

Electronic and magnetic properties of iron-based superconductors



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This thesis presents experimental studies of the electronic and magnetic properties of several iron-based unconventional superconductors, primarily using the techniques of magnetotransport and torque magnetometry in high magnetic fields and synchrotron-based angle-resolved photo-emission spectroscopy (ARPES).

Superconductivity in the iron-based superconductors is always found in proximity to a magnetic phase, and the details of the electronic structure and Fermi surface are also important in determining the strength of interactions, and ultimately superconductivity. This motivates the experimental studies of electronic, magnetic and superconducting properties of Fe-based superconductors presented in this thesis.

First, quantum oscillation measurements using high-field torque magnetometry are used to provide a partial determination of the Fermi surface of superconducting LiFeAs. The data are compared with density functional theory calculations, finding strong mass enhancements on the observed electron bands, however the hole bands are not observed.

A large portion of this thesis concerns experiments on FeSe, which uniquely has a structural transition but is not magnetically ordered at any temperature. High field magnetotransport measurements show quantum oscillations, revealing small quasi-two dimensional Fermi surfaces, and it is argued that both hole and electron pockets are observed. The low-temperature Fermi surface consisting of one hole pocket and two electron pockets is also deduced from low-field magnetotransport. ARPES studies show that both hole and electron pockets undergo a significant elongation when cooling through the structural transition at ~ 90 K, interpreted as the result of orbital order. Measurements of the resistivity anisotropy above the structural transition are used to show that the structural distortion is electronically-driven. By combining these data sets, a complete picture of the symmetry-broken electronic structure of FeSe is constructed.

The final chapter concerns another iron-based superconductor with a more complex crystal structure, the so-called “10-3-8” phase, and in particular finds an unusual field-induced magnetic transition.

Acknowledgements

This is the story of a thesis, conceived by an enthusiasm for physics, a desire to continue the student lifestyle and a total naivety about what was to come. It was schooled by the arxiv, wikipedia, and Shoenberg. It learned by trial and error- a lot of both. It was sustained by lunch and tea breaks in the canteen, and harder stuff in the pubs of Oxford. It got fat in the late hours in office 105. It became demanding and frustrating, but ultimately fulfilling. It was submitted in 2015 to the vaults of the Bodleian to collect more dust than citations, in the hope of exchange for just five letters - DPhil - and a lifetime of Dr Watson jokes.

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“You have student written all over you”

Bob Laughlin, Nobel Prize in Physics 1998

I will never leave you nor forsake you.

Joshua 1:5

To my future wife, or dog.

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Chapter 1

Introduction

Superconductivity is a phenomenon which occurs at low temperature in a large number of metallic elements and compounds, characterised by zero resistivity and expulsion of magnetic field lines, and is one of the most dramatic phase transitions to occur in the solid state. The discovery in 1911 by Kamerlingh Onnes of zero resistivity in mercury below 4.2 K set in motion a worldwide effort to characterize and understand superconductors which has lasted now more than a century. The famous Nobel prize-winning theoretical description formalised in 1957 by Bardeen, Cooper and Schreiffer (BCS) [1] was able to describe the phenomenon very satisfactorily in terms of the pairing of electrons induced by a weakly attractive interaction mediated by phonons, and superconductivity was for some time considered to be a solved problem. A great number of superconducting materials was found and characterised in the decades following Onnes' initial discovery, but by the start of the 1980s the highest critical temperatures found in "A15" compounds [2] were found to be just over 20 K. Many thought that these represented nature's best case scenario for superconductivity: technologically useful but not revolutionary. Nobody could have anticipated that before the end of that decade the record T_c would be pushed well over 100 K with the discovery of high-temperature copper-oxide superconductors. It quickly became apparent that these new copper-oxide superconductors presented several challenges to the BCS theory and are now considered one of several examples of "unconventional

superconductivity”. The interest in understanding unconventional superconductivity arises not only from the theoretical challenge, but also because the prospect of room temperature superconductivity now seems a lot more reasonable, if still distant.

While a unifying theory of unconventional superconductivity seems to be a long way off, there are some hints of what is important: superconductivity in these materials is always found in proximity to an antiferromagnetic phase and often other competing or related phases. Moreover, they often have low carrier densities and low dimensionalities - all at odds with conventional superconductivity which favours high symmetry, high density of states, non-magnetic materials [3]. There is therefore a great need for characterisations of all parts of the phase diagrams of unconventional superconductors to understand the phases which compete with, or encourage, unconventional superconductivity.

Superconductivity in iron-based superconductors (FeBS) was first reported in 2006 in LaFePO ($T_c \approx 5$ K) [4], but it was the report of 26 K superconductivity in LaFeAsO_{1-x}F_x [5] which really caught the attention of the field and was rapidly followed by the discovery of even higher T_c materials, peaking at ~ 56 K [6]; the discovery of another family of unconventional superconductors was heralded. In contrast to experiences with the copper-oxide superconductors, single crystals of high quality were soon being produced, allowing detailed measurements of the physical and electronic properties, in particular measurements of the Fermi surface. The Fermi surface, the boundary between occupied and non-occupied electron states in the zero temperature limit which ultimately determines many physical properties, was soon the target of much experimental and theoretical effort. Quantum oscillations in high magnetic fields [7] quickly provided a general confirmation of the density-functional theory prediction of quasi-2D hole and electron pockets around the Brillouin zone center and corners respectively (with some modifications); it was also soon realised that this band structure favoured an unusual “ $s_{\pm}$ ” superconducting gap function in a

spin-fluctuation theory [8], while the magnetic state in the parent compounds could, from a purely itinerant point of view, be understood in terms of a spin-density wave transition driven by nesting between the hole and electron pockets. Since 2008 there has been an extensive effort to characterise electronic structures all across the Fe-based superconductors, with the two principle experimental methods being quantum oscillations and Angular-Resolved Photo-Emission Spectroscopy (ARPES), both of which are used in this thesis.

In this thesis I present an introduction to the iron-based superconductors in Chapter 2, including discussion of the crystal structures, phase diagrams and electronic structures, and the magnetic transitions in the parent compounds. I will also introduce LiFeAs and FeSe, which are the materials which are investigated in my subsequent chapters, and place them in the wider context of iron-based superconductors. In Chapter 3 I will discuss the various experimental methods used. However since these are numerous and generally well-documented I do not go into full details. In Chapter 4 I will discuss quantum oscillations in LiFeAs and the interpretation of the Fermi surface, also making comparison to literature reports. Chapters 5, 6 and 7 concern the properties of FeSe, a material which has been the subject of strong worldwide interest due to the opportunity to study the electronic structure in the presence of orthorhombic distortion of the lattice but without magnetic order. Chapter 5 concerns quantum oscillations measurements in very high magnetic fields, finding small Fermi surfaces which are attributable to hole and electron-like bands. Chapter 6 is an angle-resolved photo-emission spectroscopy study of FeSe, finding dramatic distortions of the Fermi surface below the structural transition. Chapter 7 consists of a study of the resistivity anisotropy of FeSe, finding a large and divergent response to an applied strain near T_s , which implies that the structural transition is electronically-driven. These three studies on FeSe are complementary and provide a complete and consistent, if slightly

complex, understanding of the development of the electronic structure. In Chapter 8 I discuss an unusual field-induced transition revealed by magnetic torque measurements in $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$, an iron-based superconductor with a rather more complex crystal structure. I finish with some general conclusions on the iron-based superconductors and FeSe in particular, and some outlook for future studies. The appendices contain characterisation measurements on FeSe, and additionally a speculative theory of why FeSe is not magnetic. The appendices will also include discussion of experimental results from earlier in my DPhil studies on $\text{Bi}_2\text{Ir}_2\text{O}_7$ and Mn-doped Bi_2Te_3 ; these systems are unrelated to iron-based superconductors and will be briefly introduced separately.

Chapter 2

Iron-based Superconductors

In this chapter I will present a broad overview of the structural, magnetic and electronic properties of Fe-based superconductors (FeBS)¹. Firstly, I will discuss the crystal structures and what is common to all FeBS, and discuss the features of the phase diagrams, and place LiFeAs and FeSe in context. I will then focus on the relationship between magnetism and the symmetry-breaking structural distortion of FeBS which relates in particular to the discussion of the experimental data on FeSe presented in Chapters. 5-7. Finally, I will discuss the understanding of the electronic structures of FeBS. Further discussion of the physics of FeBS may be found in several review papers [9, 10, 11] and a recent book [12].

2.1 Crystal structures of Fe-based superconductors

The common structural motif of Fe-based is the plane of Fe atoms arranged in a square lattice, with pnictogen (As,P) or chalcogenide (Se,Te) atoms providing tetrahedral co-ordination alternately above and below the plane, as shown in Fig. 2.1. This motif may be incorporated into several different crystal structures, forming phases with four-fold symmetry. In fact, several such compounds had been synthesised many years

¹Although the term “iron-pnictide superconductor” was widely used in early papers since As and P are from the pnictogen family, the discovery of superconductivity in Fe-chalcogenide phases (e.g. FeSe) has lead to the more general term “Fe-based superconductor” being used.

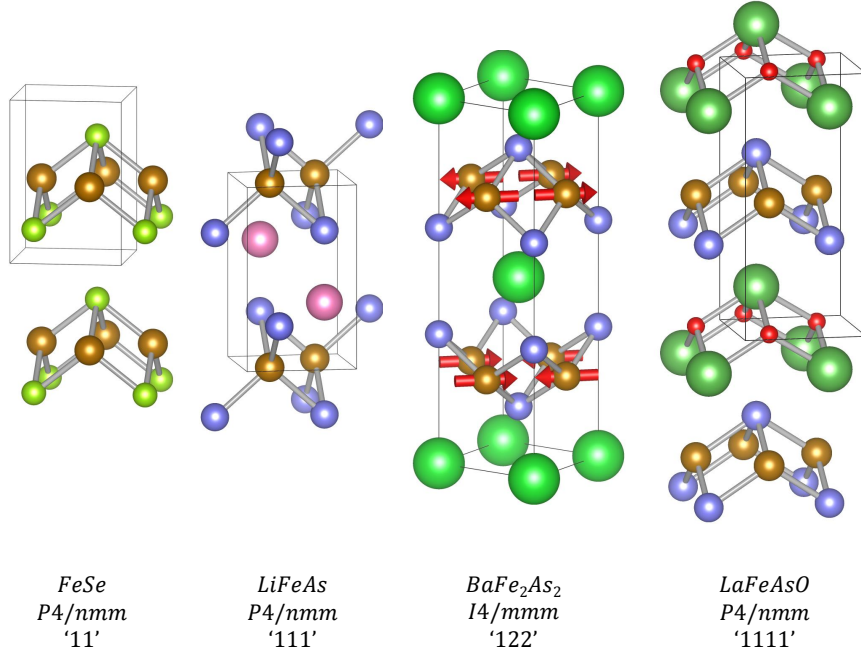


Figure 2.1: Crystal structures of selected Fe-based superconductors in their high-temperature, high symmetry phase. The crystallographic unit cell is drawn as light black lines; note that for $BaFe_2As_2$ this is a body-centered cell. For $BaFe_2As_2$ the magnetic stripe-order arrangement of the Fe spins are drawn, after Ref. [13]. Note that the low-temperature phases of FeSe, $BaFe_2As_2$ and LaFeAsO have lower symmetry due to the orthorhombicity and magnetic order.

before the discovery of superconductivity in these systems, e.g. LiFeAs in 1968 [14]. The different families are typically referred to by their stoichiometry: the '11' compounds ($FeSe$, $FeSe_{1-x}Te_x$), '111' ($LiFeAs$, $LiFeP$, $NaFeAs$), the '122' systems based on $BaFe_2As_2$, $CaFe_2As_2$, KFe_2As_2 etc. and the '1111' compounds e.g. $LaFeAsO_{1-x}F_x$ which was the first family in which high-temperature superconductivity was established in 2008 [5]. This is by no means an extensive list - it has been found that there are many possibilities for the structures separating the FeX layers, including thick perovskite layers in the '21311' phase [15], organic intercalates [16] and $Pt_{3/4}As_8$ layers as will be discussed in Chapter 8. Moreover, even within one family, the behaviour of '122' $BaFe_2As_2$ is rather different to $CaFe_2As_2$ (which has a collapsed-tetragonal phase) and $EuFe_2As_2$ (with magnetic ordering on the Eu^{2+} lattice) even though they

are formally isovalent.

This thesis is mainly concerned with ‘11’ and ‘111’ systems, however the comparisons and contrasts to the ‘122’ family in particular will be crucial to place these materials in context. Therefore the discussions in the following sections concern principally compounds based on BaFe_2As_2 as these are the most well-studied compounds. However, every family of Fe-based superconductors has their own subtleties.

2.2 Phase diagrams of Fe-based superconductors

The phase diagrams of Fe-based superconductors take a similar general form to other unconventional superconductors [17], such as heavy fermions, where superconductivity is found near the point where an antiferromagnetic phase is suppressed by a tuning parameter such as chemical substitution or pressure. The high temperature, high symmetry phase has four-fold symmetry and is paramagnetic. The superconducting phase has a characteristic dome-shaped structure. The composition with the highest T_c is commonly referred to as “optimally-doped”; the labels “under-doped” and “over-doped” are taken with respect to this point. As an under-doped sample is cooled down from the high-symmetry phase, the structural distortion breaks the four-fold rotational symmetry and subsequently the antiferromagnetic phase breaks spin-rotational and time-reversal symmetry. In the case of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, these two transitions are split by ~ 10 K, identifying a slim region which has been dubbed “nematic” due to the analogy to the nematic liquid crystal phase - the system has picked out a unique direction (x or y) but without a long-range magnetic order. In $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ this splitting of transitions is not resolved. It is clear from how the two transition lines track each other that these two transitions must be linked in some way, which is discussed in more detail in section 2.3.

It is worthwhile to consider what exactly the role of doping is. The simplest idea is a band-filling picture: the parent compound BaFe_2As_2 is a compensated metal,

having equal number of holes and electrons and the system tends to magnetic order due to nesting between the hole and electron pockets. Doping (for example by substituting an atom with more electrons than Fe onto the Fe site) will imbalance the sizes of the pockets, and disrupt the nesting such that the system does not order but retains a spectrum of antiferromagnetic spin fluctuations around the ordering vector, and these fluctuations may provide the pairing mechanism for superconductivity (see Ref. [18] and also Section 2.4). Studies which found that Ni doping (formally adding an extra 2 electrons on the Fe site) was twice as effective at destroying magnetism as Co doping [19] (which has one more electron than Fe) seemed to support these ideas. However, it is clear that this cannot be the whole story. $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ corresponds to isovalent substitution, and yet a similar phase diagram is found- although much more P on the As site is needed to reach the superconducting dome compared to Co on the Fe site. In this case it is likely that subtle changes to the electronic structure (e.g. Fermi surface alterations and relative importance of electronic interactions) cause the suppression of magnetism [20]. A similar phase diagram is also reached with isoelectronic Ru substitution onto the Fe site [21]. Furthermore, the effects of doping are very asymmetric; whereas in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ the end of the superconducting dome is reached by $x=0.13$, in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ superconductivity is found to extend right up until $x=1$, despite the end compound KFe_2As_2 having a very different Fermi surface morphology. Every phase diagram has its own subtleties, and not all features are generic - even within the subset of Fe-based superconductors deriving from BaFe_2As_2 .

As in the case of the copper-oxide superconductors, new phases continue to be found. For instance, in $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$, a new magnetic phase with restored fourfold symmetry was recently discovered [25] (not shown in the phase diagrams in Fig. 2.2). Furthermore, there are some disagreements between different reports. For instance it has been controversially claimed that tetragonal symmetry is actually broken about

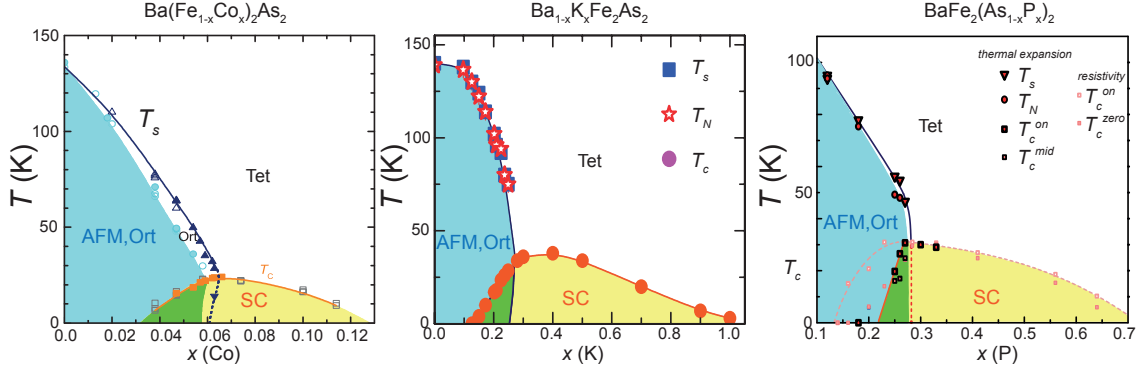


Figure 2.2: Phase diagrams of doped BaFe_2As_2 adapted from Refs. [22, 23, 24]. $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ corresponds to electron-doping. $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ is hole-doping. $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ corresponds to isovalent substitution. Note the different x axis scales between the diagrams.

100 K above “ T_s ” in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [26]. Sample homogeneity is particularly important near the crossing points of phase transition lines where there is a lot of interest in whether or not there is a nano-scale co-existence between superconductivity and magnetism.

2.2.1 LiFeAs and FeSe

Stoichiometric Fe-based superconductors have attracted a lot of interest since the crystal quality can be higher, and they are easier targets for theoretical models. In particular for quantum oscillations studies, stoichiometric systems are of interest due to the lower impurity scattering in high-quality crystals (Section 3.5). Having discussed the general features of the Fe-based superconducting phase diagrams, it is instructive to consider how the stoichiometric compounds LiFeAs and FeSe compare, since these are the subject of experimental chapters in this thesis.

LiFeAs has tetragonal symmetry at all temperatures and superconducts at ~ 18 K. However all attempts to dope it have not managed to increase the T_c [27], and furthermore a correlation has been reported between T_c and sample quality (likely to indicate the degree of stoichiometry) [28]. This information suggests that LiFeAs

roughly-speaking corresponds to an “optimally doped” composition on a general phase diagram of FeBS. In comparison, the closely related NaFeAs has a structural transition and a magnetic transition, with a small superconducting volume fraction, and may be understood to be a “slightly underdoped” composition and LiFeP, the other stoichiometric ‘111’ compound, may be considered as “over-doped” due to its lower $T_c \sim 5$ K. However there are some aspects of LiFeAs such as the large d_{xy} outer hole band which are quite unusual.

FeSe appears to sit in a very special region of parameter space, with a tetragonal-to-orthorhombic transition at ~ 90 K but no long-range magnetic order at any temperature. This has allowed a unique insight into the so-called “nematic” state with broken four-fold symmetry and is discussed at length later in this thesis. This phase is known to exist in a narrow region between the structural and magnetic transitions in under-doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ and in NaFeAs and the 1111 family. However, FeSe is certainly not near “optimal-doping” since it is known that T_c increases strongly from a modest 8 K to 37 K under pressure [29]. There is therefore no simple understanding of how FeSe compares to the Fe-pnictides and it is likely to have some unique features. It is worth also noting that there has been interest in $\text{FeSe}_{1-x}\text{Te}_x$ and $\text{FeSe}_{1-x}\text{S}_x$ ². However, FeTe is a strongly correlated non-superconducting system with a different (double-stripe) magnetic ordering [31], and the phase diagram at high Te content probably reflects different physics.

2.3 Magnetism and symmetry-breaking in the Fe-based superconductors

It is clear from the phase diagrams discussed above that a full understanding of the unconventional superconductivity in Fe-based superconductors requires an under-

²It is a little known fact amongst the quantum materials community that iron-sulfide compounds such as the end member of the $\text{FeSe}_{1-x}\text{S}_x$ series have been proposed to have been fundamental to the development of life on Earth, see e.g. Ref. [30].

standing of the magnetic state in the parent compounds - especially since the most common theories for the pairing mechanism involve spin fluctuations. The ground state of Fe-based superconductor parent phases is a single-stripe antiferromagnetic state³ as shown schematically in 2.3. The Fe spins align ferromagnetically along b and antiferromagnetically along a . This order naturally breaks four-fold rotational symmetry and would generally result in a small orthorhombic lattice distortion, as is observed. Since this thesis largely concerns electronic properties of FeBS, it is natural to take an itinerant view of the magnetism - i.e. that the magnetism in the parent compounds below ~ 150 K corresponds to a spin-density wave associated with the nesting of hole and electron sections of the Fermi surface, similar to the canonical spin-density wave behaviour in chromium [33]. However, one can also take a local-moment point of view, where the observed spin waves can be described in terms of a Heisenberg-like model, based on local magnetic interactions and usually used in magnetic insulators [32]. In reality, the magnetism is highly complex and neither the itinerant or local limits alone capture the behaviour [34, 35].

Intriguingly, in some systems, such NaFeAs and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, there is a splitting between the structural and magnetic transitions, the structural transition always occurring at a higher temperature. The question then arises - what is the origin of the structural transition in Fe-based superconductors? It has been argued that the structural transition is electronically-driven [36, 37] - meaning that this is not a regular phonon-driven structural transition, but it is the spin or charge degrees of freedom of the electrons which matter. There are, however, (at least) two competing theories, which I will refer to as “orbital ordering” and the “spin-nematic scenario” which I will discuss briefly since it is particularly relevant to the experiments on FeSe presented in this thesis. For a recent review, see Ref. [37].

As discussed, the magnetic ordering breaks both the fourfold lattice symmetry and

³An exception being FeTe[32].

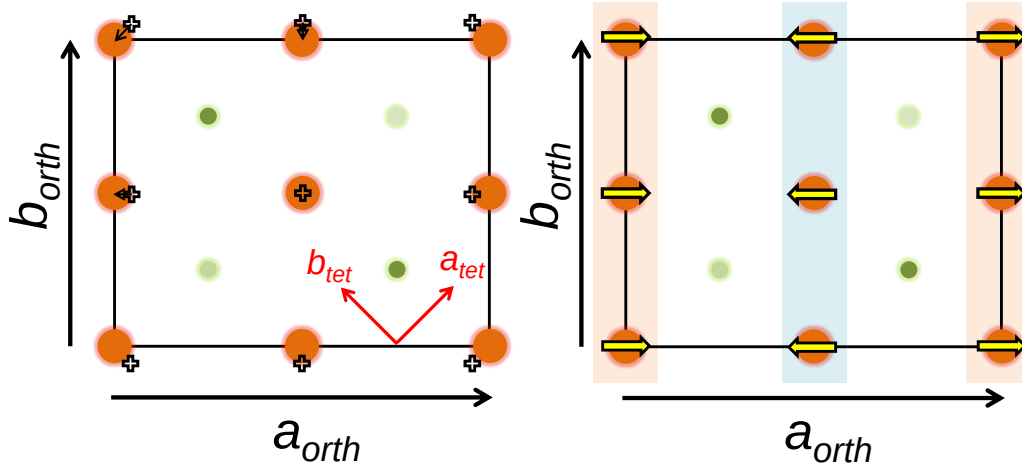


Figure 2.3: Left: Schematic of the orthorhombic transition in Fe-based superconductors. The orthorhombicity is greatly exaggerated. Below the orthorhombic transition Fe atoms (orange) undergo a fourfold-symmetry-breaking displacement from their original positions (crosses). Right: Schematic of the stripe ordering seen in iron-based superconductors. The Fe spins, which are typically $0.8 \mu_B$ are arranged ferromagnetically along the shorter b axis and anti-ferromagnetically along the longer a axis and is referred to as single-stripe order. Usually, the spins are arranged anti-ferromagnetically along the c axis (not shown).

spin-rotational symmetry as well as time reversal symmetry, and the phase diagrams show that the magnetic and structural phase transitions track each other very closely, including inside the superconducting dome (Fig. 2.2a), suggesting a close and perhaps causal connection between the two. In the spin-nematic scenario, the structural transition is driven by the same magnetic interactions as the eventual magnetic order, but a splitting between two transitions is allowed in some models which go beyond a mean-field treatment [37], where fluctuating moments correlate to break the lattice symmetry but do not order statically. These ideas have been successfully applied to various experimental data, such as the elastic constants [38], resistivity anisotropy [39, 40] and NMR data [41]. Importantly, the spin-driven scenario favours *repulsive* inter-pocket interactions⁴ and the so-called $s_{\pm}$ superconducting gap function i.e. the

⁴Here I am anticipating the fact that Fe-based superconductors have hole and electron Fermi

gap has opposite sign (or phase) on the hole and electron pockets.

The orbital scenario [42] puts less weight on the spin degrees of freedom but rather asserts that the highest energy scales in the system are the *orbital* interactions out of which one can obtain an attractive inter-pocket interaction in band-space, favouring a ferro-orbital order⁵ and s_{++} superconductivity (that is, no sign changes of the gap between pockets). In this case, any magnetic ordering is a secondary instability. Again, this theory has been shown to be able to explain various experimental data such as the elastic constants [43]; moreover the unequal occupancy of d_{xz} and d_{yz} orbitals and resulting deformation of the Fermi surface has been directly observed below T_s in NaFeAs and will be found in FeSe in this thesis.

It has been recently claimed that the origin of the structural transition FeSe is not magnetic [44, 45, 46], presenting a large problem for proponents of the spin-nematic scenario. The experiments presented in this thesis do not directly probe magnetism or magnetic fluctuations in FeSe, but are generally in support of the orbital ordering scenario. Whether or not these discoveries in FeSe have a wider applicability is a question under current debate.

2.4 Electronic structures of Fe-based superconductors

It is clear that a detailed understanding of the electronic structure of Fe-based superconductors is required to understand the mechanism behind the unconventional superconductivity and reasons for differences between materials. In this section I will use the ideas of band structure, reciprocal space and Fermi surfaces freely, which are introduced briefly in Section 3.1 and can be found in several textbooks (e.g. [47]). In Fe-based superconductors, the electronic bands near the Fermi level arise from the

surfaces at different points of the Brillouin zone as will be discussed in section 2.4.

⁵The description of “ferro-orbital order” refers to the fact that the change in orbital occupancy is the same for every Fe site.

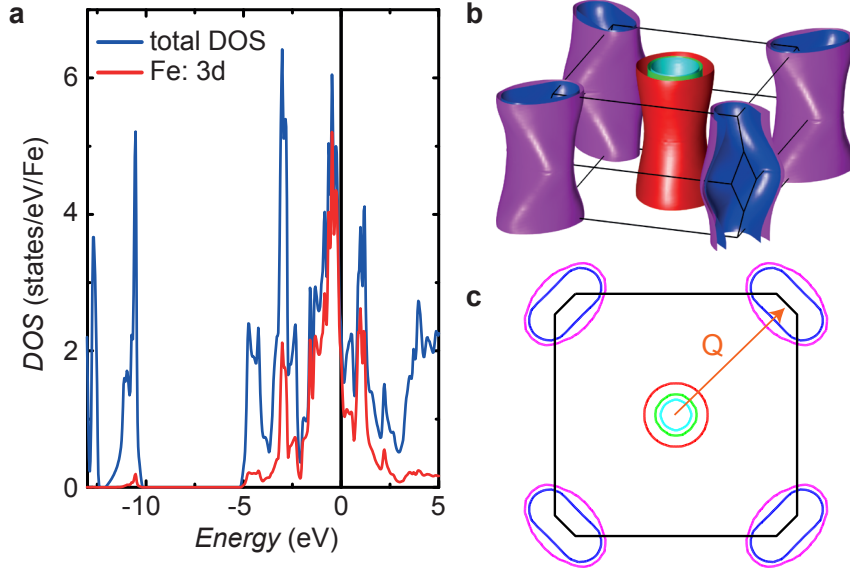


Figure 2.4: Electronic properties of BaFe_2As_2 as calculated by density functional theory (Wien2k) in the tetragonal paramagnetic phase. a) Density of States (DOS) and partial Fe-3d density of states, showing that these states dominate the bands near the Fermi level. b) Fermi surface of BaFe_2As_2 , composed of 3 hole-like bands at the Brillouin zone centre, and 2 electron bands at the Brillouin zone edge. c) Slice of Fermi surface at $k_z = 0$.

3d shell of Fe, as shown in Fig. 2.4a. Fe^{2+} has 6 electrons in the 3d shell, meaning that stoichiometric compounds such as BaFe_2As_2 and LiFeAs are compensated metals with an equal number of holes and electrons. One immediate complication is that the high-temperature primitive unit cell contains two Fe atoms per unit cell; in the literature an effective 1-Fe cell is sometimes considered by theoreticians and some of the neutron-scattering community, however in this thesis I will use the crystallographic 2-Fe unit cell unless explicitly stated.

Considering first the electronic structure of the high-symmetry paramagnetic phase, the typical picture arising both from Density Functional Theory calculations (see Section 3.6) and experiment consists of up to three quasi-2D hole pockets around the centre of the Brillouin zone with two electron-like pockets centred at a corner of the Brillouin zone, as shown in Fig. 2.4b for BaFe_2As_2 ⁶. The band structure reflects the

⁶A minor complication is that the $I4/mmm$ space group of BaFe_2As_2 is a body-centred cell; for LiFeAs and tetragonal FeSe the simpler $P4/nmm$ space group gives a simpler cuboid Brillouin zone.

layered crystal structure having poor inter-layer charge transport giving rise to the quasi-2D Fermi surfaces and means that the gross features of the electronic structure are determined by the FeAs plane and do not depend strongly on what is in between the FeAs (or FeSe etc) layers. This general picture was experimentally verified [7] for LaFePO soon after the discovery of Fe-based superconductors and forms the basis for the further discussions. One immediately apparent [8] property of this unusual quasi-2D Fermi surface is that there is good “nesting” of the hole and electron Fermi surfaces - that is, that a wavevector of $\mathbf{Q} = (\pi/a, \pi/a)$ (2-Fe cell) would map hole-like sections of the Fermi surface onto the electron sheets, as shown in Fig. 2.4c. More formally, the Lindhard dielectric response function $\chi(\mathbf{q})$ will be strongly peaked around $\mathbf{q} = \mathbf{Q}$ and this will give rise to spin-density waves with ordering vector $\mathbf{Q}$. If the nesting is imperfect, for instance due to the charge balance being altered by doping, then no static order will be formed but spin fluctuations may occur and are candidates for providing the superconducting pairing interaction between electrons [18]. However, this mechanism may depend delicately on the details of the Fermi surface - i.e. the exact sizes of the Fermi surface pockets, the quasiparticle effective masses, the orbital characters and the k_z dispersions. Experimental determinations of the electronic states near the Fermi level and their development across the phase diagram are therefore of high value, and this forms the motivation for most of this thesis, and experimental techniques for doing this will be presented in the following chapter.

Chapter 3

Theory and Techniques

In this Chapter I will introduce some of the experimental methods used in this thesis: torque magnetometry, resistivity, angle-resolved photo-emission spectroscopy and quantum oscillations, as well as techniques for the generation of high magnetic fields. Additionally, I will introduce a few theoretical concepts, such as electronic band structure, the Fermi surface and density functional theory - from the point of view of an experimentalist. While these techniques are numerous and disparate, the common theme is that these are experiments which, when applied to good single crystals and correctly interpreted, reveal information about the electron or magnetic properties of the system.

3.1 The Fermi surface

This thesis essentially concerns some properties of some metals¹. Often metals are defined by their good thermal and electrical conduction properties, but for the purposes of this thesis, they can be defined as crystalline materials with a Fermi surface. To briefly introduce this concept, which is fundamental to explaining transport and other physical properties and is probed by quantum oscillations measurements, I will make a detour to revisit the building blocks of band theory.

In a periodic lattice of atoms, the solutions of the single-electron Schrödinger

¹Which was briefly considered as the title of this thesis.

equation are Bloch waves:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (3.1)$$

where n is a band index, and $\mathbf{k}$ is the ‘crystal wavevector’ [48]. For each band, a function $\epsilon_n(\mathbf{k})$ is constructed from the eigenvalues, which is the dispersion relation for electrons in that band. The electrons obey Fermi-Dirac statistics, that is, the available energy states are filled up to a characteristic energy known as the Fermi level (at $T = 0$ K). The surface of states in $\mathbf{k}$ -space with energy equal to the Fermi level is called the Fermi surface; it is the boundary between occupied and non-occupied electron states and it is electrons near this which can scatter and dominate charge (and heat) transport in a metal, whereas in an insulator, the Fermi level sits in a gap between bands rather than in the middle of a band, and therefore there is no Fermi surface, or in secondary-school language, “no free carriers”. The dispersion relations $\epsilon_n(\mathbf{k})$ can give rise to a situation where the Fermi level sits just below a maximum of a band dispersion. Since a full band does not contribute to conductivity, it is often more convenient to consider instead of a nearly-full band of electrons, a small carrier density of *holes* which behave as if they had positive charge. The topology of a Fermi surface reflects the symmetry and structure of the lattice, for instance the iron-based superconductors have a layered structure which is reflected in the quasi-2D Fermi surfaces, as shown in Fig. 2.4; moreover the Fermi surface consists of both hole-like and electron-like carriers, in equal number for the stoichiometric compounds. The dispersion relations $\epsilon_n(\mathbf{k})$ are defined within a ‘Brillouin zone’ due to the periodicity of reciprocal space and the Bloch theorem [47].

3.2 Resistivity in metals

Measuring the resistivity of a metallic sample as a function of temperature and magnetic field is one of the most basic characterisation measurements, but contains a

large amount of information. For instance, it is obvious that both superconductivity and a metal-insulator transition will give unmissable signatures in resistivity at the transition temperature. However, even more subtle changes such as charge density-waves (e.g. in NbSe₂) or structural transitions (e.g. in Fe-based superconductors, IrTe₂) or magnetic transitions (e.g. in Mn-doped Bi₂Te₃²) will leave a signature in resistivity, as they alter either the band structure of the material or the scattering rates. Furthermore, even in the absence of any transitions, the resistivity contains important information about scattering mechanisms. For instance, at room temperature, the dominant scattering mechanism is usually scattering from phonons, whereas in the $T = 0$ limit only impurity scattering remains; therefore the residual resistivity ratio $RRR = R(300\text{ K})/R(0\text{ K})$ can be thought of as an indication of the quality of the sample since a good sample will have a low impurity scattering rate and a large RRR. Moreover, the temperature-dependence of resistivity may give information on the type of scattering processes, for example materials which behave as a Fermi liquid (with well-defined quasi-particles) should typically give rise to $\rho = \rho_0 + AT^2$ at low temperature due to electron-electron scattering.

3.2.1 Magnetoresistance and the Hall effect

Magnetoresistance, the change in resistance in response to an applied magnetic field, can provide important information about the Fermi surface, in particular when analysed in combination with the Hall effect, which is the electric field generated perpendicular to both the current and the magnetic field. The Hall effect arises due to the Lorentz force acting to change the trajectory of electrons in the presence of a magnetic field. The geometry under consideration is a current along the x axis of a sample with a magnetic field along the z axis (assumed to be a high-symmetry axis). Then, $\mathbf{E} = \rho \cdot \mathbf{j}$, where the resistivity tensor ρ relates the electric field $\mathbf{E}$ to the current density $\mathbf{j}$ and is given by

²Choosing examples which have been measured recently by me or my group.

$$\rho = \begin{pmatrix} \rho_{xx} & -\rho_{xy} \\ \rho_{xy} & \rho_{xx} \end{pmatrix} \quad (3.2)$$

Where we have $\rho_{yx} = -\rho_{xy}$ and $\rho_{yy} = \rho_{xx}$ by symmetry [48]. In the simple one-band Sommerfeld model, the Hall effect is strictly linear in magnetic field ($\rho_{xy}(B) = R_H B = -B/ne$) and dependent only on the carrier density n (i.e. independent of the scattering time), and there is no magnetoresistance ($\rho_{xx} = 1/|ne\mu|$, μ being the mobility) [48], but magnetoresistance does naturally arise when there is more than one type of carrier, and in a multiband system the Hall effect can be non-linear and additionally quantum oscillations can be observed in ρ_{xy} . This can be easily seen by considering multi-band models, where the total resistivity is given by $\rho = (\sum_i \rho_i^{-1})^{-1}$, i.e. the *conductivity* matrices (the inverse of the resistivity matrices) add³. The simplest case is a two-band model with carrier densities n_i and mobilities μ_i , where I have:

$$\rho_i = \begin{pmatrix} \frac{1}{\sigma_i} & -R_i B \\ R_i B & \frac{1}{\sigma_i} \end{pmatrix} \quad (3.3)$$

Where for convenience I have introduced $\sigma_i = |n_i e \mu_i|$ and $R_i = -1/n_i e$. Then the elements of the total resistivity tensor are given by:

$$\rho_{xx} = \frac{(\sigma_1 + \sigma_2) + \sigma_1 \sigma_2 (\sigma_1 R_1^2 + \sigma_2 R_2^2) B^2}{(\sigma_1 + \sigma_2)^2 + \sigma_1^2 \sigma_2^2 (R_1 + R_2)^2 B^2} \quad (3.4)$$

$$\rho_{xy} = \frac{(\sigma_1^2 R_1 + \sigma_2^2 R_2) + \sigma_1^2 \sigma_2^2 R_1 R_2 (R_1 + R_2) B^2}{(\sigma_1 + \sigma_2)^2 + \sigma_1^2 \sigma_2^2 (R_1 + R_2)^2 B^2} B \quad (3.5)$$

Now, ρ_{xx} has an explicit field-dependence, and ρ_{xy} can be non-linear. Furthermore, these equations suggest that in the high-field limit, the magnetoresistance should saturate, and the Hall effect should be linear. The one exception is when $R_1 = -R_2$, i.e. for a compensated system and the two carriers are now associated with electron and hole-like bands, when a cancellation in the denominator means that the magnetoresistance does not saturate; FeSe is best modelled as such a system.

³Analogously to resistors in parallel.

However, the Hall coefficient now depends on scattering times (here encoded in the mobilities), and therefore quantum oscillations may be observed in the Hall effect in a multiband system⁴. One notable feature that comes straight out of this model is that for low carrier densities, both the Hall effect and resistivity become much larger.

Extending the analysis to three or more bands makes the equations much more complex; and the matrix formulation as presented in Ref. [50] becomes helpful. Chapter 5 will make use of both 2- and 3-carrier models to understand measurements of the resistivity and Hall effect in FeSe, using simultaneous fitting to both ρ_{xx} and ρ_{yx} to extract information about carrier densities and mobilities. In order to simplify this procedure I implemented the 2- and 3-carrier fits in MATLAB with a convenient user interface. Transport in metals can be treated on many different levels of complexity [47] but for the purposes of understanding and modelling experimental data such as that presented in Chapter 5, simple models with a relatively few number of parameters can give some insight into the physics, even when some of the underlying assumptions (e.g. the relaxation time approximation) may not stand up to detailed scrutiny.

It is worth noting that if the system is magnetic, or near a magnetic or superconducting transition, there can be other contributions to the magnetoresistance which do not arise from the consideration of Lorentz forces in a metal described above. Moreover the assumption that the mobility is field-independent will not hold and the shape of the Fermi surface also becomes relevant when treating transport in a semi-classical way [47].

3.2.2 Techniques for the measurement of resistivity

Measuring the resistivity of a sample is conceptually straightforward but often practically challenging. The ideal sample morphology is a uniform, thin and long oblong

⁴Quantum oscillations in magnetotransport are usually understood to occur through oscillations in the scattering rate[49], as will be discussed Chapter 5.

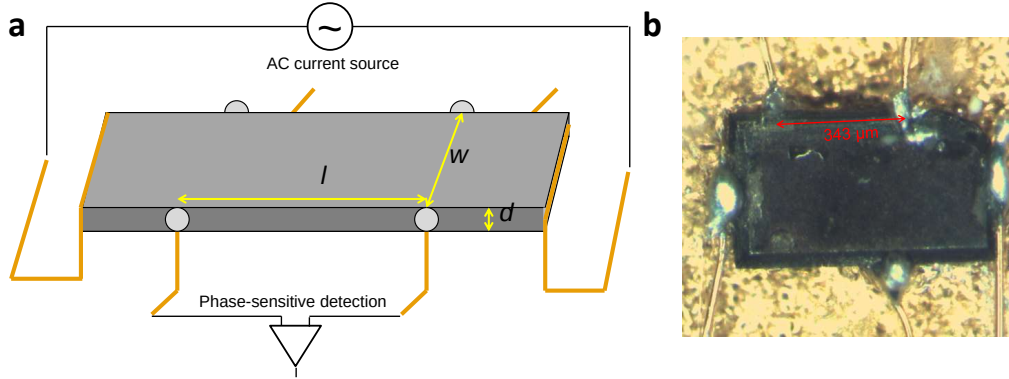


Figure 3.1: a) Idealised resistivity measurement. b) Microscope photograph of actual sample (S3) of FeSe used for resistivity and Hall effect measurements in the PPMS, presented in Chapter 5.

sample as shown in Fig. 3.1; since $R = \rho \times l/wd$ this will give a large signal to be measured. Ohmic current contacts are placed on each end of the sample, attached to a current source, and small voltage contacts are placed on the side or top of the sample. Using this four-wire measurement means that the measured voltage does not include any contribution from the lead wires or contacts⁵.

Resistivity measurements on real samples are usually much more challenging than the simple picture presented in Fig. 3.1a. The samples measured in this thesis are typically layered materials which cleave or grow to give samples of approximately uniform thickness and the top/bottom surfaces normal to the c axis - but the crystals are invariably small (usually much less than 1mm) and never form perfect oblongs. While the samples can sometimes be cut into more regular shapes, crystals can easily be damaged by such manipulations, or are too small to start with to be cut to shape.

Making good electrical contacts to small single crystal samples can often be a struggle, since it depends on surface chemistry. For the iron-based superconductors, a method of making excellent contacts between a sample and metallic lead wires (typically $25\mu\text{m}$ Au wires are used) was reported by Tanatar *et. al.* [53] (and patented

⁵Here I will describe the standard four-probe resistivity measurement, which I used in this thesis. However, both the Van der Pauw [51] and Montgomery [52] methods have advantages for certain sample geometries.

by the authors [54]) by soldering directly to the samples using pure tin and a suitable flux. Contacts made by this method are not only low resistance, but also mechanically strong and reliable when cooling the sample. In my experience, this method works very well for the “122” compounds (BaFe_2As_2) and does work on FeSe, although the contacts are less robust in that case; moreover soldering directly to samples works well for $\text{Bi}_2\text{Se}/\text{Te}_3$ compounds, and perhaps surprisingly, $\text{Bi}_2\text{Ir}_2\text{O}_7$. Indium may be used in place of tin in most cases, and requires a lower soldering iron temperature. Another technique is to use a silver-based epoxy, either curing at room temperature (e.g. Dupont 4929N) or at a higher temperature (e.g. the two-part Epotek H20E epoxy) on a hot-plate. However, these contacts (especially those made with 4929N) are electrically poor, mechanically unreliable, give noisy data, deteriorate over time and often break or give rise to spurious jumps in resistivity when the sample is cooled. Further techniques include spot welding, evaporating gold contact pads and “sparking” epoxy contacts⁶. Ideally, voltage contacts should be small compared to the sample dimensions, but it is often a good idea to try to make the current contacts sufficiently large to effectively short out each end of the sample and ensure a uniform current flow; this is especially important for samples with highly anisotropic conductivities. Measuring samples using AC rather than DC measurement techniques is an advantage not only in order to take advantage of lock-in signal recovery techniques, but additionally to negate the effect of thermal voltages [48]. Due to inevitable contact misalignment when contacts are made by hand, it is common to symmetrise data taken in positive and negative magnetic fields in order to correctly separate resistivity (ρ_{xx}) which is symmetric from the ‘Hall resistivity’ ρ_{xy} which is anti-symmetric in the applied magnetic field. Further considerations for performing good resistivity measurements may be found in Ref. [48].

⁶In some cases, the contact resistances of silver epoxy contacts can be improved from $\sim 100\ \Omega$ to $\sim 1\ \Omega$ by discharging a capacitor across the sample once or twice. However, multiple discharges tend to make the contact worse.

3.2.3 Resistivity in pulsed magnetic fields

Measuring resistivity in a pulsed magnetic field provides unique challenges. Firstly, geometrical loops in the measurement circuit give a very large pick-up proportional to dB/dt and must be avoided, and the twisted pairs which carry the current/voltage are brought as close as practical to the sample. Furthermore all wires must be fixed to avoid vibrations. Large area samples are not ideal due to eddy current heating, however having a thin sample is important for maximising the signal, and the sample should be stuck to a quartz or sapphire substrate with good thermal conductivity. The measurements are necessarily performed at high excitation frequencies, on the order of 10 kHz. However, if there are parasitic capacitances in the wiring or contacts then measurements can pick up signal in the out-of-phase channel, which must be avoided if the absolute value of resistance is important. Furthermore large currents are often used to increase the size of the signal, requiring excellent contact resistances to avoid sample heating effects. Nevertheless, I will show resistivity data obtained in pulsed magnetic fields in Chapters 5 and 8, in both cases the samples were mounted in such a way that a good signal was achieved.

In Chapter 7 I will present measurements of the resistivity anisotropy in FeSe and will describe details of the method there; however the basic considerations of a reliable, low-noise resistance measurement as described here still apply.

3.3 Magnetic torque measurements

Cantilever-based torque magnetometry has become commonly used in the high magnetic field community due to the very high sensitivity and suitability for small crystalline samples. Magnetic torque $\tau = \mathbf{M} \times \mathbf{B}$ (in the absence of field gradients [55]) is a thermodynamic probe (in the sense that it can be written as a derivative of a free energy with respect to rotation about an axis) but it is a probe of magnetic anisotropy rather than magnetization itself - which can be a rather more complex

problem. This can be seen directly from the fact that if there is no anisotropy in the sample, the magnetization $\mathbf{M}$ would point along the direction of the magnetic field $\mathbf{B}$ and their cross-product would be zero. For simple cases such as the uniaxial paramagnet, the torque follows a simple analytical formula as discussed below, but in more complex situations it can become very difficult to analyse. The great strength of torque magnetometry lies in its very high sensitivity for measuring field-induced phase transitions and quantum oscillations on small samples; the drawback is that understanding and calibrating the overall signal can be very difficult.

