

# Superconductors for magnets I

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TE-MS**

- 1. Introduction, Definitions**
  - 2. Physical properties of superconducting Materials: NbTi and Nb<sub>3</sub>Sn**
  - 3. The system NbTi, properties and fabrication**
  - 4. The system Nb<sub>3</sub>Sn**
    - A. Superconducting properties of the A15 phase**
    - B. Wire fabrication and critical current densities**
    - C. Calorimetric analysis of Nb<sub>3</sub>Sn wires**
- Annex. Thermal Stability criteria**

## 1. Introduction, definitions

Compound	Year	T <sub>c</sub> (K)	B <sub>c2</sub> (0) (T)	ξ (nm)	
<b>NbTi</b>	1960	9.6	14.5	~ 6	<b>LTS</b>
<b>Nb<sub>3</sub>Sn</b>	1953	18.3	24 - 28	~4	
<b>PbMo<sub>6</sub>S<sub>8</sub></b>	1970	15	60	2.2	
<b>Nb<sub>3</sub>Ge</b>	1972	23	38	~4	
<b>Nb<sub>3</sub>Al</b>	1975	19	33	~4	
<b>MgB<sub>2</sub></b>	2001	39	39 <sup>a</sup> <sub>bulk</sub> ; 60 <sup>a</sup> <sub>films</sub>	5	<b>HTS</b>
<b>Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1</sub>Cu<sub>2</sub>O<sub>8</sub></b>	1989	94	> 100 <sup>a</sup>	1 - 2	
<b>Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub></b>	1989	110	> 100 <sup>a</sup>	1 - 2	
<b>YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub></b>	1988	92	> 100 <sup>a</sup>	1 - 2	
<b>(Ba<sub>0.6</sub>K<sub>0.4</sub>)Fe<sub>2</sub>As<sub>2</sub></b>	2007	38	70 - >135 <sup>a</sup>	2 - 3	

## Round wires

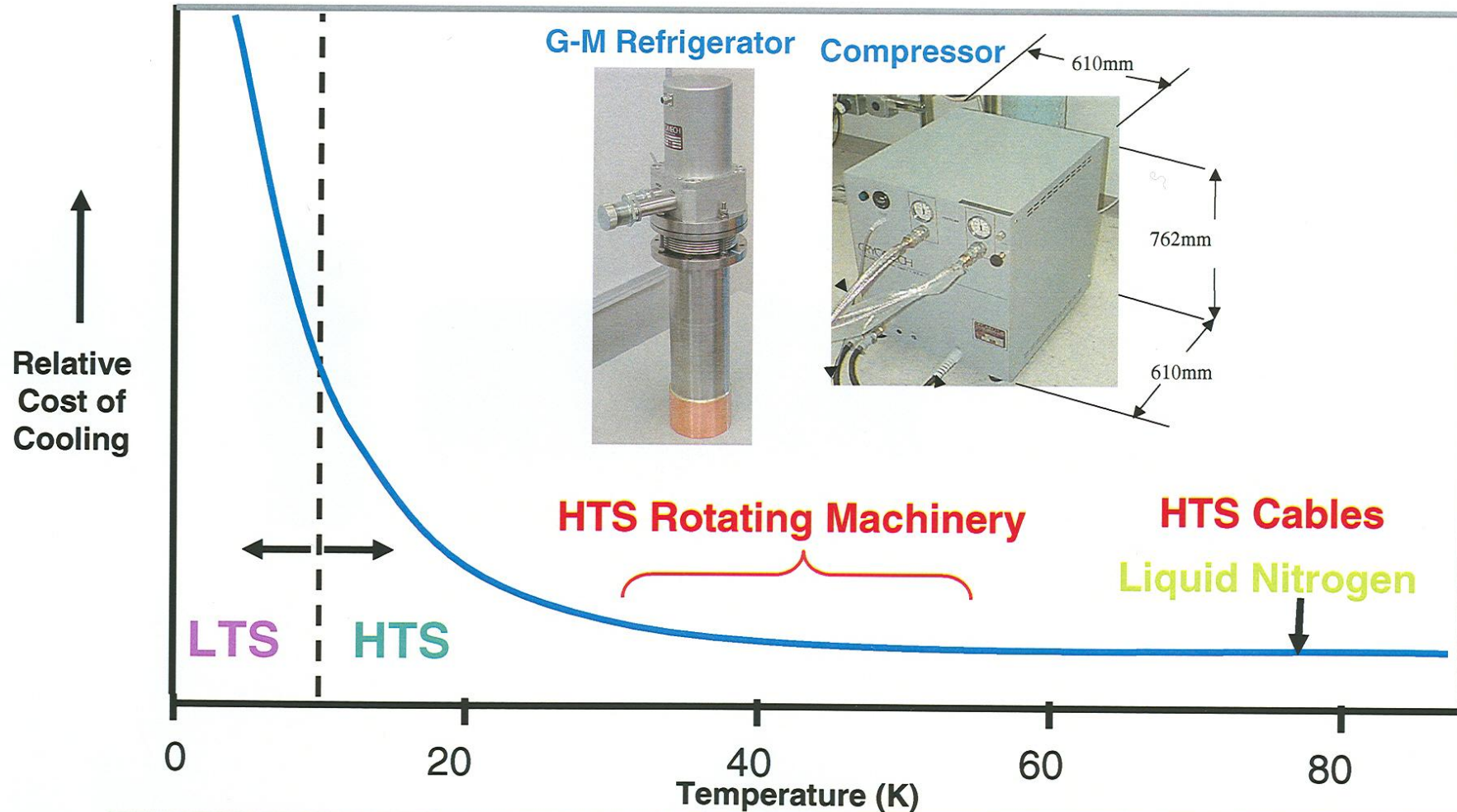
<b>NbTi</b>	Still the most used wires: ~ 90% (MRI, accelerators)
<b>Nb<sub>3</sub>Sn</b>	> 5% (NMR, lab magnets, accelerators as LHC Upgrade)
<b>MgB<sub>2</sub></b>	Low costs; Niche applications at 10 – 25 K (open MRI, LINK)
<b>Bi-2212</b>	Future accelerators at >20T. Problem: mechanical stability

## Tapes

<b>Bi,Pb(2223)</b>	Cables, motors at T < 30K. Problems: costs, < 1 T at 77K)
<b>YBCO</b>	Cables, Current limiters, Wind generators,..... (Main problems: costs, limited lengths) Commercially available: < 500 m SuperPower, USA < 500 m at Fujikura, Japan

## Other high field superconductors

<b>Ba<sub>0.6</sub>K<sub>0.4</sub>)Fe<sub>2</sub>As<sub>2</sub></b>	Pnictides: promising for high field magnets ( $B_{c2} > 70T$ ), but not yet at the industrial level. Problems: toxicity of As, complex metallurgy.
<b>PbMo<sub>6</sub>S<sub>8</sub></b>	Chevrel phases. $B_{c2} > 50T$ ! Problems: Reaction at > 1000°C, very difficult deformation, no prestress.



## Definitions

Supercond. transition temperature:

$T_c$  [K]

Critical current:

$I_c$  [A]

Critical current density:

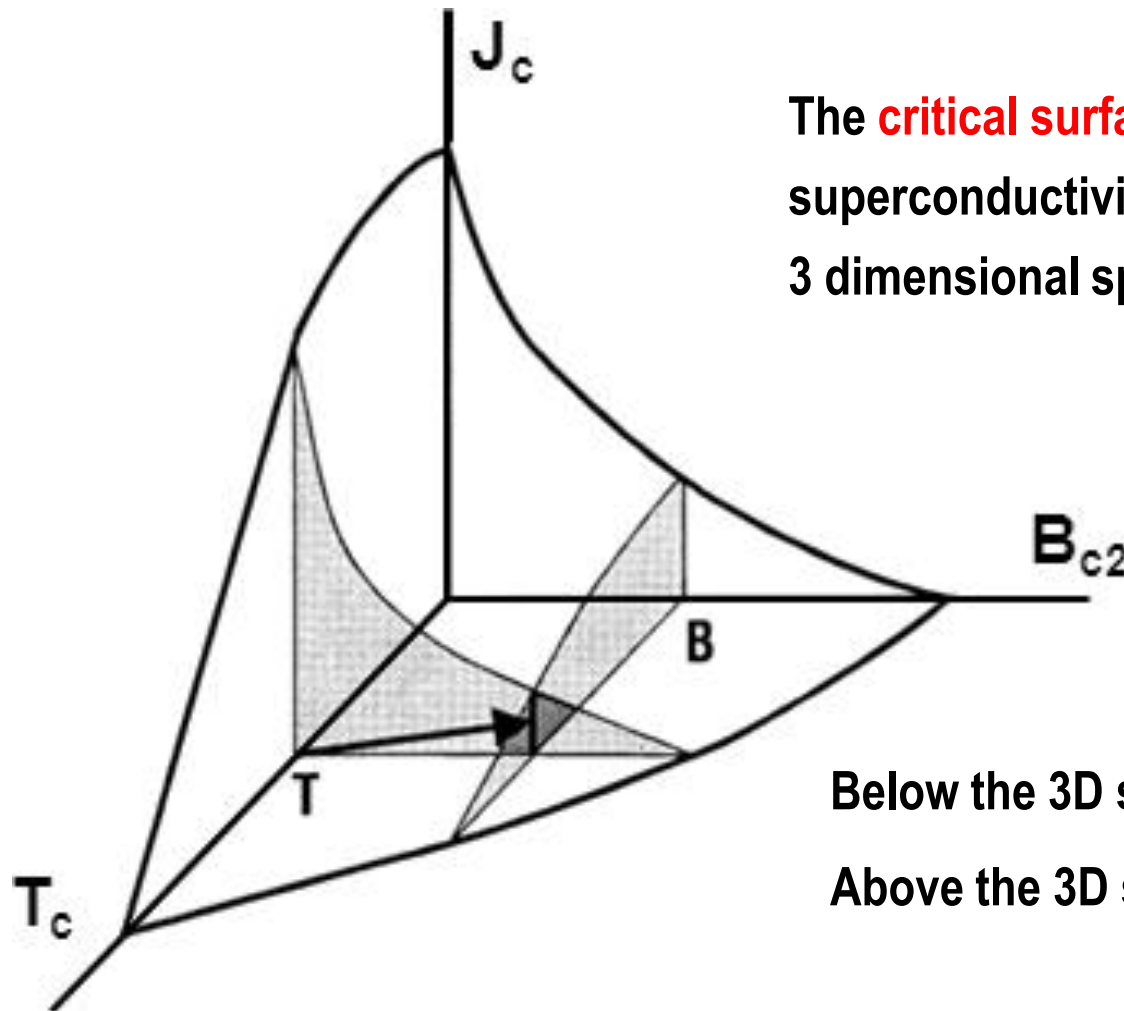
$j_c$  [A/cm<sup>2</sup>];  $j_c$  [A/mm<sup>2</sup>]

Critical magnetic field:

$B_{c2}$  [T]

Exponential  $n$  factor:

$n: U \sim I^n$



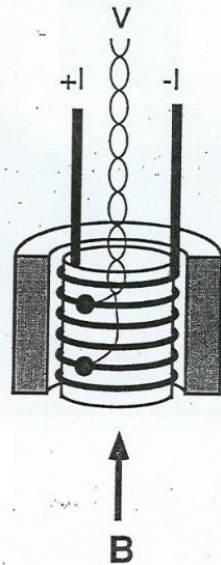
The **critical surface** is the boundary between superconductivity and normal resistivity in the 3 dimensional space.

Below the 3D surface: superconductivity.

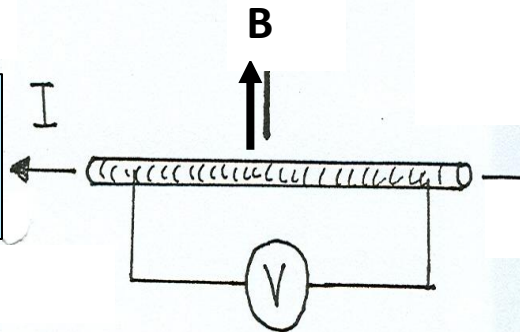
Above the 3D surface: normal state, with  $R \neq 0$ .

**Long wires**  
(length: > 0.1 m)

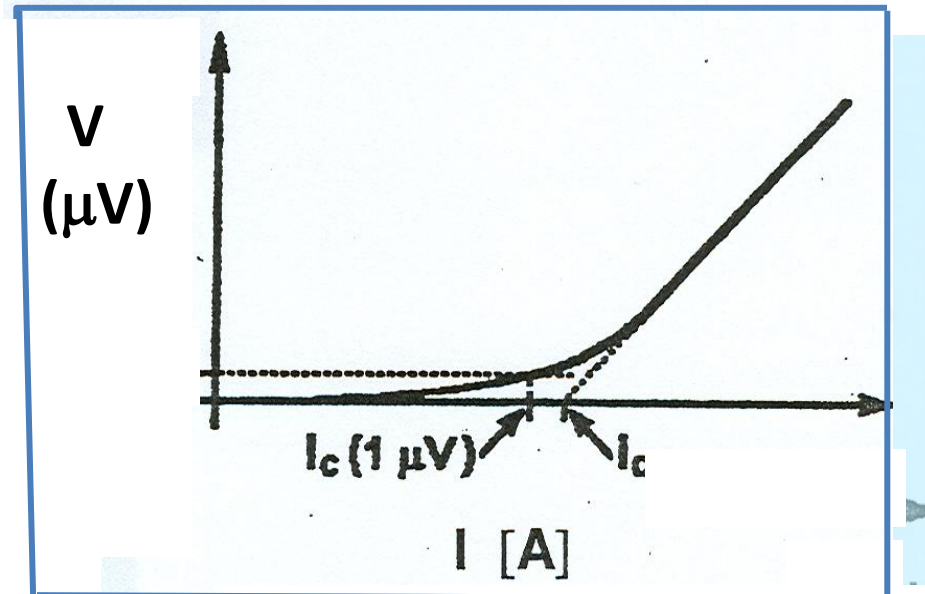
**Long wires:**  
Criterion for  $J_c$ :  
 **$0.1 \mu\text{V}/\text{cm}$**



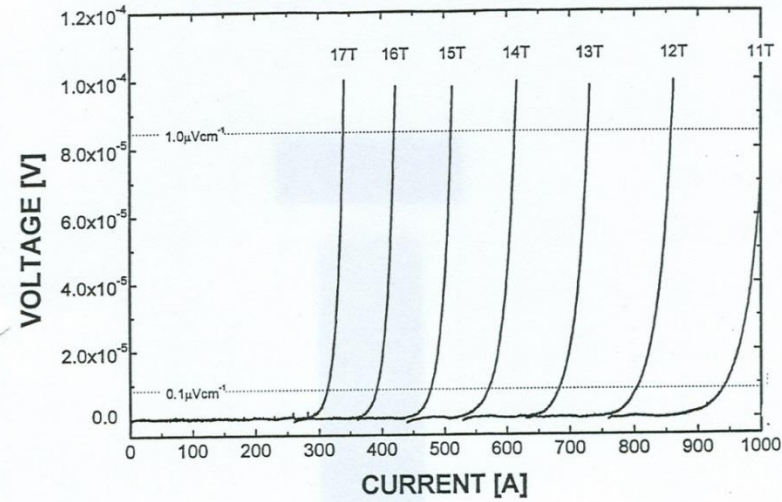
**Short wires**  
(2-3 cm length)



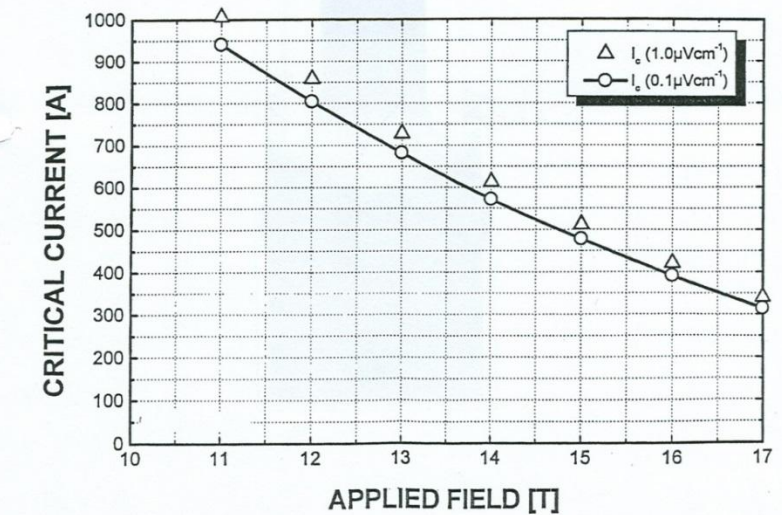
**Short wires: Criterion for  $J_c$ :  $1 \mu\text{V}/\text{cm}$**







**Resistive superconducting transition at various magnetic fields**



**Variation of critical current vs. applied magnetic field B**

## 2. Physical properties of superconducting materials: NbTi and Nb<sub>3</sub>Sn

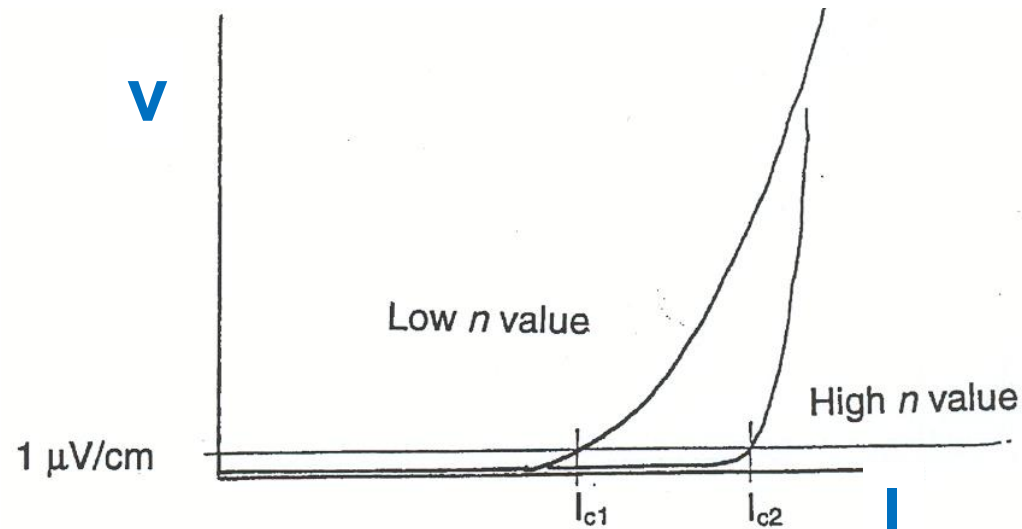
The  $n$  factor is an empirical quantity describing the quality of the wire:

- \* surface state of the filaments
- \* homogeneity along the wire axis («sausaging»)

