Physics of Transition Metal Oxides

Lecture 10

High-temperature superconductors

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Above a critical temperature, T_C, superconductors are typically normal metals, but not very good conductors. Below T_C, resistivity is zero and the material is a perfect diamagnet. Pure metals, like Pb, Ta, Sn are superconductors, while Cu, Ag, or Au are not.

This plot shows the original measurement made by Kammerlingh Onnes in Leiden in 1911.

Material	T_C (K)	Year
Hg	4.1	1911
Pb	7.2	1913
Nb	9.2	1930
$NbN_{0.96}$	15.2	1950
Nb_3Sn	18.1	1954
$Nb_3(Al_{3/4}Ge_{1/4})$	20-21	1966
Nb_3Ga	20.3	1971
Nb_3Ge	23.2	1973
$Ba_xLa_{5-x}Cu_5O_y$	30-35	1986
$YBa_2Cu_3O_{7-\delta}$	95	1987
$Bi_2Sr_2Ca_2Cu_3O_{10}$	110	1988
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125	1988
$HgBa_2Ca_2Cu_3O_{8+\delta}$	133	1993
$HgBa_2Ca_2Cu_3O_{8+\delta}$ at 25 GPa	155	1993
$HgBa_2Ca_2Cu_3O_{8+\delta}$ at 30 GPa	164	1994

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Lattice distortions:

We start by reviewing lattice distortions in perovskites, taking $BaTiO_3$ as an example. We already looked at $BaTiO_3$ earlier when discussing ferroelectric oxides. Ti (B-site) has 6 oxygen neighbors, Ba (A-site) has 12 nearest neighbor oxygens. $BaTiO_3$ has three possible crystal structures:

- **cubic**: high-temperature phase (above 200 °C) with $a = b = c = 4.0118$ Å, $V = 64.57$ Å^3

- **tetragonal**: room-temperature phase, ferroelectric, $a = b = 3.9947$ Å, $c = 4.0336$ Å, $V = 64.37$ Å^3.

- **orthorhombic** low-temperature phase (below room temperature), $a = 4.009\sqrt{2}$ Å, $b = 4.018\sqrt{2}$ Å, $c = 3.990$ Å, $V = 2(64.26)$ Å^3.

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We also need a list of ionic radii:

Small	Cu^{2+}	0.72 Å	Bi^{5+}	0.74 Å
Small-Medium	Cu^+	0.96 Å	Y^{3+}	0.94 Å
	Bi^{3+}	0.96 Å	Ti^{3+}	0.95 Å
	Ca^{2+}	0.99 Å	Bi^{3+}	0.96 Å
	Nd^{3+}	0.995 Å		
Medium-Large	Hg^{2+}	1.10 Å		
	Sr^{2+}	1.12 Å	La^{3+}	1.14 Å
Large	Pb^{2+}	1.20 Å	Ag^+	1.26 Å
	K^+	1.33 Å	O^{2-}	1.32 Å
	Ba^{2+}	1.34 Å	F^-	1.33 Å

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Cubic lattice:

The atomic positions are:
- **E site**: Ti (0,0,0) apical Ti
- **F site**: O $(0,0,\frac{1}{2})$; $(0,\frac{1}{2},0)$; $(\frac{1}{2},0,0)$ three edge-centered oxygens
- **C site**: Ba $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ body-centered Ba

E	F	C	
Ti	O_2	-	Ti at E-site, O at two F sites
O	-	Ba	O at E-site, Ba at C-site
Ti	O_2	-	Ti at E, O at two F sites

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Ba and O are almost the same size. The BaO layer (without transition metal ions) would form a close-packed cubic lattice with a lattice constant of 3.73 Å. The holes would have a radius of 0.545 Å.

Inserting the Ti ions pushes the oxygens apart, increasing the lattice constant. Replacing Ba with smaller Ca or Sr reduces the lattice constant.

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Tetragonal $BaTiO_3$

The tetragonal distortion $(c-a)/\frac{1}{2}(c+a)$ is 1%. The shift off the cubic positions is about 0.1 Å. The Ti-O-Ti bonds bend and the Ti-O distance changes. The Ti-Ti distance remains practically the same.

An orthorhombic structure can arise by distorting the a, b axis lengths, or by distorting the length of the diagonals.

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The diagonals now become the new lattice axes and the unit cell doubles in size (approximately). The lattice parameters are larger by $\approx \sqrt{2}$.

