3.13 SUPERCONDUCTIVITY

There are two properties that a material must possess to be considered a superconductor:

1. $\rho = 0$
2. $B = 0$

Zero resistivity is observed in a superconductor at all temperatures below a critical temperature, T_c, as illustrated in Figure 3.21. At T_c the material changes from a state of normal conduction to the superconducting state. In the superconducting state an induced current will flow indefinitely: without loss. This behavior has been demonstrated experimentally when a current has been run through a closed ring of a superconducting metal for over two and a half years without any measurable decay.

Superconductivity has been observed in *all* the classes of materials: metals, ceramics, and polymers. Niobium is the element with the highest T_c, 9.2 K, whereas for tungsten T_c is only 0.0154 K. An interesting fact is that metals having the highest σ, e.g., Cu, Ag, and Au, are not superconducting even at extremely low temperatures, if at all. It is the metals that are the poorer electrical conductors that make the better superconductors, albeit still at very low temperatures.

Low-temperature superconductors (LTSC) have a T_c up to about 20 K. High-temperature superconductors (HTSC) are usually defined as having a T_c above the boiling temperature of liquid nitrogen. The BCS theory (after Bardeen, Cooper, and Schrieffer) provides an explanation for superconductivity at low temperatures. The theory is complicated, but the basis is that there exists an attractive force between electrons that have about the same energy. This force causes them, under the right circumstances, to move in pairs. These are the so-called Cooper pairs. The criterion for superconductivity is that this attraction should be greater than the natural repulsion between like charges. T_c corresponds to the binding energy needed to hold the Cooper pairs together in a superconducting state.

The origin of the attractive force is that in a lattice of positive ions, an electron will attract the positive ions toward itself. In this region the lattice will be slightly denser as shown in Figure 3.22. To a passing electron the local lattice distortion will appear as an increase in positive charge density and it will be attracted toward it. The two electrons pair up in this way through their interaction with the lattice. If the lattice is vibrating through thermal effects pairing will not be possible, but at very low temperatures where the vibration amplitude is small, the attractive force can be dominant. The electrons are held together by a binding energy of only about 10^{-4} eV.

The separation of the electrons in the pair (called the coherence length) for most LTSC is 100 nm. Interatomic spacings are on the order of 0.3 nm, so two bound electrons can be as far apart as 300 lattice spaces. The large coherence length means that defects such as dislocations, GBs, and impurities are too small to have much effect on superconducting behavior. The existence of these bound electron pairs alters the energy band diagram for a superconductor by introducing a small gap at E_F, known as the superconducting gap, Δ. The difference in the band structure of a material in the superconducting state and in the non superconducting state is illustrated in Figure 3.23. The energy of this gap corresponds to the binding energy of the electron pairs. Energy 2Δis needed to break a Cooper pair. The relationship between Δ and T_c is given by the BCS theory:

$$2\Delta = 3.5\,kT_c \qquad (3.44)$$

- For LTSC Δ ~1 meV
- For HTSC Δ ~ 1–10 meV

The BCS theory predicts an ultimate limiting value of T_c of 30 K for electron pairing via lattice vibrations (phonons). This limit was enough to stop many researchers from pursuing careers in superconductivity. But clearly the BCS theory, in its entirety, cannot be applicable to HTSC where T_c >>30 K. In these materials pairing of the electrons still occurs, but the mechanism that allows these pairing needs to be determined.

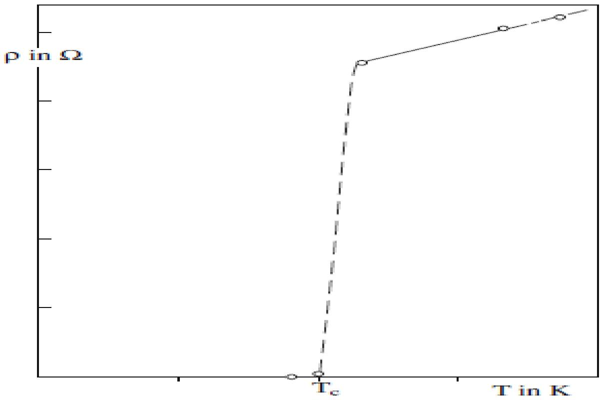


FIGURE 3.21 Plot of ρ versus T for a superconductor.

