

# **MgB<sub>2</sub> MATERIALS BY REACTIVE LIQUID INFILTRATION FOR INNOVATIVE SUPERCONDUCTING TECHNOLOGIES**

Giovanni Giunchi\*, Bekmirzaev Rahmatillo Normuradovich\*\*, Mustafaeva Marjona\*\*

\*Materials Science Consultant, via Teodosio 8, Milano, Italy (giovanni.giunchi@gmail.com)

\*\*Jizzax State Pedagogical Institute named A. Kodiriy (bekmirzaev@mail.ru)

**Abstract.** The course presents a review of the MgB<sub>2</sub> superconducting properties, together with the main preparations and the foreseen applications, as possible material substitute of the other superconductors. The focus is on the Mg Reactive Liquid Infiltration of B powders, a new preparative technique, which presents many advantages with respect to the conventional sintering of ceramic material that, otherwise, requires hot pressure sintering to reach good densification.

**Key words:** Reactive Liquid Infiltration, pressure, MgB<sub>2</sub> superconductor, materials

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**Реактив инфилтрацияси усули билан янги ўта ўтказувчилар MgB<sub>2</sub> материаллар кукунини тайёрлаш техникаси**

**Аннотация.** Ушбу ишда ўта ўтказувчилар хусусиятлари кўриб чиқилди. Реактив инфилтрацияси усули билан янги ўта ўтказувчилар материаллар кукунини тайёрлаш техникаси баён этилган. Ушбу усул керамик материалнинг анъанавий синтерланишига нисбатан жуда кўп афзалликларга эга.

**Калит сўзлар:** Реактив суюқлик инфилтрацияси, босим, ўта ўтказгич, материаллар.

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**Подготовка MgB<sub>2</sub> материалов для инновационных сверхпроводящих технологий методом инфилтрации реактивной жидкости**

**Аннотация.** Работа представляет собой обзор сверхпроводящих свойств MgB<sub>2</sub>, их приготовления и возможные применения в инновационной технологий. Основное внимание уделяется новой технике подготовки Mg методом инфилтрации реактивной жидкой порошков В, которая имеет много преимуществ по сравнению с обычным спеканием керамического материала, которое требует горячего спекания под давлением для достижения хорошего уплотнения.

**Ключевые слова:** реактивная инфилтрация жидкости, давление, сверхпроводник MgB<sub>2</sub>, материалы.

## *A1- Brief history of the superconductivity*

The discovery of the superconductivity is due to the dutch physicist H. Kammerling Onnes, just after his successful liquefaction of the Helium gas (1911) at 4.2 K. He discover that, below a critical temperature,  $T_c$ , some materials present zero electrical resistivity. Many important contributions to the understanding of the phenomena and to the discovery of new high temperature materials were done during the 20<sup>th</sup> century. The main physicists, all Nobel Laureates except prof. Meissner, are portrayed in Figure 1.

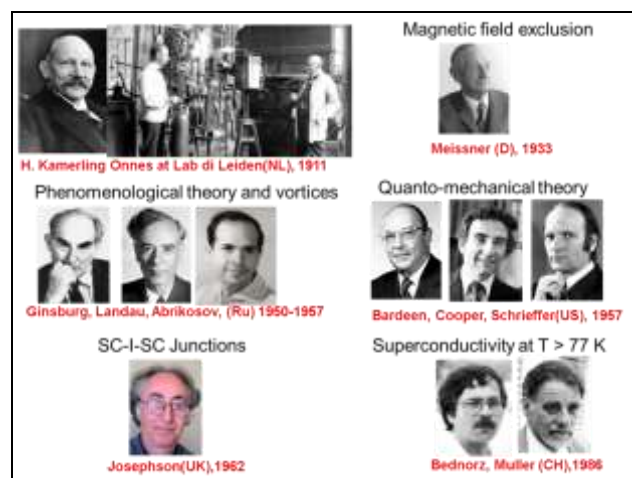


Figure 1- Important physicist for the Superconductivity developments

The route and the milestones for new materials discovery, new physical properties and applications of the superconductivity are reported in Figure 2. The field started with the Kammerling Onnes measurement of the zero resistivity of the Mercury, at the Helium liquefaction point. The most practical applications are: - from 1975, the magnets for NMR (Nuclear Magnetic Resonance) analysis of the structure of the molecules and, from 1982, the magnets for the medical MRI (Magnetic Resonance Imaging) to see in the living bodies the internal structure of organs and tissues.. The most spectacular recent achievement is the building in Geneve(CH), in 2000, of the Large Hadron Collider (LHC): a proton accelerator driven by 1232 superconducting dipole magnets placed on a circumference about 27 km long.