In case of $BaTiO_3$ the deviation from a tetragonal structure is

$$\frac{100|b-a|}{\frac{1}{2}(b+a)} = 0.22\%$$

The orthorhombic distortions changes the atomic distance in the a and b directions.

Distortions of this type are very common in High-T_C oxides: rhombal in $(La_{1-x}Sr_x)CuO_4$ and rectilinear $YBa_2Cu_3O_{7-\delta}$.

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Most of the high-T_C oxides are cuprates, some are not:

$Ba_{1-x}K_xBiO_{3-y}$

For $x > 0.25$ it forms a perovskite with $a = 4.29$ Å. Potassium partli substitutes Ba at the body center site, Bi ions are at the corners. Some of the oxygens are missing from the edge sites. K and Ba are nearly the same size. Bi valence is a mixture of Bi^{3+} and Bi^{5+}. The lattice constant is unusally large due to the large size of the Bi^{3+} ion (0.96 Å).

The T_C reaches a maximum of about 40 K at $x = 0.4$.

Although there is no copper in this structure, it has a mixed-valent transition metal and oxygen vacancies are needed for charge compensation. These features are common to all high-T_C materials.
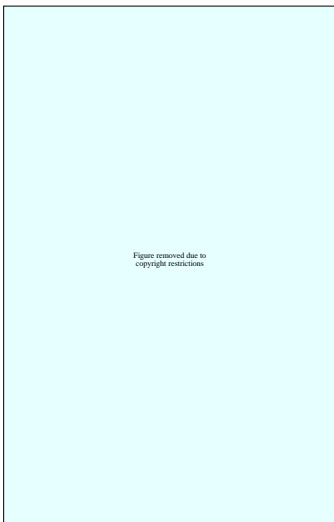
$BaPb_{1-x}Bi_xO_3$
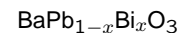
Has a T_C of up to 13 K in the range $0.05 \leq x \leq 0.3$. Only the tetragonal phase is superconducting, not the cubic phase. Otherwise has a similar charge disproportionation of

$$2Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$$

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Cuprates

Cuprate superconductors have Cu^{2+} ions in the place of the Ti ions of the $BaTiO_3$ structure. The lattice constant in the a, b plane is largely determined by these CuO_2 layers. Note that a Cu analogue of $BaTiO_3$, $BaCuO_3$, does not exist because the Cu^{4+} ion does not exist in oxides. Each compound has a unique sequence of layers in the c-axis direction.

- **superconducting layers**: [Cu O_2 -] and [- O_2 Cu]
- **insulating layers**: [Y - -] or [- - Ca]
- **hole-donating layers**: [Cu O^b -] or [Bi - O]
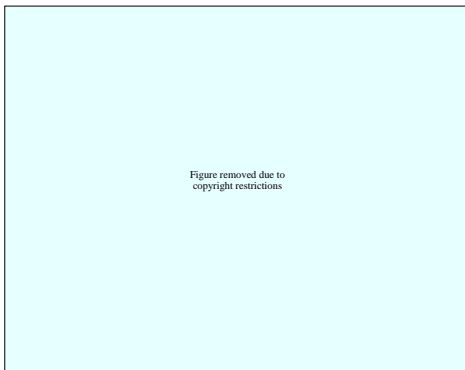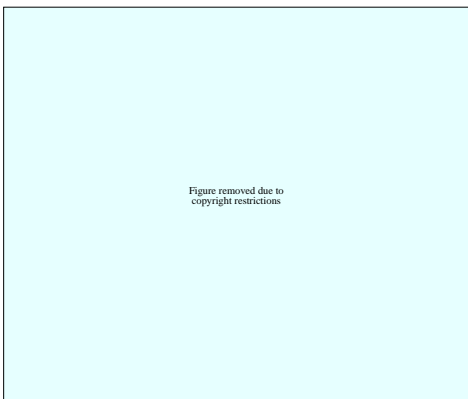
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Aligned cuprates
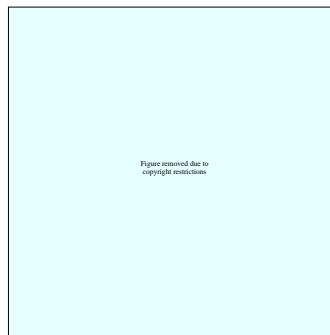
Cuprate superconductors have a σ_h horizontal reflection plane $\perp$ to the c-axis direction at the center of the unit cell. Other reflection planes are at the top and bottom of the unit cell. All atoms (except those in the σ_h plane) thus appear twice in the unit cell.

