NOTES ON SUPERCONDUCTIVITY

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I. THE DISCOVERY (1911)

The history of superconductivity is closely linked to the quest of low temperatures. In 1877 Cailletet obtained liquid Oxygen (T = 90.2 K) at ambient pressure, six years later Nitrogen was liquified (77.4 K). Liquid Hydrogen was produced in 1898 by Sir James Dewar, a professor at the Royal Institution in London, at the much lower T = 20.4 K. To store the liquid he devised a vacuum vessel, bearing his name.

Helium was discovered in the spectrum of the solar chromosphere by J. Janssen during the 1868 solar eclipse. It was then detected in gases erupted by Vesuvius and isolated in 1895 by Sir William Ramsay among the gases released by certain heated minerals.

In the late 1890s Heike Kamerlingh Onnes (1853-1926, Nobel 1913) started experiments to liquify Helium. On 10 July 1908, physicists from different countries were invited in his cryogenic laboratory in Leiden to observe the historic experiment: liquid Helium being formed at the transition temperature T = 4.2 K. The experiment lasted 16 hours and produced 60 cm^3 of liquid He through a chain of rapid expansions at colder and colder temperatures. He noticed that liquid He has very low density, about 8 times lighter than water. Helium is the only substance in nature that does not solidify at absolute zero and normal pressure.

Onnes inaugurated a new, large-scale approach to experimental physics[1]. He founded a famous school of glass-blowers and machinists and constructed a special refrigerator. For 15 years his laboratory remained the coldest and only place in the world where liquid He was produced. In Leiden's laboratory, Lev Shubnikov and de Haas discovered the oscillatory behaviour of electronic magnetic susceptivity at low T. Several experiments were done. Measurements of electrical resistances of Pt and Au showed a decrease to a residual value due to impurities. He thus tried with purified mercury in narrow vessels and, in 1911, noticed an abrupt drop of resistivity to unmeasurable small values at $T_c = 4.2\ K$. Onnes named the new state *superconductor*. Pureness was then shown to be irrelevant and superconductivity was also observed in Sn and Pb. Gold and Platinum, though very good conductors, are not superconductors.

Superconductivity is destroyed by a magnetic field above a threshold value $H_c(T)$, with experimental law

$$\boxed{\frac{H_c(T)}{H_c(0)} = 1 - \left(\frac{T}{T_c}\right)^2} \qquad (1)$$

[1] Visit www.lorentz.leidenuniv.nl/history/cold/cold.html for historical notes and photos.

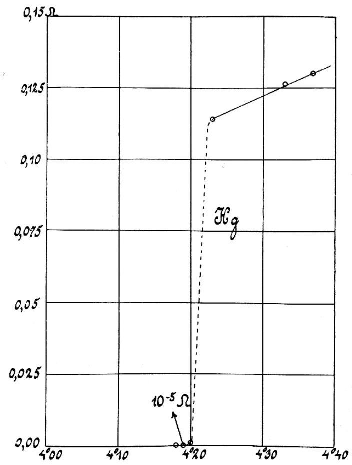

FIG. 1: The measure of resistance of Mercury (Ohm v.s. T)

Among pure metals, the highest temperature is $T_c = 9.25$ K for Niobium, and the lowest is $T_c = 325\mu K$ for Rhodium.

	T_c	T_D	H_c(gauss)
Al	1.17	420	105
Sn	3.72	195	305
Hg	4.15	87	412
La	4.87	151	98
Pb	7.19	105	803
Nb	9.25	276	2060

From *Springer's Handbook of Condensed Matter and Materials Data, 2005.* The Earth's magnetic field varies from 0.25 to 0.65 gauss.

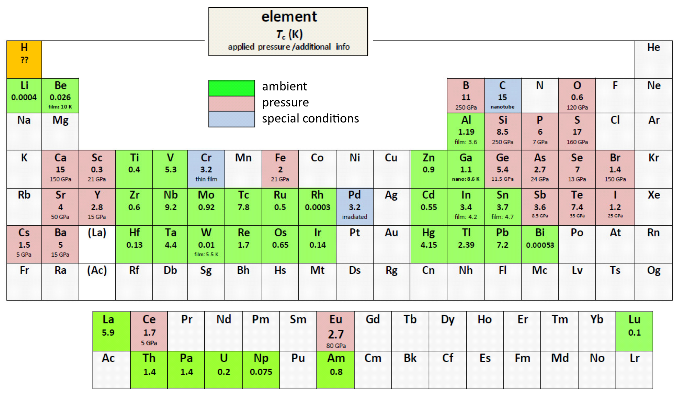

FIG. 2: Superconducting elements, T_c and P, from[32].

