

New Structural and Electronic Degrees of Freedom in Epitaxial Square-Net Materials

Thesis by
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In Partial Fulfillment of the Requirements for the
Degree of
Doctor of Philosophy



CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California

2025
Defended October 16, 2024

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ACKNOWLEDGEMENTS

There have been so many individuals who have contributed significantly to the success of my PhD. First and foremost, my thanks go to my family; my wife Zhonghui, my son Isaac, and my newborn daughter Esme, who served a most important role as my thesis writing partner. Zhonghui has given me unwavering emotional (and financial) support throughout all these years. When times were difficult, she was always there offering advice and encouragement.

I would next like to thank my parents; to my Dad for introducing me to science to my Mom for demonstrating a love for problem solving and a perseverance in the face of uncertainty. Your willingness to move across the country to help babysit our children while we both worked was absolutely essential in my success.

There are a number of scientific collaborators whom I would like to thank. First is my advisor, Joe Falson. Setting up a lab from scratch is an experience fraught with missteps and mistakes, but these make the payoff that much sweeter. You have taught me so much on the technical side, of course, but more importantly, how to approach the art of materials discovery. Your relentless optimism and leadership ability are qualities that I hope to carry with me throughout my career. I could not ask for a better advisor.

I would next like to thank the Falson group at Caltech, in particular, Veronica Show and Reiley Dorrian for helping with film growth and for carrying the mantle of square net antimonides at least a little bit farther. To Dr. Jeongrae Kim for his insights into materials growth and assiduous maintenance of the laser annealing system, Sahil Patel for his knowledge of fabrication, and to Dr. Mizuki Ohno and Sandra Glotzer for stimulating conversations on many materials topics unfamiliar to me.

There were several external collaborations without whom this thesis would not have been possible. Most important were Prof. Nick Kioussis and Dr. Jinwoong Kim (CSUN) with whom we collaborated substantially on questions of theory, as well as Prof. Salva Salmani-Rezaie (OSU) who has given us beautiful TEM data. I would also like to thank Dr. Dan Silevitch for maintaining the shared cryostats and Joe Benson for teaching me the art of machining during my early days as a grad student.

To the many friends I have made at Caltech, especially Aki Park and Duxing Hao from the Yeh group, Stephen Armstrong from the Rosenbaum lab, and Adrian Tan from the Minnich Group, all of you have left a lasting impression on me.

Lastly, I would like to acknowledge the Air Force Office of Scientific Research, the Moore Foundation and the Institute for Quantum Information and Matter, an NSF Physics Frontiers Center, for their generous support of these projects

ABSTRACT

Materials belonging to the "square-net" (SN) family of crystal structures share the structural motif of highly conducting, 2D square-planar sheets sandwiched between complex spacer layers. Materials in this class have attracted attention for their diverse array of electronic properties such as topological, magnetic, charge/spin density wave (CDW/SDW) and superconducting ground states. Familiar examples include the cuprate and pnictide superconductors, the rare-earth tellurides and the Dirac semimetals such as ZrSiS. In this thesis we exploit the abilities of molecular beam epitaxy to synthesize and study ultra-thin films of the SN compounds and uncover several unexpected behaviors.

The first compound we explore is DyTe_2 , a member of the telluride family of SN materials known for their charge density wave ground states. We begin by describing the methods to fabricate epitaxial films using MBE. The high crystalline quality allows for characterization of subtle superlattice modulations with X-ray diffraction. Combinations of this experimental data with theoretical calculations reveal the origin of this superlattice to be an ordering of Te vacancies driven by Fermi-surface nesting.

We then turn to the related compound LaSb_2 . This material is thought to undergo a CDW transition that can be suppressed under pressure and replaced by a superconducting ground state. To our surprise, thin films of LaSb_2 adopt a crystal structure distinct from that of the bulk crystals. We characterize this new structure comprehensively and find that concomitant with this new structure is an enhancement of superconducting T_c relative to the bulk.

Finally, we exploit this enhanced T_c to observe magnetic field-induced superconductivity in ultra-thin LaSb_2 doped with magnetic Ce dopants. This is the result of the unique robustness of the material to application of a parallel magnetic field. The combination of strong spin orbit coupling and reduced dimensionality allows the magnetic field to polarize paramagnetic spins, thereby reducing their deleterious impact on T_c , before the field itself destroys superconductivity. This allows a superconducting ground state to be induced from an otherwise normal metal ground state at $T = 0$.

The results of this thesis highlight the unique degrees of freedom that can be accessed via epitaxial growth of single crystalline films of quantum materials.

PUBLISHED CONTENT AND CONTRIBUTIONS

- [1] A. Llanos et al. “Field induced superconductivity in a magnetically-doped two-dimensional crystal”. In: *in preparation* (2024).
A. Llanos designed experiments, performed low temperature measurements, wrote code to analyze data and wrote the manuscript.
- [2] A. Llanos et al. “Monoclinic LaSb₂ Superconducting Thin Films”. In: *Nano Letters* 24.28 (2024), pp. 8518–8524. doi: 10.1021/acs.nanolett.4c01068.
A. Llanos designed experiments, optimized thin film growth recipes, characterized material, analyzed data and wrote all parts of the manuscript not concerning DFT calculations.
- [3] A. Llanos et al. “Supercell formation in epitaxial rare-earth ditelluride thin films”. In: *Crystal Growth & Design* 24.1 (2024), pp. 115–121. doi: 10.1021/acs.cgd.3c00755.
A. Llanos designed experiments, optimized thin film growth recipes, characterized material, analyzed data and wrote all parts of the manuscript not concerning DFT calculations.

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Chapter 1

INTRODUCTION

Over the latter half of the 20th century, all areas of physics have witnessed a period where rapid experimental discoveries of unexpected phenomena brought about conceptual leaps in our understanding of nature. These theoretical insights have motivated radical proposals for possible new phases of matter and new device functionalities. Already in the modern era have developments in materials synthesis brought about discoveries of long-sought predictions. For example, the quantum anomalous hall effect [18], superconductivity in twisted bilayer graphene [16], solid state quantum computing [35] and more recently, the discoveries of the zero-field fractional quantum anomalous hall effect in MoTe_2 [100] and Rhombohedral graphene [81], were all the results of sophisticated theoretical prediction [143, 114, 9, 8]. However, while searches for these elusive states of matter are well motivated and these discoveries quite beautiful, the development of new materials also offers the opportunity to discover something unexpected. Recent examples of the latter are the reentrant superconductivity at extremely high fields in UTe_2 [106] and the apparent field induced change in pairing symmetry recently observed in CeRh_2As_2 [58]. In order to make these kinds of discoveries, work must be done to develop the methods to synthesize new compounds which will require moving beyond the standard techniques and approaches. In this work we apply the technique of molecular beam epitaxy to grow thin films of quantum materials to draw out new behaviors in a class of crystals known as the square-net materials.

In this thesis we present our explorations into the epitaxial growth and low temperature characterization of two "square-net" (SN) compounds. These compounds form a large family of crystal structures that share the common structural motif of square planar layers sandwiched between more complex "spacer" layers. Depending on the degree of hybridization between the SN layers and the interlayers, the resulting low energy physics can be more 2D in the case of weak coupling or more 3D in the case of strong coupling. This has an impact on the crystal structure, electronic structure and low temperature ground state. In this chapter we introduce how these various permutations come about and a conceptual framework that can be used to determine candidate structures where the tools of thin film epitaxy are likely to yield ground states that differ from those found in bulk crystals of the same material. We introduce aspects of the theory of charge density wave formation and superconductivity relevant to thin film materials and review the relevant literature that motivates our studies. Our approach in this chapter will be general, saving discussions of literature relevant to

specific compounds for their respective chapters. We end with an outline of the remainder of the thesis.

1.1 Introduction to the Square Net Materials

Diversity of the Square Net

Crystal structures containing conducting square planar sheets hold an esteemed place within condensed matter physics for hosting a wide array of novel properties and ground states. Most famously, many of the exotic properties in the cuprate superconductors have been linked to the unique properties of their CuO plane [17]. The striking properties of the cuprates have motivated investigations into compounds hosting similar crystal structures. A few examples of recent discoveries in SN materials are shown in Fig. 1.1. We can roughly group the square-net materials based on their dimensionality. In the case of materials that crystallize in the ThCr_2Si_2 structure [113], the electronic structure is more three-dimensional and there is substantial hybridization between the square net sheets and the surrounding atoms. Examples of these are the iron pnictides [119] (Fig. 1.1A) and the compound CeRh_2As_2 (Fig. 1.1B). The former hosts an array of competing ground states such as spin/charge density wave that compete with superconductivity. In the latter case, the unique local inversion symmetry breaking around the rare-earth site underlies the recent discovery of a field induced transition from even parity to odd parity superconducting state [58].

In the case of more two-dimensional compounds, such as the rare-earth tritellurides [144] (Fig. 1.1C), and the nodal-line semimetal, ZrSiS [61] (Fig. 1.1D), the electronic structure largely resembles that of an isolated square lattice with hopping between p -orbitals on the atomic sites of the square sheet. These compounds have attracted attention for the existence of charge-density wave (CDW) ground states in the case of the former and, in the case of the latter, the possibility of manifesting symmetry-protected topological bandstructures featuring Dirac, Weyl points or nodal lines. Similar to the case of the protection of Dirac nodes by the C_{3v} symmetry in graphene, the degenerate points in the square-net materials are protected by the crystal symmetries of the square-net lattice. In particular, it is the non-symmorphic symmetry associated with the glide planes in the 2D sheet that allows for the preservation of these degeneracies [142].

Of the two groups of materials, the focus on this thesis will be on the latter, more two-dimensional compounds. A generic representation of the crystal structure of these materials is given in 1.2A. There is weak bonding in the c direction leading to a structure consisting of square-planar sheets that are sandwiched between corrugated layers but are electronically

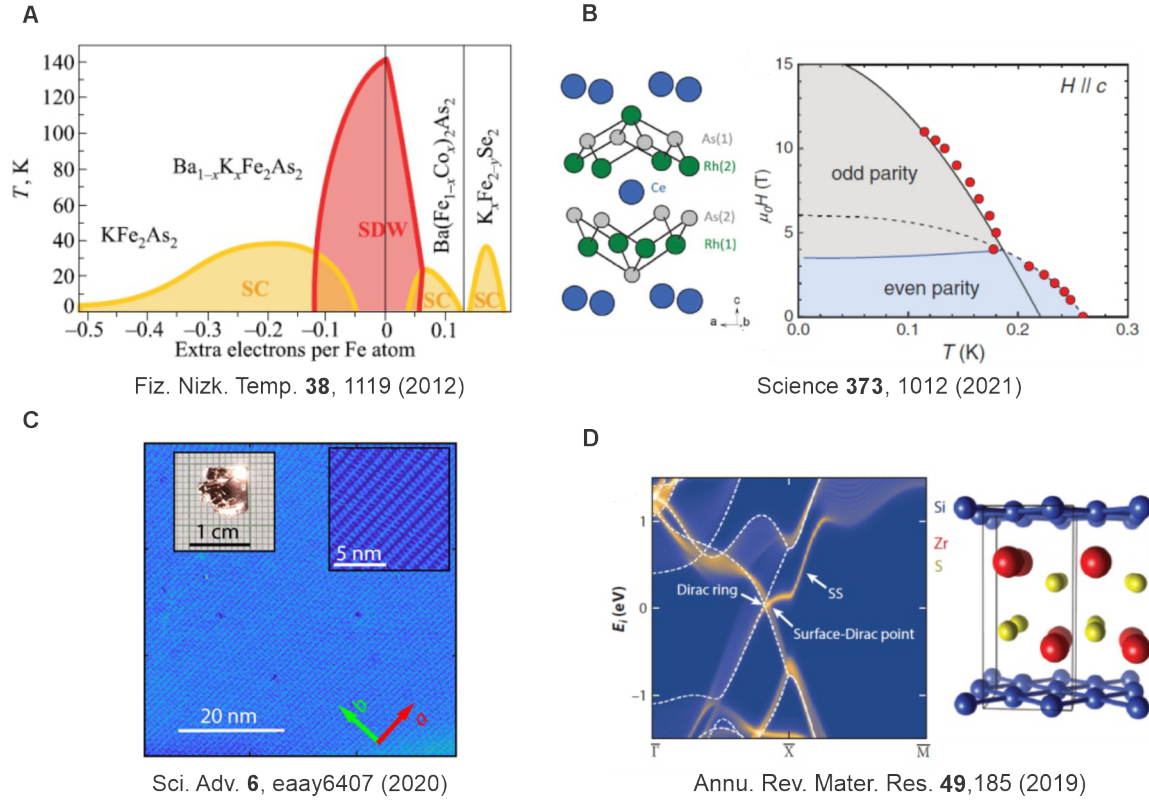


Figure 1.1: **Highlights of the diverse physics found in square net materials.** **A** Iron pnictide phase diagram. [66] **B** Exotic pairing symmetry of $CeRh_2As_2$. **C** CDW in $GdTe_3$. [74], **D** Topological band structure in $ZrSiS$. [61]. All figures reprinted with permission from sources indicated.

decoupled. The diverse array of chemical species that form square net materials can be seen in Fig. 1.2B. The stoichiometry is of the form MXZ where M is a metal, typically a rare-earth or transition metal, while X is a transition metal or p -block element. X is the element that forms the square net. Finally the Z atom is a p -block element and forms the corrugated spacer layer alongside the M atom. The larger electronegativity of the Z atom means it fills the role of accepting electrons from the electropositive M atom and as a result, the bands formed by hopping between the atoms in the corrugated layer are filled and do not contribute substantially to the electrical conduction. A comprehensive review of the various square materials and their topological properties can be found in [61]. Of course this is not always the case and hybridization can occur with the SN leading to more three dimensional behavior.

Whether a given SN compound is more 3D or 2D can be deduced from the difference between the atoms in the SN sheet d_{sq} and the distances between from those same atoms to

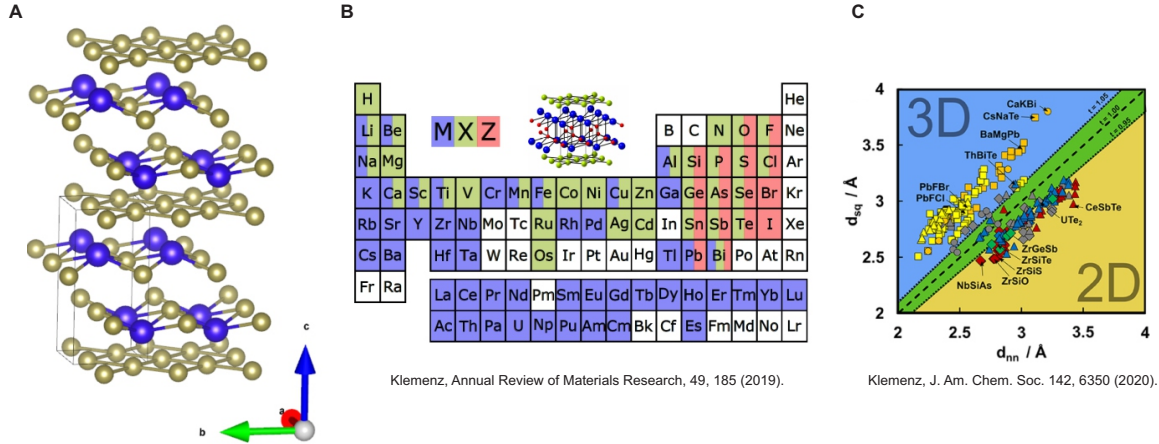


Figure 1.2: **Crystal structure and chemistry of the square nets.** **A** generic 2D square net material **B** Periodic table of elements forming square net crystal structures [61]. **C** Plot of a series of compounds based on their classification into 2D or 3D depending on bond lengths [62]. All figures reprinted with permission from sources indicated.

the nearest atoms in the corrugated layers d_{nn} . This is nicely summarized in Fig. 1.2C from the reviews by Klemenz and Schoop [62, 61]. The axes are labelled by these interatomic distances and the compounds can be classified into 2D when d_{nn} is large relative to d_{sq} and 3D when the reverse is true.

Thin Film Growth of Square Nets

This structural tunability is the primary reason underlying our interest in the growth of epitaxial thin films of square net materials. Epitaxial growth offers a few novel ways to modify material structure and behavior that are not as easily realizable in bulk or exfoliated crystals. They are as follows:

1. The ability to impose strain via substrate lattice mismatch
2. Monolayer thickness control
3. Precision doping
4. Fabrication of artificial structures such as heterostructures or superlattices
5. Engineering of interfacial phenomena such as the 2D electron gas

Of these, the first three will be of primary interest for this thesis. To illustrate by example, when films are grown on substrates of dissimilar lattice constants, the growing crystal is

strained so as to remain coherent with the interface. If the strain is compressive *in-plane*, there will be tensile strain in the out of plane direction. This would tend to decouple the layers, rendering the crystal more 2D in character. The reverse will be true for *tensile* in-plane strain. As materials are made thin, confinement effects can lead to changes in the bandstructure and doping allows for the tuning of the Fermi level thereby changing the size and shape of the Fermi surface. The latter is not unique to epitaxial films, of course, but with the technique used in this thesis, molecular beam epitaxy (MBE), doping can be controlled with extreme precision down to the ppm range or lower.

Despite these good motivations for the growth of square net materials by MBE or other techniques, examples of such thin films are relatively scarce [95, 123]. This is due to the complex crystal structure and subtle growth dynamics. In this thesis we present our investigations into the growth and low temperature transport properties of two square net compounds, DyTe_2 and LaSb_2 . We will exploit the “knobs” of thin film epitaxy to study the effects of strain, uncover new structural arrangements and finally use precision doping and thickness control to bring about a magnetic-field enhanced superconducting phase.

1.2 Outline of Thesis

Chapter 1 The remainder of this chapter is dedicated to outline the theoretical and conceptual framework we used to understand these materials. We begin with a review of the tight-binding theory in a more “chemistry-oriented” style originated by Roald Hoffman [48]. We will find this to be extremely useful in rationalizing the observed structures and reasoning qualitatively about the electronic properties and instabilities such as CDWs and defect lattices. The other major interest of this thesis is superconductivity in ultra thin films so will also describe the extensions of BCS theory in this context that may be less familiar.

Chapter 2 We describe the experimental methods used in this thesis. In particular, we motivate our approach to thin film growth by MBE by discussing the relevant aspects of the technique. Here we present our novel method for obtaining pristine substrate using laser annealing

Chapter 3 We present the results of our studies on the compound DyTe_2 . We grow films of sufficient quality to enable measurement of a superlattice resulting from vacancies in the Te sheet using a lab-based diffractometer. In collaboration with first-principles calculations, we find that the defect arrangement has a wavevector commensurate with a Fermi surface nesting condition and thereby establish the electronic origin of the defect lattice.

Chapter 4 This chapter is dedicated to our studies on the compound LaSb_2 . We find that

the crystal structure adopted by thin films differs from that taken by the bulk. The result of this is an apparent suppression of a purported CDW transition and enhancement of the superconducting T_c relative to the bulk. The combination of crystal structure analysis, electrical transport studies and DFT calculations suggest that this structure is the same as that adopted by bulk LaSb_2 under pressure.

Chapter 5 We analyze in more detail the superconducting properties of LaSb_2 focusing on the thickness dependence of the critical temperature and perpendicular critical field. We find anomalous scaling of these quantities with sample thickness and sheet resistance. Additional fitting suggests that a two-band mechanism may be needed to describe the superconducting properties.

Chapter 6 We combine the findings of the previous chapters and study superconducting LaSb_2 in the 2D limit. By magnetically doping LaSb_2 , we suppress the superconducting T_c . At a critical doping concentration, $T_c \rightarrow 0$ but is subsequently induced by the application of a parallel magnetic field. We find that this can be explained by the polarization of magnetic impurities. This polarization reduces their pairbreaking effect allowing T_c to be enhanced up to 100mK before subsequent destruction by the field itself. This rare example of *field-induced* superconductivity is the result of the reduced dimensionality and strong spin orbit coupling in LaSb_2

1.3 Introduction to the Physics and Chemistry of the Square Net

Tight binding Description of the Electronic Structure

Given the variety of structures and behaviors exhibited by the square net materials, it is desirable to develop a unified framework within which the structures and their variations can be rationalized. To this end, the tight-binding theory has been very successfully applied [127]. Despite its apparent simplicity, we will find that tight-binding arguments allow for understanding of the properties, both structural and electronic, of many intermetallic compounds. We therefore begin with a discussion of this method as it is applied specifically to the compounds of interest. We then go on to describe the "Zintl-Klemm" framework for describing the substructures that form within the unit cell. Our goal is to establish qualitative intuition for discovering new compounds as opposed to mathematical completeness. We will therefore appeal liberally to visual intuition about orbital shape and size. This discussion follows the excellent reviews by Hoffman [99, 48] and the book by Burdett [13].

We begin by reviewing the tight binding theory of bandstructure. The electronic structure of the compounds studied in this thesis are the result of partially filled bands originating from p -block elements on the square net. We thus expect the effect of strong electron

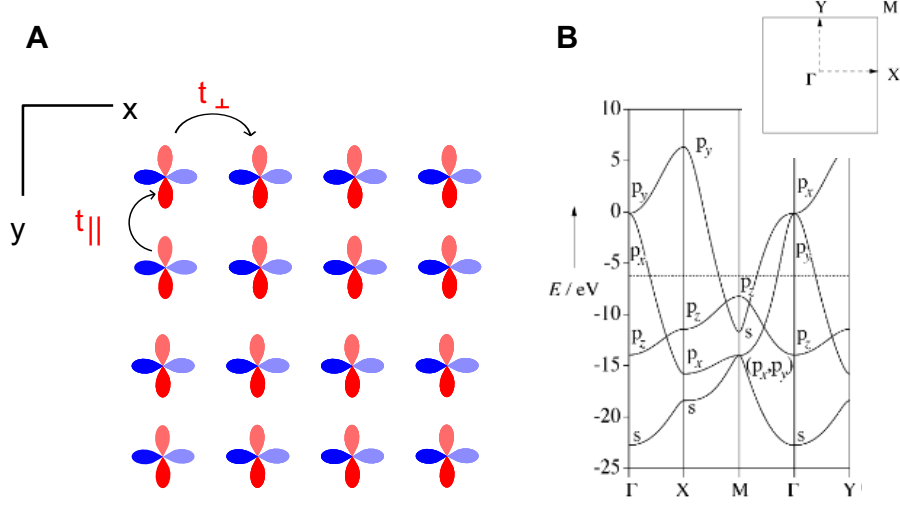


Figure 1.3: **Tight binding of the square lattice.** **A** Square net of p-orbitals. **B** Band structure of the 2D p-orbital lattice. Reprinted with permission from [99].

correlations to be relatively minor. This justifies the intuition for the electronic properties based on the bandstructure. The tight binding theory uses a basis of wavefunctions built from the Bloch formula:

$$|\psi(\vec{k})\rangle = \sum e^{2\pi i \vec{k} \cdot \vec{r}_i} |\phi(\vec{r}_i)\rangle \quad (1.1)$$

Where k is the wavevector which acts as the quantum number for the eigenstate, $\vec{r}_i$ is the position coordinate, $\phi(\vec{r}_i)$ are the atomic orbitals where $\phi(\vec{r}_i) = \phi(\vec{R} - \vec{r}_i)$ where $\vec{R}$ is a lattice vector. For the sake of simplicity we only consider hopping of p_x and p_y orbitals. Taking the matrix elements between the Bloch functions and diagonalizing the Hamiltonian yields the following basic equations for the bands.

$$\begin{aligned} E_k(k_x) &= -2t_{\parallel} \cos[(k_x) a_0] + 2t_{\perp} \cos[(k_y) a_0] \\ E_k(k_y) &= -2t_{\parallel} \cos[(k_y) a_0] + 2t_{\perp} \cos[(k_x) a_0] \end{aligned} \quad (1.2)$$

Where a_0 is the interatomic spacing and k_x and k_z are the components of the wave vector along that direction. The parameters $t_{\perp}$ and $t_{\parallel}$ are the parallel and transverse hopping amplitudes as depicted in Fig. 1.3A. The magnitude of this parameter determines the bandwidth. It is proportional to the orbital overlap in real-space and therefore if we restrict attention to the x -direction, $t_{\perp}$ which results from σ -bonding arrangements is substantially larger than $t_{\parallel}$ from the π interactions. This can be seen clearly when looking at the full bandstructure in Fig. 1.3B. The bands are labelled according to the identity of the atomic orbital from which they are built. Notice how when moving from $\Gamma - X$ (Brillouin zone

is given in the inset), the bandwidth of the p_x band is much larger compared to the p_y or exactly this reason. The former band is built from σ bonds while the latter from π -bonds when considering dispersion in this direction.

The direction in which the band “runs” can also be understood as the result of the difference in σ and π interactions. The orbitals in Fig. 1.3A are colored light and dark to indicate the regions of positive and negative phase of the wavefunction. Thus, σ bonding at Γ results in entirely out of phase (antibonding) combinations of wavefunctions in the Bloch sum. Alternatively at X , the phases of the p_x orbitals at every other site are reversed leading to maximally bonding arrangements. Thus, this band has an energy maximum at Γ and a minimum at X . The reverse is true for the π -bonded p_y orbitals. Hopping at Γ is maximally bonding while hopping at X is antibonding.

Based only on the crystal structure and atomic character, a band structure can be sketched. Furthermore, we can also understand the effects of structural perturbations. We are very much interested in the impact of strain. If one were to strain the system so that atoms were brought closer together, the interactions would get stronger. This would increase the bandwidth and decrease the density of states in the band. As the density of states is extremely important for various instabilities such as CDW, superconducting and magnetic, this picture nicely illustrates how one may expect to tune the electronic structure to enhance or suppress one of these ground states.

Electron Counting as a Way to Understand Square Net Crystal Structure

The Zintl-Klemm rules describe the possible substructures that form within crystals on the basis of electron counting arguments [112]. An illustration, due to Hoffmann, based on Sb atoms is given in Fig. 1.4A. The basic logic is that atoms form arrangements so as to locally satisfy the well-known octet rule from basic chemistry. For example, an Sb atom with a 3^- oxidation state and therefore a full p -shell, is expected to be found as an isolated atom within the unit cell. As the Sb atoms are oxidized, the structures resemble those of molecules formed by molecules with similar electron configurations. For example, a 2^- oxidation state tends toward the formation of Sb_2^{4-} dimers as encountered with the halogen atoms while a 1^- state tends to yield chains of covalent bonded Sb atoms. In contrast to the case of the dimerized pairs, this chain hosts a bandstructure that is metallic due to the partial filling of the p -orbitals. Finally, the case of a valence of 0, encountered in the elemental metal, leads to crystal structure for Sb (and also As) that consists of a network of trigonal-pyramidal sheets, reminiscent of a solid made from NH_3 molecules.

We can also rationalize the existence of higher dimensional structures using these arguments.

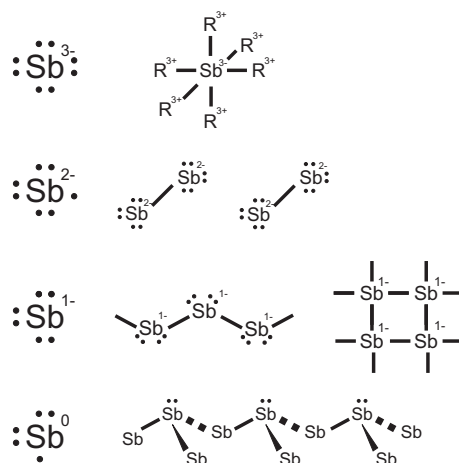


Figure 1.4: **Applications of the Zintl rules for the case of Sb.**

Of primary interest, of course, is the formation of square nets. Imagine taking a set of Sb chains with $6e^-/\text{Sb}$ and bringing them together. The two s electrons are treated as core while the two p_x electrons already occupy the bonding states due to the nearest neighbor interactions in the chain. As the chains are brought together, the interactions between the p_y orbitals between neighboring chains form bonding states which are filled by the two electrons from the Sb on either side. In summary, each Sb atom in a square-net forms 4 bonds with its neighbors using 4 out of 6 electrons. The other 2 remain as lone pairs. Thus, $6e^-/\text{Sb}$ is a stable valence for a square sheet of Sb.

This picture allows for a prediction of the effects of doping. Adding or subtracting electrons from this sheet destabilizes certain arrangements and stabilizes others. It can be extended to explain the structure of other materials hosting p -block elements [99].

Peierls Distortion, Charge-Density Waves and Defect Lattices

A natural question to ask based on the above analysis is: $6e^-/\text{Sb}$ is a stable configuration for the formation of a 2D square-net of atoms, but is also a stable configuration for an isolated chain. Under what circumstances is one configuration preferred over the other? Fortunately, while it is difficult to predict without precise calculations, the Peierls distortion provides a framework to understand whether or not a crystal distorts. Recall the problem of the dimerization of the half filled chain of s -orbitals Fig. 1.5A. Upon dimerization, the inequivalent hopping amplitudes between the “close” and “far” atoms result in a gap opening at the Fermi level, thereby lowering the overall energy if the Fermi level is placed at half-filling. Notice that from the Zintl viewpoint, it is quite natural that a half filled s -chain (i.e. a chain of H atoms) dimerizes into H_2 molecule! In the conventional nesting-driven

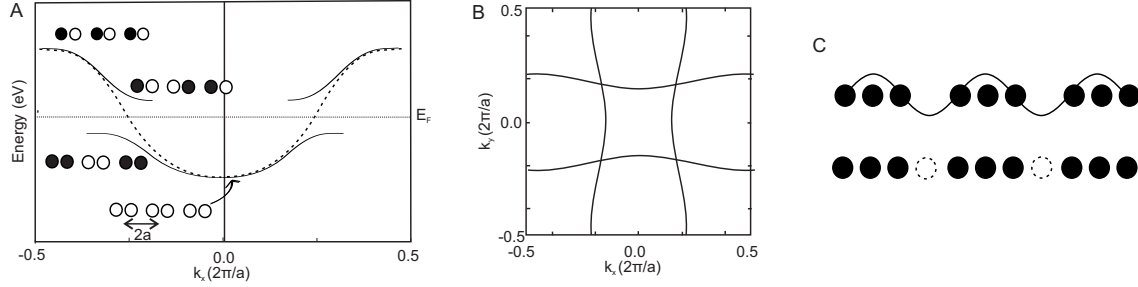


Figure 1.5: **Basics of Peierls distortions.** **A** Peierls distortion of the half-filled chain. Black and white colors represent relative phases of the orbitals on the site. **B** Fermi surface of the square net of p -orbitals. **C** Comparison between trimerized chain (top) and ordered vacancies (bottom).

picture of CDW formation, there is a peak in the Linhard response function $\chi(\vec{q})$ at a wave vector $\vec{q}$ that connects parallel portions of Fermi surface sheets (Fig. 1.5B) which gives rise to a phonon damping and ultimately a static distortion at that wavevector. This results in a gapping of Fermi surface at that wavevector which determines the new supercell size and shape. Full details of this theory can be found in [42].

For a 1D chain, there is perfect nesting of the Fermi surface because it is just two points. For a 2D lattice, the highly dispersing p bands give rise to a Fermi surface that qualitatively resembles that in Fig. 1.5B. The large, parallel portions imply that a distortion with a single wavevector $\vec{q}$ would gap large sections of Fermi surface thereby lowering the overall energy. As a result of this nesting, the square net may distort into chains, ladders or more complicated structural fragments. This type of distortion is typically known as a *commensurate* CDW because the supercell dimensions are integer multiples of the original lattice constants. However, many supercells caused by CDW distortions are *incommensurate* [107, 115] and have wave vectors with no such relation to the basic unit cell. For these ground states, the nesting picture has been called into question and it is thought that a more subtle $\vec{q}$ -dependent electron-phonon coupling is responsible [52].

Thus, a number of structures can be understood to originate as commensurate supercells of an undistorted square net driven by nesting. In fact, this picture can be taken even further to explain the origin of ordered defect superstructures. In Fig. 1.5C we show a side-by-side comparison of a trimerized chain and a chain with every fourth atom removed. Notice how the same modulation periodicity is achieved in both cases. It turns out that for a 1D chain with a fractional site occupation q and a band filling fraction z , a modulation wavevector of $q(1 - z)(2\pi/a)$ forms a gap at the Fermi level. This is known as a site-occupancy-wave (SOW). This example of a 1D chain can be extended to higher dimensional structures. More

details, including a theoretical proof of this fact can be found in [70].

Summary

This section presented a condensed and admittedly nonrigorous account of the origin of the square net and its propensities for distortion. However, we will find that on the basis of this kind of logic, we will be able to understand the structures that we observe when square-net antimonides and tellurides are grown as thin films. More quantitative (yet highly readable) discussions on this subject can be found in [127, 70, 99, 48]. Furthermore, structures following the Zintl rules are only a small fraction of interesting inter metallic compounds. So called “hypervalent” bonding arrangements are also possible which violate the octet rule but can be showed to lead to stable electron configurations [99]. We hope that the results of this thesis motivate an investigation into the properties of these materials and the possibility of modifying their unique structural arrangements when grown as thin films.

1.4 Thin Film Superconductivity

Having become acquainted with the square net materials and their structural analogues, the last topic we would like to discuss are some less familiar aspects of superconductivity in regards to thin materials. In this thesis we explore superconductivity in thin films of the square-net compound LaSb_2 . While we will assume the reader to be familiar with the basics components of Bardeen–Cooper–Schrieffer (BCS) theory, we will first briefly review several important aspects of the theory of superconductivity as it pertains to thin film materials.

The macroscopic behavior of superconductors is largely determined by a set of length scales. Recall the Ginzburg-Landau expression for the free energy density of a superconductor in a magnetic field h close to T_c [126].

$$f(\psi, \mathbf{A}) = \alpha|\psi|^2 + \beta|\psi|^4 + \frac{1}{2m} \left| \left(-i\hbar\nabla - \frac{2e}{c}\mathbf{A} \right) \psi \right|^2 + \frac{1}{8\pi} h^2$$

Where $\psi = |\psi|e^{i\phi}$ is the complex order parameter and is finite below T_c and zero above T_c . The magnitude $|\psi|$ can vary in space with the corresponding length scale given by ξ , the *coherence length*. When placed in a magnetic field, there is finite penetration of the applied field into the superconductor which goes to zero over a length scale given by λ , known as the *London penetration depth*. The ratio $\kappa = \lambda/\xi$ determines the energy associated with the formation of a domain wall between a superconducting region and a normal region. When $\kappa < 1/\sqrt{2}$, the superconductor is said to be of Type 1 character. In this case, the positive domain wall energy suppresses the formation normal domains within the superconducting

matrix and application of a magnetic field results only in finite penetration in a sheath of thickness λ on the outer wall of the material. This occurs until a critical field H_c is reached, at which point the material transitions from superconducting to normal through a first-order phase transition. If $\kappa > 1/\sqrt{2}$, the domain wall energy is negative and application of a finite field $H_{c1} < H_c$ results in a mixed state where a so-called *vortex lattice* of normal regions of diameter $\sim \xi$ thread through the material. Each vortex core carries a single magnetic flux quantum Φ_o . Because each vortex core carries a single flux quantum, increasing the magnetic field results in the formation of increasing number of vortex cores until they overlap at a field H_{c2} at which point the material no longer shows zero-resistance. H_{c2} is related to ξ through the equation $\xi = \sqrt{\frac{\Phi_o}{2\pi H_{c2}}}$.

While λ and ξ are the intrinsic length scales associated with the superconducting condensate, material-dependent parameters are also relevant for understanding the behavior of a superconductor. These *extrinsic* length scales are the sample mean free path l for electron scattering, which determines the normal state resistivity, and the sample thickness t . In the *dirty limit* when $l < \xi$, ξ and λ are modified such that $\xi_{dirty} \sim (\xi_{clean} l)^{1/2}$ and $\lambda_{dirty} \sim \lambda_{clean} \xi / l$. We see that decreased mean free path for electron scattering both reduces the coherence length (increases the critical field) as well as increases the penetration length of the magnetic field into the superconductor (decreases the superfluid density).

Finally, it is the thickness of the material t , which determines the dimensionality of the superconductor. When $t < \xi$, the material is said to be in the 2D limit. Because ξ can range from a few nm to several hundred nm, the 2D limit can be entered, even for relatively "thick" films.

1.5 Pairbreaking in Thin Film Superconductors

As described previously, in bulk superconductors, the transition from superconducting to normal in a magnetic field is generally thought of two ways. For type I materials, the transition occurs when the diamagnetic energy associated with the Meisner effect becomes larger than the condensation energy as given by the gap Δ . In type II materials, a intermediate state emerges above H_{c1} with vortices (radius $r \sim \xi$) carrying a single flux quantum threading through the bulk of the the material. The density of vortices grows with increasing field until the vortex cores overlap rendering the material normal.

In thin film superconductors, the response to the magnetic field is rather different. Because the magnetic field penetrates into a superconductor over a distance given by λ , Cooper pairs in films with thickness $t \ll \lambda$ directly feel the influence of the field on the electrons themselves. This results in "pair breaking" perturbations. This pair breaking occurs because

Cooper pairs form between electrons of equal and opposite momenta and spin according to BCS theory (singlet pairing). Thus, perturbations that are not symmetric under time reversal act differently on each member of the Cooper pair and destabilizes it.

The impact of time-reversal asymmetric perturbations on the condensate was first explored in the context of magnetic doping of superconductors. Abrikosov and Gor'kov (AG) were the first to address the effects of scattering from such impurities [3], in which they found that the exchange scattering on magnetic impurities strongly suppresses the superconducting state in conventional superconductors [89, 88]. This is expressed in the formula:

$$\ln\left(\frac{T_{co}}{T_c}\right) = \psi\left(\frac{1}{2} + \frac{\hbar}{\tau_s \pi T_c}\right) - \psi\left(\frac{1}{2}\right) \quad (1.3)$$

Where $1/\tau_s = \nu_s$ is known as the pair breaking scattering rate, T_{co} is the T_c in the absence of any pair breaking perturbation, and T_c is the critical temperature in the presence of pair-breaking. ψ is the digamma function. For the case of magnetic impurity scattering,

$$\nu_s = 2\pi N_F J_{ex}^2 J(J+1) n_s \quad (1.4)$$

where J is the total impurity angular momentum in the strong spin-orbit coupling limit, N_F the density of states at the chemical potential, J_{ex} is the exchange coupling constant.

In contrast to other pair breaking mechanisms such as applied magnetic fields, proximity to a normal metal [47] or the application of large current [86], magnetic ions are unique as they respond dynamically to an applied magnetic field (H) and temperature (T) of the system, thereby setting up a situation where different pair-breaking mechanisms may suppress or augment one another. All of the investigations in this thesis make use of ultra-thin materials, thus it is worthwhile reviewing the unique ways in which various time-reversal symmetry breaking perturbations disrupt and ultimately destroy superconductivity. Our approach will follow the original arguments of DeGennes, Abrikosov and Maki as described in DeGennes' book [39]. In an attempt to distill the essential physics, it is kept rather heuristic. A full formal treatment of this subject can be found in the review by Maki [102]. This means that several of the models used to fit the data will be stated without proof. However, we hope that the sketches provided in this chapter give physical insight into otherwise rather complicated formulae.

1.6 Theoretical Background: Time Reversal Symmetry Breaking in Superconductors

We will begin the discussion by focusing on the effect of magnetic impurities on T_c . Throughout this discussion, $k_B = 1$. The formal treatment of scattering from magnetic

impurities was first given by Abrikosov and Gorkov using methods of quantum field theory. Given the complexity of the calculation, we instead opt for a more pedestrian approach, which is also due to Abrikosov [2]. This approach involves postulating a finite lifetime τ_s for the Cooper pair and deducing its effect on T_c . It is therefore quite general and makes no assumptions about the nature of the processes leading to τ_s . We begin by recalling the expression which gives the superconducting gap as a function of temperature in the isotropic BCS model

$$1 = \frac{1}{2} g v(\mu) \int_0^{\omega_D} \frac{\tanh[(\xi^2 + \Delta^2)^{1/2}/2T]}{(\xi^2 + \Delta^2)^{1/2}} d\xi \quad (1.5)$$

where ω_D is the Debye frequency, $v(\mu)$ is the density of states at the chemical potential, Δ is the gap, T the temperature and ξ the energy which is being integrated over.

Which in the limit $T \rightarrow T_c$ gives

$$1 = \frac{1}{2} g v(\mu) \ln\left(\frac{2\hbar\omega_D\gamma}{\pi T_c}\right) \quad (1.6)$$

and the well known result, where $\gamma \approx 1.78$

$$T_c = \frac{2\hbar\omega_D\gamma}{\pi} \exp\left(\frac{-2}{g v}\right) \quad (1.7)$$

writing 1.5 using the series representation

$$\tanh(\pi x) = \frac{4x}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)^2 + x^2} \quad (1.8)$$

gives

$$1 = 2g v(\mu) T \sum_{\omega_k=\pi T}^{\hbar\omega_D} \int_0^{\infty} \frac{d\xi}{\omega_k^2 + \xi^2 + \Delta^2} \quad (1.9)$$

Where $\omega_k = \pi T(2k-1)$. Readers familiar with the finite temperature formalism of QFT will recognise this as the fermionic Matsubara frequency with poles at $\pm i(\xi^2 + \Delta^2)^{1/2}$. We can introduce a finite lifetime by inserting a small imaginary part to this pole such that it is shifted to $\pm i(\xi^2 + \Delta^2 \pm i\hbar\tau_s^{-1})^{1/2}$ and we will find that we can associate τ_s with the Cooper pair breaking rate.

To obtain T_c , we set $\Delta = 0$ and perform the intergral over ξ which gives:

$$1 = 2g v(\mu) T \sum_{\omega_k=\pi T}^{\hbar\omega_D} \frac{1}{\omega_k + \hbar\tau_s^{-1}} = g v(\mu) \sum_{k=1}^{\hbar\omega_D/2\pi T} \frac{1}{2k-1 + \rho} \quad (1.10)$$

where we have reexpressed $\omega_k = \pi T(2k - 1)$ and have introduced $\rho = \hbar/\tau_s \pi T$. To obtain the final AG formula, we use one more mathematical trick and add and subtract another summation instead with $\rho = 0$ which gives:

$$1 = \frac{1}{2} g \nu \ln \left(\frac{2\hbar\omega_D \gamma}{\pi T_c} \right) + g \nu \sum_{k=1}^{\hbar\omega_D/2\pi T} \left(\frac{1}{2k-1+\rho} - \frac{1}{2k-1} \right) \quad (1.11)$$

The first term comes from noticing that summation over $1/(2k - 1)$ is the series representation of 1.5 when $\Delta \rightarrow 0$, in the vicinity of the critical temperature. The summation limits in 1.11 can be replaced by ∞ because this sum rapidly converges and is therefore the series representation of the digamma function. Moving the first term to the LHS in 1.11 gives the ratio of the intrinsic T_c (T_{co}) given by 1.7 to the new T_c . Thus we can rearrange the formula and obtain the AG expression 1.3.

$$\ln \left(\frac{T_{co}}{T_c} \right) = \psi \left(\frac{1}{2} + \rho \right) - \psi \left(\frac{1}{2} \right) \quad (1.12)$$

When $\nu_s \sim T_{co}$, $T_c \rightarrow 0$. The precise value can be obtained by consider the asymptotics of ψ when $\rho \gg 1$. The result is

$$\frac{\hbar}{\tau_s} = \nu_s \approx \frac{\pi T_{co}}{2\gamma} \approx 0.89 T_{co} \quad (1.13)$$

The above derivation made no reference to the specific form of ν_s . It is simply a general "pair breaking" parameter. In fact, it was shown by Maki and DeGennes [86] that all pair breaking perturbations are "equivalent" in thier effect on T_c in that that they all follow and AG type expression with a generalized $\nu_s = \hbar/\tau_s$.

