ELECTRONIC BAND STRUCTURE, PHONONS 
AND EXCITON BINDING ENERGIES OF 
HALIDE PEROVSKITES CsSnX₃ WITH X=Cl, 
Br, I 

by 

LING-YI HUANG 

Submitted in partial fulfillment of the requirements 
For the degree of Doctor of Philosophy 

Dissertation Advisor: Walter R. L. Lambrecht 

Department of Physics 
CASE WESTERN RESERVE UNIVERSITY 

August, 2015
CASE WESTERN RESERVE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

We hereby approve the dissertation of

Ling-yi Huang

candidate for the Doctor of Philosophy degree*.

Committee Chair : Walter R. L. Lambrecht, Ph.D.
Professor,
Dissertation Advisor

Committee :
Philip L. Taylor, Ph.D.
Professor,
Department of Physics

Committee :
Kathleen Kash, Ph.D.
Professor,
Department of Physics

Committee :
Clemens Burda, Ph.D.
Professor,
Department of Chemistry

June 19th, 2015

*We also certify that written approval has been obtained for any
proprietary material contained therein.
Contents

List of Figures

1 Introduction

1.1 Motivation .................................................. 1
1.2 Phase transitions ........................................... 6

2 Electronic band structure

2.1 Introduction .................................................. 10
2.2 Computational method ....................................... 11
   2.2.1 Density Functional Theory (DFT) ....................... 12
   2.2.2 Local Density Approximation (LDA) and Generalized Gradient
       Approximation (GGA) .................................... 13
   2.2.3 GW approximation ....................................... 14
   2.2.4 Quasiparticle Self-consistent (QS) GW approximation ... 20
   2.2.5 Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) method 21
2.3 Results ..................................................... 25
   2.3.1 Band structures ......................................... 25
      2.3.1.1 Inverted band structure ........................... 25
      2.3.1.2 Band structures in different phases ............... 34
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.1.3</td>
<td>Band structures in different (A and B) compounds (ABI₃)</td>
<td>41</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Effective masses and exciton binding energies.</td>
<td>47</td>
</tr>
<tr>
<td>2.3.2.1</td>
<td>Theoretical treatment</td>
<td>47</td>
</tr>
<tr>
<td>2.3.2.2</td>
<td>Choice of dielectric constant</td>
<td>50</td>
</tr>
<tr>
<td>2.3.2.3</td>
<td>Comparison to the reported (experimental) exciton binding energy</td>
<td>53</td>
</tr>
<tr>
<td>2.4</td>
<td>Conclusions</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>Zone Center Phonons I: Zone center phonons in cubic, tetragonal, and orthorhombic phases</td>
<td>58</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>58</td>
</tr>
<tr>
<td>3.2</td>
<td>Computational method</td>
<td>59</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Interatomic force constant, dynamical matrix, phonon frequency, and eigendisplacement</td>
<td>60</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Electronic dielectric susceptibility tensor and high frequency dielectric permittivity tensor</td>
<td>61</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Born-effective charge tensor</td>
<td>62</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Oscillator strength tensor and static dielectric permittivity tensor</td>
<td>63</td>
</tr>
<tr>
<td>3.2.5</td>
<td>LO–TO splitting</td>
<td>63</td>
</tr>
<tr>
<td>3.2.6</td>
<td>Infrared spectra</td>
<td>64</td>
</tr>
<tr>
<td>3.2.7</td>
<td>Raman tensor and Raman spectrum</td>
<td>65</td>
</tr>
<tr>
<td>3.2.8</td>
<td>Computational details</td>
<td>66</td>
</tr>
<tr>
<td>3.3</td>
<td>Results</td>
<td>67</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Group theory analysis</td>
<td>67</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Calculated results</td>
<td>68</td>
</tr>
</tbody>
</table>
3.3.3 Comparison with IR experimental data for $\alpha$-CsSnCl$_3$ and $\alpha$-CsSnBr$_3$ ................................................. 86

3.3.4 LO-plasmon coupling effect ........................................ 89

3.4 Conclusions .............................................................. 92

4 Zone center phonons II: First-principles calculations of phonons and Raman spectra in monoclinic CsSnCl$_3$ 94

4.1 Introduction .............................................................. 94

4.2 Computational method .................................................. 95

4.3 Results ................................................................. 96

4.3.1 Lattice parameters .................................................. 96

4.3.2 Group theory analysis and internal coordinates. ................. 98

4.3.3 Infrared modes ...................................................... 100

4.3.4 Raman modes and comparison with experiment ................. 109

4.4 Conclusions .............................................................. 123

5 Full phonon band structures and their relation to the phase transitions 125

5.1 Introduction .............................................................. 125

5.2 Computational method .................................................. 127

5.3 Results ................................................................. 128

5.3.1 Calculated full phonon band structures .......................... 128

5.3.2 Soft phonon modes and phase transitions ....................... 132

5.4 Conclusions .............................................................. 138

6 Conclusions .............................................................. 140

Bibliography 144
List of Figures

1.1 Crystal structures of a perfect cubic perovskite. ........................................ 2

1.2 A mesoscopic/sensitized halide perovskite solar cell with mesoporous (MP) TiO$_2$ layer is shown on the left. Shown on the right is a planar halide perovskite solar cell without a mesoporous TiO$_2$ layer. FTO, TF, and HTM stand for fluorine doped tin oxide (FTO), thin film (TF), and hole transporting material (HTM). In the mesoscopic/sensitized structure, electrons can be collected directly and/or via TiO$_2$ layer [1]. 3

1.3 Temperature dependent phase transitions in CsSnX$_3$. .............................. 7

1.4 Crystal structures of $\alpha$-CsSnI$_3$ (left), $\beta$-CsSnI$_3$ (middle), and $\gamma$-CsSnI$_3$ (right). Green spheres are Cs atoms, purple spheres are I atoms, and grey sphere are Sn atoms. Octahedrons formed by a Sn atom and six I atoms are highlighted in grey. The $c$-axis points out of page in the top figures (top view), and the $c$-axis points upward in the bottom figures (side view). ................................................................. 8

2.1 The Feynman diagrams, from top to bottom, represent the electron self-energy, (exact) electron propagator, (exact) photon propagator, electron vertex function, and photon self-energy, respectively. These five diagrams represent the Hedin’s equations. ........................................ 19
2.2 QSGW band structures and partial densities of states of α-CsSnI₃, α-CsSnBr₃, and α-CsSnCl₃. ................................................. 28

2.3 Energy bands of CsSnI₃ in the QSGW method near the gap including spin-orbit coupling. .................................................. 29

2.4 Dominant orbital character of CBM (upper figure) and VBM (lower figure) for α-CsSnI₃. For the selected orbitals φᵢ mentioned in the figure, the figure plots k and E resolved “spectral functions”, A(k, E) = |⟨φᵢ|ψₙk⟩|^2δ(E − Eₙk) with the δ-function replaced by a Gaussian, using the color scale shown on the right. So, the light green areas and white areas indicate zero contribution from that orbital while the red areas indicate a strong contribution of that orbital. The red thin lines show the band superposed on the color graph. ............................................ 31

2.5 Schematic drawing of the anion p-orbitals pointing toward Sn-s at center of unit cell for the VBM Bloch state at the point R at the corner of the Brillouin zone. ................................................. 32

2.6 Band gap vs. lattice constant. .................................................. 34

2.7 LDA band structure of α-CsSnI₃ (upper left), β-CsSnI₃ (upper right), γ-CsSnI₃ (lower left) and Y-CsSnI₃ (lower right). ................. 36

2.8 (From left to right) Brillouin zone of cubic (α-phase), tetragonal (β-phase), and orthorhombic (γ- and Y-phase) structures, respectively. 36

2.9 QSGW band structure of β-CsSnI₃ (red solid line) and β-CsSnBr₃ (blue dashed line). .................................................. 37

2.10 LDA band structure of M-CsSnCl₃. .................................................. 39

2.11 QSGW band structure with SO of cubic CsSiI₃ (upper left), CsGeI₃ (upper right), CsSnI₃ (lower left), CsPbI₃ (lower right). ................. 43

2.12 A closer view of the band edge of CsSiI₃ (shown in Fig. 2.11). .... 44

2.13 QSGW band structure with SO of CsPbI₃ (left) and MAPbI₃ (right). 46
3.1 The real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\alpha$-CsSnI$_3$ (top), $\alpha$-CsSnBr$_3$ (middle) and $\alpha$-CsSnCl$_3$ (bottom). ......................... 72

3.2 The real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\beta$-CsSnI$_3$ when non-analyticity is applied in the $x$- or $y$-direction ($E_u$, top figure) and in the $z$-direction ($A_{2u}$, bottom figure). Please note that we omit the soft $E_u$ mode. ................................. 76

3.3 The real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\beta$-CsSnBr$_3$ when non-analyticity is applied in the $x$- or $y$-direction ($E_u$, top figure) and in the $z$-direction ($A_{2u}$, bottom figure). Please note that we omit the soft $E_u$ mode. ................................. 77

3.4 The displacement pattern of the soft phonon $E_u^1$ in $\beta$-CsSnI$_3$. The green spheres are Cs atoms, the grey ones are Sn atoms, and the purple ones are I atoms. The displacements of Cs atoms are represented by green arrows, while the displacements of I atoms are represented by purple arrows. ........................................ 78

3.5 Predicted Raman spectra of $\beta$-CsSnBr$_3$ (red line) and $\beta$-CsSnI$_3$ (blue line) in the $\bar{\varepsilon}(x,x)z$ configuration. In each spectrum, the lower frequency mode is the $A_{1g}$ mode with stronger intensity while the higher frequency mode is $B_{1g}$ modes with weaker intensity. Two $A_{1g}$ peaks in two materials are scaled to equalize intensity. .................... 79

3.6 Figures, from top to bottom, show the real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\gamma$-CsSnI$_3$ in the $x$-direction ($B_{3u}$), $y$-direction ($B_{2u}$), and $z$-direction ($B_{1u}$), respectively. ............................. 83
3.7 Figures, from top to bottom, show the real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $Y$-CsSnI$_3$ in the x-direction ($B_{3u}$), y-direction ($B_{2u}$), and z-direction ($B_{1u}$), respectively.

3.8 The upper figure shows the simulated Raman spectra of $\gamma$-CsSnI$_3$, while the lower one shows the simulated Raman spectra of $Y$-CsSnI$_3$. The different tensor components are scaled by different factors so as to normalize their strongest peak.

4.1 Crystal structure of $M$-CsSnCl$_3$ in a unit cell. The large blue spheres are Cs atoms, the intermediate size green ones are Sn atoms, and the small red ones are Cl atoms. The red horizontal arrow is in the $a_1$ direction, the green one (vertical in top two figures, and out of page in bottom one) is in the $a_2$ direction, and the blue one (out of page in top two and vertical down in bottom one) is in the $a_3$ direction. The top figure shows only the shortest Sn-Cl bonds highlighting the Sn-Cl tetrahedral units, while the lower figure includes the longer Sn-Cl bonds so as to show the distorted octahedral environment, indicating edge-sharing octahedra. The bottom picture is a projection along $a_2$.

4.2 Figures, from top to bottom, show the real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $B_u(x)$, $B_u(y)$, and $A_u$ mode, respectively, in $M$-CsSnCl$_3$. 
4.3 Upper figure shows the displacement patterns of $B_u^6$(TO) mode, at 93 cm$^{-1}$, without non-analyticity. The lower figure shows the displacement pattern of the mode at 229 cm$^{-1}$ when the non-analyticity is in the $y$ direction. The large blue spheres are Cs atoms, the medium green ones are Sn atoms, and the small red ones are Cl atoms. The red arrow is in the $a_1$ direction, the green one is in the $a_2$ direction, and the blue one is in the $a_3$ direction.

4.4 Upper figure shows the angular dependence of each $B_u^i$(LO) mode, where $i=1$ to 13 from low to high frequency. The abscissa $\theta$ is the azimuthal angle measured from the $x$-axis. The lower figure shows the angular dependence of the static dielectric constant $\varepsilon_0$, the high-frequency dielectric constant $\varepsilon_\infty$, and $\prod_i \left( \frac{\omega_{Li}}{\omega_{Ti}} \right)^2$.

4.5 This figure shows the meaning of mode crossing. What we mean, for example, is that the eigenvector of mode $B_u^{10}$ on the left of the apparent crossing (say for 30 degrees) is closer to that of mode $B_u^{11}$ on the right of the crossing (say for 60 degrees) and vice versa.

4.6 Simulated Raman spectra for $M$-CsSnCl$_3$. The different tensor components are scaled by different factors so as to normalize their strongest peak.

4.7 Digitized plot of the experimental Raman spectra from Kuok et al. [2; 3; 4]. Note the sharpness of spectrum 2 is mostly due to the low temperature (10K).

4.8 Displacement patterns for modes $B_g^1, A_g^1$ and $A_g^2$ from top to bottom. Note the different orientation of the axes.

4.9 Comparison of calculated (cal.) $A_g$(yy) spectrum with experimental (exp.) polarized Raman spectrum from Kuok [3].

4.10 Simulated $B_u^{LO}$ spectrum compared to experimental spectra 2 and 3.
4.11 Simulated forbidden LO mode contribution to the Raman spectrum compared with experimental spectrum 1 (dashed), 2 (solid) and 3 (dotted) where the numbering corresponds to Fig. 4.7 ...

5.1 Phonon band structure with phonon DOS of $\alpha$-CsSnI$_3$ (upper left), $\beta$-CsSnI$_3$ (upper right), $\gamma$-CsSnI$_3$ (lower left) and Y-CsSnI$_3$ (lower right). ...

5.2 Phonon band structure with phonon DOS of $\alpha$-CsSnBr$_3$ (top), $\beta$-CsSnBr$_3$ (middle), and (predict) $\gamma$-CsSnBr$_3$ (bottom)....

5.3 Phonon band structure with phonon DOS of $\alpha$-CsSnCl$_3$ (upper) and $M$-CsSnCl$_3$ (lower)....

5.4 From left to right shows the displacement patterns of soft phonon mode $M_2^+$, $R_a$, $R_b$, and $R_c$, or $R_{25}$, in the cubic phase, respectively. The green spheres are Cs atoms located at the corners of cubic unit cells, the gray ones are Sn atoms located at the center of unit cells, and the purple ones are X, X=I, Br, or Cl, located at the surface centers of unit cells. The displacements are represented by gray arrows. ...

5.5 The displacement pattern of the soft phonon mode at the $k$-point $Z$ in the $\beta$-CsSnI$_3$. The green spheres are Cs atoms, the grey ones are Sn atoms, and the purple ones are I atoms. The displacements of Cs atoms are represented by green arrows, while the displacements of I atoms are represented by purple arrows. For clarity, we only show the displacements of I atoms in the central octahedron. The phonon mode is named $Z_5^-$. ...

5.6 The proposed crystal structure of CsSnBr$_3$ in the $D_4^2$ space group No. 90. The $\Gamma_1^-$ deformation distorts the octahedra compared to the $\beta$-phase. The green spheres are Cs atoms, the grey ones are Sn atoms, and the brown ones are Br atoms. ...
Acknowledgements

I would like to express the greatest gratitude to the people who have helped and supported me through my Ph.D. journey. I am thankful to Prof. Walter R. L. Lambrecht, my research advisor, for his guidance over my years at Case Western Reserve University. I would also like to thank the members of my committee, Prof. Philip L. Taylor, Prof. Kathleen Kash, and Prof. Clemens Burda, for their precious time and thoughtful suggestions. I wish to thank my colleagues and the staff at Case Western Reserve University for their help with so many little things. I also owe many thanks to my friends in Cleveland for their friendship during my time in the US. Finally, I wish to thank my family, including my parents, my wife, and my son for supporting me while I lived and studied abroad. Without you I could not be receiving my Ph.D.
Electronic Band Structure, Phonons and Exciton Binding Energies of Halide Perovskites CsSnX$_3$ with X=Cl, Br, I

Abstract

by

LING-YI HUANG

Halide perovskites (ABX$_3$) have attracted a large amount of attention since 2009 due to their important applications in solar cells. Though high power conversion efficiencies have been achieved, the underlying reasons for the success are not fully understood. Moreover, some important issues have not yet been resolved, mainly stability issues resulting from phase transitions in halide perovskites. In this thesis, we used the Full-Potential Linear Muffin-Tin Orbital method with Quasiparticle Self-consistent $GW$ (QSGW) to study the electronic band structures and related properties in one family of halide perovskites: CsSnX$_3$ with X=I, Br, and Cl. We also used density functional perturbation theory to perform phonon calculations for these materials. Our first-principles calculations are compared with experimental data. The main purpose of this study is to understand the fundamental physical properties in these materials and the underlying reasons for the success of these materials in solar cells, and eventually to elucidate information about phase transitions in these materials with the goal of resolving the stability issues.

Our QSGW band gaps are in good agreement with experimental gaps. An extremely interesting finding is that the halide perovskites have an “inverted” band structure; i.e. in contrast to most conventional semiconductors, their valence band has a strong Sn-s like character (antibondingly mixed with X-p) while their conduction band has Sn-p character. The unusual characteristic explains (i) the strong luminescence, (ii) the relatively weak band gap dependence on anions, (iii) why the
valence band maximum occurs at the $\mathbf{R}$-point, and (iv) the anomalous dependence of the band gap on lattice constants. We also find that the small effective hole mass results in high hole mobility. The free-exciton binding energy was estimated to be of the order of 0.1 meV for CsSnI$_3$. Strong LO–TO splittings and large static dielectric constants are found. LO phonons contribute to infrared absorption spectra of $\alpha$-CsSnBr$_3$ and $\alpha$-CsSnCl$_3$ and Raman spectra of $\gamma$-CsSnI$_3$ and $M$-CsSnCl$_3$. Strong LO–plasmon couplings are expected in these materials because the plasmon frequencies are comparable to the LO phonon frequencies. We find soft phonons, which are phonons with imaginary phonon frequencies, in cubic and tetragonal phases, but not in orthorhombic and monoclinic phases. The phase transitions from the $\alpha$ phase to the $\beta$ phase and then to the $\gamma$ phase can be summarized, in terms of space groups and soft phonons, as follows

\[ O_{1h} \xrightarrow{M_2^+} D_{4h}^5 \xrightarrow{Z_5^-} D_{2h}^{16}, \]

where the $M_2^+$ and $Z_5^-$ are the soft phonons in the cubic and tetragonal phases, respectively. The displacement pattern of the $M_2^+$ mode is shown in Fig. 5.4 while the displacement pattern of the $Z_5^-$ mode is shown in Figure 5.5. The notation $M_2^+$ means that the phonon at k-point $M$ of the cubic Brillouin zone belonging to the irreducible representation 2+ of the point group of that k-point, $D_{4h}$, leads to the transformation of the crystal to a new one with the $D_{4h}^5$ subgroup as spacegroup and similar for the second step.
Chapter 1

Introduction

1.1 Motivation

Halide perovskites are of interest because their perovskite structure gives them many unusual properties. Fig. 1.1 shows the crystal structure of a perfect cubic perovskite $ABX_3$. The A cations are represented by the green spheres at the corners of the unit cell, the B cation is represented by the grey sphere at the body center, and the X anions are represented by purple spheres at the face centers. Note that the B cation and the six nearest X anions form a octahedron (shown in the Figure 1.1, highlighted in grey). This structure is common in many complex oxides for which interesting properties have been found, including phase transitions, ferroelectricity, High-$T_c$ superconductivity, colossal magnetoresistance, metal insulator transitions, multiferroic properties, etc.

Another point of interest is that halide perovskites have promising applications in solar cells [5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16; 17; 18]. Figure 1.2 shows two typical structures of halide perovskite solar cells based on the dye-sensitized solar cell architecture, also known as the Grätzel’s cell. In both cases, halide perovskites act as light absorber in which electrons ($e$) and holes ($h$) are generated after incidence of
sunlight (with photon energy $h\nu$). When a load is placed across the cell as a whole, holes go to the p-type hole transporting material (HTM) while electrons go to the n-type thin film (TF) directly and/or via the mesoporous (MP) TiO$_2$ layer. The electrons lose energy while moving through the external circuit, and then flow back into the p-type HTM where they can once again re-combine with holes. In this way, sunlight creates an electrical current. Compared to traditional silicon solar cells which require high temperature (about 1300 Kelvin), vacuum, and high-level cleanrooms in processing, halide perovskite solar cells are much easier to manufacture. Two main methods are used to produce halide perovskite solar cells; one is solution processing, which is extremely simple (Fig. 1.2, left) and the other is vapor deposition, which requires temperatures of only 500 Kelvin during processing (Fig. 1.2, right).

Although halide perovskites have been known for several decades, the halide perovskite solar cell was first developed by Miyasaka et al. [19] in 2009. They used A=CH$_3$NH$_3$ (methylammonium, or briefly MA), B=Pb, and X=Br and I. The power conversion efficiency (PCE) of their solar cell was only about 3.8% and the solar cell was stable for only a few minutes due to a corrosive liquid electrolyte. Two year later, Park et al. [20] slightly increased the PCE to 6.5%. At the time of their development, because of the low PCE and extreme instability, there was little interest in using halide perovskites for solar cell applications. However, because halide perovskite solar cells were extremely cheap to produce and simple to manufacture,
a few research groups continued to focus their attentions on the halide perovskites. Then three important breakthroughs came in 2012 which triggered a renewed interest in halide perovskite solar cell research. First, in order to solve the stability issue resulting from the use of organic liquid electrolytes, Kanatzidis et al. [5] used A=Cs, B=Pb, and X=I in their solar cell design and achieved a more than 10% (more precisely 10.2%) PCE. Second, in August of the same year (2012), Park’s group in South Korea cooperated with Grätzel’s group in Switzerland and reported 9.7% PCE with 500 hours of confirmed stability in CH$_3$NH$_3$PbI$_3$ [7]. Third, in October 2012, Snaith and Miyasaka published a paper [9] showing that halide perovskite was stable if put in contact with a solid-state hole transporter and showed a power conversion efficiency of 10.9%. They also replaced the conventional TiO$_2$ layer with Al$_2$O$_3$ to show that TiO$_2$ was not necessary for electron transport. This work and later works [10; 11; 21; 22; 23] suggest that halide perovskite itself is a good electron and hole transporter and, therefore, a planar thin film halide perovskite solar cell can be realized. Approximately 15% PCE was achieved in 2013 in Grätzel’s group [24] by using mesoscopic/sensitized architecture and in Snaith’s group [12] by using
planar architecture. In 2014, Yang et al. [25] claimed about 19.3% PCE in their planar thin-film-architecture-based solar cell, and the National Renewable Energy Laboratory (NREL) confirmed a non-stabilized efficiency of 20.1% from researchers at the Korea Research Institute of Chemical Technology (KRICT). From 2009 to 2014, the PCE of halide perovskite solar cells soared from only 3.8% to above 20%, making halide perovskite solar cells currently the fastest advancing solar technology. Their high efficiencies and easy processing, hence low costs, make halide perovskite solar cells extremely attractive for commercialization. Actually, Oxford Photovoltaics Limited (Oxford PV, Professor Henry Snaith is a co-founder) plans to commercialize perovskite solar cells before 2017.

Although halide perovskites have had great success in solar cell applications, the underlying reasons are not well understood. Some interesting reported properties are not understood either. For example, Kanatzidis et al. [6] found that CsSnI$_3$ shows strong photoluminescence and is a high-hole-mobility semiconductor. Inspired by this paper, we decided to first focus our attention on the more fundamental case CsSnX$_3$ with X=I, Br, and Cl (compared to methylammonium or formamidinium, HC(NH$_2$)$_2$, or other such halide perovskites). Because the existence of methylammonium or formamidinium increases the degree of freedom compared to the A=Cs case, one would expect the complexity to increase as well. For example, one would expect that there are internal phonon modes of methylammonium or formamidinium which will not exist in the A=Cs case. Upon discovery of the basic properties of CsSnX$_3$, we can understand more about the methylammonium and formamidinium halide perovskites by comparison. For this reason, although we did some calculations on methylammonium halide perovskites, this thesis will focus on CsSnX$_3$, where X can be I, Br, and Cl.

Recently, a few of the unusual properties of CsSnI$_3$ have attracted interest for solar cell applications. First, the strong luminescence at a band gap close to that of
Si and strong absorption at shorter wave lengths (see Fig. 5 in Ref. [6] and Fig. 5 in Ref. [26]) make CsSnI$_3$ attractive as a solar luminescent concentrator material [27], or as solar cell absorber [28]. Second, it was recently shown [5] that its high hole mobility [6] makes it an excellent all solid-state replacement for the electrolyte in a dye sensitized Grätzel type solar cell with TiO$_2$. It was found that the CsSnI$_3$ itself strongly contributes to the optical absorption, although the overall performance was still aided by the organic dyes.

However, many of its properties are still rather poorly understood. For instance, it is presently not clear whether the strong luminescence is intrinsic, i.e. due to free excitons, or due to defect bound excitons. The effects of crystal structure on the luminescence strength are poorly understood and are crucial for the indicated solar cell concentrator approach. Until recently, [6] progress in this field was hampered by the difficulty in obtaining phase pure CsSnI$_3$ material and the rapid conversion to the yellow phase of CsSnI$_3$ in air. The electrical conductivity is only poorly understood. Although a high hole mobility of $\sim 585 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was reported, a relatively low carrier concentration on the order of $10^{17} \text{ cm}^{-3}$ and a metallic like decreasing conductivity with temperature were obtained by Ref. [6].

Besides the few applications presently under investigation, other possibilities for halide perovskites have not yet been fully explored. In view of close structural similarities with oxide perovskites, the halide perovskites may have interesting piezoelectric or even ferroelectric properties in the lower symmetry phases. The relatively heavy ions combined with strong ionic bonding lead to low frequency modes [29; 30], which may result in a large phonon enhancement of the dielectric constant. Recently [31] third order enhanced Raman spectra were reported for CsSnI$_3$. Heavy ions like Cs also make these materials suitable for capturing $\gamma$-rays and, combined with their strong luminescence, may be excellent scintillation materials for detectors. This idea was recently proposed by Sing [32] for the closely related Tl containing compounds,
TlGeI₃, TlSnI₃ and TlPbI₃.

1.2 Phase transitions

Like the more well studied oxide perovskites, almost all halide perovskites undergo structural phase transitions with temperature changes. Figure 1.3 shows the temperature dependence of the well known phase transitions in CsSnX₃ [6; 33; 34; 35; 36]. In this figure, the c-axis points out of the page, the large green spheres are Cs atoms, and the small purple spheres can be I, Br, or Cl. The small bright green spheres are Cl atoms in the top right figure. Sn atoms are in the center of octahedrons highlighted by solid grey quadrangles in the plane. For CsSnI₃, at high temperatures, above 432 K, CsSnI₃ is in the cubic phase, or the so-called alpha (α) phase (Figure 1.3, top left). When the temperature is cooled down to about 432 K, CsSnI₃ undergoes a phase transition to the tetragonal phase, or the so-called beta (β) phase (Figure 1.3, middle left). At even lower temperatures, below 352 K, CsSnI₃ goes from the tetragonal phase to an orthorhombic phase, called gamma (γ) phase (Figure 1.3, bottom left). Then, the exposure of this gamma phase CsSnI₃ in air for several hours leads to another orthorhombic phase, called yellow (Y) phase (Figure 1.3, bottom right). In the X=Br case, CsSnBr₃ undergoes a phase transition from the cubic (α) phase to the tetragonal (β) phase when at temperatures lower than 292 K. In the X=Cl case, CsSnCl₃ goes from the cubic (α) phase to the monoclinic (M) phase (Figure 1.3, top right) below 390 K.

More detailed crystal structures of α-CsSnI₃ (left), β-CsSnI₃ (middle), and γ-CsSnI₃ (right) are shown in Figure 1.4. Again, large green spheres are Cs atoms, small purple spheres are I atoms, and small grey spheres are Sn atoms. Each octahedron formed by a Sn inside six I atoms is highlighted in grey. In the top figures, the c-axis points out of page, while the c-axis points upward in the bottom figures. As one
Figure 1.3: Temperature dependent phase transitions in CsSnX₃.
can see, the $\beta$ phase results from a rotation of octahedrons about the $c$-axis in the $\alpha$ phase. In the $\gamma$ phase, the octahedrons rotate or tilt about the axis in the $xy$ plane and the Cs atoms are also displaced.

From Figure 1.3 and Figure 1.4, we can see that the structural changes that occur between the $\alpha$ phase to the $\beta$ phase and then to the $\gamma$ phase only involve rotations and distortions of octahedrons; all octahedrons are corner shared. However, the yellow phase and the monoclinic phase are quite different from $\alpha$, $\beta$, and $\gamma$ phases because they have edge-sharing parts which imply that rebonding is required.

Phase transitions occur not only in CsSnX$_3$ but also in other halide perovskites, including MAPbX$_3$. The biggest challenge for halide perovskite solar cells is the instability resulting from phase transitions. According to our electronic band-structure
calculations (Chapter 2) and experimental data, $\gamma$-CsSnI$_3$ has band gap about 1.3 eV, which is suitable for photovoltaic applications. However, as mentioned before, CsSnI$_3$ has an end stage transformation to the yellow phase (in air) whose band gap is much larger than that of the $\gamma$ phase, which means that the yellow phase is not suitable for solar cell application. Avoiding phase transitions that lead to degradation of PCE is of prime importance in halide perovskite solar cell designs. Therefore, understanding all possible phase transitions and structures in halide perovskites is necessary to achieve long-term stability in solar cells. To this end, it is important to understand the phonons. Therefore, we present our phonon calculations in Chapters 3, 4, and 5. Because zone center phonons can be directly measured by infrared (IR) and Raman spectroscopy and are easier to calculate, compared to the full phonon band structure, we first present zone center phonon calculations in Chapters 3 and 4. We initially tried to search for all possible IR and Raman experimental data for CsSnX$_3$ in different phases, but, unfortunately, only the IR frequencies for $\alpha$-CsSnBr$_3$ and $\alpha$-CsSnCl$_3$ and the Raman spectra for $M$-CsSnCl$_3$ are available. So, in Chapter 3, we present our zone center phonon calculations for CsSnX$_3$ in all phases except for $M$-CsSnCl$_3$ and compare our calculated results with the available IR experimental data for $\alpha$-CsSnBr$_3$ and $\alpha$-CsSnCl$_3$. For $M$-CsSnCl$_3$, we present our zone center phonon calculations in Chapter 4 and compare them with available experimental Raman spectra. In order to understand stability in each (separate) phase and to study the relationship between phase transitions and soft phonons, we need to calculate the full phonon band structure for all phases. Thus, we present our full phonon band structure calculations in Chapter 5.
Chapter 2

Electronic band structure

2.1 Introduction

In the perovskite structure, see Fig. 1.1, the SnX$_6$ octahedra corner-sharing and thus each halogen ion counts for 1/2, resulting in the formula CsSnX$_3$. The cubic structure can be understood as a CsCl packing of large Cs$^+$ ions and SnX$_3^{-1}$ units. It means that the Sn in the compounds is divalent. The bonding thus can be viewed as strongly ionic. Nevertheless the band gaps are relatively small, of order 1–3 eV, compared to for example Cs halides, and most surprisingly only relatively small changes occur especially from one halide to the next, especially in the Br to the I case (1.38 to 1.01 eV). As we will show in this chapter, a number of its unusual properties result from the intra-cluster SnI$_6$ bonding. Interestingly, Cs in the structure can be replaced by other large monovalent ions, for example, Rb, Tl, or even organic radicals [35], such as methylammonium CH$_3$NH$_3^+$ and formamidinium NH$_2$CH=NH$_2^+$.