II. MEISSNER-OCHSENFELD EFFECT (1933)

In 1933 Meissner and Ochsenfeld[2] in Berlin observed that if the temperature of a superconducting material in a weak magnetic field H is lowered below $T_c(H)$, then *the field is expelled from the volume.* This showed as a sudden change of the orientation of magnetic needles visualising the lines of force in the exterior of the volume, becoming tangent to the body.
Gorter made the statement that *superconductors are perfect diamagnets*

$$\boxed{\mathbf{B}=0}$$

In bulk the magnetic field is zero, and vanishes within a thin surface layer whose thickness δ (*penetration length*) is of the order of 10^{-5}-10^{-6} cm (Abrikosov). Experiments give:

$$\frac{\delta(T)}{\delta(0)}=\frac{1}{\sqrt{1-(T/T_c)^4}} \tag{2}$$

Superconductivity is also destroyed by strong electric currents[30]. By Ampere's law, the field at the surface $r=a$ of the wire produced by a current I is $H(a)=I/(2\pi a)$. Silsbee's criterion (1916) for a wire states that $I_c=2\pi a H_c(T)$. If J flows in a surface layer of thickness $\delta(T)$, it is

$$J_c(T)=\frac{I_c}{2\pi a\delta}=\frac{H_c(T)}{\delta(T)}=J_0\left[1-\frac{T^2}{T_c^2}\right]^{3/2} \tag{3}$$

Measures of J_c at CERN on cables Nb-Ti at 6 Tesla and $T=4.2K$ give 2300 A/mm^2.

A mixed phase, where the field coexists in thin flux tubes of normal matter in the superconductor, was discovered in superconducting alloys before 1936 by Lev Shubnikov in Kharkov. There, he established the first cryogenic laboratory in U.S.S.R. and liquified He. Landau was the director of the theory group. In the same years, low-T physics was started by Kapitza in Moscow[2].

III. THERMODYNAMICS

Superconductivity is a thermodynamic state of matter: it can be specified by parameters that are independent of the history and can be modified reversibly.

In absence of electric fields, and neglecting volume variations, the change of free energy in a solid is:

$$dF=-SdT+\frac{1}{4\pi}\int d^3x\,\mathbf{H}\cdot\delta\mathbf{B}.$$

S is the entropy and $\mathbf{H}$ the applied field.
$\mathbf{H}\cdot\delta\mathbf{B}=\mathbf{H}\cdot\mathrm{rot}\,\delta\mathbf{A}=\mathrm{div}(\mathbf{H}\times\delta\mathbf{A})+\delta\mathbf{A}\cdot\mathrm{rot}\,\mathbf{H}$. Neglecting the surface term and using Maxwell's equation it is: $F=-SdT+\frac{1}{c}\int_V d^3x\,\mathbf{J}\cdot\delta\mathbf{A}$ and

$$\frac{\delta F}{\delta\mathbf{A}(\mathbf{x})}=\frac{\mathbf{J}(\mathbf{x})}{c}.$$

Where the external currents are zero, it is $\delta F/\delta\mathbf{A}(x)=0$. This is general for bodies in equilibrium[28].
Since the magnetic induction $\mathbf{B}=\mathbf{H}+4\pi\mathbf{M}$ requires knowledge of the magnetic response to $\mathbf{H}$, the Gibbs free energy density is introduced: $G=F-\frac{1}{4\pi}\int d^3x\,\mathbf{H}\cdot\mathbf{B}$, with variation

$$dG=-SdT-\frac{1}{4\pi}\int d^3x\,\mathbf{B}\cdot d\mathbf{H}.$$

For a cylinder of superconducting material in a field $\mathbf{H}$ parallel to the axis, the induction field $\mathbf{B}$ is also parallel to it. Keeping T constant, let us vary H. If H_c is the critical field at temperature $T<T_c$, the Gibbs' free energy density is:

$$g(T,H)-g(T,H_c)=-\frac{1}{4\pi}\int_{H_c}^{H}B(H')dH'$$

In the superconducting phase $B=0$, so that $g_s(T,H)$ is independent of H. In the normal phase, if magnetization is negligible, it is $B=H$. Then $g_n(T,H)-g_n(T,H_c)=-\frac{1}{8\pi}(H^2-H_c^2)$. At $(T,H_c(T))$ the s and n phases are in equilibrium: $g_s(T,H_c)=g_n(T,H_c)$. The Gibbs' free energies are then related by

$$g_s(T,H)-g_n(T,H)=\frac{1}{8\pi}(H^2-H_c^2(T))$$

For $H<H_c(T)$, the s phase occurs.

