THE CLASSICAL SUPERCONDUCTIVITY: PHENOMENOLOGY OF LOW TEMPERATURE SUPERCONDUCTORS

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1. INTRODUCTION

When hearing about persistent currents recirculating for several years in a superconducting loop without any appreciable decay, we realize that we are dealing with a phenomenon which in nature is the closest we know to the perpetual motion.

The zero resistivity and the perfect diamagnetism in Mercury at 4.2 K, the discovery during 75 years of several hundreds of superconducting materials, finally the revolution of the "liquid Nitrogen superconductivity": Nature discloses drop by drop its intimate secrets.

Nobody can exclude that the last final surprise must still come.

2. THE ELECTRICAL RESISTIVITY AND THE ONNES DISCOVERY

One of the richest phenomena in nature is the electrical conduction in solids.

As it appears in fig. 1 the resistivity is a physical quantity that can assume values within an enormous range of variation, about 10^{24} orders of magnitude.

In connection with this it is surprising that Ohm's law

$$\vec{J} = \sigma \vec{E}$$

in its simplicity can satisfy, even if with some limitations, such a wide set of substances with almost rigourous agreement.

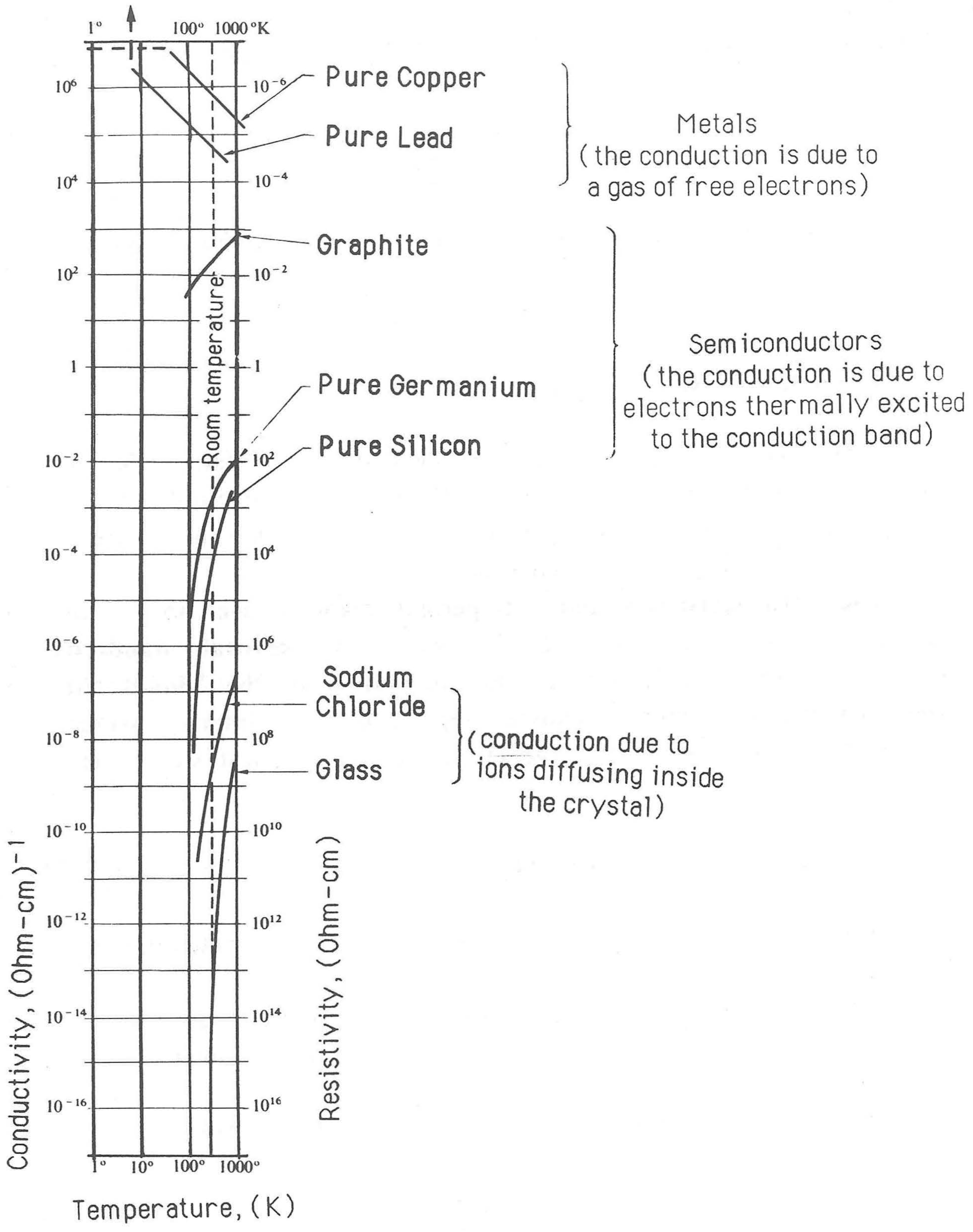


Fig. 1: *The electrical resistivity versus temperature of some common materials.*

A simple classical model, performed by P. K. L. Drude in 1900, cuts our way toward a phenomenological understanding of the problem of electrical conduction in metals. Such a model, also if with some deficiency, works very good in many cases.

Based on the hypothesis of a gas of free electrons scattered by the atoms, the model assumes that electrons wonder freely through a background of positive ions strongly pinned in ordered positions, making random collisions so that the average velocity in any specific direction is zero.

We can imagine two pin-table players of equal skill, facing each other. If they play a very high numbers of marbles, challenging each other for a very long time, they will score an equal number of goals. But if some one is tilting the table, unbalancing the level of the two nets, it will appear a favoured player since more marbles will drift into the net of his adversary.

On the same way, as shown in fig. 2, an electrical field applied to the metal will bias the electron motion and make them drifting, along the direction of the field, toward the positive electrode. In their diffusive path, electrons scatter with ions of the crystal lattice and at any collision they loose the energy borrowed from the field.

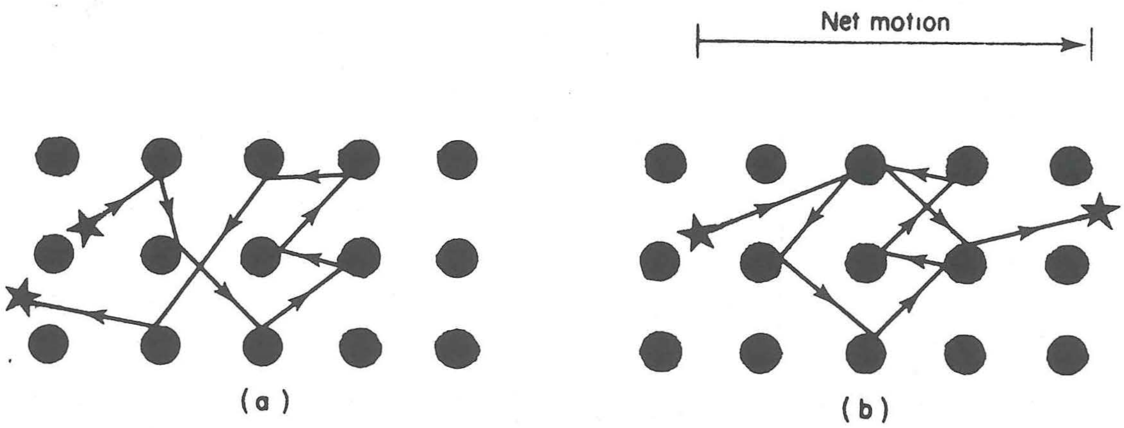


Fig. 2: *a)* *The electron motion is random for zero electric field.*
b) *A net drift toward a preferential direction appears when an electric field is applied.*

The electrical resistance is a measure of the energy that is degraded into heating since transferred by electrons from the electric field to the ions by means of lattice vibrations.

Electron collisions are determined by the quantized lattice vibrations (phonons), and by randomly-distributed crystal imperfections such as impurities, lattice irregularities or grain boundaries. Only phonons give a temperature-dependent contribution to resistivity since they get frozen when lowering the temperature. On the contrary imperfections contribute to resistivity by means of a temperature-independent residual term

$$R(T) = R_{ph}(T) + R_{res} .$$

This relation, known as the Matthiessen rule, states that the resistivity at low temperatures approaches a constant residual term, as shown in fig. 3: such a constant value depends strongly on the imperfections and the impurities content of the metal.

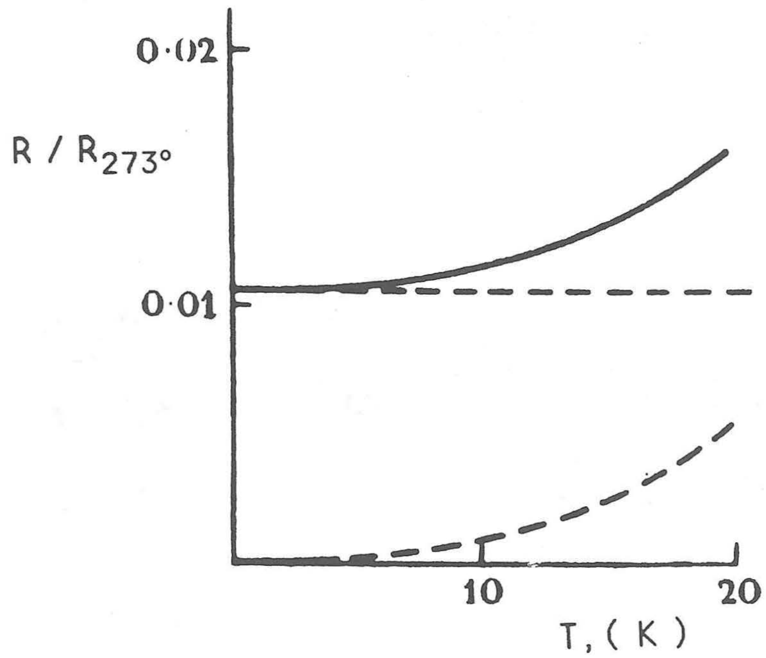


Fig.3. *The phonons contribution to the resistivity (dashed line) represents the resistivity due to lattice vibrations for a perfectly pure, strain free specimen; the resistivity measured experimentally (continuous line) is the sum of this ideal term and a temperature independent residual one.*

Although Matthiessen experiments were dated on 1864, at the beginning of this century, the theory of electrical resistance was in a rather rudimentary state: even each of the three forms of the temperature variation of the resistance, as sketched in fig. 4, seemed possible.

