CHAPTER ONE

History and Introduction

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1. HISTORY AND INTRODUCTION

The discovery of superconductivity by Kamerlingh Onnes in 1911 [1] followed closely on his technological advance of liquefying helium in 1908. Little was known in detail about the low-temperature behavior of the electrical resistivity of metals at that time and Onnes had undertaken to study this. He felt that the purity of the metal would affect the result as apparently it did in the cases of Au and Pt which he had measured, and so he opted to study the metal Hg which he felt could be prepared in very high purity. The abrupt vanishing of the electrical resistivity of Hg below 4.15 K [2] and subsequently found not to be critically sensitive to impurity level, signaled a new state of matter, a state Onnes labeled superconductivity.

This initial discovery seeded the growth of an area of materials research which continues to produce unexpected results until today. The initial low-temperature search for new superconducting materials had expanded the number of known superconducting elements by 1951 to 21, mostly through measurements to ever lower temperatures. Advances in measurement techniques at high pressures and low temperature has vastly expanded this number since that time, with the current number of elements which are or can be made to be superconducting being 52, 53 if one includes Xe-expanded films of Cr. The present status of affairs is summarized in Fig. 1.1 [3].
Figure 1.1 Periodic table of the elements indicating the occurrence of superconductivity at ambient and elevated external pressure (from Ref. [3]).
It was not until 1933 that the major discovery of magnetic-flux expulsion below the superconducting transition temperature $T_c$ was made by Meissner and Ochsenfeld [4]. This is not a result of zero resistance. Rather it is a sign of something much more fundamental and confirming that superconductivity is indeed a thermodynamically stable state. This immediately also made it clear, why, as observed experimentally before, superconductivity may be destroyed by an external magnetic field. The existence of a critical magnetic field $H_c$, depending on temperature below $T_c$ above which a superconductor would become normal is then expected, because it costs energy to exclude magnetic field from the bulk of the superconductor. Fritz London early appreciated the fundamental quantum nature of the superconducting state and, in 1935, developed, with his brother Heinz, the London-equation modification to Maxwell’s equations to describe this flux exclusion, leading to the so-called London magnetic field penetration depth in superconductors $\lambda_L$ [5]. At the same time, Fritz London suggested a quantum mechanical approach to justify what is now known as the London equation [6]. Only after World War II, Pippard recognized that although $T_c$ was not much influenced by impurities, the penetration depth was indeed and thus implied a significant modification of the original London equation [7].

Another significant theoretical advance, in 1950, was the Ginzburg–Landau superconducting free energy expression based on Landau’s theory of second-order phase transitions [8]. At first not much appreciated in the Western world, the approach was based on characterizing the superconducting state via a complex order parameter $\Psi$ which is a function of position in the superconductor. This leads to a second length scale, the coherence length $\xi$, the distance over which the order parameter can have a significant variation. Later, Abrikosov pointed out [9] that for values of $\kappa = \lambda_L / \xi > 1/\sqrt{2}$, magnetic flux would penetrate a superconductor as flux quanta below an upper critical field but above a lower critical field, below which the Meissner–Ochsenfeld state persisted. This lead to the discovery and classification of superconductors into two classes, type I and type II (Fig. 1.2). In external magnetic fields and depending on sample geometry, the type I superconductors adopt what is termed an intermediate state and type II superconductors exhibit a mixed state. They differ characteristically in the distribution of the penetrating field in the superconducting state. Type I superconductors exhibit a lamellae-type distribution of normal and superconducting regions while in type II superconductors, the field penetrates in vortices above $H_{c1}$ (see Fig. 1.2). It is interesting to note that the original theory of London is suitable for type II superconductors while the early
known type I superconductors are best described by Pippard's modified version.

The basic difficulty of a microscopic theory of superconductivity is the small difference in energy of the ensemble of conduction electrons between the normal and the superconducting state. The large and futile theoretical effort that had been expended on finding such a theory of superconductivity by the mid-1950s prompted a suspicion that the lack of success, in spite of so many fine minds working on the problem, meant that the solution would only come by somebody guessing the answer. This proved to be the case. In a short note in 1956, Cooper [10] showed that a pair of electrons placed above a free electron Fermi surface with arbitrarily small attractive interaction could form a bound state with energy less than the Fermi energy, signaling that the Fermi surface was unstable against pair formation. This important result contained two interesting aspects: the electrons were paired into something that resembled a boson, bound by an arbitrarily small attractive interaction, intuitively impossible between two negatively charged particles. The full theory of Bardeen, Cooper, and Schrieffer (BCS) building on this observation followed in 1957 [11]. This theory took the electron–phonon interaction as the attractive interaction, a possibility that was promoted already in 1950 by Fröhlich [12]. That claim was, independently, anticipated in the same year by the observation of an isotope effect on $T_c$ varying as $1/\sqrt{M}$, with $M$ as the mass of the atoms in the crystal lattice. Maxwell [13] and Reynolds and others [14] made this observation by probing $T_c$ of different available Sn isotopes. The BCS state of superconductivity has the conduction electrons paired with zero momentum and spin. BCS also predicted that a gap in the excitation spectrum of the conduction electrons opened across the entire Fermi surface below $T_c$, a prediction with many experimental consequences which were rapidly
verified. Subsequently, Gor'kov was able to show in a tour de force how the macroscopic Ginsburg–Landau theory followed from the microscopic BCS theory [15] and Eliashberg further generalized the BCS theory with a field-theoretical approach [16].

