
Exploring the Fermi surfaces of novel quantum
materials using high magnetic fields



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Abstract

This thesis presents the results of torque magnetometry and resistivity measurements of the electronic structure of novel quantum materials, specifically using the techniques of quantum oscillations and angle-dependent magnetoresistance oscillations. Measurements of the Fermi surfaces of these materials, alongside comparisons to the electronic structure predicted by density functional theory calculations, can elucidate much about the novel physical properties they exhibit and the competing interactions which govern their phase diagrams.

The first system studied is the Iron-based superconductor $\text{FeSe}_{1-x}\text{S}_x$, an isoelectronically doped version of a system of much current interest, FeSe. Doping up to $x = 0.2$ is found to suppress the structural transition in this system entirely, with superconductivity continually present at low temperatures. Shubnikov-de Haas measurements across this range find a small quasi-two dimensional Fermi surface that increases in size and warping continuously with doping, with orbital dependent effective masses that do not change significantly within the orthorhombic phase.

The second material studied is the antiferromagnetic intermetallic CeZn_{11} which, featuring an unpaired $4f$ electron, is considered a possible candidate for heavy fermion behaviour. De Haas-van Alphen oscillations are seen once the antiferromagnetic phase is suppressed, and comparable frequencies of oscillation are measured in the non-magnetic analogue LaZn_{11} , although with relatively smaller effective masses. GGA+ U calculations, once magnetic breakdown is considered, match well the measured frequencies, confirming CeZn_{11} to be a localised moment system with the $4f$ electron well below the Fermi level.

The final material studied is the transition metal dichalcogenide IrTe_2 , which undergoes dimerisation upon cooling into a number of possible charge modulated structures. Low temperature de Haas-van Alphen measurements find multiple domains of a quasi-two dimensional Fermi surface, no longer perpendicular to the lattice planes. Angular-dependent magnetoresistance oscillations observe a similarly tilted quasi-one dimensional Fermi surface, again with many domains present. Together these measurements confirm the unusual dimensionality of the dimerised Fermi surface of IrTe_2 .

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*Pour qu'une chose soit intéressante,
il suffit de la regarder longtemps.*

— Gustave Flaubert

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Chapter 1

Background

This chapter serves as an overview for the motivation of the study of quantum materials, introducing the idea of a Fermi surface and a Fermi liquid and looking at the unusual phenomena that can occur at the crossover between different phases of a material when the Fermi liquid model breaks down. Specific introductions to the families of materials studied in this thesis – Fe-based superconductors, heavy fermion materials and transition metal dichalcogenides – can be found at the start of their relevant chapters. Here I also discuss the theoretical concepts and experimental techniques that underpin the work in this thesis, specifically density functional theory, quantum oscillations, angle-dependent magnetoresistance oscillations, torque magnetometry and resistivity measurements.

1.1 Introduction

The content of this thesis – and indeed much of condensed matter physics, the field of study to which it belongs – is essentially concerned with working out what electrons get up to inside of metals. This is not a straightforward question: although quantum mechanics is able to solve exactly the interaction between a single electron and positive ion, it is not analytically or numerically possible to do so if there are of the order of 10^{20} of them. Therefore a number of vastly simplified models are used which, with a surprising amount of success, are able to predict the electronic properties exhibited by solids. Determining where these models succeed and, more importantly, where they fail

is the key to understanding the nature of electronic behaviour in solid state systems and to discovering new, unusual and potentially incredibly useful electronic properties, such as high temperature superconductivity.

Fermi liquid theory

Perhaps the simplest theory that has had some success in explaining the behaviour of real metals is the Drude-Sommerfeld model, or the free electron gas. As the name suggests, this model treats a metal as a gas of free electrons, which may undergo instantaneous collisions with the fixed positive ions but are otherwise entirely unaffected by any interactions – either with the positive ions or the other electrons in the material. Excepting the energy distribution – which takes into account the fermionic nature of the electrons – this is an entirely classical model, yet despite both this and its simplicity it is remarkably successful in predicting the electronic and thermodynamic properties of many metals, especially the ‘simple’ alkali metals with their single, s -orbital valence electron.

Rather than ignoring the electrons’ interactions (excepting collisions) entirely, instead – assuming the metal is a perfect crystal – the periodicity of the underlying ionic lattice can be exploited to define a periodic potential $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$ for all Bravais lattice vectors $\mathbf{R}$, giving a single electron Hamiltonian:

$$\mathcal{H}\Psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right) \Psi(\mathbf{r}) \quad (1.1)$$

which has the solution:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (1.2)$$

where $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$ (the Bloch function) has the same periodicity as the potential and hence the ionic lattice. This is Bloch’s theorem [1]: each electron has its own individual eigenstate described by a crystal momentum $\mathbf{k}$ (within the first Brillouin zone) and a band index n . For each value of n , the dispersion relation of the energy eigenvalues $E_n(\mathbf{k})$ will form a ‘band’ of continuous states with the periodicity of the reciprocal lattice; taken together these are the ‘band structure’ of a material. Despite the introduction of

a periodic potential, the electrons within these bands can be treated as free particles, albeit with an altered, ‘band mass’ dependent on the band dispersion:

$$m_b = \hbar^2 \left(\frac{\partial^2 E(\mathbf{k})}{\partial k^2} \right)^{-1} \quad (1.3)$$

The shape of these bands – and hence the band masses – depends on the form of $V(\mathbf{r})$ and so the symmetry of the lattice and the ions it contains. Many methods exist to calculate this computationally – some of which are described in Section 1.2.2 – and, despite neglecting any kind of electron-electron interactions, these have been able to accurately predict the electronic properties of the vast majority of materials. The reason for this success was explained phenomenologically by Landau [2]: the above band structure picture is built upon the existence of non-interacting fermions, however nowhere does it require these fermions to be electrons; if the net effect of the interactions is to produce a fermionic, spin- $\frac{1}{2}$ ‘quasiparticle’ of unit charge, then the dispersion relation that results from the Hamiltonian of Equation 1.1 will still be valid in the vicinity of the Fermi surface, although with an enhanced ‘effective’ mass m^* arising from the electron-electron interactions. Nearly all crystalline metals have a ground state well described by this Fermi liquid theory, and even superconductivity – in its conventional, BCS form – still arises from the coupling of phonons with a Fermi liquid.

Nevertheless, there are still a few metallic systems where the universal low temperature predictions of Fermi liquid theory – a constant magnetic susceptibility $\chi = \chi_0$, a linear specific heat $C = \gamma_0 T$ and a quadratic resistivity $\rho = \rho_0 + AT^2$ – do not hold true [2]. Although these systems have strong electron-electron interactions, their presence is a necessary but not sufficient condition: many intermetallic compounds containing $4f$ or $5f$ valence electrons have very strong electron-electron interactions, but are often still well described by Fermi liquid theory with colossal mass enhancements of the order $m^*/m_b = 100\text{-}1000$ – hence their collective sobriquet of heavy fermion systems. Instead a competition between interactions appears to be important, with non-Fermi liquid behaviour often occurring in the proximity of a phase transition, especially when the phase transition is suppressed to $T = 0$ – a ‘quantum critical point’.

To give some examples of systems showing non-Fermi liquid behaviour:

- **Fe-based superconductors** feature a structural and antiferromagnetic transition in close proximity; when both of these are suppressed to $T = 0$ a superconducting region emerges with non-Fermi liquid behaviour above [3].
- The aforementioned **heavy fermion compounds** feature an antiferromagnetic transition that can also be suppressed to induce non-Fermi liquid behaviour and superconductivity (although with considerably smaller transition temperatures) [4].
- Some **layered transition metal dichalcogenides** possess multiple charge density wave phases and a low temperature Mott insulator phase, again with a region of superconductivity and non-Fermi liquid behaviour when these are suppressed to $T = 0$ [5].

Phase diagrams in novel quantum materials

In many of these systems the unaltered ‘parent’ compounds themselves may be some way from non-Fermi liquid behaviour – some tuning parameter must be varied to lower the transitions and induce the non-Fermi liquid regime. The effect of the tuning parameter can be to change the number of charge carriers in the system (electron doping, hole doping) or the lattice parameters (isoelectronic doping, pressure), though not all will necessarily lead to a suppression of the phase transition [4]. To visualise the influence of the tuning parameter on the system a phase diagram can be plotted, with temperature on the y -axis and the tuning parameter on the x -axis. Despite the varied nature of the systems showing non-Fermi liquid behaviour, their phase diagrams are remarkably qualitatively similar; a generic example, applicable to all the listed examples, is shown in Figure 1.1 (specific examples for each of the listed examples are shown in the later, system-specific background discussions: Figure 2.2, 3.1 and 4.2b)). All systems show the suppression of an ordered state to a potential quantum critical point, which is obscured by a superconducting dome; above the apex of this dome is a region of non-Fermi liquid behaviour. The presence of a quantum critical point beneath the superconducting dome

is not a given: the superconductivity may not coexist with the ordered state, so the ordering phase transition no longer goes to $T = 0$ and a quantum critical point is not present; conversely the two may be able to coexist and so the quantum critical point still exists, demarcating the boundary between two distinct superconducting phases within the dome [4].

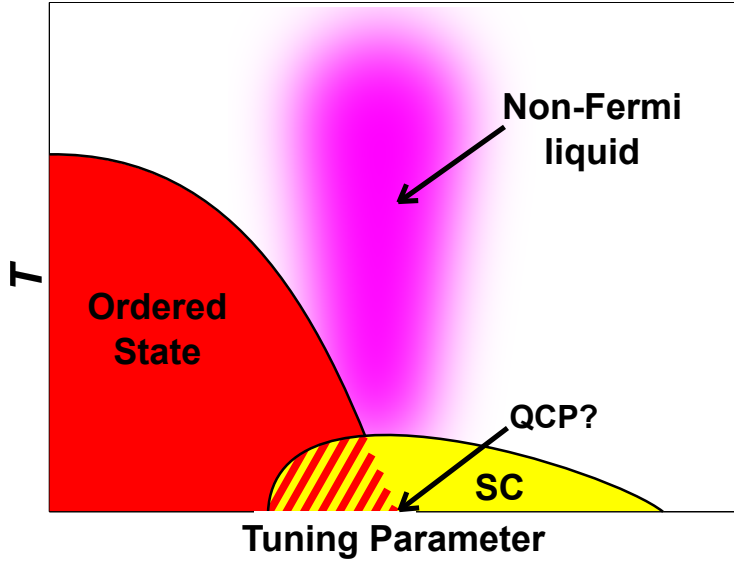


Figure 1.1: **Generic phase diagram for a non-Fermi liquid system**, showing the appearance of superconductivity and non-Fermi liquid behaviour around the suppression of an ordering transition and a possible quantum critical point.

Although the presence of the superconducting dome presents a major obstacle to experimental probes of the low temperature electronic behaviour around the non-Fermi liquid region, measurements of the electronic structure outside of the superconducting phase – achieved either by tuning the system away from the superconducting region, or by suppressing the superconductivity with a large enough magnetic field – can still offer clues towards the competing interactions that may be causing the novel behaviour. Furthermore the superconductivity shown by these non-Fermi liquid systems is not described by conventional BCS theory – for this reason it is known as unconventional superconductivity – and can, in some cases [6], display far higher critical temperatures. Therefore characterising the electronic structure of these systems may also be able to point towards the necessary features required to achieve the potential technological panacea of room temperature superconductivity.

The three systems whose study makes up the experimental chapters of this thesis – Fe-based superconductor $\text{FeSe}_{1-x}\text{S}_x$, potential heavy fermion compound CeZn_{11} and layered transition metal dichalcogenide IrTe_2 – all belong somewhere on a phase diagram like that shown in Figure 1.1, although with differing degrees of proximity to any superconductivity or non-Fermi liquid behaviour. There are, however, wide differences in the crystallographic structures and underlying interactions within these systems, with little in the way of common themes or idioms that have not been discussed here already. For this reason I will introduce each system, and discuss the broader family of materials to which it belongs, individually, at the start of each experimental chapter. The ideas discussed here – of unconventional superconductivity, quantum criticality and non-Fermi liquid behaviour – are of varying applicability to these three systems, however the hope of exploring possible electronic behaviour in metals beyond the Fermi liquid model provides a common initial motivation for their study.

1.2 Theoretical concepts

1.2.1 The Fermi surface

The Pauli exclusion principle states that two identical fermions cannot occupy the same quantum state simultaneously. Therefore the $n, \mathbf{k}$ electronic (or quasiparticle, in the case of Fermi liquid theory) eigenstates of the bandstructure of a crystalline material will, in the ground state configuration, be occupied up to a certain ‘Fermi level’ E_F , and unoccupied above it. The lowest energy excited states of this system correspond to promoting electrons from just below the Fermi level to just above it, and so it is these states around the Fermi level that will be involved in the electronic responses of a material: only electrons within $k_B T$ of the Fermi level will contribute to the specific heat; similarly only those within $\mu_B B$ of the Fermi level will contribute to the Pauli paramagnetic susceptibility. Most fundamentally, if the Fermi level lies within a band then there will be a high density of states in its vicinity and so a large number of possible low energy excitations – the material is a metal. Conversely if the Fermi level lies within

a gap considerably larger than $k_B T$ between bands then there will be no possible excited states – the material is an insulator.

Fermi surface topology

As well as the density of states at the Fermi level, their values of $\mathbf{k}$ will also play a role in determining the physical properties of a metal. The location of these states in reciprocal space can be visualised as a constant energy surface at E_F within the first Brillouin zone – this is the ‘Fermi surface’ of a metal (insulators, by definition, have no Fermi surface as no bands cross the Fermi level). It is the topology of this Fermi surface which then determines the physical properties, for example:

- A low dimensional Fermi surface, broadly isotropic in one (quasi-two dimensional) or two (quasi-one dimensional) directions, will lead to a large decrease in conductivity along the isotropic direction(s).
- Open sections of Fermi surface – regions around which an electron may perform an open orbit, never repeating its path – result in a magnetoresistance $\rho_{xx} \sim B^2$ when the field is applied perpendicularly; closed sections result in a magnetoresistance that saturates at high fields [1].

Figure 1.2 shows cartoon quasi-one dimensional, quasi-two dimensional and quasi-three dimensional Fermi surfaces, with electron orbits indicated to illustrate the second point. All sections of the quasi-one dimensional Fermi surface are open, so for all field orientations there will be a quadratic magnetoresistance; conversely for the quasi-three dimensional Fermi surface all sections are closed, so for all field orientation the magnetoresistance will saturate. However, for the quasi-two dimensional Fermi surface if the field is in-plane (shown in blue) then open orbits are possible, for all other orientations (such as that in red) all orbits are closed – the magnetoresistance of this material will depend strongly on the direction of the applied field. The concept of Fermi surface dimensionality will be returned to throughout this thesis, while further experimental signatures of open orbits are discussed in Section 1.2.4.

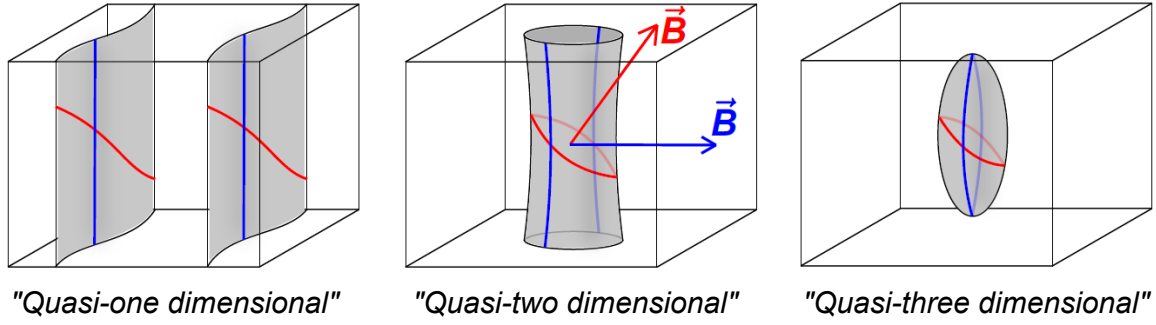


Figure 1.2: **Cartoon Fermi surfaces illustrating reduced dimensionality and open and closed sections** for quasi-one, quasi-two and quasi-three dimensional examples.

As well as affecting the electronic transport properties of the system, the topology of the Fermi surface can also drive electronic phase transitions in the material, or point towards the origin of electron-electron (or quasiparticle-quasiparticle) interactions. A Fermi surface which features large, flat, parallel sections that cannot be joined by a reciprocal lattice vector shows ‘Fermi surface nesting’, essentially a periodicity in the electronic structure that is not present in the crystal structure. If the crystal structure undergoes a small ‘Peierls distortion’ these nested sections can be placed at the Brillouin zone boundary; they will then be lowered in energy beneath the Fermi level by the band gap that opens up along the boundary. Thus a Fermi surface with significant nesting will cause a low temperature ‘charge density wave’ phase (discussed in more detail in Section 4.1.1), with a distorted crystal structure and a reduced density of states at the Fermi level. Furthermore the fluctuations associated with this Fermi surface nesting provide the pairing mechanism in both of the competing theoretical explanations for unconventional superconductivity in the Fe-based superconductors (discussed in more detail in Section 2.1.1).

Determining the Fermi surface of a material therefore imparts a great deal of information about its physical properties and the interactions which govern its behaviour. By iteratively computing the form of $V(\mathbf{r})$ in Equation 1.1 the Fermi surface expected from Bloch’s theorem can be calculated, and in the majority of metals this provides a very good approximation to the actual Fermi surface of the material. However in the case of

strong electron-electron interactions, or at the very boundaries of the Fermi liquid model, these calculated Fermi surfaces can be entirely at odds with the behaviour exhibited by the material. In these cases experiments to measure the Fermi surface directly can shed a great deal of light on the competing interactions within the system, and probe the origin of any novel electronic behaviour.

1.2.2 Density functional theory

The Kohn-Sham equations

To begin to compute the band structure of a material from Equations 1.1 and 1.2 a choice needs to be made of the form of the periodic potential $V(\mathbf{r})$ and the single electron wavefunction $\Psi_{n\mathbf{k}}(\mathbf{r})$, from which the energy can be minimised iteratively to find the stable ground state. By far the most popular, and historically the most successful, method for achieving this is ‘density functional theory’ (DFT), and this is the technique used to calculate band structures throughout this thesis.

The key assumption of DFT – from which it takes its name – is that the total energy of the system is a functional of only the electron density $n(\mathbf{r})$, related to the individual electronic wavefunctions by:

$$n(\mathbf{r}) = \sum_{n,\mathbf{k}} |\Psi_{n\mathbf{k}}(\mathbf{r})|^2 \quad (1.4)$$

This reduces the problem from one of N electrons with $3N$ variables, $E = F[\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)]$, to one of 3 variables only, $E = F[n(\mathbf{r})]$ [7]. The single electron Hamiltonian of Equation 1.1 then takes the form¹ :

$$\left(-\frac{1}{2}\nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \Psi_{n\mathbf{k}}(\mathbf{r}) = E\Psi_{n\mathbf{k}}(\mathbf{r}) \quad (1.5)$$

¹To get the Hamiltonian in this simplified form energy, distance and mass must be expressed in units of Hartree (1 Ha = 27.2 eV), Bohr radius and electron mass respectively.

There are now three terms in the periodic potential, these are:

- The nuclear interaction potential $V_n(\mathbf{r})$, which accounts for the Coulomb attraction between the electron and the I fixed, positive ions in the unit cell:

$$V_n(\mathbf{r}) = - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \quad (1.6)$$

- The Hartree potential $V_H(\mathbf{r})$, which approximates the total Coulomb repulsion from every other electron in the system to be equal to the potential arising from the electron density. This can be calculated by integrating Poisson's equation:

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}) \quad (1.7)$$

and is known as the mean field approximation.

- The exchange-correlation potential $V_{xc}(\mathbf{r})$, which arises from facets of the electron-electron interaction not accounted for by the mean field approximation: firstly there is an exchange potential, arising from the Coulomb repulsion between a spin up and spin down electron occupying the same state; secondly there is a rather less specific correlation potential, which accounts simply for any aspects of the electron-electron repulsion not covered by the mean field approximation. Unlike the other terms, the exact form of this potential is not known. However it will be related to the total exchange-correlation energy $E_{xc}[n]$ by:

$$V_{xc}(\mathbf{r}) = \left. \frac{\partial E_{xc}[n]}{\partial n} \right|_{n(\mathbf{r})} \quad (1.8)$$

The accuracy of DFT therefore depends on the accuracy of the approximation of $E_{xc}[n]$.

Together Equations 1.4-1.8 are known as the Kohn-Sham equations [8]. Beginning with the known ionic positions in the unit cell and an initial guess of $n(\mathbf{r})$ – usually taken to be the electron density of isolated atoms placed at the ionic positions – Equations

1.5-1.8 can be used to find the electronic wavefunctions $\Psi_{n\mathbf{k}}(\mathbf{r})$ which minimise the total energy of the system. These $\Psi_{n\mathbf{k}}(\mathbf{r})$ then define a new $n(\mathbf{r})$ from Equation 1.4, and the process is repeated until $n(\mathbf{r})$ is self-consistent, within a specified tolerance, between calculations. By this iterative process DFT is able to calculate the predicted ground state band structure of a material.

The local density approximation

The accuracy of the band structure calculated by DFT depends on the choice of $E_{xc}[n]$ and the basis set of wavefunctions for $\Psi_{n\mathbf{k}}(\mathbf{r})$. Although the form of $E_{xc}[n]$ is not known for the electrons of an arbitrary solid, it can be calculated in the case of an homogeneous electron gas. Given a density n and volume V the exchange energy is given by the formula [9]:

$$E_x^{\text{HEG}}(n) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{4/3} V \quad (1.9)$$

The correlation energy cannot be similarly described by an analytical expression, however it can be computed numerically by solving the many-particle Schrödinger equation and removing the known kinetic, Hartree and exchange energies [10]. These values of correlation energy can then be parameterised to define a function also dependent on the electron density, $E_c^{\text{HEG}}(n)$ [11].

The results for a homogeneous electron gas – where the electron density n is constant – can be applied to the case of electrons in a crystalline solid – where the electron density $n(\mathbf{r})$ varies periodically – under the assumption that the electron density is only slowly varying, so that at each point $\mathbf{r}$ there is volume $d\mathbf{r}$ with constant local density $n(\mathbf{r})$. The exchange-correlation energy of Equation 1.8 will then be given by:

$$E_{xc}[n] = \frac{1}{V} \int_V (E_x^{\text{HEG}}[n(\mathbf{r})] + E_c^{\text{HEG}}[n(\mathbf{r})]) d\mathbf{r} \quad (1.10)$$

This is the local density approximation (LDA). To loosen the assumptions for systems where the electron density may not be so slowly varying, an elaborated version of LDA is used, known as the generalised gradient approximation (GGA) [12], where the functional

also depends on the gradient of the electron density, $E_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$. This GGA form of the exchange-correlation energy is perhaps the most commonly used, and all the DFT calculations in this thesis employ it.

The linearised augmented plane wave method

Finally a basis set of wavefunctions must be chosen for $\Psi_{n\mathbf{k}}(\mathbf{r})$ that serve as a good approximation of the electronic states and exhibit the periodicity required by Bloch's theorem (Equation 1.2). Well away from the ions, in the 'interstitial' region, the electrons will move relatively freely, so their wavefunction can be approximated to a plane wave:

$$\phi_{\mathbf{k}_n}(\mathbf{r}) = A e^{i\mathbf{k}_n \cdot \mathbf{r}} \quad (1.11)$$

Closer to the ions the electrons will be far more tightly bound, so their wavefunction can be approximated to a linear combination of atomic wavefunctions:

$$\phi_{\mathbf{k}_n}(\mathbf{r}) = \sum_{l,m} \left(A_{lm,\mathbf{k}_n} R_{nl}(r) + B_{lm,\mathbf{k}_n} \dot{R}_{nl}(r) \right) Y_{lm}(\hat{\mathbf{r}}) \quad (1.12)$$

where $R_{nl}(r)$ and $\dot{R}_{nl}(r)$ are the radial functions and their derivatives with respect to energy, and $Y_{lm}(\hat{\mathbf{r}})$ are the spherical harmonic functions. $A_{lm,\mathbf{k}_n}$ and $B_{lm,\mathbf{k}_n}$ are chosen so that the wavefunction and its gradient are continuous between the localised and interstitial regions. The position of the boundary between the two regimes is then decided by the choice of radius of the 'atomic sphere' – within the atomic sphere centred on each lattice site the atomic wavefunctions are used, outside the plane waves. $\Psi_{n\mathbf{k}}(\mathbf{r})$ is then constructed from a linear combination of these two basis sets; this construction is known as the linearised augmented plane wave (LAPW) method [13].

Spin-orbit coupling

These various approximations to the Hamiltonian and wavefunction provide a rigorous method of calculating the band structure of a material, and prove very successful at predicting the electronic structures for many materials. However all the treatments so

far have only dealt with the charge of the electrons, their spins have been completely ignored. For non-magnetic compounds comprised of relatively light elements this turns out to be a valid approximation, but for many other materials the electron spin must be accounted for to reproduce the experimental band structure with any accuracy.

Neglecting (for now) any effect of the spin on the terms in the Kohn-Sham Hamiltonian of Equation 1.5, a correction term can instead be added to account for the interaction between the spin and the potential $V(\mathbf{r})$ it passes through. This ‘spin-orbit coupling’ takes the form:

$$\Delta\mathcal{H}_{\text{so}} = \frac{1}{2c^2} \frac{1}{r} \frac{dV(\mathbf{r})}{dr} \mathbf{l} \cdot \mathbf{s} \quad (1.13)$$

in the case of a Coulomb-like potential, where $\mathbf{l}$ is the orbital angular momentum of the electron and $\mathbf{s}$ the spin. Far away from ionic positions the potential will be relatively constant, so $dV(\mathbf{r})/dr$ will be negligible. Therefore the spin orbit term is taken to be zero in the interstitial region, while in the atomic spheres the relevant, Coulomb-like potential is taken to be the nuclear interaction potential $V_n(\mathbf{r})$ of the central ion, as defined in Equation 1.6 (with the sum over only one ionic site). The effect of spin-orbit coupling is greatest for heavy elements – where the potential $V(\mathbf{r})$ is largest and higher $\mathbf{l}$ quantum numbers are possible – and often acts to split the degeneracy of bands at high symmetry points.

The local spin density approximation

In many cases the small adjustments resulting from the inclusion of spin orbit coupling are enough to engender a good correspondence with the experimental band structure. However for the case of magnetic materials a more holistic approach to spin is required, and the Kohn-Sham equations must be modified to include a spin dependence. Unlike charge, spin is a vector property, so it cannot be described by a scalar density analogous to the charge density $n(\mathbf{r})$. If, however, the spins are collinear – that is they are all aligned along the magnetic easy axis of the material, either spin up or spin down – then the scalar density description can still be applied, and the energy will be a functional $E = F[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), s_{\uparrow}(\mathbf{r}), s_{\downarrow}(\mathbf{r})]$, where the charge density $n(\mathbf{r})$ and the spin density $s(\mathbf{r})$

are now spin-polarised – up and down spins are treated separately. This is the basis of the local spin density approximation (LSDA). The first three terms in the Kohn-Sham Hamiltonian of Equation 1.5 have no spin dependence, so the effect of any spin interactions must be included in the exchange-correlation potential. In fact the new, spin dependent exchange correlation potential can be split into two terms [14]: the first, solely charge-dependent, is simply $V_{xc}(\mathbf{r})$ from the LDA case; the second, solely spin dependent, is given by:

$$V_{xc}^{\text{LSDA}}(\mathbf{r}) = \mu_B \boldsymbol{\sigma} \cdot \mathbf{B}_{xc}(\mathbf{r}) \quad (1.14)$$

where $\mathbf{B}_{xc}(\mathbf{r})$, the ‘exchange-correlation magnetic field’, can be viewed as the effective magnetic field generated by the other electrons in the system, and is a functional $\mathbf{B}_{xc}(\mathbf{r})[s_{\uparrow}(\mathbf{r}), s_{\downarrow}(\mathbf{r})]$ with a numerically calculated parameterised form [14]. For magnetic materials where the spins are collinear (so ferromagnetic or antiferromagnetic ordering) LSDA calculations – or those using an adapted GGA method, which incorporates the spin density gradients $\nabla s_{\uparrow}(\mathbf{r}), \nabla s_{\downarrow}(\mathbf{r})$ into the functional – are often able to predict the correct magnetic structure and total moment.

Density functional theory+ U calculations

As the charge density becomes spin-polarised in LSDA calculations, this affords the opportunity for a more careful consideration of the exchange potential. In the course of calculating the exchange energy in the L(S)DA (or GGA) method it is assumed, in Equation 1.9, that there are an equal number of spin up and spin down electrons, both occupying the same energy states. However the exchange term itself actively penalises this configuration, assigning an energy cost for doubly occupied states equivalent to the Coulomb repulsion. In systems with strongly correlated d or f electrons – such as rare earth compounds and transition metal Mott insulators – this energy cost is large enough to change the occupancy of the states, and so L(S)DA calculations are unable to reproduce the measured electronic structure. To account for the exchange interaction at each

individual site, a Hubbard term can be added to the total energy of the system:

$$E = E_{\text{LDA}} + \frac{1}{2}U \sum_{i=1}^N n_{i\uparrow}n_{i\downarrow} - \frac{1}{2}UN(N-1) \quad (1.15)$$

where U is the energy cost of a doubly occupied state and the final term is a ‘double counting correction’ which removes the energy cost of the doubly occupied states already accounted for in the LDA exchange energy of Equation 1.9. The sum is typically conducted over only the d and f electronic sites [15]. The effect of this additional Hubbard term is to lower the energy states of one spin configuration and raise those of the other (the choice of which is arbitrary); if U is chosen to be large enough this then has the effect of localising the d and f electrons of the system. These LSDA+ U and GGA+ U calculations are able, with a carefully chosen U , to reproduce the electronic structure for many systems where the usual LSDA and GGA calculations comprehensively fail.

A number of off-the-shelf software packages exist that perform the DFT calculations outlined here, taking an input of ionic positions in the unit cell and calculating the electronic structure using the LDA or GGA method, with the possibility of adding spin-orbit coupling, spin-polarisation or the Hubbard U term. It is through this framework that the DFT calculations in this thesis were performed, with details given in Section 1.3.1 of their implementation. The successes and failures of DFT in this thesis mirror those seen across condensed matter physics: for non-magnetic materials with relatively light elements the GGA method (with spin-orbit coupling) can be a highly accurate determiner of the electronic structure; for materials with heavier d or f orbital elements the spin-polarised GGA+ U method can still be tuned to produce much of the experimental band structure; while for materials with stronger electronic correlations DFT calculations, even with a few manual shifts to the resulting band structure, are at best only able to provide a rough semblance to the measured electronic structure. Despite this, DFT still currently provides the most universally applicable framework for calculating the electronic properties of any solid state system, and the success of its individual electron approach

is testament to the breadth of Fermi liquid theory. Even for systems where its success is limited, the exact nature of the discrepancies between it and the measured electronic structure can still be indicative of the origin of the strong electronic correlations present.

1.2.3 Quantum oscillations

Perhaps what could be classed as the first real ‘observation’ of a Fermi surface occurred in 1930 at the University of Leiden in the cryogenics laboratory of Kamerlingh Onnes which, for a time, was the coldest place on Earth thanks to its ability to liquify Helium. While measuring the low temperature properties of Bismuth Wander Johannes de Haas, alongside his student Pieter van Alphen and the visiting Lev Shubnikov, observed oscillations in the magnetic field dependence of both the conductivity, the Shubnikov-de Haas effect [16], and the magnetisation, the de Haas-van Alphen effect [17]. The significance of these results was not noted until 1952 however, when Lars Onsager determined they arose from quantised electronic orbits around the Fermi surface [18], with a full derivation given by Ilya Lifshitz and Arnold Kosevich in 1956 [19].

Landau tubes and Fermi surface areas

These ‘quantum oscillations’ seen in the low temperature physical properties of metals arise from the quantising effect of an applied magnetic field on the electronic states near the Fermi surface. Considering first the simplest case of a free electron gas, when a magnetic field² is applied along the z -direction, $\mathbf{B} = B \hat{\mathbf{z}}$, k_x and k_y are no longer good quantum numbers – instead a free electron will travel in helical cyclotron orbits around the applied field, described by quantum numbers l and (the unchanged) k_z . The energy of this free electron will then be given by [1]:

$$E(k_z, l) = \frac{\hbar^2}{2m_e} k_z^2 + (l + \frac{1}{2}) \hbar \omega_c \quad (1.16)$$

²In this thesis I will refer to the magnetic field as $\mathbf{B}$ (units Tesla), which is the externally applied magnetic field – that determines, amongst other things, the frequency of quantum oscillations – related to the H -field of the sample by $\mathbf{B} = \mu_0 \mathbf{H}$. This is different to the B -field of the sample, given by $\mathbf{B}_s = \mu_0(\mathbf{H} + \mathbf{M})$.

where $l \in \mathbb{N}$ and the cyclotron frequency is given by:

$$\begin{aligned}\omega_c &= \frac{eB}{m^*}, \\ m^* &= \frac{\hbar^2}{2\pi} \frac{\partial A(E, k_z)}{\partial E}\end{aligned}\tag{1.17}$$

with $A(E, k_z)$ the in-plane area (in reciprocal space) of the electronic orbit.

The in-plane motion is therefore confined to a number of ‘Landau levels’ described by quantum number l . The difference in energy between adjacent Landau levels then follows from Equations 1.16 and 1.17:

$$\begin{aligned}E(k_z, l+1) - E(k_z, l) &= \frac{2\pi eB}{\hbar} \frac{\partial E}{\partial A(E, k_z)} \\ &\approx \frac{2\pi eB}{\hbar} \frac{E(k_z, l+1) - E(k_z, l)}{A(E(k_z, l+1), k_z) - A(E(k_z, l), k_z)}\end{aligned}\tag{1.18}$$

assuming that the energy of adjacent Landau levels is far greater than the difference between them, which should be the case near the Fermi level. Rearranging this gives the difference in area between adjacent orbits to be:

$$\Delta A_{l+1, l} = \frac{2\pi eB}{\hbar}\tag{1.19}$$

This is known as the Onsager relation.

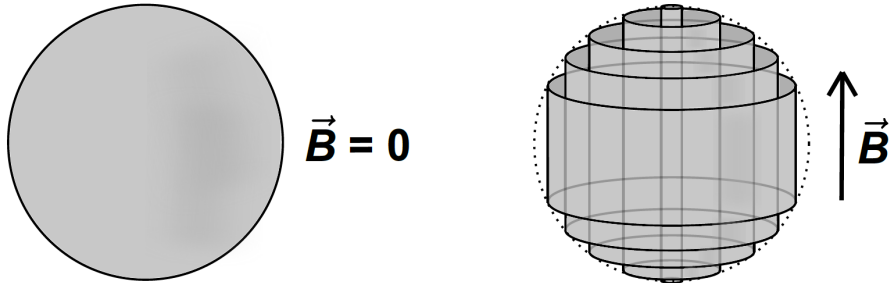


Figure 1.3: **The formation of Landau tubes with applied magnetic field for a free electron gas.** Shown is the Fermi sphere of occupied states and the Landau tubes formed within this sphere when a magnetic field is applied.

The effect of the applied magnetic field is therefore to confine the allowed electronic states to a number of ‘Landau tubes’ in reciprocal space, of cross-sectional area $A_l = 2\pi eB(l + \lambda)/\hbar$ (where λ is a constant). Figure 1.3 shows these Landau tubes for the free

electron gas: with no applied field the allowed states of this completely isotropic system form a ‘Fermi sphere’; with the application of field these states become a series of coaxial Landau tubes along the field direction, all still within the Fermi sphere. In both cases the Fermi surface is the same – the sphere indicated with a dashed line encompassing the Landau tubes. Generalising to the case of a Fermi liquid, the occupied states no longer form a Fermi sphere but instead an arbitrarily shaped Fermi surface. However the Landau tube picture is still – at least in the vicinity of the Fermi surface – valid, although instead of coaxial cylinders the tubes will now follow the contours of a constant (neglecting the k_z contribution) energy surface through the Brillouin zone [1].

From the Onsager relation of Equation 1.19 it is clear that the size of the Landau tubes, and hence the energies of the occupied electronic states, will vary with the size of the applied magnetic field. Reverting back to the case of a free electron gas, from Equation 1.18 the in-plane area of the electronic states around a Landau tube is given by $\delta A = 2\pi eB/\hbar$, so, taking the number of states per unit k -space to be $V/4\pi^3$ [1], the number of states per Landau tube within a slice (width δk_z) perpendicular to the magnetic field will be:

$$N_l = \left(\frac{2\pi eB}{\hbar} \right) \left(\frac{V}{4\pi^3} \right) \delta k_z = \frac{eBV}{2\pi^2\hbar} \delta k_z \quad (1.20)$$

The total energy of the occupied electronic states within the slice will be given by:

$$E_{\text{slice}} = \sum_{l=0}^{L-1} N_l E(k_z, l) \quad (1.21)$$

where L is the number of occupied Landau tubes. Substituting in Equations 1.16, 1.17 and 1.20 gives:

$$\begin{aligned} E_{\text{slice}} &= \sum_{l=0}^{L-1} \left(\frac{eBV}{2\pi^2\hbar} \delta k_z \right) \left(\frac{\hbar^2}{2m_e} k_z^2 + \left(l + \frac{1}{2} \right) \frac{\hbar eB}{m^*} \right) \\ &= \left(\frac{eBV}{2\pi^2\hbar} \delta k_z \right) \left(\frac{\hbar^2}{2m_e} k_z^2 L + \frac{\hbar eB}{2m^*} L(L+1) + \frac{\hbar eB}{2m^*} L \right) \\ &= \frac{e^2 B^2 V}{4\pi^2 m^*} \delta k_z \left(L^2 + 2L + \frac{\hbar m^*}{e B m_e} k_z^2 L \right) \end{aligned} \quad (1.22)$$

The number of occupied Landau tubes L can be calculated by simply rearranging the Onsager relation:

$$L = \lfloor \frac{\hbar A_F}{2\pi e B} (-\lambda) \rfloor \quad (1.23)$$

where the floor function $\lfloor x \rfloor$ returns the largest integer $\leq x$ and A_F is the Fermi surface area within the slice (λ is an arbitrary constant).

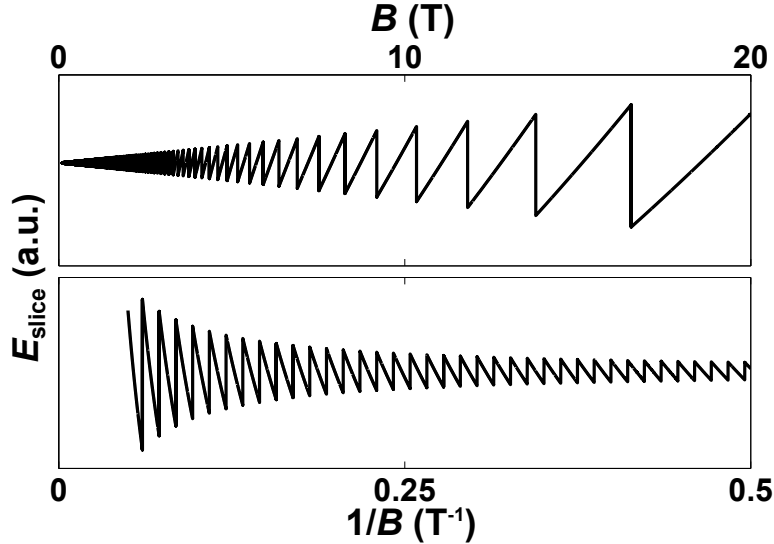


Figure 1.4: **Energy variation with magnetic field for the occupied states beneath the Fermi level**, calculated from Equation 1.22 for a Fermi surface pocket that takes up 0.5% of a $(5 \text{ \AA})^3$ Brillouin zone.

This discrete variation of L leads to sawtooth oscillations in the energy, shown in Figure 1.4: the Landau tubes increase in size with increasing field, so for a constant L the energy increases as $\sim B^2$; however every time a Landau tube passes through the Fermi surface, decreasing L by one, its electronic states empty and there is a sudden drop in the energy. These oscillations are periodic in $1/B$, with a frequency given by Equation 1.23 of:

$$F = \frac{\hbar}{2\pi e} A_F \quad (1.24)$$

essentially a restatement of the Onsager relation. This does mean, however, that each cross-section of the Fermi surface perpendicular to the applied field will produce oscillations in the total energy of the system, with a frequency F on the order 10^0 - 10^4 T, depending on the Fermi surface size. This concept of a Fermi surface frequency – essentially a measure of its cross-sectional area perpendicular to an applied magnetic field – is

the keystone of the quantum oscillations lexicon used throughout this thesis.

To consider the effect of the Landau tube quantisation on the total energy of the system, rather than just the energy of a single slice of the Fermi surface, it is necessary to integrate Equation 1.22 over all k_z within the first Brillouin zone. The variation in the Fermi surface area $A_F(k_z)$ will render this integral a sum of the oscillations of Figure 1.4 over all possible frequencies $F(k_z)$ of the Fermi surface. The destructive interference between these frequencies means that only the regions where the frequency varies little with k_z – i.e. $\partial F(k_z)/\partial k_z$ is smallest – will have a net contribution to the total energy. To be explicit, only ‘extremal’ Fermi surface areas – i.e. local minimum or maximum in $F(k_z)$ – will produce oscillatory behaviour in the total energy. Therefore the frequencies observed in quantum oscillations experiments are a direct measure of the extremal cross-sectional areas of the Fermi surface perpendicular to the direction of the applied field. Furthermore these oscillations will only be present for Fermi surfaces with closed sections – if a Fermi surface has only open sections at a certain field configuration then all cross-sectional areas will be infinite, and no oscillations will be observed.

The Lifshitz-Kosevich equation

The above analysis is conducted for the entirely hypothetical case of a free electron gas, considers only the total energy of the system rather than any measurable properties and ignores entirely any damping effects that may be present. However a far more rigorous derivation [19] returns the same fundamental behaviour – oscillations, periodic in $1/B$, with frequencies that correspond to extremal areas of the Fermi surface. For this more general case the Landau free energy is given by the Lifshitz-Kosevich equation:

$$\Omega = \left(\frac{e}{2\pi\hbar}\right)^{3/2} \frac{e\hbar V B^{5/2}}{m^* \pi^2} \sum_{A_{\text{ext}}} \left| \frac{\partial^2 A_{\text{ext}}}{\partial k_{\perp}^2} \right|^{-1/2} \sum_{p=1}^{\infty} p^{-5/2} R_T R_D R_S \cos \left(2\pi p \left(\frac{F}{B} - \frac{1}{2} + \frac{\phi_B}{2\pi} \right) \left[\pm \frac{\pi}{4} \right] \right) \quad (1.25)$$

where R_T , R_D and R_S are damping terms. The first sum extends over all extremal Fermi surface areas perpendicular to the applied field A_{ext} and the second over all p harmonics of the fundamental oscillation frequency; the phase shift in brackets is only present for

a quasi-three dimensional Fermi surface. $|\partial^2 A_{\text{ext}}/\partial k_{\perp}^2|^{-1/2}$ is known as the ‘curvature factor’, and accounts for the curvature of the Fermi surface: an extremal orbit around which the Fermi surface area hardly changes, so $|\partial^2 A_{\text{ext}}/\partial k_{\perp}^2|$ is small, will have many more states contributing to its amplitude than an extremal orbit where the area changes sharply, where $|\partial^2 A_{\text{ext}}/\partial k_{\perp}^2|$ is large.

The temperature damping term

The first damping term, R_T , arises from the thermal broadening of the Fermi-Dirac distribution with temperature. At non-zero temperatures the step function at the Fermi level will be broadened over a range $k_B T$, so the Fermi surface is no longer a well defined demarcation between occupied and unoccupied states. This ‘smearing’ of the Fermi surface results in a superposition of multiple oscillations around the Fermi surface frequencies, constructively interfering to reduce the amplitude of oscillation. This thermal damping is given by [20]:

$$R_T = \frac{X}{\sinh(X)}, \quad (1.26)$$

$$X = \frac{2\pi^2 k_B T p m^*}{e \hbar B}$$

Intuitively R_T depends on $X \propto k_B T / \hbar \omega_c$, so the damping will be large when the thermal broadening is comparable to or greater than the spacing between adjacent Landau levels. Therefore both low temperatures and high fields are required to reduce the thermal damping so that oscillations may be observed – Figure 1.5a) shows the field dependence of the total amplitude of oscillation, taking a typical effective mass of $m^* = 1 m_e$, at a variety of temperatures to illustrate this point. In fact R_T contains the entire temperature dependence of Equation 1.25, and so by fitting the temperature dependence of the amplitude, for a fixed value of field, to Equation 1.26 the effective mass m^* can be extracted. Figure 1.5b) shows examples of these ‘Lifshitz-Kosevich fits’ for a range of values of m^* .

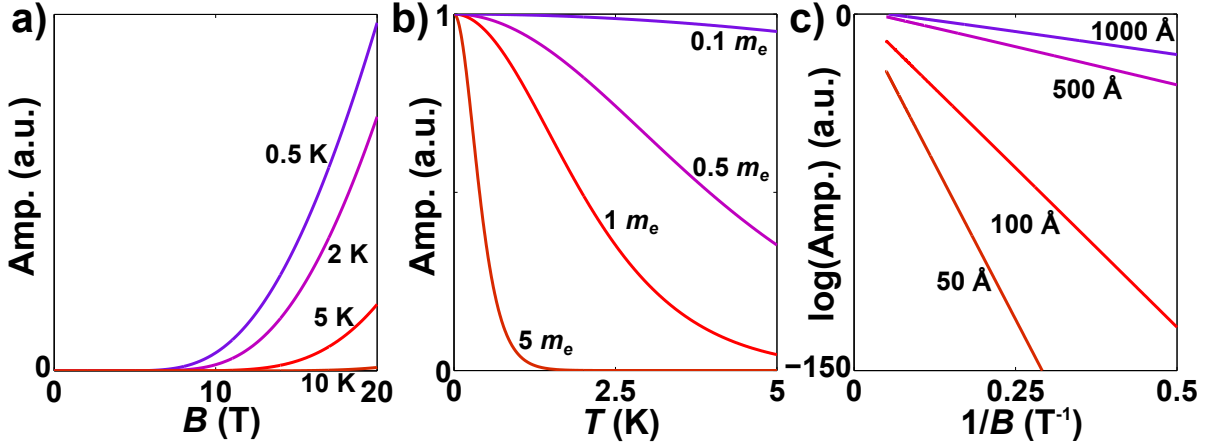


Figure 1.5: **Effect of damping terms on quantum oscillation amplitude.** a) Temperature and field dependence of the amplitude, calculated for $m^* = 1 m_e$, $F = 500$ T, $l_D = 500$ Å. b) Lifshitz-Kosevich plot of the temperature dependence of the amplitude for different effective masses, calculated at $B = 13.3$ T. c) Dingle plot of the impurity scattering term, calculated for $F = 500$ T.

The impurity damping term

The second damping term, R_D , known as the Dingle term, arises from inhomogeneity and impurity scattering within the material. Due to these processes, an electron close to the Fermi level will occupy an eigenstate for a finite lifetime τ before being scattered³. By the uncertainty principle this finite lifetime leads to an approximately Lorentzian broadening of the energy levels, which again leads to a smearing of the Fermi surface. Assuming that τ is independent of energy – valid at the Fermi level where the Landau tubes are closely spaced – this damping takes the form [20]:

$$R_D = \exp\left(-\frac{\pi p m_b}{e B \tau}\right) \approx \exp\left(-\frac{2\pi^2 \hbar \sqrt{F}}{e l_D B}\right) \quad (1.27)$$

where for the approximate equality the mean free path is defined as $l_D = \tau v_F = \tau \hbar k_F / m_b$ and the orbit is approximated to a circle such that $\pi k_F^2 = A_{\text{ext}} = (2\pi e / \hbar) F$. Again this damping decreases with increasing field, but it also depends on the mean free path l_D of the system, indicative of the sample quality. In the field range achievable experimen-

³This ‘quantum lifetime’ τ is different to, and intrinsically shorter than, the ‘classical lifetime’ of Drude-Sommerfeld theory, which requires multiple scattering events to fully randomise the momentum – the two can sometimes differ by orders of magnitude [21].

tally a relatively small difference in l_D can have an enormous effect on the amplitude of oscillation: taking $F = 500 \text{ T}$ and $B = 20 \text{ T}$, $R_D(l_D = 500 \text{ \AA})/R_D(l_D = 100 \text{ \AA}) \approx 2500$. Therefore high sample quality is paramount for the observation of quantum oscillations. To extract the value of l_D from the quantum oscillation amplitude, a ‘Dingle plot’ of the log of the amplitude (or more accurately the amplitude divided by R_T , if both T and m^* are known) against inverse field can be made, as shown in Figure 1.5. The gradient of this line then, for a known frequency, gives l_D from Equation 1.27. This is useful both as a measure of sample quality and an indicator of the scattering processes within the material.

The spin splitting term

The final damping term, R_S , is due to the Zeeman splitting of the energy levels by the applied magnetic field. Rather than a smearing of the Fermi surface, as was the case for R_T and R_D , this spin splitting will instead result in a separation of the Fermi surface – of magnitude $\Delta E = g\mu_B B/2$ – into separate spin up and spin down components, whose frequencies will then interfere. The net result of this interference is an attenuation given by [20]:

$$R_S = \cos\left(\frac{\pi g p m_{ss}^*}{2m_e}\right) \quad (1.28)$$

Unlike the other damping terms R_S shows no variation with field or temperature, and would instead appear to be a constant for a given frequency. However any variation in gm_{ss}^* will effect the amplitude of this term, indeed when $g p m_{ss}^*/m_e = 2n + 1$, $n \in \mathbb{N}$ the spin splitting will reduce the amplitude completely to zero, known as a ‘spin zero’. The effect of the spin splitting in a quasi-two dimensional system, where $m_{ss}^*(\theta)$ varies with angle, is explored in Section 2.3.3.

Mass enhancement

Each of the three damping terms described include a different mass: m_b , m^* and m_{ss}^* . The first of these m_b – which determines R_D – is simply the band mass, arising from the dispersion of the band structure and taking no account of any electronic correlations.

This was defined back in Equation 1.3, where the energy bands are calculated without any correlation terms, and so will be the mass obtained from DFT calculations. Taking $\pi k_F^2 = A_{\text{ext}}^{\text{DFT}}$, where $A_{\text{ext}}^{\text{DFT}}$ is the Fermi surface area found by DFT calculations, this can be rewritten as $m_b = (\hbar^2/2\pi) \partial A_{\text{ext}}^{\text{DFT}}/\partial E$.

Under Landau Fermi liquid theory the presence of any electronic correlations will lead to an enhanced effective mass greater than m_b . For an isotropic system of mutually interacting electrons – which serves as a reasonable approximation to a correlated metal – the effect of symmetric electron-electron interactions is an enhancement to the mass of $m'_b = (1 + \lambda_{ee}^s) m_b$, where λ_{ee}^s is therefore a measure of the electron-electron correlations in the system. For the thermal effective mass m^* – which determines R_T and also appears in the heat capacity [1] – electron-phonon coupling enhances the mass in a similar form; for the spin susceptibility effective mass m_{ss}^* – which determines R_S and the Pauli susceptibility – electron-phonon coupling does not contribute, but instead the effective mass is normalised by the antisymmetric electron-electron correlations. These various mass enhancements are given by [22]:

$$\begin{array}{ccc}
(1 + \lambda_{ee}^s + \lambda_{ep}) m_b & & \\
\mathbf{m}^* & & \\
\nearrow & & \\
\mathbf{m}_b \longrightarrow \mathbf{m}'_b & & (1.29) \\
\frac{\hbar^2}{2\pi} \frac{\partial A_{\text{ext}}^{\text{DFT}}}{\partial E} \quad (1 + \lambda_{ee}^s) m_b \searrow & & \\
\mathbf{m}_{ss}^* & & \\
\left(\frac{1 + \lambda_{ee}^s}{1 + \lambda_{ee}^a} \right) m_b & &
\end{array}$$

Therefore comparing the band mass obtained from DFT calculations, m_b , with the effective mass determined from the temperature dependence of the oscillation amplitude, m^* , can give a measure of the strength of the total correlations in the system, $\lambda_{ee}^s + \lambda_{ep}$. Similarly if the spin susceptibility effective mass, m_{ss}^* , can be obtained from the spin

splitting term, then this can give a measure of the electron-electron interactions in the system, $(1 + \lambda_{ee}^s)/(1 + \lambda_{ee}^a)$.

The Berry phase

The other factor not yet considered in Equation 1.25 is the phase shift ϕ_B , known as the ‘Berry phase’. This is equal to the phase gained by the wavefunction of an electron over the course of a single closed orbit of the Fermi surface, and depends solely on the geometry of the orbit, with no time dependence. For all frequencies the Berry phase is trivially zero unless their orbit encompasses a degeneracy in energy, i.e. a point at which two bands cross. These are known as ‘Dirac points’, as band crossings with linear dispersions are capable of producing massless ‘Dirac fermion’ quasiparticles. For each Dirac point encompassed a Berry phase of $\phi_B = \pi$ is gained [23]; therefore only orbits encompassing an odd number of Dirac points, $\phi_B = (2n + 1)\pi$ where $n \in \mathbb{N}$, will produce a non-trivial Berry phase in their oscillations. Alongside a non-trivial Berry phase, very light effective masses and high conductivities are further indicators of a Dirac point within a material, both due to the near-massless properties of Dirac-like fermions [24].

Higher order harmonics

Alongside the fundamental frequencies F that correspond to the extremal orbits of the Fermi surface, Equation 1.25 also produces an infinite number of harmonics with frequencies pF . This multiplicative factor p also appears alongside the mass in all three damping terms of Equations 1.26, 1.27 and 1.28, so these harmonics can be thought of as having enhanced effective masses pm_b , pm^* etc. Because of these enhanced effective masses, as well as the $p^{-5/2}$ term in Equation 1.25, the harmonics will have significantly reduced amplitude compared to the fundamental frequency. Nevertheless second order and higher harmonics are seen fairly frequently experimentally – careful comparison of frequency and mass should be able to ascertain their presence.

Magnetic breakdown

Additional, non-fundamental frequencies may also be generated at high enough fields, when the spacing between adjacent Landau levels becomes comparable to the gaps between different bands of the Fermi surface at certain points within the Brillouin zone. At these points an electron, rather than continuing along its fundamental orbit, may instead tunnel across the k -space gap to the nearby band and pursue an orbit along a different part of the Fermi surface. This ‘magnetic breakdown’ will lead to additional frequencies, at high enough fields, in the quantum oscillations spectrum, corresponding to closed orbits – still contained within slices perpendicular to the applied field – around multiple bands of the Fermi surface.

Figure 1.6 shows a schematic diagram of two Fermi surface orbits, in blue and red, centred on $\mathbf{k}_x$ either side of the origin and separated by a minimum k -space gap of k_g . Rather than continuing along the same orbit an electron may instead tunnel across the region $-k_g/2 \leq k_x \leq k_g/2$, along a path such as that indicated with a dashed black line. The probability of a tunneling event occurring depends on the exact form of this path, and explicitly the variation in k_y over its course. The contribution of this variation to the energy, proportional to k_y^2 , can be seen as a weakly varying potential across the path, and so the probability of tunneling is given by the WKB approximation [25]:

$$\begin{aligned} P &= \exp \left(-2 \int \sqrt{\frac{2m(E - V(r))}{\hbar^2}} dr \right) \\ &= \exp \left(-2 \int \sqrt{-k_y^2} dr \right) \end{aligned} \quad (1.30)$$

where the integral extends along r over the length of the tunneled path.

In the vicinity of the tunneling points the two orbits can be approximated to circles, of radii $1/a$ and $1/b$ respectively. Taking the explicit example of the point (k_x^a, k_y^a) , on the blue orbit, indicated in Figure 1.6 this gives:

$$\begin{aligned} k_y^a{}^2 &= \left(\frac{1}{a} \right)^2 - \left(k_x^a - \left(-\frac{k_g}{2} - \frac{1}{a} \right) \right)^2 \\ &\approx -\frac{2}{a} \left(k_x^a + \frac{k_g}{2} \right) \end{aligned} \quad (1.31)$$

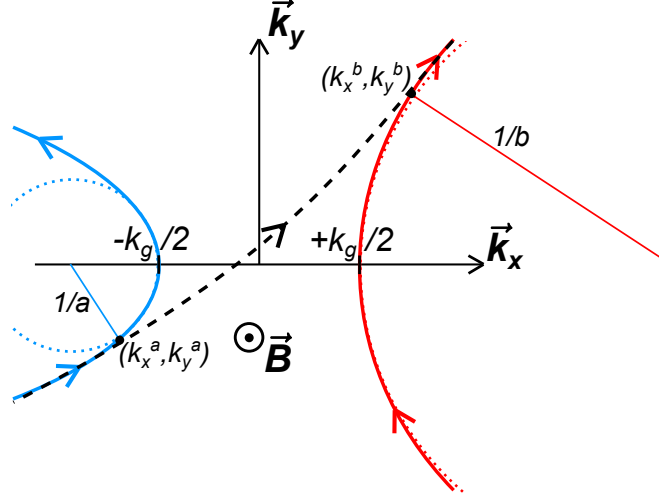


Figure 1.6: **Schematic diagram of orbit tunneling by magnetic breakdown**, shown for the simplified case of two orbits separated by k_g along $\mathbf{k}_x$. In large enough fields the electron may tunnel between two separate bands of the Fermi surface (in blue and red), with a possible path indicated by the black dashed line.

where, as $1/a \gg k_g$ for a real case of magnetic breakdown (i.e. the gap between the orbits is far smaller than the orbits themselves), the second order term is ignored. Similarly at the point (k_x^b, k_y^b) on the red orbit, close to the tunneling point, the orbit can be described by:

$$k_y^{b\ 2} \approx -\frac{2}{b}(-k_x^b + \frac{k_g}{2}) \quad (1.32)$$

At its limits of $k_x = \pm k_g$ the tunneling path must join up with the orbits, and so must satisfy Equations 1.31 and 1.32 respectively, along with their derivatives, for the slope to be continuous. This can be achieved by two parabolic functions of the form:

$$-k_y^2 = \begin{cases} \frac{k_g}{(a+b)} \left(1 - \frac{(a+b)^2}{k_g^2 a^2} (k_x - k_1)^2 \right) & -k_g/2 \leq k_x \leq k_1 \\ \frac{k_g}{(a+b)} \left(1 + \frac{(a+b)^2}{k_g^2 b^2} (k_x - k_1)^2 \right) & k_1 \leq k_x \leq +k_g/2 \end{cases} \quad (1.33)$$

which are of equal heights and zero slope at the cross over point $k_1 = k_g/2 (a - b)/(a + b)$.

