

## Superconductivity:

**1. Overview:** Roughly  $\frac{1}{2}$  of the elements exhibit superconductivity, though some only under extreme pressure. The elements tend to be type I; see the last page for more detail about the distinction between Type I and Type II. Hg, Sn, and Pb superconductors were discovered by Onnes roughly 100 years ago. Among bulk elements Nb has the highest  $T_c$ ; Nb is sometimes used for microfabricated SQUID sensors such as for magnetometers. On the other hand, copper, silver, and gold, the best normal conductors, cannot be made superconducting at all. (The reason: electron-phonon coupling normally drives electron pairing in superconductors, but the interaction is weak in noble metals, also reducing phonon-driven resistivity.) Magnetic materials also generally do not superconduct since magnetism and superconductivity work at cross-purposes.

**Table I:** Better-known elemental superconductors; Nb has the highest  $T_c$ .

Element	$T_c$ (K)	$H_c$ (T)
Gallium (Ga)	1.1	0.005
Aluminum (Al)	1.2	0.01
Tin (Sn)	3.7	0.03
Mercury (Hg)	4.2	0.04
Lead (Pb)	7.2	0.08
Niobium (Nb)	9.3	0.82

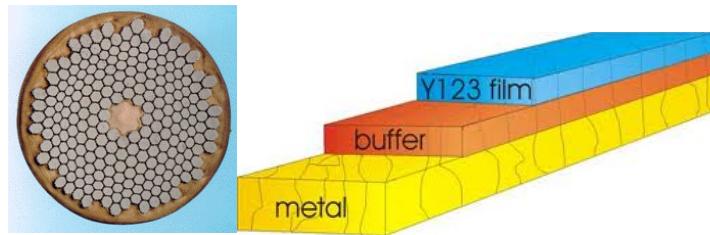
Alloys are type-II superconductors, with isolated exceptions. Because of the much higher critical fields, type II superconductors are used for high-current applications such as magnets and power transformers. A brief list of “non-high  $T_c$ ” type II superconductors is in Table II.  $\text{PbMo}_6\text{S}_8$  is a Chevrel phase material; these attracted interest in the 1980s (pre-high  $T_c$ ) as potential high-current superconductors because of their tolerance for magnetism.  $\text{UPt}_3$  and  $\text{CeCoIn}_5$  are “heavy Fermion” superconductors, in which superconductivity grows out of an exotic metallic state strongly influenced by interacting magnetic ions, and magnetic excitations appear to cause the superconducting state, in contrast to the phonon pairing in traditional superconductors.

**Table II:** Brief list of non-high- $T_c$  superconducting compounds.

compound	$T_c$ (K)	compound	$T_c$ (K)
$\text{Nb}_3\text{Sn}$	18	$\text{MgB}_2$	39
$\text{Nb}_3\text{Ge}$	23	$\text{PbMo}_6\text{S}_8$	15
$\text{NbN}$	16	$\text{UPt}_3$	0.48
$\text{Nb}_{0.6}\text{Ti}_{0.4}$	9.8	$\text{CeCoIn}_5$	2.3

The Nb alloys in the table II are standard materials for magnets and high-current. Nb-Ti is easy to work with, for applications such as MRI magnets.  $\text{Nb}_3\text{Sn}$  is used for higher fields but it is very brittle and cannot be drawn like ordinary wire. Pictured below at the left is a Nb-Ti wire for magnets (CERN website) with 6300 strands of  $6 \mu\text{m}$ -diameter Nb-Ti drawn in a copper matrix; the small filaments must be used to minimize the motion of superconducting vortices, since

dissipative motion of vortices can quench the wire to a normal state. On the right is a schematic of a tape developed more recently for high-T<sub>c</sub> YBCO cables.

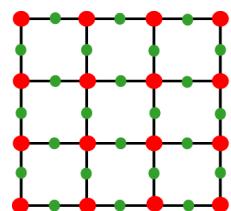


"High- $T_c$ " often refers specifically to the copper-oxide materials. The first discovered was  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ,  $T_c = 38$  K, by Bednorz and Müller (Nobel prize 1987) -- see Table III. There have since been a large number of high- $T_c$  compounds synthesized.