The difference of entropy densities is

$$s_s(T,H)-s_n(T,H)=\frac{1}{4\pi}H_c(T)\frac{\partial H_c}{\partial T}$$

It is experimentally observed that $H_c(T)$ is a decreasing function of T then, in the s phase, it is $s_s<s_n$.
Note that, by Nernst' theorem, it is $(\partial H_c/\partial T)_{T=0}=0$.

The quantity $T[s_s(T,H_c)-s_n(T,H_c)]<0$ is the latent heat, i.e. the heat liberated during the transformation from the n to the s phase on the cohexistence line. It is zero only for $H_c(T)=0$, i.e. at $T=T_c$.

The specific heat per unit volume, $c=T(\partial s/\partial T)$, for $H=0$ is:

$$c_s(T,0)-c_n(T,0)=\frac{T}{4\pi}\left[\left(\frac{\partial H_c}{\partial T}\right)^2+H_c(T)\frac{\partial^2 H_c}{\partial T^2}\right]$$

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[2] During a Stalinian purge Shubnikov was killed with other scientists. Landau escaped to Moscow but was arrested in 1938 and jailed for one year. He was freed by the intervention of Kapitza, who was investigating the superfluidity of Helium II (1938) (he gained the Nobel prize in 1978). Landau formulated the theory of superfluidity (1940-41) and received the Nobel prize for this, in 1962.

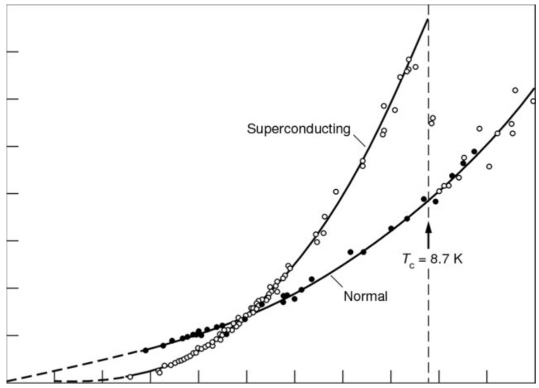

FIG. 3: The specific heat of Nb. The normal phase is in presence of a magnetic field (from[33]).

At the transition $T = T_c$ there is a jump (Rutgers, 1933):

$$c_s(T_c, 0) - c_n(T_c, 0) = \frac{T_c}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)^2_{T=T_c}$$

If the empirical law (1) is used, with the facts that $c_s(T)$ is exponentially small near $T = 0$ while $c_n(T) = \gamma T$, one obtains $\gamma = \frac{1}{2\pi}H_c^2(0)/T_c^2$. Therefore, at $T = T_c$: $(c_s - c_n)/c_n = 2$. The prediction of B.C.S. theory is $(c_s - c_n)/c_n \approx 1.43$. The jump was measured in 1932 by Keesom and Kok for Tin and Thallium.
These facts describe the $s-n$ phase transition as a second order one if $H = 0$, and a first order one if $H \neq 0$.
With $f(T, 0) = g(T, 0)$, the difference

$$f_s(T, 0) - f_n(T, 0) = -\frac{1}{8\pi}H_c^2(T),$$

is named the *condensation energy* per unit volume.

IV. LONDON EQUATIONS (1935)

Fritz and Heinz London were in Oxford to escape racial persecution. They described a superconductor as an incompressible fluid of particles with density n_s, charge e_s, mass m_s, velocity field $\mathbf{v}_s$, and free energy

$$F_s = F_n + \int d^3x \left[\tfrac{1}{2}m_s n_s v_s^2(\mathbf{x}) + \frac{B(\mathbf{x})^2}{8\pi}\right]$$

