## Thermodynamics and Strong-coupling Superconducting Energy Gaps

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### Abstract

Superconductivity is a field where much research has been conducted into explaining all aspects of this phenomenon in many materials. BCS theory provided the principal understanding of superconductivity in conventional materials yet fails to entirely describe those which exhibit greater coupling-strengths as well as the more unconventional superconductors. Formulations have been proposed which extend BCS theory in various ways such as scaling the predicted energy gap by values representative of greater coupling strengths.

In order to further extend such formulations we applied our own theory which recalculates the energy gap based solely on thermodynamic parameters, in the hope of improving their accuracy. Comparisons of this energy gap calculated from existing criticalfield measurements as well as computational predictions for a range of weak- to strong-coupling type I *s*-wave superconductors were made with experimental tunnelling measurements. Our thermodynamic theory provided an accurate temperature-dependence of the energy gap for all these superconductors except for the strongest coupler which produced erroneous predictions.

An extra-strong-coupling superconductor  $Pb_{0.7}Bi_{0.3}$  was synthesised and it's criticalfield measured in order to rigorously test our theory in the strong-coupling regime. It exhibited type II superconductivity contrary to our belief and as such measurements were insufficient for an accurate comparison. However, computational calculations predicted an accurate temperature-dependence for the energy gap of  $Pb_{0.7}Bi_{0.3}$  when compared with experimental tunnelling measurements. Thus our theory appears to apply for this extra-strong-coupling type II superconductor and not for the strong-coupling type I superconductor, which prompts further investigation. These comparisons depend upon the accuracy with which the temperature-dependence of the energy gap can be measured - not an easy task.

Extension was also made to *d*-wave superconductivity where our theory provided little improvement over a scaled BCS interpretation for several overdoped samples of

the unconventional Bi-2212 superconductor. However, and this is a most important conclusion, this is due to the weak nature of the coupling in this material which we were able to establish.

Thus our theory appears to provide several promising first-order results and warrants further investigation and application to a range of superconductors.

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## Chapter 1

## Introduction

Superconductors in general are a class of materials which exhibit the phenomenon of absolutely zero electrical resistance once they are cooled below their critical temperature,  $T_c$ . This superconducting state is characterised by the pairing of electrons into Cooper pairs which breaks gauge symmetry and causes a energy gap,  $\Delta$ , to open in the density of states. Historically this superconducting state was initially well described by Bardeen, Cooper and Schrieffer in a complex theory from which the central results successfully applied to most conventional low temperature superconductors.<sup>13</sup> BCS theory, as it has been termed, whilst quite successful has its shortcomings. In conventional superconductors the Cooper pairs consist of electrons with equal and opposite momentum yielding s-wave symmetry for the energy gap. This electron pairing is mediated via the exchange of a boson which is identified in conventional superconductors as a phonon within the crystal lattice.<sup>13</sup> BCS theory describes superconductors well when this interaction is weak, the so-called weak-coupling limit, yet discrepancies begin to arise once the strength of this coupling increases. The theory also did not account for the advent of a new generation of unconventional high temperature superconductors which exceeded its theoretical limits. In these unconventional superconductors the momenta of the coupled electrons are still equal and opposite yet have an overall nonzero angular momentum and thus yield an anisotropic energy gap with d-wave symmetry with the pairing mechanism remaining unidentified even today.<sup>14</sup> Much research has been conducted over the last couple of decades in an attempt to accurately describe superconductivity in all its forms with much progress being made but several central issues still remain unresolved.

Padamsee, Neighbor and Schiffman presented a formulation based on BCS theory which accurately describes the behaviour of several properties for conventional *s*-wave superconductors regardless of their coupling strength.<sup>2</sup> It assumes the superconductor is a system of independent fermion quasiparticles from which the electronic entropy can

be calculated. The energy spectrum is taken to be the same as in BCS theory with the gap to  $T_c$  ratio value,  $\alpha$ , representative of the coupling strength being an adjustable parameter. This model provides a good match to experimental data for a range of coupling strengths yet its validity remains to be seen when compared with extra-strong coupling superconductors.

In this thesis we test the application of a theory put forward by our group similar to Padamsee but extending it beyond its reliance on the BCS energy spectrum. Our theory relies solely on the use of thermodynamic functions in order to calculate the temperature dependence of the superconducting energy gap,  $\Delta(T)$ , for a range of superconductors. Ferrell's work<sup>15</sup> has primarily been drawn upon in the formulation of this theory. Ferrell working from the BCS Hamiltonian transformed the equations to obtain an expression for the free energy in terms of an integral of the temperature dependence of the superconducting energy gap squared. Ferrell's intention was to input a model  $\Delta(T)$ , such as BCS, and to calculate the temperature dependent free energy. Yet we can easily determine the free energy from thermodynamic critical-field data, so our theory inverts Ferrell's process and calculates an accurate  $\Delta(T)$  for any superconductor based on the thermodynamic functions  $\Delta F$  and  $\Delta S$ . In terms of simulating the results numerically we too make use of the electronic entropy such as Padamsee and derive from this the Helmholtz free energy in order to deduce  $\Delta(T)$  using our theory. Utilising the BCS energy gap as a starting point the zeroth iteration of the program should produce the same thermodynamic results as Padamsee for a range of coupling strengths. Our theory allows us to then deduce a new energy gap temperature dependence from these thermodynamic functions and feed this back into the program as the starting gap and recalculate. The first additional iteration tested appears to produce a  $\Delta(T)$  which more accurately reflects the departure seen from BCS theory exhibited by stronger coupling superconductors. It is hoped that multiple iterations will settle on a stable solution for  $\Delta(T)$  which will accurately match tunnelling and critical-field data for a range of superconductors.

It is our intention to compare numerical results from our program and apply this theory to existing data for a range of weak- to strong-coupling *s*-wave superconductors. In order to provide a rigorous test for our theory we also synthesised an extra-strong coupling superconductor,  $Pb_{0.7}Bi_{0.3}$ , and measured critical-field data for a range of pressures utilising a standard clamp cell with which to compare to numerical calculations. Finally we hope to extend our theory to represent the more unconventional *d*-wave superconductors as well.

## Chapter 2

## Background

## 2.1 BCS Theory Overview

The phenomenon of superconductivity where certain conductors suddenly exhibit absolutely zero electrical resistance when cooled below a critical temperature,  $T_c$ , remained a great mystery for many decades after its initial discovery by Kamerlingh Onnes in 1911.<sup>1</sup> It was not until 1957 when Bardeen, Cooper and Schrieffer published their iconic work<sup>13</sup> that a reasonable theory for superconductivity which predicted experimental findings was accepted. In the formulation of BCS theory several clues were central. Firstly, the observed transition from the normal to superconducting state was so sharp that it could only be described if the electrons condensed into a coherent, ordered state which extended for long distances across atoms. Thermodynamically, it is a second-order phase transition.<sup>16</sup> Secondly, the isotope effect observed experimentally in 1950 gave a linkage between superconductivity and the atomic lattice of a superconductor. The isotope effect was discovered when experimenting with the dependence of  $T_c$  on the isotopic mass M of the atoms in a superconductor and found that<sup>17</sup>

$$T_c \propto \frac{1}{\sqrt{M}} \tag{2.1}$$

Thus the isotope effect shows the mass of atomic nuclei affects  $T_c$  and that the vibrating atoms in the lattice must somehow be involved with superconductivity.

Cooper was the one to propose that superconductivity is associated with a bound pair of electrons in a metal with equal and opposite spin and momentum.<sup>13</sup> The question was how do these electrons pair when they normally would repel one another via the coulomb interaction? The isotope effect indicated that the development of the superconducting state was related to the vibrations of the lattice and thus phonons became the most likely candidate for this interaction mechanism. Exchange of momentum between two electrons

via a virtual phonon allows them to experience a mutual attraction at a distance and form what has become known as a Cooper pair. The distance over which phonon-electron coupling occurs is known as the coherence length,  $\xi$ , a concept proposed in Ginzburg-Landau theory<sup>16</sup> which can also be derived from BCS theory. Experimental analysis determined that in conventional superconductors the coherence length is around  $10^{-4}$  cm and thus the influence of any one Cooper pair extends over this macroscopic distance.<sup>1</sup> There exist very many Cooper pairs within the coherence length and as such the waves associated with all of these pairs overlap with one another. Cooper pairs no longer exist in isolation but are continually swapping partners with one another due to this extensive overlap forming a single coherent condensed state of the superconductor.<sup>1</sup> Fluctuations out of the paired state (or into the paired state from the normal state) become significant when the condensation energy is comparable to  $k_BT_c$ . Using Ginzburg-Landau theory this criterion can be reexpressed in terms of the number of Cooper pairs within a coherence volume. Should this be comparable to unity then strong superconducting fluctuations will be present up to  $\sim 2T_c$ . In conventional superconductors there is a large number of overlapping pairs so critical fluctuations are suppressed. One could think of this as being, in a sense, close to the "thermodynamic limit" for Cooper pairs. Where fluctuations are weak the transition is very sharp.<sup>18</sup> However, in high- $T_c$  superconductors the very short coherence length means there are just a few pairs that overlap and fluctuations become very significant. Thus coherence leads to the superconductor acting like a single macroscopic quantum state. Cooper pairs can all occupy this single state as they consist of two fermions with opposite spin making them bosons and hence do not obey the Pauli exclusion principle.

The energy within this coherent state is lower than that of normal conduction electrons in a metal due to the higher degree of order from the formation and interaction of the Cooper pairs. As a result an energy gap of  $2\Delta$  opens in the excitation spectrum at the Fermi level separating the superconducting condensate from the normal electron state. In order to excite an electron from the superconducting-state to the normal-state requires breaking apart a Cooper pair from within the condensate, so naturally a finite amount of energy is required to free a single electron from both its pair and the coherent state. One of the famous results of BCS theory is that it links this energy gap at absolute zero,  $\Delta(0)$ , to the experimentally observed  $T_c$ , irrespective of the  $T_c$  value.<sup>16</sup>

$$2\Delta(0) = 3.528k_B T_c \tag{2.2}$$

The relation holds for a range of conventional superconductors which exhibit *s*-wave symmetry for their Fermi surfaces. BCS was originally formulated to describe such conventional superconductors but failed to adequately account for the processes later discovered in unconventional superconductors. In particular these unconventional superconductors exhibit *d*-wave symmetry and the Cooper pairs have an overall non-zero angular momentum.<sup>14,19</sup> However it is still possible to extend BCS theory in order to obtain an estimate of the amplitude of the energy gap at absolute zero.

$$2\Delta(0) = 2.14k_BT_c \tag{2.3}$$

Where the gap is now k-dependent around the Fermi surface and  $\Delta(T, k) = \Delta(T)cos2\theta$ where  $\theta$  is the angle around the Fermi surface. BCS theory also provides an accurate estimate of the temperature dependence of this energy gap  $\Delta(T)$  in the conventional superconductors. At any finite temperature there will be some electrons with enough energy to be thermally excited across the energy gap reducing the number of Cooper pairs and raising the pairing energy of the coherent superconducting-state. As the temperature is increased and the energy gap grows smaller more electrons are thermally excited out of the superconducting-state until eventually at  $T_c$  no pairs remain and the superconductingstate vanishes as illustrated in Figure 2.1.<sup>1</sup> The derivation of the energy gaps from the energy spectrum or density of states for both s- and d-wave symmetry is described in more detail in Section 2.2. BCS theory was formulated such that it applies in the so-called weak-coupling limit. In this limit it is assumed the electron-phonon coupling constant obeys Equation 2.4.<sup>16</sup>

$$\lambda = N(E_F)V < 1 \tag{2.4}$$

Where  $N(E_F)$  is the number of states at the Fermi level and V is the electron-phonon interaction strength which is assumed to be constant up to some high cut-off energy.

BCS theory does indeed reasonably hold for a range of conventional superconductors

yet discrepancies begin to arise when the strength of the coupling interaction increases and Equation 2.4 no longer holds. Thus new theories which modify the central results of BCS theory are needed in order to adequately describe superconductors which exhibit stronger coupling. BCS theory also does not adequately describe the new generation of unconventional high-temperature superconductors that have been discovered since its formulation. These unconventional superconductors exhibit  $T_c$ 's much higher than the theoretical limits predicted by BCS theory and the pairing mechanism of their Cooper pairs has as of yet not been conclusively identified. Using the Eliashberg extension of BCS theory to strong coupling McMillan predicted an upper limit of  $T_c$  of 28 K for the Nb alloys and 40 K for V<sub>3</sub>Si.<sup>20</sup> Thus much research has been conducted in the field of superconductivity over the last couple of decades in an attempt to formulate a theory to adequately describe superconductivity in all of its forms.<sup>1</sup>



**Figure 2.1** The temperature dependence of the superconducting energy gap  $\Delta(T)$  scaled by the gap at absolute zero  $\Delta(0)$  as predicted by BCS theory. Overlaid with experimental measurements of the energy gap for an indium-bismuth alloy to show good agreement with theory.<sup>1</sup>

## 2.2 Density of States

#### **2.2.1** *s*-wave

In 3D Fermi-liquid-like metals the Density of States (DOS) is proportional to  $\sqrt{E - E_F}$ provided the dispersion is free-electron like. But for energies close to  $E_F$  we approximate the DOS as a constant. In an *s*-wave superconductor electrons with equal and opposite momentum pair up into Cooper pairs breaking gauge symmetry and causing an energy gap,  $\Delta$ , to open up in the DOS. We can deduce a formula for the superconducting-state DOS, N(E), by counting all states over momentum *k*-space with particular energies, *E*. We start with a relation from the BCS Hamiltonian<sup>13</sup> linking the superconducting-state energy,  $E_k$ , the normal-state or free particle energy,  $\varepsilon_k$ , and  $\Delta$  which is isotropic for *s*wave superconductors.

$$E_k = \sqrt{\varepsilon_k^2 + \Delta^2} \tag{2.5}$$

$$N(E) = \sum_{k} \delta(E_k - E)$$
(2.6)

$$= N(0) \int \delta(\sqrt{\varepsilon_k^2 + \Delta^2} - E) d\varepsilon_k$$
(2.7)

The DOS can now be calculated as an integral over  $\varepsilon_k$  where N(0) is the magnitude of the normal state DOS at the Fermi level. It is more convenient however to change variables and integrate over the superconducting state energy,  $E_k$ .

$$d\varepsilon_k = \frac{E_k dE_k}{\sqrt{E_k^2 - \Delta^2}} \tag{2.8}$$

$$N(E) = N(0) \int \frac{E_k}{\sqrt{E_k^2 - \Delta^2}} \delta(E_k - E) dE_k$$
(2.9)

$$= N(0) \frac{|E|}{\sqrt{E^2 - \Delta^2}}$$
(2.10)

Thus we now have a useful form for the *s*-wave superconducting DOS. The number of states must of course be the same in both the normal- and superconducting-state in order for entropy to be conserved within the system. In order to account for the reduced DOS at low energies due to the gap opening the DOS becomes large immediately above the gap



**Figure 2.2** *s*-wave superconductor DOS in superconducting- (line) and normal-states (red dashed). Hatched areas represent the equivalent number of states in the normal- and superconducting-states.

forming a singularity at  $E = \Delta$ , which we can see qualitatively illustrated in Figure 2.2.

#### **2.2.2** *d*-wave

In unconventional superconductors the electrons forming Cooper pairs still have equal and opposite momentum but overall non-zero angular momentum and so the energy gap which opens is no longer isotropic and exhibits lower symmetry in k-space, typically though not exclusively p-wave or d-wave. Generally unconventional superconductors exhibit a layered structure which gives rise to quasi-2D electronic behaviour. As such the  $k_z$  dispersion varies only slightly and is usually neglected. A d-wave gap opens above and below the Fermi surface in k-space, a constant energy contour projected onto the  $(k_x, k_y)$ plane, and can be described by the relation<sup>16</sup>

$$\Delta_k = \frac{\Delta}{2} (\cos k_x - \cos k_y) \tag{2.11}$$

Where it exhibits nodes at the diagonals of the zone,  $k_x = k_y$ , as illustrated in Figure 2.3. We can however represent these co-ordinates within k-space in terms of an angle,  $\theta$ , made to the  $k_y$  axis.

$$\theta = \arctan\left(\frac{\pi - k_x}{\pi - k_y}\right) \tag{2.12}$$



**Figure 2.3** The Fermi surface (red) and energy gap (blue) which opens up along it at the zone diagonals of a *d*-wave superconductor. The same size gap opens up below the Fermi surface but is not shown here for clarity.

