6 What Causes Superconductivity?

Following Kamerlingh Onnes' discovery of zero resistance, it took a very long time to understand how superconducting electrons can move without hindrance through a metal. Attempts to explain from first principles how superconductivity comes about proved to be one of the most intractable problems of physics. Progress required more than just new data; it needed an innovative theoretical framework built around radical new ideas. There are inherent difficulties in achieving this. Fundamentally new concepts are not discovered by observation alone but require new modes of imaginative thought, which by their very nature are unpredictable and elusive.

One day in 1955, when John Bardeen, Bernd Matthias and Theodore Geballe were driving between Murray Hill and Princeton, the question was raised: "What are the most important unsolved problems in solid state physics?" After a characteristic lengthy pause, Bardeen suggested that superconductivity must be a candidate. Later in 1957, in collaboration with Leon Cooper and Robert Schrieffer, he was to provide a most ingenious, and generally accepted, explanation of superconductivity founded on quantum mechanics. The physical principles underlying this BCS theory are the concern of this chapter. It has become evident that while the BCS theory gives a reasonable description of superconductivity in the "conventional" superconductors, known at that time, that is not the case for more recently discovered "unconventional" materials, such as the high temperature superconducting cuprates (which will be discussed separately in Chapter 11).

BCS theory has established that superconductivity in conventional materials arises from interactions of the conduction electrons with the vibrations of the atoms. This interaction enables a small net attraction between pairs of electrons. Before insight into this electron pairing and a subsequent ordering can be gained, some characteristics of superconductors need to be brought to mind.

Superconductivity is a common phenomenon; at low temperatures many metals, alloys and compounds are found to show no resistance to flow of an electric current and to exclude magnetic flux completely. When a superconductor is cooled below its critical temperature, its electronic properties are altered appreciably, but no change in the crystal structure is revealed by X-ray crystallographic studies. Furthermore, properties that depend on the thermal vibrations of the atoms remain the same in the superconducting phase as they were in the normal state. Superconductivity is not associated with any marked change in the behavior of the atoms on the crystal lattice. However, although superconductivity is not a property of particular atoms, it does depend on their arrangement. For example white, metallic tin is a superconductor but grey, semiconducting tin is not. Another of the many examples illustrating an involvement of the atomic arrangement is that while the usual semimetallic form of bismuth is not superconducting, even at a temperature as low as 10^{-2}K, several of its crystalline forms, which can be obtained under high pressure, are. Although the atomic arrangement is important, it need not be regular in the crystalline sense; even some glassy materials can become superconducting. For example, bismuth when condensed onto a cold finger surface at 4K forms an amorphous film; in this form it is superconducting. Amorphous metals have recently become very important materials. Alloys can be frozen in an amorphous state by cooling them extremely quickly from the melt; some are superconductors.

The conduction electrons themselves must be responsible for the superconducting behavior. A feature which illustrates an important characteristic of these superconducting electrons is that the transition from the normal to the superconducting state is very sharp: in pure, strain-free single crystals it takes place within a temperature range as small as 10^{-3}K. This could only happen, if the electrons in a superconductor become condensed into a coherent, ordered state, which extends over long distances compared with the distances between the atoms. If this were not so, then any local variations from collective action between the electrons would broaden the transition over a much wider temperature range. A superconductor is more ordered than the normal metal; this means that it has a lower entropy, the parameter that measures the amount of disorder in a system. In an analogous way, the entropy of a solid is lower than that of a liquid at the same temperature; solids are more ordered than liquids. A crucial conclusion follows. When a material goes superconducting, the superconducting electrons must be condensed into an ordered state. To understand how this happens, we need to know how the electrons interact with each other to form this ordered state. That mechanism is the essence of the BCS model.

The Isotope Effect

In the search for the nature of the interaction that binds the electrons together, there was a key question to answer. How do the atoms or their arrangement in a solid assist in the development of superconductivity? An important clue to the form of the way in which they interact with the electrons came from experimental observations in 1950 that the critical temperature T_c depends on the isotopic mass M of the atoms comprising a sample. Many elements can have nuclei having different numbers of neutrons and so have different masses. These isotopes of a given element have identical electronic structure and chemical properties. If the atoms are involved, then changing their mass might be expected to have an effect on superconducting properties. Kamerlingh Onnes himself had looked at this possibility as early as 1922. At that time there were available to him two naturally occurring forms of lead (Pb) having different masses; the more abundant, with an atomic mass M of 207.2, comes from non-radioactive ores, the other from uranium (U) derived lead has a mass M of

206. These two forms of lead differ in mass because they are made from different mixtures of isotopes. In those early days the sensitivity of Onnes' measuring equipment was not good enough to enable him to detect any difference between the superconducting transition temperatures T_c of specimens containing different amounts of lead isotopes. Later experiments made by others, again using lead, were also unable to detect an effect of atomic mass on transition temperature T_c. However with the development of nuclear reactors after World War II, it became possible to make artificial isotopes in sizeable quantities and in turn samples having wider mass differences; at last experiments could be carried out which were able to detect the effect of the atomic mass on transition temperature T_c. The required high sensitivity of measuring temperature is illustrated by the fact that for mercury T_c varies only from 4.185K to 4.146K as the atomic mass is changed from 199.5 to 203.4.

The measurements made on mercury samples having different isotopic masses, and later on lead and tin, showed that the superconducting transition temperature T_c is proportional to the inverse square root of the atomic mass M (that is T_c is equal to a constant divided by $\sqrt{M}$). Therefore the critical temperature of a sample composed of lighter isotopes is higher than that for a sample of heavier isotopic mass. Changing the isotopic mass alters neither the number nor the configuration of the orbital electrons. This *isotope effect* shows that the critical temperature T_c does depend upon the mass of the nuclei, and so the vibrating atoms must be involved directly in the mechanism which causes superconductivity. The argument is greatly strengthened by the fact that the frequency of atomic vibrations in a solid is also inversely proportional to the square root ($\sqrt{M}$) of the nuclear mass: this correlation strongly suggests that the lattice vibrations must play an important role in the process leading to the formation of the superconducting state.

It is firmly established that the electron–lattice interaction plays a central role in the mechanism of superconductivity in conventional materials. Now at low temperatures, the lattice vibrations, which carry heat or sound, are quantized into discrete energy packets called phonons (from the Greek *phonos* for sound). It is usual to talk about the electron–phonon interaction. In 1950, Herbert Fröhlich from Liverpool University, yet another émigré from Nazi Germany, first tried to produce a theory of the superconducting state based on electron–phonon interactions, which yielded the isotope effect but failed to predict other superconducting properties. Fröhlich realized that electron–phonon interactions could explain the paradox that those elements that are the best conductors of electricity (copper, silver and gold) do not become superconductors even at temperatures as low as 10^{-3} while poorer conductors like lead (T_c = 7.2K) and niobium (T_c = 9.5K) have the highest transition temperatures of the elements. A strong electron–phonon interaction results in a high scattering level of electrons by the thermal vibrations and hence comparatively poor conductivity – but it does enhance the likelihood of superconductivity. By contrast the noble metals copper, silver and gold are good conductors because the scattering of electrons by phonons is weak – so weak an interaction that in fact it precludes them from being superconducting. A somewhat similar approach to constructing a theory based on electron–phonon interactions made independently in 1950 by Bardeen at the University of Urbana, Illinois in the U.S. also ran into difficulties. Fresh ideas were needed.

Working Towards a Successful Theory

The next crucial step towards an acceptable explanation of how superconductivity occurs at the microscopic level was made in 1956 by Leon Cooper – guided by Bardeen. The crucial realization is that superconductivity is associated with a bound pair of electrons, each having equal but opposite spin and angular momentum, travelling through the metal. Building on this idea, Bardeen, Cooper and Schrieffer, working at the University of Urbana, Illinois, produced a theory in which superconductivity is considered to arise from the presence of these "Cooper pairs". Of the three men, John Bardeen was by far the most senior and eminent. For much of his scientific career he had been intrigued by superconductivity. He recognized that a complete theory required the use of more sophisticated techniques such as quantum field theory, which was then just beginning to be introduced. To develop the required expertise, he had attracted Cooper, an expert in this area, to Urbana in 1955. Together with J. Robert Schrieffer, who had arrived at Illinois in 1953 as a graduate student from MIT, Bardeen and Cooper began a comprehensive assault on developing a microscopic theory of superconductivity. They were spurred on by the realization of competition from several other physicists studying the same problem, among them Richard Feynman, one of the most innovative and inspirational theoreticians of his generation.

Towards the end of 1956, success for the three seemed to be as far away as ever and Schrieffer confided in Bardeen that he was beginning to turn his efforts towards other more tractable problems. After all scientific progress is made by working on soluble problems! At the time, Bardeen was about to travel to Stockholm to receive the Nobel Prize for physics for the invention of the transistor. He received this award jointly with Walther Brattain and William Shockley for work that the three of them had carried out at the Bell Telephone Laboratories in Murray Hill, New Jersey in the late 1940s. Bardeen encouraged Schrieffer to continue with the superconductivity problem since he felt that they were close to success. The turning point came early in 1957 when they managed to deduce what is known as the correct ground state wave function for the superconducting electrons. This was followed by a frantic effort on the part of all three men as the details of the theory were worked out. After a preliminary note submitted to the journal *Physical Review* in February 1957, they worked on a much more substantial paper which appeared in the same journal in October of that year. This second paper, elegantly written and comprehensive, has become one of the classic papers of condensed matter physics, widely quoted and influential. The BCS theory accounted for many of the experimental observations, such as the existence of an energy gap $2\Delta(0)$ between the superconducting and normal states. A large number of experiments have confirmed this predicted value of the energy gap in the conventional superconductors. Recognition of the significance of their work came with the award of the 1972 Nobel Prize in Physics to Bardeen, Cooper and Schrieffer. For John Bardeen this was his second Nobel Prize in Physics, the only person ever to be so honored. For one person to develop the theory of both semiconductors and superconductors is a truly remarkable intellectual achievement and places Bardeen among the greatest physicists of the twentieth century.

In the next section the physical principles, which underlie the BCS theory are described in more detail. This requires a more theoretical argument; if this is not your scene at all, and you are happy with accepting the fact that exchanging phonons (heat) can hold a pair of electrons together then do not bother to read the accompanying boxes!

Physical Principles of the BCS Theory

One of the first steps to take when developing any theory of a physical phenomenon is to make an assessment of the energy involved. Superconductivity takes place at a lower temperature than normal state behavior; when a superconducting solid is heated above its critical temperature T_c, it goes into the normal state. Therefore, to drive a superconductor normal, energy is needed; this would be thermal energy, if the superconducting state is to be destroyed by increasing the temperature above the critical temperature T_c. However, it is also possible to drive a material normal by applying a magnetic field equal to a critical value. This magnetic behavior makes it easy to determine the energy difference between normal and superconducting states: all that is required is to measure the value of the critical magnetic field that destroys superconductivity. When this is done, it is found that the energy difference between the normal and the superconducting states is extremely small. For many pure metals, the critical magnetic flux density (B_c) at the 0K limit required to destroy superconductivity is of the order of only 0.01Tesla. This leads to an order of magnitude estimate of the condensation energy ($=\mu_0 B_c^2$) of only 10^{-8}eV per atom. To physicists struggling with the development of a theory of superconductivity, such a very small value of the superconducting energy presents a major obstacle: it is several orders of magnitude smaller than the energies involved in many processes always present in metals (for example, Coulombic interactions between the electrons lead to a comparatively enormous correlation energy of the order of 1eV per atom). The small energy difference between the normal and superconducting states may also be compared with the energy of about 5eV for the conduction electrons in the normal metal. It is simply not possible to calculate the energy of the normal state electrons to the accuracy required to be able to separate off the tiny change due to the normal to superconducting transition. Any attempt at calculation of the condensation energy seems bound to fail because the much larger energy of other processes would be expected to mask that of the interaction responsible for the superconducting state. To avoid this dilemma, Bardeen, Cooper and Schrieffer assumed that the only important energy difference between the normal and the superconducting states arises from the interaction leading to superconductivity: they took the only reasonable theoretical approach of assuming that all interactions except the one causing superconductivity (i.e. Cooper pairing in the BCS theory) are unaltered at the normal to superconducting state transition. They assumed that the only energy change involved when a material goes superconducting is that due to *the formation and interaction of the Cooper pairs.*

That electrons in a metal can pair at all is remarkable because they have the same charge and normally repel each other. So it is no surprise that the energy of electron pairing is extremely weak. In principle, only a small rise in temperature is enough to break a pair apart by thermal agitation and convert it back to two normal electrons. Nevertheless if the temperature is taken down to a sufficiently low value, the electrons do their best to get into the lowest possible energy states, so some pair off. The repulsion between electrons is overcome in two ways. First, some of the negative charge of an electron is blocked off or screened by the motions of other electrons. Second, an intermediary can bring the electrons together into pairs, which then behave more or less like extended particles. The first step in the formulation of a theory of superconductivity is to describe the nature of the interaction, which causes the pairs to form. A simple, commonly used analogy for such an interaction is given by two rugby football players, who can pair by passing the ball back and forth between them to avoid being tackled as they run up-field. The question is what corresponds to the ball in a superconductor? Answer: a phonon, the quantized packet of heat. You can find out more about phonons in Box 4.

