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Developments in Superconductivity¹

Douglas Finnemore

Abstract. Key experiments leading to our present understanding of superconductivity are reviewed.

Superconductivity is a low temperature metallic state characterized, as the name suggests, by an immeasurably large electrical conductivity. Historically this phenomenon was discovered by Kamerlingh Onnes in 1911 during an investigation of the electrical resistivity of very pure mercury. He noted a precipitous drop in the resistance of his sample in a temperature interval of a few thousandths of a degree Kelvin (see Figure 1). The drop was at least a factor of 10^5 , and, within the accuracy of his experiment, the resistivity went to zero. He further noted that the effect was relatively insensitive to additions of small amounts of impurity, thus ruling out the possibility of its being due to the presence of a perfect lattice. The conclusion was that the metal had transformed into a new "superconducting" state. More sophisticated measurements capable of detecting resistivities 10⁻¹² times the resistivity of very pure copper have failed to show any trace of resistance. The importance of this discovery, both from the fundamental aspect of understanding how electrons can traverse a metal with no energy loss, and from a practical aspect of relieving difficulties which arise from Joule heating, is readily apparent.

In the years following the initial discovery, it was determined that temperature and magnetic field are two important parameters governing the occurrence of superconductivity. The situation may be briefly summarized as follows. In zero magnetic field, certain metals and alloys enter the superconducting state at the critical temperature, T_c , and remain superconducting at lower temperatures. The value of T_c is a characteristic physical property of the substance, ranging in value from 0.14° K for iridium to 18.0° K for Nb₃Sn. At temperatures below T_c , the application of a sufficient magnetic field destroys the superconductivity and the metal reverts to the normal state, having substantially the characteristics of the metal above T_c . The field strength necessary to quench superconductivity, when plotted as a function of temperature (Figure 2) forms a phase boundary entirely analogous to the solid-liquid phase boundary in a sub-

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stance such as water. This boundary, characteristically varying from zero to a few hundred gauss, is called the critical field curve.¹

Consider for a moment a model we might use for a metal at low temperatures. Take for instance a cube of lead 1 cm on a side. The lead nuclei are distributed on a cubic lattice approximately 2Å apart with the core electrons remaining bound to the nuclei in much the same manner as in a free atom. The valence electrons, however, are to a good approximation free to roam throughout the crystal. Thus we have a picture of free electrons moving in a background of a positively charged lattice. In a real crystal at a temperature above absolute zero, there will, of course, be impurities, dislocations, and lattic vibrations to scatter electrons as they move through the crystal. For each free electron there will be a quantum state describing its motion. and. by the Pauli Principle there will be only one electron per state. Knowing the equations of motion and the boundary conditions, one can compute these electronic energy levels and fill them, starting from the lowest energy state, until all the valence electrons are placed in the metal. The highest energy state used for an electron (at 0°K) is called the Fermi Energy or Fermi Level. There are in general more quantum states for the electron just above the Fermi Energy which can be excited thermally or by an external stimulus. The task we set for the remainder of this talk is to obtain clues as to how electrons in a superconductor can flow through a metal in the presence of impurities and lattice vibration with no energy loss.

An important breakthrough came in 1933 when Meissner and Ochsenfeld² inferred from their experiments that a simply connected superconductor (i.e. one with no holes) has zero magnetic field, B, in the interior of the sample regardless of the magnetic and thermal history. Before this experiment it was thought that a substance having zero resistance would, by Lenz's Law, trap whatever flux was present in the sample at the time of transition. That is, 'Lenz's Law would not permit any change in the flux linkage after the zero resistance state was established. Thus it was thought that the state of magnetic induction would depend on the history of the sample and that the transition would be irreversible in a thermodynamic sense. The Meissner and Ochsenfeld experiment, however, indicated that the flux was pushed out or excluded from the sample when a transition was made in a finite magnetic field. Further quantitative experiments have shown that the flux is excluded from all but a layer approximately 10⁻⁶ cm thick on the surface of the specimen. In this surface layer are the so-called supercurrents which cancel the external field to give zero field inside. It might be

