



Superconducting Materials - Something new, something old



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University of Wisconsin

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Collaborators and Acknowledgements

MgB₂:

Groups of Eric Hellstrom, Chang-Beom Eom and Susan Babcock at UW

Groups of Robert Cava (Princeton) and Paul Canfield (Ames)

X.Y. Cai, J. Choi, L.D. Cooley, A. Gurevich, J.Y. Jiang, M. Naus, S. Patnaik, A.A. Polyanskii, M. Rikel, X. Song,

Applied Superconductivity Center, University of Wisconsin-Madison,

Supported by: NSF-MRSEC, AFOSR, DOE

Nb₃Sn:

Peter Lee, Michael Naus, Chris Hawes and Chad Fischer,

Lance Cooley, Alex Squitieri and Bill Starch

Ron Scanlan at LBNL and the Conductor Development Program

Supported by DOE-HEP and Fusion

Recent Relevant Papers

MgB₂

D. C. Larbalestier, L. D. Cooley, M. O. Rikel, A. A. Polyanskii, J. Jiang, S. Patnaik, X. Y. Cai, D. M. Feldmann, A. Gurevich, A. A. Squitieri, M. T. Naus, C. B. Eom, E. E. Hellstrom, R. J. Cava, and K. A. Regan, "Strongly Linked Current Flow in Polycrystalline Forms of the Superconductor MgB₂," *Nature*, **410**: 186-189, 2001.

C.B. Eom, M.K. Lee, J.H. Choi, L. J. Belenky, X. Song, L.D. Cooley, M.T. Naus, S. Patnaik, J. Jiang, M. Rikel, A. Polyanskii, A. Gurevich, X.Y. Cai, S.D. Bu, S.E. Babcock, E.E. Hellstrom, and D.C. Larbalestier, "Very High Critical Current Density and Enhanced Irreversibility Field in Magnesium Diboride Films", *Nature* **411**: 558-560, 2001

S. Patnaik, L.D. Cooley, A. Gurevich, A.A. Polyanskii, J.Y. Jiang, X.Y. Cai, A.A. Squitieri, M.T. Naus, M.K. Lee, J.H. Choi, L. Belenky, S.D. Bu, J. Letteri, X. Song, D.G. Schlom, S. E. Babcock, C. B. Eom E.E. Hellstrom and D. C. Larbalestier "Electronic Anisotropy, Magnetic Field-Temperature Phase Diagram and their Dependence on Resistivity in c-Axis Oriented MgB₂ Thin Films", *Superconductor Science and Technology* **14**, 315-319, (2001).

Nb₃Sn

C. D. Hawes, P. J. Lee, and D. C. Larbalestier, "Measurement of the Critical Temperature Transition and Composition Gradient in Powder-In-Tube Nb₃Sn Composite Wire," *IEEE Transactions on Applied Superconductivity*, **10**: 988-991, 2000.

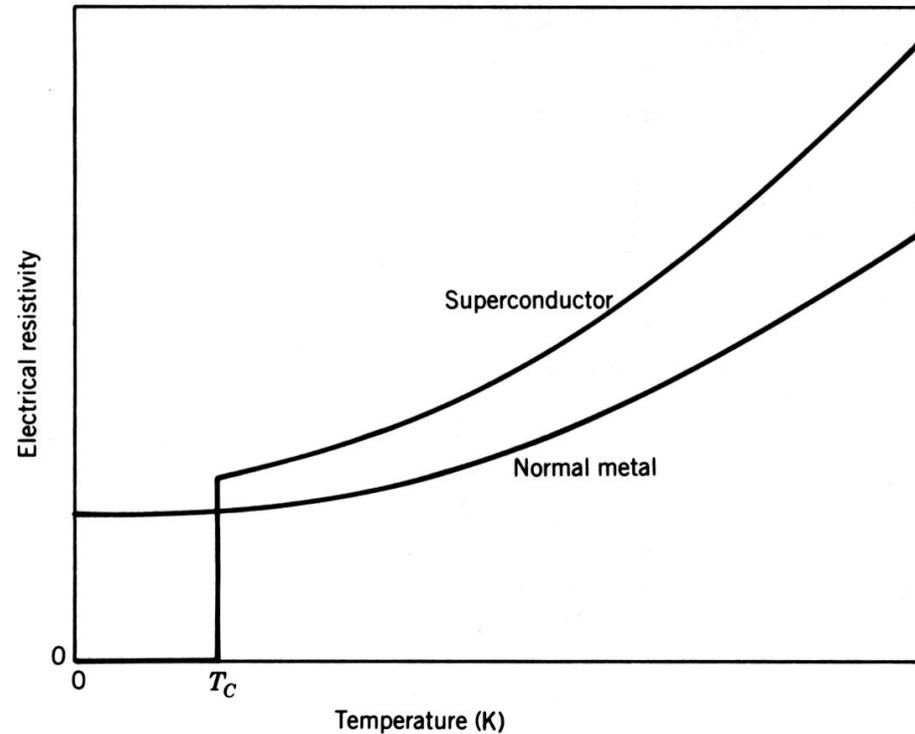
P. J. Lee, A. A. Squitieri, and D. C. Larbalestier, "Nb₃Sn: Macrostructure, Microstructure, and Property Comparisons for Bronze and Internal Sn Process Strands," *IEEE Transactions on Applied Superconductivity*, **10**: 979-982, 2000.

P. J. Lee and D. C. Larbalestier, "Compositional and Microstructural Profiles Across Nb₃Sn Filaments Produced by Different Fabrication Methods," *IEEE Transactions on Applied Superconductivity*, **11**: 3671-3674, 2001.

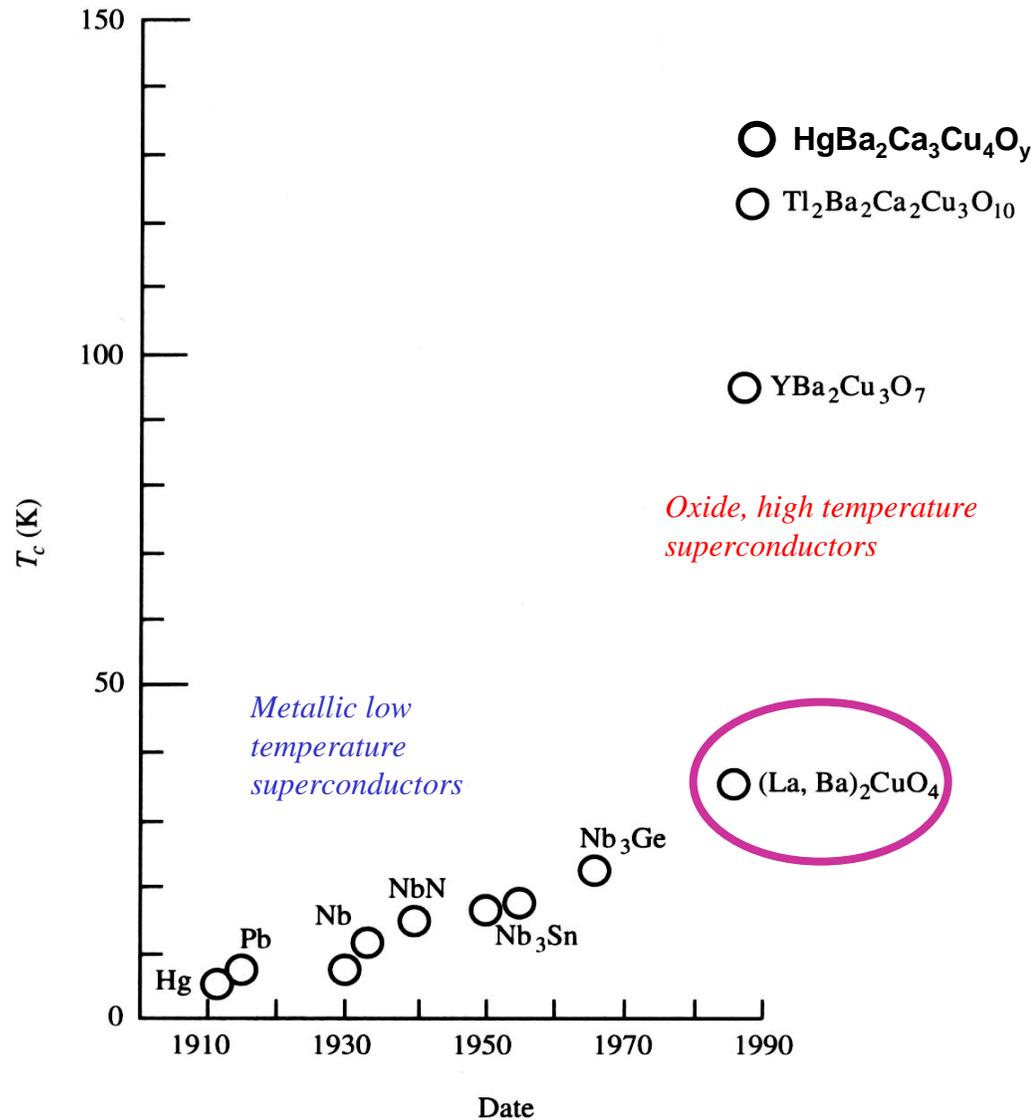
M. T. Naus, P. J. Lee, and D. C. Larbalestier, "The Influence of the Starting Cu-Sn Phase on the Superconducting Properties of Subsequently Reacted Internal-Sn Nb₃Sn Conductors," *IEEE Transactions on Applied Superconductivity*, **11**: 3569-3572 2001.

“Zero Resistivity”

- Non-Superconducting Metals
 - $\rho = \rho_0 + aT$ for $T > 0 \text{ K}^*$
 - $\rho = \rho_0$ Near $T = 0 \text{ K}$
- *Recall that $\rho(T)$ deviates from linearity near $T = 0 \text{ K}$
- Superconducting Metals
 - $\rho = \rho_0 + aT$ for $T > T_c$
 - $\rho = 0$ for $T < T_c$
- Superconductors are more resistive in the normal state than good conductors such as Cu



Transition Temperature T_c



X-Sender: mrikel@facstaff.wisc.edu

X-Mailer: QUALCOMM Windows Eudora Version 4.3.2

Date: Wed, 24 Jan 2001 08:16:12 -0600

To: David Larbalestier <larbales@engr.wisc.edu>,
"Eric E. Hellstrom" <hellstrom@engr.wisc.edu>

From: Mark Rikel <mrikel@facstaff.wisc.edu>

Subject: Tc = 40 K in MgB2

Subject: Tc = 40 K in MgB2

David, Eric

I have a mail (in Russian) from my former colleague xxxxxx who is currently in Japan.

Superconductivity in MgB2 at ~40 K was discovered, and for two last days, people in his lab were measuring Tc and Hc2 of the powder bought in the nearest chemistry store.

They confirm Tc~38.5 K and dHc2/dT ~ 0.5 T/K.

The reported problem: in air MgB2 is oxidized to MgO.

Mark

Date: Mon, 29 Jan 2001 11:31:22 -0600

To: David Larbalestier <larbales@engr.wisc.edu>,
"Eric E. Hellstrom" <hellstrom@engr.wisc.edu>,
jianyijiang@facstaff.wisc.edu,
"Cai Xueyu Y." <xcai@facstaff.wisc.edu>,
Tolya Polyanskii <polyansk@engr.wisc.edu>, agourevi@facstaff.wisc.edu
From: Mark Rikel <mrikel@facstaff.wisc.edu>
Subject: Fwd: Tr: **New superconductor?!?!?!?!?**

David, Eric, Jianyi, Cai, Tolya, and Sasha

> The news of superconductivity of MgB₂ is true. I have already known more
> than two institutes who confirmed the superconductivity of the material
> around 39K by using SQUID. **The discovery was made by Prof. Akimitsu. He**
> **presented his discovery at a meeting in Sendai on Jan. 9 or 10, I don't**
> **remember correctly.** I heard the meeting was crowded because some people
> heard in advance that a new discovery of ROOM TEMPERATURE SUPERCONDUCTOR
> will be presented. But the T_c was 40K in this presentation. I myself knew
> this news at a meeting at Tokyo on Jan 18. I heard that the people in the
> Physics side are excited about this discovery very much whereas the people
> in the application side are rather cool at this moment because of the rather
> low T_c. I myself think this discovery is of course very important because
> the system is totally different from the conventional HTS.
>> **As long as I knew, Prof. Akimitsu commented that he will not make any**
> **presentation about this discovery after Sendai meeting and he will NOT**
> **publish a paper for this discovery, MgB₂.**

Snowmass July 5, 2001

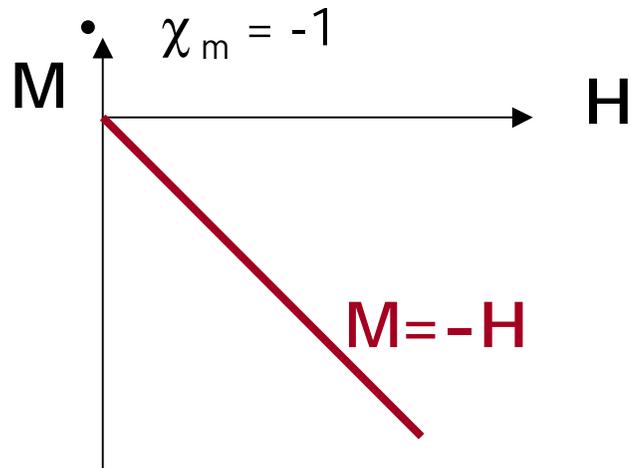
Available Conductor Materials

- Nb-Ti
- Nb₃Sn
- (Bi,Pb)₂Sr₂Ca₂Cu₃O₁₀

Potential Conductor Materials

- YBa₂Cu₃O₇
- MgB₂

Perfect Diamagnetism

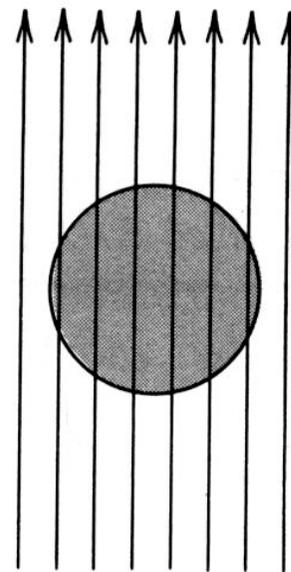


- Means:

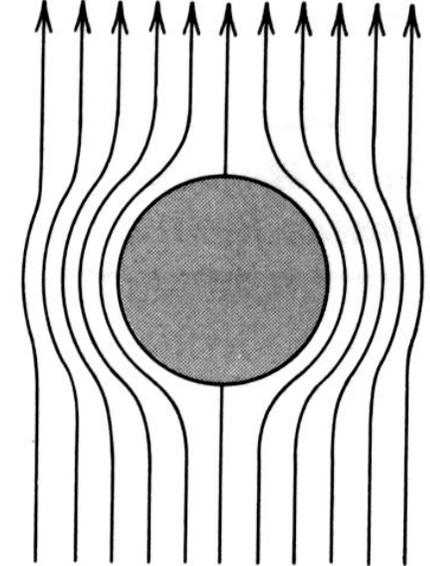
$$B = \mu_0(H + M)$$

$$B = \mu_0(H + \chi_m H)$$

$$B = 0$$



Normal Metal

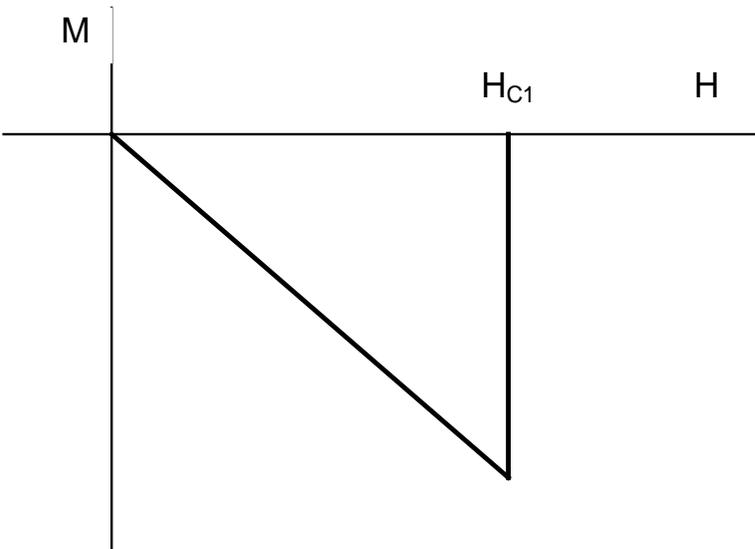


Superconductor

Flux is excluded from the bulk by supercurrents flowing at the surface to a penetration depth (λ) ~ 200-500 nm

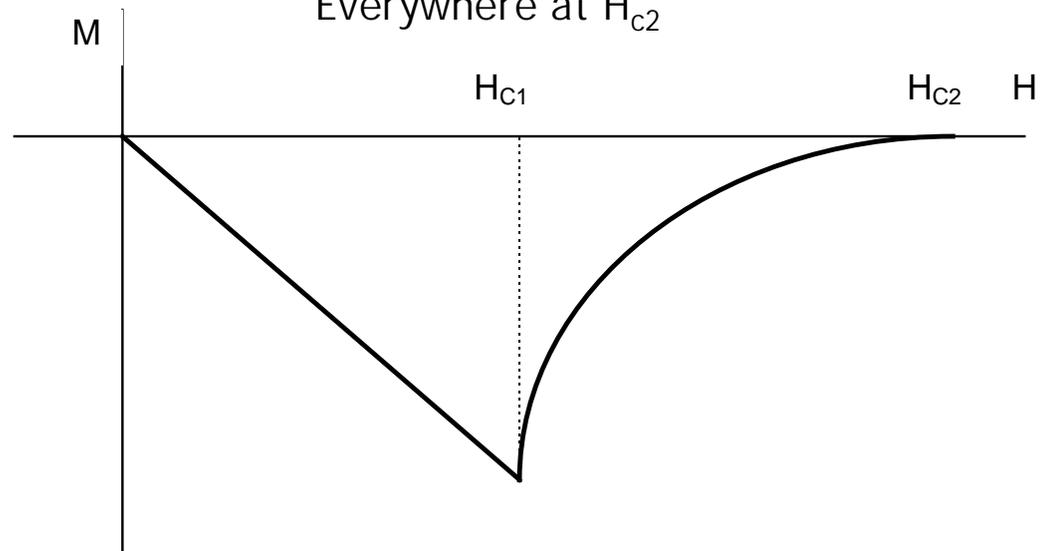
Type I and Type II

- Type I
 - Material Goes Normal Everywhere at H_c



Complete flux exclusion up to H_c , then destruction of superconductivity by the field