Using this form of $-k_y^2$, the integral of Equation 1.30 can be solved exactly [25]:

$$\begin{aligned} \int \sqrt{-k_y^2} dr &= \int_{-k_g/2}^{+k_g/2} \sqrt{-k_y^2} \frac{\hbar}{eB} dk_x \\ &= \frac{\pi}{4} \left(\frac{k_g^3}{a+b} \right)^{1/2} \frac{\hbar}{eB} \end{aligned} \quad (1.34)$$

using $\hbar \dot{\mathbf{k}} = -e\mathbf{r} \times \mathbf{B}$ for the change of variables. The tunneling probability is therefore given by:

$$\begin{aligned} P &= \exp \left(-\frac{\pi \hbar}{2eB} \left(\frac{k_g^3}{a+b} \right)^{1/2} \right) \\ &= \exp \left(-\frac{B_{BD}}{B} \right) \end{aligned} \quad (1.35)$$

where B_{BD} can be thought of as a ‘breakdown field’ above which tunneling events become significant and breakdown orbits may be observed. In the nearly-free electron model $(a+b) \sim 1/k_g$ and $k_g/k_F \sim E_g/E_F$ [20] – where E_g is the energy gap between the bands – so, relating the field to the cyclotron frequency of the Landau tubes by Equation 1.17, the raised term in Equation 1.35 reduces to $B_{BD}/B \sim \pi(E_g^2/E_F)/(\hbar\omega_c)$, with the same result returned by a far more rigorous derivation [26]. As expected, when the energy spacing between Landau levels $\hbar\omega_c$ is comparable to the energy gap E_g between bands the tunneling will have high probability, but in fact this criterion is much more generous than that: $E_F \gg E_g$, so breakdown orbits will be accessible when $\hbar\omega_c$ is only a fraction of E_g . Therefore, for Fermi surfaces with bands in close proximity, magnetic breakdown orbits are readily accessible at experimental magnetic fields, and can play a significant role in determining the quantum oscillations spectrum.

The de Haas-van Alphen effect

To obtain the exact form of the oscillations observed experimentally, the measured property must be obtained from the Landau free energy of Equation 1.25. For the de Haas-van Alphen effect this is the magnetisation, which is a function of state and so can be directly related to Ω . The oscillatory component of the magnetisation parallel to the applied field is given by [20]:

$$\begin{aligned} \tilde{M}_{\parallel} &= - \left(\frac{\partial \Omega}{\partial B} \right)_{\mu} \\ &\approx \left(\frac{e}{\hbar} \right)^{3/2} \frac{e \hbar F V B^{1/2}}{\sqrt{2} m^* \pi^{5/2}} \sum_{A_{\text{ext}}} \left| \frac{\partial^2 A_{\text{ext}}}{\partial k_{\perp}^2} \right|^{-1/2} \sum_{p=1}^{\infty} p^{-3/2} R_T R_D R_S \sin \left(2\pi p \left(\frac{F}{B} - \frac{1}{2} + \frac{\phi_B}{2\pi} \right) \left[\pm \frac{\pi}{4} \right] \right) \end{aligned} \quad (1.36)$$

where the derivative is only taken of the rapidly varying, sinusoidal part as this will be by far the dominant contribution. However the torque on the sample in an applied field – the technique used in this thesis to measure the magnetisation – depends on the component of the magnetisation perpendicular to the applied field: $\boldsymbol{\tau} = \mathbf{M} \times \mathbf{B}$. This is given by [20]:

$$\begin{aligned}\tilde{M}_{\perp} &= -\frac{1}{B} \left(\frac{\partial \Omega}{\partial \theta} \right)_{\mu, B} \\ &\approx -\frac{1}{B} \frac{\partial F}{\partial \theta} \left(\frac{\partial \Omega}{\partial F} \right)_{\mu, B} \\ &\approx -\frac{1}{F} \frac{\partial F}{\partial \theta} M_{\parallel}\end{aligned}\tag{1.37}$$

where again it is assumed that the sinusoidal term dominates the derivative, so only the angular dependence of $F(\theta)$ (and not $R_T(\theta)$, $R_D(\theta)$ etc.) is considered. This oscillatory component $\tilde{M}_{\perp}$ appears in addition to the ‘background’ magnetisation of the material, and so the total magnetisation measured by torque will be the sum of the oscillatory and background components. The prefactor in Equation 1.37 can be considered as an additional damping term that only occurs for torque measurements: $R_{\tau} = -(1/F)(\partial F/\partial \theta)$. For a perfectly three-dimensional Fermi surface F is independent of angle, so $R_{\tau} = 0$ and no oscillations will be observed; for a two-dimensional Fermi surface $F = F(0)/\cos(\theta)$ (where θ is the angle made with the high symmetry axis), so $R_{\tau} = \tan(\theta)$ and no oscillations will be observed when the field is along the high symmetry direction.

The Shubnikov-de Haas effect

The conductivity of the material, σ_{xx} , is not a function of state, so cannot be calculated so easily from the Landau free energy. Instead it is determined by the scattering processes in the material, with each scattering event corresponding to an electron close to the Fermi level changing its eigenstate. By Fermi’s golden rule the rate of transition between eigenstates is proportional to the density of final states, so the scattering rate in the material will be proportional to the density of states at the Fermi level. The Landau free energy at an arbitrary energy E is simply (assuming $T = 0$) the sum of the energies of

all states below E [20]:

$$\Omega(E, T = 0) = \int_{-\infty}^E (\varepsilon - E)g(\varepsilon)d\varepsilon \quad (1.38)$$

Differentiating this twice with respect to E therefore gives the density of states in terms of $\Omega(E)$:

$$g(E) = -\frac{\partial^2 \Omega(E, T = 0)}{\partial E^2} \quad (1.39)$$

Evaluating this at the Fermi level obtains the density of states at the Fermi level in terms of the Landau free energy $\Omega = \Omega(E_F, T)$ of Equation 1.25:

$$\begin{aligned} g(E_F) &= -\left(\frac{\partial^2 \Omega(E, T = 0)}{\partial E^2}\right)_{E=E_F} \\ &\approx -\frac{\partial F}{\partial E} \frac{\partial}{\partial F} \left(\frac{\partial F}{\partial E} \frac{\partial}{\partial F} \left(\frac{1}{R_T} \Omega\right)\right) \\ &\approx -\left(\frac{m^*}{e\hbar}\right)^2 \left(\frac{2\pi p}{B}\right)^2 \frac{1}{R_T} \Omega \end{aligned} \quad (1.40)$$

where again only the derivative of the sinusoidal component is taken, and Equations 1.24 and 1.17 give $\partial F/\partial E = (\hbar/2\pi e) \partial A_F/\partial E = m^*/(e\hbar)$. As $\Omega(E, T = 0)$ is evaluated at zero temperature, the thermal damping term has no effect ($R_T = 1$) and so is divided out. Therefore the oscillations seen in the Landau free energy of the system are also seen in the density of states at the Fermi level. These oscillations are then also present in the conductivity, although π out of phase – when there is a maxima in $g(E_F)$ the rate of scattering will be highest, so there will be a minima in σ_{xx} . Furthermore as the number of available states for scattering around E_F increases with increasing temperature, the temperature damping term R_T is reinserted into the amplitude for Shubnikov-de Haas oscillations. A far more rigorous derivation [27] returns essentially the same result:

$$\tilde{\sigma}_{xx} \sim \left(\frac{m^*}{e\hbar}\right)^2 \left(\frac{2\pi p}{B}\right)^2 \Omega \quad (1.41)$$

with the same dependence seen in the resistivity. Again this is only the oscillatory component of the conductivity, there will also be a background term; unlike the magnetisation

however, the total conductivity is the product of the oscillatory and background components, not the sum. Otherwise – excepting the phase difference from the $\sin()$ and $\cos()$ terms respectively – de Haas-van Alphen and Shubnikov-de Haas oscillations are rather similar, both containing the same information about Fermi surface size, shape and correlations. Therefore the choice of which to use depends on the system: typically the de Haas-van Alphen effect is larger [20], and can be measured on samples too small to contact for resistance measurements; however in systems with low carrier densities and high mobilities the Shubnikov-de Haas effect will instead be the bigger of the two, and is often easier to measure in materials with a very large magnetic background. The additional, Fermi surface anisotropy-dependent damping term R_τ also means that less anisotropic (i.e. more quasi three-dimensional) Fermi surfaces will also be seen less strongly in the de Haas-van Alphen effect.

1.2.4 Angle-dependent magnetoresistance oscillations

Through the medium of Shubnikov-de Haas oscillations, magnetoresistance measurements are able to discern a good deal of information about the size and shape of a Fermi surface. However only extremal closed orbits of the Fermi surface contribute to these oscillations, so the majority of the Fermi surface is not involved in their generation. Instead orbits around most of the Fermi surface contribute only to the background magnetoresistance, and in systems where there are no extremal orbits, or the effective masses are too heavy and mean free paths too short, only this background magnetoresistance will be present. Nevertheless, this background magnetoresistance – and specifically its dependence on the direction of the applied magnetic field – can exhibit many features that arise from the geometry and corrugation of the Fermi surface, albeit whose origin may not be as manifest as for quantum oscillations.

Beginning in the 1980s, angle-dependent magnetoresistance measurements (AMR) have been used to look for various Fermi surface signatures, most commonly in the quasi-one dimensional organic conductors [28] but also in materials with large quasi-two dimensional Fermi surfaces such as the cuprate superconductors [29]. In these measurements

the resistivity of the material is measured as the sample is rotated in a constant magnetic field, and – at high enough fields and low enough temperatures – clear features are seen in the angular dependence of diminished or enhanced amplitude. These ‘angle-dependent magnetoresistance oscillations’ (AMRO) are oscillations in the background magnetoresistance, and may appear alongside – but unrelated to – Shubnikov-de Haas oscillations, which will also be present in the AMR if the oscillation frequency varies with the rotated angle.

Lebed magic angles

The conductivity at a certain orientation of magnetic field will be determined by the paths – and specifically the velocities – of the cyclotron orbits the electrons traverse around the field. Explicitly the conductivity tensor is given by the Boltzmann transport equation [1]:

$$\sigma_{ij} = e^2 \int \frac{d\mathbf{k}}{4\pi^3} v_i(\mathbf{k}) \left(-\frac{\partial f(\mathbf{k})}{\partial E(\mathbf{k})} \right) \int_0^\infty dt e^{-t/\tau} v_j(\mathbf{k}(t)) \quad (1.42)$$

where the first integral is simply a sum of all electron velocities and the second integral – assuming an (energy dependent) relaxation time τ – accounts for the probability of scattering from velocity state $v_i(\mathbf{k})$ to $v_j(\mathbf{k})$; $f(\mathbf{k})$ is simply the Fermi function. Only electrons close to the Fermi level will have a non-zero contribution to the integrals of Equation 1.42, as those more than $k_B T$ below the Fermi level will still be completely occupied and so are collectively inert. Therefore it is the orbits of electrons close to the Fermi level that determine the conductivity of the system.

In the band structure model of electronic states the velocity depends on the dispersion of the bands, as [1]:

$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial \mathbf{k}} \quad (1.43)$$

Therefore the electron velocity at the Fermi level will be normal to the surface of constant energy, i.e. the Fermi surface. In an applied field the force on the electron is given by [1]:

$$\hbar \frac{\partial \mathbf{k}}{\partial t} = -e \mathbf{v}_n(\mathbf{k}) \times \mathbf{B} \quad (1.44)$$

so the electronic orbits in reciprocal space are perpendicular to the electron velocity and are therefore contained on the Fermi surface. These orbits must also be perpendicular to the applied field, so the field orientation will determine the possible orbits around the Fermi surface of a material, the velocities and scattering processes of which – through Equation 1.42 – determine the conductivity of the material.

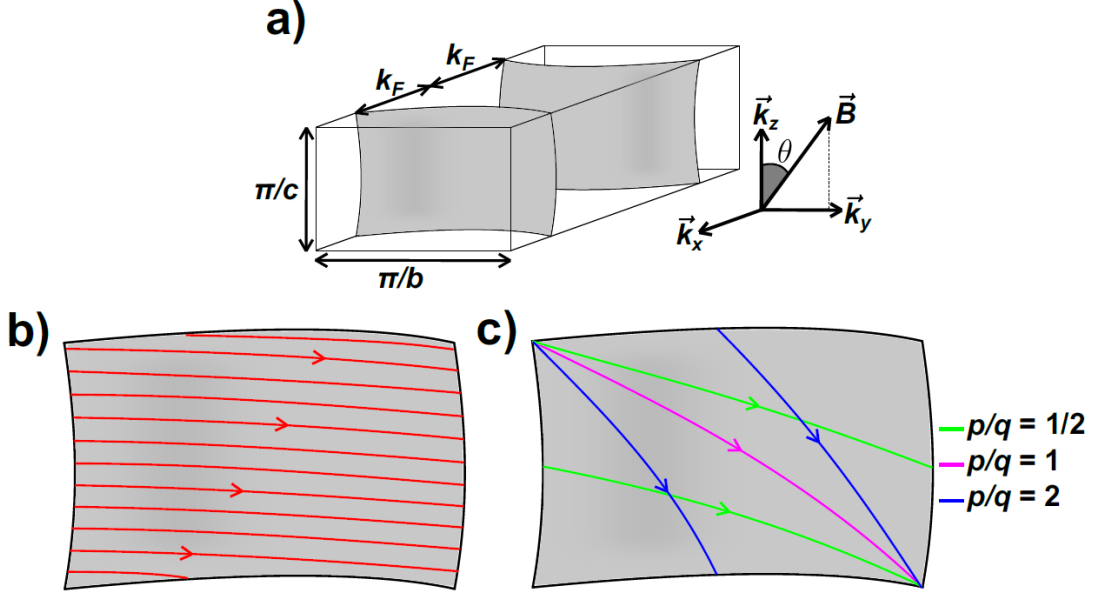


Figure 1.7: **Electronic orbits on a Fermi surface sheet for a magnetic field applied within the sheet**, for the simple case of an orthorhombic structure. **a)** Cartoon Fermi surface of two corrugated sheets perpendicular to $\mathbf{k}_x$, located at $\pm k_F \hat{\mathbf{x}}$. **b)** Electronic orbit for an arbitrary (p/q irrational) field orientation. **c)** Electronic orbits for field orientations corresponding to $p/q = 1/2, 1, 2$.

Figure 1.7a) shows the simple case of a quasi-one dimensional Fermi surface arising from an orthorhombic crystal structure. The cartoon Fermi surface consists of two corrugated sheets normal to the low symmetry axis $\mathbf{k}_x$, located at $\pm k_F \hat{\mathbf{x}}$ either side of the Γ point. If the magnetic field is rotated in the plane of the Fermi surface sheets, perpendicular to $\mathbf{k}_x$, the allowed electronic orbits will all be open, forming straight lines in the $\mathbf{k}_y$ - $\mathbf{k}_z$ plane. At an arbitrary field orientation – for which the orbits travel an irrational portion of π/b in $\mathbf{k}_y$ or π/c in $\mathbf{k}_z$ each time they cross the Brillouin zone – the electron must cross the Brillouin zone an infinite number of times to return to the same position and complete its orbit, as shown in Figure 1.7b). Therefore a single orbit will traverse the entirety of the Fermi surface sheet, and the contribution of every orbit to the conductivity of Equation 1.42 will be identical and independent of field orientation – an integral

over the entire Fermi surface sheet, acting to average out the velocities and scattering processes for all the states at the Fermi level.

However at a select few field orientations, known as Lebed magic angles [30], the orbits will cover a fraction $1/p$ of π/b in $\mathbf{k}_y$ and $1/q$ of π/c in $\mathbf{k}_z$ each time they cross the Brillouin zone. The electron must then cross the Brillouin zone a finite, integer, p or q number of times to return to its position, and so each orbit covers only a small portion of the Fermi surface sheet. Figure 1.7c) shows example orbits for the cases $p/q = 1/2, 1$ and 2 . At these field orientations the integrals of Equation 1.42 will no longer be over the entire Fermi surface, so the velocity averaging and scattering processes will vary with different orbits, leading to significant changes in the conductivity at these field orientations. For the orthorhombic Fermi surface of Figure 1.7a), basic trigonometry finds the Lebed magic angles occur at:

$$\tan(\theta) = \frac{p}{q} \frac{b}{c} \quad (1.45)$$

with θ the angle between the magnetic field and $\mathbf{k}_z$, as shown in Figure 1.7. The more general case for a triclinic system is given later in Equation 4.2.

Resistivity dips at Lebed magic angles

The exact origins of the conductivity changes at Lebed magic angles are not completely understood, however some simple models are able to qualitatively explain why the orbit paths may affect the velocity and scattering terms in the integrals of Equation 1.42 [28]. Figure 1.8a) shows a Fermi surface sheet normal to $\mathbf{k}_x$ with corrugation along $\mathbf{k}_z$. For an orbit which covers the entire Fermi surface – such as that shown on the left, with a section of the orbit plotted and the velocities indicated by black arrows – the effect of this corrugation will be averaged out, such that the average velocity across the orbit is still parallel to $\mathbf{k}_x$. However for an orbit at a Lebed magic angle this is not the case: for the different orbits shown on the right of Figure 1.8b) – which correspond to the extreme case of $p/q = \infty$ – the average velocity across two of the three orbits will have an in-sheet component, in this case along $\mathbf{k}_y$. Therefore these orbits are able to contribute to the conductivity in the $\mathbf{k}_y$ direction, and so there will be a dip in resistivity at this Lebed

magic angle. A far more rigorous derivation [31] finds essentially the same result, that for any combination of Fermi surface corrugations there will be a dip in the resistivity at Lebed magic angles.

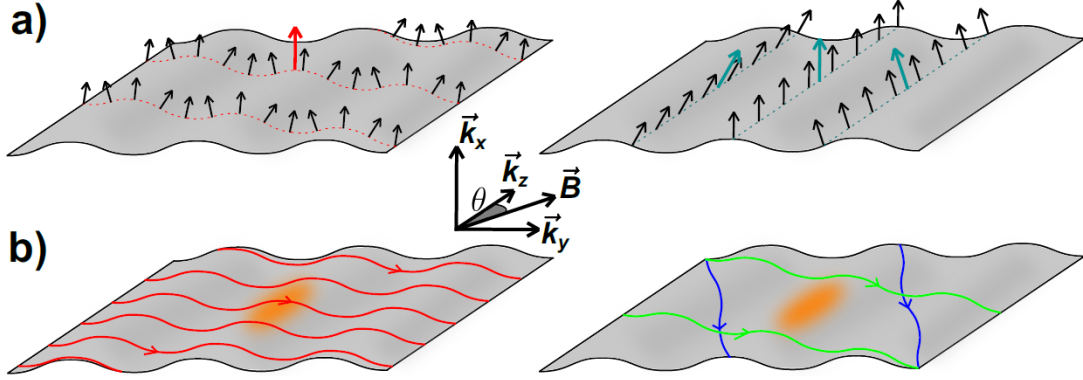


Figure 1.8: **Possible origins of resistivity dips at Lebed magic angles** [28]. **a)** For a corrugated Fermi surface the average (coloured arrows) of the individual (black arrows) velocities across an orbit has no net in-plane component (left), unless the field is oriented at a Lebed magic angle (right). **b)** For a Fermi surface with a ‘hot spot’ of enhanced scattering (marked in orange), all orbits will pass through the hot spot (left), unless the field is oriented at a Lebed magic angle (right).

Concurrently the orbit paths traversed by the electrons will also determine the rate at which they scatter. As the scattering rate is proportional, by Fermi’s golden rule, to the density of states to scatter into, a Fermi surface ‘hot spot’ with a significantly increased density of states – arising where particularly shallow bands cross the Fermi level – or additional scattering processes will have a similarly increased scattering rate. Figure 1.8b) shows such a hot spot (marked in orange) on a Fermi surface sheet. Away from Lebed magic angles the orbits traverse the entire Fermi surface, so all pass through the hot spot and see an increase in their scattering rate – as shown on the left of Figure 1.8b). However at the Lebed magic angles the orbits cover only a small portion of the Fermi surface, so many will miss the hot spot entirely and see no increase in their scattering rate – as shown on the right in Figure 1.8b). This decrease in scattering across multiple orbits will also produce a dip in the resistivity at Lebed magic angles [32].

The positions of the Lebed magic angles are, from Equation 1.45, independent of field, so depend only on the geometry of the system and not the form of the Fermi surface – beyond the fact that it must be a quasi-one dimensional sheet. With larger order p/q

each orbit covers more of the Fermi surface, so the magnitude of the resistivity dips will tend to decrease, vanishing for higher orders. The lower order p/q resistivity dips will occur as long as there is an in-sheet field component, so the field does not necessarily have to be entirely within the Fermi surface sheet, although at that configuration the effect will be strongest. In this more general case Equation 1.45 will now read $\tan(\theta) \sin(\varphi)$ to the left of the equality, where θ is still the angle between the magnetic field and $\mathbf{k}_z$ and φ is the angle between the magnetic field and $\mathbf{k}_x$, the normal to the Fermi surface sheet.

Further AMRO effects

When the field is no longer within the Fermi surface sheet other AMRO effects are also possible, arising from velocity averaging over the corrugated Fermi surface sheets. These are less relevant to the measurements presented in this thesis however, and so are only mentioned in passing. Danner-Kang-Chaikin (DKC) oscillations [33] can occur for $\mathbf{k}_x$ - $\mathbf{k}_z$ rotations – i.e. from the normal to the Fermi surface sheet to the axis of corrugation – and take the form [31]:

$$\tan(\theta) = \frac{\pi \hbar v_F}{2 t_y c} \left(n - \frac{1}{4} \right) \quad (1.46)$$

where t_y is a measure of the corrugation of the Fermi surface and $n \in \mathbb{N}$. For a weakly corrugated Fermi surface the DKC oscillations will be slight, and away from the $\mathbf{k}_x$ - $\mathbf{k}_z$ plane – where there are no Lebed magic angles – the Lebed dips will dominate. A third angular effect (TAE) [34] may also be observed for rotations in the $\mathbf{k}_x$ - $\mathbf{k}_y$ plane, where both the Lebed magic angles and DKC oscillations disappear. Rather than a succession of features this is just a single resistivity dip, with a position given by:

$$\tan(\theta) = \frac{2 t_y b}{\hbar v_F} \quad (1.47)$$

Again the size (and position) of this dip depends on the Fermi surface corrugation.

Increasing the magnetic field will increase the size of the various AMRO resistivity dips as the cyclotron frequency increases, while lower temperatures will also increase

their size as the conduction electrons become tightly contained at the Fermi level and the thermal scattering decreases [31]. Unlike quantum oscillations however, AMRO does not require such a sharply defined Fermi surface ($k_B T \ll \hbar \omega_c$), so the reduction in amplitude with temperature is rather more gradual. AMRO effects are therefore visible at much higher temperatures than quantum oscillations, and of course provide information about the open orbits (of often quasi-one dimensional Fermi surfaces), complimentary to the information about the closed orbits (of quasi-two or quasi-three dimensional Fermi surfaces) provided by quantum oscillations.

1.3 Experimental Techniques

1.3.1 Density functional theory calculations

The Wien2k package

The density functional theory calculations conducted throughout this thesis were performed with the Wien2k software package [13], run in parallel on the ARCUS super-computer in Oxford. This uses the mean field approximation and LAPW method, as outlined in Section 1.2.2, to iteratively calculate the electronic structure, with a choice of either the LDA or GGA form for the exchange-correlation energy (the latter is used for the calculations in this thesis). From a user-generated input file containing the crystal structure (i.e. the lattice parameters, atomic positions and spacegroup) these programs, called through the command line (although a web interface also exists), generate the necessary input files for a calculation. This initialisation process prompts the user to define a number of parameters that define the exact form of the LAPW basis set, such as the atomic sphere radius and the strength of the potential within it; however for most calculations the default values given are sufficient – only when the process generates error messages will these values need to be adjusted, with the general procedures outlined in [13]. The parameter that does require some thought on the user’s behalf is the number of k -points included in the calculation – too small a number and the resulting electronic structure will have poor resolution, too large a number and the calculation will take too

long to complete. A value of about 4×10^4 (a $34 \times 34 \times 34$ k -space grid) generally proves sufficient, with the running time further reduced by converging an initial calculation on a smaller number of k -points (normally 10^3) to provide a starting point for the larger calculation. Finally, the choice of convergence criteria also determines the accuracy and running time of the calculation, with the user providing a maximum difference between iterations that defines the self-consistency. These convergence criteria can be for charge ($n(\mathbf{r})$) or energy ($E(\mathbf{r})$), typically a value of 10^{-5} (in units of e and Ry) is chosen for both. With the values given here a calculation may run through around 40 iterations until convergence for the initial 10^3 k -point calculation, then two or three more until the full, 4×10^4 k -point calculation is converged; run on ARCUS this process takes at most a couple of hours.

On top of this base procedure Wien2k is also able to include the spin-orbit coupling term – which can be turned on for individual atoms – and perform LSDA/spin polarised GGA and LSDA+U/GGA+U calculations – which require a user specified value of U ; the orbital contributions to the density of states at each k -point can also be calculated to determine the orbital character of the energy bands. A number of ancillary programs also exist as part of the Wien2k package, which are able to make one dimensional ‘spaghetti’ plots of the band structure (with energy on the y -axis and some path in k -space on the x) and calculate the density of states and other band structure-determined physical properties; these are the source of the density of states plots and values contained within this thesis.

Fermi surface visualisation and orbit calculation

The Fermi surface may be visualised from the Wien2k output files by the program XCrySDen, which creates its own ‘.BXSf’ file of the band structure. However the options for plotting the electronic structure are rather limited and the colour scheme is very ’90s – all fluorescent colours and white lines on a black background. Therefore for both practical and aesthetic reasons the Fermi surface figures in this thesis are instead plotted with the program FSPlotter (written by myself, based on code by Ed Yelland, for my MPhys

project), which is written in Matlab and so features all of its plotting capabilities, as well as the option of projecting orbital character and Fermi velocity contour plots onto the Fermi surface.

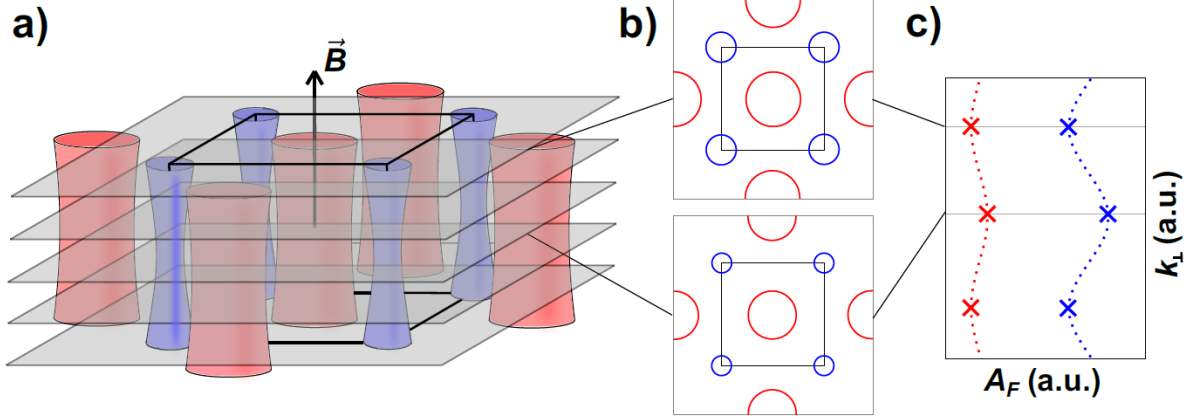


Figure 1.9: **Frequency determination for density functional theory calculated Fermi surfaces.** **a)** The Fermi surface is plotted within a multi-Brillouin zone supercell. **b)** Slices are taken of the Fermi surface perpendicular to the applied field direction, with the Brillouin zone outlined in black; for each slice closed orbits are determined and areas calculated. **c)** Areas are sorted into branches dependent on their size and location; local minima and maxima of individual branches give the extremal areas observed in quantum oscillations.

To calculate the frequencies arising from the DFT calculated Fermi surface, the cross-sectional areas perpendicular to a given field orientation must first be calculated and then compared to determine which are extremal – Figure 1.9 shows the approximate procedure. As orbits may extend out of the first Brillouin zone (although, by the periodicity of the electronic structure, cannot be larger in size than the cross-sectional area of the Brillouin zone) a larger k -space ‘supercell’ is created of multiple tiled Brillouin zones, through which many evenly spaced slices are taken perpendicularly to the applied field, as shown in Figure 1.9a). For each slice the closed orbits are determined – by mapping out, band by band, between which adjacent k -points the Fermi level is crossed, and following these crossings around the slice until the initial crossing is returned to – and the areas they enclose calculated. By comparing the centre-point and size of orbits between slices the areas can then be sorted into branches, such that one branch tracks the evolution of a certain Fermi surface feature as the slices progress along the field direction. For example, in Figure 1.9b) the red orbit at the centre of the Brillouin zone belongs to one branch –

as the orbit around the hole cylinder – while the blue orbits at the four corners of the Brillouin zone belong to four separate branches – as the orbits around the four symmetry equivalent electron cylinders. The local minima and maxima of these Fermi surface areas A_F as a function of $k_\perp$, the distance along the field direction, will then be the extremal areas observed by quantum oscillations; these can be converted to frequencies by Equation 1.24. Figure 1.9c) shows this procedure for the Fermi surface of Figure 1.9a): as expected, each warped cylinder produces two values of extremal area, marked with an ‘x’, corresponding to the narrowest and widest sections of its warping. Calculating the second derivative of this area evolution $|\partial^2 A_F / \partial k_\perp^2|$ gives the curvature factor of Equation 1.25, while by repeating the procedure at energies either side of the Fermi level $\partial A_F / \partial E$ and hence, from Equation 1.17, the band mass can also be determined.

For the DFT calculations in this thesis the frequency finding routine is performed by FSPlotter, with one exception: for the low symmetry calculations of Section 4.2.3 FSPlotter is not (yet) able to convert the electronic structure – Wien2k returns the energies for the smallest possible set of inequivalent k -points, so the symmetry operations (which have not yet been encoded into FSPlotter for lower symmetry spacegroups) of the lattice must then be used to fully repopulate the Brillouin zone – so instead the SKEAF program [35], which follows the same procedure but is written in Fortran, is used; this takes the input of an XCrySDen generated .BXSf file, during the construction of which the Brillouin zone repopulation has already been performed. For a simple Fermi surface producing only a few frequencies of reasonable size – such as the example of Figure 1.9 – this frequency finding routine is pretty robust, however for more complex Fermi surfaces with many (often small) frequencies and intricate features – such as those encountered in Section 3.3.2 – the routine can struggle, missing some frequencies or identifying others spuriously. This is a result of the resolution, with the finite k -space grid limiting the size and smoothness of the Fermi surface features rendered. A larger number of k -points in the Wien2k calculation (for the Fermi surfaces of Section 3.3.2 10^5 k -points, a $46 \times 46 \times 46$ grid, is used), coupled with a smooth (cubic or spline) interpolation to generate a larger k -space grid for the frequency determination, is somewhat able to remedy this.

Magnetic breakdown calculations

To calculate the possible orbits that may arise from magnetic breakdown, an additional step is inserted into the procedure. Once the orbits are determined within a slice, all the potential tunneling points are identified – positions where two different bands of the Fermi surface are separated by less than a specified k_g – and the regions of orbit either side of the tunneling points fitted to a circle to obtain the radii of curvature $1/a$ and $1/b$. Together, by Equation 1.35, k_g , $1/a$ and $1/b$ then determine the breakdown field for the tunneling point. The possible magnetic breakdown orbits are then, for each set of interconnected bands, generated by propagating an electron around an orbit and, upon reaching each tunneling point, creating a copy, such that one electron continues along the original orbit and one tunnels across the gap. In this way an array is generated of electrons traversing every possible magnetic breakdown orbit within the slice, with each orbit halted either when the electron returns to a previous position (so a closed orbit has been generated), traverses too many tunneling points (from Equation 1.35 these orbits are improbable) or travels too far from the first Brillouin zone (so the orbit is, if not open, at least very large, so unlikely to be seen in quantum oscillations). The closed orbits generated by this procedure are then the magnetic breakdown orbits of the slice (alongside the fundamental orbits also). The extremal magnetic breakdown orbits are then calculated by the same method, illustrated in Figure 1.9, as the fundamental orbits – by repeating this process across multiple slices and sorting the orbits into branches.

Comparison between these calculated frequencies and those obtained from quantum oscillations measurements is then instructive towards generating a complete picture of the Fermi surface from only the extremal areas detected by experiment, while any enhancement in the measured effective masses compared to the calculated band masses can, through ‘Equation’ 1.29 give some measure of the correlations in the system. In some strongly correlated systems, notably the Fe-based superconductors [3], although DFT may not on its own be able to reproduce the measured electronic structure, with the application of ‘rigid band shifts’ it can still produce a good correspondence. These

rigid band shifts are shifts either up or down in energy with respect to the Fermi level, chosen and applied individually to each band such that the Fermi surface size matches that observed in quantum oscillations, but also that the Fermi surface remains charge compensated – possessing an equal number of hole and electron states. These arbitrary shifts can be qualitatively justified if the effect of correlations on the system is envisaged as simply a constant offset in energy, applied uniformly to all electrons within a band.

1.3.2 Low temperatures and high magnetic fields

The two main techniques used in this thesis for the measurement of Fermi surfaces – quantum oscillations and AMRO – need both low temperatures and high magnetic fields to be observed. Both of these are provided by the variety of cryostats used for the measurements, in which the sample(s) to be measured are placed – at the end of a long probe, enclosed in an evacuated jacket – at the centre of a solenoid, immersed in a bath of Helium-4.

Temperature control

To control its temperature, the probe sits in a variable temperature insert (VTI), connected to the main bath by a needle valve but otherwise insulated by a vacuum space. For temperatures above the boiling point of Helium-4, 4.2 K, a heater in the VTI can warm the probe, with the cooling power provided by a variable flow of Helium-4 through the needle valve. For temperatures below 4.2 K a volume of Helium-4 is introduced into the VTI, which is then pumped on; this lowers the pressure and hence the boiling point of Helium-4 and, depending on pump rate, can achieve temperatures down to 1.4 K. Ideally the needle valve can be kept very slightly open during these measurements – such that the rate at which Helium-4 enters the VTI matches the rate at which it is pumped out – and the low temperatures can be achieved indefinitely, however finding the perfect balance is difficult, so most often the VTI is simply filled with Helium-4 and then pumped, thus providing low temperatures for a few hours until it is emptied. For temperatures lower than 1.4 K the cryostat may be fitted with a Helium-3 insert, and – as a result of its lower

ambient boiling temperature and higher vapour pressure – pumping on this volume of Helium-3 may reduce the temperature to around 320 mK. Due to the far greater cost of Helium-3 ($\sim 200 \times$ that of Helium-4) these systems operate on a self-contained reservoir – so the Helium-3 must be recondensed between measurements – and tend to be used only when sub-1 K temperatures are crucial for the measurement.

High magnetic fields

To generate high magnetic fields a large current must be passed through the solenoid, which is either superconducting or resistive. In the superconducting case the solenoid consists of wires made of a type-II conventional superconductor (such as Nb_3Sn), which are cooled below their superconducting temperature by virtue of being submerged in Helium-4. As the solenoid itself has no resistance these systems are very efficient to run – with the main cost being the Helium-4 required to keep the solenoid cold – and capable of producing stable, homogeneous fields. However the critical current of the superconducting wires sets an upper limit on the fields these magnets are able to produce, capped at about 21 T. Beyond this the solenoid will suddenly become resistive, and discharge all its newfound energy into its cooling cryogens, rapidly boiling off the surrounding Helium-4 and Nitrogen. This magnet ‘quenching’, as well as wasting a large amount of time and cryogens, can also permanently damage the magnet itself, although most newer systems are designed to withstand it.

Therefore to generate fields in excess of 21 T resistive solenoids must be used, which follow the Bitter design of stacked conducting plates through which the current passes helically. These magnets require vast amounts of power to run, typically around 20 MW at maximum field, and large quantities of pressurised cooling water to prevent overheating. Because of the infrastructure required for their operation, these resistive magnets are located at purpose-built facilities for high magnetic field research: the National High Magnetic Field Laboratory (NHMFL) of Florida State University, Tallahassee has the record for the highest (DC) field of 45 T, achieved by a ‘hybrid’ combination of an 11.5 T superconducting outsert and a 33.5 T resistive magnet; while the High Field Magnet

Laboratory (HFML) of Radboud University, Nijmegen has the record for the highest (DC) field achieved by a solely resistive magnet of 37.5 T.

For the measurements in this thesis four magnet systems were used, two located in Oxford and two at the aforementioned facilities: a Quantum Design Physical Property Measurement System (PPMS) with a 14 T superconducting magnet; a 21 T Oxford Instruments superconducting magnet which was used to generate fields up to 18 T (the final 3 T can be achieved by pumping on the lambda plate to reduce the temperature of the solenoid); a 33 T resistive magnet at HFML, fitted with a Helium-3 insert; a 45 T hybrid magnet at NHMFL, also fitted with a Helium-3 insert. The choice of system really depends on the material being measured – although the high fields and lower temperatures provided by the resistive magnets at HFML and NHMFL are of course preferable, if the effective masses in a material are small and the mean free paths long, most if not all the quantum oscillation features can be observed by much lower fields and there is little intrinsic benefit, excepting greater signal-to-noise, to using the much more expensive (and proposal requiring) resistive systems.

Rotator probe design

To map the Fermi surface of a material with quantum oscillations and put the ‘A’ in AMRO, the sample orientation must be changed with respect to the magnetic field. To this end the samples are mounted on a sample platform, which may be rotated from the top of the probe while it remains in the cryostat. Figures 1.10a) and b) show some examples of the rotating mechanisms used for the measurements in this thesis, while Figure 1.10c) illustrates the possible angles of rotation. Figure 1.10a) shows a single axis ‘Swedish’ rotator, where the angle θ may be varied by turning a dial at the top of the probe: the dial is attached to a rotating rod, the end of which locks into a row of teeth around the outside of a cup within which the sample platform sits; rotating the dial therefore rotates the cup, with about a $\sim 270^\circ$ angular range accessible. Through this method the angle θ may then be changed discretely between measurements by manually turning the dial, with the dial value – read off the top of the probe – to angle calibration

determined with a Hall probe.

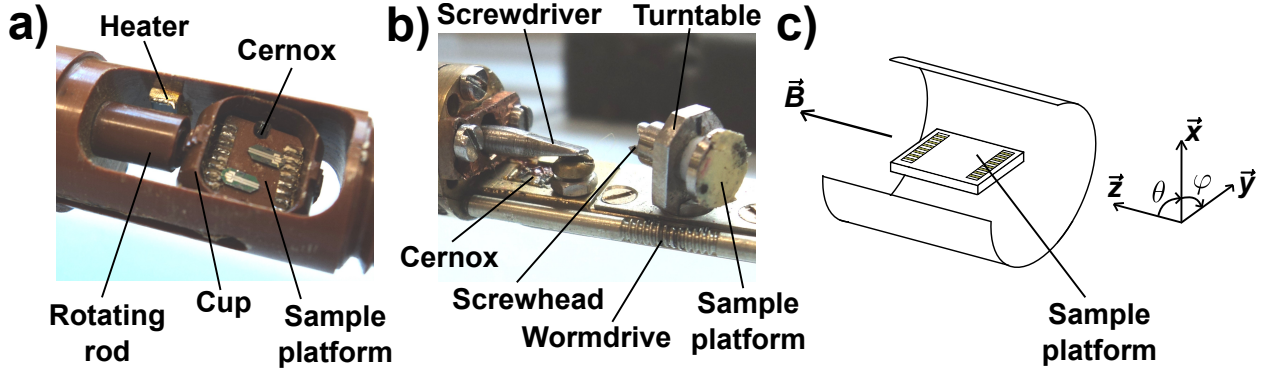


Figure 1.10: **Rotator probe designs.** a) Single axis Swedish rotator: a rotating rod turns a cup containing the sample platform. b) Two axis rotator: a wormdrive rotates a turntable with the sample platform attached; a screwdriver rotates the sample platform with respect to the turntable. c) Schematic of a sample platform, illustrating the angles of rotation.

Figure 1.10b) shows a two axis rotator, where both the angles θ , continuously, and φ , discretely, may be varied. The sample platform is mounted to a turntable, which is connected, by a wormdrive, to an electric motor mounted at the top of the probe. Applying a current to this motor then rotates the turntable continuously over a 360° range – provided there is enough slack in the wiring to the sample platform – with a (Hall probe calibrated) potentiometer attached to the motor providing the value of θ . On the reverse side of the turntable to the sample platform is a screwhead, which rotates the sample platform with respect to the turntable. If θ is set so the screwhead faces towards the top of the probe, it aligns with a screwdriver which may then, by turning a dial at the top of the probe, be used to turn the screwhead, discretely varying φ over a 360° range.

The rotator probes shown in Figure 1.10 were both used in the 21 T superconducting magnet, however similar probes were also used in the measurements conducted in different systems: a single axis wormdrive rotator, allowing for continuous rotation of θ , was used for PPMS measurements; a single axis Swedish rotator was used for measurements at HFML and NHMFL, with the latter controlled by a motor. In all cases a resistance thermometer (usually a Cernox) is mounted close to the sample platform to monitor the sample temperature (via a LakeShore temperature controller and the known calibration),

and a resistive heater may also be close by to heat the samples directly. The piezo-levers (as can be seen in Figure 1.10a)) or transport samples are then soldered onto the gold pads on the sample platform, and, by twisted pair wiring spanning its length, these pads correspond to the pins of a Fischer connector at the top of the probe.

1.3.3 Torque magnetometry

As already seen in Section 1.2.3, the torque produced by the interaction between a sample's magnetisation and an external applied magnetic field, $\boldsymbol{\tau} = \mathbf{M} \times \mathbf{B}$, provides a straightforward way to measure the de Haas-van Alphen effect, with the oscillations described by Equation 1.37. Torque is not a direct measure of the magnetisation however, but rather the component of the magnetisation perpendicular to the applied field. In this sense it is a measure of the magnetic anisotropy of the sample, for in a system with no anisotropy the magnetisation will align with the applied field and so the torque will be zero.

The background magnetic torque

For an anisotropic paramagnetic system, the magnetisation will be given by a field-independent susceptibility tensor $\mathbf{M} = \chi \mathbf{H}$. If the magnetisation is then uniaxial, the free energy can be written as [36]:

$$\begin{aligned} F &= -\frac{1}{2}\mu_0 \mathbf{M} \cdot \mathbf{H} \\ &= -\frac{1}{2}\mu_0 H^2 (\chi_{\parallel} \sin^2(\theta) + \chi_{\perp} \cos^2(\theta)) \end{aligned} \tag{1.48}$$

where θ is the angle between the magnetic field and the uniaxial axis. The torque is then given by:

$$\begin{aligned} \tau &= -\frac{\partial F}{\partial \theta} \\ &= -\frac{1}{2}\mu_0 H^2 (\chi_{\parallel} - \chi_{\perp}) \sin(2\theta) \end{aligned} \tag{1.49}$$

Although this is a very simplistic case, many real systems – especially those of layered crystal structures with quasi-two dimensional Fermi surfaces – show a background torque

that varies as $\tau \sim B^2$ (trivially depicted in Figure 1.11a)) and a $\sin(2\theta)$ angular dependence for rotations in constant field.

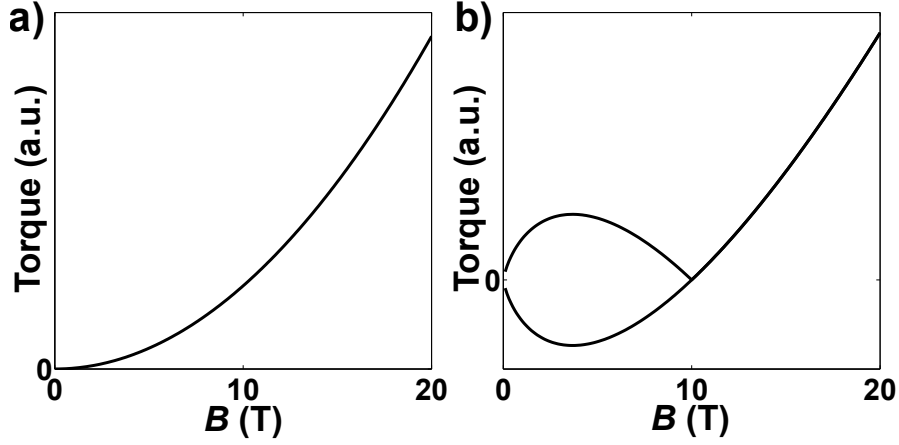


Figure 1.11: **Background torque in anisotropic systems.** **a)** An anisotropic paramagnet shows a B^2 background, simulated from Equation 1.49. **b)** An anisotropic type-II superconductor shows hysteretic behaviour beneath $H_{c2} = 10$ T, simulated from Equation 1.50.

For an anisotropic (type-II) superconducting system however, the material will no longer be paramagnetic at low fields; instead $\mathbf{M} = -\mathbf{H}$ in the perfectly diamagnetic state beneath H_{c1} , and increases between H_{c1} and H_{c2} such that, at H_{c2} , $\mathbf{M} = 0$. In this case the torque is given by [36]:

$$\tau \sim H \ln \left(\frac{\eta H_{c2}(\theta)}{H} \right) \frac{\sin(\theta) \cos(\theta)}{(\sin^2(\theta) + \gamma^2 \cos^2(\theta))^{1/2}} \quad (1.50)$$

where the effective masses determine the anisotropy parameter $\gamma = (m_{\parallel}^*/m_{\perp}^*)^{1/2}$ and η depends on the vortex lattice structure. Additionally the torque is hysteretic beneath H_{c2} , changing sign between up and down field sweeps, which leads to a hysteresis loop like that shown in Figure 1.11b); subtracting the up and down field sweeps then gives the position of H_{c2} .

Torque is also sensitive to magnetic transitions in the material, which will manifest themselves as changes in the gradient, either as a function of magnetic field or, in a constant applied field, temperature. Peaks in the differential of the torque may then be used to map out these transitions (as is performed in Section 3.3.1), either to determine their anisotropy or to construct a phase diagram. Non-magnetic structural transitions

will be less clear in the field or temperature dependence of torque, however any change in the anisotropy, density of states or crystal axes will be apparent in the amplitude and the phase of the anisotropy of the torque, assuming it takes a form similar to Equation 1.49. Therefore rotations in constant field can be used to track the evolution of these parameters across a structural transition, this method is used in Section 4.2.1.

Torque measurement with piezo-levers

The torque measurements conducted in this thesis were performed with piezoresistive cantilevers (piezo-levers), specifically the Seiko PRC-400 (and sometimes the shorter PRC-120) self-sensing microcantilever chip⁴. The chip design, shown in Figure 1.12, consists of a $400\text{ }\mu\text{m}$ long cantilever upon which the sample is mounted, alongside an empty ‘dummy’ lever. Both these levers are attached to the body of the chip by piezoresistive arms, whose resistance will depend on the torque experienced by the levers. As shown in Figure 1.12a), these piezo-levers form one half of a Wheatstone bridge, completed by one fixed and one variable resistor. The potential across the Wheatstone bridge circuit will depend upon the difference in resistance between the two current paths, and so the difference in the piezoresistance between the sample lever and the dummy lever. Any contribution to the piezoresistance from the levers themselves will be felt by both the sample lever and the dummy, so their difference, and hence the measured voltage, will depend only on the torque produced by the sample. Typically these differences in piezoresistance are very small, so to maximise sensitivity the Wheatstone bridge is balanced – by changing the variable resistor so that the measured voltage is zero – before a measurement is performed.

A small AC current (not in excess of $100\text{ }\mu\text{A}$) is used to prevent sample heating, provided by either a (Keithley 6221) current source or the output voltage of a (Stanford Research SR830) lock-in amplifier, applied in series over a large resistance. The same lock-in is then used to measure the voltage signal, which is typically amplified $100\times$ by

⁴Both these products have been recently discontinued by Seiko, which – as these levers invariably eventually break as a result of underestimated magnetic transitions or sample mounting cackhandedness – may curtail the use of piezo-levers for torque magnetometry, unless an alternative provider is found.

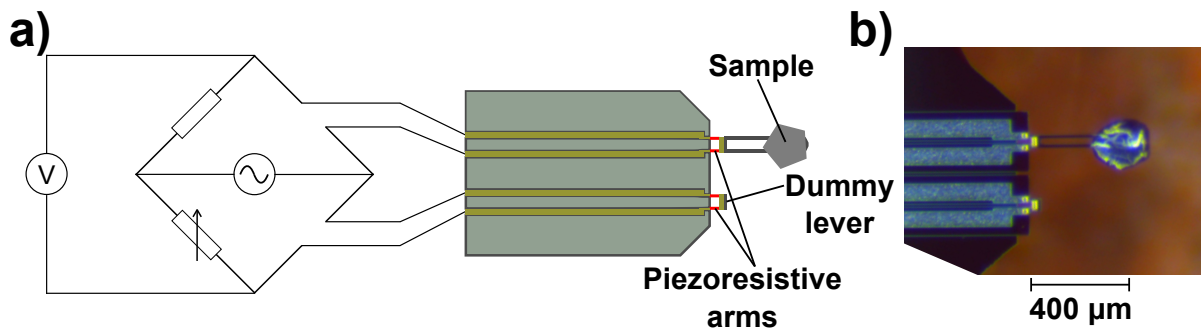


Figure 1.12: **Circuit design for piezoresistive cantilever measurements.** a) Schematic of a piezo-lever, attached to a Wheatstone bridge circuit for accurate measurement. b) Photograph of a piezo-lever with a sample (IrTe_2) mounted.

either a transformer or a pre-amplifier. The sample is affixed to the lever by Apiezon N grease, which is soft at room temperature to allow the delicate positioning of the sample (performed with a hair⁵ taped onto the end of a cocktail stick) but freezes upon cooling to fix the sample in place. The Sekio PRC-400 lever is $400\text{ }\mu\text{m}$ in length, so this places a maximum limit on measurable crystal size of perhaps $300 \times 300\text{ }\mu\text{m}^2$ for the mounted face.

For small deflections of the lever of less than $\sim 1^\circ$, the change in resistance, and so the voltage signal, is proportional to the torque felt by the sample [37]. For deflections far in excess of $\sim 1^\circ$, in addition to the non-linear piezoresistive response, the large deflection will also change the position of the sample relative to the field, and thus the torque it experiences. This ‘overcritical torque interaction’ effectively changes the sample orientation as a function of field, and so can lead to unexpected, and unwanted, effects with increasing field, such as sawtooth-like quantum oscillations [38]. For magnetic or strongly oscillating samples these effects can be a problem if too large a sample is chosen.

Although in the usual measured deflection range the voltage is linearly related to the torque, the exact form depends on the specific cantilever. As torque measures only the field orientation-dependent perpendicular component rather than the total sample magnetisation, calibrating an individual lever is not straightforward. Because of this the torque is typically given in arbitrary units (a.u.) – which is the case throughout this thesis – and is generally used to measure transitions and oscillatory effects, where only

⁵In my experience the finer end of an eyelash or eyebrow is best suited for this purpose, although with the downside that one can come out of a long sample preparation session looking rather alopecic.

the relative amplitude is important, rather than to probe the bulk magnetisation.

1.3.4 Resistivity measurements

Measuring the resistivity as a function of temperature or field is of course the most direct way of characterising a metal, depending on both the availability of conduction states and the various scattering processes that may effect them. Superconductivity and metal-insulator transitions are unmistakable in the resistivity – causing the disappearance of and a sudden large change in resistivity respectively – but structural, magnetic and charge-ordering transitions can also leave signatures in the resistivity, with changes of the electronic structure or scattering processes resulting in a change of gradient – the position of the transition can then be determined from the peak in the first derivative. As discussed in Sections 1.2.3 and 1.2.4 Shubnikov-de Haas oscillations and AMRO may also be observed in the field and angular dependence of the resistivity, conveying much about the nature of the Fermi surface.

The background resistivity

If no transitions – and so no changes in the density of states at the Fermi level – are present, then the change in resistivity with cooling depends on the scattering processes in the material. At room temperature phonon scattering dominates, but at lower temperatures the thermal vibrations of the lattice reduce and electron-electron scattering becomes the important term, leading to the $\rho \sim T^2$ dependence expected for a Landau Fermi liquid [1]. At very low temperatures this term will also be much reduced, and so the main contribution to the resistivity comes from impurities in the sample, which leads to a constant, temperature-independent resistivity. Therefore the ‘residual resistivity ratio’ (RRR) of $\rho(300\text{ K})/\rho(0\text{ K})$ can be used as a measure of sample purity, where $\rho(0\text{ K})$ can be extrapolated from the lowest temperature non-superconducting resistivity data – a high RRR means little impurity scattering and so a relatively clean sample, a low RRR means the opposite. The RRR is thus used as a way of screening samples in zero-field, so that the cleanest samples may be selected for Shubnikov-de Haas measurements (whose

amplitude, through the Dingle term of Equation 1.27, depends on the mean free path).

Sample preparation

The resistivity measurements presented in this thesis have been performed on the layered compounds $\text{FeSe}_{1-x}\text{S}_x$ and IrTe_2 , both of which form thin, plate-like samples typically up to 1 mm (but sometimes as small as $200\text{ }\mu\text{m}$) in breadth and around $10\text{ }\mu\text{m}$ in thickness, with the crystallographic c -axis normal to the large top and bottom faces of the crystal as well as the lattice planes. From the sample geometry it is therefore easy to define an in-plane and an out-of-plane measurement configuration for the resistivity ρ_{xx} : for an in-plane measurement, shown in Figure 1.13a), a current contact is placed at each end of the sample while a pair of voltage contacts are placed on the top, this will measure the resistivity within the lattice planes; for an out-of-plane measurement, shown in Figure 1.13b), the current contacts are placed approximately opposite each other on opposing sides of the sample and the voltage contacts similarly, this will measure the resistivity normal to the lattice planes. Figure 1.13c) shows a (rather large) sample of $\text{FeSe}_{0.95}\text{S}_{0.05}$ contacted for in-plane measurements. A second pair of voltage contacts are present for Hall effect measurements of the resistivity perpendicular to the applied current, ρ_{xy} . Due to misalignments of the contacts the measured resistivities in both orientations will give some combination of ρ_{xx} and ρ_{xy} , so to isolate the components the data must be symmetrised by performing measurements at both positive and negative fields: ρ_{xy} changes sign when the field direction is reversed, ρ_{xx} does not. The resistivity measurements in this thesis, however, are only concerned with the occurrence of oscillations on top of the resistivity background, and so a simple unsymmetrised measurement – as pictured in Figures 1.13a) and b) – is sufficient to observe this behaviour.

To measure the resistivity an AC current of a few mA – typically 1 or 2 mA, with anything in excess of 5 mA accompanied by a risk sample heating, depending on the contact resistances – is applied by either a current source or a lock-in amplifier; the voltage signal is amplified $100\times$ by either a transformer or pre-amplifier, and then measured with a lock-in, in a similar procedure to torque measurements. The voltage signal may then

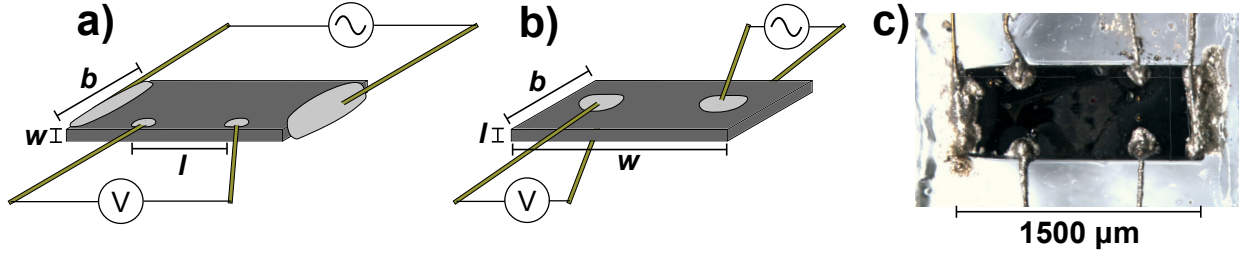


Figure 1.13: **Contact configurations for resistivity measurements.** a) Contact configuration for in-plane measurement. b) Contact configuration for out-of-plane measurement. c) Photograph of a sample (FeSe_{0.95}S_{0.05}) contacted for in-plane resistivity measurements (and Hall effect). Relevant dimensions for the calculation of resistivity are indicated.

be converted to a resistance from the measurement current and amplification, and this resistance converted to the resistivity from the dimensions of the sample: $\rho = RA/l$, with $A = w \times b$ and l the dimensions indicated in Figure 1.13a) and b), measured under a microscope. For in-plane measurements the voltage contacts should be kept small so a larger l , and so portion of the sample, is measured, but the current contacts should span much of the breadth of the sample to ensure a uniform current flow across the layers; these considerations are less important for out-of-plane measurements as both pairs of contacts necessarily span the two faces of the crystal.