Box 4

Phonons, the quantized packets of heat vibrations

Heat and sound are propagated in solids as thermal waves. Such lattice, or thermal, vibrations are waves propagated by displacement of the ion cores. The energy and momentum of these waves are quantized; thermal vibrations of frequency ν_q may be treated as wave packets with energy $h\nu_q$. These quantized packets are called "phonons" by analogy to the "photons" of electromagnetic radiation. The word photon was devised from the Greek *photos* for light, phonon from that *phonos* for sound. Since a phonon has both direction and magnitude, it has to be described as a vector quantity **q**, which is called the phonon wave-vector and has a value of $2\pi/\lambda$, λ being the wavelength of the associated thermal wave. This wave-particle duality of heat and sound arises as a result of the de Broglie hypothesis, which relates the momentum **p** ($=mv$) of a particle of mass m and velocity v and the wavelength λ, by:

$$p = h/\lambda,$$

where h is the Planck constant. Hence, since the value of **q** is $2\pi/\lambda$, the phonon momentum is $\hbar\mathbf{q}$, where the usual practice of writing $\hbar$ for $h/2\pi$ has been adopted. The energy of a phonon is much less than that of the conduction electrons in a metal, which are those electrons at the Fermi level and have the highest energy.

The discovery of the isotope effect suggested that interaction between electrons in states near the Fermi level and phonons is closely connected with the development of the superconducting state. In the case of an electron pair the "rugby football" being passed between two players and holding them together is a phonon. Electrons remain paired by exchanging phonons. The electron−phonon pairing mechanism, when embodied in the BCS theory, works extremely well for explaining superconductivity in conventional materials. The phonon acts as the "matchmaker" bringing the electrons together into pairs. The interaction between an electron and a lattice vibration can be treated as a collision between particles. Figure 6.1(a) illustrates this collision or scattering process, which is treated in more detail in Box 5.

Box 5

Interaction between electrons and phonons in Cooper pairs

On collision with a phonon, an electron of wavevector **k** absorbs the phonon and takes up its energy $h\nu_q$ (which is in general much less than that of the electron) and is scattered into a nearby state of wavevector $\mathbf{k}'$. Essentially, the electron has absorbed heat from the lattice and is now in a quantized state of different energy. The energy must be conserved in the process so that the new energy $E(\mathbf{k}')$ of the electron is the sum of its former energy $E(\mathbf{k})$ and that $h\nu_q$ of the absorbed phonon:

$$E(\mathbf{k}') = E(\mathbf{k}) + h\nu_q. \tag{1}$$

When the electron absorbs the phonon, it also takes up its momentum and changes its direction; this process is illustrated in Figure 6.1(a). Another basic law of the physical world has also to be obeyed: momentum must also be conserved:

$$\therefore\ \hbar\mathbf{k} + \hbar\mathbf{q} = \hbar\mathbf{k}' \text{ or } \quad \mathbf{k} + \mathbf{q} = \mathbf{k}' \tag{2}$$

just as it would be for collision between two billiard balls. However, electrons are different from billiard balls: not only can an electron moving through a crystal lattice absorb phonons, it can also emit them. In this case, illustrated in Figure 6.1(b), the conservation of momentum leads to

$$\mathbf{k}' = \mathbf{k} - \mathbf{q}. \tag{3}$$

Particularly important in the BCS theory are so-called "virtual phonons". A solid can be thought of as teeming with virtual phonons, which exist only fleetingly. Indeed an electron moving through a lattice can be considered as continuously emitting and absorbing phonons: it is "clothed" with virtual phonons. Virtual states can be thought about in terms of the Heisenberg uncertainty principle in the form $\Delta E \Delta t \approx \hbar$. A phonon, which remains in a state for a time Δt, has an energy uncertainty ΔE. If the lifetime Δt of the phonon is very short, the energy uncertainty ΔE is very large and the phonon can transfer more energy than allowed by the law of conservation of energy. Over a period of time long compared with $\hbar/\Delta E$ energy must be conserved.

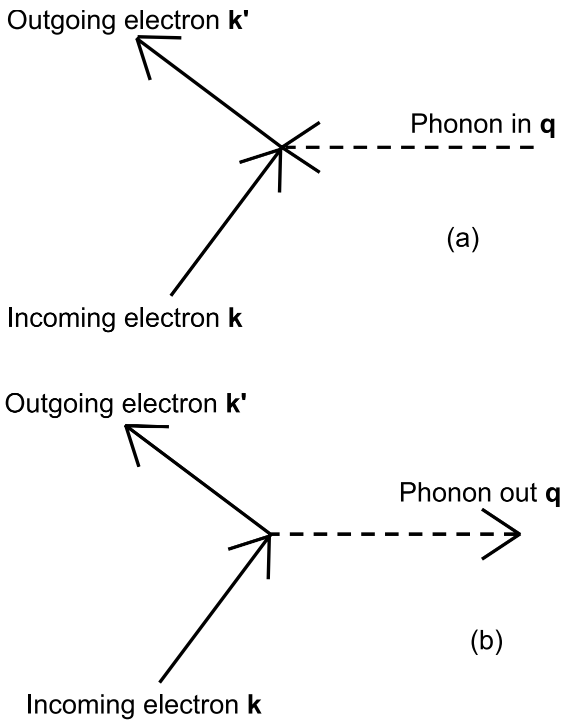

Figure 6.1 (a) Absorption of a phonon of wave-vector **q** by an electron in a state of wavevector **k**. The incoming phonon **q** is shown as the dotted arrow and the incoming (**k**) and outgoing (**k**′) electron as the filled arrows. (b) When an electron in a state **k** gives out a phonon of wave-vector **q**, it loses the energy of the phonon and goes into a new state **k**′.

Electron-virtual phonon processes play a central role in the development of the superconducting state. Cooper showed that electrons may be considered as being bound together in pairs by mutual exchange of virtual phonons. The process involved is illustrated in Figure 6.2. An electron in a state $\mathbf{k}_1$ near the Fermi surface emits a virtual phonon **q** and scatters into a state $\mathbf{k}_1'$. The law of conservation of momentum requires that for this process:

$$\mathbf{k}_1' = \mathbf{k}_1 - \mathbf{q}. \tag{4}$$

Another electron in a state of $\mathbf{k}_2$ absorbs the virtual phonon and is scattered to a state $\mathbf{k}_2'$ which is defined as:

$$\mathbf{k}_2' = \mathbf{k}_2 + \mathbf{q}. \tag{5}$$

The two electrons, which exchange virtual phonons in this way, have interacted dynamically. Momentum must be conserved for the whole process; therefore from equations (4) and (5) above:

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2' = \mathbf{K}. \tag{6}$$

Here **K** is the total momentum of the pair. In principle the interaction between the electrons may be either repulsive or attractive, the determining factor being

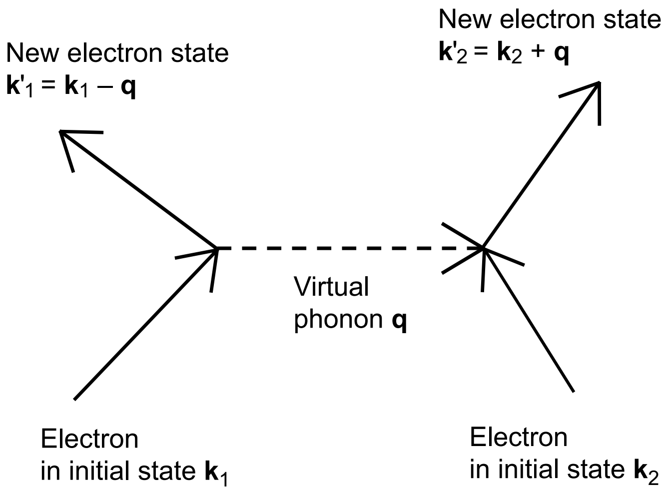

Figure 6.2 The process which binds two electrons into a Cooper pair. It is an interaction between the two electrons, which are in initial states with wave-vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, by exchange of a virtual phonon of wavevector **q**. The electrons go into new states $\mathbf{k}_1'$ and $\mathbf{k}_2'$.

the relative magnitudes of the phonon energy $h\nu_q$ and the energy difference between the initial and final states of the electrons. Cooper demonstrated that a weak attractive force could exist between pairs of electrons in a metal at low temperatures. For bonding between electron pairs to occur, the net attractive potential energy ($-V_{ph}$) arising from virtual phonon exchange must be larger than the Coulombic repulsive energy (V_{rep}) between the electrons. Therefore, using the convention that a negative potential energy gives rise to attractive forces, the energy balance being:

$$-V_{ph} + V_{rep} < 0.$$

A simple picture illustrates how an attractive force might arise between electrons in a lattice. As an electron moves through the lattice of positively charged ions, motion of the ions is disturbed in the near vicinity of the electron. The positive ions tend to crowd in on the electron: a screening cloud of positive charge forms around the electron. A second electron close by can be attracted into this region of higher positive charge density. The process in a two-dimensional square lattice is illustrated in Figure 6.3. If the ionic vibrations and the charge fluctuations produced by the first electron are in the correct phase, then the Coulombic repulsion between the two electrons is counteracted and the electrons are attracted into each other's screening clouds. The attractive energy between the electrons is increased when the electrons have opposite spin. By the process of exchanging phonons, the electrons in a Cooper pair experience mutual attraction at a distance.

The average maximum distance at which this phonon-coupled interaction takes place in the formation of a Cooper pair is called the *coherence length* ξ. In the early 1950s the Russian theorists Vitaly Ginzburg and Lev Landau produced an important phenomenological description of superconductivity, which had first introduced this concept of a coherence length. Their compatriot Lev Gorkov later showed that the

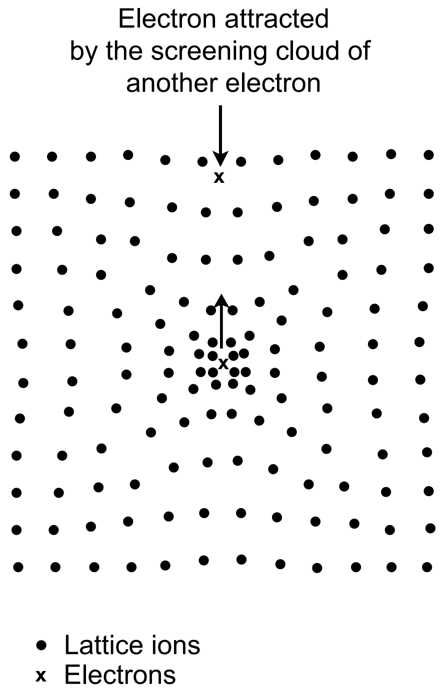

Figure 6.3 Attraction of an electron, shown by the cross (×), into the screening cloud of positive ions pulled in towards another electron (×) at the center of the picture. The sketch is very diagrammatic. The process of interaction is dynamic and both electrons distort the lattice.

Ginzburg–Landau theory can be derived from the BCS theory: both give equivalent results close to the superconducting critical temperature. The coherence length is fundamental to superconductivity and emerges as a natural consequence of the BCS theory.