The band structures have been studied theoretically in a few previous papers [37; 38; 39; 40]. These papers focused mostly on the changes in band structure with crystal structure and because they were based on density functional theory (DFT) in the local density approximation (LDA) strongly underestimated the gaps. In the early
literature, there is even significant discussion on whether they are semiconductors or semimetals \[37; 38\]. Only in the most recent study \[6\], the screened exchange method was used which gave larger gaps for CsSnI\(_3\) but still it obtained a smaller gap than experimental results for the black phase.

Here we present a study of the electronic band structure using the quasiparticle-self-consistent \(GW\) method (QSGW) \[41; 42\]. We first present the basic band structures in the cubic perovskite structure. Analyzing the atomic orbital character of the bands provides immediate insights into some of the questions mentioned above. These are all explained in terms of the intra-SnI\(_6\) cluster nature of the band gap. The changes seen with crystal structures are found to be in fair agreement with previous theory work. However, it is only after adding the QSGW quasiparticle corrections that we can make a quantitative comparison of the gaps with experimental results. Next, we address another anomaly in the exciton binding energy \[43\]. We will show that a large exciton binding energy (on the order of 12 meV) is indeed obtained if the electron-hole interaction is only screened by the high-frequency dielectric constant. However, we find that the phonons increase the dielectric constant by a factor 9.9 and hence lead to two orders of magnitude smaller exciton binding energy if their contribution to the screening is included. The analysis of the previous experimental data is then revised.

2.2 Computational method

The starting point for our band structure calculations is the local density approximation (LDA) of the density functional theory (DFT). Because the LDA underestimates band gaps, we next use the quasiparticle self-consistent (QS) \(GW\) method to recalculate the band structures more accurately. The full-potential linearized muffin-tin orbital method (FP-LMTO) with implementations of QSGW was used for the band
structure calculations. We will introduce DFT, LDA (and GGA), (QS)GW, and FP-LMTO method in this section. A detail method for calculating zone center phonons in cubic CsSnX₃ is presented in the next chapter.

2.2.1 Density Functional Theory (DFT)

Instead of solving the formidable many particles Schrödinger equation for $N$ electrons in a solid with the Hamiltonian \[44; 45; 46\]

\[
H_{el} = -\frac{1}{2} \sum_i^N \nabla_i^2 + \frac{1}{2} \sum_{i,j}^N \frac{1}{|r_i - r_j|} + \sum_i^N V_{ext}(r_i) \tag{2.1}
\]

where, based on the Born-Oppenheimer approximation, we omit the Hamiltonian for nuclear parts and describe the Coulomb interaction between a nuclei and an electron by an external potential $V_{ext}(r_i)$ seen by the electron at position $r_i$, the density functional theory (DFT) \[45; 46\] shows that it is adequate for solving the following one-particle Schrödinger equation, the so called Kohn-Sham equation (here we use $h=1, m=1,$ and $e=1$),

\[
\left\{ -\frac{1}{2} \nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}[n(r)] \right\} \psi_i(r) = \epsilon_i \psi_i(r), \tag{2.2}
\]

where

\[
V_H(r) = \int d\mathbf{r}' \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|} \tag{2.3}
\]

with the density of electrons in the solid

\[
n(r) = \sum_{i=1}^N |\psi_i(r)|^2, \tag{2.4}
\]
and

\[ V_{xc}[n(r)] = \frac{\delta E_{xc}}{\delta n(r)} = \frac{\partial (n \epsilon_{xc}[n])}{\partial n} \]  \hspace{1cm} (2.5) \]

is the exchange and correlation potential with \( \epsilon_{xc} \) being the exchange and correlation energy per electron and the (total) exchange and correlation energy

\[ E_{xc}[n] = \int \text{d}r \ n(r) \ \epsilon_{xc}[n(r)] ; \]  \hspace{1cm} (2.6) \]

we will discuss the physical meaning of the exchange-correlation energy later. The DFT was first proposed by Kohn and Sham and is based on two theorems proven by Hohenberg and Kohn: (i) \( V_{\text{ext}}(r) \) is a unique function of \( n(r) \) (apart from a trivial additive constant), and vice versa and (ii) the ground state energy \( E \) can be obtained by minimizing the energy over all possible densities. Therefore, the Kohn-Sham equation can be solved self-consistently; with an assumed \( n(r) \), Eq. (2.2) gives us new \( n(r) \). The (total) energy is given by

\[ E = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2} \int \int \text{d}r \text{d}r' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n] - \int \text{d}r \ n(r) \ V_{xc}[n(r)]. \]  \hspace{1cm} (2.7) \]

### 2.2.2 Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA)

An important issue that needs to be addressed in DFT calculations is that the exact exchange-correlation functional is unknown; how to choose an approximated exchange-correlation functional becomes a crucial factor that influences the accuracy of DFT calculations. There are two main approximations: (i) the local density approximation (LDA) and (ii) the generalized gradient approximation (GGA). In LDA, \( \epsilon_{xc} \) in Eq. (2.9) depends only on the density [47], while in GGA, \( \epsilon_{xc} \) depends
both on the density and its gradient \cite{48}; more precisely

\[ E^{LDA}_{xc} = \int d\mathbf{r} \, n(\mathbf{r}) \, \epsilon_{xc}(n(\mathbf{r})), \quad (2.8) \]

and

\[ E^{GGA}_{xc} = \int d\mathbf{r} \, n(\mathbf{r}) \, \epsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|). \quad (2.9) \]

The explicit forms of the LDA and GGA functionals are derived from the assumption that the electron gas is homogeneous for LDA and slowly varying for GGA.

### 2.2.3 GW approximation

Until this point, we have not discussed the physical meaning of exchange-correlation energy (potential). Considering putting an electron in an electron gas, the electrons already in the gas try to avoid the new electron via electron repulsion and the Pauli exclusion principle. The Pauli exclusion principle requires the antisymmetry of the many-electron wave functions and contributes to the exchange energy. The electron repulsion between electrons gives rise to the correlation energy. However, the exchange-correlation energy (potential) terms in LDA and GGA do not involve any dynamic excitations, so both LDA and GGA are only suitable to study ground state properties. In the DFT, one focuses on the mean-field average of the exchange-correlation energy resulting from the interactions as it enters the total energy of the system.

To deal with the excitations in condensed matter, we need another approach, the so-called many-body perturbation theory. The central quantity in this theory is \( G(t_2, \mathbf{r}_2; t_1, \mathbf{r}_1) \), the electron propagator. It gives the probability amplitude to create an electron at position \( \mathbf{r}_1 \) at time \( t_1 \) from the ground state, subsequently traveling to another position \( \mathbf{r}_2 \) at time \( t_2 \) where it is annihilated. Its Fourier transform
from time to energy describes a spectral function with peaks at the quasiparticle energies. These are the excitation energies for an electron which we conventionally call “the band structure”. To be more precise, the above describes the motion of an added electron to the first available empty state, as would be measured in inverse photoemission. One may also conversely first annihilate an electron and then recreate it, or in other words, describe the motion of a hole in the occupied bands. The effects from the interaction of the electron or hole with the other electrons as it propagates are embodied in the so-called self-energy operator, which describes all interactions beyond the Hartree potential. Hedin\cite{49} proposed a method to calculate the self-energy in terms of the screened Coulomb interaction $\mathcal{W}$. In his $GW$ approximation, the product of $G$ and $\mathcal{W}$ is the electron self-energy, usually denoted by $\Sigma$. The Green’s function or propagator can be written in terms of a quasiparticle wave function. The quasiparticle excitation energies and wavefunction can then be obtained from

\[
\begin{align}
-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) \phi_i(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_i^{GW}) \phi_i(\mathbf{r}') &= \epsilon_i^{GW} \phi_i(\mathbf{r}). \tag{2.10}
\end{align}
\]

This equation closely resembles the Kohn-Sham equation of DFT but this is deceiving. At first sight it appears that the exchange correlation potential is replaced by a non-local and energy dependent self-energy operator term. However, the meaning of both equations is different. The Kohn-Sham equation merely describes the energies of fictitious non-interacting particles in an effective potential which happen to have the same density as the real interacting electrons in the external potential and is used only as an intermediate step to obtain the ground state total energy. On the other hand, Eq. \(2.10\) describes the actual excitation energies that would be probed by one-particle spectroscopies, such as photo-emission and inverse photo-emission.

Nonetheless, the close resemblance between both equations is exploited in practice to solve Eq. \(2.10\). It is usually solved by perturbation theory starting from the
Kohn-Sham equation. In that sense, the electron self-energy provides a shift of the Kohn-Sham one-electron eigenvalues as well as a lifetime through its imaginary part. Assuming the wavefunctions of Eq. (2.10) are the same as those in Eq. (2.2), the eigenenergy of Eq. (2.10) is

$$\epsilon_{GW}^i = \epsilon_{LDA}^i + \langle \psi_{LDA}^i | \left[ \Sigma (r, r', \epsilon_{GW}^i) - V_{LDA}^{xc}(r) \right] | \psi_{LDA}^i \rangle$$  \hspace{1cm} (2.11)

Expanding the $\Sigma$ around $\epsilon_{LDA}^i$, we have

$$\epsilon_{GW}^i = \epsilon_{LDA}^i + Z_i \langle \psi_{LDA}^i | \left[ \Sigma (r, r', \epsilon_{LDA}^i) - V_{LDA}^{xc}(r) \right] | \psi_{LDA}^i \rangle$$  \hspace{1cm} (2.12)

where $Z_i = \left( 1 - \langle \psi_{LDA}^i | \frac{\partial}{\partial \epsilon} \Sigma (r, r', \epsilon) \big|_{\epsilon = \epsilon_{LDA}^i} | \psi_{LDA}^i \rangle \right)^{-1}$ is the renormalization factor. However, as will be discussed in the next section, this means that the result still depends on the starting point. In the so-called quasiparticle self-consistent $GW$ method, this problem is addressed.

Now let us slightly extensively talk about the electron self-energy, $\Sigma$, and the $GW$ method. Hedin [49] used the one-electron Green’s function and functional derivatives to derive a set of equations for the electron self-energy. The results can be represented by the Feynman diagrams shown in Fig. 2.1. Hedin’s approach is based on functional derivatives of various quantities vs. the Green’s function. The central idea is to expand the relevant quantities such as the Green’s function, self-energy, etc. in the screened Coulomb interaction $W$, rather than the bare Coulomb interaction. Thus, this embodies the key physical concept of screening, which weakens the interactions. The functional derivatives approach is equivalent to formally summing various infinite series of perturbation terms. Manipulating the many-body perturbation equations, Hedin came up with a set of self-consistent equations between the one-electron Green’s function $G$, the self-energy $\Sigma$, the polarization $\Pi$, defining the
screening, which in turn defines the screened Coulomb interaction $W$, and a so-called vertex function, which is defined by $\Gamma = -\delta G^{-1}(12)/\delta V(3)$. The Hedin equations (using $\hbar=1$, and $1 \equiv (t_1, r_1, \sigma_1)$, where $\sigma$ is spin index) are:

\begin{align}
\Sigma(1, 2) &= i \int d(34) G(1, 4) W(1, 3) \Gamma(4, 2, 3), \quad (2.13) \\
G(1, 2) &= G_0(1, 2) + \int d(34) G_0(1, 3) \Sigma(3, 4) G(4, 2), \quad (2.14) \\
W(1, 2) &= v(1, 2) + \int d(34) v(1, 3) \Pi(3, 4) W(4, 2), \quad (2.15) \\
\Gamma(1, 2, 3) &= \delta(1, 2) \delta(1, 3) + i \int d(45) W(1, 2) G(1, 4) G(5, 2) \Gamma(4, 5, 3) + \ldots (2.16) \\
\Pi(1, 2) &= -i \int d(34) G(1, 3) \Gamma(3, 4, 2) G(4, 1), \quad (2.17)
\end{align}

The Hedin equations can be summarized by several Feynman diagram equations shown in Fig. 2.1. In the Eq. (2.13) (Fig. 2.1, first diagram), apart from the already mentioned $G$ and $W$, the electron vertex function $\Gamma$ is also included in the more general form of the electron self-energy. In the Eq. (2.14) (Fig. 2.1, second diagram), $G_0$ represents the electron propagator without any interaction, while the second term includes the possibility that between $(t_3, r_3)$ and $(t_4, r_4)$ the electron experiences interactions with the other electrons in the system, via the screened Coulomb interaction, which is represented by the heavy wavy line. In an analogy with standard quantum electrodynamics, this can be thought of as the electron becomes an electron plus a photon. The “photon” here is the non-retarded, but screened, Coulomb
interaction $W$. The same physical meaning applies to the photon propagator, in the Eq. (2.15) (Fig. 2.1, third diagram), $v$ represents the photon propagator without any interaction (bare Coulomb interaction), while the second term includes the possibility that the photon can become two electrons between $(t_3, \mathbf{r}_3)$ and $(t_4, \mathbf{r}_4)$, which is called the photon self energy represented in the Eq. (2.17) and Fig. 2.1, fifth diagram). This has the meaning of the polarization operator here. The first term in the right-hand side of the fourth diagram represents no vertex correction, which is the first term in the Eq. (2.16).

The $GW$ approximation then becomes a first approximation to this set of equations, in which we assume $\Gamma (1, 2, 3) = \delta (1, 2) \delta (1, 3)$ only; then we have

$$\Sigma (1, 2) = iG (1, 2) W (1, 2), \quad (2.18)$$

$$\Pi (1, 2) = -iG (1, 2) G (2, 1). \quad (2.19)$$

Furthermore, Eq. (2.15) can be written as (the so-called random phase approximation, RPA)

$$W = (1 - v\Pi)^{-1}v \equiv \epsilon^{-1}v. \quad (2.20)$$

where $\epsilon$ is the (screening) dielectric function; hence, the physical meaning of $\Pi$ can also be interpreted as the polarization. Eqs. (2.18), (2.19), and (2.20) are the central/main equations used in our $GW$ calculations, and note that $\Sigma$ is a function(al) of $G$ in the current approximation. Even in the simplest approximation, solving the $GW$ equations is time consuming and usually done by perturbation theory as discussed earlier.
Figure 2.1: The Feynman diagrams, from top to bottom, represent the electron self-energy, (exact) electron propagator, (exact) photon propagator, electron vertex function, and photon self-energy, respectively. These five diagrams represent the Hedin's equations.
2.2.4 Quasiparticle Self-consistent (QS) GW approximation

From Eq. (2.11), we can see that the accuracy of GW calculations depends on the starting point. The so-called Quasiparticle Self-consistent GW (QSGW) formalism was proposed by Van Schilfgaarde et al. [41; 50] to rectify this problem. The starting point for the GW approach is defined in terms of a zero-th order Hamiltonian, which is usually taken to be the DFT Kohn-Sham equation

\[ H^0 \psi_i \equiv \left( -\frac{\nabla^2}{2} + V_{\text{eff}} \right) \psi_i \equiv \left( -\frac{\nabla^2}{2} + V_{\text{ext}} + V_H + V_{xc} \right) \psi_i = \epsilon_i \psi_i. \]  

(2.21)

It provides the corresponding Green’s function \( G^0 \)

\[ G^0 = \frac{1}{\omega - H^0 \pm i\delta}. \]  

(2.22)

where, with small \( \delta \), the \( \pm \) sign depends on whether \( \omega > \mu \), or \( \omega < \mu \) with \( \mu \) the chemical potential or Fermi level. Once \( G^0 \) is determined, we can then calculate the electron self-energy and the following “Hamiltonian”

\[ H(\omega) = -\frac{\nabla^2}{2} + V_{\text{ext}} + V_H + \Sigma \left[ G^0(\omega) \right]. \]

(2.23)

This is the operator entering the quasiparticle equation Eq. (2.10). Because it is energy dependent and contains the complex \( \Sigma(\omega) \), it is actually a non-hermitian operator. This is solved in perturbation theory and will thus be the more accurate, the closer the \( H^0 \) is to \( H \). Using some suitable measure for what it means to be close, van Schilgaarde and Kotani, came up with with a prescription to obtain a new \( H^0 \) from the self-energy \( \Sigma \). The new \( H^0 \) is defined in terms of a non-local and energy
independent exchange-correlation potential $V_{xc}$ in the following way

$$V_{xc}^{QSGW} = \frac{1}{2} \sum_{i,j} |\psi_i\rangle\langle\psi_i| \left\{ \text{Re} \left[ \Sigma (\epsilon_i) \right] + \text{Re} \left[ \Sigma (\epsilon_j) \right] \right\} |\psi_j\rangle\langle\psi_j| \quad (2.24)$$

where $\text{Re}$ signifies the Hermitian part; $\psi_i$ and $\epsilon_i$ are eigenfunctions and eigenvalues in Eq. (2.21). Note that it simply takes the average of the off-diagonal elements of $\Sigma$ in this basis set evaluated at the two energies. Including these off-diagonal elements, however, is a significant step beyond Eq. (2.12). It allows the eigenstates of the original $H^0$ to become intermixed, so that the final solutions may be farther away from the DFT starting point of $H^0$. The new $H^0$ then defines a new $G^0$, which gives a new $\Sigma$, a new $V_{xc}^{QSGW}$ and the set of equations can be iterated to convergence. This ultimately makes the method independent of the starting point and the eigenvalues of the $H^0$ converge to those of the quasiparticle equation. Of course, the actual energy dependent self-energy $\Sigma(\omega)$ still contains additional information on the lifetime and possibly even a more complex spectral shape than a simple broadened quasiparticle peak. It may contain for example satellite structures. In this way, QSGW provides better accuracy than one-shot $GW$ and should not be dependent on the starting point. Van Schilfgaarde et al. demonstrated that, for most semiconductors, band gaps calculated by QSGW showed excellent agreement with experimental ones [41; 50; 42].

2.2.5 Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) method

The Muffin-Tin Orbital (MTO) method is one of two major methods used to solve the single-particle Schrödinger equation with periodic boundary condition. The other is pseudopotential plane wave method. In MTO method, space is divided into two
parts: (i) spheres around atomic sites, called muffin-tin spheres, and (ii) the interstitial region between spheres. Though, instead of using an approximated muffin-tin potential in usual MTO method, we use the real ”full potential” in the so-called Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) method, the basis function is constructed conceptually according to the geometrical separation and can be written as follows \cite{51, 52}

\[
\psi_i(r) = \mathcal{H}_i(r) + \sum_{R,l,m} \left[ \Phi_{ilm}(r-R) - \mathcal{H}_{ilm}(r-R) \right].
\] (2.25)

Where $\mathcal{H}$ is a smoothed Hankel function convoluted from Gaussians and standard Hankel functions that are originally solutions to the Schrödinger equation in the interstitial region and are called envelope functions; in practice, the smoothed Hankel function can be characterized by the function decay parameter $\kappa$ and its smoothing radius $R_{sm}$. The smoothed Hankel function in the first term in Eq. (2.25), $\mathcal{H}_i(r)$, is a smoothly varying function defined in the whole cell. In the muffin-tin sphere at $R$ with radius $S_R$, $\mathcal{H}_{ilm}(r-R)$ is the expansion of the smoothed Hankel function in spherical harmonics times radial functions. It is then “augmented”, which means it is replaced inside the sphere by $\sum_{l,m} \Phi_{ilm}(r-R)$, which is a linear combination of numerical solutions of the Schrödinger equation inside the sphere for the actual potential in that sphere. In the linear theory, a radial solution $\phi$ of the Schrödinger equation and its energy derivative, $\dot{\phi}$, are calculated for a given $R$ and $l$, and $\Phi_{ilm}(r-R)$ is constructed out of the linear combination which matches value and slope of $\mathcal{H}_{ilm}(r-R)$ at $S_R$. Note that the basis function shown in Eq. (2.25) is continuous and differentiable everywhere in all space. Having defined a suitable basis function set, expected to be quite complete because it is already constructed out of solutions of the Schrödinger equation, which are valid over a reasonably wide energy range inside each sphere and corresponding to the solutions for a flat potential in
between them, the Hankel functions, one then applies the usual variational method. This requires matrix elements of the Hamiltonian and the overlap matrix. The expectation value of an arbitrary operator $\hat{O}$ is given in the following form \[51; 52\]

$$
\langle \psi_i (r) | \hat{O} | \psi_j (r) \rangle = \int_{all \ space} dr \langle \mathcal{H}_i (r) | \hat{O} | \mathcal{H}_j (r) \rangle \\
+ \sum_{R,l,m,l',m'} \int_{r < S_R} dr \left[ \langle \Phi_{ilm} (r - R) | \hat{O} | \Phi_{j'l'm'} (r - R) \rangle - \langle \mathcal{H}_{ilm} (r - R) | \hat{O} | \mathcal{H}_{j'l'm'} (r - R) \rangle \right].
$$

The first term in Eq. (2.26) is evaluated through all space by direct summation over a mesh of points on which the functions are evaluated, while the second and the third terms, local terms, are integrated inside the muffin-tin spheres. The first and third terms are both related to the smoothed Hankel functions, which are characterized by two ($\kappa, R_{sm}$) and are slowly varying. The second term contains real full-potential inside muffin-tin spheres and is rapidly varying near cores. So, the local parts turn on smoothly and become non-negligible only for $r$ significantly smaller than $S_R$.

When $r \to S_R$, only high $l$ wave functions contribute significantly (non-negligibly) to expectation value; this scheme has a very rapid $l$ convergence and, hence, is less time consuming. Please note that, in this scheme, no cross terms of $\mathcal{H}_i (r)$, $\Phi_{ilm} (r - R)$, and $\mathcal{H}_{ilm} (r - R)$ appear in the integrals. Again, this avoids time consuming calculations present in different earlier formulations of the full-potential methods. It also avoids any awkwardly shape-dependent integral for the interstitial region, which is difficult to calculate because of its complicated shape. With this scheme, the FP-LMTO method provides excellent efficiency as well as accuracy. The latter is competitive with the so-called linearized augmented plane wave (LAPW) method, one of the most accurate band structure methods.

In the present calculations, we use two ($\kappa, R_{sm}$), the first for $spd$ and the second
for $sp$ orbitals, on Cs, Sn and the halogen ion. For Cs, we treat the $5p$ states as bands. A $6p$ orbital was added as a local orbital in some test calculations, but was found to have little effect. For Br, I, we include the $4s$, $5s$ semi-core orbitals as local orbitals and the empty $5s$, $6s$ as band orbitals. Inside the spheres augmentation is done up to $l_{\text{max}} = 4$. Brillouin zone integrations are done with a $10 \times 10 \times 10$ k-point mesh.

To perform QSGW calculation within the FP-LMTO method, we need some additional implementations. One unique implementation is the mixed product basis set. The motivation came from the expansion of the screened Coulomb interaction, $W$, where one encountered an interaction like $\langle \psi \psi | v | \psi \psi \rangle$. In the interstitial region, eigenfunctions are expanded in plane waves, while, inside the muffin-tin spheres, eigenfunctions are expanded by Bloch sums of solutions to the radial Schrödinger equation. The product of two plane waves results in a new plane wave; so, the mixed product basis set is generated by (i) interstitial plane waves and (ii) the Bloch sum of the product of solutions of the radial Schrödinger equation inside the muffin-tin spheres. This so-called product basis is further reduced by excluding linearly dependent terms and orthogonalized. The use of the product basis was originally introduced by Aryasetiawan and Gunnarsson [53]. Details of the implementation can be found in Ref. [42].

All in all, the most important point here is that the QSGW approach used in conjunction with the FP-LMTO implementation allows us to obtain a real space representation of the $\Sigma$ in the basis of atom-centered muffin-tin orbitals. By a reverse Fourier transform, this then allows calculating the $GW$ corrections at arbitrary $k$-points, even if the $GW$ calculation is performed only on a relatively coarse $k$-point mesh. This allows us to display the full band structure at the $GW$ level, and to extract reliable effective masses from the band dispersion. The convergence of the results with the $GW$ $k$-point mesh used was carefully studied as well as its dependence
on the parameters of the LMTO basis set. Slightly more localized basis functions 
are used than for the total energy LDA calculations and a mesh of $5 \times 5 \times 5$ was 
found to be adequate for the cubic perovskite structure. For the tetragonal $\beta$-phase, 
a correspondingly dense mesh is used. Spin-orbit (SO) coupling (calculated at the 
LDA-level) can be added as a separate term in the Hamiltonian.

### 2.3 Results

#### 2.3.1 Band structures

Sections 2.3.1.1 and 2.3.1.2 but not 2.3.1.3 are based on material published by the 

The LDA usually slightly underestimates the lattice constants. In the present 
case, for the cubic phases, we obtained an underestimate of the lattice constant 
by about 1.5-2% using the all-electron LMTO method. Therefore we prefer to use 
the experimental lattice constants for our band structure calculations. In Tables 
2.1 and 2.2 the lattice constants and internal parameters used in our calculations 
are summarized. For the $\beta$-phase of CsSnI$_3$ we also performed LDA calculations to 
minimize the structure with respect to the internal parameters and found excellent 
agreement with the experimental values to 0.001 precision.

For CsSnCl$_3$ we also performed LDA calculations for the monoclinic phase, which 
has a rather different crystal structure [56], and we also calculated the band structure 
of the yellow phase of CsSnI$_3$ in the LDA.

#### 2.3.1.1 Inverted band structure

We start analyzing the band structures in the cubic perovskite phase. Fig. 2.2 shows 
the band structures of CsSnX$_3$, with X=Cl, Br, I obtained in the QSGW method
Table 2.1: Lattice constants for CsSnX$_3$. Note that $\alpha$, $\beta$ and $\gamma$-phases are cubic, tetragonal and orthorhombic respectively, while the $M$-phase is monoclinic and the $Y$-phase is orthorhombic.

<table>
<thead>
<tr>
<th>Material</th>
<th>Space group</th>
<th>Lattice constants (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-CsSnCl$_3$ [55]</td>
<td>$Pm\overline{3}m$</td>
<td>$a = 5.56$</td>
</tr>
<tr>
<td>$M$-CsSnCl$_3$ [56]</td>
<td>$P2_1/n$</td>
<td>$a = 16.10$, $b = 7.425$, $c = 5.74$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta = 93.2^\circ$</td>
</tr>
<tr>
<td>$\alpha$-CsSnBr$_3$ [55]</td>
<td>$Pm\overline{3}m$</td>
<td>$a = 5.804$</td>
</tr>
<tr>
<td>$\beta$-CsSnBr$_3$ [57]</td>
<td>$P4/mbm$</td>
<td>$a = 8.195$, $b = 5.805$</td>
</tr>
<tr>
<td>$\alpha$-CsSnI$_3$ [33]</td>
<td>$Pm\overline{3}m$</td>
<td>$a = 6.219$</td>
</tr>
<tr>
<td>$\beta$-CsSnI$_3$ [33]</td>
<td>$P4/mbm$</td>
<td>$a = 8.772$, $b = 6.261$</td>
</tr>
<tr>
<td>$\gamma$-CsSnI$_3$ [33]</td>
<td>$Pnam$</td>
<td>$a = 8.688$, $b = 8.643$, $c = 12.378$</td>
</tr>
<tr>
<td>$Y$-CsSnCl$_3$ [36]</td>
<td>$Pnam$</td>
<td>$a = 10.328$, $b = 17.677$, $c = 4.765$</td>
</tr>
</tbody>
</table>

Table 2.2: Atomic coordinates of $\beta$- and $\gamma$-CsSnI$_3$. The column Position gives the Wyckoff position and site point group [33].

<table>
<thead>
<tr>
<th>Material</th>
<th>Atom</th>
<th>Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-CsSnI$_3$</td>
<td>Cs</td>
<td>2d(mmm)</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>$\beta$-CsSnI$_3$</td>
<td>Sn</td>
<td>2b(4/m)</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>$\beta$-CsSnI$_3$</td>
<td>I(1)</td>
<td>2a(4/m)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\beta$-CsSnI$_3$</td>
<td>I(2)</td>
<td>4h(mm)</td>
<td>0.210</td>
<td>0.290</td>
<td>0.5</td>
</tr>
<tr>
<td>$\gamma$-CsSnI$_3$</td>
<td>Cs</td>
<td>4c(m)</td>
<td>0.006</td>
<td>-0.040</td>
<td>0.25</td>
</tr>
<tr>
<td>$\gamma$-CsSnI$_3$</td>
<td>Sn</td>
<td>4b(T)</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\gamma$-CsSnI$_3$</td>
<td>I(1)</td>
<td>4c(m)</td>
<td>0.476</td>
<td>0.000</td>
<td>0.25</td>
</tr>
<tr>
<td>$\gamma$-CsSnI$_3$</td>
<td>I(2)</td>
<td>8d(1)</td>
<td>0.294</td>
<td>0.705</td>
<td>-0.019</td>
</tr>
</tbody>
</table>
without spin-orbit coupling and the corresponding partial densities of states. The dominant orbital character of the bands can be described as follows. At about $-15$ eV below the VBM, in CsSnI$_3$, we find the I-5$s$ bands. In the CsSnBr$_3$ and CsSnCl$_3$ cases these bands move further down reflecting the deeper atomic energy levels in the earlier elements of the periodic table. The next narrow band corresponds to the Cs-5$p$ semicore levels. Then we find a band which is a bonding combination of Sn-5$s$ and I-5$p$, followed by mostly I-5$p$ states and a band which is antibonding between Sn-5$s$ and I-5$p$. The conduction band minimum is dominated by Sn-5$p$ states but higher up there are also I-5$p$ antibonding orbital contributions and above 5 eV, there is a significant Cs-5$d$ contribution. The energy levels at the $R$-point where the minimum direct gap occurs are symmetry labeled for the CsSnI$_3$ case and the same labels apply for the other cases.

