

# TECHNOLOGY OF SUPERCONDUCTING MATERIALS

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**Abstract.** *The present superconducting materials find hard hurdles to find applications for the real life, mainly due to the cryogenic issues. Waiting for future room temperature superconductors, the low temperature of the present materials is a condition that limits a lot the applications in the real life. The liquid He and the liquid N<sub>2</sub>, used to cool down the LTS materials, impose severe conditions to perform safely their containment and their transfer. The present worldwide use of superconducting magnets are for the human diagnostics with MRI magnets and the chemical analysis with NMR Magnets.*

**Key words:** *jet inflatsii of a liquid, pressure, superconductor materials.*

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## **Ўта ўтказгич материаллар тайерлаш технологияси**

**Annotasiya.** *Хозирги пайта ўта ўтказувчи материаллар жуда кўп соҳаларда ишлатилмоқда. Асосий мақсад эса келажакда хона ҳароратидаги ўта ўтказувчи материалларни яратишидир. Ушбу ишда хона ҳароратидаги ўта ўтказувчи материалларни тайерлаш технологияси кўриб чиқилган.*

**Калим сўзлар:** *Реактив суюқлик инфилтрацияси, босим, ўта ўтказгичли материаллар*

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## **Технология подготовки сверхпроводящих материалов**

**Аннотация.** *Существующие в настоящее время сверхпроводящие материалы сталкиваются с некоторыми трудностями при применении в реальной жизни. Это обусловлено, в основном из-за криогенных проблем. В настоящее время создания сверхпроводящих материалов при комнатной температуре. В работе были рассмотрены вопросы подготовки и технология сверхпроводящих материалов.*

**Ключевые слова:** *реактивная инфильтрация жидкости, давление, сверхпроводниковые материалы.*

## **Introduction**

With the advent of the High Temperature Superconductors (HTS) in 1986[1], a big hope was created by the possibility to realize a superconductivity free from the need of a liquid Helium cryogenics. Indeed, its low temperature (4.2K) requires highly efficient and safe insulation and high cost of the cryogenic liquid. Furthermore, in a long term, it must be considered the disappearance of the natural reservoirs of Helium. Instead Liquid Nitrogen (77K) appeared as a more friendly cryogen to be used. Unluckily the Cuprates, that have T<sub>c</sub> higher than 77K, have difficulties in the applications, for several reasons: a) the too low critical current densities in usable magnetic field at 77K, b) a ceramic brittleness, c) the need of

grain boundary orientation, d) an high cost of the manufacturing of the superconducting elements. All these issues make today of interest to study an intermediate critical temperature material, like  $\text{MgB}_2$  having  $T=39$  K.

In Figure 1 the history of the superconducting materials discoveries has been put in graph. It is worthwhile to comment that only few materials have been extensively used in practical applications (Nb, NbTi and  $\text{Nb}_3\text{Sn}$ ) and they are named Low Temperature Superconductors (LTS), because are generally used at 4.2 K or below. Indeed, there was a big delay between the time of the discovery of the material and the time of its application, due to the technological problems regarding the low temperature ambient where they work and their intrinsic instabilities. In the graph are also reported the temperatures of existence of the cryogenic liquid, potentially useful to cool the superconductors. In practice, at this time only liquid He is extensively used.