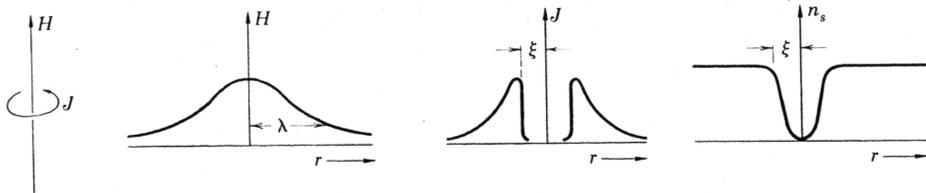
- Type II
 - Material Goes Normal Locally at H_{c1} , Everywhere at H_{c2}



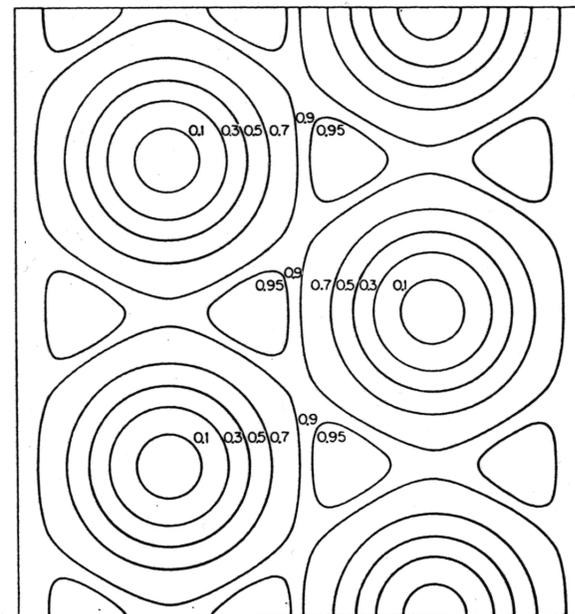
Complete flux exclusion up to H_{c1} , then partial flux penetration as vortices

Current can now flow in bulk, not just surface

Vortex properties



- Two characteristic lengths
 - coherence length ξ , the pairing length of the superconducting pair
 - penetration depth λ , the length over which the screening currents for the vortex flow
- Vortices have defined properties in superconductors
 - normal core dia, $\sim 2\xi$
 - each vortex contains a flux quantum ϕ_0
 - currents flow at J_d over dia of 2λ
 - vortex separation $a_0 = 1.08(\phi_0/B)^{0.5}$



$$H_{c2} = \phi / 2\pi\xi^2$$

$$\phi_0 = h/2e = 2.07 \times 10^{-15} \text{ Wb}$$

$$B/B_{c2} (=b) \sim 0.2$$

Discovery: Akimitsu Jan. 2001

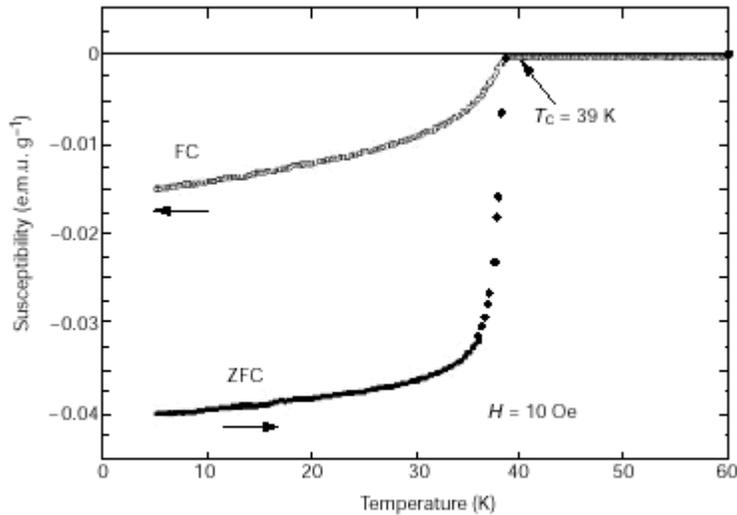


Figure 3 Magnetic susceptibility χ of MgB_2 as a function of temperature. Data are shown for measurements under conditions of zero field cooling (ZFC) and field cooling (FC) at 10 Oe.

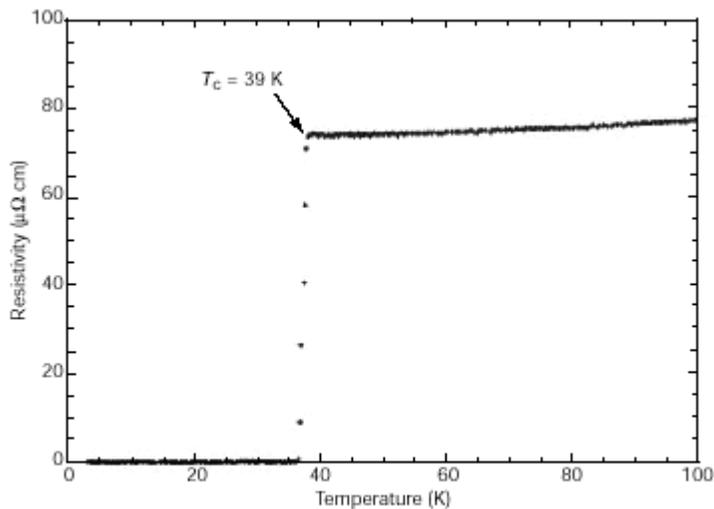


Figure 4 Temperature dependence of the resistivity of MgB_2 under zero magnetic field.

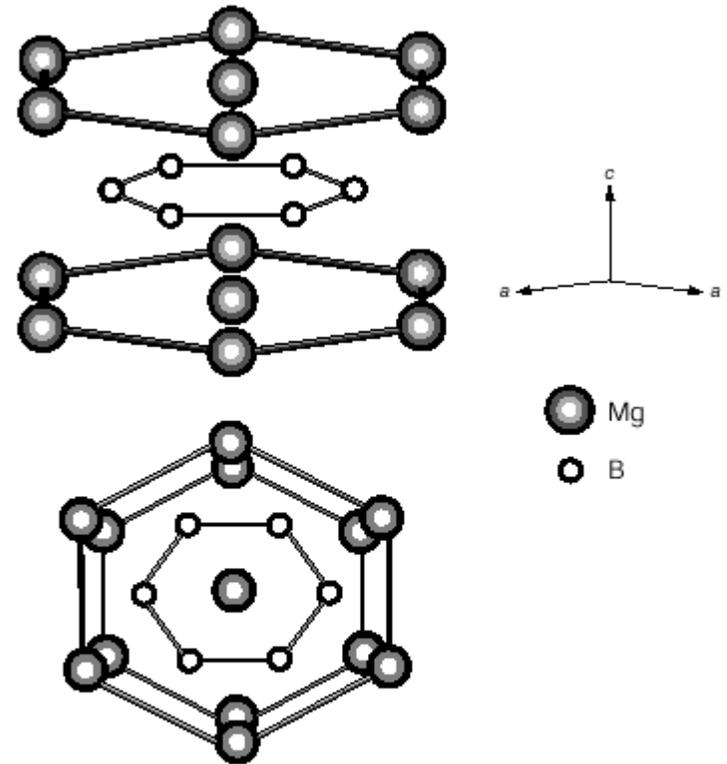


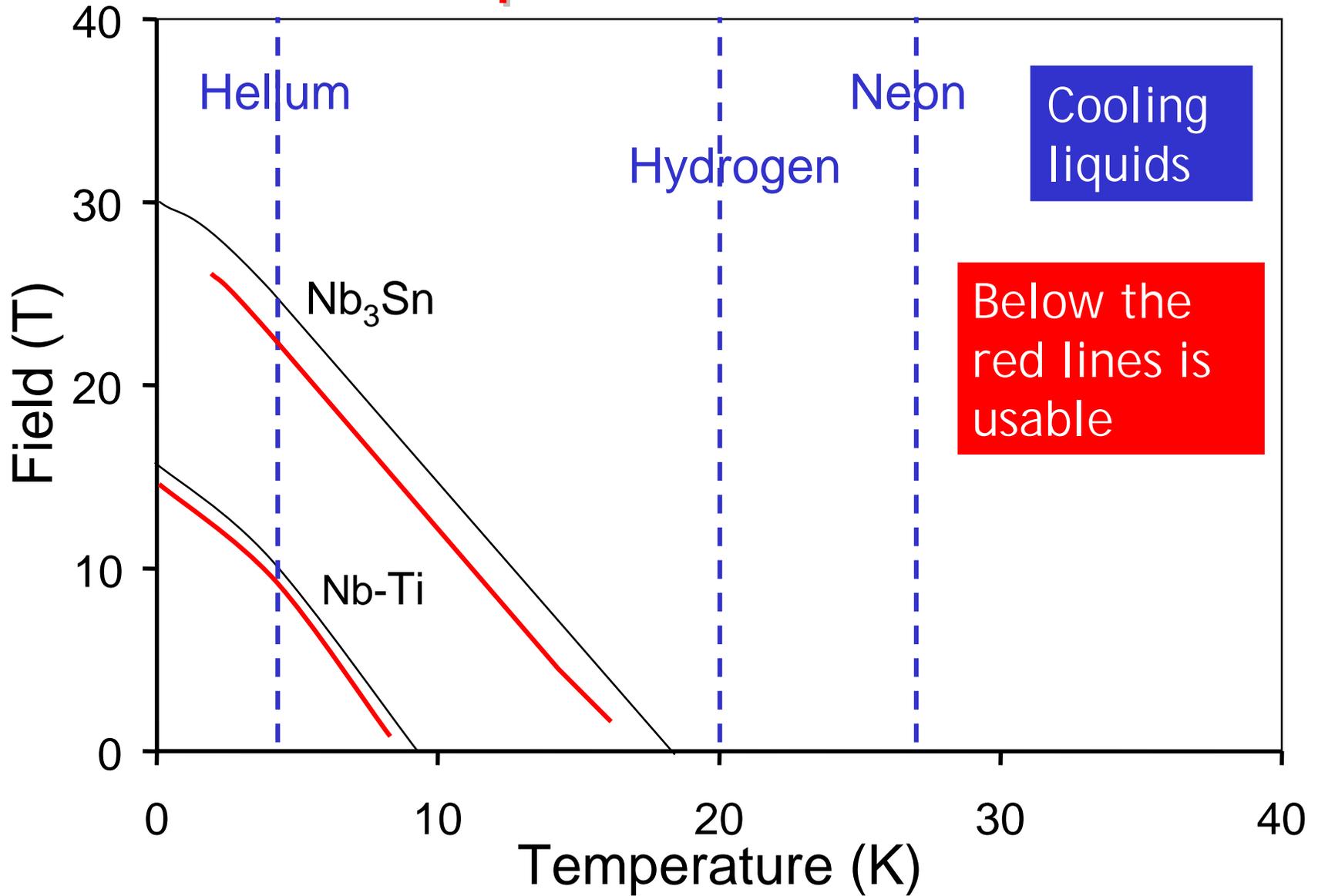
Figure 2 Crystal structure of MgB_2 .

$$a = 3.1432 \text{ \AA}$$

$$c = 3.5193 \text{ \AA}$$

$$r = 2.55 \text{ g/cm}^3$$

H-T plane for LTS



MgB₂ at UW - January

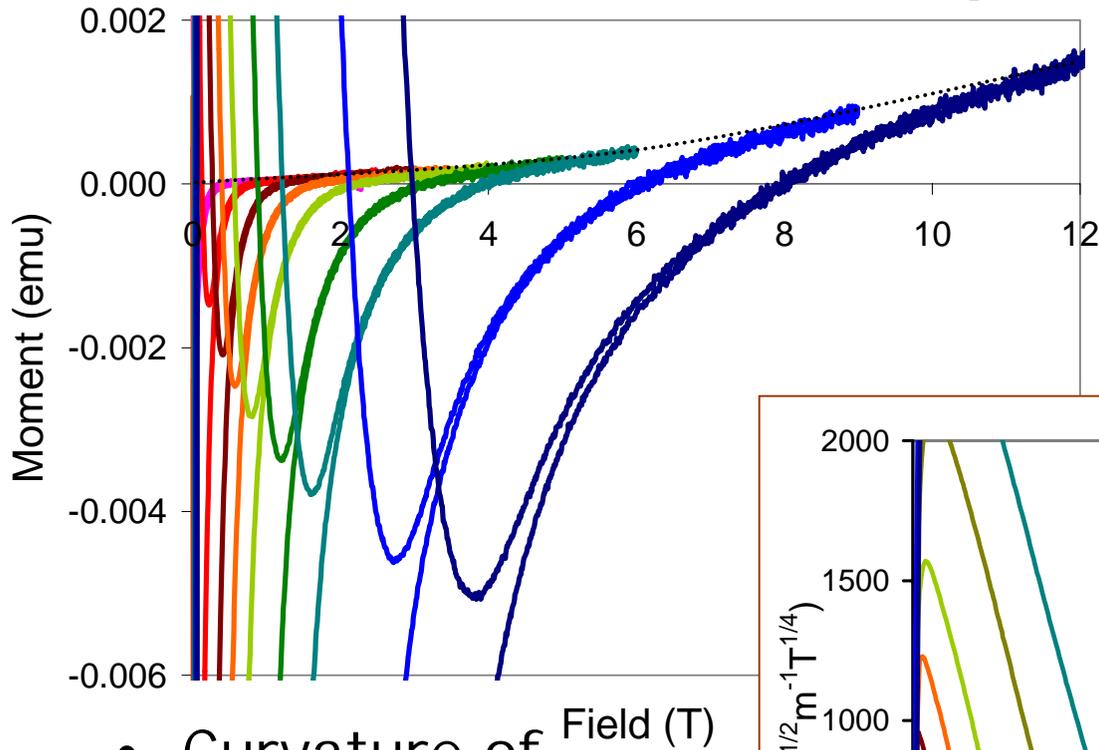
- People: Eric Hellstrom, Chang-Beom Eom and our groups
- Bulk samples
 - Drive to Milwaukee, pick up borides at Aldrich
 - sinter to form quasi-dense pack
 - Scrounge B and Mg and react together
 - Bob Cava (Princeton) called up
 - Samples offered by Canfield (Ames), Kumukura (NIMS)
Thin Films at UW
- Thin films (Eom)
 - Pulsed Laser Deposition at RT and subsequent annealing in Mg vapor

Our Questions

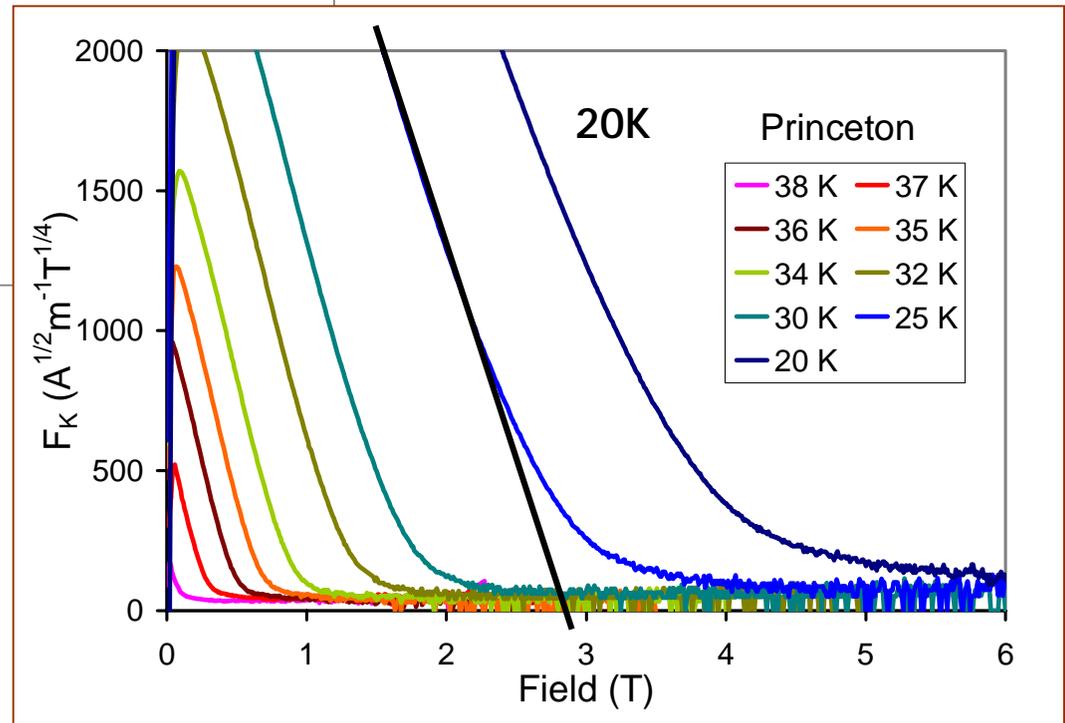
- With a 39K T_c , surely H_{c2} should vanquish Nb_3Sn ?
- High- T_c cuprates have a mammoth problem: Grain Boundaries (GBs) tend to obstruct current
- GBs are benign in Low- T_c materials
- How would GBs in MgB_2 behave?