**Definition:**

$$V \sim I^n$$

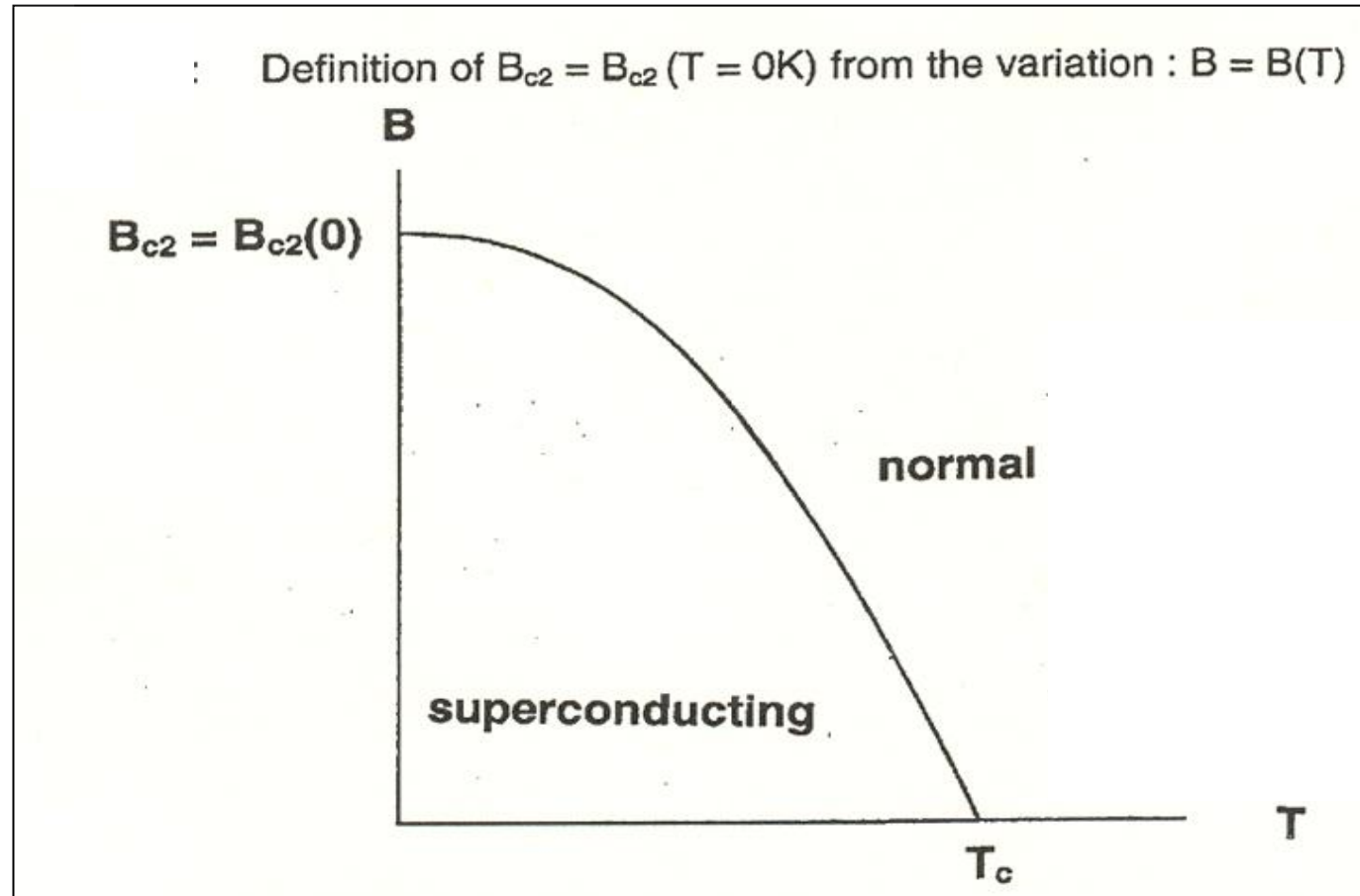
at a given operational B and T

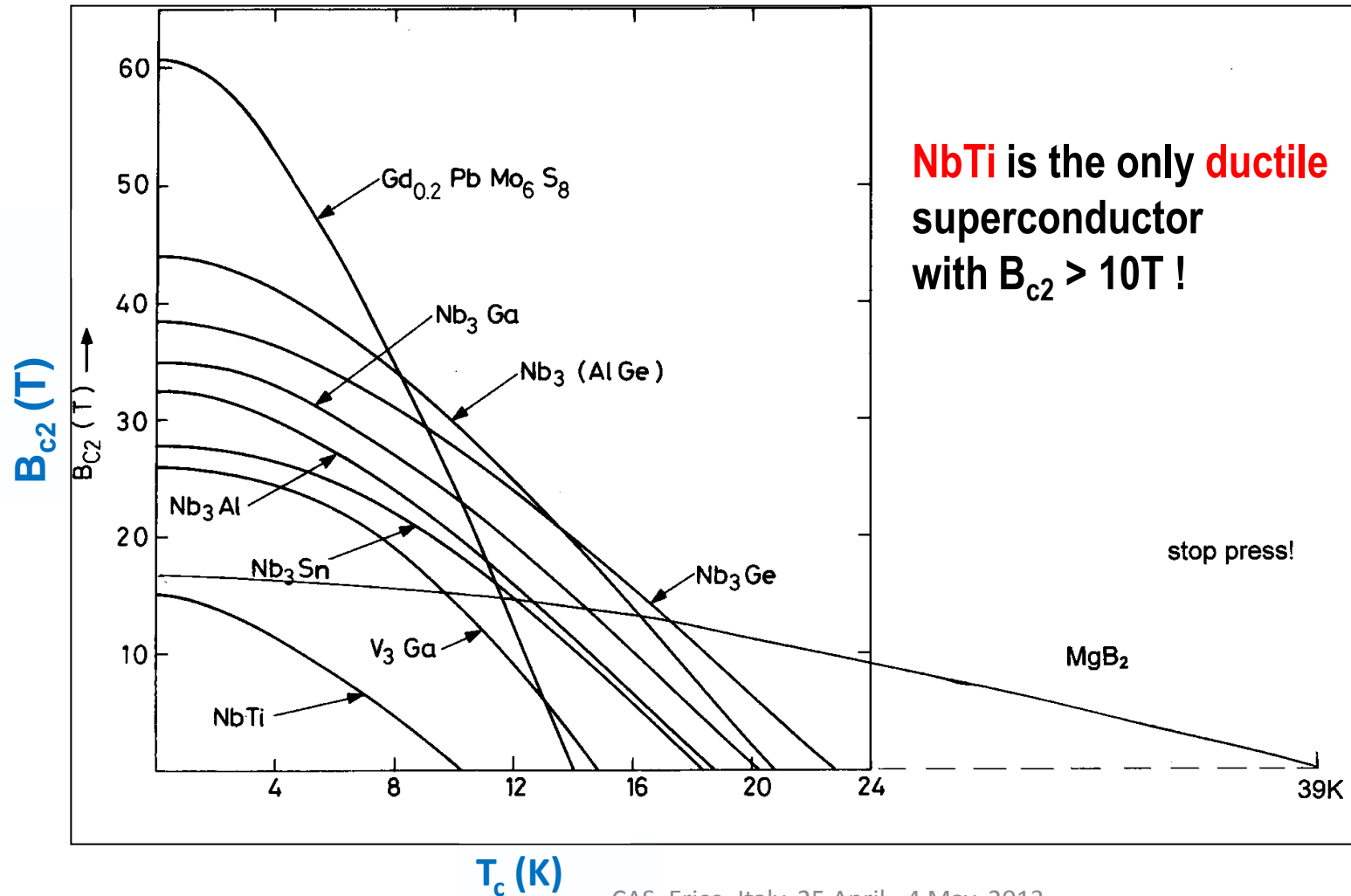


In general, a high  $n$  value corresponds to a wire of higher quality

Required:  $n > 30$  at operational B and T.

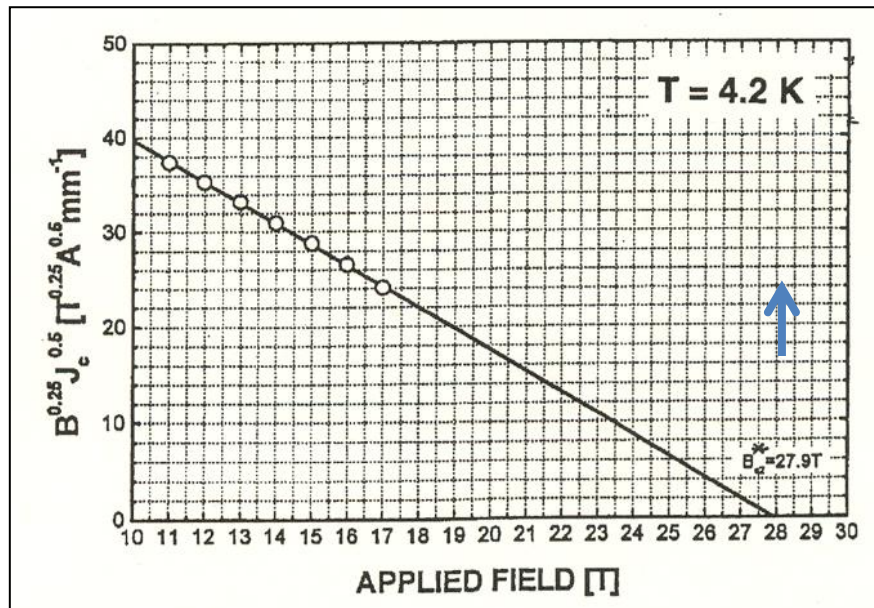
Highest  $n$  values for NMR magnets





$B_{c2}(0)$  is determined by measuring  $B_{c2}(T)$  either **resistively** or **inductively**.

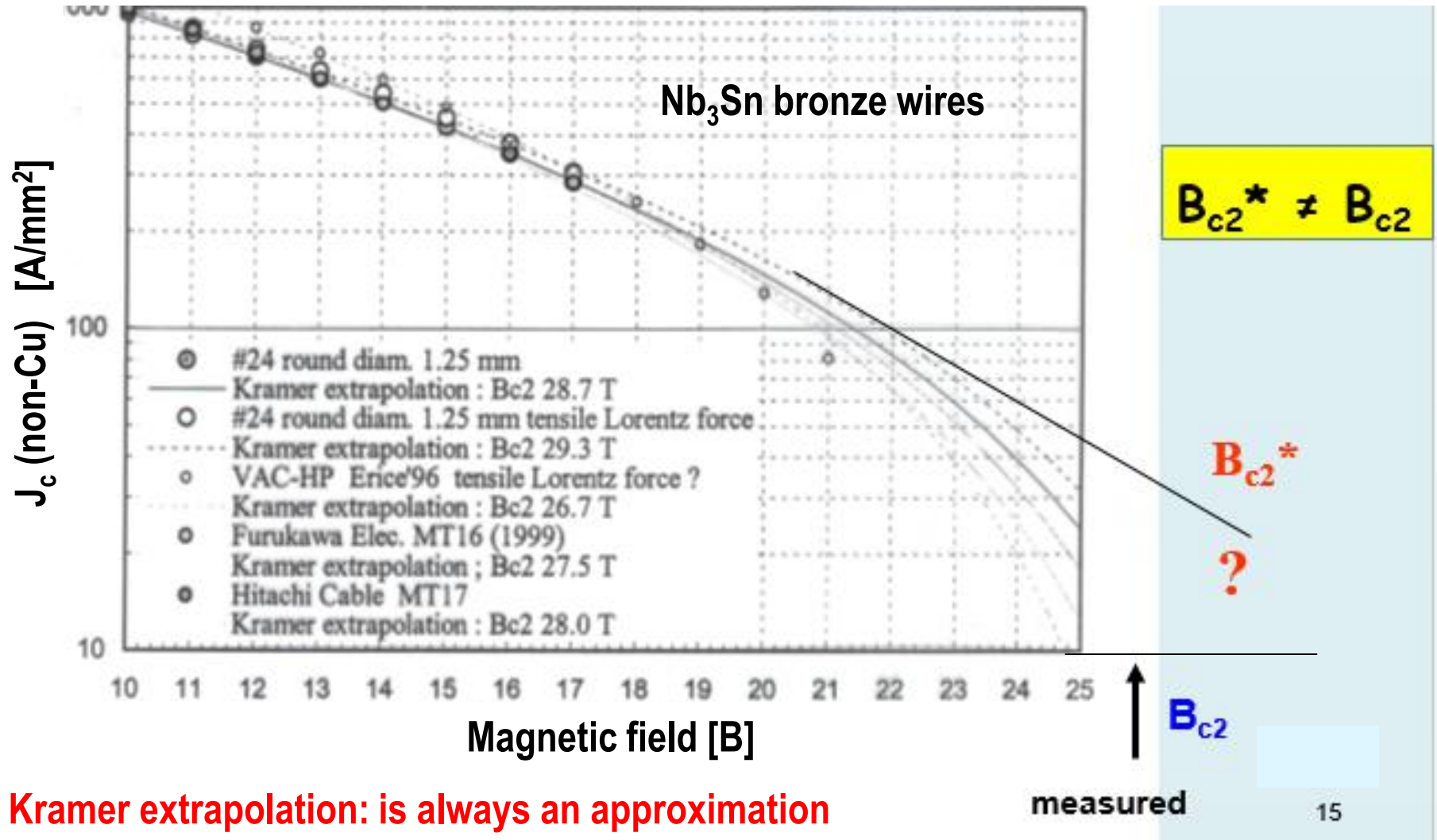
In the case of wires, where  $I_c$  is known, one uses the Kramer extrapolation:  
 the function  $B^{3/4} I_c^{1/2} (T)$  vs.  $B$  is extrapolated to  $B = 0 \rightarrow B_{c2}^*|_T$



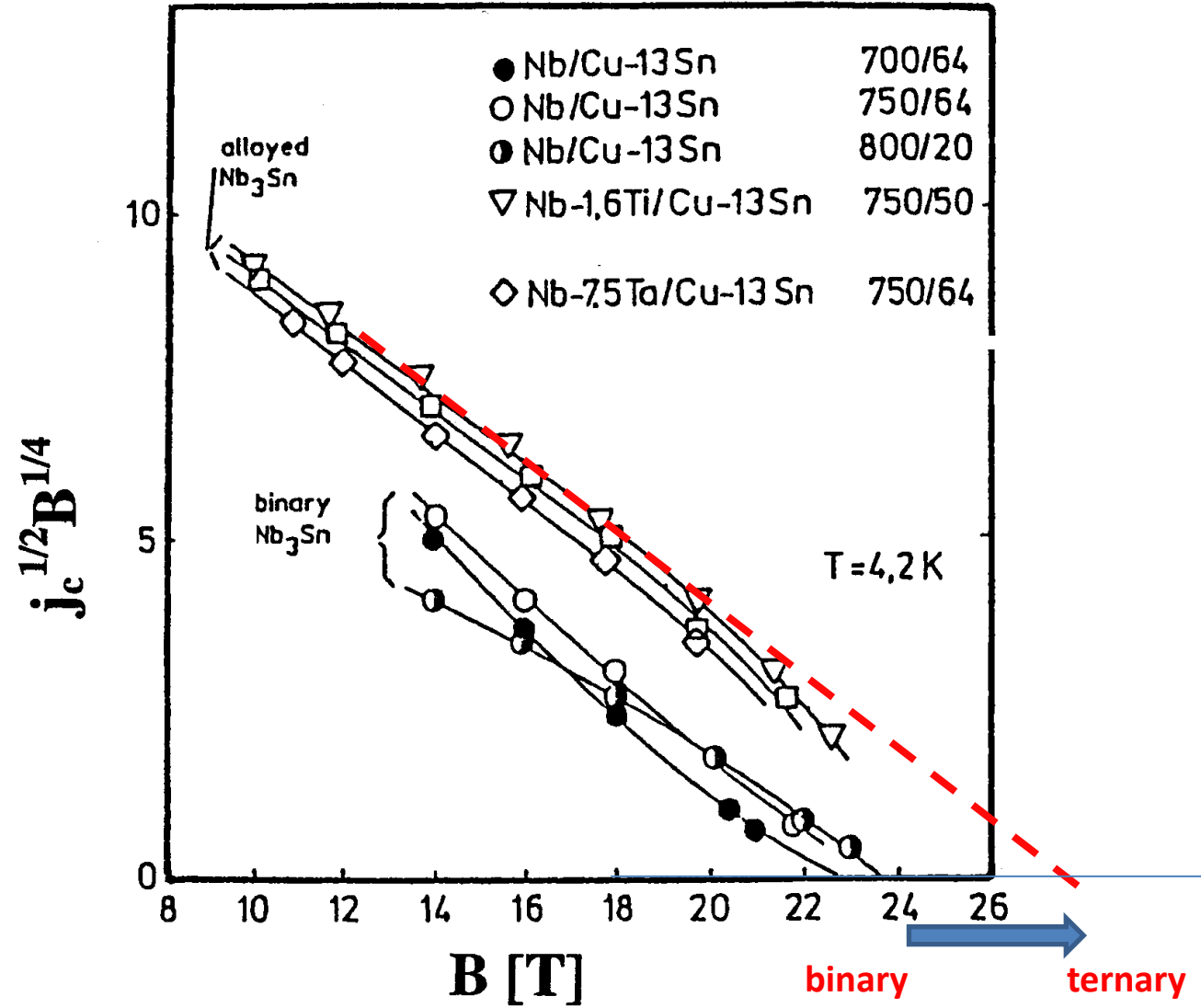
For magnets, one defines usually:

**NbTi :  $B_{c2}^*(1.9 K)$ ,**  
**Nb<sub>3</sub>Sn :  $B_{c2}^*(4.2K)$ .**

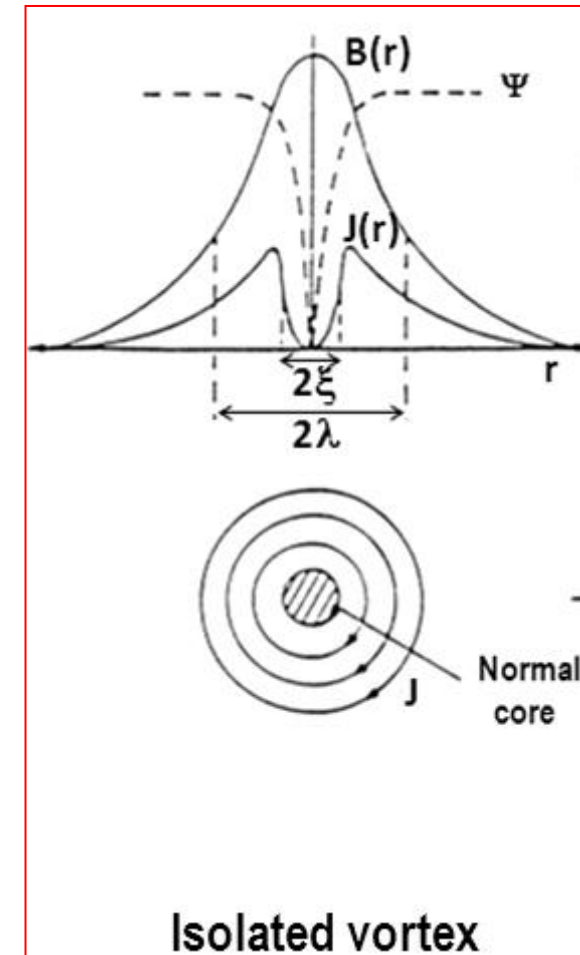
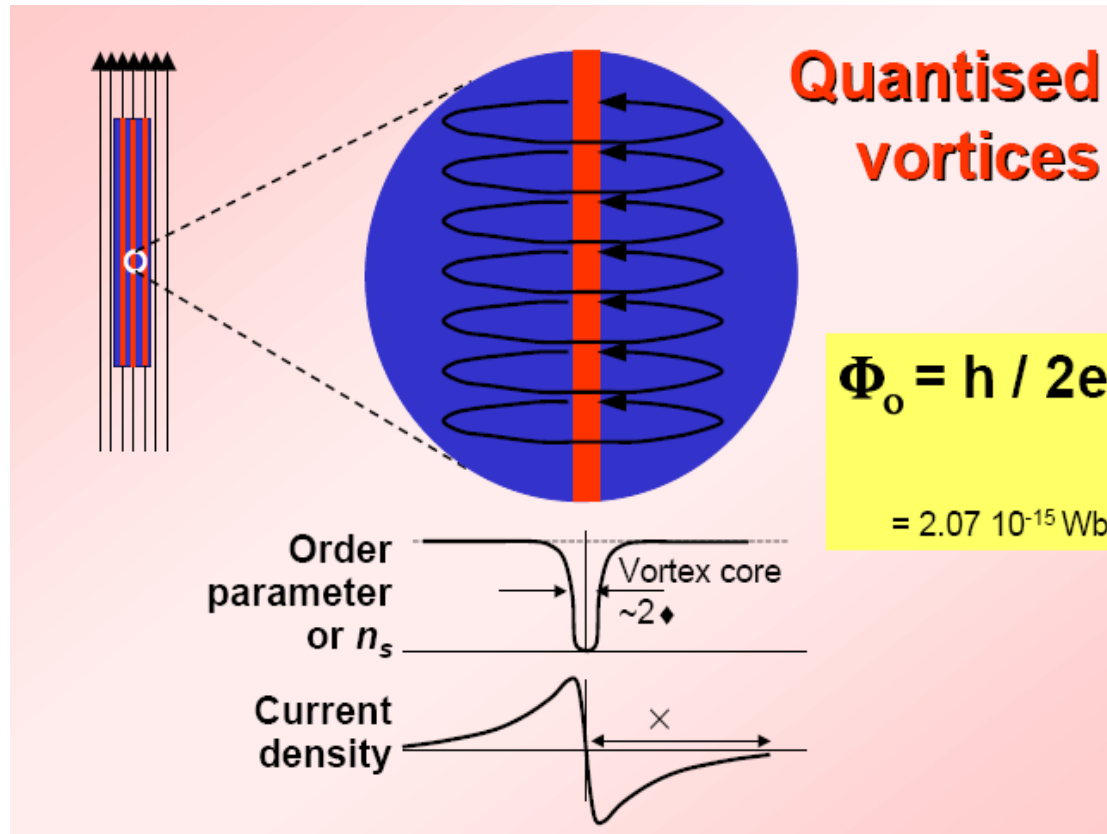
These extrapolated values may differ from  $B_{c2}(4.2K)$  or  $B_{c2}(1.9K)$  determined by a direct measurement.

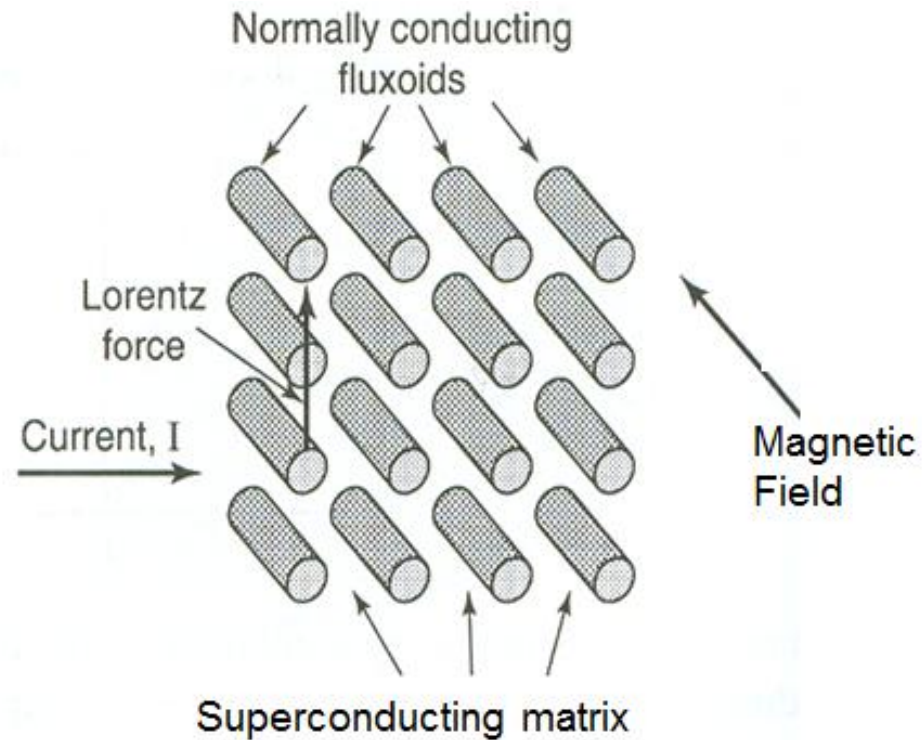


**Kramer extrapolation: is always an approximation**









## Tornado

- \* Speed zero at the center
- \*  $V_{\max}$  outside of the tube \*
- Diameter: > 100 m**

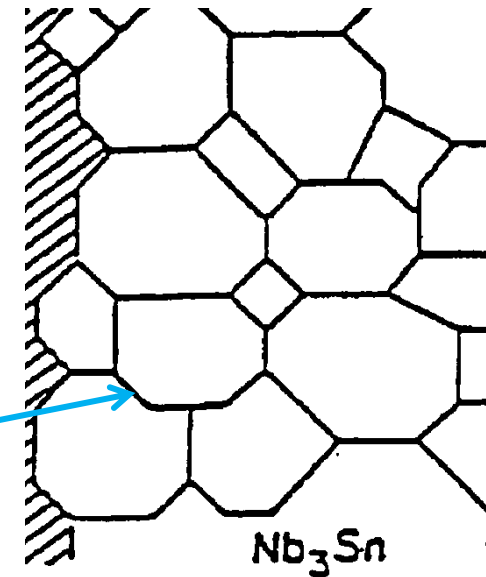
## Vortex

- \*  $T_c = 0$  inside (normal)
- \*  $J_c \neq 0$  outside of the vortex
- \* « Diameter »: < 10 nm

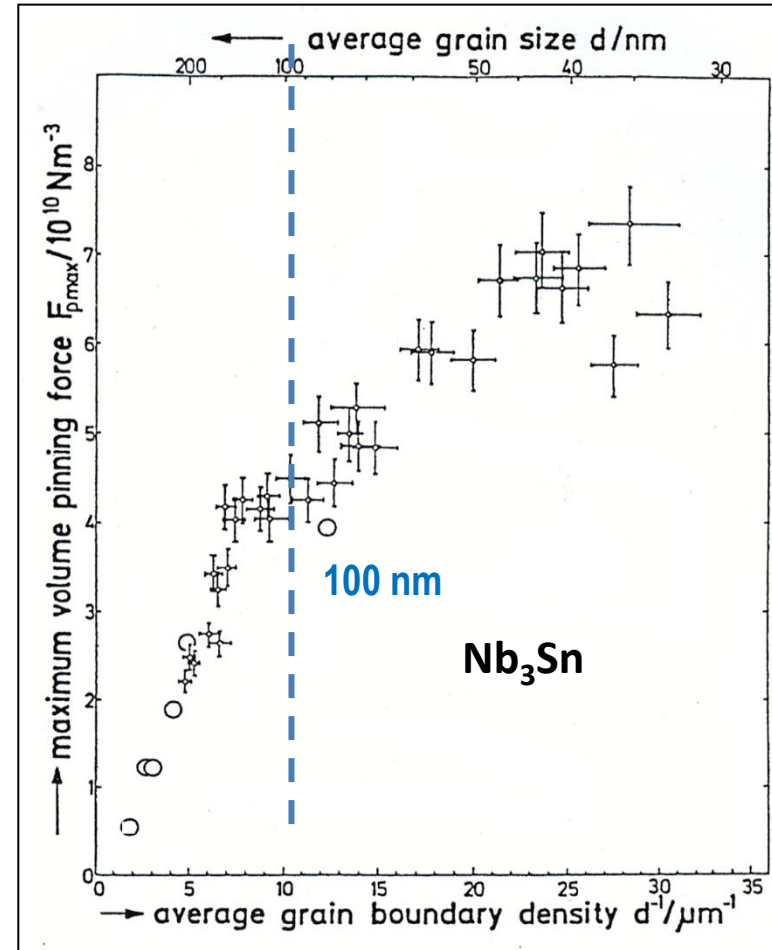
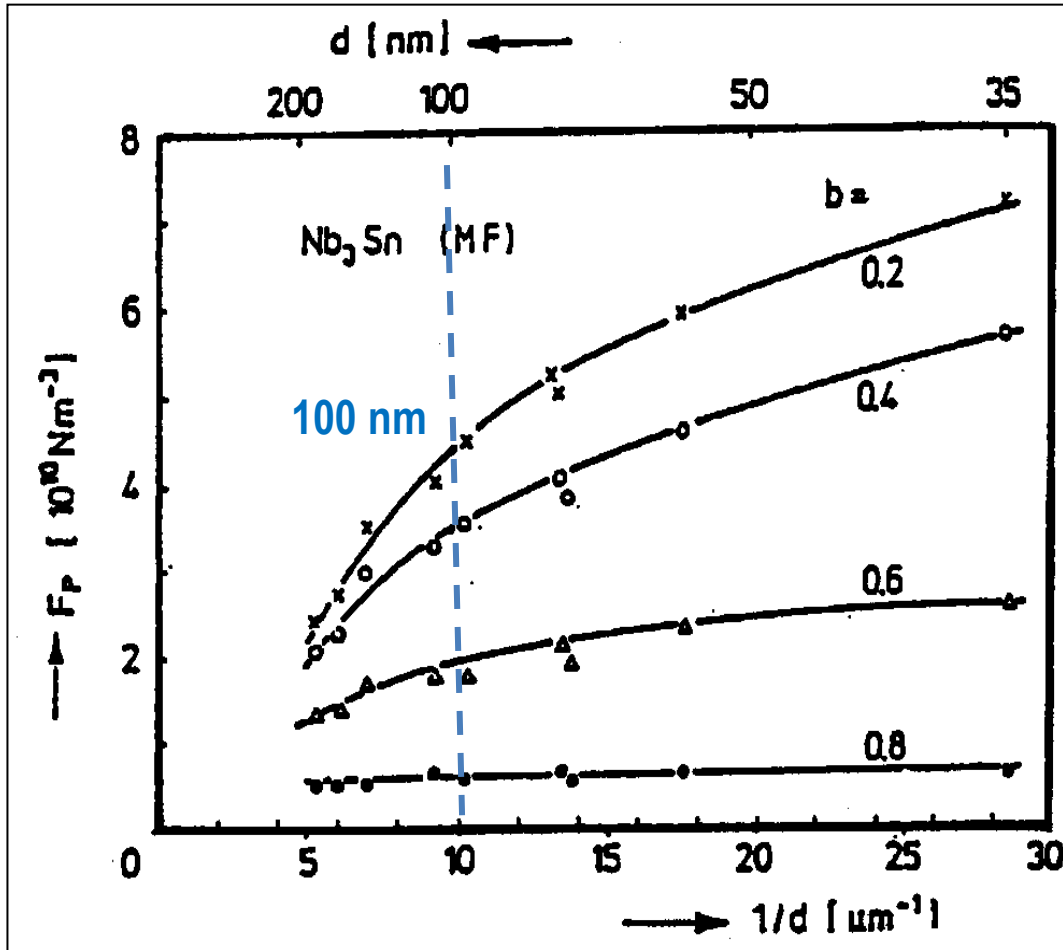
$J_c$  in a wire is **zero**, unless vortices can be «pinned» !

Microscopic defects provide pinning sites:

- Precipitates
- Dislocations
- Twin boundaries, stacking faults
- Irradiation tracks
- Grain boundaries



**Grain boundaries: main contribution to pinning in LTS**



Nb<sub>3</sub>Sn  
bronze  
route wire



**800 °C/48h**

$d_k = 200 \text{ nm}$

$$F_{pmax} = 2.5 \times 10^{10} \text{ Nm}^{-3}$$

**680 °C/48h**

$d_k = 85 \text{ nm}$

$$F_{pmax} = 5.1 \times 10^{10} \text{ Nm}^{-3}$$

**600 °C/200h**

$d_k = 40 \text{ nm}$

$$F_{pmax} = 6.8 \times 10^{10} \text{ Nm}^{-3}$$

**Increase of grain size with reaction temperature**

The motion of a flux line submitted to a magnetic field can be stopped by introducing pinning centers, thus leading to an energy reduction.

Maximum pinning force per flux tube :

$$\vec{f}_p = -(\vec{j}_c \times \vec{\Phi}_0)$$

Maximum pinning force per volume :

$$\vec{F}_p = n \vec{f}_p = -(\vec{j}_c \times \vec{B})$$

In a type II superconductor in the mixed state,  $j_c$  is limited by the motion of flux lines.

Lorentz force on each flux line :

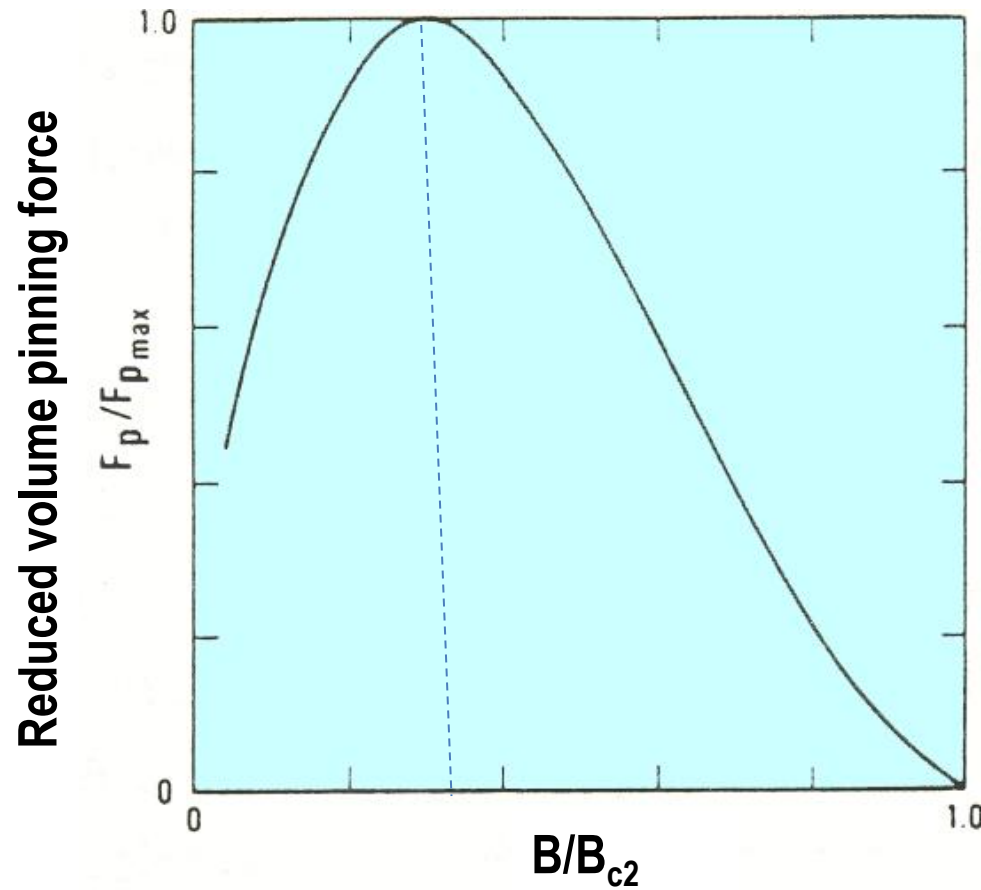
$$\vec{F}_L = \vec{j} \times \vec{\Phi}_0$$

Flux motion leads to energy dissipation, thus to local heating.

Energy dissipation :

$$P = \vec{j} \cdot \vec{E} = \vec{j} \cdot (\vec{v} \times \vec{B})$$

There is energy dissipation when  $F_p > F_L$ , i.e. when the Lorentz force is larger than the pinning force.

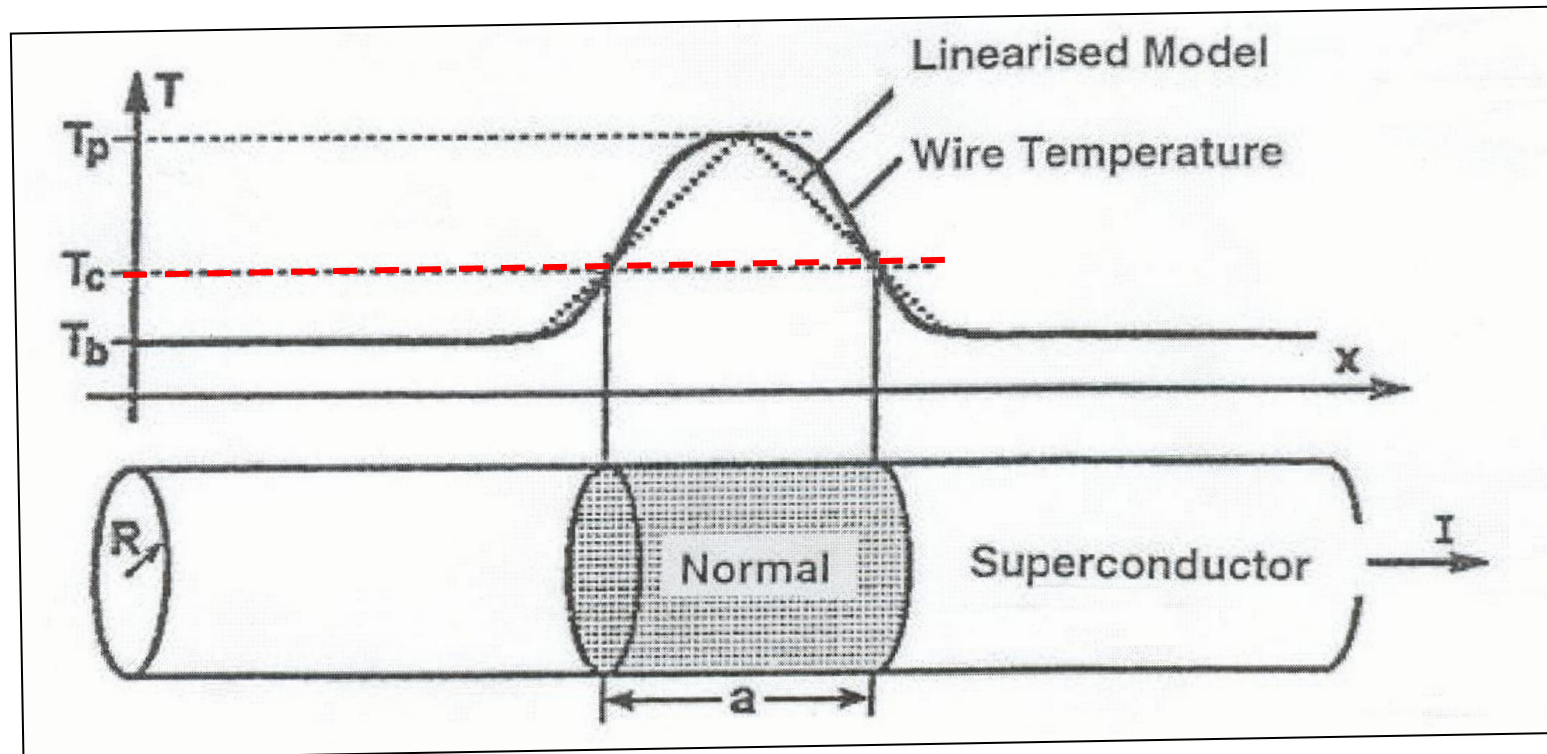


**Reduced field:  $b = B/B_{c2}$**

$$F(b) \sim b^p(1-b)^q$$

Local and/or temporary **perturbations** may lead to **thermal instability** and to a **quench**.