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Atomic layers in $YBa_2Cu_3O_7$

$YBa_2Cu_3O_7$ is often referred to as YBCO or simply 123. It has a T_c of 92 K.

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The unit cell consists of three perovskite units: $BaCuO_3$, $YCuO_2$, and $BaCuO_2$, with some missing oxygen. This explains why the c-axis length (11.68 Å) is $\approx 3\times$ the a-axis (3.83 Å) or b-axis (3.88 Å) length. Only the orthorhombic structure (copper-oxygen chains) is superconducting. the oxygens are randomly distributed along the a and b axes in the tetragonal phase.

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The Cu(1) ions in the chains have a square-planar coordination. The two other Cu(2) copper sites have a fivefold pyramidal coordination.
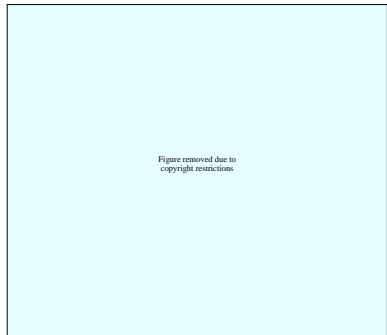
Oxygen stoichiometry is very important. The formula is usually written as $YBa_2Cu_3O_{7-\delta}$. When $\delta < 0$, the extra oxygen will go into the a-axis sites in the chain layers, resulting in a superconducting phase with T_c=60 K.
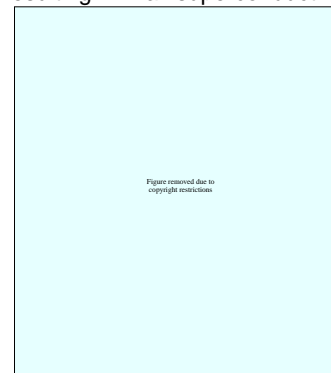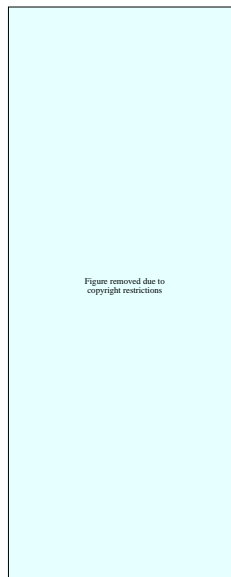
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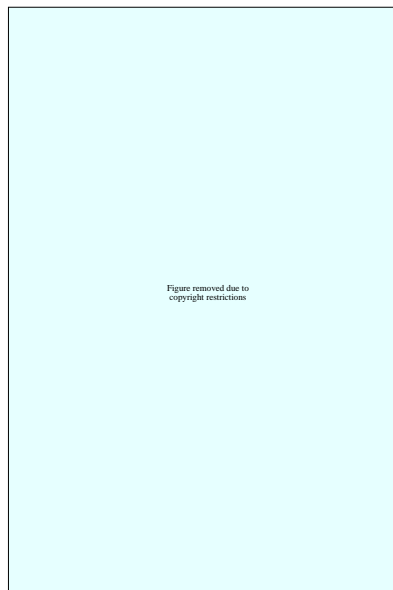
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Charge distribution

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It is clear that the Y^{3+} and Ba^{2+} ions are completely ionized. Cu and O have large overlap. The chain sites are clearly visible. The weakest Cu-O bond is between the Cu(2) and apical O(4) sites. The calculation gives an average charge of +1.62 for copper and -1.69 for oxygen.

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Oxygen stoichiometry

Oxygen can be loaded into or removed from the $YBa_2Cu_3O_{7-\delta}$ structure by annealing in pure oxygen or in a vacuum.

Extra oxygen or vacancies directly affect the chain sites in the structure but there is a significant amount of charge transfer between the copper layers.

There are two superconducting phases, depending on the oxygen content, with T_c of 92 K and 60 K. Superconductivity disappears in $YBa_2Cu_3O_{6.4}$. At this point the average copper oxidation state is below 2.

