

Ultrafast spectroscopy and control of correlated quantum materials

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Abstract

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Acknowledgements

Preface

The physics of solids is, to me, one of the most important and fundamental fields of modern science. This might seem, to some, a bit of a hot take. After all, by studying condensed matter physics, one learns next to nothing about, say, the formation of the stars and planets, or the origin of the universe. Nor does one learn about life, death, consciousness, disease, ethics, God, or any other question that perhaps puzzled humanity prior to about five hundred years ago. Certainly no one would argue that condensed matter physics is quite *useless*, given that nearly every device we interact with in modern life required some condensed matter physicist somewhere along the way to make one brilliant discovery or another – yet when the human mind starts to wander, and our thoughts turn to the metaphysical, we tend to look up, not down.

In my work I have taken a quite different view. Condensed matter physics, to me, is ultimately the study of how *truly boring* objects, when brought together in large quantities, *become* interesting, seemingly in spite of themselves. When electrons are put together in a lattice and allowed to interact slightly with the massive nuclei, at low enough temperatures they pair, the low-energy excitations become gapped, and current can flow for infinite times and with absolutely zero energy loss. Those same electrons, with some other set of interactions, may instead ionize (the opposite of pairing!) to create an electrically insulating state, whose low-energy excitation spectrum is nevertheless gapless and consisting of charge-neutral spin- $1/2$ particles. In all such cases, these systems exist in otherwise ordinary-looking rocks, fit in the palm of a hand¹, and are more or less indistinguishable from something you might find sticking into the bottom of your shoe.

While such systems may not tell us a lot² about the early universe, considering these and related problems lets us ask deep, fundamental questions about the world we live in – like, why is this thing a metal, but this thing is an insulator? What do those terms even mean? – that I don't think we would try to ask otherwise. To me, focusing our attention on

¹Hopefully, gloved.

²This discussion is obviously intentionally reductive. In truth there is still quite a bit one can learn about, e.g. the early universe by studying condensed matter physics, see the Kibble and Pickett [31].

these problems, despite their obviously terrestrial nature, is not a waste of time; rather, I think they remind us that even the most mundane aspects of the human experience involve a level of complexity far beyond what we are capable of understanding absent the pursuit of science.

Throughout the seven years of my Ph.D., I hope to have made a few contributions to this pursuit. As the title of this work implies, I have mainly focused on the application of ultrafast techniques to the study of correlated quantum materials, which I loosely define as those materials in which the interaction between particles is large enough so as to compete with the kinetic energy of those particles. It is in these materials that I think lies the true frontier of condensed matter physics; here, much of our basic intuition about non- or weakly-interacting theory fails, and more complicated notions of phase competition, phase separation, disorder, pairing, coherence, etc. are needed to properly describe the relevant physics.

In my own view, and in the view of many scientists in this field[1], the main question for strongly correlated physics amounts to: “Given a correlated system with some defined combination of different interaction strengths, is there a general theory which allows us to predict the phase diagram of this system *a priori*?” Related of course are questions about the origins of high- T_c superconductivity, strange metallicity, quantum spin liquids, and other exotic phases that we find emerging from strongly interacting systems. Since such a theory does not currently exist, at least with the level of predictive power that I think most would find satisfactory, new advances in this field typically come directly from experiment. Ultrafast optics plays a special role in this regard, for reasons that I will explain in chapter 1.

Progress thus happens in this field somewhat unsystematically, with small pieces of the puzzle added at random, but not infrequent, intervals. Usually it is either new techniques or new materials that are the driving force here. To this end, I have tried to pursue both directions in my Ph.D. Appearing also in chapter 1 is thus a description of the materials I studied the most during my thesis, two of them, CuBr₂ and CaMn₂Bi₂ I consider criminally understudied. On the technique side, almost all of the work presented in this thesis was done using time-resolved second harmonic generation (tr-SHG), a relatively new, nonlinear optical technique which, at the most basic level, probes the point group assumed by the charge distribution function $\rho(\mathbf{x})$ at any given point in time. Second harmonic

generation (SHG) and tr-SHG are tricky techniques, with many pitfalls both practically and theoretically; chapters 2 and 3 are thus devoted to what I hope is a useful, if not fully comprehensive, description of the technique. Chapter 4 is devoted to work that we did developing a new way to control the polarization of the light in a tr-SHG experiment using stepper motors. My hope is that these chapters are useful not only for the new student trying to build their own setup or analyze their own SHG data, but also for people for whom SHG is not a focus but nevertheless want to learn about it in slightly more detail than one would get from a typical paper or review article.

What follows, then, is a description of the three main research works I contributed during my Ph.D.. The first, which I describe in chapter 5, involves work that I did during my second and third years on 1T-TaS₂, a very interesting charge density wave (CDW) material that, among other things, undergoes a mirror symmetry breaking CDW transition at 350 K that shows up in the SHG as a sudden distortion of the flower pattern at that temperature. Since this transition breaks mirror symmetry, two energetically degenerate domains should be present, corresponding to two opposite planar chiralities; in this work, we showed that SHG could differentiate between these two domains (i.e. the flower pattern in either domain looks different).

The second and third works, which I describe in chapters 6 and 7, in contrast to the 1T-TaS₂ work, both involve taking the system out of equilibrium to study the dynamics. In CaMn₂Bi₂ (chapter 6), we discovered that photoexcitation causes the antiferromagnetic (AFM) order in that compound to reorient (relative to equilibrium) to a metastable state which is impossible to reach from the equilibrium state thermodynamically. Light is thus used to *control* the magnetic order in this material.

In CuBr₂ (chapter 7), light is not used to control the order parameter like in CaMn₂Bi₂, but it does excite coherent oscillations of the collective modes of the multiferroic order (electromagnons), whose frequency, amplitude, damping, etc. may be probed in tr-SHG as a function of temperature – a methodology referred to as ultrafast *spectroscopy*. In doing so, we found that one of these collective modes is actually quite special, as it is in fact the analogue of the Higgs mode of particle physics in the context of a multiferroic material.

I conclude with various remarks in chapter 8, as well as an appendix, in which I enumerate briefly all of the null-result experiments I performed

during my Ph.D., in the hopes that future scientists don't have to waste time on what we already know are fruitless pursuits. If you have any questions about this or any other section of this thesis, please do not hesitate to reach out via email.

Contents

Contents	ix
List of Figures	xi
List of Tables	xii
1 Ultrafast optics in correlated electron systems	13
2 Second harmonic generation: theory	15
2.1 Space groups, point groups, and Neumann's principle	15
2.2 A classical understanding of SHG	19
2.3 SHG in quantum mechanics	21
2.4 SHG in the Ginzburg-Landau paradigm	25
3 Second harmonic generation: practical	29
3.1 Description of the setup	29
3.2 Before you build	32
3.2.1 Spot size	32
3.2.2 Oblique vs. normal incidence	33
3.2.3 Choice of detector	34
3.3 tr-SHG: methodology	35
3.4 Data analysis	37
3.4.1 Static RA-SHG patterns	37
3.4.2 Modeling χ_{ijk} : the simplified bond hyperpolarizability model	40
3.4.3 Fitting time traces in tr-SHG	41
4 Automated polarization rotation for multi-axis RA-SHG experiments	45

4.1	Preface	45
4.2	Abstract	45
4.3	Introduction	46
4.4	Design	50
4.4.1	Slip Ring	51
4.4.2	Miniature Stepper Motor	53
4.5	Validation and Discussion	55
5	Second harmonic generation as a probe of broken mirror symmetry in 1T-TaS₂	57
5.1	Preface	57
5.2	Abstract	57
5.3	Introduction	58
5.4	Results and discussion	61
5.5	Conclusion	68
5.6	Acknowledgments	68
5.7	Supplemental material	69
5.7.1	Probing broken mirror symmetry with RA-SHG	69
5.7.2	Physical importance of the P _{in} -S _{out} channel	73
5.7.3	Generalization to other mirror symmetry-breaking transitions	75
5.7.4	Probing the sense of planar chirality with RA-SHG	77
5.7.5	Bulk broken mirror symmetry in 1T-TaS ₂	79
5.7.6	Methods	83
6	Light-induced reorientation transition in the antiferromagnetic semiconductor CaMn₂Bi₂	85
7	Amplitude-mode electromagnon in the XXZ chain CuBr₂	87
8	Concluding remarks	89
	Bibliography	93

List of Figures

3.1	Schematic drawing of the SHG setup used in this research.	30
3.2	Photograph of the SHG setup.	31
4.1	A demonstration of RA-SHG in the test sample GaAs	48
4.2	A diagram of the full second harmonic generation setup	50
4.3	Exploded-view diagram of one of the automated polarization rotators	52
4.4	A 3-dimensional rendering of the automated polarization rotators	54
4.5	Demonstration of the automatic polarization rotators	55
5.1	Structure of 1T-TaS ₂ and schematic of the SHG setup	60
5.2	SHG in 1T-TaS ₂ above and below $T_{\text{IC-NC}}$	63
5.3	SHG in NC-TaS ₂	64
5.4	RA-SHG in the $S_{\text{in}}S_{\text{out}}$ polarization channel in 1T-TaS ₂	67
5.5	RA-SHG of 1T-TaS ₂ : all polarization channels	69
5.6	Intuition for mirror symmetry breaking in SHG	74
5.7	RA-SHG in the α and β phases of 1T-TaS ₂	78
5.8	Electron diffraction of 1T-TaS ₂	81
5.9	Electric quadrupole RA-SHG in 1T-TaS ₂ ($T = 295$ K)	82
5.10	Electric quadrupole RA-SHG in 1T-TaS ₂ ($T = 356$ K)	82

List of Tables

3.1	Vector definition of polarization channels.	38
5.1	Indicators of broken mirror symmetry in RA-SHG	76

Chapter One

Ultrafast optics in correlated electron systems

Chapter Two

Second harmonic generation: theory

2.1 Space groups, point groups, and Neumann's principle

The utility of SHG in studying condensed matter systems is derived from the following simple statement, attributed to Franz Neumann[44] and later Pierre Curie[14]:

Theorem 2.1.1 (Neumann's principle) *Let P_G be the symmetry group of a crystal structure and P_H the symmetry group of some physical property of that crystal. Then, P_G is a subgroup of P_H .*

There are a few things to digest here. Let us start by understanding the meaning of the phrase “symmetry group”. For any given crystal, there exists some infinitely large set of operations G under which the crystal structure is symmetric. Each of these operations may be decomposed into two parts: a “point-preserving operation” R , corresponding to either the identity, rotation, inversion, mirror, or the product of mirror and rotation, followed by a translation by some vector τ :

$$G = \{(R|\tau)\} \tag{2.1}$$

where $(R|\tau)$ means “Perform R , then translate by τ ”. Clearly, the set G forms a group, since if both g_1 and $g_2 \in G$ leave the crystal structure

invariant, so does the product $g_1 g_2$, and so $g_1 g_2 \in G$. Thus, G is called the *space group* of the crystal. In three dimensions, there are 230 crystallographic space groups, which are tabulated in a number of places, most usefully Wikipedia[12].

For 73 of these groups, the translation parts of the τ 's in Eq. 2.1 are only ever linear combinations of integer multiples of the lattice vectors a , b , and c ; these are called *symmorphic* space groups. The remaining 157 groups involve translations that are not integer multiples of the lattice vectors; these are one's screw axes and glide planes, and so these groups are called *asymmorphic*.

Importantly, the “physical properties” of theorem 2.1.1 refer to the truly macroscopic properties of the crystal, like its conductivity, dielectric, or pyroelectric tensors. Consider, for example, that in SHG, we are typically studying the sample at optical wavelengths, where the wavelength of light is three or four orders of magnitude larger than the lattice spacing. Clearly, then, these properties do not care whether the correct symmetry is $(R|\tau)$ or $(R|\tau + a/2)$. A more useful group, then, is the *point group* of the crystal

$$P_G = \{R \text{ s.t. } \exists \tau \text{ s.t. } (R|\tau) \in G\} \quad (2.2)$$

i.e., the point group is the set of point-preserving operations R for which R appears in G , regardless of whether you need to perform a translation with it. Once can show that P_G is also a group, and thus it is P_G which is involved in Neumann’s principle for all intents and purposes¹.

The last ingredient that we need to understand theorem 2.1.1 is the concept of what is meant by “physical property”. The idea is that the response of the crystal $J_{i_1 i_2 \dots i_n}$ (i.e., the current J_i , or the quadrupole moment Q_{ij}) is proportional to some field $F_{i'_1 i'_2 \dots i'_m}$ via some tensor χ :

$$J_{i_1 i_2 \dots i_n} = \chi_{i_1 i_2 \dots i_n i'_1 i'_2 \dots i'_m} F_{i'_1 i'_2 \dots i'_m}. \quad (2.3)$$

For example, the conductivity σ_{ij} relates a current density J_i to an applied electric field E_j :

$$J_i = \sigma_{ij} E_j. \quad (2.4)$$

¹Of course this breaks down when the wavelength of light is comparable to the lattice spacing; in that case you need to consider the full space group.

Likewise, the polarization P_i due to the pyroelectric effect is related to the a temperature difference ΔT by a tensor p_i :

$$P_i = p_i \Delta T. \quad (2.5)$$

The tensors σ_{ij} , p_i , and generally, $\chi_{i_1 i_2 \dots i_n i'_1 i'_2 \dots i'_m}$ are commonly referred to as *matter tensors*[50], to emphasize the fact that they are the only part of the response equations that depend on the material. It should be noted that matter tensors generically come in two types: those that transform like a vector under inversion and those that transform like a pseudovector under inversion. You can tell which is which by applying inversion to either side of the response equation. For example, the tensor ϵ_{ij} relating the displacement field to the electric field

$$D_i = \epsilon_{ij} E_j \quad (2.6)$$

is a polar tensor, whereas the tensor χ_{ij}^{me} describing the magnetoelectric effect

$$M_i = \chi_{ij}^{me} E_j \quad (2.7)$$

is an axial tensor.

We are now ready to restate theorem 2.1.1 in a slightly more useful form, using the terminology we have developed about point groups and matter tensors:

Theorem 2.1.2 (Neumann's principle, restated) *Let P_G be the point group of a given crystal, and let χ be a matter tensor describing some response function of that crystal. Then, for all $g \in P_G$, we have*

$$g(\chi) = \chi. \quad (2.8)$$

Eq. 2.8 can be more usefully expressed if we know the matrix R_{ij}^g corresponding to g . For example, if g is “threefold rotation about the z axis”, we have

$$R_{ij}^g = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (2.9)$$

in which case one can show that Eq. 2.8 reads

$$(\det R^g)^t R_{i_1 i'_1}^g R_{i_2 i'_2}^g \cdots R_{i_n i'_n}^g \chi_{i'_1 i'_2 \dots i'_n} = \chi_{i_1 i_2 \dots i_n}, \quad (2.10)$$

where t is 0 if χ is a polar tensor and 1 if χ is an axial tensor. Theorem 2.1.2 tells us that there is one copy of Eq. 2.10 for each $g \in P_G$.

Apparently, each element $g \in P_G$ gives us a *constraint* on the numbers $\chi_{i_1 i_2 \dots i_n}$, in that they have to satisfy Eq. 2.10. This is a remarkably useful fact. Since different point groups enforce different constraints on χ , that means the *form* of χ (e.g. when written as a list of numbers) depends quite sensitively on the point group of the crystal we are studying. As an example, here is the dielectric permittivity tensor for crystals with the point group (in Schoenflies notation) C_2 :

$$\epsilon_{ij} = \begin{pmatrix} a & 0 & e \\ 0 & b & 0 \\ e & 0 & c \end{pmatrix}_{ij} \quad (2.11)$$

versus in the point group D_{3d} :

$$\epsilon_{ij} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix}_{ij}. \quad (2.12)$$

Clearly, any *measurement* of ϵ_{ij} will be able to easily differentiate a crystal with point group C_2 from one with point group D_{3d} . This is the fundamental basis, then, for SHG. In SHG, we measure the tensor χ_{ijk} corresponding to the response equation²

$$P_i(2\omega) = \chi_{ijk} E_j(\omega) E_k(\omega); \quad (2.13)$$

the numbers χ_{ijk} thus tell us about the crystallographic point group we are measuring from.

There are a couple of advantages to measuring χ_{ijk} over any other matter tensor in a given system. For one thing, χ_{ijk} is a third rank tensor, which means it has a few more degrees of freedom to work with compared to ϵ_{ij} , and thus does a better job at uniquely specifying each point group. It also doesn't have *too many* degrees of freedom, so that most of the time your experiment will be able to tell you all of your tensor elements³. In addition, since we are typically doing SHG at optical wavelengths, the

²This discussion is a bit simplified in the sense that there are actually *many* response functions which will give you light at 2ω ; for a more detailed discussion, see section 2.2.

³Quadrupole SHG has this problem, see section 2.2.

form of χ_{ijk} reflects the symmetry of the *charge distribution* $\rho(\mathbf{x})$, in contrast to e.g. x-ray diffraction, where the relevant tensors will tell instead you about the electron distribution, $n(\mathbf{x})$. This can be advantageous in cases where the long range order you are trying to study involves an ordering of the valence electrons but not the electrons in the cores of atoms. This is entirely the result of the fact that Neumann's principle, as expressed both in theorem 2.1.1 and theorem 2.1.2, tells us that the point group of our crystal is a *subgroup* of the point group we get from our measurement – the measurement can always be more symmetric than the crystal!

As another example of this fact, let us note that the response equation given by Eq. 2.13 clearly has an additional symmetry $j \leftrightarrow k$, since the two copies of the electric field on the right hand side are equivalent. Obviously this is not a result of the material we are studying, it is simply a fact of doing SHG. Thus, in addition to the constraints given by Neumann's principle and Eq. 2.10, we have the additional constraint

$$\chi_{ijk} = \chi_{ikj} \forall i, j, k. \quad (2.14)$$

This is known as *particularization*[7].

2.2 A classical understanding of SHG

In the last section we considered the SHG response function given by Eq. 2.13. Where does this relationship come from, and how is $P(2\omega)$ eventually measured? Our starting point in the classical treatment will be the inhomogenous electromagnetic wave equation

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) E_i(\mathbf{x}, t) = S_i(\mathbf{x}, t), \quad (2.15)$$

which we understand as defining the field $E_i(\mathbf{x}, t)$ radiated by the source term $S_i(\mathbf{x}, t)$, which is induced by the incident field. To lowest order in a multipole expansion, $S_i(\mathbf{x}, t)$ is given by[30, 32]

$$\mu_0 \frac{\partial^2 P_i(\mathbf{x}, t)}{\partial t^2} + \mu_0 \left(\epsilon_{ijk} \nabla_j \frac{\partial M_k(\mathbf{x}, t)}{\partial t} \right) - \mu_0 \left(\nabla_j \frac{\partial^2 Q_{ij}(\mathbf{x}, t)}{\partial t^2} \right) \quad (2.16)$$

where $P_i(\mathbf{x}, t)$, $M_i(\mathbf{x}, t)$, and $Q_{ij}(\mathbf{x}, t)$ are the induced electric dipole, magnetic dipole, and electric quadrupole densities, and ϵ_{ijk} is the Levi-Civita tensor.

If the incident electric field is small, then the terms $P_i(\mathbf{x}, t)$, $M_i(\mathbf{x}, t)$, and $Q_{ij}(\mathbf{x}, t)$ are linear functions of that electric field. However, for larger incident fields (such as those generated by pulsed lasers), they may be more generally written as a Taylor series:

$$P_i = \chi_{ij}^{ee} E_j + \chi_{ij}^{em} H_j + \chi_{ijk}^{eee} E_j E_k + \chi_{ijk}^{eem} E_j H_k + \dots \quad (2.17)$$

$$M_i = \chi_{ij}^{me} E_j + \chi_{ij}^{mm} H_j + \chi_{ijk}^{mee} E_j E_k + \chi_{ijk}^{mem} E_j H_k + \dots \quad (2.18)$$

$$Q_{ij} = \chi_{ijk}^{qe} E_k + \chi_{ijk}^{qm} H_k + \chi_{ijkl}^{qee} E_k E_l + \chi_{ijkl}^{qem} E_k H_l + \dots \quad (2.19)$$

where we have suppressed the arguments \mathbf{x} and t for brevity.

