EXPLORING MANY BODY INTERACTIONS WITH RAMAN SPECTROSCOPY

by

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Abstract

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Many-body interactions are cornerstones of contemporary solid state physics research. Especially, phonon related interactions such as phonon-phonon coupling, spin-phonon coupling and electron-phonon coupling constantly present new challenges. To study phonon related many-body interactions, temperature dependent Raman spectroscopy is employed. Firstly, a new design and construction of a Raman microscope aimed at high collection efficiency, positional and thermal stability is discussed. The application of the home-built Raman microscope is shown in the context of two types of novel materials; \( \text{Cr}_2\text{Ge}_2\text{Te}_6 \) (spin-phonon coupling) and \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \) (phonon-phonon coupling). \( \text{Cr}_2\text{Ge}_2\text{Te}_6 \) is one of the rare class of ferromagnetic semiconductors and recent thermal transport studies suggest the spin and lattice are strongly coupled in its cousin compound \( \text{Cr}_2\text{Si}_2\text{Te}_6 \). In this work, the spin-phonon coupling in \( \text{Cr}_2\text{Ge}_2\text{Te}_6 \) has been revealed in multiple ways: we observed a split of two phonon modes due to the breaking of time reversal symmetry; the anomalous hardening of an additional three modes; and a dramatic enhancement of the phonon lifetimes. It is well-known that the phonon-phonon interaction plays a significant role in determining the thermal transport properties of thermoelectrics. A comprehensive study of the phonon dynamics of \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \) has been performed. We found that the unusual temperature dependence of different phonon modes originates from both cubic and quartic anharmonicity. These results are consistent with the resonance bonding mechanism, suggesting that the resonance bonding may be
a common feature for conventional thermoelectrics. In the Raman spectra of Bi$_2$Te$_2$Se, the origin of the extra Raman feature has been debated for decades. Through a temperature dependent Raman study, we were able to prove the feature is generated by a Te-Se antisite induced local mode. The anomalous linewidth of the local mode as well as the anharmonic behavior were explained through a statistical analysis. Then, a wavelet transform and data clustering based spike-removal algorithm is proposed to resolve the erroneous spikes caused by cosmic rays in Raman spectra. Data sets from real measurements were analyzed to demonstrate the capability of the algorithm. Finally, the results of a minor project are presented. Thin films of the high dielectric material SrTiO$_3$ grown via a new method on silicon(100) are studied by ellipsometry. The results suggest that two layers of SrTiO$_3$ are formed during the growth.
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Chapter 1

Introduction

1.1 Many-body interactions with phonons

Fundamental excitations and many-body interactions are cornerstones of contemporary solid state physics research. Although phonons, as the collective vibration of atoms in solids, are one of the most extremely studied quasiparticles, phonon related interactions such as phonon-phonon coupling, spin-phonon coupling and electron-phonon coupling constantly present new physics and challenges. The most famous example might be conventional superconductors where the electron-phonon coupling provides the “glue” for Cooper pairs. Thus, studying phonon related many-body interactions will push the knowledge boundary forward in condensed matter physics. Besides, from the perspective of real applications, these interactions also play an important role in determining the fundamental properties of materials (i.e. thermal expansion, thermal and electrical conductivity, magnetostriction, multiferroics and piezoelectric effects) which give birth to various types of devices (i.e. thermoelectric cooling, magnetostrictive and piezoelectric devices). Therefore, these studies can also have a great impact on industry.

One natural way to study these phonon related interactions is to track the temperature dependence of phonon frequencies and linewidths that should reveal the temperature
renormalization of the self-energy of the phonon modes. However, from the experimen-
tal perspective it is very challenging due to the small temperature dependent changes (typically a few 100 $\mu$eV), posing strict requirements on the **resolution**. Inelastic light scattering, especially variable temperature Raman scattering, provides numerous advan-
tages including: non-destructive and contactless probe, spectra that directly reflect the
intrinsic response of the sample, and high temperature and spectral resolution. Raman
scattering measures the energy difference between incoming and outgoing photons and
the difference corresponds to a fundamental excitation in the materials. Through track-
ing the temperature dependent phonon frequencies and linewidths one can gain profound
insights into the interactions.

### 1.2 Scope of the thesis

In this thesis we present a complete doctoral work with three aspects: instrumentation,
algorithm, and studies of various materials. The instrument developed was used to study
phonon-phonon coupling and the spin-phonon coupling in several materials.

Chapter 2 discusses the general theoretical background for the following chapters.

Chapter 3 starts with a discussion of the fundamental operating principles of Raman
spectroscopy. Although there are many commercial variable temperature Raman micro-
scopes available, the current designs suffer from mechanical and thermal stability issues,
low light collection efficiency, and high cut-off energy. These drawbacks usually become
a bottleneck to research, limiting our capacity to study materials with Raman scattering.
Consequently, a home-built variable temperature Raman microscope which can overcome
these downsides is necessary. A new design aiming to achieve high collection efficiency,
high mechanical and positional stability as well as automated functions is presented.
Tests on two challenging materials, Bi$_2$Se$_3$ and V$_2$O$_3$, are also given to demonstrate the
overall capability of the setup.
Chapter 1. Introduction

The application of the home-built Raman microscope is first shown in chapter 4 in the context of a ferromagnetic semiconductor Cr$_2$Ge$_2$Te$_6$. Cr$_2$Ge$_2$Te$_6$ has been of interest for decades as it is one of only a few ferromagnetic semiconductors. Recently this material has been revisited due to its potential as a two dimensional semiconducting ferromagnet, and a substrate to induce anomalous quantum Hall states in topological insulators. Furthermore, it has been shown that Cr$_2$Ge$_2$Te$_6$ and its cousin compound Cr$_2$Si$_2$Te$_6$ have negative thermal expansion coefficients upon cooling, and the thermal conductivity is very low even comparable to thermoelectrics, indicating that the spins and the lattice are strongly coupled. However, the phonon dynamics and the interplay between magnetism and phonons remain unknown even in bulk Cr$_2$Ge$_2$Te$_6$. In this chapter we investigate temperature dependent phonon behavior in Cr$_2$Ge$_2$Te$_6$ using polarized temperature dependent Raman scattering. Seven features are observed. Two modes split and are ascribed to spin ordering induced time reversal symmetry breaking. For the other five modes the temperature dependence agrees well with Klemens’s model above $T_C$. However, below $T_C$ three out of the five modes deviate from the anharmonic prediction. The spin-phonon coupling coefficients of the three modes are obtained. These results confirm that the spins and phonons are strongly coupled and also suggest a potential method to study spin-phonon coupling in exfoliated Cr$_2$Ge$_2$Te$_6$ 2D atomic crystal with Raman scattering.

Thermoelectrics are another interesting class of materials from the perspective of both physics and engineering. These materials are known for their very low thermal conductivity which originates from the large phonon-phonon scattering processes. Temperature dependent Raman scattering is an ideal tool to study the dynamics of phonons at the $\Gamma$ point of the Brillouin zone. Chapter 5 discusses Raman results from single crystals Bi$_2$Te$_3$, Bi$_2$Te$_2$Se and Bi$_2$Se$_3$ over the temperature range from 4 K to 293 K. Similar Raman spectra were observed which can be attributed to the similarity in lattice structure. Klemens’s model is employed to explain the renormalization of the phonon linewidths.
For Bi$_2$Te$_3$ and Bi$_2$Se$_3$, the temperature dependent phonon frequencies are discussed in detail with the consideration of both the lattice expansion and the quartic anharmonicity explicitly. A detailed analysis of the three phonon modes reveals dramatically different behavior. These findings are all consistent with the theoretically suggested resonance bonding mechanism, confirming its prevalence in the IV-VI, V$_2$-VI$_3$ thermoelectrics.

The small defect formation energies in Bi$_2$Te$_{3-x}$Se$_x$ often result in large carrier densities, causing the bulk conductance to dominate over the surface conductance. A transition from p-type to n-type behavior in the Bi$_2$Te$_{3-x}$Se$_x$ solid solution has been known for decades. Further studies have revealed that when $x$ is close to 1, namely Bi$_2$Te$_2$Se, the crystal structure is ordered. Recently, a new method was developed to grow Bi$_2$Te$_2$Se with large resistivity. However, further studies using X-ray diffraction and scanning tunneling microscopy both showed that the defect formation is inevitable in Bi$_2$Te$_2$Se. Chapter 6 starts with a discussion about a Raman mode whose origin has been debated for decades. Via its temperature dependence, as well as a comparison to other modes, the mode is proven to be a Te-Se antisite defects induced local mode. In addition, the phonon dynamics of all four modes are discussed in detail. Especially, through statistical analysis, the anomalous phonon linewidth of the local mode is well explained.

Because CCD detectors used in Raman microscopes are vulnerable to cosmic rays, a normal dispersive Raman microscope suffers from spikes caused cosmic rays. As a result, many spurious spikes occur in the measured spectra, creating an obstacle in the analysis. In chapter 7, we outline a new method featured at automatic removal of these spikes. Specifically, wavelet transform and data clustering are employed in the spike-removal algorithm. The algorithm has been shown to generate spike-free spectra with negligible spectral distortion on the real spectra. The reduced dependence on the selection of wavelets and intuitive wavelet coefficients adjustment strategy enable non-experts to employ this powerful spectra-filtering technique.

*The Roman numerals denote the column number of the elements in the periodic table and the subscripts indicate the number of atoms per unit cell.
Chapter 8 discusses an ellipsometry study of a SrTiO$_3$ film on silicon(100). SrTiO$_3$ is an important high dielectric material for a wide range of applications. Epitaxial buffer layers enable the many functionalities found in perovskites to be integrated with silicon. However, epitaxial growth of SrTiO$_3$ on silicon is tricky and has so far only been achieved by molecular beam epitaxy. Nonetheless, previous investigations of these films were limited by the amorphous layer occurring at the interface. Through a combination of improved interface quality and an improved model, we report the optical properties of SrTiO$_3$ films on Si(100) investigated by spectroscopic ellipsometry. We find the data is best described by a model with two different SrTiO$_3$ layers, potentially resulting from variations in the oxygen content.

In the end, we present our conclusions and also suggest future experiments for furthering the understanding of the materials studied in this thesis.
Chapter 2

Theoretical framework

2.1 Introduction

Due to the diversity of the techniques and areas covered in this thesis, we will describe general physics such as the principle of Raman scattering and the theory of anharmonicity in this chapter and leave more specific theoretical background to the individual chapters.

2.2 Raman scattering and selection rules

As mentioned above, the Raman effect is the inelastic scattering of photons. The process of spontaneous Raman scattering can be illustrated in FIG. 2.1. We can see from the figure the transition between the many-body states $|s'\rangle$ and $|s\rangle$ is mediated by an intermediate state $|i\rangle$ and the energy difference between the incoming photon and outgoing photon corresponds to the energy ($\Delta E$) of the excited states. Mathematically, this process can be described by the following transition matrix between $|s'\rangle$ and $|s\rangle$,

$$H_{s',s}^R = \sum_i <s'|H_{int}|i> <i|H_{int}|s> \frac{\hbar \omega - (E_i - E_s)}{\hbar \omega}$$

(2.1)
where \(|i>|\) is an intermediate state, \(E_i\) and \(E_s\) are the energies of the corresponding states, \(\omega\) is the excitation photon energy and \(H_{int}\) is the electron-photon interaction Hamiltonian. The electron-photon coupling can take the form \(\vec{E} \cdot \vec{r}\) in the dipole approximation, since the wavelength of the light source (typically a laser) used in Raman scattering is much longer than the lattice constant. Usually for Stokes scattering, \(|s>|\) is the ground state and of \(E\) (identity) symmetry. For Raman scattering caused by phonons in solids, the final state \(|s'>|\) contains information about the symmetry of the phonon mode. If \(\Gamma_\vec{r}\) is the representation that \(\vec{r}\) belongs to, according to the matrix-element theorem[3], the intermediate state \(|i>|\) should belong to the \(\Gamma_\vec{r}\) representation (\(\Gamma_\vec{r} = \Gamma_\vec{r} \otimes \Gamma_E\)). Consequently, the final state \(|s'>|\) should belong to the following representation,

\[
\Gamma_\vec{r} \otimes \Gamma_\vec{r} = \Gamma_{\vec{r}\vec{r}} \tag{2.2}
\]
Thus for a mode to be Raman active, the basis functions of its irreducible representation have to include bi-linear functions (i.e. $x^2, y^2, xy$). These are the selection rules that Raman scattering obeys. Similar statements hold for Anti-Stokes scattering too.

We can see the transition matrix element is associated with the polarization of both incoming and outgoing photons. The light scattering probability is proportional to the square modulus of the transition matrix element. Thus the Raman intensity of a phonon mode can be expressed by a more compact form,

$$I_R = |\vec{e}_i \cdot \mathbf{R} \cdot \vec{e}_o^T|^2$$

where $\mathbf{R}$ is called the Raman tensor, and $\vec{e}_i$ and $\vec{e}_o$ are the polarization of the incoming and outgoing photons respectively. As we discussed, the transition matrix of a phonon mode is determined by the irreducible representation it belongs to. Since there is a one to one correspondence between $\mathbf{R}$ and transition matrices, the symmetry of a phonon mode can also help us in determining $\mathbf{R}$. For example, the silicon Raman active mode is of $T_{2g}$ symmetry. The basis functions of the $T_{2g}$ irreducible representation are triply degenerate as $(xy, xz, yz)$. Consequently, the three Raman tensors of this phonon mode will take the following forms.

$$\mathbf{R}_{T_{2g}} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}$$

On the other hand, by measuring the Raman response for various configurations of $\epsilon_{i,o}^\gamma$ as well as at different angles with respect to the sample, one should be able to access the individual elements in $\mathbf{R}$. Consequently, the symmetry of the excitations can be revealed. One example is shown in chapter 4 where the symmetry of the phonon modes is determined in this way.
2.3 Anharmonicity

Since the anharmonicity induced changes to the self energy of phonon modes are one of the central topics in most parts of thesis, we outline the underlining theory and physics in this section.

As we know, anharmonicity (phonon-phonon interactions) plays a significant role in solids. Without anharmonicity, solids cannot expand and their thermal conductivity will be infinite which is apparently unphysical. Usually, the phonon Hamiltonian in crystal can be written as[4],

\[
H = H_0 + H_A
\]

\[
H_0 = \sum_{\vec{q}, j} \hbar \omega(\vec{q}, j) (a_{\vec{q}, j}^\dagger a_{\vec{q}, j} + 1/2)
\]

\[
H_A = \sum_{\vec{q}_1, \vec{q}_2, \vec{q}_3, j_1, j_2, j_3} V \left( \begin{array}{ccc}
\vec{q}_1 & \vec{q}_2 & \vec{q}_3 \\
 j_1 & j_2 & j_3 
\end{array} \right) A(\vec{q}_1, j_1) A(\vec{q}_2, j_2) A(\vec{q}_3, j_3) + \\
\sum_{\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4, j_1, j_2, j_3, j_4} V \left( \begin{array}{cccc}
\vec{q}_1 & \vec{q}_2 & \vec{q}_3 & \vec{q}_4 \\
 j_1 & j_2 & j_3 & j_4 
\end{array} \right) A(\vec{q}_1, j_1) A(\vec{q}_2, j_2) A(\vec{q}_3, j_3) A(\vec{q}_4, j_4)
\]

where \(H_0\) (\(H_A\)) denotes the harmonic (anharmonic) contribution, \(\vec{q}_i\) and \(j_i\) are the momentum and phonon band index, \(\omega(\vec{q}, j)\) is the harmonic phonon energy, \(V\) is the anharmonic coefficients derived from the lattice potential energy of deformation at constant volume, \(a^\dagger\) (\(a\)) is the phonon creation (annihilation) operator, and \(A(\vec{q}_i, j_i)\) can be expressed as follows,

\[
A(\vec{q}_i, j_i) = a^\dagger_{-\vec{q}_i, j_i} + a_{\vec{q}_i, j_i}
\]

The first term in equation 2.6 denotes the cubic anharmonicity and the second term comes from the quartic anharmonicity. The sum of the momenta in each term equals 0.
(\sum_i \vec{q}_i = 0) due to the conservation of momentum.

2.3.1 Self energy of phonon modes

Typically the one-phonon scattering process observed in Raman spectra is generated by the creation of phonon modes located at the \( \Gamma \) point (\( \vec{q} = 0 \)) of the Brillouin Zone. According to the standard perturbation theory, it can be shown that the effect of the anharmonic interactions (equation 2.6) is to add a temperature dependent self energy (\( \Sigma(0,j;\omega,T) \)) to the harmonic phonon energy \( \omega(0,j) \) of the Raman-active phonon[5]. The real part (\( \Delta(0,j;\omega,T) \)) of the self energy causes a temperature dependent frequency shift to the phonon mode and the imaginary part (\( \Gamma(0,j;\omega,T) \)) induces a temperature dependent broadening to its linewidth. The major components of the self energy are[6],

\[
\Sigma(0,j;\omega,T) = \Delta_2(0,j;\omega,T) + \Delta_3(0,j;\omega,T) + \Delta_4(0,j;\omega,T) + i\Gamma_3(0,j;\omega,T) + i\Gamma_4(0,j;\omega,T)
\]

(2.7)

where \( \Delta \) and \( \Gamma \) are the real parts (phonon frequency) and imaginary parts (phonon linewidth) of the self energy respectively, \( \omega \) is the phonon frequency, and \( T \) is the temperature. The subscript 2 denotes the quasi-harmonic contribution which comes from the temperature dependent lattice expansion. Subscripts 3 and 4 indicate the temperature dependent correction due to the cubic and quartic anharmonicity respectively. The lattice expansion induced phonon frequency can be expressed with Grüneisen parameter \( \gamma \) and thermal expansion coefficients \( \alpha \) which reads[7]

\[
\Delta_2(0,j;\omega,T) = \Delta(\omega,T)_{lattice} = \omega(0)(\exp^{-\gamma \int_0^T \alpha_a(T') + \alpha_b(T') + \alpha_c(T')dT'} - 1)
\]

(2.8)

where the subscripts of \( \alpha \) indicate the crystal axes and \( \omega(0) \) is the phonon frequency at 0 K.
For the cubic anharmonicity both phonon frequencies and linewidths are renormalized by the temperature due to the second-order perturbation[7],

\[
\Delta(0, j; \omega, T) = -\frac{18}{\hbar^2} \sum_{\vec{q}, j_1, j_2} |V(0, \vec{q} - \vec{q})|^2 R(\omega) \tag{2.9}
\]

\[
R(\omega) = \frac{n_B(\vec{q}, j_1) + n_B(-\vec{q}, j_2) + 1}{\omega - \omega(\vec{q}, j_1) - \omega(-\vec{q}, j_2)} - \frac{n_B(\vec{q}, j_2) - n_B(-\vec{q}, j_1)}{\omega - \omega(\vec{q}, j_1) + \omega(-\vec{q}, j_2)} - \frac{n_B(\vec{q}, j_1) - n_B(-\vec{q}, j_2)}{\omega + \omega(\vec{q}, j_1) - \omega(-\vec{q}, j_2)} \tag{2.10}
\]

\[
\Gamma(0, j; \omega, T) = \frac{18}{\hbar^2} \sum_{\vec{q}, j_1, j_2} |V(0, \vec{q} - \vec{q})|^2 L(\omega) \tag{2.11}
\]

\[
L(\omega) = (n_B(\vec{q}, j_1) + n_B(-\vec{q}, j_2) + 1) \delta(\omega - \omega(\vec{q}, j_1) - \omega(-\vec{q}, j_2)) - (n_B(\vec{q}, j_2) - n_B(-\vec{q}, j_1)) \delta(\omega + \omega(\vec{q}, j_2) - \omega(-\vec{q}, j_1)) - (n_B(\vec{q}, j_1) - n_B(-\vec{q}, j_2)) \delta(\omega - \omega(\vec{q}, j_1) + \omega(-\vec{q}, j_2)) \tag{2.12}
\]

where \( n_B \) is the Bose factor \( n_B(\vec{q}, j_i) = \frac{1}{\exp[\beta \omega(\vec{q}, j_i)] - 1} \). The cubic anharmonic terms in \( \Delta \) and \( \Gamma \) consist of both decay (the first term in \( R(\omega) \) and \( L(\omega) \)) and coalescence (the last two terms in \( R(\omega) \) and \( L(\omega) \)) processes (see FIG. 2.2). The coalescence process requires the participation of a second phonon to fuse into a third phonon. The possibility of this process is very low, especially at low temperatures because the requirements of thermal population of the second phonon[8]. Unless the phonon bands have a very unique structure (i.e. the phonon bands of PbTe[9]), the coalescence process can be neglected. If the coalescence process is neglected the quartic terms of phonon self energy will have
the following form[7],

\[
\Delta(0, j; \omega, T) = \frac{24}{\hbar} \sum_{\vec{q}, j_1} V \begin{pmatrix} 0 & 0 & \vec{q} & -\vec{q} \\ j & j & j_1 & j_1 \end{pmatrix} (2n(\vec{q}, j) + 1) - \\
\frac{96}{\hbar^2} \sum_{\vec{q}, j_1} |V| \begin{pmatrix} 0 & \vec{q}_1 & \vec{q}_2 & -\vec{q}_1 - \vec{q}_2 \\ j & j_1 & j_2 & j_3 \end{pmatrix}^2 \times \\
(n_B(-\vec{q}_1 - \vec{q}_2, j_3) + 1)(n_B(\vec{q}_1, j_1) + 1)(n_B(\vec{q}_2, j_2) + 1) - n_B(-\vec{q}_1 - \vec{q}_2, j_3)n_B(\vec{q}_1, j_1)n_B(\vec{q}_2, j_2) \omega - \omega(-\vec{q}_1 - \vec{q}_2, j_3) - \omega(\vec{q}_1, j_1) - \omega(\vec{q}_2, j_2)
\]

(2.13)

\[
\Gamma(0, j; \omega, T) = \frac{96}{\hbar^2} \sum_{\vec{q}, j_1} |V| \begin{pmatrix} 0 & \vec{q}_1 & \vec{q}_2 & -\vec{q}_1 - \vec{q}_2 \\ j & j_1 & j_2 & j_3 \end{pmatrix}^2 \times \\
(n_B(\vec{q}_1, j_1) + 1)(n_B(\vec{q}_2, j_2) + 1)(n_B(-\vec{q}_1 - \vec{q}_2, j_3) + 1) - n_B(-\vec{q}_1 - \vec{q}_2, j_3)n_B(\vec{q}_1, j_1)n_B(\vec{q}_2, j_2) \delta(\omega - \omega(-\vec{q}_1 - \vec{q}_2, j_3) - \omega(\vec{q}_1, j_1) - \omega(\vec{q}_2, j_2))
\]

(2.14)

We can see that the second-order perturbation by quartic anharmonicity contributes to both \(\Delta\) and \(\Gamma\), while the first-order perturbation only contributes to \(\Delta\).
Consequently, the renormalization of the phonon linewidth $\Gamma$ is free of lattice expansion as well as the first order correction to quartic anharmonicity. Besides, $\Gamma$ is also directly proportional to the phonon joint density of states because of the requirement of conservation of energy ($\delta$ function in equation 2.12 and 2.14). So, phonon linewidths are simpler than phonon frequency shifts and contain more intrinsic information about the sample and anharmonicity.

