gaussian. The major difference is that the tip of the distribution is slightly flattened and it is anisotropic, which suggests that Pb is located in a pseudo-harmonic, but slightly flattened potential. Our ab-initio molecular dynamics simulations (for details see Appendix) support this interpretation, though the resulting probability distribution (Fig. 1g) is more isotropic than that of any of the displaced models. Our calculated average displacements (Figure A1 in the Appendix) are negligibly small.

### Table I

Overview of the results of the average structure refinements and of the MD simulations. Displacement parameters $U$ are given in $\AA^2$ units and the split parameter $x$ is given in $\AA$. Harmonic and split model root mean square displacements of the atoms from their high-symmetry Wyckoff positions.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Harmonic model</th>
<th>Split model</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>6.538</td>
<td>6.527</td>
</tr>
<tr>
<td>250</td>
<td>6.4546(2)</td>
<td>6.4546(2)</td>
</tr>
<tr>
<td>200</td>
<td>6.4489(3)</td>
<td>6.4494(1)</td>
</tr>
<tr>
<td>100</td>
<td>6.4549(3)</td>
<td>6.4550(3)</td>
</tr>
<tr>
<td>50</td>
<td>6.4724(3)</td>
<td>6.4723(3)</td>
</tr>
</tbody>
</table>

Note that the values of $U$ for the split models $(xxx)$ and $(xx0)$ are not a misprint but truly found in the refinements. The lattice parameters reported are the displacement parameters from the MD simulations are calculated as mean-square displacement of the atoms from the high-symmetry Wyckoff positions.
FIG. 1. Probability density functions of Pb. a) - d) show two-dimensional sections through the probability density functions at room temperature for the different split models indicated with the color scale representing the probability density in Å$^{-3}$. e) and f) show scans through the center along the a-axis at 125 K and at room temperature; (g) and (h) show the 2d section and scan through the center along the a axis for our MD simulations both at 300 K, where the red line in (h) represents a Gaussian fit.
for both Pb and Te atoms (consistent with the earlier molecular dynamics simulations discussed above) and the probability density for the lead atoms (panel (g)) indicates that they are centered on the rocksalt high-symmetry positions. However, we do not have enough statistics to definitely assess whether the tip of the distribution is flattened (panel (h)).

Figure 2 shows the temperature evolution of the ADPs compared with the temperature-corrected data by Knight\(^7\) of the original data of Ref. 2. Our refined ADPs show a linear dependence on temperature over the full examined temperature range, however with a larger slope than the data of Ref. 2, which were collected with powder samples. Moreover, they nicely linearly extrapolate to close to zero at 0 K. We also extracted the ADPs from the MD simulations as the mean squared displacements from the average positions. They exhibit the same linear dependency and are consistently larger than those expected from a harmonic model using the \(T = 0\) K DFT phonons (computed using the Phonopy\(^\text{22}\)) pointing to anharmonic effects. While our calculated Te ADPs are severely underestimated in our MD simulations, due to their extreme sensitivity to the soft mode phonon frequencies and correspondingly to our supercell size (the open triangle at 300 K shows the result for a larger supercell) and neglect of spin-orbit coupling.

In summary, we find good agreement in the temperature evolution of the average structure between our single-crystal Bragg measurements and \textit{ab-initio} MD simulations, as well as with the earlier literature reports; as expected the average structure is rocksalt. In particular, our calculated and measured ADPs are consistently larger than those calculated within a harmonic model. Our fits are unable to distinguish between split and single-minimum harmonic models, giving similar quality refinements in both cases. Therefore, while our average structure analysis certainly points to anharmonic behavior, it does not shed light on the question of the existence or nature of local off-centering.

\section{Local Structure}

We now analyze our diffuse scattering measurements and \textit{ab-initio} MD simulations to determine the local structure.

\subsection{Observations and qualitative interpretation of diffuse scattering and 3D-\(\Delta\)PDF patterns}

The diffuse scattering pattern is dominated by a system of alternating weak and strong diffuse planes perpendicular to the cubic main axes. The planes are narrow but not sharp (Fig. 3). The diffuse intensities are strongest beneath the Bragg reflections that are not extinct by the Bravais lattice. The overall intensities of the planes tend to increase with increasing diffraction vector, which is a characteristic pattern of displacive disorder with sub-Ångstrom amplitude. The weak diffuse intensities seen in the upper row in Fig. 3 can be understood as diffuse scattering from optical phonons, which scatter close to the Brillouin zone boundary. This is an interesting observation, because the typically small optical phonon amplitudes rarely allow measurements of corresponding diffuse scattering. In addition, some structured band and square-like diffuse scattering is visible in higher layers (for an example see the lower row in Fig. 3). It is interesting that the diffuse diffraction patterns show almost no variation within the investigated temperature range, apart from a decrease in the total diffuse intensity with decreasing temperatures. Therefore, it can be assumed that the qualitative local-order model is valid over the complete examined temperature range, \(125 \leq T \leq 298\) K, with the amplitude of the displacements decreasing with decreasing temperature in this temperature range.

Next, we focus on the interpretation of the 3D-\(\Delta\)PDF maps, obtained as the Fourier transform of the diffuse diffraction pattern, with the Bragg reflections cut out from the diffraction pattern (see Appendix for details). The 3D-\(\Delta\)PDF indicates where and how pair correlations of the real structure differ from the average structure model as obtained from the Bragg reflections alone. Positive values mean that finding an atom at the end of the corresponding inter-atomic vector is more likely than in the space and time averaged structure, while the probability is lower if the 3D-\(\Delta\)PDF density is negative. For example, in the case that two atoms tend to move in-phase (positive correlation) the corresponding 3D-PDF peak is narrower than in the Bragg scattering based 3D-PDF map. Thus the 3D-\(\Delta\)PDF peak shows positive values in the center and negative in the next neighborhood (looking like a Mexican hat pattern in the cross-section). If atoms move in anti-phase (negative correlation) the behaviour is inverse (upside-down Mexican hat). At large distances 3D-\(\Delta\)PDF densities approach zero, because pair correlations of the real and the average structure become very similar due to the spatial loss of displacement correlations\(^\text{23}\). Figure 4 shows the \textit{x}y0 section
FIG. 3. Reciprocal space reconstructions of the diffuse scattering at room temperature (left panels) and 125 K (right panels). For an economic representation only the sections $hk0$ (upper panels) and $h0k.2$ (lower panels) are selected from the full data set having $360 \times 360 \times 360$ voxels. Observed intensities (obs, upper left of each panel), results from the YELL refinement (refined, upper right) and difference (lower) intensities of the diffuse scattering are compared. The patterns at 150 K, 200 K and 250 K, which are not shown here, are comparable. The truncation ripples in the refined $hk0$ sections are due to incomplete coverage of the 3D-PDF maxima. The color wedges were linearly scaled by trial and error to allow a better qualitative comparison of the diffuse scattering patterns at different temperatures; the absolute diffuse intensities decrease with decreasing temperature as expected from the evolution of the ADPs. The white squares in the $hk0$ layers at $h, k = \text{even}$ are the cut-out Bragg reflection regions. Note that all quadrants include $000$ and $00.2$ or $03.2$ and $03.2$ pixels, respectively, such that the pixels oriented up/down or left/right to the white lines separating the four sections in each panel have the same coordinates.

of the 3D-$\Delta$PDF map at different temperatures. The 3D-$\Delta$PDF signals are found close to integer and half-integer lattice coordinates, corresponding to the average interatomic vectors of the rocksalt structure. Signals at $x+y+z = \text{integer}$ correspond to Pb/Pb and Te/Te interatomic vectors, which overlap perfectly, while those found at $x+y+z = \text{half-integer}$ represent Pb/Te vectors. The PDF signals at overlapping homoatomic pairs are strongly dominated by local order properties of Pb/Pb pairs, because Pb has both a stronger scattering power and larger ADPs, and therefore contributes more to the diffuse scattering and 3D-$\Delta$PDF maps. The homo- and hetero- interatomic vectors contribute similarly to the 3D-$\Delta$PDF, with the correlations strongest along $(100)$ directions and (see next section) weakest along $(111)$, although some minor differences can be observed after careful inspection. In general the 3D-$\Delta$PDF shows positive signals at average interatomic distances and negative signals along its radial neighborhood, which, as discussed above, is a typical signature for positive displacement correlations, i.e. it is consistent with a 3D-$\Delta$PDF pattern dominated by acoustic phonons.

B. Pair correlations

In this section we compare and analyze the pair correlations between atomic displacements as obtained from the 3D-
FIG. 4. 3D-ΔPDF x0y0 layer at room temperature (top panel) and 125 K (bottom panel). Observed densities (obs), results from the YELL refinement (refined) and difference 3D-ΔPDF densities are compared. The patterns at 150 K, 200 K and 250 K, which are not shown here, are comparable. The color wedges were linearly scaled by trial and error to allow a better qualitative comparison of the 3D-ΔPDF densities at different temperatures. Note that absolute 3D-ΔPDF densities decrease with decreasing temperature. Strongest disagreements between observed and refined densities are at ⟨x00⟩ coordinates. The origin may be anharmonic pair correlations that are not covered by our harmonic 3D-ΔPDF model, but the resolution is not good enough to allow a clear conclusion. The negative densities at large PDF distances come from artifacts due to masking diffuse scattering next to Bragg reflections. Note also that all quadrants include x00 and y00 pixels, such that the pixels oriented up/down or left/right to the white lines separating the four sections in each panel have the same coordinates.
The displacive pair correlations were described in the harmonic approximation and refined with the program YELL. For each symmetry independent average interatomic vector up to about 60 Å we have refined the corresponding 3D covariance coefficients to minimize the difference between the experimental diffuse scattering and the one calculated from the covariances. A detailed description of the 3D-ΔPDF model and the refinement strategy is found in the Appendix. The PDF and reciprocal space results of the YELL refinements are shown in Figs. 3 and 4. The most significant pair correlations resulting from the YELL refinement are depicted in Fig. 5, and compared to the results extracted from our MD simulations.

![Graphical representation of the displacive pair correlations as obtained from the 3D-ΔPDF refinement and from the MD simulations at RT and 300 K, respectively. The diagram shows the strength and direction of correlations, with homo-atomic pairs represented by blue ellipsoids and hetero-atomic pairs by red ellipsoids.](image)

FIG. 5. Graphical representation of the displacive pair correlations as obtained from the 3D-ΔPDF refinement and from the MD simulations at RT and 300 K, respectively. The plot shows pair correlations in the x00 layer. Blue ellipsoids represent correlations between homo-atomic pairs, while red ellipsoids show correlations between Pb and Te. Sizes and orientations of the ellipsoids indicate the strength and direction of correlations, i.e., the strongest correlations found are along the main crystallographic axes. The large blue circle in the bottom-left represents the correlation of an atom to itself, with definition in unity. The diagonal line separates experimental and simulation results and coincides with a crystallographic mirror plane. All of the shown pairs are positively correlated along all directions. Missing ellipsoids in the simulated data have at least one, in all cases very weak, negative component indicating presence of some small negative correlations. Table A1 in the Appendix presents an extended overview of the numerical values of the pair correlations.

In agreement with the qualitative interpretation it is seen that the correlations are very strong for pairs separated by ⟨x00⟩ vectors with strong longitudinal correlations. Most importantly, pair correlations extracted from our MD match almost perfectly (see Fig. 6). In general the correlations decay quickly (Fig. 6), but with the formation of “steps” – indicating that pairs of neighboring atoms have strongly correlated motions. Furthermore, correlations of the homo-atomic pairs are generally stronger than those of the hetero-atomic pairs. In agreement with our qualitative interpretation it is clear that the correlations are mostly independent of temperature over the temperature range studied. The amplitudes of the displacements change, however, in accordance with the changes in the ADPs.

We now discuss a microscopic mechanism that is consistent with these pair correlations (see Fig. 7). As presented above, the 3D-ΔPDF shows signatures of displacement correlations that are typical for acoustic phonons. These would generate positive pair correlations decaying with distance because of the short-range nature (green triangles in the figure). Optical phonon-like displacements, on the other hand, have pair correlations that alternate in sign (light blue diamonds). A superposition of both kinds of displacements, taking into account that in the real system the acoustic phonons dominate, gives rise to steps, with correlations of the homo-atomic pairs stronger than those of the hetero-atomic pairs. This displacement pattern suggests a Pb-Te dimerization along the ⟨100⟩ direction, that results in a local polarity.

The presence of optical phonon-like displacements, which are usually not detected in diffuse scattering, implies not only that the optical phonons are active but also that their amplitude is big enough to be detected. We propose that this is possible in PbTe, because of the soft TO mode. To test this hypothesis we performed the same analysis using a literature Buckingham effective potential, with parameters fit to ab initio calculations for PbTe. This potential was shown to reproduce reasonably the mechanical and phonon properties of bulk PbTe, except that the optical phonons calculated with the Buckingham potential are much harder than those in DFT. In particular, the TO mode at Γ is in the order of 3 THz instead of about 1 THz in DFT. Moreover, the optical and acoustic phonons are clearly separated in energy (Fig. 8(a)), so that a coupling between them is unlikely. We performed classical molecular dynamics with this potential as implemented in LAMMPS using a 10×10×10 supercell [we checked the results also with the 6×6×6 supercell to make sure that the results in this supercell are not affected by finite-size effects] and, when possible, the same settings as we used in our ab-initio MD calculations. As expected, the pair correlations are found to decay smoothly without the formation of any steps (Fig. 8(b)).

Interestingly, inelastic neutron scattering experiments by Delaire et al. reported a strong coupling between the ferroelectric TO mode and the longitudinal acoustic (LA) modes. One of its signatures – the avoided crossing between TO and LA – is also captured by our MD simulations. Figure 9 presents the power spectrum Z(q, ν) at 300 K computed as described in Ref. 12, that can be directly compared to the inelastic neutron scattering intensities. The right panel shows the dispersion relation along the A direction; although the T = 0 K DFT bands (white lines) have an LA-TO crossing, the MD results show a repulsion between LA and TO leading only to a contact between the two bands roughly midway along the Γ to X line. The left panel presents the power spectrum at the Γ point. The peak is very broad and a splitting...
starts developing. Since these features are already highly enhanced with respect to a $3 \times 3 \times 3$ supercell, we expect that an even larger supercell would allow a good description of the emergence of the additional phonon mode, as in previous experiments and (classical) MD simulations\textsuperscript{3,12–14}.}

Finally for this section, we show the effect of the displacement pattern linked with the pair correlations on the electronic structure, by plotting in Fig. 10 the calculated electron localization function (ELF) for a static configuration consistent with the inset at the lower right of Fig. 7. The ELF provides a measure of the valence charge density, weighted to emphasize regions of higher electron localization, and has been used effectively to analyze the electronic structure in the related ferroelectric IV-VI chalogenides\textsuperscript{28}, where their stereochemical activity drives the dipole formation in the ferroelectric state. The central Pb atom is the most strongly displaced from its high-symmetry position (indicated by the black dashed line) with the distortion amplitudes gradually reducing with distance from the center. In the top panel (a) the scale is chosen to illustrate the enhancement of the Pb-Te chemical bond as the Pb ions displace to the right towards their Te neighbors (at the centers of the orange regions). In the lower panel (b) the scale is chosen to emphasize the red “banana-shaped” localized electrons to the left of the displacing Pb ions, which form the stereochemically active lone pair. The stereochemical activity of this lone pair of electrons drives the displacement of the Pb ions and prevents the Te

---

**FIG. 6.** Longitudinal correlation coefficients along the cubic axis: (a) comparison at 300 K between diffuse-scattering extracted quantities (red triangles), and MD values [with the $6 \times 6 \times 6$ supercell]. The plateau and even small increase in the MD correlations for distances $2.5a$ and $3a$ is a consequence of periodic boundary conditions. (b) Temperature evolution of the experimental correlation coefficients. Whether the small temperature dependent spreads at a given distance are significant or if they are artefacts from incomplete models is not fully understood.

**FIG. 7.** Cartoon of pair correlations expected for different “phonon modes” along the (100) direction; in green for acoustic-like displacements, in light-blue for optic-like, and in purple for a superposition of the two. The effects are exaggerated to visualize the formation of steps.

**FIG. 8.** Properties derived from the Buckingham potential of Refs. 25 and 26. (a) Phonon density of states (DOS) [computed using the Phonopy package\textsuperscript{22}]; in blue with the Buckingham potential, in dashed red with CP2K. (b) Longitudinal correlation coefficients along the cubic axis at 300 K [with the $10 \times 10 \times 10$ supercell] computed using the Buckingham potential.
FIG. 9. Power spectrum $Z(q, \nu)$ at 300 K computed from the 6 × 6 × 6 supercell using ab-initio MD. The left panel shows $Z(q, \nu)$ at the $\Gamma$ point (arbitrary units are used). The right panel shows the dispersion relation along the $\Delta$-line. White lines correspond to $T = 0$ K DFT calculations.

ions from acquiring a similar displacement leading to dipole formation.

Note that our calculations are consistent with the reported long-ranged interactions along (100) through resonant bonding\textsuperscript{30} (or equivalently lone pairs) and the recent report of anisotropic microstrain along (100) in all lead chalcogenide systems by Christensen et al.\textsuperscript{31}. The latter paper argued that microstrain is a manifestation of the structural transition to an orthorhombic phase under pressure (in fact, the major atomic displacements in that phase transition are along (100)\textsuperscript{31}), based on what they call "anion-mediated Pb(6s)-Pb(6p) interaction", another term for the (revised) lone pair\textsuperscript{30} or resonant bonding\textsuperscript{30} concept.

C. Higher-order correlations

The correlation of bond lengths provides valuable information about the local dipoles present in the structure. However, bond-length correlations represent a many-body problem, which cannot be easily extracted from Bragg and diffuse scattering alone\textsuperscript{33}. To exceed this limitation we analyze the bond-lengths correlations from our MD simulations. Since we have shown that our MD reproduces the experimental pair correlations well, we are confident that our calculated higher-order correlations are physically relevant. Fig. 11 shows all computed correlations. To quantitatively assess the kind of correlation present between each pair of bonds we compared to a reference state in which the bonds are uncorrelated (see Fig. A2 in the Appendix); the latter was computed by considering all pairs of bonds at least 15 Å apart.

We start by showing the three-body correlations, i.e. the correlations between bonds that share an atom (Fig. 12; for our notation see Fig. 11). In general, the correlations should depend on the type of shared atom, so we present our results for both Pb and Te shared. Fig. 12 shows probability densities for three-body correlations. Bonds $B_3^3$ (lower panel) show a clear negative correlation – if one bond is longer than on average the other tends to be shorter. Note also that when the shared atom is Pb (d) the distribution is more elongated than for Te (e) – as already discussed Pb is more polarizable, leading to a larger variability in the bond distribution. In the same way, $B_1^3$ bonds (upper panel) show a negative correlation, even though the deviations from the reference state are smaller. However, here larger deviations are observed for

FIG. 10. Electron localization function (ELF) computed with the VASP\textsuperscript{29} code for a structure distorted according to the pattern of pair correlations shown in Fig. 6 with the central Pb ion in the 15×1×1 supercell given the largest distortion from its high symmetry position (vertical dashed line). The displacements towards the right of the figure are exaggerated to amplify the effects. Different magnitude ranges are chosen for the upper and lower panels to illustrate the increased Pb-Te bonding as the Pb moves right towards its neighboring Te (a) and the formation of the lone pair (small red lobe) left of the Pb ions (b).

FIG. 11. Notation of our computed higher-order correlations between pairs of nearby bonds. The reference bond (Bond 1 in the probability-density plots) is marked in black, with three-body correlations in green, four-body in purple, and correlations between diagonal bonds in orange. The lower panel shows a crystal plane lying above or below the upper panel (with the gray bond lying just on top or below the reference black bond). The upper index in our notation for higher-order correlations indicates the type of correlation (three- or four-body), and the lower enumerates them.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig11.png}
\caption{Notation of our computed higher-order correlations between pairs of nearby bonds.}
\end{figure}
FIG. 12. Difference probability densities of three-body correlations calculated from MD. The upper panel presents bonds $B_1^3$; the lower panel bonds $B_2^3$. The first and second columns show difference densities with respect to the reference when the shared atom is Pb and Te, respectively, while the third column shows the difference between the first and second column. The color scale represents the probability density in $\AA^{-3}$.

We next analyze the further apart bonds shown in Fig. A4 in the Appendix. By close inspection of the four-body correlations' probability densities, the following local picture can be derived (Fig. 13): The horizontal [100] line containing the reference bond shows a clear alternation of short and long bonds (i.e. negative correlations), resulting in a local "ferroelectric-like" arrangement of electric dipoles. The neighboring, parallel [100] lines show the same pattern with a "ferroelectric" coupling to the reference [100] line. The only exception is the $B_2^3$ bond which has a weak tendency to a positive correlation – strain and dipolar interaction are strong enough to counterbalance the ferroelectric coupling that would favor a negative correlation. On the other hand, the vertical [010] line also presents a ferroelectric-like arrangement of bonds, but with the formation of a "head-to-head domain wall" at the reference [100] line.

Note that the formation of ferroelectrically coupled ferroelectric-like [100] lines is not expected from the long-range dipole-dipole interaction, which would favor an antiferroelectric coupling of ferroelectric [100] lines. The origin of such a coupling may be found in short-range interactions depending on the chemistry of the environment, in this case the stereochemical activity of the lone pair. A similar competition was noted for the bulk ferroelectric behavior in perovskite BaTiO$_3$ by Nishimatsu et al. with the construction of an effective Hamiltonian. The authors showed that when only the dipole-dipole interaction is considered the most unstable phonon mode corresponds to the $M$ point – the most stable structure consists of an antiferroelectric cell-doubling state. Only when the short-range interactions are also included is the most unstable mode found at $\Gamma$ producing the actual ferroelectric state.

At first sight our findings in this section could seem in contradiction with our earlier discussion that the average structure remains high-symmetry rocksalt. However, the bond lengths averaged over all higher-order correlations are unchanged from those of the reference state, with the most probable bond length still found at $a/2$ (see Figs. A2-A4 in the Appendix). This hints at a reconciliation between the
conflicting descriptions – anomalous anharmonicity or off-centering – which we will explore further in the next section.

D. Local off-centering

Next we discuss the implications of these correlated dipoles in the context of the proposed off-centering. In particular, we show that the existence of correlated local dipoles is consistent with an average local Pb position which is centered in the Te coordination polyhedron. Figure 14 presents the deviations of the Pb atoms from the center of gravity of the PbTe$_6$ octahedra. Since it is also a many-body problem this information is not directly accessible from the diffuse scattering or the 3D-APDF data. Therefore we show only results from our MD simulations, which we justify by the good agreement in the local structure between MD and 3D-APDF. Clearly, the distribution is centered on the origin and a Gaussian profile cannot be excluded. Here, only the x − y plane is shown but the same conclusions are obtained also for all inequivalent [100], [110], and [111] directions. The same picture is obtained when considering the displacement of Te atoms with respect to the TePb$_6$ octahedra. So, we see that on average both Pb and Te atoms are not off-center but sit in the center of their coordination polyhedra, consistent with our previous finding of the most probable bond being at a/2

We next link this result with our previous discussion about correlated dipoles. In a specific unit cell, as we have just seen, the probability distribution for distortions is Gaussian without any preferential direction. As soon as one unit cell has chosen a distortion direction, however, the neighboring unit cells are no longer free to choose their distortion directions, since the pair and higher-order correlations impose a preferred orientation. The result is the development of regions of local polarity composed of correlated dipoles along the ⟨100⟩ directions. These distorted regions are randomly distributed in the crystal, however, such that averaging over them results in an (undistorted) rocksalt structure. From the decay of the higher-order correlations’ strength we can roughly estimate the extent of these correlated dipoles regions to be around 30 Å. These correlations may resemble local distortions in relaxor ferroelectrics, as in the analysis of the diffuse scattering by Bosak et al.$^{36}$

We emphasize the distinction from a static local off-centering, in which the interatomic potential would not have a single minimum, but would show other (meta-)stable states. This could result in an alternation of long and short bonds, with the formation of one shoulder on each side of the PDF peaks, or even of multi-valued peaks. Moreover, the distribution of the deviations with respect to the coordination polyhedra shown in Fig. 14 would not be Gaussian and may show multiple peaks.

We propose that our finding of correlated local dipoles combined with centered average Pb environments automatically resolves some of the controversy in the literature, which has been caused by differing interpretations of the meaning of “off-centering”, such as the root mean square$^{11}$ or absolute$^{10,12,13,15}$ displacement from the rocksalt positions. Here we show that the phenomenon called emphanisis is associated with the formation of correlated local dipoles which can both vary in orientation throughout the structure and fluctuate in time. As a result the positions of the ions are centered on average. The effect might be better referred to as correlated local dipole formation to avoid confusion in future works.

E. Radial pair distribution function analysis

Finally we show that our finding of local correlated dipoles is largely consistent with the peculiar features of the original pair distribution function (PDF) of Božin et al.$^{2}$ with the exception that the shoulders in the peaks are not reproduced by our MD simulations. To do this, we first compare the radial PDF $G(r)$ extracted from our MD simulations with the original data. We computed the PDF from the MD as a histogram of the interatomic distances and by taking into account the neutron scattering lengths (9.405 fm for lead and 5.80 fm for Te$^{37}$), with the experimental termination error from the finite $Q$ range of the Fourier transform ($Q_{\text{max}}$ set to 35 Å$^{-1}$), and scale by a factor of 0.89 to take into account the arbitrary scaling introduced by some of the applied data corrections.$^{38}$ Figure 15 compares the MD and measured PDFs at three different temperatures, 50 K (a), 450 K (b) and 300 K (c). As can
be seen, at the lowest temperature shown, 50 K (panel (a)), our MD calculations underestimate slightly the width of the nearest-neighbor peak – this may be ascribed to the underestimation of the ADPs originating, at this low temperature, from the lack of zero-point motion in the MD simulations. On the other hand, at the other two temperatures shown the agreement is remarkably good. Only the shoulder on the high-$r$ side of the peak at 450 K (panel (b)) is not captured. (The two small shoulders appearing at approx. 2.8 and 3.6 Å in the experimental data are probably artifacts; their position is consistent with the periodicity of the wiggles from the finite $Q$ range of the Fourier transform.) In particular, Fig. 15(c) shows that our MD simulations at 300 K capture not only the correlated motion of the nearest-neighbor peak at ~3.2 Å, but also the intriguing overly sharp lattice-repeat-distance peak of the original data. In Fig. 16 we compare our 300K MD data with a model that neglects correlated motion. We find the largest differences for the first and fourth peaks (marked by the red arrows in the figure), which are sharper (their calculated width, not shown, is smaller) than the second, third, fifth, and so on. The sharper peaks correspond to interatomic distances between atoms lying along the $\langle{100}\rangle$ directions, and their sharpness is a result of the pair correlations being positive, and strongest along the $\langle{100}\rangle$ direction.

While visual inspection suggests that the MD peaks are less asymmetric than the data, our quantitative analysis shows that the asymmetry is actually captured quite well, in particular the trend towards more asymmetric peaks with increasing temperature. For the computation of the asymmetry we first transform the PDF $G(r)$ to the radial distribution function (RDF) $R(r)$, such that its peaks’ shapes describe the underlying pair-probability distribution (for a Gaussian probability distribution the peaks are symmetric) and the baseline lies at zero. We define asymmetry in two different ways, the first being:

$$\Delta R_{ASYM} = \frac{\int_{r_0}^{r_0+\delta r} [R(r_0 + r) - R(r_0 - r)] \, dr}{\int_{r_0}^{r_0+\delta r} [R(r_0 + r) + R(r_0 - r)] \, dr},$$

the second defining a “relative error” with a Gaussian function,

$$\Delta R_{GAUSS} = \frac{\int_{r_0-\delta r}^{r_0+\delta r} R(r) - N_c \cdot e^{-((r-r_0)^2/2m_2^2)/\sqrt{2\pi m_2^2}} \, dr}{\int_{r_0-\delta r}^{r_0+\delta r} e^{-(r-r_0)^2/2m_2^2}/\sqrt{2\pi m_2^2} \, dr},$$

where $N_c = \int_{r_0-\delta r}^{r_0+\delta r} R(r) \, dr$ is the coordination (area of the peak), and $m_2$ is the variance of the peak. If the peak is not only asymmetric but also displays shoulders, the Gaussian parameter, $\Delta R_{GAUSS}$ should be a better indicator than others relying on a difference between high- and low-$r$ sides. Figure 17 shows the temperature evolution of the two asymmetry parameters calculated from our ab-initio MD simulations (blue), from the original data by Božin et al.\textsuperscript{2} (red), and from the Buckingham potential (green). Both asymmetry parameters deliver a constantly increasing asymmetry with temperature for the nearest neighbor peak in good agreement with the experimental data by Božin et al.\textsuperscript{2}. The next nearest neighbor peak is more symmetric, but shows increasing deviations from a Gaussian profile too. Note that using the skewness as a measure of the asymmetry leads to the same conclusions.

Next, we subject the PDFs obtained from our MD simulations to the same small-box fitting protocols as in the original PDF study.\textsuperscript{2} We used the PDFgui package and set all experimental setup related parameters (scale factor, $Q$-space resolution and related damping in $r$-space) to ideal values. Various models were refined over a narrow $r$-range up to 6 Å,
FIG. 17. Asymmetry parameters of the first two peaks of the RDF as a function of temperature. The top panels (a)-(b) show the asymmetry parameters for the nearest-neighbor peak, while the bottom panels (c)-(d) for the next nearest neighbor peak. The left panels (a) and (c) present the asymmetry parameter $\Delta R_{\text{ASYM}}$, while the right panels (b) and (d) $\Delta R_{\text{GAUSS}}$. Blue symbols are obtained from our ab-initio MD simulations (blue stars correspond to the larger supercell), red symbols are from the original data of Božin et al.\textsuperscript{7}, and green symbols are from the Buckingham potential.

FIG. 18. Comparison of different structural models fit to our MD simulations. (a) Quality of the fit through the $\chi^2$ goodness parameter; (b) “off-centering” displacement, $\Delta r$, extracted for the two most probable (split) models compared to the data extracted from the study by Božin et al.\textsuperscript{7} with the temperature correction proposed in Ref. 7.

FIG. 19. Representation of how anharmonicity can be introduced in real-space refinement utilities through split models.

some with lead displacements allowed and some not: the cubic $Pn3m$ rocksalt ($\langle 000 \rangle$); $\langle 100 \rangle$ and ($111$) models, where the lead sublattice is allowed to shift with respect to the Te sublattice in the specified direction; a $\langle 100 \rangle$ PbO-like model, where a tetragonal cell is used and lead is allowed to displace in a pattern similar to that in PbO. In Fig. 18(a) we show the quality of the fits, measured by the $\chi^2$ parameter, as a function of temperature for the various models. We see that the cubic model does progressively worse with increasing temperature, while the best fit is produced by the $\langle 100 \rangle$ PbO-like model in particular at higher temperatures, consistent with the original experimental observation\textsuperscript{5}. Note that the $\langle 111 \rangle$ model also gives reasonably good fits. Next we extract an “off-centering” displacement from the two best models and show our results in Fig. 18(b). The resulting values are in good agreement with the original reported values in Ref. 2 (light blue symbols).

While this finding of off-centering might seem to contradict our finding above that the Pb ions are at the center of their Te coordination polyhedra, in fact it is a consequence of the interpretation and use of split models in current real-space refinement utilities. In fact, the small-box modeling software, PDFgui, is not designed to handle anharmonic effects, and instead uses Gaussian distribution shapes. Instead of accounting for anharmonic effects directly, these effects are handled indirectly via discrete bond-length distributions and partial occupancies (split models). Consider the situation shown in Fig. 19: on the left a split model is considered, with each split position (50% occupancy) described by a Gaussian and separated by the “off-centering” $2\Delta r$. However, the sum of the two Gaussians (right) results in a pseudo-Gaussian distribution that mimics an anharmonic potential. This means that if the final distribution of a split model is not multivalued, anharmonicity and off-centering can not be distinguished. It would be therefore desirable to upgrade real-space refinement procedures with anharmonic features to avoid confusion in the description of strongly anharmonic systems such as the group IV chalcogenides.

F. Origin of the peak asymmetry

Finally, we discuss the origin of the unusual behavior and conflicting literature reports in light of our new measurements and calculations. First we address the relationship between the asymmetry of the peaks and the anharmonicity of
the PbTe potential. In the previous studies that did not find any off-centering\textsuperscript{10,12–15}, the well-known anharmonicity of PbTe was considered to be the sole cause of asymmetry. Indeed, an anharmonic potential, such as the Buckingham potential used above, can explain alone (part of) the asymmetry. Figure 17 shows that also the Buckingham potential produces an increased asymmetry with good agreement with the data from Ref. 2. On the other hand, anharmonicity alone is not enough to explain the peculiar decay of the pair correlations presented in Fig. 6, since we showed that the Buckingham potential does not lead to steps in the pair correlations (see Fig. 8).

