



Outline

A brief introduction to A15 superconductors

Nb₃Sn: the pathway to industrialization

Towards the ultimate performance of Nb₃Sn

• the Future Circular Collider study @



Not only critical current !!

Focus on the electromechanical properties

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An introduction to A15 superconductors

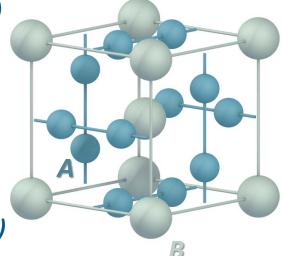
• A15 are intermetallic compounds with A₃B formula

• V_3 Si is the earliest example, $T_c = 17.1$ K (Hardy, 1954)

The Superconductivity of Some Transition Metal Compounds*

George F. Hardy† and John K. Hulm Institute for the Study of Metals, University of Chicago, Chicago, Illinois (Received November 23, 1953)

About eighty transition metal compounds comprising borides, carbides, nitrides, oxides, silicides, and germanides of metals of Groups 4A, 5A, and 6A were tested for superconductivity down to 1.20°K, using a magnetic method. Among the specimens were most of the known compounds of the above type not examined and the specimens were most of the known compounds of the above type not examined the specimens were most of the known compounds of the above type not examined the following eleven new superconductors were discovered, parentheses: W₂B (3.10°), Nb₂C (9.18°), Ta₂C (3.26°), parentheses: W₂B (3.10°), Mo₃Ce (1.43°), α-ThSi₂ (3.16°), β-ThSi₂ (2.41°), and the first superconducting germanides, V₃Ge and Mo₃Ge, which, together with V₃Si and Mo₃Si, crystallize in the cubic β-tungsten structure. The transition temperature of V₃Si is apparently the highest known for any binary superconducting compound.



Nb₃Sn came 6 month later, $T_c = 18 \text{ K (Matthias, 1954)}$

PHYSICAL REVIEW

VOLUME 95, NUMBER 6

SEPTEMBER 15, 1954

Superconductivity of Nb₃Sn

B. T. Matthias, T. H. Geballe, S. Geller, and E. Corenzwit Bell Telephone Laboratories, Murray Hill, New Jersey (Received June 10, 1954)

Intermetallic compounds of nichium and tantalum with tin have been found. The superconducting

Nb₃Sn at 18°K

VOLUME 6, NUMBER 3

PHYSICAL REVIEW LETTERS

FEBRUARY 1, 1961

 ... and Nb₃Sn exhibited very high in-field J_c (Kunzler, 1961) SUPERCONDUCTIVITY IN Nb₃Sn AT HIGH CURRENT DENSITY IN A MAGNETIC FIELD OF 88 kgauss

J. E. Kunzler, E. Buehler, F. S. L. Hsu, and J. H. Wernick Bell Telephone Laboratories, Murray Hill, New Jersey (Received January 9, 1961)

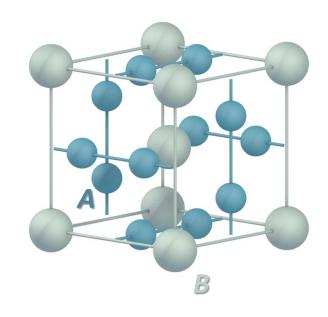
exceeding 100 000 amperes/cm² in magnetic fields as large as 88 kgauss.



An introduction to A15 superconductors

• More than 50 superconductors, 10 of them with $T_c \ge 15 \text{ K}$

	Ti	Zr	V	Nb	Та	Cr	Мо
Al			11.8 K	18.8 K			0.6 K
Ga			16.8 K	20.3 K			0.8 K
In			13.9 K	9.2 K			
TI				9.0 K			
Si			17.1 K	19.0 K			1.7 K
Ge			11.2 K	23.2 K	8.0 K	1.2 K	1.8 K
Sn	5.8 K	0.9 K	7.0 K	18.0 K	8.4 K		
Pb		0.8 K		8.0 K	17.0 K		
As			0.2 K				
Sb	5.8 K		0.8 K	2.2 K			
Bi		3.4 K		4.5 K			
Тс							15.0 K
Re							15.0 K
Ru						3.4 K	10.6 K
Os			5.7 K	1.1 K		4.7 K	12.7 K
Rh			1.0 K	2.6 K	10.0 K	0.3 K	
lr	5.4 K		1.7 K	3.2 K	6.6 K	0.8 K	9.6 K
Pd			0.08 K				
Pt	0.5 K		3.7 K	10.9 K	0.4 K		8.8 K
Au		0.9 K	3.2 K	11.5 K	16.0 K		

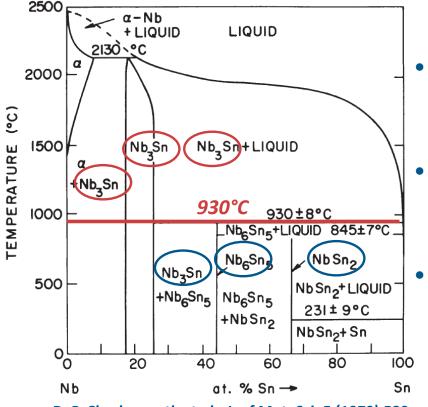


- V₃Ga, Nb₃Sn and Nb₃Al can be produced as practical conductors
- Nb₃Ge held the record for the highest
 T_c (23.2 K) until 1986



The Nb-Sn phase diagram

Implications for practical conductors



- Three stable phases: Nb₃Sn, Nb₆Sn₅ and NbSn₂
- Below 930°C NbSn₂ and Nb₆Sn₅ have a more rapid kinetics of formation
- Above 930°C the only stable phase is Nb₃Sn

D. P. Charlesworth et al., J. of Mat. Sci. <u>5</u> (1970) 580

The practical consequence of this phase diagram is that the reaction to form Nb_3Sn needs to be performed at $T > 930^{\circ}C$



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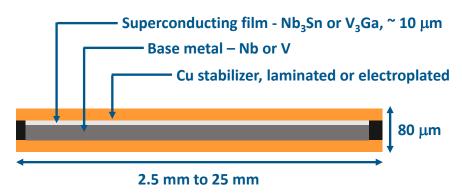
Not only critical current !!

Focus on the electromechanical properties

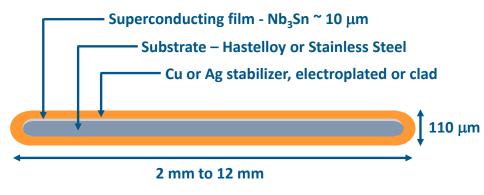


1963-1964: Nb₃Sn coated conductors (!!)