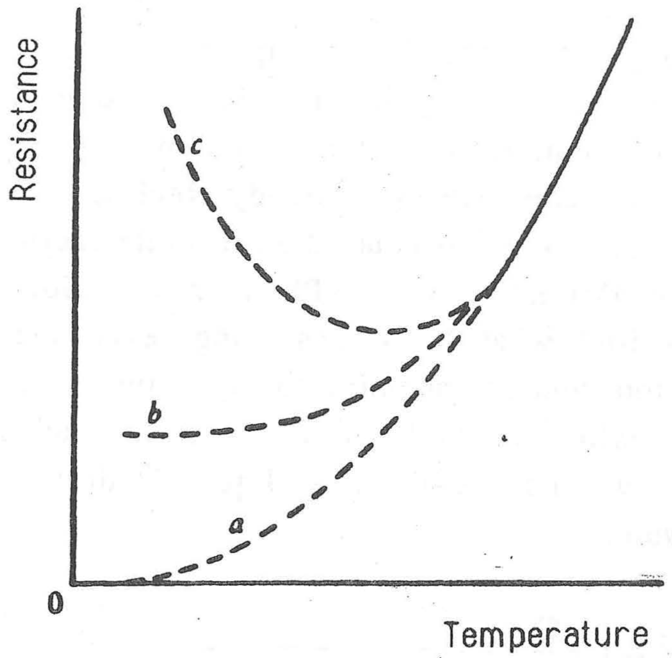


Fig. 4 *The Resistivity behaviour as predicted by Dewar (curve a), by Matthiessen (curve b) and by Kelvin (curve c).*

According to the idea of Sir James Dewar, the resistance was caused by the obstruction of Plank thermal vibrations on the motion of the free electrons: hence it had to decrease, when temperature was lowered, vanishing at the absolute zero.

Different it was the rule stated in 1902 by Lord Kelvin, convinced that at low temperature all metals should become insulators. The electrons were supposed to become free due to the thermal vibrations and only when free they could conduct current. Therefore he predicted a minimum occurring at low temperatures due to the rapid fail off of the number of free electrons as they condense on atoms.

In 1908 at the University of Leiden, H. Kamerlingh Onnes succeeded in realizing the dream that Dewar pursued unsuccessfully for the last years of his cryogenic career: Helium was liquefied, its boiling temperature about *4.2 K* was found and the record ultimate temperature of *1.7 K* was reached pumping on the liquid. The liquefaction apparatus was composed of separated closed cooling systems set in "cascade": liquid Oxygen was used in order to cool Nitrogen, used in order to cool Hydrogen, used in order to cool Helium. Each of these systems was a separate circuit with its valves, compressors, exhaust pumps, gasometers, liquefiers, and cryostats.

The technology of these low temperatures were for a certain numbers of years uncontested domain of Leiden laboratory, so that Onnes could embark experimentally on the problem of resistivity at low temperatures with no concurrents. Already inclined to the idea that resistance would tend to vanish at the absolute zero, he started by reproducing some of Dewar results on Platinum and Gold, but he quickly discovered that, to find what he was seeking, even the purest gold he could obtain was too much contaminated by impurities. Hence Mercury was chosen, since extremely high purity could be achieved distiling it several times. Moreover its resistivity at liquid Hydrogen is high enough to be easy to measure.

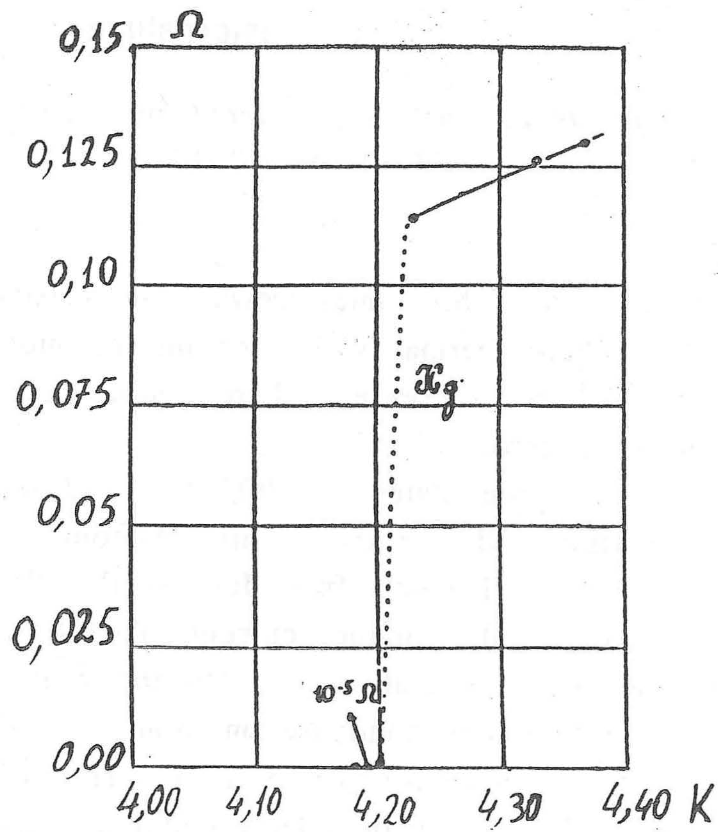


Fig. 5 *The resistance of Hg showing the transition to superconductive state (H. Kamerlingh Onnes, 1911).*

On April 28, 1911 the measurement was performed: the electrical resistance of Mercury was slowly and steadily decreasing with temperature, when at a temperature slightly below *4.2 K*, (fig. 5), it vanished abruptly failing to inappreciable values. "Mercury has passed into a new state that for its extraordinary properties may be called the superconducting state".

Another month of experiments showed to Onnes that the electrical resistivity collapses to zero in the space of few hundredths of degree and that a considerable amount of impurities added to mercury did not inhibit the drop to zero resistance.

Onnes found that many other metals became superconducting at temperatures achievable by his cryogenic apparatus (fig. 6).

Moreover in order to establish if the resistance in the superconducting state was really zero or not, he made a superconducting loop in which a current flow was induced; when the power supply was removed from the circuit, instead than an exponential decay of the current as it happens for normal metals, no detectable decay of the recirculating current was verified. This is a phenomenon which in nature is the closest we observe to the perpetual motion. The same method permitted to Collins in 1956 to place the upper limit of 10^{-21} *Ohm cm* for the resistivity in the superconducting state.

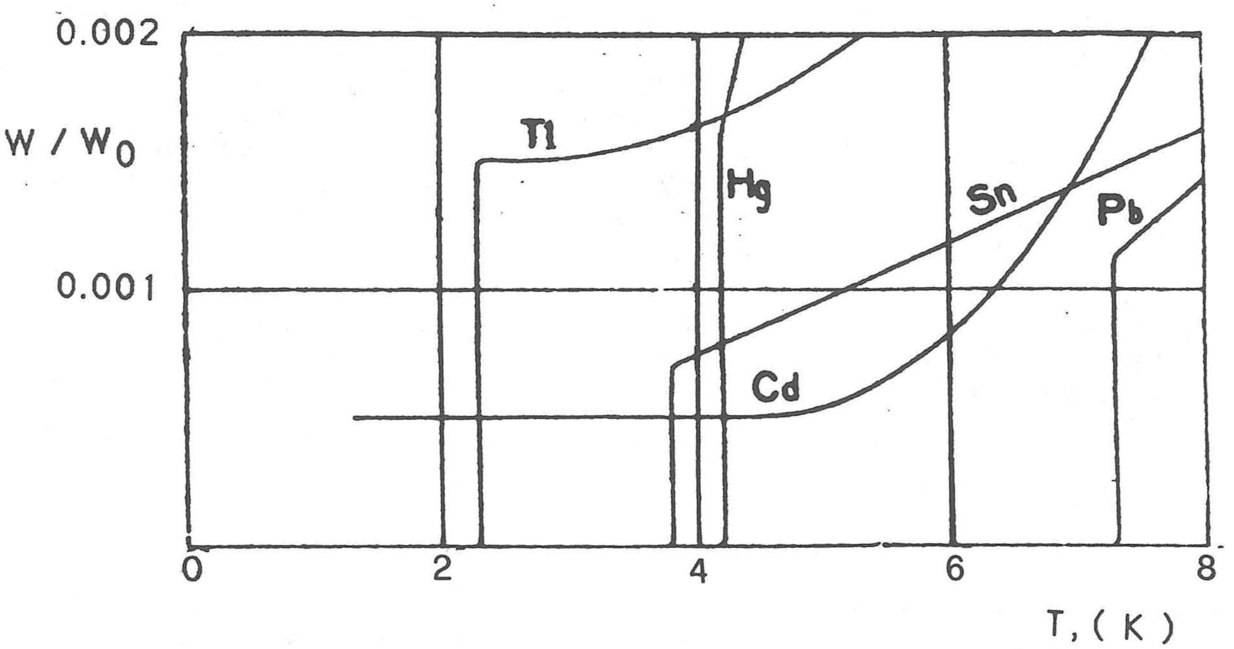


Fig. 6 *The resistive superconducting transition of other elements investigated by Onnes.*

The critical temperature is a peculiar characteristic of the element. Many simple elements in the periodic table are found to be superconducting (Table I); even some of them become superconducting under pressure. While it is endless the number of alloys that undergo the superconducting transition.