Consider a wire with  $T_c$  submitted to  $I$  in bath  $T_b$ . Stable operation conditions:  $T_c > T_b$





- 1 : Chemical stability
- 2 : Mechanical stability :
  - Bulk superconductors (except NbTi) break at  $\varepsilon < 0.05 \% !$
  - microcomposite (multifilamentary) configuration
  - Filament size:  $< 5 - 30 \mu\text{m}$
  - Wires: Irreversible strain:  $\varepsilon_{\text{irr}} > 0.4 \%$
- 3 : Cryogenic stability : presence of Cu as stabilizer
  - High thermal conductivity of Cu
  - a minimum quantity of stabilizer is required ( $> 23\% \text{ Cu}$ )
- 4 : Electromagnetic stability :
  - Low AC coupling losses required → Twisting of wires
- 5 : Low material costs
- 6: Length:  $> 1 \text{ km}$

**Typical wire configuration: 1'000 -10'000 filaments**  
**5 - 30 mm filament size**  
**25 cm twist pitch**

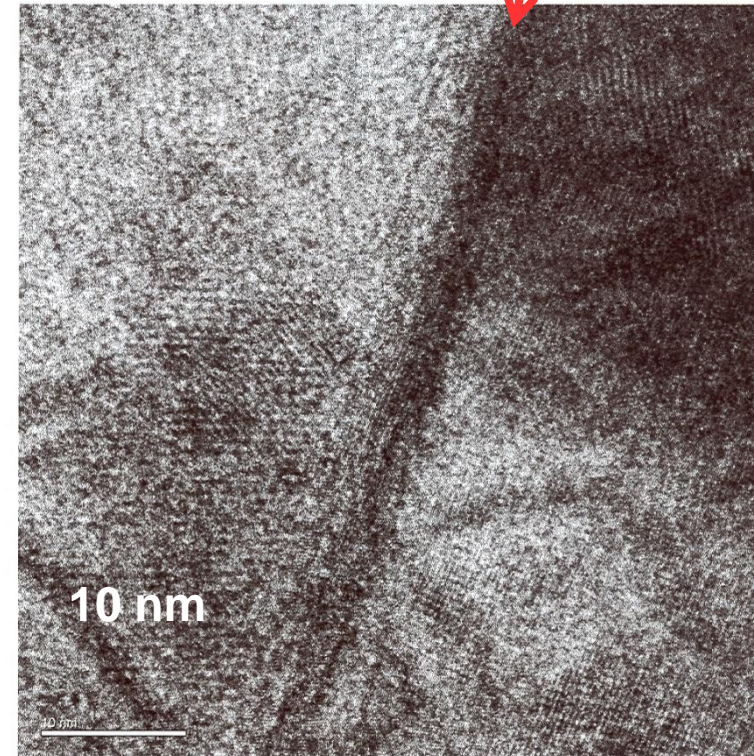
## Intergrain boundary at the high Sn limit of Bronze Route Wires

**LTS:**

**Defects at grain boundaries:  
breakage of periodicity creates  
normalconducting regions:  
Vortices, will pin the flux lines**

**Grain boundaries are the main  
factor for the enhancement of  $J_c$  in  
superconducting wires**

Boundary between  $Nb_3Sn$  grains



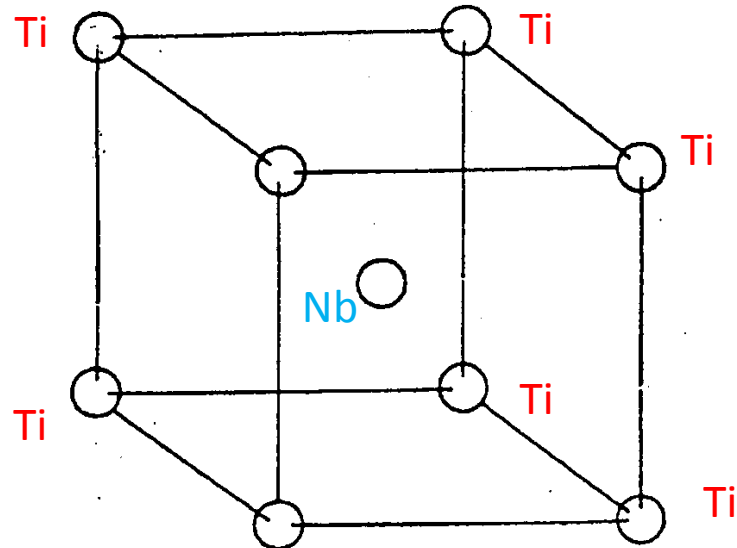
**4 nm: ~ Coherence length  $\xi_0$**

R. Flükiger and M. Cantoni, 2005

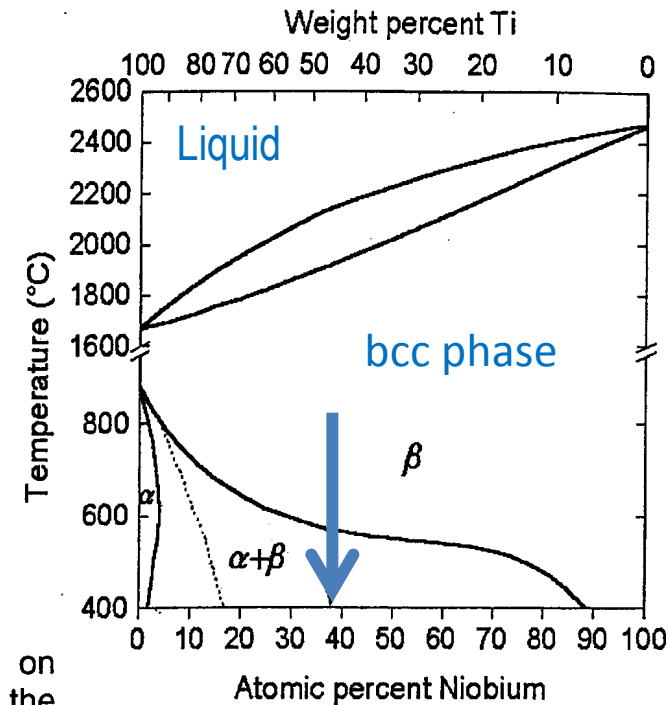
## 3. The system NbTi

**NbTi:  $T_c = 10$  K,  $B_{c2} = 14$  T**

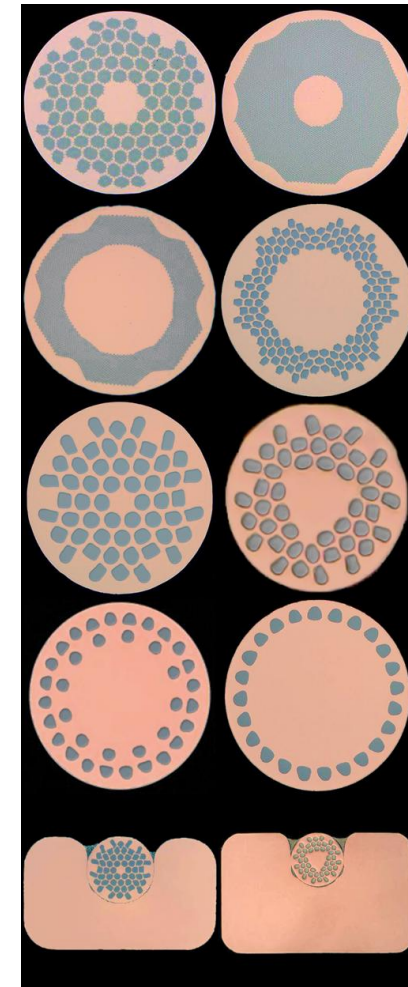
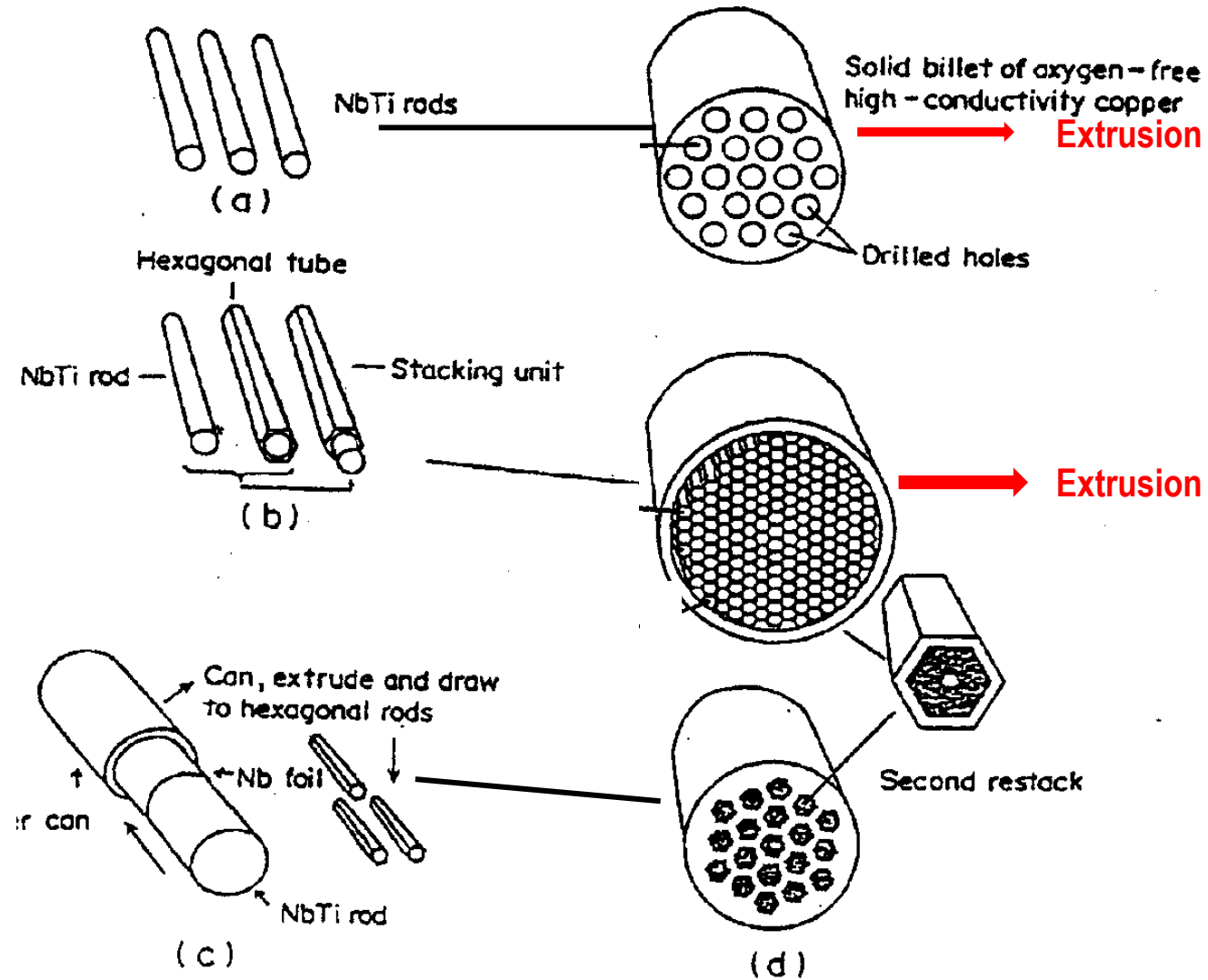
**Body cubic cented structure**

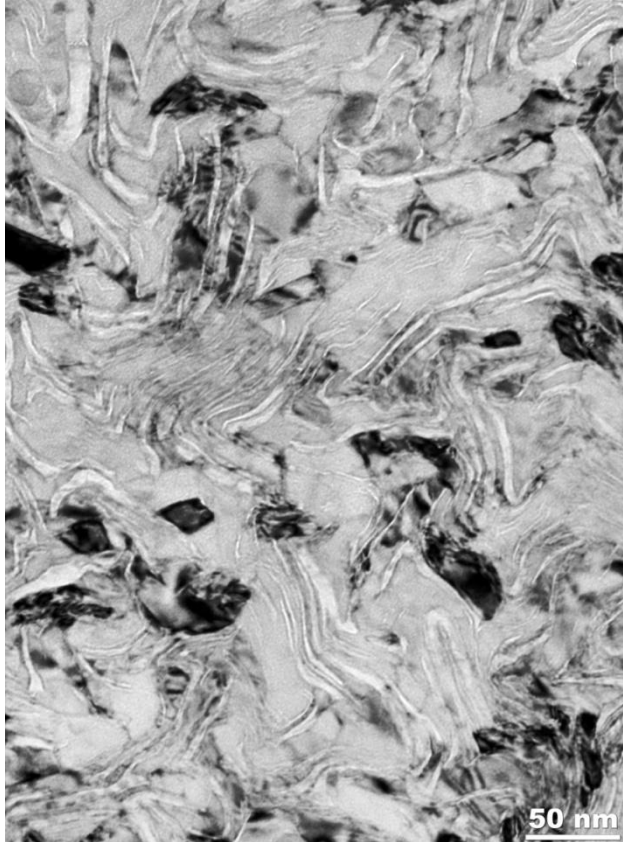


**Phase diagram**



Nb-Ti phase diagram. The low temperature boundaries are based on calculations by Kaufman et al. The dashed line represents the martensitic transformation inferred by Moffatt and Larbalestier.





**$\alpha$  – Ti ribbons: form spontaneously during wire deformation**

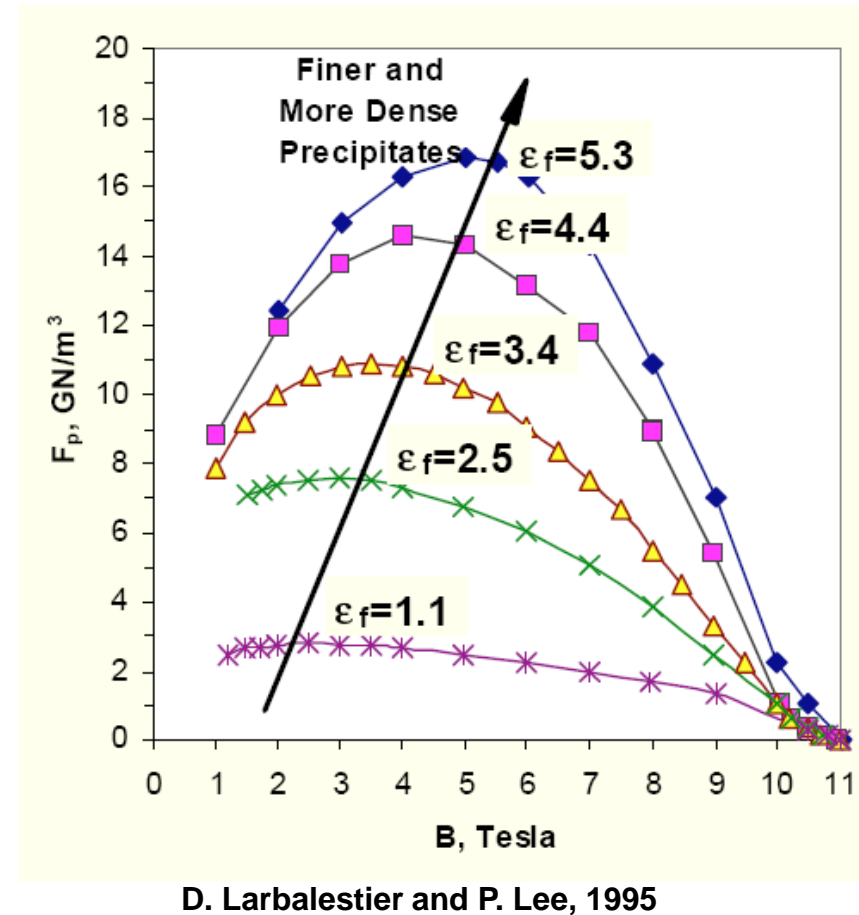
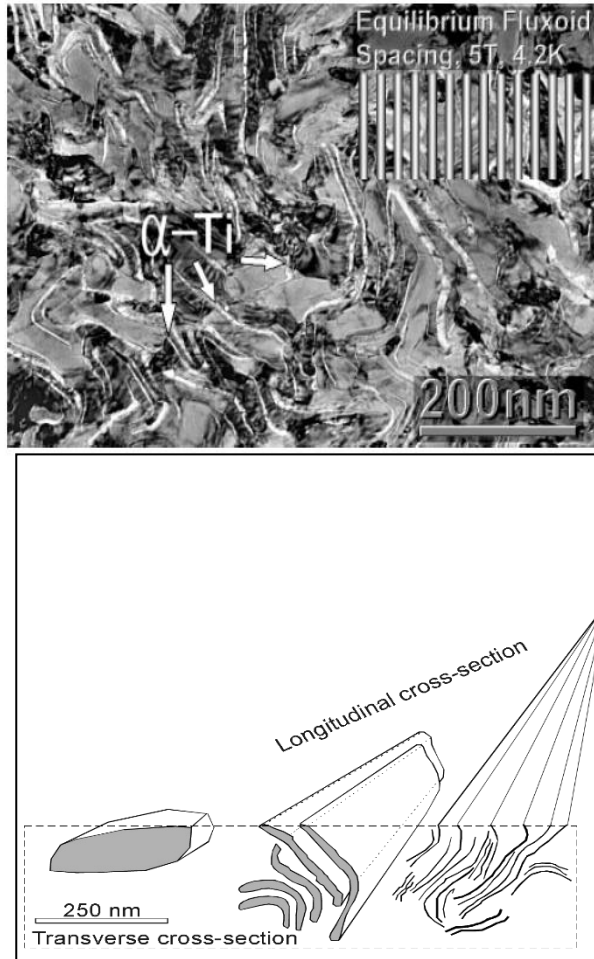
**TEM image of the microstructure (transverse cross-section) of a 3700 A/mm<sup>2</sup> (5 T, 4.2 K) multifilamentary strand from Oxford Instruments (OST).**

**This image shows the dense array of folded  $\alpha$ -Ti ribbons (lighter contrast) that create the strong vortex pinning.**

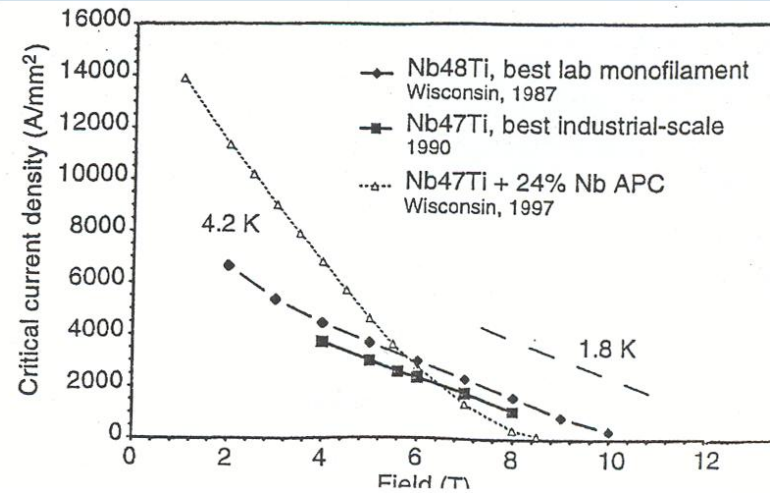
Courtesy Oxford Instruments

D. Larbalestier and P. Lee, 1995

**Artificial pinning:** Introducing defects having sizes comparable or smaller than  $\xi_0$



Progress in  $j_c$  of Nb-Ti wires  
with Nb APC (L. Cooley,  
D. Larbalestier)



Today, NbTi is used

- \* for **NMR** up to 9T,
- \* for a **background field** in high field magnets

and

- \* for **accelerator magnets** (LHC)

No further work is performed for a further enhancement of  $J_c$  in industrial NbTi wires.

