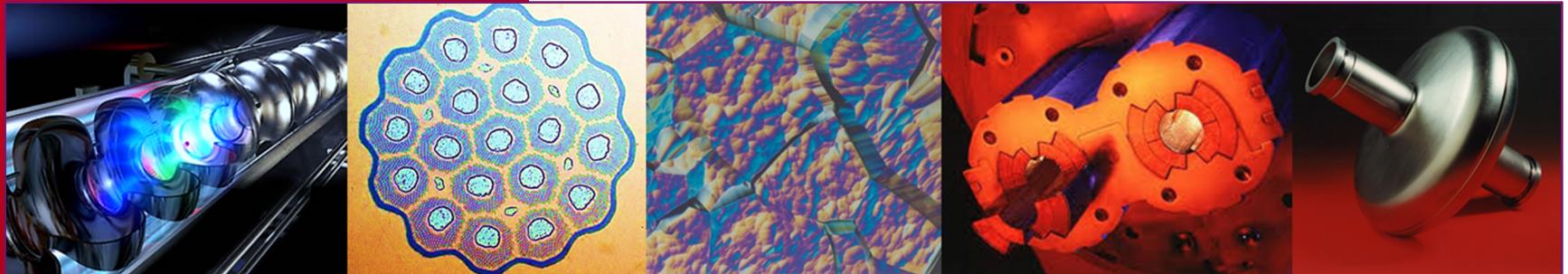


DE LA RECHERCHE À L'INDUSTRIE



MATERIALS FOR SUPERCONDUCTING ACCELERATORS: BEYOND BULK Nb



www.cea.fr

SRF 2019 Tutorials

C.Z. Antoine

+ some material gathered by A.M. Valante-Feliciano

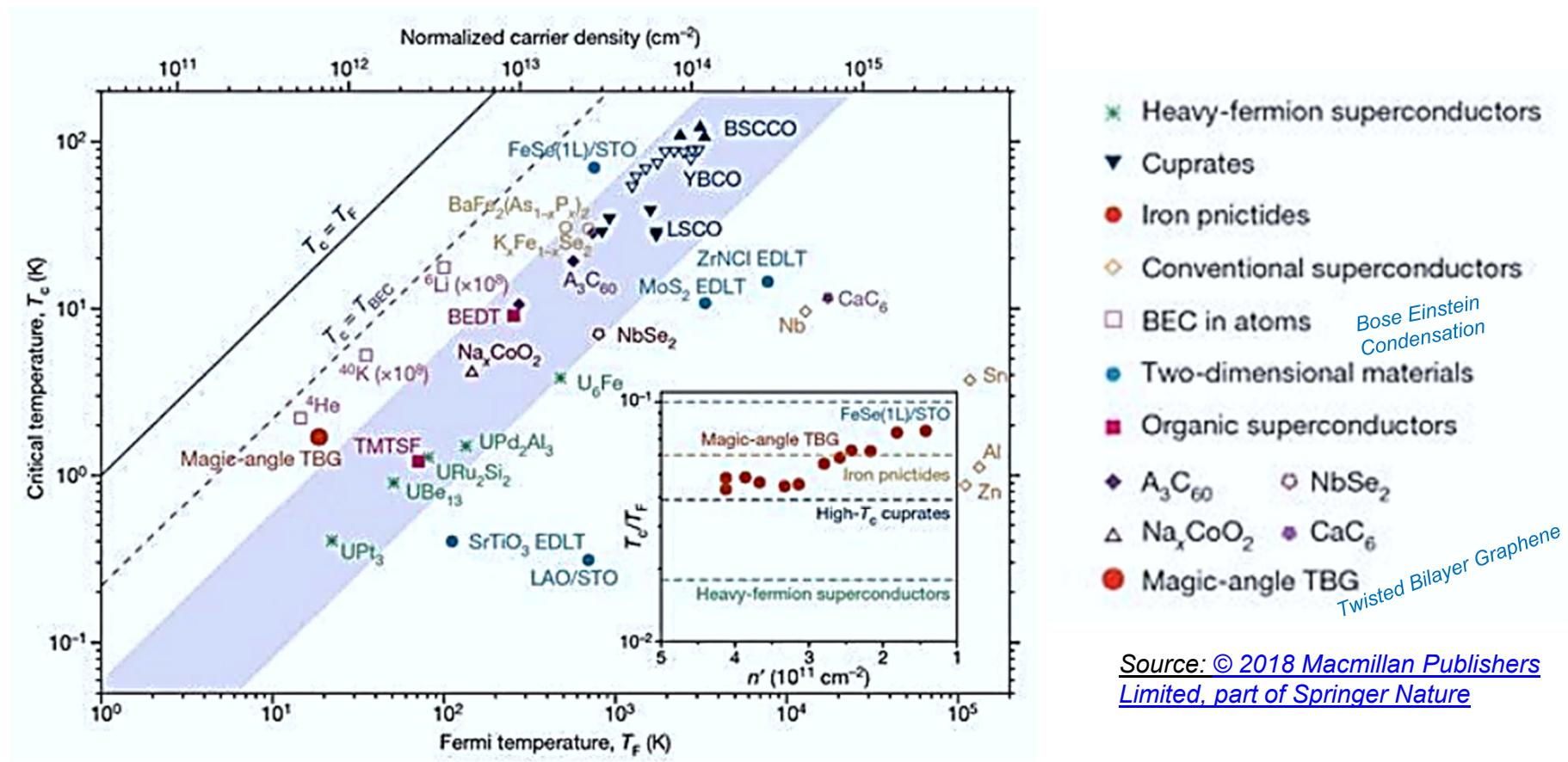


CHOICE CRITERIA ?

THOUSANDS OF SUPERCONDUCTORS ...



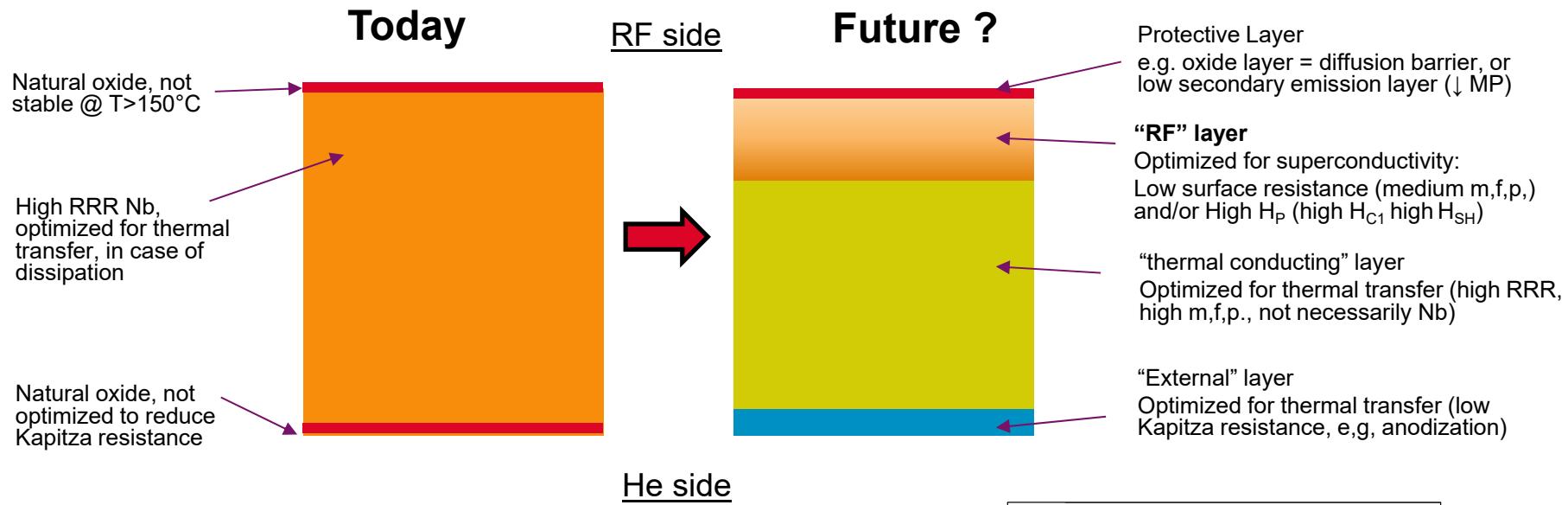
Thousands of SC exist, ~10 are currently used for applications, only bulk Nb works well for SRF !!!



IDEAL SRF MATERIAL: TAILORED FOR APPS

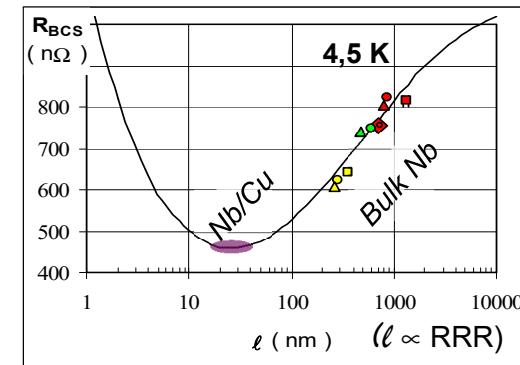


High RRR not required for superconductivity
but for thermal stabilization in case of defects



- **"RF" layer optimized for superconductivity:**
 - Low surface resistance (medium m.f.p.)
 - and/or*
 - High H_P (high H_{C1} or high H_{SH})

*Depends on the application



ULTIMATE LIMITS IN SRF-1

Niobium superconducting radiofrequency cavities

■ Performances

- $E_{acc} \propto H_{RF}$
- $Q_0 (\propto 1/R_S) \propto T_C \Rightarrow \text{Nb}_3\text{Sn}, \text{MgB}_2, \text{NbN} \dots$ (but not YBCO)
- Limit = magnetic transition of the SC material @ H_{peak}

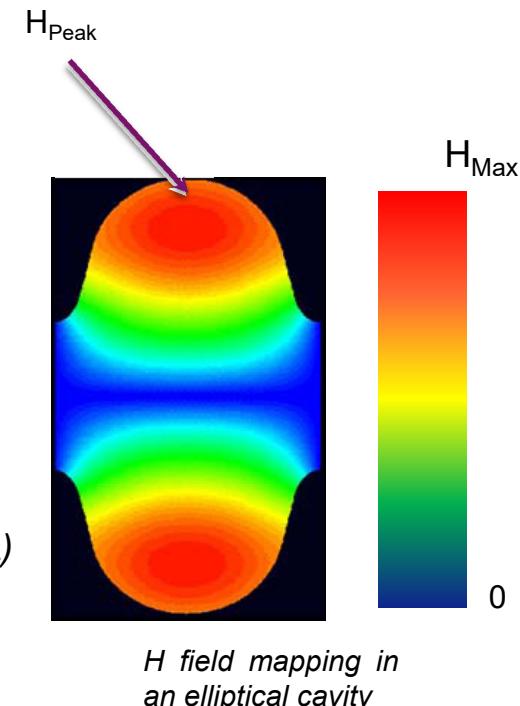
■ Superconductivity only needed inside :

- Thickness $\sim 10 \lambda, \sim < 1 \mu\text{m} \Rightarrow$ thin films (*onto a thermally conductive, mechanically resistant material, e.g. Cu*)

■ Today :

- Thin films exhibit too many defects
- Only Bulk Nb has high SRF performances (*high Q_0 and high E_{acc}*)

■ Issues : getting “defect free” superconductors



(Yes but not all defects are detrimental... See doping !)

■ SC phase diagram

- All SC applications except SRF: mixed state w. vortex
 - Vortices dissipate in RF !
- SRF => Meissner state mandatory !

■ Limit ?

- H_{C1} = limit Meissner/mixed state
 - Nb: highest H_{C1} (180 mT)

Or

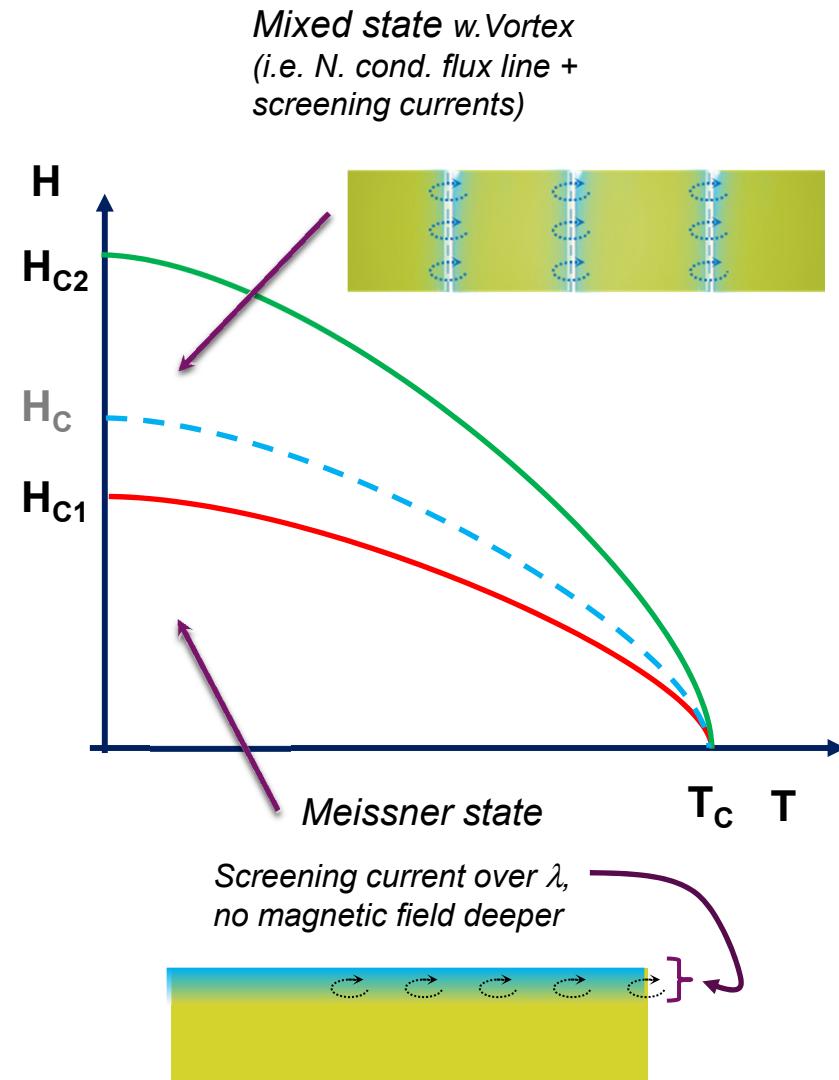
- H_{SH} "Superheating field": Metastable state favored by H // to surface
 - Difficult to get in real life !



■ Surface resistance:

$$R_{BCS} = A(\lambda_L^4, \xi_F, \ell, \sqrt{\rho_n}) \frac{\omega^2}{T} e^{-\Delta/kT}$$

- High T_c is better
- $T \ll T_c$ is better ($e^{-\Delta/kT}$)
- Metallic character in NC state is better (ρ_n)
- Dirty is better than high RRR (ℓ) ? (e.g, doping, but more complex than that !)

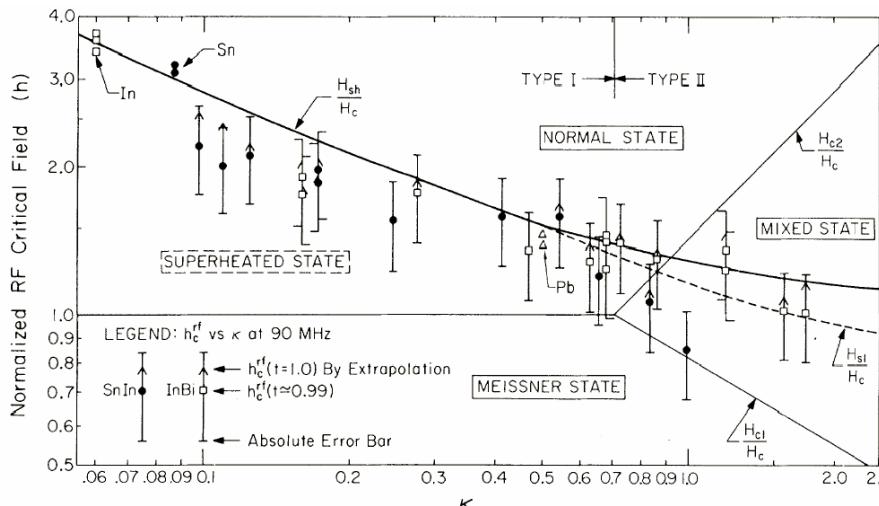


SUPERHEATING FIELD



Metastable Meissner state above H_{c1}

- observed close to T_c in DC/AC



Physical Origin

- normal zone nucleation $\sim 10^{-6}$ s ?
- RF $\sim 10^{-9}$ s *

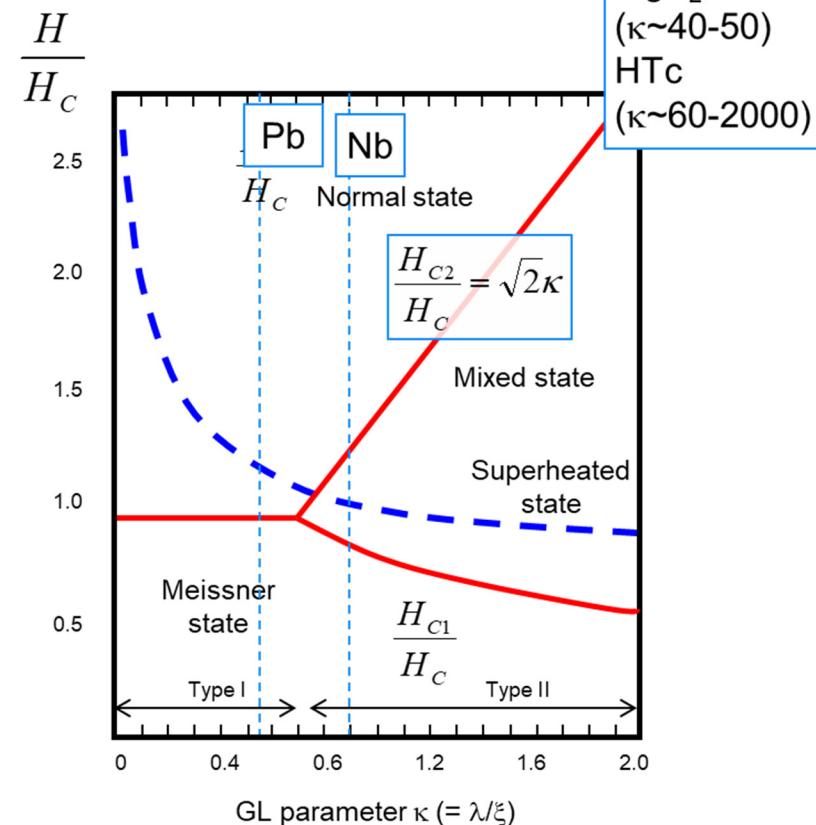
but in fact

- 1! vortex penetration $\sim 10^{-13}$ s **
- SH state favored by $H//$ surface (BL barrier) ***

* H. Padamsee, J. Knobloch, and T. Hays, "RF superconductivity for accelerators". 1998: J. Wiley & son.

** Gurevich, Brandt, Smethna...

*** C. P. Bean and J. D. Livingston, Phys. Rev. Lett. 12, 14 (1964).



$H_{SH} \sim 1,2.H_c$ pour $\kappa \sim 1$
 $H_{SH} \sim 0,75.H_c$ pour $\kappa \gg 1$
(Thermodynamics)

SUPERCONDUCTORS FOR SRF ?



Material	T _C (K)	ρ _n (μΩcm)	μ ₀ H _{C1} (mT)*	μ ₀ H _{C2} (mT)*	μ ₀ H _C (mT)*	μ ₀ H _{SH} (mT)*	λ (nm)*	ξ (nm)*	Δ (meV)	Type
Pb	7,1		n.a.	n.a.	80		48			I
Nb	9,22	2	170	400	200	219	40	28	1.5	II
NbN	17,1	70	20	15 000	230	214	200-350	<5	2.6	II
NbTi			4-13	>11 000	100-200	80-160	210-420	5,4		
NbTiN	17,3	35	30				150-200	<5	2.8	II
Nb ₃ Sn	18,3	20	50	30 000	540	425	80-100	<5	<5	II
Mo ₃ Re	15	10-30	30	3 500	430	170	140			II
MgB ₂	39	0.1-10	30	3 500	430	170	140	5	2.3/7.2	II- 2gaps**
2H-NbSe ₂	7,1	68	13	2680-15000	120	95	100-160	8-10		II- 2gaps**
YBCO/Cuprates	93		10	100 000	1400	1050	150	0,03/2		d-wave**
Pnictides Ba _{0.6} K _{0.4} Fe ₂ As ₂	38		30	>50000	900	756	200	2	10-20	s/d wave**

* @ 0K

** 2D => orientation problems ?

VORTEX PENETRATION WITH $B \parallel$

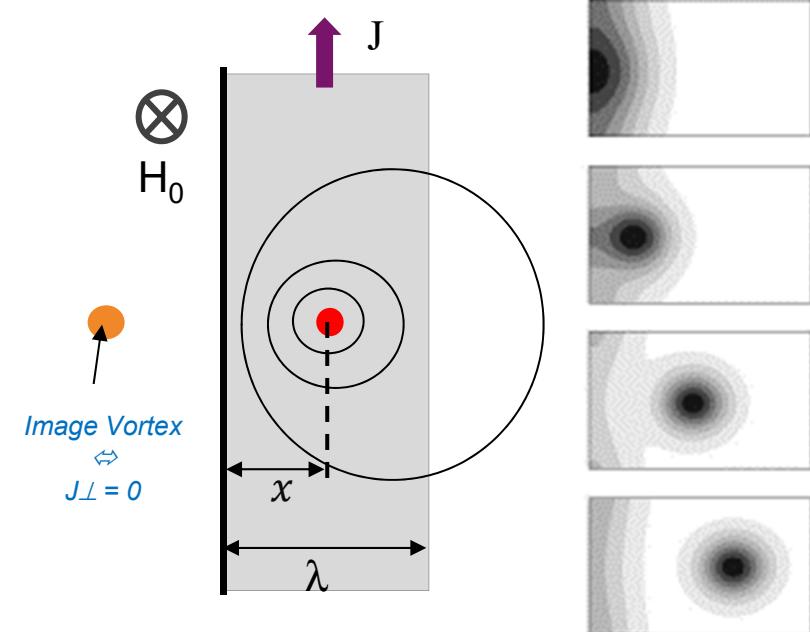
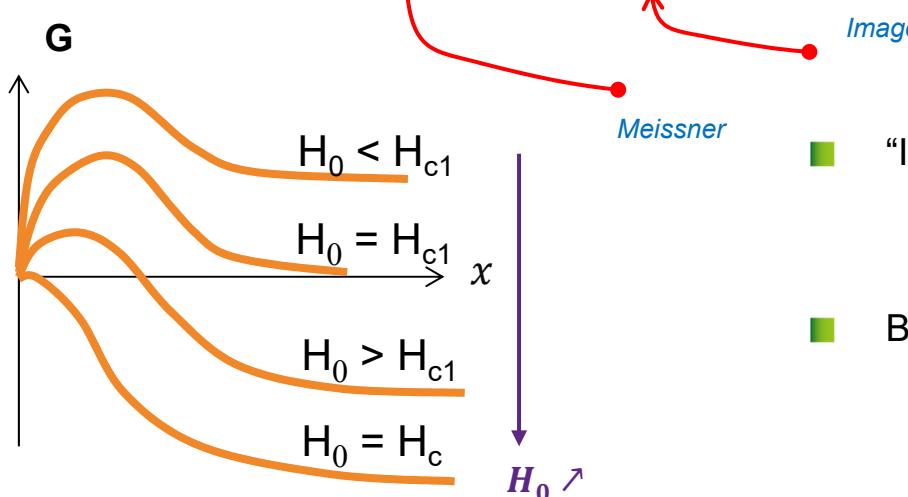


Surface barrier

(Bean & Livingston, 1964)

- Boundary condition. ($J_{\perp} = 0$) \equiv “image” vortices
 - Supercurrent tends to push V_x inside
 - Image antivortex tends to pull it out
- Before entering the material V_x have to cross a surface barrier:
 - V_x thermodynamic Potential :

$$G(x) = \phi_0 \left[H_0 e^{-x/\lambda} - H_v(2x) + H_{c1} - H_0 \right]$$

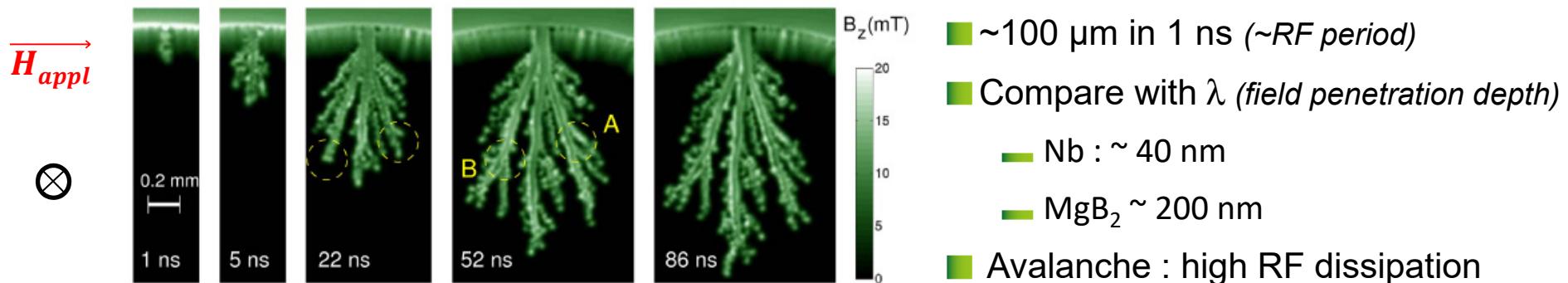


- “Ideal surface”
 - Barrier disappears only at $H_{SH} \sim H_C > H_{c1}$
 - Rationale used to predict SRF limits
- BUT
 - If \exists localized defect w.: $H_C^{Local} \ll H_C^{bulk}$ (or $T_C^{Local} \ll T_C^{bulk}$) \Rightarrow early penetration of 1 or several Vx there

WHAT IS THE ACTUAL LIMIT ($H_p/H_{C1}/H_{SH}$) ?