Assuming the incident field is monochromatic,

$$E_i(\mathbf{x}, t) = E_i(\omega) e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} + \text{c.c.} \quad (2.20)$$

$$H_i(\mathbf{x}, t) = H_i(\omega) e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} + \text{c.c.} \quad (2.21)$$

the induced sources are also monochromatic, and (keeping only terms proportional to $e^{i2\omega t}$) we thus get

$$P_i(2\omega) = \chi_{ijk}^{eee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{eem} E_j(\omega) H_k(\omega) \quad (2.22)$$

$$M_i(2\omega) = \chi_{ijk}^{mee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{mem} E_j(\omega) H_k(\omega) \quad (2.23)$$

$$Q_{ij}(2\omega) = \chi_{ijkl}^{qee} E_k(\omega) E_l(\omega) + \chi_{ijkl}^{qem} E_k(\omega) H_l(\omega). \quad (2.24)$$

Since Eq. 2.15 is linear, the electric field radiated by $S_i(\mathbf{x}, t)$ is simply proportional to it. In the limit where the first term of Eq. 2.22 dominates, the intensity measured at our detector thus satisfies

$$I(2\omega) \propto |\hat{e}_i^{\text{out}} \chi_{ijk}^{eee} \hat{e}_j^{\text{in}} \hat{e}_k^{\text{in}}|^2, \quad (2.25)$$

where \hat{e}^{in} and \hat{e}^{out} are unit vectors in the direction of the incoming and measured electric fields⁴. χ_{ijk}^{eee} does typically dominate when inversion symmetry is broken, but if not, you have to consider all of the terms in Eqs. 2.22–2.24. Actually, each of these terms needs to be considered twice, since there is both a surface contribution and a bulk contribution⁵. In my experience, the hierarchy of contributions (from most to least important, and assuming everything is allowed by symmetry) is typically:

⁴Usually there are polarizers in the experiment which define these directions.

⁵The space group which constrains the surface contributions is the bulk space group less the operations which involve some change in the z coordinate.

1. Bulk electric dipole
2. Surface electric dipole, bulk electric quadrupole, and bulk magnetic dipole, at the same order⁶
3. Everything else

I've never seen anything outside of items 1 and 2, but in rare cases an electronic resonance may cause an enhancement in one of the other contributions[20].

Let us take a moment now to emphasize the following extremely common misconception about SHG: just because you see SHG in your experiment, that does not mean that inversion symmetry is broken in your material! It also does not mean that your material is a ferroelectric, or really that there's anything special at all about your material, at least before you've done any further analysis. Similarly, if you *don't* see SHG, that doesn't mean inversion symmetry is preserved, either. I have repeatedly seen large electric quadrupole SHG show up in materials with inversion symmetry, while materials which definitely break inversion symmetry have absolutely zero SHG observable in the experiment. The reason for this is ultimately due to resonance, a topic which I will discuss in section 2.3, but I mention it here because it is truly quite common in the literature and it is surely a mistake worth avoiding. You are "allowed" to say your material breaks inversion symmetry only if there is no other contribution in Eqs. 2.22–2.24 which fits your data, and you are basically never allowed to say that your material preserves inversion symmetry when there is no SHG (a fact that should be obvious on a careful reading of theorem 2.1.1).

2.3 SHG in quantum mechanics

The description of SHG in the previous section is probably the most useful for understanding SHG from an "optics" perspective, but it gives little insight into the true microscopic origin of the SHG intensity. The

⁶Somehow the bulk electric quadrupole and magnetic dipole contributions have been labelled "exotic" by some in the community, but that has not been my experience. If I had to guess, almost half of the materials I have measured with inversion symmetry show electric quadrupole SHG.

quantum description, on the other hand, will tell you exactly where the SHG is coming from microscopically, but only if you have access to the eigenfunctions $|\psi\rangle$ of your hamiltonian – it is of little use otherwise. Nevertheless, we can still gain intuition about the dependence of our SHG intensity on the frequency of the light in the quantum picture, which will be useful for clearing up a whole other slew of misconceptions that have somehow made their way into the SHG literature. This treatment closely follows that of Boyd [10].

The starting point is to describe the system under study as a statistical ensemble specified by a Hamiltonian

$$H = H_0 + \lambda V \quad (2.26)$$

and a density matrix

$$\rho(t) = \sum_i p_i(t) |\psi_i(t)\rangle \langle \psi_i(t)| \quad (2.27)$$

where the $p_i(t)$'s specify the classical probability of the system being in state i at time t , and the $|\psi_i\rangle$'s are wavefunctions given by

$$|\psi_i(t)\rangle = \sum_n c_n^i(t) |n\rangle \quad (2.28)$$

for some $\{c_n^i(t)\}$, where

$$H_0 |n\rangle = E_n |n\rangle \quad (2.29)$$

for all n . In the presence of damping, the elements

$$\rho_{nm} = \langle \psi_n | \rho | \psi_m \rangle \quad (2.30)$$

of ρ satisfy the differential equation

$$\dot{\rho}_{nm} = \frac{1}{i\hbar} [H, \rho]_{nm} - \gamma_{nm} (\rho_{nm} - \rho_{nm}^{(eq)}), \quad (2.31)$$

where γ_{nm} is a matrix of (phenomenological) damping parameters⁷, and $\rho_{nm}^{(eq)}$ is the density matrix corresponding to the equilibrium steady state of the system.

⁷This is just one choice of $p_i(t)$.

We consider the case where V may be treated as a perturbation on top of H_0 , i.e. where λ is small. In this case, Eq. 2.31 can be written

$$\dot{\rho}_{nm} = -i\omega_{nm}\rho_{nm} + \frac{1}{i\hbar} \sum_k \lambda(V_{nk}\rho_{km} - \rho_{nk}V_{km}) - \gamma_{nm}(\rho_{nm} - \rho_{nm}^{(eq)}), \quad (2.32)$$

where $\omega_{nm} = E_{nm}/\hbar$, and we seek a solution

$$\rho_{nm} = \rho_{nm}^{(0)} + \lambda\rho_{nm}^{(1)} + \lambda^2\rho_{nm}^{(2)} + \dots \quad (2.33)$$

Turning the crank (see Boyd [10] for details) gives us the solution

$$\rho_{nm}^{(N)}(t) = \int_{-\infty}^t \frac{1}{i\hbar} [\lambda V(t'), \rho^{(N-1)}(t')]_{nm} e^{(i\omega_{nm} + \gamma_{nm})(t' - t)} dt'. \quad (2.34)$$

Carrying out this series to second order in λ with the perturbation $V(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t)$, where $\boldsymbol{\mu}$ is the dipole moment and $\mathbf{E}(t) = \sum_q \mathbf{E}(\omega_q) e^{-i\omega_q t}$ is the incident electric field, we get an expression for the density matrix $\rho_{nm}^{(2)}(t)$ as a function of the dipole matrix elements

$$\boldsymbol{\mu}_{nm} = \langle n | \boldsymbol{\mu} | m \rangle, \quad (2.35)$$

the frequencies ω_q , the damping constants γ_{nm} , and $\rho_{nm}^{(0)}$.

Once we have $\rho_{nm}^{(2)}(t)$, we can compute the expectation value

$$\langle \boldsymbol{\mu}(t) \rangle = \sum_{nm} \rho_{nm}(t) \boldsymbol{\mu}_{nm}, \quad (2.36)$$

from which the susceptibility can be computed by taking two derivatives with respect to the electric field amplitudes⁸. Reproducing the final answer

⁸We are specializing here to the case of electric dipole SHG, although the calculation proceeds similarly for magnetic dipole and electric quadrupole.

here (again, from Boyd [10]):

$$\begin{aligned} \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) = & \frac{1}{2\epsilon_0 \hbar^2} \sum_{lmn} (\rho_{ll}^{(0)} - \rho_{mm}^{(0)}) \times \left\{ \right. \\ & \frac{\mu_{ln}^i \mu_{nm}^j \mu_{ml}^k}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}] [(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \\ & + \frac{\mu_{ln}^i \mu_{nm}^k \mu_{ml}^j}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}] [(\omega_{ml} - \omega_q) - i\gamma_{ml}]} \\ & + \frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}] [(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \\ & + \frac{\mu_{ln}^k \mu_{nm}^i \mu_{ml}^j}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}] [(\omega_{ml} - \omega_q) - i\gamma_{ml}]} \\ \left. \right\}, \end{aligned} \quad (2.37)$$

where $\omega_{nm} = \omega_n - \omega_m$. The SHG susceptibility tensor is then obtained by taking the limit $\omega_p = \omega_q$.

We learned two things by doing the quantum calculation. First of all, clearly if we know all of the eigenfunctions $|n\rangle$ of our unperturbed Hamiltonian, we can calculate the susceptibility tensor *a priori*, although this is obviously difficult except in the simplest of cases. Secondly, we notice that there are two types of denominators in Eq. 2.37: those occurring at 2ω (remember we have set $\omega_q = \omega_p$) and those occurring at ω . Both can cause resonances in the SHG intensity and are observed abundantly in experiment[20]. The existence of resonances in the SHG spectrum makes comparison between different materials quite difficult if reference is made only to the SHG intensity at a single color. In one infamous example, Wu et al. [68] incorrectly attributed the large SHG amplitude at optical wavelengths in TaAs to the presence of Weyl nodes near the Fermi level; later SHG spectroscopy measurements demonstrated that the enhancement was due to a simple band resonance at the excitation frequency used in that paper[46]. The emerging consensus is that the SHG intensity at optical frequencies has more or less nothing to do with the low-energy excitation spectrum or its topology.

2.4 SHG in the Ginzburg-Landau paradigm

While Eq. 2.37 is quite general and completely correct microscopically, it obviously lends very little intuition into what kind of phenomenology we can expect to find in the SHG signal, say, across a phase transition, where the dipole matrix elements which determine Eq. 2.37 certainly change but may not do so in a simple or straightforward way. An alternative approach is to treat SHG in a generalized Ginzburg-Landau paradigm, in which all of the physics of the system is cast in terms of an order parameter $\mathcal{O}_{i_1 i_2 \dots i_r}$. This approach was mainly developed by Sa et al. [53], based off of early work by Pershan [47] in the 1960s.

The key insight of Pershan is that one can define a “time-averaged free energy” in nonlinear optics by considering the term (assuming the incident field $E^{\text{in}}(t)$ is monochromatic with frequency ω)

$$F_{\text{SHG}} = -P_i(2\omega)E_i^{*\text{out}}(2\omega) + \text{c.c.} \quad (2.38)$$

$$= -[\chi_{ijk}E_i^{*\text{out}}(2\omega)E_j^{\text{in}}(\omega)E_k^{\text{in}}(\omega) + \text{c.c.}] \quad (2.39)$$

Since F is a free energy, it must be a real, totally symmetric scalar, and Eq. 2.39 thus gives us a way to *derive* the form of the tensor χ_{ijk} in a particular point group using similar arguments as in section 2.1.

In the context of a (spontaneous) symmetry-breaking transition at T_c , the Ginzburg Landau paradigm asserts that the free energy of Eq. 2.39 still obeys the symmetry group of the high temperature phase, even though the low temperature phase explicitly breaks some of those symmetries. This is because the spontaneous symmetry breaking is considered a property of the *solution* of the free energy minimization problem, rather than a property of the minimization problem itself. Thus, a valid expression for the free energy in the low temperature phase is given by

$$F = -[\chi_{ijkl_1 l_2 \dots l_r}(T > T_c)E_i^{*\text{out}}(2\omega)E_j^{\text{in}}(\omega)E_k^{\text{in}}(\omega) + \text{c.c.}] \mathcal{O}_{l_1 l_2 \dots l_r}. \quad (2.40)$$

Comparing Eqs. 2.39 and 2.40, we have an equation for the SHG susceptibility tensor in the low temperature phase

$$\chi_{ijk}(T < T_c) = \chi_{ijkl_1 l_2 \dots l_r}(T > T_c) \mathcal{O}_{l_1 l_2 \dots l_r}. \quad (2.41)$$

In light of Eq. 2.41, let us consider the consequences of the symmetry of \mathcal{O} on the SHG signal. For simplicity, let us consider a situation that

resembles a ferroelectric phase transition; i.e., the high temperature phase preserves inversion symmetry, but the low temperature phase involves the emergence of a rank-1 order parameter \mathcal{O}_l which is odd under inversion. In that case, we have

$$\chi_{ijk}(T < T_c) = \chi_{ijkl}(T > T_c)\mathcal{O}_l(T), \quad (2.42)$$

i.e. the SHG at low temperature is simply a product of a high-temperature tensor and the order parameter \mathcal{O} . We of course need to check that χ_{ijkl} is allowed in the high temperature phase; here, we need χ_{ijkl} to be an even rank polar tensor, which is allowed in the presence of inversion symmetry (see Eq. 2.10).

Let us now imagine that the polarization \mathcal{O}_l is known to be directed along the y axis, i.e.

$$\mathcal{O}_l = (0, P_0, 0)_l, \quad (2.43)$$

for some P_0 . Then, by Eq. 2.42, we have

$$\chi_{ijk}(T < T_c) = \chi_{ijky}(T > T_c)P_0. \quad (2.44)$$

Besides telling us that the susceptibility tensor is linear in the polarization magnitude P_0 , what this formulation gets us is also that the elements of χ_{ijk} are just the elements of χ_{ijkl} with $l = y$. In many cases this is more information than you would have if you only knew the point group of the low temperature phase!

Eq. 2.41 is also quite useful in the case where the low temperature phase is heterogenous; i.e. the order parameter \mathcal{O} varies spatially from one point to another. This is commonly the case in magnets, for example, where rotational symmetry is spontaneously broken at T_c and the low temperature free energy thus consists of multiple energetically degenerate states related to each other by elements R of the high temperature point group which are broken at low temperature. These states have the same free energy since, again, the symmetry-breaking is due to the order parameter, not due to the free energy itself. The order parameter in the different domains are thus related to each other via

$$\mathcal{O}_{i_1 i_2 \dots i_r}(\mathbf{x}_1) = R[\mathcal{O}_{i_1 i_2 \dots i_r}(\mathbf{x}_2)], \quad (2.45)$$

where the right hand side is given by Eq. 2.10. Combining Eq. 2.41 and Eq. 2.45, the SHG tensor thus satisfies

$$\chi_{ijk}(\mathbf{x}_1) = R[\chi_{ijk}(\mathbf{x}_2)]. \quad (2.46)$$

Eq. 2.46 is the fundamental basis for our SHG works on 1T-TaS₂ and CaMn₂Bi₂, discussed in chapters chapter 5 and chapter 6.

Chapter Three

Second harmonic generation: practical

3.1 Description of the setup

In the last chapter we saw that the SHG intensity in a given crystal is related to the point group, order parameter, band structure, etc. of that crystal via the susceptibility tensor χ_{ijk} . It is also obvious from section 2.1 that the ideal scenario is to be able to measure as many of the numbers χ_{ijk} as possible; after all, if you only measured the xx component of Eqs. 2.11 and 2.12, you would have obtained essentially no information about your crystal whatsoever. The SHG setup that we built (whose design is mostly credited to Torchinsky and Hsieh[63], with some improvements by us which I will discuss below) was designed with exactly this goal in mind. There are two key insights which make this design work: one, the light is obliquely incident on the sample so there is some component of E^{in} directed along the sample normal, and two, we rotate the plane of incidence so that the in-plane field direction sweeps an entire 360° . The first point allows us to measure elements of χ_{ijk} with z indices¹, and the second point makes sure we get all of the x and y elements of χ_{ijk} too. All of the tensor elements are thus given a chance to contribute to the SHG intensity in a given experiment.

With those considerations in mind, let me proceed to give a schematic description of our SHG setup (see Figs. 3.1 and 3.2). Some of the choices

¹Here and unless otherwise noted I define the sample normal to be the z axis.

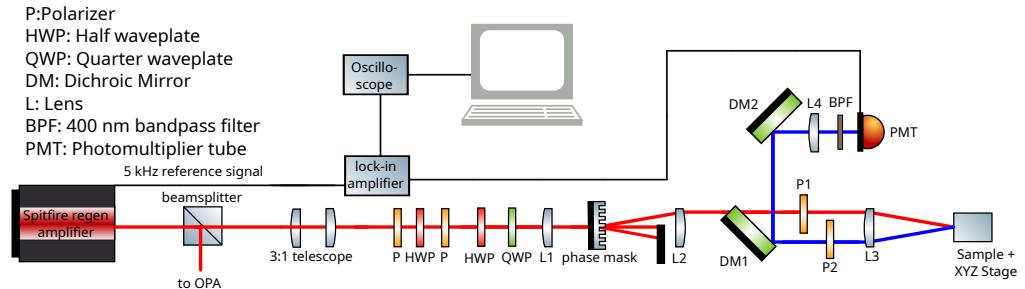


Figure 3.1: Schematic drawing of the SHG setup used in this research. After Morey et al. [42].

we made may seem arbitrary right now, but I will go over them in detail in section 3.2. The starting point is our regenerative amplifier (Spectra-Physics Spitfire Sptf-100f-5k-xp), which produces 100 fs 800 nm pulses at a 5 kHz repetition rate from an 86 MHz seed laser (Spectra-Physics Tsunami 3941-M1S). 90% of the beam is split off to power an optical parametric amplifier (OPA), and the remaining 10% is used for the SHG probe beam. After passing through an optical telescope, which creates a collimated beam of width 1 – 2 mm, this beam is attenuated with a polarizer - half-wave plate - polarizer triplet, and then elliptically polarized with a quarter-wave plate and half-wave plate in series. The ellipticity at this stage is set so the light is perfectly circularly polarized following transmission through a phase mask, as described below.

After passing through these polarization optics, the beam is focused with a lens onto the aforementioned phase mask, which acts as a transmissive diffraction grating and separates the beam into multiple different diffraction orders. The +1 order diffraction comes off at an angle of roughly 7°, while the other orders are blocked with anodized aluminum foil. This (diverging) beam then propagates at 7° to the optical axis before meeting a lens set at the appropriate distance so as to both collimate the beam and rectify the 7° propagation angle. Then, the light passes through a dichroic mirror (which transmits 800 nm and reflects 400 nm), becomes linearly polarized by a wire-grid polarizer, and is then focused onto the sample at a 10° angle of incidence by passing through the edge of a 1 in-diameter 50 mm achromatic focusing lens. The interaction between the light and the sample causes SHG to be radiated in reflection at the same

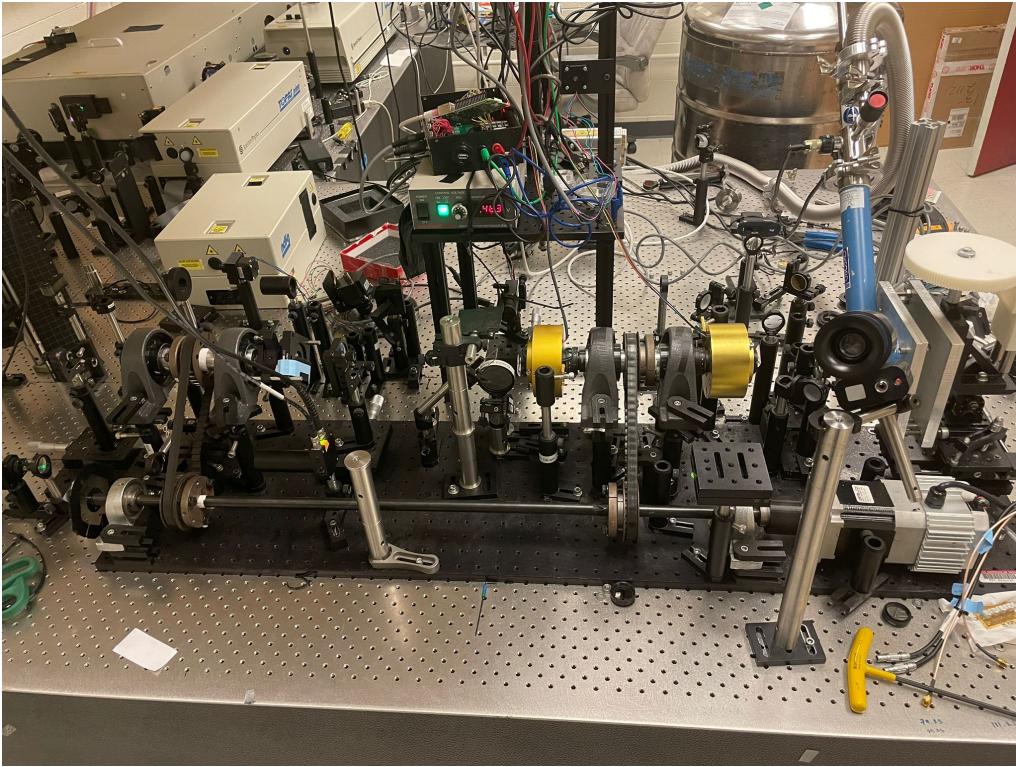


Figure 3.2: Photograph of the SHG setup used in this research. The sample lies in the blue cryostat on the right side of the image. The phase mask is mounted in a black holder with blue masking tape on the left side, and the polarizers are mounted in the two gold-colored slip rings (described in chapter 4).