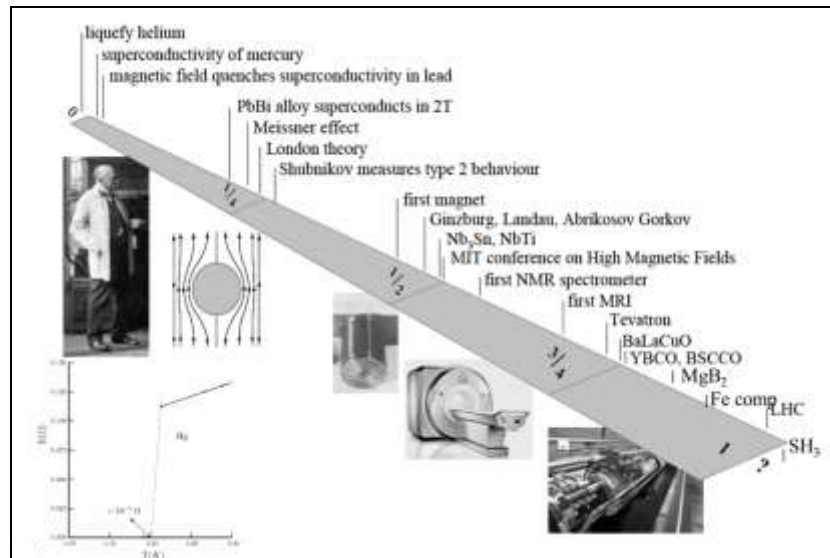


Figure 2 –One century of Superconductivity

### ***A2- Superconductivity and magnetic fields***

The magnetic fields are a vital component of the electromagnetic phenomena and have an important impact on our life. The magnetic field induction is measured in Tesla (T), in the SI units, and in Gauss (G), in the cgs units. The relation between the two units is : 1 T = 10.000 G. As a reference, the Earth magnetic field is about 0.5 G. In Figure 3 are shown the intensities of the magnetic field that we encounter in the real life.

Soon after the superconductivity discovery, Kamerling Onnes realized that high currents could not be inserted in the known metallic superconductors when  $H > H_c$ (critical field). In this event the superconductivity disappeared suddenly. This was an hard blow to its expectation to apply the superconductors in a real life as energy saving materials. Later, it was discovered the dependence of  $H_c$  with the temperature, valid for the metallic superconductors, which is given by the formula:

$$H_c = H_o [1 - (T/T_c)^2]$$

and is displayed, for several metals, in Figure 4.

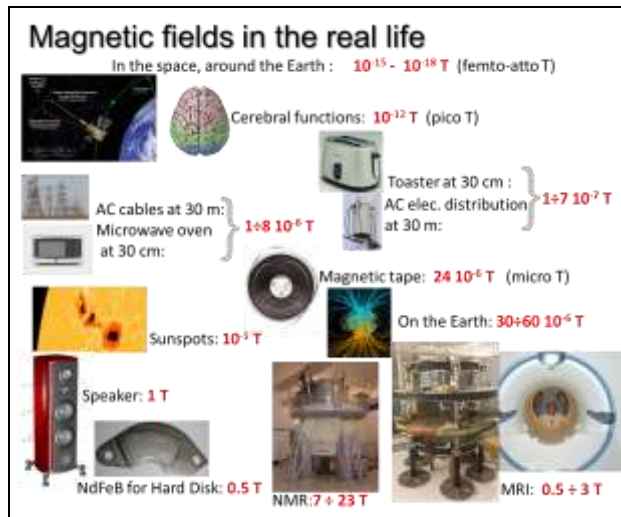


Figure 3 – Impact of the magnetic fields in the real life

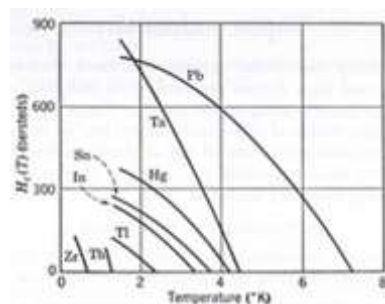
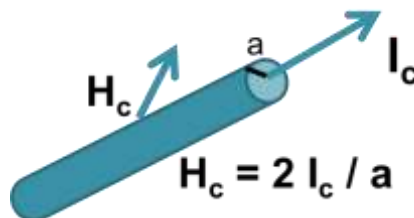


Figure 4 – Magnetic critical field vs. Temperature

The behavior of the superconducting currents in a metallic superconductor, in presence of a magnetic field, was rationalized by Silbee (1916) admitting that the critical field  $H_c$  and the critical current intensity,  $I_c$ , were linked by the well know electrodynamic relation between the current in a wire and the magnetic field at the radius of the wire.



