Chapter 1

Introduction.

In this chapter I will review the history of superconductivity, and its basic properties. The discovery of high temperature superconductor follows and the chapter ends with a section on the structure of these new superconductors.

Superconductors are a class of materials whose dc resistivity goes to zero below a certain temperature T_c, called the critical temperature. This incredible behavior, called superconductivity, was discovered in 1911 by the Dutch physicist H. Kamerlingh Onnes (1).He and one of his graduate students found that the dc resistance of purified mercury dropped abruptly to zero at a temperature of 4.15 K, as shown in Figure 1.1. Above this temperature the resistivity is small, but finite, while the resistivity below this point is so small that it is essentially zero. When it was cooled through the transition temperature in the absence of any external magnetic field, it became superconducting. Onnes won the Nobel Prize in 1913 for the discovery of superconductivity, and for the liquefaction of helium.

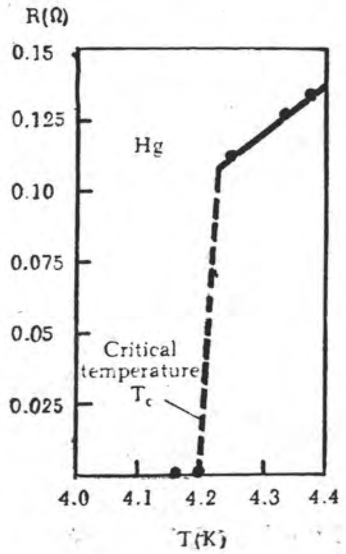


Fig.1.1 Resistance versus temperature for mercury. The graph follows that of a normal metal above the critical temperature. The dc resistance drops abruptly to zero at the critical temperature, which is 4.15 K for mercury (2).

Following Onnes's discovery, many new materials (both elements and compounds), were found to be superconductors, each with own critical temperature T_c.

Over the years after Onnes's discovery, intense theoretical and experimental efforts have been devoted to study superconductivity. It is found that when a normal metal becomes superconducting, its superconducting properties are very different from normal metal behaviors.

Basic Properties of Conventional Superconductors

Various experiments on superconductivity in many metals and compounds have shown that the nature of the superconducting state is very different from that of metals. For example,

1. A superconductor exhibits infinite conductivity (2).

2. A bulk specimen of metal in the superconducting state exhibits perfect diamagnetism, with the magnetic induction $\vec{B}=0$. This is the Meissner effect (2). The external magnetic field will penetrate the surface of the specimen over a distance determined by the penetration depth, λ (2).

3. There are two types of superconductors, I and II. In a bulk specimen of type I superconductor, the superconducting state is destroyed and the normal state is restored by application of an external magnetic field in excess of a critical value H_c. A type II superconductor has two critical fields, a vortex state exists in the range between H_{c1} and H_{c2} (2).

4. The charge carriers in the superconducting state have charge -2e and are hence formed by pairs of electron. The average separation of the electrons making up the pairs is given by the intrinsic coherence length ξ_o . Type II superconductors have $\xi_o << \lambda_o$ (2).

5. In the superconducting state, an energy gap $E_g = 3.5\ k_B T_c$ separates superconducting electrons below from normal electrons above the gap. The gap is detected in experiments on heat capacity, infrared absorption, and tunneling (2).

6. In many superconductors, the critical temperature varies with isotopic mass M as $T_c \propto M^{-1/2}$ (2).

7. Magnetic impurities such as Gd in $LaAl_2$ destroy the superconductivity at very small concentrations (2).

Since the discovery of superconductivity in metals by Onnes, there has been a substantial effort to increase the transition temperature by alloying intermetallic compounds in many laboratories.

For many years, all efforts to enhance T_c over the 23.3 K reached by Gavaler (3) and Testardi et al.(4) in thin films of Nb_3Ge failed. This situation led one to the conviction that the efforts in intermetallic compounds should not be pursued further.