D. C. Larbalestier, L.D. Cooley, M. Rikel, J. Jiang et al., "**Strongly Linked Current Flow in Polycrystalline Forms of the Superconductor MgB_2** ," *Nature*, **410**: 186-189, 2001.(March 8, 2001)

Bulk samples - I

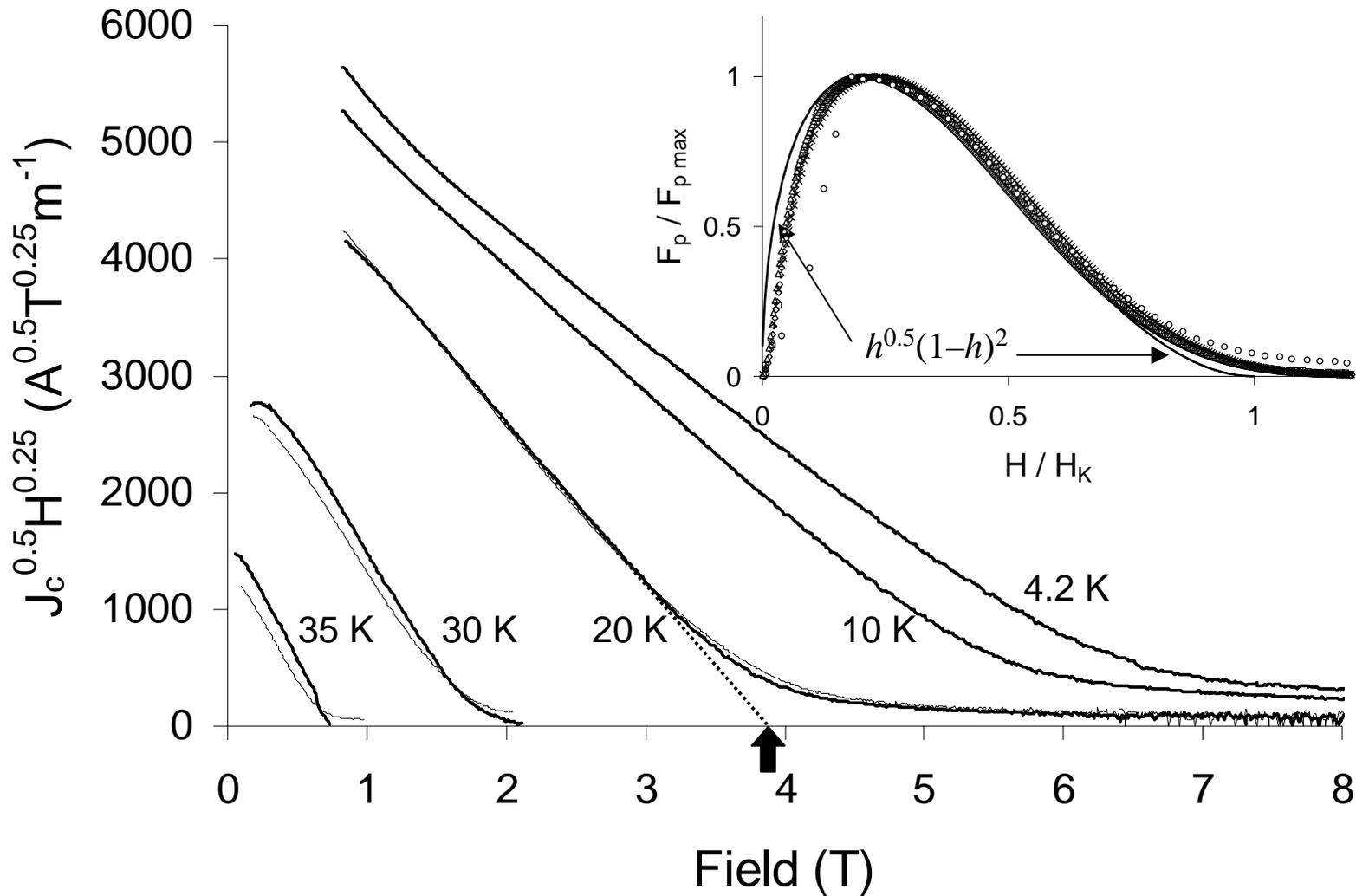


- Curvature of reversible $m(H)$
- Tails on Kramer plots

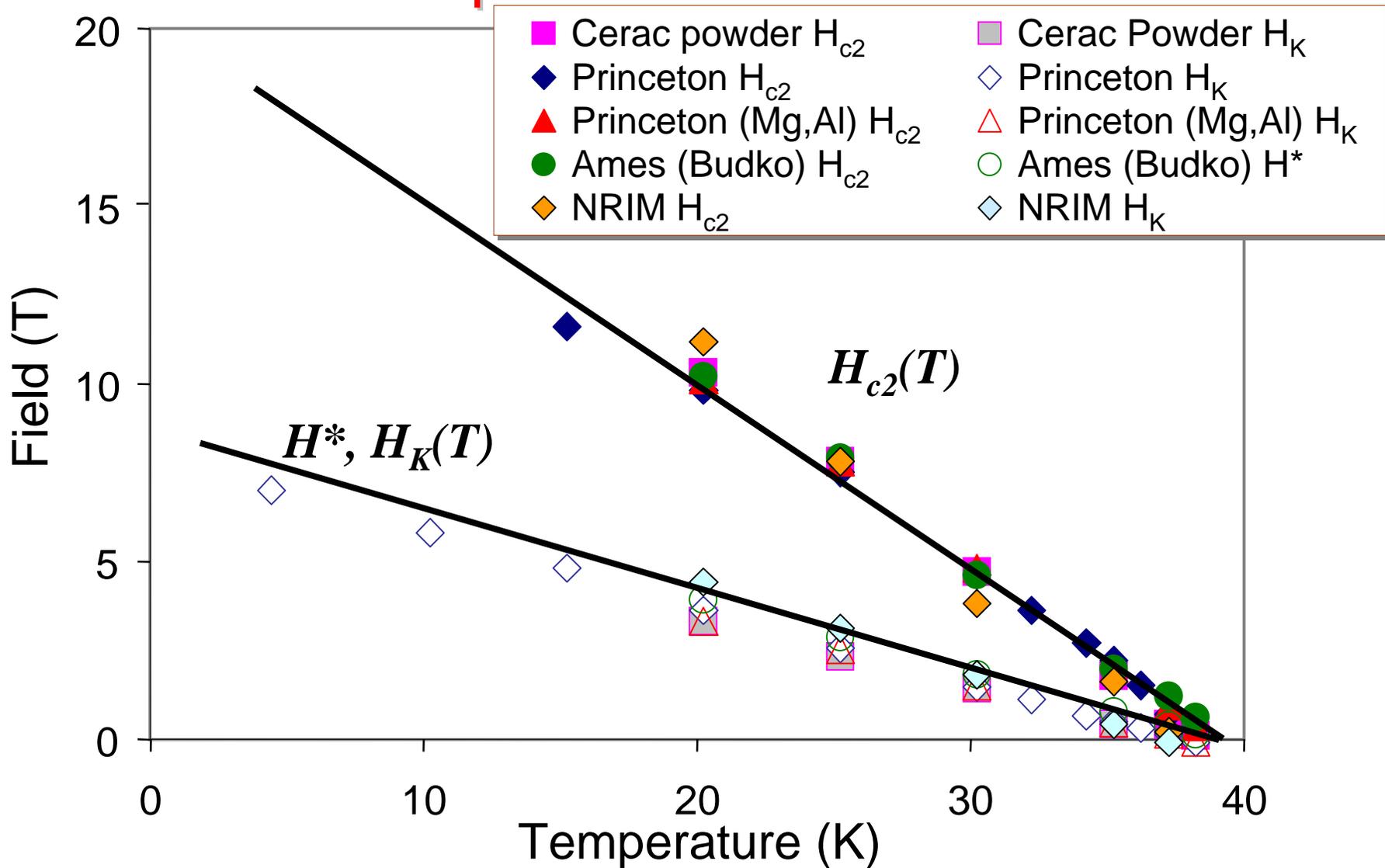


Bulk Samples-II

Strong Flux Pinning and High J_c !



Common Bulk Properties despite big sample differences?



The Irreversibility Field

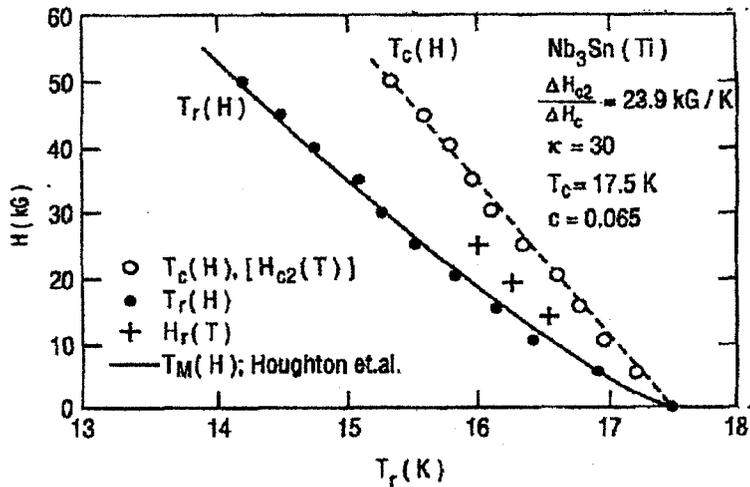


FIG. 3. $T_r(H)$ and $T_c(H)$ [$H_{c2}(T)$] for Nb_3Sn ($\sim 3.5 \mu\text{m}$) and the melting temperature $T_M(H)$ from Eqs. (1) and (2). The crosses are the irreversibility fields $H_r(T)$ as determined from hysteresis measurements at constant temperature.

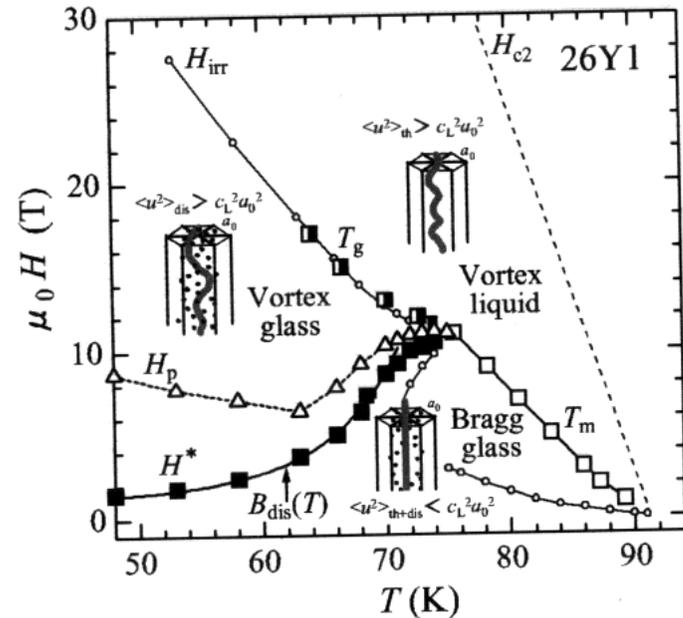


Figure 7. The vortex-matter phase diagram in untwinned $\text{YBa}_2\text{Cu}_3\text{O}_y$. The transition lines $T_m(H)$, $T_g(H)$, and $H^*(T)$ terminate at the critical point and divide into three different phases of the vortex liquid, the vortex glass, and the Bragg glass. The full curve is a fit to the field-driven transition line $B_{\text{dis}}(T)$.

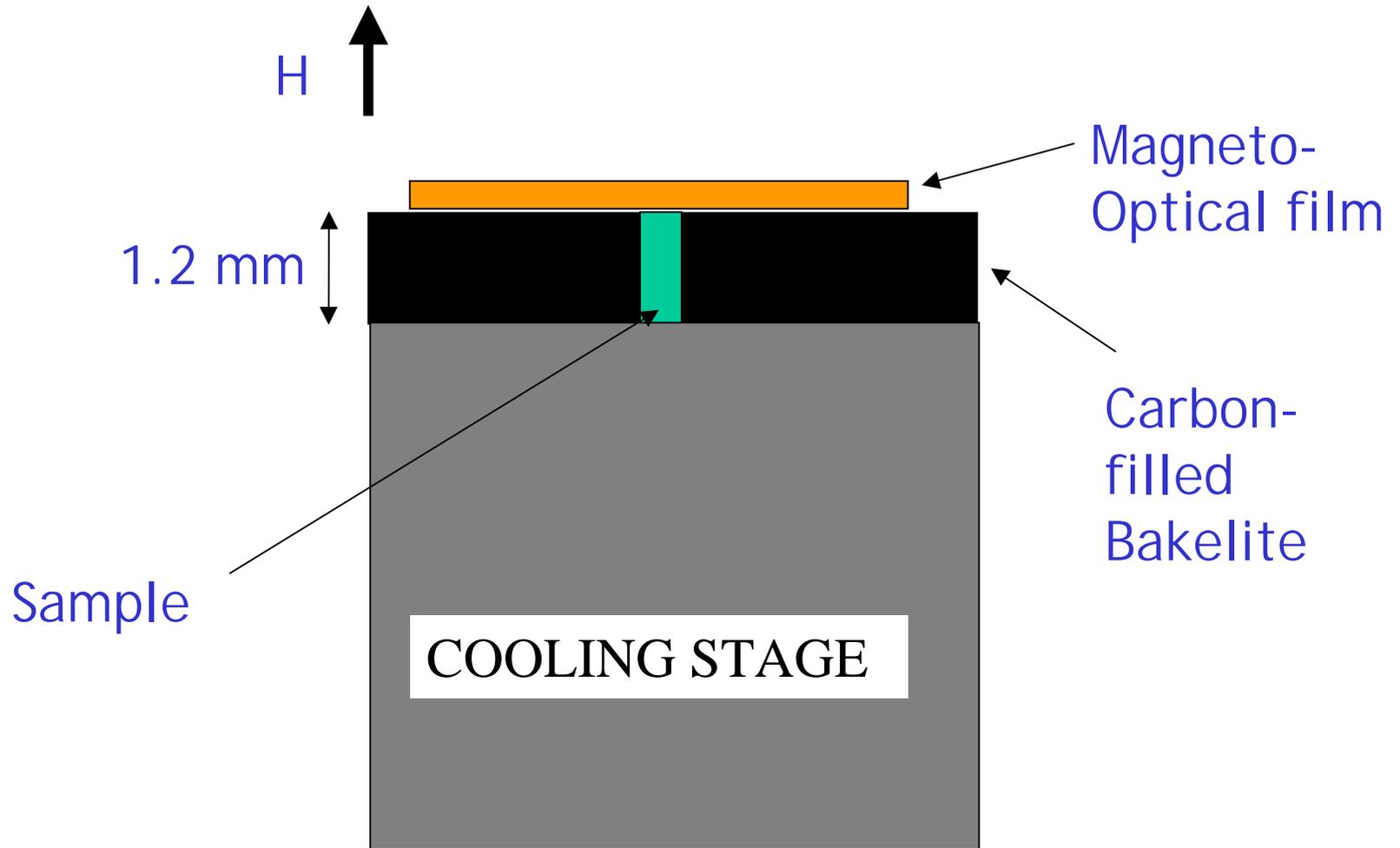
Simple H-T diagram for LTS:

Suenaga, Ghosh, Xu, Welch PRL 66, 1777 (1991)

Complex H-T diagram for HTS

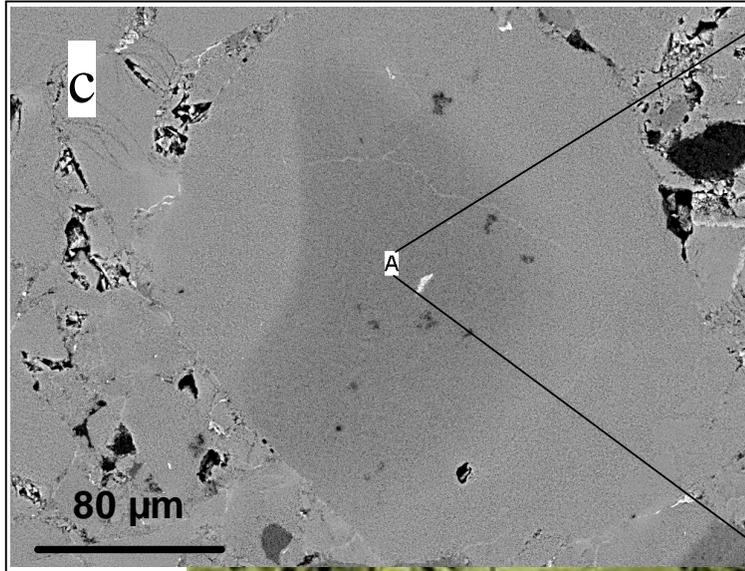
Nishizaki and Kabayashi SuST 13, 1 (2000)