Depairing in the Presence of Scattering

The essence of depairing under the influence of time-reversal asymmetric perturbations is the disruption of phase coherence due to the difference in energy of electrons of momentum $\vec{k}$ and $-\vec{k}$. This follows from the fact that the phase difference will evolve as $e^{-i\Delta E t/\hbar}$, where ΔE is the difference in energy between the members of the Cooper pair. For concreteness, we study the effect of a magnetic field on the superconducting condensate within a thin film. This argument is due to Tinkham [126].

If we consider a film of thickness $t \ll \lambda$, the London penetration depth, then the magnetic field will penetrate in to the superconductor. Additionally, assume the field is directed parallel to the a-b plane such that there is no vortex structure and the order parameter is

uniform. In this case, the perturbation is given simply by :

$$H_{\text{int}} = \frac{e}{2m} \sum_i (\mathbf{p}_i \mathbf{A} + \mathbf{A} \mathbf{p}_i) - \mu_B \sum_i \sigma_i \mathbf{H} \quad (1.14)$$

If we restrict the analysis to the orbital contribution (first term on the RHS) at first order, the phase evolves according to:

$$\frac{d\phi}{dt} = \frac{2e}{mc} \vec{p}_k \cdot \vec{A} \quad (1.15)$$

Where $\vec{p}_k$ is the particle momentum and $\vec{A}$ is the magnetic vector potential. In a real material, there is scattering from impurities that occurs on a time scale given by $\tau \sim l/v_F$, where v_F is the Fermi velocity and l is the mean free path. For isotropic scattering, p_k will change directions every τ seconds causing the change in phase to average out to zero. For a perturbation to be effective at pairbreaking, therefore, the time scale associated with the perturbation of strength E_{int} must satisfy $\hbar/E_{\text{int}} \ll \tau$. For the case described by 1.15, a full calculation of the field effect on the superconductor gives:

$$\frac{1}{\tau_s} = \nu_s = \frac{De^2 H^2 d^2}{6\hbar c^2} \quad (1.16)$$

Where D is the diffusion constant, d is the film thickness and H is the applied field. Since $D = \frac{1}{3} v_F^2 \tau$, we see that reducing the film thickness d as well as increasing disorder will both suppress pair breaking leading to an enhancement in the critical field.

The second term in 1.14, acts directly on the Cooper pair spin. It is known as the paramagnetic effect. Polarizing the electron spins to be parallel would also violate time reversal symmetry, breaking the Cooper pair. In this case however, the relevant scattering time opposing the pair breaking is no longer the transport scattering time τ but instead the spin-orbit scattering time τ_{SO} . Spin-orbit scattering (SOS) would serve to scramble the electron spin yet preserve time reversal symmetry. It therefore does not break pair but allows for a weakening of the paramagnetic effect. The pair breaking rate is given by:

$$\frac{1}{\tau_s} = \nu_s = \frac{\tau_{SO} e^2 \hbar H^2}{m^2 c^2} \quad (1.17)$$

A commonly quoted "limit" on the critical field of a superconductor is the Pauli limit of $H_{c2} \approx 1.84 T_c$ which is obtained by equating the Zeeman energy of a Cooper pair with the condensation energy given by Δ . The above discussion, however, implies that such a limit can be broken through a combination of a very thin film of a highly spin orbit coupled material to suppress the orbital effect and paramagnetic effect, respectively. Many thin film materials have been found to violate the Pauli limit. Depending on the magnitude of

the degree of breaking, a value for τ_{SO} can be obtained. Because $\tau \gg \tau_{SO}$, cases where large Pauli violation imply $\tau_{SO} \sim \tau$ could signal the possibility of more exotic mechanisms for preservation of superconductivity than simple spin orbit scattering. When multiple pair-breaking mechanisms are present, their contributions can usually be simply summed to obtain ρ in 1.12 [86].

Full details leading to the calculation of 1.17 and 1.16 can be found in the book by DeGennes [39].

Combining these results led Werthamer, Helfand and Hohenberg [136] to derive the following formula for the effect of a perpendicular applied magnetic field on the suppression of T_c

$$\ln(t) = \left(\frac{1}{2} + \frac{i\lambda_{so}}{4\gamma} \right) \psi \left(\frac{1}{2} + \frac{\bar{h} + \frac{1}{2}\lambda_{so} + i\gamma}{2t} \right) + \left(\frac{1}{2} - \frac{i\lambda_{so}}{4\gamma} \right) \psi \left(\frac{1}{2} + \frac{\bar{h} + \frac{1}{2}\lambda_{so} - i\gamma}{2t} \right) - \Psi \left(\frac{1}{2} \right) \quad (1.18)$$

where

$$t = \frac{T_c}{T}, \bar{h} = 2eH (v_F \tau / 6\pi T_c), \quad \gamma = \left((\alpha \bar{h})^2 - \left(\frac{1}{2}\lambda_{so} \right)^2 \right)^{\frac{1}{2}}, \alpha = 3/2 m v_F^2 \tau \quad (1.19)$$

$$\lambda_{so} = 1/3\pi T_c \tau_{SO}$$

This equation accounts for both the orbital effect as well as the effect of spin paramagnetism through the term λ_{so} . The parameter α , is the way material quality enters into the equation. Smaller values of τ imply robustness to the applied field. Small values of α (long τ) reduce the formula to original AG formula with v_s given by 1.16.

Chapter 2

EXPERIMENTAL METHODS

2.1 Introduction

The technique used in this thesis to prepare films is molecular beam epitaxy (MBE). MBE is a crystal growth technique that has an esteemed place as being able to produce very high quality crystals. However, such materials that can be grown with that level of quality are few and far between. As described in the previous chapter, our goal with this research is to widen the range of materials that can be grown in high quality with MBE. We will begin by describing the technique and highlight its benefits and drawbacks. We will highlight the lessons learned from these "greatest hits" to motivate the approach we will take in later chapters. We will then go on to describe the unique abilities of our MBE system for preparing pristine substrates using laser annealing.

After describing the MBE technique, we will continue by discussing the methods we use to study these materials, in particular, *in-situ* electron diffraction, high resolution x-ray diffraction and electrical transport.

2.2 Molecular Beam Epitaxy

Molecular Beam Epitaxy is a thin film growth technique that takes place in a UHV ($\sim 10^{-10}$) mbar environment. The technique is a physical vapor deposition process where source material is thermally evaporated from effusion cells. Coils made from refractory metals heat source material housed in ceramic or refractory metal crucibles. These cells are highly engineered to produce fluxes that are stable over long ($\sim$ hours) growth periods. The substrate is typically a high-quality semiconducting or oxide single crystal and is placed within the manipulator and is heated by a SiC heating element. Finally, the UHV environment allows for *in-situ* characterization of the growth process using a technique called Reflected High Energy Electron Diffraction (RHEED). This technique scatters high-energy electrons off the surface at grazing angles. Diffraction from the surface structure gives rise to characteristic patterns when projected onto a phosphor screen. More details of this technique will be described in a later section. A schematic of the apparatus is given in Fig. 2.1A. In Fig. 2.1B, we show a photograph of the actual MBE chamber used for the growth of these materials. Finally in Fig. 2.1C, a top down view of the whole cluster is given. There are two growth chambers, one for intermetallics that will be used for the growth of the materials in these studies and a complex oxide chamber used to grow ultra-pure oxides. The entire

cluster is interfaced with a glovebox where the atomic-force microscope (AFM) is housed that we use study surfaces without air-exposure. The chamber was manufactured by DCA instruments and was installed and commissioned by the author and Prof. Joseph Falson in December 2020.

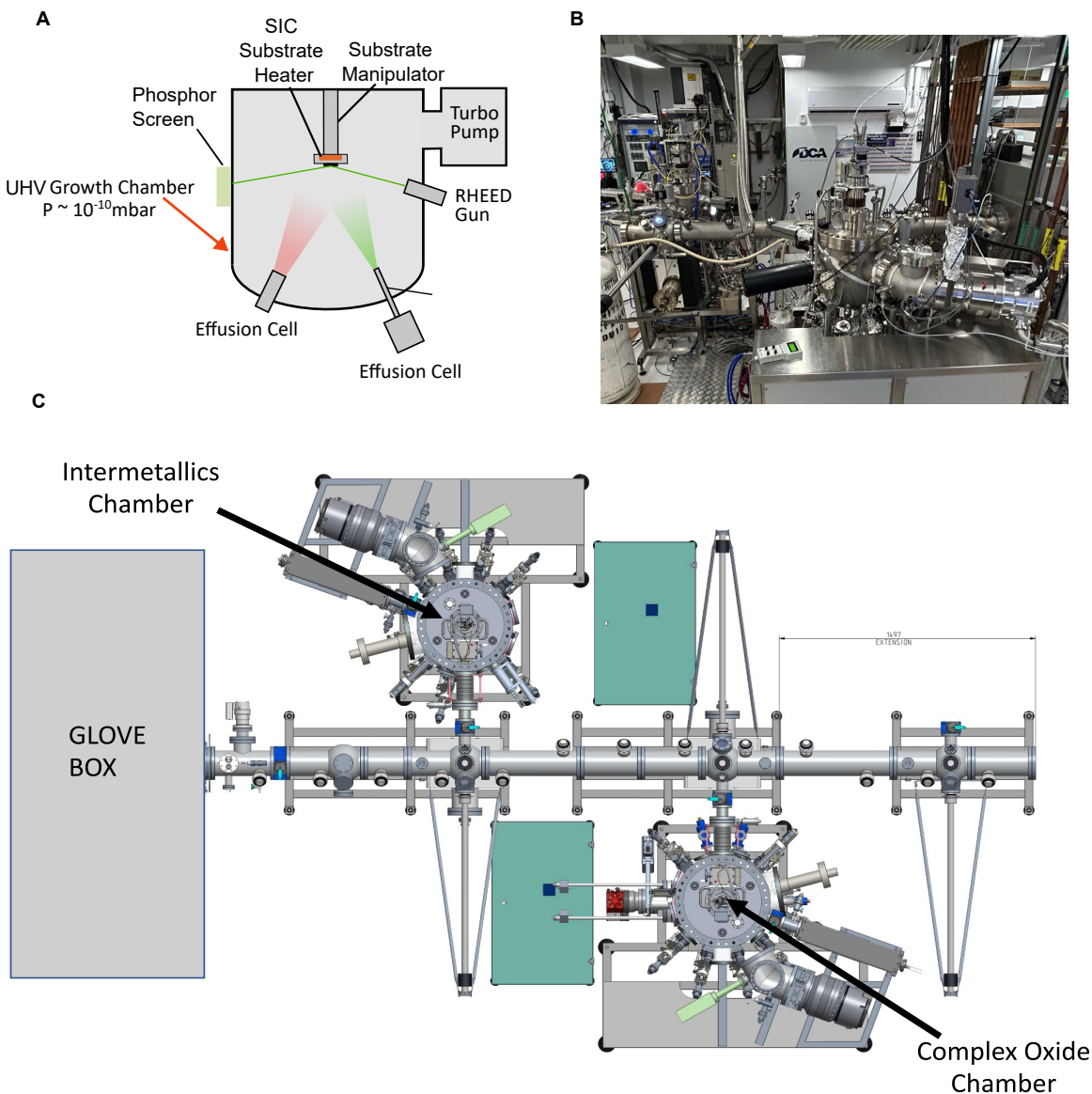


Figure 2.1: **Overview of the Falson Lab MBE system.** **A** Schematic of an MBE chamber. **B** MBE chamber in the Falson Lab. **C** Top view CAD rendering of the MBE in the Falson lab.

The ultra-clean UHV environment of MBE offers combined with the extremely stable fluxes of high-purity elements from the effusion cells offer unique tuning knobs with which to perturb the electronic structure. However, the technique is not without its drawbacks. These drawbacks are the result of the complex interaction between the thermodynamics which

govern phase formation (as captured by the bulk phase diagram), the surface energetics governing the film-substrate interface and the dynamic deposition-re-evaporation processes that is constantly occurring during growth. This means that compared with bulk single crystal growth, there are many crystal structures that would be either impossible to grow or would be so difficult that high quality could never be achieved. We will be using MBE as a materials discovery technique throughout this thesis and it therefore pays to examine what makes a material “good” for MBE growth.

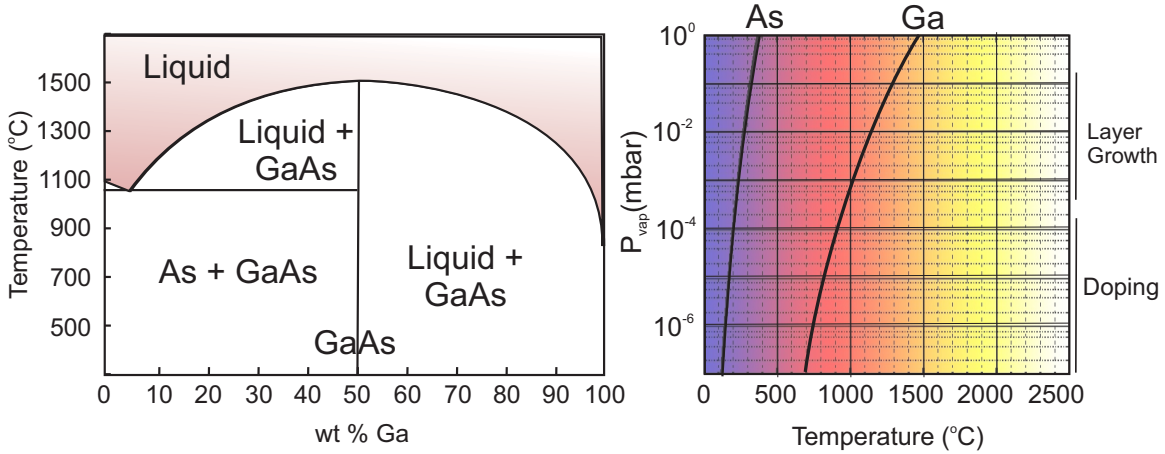


Figure 2.2: **Thermodynamic properties of GaAs.** **A** Phase diagram of the Ga-As system. **B** Plot of the vapor pressures of Ga and As.

To date, the highest purity material grown by MBE is the GaAs-AlGaAs quantum well [21], which has enabled discoveries of some of the most exotic phases of matter, most notably, the fractional quantum hall effect (FQHE) [120]. The underlying reason for the ability to synthesize such high-purity crystals comes down to the unique aspects of the bulk thermodynamics and the kinetics governing the evaporation of the constituent elements. In Fig.2.2A, we display a bulk phase diagram for GaAs [27]. Notice how GaAs only forms along a line of perfect stoichiometry. It is therefore known as a “line compound”. If one were to set up growth conditions to the left, in the As-rich regime and solidify, phase segregation into stoichiometrically pure GaAs, and elemental As would occur. Of course, it is impossible to achieve true 50:50 ratios of element fluxes, but the nature of the evaporation of the constituent elements means that this is unnecessary. In Fig.2.2B we show the vapor pressures of the Ga and As source elements (source: MBE Komponenten). Because As has orders of magnitude larger vapor pressure, it evaporates far more readily. Achieving GaAs merely requires that enough As is supplied so as to be located in the left region of the phase diagram. Then, by heating the substrate to $\sim 600^\circ\text{C}$, whatever As is not incorporated into the stoichiometric GaAs crystal simply re-evaporates leaving behind

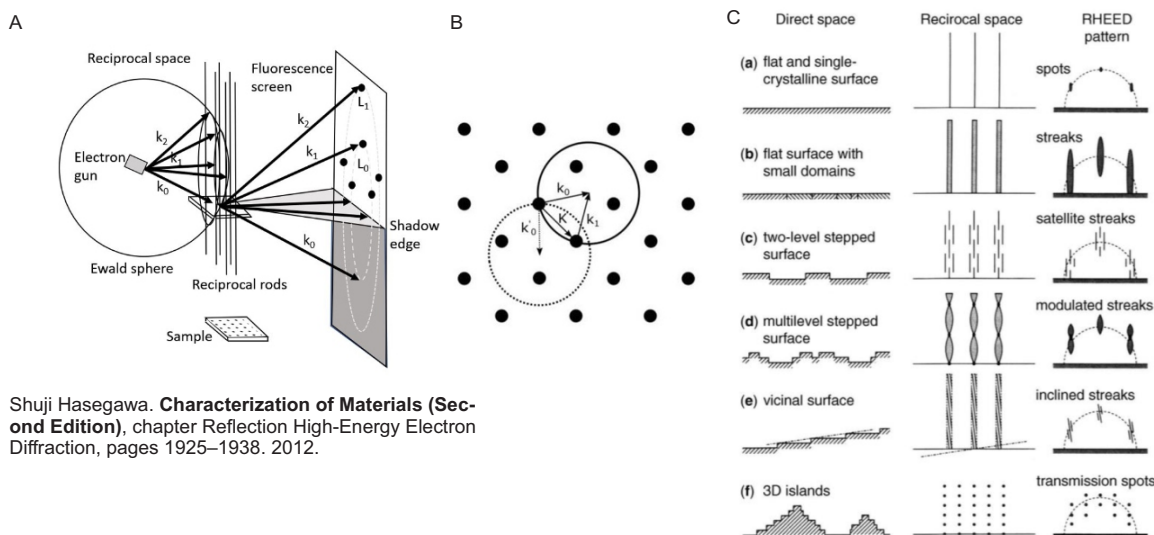
a perfect crystal. This is known as adsorption controlled growth and is the optimal regime for crystal growth because it means that precise flux calibration is no longer necessary. Finally, the last elements needed for extremely clean films is ultra-pure source material and a high quality substrate. Both of these are available in the case of GaAs-AlGaAs since films are grown on GaAs wafers and the purity of the source materials reach as high as 7N (99.99999) or higher. Conversely, crystals that do not live on the “side” of the phase diagram or that have elements with comparable vapor pressures pose a challenge due to the precise flux calibration necessary. Finally, a lattice-matched, high quality substrate is essential to stabilize the desired phase in single crystalline form. The preparation of the substrates for these experiments will be discussed in a later section.

Optimizing Film Quality

The processes of optimization of film quality is often referred to as finding the “growth window”, i.e. the window of optimal ratios of source material fluxes and substrate temperature during growth. This processes is iterative and relies on a variety of *in-situ* and *ex-situ* characterization techniques. Many of these techniques are common across various fields of materials research and so we will only briefly outline them. The primary techniques used in this thesis are as follows.

1. X-ray Diffraction : crystal structure determination and epitaxial relationship
2. Atomic Force Microscopy : Surface roughness
3. Electrical Transport : Residual resistivity ratio as a measurement of crystal quality, Hall effect to measure carrier type and mobility
4. Transmission Electron Microscopy : High resolution images of atomic structure
5. Rutherford Back Scattering : Quantitative characterization of materials stoichiometry
6. Reflection high energy electron diffraction (RHEED) : *in-situ* measurement of surface crystal structure

Each technique has its domain of relevance and will be discussed in more detail in the relevant section. However, we will give a brief introduction to RHEED here as it is likely to be unfamiliar to readers not acquainted with MBE.



Shuji Hasegawa. **Characterization of Materials (Second Edition)**, chapter Reflection High-Energy Electron Diffraction, pages 1925–1938. 2012.

Figure 2.3: **Overview of the RHEED technique.** **A** Geometry of RHEED. **B** Ewald sphere construction for the 2D lattice. **C** Effect of real space non-ideality on the diffraction pattern. Reprinted with permission from [46].

in-situ RHEED Analysis of Growth

Reflected High Energy Electron Diffraction (RHEED) is among the most powerful techniques for establishing growth conditions [46]. It is a diffraction technique that is used to characterize the surface crystallinity. The technique elastically scatters high-energy electrons $\sim 20\text{keV}$ at a grazing incidence from the surfaces of the growing film Fig.2.3A. The diffraction conditions are given by the intersection of the Ewald sphere (radius set by the electron energy) with the “rods” of the 2D reciprocal lattice (Fig. 2.3A,B). Scattered electrons hit a phosphor screen at the other side of the UHV chamber and form a diffraction pattern. The nature of this diffraction pattern gives additional information about real space features of the surface. This is depicted in Fig. 2.3C. For example an ideal, flat crystalline surface yields a pattern consisting of spots in a ring corresponding to the intersection points of the reciprocal lattice rods with the Ewald sphere. More commonly observed is the case displayed in the second row. Finite sized domains of an otherwise flat surface yield broadening of the reciprocal lattice rods. This yields a pattern of “streaks”. The other common observation is that depicted in the bottom row of Fig. 2.3C. This is the case of island growth and the RHEED streaks break up into a series of spots, reminiscent of a TEM pattern. The reason for this is that the electrons are no longer scattering from a 2D surface but are being transmitted *through* the island.

2.3 Preparation of MgO Substrates with Laser Annealing

MgO as a Substrate for Square Net Materials

It is difficult to overstate the importance of substrate preparation. Without a flat, clean, lattice matched substrate, films will grow poorly. Lack of availability of substrates is often what limits the ability to grow complex materials. Luckily, the materials of interest in this thesis can be grown on Magnesium Oxide (MgO)

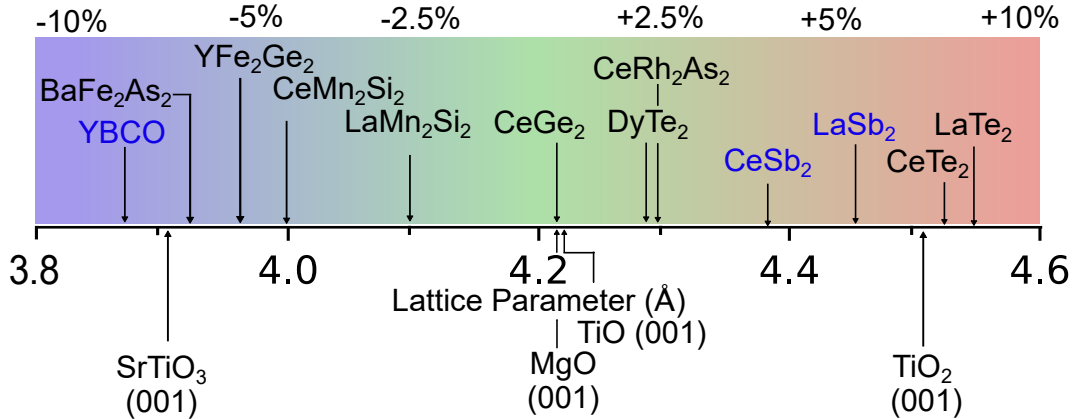


Figure 2.4: A graphical depiction of the lattice constant mismatch between square net materials of interest and commercially available substrates.

Magnesium Oxide substrates have found application in the thin film growth of strongly correlated oxides and magnetic thin films for spintronic applications. With a lattice constant of 4.21Å, MgO is unique among commercially available oxide substrates for its large lattice constant and rocksalt crystal structure. However, this lattice constant value makes MgO an attractive candidate for the growth of quantum materials. In Figure 2.4, a variety of candidate crystals that have shown interesting properties in bulk are displayed alongside the values of various substrates. These materials are members of either the square-net family as described in the introductory chapter or originate from the ThCr₂Si₂ family [113] and often host strongly correlated electrons. Notably, the square net materials DyTe₂ and LaSb₂ which form the focus of this thesis have values close to that of MgO. It was therefore selected as a substrate for these experiments. Alternative substrates such as TiO₂ could be used, however, the comparably more complex crystal structures and high cost further justify the choice of MgO as a substrate of choice.

2.4 Laser Annealing of Oxide Substrates

MgO substrates are known to be challenging to prepare with conventional methods (furnace annealing) due to their hydrophilicity. First pioneered in the work of Braun et. al [10], laser

annealing is a fast, ultra-clean method that allows for *in-situ* preparation of oxide surfaces. The technique makes use of a $10\mu\text{m}$ free space CO_2 laser rated to 1kW. A schematic of this set up is given in Figure 2.5. The high absorption coefficient of MgO at these wavelengths allows effectively unlimited substrate temperature to be reached.

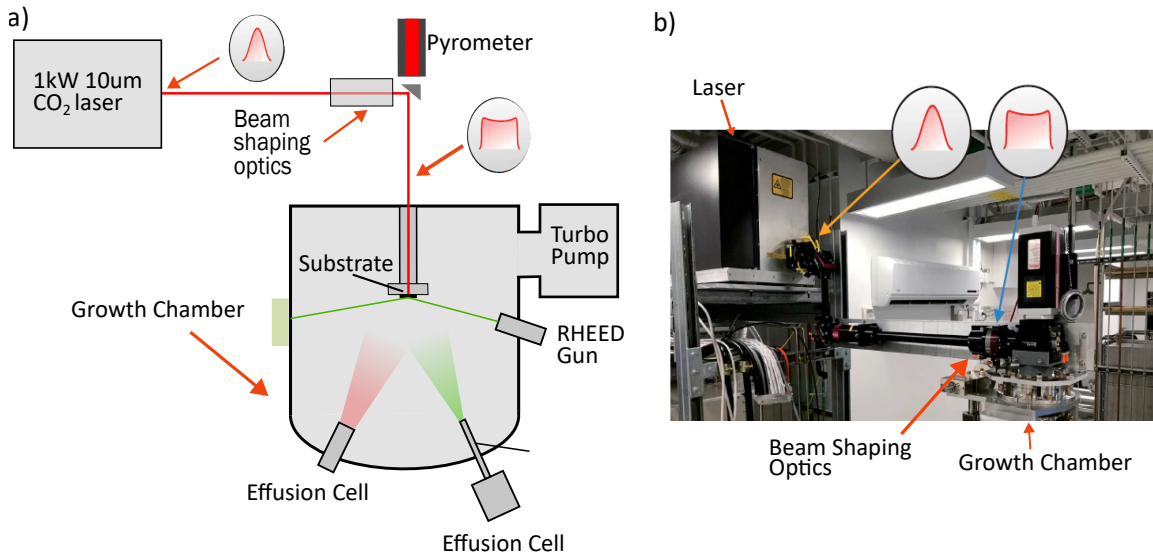


Figure 2.5: **Overview of the Laser Heating System** **A** Schematic of the beam path and optics used to first shape the beam into a quasi-flat top profile and direct it down to the substrate. A pyrometer ($5\mu\text{m}$) is used to read the substrate temperature from the back. **B** A photograph of the setup from the lab.

The beam path consists of two initial mirrors to direct the beam down an enclosed beam path toward the chamber. The initial gaussian-shaped beam is first passed through a beam shaping optical element to form a flat-top shape. It is then focused to a spot size of $\approx 15\text{mm}$ so as to uniformly illuminate the 10mm substrate. A pyrometer ($5\mu\text{m}$) is used to monitor the temperature at the back of the substrate. In doing so, ambiguity resulting from changes in emissivity of the front of the substrate during film growth are eliminated.

2.5 Preparation of Oriented Substrates

In this thesis we study growth of SN materials on both well oriented (offcut angle $<0.5^\circ$) and on substrates with intentional miscuts away from the (001) direction. To begin, we discuss the annealing of oriented substrates with the goal of obtaining step-and-terrace morphology with single monolayer height.

The process for preparing step-and-terrace morphology MgO is as follows;

1. Substrates are rapidly brought to annealing temperature at $250^\circ\text{C}/\text{min}$

2. Substrates are held at annealing temperature for 10 minutes and rotated at 5rpm for uniformity
3. Substrates are brought back to room temperature at 250°C/min

Upon completion of this process, they are then moved into a glovebox and finally transferred to a separate substrate holder for film growth. A schematic of this process is given in Figure 2.6

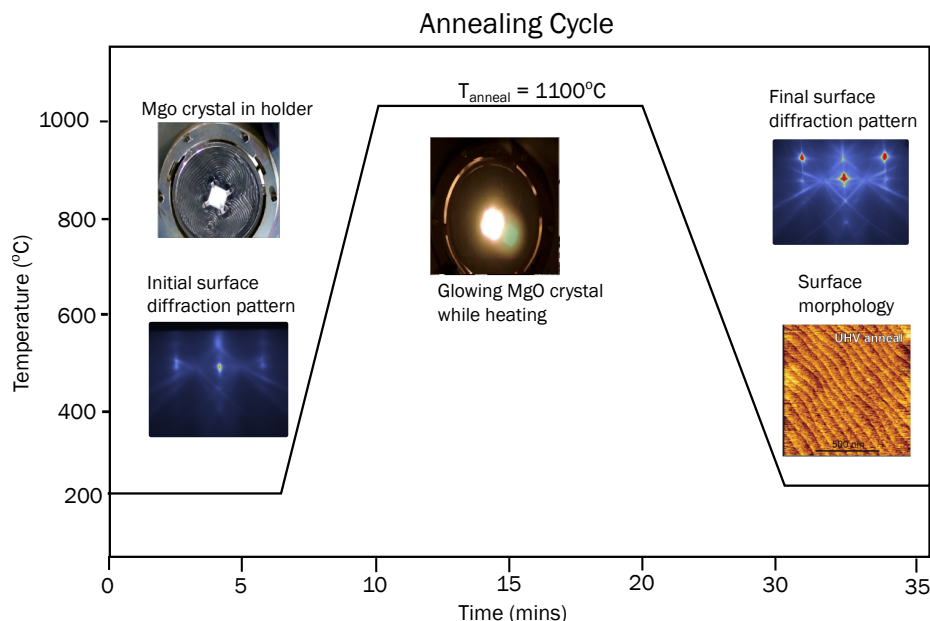


Figure 2.6: **Schematic of the annealing process.** Inset figures show RHEED patterns before and after annealing, as well as an AFM image of the final surface morphology.

RHEED monitoring is used to observe the surface quality *in-situ*. Clear improvement in surface morphology as revealed by intensity and high contrast of diffraction spots (Inset of Figure 2.6).

Determination of optimal annealing temperature was performed by imaging annealed surfaces in AFM in an inert glovebox. As can be seen in Figure 2.7, obtaining surfaces with single monolayer step height can be done with an annealing temperature ranging from 1050° up to 1125°C. Below this temperature range, substrate surfaces remain disordered with step terraces beginning to form. At optimal conditions, straight, monolayer-height terraces are obtained. Above this range, step bunching is observed and is not well controlled. Thus for oriented substrates, we take the optimal temperature to be 1100°C. It was found that variation due to MgO manufacturing and polishing had an impact on the final morphology. However, 1100°C gave the most consistent results and was used because every substrate

could not be checked before growth. The optimal annealing temperature was periodically checked to ensure proper behavior.

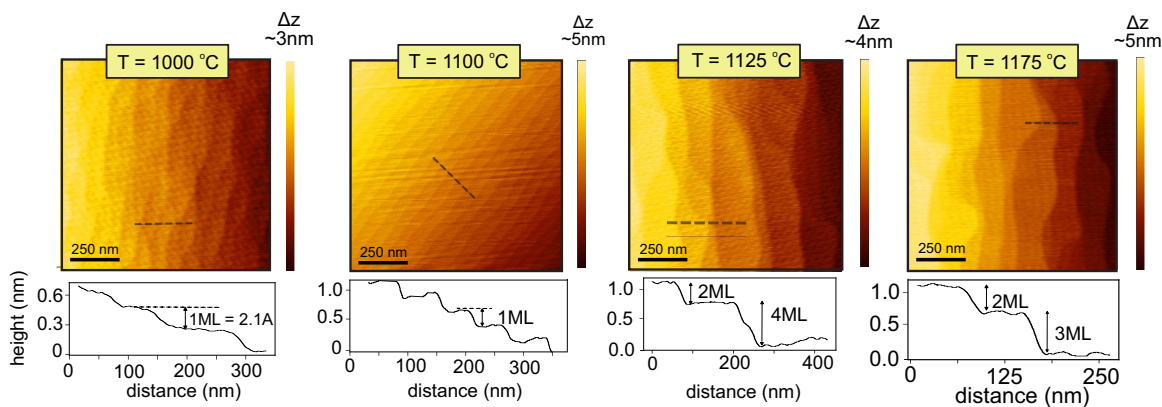


Figure 2.7: Optimization of MgO surface morphology with laser annealing. Images show surfaces of laser-annealed MgO at various temperatures with representative linecuts below, showing the changes in surface morphology as temperature is increased.

Chapter 3

SUPERCELL FORMATION IN DYSPROSIUM DITELLURIDE THIN FILMS

3.1 Introduction to the Rare Earth Tellurides

Layered compounds sharing the square-net structural motif support a myriad of electronic phases including superconductivity [146], topologically protected modes [61], magnetism [111, 72], and charge density waves (CDW) [107, 115, 73]. Among this class of materials, rare-earth tellurides (LnTe_x , where Ln is a lanthanide and $x = 2, 3$ most commonly), have attracted attention due to the interplay between itinerant carriers [74] and magnetism, superconductivity and CDW-order [144]. Sandwiched between corrugated quasi-ionic Ln-Te layers, the electronic structure of the covalently bonded two-dimensional square Te sheet can be conceptualized by a partially filled p-orbital manifold which obtains extra charge from an imbalance in valence states within the corrugated layer [127, 48]. Modifying Ln acts to exert chemical pressure and influences both the structural and electronic properties of the material. For example, in the case of the rare-earth tritellurides, chemical pressure acts to modify the CDW wavevector q , the CDW-ordering temperature, and the orthorhombicity of the crystal, which ultimately reveals two orthogonal CDW with dissimilar ordering temperatures [107, 144]. Ultra-fast optical probes have demonstrated transient expression of competing CDW orders, suggesting a complex energy landscape governs their stability [64]. Studies on the effect of hydrostatic pressure have revealed that CDW order can be further suppressed with superconductivity being promoted, all in the presence of rare-earth-derived (antiferromagnetic) ordering [144].

The related LnTe_2 exhibit behaviors similar to the tritellurides, but differ in key ways due to their electron filling of $7e^-/\text{Te}$ in the square planar layers [127, 59]. In contrast to the tritellurides, which form stoichiometric crystals, the ditellurides have a substantial width of formation and tend to form Te-deficient crystal structures with a range of stoichiometries and resulting superstructure modulations [93, 101, 115, 104]. These modulations are often commensurate with the parent structure and result from an ordering of Te vacancies within the Te sheet. However, incommensurate modulations have also been observed in $\text{LaTe}_{2-\delta}$ and $\text{CeTe}_{2-\delta}$ [115]. Electrical transport ranging from metallic [121] to semiconducting [55, 67] for similar nominal compositions and photo emission studies reporting both pseudogap [115, 20] and fully-gapped [38] Fermi surface structures further demonstrate the complexity

of the ditelluride system. Superconductivity has also been reported in CeTe_2 at 0.2 GPa [54] and in Sb-doped LaTe_2 at approximately 3 GPa [19]. The subtle dependence on defect stoichiometry and applied pressure motivates an investigation into the role that epitaxial strain and dimensionality play in the stabilization of lattice distortions and the resulting ground state of the electron-phonon system.

3.2 Structure and Basic Properties of the Rare Earth Tellurides

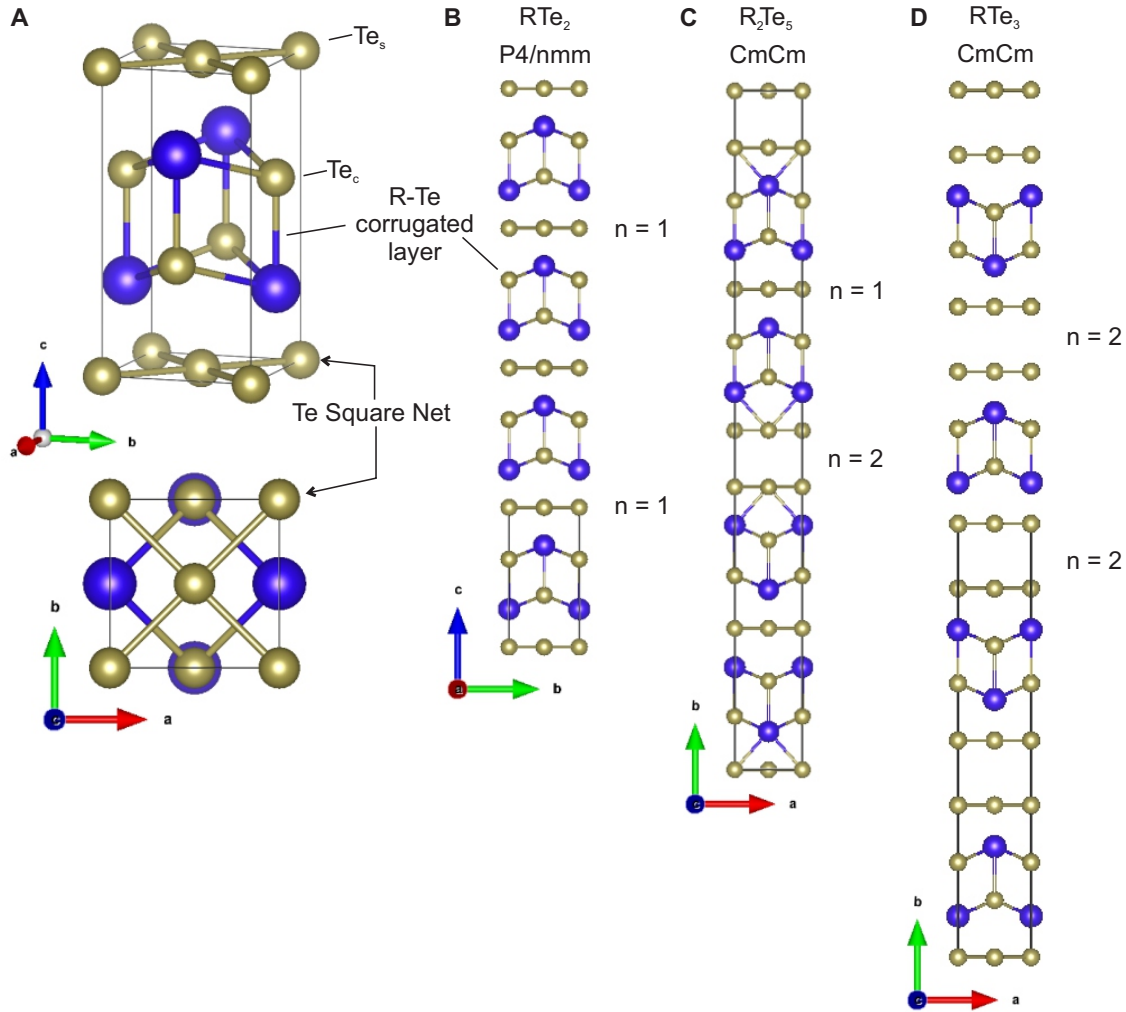


Figure 3.1: **Overview of the structure of rare-earth telluride compounds.** A View showing the tellurium sheet (Te_s) layer and the corrugated layer containing Te (Te_c) and the rare-earth ion. Layering sequence and space group corresponding to B the RTe_2 , C R_2Te_5 and D RTe_3 configurations.

Structure

The rare earth tellurides RTe_x ($x = 2, 2.5, 3$) form a family of related crystal structures with the main common structural motif being the presence of a square planar Te sheet sandwiched between "corrugated" R-Te layers. The basic structural building block is shown in Fig 3.1A. The two inequivalent tellurium atoms in the unit cell are labelled Te_s and Te_c to indicate whether they reside in the square-net sheet or corrugated layer, respectively. We will refer to this building block as a quintuple layer (QL) through the remainder of this chapter. Increasing x in the RTe_x formula results in crystal structures with differing number of stacked Te sheets (indicated by n in Fig 3.1. For example $n = 1$ in RTe_2 , while $n = 2$ in RTe_3 . R_2Te_5 features an alternating $n = 1, n = 2$ stacking sequence along the c -axis direction.

The RTe_2 crystals can be considered the "parent" compound with the simplest structure with the highest symmetry. It is a tetragonal crystal that belongs to the space group $P4/nmm$ and both a and b axes are equivalent. The next simplest to describe is the RTe_3 crystal. This structure is orthorhombic with space group $Cmcm$. The reduction in symmetry is the result of an offset between neighboring blocks as they are stacked along c . If one were to take two QL blocks and stack them such that they are displaced by $a/2$, one arrives at the RTe_3 structure. The effect of this operation can be seen by looking at the RTe_3 unit cell in Fig3.1D. As one moves along the b direction (for centered orthorhombic lattices, the convention is that the centered face is considered the c face thereby making the long axis the b -axis in the RTe_3 and R_2Te_5 materials), one can see the lower corrugated layers is "pointing up" with the next layer "pointing down". This is caused by the $a/2$ phase shift and breaks the symmetry between the a and c axes, rendering the crystal orthorhombic. It has been found that this also results in a very small discrepancy between the a and c lattice constants though the electronic structure is typically discussed ignoring this deviation [107]. Finally R_2Te_5 can be conceptualized as a stacking of RTe_2 double layers which have again been offset by $a/2$ with respect to one another.

One attractive feature of the rare earth tellurides is their flexibility with respect to the identity of the rare earth element. Nearly every rare earth element form an RTe_x phase though there are some that only form $x = 3$ (Ho [144]). As one moves from lighter to heavier rare earths, the lattice constant is seen to reduce quite readily. This is a phenomenon known as "lanthanide contraction". Due to the poor screening of the nuclear charge by the f -electrons that are filled as one moves toward the heavier elements, this nuclear charge is felt more strongly by the other electrons in the crystal, causing it to contract. Given lattice constant values ranging from $a = 4.51\text{\AA}$ for LaTe_2 to $a = 4.28\text{\AA}$ for DyTe_2 , MgO ($a = 4.21\text{\AA}$) should

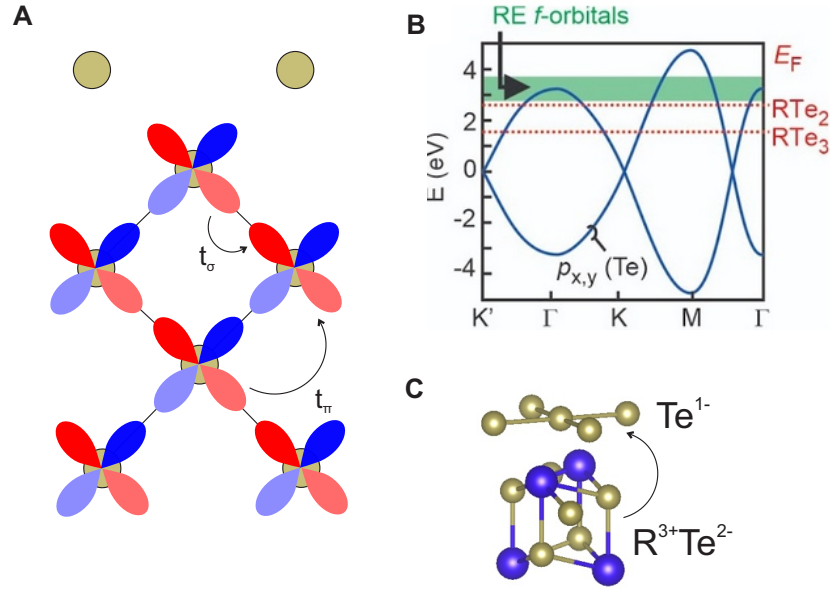


Figure 3.2: **Electronic Properties of Rare Earth Tritellurides** **A** Hopping between p -orbitals on the Te square net. **B** Schematic band structure showing the positions of the Fermi level for different RTe_x materials due to the difference in charge density. **C** Schematic of the origin of the electron filling of the Te sheet. The additional electron from the R^{3+} is donated to the Te sheet.

serve as an excellent substrate to grow a variety of epitaxial films. Finally, it has also been observed that incorporation of heavier rare earth elements reduces ambient stability.