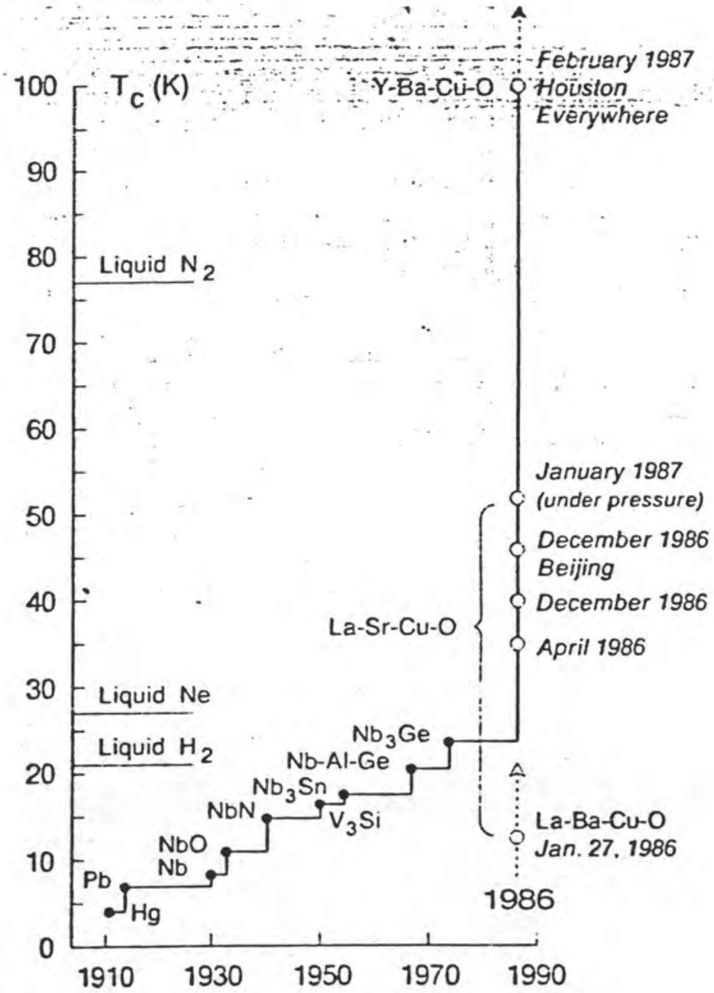
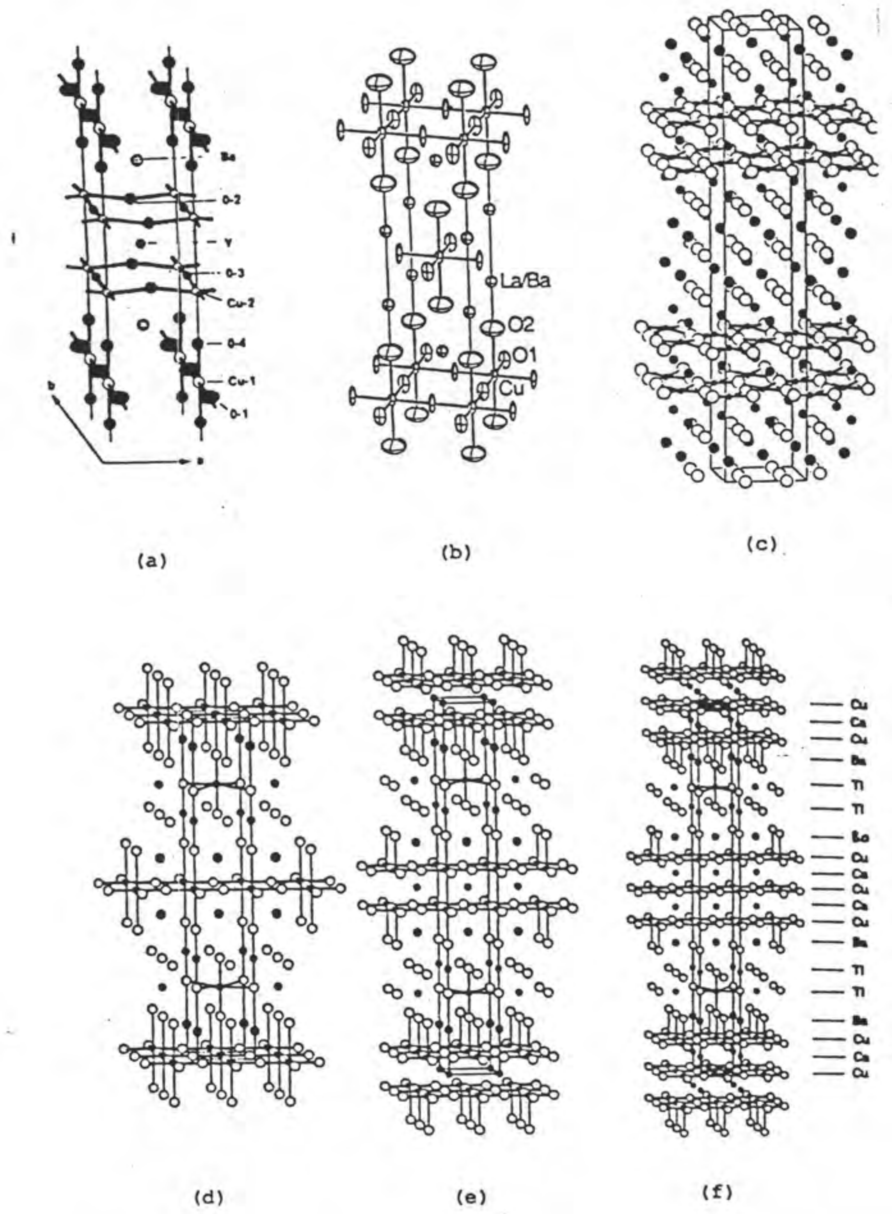