Next, we show that the correlated dipoles can further amplify the peak asymmetry. Figure 20 shows results of calculations using VASP for a cubic supercell containing one long and one short bond. The length of these two bonds was chosen to differ by about 10\% from the equilibrium bond length, giving values of 3.5 Å and 2.94 Å. The large weight in the probability densities of Fig. 12(d)-(e) corresponding to these bond lengths shows that they are a reasonable choice. One of the bonds was changed, while the other was kept fixed, and the energy was calculated. One can see that when the short bond is varied (fixed long bond) the energy curve is steeper than when the long bond is changed (fixed short bond), because of the asymmetry of the crystal field. This produces a narrower distribution for short bonds than long ones, resulting in an overall asymmetric distribution of bonds (see right panel in Fig. 20). Thus, the alternation of short and long bonds provides another microscopic contribution to peak asymmetry.

We note that the previously reported shoulder on the first PDF peak, which was interpreted as a local off-centering of the Pb-Te bonds, is not reproduced either in our molecular dynamics simulation or diffuse scattering (nor elsewhere in the literature). Therefore, any additional physics associated with the existence of this peak are not captured by our analysis. Possible reasons for its absence in our molecular dynamics simulations are an insufficiently large supercell, or the absence of spin-orbit coupling in the calculations. We note, however, that the existence of such a shoulder is not essential for emphanitic behavior, which we find in our MD simulations and which has been reported for other materials such as CsSnBr\textsubscript{3}\textsuperscript{37}, where shoulders are lacking.

**III. RELEVANCE FOR THERMOELECTRICITY**

In this last section, we discuss the relevance of our findings for the well-known thermoelectric performance of PbTe\textsuperscript{40–47}. The fluctuating correlated local dipoles will likely contribute to phonon scattering; here we show that they should also influence the electronic behavior. It is well-known that lone-pair expression is beneficial for thermoelectric performance\textsuperscript{38,49}, since it tends to open electronic band gaps and suppress bipolar conduction of carriers. The electronic structure of PbTe indicates a further mechanism to increase its performance, that is the presence of a secondary pocket along the Σ line with an energy slightly lower than those of the $L$ pocket, where the band gap can be found\textsuperscript{50}. By reducing the band offset between $L$ and Σ pockets the valley degeneracy can be increased ($L$ pockets have a valley degeneracy of 4, while that of Σ pockets is 12), and consequently also the power factor\textsuperscript{42,43,49,51–53}. Experimentally, in pristine PbTe this decrease in the offset happens with increasing temperature, with a proposed convergence at about 700 – 800 K\textsuperscript{46,57}. The band offset can also be controlled by K or Na co-doping such that the thermoelectric power factor is enhanced through the tuning of the interaction between the $L$ and Σ bands\textsuperscript{42}.

In an attempt to link the correlated dipoles to the high thermoelectric performance of PbTe we show in Fig. 21 the band gap and band offset between $L$ and Σ pockets as a function of a polar distortion along ⟨100⟩. Here we use a structure with the extreme situation of a ferroelectric distortion along ⟨100⟩, with aligned static stereochemically active lone pairs\textsuperscript{46}. As expected, we find that lone-pair expression is accompanied by an increase of the band gap (panel (a)). More importantly, the band offset (panel (b)) decreases with increasing distortions, so that the band gap becomes indirect for displacements above about 0.2 Å. While the cooperative ferroelectric distortion analyzed here of course differs from the actual correlated local dipole behavior, we expect that the trends will be similar, with the amplitude of distortion in our calculations playing the role of temperature in the experiments. Thus, the correlated dipole regions likely contribute to the high thermoelectric performance of PbTe by affecting both the electronic and phononic components.
IV. SUMMARY

In summary, we have performed a combined x-ray scattering and \textit{ab initio} molecular dynamics study of the lattice behavior of PbTe, and analyzed our results in the context of earlier PDF studies that suggested a local Pb-Te off-centering. The presented 3D-\textDelta PDF analysis provides a detailed quantitative picture of the atomic pair correlations up to distances of about 60 Å. This allows a comprehensive insight into the local structure of PbTe, and also demonstrates the power of the 3D-\textDelta PDF method for analyzing the local structure of disordered crystals.

We find a close consistency between our Bragg and diffuse x-ray scattering measurements and our molecular dynamics simulations. At the bulk level, both our Bragg scattering measurements and our calculations yield non-Gaussian peaks, indicative of significant anharmonic behavior. At the local level, both our diffuse scattering and MD simulations find a distinctive and unusual stepwise decay with distance in the pair correlation functions. This excellent match allows us to further analyze our molecular dynamics results to extract detailed information about the atomic positions and dynamics – including higher-order correlation functions – that can not be easily obtained from experiment.

Our main finding is the unusual correlated local dipole formation, exemplified by Fig. 6, in which a displacement of an ion along a cubic axis causes correlated displacements in the atoms in neighboring cells that do not show the usual smooth decay with distance. Instead, the correlations indicate a tendency for anion-cation dimerization, and the resulting formation of local dipoles, in the direction of displacement. This behavior can be interpreted as a superposition of an acoustic phonon mode, which alone would displace all atoms in the same direction and would decay smoothly with distance, with an optical phonon mode, which causes opposite atomic displacements and therefore is responsible for the step-like behavior. Thermal activation of an optical phonon mode is clearly required for such an effect, and is possible in PbTe because of the soft transverse optical phonon mode associated with the proximity to the ferroelectric phase transition. Since the essential ingredient for the observed local structure is a coherent superposition of soft optic phonon modes with acoustic modes, similar behavior should occur, in principle, close to any ferroelectric phase transition. In this respect, it would be interesting to search for such correlated local dipole behavior above the transition temperature in ferroelectric phase transitions that have been previously regarded as displacive. The finding using EXAFS spectroscopy that the local distortions associated with the ferroelectric state in GeTe persist essentially unchanged on heating to the paraelectric phase, might indeed be an indicator of emphasis\textsuperscript{38}.

Importantly, this correlated dipole formation does not translate into an average off-centering of the ions from the centers of their coordination polyhedra. Analysis of our simulations indicates that the most probable ionic position, averaged over time or space, is at the center of the polyhedron, with a smooth decrease in probability away from that point. This is consistent with different regions of the material having different orientations and amplitudes of correlated dipole formation, and with a local but not global symmetry breaking of the cubic symmetry. The question of "off-centered or not" that has recurred throughout the literature is therefore perhaps not the right question to ask in this case.

Finally, we suggest that the correlated dipoles and the associated distortions along \text{\langle 100 \rangle} are beneficial for the high thermoelectric performance of PbTe. First, the coupling between acoustic and optic phonons (as was already shown in Ref. 4) and the regions with different orientations of the correlated dipoles in the crystal may increase the phonon scattering, consequently decreasing the thermal conductivity. Second, the distortions along \text{\langle 100 \rangle} may explain two electronic features that are thought to be necessary to explain the thermoelectric performance, the increase of the band gap with temperature and, at the same time, the band convergence of the \text{L} and \text{\Sigma} pockets.

ACKNOWLEDGMENTS

BS, MF and NAS acknowledge support from ETH Zürich, the ERC Advanced Grant program (No. 291151), and the Swiss National Supercomputing Centre (CSCS) under project IDs s307, s624 and p504. We thank Joost VandeVondele for helpful discussions, in particular regarding the use of the CP2K code. TW thanks the staff of the X06SA beamline at the Swiss Light Source, Villigen, Switzerland for giving access to the beamline and for helping with the experiments. Work at Brookhaven is supported by the U.S. DOE under contract No. DESC00112704.

2 E. S. Božin, C. D. Malliakas, P. Souvatzis, T. Proffen, N. A. Spaldin,

APPENDIX

Appendix A: Methods

1. Sample Preparation

Single crystals of PbTe were prepared by mixing stoichiometric amounts of Pb (Rotometals, at 99.9 % purity) and Te (Plasmatreat GmbH, at 99.999 % purity) in an evacuated fused silica ampoule. The total amount of PbTe was 15.346 g and the length of the ampoule was approximately 18 cm. The ampoule was placed in a box furnace, heated to 1050 °C over 16 h, and held at that temperature for 36 h. The sample was then cooled to room temperature in 24 h. Small single crystals (10 – 100 µm) were formed on the top part of the ampoule. Several crystals were screened on a STOE IPDS 2T diffractometer for quality evaluation.

2. X-ray diffraction

The single crystal used for the X-ray experiments was an irregularly shaped fragment with an average diameter of about 42 µm. The experiment was done at the X06SA beamline at SLS, Villigen, Switzerland, which was equipped with a single axis goniometer and a PILATUS 6M detector. The synchrotron storage ring was operated in top-fill mode to deliver constant primary intensities. Full data sets (3600 frames, 0.1° rotation and 0.1 s exposure time per frame, wavelength 0.7085 Å, crystal - detector distance 185 mm) were recorded in the sequence room temperature, 250 K, 200 K, 150 K and 125 K. The experimental setup did not allow access to temperatures above room temperature. The primary beam was normal to the rotation axis and to the detector plane. The detectors’ energy threshold for accepting X-rays photons was set to 16 keV (energy of primary beam 17.5 keV) to suppress fluorescence scattering as much as possible. In addition, 100 frames were collected under the same conditions as in the diffuse scattering measurements, but without sample and sample holder. These frames were averaged and taken as a model for background scattering.

A Bragg data set collected with a strongly attenuated beam did not deliver satisfactory results, as the internal R-value was well above 0.2 (the internal R-value is defined as \( R_{\text{int}} = \frac{\sum |F_h| - |\langle F_h \rangle|}{\sum |F_h|} \)), where the summations run over all reflections for which more than one symmetry equivalent reflection is averaged, \(|F_h|\) is the corrected intensity of a reflection and \(|\langle F_h \rangle|\) is the corresponding symmetry-averaged intensity)

even for the triclinic Laue group. Reasons may be strong multiple scattering effects and/or unresolved saturation problems of the detector. We therefore repeated the Bragg data collection using our in-house Xcalibur Oxford Diffraction diffractometer (Mo Kα radiation, graphite monochromator, sealed tube, Onyx CCD detector, \(\theta_{\text{max}} = 45.3°, -12 < h, k, l < 12\) same crystal and temperatures as used in the synchrotron experiments).

3. Diffuse scattering data reduction

Reciprocal space reconstructions were done with the program XCAVATE\(^{27}\). Reconstructions were mapped onto a 360 × 360 × 360 voxel volume covering the reciprocal space within the limits \(-9 \leq h, k, l \leq 9\). Since the half-widths of the Bragg reflections were significantly smaller than the pixel size of the reconstructions, it was assumed that the experimental reciprocal space resolution function can be ignored to a good approximation. In contrast to the Bragg data, the diffuse scattering was corrected using a spherical absorption model for sake of simplicity. It is not expected, however, that this simplification will introduce significant systematic errors. For comparison, Bragg data corrected by spherical absorption correction resulted in slightly higher \(R_{\text{ex}}\) values (0.11 vs. 0.078 using the analytical approach, see below), but the refined structure parameter values from those data changed only by a few percent compared to the results obtained with analytical absorption correction. It is not expected that the choice of the absorption correction method would have a large impact on the results extracted from the diffuse data. Finally, the data were averaged following the Laue symmetry \(m\overline{3}m\). Individual voxels were rejected as outliers according to the procedure described in Blessing\(^{60}\). A voxel was rejected if its difference to median value of symmetry equivalent voxels was more than about six times the median difference (for details see Ref. 60, Eqs. 16, 17 with \(c_1, c_2, c_3 = 0, c_4 = 6\)). This procedure turned out to be very helpful in eliminating most of the parasitic scattering that is not compatible with the Laue symmetry of the single crystal diffraction pattern, such as scattering from small grains attached to the surface or secondary air scattering from strong reflections. Finally, the background was subtracted from the diffuse data. It was expected that the empirical experimental background obtained as described above would show slightly smaller background intensities compared to the background seen with the crystal, because scattering from the sample

\[\sum |F_h| - |\langle F_h \rangle| / \sum |F_h| \]
holder and from glue were not included in the background measurements. To our surprise we found, however, that the empirical background determination showed slightly larger intensities compared to those observed in the diffuse scattering measurements. This observation may be explained by the fact that the primary beam gets attenuated by the crystal and therefore the air scattering coming from the pathway between crystal and beam stop is reduced. To partly compensate this effect we multiplied the empirical background by a factor of 0.9 to avoid larger regions of negative intensity after correction.

4. Bragg data absorption correction

The high absorption coefficient of \( \mu = 75.5 \text{ mm}^{-1} \) required careful absorption correction. Various strategies provided by the program CrysAlisPro were tried, namely analytical absorption correction based on a graphical estimate of the crystal’s morphology and its orientation relative to the diffractometer coordinate system, spherical absorption correction, empirical absorption correction and combinations of analytical/empirical, spherical/empirical and analytical/optimised crystal shapes approaches. The best internal R-value \( (R_{\text{int}} = 0.064) \) was obtained from the analytical/optimised crystal shapes method, however, the optimised crystal shape did not well match the morphology of the sample and the results were therefore rejected to avoid overcorrection. The second best results were obtained from the analytical approach and from the combination analytical/empirical absorption correction \( (R_{\text{int}} = 0.078 \text{ in both cases}) \). Since the latter did not deliver better data, the results obtained from the analytical correction method were used in our refinements.

5. Computational details

Our ab-initio molecular dynamics simulations were performed using the CP2K code with the hybrid Gaussian and plane wave (GPW) scheme. Gamma-point only calculations were performed with a plane wave cut-off of 500 Ry. We performed GGA calculations with the PBEsol exchange-correlation functional (shown to provide the best overall agreement with experimental structural and electronic properties) and Goedecker-Teter-Hutter (GTH) pseudopotentials. We used valence electron configurations \( 6s^{2}6p^{2} \) for lead, and \( 5s^{2}5p^{4} \) for tellurium. Spin-orbit coupling was not included. Calculations were performed with a \( 3 \times 3 \times 3 \) supercell of the conventional (cubic) cell (216 atoms) at temperatures between 50 K and 500 K in steps of 50 K. Long simulations (150 ps) in the isothermal-isobaric \( (NpT) \) ensemble using the thermostat developed by Bussi et al. and the Berendsen barostat were performed, followed by 150 ps production runs in the microcanonical \( (NVE) \) ensemble. The timestep used was 2 fs. To check for finite-size effects, one run with a \( 6 \times 6 \times 6 \) supercell (1728 atoms) was performed at 300 K with a reduced simulation time of \( 60 \times 60 \text{ ps} \); this run was also used to analyze in detail the local structure.

VASP calculations were performed using the PAW implementation of density functional theory (DFT). We used the PBEsol exchange-correlation functional and a plane-wave energy cutoff of 600 eV. For the \( 1 \times 1 \times 1 \) supercell we used a \( 1 \times 1 \times 1 \) centered \( k \)-point mesh, while for the \( 3 \times 1 \times 1 \) supercell we used a \( 5 \times 15 \times 15 \) \( k \)-point mesh. Spin-orbit coupling was not included. We used valence electron configurations \( 5d^{10}6s^{2}6p^{2} \) for lead and \( 5s^{2}5p^{4} \) for tellurium. The unit cell volume was fixed to the equilibrium value (lattice constant of 6.44 Å to be compared with the experimental lattice constant of 6.43 Å) obtained with a full structural relaxation.

LAMMPS MD simulations were performed with a \( 6 \times 6 \times 6 \) and a \( 10 \times 10 \times 10 \) supercell of the conventional (cubic) cell (1728 and 8000 atoms) at temperatures between 100 K and 500 K in steps of 50 K. 150 ps simulations in the isothermal-isobaric \( (NpT) \) ensemble using the thermostat developed by Bussi et al. and the Berendsen barostat were performed, followed by 150 ps production runs in the microcanonical \( (NVE) \) ensemble. The timestep used was 2 fs.

6. Design and refinement of the 3D-APDF model

The 3D-APDF maps were obtained as the Fourier transform of the diffuse diffraction pattern, with the Bragg reflections cut out from the diffraction pattern as follows: To be sure that the tails from very strong Bragg peaks were eliminated, volumes of \( 3 \times 3 \times 3 \) voxels centered at the Bragg positions were set to zero. As the strong diffuse scattering maxima coincide with the Bragg peaks it is not possible to cleanly separate Bragg from diffuse scattering without having additional information available. The impact of cutting the Bragg peaks and diffuse scattering at the same time was shown to only significantly impact the long 3D-APDF vectors, while densities at short vectors are almost unaffected by this procedure. In contrast to Refs. 73 and 74 we did not fill the punched Bragg regions with the average of the surrounding, but with zero values. As a consequence some artifacts are present at larger PDF vectors, where the 3D-APDF densities are expected to become very weak. In the least squares 3D-APDF refinements, the cut-out volumes were ignored by giving them zero weights.

Theory: The local structure properties of PbTe were refined with the 3D-APDF modeling program YELL. In the following we summarize the fundamentals of the 3D-APDF theory of displacive disorder.

In the harmonic approximation, the diffuse scattering of a compound showing displacive disorder may be calculated as:

\[
I_{\text{d},\text{diff}}(h) = \sum_{R_{\text{iso}}} \sum_{\text{cell}} \left[ \exp(-h^2 \beta_{\text{iso}} \text{R}_{\text{iso}}^2) - \exp(-h^2 (\beta_{\text{iso}} \text{R}_{\text{iso}}^2 + \beta_{\text{cont}} \text{R}_{\text{cont}}^2)) \right] f_{m}(h) f_{n}(h) \cos[2 \pi h (R_{\text{iso}} + \text{R}_{\text{cont}})].
\]

(A1)
The summations run over all atomic pairs with significantly correlated displacements. \( \mathbf{r}_{uw} \) is the lattice vector between the unit cells hosting the correlated atoms \( m \) and \( n \) and \( r_{mn} \) is the average distance between the sites \( n \) and \( m \) within a unit cell, i.e. \( \mathbf{r}_{uw} + r_{mn} \) is the average vector between atoms \( m \) and \( n \). The average ADPs \( f_{u}^m \) and \( f_{u}^n \) as well as \( r_{mn} \) are taken from the average structure and \( f_{u}^m \) and \( f_{u}^n \) are the conventional atomic form factors. The structural information about displacive correlations is stored in the 3×3 matrix \( \beta_{uw}^{mn} \), whose elements are defined as

\[
\beta_{uw,i}^{mn} = (u_i^n - u_i^m)(u_i^n - u_i^m)_{uw} \\
= \beta_{u,i}^m + \beta_{u,i}^n - 2(u_i^m u_i^n)_{uw} \tag{A2}
\]

where \( u_i^n \) is the \( i \)-th vector component of the displacement of atom \( n \) from its average position in fractional units and \( \langle \cdots \rangle_{uw} \) indicates space and time averaging of joint displacements of all atoms \( m \) and \( n \) that are \( uw \) unit cells apart. The displacement covariances

\[
\text{Cov}_{uw,i}^{mn} = \langle u_i^m u_i^n \rangle_{uw} \tag{A3}
\]

are the structural variables that are optimized in YELL. For a more convenient comparison of the joint displacements of atoms we define the correlation matrix \( \text{Cov}_{uw,i}^{mn} \) with the matrix elements

\[
\text{Cov}_{uw,i}^{mn} = \frac{\langle u_i^m u_i^n \rangle_{uw}}{\sqrt{\beta_{u,i}^m} \sqrt{\beta_{u,i}^n}} \tag{A4}
\]

whose numerical values may range between -1 and 1. The extreme values represent perfect anti- and in-phase correlations, respectively.

**Defining the model.** For modeling the real structure we refer to the harmonic average structure displacement model, because it implies no arbitrary constraint such as \( U_{iso} = U_{iso} \). Furthermore, the probability density functions of the harmonic and split models are very similar and the choice of the average structure model is not expected to have a major impact on the extracted information.

The exponential decay was assumed to be along the main crystallographic axes, because the 3D-APDF maps clearly indicate that the correlations are strongest along such directions. In the case of very weak signals it was not possible to refine \( a_{u}^{mn}_{uw,ij} \) and \( b_{u}^{mn}_{uw,ij} \) independently without obtaining strong numerical correlations. Reasonable fits were then obtained with the constraint \( b_{u}^{mn}_{uw,ij} = 1 \), which was found by trial-and-error, and only \( a_{u}^{mn}_{uw,ij} \) was refined. The Laue symmetry \( m\overline{3}m \) was applied to all pair correlations. The final model comprised 363 independent parameters to be optimized against the diffuse diffraction data at each temperature. Even with this reduced number of parameters, computer memory limitations did not allow refinement of all parameters at the same time, given the large number of voxels in the refinement. The models were therefore refined in blocks of about 30 parameters and the process was repeated until no further improvements could be observed. A single least-squares run took about one to two hours on a modern computer.
desktop computer. In total a full refinement took about two working days per temperature point. The results of the refinements are shown in Figs. 3 and 4. In general the agreement between the observed and refined intensities or PDF densities is very good and the R-values are very low given the weak diffuse intensities \( R(125\,\text{K}) = 0.20, R(150\,\text{K}) = 0.19, R(200\,\text{K}) = 0.17 \), \( R(250\,\text{K}) = 0.15 \), \( R(293\,\text{K}) = 0.14 \); here R-values are defined as \( R = \frac{\sum (I_{obs,i} - I_{ref,i})^2}{\sum I_{obs,i}} \), where the summations run over all \( i \) voxels that were observed and not cut-out. The increase of R-values at lower temperatures might be explained by the decreasing integral diffuse scattering intensities, which lead to lower signal-to-noise levels in the experimental diffuse data. Major disagreements between observed and refined \( \Delta \text{PDF} \) densities are found along the \( \langle 100 \rangle \) directions, probably due to anharmonic contributions in the pair correlation functions that are not covered by our harmonic 3D-\( \Delta \text{PDF} \) model. The anharmonicities are extended over long distances and increase as a function of temperature, consistent with the observations of Ref. 2. As a consequence of computational and experimental limitations the achievable PDF space resolution is much lower in the single crystal cases as compared to powder PDF studies. Thus, a more detailed analysis of the anharmonic effects is not possible in the present case. The observation of long correlation lengths of anharmonic displacements clearly supports the interpretation of Ref. 2 that this anharmonicity is not just a consequence of asymmetric pair potentials, but reflects some collective structural distortion over long distances. The anharmonic pair correlations are also seen in the \( I_{obs} \sim I_{\text{ref}} \) maps, where significant asymmetries along \( h00 \) directions with respect to integer \( h \) positions are observable. A size-effect like distortion, which is frequently made responsible for such asymmetries, can be excluded because of the absence of substituitional disorder.

Appendix B: Comparison of the obtained pair correlations

Table A1 presents an overview of our refined and calculated pair correlations for distances up to two unit cells along each direction. Note the good agreement between the 3D-\( \Delta \text{PDF} \) and the MD values.

Appendix C: Average atomic displacements from the MD simulations

Fig. A1 shows the average displacement of the atoms from the rocksalt positions during the simulation at 300 K. Consistent with previous MD simulations they are negligibly small.

Appendix D: Higher-order correlations

In this section we present probability densities for the higher-order correlations that were not shown in the main text. We start by showing in Fig. A2 the reference state, which represents the uncorrelated bonds; for its computation all pairs of bonds at least 15 Å apart were considered. One can see that the most probable bond length can be found at \( a/2 \). Note also the asymmetry in the distribution with a longer tail in the direction of longer bonds, consistent with the asymmetry of the nearest-neighbor PDF peak. In fact, by integrating out one of the bonds we directly obtain the radial distribution function \( R(r) \). Next, in Fig. A3 we show the probability densities for the three-body correlations. The dependence on the type of shared atom can be clearly recognized. Note that the negative correlation of \( B_2^3 \) bonds can be observed already by visual inspection. This is not the case for more distant four-body correlations.

Finally, Fig. A4 presents all computed four-body correlations. Note the different color scale in the different panels showing the decay in correlation strength.
FIG. A4. Difference probability densities with respect to the neutral reference of four-body correlations. The color scale represents the probability density in Å⁻². Note the different color scale in the panels showing the decay in correlation strength.
TABLE AI. Pair correlation coefficients \( \rho(x, y, z) \) within the asymmetric unit of the 3D-PDF space up to a maximum distance of two unit cells along each direction; \( \Delta x = (u, v, w) \) is the interatomic vector in fractional units. The 3D-APDF values (labeled as Exp.) were obtained at room temperature, while the MD values at 300 K. In the experimental results Pb/Pb and Te/Te correlations cannot be distinguished but are subject of a combined refinement as described in Appendix A.6. The definition of the correlation coefficients is also described there.

<table>
<thead>
<tr>
<th>( \Delta x )</th>
<th>Pairs</th>
<th>Source</th>
<th>( \rho_{11} )</th>
<th>( \rho_{12} )</th>
<th>( \rho_{13} )</th>
<th>( \rho_{23} )</th>
<th>( \rho_{33} )</th>
<th>( \rho_{22} )</th>
<th>( \rho_{32} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>Homo</td>
<td>Exp.</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.5</td>
<td>PbPb</td>
<td>MD</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.4879</td>
<td>0.1602</td>
<td>0.1602</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0178</td>
<td>0.0499</td>
<td>0.0499</td>
<td>0.0060</td>
<td>0.0060</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>0.0178</td>
<td>0.0499</td>
<td>0.0499</td>
<td>0.0060</td>
<td>0.0060</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>0.0178</td>
<td>0.0499</td>
<td>0.0499</td>
<td>0.0060</td>
<td>0.0060</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.0853</td>
<td>0.0853</td>
<td>0.0853</td>
<td>0.0074</td>
<td>0.0074</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Homo</td>
<td>Exp.</td>
<td>0.1079</td>
<td>0.0333</td>
<td>0.0333</td>
<td>0.0054</td>
<td>0.0054</td>
<td>0.0054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>0.1079</td>
<td>0.0333</td>
<td>0.0333</td>
<td>0.0054</td>
<td>0.0054</td>
<td>0.0054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>0.1079</td>
<td>0.0333</td>
<td>0.0333</td>
<td>0.0054</td>
<td>0.0054</td>
<td>0.0054</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.0873</td>
<td>0.0278</td>
<td>0.0198</td>
<td>0.0052</td>
<td>0.0052</td>
<td>0.0052</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0178</td>
<td>0.0499</td>
<td>0.0499</td>
<td>0.0060</td>
<td>0.0060</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>0.0178</td>
<td>0.0499</td>
<td>0.0499</td>
<td>0.0060</td>
<td>0.0060</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>0.0178</td>
<td>0.0499</td>
<td>0.0499</td>
<td>0.0060</td>
<td>0.0060</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td>Ax</td>
<td>Pairs</td>
<td>Source</td>
<td>(C_{\alpha_1})</td>
<td>(C_{\alpha_2})</td>
<td>(C_{\alpha_3})</td>
<td>(C_{\alpha_1})</td>
<td>(C_{\alpha_2})</td>
<td>(C_{\alpha_3})</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
<td>--------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>2.0 0.5 0.5</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0391</td>
<td>0.0184</td>
<td>-0.0125</td>
<td>0.0040</td>
<td>0.0040</td>
<td>0.0027</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>0.0376</td>
<td>-0.0008</td>
<td>0.0021</td>
<td>0.0015</td>
<td>0.0020</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>0.0568</td>
<td>0.0053</td>
<td>-0.0092</td>
<td>0.0015</td>
<td>0.0020</td>
<td>0.0012</td>
<td></td>
</tr>
<tr>
<td>2.0 1.0 0.0</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0583</td>
<td>0.0215</td>
<td>0.0128</td>
<td>0.0073</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>0.0365</td>
<td>-0.0041</td>
<td>-0.0072</td>
<td>0.0062</td>
<td>0.0004</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>0.0379</td>
<td>-0.0030</td>
<td>-0.0061</td>
<td>0.0036</td>
<td>0.0000</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>2.0 1.0 0.5</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.0420</td>
<td>0.0212</td>
<td>0.0141</td>
<td>0.0028</td>
<td>0.0015</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MD</td>
<td></td>
<td>0.0193</td>
<td>-0.0057</td>
<td>-0.0073</td>
<td>0.0013</td>
<td>0.0003</td>
<td>-0.0001</td>
<td></td>
</tr>
<tr>
<td>2.0 1.0 1.0</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0308</td>
<td>0.0156</td>
<td>0.0156</td>
<td>0.0027</td>
<td>0.0027</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>0.0070</td>
<td>-0.0021</td>
<td>-0.0132</td>
<td>0.0017</td>
<td>0.0010</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>0.0100</td>
<td>-0.0029</td>
<td>-0.0133</td>
<td>0.0001</td>
<td>-0.0011</td>
<td>0.0013</td>
<td></td>
</tr>
<tr>
<td>2.0 1.5 0.0</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.0329</td>
<td>0.0202</td>
<td>0.0114</td>
<td>0.0054</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MD</td>
<td></td>
<td>0.0040</td>
<td>-0.0046</td>
<td>-0.0109</td>
<td>0.0045</td>
<td>0.0001</td>
<td>-0.0002</td>
<td></td>
</tr>
<tr>
<td>2.0 1.5 0.5</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0274</td>
<td>0.0168</td>
<td>0.0099</td>
<td>0.0050</td>
<td>0.0016</td>
<td>0.0016</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>-0.0010</td>
<td>-0.0053</td>
<td>-0.0103</td>
<td>0.0023</td>
<td>0.0018</td>
<td>0.0019</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>0.0020</td>
<td>-0.0047</td>
<td>-0.0125</td>
<td>0.0013</td>
<td>0.0004</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>2.0 1.5 1.0</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.0230</td>
<td>0.0152</td>
<td>0.0113</td>
<td>0.0025</td>
<td>0.0015</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MD</td>
<td></td>
<td>-0.0066</td>
<td>-0.0102</td>
<td>-0.0124</td>
<td>0.0003</td>
<td>0.0005</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>2.0 1.5 1.5</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0163</td>
<td>0.0104</td>
<td>0.0104</td>
<td>0.0023</td>
<td>0.0023</td>
<td>0.0020</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>-0.0117</td>
<td>-0.0107</td>
<td>-0.0131</td>
<td>0.0006</td>
<td>0.0012</td>
<td>0.0020</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>-0.0121</td>
<td>-0.0121</td>
<td>-0.0160</td>
<td>0.0006</td>
<td>-0.0002</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td>2.0 2.0 0.0</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0211</td>
<td>0.0211</td>
<td>0.0062</td>
<td>0.0081</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>-0.0043</td>
<td>-0.0032</td>
<td>-0.0226</td>
<td>0.0073</td>
<td>-0.0039</td>
<td>-0.0033</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>-0.0068</td>
<td>-0.0050</td>
<td>-0.0217</td>
<td>0.0022</td>
<td>0.0004</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>2.0 2.0 0.5</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.0187</td>
<td>0.0187</td>
<td>0.0076</td>
<td>0.0042</td>
<td>0.0005</td>
<td>0.0005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MD</td>
<td></td>
<td>-0.0078</td>
<td>-0.0074</td>
<td>-0.0208</td>
<td>0.0015</td>
<td>0.0007</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>2.0 2.0 1.0</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0150</td>
<td>0.0150</td>
<td>0.0069</td>
<td>0.0034</td>
<td>0.0012</td>
<td>0.0012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>-0.0111</td>
<td>-0.0109</td>
<td>-0.0202</td>
<td>0.0004</td>
<td>0.0014</td>
<td>0.0007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>-0.0110</td>
<td>-0.0110</td>
<td>-0.0203</td>
<td>0.0001</td>
<td>0.0009</td>
<td>0.0009</td>
<td></td>
</tr>
<tr>
<td>2.0 2.0 1.5</td>
<td>PbTe</td>
<td>Exp.</td>
<td>0.0121</td>
<td>0.0121</td>
<td>0.0079</td>
<td>0.0017</td>
<td>0.0011</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MD</td>
<td></td>
<td>-0.0134</td>
<td>-0.0145</td>
<td>-0.0206</td>
<td>0.0003</td>
<td>0.0006</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>2.0 2.0 2.0</td>
<td>Homo</td>
<td>Exp.</td>
<td>0.0079</td>
<td>0.0079</td>
<td>0.0079</td>
<td>0.0012</td>
<td>0.0012</td>
<td>0.0012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbPb</td>
<td>MD</td>
<td>-0.0234</td>
<td>-0.0187</td>
<td>-0.0163</td>
<td>0.0010</td>
<td>-0.0005</td>
<td>-0.0010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TeTe</td>
<td>MD</td>
<td>-0.0219</td>
<td>-0.0231</td>
<td>-0.0179</td>
<td>0.0008</td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
</tbody>
</table>
In this section I present some additional material that was not included in the paper. I start by discussing the thermal expansion obtained from my MD simulations. Figure 4.3 presents the evolution with temperature of the lattice constant. Blue symbols show the calculated size of the $NpT$ unit cell, green symbols the lattice constant extracted from the single-crystal x-ray diffraction study performed by T. Weber presented in the previous section, and red symbols the temperature corrected data by Knight [56] of the original neutron diffraction based data by Božin et al. [35]. Continuous lines are fits to the saturating function used in Ref. [56] (see main text). The experimental errors are smaller than the size of the symbols.

![Figure 4.3](image_url)

**Figure 4.3**: Temperature dependence of the lattice parameter. Blue symbols represent MD results, green symbols the single-crystal x-ray diffraction results of T. Weber, and red symbols temperature corrected data by Knight [56] of the original neutron diffraction based data by Božin et al. [35]; continuous lines are fits to the saturating function used in Ref. [56] (see main text). The experimental errors are smaller than the size of the symbols.