**Table III:** High- $T_c$  cuprates, Fe pnictides, and related materials.

Compound	$T_c$ (K)	Compound	$T_c$ (K)
$(\text{La},\text{Sr})_2\text{CuO}_{4,\delta}$ (LSCO)	38	$\text{LaFeAs}[\text{O}_{1-x}\text{F}_x]$	26
$\text{YBa}_2\text{Cu}_3\text{O}_{7,\delta}$ (YBCO)	95	$\text{GdFeAsO}_{1-x}$	53
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_9$ (BSCCO 2212)	110	$\text{BaFe}_2\text{As}_2$	38
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (BSCCO 2223)	110	FeSe	8.5
$\text{Hg}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	134	$\text{Sr}_2\text{RuO}_4$	0.93

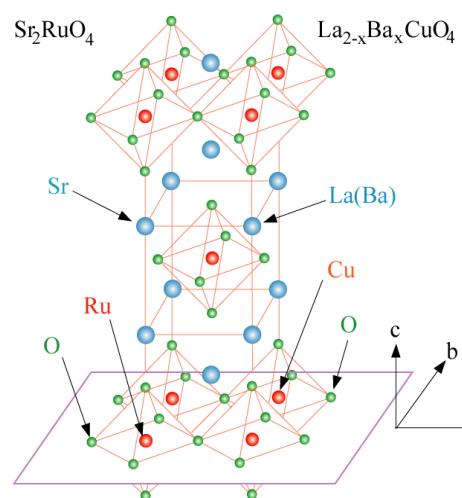
The second material in Table III,  $\text{YBa}_2\text{Cu}_3\text{O}_{7,\delta}$  (YBCO), was discovered by Paul Chu shortly after the discovery of LSCO. It is important since its  $T_c$  is above 77 K (liquid N<sub>2</sub> boiling point). An application for cuprates to date has been coils in high-efficiency microwave filters commonly used in cell-phone towers. BSCCO materials are considered



important for next generation high-current cables, but these are still limited to niche applications and demonstration projects.

The cuprates have planes containing  $(\text{CuO}_2)$  units, shown at left, while below is pictured the full structure [ref. 1]: labeling is for  $(\text{La},\text{Ba})_2\text{CuO}_{4,\delta}$  on the right, and  $(\text{Sr})_2\text{RuO}_4$  on the left.

In the formula  $(\text{La},\text{Ba})_2\text{CuO}_{4,\delta}$ ,  $\delta$  indicates that some oxygen ions are missing, which has the effect of creating holes. It is usually the holes that conduct; otherwise  $\text{La}_2\text{CuO}_4$  and other cuprates are insulating antiferromagnets.



Most cuprates are electronically two-dimensional: from a band perspective, the masses are very large in the  $c$  direction. The behavior is often modeled as parallel 2D superconducting sheets (the Cu-O planes) for which superconducting pairs can move in the  $c$  direction only by tunneling. (Tunneling of pairs, rather than single electrons, is Josephson tunneling.) This also can also decouple magnetic vortices between layers, and makes flux pinning for high currents difficult.

The microscopic parameter  $\kappa$  (defined below) is particularly large for the cuprates, for example in YBCO  $\lambda$  and  $\xi$  are approximately 100 nm and 1 nm, respectively, giving  $\kappa = 100$ . For comparison in type-I aluminum  $\lambda$  is 20 nm and  $\xi$  is 1000 nm.  $\lambda$  does not vary greatly between materials, but  $\xi$  varies much more since it is related to the pair binding energy.

“Iron pnictide” superconductors [see ref. 2] are also listed in the right-hand column of Table III. The initial 2008 report of La[O<sub>1-x</sub>F<sub>x</sub>]FeAs with a surprisingly high  $T_c$  led to great recent/current interest in understanding these materials. Iron-containing BaFe<sub>2</sub>As<sub>2</sub>, LiFeAs, and FeSe superconductors have been demonstrated. They contain magnetic Fe ions, and unconventional superconductivity that shares some common features with that of the cuprates.

