

# High-Pressure Studies of Some Heavy Fermion Materials



Oliver Squire

Department of Physics  
and Jesus College,  
University of Cambridge

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# Declaration

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the preface and specified in the text. It is not substantially the same as any work that has already been submitted, or, is being concurrently submitted, for any degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the preface and specified in the text. It does not exceed the prescribed word limit for the relevant Degree Committee.

# Summary

This thesis presents the results of measurements on three heavy fermion materials under pressure: CeSb<sub>2</sub>, YbPtBi and CeAgSb<sub>2</sub>. In Chapter 1, I give an introduction to the key concepts involved in this work, such as unconventional superconductivity, quantum critical points and quantum oscillations, and I explain why heavy fermion materials under pressure are good systems for studying these effects. Chapter 2 describes the experimental techniques used in my measurements. I give an overview of anvil pressure cell techniques, the tunnel diode oscillator circuit and the various cryostats and magnets which were used to generate the low temperatures and high magnetic fields needed to study heavy fermion materials.

CeSb<sub>2</sub> undergoes a transition under pressure into a structure hosting a heavy fermion state with a large effective mass and antiferromagnetic order. Antiferromagnetism can be suppressed to a quantum critical point around 30 kbar, where there exists a dome of superconductivity with  $T_c \approx 0.2$  K. Chapter 3 focuses on this superconducting phase, which has a large upper critical field, exceeding the conventional Pauli limit, with an unusual temperature dependence. Chapter 4 contains an analysis of the pressure, temperature and magnetic field dependence of the normal state resistivity of CeSb<sub>2</sub>, which provides insights into the material's electronic and magnetic properties.

YbPtBi has traditionally been interpreted as a heavy fermion material with an extremely large effective mass due to its very large low-temperature heat capacity. However, quantum oscillations detect light masses, and an alternative scenario is possible in which  $f$  electrons act as local moments. Chapter 5 presents quantum oscillation measurements on YbPtBi; at ambient pressure, I have investigated the temperature, magnetic field and angular dependence of quantum oscillations to investigate the role of  $f$  electrons in the electronic structure, and I have extended these measurements to high pressures.

CeAgSb<sub>2</sub> is a clean ferromagnet at ambient pressure, with a ferromagnetic quantum phase transition and antiferromagnetic phase under pressure. In Chapter 6, I discuss phase transitions seen under pressure and my attempts to observe quantum oscillations near pressure-induced quantum phase transitions.

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# Chapter 1

## Introduction

In this chapter, I give a brief overview of superconductivity, quantum phase transitions, quantum oscillations and the realisation of these concepts in heavy fermion materials.

### 1.1 Basic properties of metals

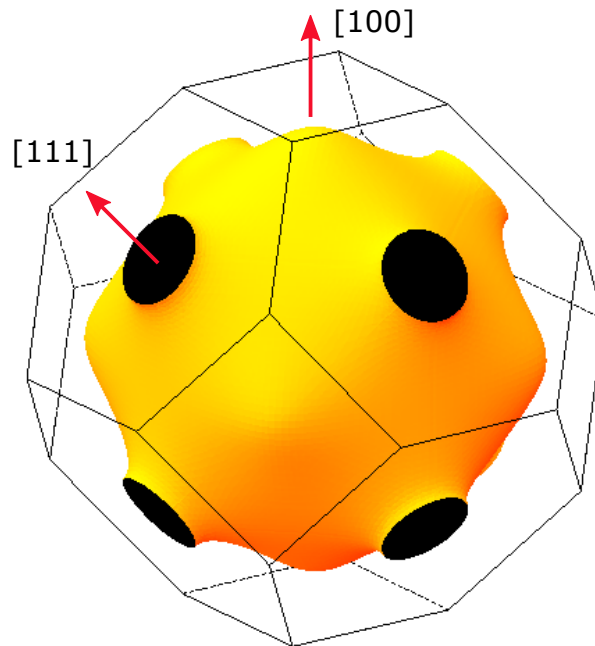


Figure 1.1: Fermi surface of copper, from the *Fermi Surface Explorer* project [1].

A convenient starting point for an understanding of the electrons in metal is a gas of free electrons. The electrons occupy the energy levels up to the Fermi energy  $E_F$ , resulting in a spherical Fermi surface in  $\mathbf{k}$ -space, separating occupied and unoccupied states. Interactions between electrons and the lattice of positive

ions results in changes in energy levels, so the Fermi surface's shape becomes non-spherical (e.g. the Fermi surface of copper shown in Figure 1.1).

In the Drude model, the resistivity of a metal is related to its effective mass  $m^*$ , carrier concentration  $n$  and scattering time  $\tau$  by

$$\rho = \frac{m^*}{ne^2\tau} . \quad (1.1)$$

Matthiessen's rule says that total scattering rate is the sum of the scattering rates from each electron scattering process:

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{impurities}}} + \frac{1}{\tau_{\text{electrons}}} + \frac{1}{\tau_{\text{phonons}}} + \dots \quad (1.2)$$

At low temperatures, the resistivity is dominated by scattering from impurity scattering and electron-electron scattering. Impurity scattering has a temperature-independent scattering rate, producing a residual resistivity  $\rho_0$ . The scattering cross-section for electron-electron scattering has a  $\sigma \propto (k_B T/E_F)^2$  temperature dependence [2], so the scattering rate  $\tau_{\text{electrons}} = 1/n\sigma v_F \propto m^{*3}/T^2$  results in an electron-electron resistivity contribution

$$\rho_{\text{e-e}} = AT^2 , \quad (1.3)$$

where the  $A$ -coefficient is related to the effective mass by

$$A \propto m^{*2} . \quad (1.4)$$

In the presence of electron-electron interactions, the electrons can no longer be treated as independent particles. The effects of these interactions in most metals are well described by Fermi liquid theory, where the electronic excitations are quasi-particles, which behave in a similar way to non-interacting electrons, but with a renormalised effective mass. The low-temperature heat capacity of a Fermi liquid is

$$C = \gamma T , \quad (1.5)$$

like a free electron gas but with an increased Sommerfeld coefficient

$$\gamma \propto m^* . \quad (1.6)$$

Although electron-electron interactions can in principle change the geometry of a Fermi surface, often these changes are not large because the symmetry of the lattice strongly constrains the shape of the Fermi surface, and because according to Lut-

tinger's theorem, the volume enclosed by the Fermi surface, which is proportional to the density of charge carriers, cannot change in the presence of electron-electron interactions [3].

## 1.2 Superconductivity

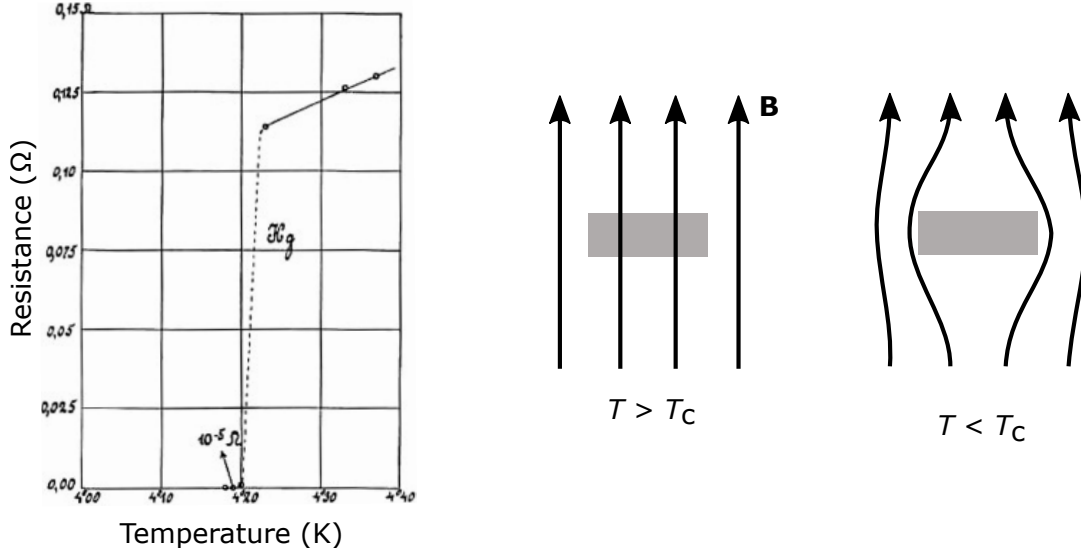


Figure 1.2: Left: superconducting transition in the resistivity of mercury from Onnes [4]. Right: magnetic field lines penetrating a sample in its normal state, and expelled from the sample in its superconducting state due to the Meissner effect.

Some metals at low temperatures display superconductivity. This effect, first seen in mercury in 1911, arises from the microscopic quantum mechanical interactions between electrons, and is characterised by properties such as zero electrical resistivity and the Meissner effect (Figure 1.2). The physics of superconductivity is not completely understood, especially in strongly correlated materials where the interactions between electrons can produce complex phases of matter, such as exotic unconventional superconducting states.

Superconductivity also has a range of applications, such as the production of large magnetic fields in MRI machines or sensitive magnetometers formed from superconducting junctions. Applications are limited by the low critical temperatures of current superconducting materials, usually requiring temperatures below a few kelvins. The discovery of materials which superconduct at higher temperatures, possibly up to room temperature, would allow the wider use of superconductor-based technology. To achieve this, it is desirable to gain a deeper understanding of the different mechanisms that could cause superconductivity, to guide the search for new superconducting materials.

### 1.2.1 Phonon-mediated superconductivity

Superconductivity arises from an attractive interaction between electrons, which causes the formation of pairs of electrons called *Cooper pairs*. These pairs behave like bosons and form a condensate at low temperatures, somewhat similar to a Bose-Einstein condensate, which carries current without dissipation.

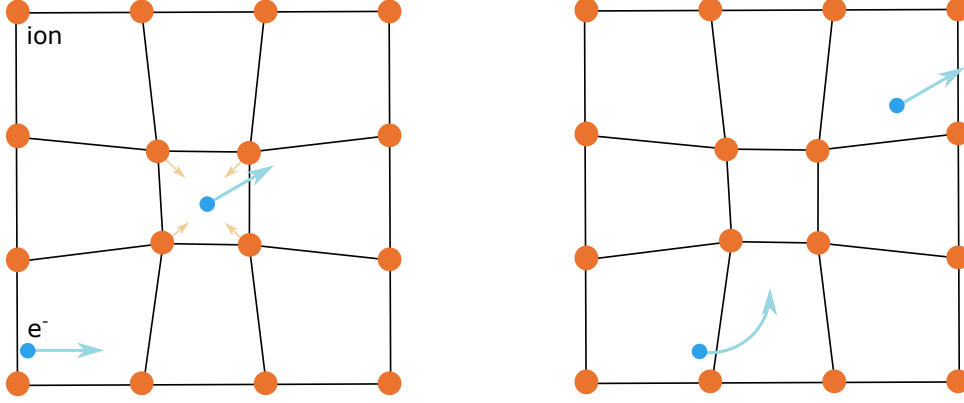


Figure 1.3: Illustration of an attractive interaction between two electrons mediated by phonons. Left: the lattice of positive ions is attracted towards the first electron. Right: after the first electron leaves, a region of positive charge is left behind, which attracts the second electron.

In conventional superconducting materials, the attractive interaction between electrons is mediated by phonons. Figure 1.3 illustrates how the distortion of the lattice of ions by one electron produces a region of net positive charge which can attract another electron. The interaction needs to be retarded to produce an attraction, i.e. there must be a time delay between the electrons, to overcome the Coulomb repulsion between the electrons that would occur if they were at the same place at the same time.

The microscopic quantum mechanical theory for phonon-mediated Cooper pairing with weak electron-phonon coupling is known as *BCS* (Bardeen-Cooper-Schrieffer) theory. This theory finds that the excitations in the superconducting state are gapped (Figure 1.4), meaning that an energy larger than  $2|\Delta|$  is needed to break apart the electrons in a Cooper pair. This gap protects the superconducting condensate from scattering, allowing it to conduct electricity without dissipation. The gap at each wavevector  $\mathbf{k}$  is given by the magnitude of the complex gap function  $\Delta_{\mathbf{k}}$ , which is determined by the pairing interaction between electrons:

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2\sqrt{(E_{\mathbf{k}} - E_{\mathbf{F}})^2 + \Delta_{\mathbf{k}}^2}} V_{\mathbf{k}'\mathbf{k}}, \quad (1.7)$$

where  $V_{\mathbf{k}'\mathbf{k}}$  is the interaction between electrons with wavevectors  $\mathbf{k}'$  and  $\mathbf{k}$ , and  $E_{\mathbf{k}}$  is

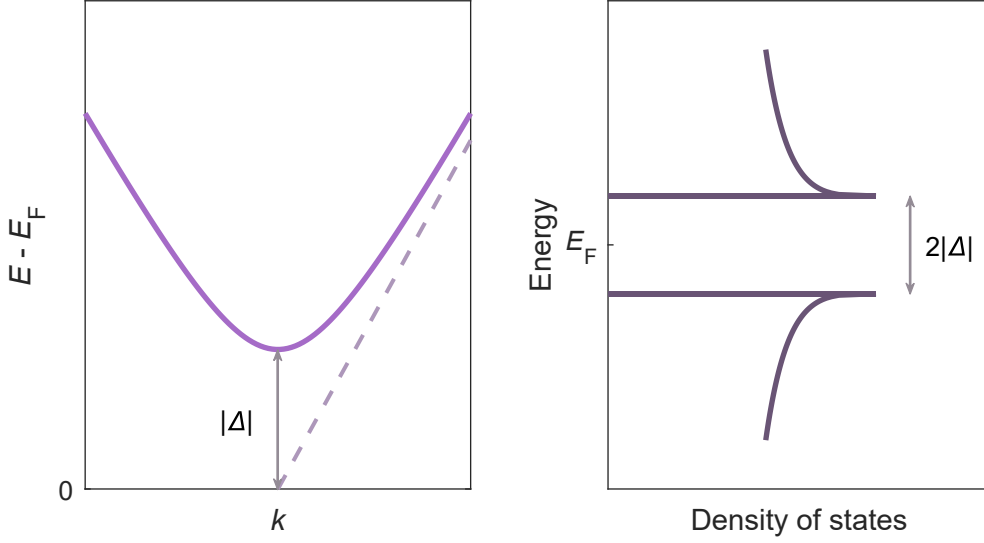


Figure 1.4: Left: dispersion for electronic excitations in the superconducting state (solid line) compared to the electronic dispersion in the normal state (dashed line). Right: density of states around the Fermi energy is gapped by  $2|\Delta|$  in a BCS superconductor.

the normal state electron energy. In BCS theory, this equation is solved by assuming  $V_{\mathbf{k}'\mathbf{k}}$  is a constant, which results in a gap function  $\Delta_{\mathbf{k}} = \Delta$  with no  $\mathbf{k}$ -dependence, and therefore a real-space gap function which is largest at  $\mathbf{r} = 0$ . In BCS theory, each Cooper pair has a singlet spin state and zero orbital angular momentum. The  $s$ -wave wavefunction  $\psi \propto \Delta$  is largest at zero displacement, reflecting the fact that the pairing interaction is strongest when the electrons are at the same location.

The formation of Cooper pairs mixes together states within a distance  $\delta k$  of the Fermi surface. The slope of the normal state dispersion  $E_k$  (the dashed line in Figure 1.4) is related to the Fermi velocity by  $dE_k/dk = \hbar v_F$  at  $E = E_F$ , so  $\delta k \approx \Delta/\hbar v_F$ . From this, the typical real-space size of the Cooper pairs can be estimated as  $\delta x \approx 1/\pi\delta k$ , known as the *coherence length*:

$$\xi = \frac{\hbar v_F}{\pi \Delta}. \quad (1.8)$$

The coherence length is usually much larger than the lattice spacing. For example, the coherence length in tin is  $\xi \approx 2000 \text{ \AA}$  [5]. Therefore, the superconducting state is formed of overlapping Cooper pairs and, unlike a Bose-Einstein condensate, cannot be thought of as simply a condensate of individual bosons.

BCS theory finds that at zero temperature, the gap is related to the transition

temperature by

$$\Delta_0 = 1.76 k_B T_c \quad (1.9)$$

and the condensation energy difference between the normal and superconducting states is

$$\Delta E = \frac{1}{4} g(E_F) \Delta_0^2, \quad (1.10)$$

where  $g(E_F)$  is the total normal-state density of states at the Fermi energy.

BCS theory, and its extension to strong electron-phonon coupling, has been successful in explaining the physical properties of many superconductors, such as elemental superconductors (e.g. mercury, tin and lead) or  $\text{MgB}_2$ , which is the highest-temperature ambient-pressure phonon-mediated superconductor with  $T_c = 39$  K [6]. In recent years, phonon-mediated superconductivity has been discovered in hydride materials at high pressures with transition temperatures approaching room temperature:  $\text{H}_3\text{S}$  with  $T_c = 203$  K [7] and  $\text{LaH}_{10}$  with  $T_c = 260$  K [8, 9]. The light masses of the hydrogen atoms in these materials mean high phonon frequencies which can produce strong superconductivity, but mean that these materials are not stable at ambient pressure. It is not impossible that phonon pairing could produce in a room-temperature, ambient-pressure superconductor, but a pairing mechanism based on magnetic fluctuations offers an alternative avenue of research.

### 1.2.2 Unconventional superconductivity

In unconventional superconductors, magnetic fluctuations can provide the pairing interaction between electrons. This is the case in heavy fermion superconductors such as  $\text{CeCu}_2\text{Si}_2$  [10], which was the first unconventional superconductor to be discovered, and cuprate superconductors, which have the highest ambient-pressure transition temperatures of all superconductors. A similar effect occurs in He-3, where magnetic fluctuations bind He-3 atoms into Cooper pairs which form a superfluid condensate with zero viscosity below  $\sim 1$  mK. Magnetic interactions in materials can have high energies, and can possibly be exploited to produce superconductivity at high temperatures.

Whereas phonon-mediated pairing relies on a retarded interaction which is largest at zero separation, a magnetic pairing interaction is attractive at a finite separation. Therefore the electrons avoid each other in space, rather than time, to overcome the Coulomb repulsion between them. An antiferromagnetic pairing interaction, shown in Figure 1.5, oscillates in space with a wavelength related to the ordering wavelength of the antiferromagnetism. Depending on the distance between the electrons, the interaction can be either attractive or repulsive. Therefore, the interaction  $V_{\mathbf{k}'\mathbf{k}}$

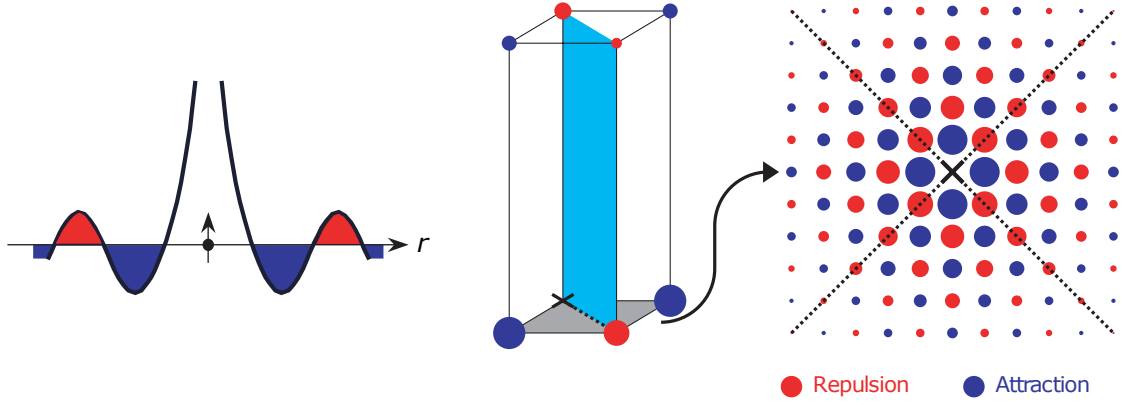


Figure 1.5: Left: magnetic interaction experienced by a ‘down’ spin as a function of distance away from an ‘up’ spin. Right: magnetic interaction experienced by electrons at other lattice sites due to the electron at the origin marked by the cross. The dashed diagonal lines indicate the nodes of a  $d$ -wave gap. This figure has been adapted from Monthoux *et al.* [11].

cannot be treated as a constant, so Equation 1.7 results in a gap  $\Delta_{\mathbf{k}}$  which is a function of  $\mathbf{k}$ .

The total wavefunction of the Cooper pairs must be antisymmetric under exchange of the electrons, so a singlet spin wavefunction is accompanied by a spatial wavefunction with  $L = 0, 2, 4, \dots$  etc. In many unconventional superconductors, such as cuprates, it is thought that the gap has a  $d$ -wave symmetry (i.e.  $L = 2$ ). In Figure 1.5, the diagonal dashed lines indicate the positions of the nodes of a  $d$ -wave gap, i.e. the points where the amplitude of the Cooper pair wavefunction goes to zero, and the size of the red or blue points indicates the strength of the repulsive or attractive interaction due to antiferromagnetic spin fluctuations. The amplitude of the  $d$ -wave gap is largest where the interaction is attractive, and disappears where it is most repulsive. Therefore a  $d$ -wave superconducting state can have a lower energy than a conventional  $s$ -wave state. A spin-triplet Cooper pair must have  $L = 1, 3, \dots$  etc. A spin-triplet  $p$ -wave state is thought to exist in some U-based superconductors where superconductivity is found within or close to a ferromagnetic state.

Other, more complicated, pairing states are possible in materials with multiple bands, such as the  $s_{+-}$  pairing state which might exist in iron-based superconductors, where the gap is  $s$ -wave but changes sign between different Fermi surface pockets. The frequency-dependence of a superconductor is often assumed to be even, i.e. the wavefunction is even under time reversal, but other pairing states are possible if the state has an odd frequency dependence. For example an odd-frequency, spin-triplet,  $d$ -wave state is theoretically possible.

If the spatial Cooper pair wavefunction changes sign, there are parts of  $\mathbf{k}$ -space where the gap goes to zero. In this case, impurities in the material can scatter

electrons into wavevectors where the superconducting condensate is not gapped, destroying the superconducting state. Therefore, unconventional superconductors where  $\Delta_{\mathbf{k}}$  has nodes are often found to be highly sensitive to disorder and need to be grown with sufficiently low residual resistivities to observe superconductivity [12, 13]. A simple criterion for the observation of unconventional superconductivity is

$$l > \xi, \quad (1.11)$$

where  $l$  is the mean free path and  $\xi$  is the coherence length.

### 1.2.3 Critical field

The superconducting state has a complex order parameter  $\psi$ , which can be thought of as a macroscopic quantum wavefunction for the superconducting condensate, and is related to the superconducting gap function  $\psi \propto \Delta$ . The free energy density of a superconductor can be written as

$$f = \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}|(-i\hbar\nabla - q\mathbf{A})\psi|^2 + \frac{1}{2\mu_0}(\mathbf{B} - \mathbf{B}_e)^2, \quad (1.12)$$

where  $\alpha > 0$  in the normal state and  $\alpha < 0$  in the superconducting state,  $\beta > 0$ ,  $q = -2e$  is the charge of a Cooper pair,  $\mathbf{B} = \nabla \times \mathbf{A}$  is the magnetic field inside the superconductor and  $\mathbf{B}_e$  is an external applied magnetic field. For a spatially uniform  $\psi$ , this free energy expression gives  $|\psi| = 0$  in the normal state, and  $|\psi| = \sqrt{|\alpha|/\beta}$  in the superconducting state. If  $\psi$  is allowed to vary in space, an analysis of this free energy expression gives a characteristic length scale for variations in the order parameter,

$$\xi = \frac{\hbar}{\sqrt{2m|\alpha|}}. \quad (1.13)$$

This distance is equivalent to the coherence length discussed in Section 1.2.1. An analysis of the spatial variation of magnetic fields in a superconductor finds that, although the magnetic field is zero in the bulk of the superconductor, it penetrates a distance

$$\lambda = \sqrt{\frac{m\beta}{2\mu_0 q^2 |\alpha|}}, \quad (1.14)$$

below the surface of the superconductor, called the *penetration depth*.

The free energy equation 1.12 shows that there is a condensation energy gain (i.e. a lowering of the free energy) associated with having a non-zero  $\psi$  and an energy cost from the expulsion of magnetic field. The response of the superconducting state to an applied magnetic field  $B_e$  is determined by the relative sizes of the coherence length

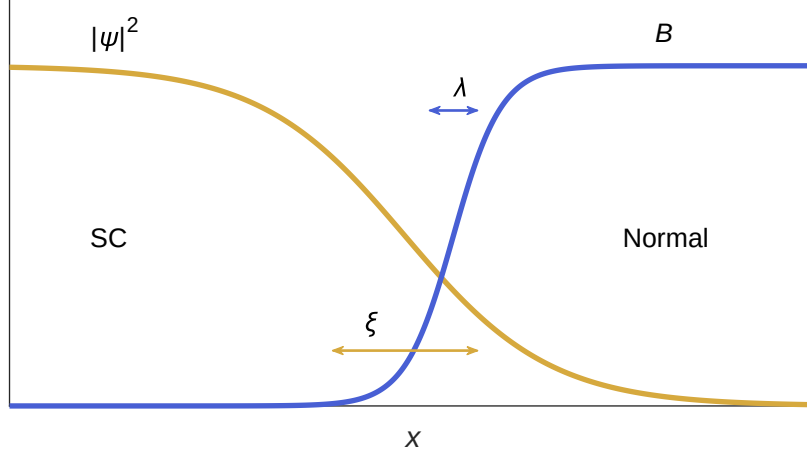


Figure 1.6: The spatial variation of the magnetic field  $B$  and superfluid density  $|\psi|^2$  at the boundary between a superconducting (SC) and normal region in a metal. Arrows indicate the coherence length  $\xi$  and penetration depth  $\lambda$ .

and penetration depth (Figure 1.6). At a boundary between a superconducting and normal region, the magnetic field will go from zero to  $B_e$  over a distance  $\lambda$ , whereas the superfluid density will go to zero over a distance  $\xi$ . If  $\xi \gg \lambda$ , there is a large region where the magnetic field and  $|\psi|^2$  are both zero. This region does not gain any condensation energy and pays the energy cost of field expulsion, so there is an overall energy cost associated with the boundary. In this case, known as *type-I* superconductivity, the superconductor will minimise the number of boundaries by expelling the magnetic field from its entire interior to produce a Meissner state. If  $\xi \ll \lambda$ , there is a region with nonzero  $|\psi|^2$  and magnetic field, so the boundary has a negative energy associated with it. In this case, known as *type-II* superconductivity, it may be advantageous to form a mixed state in a magnetic field, where some magnetic field can penetrate the material and form vortices with normal cores. This state lowers the overall energy of the superconductor due to the negative energy of the normal-superconductor boundaries inside the vortices. The vortices in a type-II superconductor have a quantised flux through their cores, which must be an integer multiple of  $\phi_0 = h/2e$  for the order parameter to be single-valued around the vortex. A full comparison of the energies finds that the precise condition for type-II superconductivity is  $\xi < \sqrt{2}\lambda$ . As  $\xi \propto v_F \propto 1/m^*$ , type-II superconductivity is more common than type-I superconductivity in strongly-correlated materials with large effective masses.

Figure 1.7 shows the magnetic field-temperature phase diagram of a type-II superconductor. At low fields, below its *lower critical field*  $B_{c1}$ , the Meissner state has lowest energy because of an energy cost associated with vortices from the third term

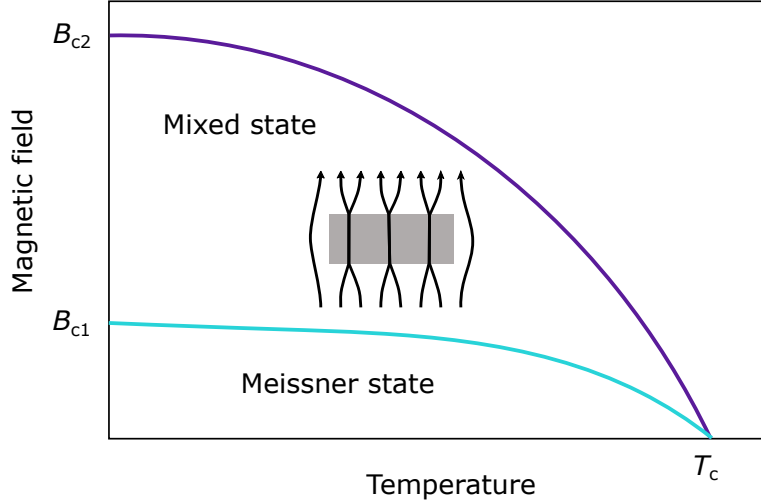


Figure 1.7: Temperature-magnetic field phase diagram of a type-II superconductor

in Equation 1.12. At higher fields, the vortex state becomes energetically favourable. This vortex state has zero resistivity, like the Meissner state; in theory the movement of vortices could cause a non-zero resistivity, but this does not usually happen because they are pinned by defects in crystals. Above the *upper critical field*  $B_{c2}$ , superconductivity is destroyed.

There are two mechanisms for the destruction of the superconducting state at  $B_{c2}$ . The first effect, orbital depairing, is related to overlapping vortex cores. Assuming the magnetic flux through a vortex is  $\phi_0 = \pi r^2 B$ , where  $r$  is the outer radius of the vortex, superconductivity will be destroyed with  $r = \xi$ , which occurs at

$$B_{\text{orb}} = \frac{\phi_0}{2\pi\xi^2}. \quad (1.15)$$

A more detailed calculation of this effect finds that this zero temperature critical field is related to the slope of the critical field curve at low fields,  $B'_{c2} \equiv dB_{c2}/dT$ , by

$$B_{\text{orb}} = 0.73 |B'_{c2}| T_c \quad (1.16)$$

for a clean superconductor [14]. Therefore,  $|B'_{c2}| \propto 1/\xi^2 \propto m^{*2}$ , so the slope of the critical field at low fields gives an indication of the effective masses of electrons.

The second mechanism is paramagnetic depairing. In a magnetic field, the energy of a paramagnetic normal state is reduced, as the magnetic moments align with the applied field. This normal state energy reduction increases with field, and a transition from the superconducting to normal state is expected when the paramagnetic energy reduction is equal to the superconducting condensation energy. This

occurs when

$$\frac{1}{2}\mu_0(\chi_n - \chi_s)H_P^2 = \frac{1}{4}g(E_F)\Delta_0^2. \quad (1.17)$$

In a BCS superconductor,  $\Delta_0 = 1.76 k_B T_c$  and  $\chi_s = 0$  at zero temperature. Using the Pauli paramagnetic susceptibility  $\chi_n = \mu_0 \mu_B^2 g(E_F)$  gives the conventional Pauli limit [15]

$$B_P = 1.84 T_c \text{ TK}^{-1}. \quad (1.18)$$

In many conventional type-II superconductors, the orbital critical field is lower than the Pauli limit, so Pauli depairing effects are not relevant. For example, vanadium has  $T_c = 5.4 \text{ K}$ , so  $B_P = 10 \text{ T}$ , whereas the measured upper critical field at zero temperature is  $0.27 \text{ T}$  [16]. In strongly correlated materials with large effective masses, the coherence length is small, so  $B_{\text{orb}}$  is large and can be comparable in size to  $B_P$ , so paramagnetic depairing effects are important.

In a spin-triplet superconductor, the parallel spins in a Cooper pair can rotate in a magnetic field, so the spin susceptibility in the superconducting state  $\chi_s$  is non-zero. The superconducting susceptibility depends on the direction of the field relative to the Cooper pair spins. For some directions  $\chi_s = \chi_n$ , so  $B_P$  is infinite and there is no paramagnetic depairing.

### 1.3 Quantum phase transitions

One of the most successful recipes for finding new unconventional superconductors, and for explaining why some materials superconduct and others do not, is the concept of a *quantum critical point* (QCP).

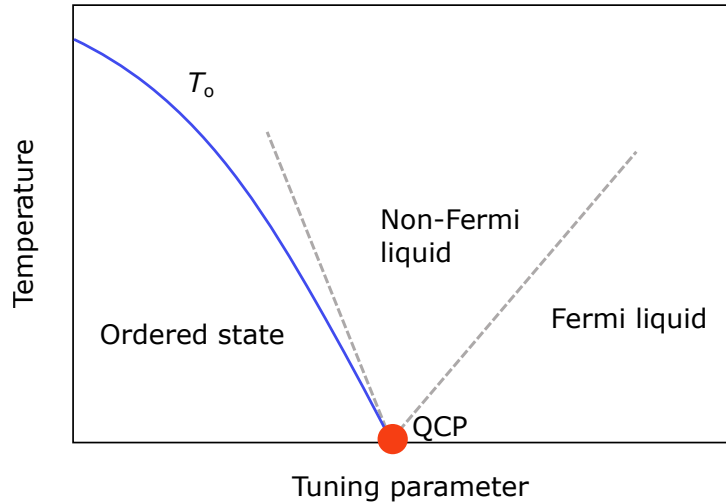


Figure 1.8: Typical phase diagram with a quantum critical point (QCP) and a fan of non-Fermi liquid emanating from it.

Figure 1.8 shows a typical phase diagram where an ordered phase is tuned by a parameter such as hydrostatic pressure, uniaxial strain, chemical substitution or magnetic field. In this phase diagram, there is a point where the second order transition into the ordered state at  $T_0$  is tuned to zero temperature, to produce a QCP. At a finite temperature second order transition, thermal fluctuations drive a divergence of the correlation length and correlation time. At a QCP, as the material is tuned from the disordered to ordered state at zero temperature, the transition is driven by quantum mechanical fluctuations. These quantum fluctuations are very different from finite-temperature thermal fluctuations and can produce electronic behaviour which deviates from Fermi liquid theory. The energy of the fluctuations  $\hbar\omega$  goes to zero at the QCP, so thermally excited quantum critical fluctuations, which exist when  $k_B T > \hbar\omega$ , produce *non-Fermi liquid* behaviour in a fan-shaped region of the phase diagram above the QCP. If the transition at  $T_0$  is first order at zero temperature, quantum fluctuations are generally not produced, although there may still be some quantum critical behaviour if the transition is only weakly first order. A zero temperature phase transition is more generally known as a *quantum phase transition*, but it must be second order to be a quantum critical point.

### 1.3.1 Superconductivity at antiferromagnetic QCPs

At an antiferromagnetic QCP, the quantum critical fluctuations can act as a ‘magnetic glue’ which binds electrons into Cooper pairs to form an unconventional superconducting state. For example, in  $\text{CePd}_2\text{Si}_2$  the second-order antiferromagnetic transition at  $T_N = 10$  K can be suppressed to zero temperature to produce a quantum critical point at 28 kbar (Figure 1.9). A dome of superconductivity exists only in a narrow range of pressures around the QCP, strongly suggesting that spin fluctuations associated with the QCP are responsible for the superconductivity (Figure 1.9, left) [17]. Superconductivity has been found at antiferromagnetic QCPs in many other Ce-based materials, all with relatively low transition temperatures  $T_c < 2.5$  K, as I will discuss further in Section 1.5, and in many other families of materials, such as organic and iron-based superconductors. The phase diagram of hole-doped cuprates (Figure 1.9, right) might also have a QCP at  $p^*$  associated with the disappearance of the pseudogap, where parts of the Fermi surface are gapped. This QCP could be responsible for high-temperature superconductivity and the non-Fermi liquid ‘strange metal’ region of the phase diagram [19], although this idea is controversial [20, 21].

Chemical substitution is sometimes used to tune the properties of materials by introducing additional electron or hole charge carriers, or through ‘chemical pressure’, where a smaller or larger isovalent element is introduced to shrink or compress

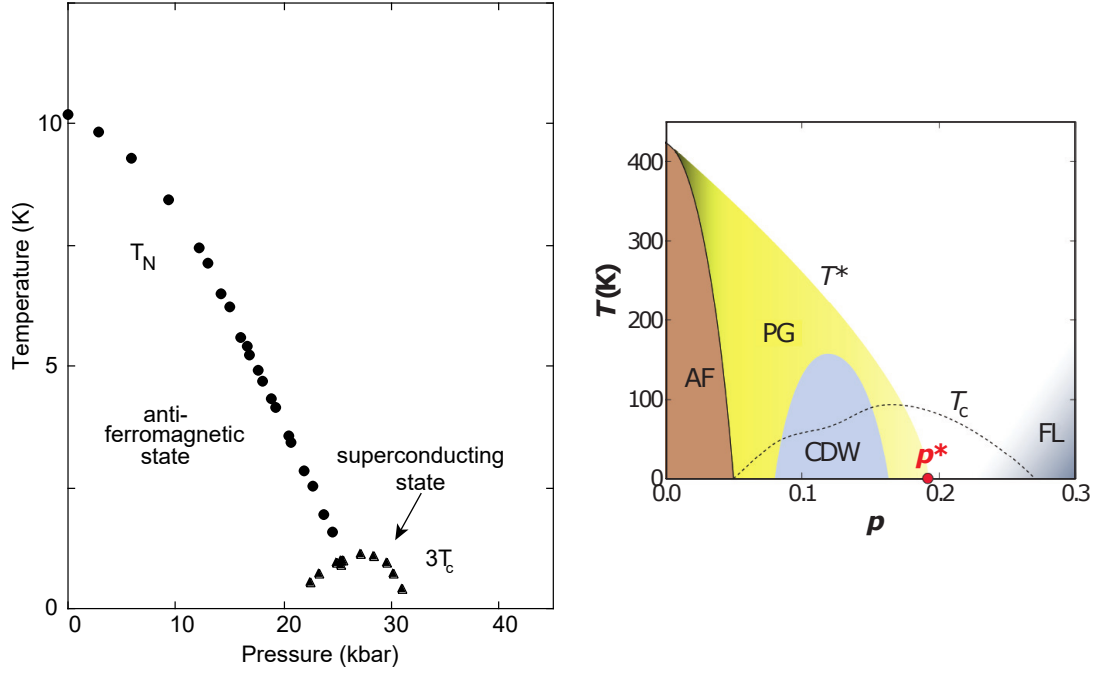


Figure 1.9: Left: pressure-temperature phase diagram of  $\text{CePd}_2\text{Si}_2$  from Mathur *et al.* [17]. Right: schematic doping-temperature phase diagram of hole-doped cuprate superconductors from Proust and Taillefer [18]. AF, PG, CDW, SM and FL indicate antiferromagnetic, pseudogap, charge density wave, strange metal and Fermi liquid regions of the phase diagram.

the lattice. However, chemical substitution introduces disorder into materials, which shortens mean free paths and can prevent the formation of a superconducting state if  $l < \xi$ . Hydrostatic pressure is an alternative, cleaner tuning parameter. It pushes the atoms in the lattice closer together, changing the strengths of interactions between electrons and electronic bandwidths. By doing this, it is often possible to weaken or strengthen different ordered phases, to produce QCPs and search for superconductivity. Measurements under pressure can be significantly more challenging than at ambient pressure, but a range of techniques have been developed to measure various different physical properties in pressure cells.

Magnetic field is another clean tuning parameter, but its effects are often different from pressure. Magnetic field alters the properties of a material by polarising its magnetic moments and shifting energy bands. This can generate quantum critical points, but applied field also weakens superconductivity, due to the critical field mechanisms described in Section 1.2.3. There are a few examples of field-induced superconductivity, such as the spin-triplet superconductor URhGe [22], but it is rare. Applying both pressure and field at the same time allows a great degree of control over a material's properties, to investigate behaviour at different points in a three-dimensional  $p$ - $B$ - $T$  phase diagram.

### 1.3.2 Non-Fermi liquid behaviour

One of the simplest models for non-Fermi liquid behaviour at a magnetic QCP is given by self-consistent renormalisation theory [23–25]. In this model, the effects of spin fluctuations at finite temperature, which are weakly coupled to each other, can be calculated, resulting in a temperature dependent resistivity  $\Delta\rho \equiv \rho - \rho_0 \propto T^n$  which deviates from the  $n = 2$  Fermi liquid result. In the simplest calculations in three dimensions, this gives  $n = 5/3$  for ferromagnetic fluctuations, and  $n = 3/2$  for antiferromagnetic fluctuations. In two dimensions, which may be more relevant for layered materials, the calculations give  $n = 4/3$  for ferromagnetic fluctuations, and  $n = 1$  for antiferromagnetic fluctuations. Non-Fermi liquid effects also show up in other physical properties, such as heat capacity. For example, a logarithmic  $C/T \propto -\ln T$  is predicted at a two-dimensional antiferromagnetic quantum critical point.

Non-Fermi liquid behaviour has been observed around antiferromagnetic QCPs in many different materials. For example,  $\Delta\rho \propto T^{1.2}$  is seen in  $\text{CePd}_2\text{Si}_2$  under pressure [17],  $\Delta\rho \propto T$  in the organic material  $(\text{TMTSF})_2(\text{PF})_6$  under pressure [26] and  $\Delta\rho \propto T$  in  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  [27]. Some hole-doped cuprate superconductors exhibit non-Fermi liquid ‘strange metal’ behaviour ( $\Delta\rho \propto T$ ) up to several 100 kelvins, which could be related to 2D antiferromagnetic fluctuations. However, an alternative theory for the linear resistivity seen in cuprates and other materials is the theory of Planckian dissipation, which proposes that there is an upper limit on the scattering rate,  $\hbar/\tau = k_B T$ , which produces the same result:  $\Delta\rho \propto T$  [28, 29].

### 1.3.3 Other types of QCP

Ferromagnetic quantum criticality is more complicated. In most clean ferromagnets, such as  $\text{UGe}_2$  [30] and  $\text{ZrZn}_2$  [31], the transition is found to become first order just before the critical point, preventing the formation of a ferromagnetic QCP. This experimental result has been explained by theoretical calculations which find that the nature of fluctuations at a ferromagnetic quantum phase transition force the transition to become first order [32, 33]. The exceptions to this rule are  $\text{YbNi}_4(\text{P}_{1-x}\text{As}_x)_2$  [34] and  $\text{CeRh}_6\text{Ge}_4$  under pressure [35, 36] where the transition seems to remain second order down to the lowest temperatures, which may be related to their quasi-1D crystal structures. However, superconductivity has not been found at the ferromagnetic QCPs in either of these materials.

Other, non-magnetic, types of QCP are possible. A structural QCP is thought to exist in  $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$  under pressure [37] and  $(\text{Ca}_x\text{Sr}_{1-x})_3\text{Rh}_4\text{Sn}_{13}$  [38], where a second order superlattice structural transition is suppressed to zero temperature. Conven-

tional, phonon-mediated superconductivity is enhanced and a  $\Delta\rho \propto T$  resistivity is seen near this QCP. In many iron-based superconductors, a nematic state exists, in which the electrons drive a breaking of rotational symmetry. In most cases, this nematic phase is found close to antiferromagnetism, making it difficult to separate the two phases. Nematic QCPs without any magnetism are found in  $\text{FeSe}_{1-x}\text{S}_x$  and  $\text{FeSe}_{1-x}\text{Te}_x$ , and the effects of nematic fluctuations on superconductivity in these materials is an area of active research [39, 40]. Ferroelectric quantum criticality has been studied in  $\text{SrTiO}_3$ , where it leads to anomalous behaviour in the dielectric susceptibility [41, 42].

## 1.4 Quantum oscillations

When a magnetic field is applied to a single crystal of a metal at low temperatures, *quantum oscillations* can sometimes be seen in its physical properties, periodic in inverse magnetic field, with a frequency related to the cross-sectional area of the Fermi surface. These oscillations can be used to determine the geometry of a metal's Fermi surface, as well as other electronic properties such effective masses and mean free paths. In this section, I give a brief overview of the theory of quantum oscillations.

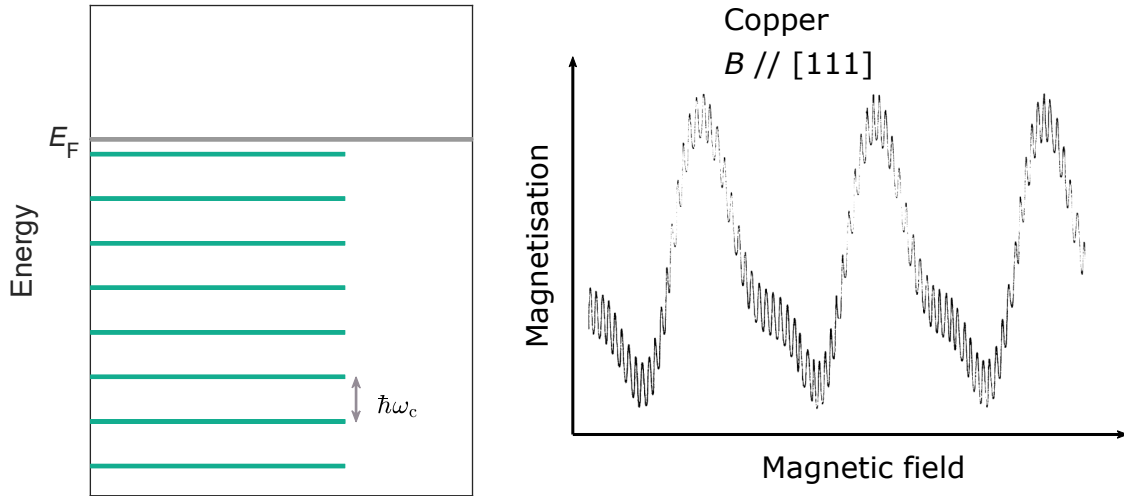


Figure 1.10: Left: schematic diagram of occupied Landau levels below the Fermi energy. Right: quantum oscillations in the magnetisation of copper for field applied along the [111] direction, from Joseph *et al.* [43].

The energy levels of an electron in a metal are quantised into *Landau levels* in

the  $x$ - $y$  plane when a magnetic field is applied along the  $z$ -direction:

$$E = \left( \lambda + \frac{1}{2} \right) \hbar \omega_c + \frac{\hbar^2 k_z^2}{2m^*}, \quad (1.19)$$

assuming no lattice potential, where

$$\omega_c = \frac{eB}{m^*} \quad (1.20)$$

is the cyclotron frequency. These levels are occupied up to the Fermi energy (Figure 1.10, left). With increasing field, the spacing between the Landau levels increases, and when the highest level passes through the Fermi energy, it depopulates, i.e. the electrons that were in the highest Landau level now occupy lower levels. As successive Landau levels pass through the Fermi energy, the population and depopulation of these levels causes the density of states, and therefore the magnetisation of the metal to oscillate.

A full calculation of the quantum oscillations in the magnetisation of a metal (known as the *de Haas-van Alphen* effect) in the presence of a lattice potential finds that the frequency of oscillations is proportional to an extremal cross-sectional area of the material's Fermi surface perpendicular to the applied field (see the book by Shoenberg [44]). The total oscillatory signal is the sum of the signal from all extremal areas, which could come from different Fermi surface pockets, or from different extremal areas on the same pocket. For example, the Fermi surface of copper (Figure 1.1) has neck and belly extremal areas perpendicular to the [111] direction, producing two different oscillation frequencies (and harmonics) in the magnetisation (Figure 1.10, right).

The oscillating magnetisation parallel to the direction of the applied field from one frequency is given by the Lifshitz-Kosevich formula,

$$\tilde{M} \propto \frac{FB^{1/2}}{m^*(A'')^{1/2}} \sum_{p=1}^{\infty} \frac{R_T R_D R_s}{p^{3/2}} \sin \left( \frac{2\pi p F}{B} + \phi \right). \quad (1.21)$$

The  $p = 1$  term is the largest, but higher  $p > 1$  harmonics can sometimes be seen at high fields. The oscillation frequency is

$$F = \frac{\hbar A}{2\pi e}, \quad (1.22)$$

where  $A$  is the extremal cross-sectional area of the Fermi surface parallel to the

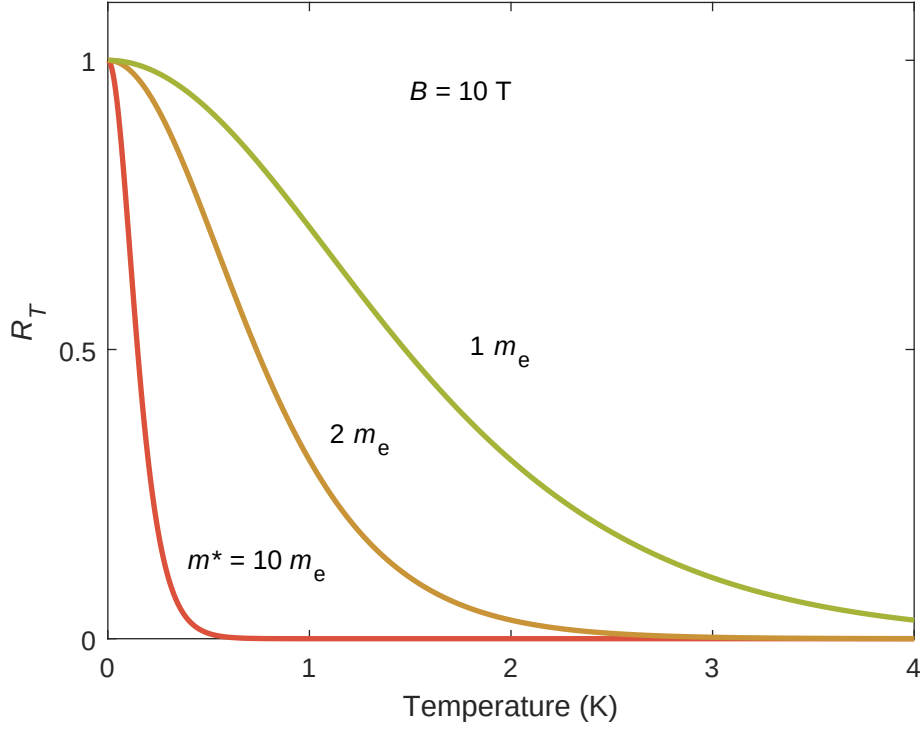


Figure 1.11: Temperature dependence of the thermal damping factor  $R_T$  at 10 T for different effective masses.

applied field.

$$A'' = \left| \frac{\partial^2 \mathcal{A}}{\partial \kappa^2} \right|, \quad (1.23)$$

where  $\kappa$  is the  $\mathbf{k}$ -space coordinate along the direction of the field, and the second derivative is evaluated at the  $\kappa$  value where the cross-sectional area  $\mathcal{A}$  is extremal.

The thermal damping factor is

$$R_T = \frac{2\pi^2 p m^* k_B T / e \hbar B}{\sinh(2\pi^2 p m^* k_B T / e \hbar B)}, \quad (1.24)$$

which arises from the smearing of the Fermi-Dirac distribution with increased temperature. By fitting the temperature-dependence of the amplitude of each frequency with this function, it is possible to determine the effective masses of different Fermi surface sheets. The factor is a function of  $m^* T / B$ , so heavier masses require higher  $B/T$  to observe oscillations (Figure 1.11).

The Dingle factor is

$$R_D = e^{-\pi p m^* / e B \tau}, \quad (1.25)$$

so materials with longer scattering times, i.e. higher purity, require lower fields to

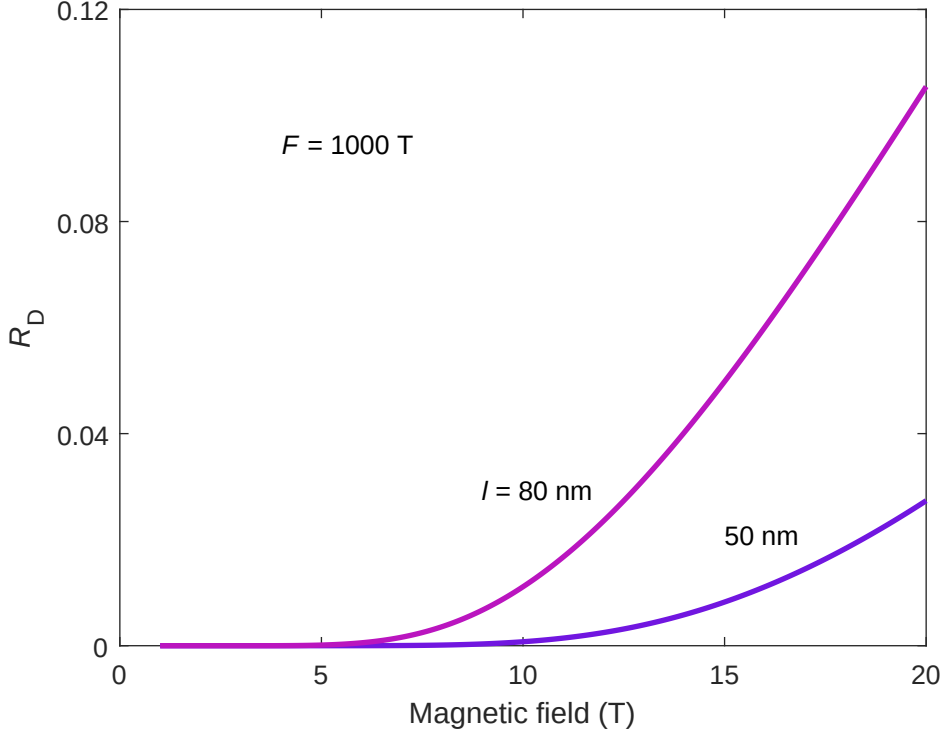


Figure 1.12: Field dependence of the Dingle factor  $R_D$  for a spherical Fermi surface pocket with  $F = 1000$  T with two different mean free paths.

observe oscillations. The Dingle factor is often written as

$$R_D = e^{-B_0/B} . \quad (1.26)$$

For a spherical Fermi surface pocket,

$$B_0 = \frac{\pi p}{l} \sqrt{\frac{2\hbar F}{e}} , \quad (1.27)$$

so higher frequencies have their amplitude damped more strongly, and therefore require higher fields or purer crystals to observe them. The exponential dependence of  $R_D$  on the mean free path means that a small increase in sample purity can produce a large increase in oscillation amplitude (Figure 1.12). Therefore, a great amount of effort is often taken to prepare single crystals with long mean free paths for quantum oscillation experiments.

The spin splitting factor is

$$R_s = \cos \left( \frac{1}{2} p \pi g m^* / m_e \right) , \quad (1.28)$$

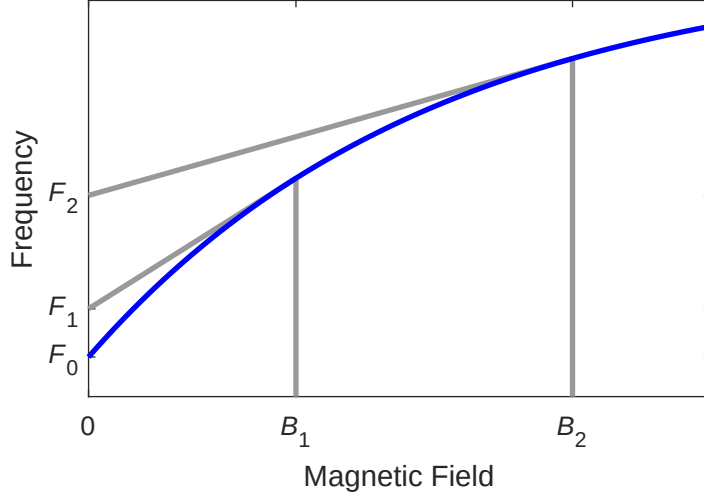


Figure 1.13: Relationship between a field-dependent  $F(B)$  and the measured quantum oscillation frequency. The curved blue line indicates  $F(B)$  and  $F_0$ ,  $F_1$  and  $F_2$  are the back-projected measured frequencies at 0,  $B_1$  and  $B_2$ .

which arises from the Zeeman splitting of energy levels in a magnetic field.

If the Fermi surface changes with magnetic field, some field-dependence of the quantum oscillation frequency might be expected. A field-dependent extremal area produces a field dependent  $F(B) \propto A(B)$ . However, the measured quantum oscillation frequency is different; it is related to the rate of change of quantum oscillation phase  $\Phi$  with respect to  $1/B$ :

$$F_{\text{measured}}(B) \equiv \frac{1}{2\pi} \frac{d\Phi}{d(1/B)} = F(B) - B \frac{dF}{dB} \quad (1.29)$$

for the first harmonic. Therefore, the measured frequency is a back-projection of the true frequency, as illustrated in Figure 1.13. A linear  $\Delta F \propto B$  field dependence, expected from simple Pauli paramagnetism in a metal, does not produce a measurable change in frequency. Only rarer nonlinear Fermi surface changes can produce field-dependent quantum oscillation frequencies.

The observation of quantum oscillations in the electrical resistivity of a metal is known as the *Shubnikov-de Haas* effect. The details of electrons scattering in a magnetic field are difficult to calculate, but the resistivity is determined by the probability of electron scattering, which is proportional to the density of states at the Fermi energy. As the density of states oscillates with a frequency  $F \propto A$ , periodic in inverse field, so does the electrical resistivity. The amplitude of the oscillations in the conductivity is roughly

$$|\tilde{\sigma}|/\sigma \approx R_T |\tilde{N}(E_F)|/N_0(E_F), \quad (1.30)$$

where  $N_0(E_F)$  is the total density of states from all sheets at the Fermi energy. For a spherical Fermi surface,

$$\frac{|\tilde{N}(E_F)|}{N_0(E_F)} = R_D R_s \left( \frac{B}{2F} \right)^{1/2}, \quad (1.31)$$

so larger resistivity oscillations arise from smaller Fermi surface pockets.

As all physical properties of a metal depend on its density of states in some way, quantum oscillations can in principle be observed in many other physical properties, such as heat capacity and sample length, but these are not as commonly measured as magnetisation and electrical resistivity. A range of experimental techniques, such as torque magnetometry and AC field modulation, are used to measure with the high sensitivity usually required to observe oscillations. One experimental technique, the tunnel diode oscillator, will be discussed in detail in the next chapter.