My MD simulations overestimate the lattice constants by 1% and reproduce the linear thermal expansion coefficient quite well. I obtain a value of $1.8 \times 10^{-5} \text{ K}^{-1}$ at 300 K, to be compared with $1.9 \times 10^{-5} \text{ K}^{-1}$ for the data from Ref. [35] and $2.6 \times 10^{-5} \text{ K}^{-1}$ for the data from the single-crystal x-ray diffraction study performed by T. Weber. Moreover, we do not observe any anomalous behavior, such as a kink, in the temperature evolution.
Next, I discuss the temperature evolution of the zone-center TO frequency. For a second-order phase transition the soft-mode theory of ferroelectricity \cite{38} predicts that
\[ \omega_{TO} \propto (T - T_c)^{1/2}. \]
(4.3)

Thus, if we plot the square of the TO frequency as a function of temperature, we should get a linear behavior. This is done in Fig. 4.4, where we compare with the experimental results of Jensen et al. \cite{33}. The hardening of the frequencies with temperature reflects the incipient ferroelectricity of PbTe. The linear extrapolation of my data gives a Curie temperature \( T_c \approx -755 \) K to be compared with the experimental extrapolation of \(-155\) K. The huge difference is caused by the overestimation of the TO frequency in DFT. On the other hand, the slope of the linear fit is reproduced quite well; I obtain a value of 4.8 meV\(^2\) K\(^{-1}\) which is off by 7% from the experimental value.

Finally, Fig. 4.5 presents more details about the asymmetry analysis of the PDF peaks. The top panels show a simple way to visualize and understand the peaks’ asymmetry. Panel (a) compares the extracted peaks’ mean value with the simulation cell size; all peaks show a larger increase than the simulated lattice constant, which is indicative of a local lattice expansion. Panel (b) makes the same comparison but for the mode of the peaks, i.e. the position of the maximum; all peaks’ modes increase following the simulated lattice constant except for the first peak, where the mode stays constant. This explains the asymmetry of the first peak: the position of the maximum does not change, but the mean value
Figure 4.5: Asymmetry analysis of the PDF peaks as a function of temperature. The color legend shown in (a) applies to all four plots. (a) Evolution of the mean of the peaks compared with the simulation cell; (b) evolution of the mode of the peaks compared with the simulation cell; (c) evolution of the skewness of the peaks; (d) evolution of the excess kurtosis of the peaks. Note that with increasing temperatures the third and fourth peaks are merging with the neighboring peaks and thus their analysis is more difficult.

increases. Thus, the high-$r$ side of the peak gets more weight. This is confirmed by the calculation of the skewness (c): the first peak has a positive skewness that increases with temperature. The other peaks stay almost symmetric over the whole temperature range. On the other hand, the kurtosis (d) shows some deviations from a Gaussian profile for these peaks too. However, at higher temperatures the analysis of the third and fourth peaks is not straightforward because the peaks can not be separated anymore (they start merging together). Thus, the results depend on the distance range used for the analysis, in particular for the higher moments like the kurtosis, since they are more sensitive to the peaks’ tails.

4.7 Comments on the presented MD simulations

When I started to run MD simulations we had some concerns regarding the settings to be used. For example, we wondered if the starting structure would influence the outcome of the analysis because the simulation time in ab-initio MD is relatively short. We thought that 100 ps may not be enough to observe the emphanitic “phase transition”, because the required time scales may be longer. For that reason I tried some starting structures where the lead atoms were randomly displaced along the cartesian axis. They all failed to produce an off-centering, but are consistent with the correlated dipoles presented in section 4.5.
that anyway I already performed longer simulations than for usual first-principles simulations, which are on the order of few tens of picoseconds.

Another issue arising in ab-initio simulations concerns the system’s size. Since at every timestep a DFT calculation is performed, the simulated system is quite limited in size. The $6 \times 6 \times 6$ cubic supercell should be large enough to prevent size effects. In any case it would be nice to run larger systems to check for the extent of the correlated dipoles’ regions and to understand their dynamics and temperature evolution. In the next chapter I will show our attempt at building an effective potential for that purpose.

The close agreement between my simulations and the single-crystal x-ray diffraction experiments shown in section 4.5 gives me confidence that my simulations are capturing the experimental situation.

Finally, I comment on the absence of error analysis of the extracted quantities. Usually, in the first-principles literature one does not find ab-initio MD with an error analysis because the simulated times are too short and do not produce enough independent data points. The problem is that the temporal series produced by MD are autocorrelated, because they are computed as a time evolution. Thus, we can not use directly the error estimates of standard statistics (like the Central Limit Theorem) because they assume independent observations. If we ignore the autocorrelation we would underestimate the errors. Moreover, different quantities can have different autocorrelation times. Thus, the error analysis has to be performed from scratch for every extracted quantity.

To better understand this, I briefly describe how one would estimate the errors for simple scalar quantities, e.g. the temperature. One of the best and easiest methods is the block-average method (see, e.g., Ref. [225]). One starts by computing the standard deviation of the original population. Then, one averages neighboring observations and computes the standard deviation of the new (halved) population. One continues doing the same until the population is too small for an accurate statistical analysis. At the beginning the standard deviation will increase, but at some point it will level out creating a plateau. This gives an estimate of the standard deviation of the sample mean and also the number of averages one needs to remove significant correlations. The problem with ab-initio MD is that usually the simulation time is not long enough for the block-average method to work. This does not allow one to extract a meaningful confidence interval on the computed quantities. The only solution would be to run longer simulations that would need a much higher computation time. Furthermore, in some cases the autocorrelation time is longer than estimated from a “short” run because the system could jump between different local minima if allowed to run longer.

The situation is more complicated for more complex quantities like the pair distribution function (PDF). Here more cumbersome methods like the Jackknife method [226] have to be used. In some cases the computation of the error could be far more time-demanding than the computation of the quantity itself. Another possibility would be to perform several independent MD simulations and average
4.8 Conclusions & Outlook

In this chapter I presented a detailed study of the local structure of lead telluride. We do not find any lead off-centering in the strict meaning of the word, but instead a peculiar local dynamic arrangement of the atoms giving rise to correlated dipoles oriented along \((100)\). We reproduce the increased asymmetry of the PDF peaks, but they are not structured as in the original paper [35]. Either our MD simulations do not capture the underlying physics or the reported structures were just artifacts of the PDF (Fourier transform) analysis.

In any case, we show that the alternation of short and long bonds associated with these dipoles is, in principle, able to produce structured PDF peaks. The strength of the higher-order correlations is probably the parameter tuning the appearance of shoulders in the PDF peaks. And, after all, the structured peaks may not be so important for an emphanitic behavior; the emphasis is reported in CsSnBr\(_3\), for example, develops without any shoulder [61]. Thus, our model is consistent both with the original report [33, 35] and the subsequent studies [48–57], and we think that the controversy has been resolved.

We show two aspects that help to understand and settle the off-centering controversy. First, we specify what one should understand by off-centering, namely atomic displacements with respect to the (local) nearest-neighbor environment. Second, we identify a possible source of the off-centering claim in the misinterpretation of the modeling of the PDF, namely the inability of the PDFgui package to handle anharmonicity.

We identify the underlying mechanism for the formation of correlated dipoles to be a (strong) coupling between acoustic and optic phonons caused by soft optic modes (with large amplitudes). We reproduce the signature of such a coupling, namely the avoided crossing between the LA and TO modes [34], and show that the zone-center TO mode develops a split peak. The origin of the splitting may be found in the strong anharmonic phonon coupling or, equivalently, in the local-symmetry breaking produced by the correlated dipoles.

We speculate that this phenomenon may be more general and could describe any system in the vicinity of a ferroelectric transition, i.e. in the paraelectric phase where the TO mode is very soft. In this respect, it would be interesting to search for the correlated-dipoles behavior in phase transitions that traditionally have been regarded as displacive. If this phenomenon were found there, the transition would acquire some order-disorder character; if not our understanding of the underlying mechanism may be incomplete or even wrong.

This work is a further step towards an understanding of the peculiar properties of PbTe, but obviously there are still open questions. Our work was not able to discuss conclusively the extent of the regions with correlated dipoles and their dynamics. To study these properties from the computational side, larger
supercells are needed, which with current computational power is not feasible from first-principles. A viable route is the use of classical potentials; in the next chapter I will show our attempt at fitting a Tersoff potential for PbTe.

A very interesting open issue is the role of the correlated dipoles in the thermoelectric performance. By simple arguments we show that they may be beneficial and may contribute to the opening of the band gap [10] and the band convergence [11] observed with increasing temperature. More realistic computations are needed to fully explore their role and significance for applications.

Finally, my MD simulations, as well as those previously published, treated PbTe as a stoichiometric compound. It is not clear yet how vacancies, or even impurities, would affect the discussed quantities; in particular, whether vacancies would produce shoulders in the PDF peaks. Further first-principles studies incorporating vacancies are needed to gain a satisfactory understanding of PbTe.
Effective potentials for PbTe

In this chapter I discuss effective potentials for PbTe and their usefulness and limitations for the description of average and local properties. The great advantage of classical potentials is that they allow much faster computations than first-principles methods. In this way bigger systems can be simulated for much longer times; thus, systems with nano-domains and phase transitions can be studied, in principle, more easily. On the other hand, an effective potential does not guarantee an accurate description of the true quantum mechanical potential of a solid system. The introduced approximations may in some cases be too crude and the obtained physical picture too simplified, or even wrong. As usual in the field of computational materials, a balance between computational time and accuracy has to be chosen depending on the applications that one has in mind. In the case of PbTe, I explore the route of effective potentials, because they allow detailed study of the dynamics of our correlated dipole regions that span several unit cells. This is at the moment not accessible with the available computer power within ab-initio methods. However, the difficulty lies in finding an interatomic potential that is able to capture such physics.

In the literature, to my knowledge, only two types of interatomic potentials were developed so far for PbTe [227–229]; both of them are isotropic potentials, i.e. they depend only on the distance between the atoms. The first potential [227] is a Coulomb-Born-Mayer-Huggins potential [230–232] within the parametrization of Fumi and Tosi [233, 234], while the second [228, 229] is a Coulomb-Buckingham potential. In this chapter I will discuss only the second, because it is directly available in the LAMMPS package [162].

If we extend the search for an interatomic potential to materials related to PbTe, we find another promising approach in GeTe. There, a recent work proposed an interatomic potential of the Tersoff type [235–237] that is able to describe in a reasonable way all the bulk properties of GeTe [238]. Interestingly, it also captures its ferroelectric transition, which occurs experimentally at 670 K [40]: Zipoli and Curioni [239] showed that when the temperature is increased the bond distribution changes from bimodal to unimodal. The transition temperature is underestimated, but this is expected since the dipole-dipole interaction is missing in the model and therefore the associated energetics is not captured well. On the other hand, it would not be too difficult to add that part to the potential.

Keeping in mind that we want to describe a possible off-centering, we thought that the approach was very promising and decided to apply it also to PbTe. For
that reason we started a collaboration with the authors of the interatomic potential for GeTe, Federico Zipoli and Alessandro Curioni at IBM Research – Zurich. In this work we developed a Tersoff potential for PbTe that is presented in this chapter. At this point it is fair to mention that the actual fitting of the potential was done by Federico Zipoli using my ab-initio MD trajectories.

The chapter is rather technical and is structured as followed: I start by discussing the Coulomb-Buckingham potential fitted in Refs. [228, 229] and compare the extracted properties with my ab-initio MD simulations. In the second part, I present our Tersoff potential and critically discuss its advantages and limitations with respect to the Coulomb-Buckingham potential.

5.1 Computational details

The calculations shown in this chapter were performed using the LAMMPS code [162]. Calculations were performed with a $6 \times 6 \times 6$ supercell of the conventional (cubic) cell (1728 atoms) at temperatures between 100 K and 500 K in steps of 50 K. 150 ps simulations in the isothermal-isobaric ($NpT$) ensemble using the thermostat developed by Bussi et al. [154] and the Berendsen barostat [155] were performed, followed by 150 ps production runs in the microcanonical ($NVE$) ensemble. The timestep used was 2 fs.

The DFT computations were performed using CP2K [161] with the same settings as in chapter 4.

The analysis of the MD simulations was performed with a self-written C++ code as described in section 4.1. The methods used to compute the pair distribution function (PDF) and the phonon spectrum are presented in Appendix B.

The $T = 0$ K phonon properties were computed using the supercell approach with the finite-displacement method as implemented in the Phonopy package [195].

5.2 Validation of Coulomb-Buckingham potential for PbTe

In this section I present the Coulomb-Buckingham potential fitted for PbTe in Refs. [228, 229] [in the following I will call it just Buckingham potential]. It consists of the usual (short-range) Buckingham potential [240], with the addition of a long-range Coulomb term

$$V(r_{ij}) = A_{ij} e^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}},$$

(5.1)

where $r_{ij}$ is the distance between atoms $i$ and $j$, $q_i$ the effective atomic charge, and $A_{ij}$, $C_{ij}$ and $\rho_{ij}$ are potential parameters. Figure 5.1 shows a Buckingham potential for typical parameters. The potential resembles the Lennard-Jones potential, but the repulsive part $1/r_{ij}^{12}$ is replaced by an exponential function that should describe more realistically the repulsion of closed electronic shells.
5.2 Validation of Coulomb-Buckingham potential for PbTe

Figure 5.1: Example of a Buckingham potential (blue), along with its different contributions, the repulsive (exponential) part (dashed green), the attractive part (dash-dotted orange), and the Coulomb term (dotted red).

On the other hand, at small distances the exponential term tends to a constant value, such that an unphysical turnover happens. If the atoms could overcome the repulsive barrier, they would become tightly bound at zero distance; this is sometimes called the “Buckingham catastrophe”.

Table 5.1: Fitted parameters of the Buckingham potential as reported in Refs. [228, 229]. The effective charges are +0.666 and −0.666 for Pb and Te, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$A$ [eV]</th>
<th>$\rho$ [Å]</th>
<th>$C$ [eV·Å$^6$]</th>
<th>Range [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-Pb</td>
<td>84203.2</td>
<td>0.0754</td>
<td>61.01</td>
<td>16.0</td>
</tr>
<tr>
<td>Pb-Te</td>
<td>92131.5</td>
<td>0.2552</td>
<td>585.70</td>
<td>16.0</td>
</tr>
<tr>
<td>Te-Te</td>
<td>1773611.7</td>
<td>0.2565</td>
<td>0.61</td>
<td>16.0</td>
</tr>
</tbody>
</table>

In the case of PbTe Qiu et al. [228, 229] determined the parameters with a fit to the total energy surface and the experimental elastic constant value. The atomic charges $q_i$ were computed through a Bader charge analysis to give a value of +0.666 and −0.666 for Pb and Te, respectively; the deviations from the nominal charges of ±2 reflect the covalent nature of the bonding in PbTe. The Buckingham part is short-ranged and is limited by a cutoff at 16 Å, while the Coulomb part is long-ranged and is computed using the Ewald summation [241]. The parameters of the potential are summarized in Table 5.1.

In the following I evaluate the quality of the potential by comparing to DFT computations.
5.2.1 $T = 0\, K$ properties

I start by showing the equation of state $E(V)$ and the extracted lattice constant and bulk modulus. To this end I fitted the equation of state using the parametrization of Birch and Murnaghan, Eq. (3.1). The equation of state is shown in Fig. 5.2 and the obtained structural properties in Table 5.2. One sees that the lattice constant

![Equation of State](image)

Figure 5.2: Calculated equation of state $E(V)$ for the Buckingham potential of Refs. [228, 229] (blue circles) and DFT (green triangles). Both curves are plotted with the zero of energy at the equilibrium position.

Table 5.2: Calculated structural properties for the Buckingham potential of Refs. [228, 229] compared with calculations done in CP2K using the PBEsol functional, and with experiments. $a_0$ is the equilibrium lattice constant, $B_0$ the bulk modulus, $B'_0$ the pressure derivative of the bulk modulus, and $\Gamma$ the $\Gamma$-point-frequency of the transverse optic mode at the equilibrium volume.

<table>
<thead>
<tr>
<th></th>
<th>Buckingham</th>
<th>CP2K/PBEsol</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ [Å]</td>
<td>6.52</td>
<td>6.51</td>
<td>6.43$^{35}$</td>
</tr>
<tr>
<td>$B_0$ [GPa]</td>
<td>43.26</td>
<td>42.49</td>
<td>38.39$^{197}$</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>7.02</td>
<td>4.55</td>
<td>–</td>
</tr>
<tr>
<td>TO [THz]</td>
<td>3.3</td>
<td>1.2</td>
<td>0.7$^{33}$</td>
</tr>
</tbody>
</table>

and the bulk modulus are reproduced very well. However, the pressure derivative of the bulk modulus is severely overestimated compared with DFT; on applying pressure the Buckingham system is much less compressible.
The next step is the computation of the phonon spectrum, which I have shown in the previous chapter to play a fundamental role in the determination of the local structure. Figure 5.3 shows that the frequencies of the optical phonons are overestimated by the Buckingham potential, in particular at $\Gamma$ with a factor of almost 3 (see Table 5.2). Therefore, with the Buckingham potential PbTe is much further away from a ferroelectric instability than in DFT and experiments. Moreover, also the acoustic frequencies are severely overestimated at the $X$ point, in particular the longitudinal acoustic (LA) mode by a factor of almost 2.

The harder TO mode has another important consequence: as the DOS in Fig. 5.3 shows, the acoustic and optic bands are clearly separated from each other and, therefore, a coupling between them is very unlikely. In fact, also the related band crossing between LA and TO along the $\Delta (\Gamma - X)$ line found in DFT is not reproduced. This finding contradicts experimental reports of a strong coupling between acoustic and optic modes [34], and, as I already showed in section 4.5, has profound implications on the local structure. I will come back to this in the next section.

### 5.2.2 Finite temperature properties

In this section I present MD simulations performed using LAMMPS in order to further validate the Buckingham potential. For that I compare the extracted finite-temperature properties with ab-initio MD simulations performed with CP2K (labeled in the following as DFT). Figure 5.4 presents the thermal expansion and the atomic displacement parameters (ADPs), i.e. the mean square displacements. The evolution of the lattice constant is captured quite well with, however, a larger slope resulting in an overestimation of the experimental thermal expansion.
Figure 5.4: Lattice constant (a) and atomic displacement parameters (ADPs), $U_{iso}$, (b) as a function of temperature from MD simulations with the Buckingham potential and DFT. The lattice constant was extracted as the unit-cell size from $NpT$ simulations, while the atomic displacement parameters (ADPs) were extracted from subsequent $NVE$ simulations.

coefficient of almost 50%. The ADPs from the Buckingham potential are underestimated, consistent with the harder phonon spectrum, and show a small kink (change in slope and curvature) at higher temperatures.

Figure 5.5 shows the phonon band structure extracted from MD through the computation of the power spectrum $Z(q, \nu)$ (see Eq. (B.6)), which can be compared with what is measured in inelastic neutron scattering (INS) experiments [52]. Finite temperatures give rise to interactions between the phonon modes, and the related many-body renormalizations can be observed as broadening and shift of the peaks in the power spectra. The left panel (a) shows the dispersion along the $\Delta$-line at 300 K. The acoustic branches are unaffected by temperature (the white lines correspond to the dispersion shown in Fig. 5.3),
while the optic branches are shifted to lower frequencies. Moreover, the TO mode at $\Gamma$ does not show any splitting or broadening, in contrast to ab-initio MD (see Fig. 9 in section 4.5) and experiments [32, 33]. The right panel (b) shows the temperature evolution of the TO frequency at $\Gamma$; the frequencies extracted from the Buckingham potential (blue circles) decrease with increasing temperatures, in contrast to the incipient ferroelectricity observed in experiments [32, 33] and in ab-initio MD (green triangles), whose signature is a hardening of the TO mode with increasing temperatures.

Next, I discuss quantities related to local properties. Figure 5.6 shows the pair distribution function (PDF) at two temperatures, 300 K (a) and 500 K (b). At both temperatures we can observe an underestimation of the peaks’ widths that can be related to the harder phonons of the Buckingham potential. On the other hand, as one sees in Fig. 5.7, the asymmetry-related parameters are captured quite well and show an increased asymmetry with increasing temperatures.

![Figure 5.6](image)

Figure 5.6: Calculated pair distribution function, $G(r)$, for the Buckingham potential (blue) and DFT (dashed green) at two different temperatures, (a) 300 K and (b) 500 K.

![Figure 5.7](image)

Figure 5.7: Asymmetry parameters of the first two peaks of the PDF as a function of temperature. Open symbols represent data for the Buckingham potential, while filled symbols are from DFT. The asymmetry parameters $\Delta R_{ASYM}$ (a) and $\Delta R_{GAUSS}$ (b) are defined in Eqs. (5.2)-(5.3).
For convenience I repeat the definition of the asymmetry parameters given in the paper [213] in section 4.5. The first parameter is defined as

$$\Delta R_{\text{ASYM}} = \frac{\int_{r_0+\delta r}^{r_0-\delta r} [R(r_0 + r) - R(r_0 - r)] \, dr}{\int_{r_0+\delta r}^{r_0-\delta r} [R(r_0 + r) + R(r_0 - r)] \, dr},$$

where $R(r)$ is the radial distribution function (RDF). The second parameter defines a “relative error” with a Gaussian function,

$$\Delta R_{\text{GAUSS}} = \frac{\int_{r_0+\delta r}^{r_0-\delta r} [R(r) - N_c \cdot e^{-(r-\mu)^2/2m_2} / \sqrt{2\pi m_2}] \, dr}{\int_{r_0+\delta r}^{r_0-\delta r} [R(r) + N_c \cdot e^{-(r-\mu)^2/2m_2} / \sqrt{2\pi m_2}] \, dr},$$

where $N_c = \int_{r_0+\delta r}^{r_0-\delta r} R(r) \, dr$ is the coordination (area of the peak), and $m_2$ is the variance of the peak.

The behavior of the asymmetry parameters seems very promising in view of the peculiar local structure, namely the correlated dipoles, described in section 4.5. However, a severe consequence of the underestimated coupling between acoustic and optic phonons (see Fig. 5.3) is the smooth decay of the pair correlations (Eq. (4.2)), i.e. without the formation of steps, shown in Fig. 5.8(a). This, in turn, is indicative of acoustic phonon-like displacements only without any superposition of optical-like displacements. Panel (b) shows the temperature evolution of the pair correlations; we can observe a large variability with temperature without a clear trend with increasing temperature. As already discussed in section 4.5 the increased asymmetry of the PDF peaks can be explained just by the anharmonicity intrinsic to the Buckingham potential, without the need of fancier explanations, like the correlated dipoles.

Finally, Fig. 5.9 shows the Buckingham potential probability densities for the higher-order correlations along the $\langle 100 \rangle$ direction. First of all, we can observe that the color scale includes here a somewhat larger range of values than DFT (see Figs. 12 and A4 in section 4.5) for the two nearest bond-correlations, $B_2^3$(Pb) and $B_1^4$, indicating that the nearest bond-correlations are stronger than in DFT.

Figure 5.8: Calculated longitudinal pair correlations along the cubic axis; (a) comparison between the Buckingham potential (blue circles) and DFT (green triangles) at 300 K, (b) temperature evolution from the Buckingham potential.
5.2 Validation of Coulomb-Buckingham potential for PbTe

Figure 5.9: Difference probability densities with respect to the neutral reference state at 300 K for the higher-order correlations along the (100) direction obtained with the Buckingham potential. The notation for the bond correlations is defined in Fig. 11 in the paper in section 4.5. Here I show only the three-body correlations for shared Pb atoms; the probability density for shared Te would be similar, even if slightly less pronounced, as in Fig. 12 in section 4.5. The color scale represents the probability density in Å\(^{-2}\). Note the different scale in the three panels showing the decay in correlation strength.

On the other hand, the decay of the correlation strength is faster here, as the color scale of the third bond-correlation, \(B_4^2\), proves. Thus, the correlations on a (very) short range are stronger, but they also decay more quickly\(^1\).

Moreover, Fig. 5.9 also confirms what we were already expecting from the pair correlations: there is no alternation of short and long bonds in the system. Instead, if the reference bond is longer than on average, all neighboring bonds along the [100] line tend to be shorter than on average. At first this can sound counter-intuitive, as with positive pair correlations all atoms should displace in the same direction, but can be understood as follows: if two neighboring atoms are pushed apart and form a longer bond than on average, then the next bond lengths are shorter than on average to compensate the local strain\(^2\). In the same way, this fact shows that it is not (always) straightforward to switch between the pair-correlation picture and the bond-correlation picture. Considering only the pair correlations, positive coefficients indicate that the atoms tend to move in the same direction, but one can not say if the bonds get longer or shorter than on average.

All in all, even if the Buckingham potential reproduces reasonably well all bulk properties, it fails in reproducing the peculiar local structure described by the formation of the correlated dipoles. This is not completely unexpected if one thinks about the form of the potential. The only long-range part is the Coulomb contribution, and, while the cutoff of the Buckingham part is quite large (16 Å), it is still smaller than the extent of the pair correlations shown in Fig. 6 in section 4.5 [16 Å correspond to about 2.5 \(a\)]. Moreover, the potential is two-body

---

1 This can be proven by considering all higher-order correlations defined in Fig. 11 in section 4.5 that, however, are not shown here.

2 This effect is amplified in our calculations by periodic boundary conditions and the fixed unit cell; if one bond is longer, and there is no alternation of long and short bonds, the other bonds have to be shorter to compensate for the larger amount of space occupied by the longer bond.
and isotropic. Therefore, it is not able to describe the polarizability originating from the lead lone pair. Expecting such a potential to describe anisotropic features relying on the local environment and bonding strength and orientation that extend over several unit cells is obviously asking too much.

5.3 Construction and validation of a Tersoff potential

Next, I present our attempt to construct a better effective potential for PbTe. As already mentioned this part was done in collaboration with F. Zipoli and A. Curioni at IBM Research – Zurich. While Tersoff potentials describe GeTe well, we find that they are not able to capture the peculiar local structure of PbTe. During the validation part we extracted valuable information for the search of better potentials that should incorporate the lead lone pair physics.

5.3.1 Introduction into Tersoff potentials

In the search for a good description of covalent-bonded systems, Abell [242] derived a model for interatomic interactions based on chemical pseudopotential theory. Abell assumed that the interatomic interactions can be represented by a sum of bond energies described by a repulsive and an attractive component parametrized by exponential functions (giving rise to a Morse-like potential [243]) and only nearest-neighbor couplings retained. The basic idea is that covalent bonding depends strongly on the geometry of the environment and that the more neighbors an atom has, the weaker the resulting bonds will be. The most relevant variable that determines the bond strength (or bond order) seems to be the coordination number (indeed potentials like the Tersoff potentials are of the bond-order type). Based on these findings, Tersoff [235–237] developed the well-known potential under his name to describe covalent bonds in Si. Tersoff extended Abell’s formulation by including also the effects of bond angles, giving rise effectively to a three-body term, and also incorporating symmetry in the bond-order term. In its formulation the total energy $E$ of the system can be written as

\[
E = \frac{1}{2} \sum_{i \neq j} V_{ij},
\]

where $V_{ij}$ are generalized Morse potentials [for simplicity, I already use the notation defined by Billeter et al. [244] for the different terms]. For an atom pair $i$ and $j$, of type $I$ and $J$, separated by a distance $r_{ij}$ the pair interaction is given by

\[
V_{ij}(r_{ij}) = f_{ij}^{IJ}(r_{ij}) \left[ A_{IJ} e^{-\lambda_{IJ} r_{ij}} - b_{ij}^{IJ} B_{IJ} e^{-\mu_{IJ} r_{ij}} \right].
\]
The function \( f_{ij}^{IJ} \) defines a cutoff for the range of interaction (usually limited to nearest neighbors of type \( I \) and \( J \))

\[
f_{ij}^{IJ}(r_{ij}) = \begin{cases} 
1 & \text{if } r_{ij} \leq R_{IJ}, \\
\frac{1}{2} \left[ 1 + \cos \left( \frac{\pi (r_{ij} - R_{IJ})}{S_{IJ} - R_{IJ}} \right) \right] & \text{if } R_{IJ} < r_{ij} \leq S_{IJ}, \\
0 & \text{if } r_{ij} \geq S_{IJ},
\end{cases}
\] (5.6)

where \( R_{IJ} \) and \( S_{IJ} \) are appropriate cutoff radii. The coefficients \( A_{IJ} \) and \( B_{IJ} \) (defining the strength of the repulsive and attractive part of the Morse-like potential, respectively), the inverse decay lengths \( \lambda_{IJ} \) and \( \mu_{IJ} \), and the cutoff radii \( R_{IJ} \) and \( S_{IJ} \), depend only on the type of the interacting atoms. Three-body effects (bond angles) are included into the damping factors \( b_{ij}^{IJ} \) of the attractive potential, which are monotonic decreasing functions of an effective coordination number \( \beta_{I} \zeta_{ij}^{IJ} \)

\[
b_{ij}^{IJ} = \chi_{IJ} \left[ 1 + \left( \beta_{I} \zeta_{ij}^{IJ} \right)^{n_I} \right]^{-1/2n_I},
\] (5.7)

where \( \chi_{IJ} \) is a coefficient depending only on the type of the interacting atoms and

\[
\zeta_{ij}^{IJ} = \sum_{k \neq i,j} f_{ik}^{IK} e_{ijk}^{IJK}. \tag{5.8}
\]

If only the term \( f_{ik}^{IK} \) were present, then \( e_{ij}^{IJK} \) would count the number of bonds to atom \( i \) besides the bond \( i \) \( - \) \( j \). The term \( e_{ijk}^{IJK} \) describes the competition of two neighbors \( j \) and \( k \) of atom \( i \) to form a bond with atom \( i \)

\[
e_{ijk}^{IJK} = \phi_{ij}^{m_I} (r_{ij} - r_{ik})^{m_I}, \tag{5.9}
\]

where \( m_I \) is an integer originally fixed to 3. Specifically, if the distance \( r_{ij} \) is much shorter than \( r_{ik} \), then the weakening of bond \( i \) \( - \) \( j \) caused by atom \( k \) is drastically reduced.

The effects of bond angle \( \theta_{ijk} \) between atoms \( j \) and \( k \) around atom \( i \) are incorporated into the term \( t_{ijk}^{I} \),

\[
t_{ijk}^{I} = 1 + \frac{c_I^2}{d_I^2} - \frac{c_I^2}{d_I^2} \left[ h_I - \cos(\theta_{ijk}) \right]^{2}. \tag{5.10}
\]

The coefficients \( c_I \) and \( d_I \) specify the strength of the angular penalty function, while \( h_I \) describes the cosine of the energetic optimal angle, but is allowed to lie outside the interval \([-1, 1]\).

Recently, an augmented Tersoff potential for SiONH systems was proposed by Billeter et al. [244]. The expression \( e_{ijk}^{IJK} \) in Eq. (5.9) was modified to

\[
e_{ijk}^{IJK} = \phi (\mu_{I} r_{ij} - \mu_{K} r_{ik})^{m_I}, \tag{5.11}
\]
such that each interatomic distance is measured with its own characteristic length. Furthermore, the total energy was augmented by the core energies $E^C_I$ (to allow a fit to configurations with different numbers of atoms and elements) and a penalty function $E^c_i$ for under- and overcooordination as

$$
E = \frac{1}{2} \sum_{i \neq j} V_{ij} + \sum_I N_I E^0_I + \sum_i E^c_i,
$$

$E^c_i = c_{I,1} \Delta z_i + c_{I,2} \Delta z_i^2,$

with $N_I$ the number of atoms of type $I$, and $\Delta z_i$ the deviation from the expected coordination number $z_i^0$. The coordination $z_i$ is defined as

$$
z_i = \sum_{j \neq i} f_{ij} b_{ij}^{IJ}.
$$

The deviation $\Delta z_i$ from $z_i^0$ is defined as

$$
\Delta z_i = \text{int} \left( |z_i - z_i^0| \right) + f_s(z),
$$

where $z = (|z_i - z_i^0|) - \text{int} (|z_i - z_i^0|)$ and

$$
f_s(z) = \begin{cases} 
0 & \text{if } |z| \leq z_T - z_B, \\
\frac{1}{2} \left[ 1 + \sin \left( \frac{\pi}{2} \frac{|z| - z_T}{z_B} \right) \right] & \text{if } z_T - z_B < |z| \leq z_T + z_B, \\
1 & \text{if } |z| \geq z_T + z_B.
\end{cases}
$$

$z_T$ and $z_B$ are atom-independent parameters and $\text{sgn}(f_s(z)) = \text{sgn}(z)$. The deviation $\Delta z_i$ is set constant for values $z > z_{\text{cut}}$. The linear term $\Delta z_i$ in Eq. (5.12) differentiates under- from overcoordination, while the quadratic term $\Delta z_i^2$ prevents a favoring of undercoordination.