10° angle of incidence, so that the SHG beam passes through the opposite side of the 50 mm lens before passing through a second, independent polarizer which is used to control the polarization of the measured light.

Finally, the polarized output reflects off of two dichroic mirrors (oriented in such a way as to cancel the differing effect of the Fresnel equations on the reflectivity of S and P polarized light) and is focused through a 400 nm bandpass filter onto a photomultiplier tube (PMT) by a 400 mm lens. The current output of the PMT is filtered by a lock-in amplifier (for static SHG, set to the 5 kHz repetition rate of the laser) and read out on an oscilloscope. The phase mask, incoming polarizer, and outgoing polarizer

are mounted on rotating lens tubes which are connected via pulley to a common motor shaft driven at ~ 5 Hz by a brushless DC motor. The motor thus continuously rotates the plane of incidence of the experiment, since the latter is entirely defined by the phase mask and the polarizers. The rotation angle is tracked as a function of time by an optical rotary encoder, consisting of a laser pointer passed through a chopper wheel (with 100 slots) mounted at the end of the motor shaft and detected via photodiode. The encoder signal and the lock-in signal are both sent to a homemade oscilloscope (an Arduino Uno microcontroller which separates the lock-in signal into different individual rotations by looking for peaks in the encoder signal), the output of which is sent to a computer for further data processing.

3.2 Before you build

I list here a few essential aspects of SHG that should be considered before designing a new setup.

3.2.1 Spot size

One of the most important quantities in an SHG setup is the diameter of the probe spot. Ideally, this diameter is as small as possible, so as to measure the smallest samples or domain sizes. However, there is an important caveat: for constant fluence (i.e. supposing we are limited by the sample damage threshold), the SHG signal to noise ratio scales linearly in the area excited by the probe, and thus SHG microscopes have a difficult time measuring small SHG signals compared to traditional SHG setups with a larger excitation area. To see this, let us say that our detector measures the number of photons per SHG pulse, which is proportional to the pulse energy $U_p(2\omega)$. Assuming the input and output pulse intensity profiles have the shape of a square wave with width τ and height $I_p(\omega)$ and $I_p(2\omega)$, respectively, we have

$$U_p(2\omega) = AI_p(2\omega)\tau \quad (3.1)$$

and

$$U_p(\omega) = AI_p(\omega)\tau \quad (3.2)$$

where A is the area of the beam at the sample surface. The SHG intensity is proportional to the square of the input intensity

$$I_p(2\omega) \propto I_p^2(\omega) \quad (3.3)$$

so that

$$U_p(2\omega) \propto \frac{U_p^2(\omega)}{A\tau}. \quad (3.4)$$

Substituting for the fluence f

$$f(\omega) = \frac{U_p(\omega)}{A} \quad (3.5)$$

we have

$$U_p(2\omega) \propto \frac{f^2(\omega)A}{\tau} \quad (3.6)$$

i.e., if we hold the fluence constant at the sample damage threshold, the number of photons in the generated SHG pulse is proportional to the excitation area and inverse to the pulse width. The signal to noise ratio is then given by

$$\text{SNR} \propto \frac{U_p(2\omega)}{\sqrt{r}} \quad (3.7)$$

where r is the system repetition rate.

3.2.2 Oblique vs. normal incidence

While all of the results presented in this thesis utilized the setup in Fig. 3.1, where the incident beam makes a small angle with respect to the sample normal, plenty of groups use a different approach where that angle is set to 0° . This has the obvious disadvantage of not specifying all of the tensor elements, since any element χ_{ijk} with $i, j, k = z$ is not accessible in this geometry. However, in some cases this can actually be something of an advantage. For example, sometimes unwanted SHG contributions (see section 2.2) may be avoided in the normal incidence geometry, assuming the numerical aperture (NA) of the focusing optic is small enough that longitudinal components of the electric field are nearly zero. Furthermore, in some materials the order parameter only couples to one or two elements of χ_{ijk} ; if none of these elements have a z index, it is needless to complicate the analysis with oblique incidence.

In my experience, oblique incidence seems to be useful in two broad cases. For one thing, some order parameters only show up in the z components of χ_{ijk} (this is the case in 1T-TaS₂, see chapter 5), in which case one obviously needs a nonzero angle of incidence to access these components. A more subtle point is that, even if in practice all of the phenomenology of a particular sample only shows up in the x and y indices of χ_{ijk} , still one must measure the full tensor to *rule out* unseen phenomenology in the other indices. Both the CaMn₂Bi₂ (chapter 6) and CuBr₂ (chapter 7) works presented in this thesis are examples of exactly this point, where the main scientific arguments involve either comparing SHG patterns in two domains or comparing oscillation amplitudes in different polarization channels. Clearly one needs to know all of the tensor elements to make those arguments exact.

3.2.3 Choice of detector

Our setup is somewhat unique in using a PMT for data collection rather than an electron multiplying charge coupled device (EM-CCD), which is the slightly more traditional method. Frankly, this decision was not based on the detection efficiency, but rather the fact that PMTs typically cost about two orders of magnitude less than EM-CCDs. However, the setup construction with a PMT is slightly different than with an EM-CCD, so you should probably decide which you want to use before you start building your setup. With an EM-CCD, the beam is sent into the device without focusing (L4 in Fig. 3.1) so that the beam traces a circle on the sensor as a function of time[24]. The rotational anisotropy signal is read off by performing a radial integration of the camera image (after masking the part of the image which is outside from the circle traced by the beam). In this way, the rotation angle of the motor is correlated with the SHG signal via the azimuthal degree of freedom on the camera image. In contrast, with a PMT the SHG signal is read out as a function of time on an oscilloscope (see section 3.1), and must be correlated with the rotation angle of the motor by some other method. We use an optical chopper wheel attached to the motor shaft; a beam from a laser pointer is directed through the chopper wheel and onto a photodiode, which produces a square wave signal that is used to trigger the oscilloscope. One must also be careful that the PMT is aligned as close to normal as possible to the axis

defined by DM2 and L4 in Fig. 3.1, as the PMT output is actually quite sensitive to the angle of incidence of the input radiation.

As for the detection efficiency of the two devies, an EM-CCD is basically an *array* of PMTs – thus, there is no fundamental difference in the detection efficiencies of the two methods, although having never used an EM-CCD I cannot speak to any specific considerations that might favor one over the other.

3.3 tr-SHG: methodology

Polarization control

The main limitation for doing tr-SHG is simply that the experiment becomes longer. Each measurement of χ_{ijk} requires averaging four different polarization channels ($P_{\text{in}}P_{\text{out}}$, $P_{\text{in}}S_{\text{out}}$, $S_{\text{in}}P_{\text{out}}$, and $S_{\text{in}}S_{\text{out}}$), which, depending on the signal to noise ratio, can take as long as 2 – 3 minutes each. In a time-resolved experiment, that procedure must be repeated at least once for each time delay; in fact, it us often useful to sweep the delay stage multiple times to reduce the extent to which systematic drifts in in the laser power, alignment, etc. affect the time trace. Not only is this time-consuming (typically taking ~ 12 hours to get a good dataset), but it also requires four rotations of the polarizers at each delay, which is simply not feasible if the polarizers are to be rotated manually. Unfortunately, automated polarizer rotation is difficult in the rotational anisotropy SHG (RA-SHG) experimental geometry because the polarizers must be rotated relative to a lens tube which is *itself* rotating at 5 Hz. The traditional method of rotating polarizers via stepper motor is thus not possible, unless one finds a method to transmit power between the stationary laboratory frame and the rotating frame that the polarizer lives in. Myself and Karna Morey designed such a method using an electronic device known as a hollow-bore electric slip ring, which uses ring-shaped conductive pads in combination with low-friction metallic brushes to conduct electricity between two rotating objects. In my opinion, such a design is essential to doing tr-SHG unless one is satisfied with only measuring a single polarization channel; thus, I have dedicated the entirety of chapter 4 to our solution, which in my opinion represents the largest contribution we made to SHG methodology during this thesis.

The pump beam path

Having discussed the modifications needed for tr-SHG on the probe arm, let us now describe the pump beam path. 100 fs pulses from the regenerative amplifier (Spectra-Physics Spitfire Sptf-100f-5k-xp) are split by 90 : 10 beamsplitter (with the 10% becoming the probe beam, see section 3.1) and are used as input to an OPA (Light Conversion TP8F1N3) which produces light of variable wavelength between 1100 and 2080 nm. The output of the OPA is directed through a wire-grid polarizer (to pick out the signal or idler, as needed) to an optical delay line (Newport DL125 with SMC100 motion controller) and a second polarizer to vary the beam power. The beam then passes through a NIR (near-infrared) longpass filter to remove unwanted visible wavelengths that are output by the OPA. A 400 nm lens focuses the beam past two mirrors (one mounted with epoxy onto the focusing lens L3 of Fig. 3.1²) and finally onto the sample. The diameter of the pump beam at the focus is set by moving the lens position along the beampath and monitoring the beam shape with a CCD camera. The pointing of the beam is aligned so that the light reflected off the sample is perfectly backscattered. Pump scatter is avoided by mounting a small black circular disk in the center of L3, and by subtracting “dark” scans without the probe beam from the final dataset.

An optical chopper wheel is placed somewhere in the pump beam path which blocks every other pulse from the OPA, so that the effective repetition rate of the pump pulsetrain is 2.5 kHz. The output of the PMT (see Fig. 3.1) is sent to a lock-in amplifier synced to this frequency, so that the output of the lock-in is proportional to

$$I_{\text{Pump+Probe}}^{\text{SHG}} - I_{\text{Probe}}^{\text{SHG}} \quad (3.8)$$

i.e. the output of the lock-in is the pump-induced change in the measured SHG intensity.

Finally, the pump-probe time delay is varied, and for each delay the rotational anisotropy in the SHG intensity is measured in each of the four polarization channels. Alternatively, the motor rotation may be parked at a fixed angle and the SHG intensity at this angle measured as a function of delay time.

²Remember that the probe beam is arriving at oblique incidence and thus passes through the edge, rather than the center, of L3.

3.4 Data analysis

Finally, we discuss the analysis of SHG data, first in the static limit and then in the context of tr-SHG.

3.4.1 Static RA-SHG patterns

The typical static RA-SHG dataset consists of a set of points $\{(\phi_n, I_n^p)\}$, $n \in \{0, 1, \dots, N - 1\}$ and standard errors $\{\sigma_n^p\}$ for each of the four independent polarization channels

$$p \in \{P_{\text{in}}P_{\text{out}}, P_{\text{in}}S_{\text{out}}, S_{\text{in}}P_{\text{out}}, S_{\text{in}}S_{\text{out}}\}.$$

By Eq. 2.13, each of these patterns may be modeled by an equation³

$$I^p(\phi) \propto |\hat{e}_i^{p,\text{out}}(\phi) \chi_{ijk} \hat{e}_j^{p,\text{in}}(\phi) \hat{e}_k^{p,\text{in}}(\phi)|^2, \quad (3.9)$$

where \hat{e} is a unit vector in the direction of the corresponding electric field. These unit vectors are given as a function of ϕ and the angle of incidence θ in table 3.1.

³I will focus on electric dipole SHG for now, although note that the equations for electric quadrupole and magnetic dipole SHG (Eqs. 2.23 and 2.24) are different – by Eq. 2.16, both involve a factor of the incident wavevector \mathbf{k} , and the magnetic dipole term has a cross product.

Table 3.1: Vector definition of polarization channels. θ is the angle of incidence and ϕ is the angle of the plane of incidence with respect to the \hat{x} axis.

Input	Output	$\hat{e}^{\text{in}}(\phi)$			$\hat{e}^{\text{out}}(\phi)$		
		$\hat{e}_x^{\text{in}}(\phi)$	$\hat{e}_y^{\text{in}}(\phi)$	$\hat{e}_z^{\text{in}}(\phi)$	$\hat{e}_x^{\text{out}}(\phi)$	$\hat{e}_y^{\text{out}}(\phi)$	$\hat{e}_z^{\text{out}}(\phi)$
P	P	$\cos \phi \cos \theta$	$\sin \phi \cos \theta$	$-\sin \theta$	$-\cos \phi \cos \theta$	$-\sin \phi \cos \theta$	$-\sin \theta$
P	S	$\cos \phi \cos \theta$	$\sin \phi \cos \theta$	$-\sin \theta$	$-\sin \phi$	$\cos \phi$	0
S	P	$-\sin \phi$	$\cos \phi$	0	$-\cos \phi \cos \theta$	$-\sin \phi \cos \theta$	$-\sin \theta$
S	S	$-\sin \phi$	$\cos \phi$	0	$-\sin \phi$	$\cos \phi$	0

Let us assume that we know the point group P_G of our material. Then, the first step is to constrain the values of χ_{ijk} using the arguments of section 2.1. One can do this manually by solving the system of equations defined by Eq. 2.10, or one can simply look up the answer in one of a number of tables (e.g. Boyd [10])⁴; in the end we are left with a tensor $\chi_{ijk}^{P_G}$ with M independent elements $\{\chi_i, i \in 0, 1, \dots, M - 1\}$.

The goal is to simultaneously fit the four patterns $\{(\phi_n, I_n^p)\}$ to Eq. 3.9 using the χ_i 's. Our objective function is thus

$$f(\{\chi_i\}) = \sum_{\substack{p \in \{P_{\text{in}} P_{\text{out}}, P_{\text{in}} S_{\text{out}}, \\ S_{\text{in}} P_{\text{out}}, S_{\text{in}} S_{\text{out}}\}}} \sum_{n=0}^{N-1} \left(\frac{I^p(\phi_n) - I_n^p}{\sigma_n^p} \right)^2 \quad (3.10)$$

with $I^p(\phi)$ defined in Eq. 3.9. Unfortunately, such a function is quite difficult to minimize. The reason is that $I^p(\phi)$ is ultimately a sum of products of trigonometric functions of ϕ (due to table 3.1) which can be difficult for typical minimization algorithms. An alternative is to cast the problem in terms of the Fourier transforms (FTs)

$$\hat{I}^p(k) \equiv \frac{1}{2\pi} \int_0^{2\pi} I^p(\phi) e^{-ik\phi} d\phi \quad (3.11)$$

of $I^p(\phi)$ and the discrete Fourier transforms (DFTs)

$$\{(k, \hat{I}_k^p)\}, \quad (3.12)$$

of $\{(\phi_n, I_n^p)\}$, where⁵

$$\hat{I}_k^p \equiv \frac{1}{N} \sum_{n=0}^{N-1} I_n^p e^{-ik\phi_n}. \quad (3.13)$$

Since the DFT is unitary, the uncertainties $\hat{\sigma}_k^p$ are simply the DFT of the σ_n^p 's. Thus, our new objective function is

$$f(\{\chi_i\}) = \sum_{\substack{p \in \{P_{\text{in}} P_{\text{out}}, P_{\text{in}} S_{\text{out}}, \\ S_{\text{in}} P_{\text{out}}, S_{\text{in}} S_{\text{out}}\}}} \sum_{k=0}^{N-1} \left(\frac{\hat{I}^p(k) - \hat{I}_k^p}{\hat{\sigma}_k^p} \right)^2. \quad (3.14)$$

⁴Be aware that these tensors are given in just one of many choices of coordinates; a rotation of χ_{ijk} may be needed to agree with the orientation of the crystal in the experiment.

⁵I am assuming the ϕ_n 's are equally spaced.

This is a much easier function to minimize for two reasons: one, the function is now just a quadratic function of the $\{\chi_i\}$'s, and two, since there are only six factors of trigonometric functions of ϕ in $I^p(\phi)$, $\hat{I}^p(k) = 0$ for $k \notin \{-6, -5, \dots, 6\}$ ⁶ (the other terms in Eq. 3.14 just contribute an overall constant to f).

What is left then is just the choice of minimization algorithm. Unfortunately, simple gradient descent algorithms are not ideal here unless you have a really good initial guess, since Eq. 3.11 is still quadratic in the fitting parameters and the global minimum is often surrounded by many local minima which can easily cause these algorithms to become trapped. Global minimization routines are thus optimal; I have used the simulated annealing algorithm of Xiang et al. [70] with success, as well as the related “basinhopping” algorithm of Wales and Doye [66], both of which are implemented in `scipy.optimize`[64]. Ultimately, though, it is up to the experimenter to ensure they have found the true global minimum of Eq. 3.14.

As part of this thesis, I wrote a software package in Python called ShgPy which uses `sympy`[40] to compute the FT model Eq. 3.11 and `scipy.optimize`[64] to fit this model to the data via Eq. 3.14. Installation instructions and a comprehensive documentation may be found at the project home page <https://bfichera.github.io/shgpy/>.

3.4.2 Modeling χ_{ijk} : the simplified bond hyperpolarizability model

Sometimes the symmetry-constrained χ_{ijk} of section 3.4.1 is difficult to analyze (perhaps it has too many fitting parameters), in which case it might be prudent try and justify an even more tightly constrained χ_{ijk} via some a microscopic model. We have already seen two such models via Eqs. 2.37 and 2.41, but the former is typically not tractable and the latter may only be valid in the presence of a spontaneous symmetry-breaking phase transition with a well-defined order parameter. One alternative is to model the microscopic charge degrees of freedom classically – suppose most of the motion of charges in our solid occurs in the bonds between atoms, and that that motion is constrained to occur along the bond direction only.

⁶This is the case for electric dipole SHG; for electric quadrupole and magnetic dipole, we can have as much as $k = \pm 8$.

Then, the solid can be modeled as an ensemble of oscillating dipoles (one for each bond in the unit cell) with corresponding hyperpolarizabilities $\{\alpha_n\}$. Symmetry may dictate how many independent α_n 's there are in the unit cell, but otherwise these are considered unknown and to be fit to the data. The electric dipole SHG response of such an ensemble was analyzed by Powell et al. [49], and the electric quadrupole response was later considered by Bauer and Hingerl [4]; the answer in both cases is quite simple:

$$\chi_{ijk}^{eee} = \sum_n \alpha_n b_i^n b_j^n b_k^n \quad (3.15)$$

$$\chi_{ijkl}^{gee} = \sum_n \gamma_n b_i^n b_j^n b_k^n b_l^n \quad (3.16)$$

where b^n is a unit vector in the direction of bond n and the α_n 's and γ_n 's are the unknown parameters of the dipole and quadrupole models, respectively.

When valid, this simplified bond hyperpolarizability model (SBHM) is powerful for two reasons: for one, Eqs. 3.15 and 3.16 typically have fewer unknown parameters than the naive, symmetry-constrained tensor $\chi_{ijk}^{P_G}$ of section 3.4.1, and two, there is a direct connection between the unknown parameters α_n and γ_n and the microscopic degrees of freedom. One can thus draw conclusions *about* the microscopic degrees of freedom by fitting the SHG patterns to Eqs. 3.15 and 3.16 (see, e.g., Ron et al. [52]). Of course, one must be careful that the assumptions of this model – that the charges are localized to the bonds, and that the only relevant motion is along the bond direction – are actually correct before proceeding with this sort of analysis.

Myself and Karna Morey built a comprehensive interface to the SBHM in Python using pymatgen[45], which takes an arbitrary crystallographic information file (CIF) and calculates the relevant susceptibility tensors via Eqs. 3.15 and 3.16. The change to the susceptibility tensor induced by an elastic distortion mode ($\chi_{ijk}(q)$, where q is the mode amplitude) can be computed via integration with ISODISTORT[11, 59]. See the package documentation (<https://github.com/morey18k/sbhm.git>) for examples and further information.

3.4.3 Fitting time traces in tr-SHG

As the final section of this chapter, let me remark on a few aspects of fitting time-domain signals that are not necessarily specific to SHG, but are nevertheless essential for tr-SHG analysis.