The supercurrent density is $\mathbf{J}_s = e_s n_s \mathbf{v}_s$. Maxwell's equation $\mathrm{rot}\mathbf{B} = \frac{4\pi}{c}\mathbf{J}_s$ gives:

$$F_s = F_n + \frac{1}{8\pi}\int d^3x \left[\frac{m_s c^2}{4\pi e_s^2 n_s}|\mathrm{rot}\mathbf{B}(\mathbf{x})|^2 + B(\mathbf{x})^2\right].$$

Minimization with respect to the induction field gives: $\lambda_L^2 \mathrm{rot}(\mathrm{rot}\mathbf{B}) + \mathbf{B} = 0$ i.e. $\lambda_L^2 \nabla^2\mathbf{B} = \mathbf{B}$ where:

$$\lambda_L^2 = \frac{m_s c^2}{4\pi e_s^2 n_s}$$

is *London's penetration depth*, i.e. the distance that the magnetic field decades from the surface to the interior. They postulated flux quantization.
London's theory was refined by Pippard, for $T \approx T_c$.

V. GINZBURG-LANDAU THEORY (1950)

Before any clue on a microscopic mechanism, and just by assuming that superconductivity can be described by an order parameter $\psi(\mathbf{x})$, Vitaly Ginzburg (Nobel 2003) and Lev Landau (Nobel 1962) developed a theory valid near T_c. In this regime the order parameter is small and they expanded the free energy as follows:

$$F_s[\psi, \overline{\psi}, \mathbf{A}] = F_n[0] + \int d^3x \, \frac{1}{2m^\star}\left|\left(\mathbf{p} + \frac{e^\star}{c}\mathbf{A}\right)\psi(\mathbf{x})\right|^2 + a|\psi(\mathbf{x})|^2 + \frac{b}{2}|\psi(\mathbf{x})|^4 + \frac{1}{8\pi}(\nabla\times\mathbf{A})^2 \qquad (4)$$

where F_n is the free energy of the normal phase in absence of the field $\mathbf{H}$, a and $b > 0$ are parameters, $\mathbf{B} = \nabla\times\mathbf{A}$ is the induction field in the sample when it is placed in a field $\mathbf{H}$. At equilibrium, being the sample away from the macroscopic currents that generate $\mathbf{H}$[28]:

$$\frac{\delta F_s}{\delta \mathbf{A}(\mathbf{x})} = 0.$$

The condition gives the second G.L. equation, that corresponds to a Maxwell equation with a supercurrent density:

$$\boxed{\nabla\times\mathbf{B} = \frac{4\pi}{c}\mathbf{J}_s} \qquad (5)$$

$$\mathbf{J}_s = -\frac{e^\star}{2m^\star}\bar{\psi}\left(\mathbf{p} + \frac{e^\star}{c}\mathbf{A}\right)\psi + c.c. \qquad (6)$$

A surface term arising from partial integration cancels with the b.c. $\mathbf{B}\times\mathbf{n} = \mathbf{H}\times\mathbf{n}$ (continuity of the tangent component).

Minimization of F_s with respect to $\bar{\psi}$ (or ψ) gives the first G.L. equation

$$\boxed{\frac{1}{2m^\star}\left(\mathbf{p} + \frac{e^\star}{c}\mathbf{A}\right)^2\psi + a\psi + b|\psi|^2\psi = 0} \qquad (7)$$

Integration by parts produces a boundary term that vanishes if $\mathbf{n}\cdot(\mathbf{p} + \frac{e^\star}{c}\mathbf{A})\psi = 0$. The boundary conditions were rediscussed by de Gennes[20]: the physical condition $\mathbf{J}_s\cdot\mathbf{n} = 0$ at the surface is satisfied more generally if

$$\mathbf{n}\cdot\left(\mathbf{p} + \frac{e^\star}{c}\mathbf{A}\right)\psi = i\hbar\lambda\psi \qquad (8)$$

with $\lambda \neq 0$ for a s-n interface, and $\lambda = 0$ for a s-*insulator* interface.

In bulk it is $\mathbf{A} = 0$, the order parameter is constant and solves $\psi(a + b|\psi|^2) = 0$ i.e. $\psi = 0$ (normal phase) or $\psi_\infty^2 = -a/b$. Then $a < 0$ for $T < T_c$ and

$$f_s - f_n = -\frac{a^2}{2b} = -\frac{1}{8\pi} H_c(T)^2.$$

Ginzburg and Landau put $a(T) = \alpha(T - T_c)$ and b constant near T_c. This gives $\psi \propto \sqrt{T_c - T}$.