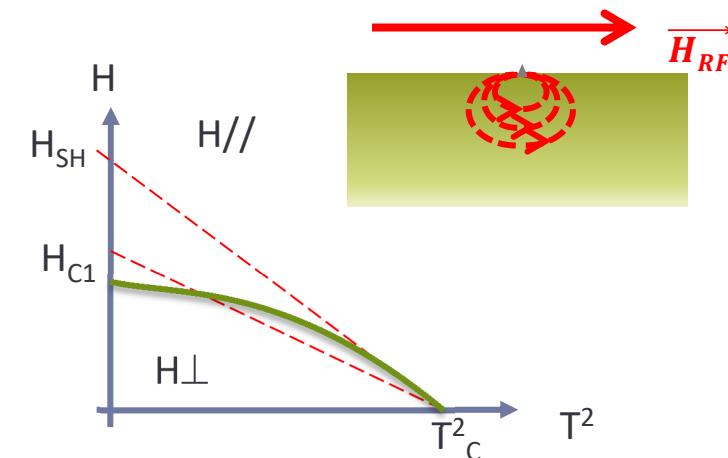
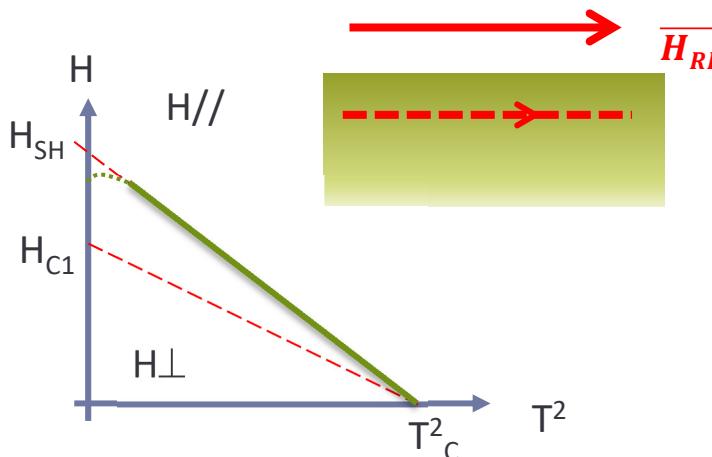
- Avalanche penetration/flux jumps



MgB_2 : http://www.nature.com/srep/2012/121126/srep00886/full/srep00886.html?message-global=remove&WT.ec_id=SREP-20121127

- In real world, cavities behavior is dominated by a few number of defects

It is very important to measure the penetration field of samples in realistic conditions



VORTICES AVALANCHES



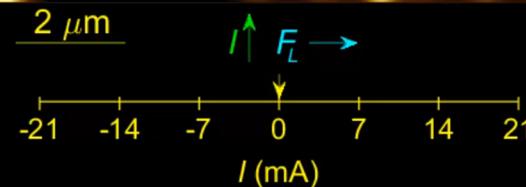
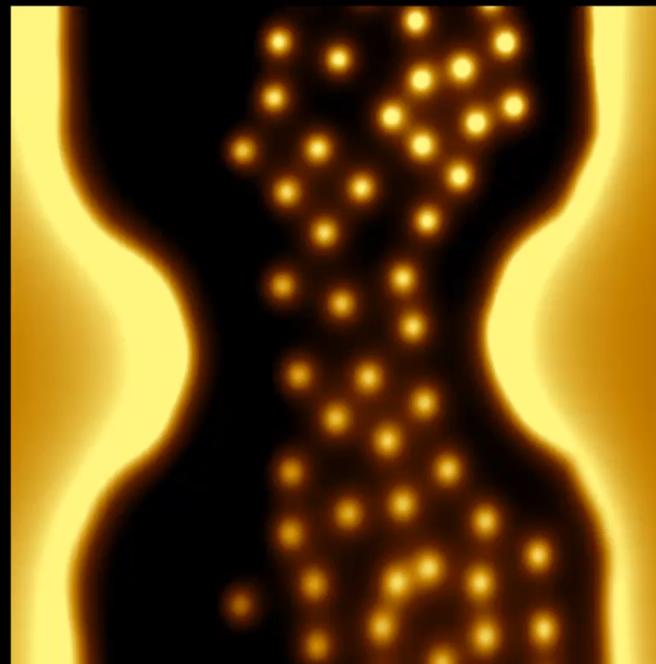
<https://www.eurekalert.org/multimedia/pub/145764.php\>

© Dr. Yonathan Anahory

Racah Institute of Physics
The Hebrew University of
Jerusalem

- Lead films
- scanning SQUID-on-tip microscopy technique
- allows magnetic imaging at magnetic sensitivity and high resolution (~ 50 nm)

Vortex dynamics in Pb film at $B_a = 2.7$ mT



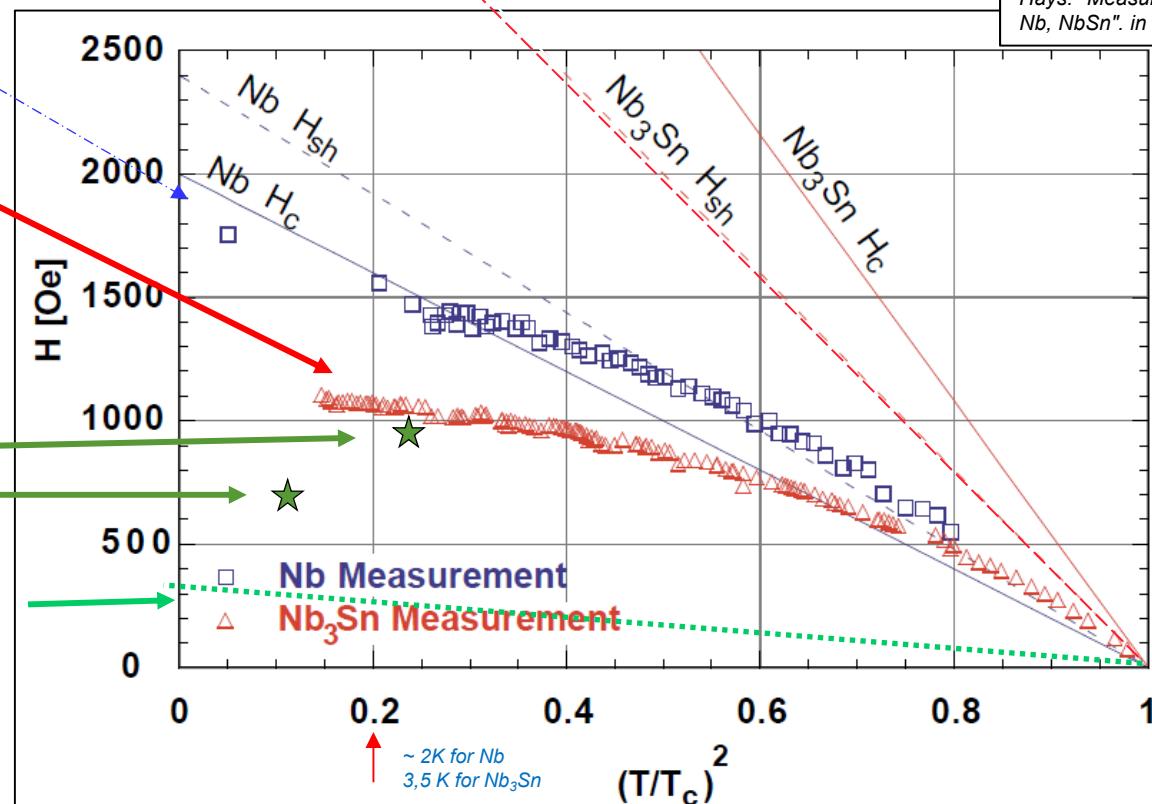
At high currents (high drives) vortices move at 20 km/s and appear as smeared line.

H_{SH} Nb₃Sn
(~ 400 mT @ 0 K)

EFFECTS OF LOCAL DEFECTS



Hays. "Measuring the RF critical field of Pb, Nb, NbSn". in SRF 97. 1997.



Vortices enter more easily at lower temperature (counter intuitive !)?

- @ $T \sim T_c$: H is low => low dissipations => easy to thermally stabilize
- @ $T \ll T_c$: H is high => even if small defect => high dissipations => Favors flux jumps

=> We have to reduce defect density (yes but which ones?)

CHALLENGES TO FACE ON THE ROUTE TOWARD OTHER SUPERCONDUCTORS: GENERALITIES

GENERAL ISSUES WITH SCs



Needed: high T_c , high H_{sh}
(by defect high H_{c1})

Advantages of niobium: pure metal.

- Highest T_c of metallic SC, H_{c1}
- Easy to form
- Uniform composition, *no phase transition in the domain of interest*
- Very large ξ : makes it less sensitive to small crystalline defects (e.g. GB)

Issues with alloyed, metallic SC compounds (e.g. NbTi)

- Higher T_c s, but smaller H_{c1} , ξ
- Still relatively easy to form (harder)
- Usually several phases, not all of them SC
- Risk of non homogeneity

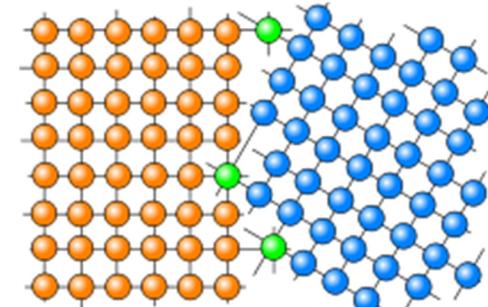
Issues with non metallic SC compounds

- Higher T_c s, but smaller H_{c1} , ξ
- Brittle, no forming is possible, only films (*OK for SRF, but a more complex fabrication route is needed*)
- Usually several phases, not all of them SC
- Risk of non homogeneity

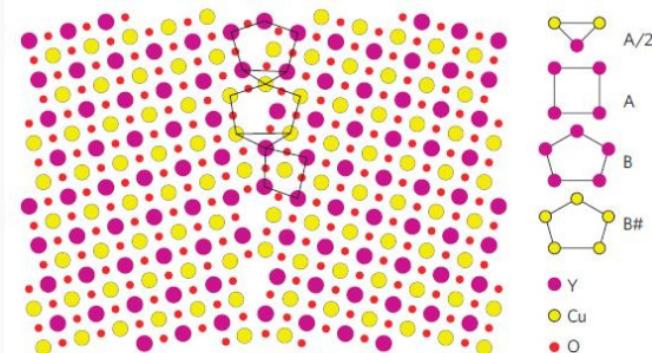
Sometimes local disorder =>

- **# local composition**, possibly non SC
- **Weak links** e.g. NC grain boundaries
= main reason why HTC do not apply in SRF .

EX. : Grain boundaries



Some nm \longleftrightarrow Compare with ξ



Top view of a (410) YBCO grain boundary calculated with molecular dynamics.

<http://www.phys.ufl.edu/~pjh/grain-boundry.html>

If you are a theoretician you prefer to talk about the "existence of nodes in the gap of d-wave superconductors": both are related to Brillouin structure



Nb : $\lambda \sim 50$ nm => only a few 100s nm of SC necessary (the remaining thickness= mechanical support) => Make thin films !

■ Advantages

- Thermal stability (*substrate cavity = copper, Aluminum, ... W*)
- Cost
- Opens route to innovative materials
- Optimization of R_{BCS} possible (e.g. by playing with m.f.p)

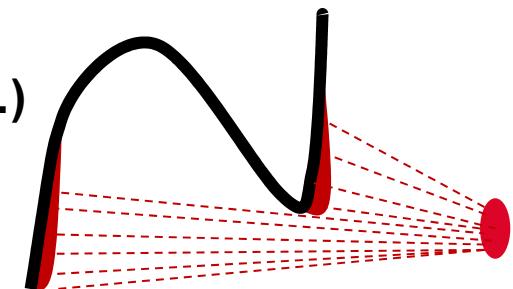
■ Disadvantages

- Fabrication and surface preparation of substrate (*at least*) as difficult as for bulk Nb
- Steep Q_0 reduction often observed by increase of RF field (*sputtered niobium films*)
- Deposition of innovative materials is very difficult (*large parameters space to be explored*)
- Most of the known SC have been optimized for wire applications (*low H_{C1} , defects, pinning centers...*) => most of the literature recipes are not fitted for SRF application ☹ ☹ ☹

DEPOSITION TECHNIQUES: 3 MAJORS FAMILIES

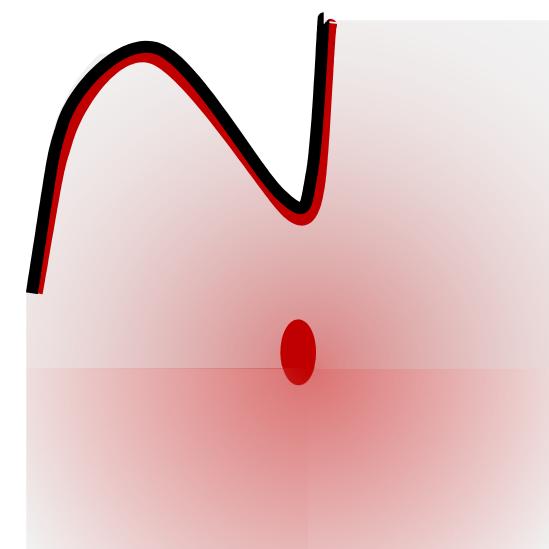
■ Physical deposition techniques (PVD, MS, DS...)

- line of sight techniques
- issues: getting uniform thickness/structure
- internal stress and adhesion
- limited for complex geometry



■ Thermal diffusion films

- limited compositions available
- non uniform composition issues (*S shaped diffusion front, differential diffusion rate with substrate grain orientation*)



■ Chemical techniques CVD, ALD

- conformational even in complex shape
- very quick for large surfaces
- issues: get the proper crystalline structure

There are two categories of films

Films: Many techniques, not possible mention all

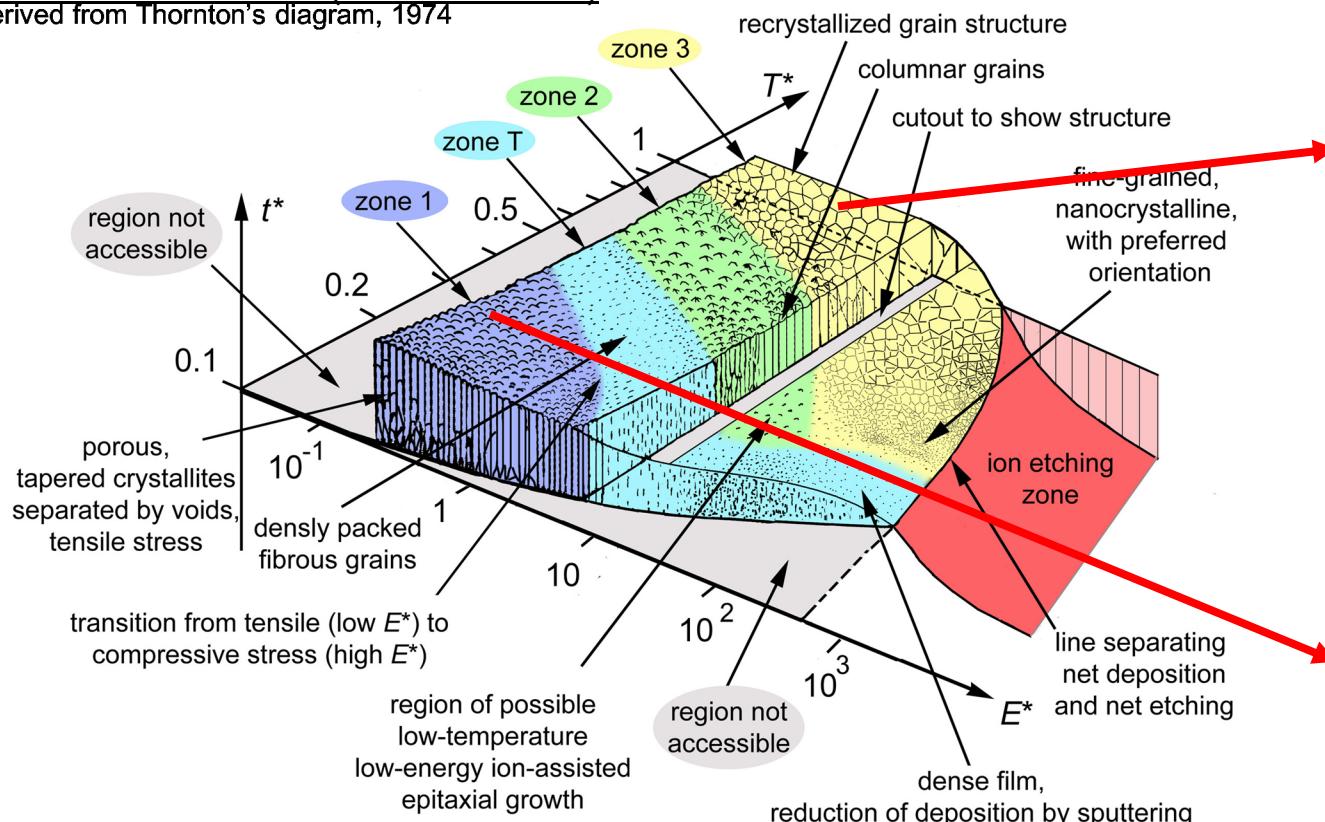
- **Films which are intrinsically films**
 - Thin, small grains, under stress
 - Problems: defects & microstructure, impurities, surface state
 - Examples: magnetron sputtered Nb films on oxidized copper
- **The general trend is to move towards films which are bulk-like**
 - Dense, large grain material
 - Examples:
 - high-energy deposition techniques
 - annealed films
 - Nb Cu-clad cavities (hydroformed cavities from bimetallic Nb (2.5 mm), Cu (0.5-1 mm) tube)

SEARCH FOR BETTER STRUCTURE



Structure zone model (from A. Anders)

derived from Thornton's diagram, 1974



© Andre Anders, 2010

A. Anders, Thin Solid Films 518, 4087 (2010).

11

*Energetic deposition
(HPIMS, CED, VAD...)
=> Bulk like films*

*Magnetron sputtering
=> A lot of defects
Cu limits annealing
temperature
recrystallization*

Unfortunately, more “bulk-like” Nb Films gave disappointing RF results. Not understood yet

THIN FILMS CHALLENGES: DEPENDS ON THE STRATEGY



Optimizing
structure/composition of the
films on samples

Optimizing deposition inside
cavities

Advantages

- Structure /composition can be optimized with conventional techniques
- Ideal structure and composition can be achieved on model sample (guide for deposition of cavities)
- Cost

Disadvantages

- RF performances cannot be directly measured
- **Specific measurement tools need to be developed** (sample cavity, magnetometer...)
- Ultimately a cavity deposition set-up will be needed, but with a known aimed composition & structure

Advantages

- RF testing easy and gives direct performance
- Work is done only once, direct cavity production

Disadvantages

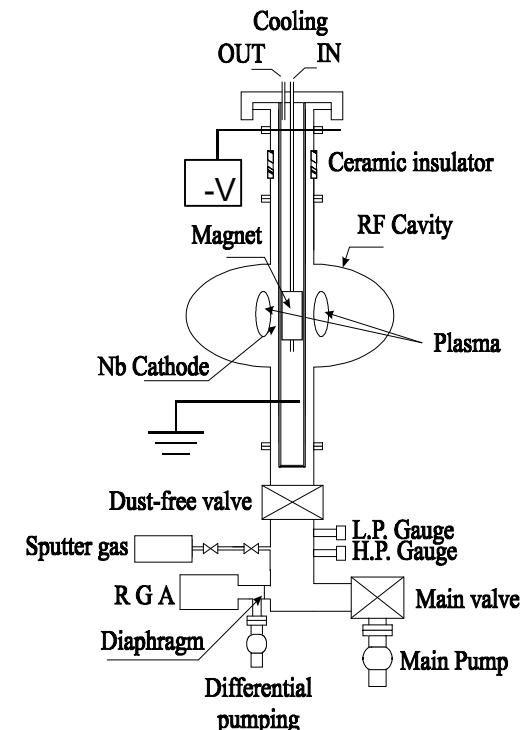
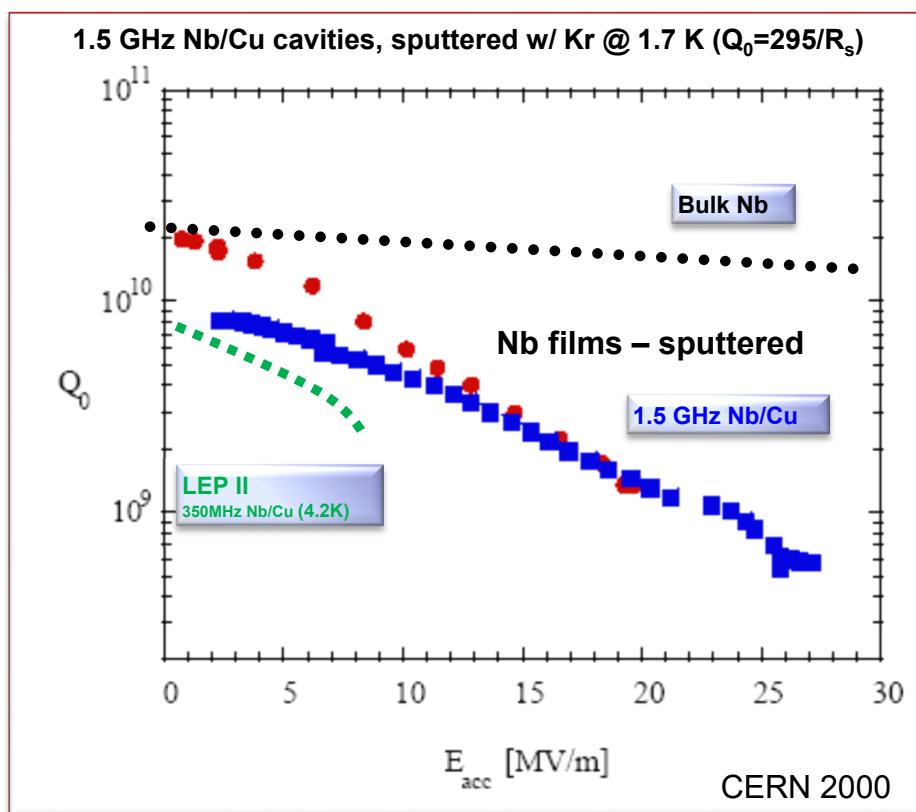
- Very heavy and lengthy, many parameters
- Need to develop a specific cavity deposition set-up
- **Difficult to optimize set-up and films together**
- Optimization of the structure/composition of the film is difficult without structure/composition info

**Nb/ Cu:
example of the issues
when dealing with thin fims**

SPUTTERED Nb FILMS



- The only Nb films deployed in accelerators were made by magnetron or diode sputtering (CERN).
 - Reached relatively low surface fields => $E_{acc} \sim 5 \text{ MV/m}$.
 - Exponential slope in R_s and Q_0



- Possible origin of the slope
 - Depinning of trapped flux
 - Low H_{c1}
 - Early vortex penetration due to roughness

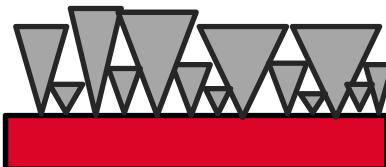
EXAMPLE OF QUALITY ISSUES OF FILMS



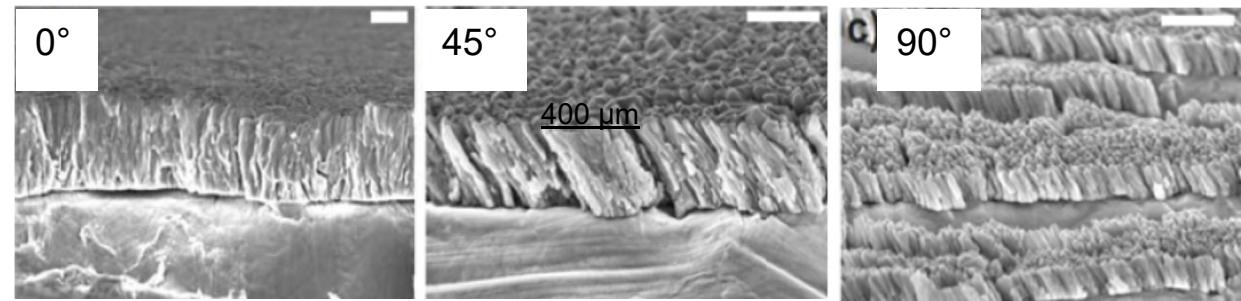
Magn. Sput. Nb

- Line of sight issues
=> porosities

[G. Rozas]

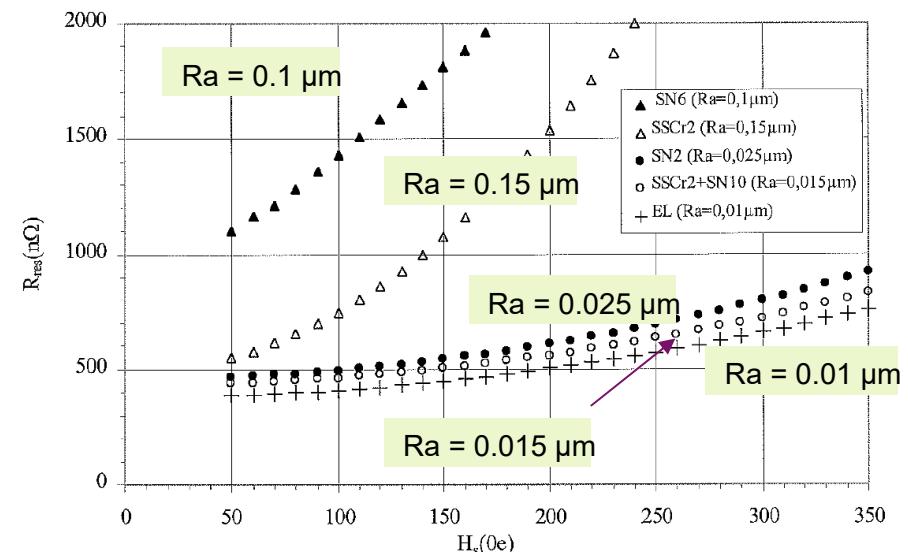


Inverted pyramid crystalline growth



- Internal stress
 - Advantage: higher Tc (*up to a certain impurity concentration*)
 - Disadvantage: adhesion issues (*peeling*)
- High impurities content
 - Nb = getter material (*nearly as good as Ti => high interstitial content*)
 - Carrier gas incorporation (Ar)

- Sensitivity to Cu roughness (*the smoother, the better*)



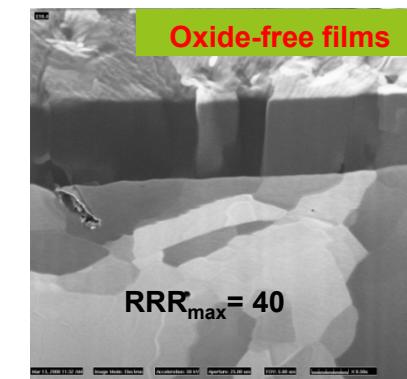
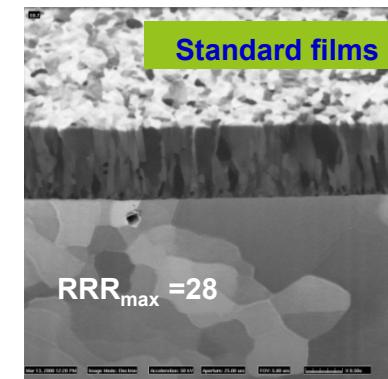
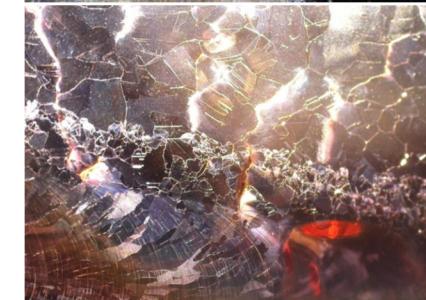
[M. Ribeaudieu, PhD]

SUBSTRATE ISSUES

- Cu and Nb not miscible (especially in presence of O)
 - Advantage: low interdiffusion
 - Disadvantage: adhesion issues (peeling)
- Best results are not always where expected:
Bulk like films did not perform better ! (*but recent
change...?*)

	Standard	Oxide-free
RRR	~10	~30
T_c (K)	9.51 ± 0.01	9.36 ± 0.04
Ar cont. (ppm)	435 ± 70	286 ± 43
Texture	(110) Fiber texture	(110), (211), (200) Hetero-epitaxy
Grain size (μm)	0.1–0.2	1–5
$\lambda/\lambda_{\text{clean}}$	1.51 ± 0.04	1.04 ± 0.09
H_{c2} (T)	1.15 ± 0.025	0.77 ± 0.01
a_0 (\AA)	3.3240(10)	3.3184(6)
Stress (Mpa)	-706 ± 56	-565 ± 78
Strain $\Delta a_{\perp}/a_{\perp}$ (%)	0.636 ± 0.096	0.466 ± 0.093

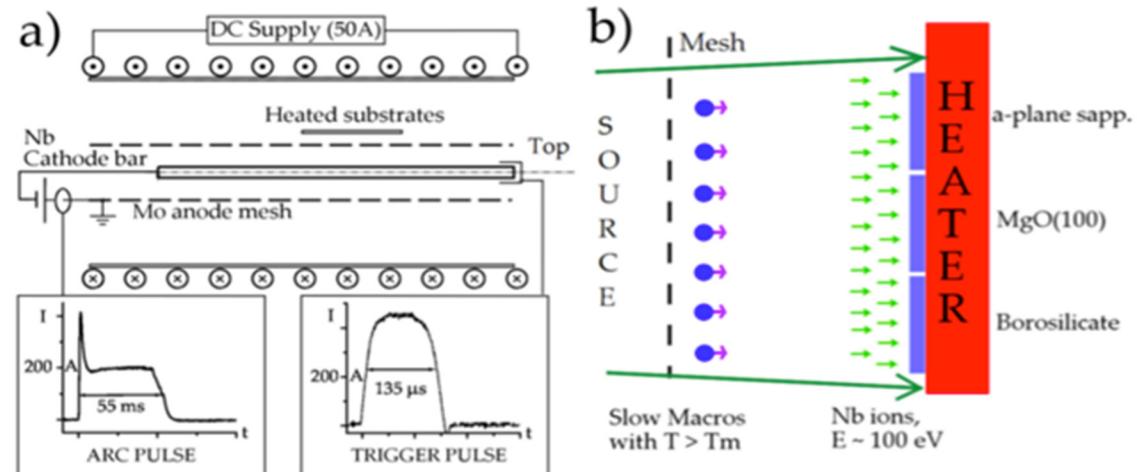
[data from CERN +
AM Valente-Feliciano]



Substrate	RRR
Single crystal insulator	
MgO (100)	176
MgO (110)	424
MgO (111)	197
a-Al ₂ O ₃	488
c-Al ₂ O ₃	247
Cu large grains	289
Record	585

- Ions Energy 60-120 eV
- Arc source is scalable for large scale cavity coatings
- UHV and clean walls important

- Bulk like RRR values
- Here again, cavities performances disappointing



Cathodic arc plasma.

