Thoughts on the Competitive Merits of Nb-Ti-Ta, Nb_3Sn and MgB_2

David Larbalestier –

Most emphasis on Nb-Ti-Ta (Peter Lee and Alex Squitieri)

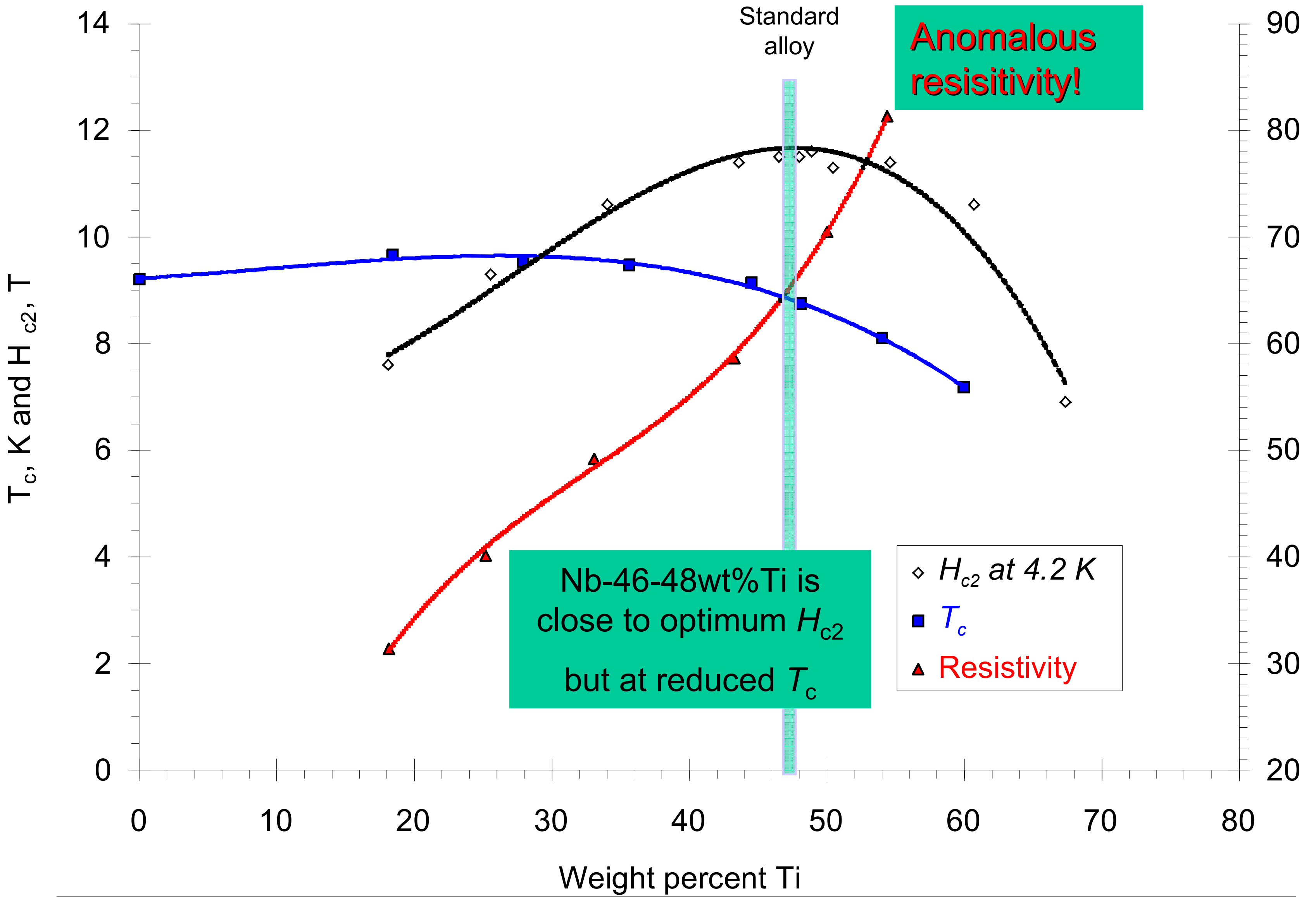
Recent very high H_{c2} results on MgB_2 (Valeria Braccini and Alex Gurevich and Chang-Beom Eom)

Some general thoughts on H^*/H_{c2} ratio

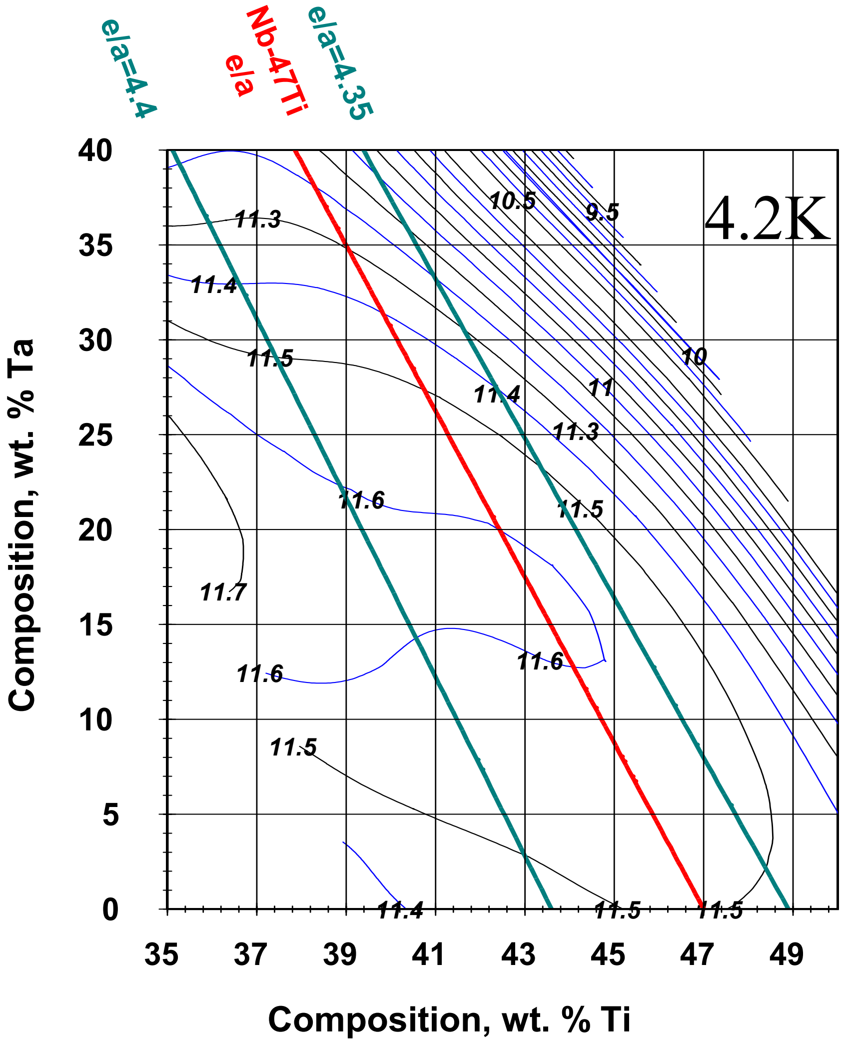
Outline of Talk

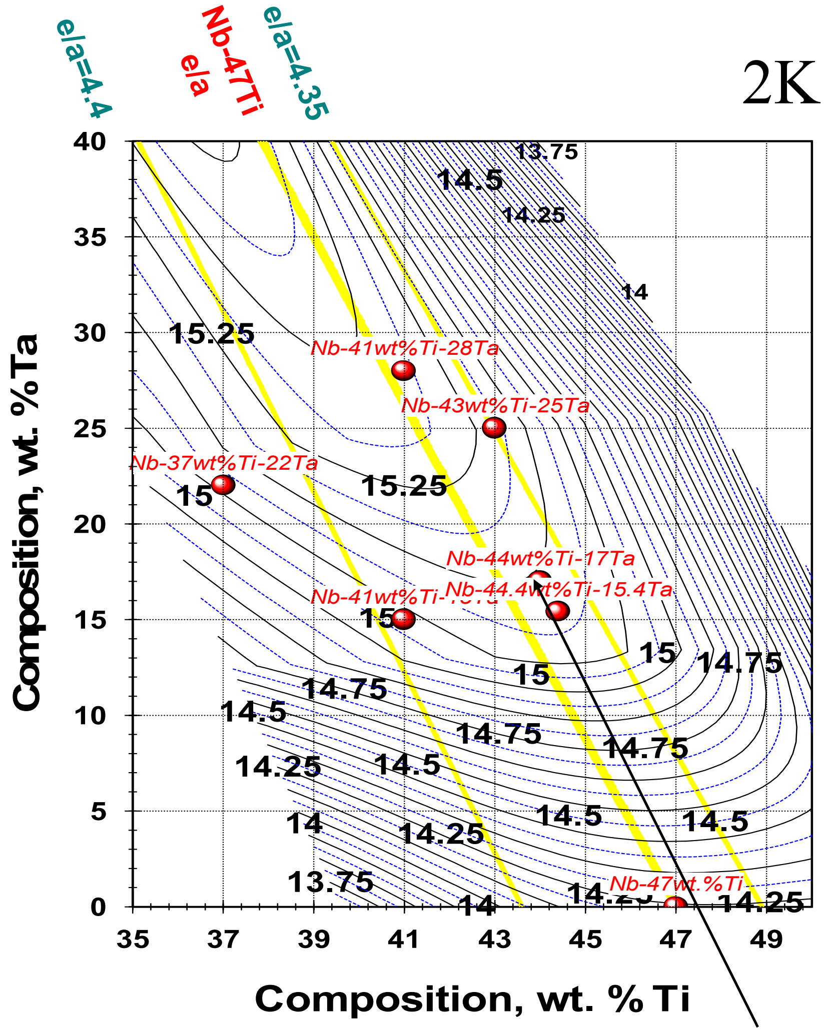
- Conductors for magnets > 10T - ??
  - Nb_3Sn
  - Nb-Ti – or **Nb-Ti-Ta**?
  - BSCCO – 2212 or 2223?
  - YBCO-CC?
  - **MgB_2**?
- Thousands of superconductors
  - …but only a few conductors………??

Nb-Ti Superconductivity



Nb-Ti-Ta – H_{c2}: 4.2K and 2K





H_{c2} data: Hawksworth and Larbalestier 1980 – 1.25 T enhancement at 2K for 25 wt.%Ta

Stages of conductor R&D

- Stage 1:

  - Develop an empirical process
- Stage 2:

  - Achieve true understanding of how the process develops desired properties
- Stage 3:

  - Apply a deep understanding to scientifically optimize the process

Scientific understanding makes scale up predictable!

Nb-Ti Development

- Stage 1: First process (1965) and empirical conductors (1965-1980)
- Stage 2: Development of true understanding of Jc (1970-1986)
- Stage 3: Application of full scientific understanding to production (1986 onwards)

Mature product since about 1990 – little R&D being done

Ternary optimization ?

APC has much higher Jc than conventional Nb-Ti, but APC fabrication is unlikely

Nb-Ti-Ta literature

- M. Suenaga, and K. M. Ralls, "Some superconducting properties of Ti-Nb-Ta ternary alloys," J. Appl. Phys., vol. 40, pp. 4457-4463, 1971.
- **D.G. Hawksworth, and D.C. Larbalestier, "Enhanced values of H_{c2} in Nb-Ti ternary and quaternary alloys," Adv. Cryo. Eng., vol. 26, pp. 479-486, 1980.**
- H. R. Segal, T. M. Hrycaj, Z. J. J. Stekly, T. A. de Winter, and K. Hemachalam, "Nb-Ti based conductors for use in 12 Tesla toroidal field coils," in *Proc. of 8th Symp. on Engineering Problems in Fusion Research*, IEEE Pub. 79-CH-1441-5 NPS, pp.255-259, 1979.
- **A. D. McInturff, J. Carson, D. C. Larbalestier, P. J. Lee, J. C. McKinnell, H. Kanithi, W. McDonald, P. O'Larey, "Ternary superconductor "NbTiTa" for high field superfluid magnets," IEEE Inter. Magnet Conf., Digest of Technical Papers, Brighton Polytechnic, U.K., p: AP15, 1990.**
- P. J. Lee, J. C. McKinnell, and D. C. Larbalestier, "Restricted novel heat treatments for obtaining high J_c in Nb-46.5wt%Ti," Adv. Cryo. Eng., vol. 36, 287-294, 1990.
- E. Gregory, T. S. Kreilick, F. S. von Goeler and J. Wong, "Preliminary results on properties of ductile superconducting alloys for operation to 10 Tesla and above," Proc. of ICEC 12, ed. R.J.Scurlock and C.A Bailey, Butterworths, Guildford, Surrey, UK, pp. 874-877, 1989.
- P. J. Lee, J. C. McKinnell, D. C. Larbalestier, "Progress in the Understanding and Manipulation of Microstructure in High J_c Nb-Ti Alloy Composites," Prog. in High Temp. Superconductivity, vol. 15, pp. 357-362, 1989.
- H. Muller, "The upper critical field of niobium-titanium," University of WI-Madison, Ph.D. dissertation, 1988.
- R. Taillard, E. Florianova, C. E. Bruzek and Hoang-Gia-Ky, "Microstructure and Properties of Simultaneously Processed Nb-Ti and Nb-Ti-Ta Superconducting Wires," Adv. Cryo. Eng., Ed. L. T. Summers, Plenum Press, NY, vol. 42B, pp. 1151-1158, 1996.
- **H. Liu, E. Gregory, K. J. Faase and W. H. Warnes, "Development of Multifilamentary Superconductors containing Nb-40wt.%Ti-18wt.%Ta and Nb-41wt.%Ti-28wt.%Ta Ternary Alloys," Adv. Cryo. Eng., ed. L. T. Summers, Plenum Press, NY, Vol. 42b, pp. 1135-1142, 1996.**
- B. G. Lazarev, O. V.Chernyj, G. E. Storozhilov, L. G.Udov, N. F. Andrievskaya, L. A. Kornienko, L. S. Lazareva, N. A. Chernyak, P. A. Kutsenko, B. K. Pryadkin, Y. A. D. Starodubov, M. B. Lazareva, V. M. Gorbatenko, "The Study Of The Microstructure And J_c In Nb-37Ti-22Ta Superconductor Produced With Different Duration Of Treatments," Proc. 7th Int. Workshop on Critical Currents in Superconductors, Alpbach, Austria, Ed. H. W. Weber, World Scientific Press, Singapore, pp. 601-604, 1994.
- G. P. Vedernikov, L. V. Potanina, V. Yu. Korpusov, V. A. Drobishev, V. S. Zurabov, A. S. Zolatarjev, A. D. Nikulin, N. I. Kozlenkova and S. I. Novikov, "An Investigation of Nb-T-Ta Alloys and Properties of the Superconductors Based on Ternary Alloys," Trans. Appl. Superconductivity, 7, pp.1751-1754, 1997.
- **P. J. Lee, C. M. Fischer, D. C. Larbalestier, M. T. Naus, A. A. Squitieri, W. L. Starch, R. J. Werner, P. J. Limon, G. Sabbi, A. Zlobin, and E. Gregory, "Development of High Performance Multifilamentary Nb-Ti-Ta Superconductor for LHC Insertion Quadrupoles," IEEE Transactions on Applied Superconductivity, 9: 1571-1574, 1999.**

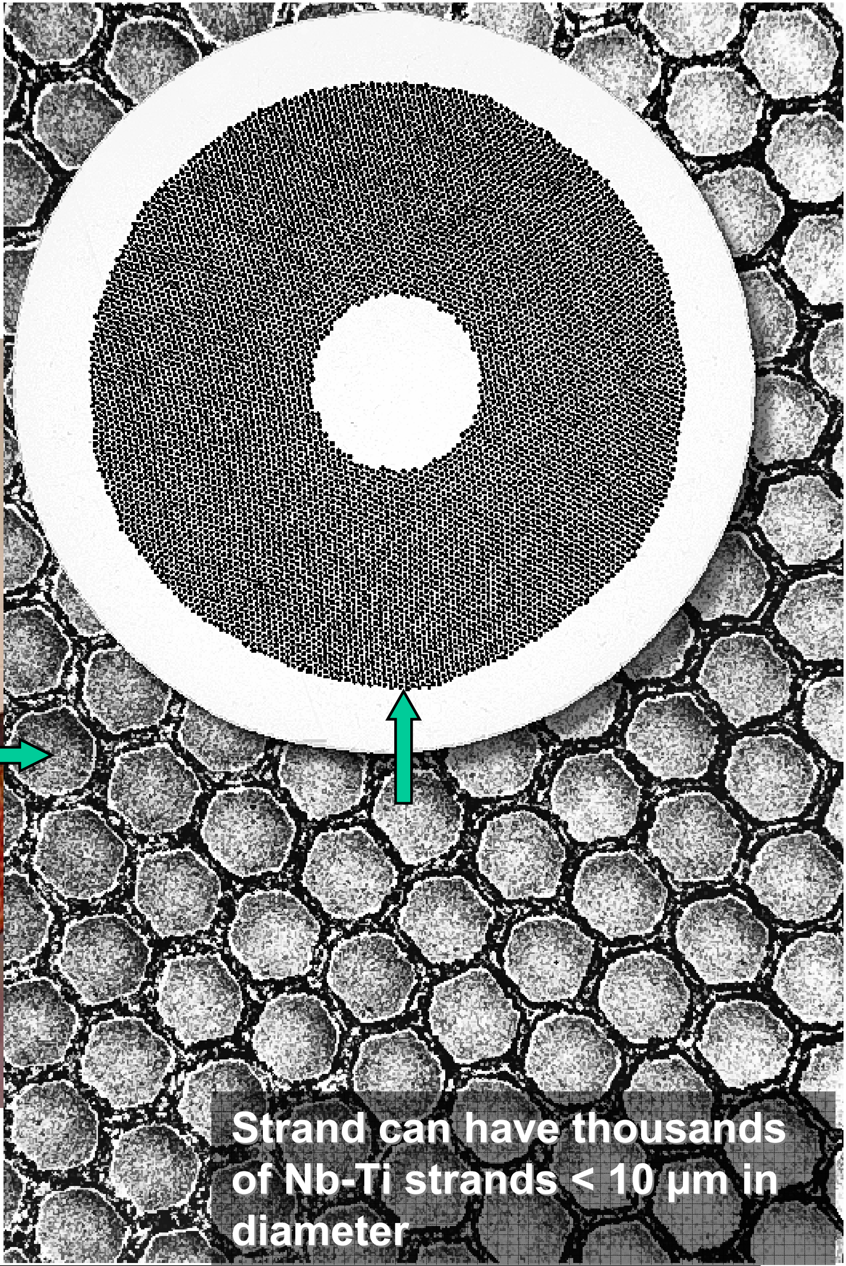
Personal Nb-Ti-Ta experience

- 1978-1982 – thesis work of David Hawksworth applied to 12T sub-cooled magnet at General Atomics
  - Low Jc, very low n-value, inhomogeneous Nb-43Ti-25Ta (TWCA)
- Fermilab quadrupole effort led by Al McInturff in 1985-1987
  - Relatively high homogeneity Nb-44Ti-15Ta (TWCA)
- Fermilab qudrupole effort led by Peter Limon using new alloys (NRC) procured by Eric Gregory (IGC) under DOE-SBIR support – mainly Nb-41Ti-17Ta
  - Careful attempt to characterize and make better

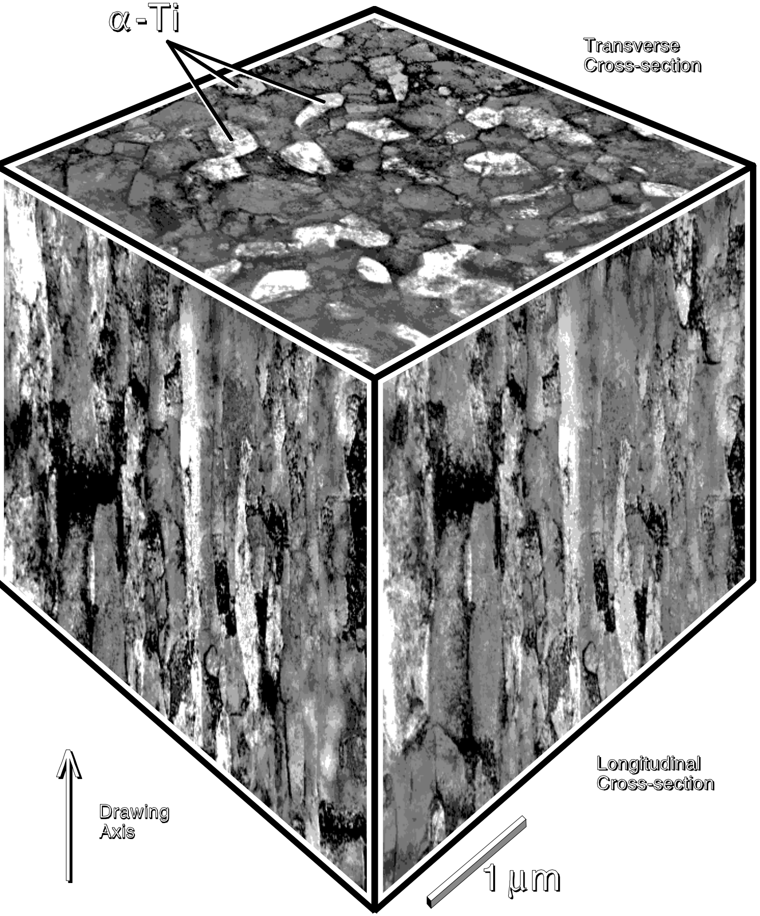
Each attempt has disappointed – why?

