

Chapter 1

Introduction

A superconductor is a material which exhibits the following two properties:

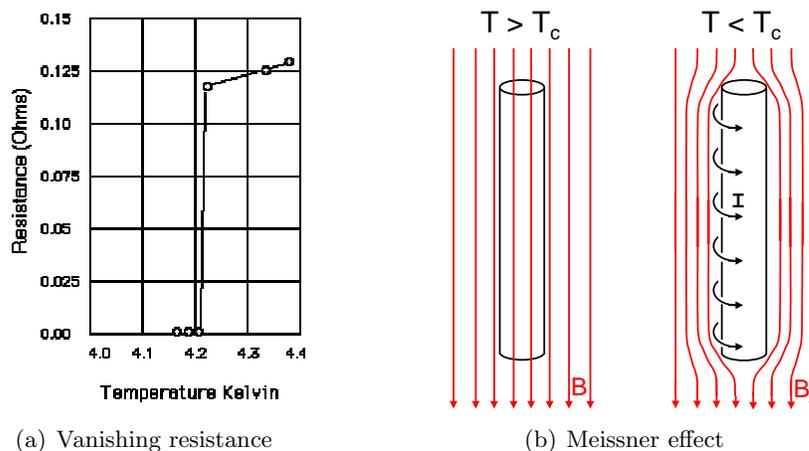


Figure 1.1: Two requirements for superconductivity: (a) vanishing of electrical resistivity below a critical temperature T_c , discovered in mercury by Kamerlingh-Onnes¹ in 1911; and (b) expulsion of magnetic flux below a critical field H_c , discovered by Meissner and Ochsenfeld² in 1933.^a

^aI attempted to find an original figure from the Meissner paper, to match this famous original figure from the Kamerlingh-Onnes paper. To my surprise, I found that despite reporting one of the most important results in experimental condensed matter physics, the original Meissner paper exists only in German, is a mere 3/4 of a page long, and contains no figures and no numerical data.

1.1 Conventional Superconductors

The phenomenon of superconductivity was first discovered in mercury by Kamerlingh Onnes¹ in 1911. As legend has it, Kamerlingh Onnes at first attributed the sudden drop in resistivity to an experimental error, such as an accidental short circuit. But careful repetition assured him that he had indeed discovered a new electronic phase. The discovery of vanishing resistivity in several other elements such as tin and lead soon followed.

The second, equally surprising characteristic of superconductivity, expulsion of magnetic flux from the superconducting state, was discovered by Meissner and Ochsenfeld in 1933.² Over the next several decades, theorists struggled to find a microscopic theory for superconductivity. Major advances were made with the London theory³ in 1935 and the Ginzburg-Landau theory⁴ in 1950. But it was not until 1957, a whole 46 years after the original experimental discovery of superconductivity, that a universally accepted microscopic theory of the phenomenon was put forth by Bardeen, Cooper, and Schrieffer.⁵

The basic idea of BCS theory is that electrons (fermions) pair via phonon coupling, and the pairs (bosons) condense into a single coherent ground state which allows the electrons to move cooperatively through the crystal without losing their forward momentum. The underlying points of the theory are that the Fermi surface is unstable to infinitesimal attractive forces,⁶ and phonon coupling provides such an attractive force.⁷ Therefore, the total energy of the system can be reduced by allowing electrons to pair, which causes an increase in kinetic energy but a much larger decrease in potential energy. The paired electrons have equal and opposite momentum, and must scatter in tandem, so the total momentum of the electrons in the system (i.e. the current) is conserved by scattering; thus the superconductivity.

Two of the key experimental facts that led to the BCS understanding of superconductivity were the following:

1. The density of states is gapped at the Fermi surface. This was determined experimentally first by the measurement of an exponential specific heat.^{8, 9} This led to the realization that some kind of pairing is occurring (i.e. electrons are thermally activated across a gap with Boltzmann probability). The gap was later confirmed by electromagnetic absorption in aluminum¹⁰ and lead.^{11, 12}
2. Phonons are involved. This was shown experimentally by the isotope effect:^{13, 14} the critical temperature T_c was found to vary as the inverse square root of the nuclear mass. Since the phonon frequency varies as $\sqrt{k/M}$, the discovery of the isotope effect

led to the realization that phonons are involved.