Magneto Optical Studies

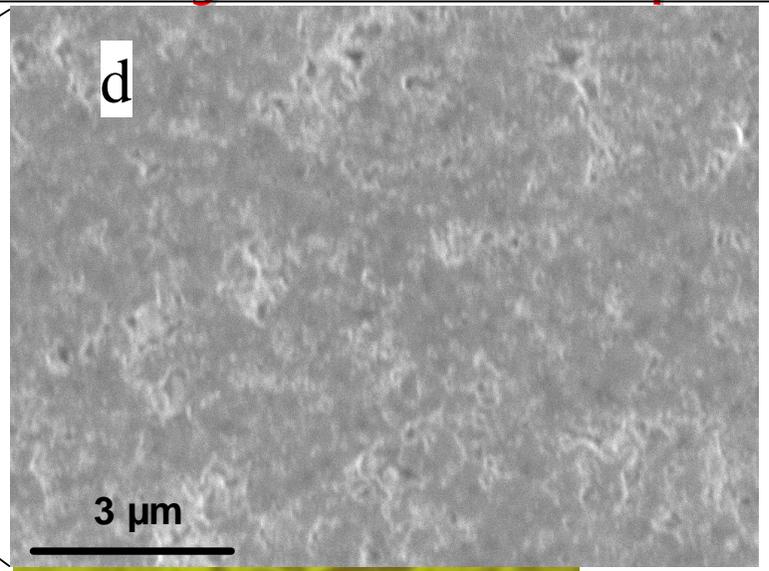


Microstructure of "January Bulk" Samples

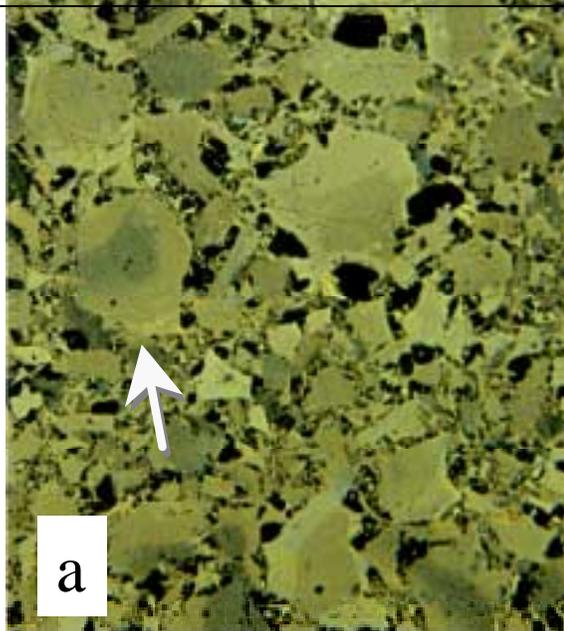
SEM



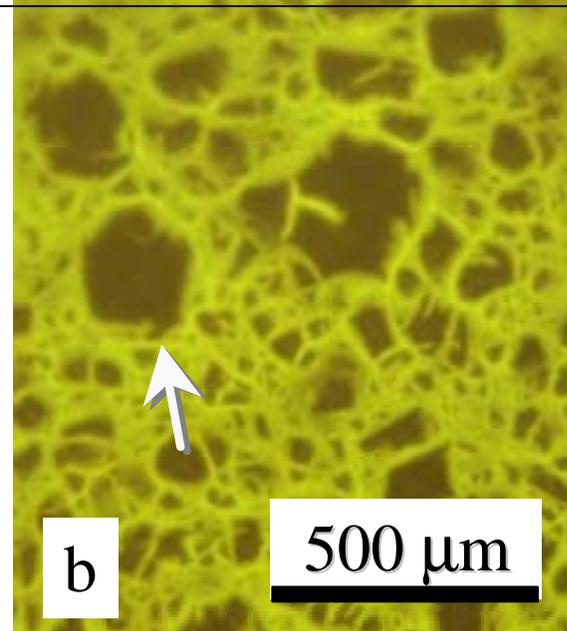
SEM



LM
Image



MO
Image



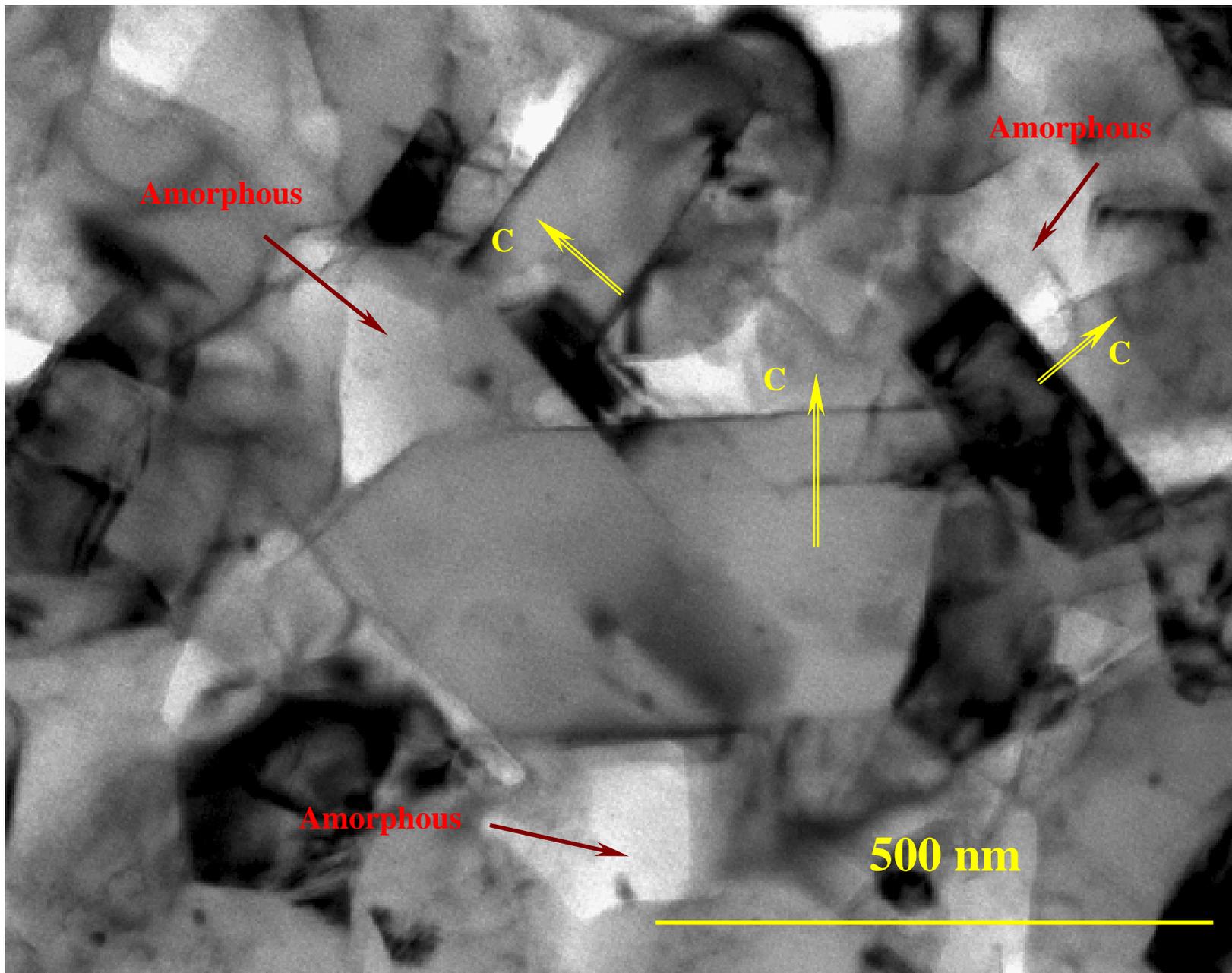
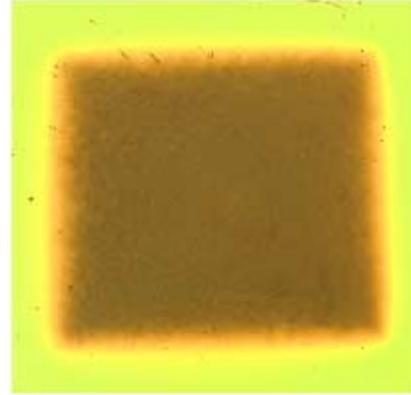
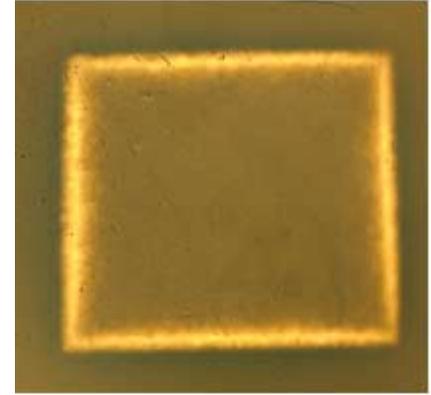


Image of H_z due to screening currents induced in MgB_2

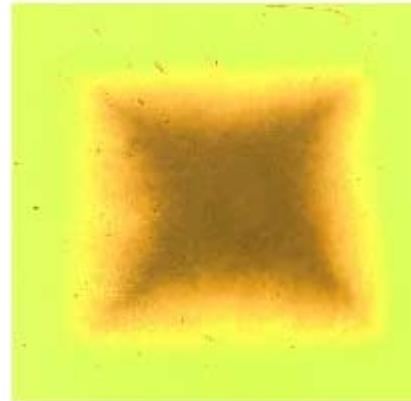
Bulk directly reacted Mg + B samples from Bud'ko and Canfield at Ames



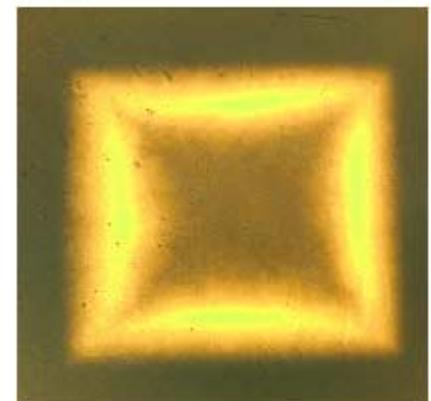
T = 20 K H = 16 mT



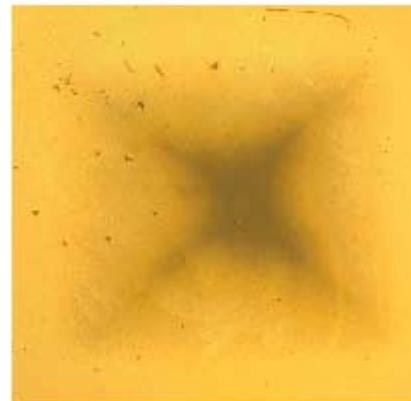
T = 20 K



T = 35 K H = 16 mT

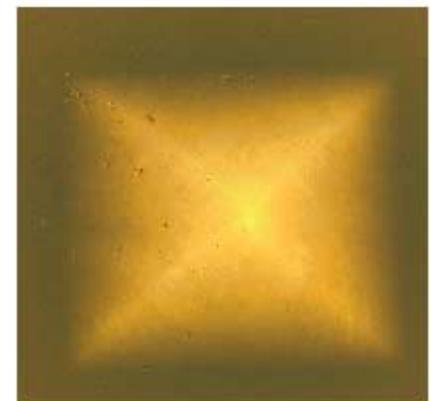


T = 35 K



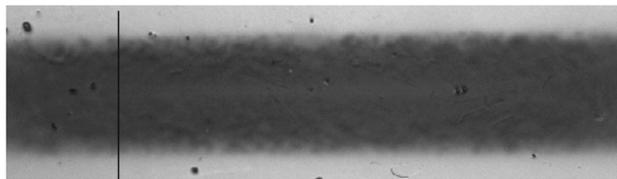
1 mm

T = 40 K H = 4 mT

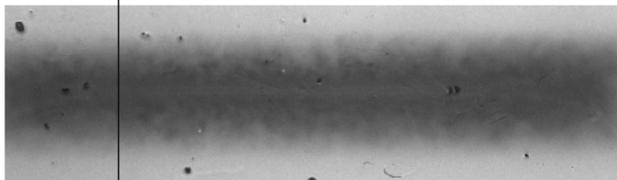


1 mm

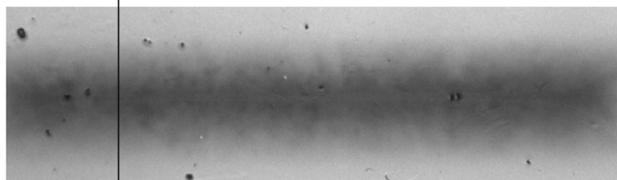
T = 40 K



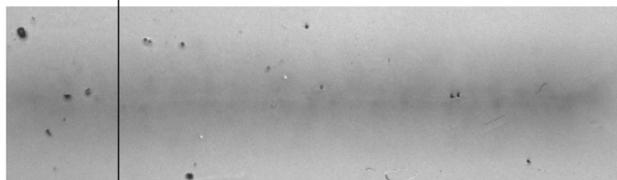
T = 10 K



T = 35 K

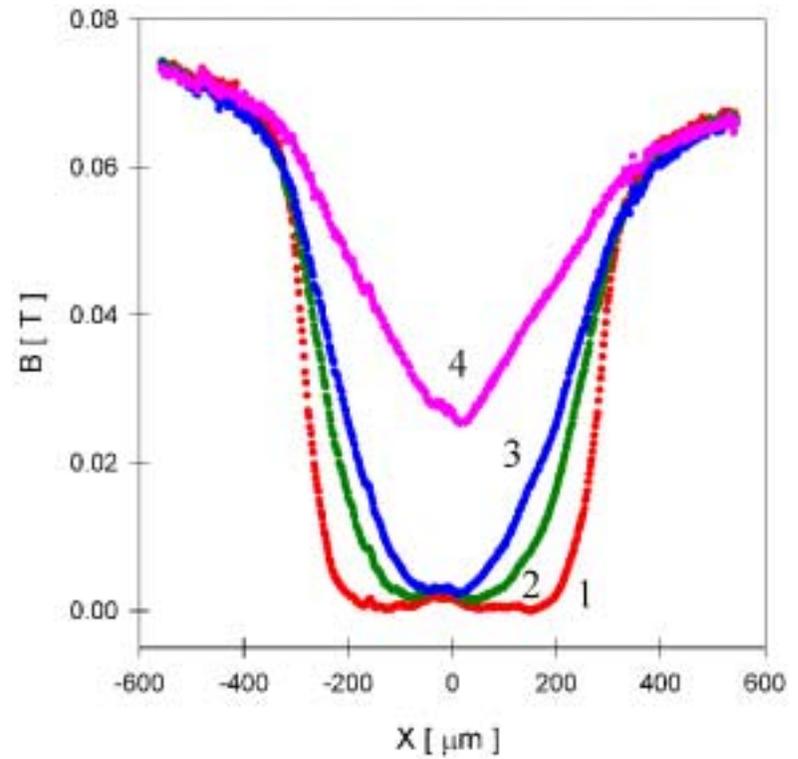


T = 37 K



T = 39 K

0.5 mm



Polyanskii et al.
Submitted

The Answers to our questions

- With a 39K T_c , surely H_{c2} should vanquish Nb_3Sn ?
 - No: peculiar H-T plane diagram
- How would GBs in MgB_2 behave?
 - Apparently benignly!

D. C. Larbalestier, L.D. Cooley, M. Rikel, J. Jiang et al., "**Strongly Linked Current Flow in Polycrystalline Forms of the Superconductor MgB_2** ," *Nature*, **410**: 186-189, 2001.(Published March 8, 2001, submitted February 8)

Mg-reacted B filament

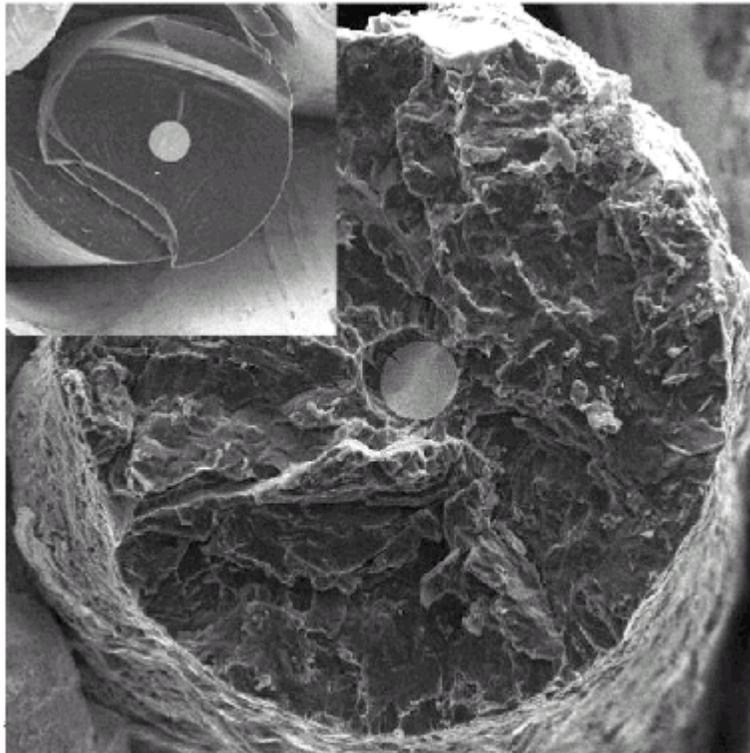


FIG. 2. Electron microscope image of cross section of grown MgB_2 wire. The diameter of the wire is $160 \mu\text{m}$. Inset: electron microscope image of the unreacted boron filament. The diameter of the filament is $100 \mu\text{m}$. For both images the wire/filament was snapped *in situ*. Note that, in both images, a central core of tungsten wire (diam $\approx 15 \mu\text{m}$) can be clearly seen.

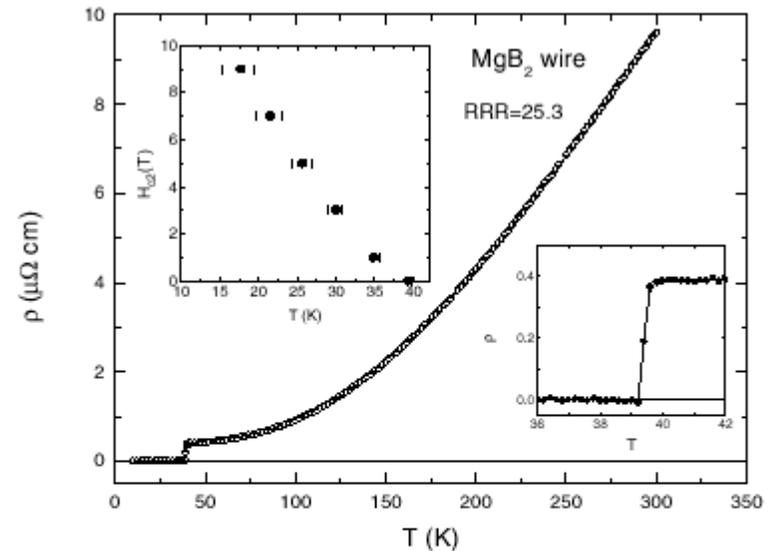


FIG. 3. Temperature-dependent electrical resistivity of MgB_2 wire. Lower inset: expanded view for temperatures near T_c . Upper inset: $H_{c2}(T)$ data inferred from temperature-dependent resistivity data taken in constant applied field upon cooling. The three symbols are for onset, maximum slope, and completion temperatures.