Fig.1.2 Evolution of the superconductive transition temperature(5).

Later studies in niobium-doped $SrTiO_3$, the first superconducting metallic oxide with a T_c of 0.3K (6)increased T_c to 0.7K (7,8). For this T_c, the carrier concentration n was only 2×10^{20} cm^{-3}, two orders of magnitude lower than in a metal, suggesting an extremely large electron-phonon coupling. In 1973, superconductivity in the Li-Ti-O system with onsets as high as 13.7 K was reported by Johnston et al.(9). Two years later, superconductivity in the mixed-valence compound $BaPb_{1-x}Bi_xO_3$, a perovskite, was discovered by Sleight et al. (10). The highest T_c in homogeneous oxygen-deficient mixed crystals occurs at 13 K, with a comparatively low concentration of carriers, $n=2\times10^{21}$ to 4×10^{21} cm^{-3}(11,12). Therefore, according to the Bardeen-Cooper-Schrieffer (BCS) theory (13), a large electron-phonon coupling was present. Thus one could expect to find still higher T_c's in other metallic oxides if the electron-phonon interactions and the carrier densities, $N(E_F)$,at the Fermi level could be further enhanced.

In 1986 Bednorz and Müller (14) discovered that La_2CuO_4 when doped with barium,is a superconductor.The dopant replaced La, and the optimum concentration is about 8% of Ba, yielding a superconductor with T_c of 35 K.

The next major breakthrough was that of Chu's group (15)in 1987. They found T_c above the liquid nitrogen temperature of 90 K for a new material, comprising the elements barium, yttrium, copper, and oxygen, which is now known to be $YBa_2Cu_3O_{7-\delta}$ and its crystallography structure is shown in Fig.(1.3).



(a) (b) (c)

(d) (e) (f)

Fig.1.3 Crystal structure of some high-T_c superconductors

(a) $YBa_2Cu_3O_7$ (16) (b) Ba-doped La_2CuO_4 (17) (c) $Bi_2Sr_2CuO_6$ (17)

(d) $Tl_2Ba_2CuO_6$ (16) (e) $Tl_2Ba_2CaCu_2O_8$ (18) (f) $Tl_2Ba_2Ca_2CuO_{10}$ (16)

Chu's material will be referred to henceforth a "YBCO" and the class of materials to which it belongs will be called collectively the "1-2-3" materials.

One of the most surprising subsequent discoveries(19) was that the yttrium in YBCO is a "passenger" for which almost any rare earth element can be substituted, with hardly any change in T_c.

For almost a year,the 1-2-3 materials have the entire stage to themselves. But some new classes(20)of copper-oxide-based materials have been discovered more recently in particular(16,17,18) the series of compounds $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n}$ with T_c's of 7 K, 80 K, and 110 K for n=1,2,3 respectively and the series of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ with T_c's of 80 K, 110 K and 125 K for n=1,2,3 respectively. In both these systems, T_c was seen to increase with the number n of CuO_2 planes per unit cell, at least in the range n=1 to 3.This has led to a suggestion that increasing n still further might provide a route to higher T_c.

Recently Ihara et. al.(21)find that T_c has a maximum around n=4 in the series of compound $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ for n=1,2,3,4 and 5 they report values of T_c respectively, 17 K, 91 K, 116 K, 122 K and less than 120 K.

Basic Structure of High-temperature Superconductors.

High-temperature superconductor has now been observed in four families of copper oxide compounds.