The GL equations contain two characteristic lengths: the coherence length ξ and the penetration length δ that respectively describe the decay of $\psi(x)$ or $B(x)$ in the transition region s-n:

$$\xi = \sqrt{\frac{\hbar^2}{2m^\star |a(T)|}} \quad \delta = \sqrt{\frac{m^\star c^2 b}{4\pi e^{\star 2}|a(T)|}} \tag{9}$$

They both diverge near T_C, but their ratio (the G.L. parameter) is independent of temperature:

$$\boxed{\kappa = \frac{\delta}{\xi} = \frac{m^\star c}{\hbar e^\star}\sqrt{\frac{b}{2\pi}}} \tag{10}$$

Mixed superconductors (1957). Alexei Abrikosov (Nobel 2003) discovered that the linearized G.L. equation admits a mixed solution, i.e. a non-zero order parameter in presence of an imposed field H.

I made my derivation of the vortex lattice in 1953 but publication was postponed since Landau at first disagreed with the whole idea. Only after R. Feynman published his paper on vortices in superfluid Helium (1955) and Landau accepted the idea of vortices, did he agree with my derivation, and I published my paper (Nobel lecture).

The highest field for this to occur is

$$H_{c2} = \kappa\sqrt{2}H_c$$

where H_c is the critical field for a pure s phase. The relation requires $\kappa > 1/\sqrt{2}$, which defines the type II superconductors[9]. In type II, diamagnetism is perfect for $H < H_{c1}$ and, for $H_{c1} < H < H_{c2}$ the field penetrates in tubes where the phase is normal and the flux is quantized. The flux tubes form a triangular array (Abrikosov lattice). Each tube is surrounded by the superconducting phase and a thin layer of supercurrents that shield it. For $H > H_{c2}$ the normal phase occurs. Type II superconductors can resist fields of the order of some tesla.

All superconducting chemical elements are Type I, with the exception of Vanadium (V, $T_c = 5.46$), Niobium (Nb, $T_c = 9.25$) and Technetium (Tc, $T_c = 7.77$) that are type II.

In high T_c superconductors the coherence length ξ of electron pairs is much smaller (1/100) than low T_c ones.

VI. COOPER PAIRS (1956)

Measurements of T_c of isotopes of Hg led independently, in 1950, Emanuel Maxwell[5] and the group of Reynolds[6] to discover the **isotope effect**: the behaviour $T_c \approx M^{-1/2}$, where M is the ionic mass. The discovery was crucial. Bardeen was informed by telephone, and published a note[3] few days later. Almost at the same time Herbert Fröhlich[4] put forward the hypothesis that phonons are relevant.

Schafroth made the hypothesis that electrons bind in charged pairs in space, and undergo B-E condensation[7].

In 1956, the american Leon Cooper showed that two electrons with an attractive potential in a shell $(\epsilon_F, \epsilon_F + \hbar\omega_D)$ in momentum space, and in presence of electrons that fill the Fermi sphere, form a bound state[8]. Such **Cooper pair** has null total momentum and spin.

In momentum space, the eigenfunctions of $H = \frac{1}{2m}(p_1^2 + p_2^2) + U$ have the form $c(\mathbf{k}_1, \mathbf{k}_2)\chi_s(\omega_1\omega_2)$ with $k_1, k_2 > k_F$ (the states in the Fermi sphere are unavailable). The function c is symmetric for $s = 0$ (singlet) and antisymmetric for $s = 1$ (triplet).

The center of mass has zero kinetic energy if $\mathbf{k}_1 = -\mathbf{k}_2 \equiv \mathbf{k}$. The total energy E is

$$\frac{\hbar^2 k^2}{m} c(\mathbf{k}) + \sum\nolimits_{\mathbf{k}'} \langle \mathbf{k}, -\mathbf{k}|U|\mathbf{k}', -\mathbf{k}'\rangle c(\mathbf{k}') = Ec(\mathbf{k})$$

Make the assumptions that the potential U is attractive and equal to $-g/V$ for electrons in the energy shell $\Gamma = \{\mathbf{k} : \epsilon_F < \epsilon_k < \epsilon_F + \hbar\omega_D\}$ (ϵ_F is the Fermi energy, and ω_D is the Debye frequency).