2.3.2 Anharmonic Models

As we discussed above, the decay process is the major contribution to the renormalization of phonon linewidths. The simplest decay channels can be considered as the decay of one optical phonon into two (three) acoustic phonons with the same energy through the cubic (quartic) anharmonic interaction. If these decay channels are the major contribution to the phonon linewidth, by setting $\omega_q = \omega_q = \omega/2$ in equations 2.11 and $\omega_{q1} = \omega_{q2} = \omega_{q2-q1} = \omega/3$ in equation 2.14 the extended Klemens model can be obtained as follows[6],

$$\Gamma(\omega,T) = A \left(1 + 2n_B(\omega_0/2)\right) + B \left(1 + 3n_B(\omega_0/3) + 3n_B(\omega_0/3)^2\right)$$ (2.15)

where $A$ (B) represents the strength of three-phonon (four-phonon) couplings, and $\omega_0/2$ and $\omega_0/3$ are the energy of the acoustic phonons that the optical phonon decays into. Since $B$ originates from the second order correction to the quartic anharmonicity, normally $B$ is one order of magnitude smaller than $A$. If the cubic anharmonicity is sufficient to fit the phonon linewidth, which is seen in chapters 5 and 6, $B$ can be set to 0 (Klemens’s model). For samples with crystalline disorder a temperature independent constant $\Gamma_0$ should be included to account for impurity induced broadening.

As for phonon frequencies, due to the complicated form in equation 2.9 and 2.13, it is hard to come up with an analytical formula directly. However, a simple assumption ($\Delta \propto \Gamma$) can be made for each decay process[10]. Consequently, the complete extended
Klemens model for both phonon frequencies and linewidths can be expressed as \[ \Omega(\omega, T) = \omega_0 + C(1 + 2n_B(\omega_0/2)) + D(1 + 3n_B(\omega_0/3) + 3n_B(\omega_0/3)^2) \] (2.16)

\[ \Gamma(\omega, T) = \Gamma_0 + A(1 + 2n_B(\omega_0/2)) + B(1 + 3n_B(\omega_0/3) + 3n_B(\omega_0/3)^2) \] (2.17)

where \( \omega_0 \) is the harmonic phonon frequency, and \( C \) (\( D \)) has the same meaning as \( A \) (\( B \)).

The models we have discussed so far have only covered the decay process induced temperature renormalization to the phonon self energy. This works well for the phonon linewidth for the reasons mentioned previously. However, as we have pointed out, other than decay processes, the phonon frequency can also have contributions from the lattice expansion as well as the first order correction from the quartic anharmonicity. In chapters 4 and 6 where we focus more on phonon linewidth these two terms are neglected. However, these two terms can play an important role in some cases (chapter 5). Now we focus on these two terms.

In theory the contribution from lattice thermal expansion can be calculated using equation 2.8 on the condition that all the parameters in the equation are known (namely thermal expansion coefficients and Grüneisen parameters, see chapter 5). However, in many cases these parameters are not available. In these cases, one usually fits the temperature dependence of phonon frequencies with equation 2.16 directly without explicitly considering the lattice expansion. This method works because the lattice expansion induced phonon frequency shifts are usually flat at low temperature and increase linearly as the temperature rises, which exactly matches the characteristic of equation 2.16. To see this more clearly, we extracted the thermal expansion contribution to the phonon frequencies of silicon and germanium from Ref. 7 and fit the data with Klemens’s model (\( D \) set to 0). The results are shown in FIG. 2.3. We can see that the thermal expansion induced Raman frequency shift can be well reproduced by the fit. This explains why temperature dependent Raman shifts can be fitted with Klemens’s model without
considering the lattice expansion contribution explicitly. However, sometimes this approach can miss interesting physics. For example, in chapter 5 we show that considering the lattice expansion explicitly can uncover the anomalous behavior from the quartic anharmonicity.

For the first order correction to the quartic anharmonicity (the first term in equation 2.13) we will prove in chapter 5 that the magnitude of this term increases much slower than that of decay processes with phonon mode energy $\omega$. For this term to be significant two conditions have to be satisfied: firstly, the Debye temperature of the sample should be low; secondly, the energy of the phonon mode should also be low. The two criteria lead us to consider this term explicitly only in Bi$_2$Se$_3$ and Bi$_2$Te$_3$, where the modes with lowest energy show interesting behavior (see details in chapter 5).

### 2.4 Voigt function

To reveal the self energy of a phonon mode, one needs to extract the phonon frequency and linewidth. For this purpose, Lorentzian is typically used to fit the Raman spectra. However, if the linewidth of the phonon mode is comparable to the instrumental resolution, Voigt function has to be employed to decouple the instrument induced broadening. The Voigt function used in the analysis of Raman spectra reads,

$$V(x, \sigma, \Omega, \Gamma) = \int_{-\infty}^{+\infty} G(x', \sigma)L(x - x', \Omega, \Gamma)dx'$$  \hspace{1cm} (2.18)

which is a convolution of a Gaussian and a Lorentzian[11]. Here the Gaussian is employed to account for the instrumental resolution and the Lorentzian represents a phonon mode. The half width $\sigma$ of the Gaussian was determined by the instrumental resolution, which is 1.8 cm$^{-1}$ in the system mentioned in chapter 3.
Figure 2.3: Temperature dependent of thermal expansion induced Raman shift of two semiconductors left: germanium, right: silicon. The fits using Klemens’s model are shown in solid blue line.
Chapter 3

Ultra-stable variable temperature Raman microscope

3.1 Introduction

Raman micro-spectroscopy is well suited for studying a variety of properties including chemical, magnetic, lattice, thermal, electronic, symmetry, and crystal orientation[12, 13, 14, 15, 16, 1, 17, 18]. As such this technique has been applied to wide-ranging areas including chemistry, physics, materials science and biology. Many interesting phenomena only emerge at low temperatures[19, 20, 21, 22], as such it is often highly desirable to measure and/or image a sample below room temperature. In addition, the temperature dependence of Raman features often reveals new information, such as the strength of phonon anharmonicity which is crucial for thermal properties[23]. For organic samples, low temperatures can immobilize the material in a near-native state, revealing much more detailed information about the samples and their interaction spectra[24, 25]. Thus numerous insights can be gained by measuring the temperature dependence of the Raman response. Typically, temperature control requires the use of cumbersome and expensive cryogenic liquids. For Raman micro-spectroscopy this can be extremely challenging, due
to a number of factors including the rapidly rising cost of helium, the low Raman scattering cross sections (typically $10^{-8}$ to $10^{-12}$)[26, 27], the requirement of high spatial and spectral resolution, as well as the need to use low laser power to prevent heating. This often creates a competing set of requirements, including long integration times, the use of high numerical aperture (NA, $NA = n \sin \theta / 2$ where $\theta$ is the angle of collection) objectives with low working distances, minimized use of helium, the need to place the sample in vacuum, and the need to keep the objective at a fixed location/temperature. To date, this has led to two different designs of low-temperature Raman microscopes. The first approach is to place the objective inside the cooling medium/vacuum, which enables high NA, but requires cryo-compatible objectives and leads to strong temperature dependence of the objective’s performance as well as its relative alignment with the sample. The second approach employs an intermediate NA, long working distance and glass compensated objective outside the cryostat. This results in higher mechanical stability of the objective, but at the cost of the large spot size, depolarization and especially the collection efficiency[24]. In addition, one also desires to make systems as automated as possible to reduce the operational errors and enable higher temperature resolution. Therefore, there has been an increasing demand for an automated system with high collection efficiency, and thermal and mechanical stability.

In this chapter, we describe a new design of Raman microscope, equipped with automated cryogenic temperature, laser power and polarization control as well as motorized imaging functions. Temperature changes in our system are based on an automated closed-cycle Cryostation, designed and manufactured by Montana Instruments Inc. For Raman excitation and collection, a Cryo-Optic module was employed, comprising a 100X, 0.9NA microscope objective, installed inside the Cryostation and kept at a constant temperature by a PID system. An Agile temperature stage was designed and installed under the sample platform, ensuring fast thermal response (less than 5 minutes from 4 K to 350 K) as well as excellent Cryostation platform mechanical (5 nm) and thermal (mKs) stability.
In addition to the small spot size and excellent collection efficiency this enables, the improved collimation by the objective provides for the use of Notch filters allowing signals down to 30 cm$^{-1}$, and excellent spectral resolution. Moreover, nearly perfect polarization response can be measured at any in-plane angle using a Fresnel rhomb. These combined features produce very reliable measurements with long integration times and continuous experiments lasting many weeks without the need for human intervention. This opens the door to widespread use of cryogenic Raman microscopy to probe nano-materials with low thermal conductivities and very weak Raman responses.

3.2 Operating Principles

Raman scattering measures the difference in energy between the incoming and outgoing photons. This difference corresponds to an excitation energy within the measured materials, enabling the use of a single wavelength light source to probe multiple excitations of a material. The basic components of a Raman microscope comprise a continuous wave laser, optical components to guide and focus the beam onto the sample, a laser filter, and a detector. After illuminating a sample, the elastic Rayleigh as well as Raman scattered light is collected by the same objective in the backscattering configuration[28]. Usually, the collected light must pass a set of filters before entering a spectrometer because of the very small scattering cross-section of the Raman processes[29].

3.3 Instrumentation

3.3.1 Optical design

We now describe in detail the overall design and layout of our Raman cryo-microscope system, which is shown in in FIG.3.1. To achieve high spatial and spectral resolution, a Laser Quantum Torus 532nm laser with a GHz-bandwidth was used as an excitation
Figure 3.1: Model of our Raman cryo-microscope. The optical breadboard and the supporting frame are hidden for clarity. Laser and collected Raman signals are shown in red and blue respectively. Components used to image the sample with white light are highlighted by the green dashed line. Details about abbreviations are shown as follow; half waveplate (HW), mirror (M), polarizer (P), stepper motor (SM), cubic beam splitter (CBS), Fresnel rhomb (FR), diffractive beam splitter (DBS), beam splitter (BS), condenser (CDS) white light (WL), diffractive notch filter (DNF), achromatic lens (AL).
source. A true zero-order half waveplate (HW1) mounted on a motorized universal rotator and a cubic polarizer (P1) were placed after the laser. Since the rotation of the half waveplate will induce a change in the polarization of the photons, the laser power after P1 can be effectively adjusted by rotating HW1, while maintaining the same polarization at the sample. In addition, the thinness of HW1 minimizes changes in the Poynting vector of the laser upon changing the power. A second true zero-order half waveplate (HW2) was placed after P1, such that the measurement configuration could be switched between collinear (XX) and crossed (XY) polarizations. Following the optical path and several silver mirrors (M), the photons were directed to a diffractive 90/10 beamsplitter (DBS) from Ondax Inc, reflecting 90 % of the excitation source, and rejecting 90% of Rayleigh scattered light after exciting the sample. The photons were then guided towards a Montana Instruments Cryostation. Before entering the Cryostation, the photons pass a double Fresnel Rhomb (Standa Inc., 14FR2-VIS-M27), which effectively acts as a broadband half waveplate.

After exciting the sample, the Raman scattered light is collected by the objective inside the Cryostation and follows the incoming path. The Raman scattered light passes through the Fresnel Rhomb and the analyzer (P2) after the 90/10 beamsplitter, as shown in FIG.3.2. As mentioned above, the selection rules provide symmetry information about the excitation as well as the crystallographic axes. However, to achieve this without the Fresnel Rhomb, one would have to rotate the sample, resulting in the loss of focus and adding more complexity to the setup. Another method would be to simultaneously rotate components HW2 and P2 (analyzer/ polarizer). However, the diffraction grating in the spectrometer is most efficient for a fixed polarization. Thus rotating P2 would inadvertently affect the signal, even for an isotropic Raman tensor. By introducing the Fresnel Rhomb, one can fix P2 to optimize the efficiency of the spectrometer, manipulate HW2 to change from cross to co-polarized configuration and use the Fresnel Rhomb to effectively rotate the sample’s crystallographic axes about the fixed axes of the optical
Figure 3.2: The light is total internal reflected four times and each time the relative phase shift $\pi/4$ between the s and p polarizations is added for a total $\pi$ phase. Thus, rotating the polarization of the incoming laser (shown in red) can be achieved through the rotation of $\lambda/2$ Fresnel rhomb (FR). The blue lines are both Raman scattered lights and Rayleigh scattered lights. Half waveplate (HW2), Analyzer (P2), 90/10 Beam splitter (DBS), Objective (O)[1]
To reject Rayleigh scattered light, and to reach a cut-off energy of 30 cm\(^{-1}\), two Ondax SureBlock volume holographic Bragg grating based diffractive notch filters (DNF) were placed after the analyzer. Using a notch filter as opposed to commonly used edge filters also allows both Stokes and anti-Stokes Raman signals to be recorded, which is a useful indicator to test local heating of the sample[30]. These two filters plus DBS result in optical density (OD) 8 attenuation to the Rayleigh scattered light. Finally, the Raman scattered light is directed to a Sine-drive spectrometer module equipped with an ultra-high resolution 2400 grooves/mm holographic grating. Prior to entering the spectrometer the light passes through an external mechanical slit mounted on a 3-axis translation stage. This allows for maximum resolution and collection efficiency by positioning the slit at the focal point of the first lens inside the spectrometer. To reduce chromatic and spherical aberration effects, an anti-reflection coated achromatic doublet lens (AL) with focal length of 50mm (Thorlabs, Inc. AC254-050-A-ML) was used to focus the light onto the slit. Ultimately, the diffracted light is detected by an Andor iDus back illumination spectroscopy charge coupled device (CCD). The detector operates in sub-image bin mode and at the lowest rate ADC channel to reduce the noise level.

To bring samples into focus during measurements, and for finding features and/or micron-size samples on a substrate, imaging the sample is necessary. To get more repeatable images, our Raman microscope is equipped with computer controlled white light illumination and imaging capabilities (highlighted by the green dashed line in FIG.3.1). Illumination lights were delivered through a multi-mode fiber to a condenser (CDS) and then reflected by a beamsplitter (BS) towards a cubic beamsplitter (CBS). A home-built motorized long range translation stage was used to move CBS in (out of) the beam path for imaging (Raman signal collection). The CBS was fixed on a linear ball bearing carrier. A NEMA 17 stepper motor (SM) coupled with a 1/4-20 acme threaded shaft was used for the translation of the linear ball bearing carrier. The motion of the motor was con-
trolled by a computer interfaced Arduino UNO microcontroller and a motor shield. Two microswitches connected to the UNO were used as stoppers for the carrier. If the CBS was moved into the beam path, the illumination light is directed onto the sample. After illumination, the reflected light follows the incoming path to the CBS, then is transmitted through the BS and ultimately directed by a mirror (M) through a lens with 15 cm focal length to form an image on a Thorlabs complementary metal-oxide-semiconductor camera (CMOS).

### 3.3.2 Cryogenic and Mechanical Design

#### Cryo-optic

To focus the excitation source on our sample, and collect (anti-) Stokes shifted radiation, we used a modified Zeiss objective, 100 X magnification and 0.90 NA with a working distance of 0.31 mm, vented to operate in vacuum. The Montana Instruments Cryostation is equipped with a Cryo-optic module designed to mount this objective, includes a low vibration cold platform (<3.5 K) for the sample, and a 60 K sample radiation shield (see FIG. 3.3). The radiation shield thermally protects the sample and helps overall temperature stability by lagging wires, fibers and other loads. Built-in Attocube 101-series xyz nanopositioners handle sample translation and focusing, providing mm translation with nm resolution. The sample radiation shield and objective housing are attached and referenced by mating together at the shield junction, all in vacuum. This bond provides a rigid positional reference, reducing the mechanical noise between the objective and the sample.

The need for a rigid mechanical connection is due to the high NA of the objective that leads to a small spot size ($\approx 1 \, \mu m$), short working distance (310 $\mu m$) and minimal depth of focus. Indeed, a key challenge for temperature dependent Raman studies is the constant need to collect from the same volume, especially for atomically thin samples (i.e. 2D atomic crystals) and/or when imaging is to be attempted. Thus the excellent collection
Figure 3.3: The cryo-optic within the low-vibration Cryostation platform. (a) Composite diagram of cryo-microscope setup highlighting critical components. (b) Photograph of an upside-down view of the entire objective housing showing 1-mm aperture in detail, from the point-of-view of the ATS sample platform, and objective radiation shield at 4K and 60 K coupled housing. The sample's radiation shield and objective housing are connected rigidly at the thermally isolated shield junction.
Figure 3.4: (a) Positional stability of the Agile Temperature stage between 4-350 K. (b) Thermal stability of the ATS over 20 minutes per setpoint.
efficiency and small spot size offered by this high NA objective, also provide a challenge for mechanical stability, while the short working distance could lead to a significant thermal load on the sample from the warm objective. Thus to ensure the sample and objective do not touch, the enclosure for the optic is threaded and allows vertical coarse positioning in air, such that the relative alignment can be optimized before cool-down. In addition, the sample radiation shield and the objective housing are thermally disconnected within the shield junction region, i.e. no direct metal-to-metal contact for heat transfer. This design leads to a rise in the sample temperature less than a few mK when the sample is brought into focus. The objective is actively temperature controlled within 500 mK through its housing, wrapped in a heat coil. This makes it immune to temperature fluctuations in the laboratory, resulting in ultrastable high quality imaging. The stability is also aided by the design of the objective radiation shield and aperture, which allow for fast thermal response. Furthermore the entire unit is isolated from room environmental conditions by the outer housing. This significantly limits mechano-thermal drift to \( \approx 40 \text{nm per K} \) over the full 350 K range (see FIG. 3.4).

**Agile Temperature Stage**

To achieve high mechanical and thermal stability of the sample platform, an Agile Temperature Stage (ATS) was developed and integrated into the Raman microscope. Figure 3.5(a) shows a rendering of the ATS, in which a 500 \( \mu \text{m} \) thick copper sample platform is surrounded by a 4 K radiation shield, and is radially supported just below the platform by G-10 thermal stand-offs. This mechanical geometry results in minimal drift in both the focal plane of the microscope, and strongly enhanced in-plane positional stability. For minimal error in sample temperature readings, a CERNOX CX-1050-HT is mounted on the bottom of the platform, thus separated from the sample by a 500 \( \mu \text{m} \) layer of OFHC copper. Moreover, the sample platform base is equipped with closed loop controllable solid state heating elements for highly isotropic heat exchange and temperature control.
This allows for precise temperature control over the sample platform, nearly independent of the cryo-cooler coldhead’s second stage, which maintains a temperature between 3 and 14 K over the full 4-350 K range of the ATS. Hence, while cycling between temperatures, the thermal stability outside of the ATS platform is only minimally affected, reducing thermal drifts within the system’s radiation shield and housing over longer time-scales. FIG.3.4a illustrates the positional stability in the $xy$-plane and along the $z$-axis, where $z$ is parallel to the Poynting vector of the laser. These data were obtained optically by thermally cycling an AFM calibration grating, while keeping the sample in focus and tracking features using closed loop positioners and recording their individual displacements.