We can see that the band gap in all three materials is direct at the point $R = (1, 1, 1)\pi/a$. The valence band maximum (VBM) is non-degenerate while the conduction band minimum is three-fold degenerate without SO coupling and splits into a doublet and a quadruplet (including spin) when SO is included as is illustrated for CsSnI$_3$ in Fig. 2.3 The spin-orbit splittings are summarized in Table 2.3. This is opposite from what is found in most compound semiconductors with tetrahedral bonding. We therefore call it an “inverted” band structure. We note that this term should not be confused with a so-called band inversion, a term recently applied to topological insulators for the case where there is actually a negative gap in absence of spin-orbit coupling because the cation-$s$ like conduction band dips below the anion-$p$ like valence band.

To obtain further insight why this happens, we analyze the atomic orbital character of the bands. This is shown in Fig. 2.4. In this figure, the color intensity indicates how much a chosen atomic orbital is present in the eigenstates at each $k$-point. One can see that the CBM is composed mostly of Sn-$p$ states. The VBM on the other
Figure 2.2: QSGW band structures and partial densities of states of $\alpha$-CsSnI$_3$, $\alpha$-CsSnBr$_3$, and $\alpha$-CsSnCl$_3$. 
Figure 2.3: Energy bands of CsSnI$_3$ in the QSGW method near the gap including spin-orbit coupling.

Table 2.3: Spin-orbit splitting in $\alpha$-structure and tetragonal crystal field splitting in $\beta$-structure in meV.

<table>
<thead>
<tr>
<th>compound</th>
<th>$\Delta_{so}$</th>
<th>$\Delta_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsSnCl$_3$</td>
<td>448</td>
<td></td>
</tr>
<tr>
<td>CsSnBr$_3$</td>
<td>437 215</td>
<td></td>
</tr>
<tr>
<td>CsSnI$_3$</td>
<td>420 254</td>
<td></td>
</tr>
</tbody>
</table>
hand, is a mixture of I-$p$ and Sn-$s$ states. These two form an anti-bonding combination. The reason why there is a strong Sn-$s$ to anion $p$-orbitals at this particular k-point is that at k-point $R$, the $p$-orbitals on opposite sites of the unit cell differ by a phase factor $e^{i\mathbf{k} \cdot \mathbf{T}} = -1$ and hence the $p$-orbitals all point with the same lobe of the orbital inward toward the Sn-$s$ as shown in Fig. 2.5. They thus belong to the same irreducible representation $a_{1g}$ of the cubic group and have a strong interaction with each other. It means that the gap is to a large extent intra-atomic between Sn-$s$ and Sn$-p$.

In fact, further group theoretical analysis, following the notation of Bose et al. [38], shows that the CBM has $R_{15}$ symmetry, while none of the I-5$p$ orbital combinations on the faces of the unit cell belong to this irreducible representation. It also does not interact with the Cs-5$p$ below. There is some interaction with the I-5$s$ states which do form a $R_{15}$ linear combination at point $R$ but which lies very deep so that the upper state has little I-5$s$ contribution. There is also some interaction with Cs-5$d$ states higher up which also belong to $R_{15}$. This interaction will tend to reduce the gap. On the other hand, the I-5$p$ with Sn-$s$ interaction leading to the two states of symmetry $R_1$ is clearly very strong because the levels are close to each other and thus there is a very strong hybridization. The Cs-6$s$ on the corners of the unit cell form a $R_{2v}$ irreducible representation, which would only interact with $f$ states at the center.

The nature of the CBM and VBM explain a number of the intriguing properties of these materials. First, it explains the “inverted” nature of the band structure. Second, it shows that strong optical transitions are expected between the VBM and the CBM because they have an allowed $\Delta l = 1$ dipole character on the same atom. Third, it shows that the gap is essentially controlled by the Sn-$s$ to I-$p$ covalent anti-bonding interaction. For instance, with increasing lattice constant, one expects this interaction to become weaker and hence the valence band width will be decreased.
Figure 2.4: Dominant orbital character of CBM (upper figure) and VBM (lower figure) for $\alpha$-CsSnI$_3$. For the selected orbitals $\phi_i$ mentioned in the figure, the figure plots $k$ and $E$ resolved “spectral functions”, $A(k, E) = |\langle \phi_i | \psi_{nk} \rangle|^2 \delta(E - E_{nk})$ with the $\delta$-function replaced by a Gaussian, using the color scale shown on the right. So, the light green areas and white areas indicate zero contribution from that orbital while the red areas indicate a strong contribution of that orbital. The red thin lines show the band superposed on the color graph.
and the gap increased. We will see below that this is confirmed directly by the calculations and it also explains the anomalous temperature behavior of the gap. It also explains why to zeroth-order the gap is not as strongly dependent on the anion as one might think. In fact, it is in some sense intra-atomic in nature on the Sn. In particular, we note that the gaps of CsSnI$_3$ and CsSnBr$_3$ are rather close, especially if we consider the fact that the larger spin-orbit coupling in I, which reduces the gap partially overcomes the expected increase in gap on going from I to Br. Still, of course, the degree of anti-bonding mixing of the anion $p$ orbital in the VBM will decrease from Cl to Br to I because the anion $p$ levels move further down. This explains the decreasing trend of the gaps from Cl to I.

Finally, we show in Fig. 2.6 the changes in band gap with lattice constant for CsSnI$_3$, CsSnBr$_3$ and CsSnCl$_3$. We confirm the already mentioned increase of gap with lattice constant. In view of the thermal expansion, this also implies an increasing band gap with increasing temperature, which is opposite from most materials. This is
Table 2.4: Gap deformation potential $a_g$ in $\alpha$-structure (in eV).

<table>
<thead>
<tr>
<th>compound</th>
<th>$a_g$ in LDA</th>
<th>$a_g$ in QS</th>
<th>GW</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsSnCl$_3$</td>
<td>5.62</td>
<td>9.05</td>
<td></td>
</tr>
<tr>
<td>CsSnBr$_3$</td>
<td>5.34</td>
<td>8.99</td>
<td></td>
</tr>
<tr>
<td>CsSnI$_3$</td>
<td>4.65</td>
<td>7.35</td>
<td></td>
</tr>
</tbody>
</table>

because in most semiconductors, the gap is between anion-$p$ and cation-$s$ dominated bands. The increasing covalent interaction between the two when atoms are brought closer together then increases the gap with decreasing lattice constant. However, here the gap is to first approximation intra-atomic. The decreasing lattice constant results in an increasing band width of the valence band, pushing up the VBM by the increased interaction between Sn-$s$ and anion-$p$. This then results in the anomalous gap behavior. Such anomalous gap behavior was reported recently for CsSnI$_3$ [27], but can also be seen in the data for the 1.72 eV CL band in Myagkota et al. [58] for CsSnBr$_3$. We find a gap deformation potential $a_g = dE_g/d\ln a$ of 4.65 eV in LDA and 7.35 in QS GW for CsSnI$_3$. For the other materials, the $a_g$ are shown in Table 2.4. While it is often assumed that the gap deformation potentials can be obtained accurately within LDA even when the gaps themselves are underestimated, because one expects similar errors for each lattice constant, the present results indicate that the GW corrections also are required for the gap changes. The increase in gap from $\alpha$ to $\beta$ structure is related to a similar effect. While the overall structure becomes denser under this transformation, we found that the Sn-halogen distance actually increases. This reduces the Sn-$s$-halogen$-p$ interaction and hence the gap increases. The change from $\beta$ to $\gamma$ is more difficult to interpret because the tilting of the octahedra makes the orbitals interactions more complex.
2.3.1.2 Band structures in different phases

Next, we consider the changes in band gap due to the structural distortions in the lower symmetry phases. The structural phases of interest can be summarized as follows. Starting from the cubic $\alpha$ phase, a rotation of the octahedra in the $xy$ plane results in the tetragonal $\beta$-phase. In Chabot et al. [39] it was pointed out that this is related to the imaginary frequency of the lowest acoustic mode at point $M$ in the Brillouin zone. It leads to a crystal field splitting of the CBM in addition to the spin-orbit coupling. The crystal field splittings are included in Table 2.3. When both spin-orbit and crystal field splitting are included for the $\beta$-phase, it leads to a splitting in 3 levels, similar to what is observed for the VBM in tetragonally distorted tetrahedrally bonded semiconductors, such as chalcopytires [59]. A further tilting of the tetrahedra away from the $z$ axis, results in the orthorhombic $\gamma$-phase.

These structural distortions have been discussed in detail in Refs. [40] and [6].

![Figure 2.6: Band gap vs. lattice constant.](image-url)
yellow phase on the other hand involves a much more involved re-arrangement of the atoms. The LDA band structures of all four CsSnI$_3$ phases are shown in Fig. 2.7. The Brillouin zones and the labeling of the high-symmetry points are shown in Fig. 2.8. Note that the relation between the $\alpha$ and $\beta$ phase involves a rotation by $45^\circ$ and a folding. The $\Gamma - M$ line of $\alpha$-phase folded about its midpoint, which we labeled $B$ in the figure becomes the $\Gamma - X$ line of the $\beta$-phase. We can clearly see in the band structure figures that the bands along $M - B$ of the $\alpha$-phase are similar in dispersion to those along the $\Gamma - X$ line in the $\beta$-phase, The point $R$ in $\alpha$ becomes folded onto the $Z$-point in the $\beta$-BZ. In fact the whole line $M - R$ is folded onto the $\Gamma - Z$ line. We included points $L$ in the middle of the $M - R$ line although it is not a higher symmetry point. It becomes equivalent to the point $H$ in the $\beta$-structure. The transformation from $\beta$ to $\gamma$ structure involves a doubling of the cell in the $c$-direction, or folding of the bands along $\Gamma - Z$ about the half-way point $H$ so that $Z$ of $\beta$ now becomes folded on to the $\Gamma$-point of $\gamma$ and $H$ point becomes the new $Z$ point where the bands are doubly degenerate because of the folding. However, the tetragonal symmetry is also broken so that $\Gamma - X$ and $\Gamma - Y$ directions become distinct.

Our results on the band-gap changes obtained in LDA are in good agreement with previous studies. For $\beta$-CsSnI$_3$ we also carried out the full QS$GW$ calculation. This allows to check that the $GW$ gap correction is not very sensitive to the structure. Although the structural changes between the $\alpha$, $\beta$ and $\gamma$-phases, are mild, the changes for the monoclinic phase of CsSnBr$_3$ and the yellow phase of CsSnI$_3$ are more severe. Nonetheless, one may argue that the $GW$-corrections are mostly dependent on the average electron density and not too sensitive to structural details. The degree to which this holds may be judged from the agreement between our thus estimated gaps for these phases with experiment. Thus, once we have obtained the gap correction for the $\alpha$-phase, we can also apply it to the gaps of the other phases. The QS$GW$ band structures of the $\beta$-phase materials are shown in Fig. 2.9 for both CsSnI$_3$ and
Figure 2.7: LDA band structure of $\alpha$-CsSnI$_3$ (upper left), $\beta$-CsSnI$_3$ (upper right), $\gamma$-CsSnI$_3$ (lower left) and $Y$-CsSnI$_3$ (lower right).

Figure 2.8: (From left to right) Brillouin zone of cubic ($\alpha$-phase), tetragonal ($\beta$-phase), and orthorhombic ($\gamma$- and $Y$-phase) structures, respectively.
CsSnBr$_3$.

![Figure 2.9: QSGW band structure of $\beta$-CsSnI$_3$ (red solid line) and $\beta$-CsSnBr$_3$ (blue dashed line).](image)

The results on the band gaps are summarized in Table 2.5. The band gap differences between $\beta$ and $\alpha$ and $\gamma$ and $\beta$ in CsSnI$_3$ are 0.158 and 0.050 eV. These are in fair agreement with Borriello et al. [40], 0.133 and 0.080 eV but less good agreement with Chabot et al. [39], 0.179 eV, 0.244 eV.

The comparison with experimental gaps requires a little discussion. For the Cl and Br materials, these are not so well established as for the I material because we rely on rather old literature data. Voloshinovskii et al. [60] presented photoluminescence (PL) and photoluminescence excitation (PLE) as well as optical absorption data for CsSnCl$_3$ in its high-temperature cubic and low temperature monoclinic forms. For the $\alpha$-phase they show a broad PL band centered around 555 nm or 2.2 eV. This is probably due to defect bound excitons rather than intrinsic. The PLE shows a peak centered at 368 nm or 3.4 eV, however, it extends clearly to about 400 nm or 3.0 eV. The absorption extends even somewhat further to 420 nm or 2.9 eV. This
Table 2.5: Band gaps for CsSnX$_3$ (eV) in various structures. Note that for the \( \alpha \) and \( \beta \)-phases, actual QSGW calculations were performed while for the other cases, they are estimates assuming a structure independent gap correction beyond LDA.

<table>
<thead>
<tr>
<th>Material</th>
<th>LDA</th>
<th>QSGW</th>
<th>QSGW+SO</th>
<th>Other calc.</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-CsSnCl$_3$</td>
<td>0.744</td>
<td>2.997</td>
<td>2.693</td>
<td>0.950(^a)</td>
<td>2.9(^b)</td>
</tr>
<tr>
<td>( M )-CsSnCl$_3$</td>
<td>2.743</td>
<td>4.7±0.1(^c)</td>
<td>2.845(^a)</td>
<td>4.5(^b)</td>
<td></td>
</tr>
<tr>
<td>( \alpha )-CsSnBr$_3$</td>
<td>0.351</td>
<td>1.690</td>
<td>1.382</td>
<td>0.58(^d)</td>
<td></td>
</tr>
<tr>
<td>( \beta )-CsSnBr$_3$</td>
<td>0.574</td>
<td>1.918</td>
<td>1.740</td>
<td>1.8(^e)</td>
<td></td>
</tr>
<tr>
<td>( \alpha )-CsSnI$_3$</td>
<td>0.295</td>
<td>1.354</td>
<td>1.008</td>
<td>0.462(^f)</td>
<td>0.348(^a)</td>
</tr>
<tr>
<td>( \beta )-CsSnI$_3$</td>
<td>0.453</td>
<td>1.494</td>
<td>1.288</td>
<td>0.641(^f)</td>
<td>0.481(^a)</td>
</tr>
<tr>
<td>( \gamma )-CsSnI$_3$</td>
<td>0.503</td>
<td>1.3±0.1(^c)</td>
<td>0.885(^f)</td>
<td>0.561(^a)</td>
<td>1.3(^g)</td>
</tr>
<tr>
<td>Y-( \text{CsSnI}_3 )</td>
<td>2.026</td>
<td>2.7±0.1(^c)</td>
<td>2.53(^h)</td>
<td>2.55(^h)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Borriello \textit{et al.} [40] GGA pseudopotential plane wave method  
\(^b\)Voloshinovskii \textit{et al.} [60]  
\(^c\)QSGW results are estimates only  
\(^d\)Bose \textit{et al.} [38] LDA with LMTO-ASA (atomic sphere approximation)  
\(^e\)Clark \textit{et al.} [61]  
\(^f\)Chabot \textit{et al.} [39] GGA pseudopotential plane wave method  
\(^g\)Chen \textit{et al.} [43]  
\(^h\)Chung \textit{et al.} [6]  

is in good agreement with our gap of 2.7 eV (with) and 3.0 eV (without spin-orbit coupling). The monoclinic phase clearly has a higher gap. The peak of the PLE and optical absorption lies near 4.46 eV [60]. We only calculated this material in the LDA, see Fig. 2.10, but assuming the same gap shift to GW as for the cubic phase, we would estimate a gap of 4.7 eV. Ohno \textit{et al.} [62] obtained two phase-material and associated a 2.11 eV PL band to \( \alpha \)-CsSnCl$_3$ with a PLE peak at 3.5 eV and onset just above 3.1 eV and a 2.65 eV PL band to monoclinic CsSnCl$_3$ with a PLE peaking at 4.23 eV.

Clark \textit{et al.} [61] report a band gap of 1.8 eV for \( \alpha \)-CsSnBr$_3$ from optical absorption and low temperature band gap luminescence at 1.72-1.75 eV depending on temperature. Myagkota \textit{et al.} [58] also assigned a peak at 1.72 eV to intrinsic luminescence of CsSnBr$_3$ in a sample that was a mixture with other phases. It is not entirely clear whether these reports correspond truly to cubic CsSnBr$_3$ or to the
Figure 2.10: LDA band structure of \( M\)-CsSnCl\(_3\).

tetragonal \( \beta \)-form, whose structure is reported in Scaife \textit{et al.} [57]. We find that our gap for the \( \beta \)-phase of CsSnBr\(_3\) agrees much better with experiment than the for the \( \alpha \)-phase. We note that our gap of \( \alpha \)-CsSnBr\(_3\) is rather close to that of CsSnI\(_3\) and hence this material is also worthwhile considering for photo-voltaic applications if it can be stabilized. In fact, as mentioned in Ref. [6] the smaller cage size in this material may lead to a stabler bonding of the Cs and hence it avoids the undesirable larger gap yellow phase of CsSnI\(_3\) but stays in a perovskite derived structure.

We note that in the past literature [63; 37; 38], it was unclear if this material was a semiconductor or semimetal. For example, in the first semi-empirical linear combination of atomic orbitals (LCAO) band structure calculation of Parry \textit{et al.} [63], and the semi-empirical pseudopotential calculation of Lefebvre \textit{et al.} [37] the Sn-\( p \) derived states at \( R \) are reversed with the Sn-\( s \) derived states, and hence the material appeared to be semimetallic, which was thought to be consistent with the high electrical conductivity. Already in Bose \textit{et al.}'s [38] LMTO calculations in the atomic sphere approximation (ASA) this was reversed and a semiconducting band
structure was concluded, but the gap was still strongly underestimated by the LDA with a gap of order 0.58 eV.

These authors noted that the main difference between the earlier empirical LCAO band structure and theirs was the absence of any Cs orbitals in the LCAO basis set. However, at the \( R \)-point where the minimum gap occurs, the Cs-6\( s \) states belong to irreducible representation \( R_{2}^\prime \) and hence cannot interact with the \( R_{1} \) VBM. The Cs-5\( d \) orbitals of symmetry \( t_{2g} \) can interact with the Sn-\( p \) at the center because they both belong to \( R_{15} \) symmetry. For example, the Cs-\( d_{xy} \) orbitals at the corners of the cell interact with the Sn-\( p_{z} \) at the center taking into account the Bloch function phase factors as discussed above. However, since the Cs-5\( d \) lie above the Sn-\( p \), omitting the Cs-orbitals or pushing them up will reduce this interaction and thus move the Sn-\( p \) CBM up, which would increase the gap. The Cs-5\( p \) states cannot interact with the Sn-\( p \) or Sn-\( s \) either. Thus we conclude that the absence of Cs-orbitals did not play a major role in the opening of the gap. However, if we shift the Sn-levels down with respect to the Br or I or Cl orbitals, we can increase the Sn-\( s \) with X-\( p \) interaction sufficiently to make the \( R_{1} \) state shift above the \( R_{15} \) state thereby closing the gap and pinning the Fermi level at the \( R_{15} \) state. Note that the X-\( s \) states at the \( k \)-point \( R \) form a state of \( R_{15} \) symmetry, which interacts with the Sn-\( p \) orbitals at the center of the unit cell and this interaction tends to increase the gap. However, this interaction is much weaker because the halogen X-\( s \) orbitals lie rather deep. Thus the origin of the wrong band structures in the early work is that the position of the Sn-\( s \) versus the X-\( p \) levels, which depends on charge transfer was not properly taken into account. In pseudopotential language, this corresponds to a too deep Sn-pseudopotential as was speculated by Bose et al. [38].

Interestingly, it was recently proposed by Yang et al. [64] that some of these materials could be close to a topological insulator condition when a strain is applied so as to induce a band inversion, i.e. negative gap. The gap would then indeed result
purely from spin-orbit coupling. These calculations however were done at the GGA level which underestimates the gaps significantly as shown here. With our present results, the strains required to induce a topological insulator behavior would be come unrealistic.

For CsSnI\textsubscript{3} our gap for the $\gamma$-phase comes rather close to the experimental value of 1.3 eV recently established. The change in gap between $\beta$ and $\gamma$-phase is rather small. In any case, our gaps are clearly all significantly larger than the LDA gaps and then the gaps reported in previous work, including the sx-LDA gap reported in Ref. [6]. With improved materials, it should become possible to probe the nature of the spin-orbit split gaps using circularly polarized light. For $Y$-CsSnI\textsubscript{3}, In Chung et al. [6] found a direct gap of 2.53 eV for the yellow phase in good agreement with the observed 2.55 eV onset of absorption but they also found a somewhat lower indirect gap of 2.46 eV. They did not report a value for the gap for the $\gamma$-phase but from their figure it appears to be about 0.7 eV, so significantly smaller than the 1.3 eV measured. Our LDA band structure of $Y$-CsSnI\textsubscript{3} is shown in Fig. 2.7. Both the direct gap, 2.026 eV, and indirect gap, 1.943 eV, are close to the $X$ point. If we add the same amount of energy change shown in $\alpha$-CsSnI\textsubscript{3} case, we will get around 2.7 eV for the band gap after QSGW and SO correction, which is close to the experimental value of 2.55 eV.

2.3.1.3 Band structures in different (A and B) compounds (ABI\textsubscript{3})

Now we discuss chemical trends in the electronic properties of halide perovskite (ABX\textsubscript{3}). We have already discussed band structures of CsSnX\textsubscript{3} with X=Cl, Br, and I in different phases. Here we will focus on band structures of CsBI\textsubscript{3} with B=Si, Ge, Sn, and Pb and APbI\textsubscript{3} with A=Cs and MA.

The QSGW band structures with SO of CsBI\textsubscript{3}, where X=Si, Ge, Sn, Pb, are shown in Fig. 2.11. A closer look at the band edge in CsSiI\textsubscript{3} is shown in Fig. 2.12.
Band gaps and spin-orbit splittings in CsBI$_3$ are shown in Table 2.6. As in the case of CsSnX$_3$ mentioned in 2.3.1.1, an important feature of the Ge, Sn and Pb based halides is that these element’s s-electrons lie deep and strongly hybridize with the halogen’s p-orbitals leading to a valence band maximum with strong Ge, Sn or Pb-s character. The conduction band minimum meanwhile is Ge, Sn, or Pb p-like. The gap is determined by the opposing trends of the increased spin-orbit coupling for heavier elements which tends to reduce the gap and the decreased valence band width for heavier elements due to the larger B-X distance, which tends to increase the gap. As we expected, from Fig. 2.11 and Table 2.6, we can see that the QS GW band gap increases (from 0.6 to 2.3 eV) when B changes from Ge to Sn, and to Pb, which results from the factor that the larger the lattice constant, the smaller the valence band width (hence, the bigger the band gap). However, from the fifth column of Table 2.6 or Fig. 2.11, we find that the spin-orbit splitting increases when B goes from Ge to Sn, and to Pb; the larger the spin-orbit splitting, the smaller the band gap. The results of the competition between these two effects are shown in the fourth column in Table 2.6. Interestingly, we find that the gaps undergo remarkably small changes (from 0.5 to 1.3 eV) due to the above mentioned compensation of spin-orbit coupling and covalent interactions. As for CsSiI$_3$, we find that the band gap is purely from spin-orbital couple effect (a true inverted electronic structure), which implies it would be a topological insulator.

Table 2.6: Band gaps and spin-orbit splitting (in eV) for cubic CsBI$_3$, where B=Si, Ge, Sn, and Pb.

<table>
<thead>
<tr>
<th>Material</th>
<th>LDA</th>
<th>QS GW</th>
<th>QS GW + SO</th>
<th>$\Delta_{so}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsSiI$_3$</td>
<td>0</td>
<td>0</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>CsGeI$_3$</td>
<td>0.256</td>
<td>0.646</td>
<td>0.465</td>
<td>0.178</td>
</tr>
<tr>
<td>CsSnI$_3$</td>
<td>0.295</td>
<td>1.354</td>
<td>1.008</td>
<td>0.420</td>
</tr>
<tr>
<td>CsPbI$_3$</td>
<td>1.261</td>
<td>2.288</td>
<td>1.331</td>
<td>1.257</td>
</tr>
</tbody>
</table>
Figure 2.11: QSGW band structure with SO of cubic CsSiI$_3$ (upper left), CsGeI$_3$ (upper right), CsSnI$_3$ (lower left), CsPbI$_3$ (lower right).
Figure 2.12: A closer view of the band edge of CsSiI$_3$ (shown in Fig. 2.11).
The QSGW band structure with SO of MAPbI$_3$ (‘MA’ stands for ‘methylammonium’) is shown in the right-hand side of Fig. 2.13. For comparison, we also show the QSGW band structure with SO of CsPbI$_3$ in the left-hand side of the Fig. 2.13. Band gaps of these two materials are shown in the Table 2.7 with other calculated results and experimental values. Though, we could find experimental gaps for CsPbI$_3$, the authors of Refs. [65] and [18] did not clearly specify the crystal structure of their samples. Therefore, we cannot be sure what structures the experimental values actually correspond to; hence, we use question marks to indicate the uncertainty. Our calculated band gap for MaPbI$_3$ is 1.675 eV, which is close to another calculated value (1.67 eV) by Frost et al. [66] and is in good agreement with the measured value of 1.61 eV from room temperature photoluminescence (PL). The band gaps of CsPbI$_3$ and MAPbI$_3$ are similar, which results from the intra-atomic (of Pb) transition characteristic. The spin-orbital splittings of these materials are close as well (Fig. 2.13). The most important change is that, in MAPbI$_3$, the band gap becomes slightly indirect, with a linear dispersion term near the $R$-point conduction band minimum. We can also see that all the bands now become spin-split away from the high-symmetry point $R$. This is related to the symmetry lowering to tetragonal symmetry. Even when we still adopt a cubic lattice structure, replacing the spherically symmetric Cs ion by a polar molecule like MA, assumed here to be oriented along the cubic axis, already breaks the cubic symmetry to tetragonal symmetry. The tetragonal symmetry of MA allows linear in $k$ terms in the Kohn-Luttinger effective Hamiltonian. The latter will be discussed in more detail in the next section on excitons. A similar splitting actually also affects the VBM at $R$, as was discussed by Brivio et al. [67]. This is related to the Rashba effect, which arises from spin-orbit coupling and is a relativistic effect on the band structure, which is particularly strong for Pb. The splitting for the VBM however, is too small to be seen on the energy scale used here.
Figure 2.13: QSGW band structure with SO of CsPbI\textsubscript{3} (left) and MAPbI\textsubscript{3} (right).

Table 2.7: Band gaps (in eV) for cubic APbI\textsubscript{3}, where A=Cs and MA at Γ. A question mark indicates uncertainty as to what structure the experimental value really corresponds to; the authors did not clearly specify a crystal structure.

<table>
<thead>
<tr>
<th>Material</th>
<th>LDA</th>
<th>QSGW</th>
<th>QSGW+SO</th>
<th>Other calc.</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbI\textsubscript{3}</td>
<td>1.261</td>
<td>2.288</td>
<td>1.331</td>
<td>1.67? [65]</td>
<td>1.73? [18]</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3}</td>
<td>1.276</td>
<td>2.557</td>
<td>1.675</td>
<td>1.67 [66]</td>
<td>1.61 [68]</td>
</tr>
</tbody>
</table>
2.3.2 Effective masses and exciton binding energies.

The exciton binding energy is of great importance in understanding the relationship between absorption and luminescence in these materials. We, therefore, discuss the exciton binding energy in this section. We will first briefly discuss how to theoretically calculate the exciton binding energy in the case where degeneracy and anisotropy occur in the band edge. Then apply the theory to our cubic phase CsSnX$_3$ to estimate the exciton binding energy. Finally, we compare and discuss our calculated results with experimental data. Portions of this subsection have been published previously in Phys. Rev. B 88, 165203 (2013) [54].

2.3.2.1 Theoretical treatment

The simplest exciton theory deals with non-degenerate valence and conduction bands in isotropic crystals. In this case, the exciton Hamiltonian can be reduced to that of the hydrogen atom with reduced mass of an electron and a hole, and then exact solutions are obtained. However, in our CsSnX$_3$ materials and in most semiconductors, for example, Si in a diamond structure, anisotropy and degeneracy occur at the band edge where the exciton is formed. Therefore, the simple exciton theory cannot be directly applied.

Because the inverted band structure in CsSnX$_3$ is rarely seen in semiconductors that are already known, we could not find any papers discussing methods to calculate the exciton binding energy in the inverted band structure case. Most of the literature discussed the exciton binding energy for diamond and zinc-blende semiconductors. In those semiconductors, the valence band maximum (VBM) is a three-fold degenerate band while the conduction band minimum (CBM) is a non-degenerate band at Γ in the absence of spin-orbit (SO) interaction. When the SO interaction is included, VBM splits into a four fold degenerate band and a two fold degenerate band with
energy difference $\Delta_0$, the so-called spin-orbit splitting. The situation is similar to our inverted band structure except for the switching of CBM and VBM. Moreover, because the point group of the diamond structure is identical to that of the cubic phase CsSnX$_3$, we can directly apply the theory for the diamond structure to our cubic phase. So, in the remainder of this section, we will briefly discuss the theoretical treatment of calculating the exciton binding energy in semiconductors with a diamond structure.