*Nb films grown by Jlab and AASC
Almeda Applied Science Corporation.*

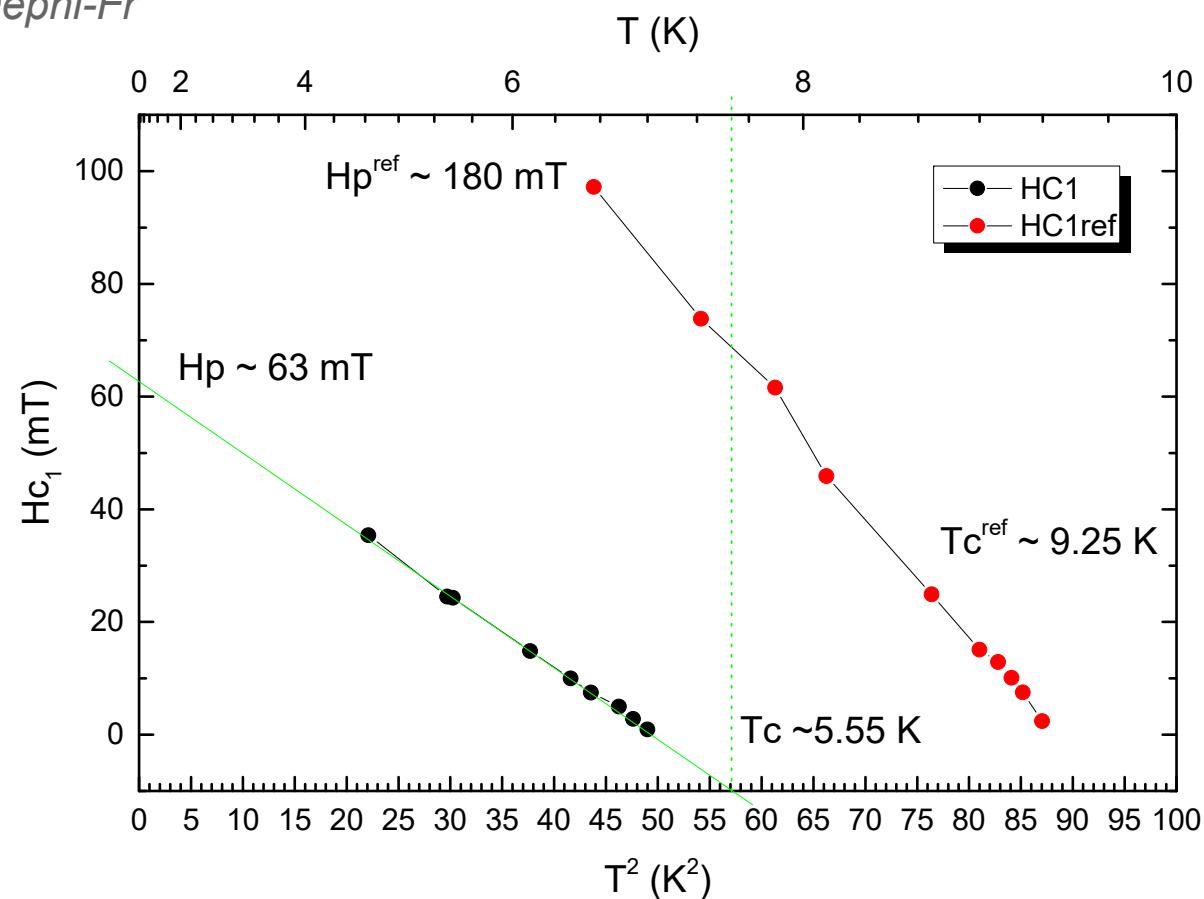
[Ch. Reece; Jlab]



Coaxial Energetic Deposition
(CED™)

Thin films

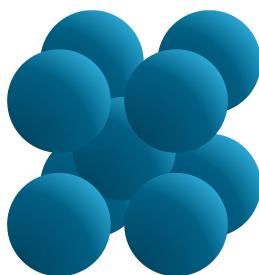
- Thin films : lower H_{C1} , higher H_{C2} / bulk values (because of high λ and low t)
- HPIMS sample from Dephi-Fr



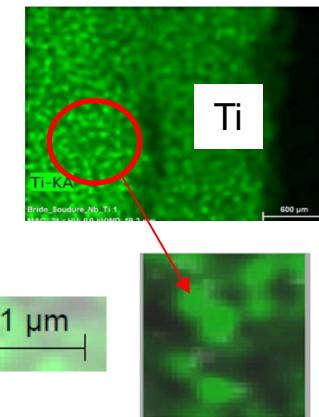
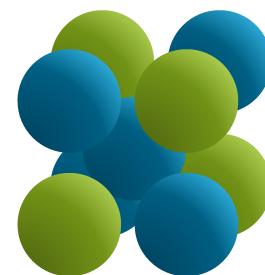
CURRENT SUPERCONDUCTORS:

- **A2** (e.g. NbTi, Transition metal alloys, BCC structures)
- **B1** (e.g. NbN, NbTiN, Transition metal carbide or nitride, NaCl structures)
- **A15** (e.g. Nb₃Sn, Compounds, NaCl structures)
- **2-D SC** (Compounds, anisotropic)
 - MgB₂
 - Cuprates, Pnictides
 - (others TaS₂, organic...)
- **SPECIAL SRF: METAMATERIALS** (Multilayers)

A2 SC ALLOYS: e.g. NbTi



BCC pure metal and solid solution alloy



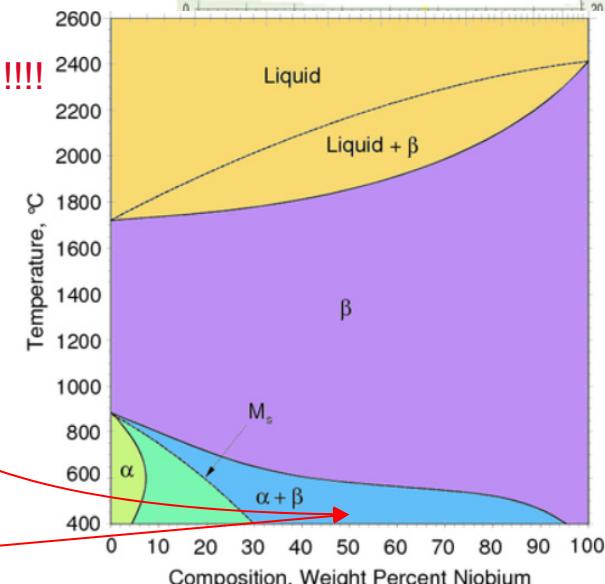
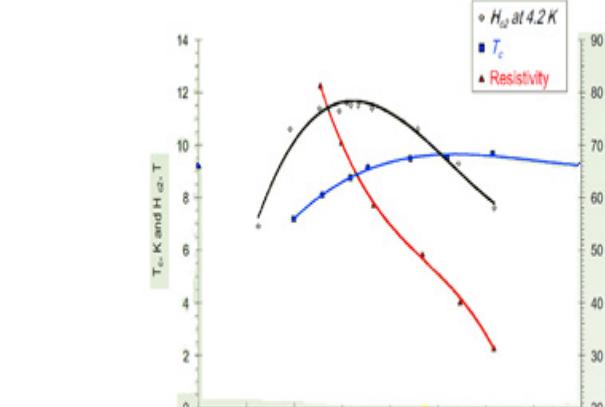
Ti precipitates ($\varnothing \sim 0.4 \mu\text{m}$)
NC Metal => RF dissipation !!!!

- NbTi widely used in coils
- Available alloys range around 45-55 % Ti
- Ti is not fully miscible inside Nb (Ti precipitates \exists at low T when $[\text{Ti}] > 5 \text{ W\%}$)

=> no RF !!!

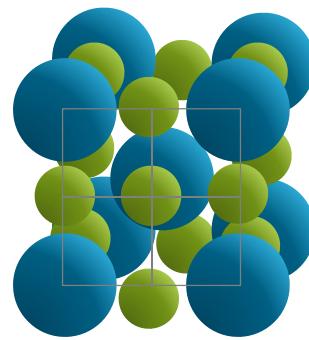
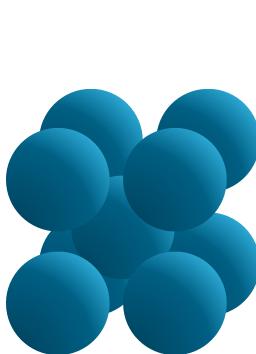
$$\text{Ti } \varnothing = \text{Nb } \varnothing$$

Ti precipitates in a niobium matrix (with a few Nb replaced by substitutional Ti) => ~ same T_c , same H_c as Nb, but not same ℓ => high κ



<http://www.dierk-raabe.com/titanium-alloys/biomedical-titanium-alloys/>

A1 SC COMPOUNDS: e.g. NbN



<https://link.springer.com/content/pdf/10.1007%2F978-1-4757-0037-4.pdf>

BCC pure metal + smaller atoms (N, C) in interstitial location => NaCl structure

- NbN cubic phase : $T_c \sim 17-18$ K
- NbTiN stabilization of cubic (SC) phase
- NbN not too sensitive to local variation of composition !
- Solid solution => relatively easy fabrication (*thermal diffusion, reactive sputtering...*)
- Good model SC
- Widely used for JJ and SC electronics

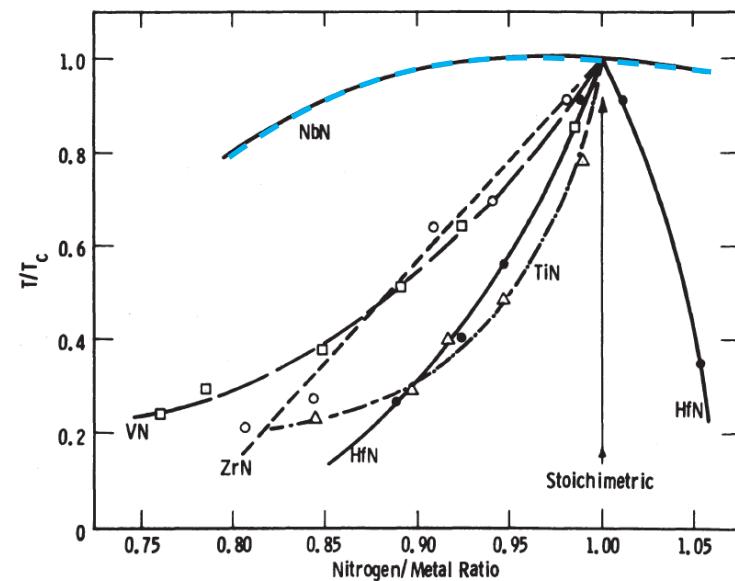


Fig. 20

Critical temperature versus nitrogen-to-metal ratio for various B1-structure nitrides of the transition metals (data assembled by Hulm and Blaugher).

Also a material of choice for the development of multilayers (see below)

A15 COMPOUNDS : HIGH T_c

compound	T _c (K)	compound	T _c (K)	compound	T _c (K)	compound	T _c (K)
Ti ₃ Ir	4.6	V ₃ Os	5.15	Nb ₃ Os	0.94	Cr ₃ Ru	3.43
Ti ₃ Pt	0.49	V ₃ Rh	0.38	Nb ₃ Rh	2.5	Cr ₃ Os	4.03
Ti ₃ Sb	5.8	V ₃ Ir	1.39	Nb ₃ Ir	1.76	Cr ₃ Rh	0.07
		V ₃ Ni	0.57	Nb ₃ Pt	10	Cr ₃ Ir	0.17
Zr ₃ Au	0.92	V ₃ Pd	0.08	Nb ₃ Au	11		
Zr ₃ Pb	0.76	V ₃ Pb	3.7	Nb ₃ Al	20.3	Mo ₃ Re	15
		V ₃ Au	3.2	Nb ₃ Ga	18.9	Mo ₃ Os	11.68
		V ₃ Al	9.6	Nb ₃ In	8	Mo ₃ Ir	8.1
		V ₃ Ga	15.4	Nb ₃ Ge	23	Mo ₃ Pt	4.56
		V ₃ In	13.9	Nb ₃ Sn	18.3	Mo ₃ Al	0.58
		V ₃ Si	17.1	Nb ₃ Bi	2.25	Mo ₃ Ga	0.76
		V ₃ Ge	7			Mo ₃ Si	1.3
		V ₃ Sn	4.3	Ta ₃ Ge	8	Mo ₃ Ge	1.4
		V ₃ Sb	0.8	Ta ₃ Sn	6.4		
				Ta ₃ Sb	0.72		

[after Due-Hugues]

Extreme brittleness !!!

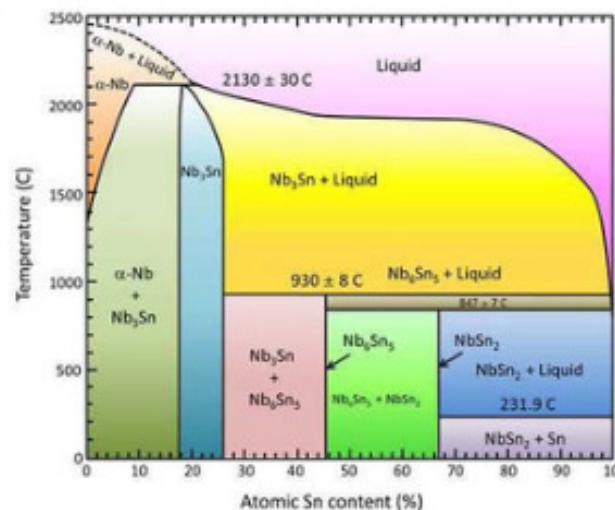
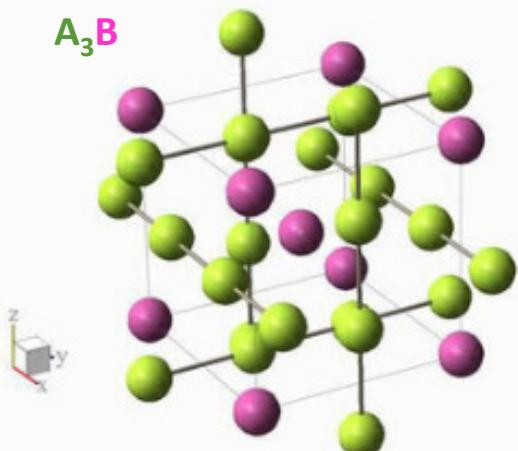
- cannot be formed
- thin/thick film route only !

nm

μm

Phases with proper stoichiometry
(A₃B) not stable in normal condition
(RT to Cryogenic temp)

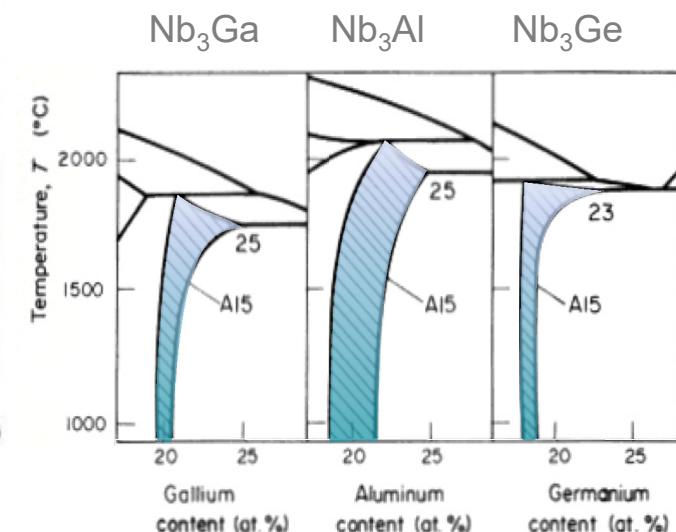
A15 COMPOUNDS : NARROW DOMAIN OF SC



B atoms occupy corners and center of BCC structure

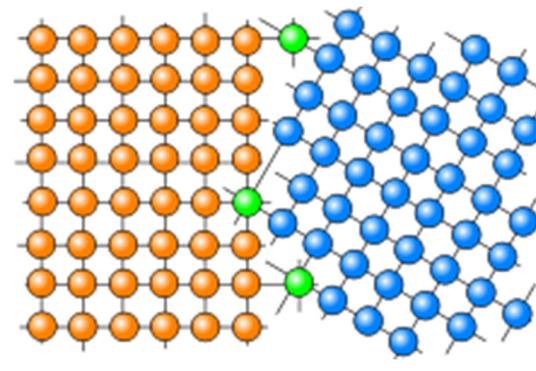
A atoms form orthogonal chains bisecting the faces of the BCC unit cell.

Linear Chain Integrity is crucial for T_c (long-range order required)



Narrow range of concentration for the SC phase:

- Highest T_c area is even narrower
- Difficult to get uniform SC phase everywhere*
- Special issues at grain boundaries: “intrinsic” local deviation of stoichiometry*
- In Nb₃Sn wires : GB exhibit degraded SC => weak links, pinning centers

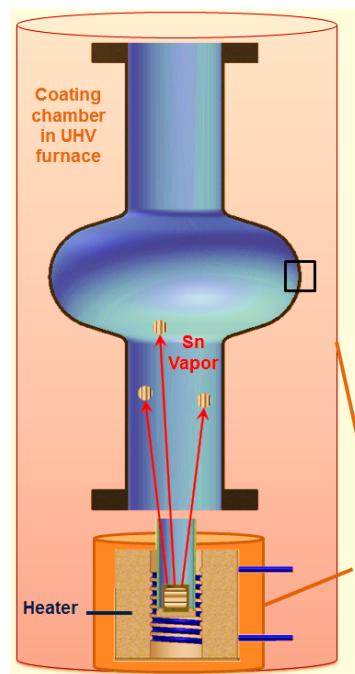
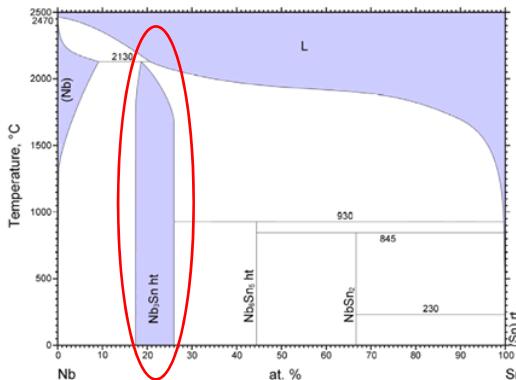


Compare with ξ

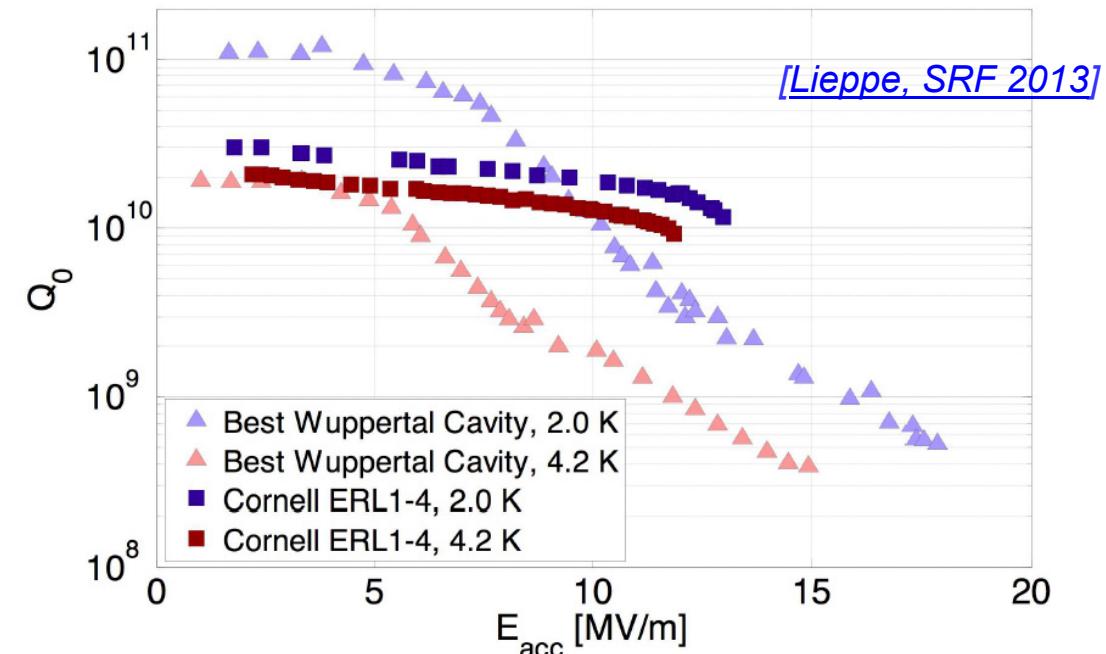


**Special interest for SRF
since the 1980's**

Nb_3Sn ON Nb (thermal way)



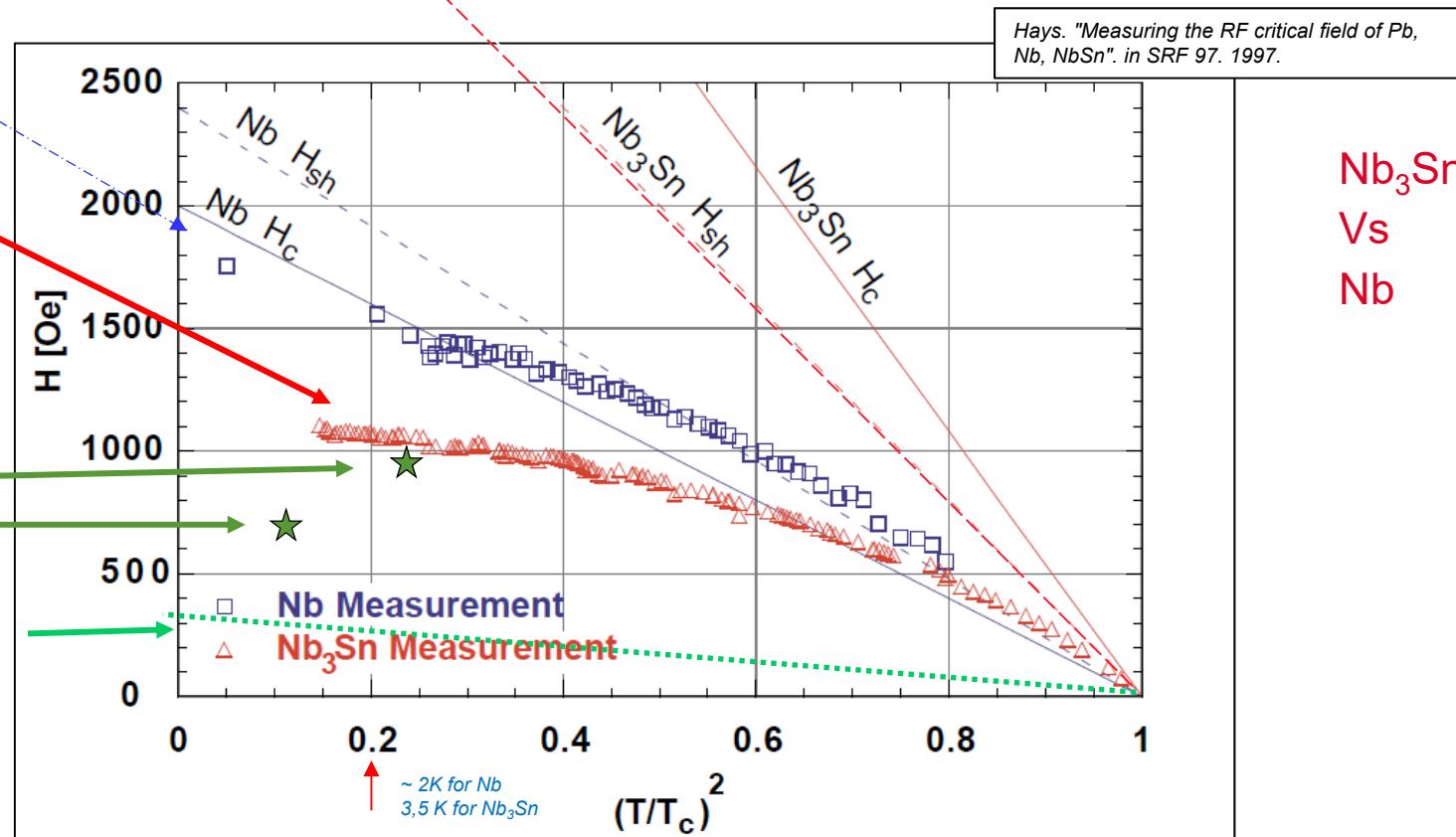
Pioneer work: Wuppertal, Cornell



- @ 4.2 K: $Q_0 \times 20$ compare to Nb, @ 2K ~ the same
- Limited in E_{acc} , best results today ~17 MV/m
- Important developments: FNAL, JLAB, CERN, PKU....

H_{SH} Nb₃Sn
(~ 400 mT @ 0 K)

EFFECTS OF LOCAL DEFECTS



=> We have to reduce defect density

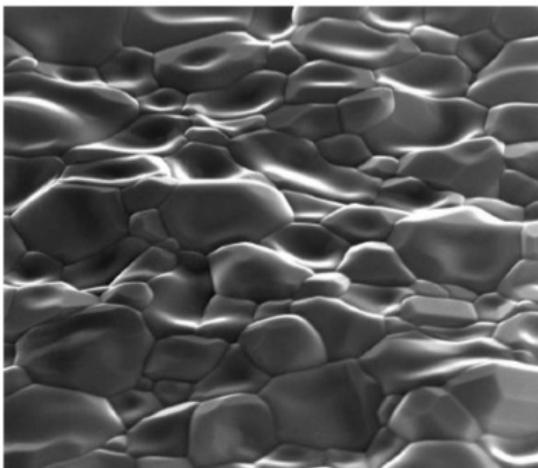
(yes but which ones?)