The earliest conductors based on Nb₃Sn



M. G. Benz, IEEE Trans. Mag. 2 (1966) 760



J. Hanak, US Pat. 3420707A (Filed Dec. 28, 1964)

Liquid Diffusion Process

Nb ribbon coated with Sn and heat treated at 900-1200°C for several hours

Developed at General Electric and used in 15 T-class R&W magnets

Vapor Deposition Process

A metallic substrate heated at 1200°C and traveling in a reaction chamber with a flow of gaseous NbCl₄, SnCl₂, H₂ and He

Developed at **RC**

A similar process is used for producing SRF cavities for accelerators based on Nb₃Sn

S. Posen and D. L. Hall, SUST 30 (2017) 033004



1966-1969: A small addition of Cu...

The Bronze Process and the development of multifilamentary wires

K. Tachikawa and his co-workers at NRIM, Tokyo, developed V_3 Ga tapes with very high in-field current by the liquid diffusion process

Tachikawa discovered that Cu was acting as a catalyst for the formation of the A15 phase, making possible the synthesis of V_3 Ga at lower temperatures

K. Tachikawa, Y. Tanaka and S. Fukuda, Japan Pat. 0670619 (Filed June 25, 1966)

K. Tachikawa and Y. Tanaka, Jap. J. Applied Physics 6 (1967) 782



Prof. Kyoji TACHIKAWA

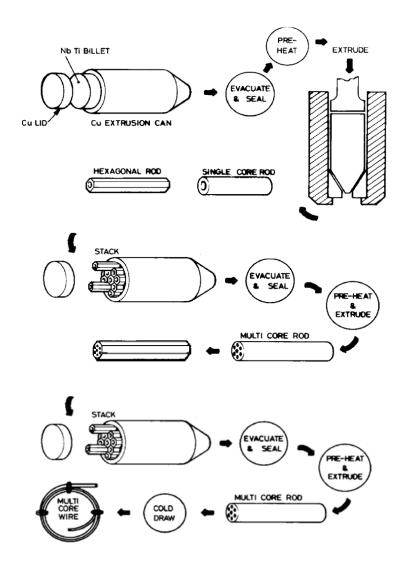
Researcher in UK and US came at the same conclusion almost at the same time

The addition of Cu lowers also the formation temperature of Nb₃Sn from above 930°C to more practical values of ~650°C

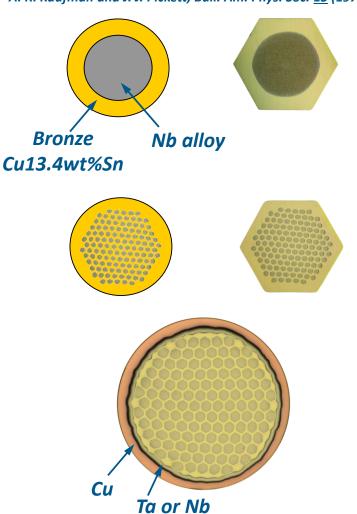
The idea was extended to the formation of Nb₃Sn by solid state diffusion at the interface of Nb and Cu-Sn alloy (bronze). This principle was used for the development of the first multifilamentary Nb₃Sn wires



The Bronze Process for multifilamentary Nb₃Sn wires



E. W. Howlett, Great Britain Pat. 52, 623/69 (Filed Oct. 27, 1969)
A. R. Kaufman and J. J. Pickett, Bull. Am. Phys. Soc. 15 (1970) 833





Industrial fabrication of multifilamentary Nb₃Sn wires Three technologies developed at industrial scale

The main difference comes from the type of Sn source



Bronze Process

Bronze is the Sn source, limited by the solubility of Sn in Cu



Internal Sn Diffusion Process

A metallic Sn rod is inserted in the subelement core



Powder-In-Tube (PIT) method

Each subelement is a Nb-alloy tube filled with NbSn₂ and Sn powders

Presently produced by BRUKER













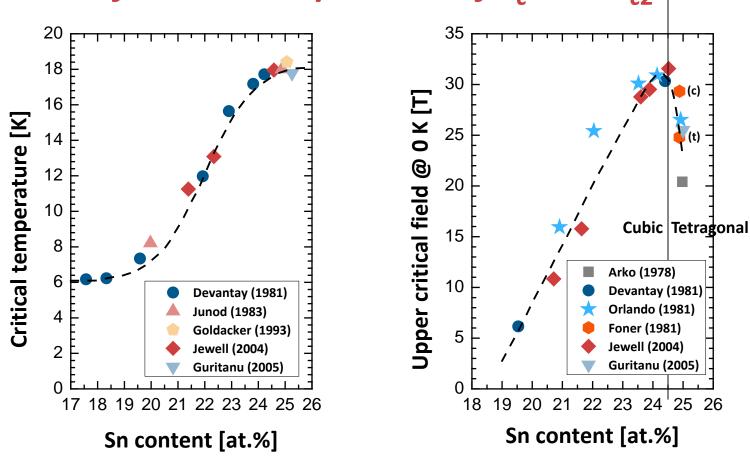


What controls the performance of Nb₃Sn

- Influence of Sn composition on T_c and B_{c2}
- Doping to further enhance B_{c2}
- Grain boundaries and vortex pinning







Adapted from R. Flükiger et al., Cryogenics 48 (2008) 293

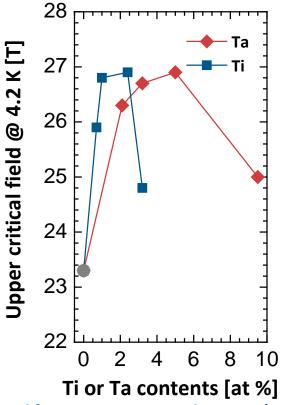
 $Nb_{3+x}Sn_{1-x}$ is superconducting also when deviates from stoichiometry



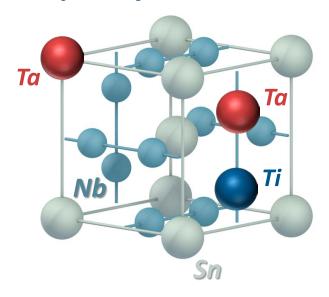


Doping to further enhance B_{c2}

The additions of Ta and Ti are particularly beneficial



Adapted from M. Suenaga et al., JAP 59 (1986) 840



From EXAFS investigations

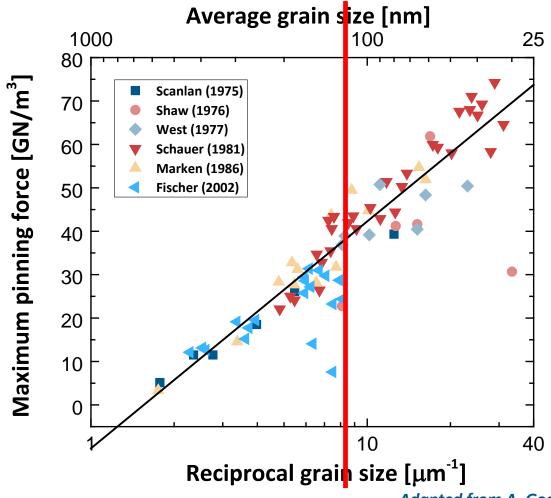
- Ti substitutes Nb
- Ta substitutes both Nb and Sn