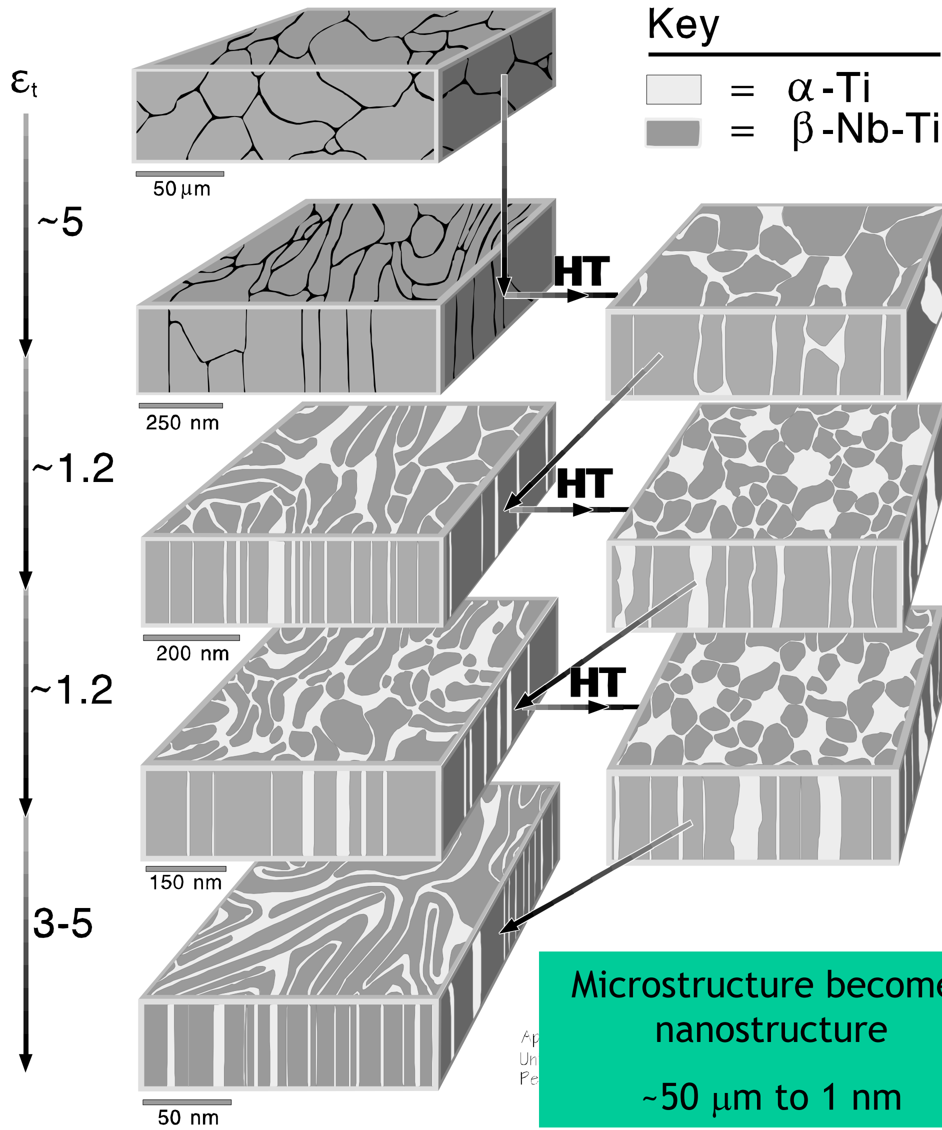
Nb-Ti review: huge size reduction

30 cm diameter



Huge microstructural Refinement



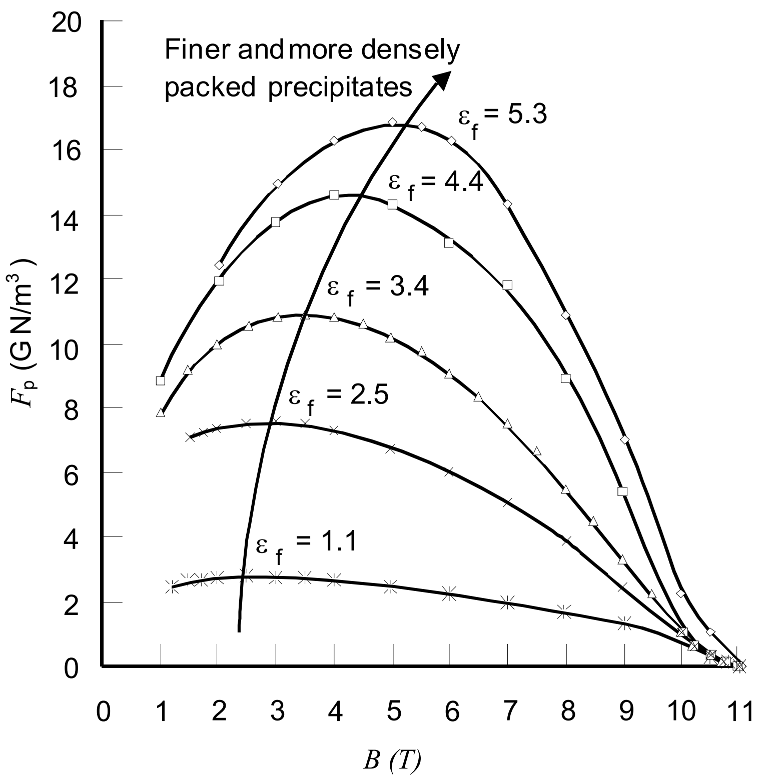


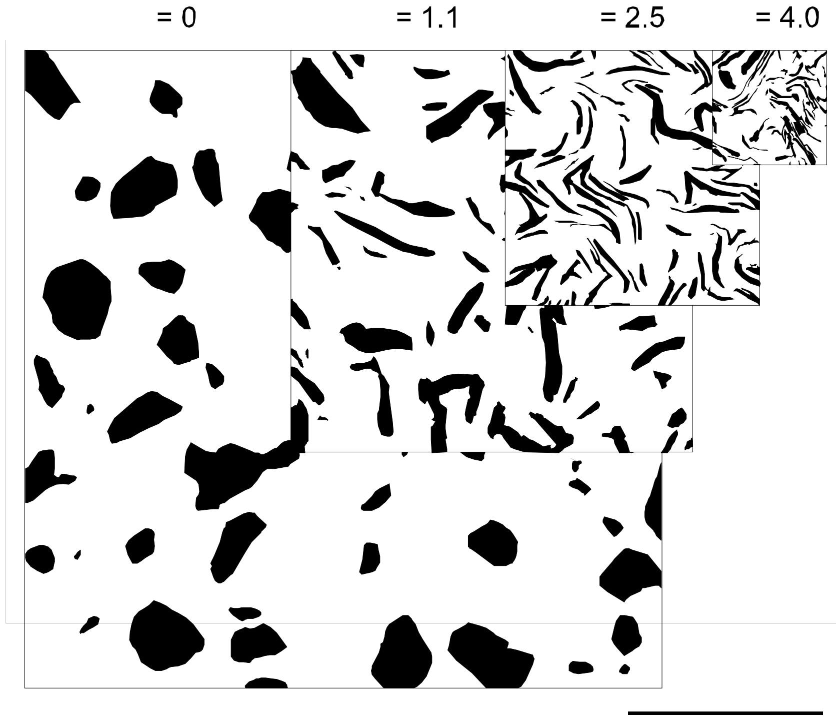
Microstructure becomes nanostructure

~50 μm to 1 nm

Montage by Peter Lee

Optimization requires a genuine nanostructure!





F_p increases with drawing strain after the last heat treatment ε_f
Precipitate size and spacing are reduced to < ξ in thickness

Meingast, Lee and Larbalestier J. Appl. Physics 1989

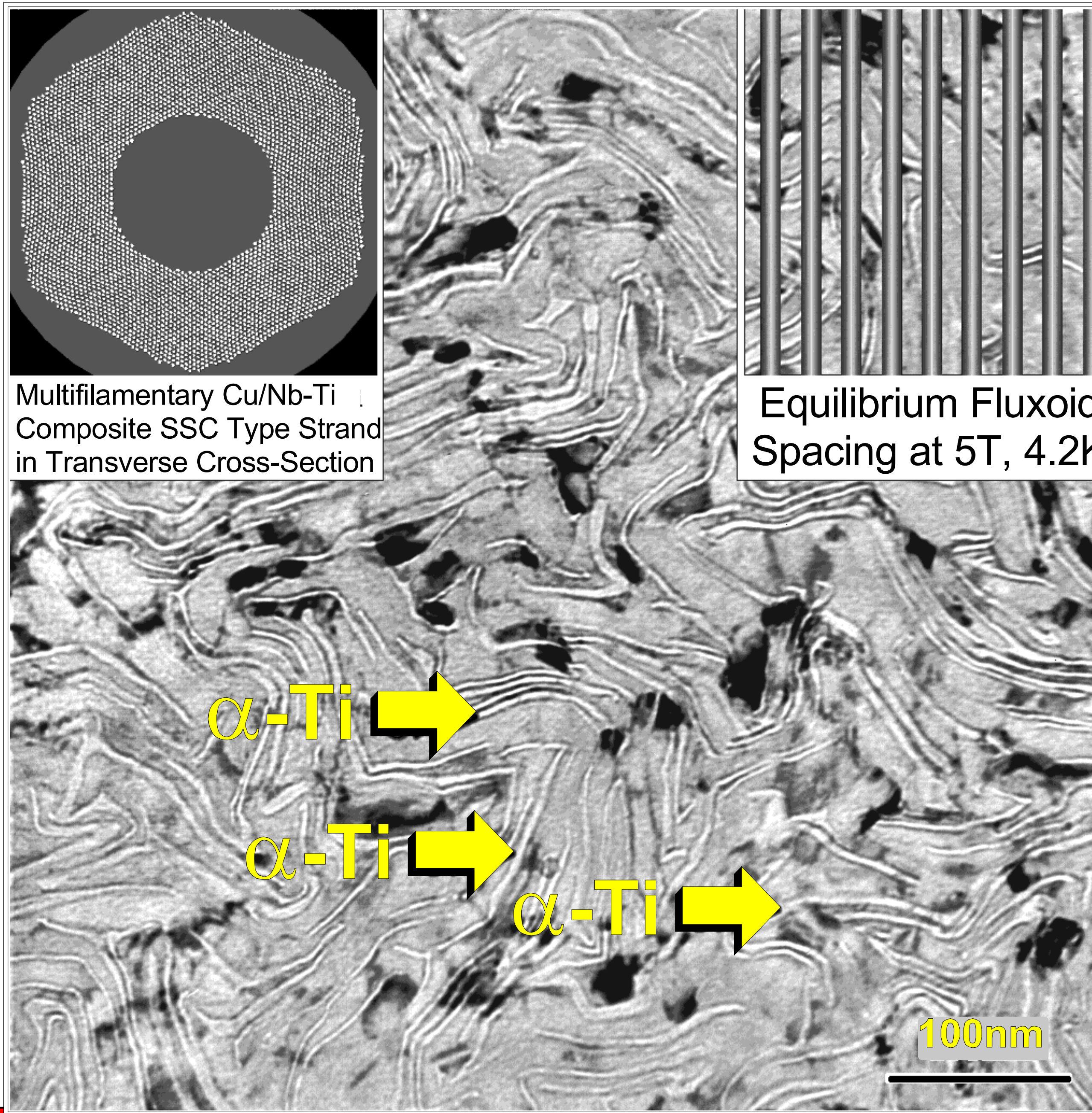
Optimized Nb-Ti strands have:

~25% α-Ti

More precipitates than fluxons (full summation)

Very strong flux pinning 5-10% Jd

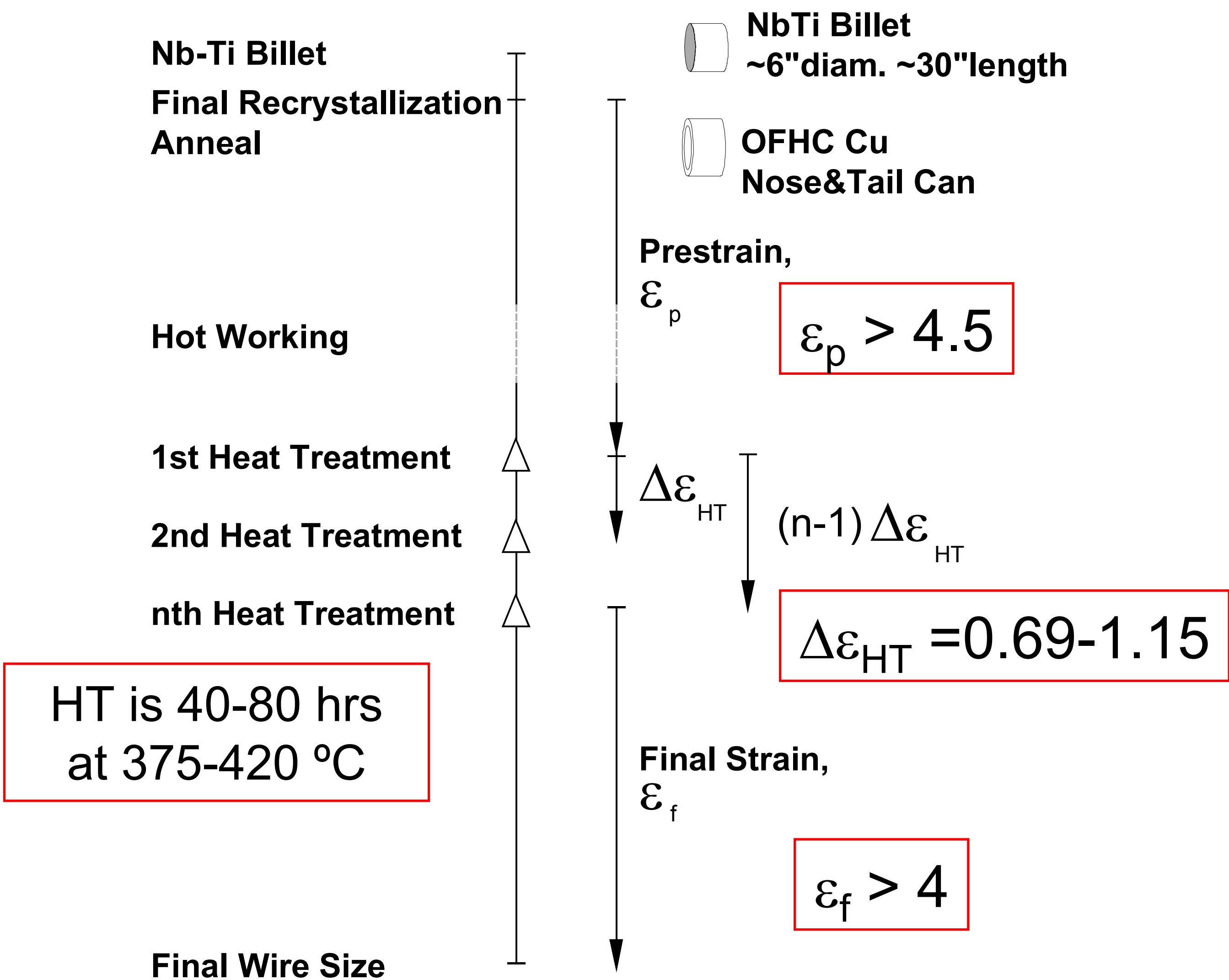
Thermodynamically unstable nanostructure



TEM by Peter Lee

True strain space: $\varepsilon = 2 \ln (D/d)$

- In general the larger the strain space the higher the J_c.
- Available strain is cold work strain after any anneal at ~850C
- Extrusion at ~600C is warm work
- All wire drawing is cold work



Avoid tree rings……….