The search for new superconducting materials had spread beyond the elements with the discovery of a small number of superconducting binary intermetallic compounds in the 1930s. By the early 1950s the hunt for higher $T_c$'s was well underway, particularly by Matthias, Hulm, and Geballe in the United States and Alekseevskii in the Soviet Union. The search continued in binary intermetallics [17], a surprising number of which were unknown in the metallurgical literature. Regularities were sought for where the highest $T_c$'s might be found. Fermi suggested to Matthias while playing tennis that he might see whether $T_c$ depended on the electron per atom count, $e/a$, since so much in the simple theory of metals depended on this. Indeed, a correlation was found [18] (Fig. 1.3) but one has never successfully explained the peaks in $T_c$ near $e/a = 4.75$ and 7. What we now know from high-pressure experiments on elemental superconductors in fact runs counter to these binary trends, particularly with $T_c = 20 \text{ K}$ of monovalent Li under pressure [19], but this early correlation points to the fundamental problem in superconducting materials: where does one go to find them? The work in the 1950s found the highest $T_c = 18 \text{ K}$ in Nb$_3$Sn [20] which crystallizes with the cubic $\beta$-W structure, a structure for the oxide W$_3$O. Trends in $T_c$ versus composition predicted that Nb$_3$Si would have a $T_c$ of 28 K if it could be made stoichiometrically. The maximum $T_c$ in the transition metal intermetallics finally reached 23 K for Nb$_3$Ge in 1973 with samples prepared using sputtering [21]. It was not clear at this time if
Figure 1.4 Part of the history of the attempts to raise $T_c$ to ever higher temperatures.

much higher $T_c$'s would be found. One theoretical argument suggested an upper limit of order 30 K, this set by lattice instability arising when the electron–phonon interaction became too strong: the lattice would distort to relieve the strong electron–phonon interaction.

Always in the background was this question of how to get to higher $T_c$'s. One might have thought that the BCS solution to the long-standing superconductivity problem would have heralded rapid advance in finding higher transition temperatures, but this was not the case. A plot of maximum $T_c$ versus year (Fig. 1.4) in fact runs smoothly through 1957, the year of publication of the BCS paper. The BCS weak coupling expression

$$kT_c = \hbar \omega_D \exp\left(\frac{-1}{N(0)V}\right)$$

[1.1]
relating $T_c$ to the Debye frequency $\omega_D$ and the product of the electronic density of states at the Fermi level $N(0)$ times the electron–phonon coupling strength $\nu$ prompted renewed search in transition metal materials, where $N(0)$ is generally larger than in simple sp-metallic conductors.

The search for new superconductors expanded out into ternary compounds in the 1970s. There was the expectation that working in the larger phase space of ternaries would lead to materials with higher $T_c$'s, but things took a different direction. It had long been known that magnetic impurities in superconductors could strongly depress $T_c$. The explanation for this came readily from the BCS theory and subsequent work of Abrikosov and Gor’kov [22]. The interaction of local magnetic moments impurities with spin $S$ in metals with conduction electrons having spin $s$ is expected to be of the form $H = -JS\cdot s$, $J$ being the strength of the interaction. So a local spin $S$ interacts with the two members of a Cooper pair with opposite sign, causing pair breaking [23].

Starting in 1958, impurity studies in magnetically doped metals had looked for the possibility of coexisting superconductivity and magnetic order, in retrospect without convincing success (Fig. 1.5). One could imagine that in an alloy system with complete solid solubility (La/Gd in Fig. 1.5) with one member (La) superconducting and the other magnetic (Gd, with a Curie temperature of 300 K), that the reduction of the respective superconducting and Curie temperatures with alloying might find some region of coexistence of superconductivity and magnetism [24]. This was not found in these simple alloying cases, but instead it was discovered in chemically ordered ternary compounds. The first to be discovered was a