S. M. Heald et al., Sci. Rep. <u>8</u> (2018) 4798

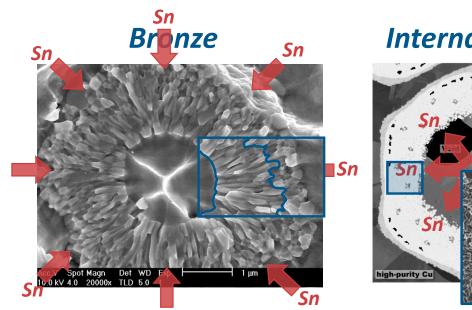
All industrial Nb₃Sn wires are doped either with Ti or with Ta



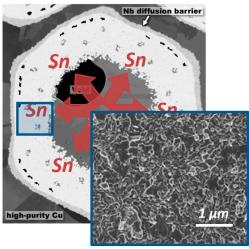
Vortex pinning at the grain boundaries in Nb₃Sn Impede vortex motion to increase J_c



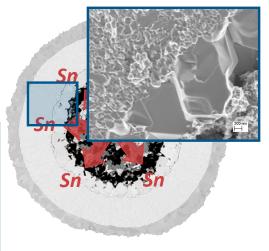
Composition and microstructure in industrial wires



Internal Sn



Powder-In-Tube



Filament size ~5 μm

Outer region Equiaxed grains ~ 150 nm Composition 21-25 at.% Sn

Inner region Columnar grains ~ 400 nm Composition 18-21 at.% Sn

Subelement size ~50 μm

Almost everywhere *Fine grains* ~ 100-150 nm Composition 23-25 at.% Sn

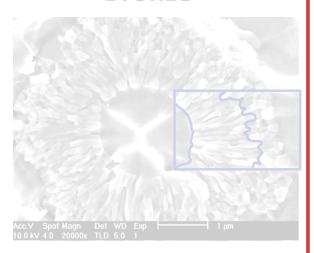
Subelement size ~50 μm

Outer region Fine grains ~ 150 nm Composition 23-24 at.% Sn

Inner region Large grains ~ 1 μm Composition 25 at.% Sn

Composition and microstructure in industrial wires

Bronze

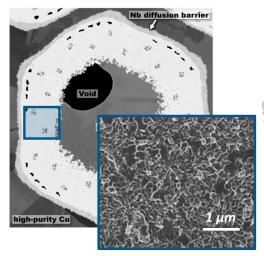


Filament size ~5 μm

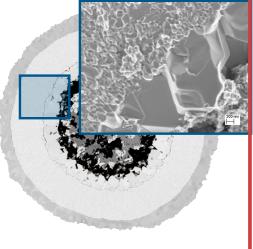
Outer region
Equiaxed grains ~ 150 nm
Composition 21-25 at.% Sn

Inner region
Columnar grains ~ 400 nm
Composition 18-21 at.% Sn

Internal Sn



Powder-In-Tube



Subelement size ~50 μm

Almost everywhere
Fine grains ~ 100-150 nm
Composition 23-25 at.% Sn

Subelement size ~50 μm

Outer region
Fine grains ~ 150 nm
Composition 23-24 at.% Sn

High performance Nb₃Sn wires

Composition 25 at.% Sn



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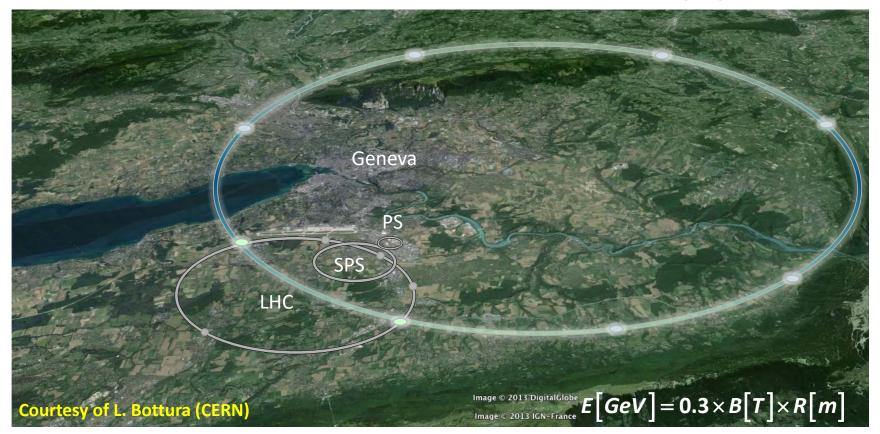
Not only critical current !!

Focus on the electromechanical properties

The Future Circular Collider Study





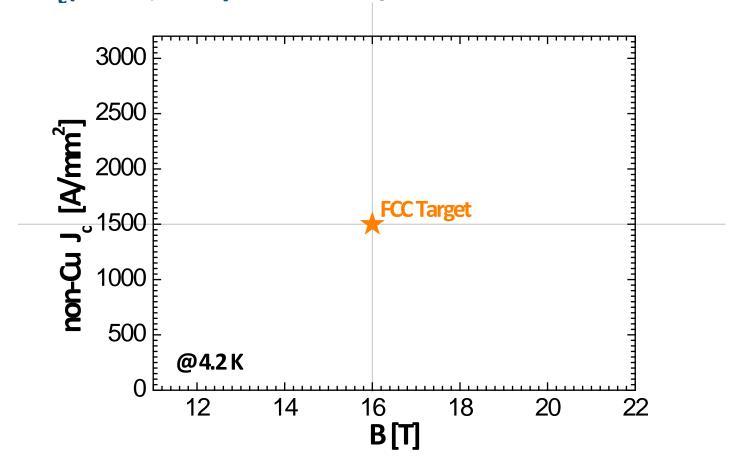


LHC 27 km, 8.33 T 14 TeV (c.o.m.) 1300 tons NbTi



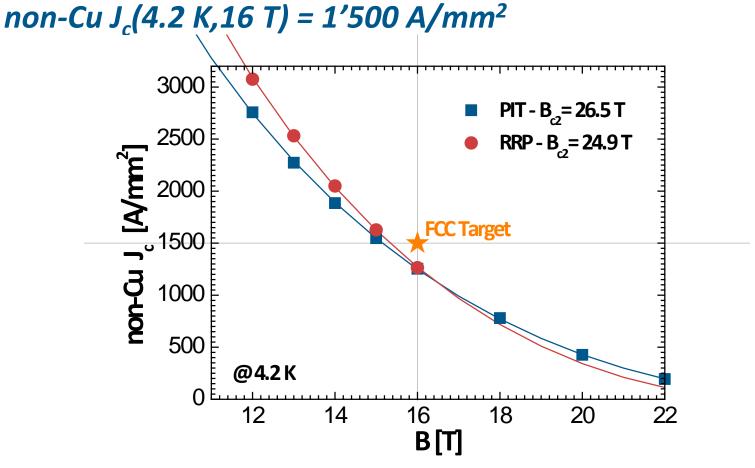


Performance target for the 16 T FCC dipoles non-Cu $J_c(4.2 \text{ K}, 16 \text{ T}) = 1'500 \text{ A/mm}^2$