**2. London equation, London penetration depth:** The London theory starts with simple assumptions: that superconducting electrons accelerate without resistance, and the internal  $B$  field of a superconductor is zero (Meissner effect). For a charge  $-q$  (which for superconducting pairs becomes  $-q = -2e$ ), with no resistance  $d\vec{v}/dt = -q/m \vec{E}$  so:

$$\frac{d\vec{j}}{dt} = \frac{nq^2}{m} \vec{E}. \quad [1]$$

Taking the curl of both sides, and using Faraday’s law ( $\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}$ ), yields

$$\frac{d}{dt} \left( \vec{\nabla} \times \vec{j} + \frac{nq^2}{mc} B \right) = 0. \quad [2]$$

Equation [2] can be solved if  $j$  and  $B$  are *time-independent*, and this led to the expectation that a perfect conductor would *retain* magnetic flux lines originally flowing through it. Fritz and Heinz London noted that instead setting the entire parenthetical expression in [2] to zero is consistent with the observation that superconductors expel fields (the *Meissner effect*). This yields the **London equation**:

$$\vec{\nabla} \times \vec{j} = -\frac{nq^2}{mc} B \equiv -\frac{c}{4\pi\lambda^2} B, \quad [3]$$

which provides a good description of the macroscopic response of superconductors to a  $B$  field. The last form of the expression defines the **London penetration depth**,  $\lambda = \sqrt{mc^2/4\pi nq^2}$ . An equivalent expression:

$$\vec{\nabla} \times \vec{\nabla} \times \vec{B} = -\frac{1}{\lambda^2} \vec{B}, \quad [4]$$

is obtained via Ampere’s law ( $\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{j}$ ). [3] and [4] lead to both  $B$  and  $j$  vanishing in the interior of a superconductor: from vector calculus the double curl in [4] is  $-\nabla^2 \vec{B} + \vec{\nabla}(\vec{\nabla} \cdot \vec{B})$ , in which the second half vanishes identically from Gauss’ law. Therefore,

$$\nabla^2 \vec{B} = \vec{B}/\lambda^2, \quad [5]$$

from which (near a flat surface)  $B$  decays exponentially as  $B = B_{ext} e^{-x/\lambda}$ . From [5] and [3] we also find that whenever the  $B$  field penetrates in a thin surface region, there is a current density  $j$  decaying exponentially near the surface in the same way as  $B$ . The value of  $\lambda$  in most materials is between 10 and 100 nm, thus the Meissner effect is accomplished by exponentially-decaying surface currents which screen the interior from applied external fields.

Finally, with  $\vec{B} = \vec{\nabla} \times \vec{A}$ , [3] is equivalent to another form of the London equation,

$$\vec{j} = -\frac{c}{4\pi\lambda^2} \vec{A}. \quad [6]$$

[6] is valid specifically in the Coulomb gauge ( $\vec{\nabla} \cdot \vec{A} = 0$ ); see Appendix G of Kittel.

**3. Interactions and pairs, BCS theory:** Superconductivity in the BCS theory (Bardeen, Cooper, Schrieffer, 1957) relies upon pairing of electrons due to an attractive interaction mediated by phonons. As an approximate way to understand this, consider the positive ions (charge  $Q$ ) as classical undamped harmonic oscillators (Einstein approximation). From classical mechanics, the displacement in response to an AC field  $\vec{E} \cos \omega t$  is

$$\vec{u} \cos \omega t = \frac{-Q\vec{E} \cos \omega t}{M(\omega^2 - \omega_o^2)}, \quad [7]$$

which includes the natural frequency of the oscillator,  $\omega_o = \sqrt{\kappa/M}$ . At frequencies higher than  $\omega_o$  there is a  $180^\circ$  phase shift. In solids we can replace  $\omega_o$  by a phonon frequency, which is small since electrons move much faster than the ions. Such reverse-phase ionic displacements can be shown to be a contribution to the dielectric function,

$$\epsilon(q) = 1 - \frac{\Omega^2}{\omega^2}. \quad [8]$$

The cutoff  $\Omega$  turns out to be the ionic plasma frequency; it is much smaller than the ultraviolet plasma frequency for charged electrons. Despite other typically positive contributions to the electrical susceptibility, [8] can dominate and give a negative dielectric function for a range of frequencies, changing the electron-electron Coulomb interaction from repulsive to attractive. This is the "overscreening" concept.