Electronic properties

As described in the introductory remarks, rare-earth tellurides provide a unique platform to study a variety of broken symmetry grounds and even topological phenomena. To understand why, we begin with a description of basic chemistry and electronic structure, using the tight-binding scheme as a first approximation.

Recall from Ch1. that the band structure can be understood as resulting primarily from the partially filled p -bands formed from the Te_s atoms in the square-net sheet. First, the out-of-plane p_z orbitals would tend to hybridize with the atoms in the corrugated layer causing their bands to be suppressed in energy and therefore filled [59]. This leaves only the p_x and p_y orbitals as the frontier orbitals to form the Fermi surface. A schematic of this arrangement is given in Fig. 3.2A. A schematic band structure of an ideal p -orbital square lattice is shown in Fig. 3.2B. As expected, the σ bonds give rise to highly dispersing bands and high mobility carriers [74].

The oxidation states in the crystal are assigned as follows. Rare earth atoms are assigned

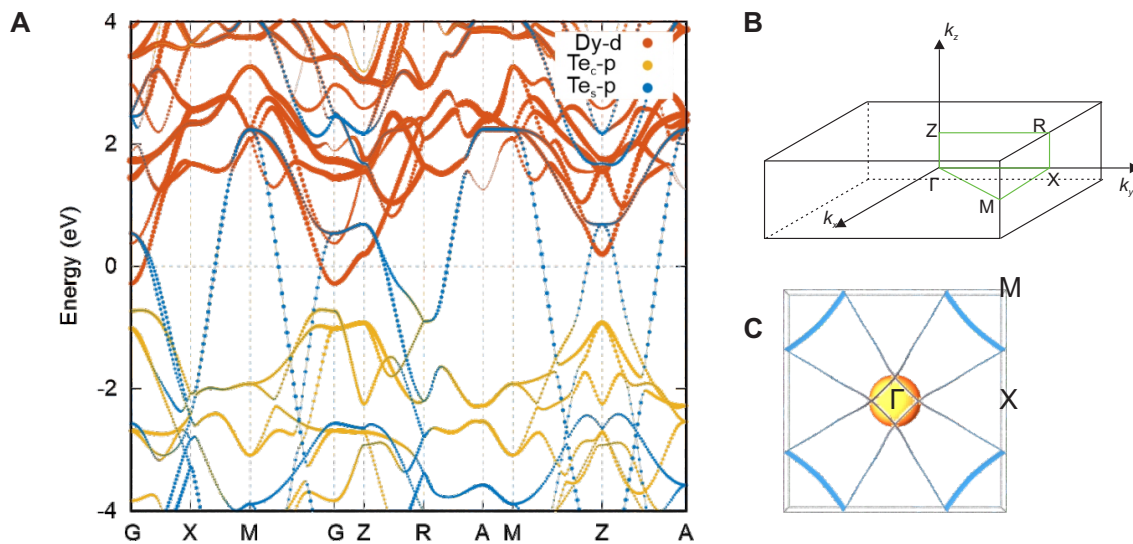


Figure 3.3: **Electronic Structure of DyTe₂** **A** Bandstructure of DyTe₂ **B** Brillouin Zone **C** Fermi Surface. Credit: Dr. Jinwoong Kim [79]

a 3+ oxidation state, while the Te_c atoms assigned a 2- oxidation state. The satisfaction of the octet rule for these atoms implies filled bands relatively low in energy. Indeed, early tight-binding calculations [59] have shown this to be true. The additional electron donated by R is transferred to the Te atoms in the square net. This is schematically represented in 3.2C. Thus, the effective charge on the Te_s atoms depends on the number of Te square nets (n). For $n = 1$ (RTe₂), there are $7e^-/\text{Te}$ while for RTe₃ there will decrease to $6.5/\text{Te}$. Such a tunability can be compared to the Ruddleson-Popper series in perovskite oxide crystals wherein charge density can be controlled by choosing how many cations are incorporated into the structure as inter layers [108]. Changing the effective charge density on the Te_s sheet is equivalent to changing the Fermi level, as is schematically represented in 3.2B. Because many novel ground states, including magnetic, superconducting and charge ordered ground states can be tuned by modifying the charge density, the rare-earth tellurides are an excellent platform for exploring novel states of matter which feature coupling between lattice, charge and spin degrees of freedom.

Of course, an ideal square-net with only p -orbitals is not possible to find in real materials. However, the rare earth tellurides host band structures that can be reasonably approximated by this picture. A calculated band structure for DyTe₂ can be found in 3.3A. This calculation was performed by Dr. Jinwoong Kim in the Kioussis group at Cal State Northridge. As can be seen in the band structure, the Fermi surface consists almost entirely of bands originating from the Te_s p -orbitals of the square-net sheet. Given the large degree of overlap between

5p orbitals, bands are strongly dispersing implying low effective carrier mass. Additionally, there is a small electron pocket originating from the Dy-5d orbitals.

3.3 Growth of DyTe₂ Thin Films

Bulk Thermodynamics

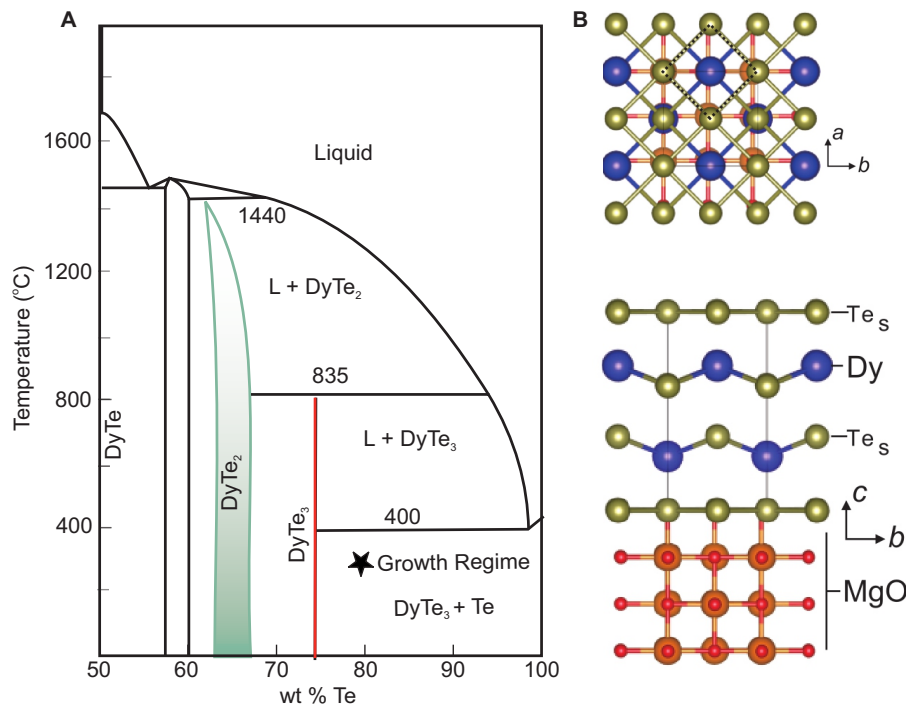


Figure 3.4: **Bulk thermodynamics and epitaxial relationship.** **A** Bulk phase diagram for DyTe₂. **B** Top and side view of DyTe₂ on MgO.

The strategy employed for obtaining high quality thin films is often very much determined by the structure of the phase diagram. As discussed in Ch 2, locating growth conditions between two line compounds on the phase diagram, results in a phase segregation and the resulting film will be of a mixed phase consisting of both compounds in proportion determined by the lever rule. Flux of elemental sources can be calibrated but is often hard to control to the level of precision required to obtain phase pure films of generic composition. The situation is changed if adsorption controlled growth becomes possible (see Ch 2). In that case, precise control no longer becomes necessary and films of the proper stoichiometry will grow provided enough of the high vapor pressure element is supplied. Luckily, this is exactly the situation for the rare-earth tellurides. The original goal for this investigation was the growth of DyTe₃ thin films. In figure 3.4A, we display the Dy-Te phase diagram. It can be seen that DyTe₃ sits at the Te-rich side of the phase diagram, with no further Te-rich phase present. Thus, we exploited this fact by supplying an overabundance

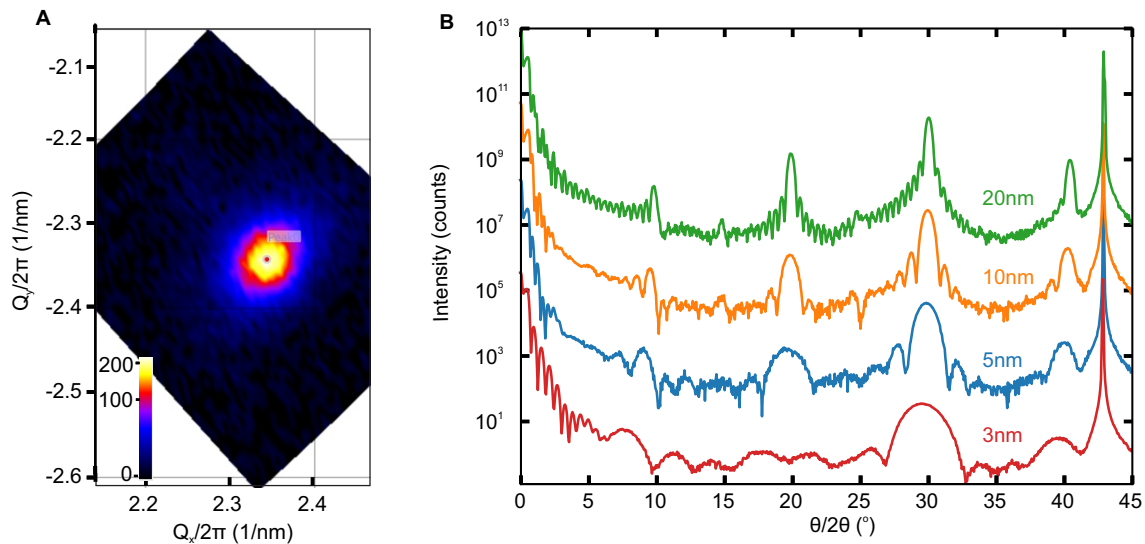


Figure 3.5: **Diffraction measurements used to characterize epitaxial DyTe₂.** **A** In-plane RSM of the (110) diffraction. **B** Symmetric scan measuring the *c*-axis lattice constants.

of Te during growth with the goal being to create growth conditions as indicated by the star in 3.4A. Given the highly differing vapor pressures, the growth rate is set by the Dy flux while the excess Te not incorporated into the growing film would simply re evaporate due to the high vapor pressure of Te even at modest temperatures (source: MBE Komponenten <https://www.mbe-komponenten.de/>). It was found that even for Te/Dy ratios in excess of 40, the DyTe₂ phase was always obtained. This phase sits to the left of DyTe₃ and displays a finite width of formation, indicating an insensitivity to off-stoichiometry.

Structural Properties of DyTe₂ Thin Films

Before describing the process by which growth was optimized to obtain high-quality films, we will discuss in more detail, the structural properties of DyTe₂ and how these can be determined experimentally. The most straightforward characterization technique is X-ray diffraction. DyTe₂ in its ideal form adopts the space-group *P4/nmm* and a representative $\theta/2\theta$ scan from a high quality sample is presented in Fig. 3.5B. Expected peak positions taken from literature values are compared to these values to confirm the structure. In addition to the main diffraction peaks, a set of 2nd order diffraction peaks were also observed. As will be discussed later in the chapter, these are indicative of a distortion of the unit cell that includes a doubling of the *c*-axis. Furthermore, Laue fringes can be observed alongside the primary peaks indicating good crystallinity and allowing for determination of sample thickness. We further verify the structure using in-plane reciprocal space mapping (RSM) of the (110) peak presented in 3.5A. From these measurements and the measurements of

other systematic extinctions, the structure can be verified. More in depth discussion will take place later on in the chapter.

In addition to XRD, RHEED analysis is used *in-situ* to study the surface structure. In 3.6, we present RHEED images taken along the two high-symmetry azimuths, [100] and [110] and index them accordingly.

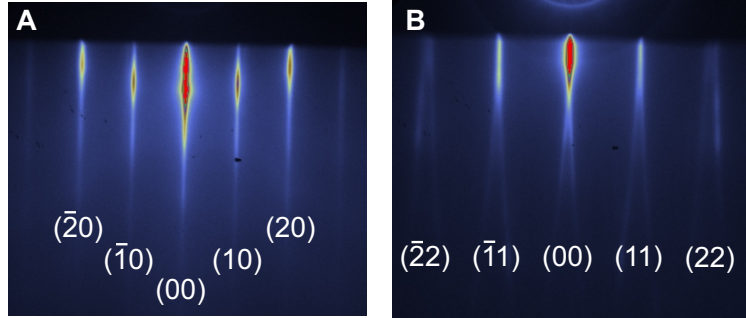


Figure 3.6: **RHEED patterns for DyTe₂** **A** RHEED pattern looking down the [100] zone axis. **B** Looking down the [110] zone axis.

A notable characteristic of the [110] diffraction pattern is the presence of arc-like streaks that intersect with the main diffraction streaks. The presence of these streaks has been observed previously in systems studying sub-monolayer adsorption onto pristine surfaces. These streaks are the result of structural disorder that primarily affects one crystal axis, or 1-D disorder. Such a phenomenon often occurs in systems displaying complex defect chemistry. As we will find, DyTe₂ is exactly such a system. Consider diffraction along the [100] zone axis of the crystal (Fig 3.6. Disorder in the lattice constant tends to both broaden the peaks, but also gives rise to diffuse background intensity along a plane orthogonal to the incident beam, i.e. the plane parallel to the plane of the paper. Thus, when the crystal is rotated to the [110] zone axis, these diffuse planes oriented along the 100 directions will intersect the Ewald sphere causing arcs with radii proportional to the angle between the diffuse planes and the incident direction as well as the radius of the Ewald sphere ($\sim 1/\lambda$) where λ is the wavelength of the electrons used for the probe. The interested reader is referred to [23] for the full details.

Growth of DyTe₂

Thin films of DyTe₂ ($a = 4.28\text{\AA}$) were grown on MgO (SG:Fm3m, $a = 4.21\text{\AA}$) substrates, selected for their 2% mismatch with DyTe₂ and were prepared using the methods of Ch. 2.

Films of DyTe₂ were grown under a Te/Dy ratio of ~ 20 . Dy was evaporated from a conventional effusion cell with Te being supplied with a thermal cracker cell. It was

found that in order for high quality films to be obtained, a two step growth method had to be employed. The necessity for such a strategy became apparent by watching *in-situ* RHEED. Growth at low temperatures films initially showed good structural quality RHEED but eventually formed rough films with domains and transmission spots indicating island growth (see Ch. 2). On the other hand, it was found that for evaporation taking place $>300^{\circ}\text{C}$ on bare MgO, films showed poor structural quality as evidenced by the poorly defined streaks and disordered diffraction pattern.

This behavior can be explained by the low sticking coefficient of Te on the bare MgO surface, despite the large Te/Dy ratio. Under the conventional model of thin film growth, incoming adatoms land on the substrate surface where they migrate toward the substrate step edges where the film is nucleated. Because Te has such a low sticking coefficient, however, during the early stages of growth, Te adatoms on MgO do not remain on the substrate for a sufficiently long time to be incorporated into the film. As a result, highly Te-deficient layers are formed with poor crystallinity. These Te-deficient layers ruin the pristine MgO surface and prevent the growth of a good crystalline film, even after MgO is completely covered.

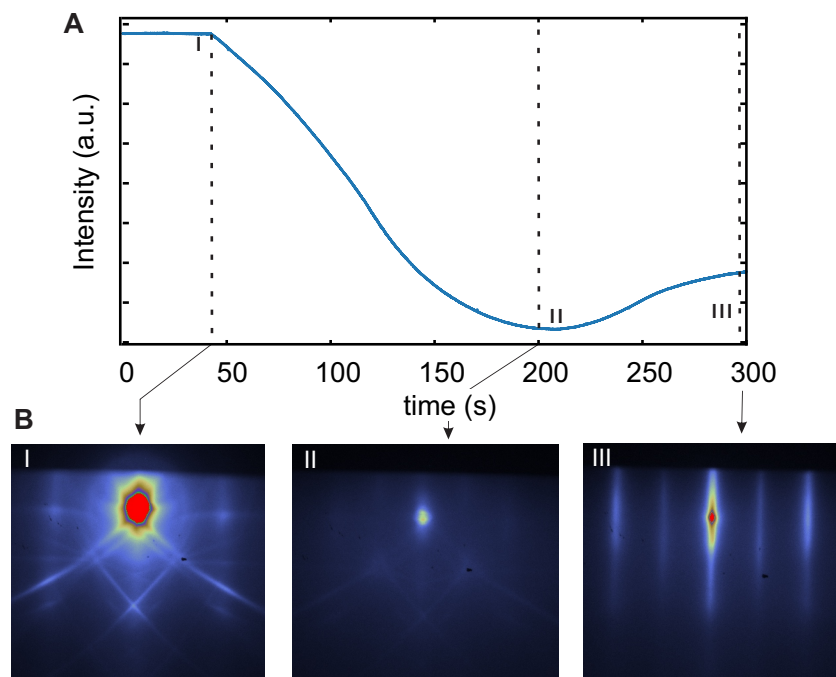


Figure 3.7: **RHEED monitoring of buffer layer growth.** **A** Intensity of specular RHEED spot as a function of time. **B** A set of representative images of I. The pristine MgO surface, II. The buffer layer at the point of minimum intensity, III. The fully grown buffer layer.

To mitigate this issue, we employed a low-temperature buffer layer consisting of a single unit cell of DyTe_2 grown at 200°C . RHEED intensity was monitored so that growth could

be stopped exactly after a single unit cell Fig.3.7. At the beginning of growth the RHEED pattern simply shows that of the MgO surface (Fig. 3.7B.I). The high crystallinity of the substrates reveals high intensity and prominent kikuchi bands. As the buffer growth proceeds, the RHEED intensity drops dramatically as the surface roughens and reaches a minimum (Fig. 3.7B.II). Gradually intensity begins to increase once again as the buffer layer crystallizes. Growth is stopped once the specular intensity reaches a maximum once again indicating the completion of the buffer layer (Fig. 3.7B.III).

The buffer layer was then heated up to growth temperature of 315°C under a constant flux of Te to prevent desorption from the buffer layer while it was heated. A schematic of the growth process is given in figure 3.8. The colored lines labelled by the respective elements represent whether the shutter for the given element is open or closed. The variation in lines representing T_g , the growth temperature gives the approximate range of values for which high-quality films were obtained.

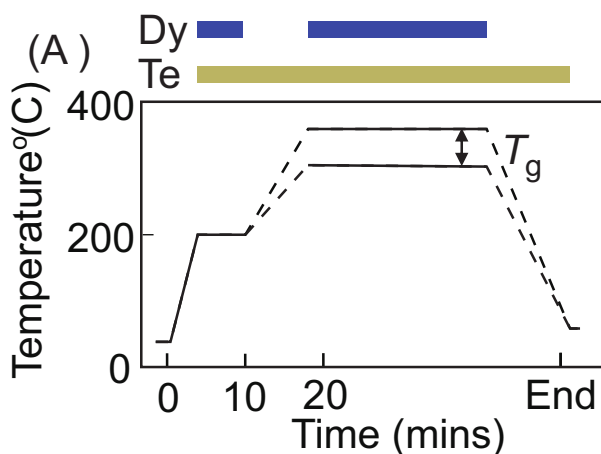


Figure 3.8: **Schematic of the growth process.** Schematic of the optimized two-step growth method to obtain phase-pure high quality DyTe₂ thin films. The plot shows the substrate temperature over time, and the colored bars labeled by elements indicate when fluxes of their respective elements were active.

Once the buffer layer was optimized, the growth window for the film was determined through a combination of X-ray diffraction and RHEED.

Proper phase formation of DyTe₂ could be accomplished using substrate temperatures for film growth ranging from 200°C up to 350°C. Within this range, XRD patterns revealed single phase films with quality comparable to that on 3.5. Rocking curve scans were further used to verify the quality and showed sharp peaks with full-width-half-max of ≈ 0.03 . Thus, XRD was no longer useful for analyzing sample quality as all growths within this regime showed comparable data.

However, RHEED analysis showed clear qualitative differences depending on growth conditions. Unlike XRD, RHEED is primarily a surface sensitive technique. However, given the enhanced cross section for electron scattering compared to x-rays, RHEED is much more sensitive to the formation of ordered defects and surface reconstructions. Furthermore, a high-quality surface is an indication of a high crystallinity film, though the converse is not always true with rough films often showing good crystallinity in XRD. In Fig. 3.9, we show a series of RHEED patterns taken on growths conducted within the temperature ranges indicated. It was found, as discussed before that growth at low temperatures caused rough, disordered surfaces with domains. At the optimal growth temperatures between 300°C and 330°C, sharp, high contrast RHEED patterns could be observed. As the temperature was increased further, RHEED patterns still displayed the proper peaks but began to reveal a hazy background, as well as a small shoulder on the (01) diffraction condition. We attribute this to variation in the lattice constant due to enhanced Te defects.

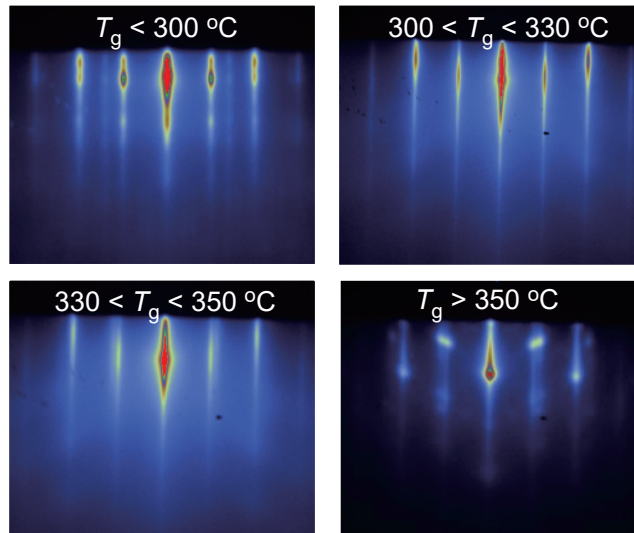


Figure 3.9: **RHEED patterns for differing growth temperatures.** Final RHEED patterns taken from films grown at varying substrate temperatures. **A** 200°C, **B** Between 300°C and 330°C, **C** Between 330°C and 350°C, **D** Above 350°C.

Of primary interest in these experiments was the possibility to epitaxially strain the square net system to enhance or suppress CDW formation and/or topological physics through dimensionality tuning. To this end, films were grown at a series of thicknesses ranging from 3nm up to 35nm. The standard reciprocal space mapping technique often employed on asymmetric peaks in the Q_x - Q_z are of insufficient intensity to be useful. Therefore to measure the in-plane lattice constants in the ultra-thin limit we used grazing incidence geometry [103] (or in-plane diffraction) to measure diffraction from $\{HK0\}$ family of

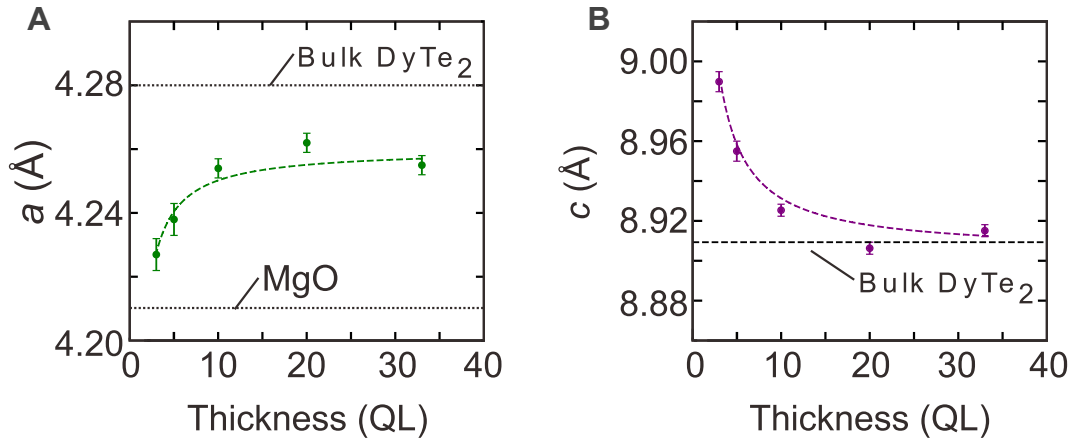


Figure 3.10: **Thickness dependence of the DyTe₂ lattice constants.** **A** a-axis and **B** c-axis lattice parameters.

peaks. This involved setting the incident angle to be only slightly above the critical angle for total external reflection, so that the beam could be strongly absorbed in the lateral direction. Alignment for this procedure is highly nontrivial making it difficult to generate the equivalent of an $\theta/2\theta$ pattern for in-plane peaks. Instead, in-plane reciprocal space mapping was performed around the (110) film peak allowing for simultaneous measurement of the $\vec{a}$ and $\vec{b}$ lattice parameters. A representative in-plane RSM taken from a 5nm film was given in Fig. 3.5A. In Fig. 3.5B, we plot a series of conventional $\theta/2\theta$ scans used to measure the c-axis lattice constants.

The results are summarized in Fig. 3.10. Because of the smaller lattice constant of MgO compared to DyTe₂, compressive in-plane strain is applied to the sample. This results in a reduced a-axis lattice constant value for ultra-thin films. In keeping with the expectations of the Poisson effect, the c-axis is dilated relative to the bulk value. As thickness increases, the lattice constant values evolve with the a saturating at about 4.26Å and c saturating around $c = 8.91\text{Å}$. As shown in Fig. 3.10, the c axis lattice constant is much closer to the bulk value compared to the a axis suggesting that unit cell volume is not strictly conserved. We attribute this to the formation of Te defects, a topic that will be returned to in a later section of this chapter. Further justification for this was given by the fact that films grown at higher temperatures showed no evidence of strain. This is attributed to the ability for defects to also accommodate epitaxial strain, causing the film to relax more quickly than those grown at lower temperatures. Unfortunately, given the material thickness, it was found to be difficult to quantify composition through conventional means such as EDX.

To conclude this section, a growth window for epitaxially strained DyTe₂ was obtained. Through a combination of X-ray diffraction and RHEED, structural quality could be thor-

oughly investigated. We will now proceed to describe the studies we performed with optimized films. Specifically, the formation of a defect lattice and its electronic origin.

in-situ RHEED Studies of Growth Dynamics

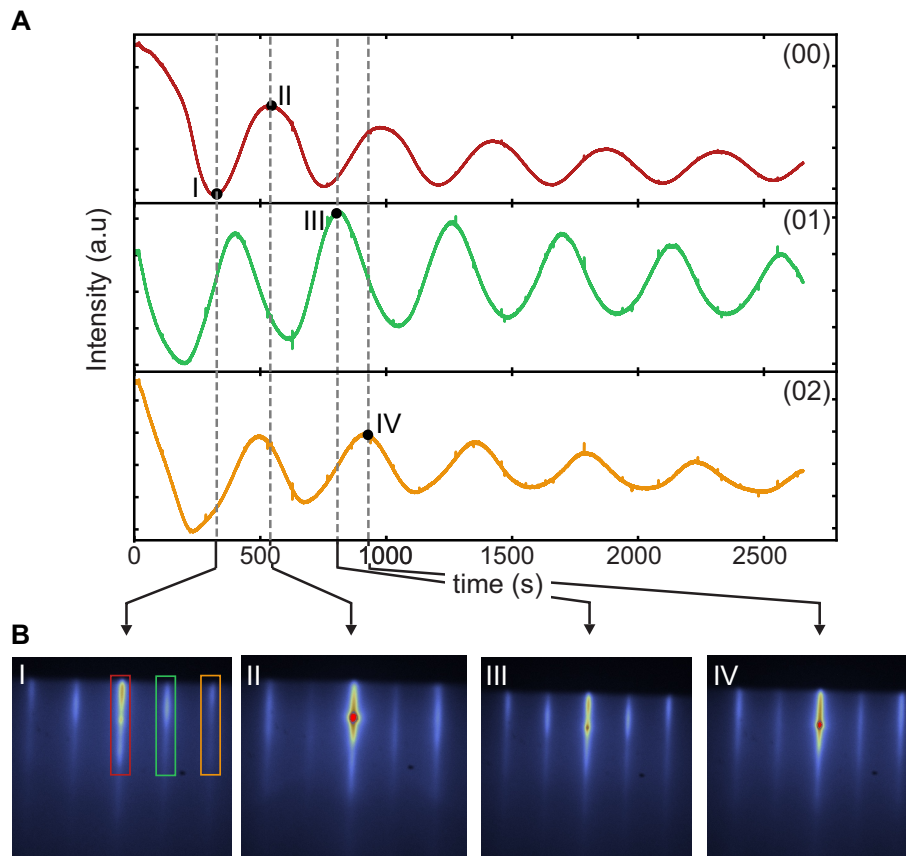


Figure 3.11: *in-situ* RHEED of growth dynamics. **A** Time-dependent intensity profiles from different diffraction conditions. **B** RHEED patterns taken at various times throughout the growth showing the phase relationship that results from the layer-by-layer growth process.

While RHEED was an indispensable tool for the establishment of the growth window allowing for the obtaining of films displaying epitaxial strain, it has a far more powerful ability to monitor growth dynamics in real time. As discussed, this monitoring has allowed for an optimization of buffer-layer growth so that a single mono layer buffer could be obtained. By monitoring the oscillations thorough the remainder of growth, further insights into the layer-by-layer growth could be obtained. As discussed in Ch 2., when electrons scatter from the growing surface, there is often an oscillation in intensity related to the periodic roughening of a growing surface.

In Fig. 3.11A, we have displayed a set of time-dependent intensity profiles of the growth by monitoring the intensity of the diffraction spots. The colors of the lines correspond to the

spot enclosed by a box of the same color in Fig. 3.11B.I. The diffraction index is also given in the upper right hand corner of the plot. The top most curve in Fig. 3.11A displays the specular intensity. It is seen to oscillate with a period of approximately 500s corresponding to the growth of a single unit cell. As time proceeds, this oscillation ultimately decaying due to equilibrium roughening. The green and orange curve represent oscillations from the (01) and (02) peaks. These are not observed to dampen as quickly because they are not as affected by surface roughness compared to the specular intensity. Several important observations can be made regarding the relationship between these three curves. Most significant is the phase shift between them. For example, while the specular intensity reaches a maximum at around 500s, as indicated as position II in the plot, the (01) reaches a maximum much later, around 800s when the specular intensity is close to a minimum (point III). Conversely, the (02) intensity is more in-phase with the specular intensity and reaches a maximum (point IV) only slightly before the specular intensity reaches its second maximum. Images of the RHEED patterns from each of these four points is given below. Of course, as growth proceeds these oscillations dampen and the peaks end with comparable intensity (see Fig. 3.6).

To understand this behavior it is useful to again consider the 2-D unit cell of a DyTe_2 surface (Fig. 3.12). DyTe_2 is assigned the primitive space group $P4/nmm$. However, this is the space group for the entire unit cell and the constituent layers in isolation host different centerings. In Fig. 3.12A, the topmost atoms of the corrugated layer are shown. The primitive centering of this cell results from the center atom and corner atoms being of different elements, Te and Dy respectively. The reciprocal lattice for this layer would therefore have no restrictions of $(hk0)$. On the other hand, the square net Te sheet reveals a centered 2D lattice consisting exclusively of Te atoms. Selection rules for a centered 2D lattice required that $h + k = 2n$. At position III on the green curve, the specular spot is close to its minimum while the (10) is at its maximum. Thus the film at this stage is rough, and the surface is terminated on the corrugated layer. Between positions III-IV, the Te square net begins to form the surface termination and the 2D reciprocal lattice of the Te sheet dominates the RHEED pattern and the 2D lattice is centered leading to suppression of the (10) intensity. Finite penetration of electrons into the lower layers cause the (10) peaks to remain visible but of diminished intensity. As growth proceeds, the surface of the film reaches an equilibrium roughness and can no longer be thought of as exclusively terminating on a given layer. Diffracted intensity will originate both from the square net as well as the corrugated layer, thereby revealing the primitive centering of the full surface unit cell with final RHEED images being the ones given in 3.6

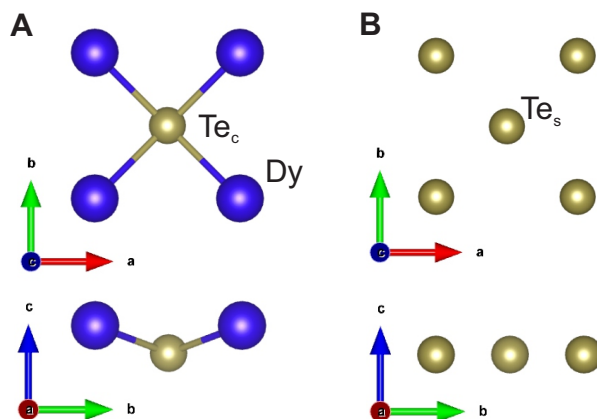


Figure 3.12: **2D unit cells of the top most atomic layers.** **A** The corrugated sheet. **B** The Te square net.

Transmission Electron Microscopy Analysis of Structure

To understand the local atomic structure of the epitaxial $DyTe_2$ films, High-angle annular dark field scanning transmission electron microscopy (TEM) was performed. Images show crystals of high crystalline quality (Fig. 3.13A) with the expected stacked layers of planar Te sheets and corrugated Dy-Te interlayers (Fig. 3.13B). The stacking sequence confirms the presence of the $DyTe_2$ phase and not $DyTe_3$. We attribute the inability for $DyTe_3$ to form to the low sticking coefficient of the Te-sheets, which evidently cannot be stacked in pairs (as is the case in the tritellurides) even with a Te/Dy flux ratio as high as 40. The film is phase pure with a sharp interface formed between the MgO and Te-square net sheet (Fig. 3.13C). The square net tellurium sheet forms the first wetting layer on the substrate, which is in line with the observations from RHEED. The high-angle annular dark-field imaging (HAADF) (Fig. 3.13B) and energy-dispersive X-ray spectroscopy elemental map (Fig. 3.13E-G) shows nominal (P4/nmm) $DyTe_2$ structure. The Dy/Te ratio with absorption and ionization cross-section correction for the foil with a thickness of 30 nm is 0.497. This ratio, at its best, has a 10-20% error because of strong channeling [84, 85]. When the beam is along the zone axis, the intensity of x-ray spectra is not a linear contribution of each element. The high resolution images also capture dissimilar intensity of Te sites along a line profile in the $DyTe_2$ [001] direction, as plotted in Fig. 3.13B. The intensity of the Te columns at the Te sheet (Te_s) and the Te columns at the corrugated layer (Te_c) is different. We attribute this to the phase space for vibrations of the atoms in the square sheet versus those in the ionic Dy-Te layer; the higher thermal vibration in the Te sheets is an indication that the atoms are loosely bound. This observation is in agreement with our experience of being unable to stabilize the tritelluride phase because we can expected higher thermal

vibrations to result in poor sticking coefficient of incoming Te atoms to the Te atoms in the square net layer. As a result, Te adatoms on a Te SN are either incorporated into the next Dy-Te layer, or re-evaporate. The growth of a second Te-interlayer is therefore suppressed in favor of the formation of a next Dy-Te corrugated layer. Such a situation highlights the profound differences between MBE growth and other growth techniques such as bulk synthesis from liquid melts. In the latter, particle number is strictly conserved while the case of MBE growth, there is a dynamical deposition-revaporation process occurring at the surface. This reevaporation of Te is what allows for adsorption controlled growth of DyTe_2 but also prevents the formation of polymorphs consisting of additional Te inter layers such as DyTe_3 or Dy_2Te_5 . Furthermore, because thin films grow (ideally) one layer at a time, the exposure of a given surface to vacuum and the specific surface energetics associated with deposition on that termination may enable, or in this case, prevent the formation of a given crystal phase.

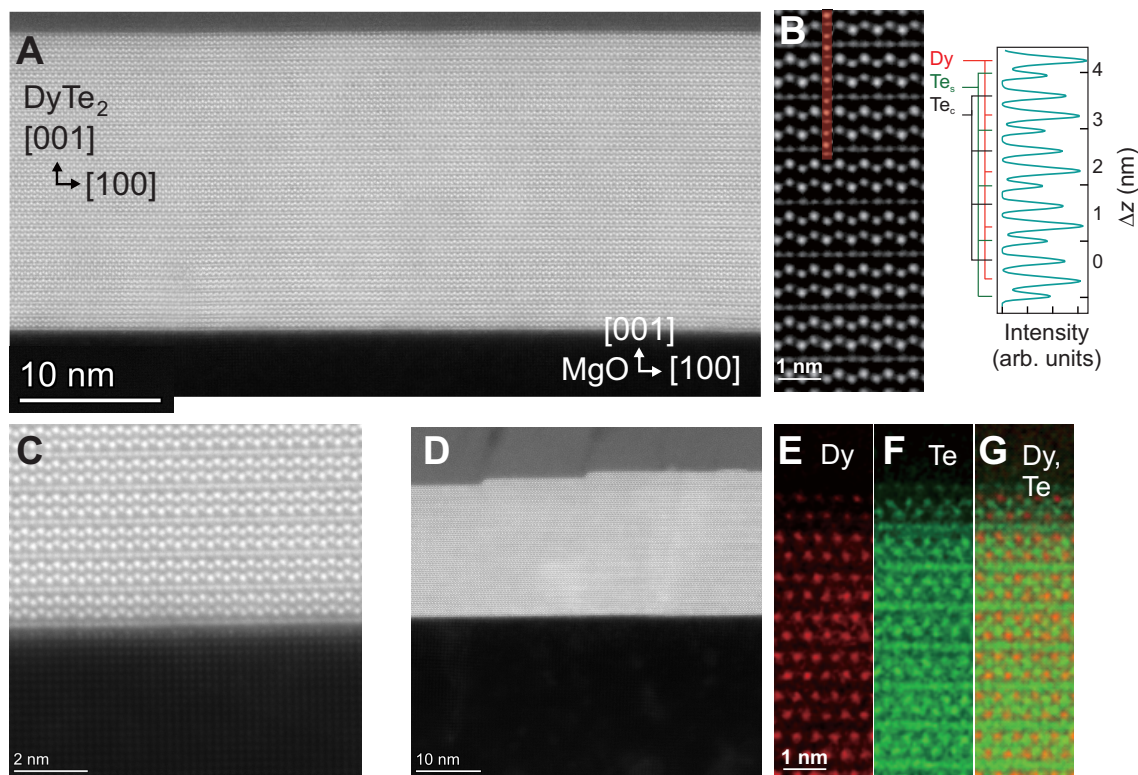


Figure 3.13: **HAADF TEM of DyTe_2 thin films.** **A** Wide area image of the DyTe_2 crystal. **B** High resolution image with line profile of the atomic species. **C** Zoom-in on the film-substrate interface revealing the Te square sheet that forms the initial wetting layer. **D** Step-terrace morphology of the surface. **E-G** Elemental mapping of the unit cell confirming the identity of the atomic species. TEM image Credit: Prof. Salva Salmani Rezaie, Prof. David Muller.

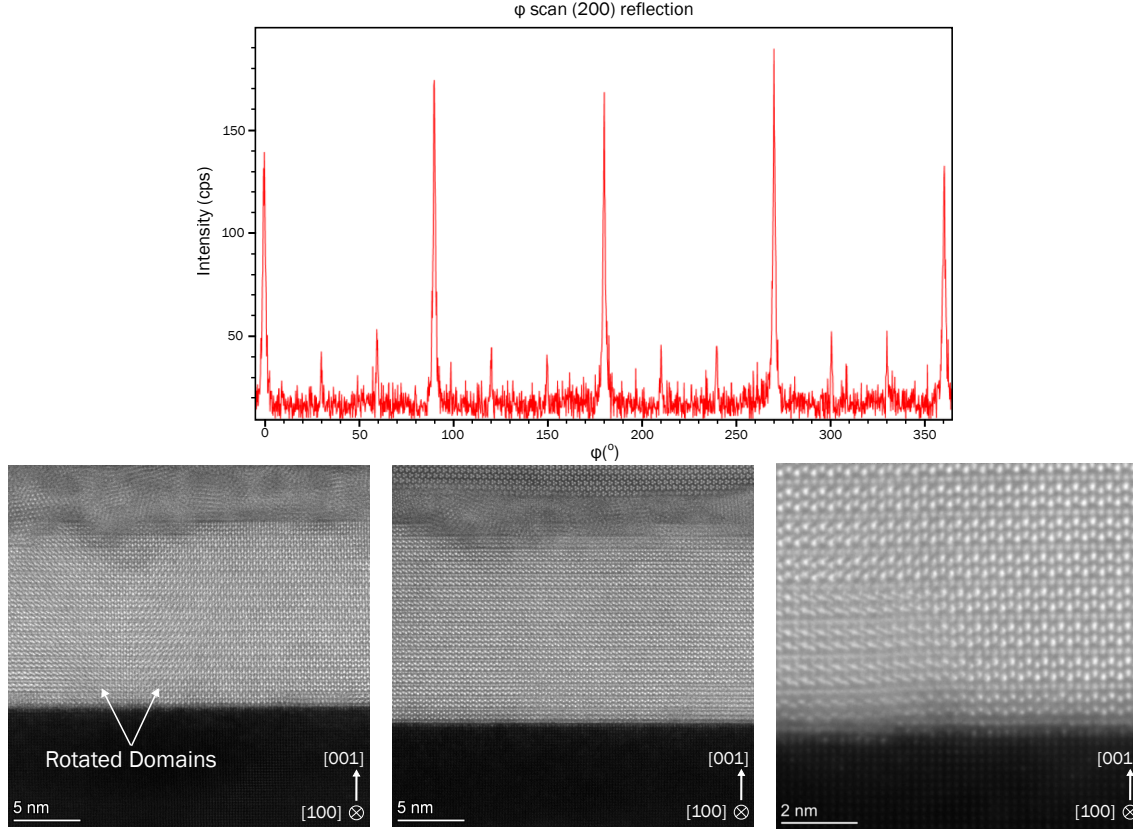


Figure 3.14: **Defect domains in DyTe_2 .** **A** Phi-scan from the (105) diffraction condition confirming the $[100]_{\text{DyTe}_2}||[100]_{\text{MgO}}$ epitaxial relationship. **B-D** TEM images of film defects.