Armed with these and other experimental facts, BCS were finally able to put the whole picture together. Numerous details were filled in over the next few decades, but the problem of superconductivity was largely considered solved by BCS in 1957.

1.2 High-Temperature Superconductors

For obvious technological reasons, the search continued for materials which could superconduct at higher temperatures. Despite much work, for decades the highest T_c 's belonged to Nb_3Sn (18K) then Nb_3Ge (23K), and the field was considered by many to be at a dead end. A history of the increase in record T_c is shown in figure 1.2.

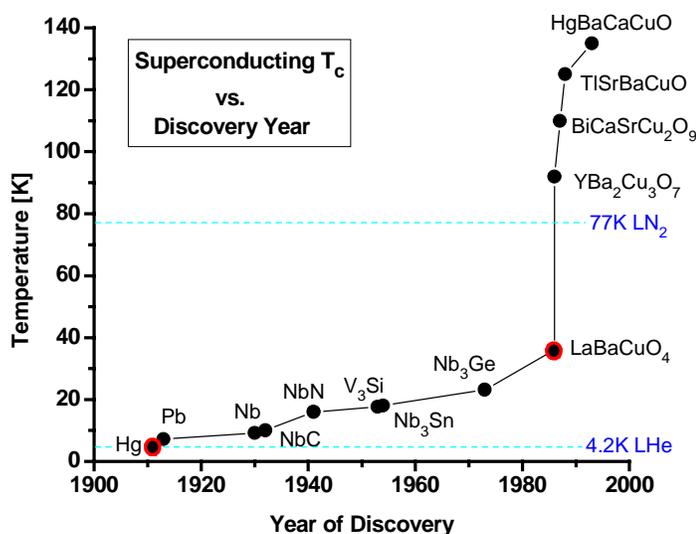


Figure 1.2: Highest T_c discovery history. (Points circled in red garnered a Nobel Prize for their discoverers: Kamerlingh-Onnes in 1913 and Bednorz & Müller in 1987.)

1.2.1 Discovery and Initial Questions

Three decades after BCS, in 1986, a startling discovery reopened the field of superconductivity research. Bednorz and Müller, working at IBM in Switzerland, discovered a new class of superconducting materials starting with LaBaCuO , which is superconducting up to 30 K.¹⁵ The following year, the liquid nitrogen temperature barrier (77 K) was broken with the discovery of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, superconducting at 90 K.¹⁶ Soon a whole host of related

materials were found. Since the common component in all these new high temperature superconductors is a CuO_2 plane, these materials are referred to as the “cuprates.”

The discovery of superconductivity in the cuprates was surprising for several reasons. No previous oxide superconductors had ever been found. Furthermore, in their stoichiometric form (with no additional oxygen or other dopant atoms added) these materials are antiferromagnetic Mott insulators. It is conventional wisdom that magnetism cannot co-exist with superconductivity. For example, Abrikosov and Gor’kov showed that magnetic impurities disrupt superconductivity and depress T_c .^{17, 18}

The obvious differences between these new high-temperature superconductors (HTSCs) and the old conventional superconductors created a great deal of excitement. Rapidly, all the old experiments which had lead to the unifying theory of conventional superconductors were repeated. But the results were often confusing and/or contradictory.

Pairing

It is now generally agreed that there is a gap in the density of states, but instead of the simple symmetric s -wave gap found in conventional superconductors, the gap is $d_{x^2-y^2}$ -wave. This was shown by flux modulation measurements in a YBCO DC-SQUID¹⁹ and then more unambiguously by flux quantization in a tri-crystal YBCO junction.²⁰ In simple terms, this $d_{x^2-y^2}$ -wave gap means that electrons traveling different directions in the crystal feel a different pairing potential.