## 1.5 Heavy fermion materials

One particularly interesting class of materials in which to study quantum phase transitions and unconventional superconductivity are heavy fermion materials. These materials contain rare earth elements, such as Ce, Yb or U, with  $4f$  or  $5f$  orbitals. The compact nature of the  $f$  orbitals produces very strong electron-electron interactions, which lead to very large effective masses of the quasiparticles in these materials, hence their name.

Many heavy fermion materials are well described by Fermi liquid theory at low temperatures, but with large effective masses of the order of 10 or 100  $m_e$ . This shows up as a large resistivity  $A$ -coefficient (Equation 1.3) and large Sommerfeld coefficient. In Fermi liquid theory,  $A \propto m^{*2}$  and  $\gamma \propto m^*$ , so  $A \propto \gamma^2$  is expected. The famous ‘Kadowaki-Woods’ plot (Figure 1.14) confirms that this relationship is roughly obeyed across a large number of heavy fermion materials. More direct experimental evidence for a heavy Fermi liquid in heavy fermion materials comes from quantum oscillation measurements. The temperature dependence of oscillation amplitudes follows the usual  $R_T$  formula (Equation 1.24) but with large a  $m^*$ , so a high  $B/T$  is needed to observe oscillations. For example, in UPt<sub>3</sub> the angular-dependence of oscillation frequencies roughly agree with density functional theory calculations, but with large effective masses ranging from 25 to 90  $m_e$  [46].

The quantum mechanical process behind the formation of the heavy Fermi liquid is similar to the single-impurity Kondo effect. In this effect, a small number of magnetic impurities is introduced into a metal, such as iron impurities in copper, and the conduction electrons hybridise with the magnetic moments through a

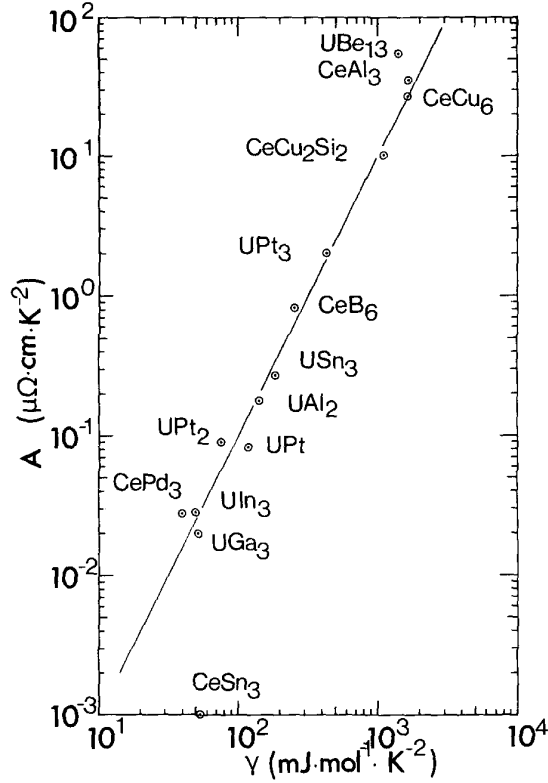


Figure 1.14: Kadowaki-Woods plot of the Fermi liquid  $A$ -coefficient against Sommerfeld coefficient for some heavy fermion materials [45].

many-body quantum mechanical effect. The resulting bound state can be pictured as a localised spin with a cloud of oppositely-polarised conduction electrons, which produces a logarithmic increase in resistivity and decrease in magnetic moment at low temperatures. Heavy fermion materials can be thought of as a *Kondo lattice* system, where a large number of magnetic impurities interact with conduction electrons through the Kondo effect. A  $\text{Ce}^{3+}$  ion has one  $4f$  electron, whereas  $\text{Yb}^{3+}$  has thirteen  $4f$  electrons, or one  $4f$  hole. Therefore Ce- and Yb-based heavy fermion systems can be pictured as a lattice of  $4f$  electrons or holes interacting with a sea of conduction electrons. The result of the Kondo effect in this case is the formation of a narrow band of width  $k_B T^*$  pinned to the Fermi energy (Figure 1.15). At temperatures above  $T^*$ , the  $4f$  states are localised, but at low temperatures, the  $4f$  states are absorbed into the Fermi sea, producing charge carriers with large effective masses  $m^* \propto 1/T^*$ .

Low temperatures  $T \ll T^*$  are required to measure heavy fermion materials, but the narrow width of the bands at the Fermi energy makes them very sensitive to tuning; only a small amount of magnetic field or pressure is required to produce changes in their free energies that are larger than  $k_B T^*$ , and therefore significantly alter their properties. Therefore, heavy fermion materials are excellent systems in

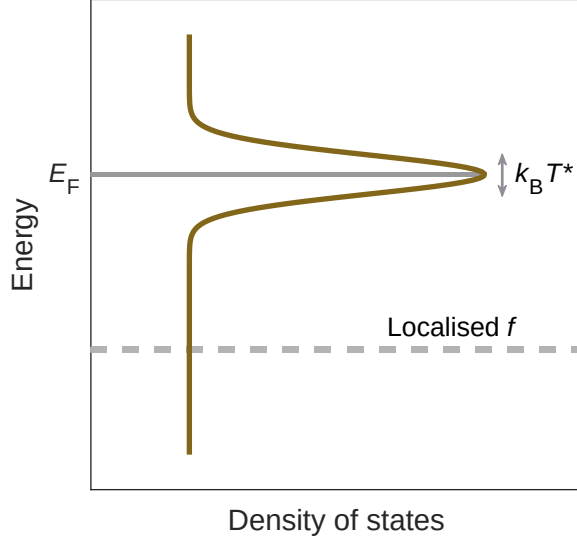


Figure 1.15: Schematic density of states for a heavy fermion material. The dashed line indicates the energy of localised  $f$  states which hybridise with conduction electrons to produce a narrow band at the Fermi energy with width  $k_B T^*$ .

which to investigate quantum phase transitions and unconventional superconductivity.

### 1.5.1 Magnetism and the Doniach phase diagram

The Doniach phase diagram (Figure 1.16) offers a simple way of thinking about the effects of tuning parameters on the electronic properties of heavy fermion materials [47]. In a Kondo lattice system, the Kondo effect competes with a tendency for the localised  $f$  moments to magnetically order. The magnetic ordering is brought about by the *RKKY* (Ruderman-Kittel-Kasuya-Yosida) interaction, where a local  $f$  moment polarises the sea of conduction electrons, which in turn interact with another local  $f$  moment, producing a net ordering interaction between local  $f$  moments. The strengths of the Kondo and RKKY interactions both increase as the strength of the exchange coupling  $J$  between  $f$  and conduction electrons increases, but the RKKY interaction is stronger for low values of  $J$ , and the Kondo interaction is stronger for large  $J$ . Therefore, magnetic order will occur for small values of  $J$  but can be tuned to zero by increasing the exchange coupling, producing a magnetic quantum phase transition at  $J_c$ .

In a Ce materials, pressure increases the degree of overlap between the  $f$  and other orbitals, so the exchange coupling  $J$  increases under pressure. Therefore, magnetic Ce-based heavy fermion materials can often be tuned to quantum phase

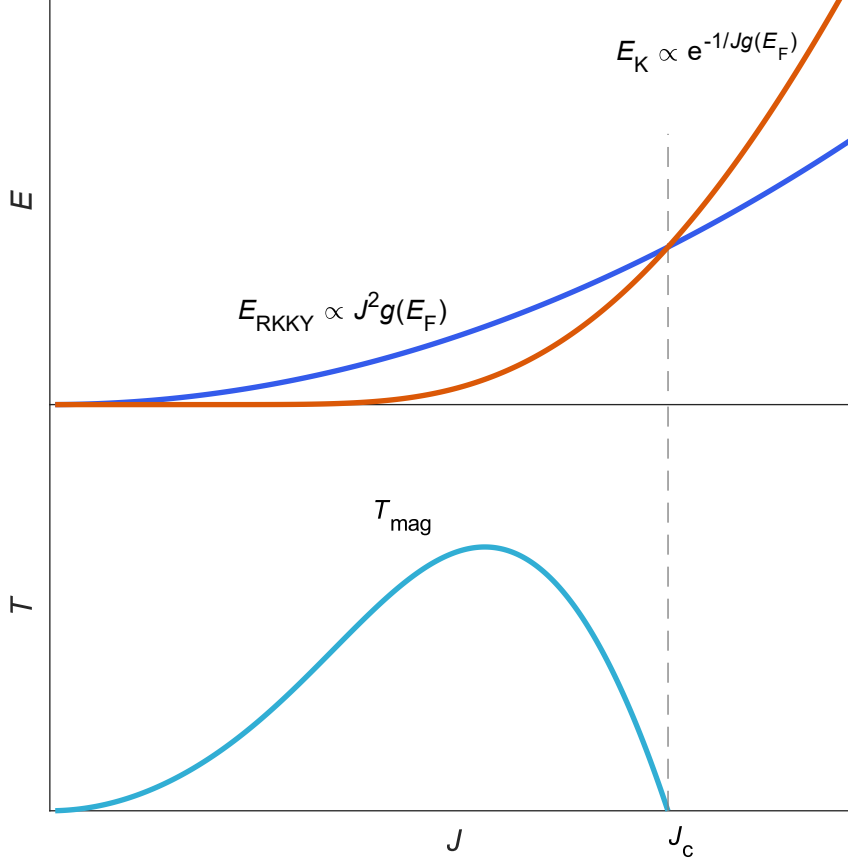


Figure 1.16: Doniach phase diagram. Top: dependence of the RKKY and Kondo interactions on the exchange coupling  $J$  between  $f$  and conduction electrons. Bottom:  $J$ -dependence of the magnetic transition temperature  $T_{\text{mag}}$ .

transitions under pressure, moving them to the right of the Doniach phase diagram. In Yb compounds, the exchange interaction between the thirteen occupied  $f$  states and conduction electrons increases under pressure, so the  $f$  hole's exchange interaction effectively decreases. Therefore, Yb-based materials move to the left of the phase diagram under pressure, and non-magnetic-to-magnetic quantum phase transitions can sometimes be induced.

### 1.5.2 Heavy fermion superconductivity

Unconventional superconductivity has been found at pressure-induced antiferromagnetic QCPs in many Ce-based heavy fermion compounds, such as CePd<sub>2</sub>Si<sub>2</sub>, CeIn<sub>3</sub> [17], CeRhIn<sub>5</sub> [48] and CePt<sub>2</sub>In<sub>7</sub> [49]. In some materials, such as CeCu<sub>2</sub>Si<sub>2</sub> [50] and CeNi<sub>2</sub>Ge<sub>2</sub> [51], no pressure tuning is needed to observe superconductivity because the system is already located very close a quantum critical point at ambient pressure. Superconductivity is rarer in Yb-based heavy fermion materials, but has been

found at very low temperatures in  $\text{YbRh}_2\text{Si}_2$  with  $T_c \approx 2 \text{ mK}$  [52]. Superconductivity has been found in several U-based materials. Many of these, such as  $\text{UGe}_2$  under pressure [53] and  $\text{UTe}_2$  [54, 55], appear to have spin-triplet superconductivity which exists close to or within a ferromagnetic state, with high upper critical fields and even field-induced superconductivity.

A comparison of  $T_c$  values between families of heavy fermion superconductors gives some indication of the different factors determining transition temperatures.  $\text{CeIn}_3$  has a superconducting dome with a low  $T_c = 0.18 \text{ K}$ , whereas the ‘115’ family of  $\text{CeTIn}_5$  ( $T = \text{Co, Rh, Ir}$ ) have the highest  $T_c \approx 2 \text{ K}$  of all Ce-based materials. The 115 crystal structure is related to that of  $\text{CeIn}_3$ , but is tetragonal rather than cubic. The  $d$ -wave gap in the tetragonal structure in Figure 1.5 can match the oscillations of the pairing interaction to minimise energy much more efficiently than in a cubic structure, which may explain the order of magnitude difference in  $T_c$  values [56].  $\text{PuCoGa}_5$  has the same 115 crystal structure but has  $T_c = 18.5 \text{ K}$  enhanced by another order of magnitude. This could be because  $5f$  electrons in Pu are less localised than the  $4f$  electrons in Ce, so bandwidths are larger, and this larger energy scale allows a higher  $T_c$  [57].

# Chapter 2

## Methods

### 2.1 Anvil pressure cells

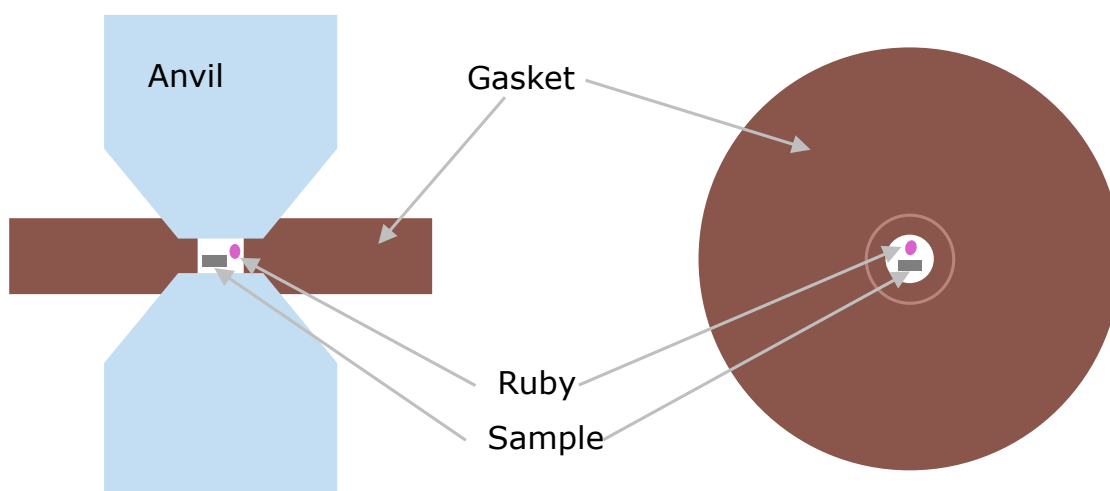


Figure 2.1: Left: side-on diagram of a gasket containing a sample and ruby squeezed between two anvils. Right: top-down view of gasket. The pale ring marks the pre-indented area.

The majority of the work in this thesis has involved the use of an anvil pressure cell. Simple diagrams to illustrate the principle of an anvil cell are shown in Figure 2.1. A gasket, which consists of a metal disc with a hole in the centre, is squeezed between two opposing anvils made of a hard material such as diamond, moissanite or sapphire. A sample to be measured is placed inside the hole, surrounded by a pressure medium. When a force is applied to the anvils, the medium transmits a hydrostatic pressure to the sample, compressing it from all sides. Forces of a few 1000 N are typically applied, and the pressure is determined by the area of the flat culets on the anvils.

Piston cylinder pressure cell are also used in our group to generate pressures

up to 30 kbar, but I have not used them during my PhD. Anvil cells are capable of generating higher pressures than piston cylinder cells, up to  $\sim 100$  kbar in our group, and up to Mbar pressures in other groups using a similar type of pressure cell. The sample space in our anvil cell measurements is around  $0.01 \text{ mm}^3$ , compared to  $10 \text{ mm}^3$  in a piston cylinder cell. This means that only one small sample can be measured at a time, with a length typically less than  $250 \mu\text{m}$ , and it means that certain measurement techniques, such as AC heat capacity or measurements involving large coils, are more difficult. Success rates for anvil cells are not high, at least not for me. However, the pain can be worth it; once a good cell has been set up, its pressure can be increased many times and the same sample can be measured over the course of months or years at a series of different pressures.

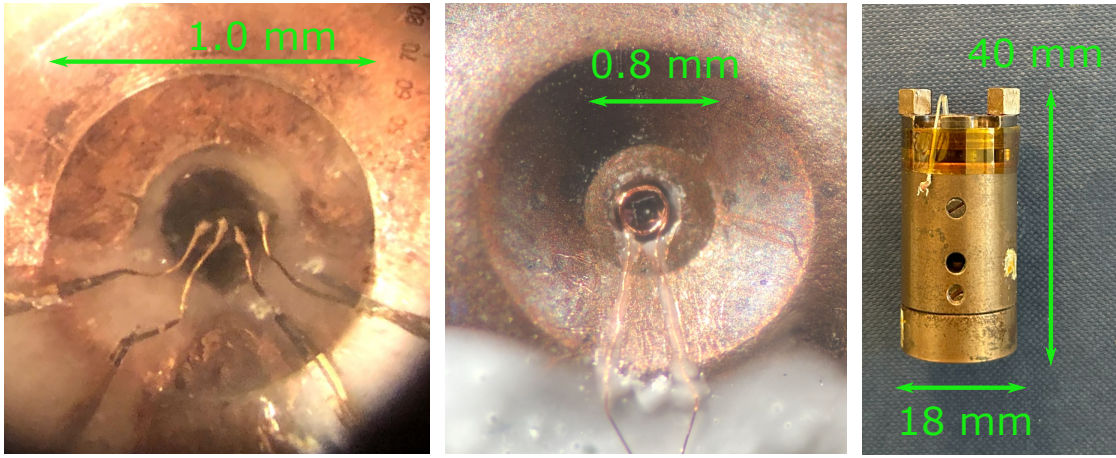


Figure 2.2: Left: sample of  $\text{CeSb}_2$  wired for a resistivity measurement inside a closed anvil cell. Centre: coil containing a sample of  $\text{CeAgSb}_2$  for a TDO measurement. Right: photograph of a closed anvil cell.

Anvil cell techniques in our group have been developed by Dr. Patricia Alireza. Details of the steps involved in setting up a cell can be found in the PhD theses of some recent PhD students in the group, such as Hui Chang [58], Matt Coak [59], Konstantin Semeniuk [60] and Puthipong Worasaran [61]. Our cells are made of Be-Cu, which has a high thermal conductivity at low temperatures. The cell body has a diameter of 18 mm, which can fit in most cryostats (Figure 2.2, right). Moissanite anvils are normally used instead of diamonds, because they are less expensive. The anvils are mounted on pistons, one of which can be pushed with screws to ensure the anvils are aligned. For the measurements in this thesis, I used culet diameters between 0.8 and 1.0 mm, gasket hole diameters half the culet diameter, and sample lengths roughly half the gasket hole diameter. I used Be-Cu gaskets which were pre-indented to ensure that the gasket fits the shape of the anvil, and to thin the gasket to ensure it operates in the stable ‘thin gasket’ regime where it does not

plastically deform under pressure [62]. Then holes were drilled and the gasket was carved with a scalpel and insulated with an alumina-epoxy mixture to protect the wires going into the hole from the high forces applied by the anvils.

For resistivity measurements in an anvil cell, four 10  $\mu\text{m}$ -diameter gold wires are attached to a sample with 6838 silver paint (Figure 2.2, left). Due to the small size of anvil cell samples, other methods for making contacts such as spot-welding are impractical. The contact resistances obtained with silver paint can be high, sometimes more than a few  $\Omega$  which can cause heating at low temperatures. This is especially problematic in an anvil cell, because the sample is surrounded by an insulating pressure medium, and the sample is only cooled through the gold wires. Contact resistances can sometimes be improved by pulsing them with the power supply of a spot welder, but this is a risky procedure which is equally likely to make contacts worse. The gold wires are attached to two twisted pairs of copper wires on the gasket, which are heat sunk around the cell body with PTFE tape. An AC current at a frequency below 100 Hz is passed through the outer two contacts, and the voltage across the inner contacts is measured with a lock-in amplifier to determine the sample's resistance.

AC magnetic susceptibility measurements or tunnel diode oscillator (TDO) measurements are performed in anvil cells using a micro-coil placed in the gasket hole (Figure 2.2, centre). A typical micro-coil has a diameter of 250  $\mu\text{m}$ , 8 turns and is made from wire with a thickness of 12  $\mu\text{m}$ . With practice, these coils can be made by winding the wire around a drill bit. For AC susceptibility measurements, the micro-coil in the hole is used as a pick-up coil and an additional 130-turn drive coil is placed on the gasket surrounding the hole. The current in the drive coil is modulated at a frequency of a few kHz, and the voltage induced in the pick-up coil, which includes a contribution from the sample's susceptibility, is measured with a lock-in amplifier. Both coils are connected to twisted pairs of copper wires which are heat sunk around the cell body. This technique was developed in our group by Patricia Alireza, initially using an additional two coils to remove the background signal [63], but these coils are no longer used due to the difficulty involved in preparing them. By placing the coil inside the gasket hole alongside the sample, a good filling factor is achieved, so a large signal from the sample can be achieved, despite the coil's small size. With this technique, superconducting and ferromagnetic transitions can be seen. Antiferromagnetic transitions and quantum oscillations have been observed in the past using the additional background-subtraction coils [64–66]. For TDO measurements, the outer drive coil is not included and the inner pick-up coil is connected to a coaxial cable rather than twisted copper wires.

The pressure is measured by placing a small piece of ruby inside the hole alongside

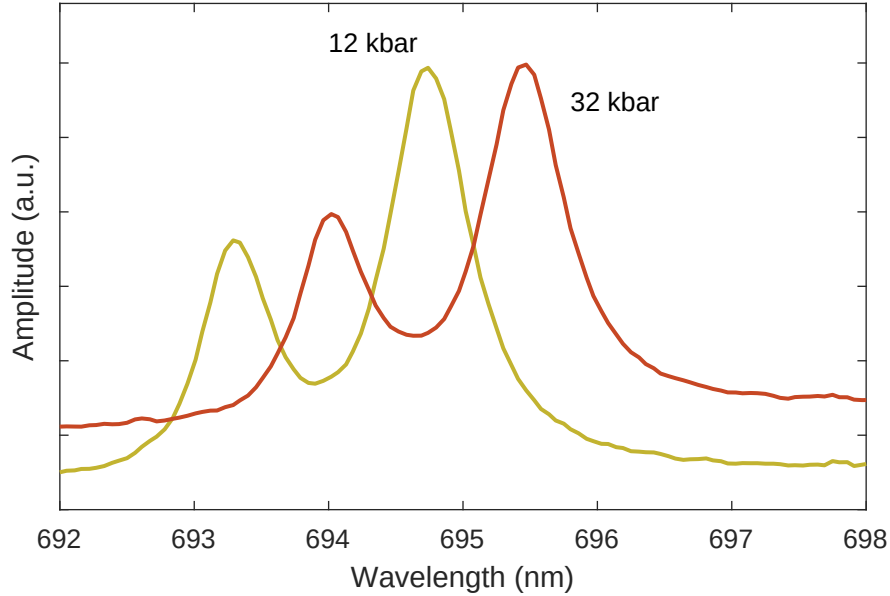


Figure 2.3: Room-temperature ruby fluorescence spectra at 12 and 32 kbar

the sample. When the ruby is excited by a 532 nm laser through the transparent anvils, two peaks are seen in the fluorescence spectrum at 693 and 694 nm. Under pressure, the peaks shift to higher wavelengths, so a measurement of the ruby spectrum can be used to determine the pressure (Figure 2.3). Ruby fluorescence measurements in our group are performed at room temperature. The thermal contraction of the different materials making up a pressure cell can in theory cause an increase or decrease in pressure upon cooling. However, AC susceptibility measurements where a piece of lead was placed inside the coil suggest that the change in pressure is negligible, at least in the range of pressures in this thesis.  $\text{CeSb}_2$  data from anvil cells and piston cylinder cells whose pressures were determined at low temperatures agree reasonably well (see Chapter 4), suggesting that the pressure change in the anvil cells was negligible.

As the pressure in a cell is increased, the pressure inside typically becomes less hydrostatic, causing pressure gradients and uniaxial stresses across the hole. The pressure where this becomes significant depends on the pressure medium used. One of the most important factors in determining this is the room-temperature solidification pressure [67]. For the  $\text{CeSb}_2$  resistivity measurements in Chapters 3 and 4 I used glycerol, which remains hydrostatic up to 50 kbar [68], and is easy to use because it is not volatile at room temperature and does not damage 6838 contacts. More hydrostatic conditions can be achieved using a 4:1 methanol-ethanol or 1:1 pentane-isopentane mixture, and the best conditions are achieved with argon or helium, but there are additional difficulties that come with using each of these pressure

media.

## 2.2 Tunnel diode oscillator

The tunnel diode oscillator (TDO) is a technique which can be used to measure phase transitions and quantum oscillations in anvil pressure cells. It has been successfully used in our group in the past for measurements of pressure-metallised NiS<sub>2</sub> [58, 60, 69, 70], and I have used it in measurements of YbPtBi, which will be presented in Chapter 5, and CeAgSb<sub>2</sub> in Chapter 6. A detailed description of the circuit theory behind the TDO circuit is available in Hui Chang's PhD thesis [58]. Other good resources are the manual by Catalin Martin [71] and the PhD thesis of Thomas Coffey [72].

### 2.2.1 $LC$ circuit

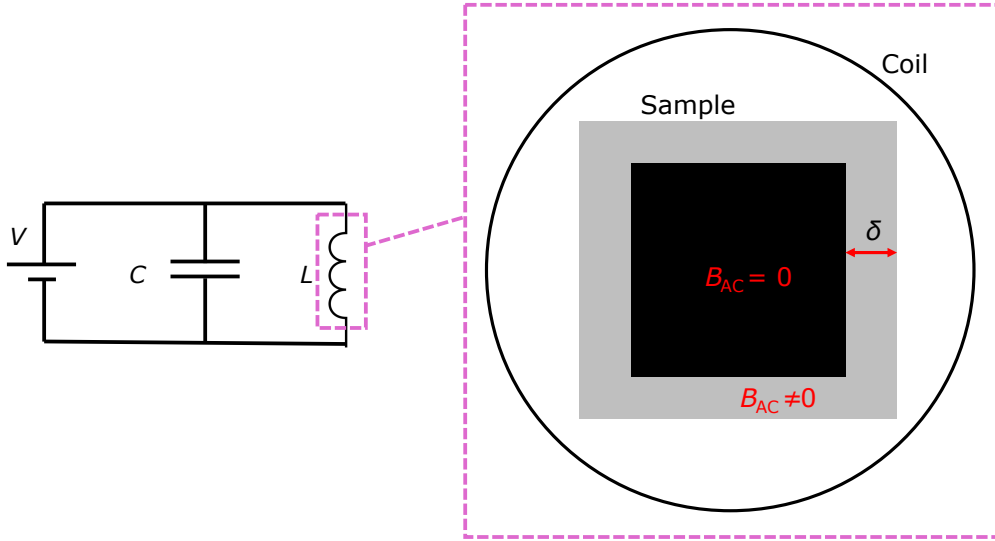


Figure 2.4: Left: simple  $LC$  circuit diagram. Right: Diagram of sample inside a coil.

The TDO circuit is an  $LC$  circuit, like the simple circuit shown in Figure 2.4. A capacitor and inductor powered by a DC voltage will oscillate at a frequency

$$f = \frac{1}{2\pi\sqrt{LC}}. \quad (2.1)$$

If a sample is placed inside the coil, the inductance of the coil, and therefore the resonant frequency of the circuit, will change when the properties of the sample change. For a metallic sample, the inductance of the coil depends on both the

sample's magnetic susceptibility and its resistivity, because its skin depth depends on its resistivity:

$$\delta = \sqrt{\frac{\rho}{\pi f \mu}}. \quad (2.2)$$

A typical sample resistivity of  $5 \mu\Omega \text{ cm}$  with a resonant frequency of 100 MHz results in a skin depth of  $10 \mu\text{m}$ , which is smaller than the size of most samples, even in an anvil cell. Therefore, the majority of the sample (the black area in Figure 2.4) is screened from the coil's AC magnetic field, so has a susceptibility  $\chi = -1$ . For a square sample with sides of length  $a$ , only an area  $4a\delta$  around the outside of the sample has a non-zero field. Therefore, if a sample in a coil has a filling factor  $\eta$ , the total inductance of the coil is

$$L = L_0 \left( 1 + \eta \left( -1 + \frac{4\delta}{a} \chi \right) \right), \quad (2.3)$$

where  $L_0$  is the inductance of an empty coil and  $\chi$  is the susceptibility of the sample. The inductance will change by

$$\Delta L \approx \frac{2L_0\eta\chi}{a} \sqrt{\frac{2\rho}{\mu f}} \left( \frac{\Delta\chi}{\chi} + \frac{\Delta\rho}{2\rho} \right) \quad (2.4)$$

when the sample's resistivity and susceptibility change by  $\Delta\rho$  and  $\Delta\chi$  respectively, assuming  $\chi \ll 1$ . This change in inductance will cause the frequency of the circuit to change by

$$\Delta f \approx -\frac{1}{2} \frac{f}{L} \Delta L, \quad (2.5)$$

so increases in  $\rho$  or  $\chi$  will cause a decrease in frequency. In this simplistic model I have treated the resistivity as a scalar  $\rho$ , but in reality, the resistivity of a single-crystalline sample is an anisotropic tensor with Hall components in a magnetic field. Therefore, the resonant frequency of an oscillator circuit measures a mixture of longitudinal and Hall resistivities [73].

Resonant frequencies are typically around 100 MHz, and noise levels of a few Hz or lower are achievable, giving a signal-to-noise ratio of  $10^8$ . This high sensitivity makes TDO a powerful technique for detecting phase transition and quantum oscillations. Contacts do not need to be made to samples, which is an advantage for small or irregularly shaped samples, and it can be extended to high pressures using a micro-coil inside an anvil cell. There are some difficulties associated with using micro-coils in oscillator circuits, as I will describe later in this section, but the technique has been successfully used by our group for quantum oscillation measurements up to 100 kbar [70], and by the group in Tallahassee up to 250 kbar [74].

This simple circuit shown in Figure 2.4 cannot produce sustained oscillations

Tunnel diode

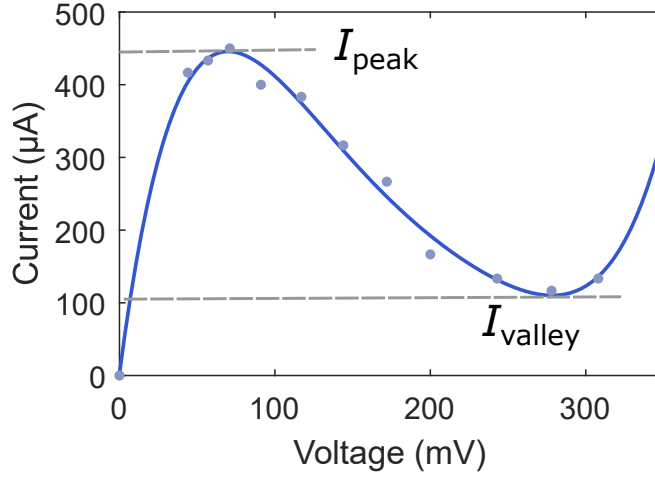


Figure 2.5: Left: tunnel diode circuit symbol. Right:  $I$ - $V$  curve of a tunnel diode.

because the resistance of the wires and coil quickly damp the amplitude of oscillations to zero. The TDO circuit overcomes this problem using a tunnel diode, a semiconductor device with a negative  $I$ - $V$  slope at some voltages (between 70 and 270 mV in Figure 2.5). This negative slope can ‘cancel out’ the positive resistances in the circuit, to produce sustained oscillations. If the slope is most negative at a voltage  $V_0$ , the current around this point can be approximated as

$$I = I_0 - g(V - V_0) + b(V - V_0)^3 \quad (2.6)$$

where  $g > 0$  and  $b > 0$  are constants which vary between tunnel diodes.

Different tunnel diodes have different peak currents  $I_{\text{peak}}$  and valley currents  $I_{\text{valley}}$ , determined by the cross-sectional area of the semiconductor  $p$ - $n$  junction inside them. A more powerful diode (i.e. a diode with a larger  $I_{\text{peak}}$  and so a larger power dissipation) will typically have a larger  $g$ . Tunnel diodes can be easily damaged with heat from a soldering iron or static electricity. A lightly damaged diode usually displays a higher valley current, which reduces  $g$  and makes it less useful. When a diode is severely damaged, the negative region completely disappears, effectively turning it into a resistor.

## 2.2.2 Circuit components

The full TDO circuit is shown in Figure 2.6. It is split into four sections, which are connected with coaxial cables. The inductor  $L$  is a coil containing a sample to be measured. The frequency of the circuit is determined by the inductor and capacitor

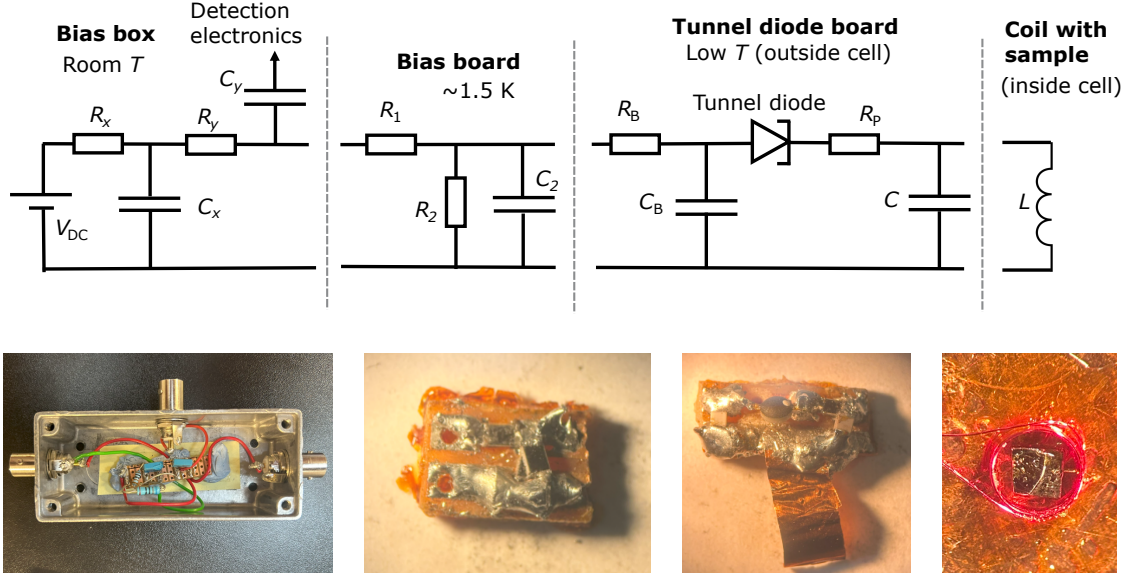


Figure 2.6: Top: tunnel diode oscillator circuit diagram split into four sections which are connected by coaxial cables. Bottom: photographs of bias box, bias board, tunnel diode board and coil containing YbPtBi sample (not inside a pressure cell).

on the right of the circuit:

$$f = \frac{1}{2\pi\sqrt{LC}}. \quad (2.7)$$

The bypass capacitor  $C_B$  helps to isolate the  $LC$  circuit on the right from any fluctuations in left side of the circuit which could cause noise. The parasitic resistor  $R_P$  makes it easier to achieve oscillations. The bias resistors  $R_1$  and  $R_2$  act as a potential divider to ensure the diode operates in the region of its  $I$ - $V$  curve with a negative slope. The capacitor  $C_2$  and the resistor  $R_B$  are sometimes included to impedance match the circuit to a coaxial cable, but are usually left out.  $R_x$  and  $C_x$  act as a low-pass filter to remove noise from the DC voltage  $V_{DC}$ , which is produced by a variable DC voltage source. The AC oscillating signal produced by the circuit is fed out through a capacitor  $C_y$  to detection electronics.

To make the circuit ‘ring’, two conditions must be satisfied. Firstly, the slope of the diode’s  $I$ - $V$  curve must be sufficiently steep to cancel out the positive resistance of the coil. An analysis of the circuit gives the condition

$$\frac{1}{g} < \frac{L}{R_L C} + R_P, \quad (2.8)$$

where  $R_L$  is the resistance of the coil [58]. At low temperatures,  $R_L$  decreases significantly, and  $g$  increases a little, so it is easier to satisfy this condition. Therefore, a circuit which does not ring at room temperature can sometimes ring at low temper-

atures. This can be tested before a measurement by dipping the circuit in a bucket of liquid nitrogen.

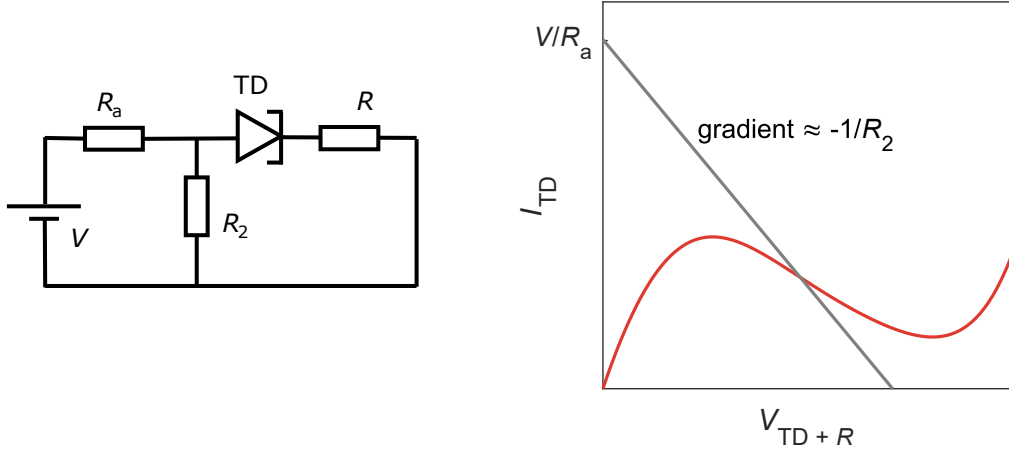


Figure 2.7: Left: DC equivalent circuit of a tunnel diode oscillator. Right:  $I$ - $V$  curve of the series combination of the tunnel diode and  $R$  and load line to determine the operating point on the curve.

Secondly, the diode must be biased by the resistors to operate in the negative part of its  $I$ - $V$  curve where the condition 2.8 can be satisfied. The condition to achieve biasing can be worked out with a load line analysis. The circuit on the left of Figure 2.7 is the TDO DC equivalent circuit, with  $R_a = R_x + R_y + R_1$  and  $R = R_B + R_P + R_L$ . The combined  $I$ - $V$  curve of the tunnel diode and  $R_b$  is shown by the red curve on the right of the figure. The operating point on this curve can be determined by considering the currents through  $R_2$  and  $R_a$ :

$$I_2 = \frac{V_2}{R_2} = \frac{V_{TD+R}}{R_2}, \quad (2.9)$$

$$I_a = \frac{V_a}{R_a} = \frac{V - V_{TD+R}}{R_a}. \quad (2.10)$$

Therefore,

$$I_{TD} = \frac{V - V_{TD+R}}{R_a} - \frac{V_{TD+R}}{R_2} \quad (2.11)$$

$$\approx \frac{V}{R_a} - \frac{V_{TD+R}}{R_2}. \quad (2.12)$$

because  $R_2 \ll R_a$ . This equation gives a straight load line with negative gradient, and the operating point on the  $I$ - $V$  curve is given by its intersection with the red curve. As the DC voltage is increased, the  $I$ -intercept of the load line increases, and the operating point moves to the right of the  $I$ - $V$  curve. For a certain range

of voltages, the operating point is in the part of the curve with a negative slope, so it may be possible to fulfil the condition 2.8 for oscillations. It can be seen from Figure 2.7 that it is only possible to sit in the negative region of the  $I$ - $V$  curve if the load line is steeper than the combined  $I$ - $V$  curve of the diode and  $R$ . A more detailed circuit analysis [58] shows the precise condition to achieve this is

$$\frac{1}{g} > R_2 + R_B + R_P + R_L. \quad (2.13)$$

If this condition is not met, the operating point will jump from the left of the peak to the right of the valley when  $V_{DC}$  is increased. Therefore it will not be possible to operate the diode in its negative region, so it will not be possible to make the circuit ring. From 2.8 and 2.13, it is clear that it is easier to make a circuit ring with a more powerful diode, but it is more difficult to bias the circuit.

There is some leeway in the precise values of the resistances and capacitances in the TDO circuit; as long as the two conditions 2.8 and 2.13 are satisfied, the circuit should ring. For a given coil, the choice of  $C$  determines the resonant frequency of the circuit. Resistances of  $50\,\Omega$  are sometimes used in the circuit for impedance matching to the characteristic impedance of the coaxial cables [75]. The value of  $C_B$  affects the size of the signal that is fed into the detection electronics. It should be large enough to isolate the  $LC$  circuit from room-temperature fluctuations, but if it is too large the signal becomes too small to measure. It is also important to consider that coaxial cables contribute significant inductances and capacitances. A flexible copper coaxial cable from Cryoandmore seems to have a capacitance of  $0.5\,\text{pF cm}^{-1}$  and an inductance of  $3\,\text{nH cm}^{-1}$ . For small coils, a long length of cable between  $C$  and  $L$  can sometimes make it easier to achieve oscillations, because it increases the total ratio  $L/C$  of the  $LC$  part of the circuit.

To give an idea of typical values, these are the components I used for one par-

ticular anvil cell measurement:

$$R_x = 680 \Omega$$

$$C_x = 150 \text{ nF}$$

$$R_y = 1 \text{ k}\Omega$$

$$C_y = 1 \text{ nF}$$

$$R_1 = 102 \Omega$$

$$R_2 = 58 \Omega$$

$$C_B = 39 \text{ pF}$$

$$\text{Diode: M-Pulse 1603 } (I_{\text{peak}} \sim 500 \mu\text{A})$$

$$R_P = 77 \Omega$$

$$C = 39 \text{ pF}.$$

### 2.2.3 Wiring

The low-temperature part of the TDO circuit is usually split into a four sections, as shown in Figure 2.6. The ‘bias box’ resistors and capacitors are contained within a diecast box next to DC voltage supply and the detection electronics. The bias resistors dissipate around 2 mW of heat, which is too large for a He-3 system or dilution refrigerator. Therefore the bias board is usually placed somewhere warmer with a large cooling power, such as a 1K pot. The tunnel diode board is placed close to the coil to avoid a long length of coaxial cable between  $L$  and  $C$ , which would introduce noise and a large background inductance. Around 50  $\mu\text{W}$  of heat is dissipated in a tunnel diode, which may raise the base temperature of a He-3 system or dilution refrigerator. Heating can be reduced by using a less powerful diode, although that may not be possible when using a small coil. Long coaxial cables connecting each section of the TDO circuit should be made of copper because it has a low resistance which prevents attenuation of the signal. More resistive stainless steel coaxial cables can be used for short distances where heat leak is particularly problematic, such as between the 1K pot and He-3 pot of the He-3 probe to be described in Section 2.3.1.

At room temperature, the AC signal is fed into a series of components for measurement of the resonant frequency. The signal is first passed through two RF amplifiers to make it large enough to measure. Then the signal at a frequency  $f$  is mixed with the signal from a local oscillator at  $f_{\text{LO}}$ , to produce frequencies of  $f + f_{\text{LO}}$  and  $|f - f_{\text{LO}}|$ . This signal is passed through a band-pass or low-pass filter to isolate the frequency at  $|f - f_{\text{LO}}|$ , which is then measured with a frequency counter.

The local oscillator frequency is chosen so that  $|f - f_{\text{LO}}|$  falls within the passband of the filter. A third amplifier, which should be placed between the filter and the frequency counter, is sometimes required if the signal is small.

#### 2.2.4 Noise

One of the main sources of noise in TDO measurements is fluctuations in the capacitance of the  $LC$  part of the circuit. This could be caused by vibrations of wires or bubbles in helium surrounding the circuit. To minimise vibrations, all wires should be firmly taped to a probe or completely wrapped in PTFE tape. Grounding the low-temperature part of the circuit to the probe also seems to reduce this source of noise by short-circuiting stray capacitances. This can be achieved with a piece of copper foil soldered to the ground of the tunnel diode board (Figure 2.6, bottom) and fixed against the probe or pressure cell body with PTFE tape. However, it is not always possible to do this if the low-temperature part of the probe is not made of metal. Grounding the circuit on the bias board or at the top of a probe seems to be less effective in reducing noise.

Voltages in the circuit can also be a source of noise. For example, voltages are induced in the circuit when sweeping a magnetic field, or there may be noise in the DC voltage source powering the circuit. This source of noise can be reduced by choosing an appropriate bias voltage. The circuit's resonant frequency often displays a stationary point as a function of  $V_{\text{DC}}$ , i.e. there is a value of  $V_{\text{DC}}$  where  $df/dV_{\text{DC}} = 0$ . At this voltage, any voltage noise should not translate into frequency noise. However, the value of this voltage often changes strongly with temperature and field, and in practice the noise is sometimes lower at a different  $V_{\text{DC}}$ , perhaps because the amplitude of the signal is bigger there.

Another source of noise is fluctuations in the temperature of the sample. This tends to be a problem when using a heater controlled by a PID loop with badly-chosen  $P$ ,  $I$  and  $D$  values or when the circuit is in contact with exchange gas. The heat dissipated by the tunnel diode can cause oscillations in the pressure of the exchange gas which make the temperature drift around. Temperature noise is more severe above base temperature where  $d\rho/dT$  is larger so  $|df/dT|$  is larger. In quantum oscillation measurements, the amplitude of the signal decreases at higher temperatures, so it is annoying that the signal often also becomes noisier.

Using a narrower band pass filter in the detection electronics sometimes reduces noise. However, this means that the signal is more likely to drift outside of the band-pass range, so the local oscillator frequency needs to be adjusted during measurements. In some measurements using a Keysight frequency counter, the noise

could be improved by mixing down to low frequency, so that a frequency below 1 MHz was fed into the frequency counter. The measured noise can often be improved by using a longer gate time on the frequency counter, but this comes at the expense of fewer data points.

Other ideas that have been suggested to improve noise include mixing and filtering the signal more than once, designing the TDO circuit to be a ‘marginal oscillator’ that only just exceeds the condition 2.8 for oscillations, or powering amplifiers at 14 V instead of the usual 15 V. These ideas may warrant further investigation, but in my experience, they do not seem to make much difference to the noise.

### 2.2.5 Difficulties of using TDO with anvil cells

There are several additional difficulties that come with using TDO in an anvil cell. Firstly, the small inductance of the microcoil makes it difficult to fulfil the condition 2.8 for oscillations. This can be overcome by using a more powerful tunnel diode, but that will generate more heat, which may limit the base temperature of the measurement. Secondly, the inductance of the coil is often small enough that it is comparable to the inductance of the coaxial cable connecting  $L$  and  $C$ . The inductance of a typical 8-turn, 250  $\mu\text{m}$ -diameter coil made from 12  $\mu\text{m}$  wire is calculated to be 40 nH, which could easily be smaller than the inductance from a few cm of coaxial cable. Therefore the sample only contributes a very small amount to the total inductance, so the frequency change from phase transitions or quantum oscillations in the sample becomes very small. These two problems become particularly significant when measuring metals with low resistivities because they have a small skin depth, so the vast majority of the sample does not contribute to the coil’s inductance. Low scattering rates are needed to observe quantum oscillations, but low scattering rates mean small skin depths in metals with high carrier concentrations and therefore small quantum oscillation signals. TDO is most effective for measurements of metals with low carrier concentrations which can have a low scattering rate but still a large resistivity, such as YbPtBi (see Chapter 5) or underdoped  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  [74].

As the pressure in a cell is increased, it sometimes becomes more difficult to make a TDO circuit ring. A decrease in the coil’s resistance can sometimes be seen at high pressures, suggesting that the coil’s turns become short-circuited to each other. A damaged coil will sometimes ring in zero magnetic field, but not in high fields. This phenomenon is not fully understood, but it might be related to the magnetoresistance of the coil, which makes it more difficult to satisfy the condition 2.8. It is possible to push this effect to slightly higher fields by adding more coaxial

cable between the cell and the tunnel diode board, to increase the overall inductance of the circuit, but even with a very long length of coaxial cable, it is often not possible to measure in high fields.

Another problem is that the sample in an anvil cell is surrounded by a thermally insulating pressure medium, making it difficult to cool. In a TDO measurement, eddy current heating from the RF magnetic field inside the coil could heat the sample. Heating could also arise from the current passing through the coil wire, which is thin and therefore has a reasonably large resistance of around  $3\,\Omega$  at room temperature. It is difficult to obtain quantitative estimates of the sizes of heating effects. Moissanite or diamond anvils have a good thermal conductivity compared to most insulators, but are worse than metals at sub-kelvin temperatures, which could cause problems in cryostats where the cell is in vacuum. In a cryostat where the cell is immersed in He-3, the anvils are cooled, but the degree of thermal contact between the anvils, sample and coil is unclear. Heating at low temperatures is problematic for quantum oscillation measurements in heavy fermion materials, as it can prevent frequencies with heavy masses from being observed, and even when frequencies are seen, can lead to a systematic underestimate of their masses. I attempted to overcome the heating problem by attaching a gold wire between the sample and the gasket to cool the sample. However I found that the cooling wire would usually become short circuited to the coil when the cell was closed, which would result in the coil becoming connected to the cell, and perhaps the whole probe. It is sometimes possible to reduce eddy current and coil wire heating by using a less powerful diode, as this reduces the size of the current flowing through the coil. A lower resonant frequency would also reduce eddy current heating. However, it may not be possible to make these changes while still satisfying the condition 2.8 for oscillations, especially if the coil becomes damaged under pressure.

## 2.3 Cryostats and Magnets

The low temperatures needed to study correlated electron materials are typically produced using helium. He-4 has a boiling point of 4.2 K, so anything immersed in liquid He-4 will be held at that temperature by the latent heat of evaporation. By pumping on the vapour above liquid He-4, the most energetic particles are removed, so the remaining liquid is cooled. This evaporative cooling process can cool He-4 to 1.5 K, or even lower. Lower temperatures can be achieved using the lighter He-3 isotope, which has a boiling point of 3.2 K and can be cooled to 0.3 K with evaporative cooling. Even lower temperatures down to a few mK can be achieved in a dilution refrigerator using a mixture of He-3 and He-4. In recent years, dry systems

which use helium contained within a closed cycle have become more popular due to the rising costs of helium. These systems can achieve temperature down to a few K by compressing and expanding the gas in a Gifford-McMahon or pulse tube cooler.

Magnetic fields are often produced using superconducting magnets. The field is produced by passing a current through a coil of superconducting wire, which sits in a bath of liquid helium to keep it below its critical temperature. Fields up to  $\sim 20$  T are achievable with these magnets, depending on the critical fields and currents of the superconducting material. Higher fields are produced using resistive magnets at specialised high-field laboratories, which will be discussed in Section 2.3.5

### 2.3.1 He-3 probe

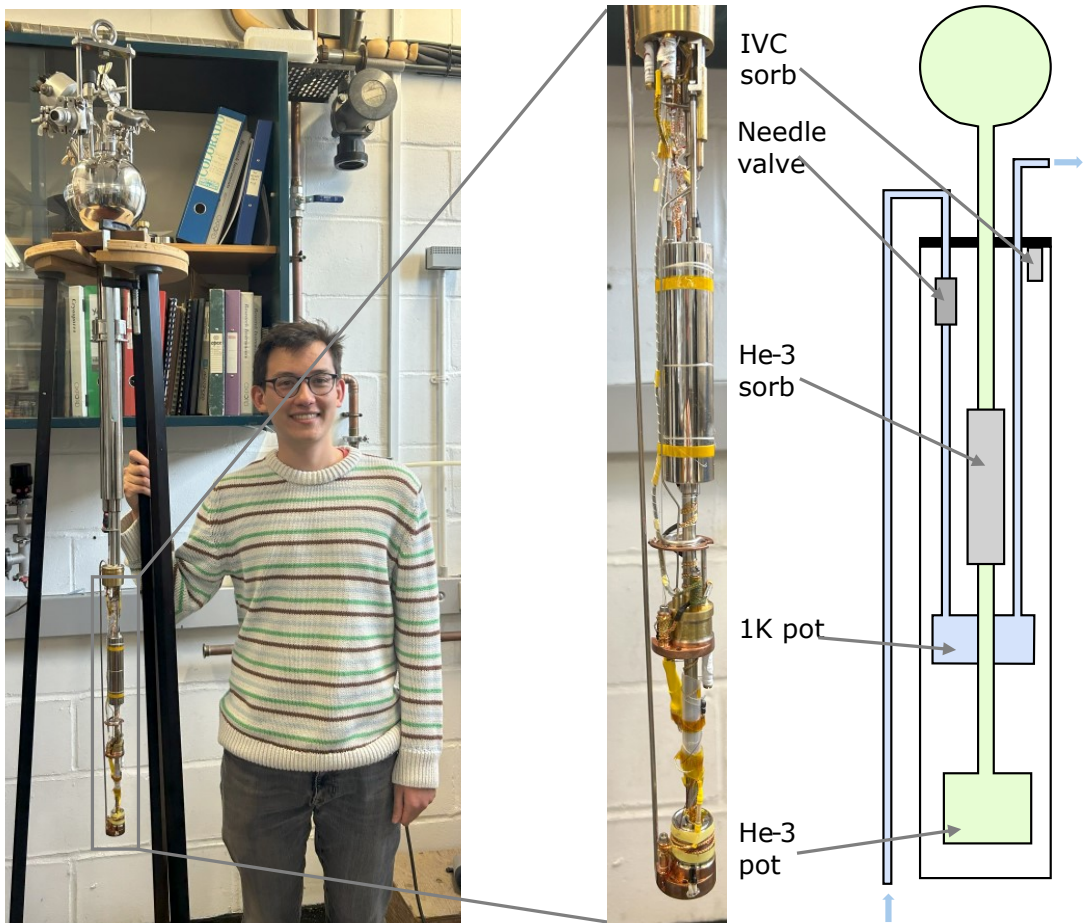


Figure 2.8: Left: photograph of He-3 probe with human for scale. Centre: enlarged photograph of the low-temperature part of the He-3 probe. Right: Schematic diagram of He-3 probe.

The TDO measurements on YbPtBi in Chapter 5 were performed with a He-3 probe from ICE Oxford (Figure 2.8). The probe is designed to be inserted into a storage dewar of liquid He-4. He-4 can be drawn through a capillary from the

dewar into a ‘1K pot’, where it is pumped on with a mechanical pump to produce temperatures of 1.5 K. He-3 is contained in a closed volume with a sorb which absorbs He-3 gas when cold and releases it when heated. The He-3 released by the sorb is condensed by the 1K pot, and liquid collects in the He-3 pot. When condensation begins, the high vapour pressure above the liquid He-3 creates a good thermal link between the He-3 pot and the 1K pot, so the He-3 pot cools to 1.5 K. After all of the He-3 has condensed, the He-3 sorb heater is turned off. As the sorb cools down, it pumps on the He-3 in the He-3 pot, reducing the temperature of the pot to a base temperature of 0.3 K. Temperatures between 0.3 and 1.5 K can be achieved by controlling the temperature of the He-3 sorb, which determines how strongly it pumps on the He-3. Samples or pressure cells are in vacuum during this process, enclosed within an inner vacuum can (IVC), and are cooled through thermal contact with the He-3 pot. There is a second sorb with a heater in the IVC to control the amount of He-4 exchange gas inside the IVC, or to produce a vacuum in the IVC when the sorb is cold.

### 2.3.2 15 T system

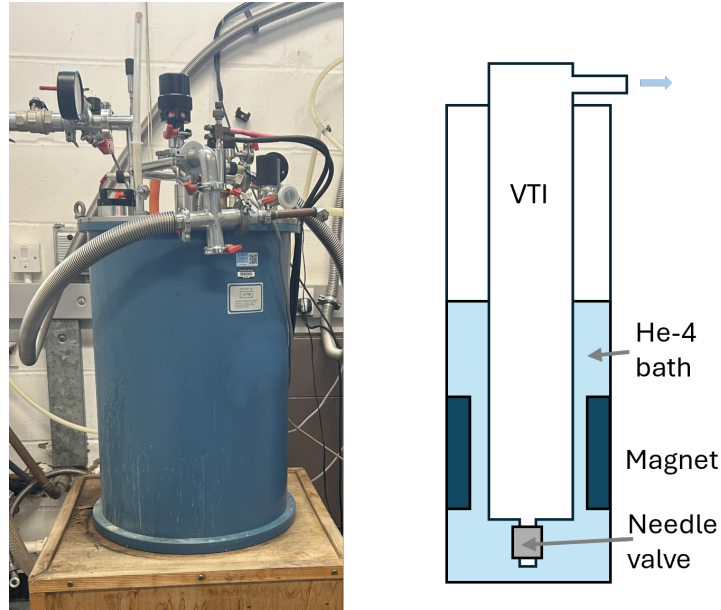


Figure 2.9: Left: photograph of 15 T system. Right: Schematic diagram of the 15 T system.

The 15 T system consists of a superconducting magnet with a He-4 variable temperature insert (VTI) (Figure 2.9). The superconducting magnet can produce magnetic fields up to 13 T under normal operating conditions. Higher fields up to 15 T can be produced using a lambda fridge, which pumps on the helium surrounding

the magnet to lower its temperature and increase its critical field. However, this process increases the helium consumption of the system. Samples to be measured are placed on a probe and inserted into the VTI. Helium is pumped from the bath into the VTI through a needle valve to achieve temperatures down to 1.5 K. The VTI is connected to the pump through a mechanical manostat, which produces a constant pressure in the VTI to stabilise at temperatures between 1.5 and 4.2 K. A rotation probe is available for the 15 T system to rotate samples in the magnetic field.