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mentioned in passing that these current densities are greater than -06 A per cm² when shielding against 100G. Energy is required to push the field out, and, as we see from the critical field curve, there is a maximum field which the superconductor is capable of pushing out. Hence measurement of the critical field curve is equivalent to measuring the energy (technically the Magnetic Gibbs Free Energy) difference between the superconducting and normal states. A simple calculation shows this energy difference to be of the order of 10⁻⁷ eV per atom. This is an exceedingly tiny energy when compared with the Fermi Energy of about 5 eV. Looking at the model described earlier, it should be pointed out that for thermal scattering (i.e. scattering energy transfer of the order of kT) only those electrons with energy within kT of the Fermi Energy can participate (Figure 3). All the other electrons buried in the Fermi sea have no empty states to which they can scatter. The fraction of electrons within kT of the Fermi level is about 10^{-4} . Combining this figure with 10^{-7} eV per atom, one concludes that the important excitation energy might be of the order of 10⁻³ eV per participating electron. This same result might also have been guessed from the fact that the average thermal energy at temperatures where superconductivity exists is of the order of 10^{-3} eV.

Another breakthrough came in the late 1950's, when Tinkham and coworkers³ found that there was a gap in the energy states available for free electrons at the Fermi Level. That is, when shining photons through a thin film of superconductor, he found that photons with energy less than approximately 10^{-3} eV were not absorbed. Above this threshold energy, absorption rose from zero to the value characteristic of the normal metal (Figure 4). Many independent experiments have corroborated these results. This experimental evidence helps our understanding of zero resistance as follows. In a normal metal we think of resistance as arising by scattering of electrons by lattice vibrations or impurities. In the superconducting phase, however, the states to which most of the electrons would scatter have been removed. There are, however, some scatterings with energy transfer larger than the gap energy and these might contribute to resistance. Therefore the existence of a gap eliminates the low energy scattering, but by itself it is not sufficient to explain the complete vanishing of resistance.

A further breakthrough came in 1961 when Deaver and Fairbanks⁴ at Stanford and Doll and Nabauer⁵ in Germany experimentally demonstrated that the flux linking a hollow superconducting cylinder is quantized. Consider for a moment the electrons induced to flow around a cylindrical shell (Figure 5) by a changing external field. The momentum associated with these



electrons should be quantized according to the familiar Bohr-Sommerfeld quantization rule

$p \cdot dl = nh.$

With a little manipulation, it is easy to show that these quantized momentum states imply that the flux linking the cylinder is quantized in units of $\frac{nhc}{dr}$, where q is the charge on the quantized entity. If q is the charge on the electron, e, then the flux quanta should be about 10⁻⁷ G cm². The experiment was carried out using cylinders with 10⁻³ cm diameter and hence 1963]

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a magnetic field quantum unit of about 0.1 G. The first striking result of this experiment is that quantization effects are manifested on a macroscopic scale. The second result is that the quantized unit is $\operatorname{not} \frac{\operatorname{hc}}{e} \operatorname{but} \frac{\operatorname{hc}}{2e}$, thus implying that the quantized entity has charge 2e.

We have said nothing about the considerable theoretical advances in the past few years. Most notable was the theory of Bardeen, Cooper, and Schrieffer (BCS) in 1957, which hinges on long range correlations between pairs of electrons to create the energy gap and to describe a current-carrying, lossless state. Thus, the flux quantization showing that the current-carrying entity has charge 2e is a striking experimental confirmation of the basic BCS pairing ideas.

The discussion above does not attempt to completely explain the phenomenon of superconductivity. Instead, some of the key experiments have been presented to display the most important aspects as we now understand them. A full explanation requires a thorough understanding of quantum mechanical processes in many-particle systems.

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Concentricity Determinations for Hollow Cylindrical Shapes Utilizing Resonant Energy¹

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Abstract. The inner to outer diameter concentricity relationship of several long, hollow cylindrical shapes was de-termined by evaluating their wall thickness uniformity. This was accomplished through the utilization of the ultrasonic resonance gauging technique.

It is difficult, if not virtually impossible, to determine the inner to outer diameter concentricity relationship of long hollow cylindrical shapes, such as tubing, by conventional methods. For this reason the following is suggested.

¹ Bock Island Arsenal, Rock Island, Ill.