Beyond overall stability, one may worry about the vibrations caused by the closed-cycle system. Their effect on the optical system was minimized by the placing the optics on a separate platform from the Cryostation, though on the same optical table. The effect on the Raman signal was checked by measuring the response of the sample at room temperature with the Cryostation compressor turned on and with it turned off. No significant difference was observed. Furthermore, the overall design of the Cryostation and the ATS minimizes the effects of vibration on the sample, as was measured using a Lion Precision CPL490 capacitive displacement sensor. With the ATS mounted on top of the positioners stack, and with the Cryostation compressor running at high power, the room temperature in-plane ($x$ and $y$) vibrations did not exceed 60 nm, and are thus below the diffraction limit of our 532 nm excitation source. While vibrations along the Poynting vector ($z$-axis) were not measured, they are unlikely to exceed the in-plane vibrations as a result of the positioner stage stack construction. White light imaging of an AFM calibration grating while the compressor was running confirmed that mechanical vibrations along $z$ were below the diffraction limit. Vibrations of the ATS were also measured in isolation of the positioners, while mounted directly to the Cryostation platform. In this arrangement, vibrations did not exceed 5 nm, and an ATS platform resonance frequency of 8.2 kHz was found.
The thermal stability of the ATS platform is shown in figure 3.4b, where each temperature point was recorded over a period of 20 minutes. We note that while the conventionally large sample platform mass passively aids thermal damping, the low drift geometrical constraints of the ATS (and thus its low mass) force it to strictly rely on a finely tuned PID loop for thermal stability, in addition to the thermal stability of the Cryostation. However, with the low platform mass of the ATS, and high thermal conductivity of copper below 50K[31], we observed temperature changes $dT/dt$ in excess of 100 K/s at low temperatures, thus imposing stringent requirements on the frequency and I/O resolution of the PID control algorithm. Our observed decline in thermal stability below 50 K coincides with a large jump in the thermal conductivity of copper, and is thus attributed to a sub-optimally tuned temperature control loop. Nevertheless, thermal stability over the full temperature range never exceeds 4.5 mK RMS (32 mK Peak-to-Peak), which easily meets the requirements for Raman microscopy, even at high temperature resolution, as shown in section 3.4.

The design of the ATS is ultimately focused on positional and thermal stability. Nonetheless it also leads to a reduction in sample cooling power compared to the Cryostation. This concern was addressed by optimizing the thermal standoff of the platform so that the ATS can easily withstand typical radiative heatloads (0.1 mW) of the Raman excitation source by several orders of magnitude, while maintaining a low base temperature. Figure 3.5(a) shows a log-log heatload map of the ATS over the full temperature range, emphasizing its low temperature cooling power. In addition to stability, the design of the ATS also allows for highly agile temperature control, resulting in minimal time loss between temperature set-points. To illustrate this agility, Fig. 3.5(b) shows a number of 20 minute thermal cycles between 4-350 K, stabilizing down to $<5$ mK RMS at both extremes of the cycle.
Figure 3.5: (a) Heatload map of the Agile Temperature Stage, installed directly on the Cryostation platform. Insert shows a rendering of the ATS, illustrating the sample platform, the radiation shield and housing, and the thermometer and heater connectors. (b) 20 Minute thermal cycles of the ATS between 4 - 350 K.
3.4 Raman Characterization

To demonstrate the performance of our setup, we measured two challenging samples, Bi$_2$Se$_3$ and V$_2$O$_3$. They are of wide interest for applications in thermoelectrics and memristive devices, as well as for their topological insulating (Bi$_2$Se$_3$)\cite{32, 33, 34} and strongly correlated behavior (V$_2$O$_3$)\cite{35, 36}. The first data set was obtained from single crystal Bi$_2$Se$_3$. The Raman response of Bi$_2$Se$_3$ is well characterized, making it a good sample to test the capability of our system\cite{2, 37, 23, 38, 16, 39}. Of particular interest is the potential for the temperature dependence of its phonons in revealing the origin of its low thermal conductivity\cite{23}. However, the low thermal conductivity, which makes it an excellent thermoelectric, also forces one to keep the laser power extremely low to avoid local heating. Thus, if the collection efficiency is not high enough, to get a sufficient signal to noise ratio is extremely challenging. The sample was freshly cleaved just before being placed into the sample chamber. The power of the laser used for the measurement was 40 $\mu$W to avoid the local laser heating. The laser spot size was 1 $\mu$m in diameter.

The primary results are shown in FIG. 3.6. Each spectra consists of an average of 5 acquisitions taken for 3 minutes each and is normalized by the height of the first phonon peak. We can see there are three phonon peaks visible in the whole temperature range. They are located at 71.7cm$^{-1}$, 131.5cm$^{-1}$ and 174.0cm$^{-1}$ at 271 K, in agreement with previous studies\cite{37}. To confirm the absence of local laser heating, we exploit the well known relationship between the ratio of the Stokes (S) and anti-Stokes (AS) intensity and the local temperature, given by: \cite{30}

$$R(S/AS) \propto \exp\left(\frac{\hbar \omega_0}{k_B T}\right)$$

(3.1)

where $\omega_0$ is the phonon energy and $T$ the local temperature. Thus we expect a linear relationship between the sample temperature and the inverse of the log of this ratio. The absence of local heating is indeed demonstrated in figure 3.7 where we plot the
Figure 3.6: Temperature dependent Raman spectra of Bi$_2$Se$_3$ in XX configuration. Excellent signal to noise is observed at all temperatures, despite the low Raman response and thermal conductivity of Bi$_2$Se$_3$. 
Figure 3.7: Temperature dependence of the inverse of logarithm ratio of Stokes and anti-Stokes of the first phonon, indicating the absence of local heating.

$log\left[\frac{R(S/AS)}{1}\right]$ versus $T$ for the lowest energy mode ($71.7 \text{cm}^{-1} \approx 103 \text{ K}$). This mode is chosen as it is the most sensitive to the temperature, nonetheless we find a good quantitative as well as quantitative agreement between the measured response and the prediction of no local heating.

To further investigate the phonon temperature dependence, the phonon positions and linewidths were automatically extracted from raw spectra using a Matlab script programmed with a peak-detection function. The results are shown in FIG. 3.8, where all three phonons are seen to harden and narrow as temperature decreases. This behavior matches well that found in a previous, independent study of a different Bi$_2$Se$_3$ crystal performed at the National High Magnetic Field Laboratory with an in-situ microscope objective based on fiber optics (see FIG. 3.9)[2]. Comparing both data sets (FIG. 3.9) re-
Chapter 3. Ultra-stable variable temperature Raman microscope

reveals a slight offset in phonon frequency, which is remedied by a temperature independent frequency shift, and can be accounted for by sample-to-sample variation or spectrometer offset. Despite the use of free-space optics, random variation in our data set is much smaller than the results obtained by fiber optics, confirming the thermal and mechanical stability of our setup.

We now turn to our measurements of a $V_2O_3$ thin film. This material is of particular interest because under normal pressure, it undergoes a first-order metal to insulator transition (MIT) and a structural phase transition[40, 41]. Although the mechanism for the transition has been widely investigated using various experimental techniques such as transport, near-field infrared spectroscopy, ellipsometry, X-Ray, and various ultrafast methods[42, 43, 44], the origin of MIT is still controversial. Variable temperature Raman spectroscopy can provide new insights into the temperature dependence of the volume fractions of each phase as well as the role of phonon-phonon interactions. However, due to the low signal level, nanometer-size domains and narrow temperature range in which the transition occurs, Raman measurements are very challenging and require very long integration times. Usually, for measurements like this, one would have to sacrifice the temperature resolution for helium cost and it is very challenging to achieve high signal to noise ratio because of thermal instability. Furthermore, the transition is first order and occurs via percolation, thus $V_2O_3$ exhibits extreme sensitivity to initial conditions as well as hysteresis, placing strict demands on thermal and positional stability. From this perspective, $V_2O_3$ is an ideal sample to test the overall capability of our setup from multiple angles, such as temperature resolution, collection efficiency, thermal and mechanical stability.

Temperature dependent Raman measurements were performed on a 200nm-thick $V_2O_3$ film grown on silicon. We found excellent reproducibility between continuous thermal cycles measured at the same location on a $V_2O_3$ film over the course of one week. Specifically, each spectrum is an average of two to four 15 minute acquisitions
Figure 3.8: The temperature dependence of Bi$_2$Se$_3$ phonon frequencies and linewidths with a laser power of 0.2 mW. The temperature resolution was chosen in the following way: below 140 K or above 180 K, the temperature steps were 15 K. In the two ranges of (from 140 K to 150 K and 168 K to 175 K), the temperature step was 2 K. Between 150 K and 168 K where the phase transition occurs, the temperature resolution was 1 K.
Figure 3.9: The temperature dependence of the third phonon of Bi$_2$Se$_3$. The data in red are extracted from Ref. 2. The data in blue are identical to “Toronto” data and offset intentionally for comparison.
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Figure 3.10: Temperature dependence of Raman intensity of V$_2$O$_3$, the structural phase transition is easily observed as are the co-existence of the two phases.

The results are shown in FIG. 3.10. Judging by the Raman spectra, there is a structural phase transition occurring as the temperature decreases. The metallic phase reveals both a broad asymmetric peak near 236 cm$^{-1}$ and a low energy continuous scattered light by free carriers. The insulating phase, on the other hand, displays four strong modes located at 233.9 cm$^{-1}$, 279.4 cm$^{-1}$, 324.9 cm$^{-1}$ and 340.4 cm$^{-1}$ respectively. Interestingly, as expected for a first-order phase transition, we can also clearly see the co-existence of both insulating and metallic phases by the presence of both sets of phonons during the transition. We also found hysteresis of the phase transition (to be discussed in a future publication) by a significant difference in the onset temperature of the transition when warming the sample.

Lastly, we turn to another important characteristic in Raman spectroscopy; polarization dependence. As mentioned in section 3.3.1, another capability of our system is to vary the polarization of incoming photons by introducing a Fresnel Rhomb. To demon-
Figure 3.11: Polarization angle dependence of Raman spectra of silicon in XX configuration. For clarity, only five spectra are shown. Legend: Polarization angle.
Figure 3.12: Polarization angle dependence of the relative Raman intensity of silicon in XX configuration.
strate this capability, we performed a measurement on commercial grade single crystal silicon at room temperature. Single crystal silicon is of space group Fd\textit{3}m-227. The mode located at 520 cm\textsuperscript{-1} at room temperature is of T\textsubscript{2g} symmetry\[45\]. The Raman tensor of this mode is
\[
R_{T_{2g}} = \begin{pmatrix}
0 & d & 0 \\
d & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

Using equation 2.3, one can show the Raman intensity should vary as $I_R = |\sin(4\phi)|^2$, where $\phi$ is the polarization angle relative to the crystal axis. The measurement results are obtained at room temperature. Each spectra was taken under laser power 0.1 mW with acquisition time of 40 s. The raw spectra are shown in FIG.3.11. From the figure, we can see two main features in each spectra: a one-phonon mode located at 520 cm\textsuperscript{-1} and a weak two-phonon mode located from 900 cm\textsuperscript{-1} to 1000 cm\textsuperscript{-1}. The one phonon mode varies with the change of polarization angle and the two-phonon modes barely change, consistent with the literature\[46\]. To confirm the relation between Raman intensity and polarization angle derived above, the area under the one phonon mode peak was extracted by the same fitting technique mentioned previously and then was plotted versus the polarization angle in FIG.3.12. From the figure, we can see the agreement between the measurements and the theoretical prediction is excellent.

3.5 Conclusion

We have presented a new design of a temperature-dependent, closed-cycle, automated, micro-Raman spectroscopy system with high collection efficiency, and excellent temperature and mechanical stability. It enables long measurement times with very high temperature, spatial and spectral resolution. The closed-cycle nature also provides ease of use and minimal operation cost. Given the automation potential of our setup, functions such
as dynamical tracking of laser power level, auto-focusing and unattended operation will be developed in the future. We have demonstrated a highly efficient, versatile automated micro-Raman cryogenic measurement platform.
Chapter 4

Spin-phonon Coupling in Cr$_2$Ge$_2$Te$_6$

4.1 Introduction

Cr$_2$Ge$_2$Te$_6$ is a particularly interesting material since it is in the very rare class of ferromagnetic semiconductors and possesses a layered, nearly two dimensional structure due to van der Waals bonds\cite{47, 48}. Recently this material has been revisited as a substrate for the growth of the topological insulator Bi$_2$Te$_3$ to study the anomalous quantum Hall effect. Furthermore the van der Waals bonds make Cr$_2$Ge$_2$Te$_6$ a candidate two dimensional (2D) atomic crystal, enabling Cr$_2$Ge$_2$Te$_6$ as a platform to study 2D semiconducting ferromagnets and for single layered spintronics devices\cite{49}. Spin-phonon coupling can be a key factor for the spin relaxation in a spintronics devices\cite{50}. Combined with the fact that understanding heat dissipation in nanodevices is crucial, it is timely and important to explore the phonon dynamics and their interplay with the magnetism in Cr$_2$Ge$_2$Te$_6$. Indeed recent studies have shown that the thermal conductivity of its cousin compound Cr$_2$Si$_2$Te$_6$ linearly increases with the temperature in the paramagnetic phase, suggesting spin-phonon coupling is crucial in these materials\cite{51}. However there are currently no direct probes of the phonon dynamics of Cr$_2$Ge$_2$Te$_6$, let alone spin-phonon coupling. Such studies are crucial for understanding the potential role of
magneto-elastic effects that could be central to the magnetic behavior of Cr$_2$Ge$_2$Te$_6$ as a 2D atomic crystal and potential nano magnetostrictive device. Polarized temperature dependent Raman scattering is perfectly suited for such studies, since it has been widely used to measure the phonon dynamics and spin-phonon coupling in bulk and 2D atomic crystals[52, 53, 54, 55, 18, 16, 56, 57, 58, 59]. Compared to other techniques, a high resolution Raman microscope can track sub-cm$^{-1}$ changes to uncover subtle physics. A demonstration of Raman studies of bulk Cr$_2$Ge$_2$Te$_6$ can be extremely meaningful for the future study of the exfoliated 2D Cr$_2$Ge$_2$Te$_6$.

In this chapter, we focus on the polarized temperature dependent Raman spectra of Cr$_2$Ge$_2$Te$_6$. The spin-phonon coupling has been confirmed in three ways: below T$_C$ (61 K) we observe a split of two phonon modes due to the breaking of time reversal symmetry;

Figure 4.1: Raman spectra of Cr$_2$Ge$_2$Te$_6$ taken in different conditions. All the spectra are taken at 300 K. Legend: the text states the condition of the sample.
an anomalous hardening of an additional three modes; and a dramatic decrease of the phonon lifetimes upon warming into the paramagnetic phase. Our results also suggest the possibility of probing the magneto-elastic coupling using Raman spectroscopy, opening a door for the further study of exfoliated 2D Cr$_2$Ge$_2$Te$_6$.

### 4.2 Experiments

Single crystal Cr$_2$Ge$_2$Te$_6$ was grown with high purity elements heated to 700°C. Detailed growth procedures can be found elsewhere[60]. The Raman spectra of the crystal were
Figure 4.3: Normalized Raman spectra of Cr$_2$Ge$_2$Te$_6$ in XX and XY geometry at 270 K.

4.3 Results and Discussion

4.3.1 Polarization Dependence

We focus on the mode symmetry assignment of Cr$_2$Ge$_2$Te$_6$ first. This analysis was complicated by the oxidation of the Cr$_2$Ge$_2$Te$_6$ surface. Indeed, many chalcogenide
Chapter 4. Spin-phonon Coupling in Cr$_2$Ge$_2$Te$_6$

Figure 4.4: Temperature dependent collinear (XX) Raman spectra of Cr$_2$Ge$_2$Te$_6$ measured in the temperature range of 10 K – 325 K. T$_c$ is indicated by the yellow dashed line.

Materials suffer from easy oxidation of the surface, which is particularly problematic as TeO$_x$ contains a strong Raman signal[61]. The role of oxidation and degradation are becoming increasingly important in many 2D materials[62]. A strong aging effect was also observed in Cr$_2$Ge$_2$Te$_6$. In FIG. 4.1 we show the Raman spectra of air-exposed and freshly cleaved Cr$_2$Ge$_2$Te$_6$ samples. The air-exposed sample reveals fewer phonon modes, which are also quite broad, suggesting the formation of an oxide. A similar phenomena was also observed in other materials[63].

The lattice structure of Cr$_2$Ge$_2$Te$_6$ is shown in FIG. 4.2. The magnetic ions Cr are located inside the octahedron formed by Te atoms. From group theory analysis, the space group of single crystal Cr$_2$Ge$_2$Te$_6$ is R-3 (No.148) and the point group is C$_3i$[60]. There are six inequivalent irreducible representations in the C$_3i$ point group. They are $A_g$, $E_{1g}$, $E_{2g}$, $A_u$, $E_{1u}$ and $E_{2u}$ respectively. All irreducible representations for the C$_3i$ point group
Figure 4.5: Raw spectra of $E_{1g}^1$ and $E_{2g}^2$ mode. Four Lorentzians (shown in dashed lines) were used to account for the splitting.

are one dimensional. However $E_{1g}$ and $E_{2g}$ are inequivalent conjugate representations. In this case, if the time reversal symmetry is not broken, the eigenstates of $E_{1g}$ and $E_{2g}$ representation are degenerate. This holds for $E_{1u}$ and $E_{2u}$ representations as well. In the Cr$_2$Ge$_2$Te$_6$ unit cell, there are 10 atoms which gives 30-phonon branches at the $\Gamma$ point of the Brillouin zone. The 30 phonon branches are $\Gamma_{acoustic} = A_u + E_{1u} + E_{2u}$ and $\Gamma_{optical} = 5A_g + 4A_u + 5E_{1g} + 4E_{1u} + 5E_{2g} + 4E_{2u}$ respectively. Because the space group R-3 has inversion symmetry, theoretically all the optical modes are either IR-active (subscript u) or Raman-active (subscript g). Here, the letter A means the phonon is non-degenerate and E means the phonon is doubly degenerate for the reason explained above.
Thus we expect to see 10 Raman-active modes, because the $E_{1g}$ and $E_{2g}$ mode are not distinguishable by energy so long as the time reversal symmetry is not broken. In the Raman spectra (FIG. 4.3), 7 modes were observed. They center at 78.6 cm$^{-1}$, 85.3 cm$^{-1}$, 110.8 cm$^{-1}$, 136.3 cm$^{-1}$, 212.9 cm$^{-1}$, 233.9 cm$^{-1}$ and 293.8 cm$^{-1}$ at 270 K. The other three modes might be too weak or out of our spectral range[64].

To obtain the symmetry of each phonon mode, we recall that equation 2.3 relates the Raman intensity to the Raman tensor $R$. The Raman tensors of phonons of $A_g$, $E_{1g}$ and $E_{2g}$ symmetry are shown below,

$A_g = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$  $E_{1g} = \begin{pmatrix} c & d & e \\ d & -c & f \\ e & f & 0 \end{pmatrix}$  $E_{2g} = \begin{pmatrix} d & -c & -f \\ -c & -d & e \\ -f & e & 0 \end{pmatrix}$

From the Raman tensors, we know that all three modes should be visible in the co-linear (XX) geometry and the $A_g$ modes should vanish in crossed polarized (XY) geometry (note the absence of off diagonal elements in the $A_g$ tensor). To gain insight into the symmetry of the modes, we compare the spectra taken at 270 K in XX and XY configurations. As can be seen from FIG. 4.3, only the two modes located at 136.3 cm$^{-1}$ and 293.8 cm$^{-1}$ vanish in XY configuration. Therefore these two modes are of $A_g$ symmetry, and the other five modes are of $E_g$ symmetry.

### 4.3.2 Temperature Dependence

The Raman spectra on single crystal $\text{Cr}_2\text{Ge}_2\text{Te}_6$ were taken over the temperature range of 10 K to 325 K. The temperature resolution was chosen to be 10 K below 100 K and 20 K above. The resulting color intensity plot of the colinearly polarized (XX) Raman spectra of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ is shown in FIG. 4.4.

