# Spectroscopy of Topological Materials

Gavin B. Osterhoudt

A dissertation submitted to the Faculty of the department of Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Boston College Morrissey College of Arts and Sciences Graduate School

November 2020

© Copyright 2020 Gavin B. Osterhoudt

#### Spectroscopy of Topological Materials

Gavin B. Osterhoudt Advisor: Kenneth S. Burch, Ph.D.

Since their first experimental realizations in the 2000s, bulk electronic topological materials have been one of the most actively studied areas of condensed matter physics. Among the more recently discovered classes of topological materials are the Weyl semimetals whose low energy excitations behave like massless, relativistic particles with well-defined chirality. These material systems display exotic behavior such as surface Fermi arc states, and the chiral anomaly in which parallel magnetic and electric fields lead to an imbalance of left- and right-handed particles. Much of the research into these materials has focused on the electronic properties, but relatively little has been directed towards understanding the vibrational properties of these systems, or of the interplay between the electronic and vibrational degrees of freedom. Further, the technological potential of these materials is still underdeveloped, with the search for physical properties enhanced by the topological nature of these materials being sought after. In this dissertation we address both of these issues.

In Chapters III and IV we present temperature dependent Raman investigations of the the Weyl semimetals  $WP_2$ , NbAs, and TaAs. Measurements of the optical phonon linewidths are used to identify the available phonon decay paths, with ab-initio calculations and group theory used to aid the interpretation of these results. We find that some phonons display linewidths indicative of dominant decay into electron-hole pairs near the Fermi surface, rather than decay into acoustic phonons. In light of these results we discuss the role of phonon-electron coupling in the transport properties of these Weyl semimetals. In Chapter V, we discuss the construction of our "PVIC" setup for the measurement of nonlinear photocurrents. We discuss the experimental capabilities that the system was designed to possess, the operating principles behind key components of the system, and give examples of the operating procedures for using the setup. The penultimate chapter, Chapter VI, presents the results of photocurrent measurements using this setup on the Weyl semimetal TaAs. Through careful analysis of the photocurrent polarization dependence, we identify a colossal bulk photovoltaic effect in this material which exceeds the response displayed by previously studied materials by an order of magnitude. Calculations of the second-order optical conductivity tensor show that this result is consistent with the divergent Berry connection of the Weyl nodes in TaAs.

In addition to these topics, Chapter II addresses the results of Raman measurements on thin film heterostructures of the topological insulator  $Bi_2Se_3$  and the magnetic semiconductor EuS. By investigating the paramagnetic Raman signal in films with different compositions of EuS and  $Bi_2Se_3$  we provide indirect evidence of charge transfer between the two layers. We also track the evolution of phonon energies with varying film thicknesses on multiple substrates which provides insight into the interfacial strain between layers.

We conclude the dissertation in Chapter VII with a summary of the main results from each preceding chapter, and give suggestions for future experiments that further investigate these topics.

# TABLE OF CONTENTS

LIST OF FIG	$\cup \mathbf{RES}$
LIST OF TAI	LES
LIST OF AB	<b>REVIATIONS</b>
ACKNOWLE	OGEMENTS
CHAPTER	
I. Intro	uction $\ldots \ldots 1$
1.1	Scope of this Dissertation
1.2	The Berry Phase and Topological Materials
	1.2.1 Weyl Semimetals
	1.2.2 Topological Insulators
1.3	Crystal Symmetry: Point and Space Groups
1.4	Raman Scattering 11
	1.4.1 Phonon Lineshapes
	1 4 2 Group Theory and Mode Classification 15
	1 4.3 Anharmonicity and Phonon Decay 17
15	Nonlinear Photocurrents
1.0	1.5.1   Connection to Topology   23
II. Charg	e Transfer in $Bi_2Se_3/EuS$ Heterostructures $\dots \dots 24$
2.1	Introduction
	2.1.1 EuS Raman Signal
2.2	Experiments
	2.2.1 Growth of Thin Films
	2 2 2 Baman Measurements 28
	2.2.2 Magnetic Measurements 20
9 2	Discussion and Analysis
2.0	2.2.1 Fabry Porot Interforence Calculations 21
	2.5.1 Fabry-refor interference Calculations

		2.3.2 Charge Transfer	38
	2.4	Strain	41
	2.5	Conclusions	43
III. F	Phone	on-Electron Coupling in $WP_2$	44
	3.1	Topological Semimetals and Mobility	44
	3.2	Crystal Symmetry and Raman Modes	45
	3.3	Polarization Dependent Raman Measurements	46
	3.4	Temperature Dependent Measurements	57
		3.4.1 Temperature Dependence of Phonon Energies	59
		3.4.2 Temperature Dependence of Phonon Linewidths .	64
	3.5	Model of Phonon Decay into Electron-Hole Pairs	69
	3.6	Electronic Band Structure and Phonon Transition Density	
		of States	71
	3.7	Selection Rules for Phonon Scattering	72
		3.7.1 Wave Vector Conservation	72
		3.7.2 Direct Product Reduction Coefficients	74
	3.8	Momentum Conservation	80
	3.9	Phonon-Electron Coupling Strengths	83
	3.10	Conclusions	87
IV. F	hono	on Scattering in NbAs and TaAs	89
	4.1	Introduction	89
	4.2	Experiments	90
	4.5	Computational Methods	91
	4.4	Lingham of the <i>D</i> . Moder	00
	4 5	Lineshape of the $B_1$ Modes	92
	4.0	Temperature Dependence of the A Linewidth	90
	4.0	Temperature Dependence of the $A_1$ Linewidth	90 100
	4.1	Dependence Counting Strength and Other Dependence	102
	4.0	diated Channels	107
	4.0	Anharmonic Fitting of Other Phonon Modes	100
	4.9	Conclusions	116
	4.10		110
<b>V.</b> F	Photo	ocurrent Measurement Apparatus	118
	5.1	Overview	118
	5.2	Requirements	119
	5.3	Components	120
		5.3.1 Laser Sources	121
		5.3.2 Water Chiller	123
		5.3.3 Mechanical Chopper	124

	5.3.4 Quarter-wave Plate $\ldots \ldots 125$
	5.3.5 Encoded Rotation Mount $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 130$
	5.3.6 Mercury-Cadmium-Telluride Infrared Detector 132
	5.3.7 Beam splitter $\ldots \ldots 136$
	5.3.8 Focusing Lens $\ldots \ldots 137$
	5.3.9 Motorized Stages $\dots \dots \dots$
	5.3.10 Breakout Boxes $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 139$
	5.3.11 PXI
	5.3.12 Lock-In Amplifiers $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 141$
	5.3.13 Multimeter $\ldots \ldots 142$
	5.3.14 Current Sources $\ldots \ldots 142$
5.4	Alignment
5.5	Photo-voltage vs Photo-current Measurements
5.6	Operating Procedures
5.7	Data Analysis
VI. Bulk	Photovoltaic Effect in TaAs
6.1	Introduction $\ldots \ldots 152$
6.2	Experimental Setup
6.3	TaAs: Crystal Symmetry and Nonlinear Photocurrents $154$
	$6.3.1  Photothermal Response \ . \ . \ . \ . \ . \ . \ . \ . \ . \ $
6.4	Device Design
6.5	Photocurrent Measurements
6.6	Elimination of Other Nonlinear Mechanisms
6.7	Comparison to Theory and Band Structure Calculations $172$
6.8	Glass Coefficient
6.9	Conclusions
VII. Concl	usions
7.1	Concluding Remarks
7.2	Suggested Further Experiments
BIBLIOGRA	PHY

# LIST OF FIGURES

# Figure

1.1	Feynman diagram showing a typical Raman scattering process. A photon of energy $\hbar \omega_{\rm c}$ is absorbed, creating an electron-hole pair	
	The electron then emits a phonon of energy $\hbar \omega$ before recombining	
	with the hole and emitting a photon of energy $\hbar\omega = \hbar\omega = \hbar\omega$	11
2.1	Feynman diagram for the first-order Baman scattering in EuS	11
2.1	In the paramagnetic state the disordered spin system provides	
	the momentum $(\mathbf{a}')$ necessary to generate the optical phonon of	
	energy $\Omega$ and momentum $\mathbf{q} = -\mathbf{q}'$	27
2.2	Raman spectra of a 5 nm thick EuS film grown on a sapphire	
	substrate. The fundamental spin-disorder mode is clearly visible	
	at 30.4 meV, as are its second and third harmonic overtones at	
	60.8 and 91.2 meV respectively.	29
2.3	Raman spectra of 7 quintuple layer (QL) $Bi_2Se_3$ with 10 nm thick	
	EuS on a sapphire substrate. While the Bi2Se3 phonon modes are	
	clearly visible at 16.5 and 21.7 meV, the EuS mode at 30.4 meV	
	is absent	30
2.4	The magnetic moment of a EuS/sapphire thin film sample in blue	
	is compared to the magnetic moment from a $\rm Bi_2Se_3/EuS/sapphire$	
	thin film in red. The diamagnetic background from the sapphire	
	substrates has been subtracted out	31
2.5	Diagram showing the rays that contribute to interference of the	
	incident laser. The black arrows show the path of the incident	
	laser, while the purple arrows indicate where multiple reflections	
	can occur for the transmitted part of the beam. The distance $y$	
	into the EuS indicates the depth at which we are calculating the	
	interference of the electric fields and will be integrated over to find	
	the total enhancement.	33
2.6	Same as the previous figure, but now showing the paths and rays	
	taken by the Raman scattered light which originates at depth $y$	
	in the EuS layer.	35

2.7	Calculated interference enhancement factor for films of varying EuS thickness, as a function of the $Bi_2Se3$ thickness. The dashed	
	line corresponds to the thickness of the $Bi_2Se_3$ for our measured samples.	37
2.8	Schematic diagram of the band bending that occurs at the in- terface between EuS and $Bi_2Se_3$ . The work function of $Bi_2Se_3$	
	$(\phi_{\text{Bi}_2\text{Se}_3} = 5.4 \text{ eV})$ is larger than that of EuS $(\phi_{\text{EuS}} = 3.3 \text{ eV})$ which leads to the formation of a Schottky barrier of height $\phi_{\text{Bi}_2\text{Se}_3}$ –	
	$\chi_{\rm EuS} = 5.05$ eV at their interface. To balance the chemical poten- tial, electrons move from EuS to the Bi <sub>2</sub> Se <sub>3</sub> resulting in a depletion region in which photoexcitation by our 2.33 eV laser is no longer	
2.9	(a) Raman spectra from bulk Bi <sub>2</sub> Se <sub>3</sub> . (b) Spectra of EuS/Bi <sub>2</sub> Se <sub>3</sub>	40
-	films on sapphire substrates. The vertical black line represents the energy of the modes from bulk $Bi_2Se_3$ . (c) Same as (b) but on strontium titanata (STO) substrates (d) Percent difference in	
	energy of the $Bi_2Se_3$ modes as a function of EuS thickness	41
3.1	Schematic diagram of the optical setup used to perform the po-	. –
3 9	larization dependent measurements of $WP_2$	47
0.2	polarization configurations	49
3.3	Polarization dependence of the $WP_2$ Raman spectra as the Fresnel rhomb is rotated.	51
3.4	Polarization dependence of the $A_1(1)$ phonon mode at 22.48 meV	
0.5	as measured on two separate faces (a) and (b)	52 V
3.5	Polarization dependence of the $A_1(2)/A_2(3)$ phonon mode at 35.84 me as measured on two separate faces (a) and (b)	eV 53
3.6	Polarization dependence of the $A_1(3)$ phonon mode at 44.89 meV	59
3.7	Polarization dependence of the $A_1(4)$ phonon mode at 49.60 meV	99
	as measured on two separate faces (a) and (b)	53
3.8	Polarization dependence of the $A_1(5)$ phonon mode at 65.00 meV	<b>.</b> .
2.0	as measured on two separate faces (a) and (b)	54
5.9	as measured on two separate faces (a) and (b), $\dots$ $\dots$	54
3.10	Polarization dependence of the $A_2(2)$ phonon mode at 32.38 meV	01
	as measured on two separate faces (a) and (b)	54
3.11	Polarization dependence of the $B_1(2)$ phonon mode at 40.47 meV.	55
3.12	Polarization dependence of the $B_2(1)$ phonon mode at 21.50 meV	55
2 1 2	as measured on two separate faces (a) and (b)	55
0.10 2.14	Polarization dependence of the $B_2(2)$ phonon mode at 45.94 meV.	00
0.14	as measured on two separate faces (a) and (b)	56
3.15	Polarization dependence of the $B_2(5)$ phonon mode at 68.90 meV	00
	as measured on two separate faces (a) and (b). $\ldots$ $\ldots$ $\ldots$	56

3.16	Temperature dependence of the $\mathrm{WP}_2$ Raman spectra in XX	58
3.17	Temperature dependence of the $WP_2$ Raman spectra in X'X'	58
3.18	Difference in phonon energy from lowest measured temperature	
	value $(\omega_0)$ as a function of temperature for the $A_2(1)$ , $B_2(1)$ , and	
	$A_1(1)$ modes	59
3.19	Difference in phonon energy from lowest measured temperature	
	value $(\omega_0)$ as a function of temperature for the $A_2(2)$ , $A_1(2)$ , and	
	$B_2(2)$ modes	60
3.20	Difference in phonon energy from lowest measured temperature	
	value $(\omega_0)$ as a function of temperature for the $B_1(2)$ , $A_1(3)$ , and	
	$B_2(3)$ modes	60
3.21	Difference in phonon energy from lowest measured temperature	
	value $(\omega_0)$ as a function of temperature for the $A_1(4)$ , $B_2(4)$ , and	
	$A_1(5)$ modes	60
3.22	Difference in phonon energy from lowest measured temperature	
	value $(\omega_0)$ as a function of temperature for the $B_2(5)$ mode	61
3.23	Phonon energy vs temperature with fits using the extended Kle-	
	mens' model as red lines for the $A_2(1)$ , $B_2(1)$ , and $A_1(1)$ modes.	61
3.24	Phonon energy vs temperature with fits using the extended Kle-	
	mens' model as red lines for the $A_2(2)$ , $A_1(2)$ , and $B_2(2)$ modes.	62
3.25	Phonon energy vs temperature with fits using the extended Kle-	
	mens' model as red lines for the $B_1(2)$ , $A_1(3)$ , and $B_2(3)$ modes.	62
3.26	Phonon energy vs temperature with fits using the extended Kle-	
	mens' model as red lines for the $A_1(4)$ , $B_2(4)$ , and $A_1(5)$ modes.	62
3.27	Phonon energy vs temperature with fits using the extended Kle-	
	mens' model as red lines for the $B_2(5)$ modes	63
3.28	Percent difference of phonon energies from the lowest temperature	
	value as a function of energy	64
3.29	A diagram showing the lowest order anharmonic decay process	
	of an optical phonon with energy $\omega$ decaying into two acoustic	
	phonons with energy $\omega/2$ and opposite but equal momentum	65
3.30	Temperature dependence of the three higher energy $A_1$ modes	
	showing behavior consistent with the anharmonic model of decay.	
	Red lines are fits to the data using the extended Klemens' model.	65
3.31	Temperature dependence of the two lower energy $A_1$ modes, as	
	well as the $A_2(2)$ mode which has an energy between the $A_1$ modes.	
	The two $A_1$ modes show anomalous linewidths consistent with	
	decay into electron-hole pairs near the Fermi surface, while the	
	$A_2$ mode shows anharmonic decay. The blue lines are fits using a	
	model of electron-hole pair decay, while the red line is a fit using	
	the extended Klemens' model.	66
3.32	Temperature dependence of phonon linewidths for the $A_2(1), B_2(1),$	
	and $B_2(2)$ modes. Red lines are fits to the data using the extended	
	Klemens' model	67

3.33	Temperature dependence of phonon linewidths for the $B_1(2)$ , $B_2(3)$ , and $B_2(4)$ modes. Red lines are fits to the data using the extended	
	Klemens' model	67
3.34	Temperature dependence of the $B_2(5)$ phonon linewidth. The red	
	line is a fit to the data using the extended Klemens' model	68
3.35	Diagram depicting interband (pink arrow) and intraband (blue arrow) transitions by optical phonons. An energy $\hbar\omega_a$ separates the initial state from the chemical potential $E_F$ . The electronic energy bands are labeled by irreducible representations $\Gamma^i$ and $\Gamma^j$ , while the optical phonon has representation $\Gamma^k$ . A transition is symmetry allowed only if $\Gamma^k$ is contained in the direct product of	
	the band representations	70
3.36	The calculated band structure of $WP_2$ along high symmetry lines.	
	The yellow shaded regions indicate cuts where transitions by I	70
2 27	Weighted joint density of states (IDOS) for vertical $(a = 0)$ tran	12
5.57	sitions between electronic states within $\pm 70$ meV of the chemical	
	notential	72
3.38	Imaginary (i-iii) and real (iv-vi) parts of the complex dielectric	
	function along the $a$ (i,iv), $b$ (ii,v), and $c$ (iii,vi) crystallographic	
	directions at T= 298 K. The vertical dotted line is drawn at $\hbar\omega$ =	
	2.33  eV, which is the energy of the laser used in our experiments.	82
3.39	Index of refraction along $a$ (i), $b$ (ii), and $c$ (iii) crystallographic	
	directions at $T = 298$ K. The vertical dotted line is drawn at $\hbar \omega =$	
0.40	2.33 eV., which is the energy of the laser used in our experiments.	82
3.40	The calculated phonon dispersion of $WP_2$ with the correction	
	to the imaginary part of the phonon self-energy due to phonon-	<b>Q</b> 1
2 /1	A zoomed in view of the phonon electron coupling strength for	04
0.41	small <i>a</i> near $\Gamma$ Only the optical modes have the coupling strength for	
	projected onto them.	85
3.42	The phonon density of states (DOS) of $WP_2$ calculated from first	
	principles.	86
4.1	Temperature dependent Raman spectra of NbAs in the XX po-	
	larization configuration from 5 to 300 K	92
4.2	NbAs XX spectra at 5 K	93
4.3	Left: Fitting to the $B_1$ modes by symmetric Voigt profiles. Right:	
	Fit to the same data but using asymmetric Fano profiles	94
4.4	Normalized $\chi^2$ fitting metric showing a quantitative improvement	~ (
	in the fit by using the Fano over the Voigt profiles	94
4.5	Temperature dependence of the Fano asymmetry parameters in	05
16	NDAS	95
4.0	ization configuration from 10 to 300 K	97

4.7	Fano asymmetry parameters $1/q$ vs temperature for the TaAs $B_1$ modes. The values obtained from these fits were computationally zero for all temperatures indicating the lack of any asymmetry in
	the lineshapes
4.8	Temperature dependent linewidths of the $A_1$ phonon mode in (a) NbAs and (b) TaAs. The solid blue lines are fits to the data using
	a model of optical phonon decay into electron-hole pairs 99
4.9	Left: Raman spectra of NbAs with light incident along the $a$ - axis, in the ZZ configuration. Right: The same surface but in cross-polarized configuration (ZX) 102
4.10	The $A_1$ phonon linewidth in NbAs as measured on an <i>ab</i> -surface (XX) and an <i>ac</i> -surface (ZZ). Both the magnitude and dependence
4.11	on temperature vary significantly between the two measurements. 105 Correction to the imaginary part of the phonon self-energy due to the electron-phonon interaction at room temperature projected onto the phonon dispersions of (a) NbAs and (b) TaAs. For both materials, there is a notable increase in self-energy along $\Lambda$ ( $\Gamma \rightarrow$ Z) and $\Delta$ ( $\Gamma \rightarrow$ X). The overall calculated self-energy is less for TaAs than NbAs, but similar wave vectors show enhanced phonon
4.12	self-energy in both materials
4.13	lines from $I$ -X and $I$ -Z
4.14	mode of NbAs
4.15	mode of NbAs
4.16	Temperature dependence of the energy for the $A_1$ mode of NbAs measured in the ZZ polarization configuration
4.17	Temperature dependence of the energy and linewidth for the $E(1)$ meda of NbAg
4.18	Temperature dependence of the energy and linewidth for the $E(2)$ mode of NbAs 112
4.19	Temperature dependence of the energy and linewidth for the $E(3)$ mode of NbAs 113
4.20	Temperature dependence of the energy and linewidth for the de- fect mode (D) in NbAs

4.21	Temperature dependence of the energy and linewidth for the $B_1(1)$ mode of TaAs
4.22	Temperature dependence of the energy and linewidth for the $B_1(2)$ mode of TaAs
4.23	Temperature dependence of the energy for the $A_1$ mode of TaAs 115
5.1	The $CO_2$ laser secured to the optical table using the custom machined mount 122
59	The quarter wave plate (OWP) mounted in our custom made
0.2	holder attached to the motorized rotation mount from Standa 130
5.3	A screenshot of the LabVIEW VI used to control the rotation mount with the OWP 131
54	MCT scan of an FTS device 133
5.5	The reflectance and power recorded by the mercury-cadmium-
0.0	telluride (MCT) and power meter respectively. The simultaneous peaks in the power and reflectance indicate OWP angles where
	left circularly polarized light was produced 135
5.6	Front panel of the LabVIEW VI for controlling the motorized
0.0	XYZ stages
5.7	Diagram showing the method by which the visible alignment laser
	and the infrared laser are aligned together. The visible laser is first
	aligned through the two apertures, the flipper mirror for it moved
	out of the path, and then the infrared laser aligned through the
	same two apertures
5.8	Photovoltage recorded as the laser was scanned over a large TaAs
	sample. The two peaks of opposite sign from the photo-thermoelectric
	effect (PTE) are clearly visible
5.9	Example polarization dependent photocurrent measurement from
	a TaAs device. Both two- and four-fold variations in the response
	are observed. The magenta line is a fit using Eq. 5.13
6.1	A schematic of the photocurrent measurement system used to
	investigate the nonlinear response of TaAs
6.2	The conventional unit cell of TaAs
6.3	Diagram of the photo-thermoelectric effect
6.4	(Left) The simulated spatial dependence of the PTE response
	when measured along two contacts. Asymmetry in the response
	can result from purely geometric effects. (Right) The measured
	spatial dependence of photocurrent measured from a TaAs device.
	The asymmetry here results from a combination of geometric ef-
	fects and additional nonlinear photocurrent generation mechanisms. 160
6.5	Resistive losses for generated photocurrent may occur if the con-
	tact separation is much larger than the spot size and the thickness
	is much larger than the penetation depth of the light

False colored SEM image of a microcopic TaAs (purple) device with Au (yellow) contacts. The device is approximately three times thicker than the penetration depth of the light used ( $\approx 750$ nm)
A Diagram of the device showing the axis along which the cur- rent is being measured. <b>B</b> , <b>C</b> , <b>D</b> Upper panel: SEM image of the device being measured and its crystal orientation. Middle/Lower panels: black dots show the measured photocurrents with the solid magnenta lines representing fits to the data using Eq. 6.22. The
crystal axis is labeled in each panel. The inset of each panel shows the relative magnitude of the $L_S$ and $L_C$ fitting terms
The reflectance and power recorded by the MCT and power meter respectively. The concurrent peaks in the power and reflectance indicate QWP angles where left circularly polarized light was pro-
duced
Power dependence of the $D, L_S$ , and $L_C$ terms from fitting. All are found to be linear
Representative current vs voltage measurements from a TaAs with (red) and without (black) laser illumination.
The first Brillouin zone (BZ) of TaAs showing the calculated Fermi surface (FS) at charge neutrality 175
The Fermi pockets of TaAs near one nearly nodal ring. The red electron and hole pockets enclose the W1 and W2 Wevl nodes.
while the grav hole pockets (H) are topologically trivial 175
The momentum space surface formed by the direct energy gap of
117 meV
Calculated values of $\sigma_{aac}^{(2)}$ as a function of doping level and incident photon energy. The dashed line indicates the energy of the laser
used in our experiments
Hall conductivity data in black with the red line showing the fit by a two-band model 178
Experimentally measured and calculated Glass coefficients for var- ious materials. Our reported Glass coefficient for TaAs is shown as a blue square in a longer wavelength range than any previously reported value, and with larger magnitude

# LIST OF TABLES

# <u>Table</u>

1.1	Character table for the $C_{2v}$ point group, equivalence representa-
	tion $\Gamma_{\text{equiv}}$ , vector representation $\Gamma_{\text{vec}}$ , and the decomposition of
	their direct product
3.1	Irreducible representations and mode energies identified from ex-
	periment. Experimental energies ( $\omega_{\text{expt.}}$ ) are compared to pre-
	dicted values $(\omega_{\text{DFT}})$ from theory. All quantities are in meV 57
3.2	Results of fitting $WP_2$ phonon energies with the extended Kle-
	mens' model
3.3	Results of fitting $WP_2$ phonon linewidths with the extended Kle-
	mens' model
3.4	Results of fitting $WP_2$ phonon linewidths with the electron-hole
	decay model, $\Gamma(T) = \Gamma_0 + F(n_F(\omega_a, T) - n_F(\omega_a + \omega_{ph}, T))$ 71
3.5	Wave vector selection rules
3.6	Character table of full group representations for $\Gamma$ , $\Sigma$ , and direct
	products of irreducible representations from $\Sigma$
3.7	Direct product decompositions
3.8	Direct product decompositions with general $k$ -points
4.1	Anharmonic coefficients obtained from fitting the NbAs energy
	and linewidth data with the extended Klemens' model 116
4.2	Anharmonic coefficients obtained from fitting the TaAs energy
	and linewidth data with the extended Klemens' model 116
6.1	Results of fitting the photocurrent data in Figure 6.7
6.2	The calculated room-temperature shift-current response tensor at
	various values of the chemical potential, including charge neutral-
	ity (chemical potential $\mu = 0$ meV), electron doping $\mu = 10$ meV,
	and hole doping $\mu = -10$ meV

## LIST OF ABBREVIATIONS

${\bf ARPES}$ angle resolved photoemission spectroscopy
${\bf BPVE}$ bulk photovoltaic effect
<b>BS</b> beam splitter
<b>BZ</b> Brillouin zone
${\bf CPGE}$ circular photogalvanic effect
$\mathbf{CW}$ continuous wave
${\bf DFT}$ density-functional theory
<b>DOS</b> density of states
<b>FIB</b> focused-ion-beam
$\mathbf{FS}$ Fermi surface
${\bf FWHM}$ full-width at half-maximum
<b>HWP</b> half-wave plate
<b>IR</b> infrared
$\mathbf{JDOS}$ joint-density of states
$\mathbf{LPGE}$ linear photogalvanic effect
$\mathbf{MBE}$ molecular beam epitaxy
MCT mercury-cadmium-telluride
MIR mid-infrared
$\mathbf{MRM}$ multi-reflection model
<b>PTE</b> photo-thermoelectric effect

 $\mathbf{PVIC}$  photo-voltage-current-conductivity

 ${\bf PWM}\,$  pulse width modulation

 $\mathbf{QCL}\,$  quantum cascade laser

 $\mathbf{QL}\,$  quintuple layer

 $\mathbf{QWP}\xspace$  quarter-wave plate

 $\mathbf{RHEED}$  reflection high-energy electron diffraction

 ${\bf SHG}$  second-harmonic generation

 ${\bf STO}\,$  strontium titanate

**SEM** scanning electron microscope

 $\mathbf{TI}$  topological insulator

 $\mathbf{TSM}$  topological semimetal

 $\mathbf{WSM}$  Weyl semimetal

### ACKNOWLEDGEMENTS

I would first of all like to extend my deepest gratitude to my advisor, Professor Kenneth S. Burch. Thank you for giving me the opportunity to work alongside you for all of these years, for your patience, and for helping me become a better scientist and stronger communicator. I could not have done this without you.

I would also like to thank the professors who graciously served on my dissertation committee, Professor Ilija Zeljkovic, Professor David Broido, and Professor Fazel F. Tafti. During my time here each of you have been giving with your time, receptive to questions, and valuable role models.

I would be remiss if I did not thank my parents, Lori and Jerry, and my brother Logan, for their unending love and support. I have never once doubted that I could fail to achieve something I had set my mind to accomplishing and this is in no doubt due to the unfaltering belief in me that you have shown for as long as I can remember.

I would like to thank Matthew Gochan for recommending that I apply to the graduate program here at Boston College. Along the same line, I would like to thank Professor Rein Uritam and the graduate committee for seeing potential in me and accepting me into the Boston College physics department.

Thank you to all of the other members of the Burch Lab that I have had the pleasure of working with over the years – Vincent M. Plisson, Yiping Wang, Erin Sheridan, Amanda Denis, Yao Tian, and Marcel Hoek. In particular I thank Mason J. Gray for the many hours of helpful discussion, laughter, and graduate student therapy. Among the Boston College physics graduate students at large I would like to thank in particular Yitzi Calm, Bryan Rachmilowitz, Victoria Gabriele, and, of course, Faranak Bahrami.

I have been lucky enough to have worked with and mentored several talented undergraduate students during my time at Boston College. There were many occasions where you posed questions that forced me to reevaluate my own perceived understanding of a topic or to distill a seemingly complicated concept down to its simpler core. So to Ryan Conrad, Kai Kharpertian, Tiffany (Chun An) Wang, and Marisa Romanelli: thank you for being driven, for being curious, for asking insightful questions, and for helping me become a (hopefully) better mentor.

I am grateful to the many collaborators I have worked with during my PhD. In particular I thank Ni Ni and Bing Shen for providing us with many high quality crystal samples, Philip J.W. Moll and his group for making wonderful devices for us, and Christina A.C. Garcia, Yaxian Wang and Professor Prineha Narang at Harvard for their excellent computational work.

I extend my thanks to the administrative staff of the Boston College physics department. Scott Bortolotto, Nancy Chevry, Jane Carter, and (formerly) Sile Ni Scanlain – this department would not function without you.

I thank Paul Dee, formerly in the machine shop, for machining numerous small parts without which many of my experiments would have been impossible.

From my time at Binghamton University I would like to thank Darshana L. Weerawrane, for showing me what it means to be a dedicated researcher and for your general kindness, Professor Bonggu Shim for allowing me to work in your lab and gain experience which proved to be invaluable in my time at Boston College, and Professor Stephen L. Levy for your guidance and support.

Lastly I would like to thank all of my friends who have been supportive over the last few years. In particular I would like to thank David S. McDonald, Benjamin Young, Trevor Crandell, Spencer Crandell, Ruoxi Zhang, Tonic, JoJo, Gin, and Olive.

### CHAPTER I

### Introduction

The profound role of symmetry in the study of physics can hardly be overstated. From Noether's theorem relating the presence of continuous symmetries to conservation laws[1, 2], to the Landau theory of phase transitions[3, 4], the symmetries of a system, and often their breaking, are crucial in understanding its properties and behavior. Yet for all the successes of symmetry in describing physical media and their phases, in the 1980s evidence began emerging that certain phenomena could not be explained on the basis of symmetry alone. After many pioneering theoretical works the picture that instead emerged was that it was the *topology* of the electronic wave functions that was crucial to describing these phenomena. Today, the combination of both symmetry and topology yields a richer and more complete understanding of materials than ever before. In this dissertation we present research into the physics of topological materials utilizing techniques that are deeply influenced by the underlying material symmetries.

### 1.1 Scope of this Dissertation

The works described in this dissertation are broken up into two main parts. The first part is primarily concerned with the use of Raman spectroscopy as a probe of phonons and phonon-electron coupling in different topological materials. Chapter II addresses Raman spectra from thin film heterostructures of the topological insulator  $Bi_2Se_3$  and the magnetic semiconductor EuS. By investigating the paramagnetic Raman signal in films with different compositions of EuS and  $Bi_2Se_3$ we provide indirect evidence of charge transfer between the two layers. We also track the evolution of phonon energies with varying film thicknesses on multiple substrates which provides insight into the interfacial strain between layers.

Chapters III and IV present temperature dependent Raman investigations of the the Weyl semimetals  $WP_2$ , NbAs, and TaAs. Measurements of the optical phonon linewidths are used to investigate the available phonon decay paths, with ab-initio calculations and group theory used to aid the interpretation of these results. We find that some phonons display linewidths indicative of dominant decay into electron-hole pairs near the Fermi surface, rather than decay into acoustic phonons. In light of these results we discuss the role of phonon-electron coupling in the transport properties of these Weyl semimetals.

The second part of the dissertation is broken into two chapters. The first, Chapter V, addresses the construction of the Photo-Voltage-Current-Conductivity or "PVIC" setup for the measurement of nonlinear photocurrents. We discuss the experimental capabilities that the system was designed to possess, the operating principles behind key components of the system, and give examples of the operating procedures for using the setup. The penultimate chapter, Chapter VI, presents the results of photocurrent measurements using this setup on the Weyl semimetal TaAs. Through careful analysis of the photocurrent polarization dependence, we identify a colossal bulk photovoltaic effect in this material which exceeds the response displayed by previously studied materials by an order of magnitude. Calculations of the second-order optical conductivity tensor show that this result is consistent with the divergent Berry connection of the Weyl nodes in TaAs.

We conclude the dissertation in Chapter VII with a summary of the main

results from each preceding chapter, and give suggestions for future experiments that further investigate these topics.

The rest of this introduction chapter will review pertinent background material. We introduce some key concepts about topological materials, Raman spectroscopy, and nonlinear photocurrents. Since symmetry and group theory feature heavily in many of the phenomena we investigate, we dedicate a fair amount of discussion to these topics. References to many invaluable resources are given, which the interested reader may pursue for more comprehensive treatments of that material.

### **1.2** The Berry Phase and Topological Materials

One of the earliest and perhaps the most well-known example of an application of topological concepts in condensed matter physics was the discovery of the integer quantum Hall effect exactly 40 years ago[5]. The quantized plateaus of the Hall conductance can be shown to be multiples of the quantum of conductance,  $e^2/h$ , and an integer topological invariant  $C_n$  called the Chern number[6–9]:

$$\sigma_{xy} = \frac{e^2}{h} C_n \tag{1.1}$$

The Chern number here is an example of what is known as a geometric or Berry phase. Named for Sir Michael Berry, who introduced and developed the concept in his seminal 1984 work[10], the Berry phase is an additional, gauge-invariant phase factor acquired by a quantum mechanical system when it adiabatically evolves through a cyclical process. The Berry phase may be expressed as[10, 11]:

$$\gamma_n = i \oint_C \langle n(\mathbf{R}) | \nabla_{\mathbf{R}} | n(\mathbf{R}) \rangle \cdot d\mathbf{R}$$
(1.2)

where  $\gamma_n$  is the Berry phase,  $|n(\mathbf{R})\rangle$  is the wave function which is parameterized by  $\mathbf{R}$ , and C is a closed loop in the parameter space ( $\mathbf{R}$  is a generalized parameter which need not be spatial). A gauge-dependent vector potential known as the Berry connection may be defined as  $\mathbf{A}_n(\mathbf{R}) \equiv i \langle n(\mathbf{R}) | \nabla_{\mathbf{R}} | n(\mathbf{R}) \rangle$ . In terms of the Berry connection we may write:

$$\gamma_n = i \oint_C \mathbf{A}(\mathbf{R}) \cdot d\mathbf{R} \tag{1.3}$$

If we consider the Berry phase as being analogous to a magnetic flux, then the Berry connection is analogous to the electromagnetic vector potential  $\mathbf{A}(\mathbf{r})$ . The path integral in Eq. 1.3 then resembles Gauss' law for magnetic fields, though written for the vector potential. This analogy can be extended further by considering the curl of the Berry connection, known as the Berry curvature,  $\mathbf{\Omega}_n(\mathbf{R}) \equiv \nabla_{\mathbf{R}} \times \mathbf{A}_n(\mathbf{R})$ . Using Stokes's theorem the Berry phase may then be rewritten as a surface integral:

$$\gamma_n = \int\limits_{S} \mathbf{\Omega}_n(\mathbf{R}) \cdot d\mathbf{R} \tag{1.4}$$

The Berry curvature is thus analogous to the magnetic field.

In the setting of crystalline solids we can identify the lattice momentum  $\mathbf{k}$  as our parameter, with the BZ serving as the parameter space[11]. The wave functions and their associated energy bands will therefore be the familiar Bloch wave functions[12]. An alternate form for the Berry curvature proves useful in these contexts:

$$\mathbf{\Omega}_{n}(\mathbf{k}) = -\mathrm{Im} \sum_{n' \neq n} \frac{\langle n(\mathbf{k}) | \nabla_{\mathbf{k}} H | n'(\mathbf{k}) \rangle \times \langle n'(\mathbf{k}) | \nabla_{\mathbf{k}} H | n(\mathbf{k}) \rangle}{(E_{n} - E_{n'})^{2}}$$
(1.5)

The denominator of this expression goes to zero when the energy gap between two bands vanishes, causing a divergence in the Berry curvature. We may thus identify such band crossings as monopoles of the Berry curvature[11]. Precisely at these points the wave functions of the two crossing bands are not well-defined, as can be seen in soluble models such as the Su-Schrieffer-Heeger model[13]. The comprehensive identification and topological classification of band crossings is a matter beyond the scope of this dissertation[14]. We will limit our discussion to two classes of topological materials: Weyl semimetals and topological insulators.

#### 1.2.1 Weyl Semimetals

Weyl semimetal (WSM) are a recently realized class of topological materials which, in the ideal case, have low energy excitations that behave like relativistic Weyl fermions[15]. These fermions are solutions to a massless version of the Dirac equation:

$$i\hbar\gamma^{\mu}\partial_{\mu}\psi = 0 \tag{1.6}$$

(where  $\gamma^{\mu}$  are the Dirac matrices) which was originally considered by Hermann Weyl in 1929[16]. In addition to being massless, Weyl fermions have a definite chirality, meaning that the spin and momentum are locked parallel or anti-parallel to one another[15, 17]. Weyl fermions are thus said to come in one of two types: right- or left-handed, depending on the relative direction between the spin and momentum. In their condensed matter realization, Weyl fermions exist as quasi-particle excitations in the vicinity of so-called Weyl nodes[18], which are band crossings with linear dispersions in three-dimensions that act as monopoles of Berry curvature. We now consider what specific material properties are required to produce a WSM.

A well-known theorem from Neumann and Wigner states that energy crossings between bands of the same symmetry are generally forbidden[19]. "Avoided crossings," as they are known, result from interactions between the two bands which lift the degeneracy and produce a band gap. However, as shown by Herring in 1937[20], band degeneracies unrelated to specific symmetries may occur in systems of three or higher spatial dimensions. Is it these "accidental" crossings that can give rise to Weyl nodes.

As noted above, these band crossings act as monopoles of the Berry curvature. The transformation properties of the Berry curvature under two fundamental symmetries: time-reversal and inversion, will determine whether a material can support the existence of Weyl nodes. Under time-reversal symmetry the Berry curvature transforms as[11]:

$$\mathbf{\Omega}_n(\mathbf{k}) = -\mathbf{\Omega}_n(-\mathbf{k}) \tag{1.7}$$

while under inversion symmetry it transforms as:

$$\mathbf{\Omega}_n(\mathbf{k}) = \mathbf{\Omega}_n(-\mathbf{k}) \tag{1.8}$$

It is clear from these relations that if a material possesses both time-reversal and inversion symmetry that the Berry curvature will be zero throughout the entire BZ. To support a non-zero Berry curvature a material must therefore break either time-reversal or inversion symmetries. In addition to this, the fermion doubling theorem of Nielsen and Ninomiya states that Weyl nodes must come in pairs of opposite chirality[17, 21, 22]. In other words, the number of sources and sinks of Berry curvature in the BZ must be the same. If a material system breaks time reversal symmetry, we thus find that the minimum possible number of Weyl nodes will be two: one left and one right chiral node. On the other hand, if a material breaks inversion symmetry we find that the minimum number of nodes must be four.

In the vicinity of the Weyl node the dispersion relation may be obtained from

the Hamiltonian in Eq. 1.6:

$$E_n = \pm \hbar v_F \mathbf{k} \cdot \boldsymbol{\sigma} \tag{1.9}$$

where  $v_F$  is the Fermi velocity and  $\sigma$  are the Pauli spin matrices. The dispersion is linear in momentum in all three-directions, with the spin polarized parallel or anti-parallel to the momentum. In the ideal case, the Weyl nodes are located at the Fermi energy and there are no other topologically trivial bands coexisting at the Fermi energy. However, finding such materials presents a challenge[23], since many WSM have trivial bands that also cross the Fermi energy[24], or have Weyl nodes that are located far from the Fermi energy[25].

The family of compounds (Nb,Ta)(P,As) were the first theoretically predicted inversion symmetry breaking WSM[26] to be experimentally confirmed. Angle resolved photoemission spectroscopy measurements of the bulk and surface band structures revealed the presence of Weyl nodes and surface Fermi arcs[27–29], and transport measurements presented evidence for the chiral anomaly[30–32] (although debate arose whether the negative magnetoresistance taken as evidence for the chiral anomaly could have been due to non-topological effects such as current jetting[33]). Since 2015 numerous other WSM have been identified, and we refer the interested reader to review articles and the references within for more information[15, 23, 34].

We lastly discuss the distinction between type-I and type-II WSM. In a type-I WSM the constant energy cross section of the Weyl cone shrinks to a point as the energy is swept through the Weyl node. In contrast, for type-II WSM the constant energy surface does not become point-like at the energy of the Weyl node due to the intersection of the electron and hole pockets that form the node[35]. The Weyl cones of a type-II WSM are therefore tilted versions of type-I Weyl cones. In Chapter III we investigate the type-II WSM WP<sub>2</sub>.

#### **1.2.2** Topological Insulators

The class of materials known as topological insulators are characterized by an electrically insulating bulk, but conducting surface states [17, 36–38]. The insulating bulk of a topological insulator (TI) has a non-zero  $\mathbb{Z}_2$  topological index [39–41] which distinguishes it from a topologically trivial insulating state such as vacuum or air. In the same way that a sphere cannot be smoothly deformed into a torus because they are topologically distinct, the bulk band structure of a topological insulator cannot smoothly deform into that of vacuum or air. At the boundary between the TI and the trivial insulator (i.e. the surface of the TI) we therefore find linearly dispersing, gapless surface states which form a two-dimensional Dirac cone [36].

The surface states may be described by the Hamiltonian [17]:

$$H(\mathbf{k}) = \begin{pmatrix} \hbar v_F \mathbf{k} \cdot \boldsymbol{\sigma} & 0\\ 0 & -\hbar v_F \mathbf{k} \cdot \boldsymbol{\sigma} \end{pmatrix}$$
(1.10)

where  $\mathbf{k} = (k_x, k_y)$  and  $\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$  (this Hamiltonian is four-dimensional). The spins of the electrons are polarized perpendicular to the momentum[42, 43], with the handedness determined by the specific crystal surface. These surface states are protected by time-reversal symmetry[41] and breaking this symmetry can lift the degeneracy at the Dirac node[44]. This corresponds to having introduced a mass term proportional to the  $\sigma_z$  Pauli matrix in the above Hamiltonian.