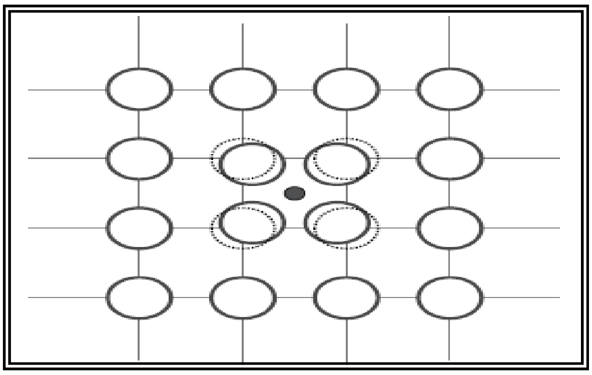


FIGURE 3.22 Illustration of lattice distortion around a free electron, which leads to the formation of Cooper pairs.

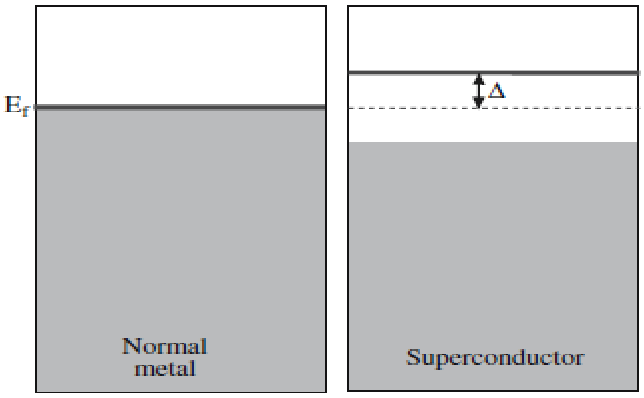


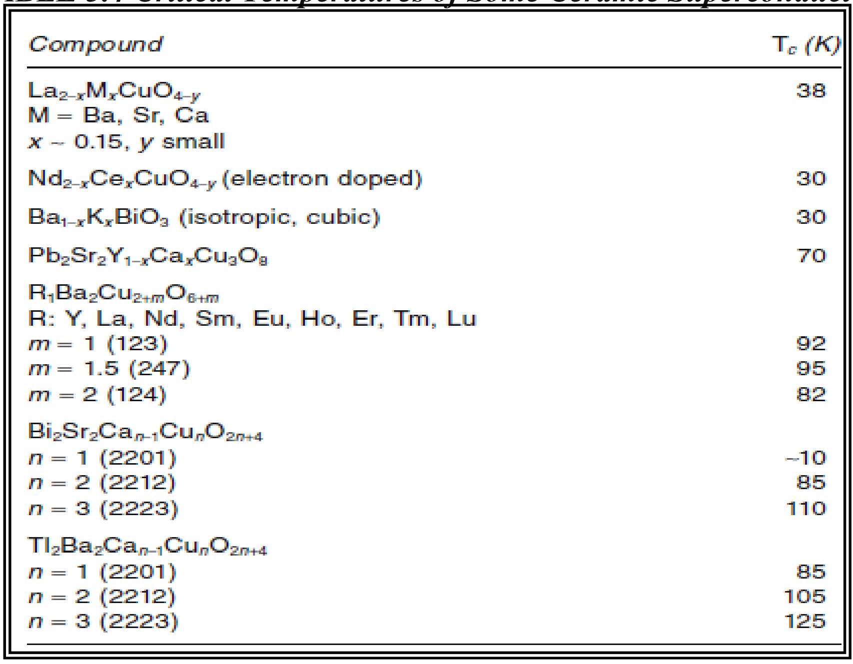
FIGURE 3.24 Band diagram for a superconductor.