The *isotope effect* was an early clue about phonon contributions: the isotope effect is a small change in  $T_c$  due to a change in isotope mass; for phonon coupling  $T_c$  is proportional to  $M^{-1/2}$ , where  $M$  is the isotope mass, and this is very close to what is observed. Careful sample preparation is required to assure that the effect is not dwarfed by other sample-dependent changes. The  $M$  dependence arises through connection to the Debye frequency, described below;  $\omega_D$  is related to the speed of sound, generally proportional to  $1/\sqrt{M}$ .

Phonon-mediated interaction is at most very weakly attractive, and in quantum mechanics a very weak attractive potential typically will not support a bound state. Cooper showed how two electrons in the presence of a filled Fermi sea can form a wavefunction with lower energy than that of two isolated electrons. Assuming a spherical Fermi surface, he took the attraction between electrons ( $V$ ) to be constant up to a cutoff energy  $\hbar\omega_D$ , the highest phonon energy in the Debye model, since the phonons cause the weak attraction. The resulting pair energy is

$$E = 2\epsilon_F - 2\hbar\omega_D e^{-2/g(\epsilon_F)V}. \quad [9]$$

Because of the exponential in [9] there is no minimum attractive energy (minimum  $V$ ) to obtain a bound state.  $V$  need only be positive, and even the very weak phonon-mediated attraction can be enough to drive an electronic phase transition. A Cooper pair is a superposition of many plane-wave states. The size of a pair for elemental superconductors is about 10000 Å, but for high- $T_c$  oxide superconductors a representative value is 20 Å. The pair size is the **coherence length**,

defined as  $\xi$ .  $\xi$  plus the London penetration depth,  $\lambda$  are the two important length scales for the description of superconductivity.

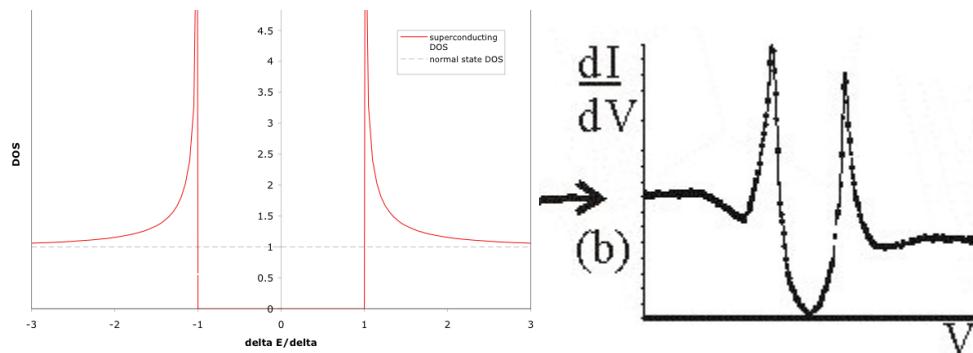
The BCS ground-state wavefunction is made by filling the metal with Cooper pairs. At zero temperature it can be written as a product state:

$$\Psi = A\Psi(\vec{r}_1, \vec{r}_2)\Psi(\vec{r}_3, \vec{r}_4)\Psi(\vec{r}_5, \vec{r}_6)\dots \quad [10]$$

where each of the pair wavefunctions in the product is identical. The operator  $A$  makes the whole wavefunction properly antisymmetric (makes the state a Slater determinant) as required for Fermions. The wavefunction hence obeys Fermi statistics for interchange of electrons.