Typically, in tr-SHG we plot the pump-induced change in the SHG intensity at a single angle ϕ_0 as a function of the delay time t ; more complicated analysis of the tensor elements themselves is possible but often unnecessary. This intensity change $\Delta I_{2\omega}(t, \phi_0)$ is related to $P(2\omega)$ via

$$\Delta I_{2\omega}(t, \phi_0) = I_{2\omega}^{\text{Pump+Probe}}(t, \phi_0) - I_{2\omega}^{\text{probe}}(0, \phi_0) \quad (3.17)$$

$$\propto |P_{2\omega}(0, \phi_0) + \delta P_{2\omega}(t, \phi_0)|^2 - |P_{2\omega}(0, \phi_0)|^2 \quad (3.18)$$

$$\propto 2P_{2\omega}(0, \phi_0)\delta P_{2\omega}(t, \phi_0) + |\delta P_{2\omega}(t, \phi_0)|^2 \quad (3.19)$$

where we have used that the signal is presumably independent of time if there is no pump pulse. When $|\delta P_{2\omega}(t, \phi_0)| \ll |P_{2\omega}(0, \phi_0)|$, this reduces to

$$\Delta I_{2\omega}(t, \phi_0) \propto P_{2\omega}(0, \phi_0)\delta P_{2\omega}(t, \phi_0). \quad (3.20)$$

The basic problem is then that we have a dataset

$$\{t_n, I_n\}, n \in \{0, 1, \dots, N - 1\} \quad (3.21)$$

with uncertainties σ_n which we wish to fit to some model, typically consisting of some (e.g. polynomial) background

$$b(t, \{b_k\}), k \in \{0, 1, \dots, K - 1\} \quad (3.22)$$

plus 1 to M damped harmonic oscillators

$$I(t, \theta) = \begin{cases} 0 & t < 0 \\ b(t, \{b_k\}) + \sum_{m=1}^M A_m e^{-t/\tau_m} \cos(2\pi f_m t + \psi_m) & t > 0 \end{cases}, \quad (3.23)$$

where θ refers to the set of unknown parameters $\{b_k\}$, $\{A_m\}$, $\{\tau_m\}$, $\{f_m\}$, and $\{\psi_m\}$. We wish to determine the model coefficients θ by minimizing the objective function

$$f(\theta) = \sum_{n=0}^{N-1} \left(\frac{I(t_n, \theta) - I_n}{\sigma_n} \right)^2. \quad (3.24)$$

Various algorithms exist to find the minimum θ_0 of f ; the Levenberg-Marquardt (LM) algorithm [34, 39] is known to have trouble with exponential functions, so it is recommended to do a Nelder-Mead search [43] first and then use LM to refine the solution. These methods also report the uncertainties $\{\sigma_i\}$ on each fitting parameter, basically by computing the curvature of the function f near θ_0 (which depends, among other things, on the data uncertainty $\{\sigma_n\}$). Importantly, however, these uncertainties are only valid when f is a linear function of the model parameters near the minimum!⁷ This is a point which is completely overlooked in the ultrafast condensed matter literature, even though there is really no reason that Eq. 3.24 should satisfy this criterion for typical uncertainty levels in pump-probe experiments.

The correct approach in this case is to note that the data set $D_0 \equiv \{t_n, I_n\}$ is just one of many possible datasets D_0, D_1, D_2, \dots that we *could* have measured during our experiment.⁸ If we could run the minimization procedure described above for each of these hypothetical datasets, we would end up with a whole distribution of model coefficients $\theta_0, \theta_1, \theta_2, \dots$ from which our measurement θ_0 was just a single draw. The spread of this distribution (or, more precisely, the spread of the distribution $\theta - \theta_{\text{true}}$) reflects exactly the quantitative uncertainty in our measurement of θ that we would like to report.

Our goal, then, is to approximate this distribution by some method. One approach (which works when we have many observations $\{t, I\}$ with the same t) is called the nonparametric bootstrap[13]. For each time t_n , let us say that we have a set of measured intensities $\{I_m^n\}$, with $m \in \{1, 2, \dots, M_n\}$. Then, we generate new hypothetical datasets $\mathcal{D}_1, \mathcal{D}_2, \dots$ by (for each t_n) drawing M_n items *with replacement* from the $\{I_m^n\}$'s. The fact that this new distribution of datasets is a faithful representation of the true distribution $\{D_0, D_1, D_2, \dots\}$ is not obvious, but theoretical work by many authors (see Wackernagel [65] for a review) has established that it is nevertheless true.

If we are confident that our model $I(t, \theta)$ is, in fact, the true model (at least for some set of coefficients θ_{true}), then rather than using the dataset D_0 to generate our hypothetical datasets, we can instead choose to use the model *itself*. The idea is to take our estimate $I(t, \theta_0)$ and generate new

⁷Here, “near” means “in a neighborhood of size σ_i .

⁸The following discussion closely follows that of *Numerical Recipes*, chapter 15[51].

datasets $\{\mathcal{D}_m\}$ essentially by adding noise:

$$\mathcal{D}_m = \{(t_n, I(t_n, \theta_0) + N_n), n \in \{0, 1, \dots, N-1\}\}, \quad (3.25)$$

for some random variable N_n which we put in by hand. This is called the parametric bootstrap, referring to the fact that we are estimating our true distribution $\{D_0, D_1, D_2, \dots\}$ via the parameters θ_0 [15]. In order for the distribution of \mathcal{D}_m 's to faithfully represent the true distribution $\{D_0, D_1, D_2, \dots\}$, obviously N_n needs to reflect the actual noise distribution of the experiment. Thankfully, in pump-probe experiments, we usually know this distribution – as long as we have enough points (t_n, I_n) with $t_n < 0$, we can estimate N_n with a normal distribution centered about 0 with variance $\langle (I_n)^2 \rangle_{<0} - \langle I_n \rangle_{<0}^2$, where $\langle \cdot \rangle_{<0}$ means “average over points with $t_n < 0$.”

Once we have the hypothetical datasets $\{\mathcal{D}_m\}$ (regardless of how we generated them), we proceed by estimating a θ_m for each one using Eq. 3.24, and then plotting the distribution $\{\theta_m - \theta_0\}$; the spread of this distribution tells us the uncertainties σ_i in each of our model coefficients. The important part is that these uncertainties are much more reflective of the true uncertainty in our measurement of θ than the curvature of Eq. 3.24 near θ_0 , which we have argued is strictly incorrect in many cases.

Chapter Four

Automated polarization rotation for multi-axis RA-SHG experiments

4.1 Preface

This chapter is based on a manuscript intended for standalone publication and modified to fit the format of this thesis. It was coauthored by myself and Karna Morey (as co-first authors), along with Baiqing Lv, Zongqi Shen, and Nuh Gedik. Karna Morey and I initiated the project, designed and built the polarization rotators, performed the demonstration experiment, and wrote the paper. Baiqing Lv and Zongqi Shen contributed to the design and helped review the manuscript. Nuh Gedik supervised the project.

4.2 Abstract

RA-SHG is a nonlinear optical technique used to probe the symmetry of condensed matter systems. Measuring the dependence of the SHG susceptibility on one or more external parameters, notably strain, field, temperature, or time delay, is an extremely powerful way to probe complex phases of quantum materials. Experimentally, extracting maximal information about the SHG susceptibility tensor requires measurements of S and P polarized input and output combinations, which naturally

involves the rotation of the polarizers during data collection. For multi-axis experiments, this has proved challenging since polarization rotation is typically done manually. Automating this process eliminates labor constraints, reduces uncertainty due to low-frequency noise, and expands the type of multi-axis datasets that can be collected; however, it is difficult due to geometrical constraints within the setup. In this work, we design and implement low-cost, high-fidelity automated polarization rotators for use in multi-axis RA-SHG. These polarization rotators utilize an electrical slip ring to transfer power to the rotating RA-SHG optical setup as well as a miniature stepper motor to perform the polarization rotation. We demonstrate this automated system in time-resolved RA-SHG measurements in the non-centrosymmetric semiconductor GaAs. For the multi-axis measurements described above, this automated system permits data averaging over longer periods, vastly expedites data collection, and expands the setup measurement capability. This ultimately opens new frontiers in probing quantum materials using multiple tunable external parameters.

4.3 Introduction

Probing the structure of crystalline solids is essential to understanding their intrinsic functionalities. Traditionally, diffraction techniques based on the scattering of e.g. x-rays are used to determine this structure; however, these techniques predominantly measure the total electron density and are thus insensitive to long-range ordering of the valence electron subsystem. In contrast, nonlinear scattering techniques at optical frequencies like RA-SHG are sensitive rather to the total charge density, and thus offer a complementary view of the electronic, magnetic, and lattice properties of quantum materials [18, 63].¹

Furthermore, due to the non-invasive nature of RA-SHG, it can also be used to investigate changes along one or more measurement axes, such as strain, field, pressure, temperature, or time delay. The phase diagram of quantum materials is heavily influenced by these independent variables, and thus, changes to the SHG response along such measurement axes are of great interest. For example, previous studies have used various

¹In this paper, we discuss RA-SHG, although the results are fully generalizable to arbitrary harmonics, e.g. third harmonic generation.

continuous experimental parameters such as pressure [35], time delay[56], and magnetic field to investigate phase transitions in quantum materials. Such measurements can illuminate the roles that charge, spin, and thermal degrees of freedom play within quantum materials.

Second harmonic generation gleans microscopic information through the coupling of an order parameter to the second harmonic susceptibility tensor (at least a third-rank tensor with 18 independent components) [10]. This tensor governs the relationship between the vector properties (i.e. polarization and intensity) of the incident radiation and the generated second harmonic, as shown in Eq. 4.1. The complexity of this tensor means that a significant amount of data is needed to fully resolve the tensor components, posing experimental challenges with data collection. The importance of resolving the tensor components can be seen by considering Neumann’s principle, which states that these tensors must be invariant under symmetry operations of the material’s point group, which constrains the tensors’ independent and nonzero elements [7]. By measuring the intensity and polarization of the generated second harmonic radiation, RA-SHG provides information about these tensor elements and thus the underlying point group. When performing experiments with more than one measurement axis, the data constraints mentioned above can often be especially burdensome, limiting the type of experiments that can be performed using RA-SHG. Thus, new methods for collecting data efficiently for multi-axis RA-SHG experiments are incredibly important.

A more detailed understanding of the information that needs to be collected to fully resolve the second harmonic susceptibility can be seen by considering Fig. 4.1. Fig. 4.1 shows a schematic of an RA-SHG setup, where near-infrared light from the laser source enters at oblique incidence and is scattered off the front of the sample, generating blue light at the second harmonic frequency. To leading order, the measured second harmonic intensity is given by

$$I(\phi) = |E_i^{\text{out}}(\phi)\chi_{ijk}^{(2)eee}E_j^{\text{in}}(\phi)E_k^{\text{in}}(\phi)|^2, \quad (4.1)$$

where ϕ is the azimuthal angle between the crystallographic axes and the plane of incidence, E^{out} and E^{in} are the polarization vectors of the outgoing and incoming light, respectively, and $\chi^{(2)eee}$ is the SHG electric-dipole susceptibility tensor. For certain values of ϕ , as shown in Fig. 4.1(a), the sample is symmetric with respect to the polarization axis of the incoming light; in this case, the second harmonic generation is constrained

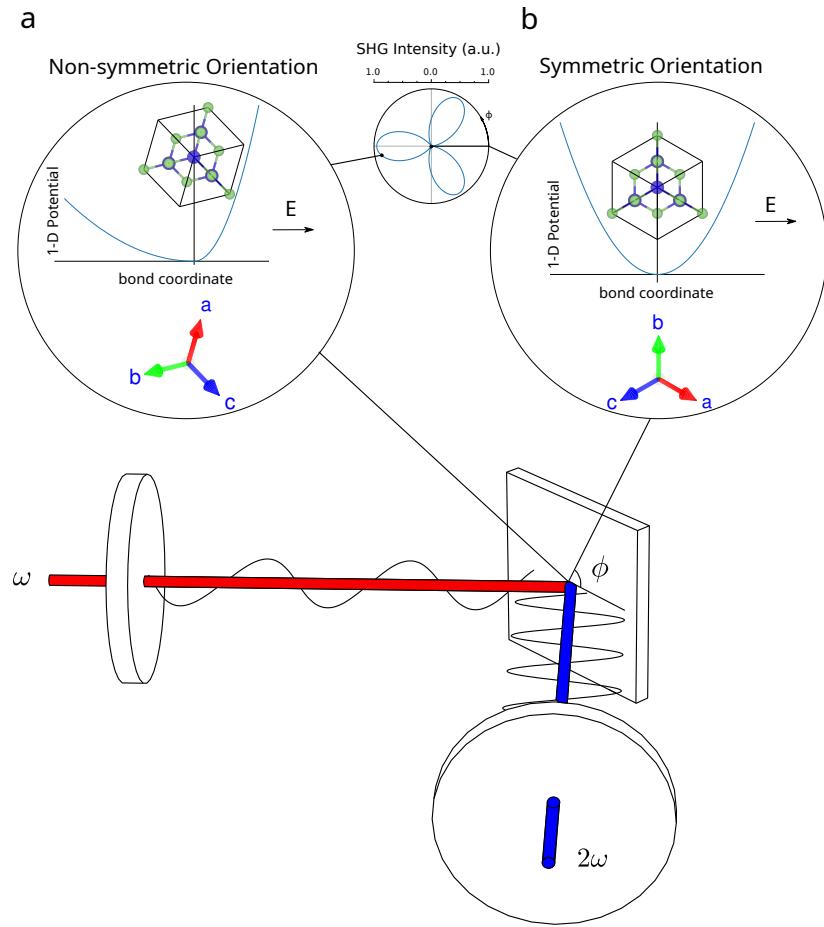


Figure 4.1: A demonstration of RA-SHG in the test sample GaAs. 800 nm light comes in at an oblique angle of incidence, after being passed through a polarizer. The polarization axis of the light is in the plane of incidence and is denoted in the insets of the figure with a black arrow. Depending on the angle of the plane of incidence relative to the crystallographic axes, as well as the polarization of the beam relative to that incoming plane of incidence, the second harmonic response to the stimuli should vary from zero points (nodes) to non-zero maxima.

to be zero, whereas in general arbitrary angles give a non-zero second-harmonic response (see Fig. 4.1(b)). Neumann’s principle dictates that Eq. 4.1 captures the symmetry considerations shown in Fig. 4.1, i.e. the symmetries of the crystal are embedded into its nonlinear susceptibility tensor $\chi^{(2)}$.

These considerations demonstrate the necessity of measuring the full rotational anisotropy of the SHG response, as well as its dependence on the incoming and outgoing polarization directions (which may be P or S-polarized, leading to four independent polarization channels). The former requires rotating the plane of incidence, which is typically done by rotating the optical setup itself rather than the sample [18, 19, 48, 63]. The geometric constraints involved in rotating the optical setup make it challenging to use electromechanical components to rotate the polarizers shown in Fig. 4.1 between S and P configurations, since naively it is difficult to transfer power to the rotating frame of reference. Because of this, switching between different polarization channels is typically done manually, resulting in time and labor constraints that often limit data collection beyond a single polarization combination [56]. Such constraints severely restrict the ability to infer tensor elements from the RA-SHG data and limit RA-SHG to studies involving often just a single tuning parameter.

Previous multi-axis RA-SHG studies typically either collected exclusively one polarization channel [56] (for more than one axis) or simply sacrificed the quantity of collected data and therefore inferred statistics. However, these approaches can often miss certain features in RA-SHG data that would be apparent if more efficient data-taking methods were available. For example, phase transitions in which the order parameter couples differently to different polarization channels through the second harmonic susceptibility [19] are best characterized by taking the full rotational anisotropy data. The benefit of collecting all four polarization combinations underscores the appeal of automated polarization control of RA-SHG setups.

In this work, we design and implement automated polarization rotators for use in multi-axis RA-SHG measurements. The devices utilize a miniature stepper motor housed in an electrical slip ring to circumvent the geometrical constraints imposed by the rotating plane of incidence. In section 4.5, we discuss the specific application of automated polarization rotation to time-resolved RA-SHG and show that it not only expedites

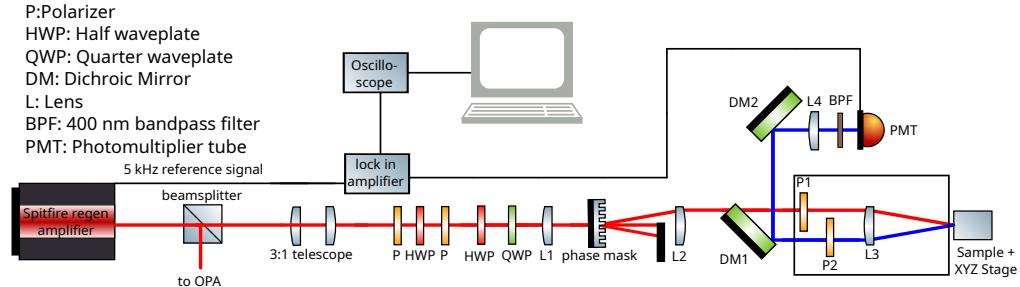


Figure 4.2: A diagram of the full second harmonic generation setup developed and described in Fichera et al. [18]. Boxed in part of the setup shows the area of interest of this work, where the incoming and outgoing polarization channels are set.

data collection but also reduces the setup's sensitivity to low-frequency noise. The advantages afforded by the automated polarization rotators exist not only for time-resolved measurements but for any measurements where an external parameter is being varied and compound rapidly as multiple parameters are varied at the same time.

4.4 Design

A detailed schematic of the RA-SHG setup is shown in figure 2. Telescopied pulses from a 5 kHz pulsed regenerative amplifier (Spectra-Physics Spitfire) are attenuated using a half-waveplate set between two polarizers and then elliptically polarized using a half-waveplate and quarter-waveplate in series. The light is then focused by a lens onto a rotating phase mask (which separates the beam into different diffraction orders), and a beam block selects the +1 order beam which is then collimated using another lens (L2). Finally, the beam passes through a dichroic mirror and a polarizer (P1) before being focused by a third lens (L3) onto the sample. The reflected radiation is passed through an analyzer (P2) and is redirected using a dichroic mirror periscope, which has equal reflectivity for S and P-polarized light and selects exclusively the 400 nm reflected radiation. The two polarizers (P1 and P2) and the phase mask are mounted on a rotating shaft coupled to an optical rotary encoder. After the dichroic mirrors, the second harmonic radiation is focused by a final lens (L4) onto a 400 nm

bandpass filter and photomultiplier tube. The signal from the photomultiplier tube is sent to a lock-in amplifier synced to the 5 kHz pulsed laser reference signal and the amplified signal is then correlated with the signal from the optical rotary encoder using a home-built oscilloscope.

Importantly, the geometrical constraints introduced by the rotating plane of incidence mean that rotating P1 and P2 between S and P configurations electromechanically is challenging, as power must be transmitted from the stationary laboratory frame to electrical components lying in the rotating frame.

To solve this problem, we utilize a hollow-bore electrical slip ring and a miniature stepper motor, shown in an exploded-view diagram in Fig. 4.3(a). A slip ring uses stationary conductive brushes sliding against a rotating through-bore cylinder to transfer power from a stationary reference frame to a rotating one, as shown in Fig. 4.3(b) [2]. To accommodate the further requirement that the beams pass through the entire device unimpeded, we employ an 8 mm stepper motor that fits in between the two beams. Fig. 4.3(c) and Fig. 4.3(d) show a front view of the device, with the wire grid polarizer in the P and S positions, respectively, and the polarization direction of the polarizer shown in arrows on the edge of the polarizer. A full rendering, to scale, of the automated system within the full setup is shown in Fig. 4.4.

4.4.1 Slip Ring

Slip rings are a standard electromechanical device for transferring power from a stationary assembly to a rotating assembly. An inner, rotating part of the slip ring can freely rotate relative to an outer, stationary part without compromising signal or power transmission. This functionality is enabled by low-friction metal brushes that slide against another set of electrical contacts, allowing free rotation while maintaining good electrical conductivity [2], as shown in Fig. 4.3(b). To allow for the uninterrupted passage of the beams through the device, we use a hollow-bore slip ring (Moflon MT3899-S040-VD) whose 38 mm inner bore rotates along with the lens tube-pulley assembly shown in Fig. 4.4. Either set screws located on the front side of the slip ring (as shown in Fig. 4.3) or a 3D-printed cylindrical hollow bore adapter (not shown) can secure the inner bore of the slip ring to the lens tube.