TEM also allows for the observation of defects and domains. Defects primarily take the form of rotational domains and regions of poor crystallinity. This is in contrast to the typical picture of relaxation in epitaxial films grown on mismatched substrates, where strain is typically relieved through the nucleation of threading dislocations. The absence of substantial dislocation formation is surprising since films do show some evidence of epitaxial strain. This would suggest that interaction between film and substrate is reasonably strong, at least compared to the case of true van-der Waals epitaxy [130] where there is no coherent strain across the substrate-film interface. As will be discussed in a subsequent section, we believe that strain is instead relieved through the tilting of the film with respect to the substrate.

In Fig. 3.14a, a grain boundary where two rotational domains meet can be observed. Because it is difficult to characterize the precise rotational domain angle using TEM, a Phi-scan diffraction pattern was obtained by rotating the film in the ϕ direction and measuring the intensity of the (200) reflection. It is found that the film grows predominantly with a

$[100]_{film} \parallel [100]_{MgO}$ epitaxial orientation with domains every 30° . Such a domain structure is often observed in films grown on hexagonal substrates due to the 60° rotational symmetry. However, in the square-on-square geometry adopted by the film, there is no obvious epitaxial relationship to explain this angle.

Tilting of Epitaxial Layers

Relaxation of epitaxial strain in thin films often manifests in the spontaneous generation of dislocations at the interface once the strain energy exceeds the energy to nucleate a dislocation [87, 26]. This strain energy is naturally thickness dependent resulting in a "critical thickness" beyond which epitaxial strain is relaxed by the formation of these defects and the film lattice constants relax to their bulk values. It was found in TEM studies that dislocation formation does not occur readily in $DyTe_2$ epilayers. Instead what appears to occur is that the entire film grows with a finite tilt with respect to the substrate. This tilt can be observed by studying the ϕ dependence of the $(00L)$ diffraction peaks. For a film grown epitaxially on a substrate, the c -axis direction of the film and substrate are ideally parallel. Thus, since the goniometer is aligned using the substrate, one expects no ϕ dependence of $(00L)$ peaks. This is, however, not what is observed for $DyTe_2$ films. In Fig. 3.15A, we present a ϕ scan of the (003) peak. Intensity shows a peak at $\phi \approx 111^\circ$ and $\phi \approx 290^\circ$. Measuring the rocking curve at $\phi \approx 111^\circ$ shows a single peak exactly at the expected diffraction condition. On the other hand, rotating the sample to $\phi \approx 201^\circ$, or exactly 90° relative, the rocking curve peak shifts by $\approx -0.6^\circ$. When rotated by -90° , the peak now appears at $\approx +0.6^\circ$. The non-uniform ϕ dependence indicates that the scattering wavevector has a small component orthogonal to the $\hat{z}$ direction. The measured position of the rocking curve peaks when rotated to 90° allow the tilt angle to be measured and give a value of $\approx \pm 0.6^\circ$. The reason for such strong ϕ dependence can be understood by recalling that the diffractometer only achieves high angular resolution within the scattering plane defined by the source and detector arms. Thus if one rotates the sample so that the tilt is oriented orthogonally to the plane of scattering, a single peak will be registered at the expected diffraction condition multiplied by the cosine of the very small tilt angle (schematically represented in 3.15C. Conversely, rotating so as to move the tilted vector into the scattering plane shifts the position of the rocking curve by an amount equal to the tilt of the sample 3.15D.

Crystallographic tilt of the layer with respect to the substrate normal is a common occurrence in semiconductor [5, 71] and oxide thin films [125, 60] grown on mismatched substrates due to differences between the vicinal step height and the c -axis lattice parameter of the epilayer [91]. Because of this mismatch, strain energy builds as the growing crystal is deformed

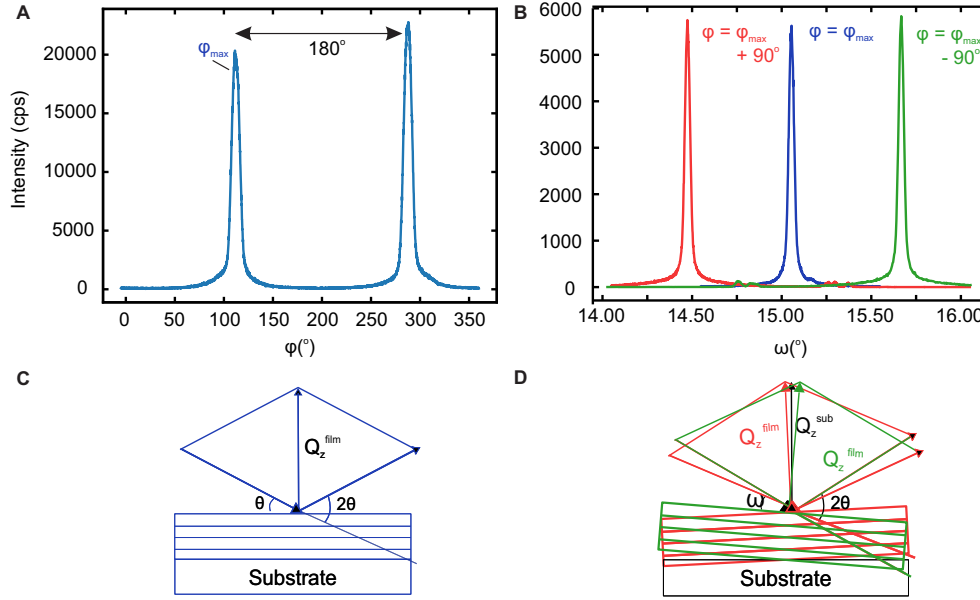


Figure 3.15: **Epitaxial tilting of DyTe₂ on MgO.** **A** Phi-scan of the (003) peak showing non-uniform intensity as the result of tilting. **B** Rocking curves taken at different ϕ angles. **C** Schematic of crystal oriented with ϕ corresponding to the maximum. **D** Schematic of crystal oriented with ϕ oriented orthogonally to the maximum. In this case, the crystallographic tilt is measurable from the offset in the rocking curve.

across the terrace. In response, a dislocation network emerges with a Burger's vector tilted with respect to the substrate terraces to relieve strain. The direction of this vector dictates the angle of tilt observed. Full details of this conventional model were worked out by Nagai [91]. However, there is reason to believe that this mechanism is not relevant in the case of DyTe₂ on MgO. First, we observe little evidence of a dislocation network forming at the interface in TEM. Secondly, the Nagai model applies to systems with mismatched but similar c-axis lattice constants with differences on the order of a few percent. In contrast, the c-axis of the film in these studies was almost 4× the length of the step terrace height. Finally many examples of tilted layers are demonstrated on highly offcut surfaces ($> 1^\circ$), all films grown in these experiments were synthesized on well-oriented MgO (offcut $< \pm 0.5^\circ$).

We therefore propose that the tilt observed is a simple consequence of the offcut angle of the polished MgO $< \pm 0.5^\circ$. Due to the large c-axis mismatch, the film simply tilts to conform to this substrate tilt, in colloquial terms, the film lays on the substrate like a blanket. The first evidence of this is that the angle of tilt is approximately equal to the quoted offcut angle of the substrate. Secondly, mechanisms that rely on strain tilting usually show thickness dependence. However, tilt on our samples has been observed in films of all thicknesses. Further evidence of this can be seen from the AFM image taken of the substrate before

growth. We see the step terraces form at an angle with respect to the substrate edge ($||[100]$). This angle is exactly that which corresponds to the ϕ scan maximum. Unfortunately, systematic exploration of these matters would require extremely high control over substrate manufacturing as common commercial MgO substrates are polished such that step terraces which form at arbitrary angles relative to the edges and often have offcut angles which can only be controlled within $\pm 0.5^\circ$. This makes the influence of crystallographic direction difficult to control for. We will conclude this section by remarking that this tilting behavior is seen in almost every high-quality DyTe₂ film that we have synthesized. Generally this tilting was most dramatic for the best quality films.

We suspect that the reason for these observations lies in the unique aspects of the RTe₂ crystal structure. These structures are not true van-der Waals materials in the same vein as TMDCs or traditional topological insulators such as Bi₂Se₃, because epitaxial strain can still be observed. However, when DyTe₂ grows, the Te sheet forms first at the interface as can be seen in the TEM images in the previous section. This Te sheet possesses weak out of plane bonding with the rest of the structure. This leads to a weakened substrate-film interaction and the film will simply exhibit global tilt so as to minimize strain across the structure. We also observe this tilting, to a lesser degree, in our studies of epitaxial LaSb₂. We conjecture that this is a ubiquitous phenomenon for epitaxial square net materials with similar bonding behaviors.

3.4 Studies on the Te-Defect Superlattice in DyTe₂

It is known that in the case of La and Ce the ditelluride structure is stable over a range of stoichiometries in the bulk, typically within the range of $x = 1.8 \sim 2.0$. The effects of such off-stoichiometries in the case of LaTe_{1.8} leads to a gap opening at the chemical potential [104]. The off-stoichiometries are known to produce a variety of structural modulations depending on Te deficiency. The most commonly observed modulation, for a Te deficiency of 20%, was a $(\sqrt{5} \times \sqrt{5} \times 2)$ superlattice of the LnTe₂ aristotype. The u.c. of this ordered defect modulation is oriented parallel to the [210] direction of the higher symmetry structure. This defect modulation is reminiscent of that observed in the insulating phase of Fe-deficient FeSe [77] and in certain oxygen-deficient surface reconstructions of SrTiO₃ [92].

Using grazing incidence X-ray diffraction (Fig. 3.16C), we are able to analyze the structural modulations present in DyTe_{2- δ} thin films, as shown in Fig. 3.16A where we plot diffraction of a 20 unit cell film in the (hk0) plane. The enhanced intensity in grazing incidence geometry for thin films enables use to resolve the presence of the $\sqrt{5} \times \sqrt{5}$ modulation of

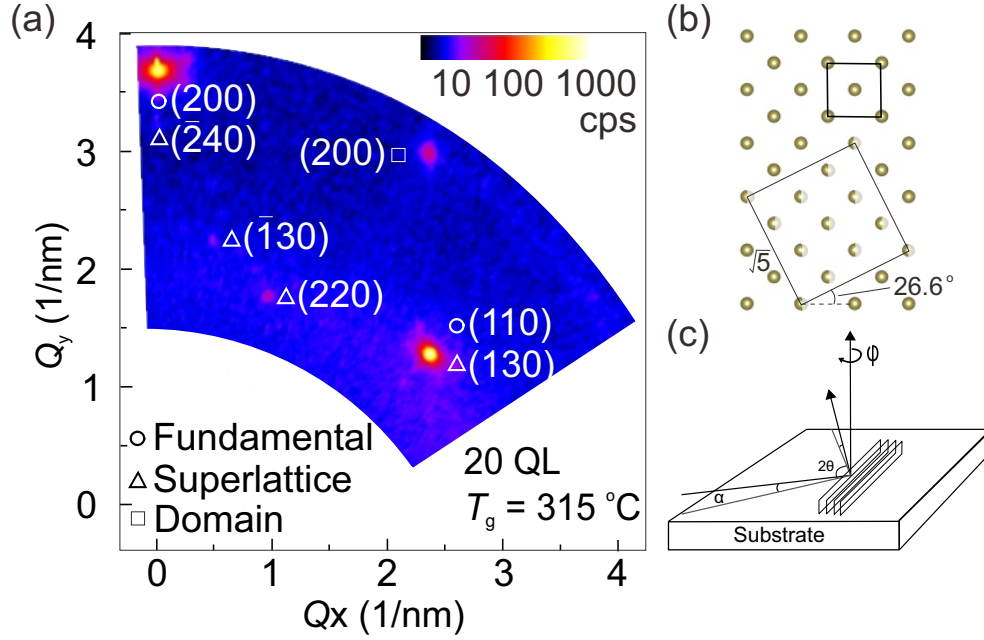


Figure 3.16: **Diffraction from the defect superlattice.** **A** In-plane RSM of the a-b plane revealing weak spots originating from the $\sqrt{5} \times \sqrt{5}$ superlattice modulation. **B** Relationship of the supercell to the base unit cell of the Te sheet. **C** Schematic of the scattering geometry.

the a-b plane, indexed by the diffraction spots identified by triangles in the figure, which are absent in the undistorted structure. The supercell wavevectors are given by $\vec{q}_1 = \frac{-1}{5}\vec{a}^* + \frac{2}{5}\vec{b}^*$, $\vec{q}_2 = \frac{2}{5}\vec{a}^* + \frac{1}{5}\vec{b}^*$ and $\vec{q}_3 = \frac{1}{2}\vec{c}^*$. Diffraction indices given by triangles are with respect to the full supercell whereas those identified by circles are referenced to the undistorted structure. The presence of the $(\bar{1}30)$ reflection in this region of reciprocal space indicates the presence of a rotated domain with modulation wavevector $\vec{q}_1 = \frac{1}{5}\vec{a}^* + \frac{2}{5}\vec{b}^*$, $\vec{q}_2 = \frac{2}{5}\vec{a}^* - \frac{1}{5}\vec{b}^*$ and $\vec{q}_3 = \frac{1}{2}\vec{c}^*$. As previously discussed, $\theta - 2\theta$ diffraction measurements revealed additional features at 0.5 reciprocal lattice units, which correspond to a doubling of the unit cell along the c -axis. Additionally in RHEED, we are able to resolve weak streaks associated with an in-plane modulation (see Fig. 3.17). Taken all together, these diffraction features provide strong evidence for the $(\sqrt{5} \times \sqrt{5}) R_{26.6^\circ} \times 2$ reconstruction being stabilized in the films. The presence of the defect lattice would imply an off-stoichiometry in the range of 10~20%, which is consistent with the EDX-obtained chemical ratios within the uncertainty of the measurement. All films with thickness greater than 10nm showed features consistent with the 2-fold modulation of the c -axis (Fig. 3.5). However, the comparably weaker diffracted intensity from films in the thin-limit combined with the intrinsically weak intensity from superlattice diffraction spots prevented the observation of the superlattice below 20 u.c. with our lab-based diffractometer. Additionally, streaks associated with this distortion were

also visible in RHEED (Fig. 3.17).

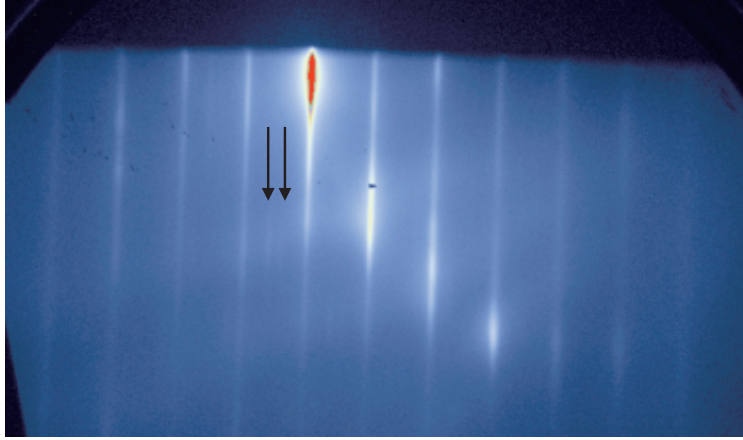


Figure 3.17: **RHEED diffraction showing the $\sqrt{5} \times \sqrt{5}$ modulation.**

In Table 3.4, a list of indexed diffraction peaks from the reciprocal space maps are given along with a comparison to values listed in the literature [104]. Lines left blank in the "Measured" column indicate reflections that could not be observed due to low intensity while those left blank in the "Reference" column indicate reflections that are not expected to show up in the absence of twins. The sections labeled "Fundamental" have indices referenced to the undistorted $P4/nmm$ structure while those labeled with "Superlattice" are referenced to the $(P4/n)$ superlattice structure. The deviation in Bragg angle can be attributed to the smaller fundamental lattice constant for the films ($a_o^{film} = 4.26\text{\AA}$ vs $a_o^{bulk} = 4.28\text{\AA}$) as discussed in the main text where a_o is the measured value of the lattice constant referenced to the $P4/nmm$ as determined from the Bragg angle from the (200) and other peaks in the Q_x - Q_z reciprocal space map. Therefore, several peaks can be indexed different ways depending on choice of unit cell. For example, The (420) of the $P4/n$ supercell corresponds to the (200) of the $P4/nmm$ fundamental structure. Both are included in the table to emphasize this relationship. Reflections from the fundamental unit cell were used as a reference for the azimuthal angle alignment and have ϕ values that are exact, as can be seen in the table. Reflections marked with an asterisk indicate reflections from rotated twins as described in the main text. The tabulation of the ϕ (measured counterclockwise relative to the Q_x direction) demonstrates the relationship between rotated twins where $\phi_{twin} = 90^\circ - \phi$ where ϕ is the azimuthal position of the given superlattice reflection.

While x-ray diffraction could provide detailed information on the crystal structure, solving the atomic arrangements is a much more difficult task with only the limited regions of reciprocal space available in thin-film scattering. Intrinsically low intensity from thin films makes

	Measured $a_o = 4.26 \text{ \AA}$		Reference $a_o = 4.28 \text{ \AA}$	
	$2\theta_B$ ($^\circ$)	ϕ ($^\circ$)	$2\theta_B$ ($^\circ$)	ϕ ($^\circ$)
<i>Fundamental (P4/nmm)</i>				
(110)	29.63	45.00	29.50	45.00
(200)	42.44	0.00	42.22	0.00
(020)	42.46	90.00	42.22	90.00
<i>Fundamental Domain</i>				
(200)	42.44	30.19		
(200)	42.44	59.81		
<i>Superlattice (P4/n)</i>				
(020)			18.54	63.43
(220)	26.54	18.44	26.33	18.37
($\bar{1}$ 30)	29.64	81.84	29.51	81.99
(130)	29.64	45.00	29.51	45.00
(420)	42.44	0.00	42.22	0.00
($\bar{2}$ 40)	42.46	90.00	42.22	90.00
<i>Superlattice Domain</i>				
(020)*	18.61	26.54		
(220)*	26.55	71.52		
($\bar{1}$ 30)*	29.65	8.16		

Table 3.1: Observed (hk0) reflections with comparison to bulk crystal report. The sections labeled “Fundamental” have indices referenced to the undistorted P4/nmm structure while those labeled with “Superlattice” are referenced to the P4/n superlattice structure.

full refinement of the structure even more difficult. To gain more insight into the atomic defect arrangement, we collaborated with Prof. Nicholas Kioussis and Dr. Jinwoong Kim who performed DFT calculations to attempt to determine the crystal structure. Several defect arrangements have been previously observed in bulk crystals of similar compounds where structural refinement could occur. A series of such candidate defect arrangements is given in Fig. 3.18(A-F). These defect arrangements feature a variety of differing Te-based fragments. The fragments are the result of removing one or two Te atoms from various positions in the expanded $\sqrt{5} \times \sqrt{5}$ supercell as labelled in 3.18a. For example the “A-B” configuration is generated by removing atoms at positions A and B and drawing bonds between nearest Te atoms in the relaxed unit cell. By calculating the total energy of the given structure as a function of lattice constant (Fig. 3.18F) we find that the lowest energy is given by the 2 vacancy “A-C” configuration. This corresponds to a stoichiometry of $\text{DyTe}_{1.8}$. We also observed (Fig. 3.5) a doubling of the lattice constant in the c-axis direction. For the A-C configuration, calculations also revealed that the position of the divacancies in adjacent Te sheets are laterally displaced by (0.5, 0.5). This explains the two-fold modulation in

the c-axis direction. As observed in Fig. 3.10, film lattice constants saturate below the bulk values of $\text{DyTe}_{2-\delta}$. This could point to additional Te defects but these are randomly distributed through the distorted Te sheet. A further insight, highlighted in Fig. 3.18F is that the presence of epitaxial compressive in-plane strain further stabilizes the defect lattice.

Within the unit cell, There are 10 Dy atoms and 10 Te_c atoms within the corrugated layer. The unit cell of the Te sheet consists therefore of 8 Te atoms and 2 vacancies. The Te fragments in the A-C configuration appear in two varieties where two Te atoms form a dimer while the other six form into two separate linear trimers. The existence of these fragments can be rationalized by electron counting and application of the Zintl-Klemm concept [99]. Using Zintl rules, we rationalize the substructures that occur within crystals by assigning oxidation states and forming fragments that locally satisfy the octet rule. We begin by assigning to Dy, an oxidation state of +3 and to Te_c an oxidation state of -2. This leaves 10 electrons to be distributed among 8 Te atoms within the sheet. Of those 8 Te, 2 are assigned a -1 oxidation state. With $7e^-/\text{Te}$, these atoms are expected to form an isolated dimer similar to the behavior of halogen atoms with $7e^-$. The remaining 6 Te atoms take the form of isolated trimers each with $4e^-$. This bonding arrangement is known as a 3 center-4 electron (3c-4e) bond and is a commonly observed arrangement for electron rich (hypervalent) molecules [99].

Electrical transport measurements on $\text{DyTe}_{2-\delta}$ epitaxial films show semiconducting transport which we present in Fig. 3.19A. However, in an undistorted DyTe_2 lattice, the assignment of at +3 oxidation state to the Dy atoms implies $7e^-/\text{Te}$ in the Te sheet which would lead to the expectation of metallic transport (in the absence of dimerization). We hypothesized that the formation of the superlattice which observed in x-ray diffraction was responsible for driving the system insulating due to the lowered symmetry of the superlattice compared to the fundamental lattice. It has further been suggested [70] that the formation of a defect lattice could be driven by energetic considerations related to the nesting of the Fermi surface, as was described in Ch 1 of this thesis.

To test whether such a mechanism was present in the case of $\text{DyTe}_{2-\delta}$ DFT calculations were performed to determine the nesting of the Fermi surface. The results of the calculations are provided in Fig3.19b-e. Since the results presented in Fig. 3.18 revealed that the "A-C" configuration was the most stable defect arrangement, calculations were performed for this structure Fig3.19D. In Fig. 3.19B, the calculated Fermi surface of undistorted DyTe_2 is presented with the Fermi energy set to be the value corresponding to be the value corresponding to the addition of $\delta = 0.2$ and the resulting electron doping. As one can see, the Fermi surface is highly 2-dimensional with large parallel sections which can be nested

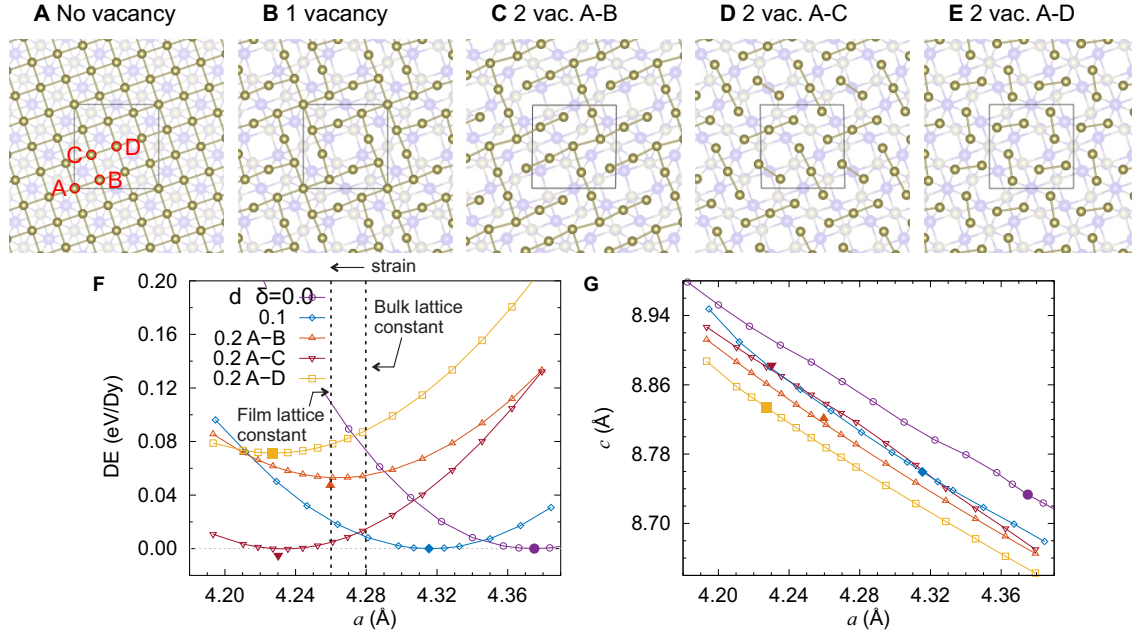


Figure 3.18: **Defect arrangements for DyTe₂.** **A** Labelled atomic sites. Atoms will be removed from these sites to form the defect arrangement, which are labelled by which sites are replaced by vacancies. **B-E.** **F**, Energy of the defect arrangement as a function of lattice constant. **G** Calculated c-axis values vs a-axis values. Credit: Dr. Jinwoong Kim.

by a single $\vec{q}$ wave vector. In figure Fig3.19C, a plot of the degree of nesting is displayed. Details for the computation of this quantity can be found in the supplementary text of [79]. The colors in this figure are mapped by the degree of nesting with the red portions corresponding to regions of higher nesting. The yellow spots correspond to the wave vector associated with the defect superlattice as measured in x-ray diffraction. Therefore, much like the arguments for the formation of conventional CDW driven by electron-phonon coupling, the energetic mechanism by which the defect lattice is formed can be explained by a gapping of highly nested regions of Fermi surface by a lattice distortion. However, in order to bring about this nesting condition, additional band filling was required and accomplished through the removal of Te. The superlattice could then be formed by arranging Te defects so as to form a superlattice with the correct modulation.

Finally, the band structure of the defective DyTe₂ is presented in 3.19E. We see that the formation of the defect superlattice results in a band structure, with a bandgap of $\approx 0.3\text{eV}$, which explains the semiconducting transport.

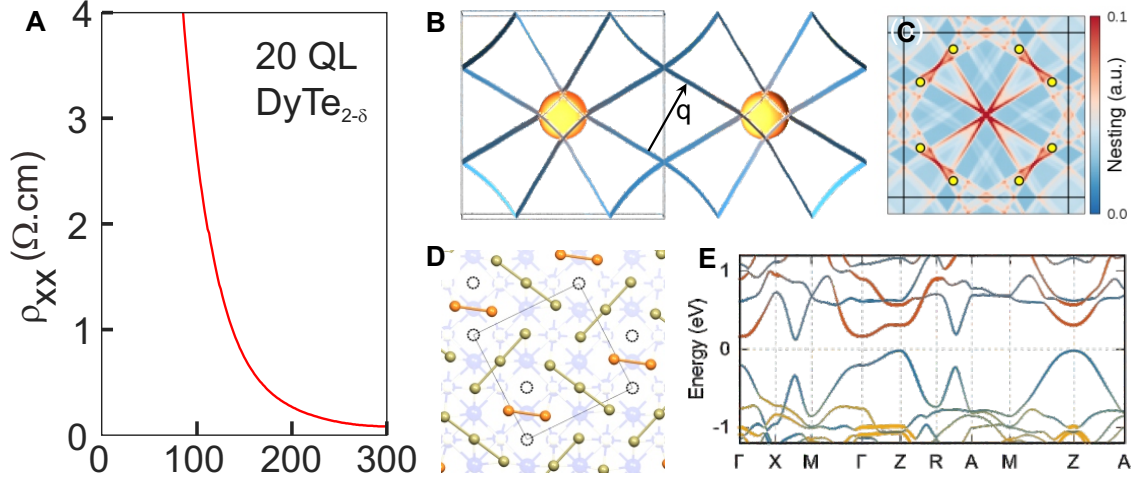


Figure 3.19: **Electronic origin of semiconducting transport behavior.** **A** Temperature dependence of resistance for DyTe₂. **B** Calculated Fermi surface with the nesting vector corresponding to the $\sqrt{5} \times \sqrt{5}$ modulation. **C** Computed nesting function, where intensity corresponds to the degree of nesting, as discussed in the text. The yellow points correspond to the $\sqrt{5} \times \sqrt{5}$ wavevector, providing evidence of a nesting origin for the defect lattice. **D** Lowest calculated energy defect arrangement. **E** Band structure of the distorted structure showing an insulating electronic structure.

3.5 Conclusions

In this chapter, we presented the first demonstration of epitaxial growth of the RTe₂ class of materials, in particular DyTe₂. We found that films could be epitaxially strained, but only for a very narrow temperature growth window. In films of optimal quality, a defect lattice originating from Te vacancies in the square-net sheet could be characterized. This allowed for DFT studies to be performed. The result of these studies was first, a proposal for the likely defect arrangement in the Te sheet as well as an understanding of the origin of the defect lattice formation, namely, the strong degree of nesting of the 2-D Fermi surface of the Te sheet at the modulation wave vector.

As discussed in the introductory chapters of this thesis, one goal of synthesizing epitaxial films of square-net materials is the ability to impose epitaxial strain. This should allow for a tuning of their structures to be more or less two-dimensional depending on whether applied in-plane strain is compressive or tensile. Furthermore, since compressive strain will increase orbital overlap, it was thought that instabilities toward density wave formation could be suppressed. However, in the case of DyTe₂ and related compounds, crystals tend to prefer the spontaneous formation of commensurate defect lattices driven by the nesting of the Fermi surface. As the calculations showed, application of compressive in-plane strain serves primarily to only further *stabilize* the defect lattice. This fact was

further emphasized by the observation that the thickness-dependent in-plane lattice constants appeared to saturate prior to reaching the bulk value. While films of high structural quality could be synthesized, these observations lead us to conclude the RTe_2 class of materials is limited by thermodynamic considerations and that effort would be better spent on materials with more favorable thermodynamics.

STABILIZATION OF MONOCLINIC LANTHANUM DIANTIMONIDE

4.1 Introduction

Structure and Stacking Arrangements of LnSb_2 Materials

In contrast to the SN telluride materials, Antimony-based LnSb_2 (Ln = lanthanide element) compounds form stoichiometric crystals and refined structural analysis [133] describes the unit cell as being formed by two quintuple layer (QL) blocks, each consisting of two Ln-Sb corrugated layers sandwiching a two-dimensional Sb square net sheet. As discussed in the first chapter, variations in electron count on the square net Sb sites as determined by the rare-earth ionization state leads to a variety of bonding and stacking arrangements [99]. In the case of EuSb_2 , the Eu^{2+} valence state causes a distortion of the Sb square net into zig-zag chains and a monoclinic crystal structure [49, 95] while the orthorhombic structure of YbSb_2 is stabilized [132] by a small admixture of Yb^{3+} ions within a predominantly 2+ network [127]. Finally, in the case of (La, Ce, Nd, Sm) Sb_2 compounds, the 3+ valence again gives rise to an orthorhombic crystal in the so-called SmSb_2 structure type [133, 12]. This latter structure differs from the YbSb_2 in the stacking arrangement of QL along the c -axis direction, which can be conceptualized by a displacement vector $\vec{d}$ within the a - b plane, as illustrated in Figure 4.1a. If one considers the displacement of consecutive QL blocks by a vector $\vec{d}$, the SmSb_2 structure is obtained by translating the second block relative to the first along the the direction $\vec{d} = \frac{\vec{a}}{4} + \frac{\vec{b}}{4}$ and the third block back along $\vec{d} = \frac{-1}{4}\vec{a} + \frac{-1}{4}\vec{b}$. The compensation of the glide by the third layer renders the structure orthorhombic. In the case of YbSb_2 , a glide along $\vec{d} = \frac{1}{2}\vec{b}$ and $\vec{d} = \frac{-1}{2}\vec{b}$ between the first and second layers respectively, gives rise to the observed atomic arrangement. Finally, a third stacking arrangement named "monoclinic YbSb_2 " is also displayed. This structure features an uncompensated glide between layers rendering the system monoclinic. It will form the focus of the present chapter and will be discussed in more detail later. These stacking sequences are illustrated in Figure 4.1 below the images of the respective crystal structures.

LaSb_2 stands out as a particularly sensitive structure which is susceptible to electronic and structural instabilities when tuning T and P . Bulk crystals grown with the self-flux method [14] form large, micaceous crystals with high residual resistivity ratios (RRR) [12, 34] and non-saturating positive magnetoresistance (MR) [12, 141]. Pronounced hysteretic electrical resistance when sweeping T is resolved under ambient P conditions [25, 82, 135,

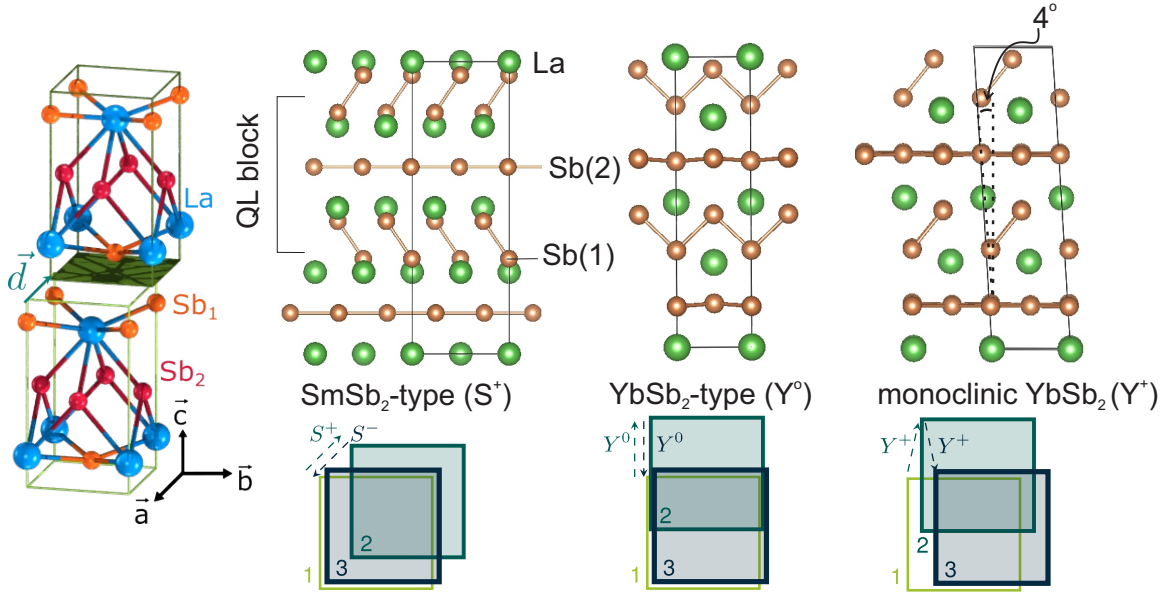


Figure 4.1: **Stacking arrangement in LaSb_2** **A** Conceptual "unit cell" with two quintuple layer building blocks displaced from one another. This displacement determines the observed crystal structure. **B** Orthorhombic " SmSb_2 " structure type **C** YbSb_2 structure **D** novel monoclinic LaSb_2 structure

98]. Under application of moderate P , the hysteretic feature is suppressed to low T and is completely absent by $P \approx 12$ kbar. Accompanying this suppression is a sharpening of the superconducting (SC) transition under P and an increase in SC critical temperature (T_c) to a maximum of $T_c \approx 2$ K [11, 44, 135]. However, due to the micacity of crystals, reliable structural analysis at high P remains challenging and therefore complicates a full understanding of correlation between structural and electronic properties.

We find that when grown as a thin film, LaSb_2 forms a novel, monoclinic phase with a superconducting $T_c \sim 2\text{K}$ and a long coherence length $\xi \sim 1000\text{\AA}$. The temperature dependence of resistance is free from resistance anomalies and the high field magnetoresistance (MR) is linear in character while the hall resistance shows evidence of multi-carrier transport. In this chapter, we discuss the growth of thin-film LaSb_2 , the structural analysis used to verify the monoclinic structure and finally, and the characterization of the basic electronic properties at low temperature. Extended discussion of the superconducting properties will take place in the subsequent chapter. We will end with a discussion about the origin of this novel phase and its relationship to the structure at high pressure.

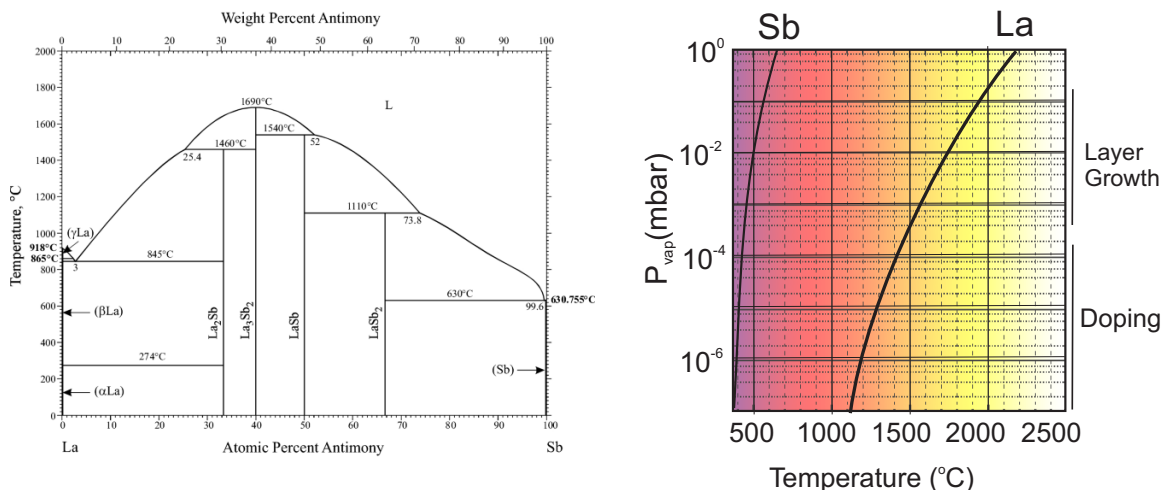


Figure 4.2: **Phase equilibria and vapor pressures of the La-Sb system.** A Bulk Phase diagram for the La-Sb system [96]. B Vapor pressures of La and Sb.

4.2 MBE Growth of LaSb_2

Optimization of Phase Purity

In contrast to LnTe_2 , the LnSb_2 materials form stoichiometric line compound on the Sb-rich side of the binary phase diagram (Figure 4.2). Thus, the approach for stabilizing LaSb_2 will be to perform growth in Sb-rich conditions at temperatures below the melting temperature of bulk LaSb_2 ($T_m \approx 630^\circ\text{C}$). To understand the effect of flux ratio on the grown film, growths were performed in varying Sb/La flux ratios. In Figure 4.3 we present x-ray diffraction on a series of films grown at varying flux ratios at a substrate temperature of 540°C . It can be seen that for flux ratios below 10, a set of impurity peaks appear. These can be indexed according to reflections from Sb-deficient phases. Thus, we select a flux ratio of 15-20 for the remainder of growths.

To verify the stoichiometry of the grown films, quantitative compositional analysis was performed using Rutherford Backscattering at the Goldwater Materials Center at Arizona State University. For films of sufficient Sb/La flux ratio, films with the expected La:Sb ratio of 1:2 are obtained.

A contrast can be drawn between this compound and $\text{DyTe}_{2-\delta}$. Whereas in the latter case, the crystal readily forms off-stoichiometry, LaSb_2 acts more conventionally and phase segregates into Sb-deficient impurity phases.

Estimation of Growth Rate

Due to the subpar lattice match for $\text{LaSb}_2/\text{MgO}_{(100)}$, higher levels of structural disorder were observed. As a result, the Laue fringes used to estimate film thickness were no longer

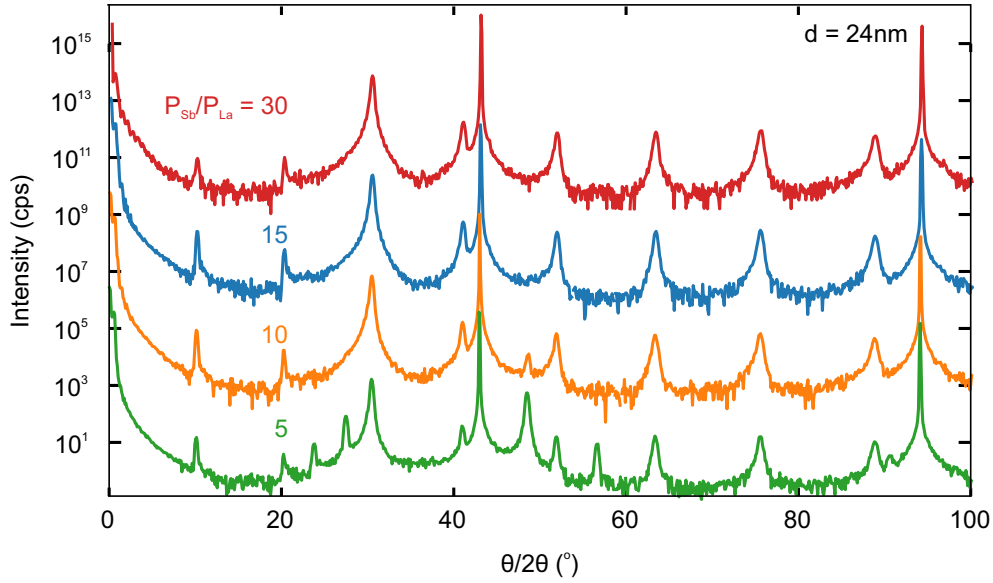


Figure 4.3: XRD taken on films growing at varying flux ratios

visible by $d \sim 22\text{nm}$. To estimate the growth rate, we plot the film thickness measured for thinner films (where Laue fringes were still visible and can be fit). As can be seen in Fig. 4.4A, the growth rate is very constant and we assume this growth rate to remain so for thick films. This assumption is justified by the observation that the post-growth beam flux pressure is identical to that at the start, even for growths as long as 12hrs. An example fit to obtain the film thickness is given in the inset.

Optimization of Structural Quality

With an understanding of the necessary fluxes to obtain single-phase films, the structural quality can now be optimized with the goal of obtaining single crystalline films with atomically flat surfaces. Due to the comparably large lattice mismatch and orthorhombic crystal structure, the growth of the antimonides was found to be far more sensitive to the growth conditions than the tellurides and it was found that non-optimal growth conditions would result in films with substantial domains. In this section we describe how we were able to obtain high-quality LaSb_2 .