The method used for contacting the samples (to either 25 μm or 10 μm gold wire, depending on the sample size) depends on the samples being measured. The lowest resistance ($< 1\Omega$), most physically robust contacts can be made by soldering directly to the sample, using an indium solder (as this has a lower melting point than tin) and flux. For materials where the solder bonds well to the surface and the samples are large enough – at my level of competency soldering becomes difficult for samples less than 500 μm in size⁶ – soldering produces the best contacts, and so the majority of the FeSe_{1-x}S_x measurements of Chapter 2 were all conducted on samples prepared this way, such as that pictured in Figure 1.13c).

For the IrTe₂ resistivity measurements of Chapter 4 the large structural distortions seen upon cooling can cause the samples to shear apart if their sides are fixed too firmly in place, so the robustness of solder contacts becomes an impediment; additionally many

⁶Below 500 μm the spacing between contacts becomes comparable to the tip size of the soldering iron (100 μm), so a level of intricacy beyond me is required to flow one contact without flowing them all.

of the samples are also too small to successfully solder. For these measurements contacts were made with silver paint (DuPont 4929N). Left to cure at room temperature these contacts can achieve resistances of $< 10\,\Omega$, but have a tendency to detach from the sample and can deteriorate over time – for a good contact the out-of-phase, capacitive component of the voltage signal should be confirmed as close to zero. Away from the sample the gold wires should be well secured in place to avoid any vibrations – especially crucial for rotation studies – however with enough slack that the thermal contraction of the sample and wiring upon cooling will not place undue tension on the contacts. If these considerations are adhered to the contacts should survive the cooling of the sample (although, as was the case for IrTe_2 , it may take multiple attempts), allowing for the possibility of low temperature magnetoresistance measurements.

1.3.5 Quantum oscillations analysis

As both de Haas-van Alphen (Equation 1.37) and Shubnikov-de Haas (Equation 1.41) oscillations take a similar form, many of the same analysis techniques can be applied to both. For a single frequency (or at a push a pair of them) the magnetoresistance can be fitted directly to the Lifshitz-Kosevich form of Equation 1.36 with a polynomial background; or alternatively differentiated to reduce the background for a direct fit, although to the differentiated form of the Lifshitz-Kosevich equation. This is particularly useful for low frequencies which display only a few periods over the measured field range, however when many frequencies are present a direct fit introduces too many free variables. Instead the frequencies of the oscillatory component are extracted by a fast Fourier transform (FFT) in inverse magnetic field, performed on the data once a low-order polynomial has been fitted to and removed – subtracted for torque measurements or divided for magnetoresistance – from the raw data.

The choice of field window determines the clarity of the features seen in the FFT: a window across the entire observable range of oscillations will produce the sharpest FFT peaks, but penalises higher frequencies which only appear (as a result of the Dingle term of Equation 1.26) at larger fields; conversely a smaller window in the high field region will

favour these higher frequencies, but leads to broader FFT peaks which may begin to merge for lower frequencies. Additionally the form of the windowing function used will effect the sharpness of the FFT peaks, typically the Hanning and Welch windowing functions are found to produce the clearest FFTs. For superconducting samples no oscillations are usually visible below B_{c2} [39], so this also places a bound on the lower limit of the field window, as well as necessitating magnetic fields in excess of B_{c2} for the observation of oscillations.

The amplitudes of each frequency obtained from the FFTs can then be used to fit to the various damping terms of Equations 1.26, 1.27 and 1.28 for the extraction of parameters such as the effective mass, with the magnetic field taken to be the average of the inverses across the field window ($1/B_{\text{ave}} = (1/B_{\text{min}} + 1/B_{\text{max}})/2$). To observe the angular dependence of the quantum oscillations the FFTs can be plotted as a function of angle: either stacked along the y -axis as a ‘waterfall’ plot; or as a ‘frequency spectrum’ with the FFT intensity determining the z -parameter for a contour plot of frequency versus angle. For the results in this thesis a set of programs, written in Matlab by Matt Watson and myself, are used to perform the FFTs, Lifshitz-Kosevich fits and angular dependence plots as described here.

Chapter 2

Evolution of the Fermi surface of $\text{FeSe}_{1-x}\text{S}_x$

2.1 Introduction

This chapter presents the results of Shubnikov-de Haas measurements of the Fermi surface of $\text{FeSe}_{1-x}\text{S}_x$ in the range $0 \leq x \leq 0.2$, an isoelectronically doped version of one of the most recently discovered, and ardently studied, Fe-based superconductors FeSe. To begin I will introduce the Fe-based superconductors, looking at their phase diagrams and Fermi surfaces with a particular focus on previous measurements of FeSe. The results of resistivity measurements follow, with superconductivity observed across the measured doping range but the structural transition disappearing before $x = 0.2$. Shubnikov-de Haas measurements find a small, unreconstructed Fermi surface which increases in size and warping with increasing doping. Their temperature dependence reveals orbital dependent effective masses, with a notably large mass enhancement that does not change significantly within the orthorhombic phase, in contrast to the case of applied pressure. Finally DFT calculations, requiring very large rigid band shifts, are found to provide a reasonable facsimile to the measured Fermi surface in FeSe, but become less accurate with increasing doping.

2.1.1 Iron-based superconductors

After the formulation of Bardeen-Cooper-Schrieffer (BCS) theory in 1957 [40], in which phonons mediate a weak attraction between pairs of electrons, for many decades superconductivity was considered to be something of a solved problem. Within conventional superconductors, whose behaviour is well explained by BCS theory, the highest possible critical temperature (T_c) is rarely more than 40 K. Although easily reachable with helium-4, this upper limit on critical temperature puts severe constraints on the applications of superconductivity, due to both the efforts required to keep the superconductor cold and the costs incurred in doing so¹. However, beginning with the discovery of superconductivity in the cuprates in 1986, many compounds have been found whose superconductivity cannot be explained by BCS theory, allowing T_c far in excess of the previous limits (for example $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_6$, $T_c = 110$ K, achievable with nitrogen) [41].

Crystal structure and phase diagrams

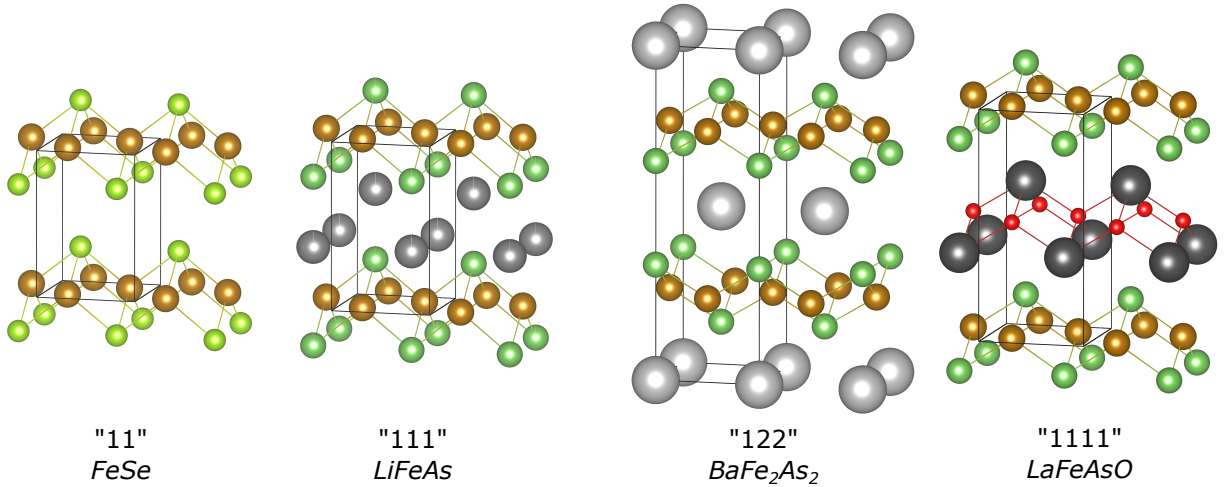


Figure 2.1: **Example crystal structures for different families of Fe-based superconductors** in the high temperature phase. The unit cell is shown by the thin black lines; as opposed to the others (spacegroups $P4/nmm$), a body centred unit cell is used for BaFe_2As_2 (spacegroup $I4/mmm$). Structural parameters taken from [42–45].

The most recently discovered members of these high temperature, unconventional superconductors are the Fe-based compounds, which became a focus of study in 2008 with

¹Although ‘high- T_c ’ gets most of the attention, high critical fields and a malleable material are of equal (if not greater) importance when it comes to practical applications.

the discovery of superconductivity ($T_c = 26$ K) in $\text{LaFeAsO}_{1-x}\text{F}_x$ [45]. Since then many more superconductors in this family have been found, all with a similar structure: planes of Fe atoms arranged in a square lattice, tetrahedrally bonded to pnictogen or chalcogen atoms. These materials are then classified into further subdivisions by their stoichiometry: the 1111 systems (such as LaFeAsO , LaFePO); the 122 systems (BaFe_2As_2 , KFe_2As_2); the 111 systems (LiFeAs , LiFeP); and the 11 systems (FeSe). Example crystal structures for each of these families are shown in Figure 2.1; all feature Fe-pnictogen/chalcogen planes separated by some kind of spacer layer, excepting FeSe which comprises of only the Fe-chalcogen planes. This list is by no means exclusive, many other spacer layers are possible, such as organic intercalates [46] and perovskite oxides [47].

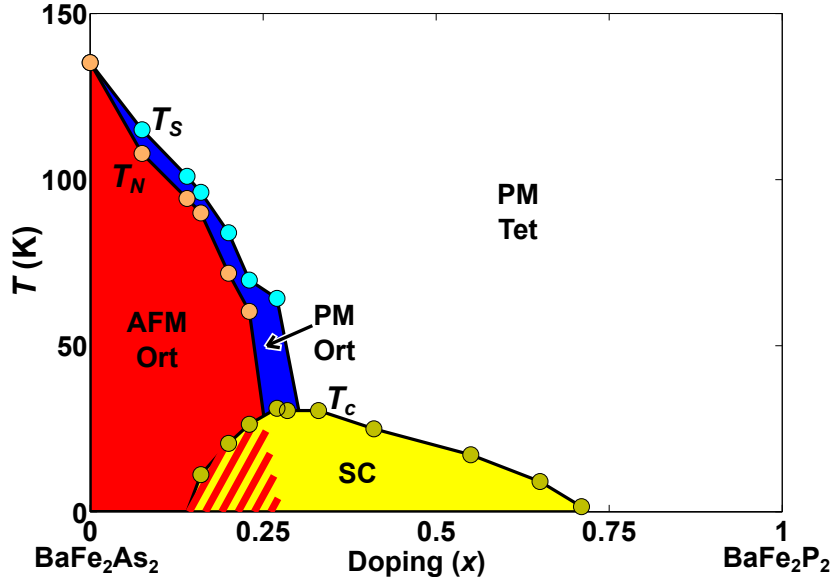


Figure 2.2: **Phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$** , showing the structural transition T_S , magnetic transition T_N and superconducting transition T_c . Data taken from [48].

To achieve maximum T_c (or in many cases any superconductivity at all) these systems can be tuned by doping – on both the Fe and pnictogen/chalcogen site or in the spacer layer – or by the application of pressure. A typical phase diagram, for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, is shown in Figure 2.2. At low dopings the first feature seen upon cooling is a structural transition, T_S , from a tetragonal to an orthorhombic structure, breaking the four-fold rotational symmetry. This is followed shortly after by a magnetic transition, T_N , from a paramagnetic (PM) to a stripe-ordered antiferromagnetic (AFM) state. In the small region between T_S and T_N the material has undergone an orthorhombic distortion along

a certain direction, but has no long range magnetic order; this is known as the nematic phase. As the system is doped both these transitions are suppressed and superconductivity emerges below T_c , with a characteristic dome shape. The apex of the dome (the ‘optimal doping’ with the highest possible T_c) occurs around the point at which the magnetic and structural transitions disappear. In the case of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ the doping is iso-electronic – As and P are both pnictogens so the doping introduces no additional charge carriers to the system – and instead the effect is one of chemical pressure, where the change in size of the anion will act to modify the lattice parameters. However electron doping (on the Fe site), $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [49], and hole doping (on the Ba site) $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [50], both produce similar phase diagrams, though with the electron doping being much more sensitive: superconductivity disappears by $x = 0.15$.

Origin of the structural and magnetic transitions

The occurrence of superconductivity in the proximity of the AFM phase naïvely seems surprising, as in conventional superconductors magnetic impurities lead to Cooper pair breaking and the suppression of superconductivity. However the occurrence of a magnetic state alongside superconductivity is a recurrent motif in unconventional superconductors – as well as the AFM phase in the Fe-based superconductors, a similar phase exists in both the cuprates [51] and heavy fermion materials [52]. Although a full theoretical description of the mechanism of superconductivity in these materials is lacking, the many theories proposed rely on fluctuations within the spin configuration of the system, equivalent to vibrations of the crystal lattice in BCS theory [53] [54]. Understanding the origin of the magnetic transition, and its relation to the structural transition, is therefore crucial to understanding the pairing mechanism beneath the superconducting dome.

As the two transitions follow each other so closely, their origin is essentially a chicken-and-egg scenario: are the magnetic interactions that form the AFM state breaking the four-fold symmetry and driving the structural transition (the ‘spin-nematic’ picture) [55]? Or are orbital interactions distorting the structure, leading to the formation of the magnetic state (the ‘orbital ordering’ picture) [56]? Both cases depend strongly on the Fermi

surface topology of the system, requiring nesting between hole and electron pockets of the Fermi surface to cause the spin and orbital fluctuations respectively. Therefore determining the Fermi surface of these materials and mapping its evolution across the phase diagram should provide clues to the cause of the transition and the nature of superconductivity in the Fe-based superconductors.

Fermi surfaces

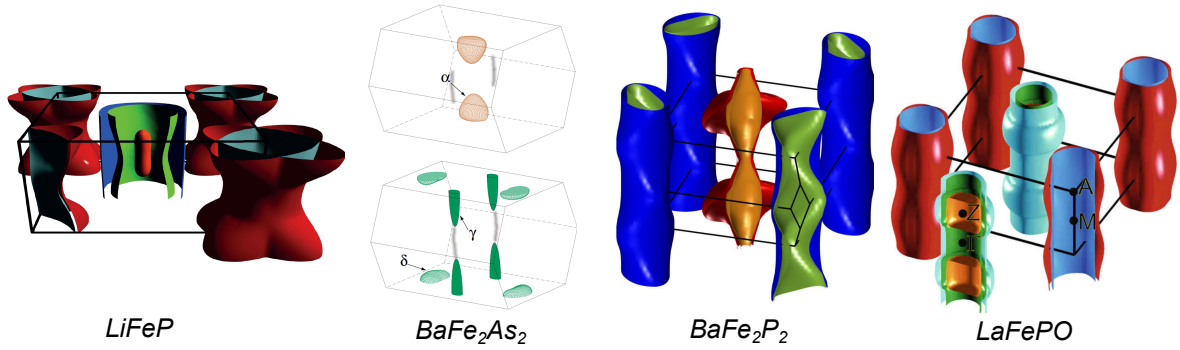


Figure 2.3: **Experimentally measured Fermi surfaces of various Fe-based superconductors.** Images taken from [57–60].

Figure 2.3 shows the experimentally determined Fermi surfaces for a variety of Fe-based superconductors- LiFeP [61], BaFe₂As₂ [58], BaFe₂P₂ [62] and LaFePO [60]. All these Fermi surfaces are constructed from the results of de Haas-van Alphen or Shubnikov-de Haas measurements², so they consequently belong to the low temperature phase of their respective materials. Considering first LiFeP, BaFe₂P₂ and LaFePO, these compounds exist on the far right side of the phase diagram in the very overdoped regime, which means that their Fermi surfaces arise from the tetragonal, PM phase. In all three cases the Fermi surface comprises of 2 - 3 quasi-two dimensional hole pockets centred on the Γ -point and 2 quasi-two dimensional electron pockets centred on the M -point. The similar size of the hole and electron pockets will favour nesting in these materials with wavevector $\mathbf{q} = (\pi/a, \pi/a, 0)$. As all the bands at the Fermi level originate from Fe 3d orbitals, the electronic structure is insensitive to the contents of the spacer layers between

²There are also numerous ARPES studies on the Fermi surfaces of Fe-based superconductors. I've not mentioned them here as only Shubnikov-de Haas results will be presented in this chapter, but qualitatively previous ARPES and quantum oscillations studies have more [63] or less [64] been in agreement.

the Fe-P planes and hence the Fermi surfaces across the Fe-based superconductors take a similar form. Typically these Fermi surfaces are relatively large, producing quantum oscillation frequencies (when the field is aligned along the axis of two dimensionality) on the order 1 - 5 kT [3].

Conversely BaFe_2As_2 is on the far left side of the phase diagram in the underdoped regime, and so at low temperatures is in the orthorhombic, AFM phase. The formation of this striped order increases the size of the unit cell, and so the quasi-two dimensional bands of the tetragonal, PM Fermi surface must be folded into a reduced Brillouin zone. The effect of the magnetic order on the Fermi surface is therefore a reconstruction into the smaller hole and electron pockets seen in Figure 2.3; at higher temperatures above T_N the Fermi surface of BaFe_2As_2 will be similar to that of BaFe_2P_2 [65]. The frequencies arising from these smaller pockets are of course smaller, with none in excess of 1 kT. Both the PM and reconstructed Fermi surfaces feature enhanced effective masses, with $(\lambda_{ee}^s + \lambda_{ep}) = m^*/m_b - 1$ taking values between 0.5 - 1.8, depending on the field orientation [3].

2.1.2 Previous work on FeSe

FeSe^3 stands out amongst the Fe-based superconductors for two reasons: as shown in Figure 2.1 it has the simplest possible structure, with only the Fe-chalcogen planes and no spacer layers; and it undergoes the structural transition T_S upon cooling but not the magnetic transition T_N . The latter point is especially interesting, as if the magnetic and structural transitions are so closely entwined in the other Fe-based superconductors then how can the magnetic transition be entirely lacking in this case? Studying this system at low temperatures gives a unique look at the nematic phase of the Fe-based superconductors and the relationship between the orbital and magnetic ordering in these systems.

³There are a number of phases of Fe_{1-x}Se in the Fe - Se system, with various hexagonal, monoclinic and orthorhombic structures possible [66]. The tetragonal, superconducting version studied here is usually referred to as $\beta\text{-FeSe}$ [66, 67], although, confusingly, $\alpha\text{-FeSe}$ has also been used in the past [68].

Phase Diagram

At ambient pressure FeSe undergoes a tetragonal to orthorhombic transition at $T_S \sim 90$ K and superconducts with $T_c = 8$ K [69], not a particularly remarkable T_c for an Fe-based superconductor. However with the application of pressure this is raised to 37 K [67], and in thin films, grown on doped SrTiO₃, superconductivity has been reported in excess of 100 K [6]. The appearance of an AFM state has also been reported at high pressures, coexisting with the superconducting state [70, 71] rather than supressing it as seen in the other Fe-based superconductors. This phase diagram is shown in Figure 2.4, unusually amongst the Fe-based superconductors (comparing, for example, to Figure 2.2) the magnetism onsets with the suppression of the structural transition, while superconductivity exists across the phase diagram.

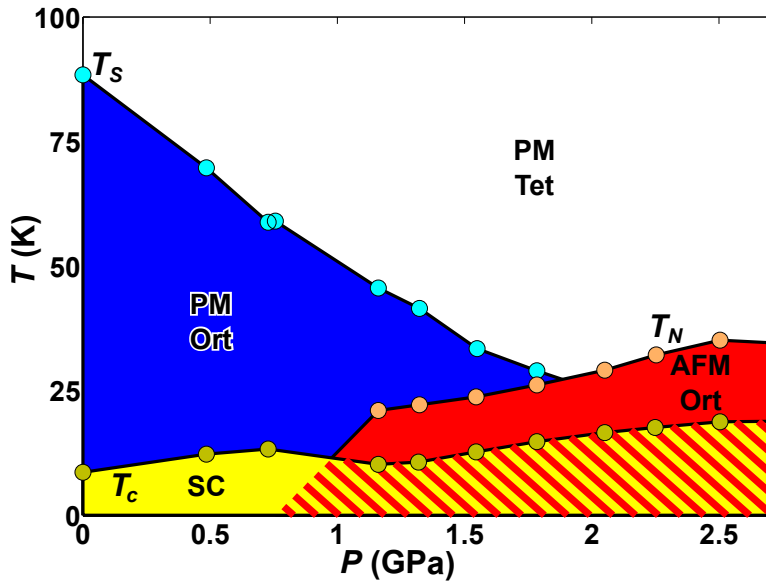


Figure 2.4: **Phase diagram of FeSe under pressure**, showing the supression of the structural transition T_S and the onset of magnetism. Data taken from [71].

The effect of both pressure and thin film growth is to change the lattice parameters [72], with the in-plane area acting as the tuning parameter of the system [73]. A similar effect can also be achieved by isoelectronic doping: inserting a smaller chalcogen ion, such as in FeSe_{1-x}S_x will decrease the size of the unit cell (and the in-plane area); inserting a larger chalcogen ion, FeSe_{1-x}Te_x, will increase it [74]. FeS itself⁴ also superconducts with

⁴FeS is also of interest as a potential catalyst for the creation of the first self-replacating organic molecules, ‘The Iron-Sulfur World Hypothesis’ [75]; however the origin of life on Earth is slightly beyond the scope of this thesis.

$T_c = 5$ K and a paramagnetic state above [76], while FeTe is magnetic at low temperatures with a double stripe AFM phase as opposed to the single stripe order seen in other Fe-based superconductors [68].

The Fermi surface of FeSe

Before considering the electronic structures of the doped compounds which form the substance of this chapter, I'll first review the work our group did in characterising the Fermi surface of the parent compound FeSe. Although I was involved in this project, the bulk of the work was done by Matt Watson and so a far more thorough description can be found in his thesis [57], along with the publications of the transport [77] and ARPES [78] data. Beginning first with the transport measurements [77], Shubnikov-de Haas oscillations were seen at high fields (> 20 T) in both DC and pulsed field measurements. Four distinct frequencies were observed (in agreement with previous reports [79]), labelled here as F1, F2, F4 and F5.⁵ By considering the effect of mobility on the relative amplitude of oscillation in the ρ_{xx} and ρ_{xy} components, combined with a positive Hall coefficient, it was deduced that frequencies F2 and F5 originated from a higher mobility hole-like band and F4 from a lower mobility electron-like band. A three carrier model is found to be necessary to fully fit the magnetotransport, with a small, high mobility electron pocket found alongside the large, relatively lower mobility hole and electron pockets already determined. This small pocket is assigned to F1.

ARPES measurements [78] were conducted both above and below T_S , with polarisation effects used to determine the orbital character of the different bands. At high temperatures two hole bands are observed at the Γ -point, both with d_{xz}/d_{yz} character, and one electron band is observed at the M -point, again with d_{xz}/d_{yz} character. Cooling below T_S the inner hole band is forced below the Fermi level by the orbital ordering, while the quasi-cylindrical Fermi surfaces of the other bands elongate along one of the in-plane lattice vectors, breaking the rotational symmetry. The presence of multiple domains in the sample leads to the appearance of cross-like Fermi surfaces, which were thought to

⁵Here I've deviated from the frequency notation(s) used in the referenced works [57, 77], as an additional frequency will later be observed in the doped compounds.

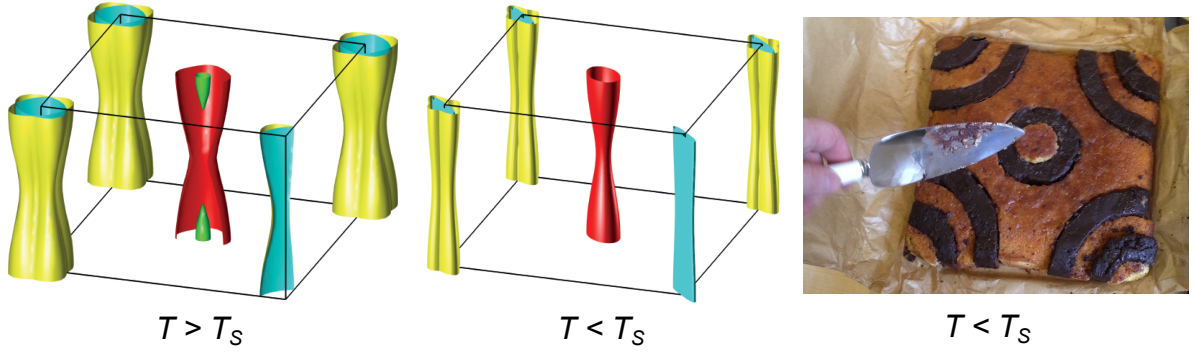


Figure 2.5: **Experimentally determined Fermi surface of FeSe above and below T_S** , in a cartoon [78] and culinary representation. Below T_S the inner electron band (green) disappears below the Fermi level and the remaining bands show an in-plane elongation.

originate from the superposition of bands distorted orthorhombically in both in-plane directions. The outer electron band, corresponding to quantum oscillation frequency F4, was not observed in this interpretation of the ARPES measurements, and this is attributed to it being of d_{xy} character which will not strongly couple with the polarisation of the incoming light. Otherwise there is good agreement with the quantum oscillations results. Figure 2.5 shows a cartoon and culinary⁶ representation of the Fermi surface above and below T_S , bringing together the results of both the quantum oscillations and ARPES measurements. This Fermi surface looks similar to the tetragonal phase of other Fe-based superconductors (shown in Figure 2.3) – at low temperatures there is only an orthorhombic distortion, not magnetic ordering, so the Fermi surface does not undergo any reconstruction below T_S .

More recently our group has also performed ARPES measurements on the doped compounds $\text{FeSe}_{1-x}\text{S}_x$, reported in [80]. With increasing doping (up to $x = 0.15$) both the size of the Fermi surface and the Fermi velocities increase (by $\sim 10\%$). Both these tie into the observed decrease in T_S : the increasing size will reduce the degree of nesting between the electron and hole pockets, while the increased Fermi velocity will reduce the density of states at the Fermi level. Together these will act to reduce the orbital ordering in the system and suppress T_S . In addition, with this reduction in orbital ordering, the inner hole band (which disappears below the Fermi level in FeSe) remains present below

⁶Note that in the culinary representation the Fermi surface sizes are overestimated due to instability of crumb issues, while the orthorhombicity is not well represented as I only own square cake tins.

T_S at high dopings ($x = 0.12$).

Although no prior quantum oscillations measurements on doped FeSe exist, a Shubnikov-de Haas study of the system under pressure (shown back in Figure 2.4) has been reported [81]. Here the four frequencies in the parent compound are observed, and these increase in size with applied pressure, in agreement with the ARPES study on $\text{FeSe}_{1-x}\text{S}_x$ – although the tuning parameters are different, the effect of both S doping and pressure is to reduce the in-plane area and suppress T_S . The effective masses also increase with pressure, and this is attributed to increasing spin fluctuations (which enhance the effective masses) as the AFM phase is approached. Upon entering the AFM phase the magnetoresistance is enhanced and only a single frequency is observed, comparable in size and effective mass to F1 but far larger in amplitude. This is attributed to the formation of a reconstructed Fermi surface with the larger unit cell of the AFM phase (much like in the case of BaFe_2As_2 , pictured in Figure 2.3), something not observed so far in the doped system.

2.2 Zero field resistivity measurements

Sample Details

Samples of $\text{FeSe}_{1-x}\text{S}_x$ for this study were provided by three crystal growers: Amir Haghighirad (AAH) at the University of Oxford; Thomas Wolf (TW) at Karlsruhe Institute of Technology; Shigeru Kasahara (SK) at Kyoto University. Details of the growth process can be found in [73]. The crystals measured span the nominal doping range $x = 0.05$ to 0.25 , with higher dopings being more difficult to grow large single crystals of. Energy dispersive x-ray spectroscopy (EDX) measurements were performed by Susie Speller at Oxford University Department of Materials to determine the actual dopings of the samples measured. Here I will refer to the samples by their actual, EDX-determined dopings (as the % S) rather than the nominal values provided by the crystal growers. Indium solder contacts were made to the samples (with in-plane dimensions between $500\text{-}1500\text{ }\mu\text{m}$ and thicknesses between $10\text{-}50\text{ }\mu\text{m}$) in an in-plane configuration. Zero field transport measurements were performed in a flow cryostat to determine T_S and T_c for

each sample.

Grower	Nominal Doping (% S)	Actual Doping (% S)	Stoichiometry (S + Se)/Fe	T_S (K)	T_c (K)
SK	5	4.4(3)	0.92(3)	83.7(2)	10.4(1)
TW	8.7	⁷	⁷	74.0(6)	11.1(2)
AAH	10	6.4(5)	1.02(12)	68.6(7)	9.7(2)
AAH	12	12.9(6)	1.06(11)	61.1(7)	10.1(1)
AAH	15	11.1(3)	0.99(5)	65.6(10)	10.6(1)
SK	20	16.4(5)	0.96(5)	45.1(8)	9.6(1)
SK	25	18.6(5)	0.88(2)	-	6.8(2)

Table 2.1: **Dopings and transition temperatures of the $\text{FeSe}_{1-x}\text{S}_x$ samples measured.** The tetragonal to orthorhombic transition T_S seems to disappear by $x = 0.18$.

Phase Diagram

Figure 2.6a) shows zero-field resistivity measurements for all dopings. T_c was taken to be the mid-point of the superconducting transition; T_S was determined from the (smoothed and) differentiated temperature dependence, in which its kink becomes a step of finite width, the mid-point of which is the transition. These values are marked on Figure 2.6a) and are given, along with the dopings and stoichiometries obtained from EDX measurements, in Table 2.1. Together these produce the phase diagram shown in Figure 2.6b).

Doping clearly suppresses the tetragonal to orthorhombic transition, with a steady decrease in T_S and no structural transition apparent by $x = 0.18$. Superconductivity persists across the measured range, though with a maximum value of ~ 11 K close to $x = 0.1$. Previous reports indicate the existence of superconductivity up to $x = 0.3$ [74, 82] (marked on Figure 2.6b)), with the values of T_c found at higher dopings somewhat larger than those presented here. The reason for this is likely twofold: the nominal doping, especially at higher values, tends to overestimate the S present in the sample; and off-stoichiometry, again an issue at higher dopings, can also effect T_c [70] by effectively hole or electron doping the sample.

⁷EDX measurements were conducted on the samples after the contacts had already been placed, in the case of 8.7% this meant there was not a large enough clean surface for an accurate measurement. Instead for this sample I will assume the nominal doping provided by the crystal grower is correct.

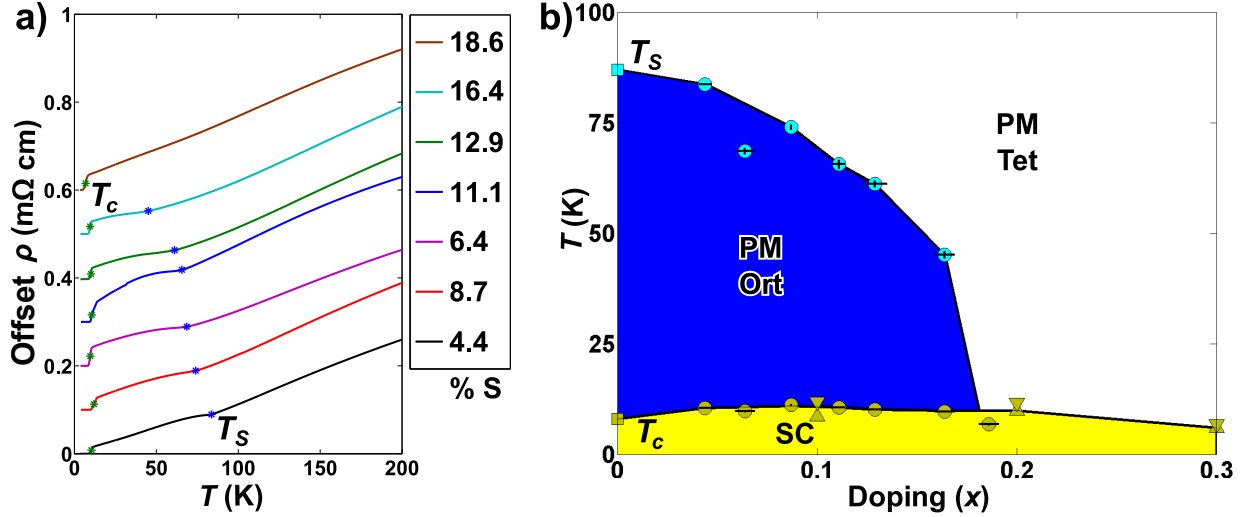


Figure 2.6: **Phase diagram of $\text{FeSe}_{1-x}\text{S}_x$ as determined by transport measurements.** **a)** Zero-field resistivity measurements for all measured dopings, with T_S and T_c marked. The resistivities have been amplified ($\times 6$) for 11.1% and 18.6% and reduced ($/3$) for 6.4% and 8.7% for display on the same scale, with a y -offset applied to all samples. **b)** The phase diagram for $\text{FeSe}_{1-x}\text{S}_x$, constructed from the transport and EDX results given in Table 2.1. FeSe data (squares) taken from [73] additional T_c points taken from [74] (triangles down) and [82] (triangles up).

Comparing the $\text{FeSe}_{1-x}\text{S}_x$ phase diagram of Figure 2.6b) with the pressure phase diagram of 2.4, there are broad similarities close to the parent compound: the ‘chemical pressure’ of doping and the application of actual pressure act to suppress T_S and, initially, slightly enhance T_c , with comparable maximum values of $T_c = 11\text{ K}$ and 13 K respectively. However at higher dopings/larger pressures the two cases diverge: applied pressure induces an AFM phase within the orthorhombic phase, and this becomes more prominent as the structural transition disappears; in the doped case the orthorhombic phase disappears entirely with no indication of magnetic order. There is also no sign of any further increase in T_c in the doped case, whereas at high pressures it is enhanced to at least 19 K . Although the effect of both applied pressure and S doping is to decrease the lattice parameters, the system is substantially more susceptible to doping: a suppression of T_S to 50 K requires $\sim 1\text{ GPa}$ of pressure, corresponding to a reduction of 3.5% in a and 5.8% in c [67]; a comparable suppression of T_S requires $x \sim 0.15$ S doping, which corresponds to a reduction of only 0.3% in a and 1.0% in c [74].

2.3 Shubnikov-de Haas oscillations

Experimental details

Transport measurements were performed in DC fields of up to 45 T at NHMFL, Tallahassee (on all samples except 11.1 %) and 33 T at HFML, Nijmegen (on all samples except 4.4 % and 6.4 %); in both cases the samples were mounted on single-axis rotators. As the 45 T measurement is achieved by the combination of a resistive magnet and a superconducting outsert, the field does not (except at the beginning and end of the day's measurement) go below the outsert field of 11.5 T. Due to the magnetoresistance of the thermometer, its resistance-temperature calibration is only valid at zero field; to calculate the actual temperature the zero field resistance must be extrapolated from the 11.5 T value using the known form of the magnetoresistance, leading to a larger uncertainty in the temperature values of the 45 T measurements. In addition a large current of 5 mA was used for the 45 T measurements for a larger signal-to-noise ratio, but accompanied by an increased likelihood of sample heating; a smaller current of 1 mA was used for the 33 T measurements, negating these effects. Due to both these considerations the 45 T data, in no small part because of the larger fields, is used in the main to determine the absolute values of the oscillation frequencies, whereas the 33 T data are used to study the temperature dependence.

2.3.1 Frequency assignment

Frequency extraction

All samples listed in Table 2.1 showed oscillations, and a representative set at base temperature ($T \sim 0.35$ K) close to $\mathbf{B} \parallel \mathbf{c}$ are shown in Figure 2.7. The raw magnetoresistance (converted to resistivity) at $T \sim 0.35$ K and close to $\mathbf{B} \parallel \mathbf{c}$ is shown in Figure 2.7a). With the exception of the higher doped samples, where $B_{c2} < 15$ T, there is a superconducting transition followed by an increasing magnetoresistance upon which, at least in the 4.4 % and 16.4 % samples, clear oscillations can already be seen. Differentiating the resistivity ($\partial\rho/\partial B$) in the high field region makes these oscillations, especially those of higher fre-

quency, clearer, as shown in Figure 2.7c). Alternatively dividing the data by a low order polynomial fit will also extract the oscillatory component ($\Delta\rho/\rho$), as shown in Figure 2.7e). Fourier transforms of both these data sets are shown in Figure 2.7f) and Figure 2.7g) respectively.

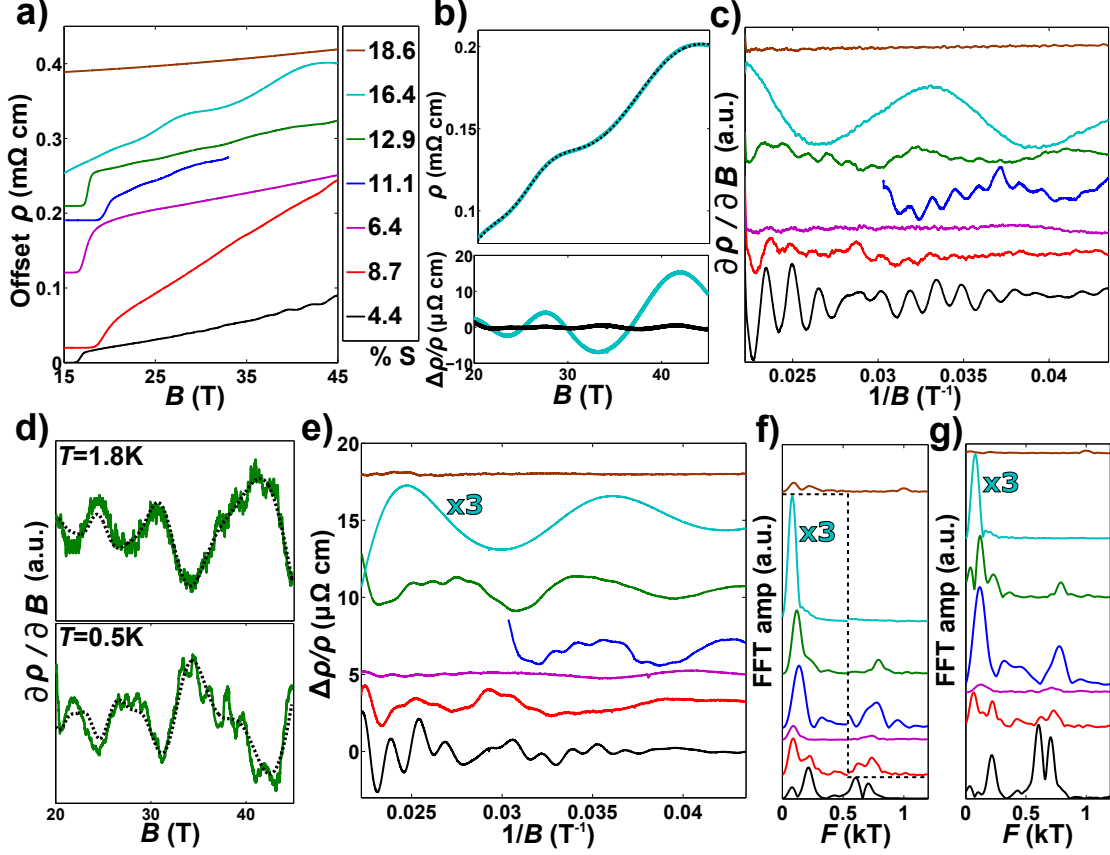


Figure 2.7: **Shubnikov-de Haas oscillations in $\text{FeSe}_{1-x}\text{S}_x$.** **a)** Magnetoresistance measurements for all samples, offset along the y -axis for clarity, conducted at $T \sim 0.35$ K close to $\mathbf{B} \parallel \mathbf{c}$, with a maximum field of 33 T for 11.1 % and 45 T for all other samples. **b)** (Top) 16.4 % fitted directly by a single low frequency and a quadratic background. (Bottom) the oscillatory part of the signal (blue) and the residual of the fit (black). **c)** The resistivities differentiated with respect to field and plotted against inverse field. **d)** Differentiated 12.9 % fitted by two low frequencies at $T = 1.8$ K and $T = 0.5$ K. **e)** The oscillatory component ($\Delta\rho/\rho$) of the resistivity, found by subtracting a 3rd-order polynomial, plotted against inverse field. The % signal has been reduced by a factor of 3. **f)** Fourier transforms of $\Delta\rho/\rho$, using a window of 22 - 33 T for 11.1 % and 22 - 45 T for the other samples. Data to the right hand side of the dashed line has been amplified ($\times 4$) to make the peaks more visible. **g)** Fourier transforms of $\partial\rho/\partial B$, with same windows as before.

Up to five separate frequencies are seen in each sample – illustrated perhaps most clearly in the 4.4 % and 8.7 % samples – in the range of 50 - 1200 T. The relative amplitudes of the low (< 500 T) frequencies dominate the divided data, while the higher

(> 500 T) frequencies are enhanced in the differentiated data. In combination these methods are used to extract the frequencies for each sample⁸, with both producing comparable values. However the Fourier transform analysis has its limitations when dealing with the lowest frequencies: as only a few periods span the measured field range the Fourier transforms will be broad and not entirely distinguishable from the background, while some of the amplitude may be lost to the background subtraction. To extract these frequencies the oscillations were, where possible, fitted directly. The fit for 16.4 % is shown in Figure 2.7b). Here the raw data are fitted by a single oscillatory component, of the form given in Equation 1.25, and a quadratic background. Values for m^* and l_D are estimated from Lifshitz-Kosevich and Dingle fits to the oscillation amplitude (discussed in more detail in Section 2.3.2) and fixed, so this is a 6 parameter fit – to the frequency, amplitude and phase of the oscillation, plus the terms in the quadratic background. When additional frequencies are present a successful fit is more difficult, as more free parameters are introduced, however two (low) frequency fits are possible to the differentiated data (where no background term is required). An example for 12.9 % is shown in Figure 2.7d): at higher temperatures the relative amplitudes of the high frequencies are reduced, so the fit at 1.8 K is better than that at 0.5 K.

Frequency values

Four of these frequencies – here labelled F1, F2, F4 and F5 – have been reported in the parent compound [78], but the fifth – F3, taking an intermediate value of ~ 450 T – is detected here for the first time. As seen in Figure 2.7f), at the lowest doping (4.4 %) F3 has by far the smallest amplitude of the observed frequencies. This may explain why it was not observed in the previous measurements on FeSe [78]: the crystals had a smaller RRR (~ 3 compared to ~ 16 in 4.4 %, from Figure 2.6a)), indicative of stronger scattering; while the pulsed field measurements conducted are typically far noisier than the DC field measurements presented here. Indeed DC measurements on FeSe do observe F3 [79], however as both the frequency and effective mass are close to double those of

⁸Although differentiating the resistivity will of course change the field dependence, the oscillatory component, and hence the frequencies, will be unchanged, excepting a phase shift.

F2 it is attributed to a second harmonic. In $\text{FeSe}_{1-x}\text{S}_x$ F3 and $2\times\text{F2}$, although having broadly comparable values, are not consistently close across the measured doping range. Furthermore by 11.1 % the amplitudes of F2 and F3 are comparable, whereas a second harmonic would be expected to have a much smaller relative amplitude. Therefore it seems that F3 is a new frequency not previously considered in this system.

The sizes of the frequencies measured close to $\mathbf{B} \parallel \mathbf{c}$ are markedly smaller than those usually seen in the Fe-based superconductors from non-reconstructed Fermi surfaces in the paramagnetic phase (taking values between 1 - 5 kT [3]); indeed the frequency range of 50 - 1200 T is closer to what might be expected for a reconstructed Fermi surface (such as BaFe_2As_2 , 100 - 900 T [58]), though of course SdH measurements on the parent compound have already confirmed that the Fermi surface of FeSe has the expected quasi-two dimensional form [77]. The relatively small values taken by the SdH frequencies in $\text{FeSe}_{1-x}\text{S}_x$ (as well as in FeSe) are therefore instead an indicator of an atypically large renormalisation of the Fermi surface of FeSe in comparison to the other Fe-based superconductors.

Doping dependence of frequencies

Using these methods the SdH frequencies close to $\mathbf{B} \parallel \mathbf{c}$ can be extracted for all samples, these are given in Table 2.2 and plotted against doping in Figure 2.8. Across much of the doping range five frequencies are observed, and these are labelled as F1 to F5, from lowest frequency to highest. In the samples where not all frequencies are observed the labels are inferred from the values of the frequency, in combination with their effective masses (discussed in detail in Section 2.3.2). The four frequencies reported in the parent compound [78] (F1, F2, F4 and F5) are seen across the measured region of the phase diagram, with the disappearance of F4 at higher dopings due to a general decrease in amplitude of the observed oscillations (as can be seen clearly in Figure 2.7g)) and an increasing proximity to the larger FFT peak of F5, rather than the disappearance of the band it originates from. Using the dashed lines as a rough guide, all five frequencies evolve continuously with doping both within the orthorhombic, PM phase and – at least

for frequencies F1, F2 and F5 – through the transition into the tetragonal PM state. No discontinuous changes in the Fermi surface appear to be accessible with (at least this range of) doping, in contrast to the case of applied pressure [81].

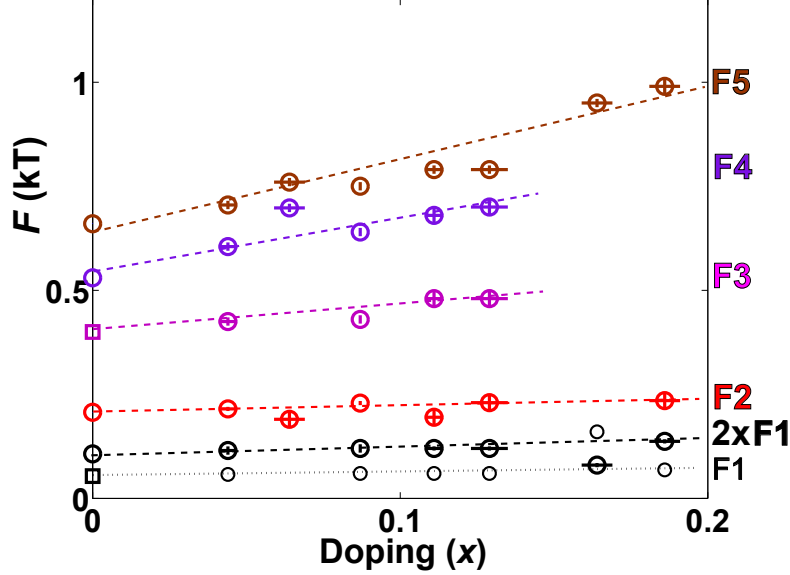


Figure 2.8: **Doping dependence of Shubnikov-de Haas frequencies in $\text{FeSe}_{1-x}\text{S}_x$.** Smaller black circles are the smallest frequency halved (or doubled for 16.4 %), dashed lines serve as a guide to the eye. Parent compound data taken from [78] (circles) and [79] (squares).

Across the measured doping range all frequencies increase in size with doping, with the effect more pronounced for the larger frequencies: between $x = 0$ and $x = 0.13$ – the highest doping at which all frequencies are seen – F1 and F2 increase by $\sim 10\%$ while F4 and F5 increase by $\sim 30\%$ and $\sim 20\%$ respectively. This qualitatively agrees with the ARPES measurements on $\text{FeSe}_{1-x}\text{S}_x$ [78], which report a $\sim 10\%$ increase in the size of the Fermi surface between $x = 0$ and $x = 0.15$ but are unable to ascertain the k_z dependence of this increase. This general increase in size with doping is expected: as the smaller S ion replaces the larger Se the Fe-S/Se bond length decreases [74, 83] and so the unit cell decreases in size; the Brillouin zone and hence the Fermi surface should therefore be expected to increase. However the greater rate of increase seen for the larger SdH frequencies reveals that as the system is doped the Fermi surfaces also become more warped. Along with the increasing size, the greater warping will also reduce the nesting in the system, likely suppressing the orbital ordering and so decreasing T_s .

Of all the measured samples 16.4 % seems to be an outlier: the data are dominated by a single oscillatory component, with an unexpectedly small frequency and incredibly large amplitude (reduced by a factor of 3 in Figure 2.7e)-g) so it can be plotted alongside the other samples). In fact a similarly small frequency is seen in DC field measurements in FeSe [79], of value 60 T compared to 80 T in 16.4 %. This is claimed to be the actual F1, with the value of 120 T reported elsewhere [78] a second harmonic. Although it may seem perverse that the second harmonic, with its smaller amplitude, is visible and the original frequency is not, the field range of 20 – 45 T in which oscillations are observed corresponds to little more than one period for a 60 T frequency. Therefore any low frequency will be indistinguishable from the background: only when the oscillation has significantly large frequency and amplitude – as is the case for 16.4 % – will the genuine F1 be visible. Plotted as smaller circles in Figure 2.8 are the measured values of F1 divided by 2, labelled ‘F1’, which line up with the low frequency of 16.4 %; similarly the double of the low frequency of 16.4 % lies on the line, labelled ‘2× F1’, through the other points. From this it seems that the measured F1, in all samples except 16.4 %, is indeed the second harmonic of the actual low frequency.

Sample	‘F1’ (T)	m^* (m_e)	F2 (T)	m^* (m_e)	F3 (T)	m^* (m_e)	F4 (T)	m^* (m_e)	F5 (T)	m^* (m_e)
4.4 %	115(10)	3.6(1)	215(5)	4.0(1)	425(10)	5.3(1)	605(10)	6.0(1)	705(10)	4.5(1)
6.4 %	-	-	190(20)	3.7(5)	-	-	698(10)	-	760(10)	4.3(5)
8.7 %	120(10)	2.5(4)	229(5)	4.0(2)	430(10)	6.1(4)	640(10)	5.8(2)	750(10)	4.5(2)
11.1 %	120(5)	3.0(1)	195(20)	4.1(3)	480(20)	-	680(20)	6.0(4)	790(10)	4.6(2)
12.9 %	120(5)	2.5(1)	230(20)	3.9(6)	480(20)	-	700(20)	-	790(10)	4.5(5)
16.4 %	80(5)	1.6(1)	-	-	-	-	-	-	950(10)	-
18.6 %	137(5)	-	235(20)	1.6(5)	-	-	-	-	990(20)	2.3(2)

Table 2.2: **Frequencies and effective masses extracted from Shubnikov-de Haas oscillations observed in $\text{FeSe}_{1-x}\text{S}_x$.** Absent frequencies and masses are likely due to oscillations being indistinguishable above the noise level, rather than any fundamental changes to the Fermi surface.

2.3.2 Temperature dependence

Effective mass extraction

The temperature dependence of the Shubnikov-de Haas oscillations was measured for all samples, in the range $T = 0.3 - 2$ K and close to $\mathbf{B} \parallel \mathbf{c}$. As discussed previously the 33 T HFML data are preferable for obtaining an accurate temperature dependence, so this data are used where possible. However, in the case where certain frequencies are only observed above 33 T (12.9 %, 16.4 %, 18.6 %) or measurements were not conducted at HFML Nijmegen at all (4.4 %, 6.4 %) the 45 T NHMFL data are instead used, although with a consistent field window for all frequencies. For both 12.9 % and 16.4 % B_{c2} can be compared between data sets to check the veracity of the NHMFL temperatures – any heating of the sample will act to lower B_{c2} . As there is no appreciable difference in $B_{c2}(T = 0.35$ K) in either sample it is fair to assume there are no heating effects in these cases. In 18.6 % however, at base temperature $B_{c2}(\mathbf{B} \parallel \mathbf{c})$ is below the lower field limit (11.5 T) of the NHMFL measurements. Instead Ginzburg-Landau fits to the anisotropy (shown in the magnified region of Figure 2.11 and discussed in more detail in Section 2.3.3) can be used to extract B_{c2} , finding a discrepancy of 1.5(5) T between the NHMFL data and HFML data both supposedly measured at $T = 0.35$ K. Taking the values of T_c and B_{c2} from the HFML measurements and assuming a near-linear temperature dependence of the upper critical field – which is the case for $\mathbf{B} \parallel \mathbf{c}$ in FeSe [79, 84] – this gives an actual temperature of 1.7(4) K, or a temperature increase due to heating of 1.4(4) K.

Figure 2.9 shows the effect of temperature on the measured SdH oscillations. As already seen, clear oscillations are observed in $\Delta\rho/\rho$ for all samples, and these decrease in amplitude with increasing temperature. Alongside the plots of $\Delta\rho/\rho$ and its Fourier transforms are Lifshitz-Kosevich fits to the temperature dependence of the amplitude of each oscillation frequency; for clear comparison between frequencies they have been scaled by their fitted intercept at $T = 0$ K. The effective masses extracted by these fits are given in Table 2.2; not all observed frequencies have an associated mass, in these cases the amplitude was not clear above the background across a broad enough range

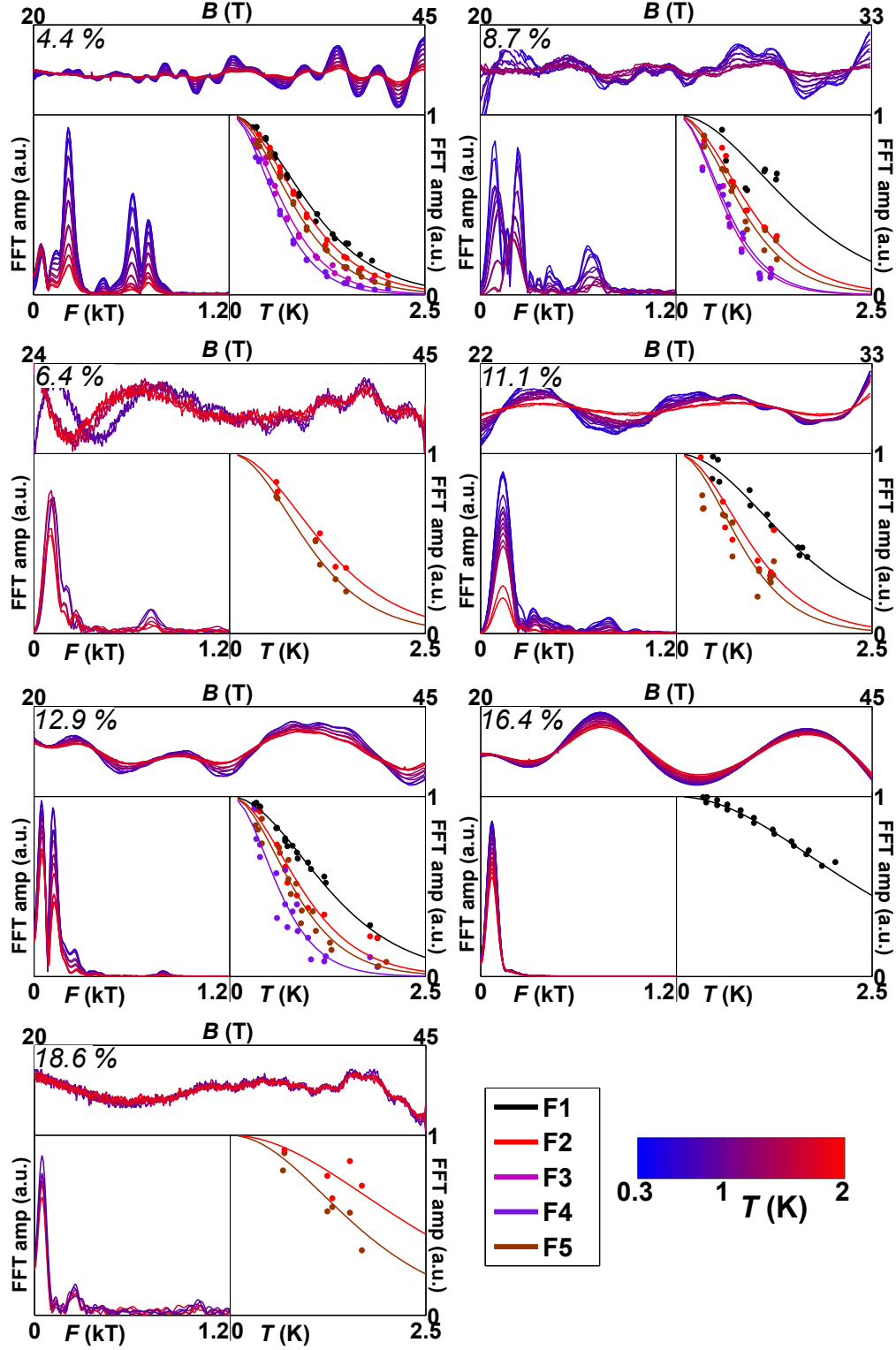


Figure 2.9: Temperature dependence of Shubnikov-de Haas oscillations in all measured samples of $\text{FeSe}_{1-x}\text{S}_x$. Shown for every sample is: (top panel) the oscillatory component ($\Delta\rho/\rho$) of the resistivity at temperatures in the range 0.3 – 2 K, measured close to $\mathbf{B} \parallel \mathbf{c}$ and coloured by temperature; (bottom left panel) Fourier transforms of $\Delta\rho/\rho$, again coloured by temperature; (bottom right panel) Lifshitz-Kosevich fits to the temperature dependence of the FFT amplitudes for all observed frequencies, scaled by the fitted intercept at $T = 0$ K.

of temperatures to produce a meaningful fit. Figure 2.10 shows the effective masses plotted against doping; the points from 18.6 % (plotted as diamonds) may systematically overestimate the masses as a result of sample heating.