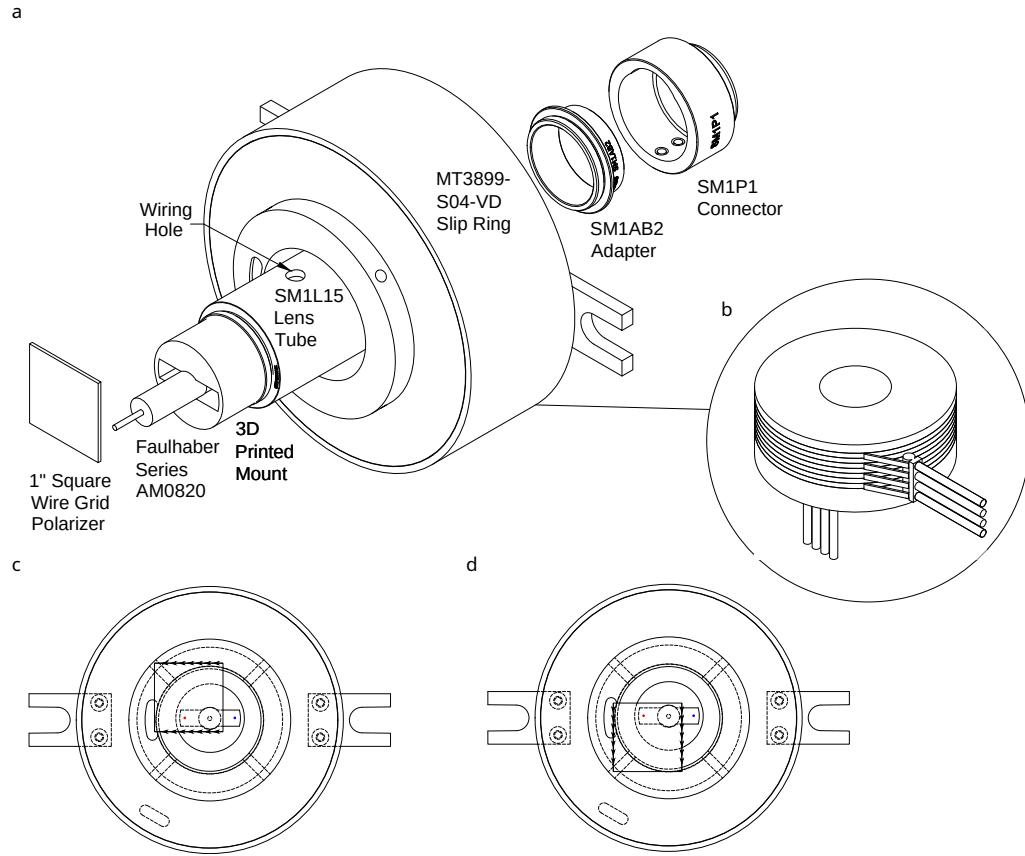


Figure 4.3: (a) An exploded-view diagram of one of the automated polarization rotators, with the individual components labeled. Each of these is a manufactured part except for the 3D-printed mount. (b) A schematic of the interior of an electrical slip ring, where low-friction metal brushes allow for electrical conduction across a rotating assembly. (c) A front view of the device, in the P-polarized state, with arrows on the edge of the polarizer indicating the polarization direction. (d) Same as Fig. 4.3(c), but in the S-polarized state.

4.4.2 Miniature Stepper Motor

The hollow bore slip ring allows for the transfer of power to the rotating shaft. To rotate the wire grid polarizer between S and P configurations while also allowing both beams to pass through the entire device, we use an 8 mm diameter Faulhaber Series AM0820 stepper motor. The stepper motor's shaft is epoxied to a 1 inch square wire-grid polarizer roughly 5 mm from the closest horizontal and vertical edges, as shown in Fig. 4.3(c) and Fig. 4.3(d). The stepper motor is mounted in the center of the SM1L15 lens tube using a custom, 3D printed mount as shown in Fig. 4.3(a). This mount, along with careful epoxying of the polarizer to the motor shaft, ensures that the incidence angle of the beam is close to normal. Furthermore, the mount ensures that the stepper motor's shaft is aligned closely to the central rotation axis of the entire assembly, minimizing torques on the motor and polarizer. This stepper motor can support up to 800 total micro-steps per revolution (0.45° per micro-step) and 0.65 mNm of holding torque, and is small enough to fit in between the incoming and outgoing beams.

The motor can then move the polarizer between the P configuration (Fig. 4.3(c)) and the S configuration (Fig. 4.3(d)) without manual intervention or the need to stop the rotation of the entire assembly. The offset placement of the polarizer on the motor shaft allows only one of the beams (either incoming or outgoing) to pass through the polarizer. The SM1AB2 and SM1P1 adapter pieces allow for arbitrary rotation relative to the longer lens tube-pulley assembly, allowing the beams to be aligned with the empty spaces in the stepper motor mount. These adapter pieces also allow for small ($\pm 20^\circ$) rotations of the polarizer about the central axis to account for factory defects which may cause the polarization axis to be misaligned with the straight edges of the polarizer.

Another copy of the same system shown in Fig. 4.3 is mounted on the other side of the lens tube-pulley assembly and controls the polarization of the reflected beam, as shown in Fig. 4.4. The back sides of both devices, shown in Fig. 4.4, are attached to the rotating lens tube-pulley-motor-shaft assembly shown in Fig. 4.4 via threads on the long central lens tube. A hole drilled in the top and bottom of the SM1L15 piece in each device shown in figure Fig. 4.3(a) allows feedthrough wires to connect the four leads of the stepper motor to the four rotating inner-bore slip ring leads. The four leads on the stationary side of each slip ring directly connect to

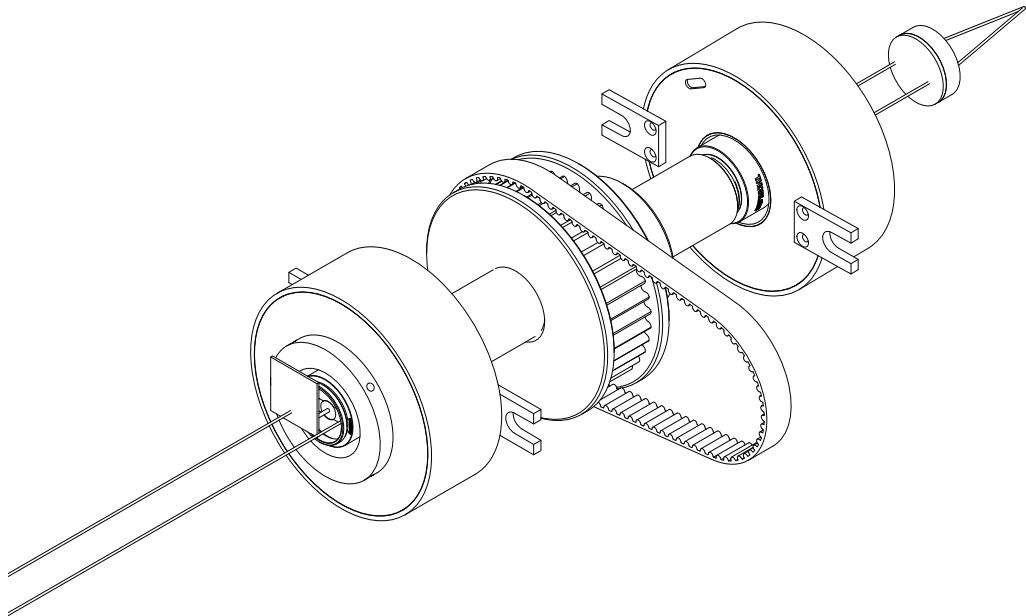


Figure 4.4: A 3-dimensional rendering of the boxed-in part of the setup in Fig. 4.2, with fully automated polarization rotators.

a Geckodrive G250X digital step driver for each device, controlled by a single Arduino Nano Every. This control circuit allows for the integration of the stepper motors with existing instrumentation software.

Whenever the stepper motors lose power, the polarizers need to be re-aligned due to the loss of their holding torque. The alignment is performed by using a reference polarizer with a known polarization axis. First, the plane of incidence of the entire assembly is positioned to the known polarization plane of the reference polarizer, then the polarizers themselves can be oriented by placing the beam through the reference polarizer and rotating the stepper motor until beam extinction (yielding an S-polarized alignment). The polarizers can then freely rotate between this S-polarized position and the orthogonal P-polarized position.

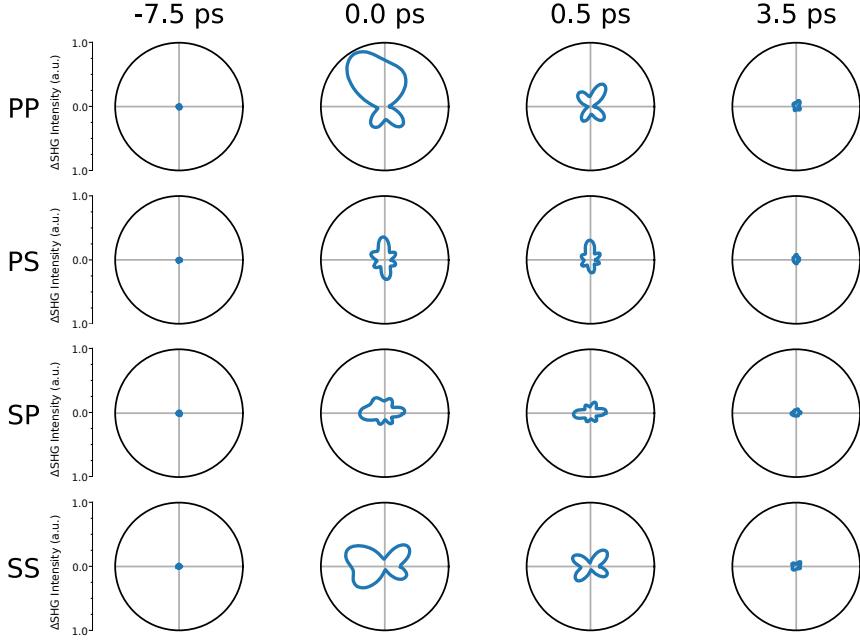


Figure 4.5: A polar plot of the change in SHG intensity (from the pre-pump state) as a function of time since zero-delay for the test sample GaAs. This is a demonstration of using the automated polarization rotators to take tr-SHG data. 55 different pump-probe delays (only four time delays are plotted) were taken in this dataset, meaning that 220 polarization rotations were performed using the automated polarizers.

4.5 Validation and Discussion

To test these automated polarization rotators, we performed time-resolved RA-SHG on the non-centrosymmetric semiconductor GaAs [17, 63]. A pump line was added to the setup shown in Fig. 4.2 by mounting a 45° mirror onto L3 so that the pump beam may be reflected directly onto the sample. The pump pulse is produced by an optical parametric amplifier (Spectra-Physics Topas) tuned to a wavelength of $1.3 \mu\text{m}$. The pump line

includes a delay stage, which controls the relative time delay between the pump and the probe pulses, and a chopper wheel, which reduces the effective repetition rate of the pump pulses to 2.5 kHz. With the pump repetition rate of 2.5 kHz and the probe repetition rate of 5 kHz, locking in at a frequency of 2.5 kHz produces a signal proportional to the change in the SHG intensity relative to equilibrium. For time-resolved measurements on GaAs, shown in Fig. 4.5, 55 different pump-probe delays were taken, resulting in 220 different automatic rotations of the polarizers. The data in Fig. 4.5 shows the change in the SHG intensity relative to equilibrium as a function of the pump-probe delay, for each of the polarization channels. The use of the polarization rotators in this validation measurement demonstrates their functionality and broad utility for multi-axis RA-SHG measurements.

This system was also used to expedite data collection in recent studies of time-resolved, temperature-dependent RA-SHG [19]. This particular type of RA-SHG measurement demonstrates the general advantages of automated polarization control in multi-axis RA-SHG measurements. To see this, note that if the rotation of the polarizers is performed manually, the best data-taking strategy involves taking the time dependence of one polarization channel in full before moving to the next. However, in the presence of low-frequency noise (due to e.g. fluctuations in the laser intensity), this is problematic as the different polarization channels will not be taken under equivalent conditions. In the automated case, in contrast, all polarization channels can be taken at each time delay. This greatly decreases the experiment's susceptibility to low-frequency noise and expedites data taking by allowing for overnight and multi-day scans.

Automated polarization rotation thus vastly improves RA-SHG data collection, eliminating the need for manual polarization rotation, especially in cases of multiple experimental axes. The roughly 1.000 \$ total cost of both devices (not including polarizers) makes them relatively inexpensive, and the design is easily implementable in existing RA-SHG setups. Multi-axis measurements are becoming increasingly important to resolve complicated phase diagrams and competing orders, and thus future measurements will increasingly rely on automated systems such as the one presented in this work.

Chapter Five

Second harmonic generation as a probe of broken mirror symmetry in 1T-TaS₂

5.1 Preface

This chapter is based on a manuscript that was published as a Rapid Communication in *Physical Review B* in 2020, again modified to fit the format of this thesis. It was coauthored by myself, Anshul Kogar, Linda Ye, Bilal Gökce, Alfred Zong, Joseph G. Checkelsky, and Nuh Gedik. Anshul Kogar and I initiated the project and took the RA-SHG data. Linda Ye and Joseph G. Checkelsky grew the samples, Bilal Gökce helped build the RA-SHG setup, and Alfred Zong took some electron diffraction data. I analyzed the data and wrote the paper. Nuh Gedik supervised the project.

5.2 Abstract

The notion of spontaneous symmetry breaking has been used to describe phase transitions in a variety of physical systems. In crystalline solids, the breaking of certain symmetries, such as mirror symmetry, is difficult to detect unambiguously. Using 1T-TaS₂, we demonstrate here that RA-SHG is not only a sensitive technique for the detection of broken mirror symmetry, but also that it can differentiate between mirror symmetry-broken structures of opposite planar chirality. We also show that our

analysis is applicable to a wide class of different materials with mirror symmetry-breaking transitions. Lastly, we find evidence for bulk mirror symmetry-breaking in the incommensurate charge density wave phase of 1T-TaS₂. Our results pave the way for RA-SHG to probe candidate materials where broken mirror symmetry may play a pivotal role.

5.3 Introduction

In condensed matter systems, phases are often classified by the symmetries that they break. Identifying these symmetries enables one to understand a system's order parameter, collective excitations, topological defects, and allowable topological indices [55, 61]. Together, these attributes allow one to predict how a material will respond to external perturbations like electromagnetic fields, heat, and mechanical forces, which is a central goal of condensed matter physics.

Specifically, the presence or absence of mirror symmetry can lead to a variety of unusual phases and properties. For example, the absence of mirror plane symmetry in noncentrosymmetric materials can give rise to gyrotropic order, which can lead to a nonzero out-of-plane circular photovoltaic effect [5]. Moreover, in certain topological crystalline insulators, such as SnTe, the presence of mirror symmetry can give rise to conducting surface states through the existence of a nonzero mirror Chern number. This topological index guarantees an even number of Dirac cones on surfaces where mirror symmetry is retained [21, 28, 60].

In other circumstances, like that in the pseudogap regime of cuprate superconductors, the existence of mirror symmetry is more controversial and has led some to seek an experimental method to serve as a binary indicator of broken mirror symmetry [27]. In principle, several tools can already do this, including resonant ultrasound spectroscopy [33, 41], X-ray, neutron, and electron diffraction [3, 16], and a recently-proposed method, shear conductivity [27]. Resonant ultrasound spectroscopy and the diffraction-based techniques are more sensitive to the ionic lattice, which makes the identification of subtle electronic symmetry-breaking challenging. And while shear conductivity has the potential to be an extremely versatile tool for identifying broken point group symmetries, experimental pursuits are currently only preliminary [27]. In this study, we focus on a nonlinear optical technique, RA-SHG, which we show is

capable not only of identifying broken mirror symmetry [26] but also of resolving its sense (left- or right-handed). Furthermore, RA-SHG is sensitive to the electronic subsystem and can be used for microscopy studies, making it an ideal experimental tool for probing phase transitions where domains may arise [25, 32].

In this direction, we choose a material, 1T-TaS₂, in which vertical mirror plane symmetry is manifestly broken across an incommensurate (IC) to nearly commensurate (NC) CDW transition [67, 71]. Using this material, we demonstrate in this Rapid Communication that RA-SHG is an effective probe of broken mirror symmetry. We also show that the sense (i.e. left- or right-handed) associated with the mirror symmetry-broken structure is encoded in the angular dependence of the RA-SHG signal. Thus, RA-SHG can be used to differentiate mirror-opposite domains. While the data presented in this work is specific to the case of 1T-TaS₂, we also show analytically that our technique is applicable to a wide class of transitions involving spontaneously broken mirror symmetry.

1T-TaS₂ is a layered material with a crystallographic structure identical to other octahedrally-coordinated transition metal dichalcogenides (Fig. 5.1(a)). The space group of the high temperature, undistorted phase is $P\bar{3}m1$ (no.164, point group D_{3d}) [58], and the point group of the surface normal to the (001) direction in this phase is C_{3v} [22, 54]. Upon lowering temperature, 1T-TaS₂ undergoes a series of CDW transitions. At $T_{IC} = 550$ K, a triple- q IC CDW forms which breaks translational symmetry but retains the surface point group symmetries of the undistorted phase [22, 54]. The effects of the CDW on the bulk symmetries in this phase are not yet understood. On further cooling, at $T_{IC-NC} = 353$ K there is a weak first-order transition to an NC CDW phase where three vertical mirror plane symmetries are broken [58] and the surface point group becomes C_3 . The NC phase has been visualized with scanning tunneling microscopy and exhibits patches of commensurate “Star of David” hexagrams that are separated by a network of discommensurations [69]. Because mirror symmetry is broken, there are two energetically equivalent CDW configurations (α and β) in the NC phase that have opposite planar chirality (Figs. 5.1(c)–d)). At even lower temperatures, $T_{NC-C} = 184$ K, 1T-TaS₂ undergoes a symmetry-preserving first-order transition, where the discommensurations disappear and the CDW locks into a structure commensurate with the underlying lattice [29].

Recent interest in the NC phase of 1T-TaS₂ has arisen due to the possi-

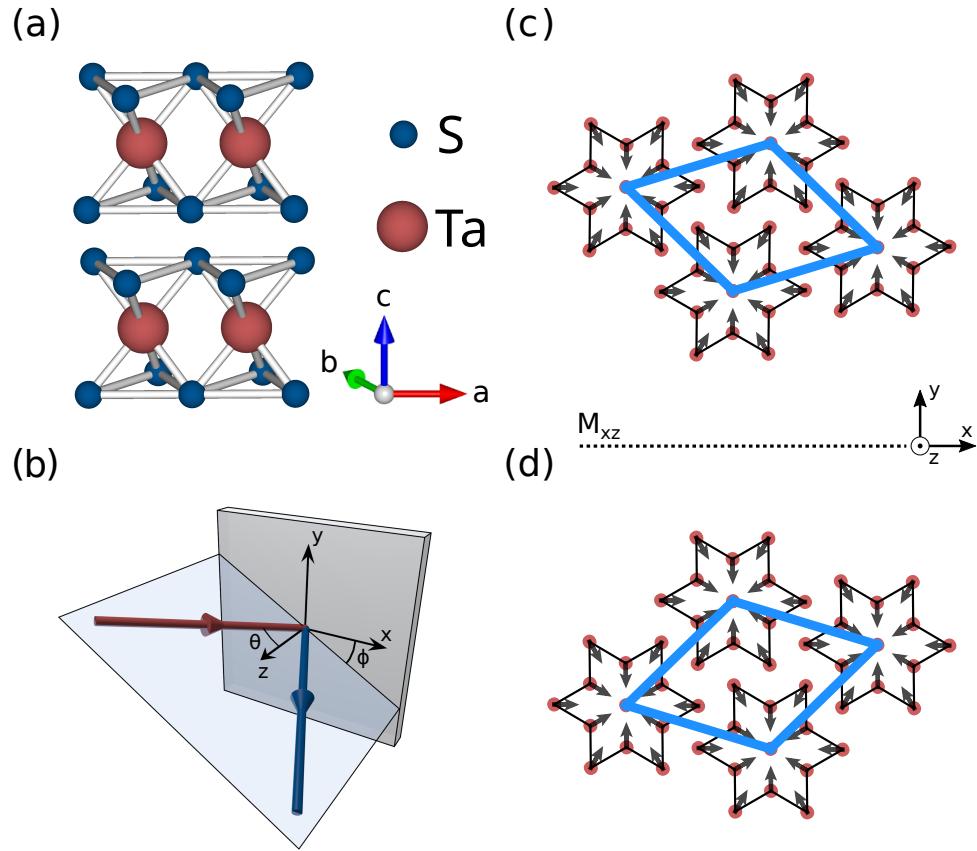


Figure 5.1: (a) Structure of 1T-TaS₂ in the undistorted phase. Ta and S atoms are depicted in red and blue, respectively. (b) Schematic of the experimental geometry. (c) (d) Structure of the CDW in the NC phase. Arrows denote the movement of the Ta atoms (red) below $T_{\text{IC-NC}} = 353$ K from their undistorted positions. The transition at $T_{\text{IC-NC}}$ spontaneously breaks mirror symmetry, so that two different CDW configurations (α and β) can form which have opposite planar chirality. The new unit cells of the two configurations are depicted in blue. M_{xz} denotes one vertical mirror plane which is broken beneath $T_{\text{IC-NC}}$. The others are related to M_{xz} by $\pm 120^\circ$ rotation about the z axis.

bility of injecting mirror-opposite domains into the CDW structure [71] which do not otherwise develop during the IC-NC transition. Zong *et al.* were able to induce these domains using a single ultrafast pulse of light, which was found to drive the material into a long-lived metastable state possessing domains of opposite planar chirality. Partly motivated by the desire to image these domains, we seek here a simple experimental method that could identify domains with opposite planar chirality.