Nb₃Sn : NON UNIFORM LAYER



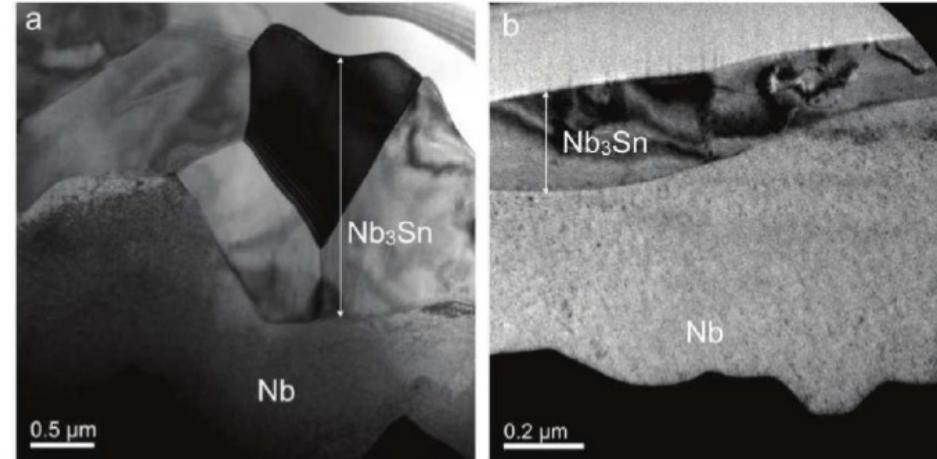
Candidates of Q-slope and quenching in Nb₃Sn

1. Surface roughness



S Posen, PhD thesis, Cornell University (2015)

2. Thin regions



Y Trenikhina et al 2018 Supercond. Sci. Technol. 31 015004

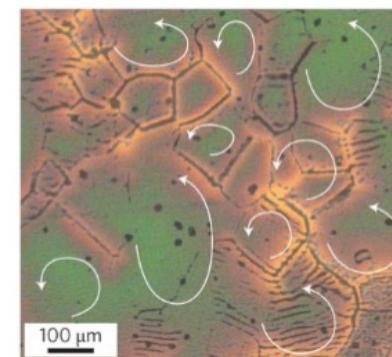
3. Composition variation (Sn-deficient region)



C Becker et al, APL 106, 082602 (2015)

[Jaeyel Lee ttc Milano meeting 2018](#)

4. Grain boundary



A. Gurevich, Nature Materials 10, 255–259 (2011)

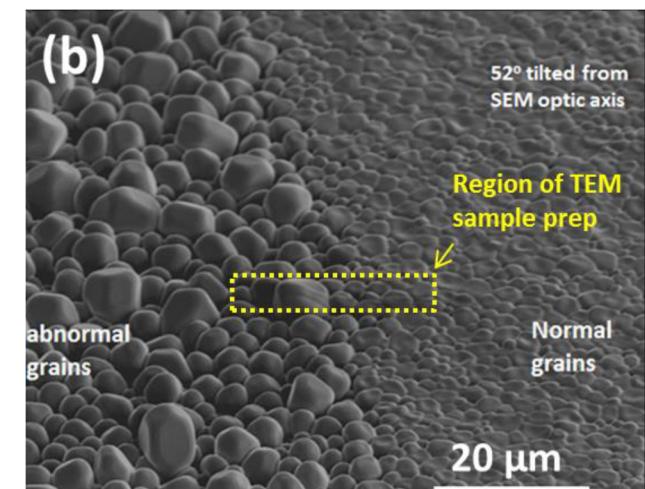
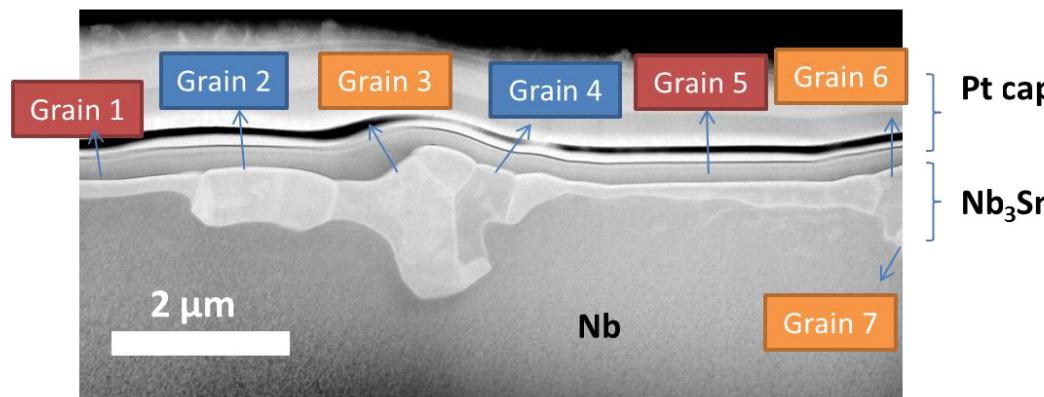
Nb₃Sn : SUBSTRATES ISSUE

Orientation A
Nb₃Sn (1̄20) // Nb (1̄11)
Nb₃Sn (002) // Nb (1̄12)

Orientation B
Nb₃Sn (1̄20) // Nb (1̄11)
Nb₃Sn (002) // Nb (23̄1)

Orientation C
Nb₃Sn (1̄20) // Nb (1̄11)
Nb₃Sn (002) // Nb (01̄1)

<https://export.arxiv.org/ftp/arxiv/papers/1807/1807.03898.pdf>



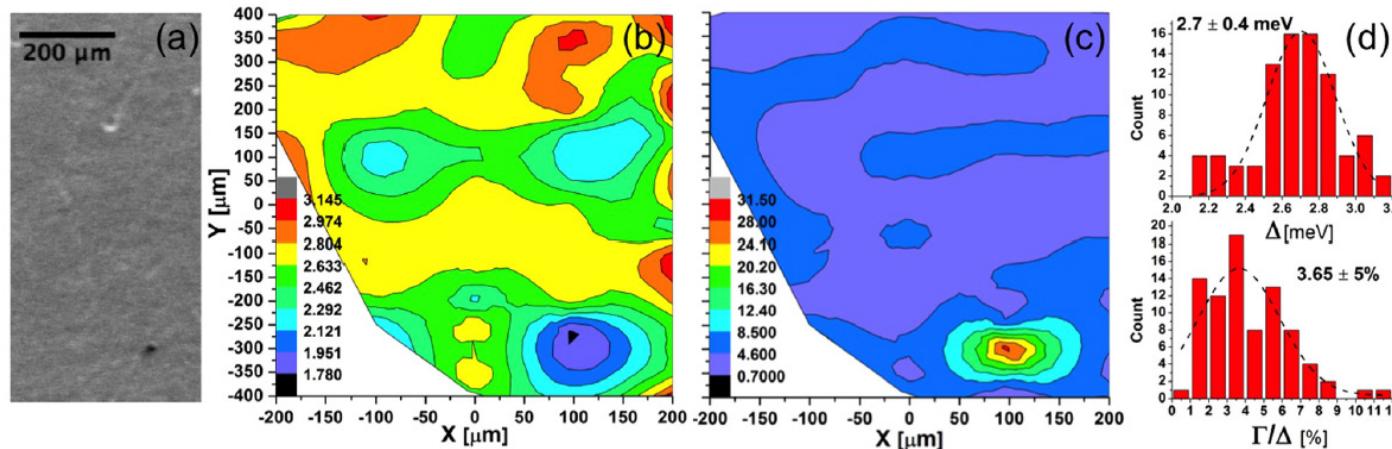
■ Nb₃S film grows in epitaxy

- Regions with poor lattice mismatch grow slower
- Thinner regions tend to be depleted in Sn => lower T_C, early transition
- Can be partially mitigated with interlayer (e.g. anodization of Nb)

■ Complex materials:

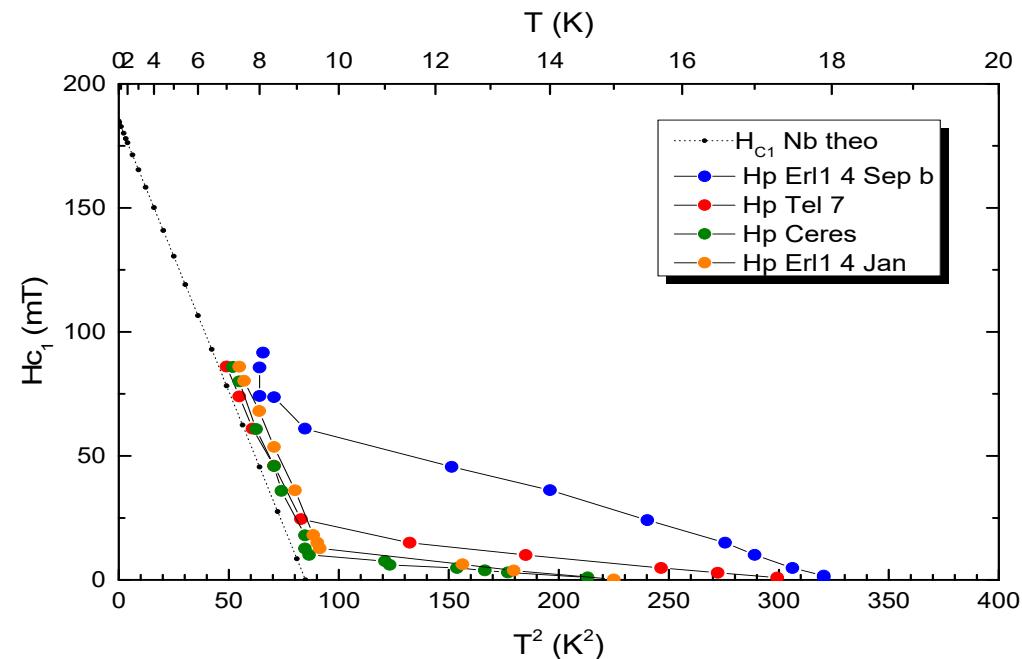
- Real difficult to master
- Very sensitive to defects

L. M.: WHAT ELSE CAN BE MEASURED



Nb₃Sn series

- Along with cavity results and PCT [*T. Proslier*]
- Magnetometry follows the trends observed on RF tests



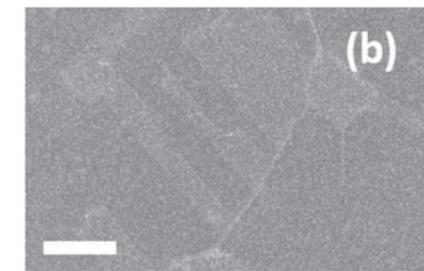
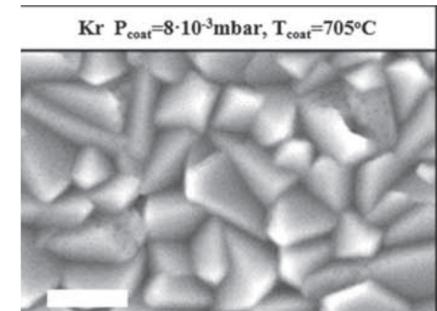
OTHER APPROACHES

Sputtered Nb₃S films on copper

- Activities at [Cern](#) and [Jlab](#)
- RT deposited films : right composition but no A15 structure
- Heating of substrate (CERN)
- And/or post annealing

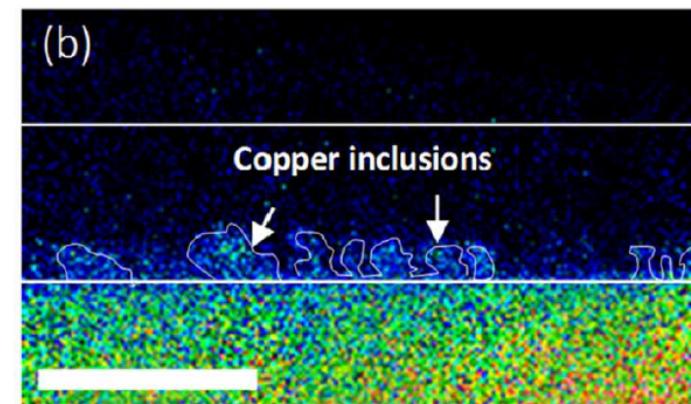
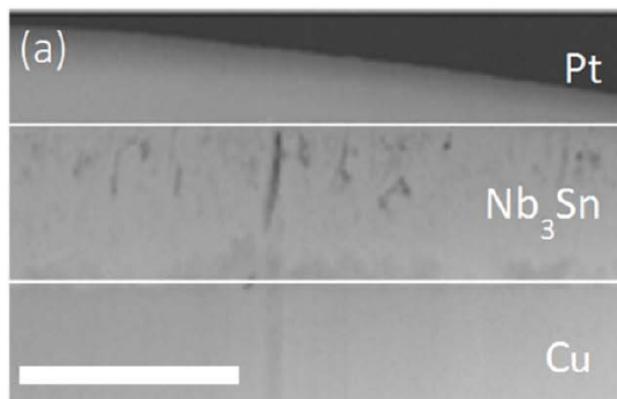
Other issues

- Cracks on the layer (*due to differential dilatation coef*)
- Diffusion of copper in the layer
- Carrier gas incorporation (*Ar, Kr*)
- Sn evaporation at higher temperature (> 1000°C)



Supercond. Sci. Technol. 32 (2019) 035002

E A Ilyina et al



OTHER APPROACHES

■ Electrochemical deposition + diffusion through copper

- Proposed at [FNAL](#)
- Inspired from wire fabrication
- Not expensive !!!!

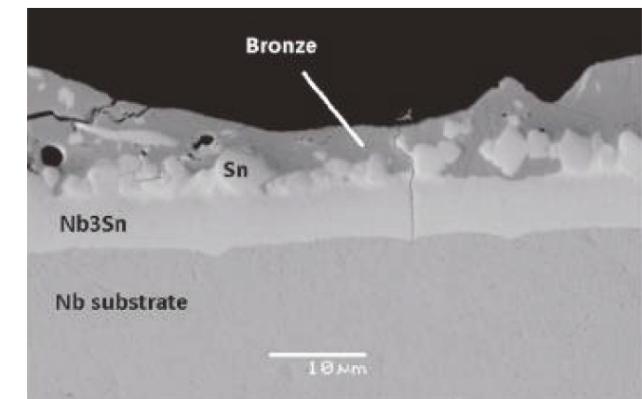
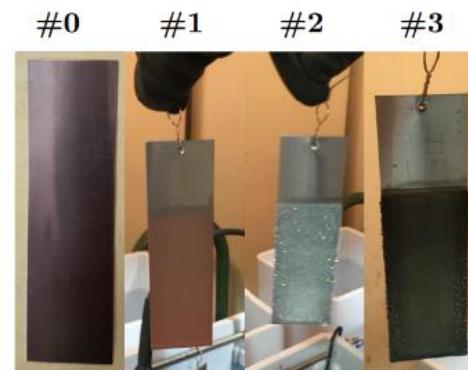
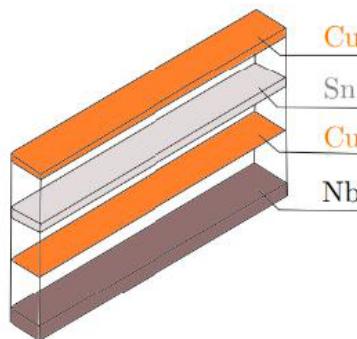


Fig. 3: Sequence of deposited layers (left), and pictures of sample at each deposition step (right).

- Multilayer is heated => solid state diffusion
- Cu lowers the formation T_p° of A15 phase and suppresses the unwanted NbSn_2 and Nb_6Sn_5 phases.

2-D SC (Compounds, anisotropic)

- MgB₂
- Cuprates, Pnictides
- Multilayers

MAGNESIUM DIBORIDE (MgB_2)



BCS type superconductor

- $T_c \sim 40 \text{ K}$, two-gap nature

Advantages:

- Very high T_c (*higher temp operation*)
- Semimetal, cheap (*fertilizer !*)
- ξ, λ of high quality* MgB_2 similar to Nb ($\sim 50 \text{ nm}$) (*transparency of GB to current flow*)
- Low ρ_n (*lower R_s*)

Disadvantages:

- Orientation issues (*in polycrystalline materials !*)
- RF dominated by lower gap ☺ !
- Still better than Nb :

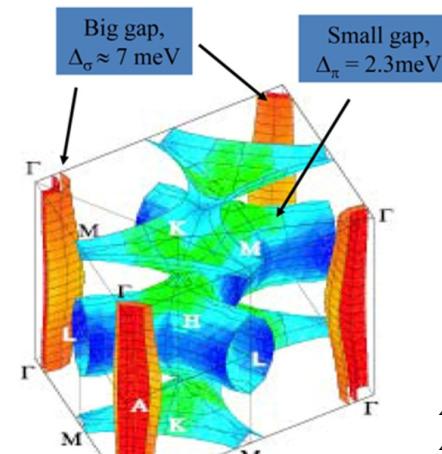
$$\Delta_{\text{Nb}} = 1.5 \text{ meV} < \Delta_{\text{MgB}_2} = 2.3 \text{ meV} < \Delta_{\text{Nb}3\text{Sn}} = 3.1 \text{ meV}$$

$$< \Delta_{\sigma}^{\text{MgB}_2} = 7.1 \text{ meV}$$

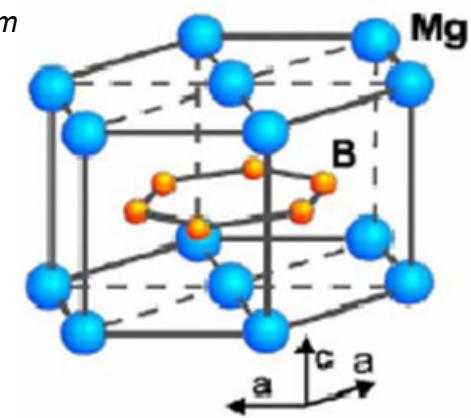
- Sensitive to H_2O (*capping necessary ?*)
- Thin film routes difficult

* wire quality MgB_2 : $\xi \sim 1-3 \text{ nm}$, $\lambda \sim 250 \text{ nm}$
 (by playing on m.f.p.: crystal structure, grain size, impurities...)

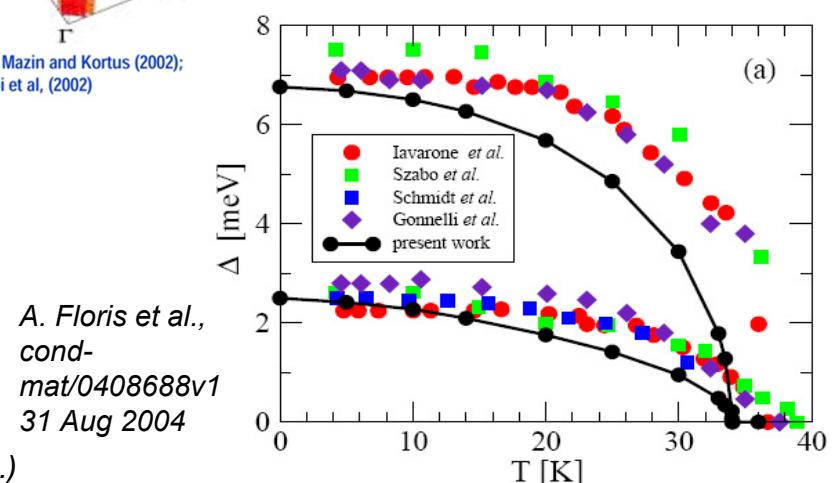
Graphite-type boron layers separated by hexagonal close-packed layers of magnesium



Liu, Mazin and Kortus (2002);
 Choi et al. (2002)



$\Delta_p = 2.3 \text{ meV}$, 2D, in-plane s-orbital
 $\Delta_s = 7.1 \text{ meV}$ 3D, out-of-plane p-orbitals



MAGNESIUM DIBORIDE (MgB_2)



Phase diagram: at low Mg pressure only extremely low deposition temperatures can be used

■ Optimal T for epitaxial growth $\sim T_{\text{melt}}/2$

- For MgB_2 $T_{\text{melt}}/2 = 540^\circ\text{C} \Rightarrow P^{\text{Mg}} \sim 11 \text{ Torr}$
- Too high for UHV deposition techniques (PLD, MBE...)

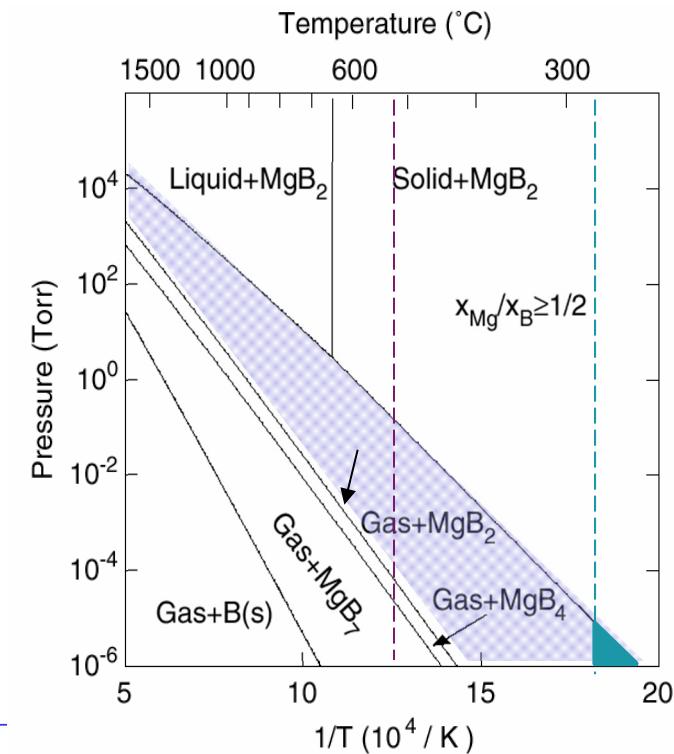
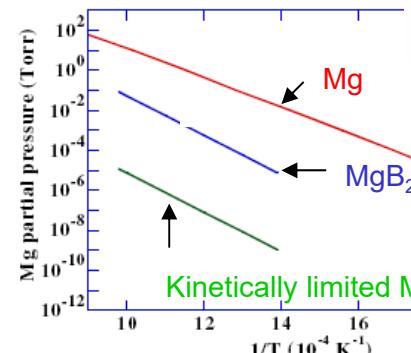
■ At $P^{\text{Mg}} = 10^{-4}$ - 10^{-6} Torr, and $T_{\text{sub}} \sim 400^\circ\text{C}$

- Compatible with MBE, and other deposition techniques
- MgB_2 is stable, but no MgB_2 formation:
 - Mg atoms re-evaporate before reacting with B

■ At $P^{\text{Mg}} = 10^{-4}$ - 10^{-6} Torr, and lower T

- MgB_2 is stable,
- If $T_{\text{sub}} > 250^\circ\text{C}$, free Mg is lost because the re-evaporation rate is higher than the impinging rate
- If $T_{\text{sub}} < 250^\circ\text{C}$
- Growth rate is very slow,
(kinetically limited by available Mg)

evaporation pressure of Mg from MgB_2 < decomposition curve of MgB_2 < Mg vapor pressure



Z.-K. Liu et al., APL 78(2001) 3678.

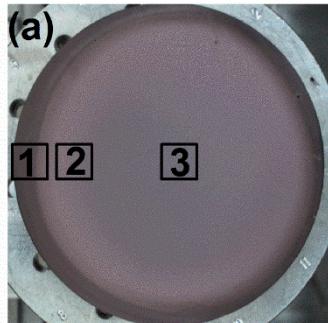
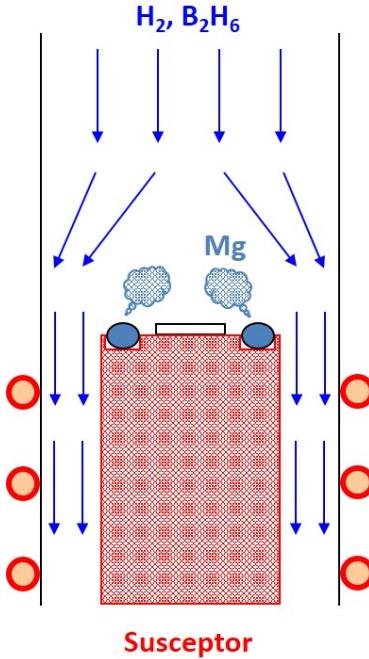
M. Naito and K. Ueda,
SUST 17 (2004) R1

MgB₂ – HPCVD ON METAL SUBSTRATES

HYBRID PHYSICAL CHEMICAL VAPOR DEPOSITION



[X. Xi- Temple University]



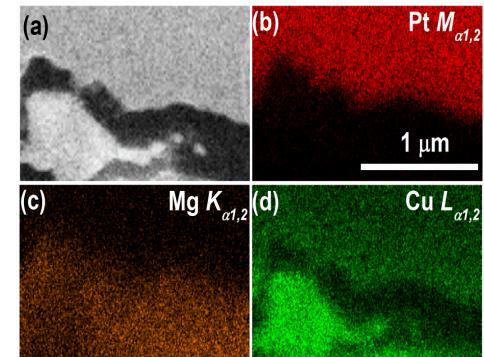
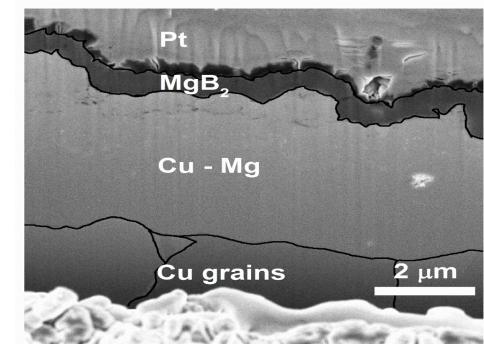
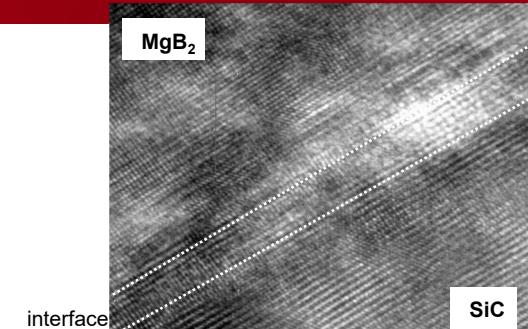
■ Polycrystalline MgB₂ films deposited:

- On stainless steel, Nb, TiN, and other substrates.
- Flat samples and tubes (*conformational*)
- Fitted for SRF apps:
 - $RRR > 80$
 - *low resistivity ($< 0.1 \mu\Omega$) and long mean free path*
 - *high $T_c \sim 42 K$ (due to tensile strain),*
 - *low surface resistance, short penetration depth*
 - *smooth surface (RMS roughness $< 10 \text{ \AA}$ with N₂ addition)*
 - *good thermal conductivity (free from dendritic magnetic instability)*

■ Keys to high quality MgB₂ thin films:

- High Mg pressure for thermodynamic stability of MgB₂
- Oxygen-free or reducing environment
- Clean Mg and B sources
- Prevent formation of spurious phase (e.g. Mg-Cu alloy islands on a Cu substrate)

Reactor/reaction designs require complex calculation in thermodynamics and hydrodynamics

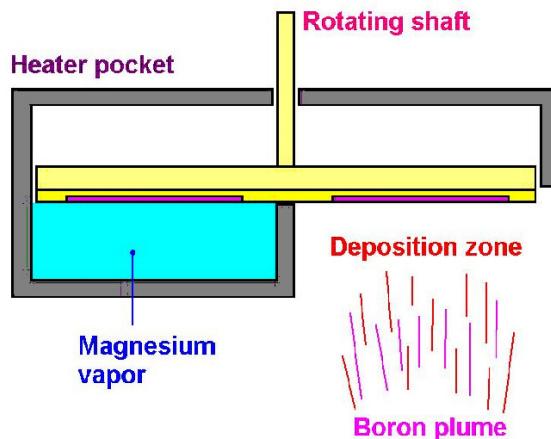


MGB₂ – OTHER ROUTE S



In-situ reactive evaporation @ 550°C

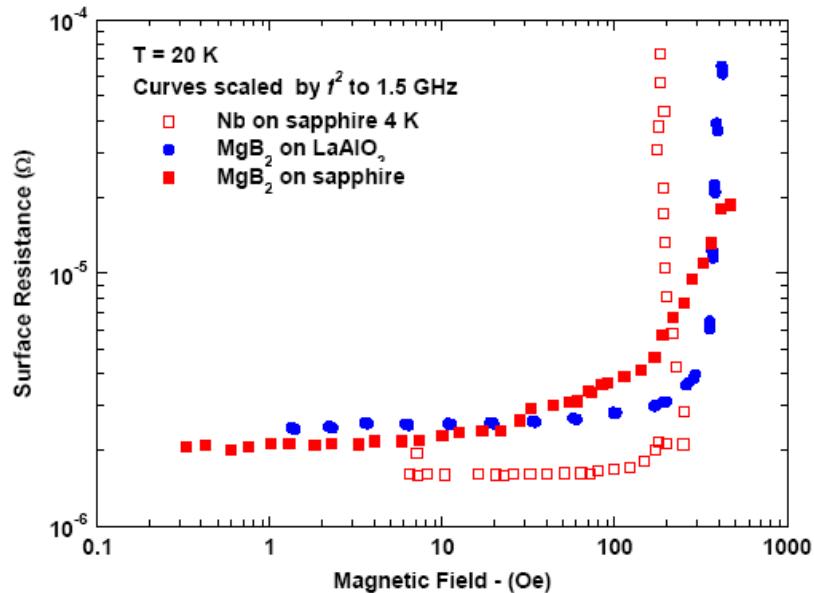
- High quality flat samples
- Difficult to apply to complex geometries



[T. Tajima, LANL]

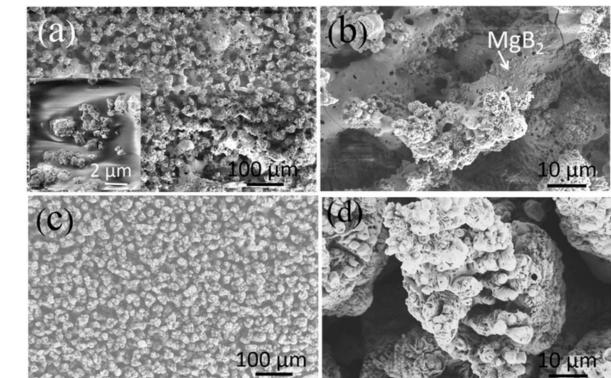
Superconducting
Technologies Inc.

