15.8 HIGH TEMPERATURE SUPERCONDUCTORS (HTS)

Extremely low critical temperatures of conventional superconductors (the low T_c type) put the most serious limitation on their use in technological applications. Working with devices that have to be cooled to temperatures in the range of liquid helium temperature (4.2 K) is obviously not viable on any count. This has kept the scientists world over relentlessly trying to discover superconductivity near room temperature. A decisive boost to this optimism came in 1986, when Bednorz and Müller synthesized metallic oxygen-deficient copper oxide compounds of La-Ba(Sr)-Cu-O system with the transition temperature of about 30 K. A vigorous activity towards the search for materials with higher critical temperatures ensued following this nobel prize winning announcement. It has resulted in the development of a variety of materials with the highest critical temperature T_c observed in the vicinity of 135 K in a mercury cuprate. Under pressure this T_c value approaches 165 K which is not far away from the temperature of the coldest regions on Earth (183 K). The T_c values being so high compared to those of conventional superconductors, these materials are called *high temperature superconductors* or *high T_c superconductors* (HTS).

The scope of this book does not permit us to do justice to the explosive development of HTS and their properties. Nevertheless, we give below an account of the structures and other salient features of some materials that represent the main classes of HTS in the order of their discovery.

15.8.1 Rare-earth Cuprates: Structural Aspect

Chu and Coworkers (1987) earned the distinction of raising T_c to 90 K in ceramics of the $Ba_{1-x}Y_xCuO_{3-y}$ system. With fastly improving methods of preparation of characterization, a ceramic alloy $Y_1Ba_2Cu_3O_{7-x}$ could be prepared even in single crystal form. In all respects including application this has emerged as the most thoroughly studied and tested system, often referred to as YBCO. A series of this class of HTS has been produced with the Y atom being replaced by other rare-earth elements such as Eu and Gd. On the basis of their stoichiometry, these types of ceramics are commonly called 123 systems.

The crystal structure of the YBCO system is illustrated in Fig. 15.26(a). It can be represented by an orthorhombic primitive cell in the superconducting state. The structure is essentially an oxygen-defect modification of the perovskite structure with about one-third oxygen positions vacant. All members of this series are axial crystals with alternating CuO_2 planes [Cu(2), O(2)] and oxygen atoms in both pyramid-type and rectangular coordination along the c-axis. Oxygen chains are formed along the b-axis with the involvement of atoms in the rectangular planar structure. We will see a little later that the oxygen vacancies in this chain may be interpreted to be actively involved in the mechanism of superconductivity.

15.8.2 Bi-based and Tl-based Cuprates: Structural Aspect

This class of HTS emerged within a year of the synthesis of 123 systems. These materials, typically represented by $Bi_2Sr_2Ca_2Cu_3O_{10}$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ systems, show still higher T_c. The main classes of ceramic superconductors with $T_c > 90$ K are compiled in Table 15.4. In accordance with their stoichiometry, Bi- and Tl-based HTS are named as 2212 and 2223 systems, respectively.

Similar to 123 systems, 2212 and 2223 systems too have a layered structure along the substantially larger c-axis. This layered structure is again considered to play a crucial role in the mechanism of superconductivity. The unit cell shown in Fig. 15.26(b) has two distinct regions, separated by two Bi–O (or Tl–O) planes. In the upper-half region, the copper atoms are located at centres while in the lower-half region they are at corners of the Cu–O planes. The T_c value is strongly controlled by the