To be able to describe the phase-change material GeTe (in particular the angle distribution in the amorphous phase), Zipoli and Curioni [238] improved the augmented Tersoff potential by allowing the parameters $c_I$, $d_I$ and $h_I$ in the angular penalty function Eq. (5.10) to depend on the type of the involved atoms and by introducing an “equilibrium” angle $\theta_{0,JK}^I$ also dependent on the atom types and a coefficient $\gamma_{IJK}$ that allows the contribution of the three-body term to be modulated, such that it can be switched off for metallic elements [for GeTe it was set to 1, but its exact value will be fundamental for PbTe]. The integer $m_I$ in Eq. (5.11) was set to 1. The final form of the three-body term $t_{ijk}^I$ is

$$
t_{ijk}^I = \gamma_{IJK} \left[ 1 + \frac{c^2_{IJK}}{d_{IJK}^2} - \frac{c^2_{IJK}}{d_{IJK}^2 + \left[ h_{IJK} \cos \left( \pi - \theta_{0,JK}^I \right) \right]^2} \right].
$$

Figure 5.10 shows different terms of the GeTe potential described in Ref. [238]. Panel (a) shows the Morse-like potential $V_{ij}$ (Eq. (5.5)) with (blue) and without
Figure 5.10: Various contributions to the Tersoff potential for GeTe described in Ref. [238]; Te-Te parameters are used. (a) Morse-like potential $V_{ij}$ (Eq. (5.5)) with (blue) and without (dashed green) cutoff function $f_{ij}$ (Eq. (5.6)) [the $b^{ij}_{ij}$ term is set to unity for the visualization]; (b) three-body term $t_{ijk}$ (Eq. (5.14)) describing the optimal bond angle for Te-Te-Te neighbors; (c) damping factor $b^{ij}_{ij}$ (Eq. (5.7)) describing the weakening of bonds with increasing effective coordination number $\beta I \zeta_{ij}^{IJ}$; (d) penalty function $E_i^c$ (Eq. (5.12)) for under- and overcoordination.
(dashed green) cutoff function $f_{ij}^{\text{IJ}}$ (Eq. (5.6)). The attractive and repulsive terms give rise to a form similar to a Lennard-Jones potential. In contrast to the Buckingham potential there is no unphysical turnover at small distances. Panel (b) presents the three-body term $t_{ijk}^{\text{IJK}}$ (Eq. (5.14)) that reflects the bond angle between Te-Te-Te neighbors. As expected for the rocksalt structure the optimal angle is about $90^\circ$ (and $270^\circ$). Panel (c) shows the damping factor $b_{ij}^{\text{IJ}}$ (Eq. (5.7)) that reflects the weakening of bonds with increasing coordination. Finally, panel (d) presents the penalty function $E_i^{c}$ (Eq. (5.12)) for under- and overcoordination. The optimal “Tersoff coordination” $z_i \approx 3$ and different steps in the penalty energy corresponding to the different coordinations can be observed.

An advantage of the Tersoff potential with respect to the Buckingham potential is the three-body term, which allows for a better description of the local geometry and bonding environment. Conversely, the Tersoff potential is shorter ranged; only the nearest-neighbors are taken into account.

5.3.2 *Method for constructing a Tersoff potential*

Two main methods exist to fit an effective potential from ab-initio calculations: (i) fit the total energies and forces of many structural configurations, and (ii) fit particular properties, like the equation of state and the elastic constants, that are considered to be important/fundamental for a correct description of the system. The latter method ensures that the relevant quantities are reproduced well, but has the drawback that properties that were not included in the fitting procedure are not guaranteed to be captured correctly. Here, we use the first method that, if the particular form of the potential is suitable, will describe reasonably well all properties. On the other hand, it could result in slightly worse agreement for properties that could be directly fitted.

I describe now in some detail the procedure used to optimize the parameters of the potential; for more details refer to Refs. [238, 244]. The starting point is the creation of a “database” with thousands of structural configurations whose energy and forces are calculated with DFT. My Born-Oppenheimer MD trajectories computed for the analysis of the previous chapter are very well-suited for that and are a good starting point. They comprise configurations at different volumes and the range of temperatures allow for a good sampling of the configurational space; in fact, MD samples the more statistically relevant configurations. In addition to these configurations I ran more $NVT$ MD simulations at different volumes (some of them also smaller than the equilibrium volume) and different temperatures. To include some information about diffusivity I also simulated at high temperatures ($1000 – 3000$ K); together with amorphous configurations (created by fast cooling the liquid phase) they are useful to model the disordered phase and to sample Pb-Pb and Te-Te bonds as well as other configurations that have higher energies than the crystalline phase. Finally, to fit the core energies of each species, $E_i^0$, I generated some configurations with Pb and/or Te vacancies.
The optimization of the Tersoff potential’s parameters is performed by minimizing the energy and force mismatch between the effective potential and DFT. The energy mismatch, \( \Delta E^2 \), is defined as the mean square error

\[
\Delta E^2 = \frac{1}{N_f} \sum_{n=1}^{N_f} (E_{\text{ter},n} - E_{\text{DFT},n})^2, \tag{5.15}
\]

where the summation is performed over all considered configurations \( N_f \), and \( E_{\text{ter},n} \) and \( E_{\text{DFT},n} \) are the energies of the \( n \)-th configuration computed with the Tersoff potential and DFT, respectively. Similarly, the force mismatch, \( \Delta F^2 \), is defined as

\[
\Delta F^2 = \frac{1}{3 \sum_{n=1}^{N_f} N_{\text{at},n}} \sum_{n=1}^{N_f} N_{\text{at},n} \sum_{i=1}^{N_{\text{at},n}} \sum_{\alpha=x,y,z} (F_{\text{ter},n,i,\alpha} - F_{\text{DFT},n,i,\alpha})^2, \tag{5.16}
\]

where \( F_{\text{ter},n,i,\alpha} \) and \( F_{\text{DFT},n,i,\alpha} \) are the forces of atom \( i \) along the cartesian direction \( \alpha \) of the \( n \)-th configuration computed with the Tersoff potential and with DFT, respectively, and \( N_{\text{at},n} \) is the number of atoms contained in the \( n \)-th configuration.

In order to fit energies and forces at the same time we minimized the weighted sum of their mismatch

\[
\Delta W^2 = w_E \Delta E^2 + (1 - w_E) r_B \Delta F^2, \tag{5.17}
\]

where \( r_B \) is the Bohr radius and \( w_E \) is the energy-mismatch weight that is allowed to take values between 0 and 1.

The optimization was performed by F. Zipoli at IBM Research – Zurich with the TERSMD code owned by IBM. The software has two methods for the minimization procedure: a steepest-descent algorithm and a simplex method [245]. The steepest-descent method computes the gradients required to describe how the energy and forces are changed by a variation in the parameters with finite differences. The simplex method is faster because the computation of the gradients is not required. However, sometimes the parameters could diverge from those having a physical meaning. This can be avoided by setting boundaries to the parameters, e.g. the parameters \( A_{IJ} \) and \( B_{IJ} \) of the Morse-like potential (Eq. (5.5)) have to be positive.

Important to mention is that the Tersoff parameters were not fitted all simultaneously and the weight \( w_E \) was also changed during the fit, but in any case it is known [244] that the forces should have a higher weight (we used weights \( w_E = 0.01 - 0.05 \)). As shortly mentioned before, a key parameter for the description of PbTe is \( \gamma_{IJK} \) that modulates the strength of the three-body term (see Eq. (5.14)). The three-body term is fundamental for the description of covalently bonded systems (see the arguments before about the influence of coordination on the bond strength), but loses significance for metallic systems. In GeTe it was set to 1, but here it had to be set to zero for Pb because of its metallicity.

The previous procedure produced many potentials (actually several thousands), from which the “best” potential had to be chosen. The first screening involved
the computation of the equation of state $E(V)$ and the comparison of the lattice constant and bulk modulus with values from CP2K (shown in Table 4.1). However, I was still left with some thousands of potentials that had an equilibrium lattice constant within a couple of percent of the DFT values. An additional selection was accomplished by comparing the phonon density of states [for that I computed the phonons in the $3 \times 3 \times 3$ cubic supercell and the density of states with a Gaussian smearing of 0.06 THz]. The best potential was finally selected with a comparison of the asymmetry of the PDF peaks and the pair correlations, Eq. (4.2). Table 5.3 presents the parameters of our best Tersoff potential.

Comment on selection process

Early in the selection process it emerged that the most effective way to select the best potential was to compare the $T = 0$ K phonons. In fact, we found that many of the obtained potentials were not able to describe reasonably well the phonon dispersions, in particular most of them produced a gap between acoustic and optic modes (as was the case for the Buckingham potential shown in the previous section). It seems that producing a soft TO mode with a resulting interaction between acoustic and optic modes is (one of) the hardest properties to obtain from “simple” interatomic potentials. This suggests that the starting point for choosing a particular potential form for PbTe should be the reproduction of the soft TO mode. One way of proceeding would be to find suitable forms that are able, at least in part, to describe the lone pair of the Pb atoms.

Federico Zipoli at IBM research – Zurich is now testing a new potential based on a Coulomb-Buckingham potential with the adiabatic core/shell model of Mitchell and Fincham [246]. In this model the ions are represented by a charged core and a (massless) charged shell linked together with an harmonic spring; all other interactions are of the Buckingham type. In this way the electronic polarizability can be, at least partly, taken into account. Usually, the shell is put only on the most electronegative element in the simulation, in our case Te, but it would be interesting to put it also on Pb to simulate the lone pair.

5.3.3 Validation of Tersoff potential

I start by showing the equation of state $E(V)$ and the extracted lattice constant and bulk modulus. To this end I fitted the equation of state using the parametrization of Birch and Murnaghan, Eq. (3.1). The equation of state is showed in Fig. 5.11 and the obtained structural properties in Table 5.4. One sees that the bulk modulus and its pressure derivative are overestimated, meaning that the Tersoff potential system is less compressible than the ab initio. The DFT lattice constant is underestimated by 2.6%.

The next step is the computation of the phonon spectrum, which I have shown in the previous chapter to play a fundamental role in the determination of the local structure. Figure 5.12 shows that while the DFT DOS is reproduced quite
Table 5.3: Fitted parameters of our Tersoff potential for PbTe. The parameters $z_T$ and $z_B$ are equal to 0.5, and $z_{\text{cut}} = 3.0$.

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Pb-Te</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ [eV]</td>
<td>5629.64205</td>
<td>18353.198</td>
<td>1785.86740</td>
</tr>
<tr>
<td>$B$ [eV]</td>
<td>5155.636</td>
<td>3213.338</td>
<td>145.39334</td>
</tr>
<tr>
<td>$\lambda$ [Å$^{-1}$]</td>
<td>1.82903</td>
<td>2.91846</td>
<td>3.07197</td>
</tr>
<tr>
<td>$\mu$ [Å$^{-1}$]</td>
<td>1.79967</td>
<td>2.14648</td>
<td>2.27362</td>
</tr>
<tr>
<td>$\beta$ [adim.]</td>
<td>$2.0686 \times 10^{-4}$</td>
<td>–</td>
<td>0.17514</td>
</tr>
<tr>
<td>$\chi$ [adim.]</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$R$ [Å]</td>
<td>1.68098</td>
<td>3.24673</td>
<td>1.07589</td>
</tr>
<tr>
<td>$S$ [Å]</td>
<td>4.73100</td>
<td>5.55203</td>
<td>4.50689</td>
</tr>
<tr>
<td>$n$ [adim.]</td>
<td>1.07866</td>
<td>–</td>
<td>1.02560</td>
</tr>
<tr>
<td>$E_0$ [eV]</td>
<td>$-94.34068$</td>
<td>–</td>
<td>$-221.59823$</td>
</tr>
<tr>
<td>$Z_0$</td>
<td>5.44755</td>
<td>–</td>
<td>2.99212</td>
</tr>
<tr>
<td>$c_1$ [eV]</td>
<td>0</td>
<td>–</td>
<td>$-0.22092$</td>
</tr>
<tr>
<td>$c_2$ [eV]</td>
<td>0</td>
<td>–</td>
<td>0.32660</td>
</tr>
<tr>
<td>$\theta_0$ [rad], $\gamma$, $c$, $d$, $h$ [adim.]</td>
<td>$X = \text{Pb}$</td>
<td>$X = \text{Pb}$</td>
<td>$X = \text{Te}$</td>
</tr>
<tr>
<td>$X = \text{Pb}$</td>
<td>$Y = \text{Pb}$</td>
<td>$Y = \text{Te}$</td>
<td>$Y = \text{Te}$</td>
</tr>
<tr>
<td>$\theta_0^{X-\text{Pb}-Y}$</td>
<td>$-0.87$</td>
<td>$-0.13$</td>
<td>$-0.82$</td>
</tr>
<tr>
<td>$\theta_0^{X-\text{Te}-Y}$</td>
<td>$-2.50$</td>
<td>$-0.89$</td>
<td>$-0.78$</td>
</tr>
<tr>
<td>$\gamma_{X-\text{Pb}-Y}$</td>
<td>0</td>
<td>0.07642</td>
<td>1</td>
</tr>
<tr>
<td>$\gamma_{X-\text{Te}-Y}$</td>
<td>5.44534</td>
<td>0.38355</td>
<td>0.00465</td>
</tr>
<tr>
<td>$c_{X-\text{Pb}-Y}$</td>
<td>26720.0</td>
<td>26720.0</td>
<td>26562.05289</td>
</tr>
<tr>
<td>$c_{X-\text{Te}-Y}$</td>
<td>728.19464</td>
<td>769.42000</td>
<td>769.42000</td>
</tr>
<tr>
<td>$d_{X-\text{Pb}-Y}$</td>
<td>33.9044</td>
<td>20.15356</td>
<td>23.72647</td>
</tr>
<tr>
<td>$d_{X-\text{Te}-Y}$</td>
<td>37.84128</td>
<td>9.70886</td>
<td>49215.12653</td>
</tr>
<tr>
<td>$h_{X-\text{Pb}-Y}$</td>
<td>$-0.20825$</td>
<td>$-0.29933$</td>
<td>$-0.49655$</td>
</tr>
<tr>
<td>$h_{X-\text{Te}-Y}$</td>
<td>$-0.52222$</td>
<td>$-0.40036$</td>
<td>$-4.22643$</td>
</tr>
</tbody>
</table>
Figure 5.11: Calculated equation of state $E(V)$ for the Tersoff potential (blue circles) and DFT (green triangles).

Table 5.4: Calculated structural properties for the Tersoff potential compared with calculations done in CP2K using the PBEsol functional and experiments. $a_0$ is the equilibrium lattice constant, $B_0$ the bulk modulus, $B'_0$ the pressure derivative of the bulk modulus, and TO the Γ-point-frequency of the transverse optic mode at the equilibrium volume.

<table>
<thead>
<tr>
<th></th>
<th>Tersoff</th>
<th>CP2K/PBEsol</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ [Å]</td>
<td>6.35</td>
<td>6.51</td>
<td>6.43$^{35}$</td>
</tr>
<tr>
<td>$B_0$ [GPa]</td>
<td>72.89</td>
<td>42.49</td>
<td>38.39$^{197}$</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>5.66</td>
<td>4.55</td>
<td>–</td>
</tr>
<tr>
<td>TO [THz]</td>
<td>2.7</td>
<td>1.2</td>
<td>0.7$^{33}$</td>
</tr>
</tbody>
</table>
well, the band structure has large deviations. The frequencies of the optical phonons are overestimated, in particular at \( \Gamma \) with a factor of 2 (see Table 5.2). Moreover, they do not show a large dispersion and are quite flat. Importantly, no gap between acoustic and optic modes can be observed; however, the overlap and crossing happens in another part of the Brillouin zone, because the TO frequency at \( \Gamma \) is overestimated. On the other hand, the acoustic modes are reproduced very well, except the LA mode at \( X \) which is slightly overestimated. We will see later that this phonon behavior does not yield the sought-for local structure.

Next, I present MD simulations performed in LAMMPS in order to validate the finite-temperature behavior of the Tersoff potential, by comparing the extracted finite-temperature properties with ab-initio MD simulations performed with CP2K (labeled in the following as DFT). Figure 5.13 presents the thermal expansion and the atomic displacement parameters (ADPs), i.e. the mean square displacements. The evolution of the lattice constant is captured quite well by the Tersoff potential except for a smaller slope resulting in an underestimation of the experimental thermal expansion coefficient of 25 %. Both Pb and Te ADPs show a larger slope than those obtained from ab-initio MD. At low temperatures Pb ADPs are slightly underestimated, while at higher temperatures they agree well. Conversely, Te ADPs are reproduced well at low temperatures, while at higher temperatures they are overestimated.

Figure 5.14 shows the phonon band structure extracted from MD through the computation of the power spectrum \( Z(q, \nu) \) (see Eq. (B.6)). The left panel (a) shows the dispersion along the \( \Delta \)-line at 300 K. Both the acoustic and optic branches are unaffected by temperature (the white lines correspond to the dispersion shown in Fig. 5.12); we can not observe any renormalization effects. In particular, the TO mode at \( \Gamma \) does not show any splitting or broadening, in con-

---

Figure 5.12: Calculated phonons for the Tersoff potential (blue) compared with DFT (dashed green). The left panel shows the band structure, the right panel the normalized density of states (DOS).
Figure 5.13: Lattice constant (a) and atomic displacement parameters (ADPs), $U_{iso}$, (b) as a function of temperature from MD simulations with the Tersoff potential and DFT. The lattice constant was extracted as the unit-cell size from $NpT$ simulations, while the atomic displacement parameters (ADPs) were obtained from subsequent $NVE$ simulations.

Figure 5.14: (a) Power spectrum $Z(q, \nu)$ at 300 K computed from MD with the Tersoff potential. The left panel shows $Z(q, \nu)$ at the $\Gamma$ point (arbitrary units are used); the right panel shows the dispersion relation along the $\Delta$-line. White lines correspond to the dispersions shown in Fig. 5.12. (b) Evolution of the TO frequency at $\Gamma$ from MD with the Tersoff potential (blue circles) and DFT (green triangles). The frequencies were extracted by fitting a Lorentzian to the peaks; the error bars correspond to the full-width at half maximum obtained from the fit.
5.3 Construction and validation of a Tersoff potential

Contrast to ab-initio MD (see Fig. 9 in section 4.5) and experiments [32, 33]. The right panel (b) shows the temperature evolution of the TO frequency at \( \Gamma \); the frequencies extracted from the Tersoff potential (blue circles) decrease slightly with increasing temperatures, in contrast with the incipient ferroelectricity observed in experiments [32, 33] and ab-initio MD (green triangles), whose signature is a hardening of the TO mode with increasing temperatures.

Next, I discuss quantities related to local properties. Figure 5.15 shows the pair distribution function (PDF) at two temperatures, 300 K (a) and 500 K (b). The agreement is quite good with a small underestimation of the peak widths.

![Figure 5.15: Calculated pair distribution function, \( G(r) \), for the Tersoff potential (blue) and DFT (dashed green) at two different temperatures, (a) 300 K and (b) 500 K.](image)

Furthermore, as one sees in Fig. 5.16, the asymmetry-related parameters are captured very well and show an increased asymmetry with increasing temperatures. Together with the absence of a gap between acoustic and optical phonons

![Figure 5.16: Asymmetry parameters of the first two peaks of the PDF as a function of temperature. Open symbols represent data obtained with the Tersoff potential, while filled symbols are from DFT. The asymmetry parameters \( \Delta R_{\text{ASYM}} \) (a) and \( \Delta R_{\text{GAUSS}} \) (b) are defined in Eqs. (5.2)-(5.3).](image)

this augurs well for the peculiar local structure, namely the correlated dipoles, described in section 4.5.

However, Fig. 5.17(a) shows that the pair correlations (Eq. (4.2)) obtained from the Tersoff potentials decay smoothly, i.e. without the formation of steps.
Moreover, the Tersoff values are systematically larger than the DFT values; the Tersoff potential seems to generate more correlated motion of atomic pairs than DFT, but the correlation strength decays faster. The decay of the pair correlations does not indicate any contribution from optic phonon-like displacements, only acoustic-like displacements are expected. Panel (b) shows the temperature evolution of the pair correlations; we observe a large variability with temperature without a clear trend with increasing temperature. As already pointed out for the Buckingham potential (see section 5.2), the smooth decay of the pair correlations is not in contradiction with the asymmetry of the PDF peaks; anharmonicity alone is enough to explain the asymmetric peaks.

Next, Fig. 5.18 shows the Tersoff potential probability densities for the higher-order correlations along the \( \langle 100 \rangle \) direction. Similar to the discussion for the Buckingham potential (see section 5.2), also here the bond correlations decay faster than in DFT. A bit surprising is that also the nearest bond-correlation, \( B_2^3(\text{Pb}) \), is weaker; moreover, in contrast to DFT and the Buckingham potential,
the correlation for shared Te presents the same strength as for shared Pb (not shown).

As with the Buckingham potential, we do not observe any alternation of short and long bonds in the system. Instead, if the reference bond is longer than on average, all neighboring bonds along the [100] line tend to be shorter than on average. As expected from the short-range nature of the Tersoff potential, the strength of the bond-correlations decays very fast, with, e.g., $B_5$ bonds already completely uncorrelated (not shown).

Finally, Fig. 5.19 presents the PDF for temperatures around the melting point $\sim 1200$ K [247, 248]. For a fair comparison ab-initio and classical MD

![Figure 5.19: Calculated pair distribution function, $g(r)$, for the Tersoff potential (blue) and DFT (dashed green) at four different temperatures, (a) 1000 K, (b) 1400 K, (c) 2000 K and (d) 3000 K. The different noise levels are a consequence of different (short) simulation times.](image)

used the same starting structure and the same (short) simulation time $\sim 10 - 20$ ps. Note that from these simulations we can not make any conclusive statement about the melting temperature, because the simulations may be too short to completely melt the system at $1200$ K. In fact, the PDF at $1400$ K (panel (b)) still shows some structure, meaning that the system has not melted yet. Only at $3000$ K (panel (d)) does the PDF show the expected behavior for a liquid. Comparing the Tersoff potential and DFT we observe quite good agreement at all temperatures, except at $2000$ K (c). Here the Tersoff potential has already completely melted and shows no structure. This is expected, since with a short-range potential it is easier to rearrange the atoms resulting in a more diffusive PDF.

All in all, our developed Tersoff potential reproduces well the bulk properties of PbTe; it is, however, not able to capture the peculiar local structure. This is not completely unexpected: even if the potential is not completely isotropic as a result of the three-body angle-dependent part, its very short-range nature (only
nearest neighbors are considered) prevents it from capturing the local physics described by the correlated dipoles that extend over several unit cells.

5.4 Comparison between Buckingham and Tersoff potentials

It is not an easy task to assess, which of the two potentials describes the properties of PbTe best; both have strong and weak points. In the following I comment separately on each property.

The equation of state parameters are reproduced better by the Buckingham potential, in particular the bulk modulus. The experimental lattice constant is reproduced well by both potentials.

The Tersoff potential has the big advantage that the phonons are reproduced much better, showing a mixing between the acoustic and optic modes, and a softer TO mode. Unfortunately, this is not enough to capture the peculiar decay of the atomic pair correlations; both potentials fail here. In a similar way, because of their short-range nature, they predict weaker bond correlations for mid-range distances.

Interestingly, the Tersoff potential reproduces better the PDF and the related peak asymmetry. However, combined with its calculated smooth decay of the pair correlations we see that asymmetry does not necessarily imply off-centering or correlated dipoles; an anharmonic potential alone is enough to produce such asymmetric peaks.

Both potentials completely fail in reproducing the temperature evolution of the TO mode. Renormalization effects are very weak: with the Buckingham potential the optic frequencies are at least shifted, even if in the wrong direction, while with the Tersoff potential they stay almost constant. Furthermore, in contrast to DFT (see Fig. 9 in section 4.5), the optic branches do not broaden at all.

5.5 Conclusions & Outlook

In this chapter I discussed two “simple” effective potentials for PbTe. While both of them reproduce well the bulk (average) properties, they fail in reproducing the local structure. In this sense there is no real winner between the two.

The peculiar local structure is the consequence of a delicate balance between the optic and acoustic phonon modes originating from the lone pair of lead atoms and produces atomic correlations that extend over several unit cells. It is not really a surprise that neither of the potentials is able to reproduce such features: they do not have any way to capture the complex lone-pair physics, are short range and, even if the Tersoff potential is anisotropic, it is not possible to include the longer-range correlations into the three-body term alone. Furthermore, in contrast to the GeTe Tersoff potential, the three-body term is freely tunable and switched off for Pb atoms.

Conversely, these failures give important hints for the search for a better potential, which should be longer range and take into account the local bonding
environment. In general one should try to reproduce best the phonon properties. A promising route would be to try to incorporate the lone-pair effects of Pb atoms into the model, such that the soft TO mode, and possibly the coupling between acoustic and optic modes, could be described reasonably well. In this sense, the approach followed at the moment by Federico Zipoli at IBM Research – Zurich could be suitable: a core/shell model with Buckingham interactions would be the first step towards an anisotropic long-range potential that can describe well the phonon properties of PbTe.

On the other hand, this suggested route leads to more complex potentials that will eventually mitigate the biggest advantage of interatomic potentials, namely their computational cost. Instead of developing an effective potential, one could also do a Taylor expansion of the DFT energies as a function of the atomic displacements up to a certain order. While this is feasible in principle, in practice it turned out to be very difficult to compute many expansion coefficients while satisfying all symmetries [249]. Ai et al. [222] recently developed a slave mode expansion that makes the Taylor expansion more tractable. This method was used by Chen et al. [52] to build a potential for PbTe that was shown to be quite effective and is able to reproduce the splitting of the transverse optic (TO) mode at \( \Gamma \). It would be interesting to check if this potential can also reproduce the local structure derived in the previous chapter, but the results shown in Ref. [52] are promising.

The complex physics associated with PbTe is probably the largest limiting factor for classical potentials, and maybe only models taking into account quantum mechanics can capture reasonably well this simple, yet very complex, material. Anyway, I think that it is still worth pursuing the route of better classical potentials for PbTe, because they allow the study of bigger systems with a longer simulation time, which at the moment is heavily limited by the available computational power in first-principles computations. This is the only way to better understand the correlated dipoles and their role for the high thermoelectric performance of PbTe.
Hole doping in PbTe

In this chapter I present a characterization of Na- and Tl-doped PbTe, with an emphasis on the electronic properties close to the Fermi energy, that finally lead to the determination of the evolution of the Fermi surface in hole-doped PbTe.

As already discussed before, within first-principles methods doped systems can be studied in two different ways: using effective medium approaches (e.g. virtual crystal approximation or coherent potential approximation) or with the explicit insertion of impurities in supercells. The former is usually chosen because it is less computationally demanding and preserves the symmetry of the undoped system; in this way a comparison with experiments, e.g. angle-resolved photoemission spectroscopy (ARPES), is straightforward. On the other hand, these methods do not account for structural relaxations originating, e.g., from changes in bond character and/or strength caused by the impurity atoms, and clustering of the impurities.

This is the clear advantage of supercell calculations; any possible effect and interaction caused by the impurities is automatically taken into account. However, this comes with a huge increase in computational cost. Furthermore, disorder can only be obtained by averaging over many different structural configurations, which demands even larger supercells.

For very low doping concentrations effective medium theories are usually the only possible choice. In this work we are also interested in studying low dopings, but the claimed charge disproportionation in Tl-doped PbTe leaves us only with the choice of supercells.

The chapter is structured as follows: I will start by discussing the used supercells and our attempts to obtain a charge disproportionated state. Next, using the band unfolding technique (see section 2.3), I will prove the validity of the rigid band approximation, at least in the case of Na doping. Afterwards, I will present the evolution of the Fermi surface in hole-doped PbTe with the help of the latter approximation. To this end, I attach a paper [209] written in collaboration with Paula Giraldo-Gallo and Ian R. Fisher from Stanford University. There, we compare the DFT-computed evolution of the Fermi surface with Shubnikov-de Haas measurements on Na-doped PbTe. Finally, I will discuss the characterization of the \( \Sigma \) pockets (not included in the paper) and present a general (quantitative) comparison with experiments.
6.1 Computational details

The computations shown in this chapter were done using the projector augmented wave (PAW) implementation [193, 194] of DFT of the VASP package [120–123]. I used the PBEsol [124] exchange-correlation functional, an energy cutoff of 600 eV, and valence electron configurations $5d^{10}6s^26p^2$ for lead, $5s^25p^4$ for tellurium, $2p^63s^1$ for sodium, and $5d^{10}6s^26p^1$ for thallium. The threshold in the forces for structural relaxations was set to $10^{-5}$ eV/Å. Calculations in the primitive rocksalt cell were done with a $\Gamma$-centered $20 \times 20 \times 20$ $k$-point grid and spin-orbit coupling was included. For calculations with supercells the $k$-point grid was accordingly scaled down and spin-orbit coupling was not included because of computational cost. The unfolding of the bands has been performed using the BandUP code [175, 176]. The calculation of DHVA frequencies and cyclotron masses has been performed by computing Kohn-Sham energies on a $140 \times 140 \times 140$ $k$-point grid as an input for the SKEAF code [250] (for details see Appendix A).

6.2 Substitutional doping with supercells

Let me start by briefly discussing the qualitative impact of a substitution of lead by either sodium or thallium on the band structure close to the Fermi energy by comparing the valence configurations of lead ($5d^{10}6s^26p^2$), sodium ($2p^63s^1$) and thallium ($5d^{10}6s^26p^1$). Figure 6.1 shows sketches of the expected density of states (DOS) of Na- and Tl-doped PbTe for different nominal charges. Remember first that in an ionic picture, the nominal charges in PbTe are Pb$^{2+}$ and Te$^{2-}$. Sodium is expected to enter as Na$^+$, resulting in an empty 3s shell; the 2p electrons lie at much deeper energies. Thus, we do not expect any strong effects on the electronic structure, except for a shift of the Fermi level into the valence
6.2 Substitutional doping with supercells

band. On the other hand, experimentally Tl seems to enter either as Tl\(^{+}\) or Tl\(^{3+}\); the former has a configuration \(6s^2p^0\), so it should affect the electronic structure close to the Fermi energy (the energy of Tl \(s\) electrons is similar to the energy of Te \(p\) electrons \([103]\)). Moreover, it has the same formal configuration as Pb\(^{2+}\), such that some stereoechemical activity may be expected. While Tl\(^{3+}\) has no lone pair, one would still expect some hybridization of the formally empty \(s\) states with the Te \(p\) states influencing the electronic structure close to the Fermi level. To complete the picture, Tl\(^{2+}\), with a configuration \(6s^1p^0\), is also expected to have a strong influence on the electronic structure close to the Fermi energy.

I used two different kinds of supercells: for most of the computations I used a \(4 \times 4 \times 4\) supercell of the primitive cell (128 atoms in total) with one lead substitution (\(x = 1.6\%\)), and, primarily as a check, a \(3 \times 3 \times 3\) supercell of the conventional cubic cell (216 atoms in total) with two lead substitutions (\(x = 1.8\%\)). In the former structure only one inequivalent substitution exists [from now on I will refer to it as a configuration], while for the latter there are nine inequivalent ways of putting two impurities (see later).

6.2.1 Structural relaxations in the small supercell

I start by discussing the full structural relaxations of the small supercell. Interestingly, the forces in the unrelaxed structure are larger for atoms along the \([100]\) direction that includes the impurity atom. The largest distortions are then expected along this direction, as confirmed by Table 6.1. Both with Na and Tl doping, Pb atoms move towards the impurity, while Te atoms move away from it. In an ionic picture we can understand this with simple electrostatic arguments\(^1\): if the impurities enter with a nominal charge of +1 instead of +2, the neighboring Te\(^{2-}\) ions are less attracted, while Pb\(^{2+}\) ions are less repelled from the impurity – a

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Te</td>
<td>3.22</td>
<td>3.22</td>
<td>TI-Te</td>
<td>3.26</td>
<td>3.22</td>
</tr>
<tr>
<td>Na-Pb</td>
<td>4.53</td>
<td>4.55</td>
<td>TI-Pb</td>
<td>4.54</td>
<td>4.56</td>
</tr>
<tr>
<td>Na-Te</td>
<td>5.58</td>
<td>5.58</td>
<td>TI-Te</td>
<td>5.58</td>
<td>5.58</td>
</tr>
<tr>
<td>Na-Pb</td>
<td>6.39</td>
<td>6.44</td>
<td>TI-Pb</td>
<td>6.42</td>
<td>6.44</td>
</tr>
</tbody>
</table>

\(^1\) In a simple geometric picture the opposite behavior would be expected: both impurities, and in particular Na, are smaller than Pb, which would favor shorter bonds with the neighboring Te (accompanied by an attractive, and not repulsive, force).
first indication that both impurity types do enter with a smaller charge than +2. We can also extract the sequence of bond lengths along the aforementioned [100] direction: a peculiar pattern of short and long bonds is obtained (see Table 6.2), reminiscent of the discussion in chapter 4. From this arrangement of bonds we

Table 6.2: Bond lengths along the [100] directions containing the impurity atom. The numeration starts from the bond containing the impurity.

(a) Na-doped PbTe. The value in the rocksalt structure is 3.22 Å.  