As would be expected from the gap in the density of states, it is generally agreed that electrons are paired. It was shown unambiguously by measurement of $h/2e$ flux quanta,²¹ which indicates that the charge carriers have charge $2e$.

It is not generally agreed what causes the pairing. Of course the first thing to look for is phonons, but tests for the isotope effect have been inconclusive, in part because it’s not clear which phonons are key. The cuprate crystal structures are much more complicated than the conventional superconductors, with typically four or five different elements per unit cell. Different atoms are involved in different phonons, so it’s not obvious which isotope should be varied. No clear dependence of T_c on isotope has been found.

Because magnetism is known to play a role in the crystal at low carrier concentration, many argue strongly that electron pairing in high temperature superconductivity is caused by magnons or other magnetic consequences. But there are also strong arguments that pairing is indeed caused by phonons.²²

Doping

Perhaps the most notable complicating factor in the high- T_c superconductors is the existence of a whole new parameter which can be tuned: carrier concentration. This leads to a 3-dimensional phase diagram rather than the simple temperature vs. B -field phase diagram of the conventional superconductors. In HTSC materials, the stoichiometric parent compounds are insulators, and it is not until charge carriers are added that these materials become superconducting. Typically charge carriers in the form of holes are added by doping oxygen interstitially (e.g. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$), by substituting a monovalent atom with a divalent atom (e.g. replacing La with Sr in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$), or by removal of oxygen from their stoichiometric positions (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$). In any case, the carrier concentration is an important variable upon which the properties of the material depend strongly. We now have a 3-dimensional phase diagram, as shown in figure 1.3.

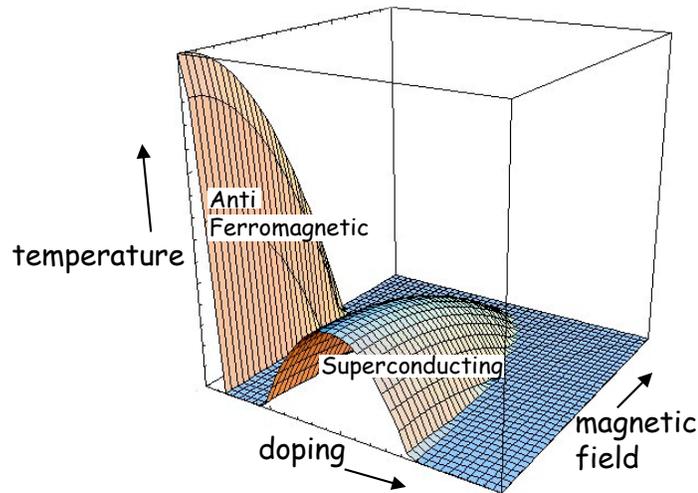


Figure 1.3: High- T_c 3-dimensional phase diagram. The state of the system is parameterized by carrier concentration (doping), temperature, and magnetic field. Two known phases are antiferromagnetism (at low doping) and superconductivity; little is known about the electronic structure throughout the rest of phase space.

There have also been discovered many electron-doped superconductors, with a phase diagram that is approximately the mirror image of the hole-doped materials. But the T_c 's of the electron-doped materials are not as high, and these materials will not be discussed in this thesis.