Choose $c(\mathbf{k}) = 0$ outside Γ, to take advantage only of the attractive interaction:

$$(E - \frac{\hbar^2 k^2}{m})c(\mathbf{k}) = -\frac{g}{V}\sum_{\mathbf{k}' \in \Gamma} c(\mathbf{k}')$$

The sum in r.h.s. is a constant, and the self-consistency equation gives the energy of the bound state:

$$1 = -g \int_\Gamma \frac{d\mathbf{q}}{E - \frac{\hbar^2 q^2}{m}} = \int_\Gamma d\epsilon \frac{\rho(\epsilon)}{E - 2\epsilon}$$

where $\rho(\epsilon) = V^{-1}\sum_{\mathbf{q}} \delta(\epsilon - \hbar^2 q^2/2m)$ is the density of states for free electrons per spin component and unit volume. Since $\hbar\omega_D \ll \epsilon_F$, the density is nearly constant at the Fermi energy. The *binding energy* $\Delta = 2\epsilon_F - E$ it is:

$$\boxed{\Delta = 2\hbar\omega_D \exp\left(-\frac{2}{\rho(\epsilon_F)g}\right)} \tag{11}$$

The size of a Cooper pair is estimated:

$$\langle r^2 \rangle = \frac{\int_\Gamma d\mathbf{k}\, c(k)(-\hbar^2\nabla^2 c)(k)}{\int_\Gamma d\mathbf{k}\, c(k)^2}$$

It gives a huge size: $r/a_0 \approx (T_F/T_c) \approx 10^4$.

VII. B.C.S. MODEL (1957)

John Bardeen, Leon Cooper and Robert Schrieffer (Nobel prize 1972) proposed the **B.C.S.**[10] theory, with attractive interaction $-g\delta(\mathbf{x}-\mathbf{y})$ for electrons in the energy shell $|\xi_k| < \hbar\omega_D$ ($\xi_k = \epsilon_k - \mu$), and variational ground state

$$|BCS\rangle = \prod_{\mathbf{k}} (u_k + v_k a^\dagger_{\mathbf{k},\uparrow} a^\dagger_{-\mathbf{k},\downarrow})|0\rangle \qquad (12)$$

which explicitly contains Cooper pairs. The variational parameters are restricted by $|u_k|^2 + |v_k|^2 = 1$ for normalization. At the time, Schrieffer was thesis student and Cooper a post-doc of Bardeen (Bardeen was former student of Eugene Wigner in Princeton, and shared the Nobel prize in 1956 with Shockley and Brattain for the discovery of the transistor).
Bogoliubov and Valatin showed that $|BCS\rangle$ is the vacuum state of canonical operators that diagonalize the B.C.S. Hamiltonian in Hartree-Fock approximation:

$$H = E_0 + \sum\nolimits_{\mathbf{k}} \sqrt{\xi_k^2 + \Delta^2}\, (\alpha^\dagger_{\mathbf{k}}\alpha_{\mathbf{k}} + \beta^\dagger_{\mathbf{k}}\beta_{\mathbf{k}}) + ...$$

E_0 is the energy of a ground state of Cooper pairs. Excitations are "bogolons" of energy $\sqrt{\xi_k^2 + \Delta^2}$.
The approach was generalised to inhomogeneous systems by Pierre-Gilles de Gennes[20].
The formation of Cooper pairs for $T < T_c$ opens an energy gap of width $2\Delta_T$ centred at the Fermi energy $\xi = 0$. The prediction of B.C.S. is:

$$\frac{2\Delta_0}{k_B T_c} = 3.53$$

The gap shows in experiments such as:
- exponential suppression of specific heat at $T << T_c$;
- *absence of absorption of infrared light* with $\hbar\omega < 2\Delta$;
- *tunneling* in n-s or s-s junctions (Giavaert[13] 1960). It provides a direct measure of the gap as the jump of the voltage versus tunneling current[14] (see fig.4)

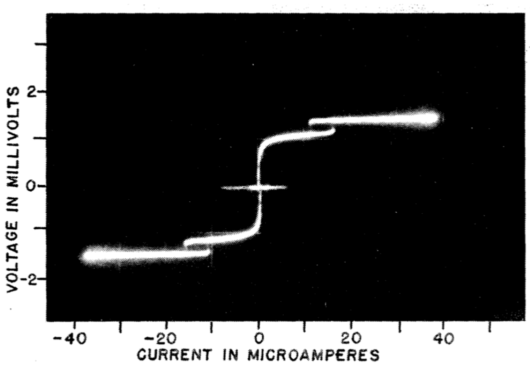

FIG. 4: the first measures of V-I (tunneling current) for an Al - Al_2O_3 - Pb sandwich at 1 K. Both Al and Pb are superconducting, separated by an insulating layer. The jump δV measures of the energy gap 2Δ of the metal with lower T_c (Al film: $T_c = 3.6K$). Fig.1 in [14].