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>3.22</td>
</tr>
<tr>
<td>2nd</td>
<td>3.17</td>
</tr>
<tr>
<td>3rd</td>
<td>3.26</td>
</tr>
<tr>
<td>4th</td>
<td>3.22</td>
</tr>
</tbody>
</table>

(b) Tl-doped PbTe. The value in the rocksalt structure is 3.22 Å.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>3.26</td>
</tr>
<tr>
<td>2nd</td>
<td>3.16</td>
</tr>
<tr>
<td>3rd</td>
<td>3.25</td>
</tr>
<tr>
<td>4th</td>
<td>3.21</td>
</tr>
</tbody>
</table>

expect to obtain stereochemically active lone pairs on Pb atoms. In fact, the charge density plot (Fig. 6.2) shows its signature in case of Tl doping, but not for Na doping. In this figure the charge density distribution in the cubic (100) plane (the diagonals in the plot corresponds to the cubic [100] directions) is presented for the uppermost Te p valence band. The impurity atoms sit at the four corners

Figure 6.2: Charge density distribution of the uppermost Te p valence band in the cubic (100) plane for (a) Na doping and (b) Tl doping. The color scale represents the charge density in Å⁻³. The (equivalent) impurity atoms sit at the four corners and the diagonals correspond to the [100] direction. Te atoms can be recognized by the red lobes, Pb atoms by the yellow lobes.

(because of periodic boundary conditions they are all equivalent images), while Te atoms correspond to sites with the red lobes. For Na doping (panel (a)) we note
that Na electrons are not contributing to this band and we observe a bit stronger
effects on Te atoms along [100] (the diagonals) with some non-spherical charge
distribution. On the other hand, for Tl doping (panel (b)) the charge density of the
nearest Te is clearly disturbed acquiring a non-spherical distribution. Moreover,
the Tl’s fourth-neighbor Pb atoms show an increase in charge density (red lobe
in the otherwise yellow region) away from Tl – a feature that can be ascribed to
the stereochemically active lone pair. This shows that Tl affects the electric prop-
erties of PbTe more strongly than Na, resulting in a more polarizable structure.
A possible reason is that Tl itself can have a stereochemically active lone pair.
We speculate that these deviations from the rocksalt structure characterized by
a stereochemically active lone pair are linked to the even higher thermoelectric
performance of the doped systems via a decrease of the thermal conductivity.

Let me now briefly comment on the charges obtained for the two kinds of
impurities. The local charge is not a completely well-defined quantity and is
extracted from the charge contained in a sphere around the atom; thus, the
charge depends clearly on the radius of this sphere. Unfortunately, there are
no unambiguous ways to define this radius; in this work I used the default
radii defined in the pseudopotentials delivered with VASP. Na fulfills the ionic
assumptions and is found to enter as Na\(^{+}\), while Tl is found to enter somewhere in
between Tl\(^{+}\) and Tl\(^{2+}\) (the difference in charge between Tl and Pb ions is less than
an electron). This is a clear indication that the ionic picture is not appropriate.

As a last thing, in Fig. 6.3 I compare the band structure between the unrelaxed
and relaxed structures. In the case of Na doping (panel (a)) the differences are

\[E - E_F [\text{eV}]\]

\[W \Gamma X L \Gamma K \Gamma\]

\[W \Gamma X L \Gamma K \Gamma\]

\[E - E_F [\text{eV}]\]

\[W \Gamma X L \Gamma K \Gamma\]

\[E - E_F [\text{eV}]\]

\[W \Gamma X L \Gamma K \Gamma\]

Figure 6.3: Comparison of the band structures between relaxed (blue) and unrelaxed
(dashed red) structures close to the Fermi energy for (a) Na doping and (b) Tl
doping.

minimal, in particular at the Fermi level, while for Tl doping (panel (b)) we can
observe significant changes. Te \(p\) bands are shifted up and contribute more to
the Fermi surface, and the bandwidth of the “impurity band” (see later for more
Hole doping in PbTe on this regard) is increased such that the density of states at the Fermi energy is decreased. This in turn suppresses any possible associated instability.

6.2.2 Comparison of different configurations of the big supercell

To tackle the charge disproportionation issue in Tl-doped PbTe, at least two impurity atoms are needed. In the following I will spend some time in characterizing Tl-doped PbTe with a doping of $x = 1.8\%$ using the bigger supercell. Because of computational cost I did not perform the same analysis for Na-doped PbTe, since we do not expect any particular additional effects when several Na impurities are explicitly inserted.

For a $3 \times 3 \times 3$ cubic supercell one can find nine inequivalent configurations to substitute two lead atoms. The first impurity can be set at one corner of the cube, chosen as the origin in the following. Because of the cubic and translational symmetry the second has to lie in the octant defined by $x \leq y \leq z$, $x \leq 1/2$, $y \leq 1/2$, $z \leq 1/2$ (in fractional coordinates) giving the following coordinates:

1. $(0, 0, 1/3)$
2. $(0, 1/6, 1/6)$
3. $(0, 1/6, 1/2)$
4. $(0, 1/3, 1/3)$
5. $(0, 1/2, 1/2)$
6. $(1/6, 1/6, 1/3)$
7. $(1/6, 1/3, 1/2)$
8. $(1/3, 1/3, 1/3)$
9. $(1/3, 1/2, 1/2)$

Figure 6.4 shows the total energy comparison of the nine different supercells without a structural relaxation. It is again interesting to see that in the most favorable configuration the two Tl sites are along the $[100]$ direction. In general, configurations where the two Tl atoms sit close are energetically favored; in this way a possible transfer of electrons between different Tl sites could be improved, which is favorable for superconductivity through charge-Kondo effect.

Because of computational cost I did not perform a full structural relaxation on all nine configurations, but I took only some of them, that I thought would be representative. I chose configurations where the two Tl impurities are nearest neighbors (nr. 2), nearest neighbors along cartesian axes (nr. 1), and furthest away (nr. 9). Using these three configurations I tried to obtain the charge disproportionated state with different methods, but all of them failed.

Remember first that Tl impurities in PbTe are thought to be negative-$U$ centers. With this in mind I started using the arguments by Harrison [103]; he found that the only way to obtain negative-$U$ behavior, and consequently charge disproportionation, is by lattice relaxations giving rise to bond disproportionation (also called breathing mode distortion), i.e. the two inequivalent Tl sites would have different sized nearest-neighbor TlTe$_6$ octahedra, one larger for Tl$^+$ and one smaller for Tl$^{3+}$. For that I manually changed the size of the octahedra by changing the nearest-neighbor Tl-Te bond lengths and computed the total energy (see Fig. 6.5). All three configurations show a monotonic increasing energy with
Figure 6.4: Total energy of the nine configurations. The inset shows the three more energetically favorable configurations. Shown is the (100) plane containing the first Tl site at the origin (green); Te atoms are drawn in gray, Pb in black. The second Tl site for the first configuration is shown in blue, for the second in red, and for the third in purple.

Figure 6.5: Total energy as a function of bond change in the breathing-mode distortion for three representative configurations.
change in bond length – a charge disproportionated state is ruled out\(^2\). Note that, even if the predicted bond length change of 0.05 Å [103] would be difficult to detect experimentally for a disordered system, it should not pose any problems for DFT calculations.

A breathing mode distortion is observed also in rare-earth nickelates RNiO\(_3\) [107, 108] (where \(R\) represents the rare-earth element), namely in a metal to insulator transition accompanied by the emergence of two types of NiO\(_6\) octahedra; half of them are compressed and half are expanded. A signature of the bond disproportionation is the different magnetic moments of the inequivalent Ni sites. Linked to this transition a charge disproportionation has been suggested: some Ni\(^{3+}\) sites would become Ni\(^{3+ \delta}\) (compressed octahedra) and some Ni\(^{3-\delta}\) (expanded octahedra)\(^3\). In this field of research it was found that standard DFT alone is not able to account for this structural distortion [252]. For some compounds in the series the initialization of the magnetic order is enough to obtain the breathing-mode distortion, for some other DFT+U is needed [253].

In the same spirit I tried both to initialize different magnetic moments on the two Tl sites and also positive and negative \(U\) values on Tl \(s\) states (\(U\) between \(-5\) eV and \(5\) eV). In contrast to the rare-earth nickelates, where this strategy was successful, here it does not produce any bond-disproportionated structure. Even though from an ionic picture one would not expect a different magnetic moment (Tl\(^{+}\) and Tl\(^{3+}\) differ just by a closed \(s\) shell), with some covalent character the two inequivalent Tl sites would not differ anymore by an integer number of electrons, giving rise to a possible difference in magnetic moments. However, the two different Tl ions are found to neither possess a different magnetic moment nor a different charge\(^4\). Partly, this can be ascribed to the DFT+U machinery that is not really developed to put a \(U\) on delocalized states, such as the \(s\) orbitals here. Furthermore, here the situation is a bit more complicated than in the nickelates, because the bond disproportionation should happen only in the (impurity) TlTe\(_6\) octahedra (the average space group does not change!), while in the rare-earth nickelates the breathing-mode distortion happens on all NiO\(_6\) octahedra with a resulting change in space-group symmetry. Therefore, in this case larger supercells may be needed to capture the effect.

On the other hand, more advanced techniques could be tried in future studies to correctly describe Tl-doped PbTe:

- a charge-constrained DFT, as was developed for VASP in Ref. [254]. This is achieved by controlling the occupation of orbitals in the DFT+U corrections;

\(^{2}\)Structures with different sized octahedra do possess a charge disproportionation, but this does not seem to be energetically favorable.

\(^{3}\)Whether a real charge order exists is currently under debate [108, 251], but this is not relevant for my discussion.

\(^{4}\)I did not try to put even larger (or smaller) \(U\) values, because the endpoints, \(\pm 5\) eV, caused a huge (nonphysical) charge transfer between the Tl sites and the neighboring Te and Pb atoms. This happened indiscriminately for both Tl sites.
• combining DFT with dynamical mean field theory (DMFT). The latter was developed to correctly describe strongly correlated materials that are not captured well by DFT.

However, also on the experimental side further studies would be needed to solve the charge (and bond) disproportionation controversy; here, techniques that can resolve the local structure, such as total scattering, could prove useful.

### 6.2.3 Electronic structure with supercells

In this section I will discuss the effects of the impurities on the electronic structure (using only the smaller supercell), focusing on regions close to the Fermi energy. Several first-principles calculations have already been carried out to study the effect of different impurities on the electronic structure in PbTe [77, 95, 96, 255–262]. Na impurities with a concentration of a few percents were shown to not greatly affect the band structure [255, 258, 261, 262], except for the lifting of the 8-fold degeneracy at the valence-band maximum; the rigid-band approximation was found to be successful. On the other hand, Tl impurities were shown to have a large impact on the states close to the Fermi energy with the formation of a resonant (impurity) band at the Fermi level [77, 95, 96, 255–257, 262]. This band originates from an hybridization of the Tl \( s \) states with the Te \( p \) states, which are known to form the upper valence bands, and was linked to the high thermoelectric performance of Tl-doped PbTe [77, 95].

In the following I focus on the low concentrations of Na and Tl impurities that were used in the experiments performed by Paula Giraldo-Gallo and Ian R. Fisher from Stanford University.

I start by showing the density of states for the two types of impurities (Figs. 6.6-6.7). As expected, Na is shown to not contribute to states close to \( E_F \) (note the small values on the \( y \) axis in Fig. 6.7(a)), while Tl \( s \) states hybridize with Te \( p \) states forming a bonding band at approx. 6 eV below \( E_F \) and an anti-bonding band just at the Fermi energy. Note that the anti-bonding state has a stronger Te \( p \) character than the bonding state that shows a high Tl \( s \) peak.

In Figure 6.8 I compare the calculated electronic band structure with (red) and without (dashed green) the impurity. The zero of energy is set at the top of the Te \( p \) valence bands. Na substitution does not affect considerably the bands close to the Fermi energy, except for a lifting of the eight-fold degeneracy at the top of the valence band, indicated by black arrows. A consequence of this shift in one of the valence bands is a shift of the Fermi energy to lower energy relative to its position in the rigid band approximation for the Na impurity. On the other hand, for the Tl impurity the original Te \( p \) bands contribute very little to the doped Fermi surface and an additional band (dotted red line) is present at the Fermi energy – the antibonding state.

Figure 6.9 shows the difference in total DOS with and without the impurity atom. For Na doping we see a distinct drop in the DOS just below the top
Figure 6.6: Density of states for (a) Na-doped PbTe and (b) Tl-doped PbTe.

Figure 6.7: Contributions of the impurity atoms to the density of states for (a) Na-doped PbTe and (b) Tl-doped PbTe.
Figure 6.8: Calculated band structure with (red) and without (dashed green) the impurity for the 128-atom supercell ($x \approx 1.6\%$). The zero of energy was set at the top of the Te $p$ valence bands. The cyan dash-dotted line corresponds to the Fermi level in the rigid band approximation. Note the lifting of the degeneracy of the top valence bands (marked by arrows).

(a) Na-doped PbTe; the Fermi energy (horizontal dashed red line) is lower than the rigid band value because of the lifting of degeneracy.

(b) Tl-doped PbTe; the antibonding band is shown as a dotted red line. Despite the lifting of degeneracy, the Fermi energy is slightly higher than the rigid band value because of the antibonding band.
of the valence band (set to 0 eV) due to band shifts caused by the presence of the impurity atom. For Tl doping the bonding and antibonding states that form through hybridization of Tl $s$ and Te $p$ states can be clearly seen as sharp peaks.

![Difference in the total DOS with and without the impurity](image)

**Figure 6.9:** Difference in the total DOS with and without the impurity, $\Delta$DOS = DOS$_{\text{with imp.}}$ − DOS$_{\text{undoped}}$; top panel for Na doping, bottom panel for Tl doping. The top of the valence band is set to 0 eV.

From these considerations, we would expect that a simple rigid-band approximation will not work for Tl-doped PbTe, while it might give qualitatively correct results for Na-doped PbTe (see more on this in section 6.3.1). In an effort to quantify the implications of the impurities on the Fermi surface I present next the unfolded band structure.

### 6.2.4 Unfolded bands with Na and Tl impurities

In this section I discuss the unfolded band structure when the doping is $x = 1.6 \%$. The main goal is to understand what are the main effects of the lifted degeneracy and the “impurity band” on the Fermi surface. For this reason I will mostly show the effective band structure close to the Fermi energy. In this way we can directly compare our supercell computations with ARPES and quantum-oscillation experiments. For this task I used the 128-atom supercell, but I checked that the general features are correctly described with the averaged effective band structure from all nine configurations of the 216-atom supercell. For a better description even larger supercells should be considered, such that clustering and many random realizations could be combined. Unfortunately, this would require a computational power that I did not have at my disposal.

Figure 6.10 presents the EBS for the Te $p$ bands. At first sight, the bands do not seem to be affected much by either impurity. Note that for Tl doping the triple degeneracy at $\Gamma$ is lost (see the different color scale). For a detailed analysis of the
Substitutional doping with supercells

Figure 6.10: Unfolded band structure of doped PbTe. The red line shows the dispersion relation of pristine PbTe shifted so that the Te $p$ valence band maxima coincide, while the color scale represents $\delta N$ (Eq. (2.19)). (a) Na doping; the largest effects can be seen at about 1 eV below $E_F$ with a smearing of the bands. Otherwise no large deviations from pristine PbTe can be seen – even at $E_F$ (for a detailed analysis see Fig. 6.11). (b) Tl doping; the Te $p$ bands stay largely unaffected. The bonding and antibonding states contribute to the dispersion only close to $\Gamma$ and $L$, respectively (for a detailed analysis see Figs. 6.11-6.12).

bands close to $E_F$ let us consider Fig. 6.11. We can observe a large smearing of the bands for Na doping approx. 1 eV below $E_F$; this is not the case for Tl doping. With both dopings we can observe contributions to the Fermi surface along the $\Sigma$ line; for Na doping this obviously stems from the Te $p$ bands, while for Tl this can be ascribed to the anti-bonding band. Note that the anti-bonding band contributes to appreciable spectral weight only close to $L$, except for some small weight along the $\Sigma$ line. This means that the decomposition of the supercell wavefunction into Bloch states of the primitive cell results in appreciable character only for $\mathbf{k} \approx L$; the supercell wavefunction does not contain any Bloch character corresponding to other regions of the primitive Brillouin zone. Moreover, the unfolded anti-bonding band shows some dispersion (which can already be observed in the supercell band structure of Fig. 6.8), pointing to the fact that the corresponding states are not completely localized (in fact, a localized state would result in a flat line). This corresponds to a conceptual difficulty intrinsic of the unfolding procedure: electrons from impurity atoms do not always contribute to or as a “normal” band.

A similar feature is observed for the bonding band of Tl-doped systems (see Fig. 6.12). In this case, spectral weight can be observed only close to $\Gamma$. We can also nicely see that the bonding band repels and pushes down the lower lying Pb $s$ bands.
Figure 6.11: Unfolded band structure of doped PbTe. The red line shows the dispersion relation of pristine PbTe shifted so that the Te \( p \) valence band maxima coincide, while the color scale represents \( \delta N \) (Eq. (2.19)). (a) Na doping; the largest effects can be seen at about 1 eV below \( E_F \) with a smearing of the bands. Otherwise no large deviations from pristine PbTe can be seen – even at \( E_F \). (b) Tl doping; the Te \( p \) bands stay largely unaffected. The anti-bonding state contributes to the dispersion at \( L \) with some weak effects along \( \Sigma \).

Figure 6.12: Unfolded band structure for Tl doping showing the bonding state. The red line shows the dispersion relation of pristine PbTe shifted so that the Te \( p \) valence band maxima coincide, while the color scale represents \( \delta N \) (Eq. (2.19)). The bonding state contributes to the dispersion at \( \Gamma \) and pushes down the lower lying Pb \( s \) bands.
Next, I present the charge distribution in real space in the cubic (100) plane (the diagonals in the plot corresponds to the cubic [100] directions) for the bonding and anti-bonding band in Tl-doped samples (Fig. 6.13). The impurity atoms sit at the four corners (because of periodic boundary conditions they are all equivalent images). One can clearly recognize that the bonding band (panel (a)) presents almost only Tl character, while the anti-bonding band shows Te character, in particular from the nearest-lying atoms. In any case, the contributions originate mostly again from atoms on the [100] direction.

**What are the consequences for the Fermi surface?** By calculating the effective band structure we can directly compare supercell calculations with experiments, in particular ARPES. For this purpose I computed the dispersion relations close to the \( L \) point along the longitudinal and transverse axes of the ellipsoid. In this way we can estimate the contribution of the split band (in case of Na doping) and the anti-bonding band (in case of Tl doping) to the Fermi surface.

Figure 6.14 shows the EBS for Na doping along the two axes. The split band is clearly recognizable as a smaller secondary pocket. By estimating its ellipsoidal axes, I was able to extract the expected maximum and minimum DHVA frequencies: \( F_{\text{max}} = 105 \pm 5 \) T and \( F_{\text{min}} = 100 \pm 5 \) T, to be compared with \( F_{\text{max}} = 335 \pm 5 \) T and \( F_{\text{min}} = 140 \pm 5 \) T of the larger pocket. The pocket originating from the split band has an almost spherical shape that would give rise to a flat angular evolution in quantum-oscillation experiments. However, it is questionable if this pocket could be detected in view of the small spectral weight, in particular along the longitudinal direction.

Very interesting is the situation for Tl doping. Figure 6.15 shows the EBS close to the \( L \) point. The split band lies about 0.25 eV below \( E_F \) (in the figure one
Figure 6.14: Unfolded band structure close to the $L = (0.5, 0.5, 0.5)$ point (in $2\pi/a$ units, with $a$ the lattice constant) for Na doping. The color scale represents $\delta N$ (Eq. (2.19)). (a) Longitudinal direction; $k_1 = (0.4, 0.4, 0.4)$ and $k_2 = (0.6, 0.6, 0.6)$. (b) Transverse direction; $k_1 = (0.4, 0.5, 0.6)$ and $k_2 = (0.6, 0.5, 0.4)$.

Figure 6.15: Unfolded band structure close to the $L = (0.5, 0.5, 0.5)$ point (in $2\pi/a$ units, with $a$ the lattice constant) for Tl doping. The color scale represents $\delta N$ (Eq. (2.19)). (a) Longitudinal direction; $k_1 = (0.4, 0.4, 0.4)$ and $k_2 = (0.6, 0.6, 0.6)$. (b) Transverse direction; $k_1 = (0.4, 0.5, 0.6)$ and $k_2 = (0.6, 0.5, 0.4)$. 
can recognize a weak dispersion at this energy), and thus does not contribute to the Fermi surface. Moreover, the anti-bonding band does not seem to contribute to the Fermi surface either, only the lower lying Te $p$ bands do. Note that this behavior would be consistent with an ARPES characterization of Tl-doped PbTe by Nakayama et al. [119]. There, the authors did not find any indications for the existence of localized impurity states at $E_F$ for $x = 0.5\%$ doped samples (a concentration which is larger than the critical concentration $x = 0.3\%$ where the hole concentration should saturate). On the contrary, they concluded that Tl doping causes hole doping in the top valence band, even though the rigid-band model is stated to be not valid. The question then arises, where the electron from the anti-bonding band has gone. As previously discussed, some spectral weight can be found also along the $\Sigma$ line. Figure 6.16 shows the EBS along high-symmetry directions that contain the $\Gamma$ point. Interestingly, the “band” originating from the anti-bonding band crosses the Fermi energy along $\Sigma$ (panel (a)), but actually only once. The same happens along $\Delta$ (panel (b)), even if the very small

![Figure 6.16: Unfolded band structure for Tl doping along high-symmetry lines that contain the $\Gamma$ point. The color scale represents $\delta N$ (Eq. (2.19)). (a) $\Sigma$, (b) $\Delta$, and (c) $\Lambda$ line.](image)
spectral weight makes it hard to recognize in the printed plot. On the other hand, along Λ (panel (c)) only the crossing of the Te p bands can be observed. Since the spectral weights are (very) small, we can not follow the dispersion of the impurity band along the whole path, and, therefore, it is difficult to tell how the corresponding Fermi surface looks like and if it would be detectable in ARPES or quantum oscillations. The trend in the dispersion relations seems to suggest that the Fermi surface would contain the K and X points, but not the Γ and L points; to identify its shape a complete scan through the region of interest of the Brillouin zone would be required. I did not proceed further in this direction because of computational cost.

On the other hand, I can not exclude that averages over many configurations of larger supercells would change the picture. Another possibility is that this is the signature of a more profound issue linked to the breakdown of the approximations at the heart of the unfolding theory, e.g. when the doped system can not be approximately described by the translational symmetry of the primitive cell. Note that this can be the case also in experiments, because for their interpretation and representation a reference Brillouin zone has to be chosen (which normally coincides with the primitive cell of the undoped system), as already discussed in section 2.3.

6.3 Fermi surface evolution

In the following I describe the evolution of the Fermi surface of hole-doped PbTe with the rigid-band approximation. In fact, we have seen that this approximation should be valid for Na-doped PbTe, while for Tl-doped PbTe we expect it to be successful only for doping smaller than the critical concentration $x_c = 0.3\%$.

For larger thallium concentrations, the hole doping of the valence band is experimentally predicted to saturate and the additional charge carriers to contribute to an impurity band [98, 99, 118], clearly invalidating the approximation. In section 6.3.1 we will show that the rigid-band approximation provides qualitative (and quantitative) agreement with experiments for Na-doped PbTe.

The starting point is the band structure of pristine PbTe (Fig. 6.17). As discussed before, we obtain a direct gap at the $L$ point, followed by a second valence band maximum along the Σ line, 70 meV below the top of the valence band.

Based on this energy dispersion we expect the following evolution of the Fermi surface when the Fermi level is moved into the valence band (Fig. 6.18):

(a) At low impurity concentrations, the Fermi surface consists only of the $L$ pockets.

(b) At intermediate concentrations, the Σ pockets also appear.

(c) At even larger concentrations the $L$ and Σ pockets merge together.
Figure 6.17: Band structure of pristine PbTe close to the Fermi energy, $E_F$. A direct gap is observed at the $L$ point, and a second valence band maximum occurs along the $\Sigma$ ($\Gamma - K$) high-symmetry line.

Figure 6.18: Evolution of the Fermi surface with representative hole concentrations, $p$.
(a) $p = 0.3 \times 10^{19}$ cm$^{-3}$; only the eight $L$ pockets contribute (shown in red).
(b) $p = 12.1 \times 10^{19}$ cm$^{-3}$; the twelve $\Sigma$ pockets contribute to most of the hole density (shown in blue).
(c) $p = 36.2 \times 10^{19}$ cm$^{-3}$; $L$ and $\Sigma$ pockets are merged together to form a “cube-shaped” Fermi surface.
Taking into account the expected morphology of the Fermi surface, suitable planes for the determination of the \( L \) and \( \Sigma \) pockets are the (110) (and also (100)) planes [118] (see Fig. 6.19). In this way, if the pockets were ellipsoidal, their axes could be directly determined:

\textbf{\( L \) pockets}  The (110) plane contains four \( L \)-pockets, while the other four are contained in a plane perpendicular to it (Fig. 6.19(a)). In this plane of rotation there are three inequivalent \( L \)-pockets giving rise to three branches in Fig. 6.20 (red lines). The minimum cross-sectional area is detected at approx. 55°, and the maximum occurs at approx. 35° and at 90°.

\textbf{\( \Sigma \) pockets}  In the (110) plane of rotation there are two inequivalent \( \Sigma \)-pockets (Fig. 6.19(b)) giving rise to two branches in Fig. 6.20 (dashed blue lines). The minimum cross-sectional area is detected at 0°, and the maximum at 0° and at 90°.

---

Figure 6.19: Sketch of the (110) plane used for the determination of the morphology of the Fermi surface. The angle \( \theta \) represents the angle formed with the \([100]\) direction. In the quantum-oscillation experiments the magnetic field was rotated from the \([100]\) (0°) to the \([110]\) (90°) direction in steps of 5°; in this way also the \([111]\) direction is sampled at about 55°. The two panels show the situation for the \( L \) pockets (a) and \( \Sigma \) pockets (b). Adapted figure with permission from Ref. [118] (page 107).
Figure 6.20: Angle dependence of the cross-sectional areas for ellipsoidal \( L \)- and \( \Sigma \)-pockets in the (110) plane. An angle of 0° corresponds to the [100] direction. The maximum (\( f_{\parallel} \)) and minimum (\( f_{\perp} \)) frequency was set to 50 T and 300 T, respectively. The \( L \) pockets produce three branches (red); \( f_{\parallel} \) can be determined at approx. 35° and 90°, \( f_{\perp} \) at approx. 55°. The \( \Sigma \) pockets produce two branches (dashed blue); \( f_{\parallel} \) can be determined at 0° and 90°, \( f_{\perp} \) at 0°.

6.3.1 Paper

The following paper, Giraldo-Gallo et al. [209] Copyright (2016) by the American Physical Society, presents the study of the evolution of the Fermi surface in Na-doped PbTe both experimentally and theoretically. The work was done in collaboration with Paula Giraldo-Gallo and Ian R. Fisher from Stanford University. I performed and analyzed all first-principles calculations, wrote the corresponding sections, and was involved in the writing of the whole paper and in the interpretation of the results.

In the paper we start by showing my DFT predictions for the Fermi-surface evolution. First, we critically assess the validity of the rigid-band approximation and discuss the dependence on computational settings and volume (see also chapter 3 and Appendix C in the paper). We find that the rigid-band approximation is in principle able to deliver only qualitative results; quantitative predictions are difficult because of the high sensitivity on computational parameters. Interestingly, we show that the evolution with doping of de Haas–van Alphen (DHVA) frequencies and cyclotron masses is not affected much by volume. We then present the detailed evolution of the Fermi surface with the expected angular evolution of DHVA frequencies and discuss non-ellipsoidal effects when the \( \Sigma \) pockets start contributing. The goal is to provide as many details as possible to guide the analysis of experiments to assess if the Fermi surface is originated by a
single band, i.e. whether the $\Sigma$ pockets contribute, and if the contributing pockets are ellipsoidal.

Next, we present the experimental results analyzed keeping in mind the signatures derived in the theoretical part. We conclude that the calculated qualitative evolution is correctly describing the experiments, except the band offset is underestimated in DFT – the measured Fermi surface is originating from solely one band for concentrations up to $x = 0.62 \%$ [this is the maximum concentration studied].
Fermi surface evolution of Na-doped PbTe studied through density functional theory calculations and Shubnikov–de Haas measurements

P. Giraldo-Gallo,1,2,3 B. Sangiorgio,4 P. Walmsley,1,5 H. J. Silverstein,1,5 M. Fechner,4 S. C. Riggs,3 T. H. Geballe,1,5 N. A. Spaldin,4 and I. R. Fisher1,5

1Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA
2Department of Physics, Stanford University, Stanford, California 94305, USA
3National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA
4Materials Theory, ETH Zurich, Wolfgang-Pauli-Strasse 27, CH-8093 Zürich, Switzerland
5Department of Applied Physics, Stanford University, Stanford, California 94305, USA

(Received 5 September 2016; published 23 November 2016)

We present a combined experimental and theoretical study of the evolution of the low-temperature Fermi surface of lead telluride (PbTe) when holes are introduced through sodium substitution on the lead site. Our Shubnikov–de Haas measurements for samples with carrier concentrations up to $9.4 \times 10^{19}$ cm$^{-3}$ ($0.62$ Na at. %) show the qualitative features of the Fermi surface evolution (topology and effective mass) predicted by our density functional (DFT) calculations within the generalized gradient approximation (GGA): we obtain perfect ellipsoidal $L$ pockets at low and intermediate carrier concentrations, evolution away from ideal ellipsiodicity for the highest doping studied, and cyclotron effective masses increasing monotonically with doping level, implying deviations from perfect parabolicity throughout the whole band. Our measurements show, however, that standard DFT calculations underestimate the energy difference between the $L$ point and $\Sigma$-line valence band maxima, since our data are consistent with a single-band Fermi surface over the entire doping range studied, whereas the calculations predict an occupation of the $\Sigma$ pockets at higher doping. Our results for low and intermediate compositions are consistent with a nonparabolic Kane-model dispersion, in which the $L$ pockets are ellipsoids of fixed anisotropy throughout the band, but the effective masses depend strongly on Fermi energy.

DOI: 10.1103/PhysRevB.94.195141

I. INTRODUCTION

Lead telluride (PbTe) is a widely known thermoelectric material and a narrow-gap semiconductor, which can be degenerately doped by either Pb (hole-doping) or Te (electron-doping) vacancies, or by introduction of acceptor or donor impurities [1–3]. Such impurity dopants have been shown to enhance the thermoelectric figure of merit $zT$ from 0.8 to 1.4 for the case of sodium doping [4–6], and to 1.5 for doping with thallium [4,7]. Ti is also the only dopant known to date that leads to a superconducting ground state in PbTe: remarkably its maximum critical temperature of $T_c = 1.5$ K is almost an order of magnitude higher than other superconducting semiconductors with similar carrier density [8–12]. Understanding the physical origin of these enhanced properties and their dependence on the choice of dopant chemistry requires a detailed knowledge of the electronic structure, in particular its evolution with changes in dopant and carrier concentrations.

The valence band of PbTe has two maxima, located at the $L$ point and close to the midpoint of the $\Sigma$ high-symmetry line (we call this the $\Sigma_3$ point) of the Brillouin zone (see Fig. 1). The enhancement of $zT$ with doping has been recently suggested to be at least in part associated with a decrease in the effective dimensionality of parts of the Fermi surface as the $\Sigma_3$ pockets connect (Fig. 2) [13]. For the case of superconductivity, an increase of the density of states at the TI concentration for which superconductivity emerges, as a consequence of the appearance of an additional band, has been invoked as a possible explanation for the enhanced $T_c$ [9]. Such hypotheses can be tested by a direct experimental determination of the Fermi surface topology and its evolution with carrier concentration. To date, such studies have been limited to quantum oscillation measurements performed in the low carrier concentration regime ($p \lesssim 1.1 \times 10^{19}$ cm$^{-3}$ for full topology) [14,15], although the enhanced thermoelectric and superconducting properties occur at considerably higher carrier concentrations. A direct measurement of the Fermi surface characteristics for these higher carrier densities is clearly needed.

In this paper we present the results of a detailed computational and experimental study of the fermiology of PbTe (Pb$_{1-x}$Na$_x$Te), with carrier concentrations up to $9.4 \times 10^{19}$ cm$^{-3}$, obtained via density functional theory (DFT) calculations of the electronic structure, and measurements of quantum oscillations in magnetoresistance for fields up to 35 T. These measurements enable a direct characterization of the Fermi surface morphology and quasiparticle effective mass for values of the Fermi energy that far exceed those available by self-doping from Pb vacancies. Our main findings are:

(i) At low temperatures, the Fermi surface is formed from eight half-ellipsoids at the $L$ points (the $L$ pockets) with their primary axes elongated along the [111] directions. The Fermi surface is derived from a single band up to the highest carrier concentration measured, $9.4 \times 10^{19}$ cm$^{-3}$.

(ii) The $L$ pockets are well described by a perfect ellipsoidal model up to a carrier concentration of $6.3 \times 10^{19}$ cm$^{-3}$. For a carrier concentration of $9.4 \times 10^{19}$ cm$^{-3}$, subtle deviations from perfect ellipsiodicity can be resolved. These deviations are qualitatively consistent with those predicted by the band structure calculations.