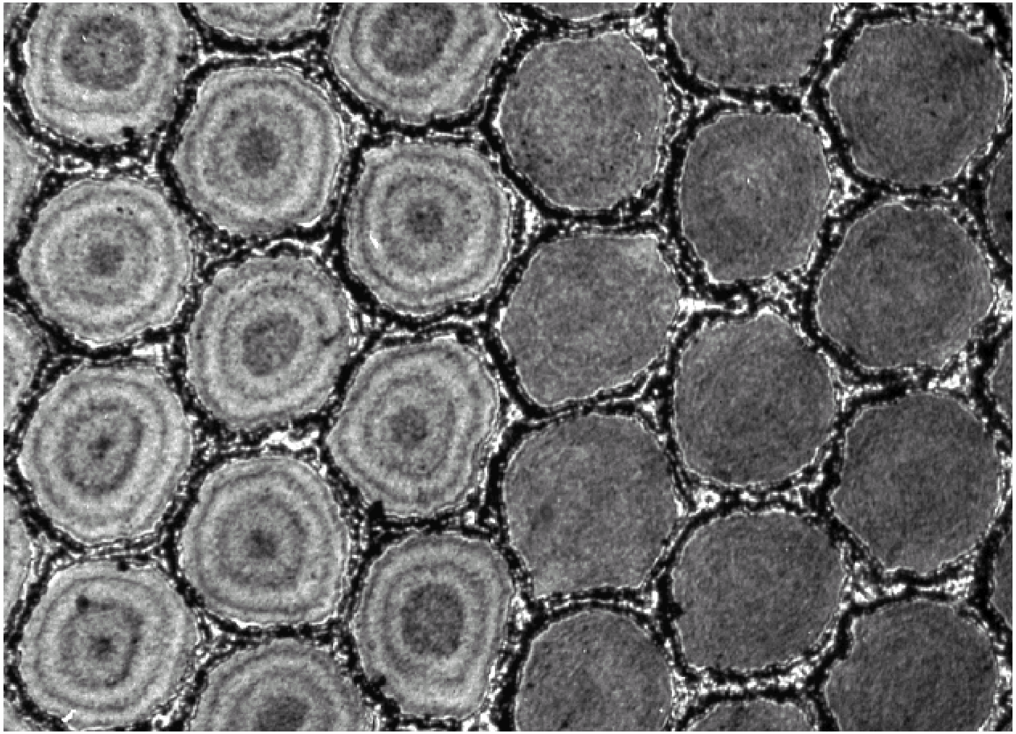
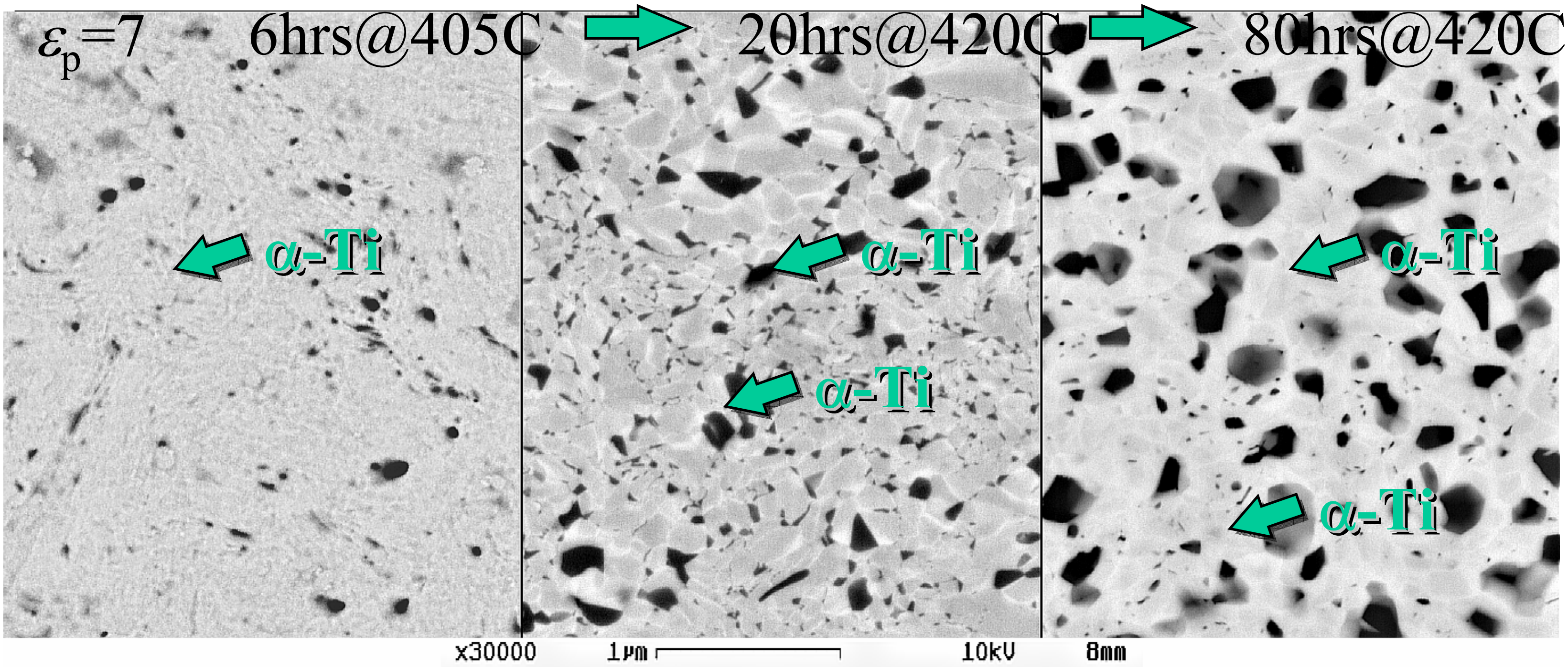


Figure B3.3.8. This billet was inadvertently stacked with Nb-Ti rods from two different raw material sources. On the left, the characteristic "tree ring" pattern indicates that these rods were not properly remelted, and have variations in local chemistry due to the large separation between the liquidus and the solidus. On the right, much more uniform chemistry is indicated by the uniform contrast of the Nb-Ti rods.

Insufficient stirring during the melt

!986 alloy – Nb44Ti15Ta: Even with relatively homogeneous alloy, we saw a large precipitate size variation



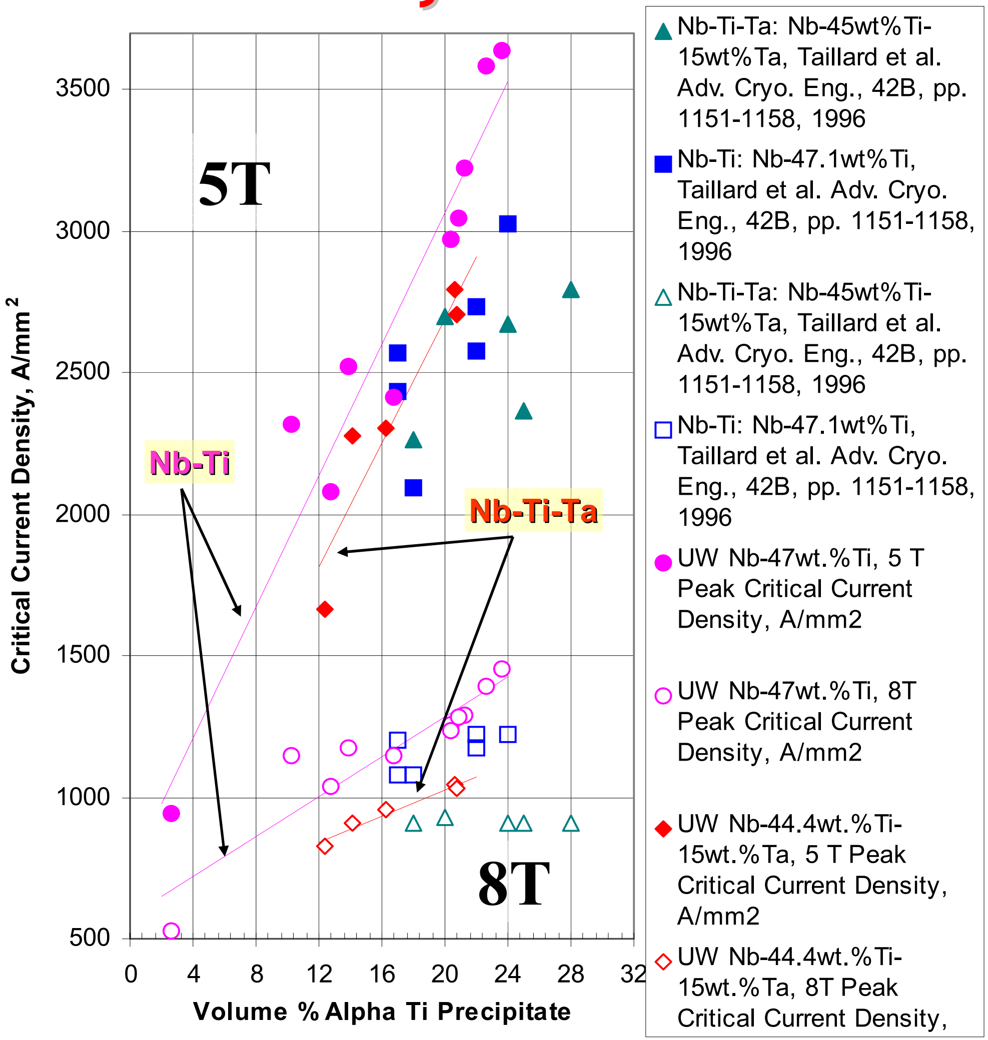
α-Ti precipitates are dark in backscatter SEM images, Nb-rich are light

The opposite of TEM contrast!

Background to 1997 study

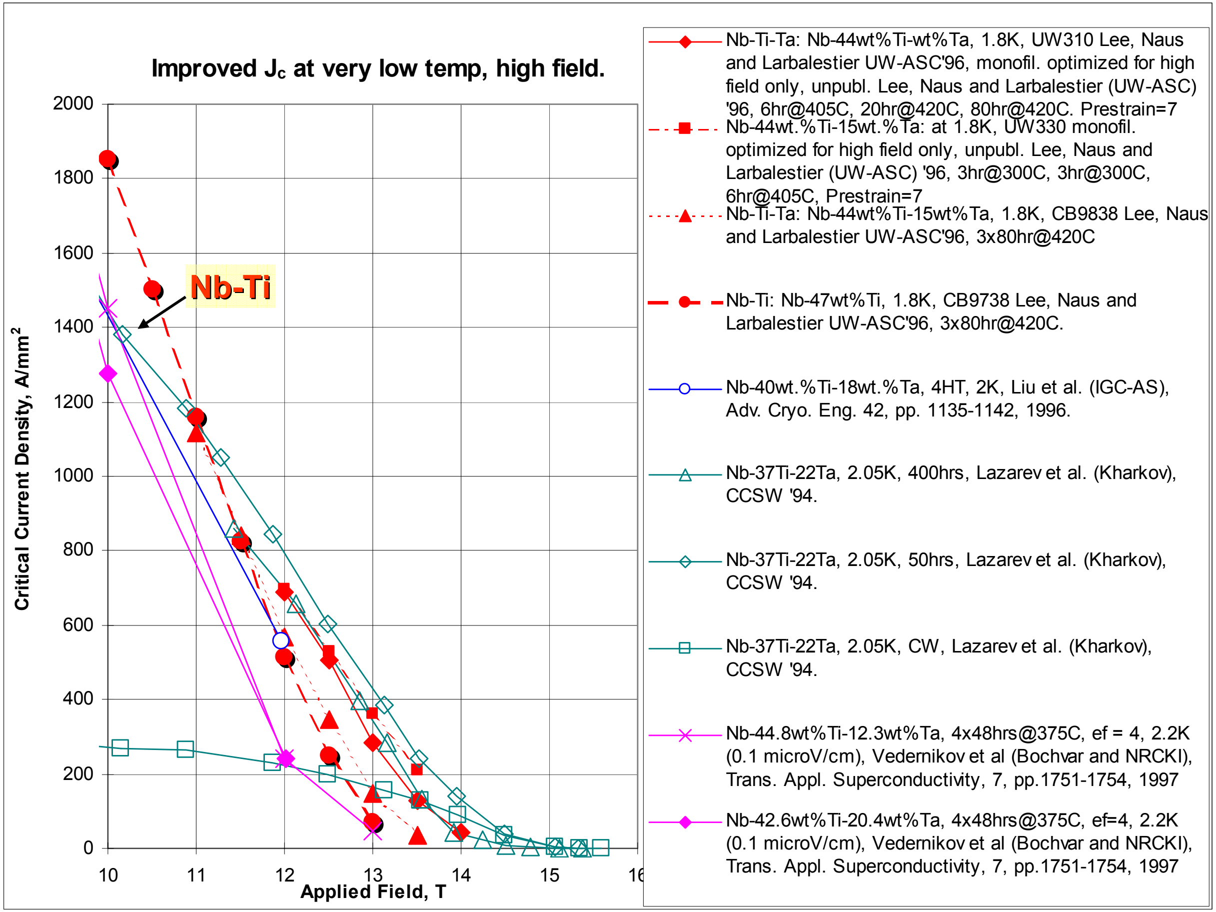
- Despite improved H_{c2} Nb-Ti-Ta has yet to achieve its promise for significant increases in high field Jc
- Why not?
  - Less precipitation or less effective precipitates?
  - larger H_{c2}-H*?
  - ??
- US-SBIR program had given Eric Gregory a Phase II SBIR to make ternary
  - FNAL interested in taking up the challenge for IR Quads again
  - Peter Limon and Gianluca Sabbi approached us for collaboration
- Better understanding and characterizations could help??

Jc(4.2K) for 15 wt.% Ta is lower than for Nb-Ti alloys with the volume % α-Ti



- The problem is NOT that the ternary does not produce enough alpha Ti!
- Slopes for binary and ternary very similar
- Flux pinning is less effective for ternary (UW and Alsthom result)

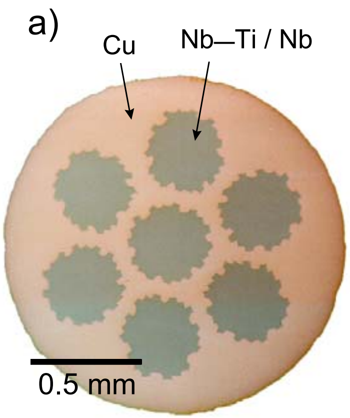
Precipitation influence on H* and H_{c2}?

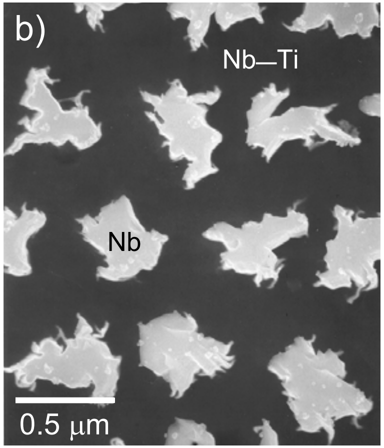


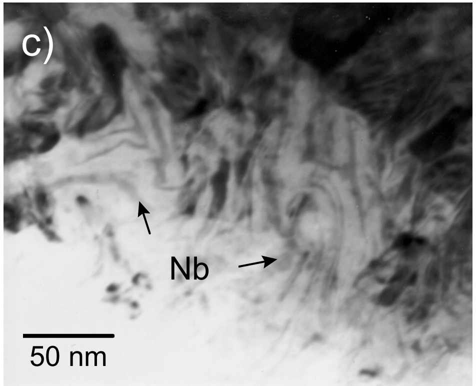
- Lazarev et al. (Kharkov) showed better high field Jc with reduced heat treatments.
- Restricted HTs (UW3xx series) yield improved current density at >11.5T
- But, aggressive HT of binary Nb-47wt%Ti produces better current density <11T

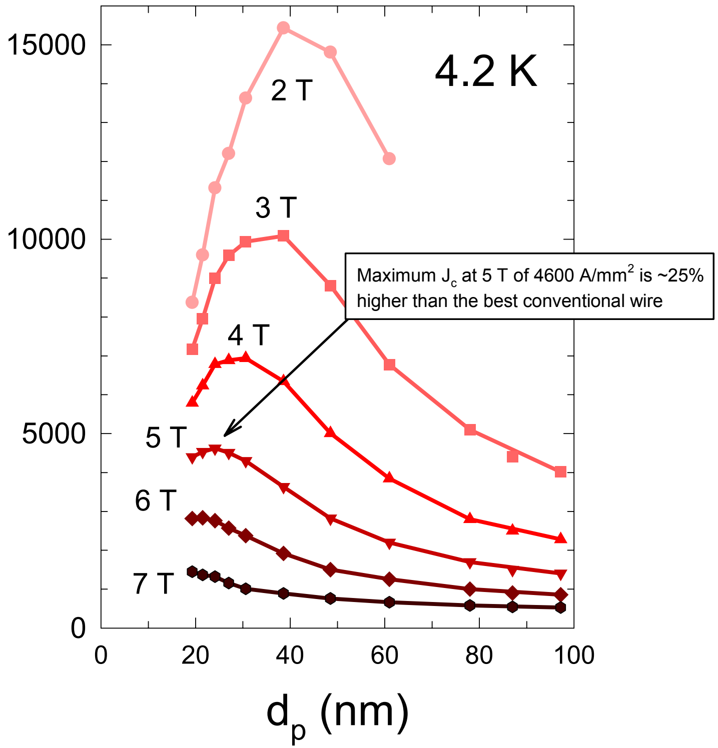
Characterization method issue – transport Jc at few points suggests where H* lies but does not define it or H_{c2}

Nb 47 wt.% Ti with strongly enhanced performance using Nb pins





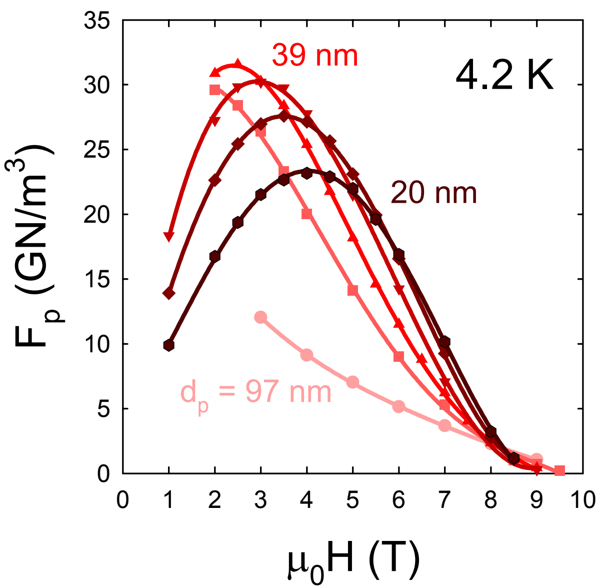




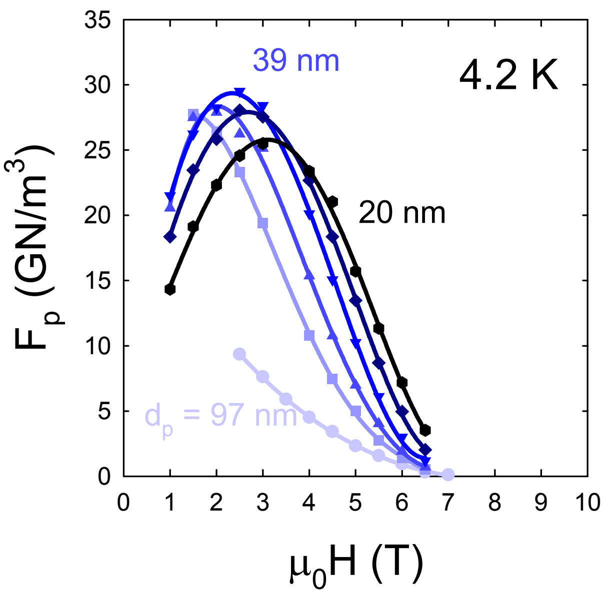
R.W. Heussner, J.D. Marquardt, P.J. Lee, D.C. Larbalestier, Appl. Phys. Lett. 70, 901 (1997)

Lesson from APC studies: Higher F_p but smaller H*

Nb 47 wt.% Ti / Nb



Nb 62 wt.% Ti / Nb



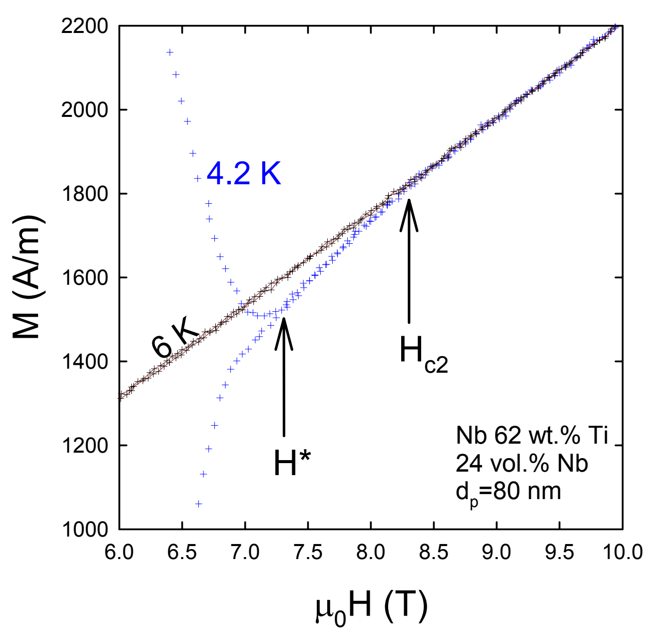
Nb47Ti/Nb APC is too Nb-rich, while Nb62Ti/Nb APC should be about Nb47Ti

Maximum Fp values are about TWICE conventional Nb-Ti

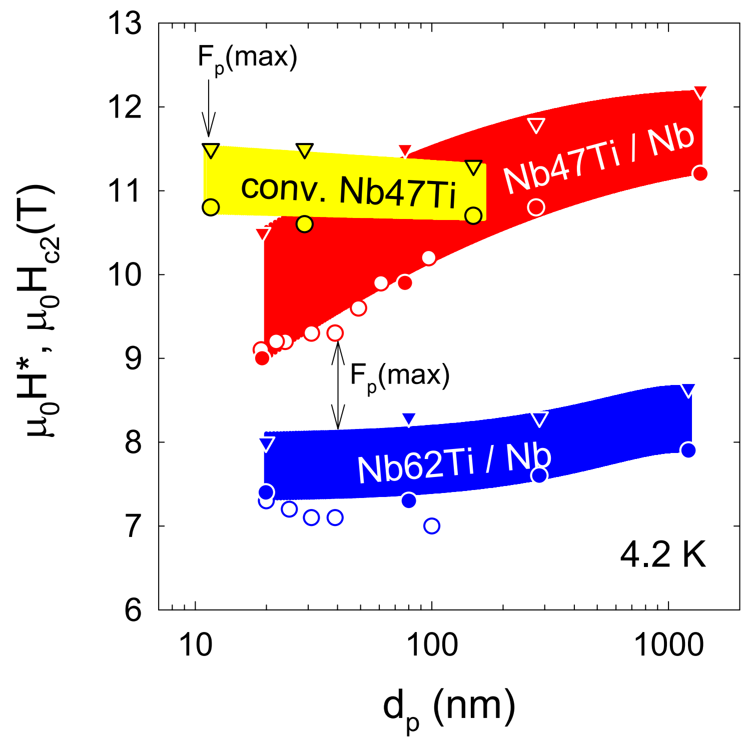
1999 Ph D Thesis work of Robert Heussner on Artificial Pinning Center Nb-Ti

The gap between H* and H_{c2} varies! – and is BIG!