Performance target for the 16 T FCC dipoles

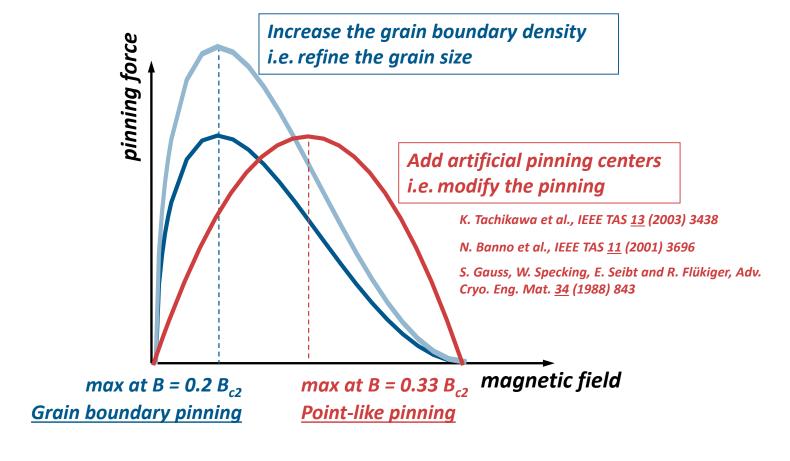


J. Parrell et al., AIP Conf. Proc. <u>711</u> (2004) 369

T. Boutboul et al., IEEE TASC <u>19</u> (2009) 2564



Strategies to increase the in-field critical current density = to enhance the pinning at high field



... but how to obtain grain refinement?



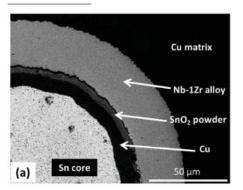
Grain refinement by Internal Oxidation in Nb₂Sn

Idea from Benz (1968) to form fine precipitates in Nb to impede the Nb₃Sn grain growth M. G. Benz, Trans. Metall. Soc. AIME, <u>242</u> (1968) 1067-1070

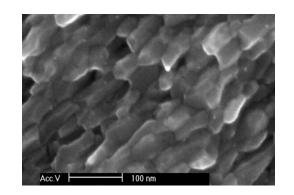
Use of a Nb-Zr alloy: Zr has stronger affinity to oxygen than Nb

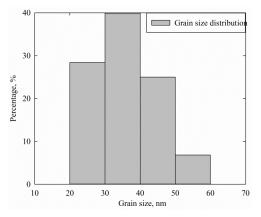
Oxygen supply added to the composite: oxidation of Zr and formation

THE OHIO STATE of nano-ZrO₂ UNIVERSITY



X. Xu et al., APL 104 (2014) 082602 X. Xu et al., Adv. Mat. 27 (2015) 1346





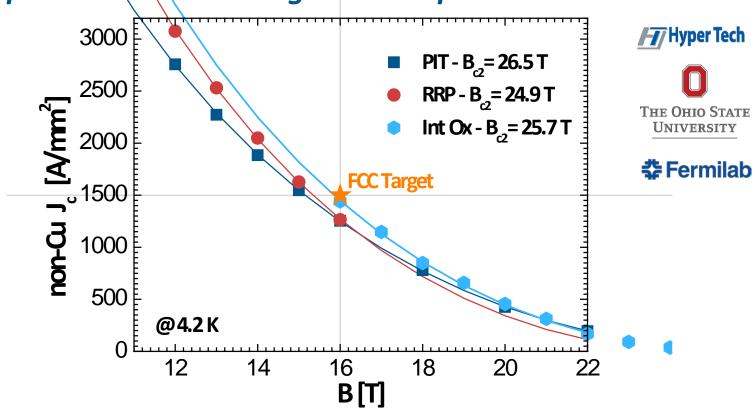
Average grain size is reduced down to ~ 50 nm in binary Nb₂Sn

Recent advances on Ta-doped Nb₂Sn 48 filaments, Zr addition, grain size 70-80 nm X. Xu et al., SuST 32 (2019) 02LT01

monofilaments, Hf addition, grain size 50-70 nm grain refinement without additional oxygen source S. Balachandran et al., SuST 32 (2019) 044006



Performance target non-Cu $J_c(4.2K,16\ T) = 1500\ A/mm^2$ First report on a wire hitting the FCC specs



X. Xu et al., arXiv 1903.08121 (2019)

J. Parrell et al., AIP Conf. Proc. <u>711</u> (2004) 369

T. Boutboul et al., IEEE TASC <u>19</u> (2009) 2564



Advances on Internal Oxidation at

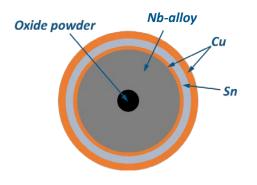


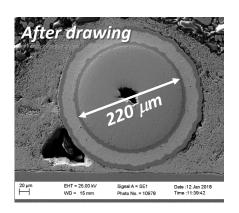
Activity funded in the frame of a collaboration with











Nb-alloy Nb-7.5wt%Ta (REF.) Nb-1wt%Zr Nb-7.5wt%Ta-1wt%Zr Nb-7.5wt%Ta-2wt%Zr

 \emptyset 220 μ m wires of Nb-alloy were prepared by cold deformation of \emptyset 12 mm rod with nano-sized powders compacted in a central hole

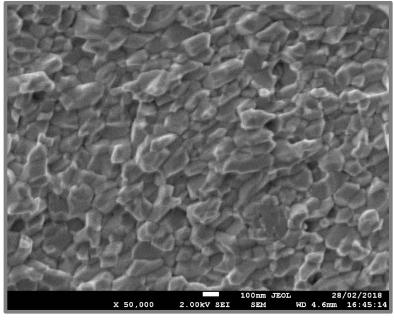
Nb alloy wire was then electroplated successively with: Cu, Sn, Cu

