Doping and strain effects in strongly spin-orbit coupled systems

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Doping and strain effects in strongly spinorbit coupled systems

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Abstract

We present Scanning Tunneling Microscopy (STM) studies on several systems in which spin-orbit coupling leads to new and interesting physics, and where tuning by doping and/or strain can significantly modify the electronic properties, either inducing a phase transition or by sharply influencing the electronic structure locally.

In the perovskite Iridate insulator $Sr_3Ir_2O_7$, we investigate the parent compound, determining the band gap and its evolution in response to point defects which we identify as apical oxygen vacancies. We investigate the effects of doping the parent compound with La (in place of Sr) and Ru (in place of Ir). In both cases a metal-insulator transition (MIT) results: at $x \sim 38\%$ with Ru, and $x \sim 5\%$ with La. In the Ladoped samples we find nanoscale phase separation at dopings just below the MIT, with metallic spectra associated with clusters of La atoms. Further, we find resonances near the Fermi energy associated with individual La atoms, suggesting an uneven distribution of dopants among the layers of the parent compound.

 Bi_2Se_3 is a topological insulator which hosts linearly dispersing Dirac surface states. Doping with In (in place of Bismuth) brings about topological phase transition, achieving a trivial insulator at x ~ 4%. We use high-magnetic field Landau level spectroscopy to study the surface state's properties approaching the phase transition and find, by a careful analysis of the peak positions find behavior consistent with strong surface-state Zeeman effects: g~50. This interpretation implies, however, a relabeling of the Landau levels previously observed in pristine Bi_2Se_3 , which we justify through *ab initio* calculations. The overall picture is of a g-factor which steadily decreases as In is added up to the topological phase transition.

Finally, we examine the effects of strain on the surface states of (001) thin films of the topological crystalline insulator SnTe. When these films are grown on closely-related substrates—in this case PbSe(001)—a rich pattern of surface strain emerges. We use phase-sensitive analysis of atomic-resolution STM topographs to measure the strain locally, and spatially-resolved quasiparticle interference imaging to compare the Dirac point positions in regions with different types of strain, quantifying for the first time the effect of anisotropic strain on the surface states of a topological crystalline insulator.

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1: Introduction

1.0 Plan of the thesis

This thesis presents Scanning Tunneling Microscopy (STM) studies on lightly doped or strained versions of several materials of recent interest in condensed matter physics. These materials all have in common the fact that spin-orbit coupling plays a key role in establishing their physical properties: the "spin-orbit Mott" state in the perovskite Iridates (Chapter 3), and the band inversion in topological insulators (Chapter 4) and topological crystalline insulators (Chapter 5).

To explain the physics of these materials and why they are interesting, we include a rather detailed exposition of the effects of spin-orbit coupling starting from the level of simple atomic physics, and proceeding through the Hall, spin Hall, and quantum spin Hall effects to topological insulators, topological crystalline insulators, and the more strongly correlated iridate compounds (Chapter 1).

The technique of STM as used in this work is described in chapter 2. We skirt through the basics of STM and quickly permit ourselves to treat the differential conductance as proportional to the sample's local density of states. (This approximation, which almost amounts to an assumption, is known to lose its validity in diverse circumstances including superconducting tips¹ and local gating of the sample², which will not concern us here.) We then describe the techniques frequently used in STM to establish the **k**-space dispersion relations of (Bloch) electrons: quasiparticle interference imaging and Landau level spectroscopy, and a relatively new technique of using STM to measure the local strain in the atomic lattice, which we apply to effect in chapter 5.

The body chapters follow, which are summarized in the abstract.

1.1 Spin-orbit coupling

Spin-orbit coupling arises from the intrinsic magnetic moment of the electron

1

$$\boldsymbol{\mu} = g \frac{e}{2m} \mathbf{S} = g \frac{e\hbar}{4m} \boldsymbol{\sigma}$$
(1.1)

where *e* and *m* are the charge and mass of the electron, **S** is the spin and σ is the vector of Pauli matrices, and *g* is the gyromagnetic ratio which for free electrons is very nearly 2. An electron moving in an electric field—for example, the field of an atom or crystal lattice—sees a magnetic field **B** proportional to $\mathbf{v} \times \mathbf{E}$, which changes its energy by

$$\Delta U = -\mathbf{\mu} \cdot \mathbf{B} \,. \tag{1.2}$$

For electrons orbiting a hydrogen-like atom (that is, a nucleus of charge Ze with potential U(r) = -Ze / r) it turns out that for reasonably small $Z\alpha$ the energy levels shift by^{3,4}

$$\Delta E \sim Z^4 \alpha^2(E_B) \tag{1.3}$$

where $E_B = 13.6$ eV is the Bohr energy, and $\alpha \approx 1/137$ is the fine structure constant. Eq. 1.3 shows that spin-orbit splitting is large only for heavy atoms, where the electron attains relativistic speeds in the potential well (i.e. where **E** and $\frac{\mathbf{v}}{c} \times \mathbf{E}$ can achieve comparable magnitudes. In hydrogen-like atoms $v/c \sim Z\alpha$.).

With the exception of SnTe, the materials studied here are all contain heavy elements: The decisive role of spin-orbit coupling is most obvious in the Iridate compounds (Z=77; chapter 3) and Bi₂Se₃ (Z=83; chapter 4).

1.2 SOC in condensed matter; the Rashba effect

Although the Rashba effect is not directly related to the experimental work shown in this thesis, it forms a convenient bridge between spin-orbit coupling in general and the more complicated effects studied later on. Furthermore, Rashba splitting is present in several noble metal surface states, the study of which played an important role in the development of STM. We briefly describe it below.

With $\mathbf{B}_{eff} = \mathbf{E} \times \frac{\mathbf{v}}{c}$ and g=2 Eq. (1.2) reduces to⁵

$$\hat{H}_{SO} \propto \mu_B \left(\mathbf{E} \times \mathbf{p} \right) \cdot \boldsymbol{\sigma} / mc^2$$
 (1.4)

For free electrons, once the Thomas correction⁶ is taken into account, the proportionality constant is one half.⁷ Clearly, \hat{H}_{SO} tends to lift the spin degeneracy of the overall Hamiltonian, and if **E** is constant over the wave packet its solutions are eigenstates of $\boldsymbol{\sigma}$ in the direction specified by $\pm \mathbf{E} \times \mathbf{p}$. (See Fig. 1.1)

In solid state physics the electrons are usually taken to be in Bloch states defined by the wavevector \mathbf{k} , the spin, and a band index. The necessary symmetries of these Bloch states limits the ability of \hat{H}_{SO} to lift the degeneracy in actual materials: Time reversal symmetry requires that $E(\mathbf{k},\uparrow) = E(-\mathbf{k},\downarrow)$ (Kramers' theorem)⁸, and if the crystal is inversion symmetric we also have $E(\mathbf{k},\uparrow) = E(-\mathbf{k},\uparrow)$. In that case the spin degeneracy is not lifted; $\langle \hat{H}_{SO} \rangle = 0$ for all states.

At the crystal surface, however, inversion symmetry is broken. Taking \hat{z} as the surface normal, we have an average electric field $\langle \mathbf{E} \rangle = E\hat{z}$, which when substituted into (1.4) gives⁹

$$\hat{H}_{SO} = \alpha \left(\hat{\mathbf{z}} \times \mathbf{p} \right) \cdot \boldsymbol{\sigma} , \qquad (1.5)$$

so that the total Hamiltonian for quasi-free electrons is

$$\hat{H} = \frac{p^2}{2m^*} + \hat{H}_{SO} = \frac{p^2}{2m^*} + \alpha \left(p_x \sigma_y - p_y \sigma_x \right).$$
(1.6)

The characteristic dispersion of this Hamiltonian is shown in **Fig. 1.1**. \hat{H}_{SO} polarizes the spins azimuthally and makes an energy gap of $2\alpha |\mathbf{p}|$ between the clockwise and anti-clockwise spins.



Fig. 1.1: Rashba-split 2DEG. The energies (orange) and spin-polarizations (red) of a Rashba-split quasi-free 2dimensional electron gas (2DEG). (a) shows the p_x -E plane; (b) shows the p_x - p_y plane. (b) roughly corresponds to the dashed horizontal line in (a).

The Hamiltonian (1.6) is a reasonably good fit for the (111) surface states of Cu^{10} , Ag^{11} , and $Au^{12,13}$. As we will discuss in great detail below (see also Chapter 4), it is also the standard low-energy approximation for the surface states of topological insulators¹⁴.

1.3 Topological insulators

We would now like to connect this simple exposition of spin-orbit coupling to the essential physics of the systems studied in this thesis: In-doped Bi_2Se_3 , $Sr_3Ir_2O_7$, and SnTe. The first of these is a topological insulator whose band inversion is directly attributed to spin-orbit coupling¹⁴, and whose phase transition with increasing In content is at least partly attributed to a weakening of the SOC.¹⁵ Although a full treatment of SOC's role in the band inversion is beyond our means, we will try to sketch out the importance of SOC to the intrinsic spin Hall effect, which was an important technological motivation of the search for topological insulators^{16,17}.

1.3.1 The spin Hall effect

The conventional Hall effect was discovered in 1879 by Edwin Hall, who imagined that the Lorentz force on a current flowing through a transverse magnetic field would create "a state of stress in the conductor, the electricity pressing, as it were, toward one side of the wire."^{18,19}

Much later (after the electron had been discovered and ascribed the property of spin), D'yakonov and Perel' argued that as the electrons moved through the conductor, spin-orbit-split scattering processes would cause an accumulation of polarized spins on the sides of the wire²⁰, with opposite spins on opposite sides. This effect, which requires defects to generate the Mott scattering²¹, is now termed the "extrinsic" spin Hall effect in contrast to the intrinsic effect, which results from the band structure itself^{22,23}.

The intrinsic spin Hall effect was predicted for GaAs in 2003¹⁶ and the Rashba-split 2DEG (Eq. (1.6)) soon after²³. In both cases it relies on the splitting of a band into branches by the spin-orbit coupling: for a single branch characterized by a definite spin orientation at each momentum **k** (e.g. the outer circle of **Fig. 1.1(b)**), the accelerating electric field tends to cant the spins in such a way as to generate a spin current ^{16,22,23}:

$$J_{i}^{i} = \sigma_{s} \varepsilon^{ijk} E_{k} \tag{1.7}$$

where **J** is the spin current (tensor), ε^{ijk} is the unit antisymmetric tensor, and σ_s is the spin Hall conductivity¹⁶. Here J_j^i represents a current flowing in in the *j* direction of spins oriented along *i*, and in particular we expect an electric field in the x-direction to cause a flow of z-oriented spins in the ydirection, and a flow of y-oriented spins in the negative z-direction. The corresponding accumulation of spins on the edges of a Hall bar or wire is shown in **Fig. 1.2**.



Fig. 1.2: The accumulation of spins at the edge of a wire under the spin Hall effect. (a) shows the top view (as of a Hall bar), and (b) shows the cross-section of a circular wire. We assume $\sigma_s > 0$.

The spin Hall effect in GaAs and InGaAs was observed^{24,25} in 2004 to much excitement²⁶ (compare **Fig. 1.2a** to Fig. 2A of ²⁴).

To make the connection with topological insulators let us point out a very important characteristic of the intrinsic spin Hall effect: the effects arising from band elements with opposite helicity tend to cancel, and it is therefore necessary that in some "net region" of **k**-space one of these elements be occupied while the other is unoccupied.^{16,23} For the Rashba Hamiltonian this is automatically the case when the Fermi energy is positive (see **Fig. 1.3**), and it was argued that in that case the Hall conductivity in the limit of zero spectral broadening achieves the precise value $e/8\pi^{23}$. This value of σ_s was later shown to be wrong^{27,28}, but the argument immediately shows the usefulness of the topological insulator surface state, and the desirability of doping or gating the TI to place the Dirac point at the Fermi level (**Fig. 1.3b**).



Fig. 1.3: Areas of k-space contributing to the intrinsic spin Hall effect. (a) In the Rashba 2DEG only that annulus contributes where the upper branch is unoccupied and the lower branch is unoccupied. (b) In the TI with $E_f=0$ entire bottom of the surface state contributes to the spin Hall effect. (The surface state Hamiltonian in Bi_2Se_3 is essentially a Rashba 2DEG with the outer branch removed.¹⁴)

1.3.2 The quantum spin Hall effect

Topological insulators have attracted such great interest that their history has already been detailed in several review articles and books^{29–34}. In 2005 Kane and Mele argued that graphene with spin-orbit coupling should show an intrinsic spin Hall effect with quantized, dissipationless $\sigma_s = e/2\pi$.³⁵ In 2006 another proposal envisioned a quantum spin Hall insulator state arising in a conventional semiconductor with a strain gradient.³⁶ That paper cleverly exploited a certain equivalence to replace the electric field in the spin-orbit coupling term ($\mathbf{v} \times \mathbf{E}$) $\cdot \mathbf{\sigma}$ with corresponding elements of the strain tensor. For spatially

varying strain this term in the Hamiltonian acts like the vector potential of a magnetic field (now it would be called a "pseudomagnetic" field^{37–39}), and a certain type of strain gradient was proposed to imitate a uniform magnetic field in in +z-direction for spin-up electrons, and the opposite for spin-down electrons. (That is, the Hamiltonian took the form $H = (p - eA\sigma_z)^2 / 2m$ where A is the vector potential of a uniform field in the z-direction.) The result of all this is that for strong strain gradients the up- and downspins are subject to the quantum Hall effect with the edge states propagating in opposite directions, and a net spin Hall conductivity of $e / 2\pi$ is achieved although the charge Hall conductivity is zero.

The main conceptual advance necessary for TI's was the topological characterization of band structures, and in particular the realization that the ordinary insulator and the quantum spin Hall insulator were topologically distinct^{40,29–31}. The topological distinctness of different filling factors of the integer quantum Hall effect (*not* spin Hall) had already been realized, and was expressed in the value of a certain integral over all occupied states in a unit-cell of **k**-space.⁴¹ In Ref.⁴⁰ the corresponding integral was a line integral around an area comprising half the Brillouin zone. The generalization of the quantum spin Hall effect and the topological band classifications to 3-dimensional systems (3D) is a bit complicated: here the band structure is characterized by four Z_2 invariants^{42,43} which, however, can usually be calculated by referring to the properties of the electronic states at the time-reversal invariant points of the Brillouin zone rather than by integration. The topological classification scheme is, however, slightly beyond the scope of this thesis and we refer the reader to the literature (e.g. Ref.⁴⁴).

1.3.3 Topological insulators

In 2006 Berenvig and Zhang proposed that the quantum spin Hall state would be realized in nanostructures consisting of a quantum well sandwich in which HgTe formed the "meat" and CdTe the bread, when the HgTe exceeded $d_c > ~6 \text{ nm}^{45}$. This prediction was experimentally verified in 2007 yielding $d_c = 6.3 \text{ nm}^{46}$. (It should be noted, however, that two-dimensional Dirac fermions at the interface

between HgTe and CdTe resulting from the mutual band inversion, as also at the interface between PbTe and SnTe, had already been predicted in the 1980's⁴⁷.)

In 2008 the first 3D topological insulator Bi_xSb_{1-x} , which had been predicted in Ref.⁴², was identified by angle-resolved photoemission spectroscopy (APRES)⁴⁸. At this point we should add that the 3-D topological insulator is characterized by metallic 2-D surface states (analogous to the 1-D edge states found in the quantum spin Hall systems^{35,45}) which makes it particularly susceptible to characterization by surface-sensitive probes like ARPES and STM. These surface states are (like their 1-D counterparts) protected against backscattering by time-reversal symmetry, which property was also verified for Bi_xSb_{1-x} in 2009, by STM⁴⁹.

However, Bi_xSb_{1-x} has a rather narrow band gap, and its surface state is rather complex: in the ARPES study it crossed the Fermi energy five times⁴⁸. (That the number of crossings should be odd is an essential characteristic of the 3D topological insulator.⁴²) A topological-insulating system without these characteristics was desirable, and in 2009 this new class of TI's, comprising Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃, was theoretically predicted and experimentally confirmed (ARPES) in two articles which (in an unusually short time-lag between theory and experiment) were published online on the same day^{50,51}.

Because Bi₂Se₃ is dealt with extensively later (and also because it is now regarded as a "prototypical" topological insulator^{52,53}) we should now describe it in some detail. Bi₂Se₃ is a layered crystal in which the basic unit is five-layer sandwich of the form Se-Bi-Se-Bi-Se. The crystal structure is shown in Fig. 1 of Ref. ⁵¹ which we reproduce in **Fig. 1.4** below. The atoms in each layer form a triangular lattice with the atomic positions in succeeding layers following an A-B-C pattern. (As a result of this pattern the lattice unit cell cuts through three quintuple layers.) The quintuple layers are weakly bonded by Van der Walls' forces, resulting in an easy cleave between quintuple layers with a Se lattice at the resulting surface. The bulk band gap is ~300 meV and the surface state consists of a single helical Dirac cone centered at $\overline{\Gamma}$ (that is, **k**=0) with noticeable curvature^{14,50,51} and the Dirac point near the bottom of the bulk band gap. For

small **p** the surface state Hamiltonian can be approximated as Eq. (1.6) with the linear, helical term dominant and the quadratic term a small correction; with increasing **p** the approximation becomes invalid before the band curves upward¹⁴. (Indeed the Hamiltonian can be further approximated as the linear term alone of Eq. (1.6), $H = \alpha \left(p_y \sigma_x - p_x \sigma_y \right)$, although we generally will not do this.)



Fig. 1.4 Crystal and electronic structure of Bi2Se3. (a) shows the crystal structure (adapted from Ref. ⁵¹) with quintuple layer indicated on the right and expanded in the lower left. (b) shows the surface state as imaged by ARPES in Ref. ⁵⁰ (c) schematizes the spin texture of the surface state, from Ref. ¹⁴.

Since its discovery Bi₂Se₃ has been thoroughly characterized by numerous experimental probes including ARPES^{51,54,55}, STM^{56,57}, and high-field transport oscillations⁵⁸, and doped and strained modifications of it have also been the object of intense study^{59,60}. Nevertheless, even in this thoroughly explored system a discrepancy between the Shubnikov-de Haas and high-magnetic-field STM studies seems to have smoldered regarding the strength of the surface state effective *g*-factor. In chapter 4 (as of September 2015, unfortunately not yet published) we are pleased to contribute to a solution of this problem.

In the years since the introduction of Bi_2Se_3 attempts have been made to optimize the material for device applications and physical research (as-grown Bi_2Se_3 is conducting in the bulk due to unavoidable Se vacancies) and also to use doping (and strain⁶⁰) to achieve new physical states. The former has led to the development of $Bi_2Te_2Se^{61,62}$ (whose crystal structure resembles Bi_2Se_3 except that the outer two layers of the quintuple layer are Te) and $Bi_{2-x}Sb_xTe_{3-y}Se_y^{63}$, in which Sb also substitutes for Bi. (For a review, see Ref. ³¹.)