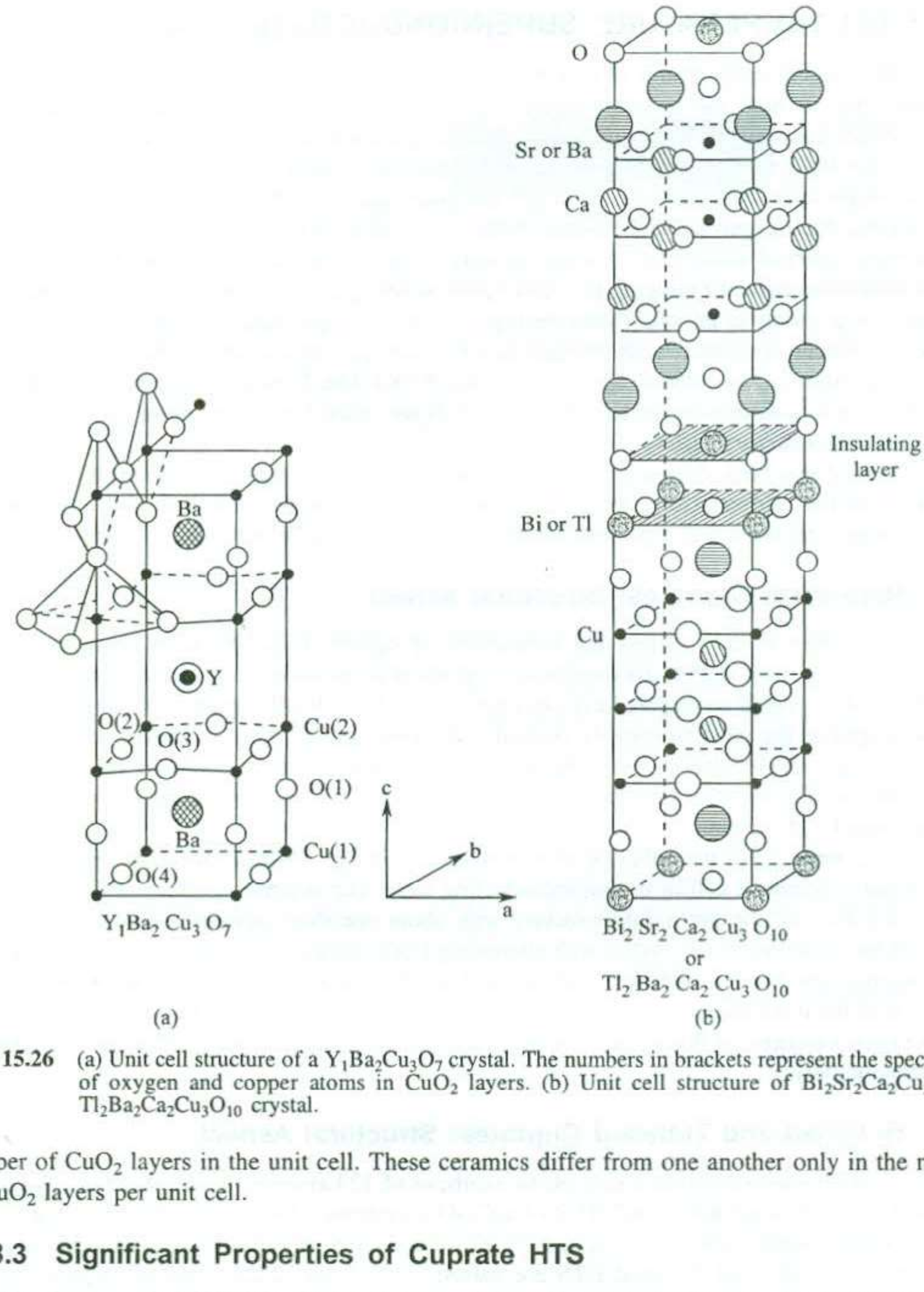

FIG. 15.26 (a) Unit cell structure of a $Y_1Ba_2Cu_3O_7$ crystal. The numbers in brackets represent the special sites of oxygen and copper atoms in CuO_2 layers. (b) Unit cell structure of $Bi_2Sr_2Ca_2Cu_3O_{10}$ or $Tl_2Ba_2Ca_2Cu_3O_{10}$ crystal.

number of CuO_2 layers in the unit cell. These ceramics differ from one another only in the number of CuO_2 layers per unit cell.