I performed some measurements using an ICE Oxford He-3 probe inside the 15 T system to combine the low temperatures and high magnetic fields of the two devices. Although the probe is designed to be inserted into a storage dewar, it can be operated in the 15 T system by filling the VTI with liquid helium to mimic the conditions in a dewar. This can be achieved by setting a constant pressure of 950 mbar on the manostat with the needle valve kept slightly open. Once the VTI has been filled with liquid and a sensible equilibrium has been reached, the He-3 probe can be operated as described in Section 2.3.1 for temperatures between 0.3 and 1.5 K. For temperatures between 1.5 and 4.2 K, the temperature of the He-3 probe can be controlled using the 15 T system's VTI and manostat. To ensure thermal contact between the sample in the He-3 probe and the VTI, the IVC needs to be filled with He-4 exchange gas and the IVC sorb needs to be heated. For temperatures above 4.2 K, a heater needs to be used, either on the He-3 probe or in the VTI.

### 2.3.3 DMS

The Dryogenic Measurement System (DMS) uses the process of adiabatic demagnetisation to cool to low temperatures down to 0.1 K. This process is illustrated in Figure 2.10 for the paramagnetic salt, chromium potassium alum (CPA), which is used as a coolant in the DMS [76]. First, a magnetic field is applied to the salt while it is kept at a constant temperature through contact with a thermal sink. During magnetisation, the magnetic moments in the salt align with the field, so its entropy decreases. Next, the salt is thermal disconnected from the sink, so its entropy is now constant, and the salt is adiabatically demagnetised. During this process, the salt's temperature decreases, with a final temperature which depends on the starting temperature and the size of the magnetic field. A 6 T superconducting magnet is used for demagnetisation in the DMS from a starting temperature of 4 K. Under these conditions, CPA can theoretically reach temperatures of 20 mK, although the lowest temperature achieved during the measurements in this thesis was 90 mK.

A sorb and helium exchange gas are used in the DMS as a heat switch, to

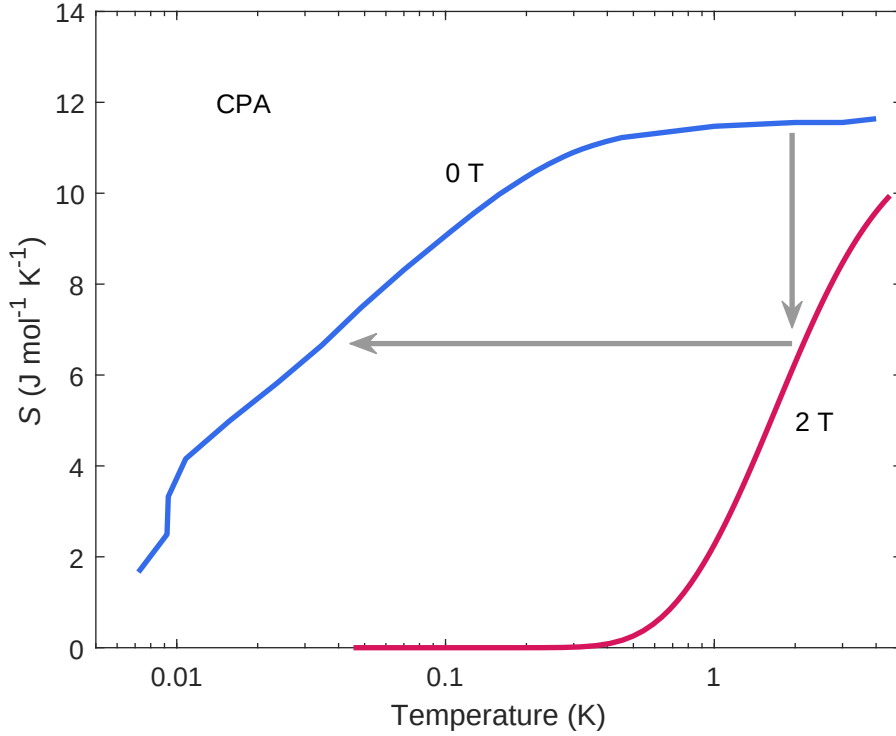


Figure 2.10: Entropy of chromium potassium alum (CPA) at 0 and 2 T. Data is from Betts [76]. Arrows indicate the processes of isothermal magnetisation and adiabatic demagnetisation.

thermally connect or disconnect the salt pill from the 4 K surroundings, which are cooled by a pulse tube cooler. There is a ‘guard pill’ of  $\text{YbPt}_2\text{Sn}$  above the CPA pill which absorbs most of the heat travelling down the probe to improve the hold time and base temperature [77]. The CPA pill is connected by copper to the low-temperature sample stage which hangs below it. A second 6 T superconducting magnet can apply a magnetic field to the sample. There are two thermometers on the low-temperature stage, a Cernox thermometer for temperatures above 0.7 K and a ruthenium oxide thermometer which can measure temperatures below 6.8 K down to the base temperature. These thermometers are located between the two magnets, where the field is zero, to ensure that they are not affected by magnetoresistance. After the system has been demagnetised to base temperature, a heater can be used to warm it to 9 K.

A low-temperature transformer is located on the DMS probe at 4 K, shielded by a superconducting lead box. By amplifying the signal at low temperatures, before some noise is introduced to the signal, a higher signal-to-noise ratio is achieved compared to the use of room temperature transformer. The peak-to-peak noise with the low-temperature transformer is typically around 10 nV after  $\times 100$  amplification

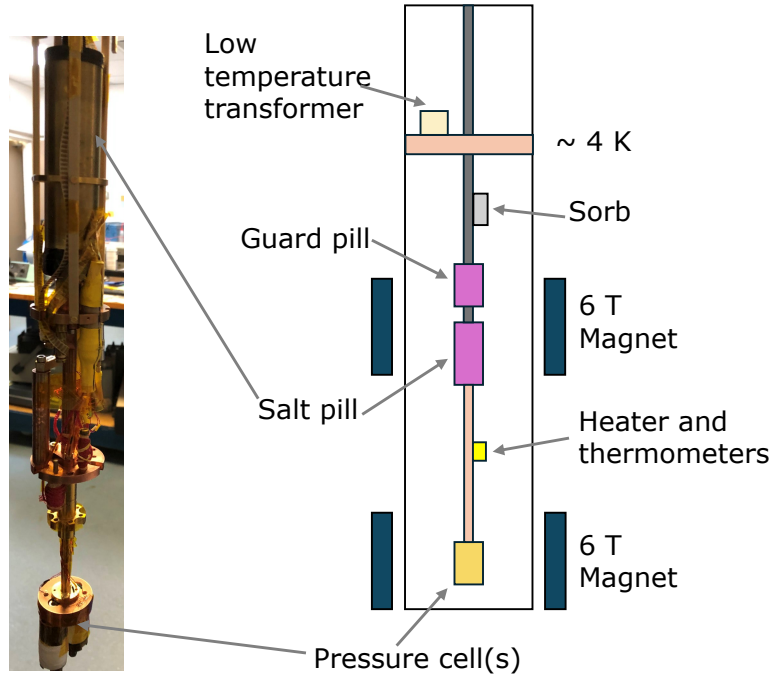


Figure 2.11: Left: photograph of the DMS low-temperature stage with two anvil pressure cells. Right: Schematic diagram of the DMS probe.

in zero magnetic field, but it becomes worse when a field is applied to the sample. Balanced current sources and superconducting measurement wires between the 4 K stage and the low-temperature stage prevent common-mode problems which can cause offsets in measured voltages. These superconducting wires mean that accurate measurements cannot be performed above 9 K.

### 2.3.4 Other systems

Our group's Physical Properties Measurement System (PPMS) from Quantum Design has a VTI for temperatures down to 1.8 K and a 9 T superconducting magnet. It operates in a similar way to the 15 T system, but it can be fully controlled by a computer, and samples are usually measured on pucks rather than probes.

The Cold Head is a table-top dry system constructed by Patricia Alireza for anvil cell measurements. Cells are screwed onto a piece of copper connected to a pulse-tube cooler, which can cool reliably to 5 K, and sometimes lower. The system takes around five hours to cool to base temperature, and can be warmed to 100 K using a heater.

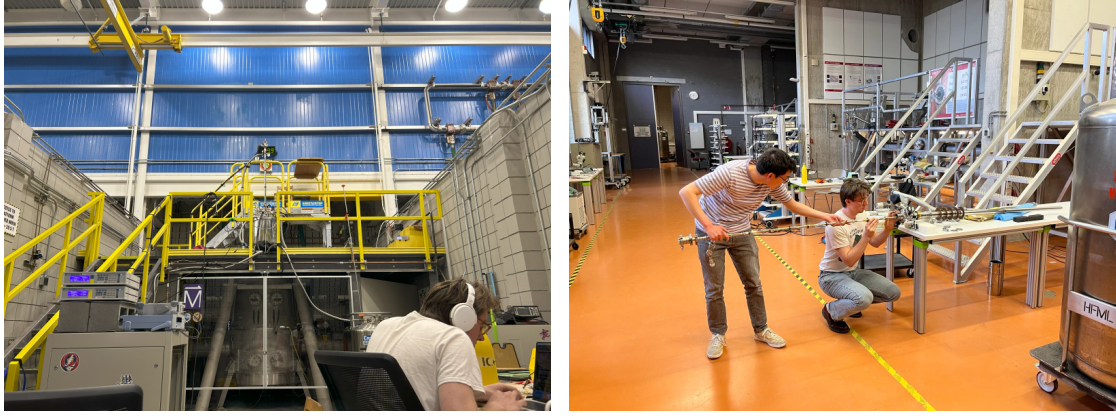


Figure 2.12: Left: 41.5 T resistive magnet (Cell 6) at the National High Magnetic Field Laboratory in Tallahassee. Right: Loading a probe into a He-3 system at the High Field Magnet Laboratory in Nijmegen, taken by Sasha Zheliuk.

### 2.3.5 High-field facilities

Resistive electromagnets are capable of achieving higher magnetic fields than superconducting magnets using a Bitter magnet design. These magnets consist of a stack of copper discs with holes in them for cooling water, and can achieve field up to 41.5 T. These magnets require large power supplies (10s of MW) and large cooling installations which pump high-pressure water through the magnets. Therefore, there are only a handful of laboratories around the world which operate these magnets. During my PhD, high-field experiments were performed at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, USA and the High Field Magnet Laboratory in Nijmegen, Netherlands. Both of these laboratories offer ‘magnet time’ to users from around the world, who visit for a few days to perform experiments.

He-3 systems, He-4 VTIs or dilution refrigerators are inserted into the bores of the magnet at high-field facilities to produce low temperatures. The He-3 systems used at these facilities are slightly different from the ICE Oxford He-3 probe described in Section 2.3.1 in that samples are in direct contact with He-3 liquid or gas. NHMFL in Tallahassee uses a top-loading He-3 system with a sorb, whereas HFML in Nijmegen uses a He-3 system with a mechanical pump. The resistive magnets with the largest fields have bores which are too small for our group’s standard 18 mm-diameter anvil cells. Narrow anvil cells have been developed in our group by Patricia Alireza with a diameter of 11 mm to fit in narrow-bore magnets, but they are more difficult to set up due to their smaller size and lack of alignment screws. Alternatively, magnets with lower fields around 30 T but wider bores are available, which are compatible with our standard anvil cells.

Higher fields up to 45 T can be achieved using a hybrid magnet which combines the fields from a 31 T resistive insert and a 14 T superconducting outsert [78]. Even

higher fields up to 100 T can be achieved in pulsed field magnets, where a field is produced by discharging the energy from a capacitor bank through a coil. These magnetic fields are only produced for a few ms, so measurements need to be performed quickly. In a metallic pressure cell, the large  $dB/dT$  produces eddy currents in the cell body which can cause very significant heating problems, limiting the base temperature of experiments to above 70 K in some cases [79]. In recent years, anvil cells with non-metallic cell bodies and gaskets have been developed in other groups to overcome this problem [79]. Hybrid or pulsed field magnets were not used in my PhD.

# Chapter 3

## CeSb<sub>2</sub>: Superconductivity

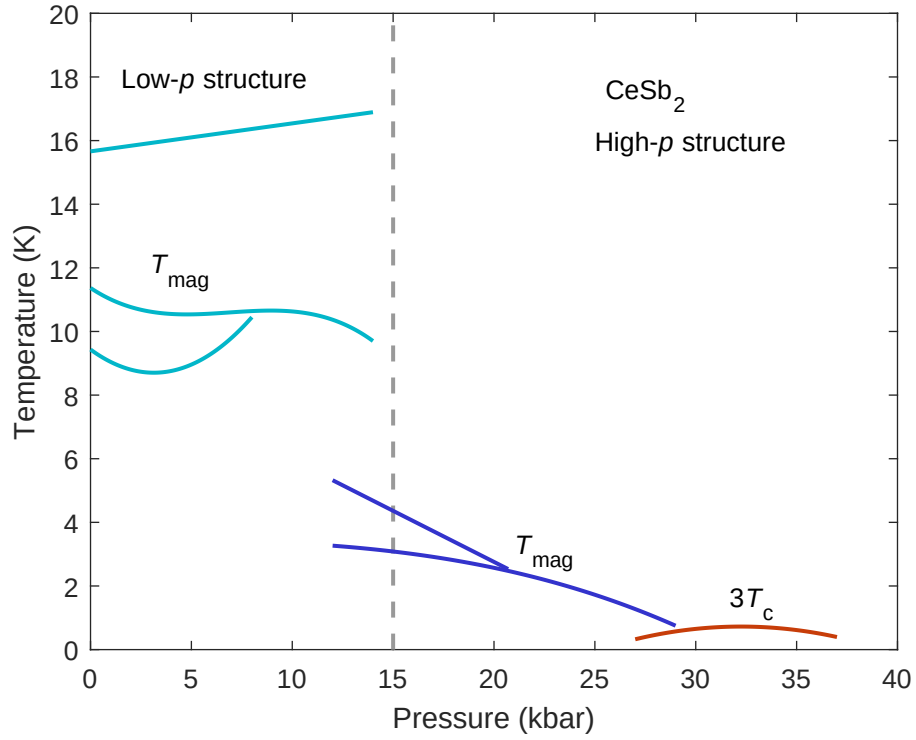


Figure 3.1: Schematic pressure-temperature phase diagram of CeSb<sub>2</sub>.

In this chapter I present low-temperature anvil cell measurements of the heavy fermion material CeSb<sub>2</sub>. These measurements resulted in the discovery of a dome of superconductivity at an antiferromagnetic quantum critical point with an unusual upper critical field. Some of these results have been published in Squire *et al.* [80].

## 3.1 Introduction to CeSb<sub>2</sub>

In this section I first give an overview of the properties of CeSb<sub>2</sub> at ambient pressure, before describing previous work in our group on the pressure-induced structural transition and high-pressure magnetic properties of CeSb<sub>2</sub>.

### 3.1.1 Low-pressure properties

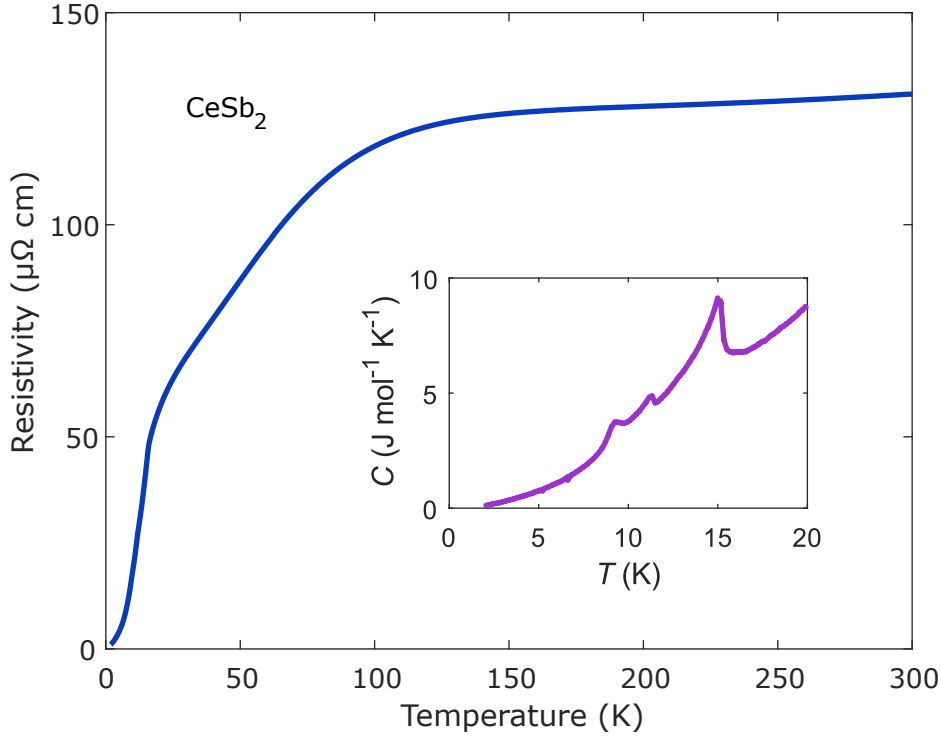


Figure 3.2: Temperature dependence of the resistivity of CeSb<sub>2</sub> at ambient pressure from Christian de Podesta. Inset: low-temperature heat capacity of CeSb<sub>2</sub> from Stephen Hodgson showing three magnetic transitions.

At ambient pressure, CeSb<sub>2</sub> crystallises in the orthorhombic “SmSb<sub>2</sub> structure” shared with other light rare-earth diantimonide materials  $RSb_2$  ( $R = \text{La-Nd, Sm}$ ) (Figure 3.3, inset). Single crystals with residual resistivity ratios  $\text{RRR} \simeq 100$  can be grown with a self flux method (Figure 3.2). CeSb<sub>2</sub> displays multiple magnetically ordered phases at low temperatures; phase transitions have been detected in resistivity, magnetisation and heat capacity measurements at 15.5 K, 11.7 K and 9.3 K (Figure 3.2, inset) [81, 82]. A possible fourth magnetic transition has also been detected at 6.5 K [83].

The nature of the magnetically ordered phases is unclear. The ground state was originally thought to be ferromagnetic on the basis of magnetisation measurements

[81], but an ordering wavevector has been detected in neutron scattering measurements leading to the suggestion that the ground state is antiferromagnetic [84]. A more recent magnetisation and scanning tunneling microscopy study has suggested that the ground state is ferrimagnetic, which is consistent with magnetisation and neutron data, but is inconsistent with the reported crystal structure at ambient pressure [85]. More work is needed to understand the different magnetic phases of CeSb<sub>2</sub> at ambient pressure. However the ambiguity over the magnetic phases of CeSb<sub>2</sub> at ambient pressure is not relevant for superconductivity CeSb<sub>2</sub> which occurs in a new high-pressure structure with completely different magnetic properties.

Previous measurements of the resistivity of CeSb<sub>2</sub> under pressure by Kagayama *et al.* found that the magnetic phases have only a weak pressure dependence up to 10 kbar. Hysteresis was seen in the resistivity between 10 and 12 kbar, which was suggested to be crystallographic in origin, but X-ray measurements to confirm this were not performed. At higher pressures, non-Fermi liquid resistivity was observed at 26 kbar, whereas the resistivity followed the more usual  $\rho = \rho_0 + AT^2$  temperature dependence at pressures on either side with  $A$  and  $\rho_0$  increasing near 26 kbar, indicating the possible presence of a quantum phase transition at that pressure [86, 87]. These results initially suggested that CeSb<sub>2</sub> under pressure might be a good system to study ferromagnetic quantum criticality, which was the original motivation for studying the material in our group.

### 3.1.2 Pressure-induced structural transition

Resistivity measurements on CeSb<sub>2</sub> in our group by Zhuo Feng [88] and Vitaly Fedoseev [89] using piston cylinder cells saw little change in the low-temperature magnetic transitions up to 15 kbar, but saw large jumps at higher temperatures (Figure 3.3), similar to those seen by Kagayama *et al.* [86]. There is significant hysteresis in these jumps, indicating that they correspond to first-order transitions, and they move to lower temperatures with increasing pressure. The transition broadens with increasing pressure and reaches zero temperature around 18 kbar. Around this pressure, the residual resistivity becomes significantly higher, indicating increased electron scattering, possibly due to a loss of crystallinity and the introduction of defects from a metastable mixture of the two crystal structures. Above  $\sim 15$  kbar, the transitions are no longer seen and the resistivity of CeSb<sub>2</sub> has a very different temperature dependence [88]; the resistivity is very flat down to 50 K, before rising to a peak at  $T_{\text{max}} = 17$  K, and then dropping very steeply at lower temperatures. This form of the resistivity is often seen in heavy fermion materials, where the position of the maximum is related to the effective mass by  $T_{\text{max}} \propto 1/m^*$ . The value

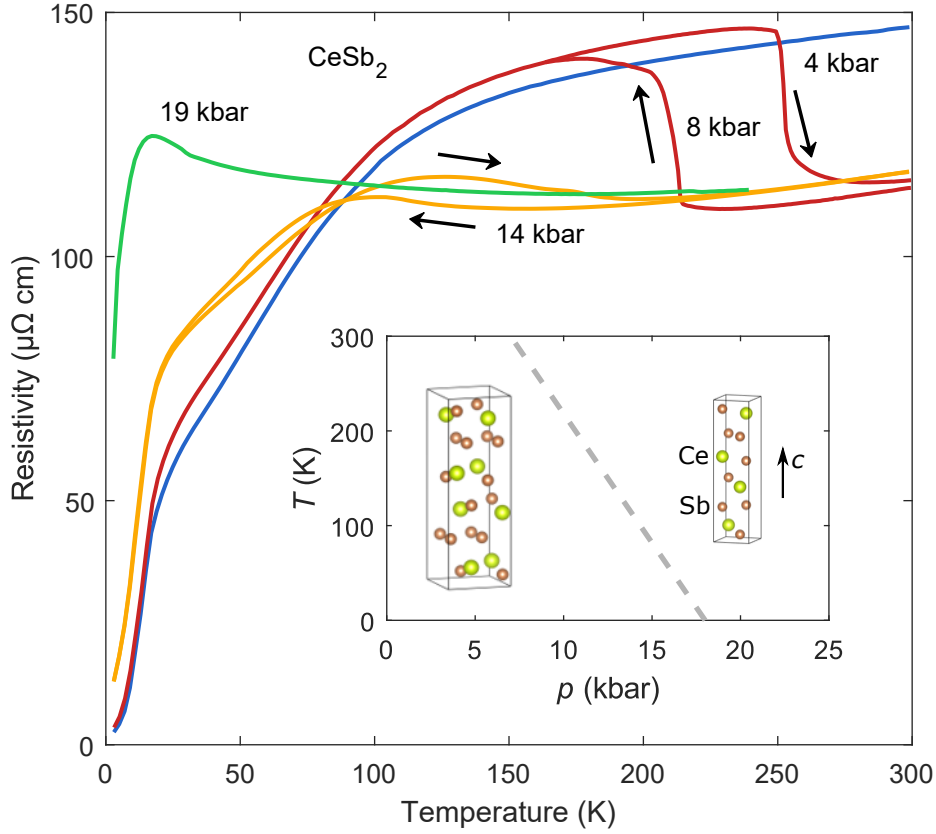


Figure 3.3: Resistivity of CeSb<sub>2</sub> at several pressures across the structural transition. Arrows indicate the direction of warming or cooling. Data was measured by Zhuo Feng [88]. Inset: schematic pressure-temperature phase diagram and crystal structures.

$T_{\text{max}}$  is lower than in most other heavy fermion materials, suggesting that the charge carriers in CeSb<sub>2</sub> have very heavy effective masses.

High-pressure powder X-ray diffraction measurements on CeSb<sub>2</sub> were performed at the Diamond Light Source, initially by Zhuo Feng, and more recently, and in more detail, by Christian de Podesta. These measurements detected a clear change in the X-ray diffraction data under pressure, confirming that CeSb<sub>2</sub> undergoes a structural transition. The change occurred at room temperature at 10 kbar, in agreement with previous resistivity data. An analysis of the X-ray data above the transitions indicates that the high-pressure structure is likely to be the “YbSb<sub>2</sub>” structure (Figure 3.3, inset). Like the ambient-pressure structure, the high-pressure structure is centrosymmetric, but lacks inversion symmetry around the Ce sites. More details of the X-ray analysis, and discussion of the likely crystal structure will be available in Christian de Podesta’s PhD thesis. In this thesis, I denote the longest axis as the *c* axis, for consistency between the high- and low-pressure structures.

### 3.1.3 High-pressure magnetism

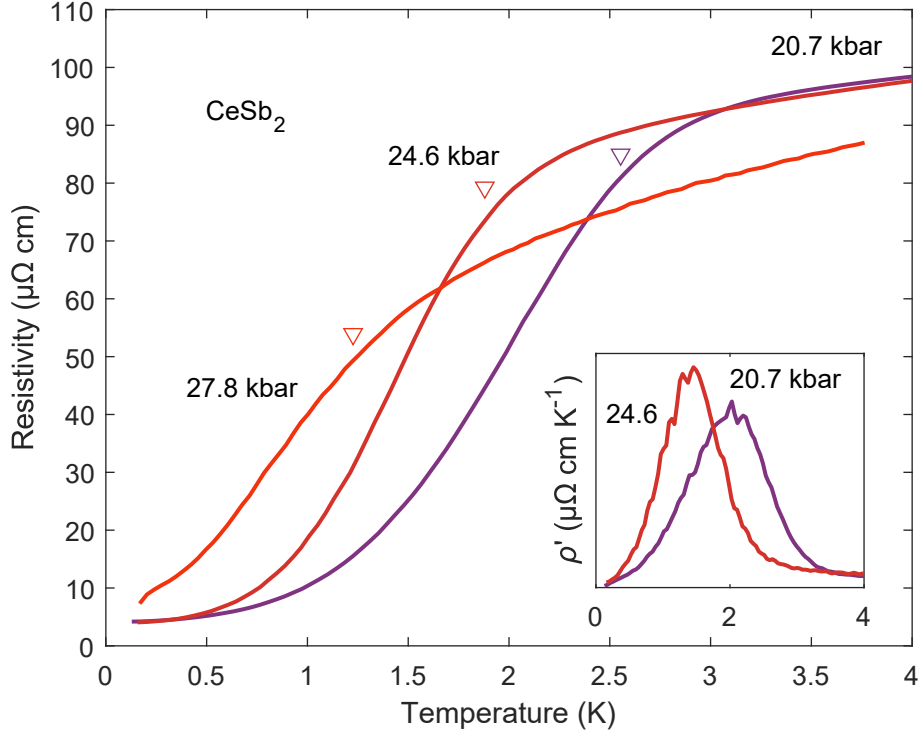


Figure 3.4: Low-temperature resistivity of high-pressure CeSb<sub>2</sub> at three pressures, showing a downturn (marked by triangles) moving to lower temperatures with increasing pressure. Inset: gradient of the resistivity. Data was measured by Vitaly Fedoseev [89].

Above 20 kbar, when the structure of CeSb<sub>2</sub> has fully converted into its high-pressure form, there is evidence for a low-temperature magnetic transition. A sudden downturn is seen in the resistivity (Figure 3.4), or a sudden rise in  $d\rho/dT$  (inset). This feature is seen at 2.5 K at 20 kbar, but moves to lower temperatures with increasing pressure. The feature extrapolates to a quantum phase transition around 30 kbar, just beyond the reach of previous piston-cylinder cell measurements in our group by Zhuo Feng [88] and Vitaly Fedoseev [89]. In one of the two samples measured by Vitaly Fedoseev, at the highest pressure of 27.8 kbar, a downturn was seen below 0.2 K, which looks like the onset of a superconducting transition, perhaps related to the nearby magnetic quantum phase transition. However, it was not possible to reach low enough temperatures, or higher pressures, to confirm this.

Recently, heat capacity measurements of CeSb<sub>2</sub> under pressure were performed in our group by Stephen Hodgson (Figure 3.5, left). These measurements were performed with a  $3\omega$  AC technique, in which a heater and thermometer are attached to a sample in a piston cylinder cell. The currents through the heater and ther-

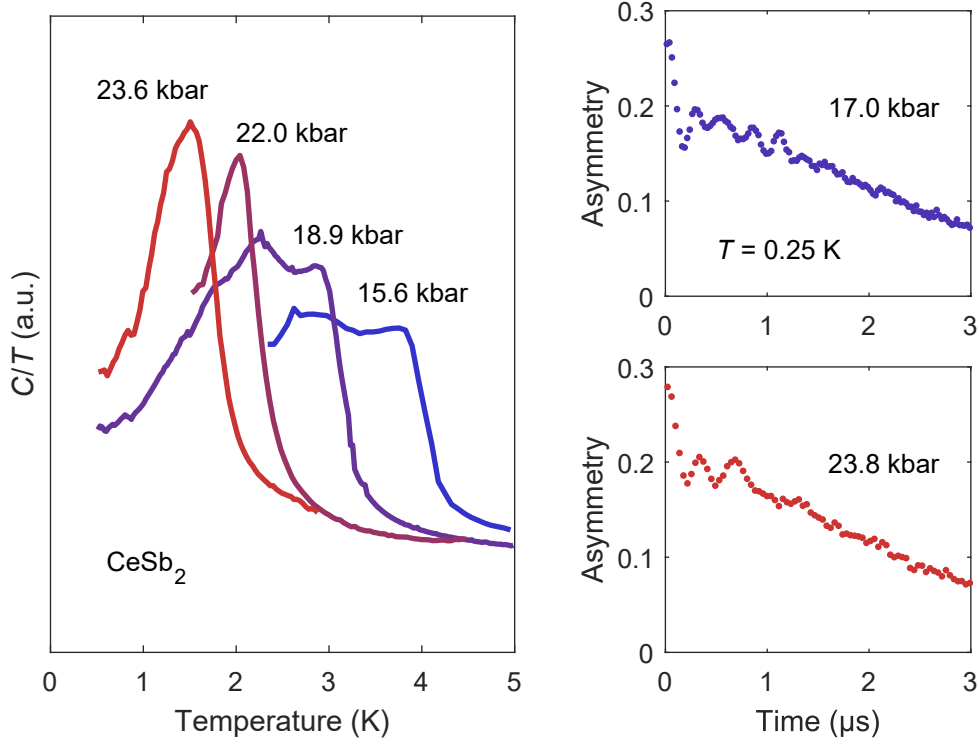


Figure 3.5: Left: heat capacity of high-pressure  $\text{CeSb}_2$  showing magnetic transitions which move to lower temperatures with increasing pressure measured by Stephen Hodgson [90]. Right: zero field muon spin rotation asymmetry at 17.0 and 23.8 kbar at 0.25 K measured by Christian de Podesta.

momenter are both modulated at a frequency  $\omega$ , producing voltage oscillations in the thermometer at a frequency  $3\omega$ , from which the heat capacity of the sample can be determined. These measurements found that the heat capacity of  $\text{CeSb}_2$  changes dramatically across the pressure-induced structural transition. In the high-pressure structure, the low-temperature heat capacity is significantly larger than at ambient pressure, although a precise quantitative measurement of the heat capacity is difficult. Between 15 and 20 kbar, two jumps are seen in the heat capacity, indicating two phase transitions. The two transitions both move to lower temperature with increasing pressure, but the distance between them decreases. At 20 kbar, the transitions merge into one transition which continues to move to lower temperatures as the pressure is increased further. Above 20 kbar, the temperatures of the transitions in heat capacity are in good agreement with the temperatures of the downturns seen in previous resistivity measurements. The shapes of the jumps in the heat capacity have a similar shape to the jumps in  $d\rho/dT$  in Figure 3.4, as expected for a magnetic transition [91], and they look like second order transitions. Assuming the transitions remain second order when pushed down to zero temperature, a quantum

critical point is produced around 30 kbar, rather than a more general quantum phase transition. Further information about the  $3\omega$  AC heat capacity technique and the heat capacity of high-pressure  $\text{CeSb}_2$  are given in Stephen Hodgson’s PhD thesis [90].

Muon spin rotation ( $\mu\text{SR}$ ) measurements under pressure confirm that the transitions seen in the high-pressure structure of  $\text{CeSb}_2$  are magnetic. These measurements were performed at the Paul Scherrer Institute in Switzerland by Christian de Podesta and Rustem Khasanov. In these measurements,  $\text{CeSb}_2$  crystals were pressurised in a piston-cylinder cell, and spin-polarised muons were implanted in them. The muons precess in any magnetic fields inside the crystals, and then decay into positrons. The direction of the emitted positrons provides information about the strengths of magnetic fields inside the crystals. Oscillations in the  $\mu\text{SR}$  asymmetry at high pressures indicate magnetic fields in the  $\text{CeSb}_2$  due to magnetism (Figure 3.5, right). The temperature dependence of the  $\mu\text{SR}$  data indicates two magnetic transitions below 20 kbar, and one transition at higher pressures, in broad agreement with heat capacity data, although the transition temperatures do not agree perfectly. Furthermore, an analysis of muons implanted into the pressure cell in these measurements suggests that the magnetism is likely to be antiferromagnetic rather than ferromagnetic. Further details of these measurements will be available in Christian de Podesta’s PhD thesis.

## 3.2 Superconducting dome

| Sample | Batch   | Measurement       |
|--------|---------|-------------------|
| A1     | SR1602  | Resistivity       |
| A2     | SR1602  | Resistivity       |
| A3     | CdP2108 | Resistivity       |
| A4     | CdP2108 | AC susceptibility |

Table 3.1: Anvil-cell samples of  $\text{CeSb}_2$ .

I set up three anvil cells for resistivity measurements of  $\text{CeSb}_2$  to search for superconductivity around the putative quantum critical point above 30 kbar. The first two cells, labelled as A1 and A2, used samples from batch SR1602 grown in our group by Jiasheng Chen, whereas A3 used a sample from batch CdP2108 grown by Christian de Podesta. I used moissanite anvils with 1 mm-diameter culets, Be-Cu gaskets and glycerol as the pressure medium. The crystals were oriented with the  $c$ -axis perpendicular to the gasket. Due to the layered nature of the crystals, the  $c$  axis at ambient pressure can be easily identified, but the  $a$  and  $b$  axes cannot.

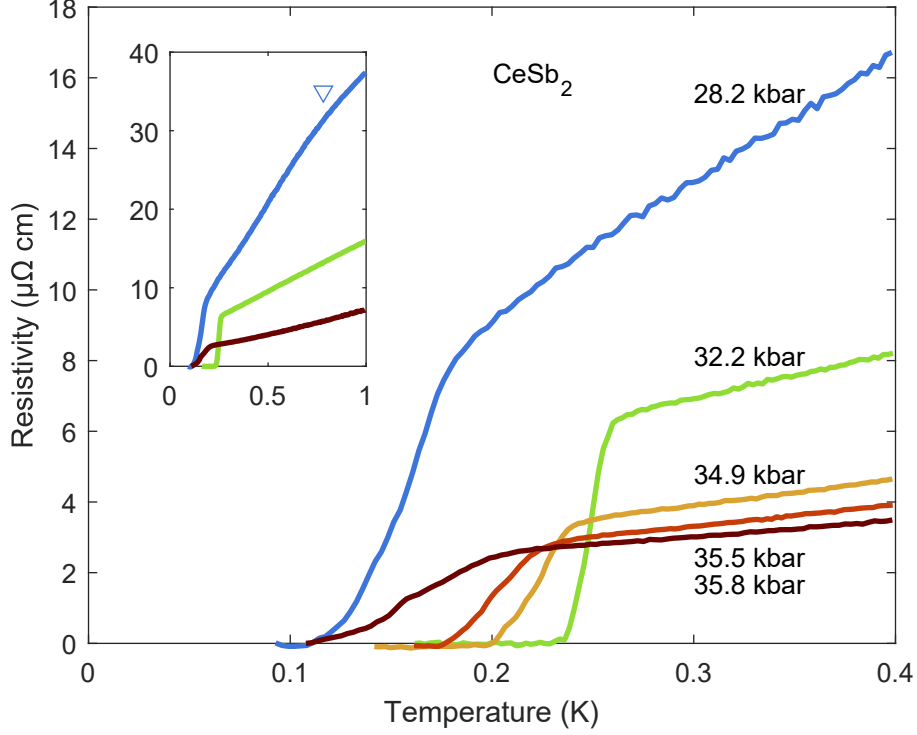


Figure 3.6: The temperature dependence of the resistivity of  $\text{CeSb}_2$  below 0.4 K at a range of pressures from 28.2 kbar to 35.8 kbar showing full resistive superconducting transitions. Inset: resistivity at higher temperatures for 28.2, 32.2 and 35.8 kbar. The triangle marks the temperature of a magnetic transition at 28.2 kbar.

The cells were measured in the DMS at temperatures down to 0.1 K. I used low currents of a few  $\mu\text{A}$ , and multiple measurements were performed with different currents to ensure there was no heating in the sample at the lowest temperatures. The signal was amplified with a low temperature transformer, room temperature transformer or preamplifier before being measured with a lock-in amplifier to provide a large signal-to-noise ratio. Complete resistive superconducting transitions were observed in a range of pressures between 28 and 36 kbar in Sample A1 (Figure 3.6) and at one pressure of 31.6 kbar in Sample A3 (Appendix Figure A.1), which was the only pressure where the cell was measured in that range. Sample A2 did not reach pressures above 27 kbar which are needed to see superconductivity.

$T_c$  values were determined from the midpoint of the drop in the resistivity, i.e. the temperature where the resistivity drops to half of its normal state value. Between 28 and 32 kbar, the transition temperature  $T_c$  increases, peaking at  $T_c \approx 250$  mK at 32 kbar, before decreasing at higher pressures, resulting in a dome-shaped superconducting phase in the pressure-temperature phase diagram. The superconducting dome in  $\text{CeSb}_2$  is at lower temperatures compared to many other Ce-based super-

conductors. While it is not as low as  $\text{CeIn}_3$  ( $T_c = 0.18$  K), which has a cubic crystal structure, it is lower than other Ce-based superconductors with quasi-two dimensional crystal structures, such as the ‘122’ and ‘115’ materials. For comparison, the maximum  $T_c$  values under pressure in  $\text{CePd}_2\text{Si}_2$ ,  $\text{CeCu}_2\text{Si}_2$  and  $\text{CeRhIn}_5$  are 0.4, 2.0 and 2.2 K respectively [17, 92, 93]. The low transition temperatures in  $\text{CeSb}_2$  may be a result of the material’s low Kondo coherence temperature which limits the energy of the superconducting state.

The variation in the width of the transitions visible in Figure 3.6 can be understood as a result of pressure inhomogeneity inside the anvil cell. At 32.2 kbar,  $dT_c/dp$  is small, so a pressure gradient across the sample  $\Delta p$  leads to a small broadening of the transition  $\Delta T_c \approx \Delta p dT_c/dp$ . However, at pressures around 35 kbar,  $T_c$  changes more rapidly with pressure, so the same pressure gradient leads to a larger spread of  $T_c$  values across the sample, and therefore a broader transition.

The normal state resistivity of  $\text{CeSb}_2$  is strongly pressure-dependent in the range of pressures where superconductivity is seen (Figure 3.6, inset). At 28.2 kbar, just below the critical pressure  $p_c$ , a kink at 0.6 K indicates the onset of magnetic order. At 32.2 kbar, just above  $p_c$ , the resistivity has an almost-linear non-Fermi liquid temperature dependence, whereas at higher pressures around 36 kbar, it is closer to the usual Fermi liquid  $\Delta\rho \propto T^2$  form. This pattern strongly suggests that the superconducting dome surrounds a quantum critical point, which is responsible for the non-Fermi liquid resistivity seen in the normal state, like in many other unconventional superconductors. The pressure and field dependence of the normal state resistivity of  $\text{CeSb}_2$  will be analysed in more detail in the next chapter.

An AC susceptibility moissanite anvil cell was prepared by Patricia Alireza and I measured it in the DMS down to 0.1 K using a current of 0.2 mA at 7333 Hz. Care was taken to ensure that the current was small enough to prevent heating in the sample at low temperatures. A clear drop in the AC susceptibility signal can be seen from the expulsion of magnetic flux as the sample becomes superconducting (Figure 3.7). The superconducting transition temperature determined from the onset of the drop in signal is  $T_c = 0.23$  K, which is in good agreement with values from resistivity measurements at similar pressures. The observation of this superconducting transition in another sample, using a different measurement technique, provides further evidence that superconductivity is intrinsic in pressurised  $\text{CeSb}_2$ .

The location of superconductivity in the pressure-temperature phase diagram of  $\text{CeSb}_2$  is shown in Figure 3.8. There is some scatter in values of magnetic transition temperatures  $T_m$ , possibly due to pressure gradients in cells and slight variations in chemical composition of samples, but there is a clear trend of decreasing transition temperature as pressure is increased towards 30 kbar. For clarity, only transition

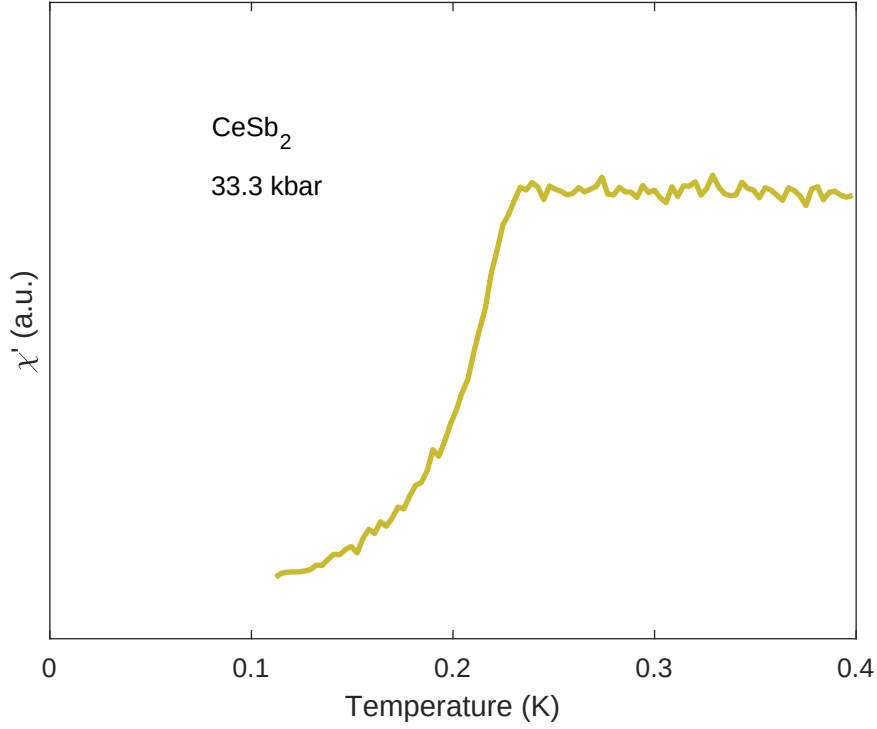


Figure 3.7: AC susceptibility signal from  $\text{CeSb}_2$  at 33.3 kbar showing a downturn at 0.23 K from a superconducting transition.

temperatures from one of the samples measured by Vitaly Fedoseev, AC heat capacity and anvil resistivity measurements have been included in the figure. The dome is tightly confined to a range of pressure around the magnetic quantum critical point. No signs of superconductivity have been seen below 27 kbar or above 37 kbar, and superconductivity has been observed in all measurements performed between 28 and 36 kbar.  $T_c$  appears to be largest at pressures around 31 kbar where the magnetic transition extrapolates to zero temperature. The location of the superconducting dome strongly suggests that magnetic fluctuations associated with the magnetic order are responsible for superconductivity.

### 3.3 Upper critical field

#### 3.3.1 Critical field along $c$

The response of the superconducting transition to a  $c$ -axis magnetic field was measured at each pressure. Raw resistivity data at four pressures across the superconducting dome is shown in Figure 3.9, all from the same sample A1. Superconducting transition temperatures in field were determined from the midpoints of the drops in

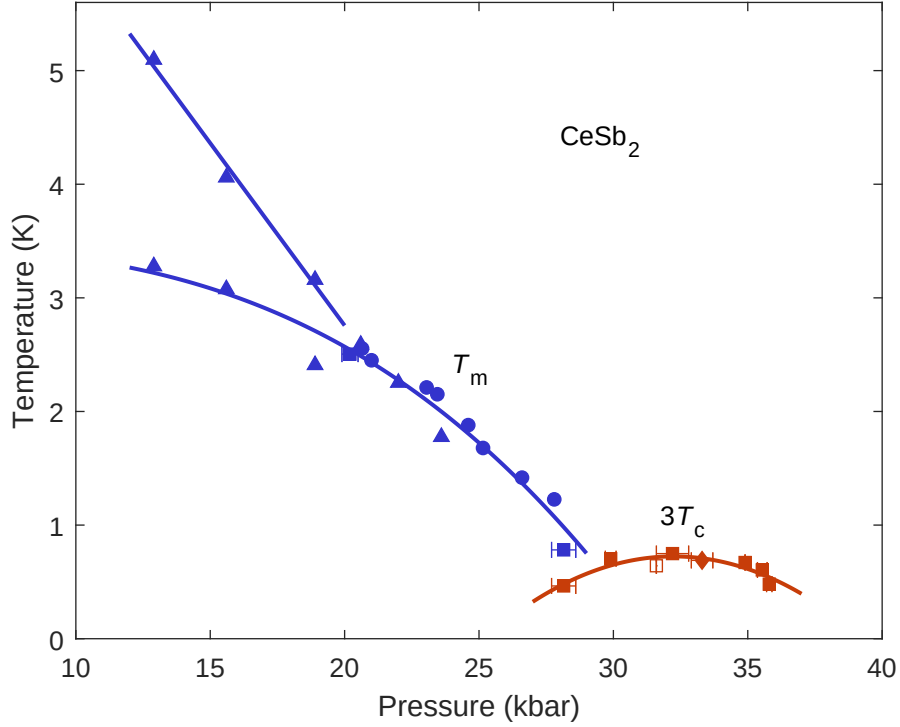


Figure 3.8: Pressure-temperature phase diagram of high-pressure  $\text{CeSb}_2$ . Transition temperatures are determined from piston-cylinder cell AC heat capacity (triangles), piston-cylinder cell resistivity (circles), anvil cell resistivity (squares) and anvil cell AC magnetic susceptibility (diamond) measurements. Filled and unfilled squares indicate transition temperatures from two different anvil cell resistivity samples. Superconducting transition temperatures  $T_c$  have been scaled by a factor of 3 for clarity.

resistivity. The resulting curves of the field dependence of  $T_c$  are equivalent to the temperature dependence of the upper critical field  $B_{c2}$  (Figure 3.10).

Additional measurements on Sample A1 were performed in a dilution refrigerator with an 18 T superconducting magnet at the National High Magnetic Field Laboratory in Tallahassee, Florida. The cell at 32.6 kbar was mounted directly in He-3/He-4 mixture with a base temperature of 22 mK, and field sweeps were performed at a series of temperatures between 22 and 300 mK to determine the upper critical field curve down to lower temperatures than could be reached in the DMS in Cambridge.  $B_{c2}$  values were determined from the midpoints of the superconducting jumps seen in the field sweep data (Figure 3.11, left), resulting in a critical field curve which reaches 4.5 T at zero temperature (Figure 3.11, right).

The magnitude of the upper critical fields in  $\text{CeSb}_2$  are surprisingly large. Antiferromagnetic spin fluctuations at a quantum critical point are expected to produce a spin-singlet superconducting state which experiences paramagnetic depairing in

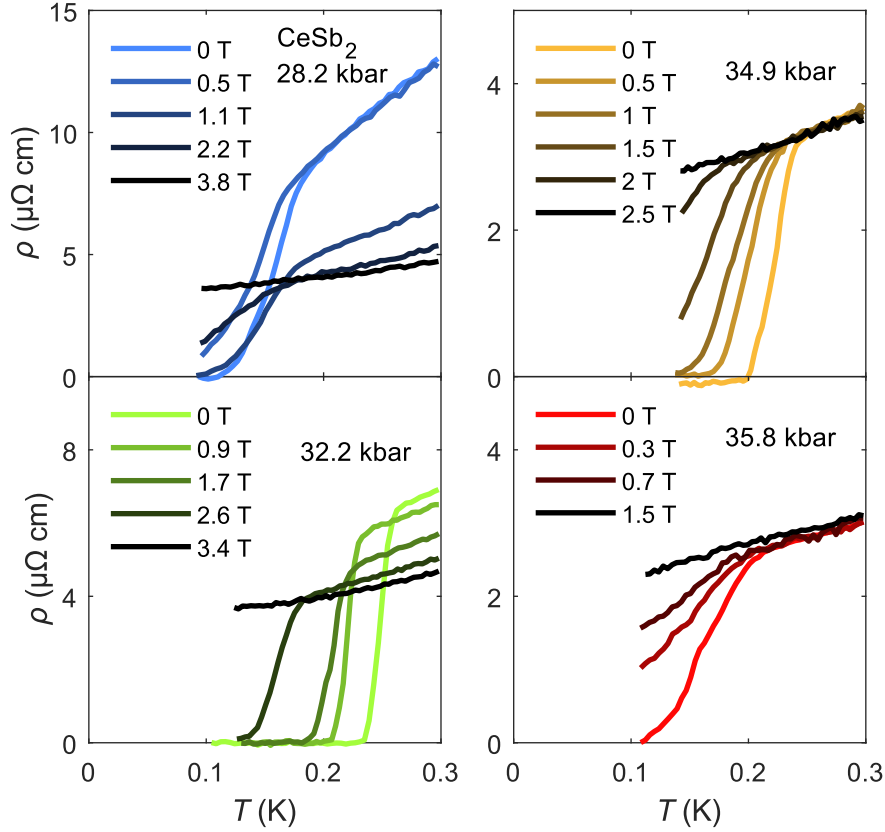


Figure 3.9: Resistive superconducting transitions in  $\text{CeSb}_2$  (Sample A1) at four different pressures in magnetic fields applied along the  $c$ -direction.

magnetic fields, as discussed in Section 1.2.3. At all pressures, the critical fields exceed the conventional Pauli limit  $B_{\text{Pauli}} = 1.84T_c$  T/K due to paramagnetic depairing effects. For example, at 32.6 kbar, the zero field value of  $T_c = 0.26$  K corresponds to a conventional Pauli limit of  $B_{\text{Pauli}} = 0.4$  T indicated by the dashed line horizontal line in Figure 3.11. The low-temperature upper critical exceeds this limit by more than an order of magnitude.

Another interesting aspect of the critical field curves is their temperature dependence. On the low-pressure side of the superconducting dome, the critical field curves have an unusual inverted S-shape (Figure 3.10, upper). For example, at 28.2 kbar,  $T_c$  initially decreases in low field up to 0.5 T, but then increase in higher fields, reaching value of  $T_c$  at 1 T similar to the zero-field  $T_c$ , before decreasing again in higher fields. The temperature dependence is less extreme in the 31.6 and 32.2 kbar critical field curves, but they still display a weak S shape. The critical fields on the high-pressure side of the dome have a more usual temperature dependence, with a constant gradient at low fields and a flatter gradient at higher fields.

The unusual inverse S-shapes on the low-pressure side of the dome make the

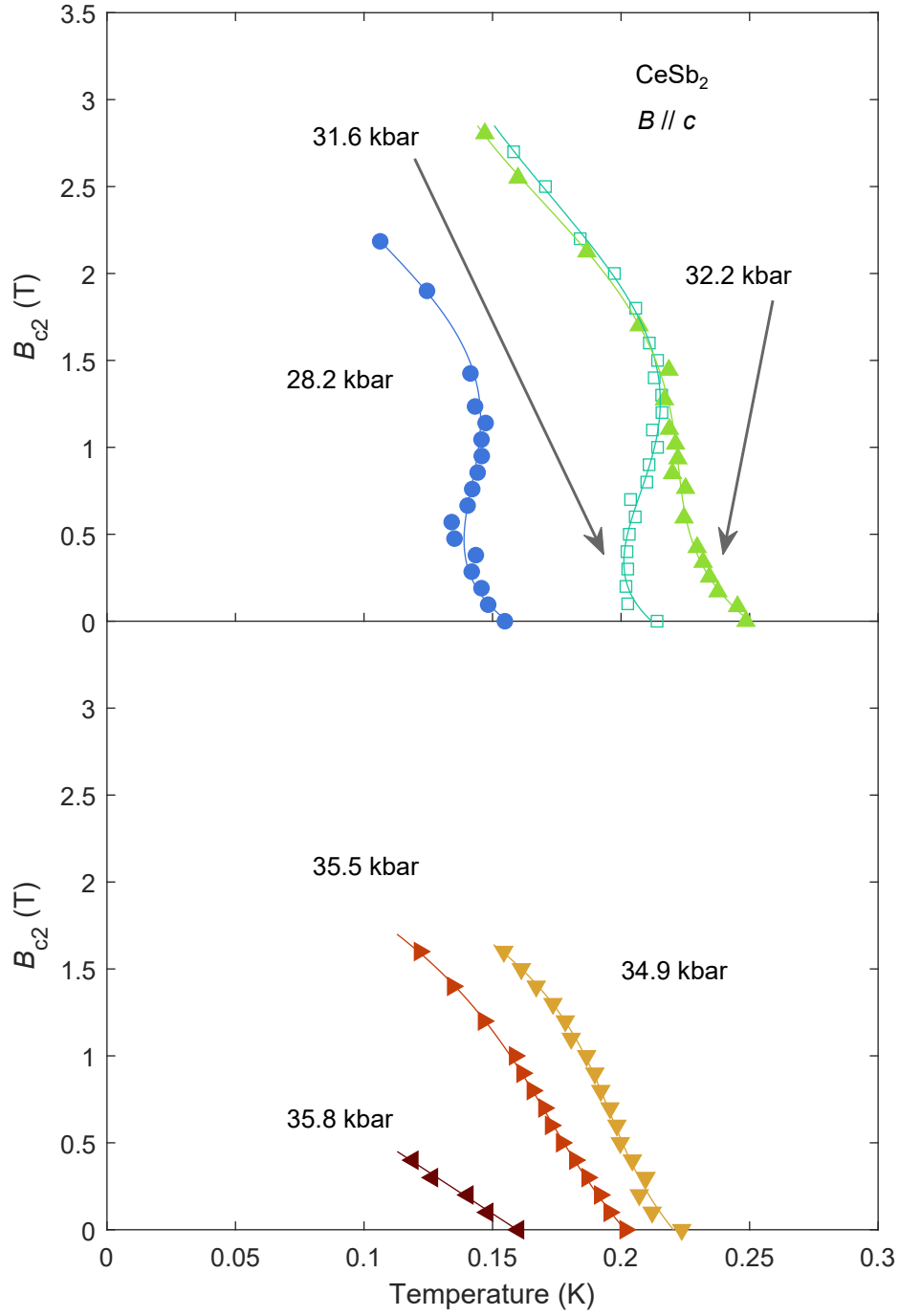


Figure 3.10:  $c$ -axis upper critical fields of  $\text{CeSb}_2$  at several pressures across the superconducting dome. Critical fields at pressures below 33 kbar (upper panel) display an S-shaped temperature dependence, whereas critical fields at higher pressures (lower panel) do not.

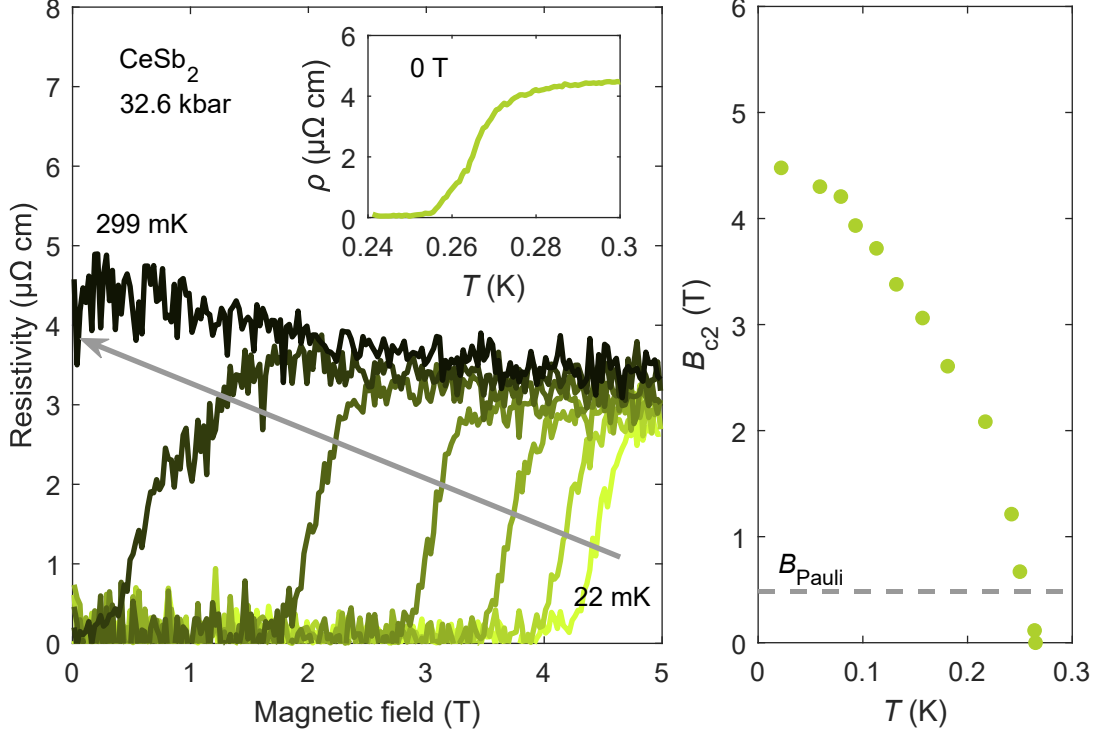


Figure 3.11: Left: superconducting transitions in the field dependence of the resistivity of  $\text{CeSb}_2$  at 32.6 kbar at a series of temperatures below 0.3 K. Inset: zero-field temperature dependence of resistivity at the same pressure showing a superconducting transition at  $T_c = 0.26$  K. Right: superconducting phase boundary from the data on the left.

curves difficult to analyse, but on the high-pressure side the curves have an approximately constant slopes at low fields, which are given in Table 3.2. Using the values of  $T_c$ , I have calculated the Pauli limiting fields  $B_{\text{Pauli}} = 1.84 T_c \text{ TK}^{-1}$ , and assuming  $\text{CeSb}_2$  is in the clean limit, I have estimated the the orbitally limited upper critical fields from  $B_{\text{orb}} = 0.73 |B'_{c2}| T_c$  [14]. At 34.9 kbar,  $B_{\text{orb}} = 4.8 \text{ T}$  gives a coherence length of

$$\xi = \sqrt{\frac{\hbar}{2eB_{\text{orb}}}} \approx 83 \text{ \AA} \quad (3.1)$$

From this value, a rough estimate of the Fermi velocity using

$$\xi = \frac{\hbar v_F}{\pi \Delta} \quad (3.2)$$

and the BCS gap  $\Delta = 1.76 k_B T_c$  gives  $v_F = 1300 \text{ ms}^{-1}$ .