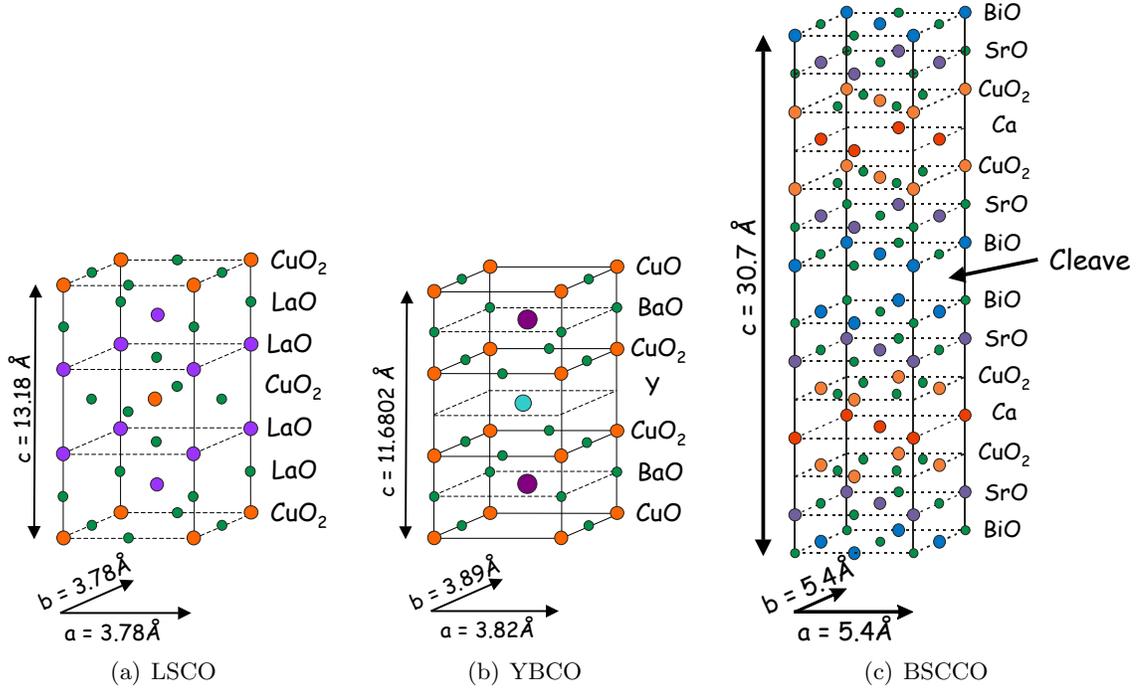


Figure 1.4: Structure of the three high- T_c cuprate superconductor families: (a) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, (b) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and (c) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

1.2.2 Materials and the Proliferation of Experiments

There are three main families of hole-doped high temperature superconductors studied today. However, much of the confusion in the study of HTSC results from the fact that each material is accessible to different experimental techniques. For example, it is easy to measure the electronic density of states of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, but harder to measure its magnetic properties. In the quest to find a unifying theory for all HTSC, it is tempting to treat these three families as one material, and combine the experimental results from all families. Because of this common practice, the field of high- T_c research is rife with conflict and apparent contradictions.

A good summary of the zoology of many of the known hole-doped HTSC materials along with an explanation of the variation in their T_c 's is given by Eisaki *et al.*²³

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

The lanthanum family of high- T_c 's was the first family of materials to be discovered, by Bednorz and Müller in 1986.¹⁵ The structure of LSCO is shown in figure 1.4(a).

LSCO is physically the hardest of the three materials, and with stronger bonds it is easier to grow large (> 1 cm!) single crystals. Neutron scattering experiments, which probe the magnetic structure of the material, are typically limited to studying LSCO because of their requirement for large single crystals.

But LSCO has not been successfully studied with an STM, because so far there has been no successful recipe to obtain an atomically flat surface with tunnel access through an insulating layer to the relevant unperturbed CuO_2 plane.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

The discovery of YBCO followed that of LSCO within a year.¹⁶ YBCO was the first material to break the 77 K (liquid nitrogen) temperature boundary. The optimal T_c is now ~ 90 K. The structure of YBCO is shown in figure 1.4(b). YBCO has perhaps been the most highly studied because it is the cleanest and most ordered crystal. But studies of YBCO can also be quite confusing because there are two CuO planes: the square plane and the chain plane. By analogy with the other HTSC families, it is thought that the superconductivity originates in the square plane, but it is hard to isolate the behaviors of the planes.

Furthermore, the one-dimensional chains complicate the study of YBCO crystals, because as-grown crystals display many domains, separated by “twin boundaries” in which the chains run orthogonal directions. YBCO crystals may be “de-twinning” by application of pressure, for more careful studies, but many existing results on YBCO are ambiguous due to twin domains.