Evaluated SnO₂ and CuO as oxygen sources, for these reasons

- high Gibbs free energy of formation
- low hardness that would make it compatible with wire fabrication
- the metal resulting from the reduction not affecting superconductivity



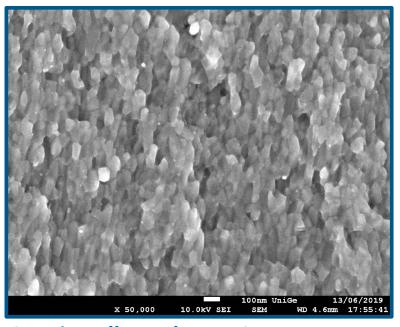
Grain morphology of Nb₃Sn



Starting alloy: Nb7.5Ta

no oxygen source

HT: 650°C/200h



Starting alloy: Nb7.5Ta2Zr

oxygen source: SnO₂

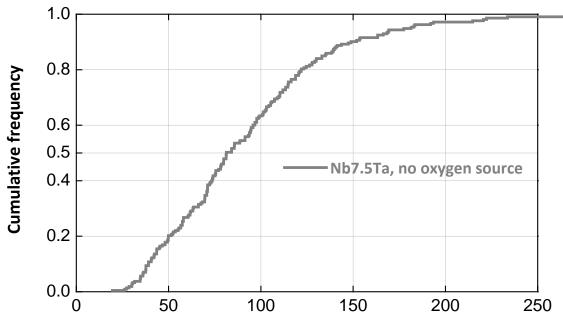
HT: 650°C/200h

Significantly smaller grains in the samples based on Zr alloys and oxygen source Elongated grains



Grain size distribution

Grain size distribution in the short axis direction



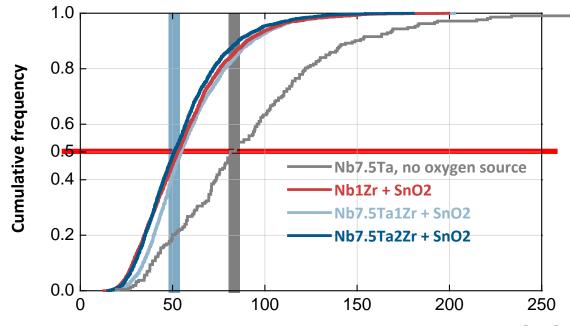
Grain boundary interept distance in the short axis direction [nm]

Linear intercept method used to obtain information regarding the grain size distribution



Grain size distribution

Grain size distribution in the short axis direction



Grain boundary interept distance in the short axis direction [nm]

Linear intercept method used to obtain information regarding the grain size distribution

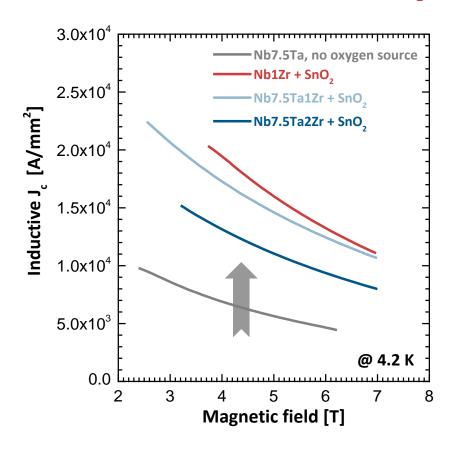
Median sizes

- Nb7.5Ta based samples ~80 nm
 - Zr containing samples ~50 nm

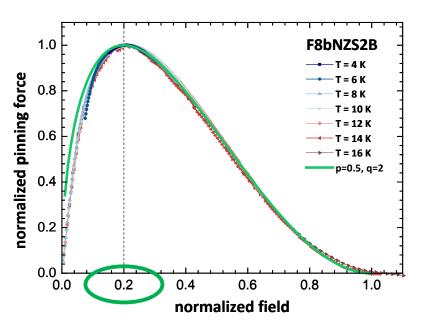
In the long axis direction the median grain size decreases from ~120 nm down to ~85 nm



Critical current density and pinning



The critical current density is strongly enhanced in the presence of Zr and O



The maximum of f_p stays close to 0.2 for all our samples, regardless of alloy, Zr content and oxygen source.

The main vortex pinning mechanism remains the same: grain boundary pinning

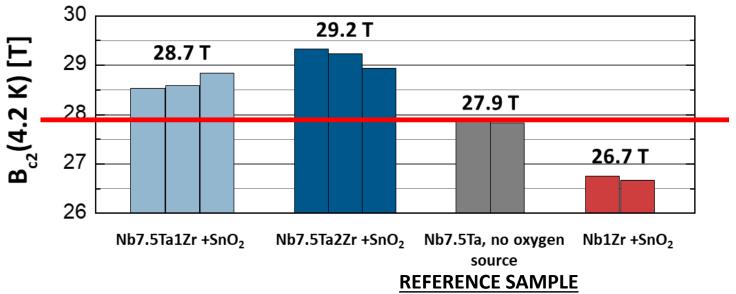


Upper critical fields at 4.2 K

Critical fields from R(B) performed at LNCMI Grenoble under magnetic fields up to 33 T







The combined presence of Ta and Zr further increases the upper critical field up to \sim 29 T , i.e. to higher values than obtained for Nb7.5Ta

This is showing that it is possible to further improve the field performance of Nb₃Sn wires



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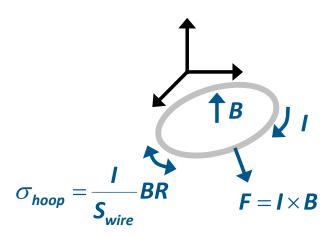


Not only critical current !!