Because of the three-fold degeneracy of the VBM in the absence of SO coupling, the masses depend on direction. Along the [100] direction, there are two bands, and we label these masses as the heavy ($hh$) and the light hole ($lh$). Similarly, in the [111] direction we also have a splitting. This situation can best be described by the following Kohn-Luttinger (KL) Hamiltonian [69; 70] based on the theory of invariants

$$\hat{H} = \frac{1}{3}\Delta_0 \vec{L} \cdot \vec{\sigma} + Ak^2 - (A - B)(L_x^2k_x^2$$
$$+ L_y^2k_y^2 + L_z^2k_z^2) - 2C(\left\{L_x, L_y\right\}k_xk_y$$
$$+ \left\{L_y, L_z\right\}k_yk_z + \left\{L_x, L_z\right\}k_xk_z),$$

(2.27)

where $\left\{L_i, L_j\right\} = (L_iL_j + L_jL_i)/2$, and $\sigma_x, \sigma_y, \sigma_z$ describes the Pauli spin matrices. The parameters $A$, $B$, and $C$ are related to the effective masses in different directions as follows:

$$A = \frac{1}{m_{lh}^*[100]},$$
$$B = \frac{1}{m_{hh}^*[100]},$$
$$A + 2B - C = \frac{1}{m_{hh}^*[111]},$$
$$A + 2B + 2C = \frac{1}{m_{lh}^*[111]},$$

(2.28)
This effective Hamiltonian describes the three valence band states near the degeneracy point. It contains all terms of order up to $k_1^2$ that are allowed by symmetry. When applied to a basis of angular momentum eigenstates with quantum number $l = 1$, it describes a $3 \times 3$ matrix whose eigenvalues gives the bands a quadratic order near $k = 0$, including the spin-orbit coupling.

Using the effective mass approximation, the exciton binding energy within the Wannier exciton theory can be obtained from the electron and hole effective masses and the screened Coulomb interaction between the electron and hole. In the simplest form of the theory, this lead to a hydrogenic model mentioned before with the binding energy being the effective Rydberg. This scales proportionally to the reduced mass and inversely proportionally to the square of the dielectric constant. This model can be further elaborated to take into account the degenerate nature of the VBM described by the Kohn-Luttinger Hamiltonian. For the diamond structure, the theory was worked out in detail using group theoretical analysis by Baldereschi and Lipari [71]. Within a so-called spherical approximation, they obtained

$$E_b = \frac{2\pi^2 \mu_0 e^4}{h^2 \varepsilon_0^2} \left[ 1 + \frac{10}{7} \left( \frac{\mu_0}{\mu_1} \right)^2 + \frac{5}{28} \left( \frac{\mu_0}{\mu_2} \right)^2 \right].$$

(2.30)

with $\mu_0^{-1} = (m^*_e)^{-1} + 2(A+2B)/3$, $\mu_1^{-1} = (A-B)/3$, and $\mu_2^{-1} = 2C/\sqrt{3}$. Here, $m^*_e$ is the effective electron mass. Note that the 2nd and 3rd terms in the square bracket are relatively small corrections and the factor up front is in fact nothing but the well known effectively scaled Rydberg energy. The electron mass is replaced by a reduced mass $\mu_0$ which involves the inverse electron mass and the average inverse hole mass. Also, note that the dielectric constant $\varepsilon_0$ is not the permittivity of the vacuum here but the static dielectric constant of the material. For a typical semiconductor, $\mu_0$ is of order 0.1 and $\varepsilon_0$ is of order 10 and becomes squared, so the effective Rydberg is on the order of 13 meV.
2.3.2.2 Choice of dielectric constant

Although we are here dealing with electrons instead of holes and with a different \( k \)-point, namely \( R \) instead of \( \Gamma \), the form of the KL Hamiltonian is still applicable here because of the cubic symmetry. We apply the above theoretical treatment of the exciton binding energy for a diamond structure to our inverted band structure of CsSnX\(_3\). According to the Eq. (2.30), the exciton binding energy is proportional to the reduced mass of hole (replace \( m_e^* \) by \( m_h^* \)) and inversely proportional to the dielectric constant squared in cubic CsSnX\(_3\). We will discuss how to obtain effective (reduced) masses in this section and directly use dielectric constants calculated in the next chapter. The detail theory and method to calculate dielectric constants will be discussed in the next chapter.

In Table 2.8 we report the effective masses obtained by fitting parabolic dispersion curves to our first-principle energy band structures. For the holes, this is straightforward because the band is non-degenerate and the band dispersion is isotropic and parabolic near the VBM. We can see that rather low hole masses are found decreasing from the Cl to the Br to the I compound. These results are obtained for the cubic phase for simplicity but they do not differ very much in the other phases. The low hole masses clearly play an important role in the observed high hole mobility, which was reported \([6]\) to be of order \( \sim 585 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \). In view of the general relation, \( \mu = e\tau/m^* \) they indicate a carrier relaxation time \( \tau \) of about \( 2.29 \times 10^{-14} \text{ s} \).

Table 2.8: Effective masses at the band gap edges (in electron mass). These correspond to the bands without spin-orbit coupling.

<table>
<thead>
<tr>
<th>sample</th>
<th>( m_h^* )</th>
<th>( m_{he}^*[100] )</th>
<th>( m_{he}^*[111] )</th>
<th>( m_{le}^*[100] )</th>
<th>( m_{le}^*[111] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-CsSnCl(_3)</td>
<td>0.140</td>
<td>0.741</td>
<td>0.272</td>
<td>0.088</td>
<td>0.149</td>
</tr>
<tr>
<td>( \alpha )-CsSnBr(_3)</td>
<td>0.082</td>
<td>0.635</td>
<td>0.201</td>
<td>0.053</td>
<td>0.084</td>
</tr>
<tr>
<td>( \alpha )-CsSnI(_3)</td>
<td>0.069</td>
<td>0.573</td>
<td>0.154</td>
<td>0.041</td>
<td>0.068</td>
</tr>
</tbody>
</table>
Because of the three fold degeneracy of the CBM in absence of SO coupling, the masses depend on direction. Along the [100] direction, there are two bands, and we label these masses as the heavy \((he)\) and light electron \((le)\) in analogy with the usual terminology for holes in usual semiconductors. Similarly, in the [111] direction we also have a splitting. Similarly to Eq.(2.29), the parameters \(A\), \(B\), \(C\) are related to the effective masses in different directions as follows:

\[
A = \frac{1}{m_{[100]}^*}, \\
B = \frac{1}{m_{[111]}^*}, \\
\frac{A + 2B - C}{3} = \frac{1}{m_{[111]}^*}, \\
\frac{A + 2B + 2C}{3} = \frac{1}{m_{[111]}^*}.
\]  

(2.31)

\[
\frac{A + 2B + 2C}{3} = \frac{1}{m_{[111]}^*},
\]

(2.32)

In Table 2.9 we list the \(A\), \(B\) and \(C\) parameters obtained by fitting to these equations.

The only remaining unknown parameter in this theory is the dielectric constant. This is a rather subtle point. If the exciton binding energy is small, it means that at the time scale of the relative motion of the electron and hole, the ions have time to relax and contribute to the screening. One should then use the static dielectric constant including the phonon contributions. On the other hand, if the time scale of the excitons is fast relative to the vibrational periods then, the phonons cannot contribute and one would use the high-frequency dielectric constant. In most

Table 2.9: Calculated inverse mass parameters \(A\), \(B\), and \(C\) of the Kohn-Luttinger Hamiltonian.
semiconductors, where the Wannier theory of excitons applies, the static dielectric constant is applicable.

However, in CsSnI$_3$ the highest optical phonon energies are of order 18 meV as we discuss in the next chapter. The static dielectric constant is larger than the high-frequency dielectric constant by a factor of 9.9, see Table 3.2. The high-frequency dielectric constant can be obtained from our $GW$ calculations. By taking the $q \to 0$ and $\omega \to 0$ limit of the $\varepsilon^{-1}(q, \omega)$ we obtain what is usually called $\varepsilon_{\infty}$. Using this high-frequency dielectric constant, we obtain an exciton binding energy $\tilde{E}_b$ of about 12 meV for $\alpha$-CsSnI$_3$. This is of the same order of magnitude as the phonon frequencies but still lower than the highest phonon frequencies. Therefore in principle at least the higher energy phonons should contribute to the screening. It is not entirely clear if we should take into account the full phonon enhancement factor of the phonons as some of the lower phonon frequencies are lower than our exciton binding energy. However, According to the Lyddane-Sachs-Teller relation

$$\prod_i \left( \frac{\omega_{Li}}{\omega_{Ti}} \right)^2 = \frac{\varepsilon_0}{\varepsilon_{\infty}}, \quad (2.33)$$

we can think as each mode contributing a factor to the enhancement of the dielectric screening. The highest modes show the highest contribution because they have the highest LO-TO splitting. They already increase the dielectric constant by a factor 1.5 so would reduce the binding energy by a factor 2.3. But then the next phonon frequency is already higher than this binding energy, so we need to also include it. Ultimately, this means a factor of 9.9 for the dielectric constant and a decrease of our exciton binding energy by a factor 98 or in other words two orders of magnitude. Thus we expect the exciton binding energy to be of order 0.1 meV. While these are all fairly rough estimates because a full dynamic theory of excitons including electron-phonon coupling is beyond present day capabilities of first-principles calculations,
the reduction of the exciton binding energy by the phonons by about two orders of magnitude should remain valid. In that case it is not at all in contradiction with Haynes’ rule, in fact even somewhat low. The same applies to the other materials which all end up with exciton binding energies of about 0.1 meV.

2.3.2.3 Comparison to the reported (experimental) exciton binding energy

Our calculated small exciton binding energy of about 0.1 meV for CsSnI$_3$ disagrees with the reported value by Chen et al. [43]. In a recent paper, Chen et al. [43] deduced the exciton binding energy from the temperature dependence of the photoluminescence intensity and found a rather high value of 18 meV. They further remarked that this implies a large deviation of the empirical Haynes’ rule, which relates exciton binding energies to band gaps. In fact on a logarithmic scale the exciton binding energies appear linear when plotted versus band gap on the linear scale. We now discuss the reasons for the discrepancy. Chen et al. [43] claimed that the exciton is a free rather than bound exciton based on their excitation power dependence study, which show a linear dependence and no saturation over several decades, and on the fact that the shape of the exciton indicates a single peak which is just shifting and broadening with temperature, rather than shifting weight from a bound exciton at low temperature to a free exciton at higher temperature. However, this is not entirely convincing because their PL is rather broad. Secondly, their approach for extracting the exciton binding energy relies on a number of assumptions. They fitted the decay of the exciton intensity as function of temperature to the expression

$$R_{\text{spon}}(T) = R_G[1 - e^{-E_b/k_B T}], \quad (2.34)$$
where $R_G$ is the generation rate of excitons, $k_B$ is Boltzmann’s constant, and the underlying assumption is that the decay is given by the dissociation of excitons as function of temperature only. In other words, no non-radiative processes are in competition with the radiative one. This equation makes sense if we assume the exciton is a bound exciton and there is no kinetic energy related to the exciton moving as a whole: the probability at temperature $T$ of decay of the exciton is then given by the Boltzmann equation and only the excitons surviving can give rise to radiation. However, they also tried to justify this equation for a free exciton. In order to arrive at the same expression under the assumption of a free exciton, they had to assume that the exciton motion is 2D so that there is a step-like density of states of exciton kinetic energies. In that case the number of excitons would be

$$N(T) = \int D(E)e^{-\frac{E}{k_BT}} \, dE \propto T[1 - e^{-\frac{E_b}{k_BT}}] \quad (2.35)$$

if we integrate up to $E_b$, which presumably one could justify by assuming that when an exciton gets kinetic energy above the binding energy it will decay. In the case of a 3D distribution the $D(E) \propto \sqrt{E}$ and we would obtain $T^{3/2} \gamma(3/2, E_b/k_BT)/\Gamma(3/2)$ with $\gamma(a, x), \Gamma(a)$ the incomplete gamma-function and gamma-function respectively \cite{72}. This must then be divided by the partition function of free electrons which is proportional to $T$ in 2D and to $T^{3/2}$ in 3D to obtain the rate of survival of excitons.

The reason is that we consider electrons to either be bound to a hole or free, but we only consider minority carriers (electrons) since the material is p-type. On the other hand, the theory of exciton decay for free excitons in a 2D quantum well was considered by Feldman et al. \cite{73}. Slightly generalizing their approach to either 2D or 3D, the decay rate of excitons is given by

$$\frac{1}{\tau} \propto \frac{E_b\mu\gamma(D/2, \frac{\Delta}{k_BT})}{M\Delta\Gamma(D/2)}, \quad (2.36)$$
where $D$ is the dimensionality of the motion, $M = m_e + m_h$ is the total mass of the exciton, $\mu$ the reduced mass, and $\Delta$ is the spread of energies of the exciton due to their non-zero kinetic energy, which arises from interaction with acoustic phonons. In other words, $\Delta(T)$, which in general depends itself on $T$, is the line width of the exciton peak. This approach appears similar that of Chen et al. [43] but is arrived at by integrating the density of excitons only up to $\Delta$ rather than to $E_b$. It turns out that for $D = 2$ this reduces to a similar form as Eq.(2.34) because $\gamma(1,x) = [1 - e^{-x}]$, but the important point is that the relevant parameter $\Delta$, in this equation, is not the exciton binding energy, but the line width of the exciton! A fit of the data to this equation with the assumption $D = 3$ would give a $\Delta \approx 30$ meV which agrees roughly with half the line width of the PL peak. The measured exciton lifetimes as function of temperature by Chen et al. [43] show a curve which is essentially inversely proportional to the exciton integrated intensity as function of temperature as expected. However, if their exciton would really be free and this theory would be applicable, then it does not tell us anything about the exciton binding energy but merely about the exciton line width!

On the other hand, the study of In Chung et al. [6] showed that after high temperature cycling (300–600K), the PL increased in intensity and this increase is also accompanied by an increase in conductivity. This indicates that chemical changes are taking place in the material, leading to an enhanced hole concentration (since the material was found to have p-type conduction). Their calculations in fact, ascribe this to the formation of Sn vacancies, $V_{Sn}$. This would then be a clear indication that the PL in question is in fact due to an acceptor bound exciton rather than a free exciton. Even material as grown before the heat treatments is already p-type with concentrations of order $10^{17}$ cm$^{-3}$. In that case, Chen et al.’s [43] first analysis in terms of a simple rate equation, assuming a single exciton binding energy but no kinetic energy of the excitons, may be considered to be valid as a way to obtain the
exciton binding energy but it is then the energy of a bound exciton and is therefore not in contradiction with our conclusion that the free exciton binding energy is two orders of magnitude smaller. Essentially, the energy is lowered by the binding energy of the acceptor, which may easily be of order 20 meV. Their analysis leading to the conclusion of a 2D motion however is clearly invalid. In fact, there is also no support for 2D motion of the electrons (or excitons) from our band structure, nor from the crystal structure.

2.4 Conclusions

In this chapter, we have presented quasiparticle self-consistent GW band structures of the family of CsSnX₃ compounds with X=(Cl,Br,I). Spin-orbit coupling effects were included. The changes in band structure with the structural distortions of the α, β and γ phases were investigated. The band gap of 1.3±0.1 eV was found to be in good agreement with experiment for γ-CsSnI₃ for which the best experimental data are available. For α-CsSnCl₃, our gap of 2.7 eV is in good agreement with the PLE data of Voloshinovskii et al. [60], giving an estimate of 2.9 eV. We also obtained good agreement for the much higher gap of the monoclinic phase (of order 4.5 eV) if we assume the same LDA to QSGW gap correction applies. For α-CsSnBr₃, our calculations predict a gap of 1.38 eV, while for the β-phase we obtain 1.7 eV in good agreement with experiment (1.8 eV) by Clark et al. [61]. While this gap is a little larger than optimal for solar cell applications, the increased stability of the desirable perovskite phase for the Br compound makes this material of further interest for photovoltaics. The Br material having a somewhat smaller lattice constant appears to avoid the competing so-called yellow phase of CsSnI₃.

The most important finding is that all these materials have a rather unusual “inverted” band structure with a non-degenerate s-like valence band and a degenerate
$p$-like conduction band. This was shown to result from the strong Sn-$s$ character of the valence band maximum, which is an antibonding state or anion-$p$ states with Sn-$s$. The reason why the VBM occurs at the Brillouin zone corner $R$ is that at this point in k-space, the anion $p$-orbitals on the corners of the octahedron surrounding the Sn atom, point with their same lobes toward the center of the octahedron and hence give the strongest interaction. The strong intra-atomic nature of the gap, explains various features: the relatively weak dependence on anion, the strong optical luminescence and band gap absorption, and the anomalous temperature dependence, increasing gap with increasing temperature.

The effective masses were determined for the band edges and the low hole mass in CsSnI$_3$ is found to be responsible for the high hole mobility observed in this material. The other materials also have relatively low hole masses and may thus also be expected to excellent p-type semiconductors.

The free exciton binding energy was estimated to be of order 0.1 meV in CsSnI$_3$ in contrast to a recent report [43] which claimed an anomalously high value of 18 meV. Our low value is obtained when using the static dielectric constant rather than the high frequency one. This is consistent with the fact that, while the vibrational frequencies are rather low, they still are expected to contribute to the dielectric screening of the electron-hole interaction. We also find no evidence for 2D motion of excitons as claimed by Chen et al. [43] and showed that their method of determining the binding energy of the excitons is flawed. Further, we propose that their PL should rather be interpreted as an acceptor bound exciton than as a free exciton.
Chapter 3

Zone Center Phonons I: Zone center phonons in cubic, tetragonal, and orthorhombic phases

3.1 Introduction

The previous chapter already relied on some of our results on phonons. Here we present the results of our zone center phonon calculations for the cubic ($\alpha$), tetragonal ($\beta$), and orthorhombic ($\gamma$ and $Y$) phases of CsSnX$_3$ with X=Cl, Br, and I. Because good experimental data are available from Raman studies for monoclinic CsSnCl$_3$, sophisticated comparison and discussion are needed; we, therefore, separately present our calculated results of $M$-CsSnCl$_3$ in the next chapter.

Zone center phonons can be directly and easily measured by infrared and Raman spectroscopy. One, therefore, may expect that there are numerous experimental infrared and Raman data available. However, this is not true. After an extensive
literature search for experimental data for all possible phases CsSnX₃, we could only find (1) the infrared spectra of α-CsSnBr₃ and α-CsSnCl₃, (2) Raman spectrum of CsSnI₃, and (3) Raman spectra of M-CsSnCl₃. The first two cases will be discussed in this chapter, while the third case will be discuss in next chapter.

### 3.2 Computational method

The method used here differs from the FP-LMTO method mentioned before; we now use the pseudopotential plane wave method to solve the single-particle Schrödinger equation, or the Kohn-Sham equation, see Eq. (2.2). This method is basically a variational method and uses pseudopotentials to describe the interactions between valence and core electrons. In this method, all eigenfunctions are expanded in terms of a set of basis functions, \( \{ \psi_G \} \), \( \psi_G = \exp\left[i(k + G) \cdot r\right]/\sqrt{\Omega_0} \), where \( G \) stands for reciprocal lattice vectors and \( \Omega_0 \) is unit cell volume) which can be varied until the minimum of the ground-state energy is found. We are interested in the response of the system to external perturbations, which, for example, can be (collective) atomic displacements or/and (homogeneous) static electric fields. Next, perturbation theory (or method) [74] is applied to the single-particle Schrödinger equation so then we can obtain the perturbed quantities in which we are interested.

In the next seven subsections, we will briefly introduce how to obtain some of the physical quantities we are interested in, based on the density functional perturbation theory (DFPT) [74]. We will also detail the parameters used in our calculations in the final subsection.
3.2.1 Interatomic force constant, dynamical matrix, phonon frequency, and eigendisplacement

The total energy of a perturbed system, $E_{\text{tot}}$, with small lattice displacements from the equilibrium positions can be written as

$$E_{\text{tot}} = E_{\text{tot}}^{(0)} + \sum_{a\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left( \frac{\partial^2 E_{\text{tot}}}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right) \Delta \tau_{\kappa\alpha}^a \Delta \tau_{\kappa'\beta}^b + ... \quad (3.1)$$

where $E_{\text{tot}}^{(0)}$ is the total energy of unperturbed system and $\Delta \tau_{\kappa\alpha}^a$ is the displacement along direction $\alpha$ of the atom $\kappa$ in the cell $a$ (with vector $R_a$), from its equilibrium position. Then, the interatomic force constant is

$$C_{\kappa\alpha,\kappa'\beta}(a, b) = \left( \frac{\partial^2 E_{\text{tot}}}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right). \quad (3.2)$$

Without loss of generality, assuming $R_a$ is at the origin, then the Fourier transform of the interatomic force constant is

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(q) = \sum_b C_{\kappa\alpha,\kappa'\beta}(0, b) e^{iq \cdot R_b}, \quad (3.3)$$

and the dynamical matrix element is

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(q) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(q) / (M_{\kappa} M_{\kappa'})^{1/2}, \quad (3.4)$$

where $M_{\kappa}$ is the mass of the atom $\kappa$. Thus the squares of the phonon frequencies $\omega_{mq}^2$ at $q$ can be obtained as eigenvalues of the dynamical matrix $\tilde{D}_{\kappa\alpha,\kappa'\beta}(q)$. Actually, $\omega_{mq}^2$ can also be a solution of the following generalized eigenvalue problem:

$$\sum_{\kappa'\beta} \tilde{C}_{\kappa\alpha,\kappa'\beta}(q) U_{mq}(\kappa'\beta) = M_{\kappa} \omega_{mq}^2 U_{mq}(\kappa\alpha), \quad (3.5)$$
where $U_{m\alpha}(\kappa\alpha)$ is the eigendisplacement of the atom $\kappa$ in the direction $\alpha$.

### 3.2.2 Electronic dielectric susceptibility tensor and high frequency dielectric permittivity tensor

The polarizability of a solid describes the density response to an applied potential; thus, in real space, we have

$$n^{(1)}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') V_{\text{ext}}^{(1)}(\mathbf{r}') d\mathbf{r}'$$  \hspace{1cm} (3.6)$$

and in the reciprocal space, we have

$$n_q^{(1)}(\mathbf{G}) = \sum_{\mathbf{G}'} \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) V_{\text{ext}}^{(1)}(\mathbf{G}')$$  \hspace{1cm} (3.7)$$

Because

$$n(\mathbf{r}) = \frac{\partial E_{\text{tot}}}{\partial V_{\text{ext}}(\mathbf{r})}$$  \hspace{1cm} (3.8)$$

we obtain

$$\chi(\mathbf{r}, \mathbf{r}') = \frac{\partial^2 E_{\text{tot}}}{\partial V_{\text{ext}}(\mathbf{r}) \partial V_{\text{ext}}(\mathbf{r}')}. \hspace{1cm} (3.9)$$

Then, the (high frequency) dielectric permittivity tensor is defined as follows

$$\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \delta_{\mathbf{G},\mathbf{G}'} + \frac{4\pi}{|\mathbf{q} + \mathbf{G}|^2} \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}). \hspace{1cm} (3.10)$$
When $q$ approaches to zero, from above equation, we have
\[
\sum_{\alpha \beta} \hat{q}_\alpha \epsilon_\alpha^{\infty} \hat{q}_\beta = \frac{1}{\epsilon_{0,0}(q)}\]
(3.11)

where $\hat{q}$ is the unit vector in the direction $q$. Thus we can conclude that the (high frequency) dielectric permittivity tensor is derived from the second-order derivative of the total energy with respect to an external static electric field.

### 3.2.3 Born-effective charge tensor

The matrix element of the Born effective charge tensor, $Z^\star_{\kappa,\beta\alpha}$, is defined as the proportionality coefficient relating the force on an atom $\kappa$ along the direction $\alpha$ and the macroscopic electric field applied along the direction $\beta$:
\[
Z^\star_{\kappa,\beta\alpha} = \Omega_0 \frac{\partial \mathcal{P}_{\text{mac},\beta}}{\partial \tau_{\kappa\alpha}(q = 0)} = \frac{\partial F_{\kappa,\alpha}}{\partial E_{\beta}},
\]
(3.12)

where $\mathcal{P}_{\text{mac},\beta}$ is the macroscopic polarization in the direction $\beta$ and $E_{\beta}$ is the macroscopic electric field in the direction $\beta$. Because the force relates to the first-order derivative of the energy with respect to atomic displacements, the Born effective charge tensor is derived from the mixed second-order derivative of the energy with respect to atomic displacements and a macroscopic electric field. In practice, in the ABINIT code [75], it is calculated from the derivative of the polarization with respect to the atomic displacement.
3.2.4 Oscillator strength tensor and static dielectric permit-
tivity tensor

The macroscopic low-frequency (static) dielectric permittivity tensor $\epsilon_{\alpha\beta}(\omega)$ is calculated by adding the ionic contribution to $\epsilon_{\alpha\beta}^\infty(\omega)$. The ionic motion (displacement) resulting from the macroscopic electric field results in the polarization in the material. Following Gonze et al. [74], the static dielectric permittivity tensor is

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2 - \omega^2},$$  \hspace{1cm} (3.13)

where $\Omega_0$ is the unit cell volume and $S_{m,\alpha\beta}$ is the oscillator strength tensor defined as

$$S_{m,\alpha\beta} = \left( \sum_{\kappa\alpha'} Z^*_{\kappa,\alpha\alpha'} U^*_{mq=0} (\kappa\alpha') \right) \left( \sum_{\kappa'\beta'} Z^*_{\kappa',\beta\beta'} U_{mq=0} (\kappa'\beta') \right).$$  \hspace{1cm} (3.14)

We can also calculate the dielectric permittivity constant along any direction, say $\hat{q}$, as follows

$$\epsilon_{\hat{q}}(\omega) = \sum_{\alpha\beta} \hat{q}_\alpha \epsilon_{\alpha\beta}(\omega) \hat{q}_\beta.$$

(3.15)

3.2.5 LO–TO splitting

The coupling between the macroscopic electric field and the polarization associated with the atomic displacements in the long-wavelength limit also leads to LO–TO splitting. The long-wavelength polarization associated with applied non-analyticity (the macroscopic electric field) contributes additional force constant term to Eq. (3.3), namely,

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(q \to 0) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(q = 0) + \tilde{C}^{NA}_{\kappa\alpha,\kappa'\beta}(q \to 0),$$  \hspace{1cm} (3.16)
where NA means non-analyticity. The explicit form of the NA term, \( \tilde{C}_{k\alpha,k'\beta}^{NA}(q \to 0) \), can be found in the Ref. [74]. Then, we diagonalize the whole force constant tensor, \( \tilde{C}(q \to 0) \) to get the LO phonon frequencies.

### 3.2.6 Infrared spectra

In this subsection, we discuss how to obtain the real and imaginary parts of a dielectric function and the method for simulating infrared absorption and reflectivity spectra. Generalizing the Eq. (3.13) to include a damping term with damping time \( 1/\Delta\omega_m \), we can rewrite the Eq. (3.13) as follows

\[
\epsilon(\omega) = \epsilon^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{|S_m|}{\omega_m^2 - \omega^2 - i\omega\Delta\omega_m},
\]

where we omit matrix label. Then the real and imaginary parts are

\[
\text{Re} \{ \epsilon(\omega) \} = \epsilon^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{|S_m|}{(\omega_m^2 - \omega^2)^2 + (\omega\Delta\omega_m)^2)}
\]

\[
\text{Im} \{ \epsilon(\omega) \} = \frac{4\pi}{\Omega_0} \sum_m \frac{|S_m| (\omega\Delta\omega_m)}{(\omega_m^2 - \omega^2)^2 + (\omega\Delta\omega_m)^2)}.
\]

Once we obtain (i) phonon frequencies, \( \omega_m \)'s, (ii) the high frequency dielectric constant, \( \epsilon^\infty \), and (iv) oscillator strengths, \( |S_m| \)'s, from DFPT and (iv) the already known unit cell volume, \( \Omega_0 \), we can calculate \( \text{Re} \{ \epsilon(\omega) \} \) and \( \text{Im} \{ \epsilon(\omega) \} \) by Eqs. (3.18) and (3.19). The \( \Delta\omega_m \) is proportional to the full width at half maximum of each peak, and, in practice, we assigned the same line width for all modes.

Once we have \( \text{Re} \{ \epsilon(\omega) \} \) and \( \text{Im} \{ \epsilon(\omega) \} \), we can calculate the infrared absorption as follows

\[
\alpha(\omega) = \frac{2\omega\text{Im}\{\epsilon(\omega)\}}{n(\omega)c},
\]

where \( n(\omega) \) is the refractive index.
where \( c \) the speed of light, and \( n(\omega) = \text{Re}\{\sqrt{\varepsilon}\} \) is the index of refraction. And the reflectivity can also be calculated in the following form

\[
R(\omega) = \left| \frac{n(\omega) - 1}{n(\omega) + 1} \right|^2.
\]

(3.21)

Based on the above four equations, we can predict the TO phonon spectra (\( \text{Im}\{\epsilon(\omega)\}\)), LO phonon spectra (\( -\text{Im}\{1/\epsilon(\omega)\}\)), infrared absorption spectra (Eq. (3.20)), and reflectivity spectra (Eq. (3.21)).

### 3.2.7 Raman tensor and Raman spectrum

In order to simulate Raman spectra for an arbitrary material, we need to know the Raman tensors \( R^m \) for each mode \( m \) in the material. Now, consider the (non-resonant) Raman scattering with incident/scattered photon frequency \( \omega_0/(\omega_0 - \omega_m) \) and polarization \( e_0/e_S \). The scattering efficiency is proportional to [76]

\[
\frac{dS}{d\Omega} = |\mathbf{e}_S \cdot R^m \cdot \mathbf{e}_0|^2 = \frac{(\omega_0 - \omega_m)^4}{c^4} |\mathbf{e}_S \cdot \alpha^m \cdot \mathbf{e}_0|^2 \frac{\hbar}{2\omega_m}(n_m + 1),
\]

(3.22)

where \( \Omega \) is the angle of collection in which the outgoing photon is scattered, \( c \) is the speed of light in vacuum, \( n_m \) is the boson factor

\[
n_m = \frac{1}{e^{(\hbar \omega_m/k_B T)} - 1},
\]

(3.23)

and \( \alpha^m \) is the Raman susceptibility defined as

\[
\alpha^m = (\Omega_0)^{1/2} \sum_{\kappa,\beta} \frac{\partial \chi}{\partial \tau_{\kappa,\beta}} U_{mq=0}(\kappa;\beta),
\]

(3.24)

where \( \chi \) is the electronic linear dielectric susceptibility tensor. From the above three equations and Eq. (3.9), we can see that Raman tensors can be obtained by third
order derivatives of total energy with respect to electric fields twice and an atomic
displacement once.