Remembering that the $E_g$ modes are doubly degenerate due to time reversal symmetry, we focus on the temperature dependence of the lowest energy $E_g$ modes in FIG. 4.5. As the temperature is lowered, additional modes appears in the spectra near $T_C$, as can
be seen from the extra feature near the $E_{g}^{1}$ mode and the extremely broad and flat region of the $E_{g}^{2}$ mode. We note that the exact temperature at which this splitting occurs is difficult to determine precisely due to our spectral resolution and the low signal levels of these modes. However, at the lowest temperatures we find a $2.9 \text{ cm}^{-1}$ splitting for the $E_{g}^{1}$
Figure 4.7: Temperature dependence of phonon linewidth (green). The red curves indicate the fit result using equation 4.2 above $T_C$. The mode located at 110.8 (136.3) cm$^{-1}$ is shown on left (right). $T_C$ is indicated by the vertical lines.

mode and a 4.5 cm$^{-1}$ splitting for the $E^2_g$ mode. V. Carteaux et al. performed the structural analysis using X-ray diffraction at both paramagnetic (270 K) and ferromagnetic phases (5 K) and no structure change was found[47]. Thus the splitting does not result from a structural phase transition. Dynamic Jahn-Teller effect, which is often ascribed to explain phonon splitting[65], is unlikely to be the reason because Cr$^{3+}$ is Jahn-Teller inactive ion.

The splitting starts near $T_C$ and becomes clear as the temperature is lowered, suggesting that the splitting is likely associated with the spin ordering. Such splitting has been observed in many magnetic materials. In chromium spinels, such as ZnCr$_2$X$_4$ ($X = O, S, Se$), a 5 cm$^{-1}$ to 20 cm$^{-1}$ splitting of phonon modes has been observed. There, the splitting was explained in terms of the spin Jahn-Teller effect[66, 67]. Magnetic order induced phonon splitting was also observed in MnO[68]. It is likely the splitting we observed is also caused by the spin ordering. As the temperature drops, the spin ordering results in the breaking of time reversal symmetry. The degeneracy of these two modes is only protected by time reversal symmetry, and thus in the magnetically ordered state the degeneracy can be lifted. Specifically, spin-phonon coupling can lead to a splitting of the phonon, as the correlation between spins becomes finite[69]. A similar effect has
been observed in CeCl$_3$ where the E$_g$ symmetry in its point group C$_{4v}$ is also degenerate by time reversal symmetry. For CeCl$_3$ it was found that increasing the magnetic field led to a splitting of two E$_g$ modes and a hardening of a second set of E$_g$ modes[70]. The phonon splitting and energy shifts (discussed later) match well with our observation in Cr$_2$Ge$_2$Te$_6$. The splitting mechanism is further evidenced by the energy of the mode. We know that the ferromagnetism of Cr$_2$Ge$_2$Te$_6$ originates from the Cr-Te-Cr super-exchange interaction where the Cr octahedra are edge-sharing and the Cr-Te-Cr angle is 91.6°[47]. The energies of these two modes are very close to the Te-displacement mode in Cr$_2$Si$_2$Te$_6$. Thus, it is very likely the E$_1^g$ and E$_2^g$ modes involve atomic motions of the Te atoms bond strength of which is very susceptible to the spin ordering, since the Te atoms mediate the super-exchange between the two Cr atoms. Thus, the splitting is likely caused by the spin ordering induced breaking of time reversal symmetry.

To further investigate the spin-phonon coupling, we turn our attention to the temperature dependence of the mode frequencies and linewidths. Our focus is on the higher energy modes, as they are easily resolved. The five modes at higher frequency (E$_3^g$-A$_2^g$) are visible throughout the entire temperature range. To gain more quantitative insights into these modes, we fit the Raman spectra with the Voigt function shown in equation 2.18. In FIG. 4.6, we show the extracted phonon energies of these modes. We can see from the figure that all phonon modes soften as the material is heated up. This result is not surprising, since the anharmonic phonon-phonon interaction is enhanced at high temperatures and typically leads to a softening of the mode. However, the phonon energies of the E$_3^g$, E$_4^g$ and A$_1^g$ modes change dramatically as we approach T$_C$. In fact the temperature dependence is much stronger than we would expect from standard anharmonic interactions. For example, a 2 cm$^{-1}$ downturn occurring from 10 K to 60 K was observed in the E$_4^g$ mode. This sudden drop of phonon energy upon warming to T$_C$ is further evidence of spin-phonon coupling in Cr$_2$Ge$_2$Te$_6$. In comparison, an electronic mechanism for the change is unlikely due to the large electronic gap (196 meV) in Cr$_2$Ge$_2$Te$_6$.[60]
The lattice expansion, which explains the anomalous phonon shifts in other magnetic materials\cite{71}, is also unlikely to be the reason, because the in-plane lattice constant of \textit{Cr}_2\textit{Ge}_2\textit{Te}_6 contracts up to 90 K\cite{47}. The spin-phonon mechanism is also confirmed by the temperature dependence of the phonon linewidth, which is not affected by the lattice deformation. In FIG. 4.7, we show the temperature dependent phonon linewidths of the \textit{E}^3_g, and \textit{A}^1_g modes due to the larger signal level. We can see the phonon lifetimes are enhanced as the temperature drops below \textit{T}_C, confirming the spin-phonon mechanism.

To uncover the spin-phonon interaction, we first attempt to remove the effect of the standard anharmonic contributions. In a standard anharmonic picture, the temperature dependence of a phonon energy and linewidth is described by the following formula according to equation 2.16

\[
\omega(T) = \omega_0 + C(1 + 2n_B(\omega_0/2)) + D(1 + 3n_B(\omega_0/3) + 3n_B(\omega_0/3)^2) \quad (4.1)
\]

\[
\Gamma(T) = \Gamma_0 + A(1 + 2n_B(\omega_0/2)) + B(1 + 3n_B(\omega_0/3) + 3n_B(\omega_0/3)^2) \quad (4.2)
\]

where \(\omega_0\) is the harmonic phonon energy, \(\Gamma_0\) is the disorder induced phonon broadening, \(C\) (\(D\)) are constants determined by the cubic (quartic) anharmonicity of the phonon energy, \(A\) (\(B\)) are those of the phonon linewidth, and \(n_B\) is the Bose-factor. The second term in equation 4.1 results from an optical phonon decaying into two phonons with opposite momentum, each with a half of the energy of the original mode. The third term describes the optical phonon decaying into three phonons with a third of the energy of the optical phonon. The resulting parameters are shown in table 4.1. The fit curves are also shown in red in FIG. 4.6. We can see that the two highest energy modes \textit{E}^5_g and \textit{A}^2_g follow the anharmonic prediction very well throughout the entire temperature range. However, for the other three modes, there is a clear deviation from the anharmonic prediction below \textit{T}_C, confirming the existence of spin-phonon coupling. Moreover, we notice that for the three modes, the phonon energies start to deviate from the anharmonic prediction even
above $T_C$ (circled in FIG. 4.6). This is probably due to the short-ranged two-dimensional magnetic correlations that persist to the temperatures above $T_C$, since finite magnetic moments were observed in $\text{Cr}_2\text{Ge}_2\text{Te}_6$ above $T_C$[60].

Table 4.1: Anharmonic interaction parameters. The unit is in $\text{cm}^{-1}$.

<table>
<thead>
<tr>
<th>mode</th>
<th>$\omega_0$</th>
<th>Error</th>
<th>Error C</th>
<th>Error D</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g^3$</td>
<td>113.0</td>
<td>0.1</td>
<td>-0.09</td>
<td>0.03</td>
<td>-0.013</td>
</tr>
<tr>
<td>$A_g^1$</td>
<td>138.7</td>
<td>0.1</td>
<td>-0.12</td>
<td>0.04</td>
<td>-0.024</td>
</tr>
<tr>
<td>$E_g^4$</td>
<td>221.9</td>
<td>0.4</td>
<td>-1.9</td>
<td>0.1</td>
<td>-0.02</td>
</tr>
<tr>
<td>$E_g^5$</td>
<td>236.7</td>
<td>0.1</td>
<td>-0.01</td>
<td>0.07</td>
<td>-0.12</td>
</tr>
<tr>
<td>$A_g^2$</td>
<td>298.1</td>
<td>0.3</td>
<td>-0.4</td>
<td>0.3</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

The spin-phonon coupling in 3d-electron systems usually results from the modulation of the electron hopping amplitude by ionic motion, leading to a change in the exchange integral $J$. In the unit cell of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ there are two inequivalent magnetic ions (Cr atoms), the spin-phonon coupling Hamiltonian to the lowest order can be written as[72, 73],

$$H_{int} = \sum_{i,\delta} \frac{\partial J}{\partial u}(S^a_i \cdot S^b_{i+\delta})u$$  \hspace{1cm} (4.3)

where $S$ is a spin operator, $u$ stands for the ionic displacement of atoms on the exchange path, the index $(i)$ runs through the lattice, $\delta$ is the index of its adjacent sites, and the subscripts $a$ and $b$ indicate the inequivalent Cr atoms in the unit cell. The strength of the coupling to a specific mode depends on hybridization and/or overlap of orbitals on different lattice sites. Different atomic motions have different influence on the exchange integral. Thus, some phonon modes do not show the coupling effect regardless of their symmetry. As mentioned above, the ferromagnetism in $\text{Cr}_2\text{Ge}_2\text{Te}_6$ is from planar and inter-planar superexchange Cr-Te-Cr interactions. So it is very likely the three modes contain the atomic motion of the Cr and Te atoms[47]. To extract the spin-phonon
coupling coefficients, we use a simplified version of equation 4.3\cite{74, 75},

$$\omega \approx \omega_0^{ph} + \lambda < S_i^a \cdot S_{i+\delta}^b > \quad (4.4)$$

where $\omega$ is the frequency of the phonon mode, $\omega_0^{ph}$ is the phonon energy free of the spin-phonon interaction, $< S_i^a \cdot S_{i+\delta}^b >$ denotes a statistical average for adjacent spins, and $\lambda$ represents the strength of the spin-phonon interaction which is proportional to $\frac{\partial J}{\partial u}$. The saturated magnetization value of Cr$_2$Ge$_2$Te$_6$ reaches 3$\mu$B per Cr atom at 10 K, consistent with the expectation for a high spin configuration state of Cr$^{3+}$\cite{60}. Therefore, $< S_i^a \cdot S_{i+\delta}^b >$ can be estimated as 9/4 for Cr$^{3+}$ at 10 K and the spin-phonon coupling constants can be estimated using equation 4.4. The calculated results are given in table 4.2. Compared to the geometrically (CdCr$_2$O$_4$, ZnCr$_2$O$_4$) or bond frustrated (ZnCr$_2$S$_4$) chromium spinels the coupling constants are smaller in Cr$_2$Ge$_2$Te$_6$\cite{67}. This is probably not surprising, because in the spin frustrated materials, the spin-phonon couplings are typically very strong\cite{67}. On the other hand, in comparison with the cousin compound Cr$_2$Si$_2$Te$_6$ where the coupling constants were obtained for the phonon at 90.5 cm$^{-1}$ ($\lambda=0.1$) and 369.3 cm$^{-1}$ ($\lambda=-0.2$)\cite{51}, the coupling in Cr$_2$Ge$_2$Te$_6$ is larger.

Table 4.2: Spin-phonon interaction parameters at 10 K. The unit is in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega$</th>
<th>$\omega_0^{ph}$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g^2$</td>
<td>113.4</td>
<td>112.9</td>
<td>0.24</td>
</tr>
<tr>
<td>$A_1^1$</td>
<td>139.3</td>
<td>138.5</td>
<td>0.32</td>
</tr>
<tr>
<td>$E_g^4$</td>
<td>221.7</td>
<td>219.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

### 4.4 Conclusion

In summary, the single crystal Cr$_2$Ge$_2$Te$_6$ was studied using polarized temperature dependent Raman spectroscopy with special emphasis on the spin-phonon coupling. Seven phonon modes were observed. The two lowest energy modes of $E_g$ symmetry split, which
is ascribed to the time reversal symmetry breaking by the spin ordering. The temperature dependence of the five modes at higher energies are studied in detail. Among the five modes, three modes indeed show the spin-phonon coupling effect. The spin-phonon coupling constants of the three modes are obtained and compared to other Cr compounds. Our results also show the possibility of studying magnetism in exfoliated 2D ferromagnetic Cr$_2$Ge$_2$Te$_6$ by tracking the frequency shift of phonon modes using micro-Raman scattering.
Chapter 5

Temperature dependent Raman study of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$

5.1 Introduction

$\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ series materials have been studied for decades, since they are good thermo-electrics. However, the physical origin of their low thermal conductivity reminds unclear. Uncovering this secret will not only have a great impact on physics research, but also be a crucial milestone for real applications. Inelastic neutron scattering studies on PbTe and SnTe suggest the giant anharmonicity induced softening of transverse optic (TO) modes not only results in a high dielectric constant in both materials (SnTe even becomes ferroelectric at low temperature), but perhaps more importantly opens a decay channel ($\text{TA} + \text{TO} \rightarrow \text{TO}$) for one of the major heat carriers-transverse acoustic (TA) modes. This may explain their thermal transport behavior[9]. Recent first-principle studies show that the resonance bonding mechanism is responsible for the softening of the TO modes and the softening also enlarges the phase-space volume, resulting in large anharmonicity. More importantly, although the mechanism is weaker, it is predicted to also be present in group V$_2$-VI$_3$ materials[76]. There is currently no direct proof of this hypothesis.
As a representative member of V₂-VI₃ thermoelectrics, verifying the resonance bonding mechanism in Bi₂Te₃₋ₓSeₓ, especially from the perspective of anharmonicity, is crucial for the whole family of V₂-VI₃ thermoelectrics. Raman spectroscopy, owing to its non-destructive probing of samples and quick access to phonon modes, has been widely used to study fundamental properties of materials for decades. Moreover, the temperature dependence of Raman scattering can provide us even more information about the lattice structure and the phonon dynamics, which are the important components in determining anharmonicity[77, 52, 53, 78, 54]. While there have been many studies on Bi₂Te₃₋ₓSeₓ using Raman spectroscopy[37, 2], a complete wide range temperature dependent study is still lacking.

In this chapter, we present a Raman study of Bi₂Te₃₋ₓSeₓ compounds, namely Bi₂Se₃, Bi₂Te₃, and Bi₂Te₂Se, over the temperature range from 4 K to 293 K. The anharmonicity of Bi₂Te₃₋ₓSeₓ is discussed from two aspects. Firstly, the temperature dependence of phonon linewidths are well explained by Klemens’s model through three-phonon interaction. The extracted anharmonic coefficients and the disorder levels are consistent with the studies of thermal transport in these materials. Secondly, the temperature renormalization of phonon frequencies of Bi₂Te₃ and Bi₂Se₃ are discussed in great detail. More specifically, to explain their temperature dependence of phonon frequencies, other than the two major contributions (quasiharmonic and three-phonon decay which explains the temperature dependence of phonon modes in most materials like silicon), the four-phonon scattering process has to be taken into account. The anharmonicity of Bi₂Te₃ and Bi₂Se₃, as well as the comparison between the two materials, is found to be consistent with the resonance bonding mechanism. Our results suggest the resonance bonding mechanism may be a common feature for V₂-VI₃ and IV-VI thermoelectrics and demonstrate the utility of Raman microscopy for establishing this mechanism in new materials. This is especially crucial as most new materials are first grown in small, polycrystalline form and thus are not amenable to neutron scattering studies.
5.2 Experimental Methods

Detailed growth procedure are described in previously published work[79]. As the preparation for measurements, all samples were freshly cleaved (111 plane) and quickly placed inside a sample chamber. Exposure to air was approximately 5 minutes. The laser power was kept as low as 40 µW to avoid laser-induced heating. This was checked at 4 K by monitoring the anti-Stokes signal as the laser power was reduced. Once the anti-Stokes signal disappeared, the power was cut an additional 50%. Detailed information on the instruments can be found in chapter 3.

5.3 Results and Discussion

5.3.1 Room Temperature Analysis

From group theory analysis, the space group of single crystal Bi$_2$Te$_{3-x}$Se$_x$ is R-3m (No.166) and the point group is D$_{3d}$. There are four optical-active inequivalent irreducible representations in the D$_{3d}$ point group. They are A$_g$, E$_g$, A$_u$ and E$_u$ respectively. The unit cell of Bi$_2$Te$_{3-x}$Se$_x$ is shown in FIG. 5.1. In the unit cell, the sites of Te2/Se2 and Te1/Se1 are not equivalent which are shown by different colors. In the mixed crystal Bi$_2$Te$_{3-x}$Se$_x$, as the Se concentration increases, Se atoms first start to fill the Te1/Se1 site, only until $x$ increases up to $\approx 1$ when Te2/Se2 sites begin to be replaced by Se atoms[79]. This is due to the radius of thSe atom being smaller so it more naturally starts to “fit” into the site 1.

Because of the inversion symmetry, all the optical modes are either IR-active or Raman-active. The IR-active modes are $2A_u + 2E_{1u}$ and the Raman-active modes are $2A_g + 2E_g$. Here, the letter A means the phonon is non-degenerate and E denotes double degeneracy. As is well established in previous theoretical and experimental studies, the first E$_g$ mode is near 39 cm$^{-1}$ in Bi$_2$Te$_{3-x}$Se$_x$[80, 81, 82]. As a result, in our spectral
Figure 5.1: Top: Raman spectra of Bi$_2$Te$_{3-x}$Se$_x$ at 4 K. The spectra are offset intentionally for clarity. The texts indicate the symmetry of the modes. Bottom: Mechanical representations of the corresponding phonon modes. Red arrows indicate the motion of atoms. Due to the double degeneracy, there are two $E_g$ representations. The atomic motion vectors of the second $E_g$ mode are perpendicular to the surface.

range (50 cm$^{-1}$ - 200 cm$^{-1}$), we expect to observe three phonon peaks from the zone center in the Raman spectra.
Chapter 5. Temperature dependent Raman study of Bi$_2$Te$_{3-x}$Se$_x$

Figure 5.2: The temperature dependent Raman spectra of Bi$_2$Te$_{3-x}$Se$_x$. From the top to the bottom are Bi$_2$Te$_3$, Bi$_2$Te$_2$Se, and Bi$_2$Se$_3$. 
Chapter 5. Temperature dependent Raman study of \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \)

The Raman spectra of \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \) at 4 K are shown in FIG. 5.1. Three sharp peaks are visible for \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \). The texts near the peaks indicate the symmetry of the modes and their corresponding mechanical representations are given at the bottom of FIG. 5.1[37]. The spectra of \( \text{Bi}_2\text{Te}_2\text{Se} \) consists of two clear peaks and a split feature at the position of the third peak. The two sharp peaks and the sharper peak in the overlapped feature have the same assignment as \( \text{Bi}_2\text{Se}_3 \)[37, 83]. The broad overlapped peak is a defect-induced mode which will be discussed in detail in chapter 6. Comparing the three spectra, we find the modes shift to higher energy with the increasing of Se doping which naturally results from the smaller mass of Se. The general trend of the phonon frequency of \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \) is consistent with previous studies at room temperature[37]. Especially, for \( \text{Bi}_2\text{Te}_2\text{Se} \) and \( \text{Bi}_2\text{Te}_3 \), the energies of the first two modes are very close. This is likely due to the fact the Se atoms only fill Te2/Se2 sites which remain at rest in vibrations. Nevertheless, the spectra of \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \) have similar features in both phonon positions and profiles of peaks, which confirms the similarity in their lattice structures.

5.3.2 Temperature Dependent Studies

For all three \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \) materials, Raman spectra were taken in the temperature range from 4 K to 293 K with 15 K resolution. At each temperature, 3 acquisitions taken for 5 minutes were averaged and the spectra were corrected for the thermal factor \((n_B(\omega)+1)\), \(n_B \) is the Bose factor). The resulting temperature dependent Raman spectra are normalized to the highest phonon peak for clarity and shown in FIG. 5.2 in the form of a color intensity plot. In all three materials, we can see all modes persist in the entire temperature range indicating no dramatic changes occurring to the lattice. Besides, they soften and broaden as the temperature is raised.

To gain more quantitative insights, we fit the Raman spectra of all three \( \text{Bi}_2\text{Te}_{3-x}\text{Se}_x \) materials with the Voigt profile function shown in equation 2.18. Three Voigt functions could be used to fit the spectra of \( \text{Bi}_2\text{Te}_3 \) and \( \text{Bi}_2\text{Se}_3 \), but four were needed for \( \text{Bi}_2\text{Te}_2\text{Se} \).
The extracted temperature dependent phonon frequencies $\Omega$ and linewidths $\Gamma$ can be used for the analysis of their anharmonicity.