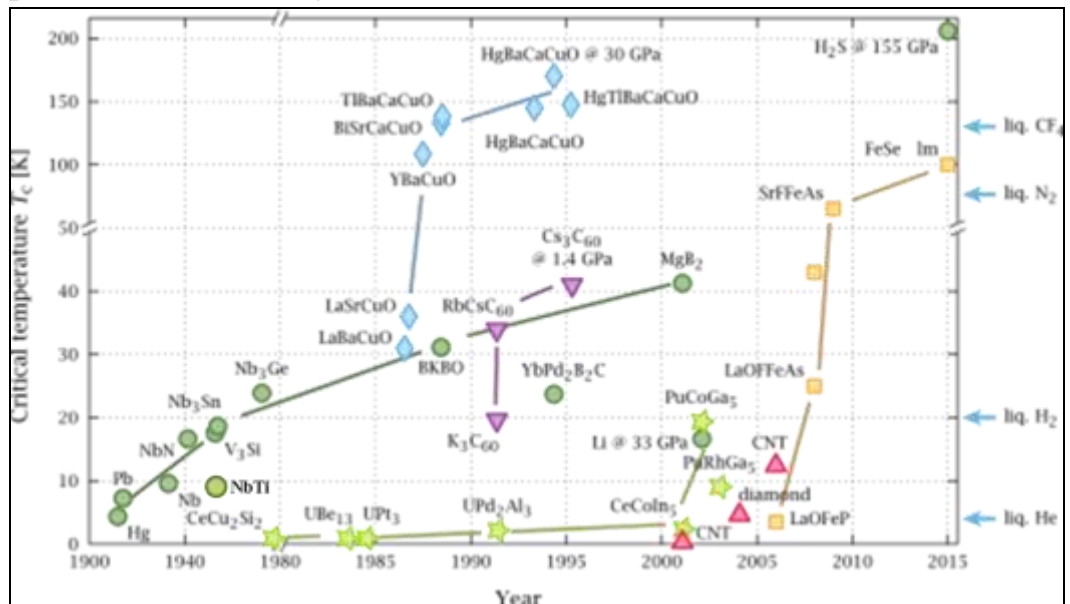


Figure 1– Time plot of the discovery of the Superconducting Materials

In the list of materials of Figure 1, there are reported materials that probably never will be used in the real earth life, as for example the high pressure hydrides, superconducting at more than 100 GPa of pressure, originated by the ideal metal hydrogen of N W Ashcroft [6], or materials reactive in the air as that containing alkali metal elements. Nevertheless these “lab superconductors” may be useful to discover all the possible ways to obtain the superconductivity. In this respect should be mentioned the attempts to explore possible mechanisms of the superconductivity on the biological molecules and in particular on the DNA and RNA [2].

### ***A5 –The main superconducting basic elements***

At the base of the manufacture of a superconducting system, like magnets, electrical conductors or other electro-technical devices, there is the fabrication of the superconducting basic elements, like fibers, cables, tapes, thin films, formed sheets or bulky pellets. These elements enter as components of the system. During more than 5 decades of evolution in the superconductor's applications, there has been many changes in the structure of the production of these elements. At the beginning several companies in the world were producing these elements, mainly superconducting cables, and only few big companies made the full superconducting systems. More recently the number of the producers of the base elements is reduced a lot and the big companies directly control the production of these elements. In Figure 1 it has been summarized the main shapes of the base superconducting elements.

The use of these elements will be exemplified in the section of the superconductive application. Here I mention the key characteristics of each element:

### ***A6 – Typical measurements of some superconducting properties***

The physical parameters that characterize a superconducting material are related to their chemical composition and are, for example, the  $T_c$ ,  $H_{c1}$ ,  $H_{c2}$ ,  $H_{irr}$  or the Coherence length and the Penetration depth. Other properties, more technological and less fundamental, are useful to design in practice the superconducting systems. Among others the main characteristics is the curves of the critical current density as a function of the temperature and of an applied magnetic field. Other important properties regard the behavior of bulk materials in magnetic fields, as the capacity of trapping a magnetic field and to maintain this field as much as possible invariant. The magnetic shielding capability or the levitation characteristics of a superconducting pellet on permanent magnets or on a more powerful superconducting magnet.

#### ***A6.1 Critical parameters measurements***

The critical temperature,  $T_c$ , can be measured in many ways, for example by the measurement of the resistance of the material during a decreasing/increasing of the temperature. At the transition, going from high temperatures to the lower one, generally it results a step wise decreasing of the temperature, with a sigmoid shape. The critical temperature is associated to the flex point of the sigmoid. With this  $R(T)$  curve, repeated at different applied magnetic fields, it is also possible to evaluate the  $H_{c1}(T)$  and  $H_{c2}(T)$  [3] at the points, respectively, of 10%R and 90%R. See Figure 2.