Basic Properties

$\rho(T_c) = 0.4 \mu\Omega \cdot \text{cm}$, $l = 60 \text{ nm}$ (RR)

~ 25 , $v_F = 4.8 \times 10^7 \text{ cm/sec}$, $n = 6.7 \times 10^{22} \text{ e/cm}^3$ (2 ϵ /unit cell)

$\Delta C = 79\text{-}84 \text{ mJ/mol.K}$

$\kappa = 26$

$\lambda(0) = 140 \text{ nm}$, $\xi(0) = 5.6 \text{ nm}$

$H_{c1}(0) \sim 200 \text{ mT}$

$H_{c2}(0) = 15\text{-}16 \text{ T}$

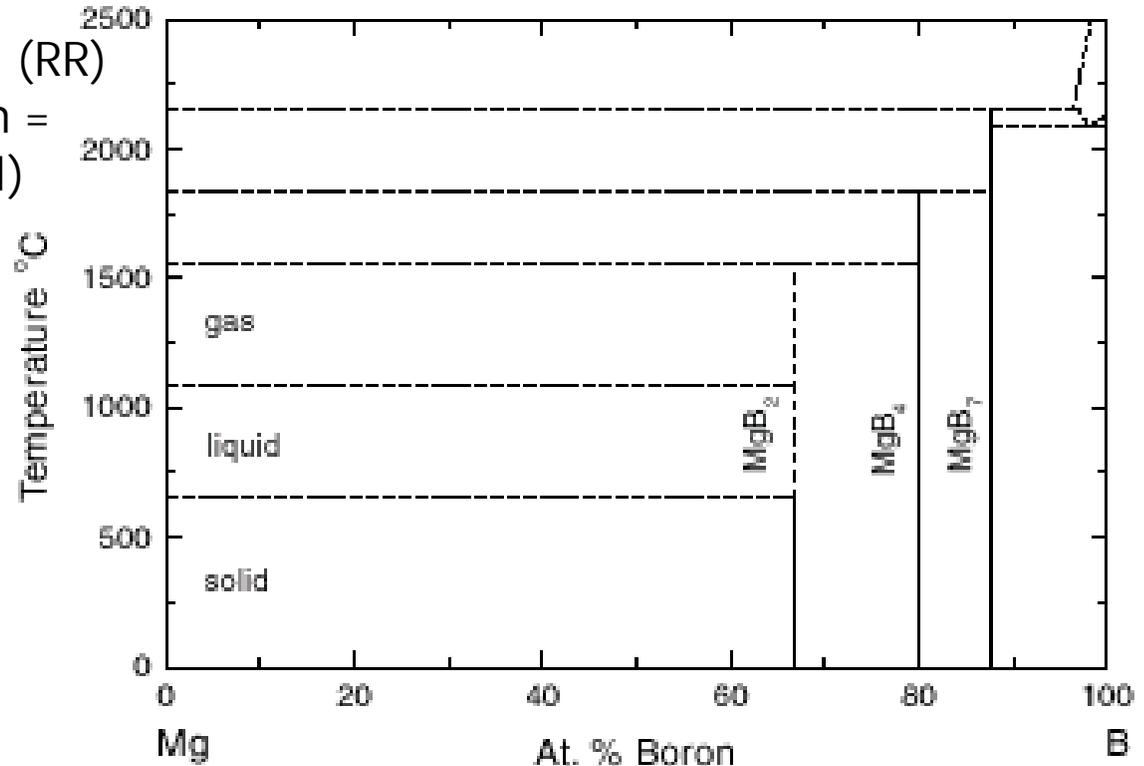


FIG. 1. Proposed, schematic, binary phase diagram for the B-Mg system (after Ref. [9]).

Thin Film Growth (Eom)

PLD at RT, Lambda Physik KrF laser, 4 J/cm² and 10 Hz

(111) oriented single crystal SrTiO₃ vacuum base pressure of 2×10^{-7} Torr

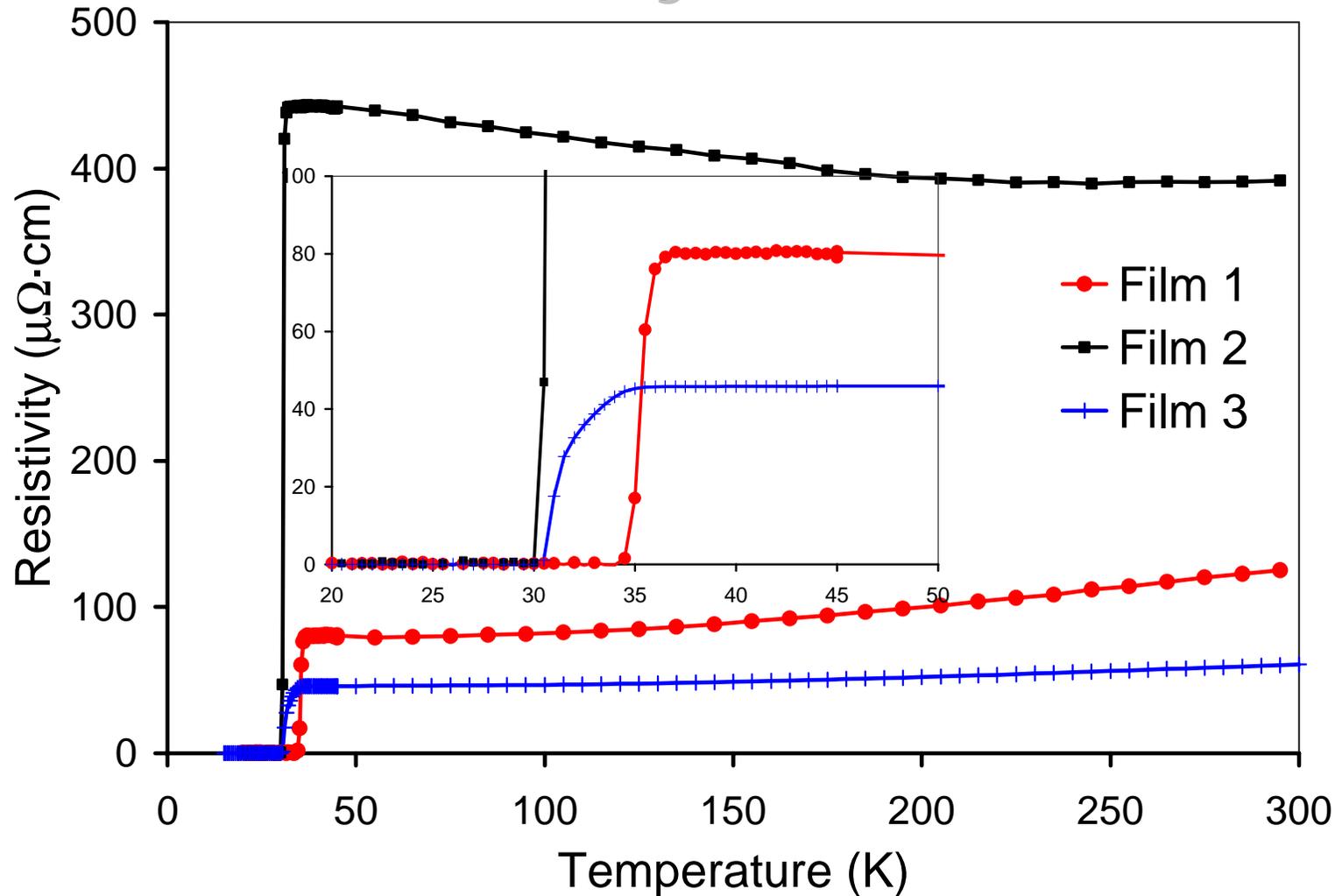
Film 1 annealed in an evacuated niobium tube (0.6 cm diameter \times 5 cm long) at 850 °C for 15 minutes.

Film 2 was annealed in an evacuated quartz tube (1.7 cm diameter \times 15 cm long) at 750 °C for 30 minutes and quenched to room temperature.

Film 3 was annealed in a tantalum envelope inside an evacuated niobium tube at 750 °C for 30 minutes.

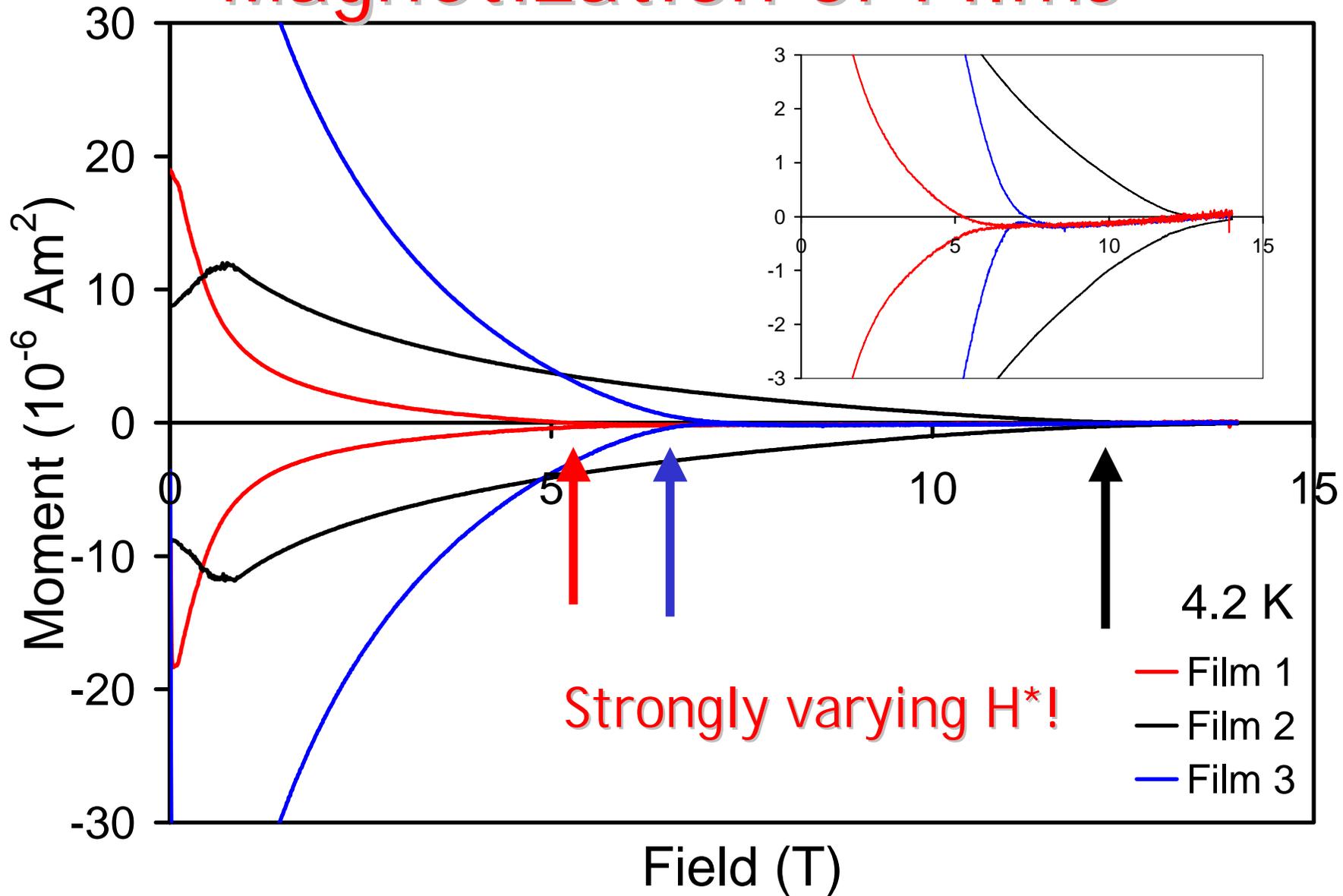
Magnesium pellets were included in each tube to prevent magnesium loss. The film thickness was approximately 5000 Å.

Resistivity of Films

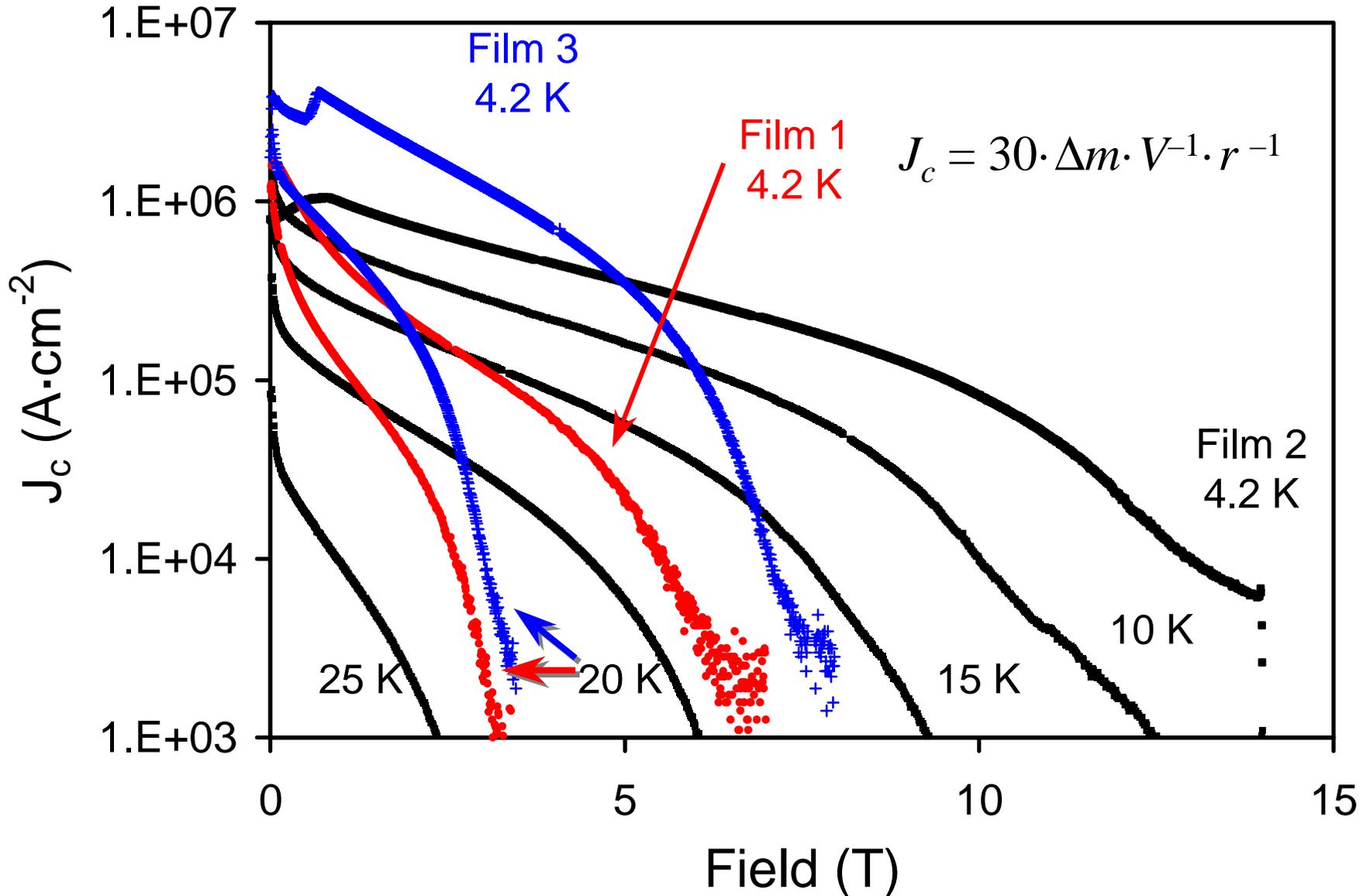


Patnaik, Cai, Cooley, Larbalestier in C-B. Eom et al., “**Very High Critical Current Density and Enhanced Irreversibility Field in Magnesium Diboride Films**” *Nature* 411: 558-560, 2001, (May 31, 2001).