The first 3D topological insulator to be experimentally identified was  $Bi_{1-x}Sb_x$ in 2008[42]. Not long after this initial discovery the so-called "second generation" of topological insulators were realized in the  $(Sb,Bi)_2(Se,Te)_3$  family of materials[45–47]. The  $Bi_2Se_3$  family in particular are layered van der Waals materials which allows exfoliation down to single atomic layers. High quality thin films can also be grown by molecular beam epitaxy (MBE) which has allowed for the creation of high quality heterostructures between TIs and other materials. One notable such example are heterostructures of ferromagnetic materials and TIs. The interfacial magnetic field produced by the magnetic material can break time-reversal symmetry at the surface of the TI, opening a gap and leading to e.g. the quantum anomalous Hall effect[48, 49].

### **1.3** Crystal Symmetry: Point and Space Groups

Group theory is a powerful mathematical tool which has many applications in the study of crystalline solids [50–52]. The groups most often discussed in this context are the point group and space group of a crystal. The space group of a crystal has as its elements the infinite group of translation operations, the finite group of rotation elements (here "rotation" also includes improper rotations such as mirror planes or roto-inversions) that are allowed by the translation symmetry of the crystal lattice, and all combinations of these allowed translation and rotation operations [53]. The point group, by contrast, consists solely of the allowed rotation elements. Unlike the group of translation operations, which is always a normal subgroup of the space group, the point group in general is not a normal subgroup of the space group. If it is the case that the point group is a normal subgroup of the space group, then the space group is said to be *symmorphic*. On the other hand, if the point group is not a normal subgroup, then the space group is said to be *non*symmorphic. In less abstract terms, a symmorphic space group is one in which none of the point group operations involve an accompanying lattice translation, while in a non-symmorphic space group at least one point group element requires a simultaneous lattice translation (e.g. a screw-axis or a glide plane).

Of considerable import to us will be the characters of the irreducible representations associated with each of these groups. The character of an irreducible representation is the trace of the matrix of that representation[51]. The translation group has as its irreducible representations the one-dimensional matrices:  $\exp(i\mathbf{k} \cdot \mathbf{R}_L)$ , where  $\mathbf{k}$  is a wave vector and  $\mathbf{R}_L$  is a lattice translation vector[53]. Since these representations are one-dimensional the characters are simply these same phase factors. For the point groups, character tables for the irreducible representations may be found in numerous references, and where necessary we will reproduce these tables such as in Section 1.4.2 below. The characters of space group representations are more cumbersome to evaluate, and due to the infinite number of translation elements it is not feasible to enumerate them. We will make use of the characters for full group representations of the space group in Chapters III and IV, with more details concerning their derivation given in Chapter III.

In Chapter VI we will also use group theory to identify the non-zero elements of response tensors. Neumann's Principle states that: "the symmetry of a physical property of a crystal must include the same spatial symmetry characteristics as the crystal structure and thus the symmetry of the matter tensor must include all of the symmetry operations contained in the point group of the crystal."[50] Mathematically this may be expressed through the relation:

$$\sigma'_{ij} = R_{ik} R_{jl} \sigma_{kl} \tag{1.11}$$

where  $\sigma_{kl}$  is the k and lth element of the original tensor  $\boldsymbol{\sigma}$ ,  $\sigma'_{ij}$  is the *i* and *j*th element of the transformed tensor  $\boldsymbol{\sigma}'$ , and  $R_{ik}$  are the elements of the matrix **R** representing a symmetry operation. If the symmetry operation **R** belongs to the point group of the crystal, then the elements of  $\boldsymbol{\sigma}'$  must be identical to those from  $\boldsymbol{\sigma}[50]$ . The relation above is valid for second-rank tensors, and similar relations may be readily derived for tensors of higher rank.

### 1.4 Raman Scattering

The inelastic scattering of light was first experimentally observed in 1928 by Sir C.V. Raman[54], a discovery for which he was awarded the 1930 Nobel Prize in Physics. In the following decades, and in particular after the advent of laser technology, Raman scattering (as it became known) developed into a canonical spectroscopic technique for the study of condensed matter systems. In this section we will introduce some of the fundamental concepts necessary for an understanding of the Raman spectra and results presented in the first few chapters of this dissertation. More specific background material will be provided where needed in the individual chapters.



Figure 1.1: Feynman diagram showing a typical Raman scattering process. A photon of energy  $\hbar\omega_i$  is absorbed, creating an electron-hole pair. The electron then emits a phonon of energy  $\hbar\omega$  before recombining with the hole and emitting a photon of energy  $\hbar\omega_o = \hbar\omega_i - \hbar\omega$ .

The Feynman diagram for a typical Raman scattering process is shown in Figure 1.1. A photon of energy  $\hbar \omega_i$  is first absorbed by an electron in the material which creates an electron-hole pair. This may occur through excitation into real or virtual electronic states, with the former potentially leading to resonant excitation via judicious choice of excitation energy[55]. The electron (or hole) then interacts with the lattice and creates a phonon of energy  $\hbar \omega$  and momentum **q**. Though not the focus of this dissertation, the excitation of magnons, excitons, and other discrete or continuous lattice excitations are also possible via Raman scattering[56– 59]. The electron and hole then recombine and emit a photon of energy  $\hbar \omega_o$   $\hbar\omega_i - \hbar\omega$ , which is often referred to as the Raman scattered light[55]. Scattering of light at longer wavelengths (lower energy) than the incident radiation is known as Stokes scattering. The reverse process where a phonon is instead absorbed leading to shorter wavelength (higher energy) scattered light is known as anti-Stokes scattering. Because anti-Stokes scattering requires the absorption of a phonon, anti-Stokes spectral features will vanish below temperatures at which there is a population of the corresponding optical phonons. Stokes scattering by contrast results in the creation of a phonon and so may be observed at any temperature. This distinction is often captured in the ratio of Stokes to anti-Stokes scattering intensity:

$$\frac{I_S}{I_{AS}} \propto \frac{n_B(\omega, T) + 1}{n_B(\omega, T)} = e^{\hbar\omega/k_B T}$$
(1.12)

where  $n_B(\omega, T)$  is the Bose-Einstein distribution function. The proportionality factor may be made into an equivalence by accounting for the distinct frequencies of the scattered light[60].

Because Raman scattering is a higher order process, the great majority of photons will not be inelastically scattered by the medium[55]. To experimentally detect the Raman scattered radiation one must generally filter out light of the original wavelength by orders of magnitude. The remaining light is dispersed by, e.g., a diffraction grating and collected by a CCD[61], with the resulting spectra plotted as CCD counts as a function of wavenumbers (cm<sup>-1</sup>) or energy (meV). Singlephonon features appear as peaks at the  $\Gamma$  point energy of the optical phonon. Two-phonon[62], electronic Raman[58], or numerous other mechanisms may also produce spectral features, although we will not discuss such topics here.

The intensity of Raman scattered light follows the well-known relation [55]:

$$I_R \propto |\hat{\mathbf{e}}_o \cdot \mathbf{R} \cdot \hat{\mathbf{e}}_i|^2 \tag{1.13}$$

where  $\hat{\mathbf{e}}_i(\hat{\mathbf{e}}_o)$  is the polarization vector of the incident (scattered) light and  $\mathbf{R}$  is the Raman tensor. The elements of the Raman tensor will depend upon the irreducible representation of the specific mode and may also be predicted by group theory[55, 63]. Through the dependence on the polarization of both the incident and scattered light, the polarization selection rules may be established for a given mode. These selection rules may be used to identify the representation of an unknown mode, a process which we will go through in some detail in Chapter III. A common notation which we will use to denote the polarization configuration of our measurements is "Porto's notation" [64]. In this notation one writes:

$$\mathbf{k}_i(\hat{\mathbf{e}}_i\hat{\mathbf{e}}_s)\mathbf{k}_s \tag{1.14}$$

where  $\mathbf{k}_i(\mathbf{k}_s)$  is the direction of propagation of the incident (scattered) light, and  $\hat{\mathbf{e}}_i$  and  $\hat{\mathbf{e}}_s$  are the direction of the polarization vector as defined above. All of our measurements were carried out in the back scattering geometry such that  $\mathbf{k}_s = -\mathbf{k}_i$ . We therefore will often omit the  $\mathbf{k}$  and simply write, for example, XX or XY, to denote the polarization of the incident and scattered electric fields.

#### 1.4.1 Phonon Lineshapes

The most common lineshape for a phonon to display in Raman spectra is the Lorentzian profile. This function takes the form[65]:

$$L(\omega;\omega_0,\Gamma,A) = \frac{2A\Gamma}{\pi(4(\omega-\omega_0)^2+\Gamma^2)}$$
(1.15)

where  $\omega_0$  is the line center,  $\Gamma$  is the full-width at half-maximum (FWHM), and A is the amplitude of the mode. To account for instrument induced broadening of this Lorentzian profile[65–67] we will use the related Voigt function in the actual fitting of our spectra. A Voigt profile is the convolution of the above Lorentzian profile with a Gaussian profile which accounts for the instrument induced broadening[65–67]:

$$V(\omega) = \int_{-\infty}^{\infty} L(\omega')G(\omega' - \omega)d\omega'$$
  
=  $A \frac{4\sqrt{\ln 2}}{\pi^{3/2}\Gamma_G} \int_{-\infty}^{\infty} \frac{\Gamma_L}{4(\omega' - \omega_0)^2 + \Gamma_L^2} \exp\left[-\frac{4(\ln 2)(\omega - \omega')^2}{\Gamma_G^2}\right] d\omega'$  (1.16)

where  $\Gamma_L(\Gamma_G)$  is the linewidth of the Lorentzian (Gaussian). This convolution does not have an analytic expression, thus efficient algorithms for highly accurate numerical approximations are used instead[66].

The other well-known but less commonly observed lineshape is the Fano profile[68]. This asymmetric profile may occur when a discrete state (i.e. the phonon) interferes with a continuum of states (often electronic). The resulting profile has the form[65]:

$$F(\omega;\omega_0,\Gamma_L,A) = \frac{2A}{q^2\Gamma_L\pi} \left[\frac{(q+\epsilon)^2}{1+\epsilon^2} - 1\right], \qquad \epsilon \equiv \frac{2(\omega-\omega_0)}{\Gamma_L}$$
(1.17)

where q is known as the Fano asymmetry parameter and is defined as [68]:

$$q \equiv \frac{\langle \Phi | T | i \rangle}{\pi V_E^* \langle \psi_E | T | i \rangle} \tag{1.18}$$

Here  $V_E$  is the electron-phonon coupling strength (we have assumed coupling to an electronic continuum), T is the transition operator,  $|i\rangle$  is the ground state,  $\langle \Phi |$  is the discrete phonon state, and  $\langle \psi_E |$  is the electronic state. In the limit that  $q \to \pm \infty$  one recovers the symmetric Lorentzian profile. This function also may be convoluted with a Gaussian to obtain an expression that accounts for the instrumental broadening[65], though as with the case for the Lorentzian profile, there is no simple analytic expression.

#### 1.4.2 Group Theory and Mode Classification

The number of phonon branches in a solid may be calculated as 3N where N is the number of atoms in the primitive unit cell[12]. The irreducible representations of these phonon branches may then be identified through the use of group theory[51]. The first step in this process is to construct the equivalence representation,  $\Gamma_{\text{equiv}}$ , by identifying which atoms are either transformed back onto their original atomic site or into an equivalent site by each of the point group operations (only one operation from each distinct class actually needs to be considered). The direct product of  $\Gamma_{\text{equiv}}$  with the vector representation  $\Gamma_{\text{vec}}$  will then produce a reducible representation which, when decomposed, will yield the irreducible representations of the phonon branches at the  $\Gamma$  point in the BZ. We will explicitly work this out as an example for WP<sub>2</sub>, a material which we will return to in Chapter III.

WP<sub>2</sub> crystallizes in the space group  $Cmc2_1$  with point group  $C_{2v}$ . There are four symmetry operations and irreducible representations in this point group, whose character table is reproduced in Table 1.1. This table also lists the reducible representations  $\Gamma_{\text{equiv}}$ ,  $\Gamma_{\text{vec}}$ , their direct product, and their respective decomposition into irreducible components. As noted above, the characters of the equivalence representation  $\Gamma_{\text{equiv}}$  may be found by acting the point group symmetry elements on the crystal lattice. If after transformation by the symmetry element an atom returns to its specific atomic site or an equivalent atomic site it is assigned a one, and if it does not then it is assigned a zero. Summing over all the atoms in the unit cell then gives you the character of  $\Gamma_{\text{equiv}}$  for that symmetry element. Since there are six atoms in the WP<sub>2</sub> unit cell, we find a character of six for the identity operation. Under the  $C_2$  operation no atoms return to their atomic sites so we have a character of zero for this operation (the  $C_2$  operation is a combined rotation and translation operation within the space group so it is no surprise that when only considering the rotation aspect none of the atoms return to an equivalent atomic site). For the other combined rotation and translation operation, the glide plane  $\sigma_v(xz)$ , we also find a character of zero, while under the  $\sigma_v(yz)$  operation all of the atoms return to an equivalent site giving a character of six.

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A <sub>1</sub>	1	1	1	1	
A <sub>2</sub>	1	1	-1	-1	
B <sub>1</sub>	1	-1	1	-1	
$B_2$	1	-1	-1	1	
$\Gamma_{ m equiv}$	6	0	0	6	$3A_1 + 3B_2$
$\Gamma_{ m vec}$	3	-1	1	1	$A_1 + B_1 + B_2$
$\Gamma_{\rm equiv}\otimes\Gamma_{\rm vec}$	18	0	0	6	$6A_1 + 3A_2 + 3B_1 + 6B_2$

Table 1.1: Character table for the  $C_{2v}$  point group, equivalence representation  $\Gamma_{\text{equiv}}$ , vector representation  $\Gamma_{\text{vec}}$ , and the decomposition of their direct product.

The  $\Gamma_{\text{vec}}$  representation may be found by identifying which irreducible representations transform as the (x, y, z) components of a vector[51]. For the case of the  $C_{2v}$  point group these are the A<sub>1</sub>, B<sub>1</sub>, and B<sub>2</sub> irreducible representations. The direct product  $\Gamma_{\text{equiv}} \otimes \Gamma_{\text{vec}}$  may then be evaluated either through the direct multiplication of the corresponding characters, or through the use of product tables for their irreducible components. In the bottom right column of Table 1.1 we show the decomposition of this direct product, which corresponds to the symmetries of each phonon branch in WP<sub>2</sub>. There are a total of 18 total modes, three of which are acoustic and have the same representations as  $\Gamma_{\text{vec}}$ . The remaining 15 modes are optical and have the representations  $5A_1 + 3A_2 + 2B_1 + 5B_2$ . This calculation may be verified by use of the automated tools found on the Bilbao Crystallographic Server[63].

The machinery of group theory may also be used to evaluate the selection rules for various scattering processes within a material[53]. These calculations are much more involved than those detailed above for the identification of phonon
mode symmetries, so we leave the relevant details to Chapter III.

#### 1.4.3 Anharmonicity and Phonon Decay

A well-known failure of the harmonic approximation is that readily observed physical properties, such as the expansion of a solid with increasing temperature, are unable to be explained[12]. The resolution to this problem lies in the incorporation of anharmonic effects into the theory. Third- and fourth-order anharmonic terms may be treated perturbatively or through the use of many-body techniques[69]. We will not explicitly discuss such theory here, choosing instead to focus on the experimentally observed consequences of anharmonicity and the models used in the analysis of these results.

The energy of a phonon will typically decrease as the temperature is raised due to both anharmonic renormalization and lattice expansion[70, 71]. At temperatures below  $\sim T_D/3$  ( $T_D$  is the Debye temperature) the phonon energy becomes independent of temperature[72], while above this temperature the decrease in energy is often found to be linear with temperature. If fourth-order anharmonic terms are significant then this decrease may become quadratic. In contrast to the energy, the linewidth of a phonon will generally increase with rising temperatures. In further contrast, the linewidth is independent of the effects of lattice expansion[70] and is solely related to the phonon-phonon or phonon-electron decay paths available to the phonon mode. Third-order anharmonic interactions describe the decay of an optical phonon into two acoustic/optic phonons, while fourth-order anharmonic interactions capture the decay into trios of acoustic/optic phonons. Energy and momentum conservation must be satisfied in such decay processes, and since Raman probes approximately zone center phonons, this will result in pairs of acoustic phonons with  $\mathbf{q}' = -\mathbf{q}'$  for the case of three interacting phonons.

The model most often used to describe these behaviors is known as the Kle-

mens' model[73], with its generalization to fourth-order effects known as the extended Klemens' model[70]. These models make some simplifying assumptions about the pairs and trios of acoustic/optic phonons involved in the optical phonon decay. For the lowest order term describing an optical phonon of energy  $\omega_0$  and momentum  $\mathbf{q} \approx 0$  into two acoustic/optic phonons with momenta  $\mathbf{q}' = -\mathbf{q}'$ , the energy of the resulting phonons is assumed to be  $\omega_0/2$ . Similarly, for the decay into trios of acoustic/optic phonons the resulting phonon energies are each assumed to be  $\omega_0/3$ . These assumptions simplify the expressions predicted to govern the temperature dependence of phonon linewidths and energies[70]:

$$\Gamma(T) = \Gamma_0 + A \left(1 + 2n_B(\omega_0/2, T)\right) + B \left(1 + 3n_B(\omega_0/3, T) + 3(n_B(\omega_0/3, T))^2\right)$$
(1.19)  
$$\omega(T) = \omega_0 + C \left(1 + 2n_B(\omega_0/2, T)\right) + D \left(1 + 3n_B(\omega_0/3, T) + 3(n_B(\omega_0/3, T))^2\right)$$
(1.20)

In Eq. 1.19 the coefficients A and B capture the strength of the three- and fourphonon processes respectively. The  $\Gamma_0$  term is included to account for any temperature independent contribution that may arise from e.g. impurity or defect scattering. The C and D terms of Eq. 1.20 for the phonon energy have a similar interpretation as A and B, although the C term will also contain contributions from lattice expansion.  $\omega_0$  is the harmonic phonon energy.

### **1.5** Nonlinear Photocurrents

The material response to an applied stimulus is often assumed to be linear. A canonical example of this is Ohm's Law[12, 74]:

$$\mathbf{J} = \boldsymbol{\sigma} \mathbf{E} \tag{1.21}$$

where an applied electric field  $\mathbf{E}$  produces a current  $\mathbf{J}$  through the material tensor  $\boldsymbol{\sigma}$ . The single power of  $\mathbf{E}$  on the right-hand side of this equation signifies that this expression describes a linear order response. However, this is not the only order response that is possible. This was made experimentally apparent in 1961 almost immediately after the invention of the laser when second-harmonic generation (SHG) was first observed[75]. To describe such effects, the response is expanded as a power series in the electric field[76]:

$$\mathbf{J} = \boldsymbol{\sigma}^{(1)}\mathbf{E} + \boldsymbol{\sigma}^{(2)}\mathbf{E}\mathbf{E} + \boldsymbol{\sigma}^{(3)}\mathbf{E}\mathbf{E}\mathbf{E} + \cdots$$
(1.22)

where  $\boldsymbol{\sigma}^{(n)}$  is the *n*th-order conductivity tensor and will be a tensor of rank n+1. In this dissertation we will limit our focus to second-order effects arising from two powers of the electric field.

Second-order nonlinear effects require broken inversion symmetry for their expression[76]. This can be seen by noting that the inversion operation, which sends  $\mathbf{x} \to -\mathbf{x}$ , will result in  $\mathbf{J} \to -\mathbf{J}$  and  $\mathbf{E} \to -\mathbf{E}$ . If the material in question possesses inversion symmetry, then from Neumann's Principle you would find  $\boldsymbol{\sigma}^{(2)} \to \boldsymbol{\sigma}^{(2)}$ . The combination of all of these yields:

$$\mathbf{J} = \boldsymbol{\sigma}^{(2)} \mathbf{E} \mathbf{E} \qquad \rightarrow \qquad \mathbf{J} = -\boldsymbol{\sigma}^{(2)} \mathbf{E} \mathbf{E}$$
(1.23)

which is only able to be satisfied if  $\sigma^{(2)} = 0$ . (This same requirement will be true for any nonlinear effect that is even in the electric field.) Second-order effects may therefore occur only in materials which lack inversion symmetry, or at the surface of a material where inversion symmetry is always broken.

Unlike linear responses, second-order nonlinear effects may occur at frequencies distinct from the applied electric fields. We explicitly write out the frequency components of each term in the following expression:

$$\mathbf{J}(\omega_1 \pm \omega_2) = \boldsymbol{\sigma}^{(2)}(\omega_1 \pm \omega_2; \omega_1, \omega_2) \mathbf{E}(\omega_1) \mathbf{E}(\omega_2)$$
(1.24)

There are two options for the response: it may occur at the sum frequency,  $\omega_1 + \omega_2$ , or it may occur at the difference frequency,  $\omega_1 - \omega_2$ . In many experiments  $\omega_1 = \omega_2$ which results in responses at  $2\omega$  and 0, which correspond to SHG and second-order photocurrents respectively. We hereafter focus exclusively on photocurrents.

Second-order nonlinear photocurrents may broadly be categorized into two types: those that arise from circularly or linearly polarized light respectively[77]. Whether a specific noncentrosymmetric material supports photocurrents of these types will be determined by the point group symmetries of the crystal via the second-order conductivity tensor. Using the generalization of Eq. 1.11 for a thirdrank tensor[50]:

$$\sigma'_{ijk} = R_{il}R_{jm}R_{kn}\sigma_{lmn} \tag{1.25}$$

we obtain a system of 27 equations for the  $\sigma'_{ijk}$  and the  $\sigma_{lmn}$  for each point group operation **R**. This system of equations may be solved to identify the non-zero and unique components of  $\sigma$ , a task which is simplified by noting that for many point groups a significant number of the elements will vanish. In addition to the constraints imposed by the point group symmetries, we have an additional constraint that arises from index interchange of the two electric field components[77, 78]. The origin of this requirement is more readily seen if we rewrite Eq. 1.24 in the Fourier frequency space and in component form:

$$J_i = \sigma_{ijk}^{(2)} E_j E_k^* \tag{1.26}$$

The current  $J_i$  is required to be real, so upon taking the complex conjugate of

each side we obtain:

$$\left(J_{i} = \sigma_{ijk}^{(2)} E_{j} E_{k}^{*}\right)^{*}$$

$$J_{i}^{*} = J_{i} = (\sigma_{ijk}^{(2)})^{*} E_{j}^{*} E_{k}$$

$$\sigma_{ijk}^{(2)} E_{j} E_{k}^{*} = (\sigma_{ijk}^{(2)})^{*} E_{j}^{*} E_{k}$$

$$(1.27)$$

from which we can see that  $\sigma_{ijk}^{(2)} = (\sigma_{ikj}^{(2)})^*$ . Writing  $\sigma_{ijk}^{(2)}$  in terms of real and imaginary components we therefore have:

$$\sigma_{ijk}^{(2)} = \sigma_{ijk} + i\eta_{ijk} \tag{1.28}$$

$$\sigma_{ijk}^{(2)} = \sigma_{ijk} + i\eta_{ijk} \tag{1.29}$$

$$\sigma_{ijk} = \sigma_{ikj} \tag{1.30}$$

$$\eta_{ijk} = -\eta_{ikj} \tag{1.31}$$

where in the last two lines we made use of  $\sigma_{ijk}^{(2)} = (\sigma_{ikj}^{(2)})^*$ . The real part of  $\sigma_{ijk}^{(2)}$ , which we have labeled  $\sigma_{ijk}$ , is symmetric under this interchange of indices while the imaginary part  $\eta_{ijk}$  is anti-symmetric. Noting that for linearly polarized light the polarization vectors will be real and that for circularly polarized light the polarization vectors will be imaginary, we find that we may associate the symmetric/real part of the tensor with photocurrents that respond to linearly polarized light (linear photogalvanic effect (LPGE)), and the anti-symmetric/imaginary part with photocurrents that respond to circularly polarized light (circular photogalvanic effect (CPGE)).

As an explicit example we consider the point group  $C_{4v}$ , which will be useful for our discussion of photocurrents in the WSM TaAs in Chapter VI. The generating elements of the  $C_{4v}$  point group are the identity operation, E; the 180° rotation around the z-axis,  $\delta_{2z}$ ; the 90° rotation around the z-axis,  $\delta_{4z}$ ; and the mirror plane normal to the y-axis,  $m_y$ . Applying the latter three operations to Eq. 1.25 in turn we find:

$$\boldsymbol{\sigma} = \begin{pmatrix} 0 & 0 & \sigma_{xzx} \\ 0 & 0 & 0 \\ \sigma_{xxz} & 0 & 0 \\ \hline 0 & 0 & 0 \\ 0 & 0 & \sigma_{xzx} \\ 0 & \sigma_{xxz} & 0 \\ \hline \sigma_{zxx} & 0 & 0 \\ 0 & \sigma_{zxx} & 0 \\ 0 & 0 & \sigma_{zzz} \end{pmatrix}$$
(1.32)

There are seven non-zero elements, of which four are unique. Next, considering the interchange of the last two indices we find:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{S} + i\boldsymbol{\eta}_{AS} \begin{pmatrix} 0 & 0 & \sigma_{xxz} - i\eta_{xxz} \\ 0 & 0 & 0 \\ \sigma_{xxz} + i\eta_{xxz} & 0 & 0 \\ 0 & 0 & \sigma_{xxz} - i\eta_{xxz} \\ 0 & \sigma_{xxz} + i\eta_{xxz} & 0 \\ \sigma_{zxx} & 0 & 0 \\ 0 & \sigma_{zxx} & 0 \\ 0 & 0 & \sigma_{zzz} \end{pmatrix}$$
(1.33)

where  $\sigma_{ijk}$  are the symmetric elements and  $\eta_{ijk}$  are the asymmetric elements. There are three unique elements for the symmetric part:  $\sigma_{xxz}, \sigma_{zxx}$ , and  $\sigma_{zzz}$ ; and only one unique element for the asymmetric part:  $\eta_{xxz}$ . From the form of this tensor we find that a LPGE may be generated along any crystal axis, but that a CPGE may only be generated perpendicular to the *c*-axis (which lacks a mirror plane). This will generally be true for any material that supports a CPGE, with the exception of materials which lack any mirror planes whatsoever. In such a case the CPGE is generated along the propagation direction of the incident light[79, 80].

#### 1.5.1 Connection to Topology

The second-order optical conductivity tensor  $\sigma(0; \omega, -\omega)$  which describes the LPGE or "shift current" is directly related to the interband Berry connection[81]. This can be intuitively understood by considering the response of an electron to photoexcitation. When an electron is excited from the valence band to the conduction band there can be a concomitant change in the real space position of the electron. This is particularly the case when the valence and conduction bands arise from orbitals associated with different atoms within the unit cell. We therefore consider the expectation value of the position operator  $\langle |\mathbf{x}| \rangle$  for the electron. Recalling that in the momentum basis the position operator may be expressed as  $\mathbf{x} = i\hbar\partial/\partial \mathbf{k}$  we find that:

$$\langle n(\mathbf{k})|\mathbf{x}|n(\mathbf{k})\rangle = i\hbar\langle n(\mathbf{k})|\nabla_{\mathbf{k}}|n(\mathbf{k})\rangle \tag{1.34}$$

which up to the factor of  $\hbar$  is the just the definition of the Berry connection.

# CHAPTER II

# Charge Transfer in $Bi_2Se_3/EuS$ Heterostructures

# 2.1 Introduction

The class of materials known collectively as "topological insulators" were the first intrinsically topological materials to be experimentally identified [45, 46]. In the ideal case these materials are insulators in their bulk, but have conducting surface states due to the bulk-boundary correspondence, and the topological phase transition that occurs when passing from the topologically non-trivial bulk to the trivial insulating state of air. These states are protected by time reversal symmetry. In particular, the  $Bi_2Se_3$  family is van-der-Waals bonded, which enables exfoliation and the creation of heterostructures with other 2D materials.

Because of these surface states there has been considerable research dedicated to creating heterostructures with these materials. For our discussion here we focus on the use of thin film ferromagnets, wherein the exchange field present at the interface between the materials can break the time reversal symmetry of the topological surface states and open a gap in their spectrum[44, 82–86]. This has lead to the observation of effects such as the quantum anomalous Hall effect[48, 49]. EuS is an insulating ferromagnet that can be grown by MBE, which has led to its wide use in creating such heterostructures.

Another effect that has been successfully used to generate novel heterostruc-

tures is the charge transfer phenomenon. When two materials are brought together, the different chemical potentials of each material must come to a common equilibrium. Depending on the material specific work functions, this can result in different functional behaviors such as Schottky barriers, etc. It has also been seen to generate metal to insulator transitions in heterostructures of LAO/STO[87], as well as enhancing the superconducting transition temperature of FeSe[88].

In the results discussed herein we provide indirect evidence, through the use of Raman spectroscopy, of a significant charge transfer in heterostructures of EuS/Bi<sub>2</sub>Se<sub>3</sub>. Raman spectroscopy is a well-suited probe for investigations of magnetic and lattice effects in such heterostructures, due to its sensitivity to both lattice and magnetic excitations, particularly in EuS. We performed measurements on a series of EuS/Bi<sub>2</sub>Se<sub>3</sub> thin films and found that the EuS Raman signal, whose presence is known to indicate the paramagnetic state of the system, is absent in all measured heterostructures. Direct measurements of the magnetic system rule out magnetic ordering at room temperature, and further calculations of the thin film interference rule out optical suppression of the mode. Using a simple model we therefore ascribe the absence of this mode to charge transfer between the EuS and Bi<sub>2</sub>Se<sub>3</sub>.

#### 2.1.1 EuS Raman Signal

Since understanding the origin of the Raman signal of EuS will be crucial to an understanding of the results presented in this chapter, we devote here a brief discussion to this topic. The appearance of first order Raman signal from EuS is unexpected. EuS has the same crystal structure as NaCl – two inter-penetrating face-centered cubic lattices. With two atoms per unit cell there are only six phonon modes, three of which are acoustic. The three optical modes are all degenerate at the zone center and, due to the lack of a unique inversion center, are odd under inversion and therefore Raman inactive. (Specifically, at the zone center they have the irreducible representation  $T_{1u}$ .) However, the entire EuX (where X = O, S, Se Te) family of materials have been experimentally observed to display first-order Raman scattering[89–92].

The explanation for this unexpected result has its roots in the coupling between the magnetic and vibrational systems. Large momentum phonons are typically unable to be generated by Raman scattering due to the need to conserve momentum and the low momentum provided by optical wavelength photons. (Two-phonon features circumvent this by generating phonons with opposite momentum such that the net is still approximately zero. However, we will here be restricting our discussion to one-phonon processes.) In the case of the EuX materials, the momentum necessary to excite phonons far from the zone center is contributed by the spin system [92]. A Feynman diagram describing the scattering process that we describe is shown in Figure 2.1. At room temperature EuS is paramagnetic and the 4f Eu spins are disordered. Incoming photons of energy  $\hbar\omega_i$  excite electrons from the 4f band to the 5d conduction band leaving behind holes. These holes are able to interact with both the lattice and the spin system, producing an LO phonon of energy  $\hbar\Omega$  and momentum  $\mathbf{q}$ , and a spin excitation with energy  $\hbar\Omega_m$ and momentum  $\mathbf{q}'$ . The hole and electron then recombine and emit a Raman scattered photon with energy  $\hbar\omega_o$ . To conserve momentum  $\mathbf{q}' = -\mathbf{q}$ , and likewise to conserve energy,  $\hbar\omega_o = \hbar\omega_i + \hbar\Omega + \hbar\Omega_m$ . In the room temperature paramagnetic phase, the different spin states are degenerate and therefore  $\hbar\Omega_m = 0$ , i.e. there is no energy cost for creating the spin excitation. However, when the crystal has long–range magnetic order, the magnons at finite  $\mathbf{q}$  now have a non-zero energy cost associated with them. And, the probability of creating a magnon via Raman scattering is proportional to  $(\hbar \Omega_m)^{-1}$ . Thus as the system passes through its Curie temperature there is an associated quenching of the Raman scattering 90, 92.



Figure 2.1: Feynman diagram for the first-order Raman scattering in EuS. In the paramagnetic state the disordered spin system provides the momentum  $(\mathbf{q}')$  necessary to generate the optical phonon of energy  $\Omega$  and momentum  $\mathbf{q} = -\mathbf{q}'$ .

### 2.2 Experiments

#### 2.2.1 Growth of Thin Films

EuS and Bi<sub>2</sub>Se<sub>3</sub> thin films were epitaxially grown in a custom-built MBE system. The base pressure of the system was  $2 \times 10^{-10}$  Torr. Effusion cells containing 5N purity Bi and Se were used to grow the Bi<sub>2</sub>Se<sub>3</sub>, while an electron beam evaporator was used for the growth of the EuS and the protective layers of amorphous Al<sub>2</sub>O<sub>3</sub>. To ensure the formation of high quality interfaces, the growth was monitored by *in situ* reflection high-energy electron diffraction (RHEED). The preparation of atomically flat substrate surfaces was also done *in situ* through several baking treatments and monitoring with RHEED. Two different substrates were used for growth, sapphire (Al<sub>2</sub>O<sub>3</sub>) and STO. As is discussed in relation to the phonon modes of Bi<sub>2</sub>Se<sub>3</sub> later, the sapphire possesses a larger in-plane lattice constant than that of Bi<sub>2</sub>Se<sub>3</sub>, while STO has a smaller lattice constant than Bi<sub>2</sub>Se<sub>3</sub>.

Once the substrates were prepared, the Bi and Se were simultaneously evaporated with a 1:15 flux ratio to the substrate, at a fixed temperature of  $240\pm5$  °C. Despite this ratio differing from the 2:3 ratio in the desired Bi<sub>2</sub>Se<sub>3</sub> phase, we note that this phase is quite stable, and self-adjusting of the final composition occurs at this elevated growth temperature. A ~1-2 Å/min growth rate was used to avoid kinetic surface roughening and provide an ultra-smooth surface. For EuS, a much faster growth rate of 0.5-0.6 Å/s from a single electron-beam source was used to help mitigate the high reactivity of Eu atoms and the dissociation problems of S. A final protective capping layer of 5 nm thick, amorphous  $Al_2O_3$  was grown on top of the  $Bi_2Se_3$  bilayers (at room temperature). All of this was done in the same deposition chamber without breaking ultra-high vacuum conditions.

#### 2.2.2 Raman Measurements

Raman measurements were performed using a WITec alpha-300R confocal Raman system. The unpolarized, 532 nm (2.33 eV) light was focused using a 100x objective to a spot size of ~1  $\mu$ m. The power was kept low at 10  $\mu$ W to avoid local heating of the Bi<sub>2</sub>Se<sub>3</sub>[93]. Any "cosmic rays" in the spectra were removed by a wavelet based algorithm[94] and the resulting spectra where then averaged and normalized by power and integration time.

The Raman spectra of a 5 nm thick EuS film on a sapphire substrate is shown in Figure 2.2. The fundamental EuS Raman peak is clearly visible in this spectrum at an energy of 30.4 meV, which is ~2% higher than the typical room temperature value of 29.8 meV[89–91]. The energy of this mode is known to decrease as the sample temperature is decreased[91]. However, these measurements were carried out at room temperature so this is unlikely to be the explanation. Inter-facial strain is also unlikely to explain the resulting shift, since the strain from the sapphire lattice would be tensile and would also cause a decrease of the mode energy. We hypothesize that the shift results from the presence of Eu-O bonds that arise from both the oxygen terminated surface of the sapphire substrate, as well as the amorphous  $Al_2O_3$  capping layer. Sulfur atoms are known to dissociate from the EuS thin films during growth, leaving behind anion vacancies[86]. These



Figure 2.2: Raman spectra of a 5 nm thick EuS film grown on a sapphire substrate. The fundamental spin-disorder mode is clearly visible at 30.4 meV, as are its second and third harmonic overtones at 60.8 and 91.2 meV respectively.

vacancies may then be occupied by O atoms during the growth of the capping layer. The O atoms are lighter than the S atoms, so the phonon mode will shift to a higher energy[91].

We now investigate the spectra of a Bi<sub>2</sub>Se<sub>3</sub>/EuS bilayer, shown in Figure 2.3. The Bi<sub>2</sub>Se<sub>3</sub> was 7 QL thick and the EuS was 10 nm thick. The two modes at 16.5 meV and 21.7 meV are the  $E_g^2$  and  $A_{1g}^2$  phonons of Bi<sub>2</sub>Se<sub>3</sub> respectively. Surprisingly, the EuS mode at 30.4 meV is absent from this bilayer. This occurs despite the thickness of EuS in this sample being twice as much as the bare EuS sample shown in Figure 2.2, which would presumably lead to a larger signal level. Raman measurements were repeated on samples with 7 QL of Bi<sub>2</sub>Se<sub>3</sub> and 2 or 5 nm of EuS (see Figure 2.9(b)), as well as samples with 5 QL of Bi<sub>2</sub>Se<sub>3</sub> with 2, 5, or 10 nm of EuS. In none of these samples was the signal from EuS observable.

#### 2.2.3 Magnetic Measurements

To determine if magnetic ordering is responsible for the absence of the EuS Raman peak we measured the magnetic moment of our samples as a function of



Figure 2.3: Raman spectra of 7 QL  $Bi_2Se_3$  with 10 nm thick EuS on a sapphire substrate. While the Bi2Se3 phonon modes are clearly visible at 16.5 and 21.7 meV, the EuS mode at 30.4 meV is absent.

temperature. Measurements were taken from 2 to 380 K using a Quantum Design MPMS in the laboratory of Professor Michael Graf. Two samples were measured, one with just EuS on sapphire, and the other with EuS/Bi<sub>2</sub>Se<sub>3</sub> on sapphire. The EuS was 5 nm thick in both films, and the Bi<sub>2</sub>Se<sub>3</sub> was 7 QL thick. While EuS is paramagnetic, with a bulk Curie temperature of 16 K[90, 92], the sapphire substrate contributes a large diamagnetic background to the overall signal. We removed this contribution by repeating the measurements on a sapphire substrate identical to the ones on which the thin films were grown. The response from the sapphire substrate was then scaled by mass to match that of the other thin films (the mass of the few nanometer thick EuS and Bi<sub>2</sub>Se<sub>3</sub> was assumed to be negligible for this calculation since the substrates were ~1 mm thick), and subtracted from the measurements on films with EuS/Bi<sub>2</sub>Se<sub>3</sub>.

The magnetic moment data thus obtained is shown in Figure 2.4, with the data from the EuS sample shown in blue, and the EuS/Bi<sub>2</sub>Se<sub>3</sub> sample in red. The two curves fall exactly on top of each other, indicating that the presence of the  $Bi_2Se_3$  does not affect the ordering temperature of the EuS. Furthermore, at 300 K



Figure 2.4: The magnetic moment of a EuS/sapphire thin film sample in blue is compared to the magnetic moment from a  $Bi_2Se_3/EuS/sapphire$  thin film in red. The diamagnetic background from the sapphire substrates has been subtracted out.

where the Raman measurements were performed, there does not appear to be any magnetic moment which indicates that the EuS is indeed paramagnetic at room temperature. From this we conclude that magnetic ordering of the EuS spins is not responsible for the absence of the magnetic fluctuation induced Raman mode in EuS and that another mechanism must be the cause.

# 2.3 Discussion and Analysis

#### 2.3.1 Fabry-Perot Interference Calculations

Having eliminated magnetic ordering as the cause for the absence of the EuS Raman mode in the spectra from our EuS/Bi<sub>2</sub>Se<sub>3</sub> thin films, we explore the possibility of interference suppressing the observation of the mode. Due to the multilayered nature of our samples, multiple reflections may occur at the various interfaces which can lead to enhancement or suppression of either or both the incident laser and the Raman scattered light. Such effects are famous for producing the multi-colored appearance of soap films. More recently in the field of 2D materials, they have also been found to explain, among other things, the variation in intensity with dielectric thickness for Raman signal from graphene[95–97], and thickness dependent Raman from exfoliated flakes of  $Bi_2Se_3[93]$  and  $MoS_2[98]$ . Here, we develop an extension of the multi-reflection model (MRM) used by Zhang *et al*[98] which accounts for the peculiarities of the thin films investigated here.

The reflection and transmission coefficients between two materials are defined as

$$r_{ij} = \frac{\tilde{n}_i - \tilde{n}_j}{\tilde{n}_i + \tilde{n}_j} \tag{2.1}$$

$$t_{ij} = \frac{2\dot{n}_i}{\tilde{n}_i + \tilde{n}_j} \tag{2.2}$$

where  $\tilde{n}_i$  is the complex index of refraction for material *i*. In general it is written as  $\tilde{n} = n + ik$  and is a function of wavelength. We define the phase propagation coefficients,  $\beta_i$  as

$$\beta_i = \frac{2\pi \tilde{n}_i}{\lambda} \tag{2.3}$$

In this expression  $\lambda$  will belong to either the wavelength of the incident light or the wavelength of the Raman scattered light – the appropriate choice is clear upon inspection.