YBCO is not an ideal material for STM studies, because it typically cleaves on the chain plane. Very nice studies can be made of the chain planes with an STM,²⁴ but this is not usually thought to access the intrinsic superconducting properties of the material.

YBCO has typically been used in nuclear magnetic resonance (NMR) studies, which probe the spatial distribution of magnetic field. This is because YBCO is so well ordered that all atoms of a particular species will live in the same electronic environment (not true for BSCCO or LSCO).

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

Finally we come to BSCCO, the favorite material for STM and ARPES. BSCCO was discovered in 1988.²⁵ BSCCO itself can have one, two, or three CuO planes, where

T_c increases with the number of planes. Bismuth can also be replaced with thallium or mercury, which results in the highest T_c material known (142K).

BSCCO competes with YBCO as the most technologically useful material. YBCO has been used in magnetic field applications because it is easier to pin flux. YBCO can be used to grow high- T_c SQUIDS with grain-boundary Josephson junctions. Their higher operating temperature than conventional SQUIDS makes them useful in the study of living biological materials. BSCCO has been more useful so far in bulk applications: it has been formed into superconducting wires (with silver) and placed into the Detroit power grid, but problems in maintaining vacuum have delayed the success of this operation.

The structure of BSCCO is shown in figure 1.4(c). Surface sensitive techniques such as STM and ARPES can study BSCCO because it cleaves easily between layers, leaving an atomically flat surface for study, and, it is thought, direct tunnel access to the relevant unperturbed CuO_2 plane. However, the down-side of the easy cleavability of BSCCO is that the weak bonds make it very difficult to grow large single crystals. Therefore, magnetic experiments such as neutron scattering, which require large crystals for measurable signals, are challenging at best, and often impossible.

1.2.3 Phase Space and the Proliferation of Theories

Because these materials have three tunable parameters (temperature T , magnetic field B , and carrier concentration p), there is a vast expanse of unexplored phase space available for theoretical prediction. We already know there are at least three phases present: antiferromagnetic, superconducting, and neither. But what other phases exist, and how do they interact? For example, is antiferromagnetism competing with superconductivity or is it somehow helping? Since doping p is tunable at zero temperature, are some phases connected by quantum critical points?²⁶

The more experiments published, the more hints of new phases, transitions, and quantum critical points seem to pop up, which in turn incites theorists to even more creative predictions. A sampling of the predicted phases includes:

1. resonating valance bond (RVB) state by Anderson (1987)²⁷
2. staggered flux phase (SFP) by Affleck and Marston (1988),^{28, 29, 30}
later work relating to SFP as a “spin gap” phase by Wen *et al.* (1996);³¹
and SFP in vortices by Kishine *et al.* (2001)³²

3. stripes by Zaanen and Gunnarson (1989);³³
later Kivelson and Emery and Zachar (1998)^{34, 35} and White and Scalapino (1998)³⁶
4. multiple “stripe” and “checkers” phases of various periodicities by Löw *et al.* (1994)³⁷
5. $SO(5)$ theory by S.-C. Zhang (1997)³⁸
6. spin density wave (SDW) by Vojta and Sachdev (1999)³⁹;
coexisting SDW + superconductivity by Demler *et al.* (2001)⁴⁰
7. time-reversal symmetry breaking phase by Varma (2000)⁴¹
8. d -density wave (DDW) phase by Chakravarty *et al.* (2001)⁴²
9. fractionalized nodal liquid (superconductivity without pairing) by Senthil *et al.* (2001)⁴³
10. QED3 phase by Franz *et al.* (2002)⁴⁴
11. gossamer superconductivity by Laughlin (2002)⁴⁵