However, the pairs themselves are identical and obey Bose-Einstein statistics: Fermions thus can act like Bosons. The BCS ground state can be regarded as a Bose-condensed fluid of identical pairs. If the magnitude of the attractive interaction between electrons were to increase, the ground state would change from a BCS-like state to one characterized by isolated electron-pair "molecules" which can also Bose condense. The latter is the regime of cooled atomic gases. The BCS regime is in the opposite extreme, where the pair wavefunction is spatially very large, such that the pairs themselves are heavily overlapping.

**4. Energy gap** With electrons paired up, there is an energy gap,  $E_g \equiv 2\Delta$  required to break a pair, and a modified density of states for the excitations (sketched below). Effectively the states "pile up" on the two sides of the gap. On the right is a figure from a tunneling measurement (STM), one method to observe the gap directly.



The transition temperature ( $T_c$ ) is related to the gap in the BCS theory according to:

$$2\Delta = 3.53 k_B T_c \quad [11]$$

**5. Ginzburg-Landau theory:** In the Ginzburg-Landau model, the superconducting state is characterized by an "order parameter"  $\psi(r)$ .  $\psi(r)$  is a pseudowavefunction: much like a wavefunction but with no microscopic features (somewhat like a Bloch wavefunction with the atomic function smeared out leaving only the long-wave oscillation).  $\psi(r)$  can be regarded as having the phase of the paired wavefunction, and an amplitude such that  $|\psi(r)|^2 = n_s$ , the density of superconducting electron pairs. This model is valid for slowly varying fields. One of the basic relations is for the electric current density, obtained assuming  $|\psi(r)|^2$  is a constant:

$$\vec{J}_{el} = -\left[ \frac{2e^2}{mc} \vec{A} + \frac{e\hbar}{m} \vec{\nabla} \phi \right] |\psi|^2, \quad [12]$$

where the phase  $\phi$  is defined according to  $\psi(r) = |\psi| e^{i\phi}$ . Eqn. [12] can be obtained directly from a quantum-mechanical result, assuming that (i) the amplitude  $|\psi(r)|^2$  is fixed, and only the phase varies vs. position, and (ii) the particles represented by the wavefunction have charge

given by  $2e$ , and mass  $2m$ , since they are *electron pairs*. The relation [12] can be used to explain phenomena such as the Josephson effect. Also note that for cases of constant phase, [12] is equivalent to the London equation.

**Flux quantization** comes naturally from this theory; integrating [14] about closed loop deep within the superconductor (where  $\vec{J}_{el}$  must be zero), and requiring the phase change to be  $2\pi$  times an integer, one can obtain the quantization condition for the magnetic flux threading the loop ( $\Phi = \int \vec{B} \cdot d\vec{s}$ ):

$$\Phi = \frac{hc}{2e} n \equiv \Phi_o n , \quad [15]$$

with  $n$  an integer. The flux quantum is  $\Phi_o = 2 \times 10^{-7} \text{ G} \cdot \text{cm}^2$ . Also as established by Abrikosov based on the G-L theory,  $\lambda$  and  $\xi_o$  are among the most important microscopic parameters. The ratio,  $\kappa = \lambda / \xi_o$ , divides **Type-I** and **Type-II** superconductors: those with  $\kappa > 1/\sqrt{2}$  are Type-II, which exhibit magnetic vortices under the application of a sufficiently large magnetic field. On the other hand Type I superconductors (with  $\kappa < 1/\sqrt{2}$ ) expel magnetic fields from their interior under all circumstances. The magnetic vortices in Type II superconductors each carry one flux quantum [15] of magnetic flux.

References from above:

- [1] Physics Today, Jan. 2001; Yoshiteru Maeno, T. Maurice Rice, and Manfred Sigrist, "The Intriguing Superconductivity of Strontium Ruthenate."; Evaluation of Spin-Triplet Superconductivity in  $\text{Sr}_2\text{RuO}_4$ , Y. Maeno et al., J. Phys. Soc. Jpn. 81 (2012) 011009.
- [2] Iron-based superconductors: Magnetism, superconductivity, and electronic structure (Review Article); A. A. Kordyuk, Low Temp. Phys. 38, 888 (2012); "Trend: High-temperature superconductivity in the iron pnictides", M. R. Norman, Physics 1, 21 (2008).