1. The $La_{2-x}AE_2CuO_4$ phases (14) where AE is a alkaline earth atom Ba, Sr or Ca, with a maximum T_c of 40 K.

2. The $YBa_2Cu_3O_7$ (1-2-3) phases (15) where Y can be replaced by other rare earths, with a maximum T_c of 93 K.

3. The $Bi_2Ca_1Sr_2Cu_2O_8$ (2-1-2-2) phases(22,23), where Bi can be replaced by Tl and Sr by Ba, with a maximum T_c around 90 K.

4. The $Tl_2Ca_2Ba_2Cu_3O_{10}$ phases (2-2-2-3)(24) with a maximum T_c of 125 K.

The most fundamental structure of superconductors is the CuO_2 plane as shown in Fig.1.4 The CuO_2 plane is a two dimensional plane formed by combining square planar units,each of which is surrounded by oxygen and has a Cu at its center. The square planars are combined through the oxygen at their apices. This plane seems to be the most important structure factor to produce superconductivity. Any of the substances such as $Y_1Ba_2Cu_3O_7$, $(BiO)_2Sr_2Ca_{n-1}Cu_nO_{2n+2}$, $(TlO)_2Ba_2Ca_{n-1}Cu_{n-1}Cu_nO_{2n+2}$, (Nd, Ce(Sr))$_2CuO_4$, and (La,Ba)$_2CuO_4$ discoverd by Bednorz-Müller, have this basic structure.

Some features of $La_{2-x}Ba_x(Sr_x)CuO_4$ and $LaBa_2Cu_3O_7$

$La_{2-x}Ba_x(Sr_x)CuO_4$ compounds (Fig.1.5) have the quasi two-dimensional K_2NiF_4 structure with tetragonally elongated Cu-oxygen octahedra. These oxides have a tetragonal structure at room temperature when $x>0.05$ and become orthorhombic around 180 K, well above the superconducting transition temperature. T_c in these oxides shows a maximum around a specific value of x (~ 0.15 and 0.2 respectively in the case of Ba and Sr). The La ion in $La_{2-x}Ba_xSr_xCuO_4$ can be replaced by other rare earth ions upto a point (<10%) without losing superconductivity. Substitution of Cu partly by Ni, Zn and such ions generally lower the T_c.