A precise estimate of the effective mass from the Fermi velocity requires knowledge about the Fermi surface geometry, which we do not have, but a very rough estimate can be obtained by assuming a spherical Fermi surface with one electron

| $p$ (kbar) | $T_c$ (K) | $B'_{c2}$ (TK <sup>-1</sup> ) | $B_{\text{Pauli}}$ (T) | $B_{\text{orb}}$ (T) | $\sqrt{-B'_{c2}/T_c}$ (T <sup>1/2</sup> K <sup>-1</sup> ) |
|------------|-----------|-------------------------------|------------------------|----------------------|-----------------------------------------------------------|
| 34.9       | 0.224     | -29.4                         | 0.41                   | 4.80                 | 11.5                                                      |
| 35.3       | 0.202     | -23.2                         | 0.37                   | 3.41                 | 10.7                                                      |
| 35.8       | 0.160     | -9.7                          | 0.29                   | 1.12                 | 7.8                                                       |

Table 3.2: Critical field parameters for CeSb<sub>2</sub> on the high-pressure side of the superconducting dome.

per formula unit. With a volume per formula unit of  $80 \text{ \AA}^3$  from high pressure X-ray measurements, this gives a Fermi wavevector of  $k_F \approx 0.7 \text{ \AA}^{-1}$  and a very large effective mass of

$$m^* = \hbar k_F / v_F \approx 600 m_e. \quad (3.3)$$

The combination of Equations 3.1, 3.2 and 3.3 gives

$$m^* \propto \sqrt{\frac{-B'_{c2}}{T_c}}, \quad (3.4)$$

which is given for each pressure in Table 3.2. As the pressure is increased away from the middle of the dome, this value decreases, suggesting that the effective mass of the charge carriers decreases as the system is tuned by pressure away from the quantum critical point. This behaviour is consistent with that usually observed at quantum critical points, and is consistent with the analysis of the normal state resistivity which I will present in the next chapter.

To check whether the superconductivity is ‘clean’ or ‘dirty’, the mean free path can be estimated from a Drude formula assuming a spherical Fermi surface,

$$l = v_F \tau = \frac{3\pi^2 \hbar}{e^2 \rho_0 k_F^2}. \quad (3.5)$$

There is some variation in  $\rho_0$  values between samples, but typical values are  $\rho_0 \approx 5 \mu\Omega \text{ cm}$ . Using the value of  $k_F = 0.7 \text{ \AA}^{-1}$  from before gives a mean free path of  $l \approx 500 \text{ \AA}$ . This is much larger than the estimated coherence length of  $\xi \approx 83 \text{ \AA}$  (calculated in the clean limit), so superconductivity in CeSb<sub>2</sub> is in the clean limit where  $l \gg \xi$ . This explains why superconductivity has been observed in all samples measured around the quantum critical point in CeSb<sub>2</sub>; the coherence length is very short, so even crystal with relatively large residual resistivities can satisfy the condition  $l > \xi$  which is typically required to observe unconventional superconductivity.

A large critical field with an unusual temperature dependence has recently been reported in the heavy fermion superconductor CeRh<sub>2</sub>As<sub>2</sub> [94]. The material has a superconducting transition temperature  $T_c = 0.26 \text{ K}$ , but a zero-temperature criti-

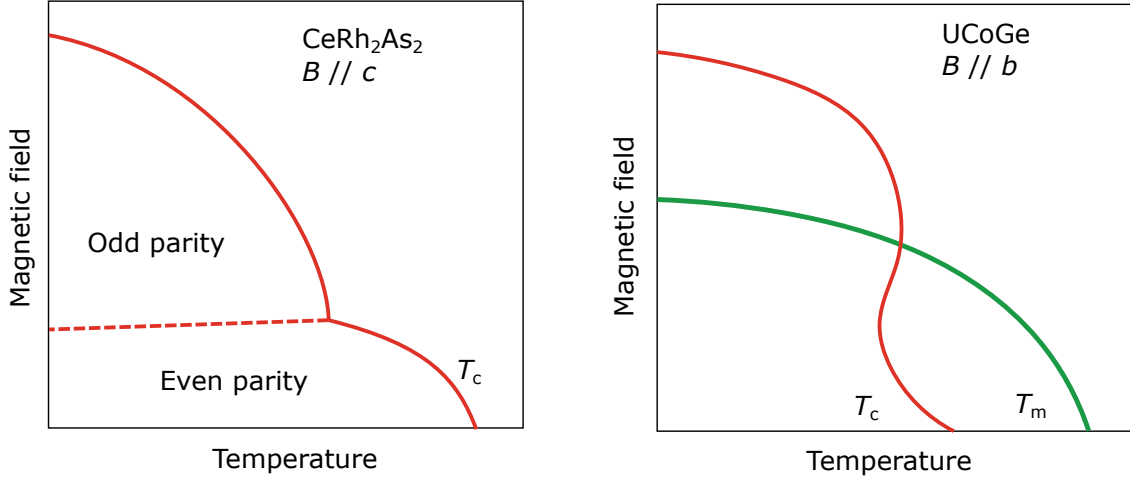


Figure 3.12: Schematic superconducting temperature-magnetic field phase diagrams for  $\text{CeRh}_2\text{As}_2$  (left) and  $\text{UCoGe}$  (right).

cal field of  $B_{c2} = 15$  T along its  $c$ -axis, which exceeds the conventional Pauli limit by a factor of 30. A first order phase transition line has been observed within the superconducting state (Figure 3.12, left) and the overall temperature dependence of the critical field resembles the S-shaped critical field seen in  $\text{CeSb}_2$  at 32 kbar. The crystal structure of  $\text{CeRh}_2\text{As}_2$  is centrosymmetric, so the superconducting state must have well defined parity, but the Ce atoms in the material are not located at the inversion centre. Therefore the structure contains two noncentrosymmetric Ce sublattices, whose electrons are presumably responsible for the material's two-dimensional electronic structure and superconductivity. If spin-orbit coupling on the sublattices is stronger than hopping between the sublattices, theoretical model calculations suggest that a field-induced transition from a low-field even parity state to a high-field odd parity state, which is not affected by paramagnetic limiting, can occur and superconductivity can survive beyond the Pauli limit [94, 95]. The transition observed within the superconducting state of  $\text{CeRh}_2\text{As}_2$  has been interpreted as this transition. However, the phase diagram of  $\text{CeRh}_2\text{As}_2$  is complicated by the possible presence of additional antiferromagnetic and quadrupolar phases [96, 97]. The high-pressure structure of  $\text{CeSb}_2$  (as well as its low-pressure structure) is similar to  $\text{CeRh}_2\text{As}_2$  in that it is centrosymmetric but lacks inversion symmetry around the Ce sites. It is therefore possible that the same physics is responsible for the unusual upper critical fields in the two materials.

A large S-shaped critical field has also been observed in  $\text{UGe}_2$  which has been explained with an alternative mechanism related to the effects of the applied magnetic field on the spin fluctuation spectrum. Superconductivity is seen in  $\text{UGe}_2$  in a dome surrounding the pressure where a  $T_x$  transition within the ferromagnetic

state is pushed to zero temperature. At pressures slightly beyond the critical pressure, a field applied along the easy  $a$ -axis ‘brings back’ the  $T_x$  transition, enhancing the fluctuations associated with the  $T_x$  state which enhances superconductivity [98, 99]. Similar behaviour has been seen in other U-based superconductors, UCoGe and URhGe, where the application of a magnetic field along the  $b$ -axis suppresses the Curie temperature by rotating the moments away from the  $c$ -axis, and superconductivity is enhanced at the field where ferromagnetism disappears. In the case of UCoGe, this results in an S-shaped critical field like in CeSb<sub>2</sub> [100] (Figure 3.12, right), whereas in URhGe the situation is more extreme; superconductivity initially disappears at low fields but reappears around 10 T when the transition is suppressed to zero temperature [22]. In all of these U-based materials, the superconductivity is thought to be an odd-parity, spin-triplet state, so there is no paramagnetic limiting and the critical fields can exceed the Pauli limit.

Although the unusual critical fields of CeRh<sub>2</sub>As<sub>2</sub> and UCoGe have been attributed to very different mechanisms, it is possible that their S-shaped curves might actually have the same origin. In CeRh<sub>2</sub>As<sub>2</sub>, the presence of antiferromagnetic order means that a mechanism related to the field tuning of magnetic fluctuations cannot be ruled out. Conversely, U-based superconductors lack inversion symmetry around the U-sites, so a mechanism related to spin-orbit coupling and an even-to-odd parity transition in field may be relevant.

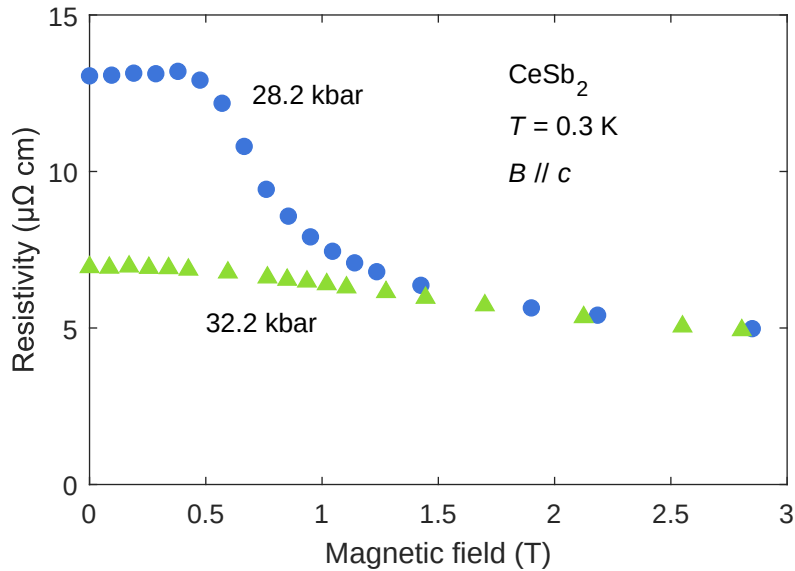


Figure 3.13: The field dependence of the resistivity of CeSb<sub>2</sub> at 0.3 K at 28.2 kbar (blue circles) and 32.2 kbar (green triangles).

The fact that an S-shaped critical field is only seen in CeSb<sub>2</sub> on the low-pressure side of the dome, where magnetism is present, strongly suggests that the mechanism

behind it is related to magnetism. Normal state magnetoresistance just above the superconducting state provides evidence for the suppression of magnetism by field along the  $c$ -axis (Figure 3.13). An anomaly in the magnetoresistance at 28.2 kbar is seen at 0.5 T, which matches up with the field in where the superconducting  $T_c$  starts to increase in field. Further evidence for the suppression of antiferromagnetism by a  $c$ -axis field can be found in data at lower pressures where  $T_N$  is larger. This will be discussed further in the next chapter.

The effects of the normal state antiferromagnetic transition on the slope of the critical field curve can be seen from an Ehrenfest equation,

$$\frac{dB_{c2}}{dT} = -\frac{C_s - C_n}{T(\partial M_s/\partial T - \partial M_n/\partial T)}, \quad (3.6)$$

where  $C$  is the heat capacity,  $M$  is the magnetisation and the subscripts  $n$  and  $s$  refer to the superconducting and normal states respectively. At the superconducting phase transition  $C_s > C_n$ , and in most superconductors  $\partial M_s/\partial T > 0$  and  $\partial M_n/\partial T < 0$  or  $\partial M_n/\partial T = 0$ , so  $dB_{c2}/dT < 0$ . A positive  $dB_{c2}/dT > 0$  requires

$$\frac{\partial M_s}{\partial T} < \frac{\partial M_n}{\partial T}. \quad (3.7)$$

Using a Maxwell relation, this inequality can be written as

$$\frac{\partial S_s}{\partial B} < \frac{\partial S_n}{\partial B}, \quad (3.8)$$

so there must be some additional field dependence of the normal state entropy to produce an increasing critical field. In CeSb<sub>2</sub>, on the low pressure side of the superconducting dome, a magnetic field tunes the material out of an antiferromagnetic state, so the entropy increases, producing the inverse S-shaped critical field curve.

There are two ways of thinking about how suppression of antiferromagnetism in field can produce an S-shaped critical field curve at 28.2 kbar. In one picture, the suppression of magnetism results in a field-induced quantum critical point at  $B_c = 0.5$  T and therefore enhanced magnetic fluctuations which increase the superconducting pairing strength. This is similar to the explanations for S-shaped critical fields in U-based superconductors, but with antiferromagnetism rather than ferromagnetism. In an alternative picture, the presence of magnetism weakens superconductivity. Therefore, when a field is applied, the antiferromagnetic phase is removed so superconductivity is enhanced, resulting in an increase in  $T_c$  in field. It is not clear which of these pictures best describes CeSb<sub>2</sub>, but in both cases the S-shaped critical field is related to the suppression of magnetism in field. At 31.6

and 32.2 kbar, no magnetic transition can be seen in the normal state resistivity, but a weak S-shaped critical field curve is still seen. This could be because magnetic fluctuations associated with the nearby magnetic order, rather than the magnetic order itself, is tuned by field in a way that enhances superconductivity.

|                                   | $T_c$<br>(K) | $B'_{c2}$<br>(TK <sup>-1</sup> ) | $B_{\text{Pauli}}$<br>(T) | $B_{c2}(0)$<br>(T) | $\sqrt{-B'_{c2}/T_c}$<br>(T <sup>1/2</sup> K <sup>-1</sup> ) | Ref.      |
|-----------------------------------|--------------|----------------------------------|---------------------------|--------------------|--------------------------------------------------------------|-----------|
| 34.9 kbar <b>CeSb<sub>2</sub></b> | 0.22         | -30                              | 0.40                      | > 3                | 11.8                                                         | This work |
| CeCoIn <sub>5</sub>               | 2.2          | -30.5                            | 4.05                      | 11.7               | 3.7                                                          | [101]     |
| CeCu <sub>2</sub> Si <sub>2</sub> | 0.77         | -14                              | 1.4                       | 2.5                | 4.3                                                          | [102]     |
| UPt <sub>3</sub>                  | 0.53         | -7.7                             | 0.98                      | 2.1                | 3.8                                                          | [103]     |
| UBe <sub>13</sub>                 | 0.95         | -45                              | 1.75                      | 14                 | 6.9                                                          | [104]     |

Table 3.3: Critical field parameters for CeSb<sub>2</sub> compared to some other heavy fermion superconductors.

In Table 3.3, the critical field of CeSb<sub>2</sub> at 34.9 kbar is compared to some ambient-pressure heavy fermion superconductors. The value of  $\sqrt{-B'_{c2}/T_c}$  in CeSb<sub>2</sub>, which is proportional to the effective mass, is larger than all other materials in the table. This is consistent with the idea that charge carriers in high-pressure CeSb<sub>2</sub> are very heavy, as seen from the low Kondo coherence temperature and the large  $A$ -coefficient discussed in the next chapter. It can be seen that in all materials in the table, the zero temperature critical field  $B_{c2}(0)$  exceeds the conventional Pauli limit  $B_{\text{Pauli}} = 1.84 T_c \text{ TK}^{-1}$ , even though several of them, such as CeCoIn<sub>5</sub> and CeCu<sub>2</sub>Si<sub>2</sub> are thought to be singlet superconductors. Some theoretical studies suggest that violations of the conventional Pauli limiting field might actually be expected in materials with a large mass renormalisation [105, 106]. The Pauli limiting field is obtained from equating the superconducting condensation energy with the energy saved by aligning spins in an applied field. In a strongly coupled heavy fermion superconductors both of these energies might be strongly modified; the energy gap might be much larger than the BCS gap  $\Delta = 1.76 k_B T_c$ , and the magnetic energy could be altered by the large density of states in a heavy fermion material.

Interestingly, some calculations for phonon-mediated superconductors show the violation of the conventional Pauli limit in heavy fermion materials can be thought of as a result of the superconducting state gaining a spin-triplet component in field [107–110]. A zero-field even parity, spin singlet, even frequency superconducting state gains an increasing odd frequency component in an applied field as the magnetic field breaks time reversal symmetry and therefore the superconducting state can have a mixture of odd and even frequency. Therefore, to preserve the overall antisymmetry of the wavefunction, an increasing spin triplet component must be mixed into the superconducting state, which is not paramagnetically limited, and

therefore can survive beyond the Pauli limit. This is similar to the situation in noncentrosymmetric superconductors, where broken inversion symmetry allows a mixture of even parity, spin singlet and odd parity, spin triplet pairing. It is possible that a similar effect may occur in unconventional superconductors like CeSb<sub>2</sub>, however a quantitative calculation of the Pauli limit in CeSb<sub>2</sub> is difficult because the Zeeman and Kondo energies are similar sizes, because the spin fluctuations which produce superconductivity are likely be strongly field dependent and because superconductivity emerges from a non-Fermi liquid electronic state which is not fully understood. Nevertheless, it is conceivable that the large violation of the conventional Pauli limit in CeSb<sub>2</sub> could be a result of the very heavy effective mass of its charge carriers.

### 3.3.2 In-plane critical field

At a few superconducting pressures I measured CeSb<sub>2</sub> with an anvil cell mounted sideways in the DMS so that the field was applied in the *a-b* plane of the sample to investigate the anisotropy of the critical field. There may have been a small misalignment of a few degrees of the *a-b* plane with respect to the field due to the sample not being completely flat in the plane of the gasket, but this is not expected to be significant. Anisotropic magnetic and electronic properties can cause anisotropy in critical fields, especially in materials with layered crystal structures like CeSb<sub>2</sub>. For example, in the cases of CeRh<sub>2</sub>As<sub>2</sub> and UGe<sub>2</sub> discussed previously, the unusual S-shaped temperature dependence is only seen when the field is applied along one particular axis.

At 34.2 kbar, the in-plane critical field is slightly different than the *c*-axis critical field at a similar pressure of 34.9 kbar (Figure 3.14), both from Sample A1. It is still significantly larger than the conventional Pauli limit  $B_{\text{Pauli}} = 0.42 \text{ T}$ , but appears to be slightly smaller than the *c*-axis critical field, and its temperature dependence displays a larger curvature at low fields. The normal state resistivity decreases more strongly in an *a-b* plane field than in a *c*-axis field, which may be due to a stronger reduction in effective mass or spin fluctuations. A strong quenching of spin fluctuations in field would explain why the critical field's temperature dependence has a strong curvature and why the critical field is lower for field in the *a-b* plane. At low fields, the gradient of the critical field curve  $dB_{c2}/dT = -30 \text{ TK}^{-1}$  in the *a-b* plane is similar to the *c*-axis critical field gradient, suggesting an isotropic effective mass at low fields.

I also measured at two different in-plane orientations to check whether any anisotropy in the *a-b* plane could be seen. Figure 3.15 compares the critical fields at

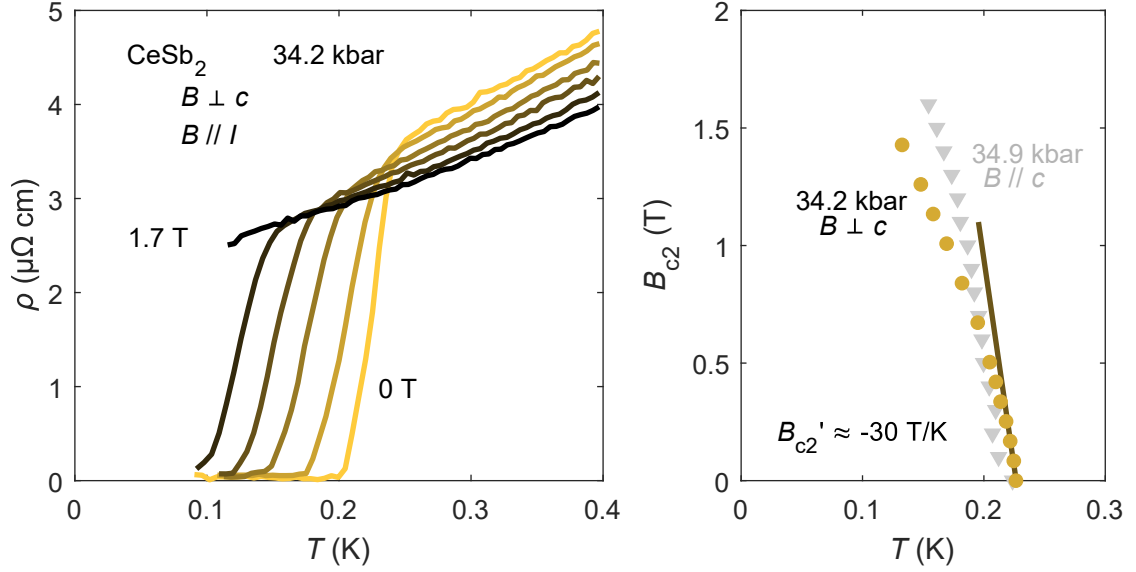


Figure 3.14: Left: response of the superconducting transition in CeSb<sub>2</sub> (Sample A1) at 34.2 kbar to a magnetic field applied in the  $a$ - $b$  plane, parallel to the current in the sample. Right: in-plane critical field curve at 34.2 kbar (yellow circles) compared to the  $c$ -axis critical field at a nearby pressure of 34.9 kbar (grey triangles). The straight line is a fit to the in-plane critical field points at lowest field giving a gradient of  $dB_{c2}/dT = -30 \text{ TK}^{-1}$ .

two nearby pressures of 33.8 and 34.2 kbar, both from measurements on Sample A1 and both with the field in the  $a$ - $b$  plane, but with the cell rotated by  $90^\circ$  between the two measurements so that the field was applied parallel to the current at 34.2 kbar and perpendicular to the current at 33.8 kbar. No difference between the two critical field curves was observed. This is not surprising because the  $a$  and  $b$  lattice constants for high-pressure CeSb<sub>2</sub> are very similar, so a large difference between the magnetic and electronic properties is not expected when rotating by  $90^\circ$  in the  $a$ - $b$  plane. It is also possible that the crystals of CeSb<sub>2</sub> become twinned in the  $a$ - $b$  plane when they pass through the structural transition under pressure, in which case no difference would be seen when the field is rotated in-plane.

Figure 3.16 shows measurements of the in-plane critical field of CeSb<sub>2</sub> at 29.9 kbar (Sample A1), with field parallel to current. Some of data, such as the 1 T data in the figure, show an incomplete superconducting transition which does not reach zero resistance, instead flattening at a non-zero value at lowest temperatures. I also observed this behaviour in measurements at 31.6 kbar on Sample A3 with an in-plane field perpendicular to current (Appendix Figure A.2), but it was not seen in the measurements around 34 kbar discussed previously. It is possible that this could be a sign of some flux flow resistivity present only on the low-pressure side of the superconducting dome from an interaction between current and superconduct-

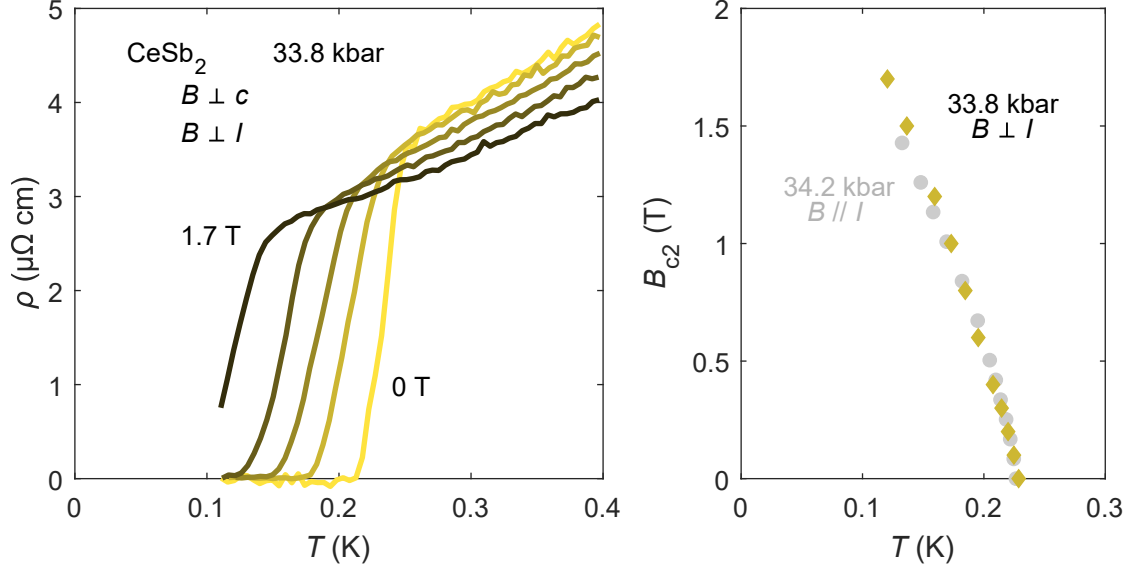


Figure 3.15: Left: response of the superconducting transition in CeSb<sub>2</sub> (Sample A1) at 33.8 kbar to a magnetic field applied in the  $a$ - $b$  plane, perpendicular to the current. Right: in-plane critical field curve at 33.8 kbar (yellow diamonds) compared to the in-plane critical field at 34.2 kbar from Figure 3.14 (grey circles).

ing vortices. A similar effect that has been reported in UGe<sub>2</sub> under pressure [98]. Alternatively, the feature could be experimental artefact from the cell not cooling below  $T \sim 0.18$  K. It is more difficult to mount cells sideways than vertical while ensuring good thermal contact with the low-temperature stage on the DMS. At lowest temperatures, heating from radiation or residual exchange gas could cause the cell to drop out of thermal equilibrium with the thermometer. Although care was taken to ensure that the cell was in good thermal contact with low-temperature stage and multiple measurement attempts were made to eliminate sources of heating, and although the flattening was only seen in measurements on the low-pressure side of the superconducting dome, I cannot completely rule out that it is caused by a heating issue. Further measurements will be required to investigate whether this feature is intrinsic to CeSb<sub>2</sub> on the low pressure side of the superconducting dome. Samples can be oriented more easily for in-plane measurements in piston cylinder cells, although it is difficult to reach high enough pressures in them to see superconductivity.

Due to uncertainty over the data at lowest temperatures, I have only included data above 0.19 K in the critical field phase diagram at 29.9 kbar (Figure 3.16, right). The critical field curve shows the same inverse-S shape that was seen on the low-pressure side of the dome with field along  $c$ , but it occurs at lower fields;  $T_c$  exhibits a local maximum at 0.3 T, compared to around 1.2 T for a  $c$ -axis field at similar

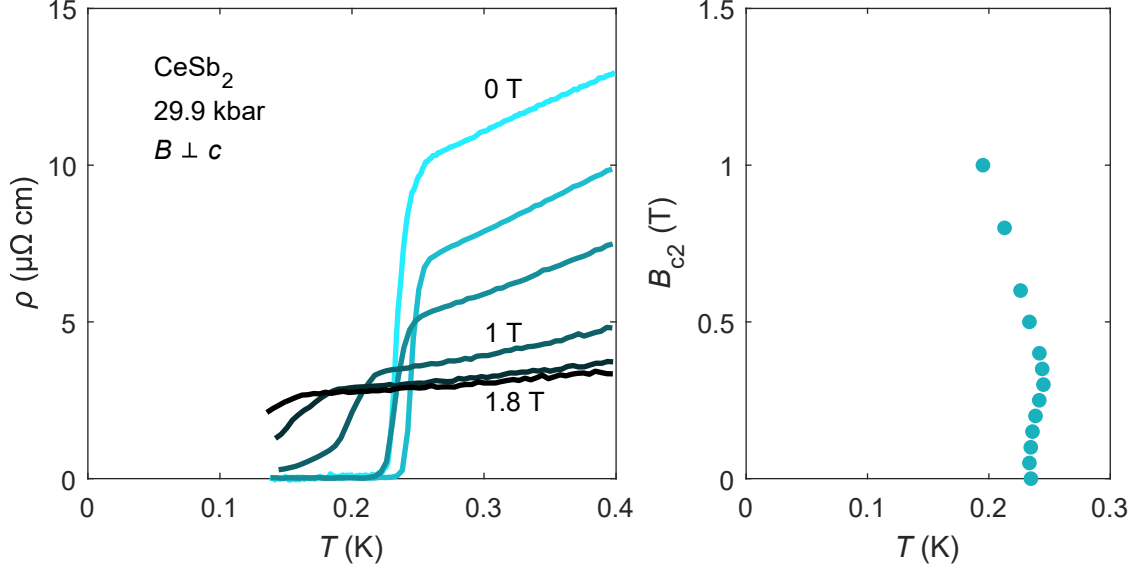


Figure 3.16: Left: response of the superconducting transition in  $\text{CeSb}_2$  (Sample A1) at 29.9 kbar to a magnetic field applied in the  $a$ - $b$  plane. Right: critical field above 0.19 K.

pressures. The S-shape is surprising, because an analysis in the next chapter of the normal state resistivity at pressures below superconductivity suggests that there is no in-plane field-induced magnetic-to-non-magnetic transition. Instead the field causes a rotation of the magnetic moments into the  $a$ - $b$  plane, so it is difficult to explain the shape of the in-plane critical field with a mechanism involving a field-induced quantum critical point. Further measurements near the quantum critical point with in-plane fields are needed to understand the interplay between magnetism and superconductivity.

### 3.4 Summary

A dome of superconductivity has been discovered surround an antiferromagnetic quantum critical point in the high-pressure structure of  $\text{CeSb}_2$ . The  $c$ -axis upper critical fields across the superconducting dome exceed the conventional Pauli limit, and the display an unusual inverse S-shaped temperature dependence on the low-pressure side of the dome. The size of the critical fields might be related to the very heavy charge carriers and the temperature dependence appears to be caused by the effects of an applied magnetic field on magnetism and magnetic fluctuations. In-plane critical fields are also large, and show a similar temperature dependence.

### 3.5 Outlook

Further measurements of the critical field of  $\text{CeSb}_2$  across the superconducting dome down to lower temperatures, either using a dilution refrigerator or by improving the base temperature of the DMS, would be interesting. By comparing the low-temperature critical field to the orbital and Pauli critical fields, it may be possible to determine the strengths of Pauli paramagnetic and orbital depairing effects, and how they change with pressure. This would give some insight into whether the superconducting state has a singlet or triplet spin state, as they are affected by paramagnetic depairing effects in different ways.

Heat capacity measurements of the superconducting transition in  $\text{CeSb}_2$  would hopefully confirm that the superconductivity is a bulk effect. Heat capacity measurements just below the critical pressure might be able to determine whether the magnetic transition remains second order as it is tuned with pressure or field, and whether it extends into the superconducting dome. However, these measurements will require further developments of the AC heat capacity technique to extend it to lower temperatures than have been reached before. Furthermore, as it is difficult to reach the superconducting dome with piston cylinder cells, it may be necessary to perform these measurements with anvil cells. AC heat capacity measurements have been performed in other groups using Au-Fe thermocouple wire [111, 112], but the decreasing sensitivity of the thermocouple at lower temperatures might make it difficult to see superconductivity in  $\text{CeSb}_2$ .

In the next chapter, I will discuss in detail the normal state resistivity of high-pressure  $\text{CeSb}_2$ . At pressures below the QCP, the response of the resistivity to magnetic field in different directions gives some insight into the nature of the antiferromagnetic order and its response to tuning with field. I will discuss how the resistivity changes with pressure towards, across and beyond the QCP, and how the mass enhancements from the Kondo effect and quantum critical fluctuations depend on pressure and magnetic field.

# Chapter 4

## CeSb<sub>2</sub>: Normal State Resistivity

The normal state resistivity of heavy fermion materials can provide valuable information about their magnetic and electronic properties. In the case of CeSb<sub>2</sub>, this information is important for an understanding of the unusual superconducting properties discussed in the last chapter, and more generally to investigate the physics of quantum phase transitions. The narrow, highly renormalised bands in CeSb<sub>2</sub> mean that the material is very sensitive to tuning with pressure and field. The system is magnetic when it first enters its high-pressure structure, and can be tuned across a large part of the Doniach phase diagram with pressure, from the antiferromagnetic state, across the quantum critical point and far into the paramagnetic state. The pressures required to do this are well within the reach of anvil pressure cells, and are sufficiently low that it can be done under hydrostatic conditions. Furthermore, the low residual resistivities of CeSb<sub>2</sub> samples mean that effects related to disorder are less important, and crystals appear to remain single crystalline in the high pressure structure, so the response to magnetic field along different directions can be studied. Therefore, CeSb<sub>2</sub> is an ideal system to investigate the physics of antiferromagnetic quantum critical points.

In this chapter, I present measurements and analysis of the normal state resistivity of CeSb<sub>2</sub> at pressures between 20 and 46 kbar. At these pressures CeSb<sub>2</sub> has fully converted into its high-pressure structure at all temperatures. The two magnetic transitions seen in heat capacity merge into one transition around 19 kbar, so only one magnetic phase is present in this range of pressures.

I have measured three anvil cell samples of CeSb<sub>2</sub>, labelled as A1, A2 and A3 using the same names from the last chapter. All three cells used glycerol as the pressure medium, and the highest pressure achieved was 46 kbar, which is within the range of pressures where glycerol is hydrostatic [68]. Low-temperature data between 0.1 and 9.0 K was measured in the DMS, and high temperature data up to room temperature was measured in the PPMS or the Cold Head. In most DMS

| Sample     | Measured by          | Scaling factor |
|------------|----------------------|----------------|
| P1.1, P1.2 | Vitaly Fedoseev [89] | 11.85, 11.72   |
| P2.1, P2.2 | Theo Weinberger      | 1.28, 1.67     |
| A1         | Me                   | 5.39           |
| A2         | Me                   | 1.33           |
| A3         | Me                   | 1.72           |

Table 4.1: Samples of CeSb<sub>2</sub> whose high-pressure normal state resistivities are analysed in this chapter. P1 and P2 are piston cylinder cells. A1, A2 and A3 are moissanite anvil cells. Each sample’s resistance in units of mΩ is multiplied by the scaling factor to obtain resistivity in units of μΩ cm.

measurements, the temperature dependence of the resistivity was measured in several different magnetic fields. A field was usually applied along the  $c$ -axis, but at a few pressures, the cell was mounted sideways so the field was applied in the  $a$ - $b$  plane. For lower pressures up to 28 kbar, I have analysed my data alongside DMS and PPMS data from piston cylinder cells measured by Vitaly Fedoseev (P1) [89] and Theo Weinberger (P2). These two piston cylinder cells each contained two samples of CeSb<sub>2</sub> with different orientations, so that magnetic field was applied in the  $a$ - $b$  plane of samples P1.1 and P2.1, and along the  $c$ -axis of samples P1.2 and P2.2. The resistance of each samples has been multiplied by scaling factor to obtain resistivity values which are consistent with the ambient-pressure, room-temperature value of 130 μΩ cm from Bud’ko *et al.* [82]. A plot of the room temperature resistivity values obtained using these scaling factors is available in Appendix B. Table 4.1 summarises the different samples in this chapter.

## 4.1 Resistivity in the magnetic state

In this section I focus on the range of pressures between 20 and 28 kbar where magnetic order is present, to investigate the nature of the antiferromagnetic order and its response to tuning by pressure and magnetic field.

### 4.1.1 Pressure dependence

As discussed in Section 3.1.3, resistivity, heat capacity and  $\mu$ SR measurements all provide evidence for antiferromagnetism in the high-pressure structure of CeSb<sub>2</sub> which extrapolates to a quantum critical point (QCP) around 30 kbar. The crystal structure of CeSb<sub>2</sub> is layered, so significant anisotropy in the material’s magnetic properties is expected. An anisotropy in exchange interactions between magnetic moments results in a gapped spin wave spectrum [113]. For a ferromagnet, scattering

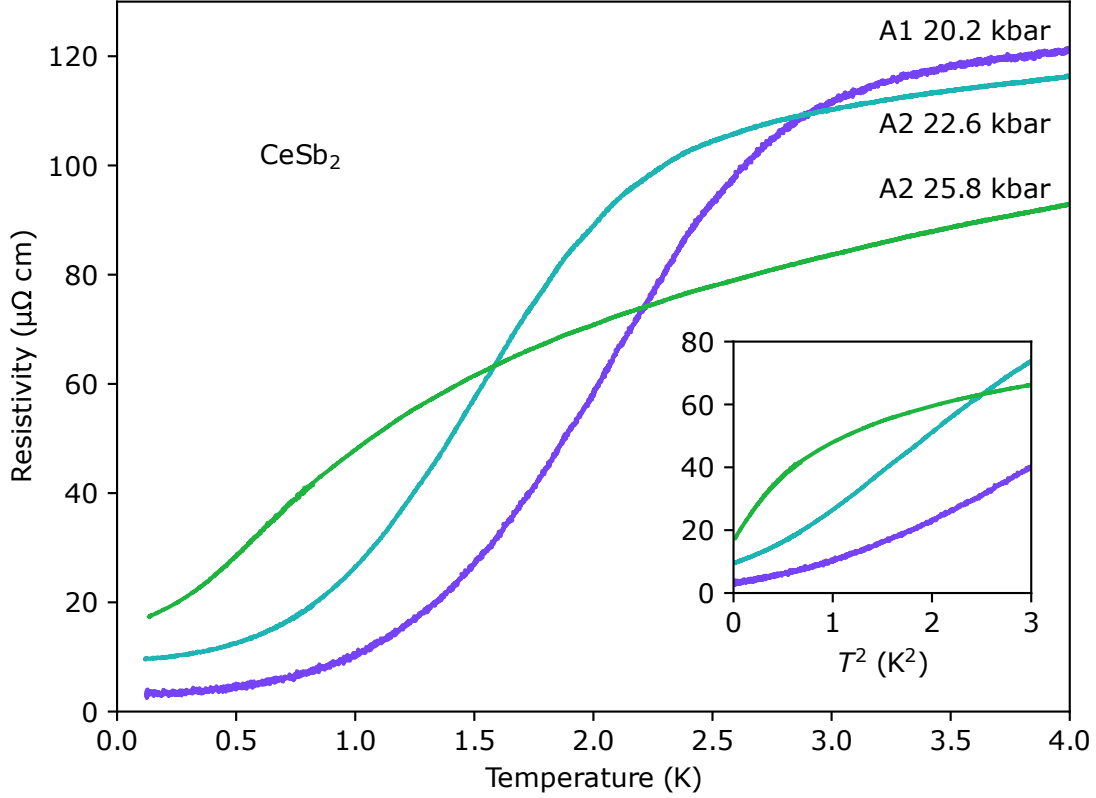


Figure 4.1: The low-temperature resistivity of CeSb<sub>2</sub> at three pressures where magnetism is present: 20.2, 22.6 and 25.6 kbar. Inset: resistivity plotted against  $T^2$  to show deviations from purely Fermi liquid behaviour.

between electrons and gapped spin waves gives a contribution to the resistivity,

$$\rho_{\text{FM}} = B\Delta^2 e^{-\Delta/T} \left[ 2 \left( \frac{T}{\Delta} \right)^2 + \frac{T}{\Delta} \right], \quad (4.1)$$

where  $B$  is a constant and  $\Delta$  is the size of the gap in the spin wave spectrum, whereas for an antiferromagnet it gives a contribution

$$\rho_{\text{AFM}} = C\Delta^5 e^{-\Delta/T} \left[ \frac{1}{5} \left( \frac{T}{\Delta} \right)^5 + \left( \frac{T}{\Delta} \right)^4 + \frac{5}{3} \left( \frac{T}{\Delta} \right)^3 \right], \quad (4.2)$$

where  $C$  is a constant, for  $T \ll \Delta$  [114]. Therefore, the temperature dependence of the resistivity in anisotropic magnetic metals can provide information about its magnetic properties and how they change with applied pressure and magnetic field. The  $C$ -coefficient is related to strength of the coupling between electrons and spin waves  $g$  by  $C \propto |g|^2$ , and it depends on the effective mass of the electrons  $C \propto m^{*2}$ , because  $\rho_{\text{AFM}} = m^*/ne^2\tau$  and  $1/\tau \propto N(0) \propto m^*$ , where  $N(0)$  is the density of states

at the Fermi energy [115].

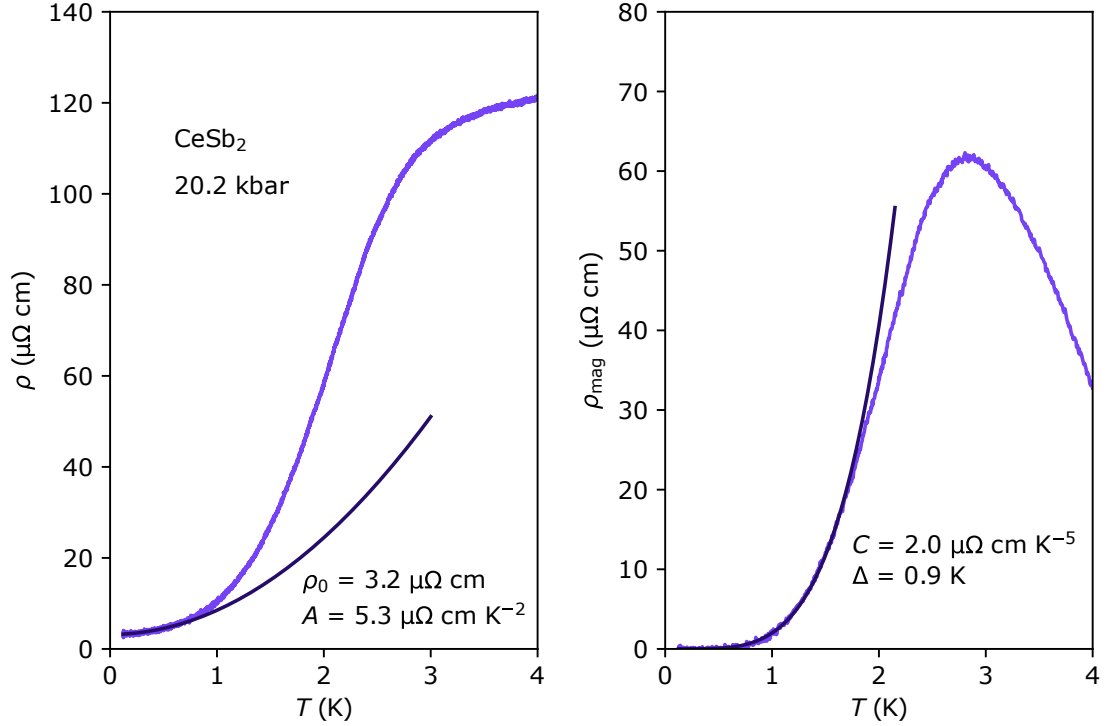


Figure 4.2: Fitting the low-temperature resistivity of CeSb<sub>2</sub> at 20.2 kbar (Sample A1). Left: Fermi liquid fit to the total resistivity at lowest temperature. Right: antiferromagnetic fit to the resulting magnetic resistivity.

The total low-temperature resistivity of CeSb<sub>2</sub> is composed of impurity, Fermi-liquid and antiferromagnetic spin wave scattering contributions:

$$\rho = \rho_0 + AT^2 + C\Delta^5 e^{-\Delta/T} \left[ \frac{1}{5} \left( \frac{T}{\Delta} \right)^5 + \left( \frac{T}{\Delta} \right)^4 + \frac{5}{3} \left( \frac{T}{\Delta} \right)^3 \right]. \quad (4.3)$$

At low temperatures, the  $e^{-\Delta/T}$  factor makes the magnetic contribution very small, so the resistivity is dominated by the first two terms. Therefore, the resistivity at lowest temperatures can be fitted with  $\rho_0 + AT^2$ . Then this Fermi liquid contribution can be subtracted from the total resistivity, leaving only the antiferromagnetic contribution, which can be fitted with Equation 4.2. At 20.2 kbar (Sample A1), this fitting procedure gives  $\rho_0 = 3.2 \mu\Omega \text{ cm}$ ,  $A = 5.3 \mu\Omega \text{ cm K}^{-2}$ ,  $C = 2.0 \mu\Omega \text{ cm K}^{-5}$  and  $\Delta = 0.9 \text{ K}$  (Figure 4.2).

The resistivity fit parameters for CeSb<sub>2</sub> at 20.2 kbar are compared to some other Ce-based antiferromagnets in Table 4.2. The  $A$ -coefficient in CeSb<sub>2</sub> is larger than in all other materials, which may be due to the very large effective masses of its charge carriers. For CeRhSi<sub>3</sub> and CeAl, antiferromagnetic resistivity fits give  $C$ -coefficients

|                                   | $T_N$ (K) | $A$ ( $\mu\Omega \text{ cm K}^{-2}$ ) | $C$ ( $\mu\Omega \text{ cm K}^{-5}$ ) | $\Delta$ (K) | Reference |
|-----------------------------------|-----------|---------------------------------------|---------------------------------------|--------------|-----------|
| 20 kbar <b>CeSb<sub>2</sub></b>   | 2.5       | 5.3                                   | 2.0                                   | 0.9          | This work |
| CeRhSi <sub>3</sub>               | 1.6       | 0.19                                  | 0.078                                 | 1.7          | [116]     |
| CeAl                              | 10        | $10^{-4}$                             | $10^{-5}$                             | 23           | [117]     |
| CePd <sub>2</sub> Si <sub>2</sub> | 10        | 0.098                                 | -                                     | -            | [118]     |
| CeRh <sub>2</sub> Si <sub>2</sub> | 36        | 0.002                                 | -                                     | -            | [119]     |
| CeIn <sub>3</sub>                 | 10        | 0.15                                  | -                                     | -            | [120]     |

Table 4.2: Magnetic resistivity parameters of CeSb<sub>2</sub> at 20.2 kbar compared to some other Ce-based antiferromagnets.

which are much smaller than in CeSb<sub>2</sub>, which could also be due to the large effective mass, or might indicate stronger electron-spin wave coupling in CeSb<sub>2</sub>.

I applied the fitting procedure to all data between 20 and 28 kbar, giving the pressure dependence of the fit parameters in Figure 4.3. There is a large amount of variation in residual resistivity  $\rho_0$  because different samples contain different amounts of disorder, but all samples shows an increase in  $\rho_0$  as the pressure is increased towards the critical pressure. The Fermi liquid  $A$ -coefficient also increases towards the critical pressure. This behaviour is often seen at quantum critical points as quantum spin fluctuations increase the scattering cross section between quasiparticles, and possibly also quasiparticle effective masses, causing increases in  $\rho_0$  and  $A$ .

The  $C$  coefficient also increases towards the critical pressure, reflecting the increase in effective mass, and possibly an increase in electron-spin wave coupling near the QCP. The spin wave gap  $\Delta$  might also have some pressure dependence, increasing towards 23 kbar before decreasing at higher pressures, although this trend is not very clear. The pressure dependence of the spin wave resistivity in CeSb<sub>2</sub> is different from that reported in CePd<sub>2</sub>Si<sub>2</sub>, where the spin wave gap remains constant, like in CeSb<sub>2</sub>, but the size of the scattering term decreases towards zero at the critical pressure, unlike in CeSb<sub>2</sub> [118]. This suggests that the nature of the interactions between electrons and spin waves might be different in the two systems.

#### 4.1.2 Effects of applied magnetic field on magnetism

The temperature dependence of the resistivity of CeSb<sub>2</sub> was measured in applied magnetic fields up to 6 T at many of the pressures discussed in the last section. In a simple picture, an applied magnetic field is expected to polarise the Ce magnetic moments along the direction of the applied magnetic field. The magnetic order in high-pressure CeSb<sub>2</sub> is most likely antiferromagnetic so an applied magnetic field should suppress antiferromagnetism by encouraging all spins to point in the same direction. As the crystal structure of CeSb<sub>2</sub> is layered, there is likely to be signif-

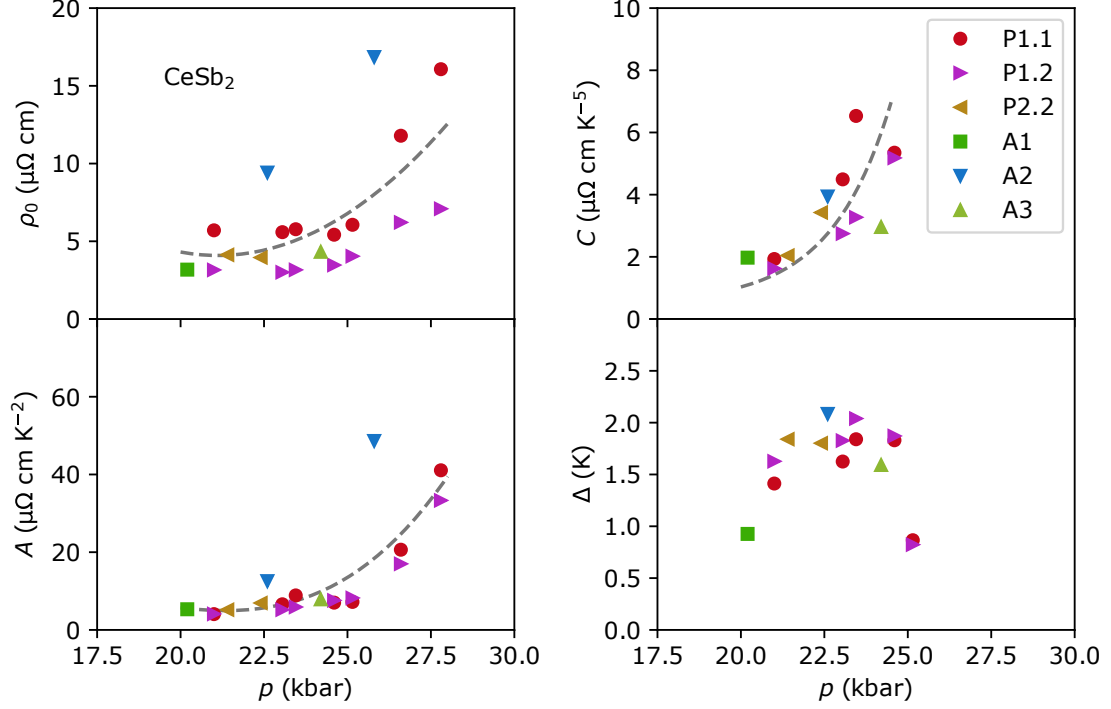


Figure 4.3: Fermi liquid and antiferromagnetic resistivity parameters obtained from fitting the low-temperature resistivity of CeSb<sub>2</sub> with Equation 4.3 at pressures between 20 and 28 kbar. Different symbols indicate different samples and dashed lines are guides to the eye.

icant anisotropy in the material's magnetic properties. Therefore the responses to magnetic fields along  $c$  and in the  $a$ - $b$  plane are expected to be different.

### Raw data

The effects of an applied magnetic field along  $c$  are illustrated by data at 20.2 kbar (Figure 4.4). At this pressure, the material has been fully converted into the high-pressure structure, and one magnetic phase is present below  $T_N \approx 2.5$  K. At high temperatures, above the magnetic transition, there is negative magnetoresistance (i.e.  $d\rho/dB < 0$ ). At lower temperatures, below the magnetic transition, the magnetoresistance is more complicated; at low fields the magnetoresistance is positive, at higher fields it is negative. The temperature where the magnetoresistance changes sign matches up with the magnetic transition temperature  $T_N$ , indicating that magnetoresistance is positive within the magnetic phase, but negative in the paramagnetic phase. Therefore, the change in the sign of the magnetoresistance with field indicates that magnetism is no longer present in high fields. This is supported by the temperature-dependence of the resistivity at lowest temperatures (Figure 4.4, upper inset); at low fields, the resistivity rises faster than  $T^2$  with increasing temperature

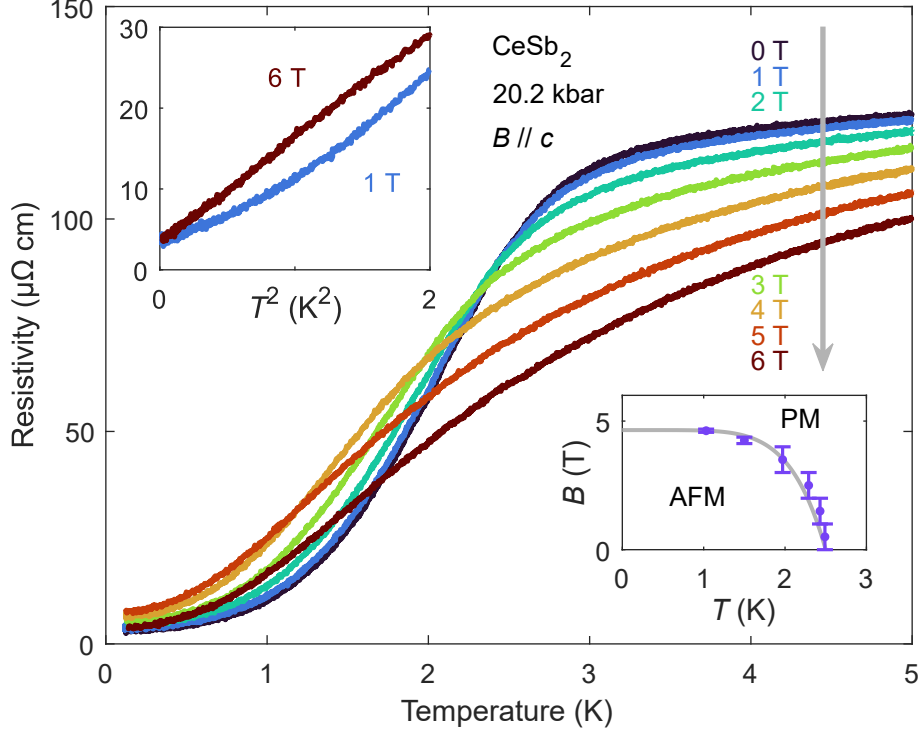


Figure 4.4: The resistivity of  $\text{CeSb}_2$  at 20.2 kbar (A1) for  $B \parallel c$ . Upper inset: resistivity at lowest temperatures plotted against  $T^2$  for 1 and 6 T. Lower inset: field-dependence of the temperature where the sign of magnetoresistance changes, which might indicate the phase boundary between the antiferromagnetic (AFM) and paramagnetic (PM) states.

due to scattering from gapped spin waves, whereas at the highest fields the resistivity has only a  $T^2$  dependence because there is no magnetic order and therefore no spin wave scattering. The temperature where the sign of the magnetoresistance changes at each field gives some indication of how the magnetic transition moves in field (Figure 4.4, lower inset), giving a zero-temperature critical field of  $B_c = 4.75$  T. At all magnetic fields, even at the critical field, the low-temperature resistivity follows a Fermi liquid  $\Delta\rho = AT^2$ . This contrasts with the non-Fermi liquid behaviour seen in the resistivity around the pressure-induced quantum critical point, which I will discuss in Section 4.2, and the behaviour seen in some other heavy fermion materials such as  $\text{YbRh}_2\text{Si}_2$  where non-Fermi liquid resistivity is seen around field-induced QCPs [121].

The effects of an in-plane magnetic field (i.e.  $B \parallel ab$ ) are very different, as illustrated by the data at 24.4 kbar in Figure 4.5. The magnetoresistance is negative for all temperatures and fields, even within the magnetic state, and the resistivity decreases much more strongly than for  $B \parallel c$ . The resistivity follows a more-than- $T^2$  temperature dependence (Figure 4.5 inset) indicating that magnetism is present at

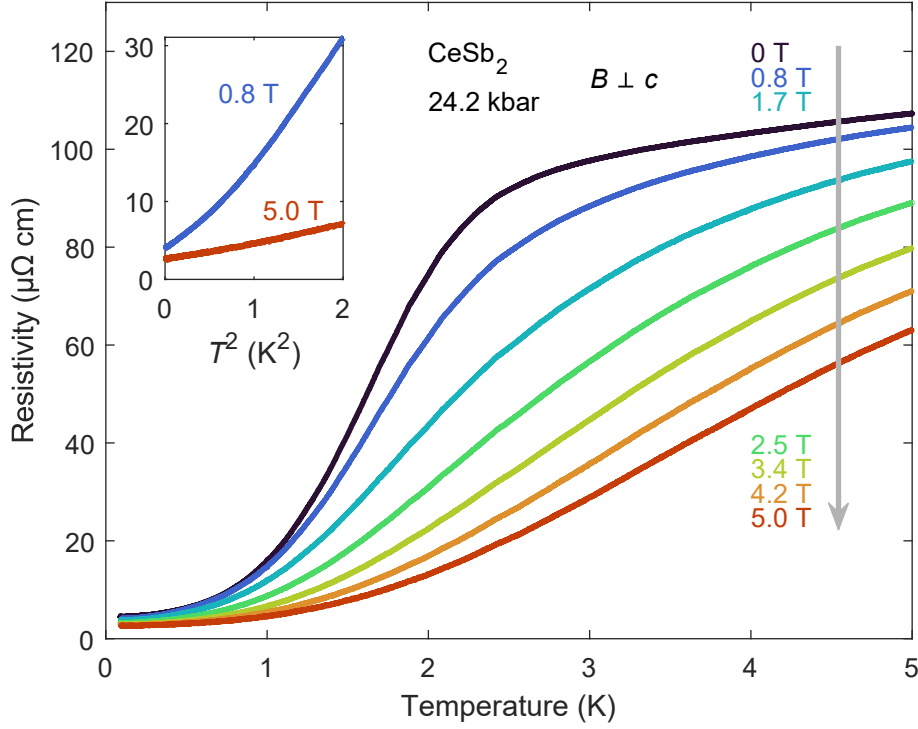


Figure 4.5: The resistivity of CeSb<sub>2</sub> at 24.2 kbar (A3) for magnetic fields  $B \parallel ab$ . Inset: the resistivity at lowest temperatures plotted against  $T^2$  for 1 and 6 T.

all fields up to 5 T.