Now, we discuss the method used to simulate Raman spectra. In practice, we
used the following equation which is transformed from Eq. (3.22) to simulate our
Raman spectra

$$RS(\omega) = \frac{(\omega_0 - \omega_m)^4}{c^4} \left| e_s \cdot \alpha^m \cdot e_0 \right|^2 \frac{h}{2\omega_m} \left[ \frac{1}{\pi} \frac{\Delta\omega_m}{(\omega - \omega_m)^2 + \Delta\omega_m^2} \right],$$

where the Cauchy–Lorentz distribution is in the square brackets with the line width
$\Delta\omega_m$ for each mode $m$. The Cauchy–Lorentz distribution gives the shape of each peak
while the remaining parts on the right-hand side of Eq. (3.25) give the intensity
of each peak. We thus can simulate Raman spectra once we obtain (i) phonon
frequencies and (ii) Raman tensors from DFPT.

### 3.2.8 Computational details

The ABINIT code [75] with norm-conserving pseudo-potentials [77] was used for
zone center phonon calculations based on the DFPT [78; 74; 76] within the LDA.
The phonons were calculated at the equilibrium lattice constants of the LDA, which
were found to be approximately several percentages lower than the experimental
values.

Our convergence studies show that the plane wave cut-off energy of about 30
Hartree is good enough for each phase. In practice, we used 28 Hartree for the
orthorhombic phase, 40 Hartree for the tetragonal phase, and 100 Hartree for cubic
phase; the latter two high cut-off energies are not necessary, but for these smaller
cells, we could afford to use a higher cut-off, which can only improve the results. And
we used a $4 \times 4 \times 4$ k-point mesh for each phase.
3.3 Results

Portions of this chapter have been published previously in Phys. Rev. B 88, 165203 (2013) [54] and Phys. Rev. B 90, 195201 (2014) [79]. Specifically, the phonon related spectra of the cubic phases and the discussion of LO-plasmon coupling were published in Phys. Rev. B 90, 195201 (2014) [79]. However, the group-theoretical analysis and infrared, Raman spectra of the phonons at Γ for the β, γ and Y phases were not previously published.

3.3.1 Group theory analysis

All that is necessary to complete the analysis is the site symmetry (or group) of the composed elements (or atoms). Decomposing the reducible representation of site symmetry to irreducible representation of the point group, we can know the irreducible representation of each site. Then the total number of normal modes of the crystal can be obtained by summing over all the irreducible representations of all composed elements. We summarize the results from this group theory analysis in Table 3.1.

For clarity, we will briefly discuss how to obtain Table 3.1 in practice. For each type of atom, we first find the Wyckoff positions, which are positions with a well-defined site point group. Next we give the standard coordinates of one of the Wyckoff positions in Table 3.1, while the other ones are obtained by applying all symmetry operations of the site point group. In the cubic phase, these positions involve no free parameters, but in other phases, these may involve parameters such as $x_1$ which have to be optimized by minimizing the energy. Now let us focus on the cubic phase. In the cubic phase, the Cs site is taken as the origin or the corner of the simple cubic unit cell, the Sn atoms correspond to the cube center and the 3c positions (of X) correspond to the face centers. Because the Cs and Sn atoms have only one site for
this Wyckoff position, but three degrees of freedom, $x$, $y$, $z$, their displacements for a three fold degenerate representation are equivalent to that of a vector at the origin, which is the $T_{1u}$ irreducible representation. For the X atom, we have 3 atoms times 3 displacements, so we obtain in total 3 triply degenerate irreducible representations. Among these irreducible representations, one corresponds to a simple translation of the whole unit cell, which corresponds to zero energy and is not really a vibrational mode. Similar considerations apply to the other structures.

All structures have inversion symmetry modes that are either even or odd with respect to inversion. The modes are only Raman active for even modes and IR active for odd modes. In Table 3.1 we explicitly show infrared active modes ($\Gamma_{IR}$) and Raman active modes ($\Gamma_{Raman}$), as well as silent modes ($\Gamma_{silent}$) and acoustic modes ($\Gamma_{acoustic}$). In this table, coordinates are actually reduced coordinates; please notice that $T$ modes are triply degenerated modes, $E$ modes are doubly degenerated modes, and $A$ and $B$ are non-degenerated (single) modes.

### 3.3.2 Calculated results

In this section, we show our calculated zone center phonon frequencies and simulated IR and Raman spectra for CsSnX$_3$ in different phases.

Table 3.2 shows our calculated phonon frequencies with some other properties for the cubic phase of CsSnX$_3$. We also analyze the Lyddane-Sachs-Teller relation:

$$\prod_i \left( \frac{\omega_{Li}}{\omega_{Ti}} \right)^2 = \frac{\varepsilon_0}{\varepsilon_\infty}$$

in the table; we can see that the static to high-frequency dielectric constant ratio is close to the expected value from the Lyddane-Sachs-Teller relation. We indeed observe a very strong contribution of the phonons to the static dielectric constant by a factor of 7 to 10, increasing from Cl to I. This is expected in view of the strong
Table 3.1: Summary of group theory analysis for different phases of CsSnX$_3$. Where "s. g." means "space group"; $x_i$, $y_i$, and $z_i$ ($i=1, 2, 3, ...$) are structural internal parameters.

<table>
<thead>
<tr>
<th>phase</th>
<th>atom</th>
<th>sym</th>
<th>coordinates</th>
<th>irreducible representation</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s. g.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$-CsSnX$_3$</td>
<td>Cs</td>
<td>1a</td>
<td>0 0 0</td>
<td>$T_{1u}$</td>
<td>3</td>
</tr>
<tr>
<td>($O_h$)</td>
<td>Sn</td>
<td>1b</td>
<td>1/2 1/2 1/2</td>
<td>$T_{1u}$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>3e</td>
<td>0 1/2 1/2</td>
<td>$2T_{1u} + T_{2u}$</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5 atoms/unit cell ($Z=1$)</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$T_{2u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$T_{1u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$3T_{1u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>no Raman active mode</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CsSnX$_3$</td>
<td>Cs</td>
<td>2d</td>
<td>0 1/2 0</td>
<td>$A_{2u} + B_{1u} + 2E_u$</td>
<td>6</td>
</tr>
<tr>
<td>($D_{2h}$)</td>
<td>Sn</td>
<td>2b</td>
<td>0 0 1/2</td>
<td>$A_{1u} + A_{2u} + 2E_u$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>X(1)</td>
<td>2a</td>
<td>0 0 0</td>
<td>$A_{1u} + A_{2u} + 2E_u$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>X(2)</td>
<td>4h</td>
<td>x,y 1/2 1/2</td>
<td>$A_{1u} + A_{2u} + 2E_u$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 atoms/unit cell ($Z=2$)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_{1g} + 2A_{1u} + A_{2g} + 2B_{1u} + 2E_u + 8E_u$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$2A_{1u} + 2A_{2u} + 2B_{1u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$3A_{1u} + 7E_u$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_{1g} + B_{1g} + B_{2g} + E_g$</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-CsSnX$_3$</td>
<td>Cs</td>
<td>4c</td>
<td>x,y 1/4 2</td>
<td>$2A_y + A_x + B_{1g} + 2B_{1u} + 2B_{2g} + 2B_{3u} + 2B_{3g}$</td>
<td>12</td>
</tr>
<tr>
<td>($D_{2h}$)</td>
<td>Sn</td>
<td>4b</td>
<td>1/2 0 0</td>
<td>$3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u}$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(1)</td>
<td>4c</td>
<td>x,y 1/4 2</td>
<td>$3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u}$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(2)</td>
<td>8d</td>
<td>x,y 1/4 2</td>
<td>$3A_u + 3A_x + 3B_{1u} + 3B_{2u} + 3B_{3u} + 3B_{3g}$</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 atoms/unit cell ($Z=4$)</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$7A_u + 8A_x + 5B_{1g} + 10B_{1u} + 7B_{2g} + 8B_{2u} + 5B_{3g} + 10B_{3u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$8A_u$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$B_{1u} + B_{2u} + B_{3u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$9B_{1u} + 7B_{2u} + 9B_{3u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$7A_u + 5B_{1g} + 7B_{2g} + 5B_{3g}$</td>
<td></td>
</tr>
<tr>
<td>$\nu$-CsSnX$_3$</td>
<td>Cs</td>
<td>4e</td>
<td>x,y 1/4 2</td>
<td>$2A_y + A_x + B_{1g} + 2B_{1u} + 2B_{2g} + 2B_{3u} + 2B_{3g}$</td>
<td>12</td>
</tr>
<tr>
<td>($D_{2h}$)</td>
<td>Sn</td>
<td>4c</td>
<td>x,y 1/4 2</td>
<td>$2A_y + A_x + B_{1g} + 2B_{1u} + 2B_{2g} + 2B_{3u} + 2B_{3g}$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(1)</td>
<td>4c</td>
<td>x,y 1/4 2</td>
<td>$2A_y + A_x + B_{1g} + 2B_{1u} + 2B_{2g} + 2B_{3u} + 2B_{3g}$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(2)</td>
<td>4c</td>
<td>x,y 1/4 2</td>
<td>$2A_y + A_x + B_{1g} + 2B_{1u} + 2B_{2g} + 2B_{3u} + 2B_{3g}$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(3)</td>
<td>4c</td>
<td>x,y 1/4 2</td>
<td>$2A_y + A_x + B_{1g} + 2B_{1u} + 2B_{2g} + 2B_{3u} + 2B_{3g}$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 atoms/unit cell ($Z=4$)</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$10A_y + 5A_x + 5B_{1g} + 10B_{1u} + 10B_{2g} + 5B_{2u} + 5B_{3g} + 10B_{3u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$5A_u$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$B_{1u} + B_{2u} + B_{3u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$9B_{1u} + 4B_{2u} + 9B_{3u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$10A_y + 5B_{1g} + 10B_{2g} + 5B_{3g}$</td>
<td></td>
</tr>
<tr>
<td>$M$-CsSnX$_3$</td>
<td>Cs</td>
<td>4e</td>
<td>x,y 1/4 2</td>
<td>$3A_y + 3B_x + 3A_u + 3B_u$</td>
<td>12</td>
</tr>
<tr>
<td>($C_{2h}$)</td>
<td>Sn</td>
<td>4e</td>
<td>x,y 1/4 2</td>
<td>$3A_y + 3B_x + 3A_u + 3B_u$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(1)</td>
<td>4e</td>
<td>x,y 1/4 2</td>
<td>$3A_y + 3B_x + 3A_u + 3B_u$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(2)</td>
<td>4e</td>
<td>x,y 1/4 2</td>
<td>$3A_y + 3B_x + 3A_u + 3B_u$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>X(3)</td>
<td>4e</td>
<td>x,y 1/4 2</td>
<td>$3A_y + 3B_x + 3A_u + 3B_u$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 atoms/unit cell ($Z=4$)</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$15A_y + 15A_x + 15B_{1g} + 15B_{1u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>no silent mode</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A_{1u} + 2B_{1u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$14A_u + 13B_u$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$15A_y + 15B_{1g}$</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2: Phonon frequencies $\omega$ in cm$^{-1}$, oscillator strength $S$ in a.u. with 1 a.u = 253 m$^3$/s$^2$, generalized Lyddane-Sachs-Teller relation and dielectric constants in $\alpha$-CsSnX$_3$. These dielectric constants $\varepsilon_\infty$ differ from the ones in Table 2.9 because they are obtained from the DFPT at the LDA level, instead of from GW.

<table>
<thead>
<tr>
<th>mode</th>
<th>TO</th>
<th>LO</th>
<th>$S$</th>
<th>$\omega_L/\omega_T$</th>
<th>$\Pi_i \left( \frac{\omega_L}{\omega_T} \right)^2$</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_\infty$</th>
<th>$\varepsilon_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsSnCl$_3$</td>
<td>$T_1^{\text{u}}$</td>
<td>25</td>
<td>32</td>
<td>$1.4 \times 10^{-5}$</td>
<td>1.311</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_2^{\text{u}}$</td>
<td>76</td>
<td>78</td>
<td>$1.3 \times 10^{-5}$</td>
<td>1.029</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_3^{\text{u}}$</td>
<td>121</td>
<td>243</td>
<td>$2.9 \times 10^{-4}$</td>
<td>2.003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_2$</td>
<td>53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsSnBr$_3$</td>
<td>$T_1^{\text{u}}$</td>
<td>19</td>
<td>26</td>
<td>$1.1 \times 10^{-5}$</td>
<td>1.381</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_2^{\text{u}}$</td>
<td>59</td>
<td>69</td>
<td>$3.7 \times 10^{-5}$</td>
<td>1.165</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_3^{\text{u}}$</td>
<td>108</td>
<td>183</td>
<td>$1.6 \times 10^{-4}$</td>
<td>1.697</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_2$</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsSnI$_3$</td>
<td>$T_1^{\text{u}}$</td>
<td>12</td>
<td>18</td>
<td>$9.5 \times 10^{-6}$</td>
<td>1.483</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_2^{\text{u}}$</td>
<td>45</td>
<td>63</td>
<td>$5.5 \times 10^{-5}$</td>
<td>1.412</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_3^{\text{u}}$</td>
<td>101</td>
<td>152</td>
<td>$1.1 \times 10^{-4}$</td>
<td>1.506</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_2$</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Born effective charges in $\alpha$-CsSnX$_3$ obtained within DFPT, in units of e.

<table>
<thead>
<tr>
<th></th>
<th>Cs</th>
<th>Sn</th>
<th>$X_{\parallel}$</th>
<th>$X_{\perp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsSnCl$_3$</td>
<td>1.162</td>
<td>4.462</td>
<td>$-3.471$</td>
<td>$-1.077$</td>
</tr>
<tr>
<td>CsSnBr$_3$</td>
<td>1.109</td>
<td>4.701</td>
<td>$-3.295$</td>
<td>$-1.258$</td>
</tr>
<tr>
<td>CsSnI$_3$</td>
<td>1.060</td>
<td>4.954</td>
<td>$-3.110$</td>
<td>$-1.452$</td>
</tr>
</tbody>
</table>
those in the previous chapter (see Table 2.9). This is not surprising because they are  
only obtained in a rather different manner, namely, from the polarization in response to a  
static electric field and only including electronic contributions and are calculated via the Berry phase method. In the previous chapter they were obtained from the  
low-frequency limit of the polarizability calculated as function of frequency in the  
region above the band gap. Furthermore that calculation was based on the QSGW band structure, while the present one uses the LDA band structure. In view of  
these widely different approaches, the agreement between the two can be viewed as  
satisfactory and certainly sufficient for our present main purpose of estimating the  
exciton binding energies in the previous chapter.

Figure 3.1 shows our simulated infrared spectra in cubic phase CsSnX₃. We will  
compare the results with experimental data in the next section.

Table 3.4 and Table 3.5 shows all zone center phonons for β-CsSnI₃ and β-  
CsSnBr₃, respectively. Please notice that \( E_{1}^{u} \) phonons are soft phonons in both  
β-CsSnI₃ and β-CsSnBr₃. The soft phonons make it difficult to calculate static dielectric constants and simulate infrared spectra. Here, we neglect the soft \( E_{u} \) mode and simulate the IR spectra in Fig. 3.2 for β-CsSnI₃ and Fig. 3.3 for β-CsSnBr₃. As in the cubic case, from these figures we can see that LO phonons contribute to the IR absorption spectra. High frequency dielectric constants are shown in Table 3.6. Unfortunately, no experimental data related to this phase can be found. We show the displacement pattern of the \( E_{1}^{u} \) soft phonon in the Fig. 3.4. We can see that this mode is dominated by the motions of the Cs atoms, so it cannot result in the \( \gamma \) phase (As we will show in Fig. 5.1, the soft phonon at \( Z \), denoted by \( Z_{5}^{-} \), has a bigger imaginary value and is responsible for the phase transition from \( \beta \)- to \( \gamma \)-phase; we will discuss this in Chapter 5).

As for the Raman active modes, we can see from Table 3.4 and Table 3.5 that there  
are four Raman active modes belonging to different irreducible representations. Upon
Figure 3.1: The real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\alpha$-CsSnI$_3$ (top), $\alpha$-CsSnBr$_3$ (middle) and $\alpha$-CsSnCl$_3$ (bottom).
closer inspection of the Raman tensor for each symmetry, we find that the Raman
tensor of each symmetry can be written in the following form

\[ A_{1g} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}, \]  
(3.27)

\[ E_g = \begin{bmatrix} 0 & 0 & c \\ 0 & 0 & c \\ c & c & 0 \end{bmatrix}, \]  
(3.28)

\[ B_{2g} = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \]  
(3.29)

\[ B_{1g} = \begin{bmatrix} -e & 0 & 0 \\ 0 & e & 0 \\ 0 & 0 & 0 \end{bmatrix}, \]  
(3.30)

where \( a, b, c, d, e \) are components of Raman tensors. According to Raman
tensors shown above, one can observe the \( E_g, B_{2g}, \) and \( A_{1g}(zz) \) modes by, for example,
\( \vec{y}(x,z)y, \vec{z}(x,y)z, \) and \( \vec{x}(z,z)x \) configurations, where we use the Porto’s notation
to specify Raman configurations. In Porto’s notation, \( k_0(e_0,e_s)k_s, \) incident light
is parallel to the \( k_0 \) direction with polarization in the \( e_0 \) direction, and one detects
scattered light which propagates in the \( k_s \) direction with the analyzer oriented parallel
to the $e_x$ direction. However, if we use the $\tilde{\varepsilon}(x,x)z$ configuration, we will see both $A_{1g}(xx)$ and $B_{1g}(xx)$ modes. We simulate the Raman spectrum in this configuration in Fig. 3.5. Because there is only one peak for $E_g$, $B_{2g}$, and $A_{1g}(zz)$ modes, it is unnecessary to simulate Raman spectra for those modes.

Table 3.4: Zone center phonons of $\beta$-CsSnI$_3$. All frequencies are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th>mode</th>
<th>freq</th>
<th>Oscillator strengths (in a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$x$ or $y$ ($E_u$(LO))</td>
</tr>
<tr>
<td>Raman</td>
<td></td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_g$</td>
</tr>
<tr>
<td>IR</td>
<td></td>
<td>$A_{2u}^1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_{2u}^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_{2u}^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_u^1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_u^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_u^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_u^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_u^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_u^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_u^7$</td>
</tr>
<tr>
<td>Silent</td>
<td></td>
<td>$A_{1u}^1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_{1u}^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_{2u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{1u}^1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{1u}^2$</td>
</tr>
</tbody>
</table>

Tables 3.7, 3.8, and 3.9 show the silent, Raman active, and infrared active phonon frequencies for $\gamma$-CsSnI$_3$ and $Y$-CsSnI$_3$, respectively. We simulate IR and Raman spectra for $\gamma$-CsSnI$_3$ and $Y$-CsSnI$_3$ in Figs. 3.6, 3.7, and 3.8. In Table 3.10, we list calculated static dielectric constant $\varepsilon_0$ and the high-frequency dielectric constant $\varepsilon_\infty$ and check the Lyddane-Sachs-Teller relation for $\gamma$-CsSnI$_3$ and $Y$-CsSnI$_3$. These materials show large LO-TO splittings and, hence, have large static dielectric constants. Again, LO phonons can be seen in IR absorption spectra, just as in the cubic
Table 3.5: Zone center phonons of $\beta$-CsSnBr$_3$. All frequencies are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th>mode</th>
<th>freq</th>
<th>Oscillator strengths (in a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>with non-analyticity in $x$ or $y$ ($E_u$(LO)) or $A_{2u}$(LO) $S_{xx}$ or $S_{yy}$ $S_{zz}$</td>
</tr>
<tr>
<td>Raman</td>
<td>$A_{1g}$</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>$B_{1g}$</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td>$B_{2g}$</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>$E_g$</td>
<td>58</td>
</tr>
<tr>
<td>IR</td>
<td>$A_{2u}^1$</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>$A_{2u}^2$</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>$A_{2u}^3$</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>$E_u^1$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>$E_u^2$</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>$E_u^3$</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>$E_u^4$</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>$E_u^5$</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>$E_u^6$</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>$E_u^7$</td>
<td>127</td>
</tr>
<tr>
<td>Silent</td>
<td>$A_{1u}^1$</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>$A_{1u}^2$</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>$A_{2g}$</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>$B_{1u}^1$</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>$B_{1u}^2$</td>
<td>72</td>
</tr>
</tbody>
</table>

Table 3.6: The high-frequency dielectric constant $\varepsilon_\infty$ of $\beta$-CsSnBr$_3$ and $\beta$-CsSnI$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\parallel x \parallel$</td>
</tr>
<tr>
<td>$\beta$-CsSnBr$_3$</td>
<td>6.99</td>
</tr>
<tr>
<td>$\beta$-CsSnI$_3$</td>
<td>8.02</td>
</tr>
</tbody>
</table>
Figure 3.2: The real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\beta$-CsSnI$_3$ when non-analyticity is applied in the $x$- or $y$-direction ($E_u$, top figure) and in the $z$-direction ($A_{2u}$, bottom figure). Please note that we omit the soft $E_u$ mode.
Figure 3.3: The real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\beta$-CsSnBr$_3$ when non-analyticity is applied in the $x$- or $y$-direction ($E_u$, top figure) and in the $z$-direction ($A_{2u}$, bottom figure). Please note that we omit the soft $E_u$ mode.
Figure 3.4: The displacement pattern of the soft phonon $E_{1u}^1$ in $\beta$-CsSnI$_3$. The green spheres are Cs atoms, the grey ones are Sn atoms, and the purple ones are I atoms. The displacements of Cs atoms are represented by green arrows, while the displacements of I atoms are represented by purple arrows.
Figure 3.5: Predicted Raman spectra of $\beta$-CsSnBr$_3$ (red line) and $\beta$-CsSnI$_3$ (blue line) in the $\bar{z}(x,x)z$ configuration. In each spectrum, the lower frequency mode is the $A_{1g}$ mode with stronger intensity while the higher frequency mode is $B_{1g}$ modes with weaker intensity. Two $A_{1g}$ peaks in two materials are scaled to equalize intensity.
Table 3.7: Silent modes ($A_u$) of $\gamma$-CsSnI$_3$ and Y-CsSnI$_3$. All frequencies are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$-CsSnI$_3$</th>
<th></th>
<th>$Y$-CsSnI$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mode</td>
<td>frequency</td>
<td>mode</td>
<td>frequency</td>
</tr>
<tr>
<td>$A^4_{u}$</td>
<td>23</td>
<td>$A^4_{u}$</td>
<td>22</td>
</tr>
<tr>
<td>$A^2_{u}$</td>
<td>31</td>
<td>$A^2_{u}$</td>
<td>48</td>
</tr>
<tr>
<td>$A^3_{u}$</td>
<td>35</td>
<td>$A^3_{u}$</td>
<td>52</td>
</tr>
<tr>
<td>$A^4_{u}$</td>
<td>37</td>
<td>$A^4_{u}$</td>
<td>63</td>
</tr>
<tr>
<td>$A^5_{u}$</td>
<td>58</td>
<td>$A^5_{u}$</td>
<td>80</td>
</tr>
<tr>
<td>$A^6_{u}$</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A^7_{u}$</td>
<td>78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A^8_{u}$</td>
<td>113</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and tetragonal phases. Interestingly, even though we have so many more modes, the IR absorption spectrum in a particular direction shows an even smaller number of peaks than in the cubic case, for example, the IR absorption spectra of the $B_{3u}$ (3 peaks) and the $B_{1u}$ (4 peaks) in $\gamma$-CsSnI$_3$. The IR spectra of $\gamma$-CsSnI$_3$ are similar to those of $\beta$-CsSnI$_3$, which probably originates from the similar crystal structures of these two phases. But the IR spectra of $\gamma$- and $Y$-CsSnI$_3$ are quite different; for example, peaks are well separated in the $B_{1u}$ and the $B_{3u}$ IR spectra of $\gamma$-CsSnI$_3$.

Another interesting point is that the strongest IR absorption peak in each direction in $\gamma$ phase is less than 100 cm$^{-1}$, while the strongest peak can be higher than 100 cm$^{-1}$ in $Y$ phase. This interesting point can also be observed in their Raman spectra.

From Fig. (3.8), we can see that it is hard to observe high frequency modes (above 100 cm$^{-1}$) in $\gamma$ phase (the strongest Raman mode is $B^5_{2g}$ at 61 cm$^{-1}$). However, it is easier to observe high frequency mode (above 100 cm$^{-1}$) in $Y$ phase, whose strongest mode is $A^9_y$ at 116 cm$^{-1}$. 
Table 3.8: Raman active phonon modes of $\gamma$-CsSnI$_3$ and Y-CsSnI$_3$. All frequencies are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$-CsSnI$_3$ mode</th>
<th>frequency</th>
<th>Y-CsSnI$_3$ mode</th>
<th>frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1^g$</td>
<td>27</td>
<td>$A_1^g$</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>$A_2^g$</td>
<td>29</td>
<td>$A_2^g$</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>$A_3^g$</td>
<td>35</td>
<td>$A_3^g$</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$A_4^g$</td>
<td>46</td>
<td>$A_4^g$</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>$A_5^g$</td>
<td>59</td>
<td>$A_5^g$</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>$A_6^g$</td>
<td>68</td>
<td>$A_6^g$</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>$A_7^g$</td>
<td>101</td>
<td>$A_7^g$</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_8^g$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_9^g$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_{10}^g$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_1^g$</td>
<td>37</td>
<td>$B_1^g$</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>$B_2^g$</td>
<td>42</td>
<td>$B_2^g$</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>$B_3^g$</td>
<td>63</td>
<td>$B_3^g$</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>$B_4^g$</td>
<td>101</td>
<td>$B_4^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_5^g$</td>
<td>110</td>
<td>$B_5^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_6^g$</td>
<td>72</td>
<td>$B_6^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_7^g$</td>
<td>112</td>
<td>$B_7^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_8^g$</td>
<td>91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_9^g$</td>
<td>117</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{10}^g$</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_1^{2g}$</td>
<td>30</td>
<td>$B_1^{2g}$</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>$B_2^{2g}$</td>
<td>35</td>
<td>$B_2^{2g}$</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>$B_3^{2g}$</td>
<td>39</td>
<td>$B_3^{2g}$</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>$B_4^{2g}$</td>
<td>49</td>
<td>$B_4^{2g}$</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>$B_5^{2g}$</td>
<td>61</td>
<td>$B_5^{2g}$</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>$B_6^{2g}$</td>
<td>72</td>
<td>$B_6^{2g}$</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>$B_7^{2g}$</td>
<td>112</td>
<td>$B_7^{2g}$</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>$B_8^{2g}$</td>
<td></td>
<td>$B_8^{2g}$</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>$B_9^{2g}$</td>
<td></td>
<td>$B_9^{2g}$</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>$B_{10}^{2g}$</td>
<td></td>
<td>$B_{10}^{2g}$</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>$B_1^{3g}$</td>
<td>39</td>
<td>$B_1^{3g}$</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>$B_2^{3g}$</td>
<td>45</td>
<td>$B_2^{3g}$</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>$B_3^{3g}$</td>
<td>68</td>
<td>$B_3^{3g}$</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>$B_4^{3g}$</td>
<td>103</td>
<td>$B_4^{3g}$</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>$B_5^{3g}$</td>
<td>114</td>
<td>$B_5^{3g}$</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.9: Infrared active phonon modes of $\gamma$-CsSnI$_3$ and $Y$-CsSnI$_3$. All TO and LO phonon frequencies are in units of cm$^{-1}$. OS means oscillator strengths (in a. u.). $B_{1u}$(LO), $B_{2u}$(LO), and $B_{3u}$(LO) phonon frequencies are obtained when we apply an non-analyticity in z-direction ($a_3$), y-direction ($a_2$), and x-direction ($a_1$), respectively, where $a_1$, $a_2$, and $a_3$ are primitive unit vectors. Therefore, oscillator strengths of $B_{1u}$ modes are in z-direction ($S_{zz}$), $B_{2u}$ modes are in y-direction ($S_{yy}$), and $B_{3u}$ modes are in x-direction ($S_{xx}$).