3.14 CERAMIC SUPERCONDUCTORS

The earliest nonmetallic superconductors were NbO and NbN. Both materials have a rocksalt crystal structure. What was significant about the discovery of superconductivity in these materials (they are of no practical use) is that they linked the phenomenon to ceramics and cubic crystal structures.

Superconductivity in a multicomponent oxide was first observed in $SrTiO_3$. Although T_c was determined to be only 0.3 K, $SrTiO_3$ has the very important perovskite structure, is the structural building block of all presently known HTSC. The beginning of HTSC started in 1986 with the discovery of superconductivity in the compound La_2BaCuO_4, which has T_c ~38 K. This discovery was of monumental importance because the classic BCS theory for superconductivity predicted a maximum value of T_c of only 30 K! Many more HTSC were simply obtained by systematic substitution of elements into the basic perovskite unit. The elements yttrium and lanthanum are interchangeable in terms of chemical properties although they differ in size. The same is true of strontium and barium in Group II of the periodic table. The idea behind the substitution of the large element for a smaller element was based on observations that T_c could be raised under an applied pressure. Substitution of a larger element for a smaller one was thought to produce an internalized pressure effect. Table 3.4 lists some of these compounds and their T_c.

TABLE 3.4 Critical Temperatures of Some Ceramic Superconductors



Compound	T_c (K)
$La_{2-x}M_xCuO_{4-y}$	38
M = Ba, Sr, Ca	
x ~ 0.15, y small	
$Nd_{2-x}Ce_xCuO_{4-y}$ (electron doped)	30
$Ba_{1-x}K_xBiO_3$ (isotropic, cubic)	30
$Pb_2Sr_2Y_{1-x}Ca_xCu_3O_8$	70
$R_1Ba_2Cu_{2+m}O_{6+m}$	
R: Y, La, Nd, Sm, Eu, Ho, Er, Tm, Lu	
m = 1 (123)	92
m = 1.5 (247)	95
m = 2 (124)	82
$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$	
n = 1 (2201)	~10
n = 2 (2212)	85
n = 3 (2223)	110
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$	
n = 1 (2201)	85
n = 2 (2212)	105
n = 3 (2223)	125

- The obvious difference is T_c. The fact that $T_c \sim 10^2$K means that the binding energy is ~10 meV, as compared to <1 meV in LTSC.

- The ceramics have higher ρ than the metals at 100 K. But ρ is comparable to some of the best ceramic electrical conductors, such as CrO_2 and TiO.

- For HTSC χ is only ~1.0 nm, which means that the pairing behavior is almost on an atomic scale and the superconducting properties will be dependent on atomic scale defects. (Compare χ with the width of a dislocation or GB.) Such defects therefore scatter the electron pairs and reduce the critical current density. For metals χ is large, e.g., χ = 1.6 μm in pure Al, χ = 38 nm in pure Nb.

- χ is anisotropic. For YBCO $\chi_{ab} \sim 1.5$ nm and $\chi_c \sim 0.4$ nm. A major problem in HTSC is to find a crystal defect that pins the flux vortices, but does not disrupt current flow.

Superconductivity essentially takes place within the CuO_2 planes. The Cu–O chains can be considered as a “charge reservoir” that is needed to transfer charge into the CuO_2 planes. Charge carriers are added by doping: adding oxygen to $YBa_2Cu_3O_6$, which enters the compound as O^{2-} and forms Cu–O chains. To maintain charge balance, electrons are removed from the Cu–O planes and the remaining holes are mobile (hence conduction) and form Cooper pairs below T_c.

In LTSC Cooper pairs, with a charge of −2e, are responsible for current flow. In most of the HTSC the Cooper pairs have a positive charge, +2e. In other words they are positive holes and the charge transfer process can be written as

$$Cu^{2+} + h^{+} \rightarrow Cu^{3+} \qquad (3.\ 45)$$

One of the consequences of a hole-hopping process involving a two-dimensional array of copper ions is that the superconducting current is very anisotropic. Hopping tends to occur between copper ions that have the smallest separation from each other, namely those in the plane. The distance between copper ions on adjacent planes is much larger than within the planes; hence charge hopping between planes is much less efficient.