The *d*-wave gap is often simplified by the approximation that  $cosk_x - cosk_y \approx cos2\theta$ yielding the *d*-wave gap equation

$$\Delta = \Delta cos2\theta \tag{2.13}$$

It is now a simple matter to deduce the DOS for a *d*-wave superconductor as at any particular  $\theta$  we have a fixed gap size akin to that of an *s*-wave superconductor. Thus utilising the same method as for the *s*-wave superconductor previously and summing over the full range of  $\theta$  we can deduce the following DOS.



**Figure 2.4** *d*-wave superconductor DOS in superconducting- (line) and normal-states (red dashed).

$$N(E) = \sum_{\theta} \sum_{k} \delta(\sqrt{\varepsilon_k^2 + (\Delta \cos 2\theta)^2} - E)$$
(2.14)

$$= \frac{N(0)}{\pi/4} \int_0^{\pi/4} \frac{E}{\sqrt{E_k^2 + (\Delta \cos 2\theta)^2}} d\theta$$
 (2.15)

The angle dependence of the energy gap and the existence of the node at the Fermi surface create a different response for the *d*-wave DOS which can be seen in Figure 2.4.

## **2.3 BCS Energy Gap Equation**

Utilising the Hamiltonian described by BCS theory it is possible to formulate the selfconsistent Equation 2.16 for the energy gap's temperature dependence as an integral over energy. This can be achieved by thermally averaging the Hamiltonian operators with quantum mechanic statistical analysis.<sup>17</sup>

$$\Delta = N(0)V \int_0^{\hbar\omega_c} \frac{\Delta}{\sqrt{E^2 - \Delta^2}} \tanh \frac{\sqrt{E^2 - \Delta^2}}{2k_B T} dE$$
(2.16)

Where V is the electron-phonon interaction strength which under BCS theory in the weak-coupling limit is constant up to some cut-off energy as mentioned in Section 2.1. That cut-off energy is  $\hbar\omega_c$  which is orders of magnitude greater than the energy of the superconducting Cooper pair condensate.<sup>17</sup> In conventional superconductors this is taken to be at the Debye frequency,  $\omega_D$ , as this is the theoretical maximum frequency of the phonons within the lattice. However this equation is self-consistent where  $\Delta$  appears on both sides of the equality and as such the only reasonable way to solve it is numerically. An initial guess for  $\Delta$  is used on the right hand side of the equation to calculate the  $\Delta$  on the left hand side, this new value is then fed back into the right hand side of the equation to recalculate  $\Delta$  once more. Many iterations carried out by a computer will eventually produce a consistent, accurate value for  $\Delta$  that matches both sides of the equation for every temperature. However this method is laborious and computationally intensive making it very inefficient for regular recalculation given modern commercial computers.  $\Delta(T)$  has already been tabulated by Muhlschlegel<sup>21</sup> to which we have made

the following fit for arbitrary T

$$\Delta = 1.764 k_B T_c \left( 1 - \left(\frac{T}{T_c}\right)^{3.49504} \right)^{0.54312}$$
(2.17)

In the first instance we shall use this approximate equation for the BCS gap and avoid the computationally intensive self-consistent calculation of Equation 2.16 unless such accuracy is necessary. Equation 2.16, as it is derived from BCS theory, holds for conventional superconductors which exhibit *s*-wave symmetry yet we may also extend this to *d*-wave symmetry to obtain a similar equation for unconventional superconductors. Utilising Equation 2.13 and integrating over all angles,  $\theta$ , we are able to carry out a similar derivation to that above and deduce the following temperature dependence of the *d*-wave energy gap.

$$\Delta = \frac{N(0)V}{\pi/4} \int_0^{\hbar\omega_c} \int_0^{\pi/4} \frac{\Delta(\cos 2\theta)^2}{\sqrt{E^2 - (\Delta\cos 2\theta)^2}} \tanh \frac{\sqrt{E^2 - (\Delta\cos 2\theta)^2}}{2k_B T} d\theta dE \quad (2.18)$$

Equation 2.18 must be solved self-consistently and thus numerical calculation is required.

## 2.4 **Tunnelling Measurements of Energy Gap**

Experimental confirmation of the energy gap as predicted by BCS theory was one of the most robust verifications of its validity. This can be done in a number of ways including microwave and infrared spectroscopy or measurement of thermal properties such as specific-heat and thermal conductivity. However one of the most direct and convenient measurements of the energy gap is through tunnelling experiments. Tunnelling experiments use the effect of quantum-mechanical tunnelling where an electron wave has a finite probability of tunnelling through a classically forbidden zone, such as a thin insulating barrier. A tunnelling junction can be manufactured as a parallel plate capacitor where two metallic layers approximately 10 nm apart are separated by a thin insulating layer. In order to measure the energy gap in a superconductor imagine one of these plate layers is the superconductor of interest and the other is a regular metal. A variable voltage can then be applied to this capacitor and the current measured. Figure 2.5<sup>1</sup> illustrates how



**Figure 2.5** Energy levels in a tunnelling junction where a superconducting plate is separated from a normal metal plate by a thin insulating layer. (a) When no voltage is applied the condensed state of Cooper pairs is aligned to the Fermi level and hence no current flows because the states are gapped there. (b) Once the applied voltage is large enough to shift the energy levels so that the excited normal states of the superconductor are at the normal metal's Fermi level then a substantial current can tunnel between the layers.<sup>1</sup>

the energy levels in the materials at each plate are affected by the applied voltage.

In a superconductor the Cooper pairs occupy a single condensed state  $2\Delta$  in energy below the excited normal-state for single electrons. When no voltage is applied this condensed state is equal in energy to the Fermi level of the regular metal on the other side of the tunnelling junction as shown in Figure 2.5 (a). Electrons are only able to tunnel through the insulating barrier when there are available states to flow into (or from) and so no current flows. As the voltage applied is increased the energy of the condensate is lowered until a certain critical voltage,  $V_{critical}$ , aligns the Fermi level in the normal metal with the excited normal-state of the superconductor. No current will flow through the junction until  $V_{critical}$  has been reached at which point there are available excited states for the electrons of the normal metal to tunnel into and so a current flows as illustrated in Figure 2.5 (b). This  $V_{critical}$  provides a direct measure of the energy gap and is equal to  $\Delta/e$ . In order to measure the energy gap at any given temperature a positive voltage is applied to the superconducting plate and increased whilst the current is measured giving a characteristic I-V curve such as Figure 2.6<sup>1</sup>, from this  $V_{critical}$  can be used to determine  $\Delta$ .



**Figure 2.6** The current-voltage characteristic curve measured for tunnelling across a superconductor/normal metal capacitor. Once  $V_{critical} = \Delta/e$  has been reached the superconducting excited state level has been depressed sufficiently to allow electrons from the normal metal to tunnel across and allow a current to flow.<sup>1</sup>

Tunnelling junctions can also be comprised of two identical superconducting plates and thus  $V_{critical} = 2\Delta/e$ . Tunnelling measurements often provide the most accurate and comprehensive measure of the temperature dependence of the superconducting energy gap for a material. As such comparisons to calculated values for the energy gap in this thesis are made to tunnelling measurements for a range of superconductors, primarily in Chapter 5.

### **2.5** The $\alpha$ Model

There have been several attempts at providing a relatively simple extension to the elegant BCS theory in order to account for the discrepancies that arise due to stronger electronphonon coupling in *s*-wave superconductors. Padamsee, Neighbor and Shiffman's attempt at this culminated in their  $\alpha$ -model.<sup>2</sup> They draw upon a similar method utilised by Finnemore & Mapother<sup>10</sup> and Swihart<sup>22</sup> which use the gap ratio

$$\alpha \equiv \frac{\Delta(0)}{k_B T_c} \tag{2.19}$$

as an adjustable parameter in BCS relations.  $\alpha$  has been taken as a measure of the coupling strength in a range of superconductors. BCS theory, which assumes weak-

coupling, has a value of  $\alpha_{BCS} = 1.764$  as could be deduced from Equation 2.2 and for other superconductors where the electron-phonon coupling is greater experimentally derived values for  $\alpha$  exceed this. The works of Finnemore & Mapother and Swihart utilise this  $\alpha$  in the BCS expression for the free energy yet this introduces thermodynamic inconsistencies and does not match the data exceptionally well.<sup>2</sup> Padamsee avoids these inconsistencies by also employing  $\alpha$  as an adjustable parameter to represent coupling strength but instead begins with the standard expression for the combinatorial entropy in a system where excited states are well-defined Fermions. Thus the electronic entropy in the superconducting-state can be calculated by

$$S_{es} = -2k_B \sum_{k} f_k \ln f_k + (1 - f_k) \ln(1 - f_k)$$
(2.20)

$$f_k = \frac{1}{\exp\frac{E_k}{k_B T} + 1}$$
(2.21)

Where  $f_k$  is the Fermi function and the quasiparticle energies  $E_k$  are given by Equation 2.5.<sup>2</sup> The energy gap  $\Delta$  is taken to be the same as in BCS theory as tabulated by Muhlschlegel<sup>21</sup> except scaled by the adjustable parameter  $\alpha$  to represent the increased coupling strength giving Equation 2.22.<sup>2</sup>

$$\Delta(T) = \frac{\alpha}{\alpha_{BCS}} \Delta_{BCS}(T)$$
(2.22)

The normal-state electronic entropy can be similarly calculated where the energy gap is zero and as such  $E_k = \varepsilon_k$  yielding a linear dependence on temperature. Thus we are now able to determine the difference in electronic entropy between the normaland superconducting-states from which we can deduce the free energy difference by integration with respect to temperature. The free energy in turn allows us to determine the critical-fields,  $H_c$ , at any given temperature by Equation 2.23.<sup>13</sup>

$$\Delta F = \frac{H_c^2}{8\pi} \tag{2.23}$$

Comparison of critical-field results of various superconductors are generally presented in terms of their deviation from a perfect parabolic temperature dependence which can be calculated via the deviation function of Equation 2.24 where  $t = T/T_c$ .<sup>2</sup>

$$D(t) \equiv \frac{H_c(t)}{H_c(0)} - (1 - t^2)$$
(2.24)

In general the deviation function is quite sensitive to small differences and as such allows a better way to observe the minute differences in  $H_c$  data between superconductors. Padamsee calculated and plotted this deviation function from the  $\alpha$ -model for a range of  $\alpha$ 's to illustrate the differences in  $H_c$  for altered coupling strengths, shown in Figure 2.7.<sup>2</sup>



**Figure 2.7** Deviations as calculated from  $H_c$  predictions of Padamsee's  $\alpha$ -model for a range of coupling strengths, indicated by the displayed  $\alpha$ -values for each curve.<sup>2</sup>

Thus Padamsee's  $\alpha$ -model provides a formalism to calculate all of the above thermodynamic variables and avoid the inconsistencies of some other models. It appears to provide a reasonable fit to critical-field data and matches  $\alpha$ -values deduced from tunnelling measurements for a fair range of different coupling superconductors. However whether it adequately describes some of the strongest coupling superconductors remains to be seen.

## 2.6 Proposed Thermodynamic Theory

We propose a theory similar to Padamsee in its formulation but which extends it beyond its reliance on the BCS energy spectrum and allows this to migrate iteratively. It relies solely on the use of thermodynamic functions in order to calculate a general superconducting energy gap,  $\Delta(T)$ , for a range of superconductors. It should be applicable to a range of s-wave superconductors with varying coupling strengths as well as unconventional d-wave superconductors.

#### 2.6.1 Theory Formulation

Ferrell's work<sup>15</sup> has been drawn upon primarily to provide a starting point in the formulation of this theory which we extend to include *d*-wave superconductivity. Ferrell, working from the BCS Hamiltonian, transformed the equations to obtain an expression for the free energy in terms of an integral of the BCS superconducting energy gap squared as shown in Equations 2.25 & 2.26.<sup>15</sup>

$$\Delta F(T) = \zeta N(0) \Delta(0)^2 t^2 \int_t^1 \frac{Q(t')}{t'^3} dt'$$
(2.25)

$$Q(t) \equiv \left(\frac{\Delta(T)}{\Delta(0)}\right)^2 \tag{2.26}$$

Where  $\zeta$  is an additional parameter included to distinguish between the *s*-wave,  $\zeta = 1$ , and *d*-wave,  $\zeta = 1/2$ , cases.  $\Delta F(T)$  being the free energy difference between the normal and superconducting states is intrinsically linked to the energy gap  $\Delta(T)$  separating them. Ferrell's intention was to adopt a model reduced-temperature dependence Q(t), such as BCS, and to calculate  $\Delta F(T)$  via Equation 2.25. However, it is relatively easy to determine  $\Delta F(T)$  from critical-field data by Equation 2.23 so we propose inverting Ferrell's calculations and instead obtaining an accurate  $\Delta(T)$  from  $\Delta F(T)$ . Thus by differentiating both sides of Equation 2.25 with respect to T and rearranging we can obtain our theoretical equation which relies solely on thermodynamic functions.

$$\zeta N(0)\Delta(T)^2 = 2\Delta F(T) + T\Delta S(T)$$
(2.27)

 $\Delta S(T)$  can be calculated by differentiating  $\Delta F(T)$  experimentally derived from criticalfield measurements and thus allows us to calculate an accurate  $\Delta(T)$ . Ferrell's calculation of the free energy is based on BCS weak-coupling yet we can attempt to extend it to strong-coupling utilising Padamsee's  $\alpha$ -model to represent this through scaling of the BCS gap. In order to achieve this the  $\Delta(T)$  in Equation 2.26 would be replaced by that calculated from Equation 2.22 which incorporates the coupling strength in the form of the  $\alpha$  ratio. We can use Equation 2.27 to calculate  $\Delta(T)$  as  $\alpha$  will be imbedded within our entropy calculation. In order to provide an initial test of the theory our group has previously calculated  $\Delta F$  and  $\Delta S$  from critical-field measurements for Pb, a strongcoupling superconductor, and calculated  $\Delta(T)$  using Equation 2.27. This calculation produced a  $\Delta(T)$  which flattens out relative to the model BCS temperature dependence and as a result more accurately matches experimental tunnelling measurements of the gap for Pb.

In order to provide a rigorous test of the theory  $\Delta(T)$  would need to be calculated from the theoretical expressions for these thermodynamic functions and iterated numerous times using each newly derived  $\Delta(T)$  in order to settle on a stable solution. Such a stable solution from multiple iterations could then be compared to experimental data and provide proof of the theory's applicability.

#### 2.6.2 Theory Computation

Padamsee's  $\alpha$ -model begins by calculating the electronic entropy for *s*-wave superconductors which requires a summation over all states in *k*-space in order to provide a thermodynamically-consistent model. We too shall begin by calculating the entropy for our system, yet a summation over *k*-space is cumbersome numerically and so we instead convert this to an integral over all energies, *E*, by inclusion of the DOS, N(E), as shown

in the Equation 2.28.

$$S = -4k_B \int_0^{E'} N(E) f_w(E, T) dE$$
 (2.28)

$$f_w(E,T) = f(E,T) \ln f(E,T) + (1 - f(E,T)) \ln(1 - f(E,T))$$
(2.29)

Where  $f_w(E,T)$  is denoted the Fermi Window function which is the same term as in Padamsee's Equation 2.20 but now the Fermi function, f, is calculated with energy and temperature inputs only rather than being deduced from k values.  $f_w(E,T)$  is a representation of the distribution of energies for thermally activated excited states within the system and so we simply need to integrate up to a sufficiently high energy E' where  $f_w$  is essentially zero. At this E' Equation 2.28 will provide an adequate numerical calculation for the entropy of the system. Inclusion of N(E) in Equation 2.28 has also generalised the entropy calculation to be used for both s- & d-wave superconductors by using the derived formula in Section 2.2. The superconducting-state entropy,  $S_S$ , can be initially calculated using N(E) with the BCS  $\Delta(T)$  scaled by  $\alpha$  as given by Equation 2.22. The normal-state entropy,  $S_N$ , is simply calculated by setting  $\Delta = 0$ . Thus we now have  $\Delta S(T) = S_N - S_S$  and by numerically integrating we can obtain  $\Delta F(T)$  producing similar thermodynamic results as Padamsee's  $\alpha$ -model for any particular  $\alpha$ .