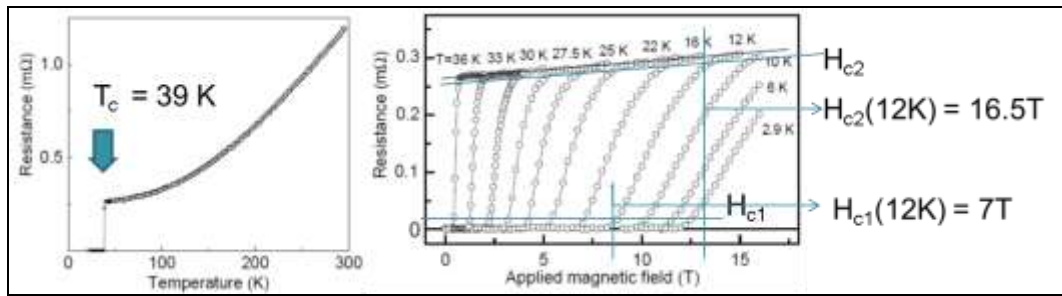


Figure 2 –Resistance measurements of the critical parameters of MgB<sub>2</sub>

Alternatively, to detect the critical parameters may be used magnetic measurements, like the AC susceptibility or DC magnetization. The AC susceptometer measures the internal instantaneous magnetization of a sample,  $H = -dM/dH$ , by applying two magnetic fields, DC plus AC. See in Figure 2 a typical diagram of the analysis. measure the dispersion due to the AC induced currents and its maximum, for variations of the AC applied field amplitude, is related to the  $I_c(T)$

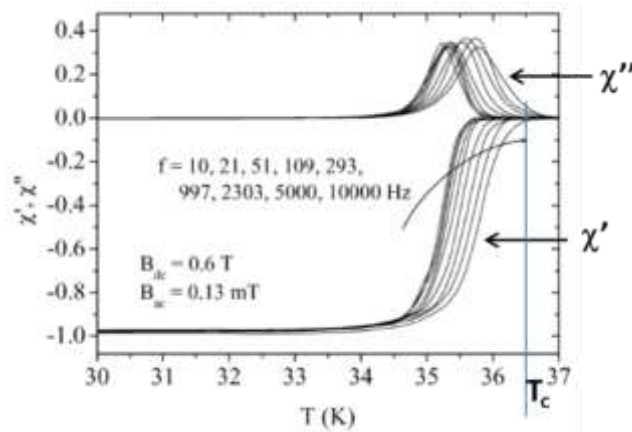


Figure 3– AC susceptibility measured for a MgB<sub>2</sub>-RLI bulk sample[9]

A measure of the  $H_{c1}$  can be done by a DC magnetization of the sample, as reported in Figure 4a. At the beginning of the magnetization  $H_{c1}$  corresponds to the applied field where the magnetization moves from the linear behavior. The critical fields  $H_{irr}$  and  $H_{C2}$  are evaluated at the closure of the cycle, respectively, at the point of closure and at the reaching of null magnetization, as shown in Figure 4b (Figures 4 a-b are respectively for YBCO and for MgB<sub>2</sub>)

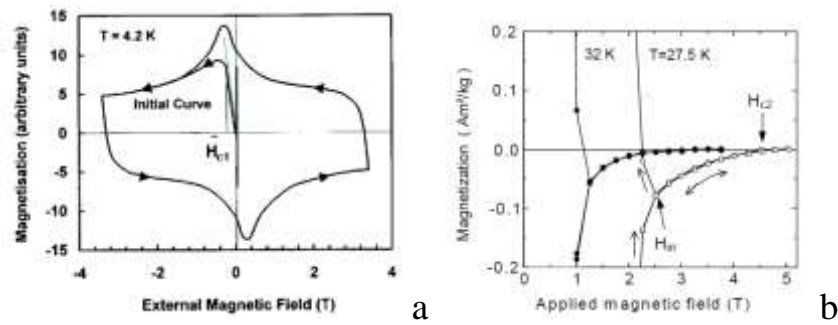


Figure 4 – DC magnetization cycle to evaluate the critical parameters: a)  $H_{c1}$ ; b)  $H_{irr}$  and  $H_{c2}$