Consider a paramagnetic sample, in the case that the system has a field-independent, uniaxially anisotropic susceptibility tensor. Although the end result would follow naturally from consideration of $\mathbf{M} = \chi \mathbf{H}$, χ being a 3×3 matrix, the free energy formulation presented here is analogous to later work on the antiferromagnetic case in Chapter 8, so I first write down a free energy, and then calculate torque:

$$F = -\frac{1}{2} (\chi_{\perp} \sin^2 \theta + \chi_{\parallel} \cos^2 \theta) \mu_0 H^2 \quad (3.6)$$

Where θ is the angle between the applied magnetic field and the uniaxial symmetry axis. Torque can be found by calculating $\tau = -\partial F / \partial \theta$. Intuitively, torque is the tendency of a system to rotate about some axis in order to minimize its free energy. Therefore

$$\tau = -\partial F / \partial \theta = \frac{\mu_0}{2} (\chi_{\perp} - \chi_{\parallel}) H^2 \sin 2\theta \quad (3.7)$$

This is a simple case, however in many layered systems a $\sim B^2$ dependence is observed in torque - including many Fe-based superconductors in their normal state (beyond any hysteretic region which is observed in magnetic torque when the sample is in the superconducting vortex lattice phase). However, note that for cubic or other symmetry the anisotropy takes a different form (due to the different symmetry constraints), and a $\sim B^2$ dependence is not to be expected in general. Note also the

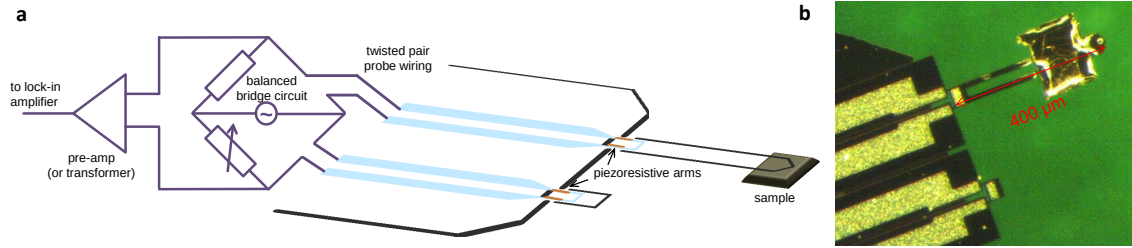


Figure 3.2: a) Schematic of the measurement of microcantilevers suitable for high magnetic field experiments. b) Photograph of a lever mounted with a sample of an iron-based superconductor.

general property that if there is no anisotropy (i.e. $\chi_{\parallel} = \chi_{\perp}$) then there is no torque.

One method of measuring magnetic torque is the piezo-resistive microcantilever technique, shown in Fig. 3.2. The cantilevers are manufactured by SEIKO systems and designed for Atomic Force Microscopy, but happen to be very suitable for this very different measurement. The model used for DC field measurements is usually the PRC400⁷, whereas for pulsed magnetic fields the shorter PRC120 lever is better due to its higher eigenfrequency [56] and strength. The cantilever is suitable for plate-like samples with typical dimensions $\sim 150 \times 150 \times 50 \mu\text{m}$ - although when a large signal is expected, e.g. for a magnetic sample with strong anisotropies, a smaller sample should be considered. My group has found that the simplest method of fixing a sample onto the cantilever is to use a very small amount of Apiezon N grease, carefully bringing the sample onto the lever by a flexible tool such as a thin piece of hair attached to a cocktail stick; the grease freezes at low temperature to secure the sample, but after an experiment the samples may be carefully replaced on the lever which is not possible with the epoxy bonds preferred by other groups. The lever is suspended from the substrate by thin piezoresistive arms; when a torque is generated in the sample the stress due to the deflection of the lever generates a small change in resistance of the arms (a linear response unless the signal becomes large).

⁷Unfortunately, SEIKO discontinued the PRC400 and PRC120 cantilevers in 2014, much to the concern of the high-field community.

The design of the cantilever includes a lever and an almost identical dummy. The small change in resistance of the piezoresistive element is measured in a bridge circuit such that any spurious signal arising from e.g. the magnetoresistance of the chip or wiring is compensated by balancing the lever against the dummy such that only the contribution of the torque of the sample is measured. A sensitive measurement is achievable by using an AC excitation (no more than $\sim 75\mu\text{A}$ for measurements in He-3 to avoid heating effects) with low-noise amplification and lock-in measurement techniques (typically using the SR830 lock-in amplifier).

This method has several advantages. Very small samples are suitable for measurement, which is desirable both because of the greater crystalline homogeneity usually possible in small crystals, and often materials of interest are only available as small crystals. Furthermore the technique can be very sensitive - a magnetic moment sensitivity of 10^{-14} J/T was estimated in Ref. [55]. The cantilevers are suitable for use in high magnetic fields, very low temperatures and in confined experimental spaces and have found widespread use in high field research, particularly for the observation of quantum oscillations (e.g. Refs. [57, 58, 7, 59]) in recent years. However the drawbacks are that they are difficult to calibrate and measure torque rather than isotropic magnetisation which can make the interpretation difficult as discussed above.

3.4 Generation of high magnetic fields

The generation of strong magnetic fields relies on the fact that a current passed through loops of wire (a solenoid) generates a magnetic field. This thesis includes data obtained in several different magnet systems, which can be classified into three groups.

Firstly, I have used superconducting magnet systems in Oxford. The current in this case is carried by superconducting wires, usually based on thin filaments of conventional Type II superconductors NbTi or Nb₃Sn inside a copper matrix; the

magnet is cooled by sitting inside a bath of liquid helium such that the wires are in the superconducting phase. The biggest superconducting magnet in Oxford can generate 21 T which is near the limit of currently commercially-available magnets. Superconducting magnets have the advantage of being relatively cheap to run (the major cost being the liquid helium required to cool the system) and tend to give good field homogeneity and stability.

However often it is desirable to reach higher magnetic fields - either to access a phase transition above ~ 21 T (e.g. H_{c2} in a high- T_c superconductor) or for the purposes of measuring quantum oscillations, the amplitude of which grow strongly with magnetic field. One method to generate such fields is to pass large currents through a resistive magnet - along with high-pressure cooling water. These DC field resistive magnets, based on the Bitter design [60], can consume large amounts of electrical power - typically 20 MW at peak field. I have primarily used 33 T magnets at the DC field facility in Nijmegen, The Netherlands, where an all-resistive 37.5 T magnet has recently been built and is the state of the art [61]. The largest DC-field magnet is the hybrid magnet in Tallahassee, which can generate 45 T with a resistive magnet inside a wide superconducting magnet which provides an extra ~ 11 T [60], which was used to collect the data presented in Chapter 4.

The final option for the generation of high magnetic fields is to generate a very large current in a coil for a short time, by discharging a large capacitor (up to 6 MJ in Toulouse, France where my pulsed field measurements were performed). This creates very large stresses on the magnets due to Lorentz forces, and the magnets will usually fail after a few hundred pulses. The measurement environment is very challenging - due to eddy current heating, vibrations and unwanted signal pick-up due to the high dB/dt . However, pulsed magnetic fields are the only method of generating magnetic fields above 45 T. This thesis includes data taken at up to 88 T in a pulsed-field magnet in Toulouse; field strengths over 100 T are now available at NHMFL, Los

Alamos, US.

3.5 Quantum Oscillations as a probe of the Fermi surface

Experimental determinations of the Fermi surface are of clear importance for understanding the behaviour of metals, and provide a target for calculations of the electronic structure. In particular, when the system undergoes an electronic instability, such as a spin-density wave or even superconductivity, detailed knowledge of the Fermi surface will help to give clues as to the mechanism. In this thesis, I use two rather different techniques to probe the electronic structure and Fermi surface - quantum oscillations and angle-resolved photo-emission spectroscopy (ARPES). Quantum oscillations may be used to study the volume and shape of a Fermi surface, and the quasiparticle effective masses, and occasionally more detailed information such as the g -factor or Berry's phase may be extracted from high-quality data sets. Furthermore for certain systems there is a field-dependence to either the frequencies [62], effective masses [63] or phase [64] of the quantum oscillations due to the presence of or proximity to phase transitions. However in general, quantum oscillations cannot provide information on the location of Fermi surfaces within the Brillouin zone, and cannot specify the type (i.e. electron or hole) of carrier. Nowadays quantum oscillations are routinely compared to Density Functional Theory calculations (see 3.6) to obtain a satisfactory understanding of the Fermi surface.

The measurement of quantum oscillations is a well-established technique for probing the Fermi surface. Oscillations in various physical properties such as the magnetisation arise from considerations of the constraints on the motion of electrons in the presence of a large magnetic field. Detailed discussions may be found in several theses [65, 66, 67] and the definitive book by Shoenberg [49]; here I reproduce only some essential features of the theory.

In the presence of an applied magnetic field, a semiclassical treatment shows that the quasiparticles move along surfaces of constant energy in $\mathbf{k}$ -space perpendicular to the applied magnetic field; moreover the *areas* of the allowed orbits in $\mathbf{k}$ -space are quantised [48]:

$$A(l, B) = (l + \lambda) \frac{2\pi e B}{\hbar} \quad (3.8)$$

The quantisation of the areas in $\mathbf{k}$ -space leads to the idea of ‘Landau tubes’ - i.e. the surfaces of allowed electronic states in the presence of a magnetic field. For an isotropic dispersion, the Landau tubes are cylinders, but in general are just defined by constant energy paths in planes normal to the direction of the applied magnetic field. The quantisation of areas corresponds to a quantisation of the energy of the Landau tubes, which are separated by $\hbar\omega_c$, where $\omega_c = eB/m^*$ is the cyclotron frequency. As the magnetic field is increased, the areas of the tubes grow and will periodically “pop out” of the Fermi surface and depopulate. In particular, whenever a Landau tube reaches an *extremal* area (for a given magnetic field direction) a large modulation of the density of states at the Fermi level will occur, with a characteristic periodicity in *inverse* magnetic field, since a Landau tube will pass through an extremal area A_{ext} with a periodicity Δ :

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar} \frac{1}{A_{ext}} \quad (3.9)$$

These ‘quantum oscillations’ are usually described in terms of a frequency F , with units of Tesla, given by:

$$F = \frac{\hbar}{2\pi e} A_{ext} \quad (3.10)$$

This is known as the ‘Onsager relation’ and is extremely powerful since it simply and directly relates the frequency of oscillations observed in thermodynamic or transport properties to extremal areas of the Fermi surface. In general there may be several

such extremal Fermi surfaces for a given material, depending on the complexity of the band structure. The depopulation which occurs as Landau tubes pass through an extremal area of the Fermi surface leads to sawtooth-like modulations of the free energy at $T = 0$ (in the absence of other dephasing factors). In order to understand the resulting experimental signatures, I begin by taking a full expression for a thermodynamic potential Ω as a function of magnetic field which is conveniently expressed as a Fourier series [65, 49] with the fundamental frequency given by Eq. 3.10:

$$\Omega = \left(\frac{e}{2\pi\hbar}\right)^{\frac{3}{2}} \frac{e\hbar B^{\frac{5}{2}}}{m_0\pi^2} \left| \frac{\partial^2 A_{ext}}{\partial k_{\perp}^2} \right|^{-\frac{1}{2}} \sum_{p=1}^{\infty} p^{-\frac{5}{2}} R_{tot} \cos \left[2\pi p \left(\frac{F}{B} - \gamma \right) + \frac{1}{2} \right] \quad (3.11)$$

Where B is the applied magnetic field (more properly H) F is the de Haas-van Alphen frequency, $\left| \frac{\partial^2 A_{ext}}{\partial k_{\perp}^2} \right|^{-\frac{1}{2}}$ is known as the “curvature factor” and R_{tot} accounts for various possible damping terms,

$$R_{tot} = R_T R_D R_s R_{mos} \dots \quad (3.12)$$

which occur due to finite temperature, impurity scattering, spin-splitting, crystal mosaicity and several other possible damping terms which can be defined.

3.5.1 Damping terms for quantum oscillations

Finite Temperatures

At $T = 0$, the Fermi surface is perfectly sharp; that is the Fermi-Dirac function which describes the occupancy of states is a step function. However, at finite temperatures, states within $\sim k_B T$ of the Fermi level may be occupied, which may be thought of as giving rise to a superposition of oscillations with slightly varying phase, causing destructive interference and suppression of the amplitude compared to the $T = 0$ case. This idea of “phase smearing” is also applicable to other damping terms, such as that caused by field inhomogeneity [49] which are not discussed here.

The thermal damping term R_T is given by

$$R_T(B, T) = \frac{X}{\sinh X}, \quad X = \frac{2\pi^2 k_B T m_{therm}^*}{e\hbar B} \quad (3.13)$$

Intuitively, X is proportional to $\frac{k_B T}{\hbar\omega_c}$ - the ratio of the thermal energy to the energy spacing of the Landau tubes. R_T is the only term which has a temperature-dependence, therefore by fitting the temperature-dependence of the amplitude of oscillation (usually extracted by Fourier analysis) to Eq. 3.13 the effective mass m_{therm}^* may be extracted.

Damping from impurity scattering

The so-called ‘Dingle term’ arises from consideration of the damping of oscillations due to scattering. Since quantum oscillations are usually measured near the $T = 0$ limit, it is usually the impurity scattering mechanism which is relevant. Via the uncertainty principle, the finite lifetime corresponds to a broadening of the Landau energy levels [49]. The ideas of phase smearing can be used again since now the Landau tubes are blurred. The scattering term R_D is given by [49]

$$R_D(B) = \exp\left(-\frac{\pi m_b}{eB\tau}\right) \quad (3.14)$$

Where m_b is a band mass, i.e. the effective mass as calculated in DFT [68] rather than the thermal mass. It is important to notice that the scattering time τ entering here corresponds to a “quantum lifetime” - that is, the time spent in a momentum eigenstate (in zero field) and includes both small and large-angle scattering processes [69]. This is likely to be a shorter time than the “transport lifetime” - i.e. the time taken to fully randomize the momentum of an electron which could correspond to several small-angle scattering processes.

Eq. 3.14 is commonly rewritten as [69, 68]

$$R_D(B) = \exp\left(-\frac{\pi}{lB} \sqrt{\frac{2\hbar F}{e}}\right) \quad (3.15)$$

where l is now the mean free path of the sample, averaged over an orbit. It is usually the impurity scattering term which determines whether or not quantum oscillations will be observed in a sample due to the exponential form of the damping. For instance, taking typical parameters of $B = 20$ T, $F = 1$ kT for measurements of iron-based superconductors, $R_D(l = 600 \text{ \AA})/R_D(l = 300 \text{ \AA}) = 20$, i.e. a factor of 2 in the impurity scattering rate can correspond to more than an order of magnitude in the amplitude of oscillation. For this reason, high quality samples are required to observe quantum oscillations - although access to very high magnetic fields will help when the scattering rate is high. Moreover there will be a natural variation of scattering rate within samples from a batch, so pre-selection of promising samples (based on e.g. RRR for transport samples) can be important. The growth technique is important; for example it was found early on that some iron-pnictides could be grown using a Sn-flux method, however these samples tended to be of a poorer quality than samples grown using a self-flux method. In certain cases, annealing crystals removes lattice strains and can decrease the scattering rate, enabling the observation of quantum oscillations [70].

In the Fe-based superconductors, studies of quantum oscillations have generally focussed on the stoichiometric compounds (e.g. LaFePO [7], LiFeAs and LiFeP [59], BaFe₂As₂ [71, 70], KFe₂As₂ [72], SrFe₂As₂ [73] and more recently FeSe [74]) because of the extra disorder when samples are doped⁸. The exception is BaFe₂(As_{1-x}P_x)₂ in which quantum oscillations have been observed over most of the over-doped side of the phase diagram [75]; it is likely that this isovalent pnictogen substitution creates less disorder than doping directly into the iron plane and disrupting the Fe 3d orbitals.

⁸As well as the fact that the superconducting critical fields can become very high at optimal dopings.

3.5.2 Measuring De Haas-van Alphen oscillations

Returning to the expression for the oscillatory potential in Eq. 3.11, the oscillatory magnetisation can be calculated from the differential of Ω with respect to the field B [65, 49],

$$\tilde{M}_{\parallel} = \left(\frac{e}{\hbar}\right)^{\frac{3}{2}} \frac{e\hbar F V B^{\frac{1}{2}}}{m_0 \pi^{5/2} \sqrt{2}} \left| \frac{\partial^2 A_{ext}}{\partial k_{\perp}^2} \right|^{-\frac{1}{2}} \sum_{p=1}^{\infty} p^{-\frac{3}{2}} R_{tot} \sin \left[2\pi p \left(\frac{F}{B} - \gamma \right) + \frac{1}{2} \right] \quad (3.16)$$

The magnetic torque measurement as described in Section 3.3 is a convenient way to measure de Haas-van Alphen oscillations - however as discussed there, torque measures the component of the magnetisation which is perpendicular to the magnetic field. Following Shoenberg again [49],

$$\tau = \tilde{M}_{\perp} B = -\frac{1}{F} \frac{\partial F}{\partial \theta} \tilde{M}_{\parallel} B \quad (3.17)$$

Therefore, this could be considered as an extra damping term specific to torque measurements:

$$R_{torq} = -\frac{1}{F} \frac{\partial F}{\partial \theta} B \quad (3.18)$$

For a quasi-2D system, this term can be approximated as $R_{torq} = B|\sin \theta|$ - meaning that there will be no oscillatory torque for a magnetic field applied along the high-symmetry c axis, although as previously discussed, there would be no background torque either in this case. In practice for quasi-2D systems this is not a big problem as one can extrapolate $F \cos \theta$ to the $\theta = 0$ limit.

In practice, oscillatory signals in magnetic torque are analysed by first subtracting a polynomial background, which usually takes a quadratic form. Then the subtracted data are interpolated using equal spacings in $1/B$, and then Fourier transformed. I developed a suite of MATLAB scripts and GUIs for the efficient treatment of de Haas-van Alphen data, which are now used in my group.

3.5.3 Measuring Shubnikov-de Haas oscillations

Quantum oscillations may also arise in transport properties of metals. The term “Shubnikov-de Haas” oscillations is used for oscillations in ρ_{xx} , but quantum oscillations have also been reported in the Hall effect, and additionally in Seebeck and Nernst effects in thermal transport measurements. When considering transport properties, one always has to consider what the scattering mechanisms are. An intuitive argument for the existence of quantum oscillations in transport properties is that the scattering rate depends on the final density of states at the Fermi level due to Fermi’s Golden Rule - and therefore oscillates in sympathy with the passing of Landau tubes through the Fermi surface - and one can simply borrow the formulae from oscillations of thermodynamic properties e.g. the Lifshitz-Kosevich formula for temperature-damping to describe oscillations in any property which depends on the scattering rate. In the simplest one-band models, the Hall resistivity is independent of the scattering rate and dependent only on the carrier density. However, as soon as you have more than one carrier type in a multiband system, there is a dependence on the scattering rates (see also Section 3.2.1) and quantum oscillations in the Hall effect may be observed. In practice, Shubnikov-de Haas oscillations can be more difficult to observe than oscillations in magnetisation [49], but are generally easier to find when the system has low carrier densities and high mobilities - the extreme cases being pure bismuth, where the first oscillations were observed by Shubnikov and de Haas in 1930, and the quantum Hall effect in two-dimensional electron gases.

3.6 Density Functional Theory

Density Functional Theory (DFT) is a very powerful tool for analysing the electronic structure of matter, and has seen widespread application across the physical sciences. Here I will introduce the concepts in the context in which it is used in this thesis - to solve the many-body problem for metals with relatively simple and known crystal

structures, and in particular to calculate the Fermi surface.

The Schrödinger equation for a many-body lattice problem consisting of nuclei and electrons may be written as

$$(T^e + T^{Ion} + V^{e-e} + V^{e-Ion} + V^{Ion-Ion})\Psi = E\Psi \quad (3.19)$$

where T^e and T^{Ion} are the kinetic energies of the electrons and ions respectively, and V^{e-e} , V^{e-Ion} and $V^{Ion-Ion}$ are the Coulomb interactions between the charged particles. The wavefunction Ψ depends on *all* the electron co-ordinates (with an additional spin index which I will drop throughout for simplicity) and *all* the nuclear co-ordinates - and it is immediately apparent that it is too complex to allow direct solution in all but the simplest cases (e.g. H_2 or He), and approximations will be necessary.

The first approximation is the Born-Oppenheimer approximation: since the nuclei are much more massive than the electrons, they are treated as decoupled from the electrons, and therefore the nuclear kinetic energy T^{Ion} and inter-ion interactions $V^{Ion-Ion}$ are dropped from the problem, and the nuclear positions are now input parameters of the problem.

The fundamental principle of DFT (from which its name is also derived) is that ground state energy - in fact any ground state property - is determined only by the ground state *electron density*, $n_0(\mathbf{r})$ (formally, a *functional* of $n_0(\mathbf{r})$). This is known as the Hohenberg-Kohn principle. The breakthrough of Kohn and Sham [76] is to map the interacting electron system onto a system consisting of non-interacting electrons subject to an effective potential. We then have wavefunctions $\phi_n(\mathbf{r})$ and a density

$$n(\mathbf{r}) = \sum_{n=1}^N \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}) \quad (3.20)$$

and the Schrödinger equation is

$$\left[-\frac{\hat{p}^2}{2m_e} + V_{ext} + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r}) \quad (3.21)$$

where V_{ext} is the external potential (including the Coulomb potential of the fixed ions), and the Hartree term V_H and the “exchange-correlation potential” V_{xc} are given by:

$$V_H = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3(\mathbf{r}') \quad (3.22)$$

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[n(\mathbf{r})]}{\partial n(\mathbf{r})} \quad (3.23)$$

Density Function Theory algorithms implement a self-consistent solution to equations 3.20-3.23. The problem is that the form of the functional $E_{xc}[n(\mathbf{r})]$ is not known, and must be approximated. The Local Density Approximation (LDA), or Local Spin Density Approximation (LSDA) when the spin degree of freedom is accounted for, provides the simplest solution by approximating the exchange-correlation energy functional $E_{xc}[n(\mathbf{r})]$ with the result for a homogeneous electron gas (or “Jellium”) and has been very successful. Various modifications or alternatives to LSDA have been suggested, the most common being the Generalized Gradient Approximation (GGA) - in particular I have used the functional proposed by Perdew, Burke and Ernzerhof (PBE) [77]. In practice, the functional is a choice and the user should beware the differences; for instance in Fe-based superconductors the size of the magnetic moment is typically larger in GGA calculations compared to LSDA.

The wavefunctions $\phi_n(\mathbf{r})$ in practice are composed from a set of basis wavefunctions which cover all of real space. There are several possible choices of basis sets. In Wien2k, the unit cell is divided into non-overlapping atomic spheres, in which hydrogen-like wavefunctions are used, and an interstitial region in which a plane wave expansion is used. Moreover, tightly bound electron states (e.g. 1s electrons) are considered separately as “core” states.

3.6.1 Implementation of DFT in Wien2k

My group uses the Wien2k [78] code, a commercial DFT code which has become popular due to its accessibility (including a beginner-friendly web-interface) and compatibility with other routines⁹. It is now reasonably common for experimental groups to have access to DFT codes, either used to compare their data to, to make predictions, or simply in order to try to think about the problem in the right way. On the other hand, the ubiquity of DFT means that theorists specialising in *ab initio* methods typically use DFT only as a starting point for more complex calculations, and rarely report straightforward DFT calculations on their own.

There are several considerations to performing meaningful DFT calculations, and caveats on the results obtained. The choice of crystal structure (i.e. atomic positions) is of obvious importance, but high-quality crystallographic data are not always available, or small disagreements may exist between experimental results. One alternative is to use DFT to “relax” the crystal structure and obtain the atomic co-ordinates which minimize the total energy. Then there are several extensions to DFT which should be considered, for instance spin-orbit coupling may be a relevant consideration. If a magnetic ground state is considered then the structure and symmetry must be carefully considered, and the calculations are computationally more expensive due to typically lower lattice symmetry and the need to calculate the spin-up and spin-down electron densities separately. Moreover, there are several cases where DFT calculations are known to fail - in the underestimation of band gaps in insulators and semiconductors, in strongly correlated electron systems in general, and in the context of Fe-based superconductors, the overestimation of the ordered magnetic moment. Therefore for the experimentalist, DFT is a useful starting point to compare to experimental data, but some discrepancies are generally to be expected.

⁹Although due to the age of the code, there are some archaisms and odd conventions such as the choice of Rydberg units, the large number of output files and unhelpful error messages. You can tell that you’ve done something seriously wrong when you get an error message in German.

The user must decide on the accuracy required for the calculation. For the purposes of Fermi surface calculations, a highly accurate convergence (typically an energy convergence of 0.00001 Ryd or better) is required, which is typically achieved after ~ 40 iterations of the self-consistency cycle. Another consideration is the density of the $\mathbf{k}$ -space grid used. Again, for Fermi surface calculations a high density is desirable - typically $0.5\text{--}5 \times 10^4$ points in the whole Brillouin zone are used to avoid later problems related to interpolation when the Fermi surface is rendered or quantum oscillations are calculated. The lattice symmetries are used to significantly reduce the number of $\mathbf{k}$ -points, by considering only the Irreducible Brillouin Zone (IBZ or ‘wedge’) of non-equivalent $\mathbf{k}$ -points. Wien2k is capable of running in parallel on a supercomputer where each k -point is assigned to a separate processor, substantially reducing the calculation time. I have run Wien2k jobs on the ARCUS supercomputer in Oxford and additionally on the supercomputing facilities in Frankfurt.

3.6.2 Predictions of quantum oscillations from DFT

After convergence, Wien2k will output energies of the electronic states in $\mathbf{k}$ -space. The Fermi surface may be rendered by taking an isosurface of these bands for an energy equal to the Fermi level, after repopulating a suitable $\mathbf{k}$ -grid based on symmetry relations to the IBZ¹⁰. However calculating the *extremal* areas of the Fermi surface which is relevant for quantum oscillations studies is a different and more complex problem - especially when considering an applied magnetic field which is not in a symmetry direction. The SKEAF algorithm [79] was designed fairly recently to fix the shortcomings of some private scripts which were being used by several groups. It works by populating a very large “supercell” in $\mathbf{k}$ -space aligned with the magnetic field direction, tiled with many copies of the reciprocal unit cell, which is sliced up to determine which Fermi surface areas are extremal, and can also account for extremal

¹⁰I have used some MATLAB codes to perform this task, originally written by Dr. E. Yelland and adapted by S. F. Blake and myself

areas which extend beyond one reciprocal unit cell. I have written a script to convert band energies from Wien2k into the (quite awkward) BXSF format used by SKEAF, and set it up to run on the ARCUS supercomputer in Oxford, and have found this to be a reliable solution to the problem.

3.6.3 Beyond DFT: DFT+DMFT

The field of physics known as “strongly correlated electron systems” principally concerns materials with partially-filled d or f shells with narrow bandwidths, and the LDA mapping onto single-electron model at a mean field level is not sufficient, often giving qualitatively wrong results. This is due to the fact that the homogeneous electron gas used in LDA as the reference system doesn’t encode the tendencies towards magnetism or localisation [18]. The LDA+U scheme accounts to some extent for onsite interactions which tend to localise electrons, which is very relevant for 4f states in lanthanides, or 3d states in transition metal oxides. A better method is to extend LDA with Dynamical Mean Field Theory, or LDA+DMFT (or DFT+DMFT). DMFT is designed to bridge the gap between the limit of non-interacting electrons in the nearly-free electron model to the localised atomic limit, and successfully described the Mott transition in the parent phase of cuprate superconductors. It works by mapping the many-body lattice problem onto a many-body *local* problem which can be solved using various “impurity” solvers. Projecting back into $\mathbf{k}$ -space, one loses the discrete energy bands obtained in DFT and replaces them with a spectral function which describes the probability of finding a quasiparticle. In the limit of weak correlations, the spectral function will have narrow dispersive features resembling the DFT band structure, whereas in the strong correlation limit the spectral weight is removed from the Fermi level and left in “Hubbard bands” at $\sim \pm U$ away - i.e. the Mott transition. The iron-based superconductors seem to be in a region of moderate correlation [80] - meaning that the spectral function consists of band-like

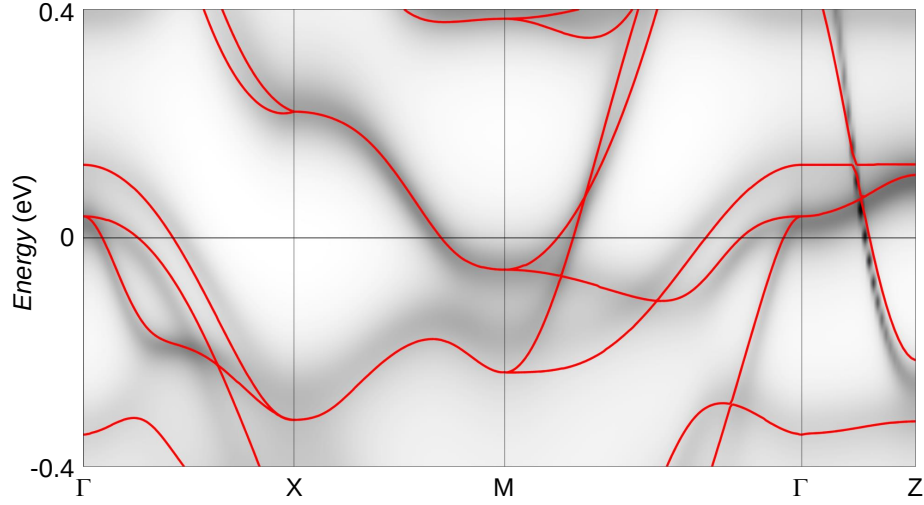


Figure 3.3: Spectral function of LiFeAs as calculated in a DFT+DMFT scheme. The DFT band structure is shown as red lines, renormalised by a factor of 2; for technical reasons spin-orbit coupling is not included in the calculation.

features (at least, near the Fermi level) but they are renormalised by a factor of typically ~ 3 compared to DFT calculations. In fact, for iron-based superconductors the Hund's rule coupling J plays a more significant role than the Hubbard U in determining the renormalisations [81] and moreover the renormalisations are orbital-dependent [81, 80] with usually the strongest correlations on bands with d_{xy} character. It is also known that the correlations are stronger on the hole-doped side of the phase diagram [80]. It should also be noted that DMFT does not account for correlations induced by long-range fluctuations.

In Fig. 3.3, I present the result of a DMFT calculation in LiFeAs, which illustrates the effect of the inclusion of on-site electron-electron interactions in a DMFT scheme ($U=3.5\text{eV}$, $J=0.8\text{eV}$). The spectral function clearly consists of dispersive features, but is renormalised compared to the DFT (the DFT band structure is renormalised here for easier comparison). Moreover, the inclusion of correlations in DMFT may induce changes to the Fermi surface, which may be seen along the Γ -X line - the outer hole pocket gets larger and the middle hole pocket shrinks. A discussion of the effect of DMFT in LiFeAs in particular may be found in Ref. [82], where some qualitative

agreement is found with ARPES experiment.

In summary - for Fe-based superconductors DFT is usually a good, but not great, starting point, and correlations will induce band renormalisations and shifts, leading to modified Fermi surfaces and heavier effective masses.

3.7 Angle-resolved photoemission spectroscopy

Quantum oscillations is the traditional method of determining the Fermi surface of materials. However, in recent years Angle-Resolved Photo-Emission Spectroscopy (ARPES) has become a very popular tool, being suitable for the layered metallic quasi-2D materials which are often of interest, including the Fe-based superconductors. It is able to measure not only the ground state Fermi surface which is probed by quantum oscillations, but all the occupied states, at a range of temperatures, also giving hints about orbital content of bands.

Photo-emission is an old story, with it now being the centenary of Einstein's 1905 *annus mirabilis* when in one of the four ground-breaking papers he wrote in that year, the photo-electric effect was explained using the concept of the photon as a particle (or packet) with energy proportional to its frequency, for which the Nobel Prize was awarded in 1921. Using energy conservation¹¹, we can write:

$$E_{kin} = h\nu - \phi - |E_B| \quad (3.24)$$

This is essentially the famous Einstein equation, relating the kinetic energy of the emitted photoelectron E_{kin} to the incident photon $h\nu$, the work function of the material ϕ and the binding energy $|E_B|$ of the initial electron state in the sample. The component of momentum parallel to the surface is also conserved in the emission process (up to a reciprocal lattice vector $G_{||}$), therefore

¹¹Here implicitly assuming a simple non-interacting electron model, see [83]. Also the small photon momentum may be neglected.

$$\mathbf{k}_i^\parallel = \mathbf{k}_f^\parallel = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \theta \quad (3.25)$$

where θ is the polar angle relating the photoelectron to the surface normal. Therefore by analysing E_{kin} and $\mathbf{k}_f^\parallel$ of the photoelectrons, the in-plane band dispersions of the initial states E_B against $\mathbf{k}_i^\parallel$ may be reconstructed.

Understanding the total intensity of ARPES signals is a more complex problem, but in general from Fermi's Golden Rule we may write the photocurrent I as:

$$I \propto \sum_i |\langle f | H' | i \rangle|^2 A_i(\vec{k}, \omega) f(\omega) \quad (3.26)$$

where $\langle f |$ and $|i\rangle$ are the final and initial electron states, H' is the perturbation Hamiltonian due to the presence of the photon, $A_i(\vec{k}, \omega)$ is the spectral function (as introduced in the context of DMFT in Section 3.6.3) and $f(\omega)$ is the Fermi-Dirac distribution. The first term is referred to as the “matrix elements effects” and the perturbation Hamiltonian H' is essentially the dipolar interaction between the incident photon and the electron. In certain circumstances, this can lead to strong selection rules - for instance, if the sample is aligned such that the scattering plane corresponds to a lattice symmetry, and additionally incident light is linearly polarised, the matrix elements may forbid transitions from particular bands because their real-space wavefunctions (i.e. orbital characters) have incompatible symmetry with dipolar transitions for light of that polarisation. This is particularly the case for Fe-based superconductors, where the bands near the Fermi level are constructed from Fe 3d orbitals. Then using the geometrical definitions appropriate for the I05 beamline with a sample aligned such that the local coordinate frame of Fe is also the scattering plane, the linear vertically (LV) incident beam polarisation picks out bands with d_{yz} character and linear horizontal polarisation picks out bands with d_{xz} character, moreover the matrix elements for transitions involving d_{xy} orbital are very small. In this context, the matrix elements can be helpful to identify bands. In other

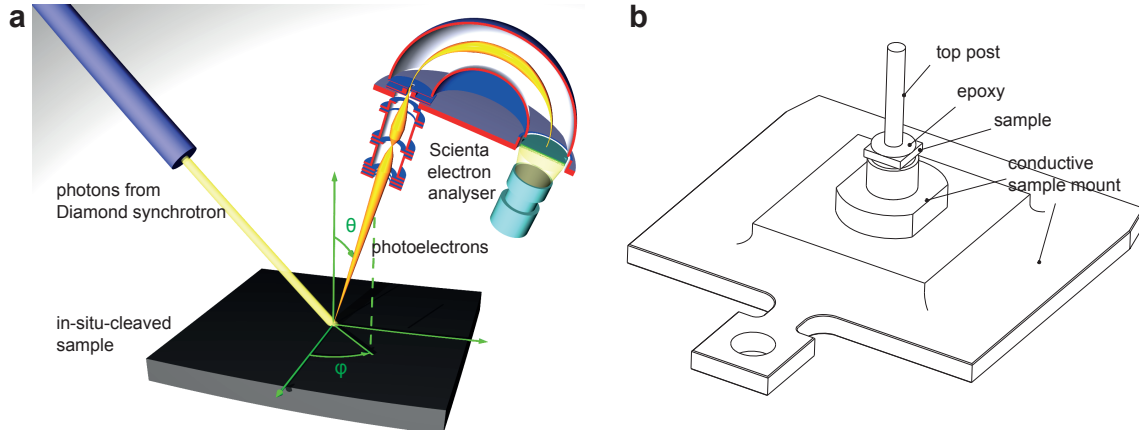


Figure 3.4: a) Schematic of an ARPES set up. Incident light generated by synchrotron radiation impinges on a sample cleaved in-situ at high vacuum, which gives off electrons by the photo-electric effect. The energy and momentum of the photoelectrons are determined by the analyser (Scientia R4000). Adapted from a wikimedia source. b) Technical drawing of the sample mount, adapted from the I05 beamline specifications.

cases it is a hindrance and can be avoided to some extent by deliberately rotating the sample lattice vectors away from the scattering plane, or using circular polarisation. A good discussion of the matrix elements appropriate for the $3d$ orbitals of Fe-based superconductors is found in Ref. [84].

Practically, there are several important factors for a successful ARPES measurement. Firstly, the samples must be good single crystals, and have a hope of cleaving in a known high-symmetry plane. Sizeable samples are required in order that they may be affixed flat to the conducting sample mount with a conducting epoxy, and have a top-post glued on top, as shown in Fig. 3.4b. When the sample is moved into the chamber with the cryomanipulator, it is cleaved by knocking the top-post off the sample, revealing (hopefully) a freshly cleaved surface, which can be brought into the centre of the beam.

The ARPES data in this thesis were taken at beamline I05 at the Diamond synchrotron, which is a state-of-the-art facility. The I05 cryomanipulator has six motor-controlled degrees of freedom - which importantly allows azimuthal rotation of the

sample for the optimisation of matrix elements effects and high-symmetry cuts. The base temperature of the sample stage is quoted as 10 K, although it can be pushed down to about 5.5 K. The use of synchrotron light allows for high intensity and choice of incident energy in the range 18-250 eV and choice of light polarisation at Diamond I05. This, in combination with the sophisticated manipulator and beamline control system, allows for complete studies of the Fermi surface, for instance detailed studies of the k_z dependence of pockets, and accessing the second Brillouin zone when using high incident energies.

In order to analyse ARPES data, first the data must be converted from the detector image into physical units (i.e. binding energy, k_x, k_y) using the above formulae and referencing the Fermi level to polycrystalline gold reference measurements. Fermi surface maps may be simply created by integrating the intensity within a few meV (i.e. the resolution) of the Fermi energy. In order to extract band dispersions from the cuts, one must attempt to fit either peaks in the momentum distribution curve (MDC - i.e. constant binding energy) or energy distribution curve (EDC - i.e. constant wavevector). Usually Lorentzian peak functions are used: physically the spectral function should have Lorentzian lineshape due to self-energy considerations. For a MDC which is expected to be symmetric, it can be useful to constrain the peaks to have equal widths. I have developed some software in MATLAB for the convenient extraction of band dispersions from multiple Lorentzian fitting to ARPES data.

In the following Chapters I will present results obtained by using all of the techniques described above. The combination of several different approaches is often beneficial and sometimes necessary for the understanding of a problem, as will be demonstrated particularly in the case of the electronic structure of FeSe. However, it does mean that I have deliberately not gone into a lot of detail about any particular technique in this Chapter.

Chapter 4

Quantum Oscillations in LiFeAs

In this chapter I present a partial determination of the Fermi surface of LiFeAs by the observation of quantum oscillations using the magnetic torque technique. I discuss the results in comparison with DFT, with the analogous LiFeP compound and with literature studies of ARPES, the Sommerfeld coefficient and quantum oscillations from another group. Some theoretical efforts to understand the Fermi surface of LiFeAs will also be mentioned. I conclude that the electron Fermi surfaces of LiFeAs are found close to their predicted sizes in DFT, albeit with sizeable effective mass renormalisations, but the hole pockets are not observed in quantum oscillations. This chapter is based on work published in Putzke *et. al.* Phys. Rev. Lett. **108**, 047002 (2012) although here I will include results from more samples and further analysis.

4.1 Introduction

LiFeAs has attracted much interest in the field of iron-based superconductivity since the stoichiometric compound is superconducting without doping, with a moderately high T_c of 18 K. LiFeAs forms in the tetragonal $P4/nmm$ space group and does not undergo any structural or phase transition, despite the fact that DFT calculations predict a magnetic ground state [85]. However, spin fluctuations have been detected around the wavevector associated with single stripe ordering [86], although possibly

slightly incommensurate [87]. The availability of single crystal samples has led to the possibility of studies of its Fermiology in angle-resolved photo-emission spectroscopy [88, 89, 90] (ARPES), quasiparticle interference [91] and de Haas-van Alphen (dHvA) measurements [59] which are reported here, and also provides a convenient target for theoretical models of the superconductivity in the system (e.g. Ref. [92]). There is therefore a lot of interest in the details of the electronic structure and Fermi surface in particular in LiFeAs - and it has not been without controversy.

In this Chapter I will present results which are the result of a collaboration with the group of Prof. Tony Carrington at the University of Bristol (who focussed on the LiFeP compound) with crystals grown in Kyoto University, Japan.

4.2 DFT Fermi surface of LiFeAs

DFT calculations were performed using the Wien2k package. Experimental atomic positions as determined in Ref. [93] were used. The GGA functional was used [77] with 40000 k -points in the Brillouin Zone for convergence. Since experimentally LiFeAs does not undergo any structural or magnetic transitions the calculations are performed using the tetragonal high-temperature structure, although various magnetic states would be lower in energy in DFT [85]. Spin-orbit coupling is included in the calculation.

DFT calculations predict what has become a well-known scenario for the iron-pnictides (see Section. 2.4), with three cylinder-like hole pockets centred at the Γ point and two electron-like hole pockets at the M point (Fig. 4.1). The electron pockets are predicted to have sizeable warping due to interlayer couplings, as shown by the cuts at $k_z = 0$ and $k_z = \pi/c$, while the outer hole band is close to a perfect 2D cylinder. The carrier density of LiFeAs as calculated by DFT is $n_e = n_h = 0.23$ electrons per Fe - i.e. the pockets occupy a large fraction of the Brillouin zone.

An unusual feature of the electronic structure is a band with Fe d_{z^2} character

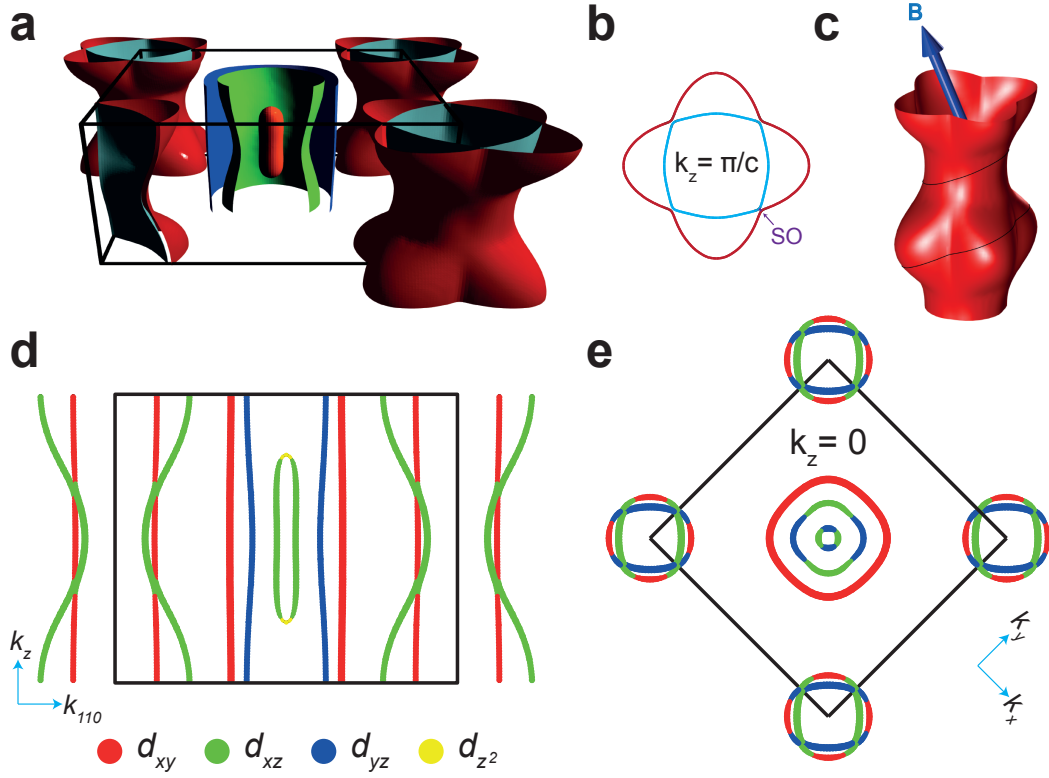


Figure 4.1: a) Fermi surface of LiFeAs, as calculated in Wien2k using the GGA functional, including spin-orbit coupling. Colours correspond to bands (not orbital character). b) Cross-section of the electron pockets around the A point, showing the splitting induced by spin-orbit coupling. c) Extremal orbits for an applied field at $\theta = 23.2^\circ$ from the c axis. d) Cut of Fermi surface in the Γ -M-Z plane, coloured by largest orbital character. e) Slice of the Fermi surface at $k_z=0$.

which disperses strongly between Γ and Z. The existence of this band has recently been confirmed by careful k_z -dependent ARPES studies [90]. This gives rise to the truncation of the inner hole pocket which would otherwise also be quasi-2D.

Including spin-orbit coupling into DFT calculations in Fe-based superconductors generally gives only a small perturbation to the band structure, but near the Fermi level it has two principle effects. Firstly, at the Γ point, there is a splitting of the d_{xz}/d_{yz} hole bands which are otherwise degenerate, and secondly the electron bands hybridise along the M-X direction, such that the electron pockets should not be considered to consist of two crossed ellipses but rather an outer and an inner Fermi

surface [94]. It is extremal orbits around these outer and inner pockets which give rise to quantum oscillations (Fig. 4.1b) - neglecting breakdown orbits which are expected to be heavily suppressed [95]. The effect of spin-orbit coupling in ARPES was recently discussed in Ref. [90], essentially supporting the conclusions of DFT.

Calculations of the quantum oscillations frequencies were performed using the SKEAF algorithm [79]. This procedure is schematically shown in Fig. 4.1c, where the extremal orbits are plotted on top of the Fermi surface for a given direction of the magnetic field. The symmetry of pockets centred on the Γ or M positions in the Brillouin zone usually leads to two extremal frequencies for a warped quasi-2D Fermi surface, arising from the “neck” and “belly” of the band. Therefore, there are 10 predicted frequencies in LiFeAs, as shown in Fig. 4.3.

The DFT Fermi surface of LiFeAs has the property of quite good Fermi surface *nesting* - i.e. matching of the sizes of quasi-2D hole and electron pockets separated by $\mathbf{Q} = (\pi, \pi)$. This is in contrast to ARPES studies, as will be later discussed.

4.3 Methods

Studies of LiFeAs are hindered by a strong air-sensitivity (due to the highly mobile Li atoms which oxidise readily) and a strong dependence of its superconducting properties to off-stoichiometry. In order to protect the samples from exposure to air, the samples were held in vials sealed under argon from the time of growth until immediately prior to the experiments, when the vials are smashed, and good samples selected and mounted as fast as possible.