Element	T_c in K	Element	T_c in K	Element	T_c in K
Aluminium	1·196	Mercury-α	4·154	Thallium	2·39
Cadmium	0·56	Mercury-β	3·949	Thorium	1·368
Gallium-α	1·091	Molybdenum	0·92	Tin	3·722
Gallium-β	6·2	Niobium	9·26	Titanium	0·39
Gallium-γ	7·62	Osmium	0·655	Tungsten	0·012
Indium	3·4035	Protactinium	1·4	Uranium-α	0·68
Iridium	0·14	Rhenium	1·698	Uranium-β	1·80
Lanthanum-α	4·9	Ruthenium	0·49	Vanadium	5·30
Lanthanum-β	6·06	Tantalum	4·483	Zinc	0·87
Lead	7·193	Technetium	8·22	Zirconium	0·546

Element	T_c in K	Pressure
Bismuth II	3·916	25,000 atm
	3·90	25,200 atm
	3·86	25,800 atm
Bismuth III	7·25	27,000 ~ 28,400 atm
Caesium	1·7	50 kbar
Germanium	4·85–5·4	~ 120 kbar
Selenium II	6·75, 6·95	~ 130 kbar
Silicon	7·9	120–130 kbar
Tellurium	~ 3·3	~ 56,000 atm
Thallium (FCC)	1·45	35 kbar
Thallium (HCP)	1·95	35 kbar

Table I *The critical temperature of superconducting elements. (From National Bureau of Standards, Techn. N. 482, 1969).*

3. MACROSCOPIC ELECTROMAGNETIC PROPERTIES OF A SUPERCONDUCTOR

In the first decades after the Onnes discovery, superconductivity appeared to be an enigmatic beautiful phenomena, of mysterious origin, but unfortunately without any practical use.

Still, in the first twenty years after the discovery only a tenth of papers about superconductivity was published.

The further investigations searching which other electromagnetic property would change simultaneously with the drop of resistivity, arrived to the conclusion that:

- The X-ray diffraction pattern does not change when crossing the transition temperature showing no transition in the lattice structure.
- Although the optical properties of normal metals are strictly connected with resistivity, no appreciable change in the reflectivity of the superconductor can be detected; moreover photoelectric properties remain unchanged too.
- The elastic properties, the thermal expansion does not change with transition and no latent heat or volume change in absence of a magnetic field are observed.

A completely new and peculiar property of superconductors was, at last, discovered in 1933 by W. Meissner and R. Ochsenfeld: When a superconducting material is cooled below the critical temperature, T_C, it behaves not only as a perfect conductor, but also as a perfect diamagnet: i. e. the sample cannot be crossed by **the magnetic field.**

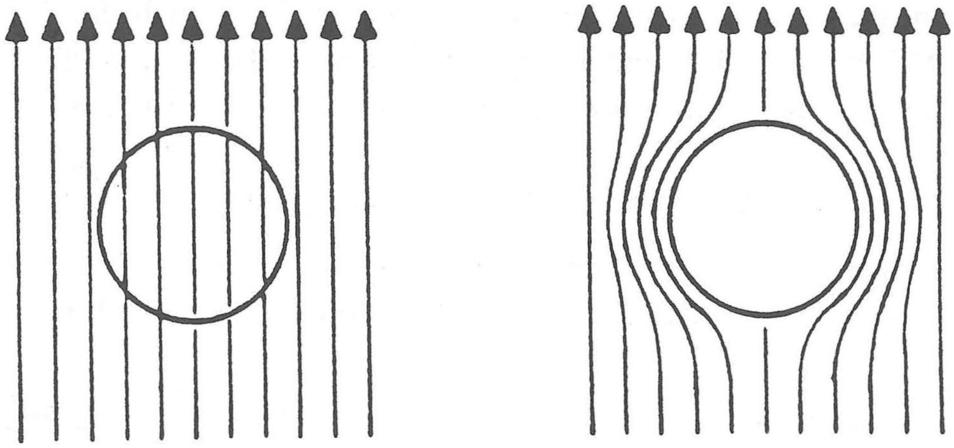


Fig. 7: *The Meissner-Ochsenfeld effect: when a material undergoes the superconducting transition, the magnetic induction B is shrunk out of the sample.*

It must be remarked that the diamagnetic effect is a phenomenon completely independent from the lack of resistivity.

Except for a small layer on the surface called the penetration depth λ, where screening surface currents are induced, the magnetic induction vector $\vec{B}$ is zero everywhere in the sample. As shown in fig. 7, the magnetic flux lines have "no licence" for getting inside the material when it is in the superconducting state. They will surround the sample in the same way a fluid, steadily flowing around the sample, will wrap it all around with its flux lines.

The Meissner-Ochsenfeld effect applies to superconductors having a multiply-connected body in a very nice way. Let us consider for instance a ring of superconducting material cooled below its critical temperature. During the transition from normal to superconducting, the flux is expelled in any direction outside of the superconductor, but the ring "does not realize" that it is closed on itself.

As shown in fig 8, some of the magnetic flux pushed out of the material will fill the hole of the ring itself and there is no reason why the flux in the hole should be expelled too. In fact the magnetic field remains sustained inside the hole by superconductive persistent currents on the surface.

It is well-known that, because $\vec{\nabla} \cdot \vec{B} = 0$, magnetic field lines are closed always onto themselves or to the infinite without possibility to get broken. On the other hand the field lines cannot cross the superconductor, therefore when the external field is removed, the magnetic flux inside the hole will remain trapped there and will not escape from the hole, unless the superconductor is quenched.

In 1935 F. and H. London predicted that if the ring is thick enough compared to the penetration depth, then the trapped flux inside the ring is quantized in integer numbers of an unitary quantity $\phi_0 = \frac{hc}{e}$.

Their hypothesis was later confirmed by Deaver and Fairbank in 1961, that using Tin films on Copper wires found that the flux is actually quantized as units of $\phi_0 = \frac{hc}{2e} \cong 2.0 \cdot 10^{-7}$ Gauss cm^2. The difference in the factor *2* from the predicted result is a good suggestion for the hypothesis that the superconducting currents are carried not by simple electrons but by electron pairs of charge $2e$.

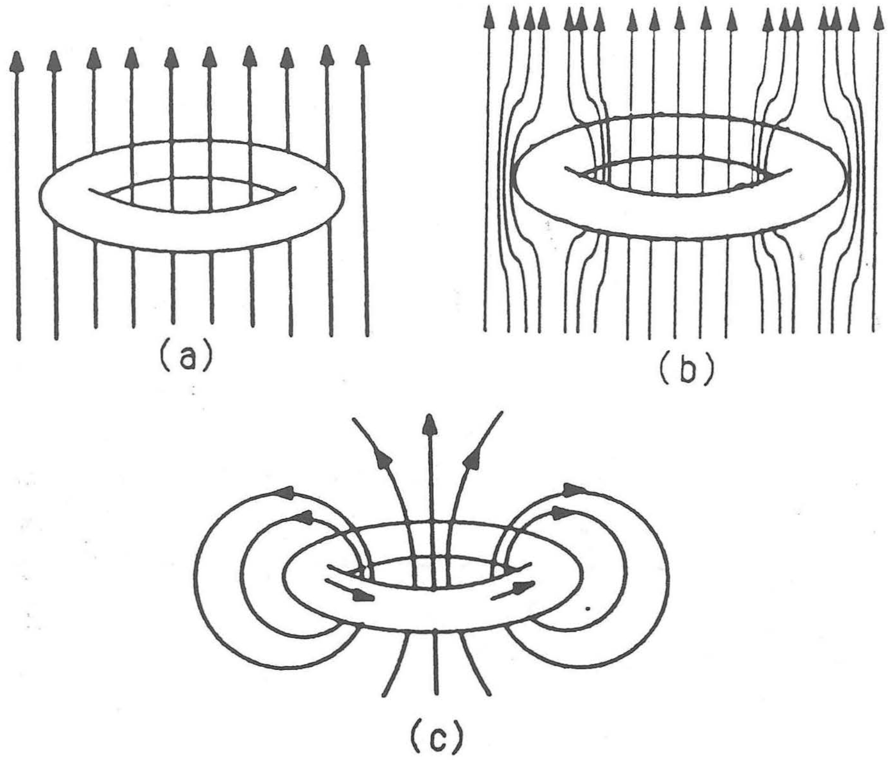


Fig. 8. *(a) The magnetic field is applied. The ring is in the normal state.*
(b) The magnetic field remains still applied, but the ring is brought into the superconducting state.
(c) The magnetic field is removed and the ring remains in the superconducting state.

4. TWO KINDS OF SUPERCONDUCTORS

Except that in a restrict set of applications making good use of the energy wasted by Joule effect, the electrical resistance represents usually a severe limitation to the technology when high performances are required for instance for high power electrical machines.

It is the case of large magnetic fields electromagnets: the magnetic field increases linearly with the current, while the energy lost by heat increases as the current square. Hundreds of kilowatts of power and an expensive elaborate cooling circuit are required to push a room-temperature electromagnet up to few tens of Kilo-Oersted, while higher and higher fields are required by research and technology.

It was readily realized by Onnes that superconductivity could be the tool for arriving to magnets of several Tesla. Nevertheless his disenchantment had to be rather strong when he discovered, by a Lead solenoid, that resistance can be restored, not only increasing the temperature above T_c, but even increasing the current up to overcome the critical current I_c. This limitation in current is related to the existence of the critical magnetic field H_c above which superconductivity is quenched. Depending on the particular superconductor, the critical current or the critical field can assume values in a rather wide range, but their existence is an universal feature for all superconducting materials.