Doping dependence of effective masses

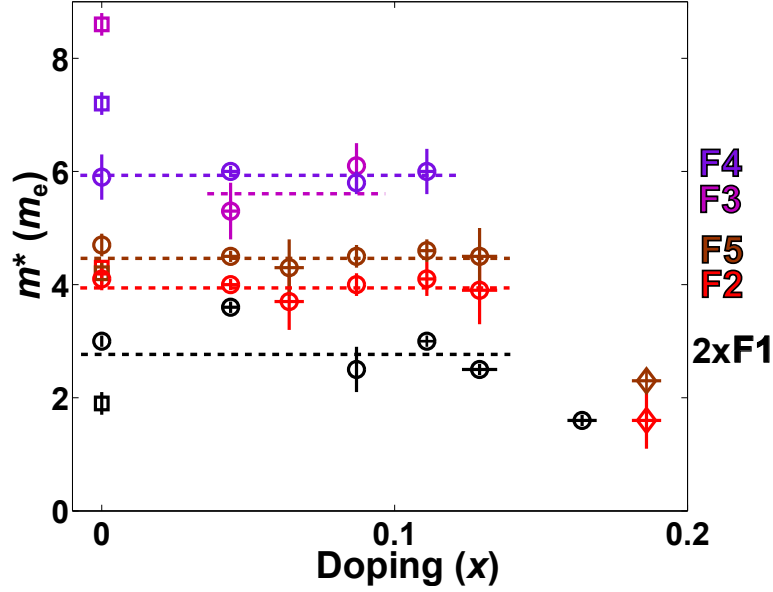


Figure 2.10: **Doping dependence of effective masses in $\text{FeSe}_{1-x}\text{S}_x$.** Some points (diamonds) may have a systematic error from sample heating, not accounted for by the error bars. Dashed lines indicate the approximately constant effective masses in the orthorhombic phase. Parent compound data taken from [78] (circles) and [79] (squares).

Across the doping range measured the effective masses fall into three categories: the smallest frequency F1 has the smallest mass of $\sim 3 m_e$; F2 and F5 take a value of $\sim 4 m_e$; F3 and F4 have the largest effective mass of $\sim 6 m_e$. This means that the frequencies paired together likely originate from the same band of the Fermi surface, being the maxima and minima of a warped cylinder. For FeSe it was determined that F2 and F5 originated from the hole band, F1 from the inner electron band and F4 from the outer electron band [77]. As F3 and F4 are of such similar effective mass they must originate from the same band, so F3 is the minima of the outer electron band, unseen, or misattributed as the second harmonic of F2 [79], in the parent compound. The reason for this misattribution is clear from Figure 2.8, as well as $F4 \approx 2 \times F2$, in FeSe (plotted as squares) $m_{F4}^* \approx 2 \times m_{F2}^*$, also required for a second harmonic. In the doped compounds

the measured m_{F4}^* is markedly less than $2 \times m_{\text{F2}}^*$ whenever it is observed, so it cannot be a harmonic. This same argument, that $m_{2\text{F}}^* = 2 \times m_{\text{F}}^*$, can also be used to confirm the previous assertion that the measured ‘F1’ is the second harmonic of the genuine F1, which is only observed in 16.4 %: as expected the effective mass measured in 16.4 %, $m_{\text{F1}}^* = 1.6(1) m_e$, is approximately half the value measured in the other samples, around $m_{\text{F1}'}^* \sim 3 m_e$.

These values of effective mass are notably larger than those usually seen in the Fe-based superconductors: typical values range between $1.5 - 3 m_e$ depending on the exact system [3], compared to $3 - 6 m_e$ in $\text{FeSe}_{1-x}\text{S}_x$ (and FeSe); this corresponds to mass enhancements of $(\lambda_{ee}^s + \lambda_{ep}) = m^*/m_b - 1 = 0.5 - 2$ in other Fe-based superconductors, versus $(\lambda_{ee}^s + \lambda_{ep}) = 4 - 5.5$ in $\text{FeSe}_{1-x}\text{S}_x$ (using the band masses calculated later in Section 2.4.2). Much like the relatively smaller size of the frequencies, these larger mass enhancements point towards a markedly larger renormalisation of the electronic structure in $\text{FeSe}_{1-x}\text{S}_x$. Furthermore there is a clear distinction in effective mass between the frequencies arising from the hole (F2, F5) and inner electron band (F1) of d_{xz}/d_{yz} character [78] – taking values in the range $2.5 - 4.5 m_e$ – compared to the outer electron band (F3, F4) of d_{xy} character – with values in the range $5.3 - 6.1 m_e$; this can be seen clearly across the measured doping range in Figure 2.10.

Considering only the samples within the orthorhombic phase, 4.4 % through to 16.4 %, there is no systematic change in effective mass for any of the frequencies with doping. This is in contrast to the case of applied pressure where, with a similar increase in frequency, the effective mass increases for all frequencies by a factor of 20 – 50% [81]. This increase is associated with an enhancement in spin fluctuations as the AFM state is approached; the fact that there is no noticeable increase with S doping suggests that an equivalent AFM state is not present in the phase diagram of $\text{FeSe}_{1-x}\text{S}_x$.

However in the highest doped, 18.6 % sample (which is without an orthorhombic transition), both observed frequencies (F2 and F5, corresponding to the hole band) are considerably reduced in effective mass. Although there is sample heating in these measurements, its presence will raise the actual temperature of the sample in relation to the

measured temperature and so overestimate the effective masses. Making the assumption that the 1.4(4) K temperature increase due to heating – calculated from B_{c2} at $T = 0.35$ K – is constant, the actual effective masses of F2 and F5 in the 18.6 % sample would be lowered further to $1.0(5) m_e$ and $1.8(2) m_e$ respectively. There therefore appears to be a clear decrease in effective mass for the highest doped, 18.6 % sample of $\text{FeSe}_{1-x}\text{S}_x$. The distinction between this sample and all the others measured is clearly evident: 18.6 % does not show a structural transition, so its Fermi surface arises from the tetragonal, ‘high temperature’ phase. The reduction in effective mass may then occur upon the entry into this state – as the system no longer undergoes an orthorhombic distortion, perhaps the coupling between the electronic structure and lattice is weaker, so λ_{ep} and hence the effective masses are reduced. However because only a single sample that did not show T_S has been measured, and because these measurements were unfortunately affected by sample heating, further measurements for $x = 0.18$ or greater dopings would need to be conducted before any firm conclusions can be drawn about the effective masses in the tetragonal phase.

2.3.3 Angular dependence

Ginzburg-Landau fits

The angular dependence of the Shubnikov-de Haas oscillations was measured for all samples over the range $\mathbf{B} \parallel \mathbf{c}$ ($\theta = 0^\circ$) to $\mathbf{B} \perp \mathbf{c}$ ($\theta = 90^\circ$), at $T \sim 0.35$ K. The results of these measurements are shown in Figure 2.11a). Shown first for each sample is the critical field (B_{c2}) anisotropy, with B_{c2} defined as the peak in $\partial\rho/\partial B$ at the transition. Although the complete range cannot be mapped for all samples (due to the limited field range of 11.5 – 45 T for NHMFL data, plotted in blue, and 0 – 33 T for HFML, plotted in green), the angular dependence is fitted well by the Ginzburg-Landau model for an

anisotropic superconductor [85]:

$$B_{c2}(\theta) = \frac{B_{c2}(0)}{\sqrt{\cos^2(\theta) + \gamma^{-2}\sin^2(\theta)}}, \quad (2.1)$$

$$\gamma = \sqrt{m_{B\perp c}^*/m_{B\parallel c}^*}$$

where γ is known as the effective mass anisotropy. $B_{c2}(0)$, the critical field at $\mathbf{B} \parallel \mathbf{c}$, can be tracked across the measured doping range and correlates well with T_c (shown back in Figure 2.6b)), notably decreasing at dopings above $x = 0.15$. The extracted B_{c2} values can also be used to check consistency between measurements, with the diminished B_{c2} observed in NHMFL measurements on 18.6 % – shown in the magnified section of Figure 2.11 (plotted in blue with a red fit, versus the HFML data plotted in green with an orange fit) – indicative of the sample heating discussed earlier.

The fitted values of the effective mass anisotropy are given for each sample in Figure 2.11a), with the doping dependence of γ shown in Figure 2.11b). Within the orthorhombic phase the effective mass anisotropy takes a relatively constant value of $\gamma \sim 1.9$, while at the highest dopings it appears to increase to $\gamma \sim 2.2$, although with fewer samples measured and larger error bars this change is not entirely clear cut. Typically in the Fe-based superconductors γ is largest close to T_c and decreases as $T \rightarrow 0$, approaching values close to $\gamma \sim 1$ [86, 87]; this is attributed to the relatively three dimensional nature of the Fermi surface, at least in comparison to the larger effective mass anisotropies of the cuprate superconductors [88]. Therefore the larger effective mass anisotropy seen in $\text{FeSe}_{1-x}\text{S}_x$ may be an indication towards the greater two dimensionality of the Fermi surface compared to the other Fe-based superconductors – the Fermi surfaces of Figure 2.5 are considerably less warped than those of Figure 2.3. However the quantum oscillation frequencies in Figure 2.8 revealed a clear increase in warping with S doping, so the effective mass anisotropy would be expected to decrease with doping, and in Figure 2.11b) this clearly isn't the case. Therefore, as the effective mass anisotropy increases as $T \rightarrow T_c$, the larger values seen in $\text{FeSe}_{1-x}\text{S}_x$ may instead be due to the relatively lower values of T_c in the material. The reduced T_c at higher dopings may then lead to the increased effective

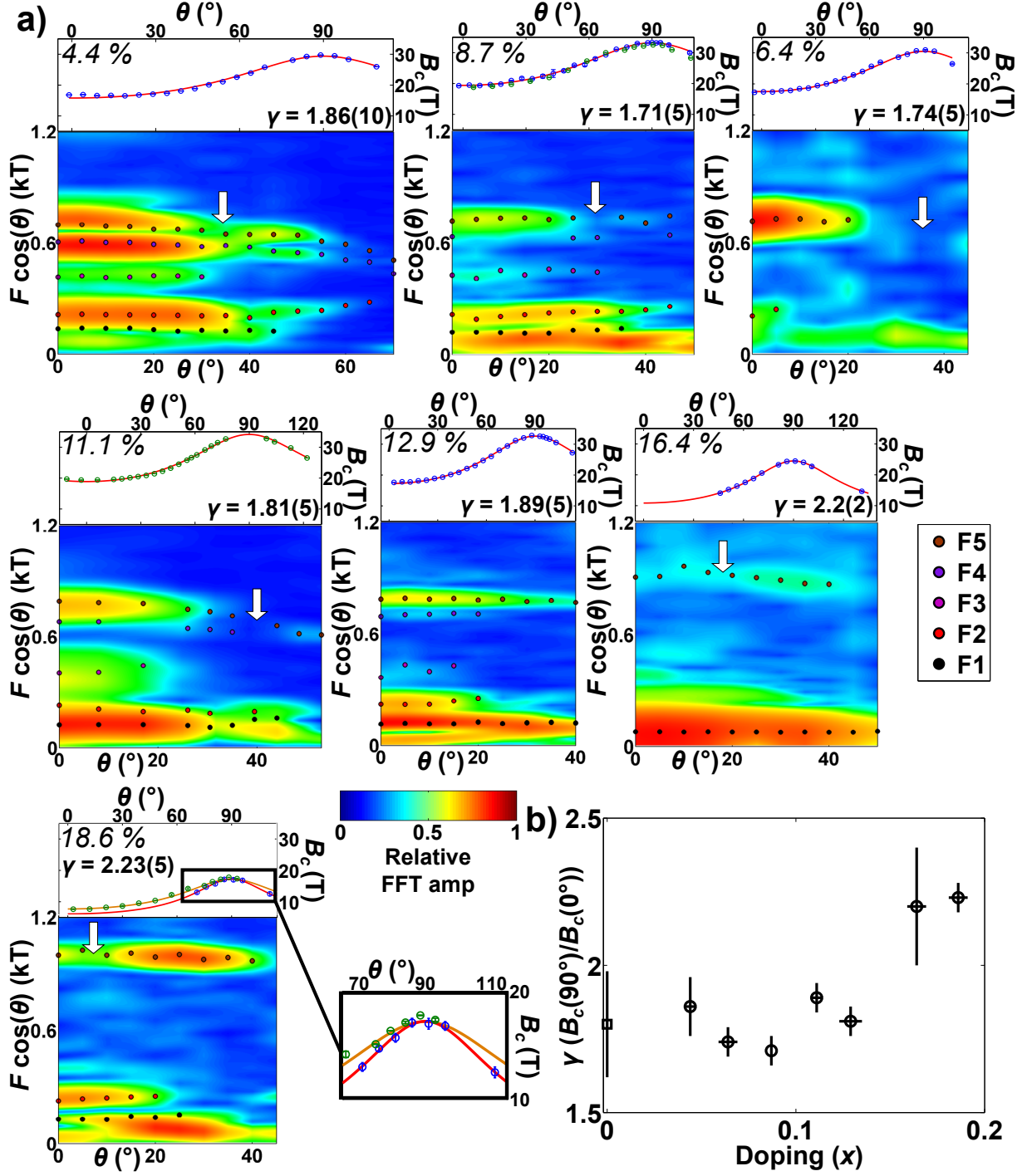


Figure 2.11: **Angular dependence of Shubnikov-de Haas oscillations in all measured samples of $\text{FeSe}_{1-x}\text{S}_x$ at $T \sim 0.35$ K, $\theta = 0^\circ$ corresponds to $\mathbf{B} \parallel \mathbf{c}$ and $\theta = 90^\circ$ to $\mathbf{B} \perp \mathbf{c}$.** a) Shown for every sample is: (top panel) Ginzburg-Landau fits to the critical field anisotropy; (bottom panel) the angular dependence of the Fourier spectrum, scaled as $F \cos(\theta)$, with the extracted SdH frequencies plotted on top. Magnified for 18.6 % is the discrepancy in critical field between NHMFL (blue points, red fit) and HFML (green points, orange fit) measurements supposedly conducted at the same temperatures, due to sample heating in the former case. b) Doping dependence of the effective mass anisotropy, obtained from the Ginzburg-Landau fits. Data for FeSe taken from [84].

mass anisotropy, and indeed $\text{Fe}_{1.11}\text{Se}_{0.4}\text{Te}_{0.6}$ shows an increased T_c of 14 K and hence a reduced $\gamma = 0.95$ at the lowest measured temperatures [88].

Angular dependence of frequencies

Plotted beneath the critical field anisotropy in Figure 2.11a) for each sample is the angular dependence of the Fourier spectrum, with peaks in intensity corresponding to SdH frequencies. Various field windows were used across the dopings, chosen for the clearest frequency resolution but also to maximise the angular range (the field window used must be consistent between runs and always above B_{c2} , which increases at higher angles). $\partial\rho/\partial B$ was used for all samples except 18.6 % (which uses $\Delta\rho/\rho$). An angle dependent scaling of $F\cos(\theta)$ is applied to the frequency on the y -axis.

For a cylindrical Fermi surface the frequency, proportional to the cross-sectional area, perpendicular to a magnetic field applied at angle θ to the normal will be $F(\theta) = F(0)/\cos(\theta)$. Therefore applying a scaling of $F\cos(\theta)$, with the assumption of quasi-cylindrical bands, can help determine the origin of the SdH frequencies: for a perfect cylinder $F\cos(\theta)$ will be constant with θ ; for the minimum of a warped cylinder $F\cos(\theta)$ will increase; while for the maximum of a warped cylinder $F\cos(\theta)$ will decrease. Applying this maxim to the Fourier spectrum of Figure 2.11 it is clear, especially from the large angular range of 16.4 %, that F2 is a minimum and F4 and F5 are maximum. Although only a small angular range is observable, F3 appears, most markedly in 8.7 %, to be a minimum; F1, most clearly visible in 11.1 % and 12.9 %, to be a maximum. This assignment agrees with the picture constructed thus far from both previous work [77] and the effective mass analysis, with F2 and F5 the minimum and maximum of the hole band, F1 the maximum of the inner electron band and F3 and F4 the minimum and maximum of the outer electron band.

Spin zeros in the highest frequency

A further feature is visible in the angular dependence of the Fourier spectrum: a large dip in the amplitude of F5 (marked by white arrows), moving from around 40° in the

lowest doped samples to 10° in the highest doped. In a quasi-two dimensional system such as FeSe, the band masses (and so also the various effective masses) vary with angle as $m_b(\theta) = m_b(0)/\cos(\theta)$ [89], similarly to the frequency. Any damping term that has a mass dependence will therefore also have an angular dependence, so – from the definitions given in Equations 1.26, 1.27 and 1.28 – R_T , R_D and R_S will all vary with angle. Combining these, the angular dependence of the damping takes the form:

$$\begin{aligned} A(\theta) &= A_0 R_T(\theta) R_D(\theta) R_S(\theta) \\ &= A_0 \frac{X}{\cos(\theta) \sinh(X/\cos(\theta))} \exp\left(-\frac{\pi m_b(0)}{eB\tau\cos(\theta)}\right) \cos\left(\frac{\pi g m_{ss}^*(0)}{2m_e\cos(\theta)}\right) \end{aligned} \quad (2.2)$$

with X defined in Equation 1.26. Both the thermal and impurity damping ($R_T(\theta)$ and $R_D(\theta)$) lead only to a general decrease in amplitude at high angles, not a brief region of zero amplitude. These regions are instead due to the spin splitting term, $R_S(\theta)$: this term will be zero (known as a spin zero) whenever $g m_{ss}^*(0)/m_e \cos(\theta) = (2n + 1)$.

Figure 2.12 shows the angular dependence of the amplitude of the Fourier transform peak corresponding to F5, extracted from the data of Figure 2.11. The 12.9% sample is not shown as the spin zero is not clear due to overlap of the amplitudes of F4 and F5. For the remaining samples, the angular dependence is fitted to Equation 2.2, with free parameters A_0 , τ and $g m_{ss}^*(0)$ ($m_b(0)$ is taken to be the value found by shifted DFT calculations, given in Figure 2.15c)). The former two parameters determine the amplitude of the angular dependence, while $g m_{ss}^*(0)$ determines only the position of the spin zero; $g m_{ss}^*(0)$ is therefore robust to deviations in the amplitude from Equation 2.2 (likely arising from deviations in temperature or uneven rotation at low angles), such as those present at low angles in 6.4%. In the 16.4% and 18.6% samples the separate branches of F4 and F5 cannot be distinguished, so there is a possibility the amplitude dip may instead arise from destructive interference between the two frequencies. However the amplitude of F4 is seen to decrease with increasing doping, while the position of the amplitude dip in these higher dopings agrees with the general trend seen in the position of the spin zero in F5 throughout the samples. It is therefore likely that the amplitude dips in 16.4% and 18.6% originate from spin zero in F5 rather than any interference

effects.

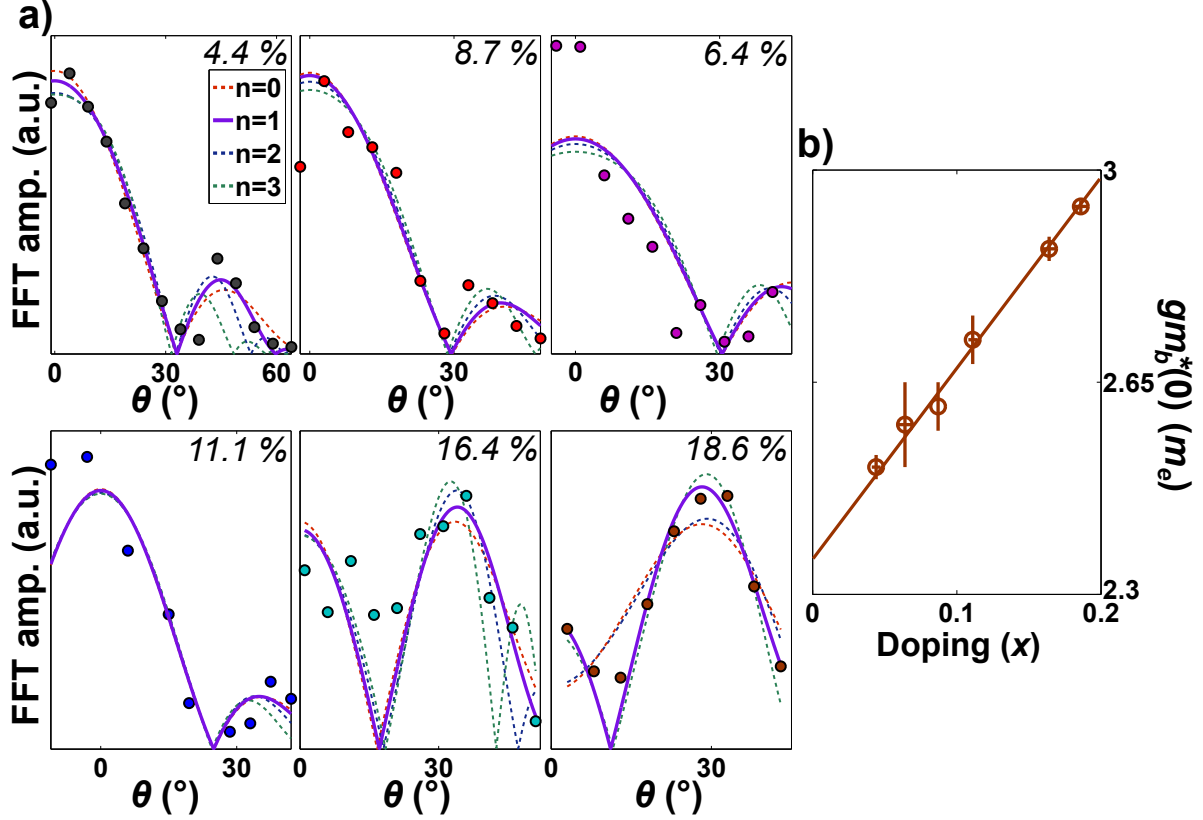


Figure 2.12: **Angular dependence of the amplitude for the highest Shubnikov-de Haas frequency in $\text{FeSe}_{1-x}\text{S}_x$.** **a)** Fits to Equation 2.2 for the amplitude of F5 in samples clearly showing a spin zero, indexed by n such that the observed spin zero occurs at $gm_{ss}^*(0)/m_e \cos(\theta) = (2n + 1)$. **b)** Doping dependence of $gm_{ss}^*(0)$, extracted from the fits, line is a guide to the eye.

There will be a local minimum in the fit every time the amplitude dip lines up with the n th spin zero, so separate fits were conducted for values $0 \leq n \leq 3$. For the 4.4 %, 16.4 % and 18.6 % samples a second spin zero (or at least the lower edge of one) is seen at higher angles, which allows for accurate determination of n : $n = 0$ places the spin zeros too far apart, while $n = 2$ and 3 place them too close together; $n = 1$ therefore provides the best fit to the measured spin zero positions. For the 8.7 %, 6.4 % and 11.1 % samples only a single spin zero is observed, so the differences between fits are rather more slight. However as the first visible spin zero corresponds to $n = 1$ in both the lower (4.4 %) and higher (16.4 %, 18.6 %) dopings, there is no reason to expect any deviation from this in the remaining samples; the $n = 1$ fit is therefore also used for 8.7 %, 6.4 % and 11.1 %.

Figure 2.12b) shows the $gm_{ss}^*(0)$ values extracted from these fits. These values increase

in size with S doping – to be expected, as the position of the spin zero moves to lower angles with increasing doping – and do so approximately linearly. Unlike the effective mass measurements, these values will be unaffected by any noise in the measurement temperature, as they depend only on the position of the spin zero. The electronic g -factor – determined as $g = 2.09(5)$ in FeSe by ESR measurements [90] – is unlikely to change significantly with doping, so the increase in $gm_{ss}^*(0)$ corresponds to an enhancement of the electron-electron interactions for F5, the maximal orbit of the hole band: using Equation 1.29 gives an increase from $(1 + \lambda_{ee}^s)/(1 + \lambda_{ee}^a) = 1.50(1)$ to $(1 + \lambda_{ee}^s)/(1 + \lambda_{ee}^a) = 1.76(1)$ over the measured doping range. Whether this enhancement arises from the suppression of the structural transition, and so peaks around $x = 0.2$, or is a general increase across the doping range is unclear; measurement at higher dopings beyond the suppression of T_S would be needed to determine this. However recently reported elastoresistance measurements on $\text{FeSe}_{1-x}\text{S}_x$ [91] find a similar increase in nematicity – and so electron-electron interactions – over the same measured doping range, which they link to the presence of a nematic quantum critical point as $T_S \rightarrow 0$. This increase in the mass enhancement of F5 was not seen in the effective masses obtained from the temperature dependence, however: of course the thermal effective mass m^* and the spin susceptibility effective mass m_{ss}^* , as defined in Equation 1.29, are not identical, relative changes between λ_{ep} and λ_{ee}^a may cancel out any changes in the thermal effective mass; additionally the thermal effective masses – obtained from fits to the often noisy temperature dependence of the frequency amplitude – have a larger error than those obtained from the positions of the spin zeros, so the change observed in m_{ss}^* may be masked by the error bars in m^* .

2.3.4 Phase analysis

Berry phase extraction

Due to the high fields used for measurement, for the smallest observed SdH frequency F1 the oscillations observed are close to the quantum limit of the system – the field, equal to the frequency of oscillation, at which the $l = 1$ Landau level passes through the Fermi surface. The first oscillation maximum beneath this field will correspond to the $l = 2$

Landau level passing through the Fermi surface, the second the $l = 3$ Landau level and so on, and the expected positions of these maxima can be easily calculated from the value of the quantum oscillation frequency, which defines their spacing in inverse field. By this method an l -value can be assigned, with some confidence, to each visible maximum in $\Delta\rho/\rho$ (and equally an $l + \frac{1}{2}$ value can be assigned to the minima)⁹. Figure 2.13a) shows $\Delta\rho/\rho$, measured at $T = 0.35$ K over a range of angles, for the samples showing a clear low frequency in the raw data. Multiple angles are plotted, with inverse field scaled as $1/(B\cos(\theta))$; for a cylindrical Fermi surface (where $F(\theta) = F(0)/\cos(\theta)$) this will align the maxima and minima at all angles. In the 11.1 % and 12.9 % samples – where F1 is a second harmonic so the deviation will be more pronounced – the oscillations become misaligned at higher angles as the Fermi surface is not a perfect cylinder, so the maxima and minima position are taken from the smallest angle at which they are visible.

Using frequency values found by direct fits to $\Delta\rho/\rho$, the maxima (dashed red lines) and minima (dashed black lines) can be assigned an l -value, in the range $l = 2 - 5.5$ for the three samples. In Figure 2.13b) these l -values are plotted against $1/B$ for the three samples. 11.1 % and 12.9 %, where the second harmonic of $2 \times \text{F1} \sim 120$ T is being fitted, lie on top of each other, though the higher field and larger signal-to-noise of 12.9 % mean a greater range of l is visible. 16.4 %, where the actual F1 is observed, has a steeper gradient as a result of the smaller frequency. The x -intercept of this plot will be the phase of the SdH oscillation (divided by a factor of 2π), which, from Equation 1.25, is $\pi - \phi_B$, the Berry phase. A nontrivial Berry phase of $\phi_B = \pi$ (rather than $0, 2\pi$) is indicative of an orbit encircling a Dirac point in the band structure, where a linear dispersion leads to massless quasiparticles. This is clearly the case for 16.4 % ($\phi_B = 0.88(5)\pi$), where the large amplitude of the frequency may be due to the enhanced mobility of a Dirac-like quasiparticle with small effective mass and no backscattering [24]. With lower doping the Berry phase becomes more ambiguous – the presence of higher frequencies and smaller amplitude increases the error bars – but for 12.9 % ($\phi_B = 1.3(1)\pi$) a non-trivial Berry

⁹The same treatment can of course be applied to higher frequencies, but as the period of oscillation is smaller and l is larger, correctly identifying l can be tricky; the large l -values also lead to a larger error in the x -intercept and hence the Berry phase.

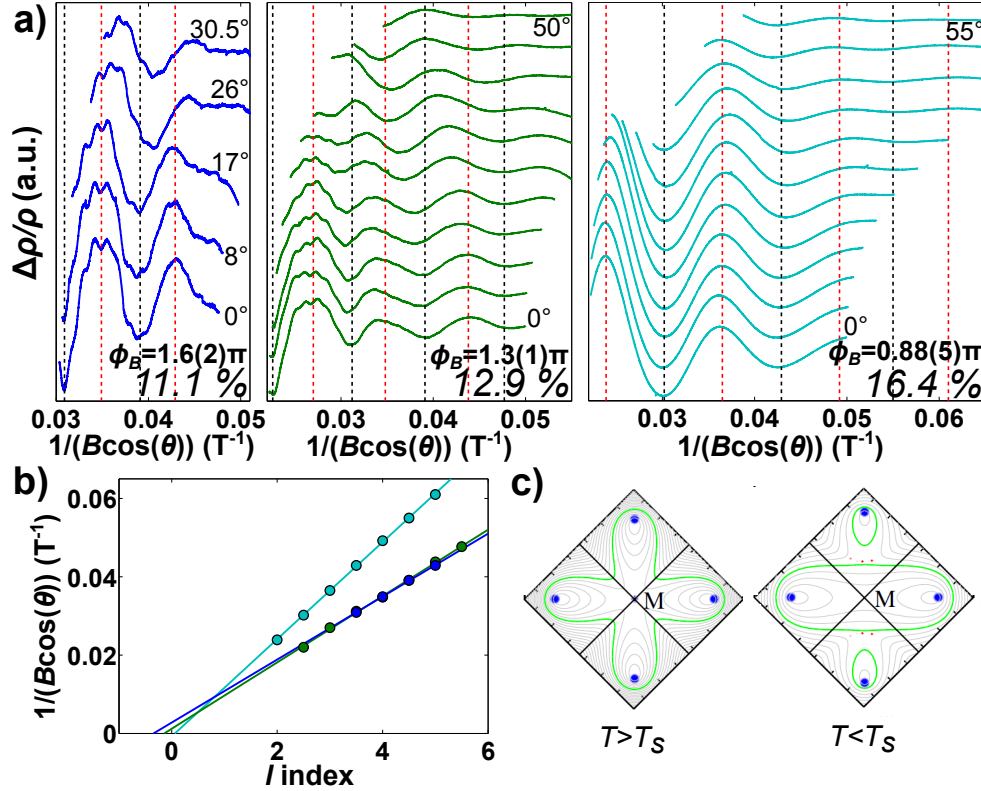


Figure 2.13: **Berry phase analysis of the lowest Shubnikov-de Haas frequency in $\text{FeSe}_{1-x}\text{S}_x$.** **a)** Subtracted resistivity data for samples showing a clear low frequency, plotted over a range of angles with field scaled as $B\cos(\theta)$. Red dashed lines indicate maxima, black dashed lines minima. **b)** Berry phase plot for the graphs of **a)**, with the maxima and minima indexed according to the frequency of oscillation. **c)** Cartoon of the possible origin of the non-trivial Berry phase, taken from [92]; orbits are in green, Dirac points in blue.

phase appears to still be present, while for 11.1 % ($\phi_B = 1.6(2)\pi$) the result is inconclusive.

Possible origin of the non-trivial Berry phase

A full study of the Dirac-like behaviour at $x \approx 0.2$ doping is presented in [92], which includes the measurements on 16.4 % presented here¹⁰. Shown in cartoon form in Figure 2.13c), the Dirac behaviour is attributed to a band crossing close to the M -point (in blue), which will be encircled by orbits around the outer electron band (in green). From the tetragonal symmetry of the system (at high temperatures) this point is four-fold degenerate, so any orbit around the electron band will not show a π Berry phase, which must encircle an odd number of Dirac points.

¹⁰The main results of this paper are from a pulsed field study I was not involved with, and the interpretation is not my own; for these reasons it does not form part of this thesis.

For this Berry phase to be present the orthorhombic transition must distort the Fermi surface enough to break down the one orbit for $T > T_S$ – which encircles four Dirac points – into three for $T < T_S$ – an elongated orbit encircling two Dirac points and two smaller orbits either side both encircling a single Dirac point. In this model the Dirac-like behaviour disappears with the orthorhombicity above T_S , and this does seem to be the case for 18.6 %, which does not have a low frequency, large amplitude oscillation dominating the signal. However, as the orthorhombicity is stronger at lower dopings the Dirac-like behaviour should also become more pronounced; this is manifestly not the case, the amplitude of the lower frequency is much reduced and the presence of a non-trivial Berry phase is dubious. Furthermore the 18.6 % sample still shows frequency F1, which should not be present in the tetragonal state. To fully confirm this interpretation the clear Fermi surface splitting shown in Figure 2.13c) (along with the Dirac points themselves) would need to be observed in ARPES measurements, while further DFT study into the effect of doping on the Dirac point and orthorhombicity would help clarify the conflicting behaviour at lower dopings.

2.4 Density functional theory calculations

Calculation details

For comparison with the experimentally measured Fermi surfaces, DFT calculations were conducted for $\text{FeSe}_{1-x}\text{S}_x$ using Wien2k [13] with the GGA form of the exchange-correlation energy and including spin-orbit coupling.

2.4.1 Density functional theory calculations for FeSe

Figure 2.14 shows the Fermi surfaces calculated by DFT for the parent compound FeSe, along with high symmetry cuts of the band structure around the Γ and Z points indicating the orbital character of the respective bands. Here two different crystal structures are used, both of the tetragonal phase: the experimentally determined structure

$a = 3.7707 \text{ \AA}$, $c = 5.521 \text{ \AA}$, $z_{Se} = 0.26668^{11}$ [73]; and the relaxed structure $a = 3.765 \text{ \AA}$, $c = 5.518 \text{ \AA}$, $z_{Se} = 0.2343$ [93]. For the relaxed structure z_{Se} has been varied (with the lattice parameters fixed to their experimental values) to minimise the energy of the system, as determined by LDA calculations; this gives a z_{Se} some way from the experimental value. Although these Fermi surfaces have of course been calculated before [78, 79, 93], they have not been quantitatively compared to quantum oscillations results, so I repeat the calculations here. Furthermore they should serve as a starting point for calculating the Fermi surfaces of the S doped compounds.

Calculations for the experimental crystal structure

Beginning first with the experimental crystal structure, shown in Figure 2.14a), five bands cross the Fermi surface: three hole bands and two electron bands, originating from Fe d_{xz}/d_{yz} (degenerate in the tetragonal phase) and d_{xy} orbitals. These have the expected quasi-cylindrical form, but are considerably larger (and more numerous) than the bands seen in the SdH measurements, with all orbits (excepting the smallest hole cylinder) well in excess of 1 kT at $\mathbf{B} \parallel \mathbf{c}$.

To transform this Fermi surface into something closer to that observed experimentally, rigid band shifts can be applied. To achieve the three band picture seen in experiment, the inner two hole bands are shifted below the Fermi level to their observed position (in the M - Γ - M cut¹²) in ARPES measurements [78], while the remaining hole and electron bands are shifted in position such that their maximal orbit (i.e. their size at the top and bottom of the Brillouin zone) matches the corresponding frequency observed in SdH measurements. These shifts are large (taking values of +131 meV, +164 meV, +224 meV, -195 meV and -188 meV for the inner/middle/outer hole band and inner/outer electron band respectively) – at least twice the size of the shifts previously necessary in other Fe-based superconductors ($< 60 \text{ meV}$) [3] – as to be expected from the smaller quantum

¹¹ z_{Se} is defined here as the height (as a fraction of c) of the Se ions above the Fe plane, which is the convention used in the literature. In the Wien2k set of programs it is conversely defined as the height of the Se ion above the origin, or $\frac{1}{2} - z_{Se}$, the previous value.

¹²The M - Γ - M cut is chosen here as these shifts will keep both hole bands below the Fermi level throughout the Brillouin zone (as observed in ARPES [78]), which is not the case if the A - Z - A cut is chosen. The converse is true for the relaxed structure, so there the A - Z - A cut is chosen.

oscillation frequencies seen in $\text{FeSe}_{1-x}\text{S}_x$, and are indicative of a comparatively large renormalisation in the FeSe system compared to the other Fe-based superconductors.

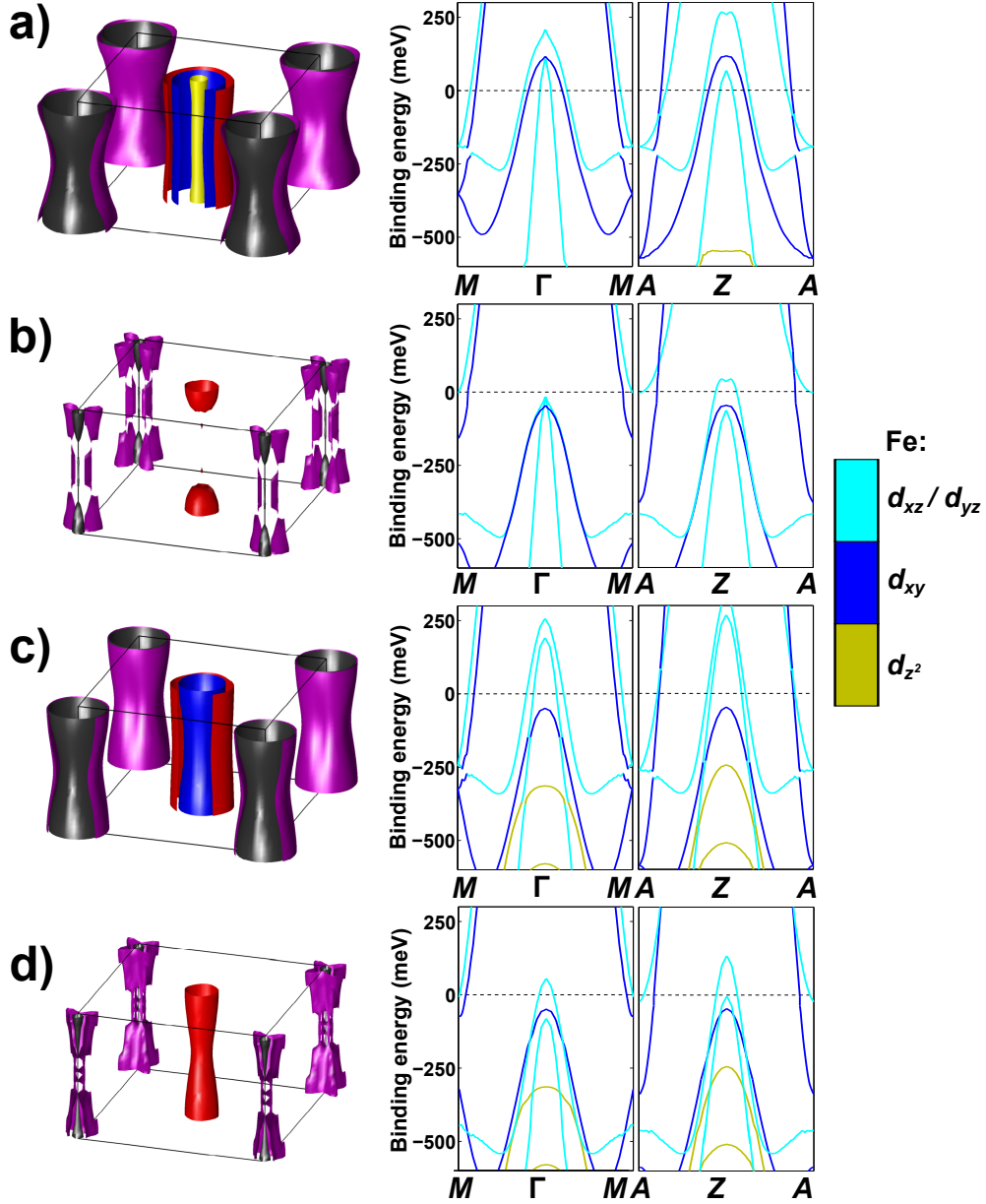


Figure 2.14: **Density functional theory Fermi surfaces for FeSe** alongside high symmetry cuts, calculated using: **a)** the experimental crystal structure; **b)** the experimental crystal structure with rigid band shifts; **c)** the relaxed crystal structure; **d)** the relaxed crystal structure with rigid band shifts. For the Fermi surfaces each band is coloured individually, in the high symmetry cuts the bands are coloured by orbital character.

The Fermi surface resulting from these shifts is shown in Figure 2.14b), and is clearly quite different from that observed in experiment: the quasi-cylindrical shape has disappeared and instead the Fermi surface comprises of pockets centered around the A and Z points. These will only produce a single, maximal quantum oscillation frequency, not

the pairs of maxima and minima observed in experiment – the extent of the warping has effectively rendered the minimal frequencies zero.

Calculations for the relaxed crystal structure

Using instead the relaxed crystal structure produces the Fermi surface shown in Figure 2.14c). Here only four bands cross the Fermi level, two hole and two electron, producing quasi-cylindrical Fermi surfaces that are slightly smaller and slightly less warped than those of the experimental crystal structure. The effect of relaxing (i.e. lowering) z_{Se} can be seen most clearly in comparing the symmetry cuts of Figure 2.14a) and c): the (blue) d_{xy} bands are shifted down, lowering the d_{xy} hole band beneath the Fermi level, while the (cyan) d_{xz}/d_{yz} bands are shifted slightly upwards; in addition two (ochre) hole-like bands of d_{z^2} character are also shifted significantly upwards, but do not yet cross the Fermi level. Although this Fermi surface is closer to that observed in SdH measurements, it is still too large (with all orbits > 1 kT) and has one hole band too many.

Again rigid band shifts can be applied, matching to the maximal SdH frequencies for the bands above the Fermi level and ARPES measurements for the bands below it; as before these are uncharacteristically large for an Fe-based superconductor (taking values of +272 meV, +204 meV, -251 meV and -246 meV for the inner/outer hole band and inner/outer electron band respectively). This produces the Fermi surface shown in Figure 2.14d): the warping is much reduced, so the hole band (red) and outer electron band (purple) are still quasi-cylindrical, as seen in experiment. The outer electron band is also very anisotropic in-plane, producing a cross-shaped Fermi surface similar to features seen in ARPES measurements [78]. There it was instead attributed to two overlapping domains of the inner, d_{xz}/d_{yz} electron band; however more recent work [94] is in agreement with the shifted band structure calculations, assigning it to a cross-shaped outer, d_{xy} electron band.

To confirm the veracity of these shifts, the calculated volumes of each Fermi surface give the following charge carrier contributions (per unit cell): $0.0149 h$ for the hole band and $0.0108 e$ and $0.0012 e$ for the outer and inner electron band respectively, summing to a

slight excess charge of $0.0029 h$. This Fermi surface is still not in complete agreement with the SdH measurements however: as can be seen in Figure 2.15a) although the minimal frequency of the hole band (F2) is reasonably well matched, the minimal frequency of the outer electron band (F3) is significantly underestimated; this discrepancy will lead to the slight excess positive charge calculated. Although the shifted Fermi surface of the relaxed crystal structure does not perfectly match all the SdH frequencies found in experiment, it does qualitatively reproduce the number of bands, shape and features observed. Therefore, of the band structure calculations so far considered, it serves as the best starting point for exploring the effect of S doping on the system.

2.4.2 Density functional theory calculations for $\text{FeSe}_{1-x}\text{S}_x$

The choice of structural parameters

The effect of S doping on the crystal structure of $\text{FeSe}_{1-x}\text{S}_x$ is twofold: it reduces the size of the unit cell as the smaller S ion replaces the larger Se, and decreases z_{Se} as the Fe-S/Se bond length decreases [74, 83]. The changes in a , c and z_{Se} are approximately linear with x (with x-ray characterisation of the dopings measured in this thesis conforming to this), so their values can be interpolated between those of FeSe and FeS. As the relaxed crystal structure provided the closest match to experiment for FeSe, the relaxed structures of FeSe and FeS [93] are used as the two points for interpolation. This gives:

$$\begin{aligned} a(x) &= 3.6735 x + 3.765 (1 - x) \text{ \AA} \\ c(x) &= 5.0328 x + 5.518 (1 - x) \text{ \AA} \\ z_{\text{Se/S}}(x) &= 0.2243 x + 0.2343 (1 - x) \end{aligned} \tag{2.3}$$

To fully account for the disorder effects of doping (as sites will be randomly populated by either S or Se ions in the ratio given by the overall composition) a large supercell, comprised of multiple unit cells containing either S or Se, must be constructed [13]. However due to its size, any calculations run on this cell will be very computationally intensive. To avoid this method, the Fermi surface of $\text{FeSe}_{1-x}\text{S}_x$ can instead be approximated to a

linear combination of the Fermi surfaces of FeSe and FeS, but calculated with the values of a , c and $z_{Se/S}$ fixed to those of $\text{FeSe}_{1-x}\text{S}_x$; this method has been used successfully before in the Fe-based superconductor $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [95]. Therefore, to determine the effect of doping on the Fermi surface of $\text{FeSe}_{1-x}\text{S}_x$, calculations were conducted for lattice parameters over the range $0 \leq x \leq 1$. The rigid shifts were recalculated, again by comparing to the maximal SdH frequencies and ARPES measurements, for $x = 0.1$ and $x = 0.2$ (beyond which there is no experimental data): the change in shift with doping was approximately (admittedly from only a three point fit) linear for all bands, so values were extrapolated across the entire doping range from this fit and applied to the calculations for each composition. Frequencies were combined as $F_{\text{FeSeS}} = F_{\text{FeS}} x + F_{\text{FeSe}} (1 - x)$ and effective masses similarly.

Doping evolution of the Fermi surface

Figure 2.15a) shows the results of these calculations, with the DFT predicted frequencies across the full range of doping plotted alongside the measured values from Table 2.2. Beneath this Figure 2.15b) shows some example Fermi surfaces for $x = 0.1$, 0.5 and 1 (at $x = 0.5$ the calculations with both Se and S are shown as they combine in equal proportion). The shifted calculations for FeSe and FeS both have the same three bands crossing the Fermi level, forming similar Fermi surfaces; there are no abrupt changes in Fermi surface, as seen, for example, with pressure [81] (though of course these changes in Fermi surface are associated with a change in symmetry and/or unit cell, neither of which are changed in these calculations). All three bands of the Fermi surface increase in size across the doping range, as expected – the rigid band shifts have been derived from this trend, at least at lower dopings. In addition a small hole pocket of d_{xz}/d_{yz} character, F0, appears by $x = 0.2$ and exists up to $x = 0.9$. Although not observed in quantum oscillations measurements (likely due to the very small, < 5 T, frequency) this pocket has been seen by ARPES at $x = 0.12$ [80].

The hole cylinder undergoes the greatest metamorphosis in the DFT calculations, with the warping of the cylinder first diminishing and then reversing so that, by $x = 0.8$,

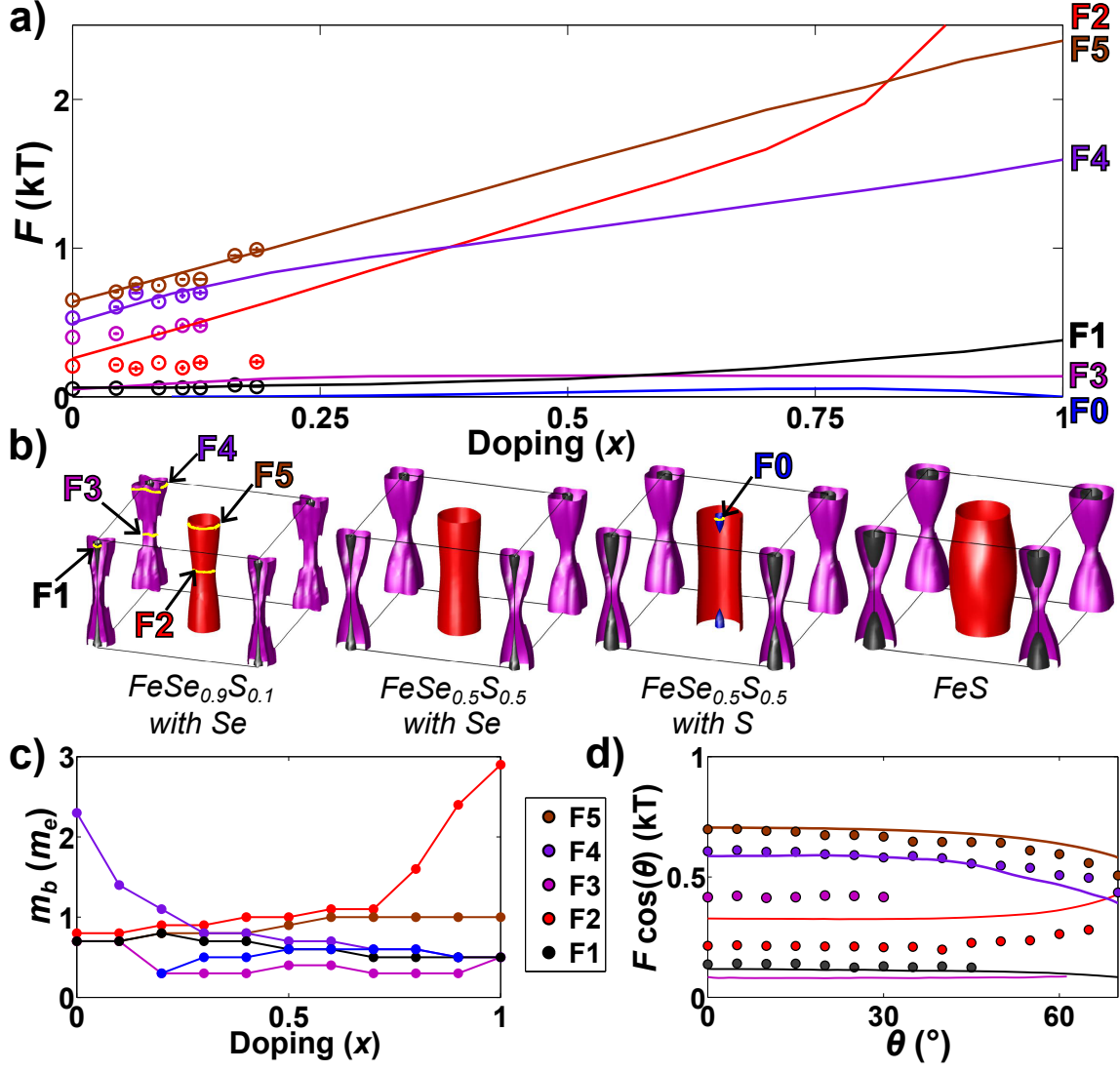


Figure 2.15: **Density functional theory calculated Fermi surfaces for $\text{FeSe}_{1-x}\text{S}_x$.** **a)** Doping dependence of quantum oscillation frequencies, calculated from DFT. **b)** Selected DFT Fermi surfaces across the doping range, with the origin of each orbit also indicated. **c)** Doping dependence of effective masses, calculated from DFT. **d)** Angular dependence of frequencies for $\text{FeSe}_{0.95}\text{S}_{0.05}$, comparing DFT (lines) with measurement (circles). DFT values for F1 have been doubled to match the second harmonic seen in measurement.

the cylinder's cross-section is largest around the Γ , rather than the Z , point. This is manifestly not the case in experiment, as can be seen by the discrepancy between the DFT (red line) and experimental points (red circles) for F2: the measured warping, at least in the range $x = 0 - 0.2$, most definitely increases. Furthermore the great increase in size adds a significant excess charge of $0.0621 h$ to the system by FeS, more than 60 times larger than the excess seen in FeSe.

The outer electron band also evolves in shape with doping, albeit more subtly than

the hole band. In the range $x = 0 - 0.3$, as seen in experiment, there is little change in warping (though it does increase at higher x); instead the clearest changes are to the in-plane anisotropy, shown by the Fermi surfaces in Figure 2.15b), which conspicuously decreases with increasing x . However quantum oscillations measurements are not able to directly confer the shape of an orbit, only its size, so it is not possible to say whether this trend is also seen experimentally.

The change in band mass with doping for these calculations is shown in the inset of Figure 2.15a). In the measured doping range the outer, d_{xy} electron band has a significantly larger mass than the other, d_{xz}/d_{yz} bands ($2.4 m_e$ vs. $0.7 - 0.8 m_e$ in FeSe). This difference is clearly observed in experiment (shown back in Figure 2.10), with F3 and F4 – originating from the outer, d_{xy} electron band – having significantly larger masses than F1 – from the inner, d_{xz}/d_{yz} electron band – and F2 and F5 – from the d_{xz}/d_{yz} hole band. For both the electron and hole bands the effective masses are significantly enhanced compared to the band masses, however the size of the enhancement is not noticeably dependent on orbital character: both F4 of the d_{xy} electron band and F5 of the d_{xz}/d_{yz} hole band show enhancements on the order of $(\lambda_{ee}^s + \lambda_{ep}) = 4 - 5.5$ in the measured doping range. Instead the larger effective masses seen in the d_{xy} electron band, already present in the shifted DFT calculations, arise from the electronic structure itself.

Over most of the doping range – and the entirety of the range measured – there is little change in the band mass for the d_{xz}/d_{yz} electron and hole bands, however the band mass of the outer, d_{xy} electron band drops rapidly, becoming no larger than the other band masses by $x = 0.3$. Over the same range the in-plane anisotropy of the outer electron band decreases markedly, and so it appears the larger band mass is linked to this anisotropy: the cross-shaped cross section of the outer electron band cuts the Fermi level at a shallower angle, and as such has a larger band mass. None of the band masses show any significant decrease across the doping range, so the drop in effective mass seen in the highest doped samples must – assuming it is physical – arise from a reduction in the mass enhancement upon leaving the orthorhombic phase.

Discrepancies with measurements

Although these DFT calculations are able to reproduce the correct form of the Fermi surface and much of its doping dependence, there are some notable aspects it falls down upon: the significant overwarping of the outer electron band and the consequent underestimation of F3; and the doping dependence of the hole band, with the warping decreasing when SdH measurements find it should increase. This discrepancy in the warping is clearest in the angular dependence of the frequencies, with Figure 2.15d) showing a comparison between DFT calculations for $x = 0.05$ and the values measured in the 4.4 % sample ($x = 0.044(3)$). For the hole band, where the warping is underestimated, the minimal frequency F2 (light red) is consistently larger in the DFT calculations, and at higher angles the maximal frequency F5 (dark red) deviates above the measured value as well. The converse is true for the outer electron band, where the warping is overestimated – the minimal frequency F3 (light purple) is smaller in DFT calculations, and the maximal frequency F4 (dark purple) deviates below the measured values at higher angles.

A k_z -dependent rigid band shift would be able to account for these warping issues, but with so many arbitrary shifts being applied to the band structure to match each and every frequency there is no real understanding to be gained from the DFT. Alternatively different starting lattice parameters, in particular z_S , may provide a better fit to the k_z -dependence, but choosing these, at least to begin with, would be a case of trial and error. However, to confirm the gradual evolution in the Fermi surface seen with doping – in contrast to the sudden changes seen with applied pressure – measurement of the Fermi surface at higher dopings, especially for the end member FeS, would be vital.

2.5 Summary

In this chapter I have presented the results of Shubnikov-de Haas measurements of the Fermi surface of $\text{FeSe}_{1-x}\text{S}_x$ in the range $x = 0 - 0.2$, alongside DFT calculations across the entire doping range. Five frequencies are observed – one more than has been seen in the parent compound – and these fully describe the Fermi surface, with no missing bands or frequencies – a problem for previous quantum oscillations and ARPES studies of FeSe. The Fermi surface comprises of three lightly warped, quasi-two dimensional bands: a hole band of d_{xz}/d_{yz} orbital character; an outer electron band of d_{xy} orbital character; a much smaller inner electron band of d_{xz}/d_{yz} orbital character. The outer, quasi-cylindrical electron band is found to have a large in-plane anisotropy in DFT calculations, producing a cross-shaped in-plane cross-section similar to ARPES observations.

The frequencies arising from this Fermi surface are much smaller than those usually seen in the paramagnetic phase of the Fe-based superconductors – taking values between 50 - 1200 T – and point towards a markedly larger renormalisation of the electronic structure in the FeSe system. This larger renormalisation also leads to heavier effective masses in $\text{FeSe}_{1-x}\text{S}_x$, which take values between 2.5 - 4.5 m_e for the d_{xz}/d_{yz} bands and 5.3 - 6.1 m_e in the d_{xy} band. These heavier masses in the outer electron, d_{xy} band are not due to a greater, orbital-dependent mass enhancement however – the values of $(\lambda_{ee}^s + \lambda_{ep}) = 4 - 5.5$, again notably large within the Fe-based superconductors, are consistent across the bands of the Fermi surface – but are instead already present in DFT calculations, associated with the considerable in-plane anisotropy of the outer electron band.