The piezoresistive microcantilever torque technique was used, as described in Section 3.3, with single crystal samples with dimensions about $200 \times 100 \times 50 \mu\text{m}$. Due to the small size of the samples and the necessity to mount the sample as soon as possible, the in-plane orientation of the samples is not known. Therefore the rotation of the sample is simply given by θ , the angle between the applied magnetic field and

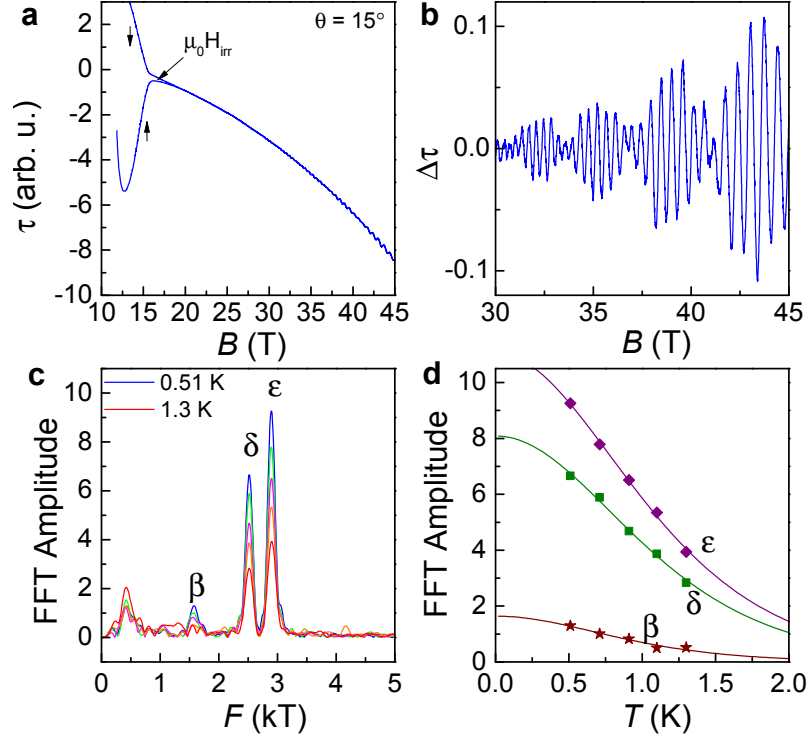


Figure 4.2: a) Raw torque signal for sample TLH A at an angle of $\theta=15^\circ$. b) The oscillatory contribution of the torque and c) its Fourier transform, clearly identifying 3 oscillation frequencies. A Welch window is used for the Fourier transform taking data between 30-45 T. d) Temperature-dependence of amplitude of oscillations, and fits to the Lifshitz-Kosevich formula (Eq. 3.13) from which the effective mass may be extracted.

the c axis, corresponding to the normal to the plane of the sample for the plate-like samples. The cantilevers were set on a rotating stage, using a ^3He cooling system to access temperatures down to 0.4-0.5 K. Measurements were performed in the 45 T Hybrid magnet at NHMFL, Tallahassee, Florida in 2011 and 2012¹. Oscillations were also detected using the capacitive torque technique (data set TLH C in Fig. 4.3b). Since these measurements were performed in the Hybrid magnet [60] in Tallahassee, the field sweeps do not extend to zero field since the outer superconducting magnet is always energised, giving a base field of 11 T.

¹Pulsed-field measurements in Toulouse were also performed by the Bristol group giving consistent results, but will not be reported here.

4.4 Quantum Oscillations analysis

Fig. 4.2a shows a typical torque measurement in LiFeAs at 0.51 K in sample TLH A. The low-field data are dominated by a large hysteresis in the superconducting state. This allows the determination of the irreversibility field $\mu_0 H_{irr}$, which for LiFeAs is ~ 16 T for $B \parallel c$. Beyond the irreversible regime, the signal is approximately quadratic in magnetic field, as would be expected for a paramagnet² (Section 3.3). Oscillations appear in the raw signal, growing in strength with magnetic field as described in Section 3.5. The oscillatory component of the torque, $\Delta\tau$, is isolated in Fig. 4.2b by subtracting a 4th order polynomial fit to the background signal. This is then treated by a Fourier transformation (FFT) as a function of inverse field, which reveals 3 oscillatory frequencies (Fig. 4.2c). For consistency with Ref. [59] these frequencies are denoted as β , δ and ϵ . One important question is whether the apparent small peak in the FFT spectrum at very low frequencies is a real quantum oscillation frequency, or a feature of the cantilever background. There are several reasons why one should be sceptical of low-amplitude, low-frequency oscillations in magnetic torque measurements in particular: the subtraction procedure may leave a slowly varying quasi-oscillatory background; there are general considerations of $1/f$ noise; and the fact that an empty cantilever can give spurious features. Moreover the feature does not have the expected temperature-dependence expected for a real peak. Therefore, although there may be reasons to expect a low frequency in dHvA (see Section 4.4.3), it has not yet been conclusively observed, and the low frequency, low amplitude ‘peak’ in Fig. 4.2c should be interpreted as an artefact.

4.4.1 Temperature dependence and effective masses

In Fig. 4.2c the amplitude of the peaks in the FFT spectrum is observed to decay with increasing temperature. Since the only term in the Lifshitz-Kosevich formalism

²Although the “paramagnetic” state of Fe-based superconductors is characterised by strong antiferromagnetic fluctuations, a long way from Curie-Weiss-type behaviour.

Table 4.1: Fermi surface parameters of LiFeAs from DFT and experiment. Note that the mass enhancements are taken with respect to the shifted values of the calculated band mass m_b at $\theta=15^\circ$. The estimated contribution of each band to the Sommerfeld coefficient γ is noted and discussed in Section 4.4.5.

DFT				Experiment				
Orbit	F (T)	m_b	γ	Label	F (T)	m^*	$\frac{m^*}{m_b} - 1$	γ
1a (h)	140	-0.330	0.15					
1b (h)	155	-0.272						
2a (h)	1617	-2.257	1.31					
2b (h)	2514	-1.557						
3a (h)	4388	-2.207	1.56					
3b (h)	4540	-2.219						
4a (e)	2386	1.191	1.45	δ	2400	5.1(4)	3.0	3.6
4b (e)	6337	2.352						
5a (e)	1574	1.594	0.92	β	1590	6.0(5)	2.4	3.9
5b (e)	2981	0.981		ϵ	2800	5.1(4)	3.8	

with an explicit temperature-dependence is R_T (Eq. 3.13), a fit to this function gives a determination of the effective mass m^* averaged around the orbit. The three frequencies β , δ and ϵ are found to have effective masses of 6.0(5), 5.1(4) and 5.1(4) respectively. These values are substantially higher than the band masses estimated by DFT using the SKEAF algorithm³. Mass renormalisation is usually considered to arise from many-body effects, in the form $m^* = (1 + \lambda)m_b$ [49] where m_b is the ‘bare’ band mass taken to be the effective mass as calculated in mean-field DFT, after shifting if necessary. The renormalised value of m^* depends on the electron-electron interactions and electron-phonon coupling [68].

An analysis of the field-dependence of the amplitude (the Dingle term, see Section 3.5.1) gives a mean free path of 450 Å for the ϵ orbit (not shown). It is this term, encoding the effect of impurity scattering as in Eq. 3.15, which kills the amplitude of oscillation for the hole pockets, which are assumed to have a higher scattering rate and exponentially damped signal.

³I performed my own DFT and effective mass fitting analysis, so there are minor differences with paper of Putzke *et. al.*

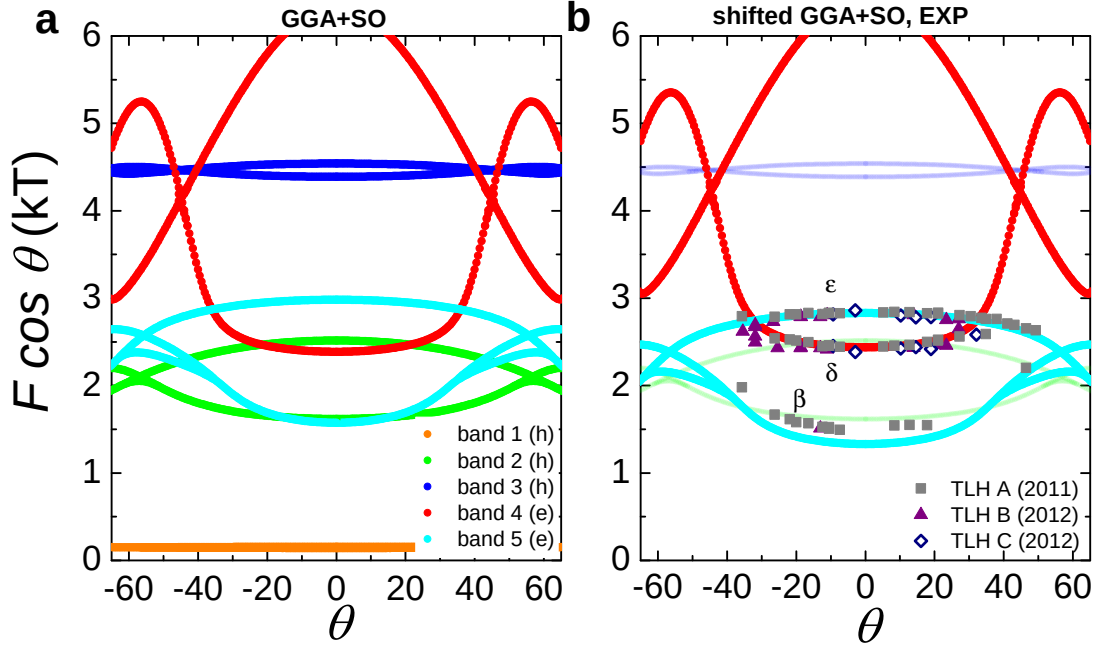


Figure 4.3: a) DHvA frequencies as calculated by DFT (GGA+SO). Colours correspond to the Fermi surface in 4.1a. b) Experimental data points, with calculated dHvA orbits from slightly shifted bands to best match experiments, as discussed in the main text. The calculated frequencies of unobserved bands are faded. Band 1 is removed from the experimental graph, since it would be observed if it did cross the Fermi level (see main text).

4.4.2 Comparison to DFT

In Fig. 4.3 the angular dependence of the observed frequencies is plotted. For an exactly 2D band, the expected angular dependence is $F = F_0 / \cos \theta$, and therefore it is convenient to plot $F \cos \theta$ against θ . Since the bands are quasi-2D, the curvature of $F \cos \theta$ against θ as plotted in Fig. 4.3 is helpful to determine whether the experimental frequency corresponds to a maximum (downward curvature of $F \cos \theta$ against θ) or a minimum (upward curvature) of a quasi-2D band. Clearly, the ϵ band corresponds to a maximum, and the β and δ arise from minima.

Since dHvA does not give information on where in the Brillouin zone an extremal frequency arises from, it is common to make assignments of frequencies to bands by comparison to DFT calculations. For instance, in BaFe_2P_2 a complete determination of the Fermi surface was possible [58] by this method. In the closely related LiFeP ,

frequencies arising from all bands were observed and matched to DFT bands requiring moderate band shifts [59].

In general, distinguishing between different calculated quasi-2D bands with similar areas may be challenging, especially when data are only available over a relatively narrow range of angles. However some bands are calculated to have quite distinctive k_z dispersions which will help with the identification, such as the “hourglass” hole pocket in BaFe_2P_2 [58] or the d_{xy} outer hole band here in LiFeAs which is particularly two-dimensional, as shown in Figs. 4.1d and 4.3a. Moreover, it can be helpful to compare to other experimental techniques and related materials. For instance, in LiFeAs the Hall effect is negative at all temperatures with $\sim 50\%$ greater mobility for the electron pockets [28], which suggests that the electron pockets are more likely to be observed in quantum oscillations measurements (this seems to be the case also in $\text{BaFe}_2(\text{As,P})_2$ [75]) primarily due to a lower scattering rate. In particular the comparison to LiFeP is useful where oscillations arising from all the bands were observed, requiring moderate shifts [59].

Therefore, one can usually⁴ match experimental frequencies with DFT bands, with a better agreement found by shifting the band structure with *rigid band shifts* and recalculating the dHvA frequencies. One should be careful that this procedure does not lead to unphysical final band structures (band crossings, large gaps, charge imbalance etc.) and furthermore while rigid shifts are the simplest mechanism to match the Fermi surfaces, a more sophisticated k_z -dependent (or orbital-character-dependent) shift may give a better match. The choice of functional and crystal structure used in DFT will of course also affect the value of the rigid band shift needed. Nevertheless the magnitude of shift required gives some indication of the degree of agreement between DFT and experiments and this analysis is used here. Physically, the deviations may be due to many-body interactions (e.g. Refs. [82, 96])

⁴An exception being FeSe , where the DFT is a particularly bad starting point, as discussed in the next Chapter.

or low-energy inter-band interactions [97].

In LiFeAs, the highest two frequencies ϵ and δ correspond to a maximum and a minimum of quasi-2D bands respectively, and are assigned to band 5 and band 4 due to their absolute values and curvature. A shift of +18 meV (-5 meV) is required to match the ϵ (δ) frequency with band 5 (band 4). The β frequency is likely to correspond to the minimum of band 5 with a good agreement without any shift. Therefore, within small errors there is a good agreement between DFT and the size and topology of the electron pockets in experiment.

Having accounted for the three observed frequencies, we conclude that the hole bands are not observed in LiFeAs. However, the results still put constraints on the possibilities for the topology of the hole bands. Since in LiFeP the signal arising from the small inner hole pocket dominates the dHvA signal [59], the *non-observation* of low frequencies suggests that band 1 does not cross the Fermi level, requiring a downwards band shift of at least ~ 60 meV. However, this downwards shift cannot occur in isolation, since band 1 and band 2 are split only by spin-orbit coupling at the Γ point. Therefore band 2 is likely to be shifted downwards by a similar value. In fact in LiFeP both of these bands have a similar downward shift (-65 and -80 eV [59]) although there the inner hole band still exists. In order to leave the system charge compensated, the outer hole band 3 must increase in size as the inner hole bands shrink (or disappear). Clearly here I am extracting a lot of information from a *non-observation* of a band - but it does provide a hint as to the possible deviations of the experimental hole bands from DFT which are not directly observed in dHvA but are observed by ARPES⁵.

⁵Here I have deviated from the original conclusion in Putzke *et. al.* where it was claimed that the hole bands were likely to be more-or-less in agreement with DFT and in disagreement with ARPES.

4.4.3 Comparison to ARPES measurements

LiFeAs is particularly suitable for ARPES studies due to the neutral cleavage plane [89]. To quickly summarise a detailed body of literature, ARPES measurements [88, 89, 90] find (with qualitative agreement, and some quantitative discrepancies) a sizeable departure of the size of the hole bands from the prediction of bandstructure as the main feature, with the outer hole band with largely Fe d_{xy} character growing in size and the inner hole band shrinking substantially. On the other hand, the electron pockets in ARPES do not differ substantially from the DFT predictions in volume. The resulting picture of the Fermi surface is one in which the ‘nesting’ (matching of size of orbits with displacement (π, π)) of the hole and electron bands is very poor or absent [89] - which has implications for the pairing mechanism. However, since ARPES is a surface-sensitive probe, it would be valuable to confirm this picture with quantum oscillations experiments in the bulk.

The dHvA measurements on LiFeAs were unable to find frequencies, corresponding to extremal areas of Fermi surface, for all of the bands. However 3 frequencies were observed and, by comparison with bandstructure calculations and the 5 K superconducting analogue LiFeP, have been attributed to the electron bands, in reasonable quantitative agreement with the predictions of LDA bandstructure. One possible route to reconciling these data sets was the observation that adding electronic correlations at the level of dynamical mean field theory (DMFT) in LDA+DMFT calculations [82] had the effect of enlarging/shrinking the hole pockets as seen in ARPES (although quantitatively not quite to the same degree), while having little effect on the sizes of the electron pockets. In Section 3.6.3 I also performed DMFT on LiFeAs, generating similar results. In this point of view, the correlations manifest as a change of the hole Fermi surfaces away from the DFT predictions, as seen by ARPES, but for the electron pockets only provide a renormalisation of the effective masses rather than any significant shifts at the Fermi level. One way to rationalise this is that at the

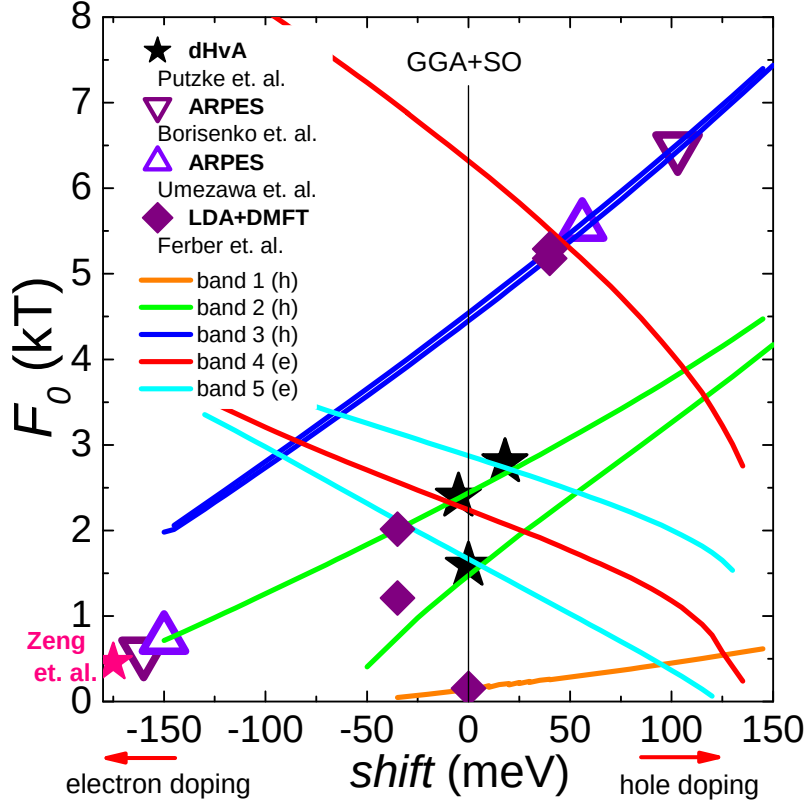


Figure 4.4: DHvA frequencies calculated in DFT (GGA+SO) as a function of rigid band shift; a positive shift increases the size of a hole pocket but reduces the size of an electron band. Experimental dHvA frequencies are plotted as stars, requiring small shifts to bring into agreement with DFT whereas the estimated frequencies from ARPES (only the hole pockets) require significant, and opposite, shifts.

electron pockets the orbital characters are very mixed, whereas for the hole pockets there is a clear distinction between the outer band with d_{xy} orbital character - which experiences the strongest renormalisations in many-body calculations [82] - and the inner bands with d_{xz}/d_{yz} character.

In Fig. 4.4 I summarise the ARPES and quantum oscillations studies (alongside DMFT) by comparing the frequencies obtained from ARPES (roughly estimated from published data) and DMFT calculations [82]⁶. As earlier discussed, the electron bands do not need very significant shifts to match ARPES data, however the hole bands as found in ARPES require large shifts of ~ 100 meV or more to bring into agreement.

⁶It should be noted that DMFT calculations usually do not account for spin-orbit coupling for technical reasons, which will have implications for the small hole pocket in these calculations.

The middle hole band 2 is found to become a 3D pocket around Z for large shifts, as is also found in the ARPES-derived Fermi surface reported in Ref. [92]. So long as these large and opposite shifts can leave the system with a compensated number of electrons and holes (as happens in DMFT by construction) then the ARPES scenario may be compatible with quantum oscillations.

4.4.4 Recent controversy: low frequency oscillations?

A recent paper by Zeng *et. al.* [98] claimed the observation of small oscillation frequencies in LiFeAs using the capacitive torque measurement technique. It is worth briefly commenting on these results, because although the detection of low frequency quantum oscillations would seem to be nicely consistent with the ARPES scenario, there are several discrepancies within their results and between their results and the results presented in this Chapter.

Two important experimental differences exist between the methods of the recent paper of Zeng. *et. al.*, and the data reported here. Firstly, the crystal growth mechanism is rather different. The growth of the crystals used in this study used Li ingots with FeAs powders in the growth, whereas Zeng *et. al.* uses Li₃As, Fe and As mixed in a ratio Li:Fe:As = 1:0.3:1 - presumably in an attempt to reduce the possibility of any excess Fe entering the LiFeAs product, which has been reported to very quickly kill the superconductivity. Secondly, the capacitive torque method used in Zeng *et. al.* is different to the piezoresistive torque measurements presented here. While both methods can be highly sensitive, the delicate piezocantilevers are suitable only for samples of order $\sim 100 \times 100 \times 50 \mu\text{m}$, whereas capacitive torque methods use larger single crystal pieces, on the order of $\sim 1\text{-}2\text{ mm}$. Therefore, there is a larger scope for impurity phases or crystal mosaicity to play a role in capacitive measurements, although with care these can be avoided.

In order to facilitate a comparison of the data sets, in Fig. 4.5 I reproduce a panel

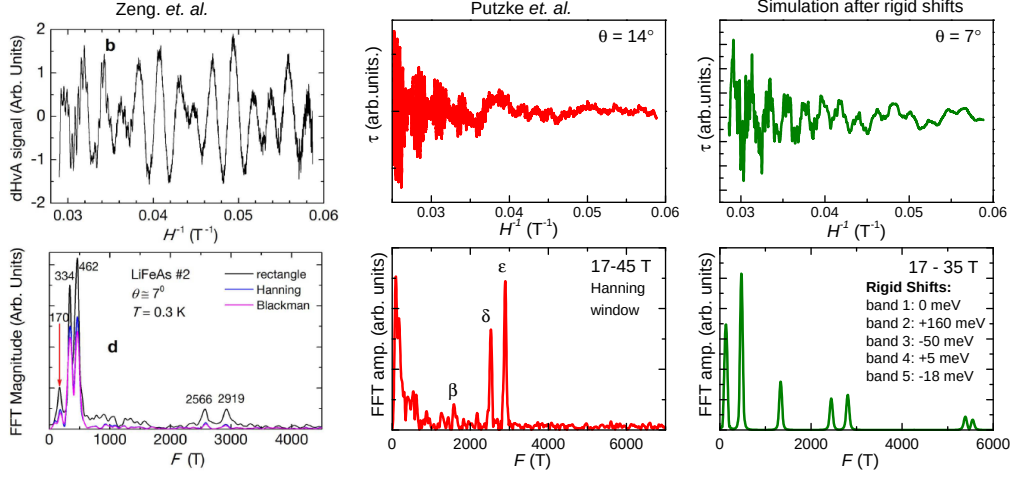


Figure 4.5: Left: Reproduction from Fig. 4 from Zeng *et. al.* Middle: Comparison of experimental data from 45 T DC field data of Putzke *et. al.* Note that the large window used is not optimal for this data, in which the β frequency becomes better resolved at higher fields. Right: Simulation of dHvA signal, assuming all bands to have the same mean free path ($=450\text{\AA}$) performing rigid shifts compatible with the data of Zeng *et. al.*

of Fig. 4. in Zeng *et. al.* alongside data at a comparable angle from sample TLH A (with measurements up to 45 T rather than 33 T). It is clear that the dominant low frequencies in Zeng *et. al.* are absent in our study, where the dominant frequency is the beating of the high frequencies. Additionally, the usual growth in signal with increasing magnetic field, parametrized by the mean free path in simulations, appears to be very small for the lowest frequencies in Zeng *et. al.*

From Fig. 5. of Zeng *et. al.*, it seems that this frequency is almost isotropic. The effective mass attributed to this frequency by using the standard Lifshitz-Kosevich formalism is given as only $(0.8 \pm 0.1) m_e$ in Table I of Zeng *et. al.*- which is rather surprisingly low, considering that the electron bands have masses $\sim 5 m_e$. Additionally, since strong correlations are known to be present, one would naively expect to find a sizeable effective mass (e.g. the DMFT mass enhancement is 2.39 for $d_{xz,yz}$ orbitals [82]), whereas in fact the reported mass enhancement compared to the (unshifted) band mass is negative. This startling fact is not commented on in Zeng *et. al.* The

fact that the low 460 T frequency is the dominant feature at all angles in the data of Zeng *et. al.*, but not observed whatsoever in this study (despite a wide-ranging angular dependence in both reports) is very peculiar. We note that this frequency was also not reported in the previous study (Li *et. al.* [99]) of torque on LiFeAs by that group, despite the observation of the electron pockets there too. Additionally, despite observing the same frequency in two samples, there is a large discrepancy between samples of the relative magnitudes of the 460 T peak and the electron frequencies (compare Fig. 3 and Fig. 4 in Zeng *et. al.*). The inconsistency between samples is hard to explain, especially since the relative amplitude of the electron frequencies from different bands are reasonably consistent.

In summary, it would appear that the low frequency reported in Zeng *et. al.* is likely to have an extrinsic origin, possibly an impurity phase. Candidates for this impurity phase with low frequency quantum oscillations are pure Fe [100] and Li₃As⁷. I will not comment on the further discrepancies in the study of Zeng *et. al.* except to note that the anomalous hysteresis they observed may have a more mundane explanation as a bad crystal mosaicity, and that the angular dispersion of their claimed 1590 T frequency is not consistent with the quasi-2D band to which the β frequency in this study is attributed.

4.4.5 Estimation of Sommerfeld coefficient

The Sommerfeld coefficient γ is the coefficient of the linear term of the specific heat at low temperature which is usually considered to arise from the contribution of the degrees of freedom of the quasiparticles at the Fermi level:

$$c_v = \gamma T = \frac{\pi^2}{3} k_B^2 T g(E_F) \quad (4.1)$$

where $g(E_F)$ is the density of states $g(E)$ evaluated at the Fermi level, summed over all contributing bands. In Ref. [101], the Sommerfeld coefficient in the normal state of

⁷I have calculated that Li₃As has a complex Fermi surface including one almost isotropic band giving rise to oscillation frequency at 460 T.

LiFeAs was estimated to be $\gamma_n = 10$ mJ/mol-K²; other reports have found significantly larger values (e.g. $\gamma_n = 17$ mJ/mol-K² in [102]) but this may be due to a significant impurity contribution [101]. Further studies of the specific heat of LiFeAs (and indeed LiFeP for comparison) would be useful.

The Sommerfeld coefficient may also be estimated from quantum oscillations data, and in particular for two-dimensional bands, it can be shown that $g(E)$ is proportional to the effective mass of the 2D band, i.e. $m^* \propto \frac{\partial A}{\partial E} \propto g(E_F)$, and therefore $\gamma \propto \sum_{bands} m^*$, adding up the contributions from all the 2D bands. For LiFeAs, we find

$$\gamma = 0.708 \sum_{bands} m^*, \quad (4.2)$$

where γ is in mJ/mol-K² and m^* is measured in electron masses and the prefactor 0.708 comes from a number of physical constants including the a lattice parameter. We can estimate the contribution of the electron bands as follows: for the inner pocket (band 5), taking the average of the effective masses of the β and ϵ frequencies gives a contribution of 3.9 mJ/mol-K², and for the outer band 4 the effective mass of the δ frequency gives a contribution of 3.6 - i.e. the total estimated contribution of the two electron pockets is $\gamma_{electron} = 7.5$ mJ/mol-K². Since there are at least 2 hole bands unaccounted for, the total γ_{QOs} is likely to exceed the experimental value of 10 mJ/mol-K², however given that the hole bands are not observed in dHvA and the discrepancies between different reports of the Sommerfeld coefficient, it is not possible to reliably state the degree to which the two techniques disagree. For reference, the Sommerfeld coefficient as estimated by DFT (as calculated using the SKEAF algorithm) is 5.33 mJ/mol-K²; the outer d_{xy} hole band is the largest single contributor.

4.5 Discussion

In $\text{BaFe}_2(\text{As,P})_2$ [75], a correlation was found between T_c and the mass enhancement, and here in LiFeAs ($T_c=18$ K) the mass enhancements are 2-3 times larger than in LiFeP ($T_c=5$ K). One possibility then, as stated in Ref. [59], is that the mass renormalisations are ultimately caused by the same interactions which drive superconductivity. This relationship is of course not a completely general statement across all Fe-based superconductors, for instance KFe_2As_2 has very large mass enhancements but a T_c of only 3 K [103], but within the family of compounds isovalent to BaFe_2As_2 (i.e. 6 electrons in the Fe-3d bands) it appears to roughly hold. One suggestion is that the mass enhancements and T_c in $\text{BaFe}_2(\text{As,P})_2$ are both linked to a quantum critical point near optimal doping [104]. Where LiFeAs fits in to this is not clear, due to the high effective masses observed in quantum oscillations but good Fermi liquid behaviour reported in transport in clean single crystals ([28]) and absence of Fermi surface shrinking effects as seen in $\text{BaFe}_2(\text{As,P})_2$ [75]. Furthermore, in the next chapters I will show that FeSe has effective masses up to 7-8 m_e , but with a moderate $T_c = 8$ K which would also appear to buck the trend. As usual, there is a lack of universality in the behaviour of different Fe-based superconductors even within nominally isovalent compounds.

In summary, I have presented an analysis of quantum oscillation measurements in LiFeAs in high magnetic fields. The observed frequencies correspond well to the DFT predictions of electron bands, but with significant mass enhancements. By contrast, ARPES studies have found that the hole bands significantly deviate from the DFT band structure, but I have shown that this scenario may in fact be still compatible with the quantum oscillations. A recent quantum oscillations study [98] claiming to observe a small hole pocket was discussed, however the reliability of this data is to be questioned. Nevertheless, a complete unambiguous *bulk* study of the Fermi surface of LiFeAs observing all the bands in quantum oscillations would be of great value

to confirm the ARPES scenario and to allow precise theoretical modelling of this (moderately) correlated and high T_c Fe-based superconductor.

Chapter 5

Hole and electron Fermi surfaces of FeSe probed by quantum oscillations and magnetotransport

In this Chapter I will briefly review the large and growing amount of work on FeSe in the literature, and then present a combined analysis of quantum oscillations in FeSe measured in both the resistivity ρ_{xx} and Hall effect ρ_{xy} . I use a novel two band analysis to determine the origin of the observed oscillation frequencies. Furthermore I present a study of the low-field magnetoresistance and Hall effect, finding evidence for a small but significantly more mobile electron pocket in addition to the electron pocket giving rise the heavy 540 T oscillation frequency. I conclude that the Fermi surface of FeSe consists of one hole pocket and two electron pockets. This Chapter contains work presented in the recent manuscript M. D. Watson *et. al.* arxiv:1502.02922 (2015), recently accepted to appear in Phys. Rev. Lett.

5.1 Literature review: FeSe

Shortly after the discovery of superconductivity in the tetragonal phase of FeSe at 8 K [105], it became clear that tetragonal β -FeSe presents several challenges to the understanding of superconductivity in the wider family of Fe-based superconductors,

despite its appealing structural simplicity. At ambient pressure, an orthorhombic distortion similar to those observed in parent and under-doped iron based superconductors occurs at ~ 90 K [106], but without an accompanying long-range magnetic ordering at any temperature. Furthermore under applied pressure, the T_c rises rapidly to 37 K [29]. The electronic structure, presumed to be the driving force behind these effects, has been of theoretical interest for some time; however earlier experimental efforts were limited by crystal quality issues, with impurity phases invariably found intergrowing with the tetragonal phase.

Recently there have been two major improvements to sample growth methods in FeSe. The development of thin-film growth has been very fruitful, with a report of superconductivity above 100 K [107] in monolayer FeSe grown on SrTiO_3 - far greater than any bulk T_c found in Fe-based systems. In addition to the thin film work, higher quality single-crystals of FeSe have been recently grown by several groups (e.g. Ref. [44]) using a low-temperature chemical vapour transport crystal growth method. Using this method, sizeable high quality crystals very near stoichiometry may be produced in the desired tetragonal structure, without impurity phases. I will therefore focus on experiments on this new generation of samples in the next few paragraphs. Details of the new method of crystal growth may be found in Appendix A.

Quantum oscillations have recently been reported [74] in FeSe, indicating the high quality of the crystals. Four quantum oscillation frequencies were found, and the authors concluded that this constituted the complete observation of the Fermi surface which most likely consisted of one hole and one electron pocket. The quantum oscillations data I will present in this thesis are largely consistent with that of Ref. [74], however my interpretation, based on a careful analysis of both quantum oscillations and ARPES, is that the low temperature Fermi surface consists of one hole pocket and *two* electron Fermi surfaces. A hint that there may be two electron pockets may also be found in magnetotransport studies, as will be presented later in this chapter, but

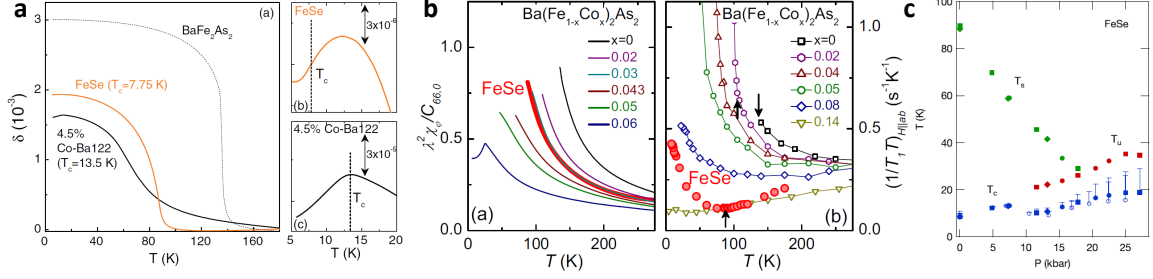


Figure 5.1: Experimental measurements of FeSe in the Literature. a) Thermal expansion measurements in FeSe, shown in comparison to Ba(Fe_{1-x}Co_x)₂As₂, highlighting in particular the lack of any significant feature at T_c . Reproduced from Ref. [44]. b) Shear modulus and NMR measurements in FeSe. The C_{66} elastic constant softens in a similar manner to the Ba(Fe_{1-x}Co_x)₂As₂ series, but there is no evidence for spin fluctuations above T_s according to the NMR measurements. Reproduced from Ref. [45]. c) Phase diagram of FeSe under pressure, reproduced from Ref. [108].

was also found in the mobility spectrum analysis presented in [109]. Several ARPES studies of varying quality and interpretation have been reported [110, 111, 112, 113] on bulk crystals. In general, these studies showed small Fermi surfaces (qualitatively consistent with the quantum oscillations), a particularly large renormalisation on the d_{xy} hole band, and a splitting of bands with d_{xz} and d_{yz} orbital character at the M point, interpreted as evidence for orbital ordering [112]. However the ARPES study that I will present in Chapter 6 constitutes the most complete study of the electronic structure of FeSe with the highest quality spectra yet reported.

In addition to the studies of the electronic structure described above, several studies have searched for clues about the origin of the structural transition in FeSe. In Ref. [44], high-resolution thermal expansion measurements were used to demonstrate a very weak coupling between the superconductivity and the orthorhombic order, reproduced in Fig. 5.1a. This suggests that the superconductivity and orthorhombic distortions are driven by different interactions. FeSe was compared to measurements in Ba(Fe_{1-x}Co_x)₂As₂, where a competition between magnetism and superconductivity [22] has been clearly demonstrated. Moreover, two NMR studies [46, 45] both concluded that there was an absence (or at least a very low level) of low-energy spin-

fluctuations above T_s . This is despite the fact that both the shear-modulus softening [45] and the orthorhombic distortion itself [44] were very similar to measurements in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, as reproduced in Fig. 5.1b. This result was intriguing, since the scaling between spin-fluctuations and shear-modulus measurements had previously been considered one of the strongest pieces of evidence for a spin-driven scenario in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [41].

To add to the anomalous results for FeSe presented above, the phase diagram of FeSe under pressure provides further peculiarities. Early experiments (on lower-quality samples) found that T_c could rise rapidly under pressure [29] up to an onset of 37 K. NMR measurements under small pressures found that the spin-fluctuations tended to increase [114] along with T_c , and a μSR study also found evidence for a pressure-induced magnetic phase [115]. Very recently, the phase diagram of FeSe under pressure has been revisited [108] (reproduced in Fig. 5.1c) on good single crystal samples, finding similar results: first the orthorhombicity is suppressed, and then a (presumably) magnetic phase is stabilised at higher pressures, while the T_c was found to rise substantially, although in a non-monotonic fashion.

Finally, there have been two recent neutron scattering reports on FeSe; since the vapour-grown samples are too small to be practically used for neutron scattering measurements these studies were performed on either powder samples [116] or large “single crystals” [117] grown by the floating-zone technique [118]. These studies found that low-temperature magnetic fluctuations corresponded to the usual $(\pi,0)$ wavevector in the 1-Fe unit cell.

5.1.1 Theoretical studies of FeSe

The experimental results detailed above, and also those described in this thesis, show that FeSe *is* different, and *how* so. The question of *why* FeSe is different has been addressed by several theoreticians. One proposal is that FeSe may correspond to

a “nematic quantum paramagnet” [119], a term coined for a system with magnetic interactions in a regime between a stripe-ordered phase and a Néel phase. Another group performed a large number of DFT calculations on FeSe in different magnetic configurations, finding that several patterns were almost degenerate in energy but all breaking rotational symmetry, suggesting that magnetic frustration was a key element in FeSe [120]. However, it is not clear how either of these interpretations corresponds to the experimental probes of magnetic fluctuations (NMR and neutron scattering) referred to above. Some would argue that the case of FeSe shows that the orbital ordering is always key element in Fe-based superconductors [42]. An alternative approach was to simply take the experimental band structure and model the low-temperature Fermi surface with a tight-binding model [121], leaving open the question of the origin of the orbital ordering effects. These numerical studies used their model electronic structure to simulate the superconducting gap and NMR spectra, with reasonable agreement with experiments. Further theoretical studies are likely to be proposed in the near future¹.

5.2 Introduction

In the following sections I will present a combined analysis of quantum oscillations in FeSe measured in both the resistivity ρ_{xx} and Hall effect ρ_{xy} . A novel two band analysis is used to determine the origin of the observed oscillation frequencies, suggesting that the 660 T (F4) and 180 T (F2) frequencies may be associated with hole-like orbits, whereas the 540 T (F3) frequency, which also has a rather higher effective mass, arises from an electron-like orbit. The observed masses are significantly renormalised with respect to the band structure calculations indicating the importance of correlations in FeSe. A study of the angular-dependence of frequencies finds that the F2 and F4 are likely to constitute the extremal areas of a single hole band, whereas

¹There were more than 50 abstracts including the word FeSe at the APS March Meeting in 2015, including several theoretical proposals. My own ideas are presented in Appendix B.

F3 is a maximum of a different band. I then present a study of the low-field magnetoresistance and Hall effect, finding evidence for a small but significantly more mobile electron pocket in addition to the electron pocket giving rise the heavy F3 oscillation frequency, concluding that there are two electron bands in FeSe. I will delay the comparison of quantum oscillations and ARPES until the next chapter, but rather make a consistent designation of bands based on completely independent logic.

5.3 Methods

Samples were grown by the KCl/AlCl₃ chemical vapour transport method. Samples S1, S2 and S5 were grown by the Karlsruhe group, and samples S3, S4 and S6 were grown in Oxford, as detailed in Appendix A. Transport measurements were performed in a dilution fridge in pulsed fields up to 56 T and also up to 88 T in helium-4 cryostats at LNCMI, Toulouse. DC field measurements were also performed up to 33 T in NHMFL, Nijmegen. Low field measurements (up to 13.5 T) were performed in a Quantum Design PPMS in Oxford. The Hall and resistivity contributions were separated by (anti)symmetrizing the data obtained in positive and negative applied magnetic fields. Good electrical contacts were achieved both by spot welding and Sn or In solder. Oscillations were observed in 4 samples with good agreement, and 2 samples were measured below 1.4 K in the dilution fridge; one of those samples (S1) was subsequently measured up to 88 T at 1.4 K. Heating effects were carefully considered by analysing the dependence of the critical field on the sample current; 1 mA was used in the dilution fridge and 10 mA in the He-4 cryostats. Samples were mounted with $B \parallel c$ only in the pulsed-field experiments, but a rotation stage was used in the DC field measurements.²

²The pulsed-field data were taken as part of a collaboration with Prof. Takasada Shibauchi (University of Tokyo) and Ass. Prof. Shigeru Kasahara and Takuya Yamashita (Kyoto University) using the crystals grown by the Karlsruhe group. I particularly thank the very dedicated local contact William Knafo, and the cryogenic technician Mark Narbonne who operated the dilution fridge. I prepared all the samples reported here (except S2, which was prepared by Shigeru Kasahara), and the two band explanation of the relative amplitude of the oscillations was also my idea. Furthermore

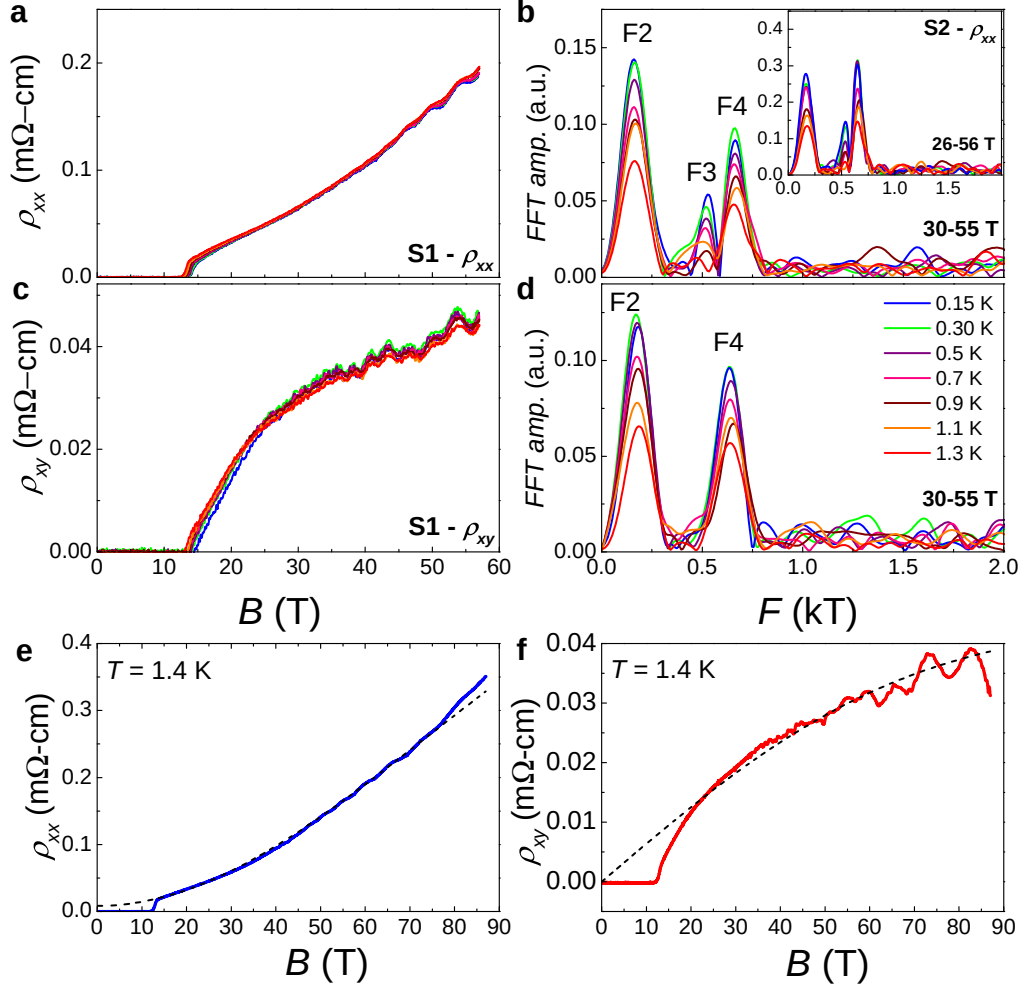


Figure 5.2: Analysis of quantum oscillations measured in a dilution fridge in pulsed fields up to 56 T. a,c) Resistivity and Hall effect measurements on FeSe sample S1. b,d) Corresponding Fourier transforms, revealing the quantum oscillation frequencies labelled F2-F4. Notably, the F3 peak is absent (or very weak) in the Fourier spectrum of the Hall Effect. Inset: quantum oscillations in the resistivity of S2, consistent with S1. In sample S1 the Hall and Resistivity components are determined by symmetrizing the data from the same pair of contacts; sample S2 was almost entirely symmetric and the Fourier spectrum is shown in the inset of b). e,f) Resistivity and Hall effect measured to 87 T. Dashed lines are a fit to the high-field data described in the main text.

I performed the low-field measurements in Oxford and the DC-field measurements in Nijmegen for which I must thank Alix McCollam for her excellent support.

5.4 Assignment of hole and electron pockets

The raw resistivity and Hall effect of sample S1 is presented in Fig. 5.2a and 5.2c where quantum oscillations can be clearly observed in the high-field region, with the Fourier transforms revealing three Shubnikov-de Haas frequencies labelled F2, F3 and F4. Note that in Ref. [74] the frequencies are labelled $\alpha - \delta$, however to avoid conflict with the ARPES bands discussed later I introduce this different notation. Although the resistivity and Hall effect are measured up to very high magnetic fields, the lower signal/noise ratio inherent to pulsed fields measurements means that observable oscillations start at a higher magnetic field and the limited window in inverse field means that the low-frequency F1 pocket reported in Ref. [74] is not resolved here.

Usually, it is impossible to determine based purely on quantum oscillations data whether a given quantum oscillation frequency arises from an electron-like or hole-like band or where it originates in the Brillouin zone, although often a comparison to band structure calculations can give a satisfactory understanding, as in Chapter 4. However, here I develop a novel argument based on a compensated two carrier model and the relative strength of oscillation peaks in ρ_{xx} and ρ_{xy} in order to argue that the F3 peak originates from an electron-like Fermi surface pocket, whereas the F2 and F4 are associated with the minimum and maximum of the hole-like band.

5.4.1 Derivation of the relative amplitude of quantum oscillations in resistivity and Hall effect measurements in a compensated semi-metal

The argument is based on the observation that the F3 orbit is missing, or at least much weaker, in the ρ_{xy} FFT spectrum compared with the ρ_{xx} , as can be directly seen from the FFT spectra from sample S1 in Fig. 5.2b and 5.2d. Note that in this sample, ρ_{xx} and ρ_{xy} are calculated by symmetrizing data from the same pair of contacts, which rules out any external explanation such as temperature gradients in the sample. In a

multiband system, ρ_{xx} and ρ_{xy} may generally be written in terms of the conductivities of the various bands. It will be shown that in a semimetal (i.e. equal number of holes and electrons which stoichiometric FeSe must have) where both the electron and hole conductivities have an oscillatory component, that the Hall Effect is *relatively* more sensitive to the oscillations of the more mobile carrier compared to resistivity; that is to say that if both electron-like and hole-like oscillations are observed in an FFT of ρ_{xx} oscillations, the FFT spectrum of ρ_{xy} will show a relatively enhanced amplitude of the more mobile carrier. In FeSe, the sign of the Hall coefficient at low temperatures and high fields is positive, i.e. the holes are (on average) more mobile, therefore the hole-like orbits are enhanced in the ρ_{xy} FFT spectrum and the missing / weak F3 peak is an electron-like orbit and both the F2 and F4 frequencies are likely to be hole-like frequencies.

In general, one may write the resistivity and Hall resistance of a two carrier system in a magnetic field as follows [122]:

$$\rho_{xx} = \frac{(\sigma_h + \sigma_e) + \sigma_h \sigma_e (\sigma_h R_h^2 + \sigma_e R_e^2) H^2}{(\sigma_h + \sigma_e)^2 + \sigma_h^2 \sigma_e^2 (R_h + R_e)^2 H^2} \quad (5.1)$$

$$\rho_{xy} = \frac{(\sigma_h^2 R_h + \sigma_e^2 R_e) + \sigma_h^2 \sigma_e^2 R_h R_e (R_h + R_e) H^2}{(\sigma_h + \sigma_e)^2 + \sigma_h^2 \sigma_e^2 (R_h + R_e)^2 H^2} H \quad (5.2)$$

Where σ_i and R_i are the conductivities and (inverse) carrier densities of the two species.