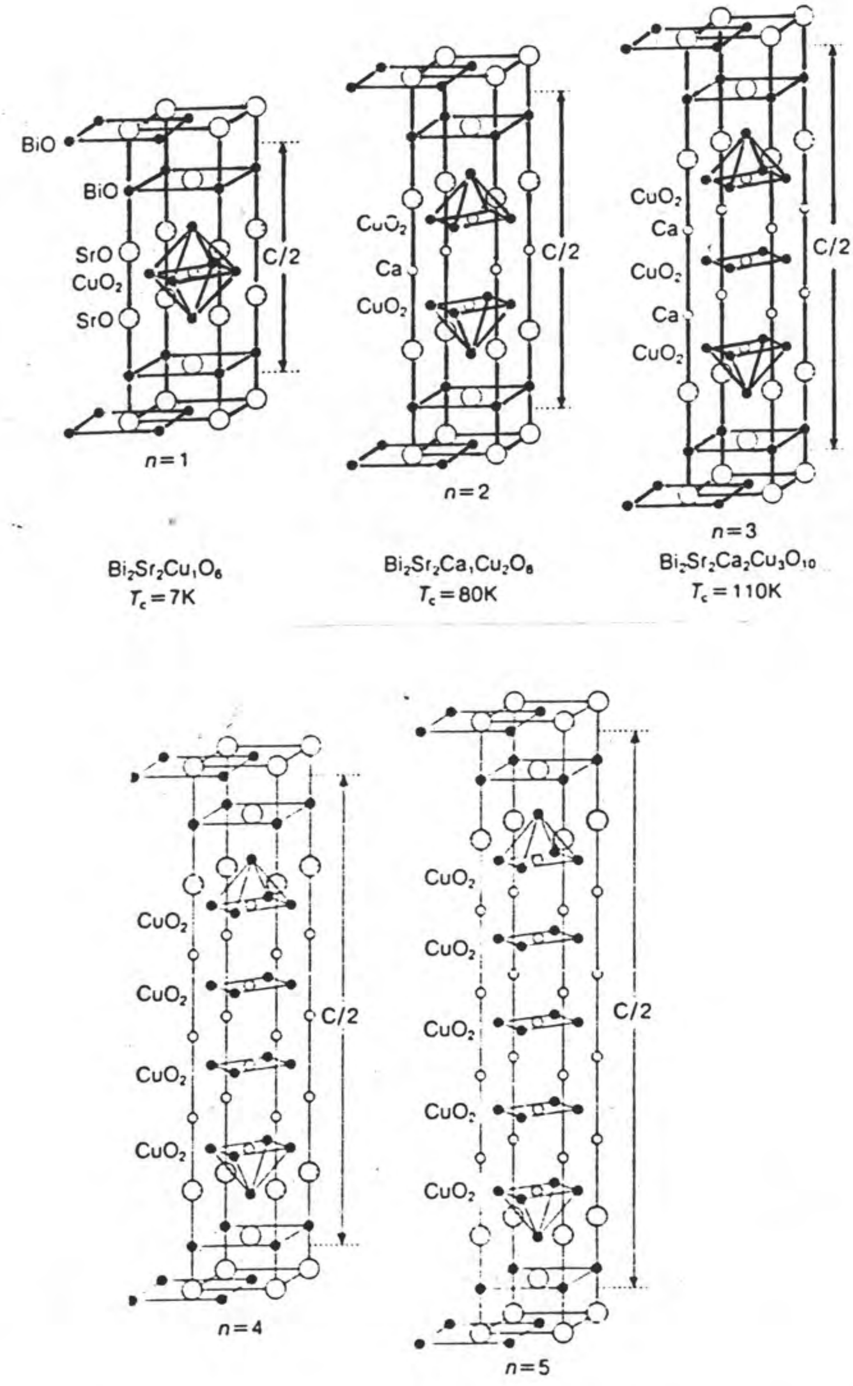


Fig. 1.4 Crystal structure of a Bi-Sr-Ca-Cu-O system (25).

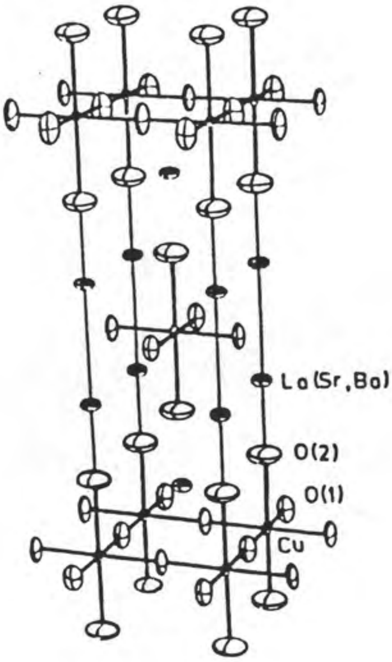


Fig. 1.5 Structure of $La_{2-x}Ba_x(Sr_x)CuO_4$ (26).

$YBa_2Cu_3O_7$ and related 123 oxides are orthorhombic (Fig.1.6), by virtue of the preferential population of the 01 sites (along the b-axis) giving rise to the Cu-O chains. Depletion of 01 oxygens or disorder between the 01 and 05 site gives rise to a tetragonal structure (Fig.1.6). The orthorhombic structure is responsible for the formation of twins; across the twin boundary, the a and b parameters seem to interchange. $YBa_2Cu_3O_{7-\delta}$ shows a progressive lowering of T_c as δ increases until the superconductivity is lost at $\delta \approx 0.6$ when the structure is tetragonal. The Cu ion in $YBa_2Cu_3O_7$ can be replaced by cations such as Zn, Fe and Ca and these substitutions generally lower the T_c because of a change in oxygen stoichiometry.