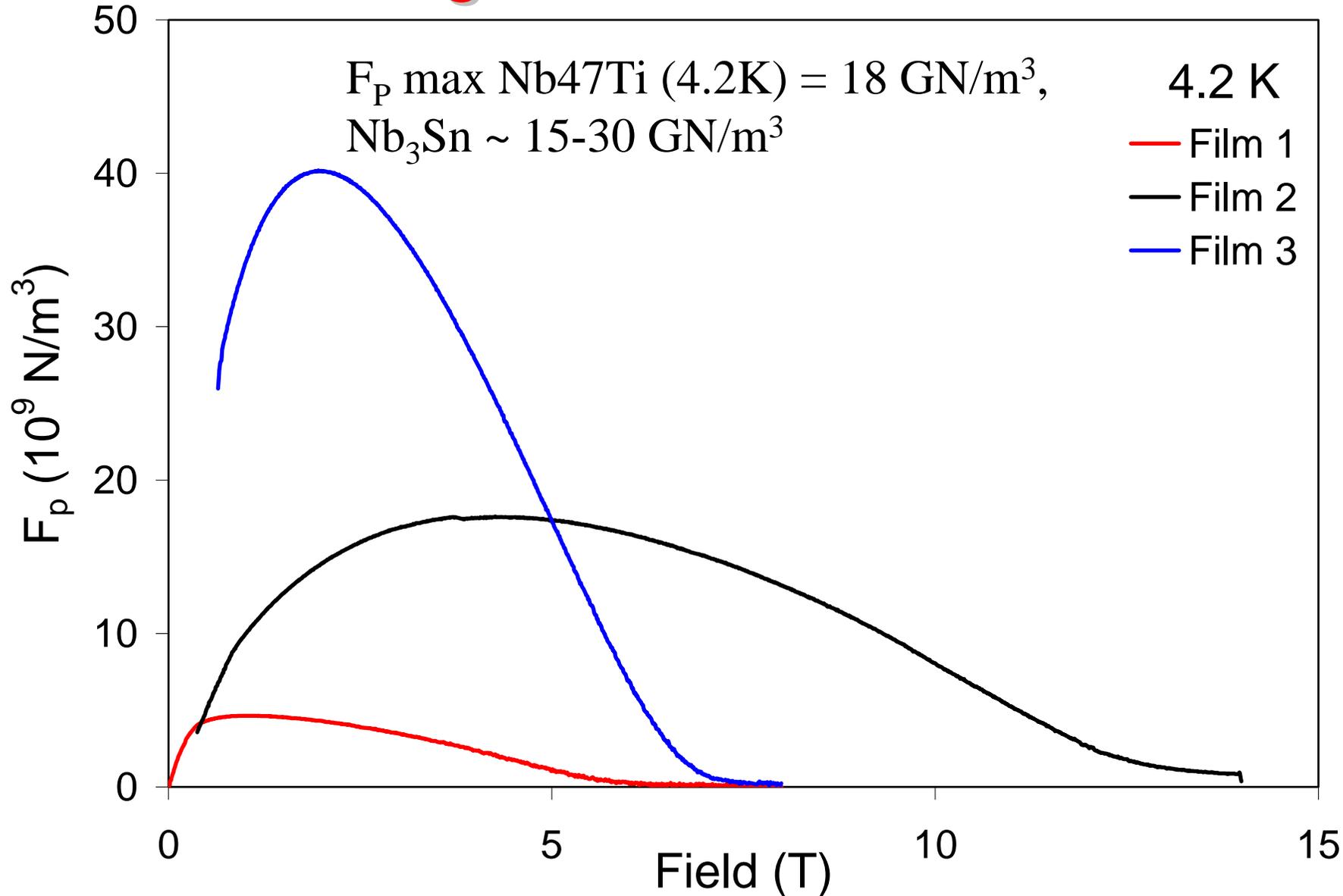
Magnetization of Films



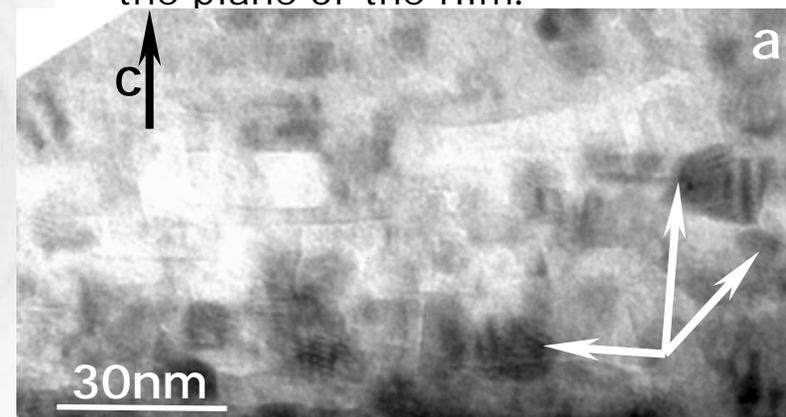
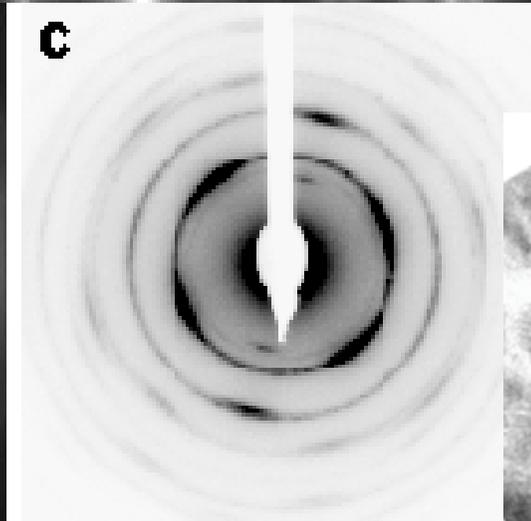
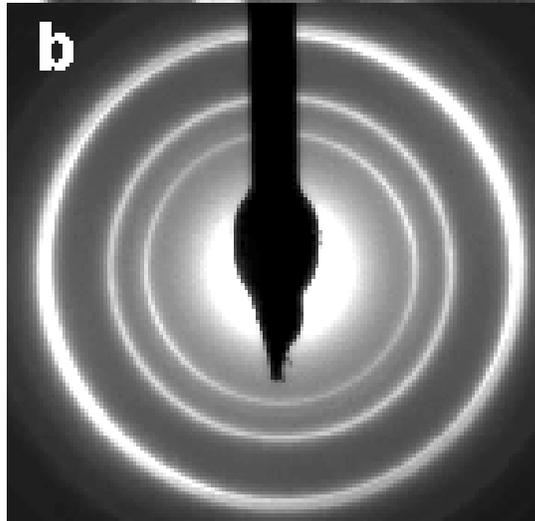
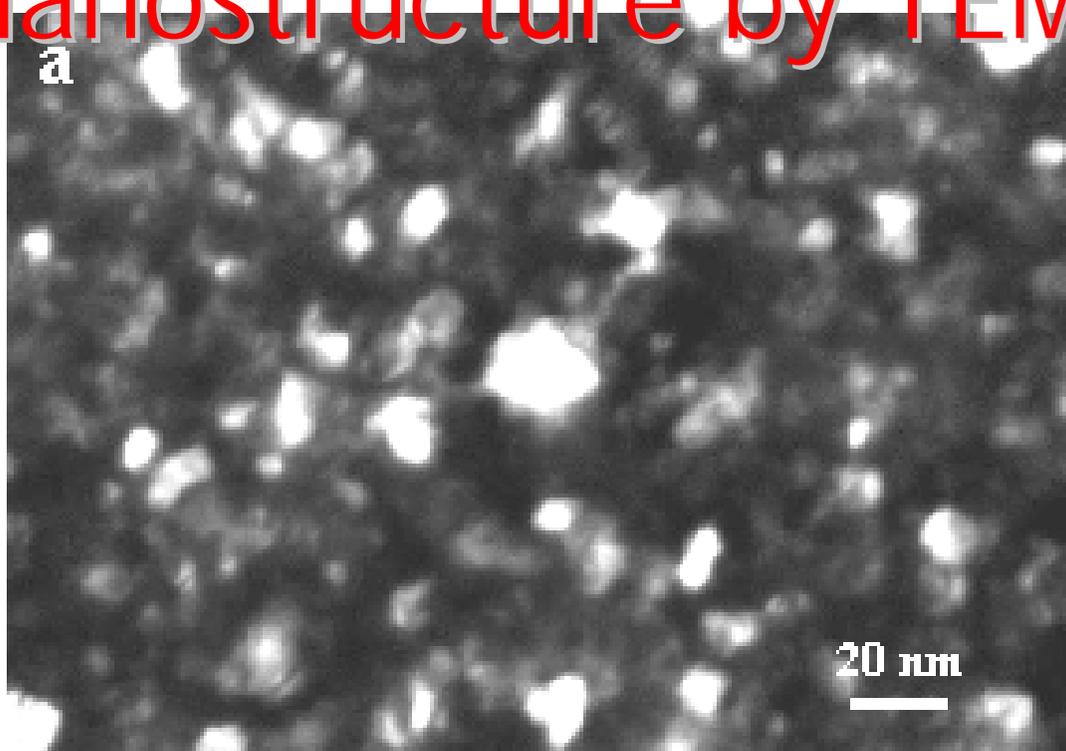
Magnetization Current Density



Pinning Force of Films



Nanostructure by TEM



(a) Dark-field image of a plan-view section of film 2

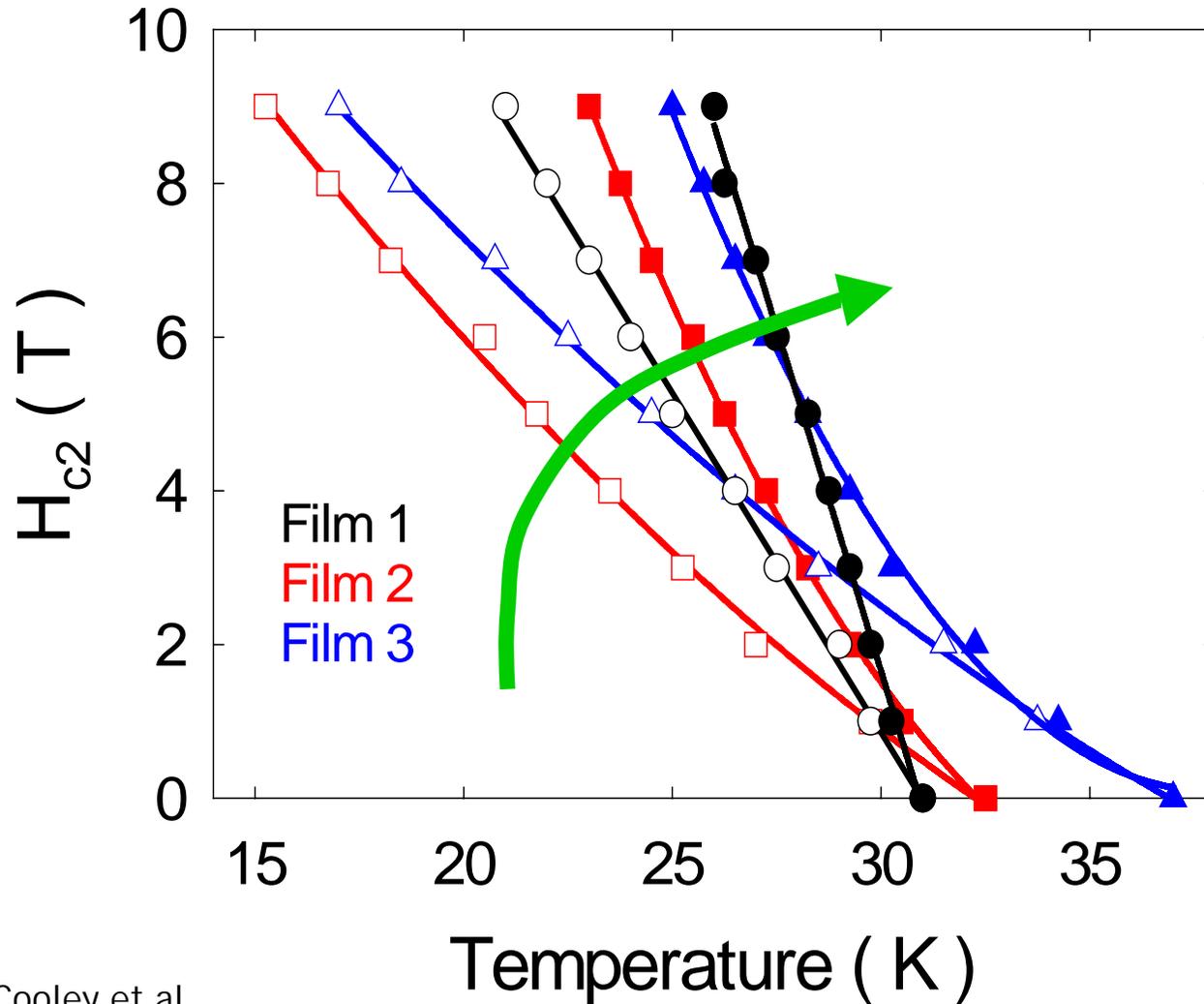
(b) and (c) SAD All rings MgB₂ or MgO.

(b) incident beam parallel to film normal. Complete rings for MgB₂ all (*hk0*) type.

(c) incident beam oriented at an angle to the film normal. Uneven distribution of intensity along all MgB₂ rings.

(00 λ) (i.e. *c*-axis) fiber texture oriented parallel to the film normal with little or no texture in the plane of the film.

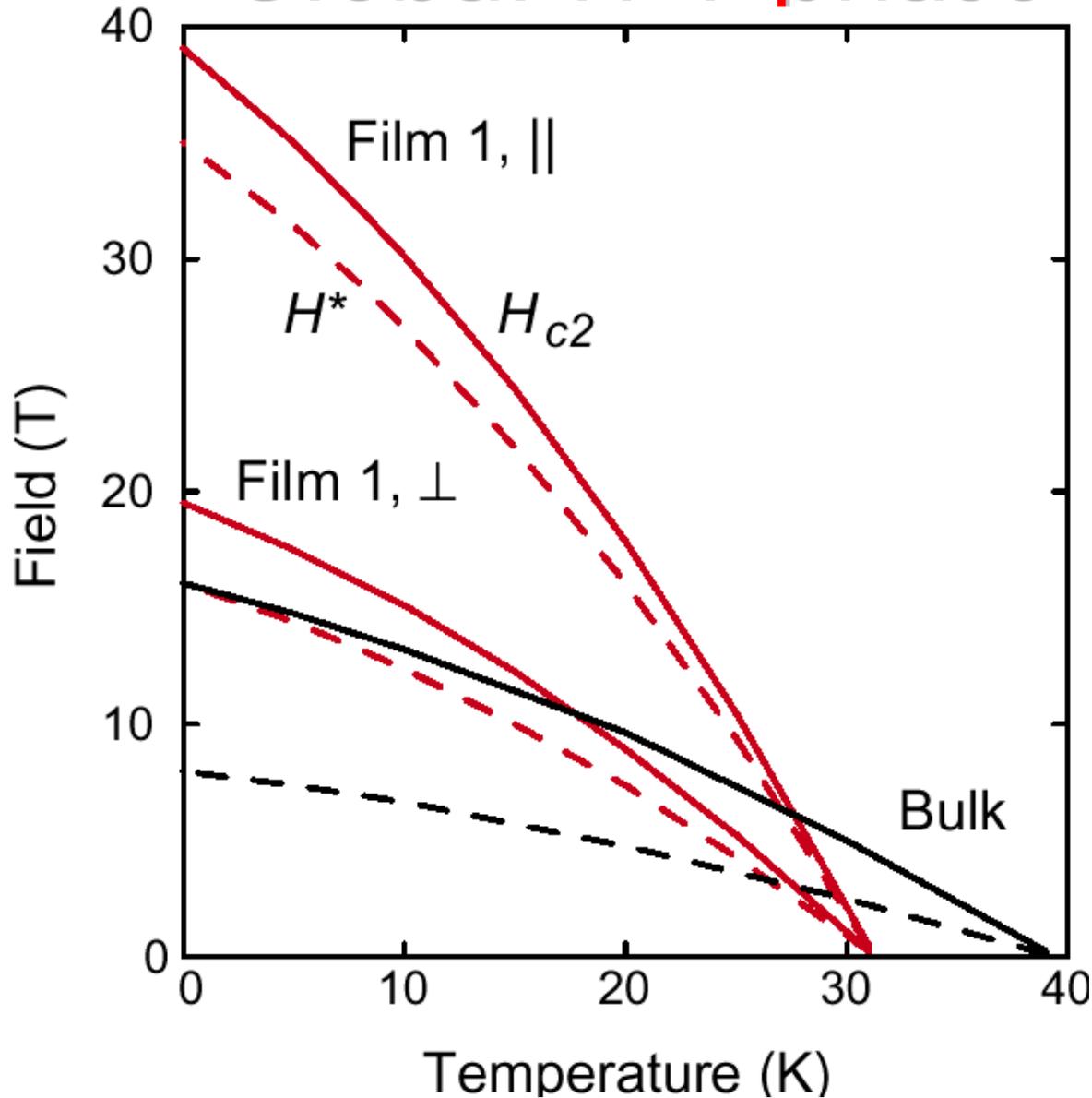
Upper Critical Fields: parallel and perpendicular



Patnaik, Cooley et al.

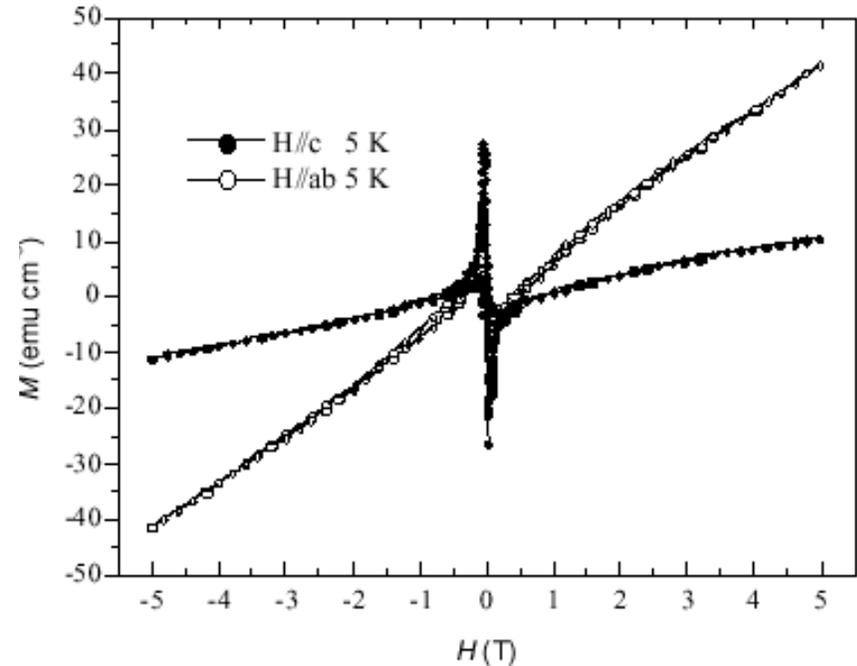
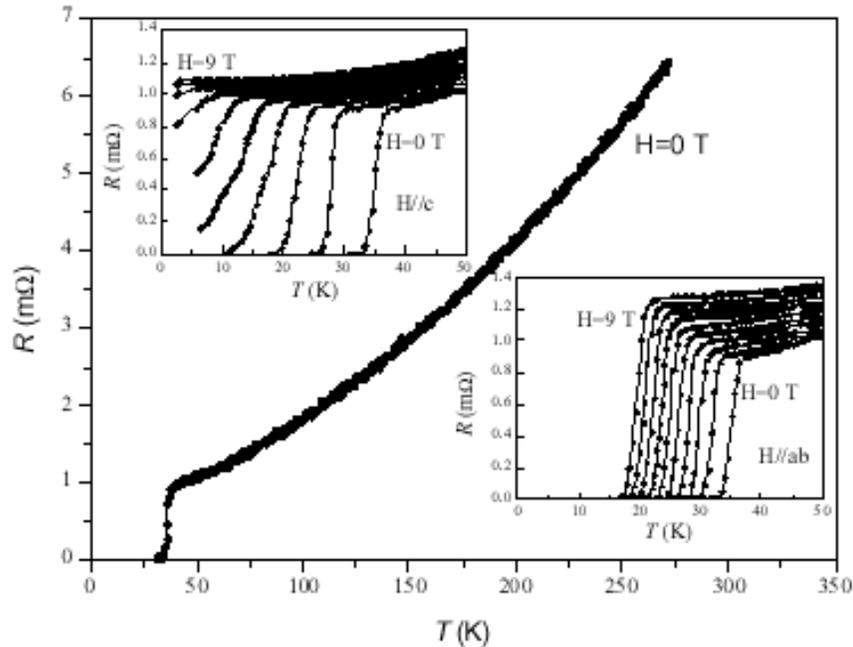
Snowmass July 5, 2001

Global H-T phase diagram



Patnaik, Cooley et al.
“**Electronic Anisotropy, Magnetic Field-Temperature Phase Diagram and their Dependence on Resistivity in c-Axis Oriented MgB₂ Thin Films**”, *Superconductor Science and Technology* **14**, 315-319, (2001). submitted April 30

Single Crystal Results: May 15



Single crystal MgB_2 with anisotropic superconducting properties

M. Xu *†, H. Kitazawa *, Y. Takano *, J. Ye *, K. Nishida *, H. Abe *, A. Matsushita * and G. Kido * Cond Mat May 15, 2001