One way of estimating a value for the coherence length is to apply a nearly critical magnetic field to a superconducting sample. Then parts of the sample near the extremities go into an intermediate state, a laminar structure composed of both normal and superconducting regions. The boundary between each normal and superconducting region is not sharp but has a finite width; physical properties also vary through the boundary. Careful examination of the boundary shows that it results from the long range of influence of the superconducting electrons over a macroscopic distance of about 10^{-4} cm., which is the coherence length.

Long-range order or coherence takes place between electrons in superconductors and is a measure of the sphere of influence of a Cooper pair. Coherence suggests that the waves associated with the pairs are macroscopic in extent and overlap considerably with each other.

This coherence results in a superconductor behaving rather as if it is a "giant molecule" i.e. an "enormous quantum state". In the early nineteenth century, when Ampère had proposed that magnetism can be understood in terms of electric currents flowing in individual atoms or molecules, it was objected that no currents were known to flow without dissipation. He has long since been vindicated by quantum theory, which gives rise to stationary states in which net current flows with no resistance. A superconductor is a dramatic macroscopic manifestation of a quantum mechanical state, which behaves like a giant molecule with no obstruction for electron flow: there is no resistance.

The Superconducting Energy Gap: a Fundamental Difference Between the Arrangements of the Electron States in Superconducting and Normal Metals

A crucial feature of the superconducting state is the existence of an energy gap at the Fermi level region of the excitation spectrum of superconductors. Electrons are not allowed to possess energies within this forbidden range of energy. The Cooper pair states exist just below the energy gap. The energy gap corresponds to the energy difference between the electrons in the superconducting and normal states. The confirmation of this long suspected feature of the arrangement of the states available for electrons in superconductors was a decisive step in the development of an understanding of superconductivity. This energy gap arises as a result of the interaction of the Cooper pairs to form a coherent state in which the superconducting electrons have a lower energy than they would have in the normal state. More formally, a central prediction of the BCS theory is that the Cooper pairs form a condensed state whose lowest quantum state is stable below an energy gap of value 2Δ, which separates the superconducting states from the normal ones. An important test of the BCS theory was to measure this gap and compare the value obtained with that predicted.

At an early stage it was noticed that a superconductor looks the same as the normal metal: there is no change in its appearance, if a metal is cooled below the critical temperature. This means that the reflection and absorption of visible radiation by a superconductor are the same as those in the normal state. However by contrast, a superconductor shows great differences in its response towards flow of a.c. and d.c. currents from those found in the normal state. Unlike normal metals, superconductors exhibit no resistance to direct current flow; but towards an alternating current they do show some resistance and this increases as the frequency goes up. If the alternating frequency lies in the infra-red region above about 10^{13} cycles/sec or beyond into the visible light range, superconductors behave in a similar manner to normal metals and absorb the radiation. That is why they look the same as normal metals in visible light.

This difference between the behavior of a superconductor towards high and low frequency provides evidence for the existence of the energy gap and suggests one way of measuring it. In normal metals, when photons of electromagnetic radiation are absorbed, electrons are excited into stationary states of higher energy. A fundamental property of superconductors is that they can absorb electromagnetic radiation only above a threshold frequency. Behavior of this type is characteristic of materials with a gap containing no allowed energy states in the energy spectrum. Electrons in states just below such an energy gap (usually said to be of value 2Δ) cannot be excited across the gap unless they absorb a photon of sufficient high energy to enable them to bridge the gap completely. The threshold frequency ν_g for absorption of radiation

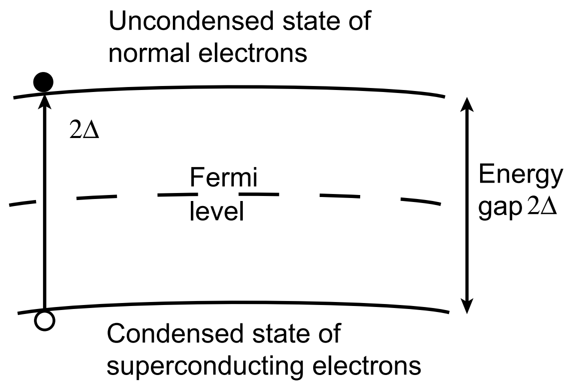

Figure 6.4 In a superconductor the energy gap is centred at the Fermi level. This diagram is an expanded small part close to the surface of the sphere shown in Figure 5.7.

is given by $2\Delta/\hbar$. Absorption of radiation beyond the threshold frequency ν_g by a superconductor occurs because pairs of electrons in the condensed superconducting state are excited by the radiation across the energy gap into states in which electrons exhibit normal behavior. From infrared absorption experiments, among others, the measured gap (2Δ) is found to be in agreement with the BCS predicted value of about $3.5k_BT_c$, k_B being Boltzmann's constant and T_c the critical temperature. The energy gap is centered at the Fermi level, as illustrated in Figure 6.4. The width of the energy gap is such that photons with a high enough energy to enable Cooper pairs to be split and surmount this threshold energy ($\hbar\nu_g$) lie in the short microwave or the long infrared region, until recently a range of the electromagnetic spectrum not readily accessible to experiment (see Chapter 9). Therefore, the gap is not that easy to observe and so its discovery was long delayed. Recognition of the existence of the gap gave a much clearer picture of the structure of the energy states in superconductors and an important indication of the type of theory necessary to explain superconductivity. In summary, in a superconductor the electron pairs form a condensed state below an energy gap that separates the superconducting states from those available for normal electrons.

The BCS Model of a Conventional Superconductor

Cooper had shown that there can be a small net attractive force between pairs of electrons; hence pairs are able to exist at low temperatures. Below the critical temperature, pairing of the electrons close to the Fermi surface is the more stable configuration in the superconducting state and reduces the total energy of the system. This is why pairing takes place. An electron pair does not behave like a point particle but instead its influence extends over a distance of about 10^{-4} cm. in agreement with the experimental measurements of the coherence length. In consequence the volume of a Cooper pair is about 10^{-12}cm^3. But there are about one million other Cooper pairs in this region: the spheres of influence of the pairs overlap extensively. It is no longer possible to talk about isolated pairs because the electrons continually exchange partners with each other; that is the same as saying that the pairs interact with each other. Overlap between the waves of the two electrons in a pair and then in turn between the waves associated with the pairs results in the coherence and produces the condensed state in a superconductor. The electron pairs collect into what may be likened to a macromolecule extending throughout the metal and capable of motion as a whole.

The BCS theory is based on this interaction between pairs of electrons to form a giant quantum state. A superconductor can be visualized as a complex square dance of Cooper pairs which are all moving in time with each other and exchanging partners continuously. This "*dance to the music of time*" comprises the condensed state that has more order and is lower in energy than that of the electrons in a normal metal. BCS propose, as the criterion for the formation of the superconducting state, that Cooper pairs are produced at low temperatures and that this is the only interaction in a superconductor that results in an energy different from that of the normal state. To simplify the problem, BCS calculate the superconducting properties for the simple model of a metal having a spherical Fermi surface, which has been described in Chapter 5 and illustrated in Figure 5.7. They make the further simplification that only those electrons near the Fermi surface need be considered in the formation of the condensed superconducting state. If the average phonon frequency in the metal is ν_g, the electrons, which can be bound together into Cooper pairs by exchange of phonons, are those within an energy $\hbar\nu_g$ of each other. Electrons within this small energy range near the Fermi surface are bound together in pairs while all the others outside this thin shell remain unpaired. This abrupt, somewhat arbitrary, cut-off usually gives satisfactory results. In fact, subsequent work indicates that the results of the BCS theory are not particularly sensitive to the form of the cut-off.

Just as all ideal gases obey Boyle's law, conventional superconductors comply with the BCS theory and behave in the same general fashion as each other.

In the BCS model the coupled pairs of electrons have opposite spin and equal and opposite momentum (see Box 6) and are condensed into a giant state of long-range order extending through the metal – such an extraordinary feature of the superconducting state that it needs to be considered further separately (Chapter 7).

Since all the pairs are in harmony with each other, the whole system of correlated electrons resists rupture of any single pair. Therefore, inherent to the system is the property that a finite energy is necessary to break up only one pair. In a normal metal, electrons at the Fermi surface can be excited by what is, to all intents and purposes, an infinitesimally small energy, whereas in a superconductor pair correlation produces a small but finite energy gap, whose value $2\Delta(0)$ at the absolute zero is given by a famous BCS formula relating the gap to the critical temperature T_c

$$2\Delta(0) = 3.5k_B T_c.$$

The 2 comes about in the left hand side of this equation because a pair of electrons has to be broken up for energy to be absorbed. Excited, single-particle, "normal" states are separated from the correlated pair states by this energy gap. A single electron is a fermion. But a bound Cooper pair acts as a boson; this is because

Box 6

Electrons in a Cooper pair have opposite momentum and spins

When the bonding between pairs is as strong as possible, the system is at equilibrium because the energy is at a minimum. Interaction between the pairs is strongest when the number of transitions of electrons from pair to pair is as large as possible. This occurs when the total momentum of each pair is the same as that of any other pair. The condition satisfying this is that the total momentum **P** is zero. Now by the de Broglie hypothesis **P** is equal to $\hbar\mathbf{K}$, so that the total wave vector **K** (see Box 5) of each electron pair is also zero. In this situation, the electrons in each pair must have equal and opposite momentum. Then

$$\hbar\mathbf{k} + \hbar(-\mathbf{k}) = \hbar\mathbf{K} = 0 \qquad \text{or} \qquad \mathbf{k} + (-\mathbf{k}) = 0.$$

A further prerequisite for minimum energy is that the electrons in each pair have opposite spin. The net spin on a pair is zero. This means that the pairs are bosons. Now bosons do not obey the Pauli exclusion principle so that they can all occupy the same state (see Chapter 5). In a superconductor all the Cooper pairs are condensed into the same state. Hence it is possible to depict the arrangement of the electron states by the simple energy level diagram shown in Figure 6.5.

if both electrons in a pair are changed, the sign of the wave function is altered twice and thus is unchanged (theoreticians say that it is invariant under this transformation). Since the pairs are bosons, all of them are contained in the same state of lowest energy. The energy levels into which electrons can go for a superconductor can be

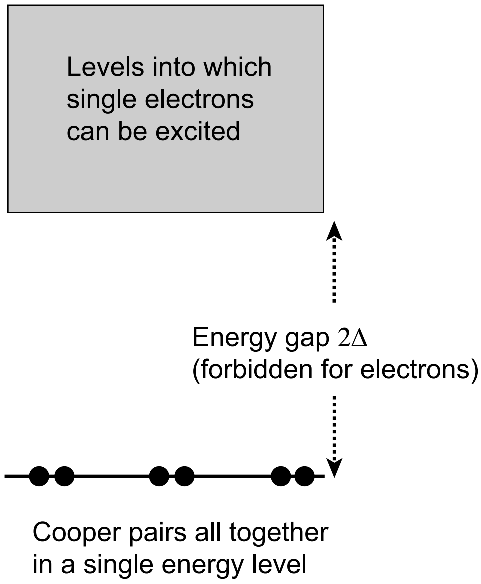

Figure 6.5 The arrangement of the energy levels in a superconductor. All the Cooper pairs collect into a single level, which is separated by the energy gap from the higher states into which single electrons can be excited.