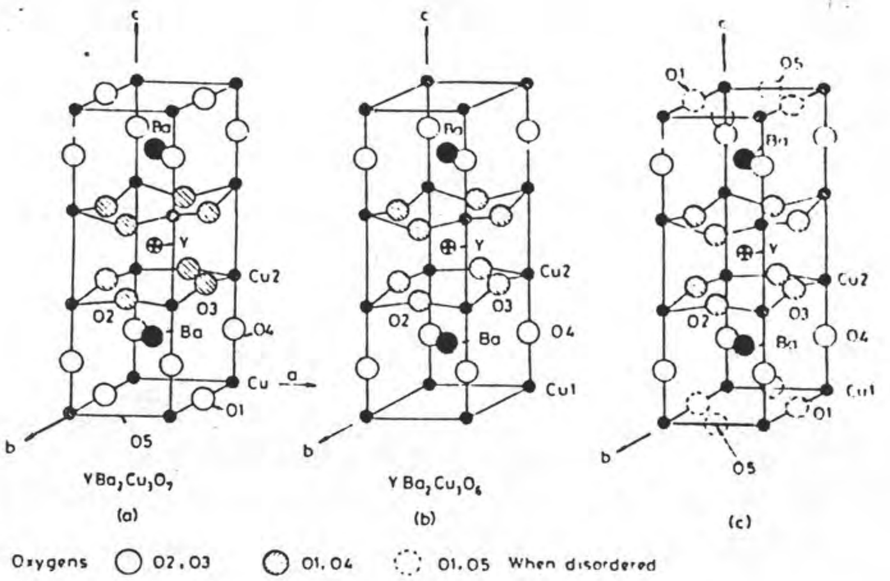


Fig. 1.6 Structure of $YBa_2Cu_3O_{7-\delta}$

(a) $\delta = 0.0$, orthorhombic; (b) $\delta = 1.0$, tetragonal;

(c) disordered tetragonal structure (26).

Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O systems

Several compositions of the Bi-Ca-Sr-Cu-O system have been studied, the member which has reproducibility shows high T_c superconductivity (zero-resistance 90 K and onset 112 K is $Bi_2(Ca,Sr)_3 Cu_2O_{8+\delta}$. By varying the Ca/Sr ratio, it is found that compositions close to $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_{8+\delta}$ with a slight Bi excess are ideal. In Fig.(1.7), electrical resistivity data of the n=2 member of the $Bi_2Ca_xSr_{n+1-x}Cu_nO_{2n+4}$ series is shown along with that of n=3 member. The n=1 member without Ca (27) has very low T_c, but with x=1, a T_c of around 80 K seems to be observed (Fig. 1.7), this n=1 member, $Bi_2CaSrCuO_{6+\delta}$, is generally in mixture with the 2122 phases. In n=3 member can be prepared in mixture with the n=2 member. The n=3 member $Bi_2Ca_2Sr_2Cu_3O_{10+\delta}$ shows a T_c of 110 K with a still higher onset temperature. The presence of the n=3 member was probably responsible for the 110 K superconductivity found in other compositions. Partial substitution of Bi by Pb upto 25% is possible, with a marginal increase in T_c in the case of the n=2 member.

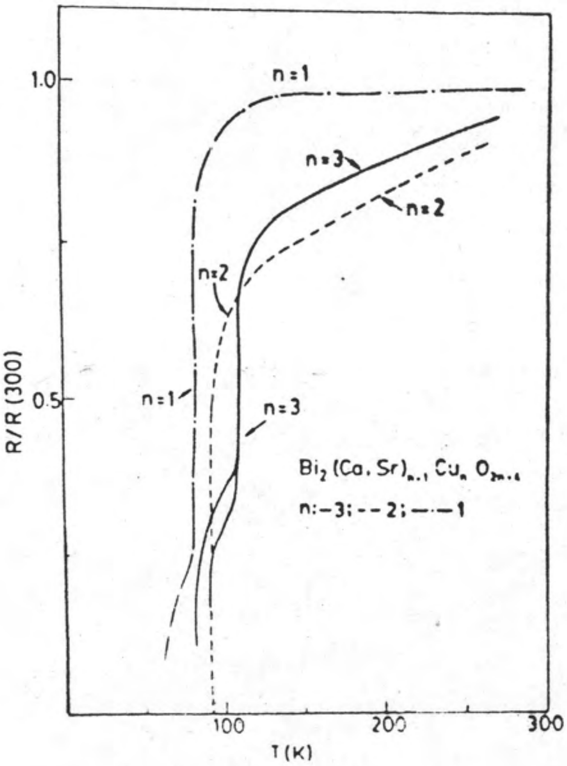


Fig. 1.7 Resistivity data of the Bi-Ca-Sr-Cu-O system (26).

The bismuth cuprates have structures similar to the family of oxides, $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$. The main difference is that we do not have Bi_2O_2 layers in the oxides. The actual structure of $Bi_2(Ca,Sr)_3Cu_{8+\delta}$ is shown in Fig.(1.8).