Upon S doping the structural transition is suppressed – disappearing by the highest measured doping of $x = 0.18$ – but the superconductivity remains, with only a slight diminishment in T_c at the highest dopings. This doping acts to decrease the size of the unit cell and the Fe-Se/S plane spacing, so the three bands of the Fermi surface become both larger and more warped. This increase in warping, and so the three dimensionality of the electron structure, is not significant enough to noticeably decrease the anisotropy in the critical field with doping; instead Ginzburg-Landau fits to the angular dependence of the critical field find a relatively consistent effective mass anisotropy of $\gamma = 1.9$, which

may increase slightly at the highest dopings as T_c approaches zero. The Fermi surface changes are monotonic with doping and there is no significant increase in effective mass – unlike the case of applied pressure, S doping does not move the system towards a magnetic phase.

Within the orthorhombic phase there is no observable change in effective mass over the measured doping range, however there appears to be a reduction in the mass enhancement upon entering the tetragonal phase – measured in the highest doped sample – although further measurements are needed to confirm this. The changing position of a spin zero with doping appears to indicate an increasing spin susceptibility effective mass in the hole band as the structural transition is suppressed, however this increase is not mimicked in measurements of the thermal effective mass. The smallest measured frequency, arising from the electron pocket, increases markedly in amplitude at $x = 0.16$ and develops a non-trivial Berry phase of close to $\phi_B = \pi$; this may originate from the presence of a Dirac point close to the M -point.

DFT calculations using the relaxed crystal structure are able to produce a reasonable facsimile of the measured Fermi surface, but require large rigid band shifts on the order 200 - 270 meV, again indicative of the significant renormalisation of the electronic structure in the FeSe system. For $\text{FeSe}_{1-x}\text{S}_x$, DFT calculations based upon a linear combination of the relaxed structures of FeSe and FeS are able to track the experimental growth of Fermi surface but categorically fail to match the warping variation. They do however reproduce the general trend of a Fermi surface increasing in size with unchanged effective masses, and confirm $\text{FeSe}_{1-x}\text{S}_x$ to have – in comparison to the other Fe-based superconductors – a strongly renormalised Fermi surface, with a rather quasi-two dimensional structure that becomes more warped with S doping, and significantly enhanced effective masses that remain unchanged within the orthorhombic phase.

Chapter 3

The contribution of $4f$ electrons to the Fermi surface of CeZn_{11}

3.1 Introduction

This chapter presents a de Haas-van Alphen and density functional theory study of the antiferromagnetic intermetallic CeZn_{11} – a possible candidate for heavy fermion behaviour – using the non-magnetic but near structurally identical LaZn_{11} as an analagous system without an unpaired $4f$ electron. First I will introduce the phase diagram of the heavy fermion systems and their signatures in quantum oscillations and specific heat measurements, and then place CeZn_{11} well within the AFM region of this phase diagram based upon previously reported measurements. To begin the experimental results I first consider de Haas-van Alphen measurements of LaZn_{11} , which has a complex, multi-band Fermi surface that is nevertheless well described by DFT calculations. The de Haas-van Alphen measurements on CeZn_{11} follow; the AFM phase is suppressed by 5 T – below the lowest field at which oscillations are seen – so the measured Fermi surface corresponds to the paramagnetic state. Many of the frequencies of this Fermi surface are similar to those seen in LaZn_{11} , though with slightly enhanced effective masses. GGA+ U calculations for CeZn_{11} with a well localised $4f$ electron are able to reproduce these frequencies, and with the consideration of magnetic breakdown frequencies the entire de Haas-van Alphen

spectrum of CeZn_{11} can be matched by calculations.

3.1.1 Heavy fermion compounds

With the discovery and characterisation of materials such as CeAl_3 [96] and CeCu_2Si_2 [97] in the 1970s, the heavy fermion compounds became one of the first families of non-Fermi liquid materials, exhibiting behaviours outside the bounds of Fermi liquid theory and featuring their eponymous strongly enhanced effective masses. These materials are intermetallics containing unpaired $4f$ and $5f$ electrons originating from lanthanide (in the aforementioned cases Ce) or actinide elements, and it is the localised moments originating from these states that may lead to heavy fermion behaviour.

Competing interactions and the Doniach diagram

Most localised moment systems form an antiferromagnetic (AFM) ground state, which exists up to the Néel temperature T_N above which a high temperature paramagnetic state forms. Adjacent localised moments do not couple directly, instead the coupling is mediated by an oscillating spin density of the conduction electrons known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [98]. The strength of this coupling, and so the size of the Néel temperature, depends on both the size of the localised (angular) moments J and the number of conduction electrons, so the density of states at the Fermi level $g(E_F)$ [99]:

$$T_N = J^2 g(E_F) \quad (3.1)$$

The addition of an external magnetic field will encourage the localised moments to align along the applied field direction, so this will favour the paramagnetic state. Increasing the magnetic field therefore suppress the AFM phase and drives the system through a quantum phase transition as $T_N \rightarrow 0$.

However if the density of states at the Fermi level is sufficiently large, the conduction electrons, rather than mediating coupling between the localised moments, can instead screen the localised moments entirely – known as the Kondo effect [100]. This screening results in a ‘Kondo lattice’ of spinless scattering centres, resulting in a drop in resistivity

and the formation of a paramagnetic state. The relevant energy scale for this effect is the Kondo temperature T_K , given by [99]:

$$T_K = D \exp\left(\frac{-1}{2J g(E_F)}\right) \quad (3.2)$$

where D is the width of the conduction band. In screening out the localised moments, the conduction electrons effectively hybridise with the previously localised unpaired f electrons. The arrival of these f states at the Fermi level results in a large increase in the density of states and the formation of quasi-particles with greatly enhanced effective masses; these are therefore the heavy fermion materials.

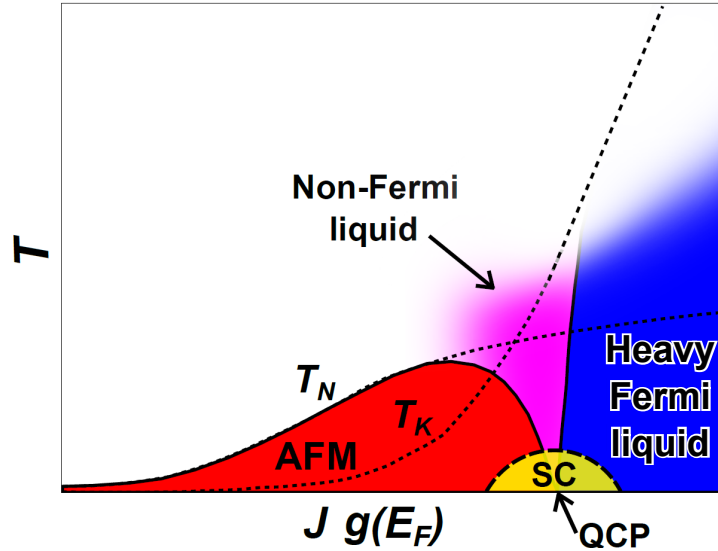


Figure 3.1: **Doniach diagram for heavy fermion materials**, showing the transition from an RKKY mediated AFM state to a PM heavy Fermi liquid, via a region of non-Fermi liquid behaviour and potential superconductivity [101].

Despite the strong interactions between the conduction electrons and the localised moments, most heavy fermion materials are still well described by Fermi liquid theory, though with mass enhancements of the order of $100 - 1000\times$ the bare electron mass. However at the boundary between the AFM and the heavy fermion phase – the region where T_N and T_K are comparable – the competition between the RKKY interaction and the Kondo effect may lead to non-Fermi liquid behaviour, with a quantum critical point – obscured by a superconducting dome – existing at $T = 0$ between the two phases. This competition between T_N and T_K can be summed up by the ‘Doniach diagram’ [101] shown

in Figure 3.1, a generic phase diagram for the heavy Fermion systems. The parameter $Jg(E_F)$ – the product of the magnetic moment and the density of states at the Fermi level – is not directly tunable, however it can be varied by doping [102], applied pressure [103] or an external magnetic field [104]. Although few materials naturally exist in the non-Fermi liquid phase, by the application of these effects many can be tuned through the quantum critical point, showing regions of AFM order, superconductivity, non-Fermi liquid and heavy fermion behaviour.

Fermi surfaces

Between the AFM and heavy fermion phases there will also be significant changes in Fermi surface. In the AFM phase the increased size of the unit cell that results from the magnetic ordering will shrink the Brillouin zone and hence the size of the Fermi surface [105]. In the heavy fermion phase there is no magnetic ordering and so no unit cell increase, and additionally the hybridisation of the f states with the conduction electrons greatly increases the density of states at the Fermi level; heavy fermion Fermi surfaces therefore have much larger surface areas. Both these Fermi surfaces are difficult to measure with quantum oscillations however: the large effective masses in the heavy fermion phase act to damp the oscillations, which are only visible at very low (< 1 K) temperatures [106]; the AFM phase is suppressed by large applied fields, which are usually necessary for the observation of quantum oscillations. If the field acts to tune the system through the quantum critical point to the right of the Doniach diagram, the high field Fermi surface will correspond to that of the heavy fermion phase. However, most certainly for materials that lie far to the left of the quantum critical point on the Doniach diagram, the field may suppress T_N without significantly increasing T_K , so the high field state will simply be the paramagnetic state that exists above the AFM phase at temperatures in excess of T_N . In this state there is no increase in unit cell size from magnetic ordering, but the f electrons remain localised and do not contribute to the density of states at the Fermi level; the Fermi surface is therefore smaller in area than that of the heavy fermion phase, with considerably lighter effective masses.

The Sommerfeld coefficient

Alongside the effective masses obtained from (the temperature dependence of) quantum oscillations, a measure of the mass enhancement in heavy fermion materials can also be garnered from the low temperature heat capacity, specifically the electronic component. At high temperatures the phonon contribution, $\propto T^3$, dominates, but at low temperatures the electronic term, $\propto T$, takes over. Specifically [1]:

$$\begin{aligned} C(T \rightarrow 0) &= \frac{\pi^2}{3} g(E_F) k_B^2 T \\ &= \frac{\pi^2 n V k_B^2}{\hbar^2} (3\pi^2 n)^{-2/3} m^* T \\ &= \gamma T \end{aligned} \tag{3.3}$$

where it's taken that $g(E_F) = (3/2)(n/E_F)$, $E_F = \hbar^2 k_F^2 / 2m^*$ and $k_F^2 = (3\pi^2 n)^{2/3}$. The linear coefficient of the heat capacity γ , known as the Sommerfeld coefficient, is proportional to the effective mass, so its size is a measure of the mass enhancement (and also the electron density n) of the system. It is obtained by plotting C/T against T – the extrapolated y -intercept (C/T at $T = 0$) is the Sommerfeld coefficient. A heavy fermion material typically has values of $\gamma > 400 \text{ mJ/mol K}^2$, compared to $\gamma \sim 10 \text{ mJ/mol K}^2$ in structurally similar compounds without unpaired f electrons [99]. For a system featuring an AFM phase there will naturally be a peak in the heat capacity at T_N , and as $T_N \rightarrow 0$ this peak will move towards $T = 0$, increasing the value of γ . If the system is far away from the quantum critical point in the Doniach diagram, γ will return to a small value once the AFM phase is suppressed and the system enters the (non-heavy fermion) paramagnetic phase. However if γ continues to increase once T_N goes to zero, then the system has entered the heavy fermion phase [104] – the field has tuned the system through a quantum critical point. The field evolution of the Sommerfeld coefficient therefore provides a clear indication of the proximity of the system to the quantum critical point at the crossover of the T_N and T_K regimes, and hence the possibility of superconductivity or non-Fermi liquid behaviour.

3.1.2 Previous work on CeZn₁₁

Similar materials

On paper CeZn₁₁ appears a promising candidate for heavy fermion behaviour and tunable quantum criticality – it is an intermetallic with a single $4f$ electron originating from the Ce atom. Many of the most well known heavy fermion compounds feature unpaired $4f$ electrons originating from Ce atoms, showing the various phases that exist on the Doniach diagram: CeAl₃, one of the first heavy fermion compounds to be characterised, exists within the heavy Fermi liquid phase, with an enhanced Sommerfeld coefficient of $\gamma = 1620 \text{ mJ/mol K}^2$ but a resistivity $\rho \sim T^2$, as expected for a Fermi liquid [96]; CeCu₂Si₂ was the first heavy fermion superconductor, with $T_c = 0.5 \text{ K}$ and $\gamma = 1000 \text{ mJ/mol K}^2$ [97]; CeCe_{6-x}Au_x can be tuned, with doping, from the AFM phase through a non-Fermi liquid region to the heavy fermion phase [107]. Additionally there exist structurally similar heavy fermion antiferromagnets, with a lanthanide or actinide atom surrounded by polyhedra of Zr or Cd (isoelectronic to Zn) atoms: U₂Zn₁₇ forms an AFM state below $T_N = 9.7 \text{ K}$, with a paramagnetic heavy fermion state, $\gamma = 535 \text{ mJ/mol K}^2$, above [108]; UCd₁₁ behaves similarly, with $T_K = 5 \text{ K}$ and $\gamma = 840 \text{ mJ/mol K}^2$ [109].

However the compound CeCd₁₁ – structurally the most similar to CeZn₁₁ – features both a Ce atom and a surrounding polyhedra of Cd atoms but shows no sign of heavy fermion behaviour: below $T_N = 0.44 \text{ K}$ CeCd₁₁ orders antiferromagnetically, but with a small Sommerfeld coefficient of $\gamma = 26 \text{ mJ/mol K}^2$ [110]. The system therefore lies far to the left of the quantum critical point in the Doniach diagram, with $T_N \gg T_K$. De Haas-van Alphen oscillations are observed in CeCd₁₁, arising from the paramagnetic state as the AFM phase is suppressed by 2.5 T. The observed frequencies are small ($< 600 \text{ T}$), with light effective masses ($< 1 m_e$) as expected from the small Sommerfeld coefficient. Similar frequencies are observed in dHvA measurements of LaCd₁₁, which is isostructural (cubic, spacegroup $Pm\bar{3}m$) to CeCd₁₁ but without an unpaired $4f$ electron. This implies that the $4f$ electron plays no role at the Fermi level in CeCd₁₁, and indeed the frequencies observed by dHvA measurements in CeCd₁₁ (and LaCd₁₁) agree well with those predicted by DFT for LaCd₁₁, arising from a complex multiband Fermi surface that results from the

large number of atoms (66) within the unit cell. Therefore the $4f$ electron is well localised in CeCd_{11} , as expected for a localised moment AFM system with a small Sommerfeld coefficient and light effective masses.

Structural details and phase transitions

CeZn_{11} crystallises in a tetragonal structure (space group $I4_1/amd$) [111] slightly different to the cubic structure of CeCd_{11} (spacegroup $Pm\bar{3}m$). This is sometimes known as a ‘caged’ structure, as each Ce atom is enclosed in a polyhedra of 22 Zn atoms as shown in Figure 3.2a). LaZn_{11} also forms the same structure, with very similar lattice parameters [112] but without an unpaired $4f$ electron. This means, rather usefully, it serves as a non-magnetic analogue for CeZn_{11} , and so can be used as a comparison to determine the role played by the $4f$ electrons in the electronic structure of CeZn_{11} .

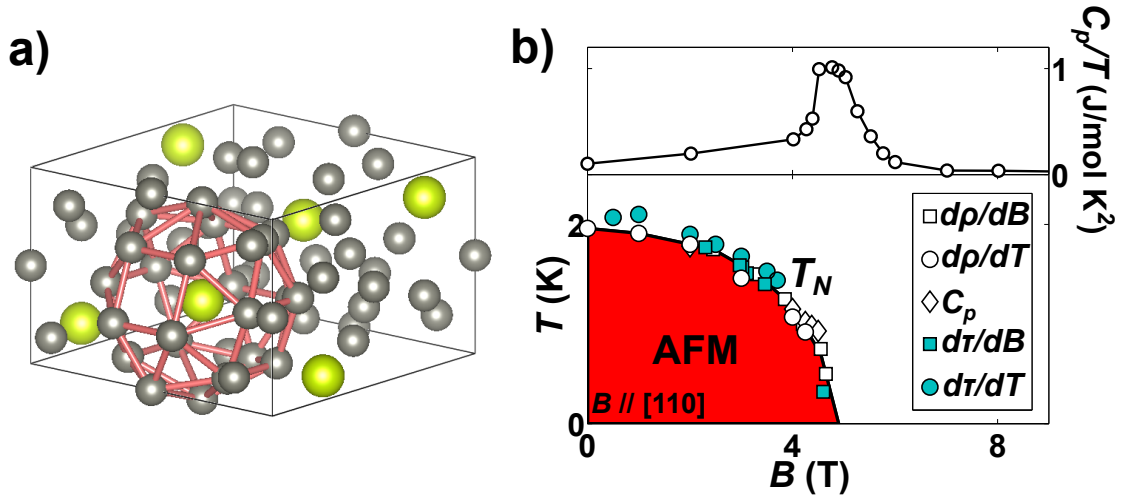


Figure 3.2: **Crystal structure and phase diagram with field for CeZn_{11} .** a) Each Ce atom is enclosed within a polyhedral ‘cage’ of 22 Zn atoms, indicated in red. b) Increasing magnetic field suppresses the low temperature antiferromagnetic phase by 5 T (bottom), leading to a peak in the Sommerfeld coefficient (top). Specific heat (C_p) and resistivity (ρ) data taken from [112], torque (τ) data from the measurements in this chapter.

Upon cooling CeZn_{11} shows a peak in heat capacity at $T_N = 2\text{ K}$, and below this temperature the magnetic susceptibility also saturates; both clear indications of a low temperature AFM phase. The saturated magnetic susceptibility takes a value of $\mu_{eff} = 2.34\mu_B/\text{Ce}$, close to the value for a free Ce^{3+} ion of $2.54\mu_B$ [113], while the magnetic entropy – calculated by integrating the heat capacity with respect to T – tends towards

a value of 12 J/mol K, slightly less than the full entropy of 14.9 J/mol K expected for the $J = 5/2$ multiplet of a $\text{Ce}^{3+} 4f^1$ configuration [112]. Thus as expected the magnetic state arises from localised moments at the Ce atoms, with a minimal reduction in magnetic entropy from crystal field effects as the surrounding polyhedra of Zn atoms provide an almost spherically symmetric local environment for the Ce atoms.

The lower half of Figure 3.2b) shows the field-temperature phase diagram of CeZn_{11} – measured along the easy $\mathbf{B} \parallel [1\ 1\ 0]$ – constructed from reported resistivity and specific heat data [112] and the torque magnetometry measurements presented later in this chapter. From a maximum at $T_K = 2\text{ K}$ the AFM phase is suppressed by $B = 5\text{ T}$, with a paramagnetic state forming above. At zero field, within the AFM phase, the Sommerfeld coefficient is small – taking a value of $\gamma = 34.6\text{ mJ/mol K}^2$ – but, as expected, this increases as the Néel temperature approaches zero – up to a value of $\gamma = 1000\text{ mJ/mol K}^2$ [112]. Beyond this however, in the paramagnetic phase, the Sommerfeld coefficient returns to a small value of $\gamma = 18\text{ mJ/mol K}^2$, comparable to LaZn_{11} with $\gamma = 10.3\text{ mJ/mol K}^2$. This field dependence of the Sommerfeld coefficient is shown in the upper half of Figure 3.2b) and is the behaviour expected for an AFM state suppressed through a quantum phase transition, rather than the increasing Sommerfeld coefficient seen in the paramagnetic phase for heavy fermion systems tuned through a quantum critical point.

CeZn_{11} is therefore – much like CeCd_{11} – a localised moment AFM system, to the far left of the Doniach diagram with $T_N \gg T_K$. As the $4f$ electrons appear to be well localised they should have no contribution to the density of states at the Fermi level, although the Sommerfeld coefficient of CeZn_{11} in the paramagnetic state is still slightly enhanced compared to that of LaZn_{11} . Quantum oscillations measurements of both LaZn_{11} and CeZn_{11} , along with DFT calculations with both localised and hybridised $4f$ electrons, will be able to directly determine both the mass enhancements in CeZn_{11} and any effect the $4f$ electrons may have on the electronic structure at the Fermi level.

3.2 The Fermi surface of LaZn_{11}

Experimental details

Samples of CeZn_{11} and LaZn_{11} for this study were provided by Halyna Hodovanets and Paul Canfield at Ames Laboratory, Iowa State University; details of the growth process are reported in [112]. Flake-like samples of size $\sim 100 \times 100 \times 20 \mu\text{m}$ were used for LaZn_{11} and $\sim 50 \times 50 \times 10 \mu\text{m}$ for CeZn_{11} (purposefully smaller due to the large magnetic signal), all with clear, flat faces whose orientation was determined by single crystal x-ray diffraction. Transport measurements on samples from the same batch report an $\text{RRR} \sim 300$ and $\rho_0 \sim 0.1 \mu\Omega\text{cm}$ for both CeZn_{11} and LaZn_{11} [112]. LaZn_{11} torque measurements were performed in DC fields up to 14 T in a PPMS, CeZn_{11} torque measurements were performed up to 18 T in a 21 T superconducting magnet and 33 T at HFML, Nijmegen; in all cases the sample was mounted on a single axis rotator. DFT calculations were conducted using Wien2k [13] with the GGA form of the exchange-correlation energy and spin-orbit coupling included; lattice parameters were taken from [112].

3.2.1 de Haas-van Alphen oscillations

Angular dependence of oscillations

Two crystals of LaZn_{11} were measured, chosen for the quality of their x-ray diffraction patterns and the high symmetry axes normal to their largest faces: LZ1, with normal $[1\ 1\ 0]$; and LZ2, with normal $[1\ 0\ 1]$. Both samples showed dHvA oscillations, with example data shown in Figure 3.3.

Figure 3.3a) shows the magnetic field dependence of torque for LZ1, measured between $\mathbf{B} \parallel [1\ 1\ 0]$ (the easy axis for CeZn_{11}) and $\mathbf{B} \parallel [0\ 0\ 1]$. At all orientations clear oscillations are visible on top of a weakly paramagnetic, slightly anisotropic background. The Fourier transforms of this data set are shown in Figure 3.3b), split into three regions, each showing a number of frequencies: at all angles measured there are multiple small frequencies with large amplitude, all below 200 T; a second strong frequency region exists just above 200 T around $[1\ 1\ 0]$, increasing with rotation away from the a - b plane, and some weaker features

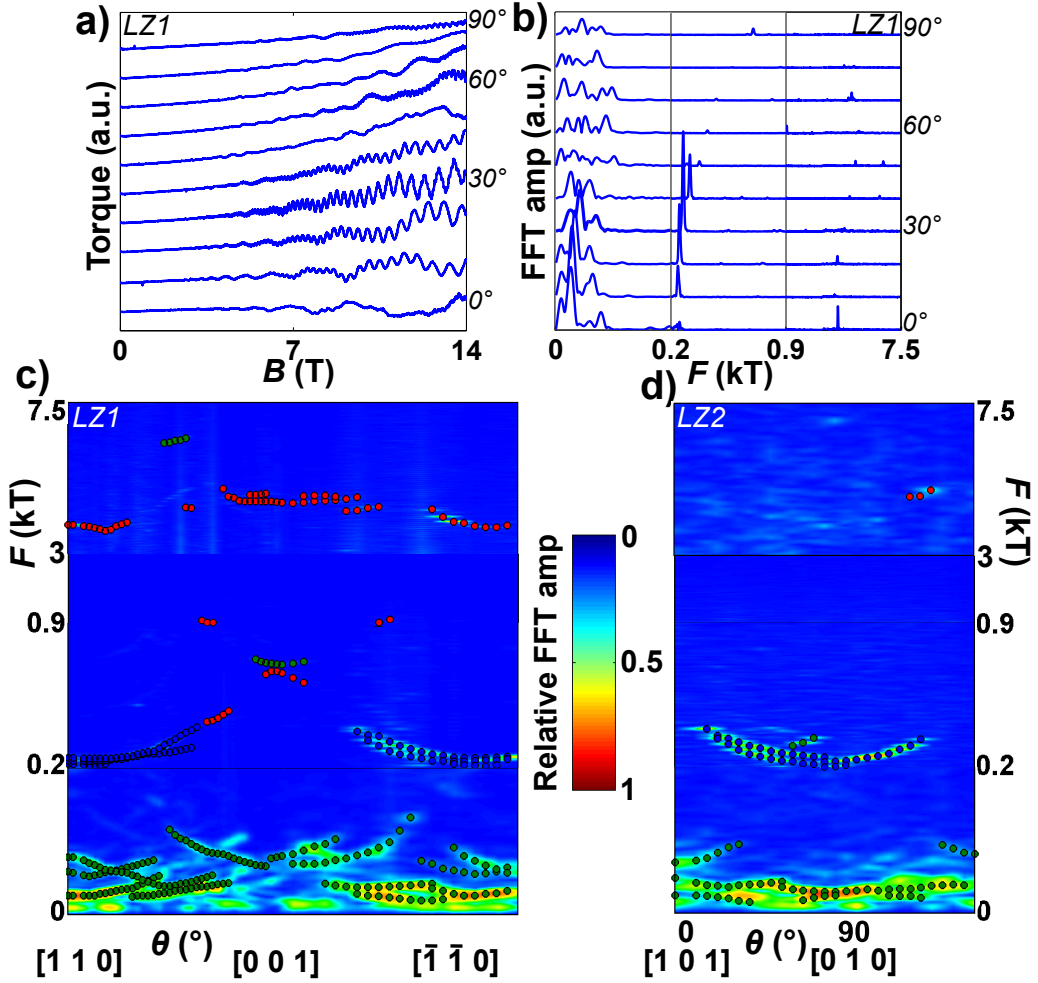


Figure 3.3: **Angular dependence of de Haas-van Alphen oscillations in LaZn_{11} .** **a)** Torque measurements conducted at 2 K on LZ1, between $\mathbf{B} \parallel [110]$ (0°) and $\mathbf{B} \parallel [001]$ (90°). **b)** Fourier transforms of the torque signal, with a field window of 4 – 14 T used up to a frequency of 3 kT and 8 – 14 T used above. **c)** Angular dependence of the Fourier spectrum for LZ1 in the range $\mathbf{B} \parallel [110] \rightarrow \mathbf{B} \parallel [001]$. **d)** Angular dependence of the Fourier spectrum for LZ2 in the range $\mathbf{B} \parallel [101] \rightarrow \mathbf{B} \parallel [010]$.

are seen at ~ 700 T close to $[001]$; finally there are also some weaker features present at higher frequencies, around ~ 4 kT close to $[110]$ and sporadically at higher frequencies closer to $[001]$.

The full angular dependence of the Fourier spectrum is shown in Figure 3.3c) for the rotation $\mathbf{B} \parallel [110] \rightarrow \mathbf{B} \parallel [001] \rightarrow \mathbf{B} \parallel [\bar{1}\bar{1}0]$ in sample LZ1. Points of high intensity correspond to dHvA frequencies, the extracted positions of these frequencies have been scattered on top of the Fourier spectrum. As expected from the crystal symmetry, the spectrum is near symmetric around the high symmetry axes (although with some differences in intensity, likely due to angular variation in the lever deflection caused by the

weight of the sample) and periodic over 180° . The sheer number of frequencies, coupled to the large variation in angular dependence, is testament to a rather complex Fermi surface in LaZn_{11} .

Figure 3.3d) shows the Fourier spectrum for the rotation $\mathbf{B} \parallel [101] \rightarrow \mathbf{B} \parallel [010]$ in sample LZ2. Although the frequencies measured differ from before as the field is applied in a different orientation, there are shared features between the two data sets: a number of small (< 200 T) frequencies; a strong feature around 200 T, again increasing away from the a - b plane; and a few large frequencies in excess of 3 kT.

Temperature dependence of oscillations

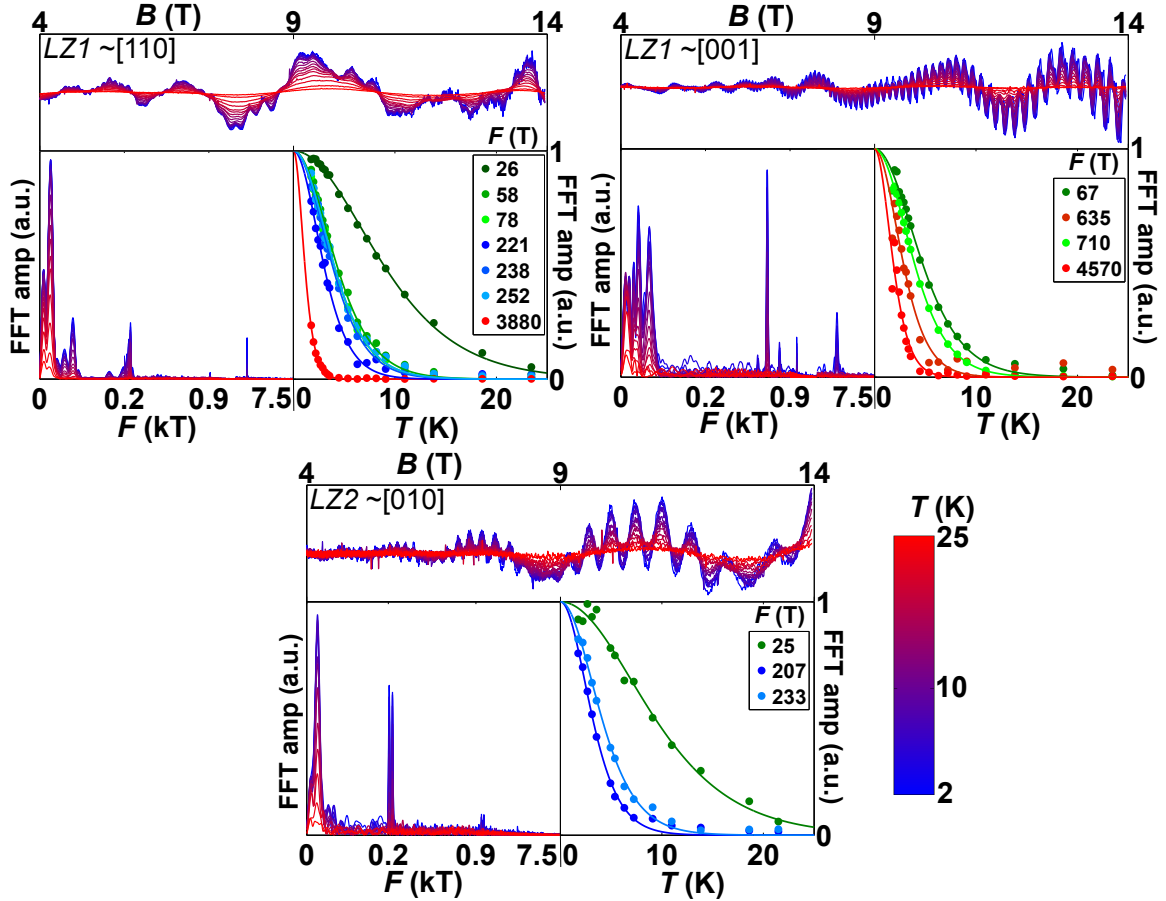


Figure 3.4: **Temperature dependence of de Haas-van Alphen oscillations in LaZn_{11}** at orientations $\mathbf{B} \parallel [110]$, $\mathbf{B} \parallel [001]$ and $\mathbf{B} \parallel [010]$. Shown for each orientation is: (top panel) the oscillatory component of the torque signal at temperatures in the range 2 – 25 K, coloured by temperature; (bottom left panel) Fourier transforms of the oscillatory component, again coloured by temperature; (bottom right panel) Lifshitz-Kosevich fits to the temperature dependence of the FFT amplitudes, scaled by the fitted intercept at $T = 0$ K.

The temperature dependence of the dHvA oscillations was measured close to the symmetry axes of $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [001]$ for LZ1 and $\mathbf{B} \parallel [010]$ for LZ2. Figure 3.4 shows the results of these measurements, with the oscillatory data plotted above the corresponding Fourier transforms and the Lifshitz-Kosevich fits to their amplitudes (the effective masses from which are listed in Table 3.1). The lowest frequency oscillations exist up to 20 K, indicative of very light effective masses, with even the largest frequencies still visible at 4.2 K. These light masses intimate a lack of any significant electronic correlations in LaZn_{11} , as expected for a Fermi level comprised almost exclusively of Zn $3d$ states.

Band	$\mathbf{B} \parallel [110]$				$\mathbf{B} \parallel [001]$				$\mathbf{B} \parallel [010]$			
	Exp.		DFT		Exp.		DFT		Exp.		DFT	
	F (T)	m^* (m_e)	F (T)	m_b (m_e)	F (T)	m^* (m_e)	F (T)	m_b (m_e)	F (T)	m^* (m_e)	F (T)	m_b (m_e)
1	221(3)	0.31(1)	216	0.29					207(2)	0.29(1)	263	0.15
1	238(2)	0.24(1)	-	-					233(3)	0.23(1)	-	-
1	252(3)	0.23(1)	266	0.21								
2	26(2)	0.10(1)	25	0.10	-	-	39	0.18	25(2)	0.10(1)	36	0.11
2	58(2)	0.22(1)	58	0.12	67(2)	0.20(1)	47	0.23	-	-	320	0.33
2	78(2)	0.23(1)	69	0.28	-	-	96	0.09	-	-	3499	0.81
2	-	-	95	0.26	710(5)	0.38(1)	606	0.20				
2	-	-	399	0.21								
2	-	-	7140	1.02								
3	3880(10)	1.34(3)	4237	1.18	635(10)	0.53(4)	731	0.56	-	-	3930	1.58
3					-	-	3849	0.29				
3					4570(1)	1.0(1)	4104	1.41				
4	-	-	242	0.36					-	-	188	0.27
4									-	-	261	0.75

Table 3.1: **Frequencies and effective masses of de Haas-van Alphen oscillations observed in LaZn_{11}** , compared with density functional theory calculations for field orientations along high symmetry axes.

3.2.2 Density functional theory calculations

With a Fermi level dominated by Zn $3d$ states, it is likely that the Fermi surface of LaZn_{11} will be well described by band structure calculations. Therefore comparison to DFT should prove valuable in disentangling the mélange of frequencies observed in the

Fourier spectra to elucidate the underlying Fermi surface.

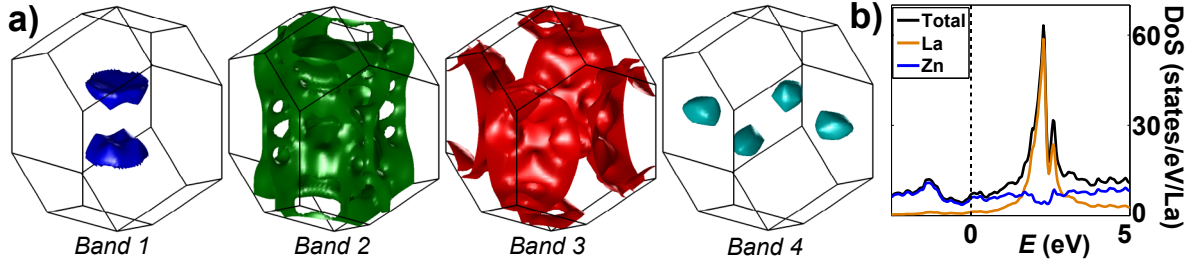


Figure 3.5: **Density functional theory calculations for LaZn_{11} .** a) The calculated Fermi surface, split into its four constituent bands. b) The density of states around the Fermi level.

Figure 3.5a) shows the DFT calculated Fermi surface for LaZn_{11} . Four bands cross the Fermi level, forming a complex, 3D Fermi surface. Figure 3.5b) shows the calculated density of states, with Zn $3d$ states dominating close to the Fermi level¹ – the peak corresponding to the La $4f$ states lies far above the Fermi energy. This conforms with the small effective masses seen experimentally.

Frequency comparison

To compare directly with the angular dependence of the measured dHvA frequencies (shown in Figure 3.3c) and d)), the frequencies arising from the DFT calculated Fermi surface of Figure 3.5a) were calculated over the same angular ranges. Figure 3.6 shows the comparison between these two sets of frequencies, coloured by their associated bands for clarity.

The hemispherical Fermi surface of band 1 accounts for the strong frequencies around 200 T, which increase in size with rotation away from the a - b plane. At angles approaching 90° the hemispherical shape will result in a very sharp curvature factor for band 1, and this, along with any increases in effective mass, acts to suppress the amplitude at the higher angles where no oscillations are seen experimentally.

The Fermi surface of band 2, with its labyrinthine assortment of protrusions and perforations, generates a wide array of small frequencies, matching roughly in form and

¹The density of state calculations with Wien2k additionally produce an ‘interstitial’ charge, not assigned to any orbital. For the purpose of these calculations these additional states are shared in proportion between the other orbitals to make up the total.

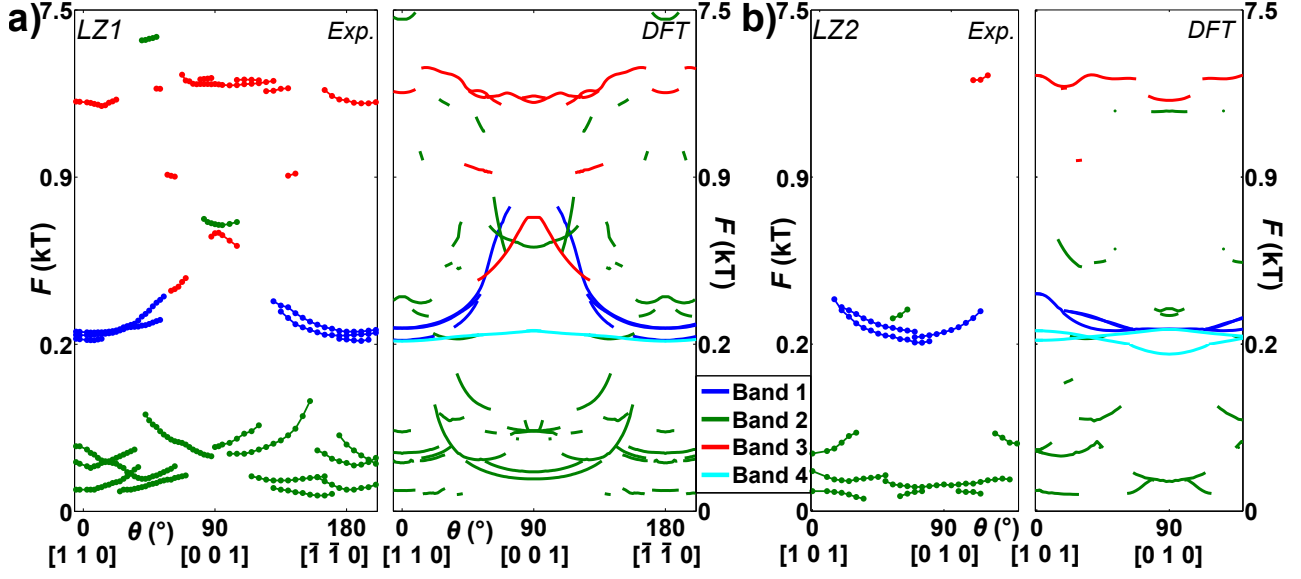


Figure 3.6: **Angular dependence of frequencies in LaZn_{11}** , from de Haas-van Alphen oscillations and density functional theory calculations. **a)** Sample LZ1, measured over the range $\mathbf{B} \parallel [110] \rightarrow \mathbf{B} \parallel [001]$. **b)** Sample LZ2, measured over the range $\mathbf{B} \parallel [101] \rightarrow \mathbf{B} \parallel [010]$.

quantity the sub-200 T frequencies observed experimentally. It also produces a number of higher frequencies, matching those observed at ~ 400 T and ~ 7 kT. Not all the frequencies found by DFT are visible in the dHvA measurements: this may again be due to geometric damping factors; however the proximity of many of the lower frequencies may inhibit their resolution, while the complexity of the Fermi surface itself means that any slight distortions, from discrepancies in stoichiometry or crystal structure, could lead to the wholesale disappearance of certain frequency branches.

The wide spread of high (> 1 kT) frequencies are well accounted for by the Fermi surface of band 3, arising from orbits around the girth of its bulbous ovoid, while its open ends at the top and bottom of the Brillouin zone produce smaller (~ 600 T) frequencies, which match those observed around $[001]$.

Together, the angular dependences of these three bands – allowing for some discrepancy in position due to slight misalignments of the measured crystals – can fully account for all the observed dHvA frequencies in LaZn_{11} . However DFT calculations predict a fourth band, band 4, which is not observed experimentally. Assuming the three measured bands of the Fermi surface take the form predicted by DFT, then band 4 must also be present for charge conservation to be met. Comparing band 4 with band 1 – whose fre-

quencies are of a comparable size but are seen clearly in experiment – the effective masses calculated from DFT are $2 - 5\times$ heavier (with values given in Table 3.1). These heavier masses will diminish the amplitude of oscillation, while further damping may occur from any enhancement in scattering for band 4.

Table 3.1 gives a detailed comparison, along the high symmetry axes, between the measured dHvA frequencies and effective masses and those simulated from the DFT calculated Fermi surface. Along with the correspondence of frequency values discussed previously, the effective mass values are also, by and large, in good agreement. Clearly in LaZn_{11} , with the $4f$ states well above the Fermi level, the Zn $3d$ dominated Fermi surface shows minimal deviation from DFT calculations, both in terms of frequencies and effective mass. This Fermi surface therefore provides an initial reference point for CeZn_{11} , with something similar expected if the $4f$ electrons are localised well below the Fermi level.

3.3 The Fermi surface of CeZn_{11}

3.3.1 de Haas-van Alphen oscillations

Comparison to LaZn_{11} measurements

Due to the strong magnetic background expected in torque measurements of CeZn_{11} (roughly $500\times$ larger than LaZn_{11}) [112], a small sample, CZ1, was selected whose largest face was normal to the easy axis $[1\ 1\ 0]$. The purpose of this was to reduce the amount of torque, to avoid any of the non-linear effects that can result from excessive deflection. Because of the smaller crystal size, the amplitudes of any oscillations observed would presumably be smaller than their counterparts in LaZn_{11} ; for this reason the CeZn_{11} sample was measured in larger fields of up to 33 T.

Figure 3.7a) shows the raw torque signal data for CZ1, measured up to 33 T at 320 mK, between $\mathbf{B} \parallel [1\ 1\ 0]$ and $\mathbf{B} \parallel [1\ 0\ 0]$. As previously reported [112] the magnetisation appears to be anisotropic within the a - b plane, being largest along the easy axis $[1\ 1\ 0]$. A clear transition is seen – whose value is taken to be the peak in the first derivative of the

torque – corresponding to the suppression of the AFM phase by the applied magnetic field. This transition is largest when $\mathbf{B} \parallel [110]$, with a temperature dependence, determined in part from these torque measurements, shown in the lower panel of Figure 3.2b).

Angular dependence of oscillations

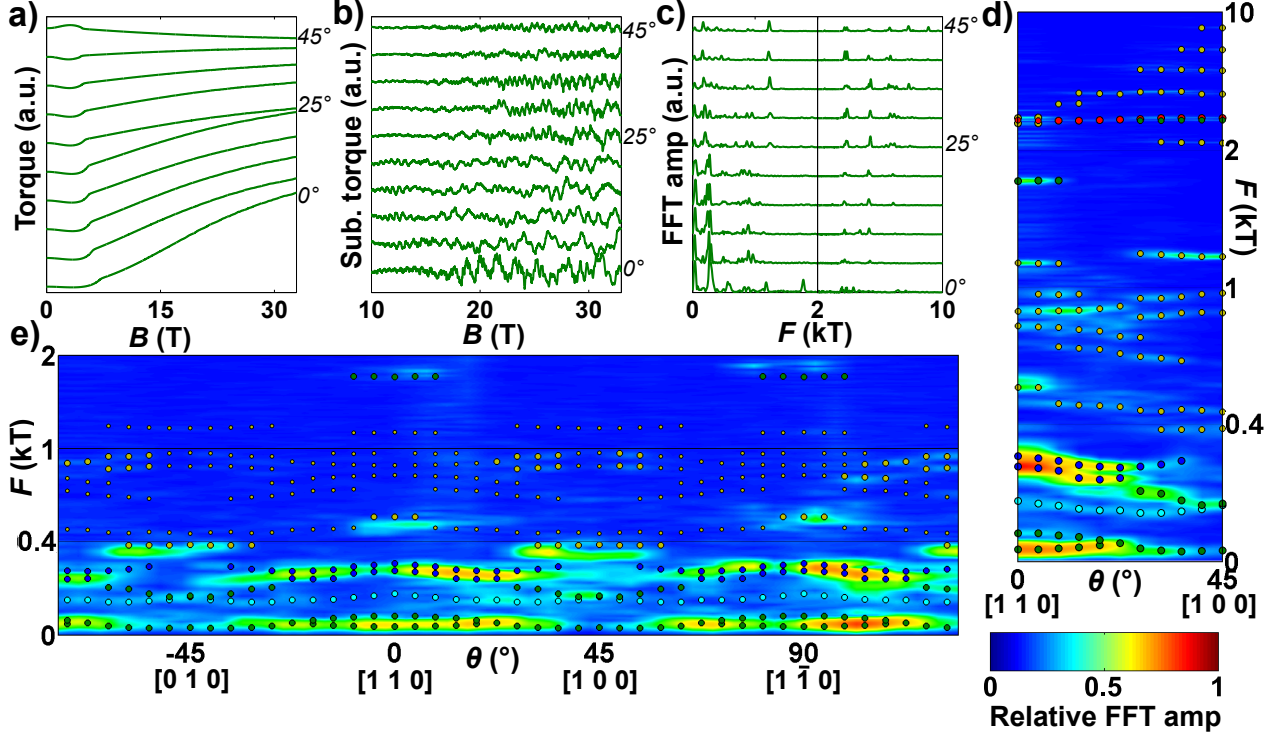


Figure 3.7: **Angular dependence of de Haas-van Alphen oscillations in CeZn_{11} .** **a)** Torque measurements conducted at 320 mK on CZ1, between $\mathbf{B} \parallel [110]$ (0°) and $\mathbf{B} \parallel [100]$ (45°). **b)** Oscillatory component of the torque signal, found by subtracting a 4th-order polynomial. **c)** Fourier transforms of the oscillatory component, with a field window of 10 – 33 T used up to a frequency of 2 kT and 20 – 33 T used above. **d)** Angular dependence of the Fourier spectrum for CZ1, measured to 33 T. **e)** Angular dependence of the Fourier spectrum for CZ1 over a broader range, with a field window of 10 – 18 T.

Figure 3.7c) shows the Fourier transforms of the subtracted data. Because of the weak oscillations and large background, any low frequencies – such as those seen below 0.2 kT in LaZn_{11} – will be hard to differentiate. In spite of this, approaching $\mathbf{B} \parallel [100]$ there is a clear peak around 0.2 kT, with features also visible below. Along with the peak seen around 4 kT across the angular range, these features are all consistent with the frequencies seen in LaZn_{11} .

However, there are a number of other features not seen in LaZn_{11} . These are most

clearly visible in the Fourier spectrum of Figure 3.7d), where the extracted frequencies have been scattered on top of the corresponding peaks in the Fourier transform (represented by intensity). Multiple branches are seen across the angular range around 1 kT, while there are a number of higher frequencies between 4 kT and 10 kT in the vicinity of $\mathbf{B} \parallel [100]$. Neither of these features are seen experimentally in LaZn_{11} , or predicted by DFT.

Figure 3.7e) shows the Fourier spectrum over a far wider angular range in the a - b plane, comprised of measurements conducted on CZ1 at 1.4 K up to 18 T. Scattered on top are the frequencies extracted from the higher field measurements of Figures 3.7a)-d) – replicated over the full angular range by symmetry operations – to act as a consistency check between the two data sets. In this lower field range the small (< 1 kT) frequencies match well, but no high (> 2.5 kT) frequencies are apparent due to the lower maximum field and higher temperature of the measurement. Many of the intermediate (~ 1 kT) frequencies are also not present, however some features are still weakly apparent. Importantly, all the features observed in this spectrum appear to be periodic over 90° and symmetric (excepting differences in intensity) around the high symmetry axes, as is necessary for the geometry of the Fermi surface from the symmetry of the crystal structure.

Temperature dependence of oscillations

Temperature dependences of these dHvA oscillations, measured close to $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [100]$, are plotted in Figure 3.8 with the oscillatory data, Fourier transforms and Lifshitz-Kosevich fits also shown for the two orientations. The effective masses found from these fits are given in Table 3.2. Values are found in the range $0.6 - 2.5 m_e$, considerably smaller than those found in heavy fermion systems, which are generally 2 – 3 orders of magnitude larger [99]. However, comparing frequencies of similar magnitude along $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [100]$, the effective masses for CeZn_{11} are 2 – 4 $\times$ larger than their counterparts in LaZn_{11} . This agrees with the previously reported specific heat measurements, where the Sommerfeld coefficient of CeZn_{11} is 3 – 4 $\times$ larger than that of

LaZn₁₁. For those frequencies with no clear counterparts in LaZn₁₁, and especially those in excess of 4 kT, the effective masses do not show the larger values expected if they originated from harmonics (where, for the n th harmonic, $m_{nF}^* = n \times m_F^*$). These additional frequencies must therefore indicate an additional facet of the Fermi surface not seen in LaZn₁₁.

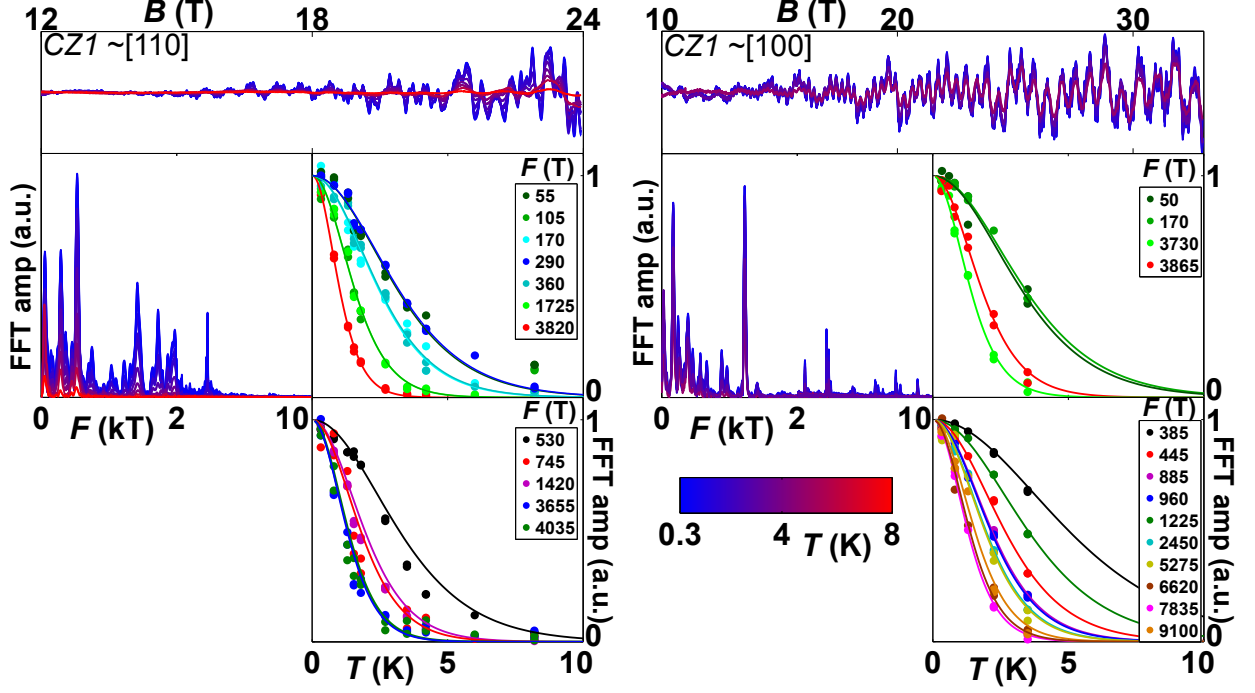


Figure 3.8: **Temperature dependence of de Haas-van Alphen oscillations in CeZn₁₁ at orientations $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [100]$.** Shown for each orientation is: (top panel) the oscillatory component of the torque signal at temperatures in the range 0.3 – 8 K, coloured by temperature; (bottom left panel) Fourier transforms of the oscillatory component, again coloured by temperature; (bottom right panel) Lifshitz-Kosevich fits to the temperature dependence of the FFT amplitudes, scaled by the fitted intercept at $T = 0$ K.

B $\parallel$ [1 1 0]					B $\parallel$ [1 0 0]			
		Exp.	DFT				Exp.	DFT
Band	F (T)	m^* (m_e)	F (T)	m_b (m_e)	F (T)	m^* (m_e)	F (T)	m_b (m_e)
1	290(10)	0.76(2)	251	0.21	-	-	298	0.12
1	360(10)	0.97(3)	297	0.18				
2	55(5)	0.77(3)	35	0.09	-	-	32	0.08
2	-	-	55	0.14	50(10)	0.71(4)	51	0.10
2	105(5)	1.5(1)	72	0.11	170(5)	0.68(2)	218	0.29
2	1725(10)	1.55(4)	1516	2.82	3730(10)	1.66(5)	3683	0.72
2	-	-	6791	0.93				
3	3820(10)	2.39(2)	4087	1.37	3865(10)	1.28(4)	3953	1.38
4	-	-	136	2.39	-	-	122	1.38
4	170(10)	0.98(3)	217	0.75	170(5)	0.68(2)	169	0.27
4					-	-	740	1.93
MB	530(10)	0.95(3)	-	-	385(10)	0.61(2)	-	-
MB	745(10)	1.7(1)	893	0.84	445(5)	1.15(3)	508	0.02
MB	1420(10)	1.57(3)	1353	0.86	885(10)	1.40(2)	-	-
MB	3655(10)	2.36(9)	3477	1.34	960(10)	1.43(2)	941	0.38
MB	4035(10)	2.29(9)	4227	1.46	1225(5)	0.87(2)	1666	0.48
MB					2450(10)	1.56(3)	2308	0.66
MB					5275(10)	1.59(8)	5640	1.13
MB					6620(10)	2.24(9)	6282	0.94
MB					7835(20)	2.37(4)	8179	0.68
MB					9100(10)	1.97(9)	9867	0.26

Table 3.2: **Frequencies and effective masses of de Haas-van Alphen oscillations observed in CeZn₁₁**, compared with GGA+ U calculations and magnetic breakdown orbits, for field orientations along high symmetry axes.

3.3.2 Density functional theory calculations

The comparisons drawn so far with the observed frequencies in LaZn₁₁ provide a useful starting point for determining the nature of the Fermi surface of CeZn₁₁: as many frequencies correspond between the two, some bands of the Fermi surface of CeZn₁₁ likely take a similar form to those of LaZn₁₁. However, as the agreement is not exact and many additional frequencies are observed in CeZn₁₁, DFT calculations for CeZn₁₁ are necessary to further clarify the picture – by varying the magnetic state of the Ce ion between calculations, the experimental Fermi surface can then be used to determine the localisation of the 4*f* electrons.

Non-magnetic GGA calculations

Initially, as the most straightforward to initiate, a nonmagnetic DFT calculation was conducted for CeZn_{11} . This calculation, using the GGA approximation, is essentially the same as that which successfully matched the Fermi surface for LaZn_{11} , but with slightly adjusted lattice parameters (to match the experimental crystal structure of CeZn_{11}) and the addition of a $4f$ electron for each Ce atom. Although this $4f$ electron is unpaired, the electron spins are for now ignored.