Defining H*, H_{c2} from M(H)



H*, H_{c2} (d_p)



Magnetization permits the whole behavior to be seen

Meingast mixing NOT seen in APC!

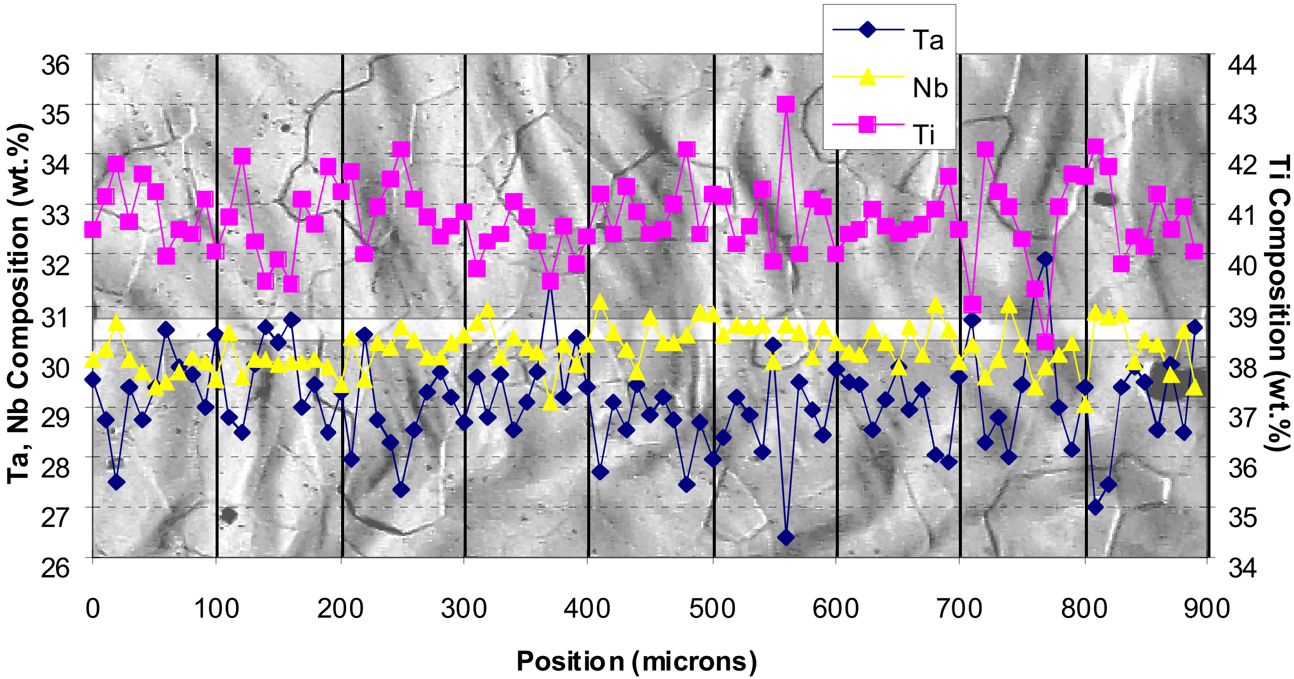
Nb-44Ti-17Ta

- A new alloy test bed.
- Chosen to have both high levels of pinning precipitate and H_{c2}.
- A new alloy source with possibly improved homogeneity.

New Nb-Ti-Ta Alloys

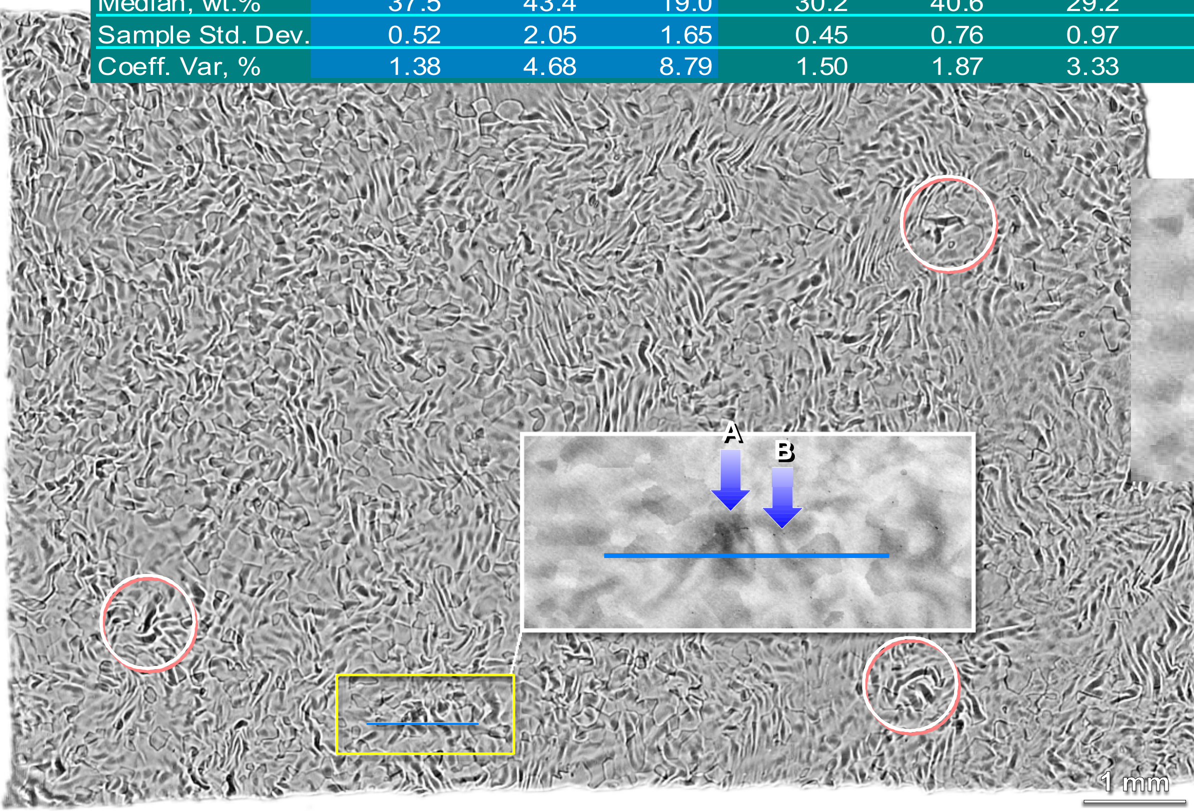
	NRC 115R5			TWC Fermi-Quad		
	Nb	*Ti*	*Ta*	*Nb*	*Ti*	*Ta*
Mean, wt%	30.16	40.73	29.11	42.25	44.33	13.42
Median, wt.%	30.18	40.63	29.17	42.21	44.32	13.44
Sample Std. Dev	0.45	0.76	0.97	0.43	0.84	0.63
Coeff. Var, %	1.50	1.87	3.33	1.02	1.90	4.71

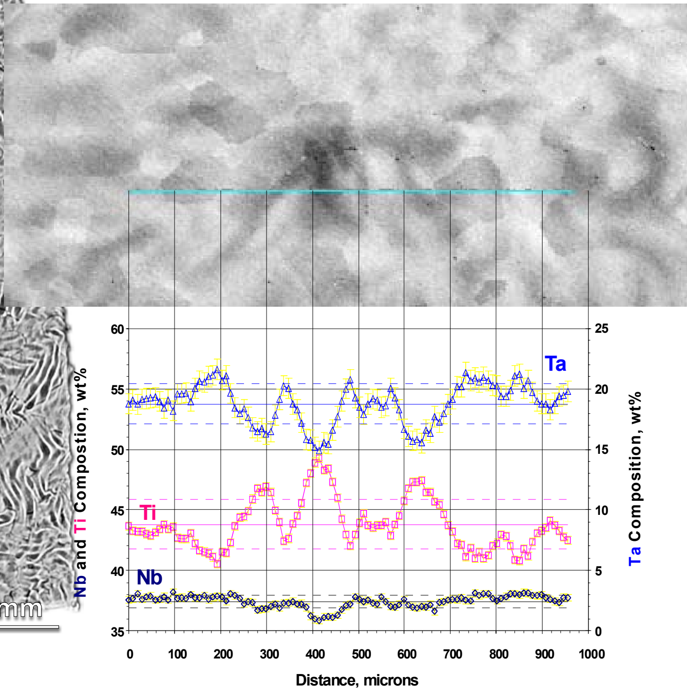
- Base NRC alloy had excellent homogeneity.



Remelts showed more inhomogeneity

	NRC 116R3			NRC 115R5			TWC Fermi-Quad		
	Nb	Ti	Ta	Nb	Ti	Ta	Nb	Ti	Ta
Mean, wt%	37.4	43.8	18.8	30.2	40.7	29.1	42.2	44.3	13.4
Median, wt.%	37.5	43.4	19.0	30.2	40.6	29.2	42.2	44.3	13.4
Sample Std. Dev.	0.52	2.05	1.65	0.45	0.76	0.97	0.43	0.84	0.63
Coeff. Var, %	1.38	4.68	8.79	1.50	1.87	3.33	1.02	1.90	4.71

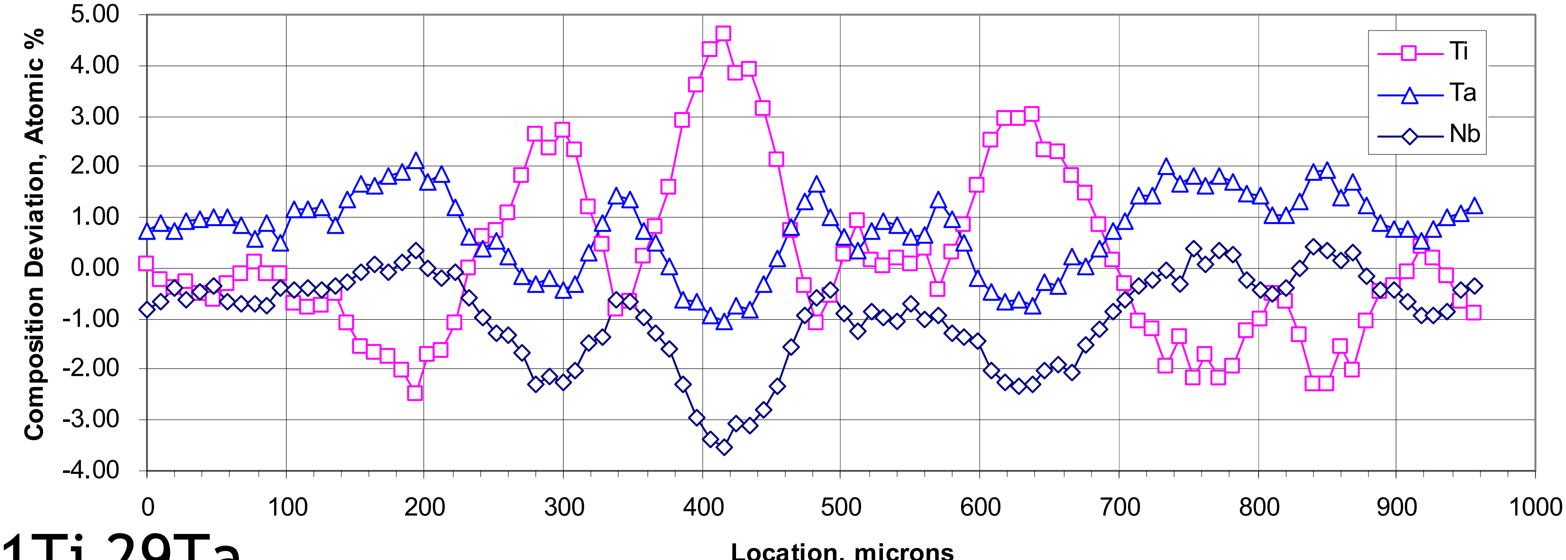




Compositional variation, in atomic %, for NRC 115R5

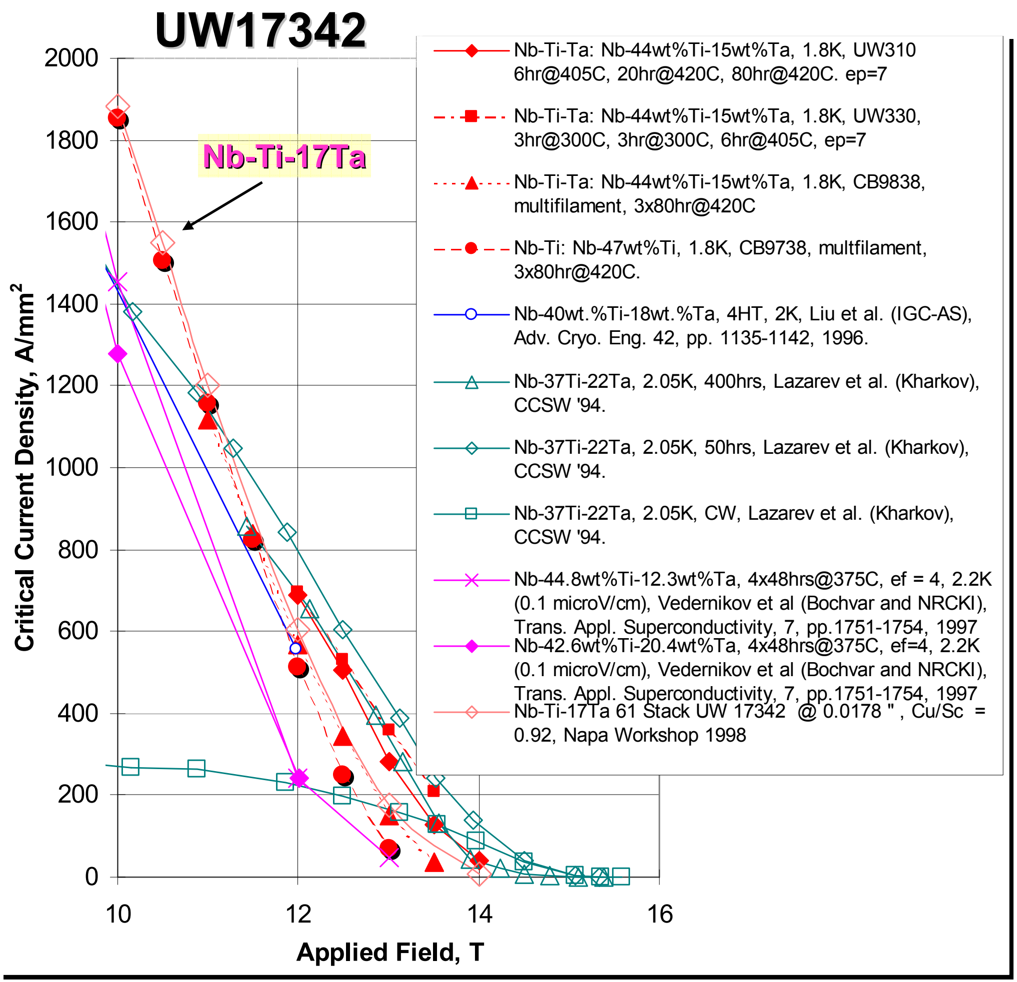
Compositional variation, in atomic %, along line scan shown as deviation from target composition for NRC 115R5

❶Areas of large Ti variation were indicated by the composition sensitive etch and confirmed by EDS analysis but these areas are small and well separated.
❷Variations in composition are larger than for NRC115R5 and the original Fermi-Quad ternary.
❸The cross-section appears to be freckle free.
❹In terms of atomic % the variations in Nb and Ta parallel each other in magnitude and position.