### Fitting the data

For each magnetic field I have performed a fit of Equation 4.3 to determine  $\rho_0$ ,  $A$ ,  $C$  and  $\Delta$ . The results for  $B \parallel c$  at 20.2 kbar are shown on the left of Figure 4.6.  $A$  initially increases with increasing field, peaks at the field where magnetism is suppressed to zero temperature, and then decreases at higher fields. The peak in the  $A$  indicates that the effective mass is largest at the field-induced quantum phase transition (QPT). Therefore, despite the absence of non-Fermi liquid resistivity at the field-induced QPT, it appears that there is still an increase in quantum fluctuations which results in increased quasiparticle masses. The residual resistivity  $\rho_0$  follows the same field-dependence as  $A$ . The field dependence of  $\rho_0$  can be explained by positive magnetoresistance in the magnetic state and negative magnetoresistance in the paramagnetic state, as discussed previously. Alternatively, the peak in  $\rho_0$  at the critical field could be a result of increased scattering at the QPT. The  $C$ -coefficient increases upon approaching the field-induced QPT, which could be caused by the increase in effective mass, or possibly an increased coupling between electrons and spin waves. This is similar to the increase in  $C$  upon approaching the pressure-induced

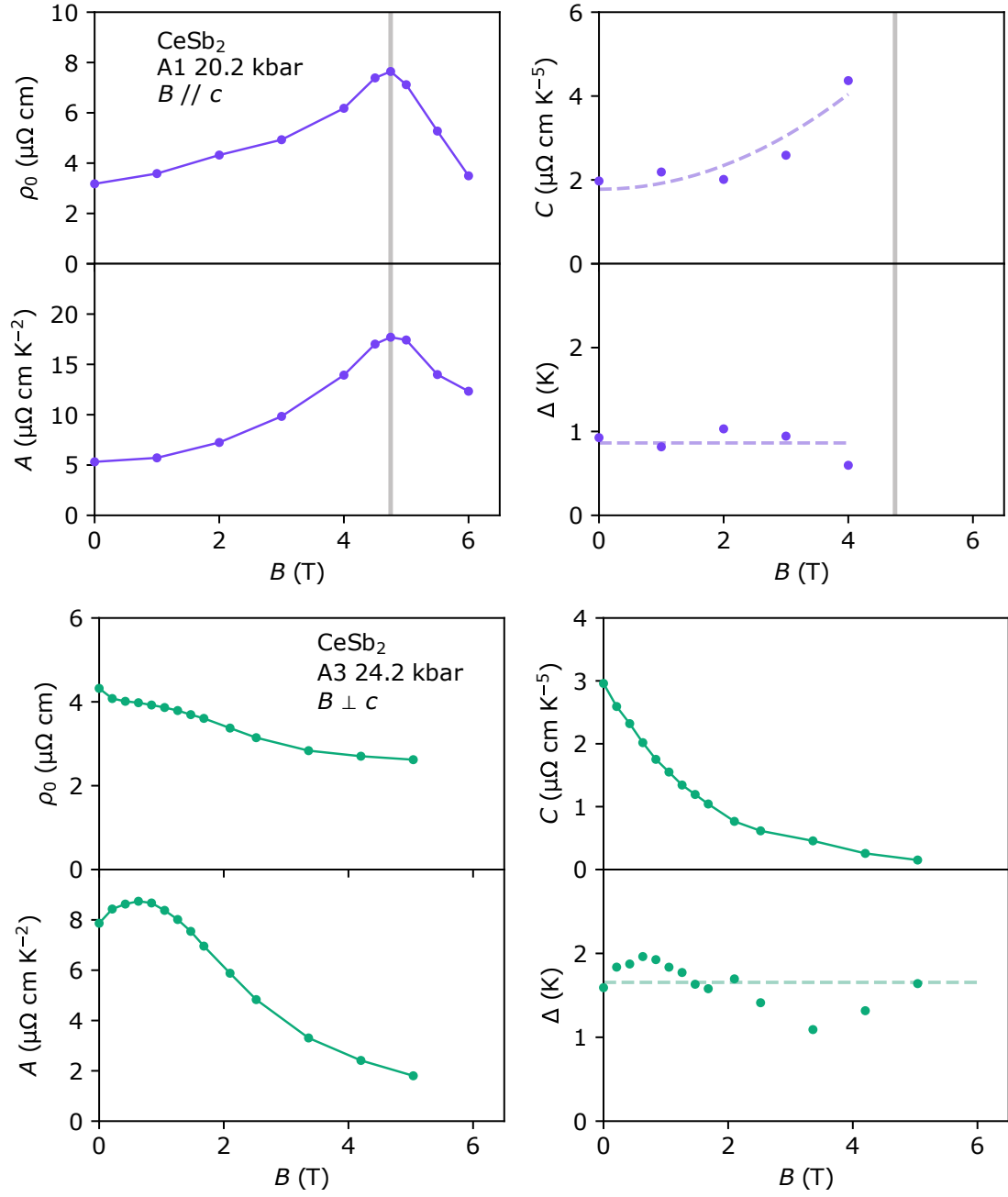


Figure 4.6: Upper: Fermi liquid and antiferromagnetic resistivity parameters obtained from fitting the low-temperature resistivity of  $\text{CeSb}_2$  at 20.2 kbar with Equation 4.3 at different magnetic fields  $B \parallel c$ . Lower: fit parameters for  $\text{CeSb}_2$  at 24.4 kbar with  $B \parallel ab$ .

QPT. The spin wave gap  $\Delta$  does not show much field dependence.

The evolution of the fit parameters for  $B \parallel ab$  (Figure 4.6, right) is very different from  $B \parallel c$ . No sharp peak is seen in  $\rho_0$  or  $A$ , consistent with the idea that there is no field-induced QPT for this field direction. There is possibly a broad hump in  $A$  around 0.5 T, but it is not a sharp feature so is unlikely to correspond to a phase transition.  $C$  decreases continuously for increasing field, unlike for  $B \parallel c$ . There does not appear to be any significant change in the gap  $\Delta$ . Overall,  $\rho_0$ ,  $A$  and  $C$  all decrease for  $B \parallel ab$ , opposite to the effects of pressure and  $B \parallel c$ .

|          | $B \parallel c$         | $B \parallel ab$ |
|----------|-------------------------|------------------|
| $\rho_0$ | Peaks at $B_c$          | Decreases        |
| $A$      | Peaks at $B_c$          | Decreases        |
| $C$      | Increases towards $B_c$ | Decreases        |
| $\Delta$ | No trend                | No trend         |

Table 4.3: The effects of an applied magnetic field on the Fermi liquid and antiferromagnetic resistivity parameters.

The effects of an applied field on the resistivity in each orientation are summarised in Table 4.3. This behaviour was seen in all samples where low-temperature in-field measurements were performed, including simultaneous measurements of samples P2.1 and P2.2 at the same pressure with field in different orientations (Appendix Figure B.3).

### Strong Ising or XY antiferromagnetism

The behaviour in field can be explained by antiferromagnetic order where either the moments are aligned along the  $c$ -direction with strong Ising anisotropy  $\chi_c \gg \chi_{a,b}$ , or the moment are aligned in the  $a$ - $b$  plane with weak XY anisotropy  $\chi_{a,b} \gg \chi_c$ .

In the Ising case, illustrated in Figure 4.7, for small field  $B < B_c$  along the  $c$ -axis (the easy axis), there is little change in the orientation of the magnetic moments because the moments are prevented from rotating by the strong uniaxial anisotropy. However for large enough fields  $B > B_c$ , a metamagnetic phase transition is induced from the antiferromagnetic state to a polarised paramagnetic state, as it becomes more energetically favourable for half of the moments to flip and point along the direction of the applied field. When a small field is applied perpendicular to the  $c$ -axis, the spins cannot align with the applied field due to the strong Ising anisotropy which constrains them to the positive and negative  $c$ -direction, but a small canting of the spins may be possible if the anisotropy is not too strong. For large enough fields, the spins can be rotated into the  $a$ - $b$  plane, and  $T_N$  can be tuned continuously to zero at a field-induced QCP. However, if the anisotropy is strong, this would occur

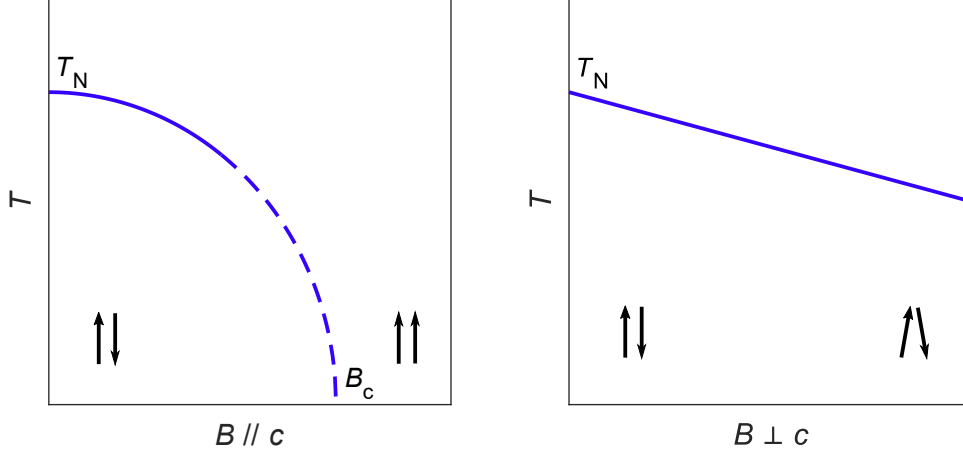


Figure 4.7: Schematic field-temperature phase diagrams showing the effect of a magnetic field applied along the  $c$ -axis (left) and perpendicular to the  $c$ -axis (right) on an antiferromagnet with strong Ising anisotropy. Solid lines indicate second order phase boundaries and dashed lines indicate first order boundaries. The arrows indicate the directions of the magnetic moments, which are ordered along the  $c$ -axis in zero field below  $T_N$ .

at very high fields, explaining why no transition was observed in my measurements.

In mean field calculations, depending on the nature of the interactions between the next-nearest-neighbour moments, a metamagnetic transition for an easy axis field can be either first or second order. For ferromagnetic next-nearest-neighbour interactions, the transition is second order at higher temperatures but first order at the lowest temperatures, whereas when all interactions are antiferromagnetic, the transition is predicted to be second order at all temperatures [122]. An Ising metamagnetic transition has been studied in detail in  $\text{CeRh}_2\text{Si}_2$  with  $T_N = 36$  K and  $B_c = 26$  T; the transition is second order above 20 K ( $B < 24$  T), and first order at lower temperatures [119]. If the transition in  $\text{CeSb}_2$  becomes first order in field, the quantum fluctuations at the first order QPT may be weaker than at a quantum critical point, which could explain the absence of non-Fermi liquid behaviour. However, there can still be some increase in spin fluctuations near a first-order QPT which produces a peak in the  $A$ -coefficient, as seen in  $\text{CeRh}_2\text{Si}_2$ , so the mechanism of field-tuned spin fluctuations responsible for the unusual S-shaped superconducting critical field discussed in the last chapter may still be valid.

For an XY anisotropy, illustrated in Figure 4.8, the moments are ordered in the easy  $a$ - $b$  plane. In this case, a  $c$ -axis field will cause a rotation of the moments, leading to a QCP, whereas an  $a$ - $b$  field will produce a metamagnetic transition where half of the magnetic moments are flipped. For this to match my measurements, the  $a$ - $b$ -plane spin-flip metamagnetic transition must occur at higher fields, above 6 T,

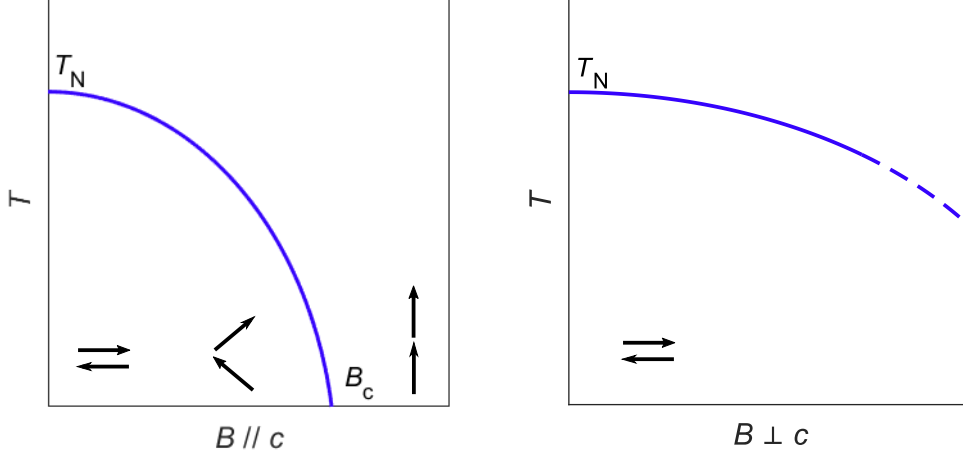


Figure 4.8: Schematic field-temperature phase diagrams showing the possible effect of a magnetic field applied along the  $c$ -axis (left) and perpendicular to the  $c$ -axis (right) on an antiferromagnet with strong XY anisotropy. Arrows indicate the directions of the magnetic moments, which are ordered in the  $a$ - $b$  plane in zero field below  $T_N$ .

than the  $c$ -axis spin rotation transition. For a strong XY anisotropy, the  $c$ -axis metamagnetic transition would be expected to occur at lower fields than the  $a$ - $b$ -plane rotation transition, like in  $\text{UPd}_2\text{Al}_3$  [123]. If the anisotropy is weak, the situation is less clear, but it may be possible for the  $c$ -axis transition to occur at lower fields, in agreement with the data. From these resistivity measurements below the QCP, it is not possible to determine which of the strong Ising or weak XY scenarios apply in high-pressure  $\text{CeSb}_2$ . However, measurements beyond the QCP, to be presented in Section 4.2.3, where the moments no longer experience a magnetic exchange field, suggest that an XY anisotropy is more likely. An XY easy-plane magnetic anisotropy is also seen in ambient-pressure  $\text{CeSb}_2$  [81, 82].

### Pressure dependence

As both pressure and magnetic fields along the  $c$ -direction suppress magnetism, it is interesting to look at the combination of these two tuning parameters (Figure 4.9). As pressure is increased towards the critical pressure, the critical field  $B_c$  for magnetism decreases, i.e. a smaller field is required to remove the magnetism when the zero-field transition temperature is lower. This results in a line in the pressure-field phase diagram separating magnetic and non-magnetic states at zero temperature which goes to zero field at the critical pressure  $p_c \approx 30$  kbar. At pressures just below  $p_c$ , the critical field for magnetism is sufficiently small that it is below the superconducting critical field, i.e.  $B_c < B_{c2}$ , so an enhancement of

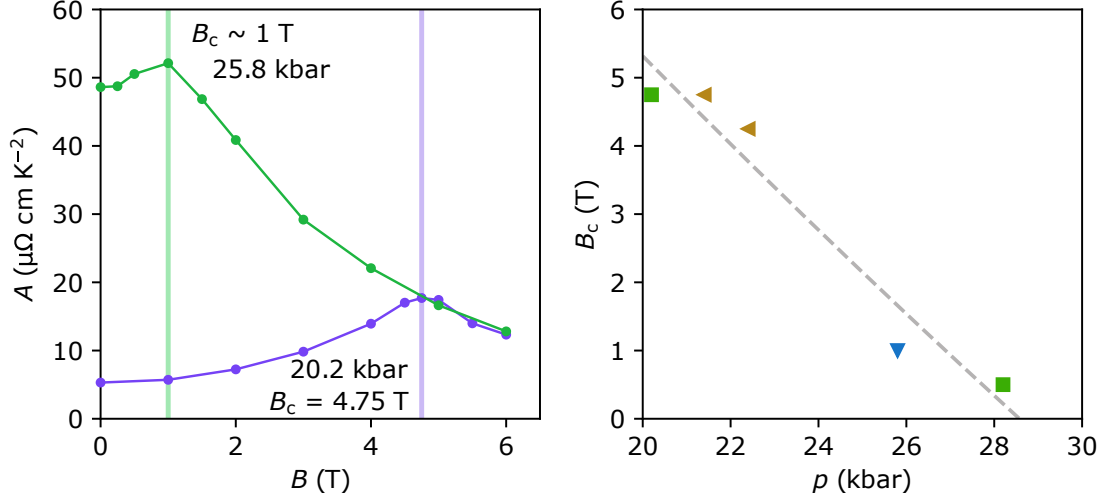


Figure 4.9: Left: Fermi liquid  $A$ -coefficient for applied fields along  $c$  at 20.2 and 25.8 kbar. Vertical lines indicate the critical field  $B_c$  for each pressure where  $A$  is largest. Right: critical field along the  $c$ -direction for magnetism at each pressure, showing a decrease in  $B_c$  as pressure is increased. Different markers indicate different samples, as in Figure 4.3. The dashed line is a guide to the eye.

superconductivity can be seen when magnetic order is suppressed by field, resulting in the unusual S-shaped critical field curve discussed in the last chapter.

## 4.2 Resistivity above and beyond the quantum critical point

### 4.2.1 Non-Fermi liquid resistivity

The low temperature resistivity and its gradient at several representative pressures around and beyond the QCP is shown in Figure 4.10. Gradients were obtained by binning the data into points separated by  $\sim 0.03 \text{ K}$  and taking the difference between these points. To analyse the normal state resistivity, I have fitted  $\Delta\rho = aT^n$  over different temperature intervals at each pressure. Each temperature interval is plotted as a point in Figure 4.11 with a colour representing the value of the exponent  $n$ . The values of the exponents at each point have been interpolated with a Kriging method to produce a two-dimensional colormap which estimates the exponent at each pressure and temperature.

At pressures below the quantum critical point, in the antiferromagnetic state, the resistivity has a Fermi liquid  $\Delta\rho = aT^2$  temperature dependence at lowest temperatures. At slightly higher temperatures, but still within the magnetic state, the fit gives an exponent  $n > 2$  due to scattering between electrons and thermally activated

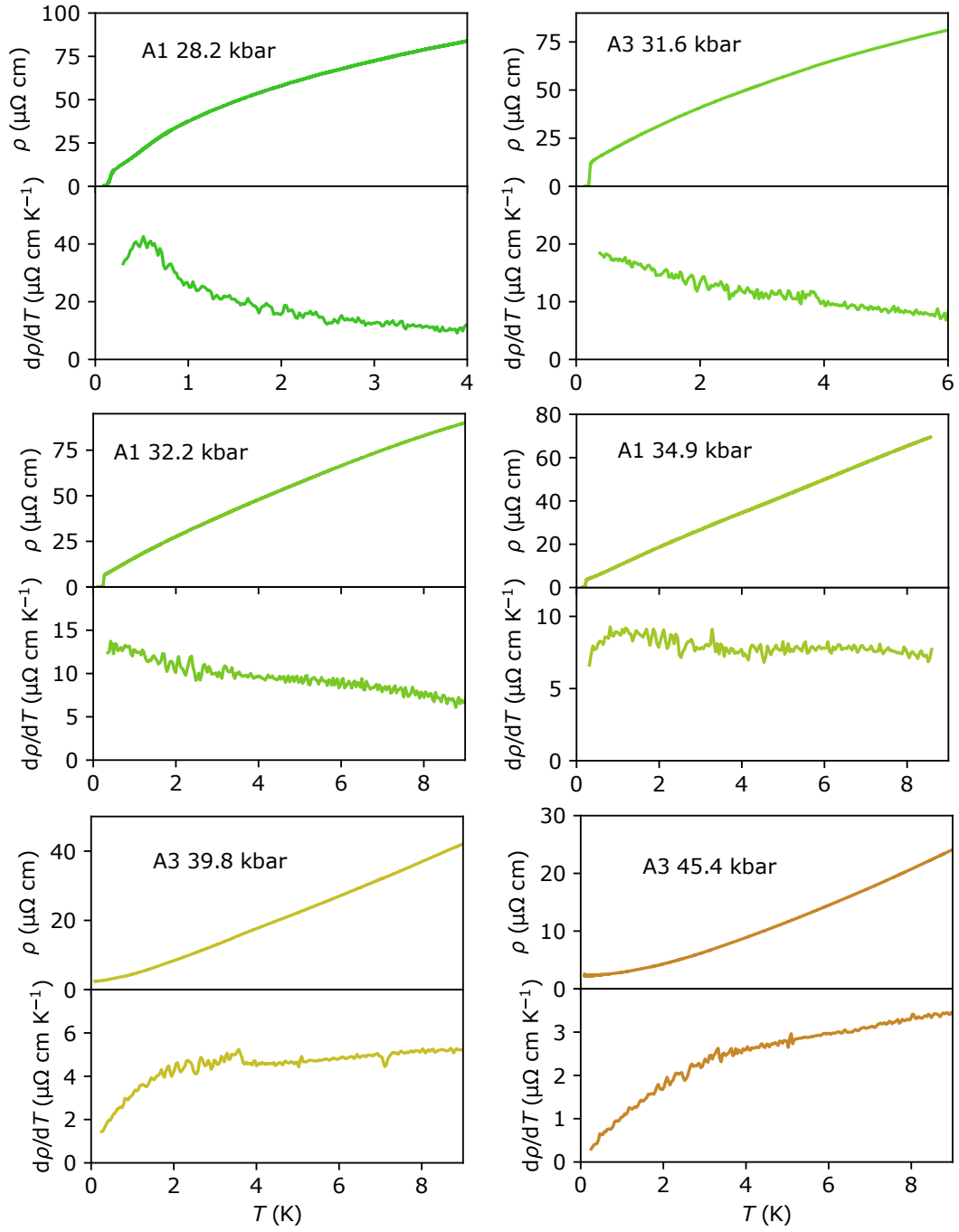


Figure 4.10: Temperature dependence of the resistivity of  $\text{CeSb}_2$ , and its gradient, at six pressures: 28.2, 31.6, 32.2, 34.9, 39.8 and 45.4 kbar.

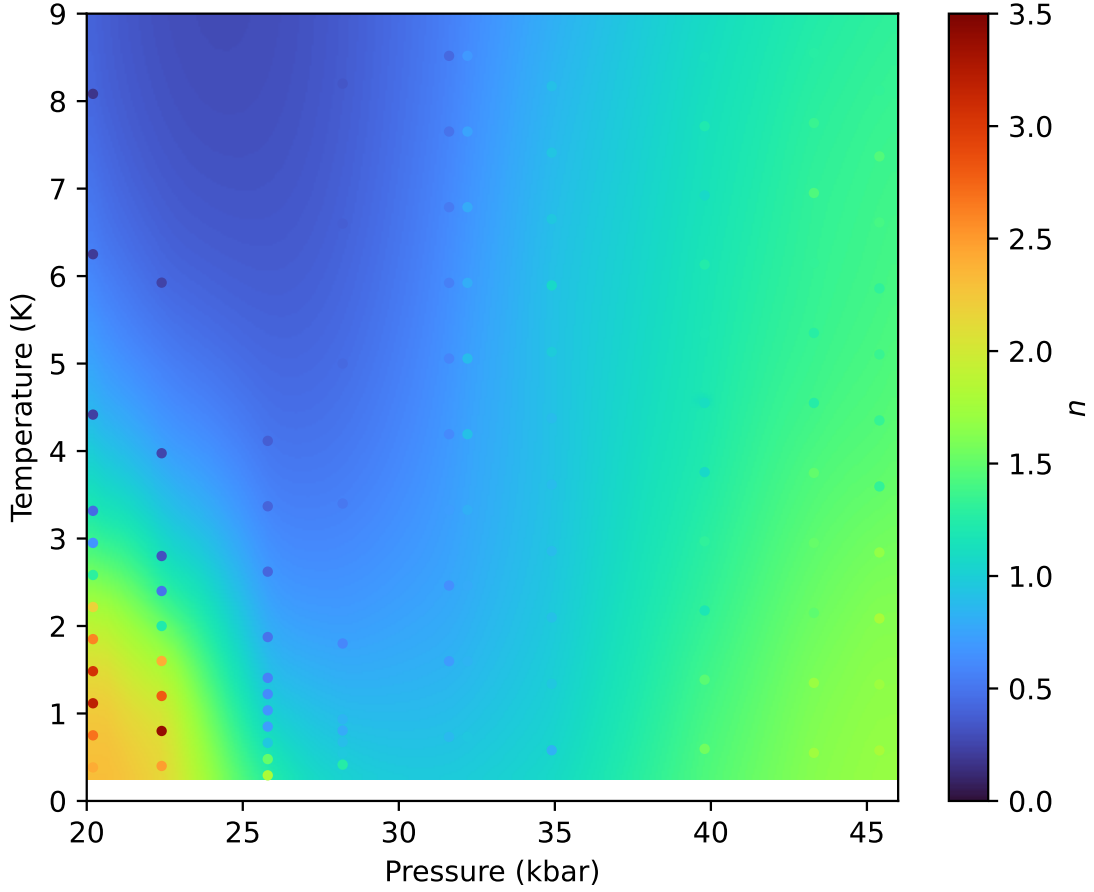


Figure 4.11: Heatmap showing the resistivity exponent  $n$  at different temperatures and pressures, obtained by fitting the zero-field temperature dependence with  $\Delta\rho = aT^n$ .

spin waves (Equation 4.2). At temperatures above the magnetic transition, the resistivity has a sublinear temperature dependence  $n < 1$  which indicates incomplete Kondo hybridisation between electrons and localised  $4f$  moments.

At 28.2 kbar, just below the QCP, a peak in  $d\rho/dT$  indicates a magnetic transition at  $T_N = 0.8$  K. At 31.6 and 32.2 kbar, no such feature is seen, suggesting that magnetism has been suppressed, and therefore the material is positioned just beyond the QCP. At those two pressures, the resistivity has a sub-linear temperature dependence down to the superconducting transition, shown by the positive slope of  $d\rho/dT$  in Figure 4.10 and the value of the exponent  $n < 1$  in Figure 4.11.

The  $n < 1$  power law in  $\text{CeSb}_2$  is different from the behaviour at pressure-induced antiferromagnetic QCPs in  $\text{CePd}_2\text{Si}_2$  and  $\text{CeCu}_2\text{Si}_2$ , where  $1 < n < 3/2$  has been observed [17, 50, 118]. In those materials, the resistivity has been interpreted in terms of antiferromagnetic spin fluctuation theory which in the simplest models gives  $n = 1$  or  $n = 3/2$  for two or three dimensional fluctuations. The normal state

resistivity in CeSb<sub>2</sub> seems more similar to CeRhIn<sub>5</sub>, where a sub-linear  $n \approx 0.85$  just above a pressure-induced antiferromagnetic quantum critical point, which is not expected from antiferromagnetic spin fluctuations [124]. It has been argued that a ‘Kondo breakdown’ quantum critical point is realised under pressure in CeRhIn<sub>5</sub>. In this type of quantum critical point, the Kondo effect disappears at the same critical pressure as antiferromagnetic order. Therefore, local on-site charge fluctuations related to the Kondo effect, as well as long-ranged antiferromagnetic spin fluctuations are present in the vicinity of the quantum critical point. Near a Kondo breakdown point,  $\Delta\rho \propto T^{2/3}$  in two dimensions or  $\Delta\rho \propto -T \ln T$  in three dimensions is predicted [125], in qualitative agreement with the observed sub-linear resistivity. Further support for Kondo breakdown in CeRhIn<sub>5</sub> comes from an isotropic scattering rate around the quantum critical point, despite the quasi-two dimensional crystal structure [124], and from quantum oscillation measurements under pressure which show a sudden change in the Fermi surface at the critical pressure, indicating a changing contribution from  $4f$  states at the QCP [126]. The similar exponents seen in CeSb<sub>2</sub> and CeRhIn<sub>5</sub> could suggest that similar physics occurs in the two systems, although this idea is speculative and it may be possible to obtain a  $n < 1$  exponent from only magnetic fluctuations.

At higher pressures  $p > 33$  kbar, the resistivity of CeSb<sub>2</sub> has a positive curvature at lowest temperatures. The exponent fit gives  $n \approx 2$ , indicating Fermi liquid behaviour. The Fermi liquid region extends to progressively higher temperatures as the pressure is increased, consistent with the behaviour usually seen when a system is tuned beyond a QCP.

At 35 kbar, the resistivity has an approximately linear  $\Delta\rho \propto T$  above the Fermi liquid region, seen as a constant  $d\rho/dT$  up to the highest temperature DMS of 9 K and an exponent  $n \approx 1$ . Measurements to higher temperatures in the PPMS indicate that the linear resistivity persists up to 10 K at 34 kbar (Appendix Figure B.4). At higher pressures around 45 kbar, the exponent is closer to  $n \approx 1.5$ . This behaviour persists over a large temperature range, so it seems to represent an extended region of non-Fermi liquid behaviour rather than simply a crossover from positive curvature at low temperatures to negative curvature at higher temperature, and is different from the  $n < 1$  non-Fermi liquid behaviour seen directly above the quantum critical point. The values of the exponents  $1 < n < 1.5$  suggest that the behaviour could arise from antiferromagnetic spin fluctuations.

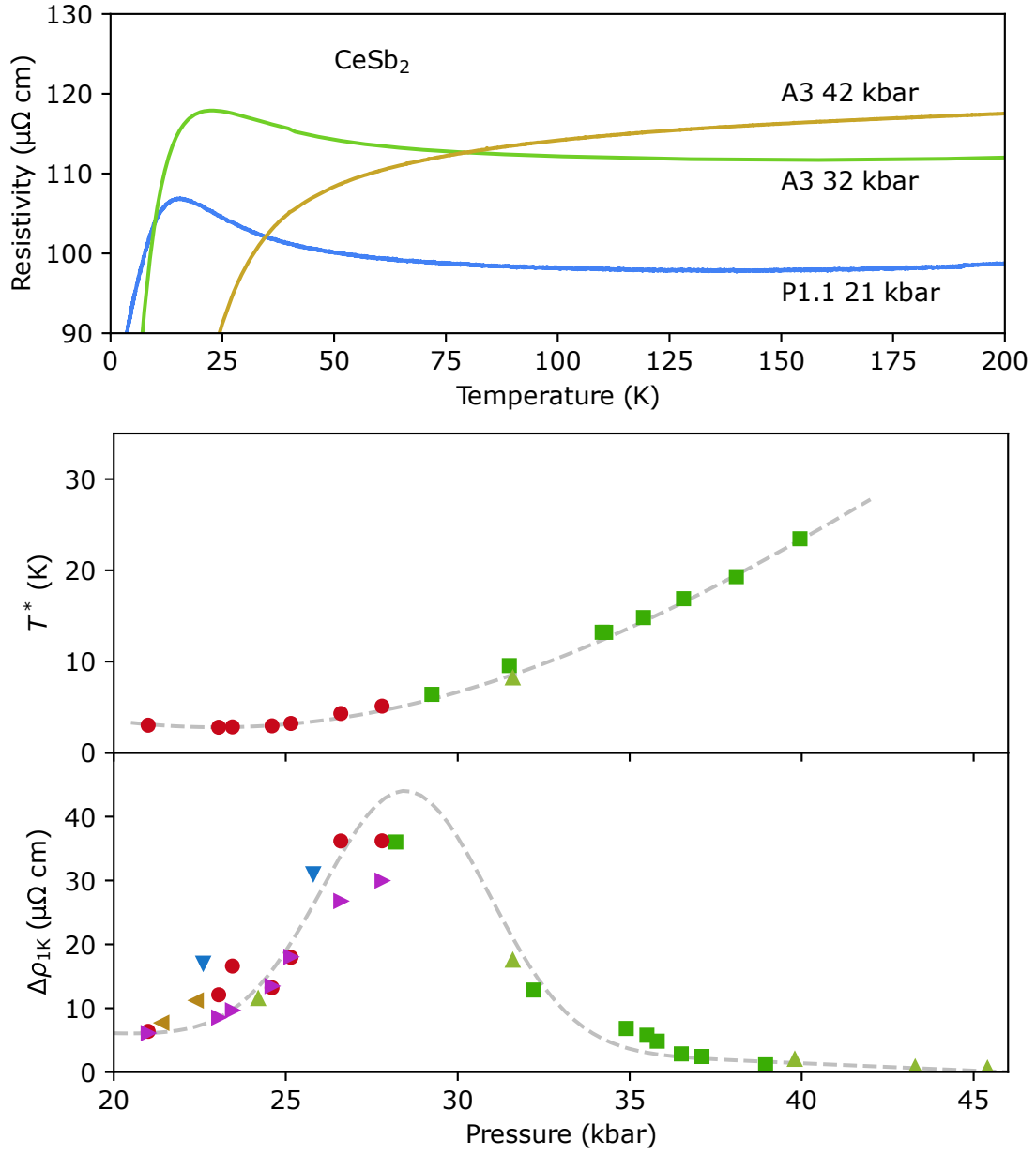


Figure 4.12: Top: resistivity of  $\text{CeSb}_2$  at higher temperatures at three pressures. Bottom: pressure dependence of the Kondo lattice coherence temperature  $T^*$  estimated as the temperature where the resistivity reaches 80% of its maximum value, and the pressure dependence of  $\Delta\rho_{1K} \equiv \rho(1\text{ K}) - \rho_0$ . Different markers indicate different samples, as in Figure 4.3.

### 4.2.2 Coherence temperature and effective mass

The resistivity of CeSb<sub>2</sub> at higher temperatures is flat, with a value that increases slightly as pressure is increased, possibly due to lattice contraction under pressure. At these temperatures, well above the coherence temperature, the  $4f$  moments are fully localised, so the large, temperature-independent resistivity arises from incoherent scattering between  $4f$  and conduction electrons. As the material is cooled, the resistivity rises to a maximum, before dropping rapidly at low temperatures. I have estimated the coherence temperature  $T^*$  up to 40 kbar as the temperature where  $\Delta\rho = \rho - \rho_0$  rises to 80% of its maximum value (Figure 4.12, bottom). For pressures above 40 kbar, an estimate of  $T^*$  is more difficult as the maximum is hidden behind a phonon background, but the high temperature resistivity still has the form of a moderate heavy fermion system. The coherence temperature represents the onset temperature for the Kondo hybridisation between  $4f$  and conduction electrons. It gives an indication of the width of the heavy  $4f$  bands at the Fermi energy, and is related to the effective mass by  $T^* \propto 1/m^*$ .  $T^*$  has a minimum around 23 kbar, indicating that the mass enhancement from the Kondo effect is largest there, at pressures below the QCP. As the pressure is increased across and beyond the critical pressure,  $T^*$  increases, indicating wider  $4f$  bands and a weaker Kondo mass enhancement.

The low-temperature  $A$ -coefficient provides an alternative measure of the effective mass, as in Section 4.1. For pressures across the QCP, the presence of non-Fermi liquid resistivity makes an analysis of the  $A$ -coefficient difficult. In Figure 4.12 I have plotted  $\Delta\rho_{1K} \equiv \rho(1\text{ K}) - \rho_0$ , which provides an alternative, less precise, measure of the effective mass.  $\Delta\rho_{1K}$  increases upon approaching the QCP, and decreases with increasing pressure on the other side of the QCP. The exact location of the peak in  $\Delta\rho_{1K}$  is unclear, but it lies close to the critical pressure  $p_c \approx 30$  kbar where magnetism disappears. Therefore, as expected for a QCP, quantum critical magnetic fluctuations, and possibly also Kondo breakdown fluctuations, provide a large mass enhancement or scattering cross section, generating a large low-temperature resistivity.

The minimum in  $T^*$  and maximum in  $\Delta\rho_{1K}$  occur at slightly different pressures of 23 and 30 kbar respectively. This could indicate that the large mass enhancement in CeSb<sub>2</sub> arises from two different mechanisms, Kondo effect and quantum critical fluctuations, which have different pressure dependences. However, the connection between  $\Delta\rho_{1K}$  and effective mass is complicated because  $\Delta\rho_{1K}$  is also influenced by other factors such as the presence of magnetic order; at pressures below the QCP, antiferromagnetism reduces the temperature dependence of the resistivity and therefore

suppresses  $\Delta\rho_{1K}$ .  $T^*$  is determined at higher temperatures so it is not affected by the presence or absence magnetic order, and therefore can have a different pressure dependence.

### 4.2.3 Fermi liquid resistivity in magnetic fields

#### Magnetic fields along $c$

The effects of an applied field along the  $c$ -axis are illustrated in Figure 4.13 for four pressures: 28.2, 31.6, 34.9 and 39.8 kbar. In field, the resistivity follows a low-temperature Fermi liquid temperature dependence  $\rho = \rho_0 + AT^2$  at all pressures, even those where a non-Fermi liquid resistivity is seen at zero field.

At every pressure and field where the resistivity follows a Fermi liquid temperature dependence at low temperature, I have fitted the resistivity to obtain an  $A$  coefficient. Points are plotted in Figure 4.14 on a colour scale to give an indication of how the effective mass  $m^* \propto \sqrt{A}$  varies across the phase diagram, and the background of the plot is an interpolation of the points. At pressures below the QCP, the mass becomes larger in field due to the field-induced magnetic to non-magnetic transition, where fluctuations are higher. As pressure is increased towards the QCP, the magnetic critical field decreases, resulting in a line of higher mass in the phase diagram which comes down to zero field at the critical pressure.

At every pressure beyond the QCP, the  $A$ -coefficient decreases with increasing field, indicating a decreasing effective mass. This behaviour can be understood for mass enhancements from both quantum critical fluctuations and from the Kondo effect. A  $c$ -axis magnetic field suppresses magnetism, so at pressures beyond the critical pressures, the system is moved even further from the QCP by an applied field. Therefore the strength of spin fluctuations decreases, and the associated mass enhancement decreases. For mass enhancement from the Kondo effect, there is a competition between the Zeeman splitting of the  $4f$  states  $\Delta E \sim \mu_B B$  and width of the heavy  $4f$  band at the Fermi energy  $\Delta E \sim k_B T^*$ . As the Zeeman splitting increases in field and becomes comparable in size to the bandwidth, the spin-up and spin-down  $4f$  bands no longer both cross the Fermi energy, so the quasiparticles lose their heaviness. For both of these mechanisms, the mass is expected to change more quickly with field near the QCP than at higher pressures, because the Kondo energy scale is smaller and there are more quantum critical fluctuations there.

At pressures close to the quantum critical point (e.g. 32.2 kbar), the 6 T magnetoresistance is negative, whereas at higher pressures (e.g. 39.8 kbar) it is positive. This behaviour can be understood as a result of the pressure dependence of the coherence temperature. Close to the QCP, the coherence temperature is low, so in

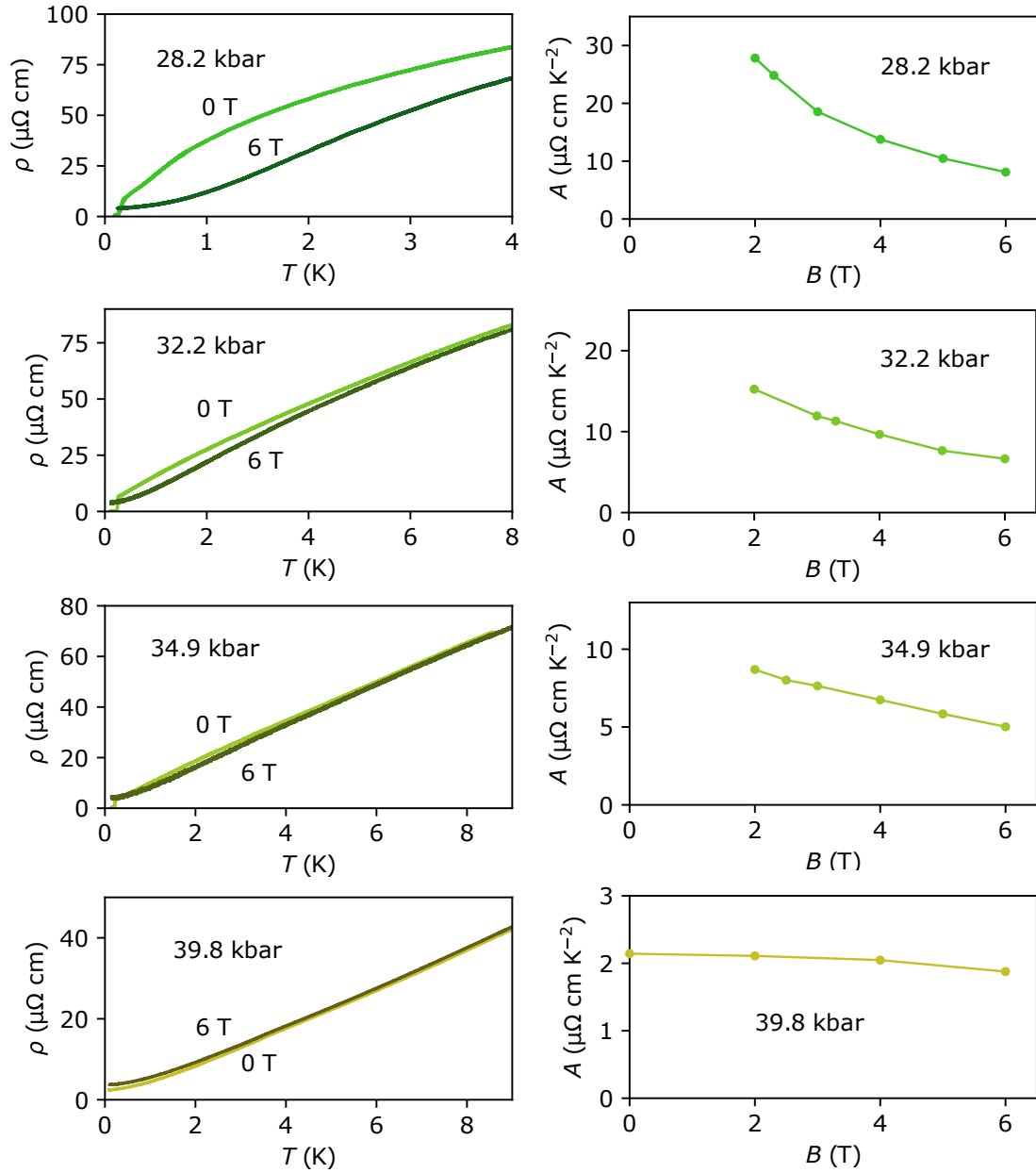


Figure 4.13: Left: Temperature dependence of the resistivity of  $\text{CeSb}_2$  in zero magnetic field and in 6 T  $c$ -axis field at four pressures: 28.2, 31.6, 34.9 and 39.8 kbar. Right: Field dependence of the  $A$ -coefficient for each pressure in the range of magnetic fields where the resistivity follows a Fermi liquid  $\Delta\rho = AT^2$  temperature dependence.

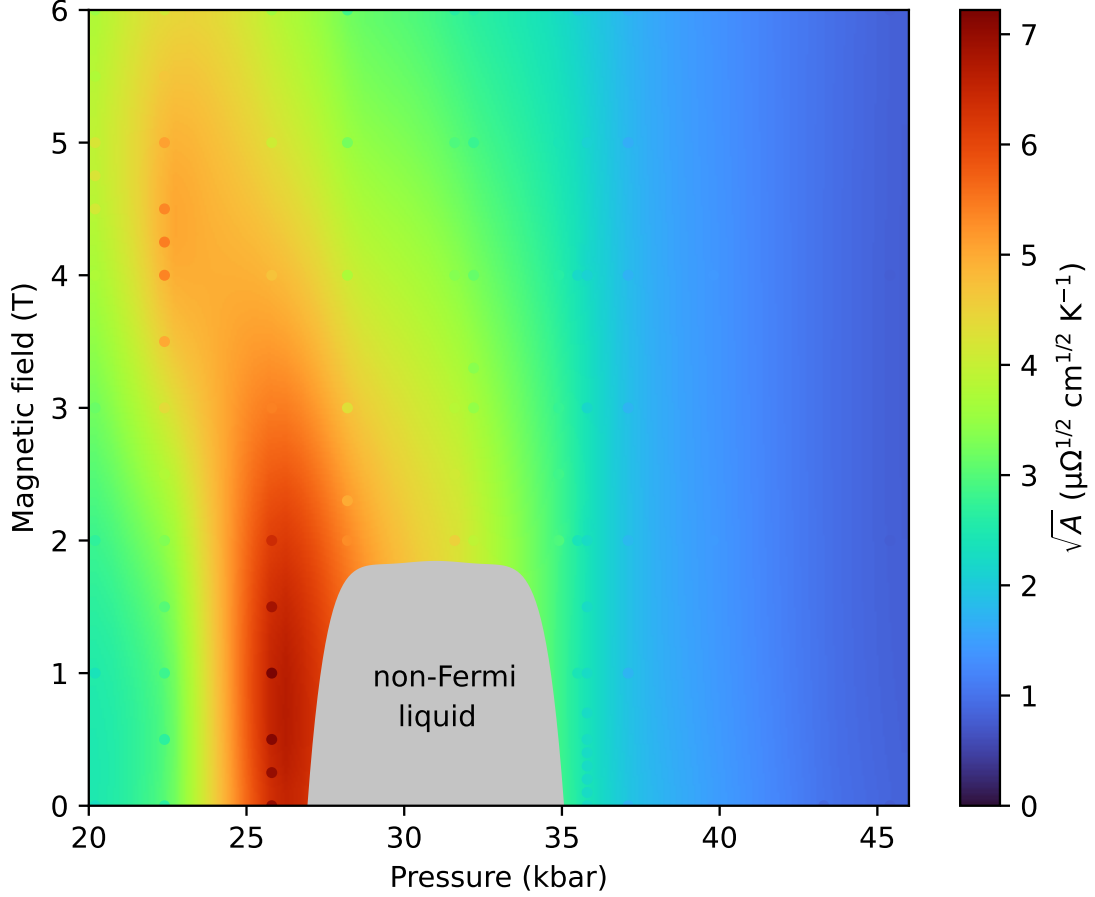


Figure 4.14: Heatmap showing the magnitude of  $\sqrt{A}$ , where  $A$  is the Fermi liquid coefficient, at different pressures and  $c$ -axis magnetic fields from fits to the resistivity at lowest temperatures. The grey area indicates pressures and fields where the resistivity does not follow a Fermi liquid temperature dependence over a sufficiently large temperature range to determine a value of  $A$ .

6 T field, the Zeeman energy is larger than the coherence energy scale. Therefore a magnetic field destroys the coherent  $4f$  bands, and instead the  $4f$  states act like field-polarised local moments. In this case, as the magnetic field is increased, the local  $4f$  moments become polarised so there is less disorder and therefore the resistivity decreases. At higher pressures the coherence temperature is larger, so the moderately heavy coherent  $4f$  bands survives up to higher temperatures and fields. This coherent heavy fermion state displays positive magnetoresistance like a normal metal. At intermediate pressures, the magnetoresistance is positive at low temperatures when  $T \ll T^*$ , but negative at higher temperatures when  $T > T^*$  (Appendix Figure B.5). This crossover in magnetoresistance is seen in other heavy fermion materials located just to the right of the quantum critical point in the Doniach phase diagram such as  $\text{CeAl}_3$  [127].

## In-plane magnetic fields

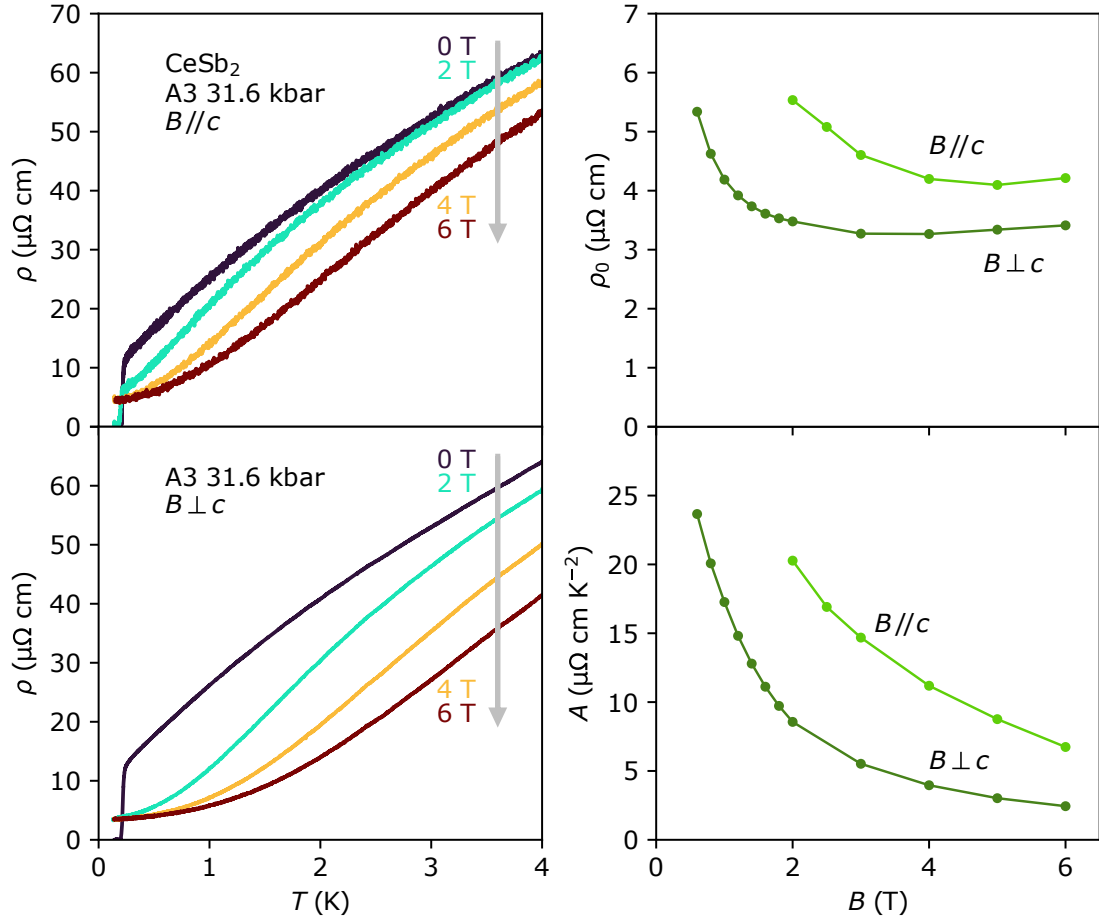


Figure 4.15: Left: resistivity of CeSb<sub>2</sub> at 31.6 kbar (A3) for magnetic fields applied along the  $c$ -direction (top) and perpendicular to the  $c$ -direction (bottom). Right: field dependence of the residual resistivity and  $A$ -coefficient from fitting the data at lowest temperatures to  $\rho = \rho_0 + AT^2$ .

At 31.6 kbar, I measured CeSb<sub>2</sub> in the DMS with field along the  $c$ -axis, and then in the  $a$ - $b$  plane (Figure 4.15). Negative magnetoresistance and the recovery of Fermi liquid behaviour is seen in both directions, but the resistivity is more responsive to in-plane fields. Fits to the Fermi-liquid form  $\rho = \rho_0 + AT^2$  show that both  $\rho_0$  and  $A$  decreases more quickly with in-plane field, indicating a stronger decrease in quantum critical spin fluctuations with field in that direction. This anisotropy can be explained by the XY anisotropy model discussed in Section 4.1; the moments can rotate more freely within the easy plane than along the hard  $c$ -axis, so spin fluctuations are quenched more quickly. The anisotropy means that the superconducting state, which is mediated by spin fluctuations, is more responsive to an in-plane field. This explains the strong curvature of the in-plane upper critical

field seen at 34 kbar, and may explain why the inverse S-feature seen in the critical field at 32 kbar appears at lower fields for  $B \parallel ab$  compared to  $B \parallel c$ .

### 4.3 Summary

At low pressures below the QCP, CeSb<sub>2</sub> is antiferromagnetic and the normal state resistivity contains contributions from scattering between electrons and gapped spin waves. In a magnetic field along the  $c$ -direction, an antiferromagnetic-to-paramagnetic transition is seen, with an increase in  $A$ -coefficient but no non-Fermi liquid behaviour seen at the critical field. For field applied in the  $a$ - $b$  plane, the transition is not seen in resistivity measurements up to 6 T.

A large low-temperature resistivity due to quantum critical fluctuations is seen at the critical pressures, whereas the Kondo coherence temperature reaches a minimum at 23 kbar then increases with increasing pressure. A non-Fermi liquid, sub-linear resistivity is seen at temperatures directly above the QCP from quantum critical fluctuations, possibly from a Kondo breakdown QCP. Fermi liquid behaviour is recovered at higher pressures, and in an applied field at all pressures, with a decreasing effective mass in field. The response to field is anisotropic, with a stronger decrease in spin fluctuations for in-plane fields, possibly indicating an XY magnetic anisotropy.

### 4.4 Outlook

Further measurements using different measurement techniques are needed to gain a deeper understanding of the magnetism and spin fluctuations in high-pressure CeSb<sub>2</sub>. Neutron scattering measurements to determine the precise ordering pattern of the antiferromagnetic phase would allow a more detailed understanding of the fluctuations responsible for superconductivity. However, the combination of high pressures above 15 kbar and temperatures below 2 K places the antiferromagnetic phase just beyond the reach of current neutron scattering capabilities. CeBi<sub>2</sub>, which has an unknown crystal structure and antiferromagnetism below  $T_N = 3.3$  K, might have the same structure and magnetism as high-pressure CeSb<sub>2</sub> [128, 129]. Therefore it could turn out to be a ‘low-pressure’ analogue of CeSb<sub>2</sub> and might present an opportunity to study the magnetism of CeSb<sub>2</sub> at ambient pressure. Alternatively, by doping CeSb<sub>2</sub>, it might be possible to stabilise the antiferromagnetic phase, and maybe even superconductivity, at ambient pressure, where it can be studied with a wider range of measurement techniques [130].

Quantum oscillation measurements in the high-pressure structure of CeSb<sub>2</sub> might be possible due to the high quality of CeSb<sub>2</sub> samples ( $\text{RRR} \sim 100$ ). These measurements could provide information about the geometry of the Fermi surface which could be compared to the anisotropy of the superconducting upper critical field. The pressure dependence of oscillation frequencies and effective masses could provide valuable information about changes in the role of  $4f$  electrons and mass enhancements from Kondo effect and magnetic fluctuations across the phase diagram. However, the very high effective masses (e.g.  $m^* \sim 600 m_e$  suggested by the slope of  $B_{c2}$  at 35 kbar) make these measurements extremely challenging, especially in a pressure cell. It is likely that the masses become lighter in very high fields, or at pressures well beyond the QCP, but they are likely to still remain large, and therefore temperatures well below 1 K are probably required to observe oscillations. Another potential difficulty could be damage to samples when they pass through the structural transition. Although the residual resistivities above 20 kbar are similar to those at ambient pressure, it is possible that the crystals become strained when passing through the transition, and it is unclear whether the samples remain single crystalline in the  $a$ - $b$  plane. So far, attempts to observe oscillations around 30 kbar with TDO in anvil cells at the National High Magnetic Field Laboratory in Tallahassee have been unsuccessful.

Hall effect measurements on CeSb<sub>2</sub> in the high-pressure structure might be interesting. Although Hall data can be difficult to interpret in heavy fermion materials, it could provide some indication of how the size of the Fermi surface evolves with pressure across the QCP. Hall measurements would not provide the same detailed information as quantum oscillations, but they are likely to be more experimentally feasible and are probably not too much more difficult than the resistivity measurements presented in this chapter.

# Chapter 5

## YbPtBi

In this chapter I present Fermi surface measurements of the Kondo lattice semimetal YbPtBi. I first review previous measurements on the material’s electronic properties to motivate and contextualise my results. Then I present ambient-pressure quantum oscillation measurements, first along the  $[100]$  direction to examine the field and temperature dependence of the oscillations, and then a rotation study to determine the shape of the Fermi surface. Finally, I extend these measurements to pressures up to 32 kbar.