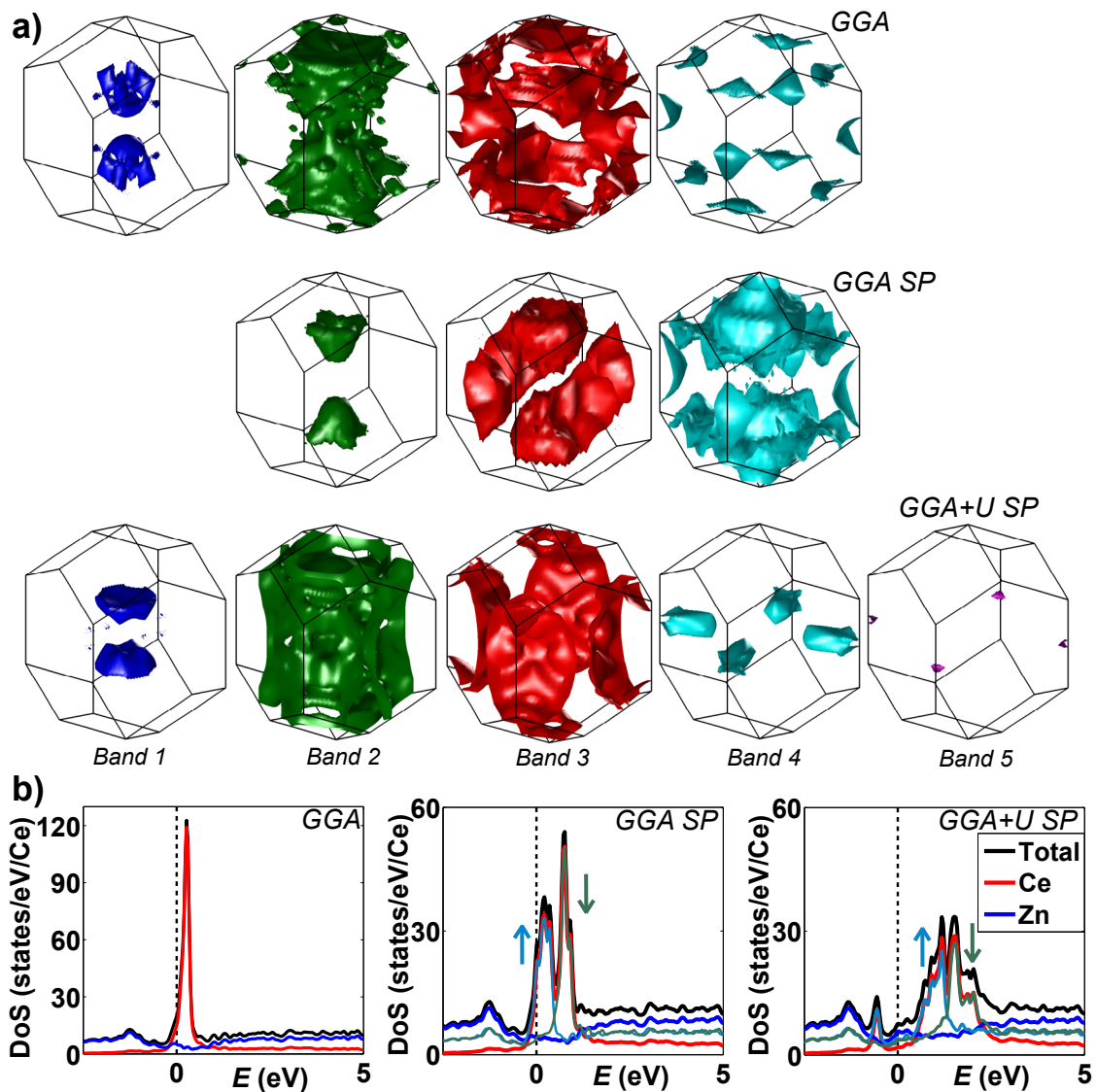


Figure 3.9: **Density functional theory calculations for CeZn_{11} .** a) The calculated Fermi surfaces, split into their constituent bands, for GGA, GGA SP and GGA+U SP calculations respectively. b) The density of states around the Fermi level found for each calculation.

Figure 3.9a) shows the Fermi surface (labelled *GGA*) this calculation predicts. As in LaZn_{11} four bands cross the Fermi level, however the morphology of the resulting Fermi surface is rather different, with many smaller pockets and a few knobbled and sinewy larger surfaces. As a result the total surface area is larger, and so correspondingly the density of states at the Fermi level must also be larger too. This is shown in Figure 3.9b): the background of Zn $3d$ states is similar to that of LaZn_{11} , however the large peak of Ce $4f$ states - whose counterpart La $4f$ states were well above the Fermi level in LaZn_{11} - now lies right on the Fermi level, with 1/14th of the Ce $4f$ states filled by the additional electron. As these $4f$ states now dominate at the Fermi level, this increases the density of states and significantly changes the morphology of the Fermi surface.

The quantum oscillation frequencies produced by this Fermi surface, in the measured range $\mathbf{B} \parallel [110] \rightarrow \mathbf{B} \parallel [100]$, are shown in Figure 3.10a). Comparing these (*GGA*) to the measured frequencies (*CZ1 Exp.*) the correspondence is poor: there is a glut of low frequencies, but all below the strongest features seen at ~ 0.4 kT; multiple frequencies are expected between 0.5–2 kT, but do not agree with the experimental angular dependence; above 2 kT only one frequency branch is seen, and this does not span the full angular range as in experiment. Further treatment of the Ce ion is therefore needed to explain the measured Fermi surface.

Magnetic GGA calculations

As indicated by the formation of an AFM ground state, magnetic interactions play an important role in CeZn_{11} : the Fermi surface may well be affected by the spins in the system, especially those of the unpaired $4f$ electrons. However the ground state AFM configuration for CeZn_{11} is not known. As each Ce ion has six nearest neighbours there are many possible AFM orderings, however all of these would at least double the size of the unit cell in the $\mathbf{a}$ and $\mathbf{b}$ lattice directions – as well as in $\mathbf{c}$ if the stacking is not ferromagnetic – reducing the size of the first Brillouin zone. All fundamental frequencies of the Fermi surface must be contained within the first Brillouin zone, so its size (and more specifically its maximum cross-sectional area) sets an upper limit on the size of

possible frequencies observable in quantum oscillations. Considering first the Brillouin zone of the non-magnetic structure, the maximum cross-sectional areas (converted to frequency) normal to $[110]$ and $[100]$ are 9.65 kT and 11.31 kT respectively – the measured frequencies are all smaller than this. However, assuming a doubling of $\mathbf{a}$ and $\mathbf{b}$ from AFM ordering reduces these areas to 4.21 kT and 5.65 kT – smaller than many of the higher measured frequencies. Therefore the highest frequencies observed in CeZn_{11} , which have no equivalents in LaZn_{11} , cannot be the result of magnetic ordering.

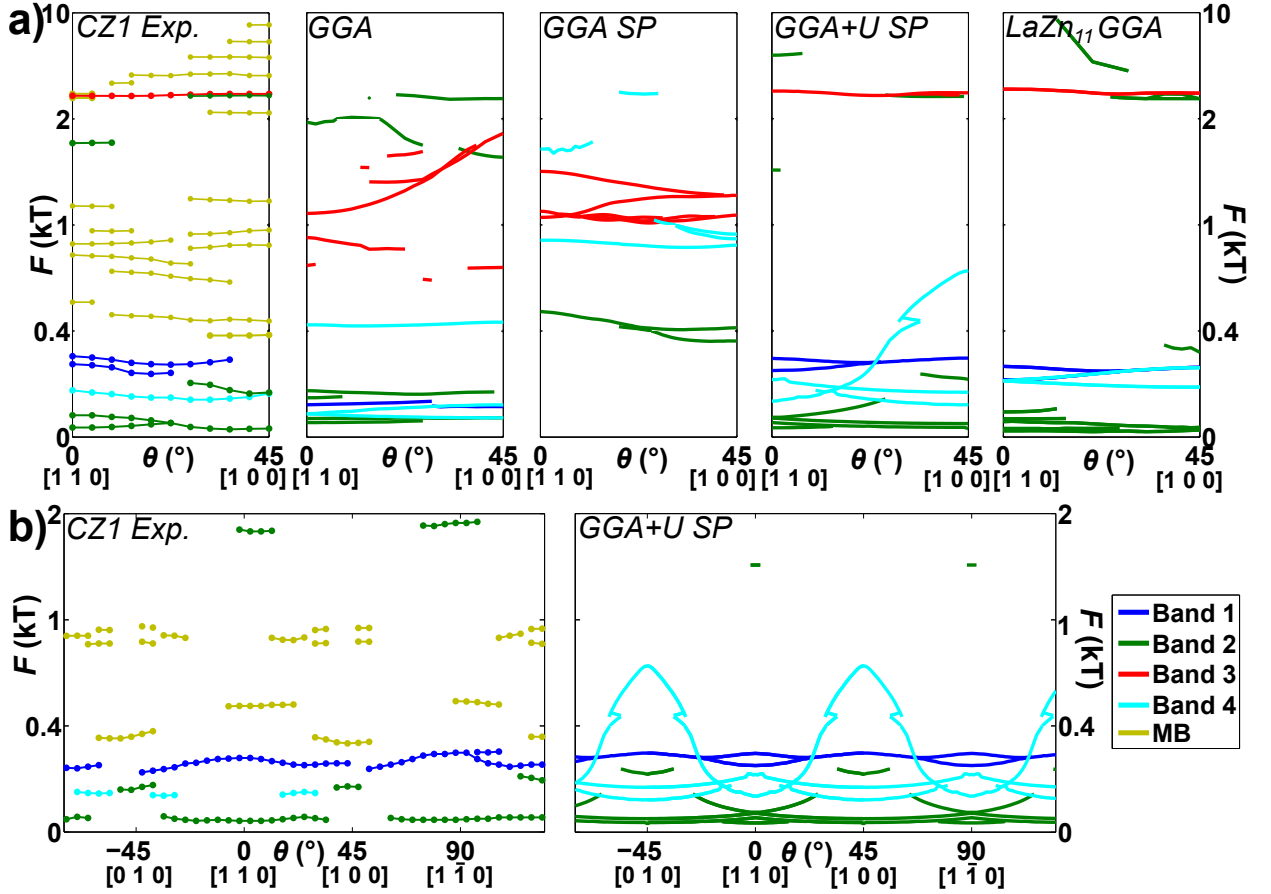


Figure 3.10: **Angular dependence of frequencies in CeZn_{11}** , from de Haas-van Alphen oscillations and density functional theory calculations. **a)** Sample CZ1, measured to 33 T over the range $B \parallel [110] \rightarrow B \parallel [100]$, compared to GGA, GGA SP and GGA+U SP calculations for CeZn_{11} , as well as GGA calculations for LaZn_{11} . **b)** Sample CZ1, measured to 18 T over the range $B \parallel [010] \rightarrow B \parallel [1\bar{1}0]$, compared to GGA+U SP calculations.

In fact quantum oscillations are only visible in fields of above ~ 10 T, above a clear transition out of the AFM state, which occurs between 4.5 – 7.5 T depending on orientation. Therefore the next Fermi surface to consider takes into account the spin density as well as the charge density, but places no constraints on their orientation at the Ce site:

this is the Fermi surface produced by spin polarised DFT calculations. As the two spin populations are considered separately, two Fermi surfaces are generated – one for spin up electrons and one for spin down.

Figure 3.9b) shows the resulting density of states for this calculation (*GGA SP*). The Ce $4f$ states still lie at the Fermi level, but they have been reduced in energy for the spin up electrons (blue arrow) and increased in energy for the spin down electrons (green arrow); the underlying Zn $3d$ states are unaffected. As a result the spin up Fermi surface – comprised of Ce $4f$ states – dominates the density of states, and is shown in Figure 3.9a)². Only three bands cross the Fermi level (counterintuitively labelled band 2, 3 and 4 for consistency between calculations), forming a simpler Fermi surface than the other calculations: all three bands produce a few large pockets; band 4 also yields a corrugated, floriferous sheet normal to the c -axis.

Figure 3.10a) (*GGA SP*) shows the frequencies expected for the spin up Fermi surface over the measured range. The lack of small pockets and continuous large features means there are few frequencies either below 0.4 kT or above 2 kT, where the strongest experimental features are seen. Instead the large pockets produce a number of frequency branches around 0.5 kT and 1 kT, but these do not match well with the weak features seen in these regions experimentally. Of all the Fermi surfaces considered, this spin up Fermi surface is the poorest match to the experimental data; a simple spin polarised DFT calculation is therefore unable to reproduce the experimental Fermi surface of CeZn₁₁.

GGA+ U calculations

Both LDA and GGA calculations are known to have problems calculating the electronic structure of systems with partially filled $3d$ and $4f$ orbitals, placing these at the Fermi level when in actuality they are localised. To overcome this the Hubbard term U of a GGA+ U can, if chosen to be sufficiently large enough, localise these d and f states. Figure

²The spin down Fermi surface – comprised of Zn $3d$ states – is near identical to the Fermi surface produced when the Ce $4f$ states are localised (labelled *GGA+ U SP* in Figure 3.9a)), so is not discussed here to save repetition. As both the spin up and spin down Fermi surfaces should match the data, the poor correspondence of the spin up Fermi surface serves to demonstrate that the spin polarised GGA Fermi surface is not seen experimentally.

3.9b) shows the density of states for a GGA+ U calculation of CeZn₁₁ with $U = 1.5$ eV (labelled *GGA+ U SP*). As before the spin up Ce 4*f* states are lowered in energy and the spin down states raised (GGA+ U calculations are necessarily spin polarised), however the Coulomb repulsion term has shifted all of these states above the Fermi level, except for a (spin up) peak of the single 4*f* electron states now localised beneath. As a result the Fermi level is now dominated by Zn 3*d* states, as was the case in LaZn₁₁.

The spin up Fermi surface produced by the GGA+ U calculation is shown in Figure 3.9a) (the spin down Fermi surface is for all intents and purposes identical). As both originate from the continuum of Zn 3*d* states, this Fermi surface is conspicuously similar to that of LaZn₁₁, with a few slight differences: the most complex band, band 2, has fewer small perforations; the pockets of band 4 extend to the edge of the Brillouin zone to form a cross-shaped Fermi surface; a very small pocket, band 5, has appeared at the edge of the Brillouin zone. The frequencies expected for this Fermi surface are shown in Figure 3.10a) (*GGA+ U SP*) alongside those calculated for LaZn₁₁ (*LaZn₁₁ GGA*) – apart from slight energy shifts of frequency branches, the only differences in the GGA+ U calculation are fewer smaller frequencies from band 2 (due to fewer perforations) and a higher frequency branch from band 4 (from its distinct cross shape). The additional band, band 5, produces frequencies < 5 T in size, too small to be observable experimentally.

Comparing with the experimental frequencies in Figure 3.10a), the frequencies of the GGA+ U calculation are able to capture all of the highest intensity features: band 1 and 2 match the strongest features beneath 0.4 kT; band 2 matches the feature close to 2 kT at $\mathbf{B} \parallel [110]$; band 2 and 3 match the high frequency branches at ~ 4 kT. In addition the weaker frequency branch at ~ 0.2 kT agrees with expected frequencies for band 4, which was not seen in measurements on LaZn₁₁. Although many of these features are also predicted by the LaZn₁₁ GGA calculations, the CeZn₁₁ GGA+ U calculation provides the best match to the absolute frequency values. Figure 3.10b) shows a comparison between the measured frequencies and the GGA+ U values over a wider angle range. Although fewer features are seen – as a result of the smaller maximum field of these measurements – the GGA+ U Fermi surface is able to explain most of the high amplitude features across

the angular range.

Table 3.2 compares the measured frequencies and effective masses at $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [100]$ with those predicted by the GGA+ U calculation: the predicted masses are of comparable size to those found in LaZn₁₁, however the measured masses are consistently larger. Due to the complexity of the Fermi surface, the calculated effective masses are very susceptible to any slight band shifts; as a result there is a good deal of variation in the mass enhancement (m^*/m_b), however the rough estimate of $2 - 4\times$ larger obtained from comparison with LaZn₁₁ appears reasonable. The single frequency branch observed for band 4 corresponds to an orbit with relatively light mass, arising from its new cross-like shape. Otherwise the frequencies of band 4 have large effective masses and so are not seen experimentally, as was the case in LaZn₁₁ where the large effective masses were postulated to significantly reduce the amplitude.

As expected from the similarities with measurements on LaZn₁₁, many of the de Haas-van Alphen frequencies observed in CeZn₁₁ arise from a Fermi surface dominated by Zn 3*d* states, with the Ce 4*f* states well localised beneath the Fermi level. This means CeZn₁₁ is well away from any heavy fermion behaviour, with the high field Fermi surface being that of the paramagnetic state with localised moments: the *f* electrons play no role at the Fermi level and there is no substantial mass enhancement, although there is a small enhancement in effective masses in comparison to the entirely non-magnetic LaZn₁₁, mirroring the enhancement seen in the Sommerfeld coefficient. However there are a number of additional weaker frequencies, plotted in ochre in Figure 3.10 and indicated as Band ‘MB’ in Table 3.2, that cannot be explained as orbits of this Zn 3*d* dominated, GGA+ U generated Fermi surface, and whose frequencies and effective masses do not correspond to higher order harmonics.

3.3.3 Magnetic breakdown

Experimental origins of non-fundamental frequencies

A number of processes, described in Sections 1.2.3 and 1.3.3, are able to produce non-fundamental frequencies, or frequency-like features, in torque measurement of the de

Haas-van Alphen effect. Already the most common effect, higher order harmonics of fundamental frequencies, has been ruled out: the effective masses (given in Table 3.2) do not show the necessary $m_{nF}^* = n \times m_F^*$ behaviour. Similarly, higher frequencies can also be generated from the superposition of different frequencies, and from the size of the high frequencies at $\mathbf{B} \parallel [100]$ this seems a promising explanation: the high frequencies (5275 T, 6620 T, 7835 T, 9100 T) are pretty evenly spaced above the highest fundamental frequency (3865 T), and this spacing is very close to another observed frequency (1225 T). However, again the masses do not show the necessary behaviour of $m_{F1+F2}^* = m_{F1}^* + m_{F2}^*$, and the frequency that corresponds to the spacing is not a fundamental frequency of the Fermi surface.

Due to the magnetic background of the torque in CeZn₁₁ and the high fields used for measurement, the forces exerted on the cantilever are very large. This could potentially lead to an overcritical torque interaction, if the deflection of the cantilever is significant enough to alter the orientation of the sample with respect to the field. This usually leads to sawtooth-like oscillations in the case of a large amplitude of oscillation [38], however in CeZn₁₁ the amplitudes of the oscillations themselves are rather small: it is instead the large magnetic background that may excessively deflect the lever. As the magnetic background grows monotonically with field so should the cantilever deflection, therefore any frequencies originating from an overcritical torque interaction should vary with field. This is not seen experimentally (for example in Figure 3.13c) and f)) and irrespectively this would only act to slightly change the fundamental frequencies observed, not to generate entirely new frequencies.

Magnetic breakdown orbits

Rather than extraneous effects, arising from particulars of the experimental setup, the additional frequencies may originate from the Fermi surface itself – in the frequency spectra of Figure 3.7e) they possess the necessary symmetry (periodic over 90° and symmetric around the high symmetry axes). Although the fundamental frequencies of the GGA+*U* calculated Fermi surface only account for about half of the measured frequencies, it may

be possible, in high enough fields, for the electrons to traverse multiple bands in the same orbit, producing numerous additional frequencies. The necessary field for an electron to tunnel between two bands of the Fermi surface was defined in Equation 1.35 as:

$$B_{BD} = \frac{\pi\hbar}{2e} \left(\frac{k_g^3}{a+b} \right)^{1/2} \quad (3.4)$$

where k_g is the k-space gap between the bands and $1/a$ and $1/b$ are the radii of curvature of the two bands at the tunnelling point. Therefore a close proximity of neighbouring bands is required for magnetic breakdown orbits to be observable in a measurable magnetic field range.

In a typical case of magnetic breakdown, a single set of symmetrically equivalent tunnelling points exist, all contained within a single, high-symmetry k -space plane. In these cases a small number of additional frequencies are generated from the combination of a pair of fundamental frequencies [114]. Due to the complexity of the Fermi surface generated by the GGA+ U calculation, this is manifestly not the case in CeZn₁₁: there are manifold tunnelling points – throughout the Brillouin zone rather than within a single plane – which link all adjacent bands. Therefore the magnetic breakdown orbits cannot simply be calculated from the combination of fundamental frequencies, but instead are calculated rigorously with the frequency finding procedure discussed in Section 1.3.1.

Orbit tunneling in CeZn₁₁

Figure 3.11 shows slices of the Fermi surface, normal to the high symmetry directions $[100]$ and $[110]$, where the bands are in closest proximity. Points where tunnelling may be possible between bands are marked with an **x**. In the simplest cases, such as slice d), the tunnelling points link two orbits of the Fermi surface that are well separated from the rest. The magnetic breakdown of these orbits will lead to two or three additional frequencies, of comparable size to the parent orbits. However a more complicated case is presented in slice c), where tunnelling via band 1 is able to link orbits of band 2 in adjacent Brillouin zones, allowing for the construction of a potentially infinite number of possible orbits. In slice a), where all parts of the Fermi surface are interconnected by

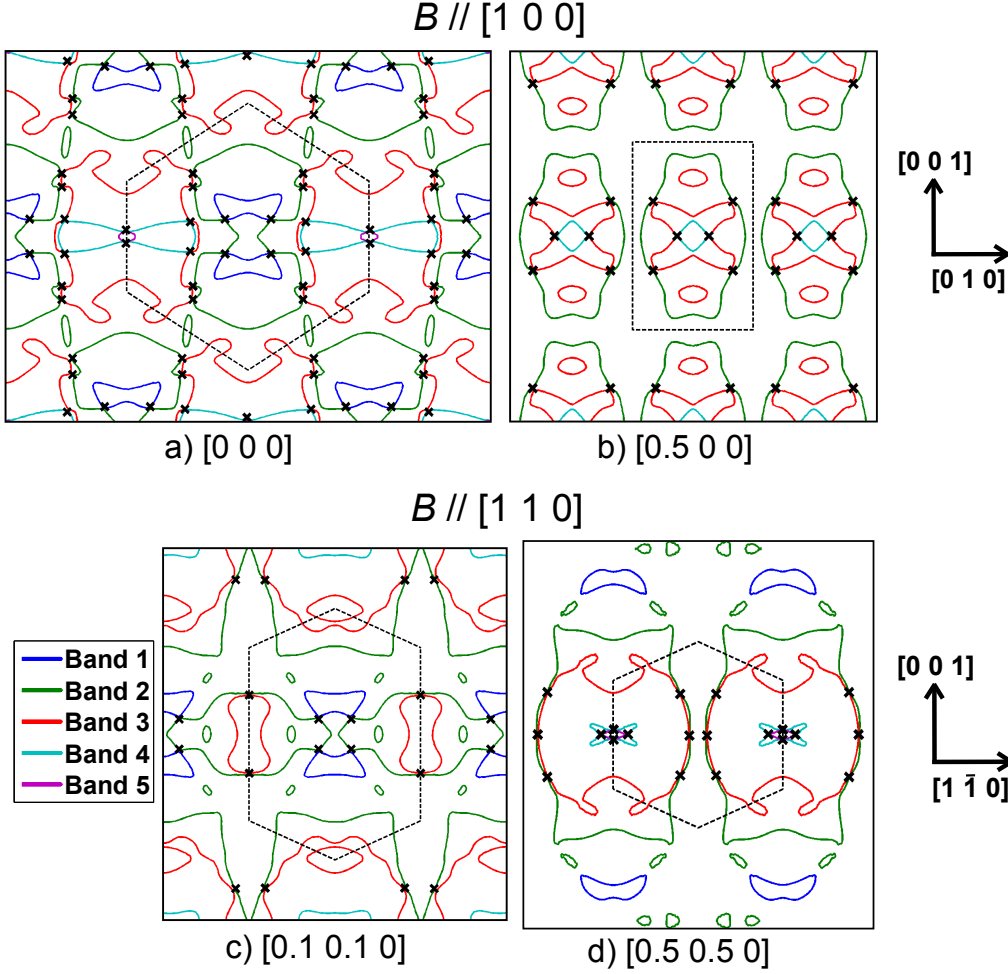


Figure 3.11: **Slices of the Fermi surface of CeZn_{11}** for the orientations $\mathbf{B} \parallel [100]$ and $\mathbf{B} \parallel [110]$. Points where tunnelling between bands may be possible are marked with an $\mathbf{x}$. Centre coordinates are given in terms of the reciprocal lattice vectors.

tunnelling points, things are even more complicated still.

Calculating an infinite number of orbits is obviously impossible, and even an intermediate number of orbits will be computationally intensive – each additional tunnelling point exponentially increases the number of orbits – and gratuitous – only a small number of additional orbits are seen experimentally. However further constraints can be placed on the orbits calculated, these are shown pictorially in Figure 3.12. In an applied field the electrons will all process in the same direction (i.e. clockwise or anti-clockwise, depending on the geometry) around the fundamental orbits, and this must also be the case for the magnetic breakdown orbits. Therefore the orbit of Figure 3.12a) is allowed – the electrons travel in the same direction for all constituent parts of the orbit – but the orbit of Figure 3.12b) is not. Furthermore band 4 is unlikely to contribute to any observable magnetic

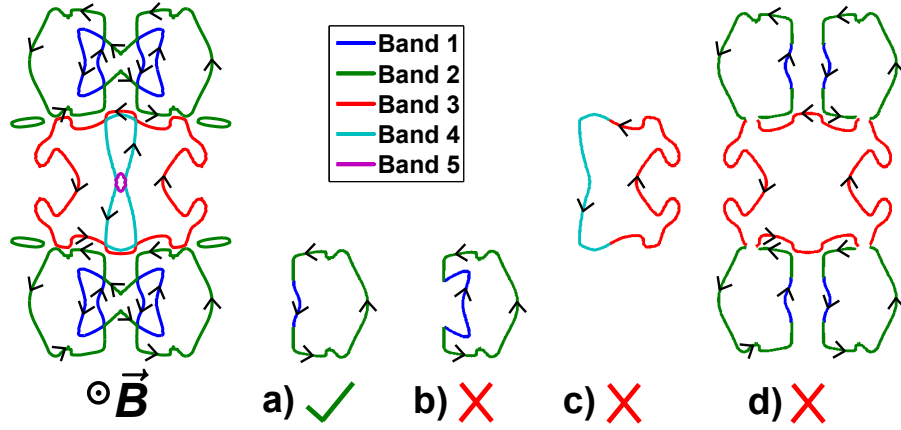


Figure 3.12: **Feasible and infeasible magnetic breakdown orbits in CeZn_{11}** , shown for a slice centered on $[000]$ for the field orientation $\mathbf{B} \parallel [100]$. Arrows denote the direction of electronic motion for the field direction indicated.

breakdown orbits: its fundamental frequencies are for the most part not observed due to their comparatively larger masses, and any magnetic breakdown orbits arising from these frequencies would be of even smaller amplitude. For this reason the orbit of Figure 3.12c) is unlikely to be experimentally observable, and so all similar orbits involving band 4 are discounted. Finally, the probability of an orbit occurring decreases with every tunnelling point passed, whether or not a tunnelling event occurs. Therefore orbits encompassing a large number of tunnelling points, such as that shown in Figure 3.12d), are highly improbable, and the amplitudes of the associated frequencies will be vanishingly small; these can also be neglected in calculations.

Magnetic breakdown along the high symmetry axes

Figures 3.13a),b) and d),e) show the magnetic breakdown orbits calculated, with the prior constraints applied, for the orientations $\mathbf{B} \parallel [100]$ and $\mathbf{B} \parallel [110]$ respectively; the frequencies seen experimentally are marked in bold. Figures 3.13c) and f) show the location of these frequencies compared to the experimental data. These values, along with their effective masses³, are given in Table 3.2, labelled ‘MB’. In Figures 3.13c) and f) Fourier transforms of the torque signal have been taken over evenly spaced 5 T windows, in

³Although there is no temperature term in Equation 3.4, it does assume that all conduction electrons are at the Fermi level, which is only true as $T \rightarrow 0$. In the measured temperature range, $T < 10$ K, this is a valid assumption, and so the temperature dependence of the magnetic breakdown frequency amplitudes is well described by the usual Lifshitz-Kosevich formula, as seen in Figure 3.8.

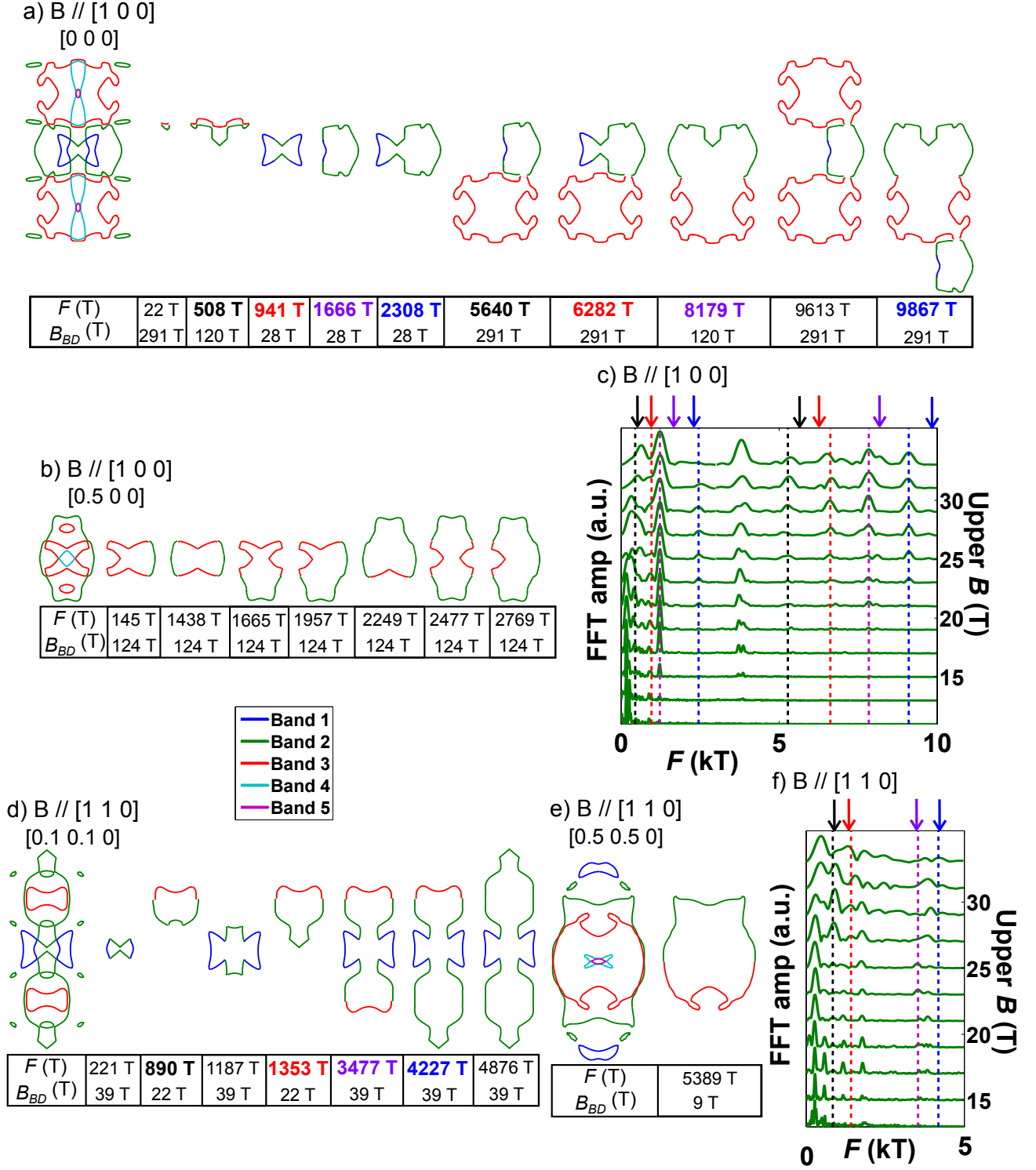


Figure 3.13: **Calculated magnetic breakdown orbits in CeZn₁₁**: a),b) The original Fermi surface and calculated breakdown orbits in the orientation $\mathbf{B} \parallel [1\ 0\ 0]$, bolded frequencies are seen experimentally. c) Fourier transforms of the torque signal at $\mathbf{B} \parallel [1\ 0\ 0]$, calculated for 5 T field windows between 6–33 T and plotted against the upper field of each window. Dashed lines indicate frequencies not matched by GGA+ U calculations, arrows indicate the corresponding magnetic breakdown frequencies. d)-f) Equivalent plots for $\mathbf{B} \parallel [1\ 1\ 0]$.

the field range 6 – 33 T, and plotted against the upper field of each window. The dashed lines indicate frequencies that are not matched by GGA+ U calculations; the arrows mark the position of the calculated magnetic breakdown frequencies. The calculated frequencies match both the number and the approximate location of the frequencies seen in experiment, with the match particularly good at $\mathbf{B} \parallel [110]$. All the high frequencies seen at $\mathbf{B} \parallel [100]$ can be explained by magnetic breakdown, arising from large, circuitous orbits that traverse multiple Brillouin zones. There are some discrepancies in the absolute frequency values, but as the large GGA+ U calculated frequencies were also slightly off the measured values for the constituent bands (as shown in Table 3.2) this is not unexpected.

Figures 3.13c) and f) also show that, compared to fundamental frequencies of similar size, the onset of magnetic breakdown frequencies occurs at higher fields. In Figure 3.13c) the fundamental frequency at ~ 4 kT is visible below 15 T, while the > 5 kT breakdown frequencies only appear above 20 T. Similarly in Figure 3.13f) the smaller (< 2 kT) breakdown frequencies are only apparent above 25 T, while fundamental frequencies of similar size are clear from 15 T. This is due to the breakdown field, B_{BD} , necessary to see the non-fundamental orbits.

For each tunneling point the required breakdown field is calculated from Equation 3.4, with k_a and k_b found by fitting the portion of each orbit around the tunnelling point to a circle. The breakdown field of each orbit is then taken to be the largest breakdown field of its constituent tunnelling points. Most of the orbits found have reassuringly low breakdown fields, in the range $22 \text{ T} < B_{BD} < 39 \text{ T}$, compared to a maximum measured field of 33 T. The exceptions to this are the orbits between band 2 and band 3 shown in Figure 3.13a), which take values of $B_{BD} = 120 \text{ T}$ and 291 T for the outer and inner tunnelling points respectively. These same orbits also showed the largest discrepancy with their measured frequency values, so it is likely that in reality bands 2 and 3 take a slightly modified form at this orientation, both lowering B_{BD} and better matching the experimental frequencies.

Not all the calculated breakdown orbits are seen, most notably those shown in Figure 3.13b) and e). In the former case the high breakdown field, $B_{BD} = 124 \text{ T}$, is likely

prohibitive; in the latter case the high frequency (5389 T) and effective mass ($1.12 m_e$) will damp the amplitude of oscillation. The few frequencies in Figure 3.13a) and d) that are not clearly seen experimentally all occur in the proximity of other frequencies, either of fundamental or breakdown origin, making them difficult to distinguish.

Angular dependence of magnetic breakdown frequencies

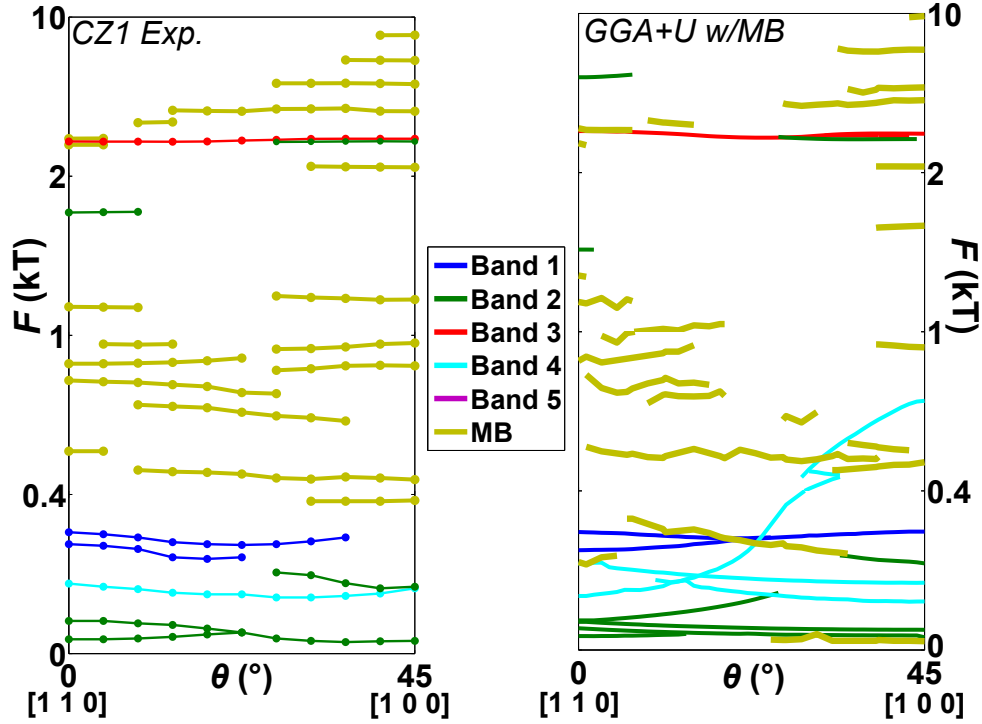


Figure 3.14: Angular dependence of magnetic breakdown orbits in CeZn_{11} . Shown for the rotation $\mathbf{B} \parallel [110] \rightarrow \mathbf{B} \parallel [100]$ are: (left panel) measured de Haas-van Alphen frequencies; (right panel) fundamental and magnetic breakdown (MB) frequencies calculated for the GGA+ U Fermi surface.

Figure 3.14 shows the calculated angular dependence of the magnetic breakdown frequencies in the measured range $\mathbf{B} \parallel [110] \rightarrow \mathbf{B} \parallel [100]$. Considering the fundamental frequencies (arising from the same GGA+ U Fermi surface) alongside the magnetic breakdown orbits, practically all features seen in the experimental angular dependence can be accounted for⁴. The most notable discrepancies occur around 30° , where the angular ranges of some frequency branches are curtailed, along with the differences in absolute

⁴The coarseness present in the calculated angular dependence arises from the finite number of slices used to calculate the possible orbits: the actual extremal orbits may not lie on considered slices, instead the values plotted are likely close to, but not exactly at, the extremal frequency.

frequency value previously discussed at $[1\ 0\ 0]$. The overestimated values of B_{BD} for tunnelling between band 2 and band 3 close to $[1\ 0\ 0]$, discussed explicitly earlier, likely leads to this curtailment; reducing it to a value within the measured field range would increase the span of these branches to something closer to the experimental case. However these disagreements are slight, from Figure 3.14 it is clear that, once magnetic breakdown orbits are considered, a GGA+ U calculated Fermi surface with a well localised Ce $4f$ electron is able to account for all de Haas-van Alphen frequencies seen experimentally in CeZn₁₁.

3.4 Summary

In this chapter I have presented de Haas-van Alphen measurements and DFT calculations of the Fermi surface of CeZn₁₁, and its non-magnetic analogue LaZn₁₁, to determine what effect, if any, the additional $4f$ electron of CeZn₁₁ has on the electronic structure.

Beginning first with LaZn₁₁, strong oscillations are seen on a weakly paramagnetic background at all measured orientations, with a multitude of frequencies taking values from 10 T to 10 kT. These frequencies are well described by GGA calculations, which predict a complex four band Fermi surface, comprised of Zn $3d$ states, that is able to replicate the number, range and angular dependence of the measured frequencies. The fourth band predicted by these GGA calculations is not seen experimentally, however its presence is necessary for charge conservation; likely higher effective masses and enhanced scattering prevent its detection within the temperature and field ranges measured. The effective masses found experimentally are also in good agreement with those predicted by DFT, taking small values with no observable mass enhancement, with a Fermi level composed almost exclusively of Zn $3d$ states.

In CeZn₁₁ the torque signal has a large magnetic background with a clear transition out of the AFM ground state, taking a value of 7 T at 320 mK along the easy axis $[1\ 1\ 0]$. On top of this background are quantum oscillations, with a superficially similar range and distribution of frequencies to LaZn₁₁. Comparing similar frequencies, the effective masses in CeZn₁₁ are roughly $2 - 4\times$ larger than their counterparts in LaZn₁₁, close

to the enhancement seen in the Sommerfeld coefficient. GGA and GGA spin polarised calculations are unable to replicate the measured frequency spectrum, with both placing the $4f$ states right at the Fermi level. However, by applying a Coulomb repulsion term $U = 1.5 \text{ eV}$, the $4f$ states can be localised beneath the Fermi level; these GGA+ U calculations produce a Fermi surface very similar to LaZn_{11} , albeit with an additional fifth band, consisting of a pocket too small to be seen experimentally. This Fermi surface is able to account for approximately half the frequencies seen in CeZn_{11} , generally those with the largest amplitude, confirming that the Fermi level is dominated by Zn $3d$ states, with the $4f$ electrons well localised and only slight mass enhancements. The low temperature localised moment AFM state of CeZn_{11} is therefore suppressed by field to a (non-heavy fermion) paramagnetic state, passing through a quantum phase transition far to the left of the quantum critical point on the Doniach diagram.

As a result of the complexity of the Fermi surface of CeZn_{11} , there are many points in the first Brillouin zone where adjacent bands come close to touching. With a large enough applied magnetic field tunnelling between these adjacent bands is possible, and this leads to the occurrence of additional magnetic breakdown frequencies. The sheer number of tunnelling points, coupled with the entwined nature of the Fermi surface, makes CeZn_{11} a particularly complex case for the determination of these frequencies; however calculations of the most probable breakdown frequencies are able to account for all the additional features seen experimentally. The breakdown fields of these orbits are found to be experimentally accessible, with most falling in the range $22 \text{ T} < B_{BD} < 39 \text{ T}$, and most experimental frequencies assigned to magnetic breakdown begin to appear around this region. With the inclusion of magnetic breakdown, the GGA+ U calculated Fermi surface is able to explain all the observed de Haas-van Alphen frequencies in CeZn_{11} , confirming the $4f$ electrons are well localised, with only slight mass enhancements.

Chapter 4

The low temperature Fermi surface of modulated IrTe₂

4.1 Introduction

This chapter presents torque magnetometry and angle-dependent magnetoresistance measurements of the transition metal dichalcogenide IrTe₂, which features a raft of structural transitions – associated with dimer formation – resulting in an unusual low temperature electronic structure with reduced dimensionality at an angle to the lattice planes. In the introductory section I discuss the structural transitions seen in some of the most studied transition metal dichalcogenides – the charge density wave materials – and the role played by the Fermi surface; following this I summarise the literature on IrTe₂, from the first observation of the structural transition to the complete description of the low temperature dimerisation. The torque magnetometry results presented are first rotations in constant field – which observe a clear change in the density of states and dimensionality at low temperatures – followed by de Haas-van Alphen oscillations. These oscillations match well to the DFT calculated Fermi surface, but only once the 6 possible domains of the low temperature structure are considered. AMR measurements display clear Lebed dips, whose location agrees with that expected for the $p/q = 1/2$ magic angle for all domains of the low temperature structure. Together the de Haas-van Alphen and AMRO

measurements confirm both the quasi-two and quasi-one dimensional Fermi surface of the low temperature structure are tilted away from the lattice planes in IrTe₂.

4.1.1 Transition metal dichalcogenides

As is clear from their name, the transition metal dichalcogenides (TMDs) take the chemical formula MX₂, with M a transition metal and X a chalcogen (usually S, Se or Te). This chemical simplicity belies a wide variety of electronic phenomena present in these materials, however structurally they are very similar, forming layered systems that exhibit quasi-two-dimensional behaviour. Figure 4.1 shows the general crystal structure of the TMDs: each transition metal ion is bonded to six chalcogen ions in an octahedral arrangement, forming hexagonal layers weakly coupled by van der Waals forces.

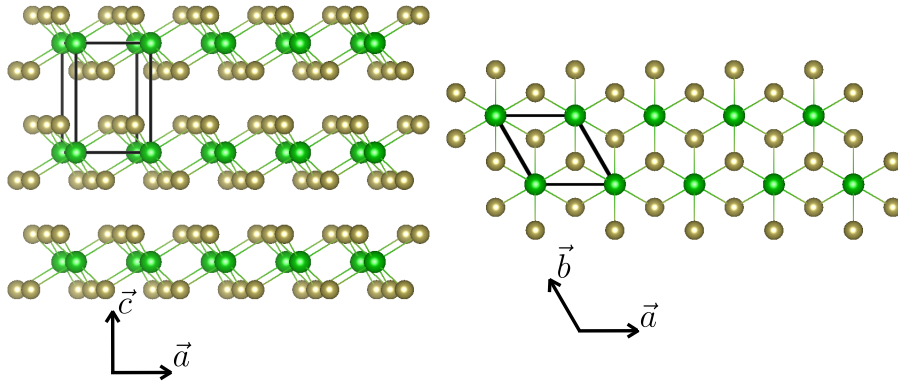


Figure 4.1: **Crystal structure of the transition metal dichalcogenides** (using the lattice parameters of IrTe₂), with the unit cell indicated in black.

This weak bonding between layers is the foundation of the main practical application of TMDs (specifically MoS₂ and WS₂): dry lubricant. However, in the wake of the surge of interest in graphene, there has been much renewed interest in the TMDs for their potential single-layer applications: due to their weak inter-layer bonding they can be exfoliated much like graphene, but show a far wider range of electronic properties. Of most interest for potential electronic applications are the semiconducting compounds such as MoS₂, MoSe₂, WS₂ and WSe₂, which have sizeable bandgaps that become direct in single layers [5]. However TMDs span the full range of electronic behaviour, from insulators (e.g. HfS₂ [115]) via semi-metals (WTe₂ [116]) to metals (NbS₂ [117]).

Charge density wave systems

Most relevant to IrTe₂ are those compounds which show novel properties, such as superconductivity and charge density waves (CDW), that originate from instabilities within the electronic structure. A typical case is TaS₂, which shows CDW order and, with applied pressure, superconductivity [118] (similar behaviour is seen in NbSe₂ and TaSe₂ [119]). Figure 4.2a) shows the temperature dependence of resistivity in TaS₂ at ambient pressure: at high temperatures TaS₂ is metallic, but upon cooling undergoes two transitions into ordered states; these are accompanied by sharp increases in resistance, and show some hysteresis. With the application of pressure these transitions are suppressed and a superconducting phase is induced, as shown in the phase diagram of Figure 4.2b).

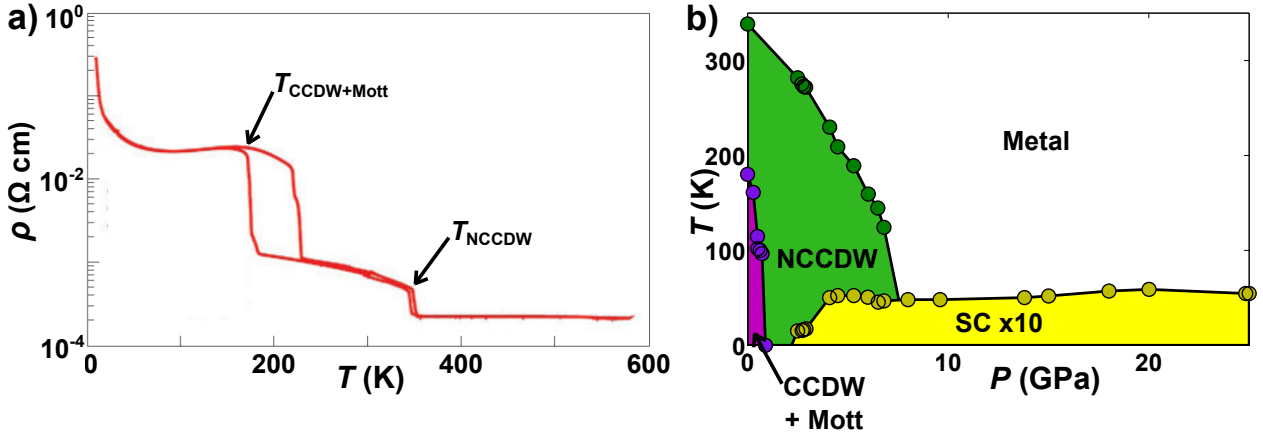


Figure 4.2: **Transitions and phase diagram with pressure of TaS₂.** a) Temperature dependence of resistivity at ambient pressure. b) Temperature-pressure phase diagram. Data taken from [118].

This charge ordering at low temperatures arises from the two-dimensional nature of the electronic structure. The Fermi surface of the high temperature, metallic state is shown in Figure 4.3b): the strongly two-dimensional structure leads to a quasi-two-dimensional Fermi surface, comprised of distorted cylinders along the $\mathbf{c}^*$ axis. The wide, flat sides of these cylinders can be joined by a vector that is not a reciprocal lattice vector – such as $\mathbf{q}_1$ in Figure 4.3a) – and so are well nested. The Peierls distortion that gaps these states is the origin of the low temperature CDW phase.

Figure 4.3c) shows, to the same scale as Figure 4.3b), the Fermi surface in the charge density wave phase of TaS₂. The CDW distortion has shrunk the in-plane size of the

Brillouin zone, and the gapping of the nested states has significantly reduced the area of the Fermi surface, and hence the density of states at the Fermi level. This reduction in charge carriers leads to the increase in resistivity seen upon forming the CDW state – as well as a sharp decrease in the paramagnetic susceptibility – with a further enhancement as the CDW phase in TaS₂ happens to be a Mott insulator. The initial transition in TaS₂, labelled T_{NCCDW} (nearly-comensurate charge density waves) in Figure 4.2a), corresponds to the first formation of regions of CDW phase, while the second transition, labelled $T_{\text{CCDW+Mott}}$ (comensurate charge density waves), corresponds to the presence of the CDW phase in the entire sample [118].

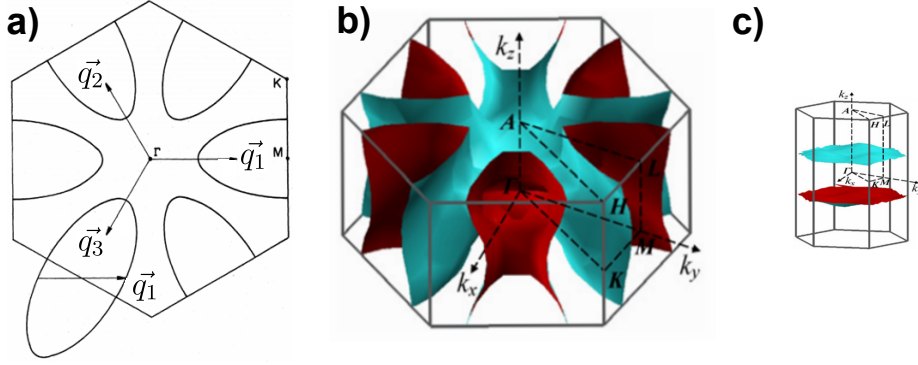


Figure 4.3: **Fermi surface of TaS₂.** a) The high temperature Fermi surface, viewed along $\mathbf{c}^*$. b) The high temperature, undistorted Fermi surface. c) The low temperature, reconstructed Fermi surface. Images taken from [120, 121]

As the electronic structure is able to drive structural distortions in the CDW state, its presence is a clear indication of large electron-phonon coupling in a material. For this reason CDW materials show a clear predilection for (BCS) superconductivity, as is the case in TaS₂. However, as the CDW phase and superconducting phase compete to gap the states at the Fermi level, the CDW phase must be partially suppressed for superconductivity to occur; it can be present (in the non-CDW regions) in the NCCDW state, but does not occur in the CCDW state, where the entire sample is in a CDW phase.

Due to the common structure, and especially two-dimensionality, of IrTe₂ and the rest of the TMDs, the CDW scenario described above for TaS₂ provides an initial point of reference for understanding any structural transitions or superconductivity that may occur within its phase diagram.

4.1.2 Previous work on IrTe₂

Structural details and phase transitions

IrTe₂ possesses the same layered structure, shown in Figure 4.1, as the rest of the TMDs, at room temperature having rhombohedral spacegroup $P\bar{3}m1$ and lattice parameters $a = 3.93 \text{ \AA}$ and $c = 5.39 \text{ \AA}$. This gives IrTe₂ a c/a ratio of 1.37, considerably smaller than the values of 1.6 – 1.8 seen in other two-dimensional TMDs [122] and suggesting of greater three-dimensionality in IrTe₂. Initial characterisation measurements of IrTe₂ found a structural transition, accompanied by an increase in resistivity and decrease in paramagnetic susceptibility, to occur at $T_S = 280 \text{ K}$ [123]. A monoclinic spacegroup of $C2/m$ was suggested beneath T_S , however it was not entirely able to reproduce the low temperature powder x-ray diffraction pattern.

Both the increase in resistivity and drop in paramagnetic susceptibility are consistent with a large reduction in the density of states at the Fermi level, as was seen with the gapping of the Fermi surface in TaS₂. When electron doping (Ir_{1-x}Pd_xTe₂ [124], Ir_{1-x}Pt_xTe₂ [125]), isovalent doping (Ir_{1-x}Rh_xTe₂ [126]) and intercalation (Pd_xIrTe₂ [124], Cu_xIrTe₂ [127]) were found to suppress T_S and induce superconductivity (max $T_c = 3 \text{ K}$), there was understandable clamour to classify IrTe₂ as another of the CDW/superconducting TMDs, analogous to TaS₂.

Photoemission spectroscopy measurements below T_S find a slight modulation in the Ir 5d electrons and a drop in spectral weight associated with bond compression [128]: both features expected for a Peierls transition. However ARPES [129] and optical spectroscopy [130] measurements find no evidence of a gap opening below T_S , while NMR measurements [131] do not see the spectral changes below T_S that would be present for an evolving order parameter. These are clear indications that CDW are not present in IrTe₂. Furthermore, the drop in the density of states is relatively small (44% [130], 40% [131]) compared to the gapping seen in CDW systems, and applied pressure increases T_S and suppresses superconductivity [132], the complete opposite of the typical CDW phase diagram shown in Figure 4.2b). In fact low temperature thermal conductivity measurements of Ir_{1-x}Pt_xTe₂ are entirely consistent with nodeless, single gap, s -wave superconductivity,

conventional in nature and tangential to the structural transition [133].

In high quality single crystals, a second resistive transition can be seen at $T_R = 180$ K, shown in Figure 4.4a) [134]. However it is only present on cooling, with the state below T_R seemingly persisting up to T_S when warming the sample. Scanning tunnelling microscopy (STM) measurements are able to map the electron density on the surface of IrTe_2 – essentially the charge distribution of the Te layer, albeit without the influence of any interplane forces – to clarify the charge modulations present below T_S and the changes occurring at T_R .

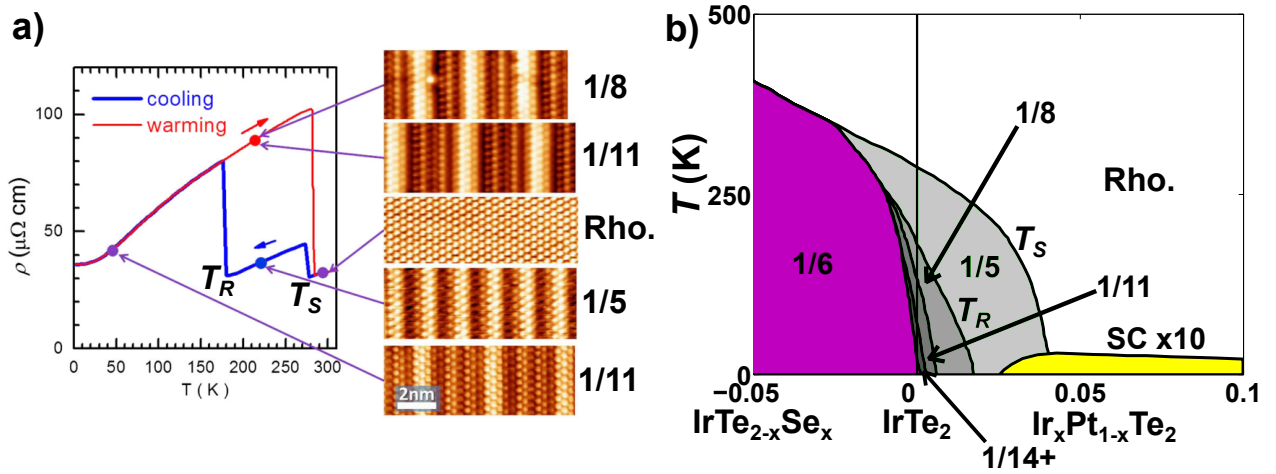


Figure 4.4: **Transitions and phase diagram of IrTe_2 .** a) Resistive transitions in IrTe_2 and corresponding surface charge modulations. Image taken from [134]. b) Phase diagram of IrTe_2 with doping, showing possible charge modulated states and superconductivity. Constructed from resistivity measurements of $\text{Ir}_x\text{Pt}_{1-x}\text{Te}_2$ [124], resistivity [122] and single crystal x-ray diffraction [135] measurements of $\text{IrTe}_{2-x}\text{Se}_x$ and STM measurements of IrTe_2 [134].

Charge modulations

Figure 4.4a), taken from [134], shows the various patterns seen on the surface of IrTe_2 . Above T_S , in the high temperature rhombohedral phase labelled as Rho., no modulation is seen. Upon cooling below T_S a striped structure forms: bright stripes, two atoms wide, of essentially unchanged electron density from the high temperature phase, separated by darker stripes, three atoms wide, where the electron density has been suppressed. This is a highly unsinusoidal charge distribution, the antipode of the modulation seen in CDW systems. As the repeating motif of this structure is five atoms wide, it is associated

with a $q_1 = 1/5$ charge modulation and labelled as such. Below T_R these bright stripes become more infrequent, and their number decreases further with cooling. This leads to innumerable possible patterns – consisting of bright stripes (two atoms wide) separated by n darker stripes (three atoms wide) – with charge modulations $q_n = (3n+2)^{-1}$. Shown in Figure 4.4a) are regions with $q_2 = 1/8$ and $q_3 = 1/11$ modulation. These higher order modulations then persist upon warming above T_R , only disappearing with the return to the unmodulated state at T_S : this explains the hysteresis seen in resistivity.

As lowering the temperature seems to favour the regions of suppressed electron density, it would seem probable that the ground state of IrTe_2 consists of $q_\infty = 1/3$. In fact, STM measurements at 4.2 K [136] find a $q_\infty = 1/6$ modulated ground state: there are slight differences in intensity profile between adjacent darker stripes. The stripes of high intensity can therefore be seen as phase slips occurring at $0, \pi$ within the modulated ground state. Doping on the Ir site suppresses the formation of these modulated states, so the lowest order $q_1 = 1/5$ modulation is favoured to lower temperatures; conversely doping on the Te site ($\text{IrTe}_{2-x}\text{Se}_x$) stabilises modulation formation, raising T_S and favouring the $q_\infty = 1/6$ state [137]. From these measurements a phase diagram can be constructed for IrTe_2 , shown in Figure 4.4b). It is important to note that although T_S and T_R are well-defined transitions, the states indicated beneath them are not mutually exclusive: until the $1/6$ modulation stabilises, many modulated states are found to coexist beneath T_R ; these states can also exist up to T_S upon warming.