The first interference factor accounts for the multiple reflections of the incident light within the heterostructure. The schematic diagram for this process is shown in Figure 2.5 The first term is represented by the red dot and is written as

$$a_1 = t_{01}^e e^{-i\beta_2 y} \tag{2.4}$$



Figure 2.5: Diagram showing the rays that contribute to interference of the incident laser. The black arrows show the path of the incident laser, while the purple arrows indicate where multiple reflections can occur for the transmitted part of the beam. The distance y into the EuS indicates the depth at which we are calculating the interference of the electric fields and will be integrated over to find the total enhancement.

where we have defined the effective transmission coefficient  $t_{01}^e$  which accounts for the possibility of multiple reflections within the capping layer. The subsequent terms are represented by the blue dots:

$$a_2 = t_{01}^e r_{23}^e e^{-i\beta_2(2d_2 - y)}$$
(2.5)

$$a_3 = t_{01}^e r_{23}^e r_{21}^e e^{-i\beta_2(2d_2)} e^{-i\beta_2 y}$$
(2.6)

$$a_4 = t_{01}^e (r_{23}^e)^2 r_{21}^e \mathrm{e}^{-i\beta_2(2d_2)} \mathrm{e}^{-i\beta_2(2d_2-y)}$$
(2.7)

$$a_5 = t_{01}^e (r_{23}^e)^2 (r_{21}^e)^2 e^{-i\beta_2(4d_2)} e^{-i\beta_2 y}$$
(2.8)

$$a_6 = t_{01}^e (r_{23}^e)^3 (r_{21}^e)^2 e^{-i\beta_2(4d_2)} e^{-i\beta_2(2d_2-y)}$$
(2.9)

where, similar to  $t_{01}^e$ ,  $r_{21}^e$  and  $r_{23}^e$  take into account multiple reflections within the capping and Bi<sub>2</sub>Se<sub>3</sub> layers respectively. Summing all of these terms to find the

. . .

overall factor we find

$$F_{inc} = \sum_{l=1}^{\infty} a_l \tag{2.10}$$

$$= t_{01}^{e} \mathrm{e}^{-i\beta_2 y} \left( 1 + r_{23}^{e} r_{21}^{e} \mathrm{e}^{-2i\beta_2 d_2} + (r_{23}^{e} r_{21}^{e} \mathrm{e}^{-2i\beta_2 d_2})^2 + \cdots \right)$$
(2.11)

$$+ t_{01}^{e} r_{23}^{e} \mathrm{e}^{-i\beta_{2}(2d_{2}-y)} \left( 1 + r_{23}^{e} r_{21}^{e} \mathrm{e}^{-2i\beta_{2}d_{2}} + (r_{23}^{e} r_{21}^{e} \mathrm{e}^{-2i\beta_{2}d_{2}})^{2} + \cdots \right) \quad (2.12)$$

$$= t_{01}^{e} \left( e^{-i\beta_2 y} + r_{23}^{e} e^{-i\beta_2 (2d_2 - y)} \right) \left[ \sum_{n=0}^{\infty} \left( r_{23}^{e} r_{21}^{e} e^{-2i\beta_2 d_2} \right)^n \right]$$
(2.13)

$$= t_{01}^{e} \frac{\mathrm{e}^{-i\beta_{2}y} + r_{23}^{e} \mathrm{e}^{-i\beta_{2}(2d_{2}-y)}}{1 - r_{23}^{e} r_{21}^{e} \mathrm{e}^{-2i\beta_{2}d_{2}}}$$
(2.14)

The effective transmission/reflection coefficients are derived in an analogous manner. For  $t_{01}^e$  we have the terms:

$$b_1 = t_{01} t_{12} \mathrm{e}^{-i\beta_1 d_1} \tag{2.15}$$

$$b_2 = t_{01} t_{12} \mathrm{e}^{-i\beta_1 d_1} r_{12} r_{10} \mathrm{e}^{-2i\beta_1 d_1}$$
(2.16)

$$b_3 = t_{01} t_{12} \mathrm{e}^{-i\beta_1 d_1} \left( r_{12} r_{10} \mathrm{e}^{-2i\beta_1 d_1} \right)^2 \tag{2.17}$$

• • •

When summed we obtain

$$t_{01}^{e} = t_{01}t_{12}\mathrm{e}^{-i\beta_{1}d_{1}}\left(1 + r_{10}r_{12}\mathrm{e}^{-2i\beta_{1}d_{1}} + (r_{10}r_{12}\mathrm{e}^{-2i\beta_{1}d_{1}})^{2} + \cdots\right)$$
(2.18)

$$=\frac{t_{01}t_{12}\mathrm{e}^{-i\beta_1 d_1}}{1+r_{01}r_{12}\mathrm{e}^{-2i\beta_1 d_1}}\tag{2.19}$$



Figure 2.6: Same as the previous figure, but now showing the paths and rays taken by the Raman scattered light which originates at depth y in the EuS layer.

where in the last line we used the relation  $r_{ij} = -r_{ji}$ . For  $r_{23}^e$  we have:

$$c_1 = r_{23} \tag{2.20}$$

$$c_2 = t_{23} t_{32} r_{34} \mathrm{e}^{-2i\beta_3 d_3} \tag{2.21}$$

$$c_3 = t_{23} t_{32} r_{34} \mathrm{e}^{-2i\beta_3 d_3} (r_{32} r_{34} \mathrm{e}^{-2i\beta_3 d_3}) \tag{2.22}$$

$$c_4 = t_{23} t_{32} r_{34} \mathrm{e}^{-2i\beta_3 d_3} \left( r_{32} r_{34} \mathrm{e}^{-2i\beta_3 d_3} \right)^2 \tag{2.23}$$

such that

$$r_{23}^e = r_{23} + \frac{t_{23}t_{32}r_{34}e^{-2i\beta_3 d_3}}{1 + r_{23}r_{34}e^{-2i\beta_3 d_3}}$$
(2.24)

This can be further simplified by using the relation  $t_{ij}t_{ji} - r_{ij}r_{ji} = 1$ ,

$$r_{23}^{e} = \frac{r_{23} + r_{34} \mathrm{e}^{-2i\beta_3 d_3}}{1 + r_{23} r_{34} \mathrm{e}^{-2i\beta_3 d_3}} \tag{2.25}$$

A similar relation is found for  $r_{21}^e$ ,

. . .

$$r_{21}^{e} = \frac{r_{21} + r_{10} \mathrm{e}^{-2i\beta_{1}d_{1}}}{1 + r_{21}r_{10} \mathrm{e}^{-2i\beta_{1}d_{1}}}$$
(2.26)

The next interference term arises from the multiple reflections experienced by the Raman scattered light as it leaves the heterostructure. As such, for these terms the  $\beta_i$  should be evaluated at the wavelength of the Raman scattered light. A diagram for this process is shown in Figure 2.6. The first term is found as

$$d_1 = e^{-i\beta_2 y} t_{21}^e \tag{2.27}$$

where we have defined the effective transmission coefficient  $t_{21}^e$  which may be shown to be

$$t_{21}^{e} = \frac{t_{21}t_{10}\mathrm{e}^{-i\beta_{1}d_{1}}}{1 + r_{01}r_{12}\mathrm{e}^{-2i\beta_{1}d_{1}}}$$
(2.28)

Subsequent terms are

$$d_3 = t_{21}^e \mathrm{e}^{-i\beta_2 y} \left( r_{21}^e r_{23}^e \mathrm{e}^{-2i\beta_2 d_2} \right)$$
(2.29)

$$d_4 = t_{21}^e r_{23}^e \mathrm{e}^{-i\beta_2(2d_2 - y)} \left( r_{21}^e r_{23}^e \mathrm{e}^{-2i\beta_2 d_2} \right)$$
(2.30)

$$d_5 = t_{21}^e \mathrm{e}^{-i\beta_2 y} \left( r_{21}^e r_{23}^e \mathrm{e}^{-2i\beta_2 d_2} \right)^2 \tag{2.31}$$

$$d_6 = t_{21}^e r_{23}^e \mathrm{e}^{-i\beta_2(2d_2-y)} \left( r_{21}^e r_{23}^e \mathrm{e}^{-2i\beta_2 d_2} \right)^2$$
(2.32)

Summing these gives us

. . .

$$F_{sc} = t_{21}^{e} \mathrm{e}^{-i\beta_{2}y} \left( 1 + r_{21}^{e} r_{23}^{e} \mathrm{e}^{-2i\beta_{2}d_{2}} + \left( r_{21}^{e} r_{23}^{e} \mathrm{e}^{-2i\beta_{2}d_{2}} \right)^{2} + \cdots \right)$$
(2.33)

$$+ t_{21}^{e} r_{23}^{e} \mathrm{e}^{-i\beta_{2}(2d_{2}-y)} \left( 1 + r_{21}^{e} r_{23}^{e} \mathrm{e}^{-2i\beta_{2}d_{2}} + \left( r_{21}^{e} r_{23}^{e} \mathrm{e}^{-2i\beta_{2}d_{2}} \right)^{2} + \cdots \right) \quad (2.34)$$

$$= t_{21}^{e} \left( e^{-i\beta_{2}y} + r_{23}^{e} e^{-i\beta_{2}(2d_{2}-y)} \right) \left[ \sum_{n=0}^{\infty} \left( r_{21}^{e} r_{23}^{e} e^{-2i\beta_{2}d_{2}} \right)^{n} \right]$$
(2.35)

$$= t_{21}^{e} \frac{e^{-i\beta_2 y} + r_{23}^{e} e^{-i\beta_2 (2d_2 - y)}}{1 - r_{21}^{e} r_{23}^{e} e^{-2i\beta_2 d_2}}$$
(2.36)

The enhancement due to the combination of these two effects at the depth y is



Figure 2.7: Calculated interference enhancement factor for films of varying EuS thickness, as a function of the  $Bi_2Se_3$  thickness. The dashed line corresponds to the thickness of the  $Bi_2Se_3$  for our measured samples.

given by the complex modulus of the product of our two terms

$$F_y = |F_{inc}F_{sc}|^2 (2.37)$$

To find the total enhancement from the EuS layer we do an integral over the depth y such that

$$F_{tot} = N \int_{0}^{a_2} |F_{en}F_{sc}|^2 dy$$
(2.38)

where N is a normalization constant. In a computational implementation of this expression the integral is replaced by a summation with  $dy \to \Delta y$  and  $\Delta y \ll a$ where a is approximately the interatomic spacing. N is found by taking the inverse of  $F_{tot}$  calculated with the Bi<sub>2</sub>Se<sub>3</sub>, capping layer, and substrate replaced by air.

The integration was numerically carried out using MATLAB for thin films of varying  $Bi_2Se_3$  and EuS thicknesses. The enhancement factors thus obtained are plotted in Figure 2.7 as a function of  $Bi_2Se_3$  thickness, with selected EuS thicknesses corresponding to those we measured. The largest enhancements are seen to occur for a Bi<sub>2</sub>Se<sub>3</sub> thickness of ~10 nm and EuS thickness of 2 nm, with the peak of the enhancement decreasing and shifting to slightly lower Bi<sub>2</sub>Se<sub>3</sub> thickness as the EuS thickness is increased. For films with 7 QL of Bi<sub>2</sub>Se<sub>3</sub>, indicated by the vertical dashed line, the enhancement decreases as EuS thickness is increased up to 10 nm. In the absence of a Bi<sub>2</sub>Se<sub>3</sub> layer (0 nm) we find an enhancement factor of 0.25 which indicates that, as expected, the Raman signal from a thin slab of EuS will be decreased compared to a bulk crystal. To obatin the expected enhancement factors for our films, we divide the value for each EuS thickness at 7 QL by the 0.25 value at 0 nm Bi<sub>2</sub>Se<sub>3</sub> to find enhancement factors of 2.5/0.25 = 10, 1.9/0.25 = 7.6, and 1.2/0.25 = 4.8 for 10, 5, and 2 nm of EuS respectively. As all of these indicate, we should expect a larger Raman signal from the EuS when the Bi<sub>2</sub>Se<sub>3</sub> is present. This is however, in clear contrast to what our Raman measurements revealed. We therefore conclude that Fabry-Perot interference is not causing suppression of the mode, and that another mechanism must be responsible.

#### 2.3.2 Charge Transfer

We now discuss how changes in the electronic structure of the EuS/Bi<sub>2</sub>Se<sub>3</sub> heterostructures could lead to suppression of the EuS Raman mode. We start by once more considering in detail the scattering processes which produce the EuS Raman signal. Light absorbed by the EuS excites an electron from the 4f valence band to the 5*d* conduction band, leaving behind a hole[92]. This hole then interacts with both the spin and vibrational systems, as depicted in Figure 2.1, before recombining and emitting the Raman scattered photon. This process depends very strongly on the energy of the incident radiation, with the resonance peak occurring quite close to the 2.33 eV of our laser[89, 99]. This type of resonance most often occurs when the electronic transitions involved in the scattering process,

like those described above, connect real energy levels instead of virtual energy levels [59]. These conditions are indeed met for bulk semiconducting EuS where the chemical potential lies within the 1.65 eV gap[99, 100]. However, as we will now address, the large difference in work function between EuS and  $Bi_2Se_3$  can cause the chemical potential within the EuS to shift to the point that it is no longer within the band gap and the electronic transitions produced by our laser are no longer resonant.

The electrical properties of an interface can be largely affected by the relative chemical potentials of the two materials. The chemical potential must smoothly transition between the materials at the interface, which can result in a transfer of charge from one material to the other. The energies of the chemical potentials are determined by their material's respective work functions, which is often identified through photo-emission measurements. In the case of EuS, the work function has been reported as 3.3 eV[101, 102], with an electron affinity of 2.35 eV[101, 102], while Bi<sub>2</sub>Se<sub>3</sub> has a reported work function of 5.4 eV[103]. The Bi<sub>2</sub>Se<sub>3</sub> is *n* doped  $(n \sim 10^{19} \text{ cm}^{-3})[86]$ , which places its chemical potential in the conduction band, so we therefore treat it as a metal, and the overall interface as metal-semiconductor.

In Figure 2.8 we show a schematic diagram of the Bi<sub>2</sub>Se<sub>3</sub> interface and the energy levels involved. On the far left and right of the diagram are flat band diagrams of the valence bands, conduction bands, chemical potentials, and work functions for Bi<sub>2</sub>Se<sub>3</sub> and EuS respectively. At the interface between Bi<sub>2</sub>Se<sub>3</sub> and EuS (the middle of the diagram) the difference in work functions leads to an imbalance in chemical potential. To even this out, electrons flow out of the EuS and into the Bi<sub>2</sub>Se<sub>3</sub>, which results in the formation of a Schottky barrier of height  $E_{bar} = \phi_{\text{Bi}_2\text{Se}_3} - \chi_{\text{EuS}} = 3.05 \text{ eV}$ . Taking the difference between the energy of the barrier and the band gap of EuS tells us that the built-in potential is 1.4 eV. In other words, the chemical potential of the EuS within the depletion region is shifted



Figure 2.8: Schematic diagram of the band bending that occurs at the interface between EuS and Bi<sub>2</sub>Se<sub>3</sub>. The work function of Bi<sub>2</sub>Se<sub>3</sub> ( $\phi_{\text{Bi}_2\text{Se}_3} = 5.4 \text{ eV}$ ) is larger than that of EuS ( $\phi_{\text{EuS}} = 3.3 \text{ eV}$ ) which leads to the formation of a Schottky barrier of height  $\phi_{\text{Bi}_2\text{Se}_3} - \chi_{\text{EuS}} = 3.05 \text{ eV}$  at their interface. To balance the chemical potential, electrons move from EuS to the Bi<sub>2</sub>Se<sub>3</sub> resulting in a depletion region in which photoexcitation by our 2.33 eV laser is no longer possible.

down by 1.4 eV, as can be seen in the central part of the diagram. The spatial extent of this region is expected to be on the order of hundreds of nanometers, which is much larger than the thickness of our EuS films. We therefore expect that the entire EuS film experiences this lowering of the chemical potential.

In bulk EuS the 2.33 eV of our laser is capable of exciting electrons from the 4f valence band into the 5d conduction band[89, 92, 99], as shown on the right side of Figure 2.8. However, in the EuS/Bi<sub>2</sub>Se<sub>3</sub> heterostructures we now find that, as a result of the shifted chemical potential,  $\approx 3 \text{ eV}$  is required to excite an electron out of the valence band. The electronic transitions available with a 2.33 eV laser are then no longer real, but virtual, and the conditions for resonance in the Raman signal are no longer satisfied. We therefore conclude that this large transfer of charge between EuS and Bi<sub>2</sub>Se<sub>3</sub> is responsible for the absence of the EuS Raman signal in our heterostructures. Future Raman measurements of similar thin films with shorter wavelength lasers, or optical transmission/absorption measurements



Figure 2.9: (a) Raman spectra from bulk  $Bi_2Se_3$ . (b) Spectra of  $EuS/Bi_2Se_3$  films on sapphire substrates. The vertical black line represents the energy of the modes from bulk  $Bi_2Se_3$ . (c) Same as (b) but on STO substrates. (d) Percent difference in energy of the  $Bi_2Se_3$  modes as a function of EuS thickness.

may be capable of confirming this hypothesis.

### 2.4 Strain

We lastly discuss the role of interfacial strain in our EuS/Bi<sub>2</sub>Se<sub>3</sub> thin films. Although the EuS Raman mode was not observed in our measurements, the Bi<sub>2</sub>Se<sub>3</sub> modes were, and through analysis of their behavior as we vary the thickness of the EuS layer or the substrate we can learn about the nature of the strain present in these films. We first measure the Raman spectra of bulk Bi<sub>2</sub>Se<sub>3</sub>, which was freshly cleaved prior to measurement. The spectra from bulk Bi<sub>2</sub>Se<sub>3</sub> is shown in Figure 2.9(a), which reveals two modes at 16.4 and 21.9 meV. As discussed earlier, these correspond to the  $E_g^2$  and  $A_{1g}^2$  modes respectively, whereas the other two Raman active modes were not observed due to the low energy cut-off of our filter.

With bulk  $Bi_2Se_3$  measured for comparison, we now turn to the spectra from  $EuS/Bi_2Se_3$  films on two different substrates, sapphire and STO. In Figure 2.9(b)

we show spectra measured on sapphire substrates with 0, 2, 5, and 10 nm thick EuS, while Figure 2.9(c) shows the same thing on STO substrates. On sapphire, the Bi<sub>2</sub>Se<sub>3</sub> modes can be seen to shift down in energy from the bulk value as the EuS thickness is increased. Similar behavior is observed for the films on STO substrates, although to a much lesser degree. The energies extracted from fitting of the peaks, expressed as the percent difference from the bulk value, are plotted in Figure 2.9(d).

These shifts in energy can be explained by interfacial strain due to lattice mismatches of the Bi<sub>2</sub>Se<sub>3</sub>, the EuS, and the sapphire and STO substrates. The Bi<sub>2</sub>Se<sub>3</sub> grows along the [0001] direction which has an in-plane lattice constant of 4.128 Å[104]. The EuS grows along the [111] direction and therefore has interatomic spacing of  $a/\sqrt{2} = 4.220$  Å. Since the lattice constant of EuS is slightly larger than that of Bi<sub>2</sub>Se<sub>3</sub>, there will be a tensile strain acting to pull the Bi<sub>2</sub>Se<sub>3</sub> atoms apart. This results in a weaker inter-atomic force and, as  $\omega \propto \sqrt{k/m}$ , a decrease in the energy of the phonon modes, in accordance with our observations.

This is further supported by observing the energy shifts of the Bi<sub>2</sub>Se<sub>3</sub> modes in the absence of any EuS. Sapphire, also in the [0001] direction, has an in-plane lattice constant of 4.785 Åwhich is greater than that of Bi<sub>2</sub>Se<sub>3</sub>, while STO has a smaller lattice constant of 3.905 Å. We would therefore anticipate that the Bi<sub>2</sub>Se<sub>3</sub> modes will decrease in energy when grown on sapphire substrates, and increase in energy when grown on STO. The measured values shown in Figure 2.9(d) are in agreement with this prediction. We note too that the out-of-plane  $A_{1g}^2$  mode appears to display a larger degree of change compared to the in-plane  $E_g^2$  mode for both substrates.

# 2.5 Conclusions

We performed a series of Raman measurements on EuS/Bi<sub>2</sub>Se<sub>3</sub> thin films. Though measurable on films with only EuS, the EuS Raman signal that indicates its degree of magnetic ordering was not found to appear on films with both EuS and Bi<sub>2</sub>Se<sub>3</sub>. While this could potentially indicate a dramatic increase in the Curie temperature of the EuS due to the proximity of spins from Bi<sub>2</sub>Se<sub>3</sub>, measurements of the magnetic moment indicate that there is no magnetic ordering present at room temperature. We instead identify charge transfer from the EuS into the Bi<sub>2</sub>Se<sub>3</sub> and the associated change in chemical potential as the mechanism suppressing the observation of this mode, while also ruling out optical interference through the use of numerical calculations. This charge transfer may be useful in future studies hoping to harness or tune the electrical response of topological insulators.

# CHAPTER III

# Phonon-Electron Coupling in WP<sub>2</sub>

## 3.1 Topological Semimetals and Mobility

The nascent field of topological semimetals is home to materials which display a range of remarkable transport phenomena, including enormous magnetoresistance and mobilities [24, 105–107]. The observation of such behavior in topological systems initially suggested that the topological nature of the electronic bands was a crucial ingredient. However, non-topological semimetals such as LaAs or PtSn<sub>4</sub> have also been found to display similar remarkable magnetoresistances and mobilities [108–110], which instead suggests that these properties are more endemic to semimetals in general. Some reports have indeed suggested that the primary factor is the near-perfect electron-hole compensation inherent to these semimetallic systems [108, 110]. In addition to their still debated origin, there is often enormous variation in the temperature dependence of these properties, indicating that temperature dependent scattering processes such as those provided by electron-phonon coupling are important.

The transition metal dipnictide WP<sub>2</sub> is an ideal semimetal in which to study the role of coupling between the electron and phonon systems. In its topological  $\beta$ -WP<sub>2</sub> phase it displays the largest magnetoresistance of any topological semimetal[106]. Further, at low temperatures there are some experiments suggesting electron hydrodynamic behavior[111], which would indicate a large degree of coupling between the electrons and phonons. In WP<sub>2</sub> the resistivity deceases by four orders of magnitude between room temperature and 2 K, while the mobility increases by five orders of magnitude over the same temperature range[106]. Over the range where the majority of this change occurs the resistivity appears to be dominated by electron-phonon scattering[106, 112]. Previous computational works have similarly suggested that electron-phonon coupling plays an important role in determining the macroscopic transport properties of WP<sub>2</sub>[113].

An important and related consideration is the phonon-electron scattering, i.e. the scattering of phonons by electrons. Evidence for strong phonon-electron coupling in topological semimetals (TSM) has been primarily reported via optical spectroscopies that directly probe the system's phonons[114–117]. However it remains unclear what combination of factors contribute to the phonon-electron scattering and thus its role in the transport behavior of TSMs. To this end we performed a combined experimental, computational, and theoretical investigation of the phonon-electron coupling in WP<sub>2</sub>. Using Raman spectroscopy, first principles calculations, and symmetry analysis, we provide evidence that phononelectron scattering dominates the linewidth behavior of certain optical phonons over a wide temperature range. The ab-initio calculations further elucidate the roles played by the relative phase space and phonon-electron coupling strength in the dominance of phonon-electron scattering.

### **3.2** Crystal Symmetry and Raman Modes

WP<sub>2</sub> may crystallize in two different structures. The  $\alpha$ -WP<sub>2</sub> phase is centrosymmetric[118], forming in the space group C12/m1 (No. 12). Due to the presence of inversion symmetry the  $\alpha$  phase is topologically trivial, although it does display many of the same defining transport characteristics such as extreme magnetoresistance and high mobility[110] like its toplogical counterpart  $\beta$ -WP<sub>2</sub>[106]. The  $\beta$  phase lacks inversion symmetry, with an orthorhombic unit cell belonging to space group  $Cmc2_1$  (No. 36). In the work presented here we focus exclusively on  $\beta$ -WP<sub>2</sub>.

The unit cell of  $\beta$ -WP<sub>2</sub> (hereafter referred to simply as WP<sub>2</sub>) contains two inequivalent W sites, such that there are six atoms (two W and four P) within the unit cell. This gives rise to a total of 18 phonon branches, of which three are acoustic and the remaining 15 optic. The four classes of symmetry operations in WP<sub>2</sub> mean there are four irreducible representations (for now we ignore the double space group operations). At the  $\Gamma$  point, group theory therefore predicts the 15 optical modes may be identified as[63]:  $5A_1, 3A_2, 2B_1$ , and  $5B_2$ . As discussed shortly, we use the distinct polarization dependence associated with each mode symmetry to assign an irreducible representation to each phonon feature in our Raman spectra.

### 3.3 Polarization Dependent Raman Measurements

Raman spectra were collected in the backscattering configuration using a custom built setup[61]. The 532 nm light from a frequency doubled Nd:YAG laser was focused by a 100X long-working distance objective to a spot size of  $\approx 2 \ \mu m$ in a Montana Instruments cryostation which enabled access to temperatures from 300 to 10 K. An incident power of ;250  $\mu$ W was used to achieve satisfactory signalto-noise ratios, with minimal laser induced heating. This was checked using the Stokes to anti-Stokes ratio at all temperatures where anti-Stokes signal was measurable ( $\gtrsim 100$  K). Any presented spectra have been averaged and had background dark counts subtracted and cosmic rays removed.

To measure the polarization dependence of the Raman modes we rotated a double Fresnel rhomb which was placed in the optical path before the sample,



Figure 3.1: Schematic diagram of the optical setup used to perform the polarization dependent measurements of  $WP_2$ .

such that the light passes through the double rhomb twice, once on the way in and again after reflection from the sample surface. The double Fresnel rhomb acts as a half-wave plate (HWP), rotating the plane of the linear polarization in a manner equivalent to rotation of the sample. The reflected and Raman scattered light then passes through a beam splitter before passing through an analyzing polarizer. A HWP placed before the beam splitter allowed us to select between XX and XY polarizations. A schematic of these optical elements is shown in Figure 3.1.

The polarization dependence of a Raman mode's intensity may be used to determine its irreducible representation. For a given mode, the intensity follows the formula:

$$I \propto |\hat{\mathbf{e}}_s \cdot \mathbf{R} \cdot \hat{\mathbf{e}}_i|^2 \tag{3.1}$$

where  $\hat{\mathbf{e}}_i(\hat{\mathbf{e}}_s)$  are the polarization vectors for the incident (scattered) light, and **R** is the Raman tensor for the phonon mode. The Raman tensors associated with

each of the irreducible representations of  $WP_2$  are [63],

$$A_{1} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$
(3.2)  
$$A_{2} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(3.3)  
$$B_{1} = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}$$
(3.4)  
$$B_{2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix}$$
(3.5)

From the form of these tensors we can see that certain modes will only appear when measured on specific crystal surfaces. For example, the  $A_2$  modes will be observable when light is incident on an *ab*-surface, but absent when measured on an *ac*-surface.

Room temperature Raman spectra of WP<sub>2</sub> in the XX (black) and X'X' (red) polarization configurations are shown in Figure 3.2. In XX there are seven visible modes, while in X'X' there are 11 modes, giving a total of 13 unique modes. The number of modes present in the spectra indicate that the measured crystal surface must not be a simple *ab*, *ac*, or *bc* surface, since at most we would expect ten modes to appear if we measured a *bc* surface (5 $A_1$  and 5 $B_2$ ). To properly describe the polarization dependence of the measured modes we will therefore have to include



Figure 3.2: Room temperature Raman spectra of  $WP_2$  in the XX and X'X' polarization configurations.

rotation matrices which transform the Raman tensors given above.

The effect of the HWP is accounted for by inserting the appropriate Jones matrices into Equation 3.1 such that we obtain:

$$I \propto \left| \hat{\mathbf{e}}_s \cdot \mathbf{H}^{-1} \cdot \mathbf{R} \cdot \mathbf{H} \cdot \hat{\mathbf{e}}_i \right|^2 \tag{3.6}$$

where  $\mathbf{H}$  is

$$\mathbf{H} = \begin{pmatrix} \cos(2\phi) & \sin(2\phi) & 0\\ \sin(2\phi) & -\cos(2\phi) & 0\\ 0 & 0 & 0 \end{pmatrix}$$
(3.7)

and  $\phi$  is the angle the HWP makes with the horizontal. To further account for an

out-of-plane sample rotation we insert the rotation matrix **O**:

$$\mathbf{O} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\alpha) & -\sin(\alpha) \\ 0 & \sin(\alpha) & \cos(\alpha) \end{pmatrix} \begin{pmatrix} \cos(\beta) & 0 & \sin(\beta) \\ 0 & 1 & 0 \\ -\sin(\beta) & 0 & \cos(\beta) \end{pmatrix}$$
$$= \begin{pmatrix} \cos(\beta) & 0 & \sin(\beta) \\ \sin(\alpha)\sin(\beta) & \cos(\alpha) & -\cos(\beta)\sin(\alpha) \\ -\cos(\alpha)\sin(\beta) & \sin(\alpha) & \cos(\alpha)\cos(\beta) \end{pmatrix}$$
(3.8)

where  $\alpha$  accounts for rotations around the *x*-axis, and  $\beta$  for rotations around the *y*-axis. (Rotations about the *z*-axis will merely introduce a phase to the HWP dependence so they are not considered here.) This gives us the final expression:

$$I \propto \left| \hat{\mathbf{e}}_s \cdot \mathbf{H}^{-1} \cdot \mathbf{O}^{-1} \cdot \mathbf{R} \cdot \mathbf{O} \cdot \mathbf{H} \cdot \hat{\mathbf{e}}_i \right|^2$$
(3.9)

The most general expressions obtained from this relation are quite cumbersome, however we found through comparison to our measured spectra that only non-zero values of  $\alpha$  were required to capture the observed polarization dependence. This suggests that the surface measured in Figure 3.2 contains an in-plane *a*-axis, with some out-of-plane *b* and *c* components.

We now derive the explicit forms of the polarization dependence for each of the irreducible representations. We assume that the light is incident along the z-axis such that our polarization vectors are given as:

$$\hat{\mathbf{e}}_s = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix}, \qquad \hat{\mathbf{e}}_i(X) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad \hat{\mathbf{e}}_i(Y) = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$
(3.10)



Figure 3.3: Polarization dependence of the  $\mathrm{WP}_2$  Raman spectra as the Fresnel rhomb is rotated.

We then find, for each of the modes in XX and XY, the relations:

$$I_{XX}(A_1) \propto \frac{1}{16} \left[ \left( (2a+b+c) + (b-c)\cos(2\alpha) \right) + \left( (2a-b-c) - (b-c)\cos(2\alpha) \right)\cos(2\phi) \right]^2 \\ \propto \left[ A + B\cos(2\phi) \right]^2$$
(3.11)  
$$I_{XY}(A_1) \propto \frac{1}{16} \left[ \left( (-2a+b+c) + (b-c)\cos(2\alpha) \right)\sin(2\phi) \right]^2$$

$$\propto \left[C\sin(2\phi)\right]^2\tag{3.12}$$

$$I_{XX}(A_2) \propto \left[d\cos(\alpha)\sin(2\phi)\right]^2 \propto \left[D\sin(2\phi)\right]^2$$
(3.13)

$$I_{XY}(A_2) \propto \left[d\cos(\alpha)\cos(2\phi)\right]^2 \propto \left[D\cos(2\phi)\right]^2$$
(3.14)

$$I_{XX}(B_1) \propto [e\sin(\alpha)\sin(2\phi)]^2 \propto [E\sin(2\phi)]^2$$
(3.15)

$$I_{XY}(B_1) \propto [e\sin(\alpha)\cos(2\phi)]^2 \propto [E\cos(2\phi)]^2$$
(3.16)

$$I_{XX}(B_2) \propto \left[f\sin(2\alpha)\sin^2(\phi)\right]^2 \propto \left[F - F\cos(2\phi)\right]^2 \tag{3.17}$$

$$I_{XY}(B_2) \propto \left[\frac{1}{2}f\sin(2\alpha)\sin(2\phi)\right]^2 \propto \left[F\sin(2\phi)\right]^2$$
(3.18)

In Figure 3.3 we show an example of the polarization dependent spectra obtained from our WP<sub>2</sub> crystals. Spectra were recorded every  $15^{\circ}$  of the incident polarization in both XX and XY (only XX is shown in Figure 3.3) from  $0^{\circ}$  to  $180^{\circ}$ . The mode intensities were extracted, and then the data from  $0^{\circ}$  to  $90^{\circ}$  was symmetrized with the data from  $180^{\circ}$  to  $90^{\circ}$  to remove any variations in intensity produced by the Fresnel rhomb. The symmetrized data were then fit with the expressions derived above to identify the modes symmetry. Where necessary, comparison to density-functional theory (DFT) was also used to assist in symmetry identification.

The symmetrized intensity data and fits are shown in Figures 3.4 through 3.15, with a summary of the mode symmetry assignments in Table 3.1. The predicted assignments agree very well with those identified experimentally. Only one  $B_1$  mode went completely unobserved in all of our measurements, likely due to the mode being too weak to observe.



Figure 3.4: Polarization dependence of the  $A_1(1)$  phonon mode at 22.48 meV as measured on two separate faces (a) and (b).


Figure 3.5: Polarization dependence of the  $A_1(2)/A_2(3)$  phonon mode at 35.84 meV as measured on two separate faces (a) and (b).



Figure 3.6: Polarization dependence of the  $A_1(3)$  phonon mode at 44.89 meV as measured on two separate faces (a) and (b).



Figure 3.7: Polarization dependence of the  $A_1(4)$  phonon mode at 49.60 meV as measured on two separate faces (a) and (b).



Figure 3.8: Polarization dependence of the  $A_1(5)$  phonon mode at 65.00 meV as measured on two separate faces (a) and (b).



Figure 3.9: Polarization dependence of the  $A_2(1)$  phonon mode at 20.37 meV as measured on two separate faces (a) and (b).



Figure 3.10: Polarization dependence of the  $A_2(2)$  phonon mode at 32.38 meV as measured on two separate faces (a) and (b).



Figure 3.11: Polarization dependence of the  $B_1(2)$  phonon mode at 40.47 meV.



Figure 3.12: Polarization dependence of the  $B_2(1)$  phonon mode at 21.50 meV as measured on two separate faces (a) and (b).



Figure 3.13: Polarization dependence of the  $B_2(2)$  phonon mode at 36.96 meV.



Figure 3.14: Polarization dependence of the  $B_2(3)$  phonon mode at 45.84 meV as measured on two separate faces (a) and (b).



Figure 3.15: Polarization dependence of the  $B_2(5)$  phonon mode at 68.90 meV as measured on two separate faces (a) and (b).

The  $A_1$  modes show a greater degree of variation in their polarization dependence between the two measured crystals. This likely results from different angles  $\alpha$  for each of the two crystals, which combined with the three unique tensor elements that enter Eqs. 3.11 and 3.12 can lead to qualitatively different polarization dependencies. The modes of other symmetries have only one unique tensor element and so their polarization dependence can only be scaled in magnitude by different angles  $\alpha$ .

We note that the mode at 35.6 meV displays a unique polarization dependence compared to the other  $A_1$  modes. We found this dependence could be well explained by assuming that this peak actually corresponds to a degeneracy (within our experimental resolution) between the  $A_1(2)$  and  $A_2(3)$  mode. Fitting the response with a sum of the intensity dependence expected from both of these representations gives an excellent fit to the data and we therefore label this mode as  $A_1(2)/A_2(3)$ . This is in slight contrast to a previous Raman work[119] which found the energies of these two modes to be marginally, but measurably different.

Mode	$\omega_{\mathrm{expt.}}$	$\omega_{ m DFT}$
$A_2(1)$	20.37	20.88
$B_{2}(1)$	21.50	21.32
$A_1(1)$	22.48	21.97
$B_{1}(1)$	NA	32.36
$A_{2}(2)$	32.38	32.70
$A_{2}(3)$	35.84	36.38
$A_1(2)$	35.84	37.03
$B_2(2)$	36.96	37.49
$B_1(2)$	40.47	42.33
$A_1(3)$	44.89	45.43
$B_{2}(3)$	45.84	47.76
$A_1(4)$	49.60	52.49
$B_{2}(4)$	55.20	58.07
$A_{1}(5)$	65.00	66.97
$B_2(5)$	68.90	70.54

Table 3.1: Irreducible representations and mode energies identified from experiment. Experimental energies ( $\omega_{expt.}$ ) are compared to predicted values ( $\omega_{DFT}$ ) from theory. All quantities are in meV.

## **3.4** Temperature Dependent Measurements

With the symmetry of each mode now identified, we begin our discussion of the temperature dependence of the Raman spectra. Spectra were recorded from 10 K to 300 K, with temperature steps of 10 K. In an initial round of measurements we also recorded spectra from 8 K to 30 K in steps of 2 K. Figure 3.16 shows the temperature dependent spectra recorded in the XX configuration, while Figure 3.17 shows the spectra in X'X'.



Figure 3.16: Temperature dependence of the  $WP_2$  Raman spectra in XX.



Figure 3.17: Temperature dependence of the  $\mathrm{WP}_2$  Raman spectra in X'X'.

#### 3.4.1 Temperature Dependence of Phonon Energies

Phonon energies will typically decrease as the temperature is raised due to a combination of lattice expansion and anharmonic renormalization[70, 73]. Deviations from this behavior can be possible signs of phonon-electron coupling, and have been observed in other topological semimetal (TSM)s[117]. A previous report observed an anomalous decrease in the mode energies of WP<sub>2</sub> below ~ 25 K[120] which was interpreted as evidence for phonon-electron coupling. In our initial run of temperature dependent measurements we also observed similar behavior. However, in repeat measurements where we allowed more time for the WP<sub>2</sub> crystals to come to thermal equilibrium with the cryostat at each temperature we found that the anomalous changes were no longer present. In Figure 3.18 through 3.22 we show the change in phonon energy from the lowest temperature value as a function of temperature for each set of measurements. As described above, the anomalous changes seen in Trial 1 are not reproduced in Trials 2 or 3. We therefore conclude that such anomalies in the phonon energy are experimental artifacts and not evidence for phonon-electron coupling.



Figure 3.18: Difference in phonon energy from lowest measured temperature value  $(\omega_0)$  as a function of temperature for the  $A_2(1)$ ,  $B_2(1)$ , and  $A_1(1)$  modes.

The quantitative behavior of the phonon energies was extracted by fitting the peaks with Voigt profiles. A Voigt profile is the convolution of a Lorentzian which



Figure 3.19: Difference in phonon energy from lowest measured temperature value  $(\omega_0)$  as a function of temperature for the  $A_2(2)$ ,  $A_1(2)$ , and  $B_2(2)$  modes.



Figure 3.20: Difference in phonon energy from lowest measured temperature value  $(\omega_0)$  as a function of temperature for the  $B_1(2)$ ,  $A_1(3)$ , and  $B_2(3)$  modes.



Figure 3.21: Difference in phonon energy from lowest measured temperature value  $(\omega_0)$  as a function of temperature for the  $A_1(4)$ ,  $B_2(4)$ , and  $A_1(5)$  modes.



Figure 3.22: Difference in phonon energy from lowest measured temperature value  $(\omega_0)$  as a function of temperature for the  $B_2(5)$  mode.

accounts for the intrinsic phonon response and a Gaussian which accounts for the instrument induced broadening. A Gaussian linewidth of 0.217 meV, determined from fitting of the Rayleigh line, was used for the fitting. We then fit the mode energies as a function of temperature using the extended Klemens' model[70, 73]. In Figures 3.23 through 3.27 we show the temperature dependence of each mode, with the red solid lines showing the fitting results. Table 3.2 contains a summary of the fitting results.



Figure 3.23: Phonon energy vs temperature with fits using the extended Klemens' model as red lines for the  $A_2(1)$ ,  $B_2(1)$ , and  $A_1(1)$  modes.



Figure 3.24: Phonon energy vs temperature with fits using the extended Klemens' model as red lines for the  $A_2(2)$ ,  $A_1(2)$ , and  $B_2(2)$  modes.



Figure 3.25: Phonon energy vs temperature with fits using the extended Klemens' model as red lines for the  $B_1(2)$ ,  $A_1(3)$ , and  $B_2(3)$  modes.



Figure 3.26: Phonon energy vs temperature with fits using the extended Klemens' model as red lines for the  $A_1(4)$ ,  $B_2(4)$ , and  $A_1(5)$  modes.



Figure 3.27: Phonon energy vs temperature with fits using the extended Klemens' model as red lines for the  $B_2(5)$  modes

Mode	$\omega_0 \; ({\rm meV})$	C (meV)	D (meV)
$A_{2}(1)$	$20.37 {\pm} 0.01$	$-0.0003215 \pm 0.0073$	$-0.004177 \pm 0.000697$
$B_{2}(1)$	$21.50 {\pm} 0.01$	$0.006153 {\pm} 0.0052$	$-0.006002 \pm 0.000527$
$A_1(1)$	$22.48 \pm 0.01$	$-0.08552 \pm 0.0106$	$-0.004248 \pm 0.0011$
$A_2(2)$	$32.38 {\pm} 0.02$	$0.03723 {\pm} 0.0128$	$-0.01504 \pm 0.0018$
$A_1(2)/A_2(3)$	$35.84 {\pm} 0.02$	$0.04342 {\pm} 0.0192$	$-0.02217 \pm 0.0029$
$B_{2}(2)$	$36.96 {\pm} 0.02$	$0.001872 {\pm} 0.0190$	$-0.01876 \pm 0.0029$
$B_1(2)$	$40.47 {\pm} 0.11$	$-0.00631 \pm 0.1132$	$-0.02334 \pm 0.0184$
$A_1(3)$	$44.89 {\pm} 0.07$	$0.09941{\pm}0.0818$	$-0.03588 \pm 0.0145$
$B_{2}(3)$	$45.84{\pm}0.01$	$-0.1535 \pm 0.0254$	$-0.2303 \pm 0.0045$
$A_1(4)$	$49.60 {\pm} 0.03$	$-0.05144 \pm 0.0363$	$-0.04046 \pm 0.0066$
$B_{2}(4)$	$55.20 {\pm} 0.06$	$-0.3878 \pm 0.0469$	NA
$A_{1}(5)$	$65.00 {\pm} 0.01$	$-0.5474 \pm 0.0102$	NA
$B_2(5)$	$68.90 {\pm} 0.01$	$-0.6249 \pm 0.0062$	NA

Table 3.2: Results of fitting  $WP_2$  phonon energies with the extended Klemens' model

We lastly discuss the percent change of the mode energies as a function of temperature. Figure 3.28 reveals that the  $A_1(1)$  mode changes by nearly 2% from 10 to 300 K, while all the other observed modes change by  $\leq 1\%$ . While this could be a sign of phonon-electron coupling in the  $A_1(1)$  mode, the temperature dependence of phonon energies contains contributions from multiple sources so an unambiguous interpretation is challenging. We therefore turn to the temperature dependence of the phonon linewidths.



Figure 3.28: Percent difference of phonon energies from the lowest temperature value as a function of energy.

### 3.4.2 Temperature Dependence of Phonon Linewidths

The phonon linewidth only contains information related to its available decay paths. The model most often assumed is that the near  $\Gamma$ -point optical phonons probed in Raman spectroscopy decay into acoustic phonons[70, 73]. A schematic of the lowest order such process is shown in Figure 3.29, where an optical phonon of energy  $\omega$  decays into two acoustic phonons with energy  $\omega/2$  and equal but opposite momentum. Due to the bosonic nature of phonons, the temperature dependence of this model is governed by the Bose-Einstein distribution function  $n_B(\omega, T)$ . The linewidths predicted by this model therefore increase monotonically with temperature as the population of phonons increases. In Figure 3.30 we show the linewidths of the three higher energy  $A_1$  modes which all display linewidths consistent with this model. The solid red lines are fits using the extended Klemens' model, and are seen to reproduce the experimental data quite well.



Figure 3.29: A diagram showing the lowest order anharmonic decay process of an optical phonon with energy  $\omega$  decaying into two acoustic phonons with energy  $\omega/2$  and opposite but equal momentum.



Figure 3.30: Temperature dependence of the three higher energy  $A_1$  modes showing behavior consistent with the anharmonic model of decay. Red lines are fits to the data using the extended Klemens' model.