Since FeSe is a compensated material, one may write $R_e = -R_h = \frac{1}{ne}$ and then the formulae reduce as follows:

$$\rho_{xx} = \frac{1 + \frac{1}{(ne)^2} \sigma_h \sigma_e H^2}{(\sigma_h + \sigma_e)} \quad (5.3)$$

$$\rho_{xy} = \frac{\frac{1}{(ne)} (\sigma_h - \sigma_e) H}{(\sigma_h + \sigma_e)} \quad (5.4)$$

Note that the denominators are the same in both equations. Now, let the conduc-

tivities have an oscillatory contribution according to the Shubnikov-de Haas effect:³

$$\sigma_i = \sigma_{i0} \left(1 + A_i \sin \left(\frac{2\pi F_i}{B} \right) \right) \quad (5.5)$$

NB there may be more than one oscillation frequency associated with each carrier species due to Fermi surface corrugation but I omit the summation for simplicity.

Calculating the oscillatory part of the signals, to first order in A (i.e. $A \ll 1$), one finds:

$$\begin{aligned} \rho_{xx}^{osc} = & \frac{\sigma_{h0}\sigma_{e0}}{(ne)^2(\sigma_{h0} + \sigma_{e0})^2} \times \\ & \left(\sigma_{e0}A_h \sin \left(\frac{2\pi F_h}{B} \right) + \sigma_{h0}A_e \sin \left(\frac{2\pi F_e}{B} \right) \right) H^2 \end{aligned} \quad (5.6)$$

$$\begin{aligned} \rho_{xy}^{osc} = & \frac{2\sigma_{h0}\sigma_{e0}}{(ne)(\sigma_{h0} + \sigma_{e0})^2} \times \\ & \left(A_h \sin \left(\frac{2\pi F_h}{B} \right) - A_e \sin \left(\frac{2\pi F_e}{B} \right) \right) H \end{aligned} \quad (5.7)$$

Note in ρ_{xx} the oscillation amplitude is multiplied by the mobility of the *other* carrier species. Therefore for a two carrier semimetal, the oscillations of ρ_{xx} are relatively less sensitive to the oscillations of the more mobile carrier; alternatively the Hall oscillations are proportionally more sensitive to oscillations of the more mobile species, which may be determined by the sign of the Hall coefficient. E.g. in FeSe since the Hall coefficient is positive (at low temperature, in the field region of interest), $\sigma_h > \sigma_e$ and the oscillations of the hole bands are enhanced over the electron bands, helping to identify the oscillation frequencies. The more mobile species are likely to have a larger amplitude (greater A_i) anyway as they scatter less: the scattering time entering the mobility also enters in the Dingle term determining the amplitude of the quantum oscillations, however in ρ_{xy} the amplitude is further enhanced relative to the amplitude in ρ_{xx} . This is demonstrated schematically in Fig. 5.3.

³The assumptions behind this will be discussed in the next subsection.

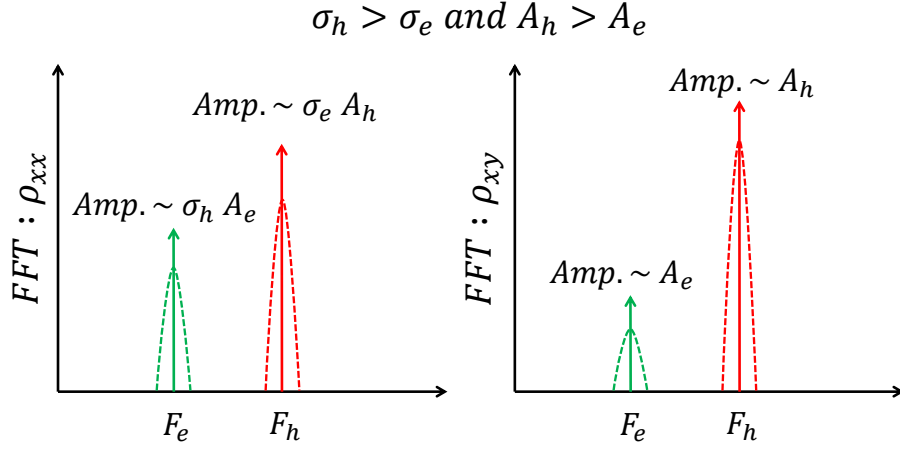


Figure 5.3: Cartoon of the relative amplitudes of quantum oscillations for a compensated semi-metal, with hole and electron contributions to the resistivity and Hall effect. As in FeSe $\sigma_h > \sigma_e$ from the sign of the Hall effect, I therefore also take $A_h > A_e$. The relative amplitudes of the oscillations can therefore be understood by general considerations of a two carrier model and suggest the nature of the carrier when the effect is large, such as in FeSe.

5.4.1.1 Notes on assumptions of the model.

There is an important assumption in this formalism, which was pointed out by Prof. Andrew Schofield (University of Birmingham) and needs to be addressed here. Usually, quantum oscillations in magnetotransport are understood to occur due to oscillations of the scattering rate [49] according to Fermi's Golden Rule; as the density of states at the Fermi level oscillates, so too does the density of final states available after a scattering process. We have assumed that e.g. the scattering rate of the hole mobility depends on quantum oscillations arising from hole pockets, but not of electron pockets, but there may well be scattering process that may transfer a carrier to the other carrier pocket, and therefore this assumption may not be valid. Indeed, in an unrelated multiband system $\text{Ca}_3\text{Ru}_2\text{O}_7$ [123] a good understanding of the oscillations in the Hall effect was found by assuming the same oscillating part of the scattering time for the two different bands - the opposite approach to the model presented above.

However, one may note that at low temperatures ~ 1 K the dominant scattering process will be impurity scattering, which resembles Rutherford scattering [48] and strongly favours low- q processes. Then, I argue based on the fact that the pockets are small and well separated in the Brillouin zone, that scattering processes will overwhelmingly leave e.g. a hole carrier in the hole band and the matrix elements for interband process are small, and that this treatment should hold. However one does have to take the ARPES or DFT view of the topology of the Fermi surface in order to know this information.

Furthermore, I have assumed a two band model here, whereas it is clear from the low-field Hall effect data that a better model is to have one hole band but two electron bands, one of which is small but has rather higher mobility carriers. Nevertheless, in the high field limit where these quantum oscillations data are taken, the two carrier fit works reasonably well (see Fig. 5.2e,f) with a substantially larger mobility for holes compared to electrons, giving us some confidence. The slight non-linearity in the Hall effect at high fields may indicate that either the system is very slightly off-stoichiometric, or that the mobilities are slightly field-dependent - noting that a compensated two carrier model is strictly linear in ρ_{xy} but also a compensated three-carrier model is linear in ρ_{xy} in the high-field limit. Nevertheless one hopes that the system is close enough to the two band model described that the assignment of hole and electron character to the quantum oscillation frequencies will be correct and it is consistent with the joint analysis with ARPES presented in the next Chapter 6.

5.5 Analysis of quantum oscillations: frequencies and effective masses

In Fig. 5.2b, A high-field window of 30-55 T (26-56 T for S2) is used to Fourier transform the oscillatory contribution to the resistivity after a polynomial background subtraction. As this is not a large window in $1/B$ it is not possible to say from these

sample	orbit	F (kT)	m^* (m_e)	A_k (%BZ)	k_F ($\text{\AA}^{-1}$)
$S2 : R_{xx}$ (27-56 T)	F2	0.171	4.20(25)	0.59	0.072
	F3	0.536	7.55(61)	1.84	0.128
	F4	0.651	4.47(30)	2.24	0.141
$S1 : R_{xx}$ (30-55 T)	F2	0.164	4.06(23)	0.562	0.070
	F3	0.528	7.25(58)	1.82	0.127
	F4	0.664	4.38(25)	2.282	0.142
$S1 : R_{xy}$ (30-55 T)	F2	0.177	4.16(23)	0.609	0.073
	F3	-	-	-	-
	F4	0.640	4.16(23)	3.88(25)	0.139
$S6 :$ (19-33 T)	F1	0.114	3.0(5)	0.392	0.059
	F2	0.200	4.1(30)	0.688	0.078
	F3	0.568	6(1)	1.953	0.131
	F4	0.664	4.7(30)	2.283	0.142

Table 5.1: Frequencies, effective masses, areas of k -space and Fermi k -vectors for 3 different samples; for sample S1 the analysis is split for the resistivity and Hall effect channels. Areas of the Brillouin Zone are relative to the high-temperature tetragonal phase.

pulsed-field data if there are any weaker frequencies below the F2 frequency at 180 T. Analysis of the temperature-dependence of the amplitude of oscillation allows the determination of the effective masses by fitting to the Lifshitz-Kosevich formula (Eq 3.13), as shown in Table 5.1. We find agreement in the values of the effective masses between samples within the error bars. The F3 orbit has a particularly heavy effective mass of 6-8 m_e , whereas the F2 and F4 orbits have effective masses of around 4 m_e , which supports the idea of the holes bands (F2 and F4) being the higher mobility species - in fact this is a weaker, but independent argument to support this assignment of electrons and holes. The experimental pockets are substantially smaller than the predictions from DFT, and the effective masses are also substantially heavier. I will discuss this comparison in detail in the next chapter, which concerns the details of the topology of the Fermi surface combining ARPES and quantum oscillation rotation studies.

5.6 Rotation study in 33 T

I now consider the angular dependence of the quantum oscillation frequencies. For this study, a sample S6 from the crystals grown in Oxford (see Appendix A) was used. These crystals appear to be of as high quality as those grown in Karlsruhe, since quantum oscillations were observed in both with comparable magnitudes. The original purpose of these experiments was to complement ARPES experiments on the same batch of single crystals. However, here I will report the angular dependence alongside the pulsed field $B||c$ data and delay the comparison between ARPES and quantum oscillations until the next Chapter.

In Fig. 5.4c, four different quantum oscillation frequencies are found, labelled F1-F4 (in ascending order), consistent with the pulsed-field data. The F1 frequency resolved here is not resolved in the pulsed field data; even though higher fields are accessed in the pulsed-field experiments, the range of *inverse* field over which oscillations is observed is actually smaller⁴. Fig. 5.4d shows the temperature-dependence of the amplitude of oscillation from which the effective masses may be determined, and stated in Table 5.1 alongside the pulsed-field data. Fig. 5.4e shows the angular-dependence of the oscillatory part of the resistance. One notable feature is that for all bands the signal appears to drop around 32° (at both positive and negative angles). One possible reason for this is a so-called “spin-zero” arising from the spin-splitting damping term as described in Refs.[49, 69]. A spin-zero at 32 degrees can be achieved with a $m_s=2.95m_e$. It is known [68] that m_s is only renormalised by electron-electron and not electron-phonon interactions which may explain why $m_s < m^*$ ⁵. The fact that all of the frequencies appear to have a spin-zero at similar angles is likely to be

⁴It should be noted that for this sample, the analysed signal was a mix of ρ_{xy} and ρ_{xx} - this happened to give the best resolution of F3 and F4. However Fig. 5.4a shows the symmetrized magnetoresistance.

⁵As described in Ref. [69] a single spin-zero is not sufficient to uniquely identify the spin-mass due to the form of R_S , however $m_s=2.95$ was the solution giving the most reasonable parameter in this case.

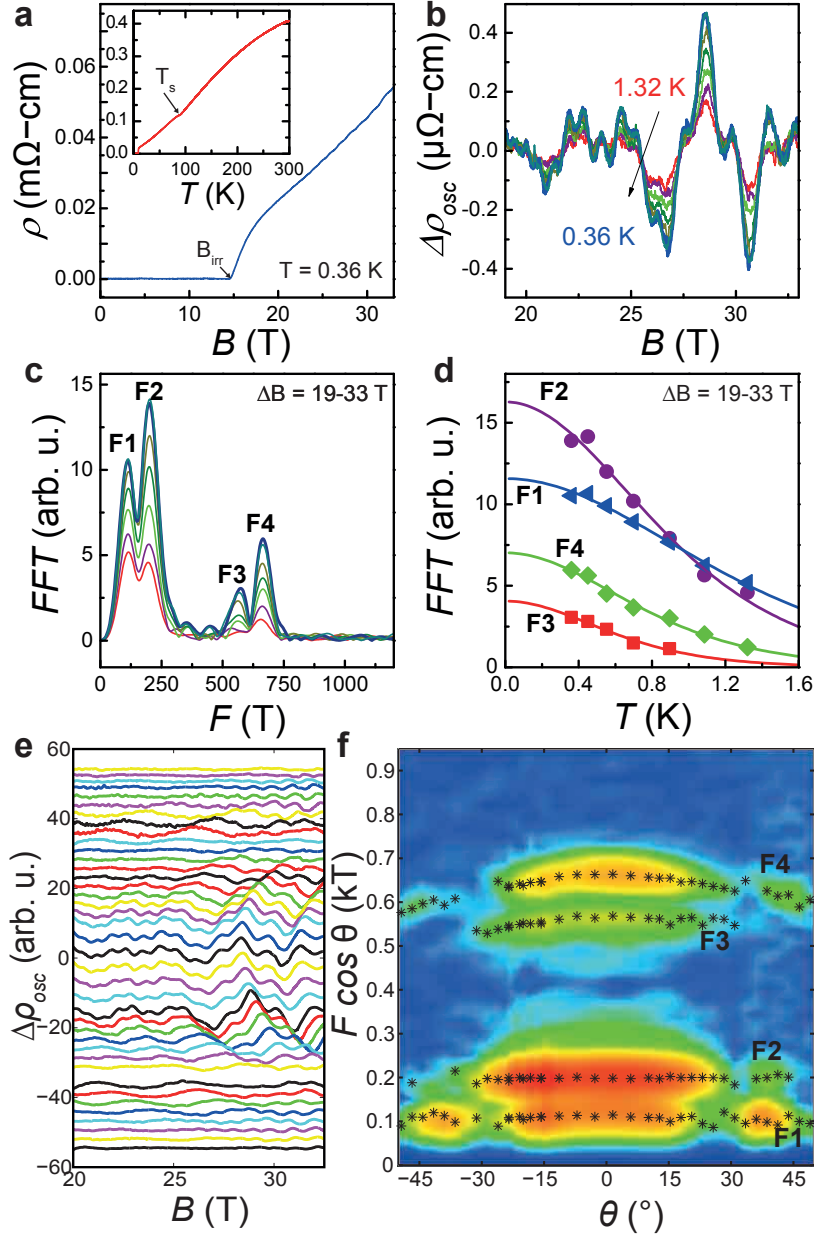


Figure 5.4: a) Magnetoresistance of FeSe for a field applied along the c axis. Above the superconducting irreversibility field at 14 T, a large magnetoresistance is observed on top of which an oscillatory signal $\Delta\rho$ is observed. b) The oscillatory part of the resistivity, obtained by polynomial background subtraction. c) Fourier transform (FFT) of the subtracted signal in b) identifying 4 quantum oscillation frequencies F1-F4, corresponding to extremal areas of the Fermi surface. d) Temperature-dependence of the amplitude of oscillation, from which the effective masses may be extracted. e) FFTs as a function of angle of applied field with respect to the c axis. Oscillations are observed to about 50° . f) By plotting $F \cos \theta$ against θ one can identify if orbits correspond to a maximum or minimum of a quasi-2D Fermi surface.

a coincidence. In Fig. 5.4f the peaks in the Fourier transformations as a function of angle are plotted, on top of an intensity plot showing the amplitude of the peaks. As in the previous Chapter on LiFeAs, it is convenient to plot $F \cos \theta$ against θ to identify whether a frequency arises from a maximum or a minimum of the quasi-2D band. Clearly F3 and F4 are both maxima, and F2 is likely to be a minimum. For F1 the situation is not clear in these data but it was found in Ref. [74] to correspond to a minimum.

There is a reasonably good agreement between the values of the frequencies and effective masses between pulsed fields and DC fields and with those reported previously in Ref. [74, 124]. However, in the case of F1 pocket there is a large disparity between the quasiparticle masses reported, probably due to the limited inverse magnetic field window available in $1/B$ (due to the superconductivity) and the problems associated with background subtraction for the analysis of low frequency quantum oscillations.

5.6.1 Comparison to DFT prediction of quantum oscillation frequencies

In the case of several iron-based superconductors which do not undergo any magnetic or structural transitions, a reasonable agreement between observed quantum oscillation frequencies and DFT predictions is observed, e.g. in LaFePO [7], BaFe₂P₂ [58] and LiFeP and LiFeAs as discussed in the last chapter (for a review, see Ref. [68]). Sometimes there are significant shifts and renormalisations required (e.g. as the superconducting dome is approached from the over-doped side in BaFe₂(As_(1-x)P_x)₂ [75]), and sometimes strong correlations may even lead to a modification of the topology of the Fermi surface compared to the DFT [126], nevertheless DFT has been almost always used as a starting point to assign the observed bands in Fe-based superconductors and it is typically not too far from experiment. However, in the case of FeSe I have not attempted the usual procedure for matching quantum oscillation

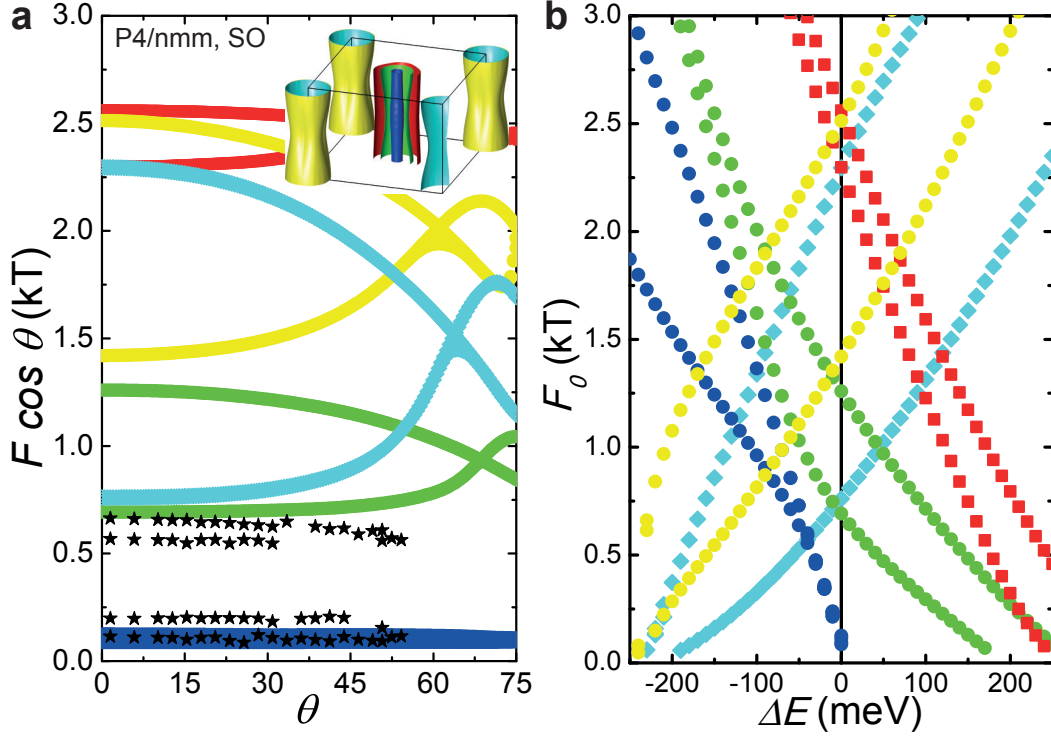


Figure 5.5: Comparison between the predicted and measured values of quantum oscillations frequencies. a) Predictions of quantum oscillation frequencies as a function of angle in FeSe, using the $P4/nmm$ relaxed structure of Ref. [125]. θ is defined as the angle of rotation from the c axis to the a axis. Black stars are experimental frequencies. Inset: corresponding Fermi surface. The predicted quantum oscillation frequencies (calculated using the SKEAF algorithm [79]) consists of frequencies up to ~ 2.6 kT arising from quasi-2D bands. The calculation does not account for the structural distortion; however even when it is included it makes very little difference to the shape of the Fermi surface or predicted quantum oscillations frequencies. b) Calculated quantum oscillation frequencies at $\theta = 0$ as a function of rigid band shift. Large shifts of ~ 200 meV would be required to bring the calculated frequencies down to the order of the experimental frequencies.

frequencies to DFT calculation since the DFT does not correctly account for the dramatic electronic anisotropy observed in ARPES and therefore does not provide a good starting point, and moreover the sizes of the pockets predicted by DFT are so much larger than observed that it is better to start without any assumptions.

As a coincidence, studies of quantum oscillations in the magnetically ordered phase typically reveal small pockets [73, 70] with comparable sizes to those in FeSe (i.e. less than 1 kT). However it is well-known from several measurements that FeSe does not

Sample	S1	S1	S3	S4
T (K)	1.4	1.4	20	9.6
B (T)	17-88	17-88	0.2-13.5	1-33
n_h (cm ⁻³)	3.81×10^{20}	3.46×10^{20}	1.47×10^{20}	2.71×10^{20}
n_{e1} (cm ⁻³)	4.66×10^{20}	3.46×10^{20}	1.25×10^{20}	2.03×10^{20}
n_{e2} (cm ⁻³)	-	-	2.2×10^{19}	6.8×10^{19}
μ_h (cm ² V ⁻¹ s ⁻¹)	1335	756	649	623
μ_{e1} (cm ² V ⁻¹ s ⁻¹)	499	401	607	456
μ_{e2} (cm ² V ⁻¹ s ⁻¹)	-	-	2570	1843
Fitting model	2-band	con. 2-band	con. 3-band	con. 3-band

Table 5.2: Comparison of 2 and 3-carrier fits to magnetotransport data. The fitting procedure simultaneously fits the Hall effect and resistivity. Constrained (con.) fits require charge neutrality, reducing the number of free parameters by one. The unconstrained 2-band model for S1 is used for the dashed lines in Fig. 5.2e,f and the 3-carrier fit to the 20 K data of S3 is plotted in Fig. 5.2d. For reference, n_h estimated from quantum oscillations is 3.6×10^{20} cm⁻³.

undergo a magnetic transition (including the absence of magnetic reconstruction in ARPES measurements) and therefore the reason for the small pockets is likely to be related to correlation effects and not magnetic reconstruction.

5.7 Low temperature, high field magnetotransport

Pulsed field measurements of ρ_{xx} and ρ_{xy} at 1.5 K up to 87 T are presented in Fig. 5.2e,f. The model used for that fitting is a two band model, where there is no restriction for the system to be compensated, but the fit converges to similar n_h and n_e which are reasonably close to the estimated $n_h = 3.6 \times 10^{20}$ cm⁻³. The constrained fit ($n_e = n_h$) cannot capture the non-linearity of ρ_{xy} however gives a similar carrier density, and the parameters can be compared in Table 5.2. These fits give us some confidence that the two carrier model is a good approximation at least at high fields, and that the argument about the assignment of the hole and electron pockets is valid, and in particular the ratio of $\frac{\mu_h}{\mu_e} = 2.7$ would give rise to a noticeable difference in amplitude of quantum oscillation in ρ_{xx} and ρ_{xy} according to the analysis presented earlier.

5.8 Low field magnetotransport

I now investigate low-field magnetotransport data at higher temperatures in order to try to understand the evolution of the electronic structure and scattering rates. The most natural model to turn to is again a compensated two band model, where the two bands represent the electron and hole pockets and charge compensation is demanded in a stoichiometric crystal; therefore there are three free parameters in the model, $n = n_e = n_h$, μ_e and μ_h . A feature of this model is that the Hall effect is strictly linear at all magnetic fields and the magnetoresistance does not saturate. This model was also used in LiFeAs [28], where it was found that the Hall effect was negative and linear up to 14 T at all temperatures, indicating that the electrons were always more mobile than the holes. The fitting routine simultaneously fits ρ_{xx} and ρ_{xy} , with equal weighting.

In FeSe at high temperatures, the holes and electrons have very similar mobilities, with subtly different temperature-dependences such that sometimes the electrons and sometimes the holes are more mobile, meaning that the sign of the Hall coefficient changes twice in the range 90-300 K. However, in this regime the two carrier fits work very well. Below ~ 75 K, the Hall effect becomes noticeably non-linear, and very dramatically non-linear by 20 K. Such behaviour cannot be understood in a two band model. The authors of Ref. [109] used a mobility spectrum analysis to demonstrate the presence of some high mobility electron carriers which could account for the non-linear Hall effect and in particular the negative sign of the Hall coefficient at low fields, but becoming positive at high fields. The FeSe data are also similar to measurements on annealed BaFe₂As₂ single crystals [127]; although the Fermi surface in the magnetically reconstructed phase is completely different, there are coincidental similarities in that there should be a compensated number of carriers and in particular a small number of highly mobile electron-like carriers. In Ref. [127] a 3-band model was used to fit their Hall effect data; here I improve on that analysis by simultaneously

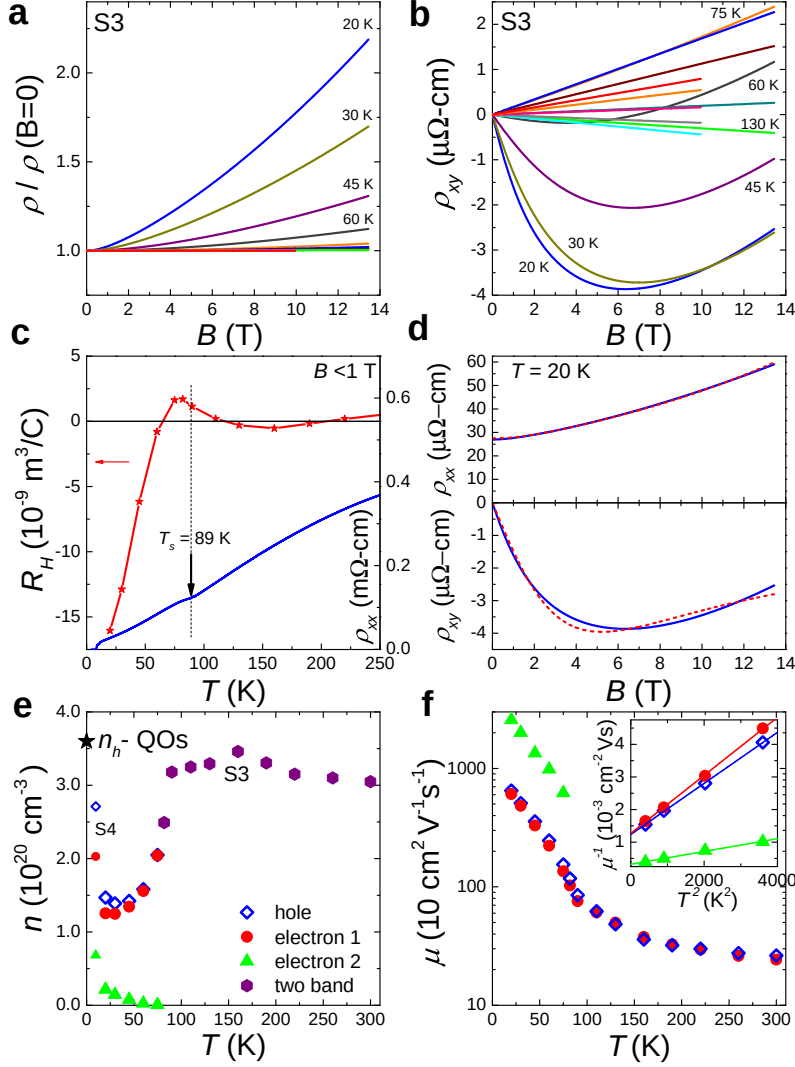


Figure 5.6: a) Magnetoresistance measured to 13.5 T in a sample S3 at temperatures between 20-300 K. b) Hall effect in FeSe. c) low-field Hall coefficient, defined by a straight-line fit to the data < 1 T. At high temperatures the Hall effect is linear but changes sign twice above 90 K. At low temperatures the Hall effect is very non-linear but the low-field Hall coefficient is negative. Also shown is the raw resistivity. d) Simultaneous fit of the magnetoresistance and Hall effect in a constrained 3-carrier model. A compensated two carrier fit to these data would be impossible. e) Temperature-dependence of the carrier density extracted from 2- and 3-carrier fits (3 carrier fits below 75 K where a noticeable non-linearity of the Hall effect sets in.) f) Temperature-dependence of mobility. Inset: the inverse of mobility, proportional to the scattering rates, appear to have a $\sim T^2$ dependence in the range of 20-60 K.

fitting ρ_{xx} and ρ_{xy} with a compensated, 3-carrier model [50] with one hole and two electron pockets, i.e. five free parameters. The result of that fitting on the 20 K data (fitting the complete data set up to 13.5 T) is presented in Fig. 5.6d. This three band model accounts for a small but highly mobile electron pocket. These data are consistent with the existence of two electron pockets: an outer d_{xy} pocket which I associate with the heavier F3 frequency in quantum oscillations, and a small electron pocket which is much more mobile.

While the two and three carrier models capture the data well, the extracted temperature-dependence of the carrier density shows a marked reduction of the carrier density below the structural transition at 90 K, dropping by a factor of ~ 2 compared to the high temperature values. Furthermore, the carrier density n_h estimated from quantum oscillations (assuming the F2 and F4 bands form the quasi-2D hole band) is $3.6 \times 10^{20} \text{ cm}^{-3}$ - similar to the high temperature carrier densities but substantially higher than the 20 K data. Below 20 K, the carrier density seems to recover to some extent, as shown by extracted parameters on a different sample S4 (Fig. 5.7), and furthermore the pulsed-field low temperature data on S1 give carrier densities from two carrier fits which are comparable again with quantum oscillations (Table 5.2).

Here, I present a *speculative* idea which may reconcile the apparent drop in carrier density below T_s with the observation from ARPES (and common sense) that the volumes of the Fermi surface should not change significantly. However, the reader is cautioned that this may not be the only possible interpretation. The suggestion is that a strongly anisotropic scattering rate may exist around the Fermi surfaces below the structural transition. If there are strong spin fluctuations (as observed by NMR below T_s [45]), parts of the hole and electron Fermi surfaces which are well nested by the antiferromagnetic ordering vector will have a dramatically increased scattering rate, similar to calculations in Ref. [128], and will be effectively shorted out by non-nested segments of the Fermi surface with a much longer scattering time

(and which may have conventional $\sim T^2$ Fermi liquid temperature-dependence of mobility, Fig. 5.6f). Therefore, the *effective* carrier density in a simple two (or three) carrier fit will appear to drop, despite no actual change in Fermi surface volume. This effect is strong, and by 30 K it appears that half of the carriers are ‘missing’. However, at very low temperatures, the scattering becomes almost isotropic (impurity scattering only in the $T=0$ limit) [128]. It is in this limit that quantum oscillations are observed, and the carrier densities from high-field two carrier fits are again comparable to the estimated n_h from quantum oscillations. Theoretical studies of transport in FeSe based on a realistic Fermi surface, as well as studies of optical conductivity to investigate these effects would be welcome.

The puzzling temperature-dependence of n notwithstanding, the mobilities have a more easily understandable temperature-dependence. Above the structural transition, the mobilities decrease with increasing temperature as the scattering rates from electron-phonon and electron-electron scattering become large. However, in the range of 20-60 K an approximate T^2 scattering rate is observed, which is consistent with the expected scattering rates for a Fermi liquid [28]. The T^2 scattering behaviour of these extracted mobilities contrasts with the resistivity having a quasi-linear temperature-dependence in this range, as also observed by other authors⁶. However according to the three-band model, the quasi-linearity occurs due to the fact that the effective carrier density is also changing in this regime and not due to any more complex reason such as quantum criticality.

5.9 High temperature, high field magnetotransport

In Fig. 5.7, I present further magnetoresistance data taken in pulsed and DC field magnets. In Fig. 5.7a,b high magnetic fields are used to measure the magnetoresis-

⁶In Ref. [129], the exponent α of resistivity $\rho = \rho_0 + AT^\alpha$ of a very clean single crystal was found to be 1.05-1.2, which is consistent with the sample I have measured.

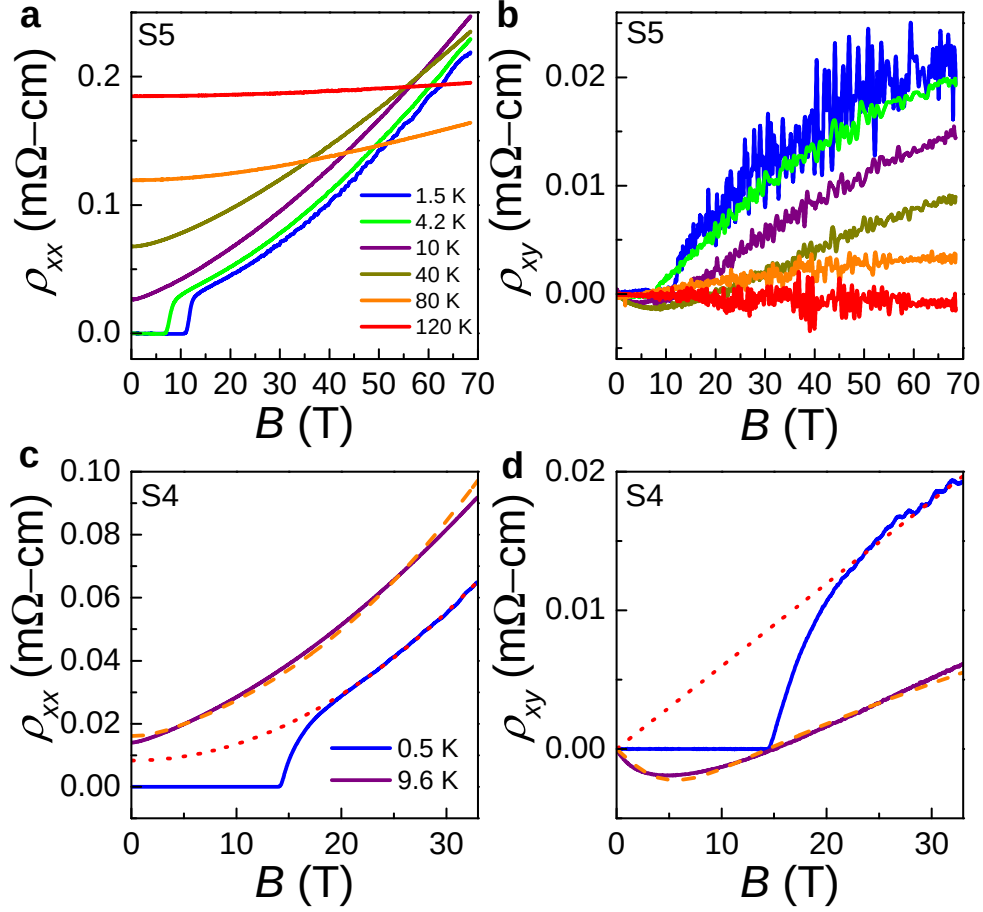


Figure 5.7: High-field magnetotransport on two further samples. a,b) Pulsed field magnetotransport measurements up to 67 T, between 1.5 K and 120 K. c,d) DC field measurements of the resistivity and Hall effect of sample S4. Orange dashed line is a fit to the 9.6 K data using a constrained 3-carrier model, with the fit parameters given in Table. 5.2. Red dotted line is a fit to a constrained 2-carrier model to the data above 20 T.

tance up to 67 T at temperatures up to 120 K. As the mobilities drop with increasing temperature, the magnetoresistance naturally drops, until at 120 K it is a small effect ($\Delta\rho(67\text{ T})/\rho(0) = 5.5\%$) but shows no sign of saturating at any temperature or field. The accompanying high field Hall effect measurements on the crystal were unfortunately hampered by experimental issues⁷, however it shows that the high-field Hall effect is always positive at least up to 80 K. Another sample S4 was measured in DC fields (allowing for a much quieter measurement), and in Fig. 5.7c,d I show the large difference in magnetotransport measurements at 0.5 K compared to 9.6 K; in addition to the superconductivity, the magnitude of the Hall effect changes markedly. At 9.6 K, a constrained 3-carrier model describes very well the behaviour of the Hall effect and resistivity (orange dashed line) and the fitting parameters are noted in Table. 5.2; it is important to include the higher mobility electron pocket to correctly describe the low-field data. However, at 0.5 K the low field data are not available due to superconductivity, and therefore I use a constrained 2-carrier model instead, fitting the data above 20 T (red dotted line) - with parameters $n_h = n_e = 4.31 \times 10^{20}\text{ cm}^{-3}$, $\mu_h = 1231$ and $\mu_e = 512\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, similar to the constrained fit of sample S1. Furthermore, quantum oscillations were observed in both samples at low temperature, in agreement with samples S1 and S2.

5.10 Discussion

Taking into account the measured quantum oscillation frequencies and the conclusions of the magnetotransport data, a schematic Fermi surface may be constructed, as shown in Fig. 5.8, indicating the assignment of quantum oscillation frequencies to extremal areas of the Fermi surfaces. The F2 and F4 frequencies were shown to arise from a hole pocket based on the relative amplitudes of oscillations in ρ_{xx} and ρ_{xy} . From the angular dependence, it was found that F4 and F2 are a maximum

⁷It is challenging to wire up a sample for Hall measurements without having open loops, whereas for resistivity measurements with contacts on the same side of the sample it is easier.

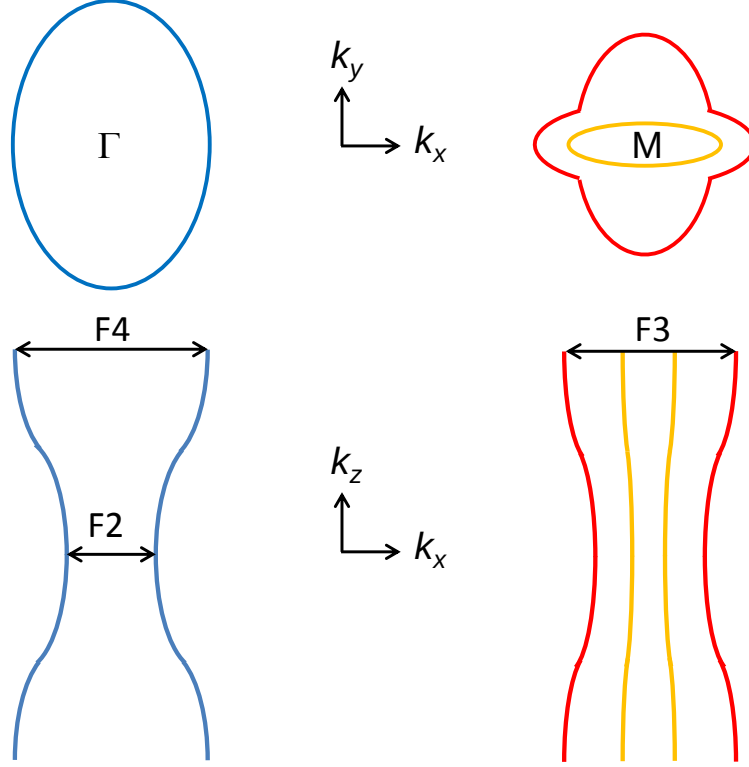


Figure 5.8: Schematic low-temperature Fermi surfaces of FeSe based on transport and quantum oscillations measurements, consisting of one hole pocket around the Γ point and two electron-like pockets around the M point.

and a minimum respectively, and therefore I assign them as the extremal frequencies of a single hole band. F3 was shown to be an electron pocket, and is a maximum. The shape of the pockets is informed by ARPES experiments in Chapter 6 but must necessarily be elongated ellipses since the four-fold symmetry is broken. The low frequency F1 pocket must originate from an electron pocket, but it is not clear which - it could be the minimum ('neck') of the outer electron band as suggested in Ref. [74], or more likely arises from the small inner electron pocket and may actually consist of two unresolved frequencies and manifests as the small high mobility pocket in magnetotransport.

One important question is whether the high magnetic fields used influence the electronic structure. It is well-known that in a paramagnet, the bands will spin-split

in the presence of a magnetic field but it is easily shown [49] that as long as the splitting is linear with magnetic field this doesn't affect the *measured* frequency; within experimental resolution I do not observe any splitting (although since the frequencies are low, one cannot exclude some small splitting). One reason for performing experiments up to some of the highest available magnetic fields in the world was to search for any field-induced transition; however no observable anomalies in magnetotransport up to 87 K were found.

In summary, I have used very high magnetic fields at low temperature to measure quantum oscillations in clean single crystals of FeSe. Three quantum oscillation frequencies are observed, at 200 T, 540 T and 660 T, with moderate to large effective masses and frequencies very much smaller to the predictions of DFT. In addition, by a novel joint analysis of the oscillations in the resistivity and Hall effect, I infer that the 540 T frequency, which has a rather larger effective mass, arises from an electron-like orbit, whereas the 200 T and 660 T are likely to arise from a hole-like band, which are the more mobile carrier in the low-temperature, high-field regime. Low-field data also indicates the presence of another small electron band with higher mobility. The low-temperature electronic structure of FeSe is crucial in understanding the unconventional superconductivity in this, structurally the simplest of all Fe-based superconductors, and these data suggest that electronic correlations strongly modify the band structure, leaving rather small and renormalised quasi-2D hole and electron-like pockets.

In order to fully determine the topology of the Fermi surface, it is desirable to also use the complementary method of ARPES. This is the subject of Chapter 6, in which I will determine the band structure of FeSe and also the changes of the Fermi surface which occur through the structural transition. I will present further discussion of the implications of this unusual symmetry-broken Fermi surface with very small carrier densities at the end of Chapter 6.

Chapter 6

The electronic structure of FeSe

In this Chapter I report angle-resolved photoemission spectroscopy (ARPES) measurements of the band structure of FeSe. I compare the high-temperature measurements to DFT calculations in the high-symmetry phase, finding moderate band renormalisations, particularly strong on a hole band with d_{xy} character, and also finding that the experimental Fermi surface volumes are significantly shrunk compared to the prediction of DFT. The temperature-dependent measurements study the dramatic changes to the electronic structure that occur below the structural transition. I compare the low temperature Fermi surface with elongated hole and electron pockets with the quantum oscillations study presented in Chapter 5. These studies reveal a distortion of the Fermi surface at the structural transition, with the low-temperature Fermi surface composed of small elliptical hole and electron-like Fermi surface pockets. Additionally, a large splitting of bands with d_{xz} and d_{yz} orbital character is observed, and is interpreted as evidence for a ferroorbital order. The low-temperature Fermi surface consists of one small and elongated hole Fermi surface and two elongated electron bands. These studies provide the essential ingredients to develop realistic models of the symmetry-breaking and superconductivity in FeSe. This Chapter is based on the work which is now published in Phys. Rev. B **91**, 155106 (2015).

6.1 Introduction

One of the most important problems in the field of unconventional superconductivity is the characterisation of the normal state from which superconductivity emerges. FeSe is structurally the simplest and yet one of the most intriguing iron-based superconductors, since in its bulk form it undergoes an electronically-driven structural transition before it becomes superconducting, whereas its single-layer form is believed to be a high-temperature superconductor. Unusually, the structural transition at $T_s=87$ K is not accompanied by a magnetic transition at any temperature, as was discussed at the start of Chapter 5. This allows a unique insight into the electronic structure of the symmetry-broken, or *nematic*, state. Using ARPES, the temperature-dependence of the electronic structure may be determined, giving insight into the nature of the symmetry-breaking instability and fully characterising the low-temperature Fermi surface along with the quantum oscillation studies presented in the previous Chapter.

6.2 Methods

Single-crystal samples were grown by Dr Amir Haghighirad and myself as described in Appendix 1. ARPES measurements (as introduced in Section 3.7) were performed at the I05 beamline at Diamond Light Source, UK. Single crystal samples were cleaved in-situ at a pressure lower than 2×10^{-10} mbar and measured at temperatures ranging from 6-120 K. Measurements were performed using linearly-polarised synchrotron light between 18-120 eV and employing a Scienta R4000 hemispherical electron energy analyser with an angular resolution of 0.2-0.5 deg and an energy resolution of ~ 3 meV. Samples were carefully aligned such that the path from Γ -M is also the scattering plane. This maximises the effect of matrix elements since the scattering plane is also the local coordinate frame of the Fe atoms (at 45° to the tetragonal in-plane axes),

and strong selection rules will hold. Additionally, it is particularly important for the cut through the M point to have this alignment otherwise a misleading cut may be obtained.

Band structure calculations were performed using the relaxed crystal structure of FeSe ($a = 3.7651 \text{ \AA}$, $c = 5.5178 \text{ \AA}$, $z_{Se} = 0.24128$ from Ref. [125]) in Wien2k (GGA) with spin-orbit coupling included. Since FeSe does not show magnetic order ARPES spectra are compared to non-spin-polarized band structure, although in DFT various magnetic orderings are lower in energy [120]. A discussion of different possible choices for the band structure calculations is presented in Section 6.7.4.

6.3 Hole bands at the Γ point

In the iron-based superconductors, studies of the electronic structure by quantum oscillations [7, 59, 58] or ARPES [89, 130] have generally found reasonable agreement with DFT - although experimentally, the bands are often shifted and renormalised compared to the calculation. However, as was hinted at in the quantum oscillations study in Chapter 5, it will be demonstrated here that DFT calculations in the paramagnetic state are not a good starting point for understanding the experimental band structure of FeSe even above the structural transition, and there are dramatic alterations below it. Therefore, experimental characterisations of the Fermi surface are crucial for developing more realistic theories.

Fig. 6.1a shows the calculated Fermi surface of FeSe in the tetragonal paramagnetic phase, which consists of three hole pockets (α , β and γ) around the Brillouin zone centre Γ and two electron-like bands (δ and ϵ), around the corner of the Brillouin zone at the M point, similar to other reports [111]. The bands which cross the Fermi level have almost exclusively d_{xz} , d_{yz} and d_{xy} character (Fig. 6.1 a,b). Both the Γ and M point have four-fold point-group symmetry in the P4/nmm high temperature unit cell, since the d_{xz} and d_{yz} are degenerate, although deliberately coloured differently

here. As detailed in e.g. Refs. [84, 130], in ARPES experiments, due to matrix effects elements the light polarization and the scattering geometry allows the selection of either mainly d_{xz} or d_{yz} bands using LH (p) or LV (s)-polarization, respectively and to identify the orbital character of the measured bands in combination with the DFT predictions. The orientation of the high-symmetry cuts to be presented in Figs. 6.1 and 6.2 are indicated in Fig. 6.1a.