Utilising Equation 2.27 we can use our theory to determine  $\Delta(T)$  from these thermodynamic functions. Yet in order to produce a self-consistent solution for  $\Delta(T)$  we need to replace the BCS  $\Delta(T)$  in N(E) with our newly calculated  $\Delta(T)$  and repeat this calculation similarly multiple times. Over a number of iterations a stable solution for  $\Delta(T)$  should eventually emerge. Whilst Padamsee's  $\alpha$ -model provides a good approximation for the gap it is not suitable for such an iterative process. It only accounts for the effect strong-coupling has on the gap size and fails to address how it also alters the electronic specific heat coefficient,  $\gamma = \partial S/\partial T$ . Our hypothesis is to extend the theory through the use of Eliashberg theory to fully account for all effects of strong-coupling and hopefully recover a realistic temperature dependence for the gap through this iterative calculation. Eliashberg theory alters the normal-state electronic specific-heat coefficient from it's Sommerfeld value to

$$\gamma_N = \frac{2}{3}\pi^2 k_B^2 N(0)(1+\lambda)$$
(2.30)

where  $\lambda$  is the electron-phonon enhancement parameter.<sup>23</sup> This enhancement parameter alters the equations for both  $\gamma_N \& \gamma_S$  such that they match the higher values measured for superconductors with stronger coupling.  $\lambda \ll 1$  for the BCS case. The specificheat coefficient can be used to find the entropy of a system by integrating with respect to temperature. As such this scalar enhancement factor would necessarily need to carry through to the entropy in order to accurately portray this effect of stronger coupling. Thus for our model we must include this enhancement factor in order to maintain full consistency with the effects of strong-coupling thereby changing Equation 2.28 into

$$S = -4k_B(1+\lambda) \int_0^{E'} N(E) f_w(E,T) dE$$
 (2.31)

In order to utilise this enhancement factor with the  $\alpha$ -model it is necessary to ensure the two are self-consistent. Determination of appropriate  $\lambda$ 's would involve performing the iterative calculation to produce stable  $\Delta(0)$ 's and then calculating the corresponding  $\alpha$ -values for each degree of coupling with Equation 2.19.

Thus our theory should allow us to simulate the full temperature dependence for the thermodynamic functions  $\Delta S(T)$ ,  $\Delta F(T)$  and  $\Delta(T)$  over a range of coupling strengths which we can compare with both critical-field and tunnelling measurement data.

## Chapter 3

## **Computational Calculations**

Computational calculations were carried out using software programs written by the author in the freely available programming language  $Python^{TM}$ . Each calculation involved creation of a particular program to carry it out and those which relied on the results from a previous calculation often imbedded that particular program into its structure. In other words, more complex programs incorporated previously written programs within them as *functions* for it to access and process as necessary. The following chapter will cover the architecture of programs created in order to undertake the calculations necessary to test our proposed theory for firstly *s*-wave and then *d*-wave superconductors.

## **3.1 Programs for** *s***-wave Symmetry**

#### **3.1.1 Density of States**

The first required quantity is the Density of States (DOS) which will be utilised by the later program Entropy. Initially the program computed this by summing states over a k-space grid of values ( $k_x = 0 \rightarrow \pi$ ,  $k_y = 0 \rightarrow \pi$ ) as described by Equation 2.6. Yet as has been mentioned in Subsection 2.2.1 this is computationally intensive and inefficient hence it proved more convenient to convert this to an integral over energy given by Equation 2.7 and calculate the DOS directly from Equation 2.10. The normal-state DOS, N(0), in this equation is a constant and is set to a value of 1.0 state/eV formula unit for the purposes of our calculations. The DOS is now calculated as a function of energy at energies  $E_i = i * dE$  for integers of i = 0 to NE. dE is determined as the range of energy divided by the number of energy values, NE, we wish to calculate. Larger values of NE will naturally produce a more accurate, detailed DOS but will be more computationally expensive. Calculation of the DOS also requires a  $\Delta$  value which we calculate using our

fit to the Muhlschlegel data given by Equation 2.17. Since  $\Delta$  is a function of temperature,  $t = T/T_c$ , the DOS must be recalculated at different temperatures. One such DOS calculated from the program can be seen in Figure 3.1 which matches the expected shape we predicted in Figure 2.2. It must be noted that due to the singularity in the DOS at  $E = \Delta$  a test condition is built into the program to avoid a computational error if this ever occurs.



Figure 3.1 Calculated Density of States versus energy of an *s*-wave superconductor with  $\Delta = 0.004$  eV.

#### 3.1.2 Entropy

Now that we have a program to calculate the DOS we are able to compute the entropy as a function of temperature utilising Equation 2.31. In order to perform this integration numerically with respect to energy we will first employ the simplest method of the trapezium rule which approximates a function as a series of trapeziums each of width dE as shown in Figure 3.2. The trapezium rule calculates the area of all of these trapeziums and thus provides an approximation for the integral given by Equation 3.1.

$$\int_{0}^{E'} f(E)dE \approx \frac{dE}{2} \sum_{i=0}^{NE-1} (f(E_i) + f(E_{i+1}))$$
(3.1)


Figure 3.2 The area under some function of energy f(E) (blue line) approximated by a series of trapeziums each of width dE.

Naturally this can underestimate or overestimate the integral in certain places but if dE is small enough it provides sufficient accuracy and is a simple and effective method for performing numerical integration. So our program cycles through a number of temperatures, NT, from 0 K to above  $T_c$  calculating the electronic entropy. At each temperature it runs the DOS function to obtain values to use in the entropy integral calculation, which is computed by the trapezium rule. The entropy calculated for the normal- and superconducting-states, as well as the difference  $\Delta S$  between these, is plotted



Figure 3.3 Calculated entropy in the normal-state (blue dotted), superconducting-state (red line) and  $\Delta S$  (green dots) versus temperature of an *s*-wave superconductor with  $T_c = 25$  K, NE = 10,000 and NT = 100.

versus temperature in Figure 3.3. The noise which is evident in the superconductingstate entropy is due to the singularity in the DOS at  $E = \Delta$ . This singularity can occur anywhere between two energy points  $E_i$  and  $E_{i+1}$ , and shifts as the temperature changes. As such the difference between the true area under the DOS and the trapeziumapproximated area can fluctuate significantly, leading to spikes in the calculated entropy. In order to minimise such noise we can simply increase NE and gain more accurate representations of the DOS. However a sufficient NE to adequately minimise noise is around 100,000 points and vastly increases the computation time. A more efficient solution is presented in the next section.

#### 3.1.3 Entropy Smoothed

In order to produce smooth noise-free results for the entropy we need to remove the DOS singularity from the calculation. This can be done quite simply through two changes of variables to produce a smooth continuous function to integrate over. Consider the following entropy integral

$$S \propto \int_{\Delta}^{E'} \frac{E}{\sqrt{E^2 - \Delta^2}} f_w(E, T) dE$$
(3.2)

where the Fermi window function,  $f_w(E, T)$ , is already a smooth continuous function. Making a change of variables to  $x = E^2 - \Delta^2$ , Equation 3.2 becomes

$$S \propto \frac{1}{2} \int_0^{E'^2 - \Delta^2} \frac{f_w(\sqrt{x + \Delta^2}, T)}{\sqrt{x}} dx$$
(3.3)

And a further change of variables to  $x = t^2$  gives

$$S \propto \int_0^{E'^2 - \Delta^2} f_w(\sqrt{t^2 + \Delta^2}, T) dt$$
(3.4)

an integral of a continuous function across the entire energy range with no singularities. Now we simply replace the dummy variable t by E and upper limit with E'. E' merely represents a large energy which is an order of magnitude or more greater than  $\Delta$  such that its effect in the upper limit is negligible. Equation 3.4 produces noise-free numerical results efficiently as can be seen in Figure 3.4 for NE values of only 1000, two orders of magnitude lower than that required by the previous calculation.



Figure 3.4 Noise-free entropy in the normal-state (blue dotted), superconducting-state (red line) and  $\Delta S$  (green dots) versus temperature for an *s*-wave superconductor with  $T_c = 25$  K, NE = 1000 and NT = 100 calculated using Equation 3.4. The change in free energy  $\Delta F$  (black dashed) is also shown.

#### 3.1.4 Free Energy

The next thermodynamic variable to be calculated is the change in free energy  $\Delta F(T)$ which we can derive directly from  $\Delta S(T)$  through integration. However in order to achieve the correct physical result from a numerical calculation we need to perform this integral from  $T_c$  down to 0 K. Above  $T_c$ ,  $\Delta S$  is zero as there is no difference between the normal- and superconducting-states in this regime and as such the  $\Delta F$  calculated would be an arbitrary constant which we can set to zero. If we instead were to integrate from 0 K up to  $T_c$  then  $\Delta F$  would begin at this zero and grow which is an unphysical result. Thus the program uses the above Entropy Smoothed function to produce  $\Delta S(T)$  from which to calculate

$$\Delta F(T) = \int_{T_c}^{T} \Delta S(T') dT'$$
(3.5)

This integration is performed numerically once again via the trapezium rule through a cumulative process in order to account for the integral from  $T_c$  down to each particular temperature, the results of which can be seen in Figure 3.4.

#### 3.1.5 Energy Gap

Now that we have programs which calculate all of the thermodynamic functions we are able to compute the full temperature dependence of the energy gap using our thermodynamic theory as expressed in Equation 2.27. Figure 3.6 illustrates how this calculation is performed. In the first iteration the program cycles through NTtemperatures from 0 K to above  $T_c$  and at each temperature it calculates the BCS  $\Delta(T)$ from our fit in Equation 2.17. The BCS  $\Delta(T)$  is used to calculate  $\Delta S(T)$  which is then in turn used to calculate the full  $\Delta F(T)$ . These thermodynamic functions are finally combined via Equation 2.27 to produce the first recalculated  $\Delta'(T)$ .  $\Delta'(T)$  is then used to replace the BCS  $\Delta(T)$  and the calculation repeated. We expect that after a sufficient number of iterations  $\Delta'(T)$  should converge to the exact BCS temperature dependence of  $\Delta(T)$  where  $\alpha = 1.764$ . As expected after the first iteration the newly calculated



Figure 3.5 Energy gap calculated from Equation 2.27 as a function of temperature. Our initial BCS fit (black dashed), first iteration result (red line) and  $40^{th}$  iteration stable solution (green line) in the BCS case where  $\alpha = 1.764$ .



Figure 3.6 Flowchart indicating the process followed by our program.

 $\Delta'(T)$  has shifted outwards slightly in relation to our rough starting fit for the BCS  $\Delta(T)$  to more accurately reflect the true temperature dependence of the energy gap, see Figure 3.5. Approximately 40 iterations produce a stable  $\Delta'(T)$  to within 0.01% of the previous iterations solution. However it is also clearly obvious that the absolute size of  $\Delta(T)$  has increased by the final iteration, particularly at 0 K. Investigation into this error found that by doubling NT this overestimate is halved, thus we are able to deduce that it arises from the trapezium rule overestimating  $\Delta F(T)$ . One remedy to this issue is to increase NT substantially to provide a more accurate estimate of the integral, yet this is computationally inefficient.

A more accurate method of numerical integration is required and thus we employ Simpson's rule. Simpson's rule is a method of numerical integration which effectively fits a quadratic polynomial across three consecutive points as shown in Figure 3.7 and performs the integral with this. Thus to provide a truly accurate representation of our



**Figure 3.7** Simpson's rule effectively fits a polynomial, P(x), to a function across three known points (a, b and their mid point m) in order to calculate it's integral instead.

integrand we make use of the composite Simpson's rule which breaks up an interval range, [a, b], into n subintervals where n must be an even number in order to perform Simpson's rule on each of these subintervals. The general formula for this composite Simpson's rule is

$$\int_{a}^{b} f(x)dx \approx \frac{h}{3} \left( f(x_{0}) + 2\sum_{j=1}^{n/2-1} f(x_{2j}) + 4\sum_{j=1}^{n/2} f(x_{2j-1}) + f(x_{n}) \right)$$
(3.6)

where  $x_j = a + jh$  for j = 0, 1, ..., n - 1, n with h = (b - a)/n and  $x_n = b$ . However the limitation of Simpson's rule is that it requires an even number of subintervals and as such it can only apply to even indexed temperature points,  $T_{2i}$  (where *i* is any integer). Yet we

also wish to calculate values at the odd indexed temperatures too. We remedy this issue by creating a hybrid numerical integration technique using both the Simpson and trapezium rules. Even indexed temperatures are calculated using Simpson's rule only but for a given odd indexed temperature,  $T_n$ , we apply Simpson's rule up to  $T_{2i} < T_n$  and the trapezium rule to the remaining  $(T_{2i+1} - T_{2i})^{th}$  subinterval as shown in Figure 3.8. Utilising this method we are able to all but eliminate the overestimation from the trapezium rule and provide a near perfect approximation to the integral for a reasonable NT.

So far we have run our program for the BCS case where  $\alpha = 1.764$ . In order to calculate  $\Delta(T)$  for each  $\alpha$ -value we need to determine the matching electron-phonon enhancement parameter,  $\lambda$ , in Equation 2.31 of the Entropy program. As discussed in Subsection 2.6.2 the  $\alpha$ -model does not account for the effect of stronger coupling on the electronic specific heat coefficient and hence the entropy. Thus we proposed including this result of Eliashberg theory in our calculations in order to ensure our thermodynamic theory correctly accounts for stronger coupling during the iterative process. If  $\lambda$  was not included the iterative process would merely cycle back towards the BCS  $\Delta(T)$ . Thus we run our Energy Gap program for a range of  $\lambda$  values and determine the corresponding  $\alpha$  from the resulting  $\Delta(0)$  with Equation 2.19.



**Figure 3.8** Simpson's rule applied to calculate integral up to an evenly indexed temperature  $T_{2i}$  (blue hatched) and for an odd indexed temperature  $T_{2i+1}$  the trapezium rule is applied for the last remaining subinterval (red shaded). Subintervals of width dT have been exaggerated for clarity.

#### 3.1.6 Deviation

We are now able to calculate  $\Delta(T)$  for any particular value of  $\alpha$  and hence a variety of coupling strengths. However the change in  $\Delta(T)$  is small and difficult to observe for these various  $\alpha$ 's and so following Padamsee we employ the deviation function which is sensitive to such minute differences.<sup>2</sup> Equation 2.24 relies on the use of  $H_c$  values yet we know that these are related to the free energy by Equation 2.23. Thus we can compute the deviation function for any particular  $\alpha$  using our simulated free energy with Equation 3.7.

$$D(t) \equiv \sqrt{\frac{\Delta F(t)}{\Delta F(0)}} - (1 - t^2)$$
(3.7)

The deviations for a range of  $\alpha$ 's were computed for a single iteration and are plotted in Figure 3.9. However comparison of this to the results of Padamsee shown in Figure 2.7 revealed a discrepancy. Our program was producing deviations for large  $\alpha$ 's with a



Figure 3.9 Calculated s-wave Deviation Function, D(t), versus  $t^2$  for the BCS case as well as a range of  $\alpha$ -values (displayed above each curve). Note the curvature of the highest  $\alpha$  curves undercutting zero near  $T_c$ .

strange curvature that undercuts the zero line near  $T_c$  where they should rather exhibit a steady linear decrease as exhibited by Padamsee's calculations in Figure 2.7.

It was determined that this error was due to the fact that our starting value for the BCS  $\Delta(T)$ , Equation 2.17, is only an approximate fit and does not accurately reflect the  $\sqrt{1 - T/T_c}$  temperature-dependence near  $T_c$ . This only became evident due to the very sensitive nature of the deviation function. The iterative method of computing new  $\Delta(T)$ 's should account for this yet is slow to converge on the true dependence near  $T_c$  and as such would require approximately 1000 iterations. Needless to say this would be highly inefficient computationally to perform for each value of  $\alpha$ . Thus instead of starting with an approximate fit for BCS  $\Delta(T)$  we can precisely calculate it directly from the BCS gap equation to use as the starting point for our program.

#### 3.1.7 BCS Energy Gap

As has been discussed previously in Section 2.3 the BCS energy gap can be calculated self consistently from Equation 2.16. Yet such a calculation involves many iterations before a suitable solution arises and as such is computationally inefficient were it to always be calculated for our program. However whilst this calculation is time intensive we in fact would only need to calculate it once for a given NT and save that data to a file.

Thus our Energy Gap program would merely open this data file, read the  $\Delta_{BCS}(T)$  and use this in Equation 2.22 to provide a starting energy gap for our calculation retaining the same processing time as previously. Thus the *s*-wave BCS energy gap was calculated with this self-consistent program for several likely values of NT and stored in separate data files to be called depending on which value of NT is requested in the Energy Gap program. The Deviation program was run using this now accurate BCS energy gap and the deviations for various  $\alpha$ -values are shown in Figure 3.10. The deviations produced from a single iteration now accurately exhibit the expected theoretical behaviour and resemble those calculated by Padamsee as well.