RF measurement @ MIT/Lincoln Lab



Plasma electrolytic oxidation (PEO)

- MgB₂ particles in suspension in an electrolyte
- MgB₂ Islands deposited on the surface
- Issues : homogeneity, purity
- To be further explored



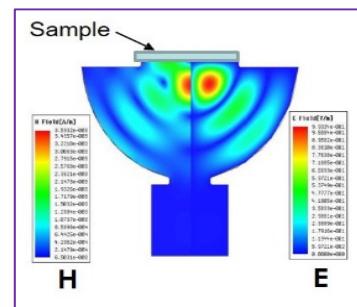
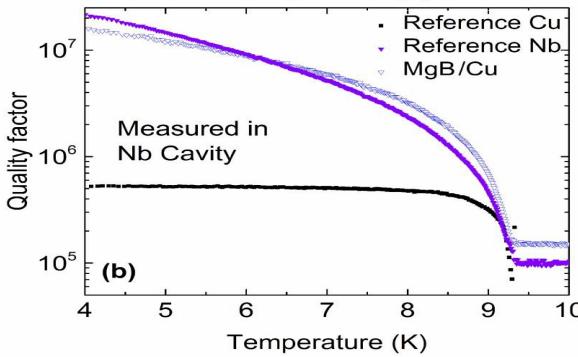
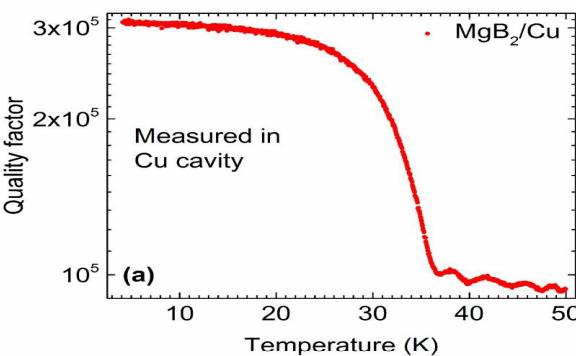
[R. Valizadeh, STFC]

HPCVD MGB₂ – RF MEASUREMENTS



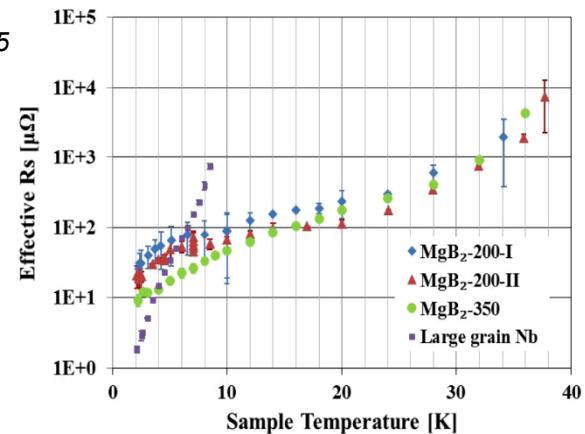
■ 11.4 GHz TE013 cavity @ SLAC

- The MgB₂ coatings were also characterized at 11.4 GHz at SLAC using a cryogenic RF system.
- The samples showed a Q factor comparable to a Nb reference sample and higher than the Cu reference sample.
- The films showed a T_c of 37 K.



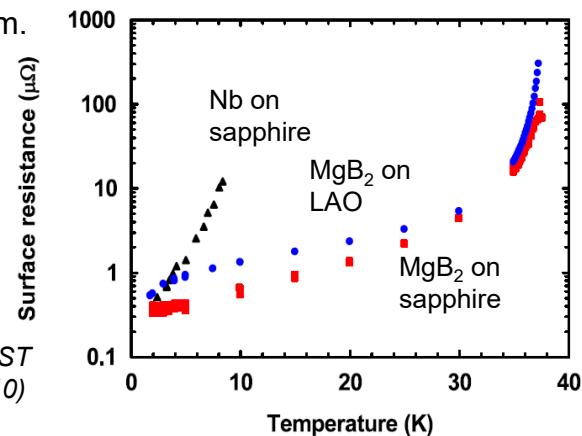
■ 7.5 GHz sapphire-loaded TE011 cavity at JLab

B.P.Xiao et al., SUST 25 (2012) 095006.



■ stripline resonator

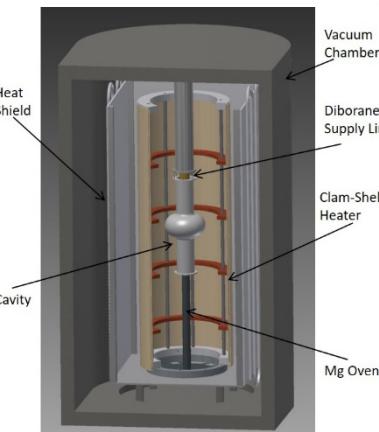
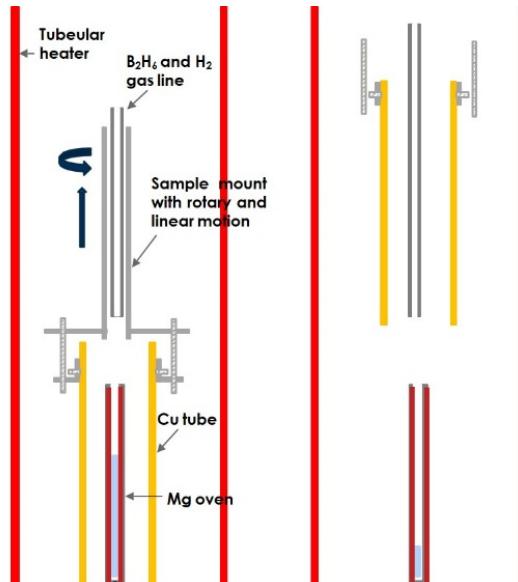
- Scaled to 1.5 Ghz
- Lower surface resistance comparable to Nb film.



Oates et al., SUST 23, 034011 (2010)

MGB₂ - SRF CAVITY COATING

Coating SRF Cavity with a 2-Step Process



[X. Xi, Temple Univ.](#)

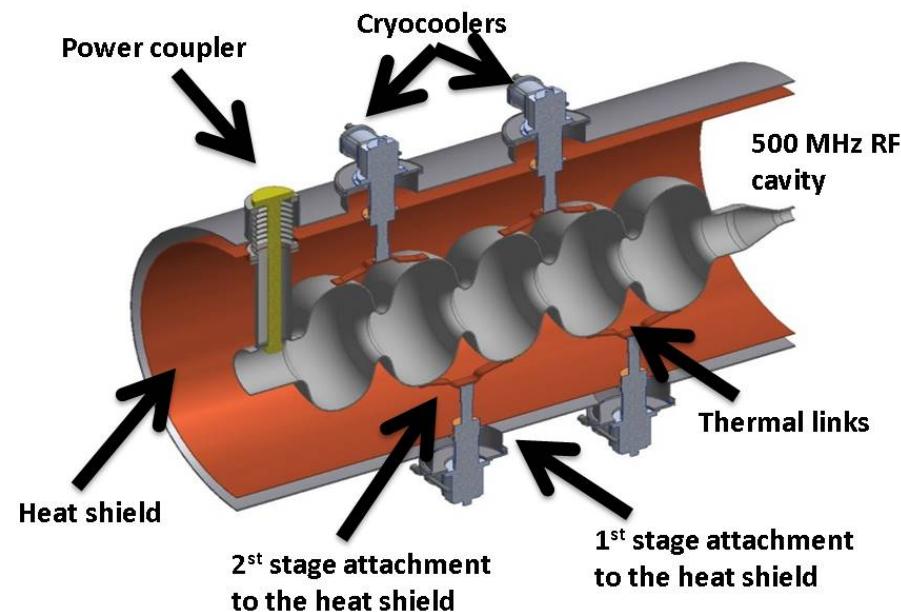
Cryocooler-Cooled MgB₂-Coated Cu Cavities

[A. Nassiri et al., ANL](#)

Coating of MgB₂ /Cu makes operation at 8-12 K possible

Temperature range can be achieved with efficient cryocoolers, providing significant benefit with reduced cost.

Goal: 500 MHz MgB₂-coated Cu cavity



HPCVD MGB₂: CU TUBE COATING-TESTING FOR 3.9 GHz CAVITY

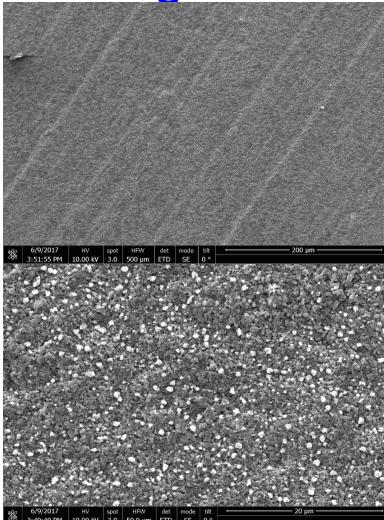


3.9 GHz mock cavity

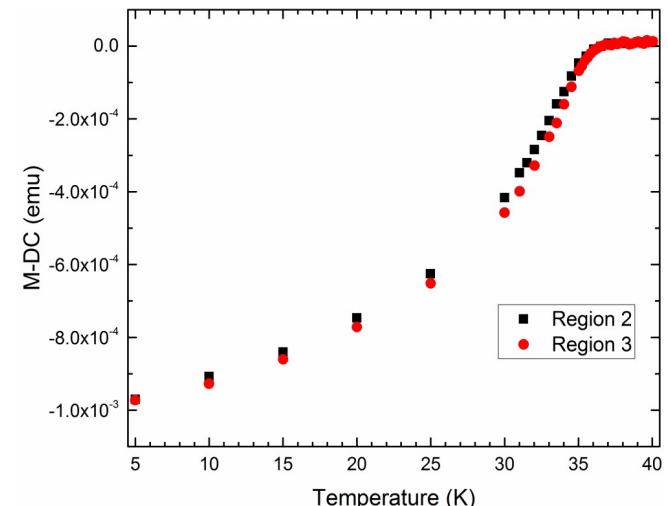
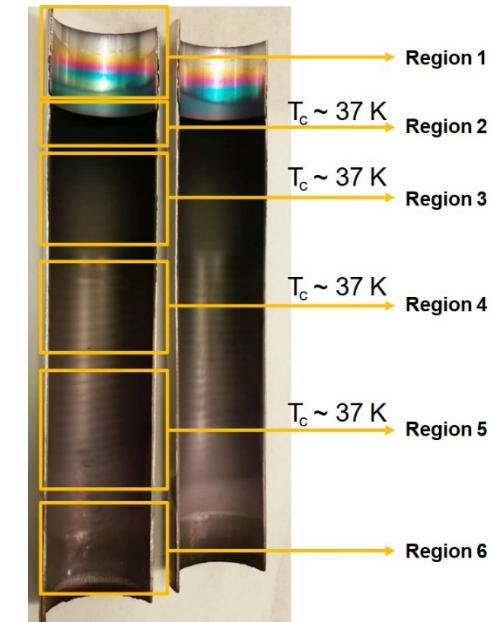
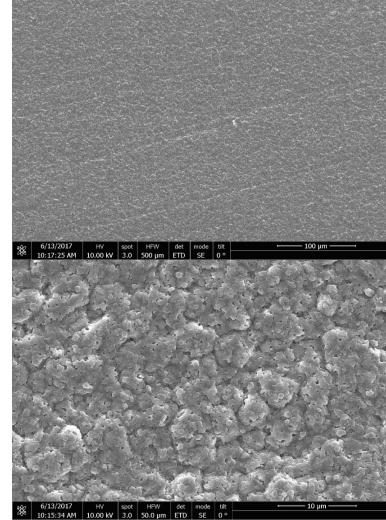
- B₂H₆ flow rate: 20 sccm
- H₂ flow rate: 100 sccm
- Total pressure: 5 Torr
- Deposition time: 20 - 30 min

Small piece from each region are tested for superconducting and surface properties

Region 2



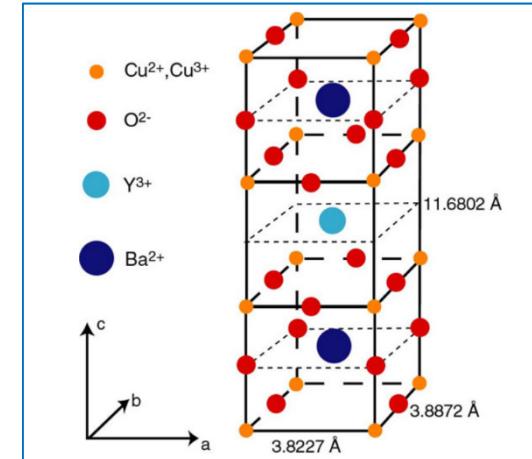
Region 3



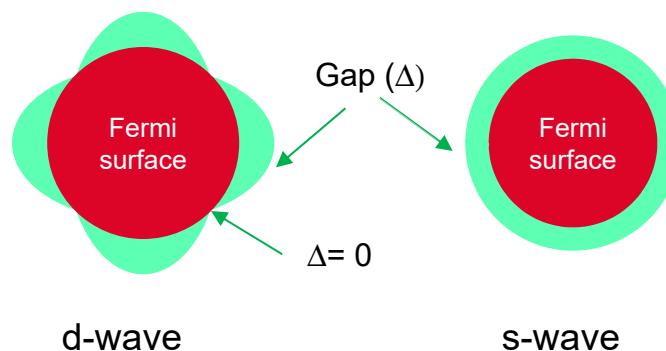
YBCO FAMILY... NOT FOR SRF !



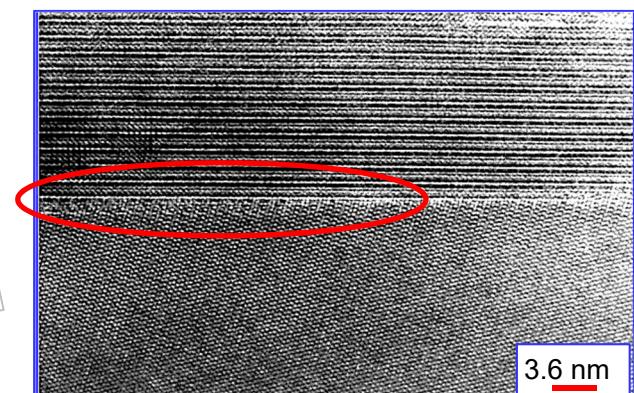
- MonoXt^{al} : Jc maximum for (a,b) planes and minimum when // c axis
 - ξ_χ (~0,03 nm) << ξ_a , ξ_b (~1-2 nm) => "layered material"
- Realistic material : polycrystalline, ceramic, fragile...
 - $\xi_c \ll$ disordered area at G.B => grains are decoupled (weak links)
 - => try to introduce preferential orientation (epitaxy): difficult to get on a cavity (but is applied to fabricate tapes for magnets)
- D-symmetry of the gap
 - superconducting gap is also anisotropic
 - = zero at four line nodes located at the diagonals of the Brillouin zone
 - $\Delta = 0 \Rightarrow$ power law for R_S : $R_S \propto T^{2-3}$
 - For the recall: gaps of conventional SC have s symmetry:
isotropic and $R_S \propto e^{-\Delta/T}$ (BCS resistance)



<http://mason.gmu.edu/~grobert1/2014syl641.htm>



Crystal structure is also related to Brillouin zones. So the relative orientation of the grains can influence the way Cooper pairs are scattered by defects



Twin boundary in YBCO

<https://areeweb.polito.it/ricerca/superconductivity/melt.htm>

PNICTIDE FAMILY... MAYBE YES ?

■ Oxypnictide base: ReOMPn

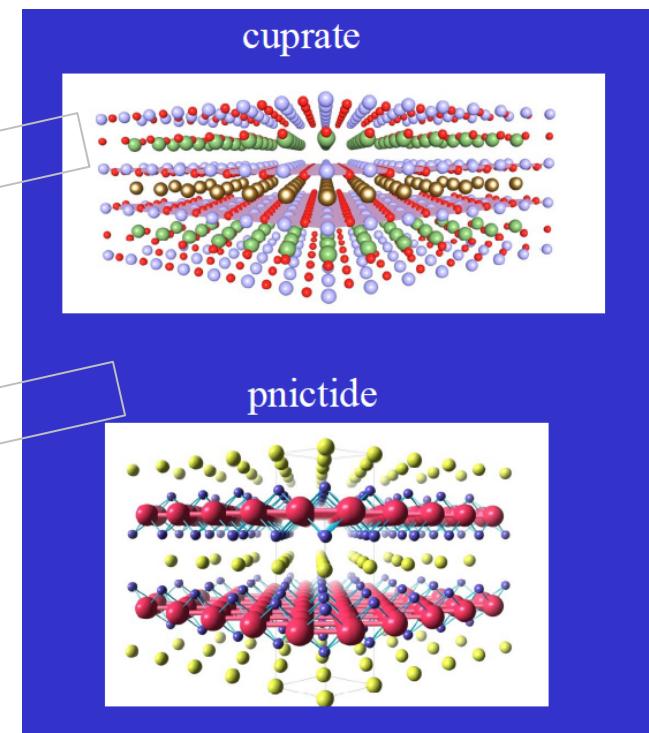
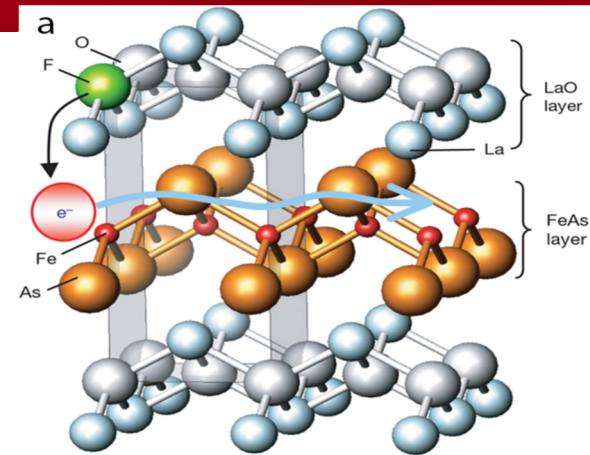
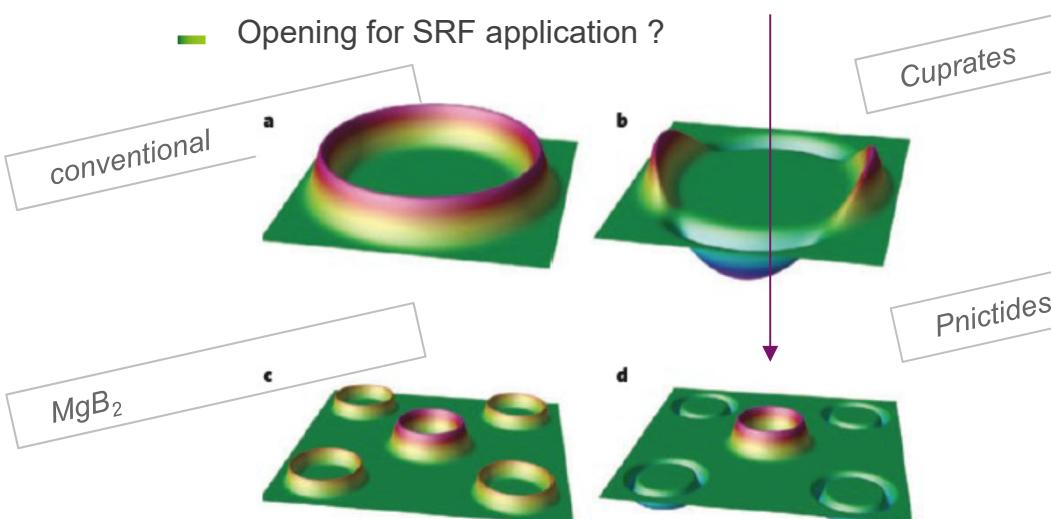
- M = Fe, Co, Ni
- Pn = As or P
- Re = La, Nd, Sm, Pr

■ A lot of common with YBCO

- High T_c (10-55 K up today)
- Layered structure
- Brittle material
- d-wave symmetry observed for some member of the family

■ But most compounds exhibit s-wave gaps...?

- Opening for SRF application ?



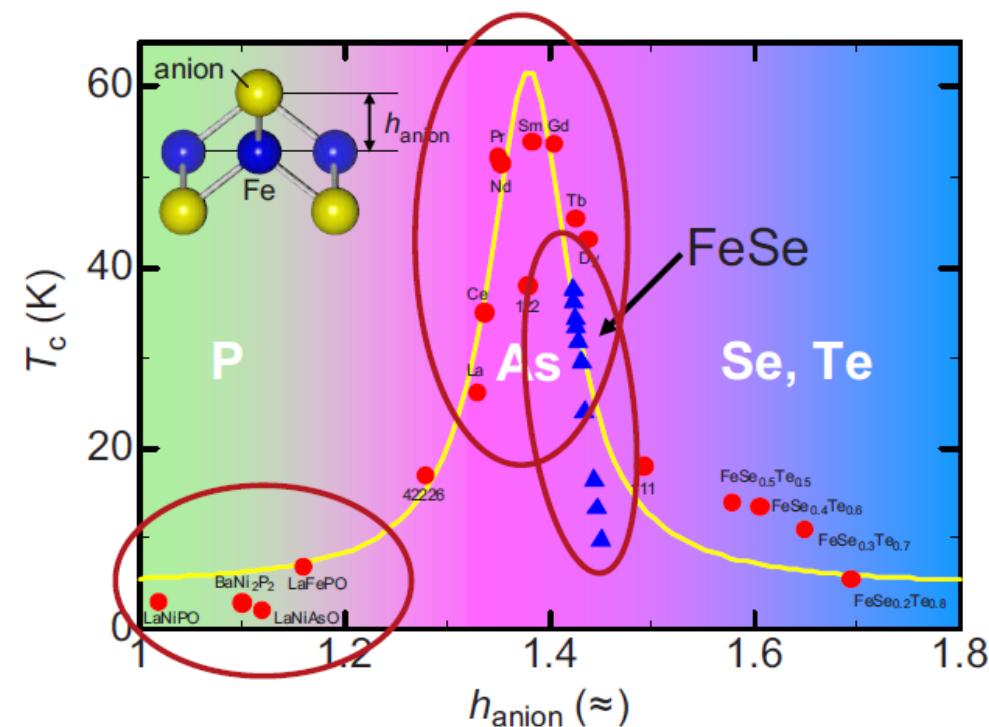
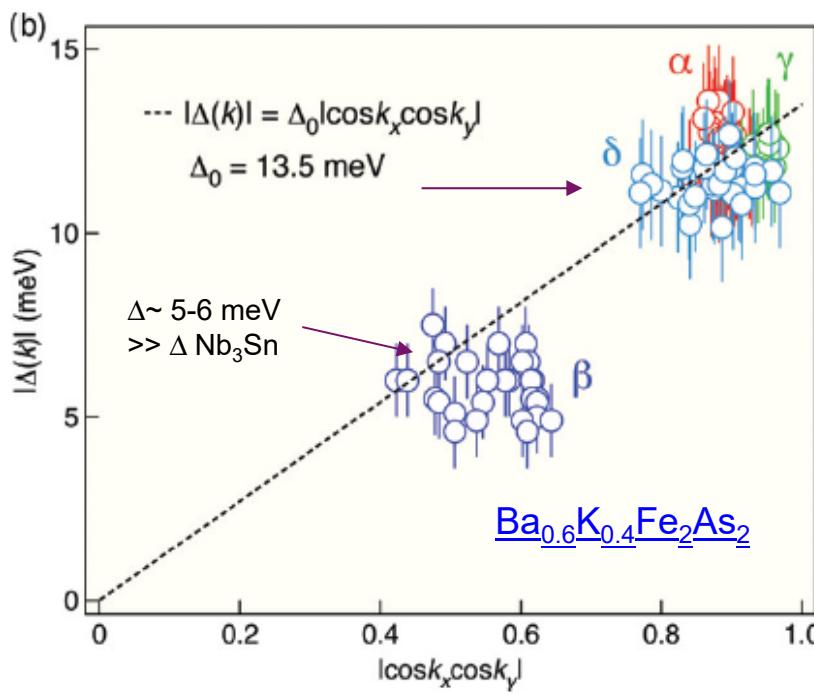
PNICTIDE FAMILY... MAYBE YES ?