### A6.2 Critical current density

There are two main ways to measure the critical current density  $J_c(B,T)$  as a function of the temperature  $T$  and of an applied magnetic field  $B$ : a **resistive** one and a **magnetic** one. Both measurements must be done in a cryostat with well controlled temperature. The resistive method is preferred for a rod or a wire having constant cross section, with a known ratio between the area of the superconducting material and that of a normal resistive matrix, eventually present. Instead the magnetic method is more suitable for a short bulk sample of regular geometry (cylindrical or parallelepiped).

The **resistive method** (otherwise named 4 points contact method) consists in the measurement of the voltage developed between two internal tips of a bar or of a wire, varying the intensity of an applied current feed on the two external leads of the bar/wire. In doing this current supply it is important to have an enough long contact with the superconducting wire, to allow a current transfer without excessive heat generation.

The variation of the voltage, as function of the current intensity, has a behavior as in figure 16, where the steeply increase of the electrical field is due to the approaching the critical conditions and to the starting of flux flow instabilities, generally described by a polynomial law:  $E(J) = E_0 (J/J_0)^n$  with the  $n$  ranging from 10 (bad) to 100 (good).

The critical current  $J_c$  may be evaluated by one of the two empirical criteria:

$$a) H = E/J \leq 10^{-14} \Omega \cdot m \quad b) E \leq 10 \text{ V/m}$$

Repeating the measurements at different temperatures and with the wire maintained at a given applied magnetic field one can obtain the  $J_c(T,B)$ , which fully describes the main technological characteristics of the superconducting material.

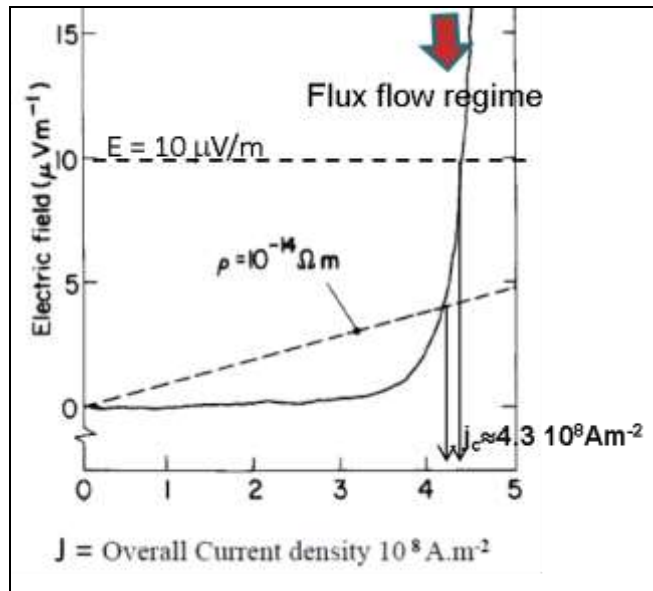


Figure 5- Typical V(I) curve to determine  $J_c$

The **magnetic method** consists in the measurement of the magnetization induced on a small superconducting sample ( few mm's high and large ) by applying a magnetic field in a cycle between  $H_{max}$  and  $-H_{max}$ . The measurements are done with an ad hoc magnetometer working in a cryostat at constant temperature. The critical current density, for each applied field, is related to the magnetization difference  $M(H) = M_{up} - M_{down}$  of a magnetization cycle. See Figure 6. There are simple relations between  $M$  and  $J_c$ , according to the shape of the sample. For a cylindrical rod of diameter  $2a$ ,  $J_c$ .