Thus we have produced a series of programs which can accurately calculate the

temperature dependence of the energy gap,  $\Delta(T)$ , for *s*-wave superconductors of various coupling strengths, as represented by  $\alpha$ , utilising our iterative thermodynamic theory.



Figure 3.10 Calculated s-wave Deviation Function, D(t), versus  $t^2$  with accurate starting  $\Delta_{BCS}(T)$  for the BCS case as well as a range of  $\alpha$ -values (displayed above each curve).

### **3.2 Programs for** *d***-wave Symmetry**

We of course would now like to generalise our calculations to apply to *d*-wave superconductors as well. It is relatively easy to do this as we merely need to include the angular dependence associated with *d*-wave superconductors into several of the previous programs calculations.

### 3.2.1 BCS Energy gap

The BCS energy gap for *d*-wave simulations could have been approximated using our fit in Equation 2.17 with the *d*-wave  $\alpha_{BCS}$  of 2.14 from Equation 2.3, except that we

have discovered this is not sufficiently accurate. Thus we instead calculate this directly using the self-consistent BCS gap equation for *d*-wave symmetry in a similar fashion to that used in Subsection 3.1.7. As has been discussed in Chapter 2 the energy gap for *d*wave superconductors is not constant in *k*-space but varies with angle  $\theta$ . Yet each single  $\theta$  value yields a different *s*-wave gap and thus under numerical integration, where we sum over  $\theta$ , this series of *s*-wave gaps gives us our *d*-wave gap. Such a treatment allows the calculation of the BCS gap Equation 2.18 which integrates over both  $\theta$  and energy to determine  $\Delta_{BCS}(T)$  via self-consistent iterations in our program. This program is run for several likely values of *NT* and the temperature dependence of the energy gap calculated is stored in several data files. Our Energy Gap program will open one of these depending on the *NT* requested and input that particular  $\Delta_{BCS}(T)$  in Equation 2.22, where  $\alpha_{BCS} = 2.14$  for *d*-wave, to use as the starting energy gap for any particular  $\alpha$  in our program.

#### **3.2.2 Density of States**

We return to calculation of the DOS for the first stage of the program as the form of this differs from the *s*-wave calculations above and may require us to perform different transformations of certain equations. Beginning with the DOS will also provide us with a useful indication of what to expect from our later simulated results. As has been mentioned previously, for a *d*-wave superconductor the energy gap has an angular component. Subsection 2.2.2 shows how we can deduce Equation 2.15 for the *d*-wave DOS in terms of an integral over the full range of  $\theta$ . The integral is performed numerically by utilising the trapezium rule which provides sufficient accuracy at this level of the calculation. Our program cycles through  $N\theta$  values from 0 to  $\pi/4$  performing this numerical integration to calculate the *d*-wave DOS which can be seen in Figure 3.11 and matches the expected behaviour we predicted in Figure 2.4.

The noise in our calculated DOS is due to the singularity issue. For an s-wave superconductor this singularity occurs in the DOS at  $E = \Delta$  which we can also see for the d-wave case as the most prominent spike. However due to our method of treating the



Figure 3.11 Calculated Density of States versus energy of a *d*-wave superconductor for  $N\theta = 200$  and  $\Delta = 0.004$  eV.

*d*-wave DOS as a sum of many *s*-wave DOS functions we have numerous singularities at different points as determined by the particular  $\theta$  used. We can reduce this noise by increasing our  $N\theta$ 's to a sufficiently large value, yet this will become computationally inefficient at some point. A solution to this issue is discussed in the next section.

#### 3.2.3 Entropy

The electronic entropy can be calculated using the DOS at each temperature with Equation 2.31 allowing us to determine  $S_S(T)$ ,  $S_N(T)$  and  $\Delta S(T)$  for our *d*-wave superconductor. However we once again encounter the issue of noise in  $S_S$  which only reduces for very large values of NE and is due to the presence of the primary singularity at  $E = \Delta$ . It however is still possible to remove this singularity from our calculations by a change of variables as we did for the *s*-wave case in Subsection 3.1.3. Such a procedure removes the DOS from the calculation and therefore the noise. The change of variables for the *d*-wave case leads to Equation 3.8 for the electronic entropy.

$$S = \frac{-4k_B(1+\lambda)}{\pi/4} \int_0^{E'} \int_0^{\pi/4} f_w(\sqrt{E^2 + (\Delta \cos 2\theta)^2}, T) d\theta dE$$
(3.8)

We now have a double integration over  $\theta$  and energy in our entropy calculation for which use of the trapezium rule provides sufficient accuracy. It was found that values of NE =1000 and  $N\theta = 200$  produce good results of our entropy calculation with no noise.

#### **3.2.4 Energy Gap & Deviations**

Now that the  $\theta$  dependence has been fully incorporated within the Entropy function the rest of the program is relatively simple and very similar to the *s*-wave case. The Entropy program calculates  $\Delta S(T)$  which is then numerically integrated via Simpson's rule, as previously, in order to determine an accurate  $\Delta F(T)$ . These two are combined in our thermodynamic theory by Equation 2.27 to produce a new  $\Delta'(T)$  which is fed back into the calculation as the new starting temperature-dependent energy gap. Multiple iterations should yield a stable  $\Delta'(T)$  which does not deviate from the starting  $\Delta(T)$  it was calculated from within some low tolerance (generally 0.01% is sufficiently stringent).



Figure 3.12 Calculated *d*-wave Deviation Function, D(t), versus  $t^2$  using a precise starting  $\Delta_{BCS}(T)$  for the BCS case as well as a range of  $\alpha$ -values (displayed above curves).

We can also produce a series of deviation curves for the *d*-wave case. We merely employ Equation 3.7 which utilises the free energy calculated by our program. The free energy values from the zeroth iteration of our *d*-wave program are utilised to produce an equivalent plot for the deviations as carried out by Padamsee and our *s*-wave calculation. Figure 3.12 illustrates the deviation functions as calculated for the BCS case and several other  $\alpha$ -values to display the effect of increasing coupling strength.

Thus we have now created a set of programs which can be used to calculate the temperature-dependent electronic entropy, free energy, energy gap and deviation functions for either s- or d-wave superconductors regardless of their coupling strength. These programs will also be used to test the validity of our thermodynamic theory through a series of iterative calculations to produce stable solutions which we will compare with experimental results for a range of superconductors.

# Chapter 4

### **Experimental Techniques**

Pb-Bi eutectic alloys have been studied in great detail in the past as they exhibit superconductivity in a range of phases.<sup>24</sup> The  $Pb_{0.7}Bi_{0.3}$  alloy in particular, which is  $\varepsilon$ -phase where the atoms form a hexagonal-close-packed structure, has been identified as an extremely strong-coupling superconductor.<sup>25</sup> In order to provide a rigorous test of our thermodynamic theory it is good to compare it with experimental data from weak- to extra-strong-coupling superconductors. Experimental data for weak- to strong-coupling superconductors. Experimental data for weak- to strong-coupling superconductor, we carried out critical-field measurements with  $Pb_{0.7}Bi_{0.3}$ . This chapter covers the experimental techniques in the synthesis, characterisation and critical-field measurements at high-pressure for our  $Pb_{0.7}Bi_{0.3}$  sample.

### 4.1 Synthesis of Pb<sub>0.7</sub>Bi<sub>0.3</sub>

In order to synthesise a crystalline sample of  $Pb_{0.7}Bi_{0.3}$  it is necessary to ensure that the correct  $\varepsilon$ -phase is achieved by consulting its phase diagram shown in Figure 4.1.<sup>3</sup> The  $\varepsilon$ -phase occurs in a narrow segment of the phase diagram and as such one has to ensure the sintering process allows the formation of the alloy within this zone. Pb and Bi powders are prone to oxidation which prevents the formation of this  $\varepsilon$ -phase. Instead we obtained Pb and Bi metal shot which are likely to have only minor oxidation on their surfaces and so will not impede the alloying process as greatly. Synthesis of this alloy was carried out under the following procedure

1. The required stoichiometric quantities of Pb and Bi shot to achieve the desired alloy were weighed out. The Pb shot was flattened using a mortar and pestle and laid along the base of an alumina crucible. Bi shot was similarly treated and placed on top of the Pb layer. Bi, which has the lower melting point of 270°C, melts first



**Figure 4.1** Phase diagram for the Pb-Bi alloy system.<sup>3</sup> Red dashed line indicates the required  $Pb_{0.7}Bi_{0.3}$  alloy from our synthesis process.

thus assisting the melting of the Pb (melting point 328°C) beneath it and allowing them to mix.

- 2. The alumina crucible was placed within a furnace at 350°C in an argon atmosphere flowing at approximately 70 mL/minute. This temperature is high enough to ensure melting of both Pb and Bi metals and the argon atmosphere helps to prevent oxidation. The mixture was sintered at 350°C for approximately 30 minutes, then cooled to 225°C in 20°C steps every 20 minutes. The alumina crucible was physically agitated approximately every 15 minutes throughout this process to promote the mixing of the molten metals.
- 3. To help formation of the  $Pb_{0.7}Bi_{0.3}$  alloy the molten mixture was further sintered at 225°C for 60 minutes, which is just above the melting point of this alloy composition.
- 4. In order to ensure formation of the  $\varepsilon$ -phase, the sample must be cooled rapidly to prevent other phases forming first. Thus the crucible was quenched in air to expose the sample to the range of conditions that border the  $\varepsilon$  segment of the phase diagram.

- 5. At this point however, it was found that partial melting has occurred with the shot pieces still remaining largely disparate and unmixed. This partial melt of metal shot was ground in a mortar and pestle for approximately 30 minutes to ensure a high degree of granular mixing. It was then pressed into a pellet using a 12 mm die at 9000 psi.
- 6. This metal pellet was sintered at 350°C for 3 hours in an argon atmosphere flowing at approximately 70 mL/minute, cooled to 225°C over 3 hours and quenched in air. Sintering times were increased from the previous sinter to help ensure adequate mixing of the molten metals.
- 7. The pellet emerged melted, particularly so at its base. The surface had dulled to a grey colour from its original metallic shine, likely due to formation of a thin oxide layer on the surface. The sample was stored under an argon atmosphere in a desiccator to avoid any further oxidation.

### 4.2 Characterisation

To ensure that our sample pellet was indeed the correct alloy and phase, the following characterisation measurements were carried out.

#### 4.2.1 SEM

In a scanning electron microscope (SEM) a material can be imaged and characterised by scanning a high energy electron beam over them. This allows the imaging of, and partially into, a sample surface on the nanometre scale as well as determination of its elemental composition through the detected signals from secondary electrons, back-scattered electrons and x-rays. Secondary electron images provide information about sample topography, whereas back-scattered electron images provide a means of atomic contrast. A sample's elemental composition can be determined using Energy Dispersive x-ray Spectroscopy (EDS) as every element has a unique atomic structure - as such they produce characteristic x-rays. These characteristic x-rays are produced as an incident electron beam can displace an inner-shell electron, creating a vacancy in a low-energy electron band. To fill this vacancy a high-energy band electron drops into this state. During this decay process a characteristic x-ray is produced, which has an energy equivalent to the difference in atomic energy levels. In this way we can distinguish different elements by their unique x-ray spectrum.



**Figure 4.2** SEM image of the melted underside of our sample illustrating that nearly the entire surface is covered by microstructure features. Inset: 100x magnification for clearer identification of both dendritic and globular-like crystal growth.

For the synthesised sample we concentrated on the melted base as this was the most likely region for alloy formation. SEM images, see Figure 4.2, revealed a dendritic and globular-like microstructure on the sample base. Energy Dispersive x-ray Spectroscopy (EDS) was also used to determine whether this microstructure was the Pb<sub>0.7</sub>Bi<sub>0.3</sub> alloy we are interested in. We acquired EDS spectra along the sample base at several different points. Due to the heavy M-line peak overlap, the L-lines of Pb and Bi were used to characterise the spectra. Using standardless quantitative analysis the Pb:Bi ratio was determined to be roughly 2:1, indicating our desired alloy has likely formed. EDS spectra also indicated

a minimal oxygen presence and thus a low concentration of oxides. Pb and Bi EDS mapping allows us to select a particular peak and scan a segment of our sample for all occurrences of that emission - producing an elemental distribution map. The base of our sample was mapped for both Pb and Bi L-line peaks and these have been overlaid in Figure 4.3 indicating that our sample is indeed a homogeneous mix of both elements.



**Figure 4.3** An EDS map at 25x magnification of the Pb (blue) and Bi (red) L-line emissions. This indicates that there is a consistent homogeneous mix of the two elements across the base of our sample, with possibly more Pb as expected for our targeted ratio.

#### 4.2.2 XRD

X-Ray Diffraction (XRD) provides a more precise means of determining the structural phase of a material. X-rays incident on a sample are scattered by its atomic structure producing a measurable diffraction pattern. This diffraction pattern is characteristic of a particular compound and is often used to identify materials by matching them against reference patterns from extensive databases. An XRD scan was run on the base surface of the sample and the diffraction pattern can be seen in Figure 4.4 (a). The diffraction spectrum indicates that the precise alloy phase of Pb<sub>0.7</sub>Bi<sub>0.3</sub> is indeed the predominant compound in our sample. It also indicates that there are trace amounts of Pb and Bi based oxides, which was expected due to the grey discolouration of the surface after the sintering



**Figure 4.4** X-ray diffraction patterns for our sample on (a) its exterior showing clear presence of  $Pb_{0.7}Bi_{0.3}$  phase (red reference pattern) but with some additional peaks indicating Pb & Bi based oxides and (b) its interior indicating no oxide phases and only the  $Pb_{0.7}Bi_{0.3}$  phase with some preferential alignment.

process. However this is believed to be merely surface oxidation and thus we removed a thin slice from the base of our sample with a scalpel revealing the shiny, metallic interior. An XRD of this interior surface revealed only the presence of the  $Pb_{0.7}Bi_{0.3}$  phase and no oxides as we hypothesised, as shown in Figure 4.4 (b). Only some of the  $Pb_{0.7}Bi_{0.3}$  reference pattern peaks are visible in this diffraction pattern, yet this is likely due to the preferential growth of the crystal along certain axis which will cause us to only be able to observe certain diffraction peaks. From the diffraction pattern we determined the unit cell parameters a = b = 0.35058 nm, c = 0.57959 nm and the ratio c/a = 1.653, which are typical of the hexagonal-close-packed structure for the  $\varepsilon$ -phase and match previously measured ratios closely.<sup>26</sup>

Further EDS measurements on this interior slice confirmed that there were no oxides and only Pb and Bi in the appropriate ratios for our alloy.

## 4.3 High-pressure Critical Field Measurements

#### 4.3.1 High Pressure Cell

It is useful to perform critical-field measurements for our sample at a range of different pressures in order to investigate the pressure-dependent superconductivity of  $Pb_{0.7}Bi_{0.3}$  whilst also testing our theory. As such we utilised a standard clamp cell made of a non-magnetic beryllium-copper alloy (BeCu).<sup>27</sup> The high tensile strength and very low magnetic background make this ideal for such sensitive high-pressure critical-field measurements. The cell has been designed with an 8.8 mm outer diameter such that it is capable of fitting within the sample bore of a Quantum Design SQUID Magnetic Property Measurement System (MPMS). The pistons within the pressure cell were made out of tungsten-carbide (WC) and the maximum pressure which can be attained by this cell is 1.2 GPa. A 2.65 mm diameter x 8 mm long teflon capsule is used as a sample holder. Figure 4.5 displays a photo of this pressure cell and its components in detail. Flourinert 77 & 70 in a ratio 1:1 were used as a pressure transmitting medium to ensure hydrostatic pressure within the sample capsule. A rectangular block (approximately 4 mm x 1 mm

x 1 mm) was cut from the interior of our sample where there is no oxidation and the phase of our material has been confirmed by XRD and EDS. A small piece of 99.9% pure tin was also cut to provide a means of determining the precise pressure that we applied to the sample within the pressure cell. The pressure dependence of the superconducting transition temperature for tin has been well documented and thus measurement of this concurrently with our sample allows determination of the pressure from Equation 4.1.<sup>28</sup>

$$P(H) = \frac{T_c(0) - T_c(H)}{0.4823}$$
(4.1)

where P is the pressure in GPa and H is the magnetic field.