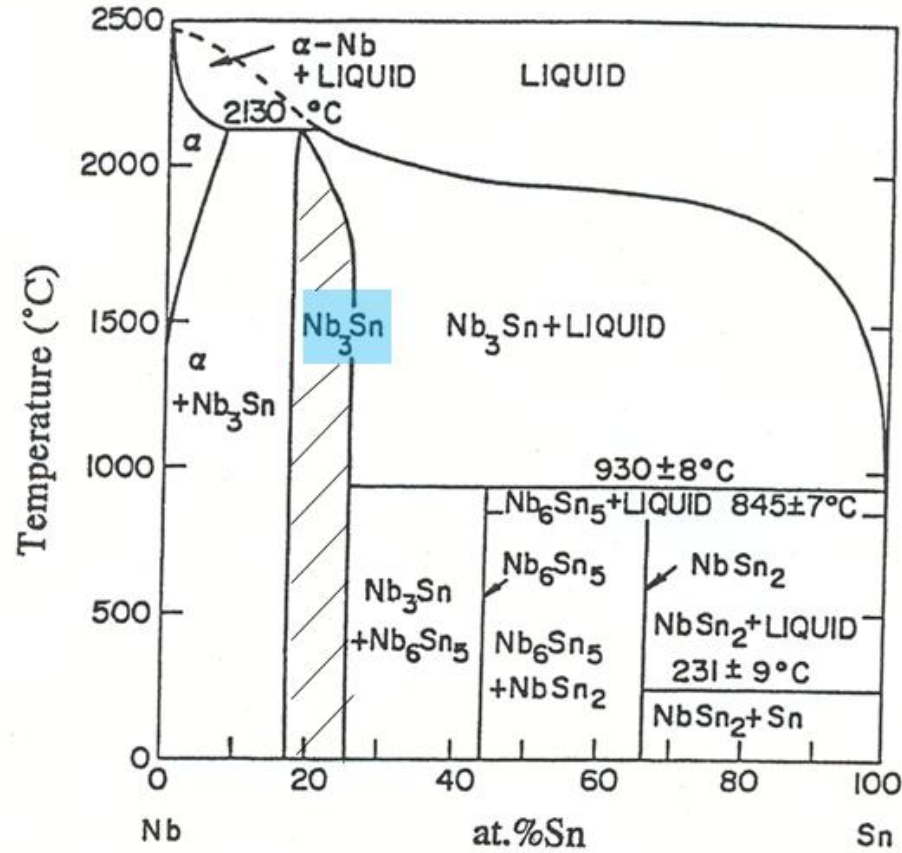
Artificial pinning in  $Nb_3Sn$  was so far unsuccessful.



## 4. The system $\text{Nb}_3\text{Sn}$

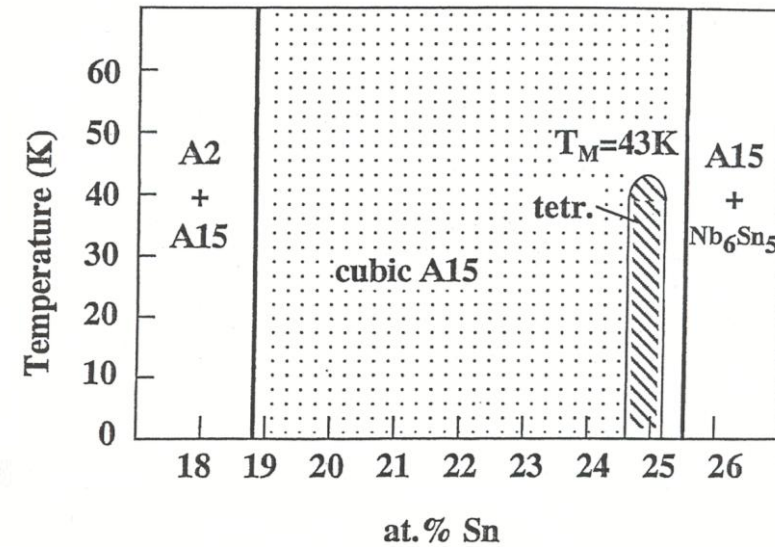
### 4 A. Superconducting properties of the A15 phase



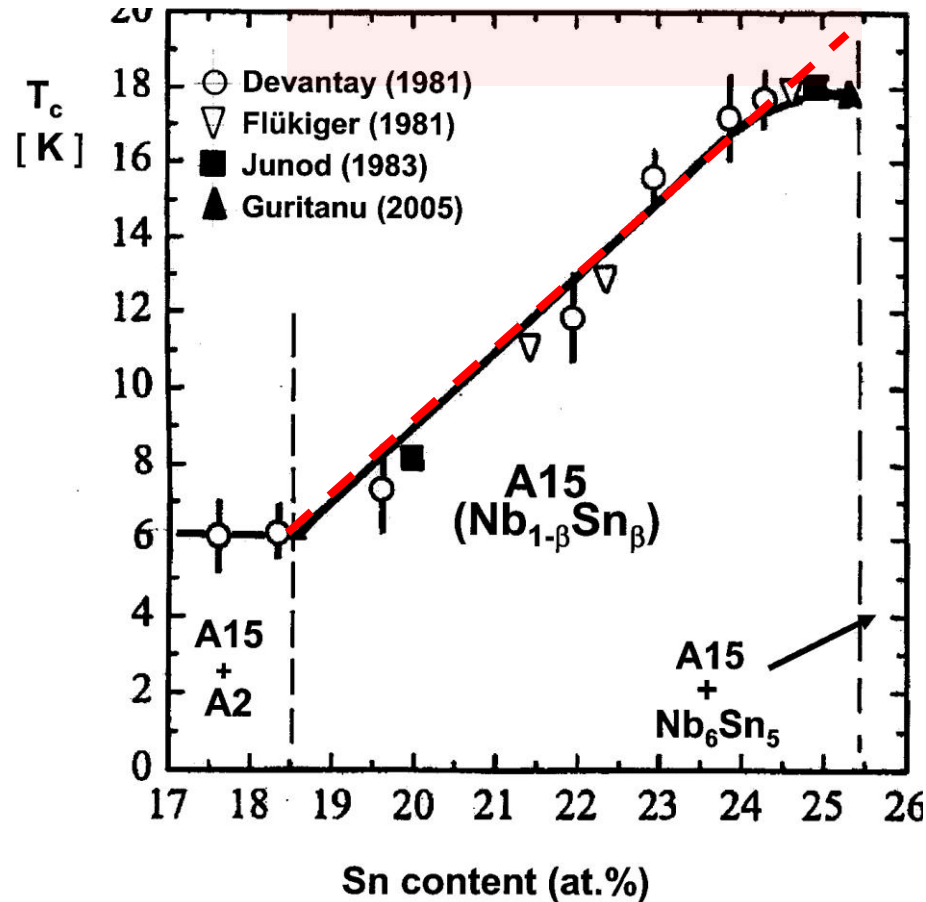


High temperature

T > 43K: cubique  
T < 43K : tetragonal



Low temperature



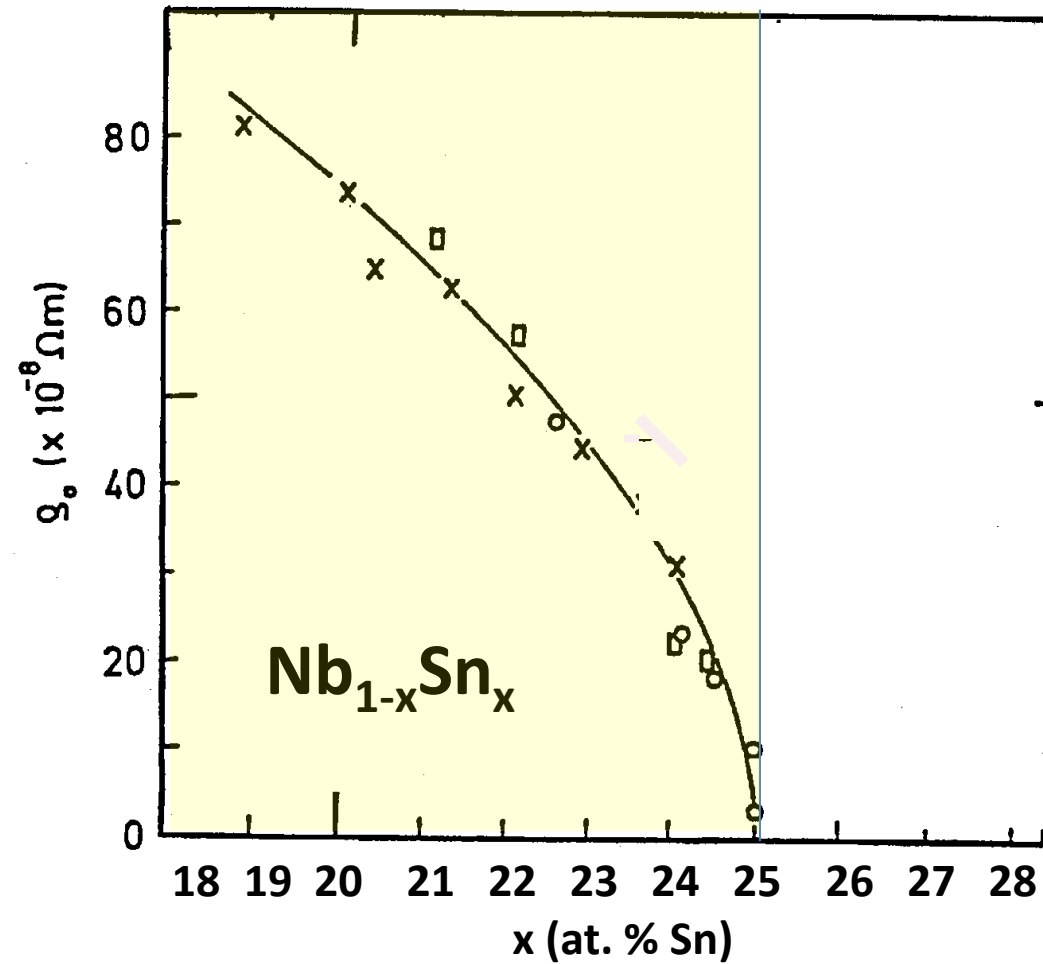
←  $T_c$  (linear extrapolation): ~ 19 K

Saturation at > 24.5 at. %:

Due to **phonon softening**

$T_c = T_c(\text{max})$  at **25 at.% Sn**

$T_c = T_{c \text{ max}} = 18.3 \text{ K}$  at the stoichiometric composition (25 at.% Sn):

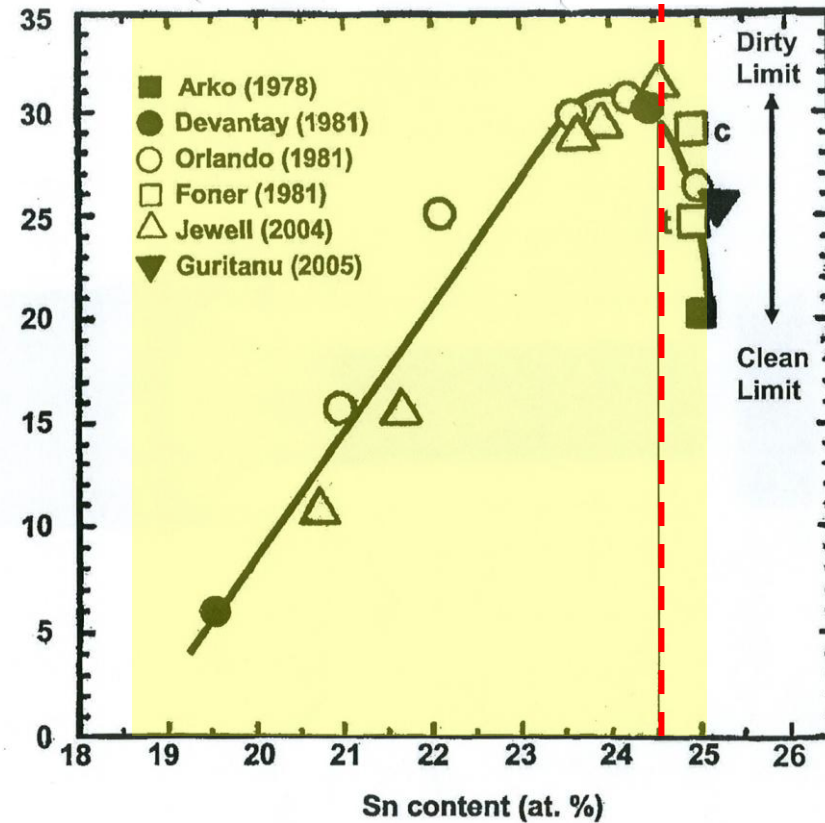


$\rho_o = \rho_o(\text{min})$   
 at **25** at.% Sn:  
 $< 10 \mu\Omega\text{cm}$

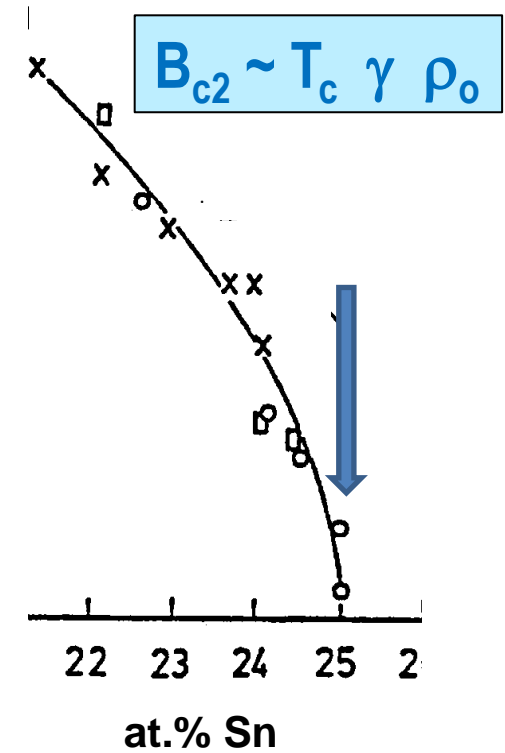
$$B_{c2} = B_{c2}(\text{max})$$

at  $\sim 24.5$  at.% Sn

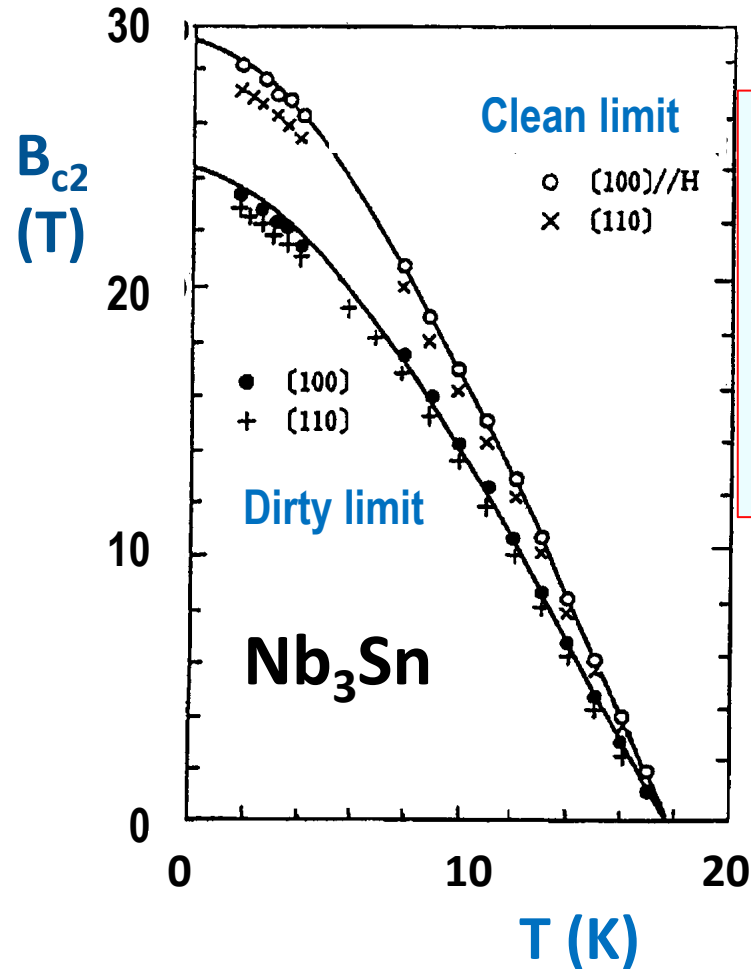
Not at 25 at.% Sn!