| Mode | $\gamma$-CsSnI$_3$ | | | | $Y$-CsSnI$_3$ | | | |
|-------|-----------------|---|---|---|-----------------|---|---|
|       | TO   | LO   | OS   |   | TO   | LO   | OS   |
| $B_{1u}^1$ | 25 | 25 | $2.0 \times 10^{-5}$ | | $B_{1u}^1$ | 22 | 22 | $7.4 \times 10^{-7}$ |
| $B_{1u}^2$ | 34 | 34 | $2.1 \times 10^{-7}$ | | $B_{1u}^2$ | 37 | 39 | $1.5 \times 10^{-5}$ |
| $B_{1u}^3$ | 41 | 41 | $1.6 \times 10^{-6}$ | | $B_{1u}^3$ | 58 | 58 | $2.0 \times 10^{-6}$ |
| $B_{1u}^4$ | 49 | 51 | $1.6 \times 10^{-4}$ | | $B_{1u}^4$ | 64 | 65 | $1.0 \times 10^{-5}$ |
| $B_{1u}^5$ | 53 | 54 | $6.1 \times 10^{-5}$ | | $B_{1u}^5$ | 71 | 74 | $3.9 \times 10^{-5}$ |
| $B_{1u}^6$ | 59 | 68 | $6.8 \times 10^{-4}$ | | $B_{1u}^6$ | 83 | 84 | $2.1 \times 10^{-5}$ |
| $B_{1u}^7$ | 68 | 108 | $1.2 \times 10^{-9}$ | | $B_{1u}^7$ | 86 | 87 | $8.0 \times 10^{-6}$ |
| $B_{1u}^8$ | 112 | 115 | $3.1 \times 10^{-5}$ | | $B_{1u}^8$ | 115 | 118 | $1.3 \times 10^{-4}$ |
| $B_{1u}^9$ | 116 | 131 | $6.0 \times 10^{-6}$ | | $B_{1u}^9$ | 123 | 142 | $1.3 \times 10^{-4}$ |
| $B_{2u}^1$ | 27 | 29 | $2.1 \times 10^{-5}$ | | $B_{2u}^1$ | 35 | 35 | $8.3 \times 10^{-7}$ |
| $B_{2u}^2$ | 33 | 34 | $1.5 \times 10^{-5}$ | | $B_{2u}^2$ | 61 | 64 | $3.5 \times 10^{-4}$ |
| $B_{2u}^3$ | 43 | 43 | $1.4 \times 10^{-5}$ | | $B_{2u}^3$ | 67 | 79 | $3.1 \times 10^{-4}$ |
| $B_{2u}^4$ | 61 | 63 | $1.1 \times 10^{-4}$ | | $B_{2u}^4$ | 79 | 125 | $7.1 \times 10^{-6}$ |
| $B_{2u}^5$ | 66 | 66 | $3.0 \times 10^{-6}$ | | | | |
| $B_{2u}^6$ | 75 | 106 | $5.9 \times 10^{-4}$ | | | | |
| $B_{2u}^7$ | 107 | 145 | $2.5 \times 10^{-5}$ | | | | |
| $B_{3u}^1$ | 27 | 30 | $1.9 \times 10^{-4}$ | | $B_{3u}^1$ | 35 | 35 | $4.7 \times 10^{-6}$ |
| $B_{3u}^2$ | 33 | 38 | $1.2 \times 10^{-4}$ | | $B_{3u}^2$ | 37 | 37 | $4.5 \times 10^{-6}$ |
| $B_{3u}^3$ | 42 | 43 | $2.7 \times 10^{-5}$ | | $B_{3u}^3$ | 39 | 39 | $2.2 \times 10^{-6}$ |
| $B_{3u}^4$ | 45 | 46 | $1.6 \times 10^{-5}$ | | $B_{3u}^4$ | 66 | 68 | $2.9 \times 10^{-5}$ |
| $B_{3u}^5$ | 54 | 54 | $1.6 \times 10^{-5}$ | | $B_{3u}^5$ | 76 | 77 | $1.9 \times 10^{-5}$ |
| $B_{3u}^6$ | 62 | 69 | $8.1 \times 10^{-4}$ | | $B_{3u}^6$ | 78 | 80 | $2.3 \times 10^{-5}$ |
| $B_{3u}^7$ | 69 | 106 | $1.0 \times 10^{-4}$ | | $B_{3u}^7$ | 88 | 88 | $4.7 \times 10^{-6}$ |
| $B_{3u}^8$ | 106 | 115 | $5.2 \times 10^{-6}$ | | $B_{3u}^8$ | 109 | 132 | $2.4 \times 10^{-4}$ |
| $B_{3u}^9$ | 115 | 133 | $8.7 \times 10^{-7}$ | | $B_{3u}^9$ | 141 | 141 | $1.4 \times 10^{-7}$ |
Figure 3.6: Figures, from top to bottom, show the real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $\gamma$-CsSnI$_3$ in the x-direction ($B_{3u}$), y-direction ($B_{2u}$), and z-direction ($B_{1u}$), respectively.
Figure 3.7: Figures, from top to bottom, show the real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $Y$-CsSn$_3$I$_3$ in the x-direction ($B_{3u}$), y-direction ($B_{2u}$), and z-direction ($B_{1u}$), respectively.
Figure 3.8: The upper figure shows the simulated Raman spectra of $\gamma$-CsSnI$_3$, while the lower one shows the simulated Raman spectra of Y-CsSnI$_3$. The different tensor components are scaled by different factors so as to normalize their strongest peak.
Table 3.10: The static dielectric constant $\varepsilon_0$ and the high-frequency dielectric constant $\varepsilon_\infty$ and generalized Lyddane-Sachs-Teller relation in $\gamma$-CsSnI$_3$, Y-CsSnI$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_\infty$</th>
<th>$\frac{\varepsilon_0}{\varepsilon_\infty}$</th>
<th>$\Pi_i \left(\frac{\omega_{\Gamma,i}}{\omega_{\gamma,i}}\right)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-CsSnI$_3$</td>
<td>76.1/9.43</td>
<td>25.1/5.29</td>
<td>42.3/7.99</td>
<td>8.08</td>
</tr>
<tr>
<td>Y-CsSnI$_3$</td>
<td>10.3/5.51</td>
<td>24.4/6.33</td>
<td>10.6/5.54</td>
<td>1.87</td>
</tr>
</tbody>
</table>

3.3.3 Comparison with IR experimental data for $\alpha$-CsSnCl$_3$ and $\alpha$-CsSnBr$_3$

The experimental data on the phonon spectra of these materials are rather scarce. For the cubic phase, in particular, there are no allowed Raman active modes. Group theory analysis shows that there are three $T_{1u}$ modes (IR active) and one silent $T_{2u}$ mode at $\Gamma$. As far as infrared studies, we found only one study for $\alpha$-CsSnBr$_3$ and CsSnCl$_3$ [80]. Unfortunately, this paper only gives a table of the modes but shows no actual spectra. The results are said to be obtained from absorption measurements on powders. The paper does not mention anything about TO-LO splittings and since they measured absorption, one would assume that these correspond to the TO-modes. A direct comparison with our calculated results in this (as will be shown later erroneous) interpretation is shown in Table 3.11 and shows discrepancies from 50 % to 72 %.

We note that the LDA underestimate of the unit cell volume may lead to an overestimate of the phonon frequencies, in particular for bond-stretch modes. To investigate this further we have calculated the fractional change in phonon frequency per fractional change in lattice volume, i.e. the mode-Grüneisen parameters, $\gamma_i = d\ln \omega_i / d\ln V$. These are also included in Table 3.11. We note that correcting the volume would shift our phonon frequencies down (except for $T_{1u}$ (TO) phonons), thus
worsening the agreement with experiment. From Table 3.11, we noted that the comparison is better between our second and third modes with their first and second modes. However, this requires explaining why the first mode was not observed and what is the higher observed third mode. We already showed in the previous section, see Table 3.2, that the oscillator strength for the lowest mode is smaller than the second one by a factor 6 in CsSnI₃ and by a factor 4 in CsSnBr₃ but not in CsSnCl₃ where they are predicted to be about equal.

To further investigate these questions, we calculated infrared spectra even though at present we have no experimental curves to compare with. Figures 3.1 shows the first-principles calculated real part and imaginary part of the dielectric function, $\varepsilon$, the imaginary part of $-1/\varepsilon$, the absorption coefficient and the normal incidence reflectivity of $\alpha$-CsSnX₃. As is well known, the peaks in the Im{$\varepsilon$} corresponds to the TO phonons while the peaks in $-\text{Im}\{\varepsilon^{-1}\}$ correspond to the LO phonons. We can see that the LO–TO splitting is negligible for the lowest $T^{(1)}_{1u}$ mode, which is consistent with its weak oscillator strength. For the second mode, the LO mode shows up in the absorption curves only as a weak shoulder for CsSnBr₃ and as a slight asymmetry of the peak in CsSnCl₃. Interestingly, the LO–TO splitting of this mode is largest for CsSnI₃ but no IR-data are available for this material. However,

Table 3.11: Direct (but erroneous) comparison of our calculated TO phonon frequencies (cal.) with experimental results (exp.) from Donaldson et al. [80]. The last column gives the mode-Grüneisen parameters. All frequencies are in units of cm⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>mode</th>
<th>cal.</th>
<th>exp.</th>
<th>error</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-CsSnBr₃</td>
<td>$T^{1}_{1u}$ (TO)</td>
<td>19</td>
<td>68</td>
<td>72 %</td>
<td>-8.6</td>
</tr>
<tr>
<td></td>
<td>$T^{2}_{1u}$ (TO)</td>
<td>59</td>
<td>118</td>
<td>50 %</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>$T^{3}_{1u}$ (TO)</td>
<td>108</td>
<td>218</td>
<td>50 %</td>
<td>-4.3</td>
</tr>
<tr>
<td>$\alpha$-CsSnCl₃</td>
<td>$T^{1}_{1u}$ (TO)</td>
<td>25</td>
<td>70</td>
<td>64 %</td>
<td>-7.7</td>
</tr>
<tr>
<td></td>
<td>$T^{2}_{1u}$ (TO)</td>
<td>76</td>
<td>172</td>
<td>56 %</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>$T^{3}_{1u}$ (TO)</td>
<td>121</td>
<td>310</td>
<td>61 %</td>
<td>-5.2</td>
</tr>
</tbody>
</table>
the third $T_{1u}^{(3)}$ shows clearly separated LO and TO peaks in absorption. Noticing that the absorption coefficient is given by:

$$
\alpha(\omega) = \frac{2\omega \text{Im}\{\epsilon(\omega)\}}{n(\omega)c}
$$

(3.31)

with $c$ the speed of light, it becomes clear that the peaks in absorption can also correspond to a zero or minimum in the index of refraction $n(\omega) = \text{Re}\{\sqrt{\epsilon}\}$ and this explains the highest peak in the experimental absorption spectrum as an LO-mode. Thus it becomes clear that the three peaks observed in the experiment are respectively, the $T_{1u}^{(2)}$ mode (averaged over TO and LO), the $T_{1u}^{(3)}(TO)$ and $T_{1u}^{(3)}(LO)$ modes.

From the Fig. 3.1, it appears however that the $T_{1u}^{(1)}$ mode has comparable intensity in absorption to the $T_{1u}^{(2)}$ mode. However, in constructing these spectra we used the same broadening for each peak. As showing in Figs. 5.2 and 5.3 we can see that the lowest mode at the Γ-point coincides with a sharp peak in phonon DOS whereas the second peak lies in a region of lower density of states (especially for CsSnBr₃). Thus we expect strong phonon-phonon scattering (or an-harmonic effects) on this mode may lead to a short lifetime or strong broadening. This would strongly reduce the peak height and might explain why this mode was not observed in the experimental absorption spectrum [80]. We can see that this mode corresponds to an almost dispersionless band corresponding to the Cs motion relative to the SnI₆ octahedron and is dominated by the Cs motion. The final comparison with experimental data using this interpretation is shown in Table 3.12. The maximum error is now reduced to 30% and occurs for the $T_{1u}^{(3)}(TO)$ mode of CsSnCl₃. The origin of this discrepancy is difficult to ascertain without reliable experimental spectra. We note that the LO-mode in both materials appears to be underestimated by our calculation. This is addressed in the next section.
Table 3.12: Comparison of our calculated phonon frequencies (cal.) with experimental results (exp.) from Donaldson et al. [80]. All frequencies are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th>mode</th>
<th>cal.</th>
<th>exp.</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-CsSnBr$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{1u}^1$(TO-LO)</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{1u}^2$(TO-LO)</td>
<td>64</td>
<td>68</td>
<td>6 %</td>
</tr>
<tr>
<td>$T_{1u}^3$(TO)</td>
<td>108</td>
<td>118</td>
<td>8 %</td>
</tr>
<tr>
<td>$T_{1u}^3$(LO)</td>
<td>184</td>
<td>218</td>
<td>16 %</td>
</tr>
<tr>
<td>$\alpha$-CsSnCl$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{1u}^1$(TO-LO)</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{1u}^2$(TO-LO)</td>
<td>77</td>
<td>70</td>
<td>10 %</td>
</tr>
<tr>
<td>$T_{1u}^3$(TO)</td>
<td>121</td>
<td>172</td>
<td>30 %</td>
</tr>
<tr>
<td>$T_{1u}^3$(LO)</td>
<td>246</td>
<td>310</td>
<td>21 %</td>
</tr>
</tbody>
</table>

3.3.4 LO-plasmon coupling effect

Although we could not find IR absorption data in the literature for CsSnI$_3$, Yu et al. [31] measured the Raman spectrum for $\gamma$-CsSnI$_3$. In Figure 1 of their paper, the Raman spectrum shows two peaks located at 258 and 472 cm$^{-1}$, respectively. They claimed the first peak is from the first-order LO phonon scattering, while the second peak is from the triply enhanced second-order Raman scattering. Comparing the experimental spectra with our simulated first order allowed Raman spectra for $\gamma$-CsSnI$_3$, see Fig. 3.8, we agree that the observed Raman spectra do not result from the first order allowed Raman modes mainly because the strongest calculated Raman peak is only at 61 cm$^{-1}$ ($B_{2g}^5$) far from the observed 258 or 472 cm$^{-1}$. Although we have already mentioned that in $\alpha$-CsSnI$_3$ none of the modes are Raman active, Raman active modes exist in the $\gamma$-phase or could be observed as LO-forbidden modes [81; 82] by means of the Fröhlich mechanism. This makes sense because the gap of the material is rather low (1.3 eV) and thus the lasers used in Raman spectroscopy in Ref. [31] are above the gap which leads to resonantly enhanced Raman scattering even for the first order Raman scattering. The resonant Raman effect is well known
to enhance the intensity of forbidden LO-modes. We also may note that because the
\( \beta \) and \( \gamma \) phases still have an inversion center, the modes derived from the \( \alpha \)-phase
\( T_{1u} \) modes remain odd with respect to inversion and therefore Raman inactive even
in the \( \beta \) and \( \gamma \) phases. The only Raman active modes in those materials will arise
from new modes at the zone center arising from folded zone-edge modes.

However, with this interpretation, there appears again to be a large discrepancy
between the measured value of the frequency, \( 258 \text{ cm}^{-1} \), and our calculated \( T^{3}_{1u}(\text{LO}) \)
mode at \( 152 \text{ cm}^{-1} \) in \( \alpha \) phase or \( B^{2}_{2u}(\text{LO}) \) at \( 145 \text{ cm}^{-1} \) in \( \gamma \) phase (see Fig. 3.6). As
we can see, this highest mode is not significantly shifting from the \( \alpha \) to \( \gamma \) phases.
The discrepancy is \( 41 \% \) and thus larger than for CsSnBr\textsubscript{3} or CsSnCl\textsubscript{3} discussed
in the previous section but we note that in all cases, our calculations appear to
underestimate the LO-mode.

Since these materials, in particular CsSnI\textsubscript{3} are known to be rather conductive by
unintentional p-type doping, we test the hypothesis that this shift could arise from
LO-plasmon coupling. The plasmon frequency can be written:

\[
\omega_p = \sqrt{\frac{4\pi ne^2}{m^*\varepsilon_\infty}},
\]

where \( n \) is the concentration of carriers, \( e \) is the electric charge, \( m^* \) is effective mass
of the carrier, and \( \varepsilon_\infty \) is the high-frequency dielectric constant in the material. In
the present case, the carriers are holes; we have calculated the effective mass of hole
and the high-frequency dielectric constant before and obtained \( m^* = 0.069 \ m_e \) and
\( \varepsilon_\infty = 4.86 \) for \( \alpha \)-CsSnI\textsubscript{3}. The remaining unknown physical quantity is the concentra-
tion of holes, \( n \). Fortunately, in the paper from Chung \textit{et al.} [6], they measured
the concentration of carriers and reported carrier concentration of about \( 10^{17} \ \text{cm}^{-3} \)
for CsSnI\textsubscript{3} at room temperature. If \( n \) goes from \( 10^{16} \) to \( 10^{18} \ \text{cm}^{-3} \), \( \omega_p \) changes as
function of \( \sqrt{n} \) from 52 to 517 cm\textsuperscript{-1}, which is comparable to the frequency of the
LO phonon modes. Thus we expect strong LO-plasmon coupling. We note that the low phonon frequencies (due to the heavy masses of the ions involved) conspire with the unusually low hole mass and low high-frequency dielectric constant in this material to produce comparable LO and plasmon frequencies even for moderate carrier concentration. We are now in a position to calculate the frequency of LO-plasmon coupled mode, denoted by $\omega_{LO-p}$. The dielectric function in the presence of the free carriers in a semiconductor is [83]

$$
\epsilon (\omega) = \epsilon_\infty \left( 1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2} - \frac{\omega_p^2}{\omega^2} \right).
$$

(3.33)

By solving the equation $\epsilon (\omega)=0$, we obtain

$$
\omega_{LO-p}^2 = \frac{1}{2} \left( \omega_{LO}^2 + \omega_p^2 \right)
$$

$$
\pm \left[ \frac{1}{4} \left( \frac{\omega_{LO}^2 + \omega_p^2}{\omega_{TO}} \right)^2 - \omega_{TO}^2 \omega_p^2 \right].
$$

(3.34)

Using our calculated $\omega_{TO} = 101$ cm$^{-1}$ and $\omega_{LO} = 152$ cm$^{-1}$ and other constants as mentioned above, we find that for hole concentrations from $10^{16}$ to $10^{18}$ cm$^{-3}$, $\omega_{LO-p}$ varies from 157 to 530 cm$^{-1}$. Clearly, this range encompasses the experimental value of 258 cm$^{-1}$, which in this model would correspond to a plausible carrier concentration of $1.92 \times 10^{17}$ cm$^{-3}$. In this case, the upper LO-plasmon coupled mode is more plasmon than LO-like. Unfortunately, we do not know independent measurements of the carrier concentration in the samples used in Ref. [31]. Our interpretation predicts that the Raman spectra could shift significantly with carrier concentration. Furthermore, In Chung et al. [6] already showed that significant changes in carrier concentration can be induced by high-temperature annealing because this creates more hole generating acceptor native defect states. We thus propose that our interpretation could be tested by measuring the Raman spectrum after annealing treatments.
Obviously, the LO-plasmon coupling effect is also expected to occur in CsSnBr$_3$ and CsSnCl$_3$ and could therefore also explain our underestimation of the LO mode when compared to the highest observed IR absorption peak. Since the highest LO mode involved in this LO-plasmon effect is a breathing mode of the octahedra, it should also be applicable to the hybrid halide perovskites.

### 3.4 Conclusions

In this chapter, we presented zone center phonon frequencies with symmetry studies and a simulation of the infrared (in the form of reflectivity, absorption and dielectric functions) and Raman spectra for CsSnX$_3$, X=I, Br, Cl for various structures. We also presented results for the static and high frequency dielectric constants. These materials have strong LO–TO splittings, which result in large static dielectric constants.

We interpreted the few available experimental data on $\alpha$-CsSnBr$_3$ and $\alpha$-CsSnCl$_3$. The three reported experimental frequencies correspond to the $T_{1u}^{(2)}(TO - LO)$ average mode, $T_{1u}^{(3)}(TO)$ and $T_{1u}^{(3)}(LO)$ modes, respectively. The lowest mode $T_{1u}^{(1)}$ at approximately 20-30 cm$^{-1}$ is shown to have low oscillator strength, low LO-TO splitting, and is expected to have a short lifetime due to coincidence with a strong peak in phonon density of states, which would broaden the transition to the extent that it becomes difficult or impossible to detect. It involves mostly the motion of the heavy Cs ion, which, in some sense, is rattling about in its too large cage. This sluggish mode is possibly of interest for thermoelectric properties because it could strongly suppress thermal conductivity. Furthermore we pointed out that in these materials a strong LO-hole-plasmon coupling can be expected because of the relatively high plasmon frequency related to the low hole mass and low high-frequency dielectric constant and low LO-phonon frequency even for moderately low carrier concentrations on the
order of $10^{17}$ cm$^{-3}$. 
Chapter 4

Zone center phonons II:
First-principles calculations of phonons and Raman spectra in monoclinic CsSnCl$_3$

4.1 Introduction

Besides the perovskite structure, which has only corner sharing octahedra, some of these materials, also possess structures in which octahedra share edges. We already showed in Chapter 1 that the so-called yellow phase in CsSnI$_3$ and the monoclinic CsSnCl$_3$ phases have very different band structures, with higher band gaps, and are hence less suitable for solar cell applications. Nonetheless, a better understanding of the lattice dynamics of these phases and their relation to the perovskite structure are important for the stability of the latter.

In this chapter, we present a study of the zone center phonons for monoclinic $M$-CsSnCl$_3$. These results were published previously in Phys. Rev. B 91, 075206
with the exception of Fig. 4.5 and the associated discussion in the text. Extensive experimental data are available in literature on the Raman spectra in this material but they have not been compared in detail with first-principles calculations.

While CsSnCl$_3$ in the perovskite structure is less suitable for solar cells because of its higher band gap than the CsSnI$_3$, it is still of interest as the end member of mixed CsSn(I$_{1-x}$Cl$_x$)$_3$ and addition of Cl has been found to increase solar cell efficiencies [9]. The reasons for this are presently not clear although they have been speculated to be due to improved crystal growth. The other reason this material is interesting is that below 390 K it undergoes a phase transition to a monoclinic structure with even larger band gap, which differs from the yellow phase occurring for CsSnI$_3$. Understanding the various possible phase transitions and structures in the trihalides is important for the long-term stability of these materials in solar cells.

### 4.2 Computational method

To calculate zone center phonon frequencies and simulated IR and Raman spectra, we use the density functional perturbation theory (DFPT) [78; 74; 76] within the local density approximation (LDA). The ABINIT code [75] with norm-conserving pseudopotentials [77] was used for these calculations. We first fully relaxed the crystal structures with respect to the lattice constants and internal parameters. Then, after iterative minimization of the ground-state total energy, the first-order perturbation of the wave functions with respect to atomic displacements and static electric fields is performed. Though, we already detailed the DFPT in previous chapter, we summarize how to obtain some important quantities below. In DFPT, the second order derivatives of the total energy with respect to atomic displacements gives us force constants, dynamical matrices, phonon frequencies, and eigendisplacements, while the second order derivatives of the total energy with respect to the static electric fields.
allow us to obtain the high-frequency dielectric tensor. The Born-effective charges are obtained by the derivatives of the total energy with respect to both atomic displacements and static electric fields. The above linear response calculations not only allow us to obtain the non-analytic LO–TO splitting at Γ, we can also extract the matrix elements for the infrared spectra once eigenvectors and oscillator strength are obtained. In order to simulate Raman spectra, we need to know the Raman tensors which can be obtained by the third derivatives of the total energy with respect to an atomic displacement and twice with respect to the electric fields. We determined that a $3 \times 9 \times 6$ k-point grid and a plane wave cut-off energy of 50 Hartree are sufficiently converged.

### 4.3 Results

#### 4.3.1 Lattice parameters

We start the (crystal) structural relaxation from the experimental crystal structure by Poulsen et al. [56] which showed that the space group of the $M$-CsSnCl$_3$ is $P2_1/c$, or $C_{2h}^5$ or No. 14 according to the International Tables for Crystallography. The crystal structure is shown in Fig. 4.1. The lattice constants are $a=16.10$ Å, $b=5.748$ Å, $c=7.425$ Å, with the angle $\gamma$ between $a_1$ and $a_2$ 93.2°, where $a_1$, $a_2$, and $a_3$ are primitive unit vectors in real space and we choose $a_1$ to coincide with the $x$-axis and $a_3$ with the $z$-axis. Our calculated lattice parameters (with experimental ones) are listed in Table 4.1. We note that LDA underestimates the lattice constants respectively by 4.5, 3.8 and 3.9 % and the volume $V = abc \sin \gamma$ by 11.8 %. Please note that this choice has the $a_2 = b$ and $a_3 = c$ lattice vectors interchanged from Ref. [56] to make the $z$-axis coincide with the 2-fold symmetry axis. Atomic positions are listed in Table 4.2.
Figure 4.1: Crystal structure of $M$-CsSnCl$_3$ in a unit cell. The large blue spheres are Cs atoms, the intermediate size green ones are Sn atoms, and the small red ones are Cl atoms. The red horizontal arrow is in the $a_1$ direction, the green one (vertical in top two figures, and out of page in bottom one) is in the $a_2$ direction, and the blue one (out of page in top two and vertical down in bottom one) is in the $a_3$ direction. The top figure shows only the shortest Sn-Cl bonds highlighting the Sn-Cl tetrahedral units, while the lower figure includes the longer Sn-Cl bonds so as to show the distorted octahedral environment, indicating edge-sharing octahedra. The bottom picture is a projection along $a_2$. 
Table 4.1: Lattice parameters of $M$-CsSnCl$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\gamma$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp. [56]</td>
<td>16.10</td>
<td>5.748</td>
<td>7.425</td>
<td>93.2</td>
</tr>
<tr>
<td>cal.</td>
<td>15.37</td>
<td>5.529</td>
<td>7.132</td>
<td>93.12</td>
</tr>
</tbody>
</table>

4.3.2 Group theory analysis and internal coordinates.

The space group of $M$-CsSnCl$_3$ is $C_{5h}^5$ or $P2_1/c$ and the point group is $C_{2h}$ or $2/m$. In relation to the International tables of crystallography, we choose the unit cell choice with unique axis $c$ and cell choice 2, labeled $P112_1/n$. The two-fold symmetry axis is along the $z$-axis and is a screw axis placed at 1/4 along the $a_1$ and $a_2$ axis, the mirror-plane is a diagonal ($n$-type) glide mirror placed at 1/4 along the $a_3$ axis. The inversion center occurs at the origin. One may easily recognize these symmetry operations in Fig. 4.1. Numbering the Cs atoms and the SnCl$_3$ units from left to right, as 1–4, the two-fold rotations relates for example 1 to 2, the glide plane relates 1 to 3 and the inversion 1 to 4.

Table 4.2: Summary of group theory analysis for $M$-CsSnCl$_3$. The atomic coordinates in parentheses are from experimental data by Poulsen et al. [56], the other ones are obtained by structural relaxation in this work.

<table>
<thead>
<tr>
<th>phase element Wyckoff position</th>
<th>reduced coordinates</th>
<th>irreducible representation total modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$-CsSnCl$_3$ Cs 4e</td>
<td>$0.1559 (0.1534)$ 0.7394 (0.7504) 0.5103 (0.5002)</td>
<td>$3A_g+3B_g+3A_u+3B_u$ 12</td>
</tr>
<tr>
<td>(C$<em>{2h}$, C$</em>{2h}$) Sn 4e</td>
<td>$0.3928 (0.3917)$ 0.2652 (0.2610) 0.4810 (0.4713)</td>
<td>$3A_g+3B_g+3A_u+3B_u$ 12</td>
</tr>
<tr>
<td>Cl(1) 4e</td>
<td>$0.2478 (0.2532)$ 0.2547 (0.2705) 0.3066 (0.3134)</td>
<td>$3A_g+3B_g+3A_u+3B_u$ 12</td>
</tr>
<tr>
<td>Cl(2) 4e</td>
<td>$0.4578 (0.4565)$ 0.2783 (0.2673) 0.1598 (0.1660)</td>
<td>$3A_g+3B_g+3A_u+3B_u$ 12</td>
</tr>
<tr>
<td>Cl(3) 4e</td>
<td>$0.3814 (0.3784)$ 0.7834 (0.8165) 0.4815 (0.4763)</td>
<td>$3A_g+3B_g+3A_u+3B_u$ 12</td>
</tr>
<tr>
<td>20 atoms/unit cell (Z=4)</td>
<td>15$A_g+15B_g+15A_u+15B_u$ 60</td>
<td></td>
</tr>
</tbody>
</table>

Γ$_{silent}$ = no silent mode
Γ$_{acoustic}$ = $A_u+2B_u$
Γ$_{IR}$ = $14A_u+13B_u$
Γ$_{Raman}$ = $15A_g+15B_g$

There are 20 atoms in the unit cell (Z=4) and thus 60 displacement degrees of freedom. Each element occupies a 4e Wyckoff position, meaning for example
that there are three distinct Cl atoms in the structure. Therefore it is sufficient to consider the decomposition in irreducible representations for one Wyckoff 4e site. The displacements of these 4 atoms build a $12 \times 12$ reducible representation which is easily seen to decompose in 3 irreducible ones of each irreducible representation, because only the identity maps the atom into itself. Thus in total $15A_g+15B_g+15A_u+15B_u$, at the zone center are predicted. Among those modes, 3 modes, $A_u+2B_u$, are acoustic modes (pure translation of all atoms) with zero frequencies because $A_u$ corresponds to a vector along $z$ and any vector in the $xy$-plane corresponds to $B_u$ irreducible representation. For the same reason, there are 27 infrared active modes, $14A_u+13B_u$.

A mode with $A_u$ symmetry can produce a long-range electric field in the $z$ direction which will affect the frequency in the $q \to 0$ limit for $q \parallel z \parallel a_3$. In other words, by including an electric field in the $z$ or $a_3$ direction, we obtain the $A_u^{LO}$ modes. For any electric field in the $xy$ plane, the $B_u$ modes will behave non-analytically for $q \to 0$ but the result will depend on which direction we choose in the $xy$ plane. In practice we choose an electric field $x$ along $a_1$ or along $y \perp x$ which is close to the $a_2$ axis. We label these as $B_u(x)^{LO}$ or $B_u(y)^{LO}$. The remaining 30 modes, $15A_g+15B_g$, are Raman active modes. No silent modes exist in this case. We summarize the results from the group theory analysis as well as our calculated and the experimental internal coordinates of the atoms in Table 4.2. The internal parameters together with the lattice parameters determine the bond lengths. Experimentally, the bond lengths of Sn-Cl in a pyramid are 2.50, 2.52, and 2.55 Å, respectively [56]. However, in our relaxed crystal structure, the bond lengths of Sn-Cl in a pyramid are 2.50, 2.55, and 2.66 Å, and are thus slightly overestimated for the longer bonds, which is a little surprising because LDA tends to do the opposite.
4.3.3 Infrared modes

In this section, we focus on the infrared modes. The latter exhibit LO-TO splittings at the zone-center which are closely related to the dielectric constant and the Born effective charges. In Table 4.3, we list the calculated static dielectric constant tensor elements $\varepsilon_{\alpha\beta}^0$ and the high-frequency dielectric constant $\varepsilon_{\alpha\beta}^\infty$ and check the generalized Lyddane-Sachs-Teller relation [85]:

$$\prod_i \left( \frac{\omega_{Li}}{\omega_{Ti}} \right)^2 = \frac{\varepsilon_{\alpha\alpha}^0}{\varepsilon_{\alpha\alpha}^\infty}$$  \hspace{1cm} (4.1)

for $M$-CsSnCl$_3$. Here the product is over all modes belonging to the irreducible representation of the direction $\alpha$. Note that the LO mode depends on the chosen direction $\alpha$. For $\alpha = z$ this means $A_u$, for $x$ or $y$ it means $B_u$ modes but the results still depend on the choice $x$ or $y$. Because the system is monoclinic, we note that there is also a non-zero $xy$ element of the dielectric tensor. Similarly, the Born effective charges have non-zero $xy$ elements although we find these to be very small because the angle $\gamma$ is close to 90°. The Born effective charges are listed in Table 4.4. We can see that they substantially differ from the nominal valence of the elements, which are +1 for Cs, +2 for Sn and −1 for Cl. The $yy$ component of Sn is much higher than the $x$ and $y$ components, meaning that the Sn atoms feel stronger long-range electrostatic forces in the $y$ direction. The same is true for the Cl(3) atoms.