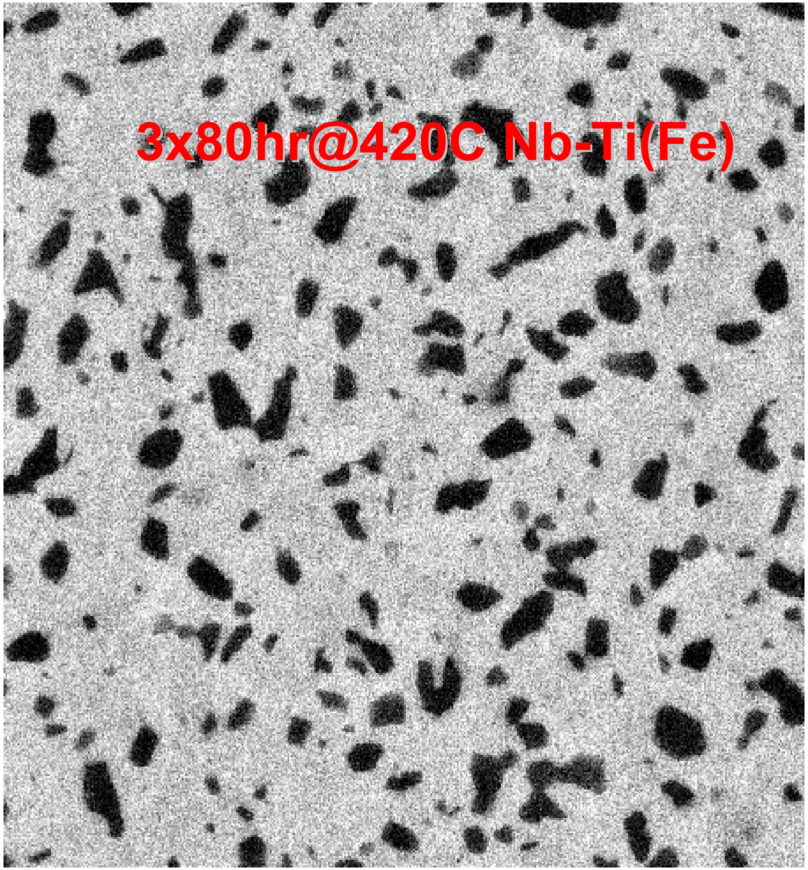
Nb 41Ti 29Ta

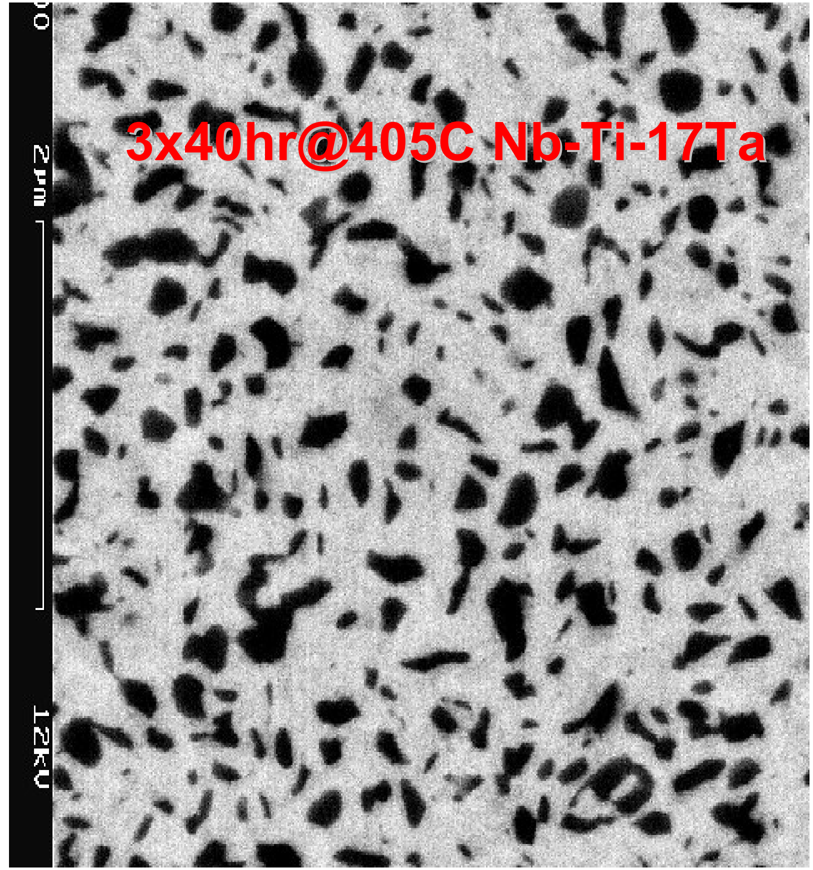
UW results on Nb-44Ti-17Ta



- Initial Test:
  - Simple 3x40hrs@405C HT
  - 61 Filament stack of cold worked rod
  - Final strain of 4.55 (optimum not yet determined).
- 1.9K performance slightly better than 3x80hrs@420C for earlier 44Ti15Ta FermiQuad.
- Full Optimization did not yield significant Jc improvements

Compare Nb-47Ti(Fe)* with 44Ti-17Ta





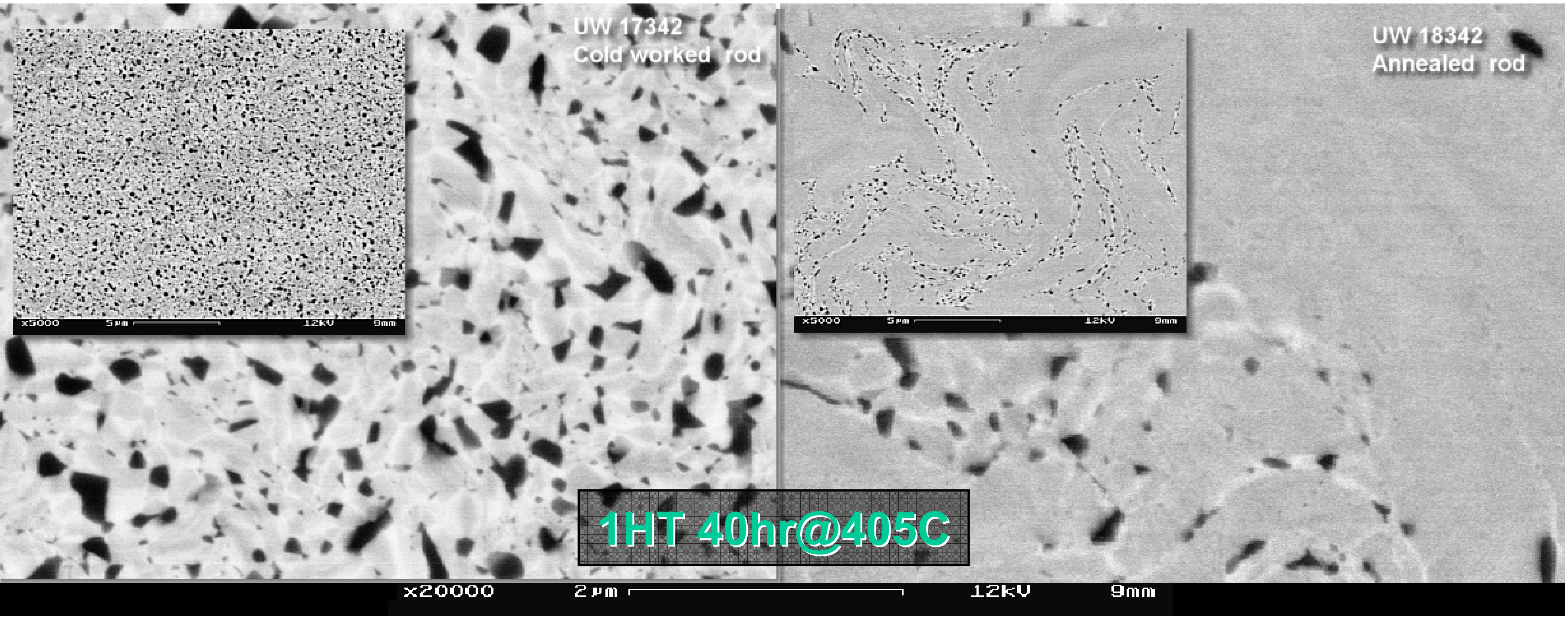
Nb-47Ti(Fe)* has 1000ppm Fe

Clearly shortage of precipitate is not a problem!

High prestrain is important for precipitate homogenization and Jc

61 stack fabricated from cold worked rod

61 stack fabricated from annealed rod

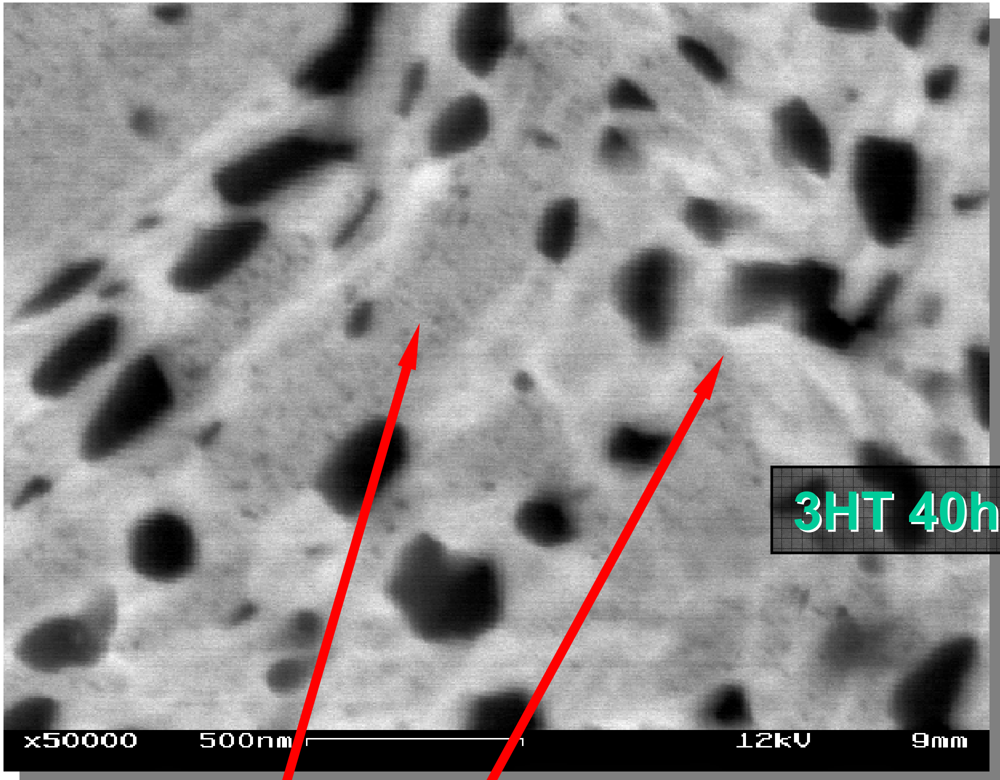


1550 A/mm² at 10.5T, 1.9K

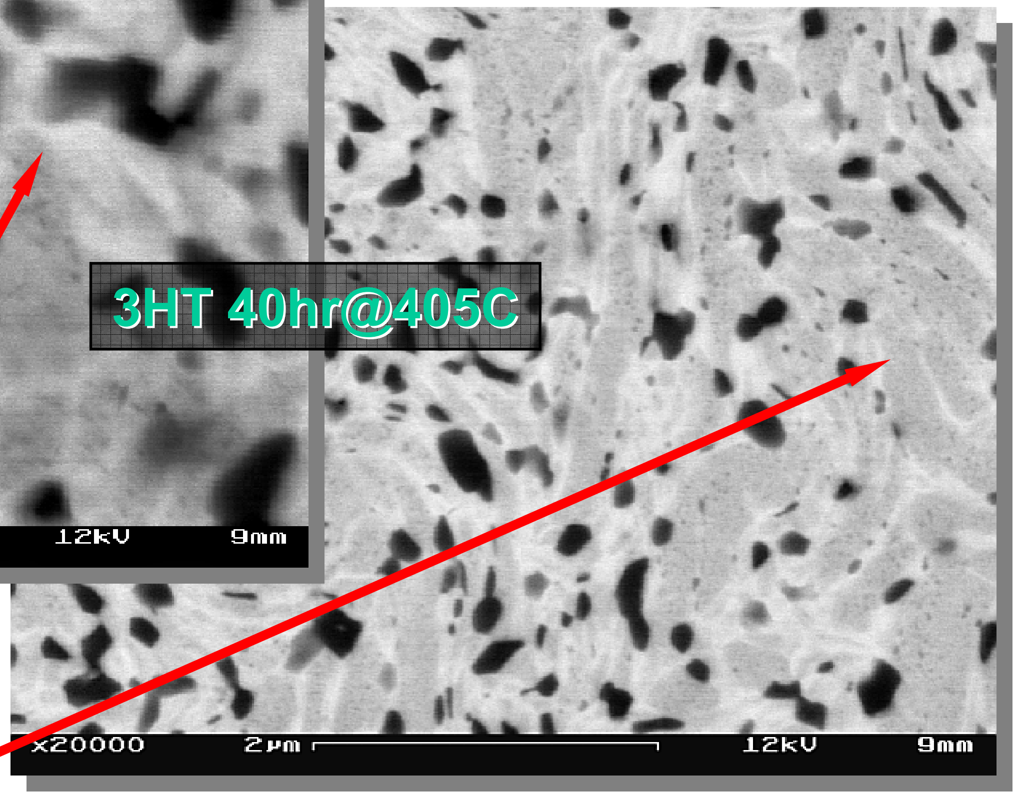
1250 A/mm² at 10.5T, 1.9K

Nb44Ti17Ta

Multiple heat treatments do not fully homogenize low prestrain microstructure



UW 18341, 61 stack fabricated from annealed rod

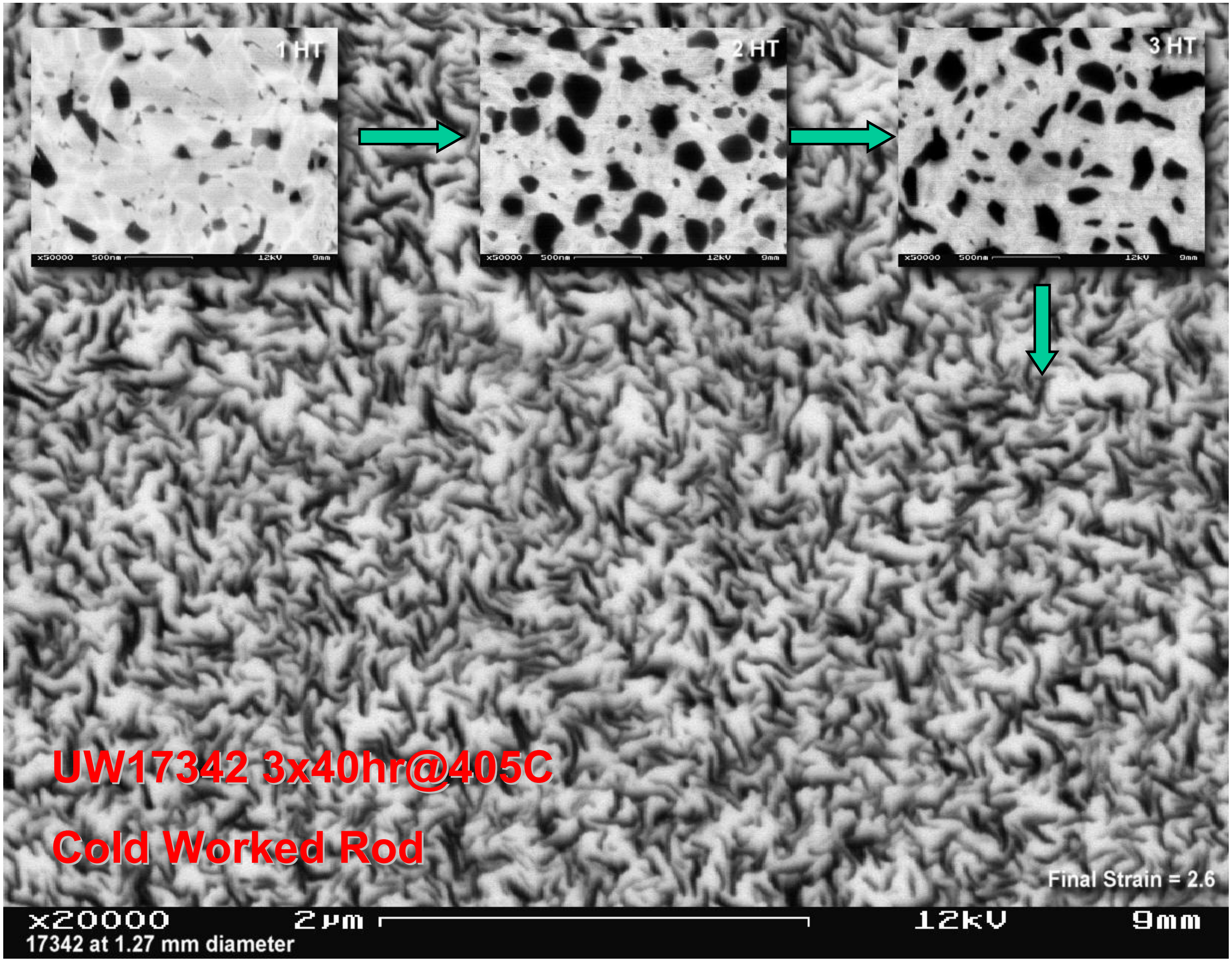


Small Intragranular α-Ti

High atomic number grain boundaries

Areas with no large α-Ti

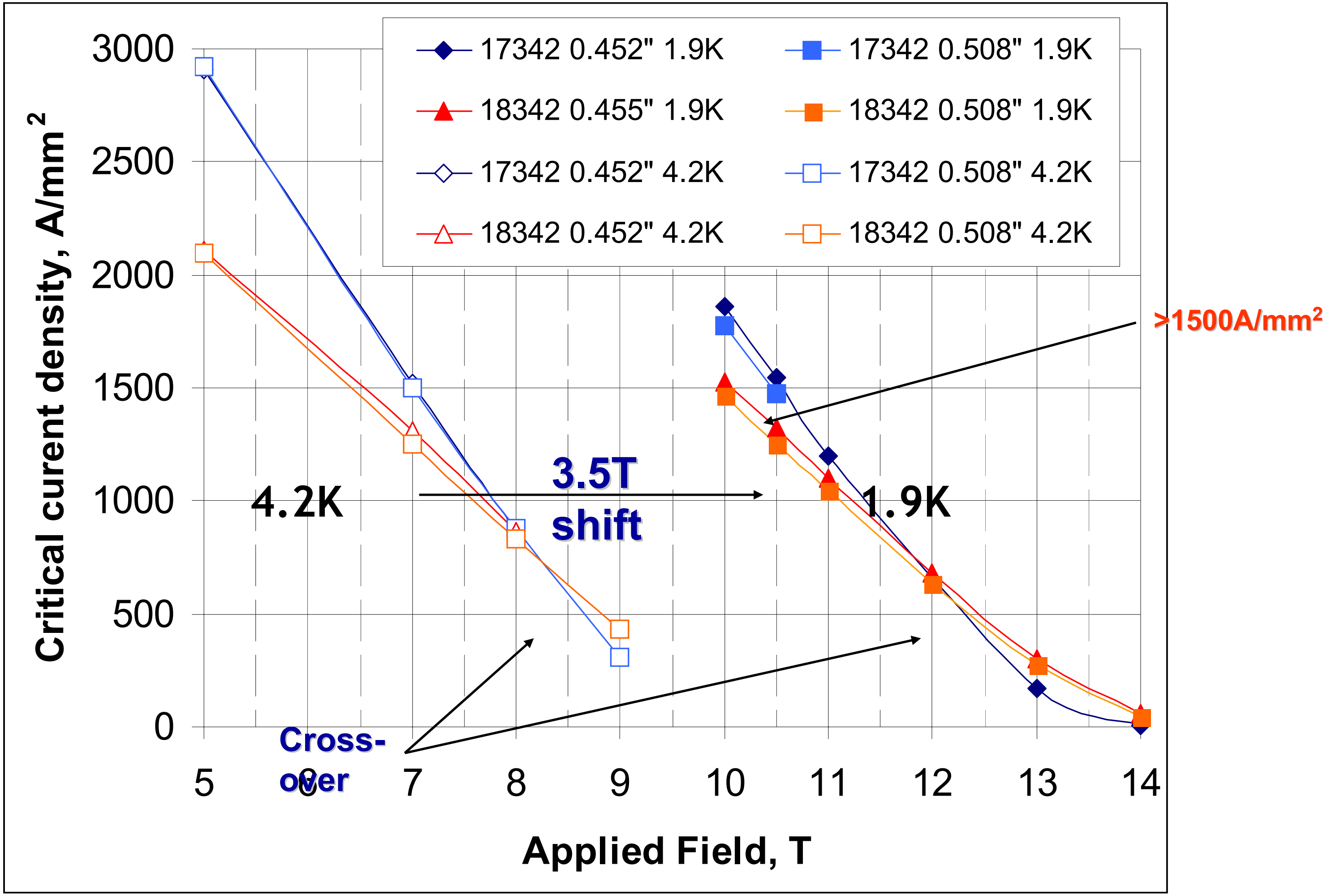
Multiple HT on cold-worked rod stock homogenize the microstructure much better