One of the interesting subjects relating to topological insulators is the phase transition which occurs between the topological insulator and the "trivial" insulating state. (An example of this was already encountered in the HgTe quantum wells.⁴⁵) In the original paper predicting that Bi₂Se₃ was a topological insulator it was found that Sb₂Se₃, which has the same crystal structure, was a trivial insulator,⁵¹ from which it follows that a phase transition should occur at some critical Sb concentration x_c . Schematically, the band-inverted insulator is regarded as having a negative band gap which, on its way to the "positive gap insulator" (Sb₂Se₃ in this case), must pass through zero^{47,64} at x_c where the topological surface state disappears. For the phase transitions in Sb- and In-doped Bi₂Se₃ this is associated with a weakening of the spin-orbit coupling with increasing concentration of the lighter element, though the difference between the relatively quick phase transition with In as compared with Sb suggests that other effects play a significant role.¹⁵ This phase transition is discussed in Chapter 4.

1.3.4 Topological crystalline insulators

Topological crystalline insulators (TCIs) are distinct from topological insulators in that the surface states are protected not by time-reversal symmetry as in the case of TI's, but by particular crystalline symmetries^{65,66}. As a result (and unlike topological insulators), symmetry-protected metallic surface states appear only on those surfaces which preserve the particular crystalline symmetry. At the time of this writing the best (and, it seems, only) known class of topological crystalline insulators are the IV-VI semiconductors (Pb,Sn)Te and (Pb,Sn)Se^{67–69} in which the (110) mirror symmetry protects the topological surface states. In these systems the low-index symmetry-preserving surfaces are the (001), (110), and (111) surfaces, each of which has its own distinct Dirac surface states⁷⁰ with multiple Dirac cones.

The close study of one of these materials (SnTe) in chapter 5 makes a detailed description necessary: The IV-VI semiconductors which are TCI's crystallize in the rocksalt structure and have band inversions at

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the eight L points of the bulk Brillouin zone^{70–72} (see **Fig. 1.5**). In the first approximation the surface state Dirac points are located at the projections of these L points onto the corresponding surface: $\overline{\Gamma}$ and \overline{M} for the (111) surface, and the two \overline{X} points for the (001) surface respectively. (We will call them \overline{X} and \overline{Y} although in **Fig. 1.5** they are labeled $\overline{X}_{1,2}$.)



Fig. 1.5 (001) and (111) surface states of TCIs. (a) shows the L points and their projections on the (111), (001), (110) surfaces; (b) shows the associated Dirac surface states for the (001) and (111) surfaces. Fig. is adapted from ⁶⁶ with panel (a) from ⁷⁰.

On the (001) surface there are at each \overline{X} point two "parent" Dirac cones offset in energy. The parent "cones" (in the $\mathbf{k} \cdot \mathbf{p}$ model) are actually elliptic cones whose anisotropy is rather small for (Pb_xSn₁. _x)Se^{72,73} but very pronounced in SnTe^{69,74,75}. Without interaction the parent cones would merge along an elliptical contour, but hybridization causes them to repel each other and reduces the surface of intersection to two points along the symmetry-protected $\overline{\Gamma} - \overline{X}$ line. This produces the double-cone structure shown in **Fig. 1.5(b)**, with four of the resulting "child" Dirac cones in the first surface Brillouin zone. The hybridization distorts the child Dirac cones (note the non-circular cross-sections in the second and third panels of **Fig. 1.6(b)**), and forces a Lifshitz transition, both above and below the "child" Dirac points, where the cones merge.



Fig. 1.6 Close-up of the (001) TCI surface states near the \overline{X} point. (a) A 3-D plot of the pair of "child" Dirac points with color indicating the orbital character, from Ref. ⁷². (b) A series of cross-sections of the surface state, from Ref. ⁶⁷. Note the Lifshitz transition between the third and fifth panels from the top.

Further, it turns out that in $(Pb_xSn_{1-x})Se$ there is a surface orthorhombic distortion which breaks one of the mirror symmetries, and endows the corresponding valley of Dirac fermions with mass^{76,77}. (Indeed $(Pb_xSn_{1-x})Se$ is a nice playground for demonstrating the capabilities of STM, and we will return to this system briefly in Chapter 2.)

Despite its complicated appearance, all of the physics described above can be captured in a 4x4 matrix Hamiltonian containing constants and terms linear in **k** which, like Eq. (1.6), can also be written in terms of (tensor products of) Pauli matrices^{67,72,73}. (This matrix, however only describes the surface states near one \overline{X} point.)

One of the most interesting features of the (001) surface states is that the (child) Dirac nodes are not locked to the time-reversal invariant momenta, but move freely as the parameters of the Hamiltonian change. Among the "knobs" that can produce such changes are chemical doping⁷⁸, temperature^{68,79}, and

strain^{80,81}. Generally speaking, compressive strain tends to increase the inverted band gap, making the system more topological and moving the Dirac nodes closer to $\overline{\Gamma}^{80}$. Moreover, for strain the response of the Dirac nodes (i.e. their shift in momentum space) is entirely analogous to an electromagnetic vector potential, and the pseudomagnetic fields resulting from spatially varying strain have been predicted to lead to exotic physics including superconductivity³⁹ (which had long ago been discovered in (001)-oriented IV-VI semiconductor junctions^{82,83}). The motion of the Dirac nodes in SnTe under two types of strain is mapped out in chapter 5.

1.4 The perovskite Iridates – Sr-327

Although the parent compound of Chapter 3, Sr₃Ir₂O₇, is both an insulator^{84,85} and a system with strong spin-orbit coupling⁸⁶, its physics is quite different from the systems described above. All of the latter could be formulated within the independent electro approximation, in which the band structure is created by the periodic potential of the lattice and electron-electron interactions are regarded as a perturbation.⁸⁷ By contrast, in the Iridates⁸⁶, and in many transition-metal oxides (TMOs) generally⁸⁸, electron correlations play a key role.

The greatest manifestation of electron correlations in TMOs is the Coulomb repulsion between electrons occupying the same lattice site. This was included as U in the famous Hubbard model⁸⁹

$$H = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$
(1.8)

where c^{\dagger} and c are creation and annihilation operators for electrons on a particular lattice site (i or j) with spin σ , and $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$ is the number of such electrons on the i^{th} site. In the first term t represents the amplitude for hopping from atom i to j (the kinetic energy term), and U represents the Coulomb energy penalty. (Note that in contrast to Eq. (1.6) the Hubbard model is an explicitly many-body Hamiltonian.) At half-filling (that is, one electron per lattice site) the ground state of the Hubbard model transitions from metallic to insulating with increasing U/t, and the resulting insulator is the Mott or Mott-Hubbard insulator (**Fig. 1.7**)^{88,90,91}. Particularly well-known Mott insulators include the parent compounds of the Cuprate superconductors⁹².



Fig. 1.7 Schematic Hubbard model phase diagram, from Ref.⁸⁸. The Mott insulator is the dark vertical line at half filling. "The shaded area is in principle metallic but under the strong influence of the metal-insulator transition, in which carriers are easily localized by extrinsic forces such as randomness and electron-lattice coupling."⁸⁸ The two ways of achieving the metal-insulator transition in this system are indicated by dark grey arrows: "filling control" (FC) and the changing of U/t at constant filling (BC).

In the study of the perovskite Iridates, particularly Sr_2IrO_4 , the insulating behavior was regarded as surprising in view of the basic *d*-orbital physics⁸⁶: as the size of the *d*-orbital increases one generally expects *t* in Eq. (1.8) to increase (from increased overlap of neighboring wave functions) and *U* to decrease, tending to render the $5d^5$ Iridates metallic. In the original proposal⁸⁶ the role of spin-orbit coupling was to split the *t2g* manifold (containing the d_{xy} , d_{yz} , d_{xz} orbitals which are split from the other two *d* orbitals by the octahedral crystal field) into $j_{eff}=3/2$ and $j_{eff}=1/2$ subbands, with four electrons in the former and one in the latter. This half-filled $j_{eff}=1/2$ is split by the Hubbard *U* into upper and lower Hubbard bands leading to an insulating state. (The $j_{eff}=1/2$ state is formed from an $L_z = \pm 1$ state of $|xz\rangle \pm i |yz\rangle$ with antialigned spin, combined with $|xy\rangle$ with aligned spin^{84,93}.)

Sr-327 is the n=2 member Ruddlesden–Popperseries $Sr_{n+1}Ir_nO_{3n+1}$, which have a layered structure depicted in Fig. 1.8. In the n=1 member, Sr-214, the Ir planes are separated by two SrO planes rendering the Ir-Ir hopping largely two-dimensional, whereas the "n=∞" member SrIrO₃ has a fully three-dimensional structure with hopping possible in all directions. In the framework of the Hubbard model this tends to increase the bandwidth, favoring metallic behavior for a given *U*. For the Iridates this leads to a "dimensionality-driven" transition from an insulartor at n=1 to a correlated metal at n=∞⁸⁴. That is, Sr-327 was predicted to be close to the metal-insulator transition in this system. In chapter 3 we study both the parent compound and the metal-insulator transition (as a function of doping, not number of layers) using STM.



Fig. 1.8 Perovskite crystal structure of the Ruddlesden-Popper Series. (a), (b) and (c) are n=1, n=2, n=3 respectively. In the Iridates the easy cleave planes are indicated by red dashed lines. The "n= ∞ " crystal structure is visible within the n=3 unit cell as indicated. The black-and-white figure is adopted from ⁹⁴. (Note that for us A, A' = Sr, B=Ir, C=O.)

Chapter 2 – Scanning tunneling microscopy

In this chapter we discuss the technique STM as employed in this thesis: low-temperature, ultrahigh vacuum (UHV) STM designed to measure the local density of states with atomic resolution. We briefly sketch the history of STM and its use as a band structure probe (and comparison with other such probes), concentrating in particular on Landau level spectroscopy and quasiparticle interference. We also explain the Lawler-Fujita drift correction procedure⁹⁵ and its use in measuring strain on an atomic scale. All of the computer code used to analyze data for this thesis was written by the author (in Java)¹, although the ideas for the various algorithms were generally originated by others.

2.1 Basics of Scanning tunneling microscopy and spectroscopy (STM/S)

Scanning tunneling microscopy is now more than 30 years old and its basic ingredients, both technical and theoretical, have been described by numerous authors^{96–98}. It is based on the phenomenon of vacuum tunneling: electrons quantum-mechanically tunnel through a (vacuum) gap of a few Angstroms between a sample surface and a sharp metallic tip. When a bias voltage is applied (in our case, to the sample while the tip is held at virtual ground) this tunneling produces a steady current on the order of pA to nA. The tip itself is moved in 3D space by piezoelectric actuators: in a typical imaging mode it scans back and forth in the horizontal plane (x-y) while a feedback loop adjusts its altitude to keep the tunneling current constant.

In the results shown in this thesis it will generally be assumed that

$$\frac{dI}{dV}(\mathbf{r}, eV) \quad \alpha \quad LDOS(\mathbf{r}, eV) \tag{2.1}$$

¹ However, publicly available math libraries were made use of. The jtransforms package for fast Fourier transforms and the Apache Commons math project deserve special mention.

where dI/dV is the differential conductance at sample bias V, **r** is the tip position, and LDOS is the local density of states as a function of position and energy: $LDOS(\mathbf{r}, E) = \sum_{i} |\psi_i(\mathbf{r})|^2 \delta(E - E_i)$ where the sum is over all states in the sample.

Eq. (2.1) can be derived from the Tersoff-Hamann theory of a spherically symmetric tip with an *s* wave function⁹⁹, in which case **r** is the center of curvature of the tip apex. Chen, however, pointed that for realistic tips this apex was so far from the surface as to be unable to account for the observed atomic corrugations on certain metals, and proposed that the tip orbital was a dangling *d* state¹⁰⁰. Generally, if the tip wave function is other than s-wave the resulting current is predicted to reflect spatial derivatives of the sample wave function at the tip position: the derivative in the *x*-direction for a *p_x* orbital, second derivatives for the *d* orbitals, and so on¹⁰¹, so that for a dangling $d_{3z^2-r^2}$ orbital the *dI/dV* would involve $(\partial^2 / \partial z^2)\psi^{100}$. For practical purposes, however, it is often sufficient (for normal-state metallic tips) to use Eq. (2.1) and regard **r** as a two-dimensional variable^{102,103}. In this thesis we regard Eq. (2.1) as valid for fixed tip position (i.e. when sweeping *V* with the tip stationary and the feedback look off), and the difficulties associated with the variation of that height with **r** as situationally negligible.

2.2 STM/S as a band structure probe – Quasiparticle interference

The designers of the STM initially conceived it as a nanoscale spectroscopic tool rather than an imaging device¹⁰⁴. (Nevertheless, its breakthrough to fame is attributed to its successful atomic-resolution imaging of the (7x7) reconstruction on Si(111)^{104,105}.) Being an inherently real-space probe, its ability to characterize Bloch states defined in **k**-space is not immediately obvious.

Early efforts in this direction included well-known studies on Cu and Au(111)^{106,107}. In both cases, scattering of electrons at a step edge created spatial modulations in the local density of states which were directly visualized by STM. In the case of Cu the wavelength of these modulations as a function of energy

directly corresponded to the band dispersion of the Cu(111) surface state (**Fig. 2.1**), although this was not so in Au¹⁰⁷.



Fig. 2.1. Band dispersion extracted from standing waves in Cu (111) and Au(111). (a) shows the dI/dV as a function of distance from a step edge on Cu(111) at different bias voltages, from Ref. ¹⁰⁶. The dashed lines are the results (Bessel functions) of a calculation for a simple 2DEG in the presence of a hard 1D potential representing the step edge. The inset shows E(k) extracted from the fits to the theory plotted with a parabolic fit. (b) shows a similar E-k plot from Ref. ¹⁰⁷, where the solid line is the surface state dispersion extracted ARPES $\equiv k_A$ and the dashed line is $k(E) = (k_F + k_A)/2$.

The practice of characterizing the band dispersion by analyzing the (energy-dependent) wave-numbers of standing waves is now called the quasiparticle interference (QPI) method¹⁰². A detailed theoretical treatment of QPI is complicated^{108–111}, but the following handwavy explanation accounts for the basic features of much of the experimental data^{49,73}: an impurity scatters the quasiparticle from some initial state with momentum \mathbf{k}_i to a final state with momentum \mathbf{k}_f . The initial and final wavefunctions interfere,

creating modulations with wavevector $\mathbf{q} \equiv (\mathbf{k_i} - \mathbf{k_f})$ in the local density of states. (This picture assumes that the initial and final states are itinerant states with well-defined \mathbf{k} and $\psi \sim e^{i\mathbf{k}\cdot\mathbf{r}}$.) In Refs. ^{106,107} the whole standing wave pattern was fit in order to extract q; nowadays one takes the Fourier transform of $dI/dV(\mathbf{r})$ and looks for peaks^{73,102}.

This intuitive picture of quasiparticle interference makes it easy to guess where in the Fourier transform the modulations will appear if $E(\mathbf{k})$ is known: simply draw arrows between states on the "Fermi contour" at that energy (constant energy contour or CEC), then translate one end of the arrow to the origin. Equivalently one can take the autocorrelation of either a drawing of the CEC, or the spectral function $A(\mathbf{k}, \omega)$ derived from a calculation (See Fig. 2.2).



Fig. 2.2. Graphical exposition of quasiparticle interference (a) shows the parabolic dispersion of a simple 2DEG, and (b) a representative constant energy contour (CEC) at $E = "E_0"$. (d) is the autocorrelation of (b), with a clear maximum at $q = 2k_0$. (c) is the actual Fourier transform of the dI/dV on Cu (111) at +2 mV (unpublished). (e) and (f)

are for the much more complicated band structure of $Sr_3Ru_2O_7$ from Ref. ¹¹², and contain theoretical CECs and an experimental Fourier ransform respectively. (Compare (b) and (c) to (e) and (f)).

The use of the Fourier transform in quasi-particle interference studies has been impactful enough to spawn a new acronym: Fourier transform scanning tunneling spectroscopy or FT-STS¹¹³. The acquisition of a dataset in FT-STS has since become something of a craft, almost independent of the particular sample, and we may briefly state its rules although some of them are obvious and others have been stated elsewhere (e.g. Ref. ¹⁰²):

The $dl/dV(\mathbf{r})$ at a given voltage being a square image made of square pixels (as is usually the case), the **k**-space resolution is isotropic and equal to $2\pi/L$ for image size *L*. To resolve fine features in **k**-space one should therefore choose a large *L*. Most scattering, however, involves states in or near the first Brillouin zone, so that the scattering vectors are no larger than a reciprocal lattice vector. Therefore, the Fourier transform need only include a region of **k**-space containing the first reciprocal lattice vectors with some margin. The extent of the Fourier transform in **k**-space is $(N/2)2\pi/L$ where N is the number of pixels, or π/a where *a* is the pixel size. The resolution therefore does not need to be very high; the high pixel density needed for good atomic resolution images would waste a large region of **k**-space. The orientation of the image is also important, especially if one is trying to fit a square reciprocal lattice into a square Fourier transform. (Care must be taken, however, that the Bragg peaks be placed not too close together taking into account that **k**-space is periodic; see section 2.4.)

Generally one tries to fix a as large as is reasonable, and then increase L until the acquisition time (which is the ultimate limiting factor as each pixel takes several milliseconds) reaches its practical limit, ultimately determined by the need to stop measurement and refill the cryostat. There is, however, no natural upper limit on L. (In our case the STMs (built by Unisoku) had a coarse motion capability and indeed we spent many days on various samples looking for flat, clean areas in which large-L datasets could be taken.) Lastly, one of the great advantages of STM (as opposed to the classic **k**-space probe, ARPES) is its spatial resolution, which among other things permits one to mask out parts of the real-space $dI/dV(\mathbf{r})$ map and compare the QPI signature in different regions. This is done extensively in Chapter 5.

2.3 Landau level spectroscopy (STS)²

This method for characterizing the band structure relies on the Landau quantization of electrons in a magnetic field^{4,114,115}. Classically, in a magnetic field the electron's motion remains free along the direction of the field (**B**) while in the perpendicular plane the trajectory is bent into a circular orbit, which is quantized into the discrete Landau energy levels. For electrons in free space the quantization is identical to that of the simple harmonic oscillator; for condensed matter systems the quantization scheme is much richer and more complicated^{116,117}. Quasi-classically, however, the behavior of Bloch electrons is somewhat analogous to those of free electrons: in free space the Lorentz force moves the electron on a circle in **k**-space, and the projection perpendicular to **B** of the corresponding real space orbit is circular; Bloch electrons traverse in **k**-space the CEC defined at their energy and k_z (the magnetic field being along *z*), and their real-space orbits mirror the (rotated) shape of the CEC¹¹⁶. As they traverse this **k**-space contour the electrons accumulate the famous Berry phase¹¹⁸, which is often mentioned in the context of topological insulators^{29,119} and whose π value distinguishes the Dirac surface state from other types of 2DEG¹²⁰.

In this thesis we will be concerned with 2D surface states, so we can afford to give a bastardized version of the theory of quantum oscillations¹¹⁶ in which the complications associated with k_z are ignored: the effect of Landau quantization is to reduce the density of states curve to a series of sharp peaks at the discrete Landau level energies. As the magnetic field is swept these peaks move in energy, and as they pass one by one through E_F they cause oscillations in the magnetization¹²¹ and transport¹²² properties of the sample. (In 2D these oscillations are intimately connected with the quantum Hall effect.) It can be

² (STS) is added in parentheses because Landau level spectroscopy is apparently much more general: a book was published with this title in 1991, well before the STM technique.¹⁸⁹

shown that semiclassically the Landau quantization encloses an equal increment of **k**-space area for each Landau level¹¹⁶:

$$A_{N} = (N + \gamma) 2\pi eB / \hbar$$
(2.2)

where A_N is the **k**-space area corresponding to the N^{th} Landau level and γ is a phase constant. As a result the oscillations in the transport properties as a function of 1/B have a definite frequency which is proportional to the area enclosed by the Fermi contour. The study of these oscillations in 3D was brought to a high degree of development by the 1960's¹¹⁶, and was a very effective and well-established method of characterizing the Fermi surfaces of metals⁸⁷ at a time when ARPES was rudimentary¹²³ and STM was a twinkle in certain workers' eyes¹²⁴.