Effect due to electronic mean free path:  $\rho_0$



$$B_{c2} \sim T_c \gamma \rho_o$$

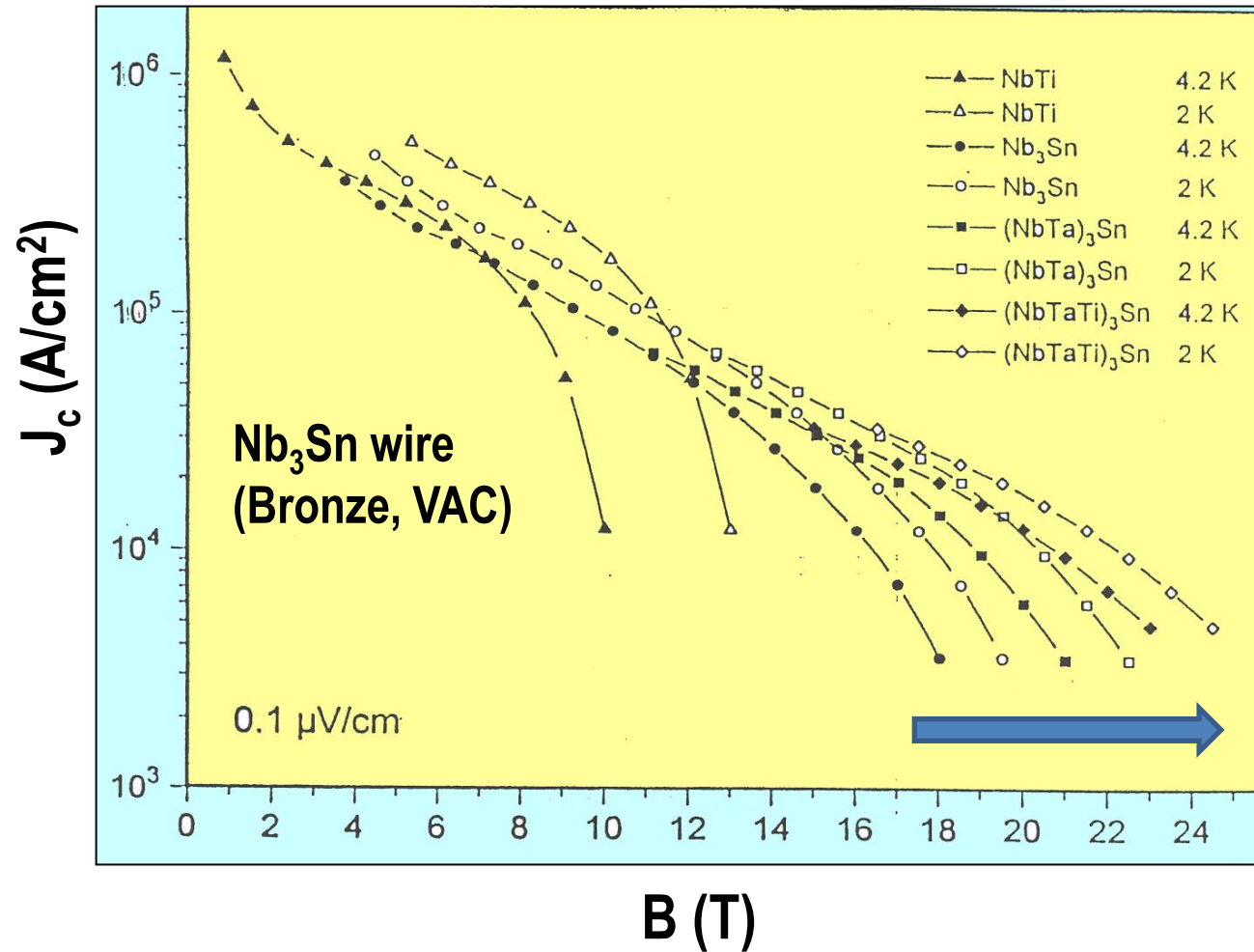


« Clean » limit: low  $\rho_o$   
 $< 5 \mu\Omega\text{cm}$   
 (very close to stoichiometry)

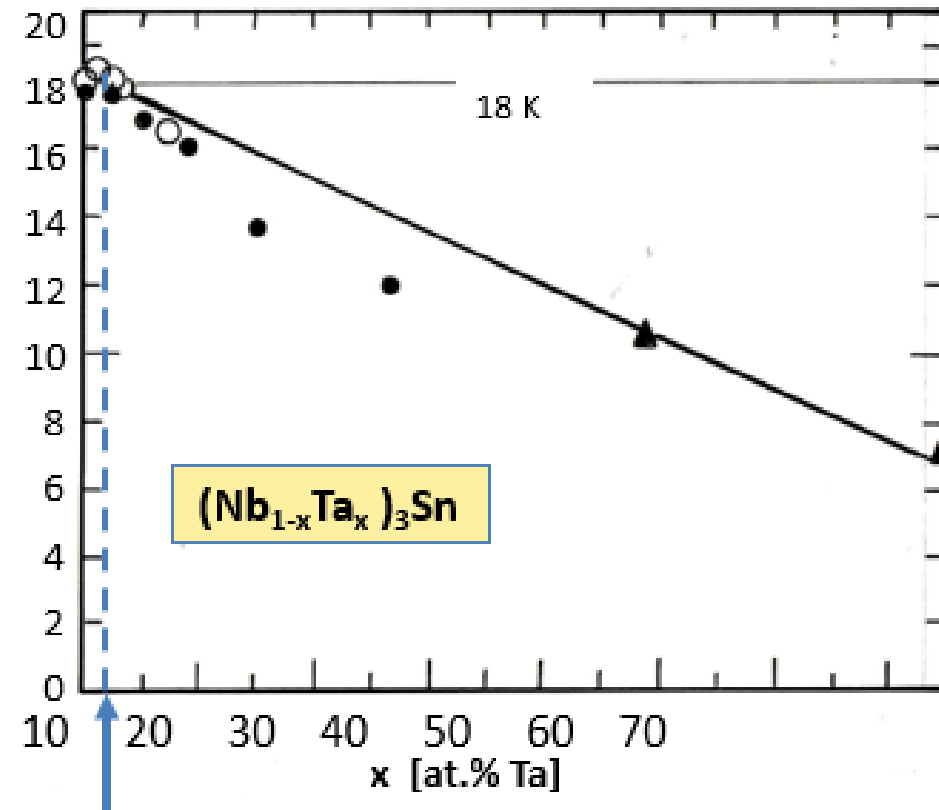
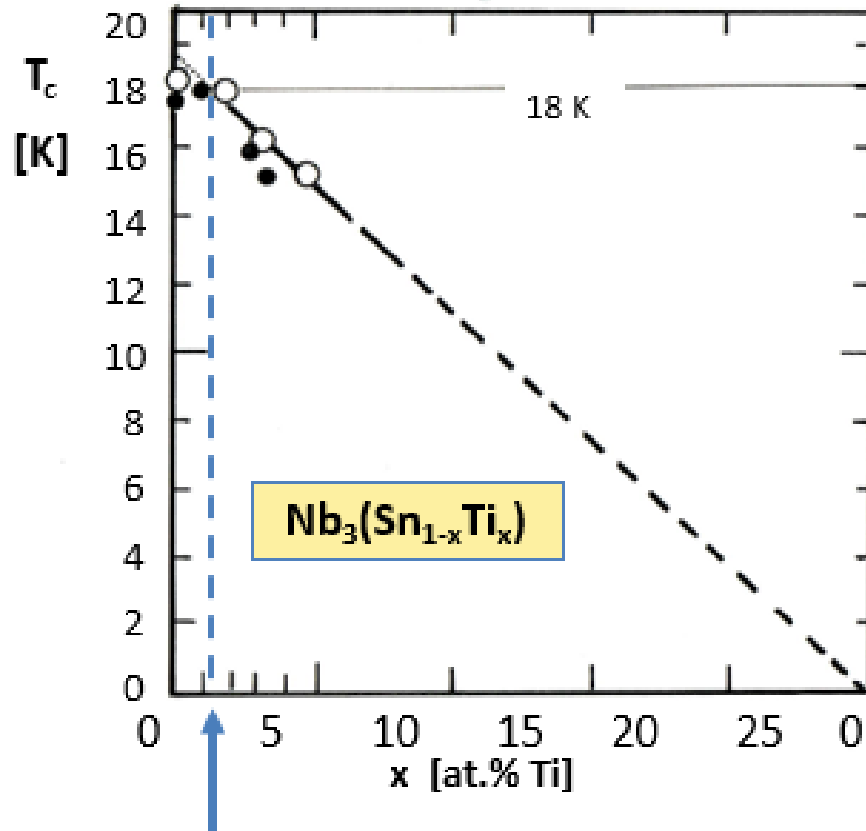
« Dirty » limit: high  $\rho_o$   
 $> 20 \mu\Omega\text{cm}$   
 (deviation from stoichiometry)

## Effect of Ti and Ta additives

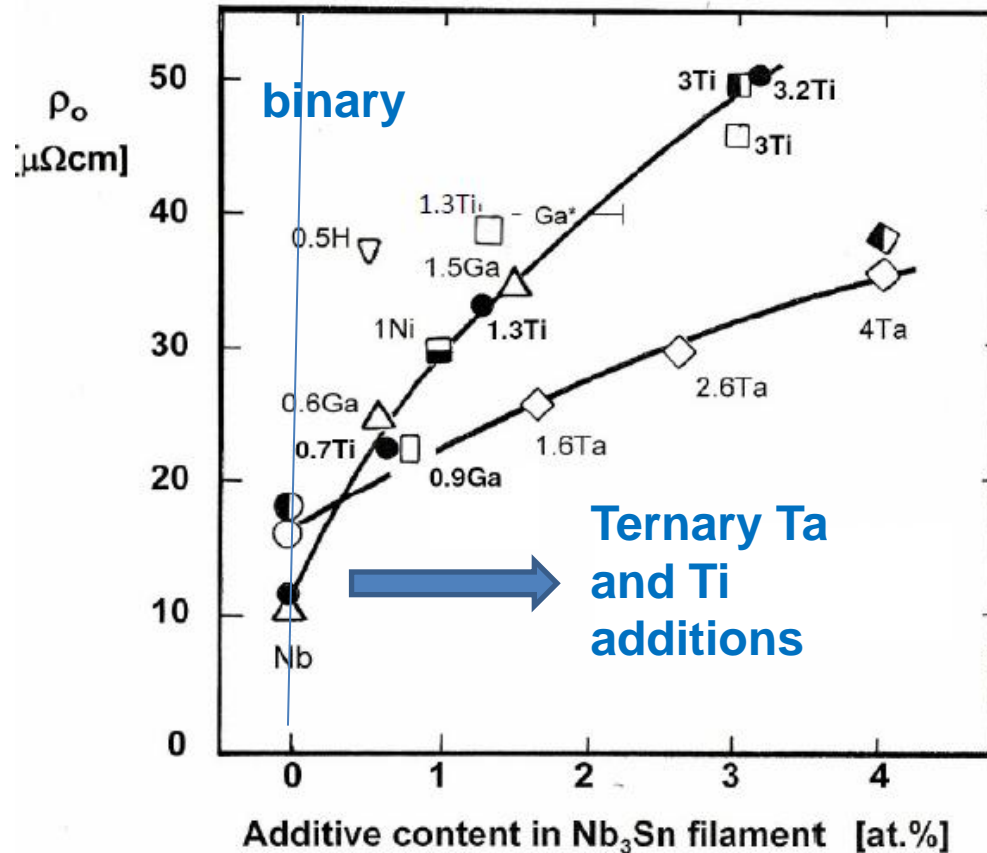
Ta: Cody et al. (1972)  
 Ti: Sekine et al. (1980)  
 Drost et al. (1985),  
 Suenaga et al., (1986),  
 Geneva group (2007)







The variation of  $T_c$  for the Ta and Ti content giving the highest values of  $J_c$  is **very small**



Effect of Ta and Ti additives:  
 Enhancement of  $\rho_0$

Since  $B_{c2} \sim T_c \gamma \rho_0$ ,  
 and  $\Delta T_c$  and  $\Delta \rho_0$  small:



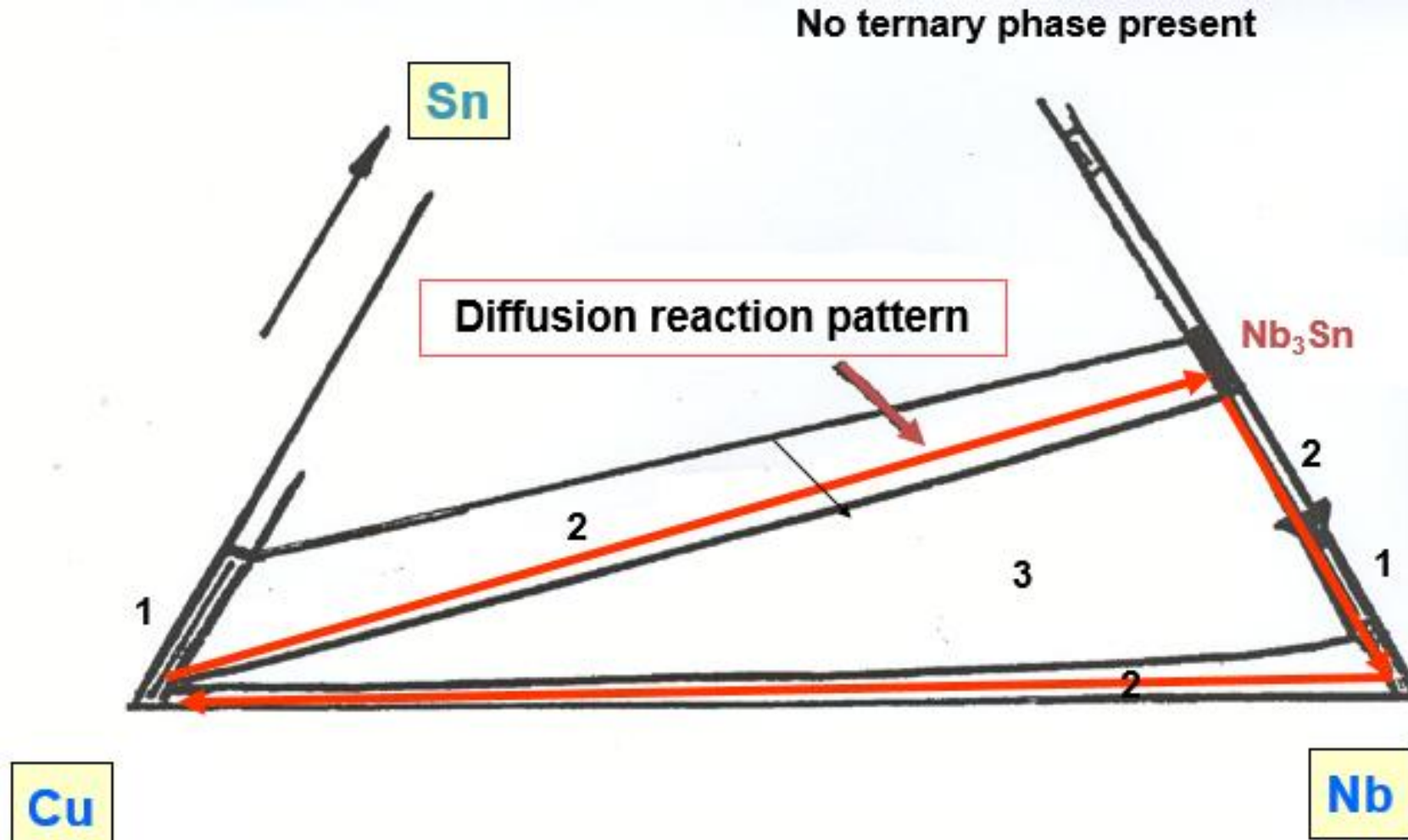
## 4B. Nb<sub>3</sub>Sn wire fabrication and critical current densities

**Industrial fabrication techniques**

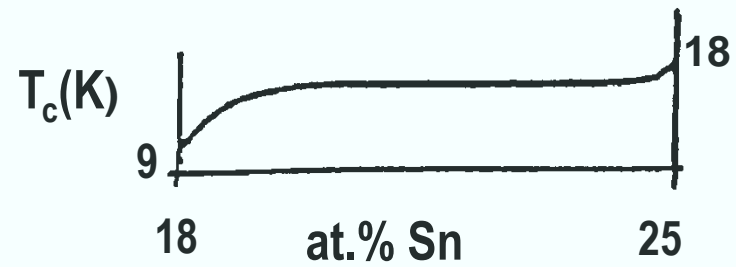
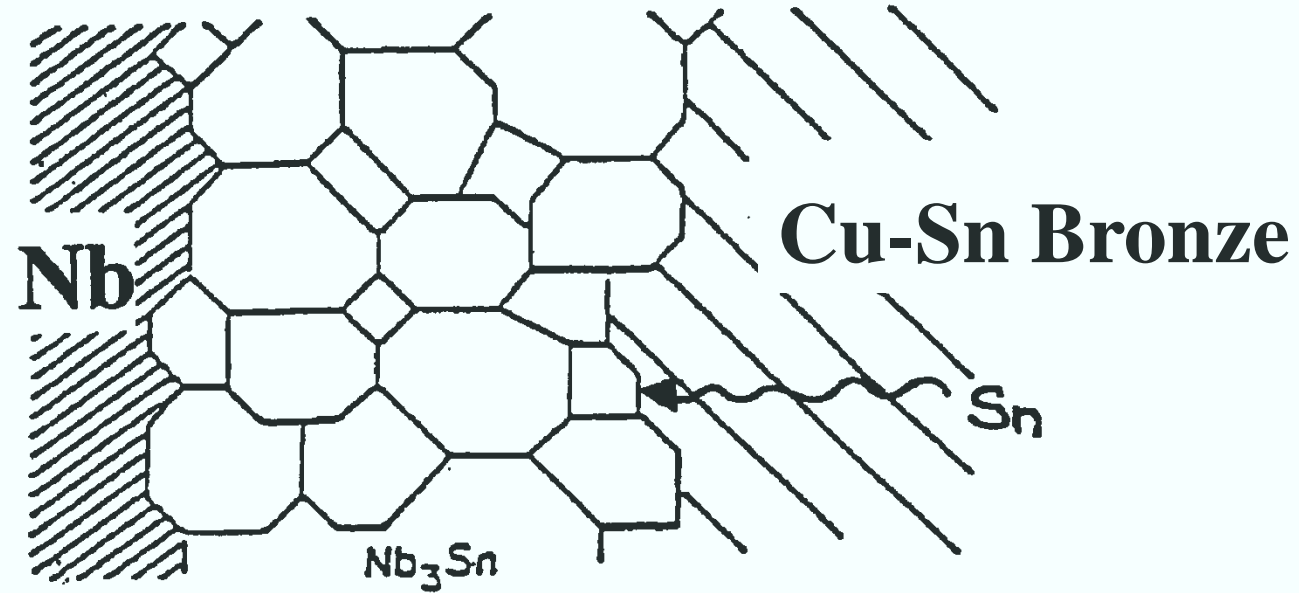
**Bronze Route**

**Internal Sn Diffusion**

**Powder in Tube (or PIT) method**



Conditions  
after  
reaction



Several different industrial modes of processing Nb<sub>3</sub>Sn wires.