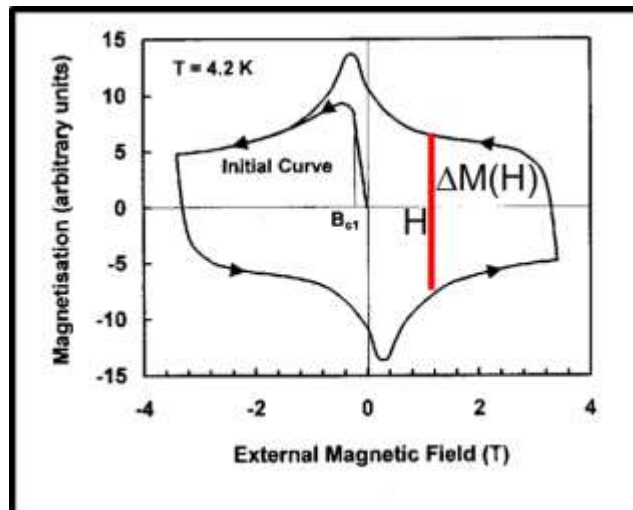


Figure 6- Magnetization cycle

The magnetic measurements does not always coincide with the resistive measurements, because the magnetization can be detected also on a sample made

by single isolated superconducting grains, not connected each other, instead the resistive measurements requires a superconductive connection between the grains.

I give an example of the  $J_c(T,B)$  measured by the magnetic method on our produced  $MgB_2$  bulk materials, of different superconductive morphology. See Figure [5]. It results that the use, in the preparation, of smaller B grains allows to obtain an higher critical current density and the results, as a function of the temperature and of the applied magnetic field can be well reproduced by an analytical function.

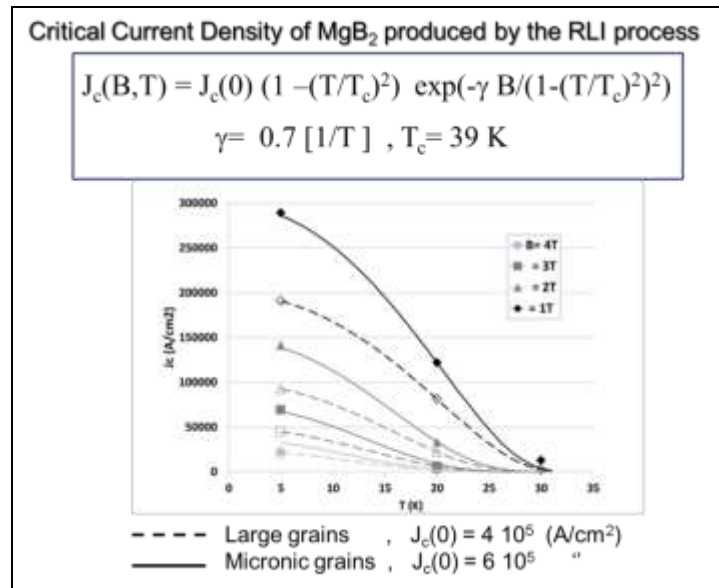


Figure 7 – $J_c(B,T)$  for two preparation of  $MgB_2$ -RLI: experiments and model fitting

### A6.3 trapped magnetic field in the bulk

The majority of the superconducting materials are of type II therefore, if exposed, in the superconducting state ( $T < T_c$ ), to a magnetic field  $B$ ,  $B_{c1} < B < B_{c2}$  they expel the field inside, except in localized points where the vortices remain pinned (pinning centers) and in each point a magnetic flux unit ( $h/2e$ ) is present (ZFC process=Zero Field Cooling). Furthermore if the magnetic field is applied at temperatures  $> T_c$  all the flux lines enter in the material and when the temperature is lowered  $< T_c$  (FC process=Field Cooling) the flux lines remains trapped in the superconductor, with the condition that the superconducting currents of the vortices are less than the critical current. This last condition may be fulfilled if strong pinning centers are present in the material, i.e. pinning centers which does not allow the vortices to move even in presence of the large currents created by the applied field. If the pinning centers are not enough strong to support the applied field, at the switching off of the field a reduction of the internal field is detected up to the point where the currents are low enough, less than their critical value. At

this point the superconducting state is stable and the material is like a permanent magnet, having a magnetic induction much higher (up to several T for Cuprates) than the classical permanent magnets, like NdFeB, which have a maximum field of about 0.3 T. Of course the high trapped fields of the superconductors are allowed only at low temperature ( $T < T_c$ ). I report in Figure 8 [6] the trapped field in an  $MgB_2$  ring by charging it with a superconducting magnet at 5 K, after the external field switched off. The behavior of the trapped field, after a temperature increase up to  $T_c$ , is also given.