The temperature dependence of the linewidths for the lowest two energy  $A_1$ modes (the  $A_1(1)$  mode at ~ 22.4 meV and the  $A_1(2)$  mode at ~35.8 meV) are plotted in Figure 3.31. In contrast to the behavior seen for the higher energy  $A_1$ modes, the linewidths of these two modes deviate from the prediction of the Klemens' model. For the  $A_1(1)$  mode we see that, at low temperatures below ~50 K, the linewidth has a nearly constant value of 0.36 meV. Above this temperature the linewidth grows rapidly, achieving a maximum value of ~0.65 meV at ~200 K, before slowly decreasing as it approaches room temperature. Though on a smaller scale, the  $A_1(2)$  mode displays similar behavior. In particular, a linewidth that decreases with rising temperature is unable to be explained by a model that assumes decay into bosonic particles. We instead identify the temperature dependence observed in these modes as resulting from decay into electron-hole pairs near the Fermi surface.



Figure 3.31: Temperature dependence of the two lower energy  $A_1$  modes, as well as the  $A_2(2)$  mode which has an energy between the  $A_1$  modes. The two  $A_1$  modes show anomalous linewidths consistent with decay into electron-hole pairs near the Fermi surface, while the  $A_2$  mode shows anharmonic decay. The blue lines are fits using a model of electron-hole pair decay, while the red line is a fit using the extended Klemens' model.

The observation of these anomalous linewidths for only the lower energy  $A_1$ modes suggests that the energy of the phonon plays a role in determining its primary decay paths. We find however, that this alone is not able to explain all of our results. In particular, we note that the  $A_2(2)$  mode at  $\sim 32.3$  meV – an energy between that of the  $A_1(1)$  and  $A_1(2)$  modes – does not display the same phonon-electron dominated linewidth, see Figure 3.31. This suggests that in order to understand why the  $A_1$  modes display these behavior, in addition to the phonon energy we must also consider the symmetry of the phonon. This is further confirmed by noting that none of the other modes of  $A_2$  or  $B_2$  symmetries display anomalous linewidths. The temperature dependence of these mode's linewidths are shown in Figures 3.32 through 3.33, with Table 3.3 summarizing the results of fitting with the extended Klemens' model.



Figure 3.32: Temperature dependence of phonon linewidths for the  $A_2(1)$ ,  $B_2(1)$ , and  $B_2(2)$  modes. Red lines are fits to the data using the extended Klemens' model.



Figure 3.33: Temperature dependence of phonon linewidths for the  $B_1(2)$ ,  $B_2(3)$ , and  $B_2(4)$  modes. Red lines are fits to the data using the extended Klemens' model.



Figure 3.34: Temperature dependence of the  $B_2(5)$  phonon linewidth. The red line is a fit to the data using the extended Klemens' model.

Mode	$\Gamma_0 \;({\rm meV})$	A (meV)	B (meV)
$A_2(1)$	$0.0804 \pm 0.0110$	$0.01825 {\pm} 0.0033$	NA
$B_{2}(1)$	$0.08718 {\pm} 0.0076$	$0.008325 {\pm} 0.0026$	NA
$A_{2}(2)$	NA	$0.06337 {\pm} 0.0062$	$0.01057 {\pm} 0.0016$
$B_{2}(2)$	$0.05661 {\pm} 0.0126$	$0.03363 {\pm} 0.0068$	NA
$B_1(2)$	$0.0524 {\pm} 0.0.0887$	$0.03557 {\pm} 0.0.0512$	NA
$A_1(3)$	NA	$0.2977 {\pm} 0.0135$	$0.01712 {\pm} 0.0053$
$B_{2}(3)$	$0.09723 {\pm} 0.0135$	$0.1469 {\pm} 0.0090$	NA
$A_1(4)$	NA	$0.1301{\pm}0.0026$	NA
$B_{2}(4)$	NA	NA	NA
$A_{1}(5)$	NA	$0.1938 {\pm} 0.0023$	NA
$B_{2}(5)$	$0.03168 {\pm} 0.0154$	$0.1816{\pm}0.0127$	NA

Table 3.3: Results of fitting  $WP_2$  phonon linewidths with the extended Klemens' model

We briefly discuss some of the odd features seen in several of the modes shown here. For the  $A_2(1)$  mode the linewidth appears to saturate above ~200 K in a manner similar to that observed for the  $A_1(1)$  and  $A_1(2)$  linewidths. While this could indicate the influence of phonon-electron decay processes, we found that, within the resolution of our measurements, fitting with the phonon-electron model did not yield a discernible improvement over the Klemens' model. We therefore assume that, while phonon-electron signatures may be present, we cannot resolve them due to the very narrow nature of this mode. Similarly, for the  $B_2(1)$  there is a sudden apparent increase of linewidth around ~200 K which could be taken as an indication of phonon-electron contributions to the linewidth. This apparent upturn however is an artifact of our least-squares fitting algorithm and the fact that this very narrow mode begins to be overlapped by the adjacent broad  $A_1(1)$ mode around 170 K, as may be seen in Figure 3.17. Lastly, for the  $B_1(2)$  and  $B_2(4)$  modes, there are several temperatures at which the linewidths appear to vary wildly. These modes were very weak in our measured spectra and an accurate estimate of the linewidth is therefore challenging. This is also the reason for the significant error bars visible for these modes.

## 3.5 Model of Phonon Decay into Electron-Hole Pairs

Linewidths indicative of optical phonon decay into electron-hole pairs have been observed in a number of semimetals, including TaAs[114, 115], NbAs[114], MoTe<sub>2</sub>[116], graphite[121, 122], and Cd<sub>3</sub>As<sub>2</sub>[117]. The model developed to describe this behavior assumes an optical phonon at the  $\Gamma$  point (q = 0) decays into an electron-hole pair via a vertical, interband transition. The linewidth therefore depends upon the difference in Fermi occupation factors between the initial and final states[123]. The initial state is often assumed to be below the chemical potential  $E_F$ , which leads to a linewidth that monotonically decreases with rising temperature as the occupancy of the electron and hole states approach the same value. This is in contrast to the behavior we observe in our linewidths, see Figure 3.31, so we find that we must modify the model accordingly.

To account for the spin-orbit split bands of WP<sub>2</sub> and the observed linewidth behavior we modify the model from its original version. In its original form the model predicts:  $\Gamma(T) \propto n_F(-\omega_{ph}/2,T) - n_F(\omega_{ph}/2,T)$ , where  $n_F(\omega,T)$  is the Fermi-Dirac distribution function, and the first (second) term refers to the hole (electron) state. We instead alter this to read as:  $\Gamma(T) \propto n_F(\omega_a,T) - n_F(\omega_a +$ 



Figure 3.35: Diagram depicting interband (pink arrow) and intraband (blue arrow) transitions by optical phonons. An energy  $\hbar \omega_a$  separates the initial state from the chemical potential  $E_F$ . The electronic energy bands are labeled by irreducible representations  $\Gamma^i$  and  $\Gamma^j$ , while the optical phonon has representation  $\Gamma^k$ . A transition is symmetry allowed only if  $\Gamma^k$  is contained in the direct product of the band representations.

 $\omega_{ph}, T$ ), where  $\omega_{ph}$  is the energy of the optical phonon and  $\omega_a$  represents the energy difference between the chemical potential and initial electron state. A schematic of the states and transitions involved is shown in Figure 3.35. The inclusion of the  $\omega_a$  term allows for the initial electronic state to be unoccupied at low temperatures. As the temperature is increased, thermal population of the state leads to a turning-on of the decay process and an increase in the linewidth. At yet higher temperatures the behavior returns to that of the original model and the linewidth decreases as a function of temperature. Fits to the linewidths using this model are shown as solid blue lines in Figure 3.31, and can be seen to reproduce the data very well. From the fitting we find  $\omega_a$  values of 24.48 ± 0.61 meV and 22.64 ± 1.73 meV for the  $A_1(1)$  and  $A_1(2)$  modes respectively. The magnitudes of the  $\omega_a$  are consistent with the assumption of our model that the transitions are occurring close to the chemical potential (on an energy scale of the optical phonons). A summary of the fitting results may be found in Table 3.4.

Mode	$\Gamma_0 \;({\rm meV})$	F (meV)	$\omega_a \; (\mathrm{meV})$
$A_1(1)$	$0.3686 {\pm} 0.0022$	$2.001{\pm}0.058$	$24.48 \pm 0.61$
$A_1(2)$	$0.2849 {\pm} 0.0028$	$0.6261 {\pm} 0.0495$	$22.64{\pm}1.73$

Table 3.4: Results of fitting WP<sub>2</sub> phonon linewidths with the electron-hole decay model,  $\Gamma(T) = \Gamma_0 + F(n_F(\omega_a, T) - n_F(\omega_a + \omega_{ph}, T)).$ 

# 3.6 Electronic Band Structure and Phonon Transition Density of States

We now examine the role played by the phonon energy in determining its linewidth behavior. In Figure 3.36 we show the calculated band structure of  $WP_2$ within  $\pm 1$  eV of the Fermi level, which agrees well with previous work |25, 113|. Along the  $\Sigma$  ( $\Gamma \to \Sigma_0$ ),  $\Delta$  ( $\Gamma \to Y$ ), and C ( $Y \to C_0$ ) cuts the gaps between neighboring bands appear to be on an energy scale similar to the optical phonons. To explicitly confirm the presence of such gaps, we calculated the low temperature, weighted JDOS for vertical (q = 0) transitions between states within an (largest) optical phonon energy  $(\pm 70 \text{ meV})$  of the Fermi level. The results of this calculation are shown in Figure 3.37, and reveal that available transitions exist across the entire optical phonon energy range, with the largest JDOS occurring between 40 and 60 meV. The  $A_1$  modes that display phonon-electron dominated linewidths have energies of 22.4 and 35.8 meV, which have a comparatively smaller JDOS. In contrast, the higher energy  $A_1$  modes that fall in the 40–60 meV range have linewidths that are dominated by phonon-phonon decay, which suggests that the availability of electronic states is not the largest contributing factor to understanding the phonon linewidths. As we discuss later, while energy conservation does play a role, we must also consider the role of momentum conservation.



Figure 3.36: The calculated band structure of WP<sub>2</sub> along high symmetry lines. The yellow shaded regions indicate cuts where transitions by  $\Gamma$  point optical phonons are allowed.



Figure 3.37: Weighted JDOS for vertical (q = 0) transitions between electronic states within  $\pm 70$  meV of the chemical potential.

## 3.7 Selection Rules for Phonon Scattering

#### 3.7.1 Wave Vector Conservation

We noted earlier that phonons of  $A_1$  and  $A_2$  symmetries display markedly different linewidth dependencies, despite occurring in the same energy range. We now evaluate the selection rules for phonon scattering by electronic energy bands to determine if there is a symmetry based reason why certain modes display anomalous linewidths and others do not. Our first step in accomplishing this is to establish which symmetry lines and points in the electronic BZ permit scattering by zone center optical phonons. We may organize wave vectors in the BZ by identifying which wave vectors are equivalent to one another under the symmetry operations of the crystal. A group of equivalent such wave vectors is called the "star" of the wave vector, and in WP<sub>2</sub> there are 19 distinct stars that may be identified[63]. Some of these represent specific points of symmetry, such as the  $\Gamma = (0, 0, 0)$  point, while others represent lines of symmetry, such as the  $\Sigma = (k, 0, 0)$  line. Scattering events typically take a particle with one wave vector into a new wave vector, with momentum conservation dictating which wave vectors may be related. The problem of identifying which symmetry lines and points allow scattering by  $\Gamma$  point phonons therefore becomes one of establishing which products contain the star of  $\Gamma$ . However, in a crystal lattice momentum is only conserved up to a reciprocal lattice vector, so care must be taken when identifying which star a wave vector belongs to.

The wave vector selection rules for the direct product of two stars may be established by evaluating the sum of each element of the first star with each element of the second star[124]. The resulting set of wave vectors consists of an integer number of complete and distinct stars. We provide an example of one such calculation below for the direct product of  $\Sigma = (k, 0, 0)$  with  $\Sigma' = (k', 0, 0)$  in WP<sub>2</sub>.

$$(k',0,0) (-k',0,0)$$

$$(k,0,0) (k+k',0,0) (k-k',0,0)$$

$$(-k,0,0) (-(k-k'),0,0) (-(k+k'),0,0)$$

From this table it is clear that there are two stars which arise from wave vector conservation:  $\Sigma'' = (k + k', 0, 0)$  and  $\Sigma''' = (k - k', 0, 0)$ . In the limit that  $k' \to k$ we note that we recover  $\Sigma''' \to \Gamma$ , and we therefore identify the  $\Sigma$  line as having the potential for scattering by  $\Gamma$  point phonons.

In the following table we enumerate some of the wave vector selection rules for the various stars in WP<sub>2</sub>. This table is not comprehensive, it leaves out many potential combinations that will not produce  $\Gamma$  or near- $\Gamma$  phonons. However since we are investigating phonons produced by Raman scattering which satisfy these limited criteria we will not require additional selection rules. For reading this table, we use the notation developed by Birman *et al.*[124] where the two wave vectors A and B involved in the direct product are represented by the bra  $\langle AB|$ , while the stars C contained in their direct product are denoted as kets  $|C\rangle$ . The number  $\langle AB|C\rangle = N$  indicates how many times the star C appears in the direct product of A and B.

Table 3.5: Wave vector selection rules

$\langle \Gamma \Gamma   \Gamma \rangle = 1$		$\langle \mathrm{EE}'   \Sigma'' \rangle = 1$	$\Sigma'' = (k + k', 0, 0)$
$\langle YY \Gamma \rangle = 1$		$\langle \mathrm{EE'} \Sigma'''\rangle = 1$	$\Sigma''' = (k - k', 0, 0)$
$\langle ZZ \Gamma \rangle = 1$		$\langle MM'   M'' \rangle = 1$	$M'' = (k_1 + k'_1, 0, k_2 + k'_2)$
$\langle \Lambda \Lambda'   \Lambda'' \rangle = 1$	$\Lambda'' = (0, 0, k+k')$	$\langle MM'   M''' \rangle = 1$	$M''' = (k_1 - k'_1, 0, k_2 + k'_2)$
$\langle TT \Gamma \rangle = 1$		$\langle NN'   M'' \rangle = 1$	$M'' = (k_1 + k'_1, 0, k_2 + k'_2)$
$\langle HH'   \Lambda'' \rangle = 1$	A'' = (0, 0, k + k')	$\langle NN'   M''' \rangle = 1$	$M''' = (k_1 - \vec{k_1}, 0, k_2 + \vec{k_2})$
$\langle SS \Gamma \rangle = 2$		$\langle \Delta \Delta'   \Delta'' \rangle = 1$	$\Delta'' = (0, k + k', 0)$
$\langle SS Y \rangle = 2$		$\langle \Delta \Delta'   \Delta''' \rangle = 1$	$\Delta''' = (0, k - k', 0)$
$\langle RR   \Gamma \rangle = 2$		$\langle BB'   \Delta'' \rangle = 1$	$\Delta'' = (0, k + k', 0)$
$\langle RR   Y \rangle = 2$		$\langle BB'   \Delta''' \rangle = 1$	$\Delta''' = (0, k - k', 0)$
$\langle DD'   \Lambda'' \rangle = 2$	A'' = (0, 0, k + k')	$\langle \mathbf{K}\mathbf{K}' \mathbf{K}''\rangle = 1$	$K'' = (0, k_1 + k'_1, k_2 + k'_2)$
$\langle DD'   H'' \rangle = 2$	H'' = (0, 1, k + k')	$\langle \mathbf{K}\mathbf{K}'   \mathbf{K}''' \rangle = 1$	$\mathbf{K}''' = (0, k_1 - k_1', k_2 + k_2')$
$\langle \Sigma \Sigma'   \Sigma'' \rangle = 1$	$\Sigma'' = (k + k', 0, 0)$	$\langle (GP)(GP') GP'' \rangle = 1$	$GP'' = (k_1 + k'_1, k_2 + k'_2, k_3 + k'_3)$
$\langle \Sigma \Sigma'   \Sigma''' \rangle = 1$	$\Sigma''' = (k - k', 0, 0)$	$\langle (GP)(GP') GP''' \rangle = 1$	$GP''' = (k_1 - k'_1, k_2 - k'_2, k_3 + k'_3)$
$\langle \mathrm{CC}'   \Sigma'' \rangle = 1$	$\Sigma'' = (k + k', 0, 0)$	$\langle (GP)(GP') GP'''' \rangle = 1$	$GP''' = (k_1 + k'_1, k_2 - k'_2, k_3 + k'_3)$
$\langle CC'   \Sigma''' \rangle = 1$	$\Sigma''' = (k - k', 0, 0)$	$\langle (GP)(GP') GP'''''\rangle = 1$	$GP'''' = (k_1 - k'_1, k_2 + k'_2, k_3 + k'_3)$
$\langle AA'   \Sigma'' \rangle = 1$	$\Sigma'' = (k + k', 0, 0)$		
$\langle AA'   \Sigma''' \rangle = 1$	$\Sigma''' = (k - k', 0, 0)$		
$\overline{\langle \Sigma(\mathrm{GP}) \mathrm{GP'}\rangle} = 1$	$GP' = (k_1 + k'_1, k_2, k_3)$	$\langle \Delta(\mathrm{GP})   \mathrm{GP'} \rangle = 1$	$GP' = (k_1, k_2 + k'_2, k_3)$
$\langle \Sigma(\mathrm{GP})   \mathrm{GP}'' \rangle = 1$	$GP'' = (k_1 - k'_1, k_2, k_3)$	$\langle \Delta(\mathrm{GP})   \mathrm{GP}'' \rangle = 1$	$GP' = (k_1, k_2 - k_2', k_3)$
$\langle C(GP) GP'\rangle = 1$	$GP' = (k_1 + k'_1, 1 + k_2, k_3)$		
$\langle C(GP)   GP'' \rangle = 1$	$GP'' = (k_1 - k'_1, 1 + k_2, k_3)$		
		•	•

We find that 18 of these selection rules either explicitly contain  $\Gamma$  or reduce to  $\Gamma$  in the limit that  $k' \to k$ . We further reduce these 18 by comparing these cuts to the Fermi surface of WP<sub>2</sub> to identify which cuts will have possible electronic transitions by optical phonons. There are three symmetry lines,  $\Sigma$ ,  $\Delta$ , and C, as well as a subset of the general k-points GP. For these four we will evaluate the direct product of their allowed representations.

### 3.7.2 Direct Product Reduction Coefficients

The selection rules for electronic transitions may be found by decomposing the direct product:

$${}^{\star}\Gamma_n^{(i)}(\mathbf{k}) \otimes {}^{\star}\Gamma_m^{(j)}(\mathbf{k}') \tag{3.19}$$

where  ${}^{*}\Gamma_{n}^{(i)}(\mathbf{k})$  is the *i*th irreducible representation in the full group representation of the star of the wave vector  $\mathbf{k}$ , associated with band *n*. A phonon induced transition between bands is allowed only for phonons with irreducible representation  ${}^{*}\Gamma^{(k)}$  contained in the above decomposition, i.e, if

$${}^{\star}\Gamma^{(k)}(\mathbf{k}-\mathbf{k}') \subset {}^{\star}\Gamma^{(i)}_{n}(\mathbf{k}) \otimes {}^{\star}\Gamma^{(j)}_{m}(\mathbf{k}')$$
(3.20)

To evaluate direct products between irreducible representations at different wave vectors we use the full-group method developed by J. Birman *et. al.*[124, 125] The characters for the full-group representations were found by consulting the Bilbao Crystallographic Server[63]. We will go through one explicit example of the direct inspection method, the other results may be found through similar means and are summarized in Table 3.7.

In the character table below the rows are labeled by irreducible representations at the  $\Gamma$  and  $\Sigma$  points, with the columns corresponding to the various symmetry operations of the double space group  $Cmc2_1$ . The final column is a combined mirror and translation operation which will be discussed in more detail shortly. For now, it is important just to note that the translation is along the same direction as  $\Sigma$ . The last five rows correspond to direct products of representations from  $\Sigma$ . To identify the irreducible representations contained in these direct products we assign a coefficient to each representation contained in the direct product (in this case,  $\Gamma$  and  $\Sigma$  representations are allowed). We then construct equations from the columns of the character table, as well as from the wave vector selection rules until we have enough linearly independent equations to solve for the various coefficients. Let us carry out this procedure for the direct product  $*\overline{\Sigma}^{(3)} \otimes *\overline{\Sigma}^{(3)}$ . Recalling the wave vector selection rules for  $\Sigma$  (and noting that here we have for simplicity set

	$\{\varepsilon 0\}$	$\{\delta_{2z} (0,0,1/2)\}$	$\{\rho_y (0,0,1/2)\}$	$\{\rho_x 0\}$	$\{\mathcal{R} 0\}$	$\{\rho_y   \mathbf{t}_1 + (0, 0, 1/2)\}$
$\Gamma^{(1)}$	1	1	1	1	1	1
$\Gamma^{(2)}$	1	1	-1	-1	1	-1
$\Gamma^{(3)}$	1	-1	-1	1	1	-1
$\Gamma^{(4)}$	1	-1	1	-1	1	1
$\overline{\Gamma}^{(5)}$	2	0	0	0	-2	0
$*\Sigma^{(1)}$	2	0	2	0	2	$2\cos(k)$
$*\Sigma^{(2)}$	2	0	-2	0	2	$-2\cos(k)$
$*\overline{\Sigma}^{(3)}$	2	0	0	0	-2	$2\sin(k)$
$\star \overline{\Sigma}^{(4)}$	2	0	0	0	-2	$-2\sin(k)$
${}^{\star}\varSigma^{(1)} \otimes {}^{\star}\varSigma^{(1)}$	4	0	4	0	4	$2 + 2\cos(2k)$
${}^{\star}\varSigma^{(1)} \otimes {}^{\star}\varSigma^{(2)}$	4	0	-4	0	4	$-2 - 2\cos(2k)$
${}^{\star}\overline{\varSigma}{}^{(3)} \otimes {}^{\star}\overline{\varSigma}{}^{(3)}$	4	0	0	0	4	$2 - 2\cos(2k)$
$^{\star}\overline{\varSigma}^{(3)}\otimes ^{\star}\overline{\varSigma}^{(4)}$	4	0	0	0	4	$-2 + 2\cos(2k)$
$\overline{\Sigma}^{(4)} \otimes \overline{\Sigma}^{(4)}$	4	0	0	0	4	$2-2\cos(2k)$

Table 3.6: Character table of full group representations for  $\Gamma$ ,  $\Sigma$ , and direct products of irreducible representations from  $\Sigma$ .

k = k') we have:

$$^{\star}\Sigma \otimes ^{\star}\Sigma = 2\Gamma \oplus ^{\star}\Sigma \tag{3.21}$$

This equation informs us that the total dimensionality of the  $\Gamma$  representations contained in this direct product will be two, while that from  $*\Sigma$  will be one. In terms of coefficients, this becomes:

$$g_1 + g_2 + g_3 + g_4 + 2g_5 = 2 \tag{3.22}$$

$$2s_1 + 2s_2 + 2s_3 + 2s_4 = 2 \tag{3.23}$$

where the  $g_i$   $(s_j)$  are coefficients corresponding to the  $\Gamma$   $(\Sigma)$  representations. The coefficients of 2 for  $g_5$ , and the  $s_i$  arise due to each of these representations being two dimensional. (The 2 on the right hand side of Eq. 3.21 arises for the same reason.) In principle, we now require seven additional linearly independent equations to uniquely solve for the coefficients. We will find however, that this number will not be required. The equations found from the columns of the character table are:

$$g_1 + g_2 - g_3 - g_4 = 0 \tag{3.24}$$

$$g_1 - g_2 - g_3 + g_4 + 2s_1 - 2s_2 = 0 (3.25)$$

$$g_1 - g_2 + g_3 - g_4 = 0 \tag{3.26}$$

$$g_1 + g_2 + g_3 + g_4 - 2g_5 + 2s_1 + 2s_2 - 2s_3 - 2s_4 = 4$$
(3.27)

(for now we will not use the final column). We now have six linearly independent equations, and nine unknown coefficients. By comparison of Eqs. 3.22, 3.23 and 3.27 it is clear that we can set  $g_5 = s_3 = s_4 = 0$ , since the coefficients by definition must be positive or zero. This leaves us with three equations and six unknown coefficients. The other equations must be found from combination rotation and translation operations. One such example is in the last column of the table from which we find:

$$g_1 - g_2 - g_3 + g_4 + 2\cos(k)s_1 - 2\cos(k)s_2 + 2\sin(k)s_3 - 2\sin(k)s_4 = 2 - 2\cos(2k)$$
(3.28)

An important thing to note in this equation is that, exact arithmetic agreement will not occur, since factors of 2k appear in the argument of the cosine function on the right hand side, while only k appears on the left hand side. However, this is to be expected, since the  $*\Sigma$  that enter the decomposition of the direct product are those at 2k and not at the original k. We may therefore treat the 2k and k as "equivalent" for the purposes of characters. (One has to be more careful when not considering k = k' and pay attention to whether it is k + k' or k - k' that is the argument of a given function.) With this final equation, our reduction problem is now trivial. From this equation alone it is clear that  $g_1 = g_4 = 1$  and  $s_2 = 1$ , while all other coefficients are zero. The other direct products may be solved through identical means. In many cases, as with the one we worked out explicitly, visual inspection of the character table will yield the coefficients without explicit arithmetic. This is particularly true if one evaluates the characters for combined rotation and symmetry operations as in the last column of the above table.

Table 3.7 summarizes the direct products and decompositions relevant to our results. The leftmost column indicates whether the transition represented by the direct product in the second column is interband or intraband, while the third column presents the decomposition of the direct product and establishes which phonons may facilitate such a transition. The labeling of these direct products as corresponding to inter- or intra-band is valid here since we only consider transitions on the energy scale of the optical phonons. The final column considers the limit where  $k \to k'$  (i.e.  $q \to 0$ ) which indicates which  $\Gamma$  point phonons are capable of interband or intraband transitions, though in the case of intraband transitions it is more accurate to say the  $\Gamma$  point representation for a given phonon branch.

Considering interband transitions first, we find from the last column of Table 3.7 that phonons of  $\Gamma^{(2)}, \Gamma^{(3)}$ , or  $\Gamma^{(4)}(A_2, B_2, \text{ or } B_1 \text{ respectively})$  representations are capable of producing interband transitions, while  $\Gamma^{(1)}(A_1)$  phonons are forbidden. For intraband transitions we instead find that  $\Gamma^{(1)}(A_1)$  phonon branches are permitted, along with  $\Gamma^{(3)}$  and  $\Gamma^{(4)}$  branches.

Transition Type	Direct Product	Decomposition	Limit $k \to k', \ (q \to 0)$
Interband	$\overline{\Sigma}^{(3)}(k,0,0)\otimes\overline{\Sigma}^{(4)}(k',0,0)$	$\Sigma^{(1)}(k+k',0,0) \oplus \Sigma^{(2)}(k-k',0,0)$	$\Sigma^{(1)}(2k,0,0)\oplus\Gamma^{(2)}\oplus\Gamma^{(3)}$
	$\overline{\Delta}^{(3)}(0,k,0)\otimes\overline{\Delta}^{(4)}(k',0,0)$	$\Delta^{(1)}(0, k + k', 0) \oplus \Delta^{(2)}(0, k - k', 0)$	$\Delta^{(1)}(0,2k,0)\oplus\Gamma^{(2)}\oplus\Gamma^{(4)}$
	$\overline{\mathrm{C}}^{(3)}(k,1,0)\otimes\overline{\mathrm{C}}^{(4)}(k',1,0)$	$\Sigma^{(1)}(k+k',0,0) \oplus \Sigma^{(2)}(k-k',0,0)$	$\Sigma^{(1)}(2k,0,0)\oplus\Gamma^{(2)}\oplus\Gamma^{(3)}$
Intraband	$\overline{\Sigma}^{(3)}(k,0,0)\otimes\overline{\Sigma}^{(3)}(k',0,0)$	$\Sigma^{(2)}(k+k',0,0) \oplus \Sigma^{(1)}(k-k',0,0)$	$\Sigma^{(2)}(2k,0,0)\oplus\Gamma^{(1)}\oplus\Gamma^{(4)}$
	$\overline{\Sigma}^{(4)}(k,0,0)\otimes\overline{\Sigma}^{(4)}(k',0,0)$	$\Sigma^{(2)}(k+k',0,0) \oplus \Sigma^{(1)}(k-k',0,0)$	$\Sigma^{(2)}(2k,0,0) \oplus \Gamma^{(1)} \oplus \Gamma^{(4)}$
	$\overline{\Delta}^{(3)}(0,k,0)\otimes\overline{\Delta}^{(3)}(0,k',0)$	$\Delta^{(2)}(0, k + k', 0) \oplus \Delta^{(1)}(0, k - k', 0)$	$\Delta^{(2)}(0,2k,0)\oplus\Gamma^{(1)}\oplus\Gamma^{(3)}$
	$\overline{\Delta}^{(4)}(0,k,0)\otimes\overline{\Delta}^{(4)}(0,k',0)$	$\Delta^{(2)}(0, k + k', 0) \oplus \Delta^{(1)}(0, k - k', 0)$	$\Delta^{(2)}(0,2k,0)\oplus\Gamma^{(1)}\oplus\Gamma^{(3)}$
	$\overline{\mathbf{C}}^{(3)}(k,1,0)\otimes\overline{\mathbf{C}}^{(3)}(k',1,0)$	$\Sigma^{(2)}(k+k',0,0) \oplus \Sigma^{(1)}(k-k',0,0)$	$\Sigma^{(2)}(2k,0,0) \oplus \Gamma^{(1)} \oplus \Gamma^{(4)}$
	$\overline{\mathrm{C}}^{(4)}(k,1,0)\otimes\overline{\mathrm{C}}^{(4)}(k',1,0)$	$ \Sigma^{(2)}(k+k',0,0) \oplus \Sigma^{(1)}(k-k',0,0) $	$\Sigma^{(2)}(2k,0,0) \oplus \Gamma^{(1)} \oplus \Gamma^{(4)}$

Table 3.7: Direct product decompositions

We also evaluate the direct products that involve wave vectors from different stars, and the direct product for wave vectors of no special symmetry, i.e. general k-points, GP. These direct products describe scattering events which may take an electron on or off a specific line of symmetry, or which occur at a general location in the BZ respectively. A general k-point respects only the identity operation, so there will be only one possible irreducible representation, or two when considering the double group space group. As a result, the selection rules for inter- and intraband transitions will be the same for any direct product that involves a general k-point. Since most of the Fermi surface in WP<sub>2</sub> exists at general k-points, we expect the selection rules derived here to describe most of the phonon mediated electronic transitions.

Table 3.8: Direct product decompositions with general k-points

Transition Type	Direct Product	Decomposition
Both	$\overline{\Sigma}^{(3)}(k,0,0)\otimes \overline{\operatorname{GP}}^{(2)}(k_1',k_2',k_3')$	$\mathrm{GP}^{(1)}(k_1'+k,k_2',k_3')\oplus\mathrm{GP}^{(1)}(k_1'-k,k_2',k_3')$
	$\overline{\Sigma}^{(4)}(k,0,0)\otimes \overline{\mathrm{GP}}^{(2)}(k_1',k_2',k_3')$	${ m GP}^{(1)}(k_1'+k,k_2',k_3')\oplus { m GP}^{(1)}(k_1'-k,k_2',k_3')$
	$\overline{\Delta}^{(3)}(0,k,0)\otimes \overline{\mathrm{GP}}^{(2)}(k_1',k_2',k_3')$	$\mathrm{GP}^{(1)}(k_1',k_2'+k,k_3')\oplus\mathrm{GP}^{(1)}(k_1',k_2'-k,k_3')$
	$\overline{\Delta}^{(4)}(0,k,0)\otimes \overline{\operatorname{GP}}^{(2)}(k_1',k_2',k_3')$	$\mathrm{GP}^{(1)}(k_1'+k,k_2',k_3')\oplus\mathrm{GP}^{(1)}(k_1'-k,k_2',k_3')$
	$\overline{\mathbf{C}}^{(3)}(k,1,0)\otimes\overline{\mathbf{GP}}^{(2)}(k_1',k_2',k_3')$	$\mathrm{GP}^{(1)}(k_1'+k,1+k_2',k_3')\oplus\mathrm{GP}^{(1)}(k_1'-k,1+k_2',k_3')$
	$\overline{\mathrm{C}}^{(4)}(k,1,0)\otimes\overline{\mathrm{GP}}^{(2)}(k_1',k_2',k_3')$	$\mathrm{GP}^{(1)}(k_1'+k,1+k_2',k_3')\oplus\mathrm{GP}^{(1)}(k_1'-k,1+k_2',k_3')$
	$\overline{\operatorname{GP}}^{(2)}(k_1, k_2, k_3) \otimes \overline{\operatorname{GP}}^{(2)}(k_1', k_2', k_3')$	$\mathrm{GP}^{(1)}(k_1 + k_1', k_2 + k_2', k_3 + k_3') \oplus \mathrm{GP}^{(1)}(k_1 - k_1', k_2 - k_2', k_3 + k_3')$
		$\oplus$ GP <sup>(1)</sup> $(k_1 + k'_1, k_2 - k'_2, k_3 + k'_3) \oplus$ GP <sup>(1)</sup> $(k_1 - k'_1, k_2 + k'_2, k_3 + k'_3)$

Table 3.8 shows the decompositions of the direct products described above. Since the electronic bands are described only by additional representations introduced by the double group, we only show the direct products involving these representations. We find that for all of the direct products considered here the decomposition contains the irreducible representation  $GP^{(1)}$ . This irreducible representation is the only possible representation for phonons at general k-points. As such, we find that any phonon branch is capable of facilitating inter- or intraband transitions of these types. As discussed above in regards to Table 3.7, these selection rules are more restrictive when only considering scattering along lines of symmetry. We therefore conclude that both interband and intraband scattering likely contribute to the observed linewidth behavior of the  $A_1$  modes, and that another feature besides mode symmetry must be found to explain the lack of observed anomalies in modes of other symmetries. Further, per these selection rules, only interband transitions with  $q \neq 0$  are possible for the  $A_1$  phonons, so we turn our attention to determining whether momentum conservation may be satisfied under our experimental conditions.

## 3.8 Momentum Conservation

For interband phonon decay into electron-hole pairs the momentum and energy conservation is trivially satisfied. As shown in Figure 3.37, interband transitions with q = 0 exist across the entire range of optical phonon energies. Interband transitions with  $q \approx 0$  will therefore have a very similar phase space. For intraband scattering we explicitly estimate both the momentum provided by the photons and the momentum required for the electronic transition. We first assume that, near the Fermi energy, the electronic bands are approximately linear[126], with a slope given by the experimentally measured Fermi velocities[111]. The change in energy and momentum are then related by the expression:

$$\Delta E = \hbar v_F \Delta k \tag{3.29}$$

where  $v_F$  is the Fermi velocity. The Fermi velocities for the different electron and hole pockets have been reported[111] as  $v_{F,\alpha} = 1.46 \times 10^5$  m/s,  $v_{F,\beta} = 1.47 \times 10^5$  m/s,  $v_{F,\gamma} = 3.78 \times 10^5$  m/s, and  $v_{F,\delta} = 3.97 \times 10^5$  m/s. The  $\alpha$  and  $\beta$  pockets intersect the  $\Sigma$  cut, while the  $\gamma$  and  $\delta$  pockets intersect  $\Delta$ , and C. We calculate the momentum required for each pocket separately.

For the  $A_1(1)$  phonon, which has energy ~22.4 meV, we find using Eq. 3.29 the required momenta:  $\Delta k_{\alpha} = 2.33 \times 10^8 \text{ m}^{-1}$ ,  $\Delta k_{\beta} = 2.32 \times 10^8 \text{ m}^{-1}$ ,  $\Delta k_{\gamma} =$   $9.00 \times 10^7 \text{ m}^{-1}$ , and  $\Delta k_{\delta} = 8.57 \times 10^7 \text{ m}^{-1}$ . Repeating this calculation for the  $A_1(2)$  phonon, which has energy ~35.8 meV, we obtain:  $\Delta k_{\alpha} = 3.76 \times 10^8 \text{ m}^{-1}$ ,  $\Delta k_{\beta} = 3.70 \times 10^8 \text{ m}^{-1}$ ,  $\Delta k_{\gamma} = 1.44 \times 10^8 \text{ m}^{-1}$ , and  $\Delta k_{\delta} = 1.37 \times 10^8 \text{ m}^{-1}$ .

We next determine the momentum provided by the laser to the phonons. In the backscattering configuration the transferred momentum is found as:

$$q \le 2\frac{2\pi n_i(\lambda)}{\lambda} \tag{3.30}$$

where  $n_i(\lambda)$  is the wavelength dependent index of refraction along the *i*th crystal direction, and  $\lambda$  is the wavelength of the optical excitation. The optical constants of WP<sub>2</sub> have yet to be experimentally reported, so we used values obtained from first principles calculations.

The index of refraction may be calculated from the dielectric function as

$$n = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}} \tag{3.31}$$

where  $\varepsilon_1(\varepsilon_2)$  is the real (imaginary) part of the dielectric function. The dielectric function was calculated from first principles using the methods outlined in Refs. [127–129]. In Figure 3.38 we show the calculated room temperature dielectric function along each crystallographic direction as a function of energy. A vertical dashed line is drawn at 2.33 eV (532 nm), corresponding to the energy of the laser used in our experiments. In Figure 3.39 the indices of refraction calculated for each crystallographic direction are shown, with values at 2.33 eV of  $n_a = 3.11$ ,  $n_b = 3.59$ , and  $n_c = 4.10$ .



Figure 3.38: Imaginary (i-iii) and real (iv-vi) parts of the complex dielectric function along the a (i,iv), b (ii,v), and c (iii,vi) crystallographic directions at T= 298 K. The vertical dotted line is drawn at  $\hbar\omega = 2.33$  eV, which is the energy of the laser used in our experiments.



Figure 3.39: Index of refraction along a (i), b (ii), and c (iii) crystallographic directions at T = 298 K. The vertical dotted line is drawn at  $\hbar\omega = 2.33$  eV., which is the energy of the laser used in our experiments.

Using Eq. 3.30 we find for the different crystal axes:  $q_a = 7.35 \times 10^7 \text{ m}^{-1}$ ,  $q_b = 8.48 \times 10^7 \text{ m}^{-1}$ , and  $q_c = 9.68 \times 10^7 \text{ m}^{-1}$ . We therefore see that, for light incident along the *c*-axis, which corresponds to the XX polarization configuration of our

measurements, the incident radiation is capable of providing enough momentum for  $A_1$  phonons to produce intraband transitions. It does however fall short for the  $A_1(2)$  phonon which suggests that while both interband and intraband processes may be available for the  $A_1(1)$  phonon, only interband processes are available for the  $A_1(2)$  phonon. Regardless, it is clear that the momentum necessary for an intraband transition by the higher energy  $A_1$  modes, which we estimate would have a minimum value of  $q \approx 1.71 \times 10^8 \text{ m}^{-1}$ , is unable to be provided by the laser, and thus only interband transitions may contribute to the phonon-electron component of their linewidths.

## 3.9 Phonon-Electron Coupling Strengths

The  $A_2$ ,  $B_1$ , and  $B_2$  representations all appear in one form or another in the selection rules derived above, yet their experimentally measured linewidths display no anomalous behavior. We therefore inspect the mode resolved phonon-electron coupling strength, calculated from first principles. Figure 3.40 shows the calculated phonon dispersion of WP<sub>2</sub>, with the effective normalized phonon-electron matrix element projected onto each mode. The acoustic branches display an overall greater coupling, while the optical modes show the largest coupling along the  $\Delta$  and T to Y to Z cuts. These cuts correspond to phonon wave vectors that connect separate parts of the Fermi surface[114].



Figure 3.40: The calculated phonon dispersion of  $WP_2$  with the correction to the imaginary part of the phonon self-energy due to phonon-electron coupling projected onto each mode.

To better understand the behavior of the modes observed in our measurements we show a close up of the phonon dispersion along the  $\Sigma$  and  $\Delta$  cuts in Figure 3.41. In this figure the coupling strength for the acoustic modes is not shown to better reveal the trends of the optic modes. At q = 0 the phonon-electron coupling strength for all optic modes is very weak, with most modes displaying a |g| on the order of 0.1 meV. This comparatively weak coupling suggests that interband transitions with q = 0 do not represent a significant source of phonon-electron scattering. For finite q we observe that, for the lower energy  $A_1(1)$  and  $A_1(2)$ modes, the coupling strength increases by an order of magnitude, while for the higher energy modes the increase in coupling strength is not as dramatic. Despite showing similar increases in coupling strength, the  $A_2(1)$  and  $B_2(1)$  modes do not display a clear phonon-electron contribution to their linewidths. This suggests that for modes of these symmetries the connection between higher phonon-electron coupling and linewidth behavior is less clear. Overall, noting that such finite q is within our experimentally accessible range, we find these trends in the coupling strength to be consistent with our measurements and interpretation of the phonon linewidths.



Figure 3.41: A zoomed in view of the phonon-electron coupling strength for small q near  $\Gamma$ . Only the optical modes have the coupling strength projected onto them.

We also discuss features of the phonon dispersion which may explain why phonon-electron decay can dominate over the usual phonon-phonon decay. The phonon dispersion in Figure 3.40 reveals that there is no energy separation between the acoustic and the lowest energy optic modes. In addition, the acoustic modes are spread over a very narrow bandwidth, and near  $\Gamma$  there is very little separation between the three acoustic branches. This latter feature is similar to the "acoustic bunching" described in the for high thermal conductivity materials[130]. The combination of these features suggest that there is a restricted phase space for phonon-phonon decay by the lowest energy optical modes, which may lead to longer phonon-phonon lifetimes. On the other hand, for the higher energy modes there are considerably more phonon-phonon decay paths available, which could contribute to the dominance of phonon-phonon behavior in the mea-

sured linewidths. To help visualize this we show the calculated phonon density of states (DOS) in Figure 3.42. As discussed heuristically above, we see that there is very little DOS below  $\sim 20$  meV, which will limit the likelihood of phonon-phonon decay for the lowest energy optical modes. In contrast, there exists considerably more DOS for the higher energy modes.



Figure 3.42: The phonon density of states (DOS) of  $WP_2$  calculated from first principles.

The bunching arguments above will also apply to the phonon-phonon scattering rates for the acoustic modes. Combined with the much larger phonon-electron coupling strengths displayed by the acoustic modes (see Figure 3.40), we expect that this could lead to the dominance of phonon-electron scattering over phononphonon scattering for these modes. Similar conclusions concerning the relative phonon-electron and phonon-phonon lifetimes have been drawn in other computational works as well[113]. Scattering of electrons by acoustic modes is generally interband (higher q and energy) or intraband (low q and energy) which can lead to intraband scattering becoming more prevalent at lower temperatures.