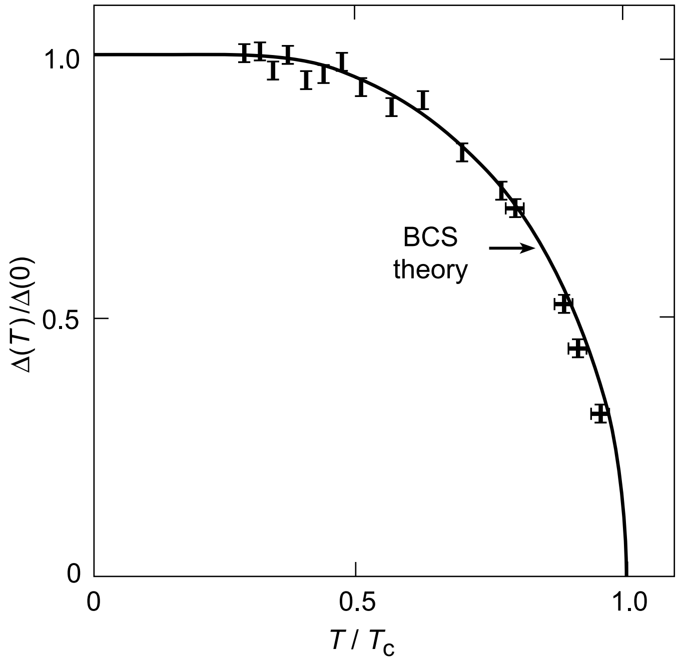

Figure 6.6 The way in which the superconducting energy gap $2\Delta(T)$ varies with temperature T. The energy gap $2\Delta(T)$ at a temperature T has been divided by that $2\Delta(0)$ at the absolute zero. This reduced energy gap $\Delta(T)/\Delta(0)$ has then been plotted as a function of the reduced temperature T/T_c. The full curve shows the BCS prediction of the temperature dependence of the energy gap. The experimental points are those found for an indium–bismuth alloy and are in good agreement with the theoretical prediction.

shown in a simple way (Figure 6.5). The Cooper pairs all exist in one level separated by the energy gap 2Δ from a higher energy band of single levels into which normal electrons (from split pairs) can be excited.

That the BCS theory should result in an energy gap and predict its magnitude was one of its major triumphs. For conventional superconductors experimental measurements of the energy gap are in good agreement with this BCS theory prediction. For example for aluminium T_c is 1.14K and the measured gap extrapolated to the absolute zero of temperature is $3.3k_BT_c$ ($\equiv 3.4\times10^{-4}$eV) while the BCS theory predicts $3.5k_BT_c$.

At any finite temperature there are always a few electrons which have been excited thermally across the gap. This reduces the number of electron pairs and the correlation energy becomes correspondingly less. Therefore, as the temperature T is increased, the energy gap $2\Delta(T)$ becomes smaller, as illustrated in Figure 6.6. At the critical temperature the energy gap vanishes, there are no pairs and the normal state is assumed.

The BCS model bears a strong resemblance to the earlier two-fluid model pioneered by Gorter and Casimir (see Chapter 2). In a superconductor at any finite temperature below the critical temperature T_c, there are two different kinds of electron states. Occupied excited states above the gap contain single electrons, while in the condensed, superconducting state below the gap the electrons are paired and the pairs are correlated. When pairs are present, they short-circuit the normal electrons: the pairs carry the "supercurrent". Now that we have acquired some of the basic ideas about the nature of superconductors, we can have a look at the mechanism by which the electrons in pair states can carry a "supercurrent" without resistance – that sensational discovery made by Kamerlingh Onnes.

Zero Resistance and Persistence of Current Flow in a Superconductor

A successful microscopic theory of superconductors must provide an adequate description of the mechanism of resistanceless flow of persistent current. The BCS model does this.

Current flow in a superconductor, which is described in more detail in Box 7, resembles that in normal metals, save for one fundamental difference: individual supercurrent-carrying electrons cannot be scattered. In the superconducting state all the electron pairs have a common momentum and there is long-range correlation of momentum. The usual situation is that resistance to current flow can only occur when scattering processes transfer electrons into empty, lower energy states with momentum in the opposite direction to the electron current. Although this process occurs in normal metals (Chapter 5 (Box 3, illustrated in Figure 5.10), it can not take place in superconductors. Figure 6.7(a) shows schematically the occupation of states in a superconductor which is not carrying current; states with opposite momentum at the Fermi level are bound into Cooper pairs. When a current is passed, there is increased momentum in the direction of the flow of Cooper pairs, as shown in Figure 6.7(b). If the electrons in the highest energy states on the right hand side of Figure 6.7(b) could be scattered into the empty states on the left hand side, this would lead to a decrease in momentum along the direction of electron current flow: there would be electrical

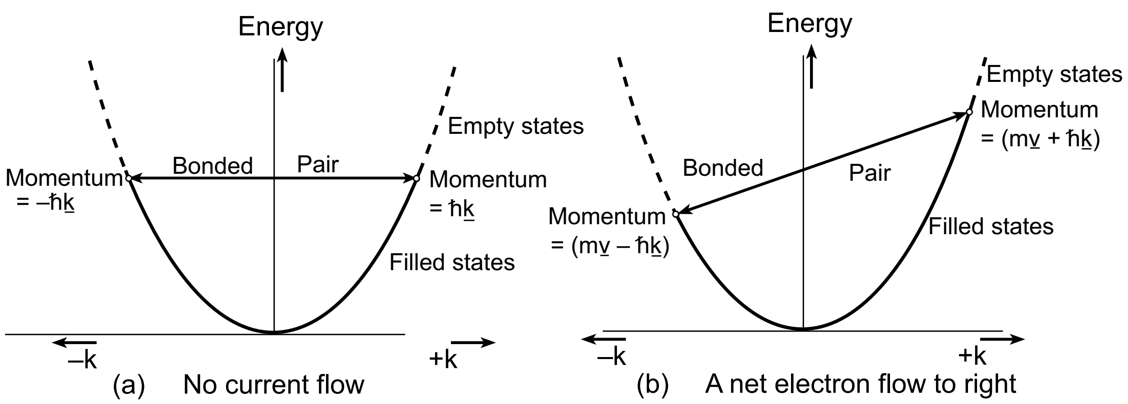

Figure 6.7 The effect of an electric field on the occupation of the available **k**-states in a one-dimensional superconductor. The full lines drawn on the lower energy states in the parabolic bands show states filled with electrons, while the dotted lines at higher energies represent empty states. The double headed arrows connect electron pairs with opposite momenta. In case (a) there is no applied field, while there is an applied field in case (b). For scattering to take place, electron pairs must be disrupted to allow electrons in the higher energy states on the right hand side to go into the empty, available, lower energy states on the left hand side. This cannot happen.

resistance. However, such scattering processes would necessitate the splitting up of electron pairs and their removal from the condensed state. It is just this process that the correlated electron pair system resists most strongly. For a pair to be broken both electrons must obtain sufficient energy to be excited across the energy gap and disturb the entire correlated system. In a superconductor the energy available from any single scattering processes by phonons (or other mechanisms) is not enough to do this. Scattering is suppressed: there is no resistance. Since the correlated pair system opposes change, current flow by the Cooper pairs is persistent.

To describe persistent current flow, Bardeen used a colorful analogy, referring to a closely packed crowd that has invaded a football field. The Cooper pairs can correspond to couples in the throng, who are desperately trying to remain together. Such a crowd is hard to stop – once set in motion – since stopping one person in the group, requires stopping many others. The crowd members will flow around obstacles, such as goalposts, with little disruption – suffering no resistance.

Box 7

Zero resistance and persistence of current flow in a superconductor

When a superconductor is not carrying a current, there is no net pair drift velocity because as many electrons go one way as the other: a pair has zero net momentum (Figure 6.7(a)). One electron in a pair has momentum $\hbar\mathbf{k}$ and the other $-\hbar\mathbf{k}$. When a current is flowing, the net drift velocity is v and net momentum mv along the direction of electron flow (Figure 6.7(b)). The energy of the current-carrying state is higher than that of the ground state. Coupling by virtual phonons now takes place between electrons with momenta $(mv + \hbar\mathbf{k})$ and $(mv - \hbar\mathbf{k})$. The total wave vectors of every pair (of total mass $2m$) are all equal (as they were before) *but now are no longer zero.* If

$$v = \hbar\mathbf{P}/2m \qquad \text{or} \qquad mv = \hbar\mathbf{P}/2$$

so that the supercurrent-carrying states are translated in $\mathbf{k}$-space by the wavevector $\hbar\mathbf{P}/2$, then the pairs have wave vectors of $(\mathbf{k} + \mathbf{P}/2)$ and $(-\mathbf{k} + \mathbf{P}/2)$. Therefore, the total wave vector of each of the pairs is:

$$(\mathbf{k} + \mathbf{P}/2) + (-\mathbf{k} + \mathbf{P}/2) = \mathbf{P}$$

and the pair momentum is $\hbar\mathbf{P}$. Scattering requires that a pair of electrons is broken up and this can only happen if a minimum energy 2Δ is supplied from somewhere to take both electrons across the gap. At low current densities, this amount of energy can not be given to the electron pairs. Scattering events which change the total pair momentum are inhibited; there is no resistance.

Another way of understanding the persistence of current flow is as follows: to take a pair of electrons away is very difficult because of the tendency of bosons to keep together in the same state. Once a current is started it just keeps going forever.

In general, the way in which superconductors behave arises because the electron pairs are bound together in a single energy level and resist removal from it. The BCS theory does account for persistence of a supercurrent. Not only can most of the known facts about superconductivity in conventional materials be explained but new properties are also predicted.

Experimental Examination of the Electron Pair Theory

An energy gap in the elementary excitation spectrum of the electrons in superconductors was postulated several years before the development of the electron pair theory. Nevertheless, the results obtained by BCS, which predicted the magnitude and temperature dependence of the energy gap are an outstanding theoretical achievement. Examination of these predictions is the most obvious way to verify the theory experimentally. Spectroscopic measurements of microwave (Chapter 9) and infrared absorption give direct evidence for the gap and its magnitude; at low frequencies there is no absorption but at a frequency ν_g such that $h\nu_g$ equals the energy gap at the temperature of measurement there is a sharp onset of absorption of the radiation: an absorption edge is observed. Thermal properties, such as specific heat and thermal conductivity, related to the energy required to excite electrons across the gap, also provide valuable information about the energy gap.

Perhaps the most striking confirmation of the energy gap comes from *electron tunnelling* experiments. Tunnelling refers to the fact that an electron wave can penetrate a thin insulating barrier, a process that would be forbidden under the laws of classical physics. If a ball is thrown against a wall, it bounces back, but an electron has a probability that it can tunnel through a forbidden region. A fraction of the electrons moving with high velocities in a metal will penetrate a barrier by tunnelling, producing a weak tunnel current on the other side of the barrier. In the late nineteen twenties some phenomena in solids were explained by tunnelling but progress in using tunnelling was slow until 1958, when a young Japanese physicist Leo Esaki at Sony Corporation pioneered the initial experiments that established the existence of the effect in semiconductors. In 1960, an engineer Ivar Giaever, working on electronic devices made by thin film technology at the General Electric Research Laboratory in Schenectady, New York, conjectured that tunnelling might also be used to great effect in the study of superconductors. In particular, he suggested that the energy gap could be measured from the current−voltage relation obtained by tunnelling electrons through a thin sandwich of evaporated metal films insulated by an oxide film. Experiments showed that his conjecture was correct and tunnelling became the dominant method of determining the energy gap in superconductors. Later Brian Josephson predicted tunnelling of Cooper pairs through a thin insulating barrier (this will be discussed in Chapter 7). In 1973 Esaki, Giaever and Josephson were awarded the Nobel Prize in Physics for their discoveries of electron tunnelling phenomena in solids.

Ivar Giaever has told of his trials and tribulations in an amusing way in his Nobel Prize lecture: neither he nor his colleague John Fisher

> "*had much background in experimental physics, none to be exact, and we made several false starts. To be able to measure a tunnelling current the two metals must be spaced no more than about 100Å apart, and we decided early in the game not to attempt to use air or vacuum between the two metals because of problems with vibration. After all, we both had training in mechanical engineering! We tried instead to keep the two metals apart by using a variety of thin insulators made from Langmuir films and from Formvar. Invariably, these films had pinholes and the mercury counter electrode, which we used, would short the films. Thus we spent some time measuring very interesting but always non-reproducible current–voltage characteristics, which we referred to as miracles since each occurred only once. After a few months we hit on the correct idea: to use evaporated metal films and to separate them by a naturally grown oxide layer*."

To prepare a tunnel junction without pinholes, these early workers first evaporated a strip of aluminium onto a glass slide. This film was removed from the vacuum system and heated to oxidize the surface rapidly. Several cross strips of aluminium (Al) were then deposited over the first film making several junctions at the same time. In this way capacitors, plate electrodes separated by a thin oxide film, were made with superconducting film. Tunnel devices now have important uses and further details of their manufacture are detailed more appropriately in Chapter 9. To obtain the current–voltage characteristic of a tunnel junction, a voltage was applied across it in the circuit shown in Figure 6.8 and the current flow measured. By April 1959, successful tunnelling experiments had been carried out that gave reasonably reproducible current–voltage characteristics. A typical current–voltage characteristic for tunnelling between two superconductors is shown in Figure 6.9; only a minute current can flow across the junction until the voltage applied is sufficient to excite Cooper pairs across the superconducting energy gap.