Cox92 p.253

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Side-centered cuprates
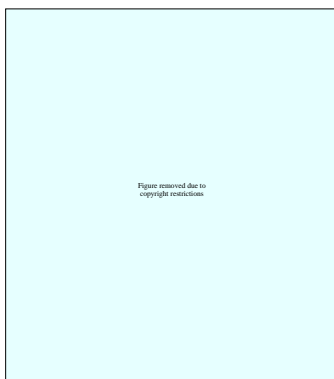
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In side-centered lattices for each atom at a position (x, y, z) there is an identical atom at a position $(x, y + \frac{1}{2}, z + \frac{1}{2})$. One example is $YBa_2Cu_4O_8$, in which we have a double layer of Cu-O chains. T_c is in the 40 to 80 K range. Another example is $Y_2Ba_4Cu_7O_{15}$, which is an ordered 1:1 intergrowth of 123 and 124 compounds. The T_c can be as high as 90 K.

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Body-centered cuprates
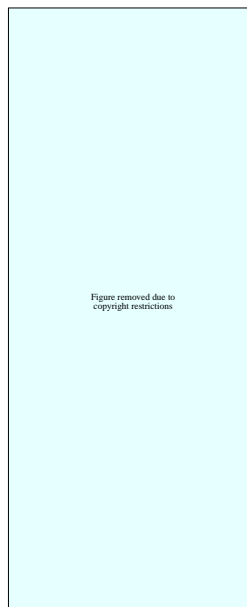
Body-centered lattices have an additional symmetry with each atom at (x, y, z) having an identical atom at $(x \pm \frac{1}{2}, y \pm \frac{1}{2}, z \pm \frac{1}{2})$. Half of the Cu-O planes are [Cu O_2 -] and half are [- O_2 Cu]. The example shown here is for $Tl_2Ba_2CaCu_2O_8$

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La$_2$CuO$_4$ and derivatives.

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The **T** phase consists of a stacking of CuO$_4$La$_2$ and La$_2$O$_4$Cu groups. The CuO$_2$ planes are mirror planes in the lattice and are thus not buckled. The parent compound La$_2$CuO$_4$ is an antiferromagnetic insulator. A superconducting composition is obtained by doping, e.g. (La$_{1-x}$Sr$_x$)$_2$CuO$_4$ with $x = 3 - 15\%$.

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The **T'** phase applies to Nd$_2$CuO$_4$. The apical O(2) oxygens in the [O - La] and [La - O] layers now move into a separate O(3) [- O$_2$ -] layer between [- - La] and [La - -] layers. The Cu octahedra have now lost the apical oxygens, leaving a square-planar CuO$_4$ layer.

While La$_2$CuO$_4$ is a hole-type superconductor, the Nd$_2$CuO$_4$ is a much less common electron-type superconductor. The best known composition is Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$.

La and Nd are both trivalent and both donate three electrons to oxygens

$$La \rightarrow La^{3+} + 3e^-$$
$$Nd \rightarrow Nd^{3+} + 3e^-$$
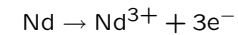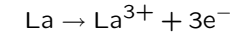
The doping is done by replacing La $\rightarrow$ Sr or Nd $\rightarrow$ Ce

$$Sr \rightarrow Sr^{2+} + 2e^-$$
$$Ce \rightarrow Ce^{4+} + 4e^-$$
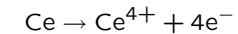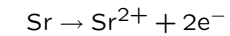
Sr doping thus decreases the number of electrons, creating a hole-doped compound while Ce doping increases the number of electrons, producing an electron-doped compound.

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Electron-doped superconductors

Almost all high-T_c cuprates are hole-type materials. The a-axis length of the hole-doped cuprates is always less than about 3.92 Å. The lattice constant of electron-doped cuprates is larger, around 3.95 Å. To achieve a superconducting electron-doped material, it is necessary to do cation doping and oxygen stoichiometry adjustment.

The best-known example is Nd$_{2-x}$Ce$_x$CuO$_{4-y}$, which achieves the highest T_c when $x = 0.15$ and $y = 0.04$. The formula could be written as

$$(Nd^{3+})_{2-x}(Ce^{4+})_x Cu^{(2-q)+}(O^{2-})_{4-y}$$
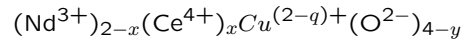
and the concentration of chemically-doped carriers is

$$q = x + 2y.$$

The highest T_c occurs when $x = 0.15$ and $y = 0.04$, giving $q = 0.23$. Both x and y are necessary to achieve superconductivity. This shows that we need the correct carrier concentration but apparently also some form of band-structure modification by (at least local) lattice distortions, like buckling of the otherwise flat CuO layers.
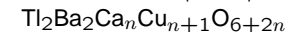
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T_c above 100 K

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Two families of compounds
$$Bi_2Sr_2Ca_nCu_{n+1}O_{6+2n}$$
$$Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$$
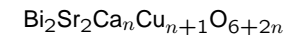
The Tl compounds shown in the figure correspond to the $n = 0, 1, 2$ members of the Tl family, also known as the 2201, 2212, and 2223 phases. The critical temperatures are 85 K for $n = 0$, 110 K for $n = 1$, and 125 K for $n = 2$.