Although STM measurements are able to clearly visualise the charge modulation on the surface Te layer, they are unable to probe the bulk behaviour of IrTe_2 , nor determine the mechanism causing this charge modulation. Electronic diffraction measurements find $q_1 = 1/5(10\bar{1})$ superstructure peaks below T_S in IrTe_2 [124], and $q_\infty = 1/6(10\bar{1})$ superstructure peaks below T_S in $\text{IrTe}_{2-x}\text{Se}_x$ (for $x \geq 0.3$) [122]. Therefore the lowest order, $q_1 = 1/5$, and ground state, $q_\infty = 1/6$, modulations both exist in the bulk, with a staircase ordering in the direction $(10\bar{1})$.

Dimerisation

Single crystal x-ray diffraction at 220 K is able to completely resolve the $q_1 = 1/5$ modulated structure, finding a triclinic $P\bar{1}$ structure [138] (the same unit cell is also reported at 270 K [139]), not the monoclinic $C2/m$ structure first reported. In this structure 1/5 of the Ir-Ir (and Te-Te) bonds are shortened, forming stripes of dimers within the lattice planes that form a staircase arrangement throughout the structure: this is the origin of the $q_1 = 1/5(\bar{1}01)$ structural modulation. Single crystal x-ray diffraction on $\text{IrTe}_{2-x}\text{Se}_x$ finds the formation of similar dimers, giving rise to the $q_\infty = 1/6(\bar{1}01)$ modulation [135].

The intermediate modulated states – such as the $q_2 = 1/8$ and $q_3 = 1/11$ modulations, readily apparent on the surface Te layers in STM measurements – are harder to achieve in the bulk crystal. Thermal cycling is able to achieve regions of these $q_{n>1}$ states below T_R in IrTe_2 , but the q_1 state still dominates much of the volume fraction [135]. Matters are further complicated by the low symmetry of the modulated states, which leads to the possibility of many domains forming below T_S . Slow cooling through the transition is in part able to counteract this [140].

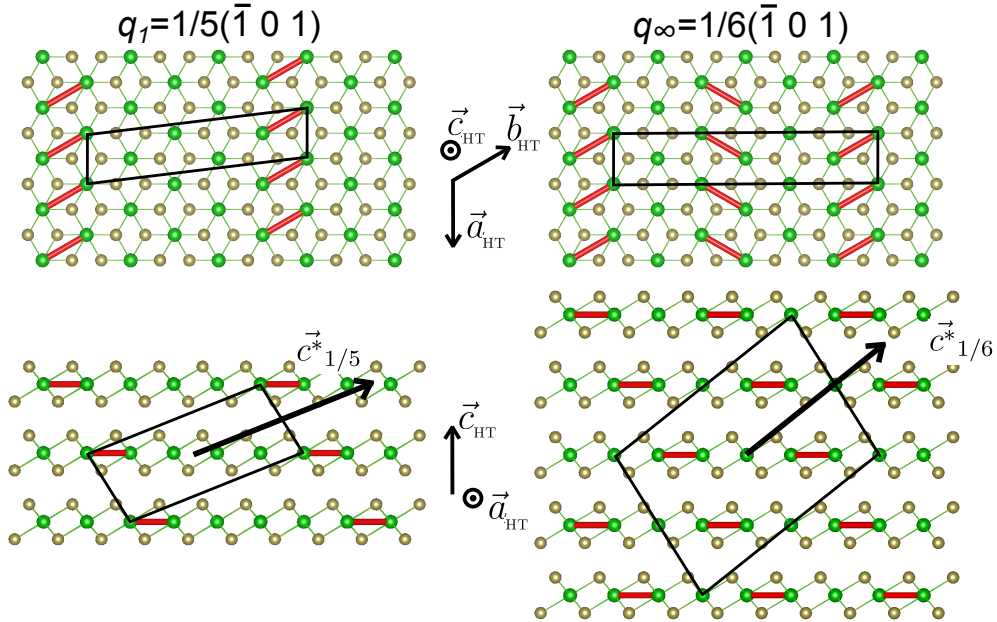


Figure 4.5: **Dimerised structure of IrTe_2** for the $q_1 = 1/5(\bar{1}01)$ and $q_\infty = 1/6(\bar{1}01)$ modulated structures. Dimerised Ir-Ir bonds are marked in red for projections in (top) and perpendicular to (bottom) the lattice planes. Unit cells are outlined in black for projections with the axis of electronic two dimensionality, $\mathbf{c}^*$, indicated; high temperature, rhombohedral axes are shown. Structures taken from [135].

Figure 4.5 shows the dimerised structures of the q_1 and q_∞ modulations, with the respective unit cells outlined. The dimerised Ir-Ir bonds are found to shorten by 20 – 23%, compared to 10 – 17% in the associated Te-Te bonds [138]. In agreement with this, optical spectroscopy [141] and x-ray absorption fine structure measurements [142] observe changes to the Ir-Ir and Ir-Te bonds below T_S , but not to the Te-Te bonds themselves; similarly resonant elastic x-ray scattering finds a Te 5*p*-Ir 5*d* covalent state beneath T_S , helping the Ir-Ir dimers stabilise the modulation in the Te layers [140].

Therefore the formation of Ir-Ir dimers – with 1/5 of adjacent bonds dimerised – causes the structural transition at T_S , and leads to the $q_1 = 1/5(\bar{1} 0 1)$ charge modulation. Below T_R these dimers become more prevalent, tending to a ground state of $q_\infty = 1/6(\bar{1} 0 1)$ – with 1/3 of adjacent bonds dimerised – as $T \rightarrow 0$. DFT calculations find the q_1 modulated state to have lower energy than the room temperature rhombohedral structure [143], and no dimer density greater than the q_∞ structure to be energetically stable [135], in good agreement with the experimental structures.

Changes in dimensionality

As a result of the staircase arrangement of the dimers, the modulated phases have a strange dimensionality: $\mathbf{c}^*$ is no longer perpendicular to the lattice planes. This is shown for the q_1 and q_∞ modulated states in Figure 4.5. If the electronic structure possesses the same dimensionality as the unit cell, this could lead to a strange situation where the electronic properties of the material are two dimensional, but tilted at an angle to the lattice planes. The phase diagram of IrTe₂ could therefore allow for the switching of conduction planes with strain (analogous to doping) or temperature. Similarly, as the q_1 modulated phase is centrosymmetric (spacegroup $P\bar{1}$) and the q_2 modulated phase is not (spacegroup $C2$), the spin polarisation of the bands (which occurs via spin orbit coupling only in non-centrosymmetric structures) can be switched on or off, potentially of use for spintronic applications [135]. Confirmation of the low temperature electronic structure of IrTe₂ is therefore necessary to determine whether or not this strange dimensionality exists.

ARPES measurements above T_S agree well with DFT, finding a distorted cylindrical Fermi surface with a relatively strong k_z dependence, due to IrTe_2 's smaller c/a ratio; however below T_S no clear features can be discerned [129, 144]. This is somewhat to be expected: ARPES is only able to probe the surface of the material, which STM studies found to consist of multiple small regions of different modulated phases and domains. Many of these phases will be present within the spot size measured, so the resulting dispersions will not be particularly coherent. Furthermore ARPES has poor resolution in the direction normal to the surface of the material, integrating over a range of values that depend on the incident photon energy. This is not a problem above T_S – the two dimensionality of the electronic structure is perpendicular to the lattice planes – but the tilted unit cells of the modulated phases will result in the significant blurring of any features.

Quantum oscillations, as a precise measurement of the extremal Fermi surfaces areas of the bulk of a material, will not suffer from the surface and resolution issues that affect ARPES. However, they are only able to detect closed orbits: any one dimensional parts of the Fermi surface will not be visible. Instead angle-dependent magnetoresistance oscillations (AMRO), also a measure of the bulk Fermi surface, can be used to look for these one dimensional features. Combined, these two techniques should be able to determine the electronic structure within the modulated state(s) of IrTe_2 .

4.2 Torque magnetometry

Experimental details

The IrTe_2 single crystals used in this study were provided by Shigeru Kasahara of Kyoto University, using the Te flux method [145]. Two platelike, approximately hexagonal samples were successfully measured with torque magnetometry: sample 1 (S1), $\sim 200 \times 200 \times 50 \mu\text{m}$; and sample 2 (S2), $\sim 100 \times 100 \times 10 \mu\text{m}$. Single crystal x-ray diffraction measurements were conducted on these samples using an Oxford Diffraction SuperNova, fitted with liquid nitrogen open-flow cooling; these results were used to orient the samples

for torque magnetisation measurements.

Torque measurements for both samples were performed in DC fields up to 14 T in a PPMS, 18 T in a 21 T superconducting magnet; S1 was also measured up to 33 T at HFML, Nijmegen. Samples were mounted on a single axis rotator to allow discrete rotation between field sweeps, and, in the case of the PPMS, continuous rotation in constant field. DFT calculations were conducted using Wien2k [13] with the GGA form of the exchange-correlation energy and spin-orbit coupling included. To calculate the quantum oscillation frequencies expected from the low symmetry $P\bar{1}$ structure, the supercell k-space extremal area finder (SKEAF) algorithm [35] was used.

4.2.1 Low temperature characterisation

Single crystal x-ray diffraction

Due to the array of possible states that can exist beneath T_S in IrTe₂, clarifying the samples' behaviour at low temperatures will help determine the possible phases and domains that may be present. Because of the small size of the torque samples, transport measurements were not performed – contacts would be difficult to place and even harder to remove without damaging the crystal – however low temperature single crystal x-ray diffraction, and torque measurements themselves, can provide some indications of the states forming below T_S . In all cases samples were cooled slowly through T_S to limit domain formation [140], with no thermal cycling so that the $q_1 = 1/5$ modulated state persists in much of the sample to low temperatures [135].

Figure 4.6 shows single crystal x-ray diffraction patterns measured above and below T_S for both torque samples. In both cases the high temperature patterns are completely fitted by the rhombohedral $P\bar{3}m1$ structure; based upon these rhombohedral lattice vectors the $0kl$, $h0l$ and $hk0$ patterns are shown. The same patterns, still defined using the rhombohedral lattice vectors, are also shown for measurements below T_S . Beginning with S1, clear superstructure peaks are seen between the high temperature peaks in the $0kl$ and $h0l$ planes. The zoomed in regions show this superstructure clearly: there are four additional peaks between each adjacent pair of high temperature peaks, seen clearly in the

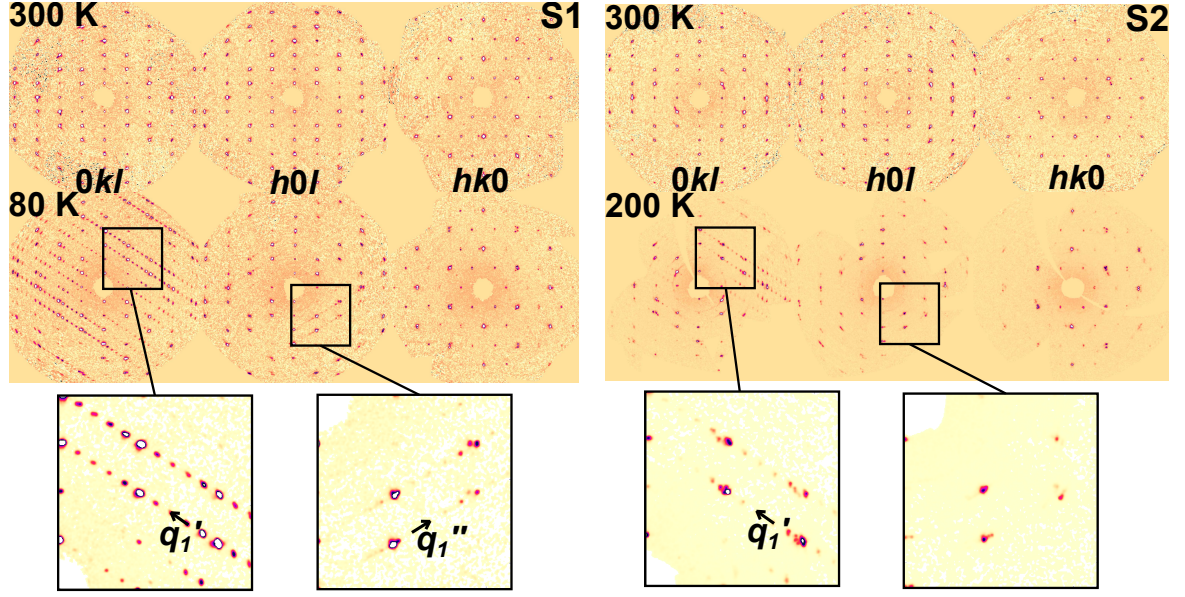


Figure 4.6: **Single crystal x-ray diffraction patterns of IrTe₂** above and below T_S . Zoomed regions show clearly the presence of superlattice peaks associated with charge modulation vectors $q_1' = 1/5(0\bar{1}1)$ and $q_1'' = 1/5(101)$.

$(0\bar{1}1)$ direction in $0kl$ and more weakly in the (101) direction in $h0l$. This is indicative of two domains of the $q_1 = 1/5(\bar{1}01)$ structure, with the q_1' domain dominating. In the considerably smaller S2, only weak peaks of the q_1' domain are seen: only one domain, of the $q_1 = 1/5$ modulation, appears to be formed upon cooling. Neither sample shows evidence of any significant regions of modulations larger than q_1 , though only S1 was measured at temperatures beneath T_R where higher order modulations may be present.

Rotations in constant field

With continuous rotation in a constant applied field, torque magnetometry is able to measure the magnetic susceptibility anisotropy of a sample. From Equation 1.49 the torque of a two-dimensional system, rotated in the a - c plane (i.e. in the plane containing $\mathbf{a}$ and $\mathbf{c}$ of the high temperature, unmodulated structure), is given by:

$$\tau = \frac{1}{2\mu_0} B^2 (\chi_c - \chi_a) \sin(2\theta - \phi_0) \quad (4.1)$$

where χ_i is the magnetic susceptibility along crystallographic axis i , θ is the angle between $\mathbf{B}$ and the normal to the lever, and ϕ_0 is a phase. Due to the weight of the sample on

the lever there will also be a gravitational term which varies as $\sin(\theta)$, but in the case of IrTe_2 this term is small – the $\sin(2\theta)$ dependence of the magnetic susceptibility anisotropy dominates the signal. Assuming the crystal is placed face down (or up) on the lever, such that the lever and lattice planes are parallel, then for a normal two-dimensional system where $\mathbf{c}$ is normal to the lattice planes, θ is the angle between $\mathbf{H}$ and $\mathbf{c}$ and hence $\phi_0 \simeq 0$. For a rotation in the a - b plane Equation 4.1 is still applicable, but with χ_{b^*} replacing χ_c . To measure in this orientation the crystal is placed on its side upon the lever, balanced (precariously) on its widest, most stable edge; this edge may not necessarily be perpendicular to a crystallographic axis, so for a - b rotations ϕ_0 takes an arbitrary value.

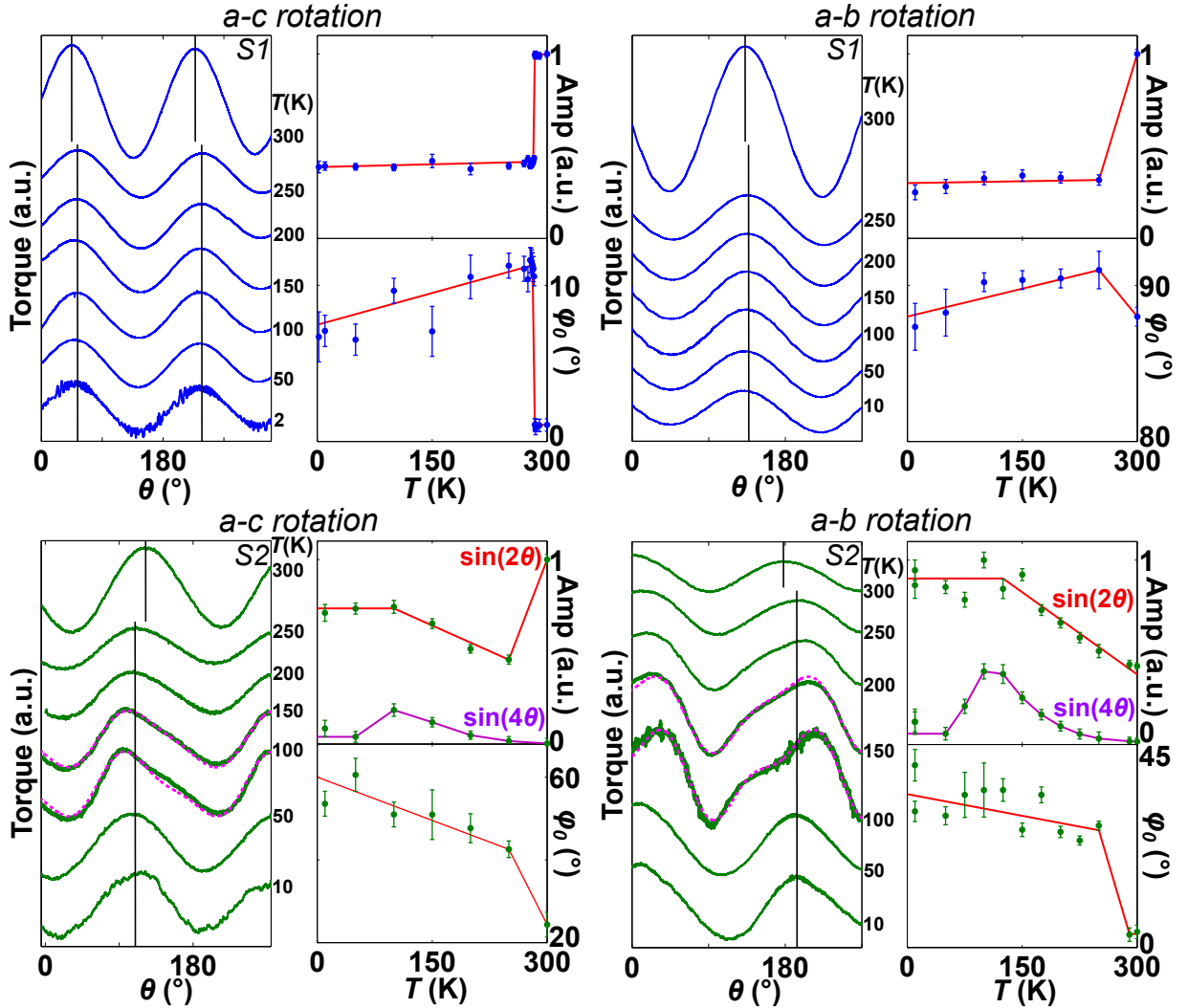


Figure 4.7: **Angular dependence of torque in IrTe_2** for a - c and a - b rotations of samples S1 and S2 at various temperatures, conducted in a constant field of 10 T. Shown alongside is the temperature dependence of the amplitudes and phases obtained from sinusoidal fits. Dashed magenta lines show fits with a significant $\sin(4\theta)$ term, black lines indicate the phase shift at T_S .

For Equation 4.1 to hold true, the rotation must be conducted within the plane containing the relevant lattice vectors. In the high temperature phase this will be the case: $\mathbf{a}$ and $\mathbf{b}^*$ are within the planes of the lattice and $\mathbf{c}$ is normal to them. However, in the modulated states below T_S the lattice vectors are tilted away from the planes of the lattice, and so are no longer contained within the planes of rotation. This is a rather less straightforward case: χ_a , χ_{b^*} and χ_c will all contribute to the torque signal, whose exact shape will depend upon the orientation of the lattice vectors with respect to the rotation plane [146]. Precisely fitting this would require knowledge of the exact modulations and domains formed with each cooldown. However there are some general features that are indicative of a change in the lattice vectors: the tilted two-dimensionality will change the value of ϕ_0 ; and a rotation plane at an angle to the lattice vectors will lead to a periodic distortion of the $\sin(2\theta)$ dependence [146].

Figure 4.7 shows the angular dependence of torque – measured at 10 T over a range of temperatures – for a - c and a - b rotations of S1 and S2, plotted along the amplitudes and phases extracted from sinusoidal fits. A clear transition is seen at $T_S = 283$ K in amplitude, along with the phase shift associated with the change of lattice vectors. Beneath T_S the phase is observed to change further, at a much slower, steadier rate; this may be linked to the stabilisation of a domain structure associated with the modulated states. For the a - b rotations a broad range of phase shifts are possible: the angle between $\mathbf{b}_{\text{HT}}^*$ and $\mathbf{b}_{1/5}^*$ is domain dependent, and $\mathbf{c}_{1/5}$ – no longer perpendicular to the plane of rotation below T_S – will also contribute to the anisotropy. However for the a - c rotations $\mathbf{c}_{1/5}$ is rotated 31° from $\mathbf{c}_{\text{HT}}$ for all domains [138]. For the phase shift, $\Delta\phi_{ac}$, to take this value $\mathbf{c}_{1/5}$ would have to lie within the plane of rotation, otherwise a smaller value – the angle between $\mathbf{c}_{\text{HT}}$ and the projection of $\mathbf{c}_{1/5}$ onto the plane of rotation – is observed. This is the case for S1 ($\Delta\phi_{ac} = 10^\circ$) and S2 ($\Delta\phi_{ac} = 19^\circ$).

The drop in amplitude below T_S corresponds to a significant decrease in the magnetic susceptibility anisotropy. Although the unit cell is tilted below T_S , the electronic structure is still predicted to be broadly two dimensional [138], so a drastic change in the ratio χ_c/χ_a or χ_c/χ_{b^*} is not expected. However a drop is also reported in magnetisation [123], and as

IrTe₂ is a (weakly) paramagnetic metal, its magnetic susceptibility is proportional to the density of states at the Fermi level [1]. NMR [131] and specific heat [130] measurements find drops in the density of states below T_S of 40 % and 44 % respectively, comparable to the decreases seen in the amplitude of the a - c rotations of 40 % for S1 and 46 % for S2. The amplitude of the a - b rotations will also be affected by the drop in the density of states, but the addition of a χ_c dependence below T_S will also have a significant effect on the anisotropy. This will be strongly dependent on the domains formed (which determine the orientation of $c_{1/5}$), and so there is substantial variation seen in the amplitude change: S1 shows a 31 % drop, while S2 actually increases below T_S .

Both above and below T_S S1 is well fitted by Equation 4.1, as is S2 for both the high and low end of the temperature range measured. Between 200 K and 50 K however, the $\sin(2\theta)$ dependence of S2 is clearly distorted. This distortion is well fitted by the next highest order sinusoidal term, $\sin(4\theta)$. Therefore the amplitude of the $\sin(4\theta)$ term, as plotted in Figure 4.7, can track the temperature dependence of the distortion: it begins to develop around $T_R = 180$ K, is strongest at 100 K and disappears by 50 K. STM measurements found T_R to be associated with the onset of higher order, $q_{n>1}$ modulations on the surface of IrTe₂ [134], so as S2 is considerably thinner than S1 these surface effects will have a larger contribution to its total magnetisation. However there is no reason to expect that a $q_{n>1}$ modulation would lead to distortion if a q_1 modulation does not; furthermore the number of $q_{n>1}$ modulations increases as $T \rightarrow 0$, while the distortion disappears below 50 K.

Instead the distortion seen in S2 is likely linked to the formation of domains of the $q_1 = 1/5$ modulated structure in the bulk. A periodically distorted $\sin(2\theta)$ dependence of the magnetic susceptibility is expected if the rotation plane does not pass through the lattice vectors [146], however the form of the distortions will vary for different domains of the sample. Any combination of $\sin(2\theta)$ terms will sum (constructively or destructively) to form a $\sin(2\theta)$ term, but over multiple domains the distortions may cancel out: S1, which x-ray measurements found to form two domains of the q_1 modulation at 80 K, shows no distortions beneath T_S ; S2, found to form one domain at 200 K, clearly does.

Therefore the onset of the $\sin(4\theta)$ term may indicate changes in the domain structure around T_R . Both the $\sin(2\theta)$ and $\sin(4\theta)$ terms increase to a maximum by 100 K, beyond which the amplitude of the $\sin(2\theta)$ term – and hence the magnetic susceptibility – is unchanged, and hence the low temperature domain structure has presumably stabilised.

4.2.2 de Haas-van Alphen oscillations

Angular dependence of oscillations

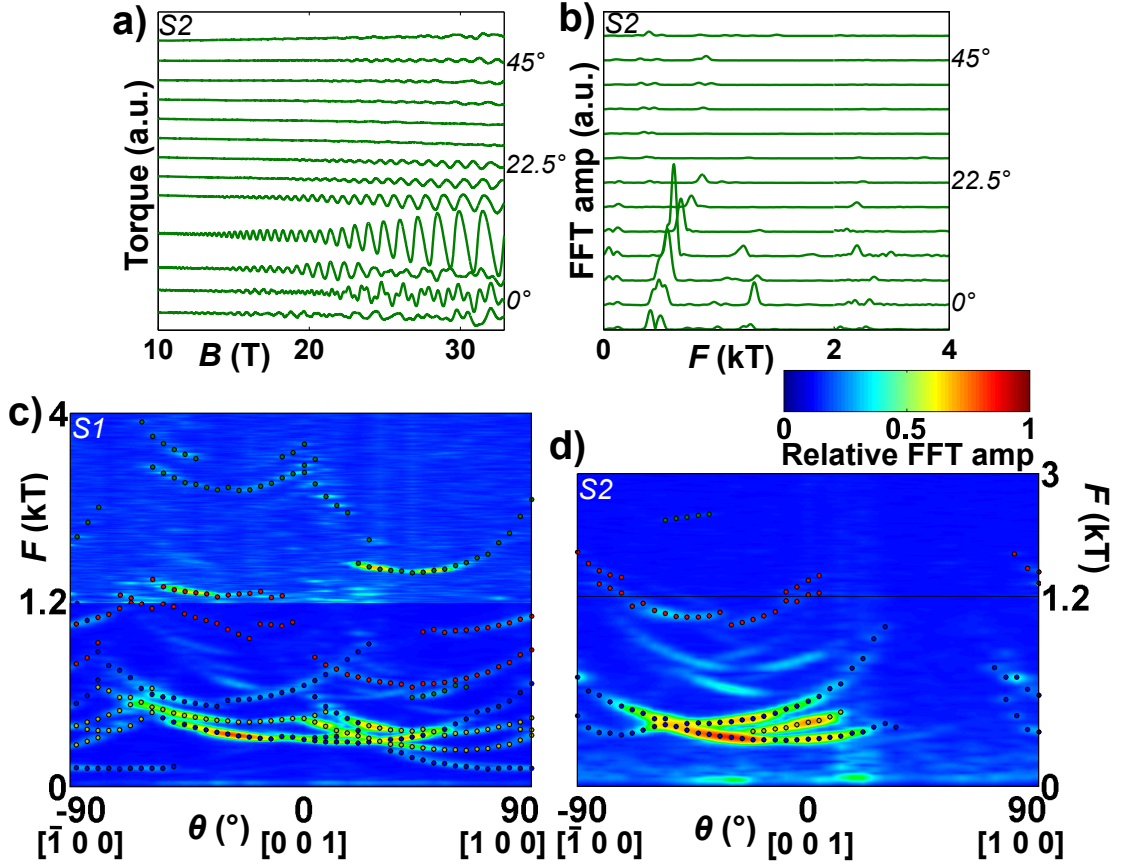


Figure 4.8: **Angular dependence of de Haas-van Alphen oscillations in IrTe₂.** **a)** Torque measurements conducted at 320 mK on S2, between $\mathbf{B} \parallel [001]$ ($\theta = 0^\circ$) and $\mathbf{B} \parallel [110]$ ($\theta = 45^\circ$). **b)** Fourier transforms of the torque signal, with a 3rd-order polynomial subtracted; a field window of 5 – 33 T is used up to a frequency of 2 kT and 20 – 33 T above. Angular dependence of the Fourier spectrum for **c)** S1 and **d)** S2 at 1.4 K, in the range $\mathbf{B} \parallel [\bar{1}00] \rightarrow \mathbf{B} \parallel [001] \rightarrow \mathbf{B} \parallel [100]$, using a field window of 8 – 18 T.

Both torque samples measured showed strong de Haas-van Alphen oscillations at relatively low fields, clearly visible against a weak paramagnetic background. Figure 4.8a) shows these oscillations in S2, measured at 320 mK up to 33 T; the corresponding

Fourier transforms are shown in Figure 4.8b). Multiple frequencies are seen in the range $0.1 - 4$ kT, but diminish in amplitude at higher angles and all but disappear by $\theta = 45^\circ$. The full angular dependence of the frequencies of S2 is shown in Figure 4.8d), alongside the same angular dependence measured for S1 in Figure 4.8c)¹; extracted frequencies are plotted on top of the data, so regions of high intensity without a scatter point correspond to 2nd harmonics. At $\theta = 0^\circ$ the magnetic field is perpendicular to the lattice planes ($\mathbf{B} \parallel [001]$ of the high temperature structure), while at $\theta = \pm 90^\circ$ the magnetic field lies within the lattice planes ($\mathbf{B} \parallel [100]$, $\mathbf{B} \parallel [\bar{1}00]$).

For a layered metal with a two-dimensional electronic structure, the Fermi surface usually consists of a number of distorted cylinders centred along $\mathbf{c}^*$, the normal to the lattice planes; as seen in the introduction, this is the case for the majority of the other TMDs. The frequencies associated with these cylinders have a minimum at $\mathbf{B} \parallel [001]$, increasing in size as the field rotates towards the lattice planes before eventually disappearing [147]. From Figure 4.8c) and d) this is clearly not the case in IrTe₂: there are frequency branches across the angular range, none of which have minima close to $\mathbf{B} \parallel [001]$. Furthermore the frequency spectrum is not symmetric around $\mathbf{B} \parallel [001]$, but is periodic over 180° : the symmetry of the observed electronic structure is significantly reduced from the high temperature case, but still retains inversion symmetry; this agrees with the $P\bar{1}$ structure expected for the $q_1 = 1/5$ modulated case, but not the noncentrosymmetric $C2$ structure of the $q_2 = 1/8$ modulated structure [135]. However many of the frequency branches still appear quasi-two-dimensional, taking a $\sim 1/\cos\theta$ form around a common minimum angle, with diminishing and eventually disappearing amplitude with rotation away. S1 appears to have two sets of these quasi-two-dimensional frequency branches, centered around $\theta \sim -30^\circ$ and $\theta \sim 45^\circ$; S2 only has the former, with frequency values in reasonable agreement with S1. This qualitative appraisal of the frequency spectrum is in agreement with the x-ray and torque characterisation measurements of S1 and S2: both appear to form the $q_1 = 1/5$ modulated structure at low temperatures, with S1 possessing

¹These measurements were performed at 1.4 K up to 18 T, rather than the 0.32 K, 33 T of Figure 4.8a) and b). This is because it was possible to measure a far larger, finer angular range at these lower fields, and no frequencies are seen by 33 T that are not already clear by 18 T.

two domains and S2 only one.

Temperature dependence of oscillations

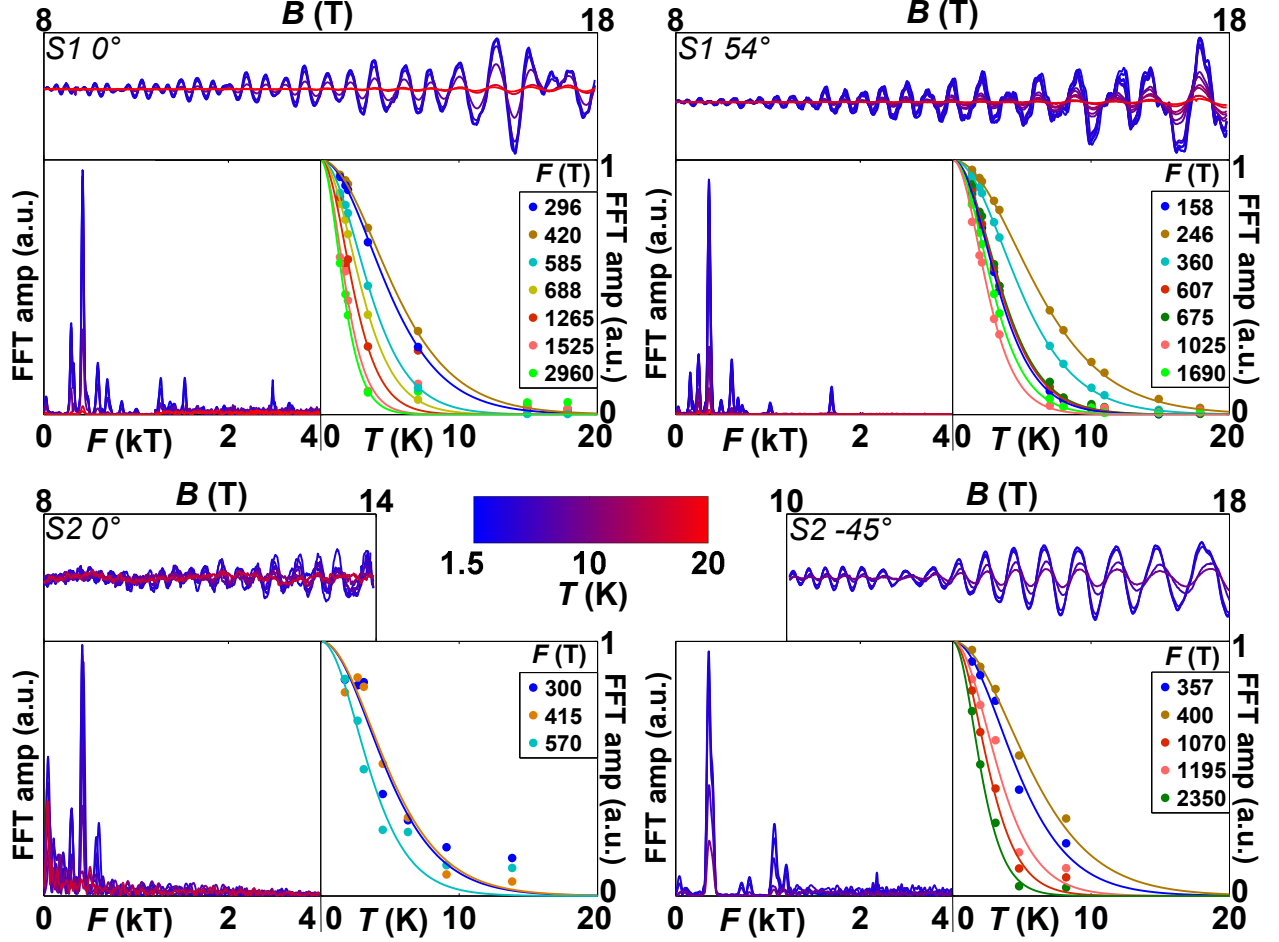


Figure 4.9: Temperature dependence of de Haas-van Alphen oscillations in IrTe_2 . Shown at orientations within the range $\mathbf{B} \parallel [\bar{1}00] \rightarrow \mathbf{B} \parallel [001] \rightarrow \mathbf{B} \parallel [100]$ for S1 and S2 is: (top panel) the oscillatory component of the torque signal at temperatures in the range 1.4–20 K, coloured by temperature; (bottom left panel) Fourier transforms of the oscillatory component, again coloured by temperature; (bottom right panel) Lifshitz-Kosevich fits to the temperature dependence of the FFT amplitudes, scaled by the fitted intercept at $T = 0$ K

Figure 4.9 shows the temperature dependence of the dHvA oscillations in IrTe_2 , alongside Fourier transforms and Lifshitz-Kosevich fits to extract the effective masses (whose values are given in Table 4.1). The temperature dependences of S2 were measured over a smaller field range than S1, so not all the frequencies seen in the angular dependence are visible; however comparing the visible frequencies at the common angle of $\theta = 0^\circ$, the masses found for both samples are in good agreement. The values found are small – between

$0.2 - 1.2 m_e$ – indicating a lack of strong correlations and a Fermi surface that should be well described by DFT. Therefore, by comparison with the calculated Fermi surfaces of the proposed low temperature structures, the dHvA oscillations should be able to clearly ascertain the low temperature electronic structure of IrTe₂, at least for the $q_1 = 1/5$ modulated state that x-ray measurements found to exist in both samples below T_S .

S1		$\theta = 0^\circ$				$\theta = 54^\circ$			
		Exp.		DFT		Exp.		DFT	
Band		F (T)	m^* (m_e)	F (T)	m_b (m_e)	F (T)	m^* (m_e)	F (T)	m_b (m_e)
1		296(5)	0.34(1)	318	0.27	158(5)	0.50(1)	194	0.33
1		585(5)	0.47(1)	655	0.59	360(5)	0.34(1)	461	0.34
2		1265(10)	0.7(1)	1305	0.73	607(5)	0.48(1)	640	0.55
2		1525(10)	0.9(1)	1426	0.88	1025(10)	0.66(2)	1032	0.58
3		2960(10)	1.0(1)	2705	0.77	675(5)	0.47(1)	658	0.58
3		-	-	2911	1.20	1690(10)	0.57(1)	1742	0.53
4		420(5)	0.31(1)	508	0.29	246(5)	0.27(1)	354	0.27
4		688(5)	0.56(1)	667	0.42	-	-	523	0.38
S2		$\theta = 0^\circ$				$\theta = -45^\circ$			
		Exp.		DFT		Exp.		DFT	
Band		F (T)	m^* (m_e)	F (T)	m_b (m_e)	F (T)	m^* (m_e)	F (T)	m_b (m_e)
1		300(5)	0.32(5)	318	0.27	357(5)	0.41(3)	391	0.37
1		570(10)	0.43(6)	655	0.59	-	-	437	0.74
2		1230(10)	-	1305	0.73	1070(10)	0.73(6)	1127	0.55
2		1435(10)	-	1426	0.88	1195(10)	0.58(8)	1501	1.06
3		2840(10)	-	2705	0.77	2350(20)	1.15(7)	2450	0.75
3		-	-	2911	1.20				
4		415(10)	0.31(3)	508	0.29	400(10)	0.34(2)	515	0.32
4		-	-	667	0.42	-	-	573	0.41

Table 4.1: **Frequencies and effective masses of de Haas-van Alphen oscillations observed in IrTe₂**, compared with values from density functional theory calculations for the triclinic $q_1 = 1/5$ modulated structure. S1 is compared to calculations for D1 and D3, S2 is compared to calculations for D1 only.

4.2.3 Density functional theory calculations

Calculated Fermi surfaces

DFT calculations were conducted for three possible structures of IrTe_2 : the rhombohedral $P\bar{3}m1$ structure of the unmodulated state above T_S ; the monoclinic $C2/m$ structure initially proposed to exist below T_S ; and the $P\bar{1}$ structure of the $q_1 = 1/5$ modulated state². The lattice parameters for these calculations were taken from [123, 138].

Rhombohedral $P\bar{3}m1$

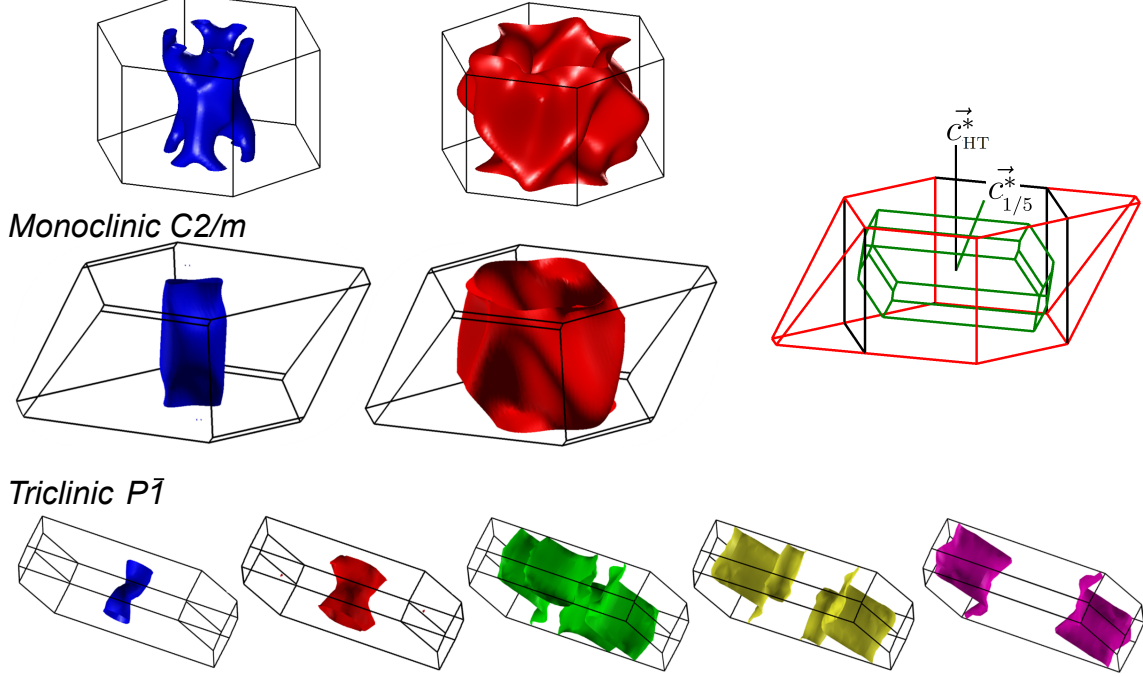


Figure 4.10: **Density functional theory calculations for IrTe_2** . Shown to scale are the Fermi surfaces calculated for the rhombohedral, monoclinic and triclinic structures, along with their superimposed Brillouin zones in black, red and green respectively.

Figure 4.10 shows the Fermi surfaces produced by these calculations, which are in agreement with previous work [130, 138]. The high temperature Fermi surface, of the unmodulated, rhombohedral phase, consists of two bands: an inner band (in blue) that shows a strong k_z dependence, with six boughs emerging plumb from a barrel centred on Γ ; and a more two-dimensional outer band (in red) in the form of a distorted cylinder. Compared to many other metallic TMDs, this Fermi surface is considerably more three

²Calculating the rhombohedral and monoclinic Fermi surfaces may seem something of a fool's errand, as these structures do not exist below T_S . However much of this work was done before the $P\bar{1}$ structure was determined, so at the time of these calculations the low temperature structure was unknown.

dimensional – a result of the smaller c/a ratio found in IrTe₂ – but there is still a broad two-dimensionality along $\mathbf{c}_{\text{HT}}^*$, normal to the lattice planes. ARPES measurements conducted above T_S , although inhibited by the three dimensionality of the inner band, are in good agreement with this Fermi surface [128, 144].

For the monoclinic structure the Fermi surface³ is much more two dimensional: the inner band (blue) now forms a flattened cylinder; while the outer (red) band, still cylindrical, is considerably less distorted. Although the Fermi surface is of a similar size to the rhombohedral case, the greater two-dimensionality results in a considerable reduction in the total area; this corresponds to a $\sim 40\%$ drop in the density of states at the Fermi level, in agreement with the measured value. However, as the two dimensionality of this Fermi surface is still along $\mathbf{c}_{\text{HT}}^*$, it should be straightforward to measure with ARPES: the k_z dependence is significantly reduced compared to the rhombohedral Fermi surface, so the features should be much clearer. The fact that this is not the case below T_S is a good indicator that the monoclinic structure does not form in IrTe₂.

The reconstructed Fermi surface predicted by the triclinic structure of the $q_1 = 1/5$ modulated phase is substantially different to that of the higher symmetry structures, in both size and shape. Five bands now cross the Fermi level, producing significantly smaller Fermi surfaces in a significantly smaller Brillouin zone, while $\mathbf{c}_{1/5}^*$ is now at an angle (31° to be exact) to $\mathbf{c}_{\text{HT}}^*$ and so is no longer perpendicular to the lattice planes. Both one- and two-dimensional features are present: distorted hole cylinders at the centre of the Brillouin zone in bands 1 (blue) and 2 (red); distorted electron cylinders at the edge of the Brillouin zone in bands 3 (green) and 4 (ochre); distorted sheets at the edge of the Brillouin zone in bands 3, 4 and 5 (magenta). The dimensionality of all these features is along $\mathbf{c}_{1/5}^*$, and so significantly tilted away from the lattice planes of the crystal. Although the Fermi surface is considerably reduced in size, the greater number of bands means that the reduction in the density of states at the Fermi level is $\sim 35\%$, close to the value for

³To calculate the Fermi surface of the monoclinic structure, the lattice parameters and atomic positions had to be converted from the $C2/m$ setting, which is not supported by Wien2k, to $B2/m$. For B -base-centred structures a reduced Bravais matrix is used [13], so the monoclinic Fermi surface in Figure 4.10 is plotted in a non-primitive Brillouin zone. This is why it is larger than the rhombohedral Brillouin zone, despite having a larger unit cell.

the monoclinic structure as well as that determined experimentally.

Domains

Domain	Monoclinic $C2/m$			Triclinic $P\bar{1}$		
	$\mathbf{a}_m$	$\mathbf{b}_m$	$\mathbf{c}_m$	$\mathbf{a}_{1/5}$	$\mathbf{b}_{1/5}$	$\mathbf{c}_{1/5}$
D1	$-\mathbf{a}_{\text{HT}} - 2\mathbf{b}_{\text{HT}}$	$\mathbf{a}_{\text{HT}}$	$\mathbf{c}_{\text{HT}}$	$\mathbf{a}_{\text{HT}}$	$\mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$	$-2\mathbf{a}_{\text{HT}} - 4\mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$
D2	$2\mathbf{a}_{\text{HT}} + \mathbf{b}_{\text{HT}}$	$\mathbf{b}_{\text{HT}}$	$\mathbf{c}_{\text{HT}}$	$\mathbf{a}_{\text{HT}}$	$\mathbf{b}_{\text{HT}} - \mathbf{c}_{\text{HT}}$	$2\mathbf{a}_{\text{HT}} + 4\mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$
D3	$\mathbf{b}_{\text{HT}} - \mathbf{a}_{\text{HT}}$	$-\mathbf{a}_{\text{HT}} - \mathbf{b}_{\text{HT}}$	$\mathbf{c}_{\text{HT}}$	$\mathbf{b}_{\text{HT}}$	$-\mathbf{a}_{\text{HT}} - \mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$	$4\mathbf{a}_{\text{HT}} + 2\mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$
D4				$\mathbf{b}_{\text{HT}}$	$-\mathbf{a}_{\text{HT}} - \mathbf{b}_{\text{HT}} - \mathbf{c}_{\text{HT}}$	$-4\mathbf{a}_{\text{HT}} - 2\mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$
D5				$-\mathbf{a}_{\text{HT}} - \mathbf{b}_{\text{HT}}$	$\mathbf{a}_{\text{HT}} + \mathbf{c}_{\text{HT}}$	$-2\mathbf{a}_{\text{HT}} + 2\mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$
D6				$-\mathbf{a}_{\text{HT}} - \mathbf{b}_{\text{HT}}$	$\mathbf{a}_{\text{HT}} - \mathbf{c}_{\text{HT}}$	$2\mathbf{a}_{\text{HT}} - 2\mathbf{b}_{\text{HT}} + \mathbf{c}_{\text{HT}}$

Table 4.2: **Possible domains for the low symmetry structures of IrTe_2** , given in terms of the lattice vectors of the high temperature, rhombohedral structure.

To directly compare these Fermi surfaces to the observed dHvA oscillations, the frequencies they produce over the measured angular range can be calculated. For the rhombohedral structure this is trivial – the orientations of the samples are defined with respect to the rhombohedral lattice vectors – however for the lower symmetry structures the measured angular range no longer corresponds to a plane defined by lattice vectors (or other high symmetry directions). Furthermore, as both the monoclinic and triclinic structures are of reduced symmetry, a number of differently oriented domains are possible. The high temperature $P\bar{3}m1$ spacegroup has 12 equivalent positions, while the monoclinic $C2/m$ structure has 4 and the triclinic $P\bar{1}$ structure has 2. Therefore there are $12/4 = 3$ possible domains of the monoclinic structure and $12/2 = 6$ possible domains of the triclinic structure. The lattice vectors of these domains, given in terms of the lattice vectors of the rhombohedral structure, are listed in Table 4.2.

Angular dependence of frequencies

Figure 4.11 shows the extracted frequencies of S1, alongside the frequencies calculated over the measured angular range for the rhombohedral structure, the three domains of the monoclinic structure and the six domains of the triclinic structure. Beneath each calculation the corresponding Brillouin zone is shown, along with the vectors defining the plane of rotation ($\mathbf{a}_{\text{HT}}$, $\mathbf{c}_{\text{HT}}^*$) and the high temperature Brillouin zone (both in black).

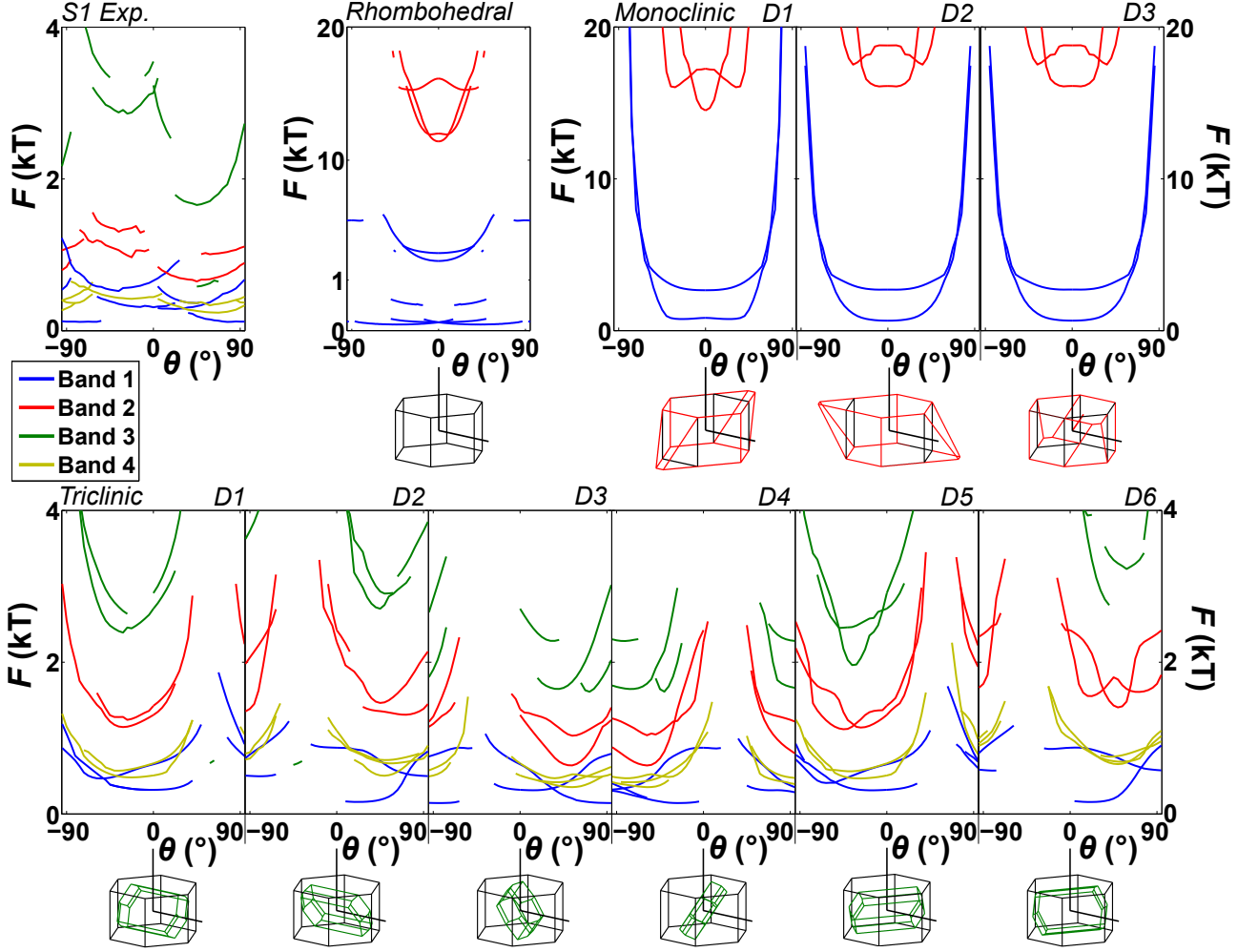


Figure 4.11: **Angular dependence of frequencies in IrTe_2** , from de Haas-van Alphen oscillations and density functional theory calculations. Shown are the experimental frequencies of S1 alongside the calculated frequencies for every possible domain of the rhombohedral, monoclinic and triclinic structures. Beneath each panel the Brillouin zone of the respective domain is shown (in red/green) on top of the high temperature Brillouin zone and the lattice vectors ($\mathbf{a}_{\text{HT}}$, $\mathbf{c}_{\text{HT}}^*$) (in black) that define the plane of rotation.

Beginning with the rhombohedral structure, only the inner (blue) band produces frequencies of comparable size to those measured, with all frequencies from the outer (red) band in excess of 10 kT. However, as the plane of rotation passes through the axis of two-dimensionality ($\mathbf{c}_{\text{HT}}^*$) of this structure, there is a clear minima at $\theta = 0^\circ$ with the frequency spectrum symmetric either side. This is in clear contrast to the measured spectrum of S1 – which has minima away from 0° and no symmetry around $\mathbf{c}_{\text{HT}}^*$ – so, as expected, the rhombohedral, unmodulated structure does not persist to low temperatures in IrTe_2 .

The three domains of the monoclinic structure all produce very similar frequency

spectra; indeed D2 and D3 are actually equivalent within the chosen plane of rotation. Although the symmetry has been reduced from the rhombohedral structure, the Fermi surfaces are broadly similar and $\mathbf{c}_{\text{HT}}^*$ is still the axis of two dimensionality. Therefore the minima at and symmetry around $\theta = 0^\circ$ is still present, but the greater two-dimensionality of the inner band means it produces a considerably simpler low frequency spectrum. As before none of these features are seen in the measured spectrum, so the monoclinic structure does not form beneath T_S – in agreement with recent x-ray studies [138, 139] that find no evidence for the low temperature monoclinic structure initially proposed [123].

For the triclinic structure the plane of rotation no longer contains the axis of two-dimensionality, so the frequency minima are dispersed across the angular range for the different domains and are not symmetric either side of $\theta = 0^\circ$. Because the Fermi surface is reduced in size the frequencies are considerably smaller – all main features occur beneath 4 kT – while the increased number of bands produces significantly more frequency branches. Considering all six domains together, the triclinic structure offers a smörgåsbord of low frequency, low symmetry features that all show minima well away from $\theta = 0^\circ$ – the main features of the measured spectra of S1 and S2.

To disentangle the multiple domains that may form within either sample, it is worth considering the low temperature x-ray diffraction measurements on S1 and S2, shown back in Figure 4.6: S1 showed superstructure peaks in two directions, a clear indication of two domains forming; S2 showed superstructure peaks in only one, indicative of a single domain. Furthermore the single domain that forms in S2, associated with modulation vector $q'_1 = 1/5(0\bar{1}1)$, also forms in S1. It is therefore likely that the frequency spectrum of S1 should be matched by two domains, one of which will also match the entire frequency spectrum of S2.