**Temperature dependence of phonon linewidths**

It is well known that the anharmonic phonon-phonon interaction leads to the renormalization of phonon lifetimes. To analyze the temperature dependence of the phonon linewidths in Bi$_2$Te$_{3-x}$Se$_x$, we use the modified Klemens’s model. In the original Klemens’s model\[84\], an optical phonon is assumed to decay into two phonons with opposite momentum. The “coalescence” process where a phonon and a second phonon fuse into a third phonon is neglected, because it requires thermal populations of the second phonon which is very small at low temperatures\[8\]. Klemens’s model works well for describing the anharmonic process in a crystal with very high purity like silicon\[6\]. As we know, Bi$_2$Te$_{3-x}$Se$_x$ contains significant levels of defects (i.e. Bi$_T$ antisites in Bi$_2$Te$_3$ which make Bi$_2$Te$_3$ heavily p-doped)\[79\]. In this case, a temperature independent disorder induced scattering term $\Gamma_0$ should be included. The modified Klemens model reads\[84\],

$$\Gamma(\omega, T) = \Gamma_0 + A(2n_B(\omega/2) + 1) \quad (5.1)$$

where $\Gamma_0$ can be interpreted as the broadening caused by crystal disorders, $n_B$ is the Bose-Einstein function, $\omega$ is the mode energy, and $A$ is the three-phonon coupling coefficients obtained through multiplying the joint density of state by the transition matrix elements. Resulting fits are shown in FIG. 5.3 to FIG. 5.5 in red. We can see that the model works very well. The complete fit parameters including errors are listed in Table 5.1. The extracted $A$ and $\Gamma_0$ are shown in FIG. 5.6 for comparison. Comparing the value of $A$ among Bi$_2$Te$_{3-x}$Se$_x$, the cubic anharmonicity does not increase monotonically as a function of Se concentration, suggesting subtle changes as Te atoms are replaced by Se atoms. Comparing the literature lattice thermal conductivity among Bi$_2$Te$_{3-x}$Se$_x$ (1.18
Bi$_2$Te$_3$, 0.60 Bi$_2$Te$_2$Se, 0.66 Bi$_2$Se$_3$ W m$^{-1}$ K$^{-1}$, at room temperature)[85], Bi$_2$Te$_2$Se has the lowest thermal conductivity. This was attributed to the effect of imperfections namely the mass fluctuation and chemical bond changing, which would generate strong scattering of the transport of phonons in Bi$_2$Te$_2$Se[85]. Imperfection effects are also observed in our Raman results. For Bi$_2$Te$_2$Se, we found that its $\Gamma_0$, which is a indicator of the crystal disorder level, is largest among Bi$_2$Te$_3$−$x$Se$_x$. For the pristine compounds Bi$_2$Se$_3$ and Bi$_2$Te$_3$, the disorder levels are relatively close to each other. Although the majority of the heat carriers are acoustic phonons, the anharmonic coefficients are still higher in Bi$_2$Se$_3$, consistent with the smaller lattice thermal conductivity in Bi$_2$Se$_3$.

Figure 5.3: Temperature dependence of the phonon linewidths of Bi$_2$Te$_3$. 
Figure 5.4: Temperature dependence of the phonon linewidths of Bi$_2$Te$_2$Se.

<table>
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<td>$E_g$</td>
<td>$A_2^g$</td>
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<tr>
<td></td>
<td>$\Gamma_0$</td>
<td>error</td>
<td>$A$</td>
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<td>0.40</td>
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<td>$A_2^g$</td>
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<td>error</td>
<td>$A$</td>
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<td></td>
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<td>0.06</td>
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<td>$E_g$</td>
<td>1.47</td>
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<td>$A_2^g$</td>
<td>0.52</td>
<td>0.12</td>
<td>1.77</td>
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Table 5.1: Anharmonic interaction parameters of Bi$_2$Te$_{3-x}$Se$_x$. The unit is in cm$^{-1}$.
Figure 5.5: Temperature dependence of the phonon linewidths of Bi$_2$Se$_3$.

**Temperature dependence of phonon frequencies**

In this section, we focus on the temperature dependence of phonon frequencies in Bi$_2$Se$_3$ and Bi$_2$Te$_3$. As we know from chapter 1, compared to phonon linewidths phonon frequencies have contributions from multiple origins. Typically, in a non-magnetic insulating material, the temperature dependence of a phonon frequency comes from two primary sources:

\[
\Delta \omega(T) = \Delta \omega(T)_{\text{lattice}} + \Delta \omega(T)_{\text{anhar}}
\]  

(5.2)

$\Delta \omega_{\text{lattice}}$ is caused by the thermal expansion and $\Delta \omega_{\text{anhar}}$ is the anharmonicity induced change. Specifically, $\Delta \omega_{\text{lattice}}$ originates from the crystal thermal expansion induced
changes in the harmonic force constants. According to equation 2.8, this term can be described by the following equation in the context of a hexagonal lattice [2],

$$\Delta \omega_{\text{lattice}}(T) = \omega(0) \left( \exp^{-\gamma \int_0^T \left( \alpha_c(T') + 2 \alpha_a(T') \right) dT'} - 1 \right)$$  \hspace{1cm} (5.3)$$

where $\gamma$ is the mode Grüneisen parameter, and $\alpha_a$ and $\alpha_c$ are the coefficients of linear thermal expansion along the $a$ and $c$ axes. To the best of our knowledge, the relevant data to calculate $\Delta \omega_{\text{lattice}}$ is absent for $\text{Bi}_2\text{Te}_2\text{Se}$; thus, $\text{Bi}_2\text{Te}_2\text{Se}$ is omitted for the discussion in this section. If the “Coalescence” process as well as the higher order terms are ignored, $\Delta \omega_{\text{anhar}}$ arises from the coupling of phonon modes through the cubic and
Chapter 5. Temperature dependent Raman study of Bi$_2$Te$_3-x$Se$_x$

Figure 5.7: Temperature dependence of phonon frequency of Bi$_2$Te$_3$. All data points are offset by the phonon frequency at lowest temperature.

quartic anharmonicity which takes the following form according to equation 2.9 and 2.13

$$\Delta \omega(T)_{\text{anhar}} = \frac{12}{\hbar} \sum_{\vec{q},j_1} V \left( \begin{array}{ccc} 0 & 0 & \vec{q} - \vec{q} \\ j & j & j_1 \end{array} \right) (2n_B(\vec{q}, j_1) + 1) - \frac{18}{\hbar} \sum_{\vec{q},j_1,j_2} |V \left( \begin{array}{ccc} 0 & \vec{q} & -\vec{q} \\ j & j_1 & j_2 \end{array} \right)|^2 R(\omega)$$

$$R(\omega) = \frac{n_B(\vec{q}, j_1) + n_B(-\vec{q}, j_2) + 1}{\omega - \omega(\vec{q}, j_1) - \omega(-\vec{q}, j_2)}$$

where $n_B$ is the Bose-Einstein function, the $V$ coefficients derived from the lattice potential energy of deformation at constant volume, and $q$ and $j$ are momentum and band index respectively. We can see that equation 5.4 has two parts: the quartic anharmonicity (the first term of equation 5.4) to first order in the perturbation theory and cubic
anharmonicity (the second term of equation 5.4) to second order. As we know, the cubic anharmonicity to the second order contributes to the phonon linewidth as well, which is the prototype for Klemens’s model. The quartic anharmonicity to the first order only contributes to the phonon frequency. In most cases, the cubic anharmonicity dominates and results in softening of the phonon frequency and broadening of the phonon linewidth as the temperature rises[54]. However, for materials with high anharmonic potentials (i.e. ferroelectrics)[86], the quartic term does play a significant role. Interestingly, the decay channel $TA + TO \rightarrow TO$ which explains the high scattering rate of one of the major heat carriers TA modes in thermoelectrics PbTe and SnTe[9, 87], was also found in some of the perovskite ferroelectrics (i.e. SrTiO$_3$, KTaO$_3$)[88, 89]. Besides, the thermal conductivity of these ferroelectrics is comparable to thermoelectrics. Therefore, it is worth seeing the relative contributions from the cubic and quartic anharmonicity more thoroughly in Bi$_2$Se$_3$ and Bi$_2$Te$_3$. To achieve this, one has to disentangle $\Delta \omega_{\text{lattice}}$ first. We calculate $\Delta \omega_{\text{lattice}}$ using equation 5.3. The mode Grüneisen parameter $\gamma$ which describes the relative shift of a phonon frequency due to the volume change of a crystal is as follows[90],

$$\gamma = B \frac{1}{\omega} \left( \frac{\partial \omega}{\partial P} \right)_T$$  \hspace{1cm} (5.6)

where $B$ is the isothermal bulk modulus, $\omega$ is the frequency of a phonon mode, and $\left( \frac{\partial \omega}{\partial P} \right)_T$ is the isothermal derivative of the mode energy to the pressure. The pressure dependent data was acquired from Ref. 91 and was linearly fit to extract $\left( \frac{\partial \omega}{\partial P} \right)_T$. The mode Grüneisen parameters are calculated using equation 5.6 and shown in table 5.3. Usually, Grüneisen parameters are only weakly dependent on the temperature[95]. Thus, the obtained $\gamma$ can used to estimate $\Delta \omega_{\text{lattice}}$ in the whole temperature range. Combining the mode Grüneisen parameters and the thermal expansion coefficients found in the references[94, 96], $\Delta \omega_{\text{lattice}}$ can be calculated for Bi$_2$Se$_3$ and Bi$_2$Te$_3$. The results for Bi$_2$Te$_3$, as well
as its $\Delta \omega_{anhar}$ which is obtained by subtracting $\Delta \omega_{lattice}$ from the experimental data are shown in FIG. 5.7. From the figure, we can see for the $A_{1g}^1$ mode, $\Delta \omega_{anhar}$ is more or less zero at low temperature and hardens as the temperature increases. For the other two modes $E_g$ and $A_{2g}^2$, $\Delta \omega_{anhar}$ is apparently negative and monotonically decreasing in the entire temperature range and increases in magnitude as the phonon frequency increases (1.2 cm$^{-1}$ for $E_g$, 2.5 cm$^{-1}$ for $A_{2g}^2$). To understand this strikingly different behavior of the modes, let us re-examine the different contributions to the anharmonicity. According to equation 5.4, the anharmonicity interaction contributes two terms: the cubic and quartic anharmonicity with different signs. These two terms can cause a phonon mode to soften or harden as the temperature increases depending on the relative magnitudes. Moreover, the two terms have different growth rates on the phonon frequency $\omega$. For the $A_{1g}^1$ mode the magnitude of the quartic term is slightly larger than that of the cubic term, which results in $\Delta \omega_{anhar}\approx 0$ at low temperatures and hardens with a raise in the temperature. Apparently, the cubic term dominates in the $E_g$ and $A_{2g}^2$ modes, leading to $\Delta \omega_{anhar}<0$. To understand the difference between the cubic and quartic anharmonicity, let us revisit the two anharmonic terms in equation 5.4. The sum (one band index $j_1$) in the quartic term of equation 5.4 is proportional to the one phonon density of states

<table>
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<th>$A_{1g}^1$ (GPa/cm$^{-1}$)</th>
<th>$E_g$ (GPa/cm$^{-1}$)</th>
<th>$A_{2g}^2$ (GPa/cm$^{-1}$)</th>
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<td>Bi$_2$Te$_3$</td>
<td>3.86</td>
<td>3.67</td>
<td>2.79</td>
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<td>Bi$_2$Se$_3$</td>
<td>3.28</td>
<td>4.19</td>
<td>2.94</td>
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Table 5.2: $(\frac{\partial \omega}{\partial P})_T$ of Bi$_2$Se$_3$ and Bi$_2$Te$_3$

<table>
<thead>
<tr>
<th>material</th>
<th>$B$ (GPa)</th>
<th>$\gamma_{A_{1g}^1}$</th>
<th>$\gamma_{E_g}$</th>
<th>$\gamma_{A_{2g}^2}$</th>
<th>$\gamma$</th>
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<tr>
<td>Bi$_2$Te$_3$</td>
<td>37.4$^a$</td>
<td>2.36</td>
<td>1.36</td>
<td>0.785</td>
<td>1.5$^a$</td>
</tr>
<tr>
<td>Bi$_2$Se$_3$</td>
<td>48.4$^b$</td>
<td>2.12</td>
<td>1.54</td>
<td>0.820</td>
<td>1.4$^c$</td>
</tr>
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$^a$: See Ref. 92 $^b$: See Ref. 93 $^c$: See Ref. 94

Table 5.3: Bulk modulus $B$ and mode Grüneisen parameters $\gamma$ of Bi$_2$Te$_3$ and Bi$_2$Se$_3$. The last row is the overall Grüneisen parameter for comparison.
(D(ω)) and that in the cubic term (two band indexes j1, j2) is proportional to the joint two-phonon density of states (JD(ω)). For simplification, one can approximate JD(ω) as D(ω - ω1) × D(ω1) where ω - ω1 and ω are the energies of the two phonon modes respectively. For a qualitative understanding JD(ω) can be further simplified using Klemens's approximation where ω1 = ω/2. Thus, eventually JD(ω) takes the form D(ω/2)^2. As a result, the cubic (quartic) term is proportional to D(ω) (D(ω/2)^2). In a simple phonon band picture, D(ω) increases monotonically with ω. If the phonon frequency ω is small, it is possible that D(ω) is equal to or larger than JD(ω), as is the case for the A1g mode. As the phonon frequency increases, JD(ω) increases much faster than D(ω). Therefore, in the Eg and A2g modes a negative Δω_anhar is observed and becomes larger in magnitude from the Eg mode to the A2g mode. This explanation is further evidenced by the fact that the IR-active Eu mode, the energy of which is lower than all three Raman-active modes, hardens from 48 cm^{-1} to 50 cm^{-1} from 15 K to 300 K, even without the subtraction of Δω_lattice[37]. This indicates Δω_anhar > 0 and the quartic term dominates for this mode.

For Bi2Se3, a similar analysis was performed and the results are shown in FIG. 5.8. We find that the thermal expansion contribution term Δω_lattice accounts for 63%, 57% and 34% of the total phonon frequency shift at room temperature for each mode, respectively. In the case of Bi2Se3, the Δω_anhar are all negative. The magnitude of Δω_anhar increases monotonically from 0.7 cm^{-1} (A1g), 1.2 cm^{-1} (Eg) to 2.5 cm^{-1} (A2g) at 295 K. This suggests the quartic term is smaller and the cubic terms dominate in all three modes. Moreover, just as for Bi2Te3, the IR-active mode Eu (65 cm^{-1} at 300 K) mode hardens as the temperature is raised, confirming the validity of our statements above.

We have shown that the quartic anharmonicity does contribute a significant amount to the temperature renormalization of phonon frequencies in Bi2Te3 and Bi2Se3. This can be understood as follow. In first-principle studies, Sangyeop Lee et al. calculated the force constant of several thermoelectrics (i.e. PbTe, Bi2Te3 and so on) and found
that the force constants are non-negligible between the atom at the origin and up to the eighth neighbour atoms. This effect was ascribed to the presence of long-ranged interactions along the \(< 100 >\) direction of rocksalt structure in PbTe and rocksalt-like structure Te1-Bi-Te2-Bi-Te1 in Bi$_2$Te$_3$[76]. The long-ranged interactions were explained by the highly delocalized electron density distribution caused by the resonance bonding of p-electrons[76]. The highly delocalized electron density distribution from the resonance bonding mechanism can also result in a delocalized potential with high anharmonicity. As was observed in another resonance bonding material Ge$_2$Sb$_2$Te$_5$, in the crystalline phase the lattice potential is highly anharmonic and shows a Mexican hat shape[97, 98]. Consequently, the high order anharmonicity coefficients which are obtained through Taylor expansion of lattice potential can be comparatively large (especially the quartic anharmonicity when one takes the Mexican hat shape into account).

For the comparison between Bi$_2$Se$_3$ and Bi$_2$Te$_3$, we first notice that the energy of the $A^1_g$ mode is lower in Bi$_2$Te$_3$ than Bi$_2$Se$_3$. Therefore, from the perspective of the phonon density of states, we expect the quartic term is more pronounced in Bi$_2$Te$_3$. Besides, the transition matrix element (the $V$ coefficients in equation 5.4) which comes from the Fourier transform of the high order coefficients of lattice potential is larger in Bi$_2$Te$_3$. To understand this part, a more quantitative approach can be taken using the method from Ref. 99, where the resonance bonding is characterized by two coordinates, namely hybridization ($r_{\pi}^{-1}$) and ionicity ($r_{\sigma'}$). As the names suggest, $r_{\pi}^{-1}$ characterizes the hybridization level between s-electrons and p-electrons and $r_{\sigma'}$ denotes the ionicity when the bond is formed between the two atoms. For the resonance bonding to prevail, both $r_{\pi}^{-1}$ and $r_{\sigma'}$ have to be within a limited range. Otherwise the distortions (by $r_{\pi}^{-1}$) or the charge localization (by $r_{\sigma'}$) would diminish the resonance bonding. To calculate these two coordinates, one can use the approach taken by St. John, Simons and Bloch
Chapter 5. Temperature dependent Raman study of Bi$_2$Te$_3$ for binary compounds[100, 101],

\[ r_{\sigma'} = r_p^A - r_p^B \]  
(5.7)  
\[ r_\pi^{-1} = [(r_p^A - r_s^A) + (r_p^B - r_s^B)]^{-1} \]  
(5.8)

where \( r_s^X \) and \( r_p^X \) denote the valence radii of the s- and p-orbital of atom X, respectively[99]. Using equation 5.7 and 5.8, the two coordinates can be calculated for Bi$_2$Te$_3$ (\( r_{\sigma'}=0.13 \), \( r_\pi^{-1}=2 \)) and Bi$_2$Se$_3$ (0.26, 2.12) by using the radii from the literature[102]. Compared to non-thermoelectric materials (i.e SiO (0.57, 3.70))[99], the values obtained for Bi$_2$Te$_3$ and Bi$_2$Se$_3$ are very similar to other thermoelectrics that can be explained by resonance bonding mechanism (i.e. PbTe (0.20, 1.75), SnTe (0.18, 1.96))[76]. Moreover, given the slightly smaller \( r_\pi^{-1} \) in Bi$_2$Te$_3$ than Bi$_2$Se$_3$, one would expect the distortion is lower. As pointed out in Ref. 99, smaller distortions can lead to more a flat box-like potential, exhibiting larger quartic anharmonicity[99]. This could be the reason why the quartic anharmonicity is larger in Bi$_2$Te$_3$.

As we mentioned, the decay channel \( TA + TO \rightarrow TO \) plays significant role in lowering the thermal conductivity, both in the perovskite ferroelectrics and other thermoelectrics (PbTe and SnTe). The common feature in two types of materials is that the \( TO \) significantly softens as the temperature is lowered. We have shown that the anharmonicity softens the \( A_g^1 \) mode in Bi$_2$Te$_3$. However, its energy is much higher than the TO modes in the perovskite ferroelectrics and PbTe, so the contribution to the scattering of \( TA \) in Bi$_2$Te$_3$ is probably negligible. As we pointed out, the first \( E_g \) mode of Bi$_2$Te$_3-x$Se$_x$ is near 30 cm$^{-1}$, which is very close in energy to the soft TO modes. It will be extremely meaningful to see the temperature dependence of this mode in future experiments.
Figure 5.8: Temperature dependence of phonon frequency of Bi$_2$Te$_3$. All data points are offset by the phonon frequency at lowest temperature.

5.4 Conclusions

In summary, we have performed temperature dependent Raman scattering measurement on Bi$_2$Te$_3$, Bi$_2$Te$_2$Se, and Bi$_2$Se$_3$. Through comparison of their Raman spectra and the temperature dependent phonon linewidths, the disorder-induced $\Gamma_0$ is found much larger in Bi$_2$Te$_2$Se than the other two compounds, which is consistent with the thermal transport measurement. The temperature dependent phonon frequencies of Bi$_2$Te$_3$ and Bi$_2$Se$_3$ are analyzed in great detail. The different growth rates between three-phonon and four-phonon interactions are responsible for the distinct temperature dependence of phonon frequencies in Bi$_2$Se$_3$ and Bi$_2$Te$_3$. The anharmonicity of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ and the comparison between these two materials show consistent behavior as is predicted by
resonance bonding mechanism, suggesting the resonance bonding mechanism may be a common feature for V₂-VI₃ and IV-VI thermoelectrics. The future experiments would focus on the first E₉ mode to prove the decay channel $TA + TO \rightarrow TO$. 
Chapter 6

Local Mode in TE BTS from charge neutral antisites

6.1 Introduction

The family of compounds, Bi$_2$Te$_{3-x}$Se$_x$, have been studied for decades as good thermoelectrics (TEs)[103]. In binary compounds like Bi$_2$Se$_3$ and Bi$_2$Te$_3$, the small defect formation energies and band gaps often result in relatively large carrier densities, leading to a bulk conductance that dominates over the surface conductance[79]. A transition from p-type to n-type behavior in the Bi$_2$Te$_{3-x}$Se$_x$ solid solution was reported decades ago[104, 105]. Further studies have revealed that when x is close to 1, namely Bi$_2$Te$_2$Se (BTS), the crystal structure is ordered[79]. The ordering was suggested to result in the dramatic reduction in defect density[106]. However, surprisingly it has been known that BTS contains a single extra mode, the origin of which remains controversial, and is suspected to be a local mode[37]. It is known that local modes play an important role in lowering the thermal conductivity of materials. Especially for TE clathrates[107] and skutterudites[108], intentionally induced local modes (rattling modes) can cause glassy behavior in phonon transport, while producing little if any effect on the electronic proper-
ties, namely phonon-glass electron-crystal. Raman spectroscopy, owing to quick access to phonon modes, has been widely used for characterization of materials for decades. Moreover, combined with temperature dependence Raman scattering can be used to probe phonon dynamics[52, 53, 78, 54], defects and defects induced local modes[109, 110, 111]. While there have been many studies on Bi$_2$Te$_{3-x}$Se$_x$ using Raman spectroscopy[37, 2], a high spectral resolution, broad temperature range dependent study on BTS is still lacking.