Table 4.3: The static dielectric constant $\varepsilon_0$ and the high-frequency dielectric constant $\varepsilon_\infty$ and generalized Lyddane-Sachs-Teller relation in $M$-CsSnCl$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_\infty$</th>
<th>$\varepsilon_0$</th>
<th>$\frac{\varepsilon_\infty}{\varepsilon_0}$</th>
<th>$\prod_i \left( \frac{\omega_{Li}}{\omega_{Ti}} \right)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{xx}$</td>
<td>3.92</td>
<td>9.86</td>
<td>2.51</td>
<td>2.51</td>
</tr>
<tr>
<td>$\varepsilon_{yy}$</td>
<td>5.84</td>
<td>37.9</td>
<td>6.50</td>
<td>6.50</td>
</tr>
<tr>
<td>$\varepsilon_{xy}$</td>
<td>-0.105</td>
<td>-3.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{zz}$</td>
<td>3.63</td>
<td>7.66</td>
<td>2.11</td>
<td>2.11</td>
</tr>
</tbody>
</table>
Table 4.4: Effective charges of compound elements in different directions in $M$-CsSnCl$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Cs</th>
<th>Sn</th>
<th>Cl(1)</th>
<th>Cl(2)</th>
<th>Cl(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$xx$</td>
<td>1.33</td>
<td>2.82</td>
<td>-1.93</td>
<td>-1.16</td>
<td>-1.06</td>
</tr>
<tr>
<td>$yy$</td>
<td>1.48</td>
<td>4.41</td>
<td>-0.777</td>
<td>-0.594</td>
<td>-4.52</td>
</tr>
<tr>
<td>$xy$</td>
<td>-0.0246</td>
<td>-0.138</td>
<td>-0.0210</td>
<td>-0.0265</td>
<td>0.210</td>
</tr>
<tr>
<td>$zz$</td>
<td>1.35</td>
<td>2.51</td>
<td>-1.29</td>
<td>-1.88</td>
<td>-0.686</td>
</tr>
</tbody>
</table>

Our calculated infrared active phonon frequencies and the corresponding oscillator strengths are listed in Table 4.5 and the simulated IR spectra are shown in Fig. 4.2, from top to bottom, for $B_u(x)$, $B_u(y)$, and $A_u$ mode, respectively.

As in the case of cubic phase CsSnBr$_3$ and CsSnCl$_3$ discussed in the previous chapter, the LO phonons which are most strikingly seen in the loss spectrum, $-\text{Im} \varepsilon(\omega)^{-1}$ also produce notable peaks in the IR absorption spectra because of the corresponding minima in the index of refraction and $\text{Re} \varepsilon(\omega)$.

Examining the infrared active modes, we can see that the lower frequency modes have low oscillator strength and correspondingly small LO-TO splittings. This is expected because they are in modes in which the Cs ions move together with the SnCl$_3$ units but show no well defined ionic bond stretches. On the other hand, several modes tend to have a dominant oscillator strength either in the $x$ or $y$ direction, which is not surprising because the monoclinic angle is close to 90°. In the spectrum corresponding to $B_u(x)$ we can see six peaks in $\text{Im} \varepsilon(\omega)$ with corresponding peaks increasingly split away by LO-TO splitting in the $-\text{Im} \varepsilon^{-1}(\omega)$. They correspond to modes 1, 2, 5, (6,7), (8,9), 12, where groups put together in parentheses form one peak because of their closeness in frequency. The highest LO-TO splitting for non-analyticity in the $x$ direction, i.e. modes that interact with a long-range electric field in the $x$-direction produced by dipoles in the $x$-direction, occurs for mode $B_u^{12}$. Its LO-TO splitting is $(247-202)=45 \text{ cm}^{-1}$. 
Table 4.5: Infrared active phonon modes of $M$-CsSnCl$_3$. All frequencies are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th>mode</th>
<th>TO</th>
<th>LO modes</th>
<th>oscillator strengths (in a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$B_u^{LO}(x)$</td>
<td>$B_u^{LO}(y)$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>33</td>
<td>33</td>
<td>13</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>43</td>
<td>43</td>
<td>3.3 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>$A_{3u}$</td>
<td>50</td>
<td>51</td>
<td>4.9 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>$A_{4u}$</td>
<td>56</td>
<td>61</td>
<td>2.5 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$A_{5u}$</td>
<td>68</td>
<td>70</td>
<td>7.2 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>$A_{6u}$</td>
<td>82</td>
<td>82</td>
<td>1.7 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>$A_{7u}$</td>
<td>88</td>
<td>88</td>
<td>2.8 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>$A_{8u}$</td>
<td>95</td>
<td>96</td>
<td>1.2 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$A_{9u}$</td>
<td>102</td>
<td>103</td>
<td>1.1 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$A_{10u}$</td>
<td>111</td>
<td>112</td>
<td>9.4 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>$A_{11u}$</td>
<td>123</td>
<td>127</td>
<td>3.3 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$A_{12u}$</td>
<td>145</td>
<td>151</td>
<td>5.3 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$A_{13u}$</td>
<td>212</td>
<td>220</td>
<td>1.3 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>$A_{14u}$</td>
<td>254</td>
<td>281</td>
<td>2.6 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>31</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>56</td>
<td>58</td>
<td>57</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>$B_{4u}$</td>
<td>77</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>$B_{5u}$</td>
<td>79</td>
<td>84</td>
<td>82</td>
</tr>
<tr>
<td>$B_{6u}$</td>
<td>93</td>
<td>94</td>
<td>95</td>
</tr>
<tr>
<td>$B_{7u}$</td>
<td>96</td>
<td>98</td>
<td>109</td>
</tr>
<tr>
<td>$B_{8u}$</td>
<td>109</td>
<td>113</td>
<td>114</td>
</tr>
<tr>
<td>$B_{9u}$</td>
<td>115</td>
<td>121</td>
<td>124</td>
</tr>
<tr>
<td>$B_{10u}$</td>
<td>125</td>
<td>126</td>
<td>157</td>
</tr>
<tr>
<td>$B_{11u}$</td>
<td>157</td>
<td>157</td>
<td>201</td>
</tr>
<tr>
<td>$B_{12u}$</td>
<td>202</td>
<td>247</td>
<td>229</td>
</tr>
<tr>
<td>$B_{13u}$</td>
<td>261</td>
<td>261</td>
<td>261</td>
</tr>
</tbody>
</table>
Figure 4.2: Figures, from top to bottom, show the real part and imaginary part of dielectric function, $\varepsilon$, imaginary part of $-1/\varepsilon$, absorption coefficient and reflectivity of $B_u(x)$, $B_u(y)$, and $A_u$ mode, respectively, in $M$-CsSnCl$_3$. 
Figure 4.3: Upper figure shows the displacement patterns of $B_u^6$(TO) mode, at 93 cm$^{-1}$, without non-analyticity. The lower figure shows the displacement pattern of the mode at 229 cm$^{-1}$ when the non-analyticity is in the $y$ direction. The large blue spheres are Cs atoms, the medium green ones are Sn atoms, and the small red ones are Cl atoms. The red arrow is in the $a_1$ direction, the green one is in the $a_2$ direction, and the blue one is in the $a_3$ direction.
The spectrum for $B_u(y)$ looks quite different. Here we see only four peaks in $\text{Im} \, \varepsilon(\omega)$ corresponding to modes 2, 5, (6,7), 10. We can see that these are the modes with highest $S_{yy}$. It is interesting to note that $B_{12}^{12}$ has a small oscillator strength $S_{yy}$ but nevertheless a large LO-TO splitting. This suggest that the $LO - y$ mode most closely corresponding to $B_{12}^{12}$ instead is $B_{11}^{11}(LOy)$. Similarly we can shift the modes $B_{u}^{7-10}(LOy)$ to $B_{u}^{8-11}(LOy)$. In fact, mode 6 has the highest oscillator strength $S_{yy}$ and is thus expected to have the largest LO-TO splitting. To test, this idea we show in Fig. 4.3 the displacement pattern of mode $B_{u}^{6}(TO)$ compared to the mode $B_{u}^{12}(LOy)$. One can clearly see that the $y$-projection of mode $B_{u}^{6}(TO)$ matches well with that of $B_{u}^{12}(LOy)$. Both show an internal vibrational mode of the SnCl$_3$ pyramid in the $y$ direction, which is in anti phase between groups related by inversion symmetry, say groups 2-3 and 1-4 counting them from left to right. On the other hand, the $B_{u}^{6}(TO)$ has a diagonal motion with also an $x$ component. Apparently the $y$ component of this mode strongly couples to the electric field in the $y$ direction which leads to the very strong $(229-93)=136$ cm$^{-1}$ LO-TO splitting. One may also note that the groups (2-3) and (1-4) which are in anti phase with each other in their motion are displaced in the $y$ direction from each other and correspond to edge-sharing octahedra in the structure as seen in Fig. 4.1b. Of course, strictly speaking all $B_u(LOy)$ modes together result from interactions of the electric field with all $B_u(TO)$ modes together and thus, the only unambiguous way of counting them is from lower to higher frequency as listed in Table 4.5. Still, the crossing of modes suggested above explains in a natural way the broad Reststrahlen band between about 100 and 200 cm$^{-1}$ seen in the predicted IR reflectivity for electric field in the $y$ direction. For the $A_u$ modes, we see a spectrum of more or less evenly separated peaks in $\text{Im} \, \varepsilon(\omega)$ with increasingly larger LO-TO splittings with increasing frequency. Unfortunately, no experimental data have been reported to the best of our knowledge on the infrared spectra.

To conclude this section on infrared spectra, we show in the upper figure of Fig.
Figure 4.4: Upper figure shows the angular dependence of each $B^i_u(LO)$ mode, where $i = 1$ to 13 from low to high frequency. The abscissa $\theta$ is the azimuthal angle measured from the $x$-axis. The lower figure shows the angular dependence of the static dielectric constant $\varepsilon_0$, the high-frequency dielectric constant $\varepsilon_\infty$, and $\prod_i \left( \frac{\omega_{\parallel i}}{\omega_{\parallel i}} \right)^2$. 
4.4 the predicted angular dependence in the $xy$ plane of the $B_{u}^{LO}$ modes. The angle $\theta = 0$ corresponds to the $x$ axis. This also very strongly suggests a crossing of the modes 10 and 11 near $45^\circ$. Strictly speaking we cannot have crossings of modes of the same symmetry and thus we really see an avoided crossing. This picture suggests a different relation between modes than the one discussed earlier purely based on the LO splitting with non-analyticity in the $y$ direction, where we identified the mode pattern of the $B_{u}^{12}(LOy)$ with the $y$ motion of the $B_{u}^{6}(TO)$. From the full angular dependence it rather appears that mode 11 only crosses 10 and possibly 9. Again, one cannot strictly speaking associate individual TO to LO modes but should consider the whole LO spectrum with a given non-analyticity because the LO spectrum with each type of non-analyticity, i.e. direction of the electric field in the plane results from the diagonalization of a different dynamical matrix with different long-range forces. Strictly speaking one cannot assign a one to one correspondence between the TO and LO modes. The LO modes of a given symmetry are just simply all the modes obtained with a different force constant matrix which includes the non-analytic effects of the long range force constants from electric fields produced by the vibrations. For example for $Bu$ modes electric fields in any direction in the $xy$ plane will produce long-range force constants. So, in what sense can we say that modes cross? What we mean, for example, is that the eigenvector of mode $B_{u}^{10}$ on the left of the apparent crossing (say for 30 degrees) is closer to that of mode $B_{u}^{11}$ on the right of the crossing (say for 60 degrees) and vice versa. This is illustrated in Fig. 4.5.

We also show the angular dependence of the static and high-frequency dielectric constants in the lower figure of Fig. 4.4. Diagonalizing the static dielectric tensor one obtains as principal values $\varepsilon_1^0 = 38.41$, $\varepsilon_2^0 = 9.35$ with the long principal axis at $97^\circ$ and the short principal axis at $187^\circ$. The long principal axis is close to the $a_2$ crystallographic direction but not quite. For $\varepsilon^\infty$, the principal axes are at $93^\circ$ and $183^\circ$, so closer to the crystal axes and the principal values are 5.845 and 3.914 very
Figure 4.5: This figure shows the meaning of mode crossing. What we mean, for example, is that the eigenvector of mode $B_u^{10}$ on the left of the apparent crossing (say for 30 degrees) is closer to that of mode $B_u^{11}$ on the right of the crossing (say for 60 degrees) and vice versa.
close to the $yy$ and $xx$ values because the $xy$ value is quite small.

### 4.3.4 Raman modes and comparison with experiment

Our calculated Raman-active phonon frequencies are shown in columns 4 and 5 of Table 4.3.4 together with their symmetry assignment based on the corresponding eigenvectors and Raman tensors. The corresponding experimental assignments in columns 1-3 will be discussed below. The last two columns show LO modes which, as we will argue occur in the spectra as forbidden LO modes through the Fröhlich scattering mechanism [86; 87; 83]. The simulated Raman spectra for specific Raman tensor components are shown in Fig. 4.6.

Table 4.6: Raman active modes. First column: experimental peak position from digitized data from Kuok et al. [2; 3; 4]; second column: type of mode [2], librational (l), translational (t), or $\nu_n$, $n = 1 - 4$ internal modes of SnCl$_3$; third column: symmetry assignment from Ref. [3]; fourth column: our calculated Raman active modes; fifth column: our symmetry assignment; seventh column: $A^LO_u$ modes; eighth column: $B^LO_u$ modes giving either range or for specifically $x$ or $y$ direction. Forbidden LO modes may occur through the Fröhlich mechanism.

<table>
<thead>
<tr>
<th>Observed</th>
<th>type</th>
<th>symmetry [3]</th>
<th>Calculated</th>
<th>symmetry</th>
<th>$A^LO_u$</th>
<th>$B^LO_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-17</td>
<td>t</td>
<td>$B_g$</td>
<td>11</td>
<td>$B_g^1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23-26</td>
<td>l</td>
<td>$A_g$</td>
<td>27</td>
<td>$A_g^1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33-35</td>
<td>l</td>
<td>$A_g$</td>
<td>33</td>
<td>$A_g^2$</td>
<td>33</td>
<td>31-33</td>
</tr>
<tr>
<td>38-40</td>
<td>t</td>
<td></td>
<td>38</td>
<td>$B_g^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td></td>
<td>$A_g$</td>
<td>43</td>
<td>$A_g^3$</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>t</td>
<td>$B_g$</td>
<td>44</td>
<td>$B_g^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48-49</td>
<td>t</td>
<td>$A_g$</td>
<td>46</td>
<td>$A_g^4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52-53</td>
<td>t</td>
<td>$B_g$</td>
<td>53</td>
<td>$B_g^4$</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>55-56</td>
<td>l</td>
<td>$A_g$</td>
<td>57</td>
<td>$A_g^5$</td>
<td></td>
<td>57-58</td>
</tr>
</tbody>
</table>

Continued on next page
<table>
<thead>
<tr>
<th>Observed</th>
<th>type</th>
<th>symmetry [3]</th>
<th>Calculated</th>
<th>symmetry</th>
<th>$A_{u}^{LO}$</th>
<th>$B_{u}^{LO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>t</td>
<td></td>
<td>62</td>
<td>$B_{g}^{5}$</td>
<td>61</td>
<td>60</td>
</tr>
<tr>
<td>68</td>
<td></td>
<td>$B_{g}$</td>
<td>73</td>
<td>$B_{g}^{6}$</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>71-72</td>
<td>t</td>
<td></td>
<td>73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>76</td>
<td></td>
<td></td>
<td>75</td>
<td>$A_{g}^{6}$</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td></td>
<td>$A_{g}$</td>
<td>79</td>
<td>$B_{g}^{7}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>81-82</td>
<td>$\nu_{4}$</td>
<td>$A_{g}$</td>
<td>82</td>
<td>$A_{g}^{7}$</td>
<td>82</td>
<td>82-84</td>
</tr>
<tr>
<td>88</td>
<td></td>
<td></td>
<td>86</td>
<td>$A_{g}^{8}$</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>93</td>
<td></td>
<td>$B_{g}$</td>
<td>92</td>
<td>$B_{g}^{8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>$\nu_{4}$</td>
<td>$A_{g}$</td>
<td>94</td>
<td>$A_{g}^{9}$</td>
<td>94-95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>96</td>
<td>$B_{g}^{9}$</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>103</td>
<td>$A_{g}^{10}$</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>104</td>
<td>$B_{g}^{10}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>106</td>
<td>$A_{g}^{11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>112-114</td>
<td>$\nu_{4}$</td>
<td>$A_{g}$</td>
<td>112</td>
<td></td>
<td>113-114</td>
<td></td>
</tr>
<tr>
<td>117</td>
<td>$\nu_{4}$</td>
<td></td>
<td>117</td>
<td>$A_{g}^{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>118</td>
<td>$B_{g}^{11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>121</td>
<td>$\nu_{4}$</td>
<td>$B_{g}$</td>
<td>121-124</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>127-129</td>
<td>$\nu_{2}, \nu_{4}$</td>
<td>$B_{g}$</td>
<td>125</td>
<td>$B_{g}^{12}$</td>
<td>127</td>
<td>126</td>
</tr>
<tr>
<td>141-149</td>
<td>$\nu_{2}, \nu_{1}$</td>
<td>$B_{g}$</td>
<td>146</td>
<td>$A_{g}^{13}$</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td>162</td>
<td>l</td>
<td></td>
<td>159</td>
<td>$B_{g}^{13}$</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>193</td>
<td>l</td>
<td></td>
<td>201(y)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>t</td>
<td></td>
<td>211</td>
<td>$A_{g}^{14}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>227-231</td>
<td>$\nu_{3}$</td>
<td>$A_{g}$</td>
<td>220</td>
<td></td>
<td>229(y)</td>
<td></td>
</tr>
<tr>
<td>249-253</td>
<td>$\nu_{3}$</td>
<td>$B_{g}$</td>
<td>239</td>
<td>$B_{g}^{14}$</td>
<td></td>
<td>247(x)</td>
</tr>
</tbody>
</table>

Continued on next page
We found three papers showing the Raman spectra for \( M\text{-CsSnCl}_3 \). They actually are from the same research group, Kuok’s group in the National University of Singapore. The first paper [2], published in 1987, shows the Raman spectra from room temperature to 85 K and concludes that no phase transition occurs within that temperature range. The second paper [3], published in 1992, shows the polarized Raman spectra from 10 K to 423 K, which provides evidence of a phase transition in \( \text{CsSnCl}_3 \) to the cubic perovskite phase at about 385 K. The third paper [4], published in 1994, studies additional phase transitions of \( \text{CsSnCl}_3 \) under high pressure. Although we do not address the phase transition under high pressure situation in this thesis, their Raman spectra at 0 kbar show the latest experimental Raman spectra we could find for \( M\text{-CsSnCl}_3 \).

Although these papers list various Raman frequencies in their discussion, the authors did not clearly label the frequencies of the peaks in their Raman spectra shown in their papers. In order to more accurately compare our calculated results with the experimental spectra, we first need to know the frequencies of all obvious peaks in the experimental spectra. To this end, we digitalize their experimental Raman spectra shown in these three papers. Figure 4.7 shows the digitized results. The first (top) spectrum, labeled by 1, is digitized from the spectrum recorded at 85

<table>
<thead>
<tr>
<th>Observed type symmetry [3]</th>
<th>Calculated symmetry</th>
<th>( A_{LO} )</th>
<th>( B_{LO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_3 ) ( A_g )</td>
<td>263-266</td>
<td>259</td>
<td>( A_{15} )</td>
</tr>
<tr>
<td>269</td>
<td>( \nu_3 )</td>
<td>269</td>
<td>( B_{15} )</td>
</tr>
<tr>
<td>278-284 ( \nu_3 ) ( B_g )</td>
<td>281</td>
<td></td>
<td></td>
</tr>
<tr>
<td>290 ( \nu_1 ) ( A_g )</td>
<td>300-316</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.6: Simulated Raman spectra for $M$-CsSnCl$_3$. The different tensor components are scaled by different factors so as to normalize their strongest peak.
Figure 4.7: Digitized plot of the experimental Raman spectra from Kuok et al. [2; 3; 4]. Note the sharpness of spectrum 2 is mostly due to the low temperature (10K).
K in Fig. 2 in the first paper [2]. The second spectrum, labeled by 2, is digitized from polarized (zz) Raman spectrum at 10 K in the Fig. 1 in the second paper [3]. And the remaining spectra, labeled by 3 to 5, are from three spectrum in the Fig. 1 in their third paper [4]. Digitalization, of course, contains some errors; for example, it looks like the frequency of the first peak in the spectrum 2 (25.3 cm$^{-1}$) is lower than the frequency of the first peak (23.8 cm$^{-1}$) in the spectrum 4. However, our purpose here is not to determine more precise mode frequencies from the experimental Raman spectra, rather we wish to associate the modes as identified in the papers with specific peaks in the spectrum so we can also discuss the corresponding intensities.

Unfortunately, the three experimental papers do not fully describe the scattering geometry. The authors specify that the crystals are needle like and with the needle axis coinciding with their choice of c axis, which is our b axis. The mentioned (zz) polarization should then correspond to our $\mathbf{E} \parallel b$ or our (yy) polarization. In the most recent paper, they only state the crystal is mounted vertical or horizontal and the beam is perpendicular to or parallel to the crystal axis. This however does not tell us the actual polarization.

In Table 4.3.4 we list the thus determined experimental peak positions as well as explicitly quoted frequencies in the papers from lower to higher frequency which allows us to see the correspondence with calculated modes based purely on frequency value. We also give the symmetry assignment made in the experimental papers. Generally speaking we find a good one-to one match and agreement to within a few cm$^{-1}$ for the low frequency modes up to about 95 cm$^{-1}$ although our assignments as $A_g$ or $B_g$ do not always agree with the experimental papers. For the higher frequency modes the discrepancies are higher and the assignments are less clear, so we discuss them later.

Kuok’s [2] analysis of the spectra is based on separating internal vibration modes of the SnCl$_3$ units at higher frequencies from crystal translational and or molecule
librational modes. The internal motions of the SnCl$_3^-$ radical, which has $C_{3v}$ symmetry were reported by Woodward and Taylor [88] but due to the lower symmetry and resulting distortions of the molecules and interactions between the molecules the modes split and the correspondence is not entirely obvious anymore. These are the modes designated as $\nu_{1-4}$. The $\nu_1$ and $\nu_2$ modes have $A_1$ symmetry of the $C_{3v}$ group while $\nu_3$ and $\nu_4$ have doubly degenerate $E$ symmetry of $C_{3v}$. In SnCl$_3^-$ radicals dissolved in ether, these occur respectively at 297, 128, 256 and 103 cm$^{-1}$. In the second paper [3] the authors based the symmetry assignment of the modes on the assumption that $A_g$ modes are generally stronger than $B_g$ modes. Obviously this cannot be applied across the board.

In Kuok [2] the modes are labeled as translational or librational where this assignment was made based on the assumption that librational modes have higher intensity. As shown in Fig. 4.8, in the first two modes we can see the Cs and SnCl$_3$ molecules move together in respectively the $b$ or the $c$ direction for the left part of the unit cell and in the opposite direction in the right part. So, these modes look like a folded acoustic mode and definitely have indeed mostly translational character. However, some distortion of the CsCl$_3$ molecules is visible in these modes as well. Kuok [2] identified two peaks at 23 and 26 cm$^{-1}$ labeled as librational and translational respectively. In his spectrum only the 23 cm$^{-1}$ is clearly visible and this mode is definitely more translational. We seem to overestimate this frequency somewhat.

The $A_{g}^{2}$ mode involves a rotation about the $c$-axis of the molecules, which could be termed librational, but also a translation of the Cs atoms relative to the molecule. The $B_{g}^{2}$ mode (not shown) also has mixed librational character involving the rotation of the molecules but has translations of the Cs atoms as well. The next $A_{g}^{3}$ mode involves a motion of Sn and two of the Cl atoms predominantly in the $a$-direction, while the other Cl and the Cs move in the $c$ direction. So, one could more call it translational and distortion than libration. The $B_{g}^{5}$ mode shows the SnCl$_3$ molecules
Figure 4.8: Displacement patterns for modes $B_9^1$, $A_9^1$ and $A_9^2$ from top to bottom. Note the different orientation of the axes.
moving relative to each other in the $b$ direction and is indeed mostly translational. These are just a few examples, the displacement patterns of all the modes are available in the Supplementary Information accompanying our recent paper [84]. We conclude that some modes have indeed predominantly translational character but many are also mixed librational and translational.

We now scrutinize this assignment further and attempt to address the higher frequency mode discrepancies by examining the intensities. We note that the $A_g(yyyy)$ spectrum is clearly the strongest and can be compared most directly with Kuok’s spectrum 2, which we do in Fig. 4.9. The strongest peaks in our calculated spectrum clearly correspond to modes $A^7_g$ and $A^9_g$ at 82 and 94 cm$^{-1}$ which match well the peaks in the experiment at 81.4 and 95.4 cm$^{-1}$. The lowest frequency modes $A^1_g$ and $A^2_g$ at 27 and 33 match the separated peaks in Kuok at 25.3 and 34.7 although these peaks are significantly smaller in our calculation compared to the experiment. As we will later argue this is because LO modes at almost the same frequency also contribute to this mode. The $A^3_g$ and $A^4_g$ are rather weak both in our calculation and experiment but still visible in the experiment. The $A^5_g$ peaks is stronger in our calculation than in experiment. $A^8_g$ mode is relatively weak in our calculation but can be seen in spectrum 4 of Kuok et al. Modes $A^{10-12}_g$ are close to each other. Only the highest mode at 117 seems to match spectrum 3 and a peak at 112 in spectrum 2 but in any case our calculated peaks appear much stronger than the experiment. In spectrum 3 one can see other separate features just below it. Our mode $A^9_g$ at 146 cm$^{-1}$ matches the experimental peak at 149 cm$^{-1}$. The big mystery at this point is what is the enormous peak at 169 cm$^{-1}$ present as a broad peak in all experimental spectra but not matching clearly any of our calculated $A_g$ or $B_g$ modes. The $A^{14}_g$ mode at 211 cm$^{-1}$ is only seen in spectrum 1.

In the high frequency region the experiment shows three clear peaks at about 230, 250 and 260 cm$^{-1}$ in all the spectra. Our calculated $A^{14}_g$ mode at 259 nicely
Figure 4.9: Comparison of calculated (cal.) $A_0(yy)$ spectrum with experimental (exp.) polarized Raman spectrum from Kuok [3].
matches the highest one in frequency but is very weak in intensity in our calculation compared to the experiment. Our calculated $B_g^{14}$ mode at 239 should be strong only in $xz$ polarization and could possibly match the 250 cm$^{-1}$ experimental peak or the 230 cm$^{-1}$ but none of these assignments seem to agree intensity-wise. Our highest $B_g^{15}$ at 269 cm$^{-1}$ is predicted to be weak for any polarization.

An alternative explanation emerges when we consider the possibility of LO-forbidden modes. We note that $B_u^{12}(LOy)$ and $B_u^{13}(LOy)$ modes at 229 and 261 cm$^{-1}$ match very closely to the 230 and 260 experimental peaks. The 250 cm$^{-1}$ experimental peak then matches the 247 cm$^{-1}$ $B_u^{12}(LOx)$. The $A_u^{13}(LO)$ mode at 220 cm$^{-1}$ may also contribute to the experimental peak which varies between 227 and 231 and has an asymmetric shape suggesting another mode could be hidden under it at lower frequency. This seems a far more plausible explanation. Furthermore if we now accept that LO modes appear as forbidden LO modes in the Raman spectrum through the Fröhlich mechanism, we should include all LO modes. We then notice that several low frequency LO modes coincide almost with allowed $g$ modes and help explain the discrepancies in intensity noticed earlier. In particular the already strong 82 and 95 cm$^{-1}$ modes would become even stronger, and also the 27 and 35 cm$^{-1}$ peaks would increase in intensity.

We thus attempt to construct a separate simulated Raman spectrum for the LO modes. Unfortunately, we do not have a fully first-principles theory available for calculating the relative intensities of these modes, although based on the nature of the Fröhlich interaction [83], we may expect it to be related to the LO-TO splitting and thus choose the amplitude proportional to

$$
\left( \frac{\omega^2_{LO} - \omega^2_{TO}}{\omega^2_{LO}} \right).
$$
This requires to establish a one-to-one correspondence between LO and TO modes which we have argued is not strictly valid. For the $A_{1u}^{LO}$ modes, there is only one LO frequency, but for the $B_{1u}^{LO}$ modes the $\omega_{LO}$ depends on the direction in the plane. For most modes, this is a small effect but as seen in Fig. 4.4 for mode 11 there is a big dispersion with angle. Based on this figure we assume the mode 11 crosses mode 10 and corresponds to the TO mode at 115 cm$^{-1}$. In that case, one might expect a peak at the average of the LO$^x$ and LO$^y$ values and a large width due to the dispersion. Using this approach, we obtain the spectrum for $B_{1u}^{LO}$ modes shown in Fig. 4.10. This simulated spectrum accounts clearly for the 165–169 cm$^{-1}$ peak which is very strong in most polarizations but also quite broad. The peak position is close to the frequency where the crossing of modes occurs in Fig. 4.4. This indicates a mode with large LO-TO splitting and oscillator strength for which we can also expect the strongest Fröhlich coupling mechanism. It also shows a good match for some of the other peaks at lower frequency but does not account well for the fine structure of the higher peaks above 200 cm$^{-1}$.