We lastly comment on the role that the topological features of  $\beta$ -WP<sub>2</sub>'s electronic structure may play in the phonon-electron decay mechanism we report on. In  $\beta$ -WP<sub>2</sub> the Weyl nodes are located hundreds of meV below the Fermi surface[25, 126]. The impact of these nodes on the transport properties of bulk WP<sub>2</sub>, which

typically are sensitive to the Fermi surface, is therefore questionable. For the particular phonon-electron decay mechanism discussed here, the nodes themselves do not seem to play any role in facilitating the effect, since the optical phonon energies are an order of magnitude smaller than the depth of the Weyl nodes. We do note though, that the spin-orbit coupling giving rise to the Weyl nodes also produces the band splitting that enables interband phonon decay paths [25]. Further evidence that this effect is not related to the topological nature of  $\beta$ -WP<sub>2</sub> may be found in another recent study of the phonon dynamics of  $\alpha$ -WP<sub>2</sub> which displayed nearly identical linewidth behavior, despite  $\alpha$ -WP<sub>2</sub> being topologically trivial [120]. While the topological nature of the material may not play a direct role in the phonon-electron behavior discussed here, the features of electronic bands in topological materials may provide the proper conditions for such behavior to occur. If crossed and linearly dispersing bands are found near the Fermi energy, then interband optical phonon decay may occur for phonons of arbitrary energy. As noted earlier, similar linewidth behavior has indeed been reported for TaAs and NbAs[114, 115], two prototypical Weyl semimetals with Weyl nodes near their Fermi surfaces. In addition, the heavy atoms with large spin-orbit coupling found in many topological materials also lead to a reduction in the bandwidth of the acoustic phonons, limiting the available phase space for phonon-phonon scattering as discussed above. We thus conclude that while the effects we observed here could be possible in a semimetallic system regardless of its topological nature, the unique features of topological semimetals may provide a canvas well-suited for their expression.

## 3.10 Conclusions

We have measured and analyzed the temperature dependent Raman spectra of the topological semimetal  $WP_2$ . Through examination of the temperature dependence of the phonon linewidths, we identified electron-hole decay as the primary path for the lowest energy  $A_1$  optical phonon modes over a broad temperature range. Through the use of group theory we further identified that such transitions result from interband and intraband scattering with finite q, which combined with the necessary energy and momentum conservation clarifies why only certain modes display this behavior. We also discussed the role of the phonon-electron coupling strength and the relative availability of phonon-phonon decay paths in facilitating these effects. The much larger phonon-electron coupling strengths calculated for the acoustic modes suggest that they may display similar behavior and scatter primarily off of charge carriers, contributing to the significant temperature dependence observed in the mobility and resistivity and potentially contributing to the development of hydrodynamic behavior. We anticipate that future investigations utilizing e.g. resonant inelastic x-ray spectoscopy, or Brillouin scattering will be valuable in furthering the understanding of phonon dynamics both in WP<sub>2</sub> and in semimetals in general.
# CHAPTER IV

# Phonon Scattering in NbAs and TaAs

# 4.1 Introduction

The family of transition metal mono-prictides comprised of (Nb,Ta)(P,As) are prototypical type-I Weyl semimetals. The electronic structure of these inversion breaking semimetals has been extensively studied using angle resolved photoemission spectroscopy (ARPES)[27–29, 31] leading to the identification of 24 total Weyl nodes throughout the first BZ. By contrast, very little effort has been made to understand the vibrational properties of these materials, or the coupling between the electronic and vibrational systems. Prior to the publication of this author's work 114 on NbAs and TaAs, only two articles investigating the Raman spectra [131, 132] had been published, and only one [133] on the infrared (IR) spectra had dealt with optical phonons. In particular, the Raman works were fairly limited in scope, focusing only on consistency with group theoretical predictions and characterization between the different (Nb,Ta)(P,As) compounds at room temperature. The IR work provided more in depth temperature analysis of the TaAs  $A_1$  phonon. They observed a temperature dependent Fano lineshape which was attributed to electron-phonon coupling between the  $A_1$  mode and the Weyl fermion quasiparticles in the vicinity of the Weyl nodes. In addition, the temperature dependence of the linewidth indicated that the  $A_1$  mode decays into

electron-hole pairs, rather than the typical decay into acoustic phonons.

In this chapter we present temperature dependent Raman spectroscopy studies of NbAs and TaAs. We place particular emphasis on the temperature dependence of the  $A_1$  mode linewidths which, like the IR work[133], display a temperature dependence indicative of phonon decay into electron-hole pairs rather than acoustic phonons. Interestingly, we find that this observation depends on the crystal surface upon which one measures the Raman spectrum of NbAs. This difference is attributed to the small but non-zero momentum imparted to the created phonon. The  $A_1$  phonons in the two measurement configurations have perpendicular momenta, and therefore have different decay channels available to them, as supported by group theoretical calculations. We also identified a temperature independent Fano lineshape of the  $B_1$  modes in NbAs, consistent with a modest degree of electron-phonon coupling in these materials. Lastly, we also discuss more general pathways in the BZ by which optical phonons can cause scattering between different parts of the FS.

### 4.2 Experiments

Single crystals of NbAs and TaAs were provided by Professor Ni at UCLA. Details on the synthesis and growth may be found in reference[134]. Specific crystal surfaces were first identified by the presence of Raman modes previously identified in[131, 132] by measurement in the WITec alpha-300R Raman spectrometer located in the Burchlab glovebox. After identifying the surface for investigation, the samples were mounted onto Montana Instruments sample holders using silver epoxy to ensure both good thermal contact and adhesion during cool down. Temperature dependent Raman measurements were carried out using the custom built Raman spectrometer described in [135]. The 532 nm light from a frequency doubled Nd:YAG laser was focused onto the samples using a long working distance 100X objective to a spot size of approximately 1-2  $\mu$ m. The power was kept below 320  $\mu$ W for NbAs and 400  $\mu$ W for TaAs to avoid local heating by the laser. The temperature was varied from 5 to 300 K for NbAs, and 10 to 300 K for TaAs.

#### 4.3 Computational Methods

The imaginary part of the phonon self-energy correction due to the electronphonon interaction is evaluated in the Migdal approximation[136],

$$\operatorname{Im}\Pi_{\mathbf{q}\alpha} = \frac{\hbar}{2\tau_{\mathbf{q}\alpha}} = 2\pi \sum_{mn} \int_{\mathrm{BZ}} \frac{\Omega \, d\mathbf{k}}{(2\pi)^3} \left| g_{\mathbf{k}m,(\mathbf{k}+\mathbf{q})n}^{\mathbf{q}\alpha} \right|^2 \times (f_{\mathbf{k}n} - f_{(\mathbf{k}+\mathbf{q})m}) \delta(\hbar\omega_{\mathbf{q}\alpha} - \varepsilon_{(\mathbf{k}+\mathbf{q})m} + \varepsilon_{\mathbf{k}n}),$$

$$(4.1)$$

This self-energy is related to the lifetime produced by scattering of phonons via the electron-phonon interaction, and is directly proportional to the corresponding phonon scattering rate. To calculate this self-energy, we use first-principles density functional theory (DFT) calculations of the electron-phonon matrix elements from JDFTx[137]. The independent electron and phonon states were calculated using fully-relativistic ultrasoft pseudopotentials[138, 139] parameterized for the PBEsol exchange-correlation functional[140]. For NbAs and TaAs, we obtain wellconverged DFT results for an  $8 \times 8 \times 8$  k-point mesh, Marzari-Vanderbilt ("cold") smearing [141] with 0.001 Hartree width, a  $4 \times 4 \times 4$  phonon supercell, and a planewave energy cutoff of 24 Hartrees for NbAs and 22 Hartrees for TaAs. Using a basis of maximally-localized Wannier functions[136], we then interpolate all energies and matrix elements to a much finer k-mesh of  $224 \times 224 \times 224$  wave vectors for room temperature in TaAs and  $200 \times 200 \times 200$  in NbAs in order to converge the necessary Brillouin zone integral for the phonon self-energy. Methods for this calculation are presented in a previous work[114].

# 4.4 Temperature Dependent NbAs Raman Spectra and Fano Lineshape of the $B_1$ Modes

The temperature dependent Raman spectra of NbAs in the XX polarization configuration from 5 to 300 K are plotted in Figure 4.1. There are three phonon modes visible in these spectra, the lower two are of  $B_1$  symmetry, and the highest is of  $A_1$  symmetry[131]. All three modes are seen to decrease in energy as the temperature is increased, in agreement with the standard expectations of lattice expansion and anharmonic interactions[70, 73]. For the sake of clarity we also plot the 5 K spectra alone in Figure 4.2. Close inspection of the tails of the  $B_1$ modes reveals a subtle asymmetry in their lineshape. The lower energy  $B_1$  mode at 29.5 meV appears to have more spectral weight on its lower energy side, while the higher energy  $B_1$  mode at 31.5 meV appears to have more spectral weight on its higher energy side. This is most clearly seen by observing how much more sharply the two modes disappear in the region between each other.



Figure 4.1: Temperature dependent Raman spectra of NbAs in the XX polarization configuration from 5 to 300 K.



Figure 4.2: NbAs XX spectra at 5 K.

In order to confirm this asymmetry we fit the spectra with both symmetric (Voigt) and asymmetric (Gaussian-broadened Fano) lineshapes and then compared the results both visually and quantitatively through the  $\chi^2$  fitting metric. The results of these fittings are shown in Figure 4.3, with the normalized  $\chi^2$  for each fit shown in Figure 4.4.

The Voigt fit to the  $B_1$  modes visibly underestimates the spectral weight on the left (right) side of the lower (higher) energy modes. On the other hand, the Fano fit clearly captures the lineshape of the modes. The improvement in fitting accuracy is confirmed by the normalized  $\chi^2$  metric where we see a 50% better result obtained with the Fano compared to the Voigt fit.

Having confirmed the presence of the Fano asymmetry in the  $B_1$  modes, we inspect the temperature dependence of the Fano asymmetry parameter q. In Figure 4.5 we see that, over the temperature range investigated, the q for each mode remains temperature independent. This is in stark contrast to the behavior that was observed in the IR work[133], where the q for the  $A_1$  mode followed the same temperature dependence as the linewidth (specifically, the difference of



Figure 4.3: Left: Fitting to the  $B_1$  modes by symmetric Voigt profiles. Right: Fit to the same data but using asymmetric Fano profiles.



Figure 4.4: Normalized  $\chi^2$  fitting metric showing a quantitative improvement in the fit by using the Fano over the Voigt profiles.

Fermi occupation functions which will be discussed in more detail shortly). While a theoretical explanation for the static temperature dependence we observed is still lacking, phenomenologically we note that the strength of the electron-phonon coupling as calculated (and discussed in more detail later) seems to be nearly temperature independent, which is consistent with such a lack of temperature dependence in the lineshape.



Figure 4.5: Temperature dependence of the Fano asymmetry parameters in NbAs.

#### 4.5 Temperature Dependent TaAs Raman Spectra

Raman spectra for TaAs measured from room temperature down to 10 K are plotted in Figure 4.6. Due to the larger mass of Ta compared to Nb, the  $B_1(2)$ and  $A_1$  modes switch order in energy[132] such that from low to high energy we have:  $B_1(1), A_1$ , and  $B_1(2)$ . Unlike both the IR work on TaAs[133] and our NbAs results, none of the phonon modes display any asymmetry in their lineshape.

A possible explanation for this is the different excitation mechanism for Raman scattering compared to IR measurements. In an IR measurement the creation of a phonon is caused directly by the absorption of light with energy equal to the phonon's energy. Likewise, the electronic continuum that couples to the phonon and produces the asymmetry is also directly excited by the light. On the other hand, in Raman scattering the energy of the incident light is typically orders of magnitudes larger than the phonon energy. (In this specific case our laser excites at 2.3 eV, compared to the phonon energies of approximately  $\approx 0.02 - 0.03$  eV). Instead, as discussed in chapter I, the phonon is created by emission (in the case of Stokes) from the optically generated electron-hole pair. If the electronic continuum is unable to be generated by such a mechanism, i.e. is Raman inactive, then the phonon would not display an asymmetry in its lineshape. It also may be possible that the  $A_1$  phonon measured in the IR and Raman measurements are at slightly different momentum, since the momentum provided by the visible wavelength laser in Raman experiments is two orders of magnitude larger than the IR light in the IR measurements.



Figure 4.6: Temperature dependent Raman spectra of TaAs in the XX polarization configuration from 10 to 300 K.

To explicitly confirm the lack of asymmetry in the  $B_1$  modes of TaAs we attempted to fit them with Fano lineshapes. If the lineshape is completely symmetric then we expect the 1/q parameter to approach zero. The 1/q values we obtained from attempting to fit the  $B_1$  modes of TaAs are plotted versus temperature in Figure 4.7. As could be expected from the visual appearance of the Raman spectra, the values are computationally zero for both modes, confirming the lack of any asymmetry in the TaAs  $B_1$  modes. While this result is not particularly illuminating on its own, it does illustrate by point of contrast the aptness of fitting the NbAs  $B_1$  modes with Fano lineshapes, since we there obtained a demonstrably non-zero value for 1/q.



Figure 4.7: Fano asymmetry parameters 1/q vs temperature for the TaAs  $B_1$  modes. The values obtained from these fits were computationally zero for all temperatures, indicating the lack of any asymmetry in the lineshapes.

#### 4.6 Temperature Dependence of the A<sub>1</sub> Linewidth

In the Raman spectra of NbAs and TaAs the  $A_1$  modes fail to display any asymmetry in their lineshape. However, the linewidth of these modes do display atypical temperature dependencies. The temperature dependence of optical phonon linewidths is typically driven by their decay into acoustic phonons[70, 73]. As a result, most optical phonons display a linewidth that is nearly constant at low temperatures, and that grows linearly at higher temperatures. (In very anharmonic materials higher order (four-phonon) decay mechanisms may also be relevant and contribute a quadratic term to the temperature dependence of the linewidth[70].) In contrast, the temperature dependence we observe for the  $A_1$ modes (a) displays a very rapid increase at relatively low temperatures and (b) more substantially, *decreases* at higher temperatures. Such a temperature dependence is clearly at odds with the established behavior for decay into acoustic phonons, and therefore necessitates an alternative explanation.



Figure 4.8: Temperature dependent linewidths of the  $A_1$  phonon mode in (a) NbAs and (b) TaAs. The solid blue lines are fits to the data using a model of optical phonon decay into electron-hole pairs.

The high temperature decrease of the  $A_1$  linewidths suggests a decay into fermionic particles, rather than bosonic. To understand why we arrive at such a conclusion, we first review some of the relevant physics concerning fermions. Fermions, unlike bosons, are subject to the Pauli exclusion principle; two fermions are unable to simultaneously occupy the exact same quantum state. As a consequence of this fundamental principle, fermions display statistics that are distinct from those of bosons. This is captured by the Fermi-Dirac distribution function:

$$n_F(\omega, T) = \frac{1}{\mathrm{e}^{(\hbar\omega - \mu)/k_B T} + 1}$$
(4.2)

where  $\hbar\omega$  is the energy of the fermion, and  $\mu$  is the chemical potential. At zero temperature, any states with energy less than the chemical potential are occupied, while states with energy above are unoccupied. At higher temperatures, some of the states below the chemical potential are thermally excited into higher energy states, with the result being that the line between occupied and unoccupied states becomes smeared. As the temperature approaches infinity, all states (or more precisely, as many states as there are electrons) become equally likely to be occupied due to this smearing.

To understand how this can result in a linewidth that decreases with increasing temperature, let us imagine that we have a simple two-state system, where the two states have an energy difference  $\Delta$ , and that we populate this system with a single fermionic particle. (To be more rigorous, we should technically assume a large number of identical such systems, but the physics we are interested in addressing is not aided by such rigor.) At zero temperature, the lower energy state is occupied and the higher energy state is unoccupied. If the fermion absorbs an energy  $\Delta$ , say from a phonon, then it will be excited to the higher energy state. If we were to assign a probability to the chances of this absorption happening (while only taking into account the occupancy of the upper and lower states as being relevant to this probability), we would assign it a probability of 1 at zero temperature. At higher temperatures, such that  $k_B T \sim \Delta$ , there is now a chance that the fermion has been thermally excited into the upper energy level. If we were to now ask what the probability of the phonon absorption is, we would find that our probability is now less than one, since when the fermion is in the higher energy state it can no longer absorb the phonon energy  $\Delta$ . From the point of view of the phonon, the probability of it being able to transfer its energy to the fermion, in other words to decay, has clearly decreased as the temperature increased. Since the phonon linewidth is directly proportional to its rate of decay (or inversely proportional to its lifetime), we find that the phonon lifetime will decrease as the temperature is increased.

The simplest model we can use to describe such a process thus assumes that the phonon linewidth is proportional to the difference in occupation functions between an initial hole state and a final electron state. We also include a temperature independent offset to account for any disorder or low temperature, residual anharmonic renormalization that may be present in the system. Our model therefore takes the form:

$$\Gamma(T) = \Gamma_0 + F\left(n_F(-\omega_h, T) - n_F\omega_e, T\right)$$
(4.3)

where  $\Gamma_0$  is the temperature independent term,  $\omega_h$  is the energy of the hole,  $\omega_e$  is the energy of the electron, and F is a factor which governs the degree to which the linewidth is renormalizd. Such a model was originally developed in the study of graphite/graphene[123], where due to the particle-anti-particle symmetry, the electron and hole energies were assumed to be equal ( $\omega_h = \omega_e$ ). However, in the case of a WSM with anisotropic, tilted Weyl bands and a finite chemical potential, this assumption is no longer likely to hold. Indeed, attempts to fit our experimental data which assumed  $\omega_h = \omega_e$  and excluded a chemical potential were entirely unsuccessful. We further generalized the above model to take into account the tilt of the Weyl nodes by allowing the electron and hole energies to be unequal. (The introduction of a chemical potential has a similar, but slightly different effect.)

Fits to the  $A_1$  linewidths are shown as solid blue lines in Figure 4.8. For the NbAs data the model is quite successful at reproducing the observed trends over the entire measured temperature range. As properly motivated later, we assume that the electron-hole pairs are being generated at the W1 Weyl nodes which lie in the  $k_z = 0$  plane. For TaAs we see some deviations from this model, with a sharper reduction in linewidth around ~ 150 K than our simple model captures, and then an upturn around ~200 K. The upturn may occur due to a transition to anharmonic dominated decay[122]. The anharmonic contribution to the linewidth is expected to grow with increasing temperature, so a cross-over between the two mechanisms is inevitable. The lack of similar behavior in NbAs over the same temperature range may be due to a larger phonon-electron contribution, as evidenced by the larger  $A_1$  linewidth in NbAs compared to TaAs.

# 4.7 ZZ NbAs Raman Spectra and Group Theory Analysis

We also performed temperature dependent measurements with light incident along the *a*-axis of the crystal in both ZZ and ZX configurations, as shown in Figure 4.9. (In the previous measurements the light was incident along the *c*-axis of the crystal, in the XX polarization configuration.) With light incident on an *ac*surface the three optical modes of *E* symmetry become active, while the  $B_1$  modes are no longer present. We also note the presence of an additional mode, which had previously been ascribed as a defect mode[132]. This assignment is confirmed via the near temperature independence of its linewidth, see Figure 4.20. The temperature dependence of the *E* modes is consistent with the usual model of anharmonic decay, as discussed in more detail in Section 4.9.



Figure 4.9: Left: Raman spectra of NbAs with light incident along the *a*-axis, in the ZZ configuration. Right: The same surface but in cross-polarized configuration (ZX).

Interestingly, the  $A_1$  mode, which is active for both crystal surfaces, has a markedly different temperature dependence when measured on this surface. In Figure 4.10 we plot the linewidth as measured on both the *ab*- and *ac*-surfaces (XX and ZZ respectively). The magnitude of the linewidth is considerably smaller when



Figure 4.10: The  $A_1$  phonon linewidth in NbAs as measured on an *ab*-surface (XX) and an *ac*-surface (ZZ). Both the magnitude and dependence on temperature vary significantly between the two measurements.

measured in the ZZ configuration, and the temperature dependence is emblematic of anharmonic decay rather than decay into electron-hole pairs. The distinct behaviors observed in these two measurements are difficult to reconcile if we make the typical assumption that optical phonons probed in Raman scattering have zero momentum[55]. Under such an assumption we would have to ascribe both observed behaviors to the same  $\Gamma$  point phonon, which is not possible. Instead, we must consider the small but non-zero momentum imparted to the phonon in perpendicular directions for each measurement configuration.

Before approaching this from a group theoretical approach, we numerically estimate the momentum of the phonons created under our experimental conditions. In the XX configuration the light is incident along the *c*-axis of the crystal, while in the ZZ configuration it is incident along the *a*- or *b*-axes, which are symmetrically equivalent. The phonons created in each of these conditions will have either  $\mathbf{q}_{XX} = (0, 0, q_c)$  or  $\mathbf{q}_{ZZ} = (q_a, 0, 0)$  (where for ZZ we will be assuming light incident along the *a*-axis). Our measurements were performed in the backscattering configuration, so the specific  $q_i$  may be calculated from the relation  $q_i \leq 4\pi n_j(\lambda)/\lambda$ , where  $n_j(\lambda)$  is the index of refraction for light of wavelength  $\lambda$  polarized along the *j*th crystal axis. The indices of refraction at the 532 nm wavelength of our laser were estimated from our first-principles calculations[127] as  $n_a = 3.43$  and  $n_c = 3.74$ . For XX we therefore estimate the phonon momentum as  $\mathbf{q}_{XX} = (0, 0, 8.11 \times 10^{-3} \text{ Å}^{-1})$ , and in ZZ we estimate  $\mathbf{q}_{ZZ} = (8.83 \times 10^{-3} \text{ Å}^{-1})$ , which are  $\sim 1.55\%$  and  $\sim 0.5\%$  of each respective Brillouin zone direction.

Having estimated the momentum of the phonons in each measurement configuration, we turn now to a group theoretical approach to our phonon scattering problem. The selection rules for phonon scattering may be established by evaluating the direct product of the irreducible representations for the initial and final electronic states. A transition or scattering event is symmetry allowed if the irreducible representation of the phonon is contained in the decomposition of this direct product[124]. We will not go into the details concerning the evaluation of the direct products here, since much of the work involved is nearly identical to that developed and discussed in Chapter III. Instead we will just provide as much detail as necessary to understand and justify the conclusions drawn from the group theoretical analysis.

The FS of NbAs and TaAs consists of multiple banana-like electron and hole pockets, with some additional small ovular electron pockets[134, 142]. The available surface for phonon decay is not too dissimilar from the FS, as can be seen in Figure 4.12. By necessity, the Weyl nodes exist at general k-points[26], and the majority of the FS does as well. In evaluating the selection rules for phonon scattering we therefore primarily consider electronic transitions between two general k-points. At general k-points the only point group symmetry operation present is the identity operation. In the double space group both the identity operation corresponding to a  $2\pi$  rotation and the operation corresponding to a  $4\pi$  rotation will be present. There will therefore be two irreducible representations at GPs (for "General Point"), the GP<sup>(1)</sup> representation and the  $\overline{\text{GP}}^{(2)}$  representation, where the bar indicates that the representation arises from considering the double space group. The electronic bands at these points will have the  $\overline{\text{GP}}^{(2)}$  representation, so we consider the direct product  $\overline{\text{GP}}^{(2)}(\mathbf{k}) \otimes \overline{\text{GP}}^{(2)}(\mathbf{k}')$ . The wave vector selection rules may be found as:

$$\overline{\mathrm{GP}}^{(2)}(\mathbf{k}) \otimes \overline{\mathrm{GP}}^{(2)}(\mathbf{k}') = \mathrm{GP}_1^{(1)} \oplus \mathrm{GP}_2^{(1)} \oplus \mathrm{GP}_3^{(1)} \oplus \mathrm{GP}_4^{(1)} \oplus \mathrm{GP}_5^{(1)} \oplus \mathrm{GP}_6^{(1)} \oplus \mathrm{GP}_7^{(1)} \oplus \mathrm{GP}_8^{(1)}$$

$$(4.4)$$

where the wave vectors for each  $GP_i$  on the right hand side are:

$$GP_{1} = (k_{1} + k'_{1}, k_{2} + k'_{2}, k_{3} + k'_{3})$$

$$GP_{2} = (k_{1} - k'_{1}, k_{2} - k'_{2}, k_{3} + k'_{3})$$

$$GP_{3} = (k_{1} - k'_{2}, k_{2} + k'_{1}, k_{3} + k'_{3})$$

$$GP_{4} = (k_{1} + k'_{2}, k_{2} - k'_{1}, k_{3} + k'_{3})$$

$$GP_{5} = (k_{1} - k'_{1}, k_{2} + k'_{2}, k_{3} + k'_{3})$$

$$GP_{6} = (k_{1} + k'_{1}, k_{2} - k'_{2}, k_{3} + k'_{3})$$

$$GP_{7} = (k_{1} + k'_{2}, k_{2} + k'_{1}, k_{3} + k'_{3})$$

$$GP_{8} = (k_{1} - k'_{2}, k_{2} - k'_{1}, k_{3} + k'_{3})$$

Since we are only capable of probing phonons with small momentum we then take

the limit  $\mathbf{k}' \to \mathbf{k}$ . In this limit we have

$$GP_{1} \rightarrow GP_{1} = (2k_{1}, 2k_{2}, 2k_{3})$$

$$GP_{2} \rightarrow 8\Lambda = (0, 0, 2k_{3})$$

$$GP_{3} \rightarrow GP_{2} = (k_{1} + k_{2}, k_{1} - k_{2}, 2k_{3})$$

$$GP_{4} \rightarrow GP_{2} = (k_{1} + k_{2}, k_{1} - k_{2}, 2k_{3})$$

$$GP_{5} \rightarrow 2B_{2} = (0, 2k_{2}, 2k_{3})$$

$$GP_{6} \rightarrow 2B_{1} = (2k_{1}, 0, 2k_{3})$$

$$GP_{7} \rightarrow 2A_{1} = (k_{1} + k_{2}, k_{1} + k_{2}, 2k_{3})$$

$$GP_{8} \rightarrow 2A_{2} = (k_{1} - k_{2}, k_{1} - k_{2}, 2k_{3})$$

where the numerical coefficients indicate how many copies of the new wave vector star are present. From these expressions we find that transitions at general kpoints by exactly  $\Gamma$  point phonons are not allowed by wave vector conservation. There are no point group symmetries relating +z to -z so the phonon must have a non-zero  $q_z = 2k_z$  component. The lack of any FS near  $\Gamma$  rules out the possibility of any small  $\mathbf{q}$  phonons that belong to the GP<sub>1</sub>, GP<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub>, A<sub>1</sub>, or A<sub>2</sub> stars contributing to the behavior observed in our measurements. Thus only  $\Lambda$  phonons with  $\mathbf{q} = (0, 0, 2k_z)$  are both capable of producing an electronic transition at a general point/near the Weyl nodes and experimentally accessible through Raman scattering. This second criteria is only satisfied if the  $q_z = 2k_z$  is within the  $\sim 1.5\%$ range of  $q_z/(2\pi/c)$  that we estimated above, which restricts us to consideration of the FS on or close to the  $k_z = 0$  plane. We note however, that the eight W1 Weyl nodes are located within the  $k_z = 0$  plane [26, 27]. Consistent with our discussion above, this suggests that the  $A_1$  phonon linewidth behavior observed in the XX measurement configuration is indicative of phonon decay via the creation of electron-hole pairs near the W1 Weyl nodes. Although they did not carry out

group theoretical calculations to confirm this behavior, the group who performed IR measurements of the  $A_1$  mode in TaAs arrived at this same conclusion[115]. By contrast, in the ZZ measurement the phonons have no  $q_z$  and only a small  $q_x$ component. They are therefore unable to satisfy momentum conservation due to the lack of any FS near  $\Gamma$  and their linewidth behavior is instead dominated by decay into acoustic phonons. The momentum conservation rules derived here from group theory, combined with consideration of the FS of NbAs and TaAs provide an explanation for the distinct linewidth behavior displayed by the  $A_1$  mode when measured on perpendicular crystal surfaces.

# 4.8 Phonon-Electron Coupling Strength and Other Phonon Mediated Channels

We now discuss the results of our ab-initio calculations of the phonon-electron coupling strength. In Figure 4.11 we show the calculated imaginary part of the phonon-electron self-energy at room temperature plotted along the phonon dispersions for (a) NbAs and (b) TaAs. Overall we note a larger magnitude of the phonon-electron self energy in NbAs compared to TaAs, which may be consistent with the presence (absence) of asymmetric lineshapes for the  $B_1$  modes in NbAs (TaAs), and with the larger magnitude of the phonon-electron dominated  $A_1$  linewidth in NbAs compared to TaAs. The largest self energy is seen to occur along the  $\Lambda$  ( $\Gamma \rightarrow Z$ ) and  $\Delta$  ( $\Gamma \rightarrow X$ ) cuts. The larger self energy along  $\Lambda$ , and particularly near  $\Gamma$ , is consistent with our observations of phonon-electron dominated linewidths for the  $A_1$  modes measured in the XX configuration, and with our group theoretical calculations. Measurements of the resistivity have also revealed anistropy between  $\rho_{xx}$  and  $\rho_{zz}[143]$  which may be consistent with the larger phonon-electron coupling calculated along the  $\Lambda$  direction.



Figure 4.11: Correction to the imaginary part of the phonon self-energy due to the electron-phonon interaction at room temperature projected onto the phonon dispersions of (a) NbAs and (b) TaAs. For both materials, there is a notable increase in self-energy along  $\Lambda$  ( $\Gamma \rightarrow Z$ ) and  $\Delta$  ( $\Gamma \rightarrow X$ ). The overall calculated self-energy is less for TaAs than NbAs, but similar wave vectors show enhanced phonon self-energy in both materials.

Although we are unable to access large momentum phonons through optical measurements, we discuss the possible scattering pathways which may contribute to the electron-phonon coupling in NbAs and TaAs. In Figure 4.12(b) and (c) we plot the surface of electronic states that are both energetically within the maximum phonon energy ( $\sim 38 \text{ meV}$ ) of another electronic state and the chemical potential. The relatively small phonon energy scale compared to the electronic energy scale results in surfaces that are not too dissimilar from the FS, with the main distinction being that the ovular electron pockets having been subsumed by the larger banana-like pockets. The **q** plotted in each figure correspond to wave vectors from Figure 4.11 which display larger phonon-electron self energy. From these figures it is clear that the phonon wave vectors with larger self energy correspond to wave vectors that connect different parts of the NbAs FS.



Figure 4.12: (a) A possible phonon-mediated transition within a single Weyl cone. (b) and (c) show the Brillouin zone of NbAs, with orange areas indicating the electronic states which are energetically within 35.8 meV (about the largest phonon energy in NbAs) of another state and the chemical potential. The q in these images indicate possible wave vectors corresponding to those with increased electron-phonon self-energy as shown in Figure 4.11. Here,  $q_1$  is a wave vector at or near  $\Gamma$ , and  $q_2$  and  $q_3$  are respectively along the lines from  $\Gamma$ -X and  $\Gamma$ -Z.

# 4.9 Anharmonic Fitting of Other Phonon Modes

In contrast to the anomalous behavior displayed by the  $A_1$  modes in NbAs and TaAs, the other observed modes displayed linewidth behavior consistent with the typical anharmonic model of optical phonons. In Figures 4.13 through 4.23 we show the energy and temperature dependence of these other modes with fits using the extended Klemens' model[70, 73].



Figure 4.13: Temperature dependence of the energy and linewidth for the  $B_1(1)$  mode of NbAs.



Figure 4.14: Temperature dependence of the energy and linewidth for the  $B_1(2)$  mode of NbAs.



Figure 4.15: Temperature dependence of the energy for the  $A_1$  mode of NbAs measured in the XX polarization configuration.



Figure 4.16: Temperature dependence of the energy for the  $A_1$  mode of NbAs measured in the ZZ polarization configuration.



Figure 4.17: Temperature dependence of the energy and linewidth for the E(1) mode of NbAs.



Figure 4.18: Temperature dependence of the energy and linewidth for the E(2) mode of NbAs.



Figure 4.19: Temperature dependence of the energy and linewidth for the E(3) mode of NbAs.



Figure 4.20: Temperature dependence of the energy and linewidth for the defect mode (D) in NbAs.



Figure 4.21: Temperature dependence of the energy and linewidth for the  $B_1(1)$  mode of TaAs.



Figure 4.22: Temperature dependence of the energy and linewidth for the  $B_1(2)$  mode of TaAs.



Figure 4.23: Temperature dependence of the energy for the  $A_1$  mode of TaAs.

As noted above, the Raman spectra of NbAs in the ZZ and ZX configurations (Figure 4.9) reveal the presence of an additional mode not predicted by group theory at  $\sim 32$  meV. In a previous report of the room temperature NbAs Raman spectra[132] this was assumed to be a defect mode. In Figure 4.20 we find that the linewidth of this mode is nearly constant over the measured temperature range which confirms this assignment.

The Klemens' model describes the decay of an optical phonon with energy  $\omega_0$ and  $\mathbf{q} \approx 0$  into two acoustic phonons of equal energy  $\omega_0/2$  and opposite momentum  $\mathbf{q}_1 = -\mathbf{q}_2$ [73]. The extended Klemens' model also considers higher order processes whereby optical phonons may also decay into trios of acoustic phonons[70]. This model predicts that the optical phonon energy as a function of temperature is given by:

$$\omega(T) = \omega_0 + C \left(1 + 2n_B(\omega_0/2, T)\right) + D \left(1 + 3n_B(\omega_0/3, T) + 3 \left(n_B(\omega_0/3, T)\right)^2\right)$$
(4.5)

and that the linewidth is given by:

$$\Gamma(\omega, T) = \Gamma_0 + A \left( 1 + 3n_B(\omega/2, T) \right) + B \left( 1 + 2n_B(\omega/3, T) + 3 \left( n_B(\omega/3, T) \right)^2 \right)$$
(4.6)

where  $n_B(\omega, T)$  is the Bose occupation factor,  $\omega_0$  is the bare phonon energy,  $\Gamma_0$  is a temperature independent linewidth contribution coming from impurity scattering, C(A) is the third order correction to the phonon energy, and D(B) is the fourth order correction to the phonon linewidth. (The C term also accounts for the effects of lattice expansion.) In Tables 4.1 and 4.2 we show the anharmonic coefficients obtained from fitting of our data with the extended Klemens' model.

Mode	$\omega_0 \; (\mathrm{meV})$	$C \;(\mathrm{meV})$	$D \ (meV)$	$\Gamma_0 \; (\mathrm{meV})$	$A \ (meV)$	B (meV)
E(1)	18.97	-0.0038	-0.0022	0.0507	0.0149	N/A
E(2)	29.56	-0.0365	-0.0096	0.1180	0.0130	N/A
$B_{1}(1)$	29.57	-0.0341	-0.0099	0.0845	0.0195	N/A
E(3)	31.57	-0.0268	-0.0089	0.0875	0.0331	N/A
$B_1(2)$	31.60	-0.0300	-0.0087	0.0789	0.0224	N/A
$A_1$	34.30	-0.1497	-0.0042	0.0678	0.0301	N/A

Table 4.1: Anharmonic coefficients obtained from fitting the NbAs energy and linewidth data with the extended Klemens' model.

Mode	$\omega_0 \; (\mathrm{meV})$	C (meV)	$D \ (\mathrm{meV})$	$\Gamma_0 \; (\mathrm{meV})$	$A \ (meV)$	B (meV)
$B_1(1)$	21.78	-0.0552	N/A	0.0494	-0.0073	0.0024
$A_1$	31.89	-0.1425	N/A	N/A	N/A	N/A
$B_1(2)$	32.63	-0.08638	N/A	0.0220	0.0101	N/A

Table 4.2: Anharmonic coefficients obtained from fitting the TaAs energy and linewidth data with the extended Klemens' model.

# 4.10 Conclusions

We performed temperature dependent measurements of the Raman spectra of both NbAs and TaAs. The  $B_1$  modes of NbAs were found to display weakly asymmetric Fano lineshapes that were independent of temperature, while the same modes in TaAs displayed no asymmetry in their lineshapes. The  $A_1$  modes in both NbAs and TaAs displayed linewidths that deviated from the usual behavior expected from anharmonic decay into acoustic phonons, which was instead interpreted as arising from decay into electron-hole pairs near the W1 Weyl nodes in the  $k_z = 0$  plane. This interpretation was supported by group theoretical calculations of the allowed decay paths, and ab-initio calculations of the phonon-electron self energy. Our calculations also revealed larger phonon-electron self energy for large momentum phonons with wave vectors that connect separate parts of the FS. Overall we find qualitative agreement between our experimental and computationally predicted results. The work presented here sheds new light on phonon scattering in these prototypical type-I Weyl semimetals and should motivate future studies into the interplay between the phonon and electronic systems.

# CHAPTER V

# **Photocurrent Measurement Apparatus**

#### 5.1 Overview

The second-order nonlinear photocurrent response is a way to probe the topological properties of a material. As discussed in more detail in the introduction, the second-order conductivity tensor which gives rise to the CPGE or LPGE is directly proportional to the Berry connection [81]. In some special cases, the CPGE may be quantized [79, 80], and other novel nonlinear effects can arise due to subthe symmetry breaking induced by the spatial properties of the beam [144] or at the edges of exfoliated materials [145]. In order to measure these nonlinear photocurrents, we needed to have an experimental setup capable of carrying out such measurements. As part of my PhD research I assembled and constructed such a photocurrent measurement setup. Informally dubbed the "PVIC" setup (short for Photo-Voltage/Current/Conductivity), this setup primarily consists of the laser sources, the various optics for controlling the beam propagation and polarization, translation stages for the sample, and the electrical measurement equipment used to detect the generated photocurrents. In this chapter we discuss the experimental capabilities that we required for the setup, the individual components that comprise the system, the procedures for alignment of the infrared lasers used in this system, the types of measurements that can be made using the system, the general operating procedures for these measurements, and some of the analysis techniques used for interpreting the data produced by the setup.

# 5.2 Requirements

The first and most obvious requirement for our photocurrent measurement setup is a laser light source for excitation of the nonlinear response. A suitable choice of laser is here informed by the particular physics that we are attempting to investigate. Photocurrents produced in Weyl semimetal systems, sensitive to the Berry connection of the Weyl nodes[81, 146, 147], are predicted to strongly depend on the wavelength of the excitation, with longer wavelengths producing a generally larger response[148, 149]. The array of long wavelength laser options, with photon energies on the scale of the Weyl nodes, is quite small. We therefore elected to use a CO<sub>2</sub> laser which emits radiation at 10.6  $\mu$ m corresponding to an energy of ~117 meV. CO<sub>2</sub> lasers have extensive academic and industrial use, due to their high power and coherence. As discussed in more detail in the following section, we also later incorporated a quantum cascade laser (QCL) with tunable wavelength from 4.4 to 5.4  $\mu$ m into our setup.

Nonlinear responses at a minimum depend on two powers of the electric field, with the specific material response determined by the *n*th order optical conductivity tensor. The polarization dependence of these nonlinear responses will be determined by the crystalline symmetries that constrain the elements of the conductivity tensors. One well-known example of this is the CPGE whereby a photocurrent is excited by circularly polarized light[150, 151]. Experimental measurement of the polarization dependence is therefore crucial to identifying the origin of a particular response. For this reason we require comprehensive tuning of the polarization in our setup by wave plates. In particular, we make substantial use of a QWP which allows for the production of circularly polarized light, controlled by an encoded and motorized mount for accurate and reproducible rotation.

Accurate and reliable positioning of the sample is also a prerequisite for our photocurrent measurements. For example, the spatial distribution of a photocurrent can reveal its generation mechanism, as commonly seen in the characteristic profile produced by the PTE[150, 152]. Motorized stages with high resolution and encoded translation were purchased to fulfill this need. Along with these stages, a custom designed adapter was machined to allow mounting of the samples to the stages.

The photocurrents we wish to measure will be electrical signals by nature so we require electrical measurement and characterization equipment. We will discuss the two types of lock-in amplifiers that we used in the development of our system. Current sources and multimeters for electrical characterization of our samples were also required.

The last main category of requirements for our setup consists of the various optical and optomechanical components necessary for building an optics setup. An example of this might be gold coated mirrors and their kinematic mounts used to guide the  $CO_2$  laser emission onto our main optical path. We will not dedicate specific discussion to most of these, since their use is generally self-evident. In the following section we will discuss the relevant details for the non-trivial components of our photocurrent measurement setup introduced above.

#### 5.3 Components

In this section we discuss the individual components that comprise the photovoltage-current-conductivity (PVIC) system.

#### 5.3.1 Laser Sources

#### 5.3.1.1 $CO_2$ Laser

The first laser used in the construction of the photocurrent setup is a CO<sub>2</sub> laser producing mid-infrared (MIR) radiation at 10.6  $\mu$ m. The laser, a model L4SL from Access Laser, has a maximum power output of ~1 W, a beam diameter of ~2.4 mm, and is horizontally polarized. The laser head is water cooled, which we discuss more in section 5.3.2. The continuous wave (CW) output from the laser is controlled by pulse width modulation (PWM) of an applied signal from its controller. In this section we will discuss some of the steps undertaken to implement safe operation of this laser, as well as some of the details concerning the mechanisms and modes by which the laser may be operated.

The L4SL is a class IV laser which produces a MIR beam invisible to the human eye. The implementation and adherence to proper safety protocols is thus vital when using such equipment. First, safety goggles which filter out MIR light were purchased, and usage of these goggles was mandated for any personnel within the optics room while the laser is operational. Second, a lighted sign outside each entrance indicates whether the laser is currently in operation or not. Third, an optical shutter was placed right after the laser in the path of the beam and connected to the room interlock system. This interlock system is connected to keypads outside each entrance to the optics room. Entrance to the room without first entering the safety code will trigger the optical shutter and block the output beam. An alarm will also sound indicating that the safety mechanism has been tripped.

Stability of the laser unit is critical for experimental use. To securely mount the laser to the optical table we designed a custom adapter plate with clear holes to screw into the bottom of the laser casing, and four clear holes to attach to



Figure 5.1: The  $CO_2$  laser secured to the optical table using the custom machined mount.

1" posts. The posts were tightly clamped to the optical table which provided a robust and vibrationally stable foundation for the laser. A picture of the unit is shown in Figure 5.1.