In this chapter, we present a Raman study of BTS over the temperature range from 10 K to 290 K. Four modes were observed in the whole temperature range. Three of them were assigned as $A_g^1$, $E_g$ and $A_g^2$ modes[37]. The extra mode, the origin of which is controversial, is proved to be the antisite defects induced local mode. The anomalous broadness of the local mode is qualitatively understood through a simulation of diatomic chains. The temperature dependence of all four phonon modes are well explained by anharmonic phonon-phonon interactions.

### 6.2 Experiments

The BTS single crystal was grown with special techniques to suppress carrier-concentration. Detailed growth procedure and characterizations are described in previously published works[79, 32, 112]. As the preparation for measurements, the BTS sample was freshly cleaved (111 plane) and quickly placed inside a sample chamber. The measurements was performed using the home-built Raman microscope. Details about the Raman microscope can be found in chapter 3. The laser power was kept as low as 40 µW to avoid laser-induced heating. This was checked at 10 K by monitoring the anti-Stokes signal as the laser power was reduced. Once the anti-Stokes signal disappeared, the power was cut an additional 50%. More details about the instruments can be found elsewhere[18, 1, 22, 113].
6.3 Results and Discussion

6.3.1 Phonon Mode Assignments

BTS is of a quintuple layer structure Te$_I$-Bi-Se$_{II}$-Bi-Te$_I$ (see FIG.6.1a)[79]. From group theory analysis, the space group of BTS is R-3m (No.166). The point group is D$_{3d}$. There are four optical-active inequivalent irreducible representations in the D$_{3d}$ point group. They are $A_g$, $E_g$, $A_u$ and $E_u$ respectively. Raman-active modes are $2A_g + 2E_g$.

As established in previous experiments, the lowest energy mode in the Bi$_2$Te$_{3-x}$Se$_x$ is typically below 50 cm$^{-1}$ which is below our low energy cut-off[80, 81, 82]. As a result, in our spectral range we expect to observe three phonon peaks from zone center modes in the Raman spectra of BTS.

![Figure 6.1: a: Schematic crystal structures of BTS. b: Raman spectra of BTS taken at 4 K and 290 K. Raw data are shown by * markers. The four individual Voigt functions are shown in different colors. The added curves are shown in thinner lines.](image)

The spectra of BTS taken at 290 K and 10 K are shown in FIG.6.1b. We can see the BTS spectra consists of two isolated peaks at lower frequencies, and two peaks at higher
energies which overlap. To quantitatively evaluate the overlapped features, the Raman spectra of BTS were fitted with Four Voigt functions. From the fit, the frequencies of the four features are: 65.12 cm\(^{-1}\), 109.1 cm\(^{-1}\), 145.0 cm\(^{-1}\) and 154.6 cm\(^{-1}\) at 10 K, in good agreement with those found by Akrap et al.[83]. However, the linewidth in our spectra are much narrower, perhaps due to the higher quality of our crystal. The first two modes plus the mode of highest energy have been assigned as \(A_{1g}\), \(E_g\) and \(A_{2g}\) modes according to the literature[37]. However, there is no consensus on the assignment of the mode at 145.0 cm\(^{-1}\), which we denote as \(V_1\) for convenience. Akrap et al. noted that a very weak mode, seen in their IR conductivity spectra, was very close to the \(V_1\) mode. From this the authors concluded that the appearance of this mode in Raman scattering is due to the activation of \(A_{2u}\) mode by disorder and symmetry breaking. If this holds, given the similar energy of the \(V_1\) mode to the \(A_{2g}\) mode, one would also expect a similar phonon linewidth and temperature dependence. However, as described below, we found that upon cooling to 10 K, the \(A_{2g}\) mode becomes much narrower, as is typically observed, while the \(V_1\) mode remains considerably broad. Perhaps more problematic, disorder or symmetry-breaking induced IR modes in Raman spectra are typically very weak[16] and cannot be as strong as ordinary Raman modes (especially when one compares the amplitude of the \(V_1\) mode to that of the \(A_{2g}\) mode at room temperature). Richter et al.[37] also observed this mode and suspected it to be a splitting of the \(A_{2g}\) mode resulting from the local change in bonds between the different chalcogenide layers (ie. Se in the middle of the quintuple versus Te in the outer layers). However, these measurements were performed at room temperature and thus could not reveal whether or not this was indeed a local mode. Defects could also enable non-zone center phonons to appear in the Raman spectra, as is typically seen in graphite (i.e. the D-band). This mechanism can generate a broad Raman profile due to the participation of multiple modes[114]. This phenomenon is usually related to an electronic resonance effect. Nonetheless this possibility also seems highly unlikely, when comparing BTS to Bi\(_2\)Te\(_3\). Specifically Bi\(_2\)Te\(_3\) has of a large
density of Bi\textsubscript{Te} antisite defects that generally lead to its heavy p-type doping\cite{115, 79}. Considering the high similarity in both electronic and phonon structure between Bi\textsubscript{2}Te\textsubscript{3} and BTS, one should also observe a “V\textsubscript{1}-like” mode in Bi\textsubscript{2}Te\textsubscript{3}\cite{82}. Nonetheless despite extensive Raman measurements by various groups, the V\textsubscript{1} mode has only been observed in samples with Se doping\cite{37, 116}.

The comparison with Bi\textsubscript{2}Te\textsubscript{3} suggests we carefully consider the role of Se in generating this new Raman mode. In theory, Se enters the Se\textsubscript{II} site and not the Te\textsubscript{I} site. Nonetheless scanning tunneling microscopy (STM) studies have established several types of defects\cite{115}: adatoms remnant from the cleavage process, Te\textsubscript{I}-Se\textsubscript{II} antisites, Te\textsubscript{I}-Bi antisites, and Se\textsubscript{I}-Bi antisites. A further study using X-ray diffraction (XRD) showed in BTS 8.5\% of Se\textsubscript{II} atoms are replaced by Te and 4.17 \% of Te\textsubscript{I} atoms are substituted by Se. The site occupancy factor of Bi is 1\cite{79}. Therefore, the Se-Te antisite is the major defect in BTS. A point defect, such as the Te-Se antisite, can cause a local mode that vibrates at its own frequency with a considerably broad linewidth\cite{111}. Such local modes have been observed in many semiconductors like Ge-Si alloys\cite{117}, CdSe\textsubscript{0.985}S\textsubscript{0.015}\cite{118}, Ba\textsubscript{y}Sr\textsubscript{1-y}F\textsubscript{2}\cite{119}, Sr\textsubscript{y}Ca\textsubscript{1-y}F\textsubscript{2}\cite{119} and so on. A key signature is the relatively small temperature dependence of their linewidth as seen by I\textsubscript{3}\textsuperscript{+} line in Iodine intercalated Bi\textsubscript{2}Sr\textsubscript{2}CuO\textsubscript{6}\cite{120}. There I\textsubscript{3}\textsuperscript{+} line narrows (19 cm\textsuperscript{-1} to 16 cm\textsuperscript{-1}) from room temperature to 30 K but remains considerably broad, very similar to our observation (14.4 cm\textsuperscript{-1} to 11.7cm\textsuperscript{-1}). Thus, we can infer the V\textsubscript{1} mode is a local mode caused by the point defect Te-Se antisite.

6.3.2 Temperature Dependence Studies of Phonon modes

To gain more quantitative insights, we focus on the temperature dependent Raman spectra of BTS over the whole temperature range (shown in the bottom of FIG. 5.2). We fit the Raman spectra with Voigt profile functions shown in equation 2.18. The extracted temperature dependent phonon frequencies \(\Omega\) and linewidths \(\Gamma\) are shown in FIG. 6.2.
From the plot, we can see all phonon modes sharpen and harden as the temperature is decreased. This naturally results from the anharmonic phonon-phonon interaction, which leads to a renormalization of phonon frequencies and linewidths. To analyze the temperature dependent behavior, Klemens's model was used. Since the cubic anharmonicity is sufficient to describe the phonon temperature dependence, we can set D and


\[ \Omega(\omega, T) = \Omega_0 + C[2n_B(\omega_0/2) + 1] \]  
\[ \Gamma(\omega, T) = \Gamma_0 + A[2n_B(\omega_0/2) + 1] \]

where \( \Gamma_0 \) can be interpreted as the contribution from the crystalline disorder, \( \Omega_0 \) is the harmonic phonon frequency, \( n_B \) is the Bose-Einstein function, and \( A \) and \( C \) are the coefficients representing three-phonon (cubic) interaction. The resulting fits are also shown in FIG. 6.2. We can see that the model works very well. The complete fit parameters including errors are listed in Table 6.1. Among all the modes, the temperature independent \( \Gamma_0 \) is dramatically larger for the \( V_1 \) mode, almost three times that of the \( A^2_g \) mode. However the \( A \) and \( C \) are comparable to the other modes. To qualitatively explain this, we employed statistical analysis which was used to handle disordered effects[121].

We can think of BTS crystal is constituted of many atomic chains. The Raman modes in BTS only involve Bi and Te\(_I\) sites[37]. Thus, a perfect chain consists of Bi and Te atoms one after the other. Since our sample has defects, some Te atoms are randomly replaced by Se atoms. The energies of the local modes in these chains have much larger dependence on the configuration of Se atoms in the chain than that of a normal phonon mode. Consequently, the observed spectra consists of many local modes with slightly different frequencies, resulting in much larger broadening than normal phonon modes.

To see the validity of above statements, a simple model adopted from Ref. 111 was used to calculate the vibrational modes of one dimensional circular diatomic chain (see FIG. 6.3). The energy of each mode is obtained by solving the lattice vibration equation,
\[ \omega^2 \ddot{u} = M^{-1/2} K M^{-1/2} \ddot{u} \]  

(6.3)

where \( K \) (\( M \)) is the force (mass) matrix, \( \ddot{u} \) is the displacement vector and \( \omega \) is the mode energy. For one dimensional circular diatomic chain, \( M \) and \( K \) take the following forms,

\[
M = \begin{pmatrix}
m_a & 0 & 0 & 0 & \cdots & \\
0 & m_b & 0 & 0 & \cdots & \\
0 & 0 & m_a & 0 & \cdots & \\
0 & 0 & 0 & m_b & \cdots & \\
\vdots & \vdots & \vdots & \vdots & \cdots & \\
\vdots & \vdots & \vdots & \vdots & \cdots & \\
\end{pmatrix}
\]

\[
K = \begin{pmatrix}
2k & -k & 0 & 0 & \cdots & \\
-k & 2k & -k & 0 & \cdots & \\
0 & -k & 2k & -k & \cdots & \\
0 & 0 & -k & 2k & \cdots & \\
\vdots & \vdots & \vdots & \vdots & \cdots & \\
\vdots & \vdots & \vdots & \vdots & \cdots & \\
\end{pmatrix}
\]

(6.4)

The original chain consists of 48 atoms of only two types atoms (a,b) with the configuration \( ...a-b-a-b... \), since the Raman modes in BTS only involve Bi and Te atoms[37]. The mass of atom \( m_a \) (\( m_b \)) was set to 2.58 (4). The force constant \( k \) was set to be 1. To simulate the local modes, two atoms \( a \) were replaced by the “defect” atoms \( c \) with mass 1.57. The masses were chosen based on the real mass ratio of Te (a), Bi (b) and Se (c) atoms. The number of the “defect” atom \( c \) was chosen to represent 4.17% disorder obtained by XRD. Since two atoms are replaced, there will be two local modes in the chain. Twenty trials were run and for each trial two sites of atom \( a \) were randomly chosen to be replaced by atom \( c \). The results of two local modes as well as a non-local mode (phonon mode) are shown in FIG. 6.4. We can see from the plot, although both local modes and the phonon mode are very close in energy among different trials, the variation of energy of the local modes is much larger than that of the phonon mode. The other phonon modes were checked as well no qualitative difference was found. Thus our observation that the \( V_1 \) mode contains a much larger \( \Gamma_0 \) than the other phonon modes is completely consistent with a mode originating from local defects.

Up to now, we have only discussed the broadening from a temperature independent
Figure 6.4: Energies of local modes and a phonon mode of the 1 dimensional circular diatomic chain. The texts denote the corresponding standard deviation.
participation of many local modes. For the temperature dependent anharmonic coupling, it has been shown that local modes can couple to lower energy modes as has already been observed in the skutterudites\cite{122}, clathrates\cite{107} and other materials\cite{111}. As the simulation shows, all the local modes are very close in energy. Therefore, one expects these modes to follow the same temperature dependence, since the temperature dependence is just coming from Bose-Einstein statistics\cite{111}. Consequently, even though the V$_1$ mode profile in theory consists of many modes, these modes broaden and soften with the same pace as the temperature rises. Thus, the temperature dependent behavior of the V$_1$ mode can still be explained by Klemens’s model.

After clarifying the origin of the anomalous linewidth of the V$_1$ mode, we focus on the anharmonic behavior. Comparing the amplitude of ‘A’ and ‘C’ among the four modes, we find that they monotonically increase with mode energy. This is because the anharmonic coefficients are determined by the phonon joint density of states, $JD(\omega) = \sum \delta(\omega - \omega_1 - \omega_2)$. Here $\omega_1$ and $\omega_2$ are the energies of the two phonons into which phonon $\omega$ decays. $JD(\omega)$ normally is a monotonically increasing function of $\omega$. Thus the anharmonic coefficients are likely to be a monotonically increasing function of $\omega$, which is consistent with the fit results.

\section{Conclusion}

In summary, we performed temperature dependent Raman scattering measurement on BTS. Four modes were observed over the entire temperature range. Three of them were assigned as the zone center modes. The extra mode was proved to be an antisite defect induced local mode. The anomalous broadness of the local mode was clarified through a simple model of diatomic chains. The temperature dependence of the four modes were explained by an anharmonic phonon-phonon interaction model.
Chapter 7

Automatic Spike-Removal Algorithm for Raman Spectra

7.1 Introduction

Raman micro-spectroscopy has been applied to wide-ranging areas including chemistry[123], physics[124, 12, 13, 14, 15, 18, 16, 1, 17], materials science[125], and biology[126] because of its simple instrumental structure and easy interpretation of Raman spectra. However, Raman measurements are often limited to low signal levels, and thus long integration times are necessary. In principle this would only lead to increased statistical noise, which could ultimately be averaged out. However, for dispersive spectrometers, Charge-coupled devices (CCD) are widely employed because of their unique advantages such as high quantum efficiency, great sensitivity, high dynamic range, linear response to photons, small thermal/readout noise and high reliability. Unfortunately these detectors are highly vulnerable to cosmic rays, resulting in extremely large spikes in the measured spectra, where the signal level on a single/few pixels becomes many orders of magnitude larger than the measured spectra. The majority of cosmic rays are muons and most of the remainder are protons and neutrons[127]. These high energy particles collide and interact electro-
magnetically with materials on a CCD chip, causing ionization and atomic or collective excitations and cannot be easily blocked by shielding[128]. Such events typically generate a charge of at least several thousand electrons on a single pixel or over a few consecutive pixels of a CCD detector[129], leading to spurious, comparatively narrow spikes[130]. Moreover, given the nature of the highly stochastic collision process, these spikes are distributed randomly both in time and space, causing further complexity for spike-removal.

To solve this problem, both software solutions as well as hardware solutions have been proposed. For example, an image curvature correction method was employed to improve the optical hardware of a spectrometer[131]. However, this is more instrumentally complex and costly. Therefore, for most Raman applications, software approaches are more widely applied.

Many algorithms have been proposed for different applications, based on either single or multiple scan. The single scan methods include smoothing, weighted moving window filtering [132], wavelet transform based filtering[129], and attempts to fit spikes with predefined profiles[133]. These algorithms rely on the assumption that the amplitudes of spikes are much higher and linewidths are narrower than real Raman features. Beyond the sometimes limited validity of this assumption, these algorithms also require a deep knowledge of spectral filtering, such that proper threshold settings can be chosen to minimize distortion. Taking the random nature of the cosmic rays into account, to some extent, multiple scan methods can overcome the above drawbacks through a comparison between consecutive scans. For example, the upper-bound spectrum method[134] and time domain comparison [135] have received a lot of attention. Nevertheless, these methods also suffer from the difficulty of properly choosing the numerous parameters involved, or the failure to explore the different local frequency characteristics between spikes and real features. As such these methods have not found widespread use due to the difficulty of implementing them, then inability to properly detect all spikes, and/or their tendency to distort the spectra.
To overcome these difficulties we have devised a new algorithm that combines wavelet transforms with data clustering methods to automatically detect and remove cosmic rays from Raman spectra. Specifically, based on the randomness of cosmic rays, spike detection was ensured by a clustering of wavelet coefficients method. By analyzing the clustering behavior, the erroneous coefficients can be reset to the most probable value. A multi-resolution analysis was also employed to enable separation of spikes and real features by different local frequency characteristics. This approach ensures the preservation of real Raman features of both broad and narrow profiles, as well as insensitivity to spike amplitude. Furthermore this automatic detection enables easy-implementation, provides a more intuitive threshold setting, and reduces dependence on the particular wavelets employed. As such our method is easily implemented by those not familiar with spectral filtering algorithms.
7.2 Theory

In this section, we outline the theory behind the two techniques used in our algorithm.

7.2.1 Wavelet Transform

Fourier transforms are well known for their superior ability to reveal the frequency composition of a series \( x(\omega) \) and thus remove periodic noise. However, because of its extended and periodic basis functions (sine and cosine), localized features in \( x(\omega) \) will strongly overlap in the frequency domain after transform. Thus, Fourier filters are unable to remove localized features, and as such are not appropriate for separating spectral spikes from Raman features, which are generally localized. To solve this problem, some authors have turned to wavelet transforms[136].

In wavelet transforms one represents localized and non-stationary signals by a set of functions called wavelets. Wavelets are a series of functions that are all localized, quickly decaying, and can be translated and scaled to be a complete basis. To gain more insight into wavelet transforms, let us consider the following formula which is used to obtain continuous wavelet transform coefficients,

\[
\text{c}(p, q) = \int x(\omega)\Psi_{p,q}(\omega)\,d\omega \\
\Psi_{p,q}(\omega) = \frac{1}{\sqrt{|p|}}\Psi\left(\frac{\omega - q}{p}\right)
\]

Here \( x(\omega) \) is the original signal, \( \Psi_{p,q}(\omega) \) is a series of wavelet functions generated by scaling and translation of the mother wavelet \( \Psi(\omega) \), \( p \) characterizes the range and local frequency (here local frequency represents how fast the signal changes locally), and \( q \) translates the center of the wavelet. An example is shown in FIG. 7.1 where one can see that as the scaling factor \( (p) \) decreases, the wavelets become more localized with a decreasing period of oscillation. Thus as \( p \) is reduced, higher local frequencies are sampled,
and only a smaller section near \( x(q) \) is included in equation 7.1. In other words, \( c(p,q) \) is capable of extracting the local frequency component of \( x(\omega) \). The frequency window (bandwidth) is controlled by the scaling factor \( p \) and as \( p \) decreases, more local/higher frequency components can be extracted. For a continuous transformation, \( p \) and \( q \) can take any positive value. From the perspective of reduction of redundant information and for real applications, discrete wavelet transforms are preferred where the values taken by \( p, q \) normally have the following relation

\[
p = 2^j \quad q = 2^j - k \quad k, j \in \mathbb{Z}
\]  

(7.3)

where wavelets \( \Psi_{p,q}(\omega) \) are denoted by \( \Psi_{j,k}(\omega) \) instead[137].

This natural ability of wavelets to separate out information at varying degrees of local variation, makes them a natural choice for removing cosmic ray induced spikes on Raman spectra. Specifically, real features are typically broader than spikes leading to a natural separation into different local frequency bands. Therefore, most of the real Raman features will appear in smaller local frequency components (i.e. lower \( j \)) than cosmic rays. If features in a series \( x(\omega) \) have different local frequency characteristics, a multi-resolution analysis can be achieved by discrete wavelet transform.