Focus on the electromechanical properties



Electromagnetic forces in a magnet

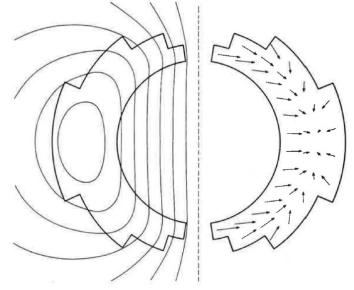


Hoop stress levels well above 100 MPa are common

Stress increases proportionally to field, current density and magnet size

In real magnets conductors are exposed to 3D stresses that combine axial tension and transverse compression



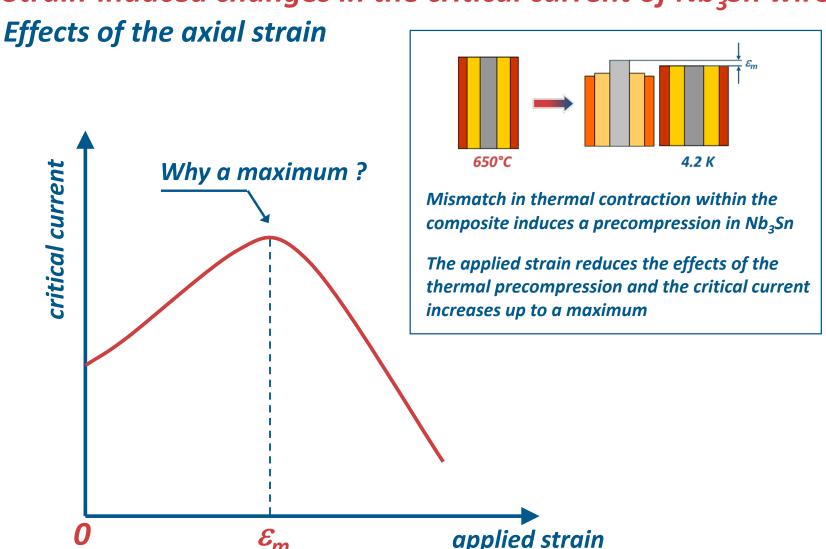


magnetic lines of force

vectors of electromagnetic force per unit volume

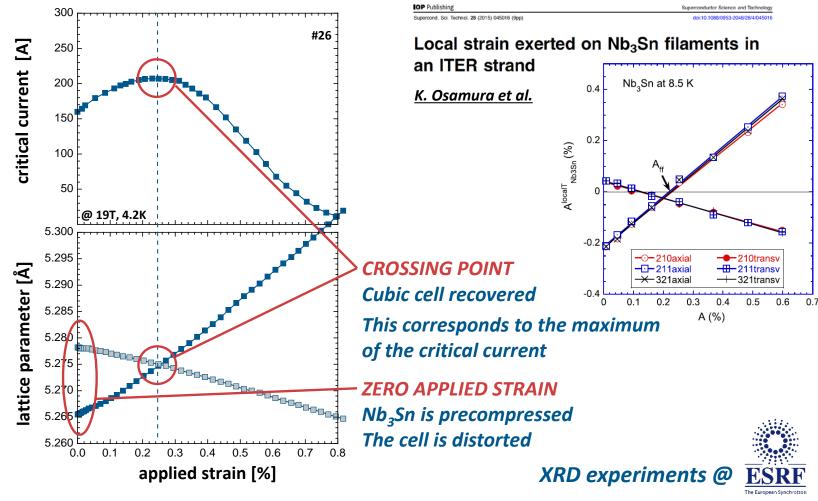


Strain-induced changes in the critical current of Nb₃Sn wires





Lattice parameters and I under axial strain



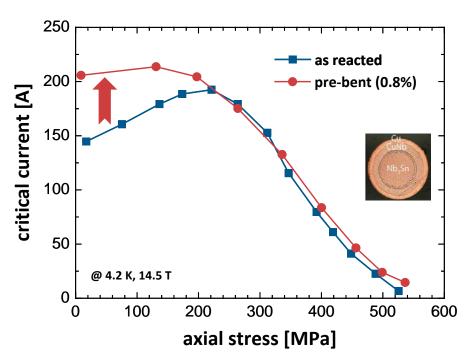
Tests on a Bronze Route wire

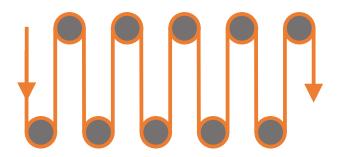
C. Scheuerlein et al., IEEE TASC 19 (2009) 2653 L. Muzzi et al., SUST 25 (2012) 054006



Prebending to remove the precompressionCuNb-reinforced Nb₃Sn wires for the 25 T cryogen-free magnet @







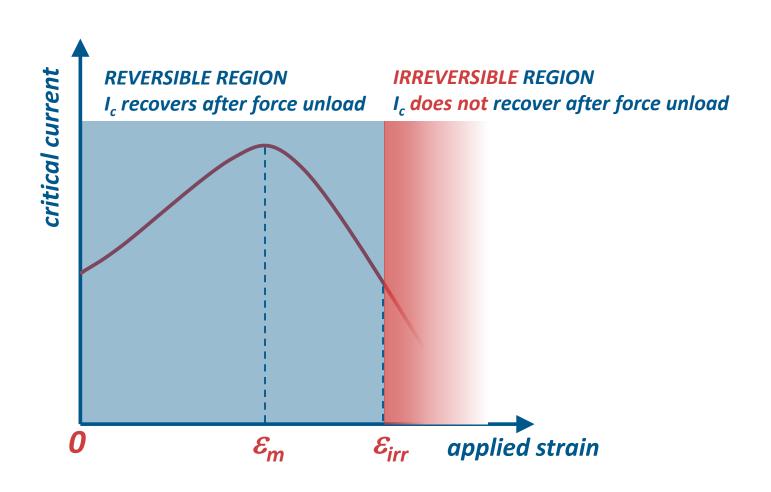
Repeated bending at room temperature after the reaction heat treatment

Adapted from H. Oguro et al., IEEE TASC <u>24</u> (2014) 8401004

The prebending leads to a precompression release in Nb₃Sn through the plastic deformation of CuNb \Rightarrow significant improvement of I_c at low applied stress



Strain-induced changes in the critical current of Nb₃Sn wires Effects of the axial strain

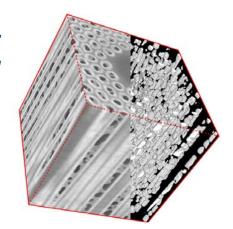




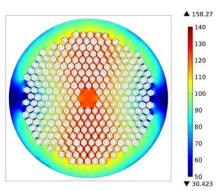
Irreversible degradation phenomena

Two mechanisms govern the irreversible degradation of the critical current

 Formation of cracks in the Nb₃Sn filaments due, for instance, to the stress concentration at the voids formed during the reaction heat treatment



 Plastic deformation of the matrix and residual stress on the Nb₃Sn filaments.





Which mechanism dominates the irreversible degradation of the critical current?