The radiation emitted by the laser is PWM, which means that it follows the on/off pattern of a TTL input with variable duty-cycle. The duty-cycle describes the percentage of the pulse cycle during which the signal is on. For example, a 100% duty-cycle corresponds to a constantly on input, resulting in a CW output, whereas a 10% duty-cycle would mean the laser only emits for 10% of each frequency cycle. The duty-cycle may be controlled through adjustment of a dial on the laser controller, which is one method by which the effective power output of the laser may be tuned. Emission from the laser always occurs at ~1 W, but depending on the duty-cycle you will achieve different time-averaged powers. Returning

to the previous examples, the 100% duty-cycle will have a time-averaged power of 1 W, and the 10% duty-cycle will have a 0.1(1 W) = 0.1 W time-averaged power. True CW output of the laser is thus only possible at maximum power, although the default frequency of the PWM is 16 kHZ, so for processes which occur on shorter time scales the output will be effectively CW. Modulation of the laser at other frequencies is possible through application of an external TTL signal of 0-5 V at frequencies from 0-400 kHz. This may be a valuable alternative to mechanical chopping of the laser when higher frequency modulation is desired.

#### 5.3.1.2 Quantum Cascade Laser

The second laser incorporated into our photocurrent measurement setup is a QCL from Daylight Solutions. The MIRCat is a tunable MIR laser source, with the two modules in it covering the 4.47–5.07  $\mu$ m and 5.00–5.41  $\mu$ m ranges respectively. The emitted radiation is vertically polarized, and can be controlled either through the use of their proprietary software, MIRCat Control, or through LabVIEW with VIs provided by the company. All of the functionality provided by their proprietary software may be reproduced using LabVIEW. The output power varies as a function of the chosen wavelength, with the peak emitted power for CW operation being ~220 mW. Emission from the MIRCat may either be pulsed or CW depending on which mode is selected. For our experiments we exclusively used the CW mode.

#### 5.3.2 Water Chiller

Both of the laser sources require water cooling to prevent their overheating. The first water chiller used in the construction of our setup was an A28/AC150 from Thermo-Fisher Scientific. To help isolate vibrations from the water chiller we placed it in the closet of our optics room and ran tubing out of feedthroughs to the closet space. The tubing was run along the length of the optic tables, with multiple branches added to allow for the addition of future equipment. (This was in fact used for additional cooling of the CCD in our Raman spectroscopy system.)

An additional water chiller was acquired with the QCL. This chiller, a Thermocube 200 from Solid State Cooling Systems was incorporated and made compatible with the  $CO_2$  laser as well. 1/4" CPC connects that run from each laser can be quickly connected or disconnected from the Thermocube depending on which laser is in operation. After the acquisition of this chiller we used the Thermocube exclusively, while the Thermo-Fisher Scientific chiller was dedicated solely to chilling of the CCD.

#### 5.3.3 Mechanical Chopper

The photocurrent signals measured in our experiments may be quite small, on the order of  $\mu$ A down to nA. In order to reliably measure these signals we introduce an ac modulation to the laser which in turn produces an ac modulation of the photocurrent. This allows us to use lock-in amplifiers to measure the resulting photocurrents and achieve higher sensitivity. The ac modulation is introduced through the use of a mechanical chopper placed in the beam path. The mechanical chopper consists of a DC motor which rotates a metal wheel with periodically spaced apertures. A photointerruptor attached to the housing detects the passing of the blades and, via the electronic controller, produces an output TTL signal which is used as the reference for lock-in measurements.

In our setup we use a SciTec Instruments Model 300CD optical chopper which consists of the control unit, the chopping head, and a set of blades that can be attached to the chopping head. The different blades have slots of different sizes, allowing the beam to be chopped over a wide range of frequencies from 5–3000 Hz. The control unit allows for manual setting of the chopping frequency by rotation
of a knob on the front of the control unit. Alternatively one can provide a 0-15 V DC signal which can control the frequency of the blades. This latter option is useful for experiments in which one wants to tune the chopping frequency of the light since it allows for straightforward automation with an appropriate voltage source.

Mechanical chopping of the beam may also be of use for double modulation experiments. A current with frequency  $\omega_1$  may be applied at the same time the light is chopped with frequency  $\omega_2$  and signals resulting from both the light and the current may be looked for at the sum or difference frequencies  $\omega_1 \pm \omega_2$ . However, drift over time of the mechanical chopper frequency necessitates care be taken in the generation of the sum or difference frequency signal.

## 5.3.4 Quarter-wave Plate

QWPs are generally known for being able to convert linearly polarized light into circularly polarized light. The principle underlying this functionality is the birefringence of the material used to construct the wave plate. Namely, light polarized along different crystal axes travels with different speeds through the crystal. We first discuss the distinctions between different polarizations of light, and we then discuss the principles behind the operation of a QWP. We conclude with some details concerning the specific QWP used in our setup.

The polarization state of an electromagnetic wave generally refers to the direction of the electric field component of the wave[74]. There are three main categories of polarization states: unpolarized light, in which there is no net direction of the electric field vector; linearly polarized light, in which the electric field vector oscillates along a single axis normal to the direction of propagation; and elliptically polarized light, in which the electric field vector rotates throughout the plane perpendicular to the direction of propagation[153]. Circularly polarized light occurs as a special case of the more general elliptically polarized light. There have been multiple systems developed to describe the polarization state of an electromagnetic wave, among these the Stokes parameters and the Jones matrices are the most commonly used[153]. In our discussion here we will make use of the Jones matrix formalism since this will allow easy connection to the nonlinear response of materials to the applied radiation.

In the Jones matrix formalism the polarization state of a wave is described by a column vector, with the three rows corresponding to the electric field component along the three Cartesian axes, see Eq. 5.1.

$$\mathbf{E} = \begin{pmatrix} E_{0x} \mathrm{e}^{i\phi_x} \\ E_{0y} \mathrm{e}^{i\phi_y} \\ E_{0z} \mathrm{e}^{i\phi_z} \end{pmatrix}$$
(5.1)

where  $E_{0i}$  is the amplitude of the electric field along the *i*th direction, and  $\phi_i$  is the phase along the *i*th direction. For light propagating along the  $\hat{z}$ -direction we will have

$$\mathbf{E} = \begin{pmatrix} E_{0x} \mathrm{e}^{i\phi_x} \\ E_{0y} \mathrm{e}^{i\phi_y} \\ 0 \end{pmatrix}$$
(5.2)

(where we have assumed propagation in a vacuum in the absence of any charge sources). Light that is linearly polarized along the x-axis will have a Jones vector:

$$\mathbf{E}_X = \begin{pmatrix} E_{0x} \mathrm{e}^{i\phi_x} \\ 0 \\ 0 \end{pmatrix} \tag{5.3}$$

while light polarized along the y-axis will have a Jones vector:

$$\mathbf{E}_{Y} = \begin{pmatrix} 0\\ E_{0y} \mathrm{e}^{i\phi_{y}}\\ 0 \end{pmatrix}$$
(5.4)

When working with light that is initially linearly polarized we will generally ignore the phases  $\phi_x$  or  $\phi_y$ . Circularly polarized light occurs when the electric field direction rotates in the (assumed) xy-plane with equal amplitudes along the xand y-directions. For left circularly polarized light the x-component leads the y-component by  $\pi/4$ , so we have (in normalized form)

$$\mathbf{E}_{L} = \frac{E_{0}}{\sqrt{2}} \begin{pmatrix} 1\\i\\0 \end{pmatrix} \tag{5.5}$$

For right circularly polarized light we have the opposite phase relation between the x and y-components such that:

$$\mathbf{E}_{R} = \frac{E_{0}}{\sqrt{2}} \begin{pmatrix} 1\\ -i\\ 0 \end{pmatrix}$$
(5.6)

The effect of an optical element such as a QWP may also be captured through the use of a Jones matrix which acts on the Jones vector of the light[153]. A QWP with its fast-axis at an angle of  $\phi$  to the horizontal has a corresponding Jones matrix:

$$\mathbf{QWP}(\phi) = \begin{pmatrix} \cos^2 \phi + i \sin^2 \phi & (1-i) \sin \phi \cos \phi & 0\\ (1-i) \sin \phi \cos \phi & \sin^2 \phi + i \cos^2 \phi & 0\\ 0 & 0 & 0 \end{pmatrix}$$
(5.7)

In the chapter VI discussion of the nonlinear response of TaAs we will make extensive use of these expressions.

We now turn to our discussion of the principles behind the operation of a QWP. As noted earlier, the central physical property of materials used to create QWPs is their birefringence. Birefringence occurs when the underlying crystal structure is anisotropic, such that light polarized along one axis travels through the crystal with a different speed than light polarized along another axis[153]. Invariably the speed of propagation along one axis is faster than the other, and this axis is referred to as the "fast-axis." When a wave plate is fabricated from a source single crystal, the crystal is cut and polished such that the fast-axis lies within the surface plane of the final wave plate. The "slow-axis" is therefore also within this plane and, depending on the orientation of the wave plate, different components of the light's polarization will experience different indices of refraction.

The critical step in the creation of a specific wave plate is then in the establishment of the wave plate thickness. Let us assume that the light incident upon the wave plate is polarized such that equal projections are made upon the slow- and fast-axes of the wave plate. Prior to its incidence upon the wave plate, these projections have a difference in phase such that they produce the specific polarization state of the light thus assumed. In traveling through the wave plate, the relative phase between the two components will change as the component parallel to the fast-axis travels faster than the component parallel to the slow-axis. The thickness of the wave plate can therefore be chosen to select for a specific difference in phase between the two components. A wave plate with thickness chosen to produce a  $\pi/2$  phase difference between the two components is called a quarter-wave plate, whereas one with a  $\pi$  phase difference is a half-wave plate. The specific thickness required for a wave plate of given phase retardance will naturally depend on the material and wavelength dependent indices of refraction.

The orientation of a QWP is typically specified in relation to the direction of the fast-axis, see Eq. 5.7. If we assume an input light of fixed polarization, rotation of the QWP in the plane normal to the propagation of light will change the relative angle between the polarization of the incident light and the fast-axis of the QWP. This will result in different projections upon the fast- and slow-axes, such that the output light is generally elliptically polarized. Assuming the convention used in Eq. 5.7, with light that is initially horizontally polarized, if the fast-axis is at an angle of  $\phi = 0^{\circ}$  to the horizontal, there will be no change in the polarization state of the beam, other than an additional phase factor applied to the horizontally polarized light. At  $\phi = 45^{\circ}$  the light will be converted to right circularly polarized, as some straightforward matrix multiplication and normalization will reveal. At  $\phi = 90^{\circ}$  we once again have no change in the polarization of the light, while at  $\phi = 145^{\circ}$  we will obtain left circularly polarized light. In total, we find that circularly light will be produced a total of four times, with left and right circular polarizations being produced twice each.

For our experiments which primarily used a  $CO_2$  laser producing horizontally polarized light at 10.6  $\mu$ m we used a QWP made from CdSe. CdSe crystallizes in the hexagonal wurtzite structure, which has unique *a* and *c* axes[154], leading to its birefringent properties. The QWP had a square shape, which required us to design and manufacture a custom holder so it could be mounted on our motorized rotation stage. Created from aluminum, the holder consisted of two annuli, between which the wave plate was secured. Through-holes in the bottom plate allowed it to be fastened to the rotation mount, while through-holes in the upper plate allowed it to be fastened to additional tapped holes in the bottom plate. Soft plastic o-rings were placed between the annuli and the wave plate to cushion and protect the wave plate. An image of the assembled structure is shown in Figure 5.2.



Figure 5.2: The QWP mounted in our custom-made holder, attached to the motorized rotation mount from Standa.

## 5.3.5 Encoded Rotation Mount

Measurements of polarization dependent responses require repeatable and accurate rotation of the polarizing optics. The goal of having automated, high measurement throughput introduces the additional requirement for a motorized implementation. To meet all of these needs we made use of an encoded, motorized rotation mount from Standa. The rotation mount, seen above in Figure 5.2, has an angular resolution of 0.00125° (4.5 arcsec), which due to the inclusion of an encoder is highly repeatable. LabVIEW sub-VIs and drivers provided by the company allowed it to be integrated into our suite of LabVIEW software for straightforward automation. In the rest of this section we discuss some of the details concerning our LabVIEW implementation of this motor.

Proper calibration of the rotation stage is vital to its operation. For this rotation mount, a file which contains the calibration information may be created using the proprietary software SMCView available from the standa.lt website. Once the proper calibration settings have been achieved, a <filename>.usm file may be output which can be loaded during control of the stage through LabVIEW.



Figure 5.3: A screenshot of the LabVIEW VI used to control the rotation mount with the QWP.

A picture of the LabVIEW VI for control of the rotation mount is shown in Figure 5.3. When initiated, the user should first click on the Find Devices button. The program will then search through the USB ports of the computer to find the correct port for the rotation mount controller. Then, the user clicks on the Load Profile button and selects the proper <>.usm calibration file which contains the settings for the controller. After this the various controls of the VI may be used to control the positioning of the stage as desired. In other LabVIEW VIs which require control of the stage we have implemented Shared Variables which link to the VI directly controlling the stage. These Shared Variables can change the Destination Position, read the Current Position, and Start the rotation of the stage. The usage of Shared Variables instead of embedding control of the stage explicitly within the other VIs grants a few benefits. One, the control architecture and initialization of the other program is simpler. Two, failure of the other program does not lead to any unintended operation of the stage. And third, the stage can be controlled independently of other programs, which can prove useful in the event of failure of other VIs. Similar program design choices were made for the translation stages onto which the samples are mounted.

## 5.3.6 Mercury-Cadmium-Telluride Infrared Detector

An MCT detector was included in our setup to measure the light reflected from the device. By recording this measurement as the sample is scanned underneath the laser we are able to obtain an intensity map of the reflected light and thus "image" the sample. Comparison of this reflectance image and the simultaneously measured photocurrent to pictures of the device taken in visible wavelength microscopes allows us to identify where on the sample a specific response is being generated. Furthermore, in measurements of the polarization dependence, variation of the reflectance as the QWP was rotated allows for precise identification of the polarization of the radiation incident upon the sample. In this section we discuss some of the basic operating principles of an MCT detector, how we incorporated the MCT into our setup, and how we identified the polarization of the laser from the reflectance measured by the MCT.

The basic principle underlying the operation of an MCT is photoconductivity. Briefly stated, illumination of the MCT crystal by infrared radiation changes its conductivity. In operational use this is detected by applying a small bias current



Figure 5.4: MCT scan of an FTS device.

and measuring the resulting voltage across the detector. A change in the conductivity will be manifested as a change in the measured voltage, since the voltage is proportional to both the applied current and the resistance of the detector. In order to guarantee that the measured voltage change results solely from a change in the resistance of the MCT detector and not from a simultaneous change of the applied current, typically a resistor with resistance much larger than the MCT is connected in series and a voltage applied across the combined system. The large resistor thus acts as a "current source" which is stable against changes in the resistance of the MCT. For our specific setup, a 1 k $\Omega$  resistor was placed in series with the detector and, during use, a voltage is applied across the resistor using a power source. A gold-coated off-axis paraboloid mirror was used to focus the reflected light onto the MCT detector, which actually consists of an array of identical detectors. In order to accurately measure the voltage across the MCT and thus the relative intensity of light incident on the detector, we modulate the light using an optical chopper. We are then able to lock-in to the measured voltage and isolate the voltage response due solely to the incident light.

An example reflectance map from a device is shown in Figure 5.4. This device consisted of an exfoliated FeTe<sub>0.5</sub>Se<sub>0.5</sub> flake with six gold contacts on an SiO<sub>2</sub>/Si wafer. The gold contacts have a much higher reflectance compared to the SiO<sub>2</sub> wafer, so the corresponding MCT signal is larger. In the grayscale colormap used in the figure the gold contacts appear as the white regions, while the darker gray regions are the SiO<sub>2</sub>/Si wafer. The relatively large spot size of the focused laser ( $\sim 30 \ \mu$ m) leads to the lack of resolution in defining the smaller features of the device.

The MCT response may also be used to identify the polarization state of the beam incident upon the sample. In polarization dependence experiments with the  $CO_2$  laser where the QWP is rotated and the sample fixed, we observe a fourfold modulation of the MCT signal with peaks occurring whenever the light is circularly polarized. This modulation occurs because of the angle of the beam splitter (BS) being used to reflect light to the MCT. The BS is at an angle of  $\sim 45^{\circ}$  to the beam path, which is close to Brewster's angle such that vertically polarized light is preferentially reflected towards the MCT. The light emitted by the  $CO_2$  laser is horizontally polarized so, when the QWP is at angle of  $0^{\circ}$ and does not change the polarization as the laser passes forward or back, the least amount of light is reflected and there is a minimum in the MCT signal. On the other hand, when the QWP is at 45° and produces circularly polarized light, when the reflected beam from the sample passes back through the QWP the light becomes polarized at  $-45^{\circ}$  to the horizontal and thus has a vertical component. This vertical polarization component is more strongly reflected by the BS and produces a maximum in the MCT signal. In Figure 5.5 we show a characteristic measurement of the reflectance as a function of the QWP angle in black, as well as the power recorded by a power meter with polarizing optics to select for left circularly polarized light in red. The four-fold variation in the MCT response is



Figure 5.5: The reflectance and power recorded by the MCT and power meter respectively. The simultaneous peaks in the power and reflectance indicate QWP angles where left circularly polarized light was produced.

clear, and the alignment of the peaks for left circularly polarized light as measured by the power meter match with two of the peaks for the reflectance.

The variation in the MCT response described above can be captured through the use of Jones matrices for the relevant optics. The Jones matrix for a QWP was given above as Eq. 5.7, but we also need to introduce the Jones matrix for back reflection:

$$\mathbf{MR} = \begin{pmatrix} -1 & 0\\ 0 & 1 \end{pmatrix} \tag{5.8}$$

and a matrix that represents the BS which preferentially reflects vertically polarized light:

$$\mathbf{BS} = \begin{pmatrix} 0.2 & 0\\ 0 & 0.9 \end{pmatrix} \tag{5.9}$$

where we have assumed for the sake of modeling that 20% of horizontally polarized

light and 90% of vertically polarized is reflected. Assuming that our light is initially horizontally polarized, we find that the light that reaches the MCT will be of the form:

$$\mathbf{E}(\phi) = \mathbf{BS} \cdot \mathbf{QWP}(-\phi) \cdot \mathbf{MR} \cdot \mathbf{QWP}(\phi) \cdot \begin{pmatrix} 1\\ 0 \end{pmatrix} = \begin{pmatrix} -0.2\cos(2\phi)\\ 0.9\sin(2\phi) \end{pmatrix}$$
(5.10)

It is important to note that the light reflected by the sample sees the QWP at an angle of  $-\phi$  as opposed to  $+\phi$ . From this we calculate the intensity

$$I(\phi) = |E|^2 = \left(-0.2\cos(2\phi) \quad 0.9\sin(2\phi)\right) \begin{pmatrix} -0.2\cos(2\phi) \\ 0.9\sin(2\phi) \end{pmatrix}$$
(5.11)

$$= 0.425 - 0.385\cos(4\phi) \tag{5.12}$$

From this expression we find that there are minima in the intensity for  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$ , and  $270^{\circ}$  degrees, corresponding to horizontally polarized light at the sample, and maxima at  $45^{\circ}$ ,  $135^{\circ}$ ,  $225^{\circ}$ , and  $315^{\circ}$ , corresponding to circularly polarized light at the sample, in agreement with the data shown in Figure 5.5. We also note that if the light is initially vertically polarized, as from the QCL, that the maxima in the MCT response will no longer correspond to circularly polarized light, but the minima will.

#### 5.3.7 Beam splitter

A BS was placed in the beam path to capture a portion of the light reflected by the sample and reflect it towards the MCT detector discussed in the previous section. We discuss here the specific criteria which informed our BS selection. First, the BS must be highly transparent across both the MIR and visible wavelength range. In particular, since we do not want a large portion of the incident beam or returning beam to be reflected (the latter to avoid unnecessary loss of power and the former to avoid damaging the MCT) we want a material with very high transmittance in the MIR. Second, since the optical path is not under vacuum we require a material which is non-hygroscopic so that it does not deteriorate due to the presence of moisture in the air. After perusing the materials available from International Crystals, we found that  $BaF_2$  was well-suited for this role.  $BaF_2$  is both highly transparent from 150 nm to 11.5  $\mu$ m and non-hygroscopic. A polished window, of 1" diameter and 2 mm thickness, was purchased from them and used as our BS.

#### 5.3.8 Focusing Lens

To focus the light down onto the sample we use a plano-convex ZnSe lens purchased from Thorlabs, Inc. The focal length of the 0.5" diameter lens was 15 mm, chosen to produce a small spot size of ~ 30  $\mu$ m at the sample. The lens has an anti-reflective coating for wavelengths 7–12  $\mu$ m.

### 5.3.9 Motorized Stages

Positioning of the sample underneath the focused beam was achieved using encoded, motorized stages. The Standa 8MT167-25 stages have a travel range of 1", with a minimum step size of 0.625  $\mu$ m, and the encoders guarantee reproducible positioning down to ~1.5  $\mu$ m. Since the minimum spot size theoretically achievable using the CO<sub>2</sub> laser is ~ 5  $\mu$ m, and our measured spot size was ~ 30  $\mu$ m, we found that this resolution was more than adequate for our scans.

The stages can be controlled using the XILab software provided by Standa or through LabVIEW. For experimental use a LabVIEW VI was written which allows control of the stages both by the user and programatically through commands sent by other VIs. The front panel of this program is shown in Figure 5.6.



Figure 5.6: Front panel of the LabVIEW VI for controlling the motorized XYZ stages.

Rough positioning of the stage can be done through manual control with the arrow buttons. For more precise control, specific coordinates may be entered and moved to using the Move To and Step To buttons. The Move To option will move the stage to the specified coordinates (shown in units of internal steps). while the Step To option will increment the stages by the amount entered below (also in steps). In addition to the commands through the front panel, additional motion control can be achieved through shared variables which allow other VIs to operate through this VI.

The samples are mounted to the stage using a custom designed adapter. The adapter was designed in the Fusion 360 CAD software and machined out of G10 garolite. This material was chosen since it is both machinable and highly insulating, preventing any unintentional electrical connections from occurring.

#### 5.3.10 Breakout Boxes

The breakout boxes used to interface the sample and our measurement equipment went through a number of iterations before the final design which is currently in use. In this section we describe the salient features of the first and last versions, and discuss the reasons why the newer, improved version was made.

The first version of our breakout boxes consisted of two  $4.7^{\circ} \times 7.39^{\circ}$  aluminum boxes, each with ten holes drilled for BNC connectors, additional holes to allow the cable from the samples into each box, and a final hole which had a connector inserted to allow for grounding of the boxes. The ten BNC connectors on each box had the inner signal line electrically isolated from the outer shield line. Inside the boxes, individual wires corresponding to each contact pad on our sample holders were soldered to the BNC connectors. The boxes while in use were kept grounded through direct connection to the building ground.

We found that, while simple, this first version of the breakout boxes had issues with grounding of the samples. Namely, when connected to this breakout box the samples were kept floating at all times. When measurement equipment such as preamplifiers were turned on for use, current surges could potentially flow through the sample and damage or destroy them if small or fragile enough. Such current surges did in fact lead to the loss of multiple samples, which set back our ability to progress with experiments since the samples were custom made by an external group.

To address this issue we made changes both to the breakout boxes and to our procedures for measuring samples. The major change implemented to the breakout boxes was the inclusion of a second BNC connector for each contact. The signal line of this second BNC was directly wired to the signal line of the first, and the outer shield line was directly connected to the box ground. A shorting cap placed on this second BNC therefore shorts the signal line from the sample to the ground of the box, leaving the original BNC connector available for connection and powering on/off of equipment while the sample remains grounded.

The procedure we now follow when using these boxes is as follows: the shorting caps are kept on the secondary BNC connectors whenever the system is not in use. This keeps every contact from the sample connected to the room ground and prevents any spruious current from flowing through the device. Prior to use, any electrical equipment is connected to the primary BNC connector and turned on. Since the shorting caps remain in place, any current surges do not flow through the sample. Once all of the measurement equipment is connected and turned on the shorting caps may be removed, with one shorting cap left in place to act as the measurement circuit ground. After the measurement has been completed, shorting caps are immediately replaced onto the secondary BNCs. Electrical equipment may then be turned off.

## 5.3.11 PXI

The PXI is a modular DAQ instrument available from National Instruments. The two modules in our unit have four BNC connections each, with the PXI-4461 module having two output and two input connections, and the PXI-4462 having four input connections. The analog output connections of the PXI-4461 module can produce voltages from  $\pm 10$  V, and can output DC and AC signals. LabVIEW is used to program each module, with the inputs on the 4462 module primarily being used for digital lock-in amplifiers, and the output of the 4461 being used as a programmable voltage source.

Of the four BNC connections on the 4462 module, one is used for the reference signal input, and the other three are used as individual lock-in amplifiers. The lock-in amplifier sub-VIs are no longer supported by National Instruments and are password protected which prevents any modification. Although the lock-in sub-VIs have a "time constant" input, which nominally should correspond to the time over which the signal is averaged, in practice this time constant does not appear to reliably affect the signal-to-noise ratio. The digital lock-ins also lack filtering options at 60 or 120 Hz. Further, since the digital lock-ins are run through LabVIEW with the the resources of the on-board CPU of the PXI (which is almost comically under-powered) the system often struggles to keep up with the demands of running its own hardware. Due to these concerns we stopped using the PXI for data acquisition and switched to the much more reliable SRS830 lock-in amplifiers.

## 5.3.12 Lock-In Amplifiers

The SR830 lock-in amplifier from Stanford Research Systems is now used as the primary instrument for photocurrent measurement in this setup. One advantage of using the SR830s over the PXI for lock-ins is the superior filtering and sensitivity provided by the SR830. The notch filters at 60 and 120 Hz, and the wide range of available time constants, result in a much higher signal-to-noise ratio compared to the virtual lock-ins on the PXI. In addition, the ability to manually select the reference frequency, using the internal oscillator of the SR830, is a feature that is completely absent for the PXI. Another advantage is the ability to output the measured signal from the SR830 so that it could be measured by a second lock-in. Lastly, since the SR830 has its internal hardware, it is not reliant on the CPU of the PXI to run.

The SR830s were connected to our computer by GPIB cables. LabVIEW VIs for controlling the SR830, available freely from SRS, were used to integrate the lock-ins with our previously developed measurement VIs.

#### 5.3.13 Multimeter

To measure DC voltages we used a HP 3478A multimeter, which was connected to our computer via GPIB cable. The minimum voltage measurable on this equipment is quoted at 150 nV, however in practice we found it was closer to 200 nV. Similar to the other equipment, LabVIEW VIs were used to automate the recording of measurements from this hardware.

#### 5.3.14 Current Sources

For sourcing current in measurements of resistance or photoconductivity we used either a Keithley 6220 or 6221 current source. The 6221 is capable of sourcing both DC and AC, while the 6220 can only source DC. The minimum output current for each of these is 2 nA, which for AC output from the 6221 will also be the minimum resolution of the signal. A reference signal for AC output from the 6221 can be manually turned on with only a little extra effort. Both of these current sources were connected to the computer through GPIB cables and controlled through LabVIEW VIs.

## 5.4 Alignment

The infrared lasers used in this setup provide a challenge for proper alignment since they cannot be seen by the naked human eye. The solution to this problem that we opted for was to first align all of our optics with a visible wavelength laser, and then ensure that our infrared laser and the visible laser were co-aligned with each other. When finished, the infrared laser is thus properly aligned with our optics. In this section we detail some of the specific steps taken to optimize this procedure and guarantee both that initial co-alignment could be achieved and that realignment would be simple.



Figure 5.7: Diagram showing the method by which the visible alignment laser and the infrared laser are aligned together. The visible laser is first aligned through the two apertures, the flipper mirror for it moved out of the path, and then the infrared laser aligned through the same two apertures.

Initial alignment was achieved through the use of two apertures, fixed in place. These two apertures were placed along the final desired optical path, with as large a distance between them as needed both to accommodate the optics to be used in the final setup and to provide filtering sensitivity to small angular deviations. We note here that, due to the relatively simple needs of our setup, only two apertures were needed for the entire optical path. If longer optical paths are needed, this procedure can be used with as many apertures as required. A diagram of this is shown in Figure 5.7.

The visible wavelength laser is first aligned through the apertures using kinematic mounts. Passage through the near aperture is tuned by the first mirror, and passage through the far aperture by the second mirror. Since the visible laser spot can be seen no special equipment is required to make sure that the beam is passing through the apertures beyond ones eyes (while following proper safety protocol). By iterating back and forth between these two apertures the visible beam can eventually be precisely steered such that it passes directly through the center of both apertures. This same procedure is then repeated with the IR laser, with the caveat that now alignment through the apertures is checked using a power meter since the beam cannot be perceived by the eye. Once the alignment of the IR laser through the apertures is completed we now know that the visible beam and the IR beam are coincident with one another. Any subsequent alignment of additional optics using the visible beam will result in alignment for the IR beam.

## 5.5 Photo-voltage vs Photo-current Measurements

Electrical measurement of a photocurrent response may be performed using one of two approaches. The first technique directly measures the induced current using a load resistor placed in series with the sample. The second technique measures the current indirectly through a measurement of the voltage generated across the sample. In this section we will discuss both of these techniques and the relative advantages and disadvantages posed by each.

Direct measurement of the current is the more commonly used technique in contemporary research. A load resistor of known resistance is placed in series with the sample and the voltage across this resistor measured using a multimeter for DC photocurrent generation or a lock-in amplifier for AC photocurrent generation. From the measured voltage and the known resistance one immediately calculates the photocurrent since the sample and the load resistor are in series. One advantage of this technique is that photo-induced changes in the conductivity of the sample that may potentially be produced will not affect the measured voltage since the voltage measurement occurs across the load resistor which is not being irradiated. This same advantage becomes indispensable if cryogenic measurements are to be performed, since the resistance of the sample will invariably change with temperature. When directly measuring the photocurrent in this manner it is crucial to guarantee the existence of only one electrical ground in the measurement circuit. If there are multiple available current paths then the measured value may not be accurate. This may be the only drawback to this method, as it limits current measurement to only one set of contacts at a time.

Measurement of the photovoltage generated across the sample allows for the measurement of multiple contacts at a time. The voltmeter should have a resistance many orders of magnitude larger than the device, and no current should flow between the two points of measurement. The voltage measured for one set of contacts should therefore be unaffected by a simultaneous measurement of another set, though care must still be taken to ensure that the measurement circuit has a single, well-defined electrical ground. The photovoltage thus measured may be converted to the photocurrent by dividing the voltage by the appropriate resistance of the sample. The resistance should be measured both with and without illumination in order to determine if there is any change in the resistance produced by the light. This can prove extremely cumbersome if the laser is being scanned over the device, as in principle the resistance should be measured at each individual laser position to properly extract the current. In cryogenic measurements this approach again has the obvious drawback that it requires a measurement of the resistance at each temperature in order to properly obtain the photocurrent.

## 5.6 Operating Procedures

In this section we give a brief overview of the measurement procedures for this system. The instructions here are not intended to be comprehensive, rather, they are intended to illustrate the typical steps taken in use of this system. For such reasons we will not delve overly deep into details concerning, for example, the individual steps required for use of a given LabVIEW VI.

The steps we enumerate here below are general to any measurement to be carried out using this system. Once appropriate, we will distinguish procedures for different specific measurements.

#### **General Start Up Procedures:**

- 1. Put on a pair of infrared safety goggles.
- 2. Turn on the room interlock system.
- 3. Check that the water lines from the chiller are connected to the proper laser, and that any vales are open.
- 4. Turn the water chiller on, and make sure that it is set to the correct temperature (typically  $\sim 20^{\circ}$ ).
- 5. Turn the laser on, and allow sufficient time (typically  $\sim 1$  hour) for the laser to warm up.
- 6. Using the power meter, set the power of the laser to the desired level.
- 7. If using the optical chopper, turn the chopper on and set the frequency to the desired rate.
- 8. If using the MCT, perform an initial filling of the MCT with liquid nitrogen, wait 30–45 minutes, and then fill it once again. Turn on the power supply to the MCT and set to the desired voltage level.
- 9. With the shorting caps of the breakout box in place, connect and then turn on any electrical measurement equipment.
- 10. Only once all of the electrical equipment is turned on, remove all but one shorting cap from the breakout box, with the remaining cap serving to designate the ground for the measurement circuit.
- 11. Open LabVIEW and the PVIC Setup Master Control Project project.

(Some of the above steps which require waiting may be performed simultaneously.) We next go through the procedure for carrying out a scan of the sample.

## **Photocurrent Scan Procedures:**

- From the PVIC Setup Master Control Project window open Three Axes Translation Stage Control.vi. Run the VI and make sure that all three stages connect and communicate properly.
- 2. Open QWP Rotation Stage Controller.vi and rotate the QWP or HWP to the angle producing the desired polarization.
- 3. Open Area Scan.vi and enter the range of coordinates to be scanned over.
- 4. Specify the file save path for the data.
- 5. Click the Calculate Area button, and then the Start Scan button.
- 6. After the scan has completed, stop the VI and place the shorting caps back on the contacts. Only once the shorting caps are back on, turn off the electrical measurement equipment.

We conclude this section with the procedure for performing a polarization dependence measurement.

## **Polarization Dependence Procedures:**

- From the PVIC Setup Master Control Project window open Three Axes Translation Stage Control.vi. Run the VI and make sure that all three stages connect and communicate properly.
- 2. Move the stages to the desired sample position.

- 3. Open QWP Rotation Stage Controller.vi and make sure that the rotation stage is functioning properly.
- 4. Open Polarization Dependence.vi and enter the range of angles to be measured and the desired angular resolution.
- 5. Specify the file save path for the data.
- 6. Run the VI.
- 7. After the measurement has completed, stop the VI and place the shorting caps back on the contacts. Only once the shorting caps are back on, turn off the electrical measurement equipment.

## 5.7 Data Analysis

The data obtained from measurements in this system may largely be categorized into two types. The first type are data sets coming from scans of the laser across the sample. Such data consists of a set of photocurrent and/or reflectance measurements, each labeled by the encoder position of the stages when that measurement was recorded. A two-dimensional "map" of the data may then be produced by plotting the individual points at grid locations according to their positions. MATLAB codes for automatic sorting and plotting these data sets were written to enable quick processing of photocurrent scans. An example of a reflectance scan may be seen in Figure 5.4, while an example of a photocurrent map is shown in Figure 5.8.



Figure 5.8: Photovoltage recorded as the laser was scanned over a large TaAs sample. The two peaks of opposite sign from the PTE are clearly visible.

Spatial scans of the photocurrent response may be useful for identifying where on the sample the photocurrent is primarily being generated. This can further be aided by comparison to an appropriate reflectance map recorded by the MCT. This can be of great use in establishing the generation mechanism responsible for the measured photocurrent. As an example of this we show a plot of the photocurrent response of a TaAs device in Figure 5.8. The two peaks visible in this scan are indicative of a response due to the PTE. The change in sign of the photocurrent results from a change in the direction of the thermal gradient produced by the laser, for more discussion see Chapter VI. Scans may also be used to identify the presence of a CPGE. A CPGE will produce a current that travels in one direction for one helicity of the light, and in the opposite direction for the other helicity. Meanwhile, other photocurrent generation mechanisms should not be sensitive to the helicity of the light. Taking the difference between a scan obtained with left and right circularly polarized light will therefore yield the response due purely to a CPGE if present[151].

The second main type of data that can be obtained from this system is the polarization dependence of the photocurrent at a specific location on the sample. The QWP is rotated incrementally and the photocurrent recorded at each angular position. A plot of the photocurrent as a function of the QWP angle may then be fit to extract the various components that are present. Depending on the symmetries of the material under investigation, different components of the photocurrent response may be associated with different generation mechanisms. The general functional form of a photocurrent response is [134, 150]:

$$J(\phi) = D + C_C \cos(2\phi) + C_S \sin(2\phi) + L_C \cos(4\phi) + L_S \sin(4\phi)$$
(5.13)

where  $\phi$  is the angle of the QWP, D is a polarization independent fitting term,  $C_{C/S}$  are the fitting terms for the two-fold responses, and  $L_{C/S}$  are the fitting terms for the four-fold responses. Circularly polarized light may generate the  $C_C$ term, while linearly polarized light can contribute to the D and  $L_{C/S}$  terms.

In Eq. 5.13 we note that there are no sine or cosine terms with odd arguments. This results from the even number of times in which circular and linear polarizations are generated by the QWP. However, in real data there may be terms with odd arguments that appear due to extraneous effects such as the precession of the beam due to rotation of the QWP. These artifacts can be removed by averaging the data from  $0^{\circ}$  to  $180^{\circ}$  with the data from  $180^{\circ}$  to  $360^{\circ}$ . Sine or cosine terms

with odd arguments are eliminated by such an averaging procedure (as can readily be pictured for a term  $\propto \sin(\phi)$ ) and the physical terms with even arguments remain. This procedure requires data be taken for a complete 360° rotation of the QWP, and in the end will reduce the data set down to only 0° to 180°.

An example polarization dependent response is plotted in Figure 5.9. The photocurrent consists of a sum of sine and cosine terms as described by Eq. 5.13, here used to produce the fit shown as a solid magenta line. Although the raw data was acquired over a full 360° rotation of the QWP, the data shown here was symmetrized using the above procedure and thus is only shown from 0° to 180°. The different values of the photocurrent at 45° and 135° indicate that there is a response to circularly polarized light, since these are the two angles for right and left circularly polarized light respectively. In addition, there is a polarization independent offset which is seen by noting that the oscillatory terms do not center around a current of zero.



Figure 5.9: Example polarization dependent photocurrent measurement from a TaAs device. Both two- and four-fold variations in the response are observed. The magenta line is a fit using Eq. 5.13.

## CHAPTER VI

## Bulk Photovoltaic Effect in TaAs

## 6.1 Introduction

Recently there has been renewed interest in the nonlinear generation of light due to its connection to electron topology[146, 155, 156]. Of particular interest here is the bulk photovoltaic effect (BPVE) or "shift current," a nonlinear mechanism where direct acceleration of electronic quasi-particles in response to linearly polarized light results in an electric current[81]. First discovered in ferroelectric insulators, the shift current was initially attributed to their built-in electric fields[157]. However, the nonlinear nature of the effect was established in the following decades[77], and its connection to topology made at the turn of the century[81]. Physically the shift current may be understood as resulting from the change in center of the Wannier function of the particle upon interband optical excitation. It is therefore closely linked to the Berry connection, which may be expressed as the expectation value of the position operator in the crystal unit cell.

Second-order nonlinear optical effects such as the BPVE require materials with a lack of inversion symmetry. Under the right conditions this same requirement may generate a WSM. The electronic structure of a WSM is characterized by the presence of three-dimensional linearly dispersing bands, coming in pairs known as Weyl nodes. The Berry connection is singular at the precise location of the node, but is generally enhanced in its vicinity. A number of materials have recently been confirmed to be WSM, with experimental evidence for the Weyl nodes and their singular Berry connection[27–29, 31]. Due to their topological properties, there have been numerous theoretical[148, 149, 158, 159] and experimental works[79, 145, 151, 160] investigating the nonlinear responses of these materials. In the work we present here, we investigate the nonlinear response of the WSM TaAs to linearly polarized light. We find that, in a reflection of its topological nature, the BPVE response of TaAs is an order of magnitude larger than any previously reported, and due to the gap-less nature of the semi-metallic system, it occurs in a wavelength range in which such effects were previously inaccessible.

## 6.2 Experimental Setup

We briefly describe the photocurrent measurement setup used to investigate nonlinear photocurrents in TaAs; a more detailed discussion may be found in Chapter V. A diagram of the setup is shown in Figure 6.1. The 10.6  $\mu$ m output from a CO<sub>2</sub> laser is modulated by a mechanical chopper so that we may use a lock-in amplifier to measure the resulting photocurrent. The light then passes through a BS which redirects reflected light towards a MCT detector, allowing us to measure the relative reflectance. A QWP on a motorized rotation stage controls the polarization of the light, which is focused onto the sample using a plano-convex ZnSe lens with a 15 mm focal length, resulting in a spot size of ~ 30  $\mu$ m. The sample itself is mounted on a motorized three-axis translation stage allowing for precise positioning of the sample underneath the incident laser. Photocurrent signals are measured using a National Instruments PXI DAQ system after amplification and frequency filtering by an SRS voltage pre-amplifier.



Figure 6.1: A schematic of the photocurrent measurement system used to investigate the nonlinear response of TaAs.



Figure 6.2: The conventional unit cell of TaAs.

# 6.3 TaAs: Crystal Symmetry and Nonlinear Photocurrents

TaAs crystallizes in the tetragonal, non-symmorphic space group  $I4_1md$  (No. 109), the conventional unit cell is shown in Figure 6.2. This structure lacks inversion symmetry which allows both for the presence of Weyl nodes within its BZ and the generation of second-order nonlinear photocurrents. The equation governing the generation of such photocurrents is:

$$J_i = \sigma_{ijk}^{(2)} E_j E_k^* \tag{6.1}$$

where  $J_i$  is the current along the *i*th crystallographic direction,  $E_j$  is the (complex) electric field polarized in the *j*th direction, and  $\sigma_{ijk}^{(2)}$  is the second-order conductivity tensor. The third-rank tensor  $\sigma_{ijk}^{(2)}$  in general contains 27 elements, however many of these will be zero or equivalent to other elements due to Neumann's principle which states that the tensor must be invariant under the symmetry operations of the crystal[50]. Applying the symmetry elements of the  $C_{4v}$  point group to this tensor we find that there are seven non-zero elements, of which four are independent. These are listed below:

$$\sigma_{aac} = \sigma_{bbc}, \quad \sigma_{aca} = \sigma_{bcb}, \quad \sigma_{caa} = \sigma_{cbb}, \quad \sigma_{ccc} \tag{6.2}$$

where we have dropped the (2) superscript. These elements may generally be complex, which we write as:

$$\sigma_{aac} = \sigma_{aac} + i\eta_{aac} \tag{6.3}$$

where  $\sigma_{aac}$  is the real part, and  $\eta_{aac}$  is the imaginary part. In addition to the crystal symmetry operations, we require an additional symmetry which is interchange of the electric field components. For the conductivity tensor, this corresponds to an exchange of indices and complex conjugation. This leads to the relations:

$$\sigma_{aac} = \sigma_{aca}^* \tag{6.4}$$

$$\sigma_{aac} + i\eta_{aac} = \sigma_{aca} - i\eta_{aca} \tag{6.5}$$

from which we find  $\sigma_{aac} = \sigma_{aca}$  and  $\eta_{aac} = -\eta_{aca}$ . On the other hand, for elements with repeated indices we find:

$$\sigma_{caa} = \sigma^*_{caa} \tag{6.6}$$

$$\sigma_{caa} + i\eta_{caa} = \sigma_{caa} - i\eta_{caa} \tag{6.7}$$

which tells us that while (trivially)  $\sigma_{caa} = \sigma_{caa}$ , and  $\eta_{caa} = -\eta_{caa} = 0$ . Summarizing we have the real elements:

$$\sigma_{aac} = \sigma_{aca} = \sigma_{bbc} = \sigma_{bcb}, \quad \sigma_{caa} = \sigma_{cbb}, \quad \sigma_{ccc} \tag{6.8}$$

and the imaginary elements:

$$\eta_{aac} = \eta_{bbc} = -\eta_{aca} = -\eta_{bcb} \tag{6.9}$$

Physically we may associate the real parts of the tensor with the response to linearly polarized light, and the imaginary parts with the response to circularly polarized light. We hereafter focus on the response to linearly polarized light.