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T_C above 130 K

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The first superconductor found was Hg metal. The highest T_C values seen in cuprate superconductors also contain Hg in a family of compounds
$$HgBa_2Ca_nCu_{n+1}O_{2n+4}$$
Compounds with $n = 0, 1, 2$ have been synthesized with T_C of 95, 122, and 133 K.

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Doping cuprates

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The undoped parent compounds of high-T_C oxides are typically antiferromagnetic insulators. This is to be expected for a regular Cu-O-Cu arrangement of atoms (superexchange).
Both n-type (Nd_2CuO_4) and p-type (La_2CuO_4 and many others).

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Resistivity above T_C

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The so-called 'high-T_C' materials are much worse conductors than good metals, like Cu or ag. The transition to superconducting state also happens in a different temperature regime, the T^5 region for simple metals, and in the linear region for high-T_C materials.

The room temperature resistivity is about 1000 times higher that pure metals. The drop from room temperature to the transition temperature is by a factor of 2 to 3 and the drop is linear in the hole-doped 123-type compounds $RBa_2Cu_3O_7$.

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The layered oxides have a very different conductivity in different lattice directions. For $YBa_2Cu_3O_7$ we have $\rho_c/\rho_{ab} \approx 100$ and for $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ the ratio can reach 10^5. The normal state resistivity can be described by

$$\rho_c = \frac{A_c}{T} + B_cT$$

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Superconductors in a magnetic field

Superconductors are perfect diamagnets in the superconducting state

$$\mathbf{M} = -\mathbf{H}$$

If a magnetic field is applied to a superconducting object, the field will be excluded from the object. If the field is applied when the material is in its normal state and the cooled, the magnetic field will be expelled from the object's interior *Meissner effect*.
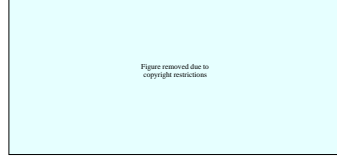
In a magnetic field, the surface layer of a superconductor would carry a shielding current. This current exists in a layer with a characteristic thickness λ.

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The penetration depth varies with material. Simple metals usually have $\lambda \approx 30 - 60$ nm. This applies to Sn, Ta, Pb, Nb, etc. and also for A15 compounds like Nb_3Sn or Nb_3Ge.

Oxide superconductors generally have larger penetration depth values, around 200 ($YBa_2Cu_3O_7$). Some metal alloys, like Nb-N have similar values.

Just like resistivity, the penetration depth is also direction dependent in layered oxides. The measured values vary a lot, depending on experiment, but for $YBa_2Cu_3O_{7-\delta}$ $\lambda_c \approx 180$ nm while $\lambda_{ab} \approx 30$ nm. Values reported for $HgBa_2Ca_2Cu_3O_{8+\delta}$ are $\lambda_c = 3500$ nm, $\lambda_{ab} = 130$ nm.

Another parameter that is very important for characterizing superconductors is the *coherence length*. This can be thought of as the spatial extent of a Cooper pair. This parameter is *very* different for traditional metallic superconductors and oxide superconductors. Some typical values are Al: 550 nm, In: 360 nm, Sn: 180 nm, Ta: 92 nm, Pb: 82 nm, Nb: 39 nm. Oxides have typical values in the 1..3 nm range. The coherence length is also anisotropic: $YBa_2Cu_3O_{7-\delta}$: $\xi_{ab} = 1.6$ nm, $\xi_c = 0.3$ nm.
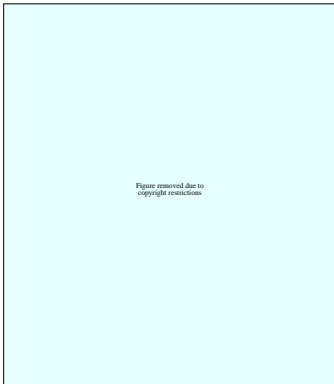
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The penetration depth and coherence length determine the *Ginzburg-Landau parameter*

$$\kappa = \frac{\lambda_L}{\xi}$$

Superconductors are divided into two groups

Type I: $\kappa < \frac{1}{\sqrt{2}}$

Below a critical field H_c there is no flux penetration into the superconductor. At the critical filed, the whole material reverts to normal state and the external field penetrates into the normal-state superconductor.