Analysis of the phenomenon in two load geometries

1 - Axial tension and the role of cracks at the voids

2 – Transverse compression, plastic deformation of the matrix and residual stress on Nb₃Sn

Analysis of the phenomenon in two load geometries

1 - Axial tension and the role of cracks at the voids

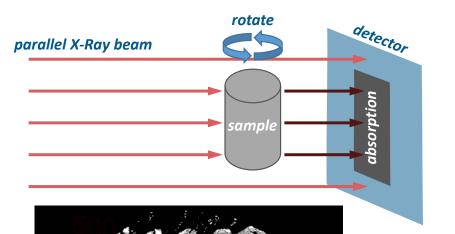
2 – Transverse compression, plastic deformation of the matrix and residual stress on Nb₃Sn



Voids detection in Nb₃Sn wires



X-ray microtomography reconstruction @ ESRF Grenoble



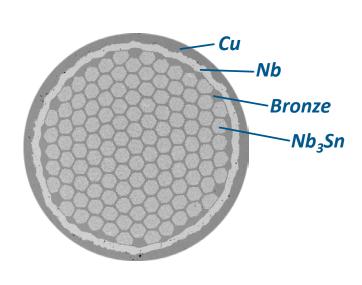
- X-ray photon energy = 89 keV
- 360° rotation of the sample
- 30'000 projections
- 2560 x 2160 pixels
- 0.57 μm/pixel resolution

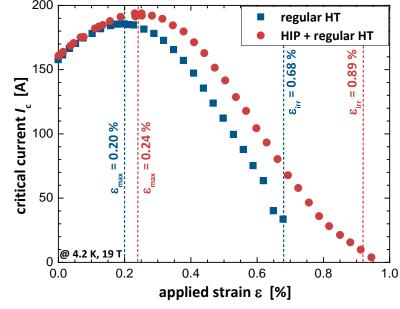


C. Barth et al., Sci. Rep. 8 (2018) 6589



A case study on Bronze Nb₃Sn wires





manufacturer	UNIVERSITÉ DE GENÈVE FACULTÉ DES SCIENCES		
wire diameter	1.25 mm		
# of filaments	121 x 121		
filament size	4.5 μm		

Regular HT:
$$600^{\circ}$$
C/ $100h + 670^{\circ}$ / $150h$

$$\varepsilon_{c} = \varepsilon_{irr} - \varepsilon_{max} = 0.48 \%$$
HIP 550° C/ $1h$ / $200MPa + Regular HT$

$$\varepsilon_{c} = \varepsilon_{irr} - \varepsilon_{max} = 0.65 \%$$

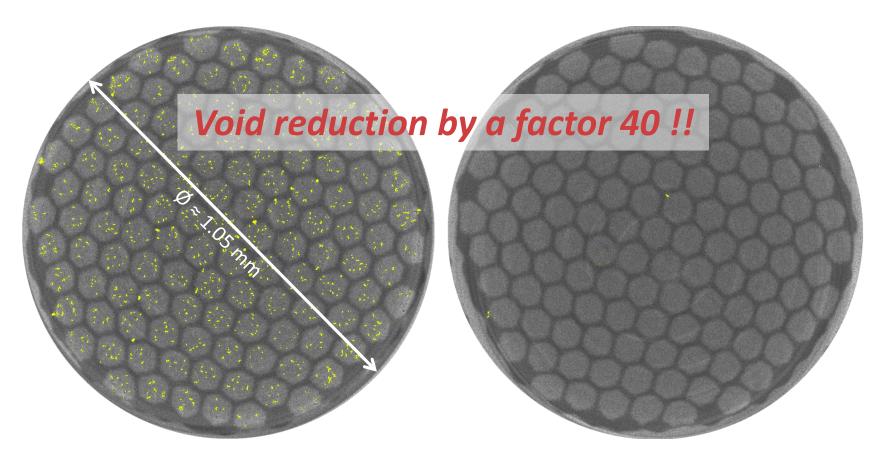
With HIP treatment ε_c increases by +0.17 %



Bronze wire: Void detection

Without HIP treatment Void fraction = 2.1 %

With HIP treatment Void fraction = 0.05 %





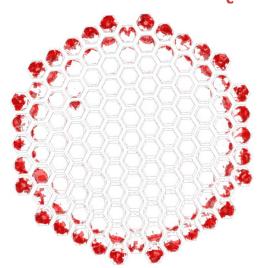
Statistical FEM analysis

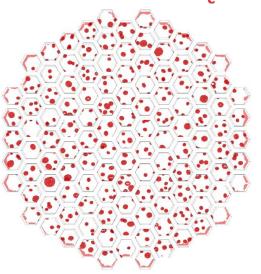
- The experimental ε_c corresponds to an irreversible reduction of I_c by 5%
- Working hypothesis: 5% of I_c degradation \equiv damage in 5% of the filaments

Wire <u>without</u> voids

SIMULATION done at $\varepsilon_c = 0.65\%$

Wire <u>with</u> voids SIMULATION done at $\varepsilon_c = 0.50\%$



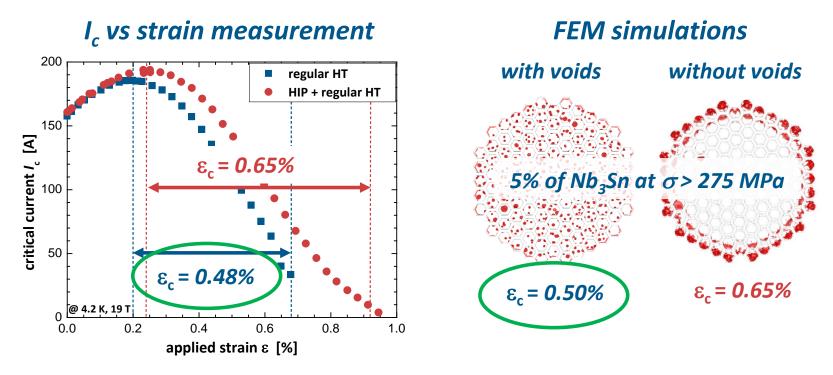


The red regions represent the 5% of the Nb₃Sn volume at the highest stress Here the red regions are at $\sigma \ge$ 275 MPa, which is the critical stress



Irreversible limit in the presence of voids

Experiment vs Prediction



The simulations predict the correct value of ϵ_c when voids are introduced Changes in the voids correlate quantitatively with the changes in the electromechanical limits



Analysis of the phenomenon in two load geometries

1 - Axial tension and the role of cracks at the voids

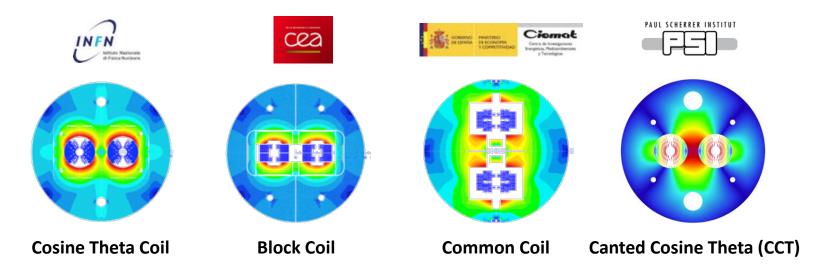
2 – Transverse compression, plastic deformation of the matrix and residual stress on Nb₃Sn



Design options for the 16 T FCC dipoles



h2020 EuroCirCol WP5, started in 2015
WP leader: Davide TOMMASINI, CERN



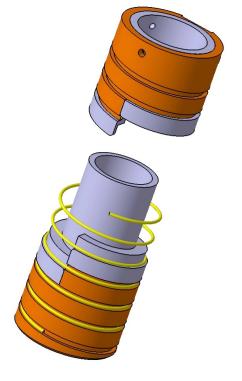
All designs for the 16 T dipoles share a peak in transverse stress at operation of 150-200 MPa

Nb₃Sn Rutherford cable for HL-LHC, 40 strands

Are the Nb₃Sn wires in the Rutherford cables able to withstand such a high stress level? Which degradation is tolerable?