A further fundamental step in the behavior of a superconductor in a magnetic field was done by the German Prof. Meissner (1933), who discovered that the

superconductors, in presence of a magnetic field  $H$ , expels the flux lines by its interior, therefore the magnetic flux inside is  $B=0$  below  $T_c$ . Therefore, the superconductors are perfect diamagnet, with magnetic susceptibility  $\chi = M/H = -1$ . Later it was discovered that this “Meissner effect” is valid only for a class of superconducting materials, named Type I superconductors.

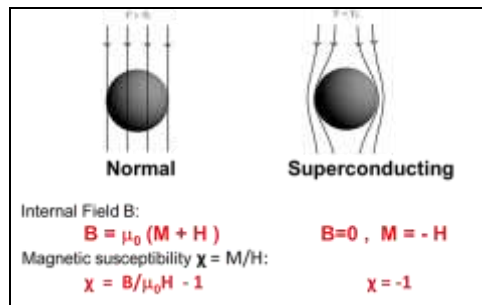


Figure 5- Meissner effect

### *A3 – A phenomenological model and full quanto-mechanical theories for the superconductivity*

One of the best books to introduce the modelling and the theories to interpret the superconductivity is by M.Tinkham (1996) [1].

F, London (1935)[2] with the aim to interpret the Meissner effect, introduced a classic model of the superconducting behavior, based on the Maxwell equations.

According to its model there are two kinds of electrons fluids:

- a) a normal one, having current density  $J_n$
- b) a superconducting one, having current density  $J_s$

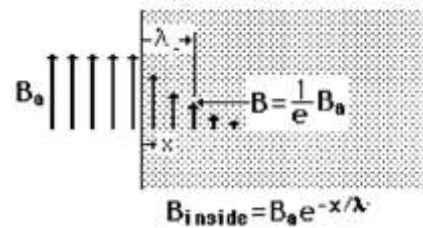
For the normal electrons is valid the Ohm's law:  $J_n = \sigma E$

For the superconducting electrons is valid an empirical law:  $\Lambda J_s = -A$

where  $A$  is the vector potential of the magnetic field.

Applying the Maxwell's equations to the two fluids, it results  $\Lambda = 4\pi/c \lambda^2 = m c/(n_s e^2)$ , where  $n_s$  is the electron density of the material and  $\lambda$  is named Penetration Depth and it is half of the thickness where the surface superconducting currents are flowing and generating, inside, a shielding of

the magnetic field. Generally, the experimental values of range from 40 to 400 nm.



Later (1950), London speculated on a possible quantization of the magnetic flux, assuming as elementary flux  $\Phi_0 = h/e$  and putting  $\Phi = n \Phi_0 = n h/e$ ,  $n$  integer (right intuition, but wrong result for a factor 2, because was not considering the possibility to realize a two electron couple) Ginzburg and Landau (1950)[3] introduced a quanta-mechanical theory of the superconducting state, assuming a new parameter to describe the size of the superconducting state:  $\xi =$  **Coherence Length**, which roughly represents the minimum size of this state. Accordingly, a full-size superconducting state exists below a first critical field  $B_{c1}$  ( $B_{c1} < B_c$ ) and localized superconducting states, roughly of dimensions  $\xi$ , well separated each other, exist up to a second critical field  $B_{c2}$  ( $B_{c2} > B_c$ ). Therefore plotting the magnetization versus the applied field  $B_a$ , instead to have a linear slope up to a single magnetic critical field  $B_c$ , there is the linear slope up to a first field  $B_{c1}$  and a decreasing magnetization up to a second critical field  $B_{c2}$ . See Figure 6.

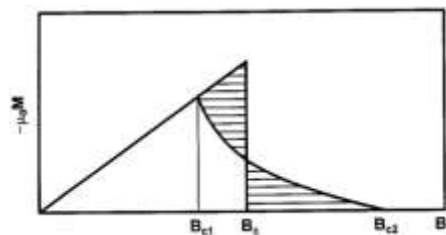


Figure 6 - Magnetization for of different superconducting materials

For each material there is the constant  $k$ , defined as  $k = \lambda/\xi$ , which differentiates the extension of the superconducting states. According to the value of this constant, the superconducting state regards all the interior of the material (Type I superconductors) or there are localized vortices (fluxons) of superconducting

electrons (type II superconductors) around point-like normal zones where the magnetic field is present.