Fig. 6.1d-f show the temperature-dependence of the high-symmetry A-Z-A cut, which is similar to the cut through Γ (Fig. 6.1c), except that the hole pockets are slightly larger and small effects may be more easily observed. In the high-temperature phase with C_4 symmetry both α and β bands cross the Fermi level, as shown by the Fermi-level momentum distribution cuts at 120 K in Fig. 6.1h. The degeneracy between the α and β bands at Γ (or equivalently Z) is lifted only by the spin-orbit coupling [94] which can be estimated from these data directly as being $\Delta_{SO} \sim 20$ meV. Both bands cross at the Z point at high temperature; it is not known conclusively if the β band also crosses at Γ at high temperatures but most likely it forms a tiny 3D pocket around Z at high temperatures. By lowering the temperature below the structural transition at 87 K the β band is pushed below the Fermi level by ~ 23 meV shown in Fig. 6.1g,h. About 50 meV below the Fermi level the presence of a broad band that is the d_{xy} band in Fig. 6.1g is also detected, which has weaker intensity due to matrix elements considerations and it is shifted significantly in relation to the high temperature predictions in Fig. 6.1b.

The effect of electronic correlations can be estimated by comparing the high temperature band structure calculations with the band dispersion in the tetragonal phase at 120 K, as shown in Fig. 6.1g. The obtained renormalisation factors for FeSe are ~ 3.2 , 2.1 and 8 for the α , β and γ pockets respectively - suggesting particularly strong orbital-dependent electronic correlations on the γ band with d_{xy} orbital character. These are close to values of 3-9 reported in another ARPES study on FeSe

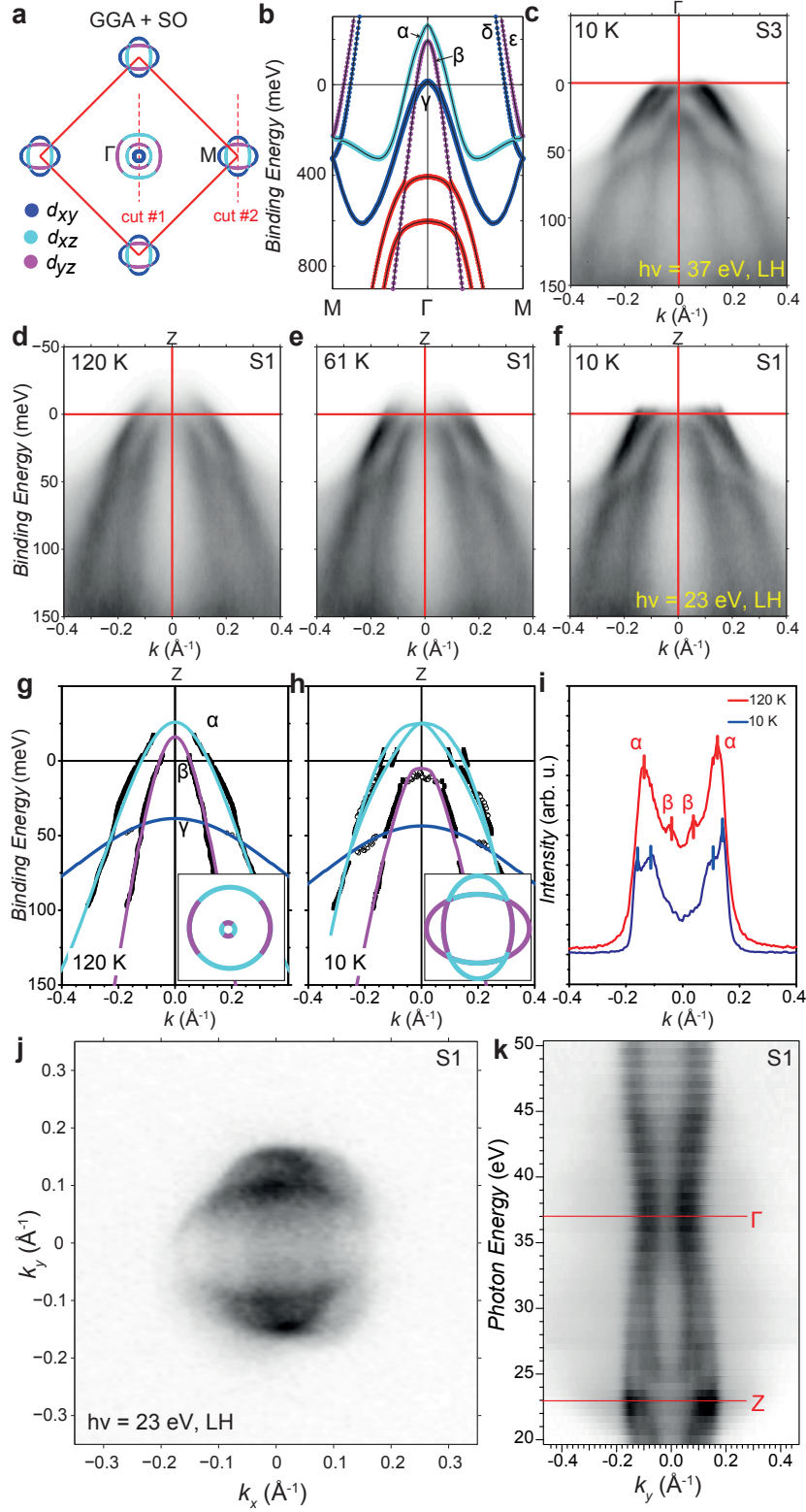


Figure 6.1: ARPES Measurements of the hole pockets around the Γ/Z point of FeSe above and below T_s . (Caption continued overleaf)

Figure 6.1: (Figure on previous page). a) DFT Fermi surface calculation for FeSe in the high-temperature tetragonal phase, projected into the $k_z = 0$ plane and coloured by dominant orbital character. The labelled cuts are the high-temperature cuts shown in Fig. 6.1 and Fig. 6.2 respectively. Calculations predict three hole pockets around the Γ point and two electron pockets around the M point, as shown also by the high-symmetry cut in b). c) ARPES dispersion through the Γ point at low temperature. The hole pockets are larger at Z, where the temperature-dependence of the cut is plotted in d)-f). g) Extracted band dispersion from constrained multiple Lorentzian fits to momentum-distribution cuts (MDC – solid symbols) or peaks in the energy dispersive cut (EDC – open symbols) from the spectra in d) and f). The outer hole band, labelled α , appears to split near the Fermi level, resulting in two crossings, as also shown in h). This is a result of elongation of the pocket combined with a duplicate rotated by 90° due to formation of twin domains, as schematically illustrated in the insets of g) and is directly observed in the Fermi surface map i). j) Photon-energy dependence of the MDC at k_F , equivalent to scanning k_z in the Γ -Z direction, from which the incident photon energies appropriate for Γ and Z are chosen.

[111]. Band structure calculations including correlations (DMFT) on FeSe [81] give sizeable band renormalisation values of ~ 2.8 for the $d_{xz/yz}$ orbitals, comparable to the measured values, although the predicted ~ 3.5 for the d_{xy} is still too small. Furthermore, adding DMFT beyond DFT calculations of FeSe does not appear to help with the fact that the experimental Fermi surfaces are much smaller than the predictions of DFT [131].

The effect of the loss of C_4 symmetry through the structural transition is very clearly observed in the detailed Fermi surface cut at the Z point, showing that the α pocket elongates to become elliptical. However, since the samples are twinned, two ellipses are observed at 90° with respect to each other, as shown also schematically in Fig. 6.1g. It is assumed that the structural domains have a smaller size than the beam spot, which is $\sim 100 \mu\text{m}$, meaning that both domains are always observed in the experiment. The ellipses are not complete, because the LH polarization is predominantly sensitive to the d_{xz} orbital character and the d_{yz} contribution around $k_y = 0$ are not picked up. In the cuts through Z (and also Γ) below T_s it is observed that the α pocket develops two crossings, corresponding to the two ellipses. By measuring the Fermi-level momentum cut as a function of incident photon energy, shown in

Fig. 6.1k, one can extract the k_z dependence of the hole pocket at low temperatures which shows that α pocket is quasi-two dimensional, in contrast the closed cigar-shaped Fermi surface around Z suggested in Ref. [111]. I will later make quantitative comparisons of the size of this single hole band with the quantum oscillations results and DFT, but it is worth noting at this point that the experimental measurements of the hole bands even at high temperatures are a long way from the DFT scenario which has three quasi-2D hole pockets with much higher Fermi surface volumes.

6.4 Electron bands at the M point

Now I focus on the temperature-dependence of the electron-like bands in FeSe shown in Fig. 6.2a, demonstrating important changes to the dispersions when cooling down through the structural transition. In the high-temperature tetragonal phase of FeSe, the band structure calculations predict two quasi-two dimensional electron pockets, as shown in Fig. 6.1a and Fig. 6.2b. The outer electron-like band δ has a dominant d_{xy} orbital character whereas the inner electron band has $d_{xz/yz}$ orbital character (d_{yz} in the experimental cut direction). At high temperatures above T_s the inner $d_{xz/yz}$ band, is clearly observed, which has a strong intensity at the M point where bands dispersing both along and perpendicular to the cut direction are degenerate, as shown in Fig. 6.2a. However, a combination of low intensity caused by matrix element effects for d_{xy} orbitals [84], as well as a possible particular sensitivity to impurity scattering [130] or strong correlations causing band incoherence, makes it difficult to see the d_{xy} band in ARPES¹.

Along the experimental Γ -M- Γ cut, the band crossing the Fermi level has d_{yz} character, whereas the downwards dispersing band has d_{xz} character. Below the

¹One of the distinguishing features of FeSe is that the orbital characters of bands seem to be particularly pure, perhaps partially arising from the absence of interlayer atoms. In other Fe-based superconductors there may be more mixing of characters which enables the detection of the outer electron band in e.g. LiFeAs [90] rather than the direct observation of weak d_{xy} matrix elements. The observation of the d_{xy} hole band γ in FeSe is similarly likely to be due to hybridisation with the d_{xz}/d_{yz} orbitals, and the intensity is strongest near anticrossings.

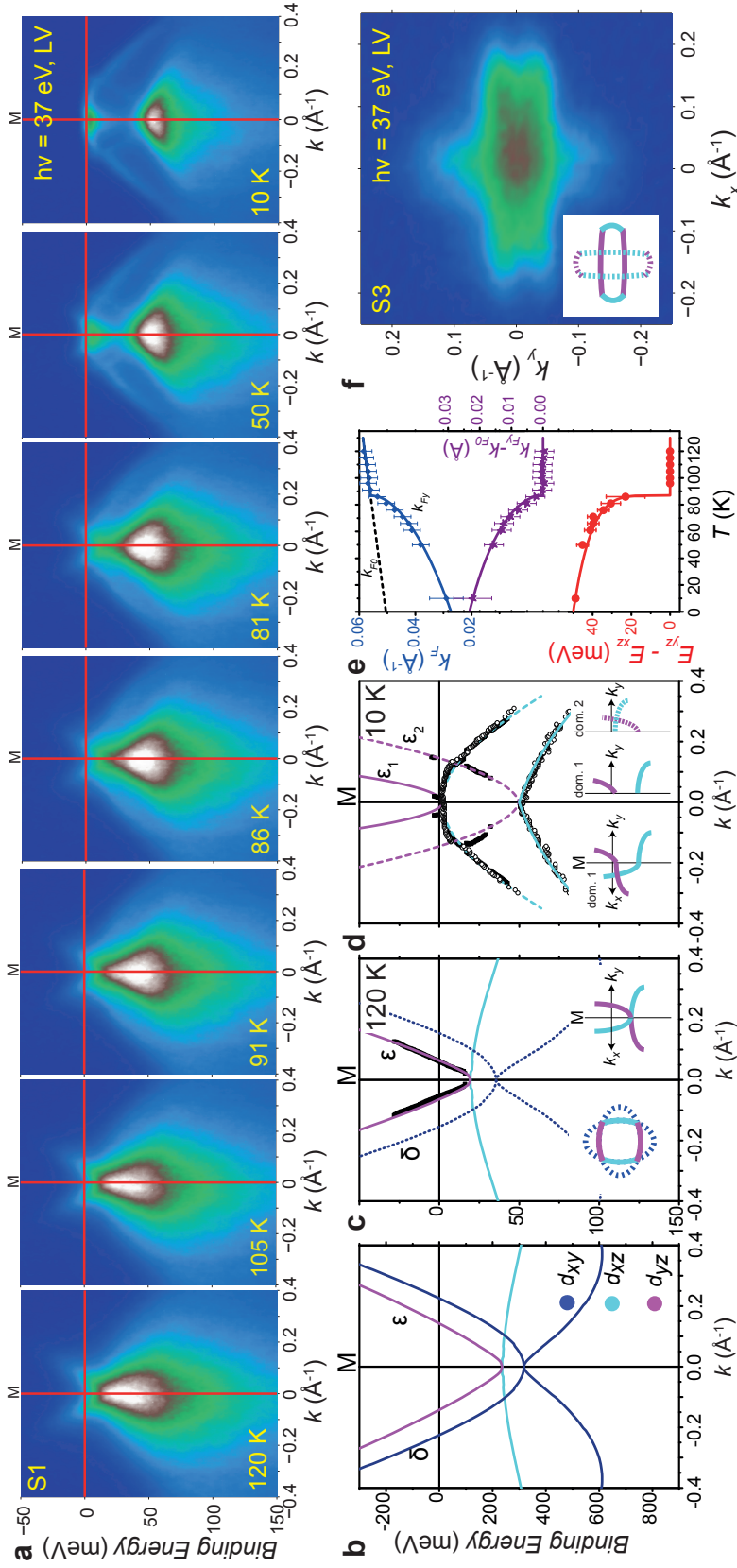


Figure 6.2: a) Temperature dependence of high-symmetry cut through M, showing the development of a splitting of intensity which results from strong orbital-dependent shifts of the band structure which onsets at $T_s=87$ K. b) Band dispersions as calculated in GGA. In c) the band structure is renormalized to fit the extracted band position from the spectrum at 120 K; the outer d_{xy} electron band δ is not observed here or at low temperature. d) At 10 K, the observed dispersions are dramatically different. Solid and dashed guides to the eye are contributions from two different domains. e) The energy splitting at M, $E_{yz} - E_{xz}$, along with the Fermi wavevectors k_F as a function of temperature; both may be considered as proxies for a ferro-orbital ordering parameter as discussed in the main text. f) Fermi surface map, integrated within 2 meV of the Fermi level; the cross-shape arises from strongly elongated Fermi surfaces in two domains, as shown schematically in the inset.

structural transition, the four-fold symmetry is broken and the degeneracy at the M point is lost; the d_{yz} band moves up, and the d_{xz} band moves down (solid guides to the eye in Fig. 6.2c). However, one must also consider the contribution of the other structural domain where the d_{xz} band moves up and the d_{yz} moves down (dashed guides to the eye) where x and y are defined in the *experimental* coordinate frame, resulting in a cut with four observed dispersions. This picture also agrees with that suggested for detwinned crystals of FeSe [112]. At the Fermi level, the resulting pocket is a very strongly elongated pocket, with a $k_{Fy} \approx 0.02$ but $k_{Fx} \approx 0.14$ - however similar to the hole pockets, the Fermi surface consists of two ellipses at 90° to each other due to twinning, resulting in the cross-shaped Fermi surface shown in Fig. 6.2e and Fig. 6.4f.

The band splitting at the M point reaches 49 meV at 10 K - a number which is far larger than the (un-renormalised) splitting of 17 meV in DFT allowing for a structural distortion of $(a-b)/(a+b) = 2 \times 10^{-3}$ [132]. As the orthorhombicity cannot account for the energy split observed by lowering symmetry it should be considered that the electronic degrees of freedom drive the structural transition in FeSe. This is supported by the measurements of the strain-derivative of resistivity presented in Chapter 7, where it is shown that the primary order parameter of the structural transition is electronic - i.e. not a regular phonon-driven structural transition.

In the context of iron-based superconductors, the mechanism of the structural transition has been much debated, with either spin or orbital degrees of freedom suggested to be ‘in the driving seat’ [37]. ARPES measurements naturally probe electronic and orbital properties but not spin, and the observation of a large splitting at the M point has been linked [112] to a ferro-orbital ordering, i.e. the development of inequivalent occupations of d_{xz} and d_{yz} orbitals. Thus the separation of the bands with d_{xz} and d_{yz} orbital character at the M point is a natural consequence of a ferro-orbital ordering. The ideas of ferro-orbital ordering may be conveniently explored in the 1-Fe

unit cell as will be briefly considered in Appendix B, however here I will stick to the crystallographic 2-Fe unit cell. The contraction of the sections of electron-like Fermi surfaces with d_{yz} character and expansion of sections with d_{xz} character will reflect in band-space the development of the ferro-orbital order parameter $\psi = n(d_{xz}) - n(d_{yz})$. Experimentally, there are two measurements which may be taken to be proxies for the ferro-orbital order parameter as a function of temperature. Firstly, there is the splitting $E_{yz} - E_{xz}$ at the M point, which reaches 49 meV at 10 K and was considered also in Ref. [112]. However, this is difficult to define at temperatures near T_s where the splitting is not very distinct, and it is also not clear exactly how this relates to the occupancy difference ψ . The other option is to measure the Fermi wavevector k_F as a function of temperature; below the transition there will be two wavevectors k_{F1} and k_{F2} , k_{F1} being more intense and easier to follow experimentally. This measurement, enabled by the high resolution of this study, is well-defined at all temperatures and also is naturally linked to the ferro-orbital order parameter since the elongation of the Fermi surface $k_{F1} - k_{F0}$ reflects the d_{yz} section of the Fermi surface contracting to reduce the orbital occupancy of d_{yz} . The temperature-dependence of these two experimental proxies for a ferro-orbital order parameters are plotted in Fig. 6.2e, with order-parameter-like guides to the eye which onset at $T_s = 87$ K.

The existence of orbital ordering effects, with a similar energy splitting ~ 50 meV, was observed over a limited temperature range between the structural transition and magnetic transition in NaFeAs [133, 134, 84]. In that case, the structural transition is a precursor to the lower magnetic transition, but in FeSe the magnetism never occurs and the underlying interactions may be different, although giving similar results. Furthermore, the electronic structure of multilayers of FeSe on SrTiO₃ [135] is quite similar to bulk FeSe, but in that case the splitting of bands at the M point was assigned to a possible formation of a spin-density wave. However, it is more likely that FeSe both in bulk and multilayers undergoes significant band splitting caused by orbital

ordering, but remain unreconstructed by static magnetic order, and therefore the spin-density wave interpretation in Ref. [135] was incorrect. Indeed a very recent ARPES study on thin films has identified the splitting with nematicity [136], analogous to the bulk system, and not a spin-density wave.

6.4.1 **Aside: schematic of the development of strongly elongated electron pockets at the M point**

Since the band structure changes around the M point are a little complicated to understand, here I explain the development of the electronic structure through the structural transition with the help of the schematic diagrams in Fig. 6.3. In Fig. 6.3a,c I show the high temperature cuts and Fermi surface around the M point. There is a four-fold degeneracy (even with spin-orbit coupling [94]) of the d_{xz} and d_{yz} bands dispersing along the k_x and k_y directions; it may be helpful to think of it as a double saddle-point. This degeneracy is lost when the four-fold symmetry of the lattice is broken, and the d_{xz} and d_{yz} bands separate. The d_{xy} band is not observed at the M point at any temperature and is therefore shown as a dashed line but not drawn at low temperature for simplicity. Below the structural transition, the band with d_{yz} orbital character moves up, whereas the d_{xz} band is pushed down away from the Fermi level as suggested by experiments on de-twinned crystals [112]. The positions of the band crossings, (band minima of the band crossing the Fermi level) are marked by black dots. Consequently, at the Fermi level, the d_{yz} portion of the Fermi surface contracts, whereas the d_{xz} portion expands. The beam spot is sufficiently large that one expects to always observe a superposition of bands in the two structural domains. The contribution of the second domain to the experimental k_y cut is equivalent to the dispersion along k_x but with orbital characters reversed ($x \leftrightarrow y$). Therefore the observed experimental cuts have four observed dispersions that result in an apparent cross-shaped Fermi surfaces in Figs. 6.2 and 6.4. The d_{xy} band is not observed at the M point but presumably it also loses its four-fold symmetry. Although it is

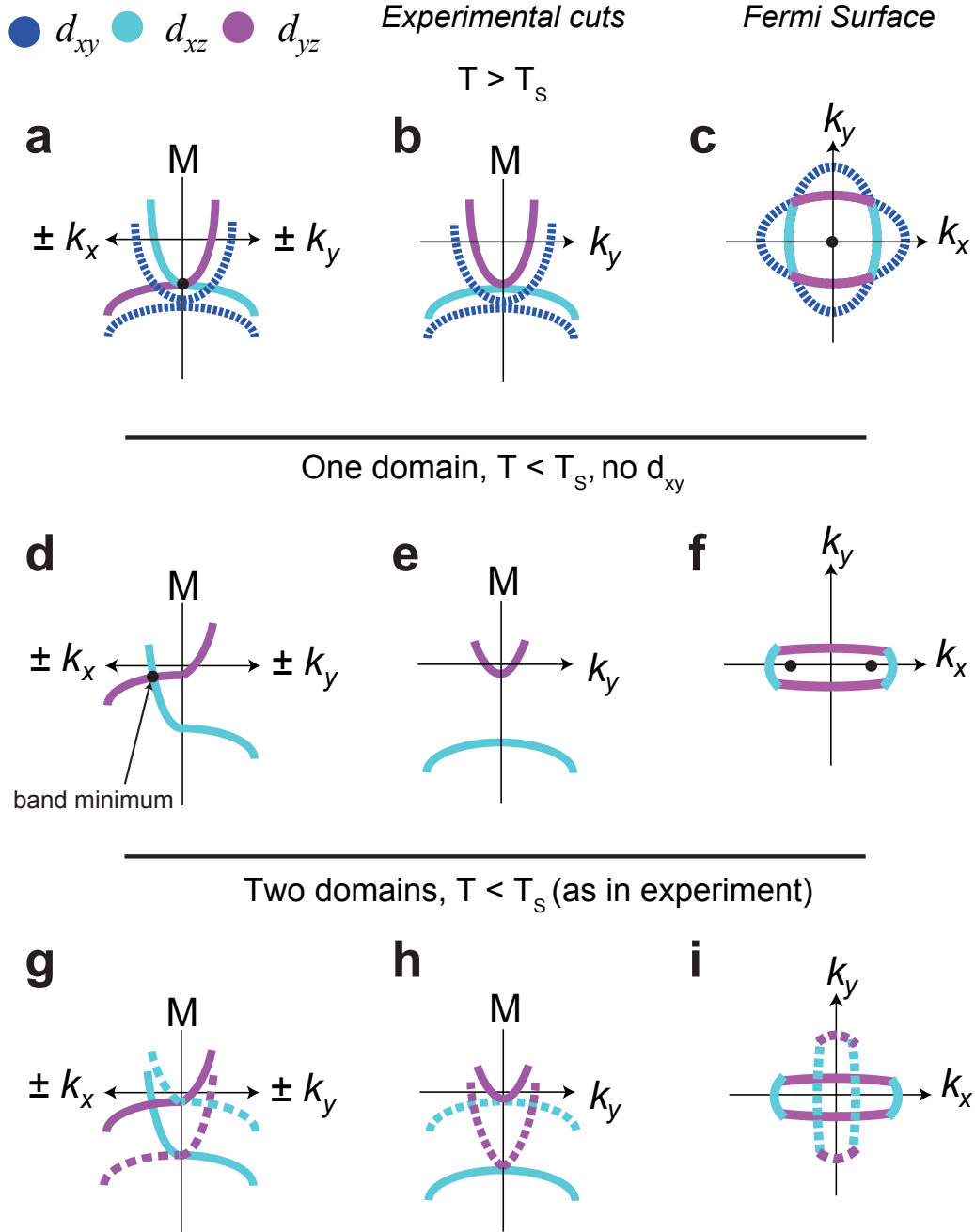


Figure 6.3: a-c) Schematic high temperature cuts and Fermi surface around the M point. d-f) Schematic of the low-temperature Fermi surface and high-symmetry cuts for one domain only when the observed pocket becomes highly elongated. g-h) Schematic of the experimental data at M, formed by a superposition of dispersions originating from twin domains that are at 90° with respect to each other.

not observed by ARPES, it must exist and is assigned to the F3 peak in quantum oscillations.

6.5 Comparison to quantum oscillations

In Chapter 5, I presented studies of the quantum oscillations in FeSe, finding four frequencies F1-F4, and showed that the F2 and F4 frequencies arise from a hole band whereas F3 arises from an electron band. That argument was independent of the assignment that arises from the comparison of ARPES data to quantum oscillations based on absolute values and other considerations which I will present here, however the assignment is in agreement.

Band structure calculations predict the existence of five different quasi-two dimensional cylinders with estimated frequencies up to 2.6 kT (see Section 5.6.1), much larger than those found in experiments (only up to 660 T).

The low temperature Fermi surface of FeSe based on these ARPES data is composed of one quasi-two dimensional hole band and likely two quasi-two dimensional electron bands. For a corrugated quasi-two Fermi surface centred at a high symmetry point, there are usually two frequencies per band belonging to the minimum and maximum extremal areas. Fig. 5.4f shows the angular dispersion of all observed frequencies in quantum oscillations.

The angular dependence of frequencies in Fig. 5.4 indicates whether a band is a maximum or a minimum (as discussed in Chapters 4 and 5) but it does not provide direct information on the position of these orbits in the Brillouin zone or the type of carrier, which is given by ARPES. Around $\Gamma - Z$, ARPES shows one quasi-two dimensional band corresponding to an hole density of $2.53 \times 10^{20} \text{ cm}^{-3}$, with only two-fold symmetry, with a maximum area around Z and minimum around Γ ; these two extremal areas will give rise to a pair of oscillation frequencies. As there are two frequencies F2 and F4 with similar effective masses, one a minimum and one a maximum, these are likely to form such a band and the size compares reasonably well to ARPES measurements. The absolute k values extracted from ARPES can be compared to those from quantum oscillations, as listed in Table 6.1. An additional

argument for this is that since there is only one hole pocket but more than one electron pocket, it is likely that largest maximum orbit observed in quantum oscillations (F4) corresponds to the hole pocket in order to maintain charge balance in the system.

ARPES gives a clear indication of the presence of a quasi-two dimensional in-plane elongated cylinder with mainly d_{xz} and d_{yz} character at M-A, but it is lacking the information concerning the behaviour of the outer electron-like d_{xy} band. However, there are some indications that the outer d_{xy} electron pocket may be the F3 frequency. The F3 frequency in quantum oscillations has a substantially larger effective mass than all the other frequencies, which is of similar value to the band renormalization found in the ARPES experiments for the d_{xy} band², suggesting that the outer electron pocket that is detected in quantum oscillations but not in ARPES has the d_{xy} character. Moreover, the estimated size of the strongly elongated small electron pocket is too small to account for F3. The inner electron band is likely to have extremal areas similar to the F1 peak, which may be in fact composed of more than one low frequency which are unresolved.

In Table 6.1 I compare the ARPES and quantum oscillations results with the assignment of orbits as described above. While there are some small discrepancies, in general the agreement is reasonable. In particular the d_{xy} electron band not observed by ARPES is observed in quantum oscillations, making for a complete determination of the low-temperature Fermi surface of FeSe. It is worth noting that quantum oscillations were observed in crystals from the same batch on which ARPES measurements were performed, grown in Oxford. This indicates their quality, and also shows that they are comparable to crystals grown by other groups since the frequencies are in agreement.

²The d_{xy} band has a large renormalisation near Γ where it is observed but is not observed near M where it would give rise to the electron pocket associated with F3, and one cannot directly compare the experimental mass and ARPES renormalisation value.

Table 6.1: Comparison of the Fermi surface properties as extracted from ARPES and quantum oscillations experiments. The effective mass m^* is obtained from a fit to the standard Lifshitz-Kosevich formula [49] for the temperature-dependence of the amplitude of oscillation. The energy shifts, ΔE , and renormalisation (*renorm*) values are obtained by comparing the relaxed DFT band structure with the high-temperature ARPES data at 120 K as shown in the main text. Due to the experimental and calculated k_z dependence being different, the shifts will be slightly different shifts required at Γ compared to Z. The Fermi surface shown in Fig. 4h is based on these renormalisation values (the unobserved δ d_{xy} electron band is treated similar to the ϵ pocket). The notably large shift and renormalisation factor on the d_{xy} band indicates that it is the most strongly correlated band.

Bands	α (Γ)-h $d_{xz/yz}$	α (Z)-h $d_{xz/yz}$	β (Z)-h $d_{xz/yz}$	γ (Z)-h d_{xy}	δ (M)-e d_{xy}	ϵ (M)-e $d_{xz/yz}$
ARPES	$T=120$ K					
k_F ($\text{\AA}^{-1}$)	—	0.126	0.052	—	—	0.057
<i>renorm</i>	—	3.2	2.1	8	—	4.1
ΔE (meV)	—	-224	-273	-320	—	+156
v_F (meV $\cdot$ $\text{\AA}$)	—	320(30)	560(80)	—	—	440(30)
ARPES	$T=10$ K					
k_F^{min} ($\text{\AA}^{-1}$)	0.033(6)	0.10(6)	—	—	—	0.02(1)
k_F^{max} ($\text{\AA}^{-1}$)	0.077(6)	0.15(6)	—	—	—	0.14(1)
A_k (10^{-3} $\text{\AA}^{-2}$)	8	49	—	—	—	9
F_{ARPES} (T)	85 (50)	510 (80)	—	—	—	95 (60)
QOs	$T < 2$ K	$B > 19$ T				
Orbits	F_2	F_4	—	—	F_3	F_1
F (T) (S4)	207	660	—	—	530	107
m^* (S4)	4.0(5)	4.0(5)	—	—	—	—
F (T) (S6)	200	664	—	—	568	114
m^* (S6)	4.1(5)	4.7(5)	—	—	6(1)	3.0(5)
A_k (10^{-3} $\text{\AA}^{-2}$)	19	63	—	—	54	11
QOs - Lit.	$T < 2$ K	$B > 19$ T				
F (T) [74]	200	670	—	—	570	60
m^* (m_e) [74]	4.5(1)	4.8(5)	—	—	7.0(7)	1.9(2)
F (T) [124]	200(10)	660	—	—	580	96(6)
m^* (m_e) [124]	2.0(4)	3.2(6)	—	—	—	0.75(2)

6.6 Discussion

Based on combined ARPES and quantum oscillations electronic structure studies, I show schematically the evolution of the Fermi surface in Fig. 6.4. The low temperature Fermi surface of FeSe consists of one hole pocket and two electron pockets, which

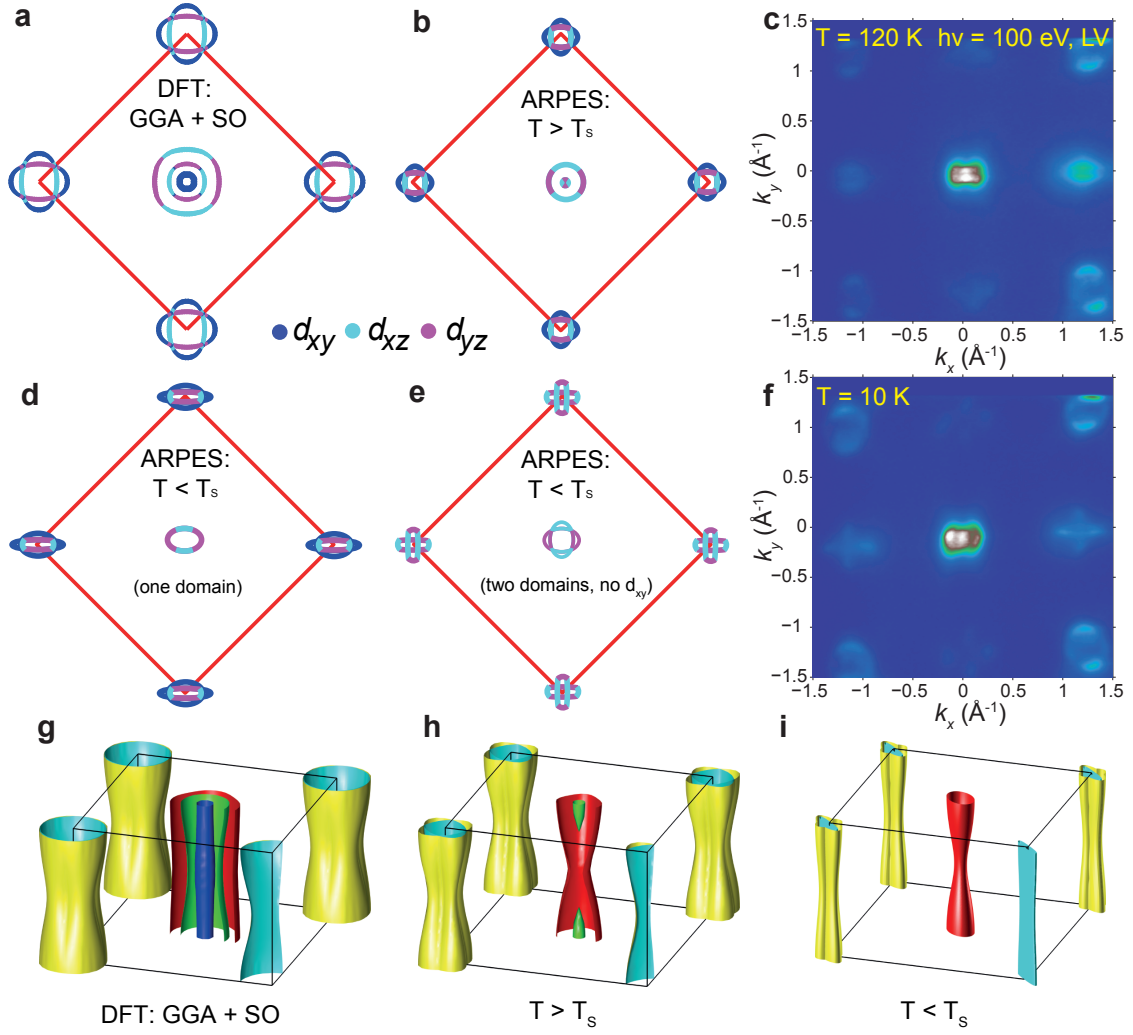


Figure 6.4: a) DFT calculation of the Fermi surface in the high-temperature $P4/nmm$ tetragonal space-group. b,c) The experimental high-temperature Fermi surface consists of significantly shrunk pockets, furthermore the d_{xy} hole band (γ) is significantly below the Fermi level and does not cross. d) Below the structural transition in the orbitally-ordered phase the low temperature Fermi surface consists of moderately elongated hole pockets and strongly elongated electron pockets. e,f) Schematic and experimental low temperature Fermi surface, which is understood by including the effect of twin domains and not considering the unobserved d_{xy} electron pocket. g-i) 3D Fermi surface representations of the schematics of a-c).

are quasi-2D but with sizes significantly shrunk with respect to the expectations from DFT. Furthermore, the ARPES measurements indicate that an orbitally-ordered electronic phase is realised at low temperatures in bulk FeSe, as shown schematically in Fig. 6.4d. However, the orbital ordering below T_s does not rule out antiferromagnetic

spin fluctuations as a possible pairing mechanism for the unconventional superconductivity at $T_c \ll T_s$, as they have been now observed in both NMR [45, 46] and neutron scattering [116].

A joint analysis of quantum oscillations with ARPES has been shown to be very useful, since the outer electron pocket with d_{xy} character is not detected in ARPES but does give rise to the F3 frequency in quantum oscillations. Otherwise, there is decent agreement between quantum oscillations and ARPES, which means that there is no significant difference between the surface electronic structure and the bulk. As the Fermi surfaces spontaneously distort from fourfold-symmetric to two-fold symmetric elliptical pockets this transition may be interpreted in terms of an orbital ordering that breaks the discrete point group symmetry of the underlying lattice. This orbitally ordered state would also exhibit distinct transport properties along the different crystal axes below the structural transition as will be discussed in Chapter 7. Indeed recent observations of strongly anisotropic scattering in quasi-particle interference measurements would be consistent with this [129].

In summary, I have shown that the Fermi surface of FeSe undergoes dramatic changes through the structural transition due to the onset of orbital ordering at T_s . The characterisation of the electronic structure is sufficiently detailed to allow for theoretical modelling (e.g. [121]) both to understand the ground state properties and also provide a quantitative test for orbital ordering theories. Given the observed small and anisotropic Fermi surfaces with low carrier densities and low effective Fermi energies [129] it is perhaps not surprising that the physical properties, including the superconducting and structural transitions are susceptible to external parameters (e.g. pressure, strain, doping) and by controlling them one can tune FeSe into a high-temperature superconductor.

6.7 Further measurements and calculations

6.7.1 The effect of matrix elements

In Fig. 6.5 I present a complete set of low-temperature high-symmetry cuts in all polarisations. The measurements were performed for two different incident beam polarizations: linear horizontal, LH, (p) (top row) or linear vertical, LV, (s) (bottom row). All samples measured were carefully aligned such that the Γ -M direction corresponded to the scattering plane (equivalently, the local coordinate frame of the Fe atoms is aligned to the scattering plane). In this geometry, matrix elements effects allow us to select predominantly bands with d_{xz} (LH) or d_{yz} (LV) orbital character; further details can be found in Ref. [84]. The d_{xy} band is observed near Γ (Z) in LH probably because the band character is not pure rather than a direct observation of d_{xy} matrix elements here, which should vanish at Γ and be small elsewhere [84]. At the Γ point there is a mixing of orbital character due to spin-orbit coupling (as described below), as shown in the LV polarisation cuts at Γ and Z in b) and d). The Z^* and A^* cuts are performed at 50 eV which is close, but not exactly at $|k_z|=\frac{\pi}{c}$ which is estimated to be 53.5 eV; this energy corresponds to the next Z point from the 23 eV used in Fig. 6.1. The photon energy (i.e. k_z) dependence reveals the degree of corrugation of the two-dimensional bands; the hole pocket α appears to be more strongly corrugated than the electron pocket around M(A).

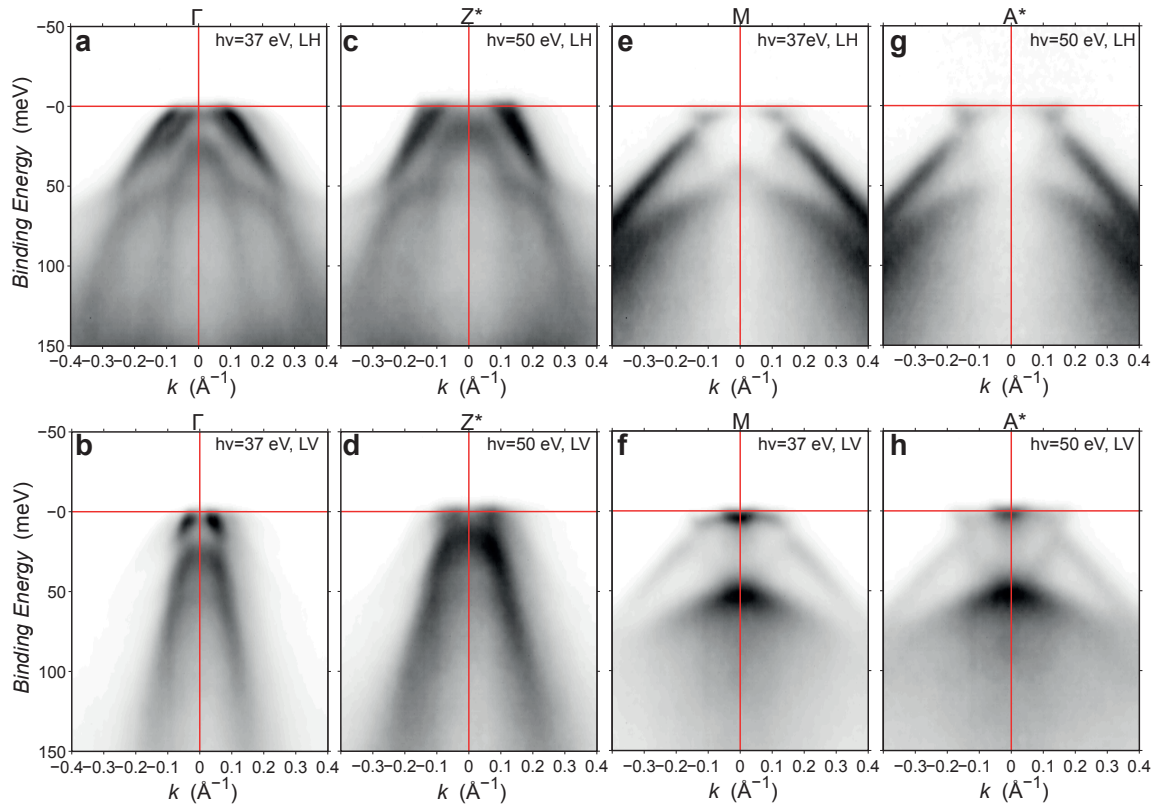


Figure 6.5: Low-temperature cuts at high-symmetry points in the Brillouin zone performed on an additional sample S3.

6.7.2 Measurement of the superconducting gap

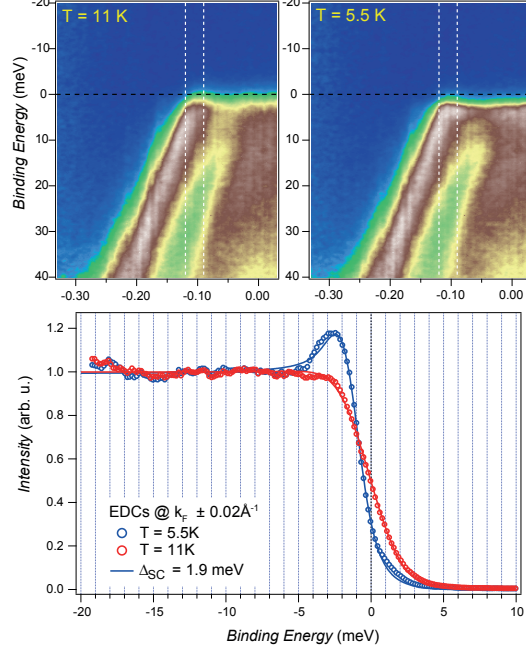


Figure 6.6: Direct measurement of the superconducting gap on the α pocket in FeSe. Top: High-resolution cut of the α pocket Fermi level crossing above and below the superconducting transition. Bottom: integrated EDCs (integrated between the white dashed lines in the cuts) showing a build-up of intensity just below the Fermi level in the superconducting state.

The energy dispersion of the hole bands above and below the superconducting transition, $T_c \sim 8$ K, for sample S2 (a second cleave on the same sample), measured in linear horizontal polarization at an incident photon energy of $h\nu=23$ eV. A pass energy of 2 meV and exit slit width of $20\mu\text{m}$ were used to optimize the resolution. In the superconducting state at $T = 5.5$ K an increase of intensity just below the Fermi level due to Bogoliubov quasiparticle formation is observed; the back-bending of the bands due to the formation of the superconducting bands may be directly seen in comparison with the normal state at $T = 11$ K. The formation of the Bogoliubov quasiparticle peak below T_c is clearly observed and a fit to these data gives the value of the superconducting gap on the α hole pocket of $\Delta=1.9$ meV, following a similar

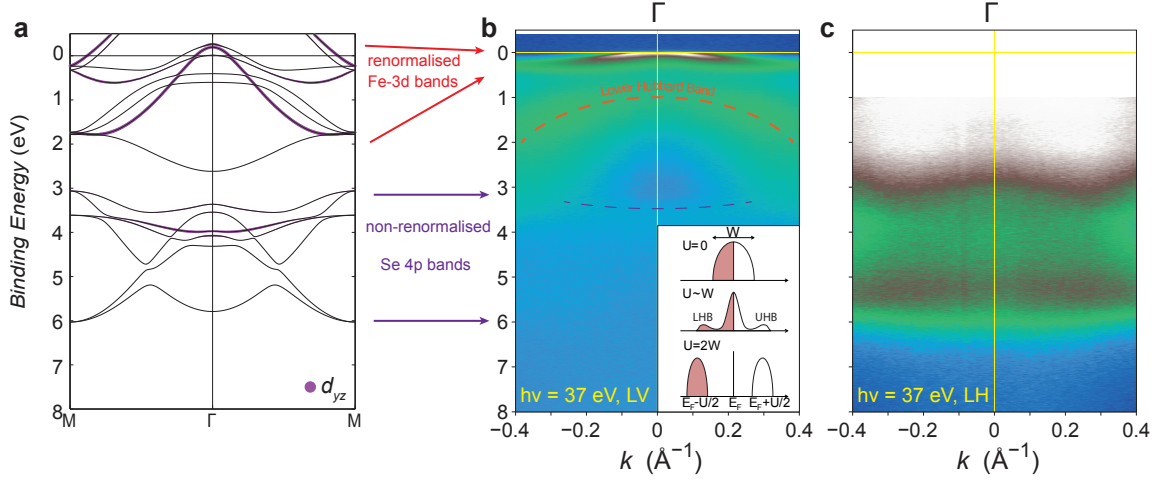


Figure 6.7: a) DFT calculation of the band dispersions for a cut through the Γ point highlighting the d_{yz} orbital character which is picked out in the LV polarisation. b) Experimental cut through the Γ point in LV polarisation to high binding energies. The intensity I is rescaled by $I^{1/4}$ to bring out weak features. c) The same experimental cut in LH polarisation. At low binding energy the spectrum is cut due to the very large intensity found there in order to focus on the weaker features at high binding energy.

procedure detailed in Ref. [137]³. This value agrees with the 2 meV previously reported in ARPES measurements on FeSe at 1 K in Ref. [111] and gives a large BCS coupling value $2\Delta/k_B T_c = 5.5$.

6.7.3 Deep measurements of bands away from the Fermi level

The primary focus of this ARPES study has been to study the band structure near the Fermi level, where sharp dispersive bands are found; typically the cuts presented have only extended to a binding energy of 150 meV to focus on this regime. However, ARPES measurements are not restricted to low binding energies, and there is information which may be extracted at higher binding energies. In Fig. 6.7b I show the result of an ARPES measurement in “swept-mode” on sample S3. In LV polarisation, near the Γ point it is primarily the d_{yz} band (β) which is observed. Compared to the DFT prediction, the bandwidth of this band, which may be taken to be repre-

³I thank Timur Kim for performing this analysis.

representative of the Fe $3d$ -orbitals in general, is strongly shrunk. About 1-2 eV below this much narrower Fe- $3d$ bandwidth, a broad “band” of spectral weight is observed which appears to have a dispersion roughly following the much sharper and more intense d_{yz} hole band near the Fermi level. This broad band of intensity is likely to correspond to the “lower Hubbard band” - a concept which arises from considerations of electron-electron interactions. In the inset Fig. 6.7b a schematic of the Mott transition is presented. For increasing U/W (i.e. onsite electron-electron repulsion vs non-interacting bandwidth), the spectral weight changes from a wide bandwidth metal in a non-interacting electron picture, into the Mott insulating state at high U . For Fe-based superconductors, the relevant interaction strength is somewhere in between, i.e. there is still spectral weight near the Fermi level in the form of renormalised quasi-particles as observed, but there is also some shift of spectral weight into the so-called Hubbard bands, which should appear to be broad and incoherent in photoemission. Within this interpretation, the observation of the lower Hubbard band at 1-2 eV suggests simplistically a U of 2-4 eV, although the magnitude of the Hund’s rule coupling J also undoubtedly plays a role in Fe-based superconductors [81]. A good theoretical tool for studying the spectral function in the case of moderate electron-electron interactions is DMFT, as introduced in Section. 3.6.3. The observation of the lower Hubbard band at binding energies of 1-2 eV is consistent with the DMFT calculations in Ref. [138].