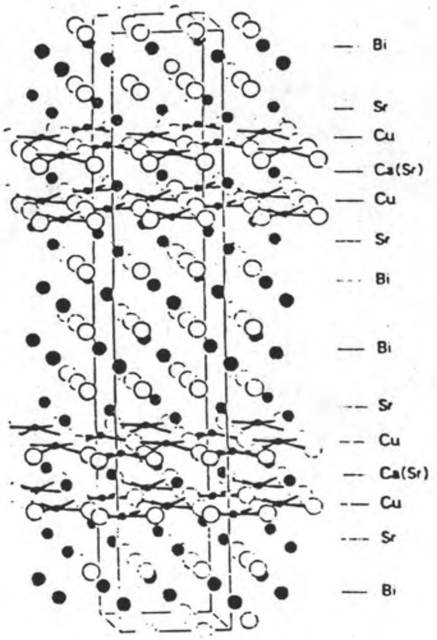


Fig. 1.8 Structure of $Bi_2(Ca,Sr)_3Cu_{8+\delta}$ (26).

In the Tl-Ca-Ba-Cu-O system, the $TlBa_2CuO_6$, $TlCaBa_2Cu_2O_8$ and $TlCa_2Ba_2Cu_3O_{10}$ are well-characterized (28,29,30) with zero-resistance T_c's around 80, 110 and 125 K for n=1,2 and 3 respectively. The Tl cuprates give very sharp resistivity and susceptibility anomalies at T_c. The structures of Tl-Ca-Ba-Cu-O superconductors are similar to those of the Bi-Ca-Sr-Cu-O superconductors. Fig.(1.9), shows the structure of $Tl_2CaBa_2Cu_2O_8$.

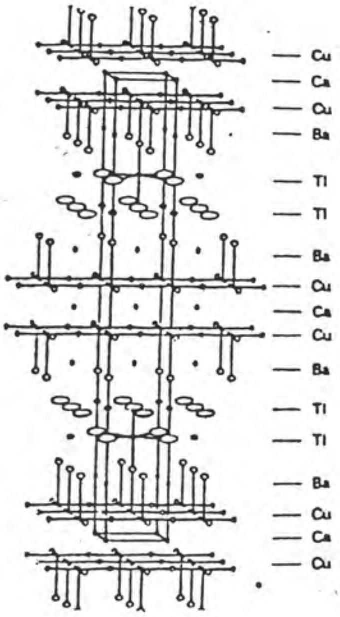


Fig. 1.9 Structure of $Tl_2CaBa_2Cu_2O_{8+\delta}$ (26).

The T_c in the Tl-Ca-Ba-Cu-O system also increases with the number of Cu-O layers. The n=4 and 5 members of this family would be expected to show T_c's of around 140 and 160 K respectively. Fig.(1.10) shows the schematic structure of the different members of Bi and Tl cuprate families to point out their similarity.

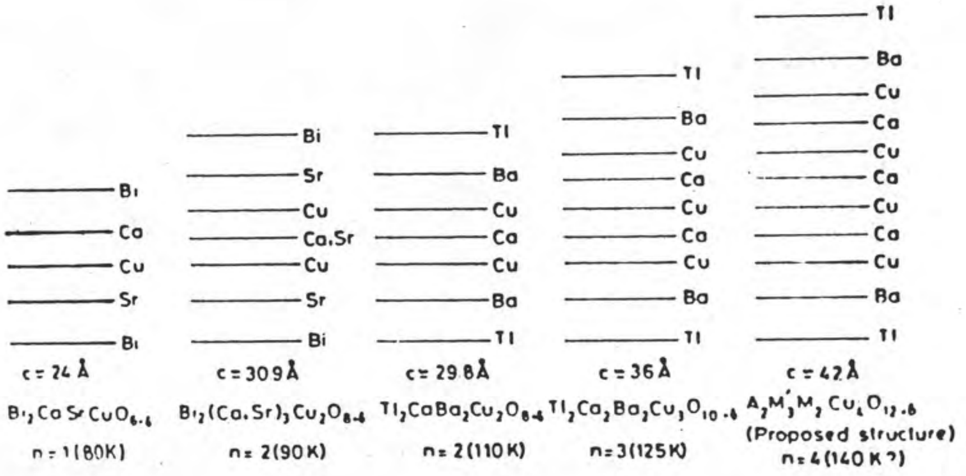


Fig. 1.10 Schematic structure of the Bi-Ca-Si-Cu-O and Tl-Ca-Ba-Ca-O families. The T_c values are shown in parentheses next to the number of Cu-O layers(n) (26).

In the Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O systems, the T_c increases with the number of Cu-O layers(n), as shown in Fig.(1.11). We could expect a T_c of 200 K only when n is 7 or higher. This is unlikely to be achieved. However, high T_c's in the 200-300 K range found in the Bi-Ca-Sr-Cu-O systems could be due to intergrowths with a large number of Cu-O layers in the unit cell(25). It appears that Bi and Tl ions do not play any significant role in the superconductivity of these cuprates, the role is mainly of oxygen and copper ions.