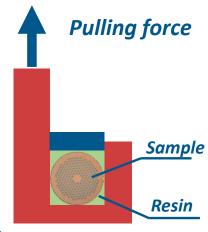


I_c vs. transverse stress on a single wire The WASP concept





4-WALL + impregnation

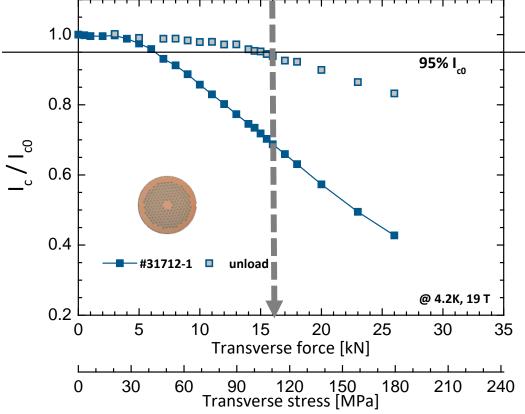


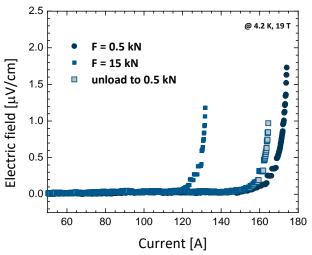
- B. Seeber et al., IEEE TASC 17 (2007) 2643
- G. Mondonico et al., SuST 25 (2012) 115002



I_c vs. transverse stress Powder-In-Tube Nb₃Sn wire + epoxy L

# of subelements	Cu/non-Cu	Diameter	I _c (16 T)
192	1.22	1.0 mm	340 A





The irreversible limit is defined at the force level leading to a 95% recovery of the initial I_c after unload

Here

$$F_{irr}(B=19T) = 16 \text{ kN}$$

The corresponding irreversible stress limit is

$$\sigma_{irr}(B=19T) = 110 \text{ MPa}$$

where

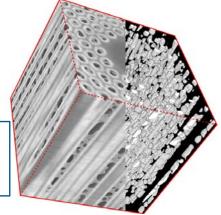
$$Stress = \frac{Force}{groove\ length\ \times groove\ width}$$

Irreversible degradation phenomena

Two mechanisms govern the irreversible degradation of the critical current

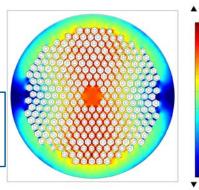
 Formation of cracks in the Nb₃Sn filaments due, for instance, to the stress concentration at the voids formed during the reaction heat treatment

Cracks generate a reduction of the current carrying cross section $\Rightarrow I_c^{unload}/I_{c0}$ is independent of the magnetic field

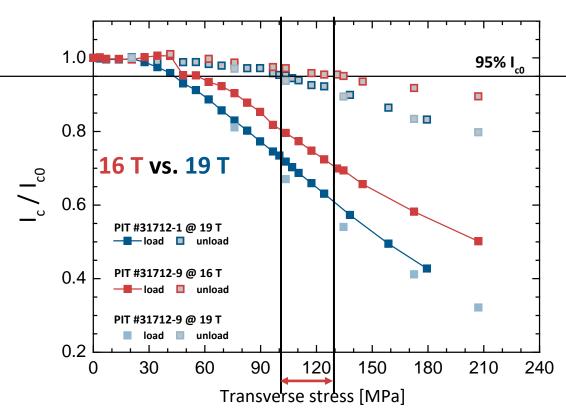


• Plastic deformation of the matrix and residual stress on the Nb₃Sn filaments.

Residual stress induces a permanent reduction of B_{c2} after unload $\Rightarrow I_c^{unload}/I_{c0}$ depends on of the magnetic field



Field dependence of the irreversible stress limit



I_c^{unload}/I_{c0} depends clearly on of the magnetic field!!

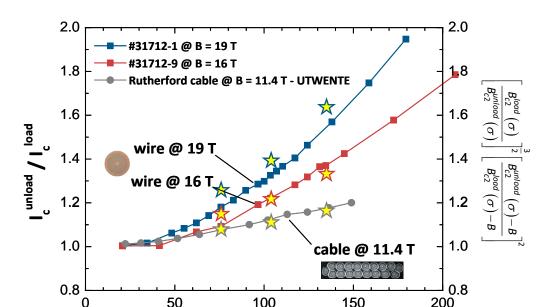
 σ_{irr} at 16 T increases by ~20 MPa compared to 19 T

Residual stress on Nb₃Sn due to the plastic deformation of the matrix dominates the irreversible degradation

 $\Delta \sigma_{irr}$ (19 T \rightarrow 16 T) \approx +20 MPa



Field dependence of the irreversible stress limit



A simple model, based only on the effects of residual stress, reproduces the experimental dependences on field and stress

It proves also that the experiments performed on the single wire are consistent with those on cables

Transverse stress [MPa]
$$\frac{I_c^{unload}}{I_c^{load}}(B,\sigma) = \left[\frac{B_{c2}^{load}(\sigma)}{B_{c2}^{unload}(\sigma)}\right]^{\frac{3}{2}} \left[\frac{B_{c2}^{unload}(\sigma) - B}{B_{c2}^{load}(\sigma) - B}\right]^{2}$$



To conclude...

65 years after the discovery there is a revamp of interest for Nb₃Sn

In particular, the FCC study is driving Nb₃Sn towards its ultimate performance

- material with refined grains and high B_{c2} is produced in several laboratories around the world
- practical solutions to implement this technologyin industrial wires are being developed

But there is still work to do also on other properties of the conductors, e.g. the tolerance to stress

- Developing tailored heat treatments to control size and distribution of the voids in the filaments
- Optimizing the filament layout in the wire by using FEM, to predict the redistribution of mechanical loads between superconductor and matrix

Not at the exclusive benefit of high energy physics, but also for fusion (DEMO), NMR and medical accelerators