Since the lower bands at binding energies of 3-6 eV consist mainly of Se $4p$ orbital weight and not Fe $3d$, these bands are not expected to be renormalised, and a couple of dispersions here are weakly observed in ARPES close to the expected binding energies in DFT. These bands would have been better studied at higher incident photon energy and away from the Γ point but a systematic study of these bands was not performed. It is worth noting that in FeSe there is a convenient gap separating the Fe $3d$ bands from the Se $4p$ bands, which makes the detection of the weak and

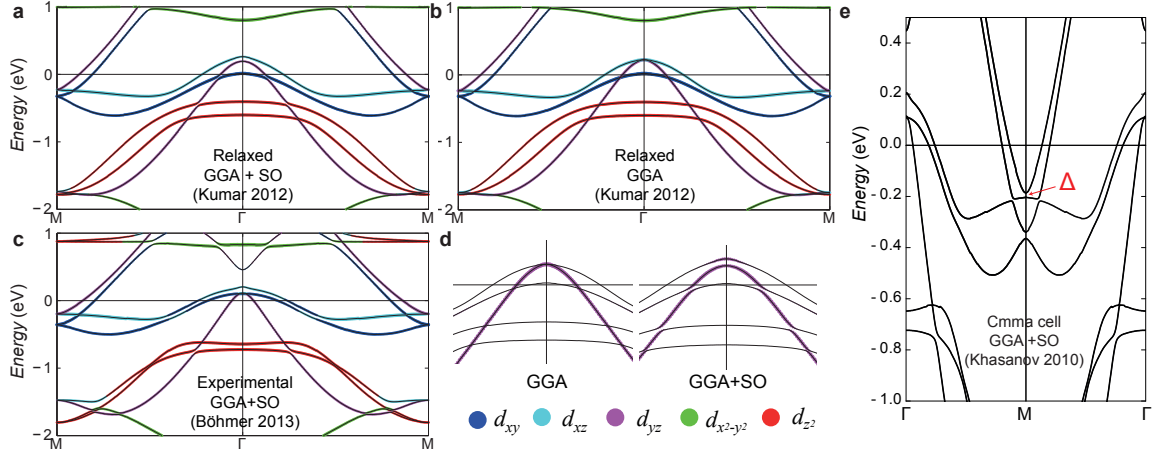


Figure 6.8: Band structure calculations of FeSe using relaxed and experimental structures performed using Wien2k [78]. a) Band structure calculations performed in Wien2k based on the relaxed crystal structure of Ref. [125] including spin-orbit coupling. A comparison to a calculation without spin-orbit coupling is presented in b) where there are no spin-orbit induced band anti-crossings, and additionally the d_{xz} and d_{yz} orbitals are degenerate at Γ . c) Calculation based on the experimental structure reported in Ref. [44], including spin-orbit coupling. d) Detailed cuts of the relaxed structure near the Γ point showing only the d_{yz} weight. As well as lifting the degeneracy at the Γ point, spin-orbit coupling mixes the orbital characters of bands near anti-crossings and also at the high-symmetry Γ point. e) Calculation of band dispersion in the low-temperature $Cmma$ space group (i.e. four-fold symmetry is broken), taking the structure of Ref. [132]. A splitting of bands at the M point is now allowed, and is calculated to be 17 meV.

broad lower Hubbard band easier.

6.7.4 Effect of and crystal structure in DFT

In the calculations presented earlier in this Chapter, I have chosen to use a relaxed crystal structure rather than the experimental one. The comparison is presented in Fig. 6.8a,c. The main difference between the two is the structural z_{Se} parameter, significantly shorter for the relaxed structure. The considered structures were:

Relaxed structure:

Kumar *et al.* (2012) [125] $a = 3.7651 \text{ \AA}$, $c = 5.5178 \text{ \AA}$, $z_{Se} = 0.24128$

Experimental structure:

Böhmer *et al.* (2013) [44] $a = 3.7707 \text{ \AA}$, $c = 5.521 \text{ \AA}$, $z_{Se} = 0.26668$

The principal effect near the Fermi level is the position of the d_{xy} hole band. In calculations using the experimental structure the d_{xy} hole band (blue) lies in between the two $d_{xz/yz}$ bands; with spin-orbit coupling included, it mixes orbital character. However, in the relaxed structure, the d_{xy} only just crosses the Fermi level and is below the two $d_{xz/yz}$ hole bands. There are further differences in the k_z dependence obtained between the two structures. In experiment, the d_{xy} hole band is ~ 50 meV below the Fermi level, well below the two $d_{xz/yz}$ bands, and therefore I choose the relaxed structure as a better starting point. The choice of structure will slightly alter the band renormalisation values stated in the main text used to match these experimental data.

In either case, DFT substantially over-estimates the size of the pockets even above the structural transition, and requires opposite shifts of the band structure for hole and electron-like bands in order to match the experimental ($T > T_s$) dispersions. Such a shrinking of bands has been widely discussed, particularly in the context of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [75], where the observed sizes of electron Fermi surface pockets shrinks as a function of decreasing x from the overdoped side of the phase diagram and is further discussed in Section 5.6.1.

6.7.5 Effect of spin-orbit coupling

It is important to include spin-orbit coupling into the band structure calculation, especially at the Γ point. As shown in Fig. 6.8, without spin-orbit coupling there are two hole bands with d_{xz} and d_{yz} orbital character which are degenerate at Γ ; including spin-orbit coupling lifts the degeneracy here by $\lambda_{SO} = 65$ meV based on these calculation. Therefore the experimentally observed splitting of ~ 20 meV in the high-temperature C_4 -symmetry state can be linked to the spin-orbit coupling constant; however below T_s the bands are allowed to split even further due to the

loss of symmetry due to orbital order and the β band moves below the Fermi level. As well as causing an anticrossing at Γ , spin-orbit coupling will also mix the orbital characters near the high symmetry point - which is probably linked to the observed “teeth” described in Section 6.7.1.

As discussed in Ref. [94], the group theory of the M point in the corner of the Brillouin zone is rather more complicated since $P4/nmm$ is a non-symmorphic space group. The spin-orbit coupling does not lift any degeneracies exactly at M; however it does introduce anti-crossings away from M, importantly between the two predicted electron bands along M-X, thus the electron pockets should be thought of as an outer and inner pocket, the outer d_{xy} not being resolved in this ARPES experiment.

Note that for the purposes of matching the band structure to the extracted dispersions in Fig. 6.1g and 5.4f of the main text, the calculation without spin-orbit coupling is used. This is because if the bands are allowed to shift and renormalise independently, they maintain artefacts from the anti-crossings of the unshifted bandstructure, where there may no longer be a band crossing. In reality there will be spin-orbit induced anti-crossings, as in fact is observed in the experiment, for example where the α and γ pockets meet.

6.7.6 Discussion of other ARPES studies on FeSe

Recently, there have been several reports of ARPES on FeSe, giving somewhat conflicting interpretations to each other and this work. Due to the strong interest within the community, here I briefly address the similarities and differences:

In Nakajama *et. al.* [110], a separation of intensity at the M point was interpreted as evidence for an electronically-driven nematic state. These measurements are roughly-speaking equivalent to this study of the temperature-dependence at the M point, however the much improved resolution in this study gives a stronger un-

derstanding of the low temperature electronic structure; in particular the second ϵ_2 d_{yz} Fermi-crossing band is not observed in their data. Moreover, their interpretation (based on a smoothed second-derivative analysis of the EDCs at M) that a splitting is observable up to ~ 110 K, greater than the structural transition of 90 K, is not supported by the results of this study, where it is found that the splitting onsets at T_s within error.

In Maletz *et. al.* [111], significant band-dependent renormalisations were observed, giving values consistent with these data. Their picture of the $\Gamma(Z)$ point is similar to ours, although importantly they do not detect the splitting of the α band Fermi level crossings. In my k_z dispersion, I find that the α pocket is quasi-2D (extending all the way through the Brillouin zone), in contrast to their claim of a closed pocket around Z. Their data shows no sign of the unusual band splitting at the M point which is the most dramatic feature of these data (and the other reports).

In Shimojima *et. al.* [112], a similar picture was described to this thesis suggesting anisotropic Fermi surfaces based on the interpretation of an orbital order which lifts the degeneracy of d_{xz} and d_{yz} orbitals, in a particularly dramatic way at the M point. In this higher quality study the d_{xy} pocket is not observed, whereas they do assign some intensity in their data to the d_{xy} electron band around M: this may be questionable. Another important issue is whether or not the d_{yz} band at M dips below the Fermi level, noting a slight inconsistency in their data between their Figs. 1 and 2. In the experiments presented in this Chapter, it is clear that it is below the Fermi level. However, their data on detwinned single crystals are very valuable and show directly that it is the d_{yz} orbital which moves up at M. Finally, the Fermi surface maps in this study show directly the anisotropic Fermi surfaces which were only really implied by Shimojima *et. al.*.

In the very recent preprint Zhang *et. al.* [113], ARPES spectra of good quality (although still inferior to this study) were reported, however the interpretation presented in that work is confused and their data is not of sufficient quality to substantiate their claim that the splitting at M persists beyond T_s .

Since FeSe has now been studied by several groups at several beamlines, it seems to be the case that the data quality obtainable at I05 cannot be matched.

6.7.7 Magnetically reconstructed Fermi surface

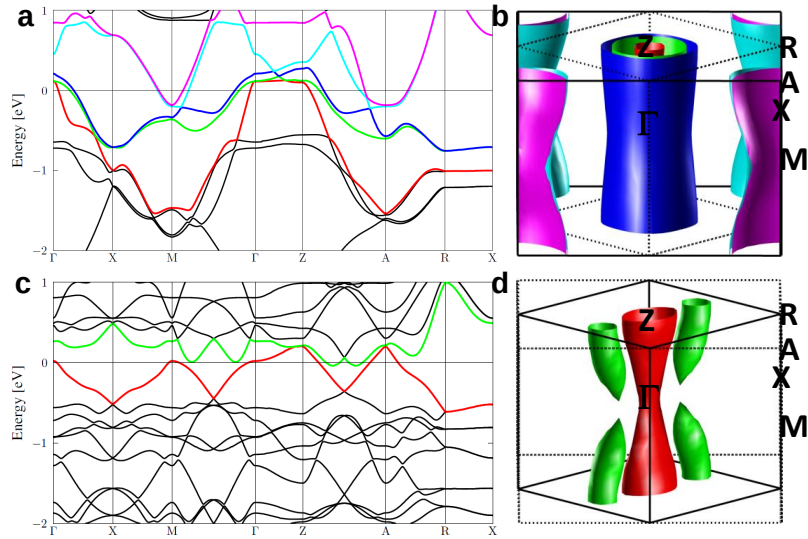


Figure 6.9: a) Band structure and b) Fermi surface of non-magnetically ordered FeSe, and c), d) a comparison with the magnetically ordered structure. Orthorhombic unit cells are used in both cases but for consistency with the ARPES experiments I maintain the same notation of positions in the Brillouin Zone as for the high temperature tetragonal cell although this is technically incorrect.

The ground state of FeSe in DFT is not the paramagnetic state, and actually not the magnetic stripe-ordered Fermi surface either as was previously thought [125] but a novel “staggered dimer” phase, although other magnetic orderings are close in energy [120]. However, given the massive discrepancy between the simple non-magnetic DFT and the experimental Fermi surface observed by ARPES at high temperature, caution is urged against taking results based on DFT too seriously in this case. Moreover,

recent neutron scattering data indicate that the only wavevector associated with magnetic fluctuations is $(\pi, 0)$ [116] and not any other less conventional orderings.

It is worthwhile to briefly consider what the magnetically reconstructed Fermi surface of FeSe would look like. While there is no magnetic ordering in FeSe, I have performed DFT in the single-stripe magnetic ordered state, space group $Pccm$. I find that allowing for a magnetic ordering gives an energy saving of 396 meV/unit cell and a magnetic moment of $1.83 \mu_B$ per Fe. The experimental crystal structures of Ref. [132] and the LSDA function is used in this case; it is well-known that the GGA function typically produces a larger magnetic moment than the LSDA (I get $2.23 \mu_B/\text{Fe}$ in GGA).

The Fermi surface and band structure of the magnetically reconstructed phase is clearly incompatible with ARPES measurements. However, by coincidence the reconstructed Fermi surface of FeSe is not far from the quantum oscillations results with small quasi-2D electron and hole pockets; calculations of the expected quantum oscillations frequencies from the Fermi surface of Fig. 6.9d gives rise to 4 frequencies all less than 1 kT for $B \parallel c$, and therefore I show it as a curiosity. Note that the smaller degree of c -axis warping in FeSe makes the reconstructed Fermi surface much more 2D than BaFe_2As_2 , where the small Fermi surface volumes left after magnetic reconstruction are very 3D [70].

It is not clear exactly why DFT fails badly for FeSe since it has been shown to be reasonably effective in other Fe-based superconductors, but the facts are: the ground state is not magnetic, in contrast to DFT; the Fermi surfaces are much smaller than predicted and the d_{xy} hole band in particular doesn't cross the Fermi level; DFT cannot account for the large splitting of bands at the M point below T_s ; and the band structure is strongly renormalised compared to DFT. The reader is therefore advised to take a sceptical view of reports on FeSe (and Fe-chalcogenides in general) that rely heavily on DFT since it is so far from the experiment, in the case of FeSe.

6.7.8 Discussion of the Sommerfeld coefficient

As discussed in Section 4.4.5, the Sommerfeld coefficient γ is the coefficient of the linear term of the specific heat at low temperature which is usually considered to arise from the contribution of the degrees of freedom of the quasiparticles at the Fermi level. For FeSe in the 2D approximation, one finds:

$$\gamma = 0.700 \sum_{bands} m^*, \quad (6.1)$$

where γ is in mJ/mol-K² and m^* is measured in electron masses and the prefactor 0.700 comes from a number of physical constants including the a lattice parameter. Therefore, an estimate of the specific heat may be made from the experimental quantum oscillations effective masses which are extracted from the temperature-dependence of the amplitude of oscillation in Fig.3d. For reference, γ is 3.5 mJ/mol-K² in DFT. In the case of a quasi-two dimensional cylinder, there are two extremal areas corresponding to a maximum and a minimum quantum oscillation frequencies, and to estimate the contribution to γ one usually averages their effective masses. A check of the validity of this approximation is to directly compare the Sommerfeld coefficient from the density of states integration using the SKEAF algorithm with the use of Eq. 6.1 taking m^* to be the average of the masses of the two extremal orbits associated with each band; similar results are found within an error of less than 10% for all bands. Note also that the formula does not rely on the band being isotropic in-plane, only that it extends through the entire Brillouin zone in the k_z direction, so it should be applicable to the in-plane distorted pockets in FeSe.

Based on ARPES and quantum oscillations, F2 and F4 quantum oscillation frequencies correspond to the α hole pocket (the only one that crosses the Fermi level at low temperatures) which gives a value $\gamma_{hole} = 0.7 \times (4.7 + 4.1)/2 = 3.1(4)$ mJ/mol-K² (using the effective mass values for sample S6). Next, the F3 frequency (a maximum) is assigned to the outer electron pocket, which is the electron d_{xy} band at M not

observed in ARPES. As it is not clear if the minimum of this band is observed in the quantum oscillations, I assume that this band is quasi-two dimensional with the contribution to γ of 4.2(7) mJ/mol-K². Finally the small and highly elongated inner electron pocket observed in ARPES should have two small frequencies with sizes comparable to the F1 frequency giving a contribution of 2.1(4) mJ/mol-K². Therefore the estimated total Sommerfeld coefficient of $\gamma_{QO} = 9.4(15)$ mJ/mol-K² is larger than the reported experimental value of 5.7 [45] or 5.73 [139] mJ/mol-K². However, I believe that there is sufficiently strong evidence from ARPES, quantum oscillations and magnetotransport for the existence of two electron pockets that the over-estimate of the Sommerfeld coefficient from the analysis of quantum oscillations masses should not be seen as a significant obstacle. Furthermore there are several examples showing discrepancies between specific heat and quantum oscillations including LiFeAs as discussed in Section 4.4.5. Therefore the Sommerfeld coefficient is not a significant obstacle to this interpretation. The Sommerfeld coefficient could also be estimated from ARPES data by looking at the Fermi velocities to estimate $\frac{\partial A}{\partial E}$. However due to the large uncertainties and also since ARPES does not observe the electron d_{xy} band (which is likely to be the biggest single contributor) I have not attempted this calculation in this thesis. However, a tight-binding model based closely on these ARPES data [121] has an estimated $\gamma_{tb}=4.3$ mJ/mol-K²⁴, suggesting that the experimentally-derived quantum oscillations masses may be systematically over-estimating the real effective masses, which would help to resolve the problem.

⁴S. Mukherjee, private communication.

Chapter 7

Electronically-driven structural transition in FeSe

In this Chapter, I present a measurement of the strain-derivative of resistivity anisotropy in FeSe (which by now needs no further introduction), finding a large response that is divergent in the vicinity of T_s , with a comparable magnitude and temperature-dependence to $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$. These measurements indicate that the structural transition in FeSe is electronically driven. Moreover given the apparent low importance of spin degrees of freedom above T_s , these measurements are consistent with the driving force for the structural transition in FeSe being a spontaneous symmetry breaking of the electronic structure and Fermi surface, which would result from an orbital order. The induced resistivity anisotropy in the tetragonal phase is positive - opposite to $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, but similar to FeTe. Below the structural transition, the sign of the resistivity anisotropy changes, which has not previously been observed in Fe-based superconductors, and a possible interpretation of this is suggested. This short Chapter is to some extent self-contained, and I present the methods and theoretical description particular to this problem here.

7.1 Introduction

Determining the origin of the tetragonal-to-orthorhombic (“nematic”) structural transition in under-doped iron-based superconductors has proved to be a difficult question.

Strong evidence for an *electronic* rather than structural (i.e. purely phonon-driven) origin of the structural transition came from resistivity measurements under applied strain, which showed a large and divergent response of the resistivity anisotropy to a small applied strain along the Fe-Fe direction in the tetragonal high-temperature phase above the structural transition in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [36]. Those measurements indicated that the structural distortion itself was not the primary order parameter, but rather that the structure responds to a symmetry-breaking *electronic* order parameter. However, there has been some controversy in determining what is really the driving force for the structural transition, with both orbital order and spin order parameters suggested to provide the primary fluctuations which drive the fourfold symmetry breaking (nematicity) [37]. Since FeSe is a special case with an orthorhombic distortion but no magnetism at any temperature, investigations of resistivity anisotropy would be an interesting test of these theoretical ideas, providing a further comparison with the 122 family to help determine what is different about FeSe.

7.2 Interpretation of induced resistivity anisotropy

The principle question which is addressed by the measurements presented in this Chapter is whether the tetragonal-to-orthorhombic symmetry-breaking transition at $T_s=90$ K in FeSe is electronically driven - i.e. the electronic degrees of freedom favour the development of a symmetry-breaking “nematic” order parameter ψ , or if there is a purely structural instability which favours an orthorhombic distortion. In the following arguments, it will be shown that these two scenarios may be distinguished by measurement of the induced resistivity anisotropy above T_s under applied strain.

The analysis of the induced resistivity anisotropy relies on the fact that the resistivity anisotropy may be used as a proxy for a nematic order parameter [140], without specifying the exact mechanism, only that somehow the nematic state has anisotropic scattering or anisotropic Fermi surface properties. Denoting the underlying nematic

order parameter ψ and the normalised resistivity anisotropy N , we have

$$\psi \propto N = \frac{(\rho_a - \rho_b)}{\frac{1}{2}(\rho_a + \rho_b)} \quad (7.1)$$

When thinking about phase transitions in a phenomenological way, it is common to use a Landau free energy approach. Here, we consider the free energy F suitable for a system with tetragonal symmetry with a possibility to develop a symmetry-breaking nematic order parameter ψ in a real system where coupling to the lattice must also be considered. Following the analysis of [36], an expression for the free energy F is given by:

$$F = \frac{a}{2}\psi^2 + \frac{b}{4}\psi^4 + \frac{c}{2}\epsilon^2 + \frac{d}{4}\epsilon^4 - \lambda\psi\epsilon - h\epsilon \quad (7.2)$$

where ϵ is the elastic strain, h is the stress (a conjugate field to strain) and λ is a coupling constant. Within this formalism, there are two possibilities for a structural transition to occur: in the case of an electronically-driven transition, it is the a parameter which tends to zero at some temperature (i.e. $a = a_0(T - T^*)$); or alternatively if the transition caused by a purely structural instability it is the c parameter which goes to zero (i.e. $c = c_0(T - T^*)$). Due to the bilinear coupling λ , a finite ψ will induce a finite ϵ , and vice-versa - and so it may not be clear which is the primary instability. An elegant experimental method of determining whether or not the structural transition is really an electronic nematic instability or a purely structural instability is to measure the induced resistivity anisotropy under the conditions of small constant strain, applied along the direction of the later symmetry-breaking distortion, i.e. [110] in the tetragonal unit cell. The strain-derivative of resistivity anisotropy above T_s , in this above model, is a measurement which is proportional to $d\psi/d\epsilon$ ¹, and is given by [36]:

$$\frac{d\psi}{d\epsilon} = \frac{\lambda}{a} = \frac{\lambda}{a_0(T - T^*)} \quad (7.3)$$

¹The temperature-dependence under constant *stress* is ambiguous, but the response under constant *strain* should only diverge for a truly electronically-driven transition, as shown in Ref. [36].

where I assume the temperature-dependence appropriate for an electronically-driven transition after the second equality sign. T^* should be interpreted as a “mean-field” transition temperature [36, 141]; in measurements the resistivity anisotropy does not truly diverge because a finite value of ψ onsets at $T_s > T^*$ due to coupling to the lattice. Physically, in the high-temperature phase tetragonal symmetry forbids any resistivity anisotropy, but by the application of a symmetry breaking field (external strain), there will be an induced resistivity anisotropy which will be large near T^* where the fluctuations of the nematic order parameter are large. Analogously, time reversal symmetry prevents the existence of a magnetic moment in a ferromagnetic material above its Curie temperature; however in the presence of a small external applied symmetry-breaking magnetic field an induced magnetic moment with the well-known Curie-Weiss $\chi = C/(T - T_C)$ temperature-dependence is observed which is large near T_C . However, if the transition were a simple structural (phonon-driven) transition, there is no reason to find a large induced resistivity anisotropy, or any strong temperature-dependence [37] - since $\frac{d\psi}{d\epsilon}$ has no dependence on the c term which goes to zero in that case². Therefore, this experiment demonstrates very clearly that the structural transition in FeSe is electronically driven, in a general sense, and the quantity $\frac{dN}{d\epsilon}$ has been dubbed the “nematic susceptibility” [36] - although I will avoid this term since there are very different measurements of elastic constants [142] which have also been given that name.

7.3 Methods

Single crystals of FeSe were grown using the KCl/AlCl₃ vapour transport growth method (Appendix A). The crystals form as platelets with natural edges corresponding to the tetragonal a and b axes; here I report measurements on a single sample

²Although this is true in theory, I am not aware of any existing studies of this “straw man” scenario but it would be an interesting proof of principle if a suitable system with an analogous tetragonal-to-orthorhombic transition driven by a structural instability could be indentified.

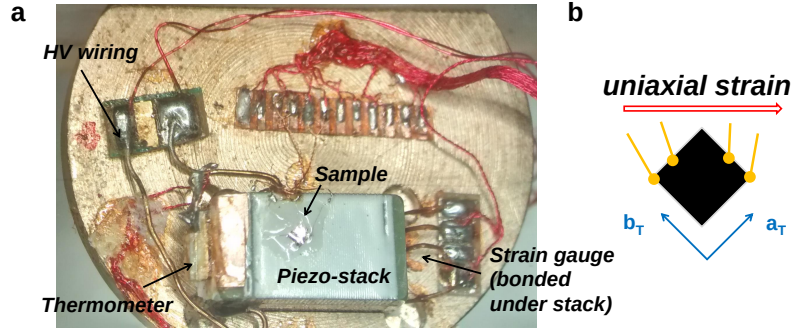


Figure 7.1: a) Set-up used for measurements of the strain-response of resistivity in FeSe. The thermometer is attached to a copper piece placed on the side of the piezostack such that the measured temperature is as close as possible to the sample. The piezo-stack sits in a groove on a brass piece without restriction on its movements and a strain gauge is bonded on the back face of the stack. The brass platform sits at the bottom of a probe inside an evacuated vacuum can, and the whole set-up is placed into liquid nitrogen (or helium) to perform this measurement. The wiring is slightly loose since I designed the brass platform to be rotatable. b) Schematic of the measurement set up, indicating the position of electrical contacts and the direction of strain on a sample cut to have square dimensions. The strain is not truly uniaxial, so sample will also be under compressive strain in the direction perpendicular to the main expansion.

with square morphology oriented with the $[1\ 1\ 0]_T$ direction parallel to the applied strain, which is provided by a piezo-actuating stack to which the crystal is stuck with a standard epoxy, as shown in Fig. 7.1. The strain ϵ (which will be more precisely defined later) is measured using a pair of strain gauges bonded to the bottom of the stack. The current path is also along the $[1\ 1\ 0]_T$ direction, which corresponds to the x/y axes of the local Fe coordinate frame (and also the Fe-Fe direction, and the lattice vectors of the orthorhombic unit cell). A high sensitivity, low noise resistivity measurement was achieved by hand-soldered indium contacts and using a transformer and lock-in amplification. The normal considerations for performing good transport measurements as described in Section 3.2.2 are applicable here; a very high sensitivity was achieved, with the noise level being limited by the digitisation of the final digit of the lock-in amplifier.

Measurements were performed under very slow cooling and warming conditions

by sweeping the voltage applied to the piezostack on a much faster time-scale than the rate of change of temperature in the system (see lower inset of 7.1a), and using data analysis routines to extract the small change of resistivity with the applied strain. In Fig. 7.2a) I show a measurement of the raw resistance of a sample mounted as previously described as a function of temperature. The temperature is changed extremely slowly, as shown in the lower inset, where the cooling rate is as low as 0.18 K/min, whereas the strain is swept at a much faster rate (approximately 20 seconds per sweep). The quasi-stable temperature condition is very important to avoid a spurious contribution from $(dR/dT)(dT/dt)$ affecting the measurement, but this method allows a large number of data points to be collected and additionally ensures minimal heat gradients in the system, which are inevitable when using a heater to stabilise a temperature. While it is true that a more reliable method would be to stabilise the temperature in e.g. a flow cryostat, my group has had mixed experiences in using this method, and if in my set-up the cooling rate is slow enough there will not be large systematic errors, which can be checked by comparing the warming and cooling curves as in Fig. 7.3; moreover this method is far less demanding on cryogenics.

In Ref. [143] it is shown that the desired quantity $d\psi/d\epsilon$ is strictly speaking proportional to the m_{66} component of the elastoresistance tensor, and that a true measurement of the elastoresistance should involve the measurement of two different samples oriented at 90° to each other and a subtraction routine is used to make small corrections to the signal obtained from just one sample. This is related to the fact that no piezostack gives a truly uni-axial strain, it is always bi-axial. N. R. Davies in my group has performed such measurements on FeSe which are presented in Ref. [144]. The strain which here I will refer to as ϵ for simplicity in my measurements is actually a bridge circuit which measures $\epsilon_{xx} - \epsilon_{yy}$, since the piezostack has a finite Poisson ratio and will contract in the y direction when expanding along the x direction. Measuring this way has the advantage of the high sensitivity intrinsic to bridge circuits

and the cancellation of temperature-dependent effects, but it is also the appropriate quantity to measure, since in Ref. [143] it is shown that $2m_{66} = \frac{\partial N}{\partial(\epsilon_{xx}-\epsilon_{yy})}$. These measurements are not of N directly, but measure only $(\delta R/R)_{yy}$, the induced change in resistance under applied strain in one direction, similar to the original report of Ref. [36]. This will be equal to $N/2$ in the case that m_{66} dominates, but there may be other small contributions to the measurement from other components of the elastoresistance tensor³. Therefore, the quantity that I will plot will be labelled as $1/R \, dR/d\epsilon$ and is approximately equal to m_{66} when it becomes large.

7.4 Induced resistivity anisotropy in FeSe above T_s

In Fig. 7.2b, the strain-derivative of resistivity anisotropy $1/R \, dR/d\epsilon$ is plotted, which shows a divergent behaviour above the structural transition (at 92 K in this sample) and a sharp anomaly at T_s . The sharp anomaly in $1/R \, dR/d\epsilon$ coincides with the more subtle anomaly in raw resistivity in Fig. 7.2b and corresponds to the tetragonal-to-orthorhombic structural transition. The regime of measurements above T_s is where the analysis presented above is valid, whereas below T_s the interpretation is more complicated, as will be discussed later, but in general some form of anomaly is expected at T_s . In Fig. 7.2b, a fit of data above 100 K to $\frac{\lambda}{a_0(T-T^*)} + \chi_0$ is plotted, which gives a T^* value of 66(2) K. This may be interpreted as a “mean-field” critical temperature [36]. However, over the relatively narrow temperature window of ~ 100 -250 K where reliable data may be obtained, a satisfactory fit to $\frac{\lambda}{a_0(T-T^*)^n} + \chi_0$ is possible for $n = 1.5$ or 2 as well as $n = 1$ and therefore over-interpretation of the meaning of the $1/(T - T^*)$ temperature-dependence or T^* itself is cautioned against. What is important is that the response becomes large in magnitude with a strong, diverging temperature-dependence, which cannot happen for a transition driven purely by structural effects.

³Only the m_{66} component is expected to have any significant temperature-dependence, so the other components will effectively give a constant offset.

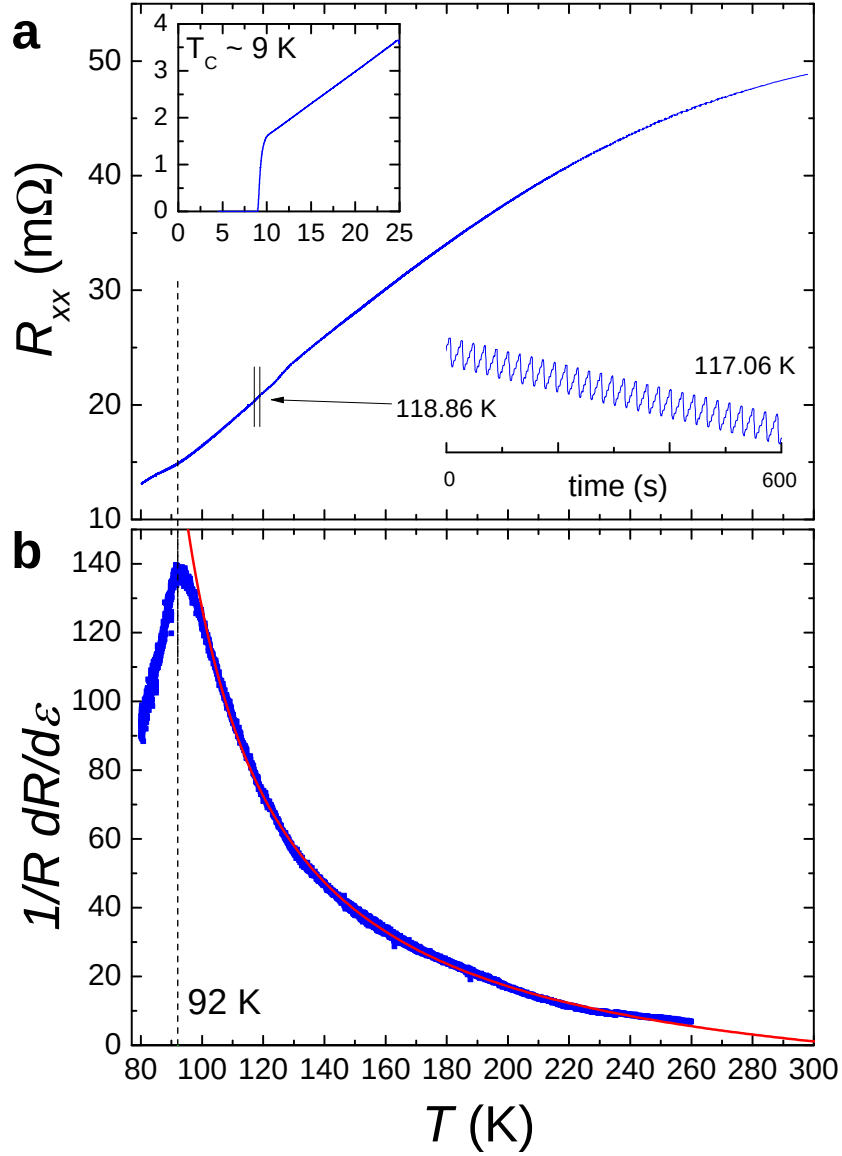


Figure 7.2: a) Raw sample resistance under frequently changing applied strain. The structural transition, at 92 K in this sample, gives an anomaly in $R(T)$, and the T_c is 9 K (top inset). Lower inset: detailed view of the measurement as a function of time, showing the fast strain sweeps compared to the temperature change. b) Extracted “nematic susceptibility” $1/R dR/d\epsilon$ showing a large absolute value and a divergent behaviour. Red line is a fit of data above 100 K to Eq. 7.3 with a constant offset.

The total amplitude of $1/R dR/d\epsilon$ at T_s is larger than that in BaFe_2As_2 , although less than the reported underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)\text{As}_2$ with similar T_s [36]. It has recently been argued in Ref. [145] that the resistivity anisotropy in the tetragonal state is independent of disorder, using a set of experiments on $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

and $\text{Ba}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ and annealed vs as-grown BaFe_2As_2 , which counters previous worries that some of the resistivity anisotropy may be due to impurities, and rather implies that it is an intrinsic effect. These samples of FeSe are very clean; the resistivity ratio $R(300\text{ K})/R(10\text{ K})=31$ for this particular crystal and quantum oscillations are observed in crystals from the same batch. Therefore, it is also unlikely to be an impurity-induced effect in FeSe.

Notably, the sign of the effect is different: in FeSe a positive strain induces a positive change in resistance (i.e. $\rho_a > \rho_b$, where $a > b$ are the orthorhombic lattice parameters) in contrast to $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)\text{As}_2$. This has been previously observed in FeTe [146], and also for certain dopings of $(\text{K}_x\text{Ba}_{1-x})\text{Fe}_2\text{As}_2$ [40], but is unusual in Fe-based superconductors. In the case of $(\text{K}_x\text{Ba}_{1-x})\text{Fe}_2\text{As}_2$, the crossover of sign of resistivity anisotropy was linked to calculations based on anisotropic spin-fluctuation scattering of electrons at particular “hot-spots” on the Fermi surface [39], whereas in FeTe it was linked to the much stronger correlations, i.e. Hund’s rule coupling J . In general, the magnitude and the sign of the resistivity anisotropy is a difficult problem, since it depends on scattering rates and mechanisms and Fermi surface sizes and curvatures, and how they change in response to small perturbations. Moreover, there may be experimental issues (such as imperfect coupling through the epoxy used to secure the sample to the piezostack) which are hard to quantify.

7.5 Measurements below T_s

A further discrepancy with literature measurements is the low-temperature behaviour, below T_s , which will be discussed below along with a possible scenario to reconcile all the observations. Below the structural transition, a numerical analysis is difficult due to twin domain formation as well as the nematic order parameter and the strain now having a finite value. However, the low temperature behaviour in FeSe is rather anomalous, since the sign of the strain response of resistivity changes, and appears to

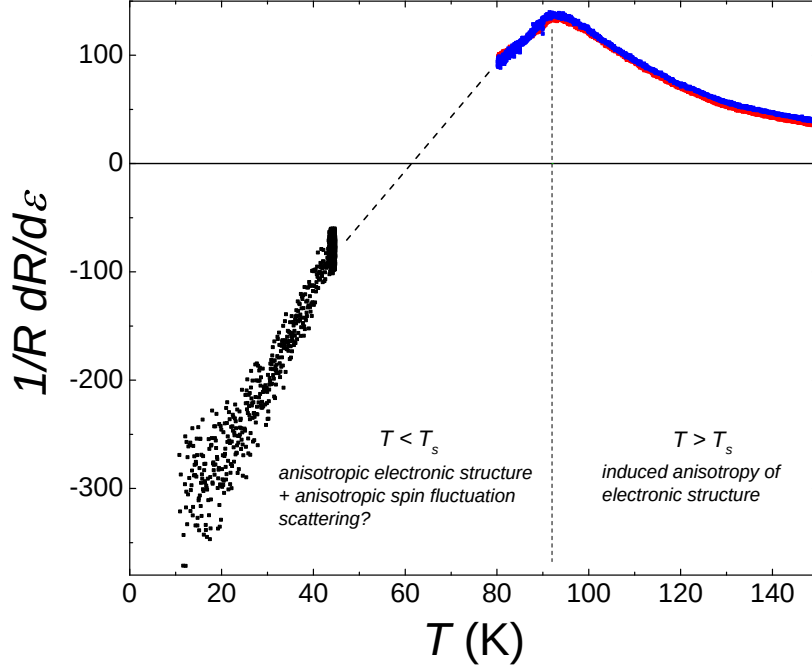


Figure 7.3: Low temperature measurement of the strain-derivative of resistivity. Since at low temperature both R and ϵ generated by the piezo-stack become small, the measurement becomes more noisy. For experimental reasons, I could not stabilize a temperature between 45 K and 78 K. Also shown above 77 K are the data from Fig. 7.2 for both cooling and warming runs which show good agreement.

continue to increase in magnitude at low temperature. A qualitative understanding of this behaviour can come from the following reasoning, although other explanations may be possible.

Equation 7.1 relates the resistivity anisotropy to a nematic order parameter, but does not specify by what mechanism this occurs. In principle, there are two mechanisms relevant to the iron-based superconductors which may provide this link - an intrinsic anisotropy of the electronic structure (which would occur in an orbital ordering scenario which breaks the symmetry of the Fermi surface), or anisotropic scattering mechanisms (in this case, naturally linked to spin-fluctuations). In most iron-based superconductors, both contribute at all temperatures. Although in most Fe-based superconductors the strain-derivative of resistivity is negative both above and below T_s or T_N (that is, $\rho_b > \rho_a$, where $a > b$) [40, 143], a sign-change has been

observed in sufficiently hole-doped Fe-based superconductors which was understood by spin-fluctuation theories using a model Fermi surface [39, 40].

However, FeSe is different since at $T > T_s$, the sign of $dR/d\epsilon$ is positive - opposite to measurements in BaFe_2As_2 but in agreement with some orbital models (e.g. Ref. [147, 148])⁴. This *may* support an interpretation that spin-fluctuations do not drive the structural transition. Spin fluctuations do not contribute much above T_s but do set in sharply below T_s , as is also observed in NMR measurements[45, 46]. A possible interpretation is that the spin-fluctuations give rise to highly anisotropic scattering and become dominant in $dR/d\epsilon$, making it now negative, similar to other pnictides. Although the interpretation below T_s is a rather complex problem, a sign change would not be expected unless the link between resistivity anisotropy N and the underlying electronic nematicity ψ changes, especially since there is no magnetic reconstruction of the Fermi surface, although it does become distorted. It is worth noting that in the case that there is a strong temperature-dependence of the mechanism relating resistivity anisotropy N to the underlying nematic physics ψ , as appears to be the case in FeSe at least below T_s , then the question of whether or not the response truly has a $N \sim 1/(T - T^*)$ temperature-dependence becomes meaningless.

7.6 Discussion

I now discuss these results in the light of several recent studies on FeSe. In FeSe, ARPES measurements have observed strongly distorted Fermi surfaces below the structural transition (see Chapter 6) - which would result in anisotropic transport properties (within one structural domain). These Fermi surfaces with only two-fold symmetry will naturally lead to anisotropic transport properties. Moreover, in Chapter. 6 it was found that a splitting of 49 meV was found between bands with d_{xz} and d_{yz} at the M point- far more than would be expected within DFT incorporating

⁴Although it is certainly true that the high-temperature Fermi surface of FeSe is substantially different to Fe-pnictides, which may affect these models.

the orthorhombic distortion. The combined conclusion of the ARPES data and these measurements is therefore that the structural transition in FeSe is certainly driven by electronic degrees of freedom.

In the context of other Fe-based superconductors, it has been postulated that anisotropic scattering in a spin-nematic state would give rise to resistivity anisotropy, with some successful predictions [40]. However, FeSe does not magnetically order at any temperature and some studies have suggested that magnetism may play only a weak role in FeSe, at least above T_s . Of particular relevance is a recent combined thermodynamic and NMR study of FeSe single crystals, which found that while their “nematic susceptibility” derived from shear modulus measurements for FeSe compared very closely to underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)\text{As}_2$, there was an apparent lack of spin-fluctuations affecting the relaxation rate in NMR measurements above T_s [45]. These measurements were suggestive of a non-magnetic origin of the structural transition in FeSe. Furthermore, in measurements of thermal expansion, a lack of coupling between superconductivity and orthorhombic distortion [44] was found, with one possible interpretation being that the structural transition is not magnetically driven in FeSe. Our measurements are complementary, indicating that the structural transition is still electronically driven in FeSe, but taking all the experimental evidence into account, that it is the spontaneous symmetry-breaking of the electronic structure itself which drives the structural transition, with the spin-degrees of freedom not playing a large role. However spin-fluctuations at low temperature $T \ll T_s$ may still be relevant to the superconducting pairing mechanism in FeSe and may also cause the unusual sign change of the resistivity anisotropy at low temperatures.

In conclusion, I have used measurements of the strain-derivative of resistivity anisotropy to demonstrate that the structural transition in FeSe is electronically-driven. The magnitude and temperature-dependence are similar to measurements in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)\text{As}_2$ but the sign is opposite. Taking into account literature data

indicating that the structural transition is not driven by magnetism, the structural transition in FeSe is driven by the tendency towards orbital order, as also indicated by ARPES measurements.

Chapter 8

Field-induced spin-flop transition in $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$

In this Chapter, I introduce the $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$ (“10-3-8”) family of Fe-based superconductors, performing an analysis of the resistivity and Hall effect across the phase diagram. I then concentrate on the high-field properties, characterising the superconducting phase diagram for a composition of $x=0.078$ and finding an unexpected field-induced magnetic transition at 22 T. The anomaly observed in magnetic torque at this field is well described by a model assuming a spin-flop contribution to the magnetic torque signal. I conclude that, across the phase diagram, the 10-3-8 family of Fe-based superconductors undergo a field-induced spin-flop-like metamagnetic transition which is likely to arise from antiferromagnetic fluctuations rather than long-range order. This chapter is based on work published in Watson *et al.* Phys. Rev. B 89, 205136 (2014)¹.

¹For this work I would like to particularly thank Alix McCollam for her support during the measurements in Nijmegen, Roser Valenti and Igor Mazin for useful discussions of magnetic anisotropy, and Ni Ni who grew the crystals.

8.1 Introduction

One of the interesting aspects of the iron-based superconductors is the large variety of structures into which a FeX (X =pnictogen or chalcogen) layer may be incorporated and yet superconductivity is found. In many families the preparation of sizeable samples has been achieved, allowing for detailed investigations into the differences between families. In the most studied ‘122’ systems (based on the parent compounds BaFe_2As_2 , CaFe_2As_2 or SrFe_2As_2) the antiferromagnetic phase is suppressed and superconductivity is found with a large variety of transition metals doping onto the iron-site. However, attempts to dope Pt into the iron layer of CaFe_2As_2 threw up an unexpected surprise; before the superconducting phase is reached a solubility limit is reached and novel Ca-Fe-Pt-As phases are formed, which also superconduct [149]. More detailed analysis revealed the existence of two distinct phases: the “10-3-8” system with chemical formula $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$ with a T_c up to 13 K, and the “10-4-8” system $\text{Ca}_{10}(\text{Pt}_{4-\delta}\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$ with a maximum T_c of 26 K [150]. The crystal structures consist of the usual (Pt-doped) FeAs layers, but stacked alternately with additional Pt_3As_8 or Pt_4As_8 layers.

In this chapter, I will concentrate on the “10-3-8” phase, explaining the unusual crystal structure, characterising a series of samples with resistivity and Hall effect measurements, and then focussing on the high-field properties of 10-3-8 where a magnetic transition at 22 T in magnetic torque measurements is revealed.

8.2 Literature survey of $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$

The crystal structure of the “10-3-8” family is shown in Fig. 8.1a - it is clear that it is structurally much more complex than the other Fe-based superconductors due to the stacking of the FeAs layer with the Pt_3As_8 layers. The overall space group is the low-symmetry triclinic $\bar{P}1$ due to the incompatibility of the symmetries of the Pt_3As_8

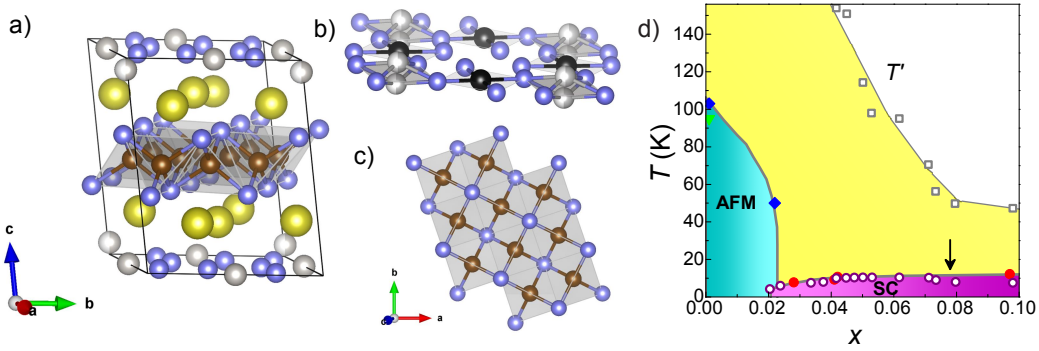


Figure 8.1: a) Unit cell of $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$, which is formed by stacking Pt_3As_8 and FeAs layers and takes the $\text{P}\bar{1}$ space group. b) Detailed view of the Pt_3As_8 layer, showing the square planar co-ordination of the Pt atoms; furthermore some of the Pt (shaded half-grey) can occupy a position either above or below the plane. c) Projection of the FeAs layer in the ab plane, showing the same structural motif as other Fe-based superconductors. d) Phase diagram of Pt-doped 10-3-8, data taken from Refs. [151, 152]. Black arrow indicates the $x = 0.076$ composition which was studied in the most detail in the following sections.

and FeAs layers. One feature which will be important later on is that the structural c -axis is not normal to the ab plane - the crystals however still cleave in the ab plane.