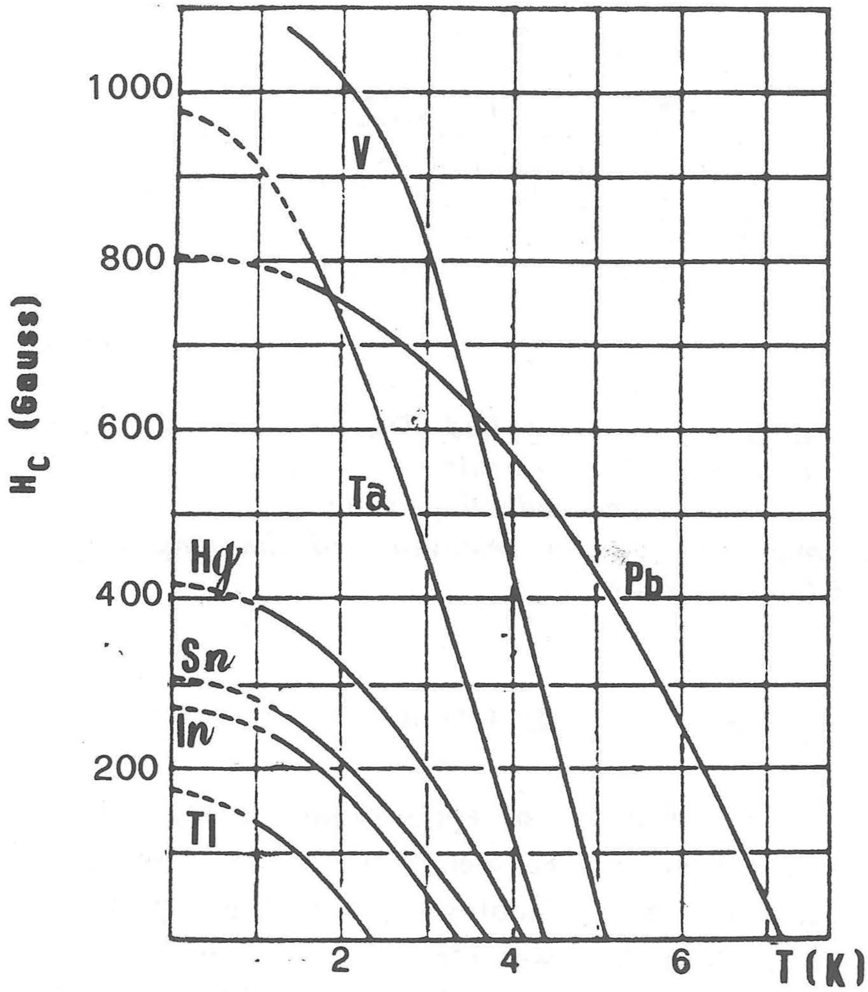


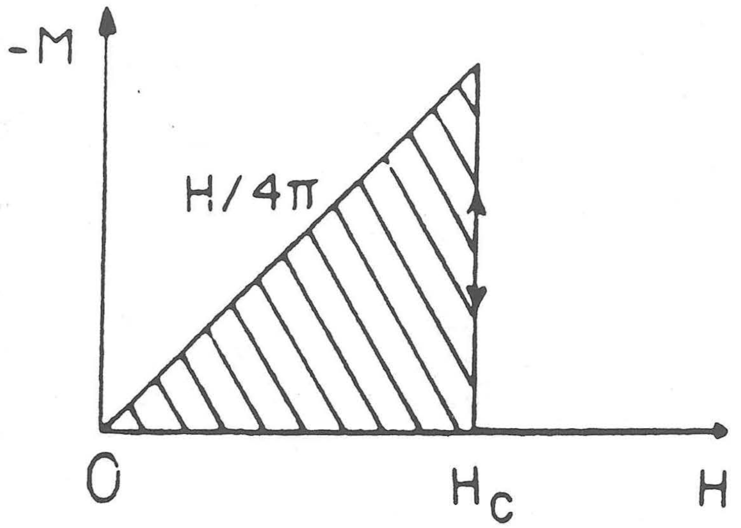
Fig. 9 *The critical field versus temperature for some superconducting elements.*

In fig. 9 the temperature dependence of H_c for some elementary superconductors is drawn; such a behaviour is well approximated by the parabola

$$H_C = H_0 \left[1 - \left(T/T_c \right)^2 \right]$$

that defines the limit of existence of superconductivity.

The diagram shown in fig 9 indicates a sharp transition from the superconducting state to the normal one. The same sharpness from one state to the other appears from the picture of magnetization versus field (fig. 10). This characteristic is peculiar only of one class of materials defined as "first type superconductors".



Fig, 10 *The magnetization in the superconducting state is equal to* $-H/4\pi$, *while it is zero in the normal state.*

The critical fields of First Kind Superconductors are quite low (always less than 10^{-1} *Tesla*) and the reason of Onnes' defeat was that he adopted just such materials to build his superconducting solenoid. Only after some decades high fields superconducting electromagnets could be prepared only by means of the "Second Type Superconductors" having high critical fields and high critical currents.

Type II superconductors are usually alloys or compounds, but the peculiarity of such a class of superconductors is displayed by their magnetic behaviour. Two critical fields enter the scene: H_{C1}(T), below which the material is entirely superconducting and an upper critical field H_{C2}(T) over which the sample is completely normal conducting (fig. 11).

The upper critical field is generally determined from measurements of the superconducting magnetization curve. In fig. 12 some high H_{C2} superconductors are compared.

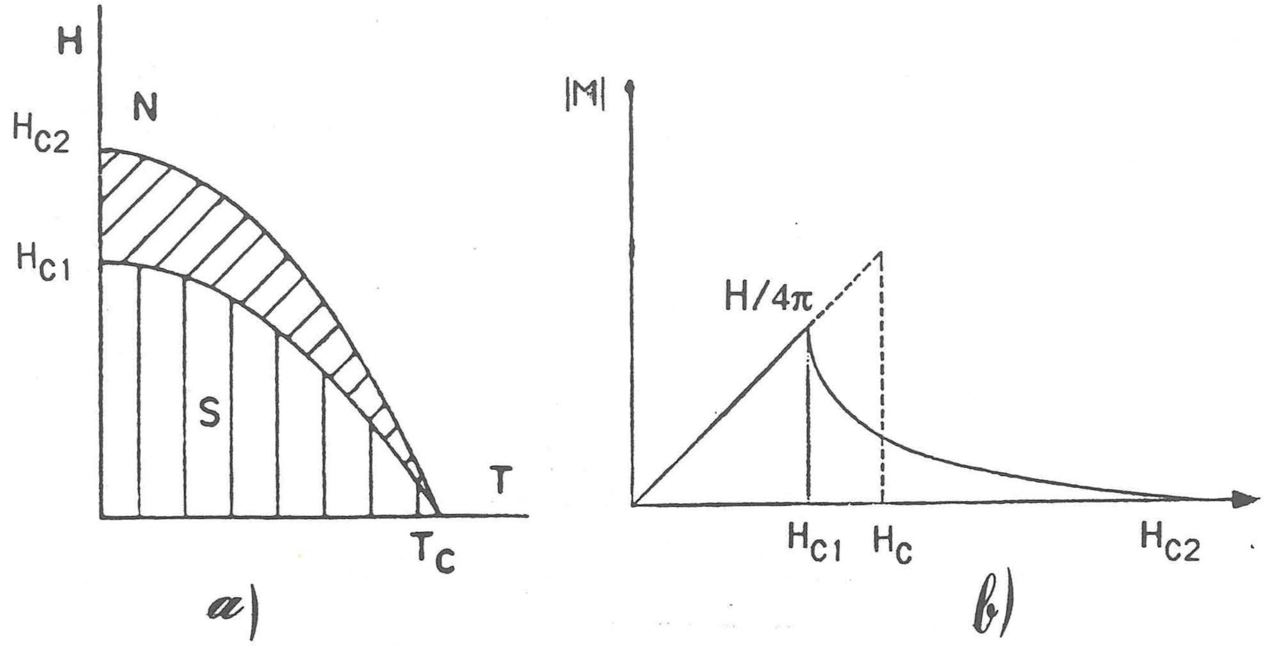


Fig 11 *a) The temperature dependence of H_{C1} and H_{C2}*
b) The magnetization versus field for Type II superconductors clearly shows a region of incomplete Meissner Ochsenfeld effect.

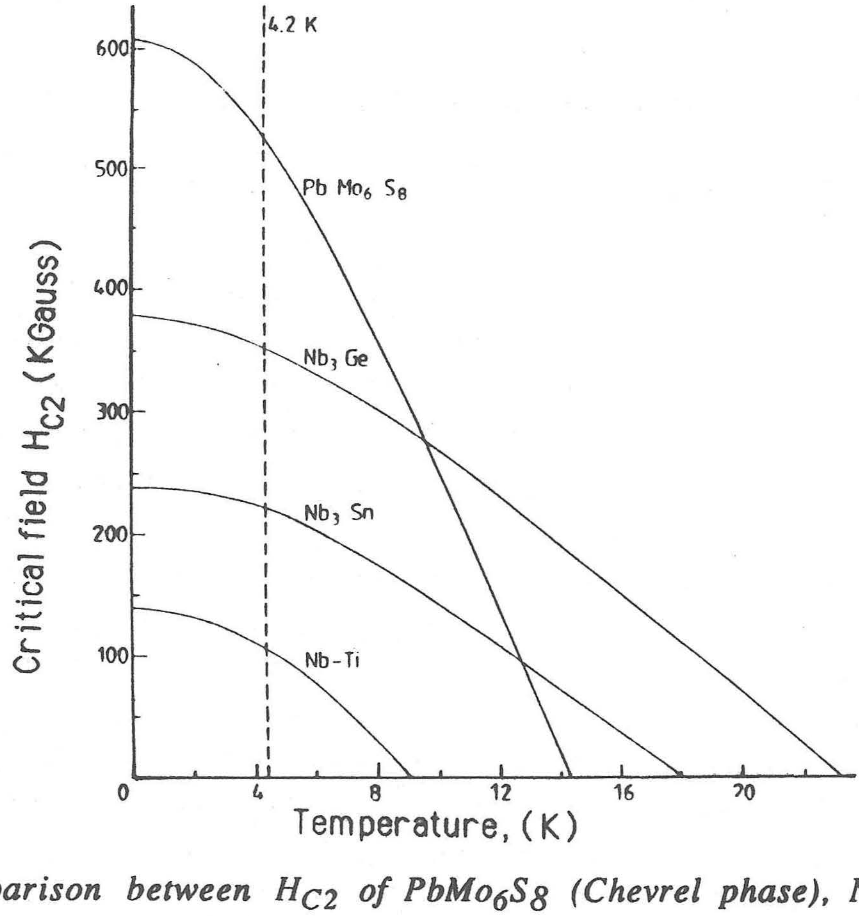


Fig. 12 *Comparison between H_{C2} of $PbMo_6S_8$ (Chevrel phase), Nb_3Ge and Nb_3Sn (A15) and Nb-Ti alloy.*

Exposed to fields between those two, the sample shows an incomplete Meissner state known as the "mixed state", characterized by a partial penetration of magnetic flux in a complicated microscopic structure of thin normal conducting filaments surrounded by superconductive regions. Such filaments are denominated "vortexes".

Each of them consists of a normal-state core containing one quantum of magnetic flux ϕ_0, channelled and sustained by persistent currents revolving around the vortex axis. The closer to the vortex axis such currents circulate, the higher it is the current value. At a certain distance from center the current is strong enough to overcome the critical value: that is why vortexes have normal core (fig. 13).