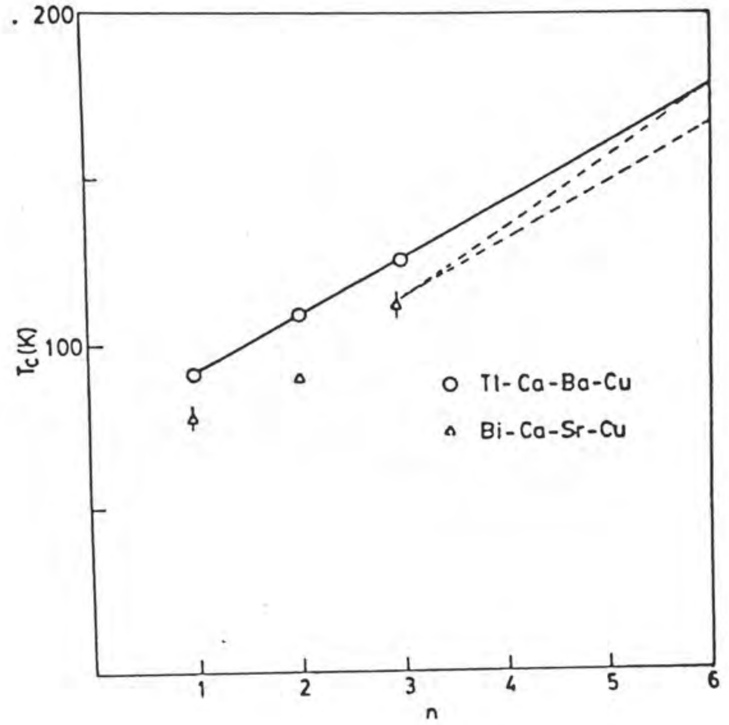


Fig. 1.11 Variation of T_c with the number of Cu-O layers, in the Bi-Ca-Sr-Cu and Tl-Ca-Ba-Ca systems (26).

Basic Properties of High Temperature Superconductors.

Some properties of the lamellar CuO_2 superconductors are identical to those of conventional superconductors. Others, however, differ quite fundamentally and this indicates that, at the minimum, the pairing mechanism itself must be quite new. Here, only the essential features are stated.

1. In zero field, the resistance is, of course, zero.

2. Meissner measurements have turned out to be surprisingly difficult in these materials. Only in high-quality samples at very low fields, typically less than 1 Oe, is a 100% Meissner fraction observed. In higher fields when the sample is cooled through T_c in

the field, strong flux pinning occurs so that there is not a complete flux exclusion. The penetration depth in the in-plane direction at low temperatures is of order 2000 A° (31).

3. All of the high-T_c materials are type II superconductors necessitating that $\xi_c << \lambda_c$. The vortices carry one quantum of flux hc/2e implying that the carriers have charge 2e.

4. Various measurements, including Josephson tunnel junctions(32), direct measurements of the flux quantum (hc/2e)(33) and the vortex array measurements(34) mentioned above all imply that the carriers are bound in pairs. However the coherence length is only about 15 A° in the plane and less than the interplanar separation perpendicular to the CuO_2 planes (31).

5. Measurement of the energy gap have proved to be extremely difficult. Various measurements can be interpreted in terms of a gap with E_g varying between $2k_BT_c$ and $8k_BT_c$. However, virtually all spectroscopic studies imply that there are significant excitations with energies less than E_g (35,36).

6. The isotope effect in the high-T_c materials is very small. Indeed, replacement of ^{16}O by ^{18}O seems to produce a decrease of T_c by about 0.3 K independent of T_c for transition temperature varying from 40 K to 110 K (37).

To date, some relations have been observed between T_c and the physical properties (25,38). First, the relation between T_c and the charge of carriers in high temperature, superconductivity is observed when the nominal charge of Cu is +2.1 to +2.3 in the case of the hole conduction. Second, the relation between T_c and the number of CuO_2 planes is now known. Although the reason is not understood yet, T_c rises as the number of layers increases from single, to double, to triple. Three layers of CuO_2 of the Tl-Ba-Ca-Cu-O system shows the zero resistance temperature, at 125 K. T_c tends to saturate and decrease as the number of CuO_2 increases further.

In the next chapter the BCS theory will be reviewed, and various works done by many researchers using different models will be discussed.