A 3.5T shift is observed for both

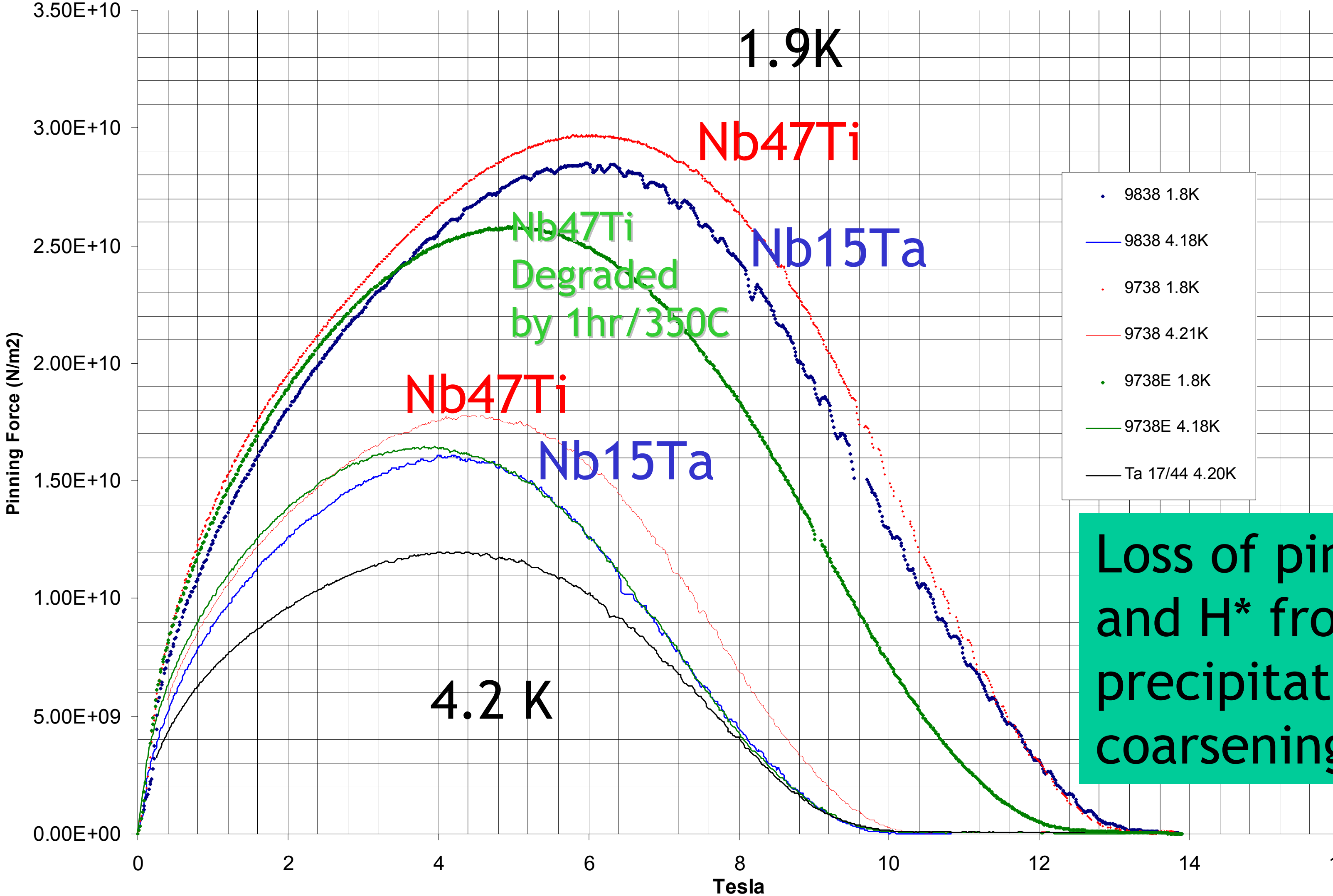
17342 – CW

18342 - recrystallized



3T shift expected for Nb47Ti, maximum of about 4.25Ti expected

2004 update



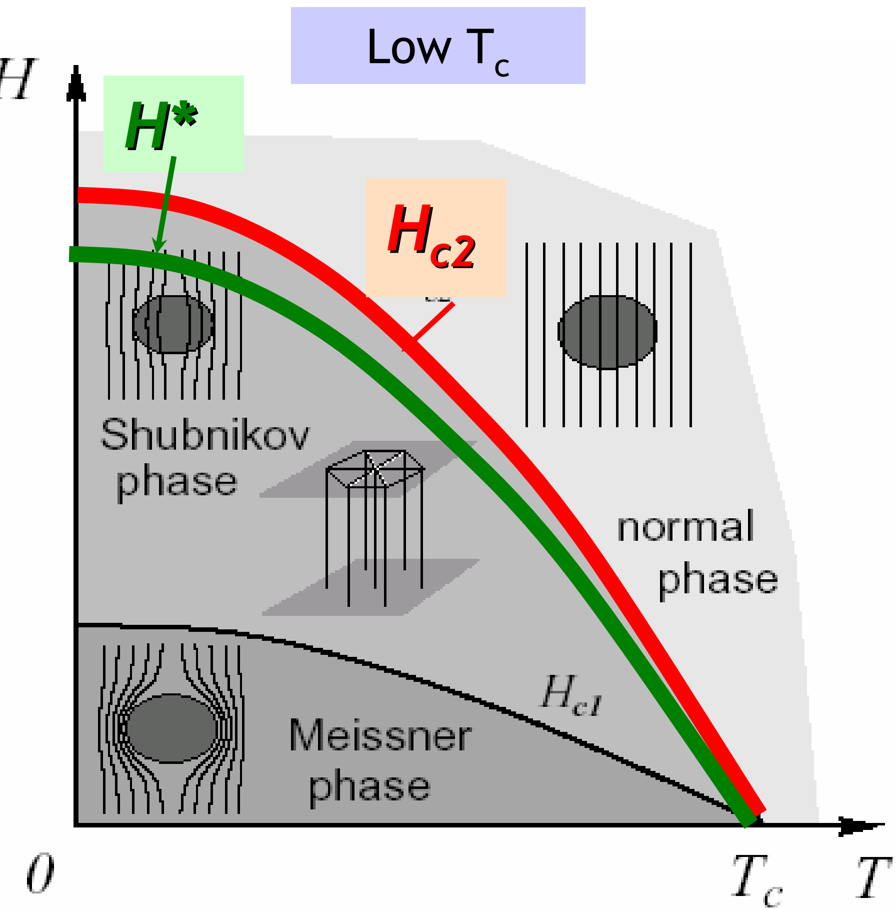
Loss of pinning and H* from precipitate coarsening

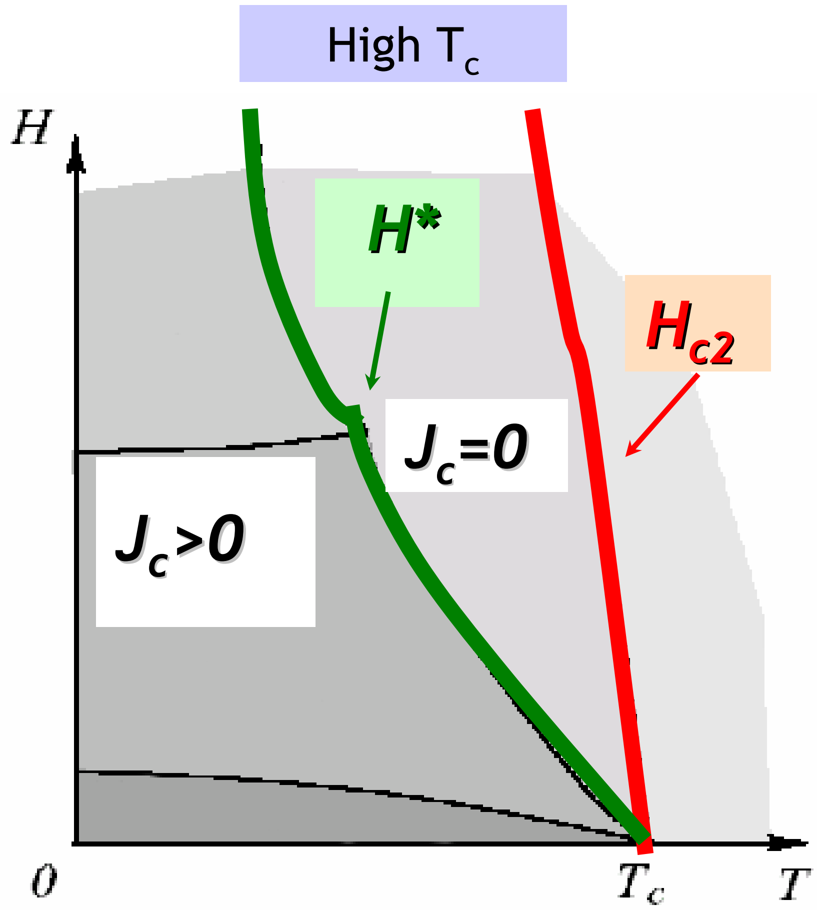
Nb-Ti lessons for Nb-Ti-Ta

- So far it seems that the best properties of Nb-Ti-Ta have not been achieved
  - Seem to have depressed H*, rather than depressed Hc2
  - Depressed H* results in good 47Ti and APC-Nb-Ti from broader spread of pinning center size
  - This suggests that further enhancement of ternary chemical inhomogeneity is vital
    - This was not done in the 1996 study
- If we assume the best properties from Nb-Ti translated to Nb-Ti-Ta, then perhaps 1000 A/mm^2 at 12 T, 1.9K are possible

Is the superconductor classical or not?

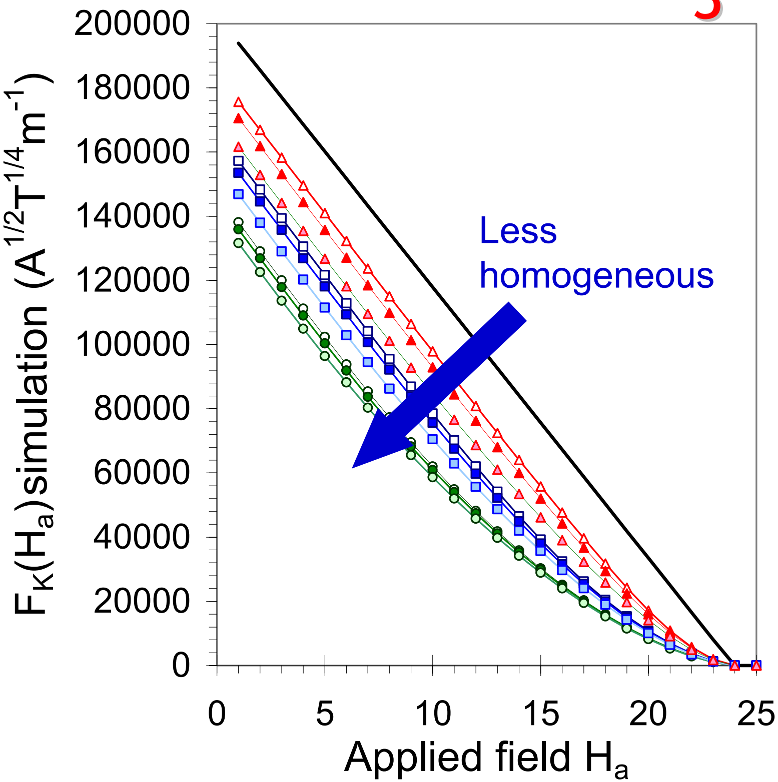
H_{c2}: bulk superconductivity disappears
H^*: J_c vanishes – irreversibility field





Blatter and Geshkenbein – Physics of Vortex Matter 2003

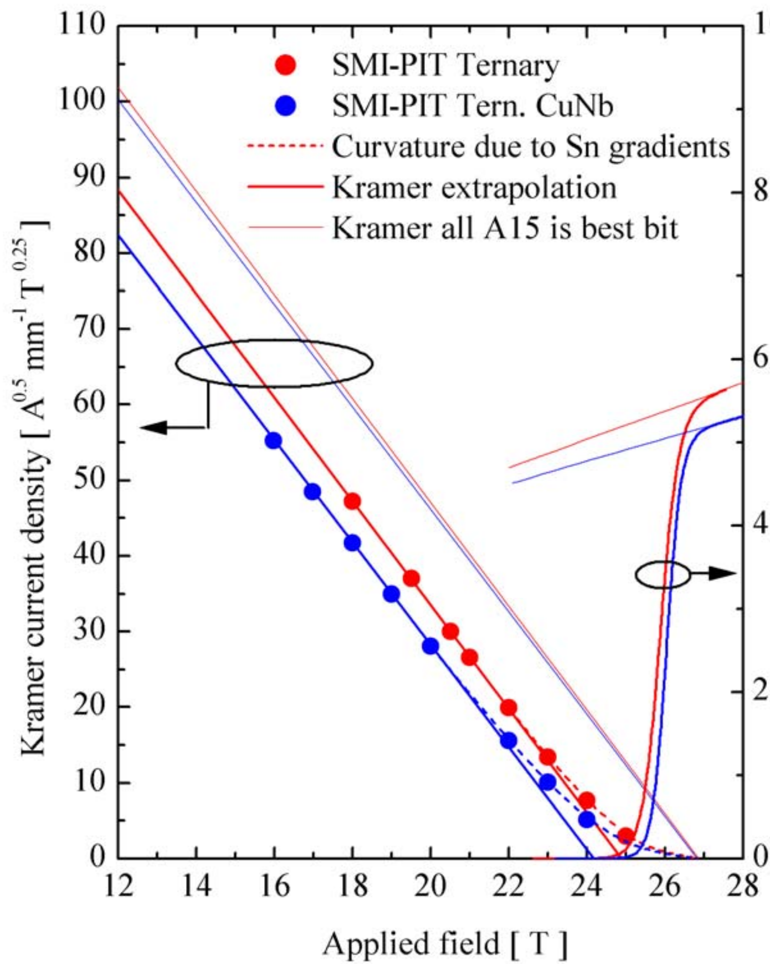
Influence of gradients on J_c and H_{c2} of Nb_3Sn



L.D. Cooley et al. (Cond Mat 0402206)

Simulation Kramer plots f(Sn gradient):

- Concentric shells of varying %Sn
- Quantitative same effect as measured



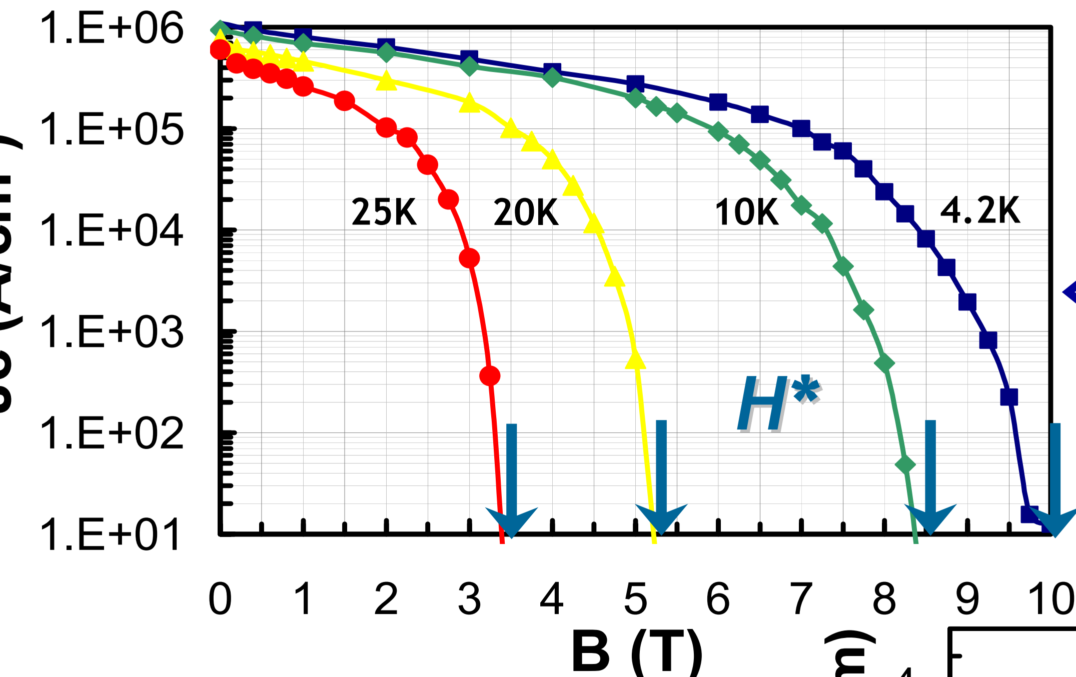
Arno Godeke PhD thesis work

MgB_2 behavior in magnetic field

- Is MgB_2 behavior in magnetic field LTS or HTS – like?
  - Important for vortex dynamics and to understand the practical capabilities of MgB_2
- Can we controllably modify MgB_2 so as to increase its magnetic field capability?
  - Alloying with impurities strongly enhances magnetic field capability in both bulk and thin films

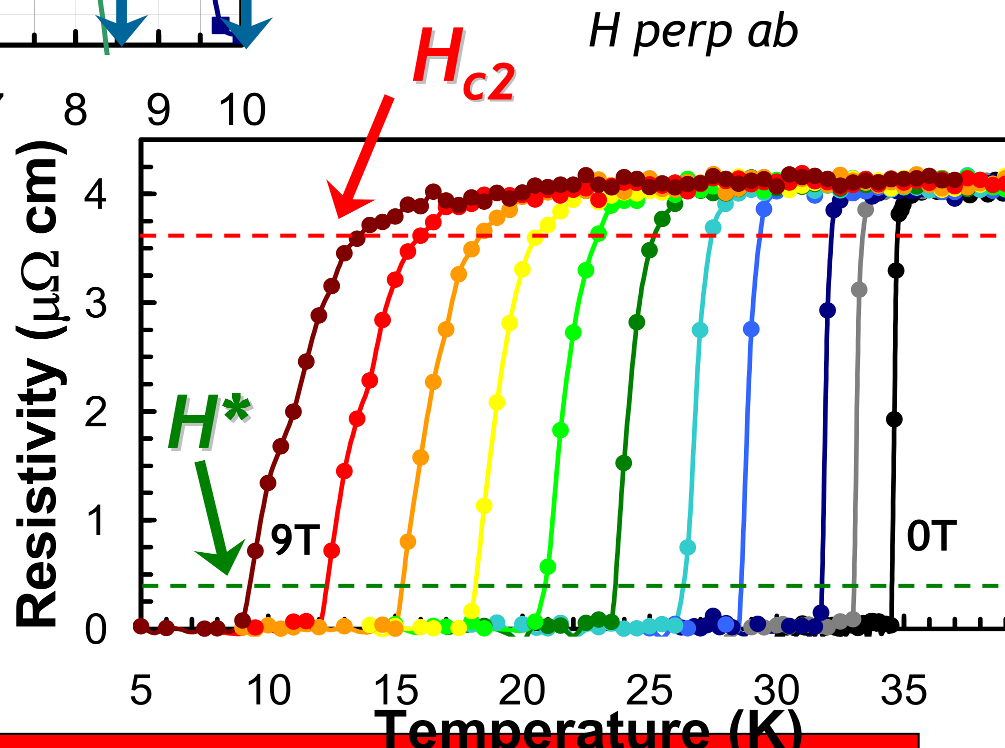
Valeria Braccini et al. post doc work Cond Mat 0402001, submitted to Phys Rev Letts. Jan 31, 2004