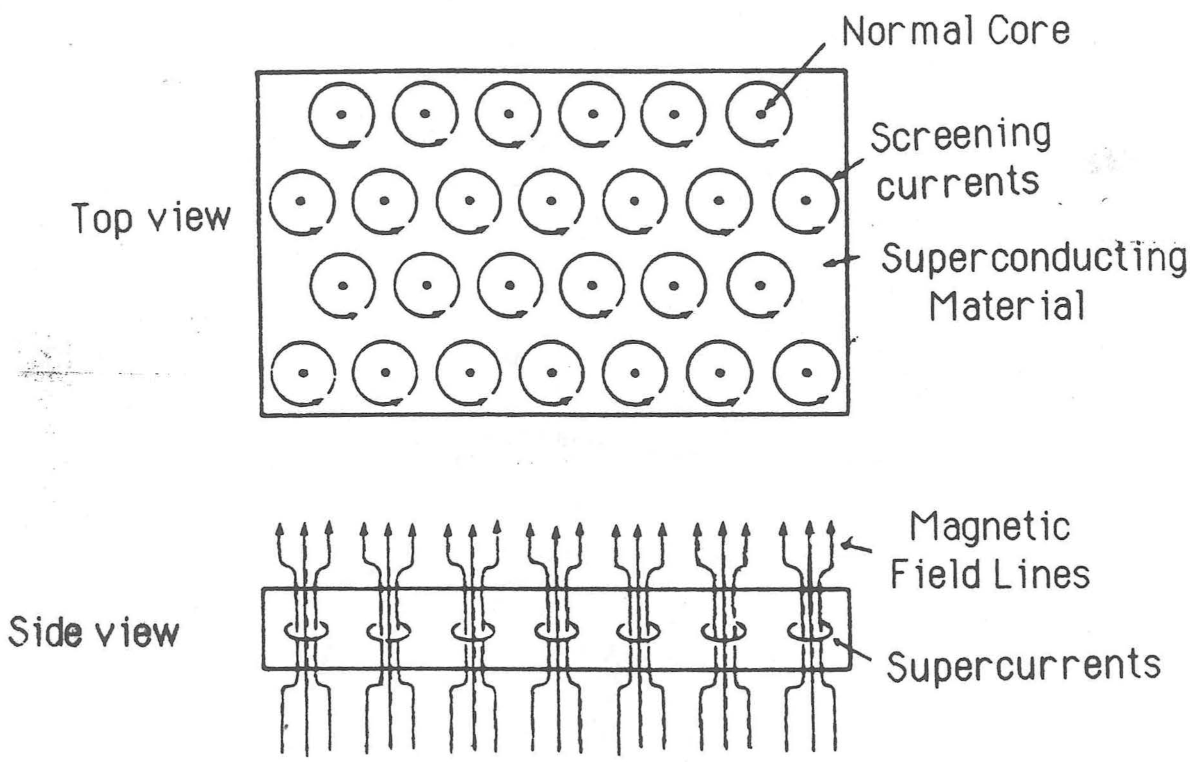


Fig. 13 *Vortexes in a Type II superconductor.*

Roughly speaking, vortexes are magnetic flux lines aligned parallelly to the applied field (if the sample is pure and defect free), perforating side by side the superconducting sample and disposed according to a triangular lattice. In the region outside vortexes superconductivity is unperturbed. Increasing the magnetic field, the number of vortexes becomes larger and larger up to when vortexes occupy all the sample surface. At that point superconductivity is completely destroyed: such a field corresponds to H_{C2} .

A current crossing the superconductor in the mixed state will act on vortexes with the Lorentz force $\vec{F_L} = \vec{J} \times \vec{\phi_0}$, making them moving. The Kinetic energy of the flux lines clearly represents a dissipation of the energy carried by the current. The flux flow of vortex lines will produce a voltage drop, hence a flow resistance equal to such a voltage divided by the current; subsequently dissipative losses as generation of heat take place inside the superconductor. Because of that, the critical current would be too small for any high-field application, if the superconductor would not contain any "pinning center" like dislocations, lattice irregularities and so on.

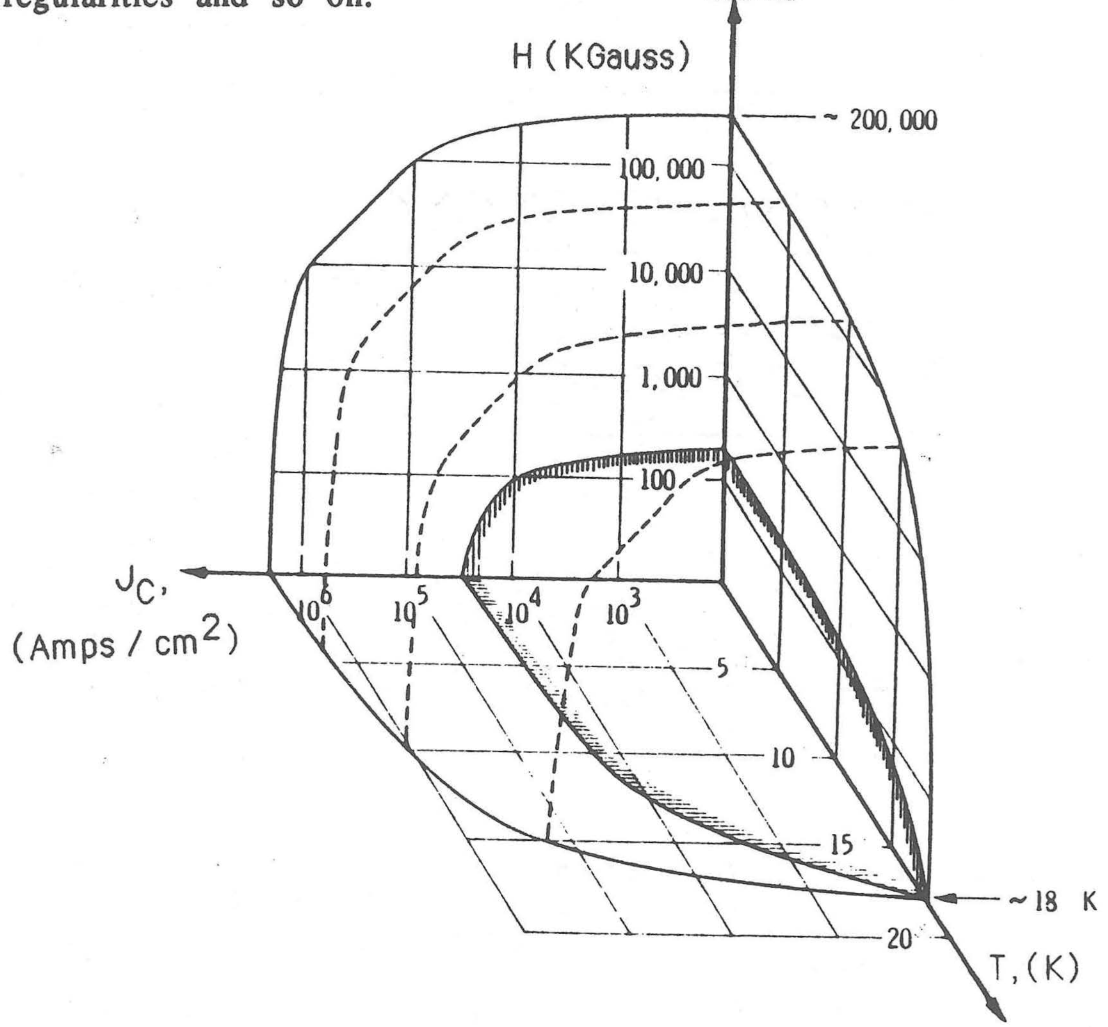


Fig. 14 *Critical current density and critical field for superconducting Nb_3Sn. The shadow line delimits the region of type I behaviour, while the type II behaviour occurs between the inner and outer surfaces.*

The addition of defects to the superconductor makes vortexes getting stuck on inhomogeneites, up the moment in which the current is strong enough for depinning. Indeed, in such a case, overcoming the critical current it means making the Lorentz force irresistible for the pinned vortexes. On the contrary a too weak current will not tear vortexes away from pinning centers, so no losses will accompany the current flow.

For *Type I* superconductors the critical current is simply the current at which the self-field generated by the current itself equals the critical field H_C.

For *Type II* superconductors the critical current is not an intrinsic microscopic property, but an extrinsic property dependent on the metallurgical history of the material, so that its value, even changing from sample to sample, cannot be predicted with absolute certainty.

In fig. 14 the critical surface current-field versus temperature is reported for Nb_3Sn.

The need for strong pinning in order to obtain high critical currents, requires that superconductors be often cold-worked materials, so that they contain residuals of different phases, even impurities. As a result they are metallurgically hard, hence sometimes they are called "hard superconductors".

5. PHENOMENOLOGICAL THEORIES.

5.1 The two fluids model.

A good deal of experiments suggest that the superconducting transition is primarily an electronic one.

In the superconducting state indeed the material properties depending on the lattice structure, such as the elastic constant or the optical reflectivity, are not shifted from their normal-state values. In the same way the lattice contributions to the specific heat and to the thermal conductivity are only slightly changed on passing through the transition.

If we extract from the curve of the specific heat versus temperature <u>the electronic component</u>, we observe that, in absence of magnetic field, a finite discontinuity is observed in C_{el}, but there is no latent heat, i.e. the transition is of the second order according to Ehrenfest' s classification.

It can be shown that this is the condition to introduce the Landau long-range order parameter ζ. Such a parameter is required to take the unitary value at the absolute zero, and to vanish at T_c.

The introduction of ζ means that the superconducting transition is characterized by the existence of long-range order.

In 1934 Gorter and Casimir provided an interpretation of ζ in terms of the so called "two fluids model", leading so to an important development for the phenomenological representation of superconductivity.

At any temperature $T < T_C$ the conduction electrons for a superconductor are shared in two components; we could say two fluids: a "cold" one, carrying no entropy, having superfluidity properties, and a "warm" one of normal electrons, responsible for Joule losses and behaving essentially as they would for $T > T_C$.

The order parameter ζ will be equal to the fraction of electrons condensed into an ordered configuration; correspondingly $1 - \zeta$ will be the fraction of normal electrons.

Therefore, as represented in fig. 15, at $T = 0\ K$, all electrons are superfluid, while at $T = T_C$ all are normal. At temperatures between $0\ K$ and T_c, the current transport in the superconducting state is a mixture of "super-electrons" and "normal-electrons". As temperature increases, the superfluid fraction increases, while the normal-fluid one decreases, remaining always constant their sum.