Figure 4.13 shows the measured frequency spectra of S1 and S2 alongside the simulated frequency spectra for the domains of the triclinic structure that provide the best match. In agreement with their x-ray diffraction measurements, S1 matches well with domains D1 and D3 and S2 matches well with D1. Table 4.1 gives a direct comparison

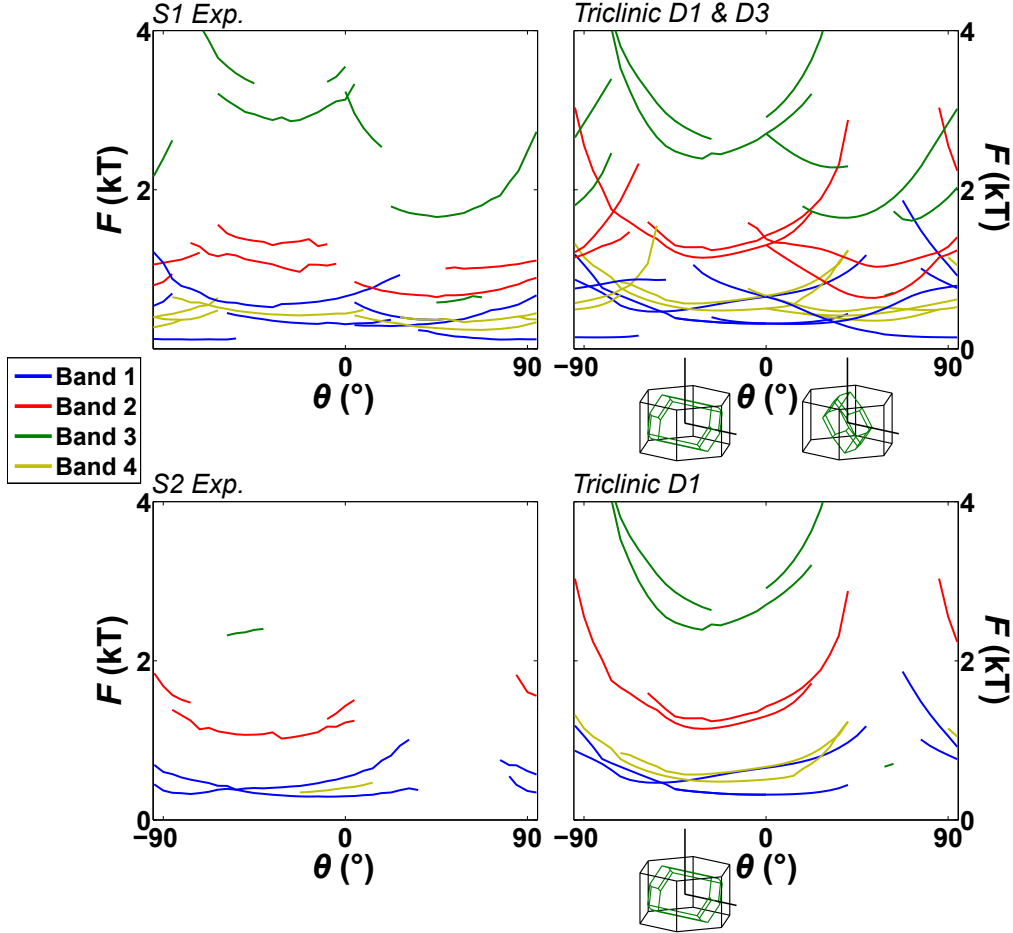


Figure 4.12: **Angular dependence of measured frequencies in IrTe₂ and simulations for matched domains.** The experimental frequencies of S1 and S2 are shown alongside the matching calculated frequencies for domains D1 & D3 and D1.

between the frequency values and effective masses for S1 and S2 and those predicted by these domains. The measured effective masses are in very good agreement with the band masses predicted by DFT, taking small values ($0.2 - 1.2 m_e$) with no significant mass enhancement. Although there are some slight discrepancies in absolute frequency values – likely due to slight misalignments of the crystals – all measured features can be accounted for by these few domains of the triclinic structure. Due to the increasing frequency and changing curvature factors, away from the frequency minima the oscillation amplitudes become weaker and so, especially for the smaller S2, the full range of predicted frequencies is not completely visible. However all quasi-two dimensional parts of the predicted triclinic structure are present, so these results are the first experimental confirmation of the strange tilted dimensionality of the electronic structure in IrTe₂ below T_S . In particular they show that (multiple domains of) the $q_1 = 1/5$ modulated structure

forms in the bulk of IrTe₂ below T_S (when no thermal cycling is applied to the sample). This is in agreement with x-ray measurements [138, 139], and in contrast to the plethora of modulations seen on the surface of IrTe₂ by STM [134, 136, 137]. Quantum oscillations are not, however, able to detect quasi-one dimensional Fermi surfaces, so to detect these features – expected for bands 3, 4 and 5 of the triclinic structure – and truly confirm the tilting of the conduction planes, a different technique must be used.

4.2.4 Comparison with other quantum oscillations studies

Concurrent to the publication of the results in this section [148], a similar paper also reported dHvA measurements of the low temperature electronic structure of IrTe₂ [149]. Here I will briefly discuss the results of [149] and compare them to the measurements and analysis presented thus far in this section.

[149] reports measurements on two batches of IrTe₂: one batch, called sample A, showed a single transition, T_S in transport measurements; the other, sample B, showed both T_S and T_R . Crystals from the two batches (but not the same crystals the transport measurements were conducted on) were then measured using torque magnetometry. dHvA oscillations were observed in both samples, with sample A determined to show the $q_1 = 1/5$ modulation and sample B both the q_1 and $q_2 = 1/8$ modulation.

In both samples an assortment of bands and domains are seen: in sample A three domains are seen of band 1, two domains are seen of band 2 and there is no evidence of bands 3 and 4; in sample B three domains are seen of bands 2, 3 and 5, one domain is seen of band 6 and there is no evidence of bands 1, 4 and 7; furthermore there are a number of frequency branches that cannot be assigned to any predicted by DFT. This is in contrast to the results presented in this chapter, where all bands are seen for all domains present, and no experimental frequencies are unaccounted for.

Part of the reason for this discrepancy in [149] arises from a misunderstanding of domain formation in IrTe₂: they claim only three domains are possible for the $q_1 = 1/5$ (and $q_2 = 1/8$) modulated structure, rather than the six that may actually form. The domains they calculate, D1, D3 and D5 by the definitions given in Table 4.2, are able to

account for all the frequencies in sample A, but only close to half in sample B. The other half of S2's frequencies show reasonable correspondence with the frequencies predicted for the $q_2 = 1/8$ structure, however they could equally arise from the domains of the $q_1 = 1/5$ calculated not considered: D2, D4 and D6. There is little difference in size between the observed bands of the q_1 and q_2 modulated structures, and the position of the frequency minima at around $+45^\circ$ and -60° lines up well with those expected for D2/D6 and D4 respectively.

The presence of the $q_2 = 1/8$ modulation in sample B, and not sample A, is justified by the observation, in transport, of the second transition T_R in sample B. However these transport measurements were only performed on a crystal from the same batch, and although T_R marks the onset of additional modulations on the surface, it is not clear it does in the bulk [134]. As will be shown in the next section, the IrTe₂ samples measured in this chapter, all from the same batch, feature a transition at T_R in transport but show no indication – in x-ray, magnetic anisotropy, dHvA or AMRO measurements – of forming anything other than the $q_1 = 1/5$ modulated state in the bulk at low temperatures. X-ray diffraction measurements found the q_2 modulation to form in (sections of) the bulk only with repeated thermal cycling [135], which was not conducted by [149].

Taking all these factors into consideration, in my opinion it seems unlikely that (without thermal cycling) dHvA oscillations would observe the $q_2 = 1/8$ modulation in the bulk of IrTe₂; instead the additional frequencies observed by [149] could well arise from additional, unconsidered domains (i.e. D2, D4 and D6) of the $q_1 = 1/5$ modulated structure. Low temperature x-ray diffraction on sample B would clear up the origin of these additional frequencies: if the $q_2 = 1/8$ modulation is present then $q_2 = 1/8(\bar{1}01)$ superstructure peaks should be visible in the diffraction patterns.

4.3 Angle-dependent magnetoresistance

Experimental details

Transport measurements were conducted on relatively large ($\sim 500 \times 500 \times 50 \mu\text{m}$) crystals of IrTe_2 , taken from the same batch as those used for the torque magnetometry measurements. Contacts were made with silver paint (rather than solder or silver epoxy) as, due to their greater malleability, they more often survived the stress on the crystal at T_S and T_R . Zero field transport measurements were performed in a flow cryostat; single plane rotations were performed at fields up to 14 T in a PPMS with a single-axis rotation stage; multi-plane rotations were performed up to 18 T in a 21 T superconducting magnet on a probe fitted with a two axis rotator, allowing for continuous rotation of θ , the angle between the normal of the lattice planes and the applied field, and discrete rotation of φ , the in-plane orientation of the crystal (these angles are shown in Figure 4.15). A small (2 mA) current was used for the measurements so any sample heating effects should be negligible.

4.3.1 Zero field resistivity measurements

To first characterise the resistive behaviour of IrTe_2 at low temperatures, zero field resistivity measurements were conducted on numerous samples. These samples were platelike in shape, so the resistivity could be measured in two configurations: in-plane, where the contacts are on the the same face of the sample and so the current passes within the lattice planes; and out-of-plane, where the contacts are on opposite faces of the crystal and so the current passes perpendicular to the lattice planes.

Figure 4.13 shows the range of behaviours seen in zero field resistivity measurements of IrTe_2 . The simplest case, that reported in the first measurements on IrTe_2 [123], is shown in Figure 4.13a): a single, slightly hysteretic transition, characterised by an increase in resistance at $T_S \approx 280 \text{ K}$ arising from the formation of the $q_1 = 1/5$ modulated state. The second transition, at $T_R \approx 170 \text{ K}$, is also seen in some cases upon cooling, with a particularly nice example shown in Figure 4.13b). This second increase in resistance, seen

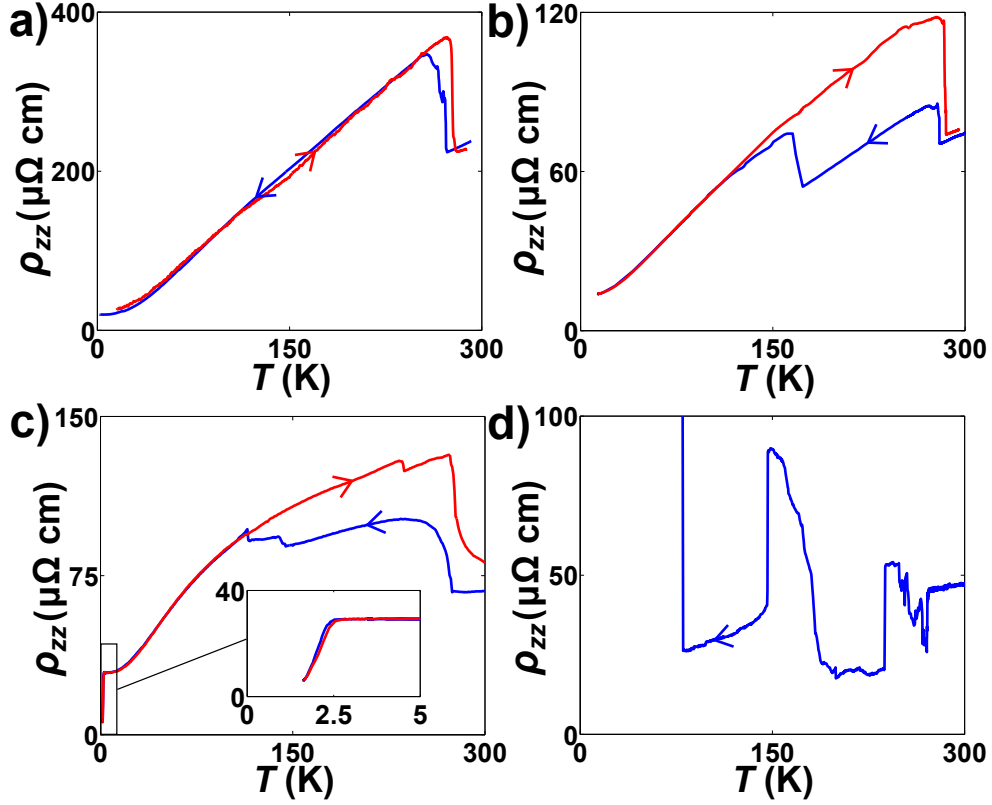


Figure 4.13: **Representative zero field resistivity measurements of IrTe₂.** a) Out-of-plane measurement showing a single, slightly hysteretic transition at $T_S = 280 \text{ K}$. b) Out-of-plane measurement showing an additional transition on cooling at $T_R \approx 170 \text{ K}$. c) Out-of-plane measurement showing both T_S and T_R but also superconductivity below $T_c = 2.5 \text{ K}$. d) A more typical measurement: contact to the sample is lost upon cooling through T_S and T_R .

in later measurements on higher quality single crystals of IrTe₂ [134], corresponds to the formation of higher order $q_{n>1}$ modulations on the surface of IrTe₂; these modulations persist up to T_S upon warming the sample, so T_R is only present upon cooling. The appearance of T_R has been linked to improved crystal quality [149], and indeed the resistivity in Figure 4.13b) (which shows both transitions) is approximately four times smaller than the resistivity in Figure 4.13a) (which shows only one transition), indicative of a cleaner crystal. However even in the cleanest samples T_R did not appear reproducibly, with its occurrence seemingly dependent upon the cooling conditions: although all samples were cooled slowly (at less than 1 K/minute) through the transitions, slower, steadier cooling favoured the appearance of T_R . This tallies with previous studies, which found the charge modulated states formed by IrTe₂ to depend heavily upon the cooling conditions [135].

Figure 4.13c) shows both T_S and T_R , with the latter occurring over a broad (115-145 K) temperature range across which higher order surface modulations are forming. In addition to this, however, the sample also superconducts beneath $T_c = 2.5$ K, shown clearly in the inset of Figure 4.13c). This superconductivity occurs repeatably for only this single sample measured in the out-of-plane configuration: it is not present in in-plane measurements, which is suggestive of filamentary superconductivity. Similar filamentary superconductivity has been previously reported in IrTe₂ [130], where it was attributed to possible Ir vacancies in the samples, and of course reducing the amount of Ir by doping (e.g. Ir_{1-x}Pt_xTe₂, Ir_{1-x}Pd_xTe₂) also induces superconductivity, with a similar $T_c \approx 3$ K [124, 125]. Therefore this superconductivity is not related to the charge modulated state that forms below T_S and instead arises from small regions of inhomogeneity within the sample.

Figures 4.13a)-c) show the range of different features seen in zero field resistivity measurements of IrTe₂; although all three are out-of-plane measurements, similar behaviour (but no superconductivity) is also seen at T_S and T_R in in-plane measurements. However, for both measurement configurations, Figure 4.13d) is unfortunately far more representative of a typical cooling curve for IrTe₂. Due to the drastic structural changes induced by dimerisation (the dimerised bonds shorten by $\sim 20\%$), the formation of modulated states at T_S and T_R places significant stress upon the crystal. Therefore, more often than not and certainly when cooling quickly, cooling through one or both transitions will result in the loss of contact(s), leading to noise, spikes, jumps and the eventual loss of signal, as seen in Figure 4.13d). Most commonly the contacts shear off the sample, often taking a bit of it with them, however (especially with stronger solder or silver epoxy contacts) the wires themselves may also break as a result of the sudden force, and sometimes the crystal itself will shear in two. To reduce the chances of things going so horribly wrong, extremely slow cooling rates (~ 0.1 K/min) through the temperatures around T_S and T_R are a very good idea, along with well secured wires, large sample contacts and nothing (except the contacts) holding the sample in place. Even adhering to all these steps a large amount of luck and perseverance is required: the sample used for the low temperature

rotation measurements presented in the next section only made it to base temperature with all contacts intact upon the twelfth attempt.

4.3.2 Rotations in applied field

Fixed φ angle-dependent magnetoresistance

To look for possible one-dimensional features in the Fermi surface of IrTe₂ at low temperatures the angular dependence of magnetoresistance (AMR) was measured for multiple transport samples. Figure 4.14 shows the results of these measurements for sample TS1, contacted in an in-plane configuration, and sample TS2, contacted in an out-of plane configuration. In these measurements θ (as defined in the diagram of Figure 4.14) is rotated while φ takes a constant, arbitrary value.

Figure 4.14a) shows the cooling curve of TS1 for these AMR measurements: only the transition at T_S is visible, with no indication of higher order $q_{n>1}$ modulations forming at lower temperatures. The AMR measured at various temperatures during this cooling process is shown in Figure 4.14b). Above T_S the AMR shows negligible anisotropy, but at lower temperatures a weak $\sin(2\theta)$ dependence begins to emerge. This corresponds to a maximum in magnetoresistance when the field is perpendicular to the lattice planes ($\mathbf{B} \parallel \vec{c}_{\text{HT}}^*$), and a minimum when the field is within the lattice planes ($\mathbf{B} \perp \vec{c}_{\text{HT}}^*$). Cooling further, additional dips appear in the AMR – marked with dashed lines in Figure 4.14 – that come to dominate by 2 K. These occur either side of the minima in the $\sin(2\theta)$ term, and are periodic over 180°. As shown in Figure 4.14c), the amplitude of these dips is strongly field dependent, but their position does not seem to vary with either field or temperature.

Similar features are also seen in the out-of-plane measurement of TS2, despite it clearly showing both T_S and T_R^4 in the cooling curve of Figure 4.14d). The $\sin(2\theta)$ dependence is much stronger in the out-of-plane measurement, so it still dominates the

⁴ T_R in this case comprises multiple jumps in resistivity (also seen in Figure 4.13c)) as different regions of the surface begin to form higher order modulations at slightly different temperatures. The large plateau from 50-100 K is not a feature of the sample however, but an overload of the lock-in amplifier: I had, presumably, gone to lunch without checking my ranges.

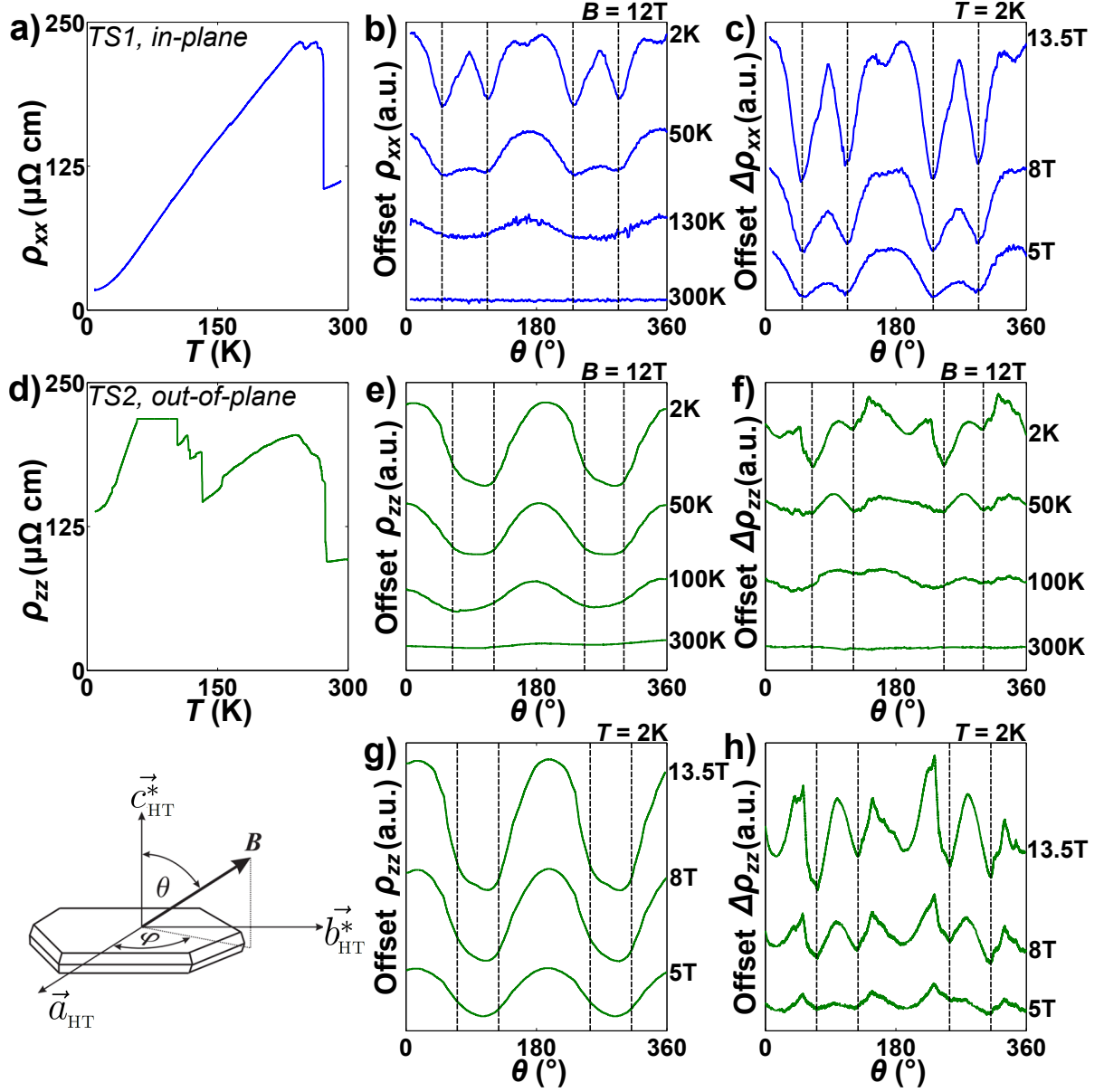


Figure 4.14: **Fixed angle-dependent magnetoresistance oscillations in IrTe₂.** a) Temperature dependence of resistivity for TS1. b) Temperature dependence of AMR for TS1. c) Field dependence of AMR for TS1. d) Temperature dependence of resistivity for TS2. e) Temperature dependence of AMR for TS2 and f) with a $\sin(2\theta)$ background subtracted. g) Field dependence of AMR for TS2 and h) with a $\sin(2\theta)$ background subtracted. AMR plots are offset along the y -axis for clarity; diagram shows the definition of angles θ and φ .

AMR in the 2 K plots of Figures 4.14e) and g). However by fitting and subtracting this $\sin(2\theta)$ dependence, the additional dips can still be clearly seen, as shown in Figures 4.14f) and h). These dips in the AMR of TS2 show the same periodicity, temperature dependence and field dependence as those seen in the AMR of TS1, while their absolute positions differ by less than 5° , within the mounting error of the sample. Therefore the

occurrence, and form, of these dips appears to be independent of both the transitions seen upon cooling – TS1 showed only T_S , TS2 showed both T_S and T_R – and the configuration of measurement – in-plane for TS1, out-of-plane for TS2.

Lebed magic angle effects

The appearance of periodic dips in the AMR is characteristic of a quasi-one dimensional Fermi surface, which can produce a variety of oscillatory features (AMRO). AMRO exist up to relatively high temperatures (as, unlike quantum oscillations, they do not require a sharply defined Fermi surface) and increase in size with magnetic field [31], both features seen in the measurements of TS1 and TS2. More specifically the AMRO features observed are likely to be Lebed magic angles [30] rather than Danner-Kang-Chaikin (DKC) oscillations [33], as the predicted quasi-one dimensional Fermi surfaces of modulated IrTe₂ shown in Figure 4.10 are not strongly corrugated: DKC oscillations depend on the corrugation of the Fermi surface sheet, so will be reduced in amplitude; Lebed magic angles are a purely geometric effect, so do not depend on the corrugation. For both these effects the current must be applied within the sheets of the quasi-one dimensional Fermi surface; in the Lebed case the field is then rotated within the sheet, while for the DKC effect the field is rotated out of the sheet. It is worth noting that AMRO is typically seen in quasi-one dimensional organic conductors, which tend to have sample resistances of the order 1-100 Ω [28]; IrTe₂, a considerably better conductor, has sample resistances of around 10 $\mu\Omega$ at low temperatures, so the features seen here are approximately six orders of magnitude smaller than when they usually occur.

As was seen for the de Haas-van Alphen effect analysis, the multiple domains of multiple modulations that can form beneath T_S – all with differently oriented lattice vectors – can make things very complicated for the low temperature Fermi surface of IrTe₂. However for the $q_1 = 1/5$ modulated Fermi surface, all three quasi-one dimensional Fermi surface sheets are normal to $\mathbf{a}_{1/5}$ (shown in Figure 4.16a)), the lattice vector that remains in the crystallographic planes beneath T_S . Therefore the Fermi surface sheets, for all domains of the q_1 modulated structure, are perpendicular to the lattice planes: $\mathbf{c}_{\text{HT}}^*$

lies within the Fermi surface sheets for all possible domains. The same is also true for the reported Fermi surfaces of the $q_2 = 1/8$ and $q_\infty = 1/6$ modulated structures [135]. In relation to the AMR measurements, this means that for the out-of-plane configuration of TS2, the current is applied within the Fermi surface sheets for all possible domains, as is required for Lebed magic angle effects. For the in-plane configuration of TS1 this is not the case, however considering the large size of the crystal – considerably larger than those used for the torque measurements, which showed one or two domains – it is likely many domains are present in the sample, and so for at least some of these domains a significant component of the current will also be within the Fermi surface sheets, allowing for Lebed-like features.

Although Lebed features are strongest when the magnetic field is rotated within the sheets of the quasi-one dimensional Fermi surface, they are also possible when the magnetic field has an out-of-sheet component as well [31]. For each domain of the q_1 modulated structure, an in-sheet rotation of the magnetic field corresponds to varying θ at a certain value of φ , which will be different for each domain. Therefore at an arbitrary φ multiple domains may contribute to the Lebed features, with the largest contribution coming from domain where the θ rotation is closest to being in-sheet. In the case of the AMR measurements of TS1 and TS2 presented in Figure 4.14, the two arbitrary values of φ produced very similar Lebed features; however for a comprehensive study of these features the AMR must be measured over a range of φ for a single sample.

Varying φ angle-dependent magnetoresistance

Figure 4.15 shows the results of AMR measurements conducted on a third sample – TS3, wired in an out-of-plane configuration – at various values of φ . To conduct these measurements TS3 was mounted on a two-axis rotator, which allows for the discrete rotation of φ without warming up and remounting the sample. Figure 4.15a) shows the resistivity as a function of temperature for these measurements, with only a transition at T_S visible. Figures 4.15b) and c) show the temperature and field dependence respectively of the AMR of TS3: as was the case in the previous out-of-plane measurement a $\sin(2\theta)$

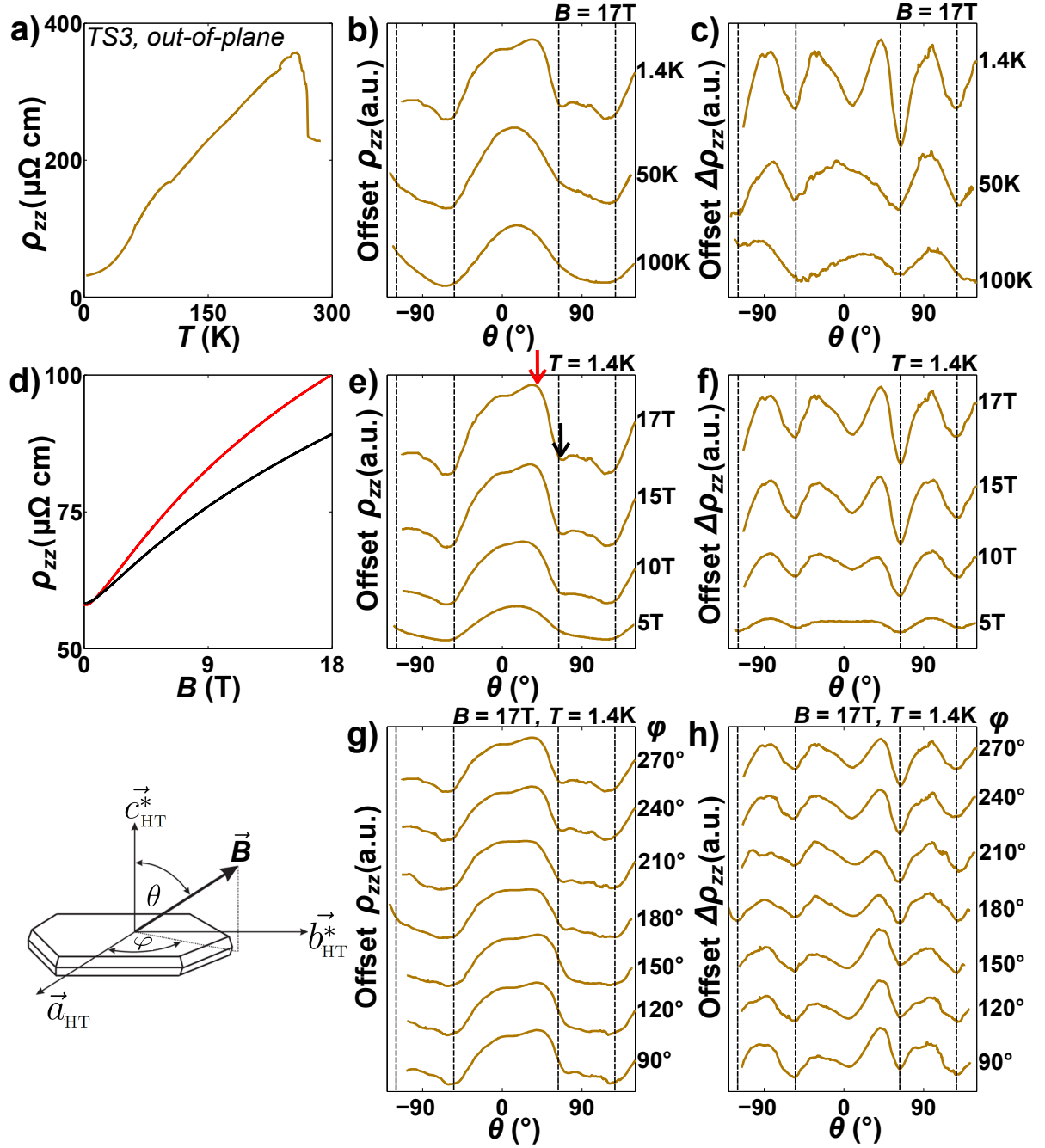


Figure 4.15: **Angle-dependent magnetoresistance oscillations in IrTe₂ with varying azimuthal angle.** a) Temperature dependence of resistivity for TS3. b) Temperature dependence of AMR for TS3 and c) with a $\sin(2\theta)$ background subtracted. d) Magnetoresistance at (black) and away from (red) Lebed dips; arrows on e) indicate the exact positions of measurement. e) Field dependence of AMR for TS3 and f) with a $\sin(2\theta)$ background subtracted. g) φ dependence of AMR for TS3 and h) with a $\sin(2\theta)$ background subtracted. AMR plots are offset along the y -axis for clarity; diagram shows the definition of angles θ and φ .

term dominates, with the resistivity largest when the field is perpendicular to the lattice planes. However once this term is fitted and subtracted the Lebed dips are once again

clear, as can be seen (marked by a dashed black line) in the residual plots of Figures 4.15c) and f). As before these dips increase in amplitude at lower temperatures and higher fields, but their position does not vary: the angles they occur at are within 5° of those seen in TS1 and TS2.

With the field orientation well away from a Lebed dip, the magnetoresistance for a single Fermi surface sheet, only capable of producing open electronic orbits, should go as $\rho \sim B^2$; at a Lebed dip, however, the magnetoresistance is expected to be substantially repressed [31]. Figure 4.15d) shows the magnetoresistance measured in these two cases for TS3, with the arrows in Figure 4.15e) indicating the exact angles of measurement. Due to the multiple quasi-one and quasi-two dimensional Fermi surfaces in IrTe₂, the magnetoresistance away from the Lebed dips, close to the maximum of the AMR (plotted in red), does not follow the $\rho \sim B^2$ dependence expected for a single sheet; at the Lebed dip (in black) however, there is still the clear reduction in the magnetoresistance that is expected.

Figure 4.15g) shows the φ dependence of the AMR, measured every 30° over a 180° range. There appears to be little to no variation, with the $\sin(2\theta)$ dependence of the background practically constant. Subtracting this away, it is a similar story for the residual plot of Figure 4.15h): the Lebed dips are present at all measured orientations, with no great changes in their angular position. This was of course to be expected: the Lebed dips seen so far in TS1, TS2 and TS3 are all very similar, despite being measured at three arbitrary (and presumably different) values of φ . However the positions, and amplitudes, of Lebed dips are supposed to be strongly angular dependent: when the magnetic field lies entirely within the Fermi surface sheet the dips are largest and closest to $\theta = 0^\circ$, rotating away from this value of φ they spread out and decrease in amplitude, before eventually disappearing [150]. To understand why this is not the case in IrTe₂, the effects of the tilted lattice parameters and the multiple domains must again be considered.

4.3.3 Lebed magic angle calculations

Defining the coordinate system

Unlike other AMRO effects, Lebed magic angles are solely geometric, depending only on the orientation of the quasi-one dimensional Fermi surfaces sheets within a material, and not on the sheets' corrugation or any further electronic properties [150]. Therefore the positions of the Lebed magic angles can be calculated from the lattice parameters of the system, and, for a generalised, low symmetry case, are given by:

$$\begin{aligned} \tan(\theta_{Lebed}) \sin(\varphi_{Lebed}) &= \frac{p}{q} \frac{b \sin(\gamma)}{c \sin(\beta) \sin(\xi)} - \cot(\xi) \\ \xi &= \cos^{-1} \left(\frac{\cos(\gamma) \cos(\beta) - \cos(\alpha)}{\sin(\beta) \sin(\gamma)} \right) \end{aligned} \quad (4.2)$$

where p and q are integers, θ_{Lebed} is the angle between the applied field and $\mathbf{c}^*$ and φ_{Lebed} is the angle between the projection of the applied field into the a - b plane and $\mathbf{a}$ (the normal to the Fermi surface sheets), as shown in Figure 4.16b). To begin with only the principal $p/q = 1$ Lebed magic angles will be considered, as this, the most straightforward case, tends to produce the most prominent features [28]. As the quasi-one dimensional Fermi surfaces arise from the $q_1 = 1/5$ modulated structure, the lattice parameters in Equation 4.2 are those of the triclinic structure. This means that θ_{Lebed} and φ_{Lebed} are not the same as the measured angles θ and φ , which are defined with respect to the rhombohedral structure. Figure 4.16b) shows both sets of angles for a single domain (D3) of the triclinic structure. For each domain the values of θ_{Lebed} and φ_{Lebed} can be calculated from Equation 4.2, which define the orientations of $\mathbf{B}$ at which Lebed magic angles are expected to appear; projecting these orientations onto the high temperature, rhombohedral lattice vectors then gives the expected Lebed magic angle positions in terms of θ and φ , the measured angles.

Lebed magic angles for $q_1 = 1/5$, $p/q = 1$

Figure 4.16c) shows the positions of the Lebed magic angles for each domain of the triclinic structure: the main plots show the positions of the Lebed magic angles projected onto

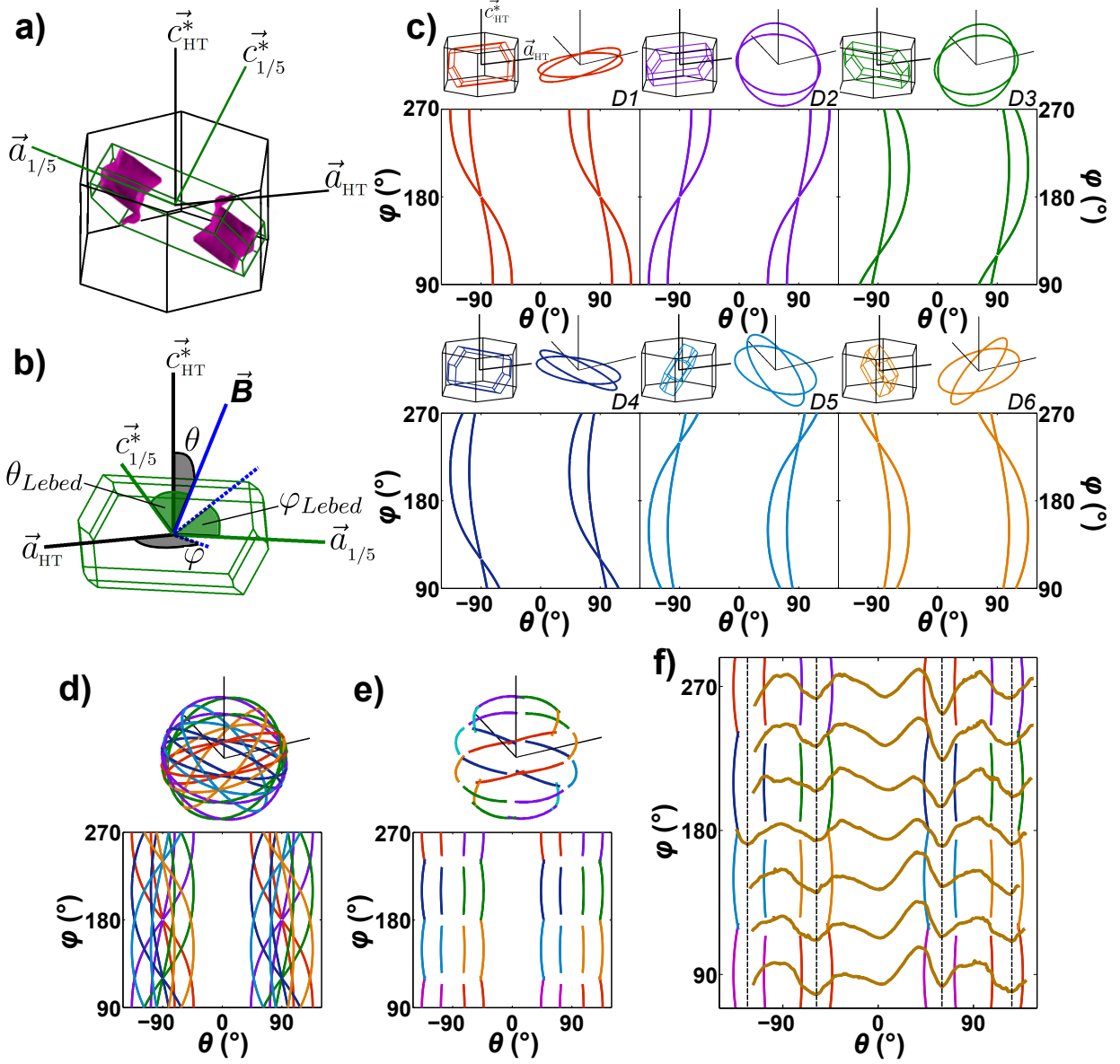


Figure 4.16: **Principal Lebed magic angles in IrTe₂** for the $q_1 = 1/5$ modulated structure. **a)** Fermi surface sheet shown within the triclinic and rhombohedral Brillouin zones, specifically band 5 for D3; note the sheet is perpendicular to $\vec{a}_{1/5}$. **b)** Measured angles θ , φ and Lebed magic angles θ_{Lebed} , φ_{Lebed} for an arbitrary field orientation $\vec{B}$, shown within the triclinic Brillouin zone. **c)** Calculated Lebed magic angles for each domain, shown in real space (top) and in the plane of θ and φ , the measured angles (bottom). **d)** Real space and θ , φ plot of Lebed magic angles for all domains. **e)** Real space and θ , φ plot of the largest amplitude Lebed magic angles for all domains. **f)** Largest amplitude Lebed magic angles compared to the measured AMR dips.

the θ , φ measured angular range; above is shown the Brillouin zone of each domain with the high temperature, rhombohedral axes $\vec{c}_{HT}^*$ and $\vec{a}_{HT}$ indicated (left), and the positions of the Lebed magic angles in real space (right). The field orientations take the expected form in real space – a pair of overlapping circles, making contact along $\vec{a}_{1/5}$ and with

the greatest separation at orientations closest to $\mathbf{c}_{1/5}^*$. At these orientations close to $\mathbf{c}_{1/5}^*$ the field is closest to being in-sheet, so the Lebed dips will be largest; at orientations close to $\mathbf{a}_{1/5}$ the field is close to out-of-sheet, so the Lebed dips will be of greatly reduced amplitude [150].

Projected onto the measured θ, φ plane, the Lebed magic angle positions for all domains are periodic over a θ range of 180° , but are not symmetric around $\theta = 0^\circ$; the same symmetries as were present in the measured Lebed dips. The projected positions do show variation with φ , however, because of the tilted $\mathbf{c}_{1/5}^*$ axis, all Lebed magic angles occur within the regions $-137^\circ < \theta < -43^\circ$ and $43^\circ < \theta < 137^\circ$ for every domain; the observed Lebed dips also occur within these regions, clustered around 90° .

The relatively large size of the transport samples measured means that many, and most likely all, domains are present below T_S . Figure 4.16d) shows the combined real space and θ, φ plots for all domains of the triclinic structure. The real space plot is a ball of confusion⁶, however plotted in the θ, φ plane the Lebed magic angles, although far more numerous and tangled, still possess the same symmetry and the same constricted angular range as the individual domains. However this plot is still some way from the spaced-out, φ -independent pairs of Lebed dips seen in the measured AMR.

What has not been considered so far is the amplitude of the Lebed dips, only the angles they occur at. Calculating their exact magnitude, especially for a triclinic system, is not straightforward [28], however in all cases the largest dips occur when the field is rotated within the plane of the Fermi surface sheet ($\varphi_{Lebed} = 90^\circ, 270^\circ$) and their amplitude becomes vanishingly small as the field approaches perpendicular ($\varphi_{Lebed} = 0^\circ, 180^\circ$). To ignore the Lebed magic angles at which the amplitude of the dips will be negligible, only those occurring in the angular ranges of $30^\circ < \varphi_{Lebed} < 150^\circ$ and $210^\circ < \varphi_{Lebed} < 330^\circ$ can be plotted, shown in Figure 4.2e). In real space the orientations of these Lebed magic angles now form two pairs of circles around $\mathbf{c}_{HT}^*$, and plotted in the θ, φ plane this reduces to two pairs of lines either side of $\varphi = \pm 90^\circ$, with almost no φ dependence. Therefore, in a sample of IrTe₂ that contains all possible domains of the $q_1 = 1/5$ modulated structure,

⁶Lebed dips moving out, Lebed dips moving in; Why?, because of the orientation of their twin... [151]

there should be negligible φ variation in the position of the Lebed dips, which was exactly the case in the AMR measurements.

Figure 4.2f) shows the φ -dependent, $\sin(2\theta)$ subtracted AMR of TS3 plotted on top of the predicted (large amplitude) Lebed magic angle positions for all domains; as in Figure 4.15 the black dashed lines mark the position of the measured Lebed dips. Although there is a common lack of φ variation, the calculations predict two sets of Lebed dips around $\theta = \pm 90^\circ$, while measurements find only one. Furthermore the measured dips lie between the two sets of predicted angles, differing from both positions by $\sim 15^\circ$. Therefore the $p/q = 1$ Lebed magic angles of the $q_1 = 1/5$ modulated structure are unable to accurately predict the location of the Lebed dips, despite appearing qualitatively similar.

Lebed magic angles for higher order modulations

Although neither x-ray diffraction or de Haas-van Alphen measurements found any evidence for higher order ($q_{n>1}$) charge modulations forming in the bulk of IrTe₂, both the $q_2 = 1/8$ and $q_\infty = 1/6$ modulated structures are predicted to have quasi-one dimensional Fermi surface sheets normal to the lattice planes [135], much the same as the $q_1 = 1/5$ modulated structure considered thus far. However as their lattice parameters differ from the q_1 modulated structure, so should the positions of their Lebed magic angles. Figure 4.17a) shows the calculated $p/q = 1$ Lebed magic angles for the $q_2 = 1/8$ and $q_\infty = 1/6$ modulated structures, plotted on top of the φ -dependent AMR of TS3; different domains are plotted in different colours, q_2 (spacegroup $C2$) may form six possible domains while q_∞ (spacegroup $C2/c$) may form three. As before a reduced angular range is plotted, neglecting the regions close to φ_{Lebed} where the amplitude of the dips becomes vanishingly small; this is chosen to be $45^\circ < \varphi_{Lebed} < 135^\circ$ and $225^\circ < \varphi_{Lebed} < 315^\circ$, as within this region both modulations show relatively little φ variation. It is plainly apparent that neither of these structures are able to match the observed Lebed dips: the Lebed magic angles of the q_2 modulation show significant φ variation for four of the six domains; the three domains of the q_∞ modulation are unable to produce consistent features across the entire φ range. Overall both modulations provide a considerably worse correspondence

to the data than the q_1 , $p/q = 1$ calculations of Figure 4.16f): the AMRO provides no suggestion of anything other than the $q_1 = 1/5$ modulated state forming beneath T_S in the bulk of IrTe₂.

Lebed magic angles for higher order p/q

Returning to the $q_1 = 1/5$ modulated structure, the other possibility that has not yet been considered is the presence of higher order, $p/q \neq 1$, Lebed magic angles. Figure 4.17c) shows the calculated positions of the $p/q = 2$ and $p/q = 1/2$ Lebed magic angles for the $q_1 = 1/5$ modulated structure, plotted on top of the φ -dependent AMR of TS3. Constraining the angular range to the regions of largest amplitude ($55^\circ < \varphi_{Lebed} < 125^\circ$ and $235^\circ < \varphi_{Lebed} < 305^\circ$ for $p/q = 2$, $5^\circ < \varphi_{Lebed} < 175^\circ$ and $185^\circ < \varphi_{Lebed} < 355^\circ$ for $p/q = 1/2$), both calculations produce two sets of approximately φ independent features, as was the case for $p/q = 1$ (shown in Figure 4.16f)). For $p/q = 2$ these two sets are some way out from the single set of Lebed dips seen in the AMR, however for $p/q = 1/2$ the two sets of Lebed magic angles occur in close proximity, and together they line up consistently well with the measured Lebed dips. Therefore the Lebed dips seen in IrTe₂ appear to occur at the $p/q = 1/2$ Lebed magic angles of the $q_1 = 1/5$ modulated state, and provide the first experimental evidence of quasi-one dimensional Fermi surfaces in IrTe₂.

It is, however, highly unusual in systems showing AMRO that the $p/q = 1/2$ Lebed features are seen and the $p/q = 1$ features are not, so to understand why this might be the case it is necessary to consider the different factors that may affect the amplitude of a Lebed dip. Beginning with the origin of the dips themselves, although the exact mechanism of the conduction increase is debated [28], it is clear that the effect arises from the comensurate nature of the electronic motion at the Lebed magic angles: when p and q are both integers each electron travels over a much reduced area of the Fermi surface sheet (in contrast to travelling the entirety when p/q is irrational). The larger both p and q are, the greater the Fermi surface area each electron travels over and hence the weaker the increase in conductivity. As a result of this, the Lebed dips should be

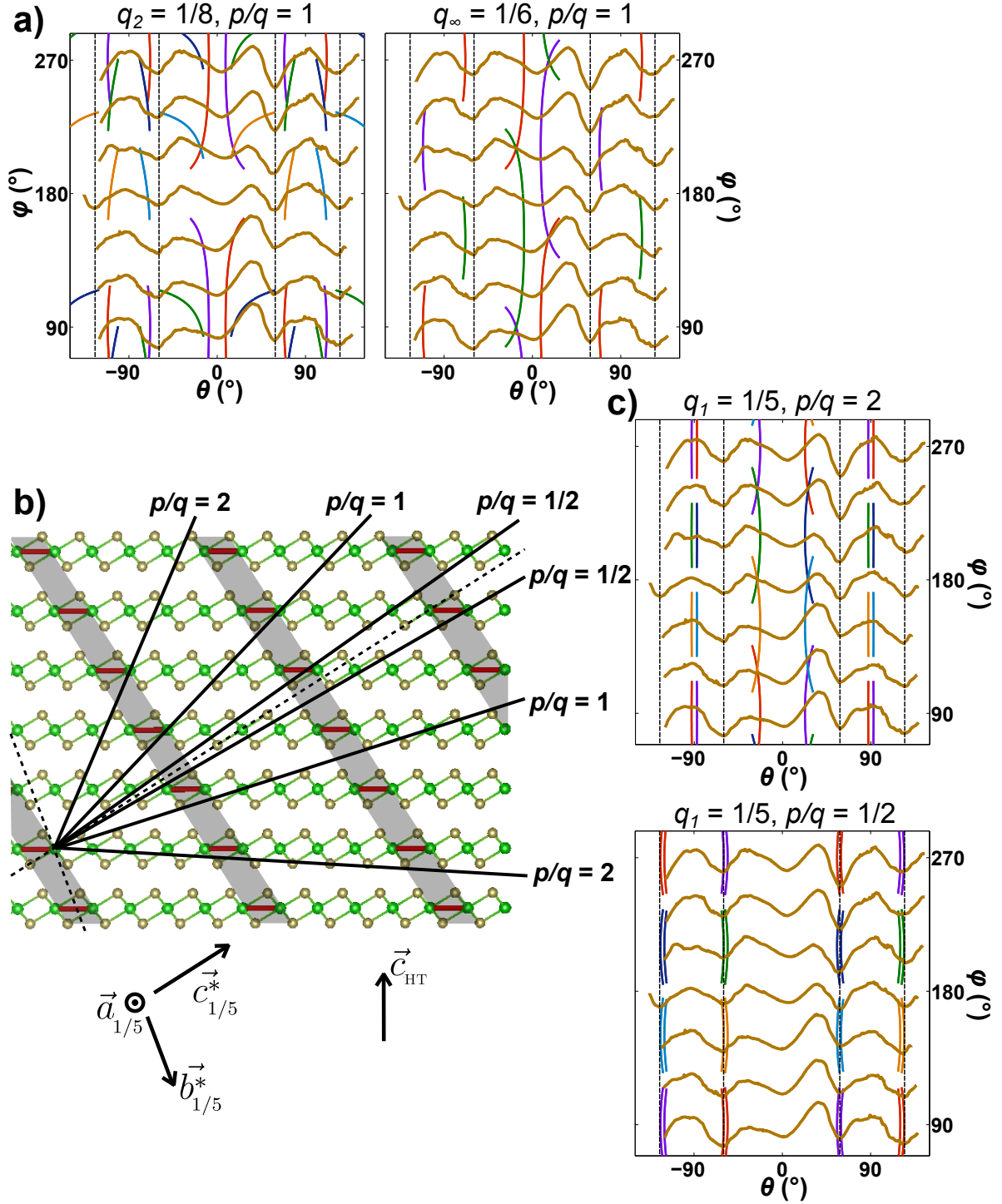


Figure 4.17: **Higher order Lebed magic angles in IrTe₂.** a) Lebed magic angle positions for the $p/q = 1$ dips of the $q_2 = 1/8$ and $q_\infty = 1/6$ modulated structures, shown for the region $45^\circ < \varphi_{Lebed} < 135^\circ$. b) Directions of electronic motion in real space at the $p/q = 1/2, 1$ and 2 Lebed magic angles for the $q_1 = 1/5$ modulated structure. Shaded regions indicate a reduced density of states. c) Lebed magic angle positions for the $p/q = 2$ and $1/2$ dips of the $q_1 = 1/5$ modulated structure, shown for the region $55^\circ < \varphi_{Lebed} < 125^\circ$ and $5^\circ < \varphi_{Lebed} < 175^\circ$ respectively.

strongest at $p/q = 1$ and decrease in amplitude with larger p and q ; this is generally the case experimentally [28], and is why the absence of the $p/q = 1$ features in IrTe₂ is so unusual.

However, the details of the crystal structure can also have a large influence on which Lebed magic angles are observed. In the quasi-one dimensional organic conductors where Lebed magic angles have been measured previously, the conductivity in the b - c plane (where the Fermi surface sheets are normal to $\mathbf{a}$) is highly anisotropic, with the values differing by up to three orders of magnitude [152]. In these cases higher order Lebed magic angles are only seen towards the more conductive direction: for example in (TMTSF)₂PF₆ the c -axis conductivity is considerably smaller, so values of $q > 1$ will be accompanied by a large increase in resistance and hence only integer (i.e. $p \in \mathbb{N}$, $q = 1$) Lebed magic angles are visible [153]. In (TMTSF)₂ReO₄ a more curious selection rule is present: Lebed magic angles are only visible when p and q are both odd integers [154]. This is because, in the b - c plane, (TMTSF)₂ReO₄ contains chains of dimers, which have a greatly reduced density of states. Even values of p and q require the electrons to travel along these dimers, so the resistance in these directions will be considerably larger (as the density of states is much smaller) and no Lebed dips will be seen.

These examples illustrate that reduced dimensionality and dimerisation are readily able to effect the observation of Lebed magic angles, and both of these are very much present in the low temperature structure of IrTe₂. Figure 4.17b) shows the $q_1 = 1/5$ dimerised crystal structure of IrTe₂ in the $b_{1/5}^*$ - $c_{1/5}^*$ plane, which shares a normal ($\mathbf{a}_{1/5}$) with the Fermi surface sheets and so contains the field orientations that produce Lebed magic angles. These field orientations – which will also be the favoured directions of electronic motion – are plotted as solid black lines for the case of $p/q = 1/2$, 1 and 2. The conductivity at these orientations will be affected by both the layered structure – which causes a reduction in the conductivity along $\mathbf{c}_{\text{HT}}$ – and the sheets of dimers – which lead to stripes of reduced density of states – indicated in grey. At the $p/q = 1/2$ Lebed magic angles the electrons travel almost perpendicularly to these dimer sheets, however for both $p/q = 1$ and $p/q = 2$ a far larger component of the electronic motion is contained

within them. As a result of their reduced density of states, the conductivity within the dimer sheets will be substantially reduced, and so electronic motion in the $p/q = 1$ and 2 directions will be more resistive than in the $p/q = 1/2$ direction. This increase in resistance may be enough to negate any decrease seen from Lebed effects, explaining why the expected dips are not present for $p/q = 1$ and 2.

Whatever the reason for the absence of the $p/q = 1$ features, it is clear that the dips seen in the AMR of all three measured samples of IrTe₂ correspond to $p/q = 1/2$ Lebed dips for the $q_1 = 1/5$ modulated structure. There is no evidence for any higher order $q_{n>1}$ modulations in the AMRO, despite some samples showing the second transition T_R upon cooling; as the same was true for the de Haas-van Alphen measurements, it seems only the $q_1 = 1/5$ modulation forms in the bulk of IrTe₂ at low temperatures, at least without the application of thermal cycling [135]. These results are a clear indication of the presence of a quasi-one dimensional Fermi surface in IrTe₂ at low temperatures, and a confirmation of the triclinic unit cell of the $q_1 = 1/5$ modulated structure determined by x-ray diffraction [138]. Furthermore this appears (to my knowledge) to be the first observation of Lebed magic angle effects outside of the field of organic metals, and certainly within the transition metal chalcogenides. Combined with the de Haas-van Alphen results, this is clear proof of the unusual electronic structure in the modulated state of IrTe₂ – with both quasi-two dimensional and quasi-one dimensional features, tilted at an angle to the lattice planes – that is predicted by DFT calculations.

4.4 Summary

In this chapter I have presented the results of torque magnetometry and angle-dependent magnetoresistance measurements, alongside DFT calculations, of the low temperature Fermi surface of IrTe₂. Through the observation of both de Haas-van Alphen oscillations and geometric effects in the angle-dependent magnetoresistance, the quasi-two dimensional and quasi-one dimensional components of the Fermi surface have both been

characterised.

Two small ($\sim 100 \times 100 \times 20 \mu\text{m}$) samples of IrTe_2 were measured using torque magnetometry, both of which showed clear superstructure peaks in low temperature x-ray diffraction – arising from a $q_1 = 1/5 (\bar{1}01)$ structural modulation – on top of the high temperature rhombohedral diffraction patterns. Torque magnetometry measurements of the magnetic anisotropy observe a clear phase shift beneath $T_S = 280 \text{ K}$, corresponding to a tilting of the two dimensionality away from the lattice planes of the crystal. The transition is also accompanied by a $\sim 40\%$ drop in the out-of-plane paramagnetic susceptibility anisotropy, of comparable size to the reported drop in the density of states and suggestive of a significant reduction in the size of the Fermi surface.

Clear de Haas-van Alphen oscillations are seen in both samples, with many small ($< 3 \text{ kT}$) frequencies that appear to be quasi-two dimensional around axes tilted well away from $\mathbf{c}_{\text{HT}}^*$, the normal to the lattice planes. Effective masses are small ($< 1.2 m_e$), indicative of a Fermi surface with negligible electronic correlations.

Calculations were conducted for the high temperature rhombohedral, low temperature monoclinic and $q_1 = 1/5$ modulated triclinic structures; due to their low symmetry, many different domains of the latter two structures need be considered. Both the rhombohedral and monoclinic structures produce Fermi surfaces that are much larger in size than those observed experimentally, and are still symmetric around $\mathbf{c}_{\text{HT}}^*$. However the triclinic, q_1 modulated Fermi surface agrees well with the measured frequencies, with the samples found to contain one and two domains respectively, in agreement with the domains found by x-ray diffraction. This Fermi surface consists of five bands, together contributing two quasi-two dimensional hole cylinders, two quasi-two dimensional electron cylinders and three Fermi surface sheets perpendicular to $\mathbf{a}_{1/5}$. These cylinders, tilted away from $\mathbf{c}_{\text{HT}}^*$, are able to explain all the measured frequencies in both samples, with the effective masses also in good agreement. This q_1 modulated Fermi surface is also about 40% smaller than that of the high temperature, rhombohedral structure, leading to the measured drop in the paramagnetic susceptibility and density of states.

Measurements on larger ($\sim 500 \times 500 \times 50 \mu\text{m}$) transport samples see transitions

at both $T_S = 280\text{ K}$ and $T_R = 180\text{ K}$, though the appearance of the latter depends greatly on cooling conditions. Irrespective of the transitions shown, all samples measured displayed clear non-sinusoidal dips in their angle-dependent magnetoresistance, which increase in size with decreasing temperature and increasing field. This, along with a clearly suppressed magnetoresistance within the dips, is the expected behaviour at Lebed magic angles, where commensurate orbits along a quasi-one dimensional Fermi surface produce periodic increases in the conductivity. The position of these dips depends solely on the lattice parameters (and the presence of a quasi-one dimensional Fermi surface), and so, once domains again are considered, can be used to confirm the low temperature bulk structure of IrTe_2 . Higher order modulated (q_2, q_∞) structures are unable to match the measured positions, however the $q_1 = 1/5$ modulated structure, with all domains present, is able to reproduce the measured features. Only one set of Lebed features are seen, however many are theoretically possible: the resistive sheets of dimers that form in the modulated phase, along with the anisotropy of the layered structure, act to suppress the appearance of Lebed features at certain orientations.

The position of the Lebed features confirms the low temperature unit cell – and, indirectly, the dimerisation – previously reported in x-ray diffraction measurements, which correspond to a $q_1 = 1/5$ modulated structure forming in the bulk of IrTe_2 . No measurements (x-ray diffraction, magnetic anisotropy, dHvA or AMRO) found any evidence of higher order modulations forming in the bulk of IrTe_2 , even though their presence has been previously confirmed on the surface. Taken together, the dHvA and AMRO results observe all aspects of the q_1 modulated Fermi surface, and confirm the unusual tilted electronic structure, unique among the TMDs, of IrTe_2 beneath T_S .

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