**Figure 4.5** The clamp pressure cell divided into its individual components (left) and in its loaded state attached to a teflon holder (right).

The  $Pb_{0.7}Bi_{0.3}$  sample along with the piece of tin were placed into the fluid filled teflon capsule which was then sealed. The capsule was lowered into the pressure cell to sit atop the lower piston and two copper rings, each at the top and bottom of the capsule, were also placed within the cell to provide a good seal under pressure. The copper rings deform around the ends of the teflon capsule when pressure is initially applied thereby sealing it and preventing the fluid medium from leaking out. In this way they also help to ensure that pressure is evenly distributed across the capsule preventing it from cracking. An upper piston is placed on top of the teflon capsule and the upper locking nut is lightly screwed into the pressure cell; it is important not to tighten this as we do not wish to prematurely apply pressure.

Pressure to the sample is applied using a 10 tonne laboratory hydraulic press. A WC push rod is used to apply load to the top piston through a hole in the upper locking nut. The load applied is increased by the press and thus so too is the pressure exerted on the sample. After reaching the desired load, the locking nut is tightened and the pressure cell is removed from the press, after releasing the load.

#### 4.3.2 Critical Field Measurements

When a normal superconductor is subjected to fields greater than the critical-field,  $H_c$ , its superconductivity is destroyed.  $H_c$  is often used to refer to the maximum criticalfield value which occurs at T = 0 K yet this falls as the temperature is increased up to the critical temperature,  $T_c$ , at ambient pressure. The critical-field measured with increasing temperature up to the zero field  $T_c$  traces a curve which marks the first-order phase boundary between the normal- and superconducting-states as shown in Figure 4.6. The critical-field is generally considered to have a roughly parabolic dependence on temperature<sup>13</sup>, yet as we have discussed in Section 2.5 many superconductors differ



Figure 4.6 Critical-field at various temperatures marking the boundary between the superconducting- and normal-states.

from this ideal case and hence the deviation function is used to distinguish them. Criticalfield values can be determined through the measurement of the temperature-dependent magnetic moment of the sample. When a material transitions into the superconductingstate it expels all applied magnetic fields (as long as these are less than the criticalfield) and becomes diamagnetic in what is known as the Meissner effect.<sup>16</sup> Thus we can determine the transition temperature,  $T_c$ , at any particular applied magnetic field by measuring the magnetic moment and observing the point where diamagnetism sets in. The most common method for determining  $T_c$  in this way is to draw a tangent at the steepest slope of the curve and extrapolate this back to the temperature axis where its intercept is taken to be  $T_c$ . Applied magnetic fields force the superconducting-state to be established at lower temperatures, thus we observe the transition temperature decreasing with increasing field as shown in Figure 4.7. The measured  $T_c$  at a given field thus allows us to map out the boundary line between the superconducting- and normal-states as we saw in Figure 4.6. Our sample's magnetic moment was measured in a Quantum Design



Figure 4.7 Illustration of susceptibility versus temperature curves for a superconductor at various applied magnetic fields (the arrow indicates shift in curves as field increased). The red dashed line illustrates determination of  $T_c$  by extrapolation of curves steepest gradient.

MPMS. To further confirm the alloy composition was in the correct  $\varepsilon$ -phase, the transition temperature  $T_c$  for the sample was measured in a standard straw holder at various fields. The measured zero field  $T_c = 8.43$  K is fairly close to the known  $T_c$  from available data.<sup>12</sup> Based on the measured  $T_c$ , in conjunction with XRD and SEM results, another piece of the sample interior was loaded in the pressure-cell and the  $T_c$  was measured from ambient to 1.2 GPa pressures with fields from 0 - 2 T and temperatures from 2 - 10 K.

# Chapter 5

### **Analysis of Weak-Strong Coupling Superconductors**

In order to rigorously test our thermodynamic theory we must compare its predictions with actual measurements of the temperature-dependent superconducting energy gap for a range of weak- to extra-strong-coupling superconductors. In this work the extra-strong-coupling superconductor Pb<sub>0.7</sub>Bi<sub>0.3</sub> has been synthesised and the critical-field measured as a function of temperature and pressure as discussed in Chapter 4. Comparisons for this extra-strong coupler will be made in Chapter 6. In the present chapter we analyse critical-field data from literature for a weak coupler Al<sup>9</sup>, intermediate couplers Sn & In<sup>10</sup> and a strong coupler Pb<sup>11</sup>. Utilising this data we make comparisons of our theory's calculated energy gap with tunnelling data from literature for Al<sup>4,5</sup>, Sn<sup>4,6,7</sup>, In<sup>6</sup> and Pb<sup>8</sup> as well as the results produced from computational calculations.

### **5.1 Calculation of** $\Delta$

Critical-field data can be utilised in order to calculate the reduced temperature dependence of the superconducting energy gap,  $\Delta(t)$ , with our thermodynamic theory. However, our theory requires use of thermodynamic quantities which can only be deduced from critical-field data by differentiation with respect to temperature. In order to perform this adequately we need a smooth function of temperature for the critical-field and so fit a Taylor power series to data for Al<sup>9</sup>, Sn, In<sup>10</sup> and Pb<sup>11</sup>. The Taylor power series expansion needs to be thermodynamically consistent and as such both the first- and thirdorder terms must be zero. If the first-order term is non-zero this yields a non-zero entropy at T = 0, and likewise a non-zero third-order term would result in a negative specific-heat coefficient,  $\gamma$ . Both of these results are unphysical and so our expansion must account for this. The Taylor expansion is truncated after the fourth-order term as this is sufficient; extension to the sixth-order showed negligible improvement in fits. In ensuring that the boundary conditions for a critical-field function are maintained, the coefficients in our Taylor expansion are deduced to be dependent upon each other yielding the general form shown in Equation 5.1.<sup>27</sup>

$$H_c(t) = H_{c0}[1 - \beta t^2 - (1 - \beta)t^4]$$
(5.1)

Which ensures that  $H_c(t) \to 0$  as  $t \to 1$  and  $H_c(t) \to H_{c0}$  as  $t \to 0$ . Here  $t = T/T_c$  and  $H_{c0}$  is the zero-temperature critical-field.

In order to determine the appropriate Taylor fit in a robust way it is most convenient to plot data as  $H_c(t)/(1 - t^2)$  versus  $t^2$ . This should vary as  $(1 + (1 - \beta)t^2)$  and allows straightforward deduction of both  $H_{c0}$  and  $\beta$ . It should be noted however that for temperatures close to  $T_c$  the denominator  $(1 - t^2)$  approaches zero and so uncertainties are magnified in this region. Thus it is sometimes necessary to exclude data points close to  $T_c$ in order to produce an accurate quadratic fit. For the sake of simplicity these plots have not been included due to the number of materials and data sets analysed. Once values have been determined for Equation 5.1 we are able to calculate a smooth function for  $\Delta F(t)$  from Equation 2.23. Differentiation of this with respect to T produces a function for  $\Delta S(t)$ . These thermodynamic functions are necessary in order for us to determine  $\Delta(t)$  with our theory as expressed by Equation 2.27. However, we also need to calculate an appropriate N(0) for each superconductor in question and so we deduce these based on the relation to the normal-state electronic specific-heat coefficient,  $\gamma_n$ .<sup>2</sup>

$$N(0) = \frac{3}{2} \frac{\gamma_n}{\pi^2 k_B^2 V_m}$$
(5.2)

Where  $V_m$  is the molar volume. Utilising published values for Al<sup>29</sup>, Sn, In<sup>10</sup> and Pb<sup>30</sup> we are thus able to calculate N(0) for each. We are now able to determine  $\Delta(t)$  with Equation 2.27 and compare this with measured tunnelling data of the energy gap for Al<sup>4,5</sup>, Sn<sup>4,6,7</sup>, In<sup>6</sup> and Pb<sup>8</sup>, which are shown in Figure 5.1.

As can be seen in Figure 5.1 the  $\Delta(t)$  calculated with our thermodynamic theory using the Taylor fit to critical-field data does reflect the general temperature dependence exhibited by tunnelling data for most of our superconductors. The available tunnelling data for the weak-coupler Al spans quite a range of values since its energy gap, and even  $T_c$ , are



**Figure 5.1** Comparison of the superconducting gap of Al<sup>4,5</sup>, Sn<sup>4,6,7</sup>, In<sup>6</sup> & Pb<sup>8</sup> from tunnelling with  $\Delta(t)$  from Equation 2.27 using  $\Delta F \& \Delta S$  deduced from critical-field data (black line). A better match is obtained by re-scaling the curve to the zero-temperature tunnelling gap (red line). The blue dashed line shows  $\Delta(t)$  from Equation 2.27 with  $\Delta F \& \Delta S$  calculated from our program assuming a rescaled BCS gap.

	$\Delta(0)$ (meV)	
	Thermodynamic Theory	Tunnelling Measurements
Al	0.178	$0.186 \pm 0.027$
Sn	0.579	$0.595\pm0.018$
In	0.545	$0.560\pm0.010$
Pb	1.213	$1.393\pm0.020$

**Table 5.1** Comparison of  $\Delta(0)$  calculated from thermodynamic theory with tunnelling measurement estimates from literature for Al<sup>4,5</sup>, Sn<sup>4,6,7</sup>, In<sup>6</sup> and Pb<sup>8</sup>.

dependent on the thickness of layers in tunnelling junctions.<sup>4</sup> Yet our calculated  $\Delta(t)$  falls within this spread of the measured gap size for Al as well as matching fairly closely to similar data for the intermediate couplers Sn and In. However, it appears that our calculation is underestimating the  $\Delta(t)$  for much of the temperature range when compared with tunnelling data. The underestimation is most evident for the strong-coupler Pb where our fit matches well near  $T_c$  but diverges from the data at lower temperatures quite markedly. The underestimation can be seen in Table 5.1 which compares the  $\Delta(0)$  from our calculation against estimations from literature based on tunnelling data. Only Al and Sn match within experimental error whereas the stronger couplers In and Pb do not. However, the absolute magnitude of our calculated  $\Delta(t)$  depends almost entirely on the values of  $\gamma_n$  from literature that we utilise to calculate N(0), some of which have errors that range as high as 5%.<sup>30</sup> Even a small amount of error in these could markedly affect the calculated values of  $\Delta(0)$  and propagate this error across the entire temperature range.

Thus in order to test if our calculation is predicting an accurate temperature dependence in absence of any potential errors in  $\Delta(0)$  we scale it by the estimated value from tunnelling measurements shown in Table 5.1. The adjusted fits are shown by the red line in Figure 5.1. The temperature dependence of our adjusted calculated  $\Delta(t)$  does appear to match the available tunnelling data quite well for Al, Sn and fairly closely for In. The adjusted  $\Delta(t)$ for Pb however, whilst greater in magnitude, does not match the temperature dependence very well at all. It appears to only match to tunnelling measurements right near  $T_c$  and for low temperatures but overestimates quite clearly over much of the intermediate range. Pb is the strongest coupler of these superconductors which is possibly why it diverges more markedly than the others. Our thermodynamic theory may not be suitable for representation of stronger coupling superconductors yet comparisons to similar strength couplers would be necessary in order to test this. Our analysis of the nominally extrastrong-coupling Pb<sub>0.7</sub>Bi<sub>0.3</sub> superconductor in Chapter 6 should provide an adequate test of the validity of the theory in the strong-coupling regime.

Comparisons with computational calculations, which utilise the iterative process to determine a stable solution for  $\Delta(t)$ , should provide a further test and will be discussed in the following sections.

# 5.2 Deviation Function

As we have discussed previously in Section 2.5 comparisons of  $H_c$  data from various superconductors are generally represented through the deviation function, Equation 2.24, which illustrates their divergence from a perfect parabolic temperature dependence. The deviation function is sensitive to the minute differences in  $H_c$  data between superconductors and its form illustrates the strength of their coupling. Thus we shall employ the deviation function to represent the relative strengths of the superconductors and compare this with computational predictions.

Chapter 3 discusses the computational program we have constructed to calculate the thermodynamic parameters  $\Delta S(t)$  and  $\Delta F(t)$  as well as  $\Delta(t)$  using our thermodynamic theory for *s*-wave superconductors. The program utilises an iterative process with our theory in order to produce a self-consistent solution for  $\Delta(t)$  yet in the first instance we shall consider results calculated from the zeroth iteration. The deviation function can be determined from the initially calculated  $\Delta F(t)$  with Equation 3.7 for a range of coupling strengths,  $\alpha$ , in a similar manner to that carried out by Padamsee.<sup>2</sup> These calculated deviations were matched against the deviation plots of critical-field data for our range of superconductors and the best fits chosen as shown in Figure 5.2. The  $\alpha$ -values of these best fits thus correspond to the coupling strength of each particular superconductor. As can be seen these fits do represent the general behaviour for each particular superconductor yet are not perfect matches. There are discrepancies in the



**Figure 5.2** Deviation function calculated from critical-field data using Equation 2.24 for Al<sup>9</sup>, Sn, In<sup>10</sup> and Pb<sup>11</sup>. Computationally calculated deviation function with best fit to data overlaid.

predicted value in certain temperature regimes yet they provide the best overall fit of all the calculated deviations. The  $\alpha$ -value for a superconductor can also be deduced from it's  $\Delta(0)$  and  $T_c$  via Equation 2.19 and thus we can determine this from the tunnelling data for each superconductor. Comparisons of  $\alpha$  from these fits by our program and those determined from tunnelling measurements are shown in Table 5.2. There is good agreement between these for Al, Sn and In but our program overestimates  $\alpha$  for Pb in the strong-coupling regime. However, what must be taken into account is that on the zeroth

	lpha	
	Computational Fit	Calculated from Tunnelling
Al	1.764	$1.61\pm0.23$
Sn	1.87	$1.81\pm0.05$
In	1.93	$1.93\pm0.03$
Pb	2.43	$2.24\pm0.04$

**Table 5.2** Comparison of  $\alpha$ 's from best computational deviation fit with those calculated from Equation 2.19 using tunnelling measurement estimates of  $\Delta(0)$  from literature for Al<sup>4,5</sup>, Sn<sup>4,6,7</sup>, In<sup>6</sup> and Pb<sup>8</sup>.

iteration our program has utilised a model BCS  $\Delta(t)$  scaled by a particular  $\alpha$ -value. As such it may not accurately reflect all the aspects of the increased coupling strength hence why we proposed our approach of recalculating  $\Delta(t)$  by successive approximations through multiple iterations. It is our hope that such a self-consistent process may produce better fits for the calculated deviation function to data as well as similar  $\alpha$ -values to those observed experimentally. Padamsee's approach of using a scaled model BCS  $\Delta(t)$ , whilst indicative, does prove to exhibit discrepancies in the strong-coupling regime in relation to actual measurements and as such is inadequate. Padamsee has shown that altering their original model to include a temperature dependence for  $\gamma$ , rather than assuming a constant value, provides improved fits and more realistic  $\alpha$ -values.<sup>2</sup> Potentially a similar alteration could also improve our programs calculated results.

## **5.3** Computational Calculation of $\Delta$

In the first instance we shall use the  $\alpha$ -values corresponding to our best fits to each superconductor for the zeroth iteration. Following Padamsee we assume a gap rescaled by these  $\alpha$ -values with Equation 2.22 from which we calculate  $\Delta S$  and  $\Delta F$ . Utilising Equation 2.27 we are thus able to deduce the first new  $\Delta(t)$ . These can be seen in the previous Figure 5.1. As with the computed deviation function we see discrepancies between  $\Delta(t)$  and experimental data. Potentially the calculated  $\Delta(t)$  for Al provides a good fit in terms of temperature dependence yet this is to be expected of a weak coupler as the starting BCS  $\Delta(t)$  already provided an adequate fit. The  $\Delta(t)$ 's for the other superconductors on the other hand exhibit systematic deviations from this initial temperature dependence. The computational results for Sn and In overestimate the values for much of the range but potentially are displaying an adequate scaled temperature dependence. However the computational  $\Delta(t)$  for Pb appears to have an erroneous temperature dependence in comparison to tunnelling measurements. Yet as we have outlined previously an iterative process utilising our thermodynamic theory should hopefully provide more accurate self-consistent  $\Delta(t)$  solutions for a range of coupling strengths.