(iii) The effective cyclotron masses increase monotonically with carrier concentration for all high-symmetry...
FIG. 1. Energy dispersion for stoichiometric PbTe along the high symmetry directions of the fcc Brillouin zone, calculated in this work using density functional theory (DFT) (for details see text). A direct gap, underestimated compared with experiment as is usual in DFT calculations, is observed at the L point, and a second valence band maximum occurs along the Σ high-symmetry line. A representative Fermi surface, which emerges as the Fermi energy is shifted into the valence band by Pb vacancies or hole-dopant impurities, is shown in the inset. For the choice of Fermi level shown (green-dashed line), the Fermi surface contains eight half-ellipsoids (shaded in red) centered at the L point and oriented along the [111] directions (L pockets), and 12 Σ pockets (shaded in blue) centered close to the midpoint of the [110] Σ line and oriented along the [100] directions.

Directions, implying that the L band is not well described by a perfect parabolic model for any carrier density. This evolution is also consistent with the predictions from our band structure calculations.

(iv) Although the qualitative evolution of the Fermi surface topology with carrier concentration is correctly predicted by band structure calculations, these calculations underestimate the band offset (between the top of the L band and the top of the Σm band).

Before detailing our experiments, we emphasize that our measurements are made in the low-temperature regime and caution should be exercised before extrapolating the results to different temperature regimes. Quantum oscillations characterize the low-temperature properties of a material, and due to the exponential damping factor, they cannot be observed above approximately 60 K in Na-doped PbTe. Hence, we do not claim that our first three findings outlined above necessarily remain valid at higher temperatures. In particular, earlier experimental studies, based on magnetoresistance and Hall coefficient measurements [16], have indicated an appreciable temperature dependence of both the band gap and the band offset (between L and Σ band maxima) in PbTe. Additionally, recent angle-resolved photoemission spectroscopy (ARPES) experiments have provided evidence for the degeneracy of the top of these two bands at high temperatures, becoming degenerate at $\sim 800$ K [17–19]. The current measurements provide a definitive determination of the morphology of the bulk Fermi surface at low temperatures, and hence provide an important point of comparison for band structure calculations, but additional measurements based on a technique that is less sensitive to the quasiparticle relaxation rate, such as ARPES, are required in order to determine whether the Σ pocket remains unoccupied at higher temperatures for the carrier concentrations studied here.

II. FIRST-PRINCIPLES CALCULATIONS

To provide a baseline with which to compare our experimental data, we first show density functional theory (DFT) calculations of the electronic structure of PbTe with and without doping. An accurate description of this compound within DFT is very challenging; in particular, the computed band structure is highly sensitive to the choice of volume, the exchange-correlation functional, and whether or not spin-orbit coupling is included. A change in lattice constant of 1%, for example, can both change the band offset by 60% and generate a ferroelectric instability. Moreover, when spin-orbit coupling is included, an unusually fine k-point mesh is needed to converge the phonon frequencies, forces, and Fermi energy. This unusual sensitivity to the input parameters in the calculation is of course related to the many interesting properties of PbTe, which is on the boundary between various competing structural (incipient ferroelectricity [20,21]) and electronic (superconductivity [10–12] and topological insulator [22,23]) instabilities. Interestingly, we show in Appendix C that the volume does not significantly affect the computed evolution with doping of the cyclotron masses and the frequencies of quantum oscillations. Therefore, experimental variations in volume, as occur for example with temperature, do not affect our conclusions.

A. Computational details

Our calculations were performed using the PAW implementation [24,25] of density functional theory within the VASP package [26]. After carefully comparing structural and electronic properties calculated using the local density approximation (LDA) [27], PBE [28], and PBEsol [29] with available experimental data, we chose the PBEsol exchange-correlation functional as providing the best overall agreement. We used a $20 \times 20 \times 20$ $\Gamma$-centered k-point mesh and to ensure a convergence below 0.1 $\mu$eV for the total energy used a plane-wave energy cutoff of 600 eV and an energy threshold for the self-consistent calculations of 0.1 $\mu$eV. We used valence electron configurations $5d^{10}6s^26p^2$ for lead, $5s^25p^3$ for tellurium, and $2p^63s^1$ for sodium. Spin-orbit coupling was included. The unit cell volume was obtained using a full structural relaxation giving a lattice constant of 6.44 Å (to be compared with the experimental 6.43 Å [20] at 15 K). Kohn-Sham band energies were computed on a fine $(140 \times 140 \times 140)$ three-dimensional grid covering the entire Brillouin zone and used as an input for the SKEAF code [30] which allows for extraction of extremal cross-sectional areas of the Fermi surface in different spatial orientations.
B. Rigid-band approximation

First, we computed the Fermi-surface evolution as a function of doping (shown in Fig. 2) by rigidly shifting the Fermi energy in the pure PbTe structure and assuming one hole per dopant. This rigid-band approximation allows very fine samplings of the Brillouin zone, which are necessary for the lower concentrations that we use in our experiments with explicit Na doping (at a concentration of 3\%\textsuperscript{19}).

The frequencies of the \(\Sigma\) pockets are shown in red, and compared with those expected in a perfect ellipsoidal model shown as black lines. The evolution of the \(\Sigma\) pockets is shown in blue. These pockets appear at a dopant concentration of \(x = 0.11\%\) (\(p_L \approx 3.5 \times 10^{19} \text{cm}^{-3}\)). In column (d), the \(\Sigma\) and \(L\) pockets have merged, forming a cube-shape Fermi surface; cross sections that cannot be identified separately with \(\Sigma\) or \(L\) are shown in purple. We plot frequencies up to 600 T, noting, however, that frequencies up to 8 kT occur, corresponding to the large-square Fermi surface orbits. As described in the main text, our quantum oscillation studies reveal that for carrier densities up to at least 9.4 \times 10^{19} \text{cm}^{-3} value, the maximum studied in this report, the Fermi surface is found to only comprise \(L\) pockets (shown in red), implying a larger band offset between the \(L\) and \(\Sigma\) pockets than predicted by these and other DFT calculations.

We show here results for a 4 \times 4 \times 4 supercell of the primitive cell containing 128 atoms (\(x \approx 1.6\%\)), with one lead ion substituted by sodium. The unit cell volume was kept the same as in pristine PbTe (it would be changed by less than 0.1\% by a full structural relaxation). We checked also that our conclusions are qualitatively unchanged for a larger 216 atom supercell (3 \times 3 \times 3 of the conventional cubic cell) in which one or two lead ions are substituted by sodium (\(x \approx 0.9\%\) or \(x \approx 1.6\%\)). The \(k\)-point mesh was accordingly scaled down and spin-orbit coupling was not included because of computational cost; the other computational settings were left unchanged.

Figure 3(a) shows the partial density of states in the region of the Fermi level from the sodium impurity for \(x \approx 1.6\%\). Note the small value on the \(y\) axis indicating that the contribution from the Na atom is very small. It does, however, have an influence on the electronic band structure which can be seen in Fig. 3(b), where we plot the difference in density of states with and without the impurity. Here we see a distinct drop in the DOS (note the higher values on the \(y\) axis) just below the top of the valence band (set to 0 eV) due to band shifts caused by the presence of the Na atom; we analyze these next.

In Fig. 4 we compare the calculated electronic band structure with and without the sodium impurity. In Fig. 4(a) we show both band structures on the same \(y\) axis with the zero of

![Diagram](image-url)

**FIG. 2.** Upper panel: Fermi surface of hole-doped PbTe calculated in this work using the rigid band approximation. Lower panel plots: The corresponding (110)-plane angle evolution of the cross-sectional areas (in frequency units) of the calculated Fermi surface pockets. The four columns correspond to monovalent impurity concentrations of (a) \(x = 0.02\%\) (\(p_L = 0.27 \times 10^{19} \text{cm}^{-3}\) and \(p_E = 0\)); (b) \(x = 0.81\%\) (\(p_L = 3.5 \times 10^{19} \text{cm}^{-3}\) and \(p_E = 8.6 \times 10^{18} \text{cm}^{-3}\)); (c) \(x = 1.56\%\) (\(p_L = 6.1 \times 10^{19} \text{cm}^{-3}\) and \(p_E = 17.4 \times 10^{18} \text{cm}^{-3}\)); and (d) \(x = 2.61\%\) (\(p_{\text{total}} = 36.2 \times 10^{19} \text{cm}^{-3}\)). The frequencies of the \(L\) pockets are shown in red, and compared with those expected in a perfect ellipsoidal model shown as black lines. The evolution of the \(\Sigma\) pockets is shown in blue. These pockets appear at a dopant concentration of \(x = 0.11\%\) (\(p_L \approx 3.5 \times 10^{19} \text{cm}^{-3}\)). In column (d), the \(\Sigma\) and \(L\) pockets have merged, forming a cube-shape Fermi surface; cross sections that cannot be identified separately with \(\Sigma\) or \(L\) are shown in purple. We plot frequencies up to 600 T, noting, however, that frequencies up to 8 kT occur, corresponding to the large-square Fermi surface orbits. As described in the main text, our quantum oscillation studies reveal that for carrier densities up to at least 9.4 \times 10^{19} \text{cm}^{-3} value, the maximum studied in this report, the Fermi surface is found to only comprise \(L\) pockets (shown in red), implying a larger band offset between the \(L\) and \(\Sigma\) pockets than predicted by these and other DFT calculations.

We show here results for a 4 \times 4 \times 4 supercell of the primitive cell containing 128 atoms (\(x \approx 1.6\%\)), with one lead ion substituted by sodium. The unit cell volume was kept the same as in pristine PbTe (it would be changed by less than 0.1\% by a full structural relaxation). We checked also that our conclusions are qualitatively unchanged for a larger 216 atom supercell (3 \times 3 \times 3 of the conventional cubic cell) in which one or two lead ions are substituted by sodium (\(x \approx 0.9\%\) or \(x \approx 1.6\%\)). The \(k\)-point mesh was accordingly scaled down and spin-orbit coupling was not included because of computational cost; the other computational settings were left unchanged.

Figure 3(a) shows the partial density of states in the region of the Fermi level from the sodium impurity for \(x \approx 1.6\%\). Note the small value on the \(y\) axis indicating that the contribution from the Na atom is very small. It does, however, have an influence on the electronic band structure which can be seen in Fig. 3(b), where we plot the difference in density of states with and without the impurity. Here we see a distinct drop in the DOS (note the higher values on the \(y\) axis) just below the top of the valence band (set to 0 eV) due to band shifts caused by the presence of the Na atom; we analyze these next.

In Fig. 4 we compare the calculated electronic band structure with and without the sodium impurity. In Fig. 4(a) we show both band structures on the same \(y\) axis with the zero of
energy set to the top of the valence band. We see that the two band structures are close to identical, except for a lifting of the eightfold degeneracy at the top of the valence band, indicated by black arrows, in the case of the explicit Na doping. A consequence of this shift in one of the valence bands is a shift of the Fermi energy to lower energy relative to its position in the rigid band approximation. We illustrate this in Fig. 4(b) where we set the zero of energy to be the Fermi energy for each case. In contrast with earlier calculations at a larger doping [36,37], the lifted band does contribute to the Fermi surface and affects the quantitative evolution of Shubnikov-de Haas frequencies with hole density, giving rise to a more complex Fermi surface having \( L \) pockets with different sizes. The folding of wave vectors and states in the supercell makes an estimation of the different ellipsoidal axes difficult. In any case, the amplitude of the quantum oscillations for the “lifited-degenerate” pockets would be weaker. From these considerations we are confident that our rigid-band calculations can be used to make qualitative predictions about the evolution of the Fermi surface with Na doping. Quantitative predictions are anyway difficult because of the previously discussed sensitivity on the parameters used for the calculations.

C. Calculated Fermi surface evolution and angle evolution of Shubnikov-de Haas frequencies

Our calculated energy dispersion for PbTe, along the high symmetry directions of the fcc Brillouin zone, is plotted in Fig. 1. As discussed above, we obtain a direct gap at the \( L \) point, followed by a second valence band maximum at the \( \Sigma_{\infty} \) point, 70 meV below the top of the valence band. Figure 2 shows our calculated Fermi surfaces, as well as the (110)-plane angle dependence of the Fermi surface pocket cross-sectional areas, or equivalently, Shubnikov-de Haas (SdH) frequencies (see Appendix A), for four impurity concentrations. The (110) plane is a natural plane to study the angle evolution of the SdH frequencies for this material, given that, in a perfect ellipsoidal scenario, it allows the determination of all the extremal cross-sectional areas of both \( L \) and \( \Sigma \) pockets. For low impurity concentrations, the Fermi surface is formed only by \( L \) pockets, which follow the angle dependence expected for a perfect ellipsoidal model. At intermediate concentrations, the \( \Sigma \) pockets appear, and clear deviations from the perfect ellipsoidal model for \( L \) pockets (and \( \Sigma \) pockets) are observed. For impurity concentrations above \( x = 1.8\% \), \( \Sigma \) and \( L \) pockets merge together to form the Fermi surface shown in Fig. 2(d). At this point, very high frequency (\( \approx 8 \) kT, corresponding to the large-square Fermi surface pieces) and very low frequency features are expected, and a whole new variety of cross-sectional areas coming from different sections of the Fermi surface make the tracking of continuous angle dependence curves more challenging.

For the \( L \) pockets, we observe a progressive evolution to nonellipsoidicity, characterized by three main features in the angle dependence plots: (i) an increasing splitting in the low frequency branch, indicative of deformations of the \( L \) pockets around the semiminor axis region; (ii) a shifting to lower values of the angle at which the maximum cross-sectional
area (maximum frequency) is found, indicative of \(L\)-pocket deformations around the semimajor axis region, and due to the formation of the tips that will eventually join with the \(\Sigma\) pockets at high enough dopant concentration; and (iii) some distortions of the dispersion branch that goes from the [100] frequency value to the maximum frequency value at 90°, generating a cusp at 90°.

Figure 5 shows our calculation of three extremal cross-sectional areas with density of holes in the \(L\) pockets \(p_{L}\) computed from the Kohn-Sham band energies. The dashed curves indicate the expected \(p_{L}^{2/3}\) behavior for perfect ellipsoidal pockets. Deviations of the computed cross-sectional areas from the perfect ellipsoidal dependence become noticeable close to hole densities in the \(L\) pockets above which the \(\Sigma\) pockets start to be populated, which is indicated by the vertical dotted lines in Fig. 5. These deviations are characterized by a shift toward lower frequencies from that expected in the perfect ellipsoidal model. Additionally, Fig. 5(c) highlights the distortions in the \(L\) pockets, which cause the shift in the maximum frequency from 35° \((f_0)\) towards smaller angles in the angle-evolution curves shown in Figs. 2(b) and 2(c).

Figure 6 shows our calculated evolution of cyclotron effective masses [Eq. (A5)] at three high symmetry directions as a function of the carrier content of the \(L\) pockets. A monotonic increase of cyclotron masses with carrier concentration is observed, implying a nonparabolicity of the \(L\) band even at the top of the band. It is interesting to note that although deviations from perfect ellipsoidicity as seen in the calculated angle evolution [Fig. 2(a)] and the calculated SdH frequencies (Fig. 5) are close to zero for the low carrier concentration regime, the variation of the effective masses at the lowest doping levels already points to the nonparabolicity of the highest valence band. Note that this was already taken into account in some transport studies of PbTe to compute its thermoelectric properties [38,39].

In summary, our density functional calculations of the evolution of the Fermi surface of PbTe with doping provide some guidelines for identifying signatures of deviations from perfect ellipsoidicity and perfect parabolicity in our quantum oscillation experiments, to be presented in the coming sections. As we mentioned previously, the main signatures in the angular dependence of cross-sectional areas of \(L\) pockets are:

(i) An increasing splitting in the low frequency branch, indicative of deformations of the \(L\) pockets around the semiminor axis region.

(ii) A shifting to lower values of the angle at which the maximum cross-sectional area (maximum frequency) is found, indicative of \(L\)-pocket deformations around the semimajor axis region, and due to the formation of the tips that will eventually join with the \(\Sigma\) pockets at high enough dopant concentration.

(iii) Some distortions of the dispersion branch that goes from the [100] frequency value to the maximum frequency value at 90°, generating a cusp at 90°.

(iv) A monotonic increase of the cyclotron effective mass of holes as a function of carrier concentration.

Our computational findings (i)–(iii) will be used in the next section in interpreting deviations from perfect ellipsoidicity in our experimental data.

Finally, we note that, although we find that doping slightly increases the unit cell volume (see Appendix B, Table III) our calculations show that our conclusions above are largely unaffected: as shown in Appendix C, even if the band-structure parameters are influenced by volume, the evolution of SdH frequencies and cyclotron masses with doping are almost unaffected.

III. EXPERIMENTAL TECHNIQUES

A. Sample preparation

\(\text{Pb}_{1-x}\text{Na}_x\text{Te}\) single crystals were grown by an unseeded physical vapor transport (VT) method, similar to that described in Ref. [11], by sealing in vacuum polycrystalline pieces of the already doped compound, with (or close to) the desired final stoichiometry. The polycrystalline material was obtained by mixing high purity metallic lead (99.999%, Alfa Aesar), tellurium (99.999+%, Alfa Aesar), and sodium (99.9%, Sigma Aldrich) in the appropriate ratios. The source materials were placed in alumina crucibles, sealed in evacuated quartz tubes, and heated up to 1000 °C, holding this temperature for 7 h, followed by a rapid quench in water. A subsequent sinter at 700 °C for 48 h was performed with the material contained in the same evacuated tube [40]. After this process, the material was removed from the crucible, ground into fine powders, and then cold-pressed into a pellet. The pellet was sealed in a quartz tube, with a small argon pressure to prevent mass transport. The pellet was then sintered again at 500 °C for 24 h, and finally it was broken into small pieces to be used in the VT stage. After the VT, millimeter-size single crystals, with clear cubic facets, were obtained. The final sodium content was estimated through the determination of the carrier concentration via Hall coefficient \((p_H)\) measurements (at \(T = 1.5\) K), assuming one hole per Na dopant. Direct determination of the dopant concentration is challenging for the low Na concentrations studied in this work (<0.62%) which are below the weight % resolution of the available electron microprobe analysis tools.
B. Magnetoresistance measurements

High-field magnetoresistance measurements of Pb$_{1-x}$Na$_x$Te single crystal samples with different $x$ values between 0 and 0.62% (carrier concentrations up to $p_H = 9.4 \times 10^{19}$ cm$^{-3}$) were taken at the DC facility of the National High Magnetic Field Laboratory (NHMFL), in Tallahassee, FL, USA, for magnetic fields up to 35 T. Pb$_{1-x}$Na$_x$Te single crystals were cleaved in rectangular shapes with faces along the [100] directions. Typical sizes of the resulting crystals were 1 mm on the longest side. Four gold pads were evaporated on one of the faces in order to improve electrical contact with the crystal. Gold wires were attached to each of the pads using silver epoxy, and the other end of each wire was pasted to a glass slide. Twisted pairs coming from the rotator 8-pin dip socket were connected to the glass slide, with special care taken to minimize the loop areas of the wires. Four-point resistance curves for different field orientations and temperatures were taken for plus and minus field sweeps (in order to extract the symmetric component of the magnetoresistance) with temperature held fixed at 0.1 K. Samples were mounted in the rotator with their (100) faces along different directions with respect to the rotator axis, depending on the desired plane of rotation. Field-sweep data was taken each 5° or 7.5°, going in one direction to prevent rotator backlash problems.

IV. EXPERIMENTAL RESULTS

We divide the results section into two parts: In Sec. IV A we show the angle dependence of the magnetoresistance as the magnetic field is rotated within a high symmetry crystallographic plane, and temperature is held fixed at (1.5 ± 0.2) K. This allows us to obtain information about the topology of the Fermi surface and its evolution with carrier concentration. In Sec. IV B we present measurements of the temperature dependence of the amplitude of oscillations in magnetoresistance along different high symmetry directions, in order to extract information about the effective cyclotron masses, and their evolution with carrier concentration.

A. High-field magnetoresistance measurements

All data presented in this section were taken at a temperature of (1.5 ± 0.2) K. For all the samples measured, large Shubnikov-de Haas (SdH) oscillations in magnetoresistance were observed starting at a field of approximately 4 T for most samples. The first column of Fig. 7 shows symmetrized measurements of resistivity $\rho$ as a function of magnetic field for Pb$_{1-x}$Na$_x$Te with (a) $x = 0$ ($p_H = 1.9 \times 10^{18}$ cm$^{-3}$), (b) $x = 0.13$% ($p_H = 2.1 \times 10^{19}$ cm$^{-3}$), (c) $x = 0.26$% ($p_H = 4.1 \times 10^{19}$ cm$^{-3}$), (d) $x = 0.4$% ($p_H = 6.3 \times 10^{19}$ cm$^{-3}$), and (e) $x = 0.62$% ($p_H = 9.4 \times 10^{19}$ cm$^{-3}$). For different field orientations in the (110) plane. As mentioned in Sec. II C, the (110) plane is a natural plane to study the angle evolution of the SdH frequencies for this material, given that, in a perfect ellipsoidal scenario, it allows the determination of all the extremal cross-sectional areas of both L and $\Sigma$ pockets. The second column of Fig. 7 shows the oscillating component of the respective magnetoresistance curves, as a function of inverse field, extracted after the following background elimination procedure: for such low carrier densities, which imply low frequencies of oscillation, the determination of the frequencies and the tracking of their evolution with angle is challenging, given that only a few periods of oscillations are observed for the field range used, and additionally, several artifacts coming from background subtractions have characteristic frequencies that are comparable to the frequencies of interest. In our data analysis, several methods for background subtraction were tested. The method that generated the best resolution in the fast Fourier transform (FFT) for all the Na-doped samples, and that we use here, was a cubic-spline fitting of the nonoscillating component. For the self-doped $x = 0$ sample, which is the sample with the lowest characteristic frequencies (as low as 8 T), the method that allowed the best resolution of the evolution of fundamental frequency branches was the computation of the first derivative.

The evolution with angle of the frequencies of oscillation is shown in the contour plots of the third and fourth columns of Fig. 7. The color scale for these plots represents the amplitude of the FFT of the corresponding curves in the second column, normalized by the maximum value of the FFT at each angle, as a function of the angle from the [100] direction, and frequency. For all samples, the fundamental frequency of the three expected branches of frequency evolution is clearly observed, and for some of the branches, the second and third harmonic can be identified. For the $x = 0$ sample, the second harmonic seems to be stronger in amplitude than the fundamental, for all three branches. This effect is likely associated with the difficulty of resolving low frequency signals. For all samples, the branch that lies in the low frequency region for all angles contributes the dominant frequency in the magnetoresistance, which is associated with its higher mobility with respect to the other two branches. For the higher concentration samples, the high frequency contributions are weaker, and a logarithmic scale in the contour plots is used in order to highlight their angle evolution. In order to determine the characteristic frequencies of oscillation, and the possible deviations of the Fermi surface from a perfect ellipsoidal model, a comparison of these plots with the frequency evolution for a Fermi surface containing eight half-ellipsoids at the L points (perfect ellipsoidal model) is shown in the fourth column plots of Fig. 7. The fundamental frequencies, as well as the second and third harmonics are shown for each sample. The splitting seen in the intermediate frequency branch for most of the samples can be successfully accounted for by a small offset in the plane of rotation. For the $x = 0$ sample, an offset of 12° about the [001] axis was considered in the perfect ellipsoidal model. For samples with $x = 0.13$, the offset is 3° about the [110] axis; and for $x = 0.4$% and 0.62%, the offset is 4° about the [110] axis.

The parameters of minimum and maximum cross-sectional areas ($f_{\text{min}}$ and $f_{\text{max}}$) used in the perfect ellipsoidal model comparison for each sample are summarized in Table I. The minimum cross-sectional area of the L pockets, associated with $f_{\text{min}}$, can be determined very accurately from the value of the fundamental frequency of oscillation at 55° from the [100] direction in the (110) plane, which is clearly observed for all the samples measured. Additionally, the maximum
FIG. 7. Magnetoresistance measurements for Pb$_{1-x}$Na$_x$Te samples of different Na concentrations [row (a) $x = 0$, row (b) $x = 0.13\%$, row (c) $x = 0.26\%$, row (d) $x = 0.4\%$, and row (e) $x = 0.62\%$] as a function of magnetic field rotated along the (110) plane. The first column shows the measured resistivity as a function of applied magnetic field. The second column shows the background-free resistivity, obtained as explained in the main text, as a function of inverse field. The third column shows the amplitude of the normalized FFT, represented by the color scale, as a function of the angle of the magnetic field from the [100] direction (horizontal axis), and the frequency (vertical axis). The last column replots column three, with a comparison to a perfect ellipsoidal model calculation superimposed (solid lines for fundamental frequencies, and dashed lines for higher harmonics). The parameters used for the perfect ellipsoidal model calculation for each set of data are summarized in Table 1. For samples with $x = 0.13\%$, 0.4\%, and 0.62\%, small deviations from the (110) plane of rotation are evidenced in the splitting of the angle evolution of the intermediate branch, and they were considered in the perfect ellipsoidal model comparison. For the two highest concentrations, combination frequency terms due to magnetic interaction effects are observed. These are identified in the fourth column plots by the light-blue-dotted lines (sum of fundamental branches) and gray-dotted lines (difference of fundamental branches).

The cross-sectional area of the $L$ pockets, associated with $f_{\text{max}}$, can be directly observed in the FFT plots of samples with Na concentration up to 0.4\%. Also, up to this concentration, the matching between the angle evolution of the frequencies of oscillation with that expected for a perfect ellipsoidal model is satisfactory. Nevertheless, for this last concentration, the maximum frequency of the ellipsoids is resolvable close to 90° from [100], but becomes blurred close to 35°. Therefore, although
TABLE I. Fermi surface parameters for Na-doped PbTe, obtained from comparison between our measured data and a perfect ellipsoidal model. $p_H$ is the Hall coefficient obtained through Hall measurements (at $T = 1.5$ K); $f_{\text{min}}$ and $f_{\text{max}}$ are the transverse and longitudinal cross-sectional areas of the $L$ pockets, respectively; $K = (f_{\text{max}}/f_{\text{min}})^2$ is the anisotropy of $L$ pockets (see Appendix D); $p_{\text{PS,Vol}}$ is the carrier concentration computed using Luttinger’s theorem (see Sec. VA).

<table>
<thead>
<tr>
<th>$x$ (at. %)</th>
<th>$p_H$ ($\times 10^{19}$ cm$^{-3}$)</th>
<th>$f_{\text{min}}$ (T)</th>
<th>$f_{[100]}$ (T)</th>
<th>$f_{\text{max}}$ (T)</th>
<th>$K$</th>
<th>$p_{\text{PS,Vol}}$ ($\times 10^{19}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.19 ± 0.001</td>
<td>8 ± 1</td>
<td>12.5 ± 2</td>
<td>25 ± 2</td>
<td>10 ± 4</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td>0.04</td>
<td>0.75 ± 0.01</td>
<td>17 ± 5</td>
<td>34 ± 7</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.13</td>
<td>2.09 ± 0.01</td>
<td>39 ± 4</td>
<td>63 ± 5</td>
<td>145 ± 7</td>
<td>14 ± 3</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>0.26</td>
<td>4.1 ± 0.06</td>
<td>60 ± 8</td>
<td>97 ± 10</td>
<td>230 ± 7</td>
<td>15 ± 4</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>0.4</td>
<td>6.3 ± 0.6</td>
<td>81 ± 4</td>
<td>132 ± 13</td>
<td>307 ± 6</td>
<td>14 ± 2</td>
<td>6.3 ± 0.2</td>
</tr>
<tr>
<td>0.62</td>
<td>9.4 ± 0.6</td>
<td>97 ± 12</td>
<td>157.5 ± 16</td>
<td>370 ± 90</td>
<td>15 ± 8</td>
<td>8.3 ± 2.1</td>
</tr>
</tbody>
</table>

the value of the maximum frequency can be determined from the 90° area, possible deviations from ellipsoidal model that could be identified around 35° cannot be resolved. However, given the round shape of the upper branch around 90°, we can say that features associated with possible departures from the ellipsoidal model are not observed [see Fig. 2(c)]. This last statement is confirmed by magnetoresistance measurements in an additional sample of the same batch as the field is rotated along the (100) plane, as shown in Fig. 8. The comparison of the FFT angle evolution and the perfect ellipsoidal model, using the same extremal cross-sectional area parameters as for the measurements with field along the (110) plane, confirms the matching of the data with the perfect ellipsoidal model for samples of this Na composition ($x = 0.4\%$). For the highest Na concentration sample measured, $x = 0.62\%$, possible deviations from perfect ellipsoidicity are observed, and will be discussed later in this section.

As can be seen in the third and fourth columns of Figs. 7(d) and 7(e), additional features in the angle dependence plots occur for the two highest Na-doped samples. Nevertheless, all of these features can be identified as the sum and difference of the fundamental frequencies of the $L$ pockets, as can be observed in the light-blue and gray curves in the fourth column plots of Figs. 7(d) and 7(e). The presence of such combination frequencies can be attributed to magnetic interaction effects, expected when the amplitude of the oscillating component of the magnetization $\vec{M}$ is comparable to $H^2/f$, in such a way that the total magnetic field $B = \vec{H} + 4\pi \vec{M}$, and not just $\vec{H}$, needs to be considered in the Lifshitz-Kosevich (LK) formalism of quantum oscillations [41] (see Appendix A).

As was suggested above, the sample with the highest Na concentration studied in this work, $x = 0.62\%$, shows possible indications of deviations from perfect ellipsoidicity. For this sample the high frequency components of the oscillations are blurred, and the evolution of the different branches can be observed only up to 400 T. As we mentioned previously, the determination of $f_{\text{min}}$ for all samples has a very low uncertainty, particularly for this sample, given that we can clearly observe up to the third harmonic of the lower branch [see Fig. 7(e)]. Fixing this value to $f_{\text{min}} = 97$ T, Fig. 9 shows a comparison between the angle evolution of the frequencies of oscillation for this sample, and a perfect ellipsoidal model using two different values of $f_{\text{max}}$. In order to better guide the comparison, both plots in this figure show the exact frequency positions of the maxima of the FFT peaks for all angles (in black-filled circles). Around the angle of 90° we observe some weight in the FFT (yellow color) around 350–370 T, which we could interpret as an indication of the value of $f_{\text{max}}$. This value is the one used in the perfect ellipsoidal model in Fig. 9(a) [as well as Fig. 7(e)]. In this figure we

FIG. 8. (a) Longitudinal magnetoresistance for a Na-doped PbTe sample with $x = 0.4\%$ and Hall number $p_H = 6.3 \times 10^{19}$ cm$^{-3}$, for different directions of the applied magnetic field, with respect to the [100] crystalline axis, as the field is rotated in the (100) plane. (b) As in (a), as a function of inverse magnetic field, after eliminating the background, therefore only preserving the oscillatory part. (c) The color scale in both plots represents the amplitude of the Fourier transform of the data shown in (b), as a function of the angle from the [100] direction (horizontal axis), and the frequency (vertical axis). For these plots, the field is rotated in the (100) plane. The right-hand side figure replots the figure in the left, but with a perfect ellipsoidal model calculation superimposed on the data, up to the third harmonic (black lines). For the model, the plane of rotation is offset by 6° (about the [100] axis). The parameters used for the calculations are the same as those used for the (110) plane of rotation data in Fig. 7(d): $f_{\text{min}} = 81.4$ T and $f_{\text{max}} = 307$ T.
FIG. 9. FFT of the background-free resistivity data of Fig. 7(e), as a function of the angle from the [100] direction and the frequency. A perfect ellipsoidal model calculation has been superimposed on the data, up to the third harmonic (black lines). In order to better guide the comparison with the perfect ellipsoidal model, the exact frequencies of the local maxima of the FFT for each angle (labeling only FFT peaks with amplitude 1% or more of the largest peak for each angle) are indicated by black dots. The parameters used in the perfect ellipsoidal model for each plot are: (a) $f_{\text{max}} = 97\, \text{T}$, $f_{\text{min}} = 370\, \text{T}$; and (b) $f_{\text{min}} = 97\, \text{T}$, $f_{\text{max}} = 460\, \text{T}$. For both plots, an offset of $4^\circ$ from the (110) plane of rotation (about the [110] axis) is considered, to account for the splitting seen in the middle branch. Additionally, the combination frequency terms are shown in light-blue-dotted lines (sum of fundamental branches) and gray-dotted lines (difference of fundamental branches). None of the fits presented here give a satisfactory description of the data, suggesting deviations from perfect ellipsoidicity.

can see that the matching between the data and the perfect ellipsoidal model is not satisfactory, especially close to the $0^\circ$ area of the plot. Interestingly, the $90^\circ$–$370^\circ$ area overlaps with the region at which the third harmonic of the lower branch passes. This could indicate that the weight observed at this region belongs to this third harmonic, and not to $f_{\text{max}}$. Figure 9(b) shows a comparison between the data and a perfect ellipsoidal model using the same $f_{\text{min}} = 97\, \text{T}$, but now using a larger value of $f_{\text{max}} = 460\, \text{T}$. These values provide a better matching between the data and a perfect ellipsoidal model for the region of $0^\circ$. However, the combination frequency terms, due to magnetic-interaction effects, suggest that this fit is not satisfactory, as the evolution of the combination frequency data points around $60^\circ$–$350^\circ$ seems to be less steep, being better matched by the fit using $f_{\text{max}} = 370\, \text{T}$, as shown in Fig. 9(a). The lack of a satisfactory perfect ellipsoidal model to describe the data can be interpreted as deviations from perfect ellipsoidicity of the $L$ pockets for this Na concentration sample. The mismatch of the data and the ellipsoidal model is observed in the intermediate branch, which is consistent with the guidelines given by the DFT calculations.