Both the staggered flux phase and the d -density wave phase may fit reasonably well with most existing data. At low energies, both the staggered flux phase³⁰ and the d -density wave phase⁴² have the same single particle spectrum as a d -wave superconductor, so experiments which measure density of states may support the existence of SFP or DDW phases. The idea of a spin density wave phase also finds strong support from neutron scattering experiments, and almost certainly plays a key role in some areas of phase space. The quantitative predictions of Demler *et al.*⁴⁰ for coexisting SDW + superconductivity in a magnetic field are particularly well matched by elastic neutron scattering experiments.⁴⁶

One phase which has garnered a lot of recent attention and vocal supporters is electronic “stripes”, a phase in which the doped holes self-segregate into one-dimensional charge rivers spaced approximately four unit cells apart. There is no doubt that some form of stripes do exist in materials closely related to high temperature superconductors,⁴⁷ but it appears that stripes are at their strongest where superconductivity is itself suppressed. Some vehemently argue that stripes are a necessary part of the mechanism of high temperature superconductivity itself,⁴⁸ while some believe that stripes are an unrelated or even competing part of the phase diagram.

1.3 Organization of this Thesis

In this thesis, I will report on experiments we have done with a scanning tunneling microscope to elucidate the nature of the superconducting quasiparticles in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. From these results we can make inferences about the phases present in the material across a range of doping and magnetic field. All measurements reported in this thesis were obtained at 4.2 K and far below the upper critical field H_{c2} , so the material was always in a bulk superconducting state.

In chapter 2, I will describe the measurements one can make with a scanning tunneling microscope. The measurements reported in this thesis were all obtained with a home-built STM mounted on a high vacuum, 250 mK ^3He fridge, constructed by Shuheng Pan and Eric Hudson, in the Davis group at Berkeley.⁴⁹ (I have also modified this design and built a UHV-compatible STM to be used for variable temperature studies. Details of this construction can be found in Appendix C and details of the vibration environment required for proper functioning of an STM can be found in Appendix B.) In addition, I will briefly summarize some other experimental techniques, such as angle-resolved photoemission spectroscopy, neutron scattering, and nuclear magnetic resonance, which can be used to measure or infer complementary information about the density of states.

In chapter 3, I will discuss the relationship between \vec{R} -space and \vec{k} -space in BSCCO. I will describe Fourier transform scanning tunneling spectroscopy (FT-STs), or how an STM can actually access both \vec{R} - and \vec{k} -space simultaneously. FT-STs is used to investigate the nature of quasiparticles in optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ at 4.2 K in zero applied field. From these studies I conclude that there is no need to invoke an alternative phase to explain results in optimally doped BSCCO.

In chapter 4, I will talk about extending the search for alternative phases, using an applied magnetic field. Although H_{c2} is too large for us to destroy bulk superconductivity, we can use our local probe to investigate the modified electronic structure within a single vortex. Here we find a periodic modulation of the electronic density of states which may signify the onset of a new phase.

In chapter 5, I will talk about extending the search for alternative phases into the underdoped side of the phase diagram. Although extremely underdoped crystals are not available for bulk studies, I will give brief evidence for inhomogeneity in underdoped samples, which enables access to nanoscale patches of far underdoped regions of phase space. I will describe the use of both intentionally introduced impurities and native defects to probe the electronic structure of the far underdoped phase.

Finally, I conclude that although no alternative phases are needed to explain the behavior of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ at low temperature, zero magnetic field, and optimal doping, there are definitely some interesting phases lurking just away from optimal doping along all three axes of phase space. The use of STM as a local probe has enabled me to obtain information about two directions in phase space (low doping and high field) for which bulk samples are currently unavailable. In both cases, I find evidence for a starkly different electronic structure than the simple d -wave superconducting order.

Forty-six years elapsed between the original discovery of low-temperature superconductivity in 1911 and its explanation by BCS in 1957. Maybe by the year $1986 + 46 = 2032$ there will be enough experimental information available for a brilliant trio of scientists to present an underlying theory for these even more complex high- T_c materials.



Figure 1.5: Perhaps the future solvers of high-temperature superconductivity are somewhere in this crowd. (Photo taken at the first International Conference on Women in Physics in Paris, France in 2002, attended by more than 250 women physicists from around the world.)