Despite the complexity, 10-3-8 contains essentially the same structural motif of the square lattice of Fe as found in other Fe-based superconductors. Therefore there have been several studies to establish whether this family behaves in a similar way to other more simple and familiar Fe-based superconductors, and to attempt to determine any interesting differences. For instance, in “undoped”² $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ a structural transition [153] in the ab plane was found, mimicking the orthorhombic distortion found in other Fe-based superconductors. A further study found anomalies in resistivity, susceptibility and specific heat which together suggested [154] a structural transition at 103 K followed by a magnetic transition at 95 K - analogous to Co-doped BaFe_2As_2 where a similar splitting of the orthorhombic and magnetic anomalies is observed. The structural transition may be suppressed by Pt-doping into the Fe layer, resulting in a superconducting dome with a maximum T_c of 13 K

²Controlling, and indeed measuring the exact excess of Pt in the system is rather difficult since there are several Pt sites.

[151, 150], as shown in Fig. 8.1d. Alternatively, by La doping onto the Ca site (also electron-doping) a higher T_c of up to 26 K has been reported [154]. The whole superconducting dome can be also reached under applied pressure [152]. Taken together, these studies suggest that the physical properties of the materials are dominated by the FeAs layer and behave similar to other Fe-based superconductors, with the structural complications not playing a large role. Indeed, this was found in ARPES measurements which found that the Fe 3d orbitals were, as usual, important at the Fermi level, and moreover the Fermi surface was found to be four-fold symmetric [155], despite this not being a symmetry of the space group - implying only weak coupling between the Pt_3As_8 and FeAs layers.

I have emphasised the fact that, despite the structural complexity and inevitable crystal quality issues associated with it, all the evidence suggests that the 10-3-8 system largely behaves like other Fe-based superconductors. Indeed the following resistivity and Hall effect characterisation measurements have similarities to other Fe-based superconductors. However, later in this chapter I will show a field-induced transition which is unique amongst iron-based superconductors which will require further discussion of what may be different about the 10-3-8 system.

8.3 Characterisation of the $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$ series

8.3.1 Zero-field resistivity and Hall Effect

Single crystal samples with typical dimensions 1000 x 600 x 40 μm were grown by Dr. Ni Ni, now at the University of California, Los Angeles. Samples were prepared for resistivity measurements using Sn solder to make good electrical contacts. Transport measurements were performed in the PPMS using temperatures down to 2 K. Hall Effect measurements were performed by stabilising the temperature, and sweeping the field between -3 T to 3 T, and taking a straight line fit to the anti-symmetric

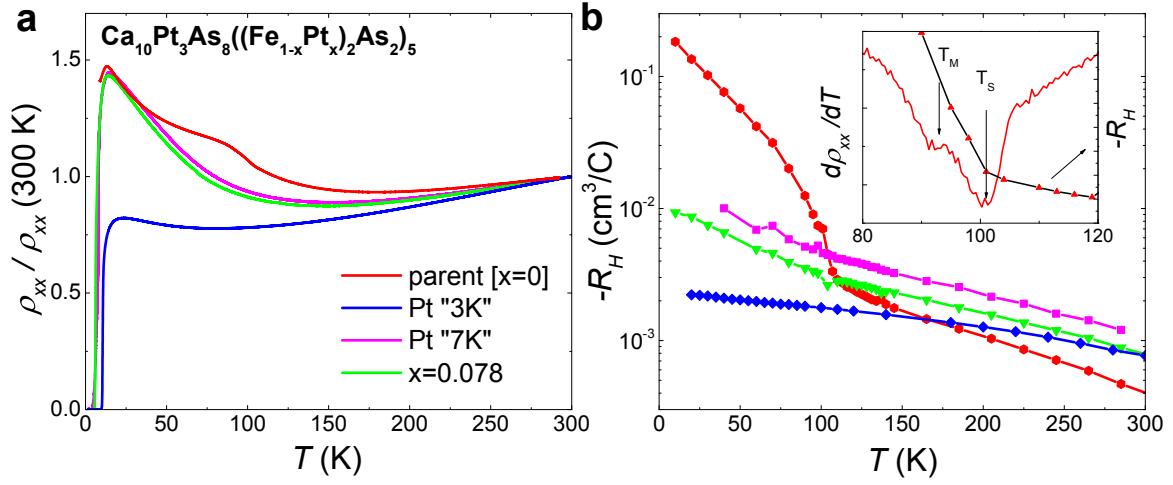


Figure 8.2: a) Zero-field resistivity measurements of the parent compound ($x=0$) and Pt-doped compositions up to $x=0.078$. b) Hall coefficient as a function of temperature. The Hall effect of the parent compound exhibits a strong anomaly at $\sim 100\text{ K}$ which corresponds to an anomaly in the resistivity, and both are linked to the structural transition at T_s .

component of the data (i.e. excluding any spurious ρ_{xx} component which is symmetric in B which may come from contact misalignment³). Samples from four batches of Pt-doped 10-3-8 were used for transport measurements. In order to determine the composition, wavelength-dispersive x-ray (WDX) measurements were performed in the group of Susie Speller, Oxford Materials, on one batch. This batch has the highest doping of the samples in this study with $x=0.078(6)$ and a T_c of $\sim 10\text{ K}$. The intermediate doping levels were never directly measured and are therefore referred to as “Pt-3K” and “Pt-7K”.

Fig. 8.2a shows the resistivity of the four batches as a function of temperature. In the parent compound, anomalies in resistivity are observed at $\sim 103\text{ K}$ and $\sim 95\text{ K}$ which are more easily observed in dR/dT plotted in the inset of Fig. 8.2b. These measurements are consistent with Ref. [154] in which they were identified as the structural and magnetic transitions respectively. A dramatic change in the Hall Effect

³This is a far more reliable method than the method suggested in the PPMS documentation, which is staying in a static field and hoping that the offset of the balance bridge in the PPMS AC transport option is temperature-independent - it never is, and therefore this method should not be used.

for the parent compound is also observed around these temperatures Fig. 8.2b. The anomaly in the temperature-dependence of the Hall coefficient due to Fermi surface reconstruction in the magnetic phase (and associated changes in mobility), reaching a high value indicative of the low carrier density found in the magnetically ordered state, with the sign indicating higher mobility for the electrons than holes. All samples have a negative Hall coefficient, but doped samples have a featureless temperature-dependence, indicating that they do not order above T_c . These findings are generally consistent with measurements in underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [156].

A feature of the zero-field resistivity for all compositions is that the resistivity remains large to low temperatures, experiencing a crossover from positive to negative dR/dT as the sample is cooled, with a minimum of resistivity defined at T' . This crossover temperature is broad, and it is found to be sample-dependent and is likely to be influenced by the high level of disorder in the samples. However measurements of one sample under applied pressure [152] found that T' tracks above the structural/magnetic transition and extends over the superconducting dome, and therefore probably reflects intrinsic behaviour. One possible explanation is that this crossover indicates the onset of spin-fluctuations, causing additional scattering; the resistivity of the “10-3-8” system may be more susceptible than other systems due to the enhanced two-dimensionality with limited inter-plane conductivity. However, there is no associated anomaly in the Hall effect at T' . On the other hand it has been pointed out that the Pt_3As_8 (as opposed to Pt_4As_8) layers are essentially semiconducting [150] which may play a role in the measurement of “in-plane” resistivity⁴, giving a more prosaic explanation. In either case one can define T' for each sample, giving values compatible with the literature measurements shown in Fig. 8.1d.

⁴Similar problems were also observed in measurements of organic superconductors where in-plane resistivity measurements were very often contaminated with the much larger ρ_{zz} component.

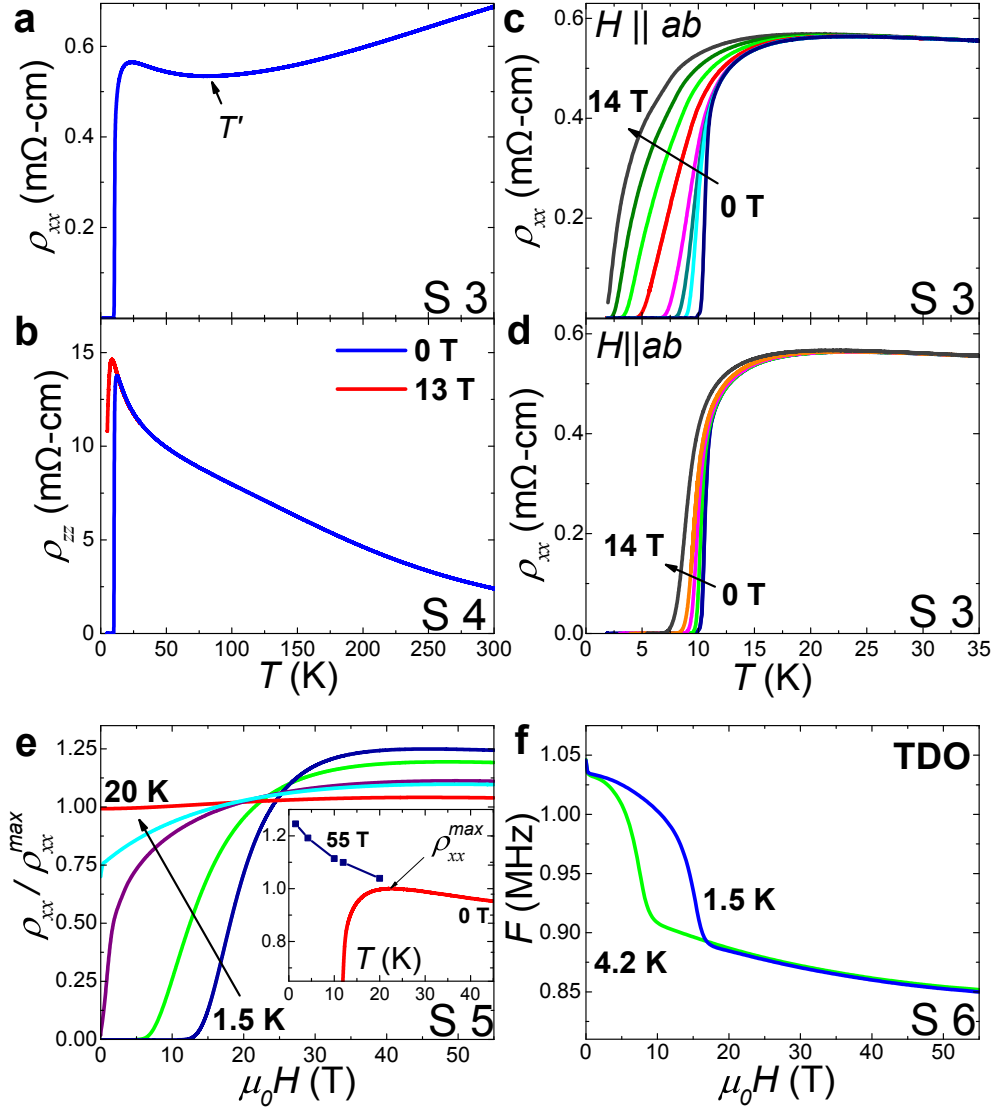


Figure 8.3: Transport measurements on single crystals of superconducting 10-3-8 ($x=0.078$). (a) Temperature dependence of the (a) in-plane and (b) inter-plane resistivity in zero field. The arrow in (a) indicates the position of the minimum in resistance at T' . Temperature dependence of in-plane resistivity in constant magnetic field (c) when $H \perp ab$ planes and (d) when $H \parallel ab$ planes. (e) Resistivity measurements in a pulsed magnetic field taken at constant temperatures. The data was normalized to the value of the sample at ρ_{max} (indicated by the arrow in inset). Inset: The normal in-plane resistivity at 55 T as function of temperature plotted together with the zero-field resistivity. (f) TDO measurements as function of magnetic field showing a superconducting transition but no further anomaly at 22 T.

8.3.2 High-field transport properties of $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{0.922}\text{Pt}_{0.078})_2\text{As}_2)_5$

I now focus on the sample with highest $T_c \approx 9.7$ K ($x=0.078$), and have performed in- and out-of-plane transport measurements to characterize the superconducting phase. Fig. 8.3a shows the temperature dependence of the in-plane resistance that has a crossover from a metallic-like to semiconductor-like regime [151] at a temperature $T' \approx 80$ K as previously discussed before it becomes superconducting at $T_c \approx 9.7$ K. A magnetic field perpendicular to the planes (Fig. 8.3(c)) causes a substantial broadening of the superconducting transition. However, there is a strong anisotropy and an in-plane field (Fig. 8.3(d)) does not suppress the transition to the same extent. This broadening indicates strong thermal fluctuations of the vortex lattice, which can be quantified by the Ginzburg number $Gi \approx 0.16$ [157], significantly higher than in typical pnictides. In contrast with the in-plane measurements, the inter-plane resistance (Fig. 8.3b) increases at low temperature by a factor ~ 6 suggesting strongly incoherent transport between the planes. In-plane resistivity (Fig. 8.3(e)) and tunnel diode oscillator measurements of the penetration depth [158] (TDO in Fig. 8.3f) in very high fields up to 55 T show no anomalies that could be associated with the magnetic transition (when $H \perp ab$), beside the expected broad transition from the superconducting to the normal state. By completely suppressing the superconductivity by a magnetic field of 55 T, the extracted normal state resistance tends to increase exponentially at low temperatures suggesting charge localization in the normal state of 10⁻³-8, as shown in the inset of Fig. 8.3e.

8.4 Field-induced magnetic transition in $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$

Fig. 8.4 shows magnetic torque data on three crystals (superconducting S1, S2 and non-superconducting parent P1) when the field is a small angle θ away from being

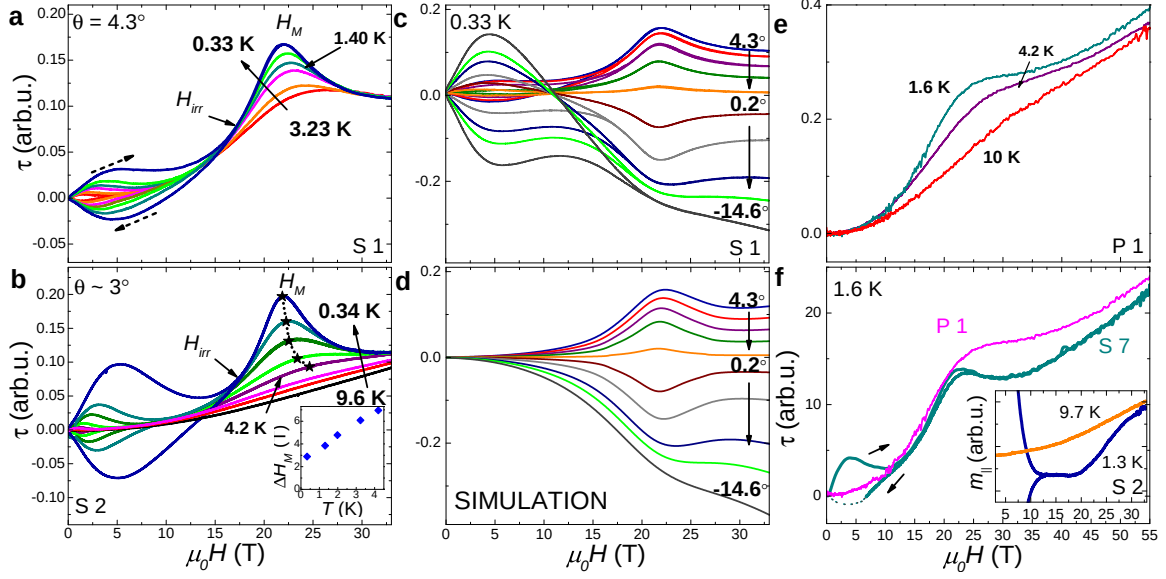


Figure 8.4: a) Magnetic torque in an applied magnetic field at constant temperatures between 0.33 K and 3.23 K for a 10-3-8 superconducting sample S1 when $H \perp ab$ (within $\theta = 4.3^\circ$, where θ is the angle between the magnetic field and the normal to the ab planes). Solid arrows indicate the positions of the irreversibility field $\mu_0 H_{irr}$ and the peak of the magnetic anomaly at $\mu_0 H_M$, dashed arrows show field sweep direction. b) Magnetic torque versus field on sample S2 up to 9.6 K. Stars indicate the position of the maxima at $\mu_0 H_M$ determined after subtraction of the 9.6 K signal. Inset: the temperature dependence of the peak width, ΔH_M , fitted to a Lorentzian. c) Field dependence of torque as function of angle θ at 0.33 K. d) A simulation of torque based on a spin-flop and a paramagnetic contribution described below, assuming the magnetic moments are aligned perpendicular to the ab plane in zero field. e) Magnetic torque measurement in the parent compound sample P1, showing a similar anomaly. f) The subtractions of the anomalous low-temperature torque and the high-temperature featureless background shows quantitative agreement between parent and doped samples. Inset: A magnetisation measurement using a torque field-gradient magnetometer described further in Ref. [55], shows a low-temperature upturn consistent with a spin-flop scenario.

perpendicular to the ab planes. The typical hysteresis that occurs in the superconducting state due to the pinning of the flux vortices allows the determination of the superconducting phase diagram from the position of the irreversibility field $\mu_0 H_{irr}$, as indicated in Fig. 8.4a,b. Furthermore, at magnetic fields above the superconducting hysteresis, there is a clear anomaly at 22 T in the magnetic torque data which becomes sharper as the temperature is lowered to 0.33 K. This effect was reproduced in

all the crystals investigated and no further anomalies were detected up to 55 T. This anomaly is well-defined only when the applied field is nearly perpendicular to the ab plane, and it is symmetric around this direction, as shown in Fig. 8.4c. The width of this peak at $\mu_0 H_M$ (the maximum in the torque signal after subtracting the featureless 9.6 K sweep), quantified by the half-width of Lorentzian fit to the subtracted data (inset of Fig. 8.4(b)), shows a linear decrease with decreasing temperature which suggests that there is a relevant energy scale with which temperatures on the order of 1 K are comparable. The observed behaviour of magnetic torque in 10-3-8 is unique and in contrast to the $\tau \sim H^2$ background torque typically observed in other FeBS above the irreversibility field and associated with paramagnetism (e.g. [7, 59]). In the parent compound ($x=0$) sample P1, shown in Fig. 8.4e) there is a similar anomaly. The peak is substantially broader in this sample of the parent compound, however experimental reasons for this difference (e.g. related to sample alignment) cannot be ruled out, otherwise the anomalies are qualitatively similar; a direct comparison in Fig. 8.4f) of the high-field raw torque shows quantitative agreement in the position of the peak to within 2 T.

The anomaly at 22 T is likely to be of magnetic origin since this is what is probed by magnetic torque, and its large magnitude compared to the superconducting hysteresis suggests that a significant fraction of the magnetic ions are involved. This anomaly is not observed in any other FeBS, and so potential explanations outside of the Fe-As layers common to the family should be considered. The first possibility is that the signal arises from a magnetic impurity phase formed in the growth and unrelated to the 10-3-8 system. However, this scenario is highly unlikely due to the magnitude of the signal, and its appearance only when the field is oriented almost exactly perpendicular to the 10-3-8 lattice planes; additionally there is no sign in X-ray or WDX for impurity phases.

Secondly, the Pt ions should be considered. They are heavy and have strong

spin-orbit coupling, and may experience large magnetic anisotropy. In the doped material, there are two types of Pt: one in the Fe plane (Pt^{4+}) and another one in the Pt-As layer (Pt^{2+})⁵. The latter are not expected to be magnetic, given the d^8 configuration of Pt^{2+} , but the former might spin polarize; even a weak polarization would provided for a measurable anisotropy of the magnetic response. For that reason, DFT calculations on a $\sqrt{5} \times \sqrt{5}$ supercell with one Fe substituted by Pt were performed by Daniel Guterding and Igor Mazin, who performed full lattice relaxation to avoid applying artificial internal pressure to the in-plane Pt. However, for both Pt positions (in-plane and intermediate layer) the calculations render completely polarization-free Pt, even though the surrounding Fe atoms acquire full polarization. Adding Hubbard $U=2.5$ eV and $J=0.5$ eV does not create spin polarization on Pt either.

Having discounted these explanations, it is necessary to explore possible meta-magnetic transition in the Fe subsystem. Motivated by studies in BaCo_2As_2 [159] and other systems, it is natural to consider the possibility of spin-flop-like physics. The spin-flop transition occurs for a magnetic field applied along the easy axis of an ordered antiferromagnet which is assumed to have uniaxial anisotropy, i.e. the field parallel or anti-parallel to the magnetic moments. At low fields, the spin directions do not change, but above a certain critical “spin-flop” H_{SF} field the energy gain from aligning spins with the magnetic field will overwhelm the anisotropy energy and the system will reorient (or “flop”) into a *canted* spin state with a net moment along the direction of the magnetic field. Treatments of the problem may be found in Refs. [160, 161]. A canonical example of a spin-flop transition in a uniaxial antiferromagnet is MnF_2 (e.g. Ref. [162]). The spin-flop transition belongs to a wider class of spin-reorientation metamagnetic transitions.

⁵The square-planar coordination of Pt in the Pt-As layer creates a strong crystal field, with a high antibonding $d_{x^2-y^2}$ band, and all other d -states occupied, so the valency of the interlayer Pt is 2^+ , as opposed to the Pt^{4+} substituting for Fe. The arsenics in the Pt_3As_8 plane form covalently bound dimers with an effective valency of 4^- per dimer so that the ionic electron count is $\text{Ca}_{10}^{2+} \text{Pt}_3^{2+} (\text{As}_2)_4^{4-} \text{Fe}_{10}^{2+} \text{As}_{10}^{3-}$.

Although there is no reported long-range antiferromagnetic order in the doped 1038 compound (see Fig. 8.1d), there are certainly antiferromagnetic fluctuations, which could become sufficiently long-lived at low temperatures to contribute to the magnetic torque. At a temperature $k_B T \lesssim K$, where K is the single-ion magnetic anisotropy energy, the fluctuating spins at zero field lie predominantly along the easy axis and may flop under an external field; this will manifest itself in magnetic torque as a peak at H_{SF} , when the field is along the easy axis. In experiments (Fig. 8.4(a,b)) the sharpness of the anomaly at H_M , which is now associated with a spin-flop field H_{SF} , varies substantially between 0.33 K and 3.23 K, and is completely featureless by ~ 10 K. Therefore a qualitative association of the temperature and magnetic anisotropy energy scales would suggest that K is of the order of ~ 1 K (86 μeV). A direct calculation of K from DFT for the Ca-10-3-8 *parent* compound ($x=0$) gives a value of $K \approx 106 \mu\text{eV}$ which is of the same order of magnitude as the measured magnetic energy scale but predicts b as the easy axis. In our experimental geometry the spin-flop explanation requires the c^* axis, perpendicular to the ab planes, to be the easy axis. However, the anisotropy energies are a subtle problem and DFT does not give the correct direction in a number of cases [163].

8.4.0.1 Simulations of magnetic torque

In order to substantiate the claim of spin-flop physics in 10-3-8, I developed a simple model with a contribution of a spin-flop term and a paramagnetic term, convoluted with a broadening function. In Section 3.3 it was shown that torque in a paramagnet may be written:

$$\tau = \frac{\mu_0}{2} (\chi_{\perp} - \chi_{\parallel}) H^2 \sin 2\theta \quad (8.1)$$

Therefore, the torque in a paramagnet is quadratic and featureless as observed for e.g. LiFeAs in Chapter 4. In contrast, I will show in the following that magnetic

torque as a function of applied field in a uniaxial antiferromagnet gives rise to a peak at the spin-flop field H_{SF} if the field is applied *parallel to the easy axis* [164]. Therefore torque is a sensitive probe of spin-flop transitions, whereas magnetization usually shows a step or slope change at the spin-flop field.

The antiferromagnetic case has been treated in the literature. Yosida in 1951 considered the case of an anisotropic antiferromagnet [160] following earlier work of Van Vleck. He considers the effect of a moderately large magnetic field, assuming that the effect of the magnetic field will be dominated by the antiferromagnetic exchange energy (i.e. J), which he assumes to be significantly larger than the anisotropy energy K . We start with a free energy which is the one derived by Yosida [160].

$$F = -\frac{1}{2} (\chi_{\perp} \sin^2 \phi + \chi_{\parallel} \cos^2 \phi) \mu_0 H^2 + K \sin^2 (\phi - \theta) \quad (8.2)$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are now defined with respect to the vector m^0 and here depend on the AFM couplings. We have also introduced a crystalline anisotropy term. In particular, in theory at least, $\chi_{\perp}$ is independent of field and temperature, but $\chi_{\parallel}$ tends to zero as T tends to zero. Therefore at low temperatures, $\chi_{\perp}$ will dominate. Note that it is the angle ϕ that enters in the first term of the free energy - not θ .

Since $\partial F / \partial \phi = 0$,

$$\begin{aligned} 0 = & -\frac{1}{2} \mu_0 H^2 (\chi_{\perp} - \chi_{\parallel}) \sin 2\phi \\ & + K (\sin 2\phi \cos 2\theta - \cos 2\phi \sin 2\theta) \end{aligned} \quad (8.3)$$

Solving gives

$$\tan 2\phi = \frac{\sin 2\theta}{\cos 2\theta - (H/H_{sf})^2} \quad (8.4)$$

Where

$$H_{sf} = \left[\frac{2K}{\mu_0 (\chi_{\perp} - \chi_{\parallel})} \right]^{1/2} \quad (8.5)$$

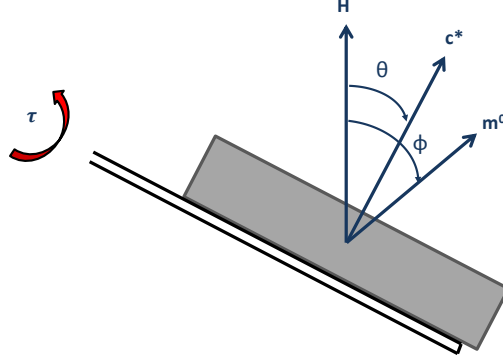


Figure 8.5: The geometry of magnetic torque analysis of spin flop transitions. Here m^0 refers to the direction of the antiferromagnetic staggered magnetisation, H is the applied field, c^* axis is normal to the ab planes and τ is the torque on the lever.

From here, one can calculate the the magnetic torque. Skipping several lines of algebra, the result is that the torque is given by

$$\tau = -\frac{\partial F}{\partial \theta} = \frac{1}{2}(\chi_{\perp} - \chi_{\parallel})\mu_0 H^2 \frac{\sin 2\theta}{\sqrt{1 - 2\lambda \cos 2\theta + \lambda^2}} \quad (8.6)$$

where

$$\lambda = \left(\frac{H}{H_{sf}} \right)^2 \quad (8.7)$$

When this is plotted, it gives a very sharp peak at $\theta \rightarrow 0$, which becomes broadened as the angle is moved away from the symmetry axis.

In Fig. 8.4d I present simulations of the angular dependence of torque in a spin-flop scenario, using Equation 8.6 and an additional term to account for a paramagnetic contribution (Equation 3.7), including a Lorentzian broadening ($\Gamma = 2.1$ T). The ratio of the contributions of the spin-flop term and paramagnetic term used are 0.8:1, i.e. almost equal. The superconducting hysteresis is not modelled. Despite the simplicity of the model, the correspondence with the experimental data is remarkable, as shown in Fig. 8.4d. Further support for a spin-flop-like interpretation comes from the magnetisation⁶ data shown in the inset of Fig. 8.4(f), where the 1.3 K data

⁶This “magnetisation” measurement uses a novel technique based on magnetic torque as described in Ref. [55].

after the large superconducting hysteresis show a clear anomaly showing the onset of increasing magnetisation above ~ 20 T, which can be interpreted as a transition from an antiferromagnetic state with zero net moment, to a canted state with magnetisation increasing with field.

It is worth noting that although the formula used for magnetic torque and the ensuing discussion are easiest to understand in terms of local moments, an itinerant analogue of the spin-flop exists [165], where the polarisation vector of the spin-density wave experiences a “flop” when a sufficiently large magnetic field is applied parallel to its initially preferred direction.

8.5 Field-temperature phase diagram of $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}/\text{Pt})_2\text{As}_2)_5$

Based on the transport and torque data, phase diagrams of the superconducting $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2)_5$ ($x = 0.078$) are constructed, as shown in Fig. 8.6a. Near T_c , the anisotropy parameter $\gamma_H = H_c^{\parallel ab}(T)/H_c^{\perp ab}(T)$ is 10, characteristic of the most 2D FeBS [166, 167]. For the in-plane magnetic field, the single-band WHH model [168] is used to fit the zero-resistance near T_c to predict $H_{c2}(0) \approx 30$ T, which is close to the irreversibility field of 32 T measured in torque at 1.5 K. For $H \perp ab$, the superconducting phase boundary shows a strong concave curvature that cannot be captured by the one-gap WHH model and is suggestive of multi-band superconductivity in this system, as seen in the closely related 10-4-8 superconducting phase [169] or other anisotropic systems such as the 1111 pnictides [170] and cuprates. The solid black arrows in Fig. 8.6b represent the favourable spin orientations for a field oriented perpendicular to the ab plane, according to the spin-flop model developed above.

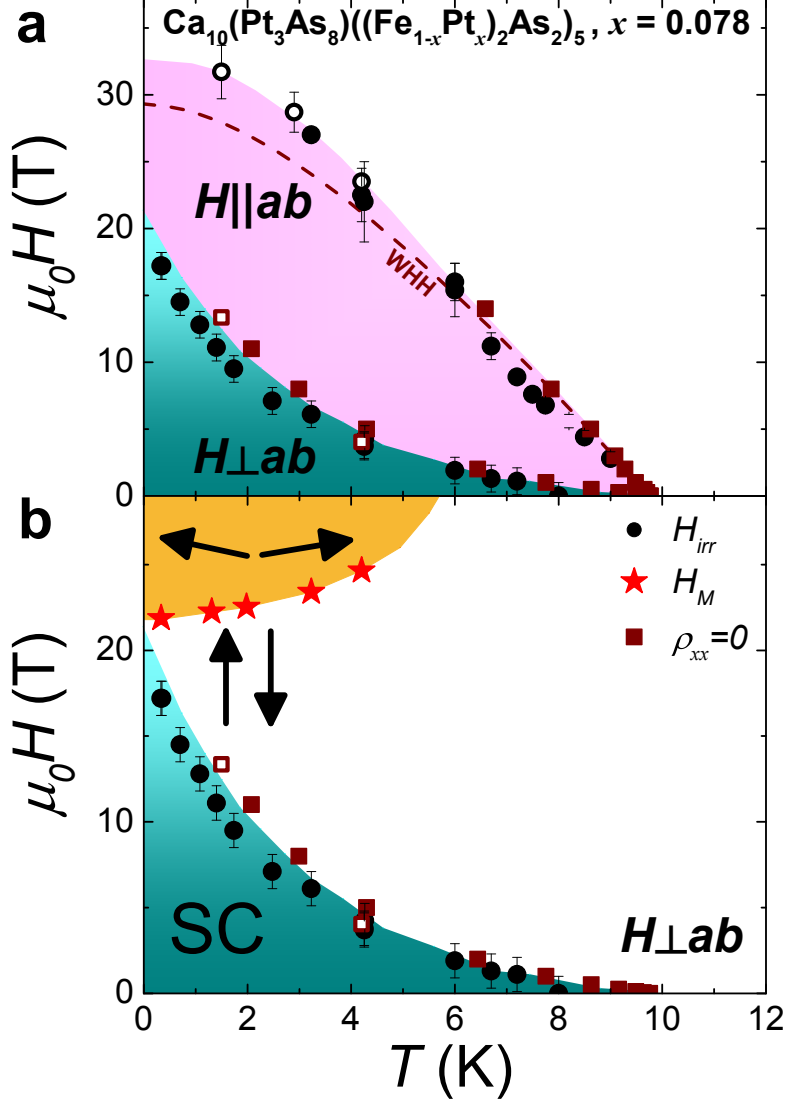


Figure 8.6: (a) The superconducting field-temperature phase diagram of $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)((\text{Fe}/\text{Pt})_2\text{As}_2)_5$ for two different orientations with respect to the (ab plane), as obtained from magnetic torque (circles) and transport measurements (squares). Open symbols indicate the pulsed fields measurements. Dashed line is the WHH fit to $H||ab$ data; the coloured phase boundaries are a guide to the eye. (b) The magnetic field-temperature phase diagram for $H\perp ab$ showing the position of the magnetic anomaly at H_M (stars - taken from Fig. 8.4b) and the irreversibility field, H_{irr} in the superconducting (SC) state. Black arrows represent the energetically favourable orientations of the fluctuating antiferromagnetic spins.

8.6 Interpretation

While the spin-flop model mathematically reproduces the data well, the physical implications of observing such a transition both in the parent and the doped compound are not straightforward. If the anomaly were associated with static magnetic moments (i.e. the classical spin flop) then it would not be expected in the doped compound without long-ranged order. Furthermore one might expect the transition to be sharper and observable right up to T_N in the parent compound. The possibility of phase separation (i.e. islands of magnetic order in the doped compound) should be considered as a possible way for the physics of ordered moments to become relevant in the nominally not-ordered system. However the doping of $x=0.078$ is high and far away from the $x \sim 0.02$ needed to suppress the antiferromagnetism so it would seem unlikely, even given some degree of inhomogeneity in x . Furthermore there is no indication in other measurements (e.g. resistivity, Hall effect, specific heat) that this is the case and WDX rules out any phase separation on a length scale greater than tens of microns. Furthermore, the static moment explanation would require the ordered spins to lie along the c^* axis in zero field. This would be in contrast to LaFeAsO, SrFe₂As₂ and BaFe₂As₂, where the spins are aligned in-plane [32] (although in NdFeAsO [171] and the related materials CaCo₂As₂ [159] and BaMn₂As₂ [172] they are along c) and would also be in contradiction with neutron scattering reports indicating the ordered spins point in the ab plane [173]. However an interpretation based on short-range antiferromagnetic correlations could be consistent with all the data. It is known in BaFe₂As₂ that the ordered Fe moment is significantly less than the total fluctuating moment, and the high-energy spin-excitations have very little change across the phase diagram (see e.g. BaFe_{2- x} Ni _{x} As₂ [174]), although the low energy spin-waves of the parent compound are suppressed and broadened as the long-range order is suppressed by doping. The hypothesis is that in 10-3-8 at low temperatures (notably, below the usual temperatures of neutron scattering experi-

ments) the antiferromagnetically correlated fluctuating moments, which exist across the phase diagram, prefer to align along the c^* axis at zero field, and experience a spin-flop transition at 22 T, above which the preferential direction is a canted state, or in-plane. Magnetic torque measurements would be able to detect such a transition of fluctuating moments through their field-dependent, anisotropic contribution to the susceptibility tensor; long-range order is not necessarily required for a signature in magnetic torque measurements. In this interpretation the ordered part of the moments in the parent compound would contribute towards the background while the fluctuations create the anomaly. Further experiments will be necessary to confirm or refute this scenario. However in the most general case, our data must reflect some form of metamagnetic transition, and to observe a peak rather than a smooth and continuous signal requires at least some of the moments in the system to align preferentially along c^* in low fields before experiencing a reorientation transition.

Chapter 9

Conclusions

The normal state electronic structures of Fe-based superconductors are of fundamental importance to understanding the mechanism of high temperature superconductors. Just as there are many possible *crystal* structures which can incorporate the Fe-As layer and exhibit high- T_c superconductivity, there are many variations of the *electronic* structure of Fe-based superconductors around the basic starting point of quasi-2D hole and electron pockets, which can have instabilities towards magnetism, orbital ordering and superconductivity tunable by external parameters such as doping and physical pressure. Precise experimental determinations of the electronic structure, and the Fermi surface in particular, give clues as to why a particular system orders, or superconducts, and provide tests for theoretical ideas. The experimental tools of high magnetic fields and high-resolution ARPES are therefore very useful for progress in the field.

In Chapter 4 I reported a partial determination of the Fermi surface of LiFeAs, observing de Haas-van Alphen frequencies associated with the electron bands. The effective masses were significantly renormalised compared to the predictions of DFT, but the absolute size of the pockets was comparable. I presented a comparison between the quantum oscillations and ARPES points of view - finding that they could be compatible. However, a recent report claiming to find low frequency hole pockets

which would appear to confirm the ARPES scenario was questioned, and therefore the question of the degree of agreement between quantum oscillations and ARPES remains open with regards to the hole Fermi surfaces of LiFeAs. Further quantum oscillations studies of LiFeAs would be valuable, however it is unlikely that the hole bands will be observed without a significant improvement in the crystal quality.

The work on FeSe in Chapters 5, 6 and 7 represents a complete study of the Fermi surface and electronic structure of FeSe. In quantum oscillations, low frequencies with moderate to large mass enhancements are observed and a novel argument was used to assign the frequencies to holes and electrons. However, quantum oscillations do not reveal the distortions of the Fermi surfaces from four-fold symmetric to two-fold symmetric elongated pockets which are observed in the ARPES studies. The joint analysis of ARPES and quantum oscillations is essential for a complete determination of the Fermi surface since there is an electron band which is not observed by ARPES but is observed by quantum oscillations. Moreover, the distortions of the electronic structure are not simply a response to a change in the lattice, but arise from an electronic instability, as indicated by the resistivity anisotropy measurements. Therefore, the structural transition T_s represents the temperature at which a non-zero orbital order parameter onsets, breaking the four-fold symmetry. The changes of the Fermi surface are particularly dramatic on the electron pockets and demonstrate that the low-temperature electronic state is orbitally ordered. However unlike any other iron-based superconductor, this state with strong symmetry-breaking in the electronic structure (with a corresponding small distortion of the lattice) persists to low temperature without the onset of magnetic ordering which reconstructs the Fermi surface.

These measurements have demonstrated the experimental fact that FeSe *is* different to other Fe-based superconductors, in several aspects. The question of *why* is

FeSe different is a difficult and currently highly controversial question. I would argue that this is one of the most important in the field right now, and is still open - but importantly, any attempt to explain the unusual properties of FeSe *must* start from a realistic electronic structure as described by these measurements, and not use DFT or models developed for other systems. My own attempt to shed some light on why FeSe does not magnetically order is presented in Appendix B.

Further studies are likely to focus on FeSe under pressure where the structural transition is suppressed before a magnetic phase is reached [108]. An alternative to applying physical pressure is to use a “chemical pressure” in the isovalent $\text{FeSe}_{1-x}\text{S}_x$ series; such studies are currently in progress in my group and others.

Finally in Chapter 8 I described unusual anomalies in high magnetic field measurements torque measurements, which arise from the magnetic degrees of freedom in a less well-known Fe-based superconductor, the 10-3-8 family. The data bear a close resemblance to the expected torque signal for a spin-flop transition, which in this case would not arise from ordered antiferromagnetic moments but rather from antiferromagnetic fluctuations.

I will conclude with a few speculations for the future of the field of superconductivity. It is a fairly safe bet that people will be arguing about the pseudogap in underdoped cuprates for many years to come, and that a new feature of the phase diagram will be discovered every few years for the next quarter-century. With regard to the Fe-based superconductors, I believe a saturation point of interest will be soon achieved, and that many researchers currently active in the field will look for new strongly-correlated bandwagons. Nevertheless, fundamental questions on the pairing mechanism rumble on. The big question is - when will theory reach a stage of being able to design new unconventional - or even conventional - high- T_c superconducting

materials? Most likely, the next family of unconventional superconductors will be discovered by chance, much like the 2008 discovery of iron-based superconductors by the Hosono group. The remarkable recent discovery of the onset of superconductivity of an apparently conventional nature at 190 K in hydrogen sulfide under extreme pressures [175] is likely to reinvigorate old ideas about high-temperature superconductivity arising from the high phonon frequencies naturally associated with hydrogen bonds, and thus the quest for the elixir of room-temperature superconductivity will go on.

Appendix A

Growth and characterisation of FeSe single crystals

In this Appendix I provide details of the crystal growth of FeSe. The FeSe samples used in this thesis came from two sources: the original crystals (used for pulsed field measurements) were grown by Thomas Wolf in Karlsruhe, with some growth details in Ref. [44]; however Amir Haghighirad and I also successfully grew FeSe single crystals of a similar high quality in Oxford. Here I will here present the details of the chemical vapour transport method used and some characterisation measurements of the resistivity, susceptibility and superconducting phase diagram which did not find a place in the main Chapters of the thesis.

A.1 Growths of FeSe in Literature

The tetragonal, superconducting β -FeSe phase is only one of many possible phases in the Fe-Se binary phase diagram [176] reproduced in Fig. A.1a, and importantly cannot be directly accessed from the liquid phase. Therefore, any attempt to grow FeSe in thermodynamic equilibrium will inevitably result in samples containing additional impurity phases, such as the hexagonal NiAs-type δ -FeSe [105]¹. Furthermore, the binary phase diagram appeared to suggest that only Fe-rich compositions (that is,

¹There has been some confusion in the literature about whether the tetragonal phase should be labelled α - or β - [105]; here we use the β - notation of the phase diagram of Okamoto [176] also adopted by the Karlsruhe group [44]

FeSe_{1-x} were possible [176], with some width of formation. Many of the experiments on FeSe were complicated by crystal growth problems, and therefore some attention was diverted to the $\text{Fe}(\text{Te}_{1-x}\text{Se}_{1-x})$ system where the tetragonal phase may be grown by conventional solid-state reactions at high Te content and superconductivity at up to 15 K may be found [31].

In order to avoid these complications, a low-temperature chemical vapour transport method was used first in the Vasiliev group in Moscow [177] and then by Thomas Wolf at Karlsruhe [44]; subsequently several groups have attained quality single crystals by this method, and it is claimed that the samples can be very close to stoichiometry [44]. Here we describe in detail the chemical vapour transport method used to grow our crystals in Oxford.

A.2 Chemical vapour transport growth of FeSe

Three batches of FeSe growth were attempted; here I will describe the method of the third and most successful growth.

Fe (99.9999 %) and Se (99.999 %) powders (Alfa Aesar) were measured out in a glove box in a molar ratio Fe:Se 1.1:1 (by weight, 1.1g Fe to 1.414g Se) and put into a quartz ampule. The transport agent was a eutectic mix of AlCl_3/KCl (ultra-dry, Alfa Aesar); the eutectic point is found for a ratio of 0.66:0.34 and the weights used were 6.21g AlCl_3 and 1.789g KCl . These chemicals are hygroscopic and therefore much care must be taken to keep them under a controlled atmosphere for the whole process. The powdered starting materials occupy approximately 50% of the volume of the ampule. The ampule containing all the chemicals is then evacuated (approximately 2×10^{-6} mbar) and sealed, and pre-reacted in a box furnace at 300°C for 2 hours.

The main part of the growth process occurs in a horizontal tube furnace shown schematically in Fig. A.1b, with independent temperature controls in two neighbouring blocks; the ampule is placed across these such that the temperature of each end

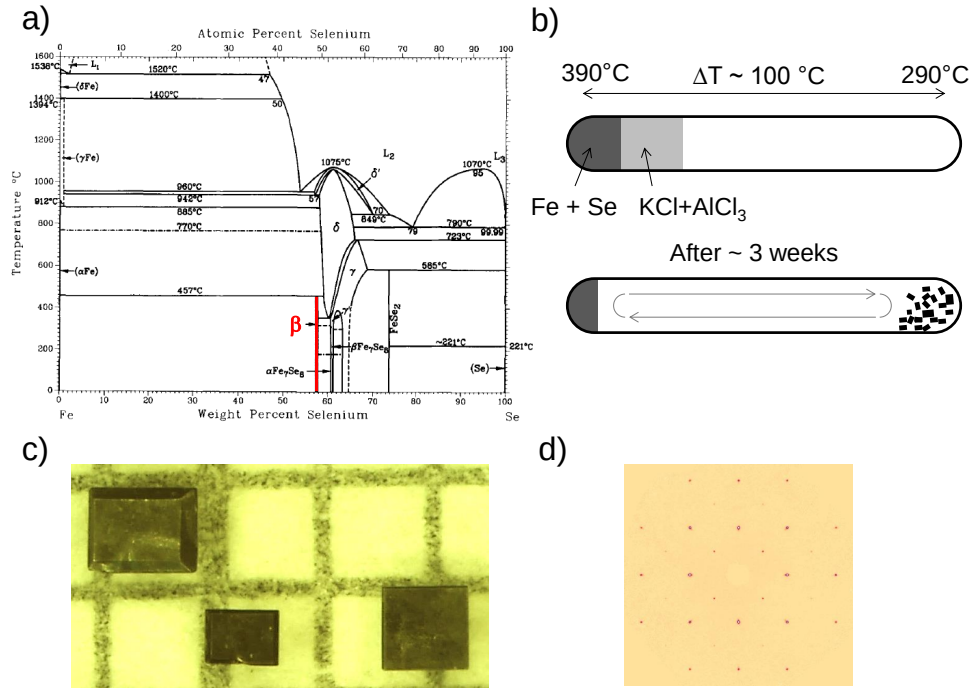


Figure A.1: a) Binary phase diagram of Fe-Se, from Ref. [176]. The desired β -FeSe phase is shown in red. b) Schematic of the chemical vapour transport method used to grow single crystals of FeSe. c) A selection of single crystals, showing particularly nice tetragonal facets. d) Projection of x-ray diffraction pattern in the $hk0$ plane from a small single crystal sample, showing four-fold symmetry without impurity phases.

of the ampule is controlled. Firstly, both ends are raised to 390°C together over 5 hours. When the temperature is stable and uniform, the empty end of the ampule is slowly cooled at $2^{\circ}\text{C}/\text{min}$ to 290°C and then held for 30 days. During this time, the Fe and Se are transported across the ampule by the flux and deposited at the cooler end in many single crystals in the β -FeSe phase. It was found that the growth was aided by tilting the furnace by about 10° from horizontal. This means that the flux which is in the liquid phase remains at the hotter end of the ampule rather than spreading all along the base of the ampule. The furnace is then turned off and the ampule removed and smashed open, and many black single crystals with tetragonal facets were harvested. Residual flux was removed with ethanol in an ultrasonic bath.

A.3 Characterisation of vapour-grown FeSe

The single crystals harvested from the batch typically grew with tetragonal facets as shown in Fig. A.1c, which is a good indication that the β -FeSe tetragonal phase has been stabilised by the vapour transport method. The natural sample edges typically corresponded to the a and b axes of the tetragonal $P4/nmm$ cell. The lattice parameters were confirmed by single crystal x-ray diffraction using the Supernova machine, as shown in Fig. A.1d. More than 10 crystals were measured with x-ray, all confirming the correct space group with no evidence for other phases. For the best sample, the single crystal refinement gives ² $a=3.7703(1)$ $c=5.5236(7)$; $z_{Se}=0.26691$ (here the site occupancy is fixed to 1:1) which are very similar to the results of Ref. [44].

I have performed many different experiments on β -FeSe single crystals; here I present some results which did not fit nicely into the earlier experimental chapters on FeSe.