The latter appear to be more clearly related to separate LO$^x$ and LO$^y$ modes. We thus also construct a spectrum simply from the LO peak positions giving each mode equal amplitude and width and at this point do not attempt to fully account for the peak intensities. The thus constructed LO spectrum is compared with the experimental ones in Fig. 4.11 and shows several peaks match at least in position. Our calculations seem to slightly underestimate the peak positions corresponding to the internal vibrational modes of the SnCl$_3^-$ molecule. This may be related to our overestimate of the bond lengths noted in Section 4.3.2.

Unfortunately, at present we do not have a fully quantitative theory for the LO forbidden peaks and some experimental features appear to correspond to LO modes for specific directions $x$ or $y$ while other seem to be better accounted for by an average in the $xy$ plane. Our assignment should thus perhaps still be taken as a working
Figure 4.10: Simulated $B_u^{LO}$ spectrum compared to experimental spectra 2 and 3.
Figure 4.11: Simulated forbidden LO mode contribution to the Raman spectrum compared with experimental spectrum 1 (dashed), 2 (solid) and 3 (dotted) where the numbering corresponds to Fig. 4.7
hypothesis. If our assignment of some peaks as forbidden LO modes is correct, one expects these peaks to become even stronger under resonant Raman conditions, i.e. when the exciting laser frequency matches an optical absorption peak such as the near gap free exciton. It may thus be very useful to explore this prediction in future experimental work.

In summary then, we conclude that the measured Raman spectrum is a superposition of first order allowed Raman modes with $A_g$ and $B_g$ symmetry with very prominent forbidden LO modes. This helps explain the discrepancies in intensity when directly comparing the allowed spectra alone and explains the presence of the broad and strong 169 cm$^{-1}$ peak and explains the high 282 cm$^{-1}$ peak.

Still there are some even higher peaks in some of the spectra at 290 and 300 cm$^{-1}$. These only appear in the oldest data in spectrum 1 and may be arising from different phases. In Kuok [2] the 300 cm$^{-1}$ mode was assigned to the symmetric stretch $A_1$ symmetry $\nu_1$ mode of the SnCl$_3$ molecule. However, in Kuok [4] this peak was no longer observed and instead the strong 165 cm$^{-1}$ mode was assigned to the $A_1$ $\nu_1$ because it is expected to be a strong mode. The authors already noted that this was surprising because of the large shift from the free molecule. In the present paper, we propose that the very strong 165 cm$^{-1}$ mode is instead a very strong oscillator LO forbidden mode. This may resolve this puzzle.

4.4 Conclusions

In this chapter, we presented a study of the zone center phonons in monoclinic $M$-CsSnCl$_3$. We provided phonon frequencies and their symmetry assignment for all 60 modes. We predict the infrared absorption and reflection spectra and investigated in some detail the angular dependence of the LO modes in the $xy$ plane. In particular we presented evidence for mode crossing behavior. Most of all we provide a detailed
interpretation of the available Raman spectra in the literature. We show that these spectra not only contain the expected even symmetry first order allowed Raman modes but also prominently show forbidden LO modes. With this interpretation, our calculated phonons agree to within a few cm\(^{-1}\) with all observed peaks in Raman but our interpretation provides new symmetry assignments to several modes. We also showed that librational and translational characteristics are thoroughly mixed in several modes. Some relation to the internal modes of the SnCl\(_3\) is still present as noted in earlier work. A complete set of mode displacement patterns is available in the Supplementary Information of our paper [84].
Chapter 5

Full phonon band structures and their relation to the phase transitions

5.1 Introduction

As discussed in the Chapter 2, the largely intra-atomic nature of the gap explains the strong optical transitions both in luminescence and absorption. However, the strong photoluminescence well separated from the absorption appears to be from a defect bound exciton rather than free exciton. As part of our study of the exciton binding energy, we needed to estimate the phonon contribution to the dielectric screening. In this chapter we provide a more complete account of the lattice dynamical properties of these materials. This chapter is based on work published previously in Phys. Rev. B 90, 195201 (2014) [79].

As mentioned in the first chapter, these perovskites are known to undergo a number of phase transitions as function of temperature [35; 34; 33; 6; 36]. The cubic phase is only stable at high temperature and at lower temperature they undergo a
series of transitions, corresponding to rotations and re-arrangements of the octahedral SnX$_6$ building blocks. As discussed in detail by Chung et al. [6] in the CsSnI$_3$ case, from high temperature to low temperature, CsSnI$_3$ changes from cubic (α) phase to the tetragonal (β) phase at around 431.5±5.7 K, and then to the orthorhombic (γ) phase at around 352±5.3 K. Exposure to air (at room temperature in 1 hour) causes a transition to another orthorhombic yellow (Y) phase. As for CsSnBr$_3$, the only commonly confirmed transition is the transition from cubic (α) phase to tetragonal (β) phase, which occurs at around 292 K [55; 57; 34]. A second transition to another tetragonal phase was found by Mori and Saito [34] at 274 K and a transition to a monoclinic phase at 247 K. For CsSnCl$_3$, the cubic (α) phase converts to a monoclinic (M) phase at around 363 K [55; 56].

Some of these transitions are well known to be related to soft modes [89; 90; 91; 92; 34; 93] and thus we investigate here whether soft modes occur and how these transitions relate to the soft mode displacement patterns. To this end, we need calculations of the full dispersion curves of the phonon modes. These transitions may turn out to be quite important for the durability of the new solar cell materials. In fact, some of the phase transition correspond to a more severe change in the lattice structure, in which the basic BX$_6$ octahedral units of the structure change from corner-sharing to side-sharing. As we already showed in Chapter 2, this leads to a large increase in the gap making the materials far less useful for photovoltaics. The key question then becomes, how to avoid these latter phase transformations. A better understanding of the stability of the various phases with respect to soft modes is required to address this question. While we are not able at this point to provide a full understanding of the transition to the so-called yellow phase of CsSnI$_3$ and the monoclinic phase of CsSnCl$_3$, we find that the γ-phase has no soft modes and is thus mechanically stable. The transitions to the undesirable phases (from a photovoltaics point of view) appears to require more complex re-arrangements and bond breaking.
and reforming. In order to design better future materials in this family, it is also important to understand their trends with different constituent ion sizes. Indeed the series of phase transitions in CsSnI$_3$ appears to generally lead to a densification of the crystal structure and hence ion sizes play a key role.

This chapter is organized as follows. In Section 5.2 we give details of the computational method. In section 5.3.1, we present our calculated phonon dispersion curves and densities of states (DOS) and discuss the relation to the phase transitions in section 5.3.2.

### 5.2 Computational method

To calculate phonon band structures, we again adopt the DFPT [78; 74; 76] within the LDA. The ABINIT code [75] with norm-conserving pseudo-potentials [77] was used for these calculations. The crystal structures are first fully relaxed with respect to the lattice constants and internal parameters. The linear response formalisms discussed in the Chapter 3 allows us to obtain the dynamical matrix at arbitrary $k$ point and also to obtain the non-analytic behavior at $k \rightarrow 0$, i.e. the LO–TO splitting. Thus we can generate the phonon band structure throughout the Brillouin zone. We use the usual approach of Fourier interpolation of the dynamical matrix from a relatively coarse mesh ($4 \times 4 \times 4$) to the points required along symmetry lines for the sake of efficiency. For the phonon density of states, interpolation to a fine mesh of $240 \times 240 \times 240$ is used.

The phonon band structure calculations are expensive calculations, especially for the lower symmetry phases which have larger unit cells. We, therefore, used a $4 \times 4 \times 4$ $k$-point grids for every phase. Actually, we checked the convergence of the $k$-point grid for the higher symmetry phases. Although small shifts in phonon-frequencies occur the qualitative conclusions about soft-modes and the nature of the IR spectra
were not affected by our choice of a relatively coarse $k$-point mesh. For $\alpha$-CsSnI$_3$, the highest phonon frequency at the $k$-point $\Gamma$, the $T_{1u}^3$(LO) phonon mode is 152 cm$^{-1}$ for the $4 \times 4 \times 4$ k-point grid, 151 cm$^{-1}$ for the $6 \times 6 \times 6$ k-point grid, and 148 cm$^{-1}$ for the $8 \times 8 \times 8$ k-point grid. Our convergence studies show that the plane wave cut-off energy of about 30 Hartree is good enough for each phase. In practice, we used 28 Hartree for the orthorhombic phase, 30 Hartree for monoclinic phase, 40 Hartree for the tetragonal phase, and 100 Hartree for cubic phase; the latter two high cut-off energies are not necessary but for these smaller cells, we could afford to use a higher cut-off, which can only improve the results.

5.3 Results

5.3.1 Calculated full phonon band structures

Figure 5.1 shows the first-principles calculated phonon band structure and phonon density of states (DOS) resolved into atomic components for $\alpha$-CsSnI$_3$ (upper left), $\beta$-CsSnI$_3$ (upper right), $\gamma$-CsSnI$_3$ (lower left) and $Y$-CsSnI$_3$ (lower right), respectively. The notation of the $k$-points is explained in Fig. 2.8. Figure 5.2 from top to bottom shows the phonon band structure and phonon DOS of $\alpha$-CsSnBr$_3$, $\beta$-CsSnBr$_3$, and our predicted $\gamma$-CsSnBr$_3$. Fig. 5.3 from top to bottom shows the phonon band structure and phonon DOS of $\alpha$-CsSnCl$_3$ and $M$-CsSnCl$_3$, respectively. We can see that in the $\alpha$ and $\beta$ phases, imaginary frequency modes indicated as negative frequencies (soft phonon modes) occur, while in $\gamma$, $Y$, and $M$ phases, no imaginary frequency modes are found. The appearance of the soft phonon modes in $\alpha$ and $\beta$ phases reflects the instability of those crystal structures at low temperatures. We should view the high-temperature phases as being stabilized by the additional entropy related to these soft phonon mode fluctuations.
Figure 5.1: Phonon band structure with phonon DOS of $\alpha$-CsSnI$_3$ (upper left), $\beta$-CsSnI$_3$ (upper right), $\gamma$-CsSnI$_3$ (lower left) and Y-CsSnI$_3$ (lower right).
Figure 5.2: Phonon band structure with phonon DOS of $\alpha$-CsSnBr$_3$ (top), $\beta$-CsSnBr$_3$ (middle), and (predict) $\gamma$-CsSnBr$_3$ (bottom).
Figure 5.3: Phonon band structure with phonon DOS of $\alpha$-CsSnCl$_3$ (upper) and $M$-CsSnCl$_3$ (lower).
We also can see that, in all three compounds, there is a dispersion-less soft phonon branch from $M$ to $R$ in the Brillouin zone of the cubic phase. The question thus arises which of these soft phonons is responsible for the phase transition. The decomposition of the DOS in different atomic contributions shows that the primary contribution to the soft phonons comes from the vibrations of the halide atoms. The absolute value of the frequency of the soft phonon modes becomes larger when the halide is changed from I to Br to Cl. This reflects the fact that the lighter mass of the atom involved, the higher the absolute value of the phonon frequency. This factor can also be used to explain why the highest phonon frequency become larger when we go from CsSnI$_3$ to CsSnBr$_3$ to CsSnCl$_3$. Furthermore, this factor explains why the vibrations of Cs (heaviest atom, compared to Sn and X) atoms only contribute to lower phonon frequency modes (say, below 100 cm$^{-1}$), while higher phonon frequency modes (above 100 cm$^{-1}$) can mainly be attributed to the vibrations of relatively lighter atoms, Sn and X. In other words, the higher phonon frequency modes come from deformations of the octahedrons, not from the relative motion of the Cs atoms and the octahedrons. However, both vibrations of octahedrons and vibrations of Cs atoms contribute to lower frequency modes.

5.3.2 Soft phonon modes and phase transitions

Now, let us investigate the displacement patterns of the soft modes in the $\alpha$ phase first. Figure 5.4, from left to right shows the displacement pattern of the soft phonon mode at the $M$ point, denoted by $M_2^+$ (corresponding to the irreducible representation notation of the Koster-Slater tables [94] for the group $D_{4h}$) (also denoted by $M_3^+$, $M_3^+$ or $M_2^+$ in different literatures depending on how the irreducible representations are ordered in the character tables [92; 34; 95; 96; 97; 98; 99], and the three-fold degenerate soft phonon modes at the $R$ point, denoted by $R_a$, $R_b$, and $R_c$, respectively.
We first may note that only the halogen ions are moving in these modes. At the M-point \((1,1,0)\pi/a\), the motions of the atoms on opposing vertical faces are opposite and thus correspond to a rotation of the octahedron about the \(c\)-axis. In adjacent unit cells, in the a-b plane, the twists are opposite leading to a new tetragonal cell rotated by \(45^\circ\) and with lattice constant \(a_t = \sqrt{2}a\). The motions at the R-point \((1,1,1)\pi/a\) at first may seem more complex, but this just reflects that now there is also a phase change for the opposite horizontal faces. So, the rotations of the octahedron in the two unit cells stacked on top of each other are opposite and may now occur about each of the cubic axes, \(a\), \(b\) or \(c\). In the literature, these are sometimes denoted as the \(R_{25}\) mode which corresponds to the Bouckaert-Smoluchowski-Wigner \([100]\) notation for the point group irreducible representations. It corresponds to the \(T_{2u}\) mode of the cubic group in the usual chemical notation \([101]\). Clearly, the \(\alpha \rightarrow \beta\) phase transition corresponds to the condensation of the \(M^{+}\) soft mode because it does not involve a doubling of the cell along the \(c\)-direction. This also means it corresponds to the Glazer tilt system \([102; 93]\) \(a^0a^0c^+\), meaning that there is only a rotation about the \(c\)-axis. The \(R_{25}\) on the other hand would correspond to Glazer tilt system \(a^0a^0c^-\) with alternating positive and negative twists about the \(c\)-axis.

The \(\gamma\)-phase is characterized by both octahedral twists about the \(c\)-axis and tilts about the tetragonal \(a\)-axis. It corresponds to the Glazer notation \(a^+b^-b^-\). The \(R_{25}\) mode corresponds to only twisting about the axes but in opposite direction in alternating unit cells. The \(\gamma\) phase can thus not be obtained directly from the \(\alpha\) phase. Inspection of the soft mode at the \(Z\)-point in the \(\beta\)-phase as shown in Fig. 5.5 reveals that not only the octahedrons rotate about the \(b\)-axis but also the Cs atoms rotate about the \(a\)-axis. The symmetry of this mode is \(Z^-_5\) in the Koster-Slater notation. It is doubly degenerate because one can either rotate the Cs about \(a\) and octahedra about \(b\) or vice versa.

The sequence of phase transitions can also be analyzed using group theory. The
Figure 5.4: From left to right shows the displacement patterns of soft phonon mode \( M_2^+, R_a, R_b, \) and \( R_c, \) or \( R_{25}, \) in the cubic phase, respectively. The green spheres are Cs atoms located at the corners of cubic unit cells, the gray ones are Sn atoms located at the center of unit cells, and the purple ones are \( X, X=I, Br, \) or \( Cl, \) located at the surface centers of unit cells. The displacements are represented by gray arrows.

Figure 5.5: The displacement pattern of the soft phonon mode at the \( k \)-point \( Z \) in the \( \beta \)-CsSnI\(_3\). The green spheres are Cs atoms, the grey ones are Sn atoms, and the purple ones are I atoms. The displacements of Cs atoms are represented by green arrows, while the displacements of I atoms are represented by purple arrows. For clarity, we only show the displacements of I atoms in the central octahedron. The phonon mode is named \( Z_{<5} \).
space group of the tetragonal phase (with space group No. 127 $D_{4h}^5$ or $P4/mbm$) is an isotropy subgroup of space group of the cubic phase (with space group No. 221 $O_h^1$ or $Pm3m$). According to group theory, the space group No. 221 can go to the space group No. 127 via four transformations [99]: $X_5^+, X_5^-, M_2^+$, and $M_3^+$ (using the notation from Stokes and Hatch [99]). But only the operation of $M_2^+$ leads to the correct atomic positions:

$$
\left( \frac{x}{2} + \frac{y}{2} - \frac{1}{4} - \frac{x}{2} + \frac{y}{2}, z \right)
$$

(in reduced coordinates) in the tetragonal phase, where $(x, y, z)$ are the reduced coordinates of an atom in the cubic phase. In fact, we may note that there is no soft phonon at the X-point the cubic BZ. In this way, the Cs atom at $(0,0,0)$ in the cubic phase transforms to the 2d (Wyckoff) positions in the tetragonal phase. The Sn atom at $(0.5,0.5,0.5)$ in the cubic phase transforms to the 2b (Wyckoff) positions in the tetragonal phase. Finally, the I atom at $(0.5,0.5,0)$ in the cubic phase goes to the 2a (Wyckoff) positions in the tetragonal phase and I atoms at $(0.5,0,0.5)$ and $(0,0.5,0.5)$ transform to 4h (Wyckoff) positions in the tetragonal phase. So the effect of condensation of the $M_2^+$ soft phonon mode is equivalent to the operation described by Eq. (5.1) in terms of a coordinate transformation.

The same analysis can be applied to the phase transformation from the $\beta$ phase to $\gamma$ phase (with space group No. 62 or $D_{2h}^{16}$ or $Pnma$). The space group No. 127 can go to the space group No. 62 via two transformation: $Z_5^-$ and $Z_5^+$. But only the operation of $Z_5^-$:

$$
(x', y', z') \rightarrow \left( y', x' - \frac{1}{2}, \frac{z'}{2} - \frac{1}{4} \right),
$$

transforms the atoms in the $\beta$ phase to the correct positions in the $\gamma$ phase. (Please notice that the y-coordinate and z-coordinate are switched compared to the notation
in the book of Stokes and Hatch [99].) The Cs atoms at 2d positions in the \(\beta\) phase transform to the 4c positions in the \(\gamma\) phase, the Sn atoms at the 2b positions in the \(\beta\) phase transform to the 4b positions in the \(\gamma\) phase, and the I atoms at the 2a and 4h positions in the \(\beta\) phase transform to the 4c and 8d positions in the \(\gamma\) phase, respectively. So the effect of condensation of the \(Z_{-5}\) soft phonon mode is equivalent to the operation described in Equation (5.2) for the coordinate transformation. The phase transitions from the \(\alpha\) phase to \(\beta\) phase, then to \(\gamma\) phase, can be summarized as follows

\[
O_{1h}^1 \xrightarrow{M_{z}} D_{4h}^5 \xrightarrow{Z_{z}} D_{2h}^{16}.
\]

(5.3)

In the paper by Mori and Saito [34] it was claimed that the \(\beta\)-CsSnBr\(_3\) (with space group No. 127) can transform to the lower symmetry phase with space group No.90 (\(D_4^2\) or \(P42_12\)) by the condensation of the \(R_{25}\) soft phonon mode. But from the group theory point of view, this appears incorrect. According to the group theory, the space group No. 127 can only transform to the No. 90 isotropy subgroup via the operation \(\Gamma_1^-\):

\[
(x', y', z') \rightarrow \left(x', y' - \frac{1}{2}, z'\right).
\]

(5.4)

However, as illustrated in Fig. 5.6, the operation of \(\Gamma_1^-\)-symmetry is related to displacements of Sn atom and I atoms just above and below the Sn along the c-axis (z-direction). It is thus not related to the rotations of the \(R_{25}\) soft phonons and does not correspond to a soft mode. Also, in this space group the c-lattice constant is not doubled, as mentioned by Mori and Saito [34]. An \(R_{25}\) soft-mode directly from the cubic phase could lead to space group 140, \(D_{18h}^{4h}\) or \(I4/mcm\) instead. So, it appears that either the space-group determination or the soft mode analysis is incorrect in Ref. [34]. We also note that the \(\gamma\)-phase has not been observed for this material but is, according to our calculations, free of soft-phonon modes and hence mechanically stable. Further work on the nature of the phase transitions in CsSnBr\(_3\) appears to
The structural changes from $\alpha$ to $\beta$, and to $\gamma$ phases only involve the rotations (with some slight distortions) of the octahedrons; all octahedrons remain corner shared. However, the crystal structure of the yellow phase and monoclinic phase are quite different from those of the $\alpha$, $\beta$, and $\gamma$ phases; they display edge-sharing of the octahedra, so re-bonding is required. It seems that the phase transitions from $\gamma$-CsSnI$_3$ to Y-CsSnI$_3$ and from $\alpha$-CsSnCl$_3$ to $M$-CsSnCl$_3$ cannot be described by condensations of particular soft phonons. In fact, we find no soft phonon modes in the $\gamma$-phase of any of these compounds. This indicates the mechanical stability of this phase. However, this does not preclude chemically induced further phase transitions.

We finally note that the series of phase transitions from $\alpha$ to $\beta$ to $\gamma$ increase the density of the crystal. They are driven by the fact that the cage size for the Cs atom in the ideal cubic perovskite is set by the Sn-I octahedron size and is slightly too large for a Cs atom. This is related to the tolerance factor $t$, defined for example in
Benedek and Fennie [103] and given by

\[ t = \frac{R_{AC}}{\sqrt{2}R_{BC}} \]  

(5.5)

with \( R_{AC} \) and \( R_{BC} \) ideal bond-lengths. Using ideal bond-lengths based on Shannon ionic radii [104], we obtain \( t \)-values of 0.987, 0.971 and 0.900 for the CsSnCl\(_3\), CsSnBr\(_3\), CsSnI\(_3\) case respectively. The fact that these are smaller than 1 indicates that rotations of the octahedra are expected and is consistent with the general trend of oxide perovskites of a transition to the \( Pnma \) phase group for materials with \( t < 1 \). The driving force for this stabilization is to optimize the environment of the \( A \)-cation. We note that for CsSnCl\(_3\), with the largest \( t \) among these materials, the transitions to the \( \beta \)-phase and \( \gamma \)-phase were not observed, but instead a transition to the differently bonded monoclinic phase occurs. For the I and Br case, the rotation angles about the \( c \)-axis in the \( \beta \)-phase, are respectively 13.89° and 12.63° based on the calculated relaxed structures. For the \( \gamma \)-phase, the rotations about the \( c \)-axis and \( a \)-axis are calculated to be 13.86° and 10.23° for CsSnI\(_3\) and 11.86° and 8.74° for CsSnBr\(_3\). Thus, the smaller \( t \), the larger the rotation as expected. We only have experimental values for CsSnI\(_3\) where the crystal structure measured by X-ray diffraction [33] correspond to an angle of 9.09° in the \( \beta \)-phase and 10.09° and 3.85° in the \( \gamma \)-phase relative to the \( c \) and \( a \) axes respectively. The calculations agree qualitatively with the experiments in terms of order of magnitude and in predicting that the rotation about the \( c \)-axis is larger than that about the \( a \)-axis.

5.4 Conclusions

In this chapter, we presented full phonon band structures and atom resolved densities of states for CsSnX\(_3\), X=I, Br, Cl for various structures. These calculations
showed soft-phonon modes between $M$ and $R$ in the cubic $\alpha$ phase and near $Z$ in the tetragonal $\beta$-phase. We showed that their normal mode displacement patterns correspond to a pure octahedron rotation about one cubic axis for the $M$ point, and an alternating rotation of octahedra back and forth along one axis for the $R$-point. The $M$-rotations which correspond to the irreducible representation $M_2^+$ are responsible for the phase transition to the $\beta$-phase. The normal mode of the soft mode at $Z$, which has $Z_5^-$ symmetry combines further rotations of the octahedrons about one axis perpendicular to the tetragonal symmetry axis and rotation of the Cs atoms about the other axis. This mode is responsible for the $\beta \rightarrow \gamma$ transition. The $\gamma$-phase is found to be mechanically stable because it displays no soft-phonon modes. We find it also to be stable in CsSnBr$_3$ and thus predict this phase might be the stable one in this material at lower temperatures. On the other hand, the yellow phase of CsSnI$_3$ and monoclinic phase of CsSnCl$_3$ involve a more complex re-arrangement of octahedra into edge-sharing octahedra, which clearly cannot be obtained from a soft-phonon mechanism. These phases themselves show no soft-phonon modes. They remain nevertheless a concern for photovoltaic applications for the ultimate stability of these materials in different chemical environments (for example moist air) because these phases have much larger band gaps.
Chapter 6

Conclusions

In this thesis we focus on studying the fundamental properties of CsSnX$_3$ with X=I, Br, and Cl by first-principles calculations. First, in the Chapter 2, we performed quasiparticle self-consistent $GW$ calculations to study electronic band structures in these materials. Spin-orbit coupling effects were included. The changes in band structures when these materials undergo phase transitions were investigated. Our QS$GW$ band gap calculations (with assuming a structure independent gap correction) show larger band gaps than previous calculations and are in good agreement with experimental results, see Table 2.5. The most interesting finding is that these materials have a rather unusual “inverted” band structure with a non-degenerate $s$-like valence band and a degenerate $p$-like conduction band. Further analysis found that the VBM has a strong Sn-$s$ and X-$p$ antibonding character while the CBM has a Sn-$p$ character. The strong intra-atomic Sn-$p$ to Sn-$s$ character explains to first order why these materials have strong luminescence and also explains the relatively weak dependence on anions (when X changes from I to Br, even to Cl). The strong Sn-$s$ and X-$p$ interaction near the VBM can explain why the VBM occurs at the $R$-point, and why these materials have the anomalous dependence of the band gap on lattice constants. Effective masses for electrons and hole were calculated. The small effective hole mass results in high hole mobility, which is confirmed in the literature. The
free-exciton binding energy was estimated to be on the order of 0.1 meV in CsSnI$_3$, which is very different from a reported high value of 18 meV [43]. Our low value is obtained by using the static dielectric constant, which is almost 10 times larger than the high-frequency dielectric constant. This is consistent with the fact that although the vibrational frequencies are pretty low, they are still expected to contribute to the dielectric screening of the electron-hole interaction. No evidence for 2D motion of excitons as claimed by Chen et al. [43] was found and, therefore, their method of determining the binding energy of the excitons is flawed. Finally, we pointed out that the PL should result from bound excitons, not free excitons.

In Chapters 3 and 4, we presented our zone center phonon calculations for CsSnX$_3$ in all known phases. All zone center phonon frequencies with symmetry assignments were provided; infrared and Raman spectra were simulated. LO–TO splittings and dielectric constants, both static ones and high frequency ones, were calculated. Generalized Lyddane-Sachs-Teller relation was tested. These materials show strong LO–TO splittings, and hence, have large static dielectric constants. LO phonons contribute to the infrared absorption spectra of these materials. This fact explained the third observed IR frequency (the highest frequency one) in $\alpha$-CsSnBr$_3$ and $\alpha$-CsSnCl$_3$ from Donaldson et al. [80] who only listed three observed IR frequencies for each case. Our simulated IR spectra for $\alpha$-CsSnBr$_3$ and $\alpha$-CsSnCl$_3$ show four main peaks for each case. It turns out that the three observed bands are our calculated $T_{1u}^{(2)} (TO – LO)$ average mode, $T_{1u}^{(3)} (TO)$ and $T_{1u}^{(3)} (LO)$ modes, respectively. The calculated lowest mode, $T_{1u}^{(1)}$ at about 20-30 cm$^{-1}$, has a short lifetime due to its coincidence with a strong peak in phonon density of states which would broaden the transition to the extent that it becomes difficult or impossible to detect. LO phonons also prominently appear in Raman spectra, whether in $\gamma$-CsSnI$_3$ or in $\gamma$-CsSnCl$_3$. In the end of the Chapter 3, we pointed out the strong LO-hole-plasmon coupling in these materials, which results from the relatively high plasmon frequency (due
to the low hole mass and the low high-frequency dielectric constant) and the low
LO-phonon frequency; in other words, the plasmon frequency is comparable to the
LO-phonon frequency. In the Chapter 4, we showed that observed Raman spectra in
$M$-CsSnCl$_3$ not only contain the expected even symmetry first order allowed Raman
modes, but also prominently showed forbidden LO modes. With this interpretation,
our calculated phonons agree to within a few cm$^{-1}$.

In the Chapter 5, we presented full phonon band structures and atom resolved
densities of states for CsSnX$_3$, X=I, Br, Cl for various structures. We found soft
phonons in cubic and tetragonal phases, but not in orthorhombic and monoclinic
phases. In the cubic phase, soft phonon modes show a dispersion-less branch from
$M$ to $R$, while soft phonon modes are near $Z$ and $\Gamma$ in the tetragonal phase. After in-
vestigating their normal mode displacement patterns, we found that $M_2^+$ corresponds
to a pure octahedron rotation about one cubic axis and, therefore, is responsible for
the phase transition from the $\alpha$ phase to the $\beta$ phase. And $Z_5^-$ symmetry combines
further rotations of the octahedrons about one axis perpendicular to the tetragonal
symmetry axis and rotation of the Cs atoms about the other axis and is responsible
for the $\beta \rightarrow \gamma$ transition. The phase transitions from the $\alpha$ phase to the $\beta$-phase,
and then to the $\gamma$ phase, can be summarized as follows

\[ O_h^1 \xrightarrow{M_2^+} D_{4h}^5 \xrightarrow{Z_5^-} D_{2h}^{16}, \]

and the atomic coordinates, Wyckoff positions, change in the following way:

\[ (x, y, z) \xrightarrow{M_2^+} \left( \frac{x + y - 1}{2}, -\frac{x + y}{2}, z \right) \equiv (x', y', z') \xrightarrow{Z_5^-} \left( y', x' - \frac{1}{2}, \frac{z' - 1}{4} \right), \]

where $(x, y, z)$ is a reduced coordinate in the cubic phase. The $\gamma$ phase is found
to be mechanically stable because it displays no soft-phonon modes. Phase transi-
tions to $Y$-CsSnI$_3$ and $M$-CsSnCl$_3$, unfortunately, cannot described by a soft-phonon mechanism because they involve a more complex rearrangement of octahedra into edge-sharing octahedra.
Bibliography


of perovskite semiconductor compound CsSnI\textsubscript{3}. *Journal of Applied Physics*, 110(6):063526, 2011. 5, 33


of the Type: ABX₃-A'BX₃, ABX₃-AB'X₃ and ABX₃-ABX'₃; X=Halogen. Z. Physik. Chem., 175:63–80, 1992. 6, 10, 125


[76] M. Veithen, X. Gonze, and Ph. Ghosez. Nonlinear optical susceptibilities, raman efficiencies, and electro-optic tensors from first-principles density func-