	$2\Delta_0/k_B T_c$
Al	3.53
Sn	3.63
Hg	3.95
La	3.72
Pb	3.95
Nb	3.65

From: L. P. Levy, Magnétisme et supraconductivité, EDP Sciences 1997.

1959. Lev Gorkov formulated B.C.S. theory in terms of thermal Green functions and obtained an expansion for $T \to T_c$, giving the G-L equations[11]. This gave way to diagrammatic techniques, that led Gerasim Eliashberg (1960) to the "strong coupling" theory[12], where the phonon exchange is accounted for, and solved the problem of Pb. An effective and widely used theory was proposed by McMillan[21]

1961. Experimental verification of flux quantization, in multiples of $hc/2e$, at Stanford[15] and in Germany[16]. A Cu wire of 1 cm and diameter 10^{-3}cm, coated with Sn is immersed in a field H parallel to the wire. Temperature is lowered until Sn is superconductor (Cu remains in the normal phase). Then H is turned off. Flux lines remain trapped in the copper region as they cannot enter the superconducting layer of tin. The flux is measured through the f.e.m. induced in two coils into which the wire is made to oscillate. ($hc/2e = 2.07 \times 10^{-7}$ gauss/cm^2)

A. Josephson effect (1962)

Brian David Josephson[17], student of P. Pippard at Cambridge University predicted the existence of a current flow $I = I_0 \sin\Delta\varphi$ that in a s-s junction, dependent of the phase difference of the order parameters in the two superconductors. The effect was observed in 1963 by Philip Anderson and John Rowell[18].
If a fixed voltage V is applied to the contact, the current is oscillatory (a.c.) with frequency $\omega_J = 2eV/\hbar$:

$$I = I_0 \sin(\omega_J t + \Delta\varphi)$$

The a.c. effect was observed by Ivar Giaever[19] (Nobel with Josephson in 1973).
A microwave of frequency ω induces quantized d.c. voltage across the Josephson junction proportional to ω.

VIII. HIGH-T_c SUPERCONDUCTORS

Cuprates (1986). Georg Bednorz and Alex Müller (Nobel prize 1987) discovered a new class of superconductors made of CuO_2 layers with Lantanum atoms between.

Metallic, oxygen-deficient compounds in the Ba-La-Cu-O system, with the composition $Ba_xLa5-xCu_5O_5(3-y)$ *have been prepared in polycrystalline form. Samples with x=1 and 0.75, y> 0, annealed below 900 C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities ..*

In 1987 Wu et al.[23] replaced Lantanum with Yttrium and found $T_c = 90K$. *A stable and reproducible superconductivity transition between 80 and 93 K has been unambiguously observed both resistively and magnetically in a new Y-Ba-Cu-O compound system at ambient pressure. An estimated upper critical field* $H_{c2}(0)$ *between 80 and 180 T was obtained.*
The progress is important as it enables liquid N (T=77K at 1 atm) as refrigerant.

A superconducting solenoid in REBCO (Rare earth barium copper oxide) has been built that produces a record field of 45.5 Tesla[27]. *For almost two decades, 45T has been the highest achievable direct-current (d.c.) magnetic field; however, such a field requires the use of a 31MWatt, 33.6T resistive magnet inside 11.4T low-temperature superconductor coils, and such high-power resistive magnets are available in only a few facilities worldwide. By contrast, superconducting magnets are widespread owing to their low power requirements. Here we report a high-temperature superconductor coil that generates a magnetic field of 14.4T inside a 31.1T resistive background magnet to obtain a d.c. magnetic field of 45.5T - the highest field achieved so far, to our knowledge. The magnet uses a conductor tape coated with REBCO (RE* $Ba_2Cu_3O_x$*, where RE = Y, Gd) on a 30μm-thick substrate, making the coil highly compact and capable of operating at the very high winding current density of 1260* A/mm^2. *Operation at such a current density is possible only because the magnet is wound without insulation, which allows rapid and safe quenching from the superconducting to the normal state. The 45.5T test magnet validates predictions for high-field copper oxide superconductor magnets by achieving a field twice as high as those generated by low-temperature superconducting magnets.*