As in the case of the tellurides, RHEED will be an important tool for the optimization of growth and characterization of the structure. Because these are the first demonstrations of thin films of LaSb_2 , we will describe the observed RHEED pattern in detail. In Fig. 4.5A, we display the RHEED pattern looking down the $[100]$ zone axis. Similar to $\text{DyTe}_{2-\delta}$, the 2-D unit cell of the LaSb_2 surface is primitive and the streaks are indexed accordingly. A notable difference between LaSb_2 and $\text{DyTe}_{2-\delta}$ is the presence of half-integer streaks along

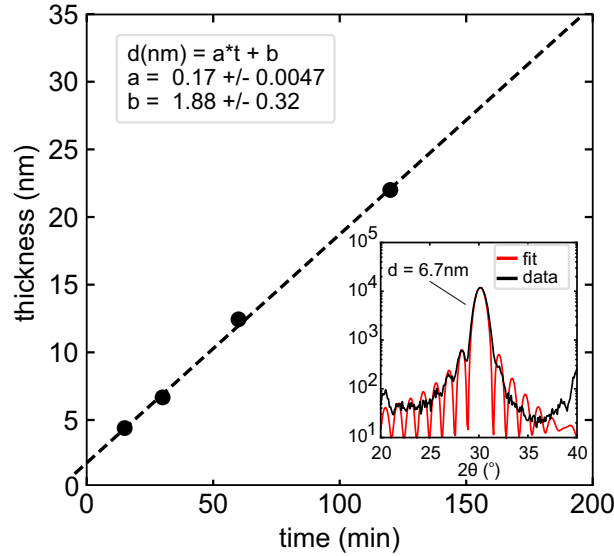


Figure 4.4: **Estimation of Growth Rate to Determine Sample Thickness.** Thickness was determined by fitting the Laue fringes of thin films (inset). A straight line was fit to the data to extrapolate the growth rate to determine thicknesses where Laue fringes were no longer visible.

this direction. A natural interpretation is that this is caused by a 2×2 surface reconstruction. However when viewed along the $[110]$ direction, the expected half order peak is absent. Instead, a set of two weak streaks can be seen in the lower half of the image. These patterns indicate the presence of a $(2 \times 1) \times (1 \times 2)$ reconstruction. A schematic of such a reconstruction is given in Fig. 4.5. The green spots indicate a surface unit cell doubled along $\vec{b}$ while the pink indicate doubling along $\vec{a}$. This kind of reconstruction is in fact a twinned structure. Only one of the two crystal axes undergoes the 2×1 reconstruction. However due to twinning between the a and b axes, this reconstruction can be viewed along any 100 zone axis. A schematic of the resulting 2D reciprocal lattice is given in Fig. 4.5. The labels correspond to the black dots and index the unreconstructed lattice. The reconstruction gives rise to half-order peaks along both the $[100]$ and $[010]$ directions but not along the $[110]$ direction. Instead, the Ewald sphere weakly intersects the half-order spots, thereby giving rise to the weak sets of two streaks observed at the bottom of in Fig. 4.5. We also note that in contrast to the observations in the tellurides, no apparent "arcs" are observed that were previously argued to originate in the disorder in the a and b lattice constants arising from the defect lattice. This is expected because LaSb_2 is a stoichiometric compound.

The primary defects that were sought to be suppressed were misoriented domains. These typically manifested as crystalline regions with a $[100]_{\text{film}} \parallel [110]_{\text{MgO}}$. This is illustrated

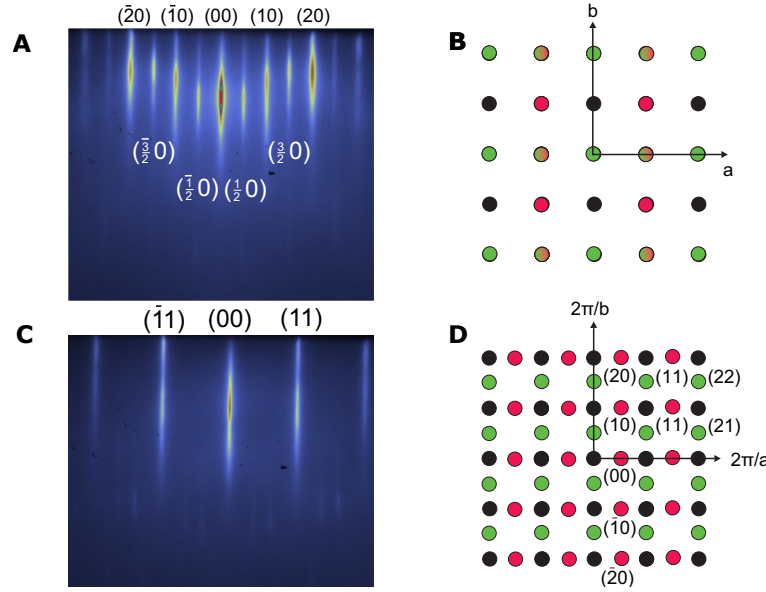


Figure 4.5: **Surface reconstruction of LaSb_2 .** **A** RHEED pattern of the $[100]$ zone axis. **B** Schematic real space lattice. Red and green dots represent the 1×2 and 2×1 reconstructions, respectively. **C** RHEED pattern along the $[100]$ zone axis. **D** Schematic of the surface 2D reciprocal lattice showing the effect of the 1×2 and 2×1 reconstructions.

later on in Figure 4.14a where in TEM the presence of domains rotated 45° is clear, especially close to the substrate-film interface. In RHEED, this manifests as a set of streaks corresponding to the $[110]$ zone axis being visible even when the substrate is oriented parallel to the $[100]$ direction. The streak spacing of these domains being $\sqrt{2}$ larger than those from the 100 planes is further confirmation of their identification as resulting from a rotated domain.

RHEED

To establish a baseline of expected “optimal” behavior, when monitoring with *in-situ* RHEED analysis, we refer to Fig. 4.6. In Fig. 4.6A, we display a series of intensity profiles taken from the streaks as oscillations begin immediately upon growth, (Fig. 3.11), in the case of LaSb_2 , a prolonged period of dropping intensity is observed. This is indicative of the formation of a poorly crystalline interface. At around 400s, corresponding to approximately 1.5 QL of growth, the intensity begins to increase as the film begins to crystallize. The streaks get sharper and more intense indicating higher structural quality. The intensity continues to climb until reaching a maximum at around 800s. The diffracted intensity then begins to oscillate weakly, however its oscillation is damped quickly and is not observed to continue beyond what is shown in the figure above. Diffraction from the other peaks follows

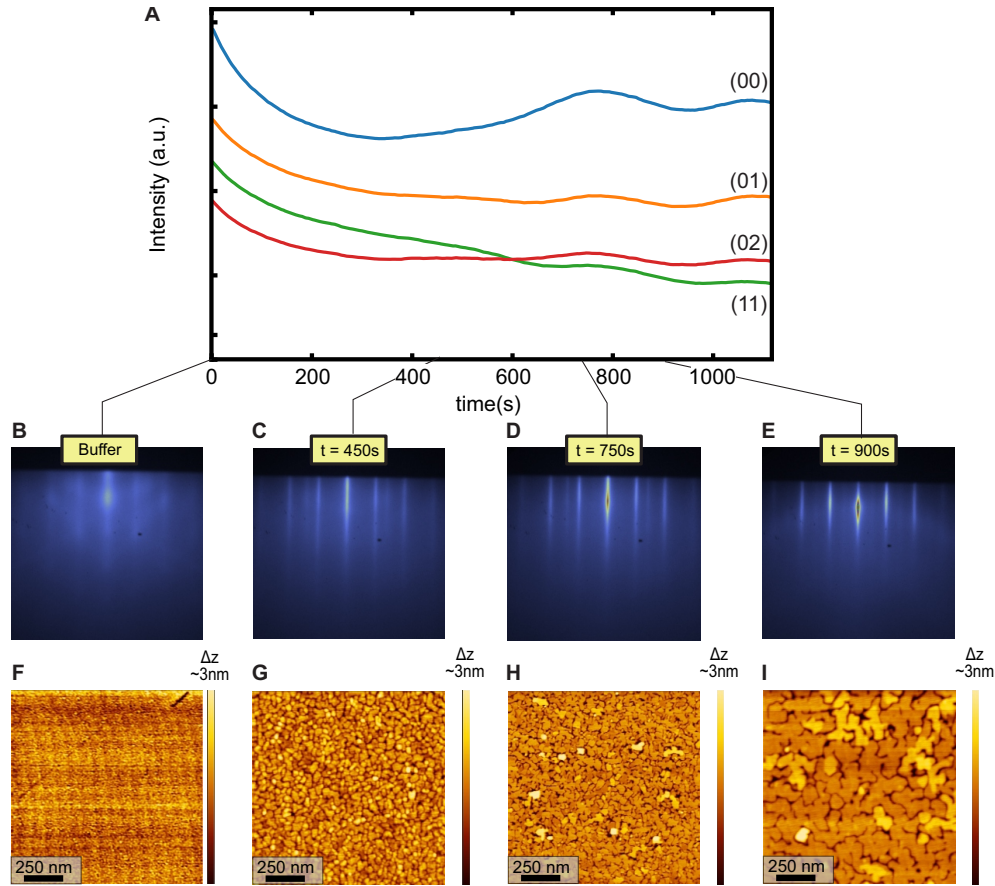


Figure 4.6: Correspondence Between Growth Time, Surface Crystallinity and Roughness. **A** RHEED monitoring of the time dependent intensity from the labelled diffraction streak. Notice the decline in intensity from the streak associated with the misoriented domain. **B-E** RHEED images taken at the corresponding times during growth. **F-I** AFM images of the film grown for the corresponding amount of time.

similar behavior. The notable exception is the behavior of the (11) peak, which continues to decline. As described, this peak is the results of an undesired domain rotated 45° . The observation of the decline of this peak implies that the domain is being suppressed as the film grows thicker. These behaviors can all be further understood by viewing Figs. 4.6B-E taken at various times throughout the growth. In particular, notice the (11) streak in the RHEED images gradually disappears as growth proceeds.

Additional insight can be gained by studying the surface morphology of grown LaSb_2 films with AFM at similar times (Figs. 4.6F-I). The relatively higher stability of LaSb_2 compared to DyTe_2 made AFM characterization possible. We see that during the early stages of growth, the films do not uniformly wet the surface. Instead, they tend to clump into a discontinuous film. While this is not true island growth, and the RHEED patterns appears “streaky”, the

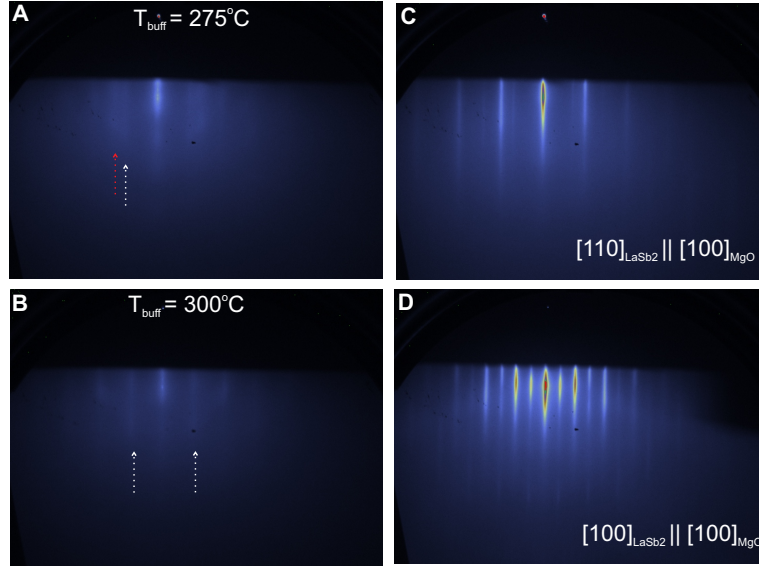


Figure 4.7: **Impact of the buffer layer.** **A** Suboptimal buffer showing a domain with the $[110]_{LaSb_2} \parallel [100]_{MgO}$ epitaxial relationship. **B** Optimal buffer showing only $[100]_{LaSb_2} \parallel [100]_{MgO}$ epitaxial relationship. **C** Film resulting from buffer in **A** that has grown with $[110]_{LaSb_2} \parallel [100]_{MgO}$. **D** Resulting film from the optimal buffer layer in **B** with expected $[100]_{LaSb_2} \parallel [100]_{MgO}$ epitaxial relationship.

film is not continuous and therefore is observed to be electrically insulating. As growth proceeds, these regions coalesce and form a flat, continuous film at the exact time that the RHEED intensity reaches its maximum. This behavior sets a lower bound on the achievable thickness that can be studied with electrical transport.

The above investigations allowed a "baseline" to be established upon which further optimization can take place. Before describing the methods, we stress that high quality growth was very sensitive to growth conditions, which often changed as the chamber was used by others and even due to the constant buildup of material on the substrate holder and manipulator. Thus, the quoted temperatures in the remainder of this section should not be taken literally. Instead, we hope the semi-quantitative correlations between the observations and nominal temperatures will guide others toward optimal parameters

Similar to the case of the tellurides, it was found that use of a buffer layer greatly enhances the structural quality of the film. Growth proceeded using a three step method. A buffer layer was grown at 300°C, for 300s then raised under Sb flux to a temperature of 615°C and then back down to $\sim 550^\circ\text{C}$. Of these steps, the most important by far was the growth of the buffer layer. RHEED images of buffer layer growth can be seen in Fig. 4.7. In Fig. 4.7B, an optimal buffer layer is shown which results in a high quality film with minimal intensity

from the $[110]_{LaSb_2} \parallel [100]_{MgO}$ by the end of growth. In 4.7A "suboptimal" buffer layer is shown. Given the poor crystallinity of this ultra thin layer, RHEED is dim and diffuse. However, streaks from the $LaSb_2$ structure were visible. In addition to the expected $\{10\}$ family of streaks, indicated by the white arrow, there were accompanying streaks from the unwanted (11) domain (red arrow). Surprisingly, the resulting film grown on top of this buffer layer grows in a $[110]_{LaSb_2} \parallel [100]_{MgO}$. It was found for similar unwanted buffer layers, the resulting film often contained a mixture of both epitaxial domains.

The last parameter to optimize was the growth temperature for the layer. The bulk phase diagram limits the growth temperature to below 630°C given by the melting point of the crystal. However as we have seen, the high vapor pressure of Sb requires sufficient over pressure to ensure stoichiometry. This limits the substrate temperature to slightly below this value. We can easily see the effect of growth temperature in Fig. 4.8. For low growth temperatures $<500^\circ\text{C}$, the RHEED streaks are broad and diffuse indicating small domain size. At the optimal temperature range $500^\circ\text{C} < T_g < 575^\circ\text{C}$, the films show bright, high-contrast RHEED patterns. Finally above 575°C , the RHEED pattern again gets dim and diffuse. It also shows obvious 45° oriented domains. While we did not investigate higher growth temperatures, it is clear that film quality would only suffer due to Sb deficiency. These images represent characteristic RHEED images for the various regimes. Because the thermocouple is subject to error due to the history of the chamber, optimal growth temperature was obtained using the following basic process:

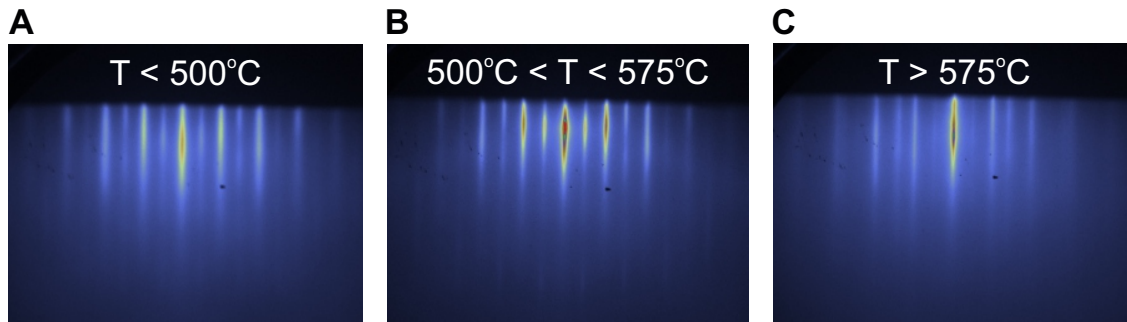


Figure 4.8: ***In-situ* characterization of the effect of temperature on surface crystallinity.** Set of RHEED images taken along $[100]$ for films grown at different temperatures. **A** Effect of low growth temperature. Hazy pattern showing broad streaks and evidence of island growth. **B** Optimal growth range. RHEED pattern is bright and high contrast. **C** Film grown at excessively high temperature. Diffuse streaks with significant domains of the $[110]_{LaSb_2} \parallel [100]_{MgO}$ relationship.

1. Sb/La ratio set to 15, T_{buffer} set to 300° , T_g set to 525°

2. Film was grown for 1hr, intensity of the diffraction conditions was monitored *in-situ*
3. T_g adjusted for next growth depending on behavior
4. Once a target set of conditions was reached, film to be used for measurement was grown

In this way, growth could be optimized without the need for external measurement techniques. For example, a film that appears "cold" based on the RHEED pattern implies that temperature should be increased for next growth. Similarly for the buffer, failure of the RHEED intensity from the (110) domain to become suppressed is evidence that the buffer layer was too cold and should be adjusted. Because the growth chamber was used for many different films, changing conditions required substantial "piloting" of the growth to obtain high-quality.

4.3 Structural Characterization

The structure of $LnSb_2$ materials is composed of QL blocks which can form a variety of stacking configurations depending on their relative displacement [133, 132]. This is depicted in Figure 4.1a with the vector $\vec{d}$ which represents the displacement in the a - b plane. Each QL contains one rare earth site, in this case La (blue), and two different Sb sites, noted as Sb₁ (orange) and Sb₂ (red). Our structural analysis indicates that $LaSb_2$ forms a previously unobserved crystal structure. We now describe how this determination was performed using a variety of techniques.

Determination of Crystal Structure

With an optimized recipe to obtain high-quality films, we can proceed to a comprehensive analysis of the film structure. Out-of-plane X-ray diffraction of films presented in Figure 4.9 b shows a single-phase, c -axis oriented film with a lattice parameter of $c = 17.62\text{\AA}$. This value is compressed relative to the value found in bulk $LaSb_2$ in the $SmSb_2$ structure where $c = 18.56\text{\AA}$ [133]. A film of thickness $t = 144\text{nm}$ was used for determination of the lattice parameters. Rocking curve analysis reveals a full-width-half max of 0.03° indicating low mosaicity. In accordance with the RHEED observations, the phi-scan using the (0 1 9) reflection reveals an $[100]_{LaSb_2} \parallel [100]_{MgO}$ epitaxial relationship with additional domains oriented $[100]_{LaSb_2} \parallel [110]_{MgO}$.

X-Ray Diffraction

Asymmetric reciprocal space mapping (RSM) (Figure 4.10) along the $h = 1$ truncation rod was used to determine the in-plane lattice constants. The data reveals a twinned crystal

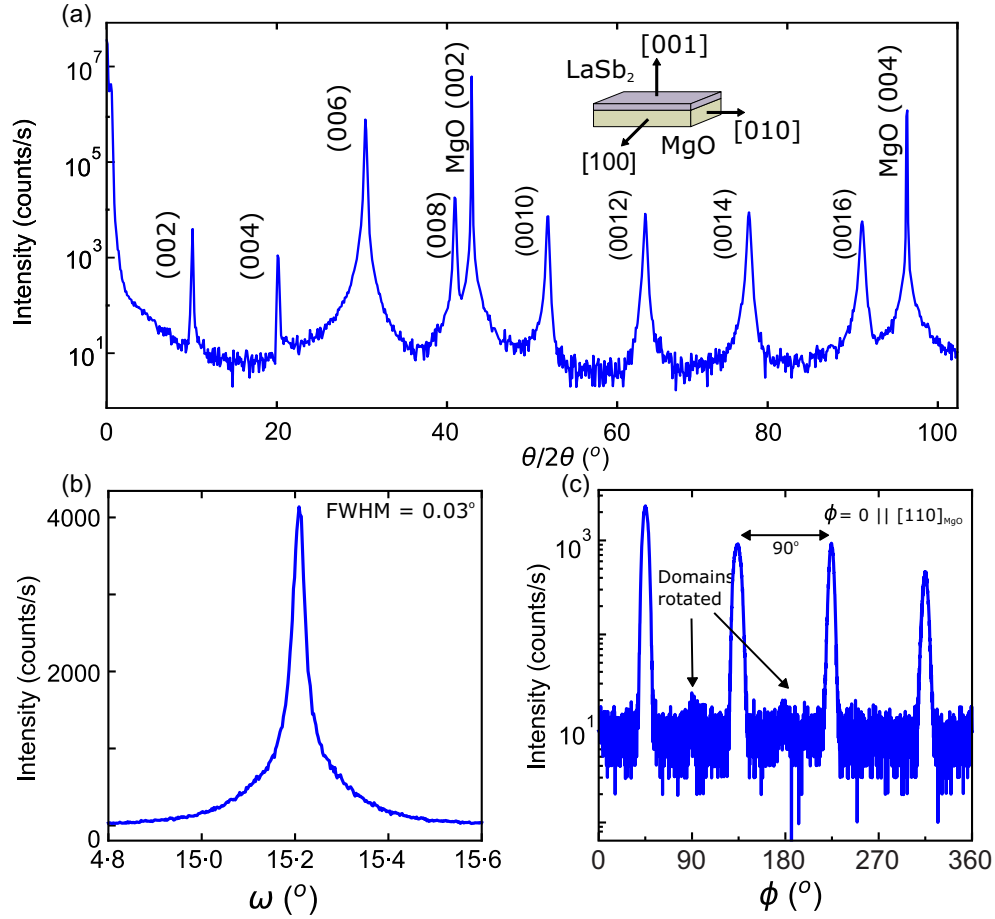


Figure 4.9: **X-ray diffraction analysis of monoclinic LaSb_2 .** **A** $\theta/2\theta$ pattern. **B** Rocking curve scan. **C** Phi-scan showing $[100]_{\text{LaSb}_2} \parallel [100]_{\text{MgO}}$ relationship.

structure with sets of spots corresponding to values from the two different crystal axes. This observation is in agreement with the observations of the $(2 \times 1) \times (1 \times 2)$ surface reconstruction in RHEED. For reflections corresponding to the a -axis, a pair of spots $((1\ 0\ 12)$ and $(\bar{1}\ 0\ 12))$ are observed, whereas intensity at $(0\ 1\ 11)$ is associated with diffraction from the b -axis. To simplify comparison with similar, bulk crystal polymorphs, we adopt a setting where the c -axis is taken to be the long axis. The corresponding a and b axis lattice constants were found to be $a = 4.52\ \text{\AA}$ and $b = 4.43\ \text{\AA}$. The similarity of the lattice constant values for the grown film ($\frac{a-b}{a} \approx 2\%$) and their $\approx 6\%$ mismatch with the cubic MgO substrate result in a relaxed film with twinned domains wherein both a and b axis predominantly align with the $\langle 100 \rangle$ directions of the substrate. For comparison, the bulk ambient phase adopts the SmSb_2 structure (space group No.64 $Cmca$) with $a = b = 4.42\ \text{\AA}$, $\gamma = 91.27^\circ$.

The distribution of the $(1\ 0\ 12)$ and $(\bar{1}\ 0\ 12)$ spots along $\vec{Q}_z$ reveals a monoclinic structure for the crystal. Recall that in a generic monoclinic crystal, $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$.

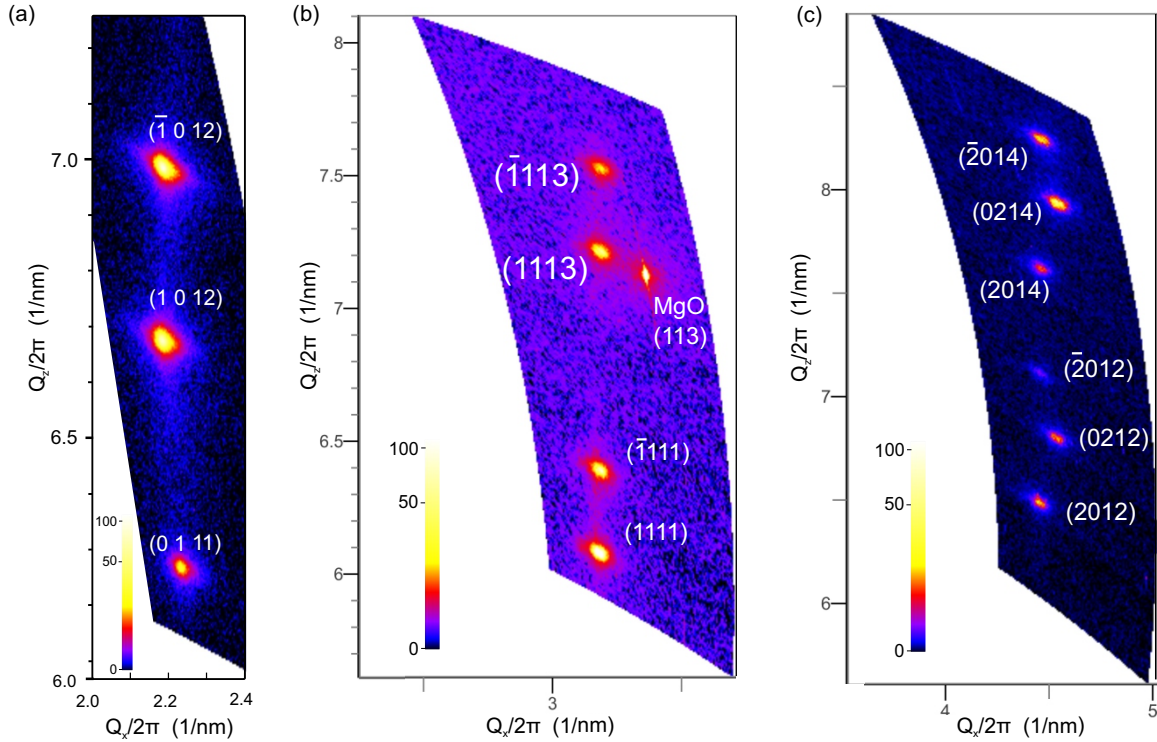


Figure 4.10: **Extended reciprocal space maps.** **A** (1 0 L), **B** (1 1 L) and **C** (2 0 L) truncation rods

When a crystal distorts from orthorhombic to monoclinic, the $\vec{a}^*$ reciprocal lattice vector forms a finite angle with $\vec{a}$ so as to maintain orthogonality with $\vec{c}$ as depicted in 4.11A. The reduced symmetry of the monoclinic structure relative to the MgO substrate leads to domains oriented 180° with respect to each other. These are depicted in 4.11A as two monoclinic crystals with shears in opposite directions. The domains are labelled by differing colors which correspond to the positions of the diffraction conditions in the schematic reciprocal space map 4.11B. Due to the presence of these domains, the appearance of both $(h0l)$ and $(-h0l)$ reflections along the same direction. Thus a single spot corresponding to $(h0l)$ in the case of an orthorhombic crystal appears to “split” along $\vec{Q}_z$ into two spots corresponding to the two rotated domains. The angle between either of these spots and the horizontal can be used to determine the monoclinic tilt which we find to be $\beta = 85.95^\circ$.

Additional reciprocal space maps were used to verify the extinction conditions and determine the space group of the grown film. The maps given in Fig4.10 imply $k+l = 2n$ for general h,k,l ; $l = 2n$ for $h, k = 0, l$; $k+l = 2n$ for $h = 0, k, l$. Comparing with the listings in the international tables (International Tables for Crystallography (2016). Vol. A, Section 1.6.5, pp. 114–128.), these conditions, along with the identification as a monoclinic crystal imply

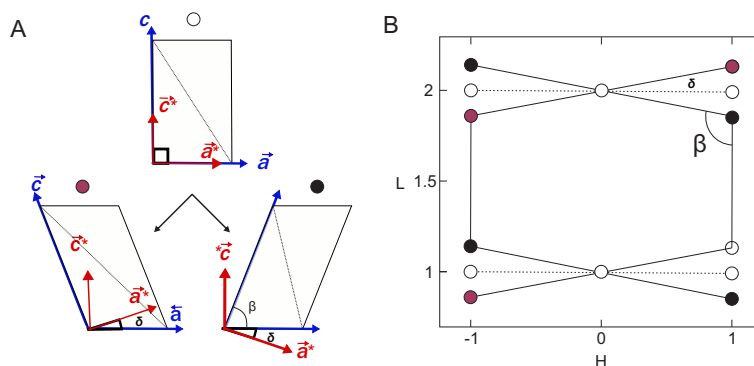


Figure 4.11: **The orthorhombic to monoclinic distortion.** **A** Schematic depiction of the results of a distortion from orthorhombic to monoclinic. **B** Impact of the distortion on the distribution of spots of the reciprocal lattice.

3 possible space groups: A2, Am, A2/m. It is the convention in crystallography to choose a setting such that the C-face is centered. However, since it facilitates comparison with other crystal structures, we choose to assign the A-face to be centered so that the long axis can remain the c-axis.

Confirmation of the Structure using TEM

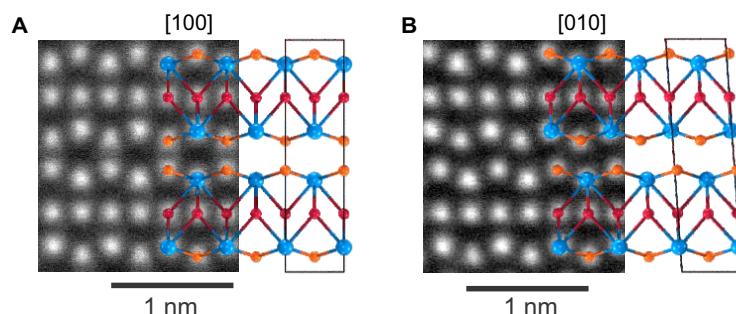


Figure 4.12: **TEM micrographs of LaSb₂.** **A** [100] and **B** [010] zone axes. Credit: Prof. Salva Salmanie Rezaie

Because XRD could not give us the atomic arrangements or uniquely determine the space group, we turned to a combination of DFT and TEM. By calculating the energies of different stacking arrangements of the aforementioned QL blocks, a candidate structure showing the expected monoclinic tilt was found by DFT. The methods used to obtain this will be described in more detail in the next section. TEM was then used to determine this structure. In Fig. 4.12 the calculated atomic arrangement, with lattice constants modified to be the true experimental values from XRD, is overlaid with TEM image. We find perfect agreement between the two, allowing the structure to be uniquely determined with the A2/m space group.

Elemental analysis also confirms the stoichiometry, which in agreement with the RBS data shows a La:Sb ratio of 2:1 within a tolerance of 10%. Elemental mapping of the structure can be found in figure 4.13A and is in agreement with expected atomic arrangement of the individual elements. In 4.13B was also present a linecut taken along the Sb sheet. Along this zone axis, the structure looks identical to the YbSb_2 structure. However in the case of the monoclinic structure, these Sb atoms form square planar sheets in contrast to the YbSb_2 structure where they are found to form slightly puckered layers. This is further confirmation that a new structure is being observed, not simply a multi-phase crystal.

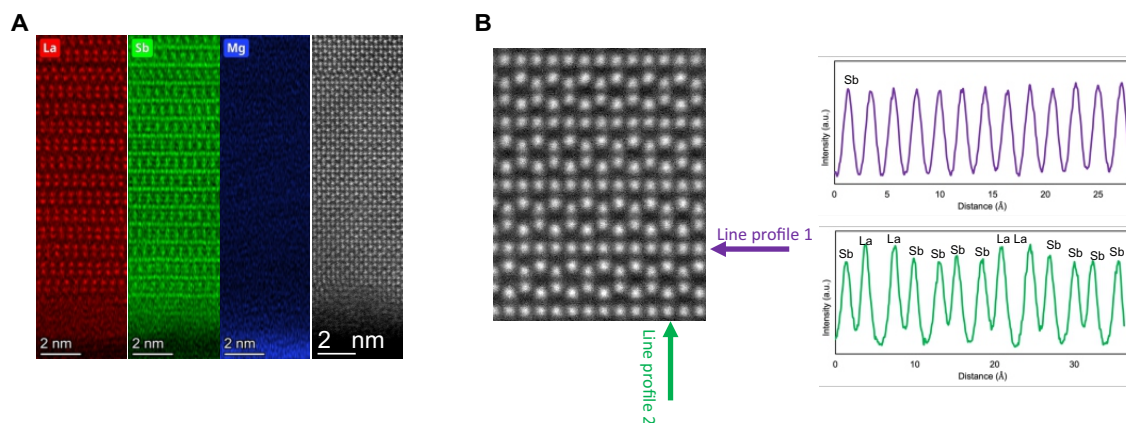


Figure 4.13: Extended TEM analysis of the monoclinic structure. **A** Elemental analysis of the unit cell showing the correct arrangement of atomic species. **B** Line cuts along the Sb square net and along the c-axis direction. The former distinguishes the unit cell from the YbSb_2 structure due to the lack of puckering of the Sb layer. Credit: Prof. Salva Salmanie Rezaie

Finally, a large-area TEM image is presented in 4.14. This image reveals a number of notable characteristics of LaSb_2 films grown on MgO . First, it confirms the domain structure discussed above, especially the observation of twinning between the a and b axes in the RSM data. We observe that throughout the region, various domains exist in about equal proportions. These regions are labelled by the relevant zone axis. The image also allows for a confirmation of several of the observations made in RHEED. In the early stages of growth, *in-situ* RHEED monitoring showed a period of decreasing intensity indicating poor crystallinity. This manifests as an interface of poor quality. Close to the MgO (See figure for labelled regions), the film is amorphous and only becomes crystalline after 1 QL of growth. This is in stark contrast to the behavior of DyTe_2 where the film crystallizes almost immediately, forming a sharp, clean interface. RHEED also revealed a diffraction streak due to misoriented domain with a $[110]_{\text{LaSb}_2} \parallel [100]_{\text{MgO}}$ epitaxial relationship. It was observed that as growth proceeded, this domain was gradually suppressed. This behavior

is nicely manifested in the TEM image. Close to the interface a substantial misoriented region with a can be seen. After approximately 5 QL with this domain, the film instead grows with the expected $[100]_{LaSb_2} \parallel [100]_{MgO}$ relationship. This thickness corresponds exactly to the time at which the RHEED intensity reaches a maximum when the film has become continuous and flat. Finally, the interface between the misoriented domain and the remainder of the film also illustrates that the fundamental crystallography unit consists of two corrugated layers sandwiching a square planar sheet. In the next section, we will discuss how stacking these fundamental units in different ways gives rise to the various observed crystal structures.

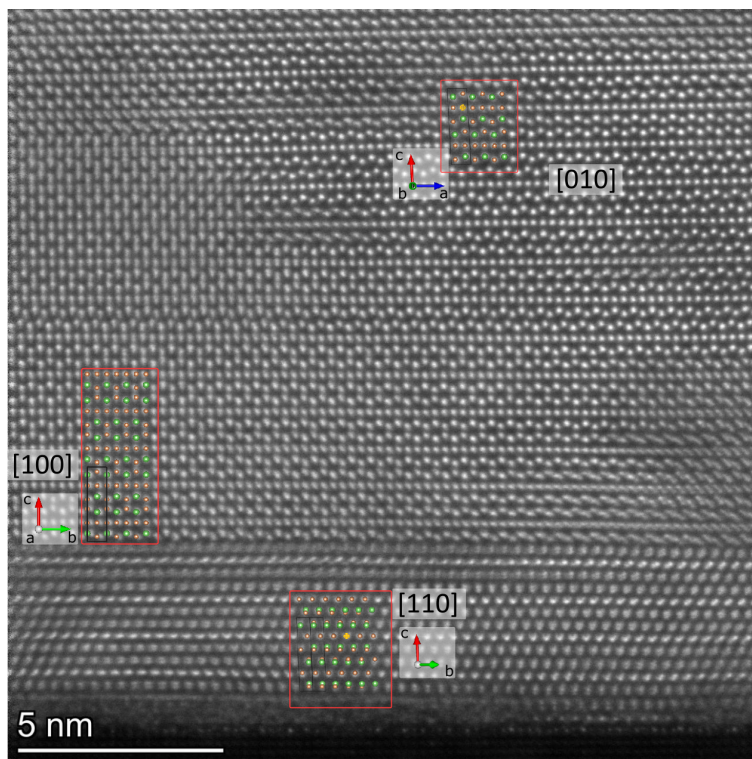


Figure 4.14: **Large area TEM highlighting the domain structure.** Prof. Salva Salmanie Rezaie

DFT Analysis of Film Structure

To further understand the origin of the monoclinic crystal structure, we again turned to DFT calculations, in collaboration with the Kioussis group at CSUN. In these calculations, the unit cell was broken similar in the way displayed previously in Fig. 5.1, where the upper block is shifted relative to the lower one by a displacement vector $\vec{d} = (d_x a_0, d_y b_0)$. This construction is in notable contrast to the case of $DyTe_2$. In those compounds, the cleavage plane was the Te sheet. In the case of the antimonides, there are relatively weak bonds

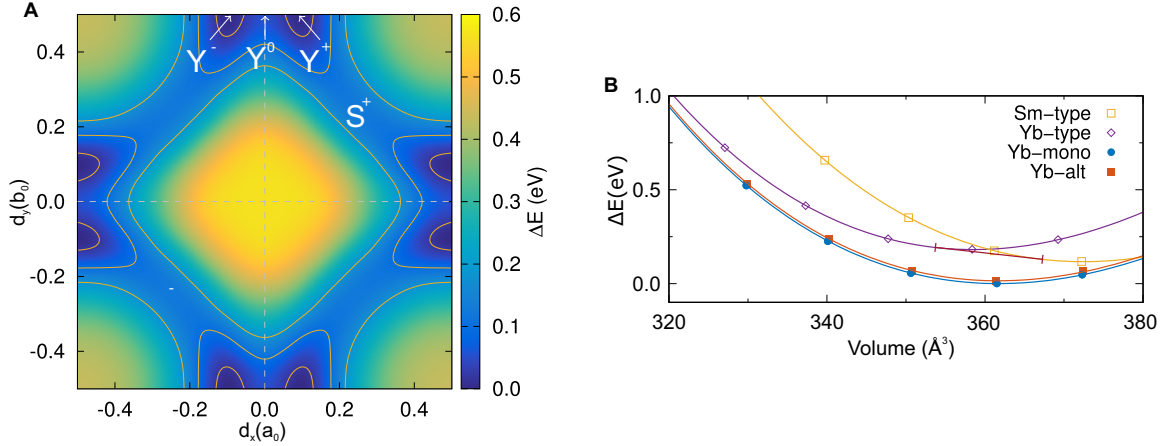


Figure 4.15: **DFT analysis of the monoclinic structure.** **A** Energy map generated by changing the relative displacement between the QL building blocks of the LaSb_2 structure 4.1 by calculating the total energy with DFT. **B** Total energy for the three structures as a function of pressure. Credit: Dr. Jinwoong Kim.

between neighboring La-Sb QL. This is substantiated by the longer inter-block La-Sb bond length ($> 3.5 \text{ \AA}$) compared to those of the intra-block bonds.

The two QL blocks were then slid relative to each other, the structure was relaxed and the total energy calculated. In this way, a map of the energy landscape on the two-dimensional (d_x, d_y) displacement space could be acquired. 4.1(a). This is obtained using a relaxed unit block slab where $a_0 = b_0 = 4.50 \text{ \AA}$ are the calculated equilibrium in-plane lattice constants, and shifting it relative to an adjacent slab, with subsequent relaxation of the atomic positions. The calculations reveal (i) four global energy minima, $Y^\pm$ and (ii) six saddle points, Y^0 and $S^\pm$. We note that the energy map preserves the C_4 rotational symmetry, inherited from the building block ($a_0 = b_0$). The vertical stacking $(d_x, d_y) = (0, 0)$ is clearly not favored. The $S^\pm$ sites, $(d_x, d_y) = (\pm 0.25, \pm 0.25)$, correspond to the displacement of the Sm-type LaSb_2 structure (space group $No.64, Cmca$) consisting of building blocks with stacking sequence of $\cdots S^+ S^- S^+ S^- \cdots$ (see also Table 4.1). The Yb-type structure (space group $No.63, Cmc$) can also be explained with the stacking sequences of $\cdots Y^0 Y^0 Y^0 Y^0 \cdots$. The two displacements between three consecutive building blocks are illustrated in Figure 4.1(b) and (c) for the Sm- and Yb-type structures, where the successive lateral displacements are compensated and both Sm- and Yb-type structures preserve orthorhombicity. The tetragonal symmetry is broken in Sm- and Yb-type LaSb_2 due to the displacement of stacking sites that breaks the C_4 symmetry of the building block. Both phases, however, do not contain the lowest energy stacking arrangement $Y^\pm$ according to these calculations. Figure 4.1(d) shows one potential structure with repeating Y^+ stacking, $\cdots Y^+ Y^+ Y^+ Y^+ \cdots$, where the

non-compensating displacement along the $\hat{x}$ direction leads to shear deformation of the out-of-plane lattice vector rendering the system monoclinic. To further validate this method, we also have applied it to the SmSb_2 and YbSb_2 structures and have found the expected stacking arrangements are reproduced.

Table 4.1: Calculated relative total energies, lattice constants, and angles of several LaSb_2 bulk phases corresponding to different stacking sequences. SG indicates the space group. The Sm-type structure is a base-centered orthorhombic cell and the lattice constants, a and b , are equivalent to the distance from the corner to the center of the conventional cell base.

System	Stacking	SG	ΔE (meV/La)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Sm-type	$\cdots [S^+ S^-] \cdots$	64	29	4.470	4.470	18.628	90.0	90.0	91.1
Yb-type	$\cdots [Y^0] \cdots$	63	45	4.477	4.546	17.607	90.0	90.0	90.0
Yb-alt	$\cdots [Y^+ Y^-] \cdots$	58	4	4.555	4.480	17.717	90.0	90.0	90.0
Yb-mono	$\cdots [Y^+] \cdots$	12	0	4.562	4.483	17.711	90.0	86.3	90.0
Bulk exp.[133]		64		4.42	4.42	18.56	90.0	90.0	91.2
This work		12		4.52	4.43	17.62	90.0	85.96	90.0

Table 4.2: Table of atomic positions within the unit cell.

Atom	x	y	z	Occ.	Site	Sym
La	0.538	0.000	0.789	1.00	4i	m
Sb1	0.481	0.000	0.459	1.00	4i	m
Sb2	0.523	0.000	0.144	1.00	4i	m

Table 4.1 lists the calculated relative total energies of the different stacking sequences, as well as experimentally obtained values for bulk crystals [133] and our thin films. The calculations point to the monoclinic structure (Yb-mono) as the ground state, with the previously synthesized Sm-type or proposed Yb-type phases exhibiting higher total energies. We note however, that this is the energy at $T = 0$, and therefore is distinct from the free energy at elevated temperatures which contains phononic, magnetic, and electronic entropic contributions. The novel Yb-mono phase is consistent with the MBE-grown LaSb_2 structure where all the calculated lattice constants and monoclinic angle β agree well with the diffraction data within an error of 1%. Combining diffraction, calculation and microscopy results, we unambiguously confirm the novel Yb-mono polymorph has been stabilized.

The calculations also reveal a new orthorhombic phase (Yb-alt in Table 4.1, space group *No.58, Pnnm*) with alternating stacking sequences of $\cdots Y^+ Y^- Y^+ Y^- \cdots$, which is close in energy to the ground state Yb-mono structure. In order to study the relative stability of the four crystal structures under hydrostatic pressure, we show in Figure 4.15B the calculated total energies as a function of volume. We find that the Yb-mono structure remains the ground state under hydrostatic pressure, which on the other hand, induces a structural phase transition from the Sm-type to the Yb-type structures at 0.749 GPa, close to the calculated value in Ref [135] of ≈ 0.5 GPa.