The total current J_{tot} is the sum of a superconducting current J_s and a normal conducting current J_n,

$$\vec{J}_{tot} = \vec{J}_s + \vec{J}_n$$

The two currents are assumed to flow in parallel. In the limit of zero frequencies, the superfluid shunts the normal component giving zero resistance in d.c..

Actually the two fluid model reflects the fact that, at temperatures different from zero, not all conduction electrons "feel superconductors".

The most evident case in which this feature can be observed is, for example, the power dissipation of a superconductor exposed to radiofrequency fields: the ideal surface resistance (that is due to the normal electrons inertia respect to rf fields) decreases with temperature, being zero only at $0\ K$, i. e. when there are no normal electrons.

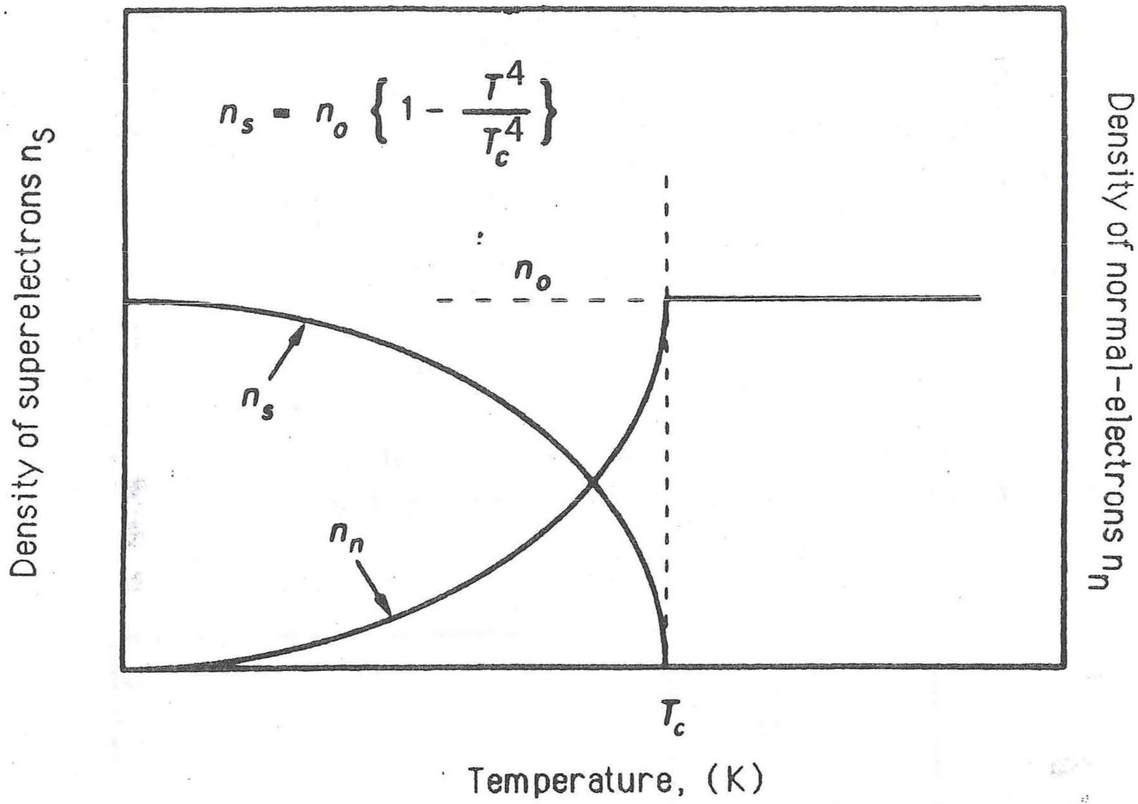


Fig. 15 *The density of superelectrons n_s and the one of normal electrons n_n versus temperature are plotted according to the dependence proposed by Gorter and Casimir,* $n_n = \left(T/T_C \right)^4$. *The great potentiality of this phenomenological approach is that it still is successfully used in many cases (especially in engineering analyses), but the forth power dependence needs to be changed with a more complex one.*

The luck of the two fluids model lays mainly beside its reformulation by Heinz and Fritz London, who, by means of simple electrodynamics, described the normal current by *Ohm's law* and the supercurrent as a system of particles flowing with no friction, arriving to two famous equations

$$\vec{\nabla} \times \vec{J}_S = - \frac{\vec{H}}{4 \pi \lambda_L} \qquad \text{and} \qquad \vec{E} = 4 \pi \lambda_L^2 \frac{\partial \vec{J}_S}{\partial t}$$

being λ_L the London penetration depth.

All London electrodynamics is contained in these two relations. Combining them with Maxwell equations the following result for static conditions is obtained:

$$\nabla^2 \vec{H} = \frac{\vec{H}}{\lambda_L^2}$$

i.e. the magnetic field decay exponentially from the surface of the superconductor with a penetration depth λ_L (fig. 16).

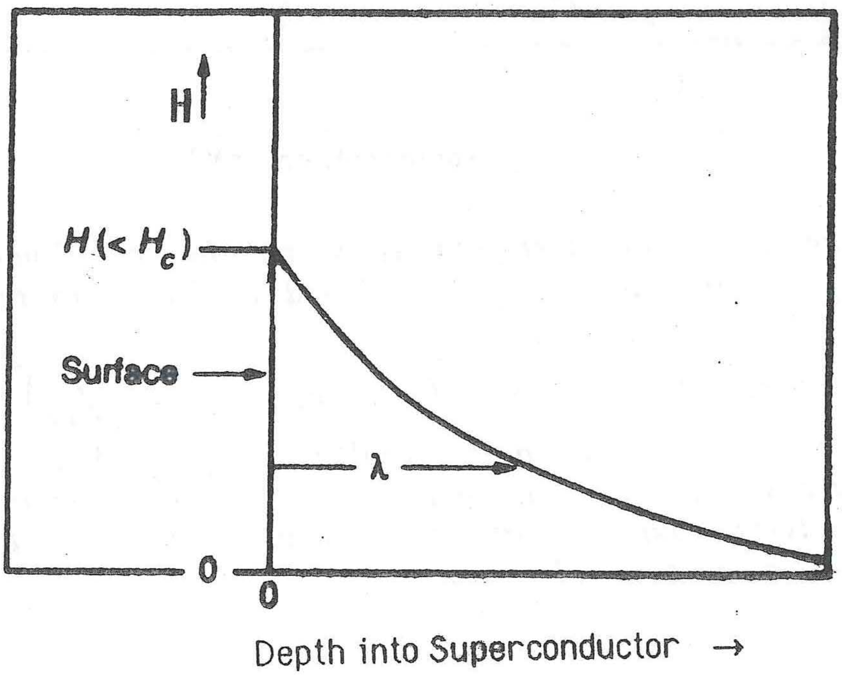


Fig. 16 *The field decays according to the relation* $H = H_0 e^{-x/\lambda_L}$ *; the quantity* λ_L *is the depth of penetration.*

It is worthwhile to recognize the similarity of the second London equation with the expression for the voltage *V* at the ends of an inductance *L* crossed by a current *I*,

$$V = L \frac{dI}{dt}$$

The inductive character of the supercurrent is therefore explicit. While $\vec{J}_n$ is in phase with the electric field $\vec{E}$, $\vec{J}_s$ has a $90°$ difference respect to $\vec{E}$. When $\vec{J}_s$ is not changing with time, the field $\vec{E}$ is required to be zero; static supercurrents can hence flow with no resistance.

For time dependent magnetic fields, the inductance of superelectrons is coupled with the normal electrons resistance, producing losses, proportional to the square of the electric field and to the square of frequency.

In 1953 just through measurements of the microwave impedance of superconductors Brian Pippard found that the reduction of the electron mean free path ℓ (m.f.p.), for instance by doping the sample with impurities, produces a very strong increasing of the penetration depth λ. On the contrary according to the London two fluid model the impurity content in a superconductor should not affect sensitively λ_L.

Pippard showed that the dependence of the penetration depth on the impurity amount could be accounted hypothesizing that the superelectrons act coherently over a distance ξ.

In such a case the equation that relates the current density with the vector potential in one point must be replaced by a non-local relation in which the current density at a point is dependent on the value of the same vector potential, but averaged over a surrounding region of size ξ.

Of course the coherence must be a function of the impurity concentration i.e. of ℓ.

Therefore an effective coherence length ξ must be defined. If ξ_0 is the coherence length for a pure metal, the experimental observed dependence for ξ is

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{\ell}$$

Depending on ℓ, an effective penetration depth λ too must be defined

$$\lambda = \lambda_L \left(\frac{\xi_0}{\xi}\right)^{1/2}$$

The Pippard non-local treatment must be necessarily applied to describe the electrodynamics of superconductors for which the characteristic length of the field variation λ is much smaller than the domain of integration ξ.

These superconductors go under the name of "Pippard superconductors"; they need a non-local treatment and the integrals supplied by Pippard must be solved.

On the contrary for superconductors for which λ is larger than ξ, the vector potential is reasonably constant within a coherence length, so the Pippard integral reduces to the local London equation. These superconductors are called London superconductors.

It can be proofed that the Pippard and the London materials correspond respectively to superconductors of the first kind and of the second kind.

In conclusion it is important to remark the existence of a class of superconductors inside the set of London-type superconductors, represented by the "dirty limit" superconductors, for which $\ell << \xi_0$.

In the dirty limit the effective coherence length is nearly equal to the mean free path. This approximation has a very wide range of applicability. Indeed the most part of superconducting alloys or composites falls into the dirty limit.

5.2 The Ginzburg-Landau theory

The two fluid model can only describe a superconducting state having a spatially constant density distribution of superconducting electrons n_s . In 1950 Vitali L. Ginzburg and Lev D. Landau formulated a phenomenological theory including the possibility to describe also states where n_s spatially varies.

The importance of Ginzburg-Landau theory is incommensurable since it permits a deep understanding of the Type II superconductors and, by means of this, the development of all the technology using this kind of superconducting materials.

The great limit of the GL theory is that it is a local theory. That determines its failure at high frequencies and at temperatures far from the critical temperature.

Indeed for $T \sim T_C$ (that is the range of validity of GL theory) the penetration depth λ is larger than the coherence length ξ and the non-local aspect of the electronic interaction becomes of secondary importance. That is why GL theory describes Type II superconductors better than Type I.