Fullerene C_{60} (1991) Hebard et al.[24] *The synthesis of macroscopic amounts of* C_{60} *and* C_{70} *has stimulated a variety of studies on their chemical and physical properties. We recently demonstrated that* C_{60} *and* C_{70} *become conductive when doped with alkali metals. Here we describe low-temperature studies of K-doped* C_{60} *both as films and bulk samples, and demonstrate that this material becomes superconducting. Superconductivity is demonstrated by microwave, resistivity and Meissner-effect measurements. Both polycrystalline powders and thin-film samples were studied. A thin film showed a resistance transition with an onset temperature of 16 K and essentially zero resistance near 5 K. Bulk samples showed a well-defined Meissner effect and magnetic-field-dependent microwave absorption beginning at 18 K. The onset of superconductivity at 18 K is the highest yet observed for a molecular superconductor.*
In 2007 the highest $T_c = 33K$ was observed in the organic superconductor $RbCs_2C_{60}$ at standard pressure.

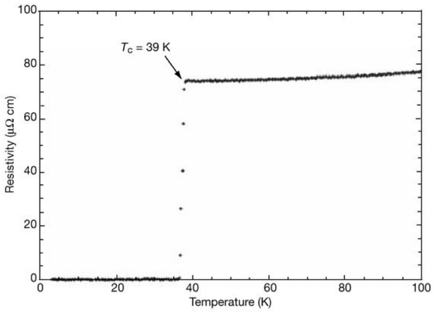

FIG. 5: Resistivity of MgB2, from[25].

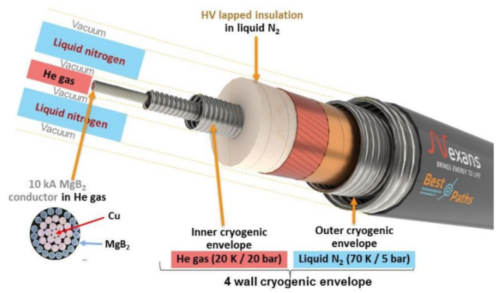

FIG. 6: Cable produced at Columbus Superconductors SpA, Genova.

MgB_2 (2001). Nagamatsu et al.[25] discovered MgB_2, with $T_c = 39K$. ... *At present, the highest reported values of* T_c *for non-copper-oxide bulk superconductivity are 33K in electron-doped* $Cs_xRb_yC_{60}$*, and 30K in* $Ba_{1-x}K_xBiO_3$. *(Hole-doped C60 was recently found to be superconducting with a* T_c *as high as 52K, although the nature of the experiment meant that the supercurrents were confined to the surface of the* C_{60} *crystal, rather than probing the bulk). Here we report the discovery of bulk superconductivity in magnesium diboride,* MgB_2. *Magnetization and resistivity measurements establish a transition temperature of 39K, which we believe to be the highest yet determined for a non-copper-oxide bulk superconductor.*

Graphene bilayers Cao et al.[26] (2018) ... *we report the realization of intrinsic unconventional superconductivity (which cannot be explained by weak electron-phonon interactions) in a 2D superlattice created by stacking two sheets of graphene that are twisted relative to each other* *by a small angle. For twist angles of about 1.1^o (the first 'magic' angle) the electronic band structure of this 'twisted bilayer graphene' exhibits flat bands near zero Fermi energy, resulting in correlated insulating states at half-filling. Upon electrostatic doping of the material away from these correlated insulating states, we observe tunable zero-resistance states with T_c up to 1.7K. The T vs carrier-density phase-diagram of twisted bilayer graphene is similar to that of copper oxides (or cuprates) and includes dome-shaped regions that correspond to superconductivity ... Moreover, quantum oscillations in the longitudinal resistance indicate the presence of small Fermi surfaces near the correlated insulating states, in analogy with underdoped cuprates. The relatively high superconducting critical temperature of twisted bilayer graphene, given such a small Fermi surface (which corresponds to a carrier density of about $10^{11}/cm^2$), puts it among the superconductors with the strongest pairing strength between electrons. Twisted bilayer graphene is a precisely tunable, purely carbon-based, two-dimensional superconductor. It is therefore an ideal material for investigations of strongly correlated phenomena, which could lead to insights into the physics of high-critical-temperature superconductors and quantum spin liquids.*

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