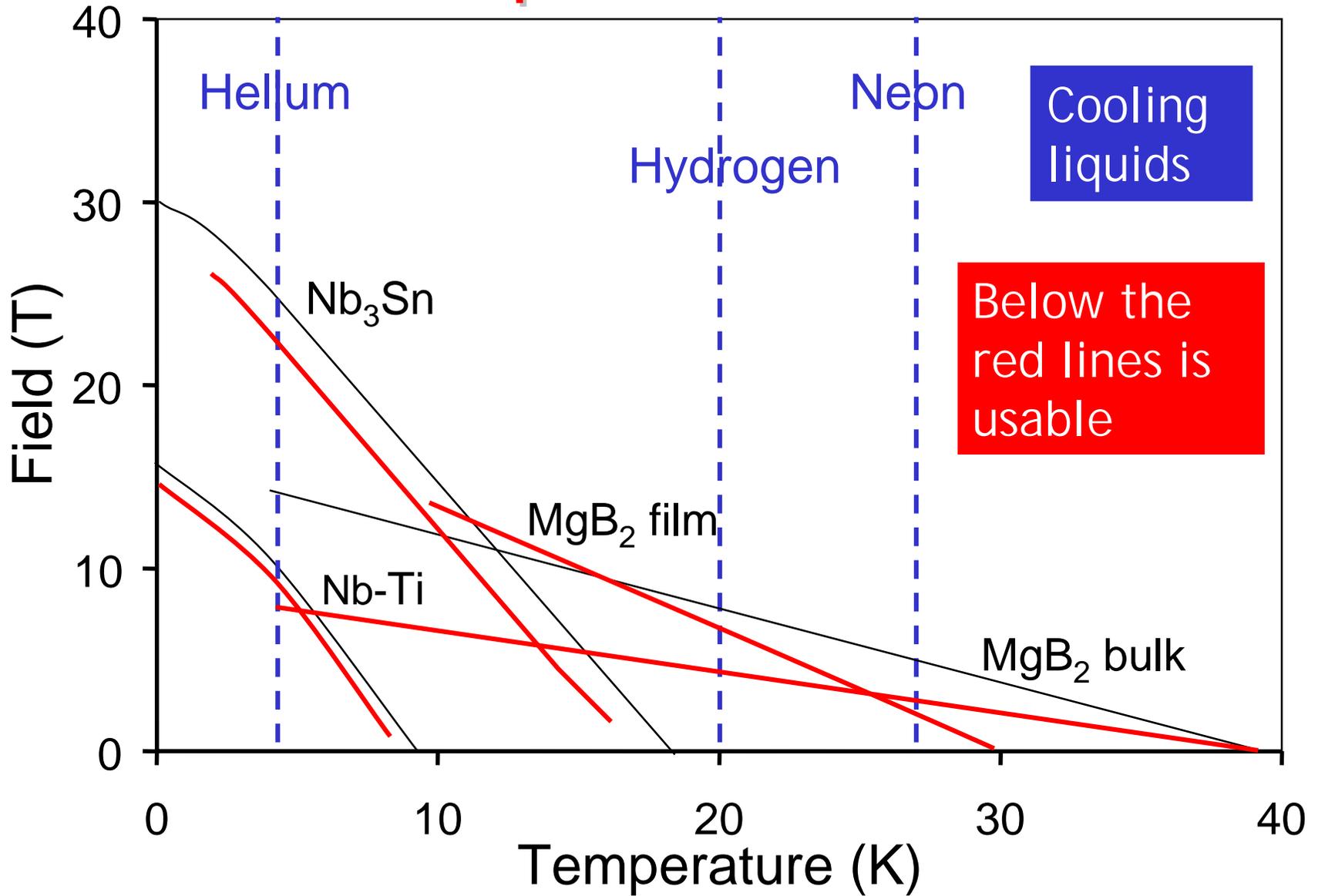
H-T plane performance

- Pure MgB₂ appears to be in the clean limit (mfp ~60 nm > coherence length ~5 nm)
 - H_{c2} can be increased by alloying (like adding Ti to Nb - H_{c2} increases from 0.3 to 11T)
 - alloying with something (O?) is increasing H_{c2} and H*
 - first proof of this is in UW thin films
- Wires have been made by Powder-in-Tube process (as used for PIT BSCCO)

Summary

- Grain boundaries are NOT obstacles to current flow
 - even in 10 nm grain sized films
- MgB₂ is anisotropic
 - H_{c2} and mass anisotropy 1.8-2.0
 - **Texture matters** because perpendicular H_{c2} is half that of parallel
- MgB₂ can be alloyed!
 - resistivity raised by about 100x
 - T_c reduced to ~30K
 - H_{c2}(0) doubled to 39T, as opposed to 17-18T for clean bulk

H*-T plane for LTS



Nb₃Sn: The issues

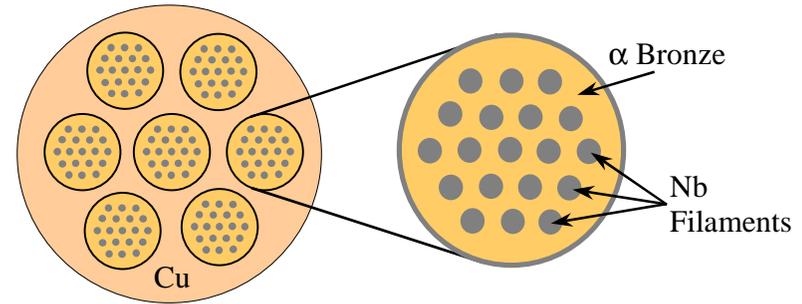
- Mainline choice for VLHC magnets
- Proven in thousands of lab magnets to >20T
- Proven in world's largest pulsed magnet
- Limits not well understood either from J_c, fabrication, or cost/performance point of view
- LBNL 14 T dipole achieved May 2001

Focus of Present HEP Program

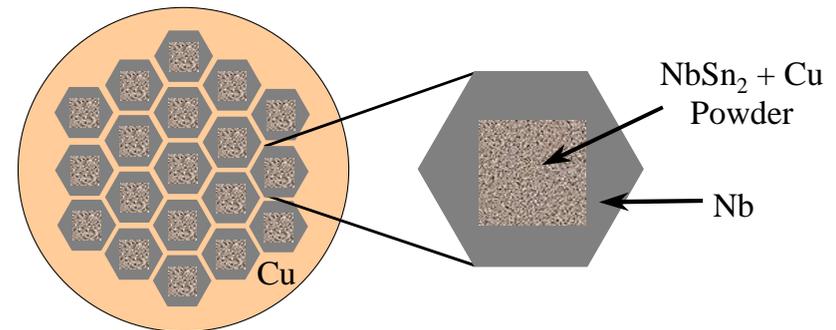
- >10 T Nb₃Sn dipoles
 - LBNL, BNL, FNAL programs
- Aggressive Industry R&D Program for conductor
 - J_c (non-copper, 12 T, 4.2 K): 3000 A/mm²
 - Effective filament size: 40 μm or less
 - Piece length: > 10 km at 0.3-1.0 mm dia.
 - Wire cost: Less than \$1.50/kA-m (12 T, 4.2 K)
- Understanding the limits of Nb₃Sn
 - Amount of Nb₃Sn that can be made from Cu-Sn-Nb package
 - quality of the Nb₃Sn and its ability to carry current

Conductor Types

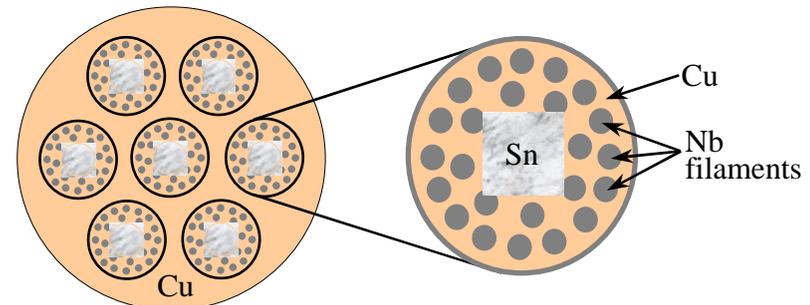
- Bronze route
 - Cu dissolves 9at.%Sn maximum while remaining single phase and ductile
 - Cu7.5at.%Sn used for years
 - NMR conductors see advantage, even for additional mechanical complexity in going to 8-8.5%Sn
- Powder in Tube method places NbSn₂ inside Nb tubes
 - least wasteful of all methods
- Internal Sn conductors use Sn, Cu and Nb as the elements
 - in principle much less Cu is present
 - components are more ductile than bronze



Bronze Process

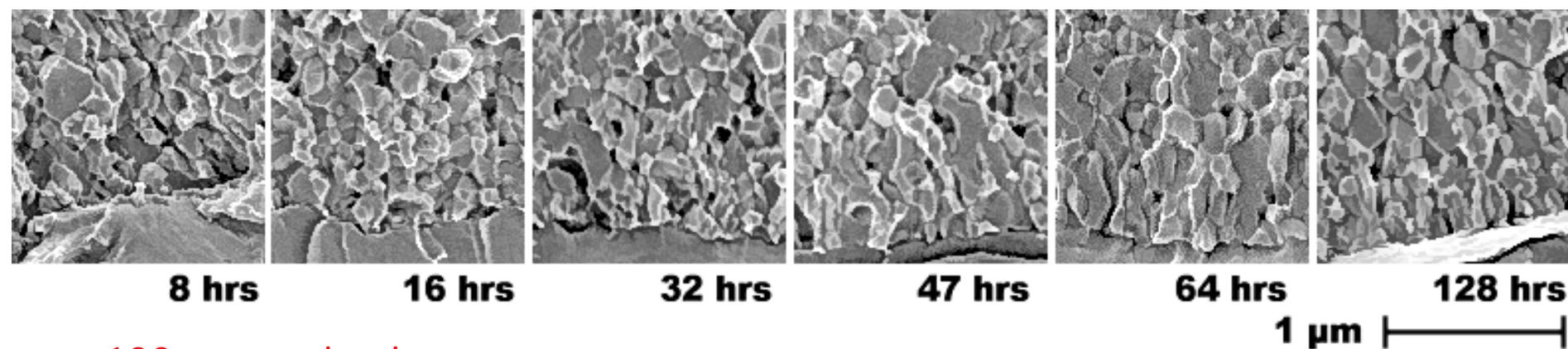
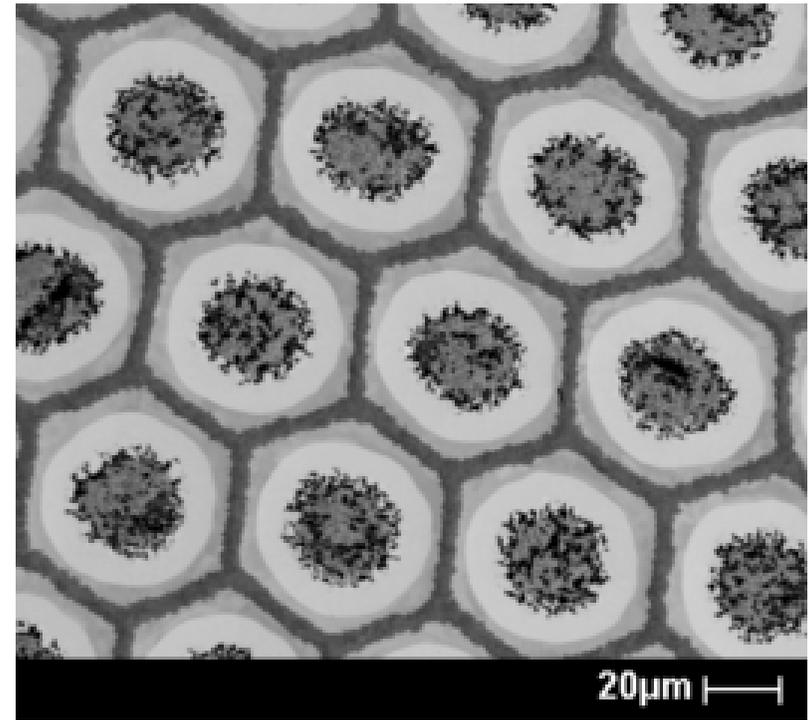
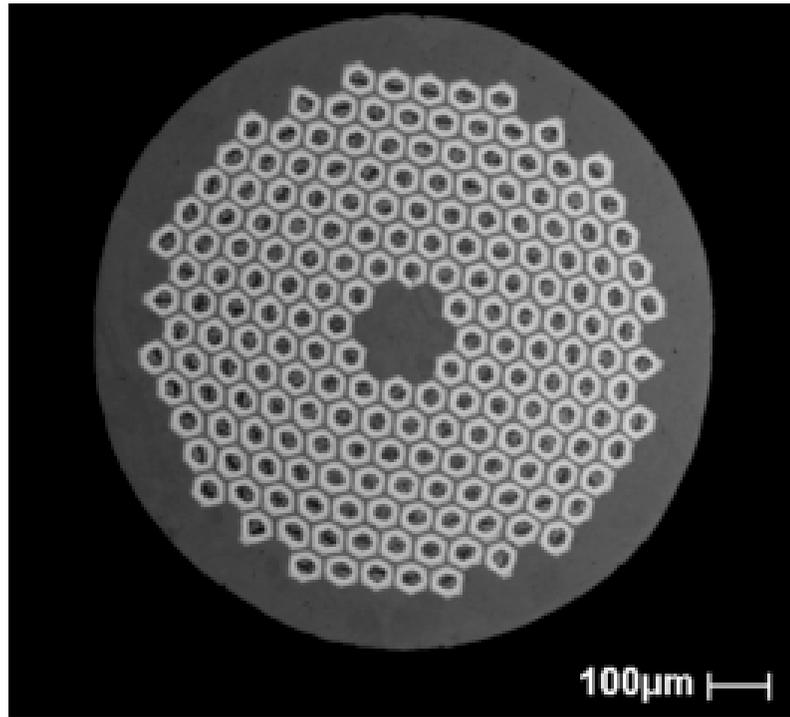


Powder-in-tube Process



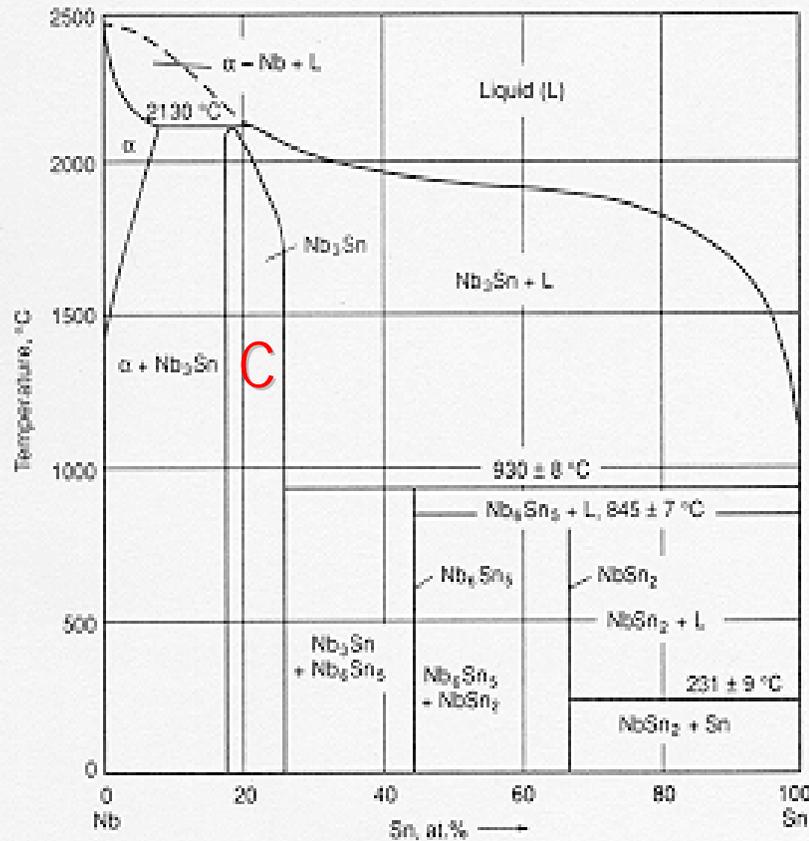
Internal Sn Process

Reaction of Cu-Nb-Sn to A15

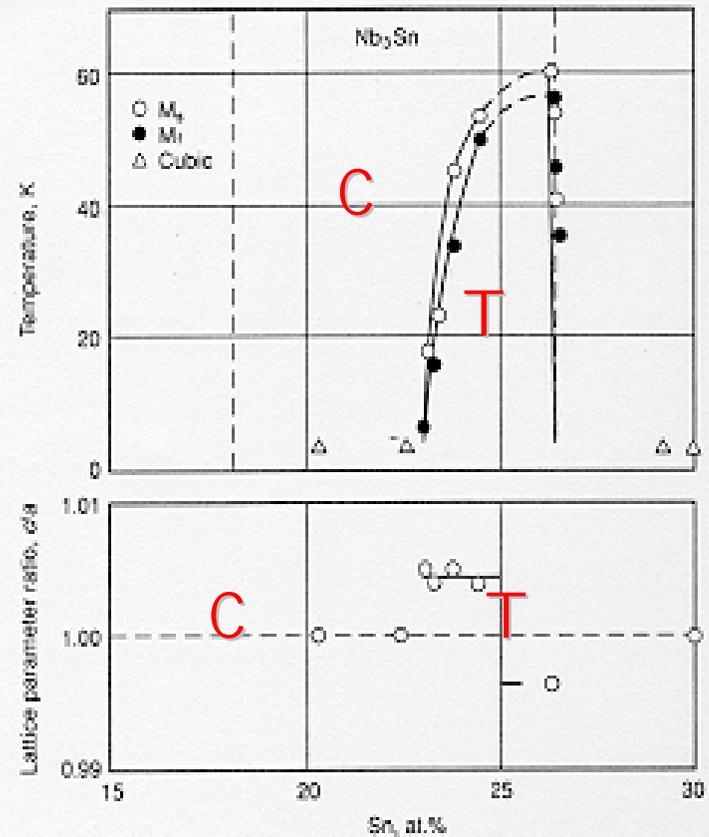


~100 nm grain size

Phase Relations in Nb-Sn System



(a)