In high-field STS the Landau level peaks appear directly in the dI/dV(V) spectrum, and as a function of field one can track them not just as they pass through E_{F_i} but throughout the energy range in which peaks are visible. It is thus possible to use STS to establish not just the area of the Fermi surface, but the area of all CECs in the energy range and therefore (if isotropic) the dispersion relation of the 2D band.

In practice the number of Landau levels observed in STS spectra is usually much smaller than in metallic quantum oscillations measurements, which can involve hundreds of Landau levels^{87,116} (**Fig. 2.3a**). Instead of sweeping the field and measuring the rate at which peaks pass through a given energy, one indexes the peaks sequentially and establishes the dispersion relation directly from Eq. (2.2). (Miller *et al.* actually did "sweep the field" in graphene, with good results¹²⁵.) Several different magnetic fields are used, but this is not essential to the technique and is usually done for two reasons: (1) to increase the density of data points enough to approximate a continuous curve, and (2) to check the indexing scheme by verifying that the A(E) curve extracted from (2.2) is indeed field-independent.



Fig. 2.3 Quantum oscillations and Landau level spectroscopy. (a) and (b) show de Haas-van Alphen oscillations in Rh and Ag, from ⁸⁷; the x-axis is the magnetic field. (c) shows Landau level peaks in dI/dV spectra taken on Sb(111), from ¹²⁶. The number of resolved STS Landau levels is usually significantly lower than in (c)^{57,76,127}.

Point (2) bears elaboration in view of the peculiarities of Landau level spectroscopy when only a few peaks are visible. The most obvious "internal" check of the correctness of an indexing scheme is that the quantity A(E) (or equivalently E(k) for isotropic systems), as extracted from the Landau level peaks, should have no dependence on the field strength. To bring this about one can shift the peak indices up and down in unit increments; in Bi₂Te₃ we even permitted ourselves to skip one of the peaks¹²⁷. But the condition itself becomes problematic when *N* is small: Eq. (2.2) was derived semiclassically and as such should be strictly valid only for N >> 1. In general it may be impossible to fit the lowest few Landau levels to a single curve using (2.2), for *any* indexing scheme. (This is so in Bi₂Se₃ when you look closely.)

In that case it is necessary to go beyond Eq. (2.2) and use knowledge derived from other sources. If one is lucky the low-energy Hamiltonian will provide an exact solution for the lowest few Landau levels (this
the case for the Bi-based topological insulators¹⁴), and one can then tweak one's indexing scheme to conform to it. (Our study of the low-index Landau levels in In-doped Bi_2Se_3 (chapter 4) obliged us to conclude that the indexing scheme originally applied in the parent compound^{56,57} indeed needed a tweaking: we had to reduce each index by one.)

Another means of distinguishing the Landau levels, which seems entirely unique to STM, is through the nodal structure of their wave functions^{128,129}. In a homogenous 2DEG each Landau level is highly degenerate, but the native spatial inhomogeneity in topological insulators^{127,129,130} (and other systems¹²⁸) lifts this degeneracy by adding a 2D potential landscape. (If this potential landscape is especially simple, for example 1D stripes or a central potential well, the well-known gauges can still be used and the problem solved more or less exactly^{127,129}.) Within this landscape the Landau orbits tend to drift along equipotential lines^{128,131}, so that when the potential gradient is steep the individual wave functions' probability density ($|\psi(\mathbf{r})|^2$) can almost be imaged directly. Generally, the index of the Landau level equals the number of nodes in its wave function (cf. the simple harmonic oscillator or indeed any 1D problem⁴) and the nodes, like the wave functions, tend to follow the equipotential lines^{128,131}.

In the topological Dirac system the situation regarding the nodes is a bit more complicated, since the solutions of the Hamiltonian are two-component spinors whose components differ by one in the number of nodes¹²⁹. In chapter 4 we present detailed first-principles calculations of the nodal structure of the wave functions in Bi_2Se_3 , showing that our tweaking of the indexing scheme is consistent with the existing experimental data¹²⁹.

2.4 Landau level spectroscopy vs. QPI

Although they both measure the same things, Landau level spectroscopy and the QPI method have certain contradictory characteristics which makes a fusion of the techniques especially difficult: QPI requires defects to generate the scattering events and produce the standing waves, whereas Landau level

spectroscopy prefers a clean sample with a long mean free path. (If the lifetime is too short the peaks will smear together.) There is also a difference in their characteristic wavelengths: In Landau level spectroscopy the characteristic wave number is $k_N \sim \sqrt{A_N} = \sqrt{N2\pi eB/\hbar}$, and the corresponding wavelength $\lambda_N = 2\pi/k_N = \sqrt{2\pi/N}\sqrt{\hbar/eB} = \sqrt{2\pi/N}\ell_B$ where ℓ_B is the magnetic length. At 7.5T (the highest field used in our lab at BC) the magnetic length is 9.7 nm, so for N=1 or 2 the expected wavelength would require a huge area to resolve convincingly in the Fourier transform (and may not give a recognizable scattering signature at all). QPI scattering vectors, by contrast, can span the Brillouin zone and have wavelengths on the order of a unit cell. Therefore, overlap between QPI and Landau level spectroscopy datasets demands a strong magnetic field, a large number of visible Landau levels, and a "Goldilocks" number of defects. It is comforting to know that in the rare cases when the two methods do overlap on the same sample, they agree with each other^{126,132}. (As the available magnets become stronger, we expect that the area of overlap will tend to increase.)

2.5 Strain measurement and the Lawler-Fujita drift correction method

In STM the relation between the piezo voltages and the tip position (with respect to the landmarks in a particular sample) is not the ideal linear relation, but a complicated one marred by nonlinearities, thermal drift and hysteretic effects (see e.g. ¹³³). As a result the atomic lattice is not uniformly periodic throughout the image, and consequently the Fourier transform of the topography or dI/dV represents **k**-space not in the sense of the reciprocal atomic lattice, but only the reciprocal piezo voltage (**Fig. 2.4**). This distinction was more-or-less tolerated until 2010, when Lawler, Fujita *et al.* needed a perfectly periodic lattice in order to search for signatures of nematicity in **k**-space⁹⁵, and developed an algorithm capable of the taking the usual, distorted type of STM image and calculating and applying the necessary "undistortion."



Fig. 2.4. An example of hysteretic effects in an STM scan. (a) is the topography, and (b) the Fourier transform. Note how near the top of (a) the vertical lines of atoms bend to the right. The corresponding smearing out of the Bragg peak in (b) is circled in red. (In principle the whole of k-space is is thus smeared out.)

The method of calculating the distortion is fairly straightforward and (as it turns out) had already been invented by transmission electron microscopists much earlier¹³⁴: The points of the ideal lattice and the actual, distorted lattice are connected by a smoothly-varying displacement field $\mathbf{u}(\mathbf{r})$, which also appears in the distorted lattice's Fourier transform. The first-order Fourier expansion of the ideal lattice is given by $A_1 e^{i\mathbf{k}_1\cdot\mathbf{r}} + A_2 e^{i\mathbf{k}_2\cdot\mathbf{r}} + \text{c.c.}$, and the real lattice, being shifted from \mathbf{r} to $\mathbf{r} + \mathbf{u}$, can be approximated similarly:

$$T(\mathbf{r}) \approx A_1 e^{i\mathbf{k}_1 \cdot (\mathbf{r} + \mathbf{u})} + A_2 e^{i\mathbf{k}_2 \cdot (\mathbf{r} + \mathbf{u})} + \text{c.c.}$$
(2.3)

where *T* represents the actual topography, and \mathbf{k}_1 and \mathbf{k}_2 are the basic reciprocal lattice vectors. If the approximation (2.3) is valid, it is very easy to find expressions proportional to $e^{i\mathbf{k}_{1,2}\cdot\mathbf{u}}$ for all **r**: simply multiply $T(\mathbf{r})$ by $e^{-i\mathbf{k}_{1,2}\cdot\mathbf{r}}$ and smooth with some length scale to average out the other, rapidly oscillating

terms. From these expressions one can extract $(\mathbf{k}_{1,2} \cdot \mathbf{u})$ for all \mathbf{r} , thence $\mathbf{u}(\mathbf{r})$ using linear algebra. (A slightly more detailed presentation is given in the appendix to chapter 5.)

It is clear that this field $\mathbf{u}(\mathbf{r})$ is conceptually identical to the displacement field of elasticity theory¹³⁵ (Indeed this was pointed out in ⁹⁵ in parentheses.): If there is genuine surface strain in the sample, that strain will necessarily appear in \mathbf{u} alongside the other effects, provided of course that the smoothing length scale is not large enough to average it out.

To separate the terms in **u** which represent genuine strain from those caused by STM-related technical issues is in general no easy task, and we believe this thesis (except for the related publication ⁷⁴) is the first to try to do it. Fortunately in the specific system we studied, SnTe thin films grown on PbSe, the strain is associated with a periodic pattern of dislocations with a quasi-lattice constant of about 15 nm. This is much smaller than the scan size used to obtain $dI/dV(\mathbf{r})$, 130 nm, and the difference in length scales made it possible to get away with subtracting from **u** (or its derivatives) a low-order best-fit polynomial in **r**. This is expected to remove the effects of nonlinearities and slow thermal drift, as well as most of the hysteresis (which the skilled STM operator can usually keep to a minimum).

We may add that the Lawler-Fujita drift correction algorithm in its original form recommends itself as a processing step in the more general analysis of STM data. In particular, by lining up the atoms on a periodic grid it makes it possible to convert pixels to atomic coordinates by simple linear algebra, which is ideal for identifying the lattice position of point defects¹³⁶; we will use it for this in Chapter 3. Also, as already mentioned it "de-smears" **k**-space and thus improves the mathematical rigor as well as the aesthetics of FT-STS.

Chapter 3 – Doping effects in Sr₃Ir₂O₇

As mentioned in the Introduction, Sr₃Ir₂O₇ (usually abbreviated Sr-327) is predicted to belong to a novel class of spin-orbit driven Mott insulators^{84,86}. The study of these systems is intrinsically interesting (and theoretically difficult) because the hopping, spin-orbit coupling and correlation effects have comparable energy scales. The analogy with the cuprates, where the doping of a Mott insulator leads to "unconventional" high-temperature superconductivity⁹², lends particular interest to doping studies in these compounds¹³⁷.

Our results fall logically into two sections: (1) the parent compound (which may however be regarded as locally doped by apical oxygen vacancies), and (2) the doping effects proper, which focuses on La-doping $(Sr_{1-x}La_x)Ir_2O_7$ and compares it to both the case of Ru-doping¹³⁸ and briefly with the La-doping of Sr_2IrO_4 .¹³⁹ The results in section (1) have been largely published already⁸⁵ although our presentation is a bit different from the reference; the results of (2) have only partly been published¹⁴⁰.

3.1 Parent compound

As mentioned in the introduction, Sr-327 lies along the dimensionally-driven metal-insulator transition between the insulator Sr-214 (n=1 in the Ruddlesden-Popper series), and the metallic Sr-113 ($n=\infty$)⁸⁴. The gap size in this compound was not clear, with the initial optical study reporting a small gap ("almost zero")⁸⁴ while a later ARPES study found a ~90 meV gap¹⁴¹. (The smaller gap had been used to account for the antiferromagnetic transition at 285K¹⁴² given the large magnon gap¹⁴³.) Other, related aspects of the ground state in Sr-327 were also unclear; the spin-orbit Mott concept was challenged in Sr-214¹⁴⁴ and Sr-327¹⁴⁵; the latter argued that the $j_{eff}=1/2$ and 3/2 bands were not sufficiently split.

Given the above, an STM study of the parent compound was highly desireable. (Also, as pointed out in ⁸⁵, STM had proved its value in revealing microscopic inhomogeneity in strongly-correlated TMOs¹⁴⁶, and no STM work on the Iridates had yet been done.)

The basic topographic features of the sample are shown in **Fig. 3.1**. The surface lattice constant is about 3.9 Å, regardless of bias voltage, indicating that the maxima in the topography correspond either to Sr or O atoms. Usually in such cases it is difficult to tell which sublattice it is, but here we have an obvious clue: in the topography (and also in the dI/dV; see below) there are defects with two orientations, which are mirror-images of each other in the *a*- or *b*-axis and whose centers are always found in the middle of a group of four surface atoms (**Fig. 3.1 (f)-(i)**). As shown in more detail below, the symmetry of these defects corresponds to the rotation about the crystalline *c*-axis of the oxygen octohedra (shown from the side in **Fig. 3.1(a)**): the rotated octahedron has a "chiral" aspect when viewed from above and breaks the mirror symmetry, and the left- and right-rotated octohedra are mirror images of each other. These considerations show that the lattice in the topography corresponds to Sr, and identify the defect site as the Ir atom, or an O atom directly above or below it. (Indeed similar conclusions were drawn in an STM study of Sr₃Ru₂O₇.¹¹²)



Fig. 3.1. Topographic images of Sr-327, from Ref.⁸⁵ (a) shows the crystal structure; note in particular the alternating rotation angle of the (brown) oxygen octahedra. The SrO plain is exposed in the cleaving process, and the step edges correspond to one bilayer (b). (c) and (d) show topographies at positive and negative bias respectively; the lattice constant corresponds to the Sr-Sr (equivalently, O-O) distance of 3.9 Å. The corresponding Bragg peaks are circled in pink (e) with a $\sqrt{2x}\sqrt{2}$ pattern's Bragg peaks in green. Two "chiral" defects are shown in (f), (g) and schematically in (h), (i).

The local density of states (LDOS) shows great unevenness in large part associated with the chiral defects (**Fig. 3.2**). To characterize the inhomogeneity of Sr-327 (and the role of the chiral defects) we took lines of spectra ("line cuts") through an isolated defect and into a region free of defects (**Fig. 3.2** (**a**)-(**e**)) in relatively narrow (**b**),(**c**) and wide (**d**),(**e**) energy ranges. Far from the defect (the bottom of panels (**a**)-(**e**) the LDOS shows a substantial insulating gap of more than 100 meV, but over the defect the gap closes and the spectrum near E_F assumes a "V" shape. The inhomogeneity in the gap size is shown even more graphically in **Fig. 3.2** (**f**)-(**h**). Here we took an atomic resolution dI/dV map in order to inspect the LDOS within a ~20nmx20nm area within +/- 180 mV of E_F . As can be seen in **Fig. 3.2(h)** (as also in panels (d)-(e)), the LDOS below E_F is fairly uniform and corresponds approximately to a pinning of E_F to the top of the valence band. Above E_F the spectra vary within a huge range including highly gapped spectra (gap \approx 180 meV; white curves in (**h**)) and fully metallic spectra (black curves) in clusters of the chiral defects.³

To fully capture this inhomogeneity we made "gap maps" (inspired by the practice in STM on the Cuprates^{147,148}) in the following manner: we define the insulating gap as the region in which the STSmeasured dI/dV is indistinguishable from zero, and for each dI/dV spectrum determine the size of the energy range in which this condition is satisfied. This produces a 2-D image as in **Fig. 3.2 (g)**. To visualize the associated variation in the spectra, we bin the 3-D dI/dV dataset against the gap map. (That is, we sort the pixels of the gap map and divide it evenly into bins; for each bin the average spectrum is the average of spectra for all pixels belonging to the bin.) The spectra far from defects (white regions in **Fig. 3.2 (g)** and spectra in **(h)**), which must show the intrinsic band structure of Sr-327, show a ~150 meV

³ See also Fig. 5 of Ref. ⁸⁵

gap, much larger than suggested¹⁴¹ even by ARPES⁴. The nanoscale metallicity induced even by a relatively small concentration of defects shows the importance of high sample quality for spatially insensity measurement techniques. (See also our study of La-doping below.)

The obvious question what the "chiral defects" are seems relatively straightforward. According to the symmetry arguments given above they must be located on the Ir site, or above or below it along the c axis. The most logical candidate are apical oxygen vacancies, since they donate two electrons each, and indeed oxygen-deficient Sr-214 was shown to undergo a transition to a (strange) metal for defect concentrations as low as $1\%^{149}$.

⁴ ARPES, however, cannot see the unoccupied states and the cited study's gap estimate was not a direct measurement.



Fig. 3.2: Electronic inhomogeneity around chiral defects. Panels (a)-(e) are from Ref. ⁸⁵. (a) shows an STM topography with an isolated chiral defect (near top); (b) and (c), and (d) and (e) show tunneling spectra taken along the dotted line indicated in a); (b) and (d) are color plots and (c) and (e) are line graphs vertically shifted to show the changing spectral shape. (f) is a constant-energy cut of a $dI/dV(\mathbf{r},E)$ map, at +180 mV bias; the chiral defects are the small blue squares (four of them circled in yellow). (g) is a gap map as defined in the main text; metallic and insulating regions are indicated by the corresponding capital letters. (h) is a collection of spectra from the dI/dV map used in (f) and (g); each spectrum color is the average of spectra at the corresponding pixel color in (g).

Before proceeding let us look a little more closely at the chiral defects. In **Fig. 3.2 (f)** one can see that the blue squares are slightly tilted with resepect to the lattice: the right- and left-most defects are slightly clockwise with the center two defects slightly anticlockwise. To characterize this rotation we carefully measured the "angles" of the impurities and found average rotations of $12 \pm 2^\circ$, consistent with the 11.8° value obtained initially from X-ray diffraction¹⁵⁰ (**Fig. 3.3**). Unfortunately this angle measurement is

probably not sensitive enough to detect small changes in the O-Ir-O binding angle, which have potentially significant effects on the hopping integrals and electronic properties.¹⁴⁹ (However, other types of impurity profile might permit more sensitive angle measurements along the same lines, e.g. the black squares in Ref. ¹¹².) To check that the tilting really corresponds to the alternating rotation of the oxygen octohedra in Sr-327, we checked the lattice position of each chiral defect and found that all defects with positive angles were on "even" lattice sites (P+Q even in **Fig. 3.3 (e)**) and vice versa.



Fig. 3.3: Tilting of the oxygen octohedra measured by STM (a) A section of the dI/dV at +130 mV, from the same area (rotated) as **Fig. 3.2 (f)**. (b) The same region topography used to acquire the dI/dV map, at -180 mV. Examples of the two subtypes of defect are circled in red and orange in (a) and (b), and indicated respectively in (c) and (d). (e) shows the top view of the crystal with rotated octohedra; the two sublattice are shaded red and yellow. (Cf. **Fig. 3.1(a)**). (f) is the actual histogram of the angle measurements with Gaussian fits superimposed, from Ref.⁸⁵

To determine what range of parameters could produce the large intrinsic gap we⁵ performed generalized gradient approximation + U (GGA+U) calculations. These results are shown in Fig. 3 of Ref.⁸⁵, here we say merely that it was necessary to assign considerable magnitudes to both spin-orbit coupling (1.7 times the value self-consistently obtained in GGA⁸⁵) and correlations (U \approx 1.5 eV). Besides being electron donors, the apical oxygen vacancies are predicted to draw the Ir atoms towards themselves, changing the crystal field noticeably; see the supplement of Ref.⁸⁵. (This is in contrast to La dopants discussed below.)