Multiple iterations for our program, as discussed in Subsection 3.1.5, require the inclusion of the electron-phonon enhancement parameter,  $\lambda$ , which accounts for the effect of stronger coupling on the entropy. If we did not include  $\lambda$  then our iterative process would cause our calculated  $\Delta(t)$  to settle back to the unscaled BCS  $\Delta(t)$  case. Each  $\lambda$  corresponds to a particular  $\alpha$  which is calculated from the stable  $\Delta(0)$  value that arises from multiple iterations with Equation 2.19. Approximately 40 iterations produced stable self-consistent  $\Delta(t)$  values for a range of  $\alpha$ -values. Thus the multiple iteration program was run utilising our thermodynamic theory for a range of  $\alpha$ -values to provide self-consistent solutions for  $\Delta(t)$ .



Figure 5.3  $\Delta(t)$  calculated computationally over 40 iterations utilising our thermodynamic theory with  $\alpha = 1.93$  corresponding to In (red line). Starting BCS  $\Delta(t)$  scaled by  $\alpha$  shown for comparison (blue dashed).

Figure 5.3 displays the starting scaled BCS  $\Delta(t)$  along with our multiple-iteration result for the  $\alpha$ -value corresponding to In chosen from deviation fits in Section 5.2. The temperature dependence has flattened out at low temperatures and migrated outwards in the intermediate regime in comparison with the BCS prediction. Our new  $\Delta(t)$  thus more accurately reflects the generally-observed dependence for a non-weak coupling superconductor, such as In, than the result of BCS theory. However the magnitude of  $\Delta(t)$  is larger than what is observed from tunnelling measurements of In superconductors. This is likely due to the fact we have chosen an  $\alpha$  based on a deviation fit from only the zeroth iteration rather than multiple iterations. Table 5.2 indicated these  $\alpha$ -values were, on average, often larger than those determined from experimental tunnelling measurements. Deviation fits from a multiple iteration result would thus likely provide a more accurate  $\alpha$ -value and predict an appropriate magnitude for  $\Delta(t)$ .

However, in the course of our computational calculations a curious artifact of the multiple iterations method arose as the coupling strength was increased. A multiple iteration result for a stronger coupling value of  $\alpha$  corresponding to Pb is shown in Figure 5.4. Whilst we are indeed settling on a stable  $\Delta(t)$  which does not deviate from the immediately previous calculated  $\Delta(t)$  it appears to cut off prematurely at the set value of  $T_c$ . This is an indication that the final iteration  $\Delta(t)$  has a higher  $T_c$  than is set by our program. Yet our computational calculation is designed to be universally applicable to all superconductors by using the reduced temperature, t.



Figure 5.4  $\Delta(t)$  calculated computationally over 40 iterations utilising our thermodynamic theory with  $\alpha = 2.43$  corresponding to Pb (red line). Starting BCS  $\Delta(t)$  scaled by  $\alpha$  shown for comparison (blue dashed).

It is necessary to examine the application of our thermodynamic theory within an iterative calculation to determine the origin of this cut off. The primary difference in

the iterative calculation is the inclusion of the electron-phonon enhancement parameter,  $\lambda$ .  $\lambda$  represents the effect of stronger coupling by enhancing the electronic specific-heat coefficient and hence the entropy as described by Equation 2.31. Essentially

$$\Delta S' = (1+\lambda)\Delta S \tag{5.3}$$

which carries through to the free energy via integration to give

$$\Delta F' = (1+\lambda)\Delta F \tag{5.4}$$

Combining these two enhanced thermodynamic parameters through our theory to determine the energy gap we see that

$$\Delta^2 \propto 2\Delta F' + T\Delta S' \tag{5.5}$$

$$\propto (1+\lambda)(2\Delta F + T\Delta S) \tag{5.6}$$

If we compare the result of Equation 5.6 to that of the BCS gap Equation 2.16 we find that

$$(1+\lambda)(2\Delta F + T\Delta S) \propto V \int_0^{\hbar\omega_c} \frac{\Delta}{\sqrt{E^2 - \Delta^2}} \tanh \frac{\sqrt{E^2 - \Delta^2}}{2k_B T} dE$$
 (5.7)

which tells us that our enhancement factor  $1+\lambda$  is essentially equivalent to V, the electronphonon interaction strength. But increasing  $\lambda$  to represent stronger coupling merely increases V and scales the BCS energy gap, effectively shifting the transition temperature higher. While our theory appears to be describing stronger coupling behaviour it is in fact just a scaled version of the weak-coupling BCS energy gap, that is being cut-off prematurely at our chosen  $T_c$ .

The essential problem is that our theory was derived from work by Ferrel where he deduced his relations from BCS theory, which is founded on the assumption of weak-coupling.<sup>15</sup> As such our theory is inevitably constrained by this and will always yield a weak-coupling result. In Figure 5.3 we did not see this similar cut off yet this is likely due to the fact that as it is for an intermediate-coupling strength the shift in  $T_c$  is not as strong. The cut-off is still there yet it is not as easily noticeable as for stronger coupling

cases. Our theory appeared to be promising for single iterations and with low strength coupling as it exhibited alterations to the temperature dependence of the gap which BCS theory did not; flattening for low temperatures and migration in the intermediate regime. However this is due to computationally calculated values of  $\Delta(t)$  converging on stable values more quickly at low temperatures than those which are closer to  $T_c$ , which in effect gave an impression of these improvements. It is now unnecessary to determine more appropriate  $\alpha$ -values from deviation fits calculated through multiple iterations as these will be invariably skewed and inaccurate due to the cut-off exhibited in our calculated values. All this points to the necessity of an energy-dependent coupling parameter,  $\lambda = \lambda(E)$ , which disallows simple scaling of the thermodynamic functions. Nonetheless, this work points to the universal flattening of  $\Delta(t)$  in the intermediate temperature range due to strong-coupling.

Under the scrutiny of multiple iterations, the proposed extension of our theory to strongcoupling has proven to be incapable of producing a self-consistent strong-coupling gap due to its origin from weak-coupling equations. Yet in similar fashion to the model of Padamsee our theory can potentially provide a good first-order approximation in the single iteration case, with some discrepancies, for superconductors of varying coupling strengths. These failings are minimal if the system is close to weak-coupling, as indeed is the case for the high-temperature *d*-wave superconductors, as we shall see in Chapter 7.

## Chapter 6

## **Experimental Analysis of Pb**<sub>0.7</sub>**Bi**<sub>0.3</sub>

In Chapter 5 we compared predictions of our theory, using critical-field data as well as calculated values, with the experimentally observed energy gap for a range of weak-to strong-coupling superconductors. In order to fully test the limits of our theory we synthesised an extra-strong-coupling  $Pb_{0.7}Bi_{0.3}$  alloy on which to perform pressure-and temperature-dependent critical-field measurements as described in Chapter 4. In the present chapter we shall analyse these critical-field measurements in the scope of our theory and make comparisons with tunnelling data from literature<sup>12</sup> as well as computational results.

## 6.1 Critical Field Measurements

#### 6.1.1 Ambient Pressure

Critical-field measurements were performed on a sample of our synthesised Pb<sub>0.7</sub>Bi<sub>0.3</sub> alloy mounted in a standard straw holder, and hence at atmospheric pressure, for a range of magnetic fields. The temperature-dependent magnetic susceptibility for these various applied fields is displayed in Figure 6.1. As expected, greater fields force the superconducting-state to be established at lower temperatures and so we see the superconducting transition temperature,  $T_c$ , falling as the applied field is increased. It is possible to deduce  $T_c$  at each field from such susceptibility curves as described in Subsection 4.3.2. The measured zero-field superconducting transition temperature  $T_c = 8.43$  K agrees fairly closely with previous values from literature<sup>12,25</sup> thus further confirming our sample is indeed the phase desired. The  $T_c$  at each particular field can be utilised to mark the first-order phase boundary between the superconductingand normal-states, essentially representing the temperature-dependent critical-field for ambient pressure. However, we can also note from Figure 6.1 that the magnitude of the


**Figure 6.1** Temperature-dependent magnetic susceptibility of a  $Pb_{0.7}Bi_{0.3}$  sample at atmospheric pressure for a range of fields. Arrow indicates increasing applied field strength from 0.2 - 1.5 T.

diamagnetic susceptibility is falling as the field is increased indicating that our sample is actually a type II superconductor rather than the simpler type I superconductors we have analysed in Chapter 5. Supporting evidence for the  $Pb_{0.7}Bi_{0.3}$  alloy exhibiting type II superconductivity can also be found in literature.<sup>31</sup>

Type II superconductors differ from type I in that they exhibit both lower and upper critical-field values,  $H_{c1} \& H_{c2}$ , as displayed in Figure 6.2. At fields below  $H_{c1}$  type II materials expel all magnetic flux in precisely the same manner as type I superconductors through the Meissner effect. However, above  $H_{c1}$  and below  $H_{c2}$  there exists a mixed state which exhibits properties of both the superconducting- and normal-states. In this mixed state magnetic flux penetrates the superconductor in quantised vortices inside which the material is in the normal-state and superconducting everywhere else. Fields greater than  $H_{c2}$  cause these vortices to overlap thus destroying the superconductivity entirely and forcing the material into the normal-state.<sup>16</sup>  $H_{c2}$  is generally much higher than  $H_{c1}$  in most type II superconductors. Thus type II superconductors are usually described in regards to their thermodynamic critical-field which is a geometric average of the lower

$$H_c \propto \sqrt{H_{c1}H_{c2}}$$

(6.1)

**Figure 6.2** Temperature dependent critical-fields for a type II superconductor. At fields below  $H_{c1}$  the material is superconducting (red shaded), between  $H_{c1}$  &  $H_{c2}$  a mixed state (blue shaded) and for fields greater than  $H_{c2}$  is in the normal-state.

It is this thermodynamic critical-field which we must utilise in our calculations in order to provide an accurate representation of the material. Unfortunately we only discovered the Pb<sub>0.7</sub>Bi<sub>0.3</sub> alloy was a type II superconductor after we had performed all of our measurements. As such we have only measured higher fields and hence only determined  $H_{c2}$  for various temperatures. Ordinarily we would also measure  $H_{c1}$  as well but due to time constraints and availability of equipment we are unable to perform these numerous additional measurements. However it is potentially possible to transform our  $H_{c2}$  measurements into corresponding thermodynamic critical-field values,  $H_c$ , through the use of the Ginzburg-Landau equation<sup>16</sup>

$$H_{c2} = \sqrt{2\kappa}H_c \tag{6.2}$$

where  $\kappa = \frac{\lambda}{\xi}$ , the ratio of the penetration depth,  $\lambda$ , to the coherence length,  $\xi$ , is the Ginzburg-Landau parameter which to a good approximation is taken to be temperature independent. Certainly in Ginzburg-Landau theory  $\kappa$  is temperature independent. The penetration depth is a measure of the distance a magnetic field penetrates the surface of a superconductor before being damped.<sup>16</sup>

Thus in order to transform our  $H_{c2}$  data we must determine an appropriate  $\kappa$  value for our superconducting Pb<sub>0.7</sub>Bi<sub>0.3</sub> alloy. We can calculate  $\kappa$  with Equation 6.2 by determining values for  $H_{c2}$  &  $H_c$  at a particular temperature. If  $\kappa$  is indeed relatively temperature-independent then determination of it will allow us to transform our  $H_{c2}$  data with ease. So we merely need to deduce  $\kappa$  for several temperatures to provide a test of this assumed temperature-independence.  $H_{c2}$  is relatively easy to determine yet to estimate the thermodynamic critical-field,  $H_c$ , we make use of the condensation energy relation.

$$U_0 = \frac{H_c^2}{2\mu_0}$$
(6.3)

The condensation energy at a particular temperature can be determined from the area under a field-dependent magnetisation curve. We are also able to easily determine the precise  $H_{c1}$  &  $H_{c2}$  based on such a measurement. Magnetisation measurements were carried out at 3 K and 5 K on our ambient pressure sample in the straw holder, one such curve is shown in Figure 6.3.



**Figure 6.3** Field-dependent magnetisation measurements at 5 K for our Pb<sub>0.7</sub>Bi<sub>0.3</sub> alloy at ambient pressure. Area under curve is equal to the condensation energy,  $U_0$  (grey shaded). Determination of  $H_{c1}$  &  $H_{c2}$  values for 5 K also shown.

The various critical-fields determined from such magnetisation measurements and  $\kappa$ 

	$H_c$	$H_{c1}$	$H_{c2}$	$\kappa$
3 K	0.1115	0.030	1.5886	10.075
5 K	0.0765	0.038	1.0919	10.093

**Table 6.1** Critical-field values (thermodynamic, lower and upper) in Tesla determined from field-dependent magnetisation measurements of ambient pressure  $Pb_{0.7}Bi_{0.3}$  sample at 3 K and 5 K.

calculated with Equation 6.2 for 3 K and 5 K are shown in Table 6.1.  $\kappa$  is practically unchanged for these two temperatures and agrees closely with the previously recorded value of 10 for the general PbBi alloy system.<sup>16</sup> Thus we appear to be justified in our assumption that  $\kappa$  is relatively temperature-independent. As such we may convert all of our measured  $H_{c2}$  values into thermodynamic critical-field values,  $H_c$ , using an average of these two  $\kappa$  values with Equation 6.2. Figure 6.4 thus shows  $H_c$  converted from measured temperature-dependent  $H_{c2}$  values for our Pb<sub>0.7</sub>Bi<sub>0.3</sub> sample at ambient pressure.



**Figure 6.4** Temperature-dependent thermodynamic critical-field,  $H_c(t)$ , determined from measurements of  $H_{c2}$  for a Pb<sub>0.7</sub>Bi<sub>0.3</sub> sample at ambient pressure (+) with Taylor fit (red line).

In order to utilise critical-field data to calculate the superconducting energy gap with our theory we require a smooth function of temperature to perform derivatives on. So once again we fit a Taylor power series expansion to the critical-field in the same manner as in Section 5.1. The Taylor fit, shown in Figure 6.4, accurately represents our data and exhibits the expected general curvature for  $H_c(t)$ . The predicted zero-temperature thermodynamic field  $H_c(0) = 0.323$  T is determined from the upper critical-field value of  $H_{c2}(0) = 1.886$  T. This value of  $H_{c2}(0)$  is approximately 50% larger than values reported in literature.<sup>31</sup> Yet there have been very few magnetic measurements on this particular phase and as such we need not be overly concerned by our larger predicted value for  $H_{c2}(0)$ . We shall utilise this smooth function in Section 6.3 in order to calculate the temperature-dependent energy gap,  $\Delta(t)$ , for our Pb<sub>0.7</sub>Bi<sub>0.3</sub> sample. We can also investigate the pressure-dependence of  $\Delta(t)$  by analysing critical-field data at a range of pressures as discussed in the following section.

#### 6.1.2 Pressure Dependent Measurements

Critical-field measurements were also performed on a separate sample of Pb<sub>0.7</sub>Bi<sub>0.3</sub> loaded into our standard clamp pressure cell. This cell allows us to apply a particular pressure hydrostatically to our sample and maintain this whilst we perform temperaturedependent measurements of its magnetic response. In this way we can use the susceptibility curves for various applied fields, similar to Figure 6.1, to determine the temperature-dependent critical-field of our sample at any given pressure. Increasing the pressure applied to our sample and repeating the measurements should also allow us to determine the pressure-dependence of the critical-field for Pb<sub>0.7</sub>Bi<sub>0.3</sub>. As has been discussed in the previous section we unfortunately only measured the upper criticalfield  $H_{c2}$  for our sample but are still capable of recovering the thermodynamic criticalfield,  $H_c$ , with  $\kappa$ . We shall assume that  $\kappa$  is also pressure-independent for now and so the value determined previously allows us to transform our  $H_{c2}$  measurements at each pressure. Figure 6.5 displays the thermodynamic critical-field determined from the  $H_{c2}$ measurements of our sample for a range of applied pressures as a function of absolute temperature T, along with the smooth Taylor fits made to each.

We can clearly see a shift of the critical-field curves indicating that as pressure is increased superconductivity in  $Pb_{0.7}Bi_{0.3}$  is pushed to lower temperatures. Our fits also indicate



**Figure 6.5** Temperature-dependent thermodynamic critical-field,  $H_c(t)$ , determined from measurements of  $H_{c2}$  at a range of pressures for a Pb<sub>0.7</sub>Bi<sub>0.3</sub> sample in our pressure cell. Taylor fits to each set of critical-field data overlaid (lines).

the zero-temperature critical-field falls with increasing pressure. Application of pressure generally stiffens the lattice of a superconductor and shifts phonon frequencies higher effectively reducing the electron-phonon coupling strength. Thus lower temperatures are required in order to establish a coherent superconducting state.<sup>32</sup> As the superconducting energy gap is directly related to  $T_c$  this falls with pressure too, along with  $\Delta F$ and ultimately the critical-field given Equation 2.23. Ideally more low temperature measurements would have been desirable in order to allow more precise fits in this temperature regime as well as better predictions for  $H_c(0)$ , but unfortunately we were limited by the available equipment. The Quantum Design SQUID MPMS utilised for magnetic measurements with our pressure cell experienced a number of maintenance issues preventing its use at temperatures below 3 K for the majority of our measurements.