Pair	d (Å)
La-La	4.167
La-Sb2	3.409
La-Sb1	3.255
Sb2-Sb2	3.226
Sb1-Sb1	2.886
Sb1-Sb2	3.964

Table 4.3: Bond lengths in monoclinic LaSb_2

4.4 Discussion

In the introductory remarks of this chapter, we discussed how varying stacking arrangements give rise to related, but structurally distinct crystal structures. The monoclinic structure

adopted by our thin films is a novel structure that has not yet been observed. In this section we will analyze the bonding arrangement and draw comparisons to the other commonly observed crystal structures adopted by RSb_2 materials.

We begin by recalling the orthorhombic structure that has been widely observed (Fig. 4.1B). The structure consists of one La site and two inequivalent Sb sites, Sb(2) in the square sheet and Sb(1) in the corrugated layers. The most salient feature of this structure, apart from the square net is the existence of Sb(1)-Sb(1) dimers that form between the Sb atoms on two separate QL layers. In [134], a full list of atomic coordinates and bond lengths is given. We can quantify the degree of dimerization by comparing the length of the dimer to the inter-dimer spacing. For orthorhombic LaSb_2 , the Sb(1)-Sb(1) distance $d_{\text{Sb1-Sb1}}$ is $2.72\text{\AA}$ is substantially smaller than the inter dimer distance d_{dd} of $5.14\text{\AA}$.

The atomic positions and bond lengths for the monoclinic cell are given in table 4.3 . It can be seen both from the values of the bond lengths in the table as well as in 4.1D, that the Sb(1) atoms no longer form such isolated dimers. This can be quantified by comparing the dimer length to the inter-dimer spacing. In monoclinic LaSb_2 , there is $d_{\text{Sb1-Sb1}} = 2.886\text{\AA}$ compared to $d_{d-d} = 3.57\text{\AA}$. This is a substantial reduction compared to the orthorhombic structure. The other structurally similar compound is YbSb_2 . In this compound $d_{d-d} = d_{\text{Sb1-Sb1}} = 2.96\text{\AA}$. In the case of YbSb_2 , the dimers have completely fused into a chain. We can therefore interpret the monoclinic LaSb_2 as being a compound occupying an “intermediate” structural position with the S^+ structure and the Y^0 structure occupying the ends of this structural parameter space.

With knowledge of a proper crystal structure, we now turn to the electronic structure as revealed through bandstructure calculations. This knowledge will be used to interpret the results of the transport experiments so we will describe it in detail. We present the results of these calculations in Fig. 4.16. In Fig. 4.16A, we display the calculations for the SmSb_2 structure type (S^+) adopted by bulk crystal LaSb_2 . A cross section of the Fermi-surface is given in Fig. 4.16B and the Brillouin zone in Fig. 4.16C. These calculations agree both with previous calculations as well as quantum oscillations experiments [40] as well as recent ARPES experiments [94]. The Fermi surface consists of highly dispersing p -orbital-like bands originating from the Sb(2) atoms on the square-net sheet. Notably, there is a Dirac point between Γ and C , and this material has been previously explored as possible topological semimetal [105]. We also note that there is minimal hybridization between the various bands as can be seen from the projected density of states. Thus, we can analyze each band in isolation. The La bands are found to be far from the Fermi level ($\approx 1\text{eV}$) while those originating from the Sb(1) atoms are fully occupied. This can be understood

by recalling the structure described in the previous section. In particular, the Sb(1) atoms exist as dimers in the orthorhombic structure. Recalling the logic from Ch 1. and [99], this structural motif results from a Peierls-like distortion of a chain of Sb^{2-} atoms. Intuitively, energy is minimized for $7e^-/\text{Sb}$ when pairs are formed thereby satisfying the octet rule. This of course results in a fully-filled band. Since the partially-filled square Sb(2) net is most stable for $6e^-/\text{Sb}$ (see Ch 1.), we assign an oxidation state of Sb^{1-} . This leaves La with the oxidation state of +3 leaving the La d-band unoccupied.

In Figure 4.16B we plot the band structure for LaSb_2 in the Y^+ crystal structure along the high symmetry directions (orange path in (F)) and the corresponding orbital-projected density of states (DOS) are displayed in Figure 4.16 where the blue, orange, and red colors denote projections on the La-5d, $\text{Sb}_1/5p$ and $\text{Sb}_2/5p$ orbitals (recall Sb(1) are on the La/Sb corrugated layer and Sb(2) are on the 2D Sb sheets in see Figure 4.1D). The Brillouin zone of the monoclinic crystal structure with the relevant high symmetry points is given in 4.16F. Similar to the S^+ structure we find highly dispersing $\text{Sb}_1/5p$ and $\text{Sb}_2/5p$ bands crossing

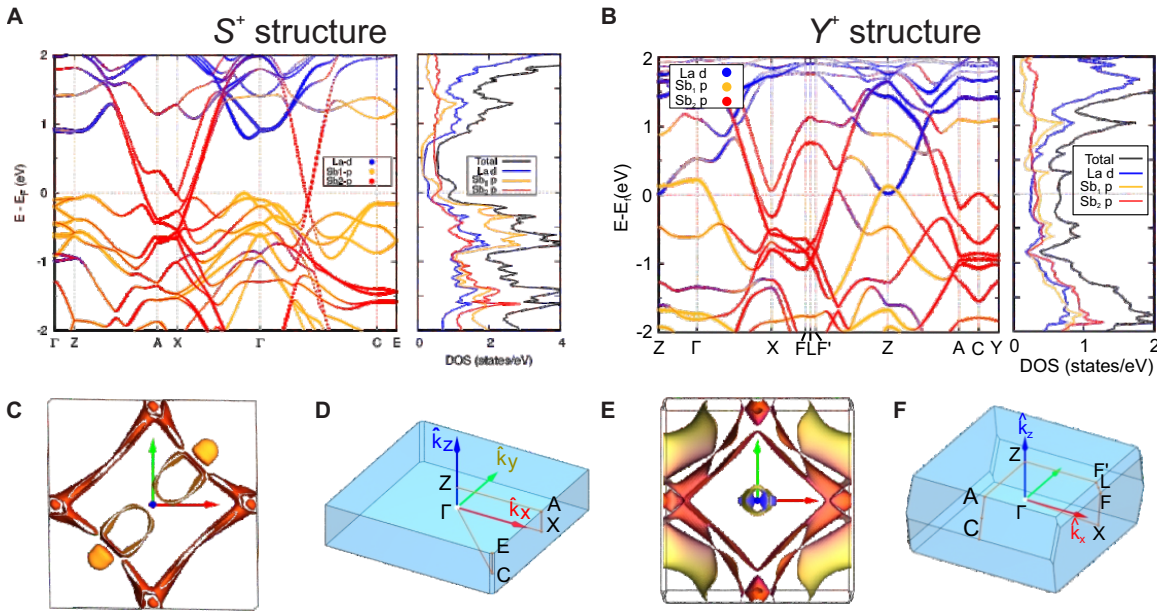


Figure 4.16: **Comparison of the monoclinic and orthorhombic band structures.** A, B for the orthorhombic and monoclinic LaSb_2 structures. C, E the corresponding Fermi Surfaces and D, F, the Brillouin zones for the two structures, Credit: Dr. Jinwoong Kim.

the Fermi level along the Γ -X and F' -Z directions, indicate high carrier mobility along the in-plane directions similar to those in the bulk orthorhombic LaSb_2 structure [109, 105, 98] and in other topological square-net materials [61]. However there are new features, most notably presence of both hole-like and electron-like pockets at the Fermi level which

originate from the different Sb atoms in the structure. As will be described in the next section, this feature is in agreement with the observation of multiple carrier types from the Hall measurements.

When the material forms in the monoclinic-YbSb₂ (Y⁺) structure, the bonding is quite different from the S⁺ structure. As described, the Sb(1) atoms no longer form dimers, instead forming extended chains. The bands from these atoms are now seen to cross the Fermi-level forming a metallic band. This behavior suggests that the Sb(1) atoms have been oxidized through interaction with the d-orbitals of La. This picture is supported by the new location of the La *d*-bands which lie close to the Fermi-level and are now hybridized with the Sb(1) *p*-bands.

This also leads to qualitatively different features of the calculated Fermi surface (Fig. 4.16D). In the monoclinic structure the strong hybridization between La-*d* and Sb(1)-*p* introduces band dispersion along the *k_z* direction which the 2D like features. Overall, the FS of the monoclinic structure is distinct from the highly nested 2D-like FS sheets of the orthorhombic Sm-type structure. The implications of this difference will be discussed in the final section of this chapter

This analysis suggests a structural transition driven by a valence instability of La. While it is difficult to strictly assign oxidation states, if one roughly assigns a 1– oxidation to Sb(1), this would be in keeping with the idealized behavior of an undistorted Sb[–] chain. Similarly, a 1– oxidation for Sb(2) is expected for 2D sheets. This would imply a reduction in the La valence to a value < 3+. In the related structure, YbSb₂, the oxidation state of Yb has been measured with magnetic susceptibility measurements. These measurements find a predominantly Yb²⁺ oxidation state with a ≈ 2% admixture of Yb³⁺ atoms. It was argued that this admixture both results in Sb(1) chains with a filling of 6e[–]/Sb and additionally stabilizes the square-net Sb(2) sheet against distorting into Sb[–] chains as well. Thus given the structural similarity between LaSb₂ in the monoclinic phase and YbSb₂ as well as the results of the bandstructure calculations, it appears that the electronic structure of LaSb₂ can be understood as intermediate between that of orthorhombic LaSb₂ and YbSb₂.

This explains the pressure-dependence of the structure as discussed in Fig.4.15 B. As the unit cell volume is reduced, there is a cross over from S⁺ to Y^o (undistorted YbSb₂ structure). As the unit cell is compressed, there is increased interaction between Sb(1)₂^{2–} dimers. This would tend to promote the formation of chains as dimer-dimer interactions grow. Additionally, the increased La-Sb(1) interactions allow for the observed hybridization of the bands, which destabilizes the La 3+ oxidation state. Epitaxial strain, which tends to compress the structure in-plane, would accomplish a similar outcome. However, a good

explanation of the observation of the monoclinic structure in thin films is still lacking. The calculations suggest that the monoclinic is the arrangement that globally minimizes the energy. Thus the question of why the bulk crystals form in the SmSb_2 structure at all is outstanding.

4.5 Electronic Transport Characterization

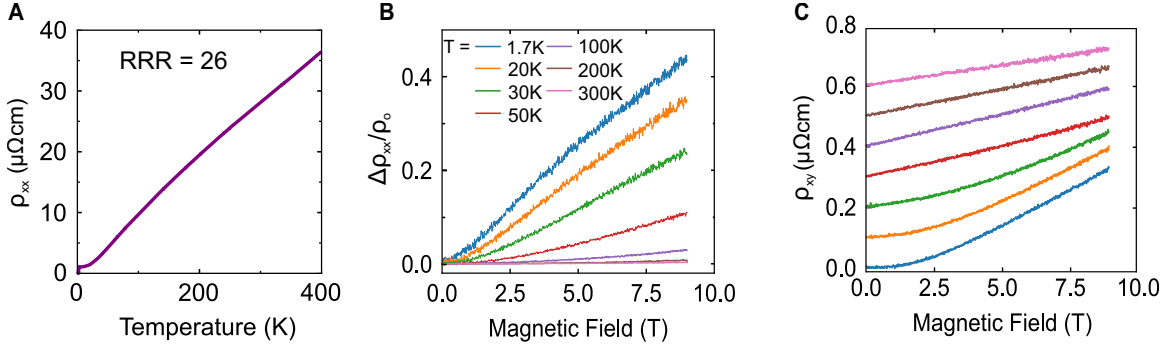


Figure 4.17: **Electrical characterization of 120nm thick LaSb_2 films.** **A** Temperature dependence of resistivity. **B** Magnetoresistance as a function of temperature. **C** Hall effect as a function of temperature, offset for clarity.

We studied the electronic properties of monoclinic LaSb_2 first using conventional low-temperature transport. Electrical data was obtained using four-point van der Pauw geometry measurements in a Quantum Design Dynacool PPMS. Samples were cut in approximately square shape of size $\approx 3\text{mm}$ and contacts were made either with pressed indium or by directly wire bonding with Al wire. Sheet resistance was obtained by numerically solving the van der Pauw equation. Excitation current of $100\mu\text{A}$ was used to attain sufficient signal to noise, given the highly metallic nature of the samples. Of primary interest to us was the electronic properties as thickness is reduced. We will postpone a discussion of thickness dependence to the next chapter and focus on the intrinsic behavior here.

To gain a first insight into the "bulk" behavior we first studied a film of thickness $\approx 150\text{nm}$ thick. In Fig. 4.17a we display the temperature dependence of resistivity which shows good metallic conduction down to low temperatures. An RRR value of 26 indicates high structural quality and is comparable to bulk crystal values ≈ 50 [12]. Bulk crystal LaSb_2 has been reported to display hysteretic resistance anomalies at around 350K which are suppressed under pressure which have been attributed to the formation of CDWs [135, 11]. Our results show no such anomalies up to 400K and display standard Fermi liquid behavior at low temperature. No anomalies appear on heating and there is minimal hysteresis between heating and cooling. We conclude that no CDW transition appears to occur in monoclinic LaSb_2 films.

Additionally, magnetotransport displays large, non saturating linear magnetoresistance of $\approx 40\%$ at the lowest temperatures. This value is reduced compared to observations in the bulk of upwards of 200% [11] [25]. The hall resistivity displays pronounced curvature at low temperatures, a featured commonly interpreted to be the result of multiple carrier types given by the formulae:

$$\rho_{xx} = \frac{1}{e} \frac{(n_h\mu_h + n_e\mu_e) + (n_h\mu_e + n_e\mu_h)\mu_h\mu_e B^2}{(n_h\mu_h + n_e\mu_e)^2 + (n_h - n_e)^2\mu_h^2\mu_e^2 B^2} \quad (4.1)$$

$$\rho_{xy} = \frac{B}{e} \frac{(n_h\mu_h^2 - n_e\mu_e^2) + (n_h - n_e)\mu_h^2\mu_e^2 B^2}{(n_h\mu_h + n_e\mu_e)^2 + (n_h - n_e)^2\mu_h^2\mu_e^2 B^2}. \quad (4.2)$$

Where n_e and n_h are the carrier densities and μ_e and μ_h are the transport mobilities for electrons and holes respectively. There is an additional constraint

$$\sigma_{xx}(B = 0) = e(n_e\mu_e + n_h\mu_h) \quad (4.3)$$

Meaning there are only 3 free parameters for the fit. Despite the fact that the MR displays linear behavior, indicating a deviation from the standard Drude model for which these formulae were derived, we fit both the MR and the hall data simultaneously. We found that only fitting to the Hall data, as is sometimes done in the literature [122, 123] gave unphysically large (or even the incorrectly signed) MR.

As can be seen in Fig. 4.18A, however, while the data can capture the curvature of the hall data, the MR were only fit adequately at higher temperatures where the MR was substantially reduced. At low-temperature, while the fits generally reproduced the order of magnitude of the MR and hall response, quantitative agreement could not be easily made. However, estimates of the carrier density and mobility were made and give physically reasonable values (Fig.4.18B,C).

The observation of multiple carrier types in the hall response is in agreement with the results of the DFT calculations previously obtained which showed an electron pocket from the Sb(1) square sheet and the hole pocket originating from the Sb(2) chains. A more careful inspection of the magnetoresistance reveals a $\Delta\rho/\rho_o \propto H^m$ with an unexpected field dependent value of m . In Fig.4.19A, we plot the MR at various temperatures on a logarithmic scale. Applying Kohler scaling [65, 2], we find that the curves all collapse when plotted vs H/ρ_o (Fig. 4.19B). The idea behind Kohler scaling is that the correction to the resistivity due to the curving of electron trajectories is of order $\sim (l/r_L)^2$ where r_L is the Larmour radius $r_L = mv_F/eH$ with v_F the Fermi velocity, m the effective mass, H the applied field

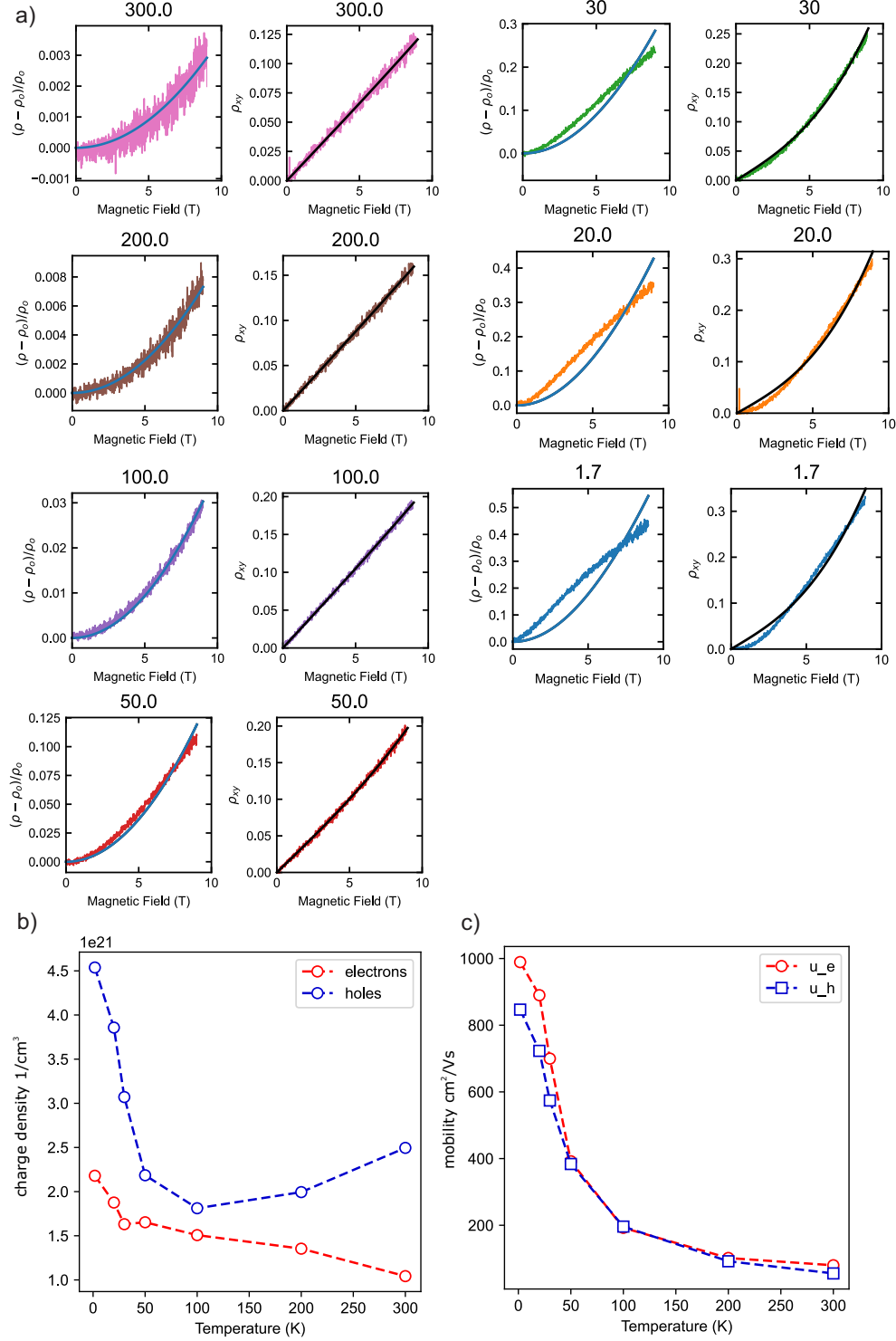


Figure 4.18: **Two carrier fits at various temperatures** **A** Fits to the longitudinal MR (left) and the Hall response (right). **B**, **C** Temperature dependence of the charge density and mobility.

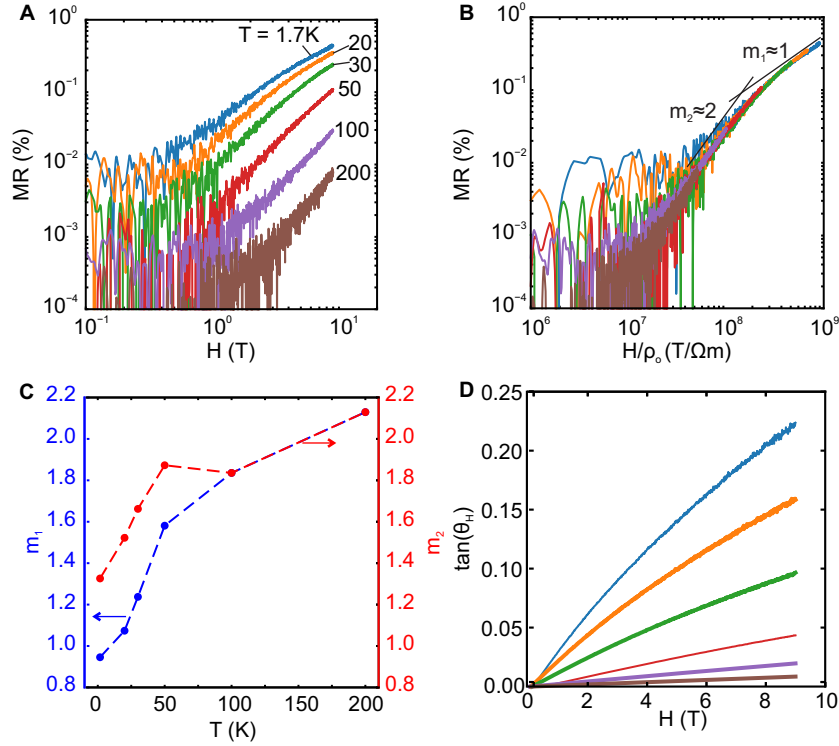


Figure 4.19: **Kohler scaling of the MR.** **A** plot of the MR for different thickness. **B** “Kohler plot” showing the change in MR exponent with field. **C** change in the apparent slope with temperature. Above 150K, there only seems to be only a slope of ≈ 2 indicating a crossover to more traditional metallic behavior with temperature. **D** the Hall angle for the experiment.

and e the electron charge. If the mean free path l is isotropic and independent of momentum, then the magnetoresistance should satisfy a universal function, $\Delta\rho/\rho = F(H/\rho_o)$ where ρ_o is the resistivity at zero field and F is an unknown function. While F is unknown, if the data follow Kohler scaling then the act rescaling the field values to $H \rightarrow H/\rho_o$ should cause all of the data to collapse to a single curve as observed. Recently, corrections to Kohler scaling have been derived to explain deviations in topological semimetals [140]. These corrections attribute this deviation to a change in carrier density as temperature is decreased. The fact that our data follow Kohler scaling indicates that the changes in MR with temperature can be attributed to the changes in the mean free path length which results from increased electron phonon scattering at elevated temperature. This observation also casts doubt on the evolution of the charge density in Fig. 4.18B. The observation in Fig. 4.18B is likely a reflection of the inadequacy of the simple two-band fit.

From the Kohler plot, the change in field scaling exponent m is more obvious. We fit these two regions for each temperature and plot the extracted values in (Fig.4.19C. Starting at the lowest temperature of 1.7K, there are two obvious scaling regimes. The high field regime,

shows approximately linear MR ($m \approx 1$). Below this field, the scaling exponent is slightly higher at around 1.3 for this temperature. As the temperature is increased, the value of m in both regimes is found to rise such that by the time $T > 100\text{K}$, there is only one scaling exponent with a value $m \approx 2$, as expected from standard Drude theory. Linear MR has been observed in LaSb_2 both in ambient conditions [12] and under pressure [11]. We note that under pressure, there also appears to be a shoulder in the MR curve, but quantitative analysis was not performed in that study [11].

Recently, linear MR has been the subject of ongoing interest due to recent observations in topological semimetals [69]. A mechanism based on guiding center diffusion in single carrier, low-disorder materials was proposed [117]. This theory requires that the hall angle $\tan(\theta_{\text{Hall}}) = \rho_{xx}/\rho_{xy}$ be constant in the linear regime, a feature that is clearly violated in LaSb_2 (Fig. 4.19D). Thus, a quantitative theoretical explanation has not been given but is clearly related to the mobility of the charge carriers as the linear portion of the curve is gradually suppressed as the temperature increases. Such a theory will likely require a first-principles approach that takes into account the anisotropic Fermi surface and electron-phonon scattering.

4.6 Superconductivity

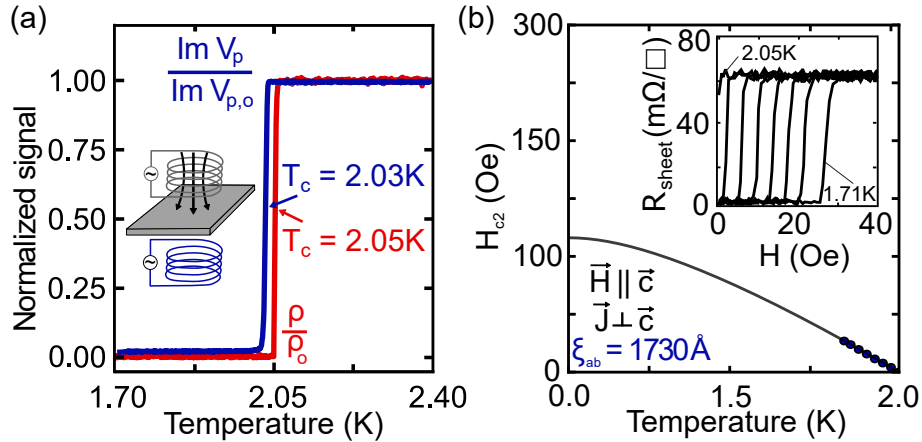


Figure 4.20: **Superconducting Properties of Epitaxial LaSb_2 .** **A** the superconducting transition. **B** the critical field behavior.

This subject of superconductivity will be discussed in much more detail in the next chapter. However, in the interest of completing the survey of transport properties of LaSb_2 we present the result of our measurements of superconductivity in thick ($\sim 120\text{nm}$) LaSb_2 film in Fig. 4.20. In 4.20A, we plot data showing the presence of a sharp superconducting transition with resistive $T_c \approx 2.05\text{ K}$. This data is plotted alongside the transition associated

with the screening of magnetic flux in a dual-coil, mutual inductance geometry. The latter was employed as a stand-in for the more standard measurement of the Meissner effect due to the difficulty in obtaining sufficient signal from a thin film.

The LaSb₂ film was held upright on the cryostat puck via a 3D printed housing. Two solenoids (5 mm in length, 2.5 mm in diameter) were inserted into the housing centered co-axially on either side of the film, and the sample was thermally and electrically grounded by a gold wire soldered to the corner of the film. An AC driving current (50 μ A at 10.13 kHz) was passed through one coil using an SR830 lock-in amplifier while the imaginary part of the first-harmonic pickup voltage (indicted as “Im V_p ” in Fig. 4b) was measured in the second coil with the same lock-in (300 ms time constant). An out-of-plane magnetic field of 10 Oe was applied to compensate for trapped flux in the cryostat system’s magnet. While sweeping the sample’s temperature at 10 mK/minute through its superconducting transition, the onset of the Meissner effect was observed as a substantial drop in the induced voltage across the pickup coil, indicating screening of the drive coil’s magnetic field by the superconducting film.

The measured T_c in the two experiments agree within 1%. In Fig. 4.20b, we plot the perpendicular critical field (measured using the resistive transition) as a function of temperature. Determination of H_{c2} was performed by fitting the resistive transition isotherms to a sigmoid function $\rho = \frac{\rho_o}{1+\exp(-k(H-H_{c2}))}$ where k , ρ_o , and H_{c2} were fitting parameters. An excitation current of 50 μ A for the critical field measurements and 100 μ A for the zero field ρ - T measurement to enhance signal/noise. These values correspond to current density values of $\approx 100 \text{ A/cm}^2$, far from the depairing threshold set by the Silsbee criterion [126] of $\approx 10^7 \text{ A/cm}^2$. While vortex dissipation may limit the upper critical current to a much lower value, the lack of impact of excitation current on measured T_c is further demonstrated by the agreement between values determined by the mutual inductance and resistivity measurements. Data were taken every 25 mK between 2.05 K and 1.71 K. The full set of critical field isotherms and fits is given in the supplementary information of [78]. We extrapolate to zero temperature by fitting the data using the single-band, Werthamer, Helfand, and Hohenberg (WHH) formula [136] in the limit where orbital pair-breaking effects dominate spin paramagnetic and spin-orbit effects. We use the extrapolated value for $H_{c2\perp}(0) \approx 110 \text{ Oe}$ to estimate the coherence length which gives $\xi_{ab} = \sqrt{\frac{\Phi_o}{2\pi H_{c2\perp}(0)}} = 1730 \text{ \AA}$. For comparison, a single-band Ginzburg-Landau model [126] gives $\xi_{ab} = 1400 \text{ \AA}$. These values are in agreement with the findings in bulk crystals under pressure [44]. The inset of Fig. 4.20b displays a subset of the isotherms used in the fitting and further demonstrates the sharpness of the transition.

4.7 Discussion

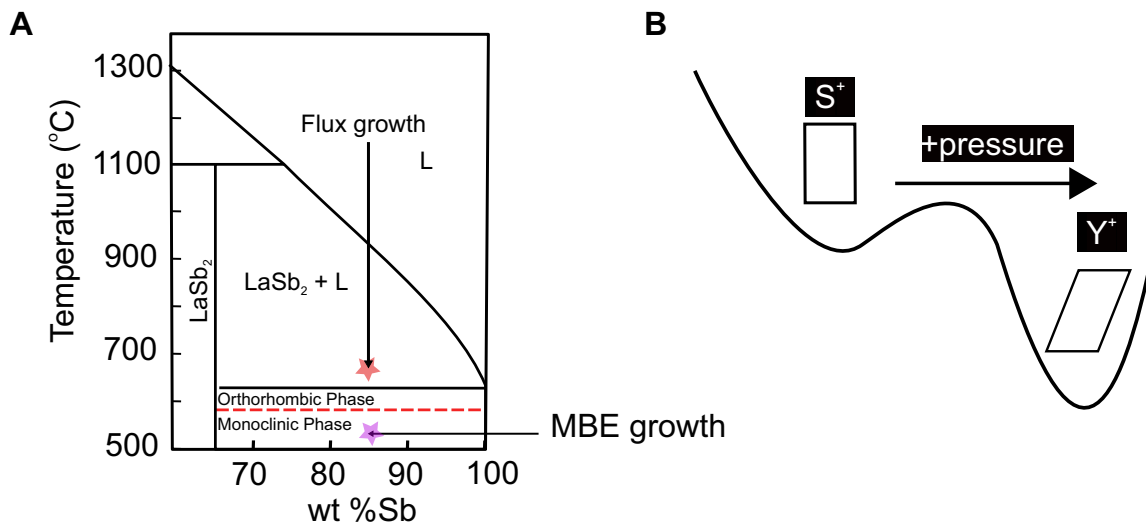


Figure 4.21: **Possible Thermodynamic Origins of Monoclinic Phase.** **A** Schematic demonstrating the difference between bulk growth and MBE growth. **B** Proposal for explaining the observation on orthorhombic structure in LaSb₂ in bulk crystals. We propose that the orthorhombic is a metastable compound that can be easily perturbed with pressure to find the global minimum.

As described in the introduction to this chapter, the rare-earth dantimonides, in particular, those containing light elements (La, Ce) have been observed to host an electronic structure that is coupled to a crystal structure that is sensitive to external perturbations such as pressure and strain. It is thus natural to ask why thin-film LaSb₂ grows with a related, but distinct stacking arrangement compared to the bulk.

One possibility for the stabilization of the monoclinic LaSb₂ is related to epitaxial strain or other perturbations induced by the substrate. The square symmetry of the MgO substrate would tend to favor layers with reduced orthorhombicity and lattice mismatch with the substrate. In the monoclinic phase, the *a* and *b* axes differ by $\approx 2\%$ compared to approximately $\approx 2.5\%$ for the ambient phase structure. However the large lattice mismatch of $\approx 6\%$ for the monoclinic structure makes it unlikely that coherent strain persists in the epilayer beyond the first 1-2 QL and therefore unlikely that the monoclinic structure be stabilized by epitaxial strain. Furthermore, the film-substrate interface is rather disordered (Fig. 3.14) making the likelihood of persistent epitaxial strain all the more unlikely. An explanation related to off-stoichiometry can also be ruled out based on the RBS measurements that were performed.

Another possibility for the observation of the monoclinic phase in thin films, yet not in the bulk crystals, is the lower growth temperature used in the MBE growth processes ($\approx 500^\circ\text{C}$

$< T_{\text{melt}} = 630^\circ$ [96]. During flux growth (the method of choice for bulk synthesis of these compounds) crystals are obtained by slowly cooling the melt from the liquidus temperature ($\approx 1000^\circ\text{C}$), over a period of tens of hours and decanting the liquid flux slightly above the solidification temperature of the desired phase [14]. Given the results of the 0 K DFT simulations, monoclinic LaSb_2 may therefore be a low-temperature crystalline phase that would be preferentially stabilized by the vapor-solid reaction of MBE. This implies that the bulk S^+ phase is a metastable phase. A structural transition from orthorhombic to monoclinic at low pressure could therefore be an explanation of the pressure dependent changes in the observed temperature dependence of resistance.

This naturally leads to the second open question, that is, whether the monoclinic structure observed in thin films is the same as that of the bulk crystals when subjected to pressure.

As of the time of writing, no single-crystal diffraction data has been reported for bulk- LaSb_2 at high P . The micacity of crystals makes such experiments challenging. Therefore, the possibility that the high-pressure phase of the bulk crystal is the same as that observed in thin films is difficult to confirm. Previous studies [135] have proposed YbSb_2 as a candidate structure for the high- P phase on the basis of DFT calculations. Our calculations agree that while the YbSb_2 structure is more stable compared to the SmSb_2 structure under pressure, the monoclinic Y^+ structure is the ground state. We propose that the application of pressure results in a structural transition to either the Y^+ polymorph or similar orthorhombic structure labelled $[Y^+Y^-]$ which is nearly degenerate.

Several pieces of circumstantial evidence allow the association of the Y^+ phase with the high-pressure phase of the bulk crystal. These are the absence of resistance anomalies at high temperature, and a sharp superconducting transition at 2K. First, in bulk LaSb_2 , large resistance anomalies have been observed in the temperature dependence of resistance. These anomalies are typically associated with CDW transitions or other structural distortions that result in gapping of sections of Fermi surface. The application of pressure is found to suppress such anomalies to zero temperature, with only modest pressures of ~ 1 GPa [11]. Our films display no such anomalies and no temperature-dependent hysteresis.

In bulk LaSb_2 , the superconducting transition is broad, with onset temperatures of about $T=2$ K, yet only reaching a fully superconducting state at $T=0.4 \sim 0.5\text{K}$ [44]. Scanning tunneling microscopy experiments have suggested that the superconductivity is more robust at the surface with a measured T_c of 1.2K [37]. This broad superconducting transition has been argued to originate from weak Josephson coupling of the 2-D -like QL building blocks of LaSb_2 [44]. The transition sharpens with P with concomitant suppression of the high temperature resistance anomaly [135, 11]. A maximum $T_c \approx 2$ K was observed

under applied pressure of 4.5kbar at which point the anomaly is completely absent [44, 135]. It was argued that the application of pressure increases coupling between the QLs causing a 2D-3D crossover [44] of the superconducting order parameter. Our bandstructure calculations also suggest that the origin of enhanced SC could be the result of the Fermi surface reconstruction that occurs on transition to the monoclinic phase. While the Fermi surface in the S^+ structure consisted almost solely of bands originating from the square net sheet, the order parameter in the monoclinic phase may well be associated with the new band originating from the Sb chains. Multi band scenarios are also possible.

The presence of a CDW transition in bulk LaSb_2 remains an open question [83]. Recent studies [94] have found no evidence of a CDW gap opening. However a scenario where the CDW competes with SC would also be ameliorated by the structural transition from orthorhombic to monoclinic. Our bandstructure calculation show that the strongly 2D-like dispersion in the other square-net systems such as SmSb_2 -type LaSb_2 is not present in our structure (Figure 4.16). This may play a role in the suppression of the resistance anomaly associated with a structural transition that competes with superconductivity. Further investigations into the superconducting phase will be explored in later chapters.

4.8 Conclusion and Future Directions

In summary, we have experimentally and theoretically presented a newly stable polymorph in the family of rare-earth dantimonides in thin films of LaSb_2 deposited on MgO (001). The films are superconducting with a critical temperature enhanced relative to reports on bulk crystals under ambient conditions. The coherence length of the superconductor is comparable to the film thickness, pointing towards this family of materials as a promising platform to study 2D superconductivity even in "thick" films (i.e. with low disorder). The ability to synthesize thin film with different lattice motifs and layering orders compared to the bulk allows for an exploration into thickness dependent properties that are otherwise inaccessible or difficult to characterize in bulk samples. This will be the focus of the next chapter.

We have also argued on the basis of first principles calculations and also on the observed the electronic properties that the monoclinic phase is the same structure adopted by bulk crystals when subjected to pressure.

The lessons of this investigation point out new directions for discovering materials that may adopt novel crystal structures when grown as thin films. As we argued, the pressure-induced valence instability found in LaSb_2 led to competing structural arrangements. Similar structural phenomena and associated electronic properties may also show up with different

anions. For example, Rare-earth dibismides [139] host similar square-net structural motifs and pressure dependent electronic properties. The enhanced spin-orbit coupling along with the much larger bandwidth from the $6p$ may reveal further interesting physics such as inverted band structures or high-mobility Dirac fermions.

Changing the rare-earth element could also lead to observation of novel phenomena. For example, the compound CeSb_2 also shows a similar orthorhombic bulk crystal structure. However, a Ce^{2+} electronic state is far less stable compared to La^{2+} . Therefore the impact of epitaxial growth on the stacking arrangement would make for an interesting comparative experiment. The addition of magnetic degrees of freedom is yet another direction for the exploration of heavier rare-earth dantimonides. Given the dependence of the valence on the rare earth element in the rare-earth dantimonides, ternary alloys consisting of two different rare-earth elements with competing valence would be yet another fruitful direction.

While it remains unclear whether it is the epitaxial growth process that promotes the formation of the monoclinic phase or simply that the observed bulk orthorhombic phase is merely a metastable phase, it is clear that epitaxial growth has unlocked a new structural degree of freedom in these compounds.

Chapter 5

THICKNESS-DEPENDENT TRANSPORT IN LANTHANUM DIANTIMONIDE

5.1 Introduction

This short chapter is a compilation of results on our studies into the thickness dependence of the superconducting and transport properties of LaSb_2 . We begin by discussing the normal state transport properties and the evolution of the magnetoresistance described in the last chapter. We then proceed to discuss the thickness dependence of the superconducting properties. We fit the data to several models and discuss their relevance for understanding the superconductivity in LaSb_2 . Among these is a fit to a two gap model, motivated by the calculations in the previous chapter showing LaSb_2 to host multiple pockets. Finally, we study the scaling of superconducting T_c with thickness and disorder and find a new scaling relationship between T_c and the sample sheet resistance.

5.2 Thickness Dependence of the Normal State Transport

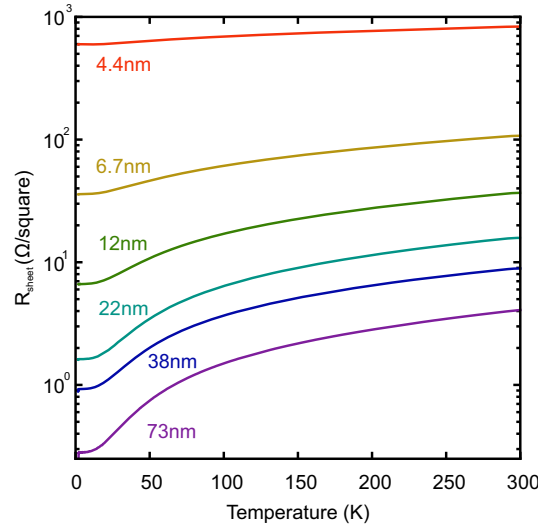


Figure 5.1: **Temperature dependence of sheet resistance for various thicknesses**

To understand the effect of thickness reduction on the normal state properties, we first studied the temperature dependence of resistance in zero applied field. The results are presented in 5.1. We find that as films are made thinner, there is a large increase in sample resistivity as well as a steep decline in RRR. Such behavior is a natural consequence of the

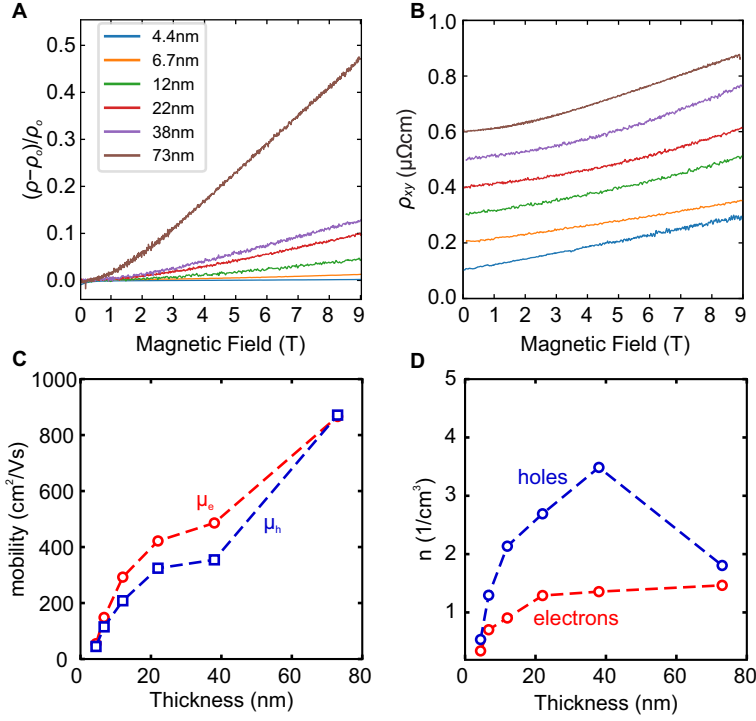


Figure 5.2: **Thickness dependence of normal state transport.** **A** MR. **B** Hall resistivity. **C** two carrier mobility. **D** Carrier density.

observations in the last chapter regarding growth. As the material initially forms on the substrate, the layers are disordered and poorly crystalline as revealed by the dim RHEED intensity. Crystallinity increases as growth proceeds leading to higher quality. To further characterize the normal state, magnetotransport measurements were performed. Data taken at 1.7K is presented in Fig. 5.2. In Fig. 5.2A, the MR is presented and shows a dramatic decline as the thickness is reduced. Concomitantly, the Hall resistance also evolves with thickness and gradually becomes more linear as thickness is reduced. We performed two carrier fitting to evaluate the transport properties as was done in the previous chapter. We find that the models fit for thin samples but are of poorer quality for the thick films, similar to the case in the last chapter. The mobility declines from its peak of around $1000\text{cm}^2/\text{Vs}$ to $\sim 50\text{cm}^2/\text{Vs}$. The carrier density also evolves and shows a decline as the thickness is reduced. However, given the poor quality of the fits of the two-carrier model for the thicker films (see previous chapter), the charge carrier numbers may not be accurate. However, despite these shortcomings, the trend of decreasing mobility with thickness is clear. Furthermore, given the reasonable fit to the low-thickness samples, more confidence can be placed in the estimates.