To explain how the energy gap can be determined, it is instructive to discuss an experiment on a capacitor which has one plate made from a superconductor while the other is a normal metal. When the capacitor plates are less than 100Å apart, a quantum mechanical tunnelling current can flow across the device. Conduction electrons in the metal plates behave as running waves, which are reflected back into the metal at the surfaces; however, there is a finite probability that an electron, on one of many "trial runs" at the surface, may tunnel through the thin layer of insulator separating the plates. The way in which the energy levels are arranged when no voltage is applied to a capacitor which has one superconducting and one normal metal plate is shown in Figure 6.10(a). As shown by the energy level diagram for a superconductor (Figure 6.5), the Cooper pairs are all contained in one level separated from the excited states by the energy gap (value 2Δ). When there is no voltage applied across the capacitor, the level containing the Cooper pairs in the superconductor is

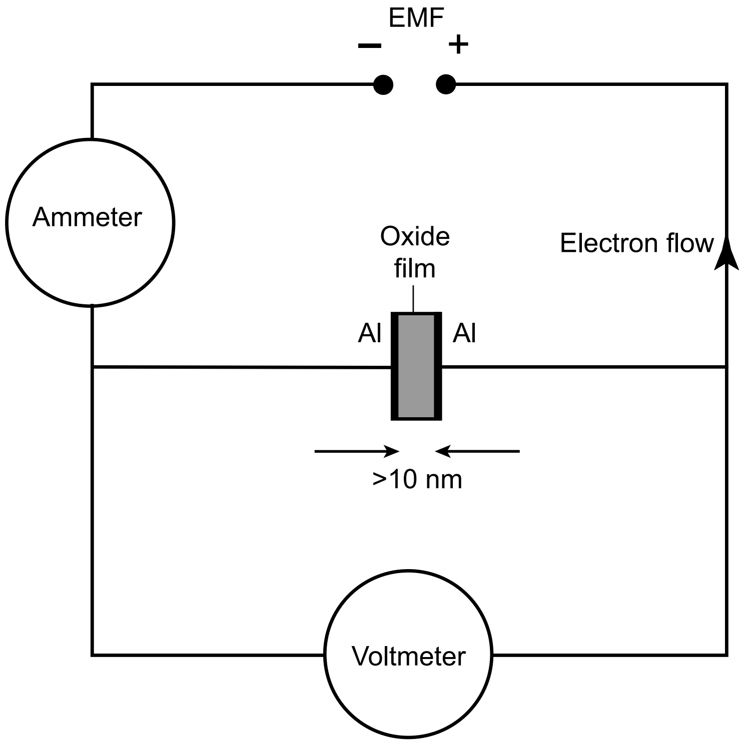

Figure 6.8 A circuit diagram for making a tunnel experiment. The device is like a capacitor whose electrodes are the superconductor under investigation (in this case aluminium (Al)) separated by a very thin, insulating aluminium oxide film. To measure the current−voltage characteristics of the device, a variable voltage (labelled EMF) is applied across it and measured using the voltmeter; the resultant current is measured with the ammeter.

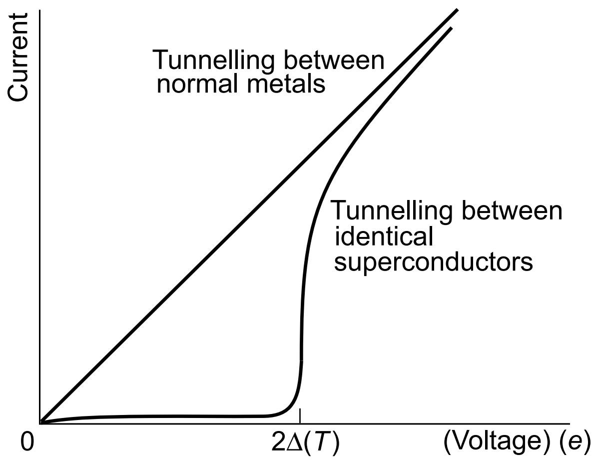

Figure 6.9 The experimental current−voltage characteristic observed for tunnelling between identical superconductors. There is a sharp increase in the tunnelling current when the applied voltage is equivalent to the energy gap at the temperature of measurement. For comparison tunnelling between two normal metals is also shown.

lined up with the Fermi level in the normal metal on the other side of the insulating barrier. Electrons can only tunnel through the insulating layer, if there are empty states for them to go into; no current flows. However, when a positive voltage is

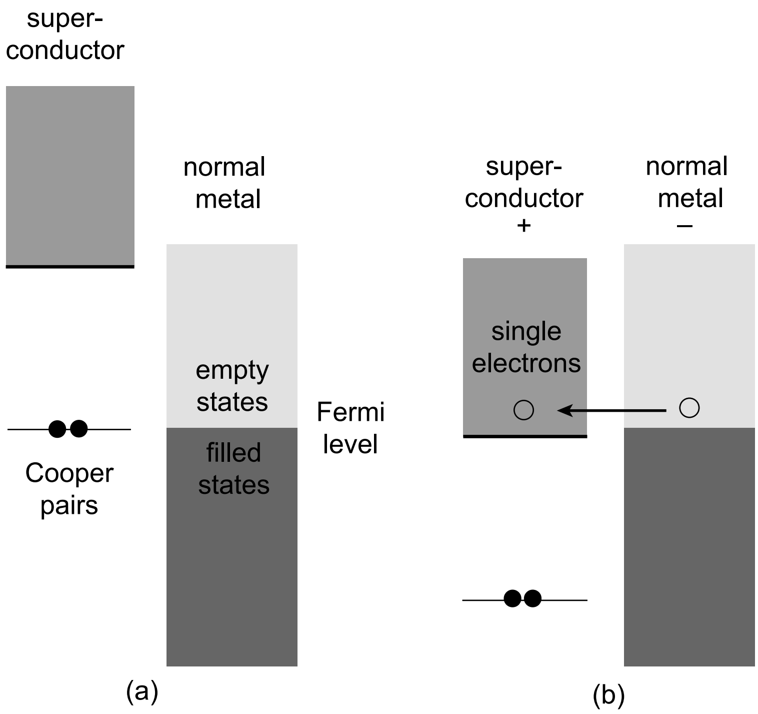

Figure 6.10 Energy level diagram for tunnelling across a device made of a superconductor separated from a normal metal by a thin insulating film. (a) No applied voltage. There are only a few excited electrons above the superconducting energy gap. The Cooper pair level is at the same energy as that of the Fermi level. (b) When the applied voltage is large enough for the states containing single electrons which face empty states above the Fermi level of the normal metal on the other side of the junction, a substantial current can flow because electrons can tunnel across into the empty states then available for them.

applied to the superconductor, the Cooper pair state is lowered (Figure 6.10(*b*)). Tunnelling still does not take place until the voltage becomes large enough for the edge to be pushed to the same level as the Fermi energy in the normal metal. Electrons at the Fermi level in the normal metal can now tunnel from the negative plate across the insulator into the empty excited states in the superconductor that forms the positive plate. A current flows.

Hence to measure the energy gap, a positive voltage V is applied to the superconducting plate. This lowers the energy levels of the superconductor relative to those in the normal plate. For a small voltage no tunneling occurs. However, when the applied voltage V is raised to a value V_{critical} equal to Δ/e, the Fermi level in the normal metal is lifted up to the lowest empty excited states in the superconductor. So at this applied voltage, which is a direct measure of one half Δ of the gap, there is a sharp increase in the current flowing across the capacitor. The current–voltage characteristic of the device is illustrated in Figure 6.11. In effect, tunneling experiments allow direct measurements of the gap with a voltmeter. The voltage is small, only of the order of a millivolt.

Giaever also observed a characteristic fine structure in the tunnel current, which depends on the coupling of the electrons to lattice vibrations. From these beginnings tunnelling has now developed into a spectroscopy of high accuracy to study in detail the properties of superconductors. The experiments have confirmed in a striking way

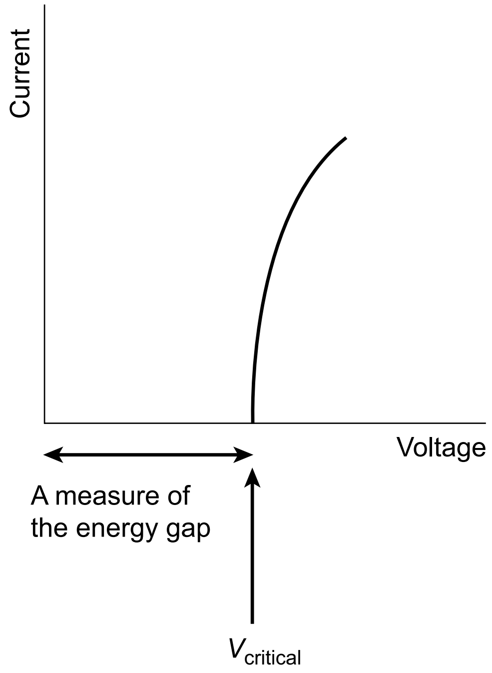

Figure 6.11 The experimental current–voltage characteristic observed for tunnelling across a capacitor made with one plate of normal metal and the other plate of superconductor. At a voltage less than that required to break Cooper pairs and excite normal electrons above energy gap no tunnelling current flows. When the voltage $V_{critical}$ is large enough to break pairs, there is a sharp increase in the tunnelling current. The critical voltage $V_{critical}$ can be used to measure the energy gap ($V_{critical} = \Delta/e$) at the temperature of measurement. Here Δ is half the gap and e is the electronic charge.

the validity of the BCS theory: extrapolated values of the limiting energy gap at 0K are between $3kT_c$ and $4.5kT_c$ for conventional superconductors. The temperature dependence of the gap usually follows quite closely the BCS predicted curve shown by the solid line in Figure 6.6.

Several other techniques have been used to determine the energy gap in superconductors. One of these is to measure the absorption of monochromatic, ultrasonic waves in the frequency range 10MHz to 1000MHz in which the ultrasound wave energy is small compared with the energy gap. Normal electrons scatter the ultrasound waves, attenuating them. So as the temperature is lowered through the critical temperature T_c, reducing the number of normal electrons, the attenuation of ultrasound waves decreases sharply. Determinations of the energy gap from ultrasonic attenuation measurements are in reasonable accord with BCS predictions. In 1964, while at the University of California, Riverside, George Saunders made ultrasonic attenuation measurements on metal single crystals, and discovered that the energy gap is anisotropic: it depends upon crystallographic direction. Typical results of the anisotropy of the energy gap are detailed in Table 6.1. This directional effect is a result of the Fermi surface also being anisotropic. It shows one limitation of the BCS theory, which, as we have seen, is based upon a spherical model of the Fermi surface and therefore cannot predict anisotropy of the energy gap.

There are also problems in the application of the BCS theory to alloys and other more complex superconductors. Phil Anderson suggests that in alloys strong scattering results in a more nearly constant interaction than that for anisotropic, pure metal superconductors. In these “dirty” superconductors the energy gap should be isotropic and the BCS theory should be obeyed closely. Measurements made by George Saunders of ultrasonic attenuation in the intermetallic, disordered alloy of composition equivalent to In_2Bi confirm this prediction. The energy gap at 0K is $(3.4\pm0.2)k_BT_c$ and, as shown in Figure 6.6, the temperature dependence of the energy gap is in reasonable agreement with that predicted by BCS. Other experimental measurements also suggest that the BCS theory is applicable to alloys. Only a few of the experimental methods used to examine the BCS theory have been surveyed here. There are numerous other techniques available. The results confirm that the generalized BCS model of superconductivity is essentially correct for many alloy superconductors.