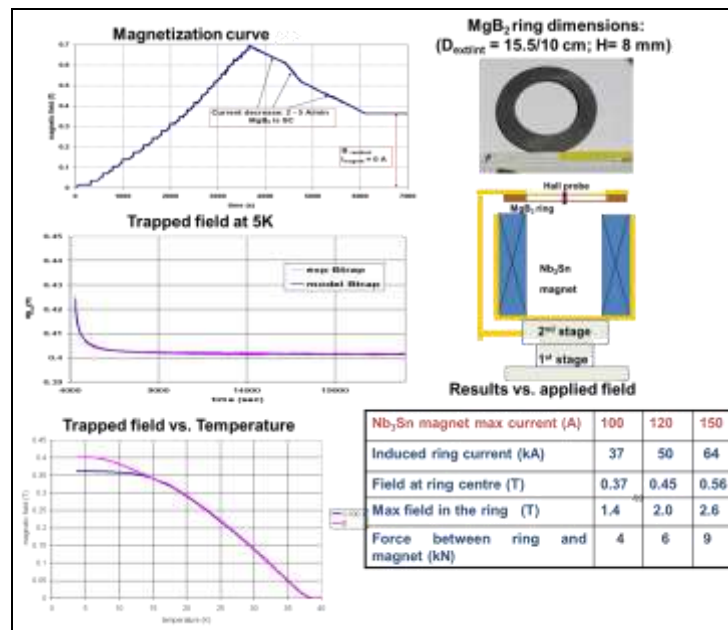


Figure 8 – Magnetization of an  $MgB_2$  –RLI ring and relative trapped field

The step-wise charging and discharging was done in order to avoid steep magnetic field changes that can induce a complete loss of superconductivity due to suddenly flux jumps, as it always occurs in the LTS materials. In this experiment no flux jump was detected. and the material behaves as a real permanent magnet giving a max central field of 0.56 T and a field on the ring edge of 2.6 T.

### ***A7 – The enemies of the superconductivity***

The present superconducting materials find hard hurdles to find applications for the real life, mainly due to the cryogenic issues. Waiting for future room temperature superconductors, the low temperature of the present materials is a condition that limits a lot the applications in the real life. The liquid He and the liquid  $N_2$ , used to cool down the LTS materials, impose severe conditions to perform safely their containment and their transfer. The present worldwide use of superconducting magnets are for the human diagnostics with MRI magnets and the



chemical analysis with NMR Magnets. Both use multilayer vacuum vessels, as cryostats, with valves and systems of gas discharging to avoid a catastrophic gas release in case of quenching of the magnet. The cryogenics must always be managed by experts and it is unsafe to install a present liquid cooled superconducting system in transportation means or in an industrial site, without an appropriate safety environment. In the last decades there are many attempts by the cryogenics industry to introduce cryogen-free systems to cool down superconducting magnets, especially dedicated to the HTS materials. Today the refrigerating power of these systems is adequate only for small magnets, at laboratory level. Another interesting recent development, always at laboratory level, is to install a compact system for a complete cycle of He liquefaction, storage, and re-condensation. This system allows a minimum use of He refill. Other cryogenic developments for the intermediate temperatures (10 ÷ 40 K) regard the use of solid cryogenics, like solid N<sub>2</sub> [7], or the use of liquid H<sub>2</sub>.

Other these cryogenic issues, there are more hurdles that must be considered in the technology developments needed to apply the present superconductors, the main are:

- Magnetic fields and magnetic relaxation
- Anisotropy and grain boundaries
- Alternate currents
- Thermal instabilities

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