A.3.1 Inter-plane resistivity

The structure of FeSe is layered and highly anisotropic, with only weak van der Waal's forces joining the FeSe layers, and from earlier in this thesis it is known that the Fermi surface is quasi-two dimensional. Therefore it is to be expected that the interlayer resistivity should vary strongly from the in-plane. In Fig. A.2 it can be seen that the room temperature inter-plane resistance is ~ 25 times larger, and furthermore the two $R(T)$ curves are rather different.³ At $T_{max}=238$ K (242 K in another sample, not shown) there is a crossover between positive and negative dR/dT . A similar feature has been observed in the 122 family at comparable temperatures, discussed at length in Ref. [179]. It is likely that details of the Fermi surface topology are relevant to understanding the inter-plane resistivity, in particular the c -axis warping, which reflects

²Thanks to Amir Haghighirad for performing the single-crystal refinement

³It has been noted [178] that one reason for anomalously high $a - c$ resistivity anisotropy can be cracks in the sample perpendicular to the c axis; without having done a systematic study it is impossible to comment whether this is relevant for these measurements on FeSe.

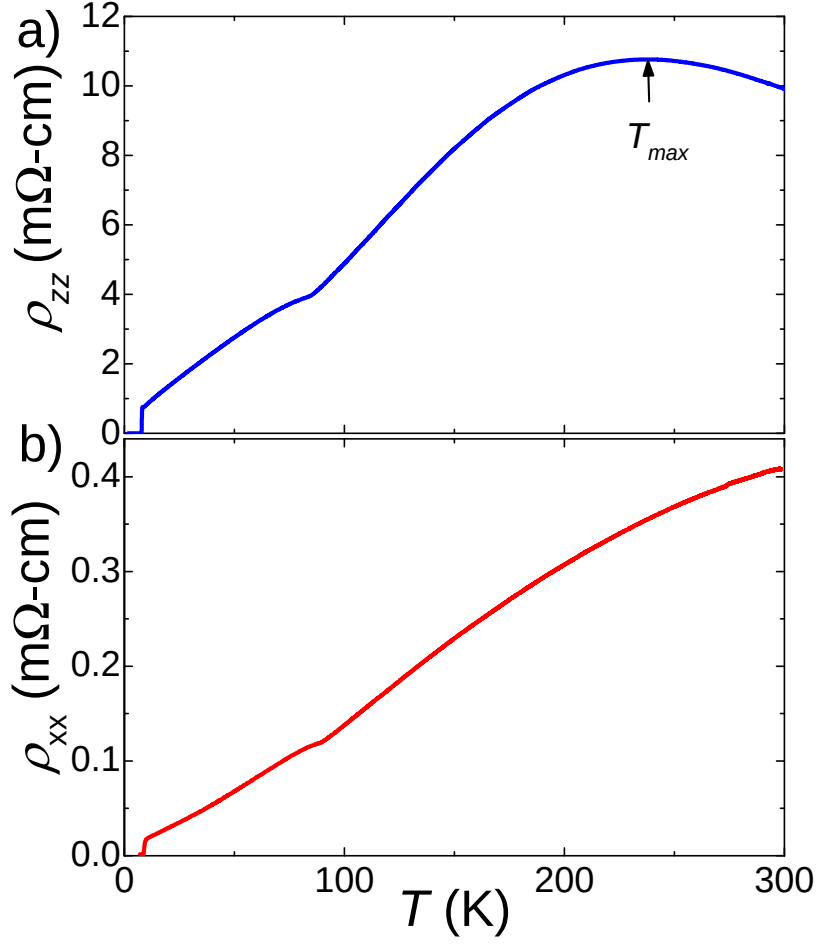


Figure A.2: a) Interplane resistivity of a sample of FeSe. b) In-plane resistivity of a different sample of FeSe for comparison.

inter-layer hopping processes. The Fermi surface of FeSe is quite two-dimensional with only a small degree of warping, compared to the 122 family which tend to have significant warping on at least some pockets. The anomaly at T_s is prominent in the interplane resistivity, possibly suggesting that there are some subtle changes of the c -axis warping through the structural transition along with the development of anisotropy in the ab plane as seen in ARPES.

A.3.2 Magnetic susceptibility of FeSe

Measurements of the magnetic susceptibility of a large single crystal of FeSe (sample mass 6.4mg) were performed in the Quantum Design MPMS. The sample was aligned

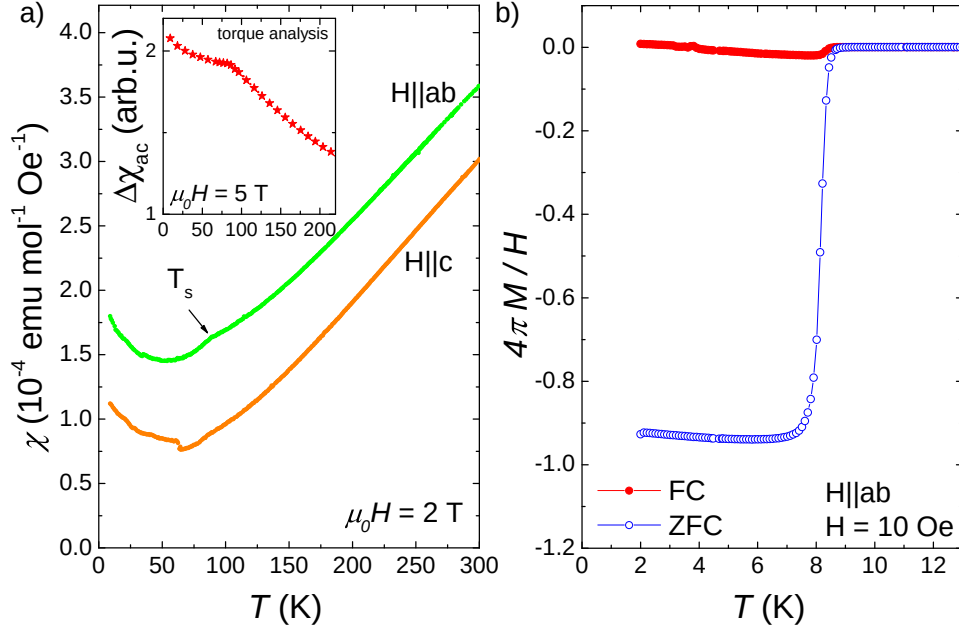


Figure A.3: a) High-temperature magnetic susceptibility of a large single crystal of FeSe, oriented with the c axis parallel and perpendicular to the applied field. Inset: Differential susceptibility as derived from magnetic torque measurements described in the text. b) Low-temperature susceptibility through the superconducting transition at 8.4 K in this sample. The screening is not equal to -1 since demagnetisation effects are not taken into account.

in two different orientations, with the applied field H applied parallel and perpendicular to the c axis of the sample. There are two different regimes to consider - above the superconducting transition the signal is small and positive (paramagnetic) and a large field (here 2 T) must be applied in order to obtain an acceptable signal/noise level, however below the transition there is a massive diamagnetism due to flux expulsion. In Fig. A.3a) the high temperature susceptibility is plotted. Above T_s , the magnetic susceptibility is linearly proportional to temperature. This is consistent with other Fe-based superconductors, e.g. BaFe_2As_2 where the linearity was confirmed even up to 700 K [180] and appears to be a universal signature in Fe-based superconductors (and also some cuprates).

An anomaly at T_s is observed weakly for $H \parallel ab$ and is barely observed in $H \parallel c$ (note that the jump at 65 K is an unexplained experimental glitch). However, this anomaly

is very significantly weakened compared to BaFe_2As_2 where the structural/magnetic transition is accompanied by a prominent drop in susceptibility [180], as a result of the fact that there is no accompanying long-range magnetic order.

The anisotropy of susceptibility may be sensitively probed by measurements of magnetic torque; as discussed elsewhere in this thesis the magnetic torque in an anisotropic paramagnet is proportional to $|\chi_a - \chi_c|B^2 \sin 2\theta$. In a full rotation of angle in an applied field of 5 T at constant temperature, the amplitude of the $\sim \sin 2\theta$ angular dependence is therefore a measurement of the anisotropy of susceptibility, and is shown for a single crystal of FeSe in the inset of Fig. A.3a).⁴ The clear anomaly observed at the structural transition reflects qualitatively the fact that the T_s anomaly in susceptibility is more prominent in $H||ab$ compared to $H||c$, and therefore clear in the subtraction.

A.4 Superconducting Phase Diagram of FeSe

The superconducting phase diagram of FeSe has attracted some controversy, particularly after the recent claim by in Ref. [129] of the existence of a so-called B-phase near H_{irr} for $B \parallel c$ based on thermal conductivity measurements. In the measurements presented in this thesis I have not found any evidence for such a phase, and so here I perform a more conventional analysis of the superconducting phase diagram.

In Fig. A.4a I present the temperature-dependence of the critical fields in FeSe as determined by resistivity measurements. When determining B_{c2} from resistivity measurements, there are several choices for the criterion used to determine the boundary of the superconducting phase; many reports use a 50% criterion however in this thesis I have used an $R = 0$ criterion largely because this is likely to correspond closely to the irreversibility criterion from the closure of the hysteresis loops in magnetic torque, as also discussed in Chapter 8. The obtained critical fields for an in-plane magnetic

⁴This measurement was repeated by David MacDougall and discussed further in his MPhys thesis (Oxford Physics, 2015).

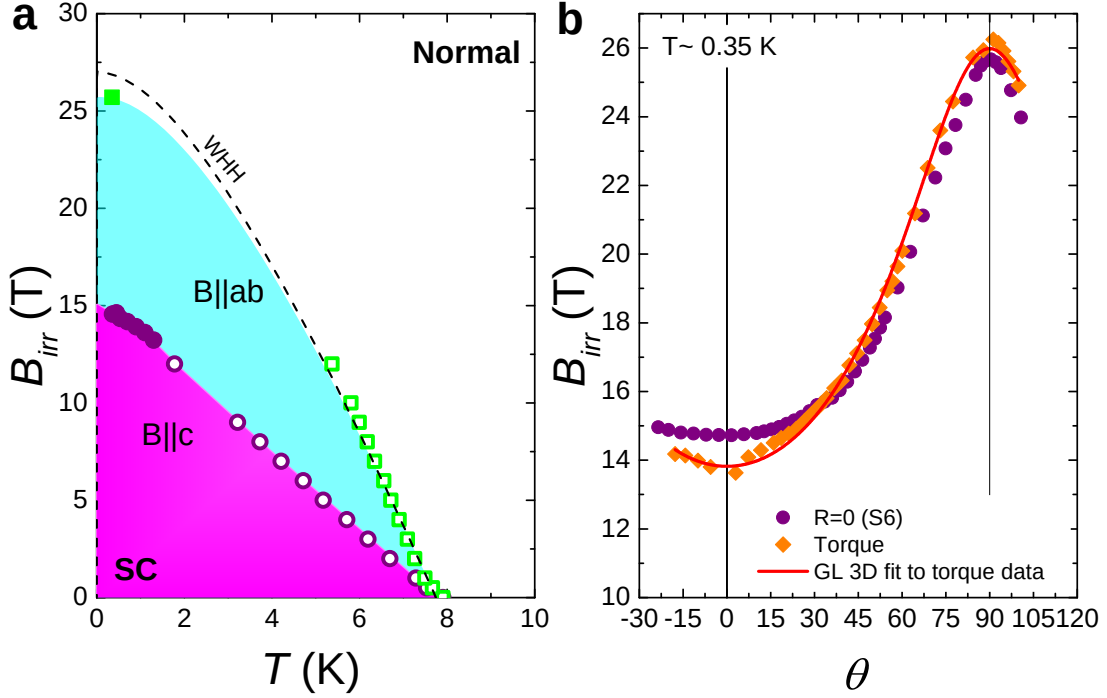


Figure A.4: a) Irreversibility field as a function of temperature for FeSe. Open symbols represent the transition to $R = 0$ in $R(T)$ measurements taken on a sample S7 in the PPMS in Oxford; closed symbols are taken from $R(B)$ measurements at HFML, Nijmegen. Dashed line is the WHH model applied to the $B || ab$ data. b) Irreversibility field as a function of angle for both torque and resistivity at $T = 0.35$ K.

field ($B || ab$) approximately follow the well-known single-band WHH model [168] assuming only orbital pair-breaking effects [181]. According to the WHH model, the temperature-dependence of the critical field down to $T = 0$ is determined solely by the T_c and $dH_{c2}/dT|_{T=T_c}$. The upper critical field may sometimes be suppressed by so-called Pauli-limiting effects, when the superconducting condensation energy is exceeded by the Zeeman spin-polarised energy [181]. Taking a maximum gap value of 2.2 meV from STM measurements [182] (which is similar to the 1.9 meV value calculated from ARPES on the hole band at 5.5 K in Chapter 6) the Pauli-limiting field is $\mu_0 H^P(0) = \Delta/\sqrt{2}\mu_B = 26.9$ T, very similar to both the experimental value of $B_{ab}^{irr}(0.35 \text{ K}) = 25.7$ T and also the extrapolated $\mu_0 H_{c2}^{orb} = 27.1$ T from the orbital-only WHH model. This suggests that paramagnetic-limiting effects are relevant in

FeSe for $B \parallel ab$ at low temperatures where the actual critical field undershoots the WHH prediction, as shown in Fig. A.4a, as was also found in [74]. In order to include both orbital and spin (Pauli) limiting effects a more detailed version of the WHH formula may be used, but these models are generally over-parametrised and are not attempted here. For similar reasons the data for $B \parallel c$ do not fit well to the simple orbital-only WHH model and the phase boundary is simply a guide to the eye. It is worth noting that the critical fields in both orientations for FeSe are within ≈ 1 T of those for LiFeAs, despite a large difference in T_c (8 K vs 18 K).

A.4.1 Anisotropy of H_{irr}

The anisotropy of the electronic structure is reflected in the anisotropy of the superconducting critical fields.

A commonly-used model (e.g. Ref. [183]) for fitting the angular dependence of the critical field is the 3D Ginzburg-Landau formula [181]:

$$H^{c2}(\theta) = H_c^{c2}(\cos^2 \theta + \gamma^{-2} \sin^2 \theta)^{-1/2} \quad (\text{A.1})$$

where θ is the angle between the applied field and the c axis, and $\gamma = H_{ab}^{c2}/H_c^{c2}$. At $T \approx 0.35$ K, the irreversibility field extracted from torque data (defined by the field at which the subtraction of the up and down sweeps drops below a small value) fits well to this formula, as shown by the solid line in Fig. A.4, giving a value of $\gamma(0.35 \text{ K}) = 1.88$. This can be compared to the ratio slopes of $dH^{c2}/dT|_{T=T_c}$; for $H \parallel ab$ and $H \parallel c$ these are 5.01 T/K and 1.8361 T/K respectively, giving $\gamma(T \rightarrow T_c) = 2.73$. Therefore FeSe has moderately high anisotropy of superconducting properties with greater anisotropy for $T \rightarrow T_c$, comparable to both LiFeAs and 1111 systems [181] although much less than the “1038” material discussed in Chapter 8.

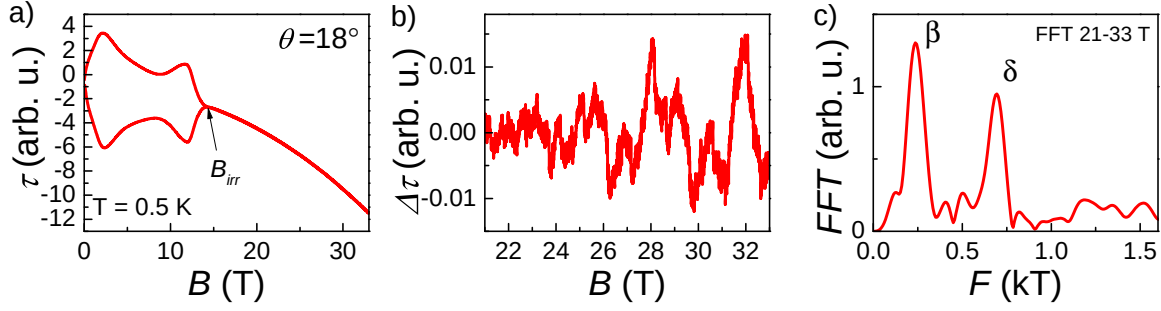


Figure A.5: a) Raw torque data at $\theta=18^\circ$. The position of the irreversibility field at 14.4 T is marked. b) Oscillatory contribution of magnetic torque, obtained by subtracting a polynomial background. The de Haas-van Alphen oscillatory signal is less than 1% of the background signal, and therefore appears quite noisy, and digitization is also unavoidable. c) Fourier transform of the oscillatory torque, identifying the β and δ frequencies also observed in the Shubnikov-de Haas measurements.

A.4.2 Clean-limit superconductivity in FeSe

The coherence lengths at $T = 0.35$ K extracted from the critical fields are $\epsilon_{ab}=3.578$ nm and $\epsilon_c=4.75$ nm. This should be compared to the mean free path, which is estimated as follows. At low temperatures, the electron / hole mobilities are on the order of $\mu \sim 1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (at 20 K). This can be equated to a scattering time via $\mu = \frac{q}{m^*} \tau$ giving $\tau_s \sim 3.4$ ps (assuming $m^* = 4$ from quantum oscillations) which is in turn related to a scattering length by taking a typical Fermi velocity from ARPES giving $l \sim 250$ nm (assuming a $v_F = 500 \text{ meV } \text{\AA}$). Since we have $l \gg \epsilon$, FeSe should be considered as a clean-limit superconductor.

A.5 Observation of quantum oscillations in magnetic torque in FeSe

One question the reader may have is why quantum oscillations were reported in magnetic torque in LiFeAs in Chapter 4 but measured in magnetoresistance in FeSe in Chapter 5. One hand-waving explanation is that the magnetoresistance (and indeed Hall effect) is large in FeSe since it is a compensated system with low carrier densities but high mobility, whereas the larger (by a factor of ~ 5) pockets in LiFeAs would give

rise to a larger signal in magnetic torque. In fact, quantum oscillations in magnetic torque were observed in one sample of FeSe in DC fields to 33 T as shown in Fig. A.5, but only the β and δ frequencies are observed and only for a limited range of angles; it seems that magnetoresistance is the more effective technique in this case.

It is also worth noting that quantum oscillations in FeSe have now also been observed with the tunnel-diode oscillator method [124], and it is good to observe a general agreement between the different techniques although there are some disparities of effective masses.

Appendix B

Why FeSe is not magnetic - an idea

In this Appendix I present some speculate ideas concerning the absence of magnetism in FeSe, based on cartoons and qualitative arguments without numerical investigations. However it can explain the mystery of the absence of magnetism in FeSe and the phase diagram under pressure. This short overview may form the basis for more detailed calculations in the future.

I will start with a toy model in the one-Fe unit cell for simplicity since it is conceptually more straightforward in the 1-Fe cell. In Fig. [B.1a](#) I draw a typical Fermi surface slice for a stoichiometric Fe-based superconductors. This includes the normal designations of orbital characters for Fe-based superconductors and consists of three orbitals: d_{xz} , d_{yz} and d_{xy} . I ignore the fact that in some systems there is d_{z^2} and $d_{x^2-y^2}$ orbital character on the Fermi surface. I will also ignore the d_{xy} hole band for now; this is certainly important in some systems, but I will not consider it for now and comment later on how it possibly comes in to these ideas. It is not present in FeSe anyway.

Notice that the two hole bands, which I will label α and β for the outer and inner bands respectively, have orbital characters opposite to each other for any given direction in k -space; furthermore they typically will have similar sizes and are circular, in comparison to the electron pockets which are elliptical in the 1-Fe unit cell. In

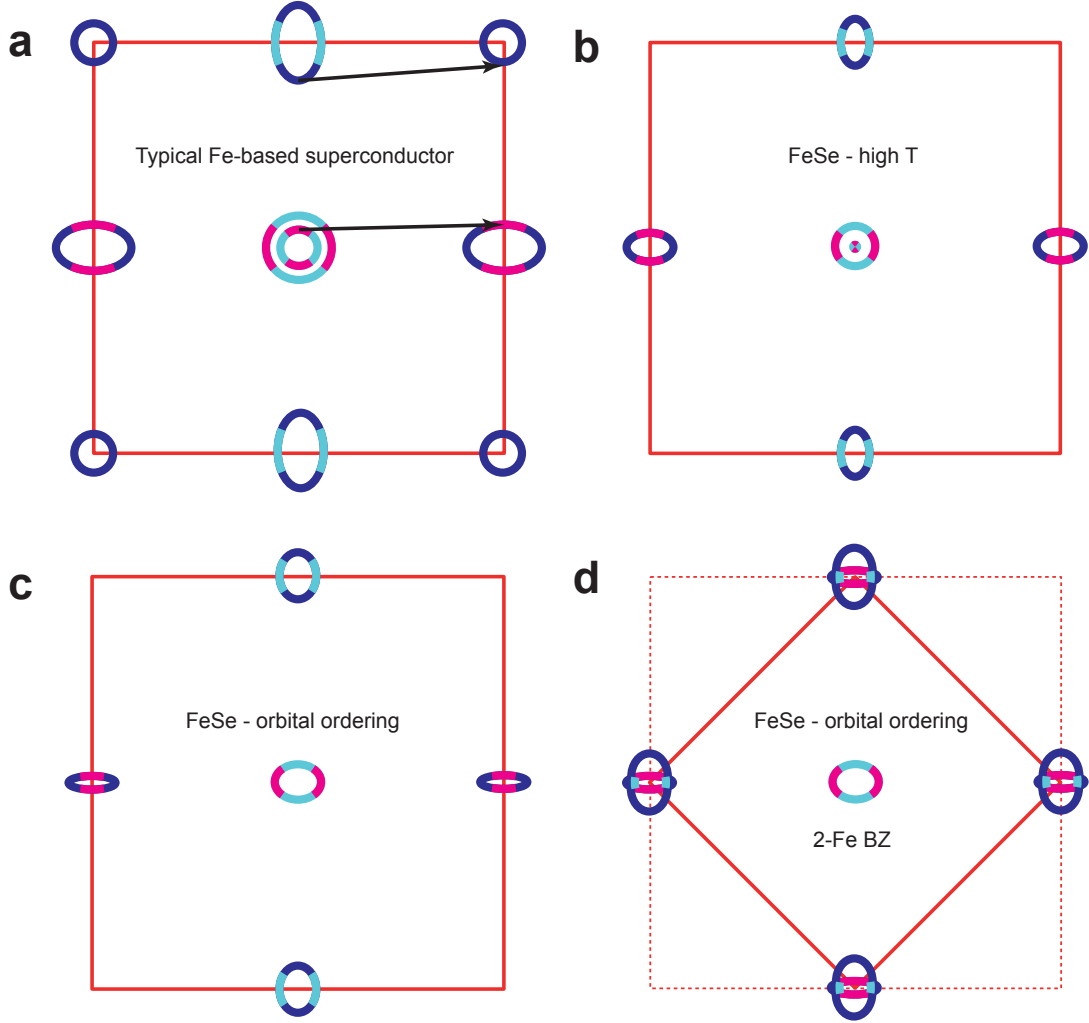


Figure B.1: a) A typical Fermi surface of an Fe-based superconductor, drawn in the 1-Fe Brillouin Zone. Black arrows represent possible nesting between segments of Fermi surface with the same orbital character. b) FeSe has very small pockets; neglecting the tiny inner hole pocket there are no possible arrows to draw. c) Fermi surface of FeSe in the 1-Fe Brillouin zone, after orbital ordering distorts the Fermi surface. d) Orbitally-ordered FeSe in the 2-Fe BZ; the electron pockets will hybridize slightly.

general, both pockets will have a good but not perfect degree of *geometrical* nesting but only one of them nests with matching orbital characters, the inner β pocket.

The outer hole pocket α has predominantly inter-orbital (U') nesting and the inner hole pocket β has predominantly intra-orbital nesting (U). Noting the different orbital characters for the two considered hole bands, I treat the hole bands independently, and more specifically make the assumption that if it is nesting from the

inner β pocket which is the leading instability, the system will magnetically order, but if the leading instability arises from the outer hole pocket this favours an orbital ordering which distorts the Fermi surface; the magnetic instability from the inner β pocket may still occur at a lower temperature. Intuitively, the orbital characters must make a difference to the inter-band interactions - i.e. the inter-*band* interactions are principally determined by the inter- or intra-*orbital* interactions since these are the highest energy scale interactions in the system.

Usually in Fe-based superconductors you have both pockets, and therefore *both* inter- and intra-orbital interactions. Now, in fact the intra-orbital repulsions are intrinsically a bit stronger (since $U > U'$), and everyone agrees that this favours magnetism, and over a significant part of the phase diagrams the magnetic state is stabilised. I also now remember that there is a d_{xy} hole pocket in some, but not all Fe-based superconductors. Exactly how this complicates the issue, I do not know. The point is, that so long as you have both α and β pockets there are necessarily *both* intra- and inter-orbital interactions which must be considered, that in general they may be of similar magnitude, and that details of the Fermi surface such as doping and size of pockets could favour one instability over the other.

So what about FeSe? FeSe is a special case because the pockets are so small, that the inner β pocket doesn't exist (in fact, it probably is a tiny 3D pocket around Z at high temperature as indicated in Fig. B.1b but that may be ignored for now). Usually, you have to have both since the pockets are split only by spin-orbit coupling at the Γ point, so if one crosses the other will. Every theoretical model I have seen has both of these pockets. However in FeSe under ambient pressure the pockets are so small that the splitting by spin-orbit coupling is enough to put the α pocket above the Fermi level and the β pocket below the Fermi level (at least at low temperature

this is true). Furthermore there is certainly no d_{xy} hole band in FeSe. *Then, the only instability that can happen comes from inter-orbital interactions which gives orbital ordering; magnetism does not occur since there are no possible well-nested segments with the same orbital character.* An alternative perspective is that while $U > U'$ is unphysical in general, in FeSe you do actually have far more U' interactions than U interactions over the Fermi surface in contrast to pretty much all other iron based superconductors, and it is known that at the RPA / mean field level for $U' > U$ you can get orbital ordering (see Ref. [184] - where the Fermi surface has both hole bands).

These ideas naturally explain the absence of spin-fluctuations in NMR data above T_s and are consistent with the idea that the structural transition is not magnetically-driven. This does not kill the spin-nematic scenario - that works pretty well in every other case, it is just that the Fermi surface of FeSe has a different instability to the other Fe-based superconductors as a result of the geometry of the hole pockets. In 122s and 111s there may be a narrow doping region which is nematic but not magnetic, but this is always near optimal doping. In fact, if the nematicity in FeSe has a different origin to the spin-driven nematicity in e.g. 122 system, this would naturally explain why stoichiometric FeSe has a low- T_c and is not near optimal doping. It could even be consistent with having spin-fluctuation mediated $s_{\pm}$ superconductivity - there are spin-fluctuations in NMR at low temperature after all, and a recent report of the neutron spin resonance in the SC state. However, in that case the superconductivity would have a different origin to the structural transition, explaining the lack of coupling between superconductivity and the orthorhombic distortion (Böhmer 2013).

What about FeSe under pressure? It seems that under pressure, first the T_s of FeSe is suppressed, and then there is probably an onset of a magnetic phase [115, 108], completely different to any other phase diagram in the Fe-based supercon-

ductors. Another fact from our preliminary data (Coldea/Shibauchi) is that the sizes of the α hole pockets increase by about 10 % in $\text{FeSe}_{0.91}\text{S}_{0.09}$ ($T_s \sim 75$ K), which is understood to mimic a small pressure effect (maybe ~ 5 kbar). Therefore, it does not seem unreasonable to suggest that as the α pocket expands, the β pocket will also exist in FeSe under pressure - and then we *can* have repulsive intra-orbital interactions which stabilise magnetism at higher pressures. At lower pressures as the β pocket emerges it competes with the orbital ordering and suppresses T_s . I also note that early NMR data suggested that the spin fluctuations increase under small applied pressure [114] which would correlate with increasing interactions tending towards magnetism, and the corresponding increase in T_c may also be explained in a spin-fluctuation pairing scenario.

Therefore FeSe really is different. The reason that the phase diagram under pressure looks so different to other Fe-based superconducting phase diagrams can be simply explained by the pretty unusual starting point which the high-temperature band structure of FeSe is, having (basically) only the α hole band at ambient pressure. From this Fermi surface, orbital ordering naturally drops out due to the usually sub-leading inter-orbital U' interactions as a result of the absence of sections which nest with the same orbital character. However under pressure as the β hole band emerges, intra-orbital U interactions also can occur, leading to magnetism at high pressures.

At the moment I have not explored these ideas numerically, however I am hoping to perform susceptibility calculations based on a 3-orbital model in the near future.

Appendix C

Detection of Ir impurities in $\text{Bi}_2\text{Ir}_2\text{O}_7$ by spurious quantum oscillations

In this Appendix I present the result of some work on $\text{Bi}_2\text{Ir}_2\text{O}_7$ which came to an unfortunate end when it was discovered that the observed quantum oscillations were consistent with pure Ir and therefore we unlikely to be intrinsic. Therefore, in this appendix I present the experimental results as a warning to any future experimentalists interested in $\text{Bi}_2\text{Ir}_2\text{O}_7$!

C.1 Introduction

Systems in which Ir $5d$ orbitals dominate the physical properties have gained much attention in the last few years, as a playground in which the bandwidth, correlation strength and spin-orbit interaction may be of comparable order of magnitude [185, 186], leading to the possibility of realising exotic phases. $\text{Bi}_2\text{Ir}_2\text{O}_7$, a metallic pyrochlore iridate, has attracted some attention [187, 188, 189, 190] as a metallic analogue of the $\text{R}_2\text{Ir}_2\text{O}_7$ series, in which a metal-insulator transition occurs; the metal-insulator transition is likely to be related to magnetic interactions favouring the “all-in-all-out” magnetic ground state and is tuned by the bandwidth of Ir t_{2g} orbitals via the size of the R atom, where R is a rare earth element (Yttrium, or a

Lanthanide) [191]. Our group performed multiple high magnetic field experiments on this material, finding quantum oscillations in magnetic torque, with frequencies generally similar to those predicted by density function theory. Unfortunately, we later discovered that the frequencies and masses were compatible with pure Ir, and that therefore the most likely explanation was that the quantum oscillations were not intrinsic to $\text{Bi}_2\text{Ir}_2\text{O}_7$, but rather that a small amount of Ir inclusions in the sample was giving rise to the oscillations.¹

C.2 High-field torque magnetometry measurements of $\text{Bi}_2\text{Ir}_2\text{O}_7$

DHvA measurements were performed with small single crystals using the microcantilever torque technique. Quantum oscillations were observed in measurements in Oxford (up to 18 T) and also at HFML, Nijmegen (up to 33 T) in several different samples with good agreement; here we focus on one high-field data set.

The general form of the magnetic torque signal is complex and can be strongly temperature-dependent, as can be seen in Fig. C.1a. Magnetic torque depends on both the temperature-dependent magnetic susceptibility and the anisotropies of the system; in a cubic system the symmetry-allowed anisotropy terms lead to a complex form for the torque even in the simplest paramagnetic case - in contrast to the simple $\tau \sim B^2 \sin 2\theta$ expected in layered systems with uniaxial anisotropy. Therefore we restrict our analysis to the de Haas-van Alphen oscillatory contribution which appears on top of this background signal, which appears at fields above ~ 12 T, except to note that the absence of any hysteresis suggests there is no superconductivity down to 0.35 K.

Above ~ 12 T, quantum oscillations may be resolved above the background magnetic torque, as shown in Fig. C.1(a). Background subtraction and standard Fourier

¹Unfortunately we came to this conclusion after presenting the results at the APS March meeting (A. I. Coldea, 2014)

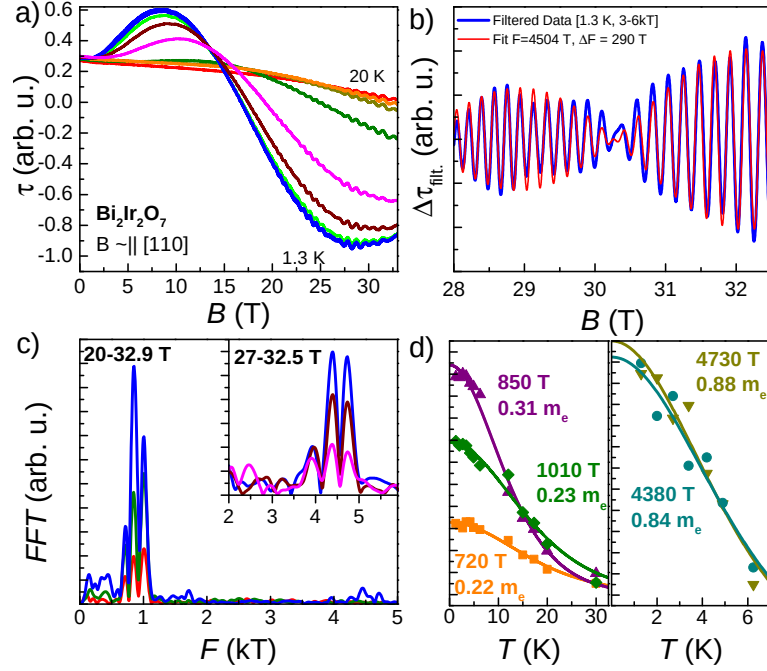


Figure C.1: a) Temperature-dependent magnetic torque. The background is strongly temperature-dependent, but quantum oscillations may readily be observed in high fields. b) As well as the low frequencies clearly visible in the raw torque, after filtering out low frequencies, further frequencies are observed around 4500 T. Red line is a fit with two close dhva frequencies. c) Fourier analysis determining the frequency of oscillations. There are high-frequencies at ~ 4500 T that are much weaker and have a split-peak structure, which is better observed by restricting the field window to only the highest fields, as in the inset. d) Temperature dependence of the amplitude of oscillations, from which fits to the Lifshitz-Kosevich formula reveal the effective masses.

transforms techniques are used to resolve the oscillations. We find that the frequency spectrum is dominated by a set of low frequencies, which cause the dominant beating oscillatory pattern in Fig. C.1. However, there are additional weaker high-frequency oscillations, which are better resolved by restricting the field window for Fourier analysis to the highest available and filtering out the low frequencies, as shown in C.1(b), where a Fourier window of 3-6 kT is taken. This high frequency data can be fitted by two closely-spaced dhva frequencies, centered around 4500 T. The relative weakness of the high frequency oscillations can be understood since it corresponds to an almost spherical Fermi surface, and it is well known that a perfect sphere would give no

	F (T)	m_b (m_e)		F (T)	m_{eff} (m_e)
DFT: [011]	4581.7	-1.22	Sample A	720	0.22(1)
	1152.8	2.47		850	0.31(1)
DFT: [001]	4725.4	-1.37		1010	0.23(1)
				4380	0.84 (7)
	790.1	1.87		4730	0.88 (7)

Table C.1: DHvA frequencies and effective masses as determined from theory and experiment. In our experiments, we always observe a split peak from spin-splitting effects, although the calculations predict only one frequency. Frequencies and masses from the Fourier transforms shown in Fig. C.1 taken from 20-32.8 T (27-32.8 T for the high frequencies).

dhva signature in magnetic torque. However, both the high and low frequencies have a split-peak structure. By fitting the temperature-dependence of the amplitude of oscillation to the standard Lifshitz-Kosevich formula, we are able to obtain effective masses for the frequencies, as summarized in table C.1.

C.3 Calculated Fermi surface and dhva orbits of $\text{Bi}_2\text{Ir}_2\text{O}_7$

In order to try to understand the origin of the observed dhva frequencies, we performed bandstructure calculations in WIEN2k [78] incorporating spin-orbit coupling, from which we derived dhva frequencies and band masses, noted in Table. C.1.

The presented calculations on $\text{Bi}_2\text{Ir}_2\text{O}_7$ are performed in the paramagnetic phase, yielding a metallic ground state. In other pyrochlore iridates such as $\text{Y}_2\text{Ir}_2\text{O}_7$, a modest $U > 1.5$ eV is required to reproduce the insulating ground state [185] with a non-collinear ‘all-in-all-out’ magnetic order. Due to the interest in the possible metallic, weakly magnetic ground state in $\text{Bi}_2\text{Ir}_2\text{O}_7$, we performed calculations in WIENncm², allowing for the all-in-all-out magnetic structure which is suggested to be the ground state in e.g. $\text{Y}_2\text{Ir}_2\text{O}_7$ [185]. While for $\text{Y}_2\text{Ir}_2\text{O}_7$ the insulating ‘all-in-all-out’ magnetic order was obtained as the ground state, in the case of $\text{Bi}_2\text{Ir}_2\text{O}_7$, we

²WIENncm is a modified version of Wien2k which allows for non-collinear magnetism.

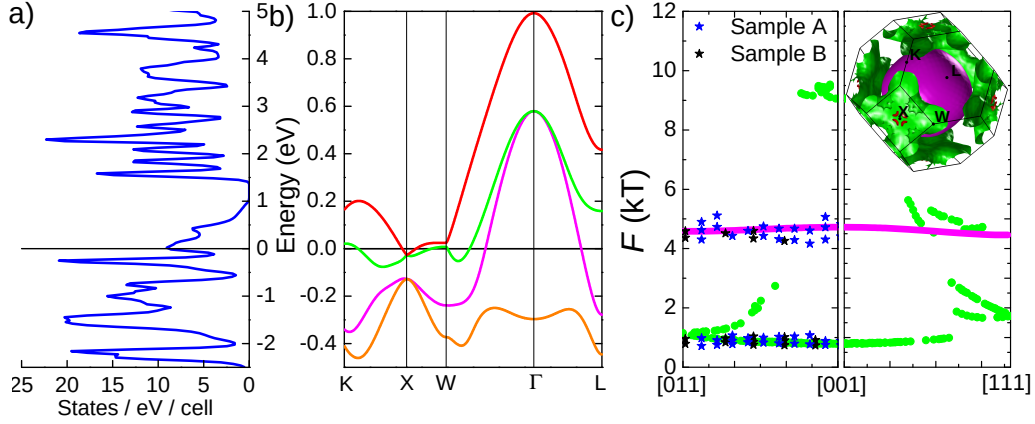


Figure C.2: a) Bi₂Ir₂O₇ Density of States (DOS) calculation, showing the Fermi level located at a peak in the DOS. b) Band dispersion calculated along high-symmetry lines. c) GGA+SO (non-magnetic) predictions of the de Haas-van Alphen frequencies with experimentally determined frequencies. The predicted very low frequencies from a third band crossing near *X* are not marked. The apparent agreement between theory and experiment is a complete coincidence since the oscillations are not intrinsic to Bi₂Ir₂O₇. Inset: Calculated Fermi surface. Calculations were performed in WIEN2k.

were not able to converge a magnetic ground state (converged moments $< 0.0001 \mu_B$) even when adding unphysically high *U* (up to 5 eV) on the Ir *d* orbitals. This was also observed in the calculations of Ref. [187].

As shown in Fig. C.2c, there is a decent agreement between the experimental frequencies and the predictions of dhva oscillations³ from the calculated Fermi surface shown in the inset of Fig. C.2c. It seems, however, that this is an unfortunate coincidence and the dhva oscillations are not intrinsic to Bi₂Ir₂O₇. One crucial problem in the comparison of the calculation and the experiment however is the fact that the experimental effective masses for the lower (~ 1000 T) frequencies are significantly smaller than the predictions from DFT (see Table. C.1). While mass *enhancements* are common in strongly correlated systems, the much smaller effective mass is impossible to justify, but is consistent with the interpretation presented below that the oscillations are due to Ir inclusions.

³Calculated using the ‘dhva’ script by Daniel Guterding

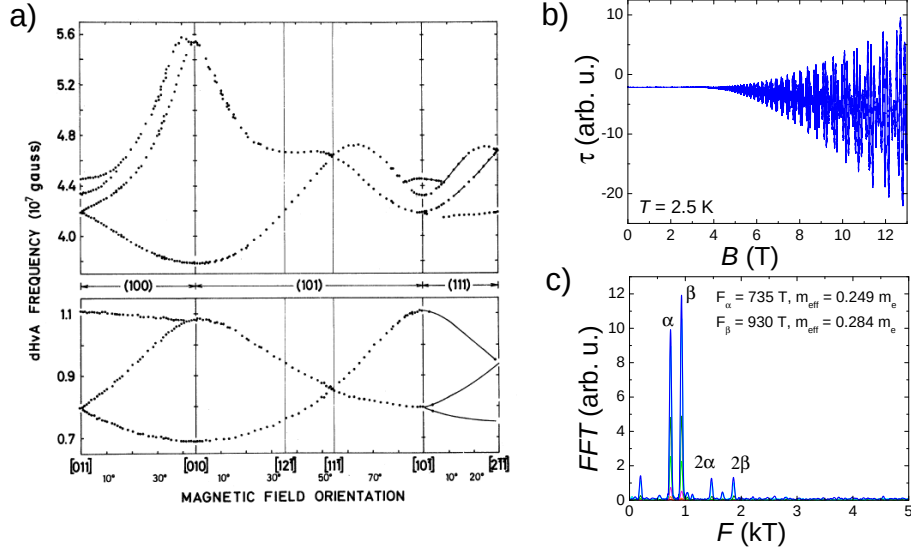


Figure C.3: a) Angular dependence of quantum oscillation frequencies in pure Ir, reproduced from Ref. [192]. b) Experimental torque measurements on a single crystal of Ir, showing a very strong signal arising from two low frequencies labelled α and β shown in the Fourier transform in c); the higher frequencies around 4500 T reported in Ref. [192] and seen at high field in our $\text{Bi}_2\text{Ir}_2\text{O}_7$ samples are not observed in this orientation.

C.4 Literature reports of quantum oscillations in Ir

A comprehensive study of the de Haas-van Alphen effect in Iridium was performed by Grodski and Dixon[192]. Not only do the frequencies match well with our experimental observations, but the experimental masses are also in agreement. We are therefore forced to conclude that this is the true origin of the de Haas-van Alphen oscillations. Note that we have no idea of the alignment of the Ir inclusions in the $\text{Bi}_2\text{Ir}_2\text{O}_7$ - and it is likely that there could be more than one orientation of Ir inclusion in any given sample, perhaps reflected in the multi-peak structure of the Fourier analysis. For comparison, we also performed magnetic torque measurements on a crystal of Ir ⁴, finding very strong oscillations at even low magnetic fields, so it is not surprising that

⁴Ir crystal provided by S. K. Choi. The sample of Ir was formed as a by-product of a growth attempt of a tertiary oxide material and is unlikely to be of high purity, nevertheless strong oscillations are observed in torque.

a small volume fraction of Ir impurities might give rise to a measurable oscillatory signal.

C.5 Conclusions

It is notable that the clear dHvA signal is observed despite the very small residual resistivity ratio (RRR) observed in transport measurements, which usually is indicative of strong scattering, and would be expected to severely dampen the dHvA signal, nevertheless we observe it in modest fields. Additionally, Shubnikov-de Haas oscillations have not been observed in magnetotransport. Both of these should be taken as pointers that the oscillations may not be intrinsic to $\text{Bi}_2\text{Ir}_2\text{O}_7$.

In conclusion, we have carried out dhva measurements on “single crystal” samples of $\text{Bi}_2\text{Ir}_2\text{O}_7$. The dhva signal comprises low frequencies at 700-1100 T and high frequencies centered around 4500 T. While there is an apparent agreement between the calculated and experimental frequencies, unfortunately this appears to be a coincidence, and the oscillations may be attributed to a fraction of pure Ir in the samples. Crystal quality is therefore likely to be an important issue in analysing other unusual properties of $\text{Bi}_2\text{Ir}_2\text{O}_7$.

Appendix D

Ferromagnetism in n -type Bi_2Te_3

One of the first projects I was involved with during my PhD was work on doped topological insulators. Since this work is not really related to the other studies presented in this thesis, here I will only write the motivation and abstract of my contribution to the study, which was a collaborative effort with the group of Thorsten Hesjedal and others and combined a number of different experimental techniques. The study was eventually published as Watson *et. al.*, New Journal of Physics **15** (2013) 103016.

D.1 Motivation

Shortly after the theoretical description of topological insulators was formalised [193], the predicted symmetry-protected surface state was found in Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 in ARPES experiments [194], where it was also shown theoretically in DFT calculations that these systems (amongst now many identified systems) have topologically non-trivial band structure. Physically, it is the large spin-orbit coupling in heavy element systems combined with narrow band gaps which make it possible to have a “band inversion”. Topological insulators have time-reversal symmetry, but one idea was to put magnetic dopants on the surface [195] or in the bulk in order to break time-reversal symmetry and induce a gap in the surface states. Therefore, there is interest in whether or not a bulk magnetic state may be induced in topological insulating materials. Within this field of magnetically-doped topological insulators, the observation

of the Quantum Anomalous Hall Effect in thin film samples of $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{1.85}\text{Te}_3$ had a large impact [196] due to the possibility of developing quantum electronic and spintronic devices based on the effect. Our study investigated the magnetic state in single crystals of Mn-doped Bi_2Te_3 and had rather less impact, but this project was carried on into thin film growths with various transition metal dopants by the Hesjedal group¹.

D.2 Abstract

In Watson *et. al.*, we presented a systematic study of the structural, magnetic and magnetotransport properties of Mn-doped Bi_2Te_3 single crystals using complimentary experimental techniques. These materials exhibit a ferromagnetic phase that is very sensitive to the structural details, with T_C varying between 9 and 13 K (bulk values) and a saturation moment that reaches $4.4(5) \mu_B$ per Mn in the ordered phase. The electrical transport data show an anomaly around T_C that is easily suppressed by an applied magnetic field due to the spin-dependent scattering in relation to the alignment of the Mn magnetic moments. Hall measurements on different crystals established that these systems are *n*-doped with carrier concentrations of $\sim 0.5\text{--}3.0 \times 10^{20} \text{ cm}^{-3}$ and a small anomalous Hall effect is detected. These measurements suggest that bulk magnetism is not restricted to the *p*-type Mn-doped Bi_2Te_3 samples previously reported. Furthermore, our magnetic torque measurements in fields up to 33 T reveal an easy axis magnetic anisotropy perpendicular to the *ab*-plane. In the ferromagnetic state the easy direction of magnetization is along the *c*-axis, in agreement with bulk magnetization measurements. This could lead to gap opening at the Dirac point, providing a means to control the surface electric transport of this magnetically doped topological insulator, which is of great importance for applications.

¹See e.g. [197] or the thesis of Liam Collins-Macintyre, Oxford Physics, 2015

List of Publications

- M. D. Watson, T. K. Kim, A. A. Haghighirad, N. R. Davies, A. McCollam, A. Narayanan, S. F. Blake, Y. L. Chen, S. Ghannadzadeh, A. J. Schofield, M. Hoesch, C. Meingast, T. Wolf, and A. I. Coldea, *Emergence of the nematic electronic state in FeSe*, Phys. Rev. B **91**, 155106 (2015).
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- A. Narayanan, M. D. Watson, S. F. Blake, Y. L. Chen, D. Prabhakaran, B. Yan, N. Bruyant, L. Drigo, I. I. Mazin, C. Felser, T. Kong, P. C. Canfield, and A. I. Coldea, *Linear magnetoresistance caused by mobility fluctuations in the n -doped Cd_3As_2* , Phys. Rev. Lett. **114**, 117201 (2015).
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