As in the case of the 120nm film studied in the last chapter, this reduction in MR and

transition to more linear hall can be explained by the reduction in electron mobility with thickness.

5.3 Thickness Dependence of the Superconducting Phase

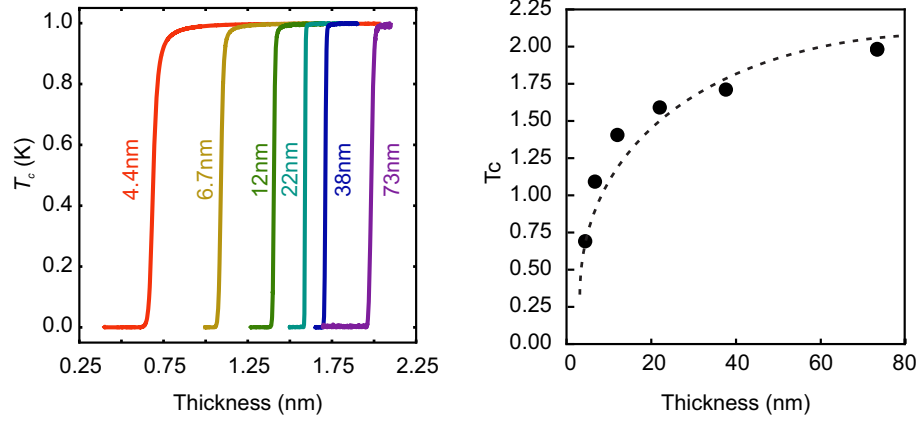


Figure 5.3: **Thickness dependence of the superconducting T_c** **A** Normalized Resistance vs Temperature. **B** Summary of T_c vs thickness.

There has been much work over the past decades on superconductivity in the 2D limit with much of the original work focused on ultra-thin, amorphous metals to study the superconductor-insulator transition [56]. More recently, advances in materials growth and device fabrication have allowed for investigations into superconductivity in ultra-clean platforms, most notably graphene. While much of this work has focused on atomically thin layers, strictly speaking, the 2D limit for superconductivity is reached once the thickness t of the material has been reduced below the in-plane coherence length ξ_{ab} . As we showed in the last chapter, LaSb₂ hosts an extremely long coherence length, comparable to some elemental type-1 superconductors [126]. According to this definition, LaSb₂ enters the 2D limit at thickness ~ 100 nm. We therefore sought to understand the impact of reduced dimensionality on the superconducting state.

In Fig. 5.3, we plot the observed T_c as a function of thickness for t ranging from 4.4nm up to 73nm. We find that reduction in sample thickness leads to a sharp drop in T_c moving from 2K down to ~ 700 mK for the thinnest film. Below this thickness, films were no longer conducting.

In Fig. 5.4, we plot the change in observed T_c against either the sheet resistance or sample thickness to determine which of these dominates the scaling of T_c . In Fig. 5.4A, T_c is plotted against $1/t$ and fit using the Simonian model [116]

$$T_c = T_{co}(1 - t_c/t) \quad (5.1)$$

Where T_{co} is the “intrinsic” T_c for the bulk material and t_c is the critical thickness below which $T_c \rightarrow 0$ and was derived using a Ginzburg-Landau model assuming $t \ll \xi$. Best fit to the data yields $T_{co} = 1.83 \pm 0.01\text{K}$ and $t_c = 2.73 \pm 0.08$. The value for T_{co} is in reasonable agreement with the observed value $\sim 2\text{K}$ yet there is notable deviation of the data from the films with larger thicknesses. This could be the symptom of the break down of the assumption that $t \ll \xi$ as t gets larger. This could also be the result of the substantially lower disorder in these films (see Fig5.1).

In 5.4B, We next considered a fit to the Finklestein model [33] given by:

$$\frac{T_c}{T_{co}} = \exp(\gamma) \left(\frac{1-X}{1+X} \right)^{1/\sqrt{2}r} \quad (5.2)$$

where:

$$\gamma = \text{Ln}(\hbar/\tau T_{co} k_B); X = \left(\frac{\sqrt{r/2}}{\frac{r}{4} + 1/\gamma} \right) \quad (5.3)$$

and:

$$r = \left(e^2/2\pi^2\hbar \right) R_s \quad (5.4)$$

Where R_s is the sheet resistance. This model was derived to explain the scaling of T_c for highly disordered films close to the superconductor-insulator transition (SIT). This model demonstrates the impact of quenched disorder (i.e. sheet resistance) on T_c and assumes nothing about the thickness. It therefore assumes a high enough degree of disorder that the disorder strength is the dominant energy scale. Given the comparably low sheet resistances for our LaSb_2 films, it is not unexpected that this model fails to fit the data entirely. The third model we consider is the universal scaling model due to Ivry *et. al* [50]. This model attempts to combine the observed dependence of T_c on both thickness and sheet resistance into a single scaling formula:

$$T_c t = A R_s^{-B} \quad (5.5)$$

Where t is the film thickness, and A and B are fitting parameters. Their analysis of data taken over the past several decades demonstrates that this formula is broadly applicable and captures the behavior of superconductors ranging from clean to highly disordered. Our fit to this model is given in 5.4C. We find that the data can be modelled with a power law of this form and we find $A = 62 \pm 1\text{Knm}$ and $B = 0.56 \pm 0.04$. While the data can be captured by this power law, the obtained values from the fits differ markedly from the observations in [50]. For the majority of the materials discovered, $B \approx 1$. Furthermore, one also finds a strong correlation between A and B . The values from our fits deviate substantially both in the magnitude and also in the relative value of A and B . Furthermore, the scatter of the data

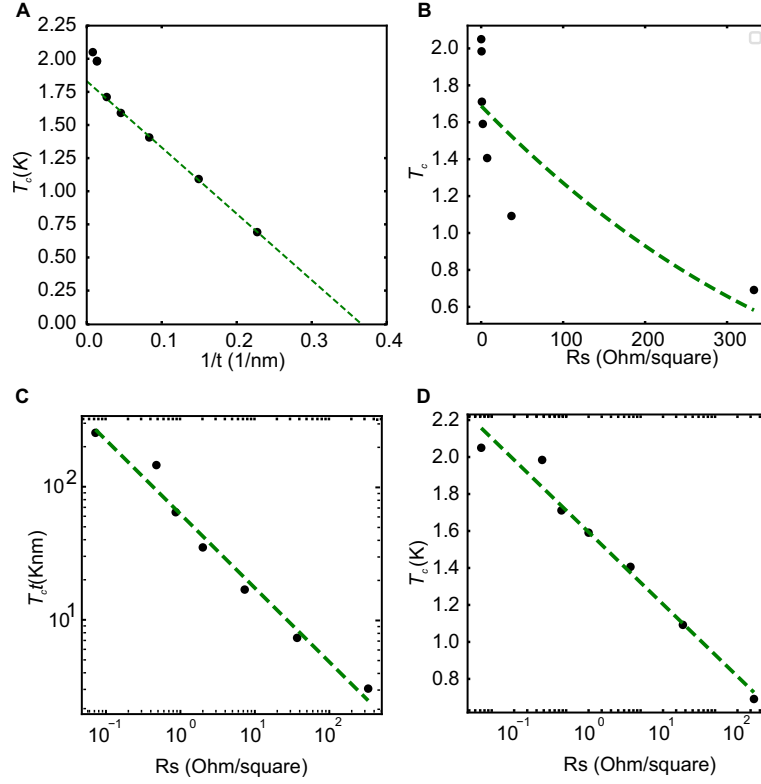


Figure 5.4: **Scaling of T_c with thickness** **A** Simmonian model [116]. **B** Finklestein model. **C** Universal scaling model. [50] **D** Novel logarithmic scaling.

about the line of best fit is clearly not entirely random. All of these observations suggest that the scaling of T_c with thickness cannot be fully understood within this paradigm.

Finally, we propose the following model

$$T_c = A \ln \left(\frac{R_o}{\gamma R_s} \right) \quad (5.6)$$

where γ and A are fitting parameters and $R_o = h/e^2$. In 5.4D, we display the fit using this formula and find $\gamma = 0.94 \pm 0.04$ and $A = 0.17 \pm 1K$. The former value indicates that the relevant scale to which we compare the sample sheet resistance is the quantum of resistance h/e^2 . Physically, this results implies that it is primarily the disorder in the material that is responsible for the reduction in T_c . It is quite surprising that this scaling appears to hold over several decades of sheet resistance. This is because it is generally believed (Anderson's theorem) that disorder that preserves TRS has minimal effect on T_c until it becomes sufficiently strong to become the dominant energy scale. This observation could be the result of the fact that the material is in the 2D limit up to quite high thicknesses.

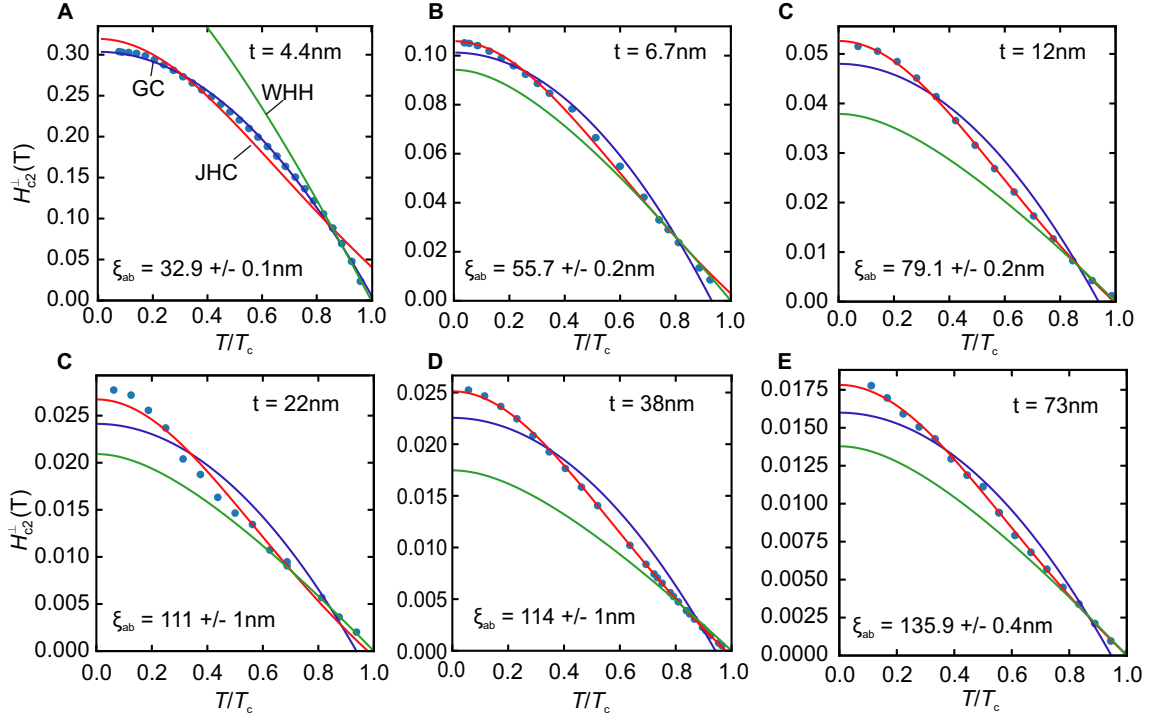


Figure 5.5: Temperature dependence of H_{c2} for various thicknesses

Critical Field Dependence

We also investigated the perpendicular critical field behavior as thickness was reduced. In Fig5.5, we plot the measured H_{c2} as a function of temperature for the various thicknesses. To each, we apply several formulae to fit their critical field behavior. A compilation of various models to fit critical field data can be found in [124]. First, we fit the modified Gorter-Casimir (GC) two fluid model [41] with the substitution $H_c \rightarrow H_{c2}$ [124]:

$$H_{c2}(T) = \frac{\Phi_o}{2\pi\xi_{ab}^2(T=0)} \left(1 - \left(\frac{T}{T_c} \right)^2 \right) \quad (5.7)$$

In this formula, the fitting parameters are ξ_{ab} , the in-plane coherence length and T_c , the critical temperature. This formula was found to only accurately capture the physics of the 4.4nm film. In all other cases, it badly fits the data and underestimates $H_{c2}(T=0)$.

The Gorter-Casimir theory also gives an expression for the temperature dependence of $\lambda(T) = \lambda(T=0)(1 - (T/T_c)^4)^{-1/2}$, the London penetration depth. When combined with the Ginzburg-Landau expression, one gets the modified formula:

$$H_{c2}(T) = \frac{\Phi_o}{2\pi\xi_{ab}^2(T=0)} \frac{\left(1 - \left(\frac{T}{T_c} \right)^2 \right)}{\left(1 + \left(\frac{T}{T_c} \right)^2 \right)} \quad (5.8)$$

This formula was originally derived by Jones, Hulm, and Chandrasekar (JHC) [53]. Again the fitting parameters are ξ_{ab} and T_c . In all other cases besides $t=4.4\text{nm}$, the films show a positive curvature near T_c . This type of critical field behavior has been observed in other layered superconductors and has been associated with multi-band effects [45, 75], or anisotropic electron-phonon coupling [30]. The possibility of multi-band effects will be explored later, but simple formulae for the effects of anisotropy are not available. It is likely that such investigations require the use of full first-principles calculations. However, our analysis finds that JHC is able to model the positive curvature. The physical reason for this could be that because the coherence length is so long, it begins to approach the London depth. As a result, the latter cannot simply be treated as constant and its temperature dependence must be taken into account.

Finally, We fit the data to the well-known WHH formula.

$$\ln(t) = \left(\frac{1}{2} + \frac{i\lambda_{so}}{4\gamma}\right) \psi\left(\frac{1}{2} + \frac{\bar{h} + \frac{1}{2}\lambda_{so} + i\gamma}{2t}\right) + \left(\frac{1}{2} - \frac{i\lambda_{so}}{4\gamma}\right) \psi\left(\frac{1}{2} + \frac{\bar{h} + \frac{1}{2}\lambda_{so} - i\gamma}{2t}\right) - \Psi\left(\frac{1}{2}\right) \quad (5.9)$$

For the WHH model, $H_{c2}(T = 0) = \Phi_0/2\pi\xi_{ab}^2$ is given by the simplified formula:

$$H_{c2}(T = 0) = -0.7T_c \left. \frac{dH_{c2}}{dT} \right|_{T \rightarrow T_c} \quad (5.10)$$

Among these formulae, the WHH is found to perform badly in all cases. This is because its temperature dependence is primarily determined by the initial slope of the $H_{c2} - T$ curve as described by eq. 5.10. In these compounds, the higher thickness films show positive curvature near T_c . As a result, WHH consistently underestimates the value of $H_{c2}(T = 0)$. For the 4.4nm case, the initial slope is much larger, likely due to the short mean free path when the film is made thin. In this case WHH gives an overestimate.

By using these fits, estimates of ξ_{ab} can be obtained and we plot the results in Fig. 5.6. We find that as the thickness is increased, the coherence length correspondingly increases. The coherence length is consistently larger than the film thickness, placing all of these films in the 2D limit. The increase in coherence length is expected because as the film is made thicker, the sheet resistance is found to decline and the RRR increase (Fig. 5.1). This implies an increase in the mean free path l_{mfp} for electron scattering. In the Ginzburg-Landau regime, ($T \approx T_c$), the coherence length for a dirty-limit ($l_{mfp} \ll \xi_{ab}$) scales as $\xi \sim (\xi_o l_{mfp})^{1/2}$ where $\xi_o = \hbar v_F / \pi \Delta(0)$ with v_F being the Fermi velocity and $\Delta(0)$ the superconducting

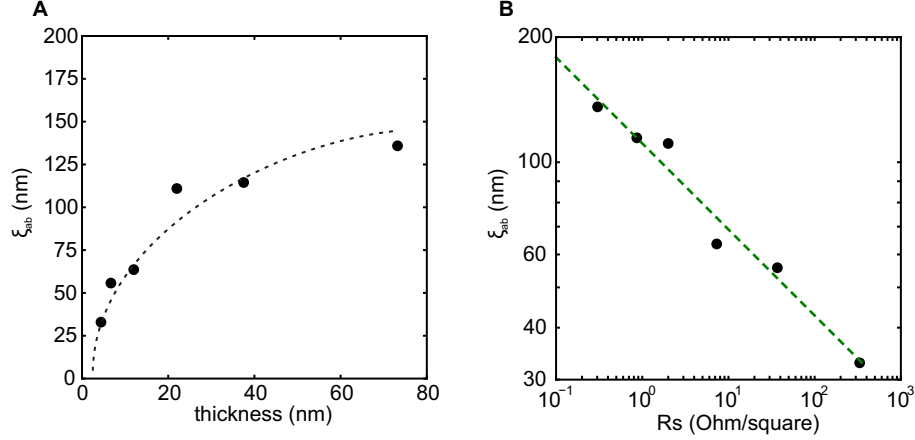


Figure 5.6: **Thickness dependence of the in-plane coherence length** **A** ξ_{ab} vs T . **B** scaling of the coherence length with sheet resistance.

gap. To determine whether this scaling holds, we plot the coherence length vs the sheet resistance $R_s \propto l_{mfp}$. The data reveal a power law relationship that goes like:

$$\xi(R_s) = AR_s^{-B} \quad (5.11)$$

Where A and B are fit parameters. While GL theory predicts $B \approx 0.5$, our data is best fit with $B = 0.201 \pm 0.003$ which is $\sim 1/5$. This anomalous dependence on sample quality could point to more subtle dependence of the superconducting state on thickness and quality. Given the formula for ξ_0 , it is generally expected that the coherence length will decrease with increasing T_c . However, in the dirty limit, the GL formula implies that coherence length is limited by the sample mean free path. This is in line with our observations. With increasing thickness, sample R_s decreases, but this causes only a logarithmic increase in T_c (5.6) but a power law increase in coherence length. These observations explain the anomalous increase in coherence length with increasing thickness and T_c .

Normal state transport is highly suggestive of multiple carrier transport. This was previously backed up by DFT calculations which showed multiple Fermi surface pockets (see previous chapter). This leads to the possibility that the superconductivity in LaSb_2 is of a multi-gap nature. It is difficult to establish this from transport alone, however, if we fit the temperature dependence of the critical field to a two gap model, we find that the results of the fit paint an appealing picture.

In Fig. 5.7, we again plot the temperature dependence of the critical field along with fits to the following formula, originally derived by Gurevich to explain the multigap properties of MgB_2 [45]. However, it has also been applied to 2D systems such as stanene [75]

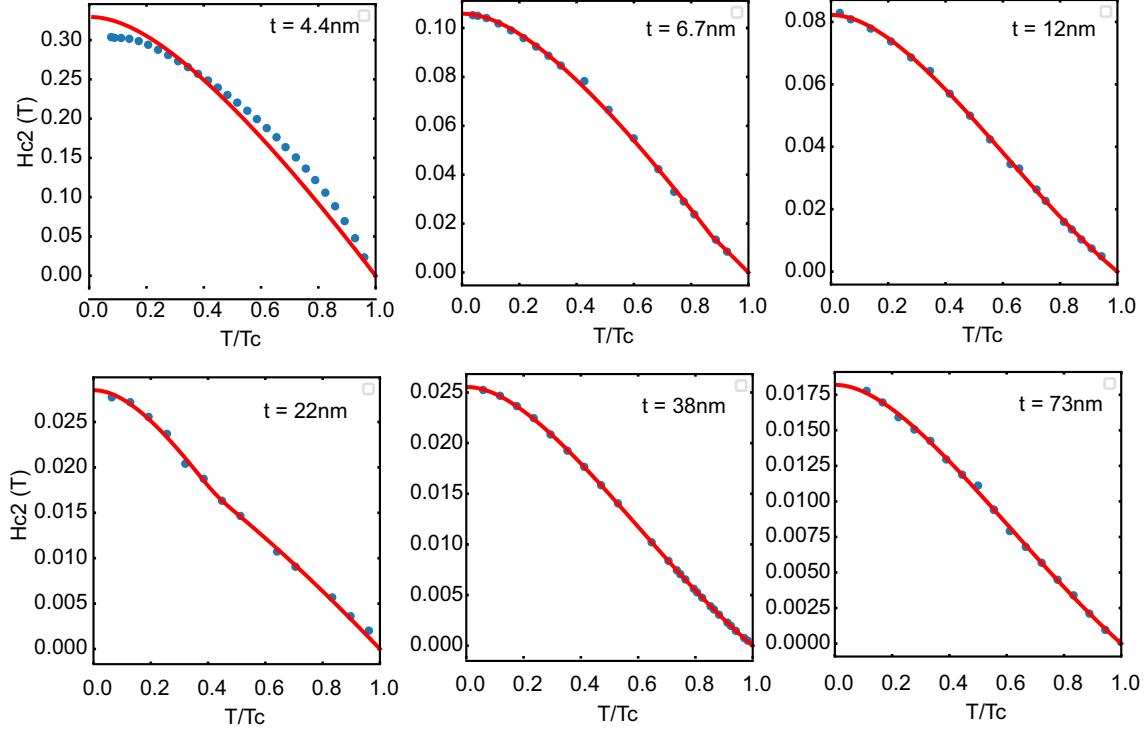


Figure 5.7: **Two gap fits as a function of sample thickness**

$$\ln \frac{T}{T_c} = - \frac{\left[U \left(\frac{eD_1\mu_0 H_{c2}}{hT} \right) + U \left(\frac{eD_2\mu_0 H_{c2}}{hT} \right) + \frac{\sqrt{(\lambda_{11}-\lambda_{22})^2 + 4\lambda_{12}^2}}{\lambda_{11}\lambda_{22} - \lambda_{12}^2} \right]}{2} + \left[\frac{\left(U \left(\frac{eD_1\mu_0 H_{c2}}{hT} \right) - U \left(\frac{eD_2\mu_0 H_{c2}}{hT} \right) - \frac{\lambda_{11}-\lambda_{22}}{\lambda_{11}\lambda_{22} - \lambda_{12}^2} \right)^2}{4} + \frac{\lambda_{12}^2}{(\lambda_{11}\lambda_{22} - \lambda_{12}^2)^2} \right]^{\frac{1}{2}} \quad (5.12)$$

Where $U(x) = \psi(x + \frac{1}{2}) - \psi(\frac{1}{2})$, λ_{11} , λ_{22} , are the electron-phonon coupling constants for the two bands and λ_{21} is the inter band coupling constant. D_1 and D_2 are the diffusivities for the two bands. If we recall the discussion of the WHH formula (1.18), we find that $U(x)$ is nothing more than the AG pairbreaking formula 1.3 for a thin film superconductor in a perpendicular field. This rather complicated looking expression is simply an extension of that model to the case of two superconducting, isotropic Fermi surfaces. The electrons in these bands have distinct mobilities as captured through the different diffusion constant and different electron-phonon coupling constants. In the limit $D_1 \rightarrow D_2$, the expression reduces to the WHH formula neglecting SOC. Even though these materials do have strong SOC, the small values of the critical field imply that the orbital contribution is the primary

pair breaker in a perpendicular field and thus SOC can be neglected.

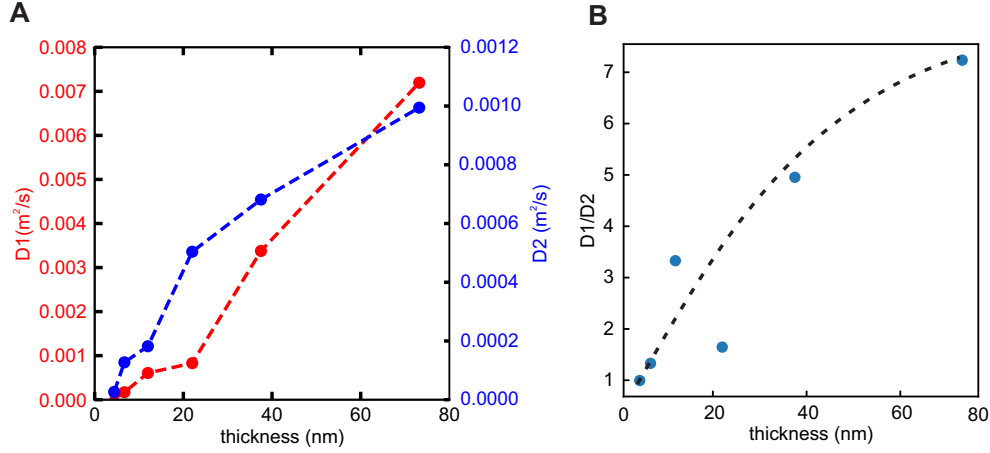


Figure 5.8: **Two gap fitting of the critical field data.** **A** evolution of fitted diffusivities for the two bands. **B** evolution of the ratio of diffusivities from the two gap fits.

The results of the fitting are given in Table 5.3. We found that the value of λ_{11} and λ_{22} converged to values that were barely different from their starting guess. The reason for this is that these two values enter equation 5.12 as the difference. Thus, the fits suggest that these values are quite close to one another. Additionally, we find that λ_{12} is quite small in all cases. This parameter also enters the formal as λ_{12}^2 . Therefore, it can be deduced that the critical field behavior does not substantially result from differences in the electron-phonon coupling. The behaviors of the diffusivities D_1 and D_2 are much more interesting. The first thing to note is that their values agree well with the estimates that could be obtained from the mobilities fit by the two band model (i.e. $D = \frac{1}{3}v_F^2\tau$ where τ is the scattering time estimated from the mobility and v_F is the Fermi velocity obtained from the charge density assuming isotropic Fermi surfaces). Again, this is a questionable approximation but given the fact that 5.12 is also the result of an isotropic model, the agreement gives confidence in the validity of the fit.

In Fig. 5.8A, we plot the values of the diffusivities from the two gap fits. We find that the diffusivities of both bands drop with sample thickness. This is again expected from the fact that l_{mfp} declines with reduced thickness. In Fig. 5.8B, a plot of the ratio D_1/D_2 is shown. We find that for large thickness, there is a substantial discrepancy between the two values leading to $D_1/D_2 \sim 7$. However as thickness is reduced, this ratio also drops quite dramatically and approaches $D_1/D_2 \sim 1$ in the thin limit. Notably, the 22nm sample appears to not follow the trend. Looking at the plot Fig. 5.7D, the critical field behavior is anomalous compared to the other sample. Therefore the values of D_1 and D_2 are likely the result of overfitting this dataset. However, despite this deviation, the remaining values scale

t (nm)	λ_{11}	λ_{22}	λ_{21}	D_1 (cm^2/s)	D_2 (cm^2/s)	D_1/D_2
4.4	0.77	0.05	0.00	0.26	0.26	1.00
6.7	0.21	0.21	0.00	1.69	1.27	1.33
12	0.21	0.20	0.01	6.06	1.82	3.33
22	0.22	0.24	0.001	8.29	5.04	1.65
37	0.20	0.17	0.02	33.77	6.82	4.95
73	0.18	0.10	0.03	71.96	9.94	7.24

Table 5.1: Fit parameters from two gap fitting

in the way described. In the thick limit, therefore, the fits suggest that there are two bands with different diffusivities that contribute to H_{c2} . These bands each have different critical field response which leads to the positive curvature of the H_{c2} vs T plot. $D_1/D_2 \rightarrow 1$ implies that there is no longer a distinction between the two bands and the material is no longer described by a two band model. It seems that as a result of the reduction in thickness and increased scattering, superconducting properties are now captured by a single band model.

5.4 Discussion and Future Directions

In this chapter, we have highlighted the results of our investigations into the thickness dependence of the transport properties of $LaSb_2$. First, the reduction in thickness is associated with a reduction in electron mobility. This is manifested both through higher residual resistivity and also through reduced MR. The linear MR observed in the thick films gradually evolves into a quadratic field dependence reminiscent of Drude physics.

It is the thickness dependence of the superconducting properties that hint toward the possibility of two-band superconductivity. First, while the critical field data can indeed be fit by simple models such as the GC and the JHC models, the scaling of the critical temperature and coherence with thickness do not appear to follow the traditional scaling expectations observed in conventional metals. Therefore the standard picture where one considers the effect of disorder on the SC condensate that is otherwise unchanged (analogous to a "rigid band approximation") does not seem to hold. As mentioned, the two-band fitting suggests that reduction in thickness is actually changing the Fermi surface in a fundamental way. This last point is further bolstered by the aforementioned reduction in the evolution from linear to quadratic MR.

Alternatively, these results seem to suggest that something unexpected is happening when a superconductor enters the "2D limit" but is not sufficiently thin that localization or quantum corrections to the normal state resistance become relevant. It is rather rare to find materials

(outside of isotropic, elemental metals) with comparably long coherence lengths. The anomalous scaling may therefore be explained as originating from 2D superconducting fluctuations in the presence of relatively clean material. This is a regime of parameters that is relatively under-explored

Unfortunately, these experiments approach the limits on usefulness of electrical transport for studying the superconducting properties. Scanning tunneling microscopy would be a particularly useful tool to determine whether two-gap superconductivity is indeed present and how it changes with temperature and applied field. It would also help to understand the effect of disorder and changes in the local density of states on the superconducting state. Measurements of the critical current may also shed light onto the vortex state but would likely require fabrication of narrow channels to reduce the required currents to sufficiently small values. The sensitivity of these materials to air and moisture makes this difficult but not impossible (e.g. through the use of dry lithographic techniques). Finally, accurate first-principles calculations of the effects of thickness reduction on the band structure as well as the electron-phonon coupling would be highly informative for understanding this material.

FIELD-INDUCED SUPERCONDUCTIVITY IN CERIUM DOPED-LANTHANUM DIANTIMONIDE

6.1 Introduction

The centrality of symmetry in the physics of superconductivity was realized soon after the development of the Bardeen–Cooper–Schrieffer (BCS) theory. The combination of time-reversal and inversion symmetry, responsible for the two-fold spin-degeneracy of the conduction electrons, is essential for preserving s-wave pairing in conventional superconductors, even in the presence of strong disorder [4]. Accordingly, superconductors with broken symmetries are prime platforms for probing unconventional superconducting behavior. Both the breaking of inversion symmetry in the presence of strong spin-orbit coupling as well as time-reversal symmetry breaking leading to spin polarization have been used as pathways to conceive microscopic mechanisms such as Ising [148], spin-triplet [6], or finite momentum pairing [36, 68]. Experimental canvassing of an array of materials has also tied the importance of symmetry to exotic pairing through the observation of extremely high upper critical fields [80, 110, 138, 24, 131], large critical field anisotropies [58, 118, 147], reentrant [106, 15, 149, 32], and even field-induced phases in magnetically ordered crystals [90, 76, 128, 7]. These phases are often probed by utilizing two-dimensional (2D) crystals, as the influence of anisotropies and crystalline symmetries are amplified in reduced dimensions while the suppression of the superconducting state in a magnetic field applied parallel to the film is weakened. And while changing layer number and chemical composition have been extensively employed for the tuning of superconducting properties, in this chapter, we study the impact of competing time reversal symmetry breaking perturbations by way of precision doping dilute paramagnetic impurities into a 2D crystalline superconductor.

In Ch 1, we introduced the concept of "pair-breaking" as a mechanism to understand the action of a time reversal asymmetric perturbation on the condensate. The primary experimental result of this chapter is the discovery of a material platform by which different pair-breaking mechanisms can be selectively tuned by the application of a magnetic field. This ultimately allows for the realization of field-induced superconductivity. Such an effect was brought about by introducing paramagnetic dopants into the crystal. A magnetic field will polarize the magnetic impurities thereby reducing the spin-flip scattering rate. This leads to a reduction in the pair-breaking strength of the magnetic impurities. Of course,

the field itself will lead to pair- breaking through the orbital and paramagnetic effects. By delicately balancing the strength of these various pairbreakers, one can use the magnetic field to enhance SC before ultimately destroying it. To understand how this comes about more quantitatively, we employ an extension of the original AG treatment that accounts for the polarization of the impurity spin. This extension was given by Khartinov and Feigelman [57]. Before describing that theory, we will begin by describing how the response of the magnetic impurities to the applied field can modify the pair breaking parameters discussed in Ch. 1.

6.2 Effect of Impurity Spin Polarization: The Khartinov Feigelman Theory

For this analysis, we treat the magnetic impurities as paramagnetic spins which respond to the applied field according to the Brillouin function.

$$\langle J_z \rangle = \left(J + \frac{1}{2} \right) \coth \left[\left(J + \frac{1}{2} \right) \frac{gH}{T} \right] - \frac{1}{2} \coth \frac{gH}{2T} \quad (6.1)$$

Where H is the applied field, $g = 2$ is the Lande g factor and T is the temperature. We have set $\mu_B = k_B = 1$ We will ignore coupling between spins as well as the Kondo effect. For rare-earth ions, the presence of strong SOC implies that only the total angular momentum J is a good quantum number.

In the mean-field approximation, the effect of these polarized spins on the conduction electrons is the generation of an internal exchange field given by:

$$H_{ex} = n_S J_{ex} \langle J_z \rangle \quad (6.2)$$

where n_S is the concentration of magnetic impurities, $\langle S_z \rangle$ is the spin polarization and J is the exchange coupling constant. It turns out that that this internal exchange field has no impact on the orbital pairbreaking term. However it does modify the paramagnetic term as follows:

$$\frac{1}{\tau_s} = \nu_s = \frac{\tau_{SO} e^2 \hbar (H - H_{ex})^2}{m^2 c^2} \quad (6.3)$$

[137]. For ferromagnetic exchange ($J_{ex} < 0$) between the impurity and itinerant spins, the action of the exchange field is to amplify the effect of the applied field. When this happens, the critical magnetic field (H_{c2}) can exhibit non-monotonic behavior reaching a maximum at moderate temperatures with subsequent reduction as $T \rightarrow 0$ due to the augmenting of the applied field by the resulting exchange field [22]. In the case of antiferromagnetic exchange ($J_{ex} > 0$), also known as Jaccarino-Peter (JP) mechanism [51], the applied external field

is compensated by the internal exchange due to the polarized impurities. This has lead to observations of not only extremely high critical fields, it has also revealed reentrant and field-induced superconductivity in samples with magnetic order [137, 32, 90, 76, 128, 7].

Central to the theory of Khartinov and Feigelman, when spins are polarized, there is a reduction in the pair-breaking scattering rate due to spin flip scattering off of magnetic impurities. The expression for the pair breaking rate is given by

$$\Gamma = \nu_S \frac{\langle J_z^2 \rangle}{J(J+1)} + \nu_S \frac{\langle J_\perp^2 \rangle}{J(J+1)} \quad (6.4)$$

where

$$\nu_S = 2\pi\nu(\mu)J_{ex}^2J(J+1)n_s \quad (6.5)$$

is the original AG scattering rate 1.3. In 6.4 the first term breaks Cooper pairs *without* spin-flip while the second term with $\langle J_\perp^2 \rangle \propto \langle J_+J_- \rangle$ or $\langle J_-J_+ \rangle$ where J_+ and J_- are the raising and lowering operators for impurity angular momentum, describes perturbations that give rise to pair breaking with spin flip. In the case of isotropic scattering, with impurity spins pointing in random directions, there is no distinction between these terms and the expression reduces to the AG formula. However, once the spins are polarized by the external field, this is no longer the case and the expression is modified and becomes

$$\Gamma = \nu_S \frac{\langle J_z^2 \rangle}{J(J+1)} + \nu_S \frac{\langle J_\perp^2 \rangle}{J(J+1)} - \delta\Gamma(\epsilon) \quad (6.6)$$

where

$$\delta\Gamma(\epsilon) = \nu_S \frac{\langle J_z \rangle}{J(J+1)} T \sum_{|\omega| > |\epsilon|} \frac{2\omega_S}{\omega^2 + \omega_S^2} \quad (6.7)$$

reduces the spin-flip scattering rate. Here $\epsilon = \pi T(2k+1)$ and $\pi T 2l$ are the fermionic and bosonic Matsubara frequencies for the electrons and spins respectively and k and l run over positive and negative integers. $\omega_S = gH$ is the Zeeman energy of the electron. In the limit $H/T \gg 1$, spins become fully polarized and the total scattering changes from $\nu_S \rightarrow \frac{J}{J+1}\nu_S$. The physical reason for this effect is as follows. As the magnitude of the applied field increases, the Zeeman splitting between the energy levels of an impurity with spin direction pointed parallel and antiparallel with the field increases. At sufficiently low temperature, spin-flip scattering is completely frozen out, leaving only pair breaking due to the non-spin flip perturbations. The effect this therefore most pronounced for $J = 1/2$ and decreases as the impurity spin gets larger.

With these expressions for the effect of magnetic field on the pair-breaking parameters, Khartinov and Feigelman obtained a formula to calculate T_c

$$\ln \left(\frac{T_c}{T_{c0}} \right) = \pi T \sum_{\epsilon} \left(\frac{1}{|\epsilon|} - C_0(\epsilon) \right) \quad (6.8)$$

where again, $\epsilon = \pi T(2k + 1)$ and C_0 is the Cooperon Green function that satisfies:

$$\left(|\epsilon| + \nu_S - \delta\Gamma(\epsilon) + \frac{1}{2} (\hat{L}_o - \Gamma_{sf}(\epsilon)) + \frac{3(h - n_S J_{ex} \langle J_z \rangle)^2}{2\nu_{SOS}} + \frac{2(p_F t)^2 h^2}{9\nu} \right) C_0(\epsilon) = 1 \quad (6.9)$$

At first glance this is a very complicated expression. However, each of the terms in the brackets on the RHS can be understood in terms of everything we have already described. The first term $\epsilon = \pi T(2k + 1)$ is again the fermionic matsubara frequency. The second and third terms describe the effect of impurity spin polarization on the exchange scattering (or spin-flip scattering) rate, the sixth and seventh terms are the familiar paramagnetic and orbital terms where the paramagnetic term has been modified by the effect of the exchange field. The numerical differences between these and the expression of Ch1. are due to choices of units. Notice in these terms, the scattering times τ and τ_{SOS} are expressed as rates ν and ν_{SOS} . The last remaining terms are

$$\Gamma_{sf} = \nu_S \frac{\langle J_{\perp}^2 \rangle}{J(J+1)} - \delta\Gamma(\epsilon) \quad (6.10)$$

is just the spin-flip part of the total scattering rate and

$$\hat{L}_0 C_0(\epsilon) = \nu_S \frac{\langle J_z \rangle}{J(J+1)} T \sum_{\omega} \frac{2\omega_S}{\omega^2 + \omega_J^2} C_0(\epsilon - \omega) \quad (6.11)$$

is an operator expression which is a convolution between the Cooperon and the spin correlation function. Because this term requires knowledge of C_0 at all energies, it must be determined self consistently. In a later section, we will describe our method for numerically solving these equations to fit the experimental data.

Finally, if we take the KF expression for the Cooperon in the limit $H \rightarrow 0$, i.e. only consider the action of the magnetic impurities, the expression reduces to

$$C_0(\epsilon) = \frac{1}{|\epsilon| + \nu_S} \quad (6.12)$$

and 6.8 reduces to 1.11.

In the AG theory, $\tau_s \sim 1/\nu_S$ gives the lifetime for the Cooper pair due to the perturbation. We can therefore interpret all the remaining terms in the Cooperon self-energy as either reducing (positive terms) or enhancing (negative terms) this lifetime and it is this lifetime that ultimately determines T_c . Because these terms have opposing dependence on the external field, the right balance of parameters allows for the inducing of superconductivity by the magnetic field.

Finally, we emphasize that the original KF theory was formulated for amorphous, disordered superconductors. It is an isotropic, s-wave theory that neglects the effect of crystal structure and Fermi-surface anisotropy. Given that LaSb_2 is of high crystalline quality, these approximations are likely not valid for this material. However, we will find that the results of the fitting qualitatively reproduce those obtained from fitting the normal state transport properties. It will therefore serve as a first step toward understanding the behavior of this material.

6.3 Magnetically Doping LaSb_2

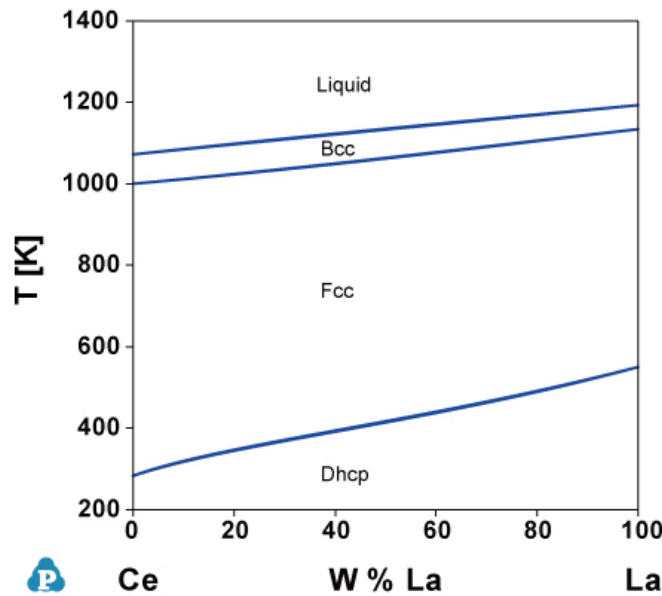


Figure 6.1: **Phase diagram of Ce-La showing a continuous solid solution between end points [43].**

Growth of Ce-doped LaSb_2

To explore the effects of time-reversal symmetry breaking perturbations and the possibility of realizing field-induced superconductivity, it is first necessary to find a magnetic dopant

that will effectively dissolve into LaSb_2 so as to minimally perturb the host crystal and its electronic structure. Such a role is very naturally served by Ce, the rare-earth element immediately to the right of La. As can be seen in Fig. 6.1, Ce forms a solid solution with La, at least when in elemental form. The expected 3+ valence adopted by Ce in this structure leaves a single f -electron bound to the Ce ion. This single f -electron should act as a local moment with $J = 5/2$. We neglect the crystal field splitting as we expect it to be small for localized f -electrons.