Multi-resolution analysis was firstly proposed by Mallat[138] in his research of computer vision. The basic idea behind multi-resolution analysis is to construct a sequence of successive approximation spaces \( V_j \) spanned by scaling functions \( \Phi_{j,k}(\omega) \). These spaces satisfy

\[
\cdots V_2 \subset V_1 \subset V_0 \subset V_{-1} \subset V_{-2} \cdots
\]  

(7.4)
Chapter 7. Automatic Spike-Removal Algorithm for Raman Spectra

with

\[ \bigcup_{j \in \mathbb{Z}} V_j = L^2(\mathbb{R}) \]  
\[ \bigcap_{j \in \mathbb{Z}} V_j = 0 \]

For an integral transform, usually it is convenient to work with orthogonal spaces. Given the relation 7.4, a series of orthogonal spaces can be constructed which is visualized in FIG. 7.2. The entire space is divided into a series of orthogonal subspaces as follow:

\[ V = V_2 \bigoplus W_2 \bigoplus W_1 \bigoplus W_0 \cdots \]

It can be shown the basis function of these subspaces have the following relation[139]

\[ W_j = \text{Span}(\Psi_{j,k}(\omega)) \]  
\[ V_j = \text{Span}(\Phi_{j,k}(\omega)) \]
\[ \Psi_{j,k}(\omega) = 2^{j/2}\Psi(2^j \omega - k) \]  
\[ \Phi_{j,k}(\omega) = 2^{j/2}\Phi(2^j \omega - k) \]

and \( \Psi_{j,0}(\omega), \Phi_{j,0}(\omega) \) satisfy the dilation equations

\[ \Psi_{j,0}(\omega) = \sum_n g[n]\Phi_{j-1,n}(\omega) \]  
\[ \Phi_{j,0}(\omega) = \sum_n h[n]\Phi_{j-1,n}(\omega) \]

where \( h[n] \) and \( g[n] \) can be taken as filter coefficients determined by different wavelet function families. Typically, \( h[n] \) is a low-pass filter and \( g[n] \) is a high-pass filter. Each of these subspaces has complementary bandwidth and by adjusting the coefficients at each complementary subspace, a multi-resolution analysis can be achieved.
\[ V_1 = V_2 \oplus W_2 \]

\[ V_0 = V_1 \oplus W_1 \]

Figure 7.2: The relationship between scaling and wavelet function spaces. The area of each ellipse denotes scaling spaces \( V \). The area between two successive ellipses represent wavelet spaces \( W \).

The coefficients obtained by projecting \( x(\omega) \) on \( \Psi_{j,k}(\omega) \) (\( \Phi_{j,n,k}(\omega) \)) are named as \( d_{j,k} \) \((a_{j,k})\). \( d \) and \( a \) are abbreviations for detail and approximation due to the local frequency characteristics of \( g \) and \( h \) explained below. The same as continuous wavelet transform, as \( j \) increases, the more coarse (low local frequency) information is represented. The mathematical details about the construction procedure of wavelet function \( \Psi \) and scaling function \( \Phi \) have been discussed in many books and are omitted here\[137\]. If the original spectrum can be considered as the approximation at level 0 by the \( a_0 \) coefficients, the Mallat algorithm tells us that the hierarchical coefficients \( a_{j+1,k} \) \((d_{j+1,k})\) can be obtained by deconvolution of \( a_{j,k} \) with filters \( h \) \((g)\) and subsequent down-sampling\[138\]. Thus, \( d_{j,k} \) \((a_{j,k})\) represents the information of the original signals in different local frequency bands. High local frequency information is stored in low level (small \( j \)) details coefficients and vice versa. More detailed theory of discrete wavelet transform and multi-resolution
analysis can be found in references[129, 137]. Once the coefficients are obtained, one can then analyze the signal at different resolution levels. This shows a clear advantage for the wavelet approach, namely the local distortion can be removed without distorting the signal resulting from non-local components. However a key difficulty in this approach is finding a reliable method for adjusting the coefficients at each level, such that only the spikes are removed. The solution to this is described in the section 7.3 via a data clustering technique.

### 7.2.2 K-Means Clustering

In our multi-resolution analysis, a data clustering technique is employed to distinguish wavelet coefficients originating from spikes from real signals. The most widely used clustering algorithm is K-means clustering. K-Means clustering is designed to partition \( n \) data points into \( K \) clusters in which each point belongs to the cluster with the nearest mean. The goal of the algorithm is to choose the cluster centroids \( (c_l) \) to minimize total intra-cluster variance, while maintaining maximum distinction between the clusters. Thus the cost function in Euclidean space is just the sum of the square distance of each data point to its corresponding centroid, given by[140] :

\[
J = \sum_{i=1}^{K} \sum_{l=1}^{I_n} |x_i^l - c_l|^2 \tag{7.14}
\]

where \( c_l \) is the centroid for cluster \( l \) and \( I_n \) is the number of data points in the cluster and \( x_i^l \) is a data point in cluster \( l \). A more detailed description can be found in Ref. 141. Nonetheless, a difficulty with this approach is that the best number of clusters is not known and has to be determined for each application of the algorithm. Another downside of K-means algorithms is that the cost function is not concave, leading to the production of local minimums, and the outcome strongly relies on the initial guess. So as to achieve a global minimum, one typically runs the K-Means algorithm multiple times
with different initial guesses and chooses the one with minimum $J$.

Figure 7.3: Raman spectra ($s$) and the corresponding wavelet coefficients ($d$ and $a$). The spikes are indicated by black arrows. The corresponding wavelet coefficients are denoted by red arrows.

### 7.3 Spike-Removal Algorithm

Firstly, to verify the capability of representing spikes by wavelet transform, the wavelet coefficients of one representative Raman spectra was obtained. The results are shown in FIG. 7.3. We can see that the spikes are indeed well locally represented by wavelet transform.

The basic idea behind our algorithm is to adjust the erroneous wavelet coefficients caused by spikes ($a_{j_0, k}^m$ and $d_{j, k}^m$, $m$ indicates the specific spectra being transformed) to the values they are most likely to be. As mentioned above, the locations of the cosmic rays are highly random leading to very low probability that two spikes are located at the same position in all spectra. Consequently, most of the coefficients representing the
real data should aggregate into a cluster. Erroneous coefficients that appear with low probability can be detected by analysis of clustering behaviors. Then, the wrong one can be adjusted to the average of the data points in an aggregated cluster. We proceed by assuming 3 or more spectra (\( h \) is the total number of spectra recorded) were measured under the same conditions for a given sample. The algorithm consists of 4 steps:

1. Wavelet transforms up to level \( n \) (determined by \( 2^{n+3} \approx \) number of data points which was found to give the best performance) are performed on each spectra individually and the resulting \( a_{j_n,k}^m \) and \( d_{j,k}^m \) (\( j \in [0,n] \), \( m \in [1,h] \)) are stored in array \( l_{j,k}^m \). With

\[
l_{j,k}^m = d_{j,k}^m, \quad j \in (0,n), \quad l_{n+1,k}^m = a_{j_n,k}^m
\]

2. Theoretically, the measured spectra should be very similar resulting in small differences among the coefficients. Thus, if one clusters the coefficients, all the coefficients should aggregate into one cluster except the erroneous coefficients caused by spikes. In practice, there will always some environmental changes or drifts (e.g. sample temperature or laser power) leading to variances between the consecutive measurements. Setting a cluster radius \( r_j \) for each each decomposition level \( j \) to allow for variance among \( h \) spectra is necessary. As mentioned in the previous section, Raman features and spikes have different local frequency characteristics and Raman features are usually broader. Thus it is safe to infer \( l_{j,k}^m \) at higher level \( j \) better represents the real features. Hence, the radius at a high level should be set larger to account for the variance among spectra. Detailed discussion about selection of \( r_j \) will be given in the section 7.5.

3. For each decomposition level \( j \) and coefficients index \( k \), adjust \( l_{j,k}^m \) based on K-means clustering process. The number of clusters \( c_{num} \) starts with one. The cluster of largest size most likely contains correct coefficients. By comparing the obtained cluster radius and the preset \( r_j \), one can decide whether the clustering is acceptable or not. If not, the algorithm will update \( c_{num} \) and repeat the aggregation procedure. On the other hand, if no cluster can be found, which is implemented by checking \( c_{num} == h \), in this case, it is likely all coefficients are real but with large variance, so no change will be made. One
Chapter 7. Automatic Spike-Removal Algorithm for Raman Spectra

An example is shown to illustrate this step in FIG. 7.4. The details of this step are shown in the following pseudocode,

**Data:** The decomposition coefficients $l_{j,k}$, total number of spectra $h$, current cluster number $c_{num}$, radius of the largest cluster $R_{C_{jm,k}}$, centroid of the largest cluster $C_{jm,k}$, preset cluster radius $r_j$

for each $j, k$ do

set $c_{num} = 1$;

while True do

use K-means method to aggregate $l_{j,k}$ into $c_{num}$ clusters.;

get the radius $R_{C_{jm,k}}$ and centroid $C_{jm,k}$ of the largest cluster, if there is more than one largest cluster, choose the one with the smallest radius;

if $R_{C_{jm,k}} \leq r_j$ then

reset the $l_{j,k}^m$ in other clusters to $C_{jm,k}$;

break to next for loop;

else

$c_{num} = c_{num} + 1$;

if $c_{num} = h$ then

no change will be made, break to next for loop;

else

continue the while loop with updates $c_{num}$;

end

end

end

4. In the end, the processed coefficients $a_{jm,k}^m$ and $d_{jm,k}^m$ will be used to perform an inverse wavelet transform to recover the $h$ spike-free spectra.
Chapter 7. Automatic Spike-Removal Algorithm for Raman Spectra

Figure 7.4: One example of step 3. a: Clustering performed at $j = 1$. $2r_1$ is visualized by the red line. In the 1st trial, the algorithm aggregated all data points into one cluster. Since the diameter (the short edge of the purple rectangle) is larger than $2r_1$, the algorithm continues. In the next trial, the data points were aggregated into two clusters. The diameter of the bigger cluster (short edge of the blue rectangle) is smaller than $2r_1$. Thus the algorithm accepts this aggregation and resets the wrong coefficients to the centroid of the bigger cluster (shown by the arrow). b: Clustering performed at $j = 5$. $2r_1$ is visualized by the blue line. Since $r_5 > r_1$, one cluster was found and its diameter (short edge of green rectangle) was accepted by the algorithm and no change was made.

Figure 7.5: Original and processed Raman spectra of Sr$_3$Ir$_2$O$_7$. The spectra are offset for clarity. The zoom-in images show details of both spectra. a: Spectra taken at 280 K. S3 spike is as high as 6000. b: Spectra taken at 125 K.

7.4 Experiments

The Raman measurements were performed using a home-built Raman microscope, the details of which can be found in chapter 3. Two single crystal samples, Cr$_2$Ge$_2$Te$_6$ and
Figure 7.6: Original and processed Raman spectra of Cr$_2$Ge$_2$Te$_6$. The spectra are offset for clarity. The zoom-in images show details of both spectra. Phonons and spikes are indicated by P and S respectively. P$_{3a}$ (P$_{4a}$) denote P3 (P4) phonon at anti-Stokes side. a: Spectra taken at 100 K. b: Spectra taken at 185 K.

Sr$_3$Ir$_2$O$_7$, were measured, chosen for their very small Raman cross-section, low thermal conductivities, and variety of Raman features (one, two-phonon as well as two-magnon). Thus in order to achieve sufficient signal to noise ratios as well as to avoid laser heating, one has to use low laser power and long exposure times, increasing the possibility of cosmic rays in the spectra. For the clustering purpose, at least three spectra taken with the same exposure time, laser power and under the same physical conditions are required.

The algorithm was implemented in MATLAB. MATLAB 2014a’s built-in wavelet transform, its inverse and K-Means clustering functions were used.

### 7.5 Results and Discussion

Cosmic rays in our Raman measurements are typically very narrow (FWHM 1.5-3 cm$^{-1}$)[129], however, the features they interfere with are of various types. In this section, we first show the processed results on four data sets with different characteristics. Subsequently, the selection of $r_j$ and the wavelets dependence on the performance will be discussed.
7.5.1 Primary Tests

The first two sets of spectra were taken on single crystal Sr$_3$Ir$_2$O$_7$ at 280 K and 125 K respectively (see FIG. 7.5). The measurement was done with the laser power as low as 0.1 mW. Each spectra was collected with 10 minutes acquisition. The processed spectral range was set to (-200,1600) cm$^{-1}$ to show both anti-Stokes and Stokes sides, resulting in 1803 data points. The central multiple peaks near 0 cm$^{-1}$ are Rayleigh scattering and artifacts of our notch filters. The Raman spectra of Sr$_3$Ir$_2$O$_7$ contain five phonons\cite{142}(centered at 143.0 cm$^{-1}$, 177.6 cm$^{-1}$, 268.4 cm$^{-1}$, 389.4 cm$^{-1}$, 586.0 cm$^{-1}$) and two broad features (710-880 cm$^{-1}$, 1307-1462 cm$^{-1}$) due to two-magnon and two-phonon excitations\cite{143} that will be the subject of a future publication. In the following texts, the amplitudes and the linewidths of both spikes and Raman features are given inside parentheses. In the first data set (shown in FIG. 7.5a), we focused on the cosmic rays overlapping with intermediately broad features (FWHM 5-10 cm$^{-1}$). There are six spikes in total visible in the spectra. Here phonons, spikes, two-magnons and two-phonons are denoted by P, S, TM and TP, respectively. From the zoom-in image in FIG. 7.5a, we can see that the processed spectra the algorithm indeed removes spikes S1 and S2 very well, while there is still some residue left in the processed spectra from S4 and S5.

In the next subsection, a strategy for the selection of $r_j$ will be discussed to minimize these residues. Compared to the first set, spikes S2-S4 (1-3 cm$^{-1}$, 200-600 counts) in the second data set (shown in FIG. 7.5b) interfere with much broader features TM ($\approx$100 cm$^{-1}$, 150 counts) and TP ($\approx$80 cm$^{-1}$, 250 counts). Broad features like this also are often observed in organic samples\cite{144, 145} and other two-particle excitations\cite{146, 22} and are more likely to be contaminated by spikes due to the broadness. Nonetheless, from FIG. 7.5b it is clear that our method was able to eliminate spikes S2-S4 from the spectra with negligible distortion of the original spectra. The results from single crystal Cr$_2$Ge$_2$Te$_6$ are shown in FIG. 7.6. The two data sets were taken at 100 K and 185 K with laser power 0.08 mW. Each spectra was collected with 15 minutes exposure and 900 data points were
acquired. As can been seen from FIG. 7.6, Cr$_2$Ge$_2$Te$_6$ contains sharper phonon lines than Sr$_3$Ir$_2$O$_7$. For example, spike S1 (2 cm$^{-1}$, 1500 counts) sits at the top of a narrow feature P1$_a$ (2.8 cm$^{-1}$, 700 counts) in FIG. 7.6a, while Spike S2 (1.4 cm$^{-1}$, 800 counts) is very near to the shoulder of P2$_a$ (2.3 cm$^{-1}$, 1100 counts). From the insets of FIG. 7.6a and 7.6b, we can see the phonon lines were well recovered. Especially noteworthy is the removal of the tiny S3 spike (see FIG. 7.6b). Moreover, in the inset of FIG. 7.6b, we can see spike S1 (2 cm$^{-1}$, 800 counts) almost overwhelms the very weak feature P3$_a$ (5 cm$^{-1}$, 50 counts). Nonetheless our method is still able to safely remove the spikes while preserving all features of the original data.

7.5.2 Selection of $r_j$

Without any doubt, $r_j$ is the most important parameter in the entire algorithm. Since $r_j$ represents the allowance of variance among spectra, a good $r_j$ should be able to keep small differences resulting from typical noise, while still filtering out cosmic rays. In the previous subsection, we already demonstrated results with different choice of $r_j$. In this subsection, we study its influence more thoroughly. One representative data set, Cr$_2$Ge$_2$Te$_6$ taken at 185 K was used for the investigation. $r_j$ was first set as a linear function of $r_s \times j$ with $r_s$ taking four different values: 5, 10, 15 and 20. The resulting spectra are shown in FIG. 7.7. For the purpose of quantitative comparison, the spikes were also removed by hand, namely adjusting the data to an approximate value. The cross-correlation[147] between the processed spectra and the corrected spectra was computed and shown in the plot. In theory, if the spectra are of high similarity except for the spikes, one would set $r_s$ as small as possible to remove all local frequency components of the cosmic rays. As shown in FIG. 7.7b, although the spike was removed in all four cases, when we take the difference between the processed spectra and manually corrected spectra, we can see that the spectra with minimum $r_s$ indeed has the best performance. Specifically, the low local frequency components (310-340 cm$^{-1}$) of the
spikes are not completely diminished in other cases. If the spectral variance is noticeable, an intermediate \( r_s \) is needed to avoid unexpected errors. This can be seen by comparing the processed spectra in FIG. 7.7d. For the bottom spectra, because the \( r_s \) was set too small, no cluster with radius \( r_1 \) smaller than 5 could be found. Consequently, no change was made for \( d_1 \) at the location of the spikes, resulting in the spikes remaining in the processed spectra. For the other three cases, the algorithm was able to aggregate \( d_1 \) with larger \( r_1 \) and reset the erroneous coefficients. Besides, in FIG. 7.7e when one compares the resulting difference between the two dashed lines where the phonon features are located, as \( r_s \) increases the ‘W’ shape in the resulting differences becomes more and more flat. Thus, if \( r_s \) is small the resulting difference is larger, and the automatically filtered spectra reveal more rapid fluctuations, indicating the modification of high local frequency components of phonon features. This results from a lack of variance allowance at low levels for high local frequency components. As such, the peak feature is better preserved for larger \( r_s \). On the other hand, just as the case discussed previously, the low local frequency components of the spike are better removed with small \( r_s \), which is shown over the spectral range -130 cm\(^{-1}\) to -70 cm\(^{-1}\) in FIG. 7.7e. So a trade-off between the allowance of variance to keep the real feature and elimination of low local frequency components of spikes has to be made, requiring one to choose an intermediate \( r_s \). This is confirmed by the highest cross-correlation (shown in FIG. 7.7a), obtained with \( 15 \times J \). One can also increase the \( r_j \) for low level clustering and reduce it at high levels for better results. In FIG. 7.8, we show the results with \( r_j \) set to \( 20 \times \sqrt{j} \) as well as the best result obtained with the previous \( r_j = 15 \times j \). For convenience, we abbreviate the \( r_j \) settings to S20 (S15) for \( 20 \times \sqrt{j} \) (15 \times j). Judging from the two curves in FIG. 7.8a and 7.8c, we can see that both settings were able to retain the real features and result in overall similar residues in between the two dashed lines (shown in FIG. 7.8b and 7.8d). However, when comparing the region outside of the lines, the residue for S15 is more significant than S20 in terms of both amplitude and oscillation. On the other hand, the residue for
S20 is more or less flat and featureless. So it can be concluded the bottom curve indeed performed slightly better in terms of eliminating the low local frequency components of the spikes, which is also checked by the calculated cross-correlation (shown in FIG. 7.8a).

<table>
<thead>
<tr>
<th>Wavelets</th>
<th>CGT_{100k}</th>
<th>CGT_{185k}</th>
<th>SIO_{280k}</th>
<th>SIO_{125k}</th>
</tr>
</thead>
<tbody>
<tr>
<td>haar</td>
<td>0.998906</td>
<td>0.996607</td>
<td>0.996441</td>
<td>0.999375</td>
</tr>
<tr>
<td>db3</td>
<td>0.998647</td>
<td>0.996882</td>
<td>0.996194</td>
<td>0.999248</td>
</tr>
<tr>
<td>sym2</td>
<td><strong>0.998980</strong></td>
<td><strong>0.997576</strong></td>
<td><strong>0.997449</strong></td>
<td>0.999204</td>
</tr>
<tr>
<td>coif1</td>
<td>0.998718</td>
<td>0.996714</td>
<td>0.996463</td>
<td><strong>0.999411</strong></td>
</tr>
<tr>
<td>bior1.0</td>
<td>0.998906</td>
<td>0.996607</td>
<td>0.996441</td>
<td>0.999375</td>
</tr>
<tr>
<td>rbio1.1</td>
<td>0.998906</td>
<td>0.996607</td>
<td>0.996441</td>
<td>0.999375</td>
</tr>
<tr>
<td>dmey</td>
<td>0.998382</td>
<td>0.995904</td>
<td>0.994815</td>
<td>0.999018</td>
</tr>
</tbody>
</table>

Table 7.1: Cross-correlation between processed and manually fixed spectra. CGT (SIO) is abbreviated for Cr$_2$Ge$_2$Te$_6$ (Sr$_3$Ir$_2$O$_7$). The maxima cross-correlation coefficient in column are highlighted.

<table>
<thead>
<tr>
<th></th>
<th>CGT_{100k}</th>
<th>CGT_{185k}</th>
<th>SIO_{280k}</th>
<th>SIO_{125k}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>0.959753</td>
<td>0.985569</td>
<td>0.873641</td>
<td>0.989123</td>
</tr>
</tbody>
</table>

Table 7.2: Correlation coefficients between original and manually fixed spectra. The spike as high as 6000 counts leads to the small correlation coefficient in SIO_{280k}.