The zero-field transition temperature at ambient pressure measured in the cell of  $T_c = 8.615$  K is curiously higher than that measured for our sample in the standard straw holder. Whilst the difference between these is small this value of  $T_c$  is in fact closer to the previously measured values from literature.<sup>12,25</sup> Furthermore, the  $T_c$  values for the

first several pressure steps still exceed the ambient pressure value determined from the straw holder. It is possible that as these are two separate samples cut from the same synthesised pellet they may have slight differences in composition which could cause these small differences in the measured  $T_c$  value. Of course they are still very similar in their observed superconducting properties. There is however one other consideration to be taken into account when analysing measurement results taken using our pressure cell; that of thermal lag. Our sample rests within the pressure clamp cell which itself is a large thermal mass within the sample chamber of the MPMS. As such, when the sample chamber stabilises at a particular temperature there will be a finite period of time before this propagates through the large thermal mass of the cell to the sample. In other words, there potentially could be a slight disparity between the measured temperature of the chamber and the true temperature experienced by the sample when we perform our measurement due to this thermal lag. Naturally, when performing measurements it would be best to allow a suitable period of time for our pressure cell to acclimatise fully to the stabilised temperature. Unfortunately this was unfeasible as the amount of data points required would cause our measurements to take an inordinately long time and restrict the range of data we were able to collect. It is possible that such a thermal lag also contributed to the differences observed in our  $T_c$  values between the straw and cell holders, although it should likely not impinge too significantly on the analysis and application of our theory.

#### 6.2 **Deviations**

In a similar fashion to that of Section 5.2 we can calculate the deviation function utilising the thermodynamic critical-field values for our  $Pb_{0.7}Bi_{0.3}$  sample. The deviation function is generally used as an indication of the coupling strength to allow comparisons between superconductors. Utilising the  $H_c(0)$  predictions from our Taylor fits we are thus able to compare and investigate the temperature-dependence of the calculated deviation functions at each pressure for our  $Pb_{0.7}Bi_{0.3}$  sample using Equation 2.24. Comparison of these deviations to those calculated by our program should also allow us to assign a particular  $\alpha$ -value to represent the coupling strength within our theory.



**Figure 6.6** Deviation function calculated from critical-field data using Equation 2.24 for  $Pb_{0.7}Bi_{0.3}$  at ambient pressure in straw holder (×) and under various applied pressures within cell. Computationally calculated deviation functions for *s*-wave BCS weak-coupling,  $\alpha = 1.764$  (red dashed), and strong-coupling,  $\alpha = 2.45$  (blue dashed), overlaid. The *d*-wave BCS weak-coupling deviation curve,  $\alpha = 2.14$ , calculated by our program also overlaid for comparison (black dashed).

The calculated deviation functions for each pressure along with those calculated by our program for several  $\alpha$ -values are shown in Figure 6.6. It is immediately obvious that our calculated deviations are atypical. Every single calculated deviation utilising our measured critical-field data falls well outside the usually observed range and implies that our sample is weaker than the predicted BCS weak-coupling result, both for either *s*- or *d*-wave cases. Even though Pb<sub>0.7</sub>Bi<sub>0.3</sub> is meant to be an extra-strong-coupling *s*-wave superconductor as determined by tunnelling measurements of its zero-temperature energy gap.<sup>12</sup> Utilising values from literature<sup>12,25</sup> of  $\Delta(0)$  and  $T_c$  we should expect a strong-coupling value of approximately  $\alpha = 2.45$ , yet our calculated deviation function implies that our sample is precisely the opposite of this and is below the weak-coupling result. Naturally this is a rather curious result, implying that perhaps something is amiss with our measurements. However, our sample has been confirmed by XRD and SEM as the precise  $\varepsilon$ -phase Pb<sub>0.7</sub>Bi<sub>0.3</sub> alloy we are interested in along with the measured  $T_c$  matching that listed in literature, indicating it is not contaminated.

Essentially the problem lies in our assumption of a temperature-independent  $\kappa$  that we used to transform our  $H_{c2}$  measurements into thermodynamic critical-field values  $H_c$  with Equation 6.2. Whilst we were able to transform the magnitude of our measurements with this assumption it did not alter their temperature-dependence which the deviation function illustrates. We can only determine that the complete mismatch of the deviations in Figure 6.6 with either *s*- or *d*-wave predictions and the expected strong-coupling nature is because  $\kappa$  is in fact temperature-dependent. In Ginzburg-Landau theory  $\kappa$  is strictly constant but the theory only applies close to  $T_c$  and we clearly see here the breakdown of this assumption. We stress again that the deviation function is very sensitive to such temperature-dependent anomalies. Thus  $H_c$  has a different temperature-dependence from our  $H_{c2}$  measurements which we can only determine if we have an accurate temperature-dependent  $\kappa$  from more measurements, or if we measure  $H_{c1}$  fully. Thus the deviation function is not suitable for the determination of an  $\alpha$ -value. Instead we shall use  $\alpha$  as deduced from tunnelling measurements in literature for the purposes of our theory.

Whilst the deviation is predicting a result contrary to our expectation we can still investigate the general pressure-dependence of critical-fields in this material. In Figure 6.6 it can be seen that most of the deviations calculated at different pressures trace out approximately the same curve indicating that they are fairly independent of pressure. Such a pressure-independence is in agreement with observations for the deviation function in other superconductors such as Al.<sup>29</sup> We have taken  $\kappa$  to be pressure-independent for our calculations yet in order to validate this fully additional measurements would need to be carried out. However, the deviations for the first several applied pressures do not agree with this approximate curve that many of the higher pressure measurements do. It is believed that this is due to two primary reasons. The first is that of thermal lag which we have mentioned previously. The critical-field measurements taken on our sample for the initial low pressures were at widely spaced temperatures and as such did not allow for much acclimatisation of the pressure cell's internal temperature. The later high-pressure measurements were taken at temperatures more closely spaced to one another thus allowing more time for the pressure cell to acclimatise. As such the lowpressure measurements likely have a greater error due to this thermal lag. This is further corroborated by the deviation calculated for our ambient pressure sample in the straw holder. It would have no thermal lag and its deviation falls precisely along the same general curve many of the high-pressure measurements follow. Following on from this, the second consideration takes into account the fewer field measurements taken for the low pressures. Taylor fits for these pressures with less data points are thus likely not as accurate as for the higher pressures for which more fields were measured. In fact the critical-field fit for the initial pressures predicts much higher values than those for the high-pressure curves as can be seen in Figure 6.5. Both of these considerations would contribute to errors in the calculated deviations for low-pressure measurements and explain their disagreement with the general curve followed by the high-pressure and ambient pressure straw holder measurements.

## 6.3 Calculation and Comparison of $\Delta$

We can still attempt to utilise the temperature-dependent fits to critical-field measurements to calculate  $\Delta(t)$  with our thermodynamic theory, in the same fashion as Section 5.1. Comparisons of its predictions as well as our computed calculations should help provide an indication of its validity in the strong coupling regime.

Again we must determine an appropriate N(0) for  $Pb_{0.7}Bi_{0.3}$  to use in Equation 2.27 in order to calculate  $\Delta(t)$ . To calculate N(0) from Equation 5.2 we require the normalstate electronic specific-heat coefficient,  $\gamma_n$ , which, for this precise alloy phase, there have been no measurements as far as we can determine. However,  $\gamma_n$  has been calculated for the general PbBi system by Clune *et al* making use of the rigid-band model.<sup>33</sup>  $\gamma_n$  is proportional to the electronic density of states at the Fermi surface and therefore should, reflect changes in the density of states upon alloying. However, we take these results to indicate that the density of states, and hence the band structure of Pb, is virtually unchanged by alloying with Bi to these concentrations, so that the rigid band model should be applicable. Thus we can make use of the quoted  $\gamma_n$  with Equation 5.2 in order to calculate N(0) for  $Pb_{0.7}Bi_{0.3}$ . It should be noted that as the rigid band model ignores the effect of electron interactions the calculated  $\gamma_n$ , and hence N(0), will be smaller by a factor of  $1+\lambda$  than those found experimentally. However in the absence



**Figure 6.7** Comparison of the superconducting gap for  $Pb_{0.7}Bi_{0.3}$  from tunnelling data<sup>12</sup> (×) with  $\Delta(t)$  from Equation 2.27 using  $\Delta F \& \Delta S$  deduced from critical-field measurements (black line). The blue dashed line shows  $\Delta(t)$  from Equation 2.27 with  $\Delta F \& \Delta S$  calculated from our program assuming a rescaled BCS gap. A better match for this computational calculation is obtained by re-scaling the curve to the zero-temperature tunnelling gap (red dashed).

of any experimental measurements we must assume that such an underestimate will not adversely affect our results; if anything it will likely only slightly underestimate the value of  $\Delta(t)$ .

Thus we use our temperature-dependent  $H_c$  fits, as determined from  $H_{c2}$  data transformed by  $\kappa$ , to determine  $\Delta S(t)$  and  $\Delta F(t)$ . Our thermodynamic theory then allows us to calculate  $\Delta(t)$  with Equation 2.27 and compare these along with our computational calculations to tunnelling data for Pb<sub>0.7</sub>Bi<sub>0.3</sub>.<sup>12</sup> As can be seen in Figure 6.7  $\Delta(t)$ determined from our fits to critical-field measurements is too large and clearly its temperature-dependence does not match that of the tunnelling data. This is due to the fact that we do not have the correct values for the thermodynamic critical-field but rather our transformed  $H_{c2}$  measurements. We already determined from the deviation function in the previous section that we cannot use a temperature-independent  $\kappa$  to convert our  $H_{c2}$ measurements to  $H_c$ . It is necessary to either determine the temperature-dependence of  $\kappa$ or measure  $H_{c1}$  as well in order to truly determine an accurate magnitude and temperaturedependence for the thermodynamic critical-field. As such the temperature-dependence and magnitude of our  $\Delta(t)$  calculated with Equation 2.27 will also be erroneous.

We can however still investigate the predicted  $\Delta(t)$  of our program which can also be seen in Figure 6.7. This calculation for a single iteration produces a  $\Delta(t)$  which is lower in magnitude but appears to exhibit a realistic temperature-dependence in comparison with tunnelling data and in particular the flatter temperature-dependence in the mid temperature range which is characteristic of strong-coupling. Scaling this computational gap by the tunnelling  $\Delta(0) = 1.81$  meV we find that its predicted temperaturedependence provides an excellent match to the tunnelling data. Thus our program appears to be producing accurate behaviour for this extra-strong-coupling superconductor. The lower predicted magnitude of  $\Delta(t)$  is likely due to our choice of  $\alpha$ . We determined  $\alpha$ from the tunnelling  $\Delta(0)$  as we were unable to match an appropriate deviation function as we did in Section 5.2 for a range of coupling superconductors. Table 5.2 indicated that in general the  $\alpha$ -values predicted from deviation fits of our program were often higher than those predicted from tunnelling  $\Delta(0)$  values. Thus if we were able to match a computational deviation function for  $Pb_{0,7}Bi_{0,3}$  measurements we would likely get a larger  $\alpha$ -value which could produce a fit for  $\Delta(t)$  of more appropriate magnitude. Interestingly, while in Section 5.1 we saw the computational fit being the least accurate for the type I strong coupler Pb it matches quite well for this type II extra-strong coupler. Such comparisons depend upon the accuracy with which the temperature-dependence of the energy gap can be measured from tunnelling which can prove difficult. Of course these predictions are only for single iterations as the multiple iteration method results in a premature cut-off and settles back to the BCS weak-coupling case as we discussed in Section 5.3. Inclusion of an energy-dependent coupling parameter,  $\lambda = \lambda(E)$ , could potentially solve this as mentioned previously.

In order to provide a truly valid test of our thermodynamic theory however we should determine accurate thermodynamic critical-field  $H_c$  data and compare the calculated  $\Delta(t)$  from this. Comparisons with other strong-coupling type I and II superconductors should also help determine the full validity of our theory in the strong-coupling regime as the results for Pb and Pb<sub>0.7</sub>Bi<sub>0.3</sub> have not proved consistent as of yet.

#### 6.4 **Pressure Dependent Quantities**

We are also interested in investigating the pressure-dependence of several of the superconducting parameters we were able to determine. Measuring the critical-field at a range of pressures using our clamp cell thus allows us to illustrate the general dependence of such quantities as can be seen in Figure 6.8. It is convenient to determine a smooth fit for the pressure-dependence of such parameters in order to allow easier use of them in certain thermodynamic derivations. Figure 6.8 (a) illustrates the pressure-dependence of the superconducting transition temperature  $T_c$ , which appears to decrease in a linear fashion as described by the best fit to data

$$T_c(P) = 8.6782 - 0.38475P \tag{6.4}$$

Thus we see that superconductivity is suppressed as the pressure is increased, resulting in the superconducting-state only being established at lower temperatures. Interestingly many high-temperature type II superconductors exhibit the opposite, where  $T_c$  increases along with the pressure. Pb<sub>0.7</sub>Bi<sub>0.3</sub> is also a type II superconductor as we have mentioned previously yet it exhibits this negative relation with pressure for its transition temperature.

The Taylor fits made to our critical-field measurements at various pressures in Subsection 6.1.2 should also allow us to determine the pressure-dependences of these useful thermodynamic quantities. Of course these have been transformed from  $H_{c2}$  measurements into the thermodynamic critical-field with  $\kappa$  yet their general pressure-dependence should hold provided  $\kappa$  is pressure-independent. Figure 6.8 (b) shows the pressure-dependence of the zero-temperature critical-field  $H_c(t = 0)$  for various pressures. A close matching smooth function to its pressure-dependence is

$$H_c(t=0,P) = 0.1113 + 0.0368 \exp(-2.1844P)$$
(6.5)

Thus we can see that  $H_c(t = 0, P)$  falls as the pressure is increased. We can immediately deduce from this that the superconducting energy gap  $\Delta(t)$  will also fall with pressure. Our thermodynamic theory depends on both  $\Delta S(t)$  and  $\Delta F(t)$  in order to calculate



**Figure 6.8** Determined values of (a)  $T_c$ , (b)  $H_c(t = 0)$  and (c)  $\beta$  from our Taylor fits to critical-field measurements taken our Pb<sub>0.7</sub>Bi<sub>0.3</sub> sample at various pressures. Best fits for data also displayed (red lines).

 $\Delta(t)$  with Equation 2.27. We have already shown that all that is necessary to perform this calculation is temperature-dependent critical-field data,  $H_c(t)$ . If  $H_c(t = 0, P)$ falls with increasing pressure then so will  $H_c(t)$  and as this is related to  $\Delta(t)$  through our thermodynamic theory then it will also fall with increasing pressure. Thus the superconducting energy gap grows smaller as the pressure is increased.

The Taylor fits we have made to our critical-field data expressed by Equation 5.1 have only a temperature-dependence, yet we may be able to incorporate a pressure-dependence into this as well. In order to do this we must deduce a smooth function for the pressuredependence of  $\beta$ . Figure 6.8 (c) shows the  $\beta$  values determined from the Taylor fit made to critical-field measurements at each pressure. The most appropriate function describing its pressure-dependence is

$$\beta(P) = 1.3307 + 0.1859 \exp(-1.9767P) \tag{6.6}$$

Thus by combining Equations 6.5 & 6.6 we are able to determine a general form of the Taylor expansion as a function of both temperature and pressure.

$$H_c(t, P) = H_c(t = 0, P)[1 - \beta(P)t^2 - (1 - \beta(P))t^4]$$
(6.7)

Equation 6.7 provides us with a consistent means of determining the critical-field at any particular temperature and pressure as well as for any other parameters we derive from it. As a smooth function of both temperature and pressure we are also able to deduce any thermodynamic variables which may require either differentiation or integration with respect to either of these variables. Of course as we have shown in earlier sections that our transformation of  $H_{c2}$  measurements to the thermodynamic critical-field is not entirely accurate it is best to deduce these relations again once further measurements have corrected this issue in order to ensure they are accurate.