Subchapter Appendix: How we measured the defect angles

We first corrected the dI/dV map using the Lawler-Fujita drift correction procedure⁹⁵. (This was necessary in order to define the crystalline axes against which the angle is to be measured.) Then we identify each square in the dI/dV map we want to measure (**Fig. 3.4 (a)**) and zoom in on it (**Fig. 3.4 (b)**). Because it has approximately the form of a bright square on a dark background we construct such an object in pure form (**Fig. 3.4 (c)**) and, after positioning and sizing artificial square to place them on top of each other we rotate the artificial square through 90 degrees and calculate the numerical correlation between the two images at each orientation. The correlation curve is always vaguely sinusoidal (**Fig. 3.4 (d)**) and the angle of maximum correlation is then selected for the impurity. This procedure eliminates the human error in direct measurement but it is time-consuming, and it requires of the impurity a certain shape, which in this case symmetry did not dictate. (See also Ref.⁸⁵, supplementary information.)

⁵ Here I mean our theoretical collaborators and not ourselves personally.



Fig. 3.4: **Angle measurement of impurities** (a) A section of the dI/dV at +130 mV, the same as **Fig. 3.2** (f). Here the dI/dV is in greyscale and the selected impurities are marked by colored circles. (b) A single impurity (indicated by the arrow in (a); (c) is its artificial square. (d) A graph of correlation versus tilt angle indicating in this case a tilt of about -12 degrees. From the supplement of Ref. ⁸⁵

3.2 La doping in Sr-327

When La is introduced into Sr-327 (Chemical formula: $(La_xSr_{1-x})_3Ir_2O_7$) there is a metal-insulator transition for $x \ge 5\%^{140,151}$. Above this point, ARPES studies^{152,153} show well-defined electron pockets whose area is proportional to *x*, as usual when adding electrons to a Fermi sea. (The bulk valence band also seems to move upwards, establishing a negative electronic compressibility.¹⁵³) We will concentrate on lower concentrations of La: 3-4.8% nominally, which straddle the metal-insulator transition and provide an opportunity to investigate how the local density of states evolves as we pass through it. Below the metal-insulator transition we see significant nanoscale inhomogeneity associated with a phaseseparated ground state¹⁴⁰; we also see some interesting phenomena relating to the individual La atoms which we describe below but cannot fully explain.

3.2.1 Topography – surface dopants

In studying the effects of light doping by STM one of the most obvious tasks is to find and identify the dopants. In La-doped Sr-327, however, the complete "dopant search" is a bit complicated: the most obvious surface defects are numerically insufficient to account for the doping concentration as estimated by the sample growers and confirmed by energy dispersive spectroscopy (EDS). They do, however, help to characterize the crystal structure and thus provide a convenient starting point for the narrative.

The "obvious" dopants are shown in **Fig. 3.5 (a)** and **(b)**, and take the form of bright squares with a slightly depressed center. These squares (which are present in STM topographs at both positive and negative bias) are centered on the topographic maxima which, given our previous experience on the parent compound⁸⁵, invites us to assume that they are La atoms substituting at Sr sites. Moreover, the defects are clearly dimorphic, and the symmetries of the two types show unambiguously that they belong to the Sr lattice (**Fig. 3.5 (c)-(e)**). This can be seen as follows: because of the alternating rotation of the IrO₆ octohedra about the *c* axis, the two Sr sites in the SrO plane are inequivalent: For one site the closest two O atoms in the IrO₂ plane are along the *a* axis, while for the other they are along the *b* axis. The immediate environment of the Sr site thus preserves reflection symmetry about the *a* and *b* axes, but is reduced from C₄ to C₂ symmetry. (This is the exact opposite of the case for the apical oxygen sites.^{85,112})



Fig. 3.5. Surface La dopants on Sr sites. (a) a 44 nm topograph at +200 mV bias; six of the C_2 -symmetric defects are circled. (b) a zoomed-in view of the six defects circled in (a). (c) A schematic showing the two types of Sr-site defect with their "long axes" indicated by arrows. (e) and (f) show representative Sr-site defects at the two sublattice sites, interpolated from (b). The two sublattice sites are shown in pink and brown respectively. (Unfortunately the lack of visible chiral defects made it impossible to clearly establish the arrow-color correspondence between (c) and the other panels; it might be reversed.)

Similarly to the apical oxygen vacancies (chapter 3; ⁸⁵) we found that the two types of defect are perfectly correlated with their lattice positions (i.e. all the "capital H" defects (**Fig. 3.5 (d**)) are on odd-numbered Sr sites, and vice versa). However, a close inspection of the topography (**Fig. 3.5(a)** and others) shows that the number of defects does not correspond to the number of expected La atoms: in **Fig. 3.5 (a)** there are slightly less than half as many as expected for $x \approx 3.2\%$. We will find the missing atoms again shortly, but in the meantime let us set them aside.

3.2.2 Nanoscale inhomogeneity in the local density of states

To study the metal-insulator crossover in La-doped Sr-327 we took atomically resolved $dI/dV(\mathbf{r}, \mathbf{V})$ maps at $x \approx 3.2\%$, 3.5%, and 4.8%. In the latter compound the spectra are gapless everywhere and show a characteristic asymmetric "V" shape, with the positive side steeper (**Fig. 3.6(b**)). In many of the spectra there is also a small "hump" at around -16 meV. For context we show the phase diagram for La-doped Sr-327 which places the 4.8%-doped sample distinctly within the metallic regime (**Fig. 3.6(b**), ¹⁴⁰).



Fig. 3.6: Line cut in metallic La-doped Sr-327 (a) A topography at +300 mV; the spectra are taken along the black-red line. (Incidentally the dimorphism of the La defects is not so evident here as in **Fig. 3.5**; our ability to detect it is somewhat tip-dependent.) (b) The dI/dV measured along the line, between -300 and +100 meV; the color of the spectrum corresponds to its position on the line. The vertical dashed line indicates the "hump."



Fig. 3.7: Metal-insulator transition in La-doped Sr-327. From Ref. ¹⁴⁰. (a) Resistivity as a function of temperature for $(Sr_{1-x}A_x)Ir_2O_7$, A = La or Ca. (b) Phase diagram of La-doped 327. From left to right the acronyms stand for antiferromagnetic insulator, metal insulator transition, and paramagnetic metal. T_{AF} is the antiferromagnetic transition temperature and T_S is the temperature of a structural distortion which accompanies the metallic state.¹⁴⁰

For the lower dopings, between 3 and 4%, the dI/dV maps are characterized by nanoscale inhomogeneity in which metallic and fully gapped insulating regions coexist. This was true of both ~3% samples. We will find that the inhomogeneity seems to be associated with another type of defect, which we identify as a subsurface La dopant. Although they were very similar in doping, and there is a clear phase separation in both samples, the degree of dopant clustering is a bit different. The individual defects are most clearly visible in the ~3.2% sample, hereafter called sample A (**Figs. 17, 21**), but the starkest clustering behavior—and also the strongest phase separation—can be observed in the 3.5% sample, sample B. Unfortunately, we will be forced to jump back and forth between the samples: we start by exhibiting the inhomogeneity in sample B, then return to sample A to introduce and characterize the defects, and finally look more closely at them in sample B. (Historically we measured sample B first, then sample A, then recleaved and measured sample B at which point the data shown in this thesis was taken.)

To examine the inhomogeneous local density of states we took $dI/dV(\mathbf{r}, V)$ maps in areas of a few tens of nanometers, covering the Fermi energy and the gap energy scale. The results of one such map (30 x 30

nm²) on sample B are shown in **Fig. 3.8.** The spectra range from fully insulating spectra reminiscent of the parent compound (Chapter 3.1; ⁸⁵) with a gap of up to 200 meV, to metallic spectra which broadly resemble the metallic system at x = 4.8% (**Fig. 3.8 (g)**). In this measurement fully two thirds of the spectra were found to be without a gap (**Fig. 3.8 (e)**), while the insulating spectra were concentrated in small patches of which the largest (or at least the roundest) was about 5 nm across. This phase separation shows that the doping-induced metal-insulator transition is first order¹⁴⁰, which is also consistent with recent theoretical work on filling-controlled phase transitions in Mott insulators¹⁵⁴.



Fig. 3.8 Nanoscale phase separation in the density of states for $x \approx 3.5\%$ **.** (a)-(d) show (smoothed) constant-voltage cuts of a a 30x30 nm $dI/dV(\mathbf{r}, V)$ map at V = -100 mV, -50 mV, 0, and +50 mV respectively (vertical lines in (g)); all four panels use the same color scale. (e) shows the gap map as defined in the main text. (f) is the simultaneous [constant-current mode] topography showing the tip altitude at the time each spectrum was taken. Note the characteristically small number of square defects, the dark patches where low density of states between the setpoint voltage and E_F and the setpoint voltage causes the tip to push inward, and the horizontal discontinuity where the state of the tip changed. (g) is a 128-bin "spectral histogram" showing the diversity of the dI/dV spectra from fully insulating (purple) to metallic (yellow and red). (h) overlays the topography (f) on the gap map (e).

However, and in contrast to the apical oxygen defects in the parent compound, this phase separation does not seem to be controlled by density fluctuations of the square-shaped La dopants (**Fig. 3.8(h)**), and a dopant count shows that their total concentration in the map area was only $\sim 1\%$. Where could the extra La have gone?

To answer this question we introduce data taken on sample A (Fig. 3.9). Between this sample and the previous one there are two obvious differences: (1) Although there are still insulating patches, the strictly gapped spectra occupy a much smaller fraction of the total area, and the transition from the insulating to metallic spectrum corresponds more to a raising up of the gap floor rather than a closing of the gap (Fig 3.9 (g)). Further (2), near E_F one can see a forest of bright atom-sized dots in the density of states (Fig. 3.9(c)), which fade in an out as the voltage is swept. Most of them line up with the observed Sr lattice, but have no clear association with the surface La dopants (Fig. 3.9(h)). They are, moreover, clearly correlated with the phase separation since far from E_F the metallic patches (bright portions of Fig. 3.9 (a) and (d)) show the greatest density of spots and vice versa.



Fig. 3.9 Phase separation and resonances at $x \approx 3.2\%$ **.** Panels (a)-(d) show constant-voltage cuts of $dI/dV(\mathbf{r}, V)$ in a 40x40nm² region at V = -80 mV, -40 mV, 0, and +40 mV respectively (vertical lines in (g)) with the same color scale in each panel. (e) is the gap map and (f) is the simultaneous topography. (g) is 64-bin plot showing the spectral diversity. In (h) we have overlaid the topography (red color scale) on the zero-bias dI/dV to show the relative positions of the La squares and the resonances.

A closer look at these bright dots is shown in **Fig. 3.10**. Each dot is associated with one or two broad peaks in the density of states as a function of energy within ± -20 meV of E_F (**Fig. 3.10(d), (e)**), whose

full width at half max ranges from 25 to 50 meV. Interestingly, some of the dots have a clear double-peak feature in which the lower peak is below and the upper peak above E_F (purple curve in **Fig. 3.10 (e)**), while in others the two peaks are barely distinguishable (orange curve) and in some cases there seems to be only one peak (red and green curves). (This is observed in both samples although we show data only from sample A.) To nail the dots down spatially, we used the Lawler-Fujita drift-correction procedure⁹⁵ to make the lattice vectors uniform, then manually picked the dot centers in the dI/d V map and plotted their lattice coordinates modulo unity (**Fig. 3.10 (f)**). This procedure is a bit crude, but the close overlap of many of the dots made spatial fitting impracticable. The vast majority of the dots were concentrated near the lattice coordinate of the surface Sr atom (center of **Fig. 3.10 (f)**).



Fig. 3.10. Spatial and energy profile of the brigh dots. (a)-(c) show the constant-voltage dI/dV cuts from a 20x20nm map at -16, 0, and +16 mV respectively. It should be evident that some, but not most of the dots visible at +16 are gone at -16, and vice versa. (d) shows dI/dV spectra taken at the four points indicated in (a)-(c), and (e) shows the background-substracted spectra—here the background was the average spectrum of the dI/dV map as a whole. (f) is a scatter plot showing the manually-obtained dot positions in lattice units. The Sr position is at the center of the box, and the apical oxygen/Iridium site is split over the corners.

What could the dots be? The most obvious answer is that they are La dopants buried beneath the surface, probably occupying Sr sites one layer down. (In the crystal structure of Sr-327 (**Figs. 3.1, 1.8**), the Sr sites of one bilayer are on the same vertical line.) Naïve theoretical reasoning suggests that the resonance features are consistent with this picture: The resonance features are near E_F which (in both samples) is the bottom of the bulk conduction band (upper Hubbard band within the spin-orbit Mott picture^{84,86}), where added electrons would be expected to sit; the La atom breaks the translational symmetry and may provide a preferential site for the donated electrons. In this case the resonances below E_F would correspond to impurity states in a semiconductor, while those above E_F correspond to electrons that left their donors and become itinerant. The double-peak feature is interesting, and may possibly be associated with the spatially inhomogeneous breakdown¹⁴⁰ of antiferromagnetic order¹⁵⁵ near the metal-insulator transition. The above is, however, speculative and the problem would benefit from the attention of a theorist.⁶

We can, however, count reliably: we identified 240 bright dots in **Figs. 3.10 (a)-(c)**, amounting to a dopant concentration of 8.5% in a nominally 3.2%-doped sample. These numbers together strongly imply that the La dopants preferentially occupy the middle Sr layer in the crystal structure (**Fig. 3.11**). If we leave interstitials out and assume that all of the observed dots are middle-layer La dopants (and that the surface layer and the third layer contain equal dopant densities, the latter being invisible to STM), the true doping formula would be

$$x = \frac{1}{3} (\text{density of dots}) + \frac{2}{3} (\text{density of squares}) .$$
 (3.1)

For sample A the densities in Eq. (3.1) are ~8.5% and ~1.5% respectively, so we obtain $x \approx 3.8\%$ which is quite consistent with the phase diagram (**Fig. 3.6(b**)) and moderately consistent with the EDS value of 3.2%. If the dots include interstitial La atoms as well, the calculated *x* would drop slightly. The

⁶ In this connection we should emphasize that for the Iridates the Mott analogy deals strictly with the Ir orbitals and lattice sites: It is the Ir 5d states which form the j_{eff} =1/2 band, and the Coulomb repulsion which splits that band is an *Iridium* double occupancy penalty, which should not apply to an occupied resonance at a La/Sr lattice site. (That is, the Hubbard term would prevent that electron from leaving the Sr lattice and entering the Ir lattice. It is not obvious that there should be a preferred spin direction of a La-site electron in the antiferromagnetic state of Sr327.)

preponderant preference for the middle layer (more than 5:1 in this case, and the figure for sample B must be comparable given its small number of squares) is striking and should be noticeable in density functional theory calculations.



Fig. 3.11 Possible sites for La dopants in Sr-327. In the bilayer the outer two SrO planes are crystallographically equivalent, and inequivalent to the middle SrO layer. The red dotted lines are cleave planes; the STM tip would come down from the top.

Appendix 3.A: La dopants in Sr-214

We have performed STM/S measurements on the La-doped n=1 member of the Ruddlesden-Popper series, $(Sr_xLa_{1-x})_2IrO_4$, which also undergoes a phase transition for small amounts of La^{139,156}. In this compound the initially stronger Mott gap (600 meV)^{157,158} is suppressed less easily; STM observes nanoscale phase separation at $x \approx 5\%$, and a detailed study shows that phase separation must persist even to significantly higher doping concentrations.¹³⁹

Here, however, we would merely like to point out that in the single-layer compound, in contrast to Sr-327, there is no "middle" Sr layer for the La dopants to hide in. Correspondingly, the number of observed La-dopant squares is higher, and actually does correspond to the nominal doping of the sample (**Fig.** **3.12(a)**). Further, the gapless regions found by STM are correlated with the local density of the square defects much more strongly than was the case in Sr-327 (**Fig. 3.12(b)-(d)**).



Fig. 3.12 STM/S data on La-doped Sr-214, from Ref. ¹³⁹. (a) shows a 12x12 nm² topography from an $x \approx 0.05$ sample; (b) and (c) are gap maps and local defect density maps from a 15x15 nm² dI/dV map in a different region from (a); the defect density was a sum of normalized Gaussians, one for each labeled defect. (d) shows a line cut along the path indicated by the black arrows in (c) and (b) and showing the transition from the insulating (black) to metallic spectra (red).

Appendix 3.B: Removal of a dopant by the tip

In STM it is sometimes difficult to tell not only the chemical species of the atoms in the imaged lattice, but also the precise identity of the impurities. In this study we were able to prove unambiguously that the square defects lay on Sr lattice sites, but their identification as La substitutions relied mainly on the correspondence between defect concentration and nominal doping (with the position of La next to Sr in the chemical formula), and on the non-observation of such defects in undoped samples. A Sr vacancy would be expected to have the same symmetry and dimorphic character as a La substitution.

In this case, however, an amusing incident occurred which helped assure us that the squares were really substitutions and not vacancies: during scanning one of these dopants was removed by the tip, and a clear "hole" left in its place (**Fig. 3.13**). The hole showed the same C_2 symmetry as the defect that had been removed, and a similar hole was subsequently identified elsewhere in the sample.



Fig. 3.13. Topography before and after removal of a defect. Defect indicated by red circle.

Appendix 3.C: Comparison with Ru-doping of Sr-327.

Our group also studied Ru-doped Sr-327 by STM/S in concert with our collaborators, who prepared the samples and characterized them using X-ray diffraction, neutron scattering, and transport measurements¹³⁸. In these samples we also found nanoscale phase separation as a function of doping (**Fig. 3.14**). Although the two cases are described in papers^{138,140}, we briefly contrast them.

Formally, the most obvious difference is that in $Sr_3Ir_2O_7$ the La substitutes at the Sr ("A") site while Ru is an Ir ("B") site dopant. Since the parent compound's band structure is determined by the Ir 5d orbitals, the Ru dopants directly destroy the j_{eff} =1/2 Mott picture locally; in contrast, the La's donate their electrons to a band structure which is not fundamentally changed. With Ru doping, metallic transport behavior is not realized until $x \approx 35\%^{138}$, and the STM measurements reveal nanoscale phase separation (**Fig. 3.14**). The spatial inhomogeneity persists through x = 50%, where the spectra, although universally gapless, range from a somewhat nondescript "V" shape (**Fig. 3.14(f)**) to a sharper V, very similar to spectra obtained on Sr₃Ru₂O₇ ("x = 1") by Lee *et al.*¹¹² (Gold curve in **Fig. 3.14(f)**; ¹³⁸). This led to the conclusion that the transition in transport properties was associated with the localized (and probably Ru-rich, although we could not see the individual dopants as in the La-doped case) metallic "puddles" percolating throughout the sample¹³⁸. This is in clear contrast to the La-doping case, where the phase separation and gross inhomogeneity were limited to $x \leq 4\%$, and quickly gave way to an essentially homogeneous metallic phase with well-defined bands^{152,153}, more-or-less consistent with the picture of a "filling-controlled" metal-insulator transition in a Mott insulator⁸⁸.