For all the measured samples, all features observed in the angle evolution of the frequencies of oscillations come from the $L$ pockets. Furthermore, the carrier concentration calculated from Luttinger’s theorem and the volume in $k$ space of the $L$ pockets (obtained through the comparison of the FFT evolution and the perfect ellipsoidal model) $\rho_{\text{PS-Vol}}$, matches perfectly (within the error bars) the Hall number (equivalent to the carrier concentration for a single band compound) for all Na-doped samples up to $x = 0.4\%$, as shown in Table I: the $L$ band contributes solely to conduction up to this Na concentration. Moreover, the small mismatch between the $L$-pocket Luttinger volume and the Hall number for the highest Na concentration sample $x = 0.62\%$ presumably comes from deviations from perfect ellipsoidicity, as previously discussed.

**B. Temperature dependence of quantum oscillations**

In order to determine the evolution of effective cyclotron masses of holes in Na-doped PbTe with carrier concentration, we measured the temperature dependence of the oscillation amplitude for samples of different Na concentrations, with the field oriented along or close to high symmetry crystallographic directions. To accurately determine the cyclotron effective masses for such a low carrier-density material, we simultaneously fitted all magnetoresistance curves to the

![Graphical representation of the data and fits.](image)

FIG. 10. Temperature dependence of the amplitude of the oscillating component of magnetoresistance for Pb$_{1-x}$Na$_x$Te samples, with magnetic field along the [111] direction ($55^\circ$ from the [100] direction, in the (110) plane). The left-column plots show the background-free data at different temperatures. The right-column plots show the fits of the data to the LK formula in Eq. (1), using the four most dominant frequencies observed in the FFT of the lowest temperature curve. From this fit, the values of cyclotron effective mass and Dingle temperature, for each frequency term, are obtained. The values obtained for the transverse cyclotron mass and Dingle temperature are summarized in Table II.
TABLE II. Cyclotron effective masses for Pb$_{1-x}$Na$_x$Te samples along different high symmetry directions. These parameters were obtained through fitting of the curves in Figs. 10, 11, and 20 to the LK formula in Eq. (1).

<table>
<thead>
<tr>
<th>$x$ (at. %)</th>
<th>$p_H$ ($\times 10^{19}$ cm$^{-3}$)</th>
<th>$\Theta_{D,\perp}$ (K)</th>
<th>$m_{1,\perp}^{\text{cy}}/m_0$</th>
<th>$m_{100}^{\text{cy}}/m_0$</th>
<th>$m_{14}^{\text{cy}}/m_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.75 ± 0.007</td>
<td>–</td>
<td>–</td>
<td>0.098 ± 0.001</td>
<td>–</td>
</tr>
<tr>
<td>0.13</td>
<td>2.09 ± 0.006</td>
<td>9 ± 4</td>
<td>0.068 ± 0.007</td>
<td>0.085 ± 0.001</td>
<td>–</td>
</tr>
<tr>
<td>0.26</td>
<td>4.1 ± 0.06</td>
<td>10 ± 3</td>
<td>0.089 ± 0.002</td>
<td>0.15 ± 0.01</td>
<td>0.29 ± 0.04</td>
</tr>
<tr>
<td>0.4</td>
<td>6.3 ± 0.6</td>
<td>9.9 ± 0.2</td>
<td>0.14 ± 0.03</td>
<td>0.172 ± 0.004</td>
<td>–</td>
</tr>
<tr>
<td>0.62</td>
<td>9.4 ± 0.6</td>
<td>9.5 ± 0.8</td>
<td>0.13 ± 0.02</td>
<td>0.225 ± 0.006</td>
<td>–</td>
</tr>
</tbody>
</table>

Lifshitz-Kosevich (LK) formula (in SI units) [41]:

$$\frac{\rho(H) - \rho_0}{\rho_0} = \sum_i C_i \left\{ \exp \left( -\frac{14.7(m_{1,\perp}^{\text{cy}}/m_0)\Theta_{D,i}}{H} \right) \right\} \times \left\{ \frac{T/H}{\sinh \left[ 14.7(m_{1,\perp}^{\text{cy}}/m_0)T/H \right]} \right\} \times \cos \left[ 2\pi f_i \frac{H}{T} + \phi_i \right],$$  \hspace{1cm} (1)

where the sum is over each frequency observed in the data, and for which a separate cyclotron effective mass $m_{1,\perp}^{\text{cy}}/m_0$ and Dingle temperature $\Theta_{D,i}$ can be obtained. For low frequency oscillations, the number of periods observed in the given field range is limited, resulting in FFTs with amplitudes highly dependent on windowing effects, variations in field range, or variations in signal sampling. In contrast to the fitting of the FFT amplitudes to the LK formula—the method widely used for the determination of effective masses of higher carrier concentration metals—the values of effective masses obtained through a direct fitting of the data to the LK formula are robust to such variations.

Figure 10 shows the temperature dependence of the oscillating component of magnetoresistance for Pb$_{1-x}$Na$_x$Te samples of different Na concentrations, for field oriented along the [111] direction, providing direct access to the transverse cyclotron effective mass $m_{1,\perp}^{\text{cy}}$, which is associated with the minimum cross-sectional area of the $L$ pockets. Least-squares fits to Eq. (1), including up to the fourth strongest frequency component, for each Na doping, and for a field range of 5 to 34 T, are shown in the right-column plots of this figure. The cyclotron masses and Dingle temperatures obtained for the fundamental frequency, i.e., $m_{1,\perp}^{\text{cy}}$ and $\Theta_{D,\perp}$, as a function of carrier concentration, are summarized in Table II, and plotted in Figs. 16 and 17, in Sec. V.

Additionally, Fig. 11 shows magnetoresistance curves at different temperatures for a sample with Na concentration of 0.26%, with the magnetic field oriented close to 35° from the [100] direction in the (110) plane. For such field orientation, one of the Fermi surface cross-sectional areas corresponds to the maximum cross-sectional area of the ellipsoids (in a perfect ellipsoidal model), which is associated with the longitudinal cyclotron mass $m_{100}^{\text{cy}}$. The value obtained for this mass is presented in Table II.

From our measurements, we can also obtain cyclotron masses along intermediate directions; these are presented in Fig. 15 of Sec. V.

V. DISCUSSION

A. Fermi surface topology

Having presented the data and the analysis performed to obtain the various Fermi surface parameters for different Na-doping levels, we now summarize them and present their evolution as a function of depth in the valence band. The parameters obtained in the previous section are summarized in Table I, where we also include data from an additional Na composition ($x = 0.04\%$) for which measurements in a more limited field range (up to 14 T) were taken.

Figure 12 shows the $L$-pockets’ Luttinger volume as a function of Hall number for the Na-doped PbTe samples studied, plus self-doped (by Pb vacancies) samples measured in previous SdH studies by other groups [14,15]. For a single-parabolic-band model, these two quantities are expected to exactly match with each other, and to lie on the dashed line shown in the figure. This is indeed the case for all the samples studied, including the self-doped ones. The deviations seen for the largest Na doping can be attributed to deviations from perfect ellipsoidicity of the pockets, as discussed in previous sections. The matching between the $L$-pockets’ Luttinger volumes and Hall numbers implies that PbTe, up to a carrier concentration of $p_H = (9.4 ± 0.6) \times 10^{19}$ cm$^{-3}$, is single band, that is, all the carriers contributing to conduction belong to the $L$ band. This result implies that the band offset between the $L$ and $\Sigma$ valence band maxima is underestimated.

FIG. 11. Temperature dependence of the amplitude of the oscillating component of magnetoresistance for a Pb$_{1-x}$Na$_x$Te sample with $x = 0.26\%$, and magnetic field oriented close to 35° from the [100] direction, along the (110) plane. For this orientation, the cross-sectional area of two of eight $L$ pockets corresponds to the maximum cross-sectional area of the ellipsoids. The left-column plot shows the background-free data at different temperatures. The right-column plot shows the fit of the data to the LK formula in Eq. (1), using the five most dominant frequencies observed in the FFT of the lowest temperature curve. From this fit, the values of cyclotron effective mass and Dingle temperature, for each frequency term, are obtained.
Na-doping is attributed to deviations from perfect ellipsoidicity. The dashed line shows the expected behavior for a single-parabolic band, for which the carrier density enclosed by the Fermi surface, as determined through Luttinger’s theorem, matches the carrier density measured using the Hall effect. All the measured samples lie on this line, and the deviations seen for the highest Na concentration are represented by a gray square, in order to emphasize that deviations from perfect ellipsoidicity can be observed.

The evolution of the three high symmetry L-pocket cross-sectional areas, in frequency units \((f_{\text{min}}, f_{\text{max}}, \text{and } f_{[100]})\), with Hall number is plotted in Fig. 13. For a perfect ellipsoidal model, all the cross-sectional areas are expected to scale with carrier concentration as \(p_H^{2/3}\). This is in fact the functional form followed by most cross-sectional areas in Fig. 13, as shown by the dashed line. The last Na-doped sample deviates from this line, confirming the departure from perfect ellipsoidicity of the pockets for this high carrier concentration. However, for carrier concentrations below \(p_H = 6.3 \times 10^{19} \text{ cm}^{-3}\), we can conclude that the L pockets are well described by a perfect ellipsoidal model, within the experimental resolution. For the highest Na concentration studied, the deviation from the perfect ellipsoidal behavior follows the expected trend predicted by our DFT calculations, as presented in Fig. 5.

Additionally, the anisotropy of the L pockets, \(K = (f_{\text{max}}/f_{\text{min}})^2\), is approximately constant with carrier concentration \((K = 14.3 \pm 0.4)\) for the range of carrier concentrations of interest, as shown in Fig. 14. The observation of a constant anisotropy of the L pockets with carrier concentration confirms previous results by Burke et al. [15] for p-type self-doped PbTe with carrier concentrations below 1 \(\times 10^{19} \text{ cm}^{-3}\) (shown as blue stars in Fig. 14), and contrasts the results by Cuff et al. [47] in self-doped samples with carrier concentrations up to 3 \(\times 10^{18} \text{ cm}^{-3}\), in which a decrease in \(K\) with increasing carrier concentration is observed. The \(K\) values reported by Burke et al. are slightly less than the average value of 14.3 ± 0.4 found in this work. However, as discussed previously, an accurate estimation of the Fermi surface parameters for the low carrier concentration regime is challenging given the few periods of oscillation observed in a limited field range. This could be the reason for the lower \(K\) value obtained for the \(x = 0\) sample measured in this work. A constant value of \(K\) with carrier concentration is expected in a perfect parabolic band model, in which the L-pocket anisotropy is equivalent to the band mass anisotropy \(K = m_{\perp}/m_{\parallel}\), where \(m_{\parallel}\) is the effective band mass along the ellipsoidal L-pocket semimajor axis (longitudinal band mass), and \(m_{\perp}\) is the effective band mass along the ellipsoidal L-pocket semiminor axis (transverse band mass) [in terms of the cyclotron effective masses \(K = (m_{\perp}^{\text{ cycl}}/m_{\parallel}^{\text{ cycl}})^2\), as shown in Appendix D]. However, a constant \(K\) value can also be obtained for specific models with

\begin{align*}
\text{FIG. 12. Carrier concentration calculated from Luttinger’s theorem and the volume of the L pockets extracted from the comparison between the data and a perfect ellipsoidal model, as a function of the Hall number, for Na-doped PbTe (black squares), and obtained using the ellipsoid parameters from previous studies in Refs. [14,15] (blue stars). The dashed line shows the expected behavior for a single-parabolic band, for which the carrier density enclosed by the Fermi surface, as determined through Luttinger’s theorem, matches the carrier density measured using the Hall effect. All the measured samples lie on this line, and the deviations seen for the highest Na doping (gray square) are attributed to deviations from perfect ellipsoidicity.}
\end{align*}
dispersion relations in which corrections for nonparabolicity of the band are considered, as we will present in the next section.

B. Effective cyclotron masses and relaxation time

As we presented in Sec. IV B, effective cyclotron masses along different high symmetry directions were obtained through direct fitting of the curves shown in Figs. 10, 11, and 20 to the LK formula in Eq. (1). For all Na compositions studied, the cyclotron masses along the transverse direction $m^{\text{cyc}}_\perp$ and [100] direction $m^{\text{cyc}}_{[100]}$ were determined through this method. Additionally, for samples with a Na concentration of $x = 0.26\%$, the longitudinal cyclotron mass $m^{\text{cyc}}_\parallel$ was also found. Supplementary to these highly symmetric masses, others along less symmetric directions of the ellipsoid can be found from different frequency terms in the measurements. Figure 15 shows the cyclotron effective masses found for all frequency terms taken into account in the LK fits of the $x = 0.26\%$ sample [Figs. 10(b), 11, and 20(c)], as a function of the angle from the (L-pocket longitudinal direction. The corresponding angle for the mass of each frequency term, with respect to the longitudinal direction of the ellipsoids, was found by identifying each frequency in the angle dependence curves, such as that presented in Fig. 7(c). Figure 15 also shows the expected angular dependence of the cyclotron effective mass (fundamental and higher harmonics) in a perfect ellipsoidal model (for more details, see Appendix D), using the average $K$ value from Fig. 14 ($K = 14.3 \pm 0.4$, which gives $m^{\text{cyc}}_\parallel/m^{\text{cyc}}_\perp = \sqrt{K} = 3.78 \pm 0.05$). Most data points lie on this curve, confirming the good agreement of the topology of the Fermi surface with the perfect ellipsoidal model for this Na concentration.

In spite of the good agreement of the anisotropy of the cyclotron effective mass with the perfect ellipsoidal model, intriguingly, the masses are not constant throughout the band: Fig. 16 shows the evolution of the longitudinal, transverse, and [100] direction cyclotron effective masses with carrier concentration. All of them show a monotonic increase with increasing carrier concentration, consistent with the predictions of the DFT band-structure calculations presented in Sec. II C. Previous SdH measurements in PbTe by Burke et al. [14,15] ($p_H < 1 \times 10^{18}$ cm$^{-3}$), and by Cuff et al. [47] ($p_H < 6 \times 10^{18}$ cm$^{-3}$), found a similar tendency for the transverse cyclotron mass. The observation of a varying effective mass with carrier concentration implies deviations from perfect parabolicity, starting from the top of the band.

A Kane model dispersion relation has been proposed before to describe the valence band of PbTe [33,39,48,50]. In this model the nonparabolicity of the band is introduced as $E \rightarrow \gamma(E) = E(1 + E/E_g)$ in the dispersion relation, where $E_g$ is the band gap. For such a model, the longitudinal and transverse effective masses depend on energy in the same way [49], implying that, although the effective masses evolve as the Fermi energy is changed, the band anisotropy parameter $K = (A_1/A_2)^2 = (m^{\text{cyc}}_\parallel/m^{\text{cyc}}_\perp)^2$ is constant. Additionally, in this model, the constant energy surfaces for any Fermi energy are ellipsoids of revolution [49], which is consistent with our observations for carrier concentrations up to $p = 6.3 \times 10^{19}$ cm$^{-3}$. The Kane model has been successful at describing the band structure near the gap of small band-gap semiconductors, for which the relevant Fermi energies are smaller than or of the same order as the band gap [51]. Our experimental results are in line with the predictions of the Kane model, ruling out other proposed models such as the Cohen model [49,52,53], at least for the low-temperature regime.
Additional to the cyclotron effective masses, we have found the Dingle temperature in the transverse direction $\Theta_{D,\perp}$, through a fitting of the data to the LK formula, as presented in Sec. IVB. In contrast to the cyclotron mass, finding this quantity along directions other than the transverse direction of the $L$-pocket ellipsoids is challenging, given that the oscillatory part of magnetoresistance is dominated by the lowest frequency component. For this dominating part of the signal, the exponential damping in $1/H$ is the only one strong enough to result in a Dingle temperature as a strong fitting parameter. Figure 17 shows the Dingle temperature associated with the transverse direction $\Theta_{D,\perp}$ as a function of carrier concentration. This quantity is constant for the range of concentrations studied, with an average value of $\Theta_{D,\perp} = (9.7 \pm 0.4) \, \text{K}$. This average value of $\Theta_{D,\perp}$ results in a value of the carrier relaxation time along the transverse direction of $\tau_{\perp} = h/2\pi k_B \Theta_{D,\perp} = (0.125 \pm 0.005) \, \text{ps}$. It is interesting to note that although the RRR value for Pb$_{1-x}$Na$_x$Te decreases by approximately 20 times from undoped PbTe to the highest Na-doping studied, suggesting a considerable increase of scattering effects, the transverse relaxation time found in this work is constant with carrier concentration. However, as suggested by the progressive decrease of the Fourier intensity of the higher frequency components as doping is increased, as can be observed in Fig. 7, the enhanced scattering could be reflected in a significant decrease of the longitudinal relaxation time. Unfortunately, a reliable determination of the longitudinal Dingle temperature, resulting in a longitudinal relaxation time, was not possible.

VI. SUMMARY AND CONCLUSIONS

In summary, we have presented a computational and experimental study of the low-temperature (1.5 to 60 K) topology and properties of the Fermi surface of Pb$_{1-x}$Na$_x$Te, and its evolution with carrier concentration, for Na dopings up to $x = 0.62\%$. We have found that:

(i) Although the band offset is underestimated by the DFT calculations, all the qualitative features of the evolution of the Fermi surface topology and effective mass are correctly predicted by our calculations. The understimation of the band offset is related to the high sensitivity of the resulting band structure to variations of parameters in the calculation, such as lattice spacing or spin-orbit coupling. This fact is presumably related to the fact that PbTe is on the boundary between various competing structural (incipient ferroelectricity [20,21]) and electronic (superconductivity [10–12] and topological insulator [22,23]) instabilities.

(ii) Up to a carrier concentration of $p = 9.4 \times 10^{19} \, \text{cm}^{-3}$ ($x = 0.62\%$ maximum studied) the Fermi surface of Pb$_{1-x}$Na$_x$Te is formed solely by eight half-ellipsoids at the $L$ points. The $\Sigma$ pockets predicted to contribute at such high carrier concentrations in our calculation and those of other groups [13,42,54–56] are not observed. Additionally, the measured Hall number and the Luttinger volume of the $L$ pockets calculated from our quantum oscillation measurements match exactly, indicating that this is the only set of
pockets that contribute to conduction in this compound at low temperatures.

(iii) The topology of the Fermi surface, formed by eight half-pockets at the L points, is well described by a perfect ellipsoidal model for carrier concentrations up to \( p = 6.3 \times 10^{19} \text{ cm}^{-3} \) (\( x = 0.4\% \)). Deviations from perfect ellipsoidicity were resolved for the highest carrier concentration studied, \( p = 9.4 \times 10^{19} \text{ cm}^{-3} \) (\( x = 0.62\% \)).

(iv) The anisotropy of the L pockets is constant for the range of concentrations studied, and has an average value of \( K = 14.3 \pm 0.4 \).

(v) The anisotropy of the cyclotron effective mass of the L pockets follows the angular dependence expected in a perfect ellipsoidal model.

(vi) The effective cyclotron masses along all high symmetry directions increase monotonically with increasing carrier concentration, implying deviations from perfect parabolicity of the band. The observation of constant geometric and mass anisotropy with carrier concentration, but an increasing effective mass, is consistent with a Kane model of nonparabolic dispersion relation for the valence band of PbTe.

Our experimental determination of the low-temperature Fermi surface and band structure parameters of PbTe is an important piece of information which needs to be considered in models that aim at explaining the evolution of a variety of electronic properties at high doping levels in PbTe, including superconductivity and thermoelectric properties.

ACKNOWLEDGMENTS

The high-field magnetoresistance measurements were performed at the National High Magnetic Field Laboratory (NHMFL), which is supported by NSF DMR-1157490 and the State of Florida. P.G.G., P.W., H.J.S., and I.R.F. were supported by AFOSR Grant No. FA9550-09-1-0583. B.S., M.F., and N.A.S. acknowledge support from ETH Zürich, ERC Advanced Grant program (No. 291151), and the Swiss National Supercomputing Centre (CSCS) under project ID s307.

APPENDIX A: QUANTUM OSCILLATIONS FORMALISM

In this Appendix we briefly outline the concepts needed to understand quantum oscillation experiments in metals. For a detailed treatment see the excellent book by Shoenberg [41]. It is well known that in a magnetic field \( H \) the allowed electronic states lie on quantized tubes in \( k \) space (Landau tubes). The tube quantization is described by the Onsager equation

\[
a(E_n,k_H) = \left( n + \frac{1}{2} \right) 2\pi eH/\hbar c,
\]

where \( a \) is the cross-sectional area of the Landau tube in a plane perpendicular to \( H \), and \( n \) is an integer. As a consequence, an oscillatory behavior with the inverse magnetic field \( 1/H \) can be observed, for example, the magnetization—the de Haas-van Alphen effect—or the resistance—the Shubnikov-de Haas effect. The period of such oscillations \( \Delta_{1/H} \) is given by

\[
\Delta_{1/H} = 2\pi e/(hcA),
\]

A being an extremal cross-sectional area of the Fermi surface in a plane perpendicular to \( H \). One can also define a frequency for these oscillations as

\[
f = 1/\Delta_{1/H} = (ch/2\pi e)A.
\]

By determining the oscillations in, e.g., the resistivity for varying orientations of the magnetic field, one can eventually reconstruct the Fermi surface.

In the semiclassical picture the electrons move along (open and closed) orbits on the Fermi surface in a plane perpendicular to \( H \). The time taken to traverse a closed (cyclotron) orbit is given by

\[
t_c = \frac{2\pi}{\omega_c} = \frac{\hbar^2 c}{e H \partial E},
\]

where one can rewrite the cyclotron frequency \( \omega_c \) in terms of a cyclotron mass

\[
m^{\text{cycl}} = \frac{\hbar^2}{2\pi^2 \partial E}.
\]

For a free-electron gas the cyclotron mass is equal to the electron mass. Experimentally the cyclotron masses are extracted using the Lifshitz-Kosevich (LK) formula (in SI units)

\[
\rho(H) = \rho_0 \sum_i C_i \left\{ \exp \left( \frac{-14.7(m_i^{\text{cycl}}/m_0)\Theta_{1D,i}}{H} \right) \right\}
\]

\[
\times \left\{ \frac{T/H}{\sinh \left[ 14.7(m_i^{\text{cycl}}/m_0)T/H \right]} \right\}
\]

\[
\times \cos \left[ 2\pi f_c H + \phi_i \right],
\]

as presented in Eq. (1).

FIG. 18. Lattice parameter of the cubic unit cell of Pb_{1-x}Na_{x}Te samples with different Na content, as a function of temperature. Filled symbols represent the experimentally determined values, and the solid lines represent a fit to a low order polynomial, as explained in the text, from which the zero-temperature lattice parameter can be extrapolated.
TABLE III. Zero-temperature extrapolated lattice parameter ($a_{T=0\, \text{K}}$) of Pb$_{1-x}$Na$_x$Te samples with different Na content. This extrapolation was done through a low-order polynomial fit of the temperature dependence of the lattice parameters, as explained in the text.

<table>
<thead>
<tr>
<th>x (Na at. %)</th>
<th>(n_h \times 10^{19} \text{ cm}^{-3})</th>
<th>(a_{T=0, \text{K}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>–</td>
<td>6.431(1)</td>
</tr>
<tr>
<td>0.26</td>
<td>4.1 ± 0.06</td>
<td>6.436(3)</td>
</tr>
<tr>
<td>0.62</td>
<td>9.4 ± 0.6</td>
<td>6.442(9)</td>
</tr>
</tbody>
</table>

APPENDIX B: TEMPERATURE AND NA-COMPOSITION DEPENDENCE OF THE LATTICE CONSTANT

In this Appendix we present an experimental determination of the cubic lattice parameter of Pb$_{1-x}$Na$_x$Te samples with different Na content, and its temperature dependence. This determination will be necessary to study the sensitivity of the DFT band-structure calculations to realistic variations in lattice constant, which we present in the next section.

The peak positions of several diffraction peaks with high 20 values were determined for different temperatures (from 300 down to 80 K), using the 2D detector of a commercial Bruker D8-Venture single crystal x-ray diffractometer. In order to minimize systematic errors, the lattice parameters at each temperature were determined through a linear fit of the calculated lattice spacing for each peak ($a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$) vs 20, and the extrapolation of this fit to 20 = 180°. These measurements were done for two Na-doped PbTe samples with Na concentrations of x = 0.26% and 0.62%. The temperature dependence of the lattice parameter of the measured samples, as well as data by Bozin et al. [20] for undoped PbTe, are shown in Fig. 18. Below 150 K, the data for x = 0.26% exhibit a greater scatter than those for x = 0.62%, reflecting poorer experimental conditions for that measurement. However, the overall trend of the temperature dependence for both compositions is similar. In order to obtain a sensible extrapolation of our data down to zero temperature, Bozin’s data for undoped PbTe samples, which goes down to much lower temperatures than ours, was fitted with a low order polynomial (solid-black line in Fig. 18). For the Na-doped samples, the data was fitted by keeping all the polynomial coefficient found for the undoped sample, except the zero-power term (vertical offset), which represents the zero-temperature lattice parameter for these Na-doped samples. The values obtained for the zero-temperature lattice parameter of these three compositions are summarized in Table III. The temperature variation of the lattice parameter, from zero temperature to room temperature, of the samples studied here, is of the order of 0.5%, whereas the compositional variation, from undoped PbTe to 0.62% Na-doped PbTe, is of the order of 0.2%.

APPENDIX C: VOLUME DEPENDENCE OF DFT RESULTS

In this Appendix we comment on the volume dependence of the band structure and quantum-oscillation parameters in our DFT calculations. Table IV shows the volume dependence of the band offset and effective masses for the range of experimental volumes of (undoped) samples at $T = 0 \, \text{K}$ (see Fig. 18 and Table III).

An increase in volume is accompanied by an increase in band offset (in contrast to the behavior expected from experiments, where thermal expansion leads to a decrease of the band offset [17–19]), and a decrease in effective masses. The latter indicates that the $L$ pocket becomes narrower, but is not able alone to predict an appreciable change in the

![Graph](image-url)

**FIG. 19.** Evolution of SdH frequencies (a) and cyclotron masses (b) as a function of density of holes in the $L$-pocket $p_L$ for two different volumes: 6.50 Å (open symbols and superscript $l$) and 6.44 Å (filled symbols and no superscript). The larger volume corresponds also to a larger band offset 120 vs 74 meV. The dashed vertical lines indicate the $L$-pocket hole density above which the $\Sigma$ pockets start to be populated.
evolution of SdH frequencies and cyclotron masses, because, as mentioned in the main text, the band is nonparabolic. To check the influence of volume on SdH frequencies and cyclotron masses, we computed their evolution with doping for two different volumes (Fig. 19), the DFT-lattice constant 6.44 Å—with a band offset of 74 meV—and a representative larger one 6.50 Å (noted with an \( l \) superscript in the figure)—with a band offset of 120 meV.

No appreciable differences in the doping dependence for the two different volumes can be observed: in fact, if the \( L \) pocket is narrower it becomes filled faster, or, the shift in Fermi energy to obtain a given density of holes is larger. The concentration at which the \( \Sigma \) pockets start contributing is also not much different for the same reason.

We conclude that unit-cell volume changes of the order of those found experimentally (due to temperature and compositional variation) do not affect significantly our DFT results.

APPENDIX D: CYCLOTRON EFFECTIVE MASS ANISOTROPY

For a given dispersion relation one can, in principle, find the relation between the geometric anisotropy of the Fermi surface and the anisotropy of the cyclotron effective mass. For a perfect parabolic band, the general anisotropic dispersion relation is given by

\[
\frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z} = E, \tag{D1}
\]

where \( m_x, m_y, \) and \( m_z \) are the band masses. For an ellipsoidal Fermi surface with the semimajor axis of the ellipse oriented along the \( z \) axis, the band masses are \( m_x = m_y = m \) (prolate ellipsoid) and \( m_z = m_e \). For such systems, the minimum and maximum cross-sectional areas are

\[
A_\perp = \pi k_{\perp,x,y}^2 \bigg|_{k_z=0} = \frac{2\pi m}{\hbar^2} E, \tag{D2a}
\]

\[
A_\parallel = \pi k_{\parallel,x,y} \bigg|_{k_z=0} = \frac{2\pi}{\hbar^2} \sqrt{m_{\parallel} m_e} E, \tag{D2b}
\]

and the ratio of maximum-to-minimum cross-sectional areas is

\[
\frac{A_\parallel}{A_\perp} = \frac{f_{\text{max}}}{f_{\text{min}}} = \left[ m_{\parallel} \right] = \sqrt{K}, \tag{D3}
\]

where \( K = m_{\parallel}/m_\perp \) is defined as the ratio of band masses, and it directly represents the anisotropy of the ellipsoidal pocket. As our experiment is a direct probe of cyclotron masses, we can find a relation between \( K \) and the extremal cyclotron masses. For a perfect parabolic band, with dispersion of the form given in Eq. (D1), the cyclotron effective mass \( m^{\text{cyc}} \) can be found from the dynamic equations and the dispersion relation, resulting in the expression

\[
m^{\text{cyc}} = \sqrt{\frac{m_x m_y m_z}{m_x \left( \frac{B_x}{|B|} \right)^2 + m_y \left( \frac{B_y}{|B|} \right)^2 + m_z \left( \frac{B_z}{|B|} \right)^2}}. \tag{D4}
\]

FIG. 20. Temperature dependence of the amplitude of the oscillating component of magnetoresistance for \( \text{Pb}_{1-x}\text{Na}_x\text{Te} \) samples, with magnetic field oriented in or close to the [100] direction. The left-column plots of each composition show the background-free data at different temperatures. The right-column plots show the fits of the data to the LK formula in Eq. (1), using the two most dominant frequencies observed in the FFT of the lowest temperature curve (three most dominant for the \( x = 0.62 \%) sample. From these fits, the values of cyclotron effective mass and Dingle temperature, for each frequency term, are obtained.
For an ellipsoid of revolution, therefore, the transverse and longitudinal cyclotron effective masses, in terms of the band masses, are

\begin{align}
m_\perp^{\text{cyc}} &= m_\perp, \\
m_\parallel^{\text{cyc}} &= \sqrt{m_\perp m_\parallel}. \\
\end{align}

(5a, 5b)

And with this,

\begin{align}
m_\perp^{\text{cyc}} / m_\parallel^{\text{cyc}} &= \sqrt{m_\parallel / m_\perp} = \sqrt{K}. \\
\end{align}

(6)

For the case of Pb$_{1-x}$Na$_x$Te, in which $K = 14.3 \pm 0.4$ for a wide range of dopings, $m_\perp^{\text{cyc}} / m_\parallel^{\text{cyc}} = 3.78 \pm 0.05$. Additionally, from Eq. (D4), we can find a general expression for the angle dependence of cyclotron mass of an ellipsoid of revolution, with respect to the main axis of the ellipsoid, and as a function of the transverse cyclotron mass, by writing the components of the magnetic field in spherical coordinates as $B_x = |\vec{B}| \sin \theta \cos \varphi$, $B_y = |\vec{B}| \sin \theta \sin \varphi$, and $B_z = |\vec{B}| \cos \theta$:

\begin{align}
m_\perp^{\text{cyc}}(\theta) &= \sqrt{K / (K - 1) \cos^2 \theta + 1}. \\
\end{align}

(7)

**APPENDIX E: EFFECTIVE CYCLOTRON MASS ALONG THE [100] ORIENTATION**

Figure 20 shows the temperature dependence of the oscillating component of magnetoresistance for Pb$_{1-x}$Na$_x$Te samples of different Na concentrations, for field oriented along the [100] direction, which provides direct access to the $m_\perp^{[100]}$ cyclotron effective mass. Least-squares fits to Eq. (1), including up to the second strongest frequency component, for each Na doping, and for a field range of 3–5 to 14 T, are shown in the right-column plots of this figure. The obtained [100] cyclotron masses are summarized in Table II, and plotted as a function of carrier concentration in Fig. 16, in Sec. V.
In the next sections I present some additional material that was not included in the paper. I start by showing a characterization of the $\Sigma$ pockets and afterwards I compare quantitatively my computed evolution with the quantum-oscillation experiments performed by Paula Giraldo-Gallo and Ian R. Fisher from Stanford University.