$$B_c = \Phi_0 / 2 \sqrt{2} k \pi \xi^2$$

$$B_{c1} \propto \Phi_0 / 4 \pi \lambda^2 = B_c / (k \sqrt{2})$$

$$B_{c2} \propto \Phi_0 / 2 \pi \xi^2 = k \sqrt{2} B_c$$

For  $k \approx 1/\sqrt{2}$ , realized when  $\lambda/\xi \geq 1$ , there is a complete Meissner flux exclusion ( $B_{int}=0$ ). Such superconducting materials are defined as Type I and are mainly metallic. For  $k \gg 1/\sqrt{2}$ , realized when  $\lambda \gg \xi$ , there are different superconducting zone distributions, as a function of the applied magnetic field. For  $B < B_{c1}$  the field is completely expelled. For  $B_{c1} < B < B_{c2}$ , it is realized an intermediate state with a lattice of magnetic points of size  $2\xi$ , surrounded by vortices of diameter  $2\lambda$  and all the rest of the material is in the superconducting state. The Figure 7 gives a schematic idea of the size of the superconducting state, represented by the wave function  $|\Psi|^2$  in a Type II superconductor, around the vortices. A further practical properties of almost all the materials of Type II, having high  $T_c$ , is the presence in the phase diagram, Figure 8, of an irreversibility line that divides a stable lattice of vortices from an unstable one in which the vortices are moving, making the superconducting state dispersive and unstable. The vortices, in a single crystal without a large number of reticular defect, are organized in a lattice, mainly of hexagonal symmetry, as reported in Figure 7.

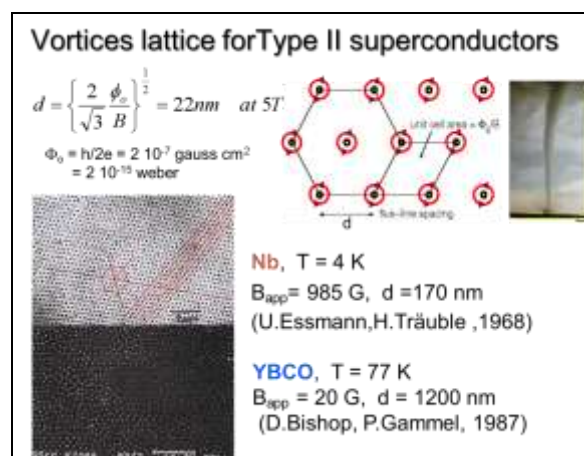


Figure 7– Lattice of vortices in single crystals

If the theories of Ginzburg-Landau describe the superconducting state as a whole, from the quanta-mechanical point of view, they were lacking a microscopic explanation of the phenomena. This explanation was set by Bardeen-Cooper-Schrieffer (1957), shortly BCS,[4] considering that the electrons in the solids, other than their coulombic repulsion due to the negative charges, can also have an attractive potential. This attraction is due to the presence in any metallic solids of the lattice of positive ions, with their mutual vibrations (phonons). One electron polarizes this ionic lattice creating a positive charge around it and this positive charge can attract a second electron. Between the two electrons it has been created an overall attractive force, higher than the coulombic repulsion as far as the temperature is very low. In such a case the link between the two electrons, each of impulse and spin  $(\mathbf{k}, \uparrow)$  creates an electron pair, Cooper pair,  $(\mathbf{k}, \uparrow; -\mathbf{k}, \downarrow)$ . These “new particles” (bosons and not fermions) can condensate forming a single macroscopic quantum state. BCS theory, with the attractive field, has introduced an energy gap,  $\Delta$ , which separates the low energy electronic states (superconducting) from the higher energy states (normal). Figure 8 describes the modification of the electronic density of state of a simple metal, with the temperature and by the presence of the superconductivity, with the  $\Delta(0)$  energy gap. To have a rough idea of the order of magnitude of these energy quantities for simple metals:  $E_F$  about 5 eV,  $K_B \Delta T$ , at 30K, about 50 meV;  $\Delta(0)$  about few meV.

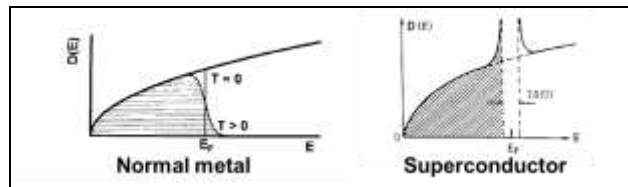


Figure 8 – Electron energy density of states

The gap is dependent from the temperature according to the general relation:

$$2\Delta(T) \cong 3.5 K_B T_c \left(1 - \frac{T}{T_c}\right)^{1/2}$$



The BCS theory has been formulated for a simple s-wave symmetry of the coupling of the electrons, as it is valid for the simple metals, but High Temperature Superconductors may present p-wave ( $\text{MgB}_2$ ) or d-wave symmetry (cuprite's) . This may modify details of the theory, but not the main message that a coupling between particles or “quasi-particles” can have a superconducting behavior by selecting the appropriate interaction between them. In the most straightforward case, the electron pairs are coupled by their interaction with the phonon field.

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