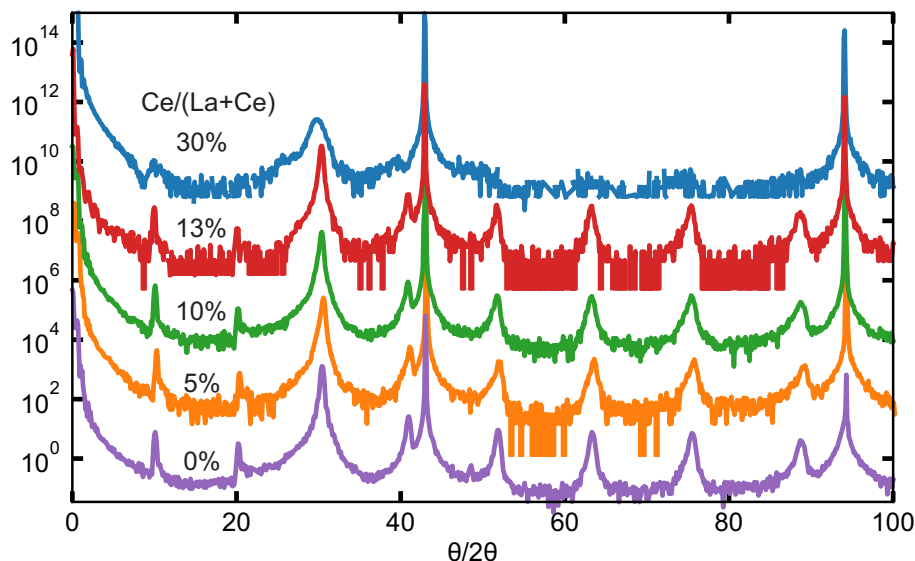


Figure 6.2: **X-ray diffraction of Ce-doped LaSb_2 thin films at varying doping concentrations.** It can be seen that the crystal quality is maintained at a high level at least as high as 13% Ce.

Because CeSb_2 in the bulk forms the identical structure as bulk LaSb_2 , it is reasonable to expect that it would substitute for La when doped into LaSb_2 . To verify that this was the case, and that it did not, for example, nucleate a second phase of CeSb_2 , we grew a series of films of varying Ce concentrations. XRD data from these growths is given in 6.2. We see that up to 30% Ce, the films adopt the expected Y^+ (monoclinic) LaSb_2 structure that was discussed in Ch 4. Beyond this concentration, structural quality suffered significantly. These growths were performed in similar conditions as described in Ch. 4. We therefore suspect that the degradation in quality was due to a shifting of the optimal growth window as Ce concentration increased. While this was not explored further, the absence of any obvious second phases even up to very high percentages gave confidence that doping of LaSb_2 would be possible.

Quantifying concentration in thin film is very challenging, especially in the ultra-dilute limit. Techniques such as EDX suffer from insufficient signal from thin films while the

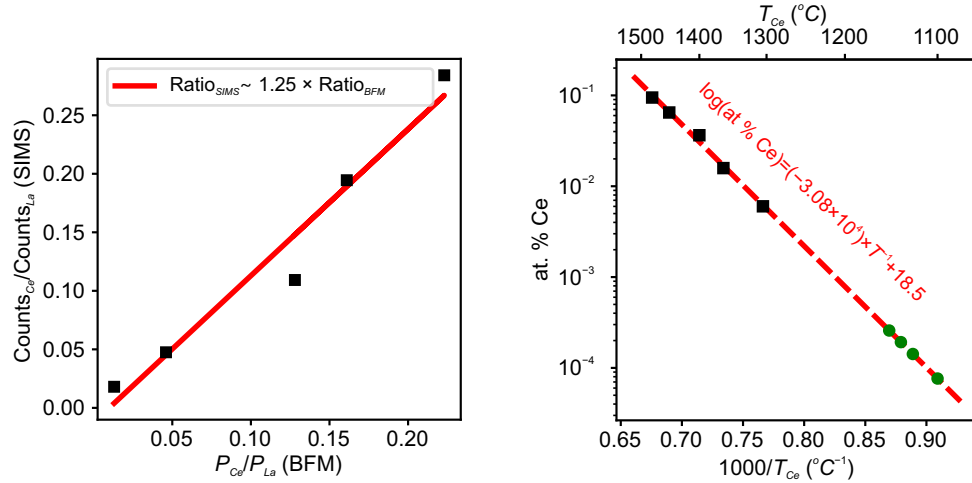


Figure 6.3: **SIMS analysis of film composition.** **A** Comparison of Ce/La ratio as measured using *in-situ* flux measurement vs the relative counts obtained in SIMS. **B** extrapolation from measured Ce concentrations to the low Ce regime used for studying the effect of dilute doping of LaSb_2 .

overlapping peaks from La and Ce in the RBS spectrum render that tool ineffective as well. Therefore, we turned to secondary ion mass spectrometry (SIMS) to study the concentration of Ce within LaSb_2 . This technique is used to investigate dilute impurities in crystal by ablating in the material in vacuum by bombarding with ionized noble gases. Atoms are released and directed through a sensitive mass spectrometer allowing them to be identified. In Fig. 6.3A, we plot the measured Ce/La peak intensity ratio ν_S that was expected from the ratio of beam fluxes. For flux ratios below 1%, the BEP of Ce was too low for the beam flux monitor to measure. However, for these concentrations, the quantification from SIMS is well in line with the expectations from the beam flux measurement.

In Fig. 6.3B, we plot the measured concentration ν_S the inverse temperature of the Ce effusion cell. Effusion cells evaporate by an Arrhenius process (see Ch. 2) which is nicely demonstrated by the linear relationship displayed by the measured points. This allows the activation energy for the evaporation to be extracted. For more dilute concentrations of Ce, however, SIMS returned unphysically large concentrations. The green dots represent a series of temperatures that will be of much interest later in the chapter. Extrapolation of the behavior observed to this temperature regime yields concentrations $\sim 0.01\%$ (100ppm). This should be easily measurable in SIMS which has a detection limit of parts-per-billion. However, when films of these concentrations were measured, concentrations $\sim 3\%$ were reported! We therefore used the extrapolated values as estimates of the Ce concentration. This assumes that the activation energy has minimal temperature dependence. This is a

reasonable assumption given that the extrapolated temperature region is only $\sim 20\%$ lower than the reliably measured temperature regime.

Kondo Effect LaSb_2

To understand the impact of magnetic doping on the electronic properties, transport measurements were performed on thicker samples to avoid the possibility of Anderson localization. In Fig. 6.4, we plot the temperature dependence of resistance, with the inset focusing on the low temperature regime. At around 10K, there is a minimum in the resistance, which begins to rise as temperature decreases.

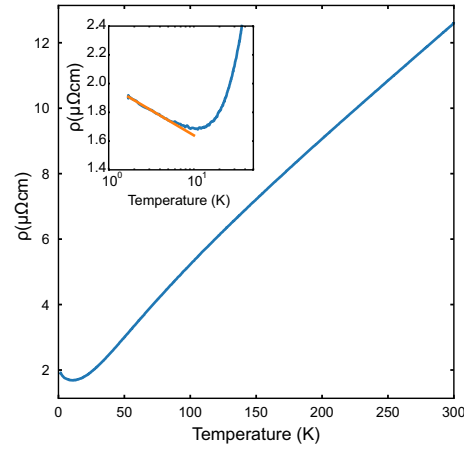


Figure 6.4: **Kondo effect in LaSb_2 .** Temperature dependence of resistance of a 1% doped LaSb_2 sample with thickness 22nm. Inset: Zoom in on the low temperature regime. Plotted in log scale to highlight the expectation from the Kondo effect.

This phenomenon is known as the Kondo effect and has been widely observed in metals with magnetic impurities [1]. It results from an antiferromagnetic exchange coupling between conduction electrons and impurities. As the temperature is lowered, scattering from the impurity is enhanced and the resistance increases with $\ln(1/T)$. This enhanced scattering eventually leads to the screening of the impurity. The Kondo temperature is the energy scale at which the magnetic impurity is maximally screened. For impurity spin $S = 1/2$, this screening is complete, while for higher spin, the screening is incomplete [129]. For the Anderson impurity model, this temperature is given by $T_k \sim D \exp(-1/J_{ex}N_F)$ where J_{ex} is the AFM exchange coupling constant and N_F is the density of states at the Fermi level. Kondo scattering is associated with a $\ln(T)$ contribution to the resistance. In the inset of 6.4, we plot the temperature dependence of resistance on a log scale to reveal this behavior. Upon reaching maximal screening, a plateau in the resistance is observed. T_k is then taken to be the temperature at which such deviation from $\ln(T)$ behavior occurs. Our data show

no deviation from $\sim \ln(1/T)$ behavior down to 1.7K suggesting that the value for T_K is much lower. This data also indicates an antiferromagnetic exchange coupling between conduction electrons and the magnetic impurity.

6.4 Field-Induced Superconductivity in Ultra-Thin LaSb₂

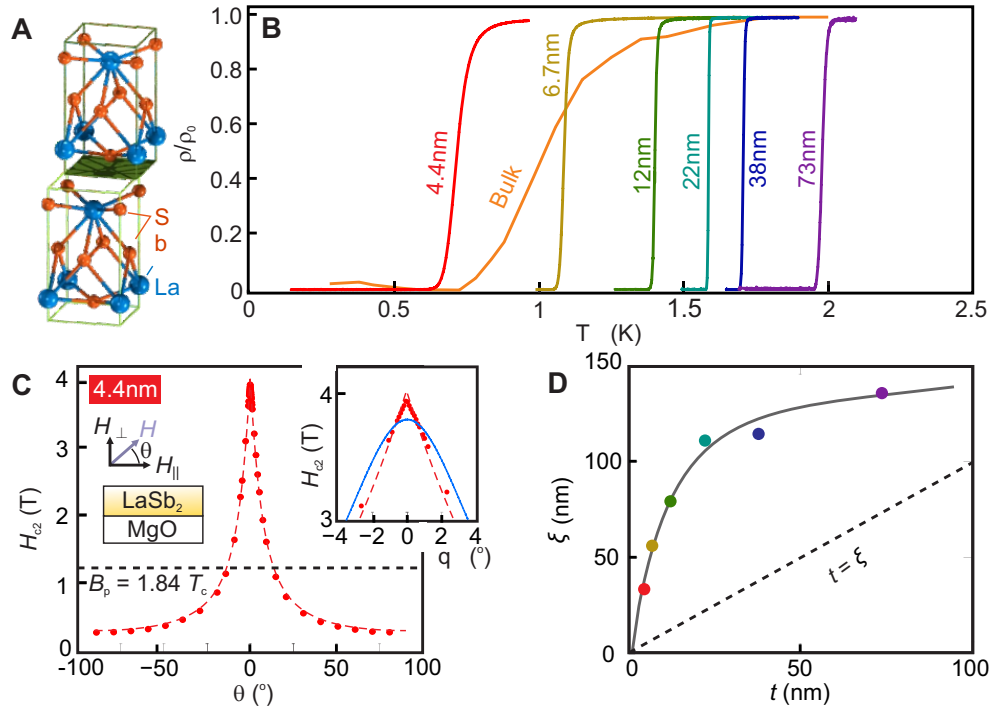


Figure 6.5: **Thickness dependent superconductivity in LaSb₂** **A** Representation of the LaSb₂ crystal structure obtained for the monoclinic structure-type. **B** Thickness dependent resistive transitions of the superconducting state. Bulk data is adapted from Ref. ([44]). **C** Tinkham analysis of a thin film with thickness of 4.4 nm. Inset shows a comparison between the Tinkham fit (red) and the anisotropic Ginzburg-Landau model (blue). **D** Coherence length ξ obtained as a function of film thickness.

Before discussing the central result of this chapter, it is worth recapitulating the results of previous investigations into LaSb₂ (space group 12, A2/m) [78]. Recall the unit cell is which is shown in Fig. 6.5 and is characterized by a monoclinic shear between the quintuple layer building blocks of the structure. The superconducting transition in a series of films with varying thickness t is plotted in Fig. 6.5 as the normalized resistance ρ/ρ_0 taken just above the transition point [44]. A notable outcome of the monoclinic structure is the enhanced T_c compared to the bulk, which we associate with an increased Josephson coupling between the quasi-van der Waals layers in the structure due to the $\sim 5\%$ compressed c-axis compared to bulk crystals. This enhancement may also be the result of the emergence of a new Sb band when the crystal is compressed. As one may have expected from the

theoretical discussion at the beginning of the chapter, creating a situation where a field enhancement superconductivity is even possible, requires the suppression of pair breaking effects of the field. This is accomplished through the use of an ultra-thin layer. We use films of thickness $t \approx 4.4$ nm, which is approximately 5 quintuple layers with around one quintuple layer surface roughness. Recall that this was about the minimum thickness that could be grown while still having a conducting film.

Although the film is far from a single atomic layer, we are still well within the 2D limit for superconductivity. Often, the 2D nature of superconductivity is verified by observing the BKT transition in critical current measurements. Given the low temperatures involved in these experiments, such currents contribute significant heating making the results difficult to interpret. Therefore, we establish the nature of 2D superconductivity by mapping H_{c2} as a function of angle θ relative to the in-plane direction. The data shown in Fig. 6.5C shows a sharp cusp when the field is applied parallel to the sample ($\theta=0^\circ$). This is in agreement with the behavior expected of a 2D superconductor according to the Tinkham formula:

$$\frac{H_c^\theta |\cos(\theta)|}{H_c^\perp} + \left(\frac{H_c^\theta \sin(\theta)}{H_c^\parallel} \right)^2 = 1 \quad (6.13)$$

as plotted by the dotted red line [126]. For comparison, a fit to a 3D anisotropic Ginzburg-Landau model was also performed and found to disagree markedly with the data. This formula, which is given by:

$$\left(\frac{H_c^\theta \cos(\theta)}{H_c^\perp} \right)^2 + \left(\frac{H_c^\theta \sin(\theta)}{H_c^\parallel} \right)^2 = 1 \quad (6.14)$$

and is plotted in blue.

Resilience to $H_\parallel$ is demonstrated by H_{c2} exceeding the Chandrasekhar-Clogston or Pauli limit $\mu_o H_{Pauli} = 1.84 T_c$ by almost a factor of 4. The Pauli limit is indicated by the horizontal line in Fig. 6.5 under the assumption that the g factor equals 2. Several examples of materials exceeding this limit have been found with mechanisms varying from strong SOS to Ising superconductivity [145]. An analysis of the out-of-plane critical fields (Fig. 5.5 allows us to estimate the coherence length ξ of samples which exceeds the film thickness shown in Fig. 6.5D. For the thinnest films considered, $\xi/t \approx 10$.

Superconductivity in Doped Ultra-Thin Layers

Having obtained high-quality, ultra-thin layers, we proceeded to dope them with Ce impurities as described in the previous section. The result is the expected suppression of T_c with doping.

Transport measurements were performed in our dilution refrigerator equipped with a 2-axis vector magnet (9-3T). Samples are in vacuum and are probed using thermally anchored thermocoax lines with additional low-temperature high frequency filters with cut off frequency of 20 kHz. The sample temperature is monitored using both a resistive ruthenium oxide and paramagnetic salt thermometer. The base temperature of the mixing chamber is around $T = 7.5$ mK, with the sample base temperature around 15 mK. Transport data was obtained on macroscopic samples approximately 5 mm^2 that are directly bonded using Al wire, with a linear 4 probe contact arrangement. Alternating current excitation of 10 nA were used below 150mK, although 100 nA was used at higher temperatures in cases where a reduction in noise was required, and voltage drops were measured using lock-in amplifiers operating between 10 and 20 Hz.

Samples were mounted vertically with the sample normal pointing parallel to the 3T, Y-magnet direction. For the measurements of the temperature dependence of resistance in a fixed parallel field (Fig. 6.7), the field was first aligned by sweeping the vector angle at a temperature close to T_c . The condition of optimal alignment was found by locating the angle which gave the minimum resistance. Sample tilt in the y-z plane was found to be 1° . While the third axis could not be aligned, deviation in that direction was estimated to be $< 5^\circ$.

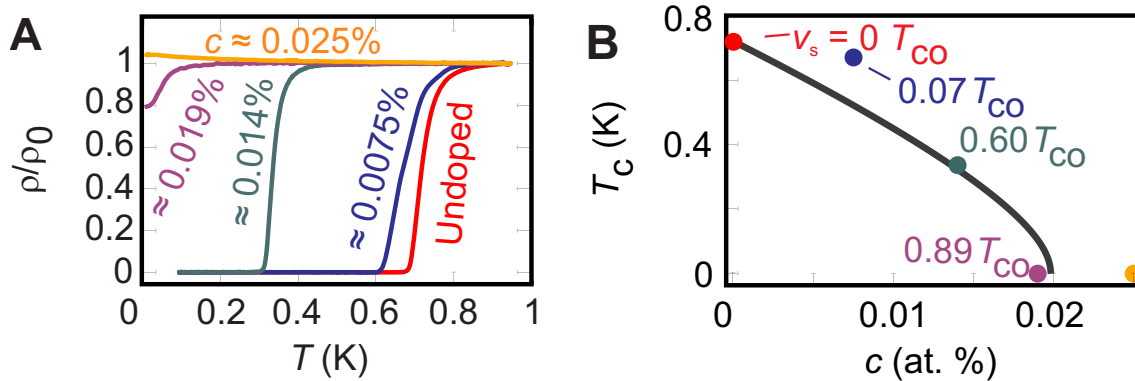


Figure 6.6: **Effect of Ce doping on T_c .** **A** Normalized resistance of different cerium concentrations as a function of temperature. **B** T_c as a function of c with the spin exchange rate v_s obtained from the KF formula annotated for the series of samples.

The effect of magnetic doping is depicted in Fig. 6.6A. As doping is increased, the T_c monotonically decreases. For the concentration $c = 0.019\%$, superconductivity (SC) is no longer observed. Only a small downturn due to vestigial SC fluctuations. Further doping causes a transition to a weakly localized metal. This reduction in T_c is summarized in 6.6B. The solid line represents a fit to the original AG formula 1.3. Based on the measured T_c ,

the AG 1.12 formula gives the corresponding exchange scattering rate. We have labeled the points as such. Because the shift in T_c is the most significant impact of the magnetic impurities, for the remainder of the discussion we will refer to the samples by their values of exchange scattering rate, ν_s , normalized by T_{c0} , the value of T_c for the undoped sample.

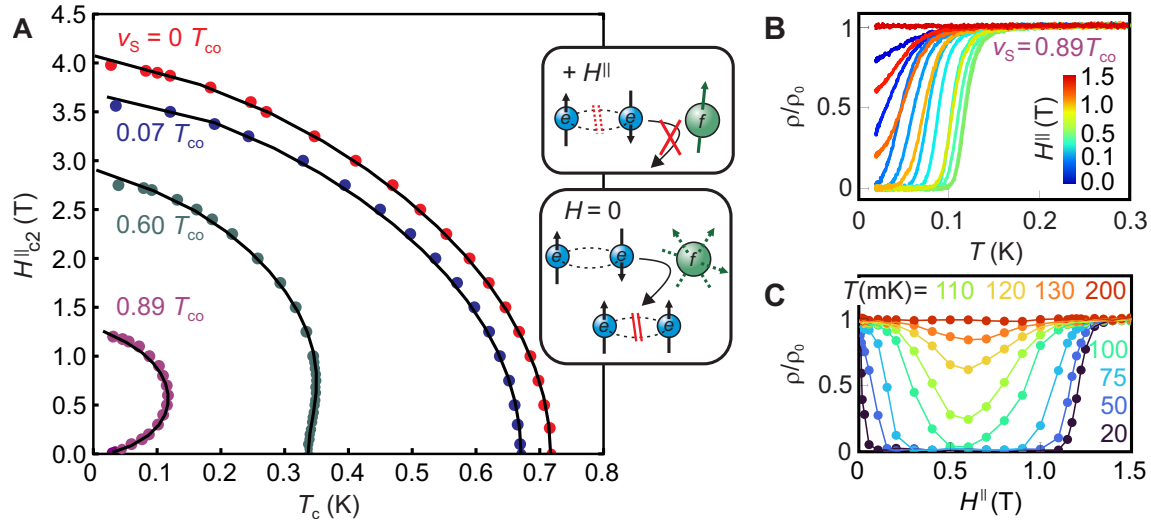


Figure 6.7: Field induced superconductivity. **A** In-plane critical field $H_{c2}^||$ as a function of T for the series of lightly doped samples. Solid lines correspond to fits according to the KF model. The $H = 0$ (lower) schematic shows a singlet Cooper pair interacting with a randomly fluctuating f -electron leading to flipping of the spin when scattering occurs, breaking the Cooper pair. The $+H^||$ (upper) schematic shows that application of a field polarizes the f -electron, suppressing the scattering channel, but leading to pair breaking between paired electrons due to the applied field. **B** Normalized resistance of the $\nu_s=0.89T_{c0}$ sample at various $H^||$ and **C** as a function of $H^||$ at various T .

Our demonstration of field-induced superconductivity is given in Figure 6.7A. The plot captures the T_c , defined as the half-point in normal resistance, in the $(H^||, T)$ -parameter space for the $t = 4.4$ nm set of samples with varying ν_s . For the lightly doped samples (small ν_s), a suppression of T_c with increasing $H^||$ is observed and can be fit by an AG-like formula with an appropriate H -dependent pair-breaking rate from the orbital and paramagnetic effects due to the external field [63]. For the $\nu_s=0.60T_{c0}$ sample, however, the response to the field is qualitatively different, with a modest increase in T_c when increasing $H^||$, pointing to field-enhanced superconductivity with T_c increasing around 20 mK between $\mu_0 H^||=0$ and 0.75 T. The field response of the $0.89T_{c0}$ sample is even more striking, as it is not superconducting at zero field, yet develops into a full zero-resistance state upon application of $H^||$. T_c continues to increase with the application of a parallel field until ≈ 0.6 T showing a maximum $T_c = 117$ mK. Fits to all these data were obtained using the Khartinov-Feigleman theory which will be discussed in detail later. For the $\nu_s=0.89T_{c0}$ sample, the resistance

as a function of temperature at a constant in-plane field is displayed in Fig. 6.7B and as a function of the magnetic field at constant temperatures in Fig. 6.7C. These show that the choice of where to define T_c (e.g 90% R_N or 10% R_N), will change the numerical value of T_c but not change the measured field values at which max T_c is obtained.

Fitting of the KF Model

To understand the data, we employ the KF theory that we described in the introduction of this chapter. Recall that this theory extends AG and JP to include finite polarizability of impurity spins and their effects on both the spin-flip scattering and the effect of the generated internal exchange field when polarized. Exchange scattering on magnetic impurities involves flipping of spin which strongly suppresses T_c , ultimately to zero when this rate becomes of order T_{co} (i.e. T_c in the absence of magnetic impurities). The competition between orbital, paramagnetic, and a variable exchange scattering rate Γ is contained in a modified Cooper pair Green function with a self-energy that contains all of these terms. It is Γ that we wish to emphasize, as its functional form when tuning temperature and applied field generates the qualitative features of our data.

Recall that we can interpret all other terms in the Cooperon self energy as either augmenting or diminishing the pair-breaking scattering rate. We obtained T_c for a given field by numerically solving 6.8. Because the expression for the Cooperon involves a convolution term ($\hat{L}_0 C_0(\varepsilon)$) that depends on knowledge of the Cooperon at all energies, we obtained the values of a Cooperon at a given self consistently. A trial Cooperon was given by AG formula $C_0(\varepsilon) = 1/(|\varepsilon| + \nu_S)$ i.e. the Cooperon with only magnetic impurity scattering considered. This trial Cooperon was then used to compute the convolution term and give full Cooperon in the presence of all other effects (orbital, paramagnetic, polarization) by numerically solving (Eq.6.9). The computed Cooperon was then used as the trial Cooperon in the next self-consistent step. This process was repeated until convergence between the trial Cooperon and the calculated Cooperon was reached. The error was obtained by computing the root-mean-square deviation between calculated and trial values. We used an error bound of 10^{-8} as it was found that the results did not change with tighter bounds. Convergence was reached within 5 self-consistent steps. Once the Cooperon for a given temperature was calculated, it was used in Eq.6.8 to numerically determine the transition temperature. We verified the accuracy of the code by reproducing the calculations in [57].

To fit the data, T_{co} is taken to be value of T_c observed in the undoped film of $T_c = 720\text{mK}$. The value for total angular momentum of the Ce atom was taken to be $J = 5/2$, The other parameters, p_{Ft} , ν , ν_{SOS} , ν_S as well as an additional parameter $\zeta = n_S |J_{ex}| S / \nu_S$ were used

as free parameters to fit the data, with the latter serving to determine the magnitude of the exchange field in the paramagnetic term. It also serves as the Born scattering parameter and should be $\gg 1$ for the Born approximation to be valid.

One important aspect of the fitting of the KF model lies in the sign of the exchange coupling J_{ex} , which we do not know *a priori*. J_{ex} enters the paramagnetic term and determines whether spin polarization acts to amplify or compensate the external field (the JP mechanism). Given our observations of the Kondo effect in a thicker film, we use a $J_{ex} > 0$, indicating an antiferromagnetic coupling of the conduction electrons to the impurity.

First, we fix ν_s based on the value of T_c at zero field. Knowing ν_s allows us to estimate the magnitude of J_{ex} using eqn. 6.5. The values for charge density from normal state transport allow us to estimate N_F based on the Drude approximation along with approximating the Fermi surface to be that of the isotropic electron gas. The magnetic impurity concentration is taken to be that given in Fig. 6.6B. We find $J_{ex} \approx 10\text{meV}$ which translates to a value for $\zeta \approx 1$. This value indicates strong scattering and the need to go beyond Born scattering and including additional effects, most notably Kondo screening.

In the KF formula, p_{Ft} and ν are not independent. We fix p_{Ft} based on the results of the transport measurements and estimation of sample thickness and charge density, assuming an isotropic Fermi surface.

Because both the paramagnetic term as well as the orbital term contribute quadratically in H to the pairbreaking, the parameters ν and ν_{SOS} were highly correlated with one another. Similarly, the ζ and ν_{SOS} terms appear together in the same term in numerator and denominator, respectively. This meant that obtaining a unique fit to the data was challenging. However, for the parameters given in Table 6.4, the data can be well reproduced using the model. The values for ν of $\sim 1000\text{K}$ implies a transport scattering time of $\sim 10^{-14}\text{s}$, in agreement with mobilities that were found from the normal state transport ($\sim 50\text{cm}^2/\text{Vs}$, see Ch. 5). Values for ν_{SOS} are consistently smaller, as expected.

Once the $0.89T_{c0}$ sample was fit, ζ was held fixed when fitting the other samples because this parameter is not expected to depend sensitively on sample quality. Using this value, we fit the remaining samples and obtain values for ν , ν_{SOS} which vary between samples but are within a factor of 2 of one another and can be explained by variations in sample quality. We also find the expected relationship $\nu > \nu_{SOS} > \nu_s$ to hold for the fit parameters.

Having access to a vector magnet allows for studies in simultaneously applied perpendicular and parallel fields. To obtain the critical field values as a function of temperature, the 9T

c (at. %)	Undoped	0.0075	0.014	0.019
ν_S/T_{co}	0	0.08	0.601	0.89
ν/T_{co}	1841	1534	1813	1032
ν_{SO}/T_{co}	99	139	174	348
ζ	0	1.25	1.25	1.25
p_{Ft}	20	20	20	20

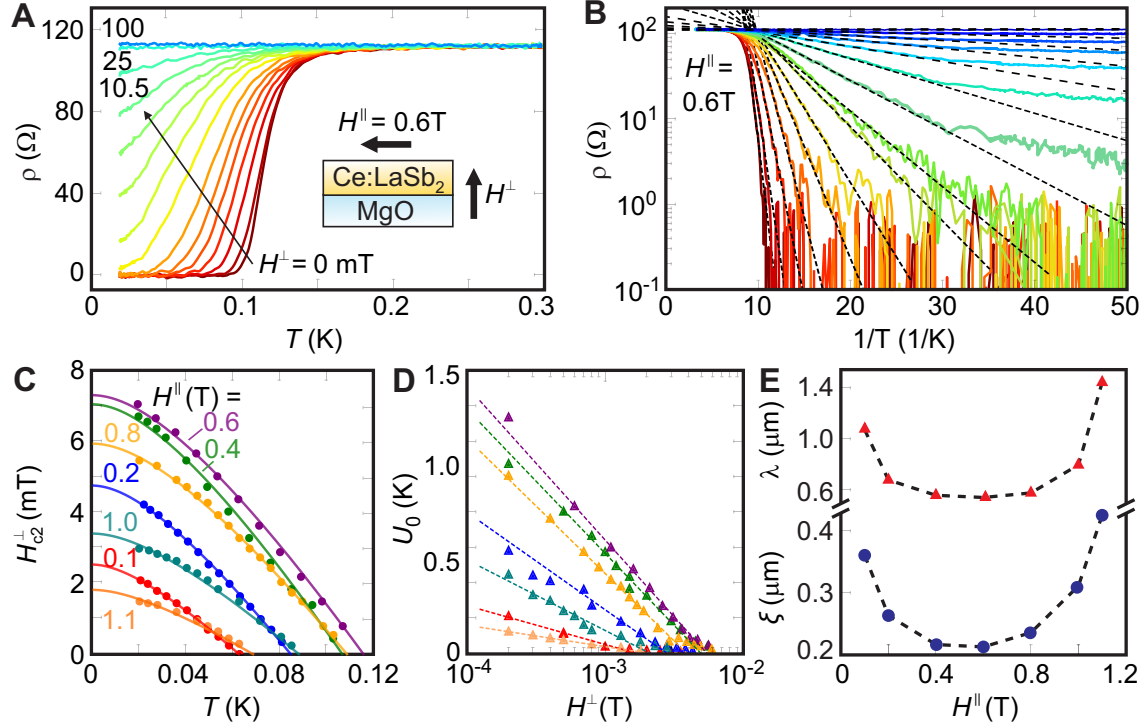
Table 6.1: Fit parameters for the $J_{ex} > 0$ (antiferromagnetic) and $J = 5/2$ 

Figure 6.8: **Perpendicular Critical Field Behavior** for sample $\nu_s=0.89T_c$. **A** $R(T)$ taken in a fixed $H_{||} = 0.6$ T in a set of H_{perp} from 0T to 0.1 T. Curves taken between 0 and 10.5mT were taken at 1-2mT intervals. **B** The same data plotted as a function of $1/T$ with dotted lines corresponding to fits of the linear regions to $R \exp(-U_0/T)$. **C** $H_{c2\perp}$ as a function of T at fixed values of $H_{||}$. Fits are to the single-band WHH model. **D** Fits of U_0 vs H_{perp} to the collective creep model $U = U_0 \ln(H/H_0)$ for a series of fixed $H_{||}$. **E** Summary of ξ (circles) and λ (triangles) as a function of $H_{||}$.

Z-magnet was kept at a fixed value while the Y-magnet was swept at 2mT/min at fixed temperature. Due to the combination of trapped fluxes and sample misalignment, the raw sweeps were found to be symmetric about non-zero values ($\sim < 10$ mT) of the Y-field. Data were therefore corrected with this value set to be true zero. Given the small critical field values of < 10 mT, parasitic contributions from the Y-field in the parallel direction would amount to < 1 mT corresponding to $< 1\%$ uncertainty in the parallel field magnitude. For

consistency, temperature dependent sweeps in a fixed parallel and perpendicular (6.8A, B) fields were also performed by fixing both the Z magnitude and varying the Y magnitude in $\sim 0.1\text{--}1\text{mT}$ steps for each sweep at low field and increased to larger increments at higher field as seen in 6.8A. The condition of zero perpendicular field was given by the Y field value that gave the maximum T_c . Temperature dependence of the critical field obtained by sweeping H at fixed T and by sweeping T with fixed H were in agreement.

With this procedure to determine proper alignment we used an out-of-plane magnetic field $H^\perp$ in addition to $H^\parallel$ to study the $\nu_S = 0.89T_{c0}$ sample in detail. Applying $H^\perp$ rapidly suppresses superconductivity through orbital effects. Figure 6.8 displays $R(T)$ with finite $H^\perp$ while $\mu_o H^\parallel = 0.6\text{ T}$, corresponding to the “nose” in 6.7A. A $\mu_o H_{c2}^\perp \sim 7\text{mT}$ is seen for the zero resistance state, which evolves into a metallic state characterized by finite resistance in the limit of $T \rightarrow 0$ [56]. In Fig. 6.8B we show the $R(T)$ behavior at fixed $\mu_o H^\parallel = 0.6\text{ T}$ on an Arrhenius plot to obtain the activation energy U_0 associated with the transition from the superconducting to the normal state. By plotting $H_{c2}^\perp(T)$ at discrete steps of $H^\parallel$ as shown in 6.8C, fits to a single band Werthamer, Helfand, and Hohenberg [136] model provide an estimate for $H_{c2}^\perp(T=0)$, allowing us to obtain ξ as a function of $H^\parallel$. Fitting the extracted U_0 obtained at a set $H^\parallel$ $\nu_S \ln(H_\perp)$ yields a linear relationship (6.8D) allowing us to extract λ using the model (Eq. 6.15) for the collective creep of vortices [28, 31].

$$\begin{aligned}
 U &= U_o \ln(H/H_o) \\
 U_o &= \phi_o^2 d / (256\pi^3 \lambda^2) \\
 H_o &\approx H_{c2}
 \end{aligned} \tag{6.15}$$

Where U is the activation energy extracted from the Arrhenius plots, d is the sample thickness, λ is the London penetration depth. These length scales are summarized in 6.8E, and confirm that the sample remains a type-II superconductor with $\lambda/\xi > \frac{1}{\sqrt{2}}$ across the parameter space. Notice that the values of $H^\parallel$ that give similar T_c do not yield similar $H_{c2}^\perp(T)$. Instead, the values obtained on the high-field side are systematically lower. A similar asymmetry is apparent in the values of λ and ξ . In the next section we will discuss how this asymmetry arises as a natural consequence of the polarization of Ce impurities.

6.5 Discussion

We summarize the results of the previous section in Fig. 6.9A. T_c increases with increasing parallel field up to a maximum value of 0.6 T whereupon it begins to decline. Similarly, the perpendicular critical field $H_{c2}^\perp$ also increases up to about $0.5\text{--}0.6\text{ T}$ where it begins to decline much faster on the high field side. We can understand both of these behaviors as

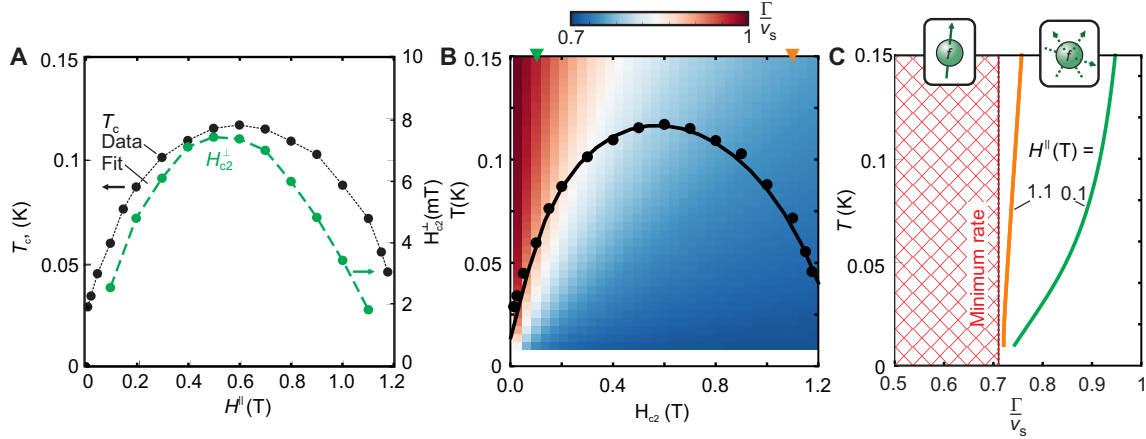


Figure 6.9: Evolution of the spin-scattering rate with temperature and applied field. A plot of dependence of T_c and H_{c2} on applied field. Fit with ferromagnetic KF model is also plotted. **B** Magnitude of the magnetic scattering term Γ normalized by the value at zero field (ν_s). **C** line cuts generated from **B** taken at 1.1T and 0.1T.

arising from the response of the magnetic impurities to the applied magnetic field. For this we use the KF theory and calculate the spin scattering rate Γ as a function of T and $H^{\parallel}$. We see that while the exchange scattering rate Γ is independent of J_{ex} , it depends strongly on both T and H . The ratio of Γ/ν_s is plotted in Fig. 6.9B, with line cuts taken at $\mu_0 H^{\parallel} = 0.1$ and 1.1 T shown in Fig. 6.9C. When $H^{\parallel}/T$ is small, the external field fails to polarize the spins. This corresponds to the upper left corner of Fig. 4B, where Γ equals ν_s as expected. When $H^{\parallel}/T$ is large, however, Γ approaches $\nu_s J/(J+1)$ as spins are readily polarized by the large field. This is the lower right of Fig. 6.9B.

In isolation this effect would produce a positive slope of $T_c(H^{\parallel})$ curve and an enhanced T_c given by the AG formula with the new Γ . We therefore refer to the low field regime (< 0.6 T in this case) as the magnetic impurity scattering regime because it is here that T_c is determined by the effects of magnetic impurities and their polarization. However, this process is in competition with orbital and paramagnetic effects due to the applied and exchange fields. The pairbreaking effect due to application of a field parallel to the film is suppressed due to the reduced film thickness. At low fields and low temperatures, the primary effect of the field is to polarize impurities. This leads to a suppression of spin-flip scattering and an *enhancement* of T_c . Eventually, spins are fully polarized and this pairbreaking is reduced as much as possible. With further increase in magnetic field, which we refer to as the field suppressed regime, the superconductivity is eventually destroyed by the normal orbital and paramagnetic effects.

The polarization of impurity spins also explains the anomalous critical field behavior. As

shown in Fig. 6.9C, Γ in the magnetic impurity scattering dominated regime continues to fall as temperature is reduced below T_c , resulting in enhanced superconductivity in the limit of $T \rightarrow 0$. This is in contrast to the field suppressed regime where the external field is sufficiently large that spins are already nearly fully polarized at T_c leaving Γ with only a weak temperature dependence [97]. The combination of small external field with an increasing degree of spin polarization as $T \rightarrow 0$ results in higher values for $H_{c2}^\perp$ in the magnetic impurity scattering regime. In other words, it is the dynamical responses of competing mechanisms to temperature and field that give rise to the asymmetric responses of $H_{c2}^\perp$, ξ and λ , obtained in the limit of $T = 0$ as one moves between pair-breaking regimes. This observation confirms that the change in spin-flip scattering due to impurity spin polarization is primarily responsible for field-induced superconductivity, and is not simply the result of the generation of an exchange field.

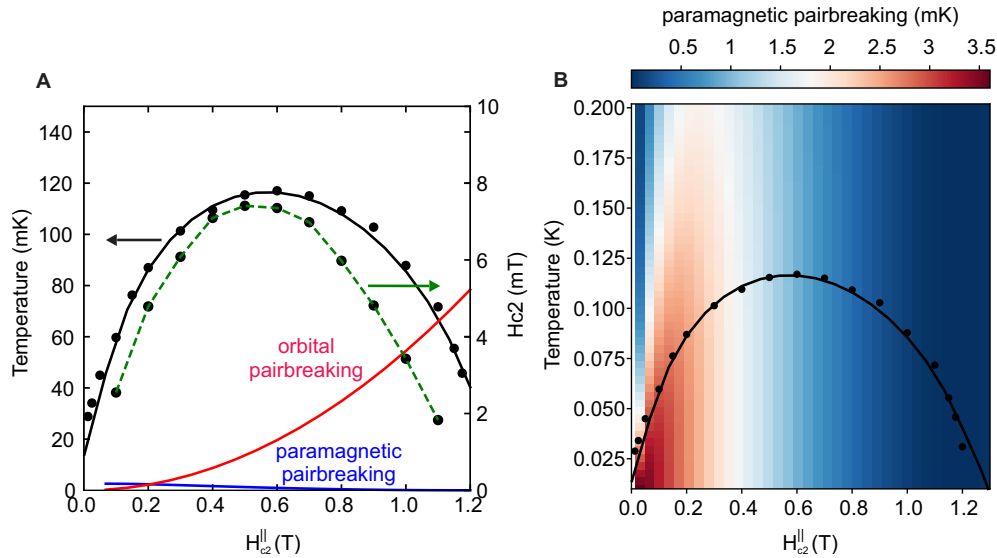


Figure 6.10: Evolution of pair breaking due to orbital and paramagnetic effects. **A** Plot of the change in T_c and $H_{c2}^\perp(T = 0)$ as a function of applied parallel field alongside the magnitude of the orbital and paramagnetic pair breaking terms evaluated at T_c . **B** Plot of the paramagnetic pair breaking across the $H^\parallel - T$ parameter space.

Further evidence that the $H_{c2}^\perp$ behavior is due to impurity spin polarization instead of the temperature dependence of the exchange field can be seen by examining the magnitude of the paramagnetic term in the $T - H$ parameter space. For the antiferromagnetic case, the paramagnetic term is seen to fall as the applied field is increased, due to the cancellation of the internal exchange field by the applied field 6.10A. Focusing on the magnetic impurity scattering regime $< 0.6T$, we find that decreasing temperature *increases* the pairbreaking magnitude of the magnetic impurities (Fig. 6.10B). As the temperature is reduced, the

impurities polarize, but in the presence of only a small applied field, leading to minimal cancellation. Alone, this would result in smaller $H_{c2}^{\perp}$ in the magnetic impurity scattering regime, in direct contradiction to the observations. Therefore, in order to explain the observations, it must be that the *decrease* in pair-breaking from the reduction in spin scattering dominates the physics as $T \rightarrow 0$ in low fields.

6.6 Conclusions and Future Directions

The focus of the above work was on the demonstration of field-induced superconductivity. Superconductors exhibiting high critical field behavior [80, 110, 29, 24, 58, 118, 147], or reentrant phases [15, 149] are the continued subject of intense investigations where the possibility of realizing exotic pairing scenarios, such as Ising, spin-triplet, and finite momentum, emerge as possible explanations. Our data demonstrate that even in the absence of such exotic scenarios, a similarly rich variety of tunable behaviors can manifest when competing pair-breaking mechanisms are present, as the KF theory is effectively an extension of BCS and neglects details of the sample. This has implications for the interpretation of qualitatively similar anomalous behaviors elsewhere, especially when there is a possibility of magnetic ion incorporation into the structure (e.g. through source material impurities). While our analysis provides a starting point for understanding this physics, the realization of the full field-induced superconducting phase in the $(H^{\parallel}, T)$ -parameter space in a chemically versatile, crystalline material in the 2D limit encourages the exploration of the effects of magnetic dopants in ultra-thin superconductors with more exotic lattice-endowed degrees of freedom in the electronic structure.

The most interesting open question motivated by these results is the nature of the exchange coupling in the ultra-thin limit. This coupling could possibly be studied by measuring the zero-bias peaks associated with the magnetic impurities in STM however the very low temperatures involved would make the experiment challenging.

Generally, there is no reason why other 2D superconductors should not be able to show similar physics. There are additional, more exotic mechanisms to preserve superconductivity against external fields. A notable recent example is the discovery of Ising superconductivity in inversion asymmetric crystals. The unit cell for LaSb_2 is inversion symmetric. However, this inversion symmetry is broken when one considers only half the unit cell. Thus, layer-number dependent studies could be very fruitful. Alternately breaking inversion symmetry by adding or subtracting layers may allow for a tuning of these more exotic effects. However, other crystal systems such as the dibismuthides may allow for even more interesting observations given their higher SOC.

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