15.8.3 Significant Properties of Cuprate HTS

Consider the example of YBCO which is the most thoroughly researched system. Its resistivity around 90 K falls most sharply to an immeasurable value for $x = 0 - 0.1$, where x denotes oxygen deficiency. On increasing x, the transition temperature decreases. For $x > 0.7$, YBCO ceramics cease to be superconductors and behave as antiferromagnetic insulators. On account of their strongly anisotropic

Table 15.4 Prominent families of high temperature superconductors with highest T_c values reached. [After R. Hott, G. Rietschel, M. Sander; *Phys. Bl.*, **48,** 355 (1992).]

Formula	*Short name*	*Highest T_c observed* (K)
$REBa_2Cu_3O_7$ (RE = Rare Earths) = Y, Eu, Gd, ...)	RE BCO or 123	92 (YBCO)
$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (+ Pb dopping)	BSCCO or Bi–22 (n – 1)n	90 (Bi–2212) 122 (Bi–2223)
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$	TBCCO or Tl–22 (n – 1)n	110 (Tl–2212) 127 (Tl–2223)
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+3}$ (A = Sr, Ba)	Tl–12 (n – 1)n	90 (Tl–1212) 122 (Tl–1223) 122 (Tl–1234) 110 (Tl–1245)
$HgBa_2Ca_{n-1}Cu_nO_{2n+2}$	Hg–12 (n – 1)n	128 (Hg–1212) 135 (Hg–1223)

* approaches 165 K under pressure.

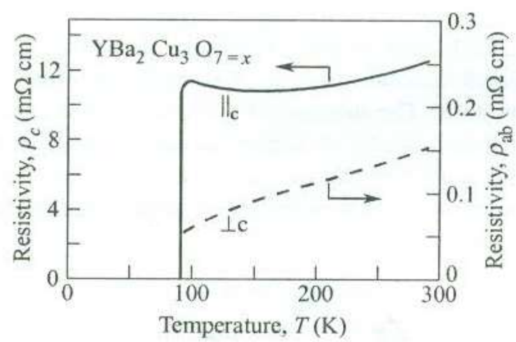

FIG. 15.27 Measured resistivity of YBCO along and perpendicular to the c-axis (ρ_a and ρ_{ab} respectively) as a function of temperature. [After S.J. Hagen, T.W. Jing, Z.Z. Wang, J. Horvath, N.P. Ong, *Phys. Rev.*, **B37,** 7928 (1988).]

crystal structure, the ceramic superconductors show highly anisotropic electronic properties. There is a large difference in the resistivities of YBCO, measured along and perpendicular to the c-axis (ρ_c and ρ_{ab} in Fig. 15.27). All the ceramic superconductors known to date show type II superconductivity for which B_{c_1} is usually less than 10 mT and the largest estimates of B_{c_2} are around 340 T.

A few extraordinary features of these HTS that might provide clue to the mechanism of superconductivity are as under:

1. The resistivity in the normal state varies linearly with temperature.
2. A near zero oxygen isotope effect is observed ($\alpha \sim$ 0–0.2). The vanishingly small isotope effect is considered an important evidence for non-phononic superconductivity in cuprates.

3. The observed energy gaps are large, nearly 20–30 meV, and $\dfrac{\Delta(0)}{k_B T_c} = 3$ to 4, which is appreciably greater than the BCS estimate equalling 1.764.
4. The thermoelectric power shows a universal behaviour as a function of hole concentration.
5. The Hall coefficient is temperature dependent.
6. An inverted parabolic relation between T_c and the hole concentration is observed.

From the data on Hall coefficient it is inferred that a Cooper pair in YBCO type and Bi- and Tl-based superconductors is a pair of holes resulting in the *p*-type superconductivity in these materials. Because of their high electronegativity, oxygen atoms act as electron acceptors. For example, in YBCO, both Y and Ba ions contribute two electrons separately to the bonding in CuO_2 layers where the oxygen atoms trap these electrons. For small x (i.e. for a less oxygen-deficient composition), there are enough oxygen atoms to swallow the electrons. This way more holes are made available in the CuO_2 planes to get bound into hole Cooper pairs. These observations point to a quasi two-dimensional charge transport in CuO_2 planes by means of holes bound in Cooper pairs. These ideas are also applicable to the Bi and Tl superconductors. Although most of the cuprates show *p*-type superconductivity, there exist a couple of systems, namely Nd_2CuO_4 and $Nd_{2-x}Ce_xCuO_4$ in which the conventional *n*-type superconductivity has been confirmed.