A lot of common with YBCO

- High T_c (10-55 K up today)
- Layered structure
- Brittle material
- but
- Most compounds exhibit s-wave gaps
- Very sensitive to impurities content (either magnetic or not)

$\text{NaFe}_{1-x}\text{Co}_x\text{As}$ ($x = 0.0175$)
= ferromagnetic

$\text{NaFe}_{1-x}\text{Co}_x\text{As}$ ($x=0.045$)
= SC



MULTILAYERS

AFTER NIOBIUM : NANOCOMPOSITES MULTILAYERS



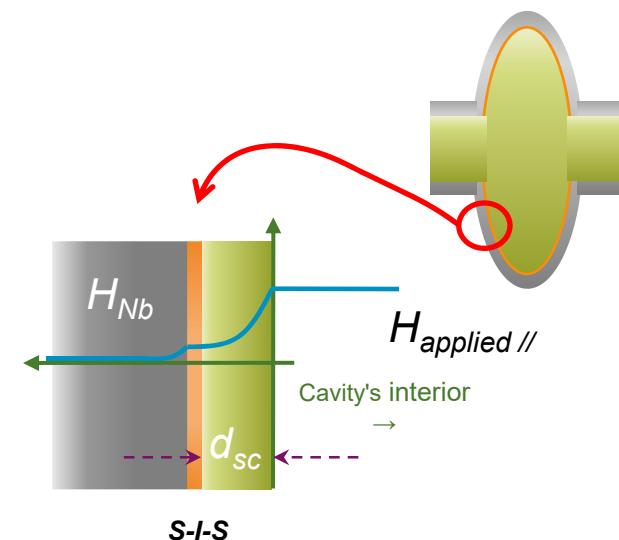
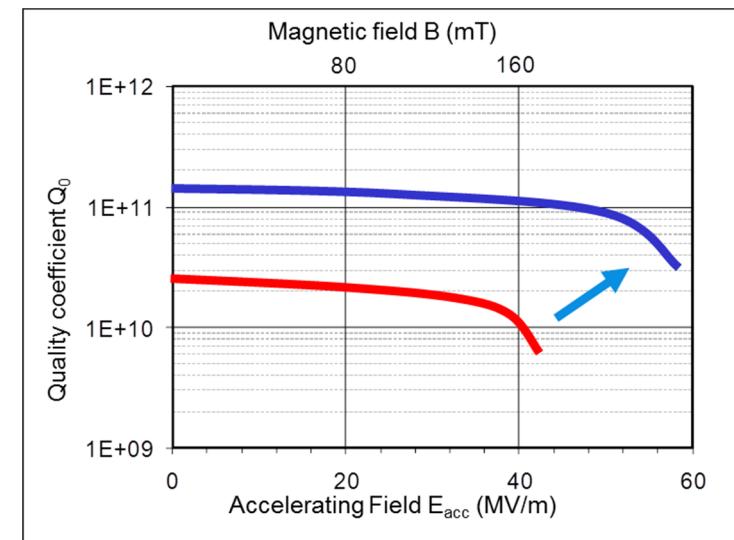
Structures proposed by A. Gurevich in 2006, SRF tailored

■ Dielectric layer

- Small \perp vortex (short \rightarrow low dissipation)
 - Quickly coalesce (w. RF)
 - Blocks avalanche penetration
- => **Multilayer** concept for RF application

■ Nanometric I/S/I/ layers deposited on Nb

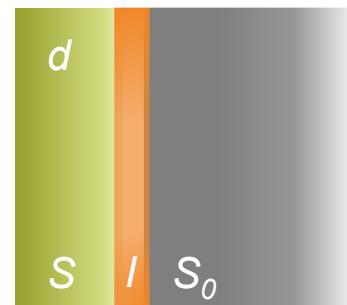
- SC nanometric layers (≤ 100 nm) $\Rightarrow H_{C1} \uparrow \Rightarrow$ Vortex enter at higher field
- Nb surface screening \Rightarrow allows high magnetic field inside the cavity \Rightarrow higher E_{acc}
- SC w. high T_c than Nb (e.g. NbN): $R_s^{NbN} \approx \frac{1}{10} R_s^{Nb}$
 $\Rightarrow Q_0^{\text{multi}} >> Q_0^{\text{Nb}}$



FIRST APPROACH: TRILAYERS

■ Meissner state stable if:

- Screening current @ both SC surface is < depairing current
- $J(0) < J_d = H_s/\lambda$ and $J(d) < J_{d0} = H_{s0}/\lambda_0$
- If d is small, H_{SH}^S is high, but most of the field reach S_0
- If d is thicker, H_{SH}^S is lower, but screening is more effective
- **exists an optimum thickness and a maximum screening field!!!**

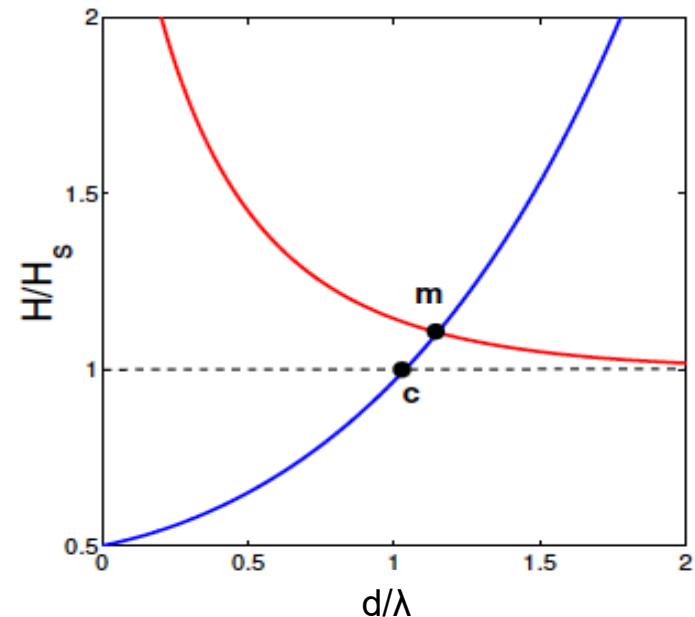


$$\frac{(e^{2d/\lambda} - k)H}{e^{2d/\lambda} + k} \leq H_s, \quad \frac{H(1+k)e^{d/\lambda}}{e^{2d/\lambda} + k} \leq H_{s0}$$

$$d_m = \lambda \ln(\mu + \sqrt{\mu^2 + k}), \quad \mu = \frac{H_s \lambda}{(\lambda + \lambda_0) H_{s0}}$$

$$H_m = \left[H_s^2 + \left(1 - \frac{\lambda_0^2}{\lambda^2} \right) H_{s0}^2 \right]^{1/2}$$

Maximum screening field H_m at the optimum S thickness $d^S = d_m$



TRILAYERS ON NIOBIUM



H_m at the optimum thickness exceeds the bulk superheating fields of both Nb and the layer material because of counterflow induced by Nb in the S layers with $\lambda > \lambda_0$. For $\lambda \gg \lambda_0$, practically for $\lambda > 160$ nm for a S layer on the Nb cavity with $\lambda_0 = 40$ nm, H_m approaches the limit

$$H_m \rightarrow \sqrt{H_s^2 + H_{s0}^2}$$

- **Dirty Nb layer:** $H_c = 200$ mT, $H_s = 170$ mT, $I = 2$ nm, and $\lambda = \lambda(\xi_0 / I)^{1/2} = 180$ nm
 $H_m = 288$ mT, $E_{acc} = 70$ MV/m, $d_m = 0.44\lambda = 79$ nm. +20% compared to $H_{SH}^{clean\ Nb} = 240$ mT
- **Nb₃Sn:** $H_s = 0.84H_c = 168$ mT and $\lambda = 120$ nm (moderately dirty):
 $H_m = 507$ mT, $E_{acc} = 120$ MV/m, $d_m = 1.1\lambda = 132$ nm $\times 2 H_{SH}^{clean\ Nb}$
- **Fe-pnictides on Nb:** $H_s = 0.84H_c = 168$ mT and $\lambda = 200$ nm:
 $H_m = 872$ mT, $E_{acc} = 206$ MV/m, $d_m = 1.78\lambda = 356$ nm $\times 4 H_{SH}^{clean\ Nb}$

Kubo et al, APL, 104, 032603 (2014); SUST, 30, 023001 (2017);
(London calculations)
Posen, et al, Phys. Rev. Appl. 4, 044019 (2015)
(London and GL calculations)
A. Gurevich, SUST 30, 034004 (2017)

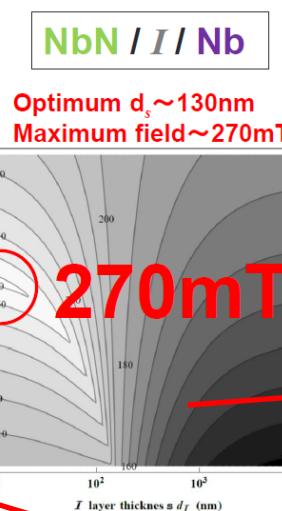
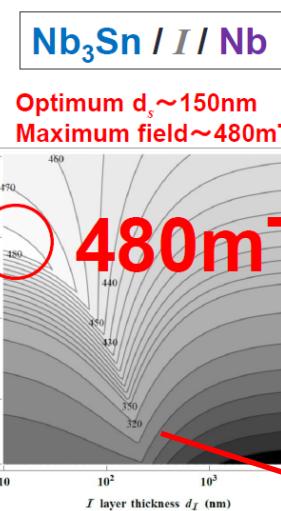
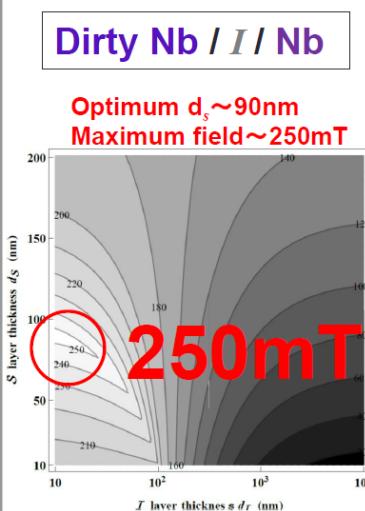
SIS OPTIMIZATION: IMPORTANCE OF MODELS



[A. Gurevich, T. Kubo](#)

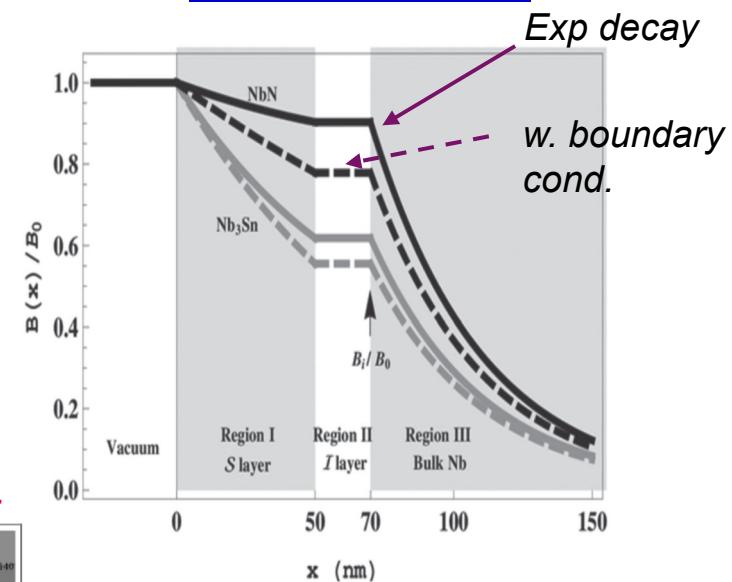
First approach: trilayers

- Boundary conditions implemented (*including effect of an insulating layer, finite thickness*)
- H_{SH} determined initial y in London approx., further improved w. quasiclassical theory (*valid @ $T \ll T_c$*)
- Initially assume “perfect conditions”
(bulk values, field // to surface)

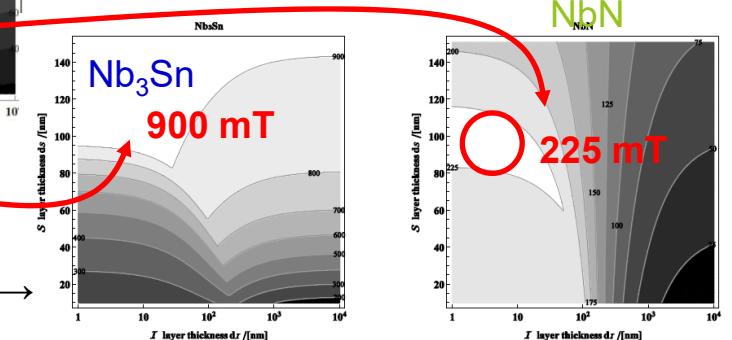


[Kubo 2013-17]

Previous calculation w. London theory only: not realistic →



← Quasiclassical Approach,
Can be further improved...



TRILAYER OPTIMIZATION (...)

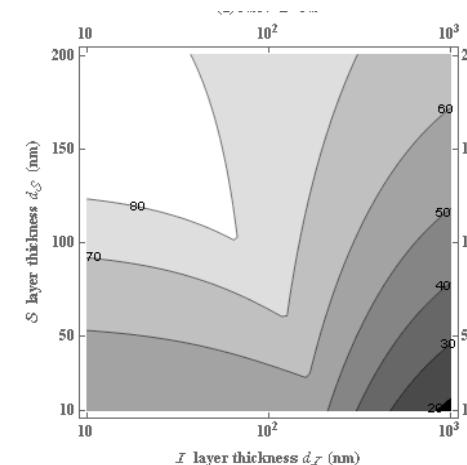
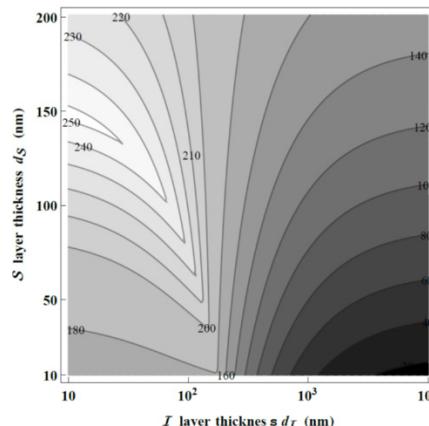


[A. Gurevich, T. Kubo](#)

■ Go for realistic condition

- layers present defects, non-negligible surface roughness, non-uniform thickness.
- $\rightarrow H_{SH}^S$ suppressed due to of the screening current enhancement.
- Introducing material suppression factor $\eta = f(\text{defect size and aspect ratio}, \xi^S)$
- $-\eta \sim 0.85$ for typical electropolished Nb surface)
- H_{SH}^{SIS} and optimal S layer thickness d_m^S can be determined w. surface topographical data

*Ideal Nb substrate
with $B_{C1}=170$ mT*



Nb with defects,
with $B_{C1}=50$ mT*

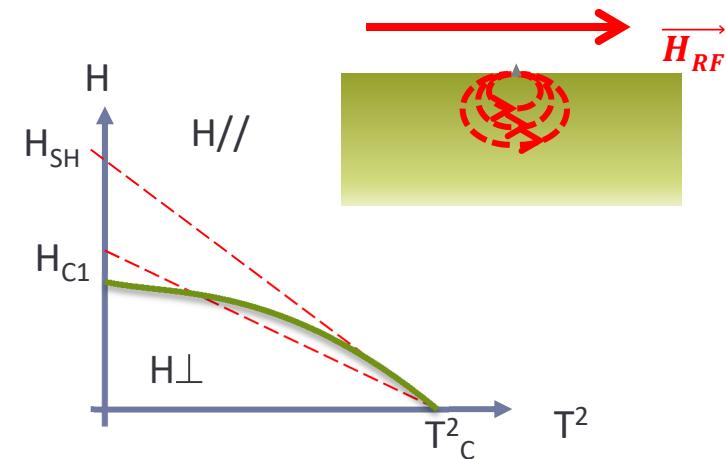
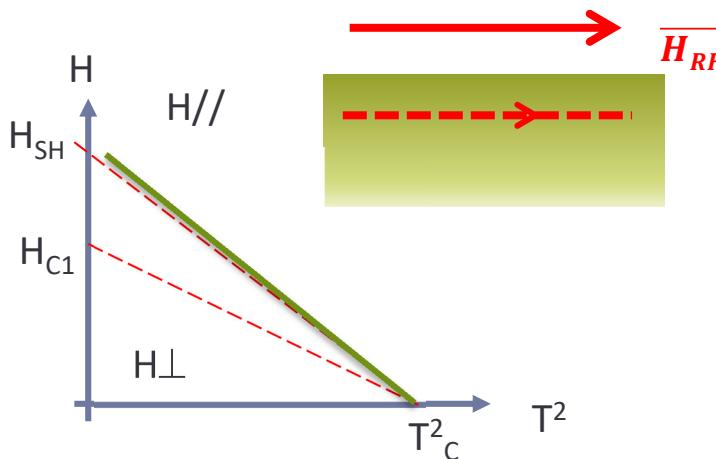
* e.g. morphologic
defects that allow earlier
vortex penetration

See exp proof later on

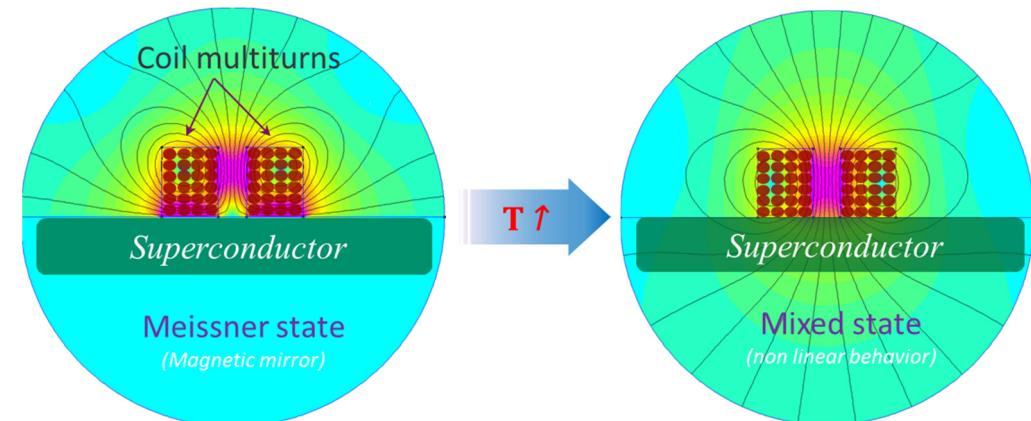
WHAT IS THE LIMIT ($H_P/H_{C1}/H_{SH}$) ?



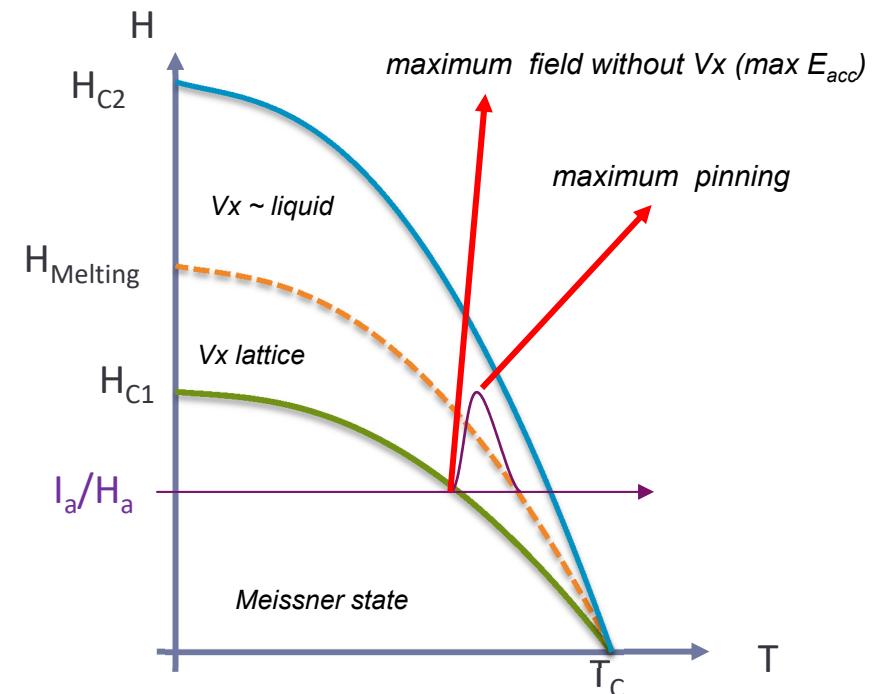
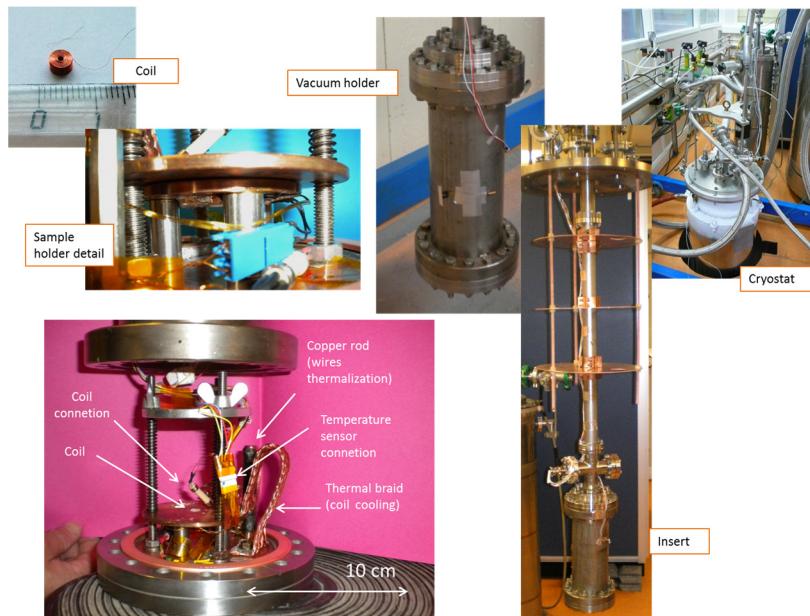
- Real world cavities behavior is dominated by a few number of defects
- It is very important to measure the penetration field of samples in realistic conditions



- Local magnetometry
- ~ Same geometry as cavities
- No shape/edge effect (vs DC/ SQUID magnetometry)
- No demagnetization effect
- Measures actual penetration field wherever it is $H_P/H_{C1}/H_{SH}$

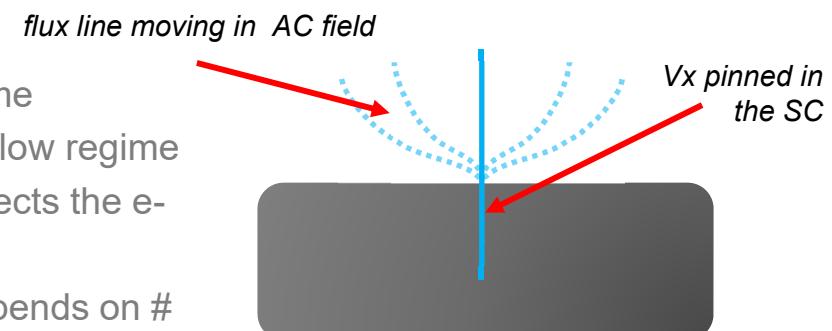


EXPERIMENTAL DETAILS



■ Low frequency \equiv DC :

- $0 < H_a < H_{C1} \Rightarrow R=0$, Meissner state
- $H_{C1} < H_a < H_M \Rightarrow Vx$ are trapped, $R=0$, Campbell regime
- $H_M < H_a < H_{C2} \Rightarrow Vx$ are moving liquid like, $R \neq 0$, Flux flow regime
- Third harmonic signal arise from flux line tension (affects the e- inside the Cu coil),
- It does not depend on dissipation inside Nb, BUT depends on # of Vx trapped there (and length).



NbN coating by Magnetron Sputtering

■ NbN single layers series

- NbN SL / “thick” Nb layer
 - Magnetron sputtered
 - MgO as dielectric layer
- Far from perfect...



Nb (nm)	MgO (nm) Calc(actual)	NbN (nm) Calc(actual)	T _c (K)
250 [†]	14	0	8.9
250 [†]	14	25	15.5
500	10 (10.3)	50 (65)	15*
500	10 (8.4)	75 (72)	14.1*
500	10 (9.8)	100 (94)	14*
500	10	125	14.3*
500	10 (6.7)	150 (132)	15.9*
500	10 (10.4)	200 (164)	15*

† Not same batch, deposited on the same conditions, but substrate = sapphire

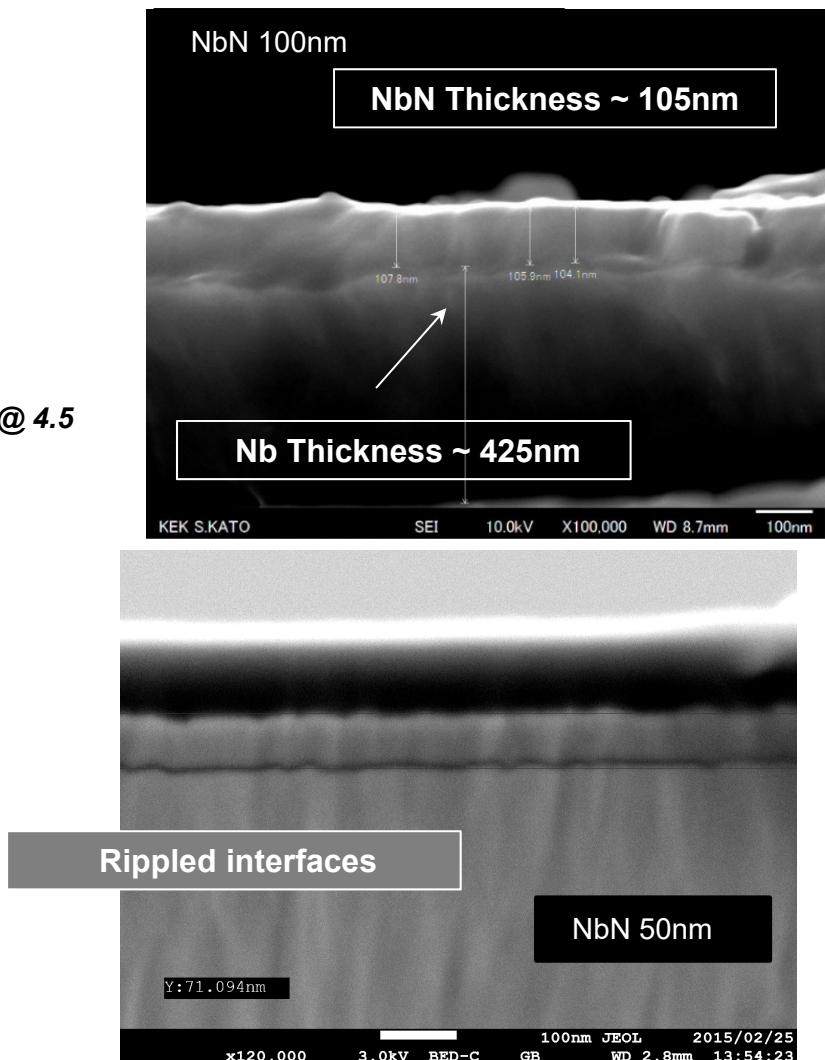
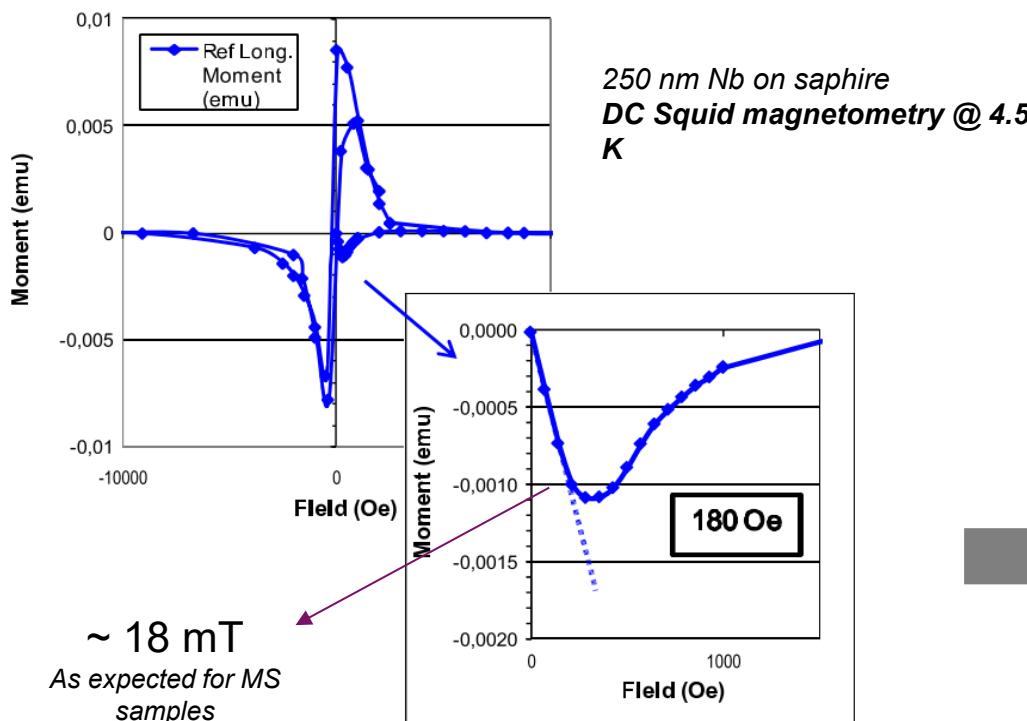
*As determined with magnetometry, see below.

SPUTTERED (DEFECTIVE) MATERIALS...



Typical defects...

- Low H_{C1}
- Thickness \neq uniform
- ...

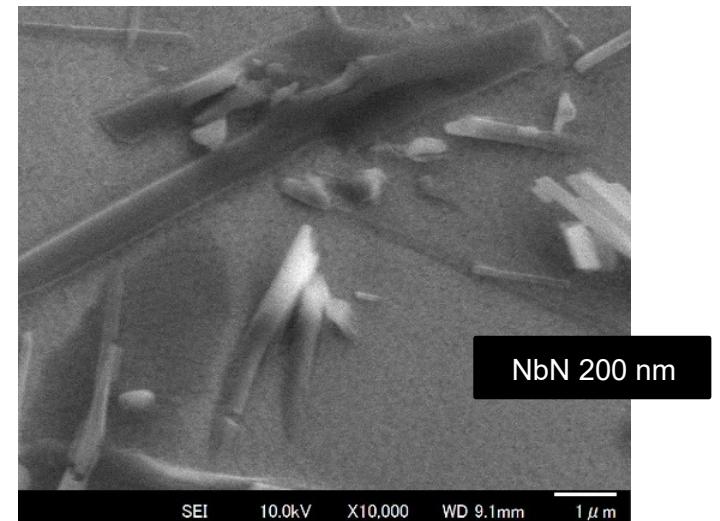
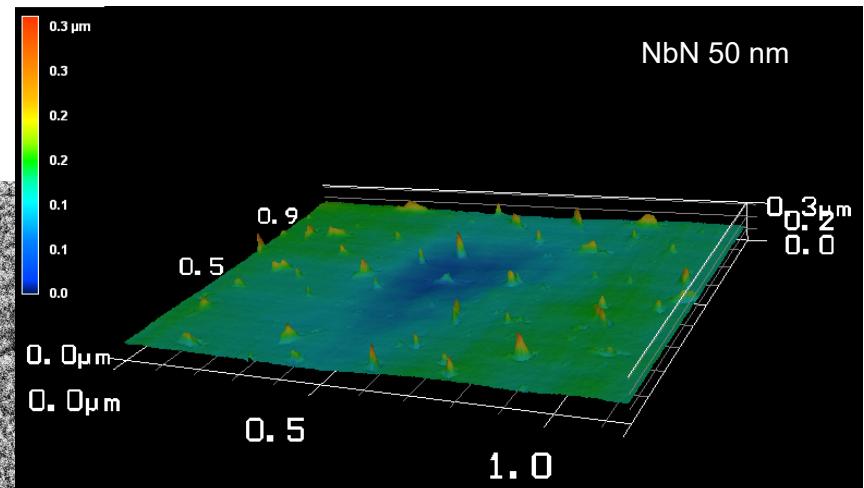
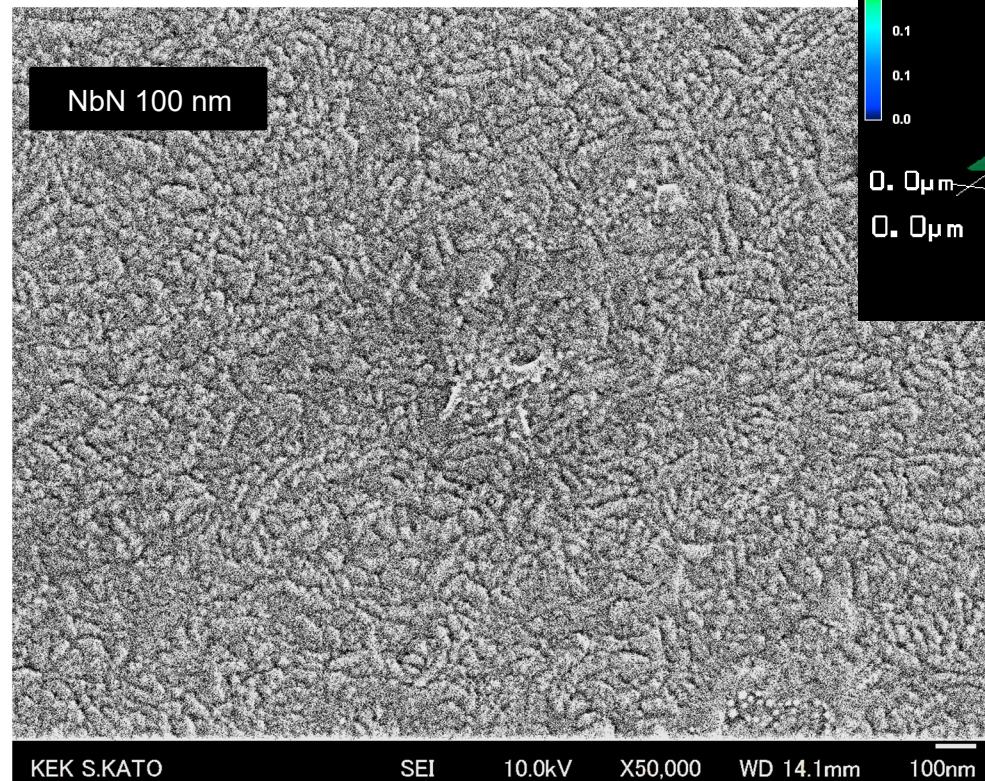


FAR FROM PERFECT...