### 5.1 Introduction to YbPtBi

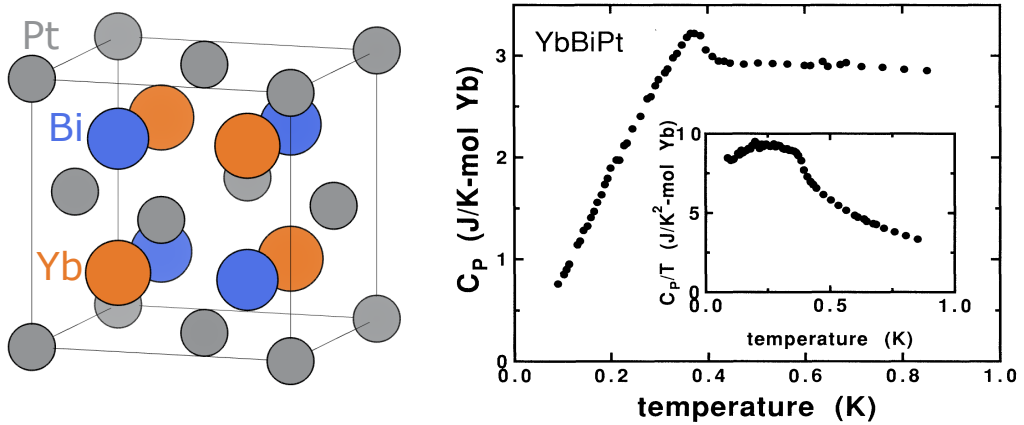


Figure 5.1: Left: conventional face-centred cubic unit cell of YbPtBi. Right: low temperature heat capacity of YbPtBi taken from Fisk *et al.* [131].

YbPtBi, also known as YbBiPt, crystallises in the cubic non-centrosymmetric half-Heulser “MgAgAs” structure with space group  $F\bar{4}3m$ . Its structure consists of

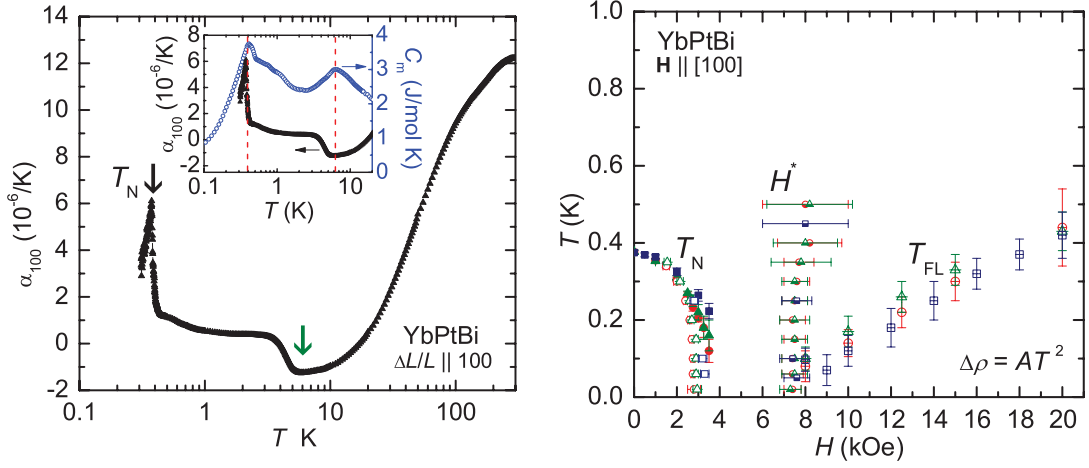


Figure 5.2: Left: thermal expansion coefficient of YbPtBi in zero field (inset: comparison of thermal expansion coefficient and heat capacity). Right: phase diagram of YbPtBi in an applied magnetic field along the [100] direction. Both subfigures have been taken from Mun *et al.* [139]

a face-centred cubic lattice with  $a = 6.5953 \text{ \AA}$  at room temperature and a basis of Yb at  $(-1/4, -1/4, -1/4)a$ , Pt at  $(0, 0, 0)$  and Bi at  $(1/4, 1/4, 1/4)a$  (Figure 5.1, left) [132].

Half-Heusler materials have attracted interest for their topological properties. They contain 18 valence electrons, so many materials in the family are band insulators or semiconductors, whereas others, like YbPtBi, are semimetals with small numbers of charge carriers from overlapping conduction and valence bands. Their band structures are very sensitive to variations in lattice constant and spin-orbit coupling, and it is possible to generate ‘band inversions’, where the energies of  $s$  and  $p$  bands are swapped, resulting in topologically protected features in their band structures [133–135].

YbPtBi has an extremely large heat capacity of  $C/T = 8 \text{ J mol}^{-1} \text{ K}^{-2}$  at low temperatures (Figure 5.1, right). Such a large heat capacity is unusual, even in heavy fermion systems, and is comparable only to  $\text{YbCo}_2\text{Zn}_{20}$  which has  $C/T = 7.9 \text{ J mol}^{-1} \text{ K}^{-2}$  [136]. If this heat capacity is produced by heavy charge carriers, it would imply effective masses similar to the mass of a proton! YbPtBi undergoes a phase transition at 0.4 K, which is believed to be a spin density wave (SDW) transition. The SDW has a small ordered moment of  $0.1\mu_B$  determined by  $\mu\text{SR}$  measurements [137], and partially gaps the Fermi surface, causing an increase in resistivity below the transition. In measurements under hydrostatic pressure, the SDW transition could no longer be seen above 1.2 kbar [138].

Cubic crystal symmetry splits the  $J = 7/2$  energy levels of an  $\text{Yb}^{3+}$  ion into one quartet and two doublet crystal electric field (CEF) levels [140]. The temperature

dependence of heat capacity shows broad bumps at 0.5 K and 6 K, which may indicate CEF levels at energies corresponding to those temperatures, and features in the thermal expansion coefficient  $\alpha = d(\Delta L/L)/dT$  are seen at the same temperatures (Figure 5.2 left) [139]. Neutron scattering results indicate that the CEF levels at energies below  $E/k_B = 20$  K consist of one doublet and quartet [141]. Recent measurements of the elastocaloric effect under applied strain are in agreement with this, and indicate that the ground state is a doublet, the first excited CEF level is the quartet at  $E_1/k_B = 1.6$  K and the second doublet is at  $E_2/k_B \sim 100$  K. However this CEF scheme cannot explain the presence of two bumps (rather than one) seen in heat capacity, or the presence of features in neutron data at 1 and 2 meV. These features may hint at an additional splitting of CEF levels which would require some symmetry breaking at low temperatures, which has not been observed in X-ray measurements [142]. Elastocaloric measurements have been interpreted to give a Kondo temperature of  $T_K \sim 10$  K, so  $k_B T_K > E_1$ . With this order of energy scales, the conduction electrons can hybridise with both the ground state doublet and the excited quartet, so a large amount of entropy is available to generate a very heavy heavy-fermion state in YbPtBi [143].

However, there is an alternative explanation for the large heat capacity in YbPtBi, in which the Kondo interaction is very weak, i.e. the Kondo temperature is around 1 K or even less. In this scenario, which is at odds with the interpretation of elastocaloric measurements, the Yb  $4f$  states are localised and hybridise only very weakly with conduction electrons at the temperatures where measurements are performed. Therefore there is not a large mass renormalisation of the conduction electrons, and the large heat capacity arises from the magnetism of the local moments and excitations of their CEF levels. A weak Kondo interaction would place the material far to the left of the Doniach phase diagram, away from a magnetic quantum critical point. It has recently been proposed that this scenario could explain the large magnetocaloric effect seen in YbNi<sub>1.6</sub>Sn [144].

In reality, the situation in YbPtBi might be somewhere between these two extremes, with some of the large heat capacity arising from a heavy Fermi liquid, and some arising from the CEF levels of local moments. An analysis of the size of the jump in heat capacity and the fraction of the Fermi surface gapped at the SDW transition was used to argue that the Sommerfeld coefficient is  $5 \text{ J mol}^{-1} \text{ K}^{-2}$ , and therefore the majority of the heat capacity arises from a heavy Fermi liquid [138]. This is roughly consistent with an analysis of the widths of CEF levels seen in neutron scattering which shows that the low lying CEF levels hybridise with conduction electrons to different degrees. Therefore some CEF levels hybridise with conduction electrons to produce heavy charge carriers, whereas others give a local-moment con-

tribution to the heat capacity [141].

In an applied magnetic field, the 0.4 K SDW transition can be suppressed to zero temperature with a critical field of 0.4 T along the [100] direction, resulting in the temperature-magnetic field phase diagram on the right of Figure 5.2. The electronic properties in the vicinity of this field-induced quantum phase transition have been studied in detail by Mun *et al.*. In applied fields between 0.4 and 0.8 T, a non-Fermi liquid  $\Delta\rho = AT^{1.5}$  resistivity was measured, whereas above 0.8 T it follows the more usual Fermi liquid  $\Delta\rho = AT^2$  temperature dependence below the temperature  $T_{\text{FL}}$  shown in the figure. The  $A$ -coefficient falls from around  $30 \mu\Omega \text{ cm K}^{-2}$  in 1 T to  $3 \mu\Omega \text{ cm K}^{-2}$  in 5 T. At low temperatures a maximum in  $d\rho/dB$  can be seen at a magnetic field  $\mu_0 H^*$ , which might correspond to a crossover of unclear origin, possibly due to a change in the volume of the Fermi surface [139]. The idea of a Fermi volume change is based on a comparison to  $\text{YbRh}_2\text{Si}_2$ , where it has been proposed that the Fermi surface changes at an field-induced antiferromagnetic quantum critical point from a zero-field ‘small’ Fermi surface without  $f$  states, to a ‘large’ Fermi surface with delocalised  $f$  states above the critical field [145].

The heat capacity in field is difficult to interpret, due to the presence of multiple contributions from electronic, magnetic, phonon and nuclear effects. In particular, the large broad bumps in the heat capacity from CEF splittings, which move to higher temperatures with increasing field, and upturns in the heat capacity at lowest temperature from nuclear Schottky effects complicate the low-temperature heat capacity. Nevertheless, Mun *et al.* have performed fits to the heat capacity to extract Sommerfeld coefficients in field, and estimated  $\gamma \sim 7000 \text{ mJ mol}^{-1} \text{ K}^{-2}$  in  $B = 1 \text{ T}$ , falling to  $\gamma \sim 120 \text{ mJ mol}^{-1} \text{ K}^{-2}$  in  $B = 5 \text{ T}$  [139].

Guo *et al.* have suggested that the heat capacity in fields above 7 T has a large  $C \propto T^3$  contribution which is too large to arise from phonons. They have suggested that this contribution arises from a linear dispersion ( $E \propto k$ ) in the vicinity of Weyl nodes in the band structure of  $\text{YbPtBi}$ . Their fits give  $\gamma = 240 \text{ mJ mol}^{-1} \text{ K}^{-2}$  in  $B = 7 \text{ T}$ , falling to  $\gamma = 90 \text{ mJ mol}^{-1} \text{ K}^{-2}$  in  $B = 13 \text{ T}$  [146]. These values of  $\gamma$  disagree with those from Mun *et al.*, but there is significant uncertainty in all values of  $\gamma$ , because they depend strongly on the fitting procedures used to subtract contributions from CEF and nuclear effects.

The Hall resistivity of  $\text{YbPtBi}$  is positive for all temperatures and fields, indicating predominantly hole-like charge carrier. At low temperatures, below the SDW transition, the Hall coefficient is  $R_{\text{H}} \sim 3.5 \mu\Omega \text{ cm T}^{-1}$ . Above the critical field, the Hall coefficient falls to  $R_{\text{H}} \sim 0.5 \mu\Omega \text{ cm T}^{-1}$ , indicating a higher carrier concentration when the Fermi surface is no longer gapped by SDW order, then rises again in higher fields and saturates at  $R_{\text{H}} \sim 3.25 \mu\Omega \text{ cm T}^{-1}$  above 6 T. The field where the

Hall resistivity is minimum matches up well with the  $H^*$  values in the phase diagram in Figure 5.2. Using a simplistic one-band model, the value of the Hall coefficient in high fields gives a small carrier concentration of  $p = 1/eR_H = 1.9 \times 10^{26} \text{ m}^{-3}$ , or 0.014 holes per formula unit [139, 147]. Alternatively, the field dependence of the Hall coefficient can be interpreted as arising from a constant carrier concentration with an anomalous contributions from magnetisation and Weyl points in the band structure [146]. For comparison, the Hall coefficient of LuPtBi at low temperatures is  $R_H = 14 \mu\Omega \text{ cm T}^{-1}$ , giving a carrier concentration of 0.003 holes per formula unit [139].

A recent study has shown that the carrier concentration can be tuned by varying the concentration of Bi flux used in crystal growth, or by substituting some Pt with Au to dope the material with electrons. More electron-doped crystals have Hall resistivities whose field-dependence can be fit with a two band model containing both electrons and holes, whereas others show single-band hole-like behaviour. Across the series of crystals in the study, hole concentrations varied from  $p = 1.5 - 4.1 \times 10^{26} \text{ m}^{-3}$  [146].

## 5.2 Previous quantum oscillation studies

Quantum oscillation measurements in YbPtBi are interesting as they could provide some insight into the question of whether the  $4f$  states act like local moments or contribute to a heavy fermion state, as the Fermi surfaces are expected to be different in the two cases.

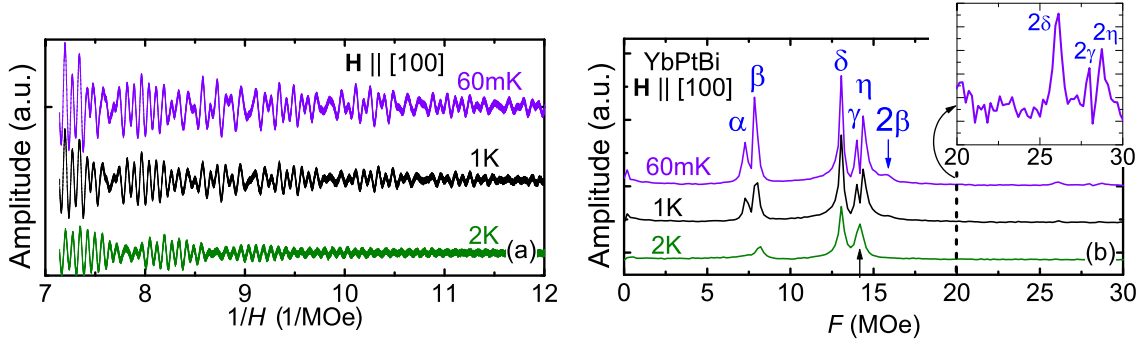


Figure 5.3: Quantum oscillations in the resistivity of YbPtBi with  $\mathbf{B} \parallel [100]$  from Mun *et al.* [148]

Quantum oscillations in YbPtBi have been measured by Mun *et al.*. The oscillations were detected in resistivity measurements between 6 and 14 T, with a base temperature of 0.06 K. Five frequencies were detected along the  $[100]$  direction, and two along the  $[111]$  direction, ranging from 0.7 to 1.8 kT (Table 5.1). Surprisingly

| $\mathbf{B} \parallel [100]$ |          |            | $\mathbf{B} \parallel [111]$ |          |            |
|------------------------------|----------|------------|------------------------------|----------|------------|
|                              | $F$ (kT) | $m^*(m_e)$ |                              | $F$ (kT) | $m^*(m_e)$ |
| $\alpha$                     | 0.73     | 1.4        | $\xi$                        | 0.90     | 1.2        |
| $\beta$                      | 0.78     | 1.6        | $\xi_1$                      | 1.79     | 0.5        |
| $\gamma$                     | 1.31     | 0.8        |                              |          |            |
| $\delta$                     | 1.40     | 0.8        |                              |          |            |
| $\eta$                       | 1.44     | 1.0        |                              |          |            |

Table 5.1: Quantum oscillation frequencies and effective masses in YbPtBi measured by Mun *et al.* for  $\mathbf{B} \parallel [100]$  and  $\mathbf{B} \parallel [111]$  [148].

the effective mass of each frequency, determined from the temperature dependence of the oscillation amplitudes, is between 0.5 and 1.6  $m_e$ , which is much smaller than expected from YbPtBi's large zero-field heat capacity [148].

Within a heavy fermion picture, the light masses can be explained if the effective masses are very field dependent, and are therefore strongly reduced from their zero-field values at magnetic fields where quantum oscillations are observed. A strongly reduced mass in field might be expected for a very heavy Fermi liquid, since bands at the Fermi energy have a very narrow width  $k_B T_K$ . Therefore only a small field is required to generate a Zeeman splitting larger than the bandwidth ( $\mu_B B > k_B T_K$ ), at which point the heavy fermion picture is no longer valid. For the Kondo temperature of 10 K suggested by Gati *et al.* [143], this effect would occur at fields around 10 T, but no field dependence was detected in the quantum oscillations. A field dependent mass might be qualitatively consistent with the field dependence of the  $A$ -coefficient and heat capacity, but a detailed comparison is not possible because the precise shape of the Fermi surface is not known, and because there is considerable uncertainty in estimates of the Sommerfeld coefficient in field. Alternatively, within the localised  $f$  moment picture, the Fermi surface is expected to be light and small, because the Yb  $4f$  states only hybridise very weakly with the conduction electrons.

|               | $F$ (kT)                             | $m^*(m_e)$      | Reference      |
|---------------|--------------------------------------|-----------------|----------------|
| YPtBi         | 0.045                                | 0.1             | [149]          |
| LaPtBi        | 0.07                                 | 0.17            | [150]          |
| CePtBi        | 0.03 (0.06 at low $T$ and high $B$ ) | 0.24 at low $B$ | [150]          |
| GdPtBi        | 0.035                                | 0.3             | [151]          |
| <b>YbPtBi</b> | 0.5 - 1.5                            | 0.8 - 1.6       | This and [148] |
| LuPtBi        | 0.08, 0.2                            | 0.11, 0.23      | [152]          |

Table 5.2: Quantum oscillation frequencies and effective masses in YbPtBi and other half-Heusler  $R$ PtBi materials for  $\mathbf{B} \parallel [100]$ .

Quantum oscillation measurements have been performed in several other half-

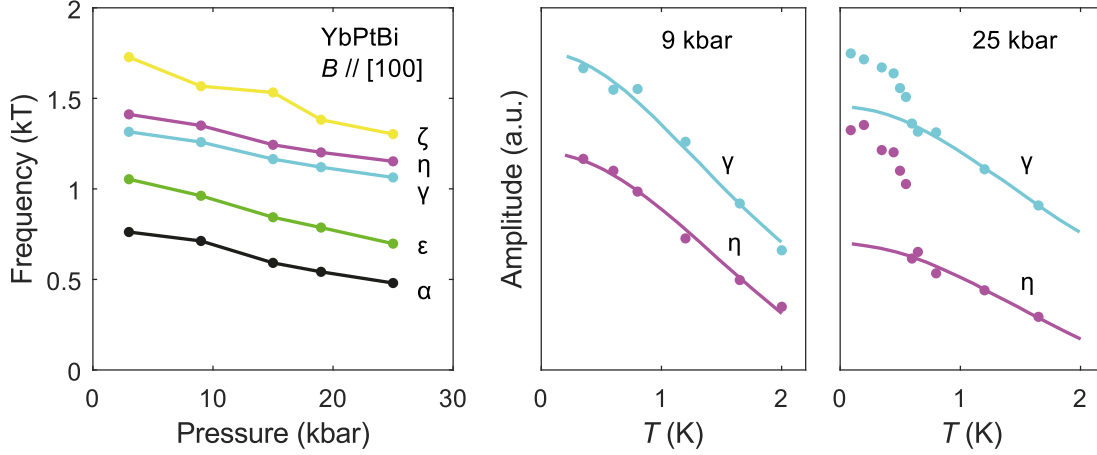


Figure 5.4: Quantum oscillation data under pressure from Huang *et al.* [153]. Left: evolution frequencies under pressure with  $B \parallel [100]$ . Right: temperature dependence of quantum oscillation amplitudes at 9 and 25 kbar, for fields between 10 and 15 T. Lines are high-temperature fits to  $R_T$  from the Lifshitz-Kosevich formula.

Heusler  $R\text{PtBi}$  materials (Table 5.2). Oscillation frequencies in YbPtBi are significantly larger than all other materials, indicating that there is something different about its electronic properties, likely due to the different role of  $4f$  states. Y and La do not contain any filled  $f$  states, while Lu contains a completely full  $4f$  shell, so its  $f$  states are not relevant in LuPtBi. The  $4f$  states in Gd compounds are completely localised, so they are not directly relevant to the electronic properties of GdPtBi.  $\text{Ce}^{3+}$  ions have one filled  $4f$  state, similar to the single  $4f$  hole in  $\text{Yb}^{3+}$  ions, so the properties of CePtBi might be expected to be similar to YbPtBi. Some field and temperature dependence of the Fermi surface has been observed in CePtBi, which was attributed to hybridisation between the conduction and  $f$  electrons, but the size of its Fermi surface is similar to the  $R\text{PtBi}$  materials without  $f$  states [150]. Therefore it seems that  $f$  electrons in CePtBi play some role, but not to the same extent as in YbPtBi.

Quantum oscillations in YbPtBi have been measured under pressure by Huang *et al.*, using a TDO circuit and a piston cylinder cell. They detected a decrease in all quantum oscillation frequencies (Figure 5.4, left). At the highest pressures, around 25 kbar, they observed a sharp increase in oscillation amplitudes below 0.6 K (Figure 5.4, right), which is not expected from the thermal damping term in the Lifshitz-Kosevich formula [153].

The previous quantum oscillation results, particularly the light effective masses and unusual temperature dependence under pressure, and the question of whether the  $4f$  states are localised or itinerant, motivated me to perform my own quantum oscillation measurements of YbPtBi. The previous results indicated that quantum

oscillations should be observable using the 15 T system and a He-3 probe. One aim was to follow oscillations down to lower fields than before, using the high signal-to-noise ratio of TDO measurements, to search for any field dependence of the Fermi surface that is expected when  $\mu_B B \sim k_B T_K$  in a heavy fermion picture. Measurements on YbPtBi were also a good opportunity to optimise the TDO technique and investigate experimental issues concerning noise and heating at low temperatures.

## 5.3 Quantum oscillations at ambient pressure

All of the measurements in this chapter were performed on single crystals of YbPtBi grown in our group by Max Daschner using a self-flux method with a molar ratio of Yb : Pt : Bi = 0.7 : 0.7 : 10. The crystals are roughly cube-shaped, with lengths around 500  $\mu\text{m}$ . The shape and size of our crystals makes it difficult to perform four-point resistivity measurements but easier to perform TDO measurements, since the cube-shaped crystals have a good filling factor inside a coil.

### 5.3.1 Oscillations for $\mathbf{B} \parallel [100]$

#### Measurements in Cambridge

|          | $F$ (kT)    |
|----------|-------------|
| $\alpha$ | 0.66        |
| $\beta$  | 0.74        |
| $\gamma$ | $\sim 1.21$ |
| $\delta$ | $\sim 1.21$ |
| $\eta$   | 1.38        |

Table 5.3: Quantum oscillation frequencies measured in the 15 T system with  $\mathbf{B} \parallel [100]$  between 8 T and 12.6 T at 0.4 K.

First, I measured a sample of YbPtBi at ambient pressure using an Ice Oxford He-3 probe in the 15 T system. The lambda fridge was not used, so the highest field was 13 T, and the lowest temperature reached by the probe was around 0.4 K. Results are shown in Figure 5.5. Five distinct frequencies can be seen in the Fourier transform in the range from 0.5 to 1.5 kT, in agreement with the results of Mun *et al.* [148]. The peaks have been labelled as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\eta$  to follow the naming convention established in that paper, and the frequencies are listed in Table 5.3. The  $\gamma$  and  $\delta$  frequencies are close together, but the presence of two distinct frequencies can be clearly seen from the shape of the peak in the Fourier transform. Likewise,  $2\gamma$  and  $2\delta$  are close, leading to a broader peak in the Fourier transform.

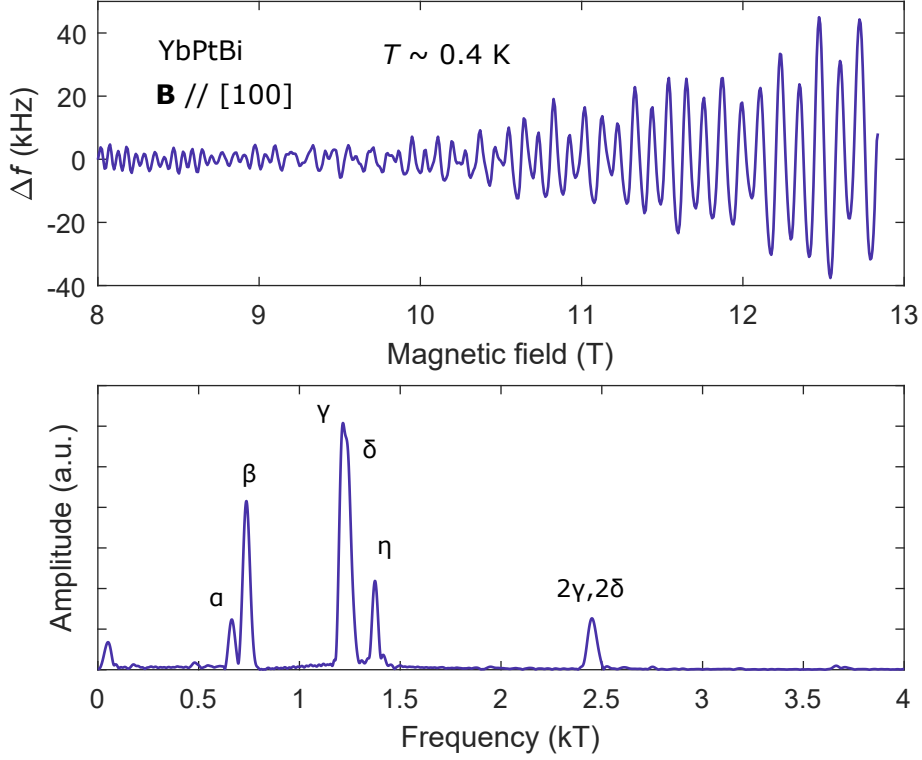


Figure 5.5: Quantum oscillations in YbPtBi measured in the 15 T system at 0.4 K in magnetic fields between 8 and 13 T applied along the [100] direction. Upper: oscillations in the TDO signal after polynomial background subtraction. Lower: Fourier transform of the data in the upper panel.

All five of the quantum oscillation frequencies are lower than the corresponding frequencies measured by Mun *et al.* by around 100 T [148]. As I will describe later in this chapter, the frequencies show some temperature and magnetic field dependence, so some of the differences could arise from different temperatures and magnetic fields used in the two measurements. However, this effect is too small to account for a frequency difference of 100 T. It is more likely that the difference in frequencies is due to a difference in carrier number arising from slightly different growth conditions.

### High field measurements in Nijmegen

I measured a different sample of YbPtBi from the same batch of crystals in a resistive magnet (Cell 1) at HFML in Nijmegen in April 2024. The sample was placed in a He-3 system, in direct contact with the He-3 liquid or gas, and the magnet was swept to 30 T in each sweep, with the field along the [100] direction. The YbPtBi sample was not in the field centre, and the position of NMR features in the TDO signal indicates that the magnetic field at the location of the sample was 96.8% of

the nominal magnetic field, giving a maximum field of 29 T. The TDO field values were scaled by this factor, and also shifted by a small amount proportional to the sweep rate (amounting to a shift of a few mT) to correct for a lag in data acquisition.

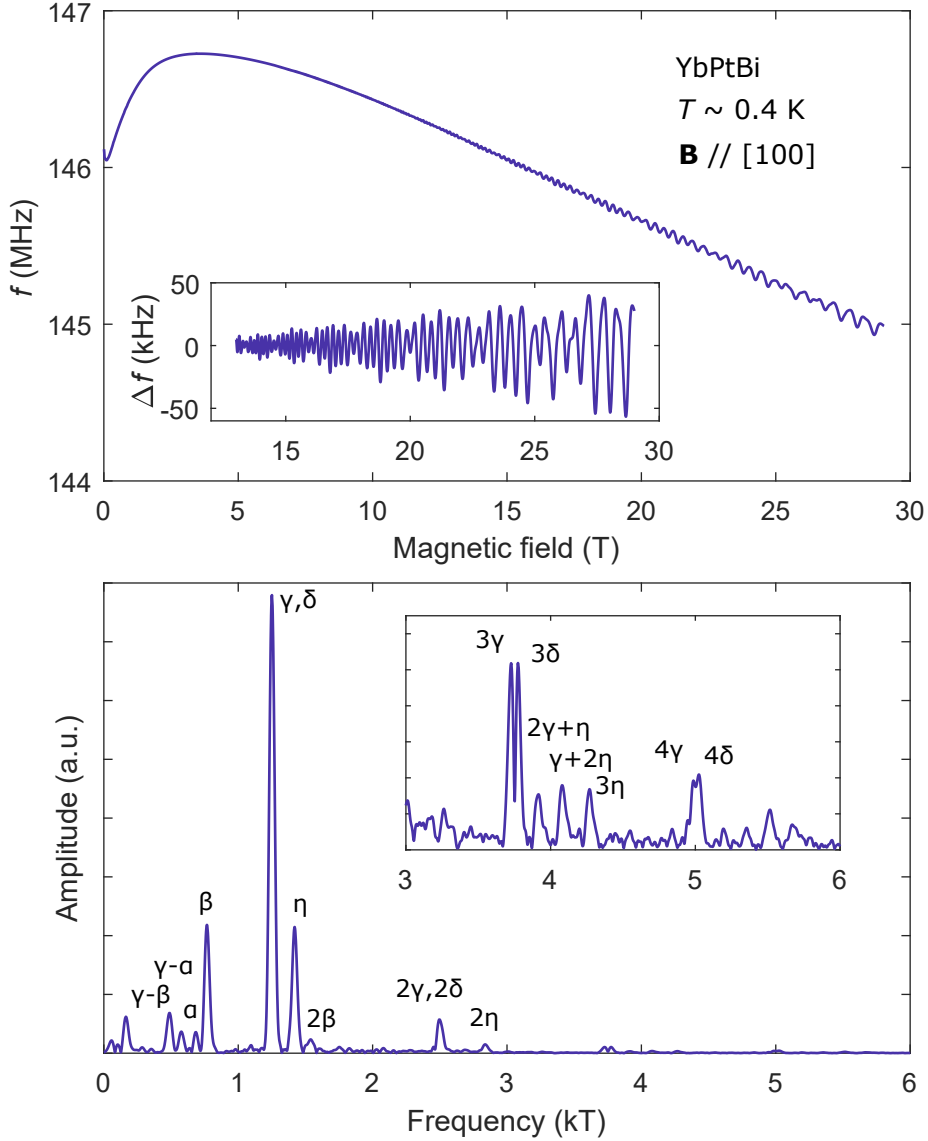


Figure 5.6: Quantum oscillations in YbPtBi measured in Nijmegen at 0.4 K with magnetic field applied along the [100] direction. Upper: Raw TDO data measured during the full sweep from 0 to 29 T. Upper inset: oscillations in the TDO signal after polynomial background subtraction. Lower: Fourier transform of the background-subtracted data. Lower inset: Enlarged Fourier transform between 3 and 6 kT showing peaks from third and fourth harmonics.

The TDO data measured in Nijmegen at base temperature is shown in Figure 5.6. The same five frequencies as before,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\eta$ , can be seen in the Fourier transform. In addition, several new frequencies can be seen, but they can all be explained as harmonics or combinations of those five frequencies, and have

|                   | $F$ (kT)    | $m^*(m_e)$      | $B_0$ (T) | $l$ (nm)   | $dF/dB$  |
|-------------------|-------------|-----------------|-----------|------------|----------|
| $\gamma - \beta$  | 0.49        | $1.23 \pm 0.16$ | 70        | -          | -0.5     |
| $\gamma - \alpha$ | 0.58        | $2.5 \pm 0.3$   | 85        | -          | 0.3      |
| $\alpha$          | 0.69        | $1.4 \pm 0.6$   | 51        | 59         | 2.1      |
| $\beta$           | 0.77        | $0.88 \pm 0.04$ | 48        | 67         | 3.2      |
| $\delta$          | $\sim 1.25$ | -               | -         | -          | $\sim 2$ |
| $\gamma$          | $\sim 1.25$ | -               | -         | -          | $\sim 2$ |
| $\eta$            | 1.42        | $\sim 0.8$      | $\sim 36$ | $\sim 120$ | $\sim 3$ |
| $2\beta$          | 1.54        | $2.4 \pm 0.4$   | -         | -          | -        |
| $2\delta$         | $\sim 2.50$ | -               | -         | -          | -        |
| $2\gamma$         | $\sim 2.50$ | -               | -         | -          | -        |
| $2\eta$           | 2.84        | $2.6 \pm 0.3$   | 60        | -          | 6.8      |
| $3\delta$         | 3.72        | $2.3 \pm 0.2$   | -         | -          | -        |
| $3\gamma$         | 3.78        | $2.0 \pm 0.2$   | -         | -          | -        |
| $2\delta + \eta$  | 3.91        | $2.2 \pm 0.6$   | -         | -          | -        |
| $\delta + 2\eta$  | 4.08        | $2.8 \pm 0.5$   | -         | -          | -        |
| $3\eta$           | 4.28        | $3.1 \pm 0.7$   | -         | -          | -        |

Table 5.4: Quantum oscillation frequencies measured in Nijmegen with  $\mathbf{B} \parallel [100]$ . The frequencies have been taken from the data at the highest fields between 15 and 29 T.

been labelled as such in the figure. The two peaks at 0.49 kT and 0.58 kT have frequencies equal to  $F_\gamma - F_\beta$  and  $F_\gamma - F_\alpha$  respectively, so they are likely to be combination frequencies arising from a mechanism such as magnetic breakdown or quantum interference, to be discussed in Section 5.3.2. They are labelled as  $\gamma - \beta$  and  $\gamma - \alpha$  rather than  $\delta - \beta$  and  $\delta - \alpha$  based on the results of the high-pressure measurements described later in this chapter (Section 5.4).

High harmonics of some of the frequencies can be seen between 3 and 6 kT. Although  $\gamma$  and  $\delta$  cannot be very clearly resolved as two separate peaks in the Fourier transform, their third harmonics  $3\gamma$  and  $3\delta$  are clearly at different frequencies. There are two peaks at 3.91 and 4.08 kT between the third harmonics of  $\delta$  and  $\gamma$  and  $\eta$ , possibly arising from magnetic breakdown. The spacing of the peaks suggests that these frequencies are more likely to arise from  $2\delta + \eta$  and  $\delta + 2\eta$  orbits, rather than  $2\gamma + \eta$  and  $\gamma + 2\eta$ , although there is some uncertainty in this identification.

### Temperature dependence

Data was taken at a series of temperatures in Nijmegen from 0.4 K to 7.0 K. Some of the data at different temperatures is shown on the left of Figure 5.7, showing a clear decrease in oscillation amplitude as the temperature is increased. In order to analyse changes in the oscillations with temperature, Gaussian functions were fitted to peaks in the Fourier transform using the data at the highest magnetic fields between 15

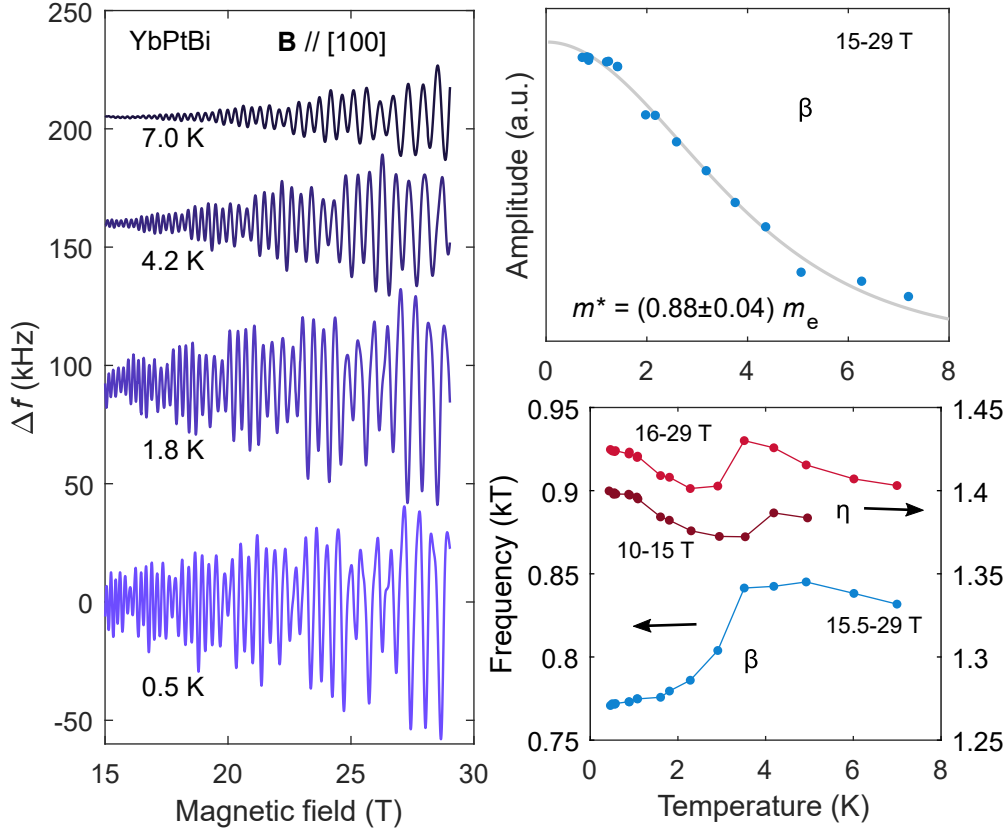


Figure 5.7: Temperature dependence of the quantum oscillations in YbPtBi measured in Nijmegen with  $\mathbf{B} \parallel [100]$ . Left: oscillations at selected temperatures after polynomial background subtraction. Right top: a fit to the temperature dependence of the amplitude of the  $\beta$  frequency gives an effective mass of  $m^* = 0.88m_e$ . Right bottom: temperature dependence of the  $\beta$  and  $\eta$  frequencies.

and 29 T, and frequencies and amplitudes were determined from the midpoints and areas under the Gaussian fits respectively. Effective masses were determined by fitting the temperature dependence of the oscillation amplitudes with the thermal damping function from the Lifshitz-Kosevich formula (Equation 1.24). An example of this fitting for the  $\beta$  frequency is shown in Figure 5.7, and the effective mass of each frequency is listed in Table 5.4. It is not possible to reliably determine effective masses of  $\delta$  and  $\gamma$ , or their second harmonics, because their frequencies are too close together. There might also be a  $2\alpha$  peak at a similar frequency to  $\eta$  which could affect the estimated mass of  $\eta$ , so it is given only as a rough estimate.

The measured masses (Table 5.4) are comparable to those reported by Mun *et al.* [148], but there are some differences. For example, for  $\beta$  my measured value of  $0.88 m_e$  compared to the value of  $1.6 m_e$  from Mun *et al.*, but these differences are not unexpected since our measured frequencies are different and, as I will discuss later

in this chapter (Section 5.4), effective masses seem very sensitive to small changes in electronic structure. Importantly, all the masses are of the order of  $1 m_e$ , which is far too small to account for YbPtBi's large low-temperature heat capacity. The masses of the harmonics are larger than the fundamental frequencies and seem to roughly follow the expected relationships, i.e. the masses of the second and third harmonics are roughly 2 and 3 times bigger than the masses of the fundamental frequencies. The masses of combination frequencies roughly follow the relationships expected for magnetic breakdown. For example, the mass of  $\gamma - \alpha$  is larger than  $\gamma - \beta$  because the mass of  $\alpha$  is larger than  $\beta$ .

As well as the oscillation amplitudes, the oscillation frequencies change significantly with temperature, as shown in the bottom right panel of Figure 5.7. The  $\beta$  and  $\eta$  frequencies have different temperature dependences, but they both show a sharp increase in frequency between 3 and 3.5 K, suggesting that there may be a rapid change in the electronic structure of YbPtBi in that temperature interval. The temperature of this feature appears to decrease with increasing field.

Temperature-dependent quantum oscillation frequencies can arise as a result of several different effects. Firstly, a material's thermal expansion can cause a decrease in the size of the Brillouin zone, and therefore a decrease in Fermi surface volumes and quantum oscillation frequencies with increasing temperature. However, the temperature dependence of the frequencies seen in YbPtBi is too large to be caused by thermal expansion; magnetostriction data from Mun *et al.* shows that the change fractional change in length between 0.5 and 1.6 K at 10 T is only  $\Delta L/L \sim 10^{-4}$ , whereas the frequencies change by several percent over the same temperature range [139]. The temperature where the oscillation frequencies show a rapid increase is similar to the temperature at which the thermal expansion coefficient of YbPtBi changes sign and the heat capacity shows a broad maximum (Figure 5.2, left). Although the change in lattice size is too small to directly cause the change in oscillation frequencies, it is possible that the same underlying effect, possibly thermal excitation of CEF levels, is responsible for both changes. However, the heat capacity maximum moves to higher temperature with increasing field [139], unlike the feature in the quantum oscillations.

In  $\text{PrOs}_4\text{Sb}_{12}$  the Fermi surface volume has been found to change, seen as changes in the frequency or phase of quantum oscillations, as the occupation of two nearby CEF levels changes with temperature or magnetic field [154]. The CEF levels in  $\text{PrOs}_4\text{Sb}_{12}$  arise from a splitting of the Pr  $4f^2$  energy levels, which are localised and do not contribute to the Fermi volume [155], but nevertheless seem to influence the measured quantum oscillation frequencies. The localised  $4f$  states in  $\text{PrOs}_4\text{Sb}_{12}$  cause a renormalisation of the charge carrier masses by a factor of 6, which is much

larger than in YbPtBi, but not large enough to account for the size of the Sommerfeld coefficient, like in YbPtBi. Temperature- and field-dependent quantum oscillations have also been observed in CePtBi, which has the same half-Heusler structure as YbPtBi, but not in LaPtBi. The only difference between CePtBi and LaPtBi is the presence of  $4f$  electrons in CePtBi, which strongly suggests that those states are responsible for the field and temperature dependence. Like in  $\text{PrOs}_4\text{Sb}_{12}$ , quantum oscillations in CePtBi indicate localised  $f$  electrons which do not directly contribute to the Fermi volume, but still alter its properties in a subtle way. It is possible that a similar effect occurs in YbPtBi.

There are several other effects that can cause temperature-dependent quantum oscillation frequencies, but they are unlikely to be relevant here. The temperature dependence of the chemical potential  $\mu(T) = E_F - \pi^2 k_B^2 T^2 / 12 E_F$  can lead to a quadratic temperature dependence  $|\Delta F| \propto T^2$ , and it has been recently proposed that an additional quadratic  $\Delta F \propto -T^2$  decrease in frequency can be seen in materials with linear dispersion ( $E \propto k$ ) near the Fermi energy such as  $\text{Cd}_3\text{As}_2$  [156]. These effects cannot explain the non-quadratic temperature dependence in YbPtBi. Frequencies could also change as a result of interactions between thermal excitations, such as thermally excited phonons in Au which cause a decrease in quantum oscillation frequency  $\Delta F \propto -T^4$  [157]. However the size of that effect ( $\Delta F/F = 10^{-4}$ ) is much smaller than seen in YbPtBi. Other mechanisms related to magnetism, such as changes in the populations of up and down spin Fermi surfaces in ferromagnets [158], are not relevant in YbPtBi due to the absence of magnetic order in high field.

## Magnetic field dependence

I have analysed the field dependence of the Nijmegen quantum oscillations at base temperature using a sliding window between  $B_1$  and  $B_2$  with fixed width in inverse field such that  $1/B_1 - 1/B_2 = 0.03 \text{ T}^{-1}$ . Each field interval partially overlaps with intervals on either side of it. The magnetic field for the sliding window was taken to be  $B = (1/2B_1 + 1/2B_2)^{-1}$ . For each field interval, Gaussian functions were fitted to peaks in the Fourier transform to determine the frequency and amplitude.

By looking at the field dependence of the oscillation amplitudes  $A$ , I have estimated the  $B_0$  parameter for some frequencies with a linear fit to  $\ln(A)$  against  $1/B$  (Equation 1.26). The results are listed in Table 5.4. For some of the fundamental frequencies, I have also estimated a value of the mean free path  $l$  (Equation 1.27). An example of this fitting is shown in Figure 5.8 for the  $\beta$  frequency. In performing these fits, I have assumed that  $m^*T/B$  is sufficiently small that there is no additional field dependence from the thermal damping  $R_T$  factor in the Lifshitz-Kosevich for-

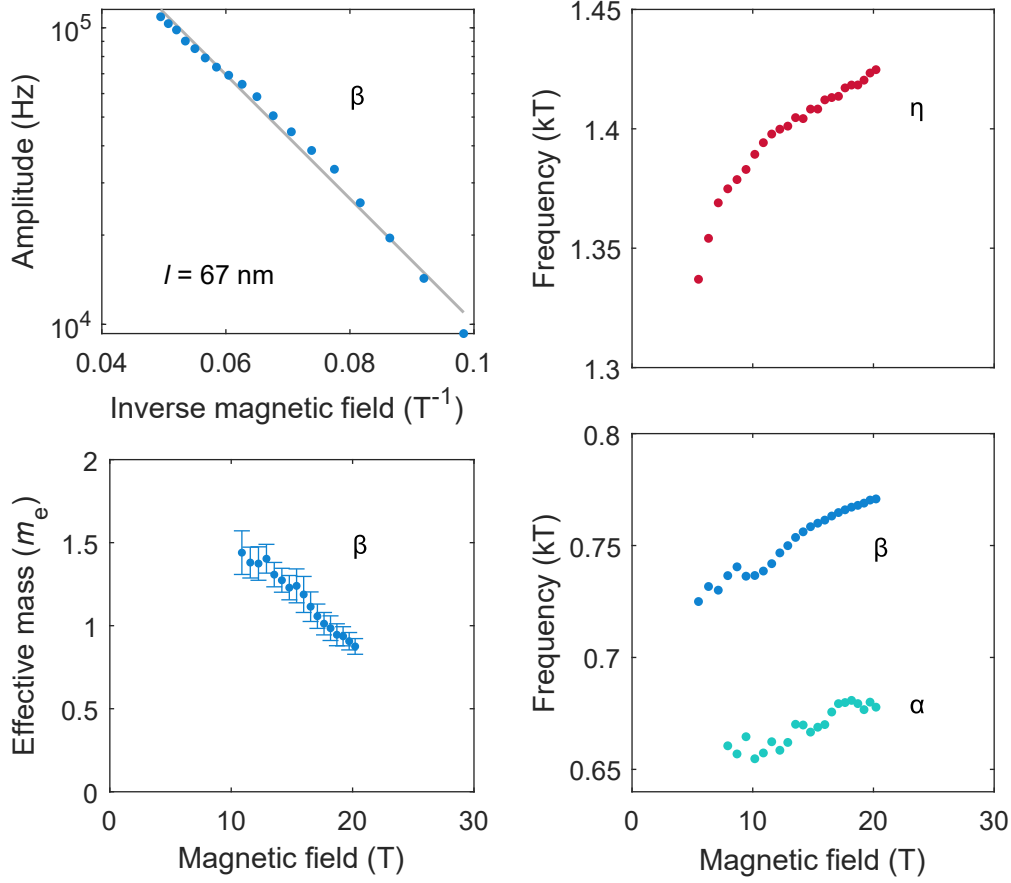


Figure 5.8: Magnetic field dependence of the quantum oscillations in YbPtBi measured in Nijmegen with  $\mathbf{B} \parallel [100]$ . Left top: a fit to the field dependence of the amplitude of the  $\beta$  frequency at 0.4 K gives a mean free path of  $l = 67$  nm. Left bottom: field dependence of the effective mass of the  $\beta$  frequency. Right: field dependence of the  $\alpha$ ,  $\beta$  and  $\eta$  frequencies at 0.4 K.

mula. There might be some errors in values of  $B_0$  and  $l$  from changes in the sample's resistivity and susceptibility with field, which would change the effective filling factor of the TDO circuit and affect quantum oscillation amplitudes. Therefore values of  $B_0$  and  $l$  should be all be taken as rough estimates. The  $B_0$  value for  $2\eta$  is close to twice the value for  $\eta$ , as expected for a second harmonic. The values for  $\gamma - \alpha$  and  $\gamma - \beta$  are larger than  $\alpha$  and  $\beta$ , indicating that those frequencies are only visible at higher fields, as expected for magnetic breakdown orbits.

All oscillation frequencies show some magnetic field dependence. All five of the fundamental frequencies show an increase with increasing field; the precise field dependence of  $\gamma$  and  $\delta$  are hard to separate, but the other three frequencies are plotted on the right of Figure 5.8, and the rates of change of all frequencies with field are given in Table 5.4. The field dependence of the frequencies gives further support to the identification of combination and harmonics since they roughly follow

the expected relationships. For example  $dF_{\gamma-\beta}/dB = dF_{\gamma}/dB - dF_{\beta}/dB$ , and  $dF_{2\eta}/dB = 2dF_{\eta}/dB$ .

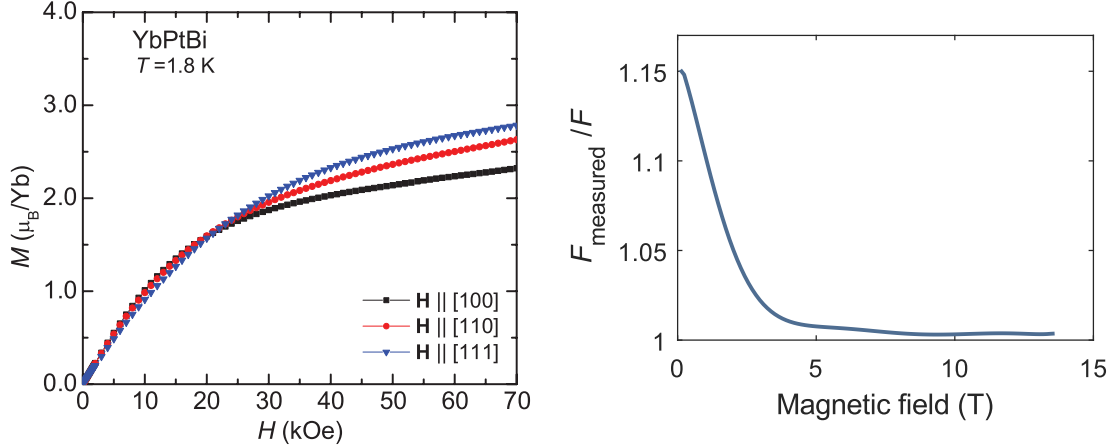


Figure 5.9: Left: field dependence of the magnetisation of YbPtBi from Mun *et al.* [139]. Right: expected field dependence of a measured quantum oscillation frequency due to the field dependence of  $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$  based on the field dependence of the magnetisation for  $\mathbf{B} \parallel [100]$  at 2 K from Guo *et al.* [146].

One potential mechanism for a field-dependent quantum oscillation frequency could be the field dependence of the magnetisation, which affects the field  $B = \mu_0(H + M)$  in the Lifshitz-Kosevich formula (Equation 1.21). As the oscillations are periodic in  $1/B$ , a field-dependent  $M(H)$  could produce a measured field dependent frequency of oscillations in  $1/H$ . The measured frequency can be calculated in a similar way to effects of a field dependent Fermi surface, as described in Section 1.4:

$$F_{\text{measured}} \equiv \frac{\mu_0}{2\pi} \frac{d\Phi}{d(1/H)} = F \left( 1 + \frac{dM}{dH} \right) \left( \frac{H}{H + M} \right)^2. \quad (5.1)$$

YbPtBi has a large magnetisation  $M$  in field from the magnetic moments of Yb ions. At low fields, the magnetisation approaches 10 percent of  $H$ , so  $M$  can have a significant effect on the quantum oscillation frequencies. The slope of the magnetisation  $dM/dB$  decreases in higher field as the magnetisation starts to saturate above 3 T (Figure 5.9, left) [139, 146]. The effect of this field dependence is a decreasing measured frequency, which changes less quickly in higher fields as  $M/H$  becomes smaller (Figure 5.9, right), so it cannot explain the increasing quantum oscillation frequencies seen in YbPtBi.

A different mechanism for the field dependent frequencies is a field dependent Fermi surface, which might be related to the field dependence of the magnetisation. As described in Section 1.4, oscillations due to a field dependent Fermi surface are difficult to interpret because they are related to the back-projected Fermi surface

area, rather than the true area in field:

$$F_{\text{measured}}(B) = F(B) - B \frac{dF}{dB}. \quad (5.2)$$

In theory, an increase in quantum oscillation frequency could be generated by either an increase or decrease in true cross sectional area. A growing Fermi surface ( $dF/dB > 0$ ) would cause an increase in measured frequency if  $dF/dB$  decreases in field, whereas a shrinking Fermi surface ( $dF/dB < 0$ ) would require  $dF/dB$  to become more negative. Quantum oscillation frequencies seem to roughly follow the field dependence of the magnetisation in Figure 5.9, changing more quickly at lower fields and saturating at higher fields. This is expected as the magnetisation shifts the energies of bands crossing the Fermi energy and changes the cross sectional areas of the resulting Fermi surfaces. A smaller  $dM/dB$  in high field indicates a decreasing  $|dF/dB|$ , and therefore increasing Fermi surfaces in field. This contradicts previous measurements of an increasing Hall coefficient in high fields [139], which suggests a decreasing carrier density ( $dp/dB < 0$ ) assuming an entirely hole-like Fermi surface. However, the Hall resistivity of YbPtBi is difficult to interpret due to possible anomalous Hall contributions.

It seems likely that the field dependence of the oscillation frequencies arises from the  $4f$  states, which produce a large field-dependent magnetisation and shift the energy levels of the conduction electrons. The temperature dependence of the oscillation frequencies is also likely caused by the  $4f$  states. However, the relationship between the field and temperature dependences is not straightforward; all oscillation frequencies increase in the same way with increasing field, while each frequency changes differently with increasing temperature. Therefore the temperature dependence of the oscillation frequencies cannot be explained simply by the temperature dependence of the high-field magnetisation (which decreases slightly with increasing temperature [146]).

Using sliding windows and Gaussian fits I have also looked at the field dependence of the effective masses. A significant decrease in the mass of the  $\beta$  frequency can be seen with increasing field (Figure 5.8, bottom left). The field dependence of the masses of other frequencies cannot be reliably investigated, since the amplitude of  $\alpha$  is too small,  $\delta$  and  $\gamma$  are too close together and  $\eta$  overlaps with  $2\alpha$ . However they all show the same decrease in  $m^*$  if these problems are ignored and the same analysis is performed.

A decrease in effective mass with increasing field is often observed in heavy fermion materials in quantum oscillation measurements, or indirectly through measurements of the Sommerfeld coefficient or  $A$ -coefficient. It can be difficult to ob-

serve a changing mass with quantum oscillations as the mass changes most quickly in low fields, while high fields are needed to observe oscillations. For example, in  $\text{YbCo}_2\text{Zn}_{20}$ , a material which has a similarly enormous zero-field heat capacity as  $\text{YbPtBi}$ , the  $A$ -coefficient decreases strongly from 100 to  $0.02 \mu\Omega \text{ cm K}^{-2}$  in 15 T, while quantum oscillation masses only fall between 5 and  $2 m_e$  at the highest fields where oscillations are visible [159]. A loss of effective mass in high field can arise from the competition between magnetic splitting and Kondo hybridisation described in the Section 5.1, but would not be expected in a localised  $f$  electron picture, even though both scenarios result in a decreasing heat capacity in field. Therefore the observation of a decrease in mass with field suggests that at least some of the large heat capacity in  $\text{YbPtBi}$  arises from heavy conduction electrons with a renormalised mass. Although the change in effective mass of  $\beta$  is far too small to account for the discrepancy between the small quantum oscillation masses and large zero-field heat capacity, it is possible that the mass decreases much more quickly at lower fields, in the same way that the frequencies change more quickly in lower field. It would be interesting to follow the oscillations down to lower field to see how much further the mass increases, but this would require crystals with longer mean free paths.

