PHYS 798C Spring 2024
Lecture 1 Summary
The Three Hallmarks of Superconductivity, Thermodynamics and Limits of Superconductivity

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I. INTRODUCTION

Superconductivity (SC) is a science which has a deep underlying theoretical basis. Almost all measurements of superconductors can be backed up with solid, essentially exact, theoretical calculations. It is very important to learn and understand this theory. One of the objectives of this class is to teach you how to do basic calculations using a variety of powerful methods. The theory of SC has also deeply influenced the approach to many other problems in condensed matter physics. The attempts to understand high temperature superconductivity, electronic pairing mechanisms, topological superconductors, and other highly correlated electron systems, are at the frontiers of theoretical condensed matter physics. All superconductors are characterized by three universal hallmarks. Anyone who claims to have discovered a new superconductor must unambiguously demonstrate that the material displays these three hallmark properties. The 3 Hallmarks of SC:

A. Zero Resistance

Zero resistance was discovered by H. Kamerlingh Onnes in 1911. Onnes was the first to liquefy He. He measured the resistance of Hg as a function of temperature, and discovered that its resistance goes to zero, $R \to 0$, at 4.2 K.

The temperature at which $R \to 0$, *in the limit of zero current* (i.e. $I \to 0$), is defined as the critical temperature, T_c. This temperature is material specific. Experimental values of T_c range from 0.3 mK for Rh, to 9.2 K for Nb, to more than 30 K for $La_{2-x}Sr_xCuO_4$, to more than 145 K for the Hg-Ba-Ca-Cu-O family of cuprate superconductors. These latter two compounds are examples of High-T_c Superconductors (HTS), and have all been discovered since 1986. The transition temperature is also a function of certain thermodynamic variables, such as pressure (pressure changes the distance between atoms in the solid, which in turn changes the degree of electron overlap and itinerancy). One interesting observation is that good metals (e.g. low resistivity metals like Cu, Ag, Au) tend to be 'bad' superconductors (i.e. no measurable T_c), whereas 'bad' metals (high resistivity) tend to be 'good' superconductors (i.e. higher T_c values). This is because sometimes the mechanism that causes scattering in the normal state is also the mechanism that produces pairing of electrons in the superconducting state.

The class web site shows plots of T_c vs. time, made in different eras. One interesting thing to note is that the recently discovered Hydrogen-rich room temperature superconductors are believed to have the same pairing mechanism as the first superconductor discovered in 1911! The other remarkable observation is that there are diferent "families" of superconductors shown in these diagrams. It is believed that different families can have quite different electron-pairing mechanisms, showing that superconductivity is a robust and general phenomenon, which is enabled by numerous different methods of pairing.

The most dramatic demonstration of zero resistance comes from measurements of persistent currents in closed superconducting rings (Onnes 1914). The circulating current creates a solenoidal magnetic field, which can be measured with great precision using a SQUID magnetometer (to be discussed later in this course). It is found that these currents show no sign of decay on the time scale of 1 year. Gough showed a resistance of less than $10^{-13}\Omega$ for a 10^3 second persistent current in a high-temperature superconductor sample.

The zero resistance state can also be used to generate very large and very stable magnetic fields by making a superconducting solenoid. This is probably the single most profitable application of superconductors today. The creation of practical superconducting solenoids did not occur until the early 1960's with the development of type-II superconductors with strong pinning of magnetic vortices. Most MRI machines and high-end NMR spectrometers use superconducting magnets. Superconducting magnetic energy storage (SMES), and electric grid voltage regulation, are also important applications of superconductors. The recent proliferation of companies promising to develop nuclear fusion reactors are utilizing HTS tapes that can carry enormous currents with zero loss at temperatures on the order of 50-75 K.

The technology for developing multi-km-long tapes of HTS wire with excellent uniformity and pinning properties has emerged over just the past few years.

Zero resistance has applications in high-current (as opposed to high-voltage) transmission lines. High voltages, and low currents, are used to transport electric power over great distances using normal metals because the Ohmic losses $P = I^2R$ are minimized. Stepping up the voltage, and down the current, minimizes the losses. Superconductors offer very limited benefit for high voltage transmission because the losses of normal conductors can be made reasonably small and the expense of cooling the superconductor is simply not justified. However, superconductors do offer benefits for high current transmission. This is demonstrated in a recent high current line installed in New York using HTS wires and cables cooled with liquid nitrogen. The Electric Power Research Institute has made extensive studies of superconducting power transmission lines.