Interesting discoveries in the field of conventional superconductors are still being made. As recently as January 2001, Professor Jun Akamitsu of the Aoyama Gakuin University in Tokyo announced at a symposium on “Transition Metal Oxides” in Sendai, Japan, that magnesium boride (MgB_2) is a binary intermetallic superconductor with a critical temperature T_c of 39K – the highest yet found for a conventional material. This discovery caused an immediate flurry of excitement as scientists worldwide attempted to verify and extend the observation. Just as the aftermath of the discovery of high temperature superconductors by Bednorz and Müller meant that many scientists communicated with each other via faxes, pre-prints and telephone conversations, so the more recent discovery led many scientists to first announce their results on the Internet; a trend which it seems is set to continue. By examining a sample containing the less abundant boron isotope (^{10}B), a group led by Paul Canfield at the Ames Laboratory in Iowa State University has already shown that MgB_2 has an isotope effect, which is consistent with the material being a phonon-mediated BCS superconductor, although such a high transition temperature might have implied an exotic coupling mechanism. Strong bonding with an ionic component and a considerable electronic density of states produce strong electron–phonon coupling, and in turn the high T_c. Other experiments such as electron tunnelling are also consistent with a BCS mechanism.

Table 6.1 The limiting energy gap at 0K in different directions in thallium (Tl) and tin (Sn) as determined from acoustic attenuation measurements. The directions in column two are given in Miller indices which are defined in standard texts on crystallography.

	Direction of propagation of ultrasonic waves	Energy gap ($2\Delta(0)/k_BT_c$)
Tl	$[10\bar{1}0]$	4.1
	$[1\bar{2}10]$	4.0
	[0002]	3.8
Sn	[001]	3.2
	[110]	4.3
	[010]	3.5

It is possible to purchase MgB_2 directly from chemical suppliers and many of the first superconducting samples were obtained in that way. The recent discovery does pose the question as to why the superconducting properties of MgB_2 were not discovered years ago. In Chapter 2, the systematic search for new superconductors by John Hulm, Berndt Matthias and others was discussed. They had great success with intermetallic compounds based on transition metals but failed to find superconductivity in any transition metal diborides that they examined. The recent discovery undoubtedly means that there will be renewed interest in other binary and ternary intermetallic compounds. Finally, an interesting ramification is that MgB_2 can be thought of as an analogue of the predicted metallic hydrogen superconductor, which many believe could have an extremely high critical temperature T_c, and which may exist in cold stars.

Summary

Within the limits imposed by the relative simplicity of the model, the BCS theory provides an acceptable explanation of the phenomenon of superconductivity in the conventional materials. The BCS model extends the concept of a "two-fluid" superconductor. At temperatures below the critical temperature T_c there are both normal and superconducting electrons. Intrinsic to the superconductor is an energy gap between the two types of particle states. The superelectrons consist of pairs of electrons coupled by phonons. Overlap between pair waves gives rise to a condensed state of long-range order capable of sustaining persistent currents; in the superconducting state, quantum effects are acting on a macroscopic scale. Experimental results on pure metal superconductors are in reasonable agreement with the theory. Certainly, measured values of the limiting energy gap at 0K ranging from $3.2k_BT_c$ to $4.6k_BT_c$ are in accordance with the prediction of $3.5k_BT_c$, and the measured temperature dependence of the gap is in general in keeping with the theory. Real metals are more complex than the idealized BCS model. The theory is framed to deal with the general cooperative nature characteristic of all superconductors. Superconductors, however complicated their energy surfaces may be in reality, are treated within the context of the same model: the BCS model is really a *law of corresponding states.*

All conventional superconductors show some departures from the BCS superconductor, but deviations are surprisingly small. Recourse to a stronger electron−phonon coupling interaction than that used in the initial theory can resolve many of the difficulties that do arise. For instance, in the strong-coupling limit the predicted energy gap of $4.0k_BT_c$ at 0K, as against the $3.5k_BT_c$, of the weak coupling theory of BCS, accords with the experimental data for mercury and lead. Thus a more realistic choice for the coupling interaction can allow for some variation in behavior from metal to metal. Agreement between experiment and theory is then much closer. The electron-pair hypothesis occasions a point of departure rather than a conclusion to the subject. Not only are known facts explained but also new phenomena are predicted.

One requirement of a theory of superconductivity is that it should predict which materials may be superconducting. In this BCS is somewhat reticent. Nevertheless, the theory does suggest that a strong interaction between the lattice and electrons is conducive to the formation of the condensed state of Cooper pairs. A strong electron–phonon interaction inhibits normal state conduction because the electrons are more strongly scattered: metals such as tin, lead, thallium and mercury, which are relatively poor conductors in the normal state, tend to be superconductors, while the best conductors of electricity, the noble metals, in which lattice scattering is weak, do not become superconductors.

7 The Giant Quantum State and Josephson Effects

One of the most fascinating and fundamentally important properties of superconductivity is its quantum behavior over large distances. Usually quantum mechanical effects are only important at low temperatures and over distances on the atomic scale, that is about 10^{-9} meters. Superconductors are an exception to this rule. As long ago as the late 1940s, Fritz London, with a great leap of the imagination suggested that for superconductors, the wave–particle duality should be able to be seen in vastly larger objects, even to a mile long superconducting loop.

As for all matter, the de Broglie hypothesis applies to Cooper pairs of electrons: there is a wave associated with them. The de Broglie wave of a Cooper pair extends over a distance of about 10^{-6} meters – some thousand times longer than the spacing between atoms in a solid. This size scale of a Cooper pair defines a coherence distance between the individual electrons forming the pairs. The essence of superconductivity is coherence between the de Broglie waves of *all* the Cooper pairs: this phase coherence extends over the whole of a superconducting body even though it may be enormous. Phase coherence corresponds to BCS telling us that *all the Cooper pairs behave in exactly the same way,* not only as regards their internal structure but also as regards their motion as a whole: they all move in time with each other. In a Cooper pair, the electrons are bound together to form an entity rather akin to a "two electron molecule". Each pair can be thought of as a wave (Figure 7.1) travelling unscattered throughout the whole volume of the superconducting metal. Each electron finds itself preferentially near another electron in a Cooper pair, which acts over such a large volume that within it there are millions of other electrons each forming their own pairs. As a result, the waves, now relating to the whole collection of pairs, overlap in a coherent manner (Figure 7.2): in addition to having the same wavelength, the pair waves are all in step: they have the same phase in time.

When there is a superconducting current flowing in a metal, all the pairs have the same momentum; the corresponding waves all have the same wavelength and all travel at the same speed. These waves (Figure 7.2) superpose on each other to form a synchronous, co-operative wave with that same wavelength. Whatever the size of the superconductor, all the electron pairs act together in unison as a wave that shows the extraordinary feature of remaining coherent over an indefinitely long distance spanning the entire superconductor. This property, known as phase coherence, is central to superconductivity and has profound consequences: indeed it can be thought of as being responsible for the curious properties of superconductors. It leads to the existence of the superconducting energy gap and is the source of the long-range order

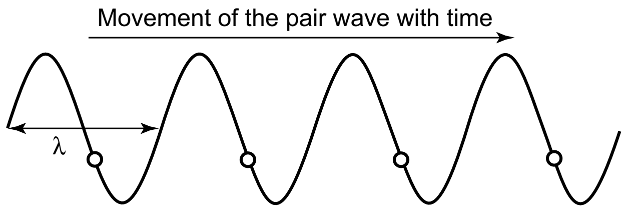

Figure 7.1 Travelling wave. A Cooper pair can be represented by a *travelling wave.* A sine wave of wavelength λ is used here as a simple way to enable "visualization" of the Cooper pair wave. If **P** is the momentum of the pair, the *de Broglie wavelength* λ of this travelling wave is $h/\mathbf{P}$. The open circles represent points of equal *phase;* this time phase is associated with the energy of the pair. Physicists use the *wave function* ψ as a mathematical tool to represent particles in quantum systems. Like any wave, this function has both amplitude and phase. $|\psi^2|$ gives the probability for a particle to be in a particular place at a particular time.

of the superconducting electrons. It is the reason why superconductors exhibit quantum effects over large distances. This coherent wave, which is identical for all the pairs throughout the superconductor, can undergo interference and diffraction effects, analogous to those observed for light waves, that are manifest in the macroscopic quantum interference effects, observed in SQUIDS (see Chapter 9) and have useful applications.

So each superconducting pair is characterized by a wave with an amplitude and a phase. The superconducting ground state is a coherent superposition of pairs – all having the same phase. Let us consider what happens if a current of electrons is set up round a ring. Motion around a ring made of a metal in the normal state causes electrons to accelerate centripetally (in an analogous manner to the moon travelling in orbit around the earth) and they continuously emit electromagnetic radiation and lose energy. By contrast, in a superconducting ring a supercurrent persists and does not lose energy by radiating electromagnetic waves. Stationary states of this kind, which do not alter with time, are governed by quantum conditions. These require the quantization of the energy of the superconducting current. This situation is analogous to the quantization of the energy levels for an electron in orbit around the proton in a hydrogen atom: in the Bohr model (see Figure 5.1) an electron remains indefinitely in its orbit with an unchanged energy and does not radiate electromagnetic waves. To increase its energy, the electron has to jump into another quantum state having a higher fixed energy. Similarly a supercurrent in a ring is quantized and can only be increased by a jump up into a state of higher fixed energy and current. One consequence of this quantization of the current round a ring is that the magnetic flux threading through the ring is quantized and we now consider the ramifications of this remarkable feature.

Flux Quantization

Flux quantization is another quantum effect of superconductors that was predicted by Fritz London. It was thought to be so bizarre that nobody paid much attention to

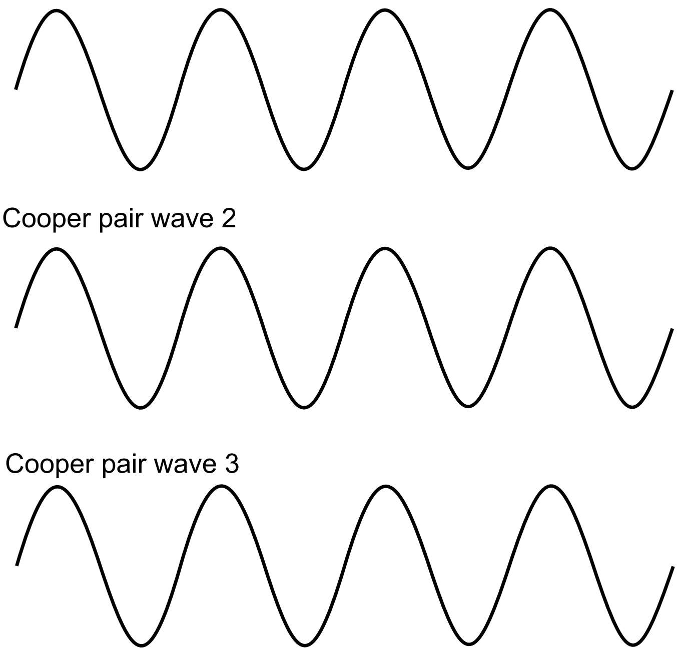

Figure 7.2 Coherence of waves. In a superconductor all the pair waves have the same phase and so these three waves should be superimposed: they are said to be phase coherent. A single wave function can then describe the entire collection of Cooper pairs.

it for many years. Fritz London, again displaying his deep insight, proposed, as part of a phenomenological theory of superconductivity, that the magnetic flux passing through the axial hole in a hollow, current-carrying, superconducting ring should be quantized in multiples of h/e (4.14×10^{-15} Weber); that is the flux can be zero, or h/e, or $2h/e$, or $3h/e$, and so on, but can have no value in between. This theoretical prediction that the flux must be a multiple of the basic quantum mechanical unit h/e is in complete contrast with classical physics, which would suggest that any current and magnetic flux can take any value at all. In his day, it was not possible to test this prediction because the available apparatus was not sufficiently sensitive to measure the small magnetic flux involved.

The advent of the BCS theory stimulated experiments to confirm the predictions made about flux quantization. It transpired that the results obtained provided convincing evidence for Cooper pairing. Careful experiments have verified that the magnetic flux is indeed quantized, but that the magnitude of the flux quantum is $h/2e$ (2.07×10^{-15} Weber): half London's predicted value. This is consistent with pairs of electrons, rather than single ones that London had originally assumed. Finding this gave an enormous boost to the acceptance of the BCS theory – being overwhelming evidence that the electrons are bound together in Cooper pairs: the result suggests that the charge on the current carriers is $2e$ (where e is the electronic charge).