![Figure 1.5 Critical temperature $T_c$ for superconductivity and Curie temperature $T_C$ for ferromagnetism in the alloy system La–Gd (from Ref. [24]).](image)
compound of the so-called Chevrel phases $\text{RMo}_6\text{Se}_8$ ($R =$ rare earth) in 1972 [25], followed by the rare-earth rhodium borides $\text{R}_{x}\text{Rh}_4\text{B}_4$ [26]. The rare-earth ions carry local magnetic moments (with certain well-understood exceptions) due to incompletely filled orbitals of $4f$ electrons. At low temperatures, the sublattice of rare earths orders magnetically in these compounds as one expects from general arguments based on the third law of thermodynamics. When this order is of antiferromagnetic type it was found to coexist with superconductivity (see Fig. 1.6), while ferromagnetic order in general did not coexist with superconductivity. This led to the situation known as reentrant superconductivity (Fig. 1.7), where existing

![Figure 1.6 Superconducting ($T_c$), ferromagnetic ($T_M$), and antiferromagnetic ($T_N$) transition temperatures in the compound series $\text{RERh}_4\text{B}_4$ (from Ref. [28]).](image1)

![Figure 1.7 Reentrant superconductivity in $\text{ErRh}_4\text{B}_4$. The lower transition reflects the onset of ferromagnetism, that is, the suppression of superconductivity (from Ref. [28]).](image2)
superconductivity disappeared when at lower temperature, ferromagnetic order set in [27].

But this story contained another twist. Not all rare-earth local moments in metals behave in the same way. Inspecting the periodic table, the 4f shell begins forming just after La, in the 5d row of the periodic table. Given the angular momentum rules for atomic structure, the 4f shell might have first appeared occupied in the 4d row but does not due to electron-electron interactions. When the 4f shell does first form at Ce, the 4f state has characteristics intermediate, depending on chemical environment, between an itinerant and a localized state. The coupling between this 4f state and the conduction electrons differs in this case from that found with the other rare earths with highly localized 4f states where \( n > 1 \): the sign of \( J \) in the interaction expression has the opposite sign, namely it is antiferromagnetic for Ce and ferromagnetic for \( n > 1 \). This has a surprising consequence: the conduction electrons in metals containing Ce act to compensate its 4f moment, an effect known as the Kondo effect [29]. In dilute alloys of Ce, below some characteristic Kondo temperature \( T_K \), the Curie–Weiss-type susceptibility behavior, characteristic of local moments, evolves into a temperature-independent paramagnetic response. For Ce, \( T_K \) is typically of order a few degrees Kelvin, but in particular cases can be orders of magnitude larger or smaller than this, depending on the local environment of the Ce ions. It was discovered that the Kondo impurity effects observed in dilute alloys of Ce persisted to high concentration in many situations where Ce was a stoichiometric component of a compound. In such dense Kondo compounds, as they came to be called, the 4f local moment spin degrees of freedom become entangled with the conduction electron degrees of freedom such that the local moment spin entropy gets shared at low temperature with the conduction electrons, forming an electronic system with a very large density of electronic states at the Fermi energy in many cases. The first compound for which this feature was identified was CeAl3 [30]. The completely surprising discovery by Steglich and coworkers was that one such compound, CeCu2Si2, became superconducting, albeit with a low \( T_c = 0.5 \) K [31]. Considering the previously mentioned detrimental effect of local moments on superconductivity, the puzzle here was how can a conduction electron state with this strong magnetic parentage become superconducting. Three 5f U-based superconductors in this class were discovered shortly afterward [32–34], the number now having expanded to perhaps two dozen, with \( T_c \) only up to 2.3 K. However, a compound which appears closely related is PuCoGa5 with \( T_c = 18 \) K [35],
suggesting the possibility of a route through these materials to moderately high $T_c$'s.

The superconductivity in these so-called heavy-fermion materials has proved to be different in a significant way from the common BCS superconductors. Namely, the pairing is not in the mentioned opposite-momentum opposite-spin (also termed singlet $s$-wave) state but rather in an opposite-spin $d$-wave state, or in some instances, a spin parallel $p$-wave state. Such states were envisioned as a possibility early after the BCS paper in materials with strong electronic correlations. Later these conjectures were discussed in more detail, for example, for elemental Pd [36]. However, it was felt that the finite angular momentum of the pairing would let that superconductivity be very sensitive to impurity and defect scattering and would only occur in very clean metals. A signature of most such nonzero angular momentum states is nodes in the superconducting gap where the superconducting order parameter vanishes. This gives rise in properties such as the specific heat, ultrasound attenuation, and NMR relaxation rates with power-law temperature dependences well below $T_c$, in contrast to the exponential dependence expected at low enough temperatures when the Fermi surface is fully gapped as for the $s$-wave case. Indeed, such power laws were found, initially in the 5f materials UBe$_{13}$[37] and UPt$_3$[38] for which reasonable size single crystals were available. Finding evidence for nontrivial or unconventional order parameters in this class of superconductors breathed new life into the field of superconductivity. What has been particularly fruitful here has been the close examination of the competition between magnetic and superconducting ground states. The current consensus is that all the heavy fermion superconductors, in the appropriate parameter space, occur in close proximity to a magnetically ordered ground state.