Fig. 3.14. Phase separation, transition, and diagram of Ru-doped Sr-327. Except for panels (c) and (d), adapted from ¹³⁸. (a) and (e) show topographs from samples with 35% and 50% Ru content respectively (white scale bar is 3 nm). (b) and (f) show point spectra from the regions shown in (a) and (e) respectively; the gold and blue spectra correspond to black and white crosses respectively. (c) shows a gap map extracted from a *dI/dV* map at x = 0.35, and (d) shows the spectra binned against the gap size (compare (b)). The red line indicates the gap cutoff. (g) and (h) show the phase diagram of Sr₃(Ir1_{-x}Ru_x)₂O₇ and a cartoon of the percolative phase transition in real space, from Ref. ¹³⁸.

Chapter 4: Strong Zeeman effects in the Landau level spectrum of (In_xBi_{1-x})₂Se₃ 4.0 Historical note

The data shown in this chapter were taken as part of an attempt to study the topological phase transition in $(In_xBi_{1-x})_2Se_3$. We tried to use Landau level spectroscopy to study the topological surface states and their transformation as one approaches (and goes through) the metal-insulator transition. Due to a complicated conspiracy of technical and experimental factors—that our field went only to 7.5T, the samples being "inherently doped" putting the Landau levels far from E_F , plus any tendency of the In atoms to disrupt the Landau orbits—we were only able to image the lowest several Landau levels. Moreover, attempts to plot the Landau levels in the usual manner (*E* vs. \sqrt{NB}) led to results which were irreconcilable with our conception of topological insulator surface states and almost totally incomprehensible.

The solution which we finally hit upon had the effect of converting our study from an investigation of the topological phase transition as such into an almost-metrology paper on Landau level spectroscopy, which focused greatly degree on the parent compound, and particularly deals with the breakdown of the semiclassical approximation (Eq. (2.2)) at low *N* and the "nonideality"¹⁵⁹ of the Dirac fermions in Bibased topological insulators. We acquired some Landau level data *beyond* the topological phase transition (at $x \sim 5\%$) which we include as an appendix, with comments.

4.1 Introduction

Three-dimensional topological insulators (3D TIs)^{42,160,161}, including Bi₂Se₃ and similar compounds^{31,50,51} have been the focus of great interest both for their rich physics and potential for future applications.³⁰ Tuning these systems by chemical doping has enabled control of the chemical potential⁵⁴, gapping of the surface state^{59,162}, and realization of the phase transition between the topological and trivial states.⁶⁴ The topological phase transition is especially interesting physically, and in $(In_xBi_{1-x})_2Se_3$ it is relatively accessible because both end-members have the same crystal structure and the critical doping level, 3% <

 $x_c < 7\%$, is relatively low.^{163,164} Besides the intrinsic interest, a recent theoretical work¹⁵ predicts clustering of the In dopants and a possible percolative nature of the phase transition.

To study the surface states of $(In_xBi_{1-x})_2Se_3$ we performed low-temperature (4K) scanning tunneling microscopy and spectroscopy (STM/S) on UHV-cleaved single crystals grown by the Bridgman method. We begin in the topological regime, and in **Fig. 4.1** show data from two samples at x=1% and x=2.5%. The two types of point defect most commonly observed are indicated by the circles in **Fig. 4.1(a)**. The number of these defects is consistent with their being In dopants, and their position with respect to the atomic lattice suggests that the dopants indicated by red and orange circles respectively are associated with In substitutions in the first and second Bi layer from the surface (see Appendix).

4.2 Landau level spectroscopy

We use Landau level spectroscopy (LLS) to characterize, in as much detail as possible, the low-energy characteristics of the Dirac surface state. Quasi-classically, the N^{th} Landau level is composed of electrons whose orbits in k-space enclose an area

$$A(E_N) = (N + \gamma) 2\pi eB / \hbar$$
 (4.1)^{116,165}.

Where $\gamma = 1/2$ for a conventional 2DEG, but zero for Dirac systems¹²⁰. E_N are the energies of the Landau levels: practically, the positions of peaks in a dI/dV spectrum at given magnetic field *B*. Spectra at several values of *B* provide a dense array of points, yielding the curve A(E), which for isotropic systems $(A = \pi k^2)$ fully characterizes the band dispersion. In that case the k-space orbit radius is proportional to $\sqrt{(N + \gamma)B}$, and for Dirac systems a plot of *E* vs. \sqrt{NB} may be directly compared with *E* vs. *k* plots obtained from e.g. ARPES.^{166,57,56}

Eq. (1) is a quasi-classical approximation which loses its validity for small N^{167} , and when extra terms are added to the Hamiltonian the $E_N(\sqrt{NB})$ are not expected to lie on the same curve. The plots retain their

usefulness, however, since the deviations from single-curvedness help to characterize the underlying physics.

Field-dependent dI/dV spectra for x=1% and 2.5% (taken at the same spatial position and setup conditions for each field strength) are shown in **Fig. 4.1(b)** and **(f)** respectively. As in pristine Bi₂Se₃, both samples showed a clear peak near the minimum of the zero-field spectrum which disperses very little with field (grey dashed line in **Fig. 4.1**), and which we initially indexed N=0^{56,57}. The resulting *E* vs. \sqrt{NB} plots are shown in **Fig. 4.1(c)** and **(g)**. Although the surface state at these dopings is still expected to be topological^{163,164}, the LLs clearly fall on different curves. To see why, we must consider the surface state Hamiltonian in greater detail.



Fig. 4.1 STM topographs and Landau level spectra in lightly In-doped Bi₂Se₃. Panels (a)-(d) and (e)-(h) show data taken from samples with 1% and 2.5% In respectively. In the topographs (a) and (e) the In dopants are visible as black triangles and bright-centered triads (red and orange circles respectively in (a)). (b) and (f) show magnetic-field dependedent dI/dV spectra acquired in In-free regions; the Landau levels are visible as small peaks and extracted following background subtraction (see supplementary information). (c) and (g) show E vs. \sqrt{NB} with the (almost) non-dispersing peak near the spectral minimum indexed as N=0; (d) and (h) show the same, indexing it as N=-1.

This is^{51,14}

$$H(k_x, k_y) = E_D + V(\sigma_x k_y - \sigma_y k_x) + Ck^2$$
(4.2)

where E_D is the Dirac point energy, V is the velocity multiplied by \hbar , σ_i are Pauli matrices in the basis of the electron spin, and the cubic term^{14,168} is omitted. In the presence of a *B* field along the z-axis, and using the ansatz that the spin-up and spin-down components bear wave functions with quantum numbers *N*-1 and *N* respectively^{14,169}, the Hamiltonian becomes¹⁴

$$H = E_D + C(2N\tilde{B}) - V\sqrt{2N\tilde{B}}\sigma_y - C\tilde{B}\sigma_z - (\mu_B gB/2)\sigma_z$$
(4.3)

where $\tilde{B} = eB / \hbar$, and in the Zeeman term $g \neq 2$ in general^{14,170}. Diagonalization yields the Landau level energies (¹⁴; see also ¹⁷¹ in which the ansatz is inverted relative to ours)

$$E_N = E_D + C(2N\tilde{B}) \pm \sqrt{\left(\tilde{B}C + (\mu_B gB/2)\right)^2 + 2N\tilde{B}V^2}$$
(4.4)

For C = g = 0, (4) reduces to the form familiar from the experimental literature. With nonzero C and g, $E_N(N,B)$ is not a function of \sqrt{NB} only; let us however express it as a function of $\xi \equiv \sqrt{NB}$ and N:

$$E(\xi, N) = E_D + 2\tilde{C}\xi^2 \pm \sqrt{D^2(\xi^2/N)^2 + 2\tilde{V}^2\xi^2}$$
(4.5)

where $(\tilde{C}, \tilde{V}) = (C, V)e/\hbar$, $D = \tilde{C} + \mu_B g/2$, and of course $\xi^2/N = B$. In **Fig. 4.1 (c)** and **(g)** the most striking feature is that the higher LLs are shifted upward in energy at constant ξ , by as much as 13 meV for N=1 to 2 (**Fig. 4.1(g)**). But, for positive LLs, (5) makes clear that if N increases at constant ξ the energy must *decrease*, regardless of the parameter values.

This glaring inconsistency led us to conclude that the naïve indexing scheme could not be applied successfully to In-doped samples. Fortunately, there is an alternative: if we decrement each Landau level, we obtain the plots in **Fig. 4.1 (d)** and **(h)**. Now the most significant features are: (1) that the N=0 LL disperses with magnetic field, about 1.8 meV/T at x=1%, and 1.6 meV/T at x=2.5%; (2) that the N=-1 LL

hardly disperses at all (although at x=2.5% it barely creeps downward at ~0.4 meV/T); (3) that for N>0 the LLs lie reasonably close to the same line. Except (2), these features can be easily reconciled with the known physics of topological insulator surface states.

The N=0 LL disperses due to the quadratic term and Zeeman effect.¹⁴ Explicitly

$$E_0 = E_D + (\tilde{C} + \mu_B g / 2)B.$$
(4.6)

(Because of the ansatz, there is no "-" solution for N=0.^{14,171}) If we ignore the quadratic term and attribute the observed dispersion solely to Zeeman coupling, the slope of E_0 yields $g \approx 61$ and 54 for x=1% and 2.5% respectively.

To characterize the surface state, and decouple the Zeeman and curvature effects on the *N*=0 LL, we performed least-squares fitting of the entire LL dataset at each doping to the four-parameter model defined by Eqs. (4.4) and (4.6). The results are shown in **Table 4.1**, and the expected Landau levels are connected by the black lines in **Fig. 4.1 (d)** and **(h)**. All fits yield $C \ge 20 \text{ eV} \cdot \text{Å}^2$, but our momentum-space range is inadequate to resolve the band curvature precisely: at $k \approx 0.025 \text{ Å}^{-1}$ a change of 3 eV·Å² in *C* moves the energy by only ~2 meV.

To overcome this limitation we fit to the model with *C* fixed at 23.7 eV·Å², consistent with ARPES for pristine Bi₂Se₃^{14,50}. When the odd *N*=-1 LL is excluded, the decline of *g* between *x*=1 and 2.5% is statistically significant. (For residuals plots, see appendix)

	C free				C fixed			
	Including $N = -1$		Excluding $N = -1$		Including $N = -1$		Excluding $N = -1$	
	1% In	2.5% In						
E_D (meV)	-275	-264	-279	-264	-274	-263	-278	-265
V (eV Å)	1.70±0.01	1.84±0.01	2.03±0.04	2.04±0.05	1.76±0.03	1.87±0.04	1.91±0.01	1.95±0.02
$C (eV Å^2)$	29.3±0.4	27.2±1.0	20.2±1.2	20.7±2.1	23.7	23.7	23.7	23.7
g	30.3±0.5	27.3±1.1	55±2.7	41±2.4	25.5±0.5	25.3±0.5	47±1.1	35.1±1.5

Table 4.1. Model parameter estimates for In-doped Bi₂Se₃. The errors were obtained by taking the standard deviation of fitting results for datasets with one point removed.

4.3 Pristine Bi₂Se₃

We have seen that in order to obtain sensible results on In-doped Bi_2Se_3 it was necessary to depart from the indexing scheme previously applied to the undoped system.^{56,57} The successful fits raise the possibility that the low-lying LLs of naively-indexed *pristine* Bi_2Se_3 bear a similar problematic feature to that revealed in **Fig. 4.1 (c)** and **(g)**, which has hitherto been overlooked. To examine this question we acquired field-dependent LL spectra on pristine Bi_2Se_3 (**Fig. 4.2**); we also carefully analyzed the previously published (and, frankly, better) field-dependent STS data on the same system^{56,57,169} (supplementary **Fig. Sx**).

The problem remains (Fig. 4.2 (c)), although it is somewhat less obvious than in the In-doped samples: the upward shift from N=1 to N=2 at constant ξ is but 9 meV instead of 13. The re-indexed LL data (Fig. 4.2 (d)) shows the same basic features as the data for x > 0. The N=0 LL disperses a bit faster, 2.0 meV/T, and the *g*-factor extracted from the least-squares fit is correspondingly a bit larger: with *C* fixed and the N=-1 Landau level excluded; the increase in *g* is statistically significant (Table 4.2).

If we accept our indexing of the pristine data, we find a coherent physical picture: The strong Zeeman coupling in the surface states of pristine Bi_2Se_3 weakens with increasing In, which reduces the spin-orbit

coupling and changes the orbital character of the bands near the Fermi energy.¹⁶³ The extent to which this picture is consistent with other evidence will be discussed below.



Fig. 4.2 Field-dependent Landau level spectroscopy on pristine Bi₂Se₃. (a) A typical, low-resolution STM topograph on the Bi₂Se₃ surface. The spectra (b) were taken along a short line in the upper-right corner of the topography. (c) and (d) are E vs. \sqrt{NB} plots with the Landau level at the spectral minimum (grey dashed line in (b)) indexed as N=0 and N=-1 respectively; Cf. Fig. 4.1 (c) and (d), (g) and (h). The black lines in (d) connect Landau levels predicted by fitting to the model (see text), with all four parameters free and including N=-1.

	0% In	1% In	2.5% In
E_D (meV)	-208	-278	-265
V(eV Å)	2.24±0.02	1.91±0.01	1.95±0.02
$C (eV Å^2)$	23.7	23.7	23.7
g	76±2	47±1.1	35.1±1.5

Table 4.2. Model parameter estimates with *C* fixed and excluding the N=-1 LL. The errors were obtained by taking the standard deviation of fitting results for datasets with one point removed.

4.4 Discussion

Quantum oscillations studies on the surface states of Bi₂X₃ TIs have been largely consistent with *g*-factors on the order of 50.^{58,159,172} A well-known early work on Bi₂Se₃ found *g*=50±10: "The associated field dependence of the *N*=0 LL should, in principle, be observable through STS measurements."⁵⁸ Subsequently Taskin and Ando¹⁵⁹ carefully analyzed Shubnikov-de Haas data for three TI systems— Bi₂Se₃, Bi₂Te₃, and Bi₂Te₂Se—and found (taking into account their opposite sign) *g*-factors ranging from 39 to 65. In a later paper, Wright and McKenzie¹⁷² calculated $g \approx 60$ and 50 for Bi₂Te₂Se and Bi₂Se₃, respectively. (We note however that a study by Xiong *et al.*¹⁷³ on BTS, cited in Ref. ¹⁷², claims a small *g*factor.) If correct, our interpretation would contribute towards harmonizing two important experimental techniques.

Can it be? The strongest evidence against it, as far as we know, is to be found in Ref. ¹⁶⁹ But before getting to that, let us make some more general comments about field-dependent STS on Bi₂Se₃, with particular reference to the earlier works^{56,57}.

In a 2D Dirac system the density of states increases linearly with energy, in both directions, from a zero value at E_D . We expect, then, that the zero-field dI/dV spectrum should take the form of a "V," with Dirac point at the nadir.⁷ In practice, however, this shape is not reliably obtained. In Ref. ⁵⁷ the zero-field spectrum (Fig. 1) was V-like, and the LL appearing near the minimum could be naturally identified as belonging to the Dirac point. In Ref. ⁵⁶, by contrast, the zero-field spectrum did not much resemble a V: In the field-dependence figure (Fig. 2) it is mostly flat, and the clearest feature is a step between the Landau levels named 0 and 1.⁸

This variability in the spectral shape is reflected in our own data: in the 1% sample the spectrum is V-shaped, while in the 2.5% sample it is mostly flat, with (as in 56) a clear step between the first two LLs,

⁷ The small, positive quadratic term should bend the left half of the "V" upwards, and the right half downwards. ⁸ In Ref. ⁵⁶, in connection with labeling the non-dispersing Landau level N=0, the supposed negligibility of the Zeeman coupling was referred to explicitly.

which is very near where our model places the Dirac point. Although it is strange that for V-shaped spectra the Dirac point should not lie precisely at the bottom (our fits generally predict 10-20 meV above it), the diversity in spectra obtained with different tips suggest that matrix elements may play a significant role in the zero-field spectral shape.

Ref. ¹⁶⁹ cleverly exploited an impurity potential to visualize the low-index Landau level wave functions directly. In Fig. 2 of that work, the authors show wave functions for LLs which they label N=0, 1, and 2. The last two of these are, as shown in great detail in the appendix, tantalizingly close to what is expected for the N=0 and 1 LLs in the presence of strong Zeeman coupling. Briefly: If (as in ¹⁶⁹) we suppress the quadratic and Zeeman terms, the Hamiltonian (3) contains terms proportional only to the identity matrix and σ_y , and its eigenstates mix spin-up and down components with equal weight. But when those terms are included, the σ_z component of (3) becomes important, and for N=1 leads to a substantial spin-polarization of the Landau levels: about 80% at 11T.

With the mandatory ansatz^{14,169,171} the N=0 LL is fully spin-polarized, and its wave function has no nodes. The N=1 LL, which without Zeeman terms contains zero- and single-noded wave functions with equal weight¹⁶⁹, now favors the noded component by a 4:1 ratio: its density of states contains a single, deep node-like depression, strikingly similar to what Ref.¹⁶⁹ calls the N=2 LL. The N=-1 LL favors the nodeless component in equal measure: its wave function should look very similar to N=0. This too is reproduced in ¹⁶⁹, although its apparent size is smaller than expected. Ref.¹⁶⁹ also reported a splitting of the N=1 Landau level, which we would label N=0. This is not consistent with the behavior of an N=0 LL in a centrally-symmetric potential, but could perhaps arise in a potential (as in ¹⁶⁹) where this symmetry is not strictly adhered to.

Although in our interpretation the decline of g with increasing In is plausible, the almost complete nondispersion of the N=-1 LL remains problematic. Part of it, probably, is due to the upward curvature of the surface state below the Dirac point from nonzero C. But (because the surface state keeps going until it merges with the bulk valence band) this curvature must become unphysical at not-very-large k. In its absence, we may only speculate. It seems possible, however, that the different orbital character of the surface state fermions above and below the Dirac point ^{52,174} might differentiate their Zeeman coefficients.

Appendix 4.A Identification and lattice position of the In dopants.

Bi₂Se₃ has a layered crystal structure⁵¹ (**Fig. 4.3**) and cleaves between the Van der Walls-bonded quintuple layers. Because of the "ABC" structure, the bismuth atoms in the first layer down are located *between* the top-layer Se atoms when viewed from above (**Fig. 4.3(b)** and **(c)**), while the second layer lie directly beneath the exposed Se. In Fig. S1d we enhanced the atomic signal (by smoothing and taking the minus second derivative) to show the atomic lattice clearly; the centers of the dark triangles (1) and lighter triplets (2) are seen to lie in between and on top of the observed lattice, respectively.



Fig. 4.3. Crystal structure and In dopants. (a)-(c) The crystal structure of Bi_2Se_3 , from ⁵¹. (d) An enhanced (smoothed second derivative) topography on $(In_xBi_{1-x})_2Se_3$ for x = 2.5%, designed to show the Si lattice clearly. The two types of In dopants referred to in the main text are indicated by the arrows "1" and "2".
Appendix 4.B Residuals for various fits to the model Hamiltonian

In **Fig. 4.4** we plot the residuals as a function of magnetic field for the four types of fits contained in Table 1 of the main text. For the fits in (d) and (h), whose results were also used in **Table 4.2** of the main text, fit generally came within +/-1.5 meV for the lower Landau levels (N=0 and N=1) regardless of magnetic field.