Transport Jc, H* and H_{c2} on textured MgB_2 film



J_c from I-V characteristics

Full critical state measurement



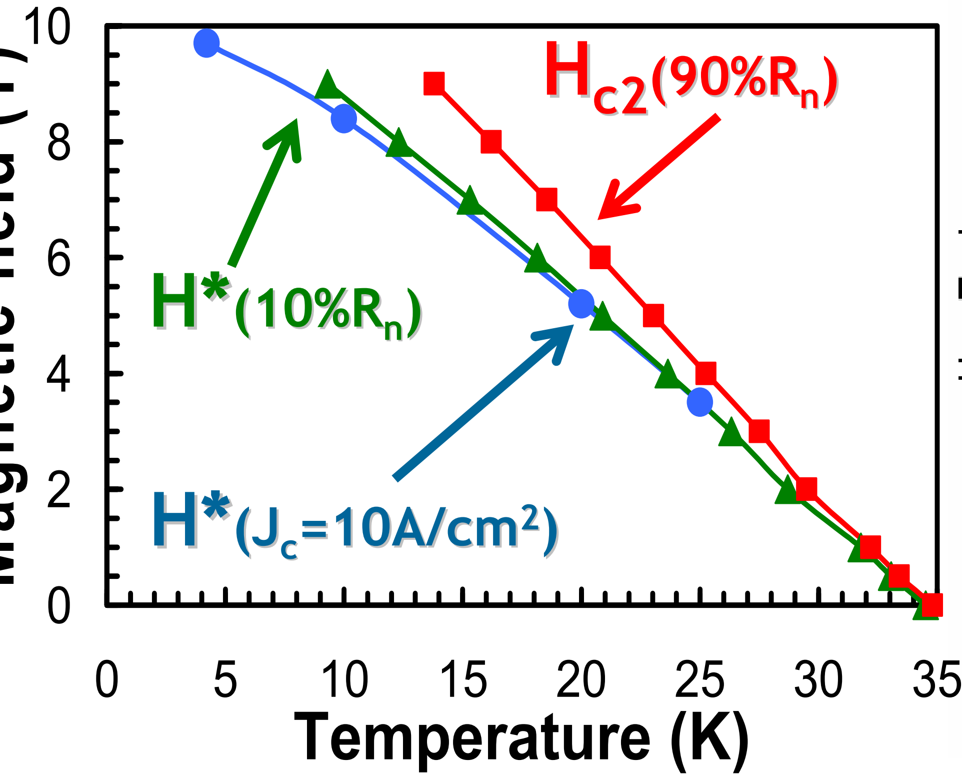
Low resistivity (~clean) thin film

Small current resistive transitions

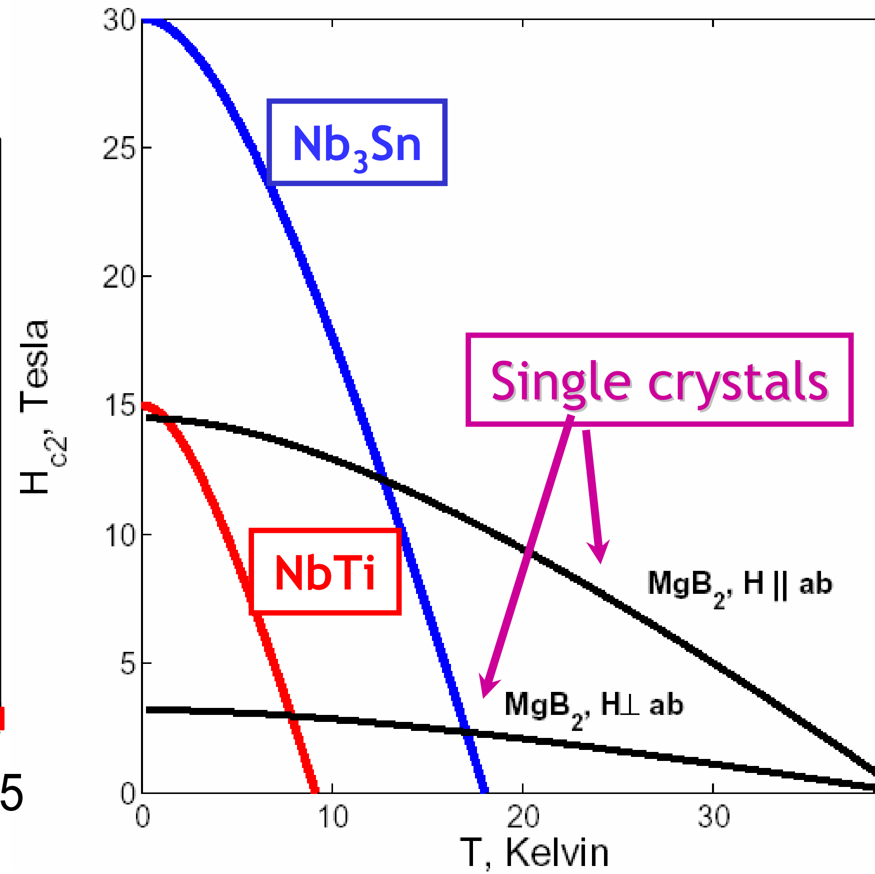
Valeria Braccini et al. on film of Giencke and Eom

MgB_2 is more like LTS

J_c goes to zero at start of H_{c2} transition occurs – just like LTS



...BUT...



Alloying required to raise H_{c2} above Nb-base superconductors

Valeria Braccini et al.

The shape of $H_{c2}(T)$ is controlled by alloying

Exact solution for $H_{c2}(T,\theta)$ with anisotropic $D_\pi(\theta)$ and $D_\sigma(\theta)$

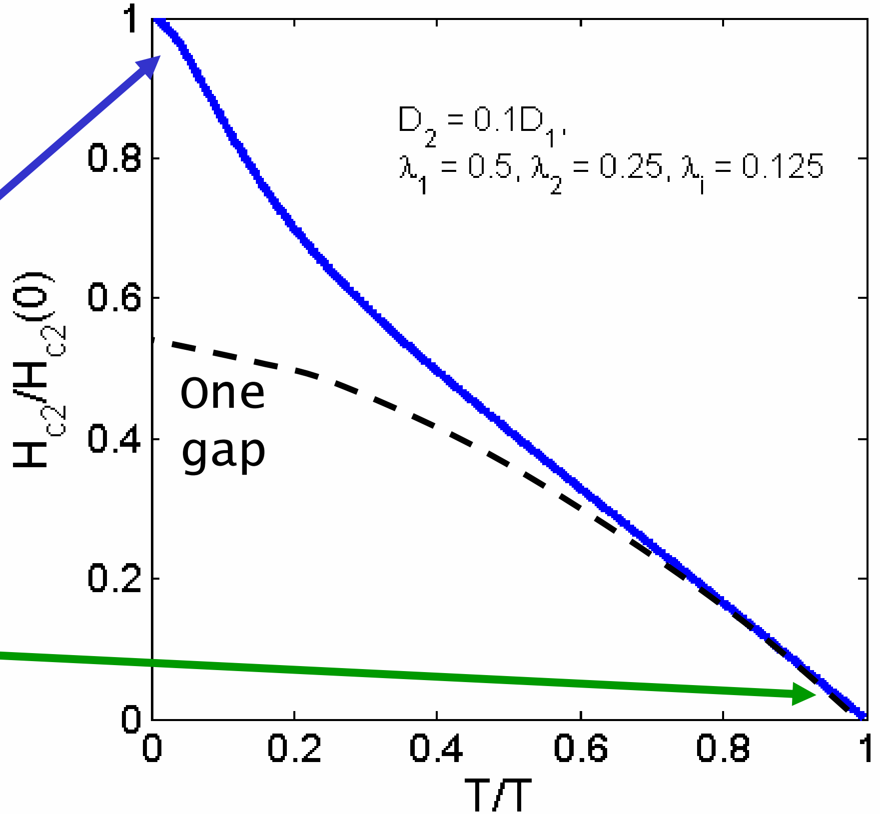
Zero-temperature $H_{c2}(0)$ is determined by the minimum diffusivity

The slope dH_{c2}/dT at T_c is determined by the maximum diffusivity

H_{c2} can be much higher than the one-band prediction:

$$H_{c2}(0) = 0.7T_cH'_{c2}(T_c)$$

*A. Gurevich, PRB **67** (2003) 184515*

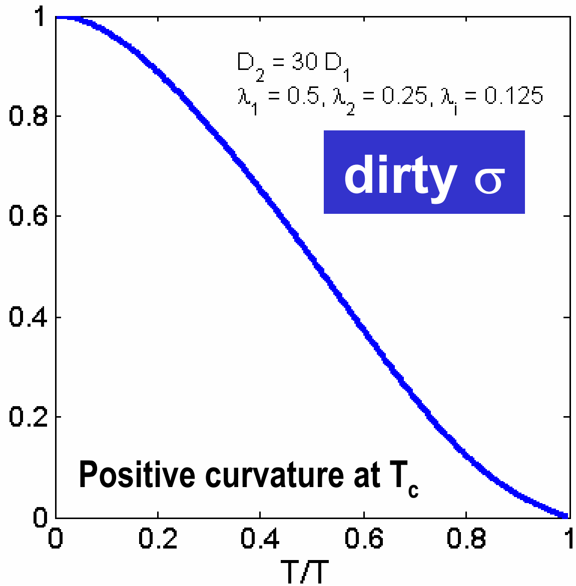


For T_c = 40 K, $H_{c2}' \approx$ 1-2T/K,

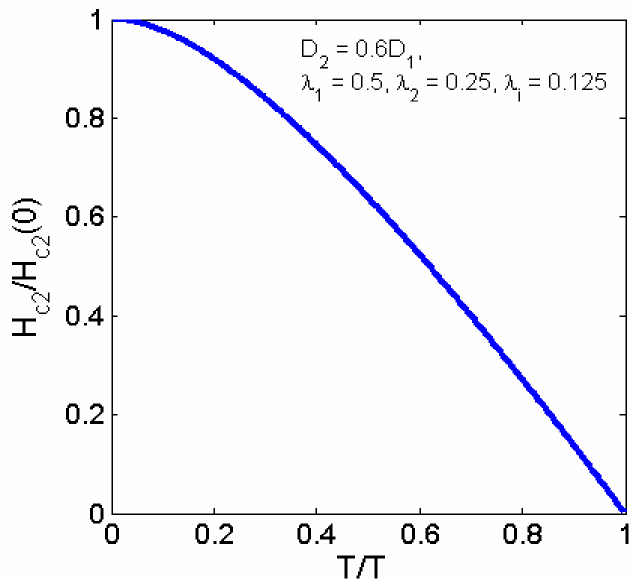
$H_{c2}(0) \approx$ 50-80 Tesla are possible

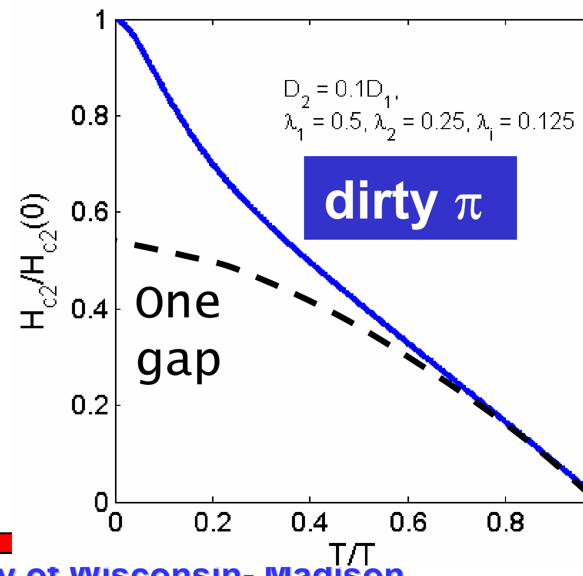
Paramagnetic limit $H_p \approx$ 70 Tesla

Interplay of different scattering channels



Strong H_{c2} enhancement by disordering Mg sublattice

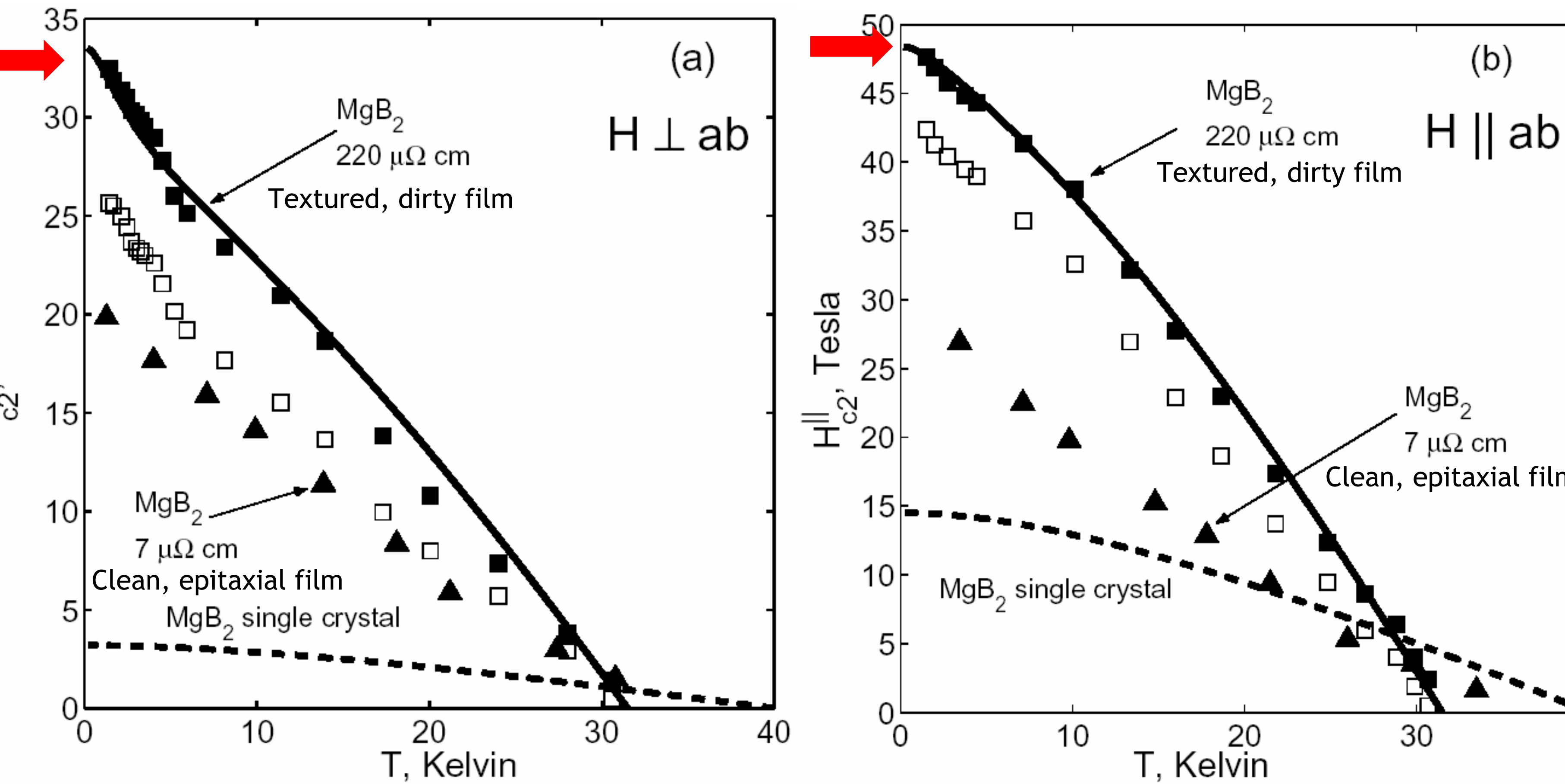




Increase π scattering relative to σ scattering

H_{c2} of high-resistivity MgB_2 film

S. Patnaik, V. Braccini et al., (UW – NHMFL - LANL collaboration)



$D_{ab}^{(\pi)} = 0.12 D_{ab}^{(\sigma)}$

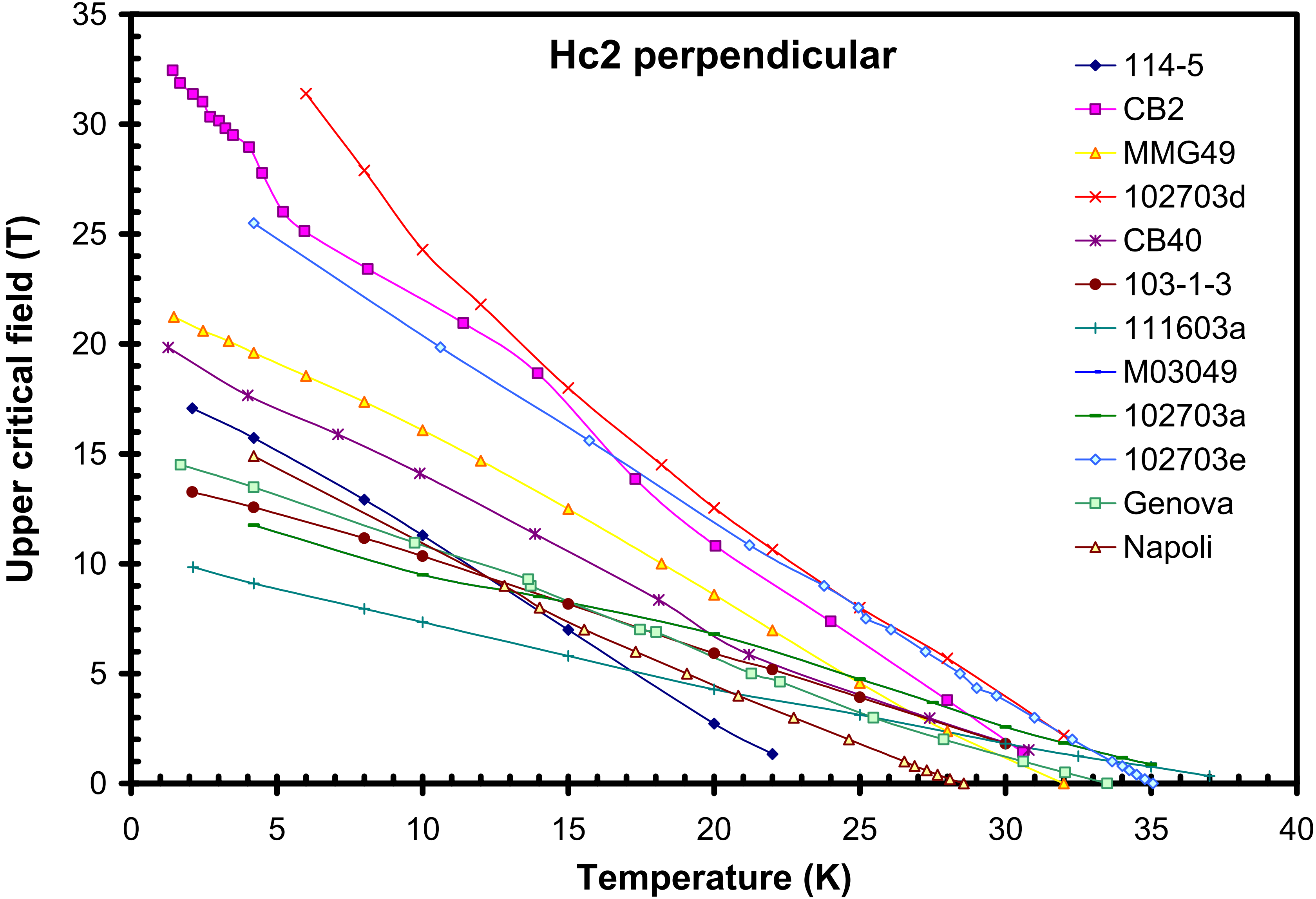
$[D_{ab}^{(\pi)} D_c^{(\pi)}]^{1/2} = 0.2 [D_{ab}^{(\sigma)} D_c^{(\sigma)}]^{1/2}$