The heavy-fermion superconductors raised anew the question as to whether a mechanism other than the electron-phonon interaction could lead to superconductivity. Various other such mechanisms, via plasmons [39], spinons [40], and excitons [41] for example, had been proposed. A vibronic interaction was suggested by Little [42] to be appropriate for molecular organic conductors. A spectacular announcement of superconductivity in the low-dimensional organic material TTF-TCNQ [43] below 70 K proved to be false, but this lead to investigations of lower dimensional organic conductors. The search resulted in the discovery of superconductivity in the so-called Bechgaard salts, first under external pressure [44] and subsequently also at ambient pressure [45]. Further studies found compounds
exhibiting superconductivity at $T_c$'s as high as 12 K and revealed remarkably complex pressure/temperature phase diagrams involving the interplay of magnetism and superconductivity with many similarities to the phase diagrams of heavy-fermion materials [46].

While the heavy-fermion and organic superconductors raised many fundamental scientific questions of great interest, the idea that much higher $T_c$'s were out there was losing adherents in the 1980s. True, there was still a very large materials space to investigate but what was a reasonable way in? There were known oxide superconductors, some with quite respectable $T_c$'s, such as those based on the spinel-type compound LiTi$_2$O$_4$ with a $T_c$ around 12 K [47]. A surprise in the 1970s had been the perovskite related Ba (Pb,Bi)TiO$_3$, with $T_c$ again near 12 K [48]. Following theoretical arguments on electron band structure and electron-phonon interaction, Mattheiss expected a significant enhancement of $T_c$ by replacing Ba with K in BaBiO$_3$. Although the corresponding alloy with a remarkably high $T_c = 30$ K was found in 1988 [49], this was eclipsed by the bombshell of superconductivity in a layered perovskite-type material announced by Bednorz and Müller in 1986 [50]. They established that in Ba-doped La$_2$CuO$_4$ superconductivity sets in near 40 K. Others took up the thread and quickly found the onset of superconductivity at $T_c = 92$ K in YBa$_2$Cu$_3$O$_7$ [51]. This latter superconducting transition temperature was far beyond what most people believed might be achieved. It now seemed possible that superconductors would have widespread technological application because of $T_c$ having passed the boiling point of liquid N$_2$ at 78 K, a readily available and easily handled refrigerant. Further searches in cuprates eventually led to a present maximum in $T_c$ of 134 K in a Hg-based cuprate [52], rising to above 150 K under pressure [53].

The superconductivity in all the cuprates appears to originate in conducting CuO$_2$ planes and to exhibit strong 2D character. Understanding the physics of these layered materials has evolved slowly and is still in development. Their properties are unlike those of simple metals and the transition-metal intermetallics. Further, harnessing the cuprates to technological application has proven extremely challenging, and the initial optimism that we were about to enjoy a new technology enabled by superconducting devices has become more sober. Still, aspects of the high-$T_c$ cuprate superconductivity raise hope that we have not probed the limits yet. The idea that the superconductivity in cuprates primarily springs from a nonphonon mechanism suggests that structural instabilities due to very strong electron-phonon interaction will not set a barrier to $T_c$. Unexpectedly high $T_c$'s in phonon-
driven superconductors, such as MgB$_2$ [54] and K$_3$C$_60$ [55], both near 40 K, suggest that even the phonon boundary has not really been probed yet.

Very recently a new class of quasi-2D materials based on Fe-pnictide layers has appeared [56]. It includes structurally related layered FeP and FeAs systems, as well as compounds with Fe-chalcogenide (FeSe) layers, with $T_c$ as high as 55 K [57]. What is interesting here is that the FeAs layers appear to be able to superconduct in a variety of crystalline environments [58], a chemical flexibility that is both reminiscent of the cuprate superconductors and at the same time appearing to be amenable to a broader chemical variation experimentally. There is so far no indication that $T_c$'s in this class of materials will surpass those found in the cuprates, but what is important is rather the excitement that one now sees the hint of new routes to manipulate the chemistry of superconducting materials.

In the following chapters some of the exciting developments after 1980 are addressed in detail. They intend to demonstrate that progress in superconductivity, not only in raising $T_c$ but also in understanding the different situations in which this fascinating phenomenon may occur and in which forms it affects the subsystem of conduction electrons in solids, is, to a large extent, due to progress in materials synthesis and characterization.

REFERENCES

[2] According to history, the discovery was made by an accidental warming up of the sample from the base temperature provided by boiling liquid$^4$He.