As explained in the main text, labeling the nondispersing Landau level N=0 leads to impossible results. However, we may still attempt the least squares procedure as shown in **Fig. 4.5**. As expected, the fit is unable to produce an increase energy with *N* at constant \sqrt{NB} . The best we can do is to draw a reasonably continuous curve through the middle of the pattern, leaving large residuals with obvious systematics for almost all *N*. At 1% In we find $E_D = -0.301$, $V = 2.16 \text{ eV}\cdot\text{Å}$, $C = 30.0 \text{ eV}\cdot\text{Å}^2$, g=-14. At 2.5% we find $E_D = -0.286$, $V = 2.21 \text{ eV}\cdot\text{Å}$, $C = 26.7 \text{ eV}\cdot\text{Å}^2$, g=-3.



Fig. 4.4 Residuals of least-squares fits. The eight panels are the residuals as a function of magnetic field for the eight columns of **Table 4.1**. The upper row (a-d) is for 1% In; (e-h) are for 2.5%. (a) and (e) are from the fitting with all four parameters free, including the N=-1 LL. (b) and (f) are the same, excluding the N=-1 LL. (c) and (g) are from fitting with *C* fixed, including the N=-1 LL. (d) and (h) fix *C* but exclude the N=-1 LL. Residuals are defined as the predicted value minus the experimental value.



Fig. 4.5 Least-squares fitting and residuals with naïve indexing. (a) and (b) are $E vs. \sqrt{NB}$ plots for the x=1% and 2.5% samples respectively, assuming that the nondispersing Landau level is N=0. (The experimental data are identical Fig. 1 (c) and (g).) The black lines connect the predicted Landau levels. (c) and (d) are the residuals plots associated with (a) and (b) respectively.

Appendix 4.C Previously published Landau levels on Bi₂Se₃

In **Fig. 4.6** we display the low-index Landau levels obtained from the published sources^{56,57,129}, as indexed by them with the non-dispersing peak N=0. To extract the Landau levels from ⁵⁶ and ¹²⁹ we digitized the spectra and applied the same peak-fitting procedure as was used for the data in the main text; T. Hanaguri kindly furnished us the data from ⁵⁷ directly.

To fit the peaks, we first subtracted the zero-field spectrum, then an additional low-order polynomial (less than 5 in all cases) to get a flat background. The peak positions were then identified approximately by eye; to find them precisely we fit a small (~5 meV) window about the optical maximum to an inverted parabola.

In all cases we see the same unacceptable increase in *E* with *N* at constant \sqrt{NB} , although its magnitude is not always the same; compare **Fig. 4.6 (b)** with **(f)**. When we re-index the Landau levels from ^{56,129} and

try to least-squares fit them, the results are correspondingly somewhat different. It is not clear why; however, in Bi_2Se_3 and Bi_2Te_3 there is often significant potential variation due to charged defects^{129,130,175}, which shifts the LLs in energy differently according to the size of their wave functions¹²⁷, which vary with *N*, and with *B* as the magnetic length changes.



Fig. 4.6 $E vs. \sqrt{NB}$ for previously published Landau levels on Bi₂Se₃. Panels (a), (c), (e) show magnetic fielddependent dI/dV spectra on Bi₂Se₃ as presented in Refs. ^{56,57,129} respectively. (Panels (a) and (c) were in the main text of their respective papers, and (e) was in the supplement.) Panels (b), (d), (f), show the respective $E vs. \sqrt{NB}$ plots. The upward shift in E with increasing N is noted in (b) and (f).

Appendix 4.D The low-index wave functions and their appearance in experiment

In this section we discuss the theory of Landau level wave functions in connection with the results shown in Ref. ¹²⁹. Their STS signature is shown in Fig. 2 of that work (here reproduced as **Fig. 4.7**), whose labeling is in accord with the very natural assumption that the N=0 LL has the smallest wave function. Although we will show that the wave functions labeled N=1 and N=2 are actually consistent with expectations for the N=0 and N=1 Landau levels, the N=-1 LL can never be made smaller than N=0, and its smallness must be ascribed to other physics, possibly matrix element effects (see also below).

Because our wave functions were defined *ab initio* as part of the calculation, we present the derivation, which is based on lecture notes by H. Murayama.¹⁷⁶

Landau level wave functions in the symmetric gauge

In the magnetic field $\mathbf{p} \rightarrow \mathbf{\Pi} \equiv \mathbf{p} - (\mathbf{e/c})\mathbf{A}$ and the Hamiltonian of a trivial, otherwise free 2DEG becomes

$$H = \frac{\Pi^2}{2m}$$

From here we suppress all dimensional constants ($m = e = \hbar = B = 1$), thus using $l_B = \sqrt{\hbar/eB}$ as the unit of length, and $\hbar\omega_c = \hbar eB/m$ as the unit of energy.

We have two sets of ladder operators

$$a = \frac{1}{\sqrt{2}} \left(\Pi_x + i \Pi_y \right), \ a^{\dagger} = \frac{1}{\sqrt{2}} \left(\Pi_x - i \Pi_y \right); \qquad b = \frac{1}{\sqrt{2}} \left(X - i Y \right), \ b^{\dagger} = \frac{1}{\sqrt{2}} \left(X + i Y \right)$$
(4.7)

which obey the usual bosonic commutation relations. Here *X* and *Y* are operators for the guiding center coordinates (for details, see 176). The basis states are defined by two quantum numbers *N* and *m* such that

$$|N,m\rangle = \frac{\left(a^{\dagger}\right)^{N} \left(b^{\dagger}\right)^{m} |0,0\rangle}{\sqrt{N! \, m!}}$$

where $|0,0\rangle$ is a certain normalized ground state. In the symmetric gauge ($\mathbf{A} = (\mathbf{B} \times \mathbf{r})/2$) the ladder operators are conveniently expressed in terms of the complex position variables z = x + iy, $\overline{z} = x - iy$:

$$a = \frac{-i}{\sqrt{2}} \left(2\frac{\partial}{\partial \overline{z}} + \frac{1}{2}z \right), a^{\dagger} = \frac{-i}{\sqrt{2}} \left(2\frac{\partial}{\partial z} - \frac{1}{2}\overline{z} \right); \qquad b = \frac{1}{\sqrt{2}} \left(2\frac{\partial}{\partial z} + \frac{1}{2}\overline{z} \right), b^{\dagger} = \frac{1}{\sqrt{2}} \left(2\frac{\partial}{\partial \overline{z}} + \frac{1}{2}z \right), \quad (4.8)$$

and the ground state is a normalized Gaussian:

$$\langle \mathbf{r} | 0, 0 \rangle \equiv W_{00}(\mathbf{r}) = N_{00} e^{-z\bar{z}/4}$$

where $N_{00}=1/\sqrt{2\pi}$. It is easy to verify that

$$W_{N0}(\mathbf{r}) = N_{N0} z^N e^{-\frac{z\bar{z}}{4}}, \ W_{0m}(\mathbf{r}) = N_{0m} \bar{z}^m e^{-\frac{z\bar{z}}{4}},$$

where $W_{Nm}(\mathbf{r}) \equiv \langle \mathbf{r} | N, m \rangle$.

The N=0 density of states

The solutions of the topological insulator Hamiltonian are two-component spinors with distinct wave functions in each channel. For the N=0 Landau level, however, the wave functions are consist solely of $W_{0m}(\mathbf{r})$; let us discuss them in some detail. (Fig. 4.8)



Fig. 4.7. Experimentally visualized Landau level wave functions; Fig. 2 of Ref. ¹²⁹. The Landau level indices are as in the original.

In Fig. 4.8(b) we see that for m > 0 the $|W_{0m}(\mathbf{r})|^2$ are appreciably different from zero in a region of size $\sim 2 l_B$. The local density of states feature measured by STM, however, should be a bit larger: The $|0, m\rangle$ states' degeneracy is split by a potential which leaves states of adjacent *m* close together in energy, and when the inverse lifetime Γ is comparable to this spacing, the observed density of states will have contributions from several *m*.



Fig. 4.8 Wave functions of the N=0 Landau level. a) Color plots of $W_{0m}(\mathbf{r})$ for several values of *m*; color scale is on the bottom left. (b) Probability amplitude $|W_{0m}(\mathbf{r})|^2$ for the same values of *m*, normalized so that all maxima are at the same height.

This additional smearing was carefully considered in Ref. ¹²⁹; see Figs. 4c and S3. We have repeated the calculation of Ref. ¹²⁹ in detail for the N=0 Landau level, using a buried Coulomb potential ($V(r) = U/\sqrt{r^2 + d^2}$ for U = 1.3 and d = 2) and Lorentzian broadening width $\Gamma = 0.05$; we calculate the energy shifts of $|0, m\rangle$ by first-order perturbation theory. The result is shown in **Fig. S7**. To correspond to ¹²⁹ as closely as possible, we took a slice of the dI/dV at the same energy (E = -0.675) and sampled the density of states as a function of *x* in the same range (**Fig. S7 (b**)), showing the contribution of the dominating eigenstate (m=5) as well as the others, and their sum (thick black curve). **Fig. S7 (b)** should therefore be entirely equivalent to the "n=0" panel in Fig. 4c of ¹²⁹.

We see that the combined density of states peak has a full with at half-max (FWHM) of 2 l_B . This corresponds almost perfectly to the dimension of the feature actually imaged in Ref. ¹²⁹, but there labeled N=1 (**Fig. S7(c**)).

We now proceed to the N=1 Landau level, for which we must write the full TI Hamiltonian.



Fig. 4.9 Density of states of the N=0 Landau level. (a) Intensity plot showing $DOS(r, E) = \sum_m |W_{0m}(\mathbf{r})|^2 L(E - E_{0m}; \Gamma)$ where L is the normalized Lorentzian with half-width Γ : $L(\omega; \Gamma) = \Gamma/\pi(\omega^2 + \Gamma^2)$. E_{0m} was determined by first-order perturbation theory. (b) Horizontal cut through the desnsity of states at E = -0.675. (the green line in (a)). The contribution of $|W_{0m}|^2$ is plotted for each m, and the total density of states in black. (Panel (b) should be equivalent to the lowest panel of Fig. 4c of ¹²⁹, except that it also shows the contributions for $m \neq 5$.) (c) Fig. 2f of ¹²⁹, annotated for comparison with (b).

Full surface-state Hamiltonian

In the magnetic field the Hamiltonian becomes

$$H - E_D = V(\sigma_x \Pi_y - \sigma_y \Pi_x) + C \Pi^2 - \gamma \sigma_z = \begin{pmatrix} C \Pi^2 - \gamma & V(\Pi_y + i \Pi_x) \\ V(\Pi_y - i \Pi_x) & C \Pi^2 + \gamma \end{pmatrix}$$
$$= \begin{pmatrix} 2C \left(a^{\dagger}a + \frac{1}{2} \right) - \gamma & iV \sqrt{2}a^{\dagger} \\ -iV \sqrt{2}a & 2C \left(a^{\dagger}a + \frac{1}{2} \right) + \gamma \end{pmatrix}$$
(4.9)

where $= g\mu_B B/2$. The relative position of *a* and a^{\dagger} in the matrix, and the requirement that the solutions be also eigenstates of the total angular momentum $J_z = (b^{\dagger}b - a^{\dagger}a) + \sigma_z/2$,^{129,176} force the ansatz

$$|\chi_{Nm}\rangle = \begin{pmatrix} \alpha | N, m \rangle \\ \beta | N - 1, m \rangle \end{pmatrix}$$
(4.10)

where $|\alpha|^2 + |\beta|^2 = 1$. We find α and β by numerically diagonalizing the matrix:

$$\widehat{H}_{ij} = \begin{pmatrix} 2C\left(N + \frac{1}{2}\right) - \gamma & iV\sqrt{2N} \\ -iV\sqrt{2N} & 2C\left(N - \frac{1}{2}\right) + \gamma \end{pmatrix} = 2CN - V\sqrt{2N}\sigma_y + (C - \gamma)\sigma_z$$
(4.11)

for N>0. For N=0 we have perforce

$$|\chi_{0m}\rangle = {\binom{|0,m\rangle}{0}},\tag{4.12}$$

so $E_0 = (C - \gamma)$. Parenthetically, regarding the sign of g: In the main text we placed $|0, m\rangle$ in the spindown slot following ¹⁴, and obtained (from $H_{Zeeman} = -\gamma \sigma_z$) $E_0 = (C + \gamma)$. In ⁵⁹, g > 0 corresponds to the N=0 LL dispersing upward with field. However, Ref. ¹⁴ has $E_0 = (C - \gamma)$; ¹⁷¹ uses $|C - \gamma|$. In any case, we now flip the sign of g relative to the main text.

N=1 spinor states

For *N*=1, the eigenspinors are

$$|\chi_{Nm}\rangle = {\alpha|1,m\rangle \\ \beta|0,m\rangle}.$$
(4.12)

The $|1, m\rangle$ wave functions are shown in **Fig. 4.10** for several values of *m*. For m > 1 they have a single radial node between two peaks in the probability density separated by very nearly 2 l_B , which agrees remarkably well with the width of the feature observed in Ref. ¹⁶⁹ and labeled N=2 (**Fig. 4.7 (i)**). The real-space probability density of the N=1 eigenspinors, however, clearly includes contributions from wavefunctions with N=1 and N=0:

$$|\chi_{1m}(\mathbf{r})|^2 = \langle \chi_{1m} | \mathbf{r} \rangle \langle \mathbf{r} | \chi_{1m} \rangle = |\alpha|^2 |W_{1m}(\mathbf{r})|^2 + |\beta|^2 |W_{0m}(\mathbf{r})|^2.$$
(4.13)

In Ref. ¹⁶⁹ it was assumed that $|\alpha|^2 = |\beta|^2 = \frac{1}{2}$, so that the lower-spin wave function largely fills in the node of the upper-spin wave function to produce a relatively featureless probability distribution (**Fig. 4.11** (b); see also ¹⁶⁹); this allowed the authors to label a nodeless feature N=1 (**Fig. 4.7 (f)**).



Fig. 4.10 Wave functions of the N=1 Landau level. a) Color plots of $W_{1m}(\mathbf{r})$ for several values of *m*; color scale is on the bottom left. (b) Probability amplitude $|W_{1m}(\mathbf{r})|^2$ for m=1, 10, and 20, normalized so that all maxima are at the same height. A 2 l_B scale bar is included for comparison with (c), from Ref. ¹²⁹.

But when the σ_z term in the Hamiltonian (4.11) becomes non-negligible the relative magnitudes of α and β (i.e. the spin polarization of the Landau level) will change considerably. (Inspection shows that the spin polarization is greatest at low *N* and high *B*; the assumption of Ref. ¹⁶⁹ is correct for large *N*.)

Explicitly, for *N*=1 we have (reverting to SI units)

$$H_{N=1} = 2C\tilde{B} - V\sqrt{2\tilde{B}}\sigma_y + (C\tilde{B} - g\mu_B B/2)\sigma_z$$
(4.13)

where $(\tilde{C}, \tilde{V}, \tilde{B}) = (C, V, B)e/\hbar$. Putting V = 2 eVÅ, $C = 23.7 eVÅ^2$, g = -60, and B = 11T (the same as used experimentally in Ref. ¹²⁹), we find $H = (8 - 37\sigma_y + 23\sigma_z)$ meV. The eigenspinors are in the *yz* plane: the +1 LL is 77% spin up, and the -1 LL is 77% spin down.



Fig. 4.11: The N=1 Landau level with and without Zeeman coupling. (a) The N=1 density of states for m=5, assuming equal weights for spin up and spin down; the + and – eigenspinors have equivalent density of states. (b) and (c) are the + and – eigenspinors for m=5 obtained from solving the Hamiltonian, with V = 2 eVÅ, C = 23.7 eVÅ², g = -60, and B = 11T.

We see that the Zeeman coupling accounts for both the nodal trough in the N=+1 LL and the nodeless appearance, but not the smallness, of the N=-1 LL. That, however, might possibly be due to matrix element effects: In the dI/dV spectra of ¹²⁹ (Fig. 1a) the peak labeled N=0 is much shorter than the others, with less spectral weight. It is tempting to speculate that this causes the wave function tails to fade into the noise background more quickly, reducing the apparent size of the wave function.

We should point out that although the relative spin polarization of the N=+1 and -1 wave functions depends on the ansatz choice (which itself involves sign factors involving *B* and the electric charge¹⁷⁶) the relative "node polarization" does not. The upward dispersion of the N=0 LL is determined experimentally, and the same coefficient of σ_z which makes $E_0 > 0$ contributes to the increase of E_{+1} . Thus, regardless of the ansatz, the N=0 and N=+1 LLs must have the same majority spin channel. (If the N=0 Landau level had dispersed downward, the situation would be reversed.)

Conclusion of Appendix 4.D

The Landau level wave functions, as imaged by STS in Ref.¹²⁹, are strikingly compatible with the indexing scheme we advance based on other arguments. A careful spin-polarized STM experiment, such as envisioned in Ref.¹²⁹, ought to be able to distinguish our indexing schemes.

Appendix 4.E: Landau levels at x = 5%

Besides the datasets at 0, 1, and 2.5% In concentration, we also acquired Landau level data on a 5% Indoped sample. This doping is at the center of the range given in Ref. ¹⁶³ for the topological phase transition—3% < x < 7%; see also¹⁶⁴, where according to the usual picture the band inversion is undone, and the fate of the topological surface state is unclear. In this sample we only saw a few Landau levels (up to 3 at 7.5T), and their distribution is qualitatively different from the three dopings discussed above.



Fig. 4.12: Landau peaks in an $x \approx 5\%$ sample. (a) A $15x15nm^2$ topography showing the area in which the line cut used for analysis was taken (green line). (b) dI/dV as a function of bias and magnetic field, averaged along the line; spectra are offset for clarity. (c) shows the background-subtracted dI/dV with fitted peaks identified as vertical blue strips. The overlaid colors match the symbol color in (d)-(f), which show E vs. $\sqrt{(N + \gamma)B}$ for two indexing schemes with $\gamma = 0$ (d) and (e), and the most natural one with $\gamma = 1/2$.

The most obvious difference is that the bottom of the rather V-shaped background spectrum (**Fig. 4.12** (b)) does not develop a non-dispersing Landau peak. Instead, the first visible peak appears 15-20 meV above the minimum and disperses sharply upward at about 2.1 meV/T; compare 2.0, 1.8, and 1.6 meV/T for our N=0 LL in 0%-, 1%-, and 2.5%-doped samples respectively. This suggests that the surface sate at 5% In is qualitatively different and perhaps a topologically trivial. (This is essentially independent of our indexing of the nondispersing peak as N=-1: if it was N=0 its disappearance would also signify the loss of the Dirac character of the surface states.)

We found empirically that when we plot the energy of the peaks against $\sqrt{(N + \frac{1}{2})B}$, i.e. use Eq. (4.1) with $\gamma = \frac{1}{2}$, the results lie reasonably close to a straight line, whose slope (about $4.0*10^5$ m/s) is quite close to the values obtained at the other dopings. (In **Fig. 4.13** we plot them all on one graph.) The apparent change from $\gamma = 0$ to $\frac{1}{2}$ seems, at first glance, like a telltale sign of the topological-trivial phase transition in a surface state whose kinematic properties remain nearly unchanged^{120,165}.



Fig. 4.13 E vs k plots for all the samples shown in this chapter. The plotting is against $\sqrt{(N + \gamma)B}$ where $\gamma = 0$ for x = 0%, 1%, and 2.5%, and $\gamma = 1/2$ for x = 5%. The 5% data did not have a C_0 and was shifted with respect to the intercept of its linear fit.