## 1: High Sn contents (>18 wt.% Sn)

<b>Internal Sn, Filaments:</b>	IGC (USA), Alsthom (F), Eurometalli (I)
<b>Internal Sn, Jelly Roll:</b>	<b>Oxford (USA)</b>
<b>Nb tube process:</b>	Showa, Toshiba (J)
<b>ECN route : powder process</b>	SMI (Ne)

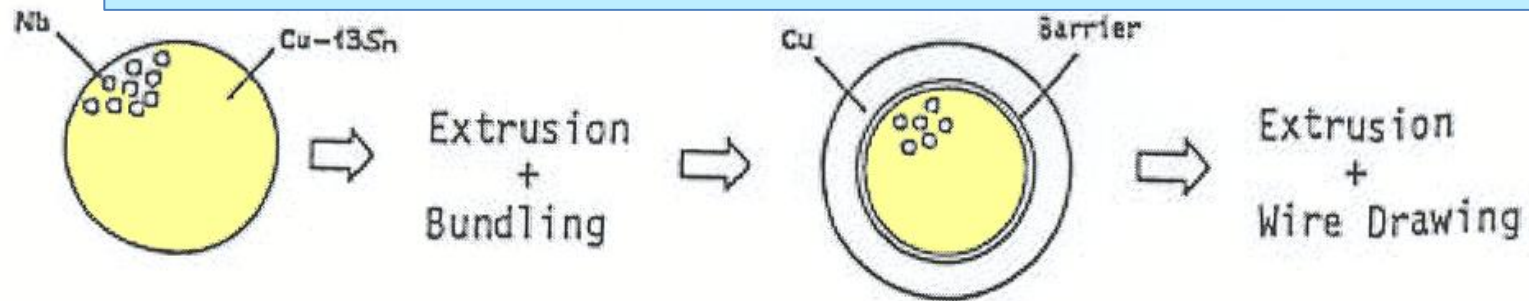
*High Sn content leads to higher values of  $j_c$  (distribution in the filaments)*

## 2: Low Sn contents ( $\leq 15.4$ wt.%Sn)

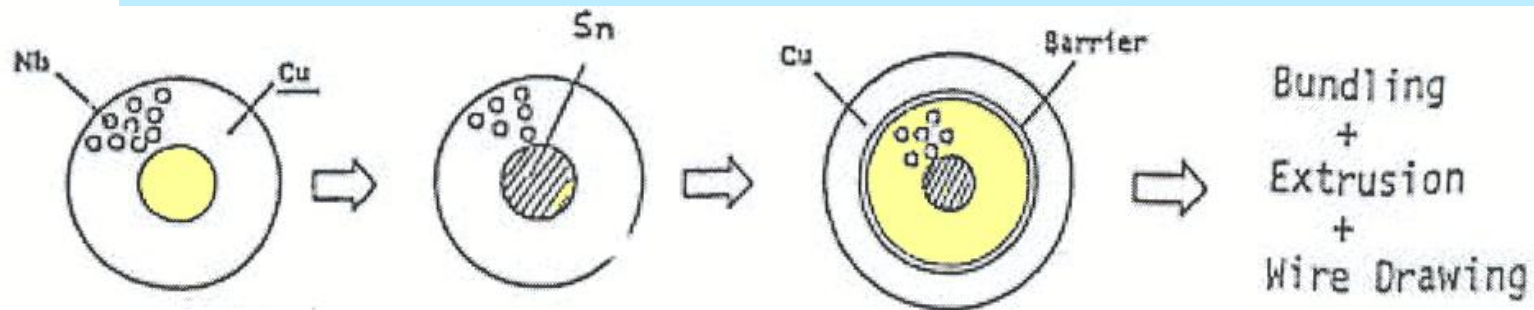
<b>Bronze route:</b>	VAC (D), Kobe Steel (J), Hitachi (J), Furukawa (J)
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The bronze route is the only one being appropriate to persistent mode operation of a solenoid, since the Ta barrier can be set at the center of the wire : the contacts between filaments of two joints occurs directly from superconductor to superconductor (the Ta barrier does not need to be etched away).

## Bronze Route: **With intermediate anneals**



## Internal Sn Diffusion method: **No intermediate anneals**



## Bronze route

### Minus

- Intermediate anneals each 50 % of cross section reduction
- Lower  $j_c$  values than Internal Sn wires at intermediate and low fields

### Plus

- Very long lengths (> 5'000 m)
  - Low effective filament diameter (< 20  $\mu\text{m}$ )
  - High longitudinal homogeneity
  - Appreciably high  $j_c$  values at high fields
  - Suitable for persistent mode applications (central Ta barrier around Cu stabilizer)
- \* Has the best mechanical properties of all  $\text{Nb}_3\text{Sn}$  wire types



## Internal Sn route

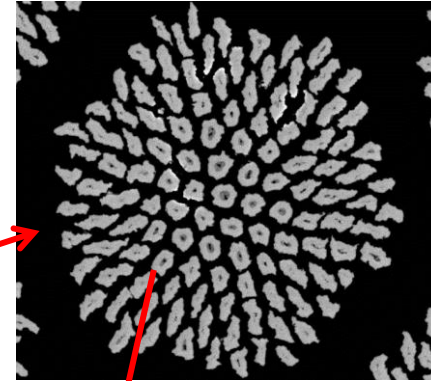
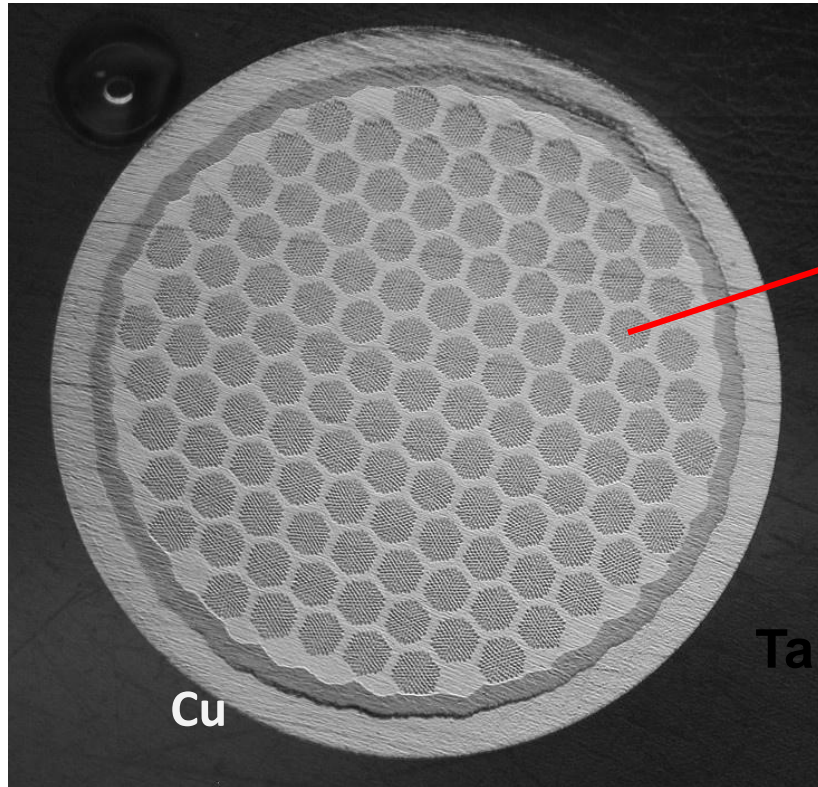
### Minus

- Effective diameter higher than for bronze route
- Longitudinal homogeneity lower than for bronze route
- Less suitable for persistent mode operation (external Ta barrier)

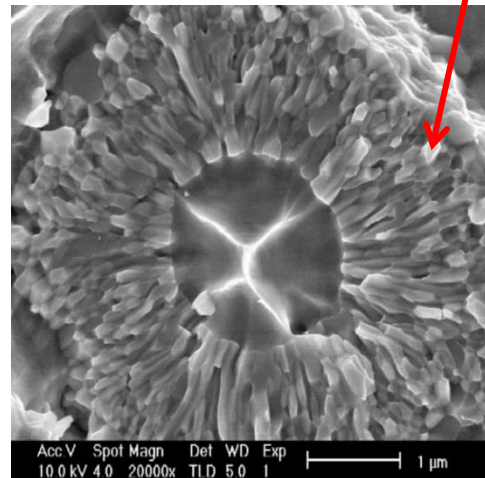
### Plus

- No intermediate anneals (lower costs than bronze route wires)
- High  $j_c$  values at intermediate fields : **> 3'500 A/mm<sup>2</sup> at 4.2K/12T**
- Appreciably long lengths ( > 1'000 m)

**Nb<sub>3</sub>Sn: T<sub>c</sub> = 18K, H<sub>c2</sub>(0) = 30T**



Filament group

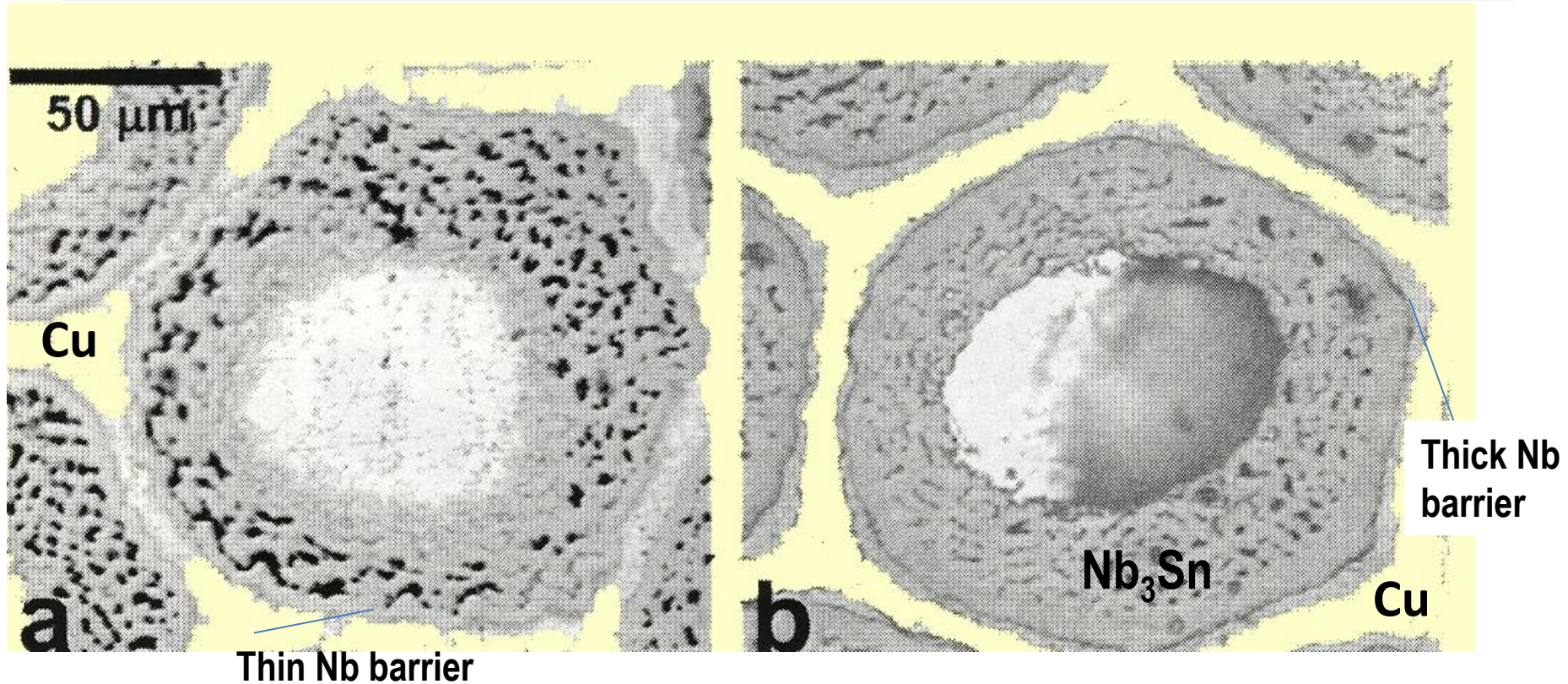


Filament diameter 4 μm)

Grain sizes: 100 – 200 nm

**Bronze type Nb<sub>3</sub>Sn wire (10'000 filaments)**

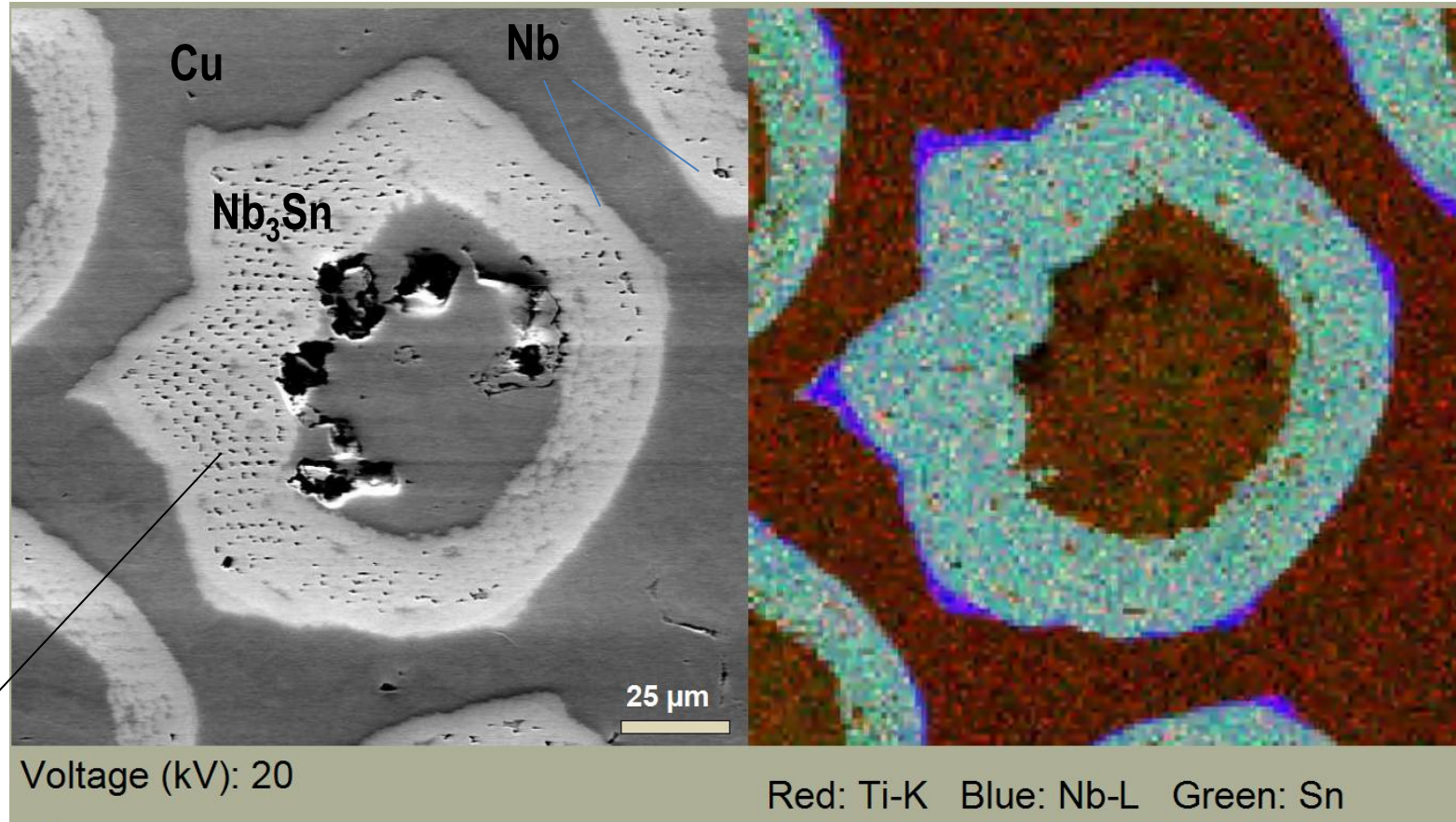
2 RRP wires with  $J_c$  (non-Cu) = 2'000 A/mm<sup>2</sup> at 4.2K/12T



a: thin Nb barrier, almost fully reacted: RRR = 10

b: thick Nb barrier, a complete unreacted Nb barrier remains: RRR = 100.