5.4 Results and discussion

1T-TaS₂ samples used in the experiment were grown using the chemical vapor transport technique, as described in Ref. [71]. We verified that the NC phase of 1T-TaS₂ was single-domain by performing electron diffraction on a sample from the same batch (see section 5.7). This is in agreement with previous works [9, 23, 67, 71].

In RA-SHG [24, 36, 37, 62], a pulsed laser beam of frequency ω and amplitude $E(\omega)$ is focused onto a sample with nonzero angle of incidence θ (Fig. 5.1(b)). The 2ω component of the radiation emitted by the sample is subsequently measured in various combinations of incoming and outgoing polarizations (either parallel (P) or perpendicular (S) to the plane of incidence) and as a function of the angle ϕ between the plane of incidence and some crystallographic axis. In noncentrosymmetric materials, the response is dominated by the bulk electric dipole moment $P_i(2\omega) = \chi_{ijk}E_j(\omega)E_k(\omega)$ [10], where χ_{ijk} is a material-specific susceptibility tensor which must be invariant under all symmetry operations present in the crystallographic point group. In centrosymmetric crystals such as 1T-TaS₂, the bulk electric dipole response is forbidden [10, 50]. In this case, the dominant response often comes from the surface of the sample, which necessarily breaks inversion symmetry [8]. SHG from surfaces of materials is described by a different susceptibility tensor, χ_{ijk}^S , which is constrained by the crystal symmetries of the surface. In addition, there can be bulk contributions from higher-order processes which are allowed in the presence of inversion symmetry, such as the bulk quadrupole response $Q_{ij}(2\omega) = \chi_{ijkl}^Q E_k(\omega)E_l(\omega)$ [32, 57]. Our experimental implementation uses a fast-rotation setup similar to that described in Harter *et al.* [24] and Torchinsky *et al.* [63]. Here, we use an 800 nm (1.55 eV) laser beam incident at 10° with respect to the (001) sample normal. Further

experimental details can be found in the supplement (see section 5.7).

To show that we are sensitive to the breaking of mirror symmetry across the IC to NC transition, we took RA-SHG data on 1T-TaS₂ in both phases. Figs. 5.2(a) and 5.2(b) show the second harmonic response from the sample above and below $T_{\text{IC-NC}} = 353$ K in two polarization channels, plotted as a function of ϕ . We are able to fit the rotational anisotropy in the IC phase using the surface point group C_{3v} (Fig. 5.2(a)), which is in agreement with previous reports [22, 54]. It should be noted that in order to fit the S_{in}-S_{out} polarization channel appropriately, we find that it is necessary to add an additional bulk quadrupole contribution to the signal. The consequences of this contribution will be discussed later, but at the moment they do not affect our conclusions.

Upon cooling into the NC phase, mirror symmetry is spontaneously broken and the surface point group reduces to C_3 [58]. As a result, the RA-SHG exhibits a marked lowering of symmetry (Fig. 5.2(b)). This lowering of symmetry can be understood by noting that the ϕ dependence of $I_{\text{PS}}(2\omega)$ under C_3 is given by (see section 5.7)

$$I_{\text{PS}}(2\omega) = (A_0 + A_1 \cos(3\phi) + A_2 \sin(3\phi))^2, \quad (5.1)$$

where A_0 , A_1 , and A_2 are functions of the susceptibility elements χ_{ijk}^S .

Symmetry considerations (see section 5.7) show that A_0 and A_1 vanish identically in the presence of mirror symmetry. The absence of these terms lead to the six-fold symmetry in the P_{in}-S_{out} channel and its alignment with the crystallographic axes as seen in Fig. 5.2(a). However, these terms can adopt nonzero values when mirror symmetry is broken. Below $T_{\text{IC-NC}}$, the RA-SHG intensity therefore exhibits a three-fold rather than six-fold symmetric pattern, arising from a nonzero A_0 . The effect of a nonzero A_1 is to rotate the RA-SHG intensity away from the high-symmetry axes, but we observe this coefficient to be zero within the resolution of our instrument. A negligible rotation of the SHG pattern should be expected, as the atomic positions of the Ta atoms only contract towards a central Ta atom and do not rotate away from their high symmetry axes to break the mirror symmetry (see Figs. 5.1(c)-d)).

The three-fold nature of the RA-SHG intensity can be quantified experimentally by performing a spectral (sine) decomposition of the intensity and extracting the third Fourier coefficient, $\mathcal{I}_{PS}^{(3)}$, of $I_{\text{PS}}(2\omega)$ (see section 5.7). Fig. 5.2(c) shows that $\mathcal{I}_{PS}^{(3)}$ appears discontinuously below

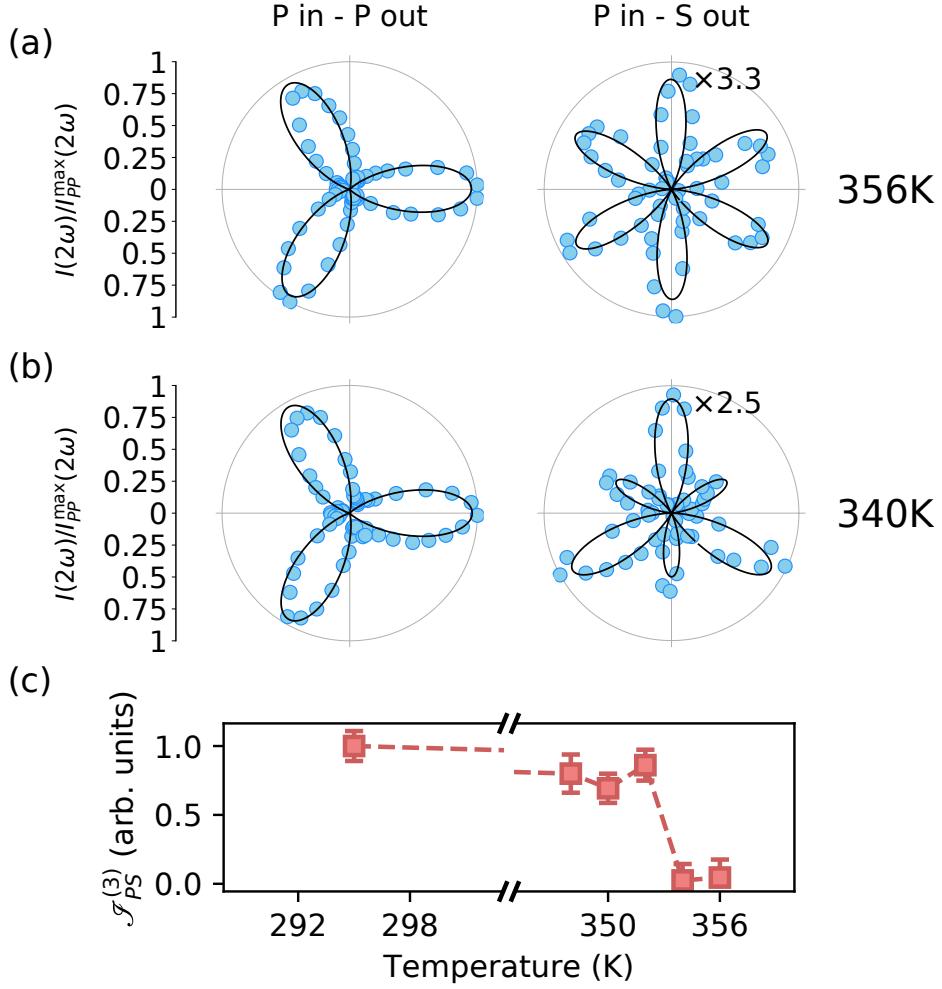


Figure 5.2: (a) (b) Second harmonic intensity from 1T-TaS₂ as a function of ϕ above (Fig. 5.2(a)) and below (Fig. 5.2(b)) $T_{IC-NC} = 353$ K. For clarity, only two polarization channels are shown; the others are reproduced in the supplement (see section 5.7). Solid lines in Fig. 5.2(a) and Fig. 5.2(b) are best fits to the data using the surface point groups C_{3v} and C_3 , respectively. Data is normalized to the maximum value of the P_{in} - P_{out} signal for each temperature. (c) Temperature dependence of the third Fourier coefficient, $\mathcal{I}_{PS}^{(3)}$, of the intensity (see main text and section 5.7 for details).

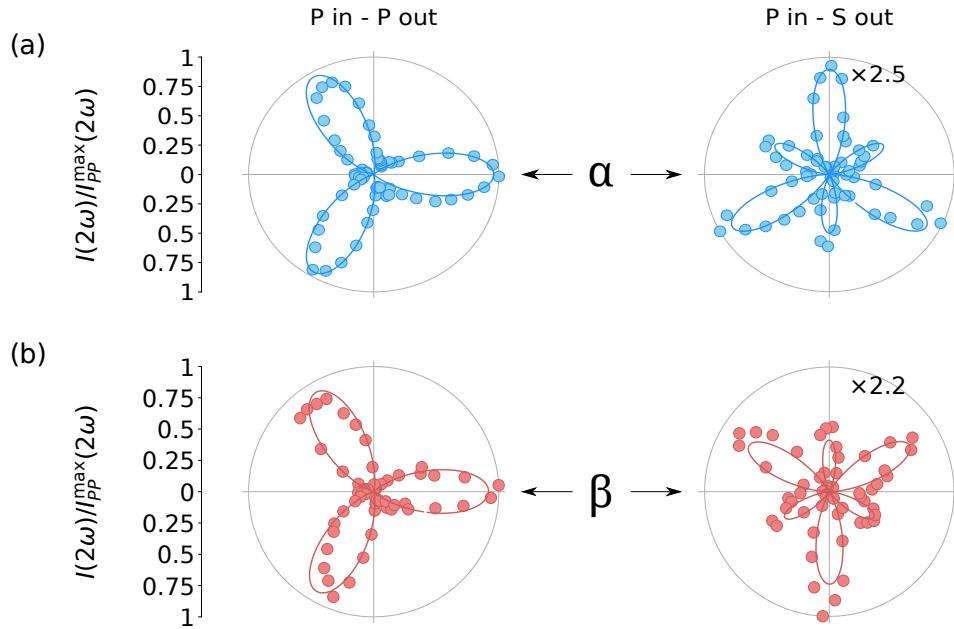


Figure 5.3: Second harmonic intensity as a function of ϕ from mirror-opposite samples of 1T-TaS₂ in the NC phase ($T = 340$ K). The labels α and β refer to the two degenerate mirror-image configurations which are allowed in the NC phase. The solid line in (a) is a fit to the data using the surface point group C_3 . The fit in (b) was generated by performing a mirror operation (see section 5.7) to the numerical susceptibility tensor obtained from 5.3(a). Data is normalized to the maximum value in the P_{in}-P_{out} polarization channel for each sample.

$T_{\text{IC-NC}}$, consistent with the first-order nature of the phase transition. Taken together, the above considerations confirm that $\mathcal{I}_{PS}^{(3)}$ is a binary indicator of broken mirror symmetry in 1T-TaS₂.

Having established that RA-SHG is sensitive to the breaking of vertical mirror plane symmetry in 1T-TaS₂, we now seek to demonstrate that it can differentiate between CDW configurations of opposite planar chirality in the NC phase. To do so, we generate two samples with opposite planar chirality by cleaving a single sample of 1T-TaS₂. We then perform RA-SHG on both sides of the same cleave. Referring to Figs. 5.1(c) and 5.1(d), cleaving the sample is equivalent to performing a 180° rotation about the x -axis, which in a single layer is equivalent to a mirror reflection about M_{xz} .

Fig. 5.3 shows the results of RA-SHG measurements in the $P_{\text{in}}-P_{\text{out}}$ and $P_{\text{in}}-S_{\text{out}}$ polarization channels as functions of ϕ , where the two mirror images are labeled α and β . As shown in the figure, whether the CDW configuration was α or β is indicated in RA-SHG by the orientation (up or down) of the pattern in the $P_{\text{in}}-S_{\text{out}}$ channel, which is determined by the sign of A_0 in Eq. 5.1 (see section 5.7). This feature constitutes an experimental observable capable of identifying the sense associated with broken mirror symmetry in 1T-TaS₂.

To validate the analysis contained above, we first fit the data for the α structure using the surface point group C_3 to generate a tensor χ_{ijk}^{α} with numerical coefficients. The fit is shown in Fig. 5.3(a). Then, we transform χ_{ijk}^{α} by a mirror reflection about M_{xz} to generate χ_{ijk}^{β} (see section 5.7); with this transformation, we find that the rotational anisotropy simulated using χ_{ijk}^{β} collapses onto the measured signal, as shown in Fig. 5.3(b).

While the data contained in this work is specific to 1T-TaS₂, the analysis is applicable to a variety of different phase transitions involving broken mirror symmetry. By understanding which Fourier coefficients of the SHG intensity adopt nonzero values in the low-symmetry phase, one can show that almost every structural phase transition involving broken mirror symmetry implies a measurable change in the symmetry of the SHG pattern (i.e. beyond a simple change in overall intensity). We have performed a symmetry analysis of all possible phase transitions involving spontaneously broken mirror symmetry and in each case identified the relevant experimental indicator(s). The results of this analysis can be found in the supplement (see section 5.7).

The final observation of this work concerns the contribution from the bulk of the sample to the measured RA-SHG signal. As mentioned above, we find that in order to fit the data in the S_{in}-S_{out} polarization channel correctly, we need to introduce an additional bulk quadrupole contribution to the SHG signal. This contribution, which is described by the effective polarization $\nabla_j Q_{ij} = 2i\chi_{ijkl}^Q k_j E_k E_l$, is the next-lowest order contribution to SHG and is allowed in the presence of inversion symmetry [32, 57]. Importantly, the quadrupole contribution is generated by the entire illumination volume and is therefore insensitive to the surface symmetry. Quadrupole SHG can be identified by examining the θ dependence of the SHG intensity in the S_{in}-S_{out} channel. For purely electric dipole SHG, the symmetry in this channel does not depend on the incident angle. The θ dependence depicted in Figs. 5.4(a) and 5.4(b) therefore establishes the presence of a quadrupole contribution in our signal.

According to diffraction measurements [22], the correct surface and bulk point groups in the NC phase are C_3 and S_6 , respectively. Fig. 5.4(a) shows our results in this phase, which are consistent with this assignment. To understand the three-fold symmetry in Fig. 5.4(a), we note that the ϕ dependence of $I_{SS}(2\omega)$ in this symmetry assignment is given by (see section 5.7)

$$I_{SS}(2\omega) = (B_0 + B_1 \cos(3\phi) + B_2 \sin(3\phi))^2, \quad (5.2)$$

where B_1 and B_2 are functions of the susceptibility elements χ_{ijk}^S and χ_{ijkl}^Q , but B_0 depends on χ_{ijkl}^Q only (and is zero when the quadrupole contribution is ignored). B_0 is then a probe of the bulk structure only and is not affected by the surface symmetry. When mirror symmetry is broken, all three coefficients are allowed and the function is three-fold symmetric as in Fig. 5.4(a).

However, symmetry considerations (see section 5.7) show that B_0 is zero in the presence of mirror symmetry. If bulk mirror symmetry were fully restored in the IC phase, we would therefore expect the signal to be six-fold symmetric. Fig. 5.4(c) shows that the RA-SHG instead remains three-fold symmetric in this phase, suggesting that the bulk breaks mirror symmetry. On the other hand, the highest-symmetry surface point group consistent with Figs. 5.2(a) and 5.4(c) is C_{3v} , which retains mirror symmetry. With RA-SHG, it is not possible to deduce the full crystal structure, but we speculate that this discrepancy between surface

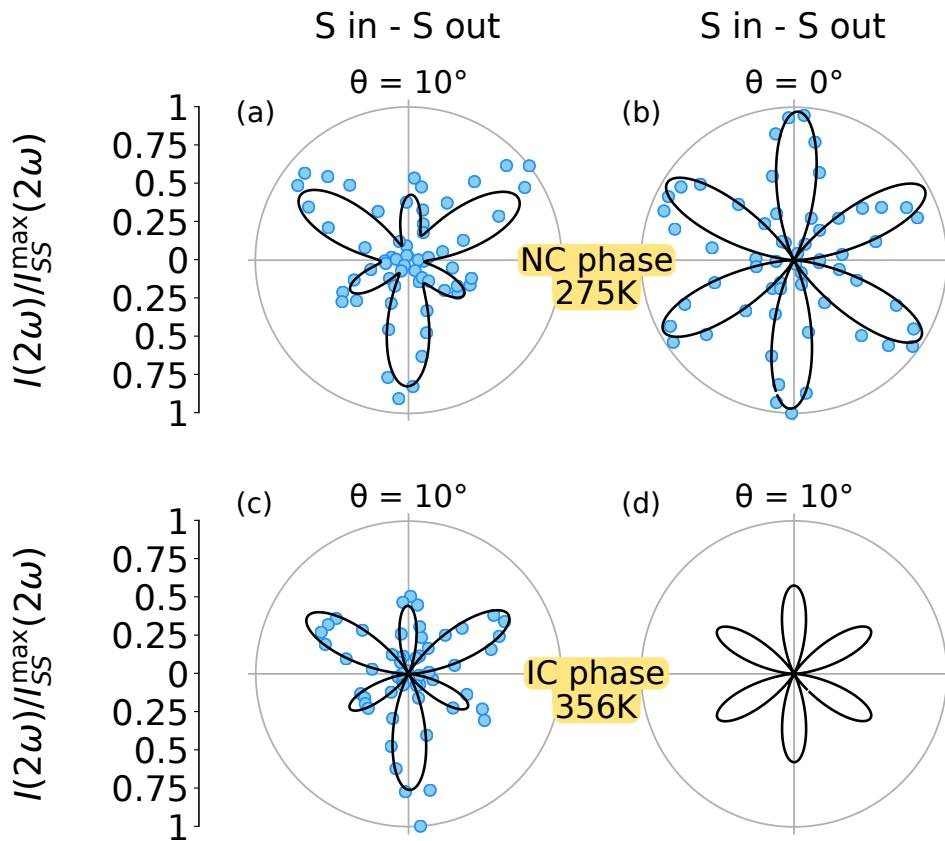


Figure 5.4: Second harmonic intensity as a function of ϕ in the S_{in} - S_{out} polarization channel. Temperatures, phases and incident angles (θ) are indicated on the figure. Also shown are fitting curves using the point group assignments (a) C_3 surface and S_6 bulk, (b) C_3 surface and S_6 bulk, (c) C_{3v} surface and S_6 bulk. (d) Best fit to data in 5.4(c) using C_{3v} surface and D_{3d} bulk. Data in all plots was normalized to one for clarity. Other polarization channels are depicted in the supplement (see section 5.7).

and bulk symmetries might be attributable to the particular stacking arrangement associated with the CDW above $T_{\text{IC-NC}}$ (see section 5.7). This would explain why the surface component, which is measuring the local structure at the surface of the sample [8], is consistent with the existence of mirror symmetry, whereas the bulk component, which measures the global structure of many layers, is not.

5.5 Conclusion

In summary, we have demonstrated here that RA-SHG can be used to identify broken mirror symmetry in crystalline materials. In addition, we have found that RA-SHG can differentiate between structural configurations related by mirror reflection. By considering the different symmetry constraints on the $S_{\text{in}}-S_{\text{out}}$ channel, we have also shown that RA-SHG is sensitive to broken mirror symmetry in the bulk of 1T-TaS₂, and have found evidence that the IC phase of this material breaks mirror symmetry in the bulk. Importantly, our analysis is generalizable beyond the specific case of 1T-TaS₂, and therefore opens up the possibility for RA-SHG to detect mirror symmetry-broken phases and their domain structures in other candidate materials.