In making such a claim, however, we must tread very carefully in view of the distinction between "nomal," topologically trivial, spin degenerate surface states and the chiral topological surface states in TI's. In the TI surface state Hamiltonian (Eq. (4.2)) the dominant, linear term directly lifts the spin degeneracy, so that the Zeeman effect only shifts the Landau peaks in energy. Contrariwise, in the conventional 2DEG these peaks are doubly degenerate without Zeeman coupling, which splits each peak in two. (For STM results see e.g. ¹²⁸, or ¹⁷⁷ for graphene.) All of the following suggestions contain features that are difficult to reconcile with the observed Landau levels:

(1) If the Dirac fermions acquired a field-independent mass term proportional to σ_z , this would not increase the dispersion of the lowest Landau level with the field: in the absence of the Zeeman and quadratic terms it would sit right at the band bottom: $E_0 = m$. (This is clear from our analysis of Eq. (4.2) and is also found experimentally⁷⁶.) Conversely (2), if the surface state Hamiltonian retained its Rashba form (4.2) but ceased to span the band gap (the quadratic bands bending back up to the valence band as in **Fig. 1.1**) the low-index Landau level spectrum should be quite indistinguishable, and in particular the N=0 Landau level would remain near the Rashba-Dirac point. If (3) an almost-linear 2DEG with spin degeneracy had taken the place of the Dirac surface states, the change in Berry phase would be explained^{120,165}, but on the other hand Zeeman coupling would lift the spin degeneracy and split the Landau levels into two branches, one of which would disperse downward with the field. (From the values used above, the splitting should be ~10-25 meV depending on the *g*-factor.)

The only scenario which avoids these difficulties is a "conventional" (in the sense of zero Berry phase around the band bottom) but near-linear 2DEG with only one spin branch. Although it is not immediately clear what the Hamiltonian of such a 2DEG would be, it is interesting to note that a recent spin-resolved ARPES study on TlBi(S_xSe_{1-x}) (which undergoes an analogous phase transition at $x \approx 0.5^{64,178}$) observed a surface state, barely on the trivial side of the phase transition, with strikingly similar properties to those required here¹⁷⁹. (See also ¹⁸⁰.) That surface state was helically spin-polarized at large *k*, but was gapped and lost its spin polarization close to $\overline{\Gamma}$, unlike the topological surface states. Further, there was no out-ofplane spin polarization even at the band bottom^{179,180}, which would have been expected had the surfacestate gap resulted from adding a mass term $m\sigma_z$ to Eq. (4.2). The zero Berry phase ($\gamma = \frac{1}{2}$) and nearlinear dispersion suggested in our own data are rather consistent with these features of the "unconventional" state of Ref.¹⁷⁹: single spin branch, incomplete spin polarization, lack of a Dirac point (**Fig. 4.14**). Indeed, the analogy between TlBi(S_xSe_{1-x}) and ($In_xBi_{1-x})_2Se_3$ is made explicitly in the supplement of Ref.¹⁷⁹, which includes ARPES data showing partial spin polarization of a gapped surface state in the latter at x = 6%.



Fig. 4.14 Schematic of the remnant surface state in TIBi($S_{\delta}Se_{1-\delta}$). From Ref. ¹⁷⁹. (a) and (b) show surface states and spin polarizations for the barely-trivial and topological sides of the phase transition, respectively. Panel (a) matches our Landau-level derived impression of the surface state at 5% In.

Chapter 5: The effects of local strain on the surface states of SnTe

5.0 Background

This chapter is essentially the draft of a paper which we wrote following an earlier publication ⁷⁴ in which we first used the Lawler-Fujita procedure to measure the 2-D strain in SnTe thin film locally, conceiving strain in the sense of an isotropic compression, ("strain" $\propto \nabla \cdot \mathbf{u}$) and showing how it affected the Dirac surface states as manifested in their quasiparticle interference patterns.

After some thought we realized that not only should it be possible to extract the whole strain tensor (given the necessary algebraic manipulations) but that the sample under study would also have regions of strong uniaxial strain with analgous effects on the surface states, which were then looked for and found. Further comments are left to the chapter body and conclusions.

5.1 Introduction

Topological crystalline insulators (TCIs) are a recently discovered^{65,67} subclass of topological insulators which harbor massless Dirac surface states tunable by temperature^{68,181} and alloying composition change⁷⁸. In contrast to Z₂ topological insulators^{29,30,42} in which the Dirac crossing is protected by time-reversal symmetry, Dirac point in TCIs is protected by a discrete set of crystalline symmetries⁶⁵. This unique crystalline protection of the surface states provides a route towards controlling their dispersion by using different types of structural deformations. Theory predicted⁷⁶ and experiments confirmed⁷⁷ that lattice distortion that breaks the mirror symmetry protecting the Dirac point in TCIs enables otherwise massless Dirac SS fermions to acquire mass. However, from both the fundamental and the applications perspectives, one of the key goals remains uncovering new pathways for manipulation of topological SS via structural deformations *without* breaking any crystalline symmetry protecting the Dirac nodes.

Theoretically, strain in TCIs is predicted to give rise to a variety of exotic phenomena, including tuning the band gap through the phase transition from the trivial to the topological state^{80,182}. Spatially

inhomogenous strain is associated with psuedomagnetic fields analogous to those observed in graphene³⁷, with intriguing potential consequences including unconventional superconductivity³⁹. In a recent study⁷⁴ we observed a quasi-periodic strain pattern on the surface of thin films of the TCI SnTe, and were able to correlate the locally-measured compressive strain with the average momentum-space distance of the Dirac points from the edges of the Brillouin zone. Here we more fully treat the influence of strain on the Dirac surface states, and obtain experimental values for two of the coefficients which determine the shift of the Dirac points as a function of strain. In particular, we unveil the effect of uniaxial strain on the Dirac surface states for the first time, which should prove helpful in developing future "straintronic" devices based on TCIs.

The effect of strain on the (001) surface states of TCIs was discussed using symmetry considerations in Ref. ³⁹. It was found that to first order

$$\mathbf{A}_{1} = \left(\alpha_{1}u_{xx} + \alpha_{2}u_{yy}\right)\hat{\mathbf{x}} + \alpha_{3}S\hat{\mathbf{y}}$$

$$\mathbf{A}_{2} = \alpha_{3}S\hat{\mathbf{x}} + \left(\alpha_{1}u_{yy} + \alpha_{2}u_{xx}\right)\hat{\mathbf{y}}$$

(5.1)

where \mathbf{A}_1 and \mathbf{A}_2 are the momentum-space shifts of the Dirac cones near \overline{X} and \overline{Y} respectively, $u_{ij} = \partial_j u_i$ are the spatial derivatives of components of \mathbf{u} (the displacement vector of elasticity theory¹³⁵), S is the shear strain $(u_{xy} + u_{yx})/2$, $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are unit vectors in momentum space, and $\alpha_{1,2,3}$ are arbitrary constants. The physical significance of Eq. (5.1) is that the diagonal elements of the strain tensor, u_{xx} and u_{yy} , shift each Dirac cone along the line connecting its time-reversal-invariant point to $\overline{\Gamma}$, while shear strain moves the cones transversely. The relative signs are chosen so that compressive strain shifts the Dirac cones inward from the zone edge, consistent with theory⁸⁰ and experiment⁷⁴ (Fig. 5.1 (c), (d)). If we define the isotropic linear compression $C \equiv (u_{xx} + u_{yy})/2$, and the uniaxial stretch $U \equiv (u_{xx} - u_{yy})/2$, we can rewrite Eq. (1) as:

$$\mathbf{A}_{1} = (\beta C + \gamma U) \hat{\mathbf{x}} + \alpha_{3} S \hat{\mathbf{y}}$$

$$\mathbf{A}_{2} = \alpha_{3} S \hat{\mathbf{x}} + (\beta C - \gamma U) \hat{\mathbf{y}}$$
 (5.2)

where $\beta = \alpha_1 + \alpha_2$ and $\gamma = \alpha_1 - \alpha_2$. Eq. (5.2) makes explicit the symmetry-derived constraint that uniaxial strain shifts the two pairs of Dirac cones in opposite directions.^{39,81}

In the following we use Fourier-transform scanning tunneling microscopy (FT-STM) to estimate the values of α_1 and α_2 , or equivalently β and γ , in SnTe. We do not consider α_3 here; we found that the shear strain in these films was about 1/3rd as strong as the other elements, and not as ordered spatially (**Fig. 5.2(h)**).



Fig. 5.1. Strain schematic. (a) The (001) surface Brillouin zone of unstrained SnTe (b); the Dirac cones are indicated by red dots. (c) and (d) In isotropically compressed SnTe the Dirac nodes move inward towards the zone center. (e) Schematic of the misfit dislocation network appearing at the interface between the PbSe (001) substrate (purple) and the SnTe film (yellow), adapted from 39 .

5.2 Experiment

The SnTe (001) thin film (~40 monolayers (MLs)) used in this experiment was grown on a PbSe (001) substrate cleaved in UHV and heated to ~300° C during deposition. The source was an electron-beam evaporator loaded with high-purity SnTe. All STM data was acquired at 4 Kelvin. It has been known for decades that many (001)-oriented heterostructures of IV-VI semiconductors exhibit grid-like quasiperiodic arrays of misfit dislocations, with associated strong strain patterns near the interface ⁸². These sub-surface dislocations manifest themselves as linear "dips" or troughs in the STM topographs directly above the line of the dislocation^{183,184}, as seen in **Fig. 5.2 (a)**. The troughs were seen consistently at both positive and negative bias voltages, consistent with their structural (rather than electronic) origin. dI/dV spectra show that the film is p-type with the Dirac point at approximately +300 mV (not shown; see Ref. ⁷⁴), consistent with an earlier report.⁷⁵



Fig. 5.2: Spatial distribution of different types of strain. (a) STM topograph of ~130 nm square region of the sample ($V_{set} = -50 \text{ mV}$, $I_{set} = 200 \text{ pA}$) (b) Schematic of the (001) surface of SnTe. Arrows in (b) denote the x- and y-axes. (c)-(f) The components of the 2 x 2 strain tensor $\nabla u(\mathbf{r})$ extracted from topograph in (a). u_{ij} denotes $\frac{\partial u_i}{\partial j}$. (g)-(j) Physically significant linear combinations of the tensor elements in (c)-(f): (g) The isotropic compression $C \equiv (u_{xx} + u_{yy})/2$; (i) the uniaxial strain $U \equiv (u_{xx} - u_{yy})/2$; (b) the shear strain $S \equiv (u_{xy} + u_{yx})/2$; (j) the local rotation angle $R \equiv (u_{xy} - u_{yx})/2$.

To experimentally determine the local strain in the topmost atomic layer, we used a phase-sensitive analysis method uniquely suited for atomic-resolution STM topographs.^{95,134} If a topograph contains a

periodic lattice, small deviations can be measured by spatial lock-in techniques: one multiplies the topography by a plane wave corresponding to one of the lattice vectors, and the (smoothed) result is a complex quantity whose phase is proportional to the shift of the atomic lattice in that direction at the given point. This phase shift, for both lattice vectors, gives the displacement field $\mathbf{u}(\mathbf{r})$ to a spatial resolution fixed by the smoothing length scale, which can be as low as a few lattice constants. The Lawler-Fujita procedure⁹⁵ also re-maps the topography onto this ideal lattice, that its Fourier transform should correspond to the true reciprocal space of a periodic system. For this reason (i.e. to measure scattering Q-vectors with respect to a uniform reciprocal lattice), we used Lawler-Fujita on the Fourier-transformed dI/dV data shown here. To measure the strain, however, we used a slightly different method based on the same principle, which calculates the derivatives of $\mathbf{u}(\mathbf{r})$ without evaluating the vector itself.¹³⁴ (See appendix for details.)

To establish the momentum-space shifts of the Dirac cones, we use the quasi-particle interference (QPI) method:¹⁰² the elastic scattering of quasi-particles produces standing waves in the density of states, which appear as oscillations of the measured dI/dV with wavevector $\mathbf{q} = \mathbf{k_i} - \mathbf{k_f}$, where $\mathbf{k_{i,f}}$ are the initial and final momenta of the quasipartle. These **q**-vectors can be directly extracted from the Fourier transform of $dI/dV(\mathbf{r}, V)$, and (the relevant band structure being known) reveal the momentum-space position of the underlying states. In the case of SnTe (001) the surface states comprise two pairs of Dirac cones near \bar{X} and \bar{Y} ; both pairs undergo Lifshitz transitions so that at the energies shown here—~200-250 meV below the Dirac point—the constant-energy-contours resemble the ellipses shown in the inset of **Fig. 5.3 (a)**.^{67,69} In this paper we will focus on the vectors labeled \mathbf{Q}_{1x} and \mathbf{Q}_{1y} in **Fig. 5.3 (a)**; each one corresponds to a single "valley" of Dirac fermions, and represents scattering across the $\overline{\Gamma}$ point between two ellipses on opposite sides.

To visualize and quantify the effect of strain on the surface states we mask the signal $(dI/dV(\mathbf{r}, V) \equiv G(\mathbf{r}))$ into regions based on the type and sign of the strain and compare Fourier transforms. From this comparison we extract the radial shifts of \mathbf{Q}_{1x} and \mathbf{Q}_{1y} , which reflect a length-wise stretching of the

ellipse-pairs at \overline{X} and \overline{Y} respectively, as predicted by Eqs. (5.1) and (5.2).⁹ Explicitly, we introduce a masking function $M(\mathbf{r}) \in [0,1]$ and Fourier-transform the mean-shifted product

$$G_M(\mathbf{r}) = G(\mathbf{r})M(\mathbf{r}) + (1 - M(\mathbf{r}))\overline{G},$$

where $\overline{G} = \int d\mathbf{r} G(\mathbf{r}) M(\mathbf{r}) / \int d\mathbf{r} M(\mathbf{r})$ is the mask-average of *G*; the sole function of the second term is to reduce ringing by using \overline{G} as the background for $G_M(\mathbf{r})$. For each mask we compute the average strain similarly: $\overline{u_{ij}} = \int d\mathbf{r} u_{ij}(\mathbf{r}) M(\mathbf{r}) / \int d\mathbf{r} M(\mathbf{r})$. With the shifts $\Delta \mathbf{Q}_{1x,y}$ and $\overline{u_{ij}}$ in our possession, we may directly fit to Eq. (5.1), remembering that because \mathbf{Q}_1 represents scattering *across* the Brillouin zone, the shift of the Dirac cones themselves is $\Delta \mathbf{Q}_1/2$.

In this paper, we use dI/dV data taken using the lock-in technique during a 130nm atomic-resolution topography at +50 mV bias. The strain fields to be averaged were computed from the same scan; the same masking functions were used on both. Although we only show data taken at +50 mV, the behavior at +25 and +75 mV are qualitatively identical, and in Ref. ⁷⁴ we found that the response to compressive strain was consistent from -50 mV to +175 mV.

5.3 Results

The strain in the 130 nm region of interest is shown in **Fig. 5.2**. The diagonal elements of the strain tensor (**Fig. 5.2 (c)** and (**f**)) each show a clear one-dimensional pattern, with blue lines of compression colocated with the troughs in the topograph (**Fig. 5.2 (a)**). The orientation of the pattern is consistent with its origin in the network of misfit dislocations at the interface. Examining **Fig. 5.1 (e)**, we see that the misfit dislocation parallel to y (which terminates in the brighter wall of the cartoon) is associated with a marked stretching of the lattice in the x-direction (i.e. with variation in u_{xx}), translationally invariant in the ydirection. Similarly, the misfit dislocations aligned along x produce variations in u_{yy} , which is ideally a function of y only. The expected pattern is reproduced in detail in **Figs. 5.2 (c)** and (**f**), with one

⁹ Although Eqs. (1) and (2) only refer to energies near the Dirac point, the physics should still apply below the Lifshitz transition.

exception: Although the discrepancy in lattice constants causes the SnTe lattice to be stretched near the dislocation line (as in **Fig. 5.1(e)**), we observe at the top surface, on the contrary, a *compression* of the lattice in the bottom of the troughs, by up to about $2\%^{74}$. An explanation of this phenomenon is beyond the scope of this paper; it probably involves the relaxation of the free top surface.¹⁸⁴

The derived quantities, *C* and *U*, each show strong variation determined by their basic constituents. The compression (**Fig. 5.2(g**)) is greatest where two troughs intersect, and smallest (negative) in the midpoint between intersections; this produces a distinctive cell pattern which resembles the topography (**Fig. 5.2(a)**). The uniaxial stretch (**Fig. 5.2(i)**) is greatest where maxima of u_{xx} coincide with minima of u_{yy} : in the troughs parallel to *y* but between the troughs along *x*; the opposite sign occurs in troughs parallel to *x* and between those parallel to *y*. These, by and large, are the orange and purple parts of **Fig. 5.2(i)** respectively.

To examine the effects of each type of strain on the QPI pattern, we applied masks which fell broadly into two types: for the individual components u_{xx} and u_{yy} the masks were a series of one-dimensional strips parallel to y and x respectively, and for the combined quantities C and U they were a two-dimensional quasi-grid of spots, one for each cell of the dislocation lattice. In both cases the maxima of the masking function could be located at an arbitrary point in the dislocation unit cell, making it possible to smoothly vary the average strain without changing the mask shape, which would distort the FFT and compromise the fitting process.¹⁰ Graphs showing the evolution of strain and ΔQ_1 as a function of this "mask position variable" are shown in **Fig. 5.4**.

¹⁰ This also makes it possible to produce movies showing the "breathing" of the FFT as a function of average strain.



Fig. 5.3 Strain-filtered Fourier transforms of dI/dV. (a) The Fourier transform of dI/dV acquired in the 130nm area shown in Fig. 5.2(a); the indicated features Q_{1x} and Q_{1y} represent scattering across the center of the Brillouin zone between the inner portions of the pockets (inset) at \overline{X} , $\overline{X'}$, and \overline{Y} , $\overline{Y'}$ respectively. (b)-(e) The Fourier transforms of masked dI/dV, with masks chosen to capture the maxima (blue in (b)-(d), orange in (e)), and minima (red in (b)-(d) and purple in (e)) of u_{xx} , u_{yy} , C, and U respectively; the arrows are guides to the eye. In (b), (c), (d) ((e)) the blue (orange) and red (purple) subsets correspond to masks coincident with the blue (orange) and red (purple) areas of Fig. 5.2 (c), (f), (g), and ((i)) respectively. (For details of the masking procedure, see supplementary information.)

Qualitatively, however, it is sufficient to compare Fourier transforms of $G_M(\mathbf{r})$ for masks capturing the extreme values of each type of strain (**Fig. 5.3**). For u_{xx} (**Fig. 5.3(b)**), we find that compression is associated with a pronounced shift of \mathbf{Q}_{1y} towards the center, while \mathbf{Q}_{1x} remains virtually unchanged. Correspondingly, compression in the *y*-direction produces an inward shift of \mathbf{Q}_{1x} (**Fig. 5.3(c)**). Taken together, these results imply that α_2 from Eq. (5.1) is much larger than α_1 ; the averaged fitting results (Table 1) show a ratio of about 5:1. The isotropic compression (**Fig. 5.3(d)**) is associated with a large inward shift of both \mathbf{Q}_1 's (as found in Ref. ⁷⁴), while uniaxial stretch shifts them in opposite directions (**Fig. 5.3(e**)). Because $\alpha_2 > \alpha_1$, the sign of the change due to uniaxial strain is opposite to what might naively be expected: pure "positive" uniaxial strain ($u_{xx} = -u_{yy} > 0$) shifts \mathbf{Q}_{1x} outward and \mathbf{Q}_{1y} inward.