The theory starts from the definition of the order parameter ζ and from the assumption that the degree of order at each point in a superconductor can be described by ζ.

According to the general theory of the second order phase transitions, an expression for the free energy of a superconductor can be constructed expanding the Gibbs potential G in powers of ζ^2.

$$G_S = G_N + \alpha|\zeta|^2 + \frac{1}{2}\beta|\zeta|^4 + \ldots.$$

being G_S and G_N respectively the Gibbs energy in the superconducting and the normal state; α and β are material dependent parameters.

The GL theory pictures a superconductor as a flexible physical system responding to applied currents and magnetic fields by adjusting its spatial distribution of order.

The equilibrium configuration of order, current and field is the one that minimizes the total energy of the system.

The theory provides two coupled equations with boundary condition giving the spatial distribution of the order parameter ζ and the vector potential $\vec{A}$ in terms of the Ginzburg-Landau parameter K_{GL} defined as ratio between the penetration depth λ and the coherence length ξ.

For different values of K_{GL} there exist different termodynamical states. GL parameter allows an estimation of the flexibility of the order parameter in presence of a magnetic field.

In fact it is possible to show that for K_{GL} values lower than $1/\sqrt{2}$, the order is relatively stiff (the concentration of superfluid is rather constant in space); for values higher than $1/\sqrt{2}$ the order is deformed by a magnetic field (vortexes penetration at fields above H_{C1}).

6. THE MICROSCOPICAL THEORY

The two phenomenological theories discussed above had the great merit of explaining the several electromagnetic properties of a superconductor in terms of a moderate number of empirical equations combined with the normal metal theory.

Nevertheless no systematic theory of superconductivity explaining the nature of the phenomenon existed up to 1957 when Bardeen, Cooper and Schrieffer (BCS) formulated a microscopical theory based on a "condensation" of couples of electrons into Cooper pairs.

Up to this moment the physics of that phenomenon resisted to all efforts of theoretical understanding. A number of talented theoretical physicists attempted to explain by quantum mechanical models the mechanism of no resistance combined with perfect diamagnetism. The reason was that it was not used the proper tool: the problem was attached in terms of quantum mechanical models of a single-electron motion. But superconductivity is a collective phenomenon: something that results from the cooperation of many atoms together. A single atom of Mercury cannot be superconducting; a cluster of Mercury atoms can. Roughly speaking superconducting electrons are organized in persistent current circulating on the sample surface just as hypothetical electrons moving in the orbital of a gigantic atom large as the whole sample.

Actually there are dynamical systems, like for example a traffic jam at cross-roads in rush hours, or a great mass of fans in a football-stadium for the World Cup final, or a water splash provocated by a stone thrown into a puddle or even the evolution of the Wall Street stock-market, that cannot be described by examining the motion of a single particle, but they need a many-body formalism. Superconductivity is one of them and before 1950 many-body theories were not yet developed.

It is indeed just the correlation between electrons the keyword to solve the enigma of the superconducting state.

Once found such a "password", Bardeen, Cooper and Schrieffer formulated a theory that gives a complete and unitary account of superconductivity, opening certainly a breakthrough in the obscurity wrapping the phenomenon.

A new thread in the field of the material research both for theorists and for experimenters was outlined. However it must be recognized that the BCS theory is a very good theory to describe superconductors already discovered, but not good enough to predict which materials would become superconducting.

In order to be introduced to the fundamental ideas of the BCS theory it is necessary to recall the concept of Fermi energy. The Fermi energy E_F is defined as that level below which, at absolute zero, all the energy states are occupied and above which all states are empty (fig. 17).

Thus at *0 K* the energy corresponding to the Fermi level is the boundary between filled and unfilled states. At temperatures different from zero the probability that a particular level of energy E above E_F would be filled by electrons is given by the well-Known Fermi-Dirac distribution function

$$\frac{1}{1 + e^{\left(\frac{E - E_F}{KT}\right)}}$$

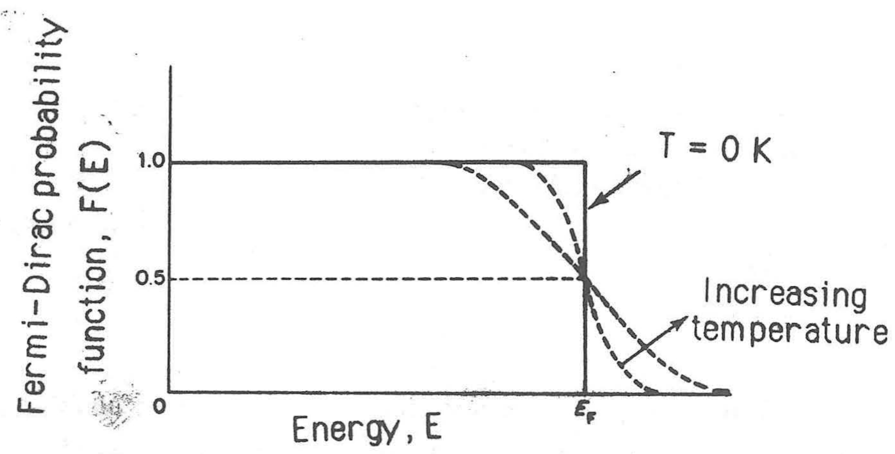


Fig.17 *a) The Fermi-Dirac distribution at 0 K, and at temperatures above 0 K.*

One basic assumption under the BCS theory is the presence of a forbidden energy gap Δ of the order of KT_C in the energy spectrum for a superconductor, just centred around the Fermi energy (fig. 18). For a critical temperature of *10 K*, KT_C is about *1 meV* , that is much smaller of the Fermi energy (which is of the order of few electron-volts).

The existence of such an energy gap has been evidenced by a variety of independent experiments.

The exponential behaviour of the specific heat and of the thermal conductivity, the sharp edge in absorption at a given angular frequency in the microwave absorption spectrum, and the extraction of the density of states by measurements of the ultrasonic attenuation, of the electron tunneling characteristic, or of the nuclear spin-lattice relaxation time all separately provide a direct measure of Δ.

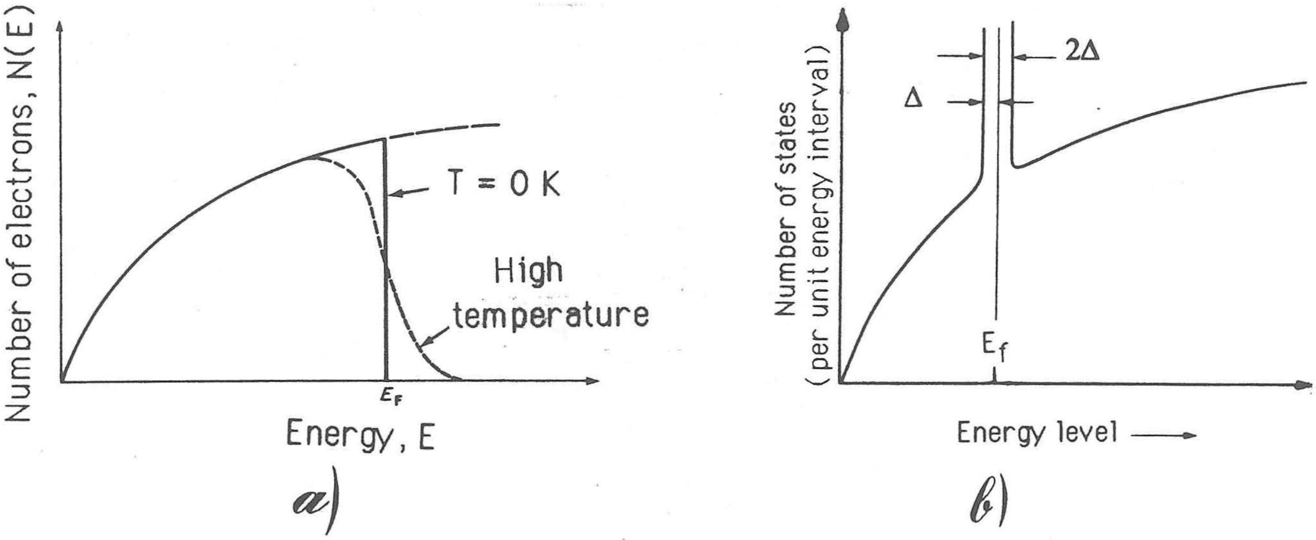


Fig. 18 *The density of electron energy states versus energy*
a) for a normal metal
b) for a superconductor.
The presence of an energy gap establishes a radical difference.

In 1956 Leon Cooper proofed that for two electrons on the Fermi surface feeling an attractive interaction, no matter how weak, it exists one stable ground state at energy below the Fermi level E_F in which the two electrons condense forming a bound pair.

Hence the other fundamental assumption of BCS is that at the absolute zero all electrons are coupled in Cooper pairs, each of them composed by electrons of opposed spins and opposed momenta.

Such Cooper pairs are bosons, and for bosons it does not occur the exclusion Pauli principle, i.e. all they are condensed into a common ground state.

Hence the fundamental state at *0 K* is not represented any more by the normal metal picture of couples of electrons, spin-up spin-down, distributed along different energy levels up to the Fermi level (fig. 19.a).

On the contrary the new fundamental state is now composed by an innumerable crowd of pairs condensed into a ground state (fig. 19.b).

At temperatures between *0 K* and T_C, increasing the temperature, electron pairs start gradually to depair breaking into quasi-particle excitations, starting to fill the energy levels above the gap, as in the usual picture for normal metals (fig. 19.c).

At T_C the gap closes and all the pairs are broken into normal electrons.