5.6 Acknowledgments

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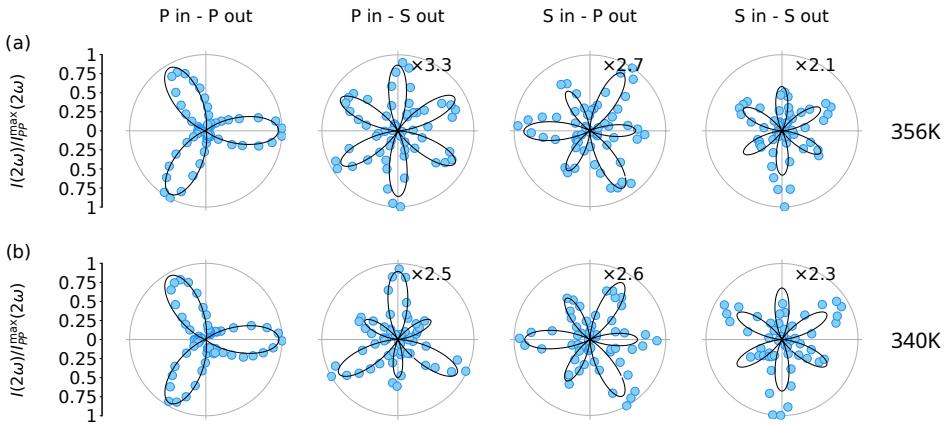


Figure 5.5: RA-SHG intensity as a function of ϕ above (a) and below (b) $T_{IC-NC} = 353K$. Solid lines are best fits to the data using electric dipole SHG in the surface point groups C_{3v} and C_3 , respectively. Data is normalized to the maximum value of the $P_{in}-P_{out}$ signal for each temperature.

5.7 Supplemental material

5.7.1 Probing broken mirror symmetry with RA-SHG

Complete RA-SHG data

In the first section of the main text, we discuss how RA-SHG is sensitive to the breaking of mirror symmetry in 1T-TaS₂. In Fig. 5.2 and Fig. 5.2(b) of the main text, we display RA-SHG data in two polarization channels: $P_{in}-P_{out}$ and $P_{in}-S_{out}$. For completeness, the other polarization channels are reproduced in Fig. 5.5. Importantly, the fits in the figure only include a surface electric dipole contribution (see main text). The inability to fit the $S_{in}-S_{out}$ polarization channel with a pure electric dipole contribution suggested to us that a second contribution was necessary in the form of a bulk electric quadrupole term. This is discussed in the main text as well as in section 5.7.5.

$\mathcal{I}_{PS}^{(3)}$ as an indicator of broken mirror symmetry

In the main text, we used the relation given by Eq. 5.1 to show that the breaking of sixfold symmetry in the P_{in}-S_{out} channel is consistent with the lowering of the surface point group from C_{3v} to C₃ during the IC to NC phase transition. In this section, we show how Eq. 5.1 is derived.

Given any crystallographic point group, it is always possible to compute the form of the susceptibility tensor χ_{ijk}^S . In C₃, the susceptibility tensor is given by [10]

$$\chi_{ijk}^S = \begin{pmatrix} a & -b & c \\ -b & -a & -d \\ c & -d & 0 \\ \hline -b & -a & d \\ -a & b & c \\ d & c & 0 \\ \hline e & 0 & 0 \\ 0 & e & 0 \\ 0 & 0 & f \end{pmatrix}_{ijk} \quad (5.3)$$

for some a, b, c, d, e , and f which are dependent on the material. Here, the threefold axis is taken to be along the z direction. In the point group C_{3v}, the susceptibility tensor is constrained by symmetry so as to take a form which is the same as Eq. 5.3, but with $b = d = 0$, i.e.

$$\chi_{ijk}^S = \begin{pmatrix} a & 0 & c \\ 0 & -a & 0 \\ c & 0 & 0 \\ \hline 0 & -a & 0 \\ -a & 0 & c \\ 0 & c & 0 \\ \hline e & 0 & 0 \\ 0 & e & 0 \\ 0 & 0 & f \end{pmatrix}_{ijk} . \quad (5.4)$$

Here, the mirror planes are taken to be the xz -plane and those related to it by rotation about the z -axis through $\pm 120^\circ$.

To compute the RA-SHG intensity in the P_{in}-S_{out} channel, we consider a frame of reference in which the plane of incidence is held fixed and the

sample is rotated about the optical axis. This reference frame is equivalent to that of the experimental setup (where the sample is fixed and the plane of incidence rotates), but it is easier to visualize and formulate mathematically. In this frame, the incoming P -polarized light at frequency ω is parallel to the vector $E_i(\omega) = (-\cos \theta, 0, \sin \theta)_i^T$, and the outgoing S -polarized light which we wish to compute is parallel to the y -axis. The RA-SHG intensity in this channel is therefore given by

$$I_{PS}^{2\omega}(\phi) \propto |P_y^{2\omega}(\phi)|^2 \propto |\bar{\chi}_{ijk}^S(-\phi)E_j(\omega)E_k(\omega)|^2, \quad (5.5)$$

where $\bar{\chi}_{ijk}^S(\phi)$ is the susceptibility tensor corresponding to the sample when it has been rotated by an angle ϕ . The relative sign in the argument of $\bar{\chi}_{ijk}^S$ is due to the different reference frame used here compared to Fig. 5.1(b), where ϕ is defined.

With the rotation matrix

$$R(\phi)_{ij} = \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}_{ij}, \quad (5.6)$$

$\bar{\chi}_{ijk}^S(\phi)$ is given by

$$\bar{\chi}_{ijk}^S(\phi) = R(\phi)_{il}R(\phi)_{jm}R(\phi)_{kn}\chi_{lmn}^S. \quad (5.7)$$

Substituting Eq. 5.7 into Eq. 5.5, we then have

$$I_{PS}^{2\omega}(\phi) \propto |R(-\phi)_{yl}R(-\phi)_{jm}R(-\phi)_{kn}\chi_{lmn}^S E_j(\omega)E_k(\omega)|^2. \quad (5.8)$$

With Eq. 5.3 as χ_{ijk}^S , we arrive at Eq. 5.1 in the main text,

$$I_{PS}(2\omega) \propto (A_0 + A_1 \cos(3\phi) + A_2 \sin(3\phi))^2, \quad (5.9)$$

where

$$A_0 = 2d \sin(\theta) \cos(\theta), \quad (5.10)$$

$$A_1 = -b \cos^2(\theta), \quad (5.11)$$

and

$$A_2 = a \cos^2(\theta). \quad (5.12)$$

Since $b = d = 0$ in C_{3v} , these equations show that A_0 and A_1 are zero in the presence of mirror symmetry, as cited in the main text. Furthermore, in C_{3v} , Eq. 5.9 reduces to

$$I_{\text{PS}}(2\omega) \propto A_2^2 \sin^2(3\phi), \quad (5.13)$$

which possesses sixfold rotational symmetry.

In the main text, we also remark that the breaking of sixfold rotational symmetry across the IC to NC phase transition can be quantified experimentally by performing a spectral (sine) decomposition of the measured intensity ($I_{\text{PS}}^{2\omega}(\phi)$) and extracting the third Fourier coefficient, which we called $\mathcal{I}_{\text{PS}}^{(3)}$. Here, we define $\mathcal{I}_{\text{PS}}^{(3)}$ explicitly and show that it is present in 1T-TaS₂ only when mirror symmetry is broken.

The spectral decomposition for any given polarization channel (Γ_{in} - Γ_{out}) is defined formally by writing

$$I_{\Gamma_{\text{in}}\Gamma_{\text{out}}}^{2\omega}(\phi) = \sum_{n=0}^{\infty} \mathcal{I}_{\Gamma_{\text{in}}\Gamma_{\text{out}}}^{(n)} \sin \left[n\phi + \psi_{\Gamma_{\text{in}}\Gamma_{\text{out}}}^{(n)} \right]. \quad (5.14)$$

This equation defines $\mathcal{I}_{\Gamma_{\text{in}}\Gamma_{\text{out}}}^{(n)}$ and $\psi_{\Gamma_{\text{in}}\Gamma_{\text{out}}}^{(n)}$ as the amplitude and phase of the n -fold Fourier component of the corresponding SHG intensity.

Using Eqs. 5.3, 5.8 and 5.14, we can then compute $\mathcal{I}_{\text{PS}}^{(3)}$ and $\psi_{\text{PS}}^{(3)}$ in the low temperature phase as

$$\mathcal{I}_{\text{PS}}^{(3)}(\chi_{ijk}^S) \propto 4\sqrt{C_1^2 + C_2^2} \quad (5.15)$$

and

$$\psi_{\text{PS}}^{(3)}(\chi_{ijk}^S) = \text{atan2}(C_1, C_2), \quad (5.16)$$

where

$$C_1 = -b \cdot d \sin \theta \cos^3 \theta, \quad (5.17)$$

$$C_2 = a \cdot d \sin \theta \cos^3 \theta, \quad (5.18)$$

θ is the angle of incidence, and

$$\text{atan2}(y, x) \equiv \begin{cases} \arctan\left(\frac{y}{x}\right) & x > 0 \\ \arctan\left(\frac{y}{x}\right) + \pi & y > 0, x < 0 \\ \arctan\left(\frac{y}{x}\right) - \pi & y < 0, x < 0 \\ +\frac{\pi}{2} & y > 0, x = 0 \\ -\frac{\pi}{2} & y < 0, x = 0 \\ \text{undefined} & x = y = 0 \end{cases}. \quad (5.19)$$

By comparing Eqs. 5.3 and 5.4, we find that

$$C_1 = C_2 = 0 \quad (5.20)$$

in the high temperature phase, so that $\mathcal{I}_{PS}^{(3)}(\chi_{ijk}^S) = 0$.

Note that Eq. 5.15 highlights an important aspect of our experiment, which is that $\mathcal{I}_{PS}^{(3)}$ requires a nonzero angle of incidence to be observed. This can be understood by noting that $\mathcal{I}_{PS}^{(3)}$ is nonzero only when the tensor element χ_{yxz}^S is nonzero. However, for such a term to be observable in the experiment, there needs to be an out-of-plane component to the incoming electric fields, which in turn requires a nonzero angle of incidence. Moreover, in a system with three-fold symmetry like 1T-TaS₂, the aforementioned tensor element can only be nonzero in a system where mirror symmetry is absent. To see that this is true, consider the term $P_y(2\omega) = \chi_{yxz}^S E_x(\omega) E_z(\omega)$. Under an $x \rightarrow -x$ mirror operation, we require that $P_y \rightarrow P_y$, $E_x \rightarrow -E_x$, $E_z \rightarrow E_z$, and $\chi_{yxz}^S \rightarrow \tilde{\chi}_{yxz}^S$. However, if this operation is a symmetry of the crystal then we have $\tilde{\chi}_{yxz}^S = \chi_{yxz}^S$, so that $P_y = -P_y$. This implies that $\chi_{yxz}^S = 0$. Therefore both a nonzero angle of incidence and broken mirror symmetry are required for a nonzero $\mathcal{I}_{PS}^{(3)}$ in the geometry of our experiment.

5.7.2 Physical importance of the $P_{\text{in}}\text{-}S_{\text{out}}$ channel

In this section we explain physically why the $P_{\text{in}}\text{-}S_{\text{out}}$ polarization channel is the most sensitive to mirror symmetry breaking in 1T-TaS₂. Consider the experimental geometry depicted in Fig. 5.6(a). A P -polarized electric field E_{in} is incident on a sample with vertical mirror symmetry about the xz plane (indicated by the sides A and B of the sample being the same color). The geometry is such that the plane of incidence makes an angle ϕ with the reflection plane. Let $\mathbf{P}_\perp(\phi)$ be the S -polarized component of the polarization resulting from second harmonic generation by the interaction of the sample with E_{in} .

Now consider applying the mirror operation both to E_{in} and to the sample (Fig. 5.6(b)). Then the resulting S -polarized component of the polarization (in the frame of the plane of incidence) will be $-\mathbf{P}_\perp(\phi)$. However, since the sides A and B in Fig. 5.6(b) are the same, by symmetry the problem is equivalent to Fig. 5.6(a) but with ϕ replaced by $-\phi$. Thus $\mathbf{P}_\perp(-\phi) = -\mathbf{P}_\perp(\phi)$, implying that $\mathbf{P}_\perp(0) = \mathbf{P}_\perp(\pi) = 0$. This along with

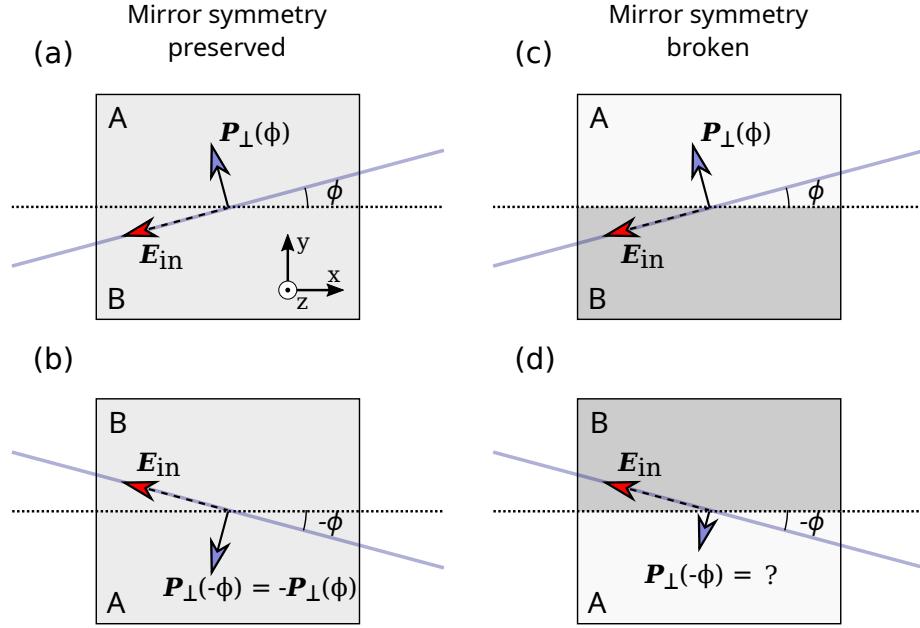


Figure 5.6: (a) Geometry referenced in showing that the $P_{\text{in}}\text{-}S_{\text{out}}$ geometry is sensitive to the breaking of vertical mirror symmetry. E_{in} is the input electric field and \mathbf{P}_{\perp} is the S -polarized component of the polarization. The arrow identifying the direction of E_{in} is dashed to indicate that there is a component in the z -direction (out of the page). The solid blue and dotted black lines represent the plane of incidence and the mirror symmetry plane, respectively, which are in the z -direction and make an angle ϕ with each other. The two halves (A and B) of the sample are the same color to indicate that mirror symmetry is present in this sample. (b) Mirror image of 5.6(a), showing that \mathbf{P}_{\perp} flips sign (when measured in the frame of the plane of incidence) under mirror reflection. (c) Same geometry as 5.6(a) with broken mirror symmetry, represented by the difference in color between sides A and B. (d) Mirror image of 5.6(c).

threefold rotational symmetry is sufficient to prove that the RA-SHG pattern from IC-phase 1T-TaS₂ in the P_{in}-S_{out} polarization channel is purely sixfold-symmetric. However, in the case where mirror symmetry is broken (Figs. 5.6(c) and 5.6(d)) the above argument no longer holds and the constraint $\mathbf{P}_\perp(-\phi) = -\mathbf{P}_\perp(\phi)$ is relaxed. Therefore in 1T-TaS₂, $\mathcal{I}_{PS}^{(3)}$ is allowed in the NC phase but not in the IC phase.

In contrast to the *S*-polarized output ($\mathbf{P}_\perp(\phi)$), the *P*-polarized output ($\mathbf{P}_\parallel(\phi)$) does not change sign (as defined in the frame of the plane of incidence) under mirror reflection. Therefore the constraint for *P*-polarized output is that $\mathbf{P}_\parallel(\phi) = \mathbf{P}_\parallel(-\phi)$. Importantly, this constraint does not forbid Fourier components like $\mathcal{I}_{PP}^{(3)}$ and $\mathcal{I}_{SP}^{(3)}$, even when mirror symmetry is present.

Finally, while the S_{in}-S_{out} channel is subject to the constraint $\mathbf{P}_\perp(-\phi) = -\mathbf{P}_\perp(\phi)$, it can also be shown (see section 5.7.5) that in the electric dipole regime, S_{in}-S_{out} is twofold-symmetric regardless of the crystallographic point group. Therefore the P_{in}-S_{out} polarization channel is especially sensitive to the breaking of vertical mirror plane symmetry in the geometry depicted in Fig. 5.6.

5.7.3 Generalization to other mirror symmetry-breaking transitions

While the argument above is effective in the case of a C_{3v} to C₃ transition (as in 1T-TaS₂), the presence or absence of other symmetries in different point groups may call for symmetry arguments which differ from those above. Therefore, to generalize this work we provide in table 5.1 a list of mirror-symmetry-breaking transitions between noncentrosymmetric point groups and identify corresponding terms (like $\mathcal{I}_{PS}^{(3)}$ in 1T-TaS₂) which adopt nonzero values in the low-symmetry phase. This table was generated using the same analysis as in section 5.7.1 for 1T-TaS₂. Note that while RA-SHG is only nonzero in noncentrosymmetric point groups, it can still be used in centrosymmetric materials because crystal surfaces necessarily break inversion symmetry.

In most of the transitions in table 5.1, $\mathcal{I}_{PS}^{(n)}$ can be used as an indicator of broken mirror symmetry for some *n*. However, for others the RA-SHG pattern rotates rather than (or in addition to) changing symmetry, which is indicated by a change in the phase $\psi_{\Gamma_{in}\Gamma_{out}}^{(n)}$ of certain Fourier components.

Initial group	Final group	Indicator(s)
T_d	T	None
T_d	D_{2d}	None
T_d	C_{3v}	None
C_{6v}	C_{3v}	$\mathcal{I}_{PP}^{(3)}, \mathcal{I}_{PP}^{(6)}, \mathcal{I}_{PS}^{(0)}, \mathcal{I}_{PS}^{(6)}, \mathcal{I}_{SP}^{(3)}, \mathcal{I}_{SP}^{(6)}, \mathcal{I}_{SS}^{(0)}, \mathcal{I}_{SS}^{(6)}$
C_{6v}	C_{2v}	$\mathcal{I}_{PP}^{(2)}, \mathcal{I}_{PP}^{(4)}, \mathcal{I}_{PS}^{(0)}, \mathcal{I}_{PS}^{(4)}, \mathcal{I}_{SP}^{(2)}, \mathcal{I}_{SP}^{(4)}$
C_{6v}	C_6	$\mathcal{I}_{PS}^{(0)}$
C_{4v}	C_{2v}	$\mathcal{I}_{PP}^{(2)}, \mathcal{I}_{PP}^{(4)}, \mathcal{I}_{PS}^{(0)}, \mathcal{I}_{PS}^{(4)}, \mathcal{I}_{SP}^{(2)}, \mathcal{I}_{SP}^{(4)}$
C_{4v}	C_4	$\mathcal{I}_{PS}^{(0)}$
D_{3h}	C_{3h}	$\psi_{PP}^{(6)*}, \psi_{PS}^{(6)*}, \psi_{SP}^{(6)*}, \psi_{SS}^{(6)*}$
D_{3h}	C_{2v}	None
D_{3h}	D_3	$\mathcal{I}_{PS}^{(3)}$
C_{3h}	C_3	$\psi_{PP}^{(1)*}, \psi_{PP}^{(2)*}, \psi_{PP}^{(3)*}, \psi_{PP}^{(4)*}, \psi_{PP}^{(5)*}, \psi_{PP}^{(6)*}, \psi_{PS}^{(1)*}, \psi_{PS}^{(2)*}, \psi_{PS}^{(3)*}, \psi_{PS}^{(4)*}, \psi_{PS}^{(5)*}, \psi_{PS}^{(6)*}, \psi_{SP}^{(1)*}, \psi_{SP}^{(2)*}, \psi_{SP}^{(3)*}, \psi_{SP}^{(4)*}, \psi_{SP}^{(5)*}, \psi_{SP}^{(6)*}, \psi_{SS}^{(1)*}, \psi_{SS}^{(2)*}, \psi_{SS}^{(3)*}, \psi_{SS}^{(4)*}, \psi_{SS}^{(5)*}, \psi_{SS}^{(6)*}$
C_{3v}	C_3	$\psi_{PP}^{(3)}, \psi_{PP}^{(6)*}, \mathcal{I}_{PS}^{(3)}, \psi_{PS}^{(6)*}, \psi_{SP}^{(3)}, \psi_{SP}^{(6)*}, \psi_{SS}^{(6)*}$
C_{3v}	C_{1h}	$\mathcal{I}_{PP}^{(1)}, \mathcal{I}_{PP}^{(2)}, \mathcal{I}_{PP}^{(4)}, \mathcal{I}_{PP}^{(5)}, \mathcal{I}_{PS}^{(1)}, \mathcal{I}_{PS}^{(2)}, \mathcal{I}_{PS}^{(3)}, \mathcal{I}_{PS}^{(4)}, \mathcal{I}_{PS}^{(5)}, \mathcal{I}_{SP}^{(1)}, \mathcal{I}_{SP}^{(2)}, \mathcal{I}_{SP}^{(4)}, \mathcal{I}_{SP}^{(5)}, \mathcal{I}_{SS}^{(2)}, \mathcal{I}_{SS}^{(4)}$
D_{2d}	S_4	$\psi_{PP}^{(4)*}, \psi_{PS}^{(4)*}, \psi_{SP}^{(4)*}$
D_{2d}	D_2	$\mathcal{I}_{PS}^{(2)}$
C_{2v}	C_2	$\psi_{PP}^{(2)*}, \psi_{PP}^{(4)*}, \mathcal{I}_{PS}^{(2)}, \psi_{PS}^{(4)*}, \psi_{SP}^{(2)*}, \psi_{SP}^{(4)*}$
C_{2v}	C_{1h}	$\mathcal{I}_{PP}^{(1)}, \mathcal{I}_{PP}^{(3)}, \mathcal{I}_{PP}^{(5)}, \mathcal{I}_{PP}^{(6)}, \mathcal{I}_{PS}^{(1)}, \mathcal{I}_{PS}^{(2)}, \mathcal{I}_{PS}^{(3)}, \mathcal{I}_{PS}^{(5)}, \mathcal{I}_{PS}^{(6)}, \mathcal{I}_{SP}^{(1)}, \mathcal{I}_{SP}^{(3)}, \mathcal{I}_{SP}^{(5)}, \mathcal{I}_{SP}^{(6)}, \mathcal{I}_{SS}^{(0)}, \mathcal{I}_{SS}^{(2)}, \mathcal{I}_{SS}^{(4)}, \mathcal{I}_{SS}^{(6)}$

* Measured from $\pi/2$

Table 5.1: Indicators of broken mirror symmetry in mirror-symmetry-breaking transitions between noncentrosymmetric point groups. Values in the rightmost column (defined in Eq. 5.14) are zero in the initial group and nonzero in the final group. In all cases, the analysis was done in a geometry such that the sample normal is parallel to the broken mirror plane (i.e. the mirror plane is vertical).