15.8.4 Fullerenes

The novel superconductors added most recently (1991) to the list of HTS are fullerenes whose prominent members are C_{60}-based molecular crystals. The transition temperatures of materials of this class range from 15 K to about 48 K. The structure of a single C_{60} molecule, as shown in Fig. 15.28, consists of 60 carbon atoms. It is a cluster of carbon atoms arranged in the shape of a truncated icosahedron with 20 hexagonal and 12 pentagonal faces (as in graphite, benzene and other organic molecules). The pentagons occur on account of the topological requirement for producing a closed structure that resembles a football.

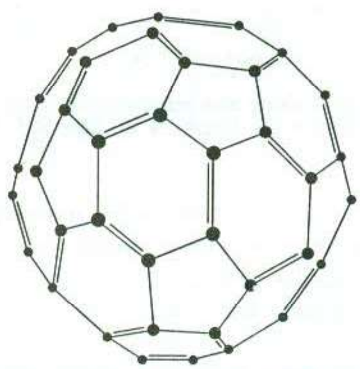

FIG. 15.28 The structure of a C_{60}-molecule.

The C_{60} clusters form the basis for a three-dimensional crystal structure of C_{60} which is characterized by an FCC unit cell. Some other interesting fullerenes have been derived from C_{60} by crystallizing C_{60} along with alkali metals whose atoms are placed in gaps between the C_{60} spheres. These are found to show superconductivity with values of T_c that justify to put them in the category of HTS. A list of such fullerenes with their T_c values is given as follows:

Fullerene	T_c(K)
K_3C_{60}	19.3
Rb_3C_{60}	28
$RbCs_2C_{60}$	33
$Rb_{2.7}Tl_{0.2}C_{60}$	48

Similar to ceramic HTS, fullerenes demonstrate the gradual onset of diamagnetism when cooled in zero magnetic field to temperatures below T_c. It has not been possible so far to carry out other experiments on fullerenes on account of their strong tendency to react with atmospheric oxygen.

Despite the availability of quality data of enormous volume and getting an exclusive attention of the entire community of solid state physicists, the theory of HTS continues to be in an uncertain shape. In view of this fact, it is appropriate to dispense with the theoretical treatment of HTS in this introductory version of the subject.

15.9 APPLICATIONS

Superconductors have tremendous potential for application. It is extremely advantageous to use them as conductors of electric current because of their nondissipative property. Applications are mostly based on conventional (liquid helium) superconductors. Although they have already found numerous applications, their utilization has been much restricted by the requirement of extremely low temperatures. It is not possible to give here a complete list of applications. The main applications are: high field magnets, SQUIDS, and some other electronic and rf devices. The NMR imaging technique employing high magnetic fields has proved far superior to CATSCAN used in medical diagnostics. High Q-cavities and various sensors are some other important devices where super-conductors are used. In addition to being employed in SQUIDS, there are a large number of applications of Josephson junctions in electronic circuitry.

In view of their higher T_c, the use of HTS in a much larger number of applications seems imminent. With considerable advancement in the methods of sample preparation (e.g. laser ablation, MOCVD, etc.), good quality wires, tapes and films of cuprates have been produced. But the low critical current and ceramic nature of HTS have seriously limited their applications. The degree of success achieved has been highest with the YBCO system, which is utilized for the fabrication of Josephson junctions and SQUIDS. With revolutionary advancement in material research, a very large number of applications spread over different areas can be realized. A high speed (~ 550 km per hour) leviating train has been tested using a conventional superconductor. But these leviating vehicles and long distance non-dissipative power transmission systems have yet to be realized in practice.

SUMMARY

1. The dc resistance of a superconductor is zero.
2. The Meissner effect ($\mathbf{B} = 0$) is complete in bulk metallic samples in the superconducting state. The London penetration depth λ_L gives the extent over which the magnetic flux penetrates from the surface of a superconductor.