Flux quantization is a direct result of the electron correlation and gives a further insight into the stability of persistent currents in superconducting rings. If a supercurrent is to decay, the flux must jump to another state with an integral quantum number: the system as a whole must be altered; many particles must change states

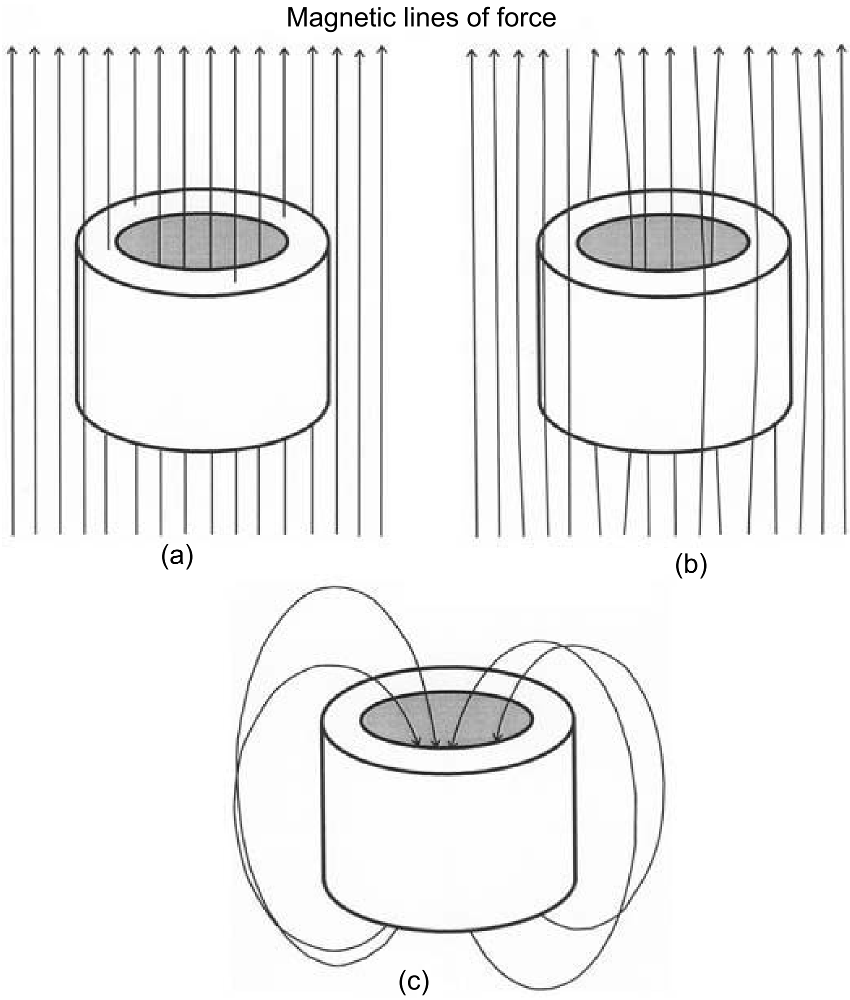

Figure 7.3 A ring in a magnetic field. (a) In the normal state: magnetic flux lines thread the ring and the metal itself. (b) When temperature is lowered below the critical temperature T_c, magnetic flux is ejected from the metal but still threads the ring. (c) As the outside magnetic field is removed, a current is induced in the ring which produces magnetic flux with the same value as before. The current and the magnetic flux persist and both are quantized.

simultaneously. The probability of this happening is vanishingly small because typical scattering processes in the solid affect only a few particles at a time. Hence supercurrents can and do persist. The nature of the flux quantization involved is a consequence of the zero resistance to a current flowing round a superconducting ring and the quantization of that current.

Let us take a ring made of a metal that can go superconducting, and place it in a magnetic field above the critical temperature, as shown in Figure 7.3(a). In the normal state magnetic field lines pass through the hole in the ring and also through the metal of the ring itself. If the ring is cooled below the critical temperature T_c, so that it goes into the superconducting state, the new situation shown in Figure 7.3(b) is produced: due to the Meissner effect, when the ring is made superconducting, the magnetic field is forced out of the superconducting metal of which the ring is made. However, flux still threads through the hole in the ring. If the external field is now removed, by Faraday's laws, as that field changes a current is induced in the ring that keeps the flux threading the ring at a constant value. This current persists round the ring. Hence the magnetic flux lines going through the hole remain trapped, as shown in Figure 7.3(c). Another novel feature is that both the current and the associated magnetic flux can only be increased in fixed steps. For the magnetic flux, drawn as a magnetic flux line, the fixed steps are now known to be $h/2e$. The **flux quantization** existing inside the ring can be visualized by fixing each magnetic field line with a value of $h/2e$ and ensuring that only an integral number of such lines can thread the hole in the ring in Figure 7.3(c).

The problem facing those experimentalists who planned to test this fundamental quantization of the current and flux in a superconducting ring is that the value of each flux quantum is extremely small: the amount of magnetic flux threading a tiny cylinder a tenth of a millimeter in diameter is about one percent of the earth's magnetic field. This makes experimental observation of flux quantization extremely difficult; to make a successful measurement, it is necessary to use very small rings. That was done. Flux quanta were first observed by measuring discontinuities in the magnitude of the magnetic field trapped in a superconducting capillary tube. In 1961 Bascom Deaver and William Fairbank at Stanford University, and at the same time Doll and Näbauer in Munich, Germany published papers in the same edition of *Physical Review Letters* reporting that they had been able to make sufficiently sensitive magnetic measurements to observe flux quanta and determine their value. The objective was to find out whether it is true that the magnetic flux threaded through a superconducting ring can take only discrete values. Both groups used very fine metal tubes of diameter only about 10μm (10^{-3}cm); then the creation of a flux quantum requires a very weak magnetic field of about 10^{-5}T, which can be handled experimentally provided that the earth's magnetic field is screened out. To carry out these superlative experiments, Doll and Näbauer used small lead or tin cylinders made by condensing metal vapor onto a quartz fiber. Deaver and Fairbank made a miniature cylinder of superconductor by electroplating a thin layer of tin onto a one-centimeter length of 1.3×10^{-3}cm diameter copper wire. The coated wire was put in a small controlled magnetic field, and the temperature reduced below 3.8K so that the tin became superconducting, while the copper remained normal. Then the external source of magnetic field was removed, generating a current by Faraday's law; as a result the flux inside the small superconducting tin cylinder remained unchanged, as shown in Figure 7.3(c). This tin cylinder now possessed a magnetic moment, which was proportional to the flux inside it. To measure this magnetic moment, a pair of tiny coils was sited at the ends of the tin cylinder and the wire wobbled up and down between them at about 100 cycles per second (rather like the behavior of the needle in a sewing machine). Then the magnetic moment was determined from voltage induced in the coils.

Deaver and Fairbank found that the flux was quantized, *but that the basic unit was only one-half as large as London had predicted on the basis of single electrons.* Doll and Näbauer obtained the same result (Figure 7.4 in which the states having 0, 1, 2 and 3 flux quanta can be seen). At first, this discrepancy from London's prediction was quite mysterious, but shortly afterwards the chief assumption of the Bardeen, Cooper, and Schrieffer theory that the superconducting electrons are paired provided the explanation of why it should be so. Everything had now come together.

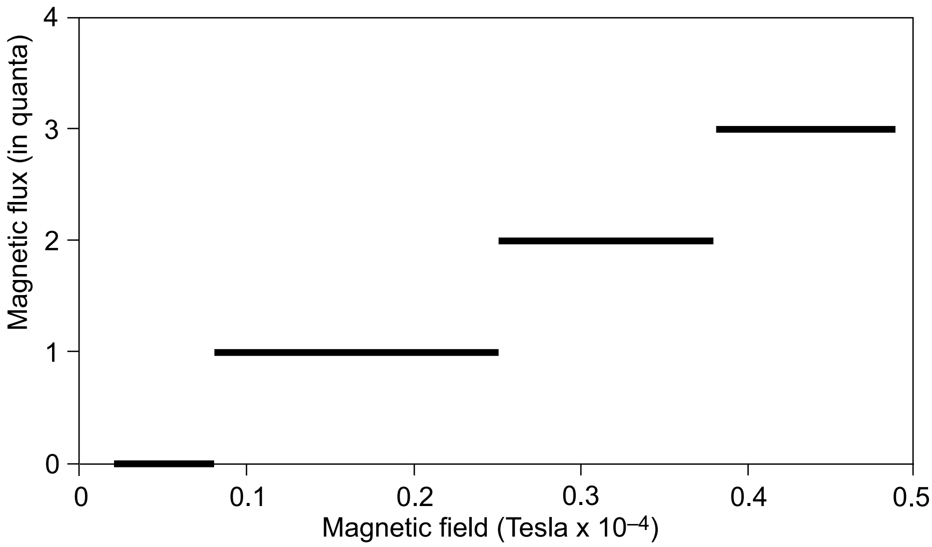

Figure 7.4 Experimental confirmation by Deaver and Fairbank of flux quantization in a tin cylinder having a very small diameter. The units of magnetic flux on the vertical scale are quanta of value $h/2e$ and the flux threading the cylinder can only take values on the lines shown, all the intermediate values not being allowed.

These experiments had verified the pairing postulate on which the BCS theory depended. All the Cooper pairs that carry the supercurrent are in the same quantum level. If Cooper pairs are caused to go into another quantum state, they must all change together. Any magnetic flux threading the hole in a superconducting ring can only exist as multiples of a quantum Φ_0, called the *fluxon,* given by

$$\Phi_0 = h/2e = 6.62\times10^{-34}\text{J s} / (2\times1.6\times10^{-19}\text{C}) = 2.07\times10^{-15}\text{ Wb.}$$

Here, the 2 in the denominator occurs because the electrons are paired. This value of a fluxon, equal to Planck's constant divided by twice the electronic charge, is extremely small. The tiny magnitude of this quantity can be put in perspective by noting that in the earth's magnetic field of about 2×10^{-5}T, the area that would be covered by a red blood corpuscle, which has a diameter of about 7μm, embraces roughly one flux quantum.

The existence of flux quantization also establishes the strict long-range phase correlation of the Cooper pairs with each other. A visual way of seeing this is shown in a simplistic fashion in Figure 7.5. A basic requirement of quantum mechanics is that a wave must be continuous and have only one value or it does not correspond to a single state. By analogy for a wave to travel round a loop of string, the string must not be cut and the ends must meet! Hence the coherent wave formed by superposition of the pair waves must complete an integral number of cycles round a ring (then the phase increases by an integral number of 2π once round the superconducting circuit). Addition of one more flux quantum into the bundle (initially containing an integral number n of flux quanta Φ_0 threading the ring) corresponds to an increase of exactly one more complete wavelength into the ring and the number of fluxons increasing to $(n + 1)$. Addition of two (rather than one) more flux quanta needs two extra complete

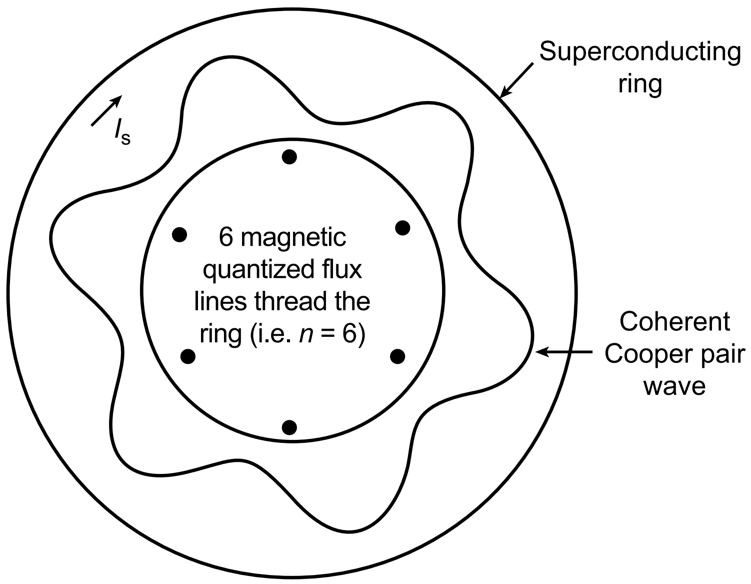

Figure 7.5 Relationship between flux quantization and phase coherence in a ring with a circulating supercurrent I_s. In this case 6 magnetic flux quanta thread the ring and there are 6 complete wavelengths round the circuit of the superconducting ring. If another flux quantum were to be added, there would then be 7 wavelengths round the ring. An intermediate state is not possible. Note the resemblance of this picture to that of the atom in Figure 5.2 but the huge difference in scale: the superconducting ring may be eight orders of magnitude (i.e. 10^8 times) larger − or even more − than the size of an atom. *Superconductivity is a giant quantum state.*

wavelengths, so that there are now $(n + 2)$ fluxons. So the observation of flux quantization also confirmed experimentally the existence of long range coherence as the large-scale quantum-mechanical behavior of electron pair waves in superconductors.