### 6.3.2 Characterization of $\Sigma$ pockets

$\Sigma$ pockets start to contribute, within DFT, to the Fermi surface at concentrations $p = 1.7 \times 10^{19}$ cm$^{-3}$ ($x = 0.12\%$). Already by visual inspection of Fig. 6.18(b) one can conclude that the $\Sigma$ pockets are non-ellipsoidal – they have a particular “bread-like” shape. This can also be seen in Fig. 6.21, where the DFT angular evolution is compared with an ellipsoidal model, where the only parameters are the maximum and minimum frequencies at $[100]$. Note that for an ellipsoidal

![Figure 6.21: Angular dependence of the cross-sectional areas for a representative $\Sigma$ pocket](image)

model we would expect to find the maximum frequency both at $[100]$ and $[110]$. The distortions are seen as marked distortions around the major-axis. As a consequence, the longitudinal orbit ($f_{||}$) at $[100]$ is not equivalent to the maximum
Hole doping in PbTe

orbit at [110], but almost equivalent (from a visual point of view) to the second-largest orbit at [110]. This shows up as a large splitting (up to 270 T for the largest concentration \( p = 23.45 \times 10^{19} \text{ cm}^{-3} \)) of the branches, in particular close to 90°. We can already conclude that the energy dispersion of the “Σ band” is non-parabolic.

Before continuing I briefly explain the notation used in the following pages for the different quantities at [100] and [110] (compare with Fig. 6.21):

[100] Properties related to the minimum frequency are labeled by \( \perp \) and those to the maximum frequency by \( \parallel \);

[110] Properties related to the smallest frequency are labeled by “min”, those to the second-largest by \( \parallel \), and those to the largest frequency by “max”.

Further evidence for the non-parabolicity of the “Σ band” is obtained from the evolution of the cyclotron masses with density of holes (Fig. 6.22). The presence of three branches, and the difference between longitudinal masses at [100] vs. [110], confirms the non-ellipsoidicity of the Σ pockets, while the variation with \( p_\Sigma \) provides a clear proof for the non-parabolicity of the Σ band on its own.

Figure 6.23 shows the evolution of extremal cross-sectional areas with density of holes in the Σ pockets (\( p_\Sigma \)) for different directions. The colored dashed curves indicate the expected \( p_\Sigma^{2/3} \) behavior (Appendix C) for perfect ellipsoidal pockets with constant anisotropy \( K = 24 \) (Eq. (C.4)) [the anisotropy was computed using the maximum and minimum frequencies at [100] and then averaged over all concentrations (Table D.2)]. The ellipsoidal evolution highly overestimates the obtained DHVA frequencies because the pockets are flattened around the longitudinal axis.
Figure 6.23: Evolution of cross-sectional areas (in frequency units) with density of holes in the Σ pockets ($p_\Sigma$) for different directions. The colored dashed curve in all the plots shows the functional dependence of $p_\Sigma^{2/3}$ (Appendix C) expected for an ellipsoid with constant anisotropy $K = 24$ (Eq. (C.4)). (a) shows the smallest, (b) the largest frequencies, respectively.

6.3.3 Comparison with experiments

In this section I present a comparison with experiments for both Tl- and Na-doped PbTe. Even though I stated earlier that a quantitative comparison is (in principle) not meaningful, I will show that the agreement is astonishingly good.

Tl-doped PbTe

In the recent quantum oscillation experiments by Giraldo-Gallo [118] resonant impurity states were proposed for concentrations larger than the critical concentration, $x > 0.3\%$. These were found to contribute to conduction, but could not be detected directly in quantum oscillations. A possible reason is that the associated electrons are either localized or they are not able to make a complete turn around the Fermi surface. My supercell calculations (as well as previously done [77, 95, 96, 255, 257, 262]) indeed indicate Tl $s$ states at the Fermi energy that contribute a large density of states. However, in supercell calculations the systems are still ordered, and the obtained Tl states generate a real band; it is not clear what would happen to this “impurity band” in a (real) disordered system. Some indications can be obtained by unfolding the bands, but a contribution to conduction and/or the Fermi surface can not be unambiguously derived: the resulting spectral functions show some dispersion, which is good for their conductivity properties, as it means that the corresponding states are (partly) delocalized, but the associated spectral weights are small, making it difficult to follow the actual dispersion. In the same way, ARPES measurements at $x = 0.5\%$ [119] did not
find any indication of impurity states. The authors of Ref. [119] commented that possible localized states should have been resolved even if the cross section for Ti electrons was relatively small. On the other hand, they stated that a rigid-band model is not appropriate to describe this compound. Note, however, that ARPES was performed at 20 K, while quantum oscillations were measured at $1.5 \pm 0.2$ K (close to the critical superconducting temperature).

I next show in Fig. 6.24 a comparison of my Fermi surface evolution with the results of quantum oscillation experiments [118]. Since in experiments the

![Figure 6.24: Comparison of the calculated evolution of DHVA frequencies with doping, and the experimental results for Ti-doped PbTe. The open symbols represent my quantities computed using SKEAF, closed symbols experimental data [118]. (a) The Hall number is used for the experimental data. (b) The Luttinger volume is used for the experimental data.](image)

hole concentration contributing to conductivity (Hall number) and the volume of the $L$ pockets (Luttinger volume) do not coincide, I show both comparisons; in panel (a) the Hall number is used, while in panel (b) the Luttinger volume. For low concentrations, the agreement is remarkably good and can be explained by the ellipsoidalicity of the $L$ pockets, both in theory and experiment. Since in an ellipsoidal model (with constant anisotropy) the evolution with Fermi surface volume depends only on anisotropy itself (Eq. (C.6)), and the obtained anisotropies are not so different (in experiments $13 \pm 4$, here 23), this is not really a surprise. Furthermore, we can observe a clear saturation of experimental DHVA frequencies for the larger concentrations, even if the experimental errors are large. This is an indication that the $L$ pockets do not seem to vary anymore, which can be explained if not all additional conducting carriers are contributing to the $L$ pockets. Since quantum oscillations did not give any indication for the presence of $\Sigma$ pockets, Giraldo-Gallo [118] concluded that additional charge carriers are present (consistent with resonant impurity levels at the Fermi level). Consistent
with that, panel (b) shows that if the Luttinger volume is used instead, the agreement with my data – and thus with an ellipsoidal model (see Fig. 5 in section 6.3.1) – is improved significantly.

Further studies are clearly needed to elucidate the presence and role of the Tl impurity states in Tl-doped PbTe.

*Na-doped PbTe*

Fewer problems in reconciling theory and experiments are expected for Na-doped PbTe. In fact, my supercell calculations did not show any large influence of Na on the bands close to the Fermi energy, something that let me conclude that the rigid-band approximation is valid. The only exception is a lifting of degeneracy that would cause the presence of two different sized $L$ pockets, with the smaller one predicted to be almost spherical. In view of the small spectral weight of the pocket originating from the split band, it is not a real surprise, that a corresponding (almost flat) angular evolution is not resolved in quantum oscillations [118, 209].

As a last thing I compare quantitatively my DFT-derived doping evolution with experiments (Fig. 6.25). Both the extremal cross-sectional areas and the cyclotron masses show a remarkably good agreement, in spite of the approximations and parameters that I used. The reason, again, is that in an ellipsoidal model with constant anisotropy $K$, the cross-sectional areas depend only on the anisotropy (Eq. (C.6)): the experimental value $K = 15 \pm 3$ is in fact quite close to my $K = 23$. But even where the ellipsoidal model is not valid anymore, the agreement stays constant because the deviations in the expected $p_L^{2/3}$ behavior are quite small (Fig. 5 in section 6.3.1).

![Figure 6.25: Comparison of the computed Fermi surface evolution with Na-doped PbTe experimental results. The open symbols represent my quantities computed using SKEAF, closed symbols experimental data [118, 209].](image)
6.4 Conclusions & Outlook

In this chapter I presented a comprehensive study of the electronic (and structural) properties of Na- and Tl-doped PbTe using supercell methods and the rigid-band approximation. It is interesting to see that both impurities tend to increase the polarizability, with the Tl compound showing clear evidence for stereochemically active lone pairs. On the other hand, DFT is not able to reproduce a charge and/or bond disproportionation for the Tl system. Either more advanced techniques are needed or the phenomenon is not present at all. Further studies, both experimental and theoretical, are needed to assess the existence of such an interesting structure. This is relevant also for the understanding of the peculiar superconducting state and the alleged charge Kondo effect that depends critically on the existence of some kind of charge disproportionation.

On the other hand, the origin of this failure could also be found in the proposed dynamic origin of the charge fluctuations that can not be captured by a static calculation. If degenerate states exist, it is a priori not possible to predict if a static calculation will favor one of them or just produce the average among them. With this respect, it may be interesting to compute indium-doped PbTe, where the charge disproportionation is proposed to be static [263–265].

Supercell computations show that the two kinds of impurities have a very different influence on the electronic structure: Na affects only minimally the band structure (by lifting the degeneracy), while Tl introduces an “impurity band” just at the Fermi level. Interestingly, unfolding of the bands suggests that the latter may not influence the Fermi surface because of its small spectral weight, in line with ARPES [119] results on Tl-doped PbTe. These experiments found that the Te $p$ bands are affected by and dependent on doping – the rigid-band approximation is not valid. In any case, it is not a priori clear if such a narrow band with large effective mass would be detectable by quantum oscillation experiments – the associated electron mean free path may not be large enough to successfully complete turns around the Fermi surface. To better understand the role of the impurity band a good strategy may be to initially forget about the alleged charge disproportionation and use effective medium theories like the coherent potential approximation (CPA). These techniques would allow one to obtain a very good understanding of the “band structure” close to the Fermi level for any doping in a reasonable amount of computer time. Afterwards, one could go back to supercell calculations, where larger systems and lower concentrations (closer to and also smaller than the critical concentration $x_c = 0.3\ %$) should be extensively studied, even in combination with more advanced techniques like DMFT.

On the other hand, I showed that the rigid-band approximation is a valid alternative for the determination and characterization of the Fermi surface in Na-doped PbTe. DFT-derived general trends for the evolution of the pockets, and in particular the fingerprints of the deviations from perfect ellipsoidalicity, can be a valuable help for analyzing quantum oscillation experiments, even if a quantitative comparison is in principle difficult.
Conclusions & Outlook

In this thesis I presented a detailed study of the structural and electronic properties of lead telluride. I find that the lead lone pair may be stereochemically active, but not in the usual (static) way. Instead, it expresses itself dynamically, giving rise to regions displaying dynamic correlated electric dipoles. Possible consequences of such a behavior are asymmetric, or even structured, PDF peaks and enhanced thermoelectric properties. The peculiar local structure is related to the incipient ferroelectricity of PbTe and may be relevant in the paraelectric phase of any ferroelectric material.

My work, as already previously noticed [34, 63–68], suggests a link between incipient ferroelectricity and enhanced thermoelectricity. The production of the band gap opening and the band convergence by the correlated dipoles are strong supporting points. Faster and bigger simulations are needed to study and understand the role of the correlated dipoles on the thermoelectric performance. For this reason the generation of classical potentials that capture the local structure produced by the lead lone pair should be pursued further.

My computations are of fundamental importance for the analysis of quantum oscillation experiments in Na- and Tl-doped PbTe. I show that the band structure extracted from DFT can be indeed used to derive meaningful DHVA frequencies and cyclotron masses. On the other hand, DFT does not seem to be adequate in describing charge disproportionated systems; more advanced techniques like DMFT might be needed.

Consistent with previous DFT studies [77, 95, 96, 255–257, 262], I find that Tl doping produces an impurity band at the Fermi energy. This questions the validity of the mixed-valence model and the related charge Kondo effect. However, the formation of an impurity band originating from a hybridization between impurity and host states should be expected in a periodic supercell calculation that always produces a coherent band structure. To fully understand the role of thallium impurities one needs to study disordered systems and to employ the band unfolding technique. My results in this respect, as well as ARPES measurements [119], are already questioning the contribution of the impurity band to the Fermi surface, but larger supercells are needed to fully dissect the issue.
Appendices

A Computation of DHVA frequencies

I extracted DHVA frequencies and cyclotron masses with the Supercell K-space Extremal Area Finder (SKEAF) code [250]. The Kohn-Sham eigenenergies have first to be computed on a uniform grid in the Brillouin zone and saved in the Band-XCrysDen-Structure-File (BXSF) format. SKEAF uses an involved algorithm to extract the morphology of the Fermi surface:

1. A cubic $k$-space supercell is constructed; it is considerably larger than the primitive Brillouin zone and aligned with the magnetic field. This allows the determination of orbits spanning a few Brillouin zones. The band energies at $k$-points in the supercell are determined by Lagrange interpolating polynomials. The density of $k$-points is usually $100 - 200$ times larger than that used in the DFT calculation.

2. The supercell is divided into slices perpendicular to the magnetic field. For each slice, the Fermi-surface orbits are identified by a predetermined path on the slice. The cross-sectional area, effective mass and orbit type (electron or hole) are recorded.

3. Orbits are matched from slice to slice, i.e. orbits on different slices with similar coordinates are averaged.

4. The extremal cross-sectional areas are determined.

Other nice features of the code include the possibility to automatically rotate the magnetic field in a specified plane and the computation of the contribution of the band to the electronic DOS at the Fermi energy.

B Analysis of molecular dynamics simulations

Molecular dynamics trajectories represent the dynamic evolution of a many-body system under given constraints and by definition are fully anharmonic. As such they are self-contained and, in principle, we can extract all possible information: mean displacements, root mean-square displacements (with access to the diffusion constant), probability density function, pair distribution function, phonon properties, etc. Here I explain how the pair distribution function and the phonon spectrum are extracted from the MD trajectories.

B.1 Pair distribution function

In this section I summarize the methods to compute the pair distribution function [182, 266, 267]. Remember the definition of the radial distribution function (RDF) given in section 2.5: \( R(r) \) gives the number of neighbors in a spherical shell of thickness \( dr \) at a distance \( r \) from an atom. Thus, we can write

\[
R(r) = \frac{1}{N} \sum_{ij} \frac{b_i b_j}{(b)}^2 \delta(r - r_{ij}),
\]

(B.1)

\( r_{ij} \) being the separation distance between two atoms at \( r_i \) and \( r_j \), \( N \) the number of atoms in the system, \( b_i \) the scattering amplitude of atom \( i \) (i.e. a measure of how strongly an atom scatters), and \( (b) = \sum_i b_i/N \). The scattering amplitudes are introduced to allow a fair comparison with experiments. In case of x-rays the \( b \) values are replaced with the atomic number of the corresponding species \(^2\); for neutron scattering they are replaced with the neutron scattering lengths, which are listed in Ref. [268]. For simplicity I will drop the \( b \) values in the derivation from now on.

In contrast to experiments, in a MD simulation it is possible to determine the PDF between any two sets of atoms, \( \text{sel}_1 \) and \( \text{sel}_2 \), and the continuous \( \delta \)-functions are replaced by a histogram

\[
R(r) = \frac{1}{N_i} \left( \sum_{i \in \text{sel}_1} \sum_{j \in \text{sel}_2; j \neq i} \sum_k \frac{h_k (r; r_{ij})}{\Delta r} \right)
\]

(B.2)

where \( N_i \) is the number of elements of the first set \( \text{sel}_1 \) (i.e. the number of atoms considered in the first sum over \( i \)), \( <> \) represents a time-average, and \( k \) runs over all bins, centered at \( r_k \) and with bin size \( \Delta r \)

\[
r_k = r_0 + k \Delta r \quad k = 0, 1, 2, \ldots
\]

\( r_0 \) is the lower bound of the histogram. The function (histogram) \( h_k \) is defined as

\[
h_k(r; r_{ij}) = \begin{cases} 
1 & \text{if } r_k - \Delta r/2 \leq r < r_k + \Delta r/2 \text{ and } r_k - \Delta r/2 \leq r_{ij} < r_k + \Delta r/2 \\
0 & \text{otherwise}
\end{cases}
\]

The PDF \( g(r) \) can then be computed as

\[
g(r) = \frac{1}{N_{\text{pairs}}/V} \left( \sum_{i \in \text{sel}_1} \sum_{j \in \text{sel}_2; j \neq i} \sum_k \frac{h_k (r; r_{ij})}{(4/3) \pi \left( r_{k+1}^3 - r_k^3 \right)} \right) \quad \text{(B.3)}
\]

with \( N_{\text{pairs}} = N_i N_j \) the number of pairs of atoms in the double sum over \( i \) and \( j \). The volume of the spherical shell is usually computed with the exact formula, instead of \( 4\pi r^2 \Delta r \) (as Eq. 2.25 would suggest). The 3D version can be derived similarly, but now a 3D histogram has to be used.

\(^2\) Actually the \( b \) values are replaced by the atomic scattering factors at \( Q = 0 \), which are proportional to the atomic numbers.
B.2 Phonon-related properties

The phonon density of states (DOS) $Z(\omega)$ can be obtained as the Fourier transform of the velocity autocorrelation function [269, 270]

$$Z(\omega) \propto \sum_n M_n \int \frac{\langle v_n(t)v_0(0) \rangle}{\langle v_n(0)v_0(0) \rangle} e^{i\omega t} \, dt,$$  \hspace{1cm} (B.4)

where $v_n$ and $M_n$ are the velocity and mass of atom $n$, respectively. Using the Wiener-Khintchine theorem [271, 272], $Z(\omega)$ can be computed as the power spectrum of the velocities [273, 274]

$$Z(\omega) \propto \sum_n \sum_{\alpha=x,y,z} M_n \left| \int v_n^{(\alpha)}(t) e^{i\omega t} \, dt \right|^2,$$  \hspace{1cm} (B.5)

where $v_n^{(\alpha)}$ is the $\alpha$ component of the velocity of atom $n$. The phonon band structure can be obtained by computing the $q$-dependent power spectrum $Z(q, \omega)$ [52]

$$Z(q, \omega) \propto \sum_{\alpha,s} M_s \frac{1}{N_q} \left| \int e^{i\omega t} \sum_j v_j^{(s,\alpha)}(t) e^{iqr_j(t)} \, dt \right|^2,$$  \hspace{1cm} (B.6)

where $s$ labels the atom type (e.g. Pb and Te), $j$ labels atoms of a specific type $s$, $r(t)$ are the time-dependent coordinates of the atoms, and $N_q$ is the number of $q$-points commensurate with the supercell. It can be understood as doing an additional Fourier transform to reciprocal space before computing the power spectrum. Strictly speaking one should use the position of the origins of the different unit cells in the supercell instead of the time-dependent coordinates. However, the time-dependency in the exponent allows the determination of phonon frequencies even if a local symmetry breaking (a local deviation from the average global structure) happens – relevant to compare with the inelastic neutron scattering experiments by Jensen et al. [33].

Power spectrum estimation

I computed the power spectrum following and adapting the computation of the periodogram as presented in Numerical recipes in C: the art of scientific computing [275].

Suppose we have a signal $c(t)$, which is sampled at $N_t$ discrete time points (with equal sampling intervals $\Delta$) to produce values $c_0, c_1, \ldots, c_{N_t-1}$ ($N_t$ is assumed to be an even integer). If we compute the discrete Fourier transform of the signal

$$C_k = \sum_{j=0}^{N_t-1} c_j e^{2\pi i j k / N_t} \quad k = 0, \ldots, N_t - 1$$  \hspace{1cm} (B.7)
the periodogram estimate of the power spectrum is defined at $N_t/2 + 1$ frequencies

$$
P(0) = P(v_0) = \frac{1}{N_t^2} |C_0|^2
$$

$$
P(v_k) = \frac{1}{N_t^2} \left( |C_k|^2 + |C_{N_t-k}|^2 \right) \quad k = 1, \ldots, \frac{N_t}{2} - 1 \tag{B.8}
$$

$$
P(v_c) = P(v_{N_t/2}) = \frac{1}{N_t^2} |C_{N_t/2}|^2
$$

where $v_k$ is defined for the non-negative frequencies

$$
v_k := \frac{k}{N_t \Delta} = 2v_c \frac{k}{N_t} \quad k = 0, \ldots, \frac{N_t}{2} . \tag{B.9}
$$

$v_c = 1/(2\Delta)$ is the Nyquist frequency, i.e. the largest frequency that can be determined from a given sampling interval $\Delta$.

To decrease the leakage from one frequency to another in the periodogram, we can multiply the input data $c_j$, $j = 0, \ldots, N_t - 1$ by a window function $w_j$ prior to FFT; in this work I chose the Welch window

$$
w_j = 1 - \left( \frac{j - \frac{N_t-1}{2}}{\frac{N_t-1}{2}} \right)^2 \quad j = 0, \ldots, N_t - 1 . \tag{B.10}
$$

Furthermore, to add more frequency bins, we can zero-pad the signal after applying the window function. This does not change the resolution of the FFT – given by $1/(N_t \Delta)$ – but it may produce a smoother-looking spectrum.

Finally, to obtain better estimates one should also split the data into several segments and average their periodograms. It can be shown that an almost optimal solution consists of adjacent segments overlapping by half of their length.

Test for the $q$-resolved power spectrum $Z(q, \omega)$

To check for a correct implementation and to visualize one simple example, I simulated a two-atom cubic unit cell with a $2 \times 1 \times 1$ supercell. Both atoms are performing a sinusoidal motion: the first atom oscillates in phase in both cells with a frequency $\nu_1 = 1.2$ THz, while the second performs an out of phase oscillation with a frequency $\nu_2 = 0.3$ THz.

Figure B.1 shows the extracted total DOS and the $q$-resolved DOS at $q = \Gamma$ and $q = X$. As expected, the $q$-resolved DOS shows peaks only at the corresponding frequencies: at $q = \Gamma$ only the in-phase motion is captured, while at $q = X$ only the out-of-phase. The small peak at $\nu = 1.5$ THz (corresponding to the sum of the two frequencies) appearing for the $q = X$-DOS is not a real feature, but a consequence of the time dependence of the position vectors in Eq. B.6. Note that the peak width is consistent with the resolution of the FFT: the standard deviation of all peaks is approx. 0.01 THz, while the resolution of the FFT is approx. 0.02 THz.
C Determination of cross-sectional areas of an ellipsoid

In this Appendix I summarize closed formulas for the intersection of a plane with an ellipsoid. For a complete analytic treatment refer to Ref. [276]. Consider an ellipsoid with three positive semi-axes $a_1, a_2, a_3$

$$\frac{x_1^2}{a_1^2} + \frac{x_2^2}{a_2^2} + \frac{x_3^2}{a_3^2} = 1,$$  \hfill (C.1)

and a plane

$$n_1 x_1 + n_2 x_2 + n_3 x_3 = \text{const}$$  \hfill (C.2)

defined by a unit normal vector

$$\mathbf{n} = (n_1, n_2, n_3)^T,$$

and containing an internal point of the ellipsoid C.1. Since the derivation of the intersection between the ellipsoid C.1 and the plane C.2 is quite tedious, I will jump directly to the result for the extremal cross-sectional area

$$A = \pi \frac{a_1 a_2 a_3}{\sqrt{\sum_i a_i^2 n_i^2}}.$$  \hfill (C.3)

Let’s consider a prolate ellipsoid with semi-axes $a_1 = a_2 =: a$ and $a_3 = c$. The anisotropy $K$ of the ellipsoid is defined by the ratio between the maximum and minimum cross-sectional areas

$$\sqrt{K} = \frac{\pi ac}{\pi a^2} = \frac{c}{a}.$$  \hfill (C.4)
It is easy to rewrite (C.3) as a function of the volume of the ellipsoid

\[ V = \frac{4}{3} \pi a^2 c, \]  

(C.5)
as

\[ A = \frac{(4V/3)^{2/3}}{\left(\sqrt{K\pi}\right)^{1/3} \sqrt{n_1^2 + n_2^2 + Kn_3^2}}. \]  

(C.6)

This means that the evolution with volume of the extremal cross-sectional areas of a prolate ellipsoid with constant anisotropy \( K \) is

\[ A \propto V^{2/3}. \]  

(C.7)

In our case the ellipsoids live in reciprocal space and their volume is proportional to the carrier density \( p = V/(2\pi)^3 \) giving an evolution of the extremal cross-sectional areas \( A \propto p^{2/3} \).

D Characterization of the \( L \)- and \( \Sigma \)-pockets

In the following tables I present a summary of the evolution of the \( L \) and \( \Sigma \) pockets obtained with the rigid-band approximation.
Table D.1: Properties of the $L$-pockets for different shifts of the Fermi energy into the valence band. $p$, and $p_L$ are the total, and $L$ density of holes; $∥$ indicates longitudinal, i.e. 35°, properties, $⊥$ indicates transversal, i.e. 55°, properties, and max indicates properties in the direction of $f_{\text{max}}$. $K$ is the anisotropy of the $L$-pockets (Eq. (C.4)).

<table>
<thead>
<tr>
<th>$\Delta E_F$ [eV]</th>
<th>$x$ [%]</th>
<th>$p \left[ 10^{19} \text{ cm}^{-3} \right]$</th>
<th>$p_L \left[ 10^{19} \text{ cm}^{-3} \right]$</th>
<th>$f_{∥}$ [T]</th>
<th>$m_{∥}^{\text{sc}} \left[ m_e \right]$</th>
<th>$f_{\text{max}}$ [T]</th>
<th>$m_{\text{max}}^{\text{sc}} \left[ m_e \right]$</th>
<th>$f_{⊥}$ [T]</th>
<th>$m_{⊥}^{\text{sc}} \left[ m_e \right]$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.004</td>
<td>0.066</td>
<td>0.066</td>
<td>15.6</td>
<td>0.11</td>
<td>15.6</td>
<td>0.11</td>
<td>3.2</td>
<td>0.03</td>
<td>24.3</td>
</tr>
<tr>
<td>0.02</td>
<td>0.010</td>
<td>0.146</td>
<td>0.146</td>
<td>26.7</td>
<td>0.14</td>
<td>26.7</td>
<td>0.14</td>
<td>5.6</td>
<td>0.03</td>
<td>23.0</td>
</tr>
<tr>
<td>0.03</td>
<td>0.018</td>
<td>0.265</td>
<td>0.265</td>
<td>39.6</td>
<td>0.16</td>
<td>39.6</td>
<td>0.16</td>
<td>8.4</td>
<td>0.03</td>
<td>22.4</td>
</tr>
<tr>
<td>0.04</td>
<td>0.029</td>
<td>0.431</td>
<td>0.431</td>
<td>54.3</td>
<td>0.18</td>
<td>54.3</td>
<td>0.18</td>
<td>11.4</td>
<td>0.04</td>
<td>22.6</td>
</tr>
<tr>
<td>0.05</td>
<td>0.044</td>
<td>0.653</td>
<td>0.653</td>
<td>71.0</td>
<td>0.20</td>
<td>71.0</td>
<td>0.20</td>
<td>15.0</td>
<td>0.04</td>
<td>22.3</td>
</tr>
<tr>
<td>0.06</td>
<td>0.063</td>
<td>0.939</td>
<td>0.939</td>
<td>89.7</td>
<td>0.23</td>
<td>89.7</td>
<td>0.23</td>
<td>19.1</td>
<td>0.05</td>
<td>22.0</td>
</tr>
<tr>
<td>0.07</td>
<td>0.117</td>
<td>1.754</td>
<td>1.303</td>
<td>110.5</td>
<td>0.25</td>
<td>110.5</td>
<td>0.25</td>
<td>23.6</td>
<td>0.06</td>
<td>21.9</td>
</tr>
<tr>
<td>0.08</td>
<td>0.245</td>
<td>3.672</td>
<td>1.756</td>
<td>133.2</td>
<td>0.27</td>
<td>135.5</td>
<td>0.30</td>
<td>28.6</td>
<td>0.06</td>
<td>22.5</td>
</tr>
<tr>
<td>0.09</td>
<td>0.464</td>
<td>6.962</td>
<td>2.446</td>
<td>163.2</td>
<td>0.30</td>
<td>169.7</td>
<td>0.35</td>
<td>35.3</td>
<td>0.07</td>
<td>23.2</td>
</tr>
<tr>
<td>0.10</td>
<td>0.806</td>
<td>12.088</td>
<td>3.505</td>
<td>202.2</td>
<td>0.34</td>
<td>216.4</td>
<td>0.42</td>
<td>44.4</td>
<td>0.08</td>
<td>23.8</td>
</tr>
<tr>
<td>0.11</td>
<td>1.078</td>
<td>16.170</td>
<td>4.380</td>
<td>229.7</td>
<td>0.36</td>
<td>250.8</td>
<td>0.46</td>
<td>51.3</td>
<td>0.10</td>
<td>25.2</td>
</tr>
<tr>
<td>0.12</td>
<td>1.323</td>
<td>19.846</td>
<td>5.209</td>
<td>252.4</td>
<td>0.39</td>
<td>285.5</td>
<td>0.71</td>
<td>57.5</td>
<td>0.11</td>
<td>27.0</td>
</tr>
<tr>
<td>0.13</td>
<td>1.563</td>
<td>23.450</td>
<td>6.078</td>
<td>272.9</td>
<td>0.40</td>
<td>327.4</td>
<td>0.93</td>
<td>63.6</td>
<td>0.12</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td>4.95</td>
<td>22.4</td>
<td>0.55</td>
<td>28.3</td>
<td>0.12</td>
<td>5.98</td>
<td>17.37</td>
<td>4.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>-------</td>
<td>------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.32</td>
<td>19.85</td>
<td>12.17</td>
<td>5.37</td>
<td>0.12</td>
<td>1.02</td>
<td>0.14</td>
<td>0.12</td>
<td>5.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.32</td>
<td>22.9</td>
<td>12.2</td>
<td>5.34</td>
<td>0.12</td>
<td>1.03</td>
<td>0.17</td>
<td>0.12</td>
<td>6.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.32</td>
<td>23.3</td>
<td>12.3</td>
<td>5.35</td>
<td>0.12</td>
<td>1.04</td>
<td>0.18</td>
<td>0.12</td>
<td>6.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.32</td>
<td>23.4</td>
<td>12.4</td>
<td>5.35</td>
<td>0.12</td>
<td>1.05</td>
<td>0.19</td>
<td>0.12</td>
<td>6.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.32</td>
<td>23.5</td>
<td>12.5</td>
<td>5.35</td>
<td>0.12</td>
<td>1.06</td>
<td>0.20</td>
<td>0.12</td>
<td>6.44</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table D.2: Characterization of the $\Sigma$-pockets in the $[100]$ direction. $d$ and $f^{\perp}$ are the total and the $\Sigma$-pockets' density of holes; $\phi$ is the density of holes that would be obtained if the pocket were an ellipsoid with given maximum and minimum cross-sectional areas.
Table D.3: Characterization of the Σ-pockets in the [110] direction; \( p \) and \( p_\Sigma \) are the total, and the Σ-pockets’ density of holes.

<table>
<thead>
<tr>
<th>( x ) [%]</th>
<th>( p ) [(10^{19} \text{ cm}^{-3})]</th>
<th>( p_\Sigma ) [(10^{19} \text{ cm}^{-3})]</th>
<th>( f_1 ) [T]</th>
<th>( m_1^{\text{cyc}} ) [( m_e )]</th>
<th>( f_2 ) [T]</th>
<th>( m_2^{\text{cyc}} ) [( m_e )]</th>
<th>( f_3 ) [T]</th>
<th>( m_3^{\text{cyc}} ) [( m_e )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>1.75</td>
<td>0.45</td>
<td>7.5</td>
<td>0.13</td>
<td>21.4</td>
<td>0.38</td>
<td>41.6</td>
<td>0.74</td>
</tr>
<tr>
<td>0.24</td>
<td>3.67</td>
<td>1.92</td>
<td>19.1</td>
<td>0.14</td>
<td>54.4</td>
<td>0.38</td>
<td>106.5</td>
<td>0.77</td>
</tr>
<tr>
<td>0.46</td>
<td>6.96</td>
<td>4.52</td>
<td>34.4</td>
<td>0.15</td>
<td>94.0</td>
<td>0.38</td>
<td>188.6</td>
<td>0.82</td>
</tr>
<tr>
<td>0.81</td>
<td>12.09</td>
<td>8.58</td>
<td>52.7</td>
<td>0.16</td>
<td>140.7</td>
<td>0.39</td>
<td>291.8</td>
<td>0.89</td>
</tr>
<tr>
<td>1.08</td>
<td>16.17</td>
<td>11.79</td>
<td>65.5</td>
<td>0.16</td>
<td>171.1</td>
<td>0.40</td>
<td>363.2</td>
<td>0.96</td>
</tr>
<tr>
<td>1.32</td>
<td>19.85</td>
<td>14.64</td>
<td>75.4</td>
<td>0.17</td>
<td>195.3</td>
<td>0.40</td>
<td>424.1</td>
<td>1.06</td>
</tr>
<tr>
<td>1.56</td>
<td>23.45</td>
<td>17.37</td>
<td>84.3</td>
<td>0.17</td>
<td>216.1</td>
<td>0.41</td>
<td>480.0</td>
<td>1.29</td>
</tr>
</tbody>
</table>
List of Publications


[278] R. Yu et al., Emphanitic-like anharmonicity in PbSe at high temperature and the anomalous electronic properties in the PbX (X=S, Se, Te) system, in preparation.
BIBLIOGRAPHY

[40] O. Madelung et al., eds., IV-VI compounds, general tables crystal structure, chemical bond and related data of GeTe, SnTe: Datasheet from Landolt-Börnstein - Group III Condensed Matter - Volume 41C: “Non-Tetrahedrally Bonded Elements and Binary Compounds I” in SpringerMaterials (http://dx.doi.org/10.1007/10681727_705), Part of SpringerMaterials.