There are many potential applications for HTSC, but the actual realization of these has in many cases not occurred. The major problem is being able to fabricate the ceramics into useful and usable shapes. Ceramics are inherently brittle and this alone makes the fabrication of long wires and tapes extremely difficult. These would be essential for domestic and industrial power transmission. The low χ also makes practical applications more difficult to achieve because we have to be concerned about defects. The most likely route to widespread practical application is to use the HTSC in the form of a thin film and utilize the Josephson Effect. The original observation of this effect was made using a junction consisting of two superconductors separated by a very thin insulating layer (~1 nm). The *I*–*V* characteristics of a Josephson junction are very nonlinear as shown in Figure 3.25. The key features are as follows:

- When $V = 0$, a direct current flows.
- When a small voltage is applied $I = 0$.
- At V_c the electrons are no longer paired and normal electron tunneling occurs with associated resistive losses.

If a Josephson junction is irradiated with microwaves of frequency *f*, the *I*–*V* behavior shows a series of steps, called Shapiro steps, as shown in Figure 3.26. These steps correspond to super currents across the junction when the condition for the absorption of microwave photons is satisfied (this is called the ac Josephson Effect). Similar behavior is seen when we expose the junction to a magnetic field.

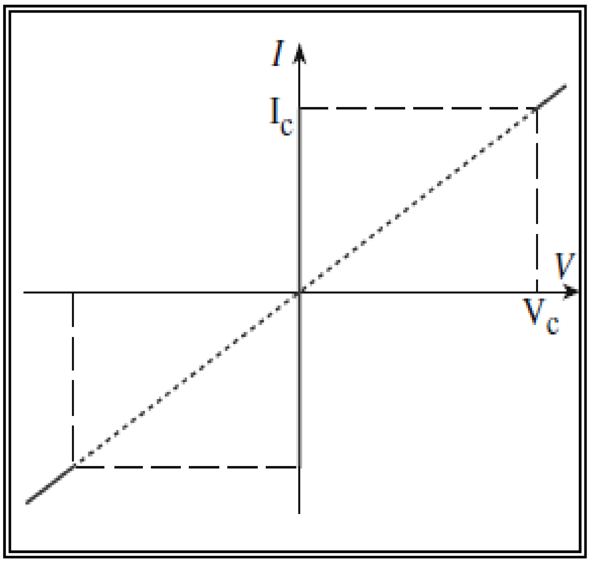


FIGURE 30.25 Illustration of lattice distortion around a free electron, which leads to the formation of Cooper pairs.

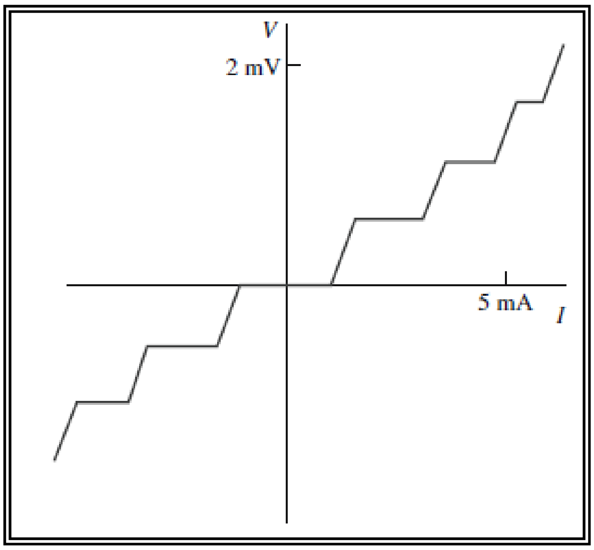


FIGURE 30.26 Effect of incident microwave radiation on the I–V characteristics of a Josephson junction.