### 5.3.2 Rotation study

#### Quantum oscillation measurements

I conducted a study of the angular dependence of quantum oscillations in  $\text{YbPtBi}$  to gain information about the shape of its Fermi surface. I performed TDO measurements on the same sample which was measured with field along [100] in Nijmegen. The measurements were performed in the 15 T system using the He-4 variable temperature insert at its base temperature of 1.5 K. Although this temperature is higher than in my previous He-3 measurements, the relatively small masses in  $\text{YbPtBi}$  mean that the oscillations still have a reasonably large amplitude at He-4 temperatures. The sample was placed on a rotating platform in direct contact with pumped He-4 liquid or gas, and the platform was rotated with a stepper motor. Quantum oscillations were measured at magnetic fields up to 13 T along two rotation directions; first the sample was positioned on the platform so field was applied between the [100] and [011] for angles between 0 and  $45^\circ$ . Then the sample was rotated by  $45^\circ$  on the platform so field was applied between [100] and [011] as the platform was rotated between 0 and  $90^\circ$ . This second rotation direction passes through the [111] direction at an angle of  $\tan^{-1}(\sqrt{2}) = 54.7^\circ$ . The raw data at selected angles is shown on the left of Figure 5.10 with corresponding Fourier transforms on the right. Negative angles correspond to the first rotation direction and positive angles to the second

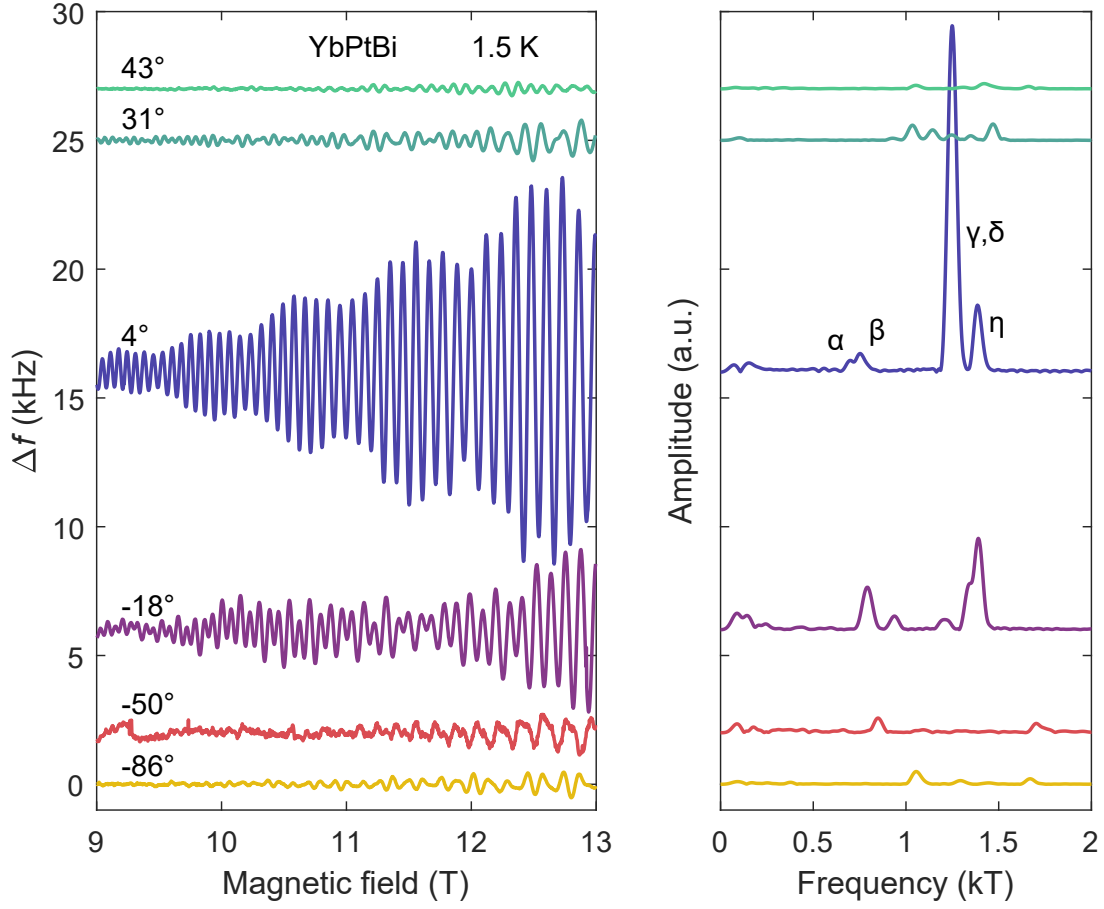


Figure 5.10: Left: Quantum oscillations after polynomial background subtraction at selected angles. Negative angles correspond to rotations between  $[011]$  and  $[100]$ , while positive angles are rotations from  $[100]$  towards  $[011]$ . Curves have been shifted vertically for clarity. Right: Fourier transform of the data on the left.

direction, with  $[100]$  at  $0^\circ$  in both cases. I also measured at some additional angles to verify that oscillations were identical along the  $[100]$  and  $[010]$  directions, and to collect more data to correct for an offset of a few degrees between the sample and platform.

The amplitudes of the quantum oscillation frequencies, particularly the  $\gamma$  or  $\delta$  frequencies, decrease strongly as the field is rotated away from the  $[100]$  direction. Such a large reduction in amplitude was not seen in the measurements of Mun *et al.*, where the amplitude of oscillations in resistivity were similar along both the  $[100]$  and  $[111]$  directions [148]. The difference cannot be explained by the different measurement temperatures as the measured effective masses are similar for both directions, but might be caused by slight variations in the orientation of samples, as the amplitude along the  $[100]$  direction is very sensitive to angle.

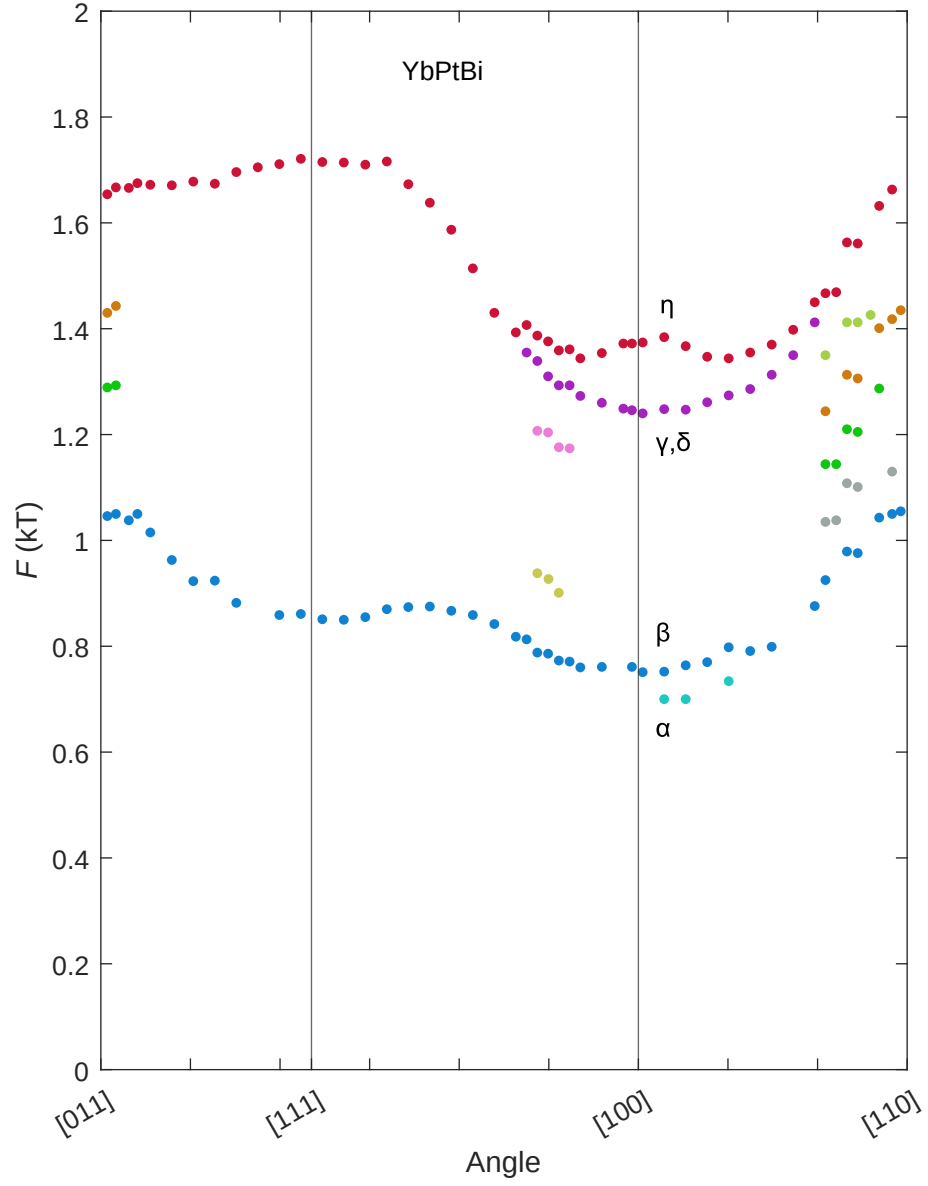


Figure 5.11: The angular dependence of quantum oscillation frequencies in YbPtBi for rotations from [011] to [100] (passing through [111]), and from [100] to [110].

The oscillation frequencies at each angle, for both rotation directions, are plotted in Figure 5.11. Two of the observed frequencies (red and blue) could be followed across all measured angles. The higher of these frequencies splits into two branches near the  $[100]$  direction, matching up with the  $\eta$  and  $\gamma$  frequencies along  $[100]$ . As discussed in Section 5.3.1, the  $\gamma$  frequency actually consists of two distinct frequencies  $\gamma$  and  $\delta$ , although the splitting of this peak could not be observed in these He-4 rotation measurements. The lower of the two frequencies seems to match the  $\beta$  frequency along  $[100]$ . Similar frequencies were observed along the  $[011]$  and  $[110]$  directions, as expected from the cubic crystal symmetry of YbPtBi. Four new frequencies appear along those directions, with all four visible near  $[110]$  and two seen along  $[011]$ . Two additional frequencies are also visible over a narrow angular range near  $-15^\circ$ .

### Comparison to calculations

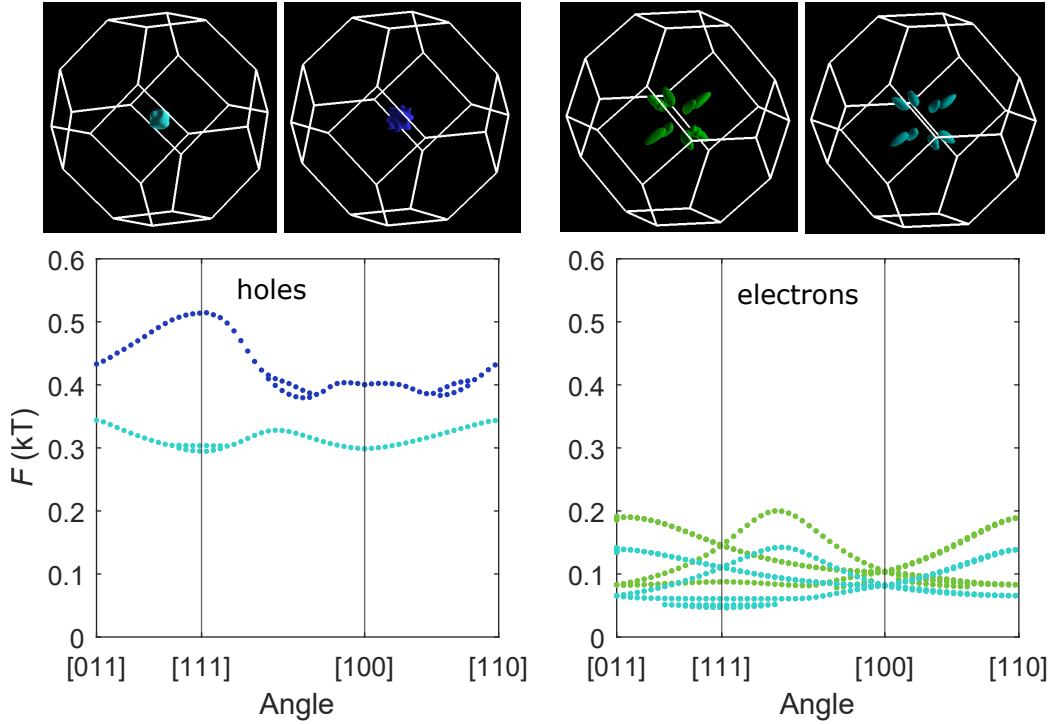


Figure 5.12: The calculated Fermi surfaces and corresponding angular dependence of quantum oscillation frequencies for YbPtBi with localised  $4f$  electrons states. Left: Two hole pockets at the centre of the Brillouin zone. Right: Two sets of eight electron pockets.

Density functional theory calculations of YbPtBi were performed in our group by Ran Tao using WIEN2k. The Fermi surfaces were visualised in XCrySDen [160] and quantum oscillation frequencies were extracted using SKEAF [161]. Calcula-

tions with itinerant  $4f$  states gives large Fermi surfaces with predicted quantum oscillation frequencies much larger than in measurements [162]. More reasonable Fermi surfaces are obtained when the  $4f$  states are treated as localised by performing a calculation of LuPtBi, but using the lattice parameter for YbPtBi. Spin-orbit coupling was included in the calculation as its effects are expected to be large due to the high atomic numbers of the constituent elements. The results (Figure 5.12) are similar to the results of the localised- $f$  YbPtBi calculation performed by Mun *et al.* [148], and similar to calculations of LaPtBi [163] and YPtBi [149]. Since YbPtBi has a noncentrosymmetric crystal structure, spin-orbit coupling breaks the spin degeneracy of each band, resulting in twice as many bands. Two hole bands and two electron bands cross the Fermi energy, giving rise to a small number of charge carriers. All four of these bands are degenerate at the  $\Gamma$  point (i.e. the centre of the Brillouin zone) indicating that they correspond to a  $J = 3/2$  quartet. Bands are also degenerate in other parts of reciprocal space. For example, the two hole bands are degenerate along the crystal axes, but only in zero magnetic field (see Kim *et al.* [149]).

The hole bands give rise to two almost-spherical Fermi surface pockets at the centre of the Brillouin zone. The electron bands give rise to two sets of eight needle-shaped pockets slightly away from the Brillouin zone centre, pointing along the  $[111]$  directions. Each hole pocket gives a single frequency between 0.3 and 0.5 kT for most angles, but at certain angles they have two extremal cross sectional areas, and therefore two frequencies. For both electron bands, the eight pockets have the same cross-sectional area along the  $[100]$  direction, but for other directions they have different extremal areas, giving rise to multiple quantum oscillation frequencies, all less than 0.2 kT. All of the calculated frequencies are too small to match the measured quantum oscillation frequencies.

A better match to experimental frequencies can be obtained if the hole bands are shifted upwards relative to the Fermi energy, causing the two hole pockets to grow. A reasonably good match to the data is obtained with  $\Delta E_F = -0.22$  eV (Figure 5.13). The first (pale blue) hole band gives a similar angular dependence to the measured  $\beta$  (blue) frequency. The second (dark blue) hole band has an angular dependence which matches the  $\eta$  (red) and  $\gamma/\delta$  (purple) data reasonably well. The two shifted hole pockets cannot explain the  $\alpha$  frequency seen close to  $[100]$ , the two frequencies that appear at a few angles between  $[111]$  and  $[100]$  or the four frequencies seen near the  $[110]$  directions.

In order to conserve charge, the electron pockets must also be enlarged, but it is difficult to do this in a way that matches the observed frequencies. When the electron bands are shifted lower, the eight pockets grow and eventually meet at the Brillouin

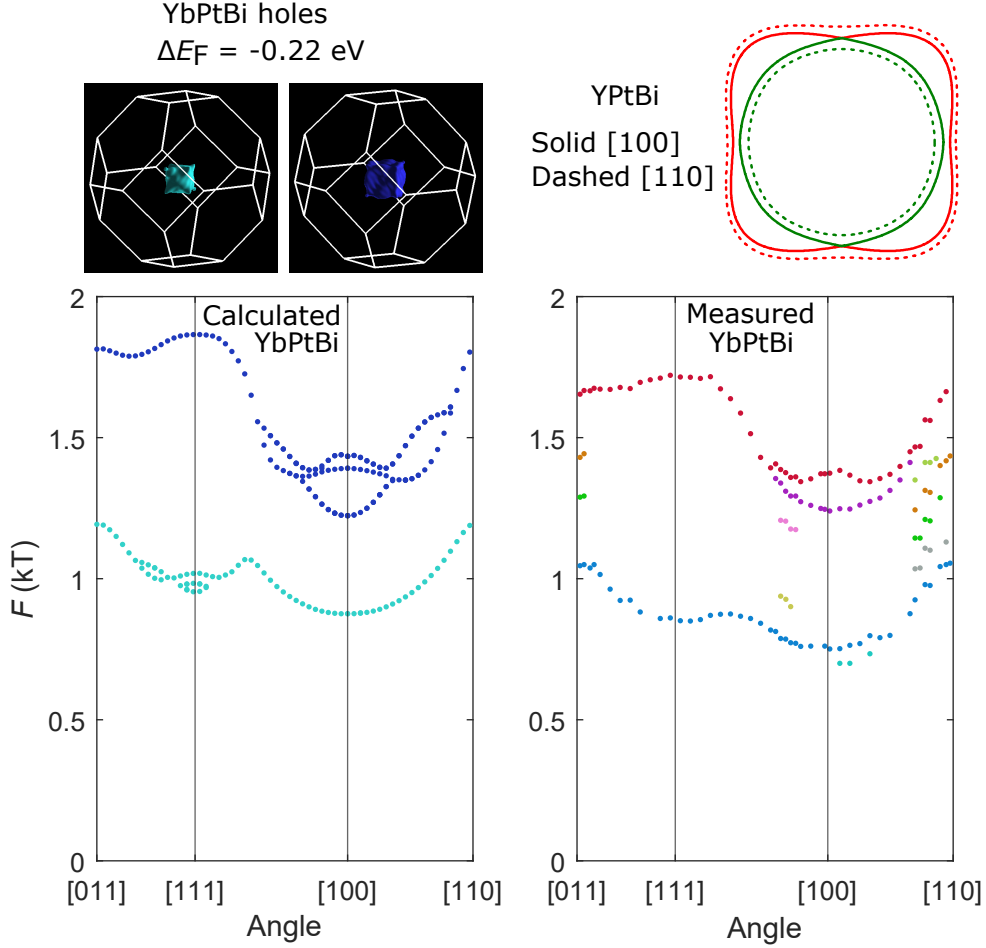


Figure 5.13: Top left: calculated Fermi surface of YbPtBi for localised  $4f$  states with the Fermi energy shifted by  $-0.22$  eV. Top right: cross sections of the Fermi surface of YPtBi from Kim *et al.* [149]. Bottom left: calculated angular dependence of quantum oscillation frequencies in localised- $f$  YbPtBi with  $\Delta E_F = -0.22$  eV. Bottom right: measured angular dependence of quantum oscillation frequencies in YbPtBi for comparison.

zone centre, forming a single electron pocket for band shifts larger than  $0.12$  eV. Shifts smaller than  $0.12$  eV give frequencies much smaller than the measured data, whereas shifts larger than  $0.12$  eV give high frequencies of  $3.5$  kT along the  $[011]$  direction and multiple frequencies along the  $[111]$  direction which also do not agree with data. Other bands away from the Fermi energy are unlikely to produce charge carriers because they would require large shifts greater than  $0.5$  eV to bring them to the Fermi energy. It is possible that additional, heavy pockets might exist which were not observed in my rotation study, but it seems unlikely because they were not observed in high-field Nijmegen measurements, or in the measurements of Mun *et al.* at dilution refrigerator temperatures [148].

Therefore, the best match to data can be obtained by just shifting the Fermi

energy relative to all bands in the calculation by  $\Delta E_F = -0.22 \text{ eV}$  so that only the two hole bands cross the Fermi energy. This shifting procedure does not conserve overall charge, and is equivalent to hole-doping the material. This is surprising because usually a large amount of doping would introduce impurities, preventing the observation of quantum oscillations. With this entirely hole-like Fermi surface, the quantum oscillation frequencies give a carrier number of around 0.036 holes per formula unit, which corresponds to a carrier concentration of  $p \approx 5 \times 10^{26} \text{ m}^{-3}$ . This is outside the range of carrier concentrations from Hall data ( $1.5 - 4.1 \times 10^{26} \text{ m}^{-3}$ ), but not too different given the approximations used to determine the values [146]. In YPtBi, quantum oscillation measurements and calculations by Kim *et al.* suggest a similar hole-doped Fermi surface, where the Fermi energy is shifted downwards to produce only two hole pockets (Figure 5.13, top right) [149].

In the absence of other bands, the additional frequencies seen at some angles must be produced by the two hole pockets, but it is difficult to draw any firm conclusions about exactly where they arise from because they can only be seen at a few angles. The real shape of the hole pockets might be slightly different from the DFT calculation of Figure 5.13 in a way that produces new extremal cross sectional areas. Alternatively, the new frequencies could arise from magnetic breakdown orbits between the two hole pockets. In YPtBi, Kim *et al.* have suggested that magnetic breakdown occurs between orbits on each hole pocket along the [110] direction due to a vanishing gap between the two pockets (Figure 5.13, top right) [149]. This could offer a potential explanation for the additional frequencies near the [110] directions in YbPtBi, although it does not give the correct number or spacing of frequencies.

Further evidence for the presence of only hole pockets comes from the difference in oscillation frequencies between my measurements and the measurements of Mun *et al.* [148]. The difference could arise from a difference in chemical potential which causes the cross-sectional areas of electron and hole pockets to change in opposite ways. All of the frequencies in my measurements are lower than in Mun *et al.*, suggesting that they all arise from the same type of charge carrier, i.e. holes.

Some of the combination frequencies seen in the high field data with  $\mathbf{B} \parallel [100]$  are difficult to explain in terms of magnetic breakdown between orbits on two hole pockets. Difference frequencies such as  $\gamma - \beta$  can only arise from tunneling between electron and hole orbits which undergo cyclotron orbits in opposite directions. Also, the combinations of  $\gamma$  and  $\eta$ , such as  $2\gamma + \eta$ , are difficult to understand in terms of breakdown if both arise from parallel orbits on the same pocket at different heights along the direction of the applied field. An alternative mechanism for combination frequencies seen in resistivity is quantum interference between quasiparticles undergoing orbits on different Fermi surface sections [164]. However, for the difference

orbit  $\gamma - \alpha$ , this would give a light effective mass  $m^* = m_\gamma - m_\alpha$ , which does not seem to match the measured mass. A recently proposed mechanism for sum and difference quantum oscillation frequencies in resistivity measurements is oscillations in the quasiparticle lifetime [165, 166]. This mechanism would also result in a light mass  $m^* = m_\gamma - m_\alpha$  that is not compatible with the data.

It seems likely that the Fermi surface of YbPtBi at high fields ( $B > 6$  T) consists of two hole pockets at the centre of the Brillouin zone. However, the Fermi surface at lower fields might look very different. The smaller Hall coefficient at lower fields suggests a larger Fermi surface, which might contain more delocalised  $f$  states, and the field dependence of the magnetisation (Figure 5.9) suggest that the Fermi surface might be different below 2 T, where magnetic moments are less polarised. At even lower fields, below the critical field for SDW order, the electronic structure is also likely to be different, as the SDW order gaps regions of the Fermi surface. Quantum oscillation measurements at lower field could be very interesting, but crystals with a higher purity would be required to achieve this.

### 5.3.3 Summary

Quantum oscillations at ambient pressure indicate small Fermi surface pockets ( $F \sim 1$  kT) and light effective masses ( $m^* \sim 1 m_e$ ) at high magnetic fields. The angular dependence of the oscillations shows good agreement with calculations, indicating localised  $f$  states and a Fermi surface consisting of two hole pockets. A field-dependent effective mass indicates some heavy fermion behaviour, which becomes more pronounced at lower fields. Field- and temperature-dependent oscillation frequencies indicate a complex role of the  $f$  states, which are localised but have some influence on the conduction electrons.

## 5.4 Measurements under pressure

I set up an anvil pressure cell with a YbPtBi single crystal from the same batch as the previous measurements. I used moissanite anvils with 0.8 mm culets, a 250  $\mu\text{m}$ -diameter seven-turn coil, and 4:1 methanol-ethanol as the pressure medium. The sample was oriented inside the coil so that field was applied along the [100] direction when measured in the 15 T system.

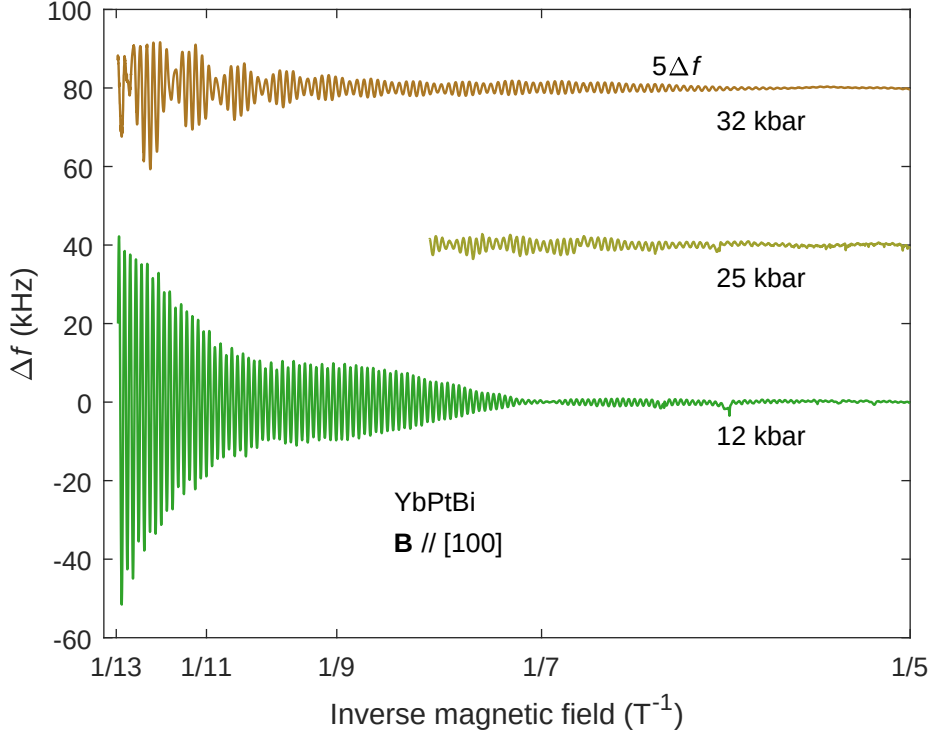


Figure 5.14: Quantum oscillations in YbPtBi under pressure with  $\mathbf{B} \parallel [100]$  at the base temperature at He-3 temperatures.

### 5.4.1 Quantum oscillations

#### Oscillation frequencies

I measured the cell at several pressures up to 34 kbar using an Ice Oxford He-3 probe in the 15 T system up to 13 T. Quantum oscillations at each pressure at the base temperature of the He-3 probe are shown in Figure 5.14. As the pressure was increased it became more difficult to measure the cell in high fields, possibly because the coil became damaged. Therefore the data at 25 kbar has a maximum field of only 8 T. I measured the cell at 12 and 25 kbar with the same TDO circuit, but I used a circuit at 32 kbar with a lower resonant frequency, so the amplitude of the oscillations is smaller.

Some beating can be seen in the data at all pressures from the two closely-spaced  $\gamma$  and  $\delta$  frequencies with similar amplitudes, even in the low-field data at 25 kbar. The frequency of the envelope  $F_{\text{envelope}} \approx (F_{\delta} - F_{\gamma})/2$  increases with increasing pressure, indicating that the  $\gamma$  and  $\delta$  frequencies move further apart.

The Fourier transform of the oscillations under pressure is shown in Figure 5.15, and the frequencies of the peaks are listed in Table 5.5. At 12 kbar, all five of the frequencies from ambient pressure,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\eta$ , can still be seen, as well as

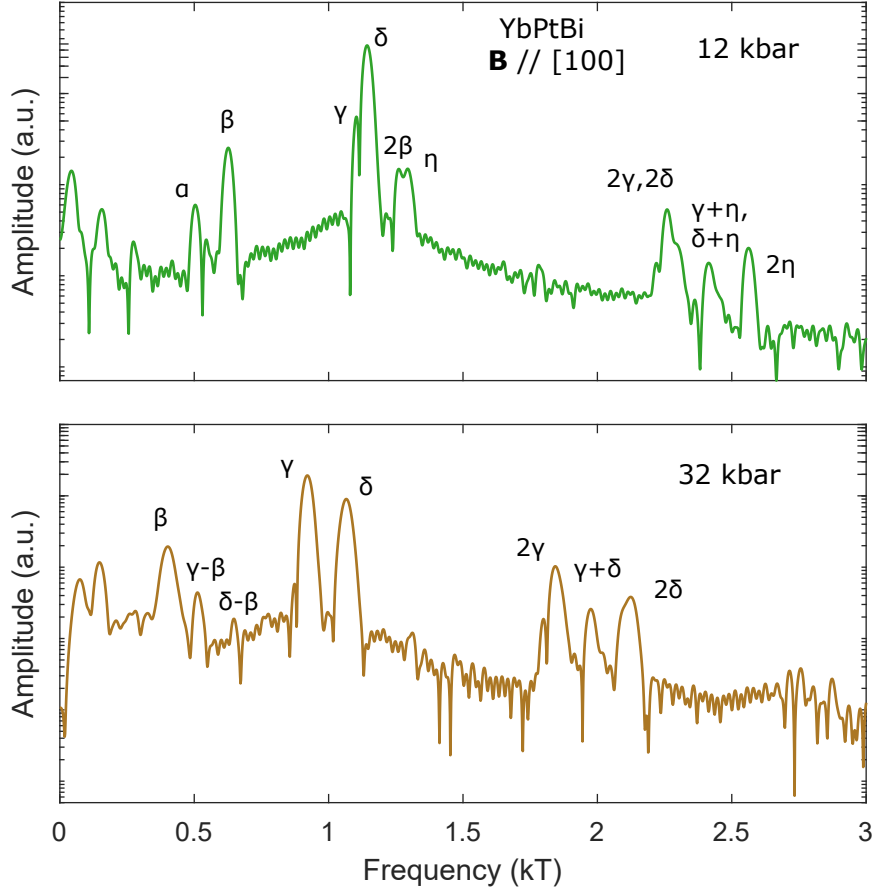


Figure 5.15: Fourier transform of quantum oscillations in YbPtBi under pressure with  $\mathbf{B} \parallel [100]$  at the base temperature at He-3 temperatures. The amplitude has been plotted on a logarithmic scale.

| 12 kbar            |          | 25 kbar   |          | 32 kbar           |          |
|--------------------|----------|-----------|----------|-------------------|----------|
|                    | $F$ (kT) |           | $F$ (kT) |                   | $F$ (kT) |
| $\alpha$           | 0.51     | $\gamma$  | 0.95     | $\beta$           | 0.40     |
| $\beta$            | 0.63     | $\delta$  | 1.10     | $\gamma - \beta$  | 0.51     |
| $\gamma$           | 1.10     | $2\gamma$ | 1.91     | $\gamma - \alpha$ | 0.65     |
| $\delta$           | 1.14     |           |          | $\gamma$          | 0.92     |
| $2\beta$           | 1.26     |           |          | $\delta$          | 1.07     |
| $\eta$             | 1.29     |           |          | $2\gamma$         | 1.84     |
| $2\gamma, 2\delta$ | 2.26     |           |          | $\gamma + \delta$ | 1.98     |
| $\gamma + \eta,$   | 2.41     |           |          | $2\delta$         | 2.12     |
| $\delta + \eta$    |          |           |          | $3\gamma$         | 3.18     |
| $2\eta$            | 2.56     |           |          |                   |          |

Table 5.5: Quantum oscillation frequencies measured in YbPtBi under pressure with  $\mathbf{B} \parallel [100]$

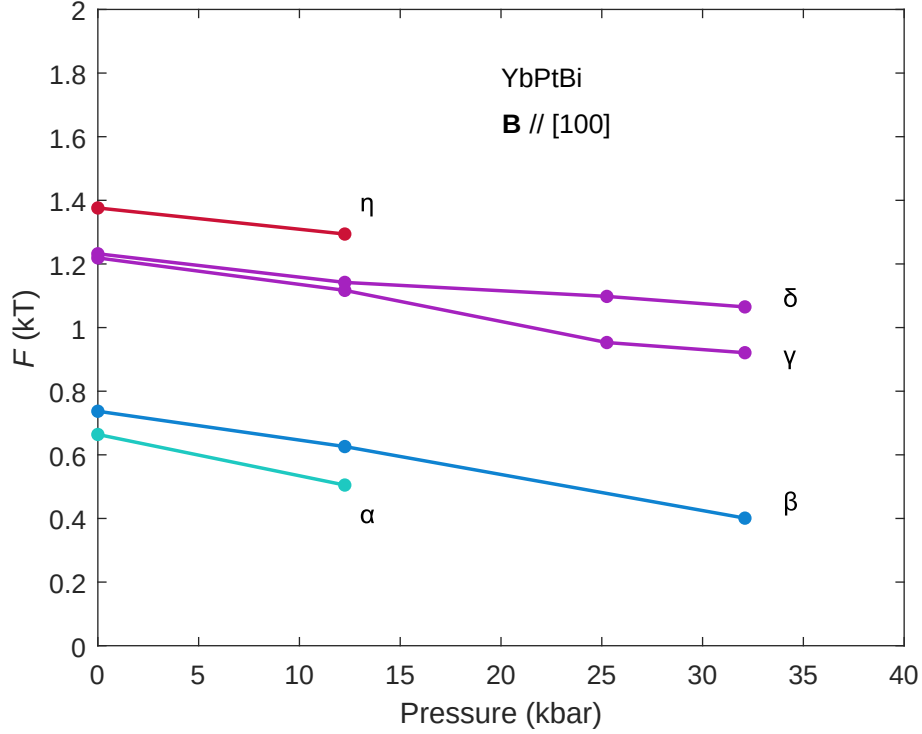


Figure 5.16: Pressure dependence of the fundamental quantum oscillation frequencies in YbPtBi with  $\mathbf{B} \parallel [100]$ .

some harmonics and combination frequencies. At 25 kbar, only  $\gamma$  and  $\delta$  could be seen, due to the lower fields in that measurement. At 32 kbar,  $\beta$ ,  $\gamma$  and  $\delta$  can be seen, but not  $\alpha$  and  $\eta$ . Unlike at ambient pressure, the  $\gamma$  and  $\delta$  frequencies are sufficiently far apart to separate their contributions to combination frequencies. A peak corresponding to  $\gamma - \beta$  can be clearly seen, and a weaker peak from  $\delta - \beta$  can also be seen just above the noise floor. A  $\gamma + \delta$  peak is also visible between the  $2\gamma$  and  $2\delta$  peaks. Therefore the data under pressure shows that magnetic breakdown is possible between  $\beta$  and both  $\gamma$  and  $\delta$ , and that breakdown is possible between  $\gamma$  and  $\delta$ .

Under pressure, all quantum oscillation frequencies decrease (Figure 5.16) in agreement with the results of Huang *et al.* [153]. Under hydrostatic pressure, the real space unit cell becomes smaller, so the Brillouin zone grows in reciprocal space. This can cause an increase in the size of Fermi surfaces, so an increase in all oscillation frequencies, which is opposite to what is seen in reality. A more complicated mechanism is needed to explain the decrease in frequencies in YbPtBi under pressure.

It is tempting to attribute the decrease in frequencies under pressure to a change in the strength of the Kondo effect. Yb-based compounds typically show a decrease

in exchange coupling between  $f$  and conduction electrons under pressure, and therefore the Kondo interaction decreases under pressure and the system moves further towards the left-hand side of the Doniach phase diagram. As this happens, the Yb  $4f$  hole contributes less to the Fermi surface, so the hole pockets shrink. However, it is not clear whether the Kondo interaction survives in high field, and this picture is not consistent with Luttinger's theorem which says that the Fermi volume cannot change continuously when the strengths of interactions changes. A shrinking Fermi surface could be consistent with Luttinger's theorem if there are both hole and electron pockets which both shrink under pressure in a way that preserves the net Fermi volume. However, ambient-pressure data seems more consistent with the presence of only hole pockets (Section 5.3.2). Therefore it seems unlikely that the change in oscillation frequencies is a result of a change in electron-electron interactions.

Under pressure, the non-interacting band structure is expected to change; as atoms are pushed closer together, electrons are more likely to hop between neighbouring atoms. This usually leads to an increase in the bandwidths. In a semimetal with both holes and electrons, this would usually lead to increased overlap between the hole and electron bands, so the volume of Fermi surface pockets, and therefore oscillation frequencies would increase. However, the case may be different in YbPtBi if the Fermi energy is shifted downwards so there are only holes. More detailed DFT calculations with different lattice parameters will be needed to further investigate the pressure dependence of the Fermi surface, and to investigate whether it is possible for charge carriers to disappear under pressure in a way that does not conserve overall charge.

### Temperature and field dependence of oscillations

In my anvil cell measurements, the  $\gamma$  and  $\delta$  frequencies have the largest amplitudes and can be measured at fields down to 5 T. The increased separation of those two frequencies under pressure allows their temperature and field dependence to be studied more easily than at ambient pressure. Other frequencies have smaller amplitudes, due to the lower fields in these high-pressure measurements compared to the ambient-pressure Nijmegen measurements, and possibly due to the effects of pressure inhomogeneities which can smear out quantum oscillation signals.

| $p$ (kbar) | $m_\gamma^*$ ( $m_e$ ) | $l_\gamma$ (nm) | $m_\delta^*$ ( $m_e$ ) | $l_\delta$ (nm) |
|------------|------------------------|-----------------|------------------------|-----------------|
| 12         | $1.12 \pm 0.09$        | -               | $0.76 \pm 0.05$        | -               |
| 32         | $0.93 \pm 0.10$        | 103             | $1.08 \pm 0.07$        | 62              |

Table 5.6: Effective masses and mean free paths of the  $\gamma$  and  $\delta$  frequencies under pressure for  $\mathbf{B} \parallel [100]$ .

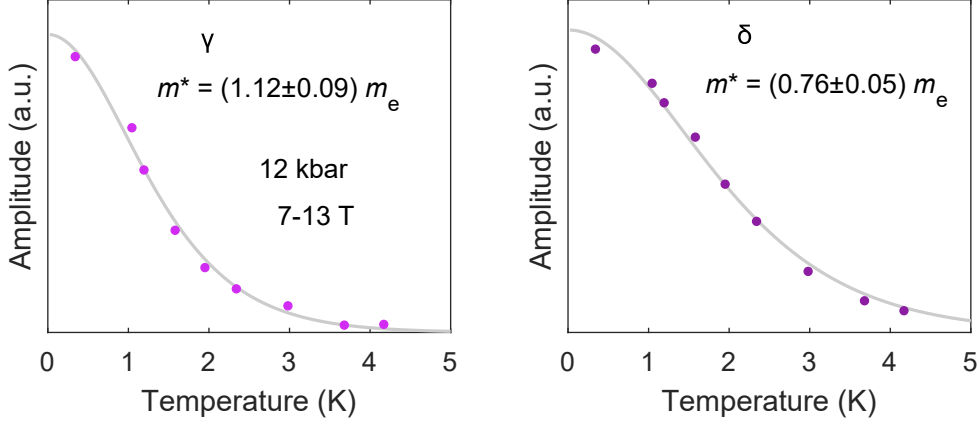


Figure 5.17: Temperature dependence of quantum oscillations amplitudes at 12 kbar for the  $\gamma$  (left) and  $\delta$  (right) frequencies and fits to obtain estimates of their effective masses.

The temperature dependence of the  $\gamma$  and  $\delta$  frequencies (Figure 5.17) appears to follow the form expected from the thermal damping factor in the Lifshitz-Kosevich formula, suggesting that there is negligible eddy current heating in the measurements. Fits give masses of  $(1.12 \pm 0.09) m_e$  and  $(0.76 \pm 0.05) m_e$  for  $\gamma$  and  $\delta$  respectively. Mun *et al.* reported  $0.8 m_e$  at ambient pressure for both frequencies (Table 5.1), in agreement with my value of  $\delta$ , but not  $\gamma$  [148].

At 32 kbar,  $\gamma$  and  $\delta$  are sufficiently far apart to allow estimates of their mean free paths, given in Table 5.18;  $\gamma$  has a longer mean free path than  $\delta$ . The mean free paths are in qualitative agreement with the field dependence of the amplitudes at lower pressures, suggesting that the order of  $\gamma$  and  $\delta$  does not change under pressure: the lower frequency is  $\gamma$  and the higher frequency is  $\delta$ . The amplitudes of the  $\gamma$  and  $\delta$  frequency oscillations both appear to roughly follow the expected Lifshitz-Kosevich form at 32 kbar (Figure 5.18, left). Fits give effective masses of  $(0.93 \pm 0.10) m_e$  and  $(1.08 \pm 0.07) m_e$  for  $\gamma$  and  $\delta$  respectively. It is interesting that the relative sizes of the two masses change significantly between 12 and 32 kbar;  $\gamma$  is heavier than  $\delta$  at 12 kbar, but lighter than  $\delta$  at 32 kbar. The mass of  $\gamma$  changes more than  $\delta$  between the two pressures, which is unexpected since its frequency changes less rapidly with pressure than  $\delta$  (Figure 5.16). The fits to the Lifshitz-Kosevich form are not perfect; the data points lie below the fits around 2.5 K but above the curves around 1 K. This deviation from could be a sign of sample heating at low temperatures which would lead to an underestimate of the effective mass. However the resonant frequency of the TDO circuit was significantly lower at 32 kbar than at 12 kbar, so the effects of eddy current heating should be much smaller in this data. Alternatively, it is possible that the deviation from the Lifshitz-Kosevich form could

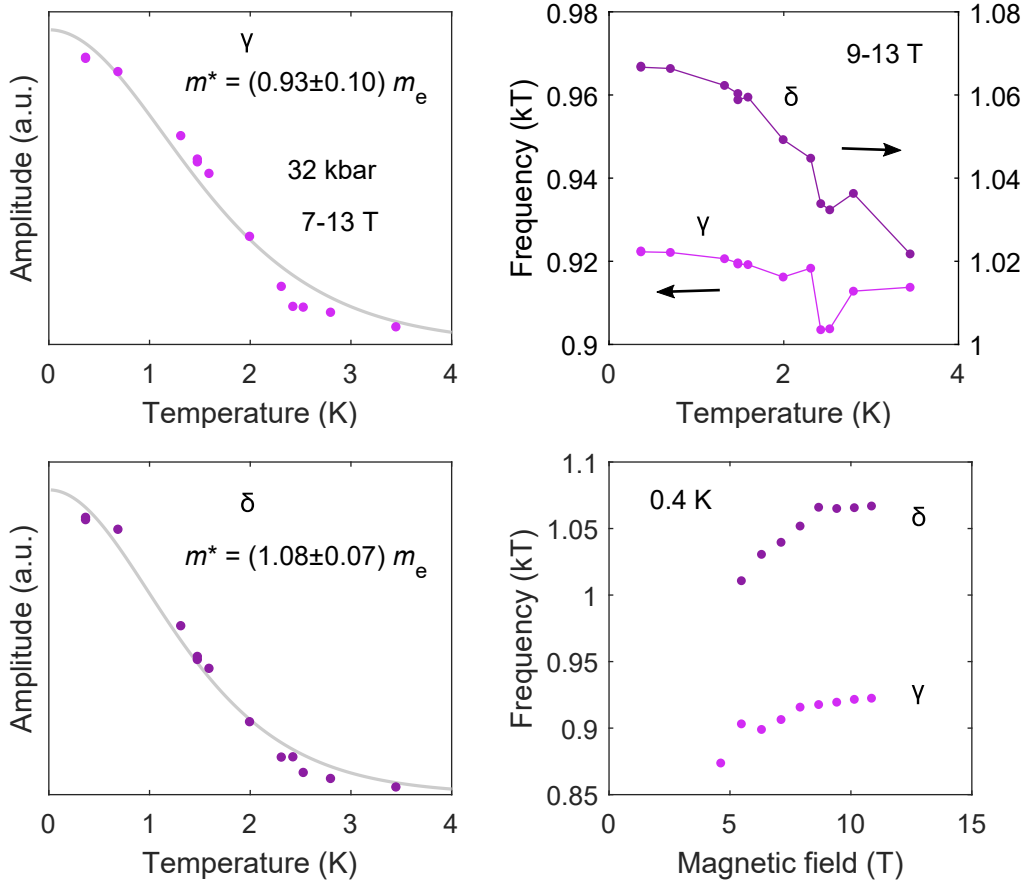


Figure 5.18: Temperature and field dependence of quantum oscillations at 32 kbar. Left: temperature dependence of the amplitudes of the  $\gamma$  and  $\delta$  frequencies and fits to obtain estimates of their effective masses. Top right: Temperature dependence of the  $\gamma$  and  $\delta$  frequencies at highest field. Bottom right: Magnetic field dependence of the  $\gamma$  and  $\delta$  frequencies at 0.4 K.

be an intrinsic effect, as reported by Huang *et al* in their TDO measurements under pressure.

Both the  $\gamma$  and  $\delta$  frequencies show temperature and field dependence (Figure 5.18, right). The  $\gamma$  frequency decreases more strongly than  $\delta$  with increasing temperature, but both frequencies show a dip around 2.5 K. This dip could be the same feature seen previously in the field dependence of the  $\beta$  and  $\eta$  frequencies, which occurred around 4 K at ambient pressure in a similar range of magnetic fields. The change in this temperature under pressure may indicate a decrease in CEF splitting under pressure. It is also interesting to note that the temperature of this dip is similar to the temperature at which the amplitude of the oscillations, particularly the amplitude of the  $\gamma$  frequency (top left panel), appears to increase rapidly. Therefore, it is possible that the temperature dependence of the frequency, and the deviation from the Lifshitz-Kosevich form could be related effects. Both frequencies increase

with increasing magnetic field, similar to the increase seen in other frequencies in the high-field ambient-pressure data, confirming that all five of the fundamental frequencies for  $\mathbf{B} \parallel [100]$  increase with increasing field.

### 5.4.2 Magnetism

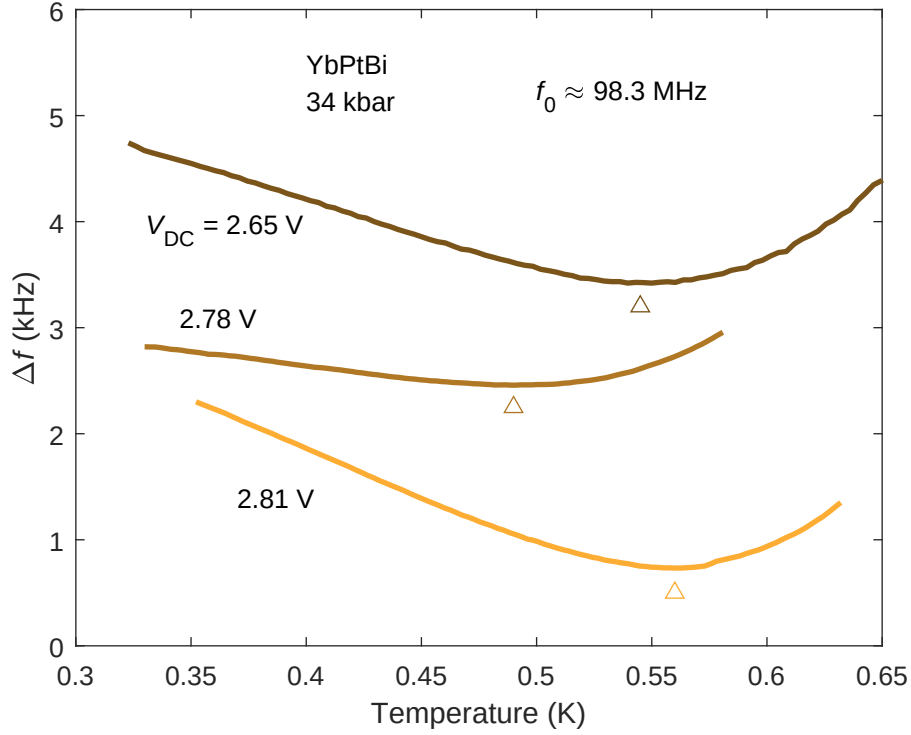


Figure 5.19: The measured TDO frequency shift from YbPtBi at 34 kbar using different DC bias voltages. The triangles indicate the measured temperatures of the minimum in the frequency, which depends on the bias voltage.

At 34 kbar I performed temperature sweeps using the He-3 probe at zero field to investigate the presence of any magnetic transitions. The results are shown in Figure 5.19 with three different DC voltages  $V_{DC}$  powering the TDO circuit. A minimum in the TDO frequency can be seen in all three curves, but the temperature of the minimum is different for each voltage. The variation in the temperature of the minimum can be explained as a result of eddy current heating in the sample induced by the AC current in the coil, which causes the sample to be at a higher temperature than the thermometer. Depending on the DC voltage used to power the TDO circuit, the tunnel diode will operate at different points on its  $I$ - $V$  curve. When the diode is operated at a point with the most negative slope  $dI/dV$ , voltage  $\Delta V_{osc}$  will generate large oscillations of the current in the coil  $\Delta I_{osc} = \Delta V_{osc} dI/dV$ . Therefore there will be a large oscillating magnetic field inside the coil, and a large amount of eddy current

heating in the sample. The data in Figure 5.19 suggests that this occurs when  $V_{\text{DC}} \approx 2.78 \text{ V}$ . When the circuit is powered with a slightly higher or lower DC voltage ( $V_{\text{DC}} = 2.81 \text{ V}$  or  $2.65 \text{ V}$ ), the diode's operating point has a less negative  $dI/dV$ , so there is a smaller  $\Delta I_{\text{osc}}$  and therefore less eddy current heating.

The minimum in the TDO frequency could be a signature of magnetic order in YbPtBi under pressure. This would contradict the results of Movshovich *et al.* who could not see any magnetic order in resistivity measurements above 1 kbar, but consistent with the data of Huang *et al.* who saw transitions in the field dependence of their TDO signal with a low-temperature critical field of 1.5 T at 25 kbar, extrapolating to zero field around 0.5 K [138, 153]. It is not clear from these measurements whether this transition is the same as the SDW transition at ambient pressure. Due to eddy current heating problems, the true temperature of the transition at 34 kbar is unknown, but the data in Figure 5.19 sets a lower bound of  $T_{\text{mag}} = 0.56 \text{ K}$ , which is higher than the reported ambient-pressure SDW transition temperature  $T_{\text{N}} = 0.4 \text{ K}$ . Further measurements under pressure, preferably using resistivity measurements to avoid heating issues, would be interesting to determine the precise pressure dependence of the SDW transition. This could provide valuable information about the strength of the Kondo interaction and the location of YbPtBi on the Doniach phase diagram.

### 5.4.3 Summary

Quantum oscillation measurements have been observed in YbPtBi under hydrostatic pressures up to 32 kbar for magnetic fields along the [100] direction, indicating a shrinking Fermi surface with increasing pressure. Some field and temperature-dependence of the oscillation frequencies is observed, like at ambient pressure. Oscillation amplitudes seem to roughly follow the expected Lifshitz-Kosevich form, although possibly some small deviations are seen. There is also some potential evidence of magnetism at zero field under pressure.

# Chapter 6

## CeAgSb<sub>2</sub>

In this short chapter I present tunnel diode oscillator (TDO) measurements of the heavy fermion ferromagnet CeAgSb<sub>2</sub> under pressure.

### 6.1 Motivation: quantum oscillations at quantum phase transitions

The primary aim of my TDO measurements on CeAgSb<sub>2</sub> was to observe quantum oscillations near magnetic quantum phase transitions, to investigate changes in Fermi surface geometry and effective masses at these interesting points of the phase diagram. This type of quantum oscillation measurement has been performed before in a handful of materials, such as at antiferromagnetic quantum critical points (QCPs) in BaFe<sub>2</sub>(As<sub>1-x</sub>P<sub>x</sub>)<sub>2</sub> using chemical pressure [167] and CeRhIn<sub>5</sub> under pressure [126] (Figure 6.1), in cuprate superconductors [168] and more recently at charge density wave transitions in TiSe<sub>2</sub> [169] and CsV<sub>3</sub>Sb<sub>5</sub> [170].

Quantum oscillation measurements under pressure could reveal information about the different mechanisms behind the large effective masses in heavy fermion materials. The mass enhancement from the Kondo effect is produced by a local, on-site interaction in real space, so is expected to produce a mass enhancement that is uniform in **k**-space. Antiferromagnetic fluctuations near a QCP have an ordering wavevector associated with them, so might only produce a mass enhancement at certain point on the Fermi surface associated with that wavevector. Therefore, a comparison of the pressure-dependence of mass enhancements on different Fermi surface sheets might provide information about the different mechanisms at play. For example, the approximately uniform increase in masses seen at the QCP in CeRhIn<sub>5</sub> suggests a local mechanism, possibly related to the breakdown of the Kondo effect, whereas at a field-induced antiferromagnetic quantum phase transition in CeIn<sub>3</sub>, the

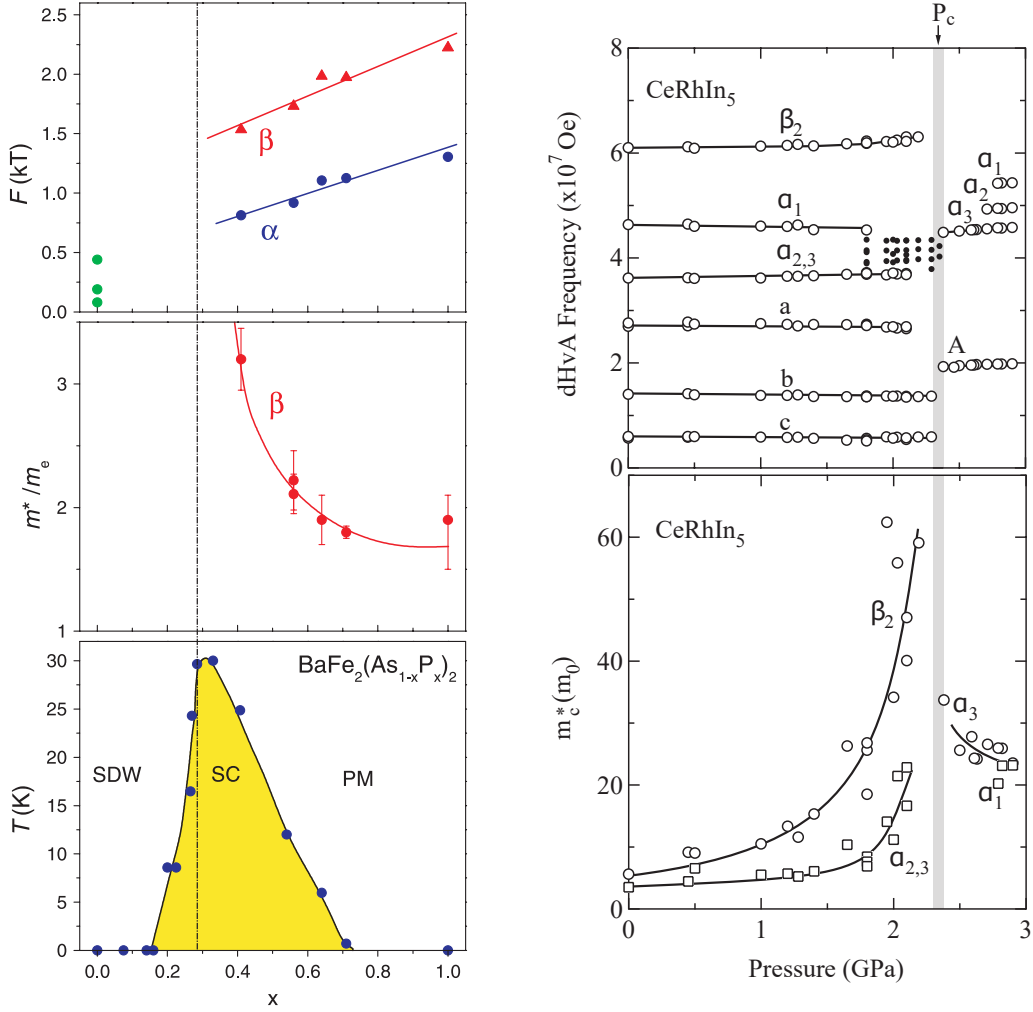


Figure 6.1: Quantum oscillations tuned to antiferromagnetic QCPs. Left: quantum oscillation frequencies, effective mass and superconducting  $T_c$  in  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  at different compositions  $x$  around the QCP at  $x_c \approx 0.3$  from Shishido *et al.* [167]. Right: quantum oscillation frequencies and effective masses in  $\text{CeRhIn}_5$  at pressures across an antiferromagnetic QCP at  $P_c$  from Shishido *et al.* [126].

mass appears to only increase at ‘hot spots’ on the Fermi surface [171].

The evolution of quantum oscillation frequencies across a phase diagram can also provide valuable information about a material’s electronic properties. Fermi surface reconstruction occurs within some ordered states: as the ordering increases the real-space unit cell so shrinks the  $\mathbf{k}$ -space Brillouin zone, leading to small Fermi surface pockets. This is seen in the different frequencies on either side of  $x_c$  in  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  in Figure 6.1 [167] and in the very different frequencies in underdoped ( $F \approx 500$  T) and overdoped ( $F \approx 18$  kT) cuprates [172, 173]. In heavy fermion materials, a sudden change in frequencies at a QCP, as seen in  $\text{CeRhIn}_5$  [126], could indicate a change in the role of  $f$  electrons, from itinerant to localised, or vice versa.

## 6.2 Introduction to CeAgSb<sub>2</sub>

CeAgSb<sub>2</sub> at ambient pressure orders ferromagnetically below  $T_C = 9.7$  K with magnetic moments pointing along the  $c$ -direction of its tetragonal crystal structure [174, 175]. High quality crystals with residual resistivities of  $\rho_0 = 0.2 \mu\Omega \text{ cm}$  can be grown with a self-flux method.

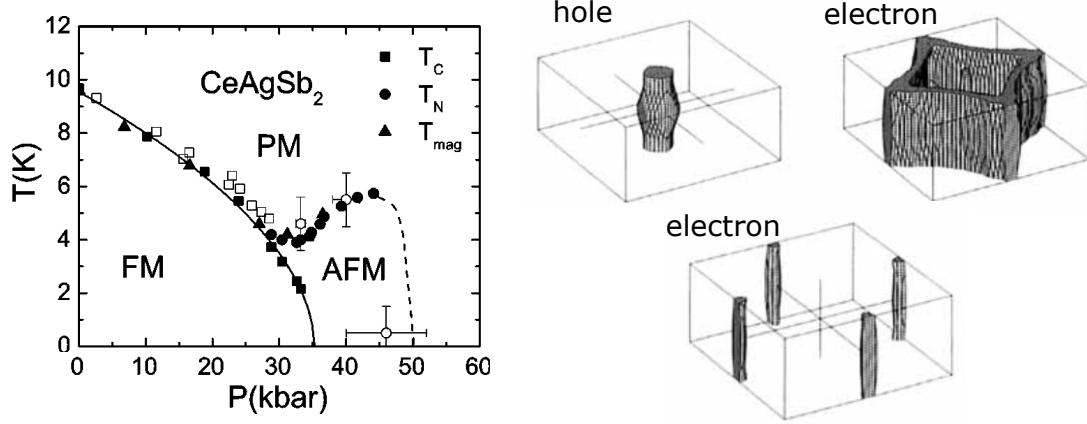


Figure 6.2: Left: pressure-temperature phase diagram of CeAgSb<sub>2</sub> showing paramagnetic (PM), ferromagnetic (FM) and antiferromagnetic (AFM) phases from Sidorov *et al.* [176]. Right: Fermi surface of CeAgSb<sub>2</sub> determined by de Haas-van Alphen oscillations from Inada *et al.* [177].