Flux quantization is not just restricted to a superconducting ring; that is, for a superconductor with a hole in it. Quantization always appears when a magnetic flux passes through any superconductor, such as those of type II, which are penetrated by an applied magnetic field in the form of fluxoids or bundles of fluxons (see Chapter 8).

As a first step in understanding the mechanism of superconductivity in the high T_c cuprates, it was vital to find out whether pairing of electrons is also involved. Several experiments have established that this is the case. One of the most compelling is the search for flux quantization carried out at the University of Birmingham by Colin Gough and co-workers shortly after the discovery of YBCO. They were able to measure the flux trapped inside a ceramic ring of YBCO. Their results are shown in Figure 7.6. They found that it is possible to excite the ring between its metastable quantum states corresponding to different integral numbers of the trapped flux. The multiphase nature of the YBCO allowed single quanta of flux to move easily in and out of the ring; this was crucial for the experiment to work successfully in the weakly superconducting material. They measured a value of $h/2e$ for the flux quantum Φ_0, hence establishing that *the superconducting electrons are also paired* in YBCO. In addition, this experiment shows that the long-range coherence of the pair waves is a property of high T_c cuprate superconductors, as it is for the more conventional materials. Hence flux quantization is a fundamental

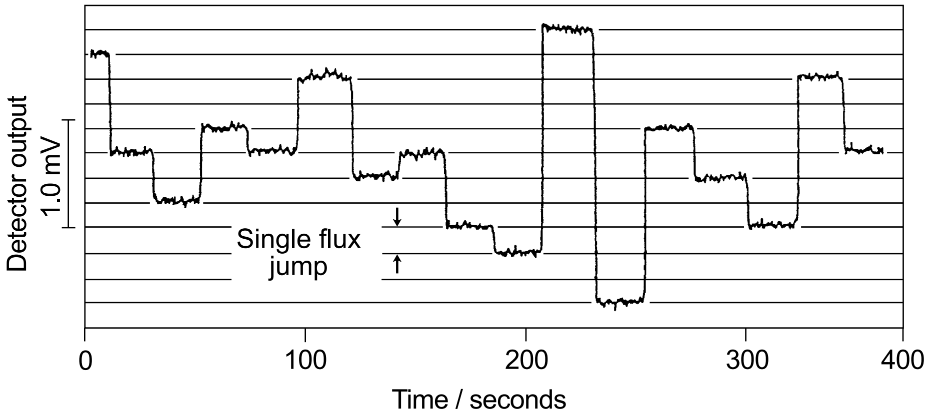

Figure 7.6 To measure the value of a flux quantum in a high T_c superconductor, a YBCO ring at 4.2K was periodically exposed (note scale on the graph abscissa is time) to a local source of electromagnetic noise causing the ring to jump between quantized flux states. The equally spaced lines shown here emphasize the quantum nature of the flux transitions because the flux jumps take place in integral numbers of a single flux quantum ($h/2e$). (Gough *et al.* (1987).)

property of all superconductors. Today, flux quanta play an important role in the many superconducting devices that depend for their operation on the so-called Josephson effects.

Josephson Effects

Age places no constraints on scientific work. While he was still a research student in the early 1960s at Trinity College, Cambridge, Brian Josephson put forward new fundamental ideas that completely changed the way in which superconductivity is viewed. The eminent American theoretical physicist Philip Anderson, who was a Visiting Professor at Cambridge at the time, has given a fascinating personal account of how Brian Josephson, then a young man of only 22 years of age, developed his far-reaching ideas and discovered the effects, which now carry his name.

Josephson considered what might happen when two superconductors are separated by a thin layer of an insulating material, which acts as a barrier to the flow of current. It had previously been recognized that, on account of their wave nature, electrons can tunnel through a thin insulating barrier between metals (see the discussion in Chapter 6 of how this phenomenon provided a powerful way of testing the BCS predictions). Tunnelling arises because the electron waves in a metal do not cut off sharply at the surface but fall to zero within a short distance outside. The electron wave leaks into the "forbidden" barrier region. Within this distance there is a small but finite probability that an electron will be found outside the metal. Therefore, when a piece of metal is placed very close (within about 10^{-7}cm) to another, electrons have a finite probability of penetrating the potential barrier formed by the insulating layer between the two metals. A small tunnelling current can be caused to flow across the junction by applying a voltage across the two superconductors (Figure 7.7).

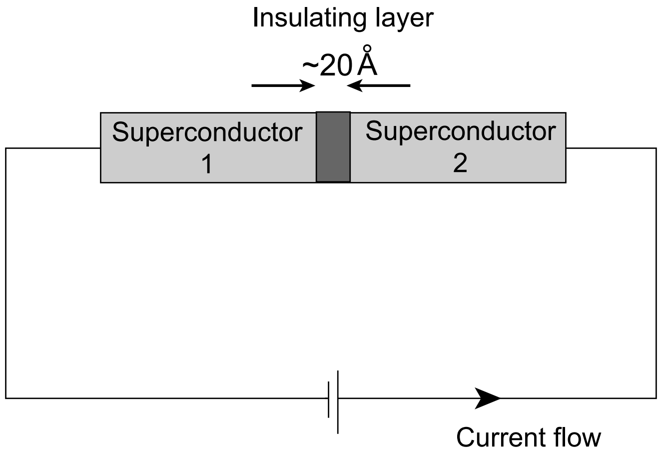

Figure 7.7 The principle of an experiment to test Josephson's prediction about tunnelling of Cooper pairs through an insulating junction between two superconductors.

In 1962, Josephson pointed out that, in addition to the ordinary single-electron tunnelling contribution, the tunnelling current between two superconductors should contain previously neglected contributions due to the tunnelling of Cooper pairs. The coherent quantum mechanical wave associated with the Cooper pairs leaks from the superconductor on each side into the insulating region. Josephson suggested that if the barrier is sufficiently thin, the waves on each side must overlap and their phases should lock together. Under these circumstances the Cooper pairs can tunnel through the barrier without breaking up. Thus, an ideal Josephson junction is formed between two superconductors separated by a thin insulating layer. The two electrons maintain their momentum pairing across the insulating gap and so the junction acts as a weak superconducting link. When there is a current flowing round a superconducting loop containing such a junction, there is a genuine supercurrent at zero voltage across the insulating layer. Josephson provided an equation for the tunnelling current (see Box 8). He was much puzzled at first as to the meaning of the fact that this current depends on the phase, which may in part explain the title of his paper reporting his work: "Possible New Effects in Superconductive Tunnelling" in the newly created journal *Physics Letters* rather than the prestigious *Physical Review Letters.*

Anderson returned home to Bell Telephone Laboratories extremely enthusiastic about what Josephson had done and eager to confirm pair tunnelling experimentally. He told a colleague John Rowell of his conviction that Josephson was right. Rowell pointed out that he had noticed suggestive things in tunnelling experiments that he had made on superconductors which could have indicated that he might actually be seeing Josephson effects. Motivated by the new ideas, he set off to study a new batch of tunnel junctions. In those days it was not easy to see the effects but he proved able to do so. Anderson and Rowell had a number of advantages going for them. In the first instance, Rowell's superb experimental skill in making good, clean, reliable tunnel junctions was especially valuable. The direct personal contact with Josephson ensured that they knew what to look for and could understand what they saw. When they came to publish their findings, they were rather more confident than young Josephson had been: now that they had understood and extended the theoretical ideas

Box 8

The dc Josephson Effect

The tunnelling current (I) was predicted by the theoretical work of Josephson to be given by the famous dc-Josephson relation, which is central to a detailed understanding of superconductivity:

$$I = I_C \sin(\theta_1 - \theta_2). \tag{1}$$

Here I_C is the maximum supercurrent that can be induced to flow, that is the critical current. This expression, also sometimes known as the sinusoidal current phase relationship, relates the current I to the phases θ_1 and θ_2 of the pair waves on each side (1 and 2) of the junction. The external current drives the difference $\Delta\theta$, equal to $(\theta_1 - \theta_2)$, between the phases of the macroscopic waves travelling in the superconductors on opposite sides, as illustrated in Figure 7.8 and defined by equation (1).

A second Josephson equation applies when an ac voltage is applied across the junction. Then the phase difference $\Delta\theta$ increases with time t as:

$$d(\Delta\theta)/dt = 2eV/h. \tag{2}$$

This effect allows a Josephson junction to be used as a high frequency oscillator or detector.

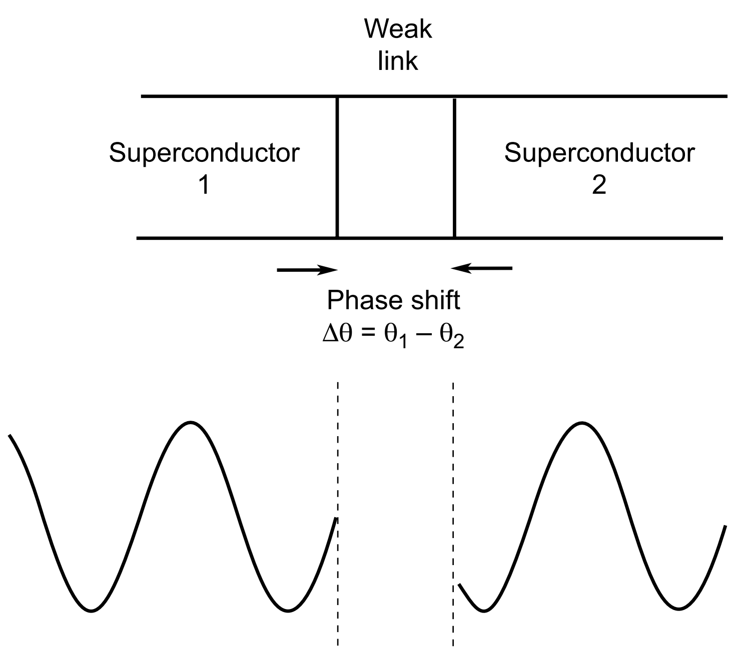

Figure 7.8 Tunnelling of a Cooper pair wave across the weak link between two superconductors. The phase shift $\Delta\theta$, equal to $(\theta_1 - \theta_2)$, across the barrier is shown diagrammatically by the two waveforms. It is not physically possible to indicate a waveform in the barrier itself.

they were able to change the title of their paper from "Possible ..." to "Probable Observation of the Josephson Superconducting Tunnelling Effect", which they published in *Physical Review Letters.*

Anderson has recalled that it was no coincidence that Josephson carried through these developments in the stimulating atmosphere of the Cavendish Laboratory. Not only did Josephson make the all-important theoretical leaps but he also explained how to observe the effects that he had predicted. Entirely by himself, he solved the Cooper pair tunnelling problem and its physical ramifications in a complete and rigorous manner.

A patent lawyer, consulted by John Rowell and Philip Anderson at Bell Telephone Laboratories, gave his opinion that Josephson's paper was so complete that no one else was ever going to be very successful in patenting any substantial aspect of the proposed effects. That was not to say that patents pertaining to working applications could not be made.

At first sight, the Josephson effects would appear to be just an esoteric part of fundamental physics far removed from the "real world" of work and business. Yet they now have applications in numerous areas (see Chapter 9), which must have been inconceivable at the start. This is one of the many examples of the spin-off from research into the fundamental properties of nature such as superconductivity.