Additionally, it should be observed that for a minority of the transitions in table 5.1, RA-SHG is not sensitive to the breaking of mirror symmetry (e.g. in the transition from T_d to T , two point groups for which the susceptibility tensor is equivalent).

5.7.4 Probing the sense of planar chirality with RA-SHG

Complete RA-SHG data

As in section 5.7.1, for completeness we reproduce in Fig. 5.7 the RA-SHG data in the α and β CDW configurations, including the two polarization channels which were truncated from Fig. 5.3 in the main text. The poor fit in the $S_{\text{in}}\text{-}S_{\text{out}}$ polarization channel again indicated to us that there was an additional bulk quadrupole contribution to the signal.

Electron diffraction confirming the sample is single domain

To confirm that 1T-TaS₂ is single-domain in the NC phase, we performed electron diffraction on a sample from the same batch as the one used for the RA-SHG measurements. The absence of CDW sister peaks in Fig. 5.8 demonstrates that the sample is single-domain, in agreement with previous reports [9, 23, 67, 71]. The thickness of the sample measured by electron diffraction was ~ 80 nm, which is approximately equal to the penetration depth of 1T-TaS₂ at 800 nm [38]. We note that recent studies have demonstrated that it is possible to inject mirror domains into an otherwise uniform sample of 1T-TaS₂ using intense pulses of light [71]. To control for this effect, we used an incident fluence of 1.4 mJ/cm² which is well below the threshold fluence 5 mJ/cm² reported in Zong et al. [71].

Fitting RA-SHG data in the α and β configurations

To fit the data in Fig. 5.3 of the main text, we performed the following procedure. First, we used the six independent elements in the C_3 susceptibility tensor given by Eq. 5.3 as fitting parameters to fit the data on the α sample (Fig. 5.7(a)) to

$$|P_i(\phi)|^2 \propto |R(-\phi)_{il}R(-\phi)_{jm}R(-\phi)_{kn}\chi_{lmn}^S E_j(\omega)E_k(\omega)|^2. \quad (5.21)$$

The fit was constrained in such a way as to forbid large changes in the susceptibility elements that exist in both phases (i.e. a , c , e , and f). This

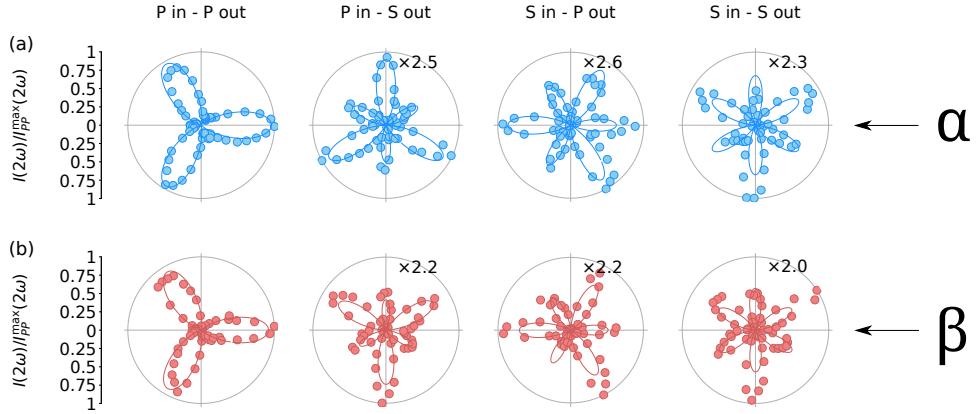


Figure 5.7: Second harmonic intensity as a function of ϕ from two samples of 1T-TaS₂ in the NC phase ($T = 340\text{K}$). The labels α and β refer to the two degenerate mirror-image configurations which can exist in the NC phase. The solid line in (a) is a fit to the data using the surface point group C_3 . The fit in (b) was generated by performing a mirror operation (see section 5.7.4) to the numerical susceptibility tensor obtained from 5.7(a). Data is normalized to the maximum value in the P_{in}-P_{out} polarization channel for each sample.

gave us a set of six numbers $\{\chi_{ijk}^{\alpha}\}$, from which we can form the tensor χ_{ijk}^{α} . The cleaving operation can be represented by the operator $\mathcal{C} = A\Gamma(\gamma)R_x$, where R_x is the operator which rotates the sample 180° about the x -axis,

$$R_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad (5.22)$$

$\Gamma(\gamma)$ is the operator which rotates the sample about the z -axis by an arbitrary angle γ ,

$$\Gamma(\gamma) = \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (5.23)$$

and A is a positive overall constant which represents minor, day-to-day fluctuations in experimental conditions. If we were able to cleave the sample exactly along the high-symmetry axis, then γ would be 0° and $\Gamma(\gamma)$ would be identity. Also note that the fact that the determinant of \mathcal{C} in the (x, y) subspace is -1 is equivalent to the statement that \mathcal{C} switches the planar chirality of the sample.

To simulate the effect of cleaving the sample, we therefore applied \mathcal{C} to χ_{ijk}^α to form $\chi_{ijk}^\beta(\{\chi_{ijk}^\alpha\}, \gamma, A)$. Formally, this amounts to computing

$$\chi_{ijk}^\beta(\{\chi_{ijk}^\alpha\}, \gamma, A) = \mathcal{C}_{il}(\gamma, A)\mathcal{C}_{jm}(\gamma, A)\mathcal{C}_{kn}(\gamma, A)\chi_{lmn}^\alpha. \quad (5.24)$$

Now, $\chi_{ijk}^\beta(\{\chi_{ijk}^\alpha\}, \gamma, A)$ is a function of only two free parameters (γ and A). We find that with the proper choice of γ and A , the signal computed with χ_{ijk}^β collapses onto the data in Fig. 5.7(b).

By applying R_x to the tensor given in Eq. 5.3, one can see that the effect of cleaving the sample is to flip the sign of b and d . By examining Eqs. 5.9–5.12, and noting that $A_1 \approx 0$ within the resolution of our instrument, we see that this reproduces the change of the orientation of the RA-SHG pattern in the P_{in} - S_{out} channel depicted in Fig. 5.3 of the main text.

5.7.5 Bulk broken mirror symmetry in 1T-TaS₂

Complete RA-SHG data at $T = 295K$

As in section 5.7.4, for completeness we reproduce in Fig. 5.9 the RA-SHG data at $T = 295K$ (NC phase) which is used in Fig. 5.4 to argue that there is a nonzero bulk electric quadrupole component to the measured signal. Furthermore, we reproduce in Fig. 5.10 the RA-SHG data at $T = 356K$ (IC phase) to show that we can fit all four polarization combinations using the surface point group C_{3v} as well as a bulk point group S_6 , which is the highest-symmetry subgroup of the undistorted point group which breaks mirror symmetry (see below). The S_{in} - S_{out} channel of Fig. 5.10 is shown in Fig. 5.4 of the main text.

Symmetry analysis of RA-SHG data

In the last section of the main text, we used the relation given by Eq. 5.2 to argue that the breaking of sixfold symmetry in the S_{in} - S_{out} polarization

channel indicates that bulk mirror symmetry is broken in the IC phase of 1T-TaS₂. Here we derive Eq. 5.2 as we did Eq. 5.1 in section 5.7.1.

As mentioned in the main text, the effective polarization for bulk electric quadrupole SHG is given by [32, 57]

$$\nabla_j Q_{ij} = 2i\chi_{ijkl}^Q k_j E_k E_l, \quad (5.25)$$

so that the total intensity in the S_{in}-S_{out} channel (including surface electric dipole) is given by

$$I_{SS}^{2\omega}(\phi) \propto \left| \left(\bar{\chi}_{yjk}^S(-\phi) + 2i\bar{\chi}_{ypjk}^Q(-\phi)k_p \right) E_j(\omega) E_k(\omega) \right|^2, \quad (5.26)$$

where

$$\bar{\chi}_{ijk}^S(\phi) = R(\phi)_{il} R(\phi)_{jm} R(\phi)_{kn} \chi_{lmn}^S, \quad (5.27)$$

$$\bar{\chi}_{ipjk}^Q(\phi) = R(\phi)_{il} R(\phi)_{pq} R(\phi)_{jm} R(\phi)_{kn} \chi_{lqmn}^Q, \quad (5.28)$$

and $E_i(\omega) = (0, 1, 0)_i^T$.

In the NC phase of 1T-TaS₂, the appropriate assignment for the surface and bulk point groups is given by diffraction measurements [58] to be C₃ and S₆, respectively. Therefore for χ_{ijk}^S we use the tensor defined by Eq. 5.3, and for χ_{ijkl}^Q we use the tensor given in Boyd [10] for the point group S₆ (which for the sake of brevity we do not reproduce here). With these tensors, we then have

$$I_{SS}(2\omega) \propto (B_0 + B_1 \cos(3\phi) + B_2 \sin(3\phi))^2, \quad (5.29)$$

with

$$B_0 = \chi_{xyxx}^Q \sin \theta, \quad (5.30)$$

$$B_1 = \chi_{yyy}^S - \chi_{xzxz}^Q \cos \theta, \quad (5.31)$$

and

$$B_2 = -\chi_{xxx}^S + \chi_{xzzy}^Q \cos \theta. \quad (5.32)$$

Importantly, if bulk mirror symmetry were restored in the IC phase we would have $\chi_{xyxx}^Q = \chi_{xzxz}^Q = 0$, and therefore $B_0 = 0$. This can be checked by inspecting the quadrupole susceptibility tensor for the undistorted bulk point group D_{3d} (which preserves vertical mirror symmetry) defined in Boyd [10].

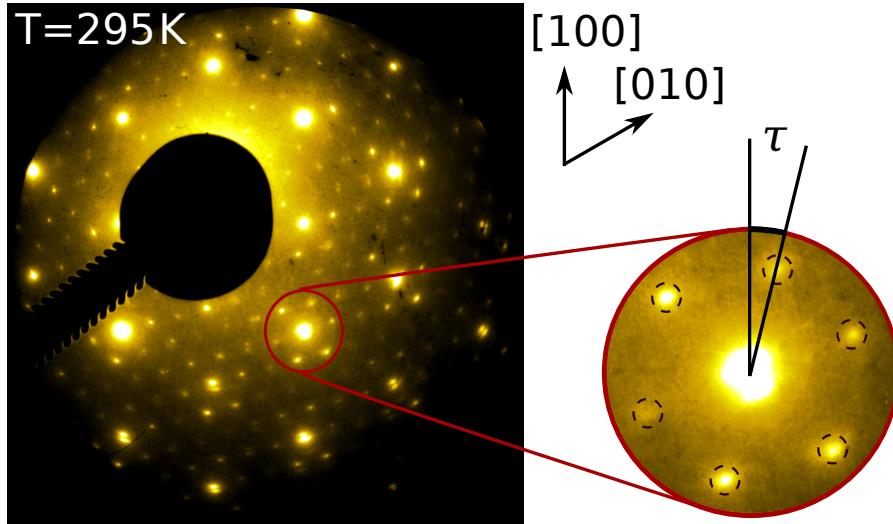


Figure 5.8: Electron diffraction data from a sample of 1T-TaS₂ in the NC phase of the same batch as the one used in RA-SHG measurements. Surrounding each Bragg reflection can be seen six CDW peaks, which are rotated about $\tau = 13^\circ$ from the high-symmetry axes. The sign of the rotation angle τ indicates whether the CDW configuration is α or β . The lack of additional CDW peaks -13° from the high-symmetry axes indicates that the sample is single-domain.

Since $B_0 = 0$ if the pattern possesses sixfold rotational symmetry (as can be seen by taking $\phi \rightarrow \phi + 60^\circ$), we have that the breaking of sixfold rotational symmetry in the RA-SHG pattern (Fig. 5.4(c) of the main text) implies $B \neq 0$. This implies that $\chi_{xyxx}^Q \neq 0$, and therefore mirror symmetry is broken in the bulk.

There are two additional important remarks which can be made about Eq. 5.29. For one, it should be noted that the θ dependence observed in Figs. 5.4(a) and 5.4(b) is consistent with Eq. 5.29, since $B_0 = 0$ for $\theta = 0$. Additionally, we see that in the absence of the quadrupole component (i.e. for purely electric dipole SHG), $B_0 = 0$ and the pattern should have sixfold rotational symmetry. Since the data in Figs. 5.4(a) and 5.4(c) clearly break

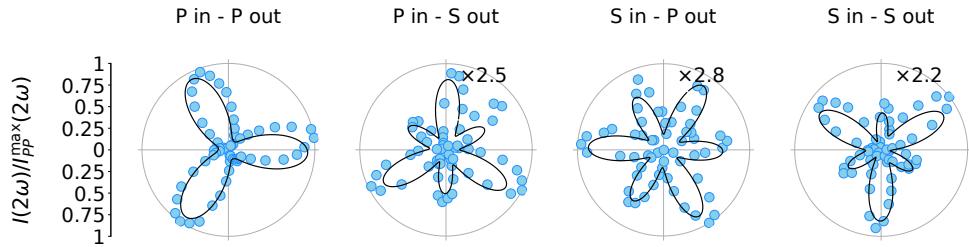


Figure 5.9: RA-SHG intensity as a function of ϕ at $T = 295K$. Solid lines are best fits to the data using a surface electric dipole term in the point group C_3 , as well as a bulk electric quadrupole term in the point group S_6 . Data is normalized to the maximum value of the $P_{\text{in}}-P_{\text{out}}$ signal.

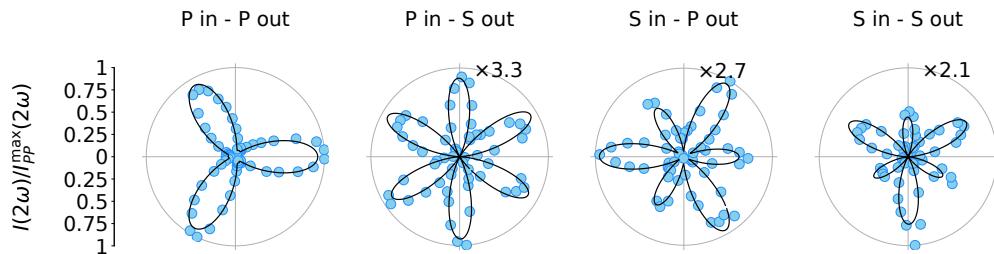


Figure 5.10: RA-SHG intensity as a function of ϕ at $T = 356K$. Solid lines are best fits to the data using a surface electric dipole term in the point group C_{3v} , as well as a bulk electric quadrupole term in the point group S_6 . Data is normalized to the maximum value of the $P_{\text{in}}-P_{\text{out}}$ signal.

this symmetry, this supports our claim that there is an extra contribution to the RA-SHG beyond the surface electric dipole contribution.

A more intuitive way to understand why the threefold spectral component in Fig. 5.4(a) and Fig. 5.4 is not allowed by pure electric dipole SHG is to note that, for purely electric dipole SHG, the rotational anisotropy always has at least twofold symmetry in the $S_{\text{in}}-S_{\text{out}}$ channel. To see that this is true, consider the effect of taking $\phi \rightarrow \phi + \pi$ in an S -polarized input geometry. In the frame where the sample is stationary, this simply changes the sign of the input field. Since the polarization is proportional to the square of the input field ($P_i(2\omega) = \chi_{ijk}E_jE_k$), then it will be symmetric under $\phi \rightarrow \phi + \pi$, as will be its projection out of the plane of incidence

(note, however, that because the component of $\mathbf{P}(2\omega)$ parallel to the direction of propagation is not visible in the experiment, the same cannot be said for the P -polarized output). Therefore, if the measured RA-SHG in the S_{in} - S_{out} channel lacks twofold symmetry, then there is a contribution to the rotational anisotropy which exists beyond the electric dipole.

For the sake of completeness, we also note here two alternative explanations for the breaking of sixfold rotational symmetry depicted in Fig. 5.4(c) which do not appeal to an additional quadrupole contribution. Firstly, it is possible that the surface of the sample was rough or nonuniform in such a way as to modulate the observed SHG intensity as a function of ϕ . In principle, this could result in a nonzero B_0 . To account for this artifact, we measured SHG on 1T-TaS₂ in multiple locations and on multiple different samples, and found that the results in this work were consistent across all measurements. Furthermore, with SHG measurements there is always the possibility of an additional contribution arising from the presence of adsorbates on the sample surface[6]. While such a contribution may be present in our experiment, we note that this too is an unlikely explanation for the nonzero B_0 because of the wavevector dependence of Figs. 5.4(a) and 5.4(b). This is because the dominant contribution from adsorbates is generally of the electric dipole type and therefore should not depend on k in S_{in} - S_{out} .

5.7.6 Methods

RA-SHG data was taken with the 800 nm pulsed output of a regeneratively amplified Ti:Sapphire laser operating at 5 kHz. The beam was scattered by a transmissive phase grating into multiple diffraction orders, and the +1-order component was steered through a polarizer and focused onto the sample with a fluence of 1.4 mJ/cm² and a spot diameter of \sim 150 μ m at a 10° angle with respect to the (001) sample normal. This experimental geometry is similar to that described in Harter et al. [24] and Torchinsky et al. [63]. The reflected light at 400 nm was directed through an analyzer and into a photomultiplier tube, where the intensity was measured with a lock-in amplifier synchronized to the 5 kHz pulsed output of the laser with a 1 ms time constant. We rotated the phase grating at \sim 5 Hz and recorded the signal as a function of time with an oscilloscope triggered on an optical rotary encoder marking 360° rotations. Each polarization combination required averaging 5000 rotations. Using the aforementioned encoder, we

expressed the corresponding time trace in terms of the azimuthal angle ϕ (Fig. 5.1(b)) to obtain the full rotational anisotropy.

The thickness of the samples used in the RA-SHG experiments was $\sim 50 \mu\text{m}$.

Chapter Six

**Light-induced reorientation
transition in the antiferromagnetic
semiconductor CaMn₂Bi₂**

Chapter Seven

Amplitude-mode electromagnon in the XXZ chain CuBr₂

Chapter Eight

Concluding remarks

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