## Ti additives introduced by NbTi rods.



Ti  
(from NbTi)

P. Lee, D. Larbalestier, J.A. Parrell, M.B. Field, Y. Zhang, S. Hong, ICMC 05, Keystone, USA

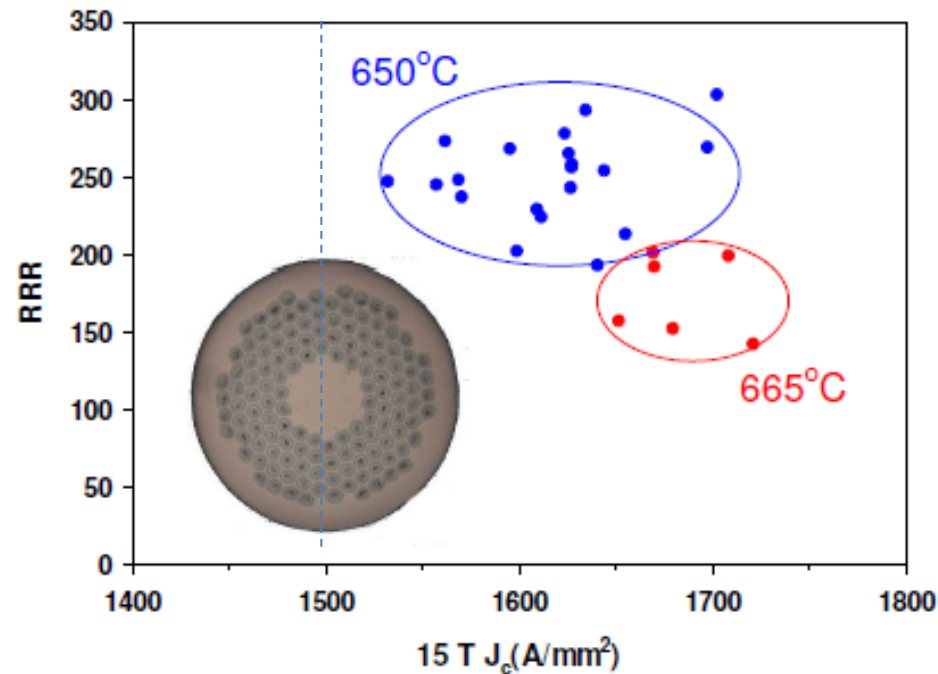
CAS, Erice, Italy, 25 April - 4 May, 2013

**Required for LHC Upgrade:  $J_c(\text{non-Cu}) = 1'500 \text{ A/mm}^2$  at 4.2K/15T**

1mm Ti doped 169 strand strand ( $D_s \sim 52\mu\text{m}$ )

Study of heat treatment temperature 665°C and 650°C

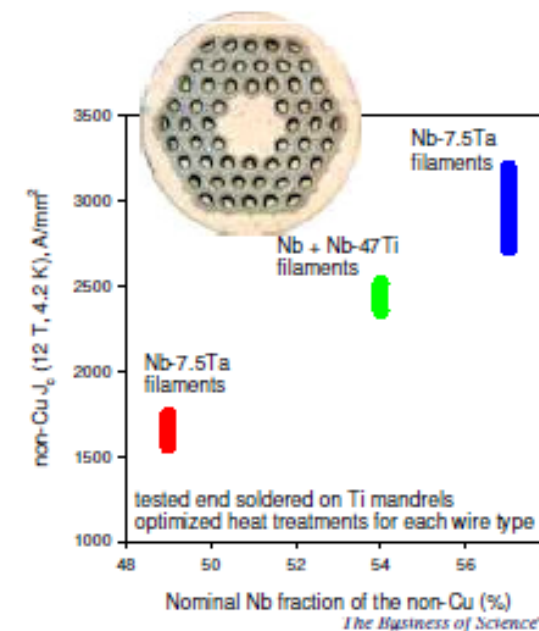
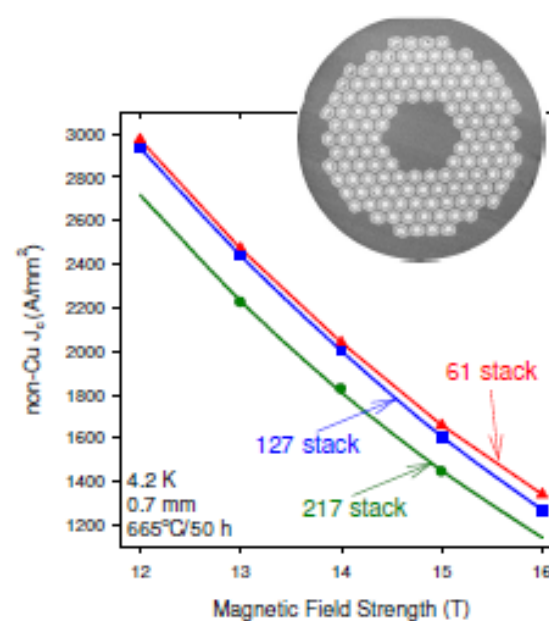
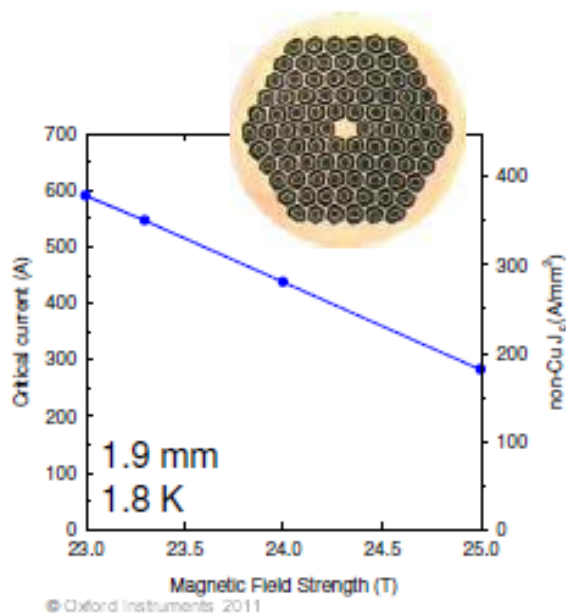
- trade small decrease of 15 T  $J_c$  to improve RRR > 200



Courtesy Parrell (OST)

## Distributed Barrier Internal Sn – RRP®

- Conductor development focused on the needs of the application
  - NMR – highest  $J_c$  at high field,  $D_{eff}$  generally not a concern
  - HEP – high  $J_c$  at mid field, but with small  $D_{eff}$
  - CICC – mid  $J_c$  at mid field, with high RRR after Cr plating
  - Lab magnets – a large  $I_c$  range (wire diameter selection), strength



## PIT technique

### Minus

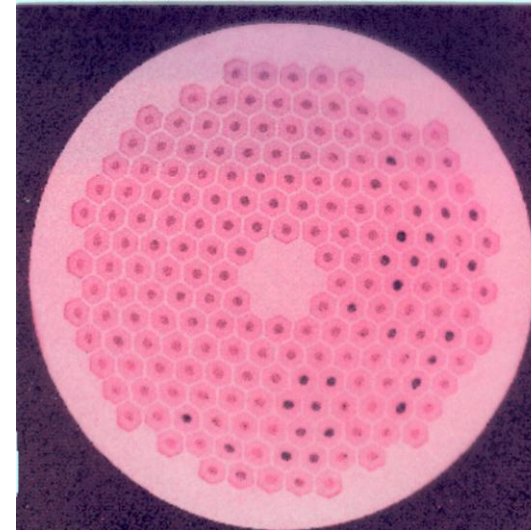
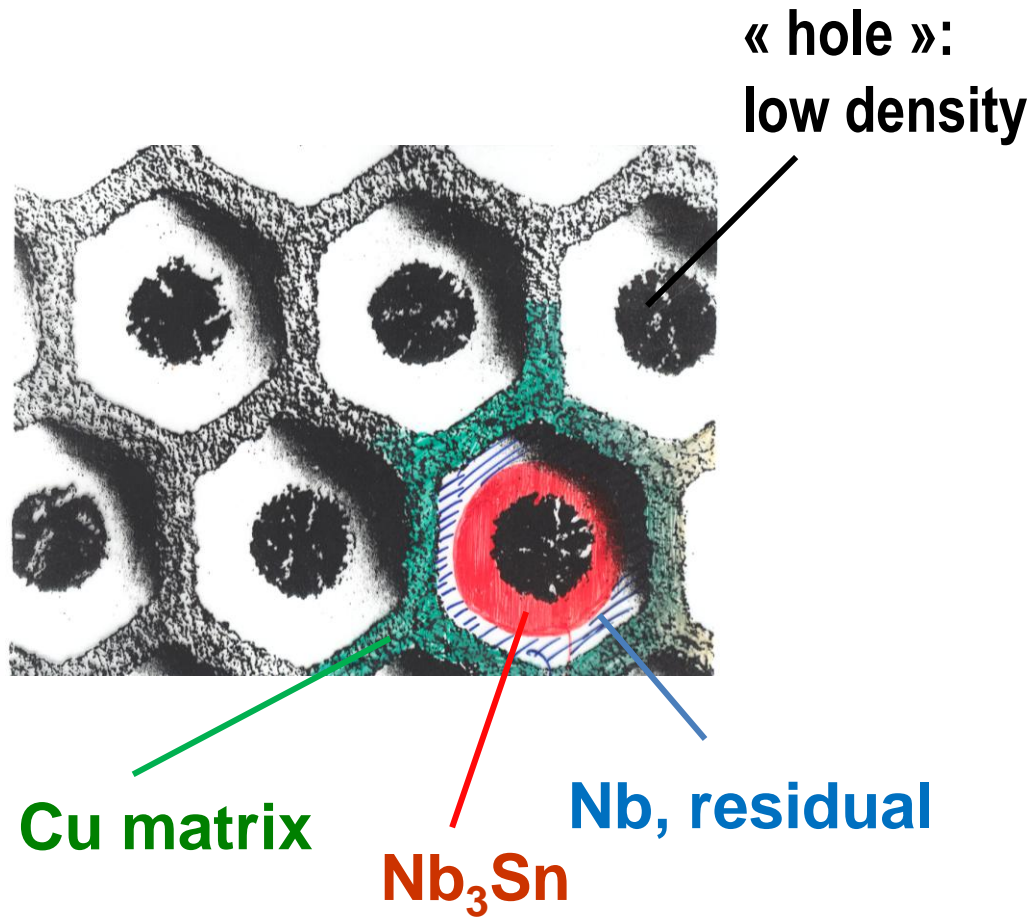
- Mechanical properties
- Large effective filament diameter
- \* Higher costs than other techniques

### Plus

- Very high Sn content → constant Sn level in the filaments
- Very high critical current densities **> 3'000 A/mm<sup>2</sup> at 4.2K/12T**

As starting material, one uses NbSn<sub>2</sub> powders, which are difficult to fabricate

 high costs





## 4C. Calorimetric analysis of Nb<sub>3</sub>Sn wires

### Specific heat measurements:

No shielding effects

Measures the totality of the superconducting volume in the wire

Measurement with the matrix (under prestress)

Up to high fields (21 T)

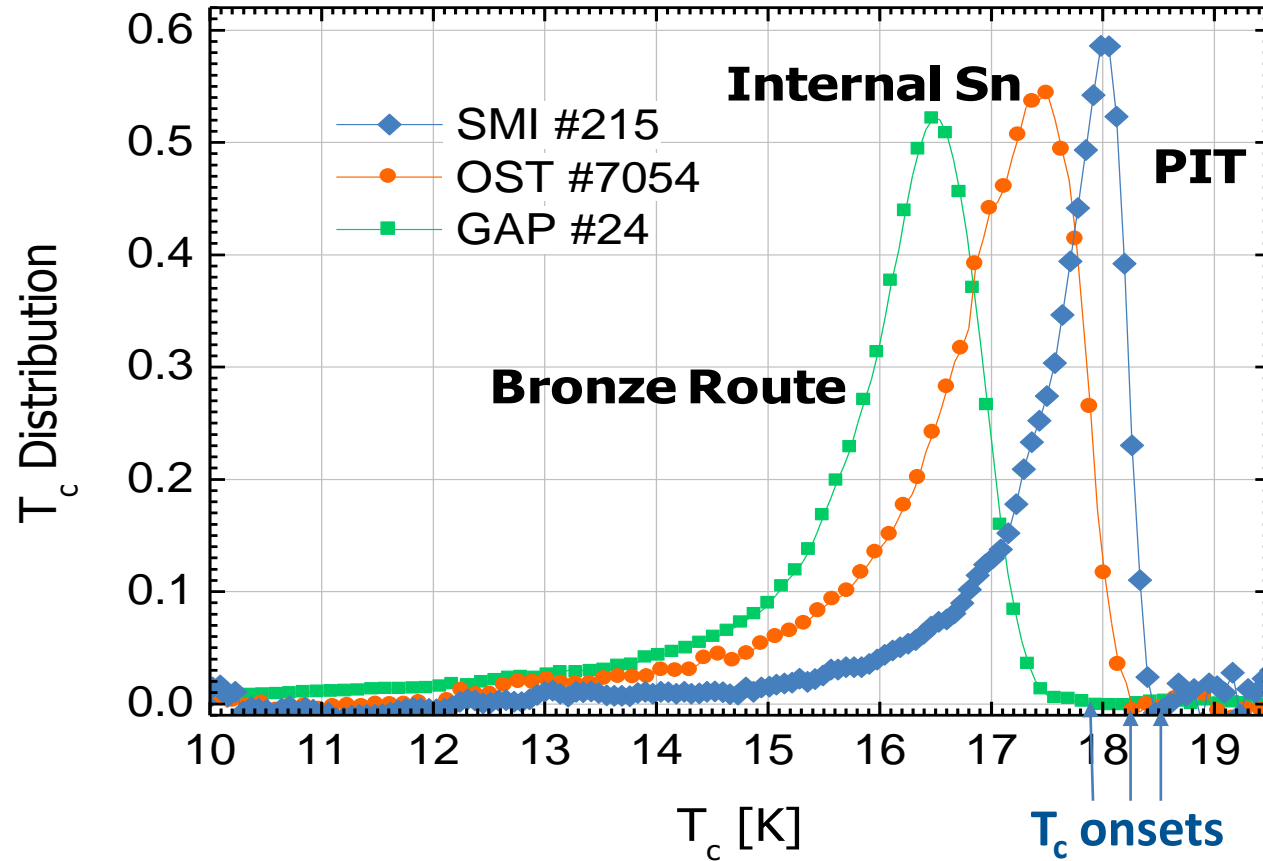
### Technique

Measurement at 0T and 14T

Subtraction, to eliminate normal conducting part

Deconvolution of the superconducting part  T<sub>c</sub> distribution

**Result:** All Nb<sub>3</sub>Sn wires are inherently inhomogeneous! Susceptibility or resistivity measurements give **only the onset value of T<sub>c</sub>!**



Clear difference between Bronze route and Internal Sn (RRP) wires:  
 Bronze Route wires have a lower  $T_c$   $\rightarrow$  lower average Sn content

## Conclusions about Nb<sub>3</sub>Sn wires (part I)

- **For LHC Upgrade, the Nb<sub>3</sub>Sn wires prepared by RRP and PIT processing are found to exhibit sufficiently high critical current densities**
- **Bronze Route wires have to be excluded, J<sub>c</sub> being too low**
- **The cost situation is at present more favourable for RRP wires, but wires of both processes are still under study.**
- **Due to the high activation of Ta due to high energy neutron irradiation, Nb<sub>3</sub>Sn wires alloyed with Ta should be avoided.**
- **Mechanical properties: see conclusions II**

**Annex.**  
**Remarks about thermal stability of superconducting wires**

Suppose a local **perturbation** causing :  $T = T_p > T_c$

- 
- \* a resistive zone develops in the wire
  - \* Joule heat is built up locally.

Energy to be **evacuated** to restore the superconducting state comprises:

- \*the energy leading to the perturbation, and
- \*the energy produced by the Joule heat.

Three different power terms have to be considered:

## 1: The Joule heat

$$P_{\text{joule}} = R_n I^2 = \rho_n a j^2 \pi R^2$$

where  $j = I / \pi R^2$ , and  $r_n =$  normal resistivity.

## 2. Heat conduction through the wire

Heat from the resistive zone to the neighbouring superconducting region:

$$P_{\text{conduction}} = 2\pi R^2 \lambda dT/dx = 2\pi R^2 \lambda dT',$$

where  $\lambda$  = thermal conductivity  
 $T'$  = temp. gradient in perturbed zone  
 $= dT/dx = 2(T_p - T_c)/a$

## 3. Heat transfer to the bath, in a slice of thickness $x$

$$dP_{\text{bath}} = 2\pi R h [T(x) - T_b] dx, \quad \text{and}$$

$$P_{\text{bath}} = 2\pi R a h [ (T_c - T_b) + a T'],$$

where  $h$  = heat transfer coefficient (to the bath)

The thermal stability limit is now given by :

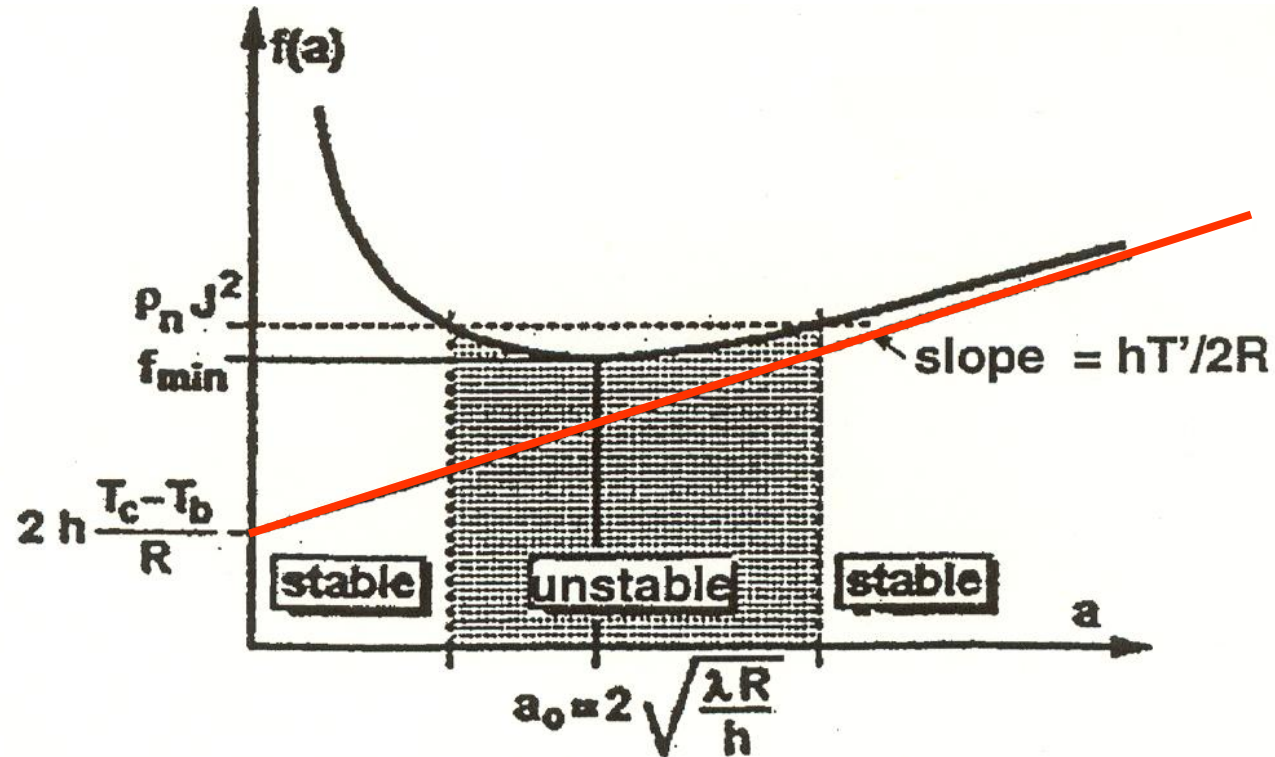
$$P_{\text{joule}} < P_{\text{conduction}} + P_{\text{bath}}$$

$$\rightarrow \rho_n I^2 < 2\lambda dT' \left( \frac{1}{a} + \frac{hT'}{2R a} + \frac{2h}{R(T_c - T_b)} \right) \equiv f(a)$$



$$\rho_n I^2 < 2\lambda dT' \left( \frac{1}{a} + \frac{hT'}{2R} a + \frac{2h}{R}(T_c - T_b) \right) \equiv f(a)$$

Graphical representation showing the regions of instability



In order to satisfy the stability criterion, following parameters have to be optimized, leading to the actual multifilamentary wire configuration :

- a : Temperature : The difference ( $T_c - T_b$ ) must be as large as possible → High  $T_c$  is important
- b : Wire radius R: **R should be as small as possible**  
→ small filament diameters, multifilamentary configuration in industrial wires
- c: Heat conductivity  $\lambda$ :  **$\lambda$  must be as high as possible**  
→ each filament in an industrial wire is surrounded by with a highly conducting Cu matrix
- d: Heat transfer h: h must be minimized  
→ The Cu matrix is also effective in providing a better heat transfer to the bath.