### 7.5.3 Selection of Wavelets

Seven wavelets were used and they are denoted by names (haar, db3, sym2, coif1, bior1.1, rbio1.1, dmey). Detailed descriptions about these wavelets can be found in MATLAB help documents. The same representative spectra on Cr$_2$Ge$_2$Te$_6$ taken at 185 K as well as the processed spectra are shown in FIG. 7.9. The $r_j$ was set as $15 \times j$. As we can see, generally cosmic rays are removed from all spectra regardless of the wavelet employed. The reduced dependence on specific choice of wavelet makes our algorithm even more user-friendly. Nonetheless, there is still slightly different behavior in terms of low local frequency residue. This can be explained by the different profiles of the wavelets. When the spikes are projected into the wavelet space using different wavelets, some wavelets can represent cosmic ray and Raman features better than others due to the different vanishing moment of wavelets.
To compare the performances and check the integrity, we computed the cross-correlation between the processed spectra and manually processed spectra for all four data sets. The calculated results including the one for original spectra are listed together in table 7.2. In general, all wavelets are capable of spike-removal and have very close performances less than 0.1-0.2%. Nonetheless, ‘sym2’ has the highest cross-correlation for the first three sets and ‘coif1’ worked best for the last data set. Thus, it can be inferred that ‘sym2’ is more suitable for spikes-removal algorithm.

7.6 Conclusion

Cosmic ray removal in Raman spectra is not a simple task due to the complex shape and large amplitude of spikes. A novel algorithm based on wavelet transform and data clustering has been proposed and validated using a wide range of experimental data. The spike detection and removal is performed by a multi-resolution data clustering of wavelet coefficients. The processed coefficients can then be used for reconstruction through inverse wavelet transform. The procedure has advantageously utilized the localization property of wavelets, which not only enable good separation of real features and spikes in wavelet space but also results in much less wavelet specific dependence. The algorithm is simple, easy to implement, has a lower dependency on the specific wavelets employed and intuitive threshold setting allowing the usage by non-experts in spectra filtering.
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Figure 7.7: Influence of $r_s$ (shown in the labels) on the resulting spectra. The original (processed) spectra are shown in blue (red). Spectra are offset intentionally for clarity. (a) Spectra processed by four $r_s$. The cross-correlations are shown in number nearby. (b)(d) The processed spectra are shown in zoom-in image. (c)(e) The difference between the processed spectra and manually fixed spectra. The black dashed lines indicate the region where phonon features and spikes are located.
Figure 7.8: Spectra processed by different threshold setting strategies $20 \times \sqrt{j}$ and $15 \times j$. (a)(c) Zoom-in images highlight the position of spikes. The numbers in the plot show the cross-correlation for the entire spectral range. (b)(d) Differences between processed spectra and manually fixed spectra. Positions of spikes and real features are indicated by the dashed lines.
Figure 7.9: Wavelets dependence of spike removal. From the bottom to top, the wavelets are ‘haar’, ‘db3’, ‘sym2’, ‘coif1’, ‘bior1.1’, ‘rbio1.1’, ‘dmey’ respectively.
Chapter 8

Optical properties of SrTiO$_3$ thin film on Silicon (100)

8.1 Introduction

SrTiO$_3$ is an important material for a wide range of applications, due to its unparalleled dielectric[148], ferroelectric[149] and piezoelectric properties[150]. The potential applications are limited, however, by the difficulty of integrating SrTiO$_3$ with silicon technology. Towards this goal, it was recently demonstrated that the perovskite SrTiO$_3$ can be grown on Si (100) directly[151], the most popular substrate in modern devices. Such integration can be used as a stepping stone to the integration of other perovskites with silicon, as SrTiO$_3$ serves as an excellent substrate for their growth. Indeed this approach has been used to incorporate BaTiO$_3$[152], Pb(Zr,Ti)O$_3$[153], BiFeO$_3$[154], PbMg$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$[155], and other important perovskites with silicon.

When these films are sufficiently thin (5-6 unit cells thick), they are commensurately strained in biaxial compression resulting in robust ferroelectric behavior. The ferroelectricity in SrTiO$_3$/Si (100) thin films is perhaps not surprising given the strong sensitivity of SrTiO$_3$ to strain[156] and chemical composition. This further suggests the electronic
and optical properties of SrTiO$_3$ films on Si (100) will be modified from their bulk values. Nonetheless, standard molecular beam epitaxy (MBE) techniques typically resulted in a complex interfacial layer. Thus previous attempts to investigate the optical properties of SrTiO$_3$ films on Si were only able to determine the average response of the film. Since recent improvements in the growth of SrTiO$_3$ via MBE have enabled films with no interfacial SiO$_2$, we have revisited the optical properties of these films. Through a combination of improved film quality and a model for analysis we have determined the dielectric function of these SrTiO$_3$ films as well as the interfacial layer.

### 8.2 Experiments

The SrTiO$_3$ thin film was prepared by MBE via a kinetically controlled growth process. The native surface oxide of the silicon substrate was thermally removed in situ prior to film growth via a strontium-assisted deoxidation process. The details of the growth can be found elsewhere[151]. The optical properties were measured using a variable angle spectroscopic ellipsometer (VASE) with a rotating analyzer and an autocompensator from J.A. Woollam Co. Inc. The VASE instrument measures the ratio of $\tilde{r}_p$ to $\tilde{r}_s$ (the complex reflectance parallel and perpendicular to the plane of incidence). This ratio is typically expressed in terms of $\Psi$ and $\Delta$ defined as

$$\frac{\tilde{r}_p}{\tilde{r}_s} = tan\Psi e^{i\Delta}$$ (8.1)

Since the optical constants of the silicon substrate are sensitive to its doping level, we also took data on a silicon substrate from the same batch. Knowing the optical constants of the substrate allowed us to precisely model the SrTiO$_3$/Si system. To prevent the interference from the substrate, the back surface of the silicon substrate is roughened intentionally[157]. Ellipsometric parameters of the SrTiO$_3$/Si film were measured from 0.75 eV to 5.5 eV with 0.05 eV resolution, except in the range 2.4 to 4.6 eV where it was
measured with 0.001 eV to properly capture the critical points of Si and SrTiO$_3$.

![Figure 8.1: Experimental data of $\Psi$ and $\Delta$ measured at various angle of incidence. Inset: Schematic view of the one layer model. Legend: Numbers indicate the angle of incidence.](image)

### 8.3 Results and Discussion

The measured $\Psi$ and $\Delta$ are shown in FIG. 8.1. From FIG. 8.1 we can see there are several features in the experimental data. The feature around 1.4 eV results from interference. The peak at 3.4 eV is the natural result of the $E_1$ critical point of the silicon substrate[158]. There are also two small features around 3.7 eV and 4.7 eV. The former
feature is due to the direct gap of the SrTiO$_3$ film and the latter one is due to the higher energy critical point of the SrTiO$_3$ film at 4.7 eV.

To properly extract the optical constants of SrTiO$_3$ as well as determine the homogeneity of the film, the dielectric function ($\tilde{\epsilon}(E) = \epsilon_1(E) + i\epsilon_2(E)$) of the SrTiO$_3$ film is defined using a sum of Tauc-Lorentz (TL) oscillators that are widely applied to interpret amorphous materials and thin films[159]. The imaginary part of the dielectric function in this model can be written as[159],

$$\epsilon_2(E) = \frac{A_L E_0 C (E - E_g)^2}{(E^2 - E_0^2)^2 + C^2 E^2} \Theta(E - E_g)$$

(8.2)

where $E_0$ is the peak transition energy, $A_L$ is the oscillator strength, $E_g$ is the band gap, $C$ is the broadening term, and $\Theta$ is the step function. The real part is obtained from a Kramers-Kronig transformation. From the formula, we see that the sudden onset of absorption due to a band gap is included via a step function multiplied by a standard Lorentz oscillator. However, in the analysis of dielectric response of crystals, the parameters of each TL oscillator itself do not have a real physical meaning, but rather function to model the behavior of dielectric function phenomenologically. What is meaningful is the optical constants described by the sum of the TL oscillators[157, 159]. Nonetheless since the same approach was applied to all materials studied, relative trends between the materials are faithfully reproduced. First, we tried to fit the data with a one layer model including only a single layer of SrTiO$_3$ thin film on the silicon substrate (shown in the inset of FIG. 8.1). The difference ($\delta \Psi = \Psi_{measured} - \Psi_{fit}$) between the measured ($\Psi_{measured}$) and the fit ($\Psi_{fit}$) with one SrTiO$_3$ layer is shown in FIG. 8.2. Similar results were seen in $\delta \Delta$. From FIG. 8.2 it is clear that the fit does not substantially improve the fit, especially in the region above the band gap of SrTiO$_3$ and at the $E_1$ critical point of silicon. Various models were tried to account for the possible strain induced by the substrate and oxygen deficiency during the growth[160]. This included a graded model where
the dielectric function varies continuously along the direction normal to the surface of the film. In addition an effective medium layer between the SrTiO$_3$ layer and the silicon substrate was added to account for a mixture of SrTiO$_3$ and silicon[161]. However, these models did not substantially improve the fit. The failure of these models led us to try a less intuitive, though simpler model where there are two layers of SrTiO$_3$ in the film with different optical constants (shown in the inset of FIG. 8.2). The improved model resulted in a dramatic improvement of reduced chi-square ($\chi^2/\nu$, where $\nu$ is the number of degrees of freedom) from 7.9 to 3.7. From FIG. 8.2 we can clearly see the dramatic reduction in $\delta \Psi$ for the second model. This is especially true at the $E_1$ critical point of the silicon substrate. The reason is a reduction in the absorption of the second layer of the SrTiO$_3$ films (see FIG. ??), which allows more light to reach the silicon substrate.

From the fit, the thickness of the top (second) layer is 75.1±0.1 nm (25.4±0.1 nm), giving a total thickness of the SrTiO$_3$ film of 100.5±0.2 nm. This is in good agreement with the nominal thickness determined from in-situ RHEED during the MBE growth of the film[160]. We present the dielectric function of both layers in FIG. ?? Data for the second layer are only displayed below 3.76 eV, since this is the energy where the penetration depth is smaller than the thickness of the top layer (see FIG. 8.4). As a comparison, the bulk SrTiO$_3$ is also measured with spectroscopic ellipsometry with resolution 0.05 eV from 0.75 eV to 5.5 eV. The optical constants of the bulk is also extracted by the sum of TL oscillators. A 3.0±0.1 nm-thick Bruggeman effective medium approximation layer was added to account for the surface roughness[162]. The extracted optical constants are in good agreement with the literature[162, 163] and plotted in FIG. ?? as well.

From FIG. ??, we can see that the onsets of $\epsilon_2(E)$ shift from the bulk value indicating the band gaps of both layers shift to lower energy. The reasons for the shifts will be discussed later.

In inset c of FIG. ?? we plot $(\epsilon_2(E) \times E^2)^2$, since in the vicinity of direct gap, $\epsilon_2(E)$ has
Chapter 8. Optical properties of SrTiO$_3$ thin film on Silicon (100)

Figure 8.2: Difference between measured $\Psi$ and the fits of the two models. A significant improvement in the quality of the fit is obtained through the two-layer model, especially near the $E_1$ critical point of silicon (3.4eV). Legend: T and O indicate two-layer and one-layer model respectively. Numbers indicate the angle of incidence.

the energy dependence ($\epsilon_2(E) \propto (E/E_g)^{-2}(E/E_g - 1)^{1/2}$)[164]. As expected we observe a linear function of energy, intercept of which gives a direct gap of 3.77±0.03 eV, close to the bulk gap value of 3.78 ± 0.12 eV determined by the same method. Since there is only limited data for the second layer, the direct gap cannot be determined. Also, at the edge of the indirect band gap, $\epsilon_2(E)$ has the energy dependence given by $\epsilon_2(E) \propto (E - E_g - E_p)^2$, where $E_p$ is the energy of phonon mode[164]. Thus, the optical indirect gap of both layers are determined by a linear fit between $\epsilon_2(E)^{1/2}$ and the photon energy[164](Inset b of FIG. ??). The results are 2.51±0.01 eV (2.28±0.01 eV) for the top (second) layer which are significantly lower than bulk value 3.04± 0.15 eV (Inset a of FIG. ??) determined in the same manner.
According to band structure calculations of bulk SrTiO$_3$[163, 165] the highest valence bands are formed by O 2p electrons and the lowest conduction bands are formed by Ti 3d electrons. The indirect gap is the transition between the Γ point and the R point and the direct gap occurs at the Γ point[163]. Reduction of the indirect gap has been reported in the literature and was attributed to the effects of strain [166, 167] and oxygen
deficiency[168, 169]. In our case, it is hard to reach a firm conclusion for the reason for the reduced indirect gap. Commensurate growth on silicon corresponds to 1.7% compressive strain at room temperature[151]. In the tight bonding approximation, as the compressive strain reduces the lattice constants of SrTiO$_3$, orbital overlap increases resulting in a reduction of the band gap. The reduction of the band gap due to the effect of strain has also been observed in SrTiO$_3$ thin films (14 nm) grown on LaAlO$_3$ (3% compressive strain)[166]. Also, substrate induced strain could also cause optical anisotropy in the epitaxial film, which is not included in the two-layer model, so the structure obtained by the two-layer model may only be an approximation.

Nonetheless we believe strain is not the cause of the two layers or reduction in the gap we observed. Specifically it is hard to see how strain relaxation would result in two distinct layers rather than a gradual change. Furthermore it has been shown that strain relaxation takes place quickly if the thickness of the SrTiO$_3$ film exceeds a critical value[170]. In particular the strain is nearly fully relaxed in films of only 50 nm (whereas our films are 100 nm). Thus, strain is less likely to be the reason for reduction of the indirect band gap. Oxygen deficiency is more likely to be the cause of the two layers we observe. Indeed it is well known that oxygen vacancies can act as shallow donors[171]. Y. S. Kim et al. investigated the effect by optical absorption spectra on 100-nm-thick SrTiO$_3$ thin films deposited with different partial pressure of oxygen ($P_{O_2}$)[169]. They find anomalous absorption peaks below the optical band gap of bulk SrTiO$_3$ and the peak shifts to lower energy as $P_{O_2}$ decreases. Based on a density-functional-theory (DFT) calculation, they argue that the effect should be due to Sr–O–O vacancy. D. Kan et al. found the oxygen deficiency of SrTiO$_3$ caused by Ar$^+$ irradiation will induce luminescence at 2.8 eV below the gap[172]. The observation of a reduced indirect gap in these experiments is consistent with our results. Moreover, the deficiency of oxygen is also consistent with the film growth procedure[160]. The oxygen was turned off at the very beginning of the growth to prevent the formation of SiO$_2$. Then the oxygen was reintroduced later. Thus
the existence of the two layers is likely caused by the deficiency of oxygen.

Figure 8.4: Penetration depth of the top layer. The red line indicates the thickness of the top layer.

8.4 Conclusion

In summary, spectroscopic ellipsometry has been performed on SrTiO$_3$ thin film grown on Si (100). The data is best described by a two layer model. The dielectric function of the second layer changes significantly from bulk. We ascribe this to the effect of oxygen deficiency at the beginning of growth.
Chapter 9

General Conclusions and Future Perspectives

9.1 Conclusion

In this thesis we first explored spin-phonon coupling and phonon-phonon coupling with Raman spectroscopy. The 2D ferromagnetic semiconductor Cr$_2$Ge$_2$Te$_6$ was studied by the highly stable and efficient home-built Raman microscope. Temperature dependent Raman spectra revealed spin-phonon coupling in Cr$_2$Ge$_2$Te$_6$ from multiple aspects: near $T_C$ we observed a split of two phonon modes due to the breaking of time reversal symmetry; an anomalous hardening of an additional three modes; and a dramatic enhancement of the phonon lifetimes. Our results show that spin-phonon coupling is crucial for the understanding of the lattice dynamics in this material. This opens the exciting possibility of studying spin-phonon coupling using Raman spectroscopy and the door for the future studies of exfoliated 2D ferromagnets Cr$_2$Ge$_2$Te$_6$.

Although the thermoelectrics Bi$_2$Te$_{3-x}$Se$_x$ have been studied for many decades, the origin of its low thermal conductivity still remains unclear. By studying the temperature dependent Raman spectra of Bi$_2$Te$_{3-x}$Se$_x$, we uncovered an anomalous anharmonic
behavior of the phonon modes, which is consistent with the recently proposed resonance bonding mechanism. Our result suggests that the resonance bonding may be a common feature for the conventional thermoelectrics. This is a very meaningful concept for the future material design of thermoelectrics. Other than the anharmonicity, we also observed an extra feature in the Raman spectra of BTS. The origin of this feature has been debated for decades. Via the temperature dependent Raman study, we were able to identify it as the Te-Se antisite defect induced local mode. The anomalous linewidth of the local mode was also explained by statistical analysis.

The cosmic-ray caused spikes in Raman spectra always pose obstacles for the analysis, resulting in a huge waste of time, and limits reproducibility. In chapter 7, we proposed an algorithm to resolve this problem. The wavelet transform and data clustering based automatic spike-removal algorithm for Raman spectra was shown to generate spike-free spectra with negligible distortion. The algorithm can be easily implemented and will be beneficial to the Raman community.

In the last chapter, a widely applicable high dielectric material SrTiO$_3$ thin film grown by a new technique on silicon (100) was investigated by ellipsometry. The growth of this material is optimized to avoid the formation of oxides in between Si substrates and SrTiO$_3$ thin films, demonstrating the possibility of replacing the current gating material SiO$_2$ in the semiconductor industry. Through modeling the ellipsometry response of the thin film, we were able to show that two layers of SrTiO$_3$ are formed during the growth process with slightly different oxygen concentration. Of particular note is the lowering of the band gap of the film, which is particularly problematic for real devices. Indeed, a smaller band gap will allow for more leakage current at a given gate voltage. To achieve better performance of devices, the growth recipe can be further explored.
9.2 Suggested further experiments

In chapter 4, we are able to show strong spin-phonon coupling in Cr$_2$Ge$_2$Te$_6$ using temperature dependent Raman spectroscopy. Cr$_2$Ge$_2$Te$_6$ is proposed to be a potential 2D ferromagnetic semiconductor through mechanical exfoliation with $T_C$ enhanced to 106 K\cite{49}. However, the small physical dimension (microns) of the exfoliated sample limits many conventional experimental techniques. To resolve this, one can probe $T_C$ and study spin-phonon coupling in the exfoliated ferromagnets Cr$_2$Ge$_2$Te$_6$ through micro-Raman spectroscopy. Besides, it has been predicted that the control of the strain can manipulate $T_C$ in the 2D ferromagnets\cite{49}, thus it will be very interesting to study the effect of substrates on the exfoliated Cr$_2$Ge$_2$Te$_6$.

In chapter 5, the large anharmonicity in Bi$_2$Te$_{3-x}$Se$_x$ is ascribed to the resonance bonding mechanism. In the original theory, PbTe and SnTe were predicted to have larger resonance bonding effect which would be more anharmonic than Bi$_2$Te$_{3-x}$Se$_x$\cite{76}. The anomalous anharmonicity was already confirmed by inelastic neutron scattering\cite{9}. However, due to the low spectra resolution and low signal levels, previous measurements were not able to track the temperature dependent phonon frequencies and phonon linewidths very well. As we already demonstrated, our Raman microscope is able to extract the temperature dependence very precisely due to the high collection efficiency and stability. Based on the temperature dependence, one would be able to uncover the contributions from different anharmonicities (cubic or quartic) in PbTe and SnTe, pushing the boundary of the knowledge of fundamental properties of thermoelectrics forward. Moreover, an instrumental upgrade can be focused on building a Fabry-Perot Interferometer for a temperature dependent Brillouin scattering study. As we mentioned in chapter 5, the heat dissipation channel $TA + TO \rightarrow TO$ has been found both in PbTe and perovskite ferroelectrics. Given the similarity between Bi$_2$Te$_{3-x}$Se$_x$ and those two types of materials, this channel may also exist in Bi$_2$Te$_{3-x}$Se$_x$. A temperature dependent Brillouin scattering measurement will be very meaningful in providing an answer to this question.
9.3 Future works on instrumentation and algorithm

When I built the polarized variable temperature Raman system, one goal I had in mind was to make the system as automated as possible. Because the Raman signal is weak, even a small operational error can result in significant changes in the Raman spectra. As we mentioned, the Raman scattering cross section is very small. To uncover the subtle many-body interactions, one should avoid any operational error as much as possible. For example, we can only extract the reliable phonon linewidths of the $E_g^4$ and $A_g^1$ in chapter 4, because the signal levels of other modes are fairly low. Via an automated data-taking scheme, we can increase the signal to noise ratio. Currently most parts of the system are motorized. However, human operations are still necessary for measurements, leading to many operational errors, especially one has to refocus the laser. Thus, future efforts can be focused on the integration of the various required software packages and full automation for more accurate and reliable measurements.

In chapter 7, the spike-removal is achieved through an preset $r_j$ which will limit the potential of full automation. K-mean clustering is one of the entry-level clustering methods in machine-learning algorithms, there should be plenty of room for improvement. Future improvement can be focused on a more intelligent clustering mechanism. Specially, a self-adaptive clustering mechanism will not only make the algorithm totally automated but also significantly improve the performance of the algorithm.
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