Pressure studies of CeAgSb<sub>2</sub> by several different groups have shown that the ferromagnetic transition is pushed to zero temperature at a critical pressure of 35 kbar [176, 178, 179]. Beyond this pressure, the residual resistivity of samples becomes significantly higher ( $\rho_0 \approx 30 \mu\Omega \text{ cm}$ ) and an additional phase was detected in resistivity and heat capacity measurements by Sidorov *et al.*, who proposed that it was an antiferromagnetic phase like in other  $R\text{AgSb}_2$  materials [174] and CeAuSb<sub>2</sub> [180]. This phase appeared to be suppressed to zero temperature at higher pressures around 50 kbar, although few measurements have been performed at those pressures. The antiferromagnetic phase was not detected in resistivity measurements by Nakashima *et al.* or magnetisation measurements in our group by Logg *et al.* [178, 179].

The Fermi surface at ambient pressure has been studied in de Haas-van Alphen measurements using a field modulation technique by Inada *et al.* [177]. They found an angular dependence which is consistent with the Fermi surface shown in Figure 6.2, indicating localised  $f$  electrons, and effective masses ranging between 1 and  $30 m_e$ . There are three two-dimensional Fermi surface pockets. One of the hole pockets has an unusual hollow diamond-shaped cross section, giving two high oscillation frequencies of 7 and 11 kT, corresponding to the inner and outer areas of that shape. Lower quantum oscillation frequencies of 25 and 300 T have been observed

in previous Shubnikov-de Haas quantum oscillation measurements [114, 181].

There are several reasons why  $\text{CeAgSb}_2$  is a good system in which to perform quantum oscillation measurements under pressure:

1. High-purity crystals of  $\text{CeAgSb}_2$  displaying quantum oscillations are available in our group.
2. The Fermi surface is relatively simple, and has been characterised in detail at ambient pressure.
3. Both ferromagnetic and antiferromagnetic quantum phase transitions are achievable at pressures within reach of our group's anvil cell techniques.

My TDO measurements were performed on single crystals of  $\text{CeAgSb}_2$  grown in our group by Christian de Podesta using a standard self-flux recipe.

### 6.3 Magnetism under pressure

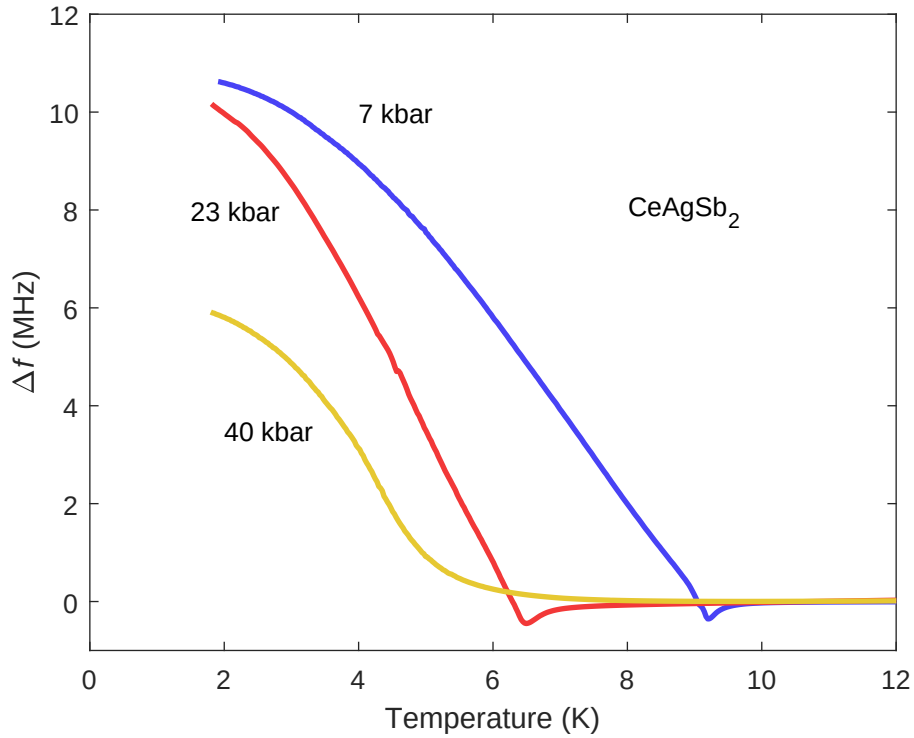


Figure 6.3: Temperature dependence of TDO frequency for the same anvil-cell sample of  $\text{CeAgSb}_2$  at three pressures: 7, 23 and 40 kbar.

I performed measurements of the temperature-dependence of the TDO signal of several anvil cells in the PPMS down to 1.8 K to investigate their magnetic transitions, and also to verify that the cells were working correctly before taking them

to high-field facilities. Figure 6.3 shows the low temperature TDO signal from the same sample of CeAgSb<sub>2</sub> at three pressures. Magnetic phase transitions are clearly visible in the TDO signal at all pressures, but the nature of the transition is different at the highest pressure of 40 kbar, indicating that it is antiferromagnetic rather than ferromagnetic. At a ferromagnetic transition, a sample’s magnetisation suddenly increases, so its susceptibility  $\chi$  spikes, and there is a gradual decrease in its resistivity  $\rho$ . The sharp increase in  $\chi$  and slow decrease in  $\rho$  results in a sharp drop then slow rise in TDO frequency, as seen at 7 and 23 kbar. For an antiferromagnetic transition, the magnetisation does not change as dramatically, so the main change is a decrease in resistivity, which produces an increase in TDO frequency, as seen at 40 kbar. Therefore my TDO measurements provide evidence for antiferromagnetism at pressures beyond the ferromagnetic critical pressure, as suggested previously by Sidorov *et al.* [176]. The transition temperatures from my TDO measurements are in good agreement with previously published data, and the with the results of high-pressure resistivity measurements in our group by Christian de Podesta, which will be discussed in his PhD thesis.

## 6.4 Quantum oscillations

Measurements of CeAgSb<sub>2</sub> were performed on three trips to international high field facilities:

1. NHFML in Tallahassee, USA in March 2023 with Christian de Podesta and Malte Grosche. We used two systems, a 31 T resistive magnet with a He-3 system (Cell 9) and a 18 T superconducting magnet with a dilution refrigerator (SCM1). We were assisted by Stan Tozer and David Graf.
2. NHFML in Tallahassee, USA in September 2023 with Christian de Podesta and Jiasheng Chen. We used a 41.5 T resistive magnet with a He-3 system (Cell 6), with help from David Graf.
3. HFML in Nijmegen, Netherlands in April 2024 with Christian de Podesta. We used a 30 T resistive magnet with a He-3 system, with help from Sasha Zheliuk.

During these trips, we performed a mixture of high-pressure TDO measurements and ambient pressure transport measurements, often simultaneously. On the first and third trips, I measured standard 18 mm-diameter anvil cells, which were set up by me. On the second trip, I measured narrow high-field anvil cells set up

by Patricia Alireza, because of the magnet’s narrow bore. Methanol-ethanol or pentane-isopentane were used as the pressure media for these TDO cells.

### 6.4.1 Ambient pressure

In ambient pressure resistivity measurements of CeAgSb<sub>2</sub> at 0.02 K, clear Shubnikov-de Haas oscillations are seen, confirming the high quality of our single crystals (Figure 6.4). For field along the  $c$ -axis, a large-amplitude 25 T frequency can be seen down to fields of 4 T. Many additional frequencies appear at higher fields, and the temperature-dependence of the oscillations gives heavy effective masses between 10 and 30  $m_e$  for each of these higher frequencies, as labelled in the figure. A detailed angle study was also performed, to determine the geometry of the Fermi surface, which is in good agreement with the de Haas-van Alphen study of Inada *et al.* [177].

In measurements on the same sample at higher fields and warmer He-3 temperatures, clear oscillations are also seen (Figure 6.5). Many of the same frequencies are seen, such as the  $F \sim 7.5$  kT frequency, but the highest, heaviest frequency is not seen, due to the lower ratio of  $B/T$  in these measurements. Some of the effective masses appear to be lower in these high-field measurements, suggesting a decreasing mass renormalisation in high fields, or possibly due to magnetic breakdown or quantum interference orbits with lower masses. For example, the 300 T frequency has a mass of only 5  $m_e$  at 25 T, compared to the masses of  $\sim 10 m_e$  for similar frequencies at lower fields. This decreased mass means that a resistive magnet and He-3 system has a sufficiently large  $B/T$  ratio to see most of the frequencies in CeAgSb<sub>2</sub>, at least at ambient pressure.

### 6.4.2 Low frequency under pressure

The low frequency seen for field along  $c$  shows up very clearly in TDO measurements, even in measurements at He-4 temperatures and low fields below 9 T in the PPMS. These quantum oscillations can be seen in measurements up to 25 kbar, showing an increase in frequency from 25 T at ambient pressure to 40 T at 25 kbar (Figure 6.6). This is in good agreement with previous measurements by Myers *et al.* [181] who saw a slight increase in frequency in resistivity measurements up to 7 kbar. It is unclear exactly which of the Fermi surface pockets causes this low frequency, but it must be a very small cross sectional area, occupying only a very small fraction of the Brillouin zone. The pocket is likely to be too small to have any significant role in determining the material’s properties. Therefore, the observation of higher frequencies, corresponding to larger Fermi surface pockets, is required to learn anything meaningful about the evolution of the electronic and magnetic properties of

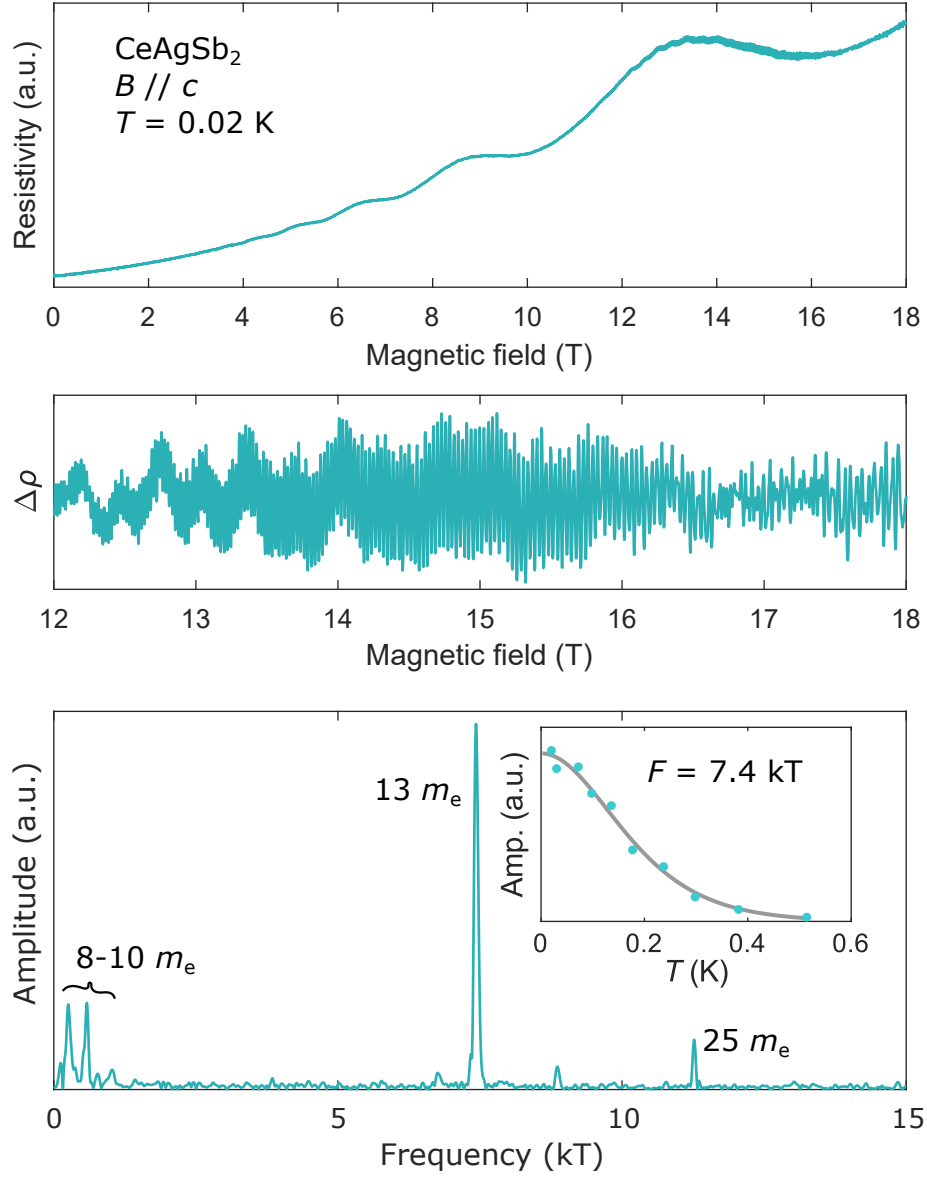


Figure 6.4: Ambient-pressure Shubnikov-de Haas oscillations in  $\text{CeAgSb}_2$  with field along  $c$  measured in a dilution refrigerator with a superconducting magnet. Top: raw signal at 0.02 K. Middle: high-frequency oscillatory signal after background subtraction. Bottom: Fourier transform of the oscillatory signal and masses of some frequencies obtained from fitting the temperature dependence of the amplitude. Inset: temperature dependence of the amplitude of the 7.4 kT frequency and fit to  $R_T$  to obtain an effective mass.

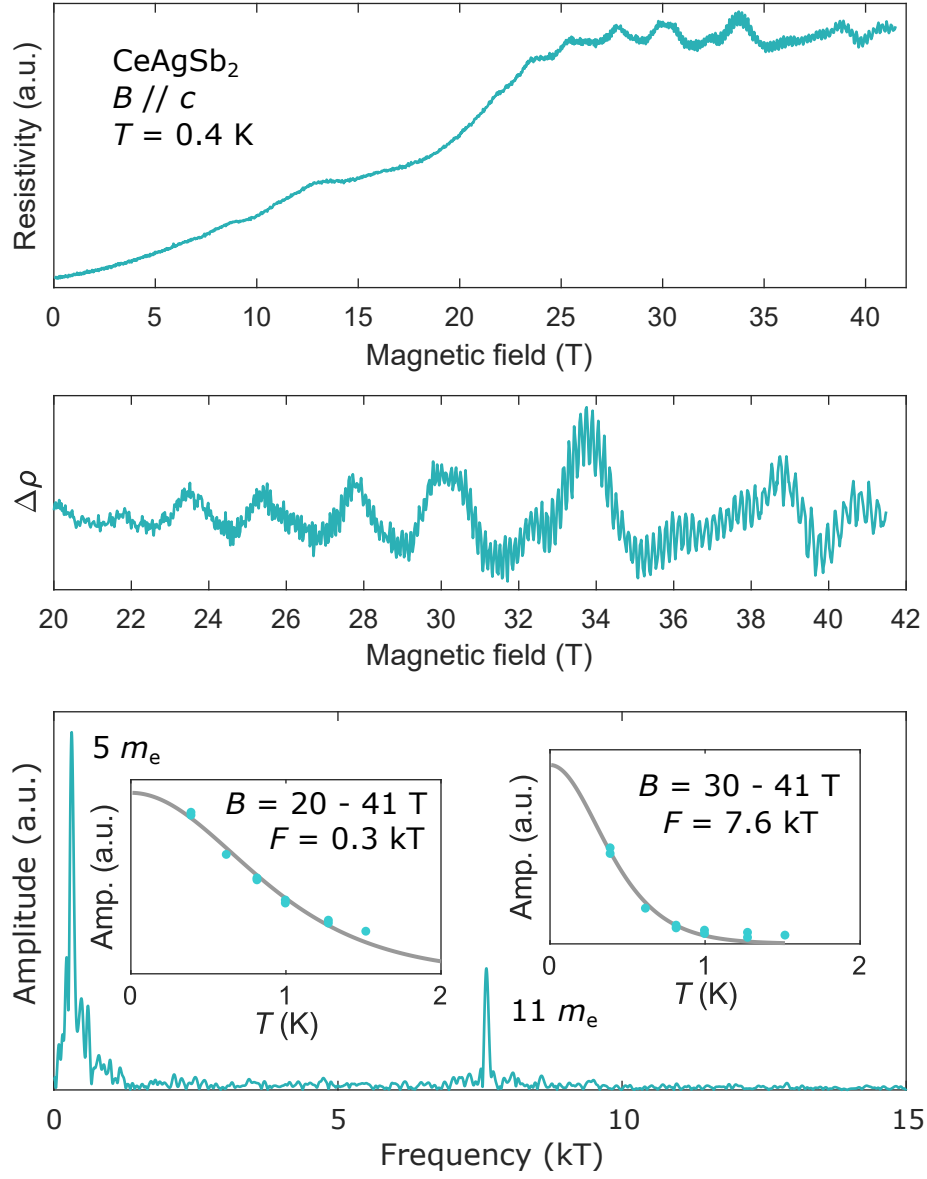


Figure 6.5: Ambient-pressure Shubnikov-de Haas oscillations in  $\text{CeAgSb}_2$  with field along  $c$  measured in a He-3 system with a resistive magnet. Top: raw signal at 0.4 K. Middle: high-frequency oscillatory signal after background subtraction. Bottom: Fourier transform of the oscillatory signal and masses of some frequencies obtained from fitting the temperature dependence of the amplitude. Insets: temperature dependence of the amplitudes of the 0.3 and 7.6 kT frequencies and fits to  $R_T$  to obtain effective masses.

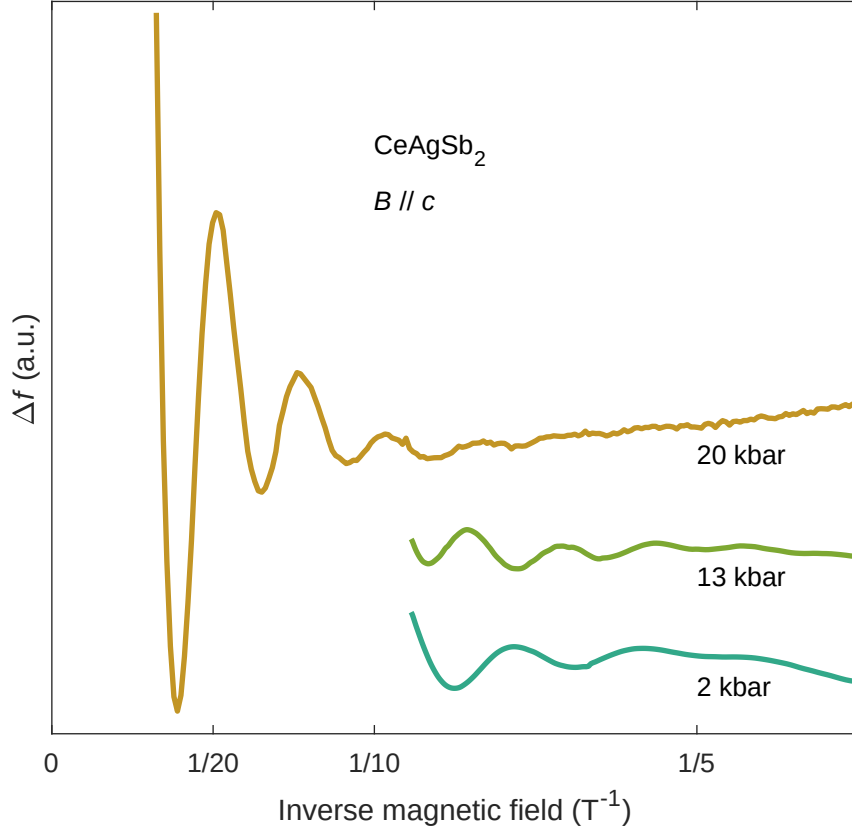


Figure 6.6: Pressure-dependence of low-frequency quantum oscillations in  $\text{CeAgSb}_2$ . The data at 2 and 13 kbar is from the same sample, measured in the PPMS, whereas the data at 20 kbar is from a different sample, measured in Tallahassee.

$\text{CeAgSb}_2$  under pressure.

### 6.4.3 High-field transition

In high-field measurements at 23 kbar, an unusual dip was seen in the TDO signal around 30 T with hysteresis, indicating a first-order phase transition in the sample (Figure 6.7). At this pressure,  $\text{CeAgSb}_2$  is ferromagnetic with  $T_C = 5.8$  K. The field was applied in the  $c$ -direction, along the direction of the ordered moments, so a field-induced ferromagnetic-to-paramagnetic transition is not expected to occur. Above the transition, quantum oscillations are seen with a frequency of  $F \sim 200$  T, which is much larger than the slow  $F \sim 40$  T oscillations seen at lower fields. This additional frequency was only seen under pressure at 23 kbar where the high-field transition was seen, suggesting that it is related to a change in electronic structure across the transition which produces a new extremal Fermi surface area. Alternatively, the high-field  $F \sim 200$  T frequency could be caused by the same Fermi surface

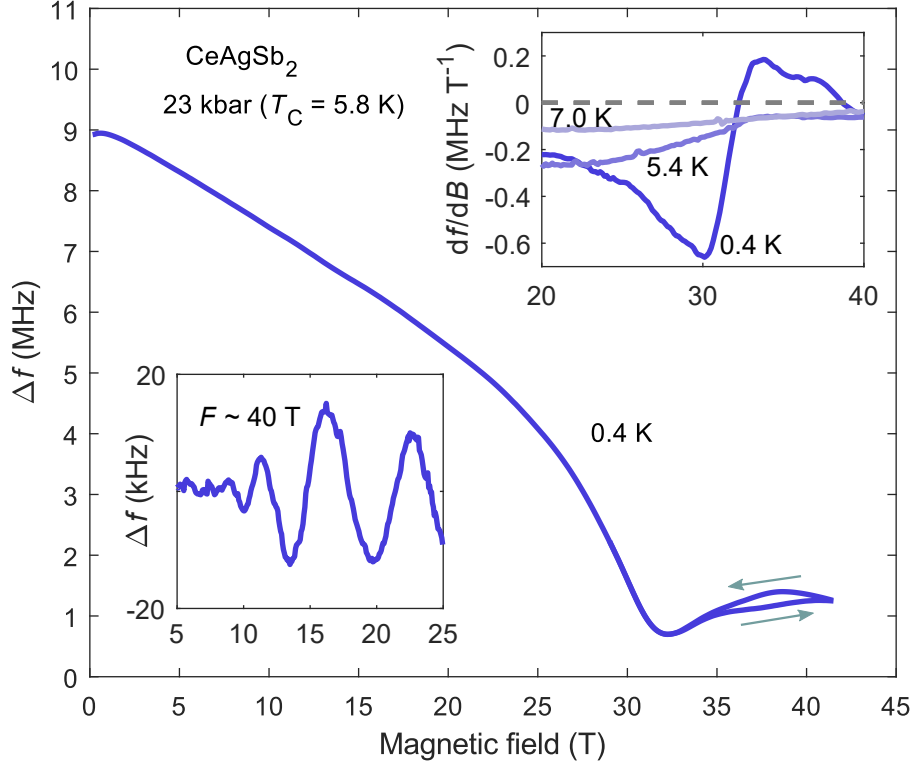


Figure 6.7: Magnetic field dependence of TDO frequency with  $\text{CeAgSb}_2$  at 23 kbar, displaying a metamagnetic transition at 30 T. Upper inset: gradient of the TDO frequency at three temperatures: 0.4 and 5.4 K below  $T_C$ , and 7.0 K above  $T_C$ . Lower inset: Background-subtracted low-field TDO signal, showing quantum oscillations with a frequency of 40 T.

pocket as the ambient-pressure 300 T frequency, which would imply an increase in mean free path across the transition, allowing the frequency to become observable. Further measurements of effective masses and the pressure dependence of quantum oscillation frequencies would allow these scenarios to be studied in more detail. This metamagnetic transition was present for all temperatures below  $T_C$ , seen as a sharp feature in  $df/dB$  which became weaker at higher temperatures and disappeared at temperatures above the ferromagnetic transition.

A possible explanation for this transition is provided by the crystal electric field (CEF) levels proposed by Takeuchi *et al.* [182]. They found that the heat capacity and thermal expansion of  $\text{CeAgSb}_2$  can be explained by a scheme where the Ce  $4f$  levels are split into three doublets, with the first and second excited states separated from the ground state by 48 and 140 K respectively. The ground level consists of  $J_z = \pm 1/2$ , the first excited state is mostly  $J_z = \pm 3/2$  and the second excited state is mostly  $J_z = \pm 5/2$ . In an applied field, their energies are Zeeman split, and at a field of 75 T, the  $J_z = -3/2$  state is expected to become the ground state (Figure

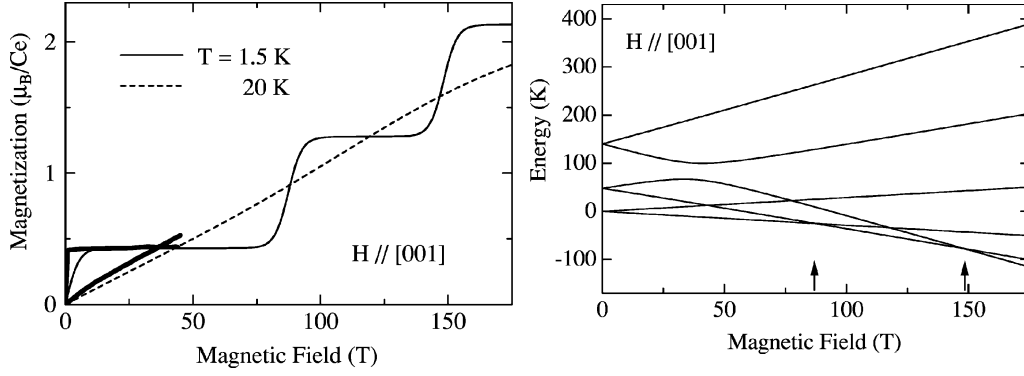


Figure 6.8: Left: expected magnetisation of  $\text{CeAgSb}_2$  along the  $c$ -direction at high fields at 1.5 and 20 K according to the material’s crystal electric field scheme. Bold lines are data and thin lines are calculated. Right: magnetic field dependence of crystal field energies. Arrows indicate the fields where levels overlap, causing the steps in the low-temperature magnetisation. This figure is adapted from Takeuchi *et al.* [182].

6.8, right). At this point, the magnetisation of the material is predicted to jump upwards (Figure 6.8, left), as the magnetic moment of the occupied ground state level is now larger, causing a spike in the susceptibility  $\chi = dM/dB$ . This spike in  $\chi$  would cause a dip in TDO frequency, as seen in the data. At higher temperatures the transition should become less pronounced due to increased thermal population of excited CEF levels. Measurements of the coherence temperature of the related material  $\text{CeAuSb}_2$  indicate that the spacing between the two lowest CEF levels decreases under pressure, which would move the metamagnetic transition to lower fields [180]. Therefore it seems plausible that the transition in  $\text{CeAgSb}_2$  could move from 75 T at ambient pressure to 30 T at 23 kbar.

Alternatively, the high-field transition could be due to a Lifshitz transition, which is a field-induced change in Fermi surface geometry. This could be caused by the Zeeman splitting of bands which can cause the appearance or disappearance of Fermi surface pockets, as seen in many other heavy fermion materials such as  $\text{YbRh}_2\text{Si}_2$  [183]. Further measurements are needed to investigate this field-induced transition and its pressure dependence, such as in the 25 to 30 kbar range where it might be expected to occur at lower, more experimentally accessible magnetic fields. It would also be useful to detect the transition in measurements of a more direct physical property, such as resistivity or AC susceptibility, rather than TDO frequency, which is more open to interpretation. These measurements would be interesting, as they could reveal information about the pressure-dependence of the CEF levels in  $\text{CeAgSb}_2$ , which are important for understanding the material’s magnetic properties. For example, it would be interesting to determine whether the energy of the first

excited level is pushed to zero at the ferromagnetic critical pressure, as that would suggest that the transition from ferromagnetism to antiferromagnetism is driven by changes in CEF levels.

#### 6.4.4 Failure to detect high frequencies

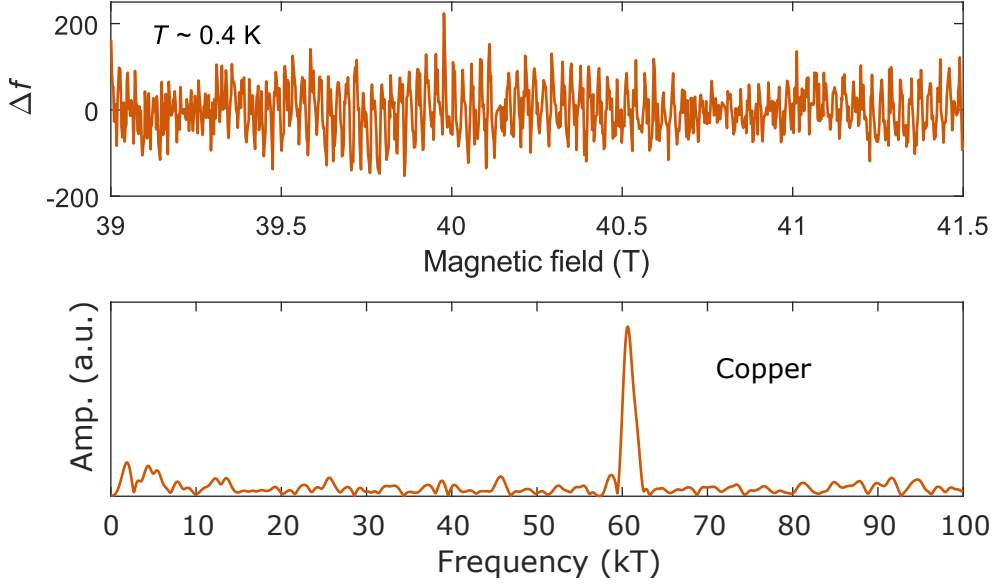


Figure 6.9: 60 kT quantum oscillations in the TDO signal of a high-pressure  $\text{CeAgSb}_2$  measurement arising from polycrystalline copper.

No frequencies, apart from the low 25 – 40 T frequency and the additional high-field  $\sim 200$  T at one pressure, were observed in any high-field measurements. In some high-pressure TDO measurements in Tallahassee, quantum oscillations with a frequency of 60 kT were seen at high fields (Figure 6.9), but these arise from polycrystalline copper [43] in the TDO coil or Be-Cu gasket. In the ambient-pressure resistivity measurements of Figure 6.5, the 300 T and 7.5 kT frequencies have large amplitudes which are around a quarter and an eighth of the amplitude of the 25 T frequency respectively. The low frequency shows up very clearly in high-pressure TDO measurements and the signal-to-noise ratio is significantly better than in ambient-pressure resistivity measurements, so it is surprising that the other frequencies are not visible. In this section, I will discuss some possible reasons for the absence of these oscillations in high-pressure measurements.

#### Hot sample

Heating of the sample is a concern in anvil-cell TDO measurements, as discussed in Section 2.2.5. The ambient-pressure effective mass plots in Figure 6.5 show that the

amplitude of the 7.6 kT frequency could easily be damped to zero by only a small amount of heating, whereas the lower 300 T frequency would require heating to temperatures above 1.5 K, which seems less likely. However, if effective masses increase under pressure, a small amount of heating could have a more serious effect; resistivity measurements show that the coherence temperature of  $\text{CeAgSb}_2$  decreases from 16 K to 8 K at 20 kbar, which suggests that effective masses might become twice as large under pressure [176]. In order to measure the entire Fermi surface of  $\text{CeAgSb}_2$  under pressure, and to accurately determine the pressure dependence of effective masses, it may be necessary to perform measurements in a dilution refrigerator, at colder temperatures where heating will become even more problematic.

### Inhomogeneous pressure

Another problem could be pressure inhomogeneity. The sample in a TDO anvil cell is often chosen to fill the coil as much as possible, to increase the signal from the sample, and the coil is often made as big as possible, to allow the TDO circuit to ring more easily. However, a large sample experiences large pressure gradients across it. As quantum oscillation frequencies depend on pressure, this causes a spread of frequencies across the sample. The sum of the oscillation signals from a spread of frequencies can result in an exponentially reduced amplitude, similar to the effects of disorder scattering [44]. This problem becomes more severe at higher pressures, as all pressure media become less hydrostatic. Lower frequencies are less sensitive to pressure inhomogeneity, which could explain why the very low 25 – 40 T frequency remains visible under pressure, while other, higher frequencies do not.

The sensitivity to inhomogeneity depends on how pressure dependent the frequencies are. For example, in high-pressure quantum oscillation measurements on  $\text{NiS}_2$  up to 100 kbar, the Fermi surface frequency was found to be only weakly pressure-dependent [70], so pressure gradients across the sample are less important. The group in Tallahassee have observed oscillations in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  up to very high pressures of 250 kbar where conditions are no longer very homogeneous [74]. However, those measurements found that the Fermi surface does not change much with pressure, with oscillation frequencies remaining relatively low ( $F \sim 700$  T), so inhomogeneity does not have a large effect. The Fermi surface of a heavy fermion material like  $\text{CeAgSb}_2$  could be strongly pressure dependent, due to large changes in electron correlations. Therefore pressure inhomogeneity in  $\text{CeAgSb}_2$  could be a serious problem and could prevent the observation of high-frequency oscillations in an anvil cell.

## High residual resistivity under pressure

A final reason for the absence of high-frequency quantum oscillations could be the increased residual resistivity in crystals of CeAgSb<sub>2</sub> under pressure; data from Nakashima *et al.* [178], Sidorov *et al.* [176] and Christian de Podesta show that the residual resistivity gradually increases from  $\rho_0 = 0.3 \mu\Omega \text{ cm}$  to  $\sim 2 \mu\Omega \text{ cm}$  at 30 kbar, before suddenly jumping to  $30 \mu\Omega \text{ cm}$  in the antiferromagnetic state. This could mean that the amplitude of oscillations is very strongly damped in the antiferromagnetic state. Resistivity data from Christian de Podesta shows that  $\rho_0$  decreases in field, but it remains much higher than at ambient pressure, even in high fields, which could prevent the observation of quantum oscillations in CeAgSb<sub>2</sub> above 30 kbar.

### 6.4.5 Outlook

Piston cylinder cells could avoid some heating-related issues, since a larger TDO coil could be used with a less powerful diode and operated at a lower resonant frequency. Their larger sample spaces might generate more hydrostatic pressures and it would be easier to cool the sample by attaching a cooling wire. However, it would not be possible to reach the ferromagnetic critical pressure in CeAgSb<sub>2</sub> using a piston cylinder cell. Anvil cell quantum oscillation measurements using four-point resistivity measurements may be possible, considering the large resistivity oscillations seen in ambient-pressure CeAgSb<sub>2</sub>. These measurements could avoid some of the heating issues associated with TDO, but might have a lower signal-to-noise ratio, and anvil cells for resistivity measurements are challenging to set up.

Other materials may be better suited for quantum oscillation measurements near pressure-induced QCPs. Systems containing *d*-electrons typically have smaller effective masses than heavy fermion materials, so issues associated with sample heating are less important. One possible candidate material for anvil cell measurements is MnP, which is ferromagnetic at ambient pressure, but becomes antiferromagnetic under pressure, and can be pushed to a QCP with a dome of superconductivity at 80 kbar [184].

# Chapter 7

## Conclusions

### CeSb<sub>2</sub>

In its high pressure structure, CeSb<sub>2</sub> can be tuned to an antiferromagnetic quantum critical point at 30 kbar. Superconductivity has been detected in resistivity and AC susceptibility measurements in a narrow range of pressures surrounding the quantum critical point, strongly suggesting that magnetic fluctuations are responsible for the superconductivity. For fields applied along the *c*-axis, the upper critical field exceeds the conventional Pauli limit by a factor of 10, which may be related to the very high effective masses of charge carriers. An unusual inverse S shape is seen in the temperature dependence of the critical field on the low-pressure side of the superconducting dome, which is likely related to the suppression of magnetism by applied field. For in-plane fields, the critical fields are slightly smaller, but remain larger than the conventional Pauli limit and displays a similar inverse S-shaped temperature dependence.

The normal state resistivity of CeSb<sub>2</sub> below the critical pressure contains a large contribution from spin wave scattering. An analysis of the field dependence of this resistivity shows a quantum phase transition for fields applied along the *c*-axis. Around the critical pressure, a non-Fermi liquid sub-linear resistivity is observed, which returns to the usual Fermi liquid form at higher pressures and in applied fields. The response to field in different directions suggests that high-pressure CeSb<sub>2</sub> might have an easy-plane magnetic anisotropy.

### YbPtBi

Quantum oscillations in YbPtBi detect light effective masses, which can be explained in a heavy fermion picture with a decreased mass in high fields, or in a local moment scenario with negligible Kondo hybridisation. Some field dependence of the effective mass and oscillation frequencies is seen, as well as temperature de-

pendence oscillation frequencies, which suggest that that  $f$  electrons play some role in the Fermi surface. The angular dependence of oscillation frequencies is in good agreement with a localised- $f$  calculations with hole doping. However, the presence of additional frequencies at some angles, combination frequencies detected at high fields and the decrease of all frequencies under pressure are difficult to explain.

### **CeAgSb<sub>2</sub>**

Tunnel diode oscillator measurements confirm the suppression of ferromagnetism in CeAgSb<sub>2</sub> under pressure and the presence of a high-pressure antiferromagnetic phase. A new high-field transition has been seen under pressure, possibly caused by a crossover in crystal field levels. Clear quantum oscillations from many Fermi surface pockets are seen in ambient-pressure resistivity measurements, but only one low frequency could be detected in high-pressure TDO measurements.

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# Appendix A

## Additional CeSb<sub>2</sub> Superconductivity Figures

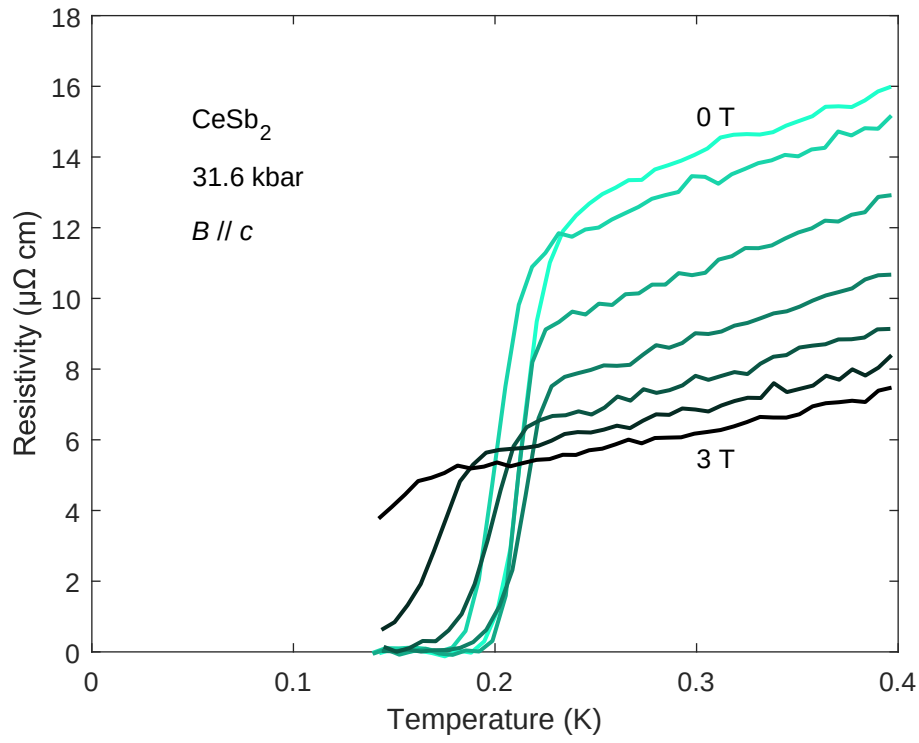


Figure A.1: The response of the superconducting transition at 31.6 kbar (Sample A3) to a magnetic field applied along the  $c$ -axis.

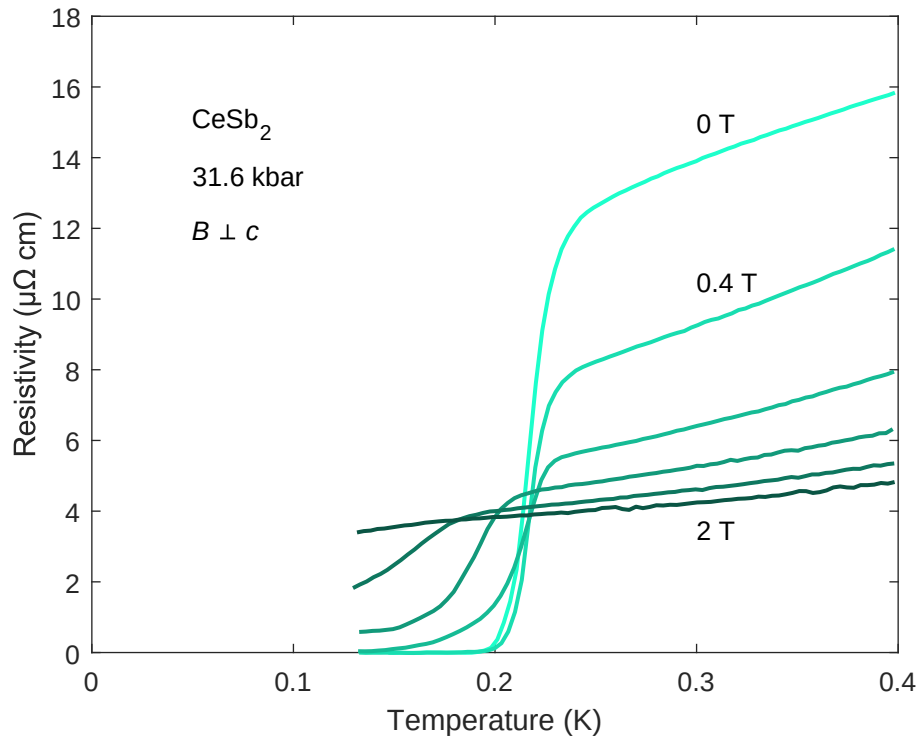


Figure A.2: The response of the superconducting transition at 31.6 kbar (Sample A3) to a magnetic field applied in the  $a$ - $b$  plane, perpendicular to current.

## Appendix B

### Additional CeSb<sub>2</sub> Normal State Figures

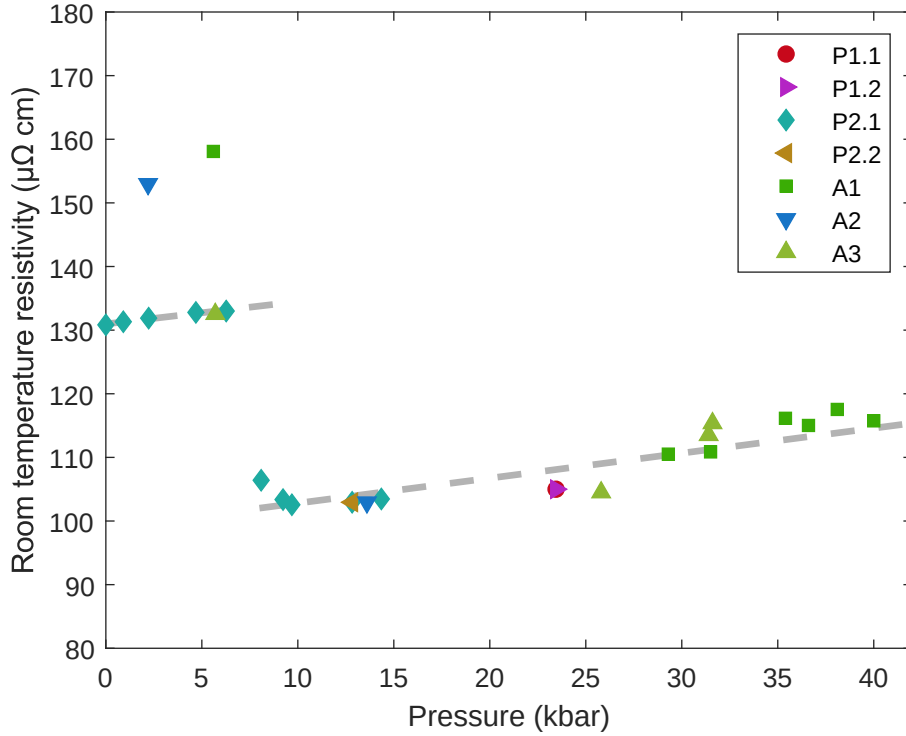


Figure B.1: The room temperature resistivity of CeSb<sub>2</sub> samples at different pressures determined using the scaling factors in Table 4.1.

Figure B.1 shows the room temperature resistivity values obtained using the scaling factors in Table 4.1. All high-pressure resistivities lie on a straight line, with an overall increase in resistivity with increasing pressure which may be caused by lattice compression. At low pressures, the values for P2.1 and A3 (grown recently by Christian de Podesta) agree well, but the values for A2 and A1 (from an

older growth by Jiasheng Chen) are larger. This suggests that crystals from different batches exhibit different changes in their resistivities when passing through the structural transition. Scaling factors have been chosen so that resistivity values at high pressures agree, because the physics of the high-pressure structure is the focus of this thesis.

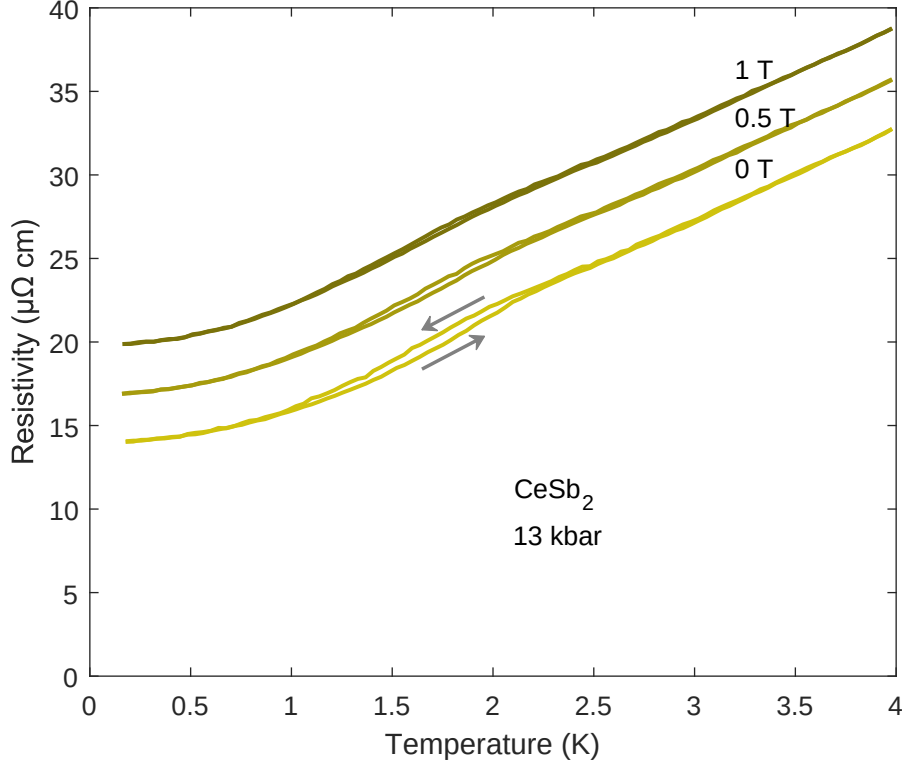


Figure B.2: Hysteresis in the low temperature resistivity of CeSb<sub>2</sub> at 13 kbar from Sample A2 in zero field, 0.5 T and 1 T applied along the *c*-axis. Arrows indicate the direction of cooling and warming. The data at 0.5 T and 1 T have been shifted by 3 and 6  $\mu\Omega$  cm respectively.

At 13 kbar hysteresis was observed in resistivity measurements of Sample A2 around 2 K, indicating a phase transition. The hysteresis loop became smaller in an applied magnetic field along the *c*-axis. This same transition was observed by Vitaly Fedoseev at similar pressures, where the sample may be in a metastable mixture of low and high pressure structures [89]. It is unclear whether this transition is intrinsic to the high or low pressure structure, but its transition temperature does not match up with the temperatures of the two high-pressure transitions seen in heat capacity.

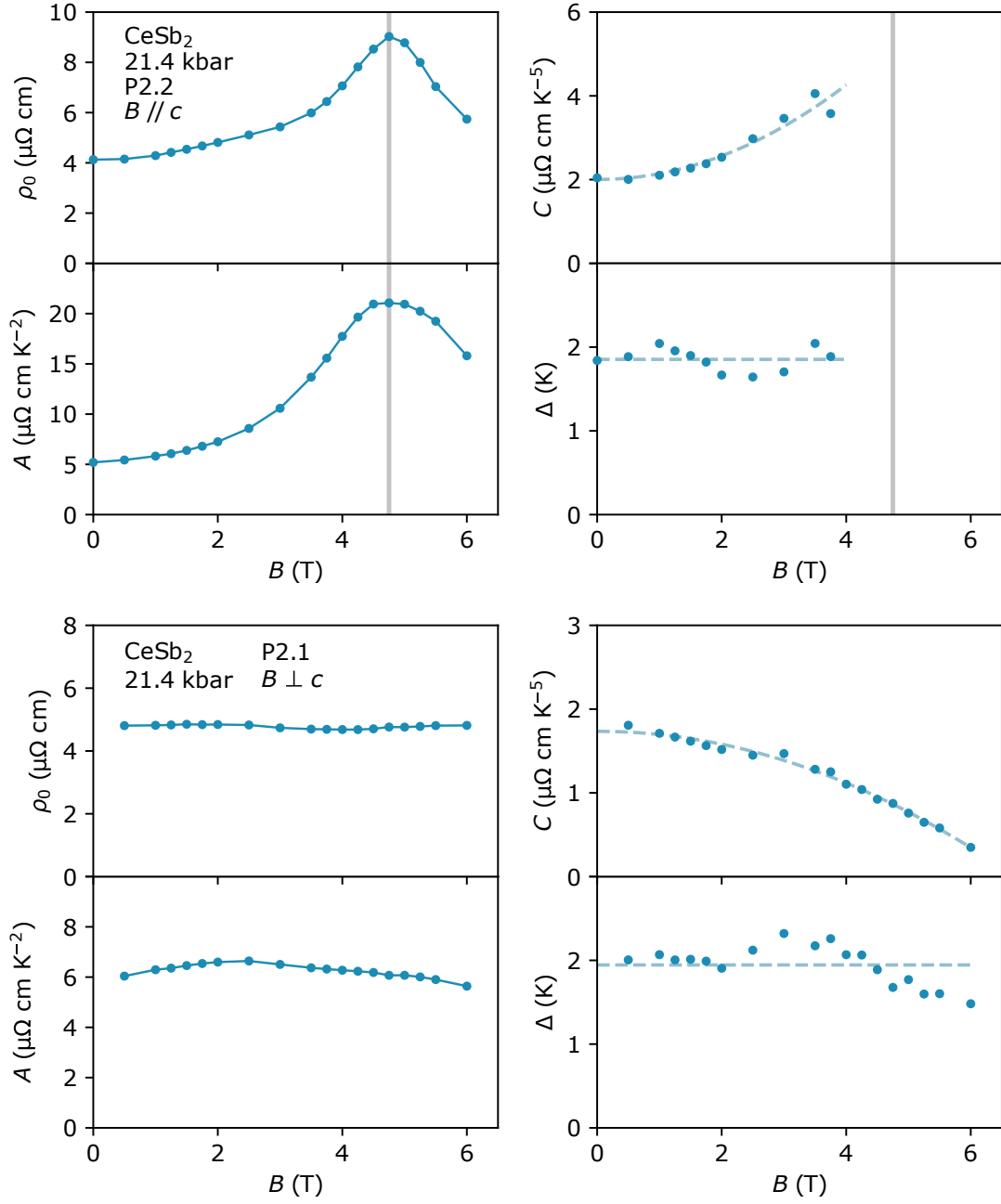


Figure B.3: Field dependence of the magnetic fit parameters for  $\text{CeSb}_2$  at 21.4 kbar with field along the  $c$ -direction (Sample P2.2) and field in the  $a$ - $b$  plane (Sample P2.1).

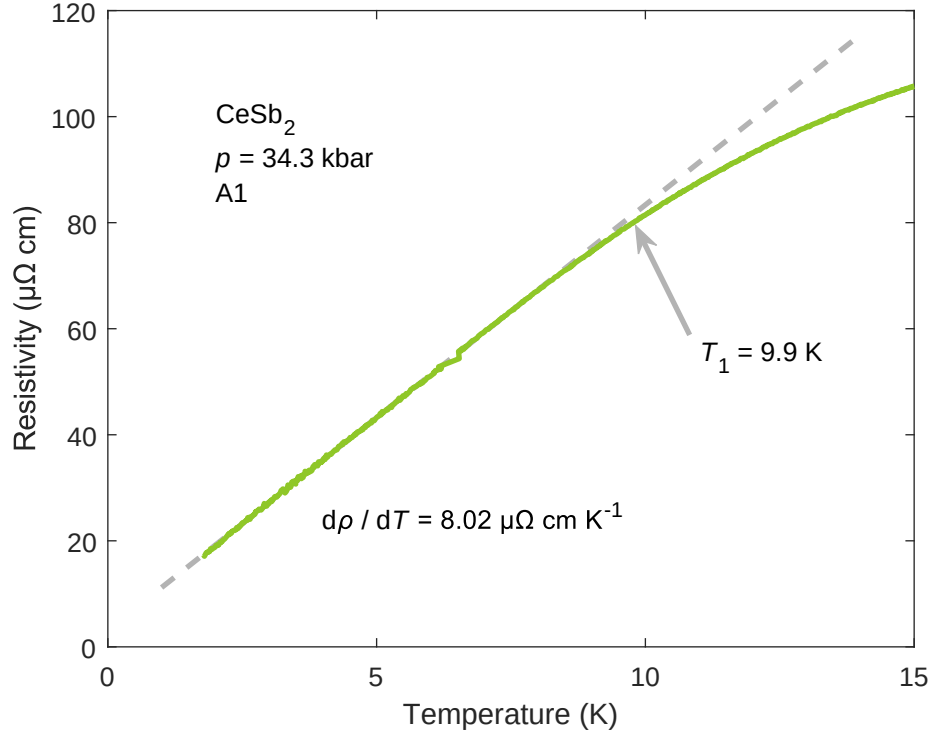


Figure B.4: The temperature dependence of the resistivity of CeSb<sub>2</sub> (Sample A1) at 34.3 kbar. The dashed line indicates a linear fit to the low temperature resistivity, and  $T_1$  indicates the temperature where the resistivity deviates from the fit by 2%.

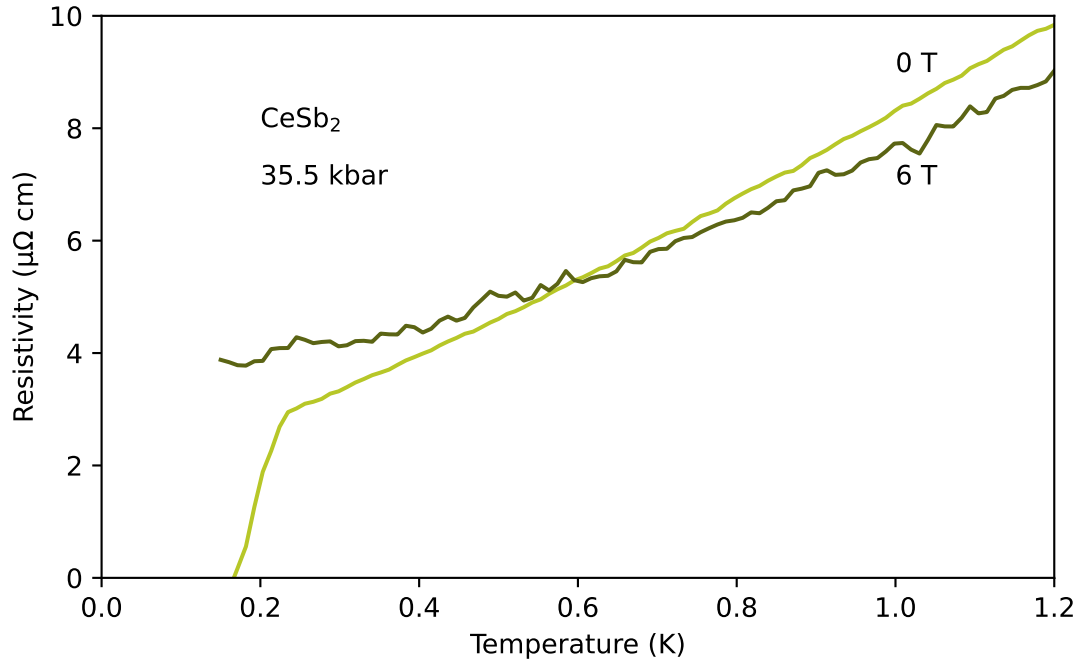


Figure B.5: Low temperature resistivity of CeSb<sub>2</sub> at 35.5 kbar (Sample A1) in 0 and 6 T field applied along the  $c$ -axis, showing a change in sign of magnetoresistance around 0.6 K.