With the second-order optical conductivity tensor elements for TaAs identified we may now derive the photocurrent expressions. We first assume that the light is normally incident on an *ac* crystal surface. The implicit sum in Eq. 6.1 then results in, for the two unique crystal axes on this surface (neglecting the CPGE terms):

$$J_a = \sigma_{aac} (E_a E_c^* + E_c E_a^*) \tag{6.10}$$

$$J_c = \sigma_{caa} |E_a|^2 + \sigma_{ccc} |E_c|^2 \tag{6.11}$$

We note that along the c-axis the response is proportional to the intensity of the

electric field along each axis, while along the *a*-axis it results from a mixture of both polarization components. This will have useful implications for our experimental ability to resolve the origin of measured photocurrents. For light incident on an *ab* surface there will be no nonlinear response due to the lack of corresponding tensor elements. The physical cause behind this is the requirement of the electric field polarization along the crystal *c*-axis – the only axis which lacks a mirror operation and can loosely be thought of as "breaking" the inversion symmetry of the crystal.

In our experiments we measured the photocurrent as the QWP was rotated. To obtain the predicted functional dependence we express the electric field components in Eq.'s 6.10 and 6.11 in terms of the angle of the QWP via its associated Jones matrix, given below:

$$\mathbf{QWP}(\phi) = \begin{pmatrix} \cos^2 \phi + i \sin^2 \phi & (1-i) \sin \phi \cos \phi \\ (1-i) \sin \phi \cos \phi & \sin^2 \phi + i \cos^2 \phi \end{pmatrix}$$
(6.12)

Assuming the incident light is polarized along a horizontal x-axis we find:

$$\begin{pmatrix}
E_x(\phi) \\
E_y(\phi)
\end{pmatrix} = \begin{pmatrix}
\cos^2 \phi + i \sin^2 \phi & (1-i) \sin \phi \cos \phi \\
(1-i) \sin \phi \cos \phi & \sin^2 \phi + i \cos^2 \phi
\end{pmatrix} \begin{pmatrix}
E \\
0
\end{pmatrix}$$

$$= E \begin{pmatrix}
(\cos^2 \phi + i \sin^2 \phi) \\
((1-i) \sin \phi \cos \phi)
\end{pmatrix}$$
(6.13)

Now, assuming the crystal *a*-axis is parallel to x and the crystal *c*-axis to y, such that we may associate  $E_a = E_x(\phi)$  and  $E_c = E_y(\phi)$ , we obtain after some simplification:

$$J_a(\phi) = \frac{1}{2}\sigma_{aac}E^2\sin(4\phi) \tag{6.14}$$

$$J_{c}(\phi) = \frac{1}{4}E^{2}\left((\sigma_{ccc} + 3\sigma_{caa}) + (\sigma_{caa} - \sigma_{ccc})\cos(4\phi)\right)$$
(6.15)

We observe that along each axis there is a distinct dependence on the angle of the QWP; along the *a*-axis it depends upon the sine of the angle, while along the *c*-axis it depends upon cosine of the angle and has a polarization independent term. As discussed below in the context of photothermal effects, we will be able to exploit this functional dependence to isolate the nonlinear response.

For the purposes of generalization we also consider an in-plane rotation of the sample by an angle  $\beta$ . We apply a rotation matrix to the electric fields in Eq. 6.13 to find:

$$\begin{pmatrix} E_{x'}(\phi,\beta) \\ E_{y'}(\phi,\beta) \end{pmatrix} = \begin{pmatrix} \cos\beta & \sin\beta \\ -\sin\beta & \cos\beta \end{pmatrix} \begin{pmatrix} (\cos^2\phi + i\sin^2\phi)E \\ ((1-i)\sin\phi\cos\phi)E \end{pmatrix}$$
$$= E \begin{pmatrix} \cos\beta(\cos^2\phi + i\sin^2\phi) + \sin\beta(1-i)\sin\phi\cos\phi \\ -\sin\beta(\cos^2\phi + i\sin^2\phi) + \cos\beta(1-i)\sin\phi\cos\phi \end{pmatrix}$$
(6.16)

Substituting these into our photocurrent equations yields:

$$J_a(\phi,\beta) = \frac{1}{2} \left( -\sigma_{aac}(\sin(2\beta) + \sin(2\beta - 4\phi)) \right)$$
(6.17)

$$J_{c}(\phi,\beta) = \frac{1}{4} \left( \sigma_{caa}(2 + \cos(2\beta)) + \sigma_{ccc}(2 - 2\cos(2\beta)) + (\sigma_{caa} - \sigma_{ccc})\cos(2\beta - 4\phi) \right)$$
(6.18)

We find that rotating the sample introduces both  $\sin(4\phi)$  and  $\cos(4\phi)$  terms along both axes, which can complicate the analysis.

#### 6.3.1 Photothermal Response



Figure 6.3: Diagram of the photo-thermoelectric effect.

In addition to the nonlinear response of TaAs we also expect to measure responses due to the PTE, a diagram of which is shown in Figure 6.3. When the laser is incident on one side of the device it produces a thermal gradient  $\nabla T$ , which in turn produces a voltage  $\Delta V$  through the Seebeck effect[151, 161]. Because this response depends upon the temperature gradient, if the laser is swept across the contacts of the device you will observe a characteristic sign change as the direction of the gradient is reversed.

We confirm this aspect through both simulations and measurements, as shown in Figure 6.4. The photocurrent measured across two contacts is plotted along the y-axis as a function of the laser position as it is swept between the contacts. Simulation and experiment produce nearly identical results, with the characteristic sign change of the PTE response being prominent in both plots. We model this response as follows: the laser spot is assumed to have a Gaussian profile and the induced temperature change is assumed proportional to the intensity. The PTE response is proportional to the temperature gradient and therefore to the



Figure 6.4: (Left) The simulated spatial dependence of the PTE response when measured along two contacts. Asymmetry in the response can result from purely geometric effects. (Right) The measured spatial dependence of photocurrent measured from a TaAs device. The asymmetry here results from a combination of geometric effects and additional nonlinear photocurrent generation mechanisms.

gradient of the Gaussian intensity profile. Fits to the response utilizing the gradient of a Gaussian are shown as solid red lines in Figure 6.4. While these fits capture most of the observed behavior, they fail to capture the asymmetry in the peak magnitudes. In the experimental measurements, we found that this asymmetry was well captured by assuming a Gaussian response centered on the device (blue line) which presumably has its physical origin in the nonlinear photocurrent generation. However, we still found asymmetries in the peak heights of the simulated PTE responses in the absence of any nonlinear responses, indicating that the asymmetry may also result from extrinsic effects such as the device geometry. We therefore find that separation of the PTE from the nonlinear response by spatial dependence alone is unsuitable and instead consider the polarization dependence of each response.

For the PTE response the laser acts as a local heat source, so we expect the response to be determined by the overall intensity of the absorbed light. We allow this to depend on the polarization of the incident light due to anisotropy from either the device or the underlying crystal structure. We write the current  $J_i$
along the *i*th crystallographic direction as:

$$J_i^{PTE} = A_i \left( \alpha_j |E_j|^2 + \alpha_k |E_k|^2 \right)$$
(6.19)

where  $A_i$  is a constant that depends on the thermal gradient, resistance, Seebeck coefficient, and other physical parameters,  $\alpha_j$  is the absorption coefficient along the *j*th crystallographic direction, and  $E_j$  is the electric field along the same direction. Using the expressions for the electric fields in Eq. 6.13 we obtain:

$$J_{a}^{PTE}(\phi) = \frac{1}{4} A_{a} E^{2} \left( (\alpha_{c} + 3\alpha_{a}) + (\alpha_{c} - \alpha_{a}) \cos(4\phi) \right)$$
(6.20)

$$J_{c}^{PTE}(\phi) = \frac{1}{4} A_{c} E^{2} \left( (\alpha_{c} + 3\alpha_{a}) + (\alpha_{c} - \alpha_{a}) \cos(4\phi) \right)$$
(6.21)

From this we can see that the polarization dependent response from the photothermal effect is identical to that from nonlinear effects along the c-axis, as in Eq. 6.15, whereas the nonlinear response along the a-axis is unique. We therefore make use of the distinction between the polarization dependence of the nonlinear response and the photothermal response along the a-axis to disentangle these two effects.

#### 6.4 Device Design

Previous measurements of nonlinear photocurrents in TaAs focused on the response to circularly polarized light and were measured on a bulk crystal[151]. As a result, the temperature range over which the CPGE was observable was limited to i100 K due to the dominance of thermal effects and resistive losses at ambient temperatures. This was explained as resulting from the competition between two length scales: the first being between the spot size of the incident radiation and the contact separation; and the second being between the penetration depth of the laser and the thickness of the crystal. Both of these are a consequence of

the photocurrent generation occurring only within the illuminated region of the samples. Laterally this is determined by the spot size and normal to the surface it is by the penetration depth. The photocurrent generated within this region spreads out until it reaches the contacts where it may be collected and measured, see Figure 6.5. Therefore if the spot size is much smaller than the contact separation, the thickness much larger than the penetration depth, or both, the measured photocurrent may be suppressed by the resistive losses that occur before reaching the contacts. Such effects were estimated as suppressing the measured CPGE by a factor of  $10^4$  in previous work[151].



Figure 6.5: Resistive losses for generated photocurrent may occur if the contact separation is much larger than the spot size and the thickness is much larger than the penetation depth of the light.

To mitigate these effects one would like a device with contact separation on the scale of the spot size, and a thickness on the order of the penetration depth. However, the penetration depth in TaAs at 10.6  $\mu$ m is ~ 250 nm[133], which is much smaller than the size of most as-grown crystals. In order to fabricate devices of such dimensions we utilized focused-ion-beam (FIB) based fabrication[162], through a process which we now describe in detail. Devices were fabricated starting from the as-grown single crystals. A FIB was used to slice a micron scale lamella out of the single crystal surface. This lamella was then transferred onto a sapphire



Figure 6.6: False colored SEM image of a microcopic TaAs (purple) device with Au (yellow) contacts. The device is approximately three times thicker than the penetration depth of the light used ( $\approx 750$  nm).

substrate with pre-made gold contacts and secured in place by a small amount of epoxy. Contacts to the sample are made by sputter-coating the sample and surrounding region with 100 nm of gold, followed by another round of FIB to cut individual contacts. A final found of FIB is used to shape the TaAs into the final device configuration (Hall bar) and thickness.

A scanning electron microscope (SEM) image of one TaAs device is shown in Figure 6.6. The thickness of the device is ~750 nm thick, approximately three times the penetration depth. Furthermore, the lateral dimensions of the Hall bar are approximately  $11 \times 2 \mu$ m such that the exposed TaAs is smaller than the minimum achievable spot size using our focusing optics. The microscopic dimensions of the device should, as discussed above, reduce the resistive losses experienced by the generated photocurrent. The particular device shown in Figure 6.6 has the crystallographic *a*-axis along the long direction of the Hall bar with the *c*axis along the short, perpendicular direction. We also fabricated a device with the crystal *a*- and *b*-axes in the plane, as well as multiple devices with smaller thicknesses (~400 nm).

### 6.5 Photocurrent Measurements

In Figure 6.7 we show three different TaAs devices from which we measured the photocurrent response. The first and third devices had *ac*-surfaces, while the second device had a *ab*-surface. This is indicated in the upper row of panels B–D, as well as a false-colored SEM image of each device. As discussed in Section 6.3 we anticipate that shift currents will be observed for the *ac*-face devices while, due to the lack of an in-plane *c*-axis, no shift currents will be generated for the *ab*-face device. In order to distinguish PTE responses from shift current, we measured the photocurrent as a function of the QWP angle. Prior to fitting, the data was symmetrized by averaging the data from 0° to 180° with that from 180° to 360°. This eliminates any sine and cosine functions with odd arguments (e.g.  $\sin \phi, \cos \phi$ ) that may result from beam precession due to rotation of the QWP from contributing, while preserving those with even arguments (e.g.  $\sin(4\phi), \cos(4\phi)$ ).

The measured photocurrents were fit by a phenomenological function of the form:

$$J(\phi) = D + L_S \sin(4\phi) + L_C \cos(4\phi) + C_S \sin(2\phi) + C_C \cos(2\phi)$$
(6.22)

where  $L_{S/C}$  capture the responses to linear polarization,  $C_S$  captures the response to circularly polarized light,  $C_C$  captures any other two-fold response, and D is a polarization independent term. In order to ensure that our fitting accurately captures the polarization dependent phase of the response we carefully calibrated the angle of the QWP. This was accomplished through two independent approaches. The first approach utilized a series of additional optics placed after the QWP: a Fresnel rhomb, a linear polarizer, and then a power meter. As the QWP was rotated, the light changes from horizontally polarized to circularly polarized, and then back to horizontally polarized. The fixed Fresnel rhomb allows the horizon-



Figure 6.7: A Diagram of the device showing the axis along which the current is being measured. **B**,**C**,**D** Upper panel: SEM image of the device being measured and its crystal orientation. Middle/Lower panels: black dots show the measured photocurrents with the solid magnenta lines representing fits to the data using Eq. 6.22. The crystal axis is labeled in each panel. The inset of each panel shows the relative magnitude of the  $L_S$  and  $L_C$  fitting terms.

tally polarized light to pass through unchanged, but alters circularly polarized light to linearly polarized at either  $\pm 45^{\circ}$  to the vertical axis depending on the light's helicity. The linear polarizer then may be used to select for light of right or left helicity. With the linear polarizer at  $-45^{\circ}$  we selected for left circularly polarized light and by recording the power as the QWP was rotated we identified the precise angles at which left circularly polarized light occurred.



Figure 6.8: The reflectance and power recorded by the MCT and power meter respectively. The concurrent peaks in the power and reflectance indicate QWP angles where left circularly polarized light was produced.

The second approach utilized the polarization dependence of the reflectance recorded by our MCT. Due to the near 45° angle of our BS, vertically polarized light is more strongly reflected than horizontally polarized light. The MCT signal therefore has a maximum whenever the input light is circularly polarized and a minimum whenever it is horizontally polarized, since in the former case the reflected light comes back from the QWP as vertically polarized.

The reflectance recorded by the MCT and the power recorded by the power meter as the QWP was rotated through 360° are shown in Figure 6.8. The four peaks in the MCT reflectance (black) correspond to the four times that circularly polarized light is achieved – left and right twice each. The two peaks in the power correspond to those for left circularly polarized light, and we can see that the data line up nicely with each other. After identification of the angles for which left circularly polarized light occurred ( $\sim 87^{\circ}$  and  $\sim 267^{\circ}$  respectively) we shifted any measured photocurrent data so that horizontally polarized light occurred at 0°.

The results of our photocurrent measurements are shown in Figure 6.7. The middle row of panels B–D show the signal measured on the longitudinal direction of each Hall bar, which correspond to the *a*-axis as indicated in each panel, while the bottom row shows measurements along the transverse Hall bar direction which correspond to the *c*-axis and *b*-axis as indicated. Inset in each panel is the normalized weight of the  $L_C$  (red) and  $L_S$  (green) fitting terms, where  $L_S$  and  $L_C$  are defined as in Eq. 6.22. We consider first the results from the *ac*-device in panels B. Along the *a*-axis of this device we find that the  $L_S$  term is five times larger than that of the  $L_C$  term, consistent with a dominant shift current response. In contrast, along the *c*-axis we find that the  $L_C$  term is dominant over the  $L_S$  term, consistent with photocurrent generated by both PTE and shift current generation mechanisms.

We next consider the response from the *ab*-face device shown in panels C. As discussed above, we expect no shift current response from such a device due to the lack of an in-plane crystallographic *c*-axis. We do however anticipate a response coming from the PTE, which should be qualitatively similar along each crystal axis. The relative  $L_C$  and  $L_S$  weights shown as insets confirm this expectation, with  $L_C$  providing the dominant response for both crystal axes, in contrast to the results from the *ac*-device.

As a check on the aptness of our technique for identifying photocurrents based off on the polarization dependence, we carried out measurements on a third TaAs device, shown in panels D, that was rotated by 90° in comparison to the previous devices. Rotation of the device by 90° will change the sign of the shift current response when compared to the original orientation, but it will not change the phase relation between sine or cosine terms, see Eq's. 6.17 and 6.18. The insets in panel D show behavior consistent with the previous ac-face device, with the

 $L_S$  term dominating along the *a*-axis, and term  $L_C$  dominating along the *c*-axis. Furthermore, the sign of the  $L_S$  term does change when rotated by 90°, consistent with the theoretical prediction. Table

Device	Crystal Axis	$D(\mu A)$	$L_S (\mu A)$	$L_C (\mu A)$
<i>ac</i> -1	a	-0.3825	-0.05318	-0.016063
	с	-0.08718	-0.02282	0.1114
ab	a	-1.388	-0.4923	2.010
	b	4.095	0.06037	0.9252
ac-2	a	0.1799	0.04937	0.03049
	с	-2.55	0.0464	-0.1496
ac-2 (rotated)	a	-2.602	-7.149	-0.799
	с	-26.31	-0.197	2.341

Table 6.1: Results of fitting the photocurrent data in Figure 6.7.

Lastly, to verify the second-order nature of the measured shift currents we measured the power dependence of the polarization independent (D), and linear sine and cosine terms  $(L_S \text{ and } L_C)$ . In addition to the expected linear power dependence from a second-order nonlinear effect, the PTE is also anticipated to be linear in power due to its dependence on the intensity of the light. Figure 6.9 shows that, over the 30 mW to 300 mW range, the response of all terms is approximately linear, in accordance with the theoretical expectations.



Figure 6.9: Power dependence of the  $D, L_S$ , and  $L_C$  terms from fitting. All are found to be linear.

# 6.6 Elimination of Other Nonlinear Mechanisms

In this section we discuss how we may rule out other nonlinear mechanisms as the source for our observed photocurrents. We consider first the photon drag[163] and the third-order nonlinear response[160]. Photon drag is an effect whereby the momentum of the incident photon is imparted to the electronic system, and is governed by the relation

$$J_i = \Phi_{ijkl} q_j E_k E_l \tag{6.23}$$

where  $q_j$  is the *j*th component of the photon's momentum, and  $\Phi_{ijkl}$  is a fourthrank tensor. The third-order nonlinear response is governed by a similar relation,

$$J_i = \sigma_{iikl}^{(3)} E_j E_k E_l \tag{6.24}$$

except the photon momentum has been replaced by a DC electric field  $E_j$ . The fourth-rank tensors in each of these processes are constrained by the same symmetries, and thus share the same non-zero and linear independent elements. We enumerate these below for the symmetric  $(\Phi_{ijkl}, \sigma_{ijkl})$ 

$$\Phi_{cccc}$$

$$\Phi_{aaaa} = \Phi_{bbbb}$$

$$\Phi_{aabb} = \Phi_{bbaa}$$

$$\Phi_{aacc} = \Phi_{bbcc}$$

$$\Phi_{ccaa} = \Phi_{ccbb}$$

$$\Phi_{abab} = \Phi_{abba} = \Phi_{baba} = \Phi_{baab}$$

$$\Phi_{acac} = \Phi_{acca} = \Phi_{bcbc} = \Phi_{bccb}$$

$$\Phi_{caca} = \Phi_{caac} = \Phi_{cbcb} = \Phi_{cbbc} \qquad (6.25)$$

and anti-symmetric components  $(\Psi_{ijkl}, \eta_{ijkl})$ :

$$\Psi_{abab} = \Psi_{baba} = -\Psi_{abba} = -\Psi_{baab}$$

$$\Psi_{acac} = \Psi_{bcbc} = -\Psi_{acca} = -\Psi_{bccb}$$

$$\Psi_{caca} = \Psi_{cbcb} = -\Psi_{caac} = -\Psi_{cbbc}$$
(6.26)

As so for the second-order photocurrents, we consider only the symmetric parts which govern the response to linearly polarized light. For the photon drag we expand the current expression for each axis to find:

$$J_{a} = \Phi_{aaaa}q_{a}|E_{a}|^{2} + \Phi_{aabb}q_{a}|E_{b}|^{2} + \Phi_{aacc}q_{a}|E_{c}|^{2} + \Phi_{abab}q_{b}(E_{a}E_{b}^{*} + E_{b}E_{a}^{*}) + \Phi_{acac}q_{c}(E_{a}E_{c}^{*} + E_{c}E_{a}^{*})$$
(6.27)  
$$J_{c} = \Phi_{cccc}q_{c}|E_{c}|^{2} + \Phi_{ccaa}q_{c}(|E_{a}|^{2} + |E_{b}|^{2})$$

$$+ \Phi_{caca} q_a (E_c E_a^* + E_a E_c^*) + \Phi_{cbcb} q_b (E_c E_b^* + E_b E_c^*)$$
(6.28)

In the geometry of our experiments, the *ac*-surface of the crystal was in-plane. Assuming the light was normally incident on this surface, we have  $q_a = q_c = 0$ , and  $E_b = 0$ . It is then clear that the photocurrent due to photon drag uniformly disappears. Our experiments were carried out at normal or near-normal incidence, so we expect that photon drag did not contribute to our measured photocurrents. Even allowing for a small degree of misalignment, the terms resembling those from the shift current  $(E_a E_c^* + E_c E_a^*)$  are proportional to  $q_c \propto \sin \theta$ , where  $\theta$  is the angle of incidence, such that at near normal incidence such terms would be heavily suppressed. We additionally note that such a term would have disappeared when the sample was rotated by 90°, yet we did not observe such behavior. We therefore rule out photon drag as being responsible for our observed photocurrents.

We now consider in detail the third-order response. As noted above, in order to generate such a response from a monochromatic light source the third electric field contribution must be a DC electric field distinct from the light, such that:

$$J_{i}(0) = \sigma_{ijkl}^{(3)} E_{j}(0) E_{k}(\omega) E_{l}(-\omega)$$
(6.29)

One possible source of the DC field could be the laser induced thermal gradients responsible for the PTE. Expanding the current relation we obtain:

$$J_{a} = \sigma_{aaaa}^{(3)} E_{a}(0) |E_{a}|^{2} + \sigma_{aabb}^{(3)} E_{a}(0) |E_{b}|^{2} + \sigma_{aacc}^{(3)} E_{a}(0) |E_{c}|^{2} + \sigma_{abab}^{(3)} E_{b}(0) (E_{a} E_{b}^{*} + E_{b} E_{a}^{*}) + \sigma_{acac}^{(3)} E_{c}(0) (E_{a} E_{c}^{*} + E_{c} E_{a}^{*})$$

$$J_{c} = \sigma_{cccc}^{(3)} E_{c}(0) |E_{c}|^{2} + \sigma_{ccaa}^{(3)} E_{c}(0) (|E_{a}|^{2} + |E_{b}|^{2}) + \sigma_{caca}^{(3)} E_{a}(0) (E_{c} E_{a}^{*} + E_{a} E_{c}^{*}) + \sigma_{cbcb}^{(3)} E_{b}(0) (E_{c} E_{b}^{*} + E_{b} E_{c}^{*})$$

$$(6.31)$$

While there are terms that do resemble those from the second-order response, we note that if the DC electric field is produced by the laser than the power dependence should be higher than linear. However as seen in Figure 6.9 the power dependence of all terms was linear. It is also possible that a built-in electric field such as that from a p - n junction could lead to observation of these third-order effects but not alter the power dependence. Measurements of the IV response of our devices both with and without illumination reveal Ohmic behavior which rules out this possibility as well. We therefore conclude that third-order responses are not the explanation for our measured photocurrents.



Figure 6.10: Representative current vs voltage measurements from a TaAs with (red) and without (black) laser illumination.

# 6.7 Comparison to Theory and Band Structure Calculations

In this section we compare our measured results to those predicted by band structure calculations. We begin with a discussion of the microscopic theory for the shift current. As shown in Eq. 6.1 the shift current is facilitated by the secondorder conductivity tensor  $\sigma_{ijk}^{(2)}$ . This tensor is non-zero only in materials which lack a center of inversion[81, 146, 155, 156, 164]. We also define the shift vector

$$\mathbf{R} = \frac{\partial \phi}{\partial \mathbf{k}} + \mathbf{A}_{cc} - \mathbf{A}_{vv} \tag{6.32}$$

where  $\phi$  is the phase of the velocity matrix element across the conduction and valence bands, and

$$\mathbf{A}_{mn}(\mathbf{k}) = i \langle \psi_m | \partial_{\mathbf{k}} | \psi_n \rangle \tag{6.33}$$

is the Berry connection between the mth and nth electronic bands at a given momentum **k**. It can be shown[81] that the second-order optical conductivity tensor is directly proportional to the integral of this shift vector over the BZ. Measurements of the tensor are therefore a way to directly measure the Berry curvature of a material.

The microscopic expression for the second-order conductivity tensor is given as[81]:

$$\sigma_{ijk}^{(2)}(\omega) = -\frac{i\pi e^3}{\hbar^2} \int \frac{dk^3}{(2\pi)^3} \sum_{n,m} f_{nm} \left( r_{mn}^j r_{nm;i}^k + r_{mn}^k r_{nm;i}^j \right) \delta(\omega_{mn} - \omega)$$
(6.34)

where *n* and *m* denote the band indices,  $f_{nm} = f_n - f_m$  is the difference in Fermi occupation functions,  $\omega_{mn} = (E_n - E_m)/\hbar$  is the energy difference between bands,  $r_{nm}^i = A_{nm}^i(1 - \delta_{n,m})$  is the interband Berry connection, and  $r_{nm;j}^i$  is the generalized derivative of  $r_{nm}^i$  defined as  $r_{nm;j}^i = \partial_{k,j}r_{nm}^i - i(A_{nn}^j - A_{mm}^j)r_{nm}^i$ . In the case of linearly polarized light with polarization along the *j*th direction, which corresponds to tensor element  $\sigma_{ijj}^{(2)}$ , the above expression simplifies to:

$$\sigma_{ijj}^{(2)} = -\frac{2\pi e^3}{\hbar^2} \int \frac{dk^3}{(2\pi)^3} \sum_{n,m} f_{nm} |r_{nm}^j|^2 R_{nm}^i \delta(\omega_{mn} - \omega)$$
(6.35)

where

$$R_{nm}^{i} = \frac{\partial \phi_{nm}}{\partial k^{i}} + A_{nn}^{i} - A_{mm}^{i}$$
(6.36)

is the *i*th component of the shift vector defined above in Eq. 6.32, and  $\phi_{nm} = -\arg[r_{nm}^j]$ . In a system with a finite gap, we expect  $\sigma_{ijj}^{(2)}$  to disappear for energies below the gap, as in the case of ferroelectric insulators[157]. However, in systems such as TaAs which have no electronic band gap and a singular Berry connection, the shift current tensor is anomalously large in the low  $\omega$  limit[148].

In our experiments the photons have energy  $\hbar\omega = 117$  meV. At this energy the dispersions near the Weyl nodes are no longer linear. In order to quantitatively model the response it is therefore important to use detailed models of the band structure from first-principles calculations, rather than a simple model of a generic type-I WSM. DFT calculations of the electronic band structure of TaAs were initially carried out using the Quantum Espresso package [165]. A 32-band tight binding Hamiltonian model was then obtained from the DFT data using the Wannier90 package [166]. The tight binding model well reproduces the low energy features of the reported band structure of TaAs, including the energy and momentum locations of the Weyl nodes, and the electron and hole pockets (see for example [167]). In Figure 6.11 we show the first BZ of TaAs with the calculated FS at charge neutrality. The 24 Weyl nodes are in close proximity to the nearly nodal rings visible along the four primary axes. The nodes are labeled in Figure 6.12 which shows a zoomed-in version of the electron and hole pockets. In Figure 6.13 we show the momentum space surface which corresponds to a direct energy gap of 117 meV. At this energy all of the Weyl nodes are enclosed by the surface which indicates that, as noted above, the band dispersion has significantly deviated from linear.



Figure 6.11: The first BZ of TaAs showing the calculated FS at charge neutrality.



Figure 6.12: The Fermi pockets of TaAs near one nearly nodal ring. The red electron and hole pockets enclose the W1 and W2 Weyl nodes, while the gray hole pockets (H) are topologically trivial.



Figure 6.13: The momentum space surface formed by the direct energy gap of 117 meV.

The second-order optical conductivity tensor was calculated from the full 32band tight binding model at room temperature. The conductivity values were calculated for doping values  $\mu = -20$  meV to  $\mu = +20$  meV. The resulting values for the tensor element  $\sigma_{aac}^{(2)}$  are shown in Figure 6.14 as a function of incident photon energy. The dashed line at 117 meV shows the energy of the laser used in our measurements. We can see that in this energy range the tensor element has a relatively constant value at no doping, and with mild hole doping, although with electron doping there is a greater degree of variation. At lower energies we see that there is a large peak in the tensor value, suggesting that future experiments with longer wavelength sources will be valuable.



Figure 6.14: Calculated values of  $\sigma_{aac}^{(2)}$  as a function of doping level and incident photon energy. The dashed line indicates the energy of the laser used in our experiments.

To properly compare our photocurrent measurements to the predicted values we calculate the carrier concentrations from measurements of the Hall resistance. These transport measurements were carried out using a custom-built transport system and AMI 9 T superconducting split-coil magnet[168]. An AC at 586.3 Hz was applied to the current leads of the Hall bar and the voltage drops across the device recorded by SR830 lock-in amplifiers. The exact value of the current was simultaneously monitored by measurement of the voltage across a known resistor in-series with the device. At 8 K we recorded the magnetic field dependence of the longitudinal and transverse voltages out to 8 T. The Hall conductivity calculated from these measurements is shown in Figure 6.15. The sharp peak at low fields and saturation at higher fields are consistent with previously published results[32]. We fit the Hall conductivity with a two-carrier model, with the results shown as the red line. From this fitting we extract the electron and hole concentrations  $n_e = 8.08 \times 10^{17} \text{ cm}^{-3}$  and  $n_h = 9.35 \times 10^{17} \text{ cm}^{-3}$  respectively, which shows that there is a very slight hole doping of our TaAs. (As an aside, the electron and hole mobilities obtained from fitting were  $\mu_e = 7.3 \times 10^4 \text{ cm}^2/(\text{V}\cdot\text{s})$  and  $\mu_h = 1.6 \times 10^4 \text{ cm}^2/(\text{V}\cdot\text{s})$ , which are consistent with measurements of bulk crystals, indicating that the FIB fabrication did not result in damages to the underlying crystal.)



Figure 6.15: Hall conductivity data in black with the red line showing the fit by a two-band model.

The values of  $\sigma_{ijk}$  for various doping levels are shown in Table 6.2. For a very slight hole doping as in our samples we see that theory predicts a value of  $\sigma_{aac} = 201 \ \mu \text{A/V}^2$ . From our experimentally measured values we calculate  $\sigma_{aac} = 32 \pm 3.7 \ \mu \text{A/V}^2$ . These values appear to disagree by approximately an

Tensor Element $(\mu A/V^2)$	$\mu = 0$	$\mu = 10 \text{ meV}$	$\mu = -10 \text{ meV}$
$\sigma^{(2)}_{aac}$	201	206	191
$\sigma^{(2)}_{caa}$	30	54	5
$\sigma^{(2)}_{ccc}$	-227	-231	-216

Table 6.2: The calculated room-temperature shift-current response tensor at various values of the chemical potential, including charge neutrality (chemical potential  $\mu = 0$  meV), electron doping  $\mu = 10$  meV, and hole doping  $\mu = -10$  meV.

order of magnitude. We note however, that this experimental value did not take into account the reflectance of TaAs and assumed that all of the incident light was absorbed by the sample. The reflectance of TaAs at 10.6  $\mu$ m is ~0.78[133], which when accounted for in our calculated of the conductivity tensor yields a value of  $\sigma_{aac} = 154 \pm 17 \ \mu \text{A/V}^2$ , in much closer agreement with the theoretically predicted value. We lastly note that in the tight-binding contributions there are two interband transitions which contribute to  $\sigma_{aac}$ . One of these is two between two Weyl bands, while the other is between one of the Weyl bands and a higher energy conduction band. The former of these contributes  $\sigma_{aac} = 251 \ \mu \text{A/V}^2$ while the latter contributes  $\sigma_{aac} = -50 \ \mu \text{A/V}^2$ . This suggests that the primary contributions to the shift current come from the Weyl nodes.

### 6.8 Glass Coefficient

In this section we discuss the calculation of the Glass coefficient which enables comparison of the shift current response of TaAs to other materials. As discussed above, the generation of photocurrent occurs only within the penetration depth of the light within the material. In order to account for the absorptive losses one typically calculates the Glass coefficient[156, 169]. Named for A.M. Glass who performed some of the pioneering work on the BPVE[169], the Glass coefficient normalizes the second-order optical conductivity by the absorption coefficient. This results in the expression

$$J = \alpha GI \tag{6.37}$$

where  $\alpha$  is the absorption coefficient, *I* the incident intensity, *J* the current density, and *G* the Glass coefficient, often expressed in units of cm/V.

From the SEM images of the device we estimate the device thickness and width to be 410 nm and 2  $\mu$ m respectively. Using  $|L_S| = 0.05318 \ \mu$ A we find a current density  $J = 64.85 \ \text{kA/m^2}$ . The absorption coefficient of  $\alpha = 7.7 \times 10^6 \ \text{1/m}$  was calculated from optical conductivity data reported in [133]. We estimate the spot size by scanning the laser across the device which resulted in an estimate for the beam radius of  $\approx 50 \ \mu$ m. The incident power was 40 mW. Using these values we calculate a Glass coefficient  $G = 1.65 \times 10^{-7} \ \text{cm/V}$ .



Figure 6.16: Experimentally measured and calculated Glass coefficients for various materials. Our reported Glass coefficient for TaAs is shown as a blue square in a longer wavelength range than any previously reported value, and with larger magnitude.

In Figure 6.16 we show previously reported and calculated values of the Glass

coefficient as a function of wavelength. Experimentally measured values are shown as circles while calculated values are drawn as lines. These materials mostly consist of ferroelectric insulators or strained semiconductors with band gaps in the visible range[77, 170–176]. Our value for TaAs is plotted as a blue square. We note that, not only is our reported value an order of magnitude larger than any previously reported Glass coefficient, it also is the first report in the mid-IR range.

#### 6.9 Conclusions

We performed measurements of the second-order nonlinear photocurrent in TaAs. By careful analysis of the polarization dependence of the response we were able to disentangle the shift current response from the PTE. Our calculated second-order optical conductivity values agree well with those predicted by first-principles calculations of the band structure. We further calculate the Glass coefficient and find that, not only is it the first Glass coefficient reported in the mid-IR wavelength range, but it is an order of magnitude larger than any previously reported value. Our microscopic theory indicates that the dominant contribution to this response comes from the Weyl nodes and their diverging Berry connection. These results suggest that WSMs could be harnessed for future use in clean energy technologies.

# CHAPTER VII

# Conclusions

# 7.1 Concluding Remarks

In this dissertation we have presented numerous works investigating multiple topological materials. In Chapter II we first reported on the Raman spectra of thin film heterostructures of the topological insulator  $Bi_2Se_3$  and magnetic semiconductor EuS. The paramagnetic Raman signal from EuS was found to be absent in the  $Bi_2Se_3/EuS$  heterostructures which was taken as indirect evidence for charge transfer between the two materials. A simple model of the band bending based on previously reported work functions for the materials suggests that such a charge transfer is likely, with electrons transferring from the EuS into the  $Bi_2Se_3$ . With the Fermi level of the EuS thus lowered into the valence band, the resonance condition for Raman scattering is no longer satisfied, explaining the absence of the mode in the heterostructures. Temperature dependent measurements of the magnetic moment and calculations of the Fabry-Perot interference further rule out magnetic ordering and interference effects respectively from preventing observation of the mode. In addition, measurements of films with varying EuS thicknesses on multiple substrates provided evidence for changes in the interfacial strain depending on the relative lattice mismatch and layer thickness.

In Chapter III we discussed the temperature dependent Raman spectra from

single crystal WP<sub>2</sub>. We found that of the 14 optical modes we observed, two of them (the lowest energy  $A_1$  modes) displayed a temperature dependent linewidth that was dominated by phonon decay into electron-hole pairs near the Fermi surface. First principles calculations of the mode resolved phonon-electron coupling strength, supported by group theoretical calculations of the scattering selection rules, indicate that both interband and intraband scattering of electrons by the finite **q** phonons contribute to this behavior. Though inaccessible in our Raman measurements, in light of the significant phonon-electron coupling strengths predicted by our computational results we discussed the role of phonon-electron scattering by the acoustic phonons in contributing to properties such as the electrical conductivity and mobility. The bunching of the acoustic mode dispersions can lead to a reduction in the phonon-phonon scattering rates, allowing phonon-electron processes to play an enhanced role. We also discussed the ways in which the topological features of the electronic band structure can facilitate phonon-electron scattering.

Chapter IV addressed our temperature dependent Raman study of the Weyl semimetals NbAs and TaAs. In NbAs we observed a temperature independent, Fano lineshape in the two  $B_1$  modes, while the same modes in TaAs displayed no such asymmetry. First principles calculations of the electron-phonon coupling strength confirm that NbAs has overall larger coupling strengths compared to TaAs, which is consistent with the  $B_1$  modes symmetry/asymmetry. The linewidths of the  $A_1$  modes in both materials were found to display the same type of phonon-electron behavior as seen in WP<sub>2</sub> when measured in the XX configuration. However when NbAs was measured in the ZZ configuration the  $A_1$ linewidth was dominated by phonon-phonon scattering. We explained this difference by using group theory to establish the wave vector selection rules for scattering of electrons by phonons. Phonons with momentum along the  $k_z$  direction (as in the XX configuration) are able to scatter electrons near the Weyl nodes in the  $k_z = 0$  plane, while phonons with momentum along  $k_x$  (as in the ZZ configuration) are unable to satisfy the necessary momentum conservation. The first principles calculations also suggested that optical phonons with large momenta could be a significant source of scattering between Weyl nodes of opposite chirality in these systems.

We then described the development of our photocurrent measurement system in Chapter V. We discussed the experimental capabilities that we designed the system to have, and detailed the various components required to achieve these goals. Since the system was constructed with MIR lasers, we addressed some of the challenges of working with these invisible light sources and the techniques we used to manage them. We considered some of the advantages and disadvantages of different approaches to measuring photocurrents, with the method of measuring the current across a load resistor in series with the illuminated sample seeming to offer the clearest benefits. We lastly provided examples of some standard operating procedures for the system, as well as techniques that can aid in analysis of the data obtained from this system.

Lastly, in Chapter VI we discussed the results of an experiment performed using the photocurrent measurement setup described in Chapter V. Our measurements of the second-order nonlinear photocurrent in the Weyl semimetal TaAs revealed the largest bulk photovoltaic effect reported to date. Careful analysis of the photocurrent polarization dependence allowed us to separate the BPVE from the coexisting photo-thermoelectric effect. First principles calculations of the second-order conductivity tensor show excellent agreement with our reported value, and suggest that the colossal BPVE we reported on arises due to the divergent Berry connection of the Weyl nodes.

# 7.2 Suggested Further Experiments

Our understanding of the phonon linewidths whose temperature dependence indicates a dominance of phonon-electron decay is far from complete. Let us start by considering the qualitative and quantitative difference between the linewidth of the  $A_1$  mode in TaAs as measured by Raman and IR spectroscopies[114, 115]. In the IR measurements, the linewidth monotonically decreases as a function of increasing temperature, in accordance with the electron-hole model developed in graphite[123]. In contrast, our Raman measurements reveal a linewidth that first increases with temperature and only then begins to decrease. In our previous discussion of this difference we ascribed the Raman behavior to a finite chemical potential compared to the IR work. However, when viewed in totality with other results it becomes clear that such a picture is not entirely justified.

The first piece of evidence suggesting that this interpretation is incomplete is the nearly identical linewidth behavior observed in WP<sub>2</sub>. In TaAs and NbAs there are Weyl nodes located near the Fermi energy so there is clear meaning to a chemical potential. However, in WP<sub>2</sub> there are no nodes near the Fermi energy. We modified the interpretation of the chemical potential term in our phonon-electron linewidth fitting function to account for this by recasting it as an "activation" energy,  $\omega_a$ , which was required for the electronic transition to be available. Yet on the energy scale of the optical phonon energies the electronic structure does not significantly change. Indeed, our calculations explicitly show that interband and intraband transitions for optical phonons at any energy are available at the Fermi energy, no  $\omega_a$  needed. The validity of either the chemical potential or the  $\omega_a$  interpretations are therefore questionable.

Second is the residual linewidth value as  $T \to 0$ . The phonon-electron model with finite chemical potential (or  $\omega_a$ ) predicts a phonon-electron contribution of zero to the linewidth as  $T \to 0$ . We have therefore claimed that the residual linewidth is due to anharmonic effects. However, the measurement of the  $A_1$ NbAs mode in the ZZ configuration suggests that this is not correct either. In the ZZ measurement the  $A_1$  linewidth very clearly follows the anharmonic trend, and even at the highest temperatures measured its value fails to reach that of the  $A_1$ measurement in XX. The low temperature values for the  $A_1$  linewidths observed across all the materials we report on here must therefore have their origins in a mechanism not captured by our current modeling.

We believe that future experiments and theoretical works could help shed light on this unresolved issue. In particular, we anticipate that temperature dependent inelastic neutron or x-ray measurements that can access a larger range of momentum values will be invaluable to understanding this behavior. We note that the distinction between the IR and Raman measurements is likely due to the difference between the momentum imparted to the phonons by each technique. In Raman the excitation source is an order  $\sim 1$  eV laser, which can provide momentum of order  $10^7$  m<sup>-1</sup>, while in IR measurements the phonon is directly created by absorption of light at its energy of order 0.01 eV, which only has momentum of order  $10^5$  m<sup>-1</sup>. If this does explain the difference between the IR and Raman measurements it will be interesting to see how broader ranges of momentum impact the phonon lifetimes as well. Raman and IR measurements performed on the same set of TaAs or NbAs crystals would also help address whether the chemical potential interpretation is valid.