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Type II: $\kappa > \frac{1}{\sqrt{2}}$

Below a lower critical field H_{c1} there is no penetration of magnetic field into the superconductor. Above the upper critical field, H_{c2}, the entire sample reverts to normal state. Between these values the flux penetrates through the superconductor in the form of filaments or vortices.
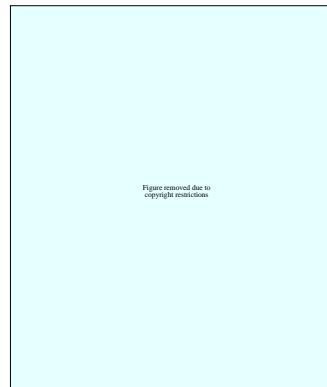

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In oxides, the lower critical field is 100 mT or less, in all crystal directions. The upper critical field can be very high, The estimated values for $YBa_2Cu_3O_{7-\delta}$ are B_c=2 T and B_{ab}=240 T

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The energy spectrum

The most widely used theory for superconductors in general is the BCS, or Bardeen, Cooper, Schrieffer theory, based on the idea of electron pairing (the *Cooper pairs*).

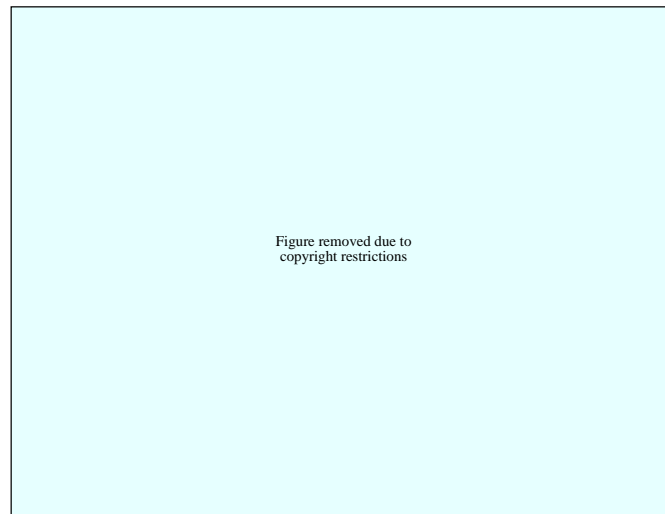Figure removed due to copyright restrictions
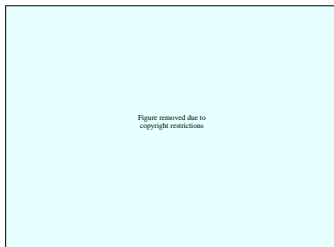
One of the predictions of the theory is that an energy gap opens at the Fermi energy when a material becomes superconducting. The gap width is tied to the critical temperature

$$\frac{\Delta_0}{k_B T_C} = 1.76,$$

i.e. $2\Delta_0/k_B T_C = 3.52$. This appears to be the case for simple metallic superconductors

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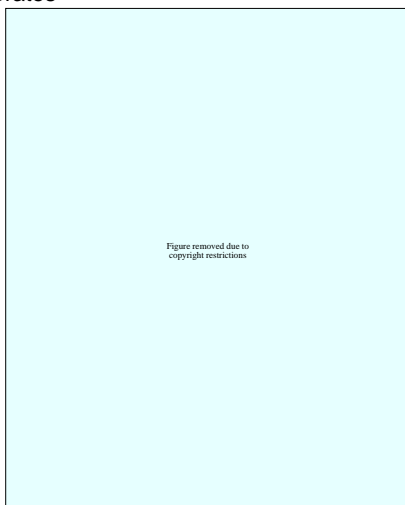Figure removed due to copyright restrictions

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The match is not good for the cuprate superconductors. The applicability of the BCS theory to cuprates is still an open question, more that 15 years after their discovery.

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Applications of high-T_C cuprates

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References:

Poole95 C. P. Poole Jr., H. A. Farach, R. J. Creswick, "Superconductivity", Academic Press, San Diego, 1995.

Cox92 P. A. Cox, "Transition Metal Oxides: An Introduction to Their Electronic Structure and Properties", Clarendon press, Oxford, 1992.

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