Fig. 5.4. $\Delta Q1$ and average strain vs. mask position. Each panel shows $\Delta Q_{1x,y}$ vs mask position for masks designed to capture variation in a particular type of strain. The types of strain varied in panels (a), (b), (c), (d) are u_{xx} , u_{yy} , C, and U respectively; the "complementary" strain type (u_{yy} , u_{xx} , U, and C respectively) are plotted for completeness. The types of strain varied in panels (a)-(d) are the same as in Fig. 5.3 (b)-(e) respectively.

To extract the desired coefficients quantitatively, we smoothly translated the various masks through the dislocation lattice, simultaneously extracting $\Delta Q_{1x,y}$ and the average strain (**Fig. 5.4**), then plotted one against the other (**Fig. 5.5**). The results are summarized in **Table 5.1**. Because we employed masks to independently measure the effect of four different types of strain— u_{xx} , u_{yy} , *C*, and *U*—we were able to obtain **two** complete sets of coefficients; we were able to perform (nominally) independent fits to Eqs. (5.1) and (5.2). The difference between the two sets of values gives an indication of the probable statistical error. On average, we find $\alpha_1 \approx 0.3$ Å⁻¹, $\alpha_2 \approx 1.5$ Å⁻¹; their sum is in good agreement with the predicted response of other IV-VI semiconductors to compressive strain.⁸⁰



Fig. 5.5 $\Delta Q1$ vs. average strain. (a)-(d) show $\Delta Q_{1x,y}$ plotted against the mask average of the average strain. The masks were chosen to maximize the variation of u_{xx} , u_{yy} , C, and U respectively; the data are the same as in Fig. 5.4 (a)-(d) respectively.

Slopes (Å ⁻¹)			Coefficients (Å ⁻¹)			
	ΔQ_{1x}	ΔQ_{1y}		From $u_{xx} \& u_{yy}$	From <i>C</i> & <i>U</i>	Average
vs. u _{xx}	-0.05	-3.15	α ₁	0.28	0.37	0.3
vs. u _{yy}	-2.53	-1.04	α2	1.42	1.57	1.5
vs. C	-3.04	-4.7	β	1.70	1.94	1.8
vs. U	2.63	-2.14	γ	-1.14	-1.20	-1.2

Table 5.1: Fitting slopes and extracted coefficients for Eq. (5.1) and (5.2).

In extracting each of the four coefficients we took the average value of slopes involving ΔQ_{1x} and ΔQ_{1y} . These, however, were sometimes quite different: compare panels (a) and (b) of Figs. 5.4 and 5.5, or the different amplitude of the variation in panel (c) of either figure. Although some of the difference could be due to tip anisotropy, one should also consider the ferroelectric transition which occurs in SnTe at low temperatures.^{75,185} In the ferroelectric phase, the symmetry which gives rise to Eqs. (1) and (2) is broken, and the two Dirac cones should in principle be affected differently by all types of strain including isotropic compression. It would be interesting to determine if the ferroelectric distortion might account for some of the asymmetry observed here.

Appendix 5.A: Measurement of the strain

The image-analysis method we used to extract the strain is derived in Ref.¹³⁴ and is closely related to the Lawler-Fujita distortion correction algorithm.⁹⁵ We describe it briefly below.

The atomic lattice in an STM topography can be expanded in a Fourier series. To first-order, $T(\mathbf{r}) \approx A_1 e^{i\mathbf{k}_1 \cdot \mathbf{r}} + A_2 e^{i\mathbf{k}_2 \cdot \mathbf{r}} + c. c.$ where \mathbf{k}_1 and \mathbf{k}_2 are the basic reciprocal lattice vectors. When the lattice is distorted the maxima corresponding to the atoms shift from \mathbf{R} to $\mathbf{R} + \mathbf{u}(\mathbf{R})$, so that the Fourier expansion becomes

$$T(\mathbf{r}) \approx A_1 e^{i\mathbf{k}_1 \cdot (\mathbf{r} + \mathbf{u})} + A_2 e^{i\mathbf{k}_2 \cdot (\mathbf{r} + \mathbf{u})} + c.c.$$

When we multiply by $e^{-i\mathbf{k}_1 \cdot \mathbf{r}}$, we obtain

$$T_1(\mathbf{r}) \approx A_1 e^{i\mathbf{k}_1 \cdot \mathbf{u}} + A_2 e^{i\mathbf{k}_2 \cdot (\mathbf{r} + \mathbf{u}) - \mathbf{k}_1 \cdot \mathbf{r}} + \cdots$$

All the terms in T_1 besides the first oscillate rapidly; they vanish upon smoothing with some length scale L, leaving $\tilde{T}_1(\mathbf{r}; L) \approx A_1 e^{i\mathbf{k}_1 \cdot \mathbf{u}}$; we similarly obtain $\tilde{T}_2(\mathbf{r}; L) \approx A_2 e^{i\mathbf{k}_2 \cdot \mathbf{u}}$. Generally, extracting \tilde{T}_1 and \tilde{T}_2 requires that in the vicinity of the Bragg peak the only significant spectral weight be due to the atomic lattice; this "vicinity" is of order 1/L.

The strain is given by the derivatives of **u**. To find these, we first normalize \tilde{T}_1 and \tilde{T}_2 throughout all space $(\tilde{N}_1 \equiv \tilde{T}_1 / |\tilde{T}_1| = e^{i\mathbf{k}_1 \cdot \mathbf{u}})$, then take the gradient and multiply by the complex conjugate:

$$\boldsymbol{\nabla}(\mathbf{k}_1 \cdot \mathbf{u}) = \frac{1}{i} \widetilde{N}_1^{\star} \boldsymbol{\nabla} \widetilde{N}_1$$

and similarly for $\nabla(\mathbf{k}_2 \cdot \mathbf{u})$. (cf. ¹³⁴ Appendix D.) To go from the derivatives $\nabla(\mathbf{k}_{1,2} \cdot \mathbf{u})$ to the $\nabla \mathbf{u}$ used in this paper (**Fig. 5.2 (b)-(e)**) requires normalization and some additional linear algebra, which is trivial if $\mathbf{k}_{1,2}$ already form a square lattice.

Experimental considerations

In the STM literature the main contributions to **u** have been not strain, but technical factors specific to STM: piezoelectric effects (nonlinearities, hysteresis, curvature of the tube) and thermal drift.⁹⁵ The hysteretic effects are often especially pronounced at the beginning of an STM scan; for the data in this paper we cropped the first 24 lines out of 1,024. The other effects vary slowly compared to the dislocation lattice, and should be approximated reasonably well by a power series in **r**. To eliminate them, we subtracted a 4th-order polynomial fit from each component of $\nabla \mathbf{u}(\mathbf{r})$.

The smoothing length *L* also plays an important role. We used Gaussian smoothing (i.e. the smoothing function $S(\mathbf{r})$ was $N_0 e^{-r^2/2L^2}$). For Fig. 5.2, we used L = 2 nm; for the mask-averaged strain (Figs. 5.4 and 5.5) we used L = 1.5 nm.

Appendix 5.B: Details of the masking procedure

The masking procedure was designed around the fact that the dislocations were well-ordered and nearly parallel to the lattice vectors $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ within the scan area (Fig. 5.6 (a)). Each "trough" in the topography was located (by finding the local maximum of the smoothed second derivative of the topography, averaged over the direction nominally parallel to it) and assigned an integer index, making the rectilinear, quasi-Cartesian grid shown in Fig. 5.6 (b). This grid defines a 2-D coordinate system which was used to formulate the masking functions $M(\mathbf{r})$.

All masking functions used are periodic with respect to this grid, and can be defined in terms of the distance between a pixel and a certain point, or locus of points, within the dislocation-lattice unit cell. For each pixel \mathbf{r} , we define the dislocation-grid distance between \mathbf{r} and the nearest point whose dislocation-

grid coordinates modulo 1 are (μ, ν) . This is

$$d(\mathbf{r}) = \sqrt{((a-\mu) - Round(a-\mu))^2 + ((b-\nu) - Round(b-\nu))^2},$$

where (a, b) are the dislocation-grid coordinates of **r** and the *Round* function rounds its argument to the nearest integer. (Clearly, $d(\mathbf{r}) \in [0, \sqrt{2}]$.)

For the one dimensional masks we are interested only in one coordinate or the other:

 $d_{a}(\mathbf{r}) = |(a - \mu) - Round(a - \mu)|,$ $d_{b}(\mathbf{r}) = |(b - \nu) - Round(b - \nu)|;$

then $d(\mathbf{r}) = \sqrt{d_a^2 + d_b^2}$. For the case $\mu, \nu = 0$ these distances are shown in **Fig. 5.6 (d)-(f)** respectively.



Fig. 5.6 Masking function ingredients (a) The drift-corrected topography at +50 mV. (b) The grid lines extracted from the topography, defining the dislocation coordinate system. (c) The raw dI/dV, simultaneously acquired with

the topography in (a). (d)-(f) are distances defined in the main text, for $\mu, \nu = 0$. The blue dots are the integer points of the coordinate system (the line-crossings in (b)), and approximately coincide with the intersection of troughs in (a). (d), (e), (f), are d_a , d_b , $d(\mathbf{r})$ respectively.

For each type of strain the mask was a well-known monotonic function of the corresponding distance; for the one-dimensional masks we used Gaussians:

$$M_{\chi\chi}(\mathbf{r}) = e^{-d_a^2/\lambda^2}, M_{\chi\chi}(\mathbf{r}) = e^{-d_b^2/\lambda^2}$$

where the subscripts denote the type of strain we want to vary, and λ is chosen so that the mask should include a certain fraction of the total spectral weight, $1/3^{rd}$ for both (i.e., $\int d\mathbf{r} M(\mathbf{r}) = 1/3$). We used $\lambda = 0.186$, found by binary search.

For the 2-D masks we used the Fermi function:

$$M(\mathbf{r}) = 1/(1 + e^{(d(\mathbf{r}) - \varphi)/T})$$

with T = 0.05 and $\varphi = 0.268$, designed so that $\int d\mathbf{r} M(\mathbf{r}) = 1/4$.

The masks were translated by varying (μ, ν) . For M_{xx} and M_{yy} , μ and ν respectively were swept from 0 to -2. For isotropic compression (μ, ν) was swept from (0,0) to (-2,-2); for uniaxial stretch the sweep was from (0, 0.5) to (-2,-1.5).

Actually, for all four types of masks the sweeps can be expressed as

$$(\mu, \nu) = (\mu_0, \nu_0) + \eta(-1, -1)$$

where the "mask position variable" η goes from 0 to 2, and is the abscissa of the graphs in **Fig. 5.4**; it also appears in the y-axis of **Fig. 5.7**. Because of the periodicity the range 1 to 2 is equivalent to 0 to 1; it was included for aesthetic reasons in **Fig. 5.4**, and in order to make the movies more watchable.

We note here that because the masked dI/dV was largely the same for adjacent values of η (d η = 0.03 for 64 points between 0 and 2) the scatter plots in **Fig. 5.5** do not represent nearly as many independent measurements of ΔQ_1 as their number of points might be taken to imply. We may guess that the number of *truly* independent measurements of ΔQ_1 is the reciprocal of the fraction of spectral weight contained in the mask: 3 for u_{xx} and u_{yy} ; 4 for *C* and *U*. Since the overlap between different masking functions is finite by design, these three or four inherently different measurements cannot be strictly separated, as in Ref.⁷⁴. Their number, however, is sufficient for fitting to a straight line.



Fig. 5.7 Masking functions. The masking functions used are shown for each type of strain, and for important values of the mask position η . The trough junctions (grid points of the dislocation lattice) are blue dots as in Fig. 5.6. For each strain type (using the sign conventions in this paper) the largest average strain occurred at $\eta \approx 0$, and the smallest (negative) at $\eta \approx 0.5$; $\eta = 0.25$ and 0.75 were approximately neutral (cf. Fig. 5.4). All masks move "to the left" (through the field of dots) with increasing η .

Appendix 5.C: Processing of the FFTs

Because $\Delta \mathbf{Q}_1$ was the shift of a rather broad peak, smeared out by mask-induced ringing, the quality and consistency of the peak-fitting procedure was important. Before fitting for \mathbf{Q}_1 the Fourier transforms of $G_M(\mathbf{r})$ were subjected to the following: (1) Reflection-symmetrization about one of the basic reciprocal lattice vectors ($\hat{\mathbf{x}}$, but since the magnitude of the FFT is inversion-symmetric using $\hat{\mathbf{y}}$ would have given the same result); (2) **k**-space smoothing on a length scale sufficient to wash out the ringing; we used Gaussian smoothing ($N_0 e^{-r^2/2L^2}$ with $L = 0.048 \text{Å}^{-1} = 10$ momentum-space pixels). Then (3) we took the Laplacian in k-space (multiplied by -1) to accentuate the peak features.

Step (1) was applied to Fourier transforms in **Fig. 5.3**. Its effect is to make the QPI feature mirrorsymmetric about the line bisecting it, so that each half-QPI peak makes it possible for each half-peak in **Fig. 5.3(b)-(e)**

The results of the three steps, as applied to the Fourier transform of the unmasked dI/dV (**Fig. 5.8(a)**), are shown in **Fig. 5.8 (b)-(d)**. The thus-processed FFTs of the masked dI/dV at $\eta = 0$ and 0.5, the same as **Fig. 5.3 (b)-(e)** of the main text, are shown in panels **Fig. 5.3 (e)-(h)**. One of the consequences of the processing is that the inner scattering peak, denoted **Q**₁' in **Fig. 5.3 (d)**, is plainly visible in the FFTs of the masked data. This vector represents intra-pocket scattering along the long axes of the ellipses, and should be equally indicative with **Q**₁ of the strain-induced shifts in the Dirac cones predicted by equations (5.1) and (5.2). The geometry of the constant energy contour (**Fig. 5.8(d)** inset) shows that the sum **Q**₁'_{x,y} + **Q**_{1x,y} = one reciprocal lattice vector, and indeed we see in **Fig. 5.8 (e)-(h)** that a significant shift of **Q**_{1x,y} of is always associated with a roughly equal shift of **Q**₁'_{x,y} in the opposite direction.

To actually extract $\mathbf{Q}_{1x,y}$ we took line cuts in the fully-processed FFT in the $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ directions (from the origin), and fit the peak to an inverted parabola; the fitting window had a half-width of 0.04 Å⁻¹, and its position shifted with η to keep the peak centered.



Fig. 5.8 Pre-fit processing of the Fourier transforms. The raw FFT (a) is symmetrized (b) by reflection about the *x*-axis (green dashed line in (a)). We smooth sufficiently to wash out the ringing introduced by the masking functions (c), and take the second derivative (d). The result clearly reveals the intra-pocket scattering feature, denoted Q_1 '. Panels (e)-(f) are thus-processed FFTs of the masked dI/dV, for mask position $\eta = 0$ (blue and orange) and $\eta = 0.5$ (red and purple); as in Fig. 3 (b)-(e) of the main text.

Appendix 5.D: Dependence of the results on the mask type

The variation in $\mathbf{Q}_{1x,y}$ and the average strain $\overline{u_{ij}}$ clearly depends on the specific functional form of $M(\mathbf{r})$. To examine this dependence, we repeated the fitting and masking procedure for compressive strain with several different functions. The results are shown in **Figs. S4** and **S5**. In **Fig. S4** one finds that tighter masking functions lead to greater variation in both the average strain and the ΔQ 's. Although there is some trend observed, with looser masks associated with slightly steeper slopes, for all five masks the slopes were within about 10% of their mean.



Fig. 5.9 Masking for compressive strain with different masks. The five panels show the variation in $\Delta Q_{1x,y}$, \overline{C} and \overline{U} against η for the masks, whose values for $\eta = 0$ are shown below the corresponding graph (color scale same as Fig. 5.7). (a),(b),(c) are Gaussian masks designed to capture $1/3^{rd}$, $1/4^{th}$, $1/5^{th}$ of the total spectral weight respectively. (That is, $M(\mathbf{r}) = e^{-d^2/\lambda^2}$ for $\lambda = 0.338$, 0.286, 0.253 respectively.) (d) and (e) are masks employing the Fermi function with T=0.05 capturing $1/5^{th}$ and $1/4^{th}$ respectively of the total spectra weight. ($\varphi = 0.267$ and 0.235 respectively.) The mask shown in (e) is the same as that used in the main paper.



Fig. 5.10: $\Delta Q1$ vs compressive strain for different mask types. The average compressive strain and ΔQ_1 values are plotted for the five mask types shown in Fig. 5.9; the shapes are indicated in the legend and the letter labels indicate the corresponding panel of Fig. 5.9. The slopes of the linear fits to the data are for ΔQ_{1x} -3.53, -3.28, -3.11, -2.93, -3.04 respectively; the slopes for ΔQ_{1y} are -5.33, -5.02, -4.76, -4.50, -4.70 respectively. All slopes are in Å⁻¹; cf. Table 5.1.

Chapter 6: Conclusions and Outlook

In all of the materials studied in this thesis, there are still many unanswered questions, and much interesting work remains to be done.

In the Ruddelsden-popper Iridates, the trend of decreasing gap size with *n*, and the rather large intrinsic gap found in Sr-327, suggests that the dimensionally-driven phase transition occurs at some intermediate *n* between 2 and ∞ , and it would be interesting to study, say, the *n*=3 compound with STM to see how the fragile, but still hard-gapped insulating state of Sr-327 evolves as one more closely approaches the 3-dimensional limit. Further, some of the predictions for exotic physics in the Iridates occur in other compounds (e.g. Na₂IrO₃^{186,187} and the pyrochlores¹⁸⁸) which are, however, perhaps more difficult to study by STM due to the lack of the easy cleave planes present in the perovskites.

Although the now-prototypical 3D TI's have been known for more than five years, chapter 4 showed that significant gaps in our knowledge remain. In both $(In_xBi_{1-x})_2Se_3$ and $TlBi(S_xSe_{1-x})^{179,180}$ there seems to be a strange, "remnant" surface state for which, as far as we know, a credible Hamiltonian has yet to be written down. Further, chapter 4 has not yet been independently published, and under the now-dominant interpretation of the STS spectra on Bi_2Se_3 the strength of the surface-state Zeeman coupling should also be regarded as a disputed point.

Of all the results presented in this thesis the study of strain effects on the (001) surface states of SnTe presents the most enticing hint of future results. The exotic states ascribed to strong pseudomagnetic fields in these heterostructures ³⁹ were predicted to occur at the (buried) interface, but chapter 5 shows that measurable and physically significant strain can also be found at the top surface. One might well imagine that with the right choice of substrate, film material and thickness the strain at the top surface would be sufficient to create manifestations of the strong pseudomagnetic fields (e.g. Landau levels) directly accessible with the STM tip. (Indeed, simple calculations show that the pseudomagnetic fields in the film studied in chapter 5 should have reached the order of 50T, though in regions hardly larger than the magnetic length; the lack of clear Landau levels in chapter 5 is *almost* surprising.) Regardless of the

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outcome of particular experiments, however, the local measurement of strain by STM seems destined to become an important part of the toolkit, and find numerous yet unforeseen uses in surface science.

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