Morphology

■ Rough surface

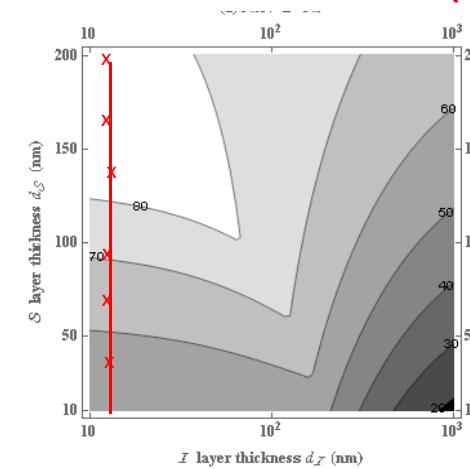
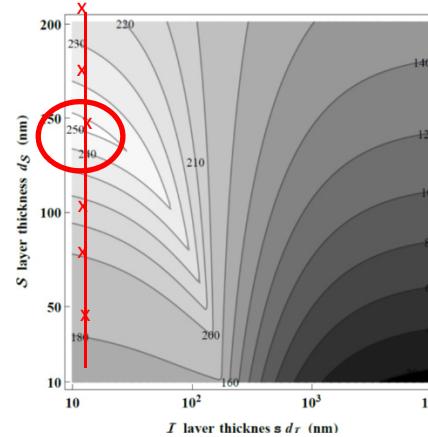


MgO needle ?
(capping material)

COMPARAISON WITH THEORY

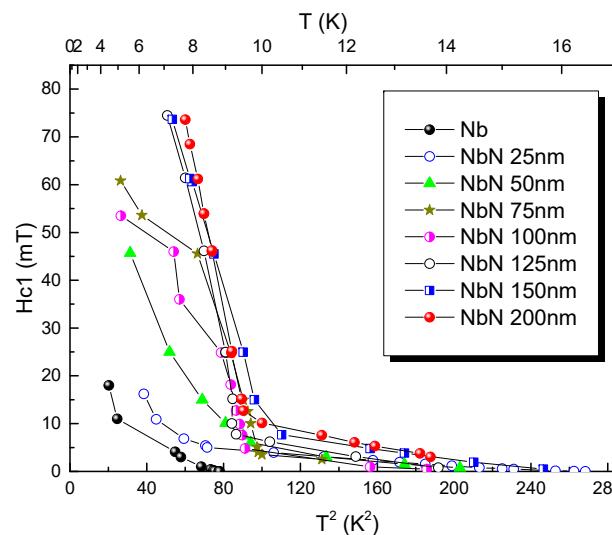
Theoretical predictions from T. Kubo (KEK)

Ideal Nb substrate
with $B_{C1}=170$ mT



Nb with defects*,
with $B_{C1}=50$ mT

* e.g. morphologic
defects that allow earlier
vortex penetration See
SST paper cited earlier

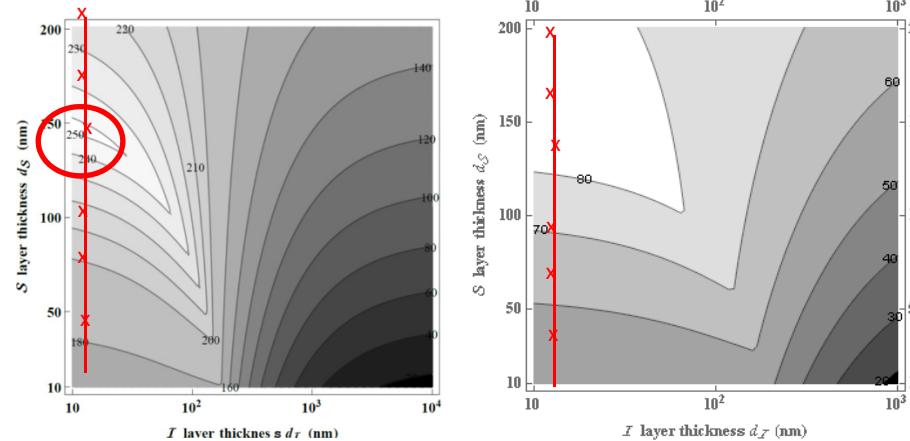


- The enhancement of the field penetration increases with thickness of NbN
- It reaches a saturation at thicknesses > 100 nm

COMPARAISON WITH THEORY

Theoretical predictions from T. Kubo (KEK)

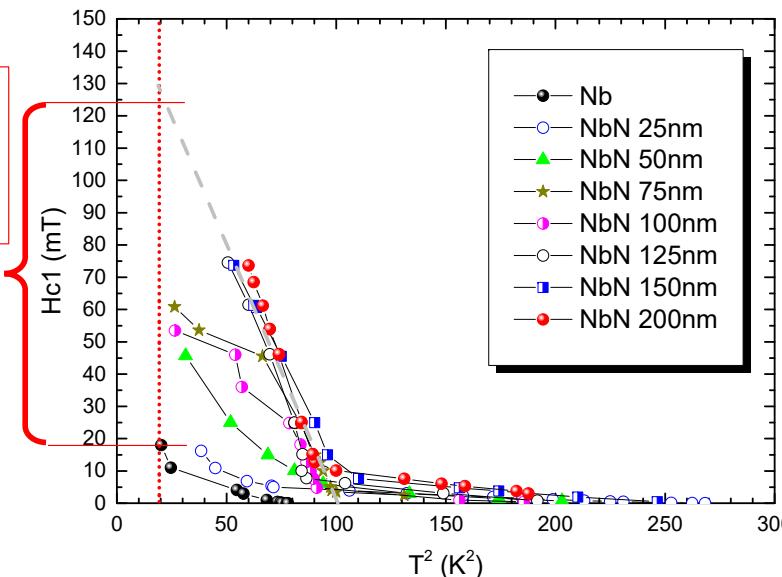
Ideal Nb substrate
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Nb with defects*,
with $B_{C1}=50$ mT

* e.g. morphologic
defects that allow earlier
vortex penetration See
SST paper cited earlier

@ 4.5 K
~ + 110 mT?
~25-30 MV/m
ILC shape

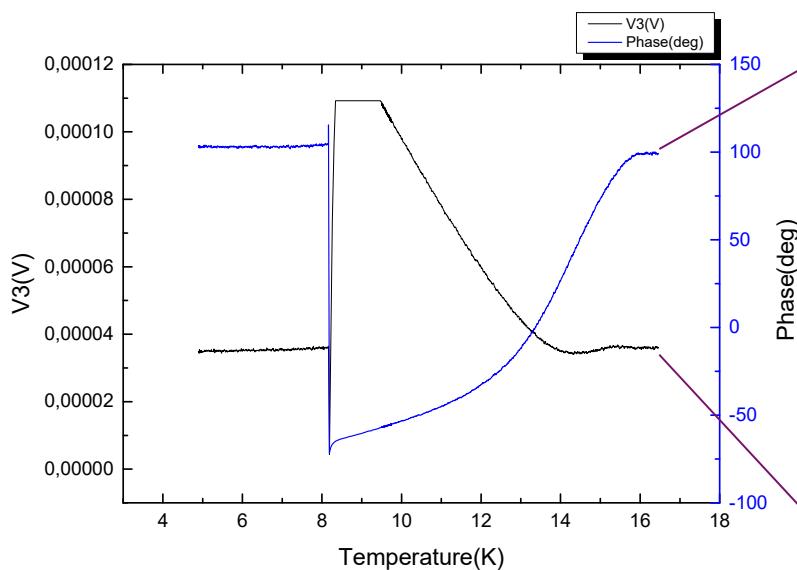


- The enhancement of the field penetration increases with thickness of NbN
- It reaches a saturation at thicknesses > 100 nm

CLOSEUP OF 3rd HARMONIC SIGNAL



- For a given H_{appl} , we observe 3 \neq transition temperatures

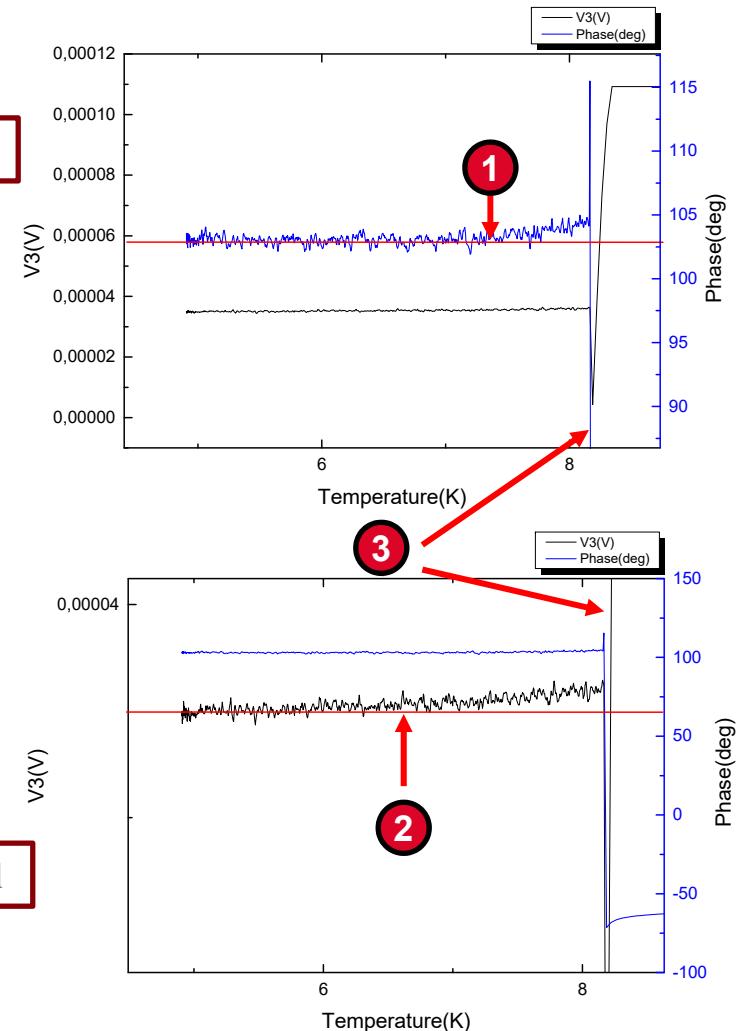


- $T_1 \sim T_2$: within noise level
- $T_3 \gg T_2$: dramatic transition

Phase signal

$T_1 \sim T_2$
 $T_3 \gg T_2$

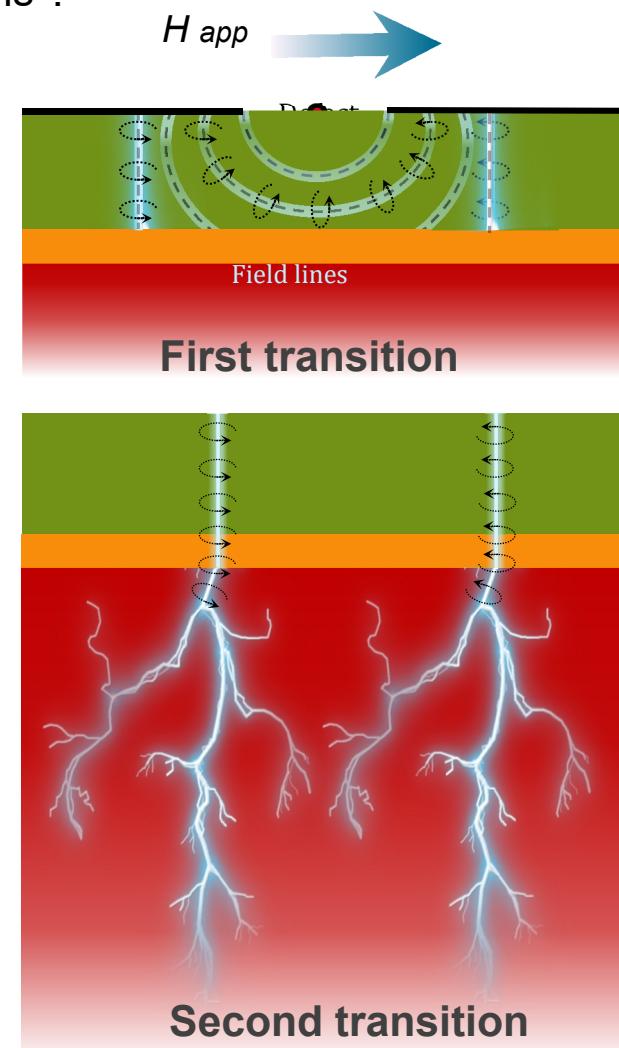
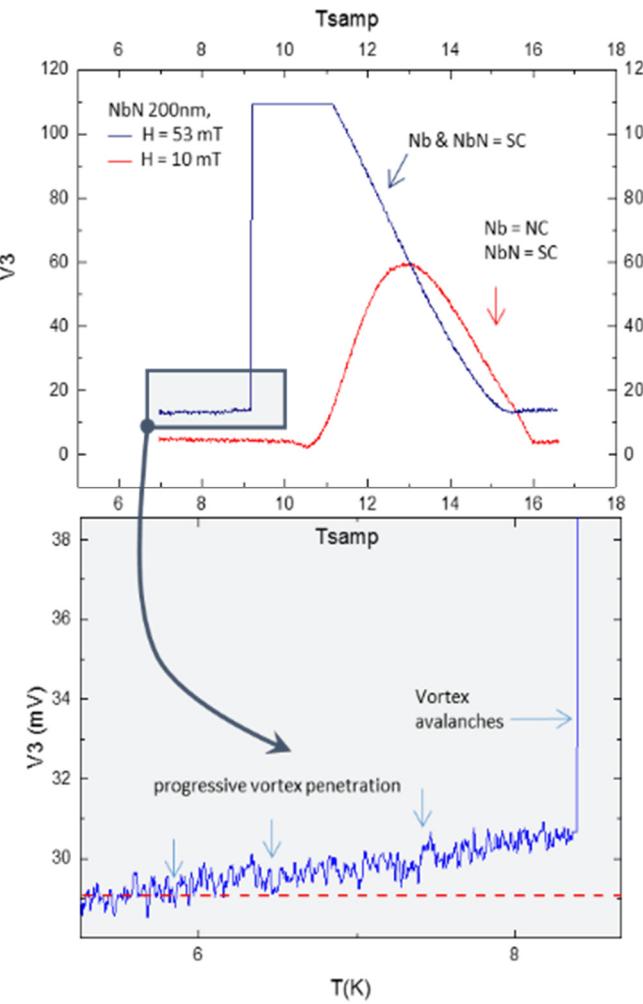
Voltage signal



ROLE OF THE DIELECTRIC LAYER !



■ Why do we have two transitions ?

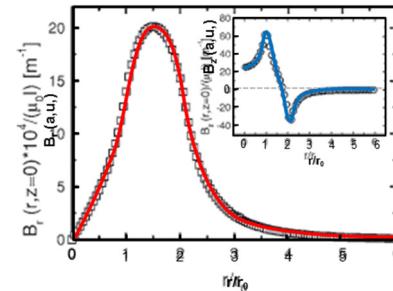
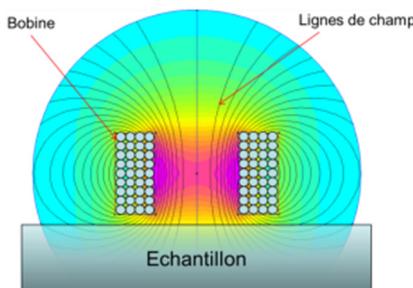


[†]B. Bean and J. D. Livingston, Phys. Rev. Lett. 12, 14 (1964).

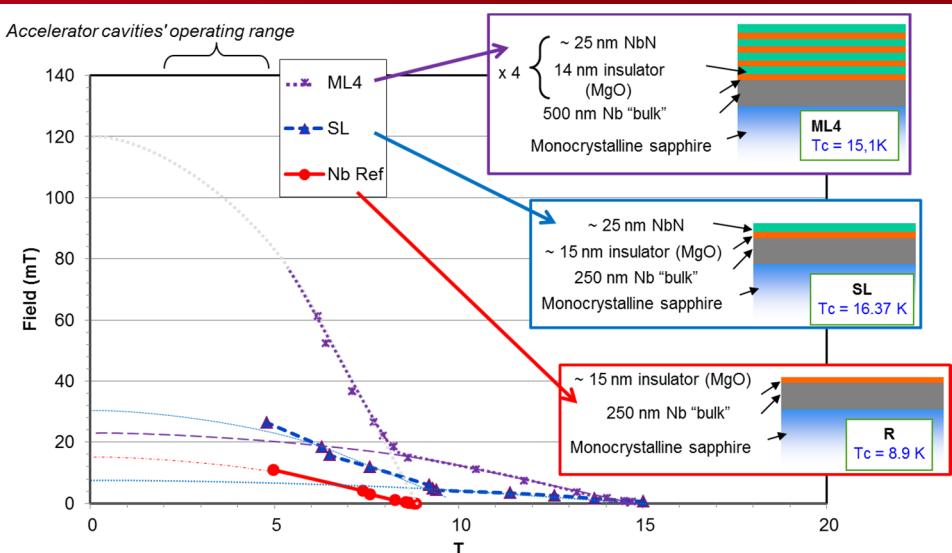
H_{c1} (E_{ACC}^{MAX}) AND R_s (Q_0^{MAX}) ESTIMATION



■ Local magnetometry:



Accelerator cavities' operating range



■ RF test (collaboration IPNO)

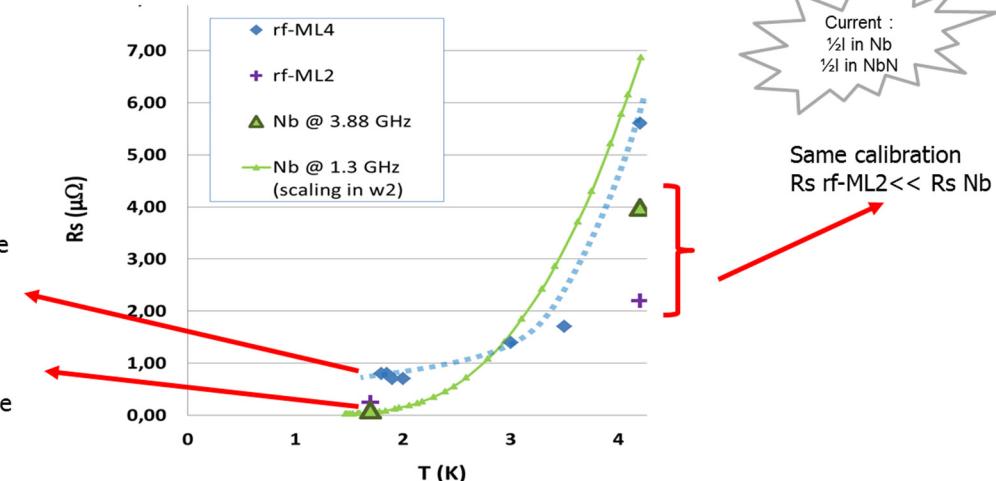
Bulk Nb TE011 cavity body

Themometric set-up

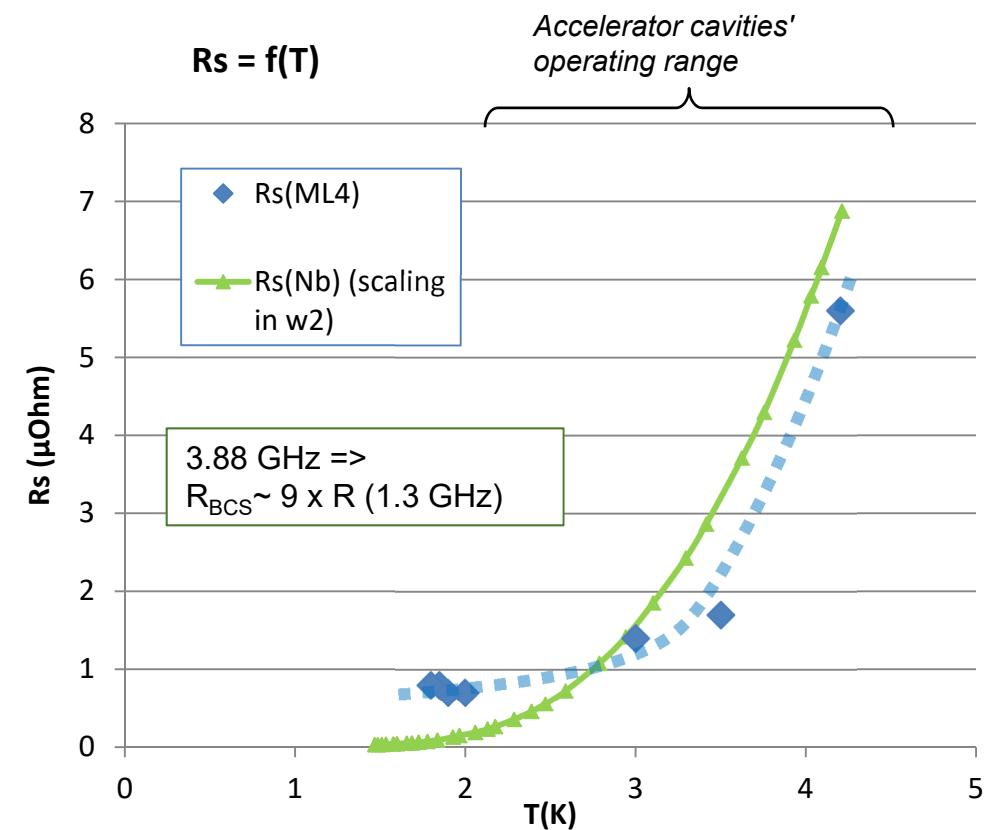
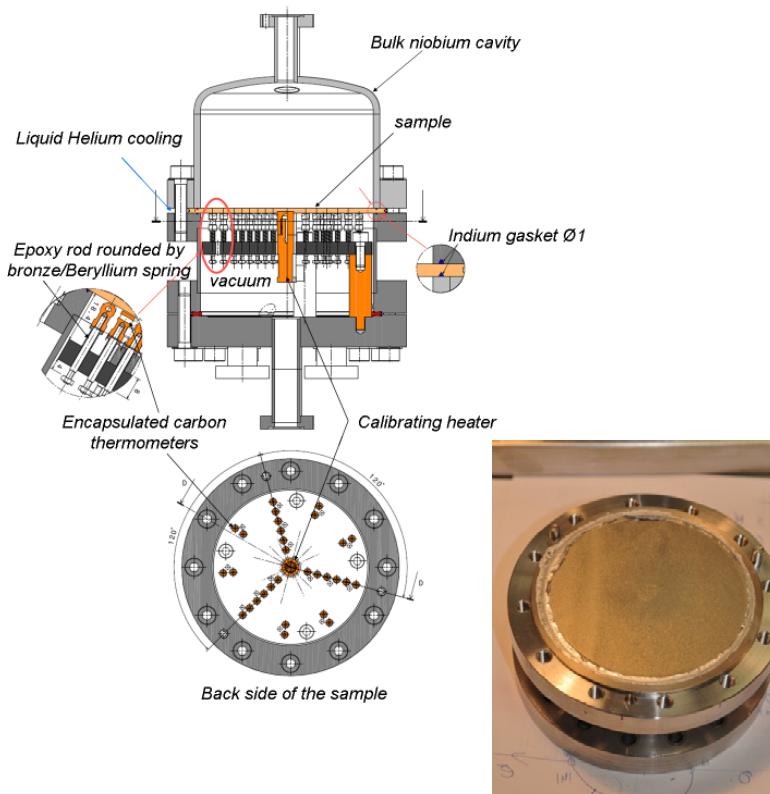


Polycrystalline Nb substrate

Large grain Nb substrate

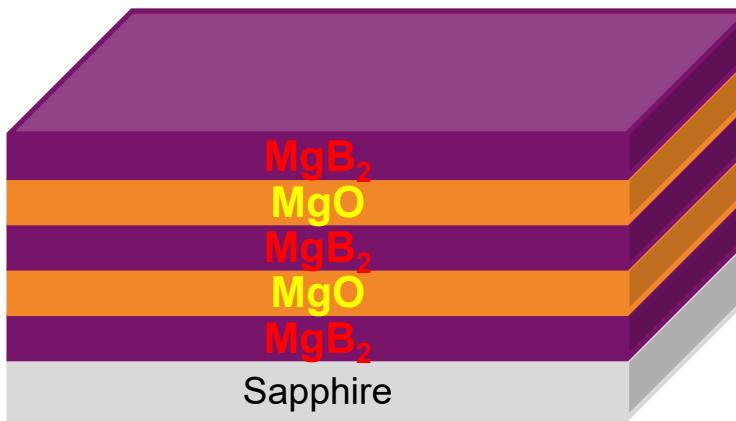


1st TEST RF @ 3,88 GHz (4 25nm NbN N LAYERS)



- Comparison is done with a high performance 1.3 GHz Nb cavity (scaling in ω^2)
- Indium gasket presents some defects measured with thermometric map => extra RF losses
- Residual resistance comes from NbN + bulk Nb substrate + indium gasket. Further investigations needed.