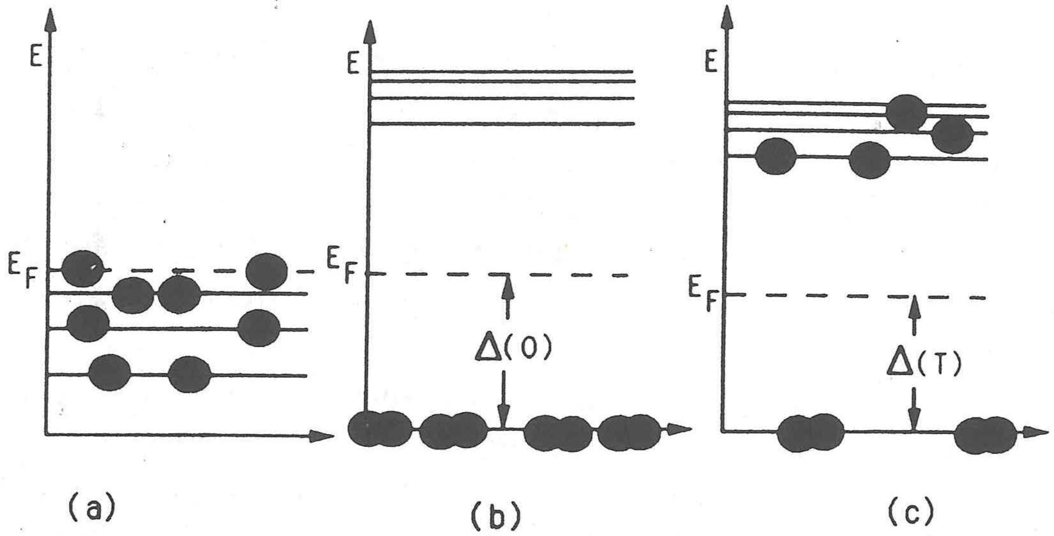


Fig 19. - *Energy spectrum for:*
(a) a normal metal. At $T = 0\,K$ all the electrons fill the lower energy levels up to E_F obeying the Pauli exclusion principle.
(b) A superconductor at $T = 0\,K$. The Fermi surface is unstable against pairs formation. The Bose condensation of Cooper pairs into one stable ground state is energetically more stable.
(c) A superconductor at $T \neq 0\,K$. Temperature excitations start to break Cooper pairs and single particle excitations go to fill the energy levels of the "normal bound"

It is obvious that, while practically no correlation between electrons exists in the case of normal metal, in the superconducting state electrons pairs are related each other by an extremely strong "long range coherence".

By means of such long range coherence Cooper pairs are, within a correlation length ξ, one connected to each other as wagons of a whole interminable train.or as stitchs of a wide-mesh net In other words the ground state is a **macroscopic quantum state.**

The size of a Cooper pair is ξ. Recalling a famous analogy: Cooper pairs are comparable to couples of "sweethearts" dancing a modern rhythm in an overcrowded discotheque. All the pairs are guided by the same music. Also if the components of each couple dance at a distance ξ.far from each other, they look at each other continuously. Moreover their steps are strongly determined by the dance of all the couples dancing in the space between them. The dance of each couple is coherent with the dance of all the others.

Now, electrical resistance in normal metals is due to the single electrons that, scattered by impurities (and by phonons if $T \neq 0$), jump from one level to the other transferring energy quanta from the fields to the lattice, with a consequent Joule effect.

In a superconductor Cooper pairs are not free as the normal electrons: within a coherence length ξ, the set of Cooper pairs must be considered as a whole single particle separated from the next excited state by Δ.

Impurities can do nothing to one single Cooper pair since it is bound to all the others. Moreover impurities do not interact either with the whole herd of pairs because the minimum energy amount that can be exchanged is Δ, and it cannot be shared into equal smaller quantities for all pairs. The movement of carriers inside the superconductor without friction leads to the lack of resistance.

At finite temperatures, but always below T_C , the Cooper pairs coexist with quasi particle excitations, but these excitations are not significant for resistivity since, as we said in section 5.1, they are shunted (in d.c.) by the superfluid, having the only effect to limit the states onto which pairs can be dispersed when decoupled.

It remains to answer to one question: how can be an attractive interaction between two electrons?

A good solution to this problem was proposed by Herbert Frölich, who suggested that the electron-electron attractive interaction could arise through a phonon exchange mediated by the lattice.

The idea was that an electron travelling through a crystal polarizes and distorts the adjacent portion of lattice giving rise to fluctuations of the lattice charge distribution. If the motion is slow enough, such electron is accompanied in its motion by a polarization cloud that surrounds it with a positive screening effective charge.

A second electron, that moves in the lattice at a distance ξ from the first one, is attracted by such a positive effective charge, feeling so a resultant attraction toward the first electron (fig. 20).

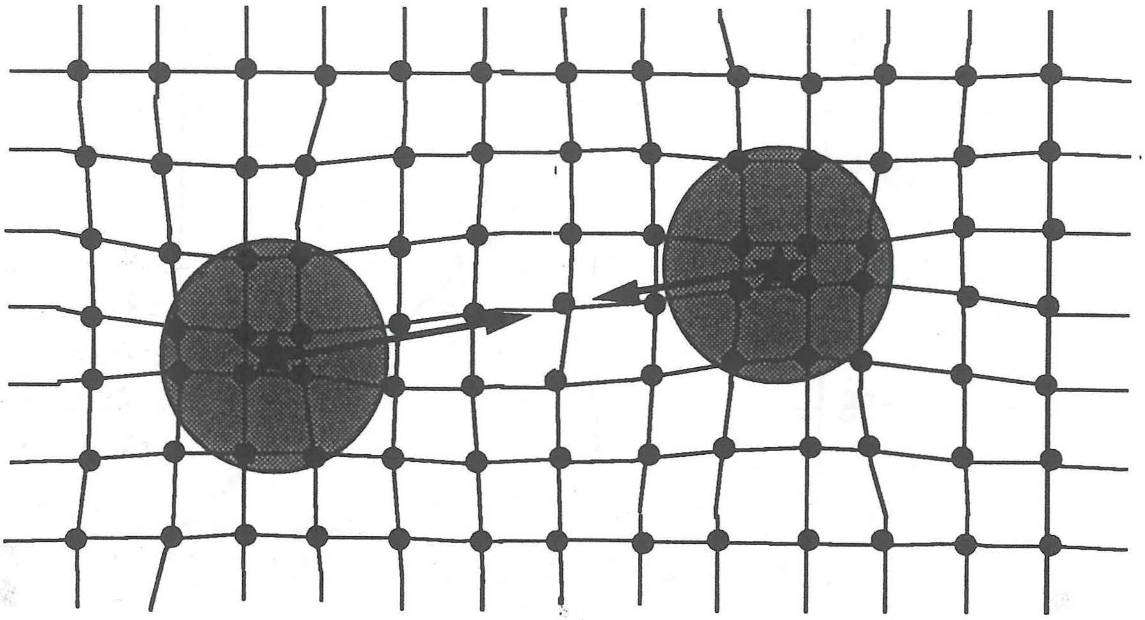


Fig. 20 *Two electrons interact attractively exchanging a phonon. The lattice behaves as the medium through which they interact. One of the two electrons "looks at" the other as a particle dressed of a positive ions cloud.*

Obviously the strength of binding of two paired electrons depends on the effectiveness of the positive screening mentioned above, but this is related to the mobility of ions around their equilibrium position inside lattice.

Hence if we take different isotopes of the same superconducting material, such a mobility would be a decreasing function of the isotopic mass M.

Thus that is the simple idea that stays beside the empirical law

$$T_C \propto M^{-1/2}$$

discovered in 1950 by Maxwell and Reynolds and known as the "isotopic effect".

In fig. 21 the phenomenon is displayed for Tin according the observations of different groups.

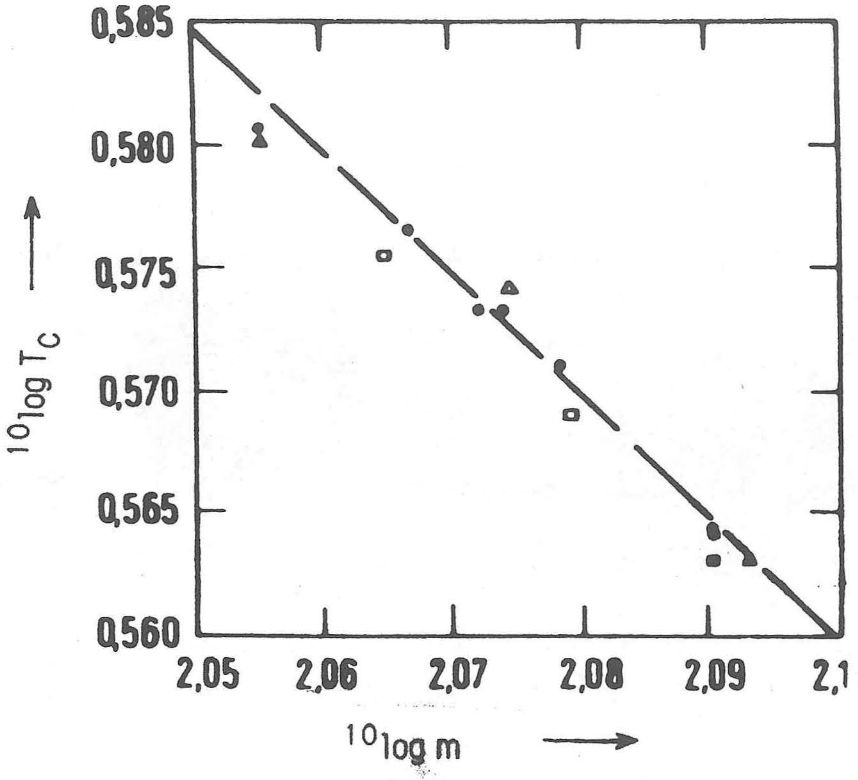


Fig. 21 *The isotope effect for Sn.*

Few exceptions there are in the framework of classical superconductors: no isotopic effect is observed for Zr and Ru and even a reversal isotopic effect is encountered in the Pd-H system.

Apart from these cases, the isotopic effect clearly indicates that the electron-phonon interaction has a major role in superconductivity: the crystal lattice structure determines the electronic properties of superconductors.

Isotopic effect was a great success for the BCS theory especially because no phenomenological model able to comprehend it existed before.

The BCS microscopical theory gave to research a significant boost on both the experimental and the theoretical side. But the real revolution laying under its formulation is that BCS theory gave to superconductivity the cloth of science.

SUGGESTED READINGS

This review is only introductory and whatever contained in it can be easily found in classical superconductivity textbooks. The purpose of this article is to give just an appetizer for who wishes a deeper understanding of the superconducting phenomenon and its technological implications.

Duo to the way in which it has been drawn up, a list of references is not provided. On the contrary the reading of some among the books listed below is warmly recommended

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