Nevertheless, we can also investigate the effect of pressure on the coupling strength in  $Pb_{0.7}Bi_{0.3}$ . Equation 2.27 allows us to determine the pressure-dependent zero-temperature energy gap  $\Delta(t = 0, P)$  simply from  $\Delta F(t = 0, P)$  as  $\Delta S(t = 0, P) = 0$ . Of course  $\Delta F(t = 0, P)$  can be found using the pressure-dependent critical-field at t = 0 as given



Figure 6.9 Pressure-dependence of  $\alpha$  as determined from Equation 6.9 for Pb<sub>0.7</sub>Bi<sub>0.3</sub>.

by Equation 6.5.

$$\Delta(t=0,P) = \sqrt{\frac{1}{N(0)\mu_0}} H_c(t=0,P)$$
(6.8)

We are able to utilise this along with  $T_c(P)$  to determine the pressure-dependent  $\alpha$ -value, and hence coupling strength, via Equation 2.19 yielding the following relation.

$$\alpha(P) = \frac{\Delta(t=0,P)}{k_B T_c(P)} \tag{6.9}$$

Figure 6.9 illustrates the pressure-dependence of  $\alpha$  as determined from Equation 6.9. We can clearly see that as the pressure increases the strength of the coupling in Pb<sub>0.7</sub>Bi<sub>0.3</sub> falls. Thus Pb<sub>0.7</sub>Bi<sub>0.3</sub> tends towards weaker-coupling with the application of higher pressures. The ambient pressure  $\alpha$ -value predicted from this is higher than that given by tunnelling measurements of approximately 2.45. No doubt this is once again due to our inaccurate representation of the thermodynamic critical-field which could be corrected with further measurements. However, the pressure-dependence should still be fairly representative of the coupling-strength response for Pb<sub>0.7</sub>Bi<sub>0.3</sub>.

## Chapter 7

#### **Extension to** *d***-wave**

Naturally we also wish to extend the use of our thermodynamic theory and calculations to other more unconventional superconductors in order to test their full range of validity. In Chapter 3 we discussed extension of our computations to represent *d*-wave symmetry which is often exhibited in such superconductors. We are thus able to compare our extension of Padamsee's  $\alpha$ -model to the experimental electronic specific-heat measurements for a series of doping concentrations of the Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub> superconductor (Bi-2212). Utilising iterative calculations we are also able to test the validity of our thermodynamic theory in comparison with this experimental data.

## 7.1 Experimental Data

Bi-2212 is a member of the high-temperature superconducting cuprate family which exhibits *d*-wave symmetry and falls into the type II classification. The onset of superconductivity can often be altered by doping the parent phase of superconductors with various elements and thus introducing additional electrons or holes. Such doping alters the superconducting behaviour and  $T_c(p)$  is observed to trace a dome shaped curve as a function of doping, *p*. There is an optimum doping level,  $p_{opt}$ , which yields the maximum  $T_c$  on this dome. We shall examine data for the hole overdoped region above  $p_{opt}$  as this is free of any obscuring effects from the pseudogap phase which is predominant in the underdoped region. Moreover, it has been shown that in this overdoped region the BCS weak-coupling ratios  $\Delta/k_B T_c^{mf}$  and condensation energy  $U_0/\gamma_n T_c^{mf^2}$  are rather well satisfied.<sup>34,35</sup>  $T_c^{mf}$  is the mean-field transition temperature that would exist in the absence of superconducting fluctuations. As such, comparisons to overdoped data will provide the most straightforward case for application of our calculations and will provide a test of just how BCS-like this material is. Up until this point we have used experimental critical-field data for our comparisons yet we are still capable of performing these with other thermodynamic measurements. Thus for a selection of overdoped Bi-2212 superconductors we utilise available detailed electronic specific-heat measurements carried out by Loram *et al.*<sup>36</sup> Specific-heat measurements allow us to determine the entropy of the superconducting-state,  $S_S$ , via integration with respect to temperature. It is also possible to determine the normalstate entropy,  $S_N$ , from such data using an ARPES-derived dispersion and a suitable pseudogap model which has already been undertaken by Storey *et al.*<sup>37</sup> The difference between these gives  $\Delta S(T)$  from which we can calculate  $\Delta F(T)$  by integrating with respect to temperature. As Bi-2212 is a type II superconductor we are interested in its thermodynamic critical-field for use in our calculations which is related to the free energy by Equation 2.23.

Thus we are able to use this experimental specific-heat data to determine the temperature dependent free energy which can be utilised to calculate the deviation function with Equation 3.7 for our comparisons.

## 7.2 Deviations

Each doping concentration of the Bi-2212 superconductor results in slightly different superconducting behaviour and as such could produce a different deviation function. We determine these deviation functions from the experimental data using Equation 3.7 and compare them with our computations. The deviation function calculated from this data for Bi-2212 produces very large values near and above  $T_c$  rather than approaching zero as we have generally seen previously. This is due to superconducting fluctuations in Bi-2212. The coherence length,  $\xi$ , we discussed in Section 2.1 is several orders of magnitude smaller in a high-temperature superconductor, such as Bi-2212, than in conventional superconductors. As a material nears its  $T_c$  small disparate regions become superconducting yet due to the small  $\xi$  do not overlap fully until lower temperatures are reached and so a single coherent superconducting-state is unable to form until  $T_c$ which lies well below its mean-field value  $T_c^{mf}$ .<sup>34</sup> This not only depresses  $T_c$  but results in a fluctuation contribution to the specific-heat which rounds off the sharp critical phenomenon generally seen for the onset of superconductivity and blurs the precise determination of  $T_c$ .<sup>34</sup> The deviation function is very sensitive especially near  $T_c$  and in the presence of superconducting fluctuations will grow rapidly there. Away from  $T_c$  its form is relatively stable and so we can hopefully match our calculated deviations to data for much of the low-temperature range, where fluctuations are negligible.

#### **7.2.1** $\alpha$ Model Extension

As discussed in Section 3.2 we have extended the  $\alpha$ -model proposed by Padamsee to superconductors with *d*-wave symmetry by including an angular *k*-dependence in our calculations. In this way we are able to calculate the theoretical temperature-dependence of both the entropy and free energy assuming a BCS energy gap  $\Delta(T)$  scaled by an  $\alpha$ value to represent the coupling strength. Thus we calculate deviations for a range of  $\alpha$ -values with our program and fit these Padamsee-like curves with the experimental measurements for Bi-2212, shown in Figure 7.1.

Here we are demanding much of data that has already had the phonon term removed, which is two orders of magnitude larger. However, overall the data is consistent with close-to-weak-coupling behaviour when compared with the BCS value of  $\Delta/k_BT_c =$ 2.14. As the doping concentration is increased we see a trend towards weaker coupling. The most curious deviation determined from data is that of p = 0.188, the closest to the critical doping of  $p_{crit} = 0.19$  where the pseudogap vanishes.<sup>36</sup> This exhibits curvature quite dissimilar from the general behaviour of the others. As can be seen, our calculated deviation function for particular  $\alpha$ -values provide fits which closely match the magnitude of the experimental data. These fits even match the temperature-dependence for some of the doping concentrations quite well, yet this is not the case for all of them. These Padamsee-like calculations over- and under-estimate the deviation function in particular temperature regimes to some degree for most of the overdoped measurements. Most notably whilst the fits are fairly good in the intermediate range they do not always accurately represent the low temperature values as well. Whilst these discrepancies are



**Figure 7.1** Deviation function calculated from electronic specific-heat data using Equation 3.7 for several overdoped samples of Bi-2212 (only every  $7^{th}$  data point shown for clarity). Calculated deviation functions utilising a scaled BCS  $\Delta(T)$  for several  $\alpha$ -values overlaid.

not particularly large they are still fairly consistent and thus do not allow as accurate a representation of the temperature dependence as would be wished. The validity of these fits to the data should of course only be considered up to approximately  $t^2 = 0.6$ , which corresponds to roughly 80% of  $T_c$ , due to the superconducting fluctuations blurring the transition zone and thus skewing the deviation functions. Calculated deviations up to this  $t^2$  value thus provide generally adequate fits with some doping concentrations exhibiting more discrepancies than others, particularly that closest to the critical doping. Again, we are asking a lot of the data and the deviation function is a very sensitive measure of any irregularities, whether systematic or experimental.

#### 7.2.2 Thermodynamic Theory

Our program allows the use of our thermodynamic theory to recalculate the temperaturedependent energy gap,  $\Delta(T)$ , via Equation 2.27. This makes use of the enhanced entropy from Equation 2.31 which includes the electron-phonon enhancement factor,  $\lambda$ , from Eliashberg theory to represent the coupling strength. The weak-coupling BCS *d*-wave gap is used as an input and for various  $\lambda$ 's we calculated the resulting  $\Delta(T)$  from one iteration. Each  $\lambda$ -value has a corresponding  $\alpha$ -value which can be calculated from the  $\Delta(0)$  of this new gap by Equation 2.19. The new gap is then utilised to re-calculate the entropy and free energy to hopefully represent their observed behaviour more closely. For this first iteration of the program we can compare the deviation function for the newly recalculated free energy to see if this more accurately matches experimental data than the Padamsee-like fits of the previous section. Figure 7.2 shows just such a comparison.



Figure 7.2 Deviation function calculated from electronic specific-heat data using Equation 3.7 for several overdoped samples of Bi-2212 (only every 7<sup>th</sup> data point shown for clarity). Calculated deviation functions overlaid which use a scaled BCS  $\Delta(T)$  for several  $\alpha$ -values (blue dashed) and a newly recalculated  $\Delta(T)$  from a single iteration of our program where each  $\lambda$  corresponds to a particular  $\alpha$  (red solid).

Interestingly we see that the deviation functions calculated from our new energy gap are in fact quite similar to those of the Padamsee-like curves from the previous section. These best fits in fact even have the same  $\alpha$ -values as determined from  $\Delta(0)$ . The curvature has shifted slightly yet for the most part they exhibit a very similar temperature-dependence. In all likelihood this is due to the fact that these overdoped samples all still exhibit fairly weak- to intermediate-coupling. The strongest coupling sample, p = 0.182, is matched fairly well to  $\alpha = 2.42$  which is an indication of still fairly weak-coupling when compared with  $\alpha_{BCS} = 2.14$ . Thus our calculation has not produced an overly different result as the coupling strength is not particularly strong. Unfortunately as a result it has not been able to better represent the low temperature curvature than our Padamsee-like fits of the previous section. Multiple iterations to recalculate the energy gap may have helped to better approximate this curvature yet as we saw in Section 5.3 such iterations in fact only result in a cut-off scaled BCS case which will provide unphysical results.

Thus we have seen that extension of the  $\alpha$ -model to a *d*-wave superconductor such as Bi-2212 does help provide a somewhat adequate representation of it with some discrepancies. Our thermodynamic theory does not provide much improvement on this representation for a single iteration most likely due to the weak nature of the coupling. Comparisons of the extended  $\alpha$ -model as well as our thermodynamic theory to *d*-wave superconductors with stronger coupling would likely yield a more rigorous test of their validity and potential improvement over one another. However, the important conclusion is that in the low-temperature region, where superconducting fluctuations are negligible, the deviation function is consistent with nearly weak-coupling mean-field behaviour with  $\alpha$ -values ranging from 2.42 to 2.28 for the five overdoped samples investigated. This is to be compared with  $\alpha_{BCS} = 2.14$  for *d*-wave symmetry. Further, the data also supports the idea that the coupling tends toward weaker values with increasing doping.

# Chapter 8

## **Conclusions and Future Work**

In this thesis we have attempted to extend the formulation put forth by Padamsee in tandem with our own proposed thermodynamic theory. Padamsee utilised a BCS  $\Delta(t)$  scaled by an adjustable  $\alpha$ -value to represent the coupling strength in various superconductors in order to calculate their thermodynamic parameters. Such an approach appeared to be fairly successful for most coupling strengths but potentially not quite so in the strong-coupling regime. Our theory extends this formulation by recalculating the  $\Delta(t)$  based on the thermodynamic functions  $\Delta S$  and  $\Delta F$  to hopefully produce a more accurate temperature-dependence for the energy gap for all coupling strengths.

Application of our theory in determining the temperature-dependent energy gap was tested for a range of weak- to strong-coupling type I superconductors exhibiting swave symmetry in two ways. Firstly by direct calculation from critical-field data and secondly by numerical calculations of thermodynamic parameters from which to deduce  $\Delta(t)$  with our theory. Comparisons of these calculated predictions with experimental tunnelling measurements of the energy gap revealed that our theory does produce a fairly accurate match of  $\Delta(t)$  for weak- to intermediate-couplers, with only some minor magnitude discrepancies. The predicted temperature-dependence flattens in the intermediate temperature range thus providing a better match to that observed experimentally. However, for the strong-coupler Pb it did not produce an accurate prediction of  $\Delta(t)$  in comparison to tunnelling measurements. Investigation into whether recalculation of  $\Delta(t)$  with successive multiple iterations would settle on a stable solution which more accurately predicted  $\Delta(t)$  in this strong-coupling regime proved fruitless and illustrated a limitation of our theory. Inclusion of the electron-phonon enhancement parameter,  $\lambda$ , in our multiple numerical calculations is merely equivalent to rescaling the BCS weak-coupling energy gap. Essentially as our thermodynamic theory is based on BCS weak-coupling it will always tend towards this through multiple iterations. However, potentially inclusion of an energy-dependent  $\lambda(E)$  should disallow such a simple scaling and could correct our theory's erroneous prediction in the strong-coupling regime. Thus  $\lambda(E)$  should be determined and incorporated into our calculations in future to hopefully remedy this issue.

To provide a rigorous test of our thermodynamic theory we also synthesised an extrastrong-coupling Pb<sub>0.7</sub>Bi<sub>0.3</sub> superconductor and measured its critical-field as a function of both temperature and pressure. Unfortunately after completing all our measurements we discovered that Pb<sub>0.7</sub>Bi<sub>0.3</sub> is in fact a type II superconductor rather than type I like the previously investigated materials. Thus our measurements only determined its upper critical-field, yet we attempted to recover the thermodynamic critical-field via a Ginzburg-Landau relation in order to utilise this with our theory. This required us to assume a temperature- and pressure-independent  $\kappa$  value, which we deduced from additional measurements. Regrettably the assumption of temperature-independence for  $\kappa$  does not appear to hold and so our deduced  $\Delta(t)$  from our transformed critical-field measurements at ambient pressure produces a highly erroneous temperature-dependence. Determination of a temperature-dependent  $\kappa$  should be carried out in future in order to allow an appropriate conversion of our measurements to an accurate thermodynamic critical-field with which to use in our theory. However, our computational calculation of the energy gap matched the experimentally observed temperature-dependence from tunnelling measurements very well. Interestingly, this implies that our thermodynamic theory is accurately predicting  $\Delta(t)$  for this extra-strong-coupling type II superconductor whereas it failed to do so for the strong-coupling type I Pb superconductor. In order to fully explore the applicability of our theory in the strong-coupling regime it would be necessary to compare with further type I and II superconductors exhibiting similar such coupling strengths.

The critical-field measurements at various pressures allowed us to deduce smooth pressure-dependent functions for both the critical-field and superconducting transition temperature,  $T_c$ . A pressure-dependent energy gap can also be determined through the use of our theory. All of these functions fall as pressure is increased indicating that superconductivity is damped in Pb<sub>0.7</sub>Bi<sub>0.3</sub> for higher pressures. Determination of the pressure-dependent  $\alpha$ -value also illustrates that as the pressure is increased the coupling

strength in  $Pb_{0.7}Bi_{0.3}$  grows weaker. Whilst we have already determined that  $\kappa$  is not temperature-independent it is likely that it is indeed pressure-independent, yet it would be prudent to perform additional measurements to confirm this assumption.

We were able to successfully extend the formulation of Padamsee, which uses the BCS  $\Delta(t)$  scaled by an  $\alpha$ -value to represent coupling strength, for application to superconductors exhibiting *d*-wave symmetry. Thermodynamic parameters calculated in this way provided an adequate representation, with minor discrepancies, for much of the temperature range when compared with experimental measurements for several overdoped samples of the high-temperature superconductor Bi-2212. Computational calculations with our theory provided little improvement to these as Bi-2212 already exhibited fairly weak-coupling. In fact as the doping concentration increases the coupling strength generally grows weaker. Comparisons of predictions from our theory to experimental data for *d*-wave superconductors with stronger coupling will likely give a clearer picture of any potential improvement it provides over the extended Padamsee formulation.

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