MgB₂-MgO MULTILAYER FILMS

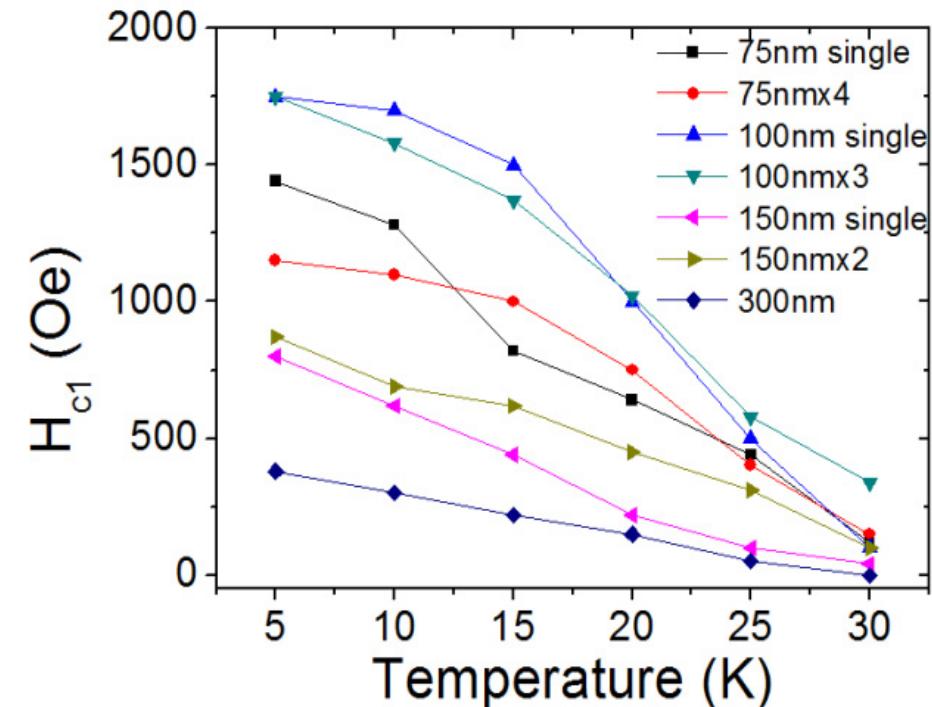


Alternating MgB₂-insulator structures have been fabricated on sapphire substrate:

- 40 nm MgO as insulating layer, sputtered.
- MgB₂ deposited by HPCVD *ex situ*. 150, 100, and 75 nm in thickness.

T_c near 40 K for 100 and 150 nm films. Lower for 75 nm film.

Multilayer films with thin MgB₂ layers show higher H_{c1} than the 300 nm film even though the total thickness are the same.

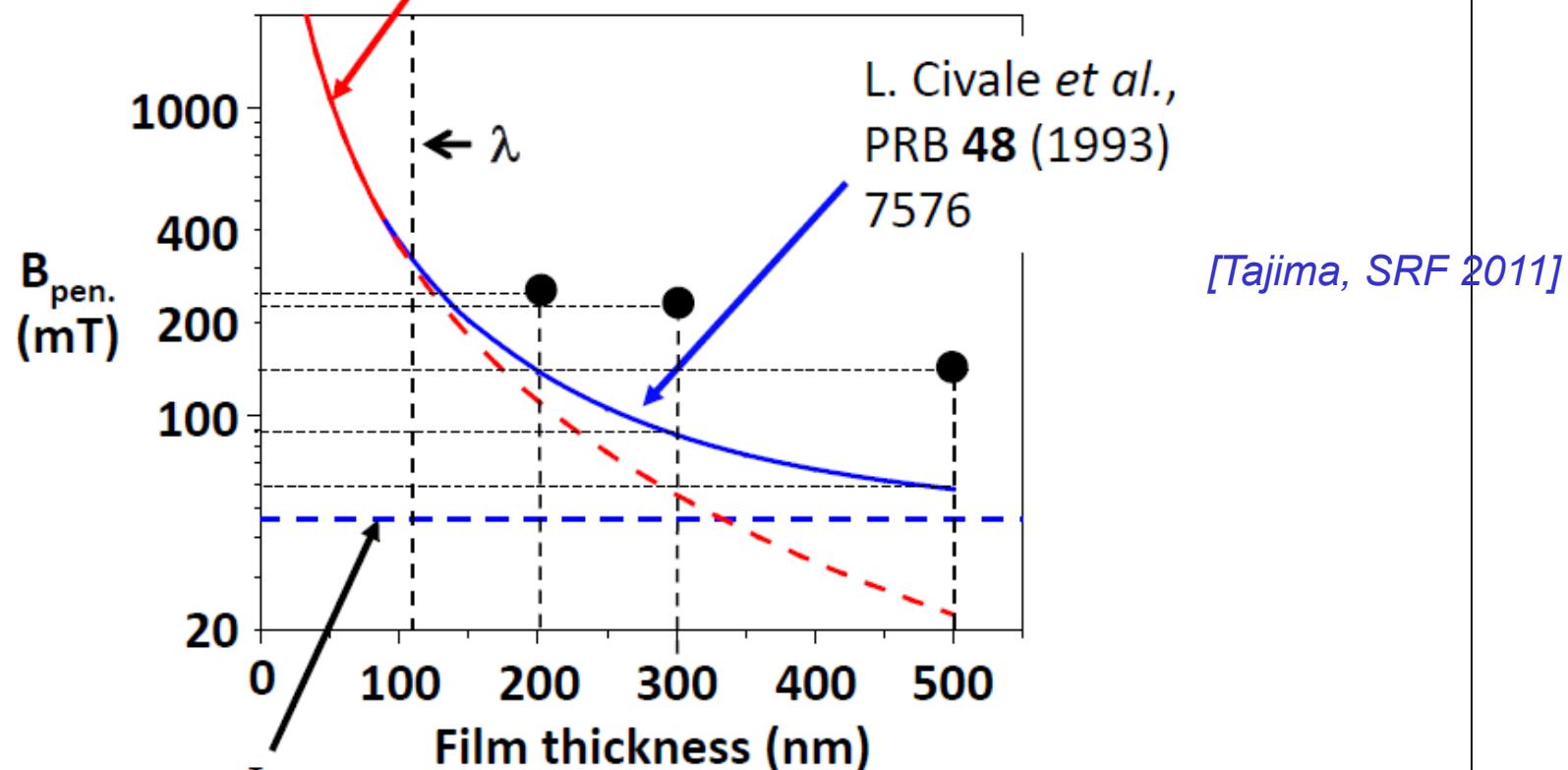


[Teng, Xi – Temple University]

EFFECT OF M.F.P.

B_{pen} data are higher than expected B_{c1} ($\lambda=110 \text{ nm}$, $\xi=6 \text{ nm}$)

$$H_{c1}(d \ll \lambda) \approx \frac{2\Phi_0}{\pi d^2} \ln \frac{d}{\xi} \quad \text{Gurevich, APL } \mathbf{88} \text{ (2006) 012511}$$



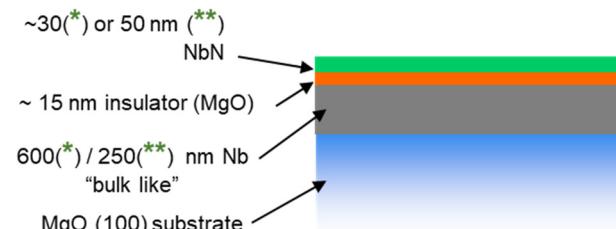
$$H_{c1}(d \gg \lambda) = \frac{\Phi_0}{4\pi\lambda^2} \ln \kappa \sim 46 \text{ mT}$$

SRF2011, Chicago, IL, USA, 25-29 July 2011

OTHER RESULTS ON NbN OR NbTiN ML

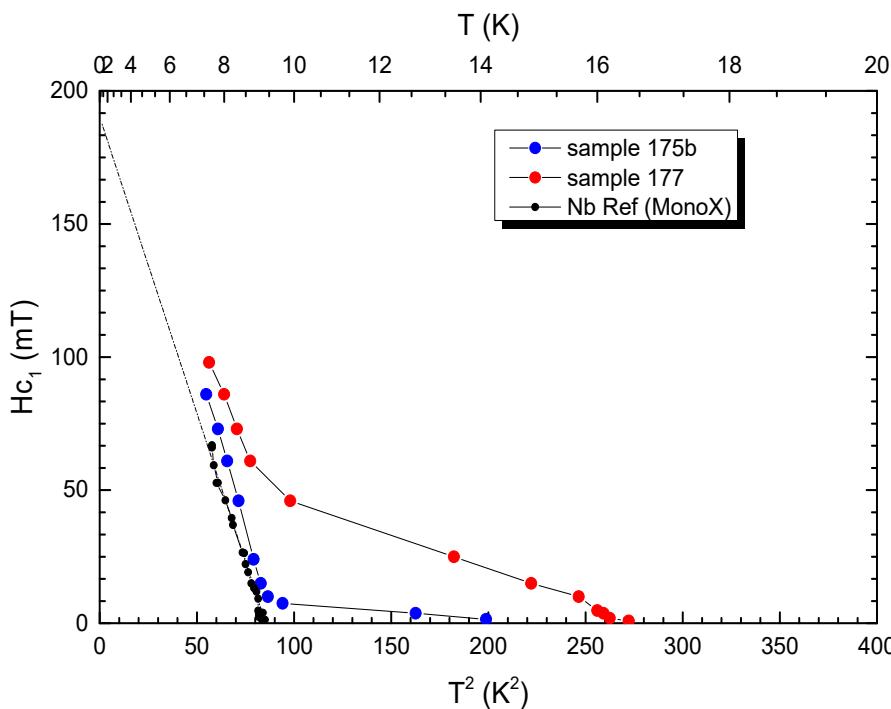
Nb/MgO/NbN Samples

[Lukaszew, 2012]

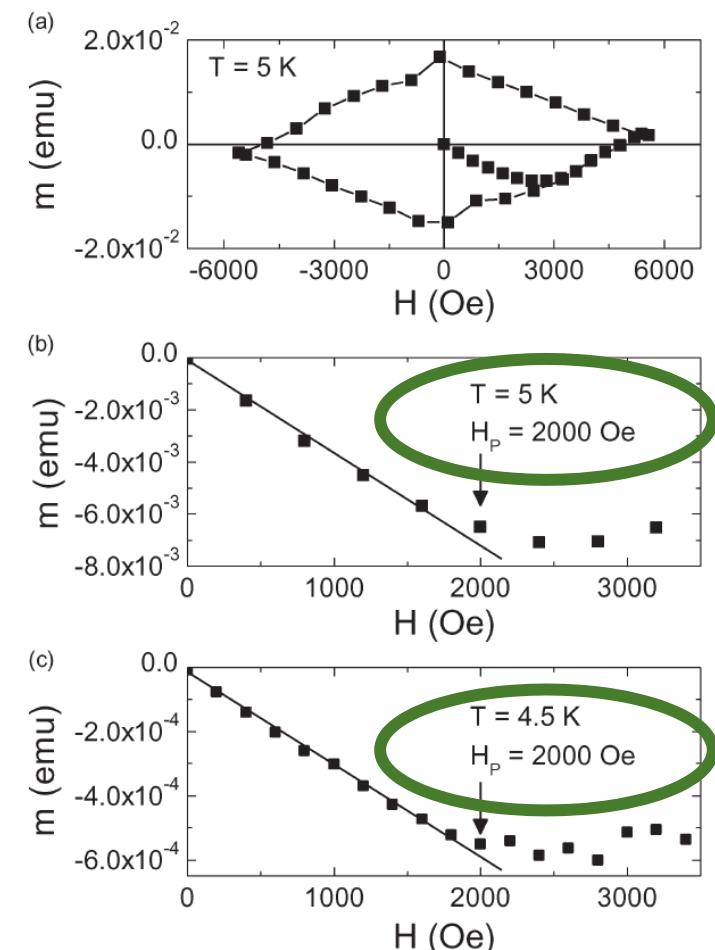


Nb bulk /AlN/NbTiN Samples

[AM Valente-Felicianno, TBP]



**



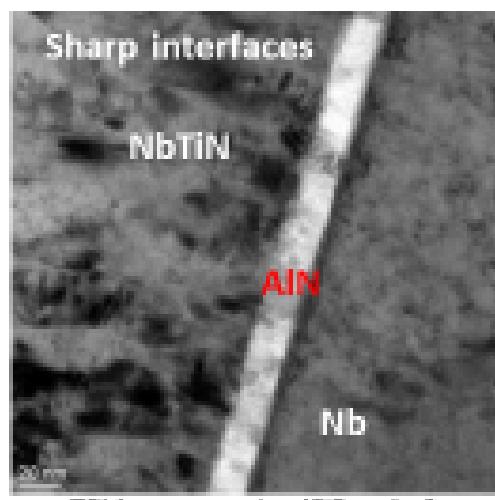
Compare with what is expected for bulk Nb : ~1300 Oe @ 4.5 K !

NbTiN/AlN/Nb structures - RF characterization

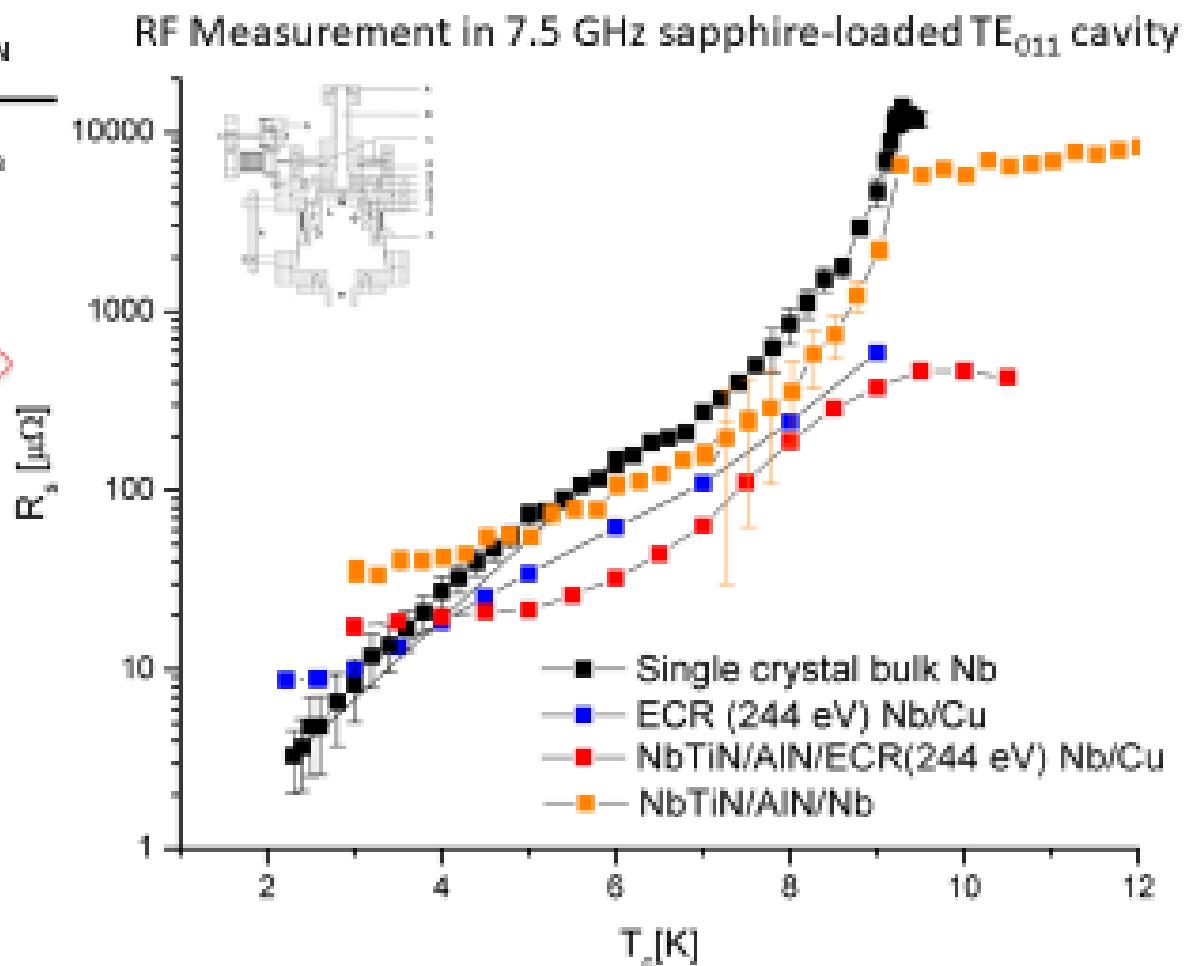
SIS structures coated on ECR Nb/Cu film and bulk Nb: 24h-bake, coating and annealing for 4 h at 450°C.

[A.M.Valente-Feliciano]

	AlN	NbTiN
N ₂ /Ar	0.33	0.23
Total pressure [Torr]	2x10 ⁻³	2x10 ⁻³
Sputtering Power [W]	100	300
Deposition rate [nm/min]	~ 2.5	~ 18
Thickness [nm]	20	150
T _c [K]	N/A	16.9



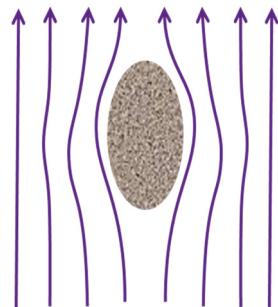
TEM cross-section (FIB cut) of
NbTiN/AlN/Nb/Cu structure



Lower BCS resistance beyond 4 K for SIS coated surfaces compared to standalone ECR film & bulk SC Nb.

ML WITHOUT DIELECTRIC INTERLAYER

μ -SR



[Junginger, SRF 2017]

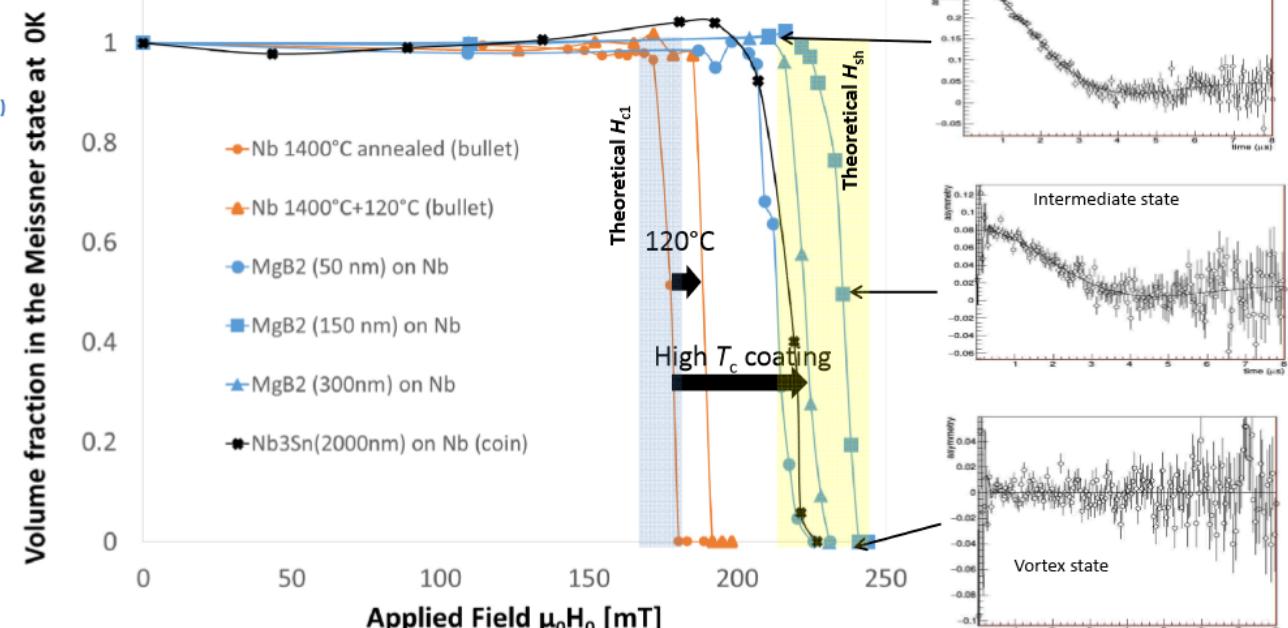
<https://arxiv.org/abs/1705.06383>



T. Junginger - Dirty layers, Bi-layers and Multi-layers: Insights from muSR - SRF17 Lanzhou, China

TRIUMF 7/15

Field of first flux entry measurements



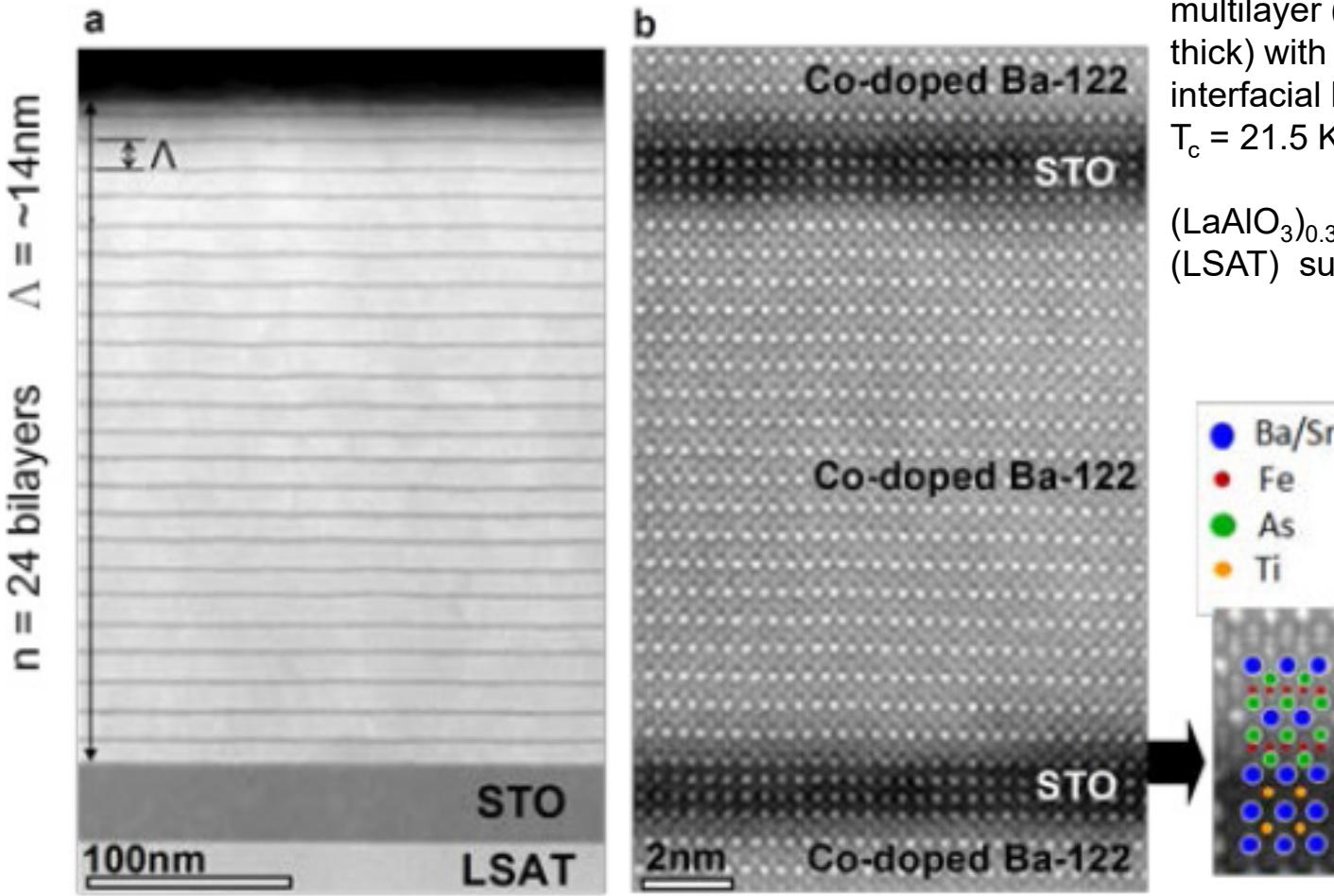
The SS boundary provides an additional barrier to prevent penetration of vortices. It would not be as robust as the I layer of the SIS structure, but it also contributes to pushing up the onset of vortex penetration.

[Kubo, SST]

SUPERCONDUCTING IRON-PNICTIDE MULTILAYERS



S. Lee et al, Nature Materials, 12, 392 (2013)



PLD grown Co-doped Ba_2As_2 multilayer (24 layers, 13 nm thick) with SrTiO_3 (1.2 nm) interfacial layers
 $T_c = 21.5\text{ K}$

$(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{TaAlO}_6)_{0.7}$
(LSAT) substrate:

Group of C-B Eom, U Wisconsin

First high quality epitaxial films have been grown by C.-B. Eom (UW)

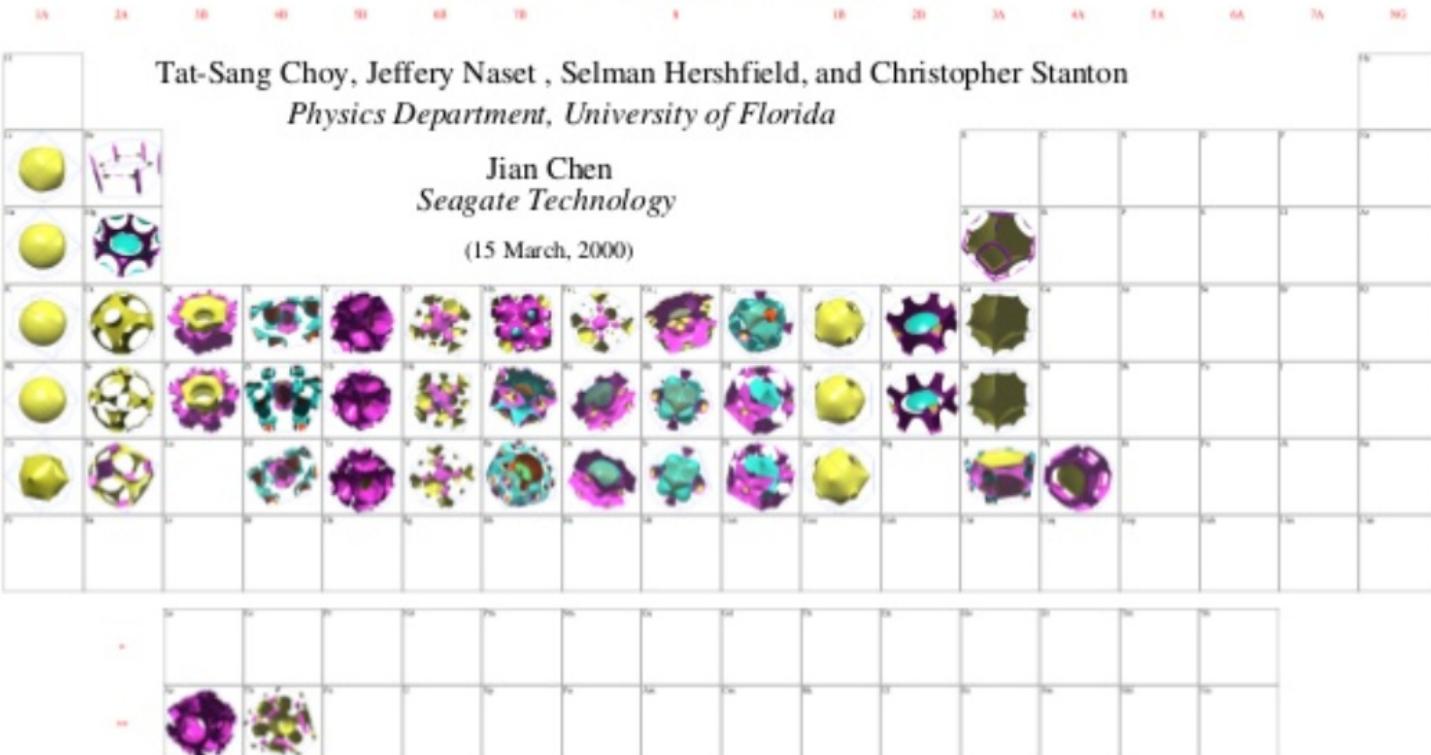
CONCLUSIONS AND PERSPECTIVES



- Superconducting cavities are dominated by their surface quality (Niobium AND other SC !)
- Niobium is close to its ultimate limits, but can be surface tailored (doping)
- H_{SH} difficult to reach in real “accelerating cavities” (low T, large scale cavity fabrication, surface defects,...)
- ML structures seem to be a promising way to go toward realistic complex materials (+ Nb cavity upgrade)
- Renewed activity on bulk-like Nb films (cost issues) and high H_{SH} SC e.g. Nb_3Sn or NbN (higher performances)
- Look for higher Q_0 , not only E_{acc} !
- WE ARE ON THE EVE OF A TECHNOLOGICAL REVOLUTION FOR SRF CAVITIES !

Periodic Table of the Fermi Surfaces of Elemental Solids

<http://www.phys.ufl.edu/fermisurface>



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Ferromagnets:



Alternate Structures :



Source of tight binding parameters (except for fcc Co ferromagnet): D.A. Papaconstantopoulos, *Handbook of the band structure of elemental solids*, Plenum 1986.

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