A. Gurevich et al., SuST to appear

EH13 #42

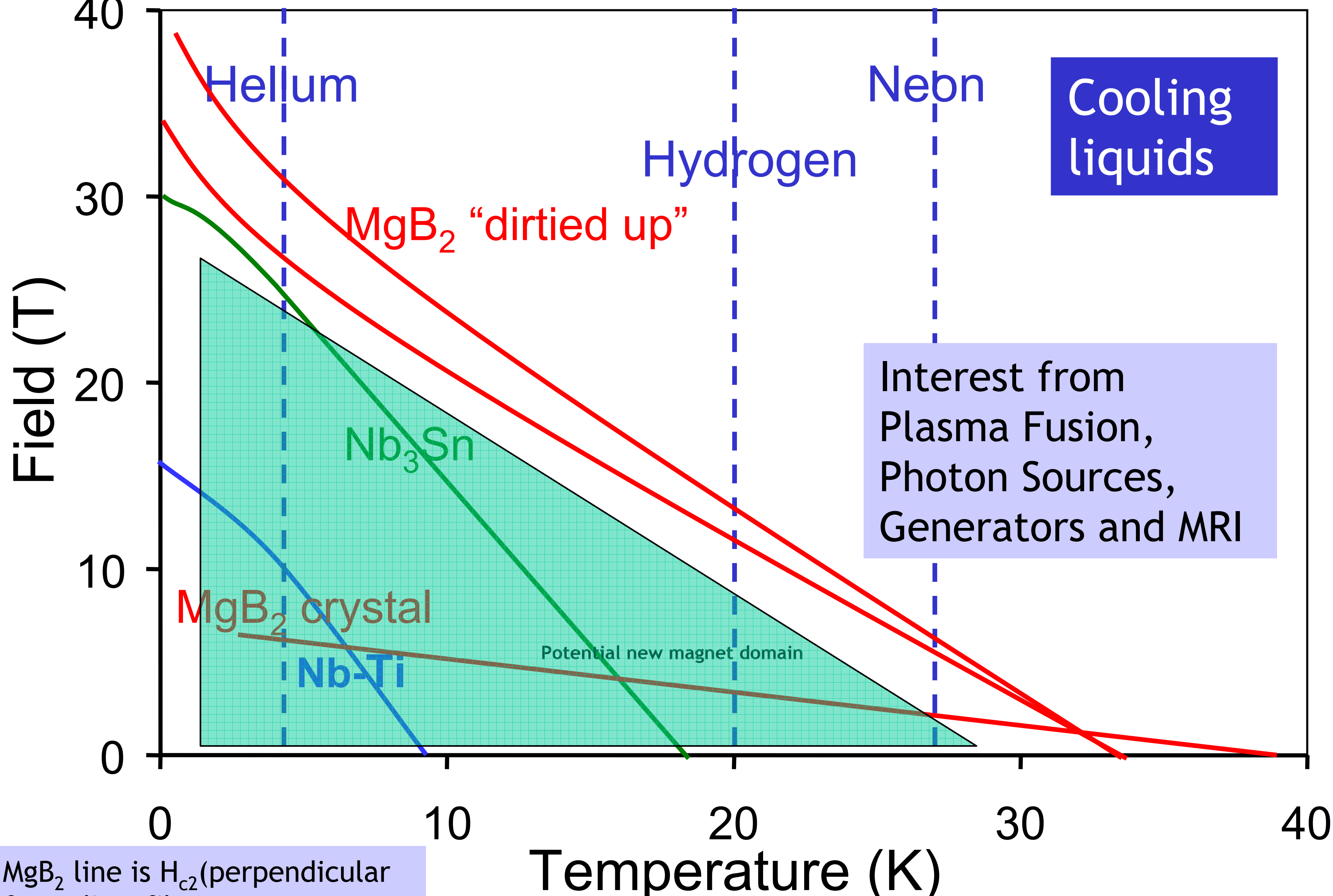
Eric Hellstrom, 05/10/2003

Very recent H_{c2} measurements



ASU-Conductus-Genoa-Penn State-Wisconsin collaboration

Potential Magnet H_{c2}-T plane for MgB_2



MgB_2 line is H_{c2}(perpendicular from dirty film)

Some summary thoughts

- Nb-Ti has been developed to a level not approached by any other superconductor
  - Nb-Ti-Ta has not
- Optimized superconductors are real nanostructures
  - Nanostructures are not easily evaluated by just one or two characterizations
- Recent attention to Nb_3Sn has made it much better
- Inhomogeneity at the nanometer scale is vital to flux pinning
  - We do NOT want long range inhomogeneities that obstruct the current paths

Recent Papers

Nb_3Sn

A Godeke, M C Jewell, A A Golubov, B Ten Haken, and D C Larbalestier ,"Inconsistencies between extrapolated and actual critical fields in Nb_3Sn wires as demonstrated by direct measurements of H_{c2}, H* and T_c", Superconductor Science and Technology **16**, 1019-1025 (2003).

M C Jewell, P J Lee and D C Larbalestier, "The influence of Nb_3Sn strand geometry on filament breakage under bend strain as revealed by metallography", Supercond. Sci. Technol. **16** 1005-1011 (2003).

L. D. Cooley, C. M. Fischer, P. J. Lee, and D. C. Larbalestier, "Simulations of the effects of tin composition gradients on the superconducting properties of Nb_3Sn conductors", Subm. to J. Appl. Phys. 2004 (Cond Mat 0402206).

MgB_2

A Gurevich, S Patnaik, V Braccini, K H Kim, C Mielke, X Song, L D Cooley, S D Bu, D M Kim, J H Choi, L J Belenky, J Giencke, M K Lee, W Tian, X Q Pan, A Siri, E E Hellstrom, C B Eom and D C Larbalestier, "Very high upper critical fields in MgB_2 produced by selective tuning of impurity scattering", Supercond. Sci. Technol. **17** 278-286 (2004).

A. Gurevich, "The theory of the upper critical field for a two gap superconductor", Physical Review B **67**, 184515 (2003)

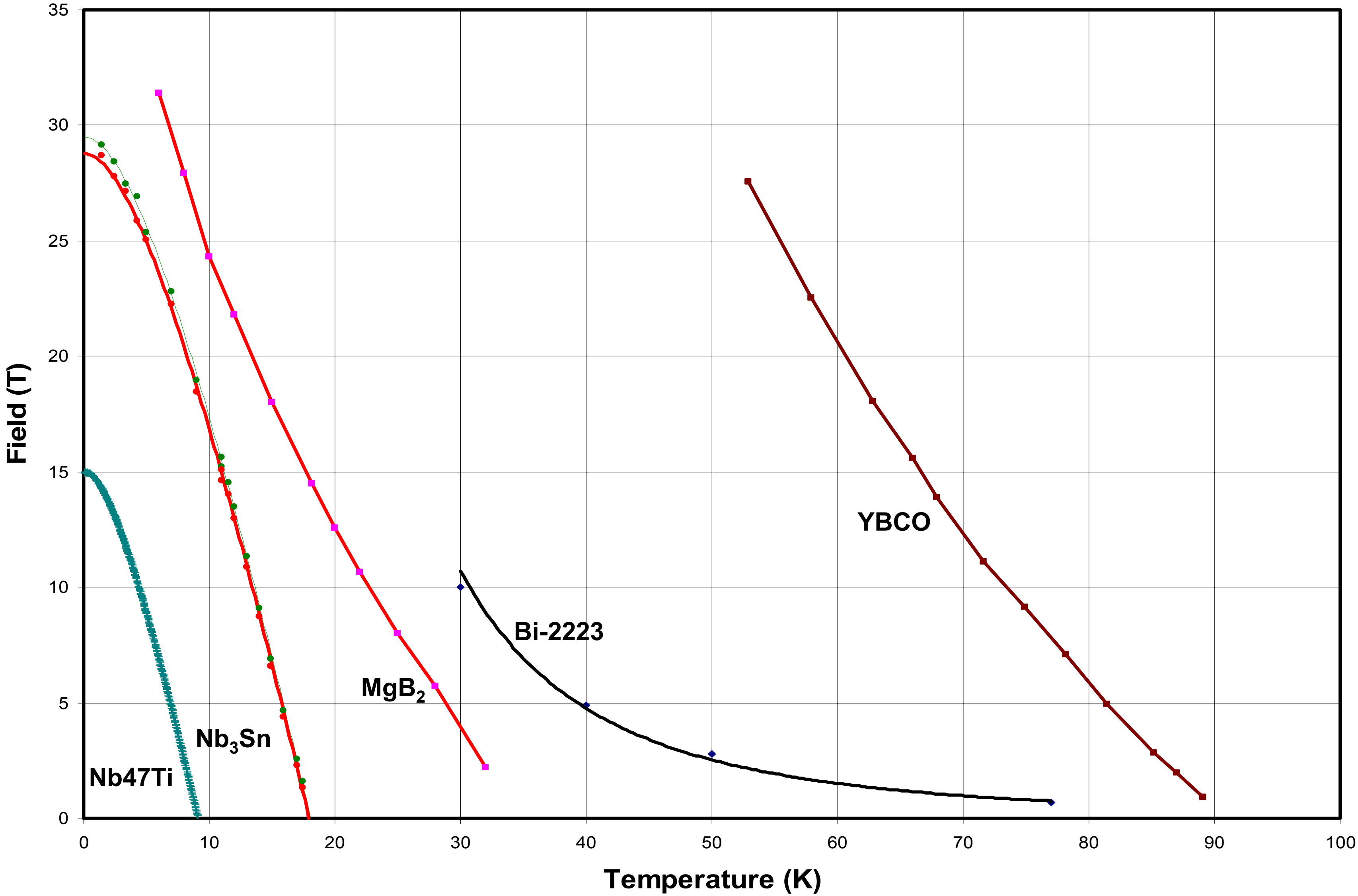
V. Braccini, A. Gurevich, J.E. Giencke, M.C. Jewell, C.B. Eom, D.C. Larbalestier, A. Pogrebnyakov, Y. Cui, B. T. Liu, Y. F.Hu J. M. Redwing, Qi Li, X.X. Xi, R.K. Singh, R. Gandikota, J. Kim, B. Wilkens, N. Newman, J. Rowell, B. Moeckly, V. Ferrando, C. Tarantini, D. Marré, M. Putti, C. Ferdeghini, R. Vaglio, E. Haanappel, "High-field superconductivity in alloyed MgB_2 thin films", subm. to Phys. Rev. Letts. January 2004. (Cond Mat 0402001)

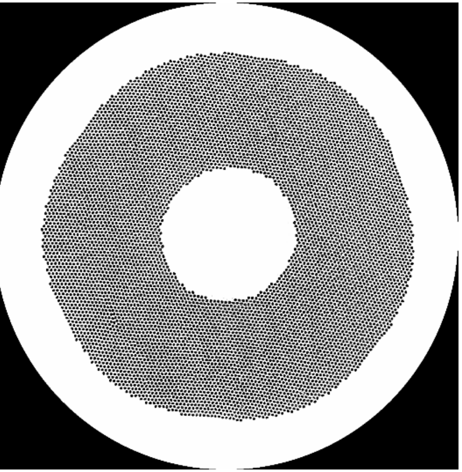
HTS – Bi-2223 and YBCO-CC

D M Feldmann, D C Larbalestier, R Feenstra, J. D. Budai, T. G. Holesinger, and P. N. Arendt, "Through-thickness superconducting and normal-state transport properties revealed by thinning of thick film ex situ $YBa_2Cu_3O_{7-\delta}$ coated conductors", Appl Phys Lett **83** 3951-3953 (2003).

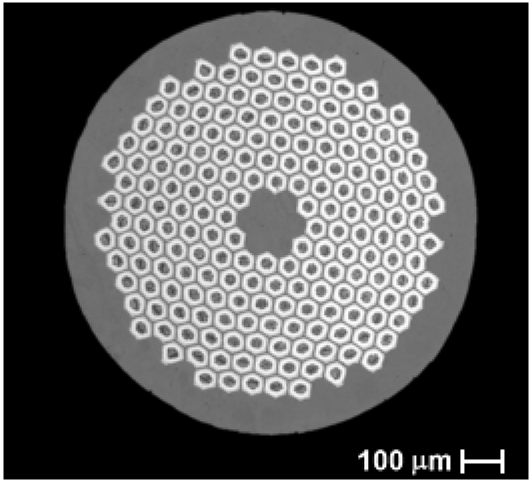
Y. Yuan, J. Jiang, X. Y. Cai, Y. Huang, R. Parrella, D. C. Larbalestier, E. E. Hellstrom, "Significantly enhanced critical current density in Ag-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10-x}$ composite conductors prepared by overpressure processing", to appear in Appl. Phys. Letts, March (2004).

The accessible H-T plane

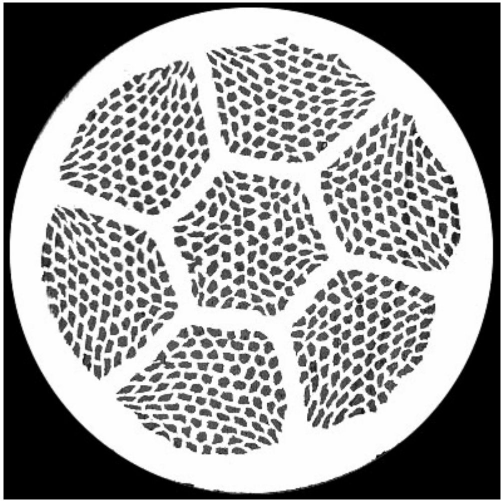




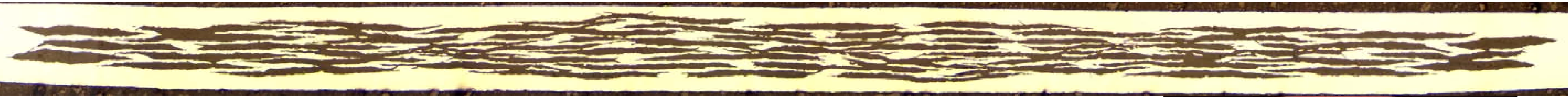
Nb47Ti



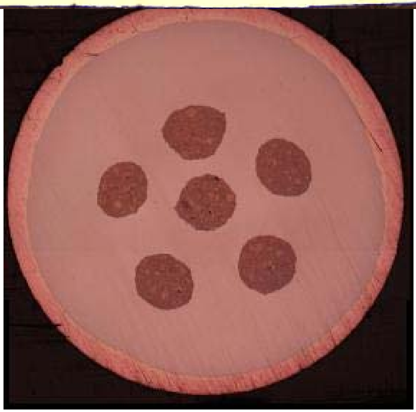
PIT Nb_3Sn



Bi-2212



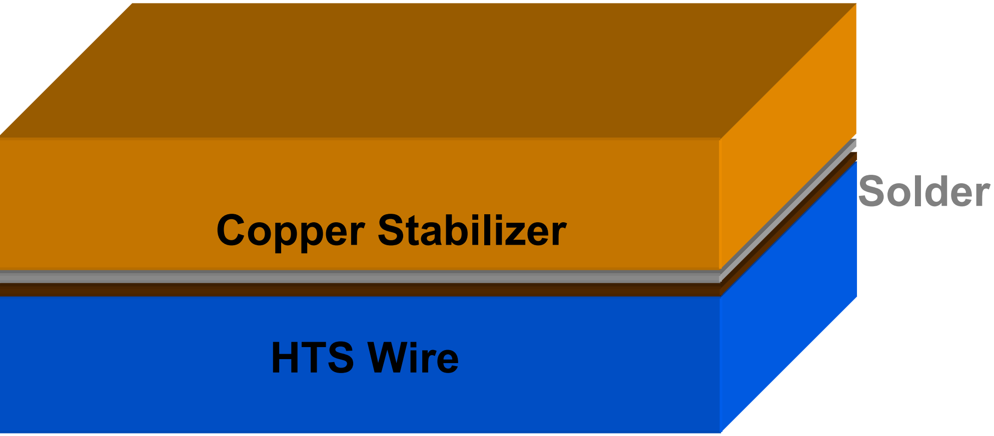
Bi-2223



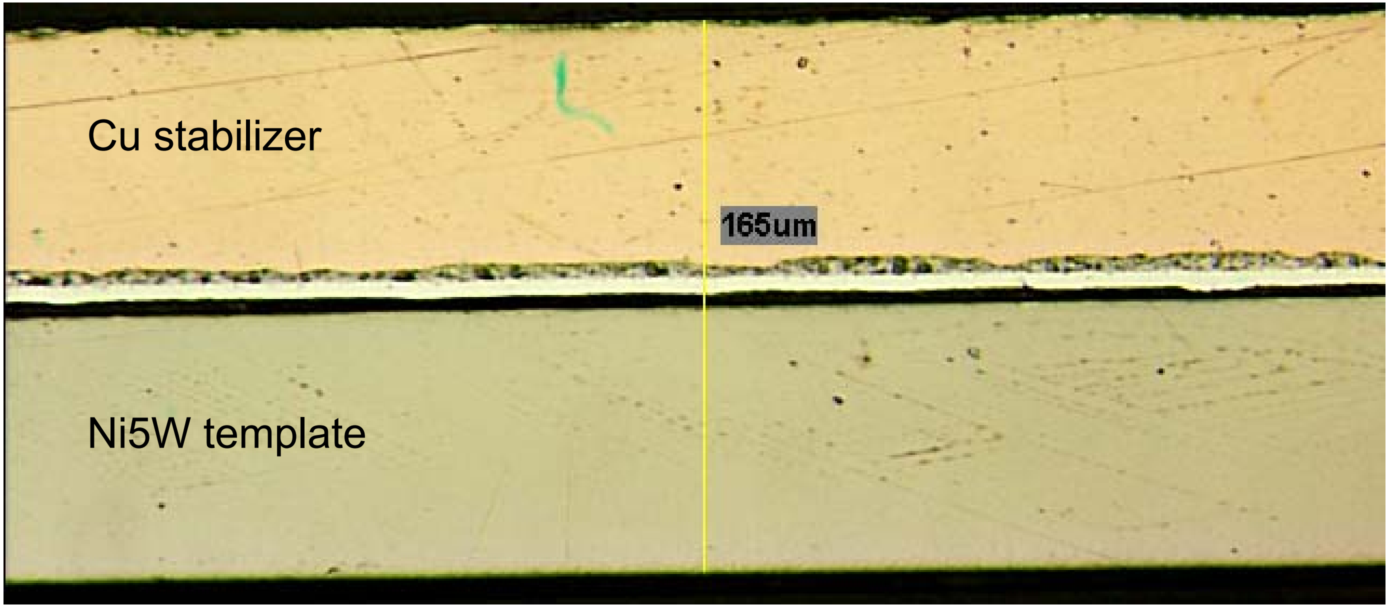
MgB_2

Representative multifilamentary conductors made from a. Nb47wt.%Ti, b. Nb_3Sn, c. Bi-2212, and d. Bi-2223 and e. MgB_2. The matrices for the conductors are high purity copper for (a), (b) and the outer sheath of (e) and pure silver for (c) and (d). The filaments of MgB_2 are surrounded by 316 stainless steel in (e). Conductors were manufactured by Oxford Instruments - Superconducting Technology (a and c), ShapeMetal Innovation (b), American Superconductor Corporation (d) and Hitachi cable in collaboration with the National Institute for Materials Science (e).

Neutral axis YBCO-CC tape



AMSC tape on Ni5W RABiTS - superconductor fill factor 1-2%



Nb_3Sn – many conductor subtypes

- Stage 1: First high field superconductor (1962). Tapes from 1964 to about 1976. Filamentary wires entered about 1974 – many processes compete even today
- Stage 2: Understanding (1962 to today). Different eras of research –
  - Pre-HTS, fusion-magnet driven to ~1995
  - HEP-magnet driven ~1997 to today
- Stage 3: Optimization of competing processes – bronze, internal tin, PIT depending on application and customer