B. The Meissner Effect

A superconductor can be distinguished from a mere perfect conductor (i.e. $R = 0$) through the Meissner effect. Consider a superconducting sphere at a temperature above T_c in a static external magnetic field. After some time, the eddy currents in the sample will have died away because of the sample's finite resistance. If the material is now cooled below T_c, it will spontaneously develop screening currents which will actively exclude magnetic flux from the interior of the sample. This is shown schematically in Fig. 1 below.

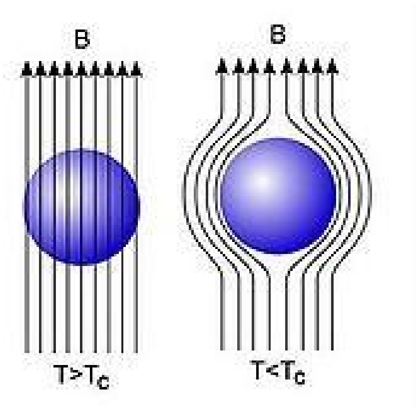

FIG. 1. A spherical metal object in the normal state ($T > T_c$) on the left and in the superconducting state ($T < T_c$) on the right. The applied magnetic field, shown by the vertical arrows, is static.

A material, which went from ordinary conductor to perfect conductor at T_c, would not show the Meissner effect in a static magnetic field. It would instead trap the magnetic flux inside itself, as it became a perfect conductor. The Meissner effect is best defined as the development of a perfect diamagnetic state in a static external magnetic field. Deep inside a superconductor in the Meissner state one has $\vec{B} = \mu_0(\vec{H} + \vec{M}) = 0$. This means that the material has generated a diamagnetic response with $\vec{M} = -\vec{H}$, and is at the root of the simple magnetic levitation effect demonstrated in class. This effect demonstrates that superconductivity and magnetism are generally (although not universally) incompatible. It implies that a large enough magnetic field applied to the sample can destroy superconductivity.

C. Macroscopic Quantum Phenomena

The superconducting state is fundamentally and uniquely a quantum state of matter. A single complex macroscopic quantum wavefunction, which is phase coherent over macroscopic distances, can be used to describe the superconductor in many circumstances. This wavefunction describes a condensate of paired electrons. The superconductor can be described by a complex order parameter $\Psi(\vec{r}) = |\Psi(\vec{r})|e^{i\phi(\vec{r})}$, where $\phi(\vec{r})$ is the position-($\vec{r}$) dependent phase factor. As such, the material can show unique macroscopic quantum phenomena such as the Josephson Effect, magnetic flux quantization, and macroscopic quantum superpositions.

Brian Josephson predicted that pairs of electrons could tunnel through a classically forbidden region (barrier) between two superconductors even at zero potential difference. The tunnel current depends on the difference in phase of the superconducting order parameter on either side of the barrier: $I = I_c \sin(\phi_1 - \phi_2)$, where I_c is the critical (or maximum) current and ϕ_i is the phase of the macroscopic wavefunction for superconductor i.

Josephson also predicted that a constant voltage difference ΔV imposed between the two superconducting electrodes will cause the phase difference to increase linearly with time as $\Delta\phi = 2e\Delta V t/\hbar$, where $\hbar$ is Planck's constant divided by 2π. This results in a current between the electrodes which oscillates with angular frequency $\omega = 2e\Delta V/\hbar$.

This order parameter must be single-valued throughout the superconductor. This in turn implies that $\phi(\vec{r})$ return to the same value (modulo 2π) for any closed circuit taken through a superconductor. Consider a superconductor with a hole in itself (like a donut or bagel). Following a path C through this material which encloses the hole (but stays entirely inside the superconductor) will lead to the conclusion that the magnetic flux $\Phi = \oint_C \vec{A} \cdot d\vec{l}$ must be quantized in integer multiples of the quantum of magnetic flux $\Phi_0 = h/2e$. This unit of flux involves only fundamental constants of nature (Planck's constant and the charge of the electron). We shall see that the factor of 2 arises from the microscopic phenomenon of Cooper pairing of the quasiparticles in the metal.

The Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity has at its heart a ground state superconducting wavefunction that includes the subtle quantum correlations between all of the electrons in the metal. The ground state wavefunction is a coherent state of the electrons and has a well defined phase, establishing a microscopic explanation for the macroscopic quantum phase discussed above.

II. THERMODYNAMICS OF SUPERCONDUCTORS

The most dramatic thermodynamic signature of superconductivity is the discontinuous jump of *electronic* heat capacity at T_c. The discontinuity is due to a fundamental re-arrangement of the electronic states that occurs at T_c. The discontinuity, or jump, in heat capacity $(c_s - c_n)/c_n$ is predicted to have a universal value for superconductors according to BCS theory, and corresponds to about a 140% increase at T_c. One can recover the electronic entropy by integrating the specific heat: $\Delta S = \int_{T_1}^{T_2} \frac{C_e(T)}{T} dT$. As shown on the class web site, the electronic entropy is lower in the superconducting state as compared to the normal state at the same temperature. The free energy density f_s is also lower than that of the normal state f_n by an amount that is maximum at $T = 0$, but decreases monotonically to 0 at T_c. This finite free energy density difference $f_s - f_n$ is known as the condensation energy, and plays an important role in the Ginzbug-Landau theory that we consider later.

III. PHENOMENOLOGY OF SUPERCONDUCTIVITY (T_c, J_c, H_c)

There are limits to the domain of superconductivity. SC is destroyed for temperatures above T_c because the thermal agitation energy breaks up the pairs which constitute the SC ground state. The superconductor is able to support large current densities, J. These currents carry significant kinetic energy because the currents flow without dissipation or scattering. There is a limit to the free energy gain of the superconducting state relative to the normal state. The critical current density, J_c, is reached when the kinetic energy in the current carried by the superconductor equals the free energy gain of the SC state over the normal state. Silsbee's rule states that when the surface self-magnetic field created by the current approaches the critical field (see below), superconductivity will be destroyed.

Similarly, due to the incompatibility of magnetism and SC, there is a limit to how large a magnetic field a superconductor can exclude in the Meissner state. This is the critical field, H_c. An estimate of the critical field comes from comparing the energy density of the magnetic field required to destroy superconductivity to the free energy gain: $\mu_0 H_c^2(T)/2 = f_n(T) - f_s(T)$ where f_n and f_s are the Helmholtz free energy densities in the normal and SC state at temperature T and zero magnetic field. It was found empirically that the critical field has an approximately parabolic dependence on temperature:
$H_c(T) \approx H_c(0)[1 - (T/T_c)^2]$. Note that $H_c(T)$ is often called the thermodynamic critical field, to distinguish it from other critical fields that will arise later.

This implies that the free energy difference goes continuously to zero at $T = T_c$, implying a second order phase transition at T_c in zero field. In finite field at temperatures below T_c there is a latent heat associated with the transition, making it first order.

There is also a spectroscopic (frequency) limit to superconductivity. The Cooper pairs that make up the superconducting correlations have a finite binding energy, so to speak. When photons with energy greater than this energy (called 2Δ) are absorbed by the superconductor, the result is a breaking of the Cooper pairs and weakening of the superconducting state. This imposes an upper frequency limit for superconducting electromagnetic response, roughly on the order of $f_{max} \sim 2\Delta/h$, where h is Planck's constant.

A. Type I, II Superconductors

Superconductors come in two flavors, Type I and Type II. They are distinguished by their response to a magnetic field. A Type I superconductor does not compromise, it is either superconducting in the Meissner state, or it is a normal conductor when the applied magnetic field exceeds the thermodynamic critical field, H_c. Depending on geometry of the sample, a type-I superconductor can enter a "compromise state"' known as the intermediate state. The regions of superconducting and normal material act in some sense like two immiscible fluids. Type II superconductors, on the other hand, will compromise with the magnetic field and create a "mixed state"' in which magnetic field is allowed to enter the superconductor but only in discrete flux-quantized bundles, called magnetic vortices.