In the case of  $WP_2$ , inelastic neutron or x-ray scattering measurements will also prove invaluable, as will other techniques such as Brillouin scattering which are able to access the acoustic modes. Although our Raman measurements and first principles calculations show that phonon-electron processes can dominate in the optical modes, direct evidence confirming or refuting this behavior in the acoustic modes would help resolve questions surrounding the origins of the hydrodynamic behavior in  $\beta$ -WP<sub>2</sub>.

There are a number of ways in which the PVIC system described in Chapter V can be improved. One non-trivial though important upgrade would be the incorporation of cryogenics to allow for sample measurement at variable temperature. The incorporation of additional light sources to allow for measurement over a larger range of excitation energies would also prove useful for this system. The MCT used for reflectance measurements could be replaced by a similar sensor that does not require liquid nitrogen cooling. This would both reduce the cost of using the system and allow for reflectance measurements over longer time scales without requiring the user to refill the MCT every few hours. The LabVIEW that was developed to control the system was written just to bring the system up to operation. However, we are certain that improvements could be made which would increase the rate of data acquisition in the system. Lastly, using lock-in techniques such a tandem or direct sideband demodulation could allow for the measurement of effects such as the photo-Hall which result from a combination of both the optical field and an applied electric field.

Many of these proposed upgrades would be useful in further investigation of the BPVE in TaAs. Temperature dependent measurements could provide information about the types of scattering processes that limit the BPVE. Measurements of the photoresponse at many wavelengths, ideally in a spectroscopic manner, could allow for comparison of the predicted second-order optical conductivity tensor to measured values. This could be particularly promising at longer wavelengths where theory predicts an even larger response due to the diverging Berry connection. Measurements of NbAs, NbP, or TaP could also be of interest, since they have similar band structures to TaAs but different degrees of spin-orbit coupling which should influence the Berry connection of each material.

### BIBLIOGRAPHY

- E. Noether, "Invariante Variationsprobleme", Nachr. Akad. Wiss. Goettingen Math.-Phys. Kl. 2, 235–257 (1918).
- [2] H. Goldstein, C. P. Poole Jr., and J. L. Safko, "Classical Mechanics", (2002).
- [3] L. D. Landau, "On the Theory of Phase Transitions", Zh. Eksp. Teor. Fiz. 7, 19–32 (1937).
- [4] R. Pathria and P. D. Beale, *Statistical Mechanics*, 3rd ed. (Elsevier, 2011).
- [5] K. v. Klitzing, G. Dorda, and M. Pepper, "New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance", Phys. Rev. Lett. 45, 494–497 (1980).
- [6] D. J. Thouless, M. Kohmoto, M. P. Nightingale, and M. den Nijs, "Quantized Hall Conductance in a Two-Dimensional Periodic Potential", Phys. Rev. Lett. 49, 405–408 (1982).
- [7] M. Kohmoto, "Topological invariant and the quantization of the Hall conductance", Annals of Physics 160, 343–354 (1985).
- [8] J. E. Avron, R. Seiler, and B. Simon, "Homotopy and Quantization in Condensed Matter Physics", Phys. Rev. Lett. 51, 51–53 (1983).
- [9] Q. Niu, D. J. Thouless, and Y.-S. Wu, "Quantized Hall conductance as a topological invariant", Phys. Rev. B 31, 3372–3377 (1985).
- [10] M. V. Berry, "Quantal phase factors accompanying adiabatic changes", Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences **392**, 45–57 (1984).
- [11] D. Xiao, M.-C. Chang, and Q. Niu, "Berry phase effects on electronic properties", Rev. Mod. Phys. 82, 1959–2007 (2010).
- [12] N. W. Ashcroft and N. D. Mermin, Solid State Physics (Harcourt Inc., United States of America, 1976).
- [13] J. K. Asbóth, L. Oroszlány, and A. Pályi, A Short Course on Topological Insulators, Band Structure and Edge States in One and Two Dimensions, 1st ed. (Springer International Publishing, 2016).
- [14] C.-K. Chiu, J. C. Y. Teo, A. P. Schnyder, and S. Ryu, "Classification of topological quantum matter with symmetries", Rev. Mod. Phys. 88, 035005 (2016).
- [15] N. P. Armitage, E. J. Mele, and A. Vishwanath, "Weyl and Dirac semimetals in three-dimensional solids", Rev. Mod. Phys. 90, 015001 (2018).
- [16] H. Weyl, "GRAVITATION AND THE ELECTRON", Proceedings of the National Academy of Sciences 15, 323–334 (1929).

- [17] T. Wehling, A. Black-Schaffer, and A. Balatsky, "Dirac materials", Advances in Physics 63, 1–76 (2014).
- [18] X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, "Topological semimetal and Fermi-arc surface states in the electronic structure of pyrochlore iridates", Phys. Rev. B 83, 205101 (2011).
- [19] J. von Neumann and E. Wigner, "ÜBER MERKWÜRDIGE DISKRETE EIGENWERTE", Physik. Z. 30, 465–467 (1929).
- [20] C. Herring, "Accidental Degeneracy in the Energy Bands of Crystals", Phys. Rev. 52, 365–373 (1937).
- [21] H. Nielsen and M. Ninomiya, "Absence of neutrinos on a lattice: (I). Proof by homotopy theory", Nuclear Physics B 185, 20–40 (1981).
- [22] H. Nielsen and M. Ninomiya, "Absence of neutrinos on a lattice: (II). Intuitive topological proof", Nuclear Physics B 193, 173–194 (1981).
- [23] M. Z. Hasan, S.-Y. Xu, I. Belopolski, and S.-M. Huang, "Discovery of Weyl Fermion Semimetals and Topological Fermi Arc States", Annual Review of Condensed Matter Physics 8, 289–309 (2017).
- [24] C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Wosnitza, Z. Liu, Y. Chen, W. Schnelle, H. Borrmann, Y. Grin, C. Felser, and B. Yan, "Extremely large magnetoresistance and ultrahigh mobility in the topological Weyl semimetal candidate NbP", Nature Physics 11, 645–649 (2015).
- [25] G. Autès, D. Gresch, M. Troyer, A. A. Soluyanov, and O. V. Yazyev, "Robust Type-II Weyl Semimetal Phase in Transition Metal Diphosphides  $XP_2$ (X = Mo, W)", Physical Review Letters **117**, 066402 (2016).
- [26] H. Weng, C. Fang, Z. Fang, B. A. Bernevig, and X. Dai, "Weyl Semimetal Phase in Noncentrosymmetric Transition-Metal Monophosphides", Phys. Rev. X 5, 011029 (2015).
- [27] S.-Y. Xu, I. Belopolski, N. Alidoust, M. Neupane, G. Bian, C. Zhang, R. Sankar, G. Chang, Z. Yuan, C.-C. Lee, S.-M. Huang, H. Zheng, J. Ma, D. S. Sanchez, B. Wang, A. Bansil, F. Chou, P. P. Shibayev, H. Lin, S. Jia, and M. Z. Hasan, "Discovery of a Weyl fermion semimetal and topological Fermi arcs", Science **349**, 613–617 (2015).
- [28] B. Q. Lv, N. Xu, H. M. Weng, J. Z. Ma, P. Richard, X. C. Huang, L. X. Zhao, G. F. Chen, C. E. Matt, F. Bisti, V. N. Strocov, J. Mesot, Z. Fang, X. Dai, T. Qian, M. Shi, and H. Ding, "Observation of Weyl nodes in TaAs", Nature Physics 11, 724–727 (2015).
- [29] L. X. Yang, Z. K. Liu, Y. Sun, H. Peng, H. F. Yang, T. Zhang, B. Zhou, Y. Zhang, Y. F. Guo, M. Rahn, D. Prabhakaran, Z. Hussain, S.-K. Mo, C. Felser, B. Yan, and Y. L. Chen, "Weyl semimetal phase in the noncentrosymmetric compound TaAs", Nature Physics 11, 728–732 (2015).

- [30] H. Nielsen and M. Ninomiya, "The Adler-Bell-Jackiw anomaly and Weyl fermions in a crystal", Physics Letters B **130**, 389–396 (1983).
- [31] C.-L. Zhang, S.-Y. Xu, I. Belopolski, Z. Yuan, Z. Lin, B. Tong, G. Bian, N. Alidoust, C.-C. Lee, S.-M. Huang, T.-R. Chang, G. Chang, C.-H. Hsu, H.-T. Jeng, M. Neupane, D. S. Sanchez, H. Zheng, J. Wang, H. Lin, C. Zhang, H.-Z. Lu, S.-Q. Shen, T. Neupert, M. Zahid Hasan, and S. Jia, "Signatures of the Adler–Bell–Jackiw chiral anomaly in a Weyl fermion semimetal", Nature Communications 7, 10735 (2016).
- [32] X. Huang, L. Zhao, Y. Long, P. Wang, D. Chen, Z. Yang, H. Liang, M. Xue, H. Weng, Z. Fang, X. Dai, and G. Chen, "Observation of the Chiral-Anomaly-Induced Negative Magnetoresistance in 3D Weyl Semimetal TaAs", Phys. Rev. X 5, 031023 (2015).
- [33] S. Liang, J. Lin, S. Kushwaha, J. Xing, N. Ni, R. J. Cava, and N. P. Ong, "Experimental Tests of the Chiral Anomaly Magnetoresistance in the Dirac-Weyl Semimetals Na<sub>3</sub>Bi and GdPtBi", Phys. Rev. X 8, 031002 (2018).
- [34] B. Yan and C. Felser, "Topological Materials: Weyl Semimetals", Annual Review of Condensed Matter Physics 8, 337–354 (2017).
- [35] D. Soluyanov Alexey A.and Gresch, Z. Wang, Q. Wu, M. Troyer, X. Dai, and B. A. Bernevig, "Type-II Weyl semimetals", Nature 527, 495–498 (2015).
- [36] M. Z. Hasan and C. L. Kane, "Colloquium: Topological insulators", Rev. Mod. Phys. 82, 3045–3067 (2010).
- [37] M. Franz and L. Molenkamp, *Topological Insulators*, 1st ed. (Elsevier, 2013).
- [38] J. E. Moore, "The birth of topological insulators", Nature 464, 194–198 (2010).
- [39] C. L. Kane and E. J. Mele, " $Z_2$  Topological Order and the Quantum Spin Hall Effect", Phys. Rev. Lett. **95**, 146802 (2005).
- [40] J. E. Moore and L. Balents, "Topological invariants of time-reversal-invariant band structures", Phys. Rev. B 75, 121306 (2007).
- [41] X.-L. Qi, T. L. Hughes, and S.-C. Zhang, "Topological field theory of timereversal invariant insulators", Phys. Rev. B 78, 195424 (2008).
- [42] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, "A topological Dirac insulator in a quantum spin Hall phase", Nature 452, 970–974 (2008).
- [43] D. Hsieh, Y. Xia, L. Wray, D. Qian, A. Pal, J. H. Dil, J. Osterwalder, F. Meier, G. Bihlmayer, C. L. Kane, Y. S. Hor, R. J. Cava, and M. Z. Hasan, "Observation of Unconventional Quantum Spin Textures in Topological Insulators", Science **323**, 919–922 (2009).

- [44] Y. L. Chen, J.-H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, "Massive Dirac Fermion on the Surface of a Magnetically Doped Topological Insulator", Science **329**, 659–662 (2010).
- [45] D. Hsieh, Y. Xia, D. Qian, L. Wray, F. Meier, J. H. Dil, J. Osterwalder, L. Patthey, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, "Observation of Time-Reversal-Protected Single-Dirac-Cone Topological-Insulator States in Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>", Phys. Rev. Lett. **103**, 146401 (2009).
- [46] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z.-X. Shen, "Experimental Realization of a Three-Dimensional Topological Insulator, Bi<sub>2</sub>Te<sub>3</sub>", Science **325**, 178–181 (2009).
- [47] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, "Observation of a large-gap topological-insulator class with a single Dirac cone on the surface", Nature Physics 5, 398–402 (2009).
- [48] C.-Z. Chang, J. Zhang, X. Feng, J. Shen, Z. Zhang, M. Guo, K. Li, Y. Ou, P. Wei, L.-L. Wang, Z.-Q. Ji, Y. Feng, S. Ji, X. Chen, J. Jia, X. Dai, Z. Fang, S.-C. Zhang, K. He, Y. Wang, L. Lu, X.-C. Ma, and Q.-K. Xue, "Experimental Observation of the Quantum Anomalous Hall Effect in a Magnetic Topological Insulator", Science 340, 167–170 (2013).
- [49] X. Kou, Y. Fan, M. Lang, P. Upadhyaya, and K. L. Wang, "Magnetic topological insulators and quantum anomalous hall effect", Solid State Communications 215–216, 34–53 (2015).
- [50] R. Powell, Symmetry, Group Theory, and the Physical Properties of Crystals, 1st ed., Vol. 824 (Springer-Verlag New York, 2010).
- [51] M. Dresselhaus, G. Dresselhaus, and A. Jorio, *Group Theory* (Springer-Verlag Berlin Heidelberg, 2008).
- [52] C. Malgrange, C. Ricolleau, and M. Schlenker, *Symmetry and Physical Properties of Crystals* (Springer Dordrecht, 2011).
- [53] J. L. Birman, Theory of Crystal Space Groups and Infra-Red and Raman Lattice Processes of Insulating Crystals (Springer-Verlag Berlin Heidelberg, 1984).
- [54] C. V. Raman and K. S. Krishnan, "A New Type of Secondary Radiation", Nature 121, 501–502 (1928).
- [55] P. Yu and M. Cardona, Fundamentals of Semiconductors: Physics and Material Properties, 4th ed. (Springer-Verlag Berlin Heidelberg, 2010).
- [56] T. Moriya, "Theory of Light Scattering by Magnetic Crystals", Journal of the Physical Society of Japan 23, 490–500 (1967).

- [57] G. F. Reiter, "Light scattering from energy fluctuations in magnetic insulators", Phys. Rev. B 13, 169–173 (1976).
- [58] T. P. Devereaux and R. Hackl, "Inelastic light scattering from correlated electrons", Rev. Mod. Phys. 79, 175–233 (2007).
- [59] M. Cardona, Light Scattering in Solids I, Introductory concepts, 2nd ed., Vol. 8 (Springer-Verlag Berlin Heidelberg, 1983).
- [60] M. Cardona and G. Güntherodt, Light Scattering in Solids II, Basic Concepts and Instrumentation (Springer-Verlag Berlin Heidelberg, 1982).
- [61] Y. Tian, A. A. Reijnders, G. B. Osterhoudt, I. Valmianski, J. G. Ramirez, C. Urban, R. Zhong, J. Schneeloch, G. Gu, I. Henslee, and K. S. Burch, "Low vibration high numerical aperture automated variable temperature Raman microscope", Review of Scientific Instruments 87, 043105 (2016).
- [62] P. A. Temple and C. E. Hathaway, "Multiphonon Raman Spectrum of Silicon", Phys. Rev. B 7, 3685–3697 (1973).
- [63] E. Kroumova, M. Aroyo, J. Perez-Mato, A. Kirov, C. Capillas, S. Ivantchev, and H. Wondratschek, "Bilbao Crystallographic Server : Useful Databases and Tools for Phase-Transition Studies", Phase Transitions 76, 155–170 (2003).
- [64] T. C. Damen, S. P. S. Porto, and B. Tell, "Raman Effect in Zinc Oxide", Phys. Rev. 142, 570–574 (1966).
- [65] S. Schippers, "Analytical expression for the convolution of a Fano line profile with a gaussian", Journal of Quantitative Spectroscopy and Radiative Transfer 219, 33–36 (2018).
- [66] F. Schreier, "Optimized implementations of rational approximations for the Voigt and complex error function", Journal of Quantitative Spectroscopy and Radiative Transfer **112**, 1010–1025 (2011).
- [67] Y. Tian, G. B. Osterhoudt, S. Jia, R. Cava, and K. S. Burch, "Local phonon mode in thermoelectric Bi<sub>2</sub>Te<sub>2</sub>Se from charge neutral antisites", Applied Physics Letters **108**, 041911 (2016).
- [68] U. Fano, "Effects of Configuration Interaction on Intensities and Phase Shifts", Phys. Rev. 124, 1866–1878 (1961).
- [69] G. D. Mahan, *Many-Particle Physics*, 3rd ed. (Springer US, 2000).
- [70] M. Balkanski, R. F. Wallis, and E. Haro, "Anharmonic effects in light scattering due to optical phonons in silicon", Phys. Rev. B 28, 1928–1934 (1983).
- [71] J. Menéndez and M. Cardona, "Temperature dependence of the first-order Raman scattering by phonons in Si, Ge, and  $\alpha$ -Sn: Anharmonic effects", Phys. Rev. B **29**, 2051–2059 (1984).

- [72] X. X. Yang, Z. F. Zhou, Y. Wang, R. Jiang, W. T. Zheng, and C. Q. Sun, "Raman spectroscopy determination of the Debye temperature and atomic cohesive energy of CdS, CdSe, Bi<sub>2</sub>Se<sub>3</sub>, and Sb<sub>2</sub>Te<sub>3</sub> nanostructures", Journal of Applied Physics **112**, 083508 (2012).
- [73] P. G. Klemens, "Anharmonic Decay of Optical Phonons", Phys. Rev. 148, 845–848 (1966).
- [74] J. D. Jackson, *Classical Electrodynamics*, 3rd ed. (John Wiley & Sons, United States of America, 1999).
- [75] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, "Generation of Optical Harmonics", Phys. Rev. Lett. 7, 118–119 (1961).
- [76] R. W. Boyd, Nonlinear Optics, 3rd ed. (Elsevier Inc., 2008).
- [77] B. I. Sturman and V. M. Fridkin, The Photovoltaic and Photorefractive Effects in Noncentrosymmetric Materials (Gordon and Breach Science Publishers, 1992).
- [78] S. Ganichev, J. Karch, M. Olbrich P. Schmalzbauer, C. Zoth, C. Brinsteiner, U. Wurstbauer, M. M. Glazov, S. Tarasenko, D. Weiss, J. Eroms, R. Yakimova, S. Lara-Avila, S. Kubatkin, and E. Ivchenko, "Photon helicity driven currents in graphene", in 35th international conference on infrared, millimeter, and terahertz waves (2010), pp. 1–1.
- [79] D. Rees, K. Manna, B. Lu, T. Morimoto, H. Borrmann, C. Felser, J. E. Moore, D. H. Torchinsky, and J. Orenstein, "Helicity-dependent photocurrents in the chiral Weyl semimetal RhSi", Science Advances 6 (2020) 10. 1126/sciadv.aba0509.
- [80] F. de Juan, A. G. Grushin, T. Morimoto, and J. E. Moore, "Quantized circular photogalvanic effect in Weyl semimetals", Nature Communications 8, 15995 (2017).
- [81] J. E. Sipe and A. I. Shkrebtii, "Second-order optical response in semiconductors", Phys. Rev. B 61, 5337–5352 (2000).
- [82] C. Lee, F. Katmis, P. Jarillo-Herrero, J. Moodera, and N. Gedik, "Direct measurement of proximity-induced magnetism at the interface between a topological insulator and a ferromagnet", Nat. Commun. 7, 12014 (2016).
- [83] Q. I. Yang, M. Dolev, L. Zhang, J. Zhao, A. D. Fried, E. Schemm, M. Liu, A. Palevski, A. F. Marshall, S. H. Risbud, and A. Kapitulnik, "Emerging weak localization effects on a topological insulator-insulating ferromagnet (Bi<sub>2</sub>Se<sub>3</sub>-EuS) interface", Phys. Rev. B 88, 081407 (2013).
- [84] A. Kandala, A. Richardella, D. W. Rench, D. M. Zhang, T. C. Flanagan, and N. Samarth, "Growth and characterization of hybrid insulating ferromagnet-topological insulator heterostructure devices", Applied Physics Letters 103, 202409 (2013).

- [85] M. Li, C.-Z. Chang, B. J. Kirby, M. E. Jamer, W. Cui, L. Wu, P. Wei, Y. Zhu, D. Heiman, J. Li, and J. S. Moodera, "Proximity-Driven Enhanced Magnetic Order at Ferromagnetic-Insulator-Magnetic-Topological-Insulator Interface", Phys. Rev. Lett. 115, 087201 (2015).
- [86] F. Katmis, V. Lauter, F. S. Nogueira, B. A. Assaf, M. E. Jamer, P. Wei, B. Satpati, J. W. Freeland, I. Eremin, D. Heiman, P. Jarillo-Herrero, and J. S. Moodera, "A high-temperature ferromagnetic topological insulating phase by proximity coupling", Nature 533, 513–516 (2016).
- [87] C. Cen, S. Thiel, C. Hammerl G.and Schneider, K. Andersen, C. Hellberg, J. Mannhart, and J. Levy, "Nanoscale control of an interfacial metal-insulator transition at room temperature", Nature Materials 7, 298–302 (2008).
- [88] L. Wang, X. Ma, and Q.-K. Xue, "Interface high-temperature superconductivity", Superconductor Science and Technology 29, 123001 (2016).
- [89] R. Merlin, R. Zeyher, and G. Güntherodt, "Spin-Disorder-Induced Raman Scattering in Europium Chalcogenides", Phys. Rev. Lett. 39, 1215–1218 (1977).
- [90] A. Schlegel and P. Wachter, "Raman effect in ferromagnetic EuS", Solid State Communications 13, 1865–1868 (1973).
- [91] P. Grünberg, G. Güntherodt, A. Frey, and W. Kress, "Raman scattering and phonon dispersion of Europium monochalcogenides", Physica B+C 89, 225–228 (1977).
- [92] G. Güntherodt, R. Merlin, and P. Grünberg, "Spin-disorder-induced Raman scattering from phonons in europium chalcogenides. I. Experiment", Phys. Rev. B 20, 2834–2849 (1979).
- [93] S. Y. F. Zhao, C. Beekman, L. J. Sandilands, J. E. J. Bashucky, D. Kwok, N. Lee, A. D. LaForge, S. W. Cheong, and K. S. Burch, "Fabrication and characterization of topological insulator Bi<sub>2</sub>Se<sub>3</sub> nanocrystals", Applied Physics Letters **98**, 141911 (2011).
- [94] Y. Tian and K. S. Burch, "Automatic Spike Removal Algorithm for Raman Spectra", Applied Spectroscopy 70, 1861–1871 (2016).
- [95] Y. Y. Wang, Z. H. Ni, Z. X. Shen, H. M. Wang, and Y. H. Wu, "Interference enhancement of Raman signal of graphene", Applied Physics Letters 92, 043121 (2008).
- [96] D. Yoon, H. Moon, Y.-W. Son, J. S. Choi, B. H. Park, Y. H. Cha, Y. D. Kim, and H. Cheong, "Interference effect on Raman spectrum of graphene on SiO<sub>2</sub>/Si", Physical Review B 80, 125422 (2009).
- [97] P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim, "Making graphene visible", Applied Physics Letters 91, 063124 (2007).

- [98] H. Zhang, Y. Wan, Y. Ma, W. Wang, Y. Wang, and L. Dai, "Interference effect on optical signals of monolayer MoS<sub>2</sub>", Applied Physics Letters 107, 101904 (2015).
- [99] P. Wachter, "The optical electrical and magnetic properties of the europium chalcogenides and the rare earth pnictides", C R C Critical Reviews in Solid State Sciences **3**, 189–241 (1972).
- [100] G. Güntherodt, P. Wachter, and D. M. Imboden, "Energy level scheme and the effect of magnetic order on the optical transitions in europium chalcogenides", Physik der kondensierten Materie **12**, 292–310 (1971).
- [101] P. Munz, "Photoemissions-Spektroskopie an Europiumchalkogeniden", Helvetica Physica Acta 49, 281–309 (1976).
- [102] D. E. Eastman, F. Holtzberg, and S. Methfessel, "Photoemission Studies of the Electronic Structure of EuO, EuS, EuSe, And GdS", Phys. Rev. Lett. 23, 226–229 (1969).
- [103] M. T. Edmonds, J. T. Hellerstedt, A. Tadich, A. Schenk, K. M. O'Donnell, J. Tosado, N. P. Butch, P. Syers, J. Paglione, and M. S. Fuhrer, "Air-Stable Electron Depletion of Bi2Se3 Using Molybdenum Trioxide into the Topological Regime", ACS Nano 8, 6400–6406 (2014).
- [104] P. Wei, F. Katmis, B. A. Assaf, H. Steinberg, P. Jarillo-Herrero, D. Heiman, and J. S. Moodera, "Exchange-Coupling-Induced Symmetry Breaking in Topological Insulators", Phys. Rev. Lett. **110**, 186807 (2013).
- [105] Z. Wang, Y. Zheng, Z. Shen, Y. Lu, H. Fang, F. Sheng, Y. Zhou, X. Yang, Y. Li, C. Feng, and Z.-A. Xu, "Helicity-protected ultrahigh mobility Weyl fermions in NbP", Physical Review B 93, 121112 (2016).
- [106] N. Kumar, Y. Sun, N. Xu, K. Manna, M. Yao, V. Süß, I. Leermakers, O. Young, T. Förster, M. Schmidt, H. Borrmann, B. Yan, U. Zeitler, M. Shi, C. Felser, and C. Shekhar, "Extremely high magnetoresistance and conductivity in the type-II Weyl semimetals WP<sub>2</sub> and MoP<sub>2</sub>", Nature Communications 8, 1642 (2017).
- [107] M. N. Ali, J. Xiong, S. Flynn, J. Tao, Q. D. Gibson, L. M. Schoop, T. Liang, N. Haldolaarachchige, M. Hirschberger, N. P. Ong, and R. J. Cava, "Large, non-saturating magnetoresistance in WTe<sub>2</sub>", Nature **514**, 205–208 (2014).
- [108] H.-Y. Yang, T. Nummy, H. Li, S. Jaszewski, M. Abramchuk, D. S. Dessau, and F. Tafti, "Extreme magnetoresistance in the topologically trivial lanthanum monopnictide LaAs", Phys. Rev. B 96, 235128 (2017).
- [109] E. Mun, H. Ko, G. J. Miller, G. D. Samolyuk, S. L. Bud'ko, and P. C. Canfield, "Magnetic field effects on transport properties of PtSn<sub>4</sub>", Phys. Rev. B 85, 035135 (2012).

- [110] J. Du, Z. Lou, S. Zhang, Y. Zhou, B. Xu, Q. Chen, Y. Tang, S. Chen, H. Chen, Q. Zhu, H. Wang, J. Yang, Q. Wu, O. V. Yazyev, and M. Fang, "Extremely large magnetoresistance in the topologically trivial semimetal α - WP<sub>2</sub>", Phys. Rev. B 97, 245101 (2018).
- [111] J. Gooth, F. Menges, N. Kumar, V. Süβ, C. Shekhar, Y. Sun, U. Drechsler, C. Zierold R.and Felser, and B. Gotsmann, "Thermal and electrical signatures of a hydrodynamic electron fluid in tungsten diphosphide", Nature Communications 9, 4093 (2018).
- [112] A. Jaoui, B. Fauqué, C. W. Rischau, A. Subedi, C. Fu, J. Gooth, N. Kumar, V. Süß, D. L. Maslov, C. Felser, and K. Behnia, "Departure from the Wiedemann–Franz law in WP<sub>2</sub> driven by mismatch in T-square resistivity prefactors", npj Quantum Materials 3, 64 (2018).
- [113] J. Coulter, R. Sundararaman, and P. Narang, "Microscopic origins of hydrodynamic transport in the type-II Weyl semimetal WP<sub>2</sub>", Physical Review B 98, 115130 (2018).
- [114] J. Coulter, G. B. Osterhoudt, C. A. C. Garcia, Y. Wang, V. M. Plisson, B. Shen, N. Ni, K. S. Burch, and P. Narang, "Uncovering electron-phonon scattering and phonon dynamics in type-I Weyl semimetals", Phys. Rev. B 100, 220301 (2019).
- [115] B. Xu, Y. M. Dai, L. X. Zhao, K. Wang, R. Yang, W. Zhang, J. Y. Liu, H. Xiao, G. F. Chen, S. A. Trugman, J.-X. Zhu, A. J. Taylor, D. A. Yarotski, R. P. Prasankumar, and X. G. Qiu, "Temperature-tunable Fano resonance induced by strong coupling between Weyl fermions and phonons in TaAs", Nature Communications 8, 14933 (2017).
- [116] A. Zhang, X. Ma, C. Liu, R. Lou, Y. Wang, Q. Yu, Y. Wang, T.-I. Xia, S. Wang, L. Zhang, X. Wang, C. Chen, and Q. Zhang, "Topological phase transition between distinct Weyl semimetal states in MoTe<sub>2</sub>", Phys. Rev. B 100, 201107 (2019).
- [117] A. Sharafeev, V. Gnezdilov, R. Sankar, F. C. Chou, and P. Lemmens, "Optical phonon dynamics and electronic fluctuations in the Dirac semimetal Cd<sub>3</sub>As<sub>2</sub>", Phys. Rev. B 95, 235148 (2017).
- [118] R. Rühl and W. Jeitschko, "ÜBER POLYPHOSPHIDE VON CHROM, MOLYBDÄN UND WOLFRAM", Monatshefte für Chemie / Chemical Monthly 114, 817–828 (1983).
- [119] B. Su, Y. Song, Y. Hou, X. Chen, J. Zhao, Y. Ma, Y. Yang, J. Guo, J. Luo, and Z.-G. Chen, "Strong and Tunable Electrical Anisotropy in Type-II Weyl Semimetal Candidate WP<sub>2</sub> with Broken Inversion Symmetry", Advanced Materials **31**, 1903498 (2019).
- [120] D. Wulferding, P. Lemmens, F. Büscher, D. Schmeltzer, C. Felser, and C. Shekhar, "Effect of topology on quasiparticle interactions in the Weyl semimetal WP<sub>2</sub>", Phys. Rev. B **102**, 075116 (2020).
- [121] P. Giura, N. Bonini, G. Creff, J. B. Brubach, P. Roy, and M. Lazzeri, "Temperature evolution of infrared- and Raman-active phonons in graphite", Phys. Rev. B 86, 121404 (2012).
- [122] H.-N. Liu, X. Cong, M.-L. Lin, and P.-H. Tan, "The intrinsic temperaturedependent Raman spectra of graphite in the temperature range from 4K to 1000K", Carbon 152, 451–458 (2019).
- [123] M. Lazzeri, S. Piscanec, F. Mauri, A. C. Ferrari, and J. Robertson, "Phonon linewidths and electron-phonon coupling in graphite and nanotubes", Phys. Rev. B 73, 155426 (2006).
- [124] J. L. Birman, "Space Group Selection Rules: Diamond and Zinc Blende", Phys. Rev. 127, 1093–1106 (1962).
- [125] L.-C. Chen, R. Berenson, and J. L. Birman, "Space-Group Selection Rules: "Rocksalt"  $O_h{}^5 \text{Fm}3m$ ", Phys. Rev. **170**, 639–648 (1968).
- [126] M.-Y. Yao, N. Xu, Q. S. Wu, G. Autès, N. Kumar, V. N. Strocov, N. C. Plumb, M. Radovic, O. V. Yazyev, C. Felser, J. Mesot, and M. Shi, "Observation of Weyl Nodes in Robust Type-II Weyl Semimetal WP<sub>2</sub>", Phys. Rev. Lett. **122**, 176402 (2019).
- [127] C. A. C. Garcia, J. Coulter, and P. Narang, "Optoelectronic response of the type-I Weyl semimetals TaAs and NbAs from first principles", Phys. Rev. Research 2, 013073 (2020).
- [128] A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard, and H. A. Atwater, "Nonradiative plasmon decay and hot carrier dynamics: Effects of phonons, surfaces, and geometry", ACS Nano 10, 957–966 (2016).
- [129] A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard III, and H. A. Atwater, "Ab initio phonon coupling and optical response of hot electrons in plasmonic metals", Phys. Rev. B 94, 075120 (2016).
- [130] L. Lindsay, D. A. Broido, and T. L. Reinecke, "First-Principles Determination of Ultrahigh Thermal Conductivity of Boron Arsenide: A Competitor for Diamond?", Phys. Rev. Lett. **111**, 025901 (2013).
- [131] H. W. Liu, P. Richard, Z. D. Song, L. X. Zhao, Z. Fang, G.-F. Chen, and H. Ding, "Raman study of lattice dynamics in the Weyl semimetal TaAs", Phys. Rev. B 92, 064302 (2015).
- [132] H. W. Liu, P. Richard, L. X. Zhao, G.-F. Chen, and H. Ding, "Comparative Raman study of Weyl semimetals TaAs, NbAs, TaP and NbP", Journal of Physics: Condensed Matter 28, 295401 (2016).
- [133] B. Xu, Y. M. Dai, L. X. Zhao, K. Wang, R. Yang, W. Zhang, J. Y. Liu, H. Xiao, G. F. Chen, A. J. Taylor, D. A. Yarotski, R. P. Prasankumar, and X. G. Qiu, "Optical spectroscopy of the Weyl semimetal TaAs", Physical Review B 93, 121110 (2016).

- [134] G. B. Osterhoudt, L. K. Diebel, M. J. Gray, X. Yang, J. Stanco, X. Huang, B. Shen, N. Ni, P. J. W. Moll, Y. Ran, and K. S. Burch, "Colossal midinfrared bulk photovoltaic effect in a type-I Weyl semimetal", Nature Materials 18, 471–475 (2019).
- [135] Y. Tian, A. A. Reijnders, G. B. Osterhoudt, I. Valmianski, J. G. Ramirez, C. Urban, R. Zhong, J. Schneeloch, G. Gu, I. Henslee, and K. S. Burch, "Low vibration high numerical aperture automated variable temperature Raman microscope", Review of Scientific Instruments 87, 043105 (2016).
- [136] F. Giustino, M. L. Cohen, and S. G. Louie, "Electron-phonon interaction using Wannier functions", Phys. Rev. B 76, 165108 (2007).
- [137] R. Sundararaman, K. Letchworth-Weaver, K. A. Schwarz, D. Gunceler, Y. Ozhabes, and T. Arias, "JDFTx: Software for joint density-functional theory", SoftwareX 6, 278–284 (2017).
- [138] A. Dal Corso, "Pseudopotentials periodic table: From H to Pu", Computational Materials Science 95, 337–350 (2014).
- [139] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, "Optimized pseudopotentials", Phys. Rev. B 41, 1227–1230 (1990).
- [140] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, "Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces", Phys. Rev. Lett. 100, 136406 (2008).
- [141] N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, "Thermal Contraction and Disordering of the Al(110) Surface", Phys. Rev. Lett. 82, 3296– 3299 (1999).
- [142] C.-C. Lee, S.-Y. Xu, S.-M. Huang, D. S. Sanchez, I. Belopolski, G. Chang, G. Bian, N. Alidoust, H. Zheng, M. Neupane, B. Wang, A. Bansil, M. Z. Hasan, and H. Lin, "Fermi surface interconnectivity and topology in Weyl fermion semimetals TaAs, TaP, NbAs, and NbP", Phys. Rev. B 92, 235104 (2015).
- [143] J. Xiang, S. Hu, M. Lv, J. Zhang, H. Zhao, G. Chen, W. Li, Z. Chen, and P. Sun, "Anisotropic thermal and electrical transport of Weyl semimetal TaAs", Journal of Physics: Condensed Matter 29, 485501 (2017).
- [144] Z. Ji, G. Liu, Z. Addison, W. Liu, P. Yu, H. Gao, Z. Liu, A. M. Rappe, C. L. Kane, E. J. Mele, and R. Agarwal, "Spatially dispersive circular photogal-vanic effect in a Weyl semimetal", Nature Materials 18, 955–962 (2019).
- [145] Q. Wang, J. Zheng, Y. He, J. Cao, X. Liu, M. Wang, J. Ma, J. Lai, H. Lu, S. Jia, D. Yan, Y. Shi, J. Duan, J. Han, W. Xiao, J.-H. Chen, K. Sun, Y. Yao, and D. Sun, "Robust edge photocurrent response on layered type II Weyl semimetal WTe<sub>2</sub>", Nature Communications **10**, 5736 (2019).
- [146] T. Morimoto and N. Nagaosa, "Topological nature of nonlinear optical effects in solids", Science Advances 2 (2016) 10.1126/sciadv.1501524.

- [147] P. Hosur, "Circular photogalvanic effect on topological insulator surfaces: Berry-curvature-dependent response", Phys. Rev. B 83, 035309 (2011).
- [148] X. Yang, K. Burch, and Y. Ran, "Divergent bulk photovoltaic effect in Weyl semimetals", arXiv:1712.09363 (2017).
- [149] C.-K. Chan, N. H. Lindner, G. Refael, and P. A. Lee, "Photocurrents in Weyl semimetals", Phys. Rev. B 95, 041104 (2017).
- [150] J. W. McIver, D. Hsieh, H. Steinberg, P. Jarillo-Herrero, and N. Gedik, "Control over topological insulator photocurrents with light polarization", Nature Nanotechnology 7, 96–100 (2012).
- [151] Q. Ma, S.-Y. Xu, C.-K. Chan, C. Zhang, G. Chang, Y. Lin, W. Xie, T. Palacios, H. Lin, S. Jia, P. Lee, P. Jarillo-Herrero, and N. Gedik, "Direct optical detection of Weyl fermion chirality in a topological semimetal", Nat. Phys. 13, 842–847 (2017).
- [152] X. Xu, N. M. Gabor, J. S. Alden, A. M. van der Zande, and P. L. McEuen, "Photo-Thermoelectric Effect at a Graphene Interface Junction", Nano Letters 10, 562–566 (2010).
- [153] E. Hecht, *Optics*, 4th (Pearson Education, Inc., San Francisco, CA, 2002).
- [154] B. Jensen and A. Torabi, "Refractive index of hexagonal II–VI compounds CdSe, CdS, and CdSe<sub>X</sub>S<sub>1--X</sub>", J. Opt. Soc. Am. B **3**, 857–863 (1986).
- [155] A. M. Cook, B. M. Fregoso, F. de Juan, S. Coh, and J. E. Moore, "Design principles for shift current photovoltaics", Nature Communications 8, 14176 (2017).
- [156] L. Z. Tan, F. Zheng, S. M. Young, F. Wang, S. Liu, and A. M. Rappe, "Shift current bulk photovoltaic effect in polar materials—hybrid and oxide perovskites and beyond", npj Computational Materials 2, 16026 (2016).
- [157] A. G. Chynoweth, "Surface Space-Charge Layers in Barium Titanate", Phys. Rev. 102, 705–714 (1956).
- [158] L. E. Golub, E. L. Ivchenko, and B. Z. Spivak, "Photocurrent in gyrotropic Weyl semimetals", JETP Letters 105, 782–785 (2017).
- Y. Zhang, H. Ishizuka, J. van den Brink, C. Felser, B. Yan, and N. Nagaosa, "Photogalvanic effect in Weyl semimetals from first principles", Phys. Rev. B 97, 241118 (2018).
- [160] J. Ma, Q. Gu, Y. Liu, J. Lai, P. Yu, X. Zhuo, Z. Liu, J.-H. Chen, J. Feng, and D. Sun, "Nonlinear photoresponse of type-II Weyl semimetals", Nature Materials 18, 476–481 (2019).
- [161] X. Xu, N. M. Gabor, J. S. Alden, A. M. van der Zande, and P. L. McEuen, "Photo-Thermoelectric Effect at a Graphene Interface Junction", Nano Letters 10, 562–566 (2010).
- [162] P. J. Moll, "Focused Ion Beam Microstructuring of Quantum Matter", Annual Review of Condensed Matter Physics 9, 147–162 (2018).

- [163] M. Glazov and S. Ganichev, "High frequency electric field induced nonlinear effects in graphene", Physics Reports 535, 101–138 (2014).
- [164] M.-M. Yang, D. J. Kim, and M. Alexe, "Flexo-photovoltaic effect", Science 360, 904–907 (2018).
- [165] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials", JPCM **21**, 395502 (2009).
- [166] A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, "An updated version of wannier90: A tool for obtaining maximally-localised Wannier functions", Computer Physics Communications 185, 2309–2310 (2014).
- [167] F. Arnold, M. Naumann, S.-C. Wu, Y. Sun, M. Schmidt, H. Borrmann, C. Felser, B. Yan, and E. Hassinger, "Chiral weyl pockets and fermi surface topology of the weyl semimetal taas", Phys. Rev. Lett. **117**, 146401 (2016).
- [168] P. Zareapour, A. Hayat, S. Y. F. Zhao, M. Kreshchuk, A. Jain, D. C. Kwok, N. Lee, S.-W. Cheong, Z. Xu, A. Yang, G. D. Gu, S. Jia, R. J. Cava, and K. S. Burch, "Proximity-induced high-temperature superconductivity in the topological insulators Bi<sub>2</sub>Se<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub>", Nature Communications 3, 1056 (2012).
- [169] A. M. Glass, D. von der Linde, and T. J. Negran, "High-voltage bulk photovoltaic effect and the photorefractive process in LiNbO<sub>3</sub>", Applied Physics Letters 25, 233–235 (1974).
- [170] V. M. Fridkin, A. A. Kaminskii, V. G. Lazarev, S. B. Astaf'ev, and A. V. Butashin, "Photorefractive effect in La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub>-Pr<sup>3+</sup> piezoelectric crystals", Applied Physics Letters 55, 545–546 (1989).
- [171] A. Zenkevich, Y. Matveyev, K. Maksimova, R. Gaynutdinov, A. Tolstikhina, and V. Fridkin, "Giant bulk photovoltaic effect in thin ferroelectric BaTiO<sub>3</sub> films", Phys. Rev. B **90**, 161409 (2014).
- [172] F. Wang, S. M. Young, F. Zheng, I. Grinberg, and A. M. Rappe, "Substantial bulk photovoltaic effect enhancement via nanolayering", Nature Communications 7, 10419 (2016).
- [173] S. M. Young, F. Zheng, and A. M. Rappe, "First-Principles Calculation of the Bulk Photovoltaic Effect in Bismuth Ferrite", Phys. Rev. Lett. 109, 236601 (2012).

- [174] J. A. Brehm, S. M. Young, F. Zheng, and A. M. Rappe, "First-principles calculation of the bulk photovoltaic effect in the polar compounds LiAsS<sub>2</sub>, LiAsSe<sub>2</sub>, and NaAsSe<sub>2</sub>", The Journal of Chemical Physics 141, 204704 (2014).
- [175] F. Zheng, H. Takenaka, F. Wang, N. Z. Koocher, and A. M. Rappe, "First-Principles Calculation of the Bulk Photovoltaic Effect in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>", The Journal of Physical Chemistry Letters 6, 31–37 (2015).
- [176] F. Wang and A. M. Rappe, "First-principles calculation of the bulk photovoltaic effect in KNbO<sub>3</sub> and (K,Ba)(Ni,Nb)O<sub>3- $\delta$ </sub>", Phys. Rev. B **91**, 165124 (2015).