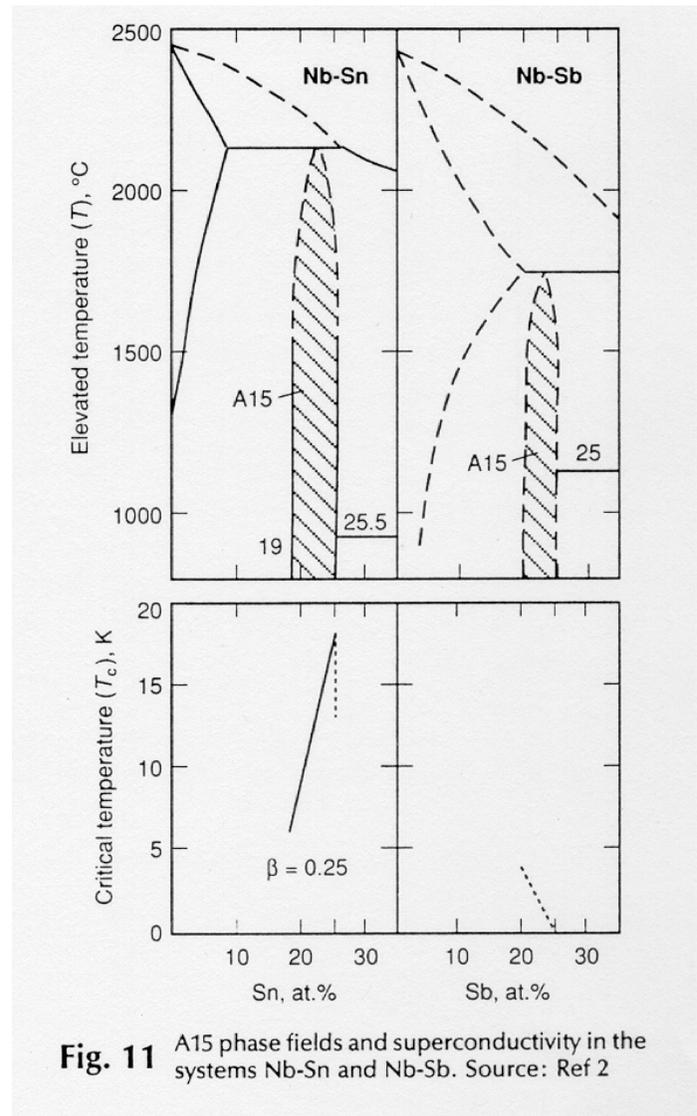


(b)

Fig. 12 Niobium-tin binary phase diagram. (a) Elevated temperatures. (b) Subzero temperatures. M_s , temperature at which martensite formation finishes during cooling; M_f , temperature at which martensite starts to form on cooling. Sources: Ref 11, 12

C: Cubic A15, higher H_{c2} phase, T: Tetragonal A15 phase

A15 Phase is not always Nb₃Sn



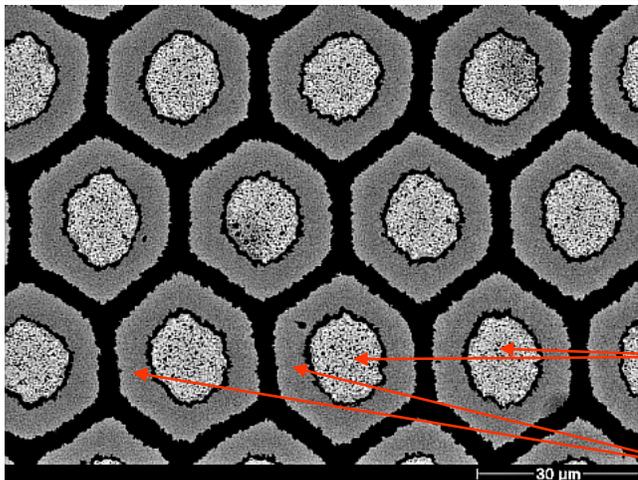
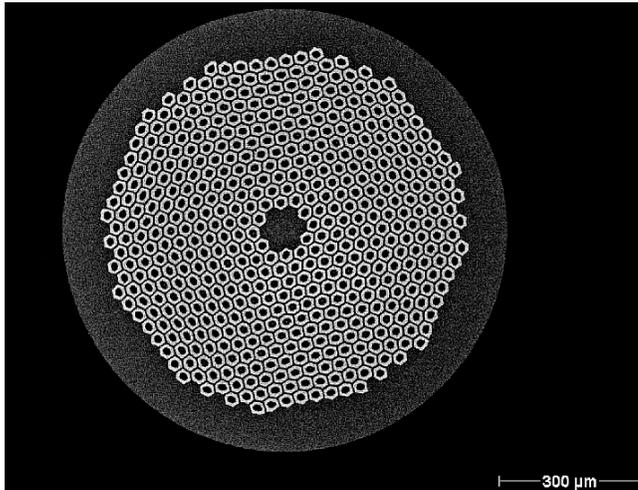
T_c decreases by about 2K/at.%Sn

Rate of decrease of H_{c2} not well known but certainly large too

Data of Devantay et al. (Flukiger (1980))

Fig. 11 A15 phase fields and superconductivity in the systems Nb-Sn and Nb-Sb. Source: Ref 2

Powder-In-Tube Strand



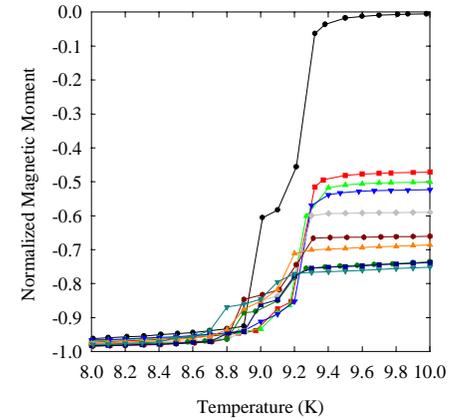
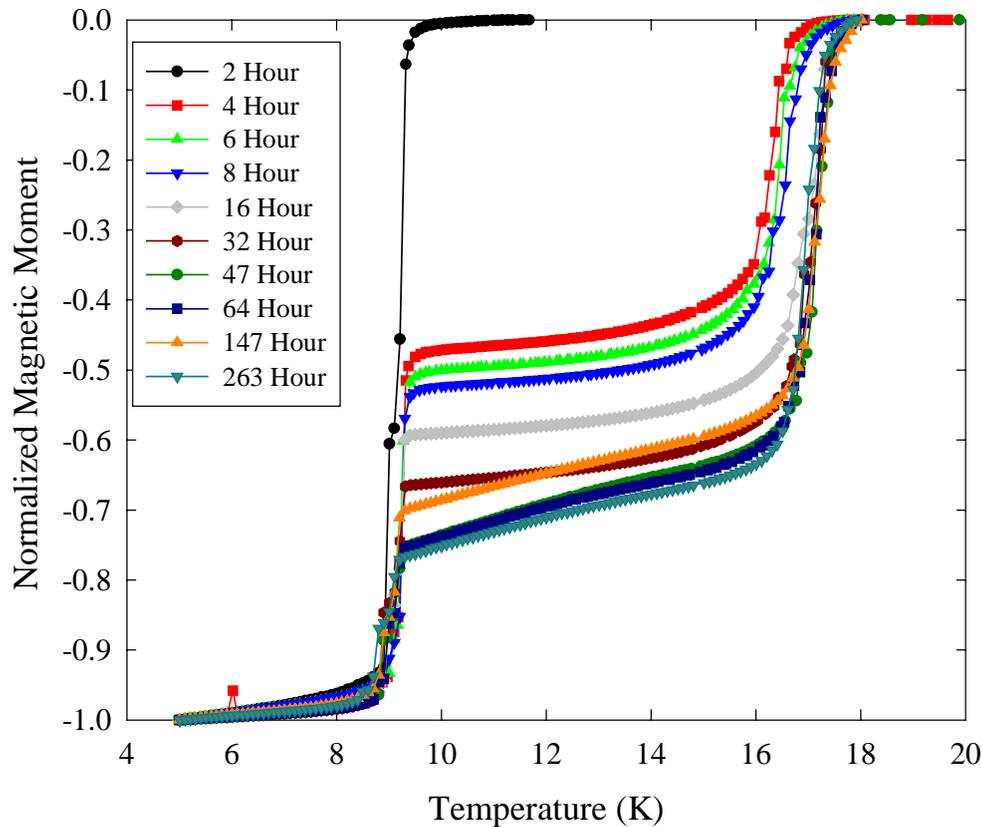
- High Sn concentration available from NbSn
- Efficient Non-Cu package with no “wasted” Cu.
- High Field Nb(Ta) based strand now available.

NbSn₂ powder + Cu powder core

Nb tubes

Inductive T_c Measurements

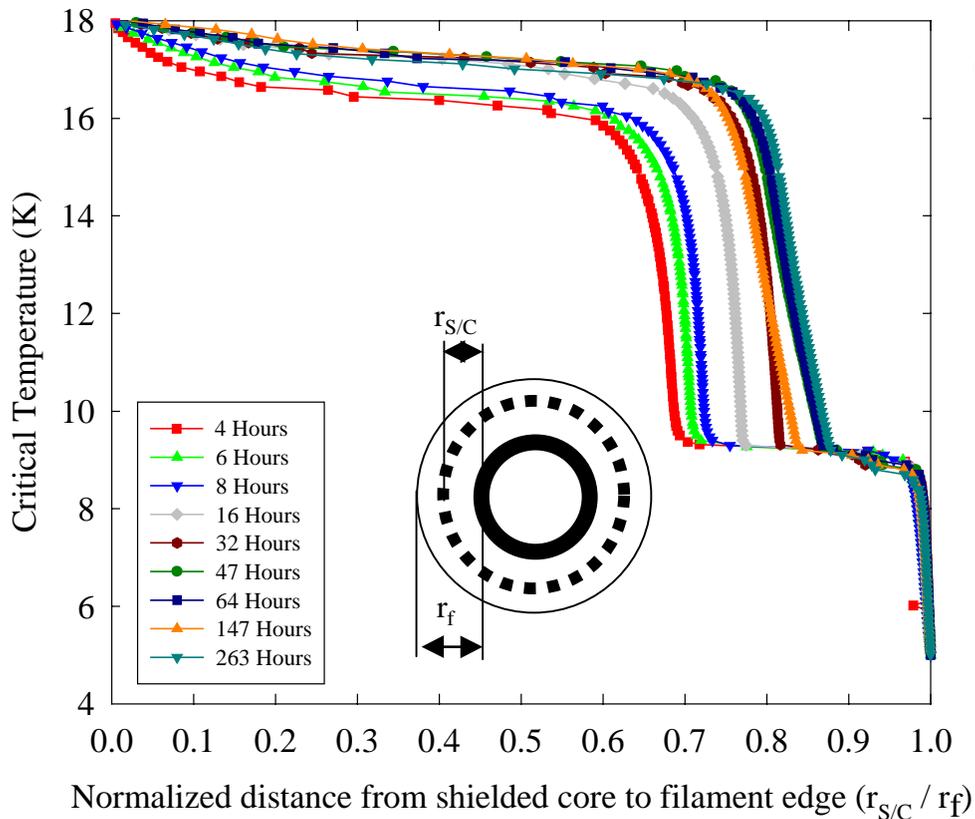
675 °C HT T_c Results



- Steady rise in Nb₃Sn T_c with HT time.
- “Nb transition” decreases and broadens with HT time.
- Nb₃Sn layer thickening.

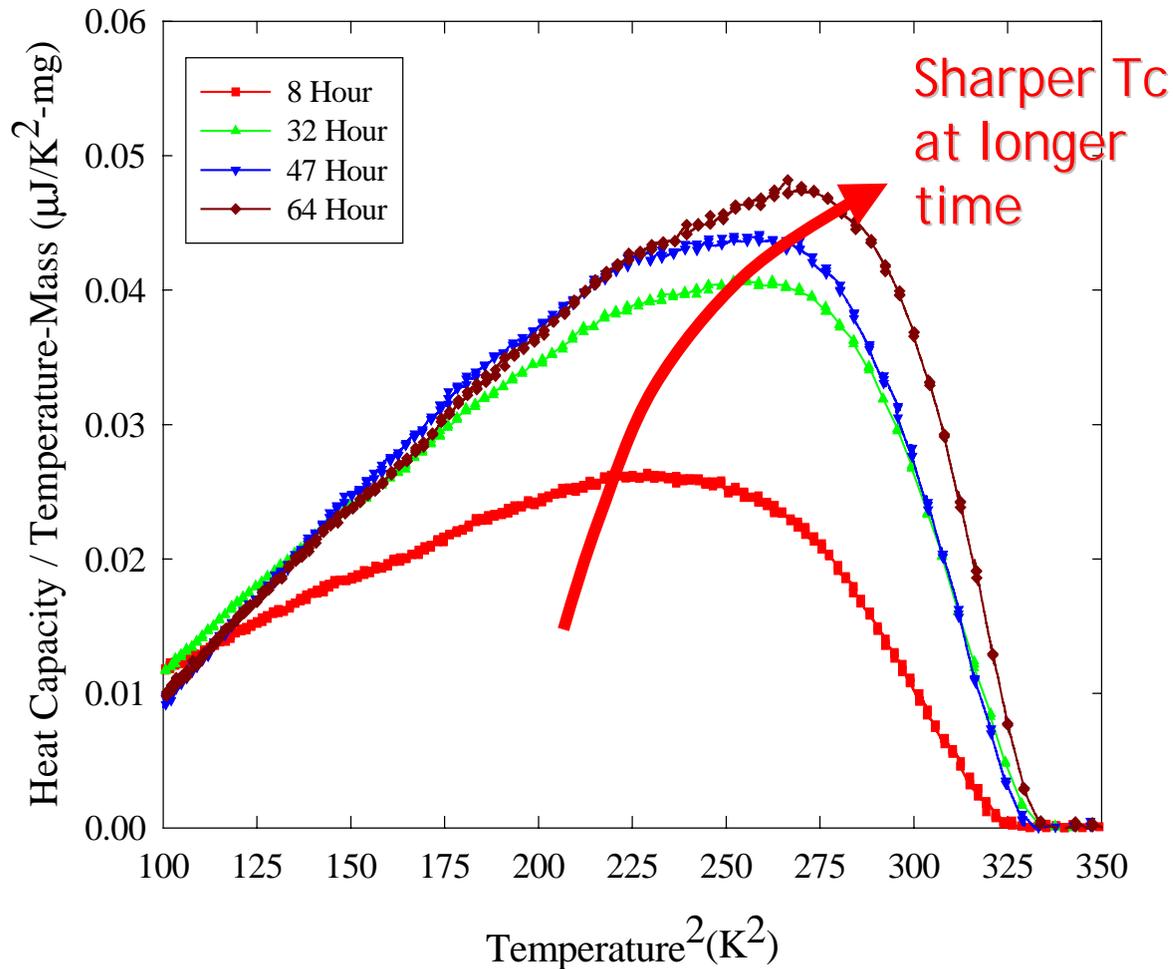
C. D. Hawes, P. J. Lee, and D. C. Larbalestier, "Measurement of the Critical Temperature Transition and Composition Gradient in Powder-In-Tube Nb₃Sn Composite Wire," IEEE Transactions on Applied Superconductivity, 10(1): 988-991, 2000.

Inductive T_c Profiles



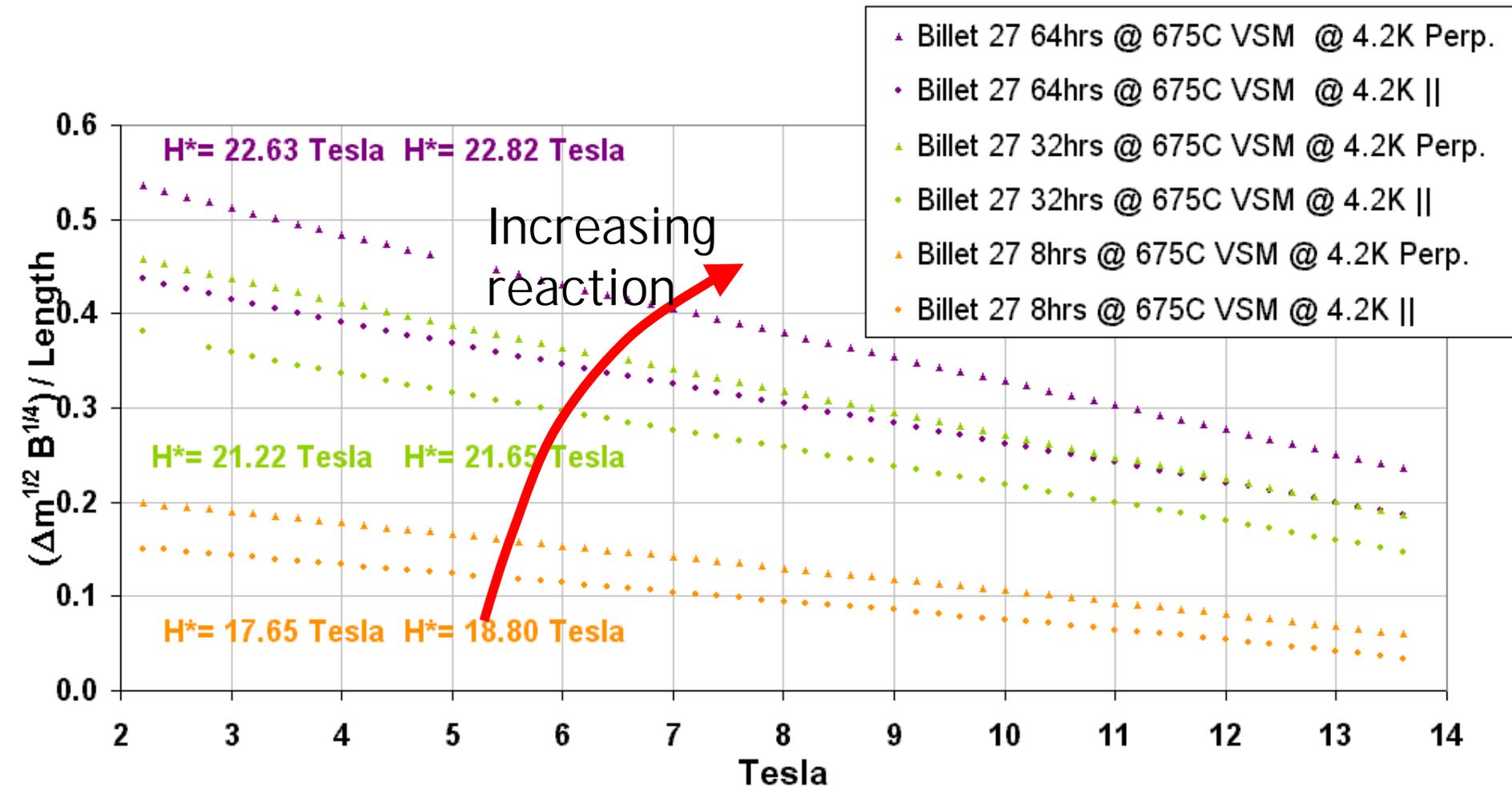
- 4-8 hour plots have a steeper slope.
- Layer growth visible.
- After 32 hours growth rate slows.
- Tail appears at ~ 14 K after 47 hour HT.

Heat Capacity Results

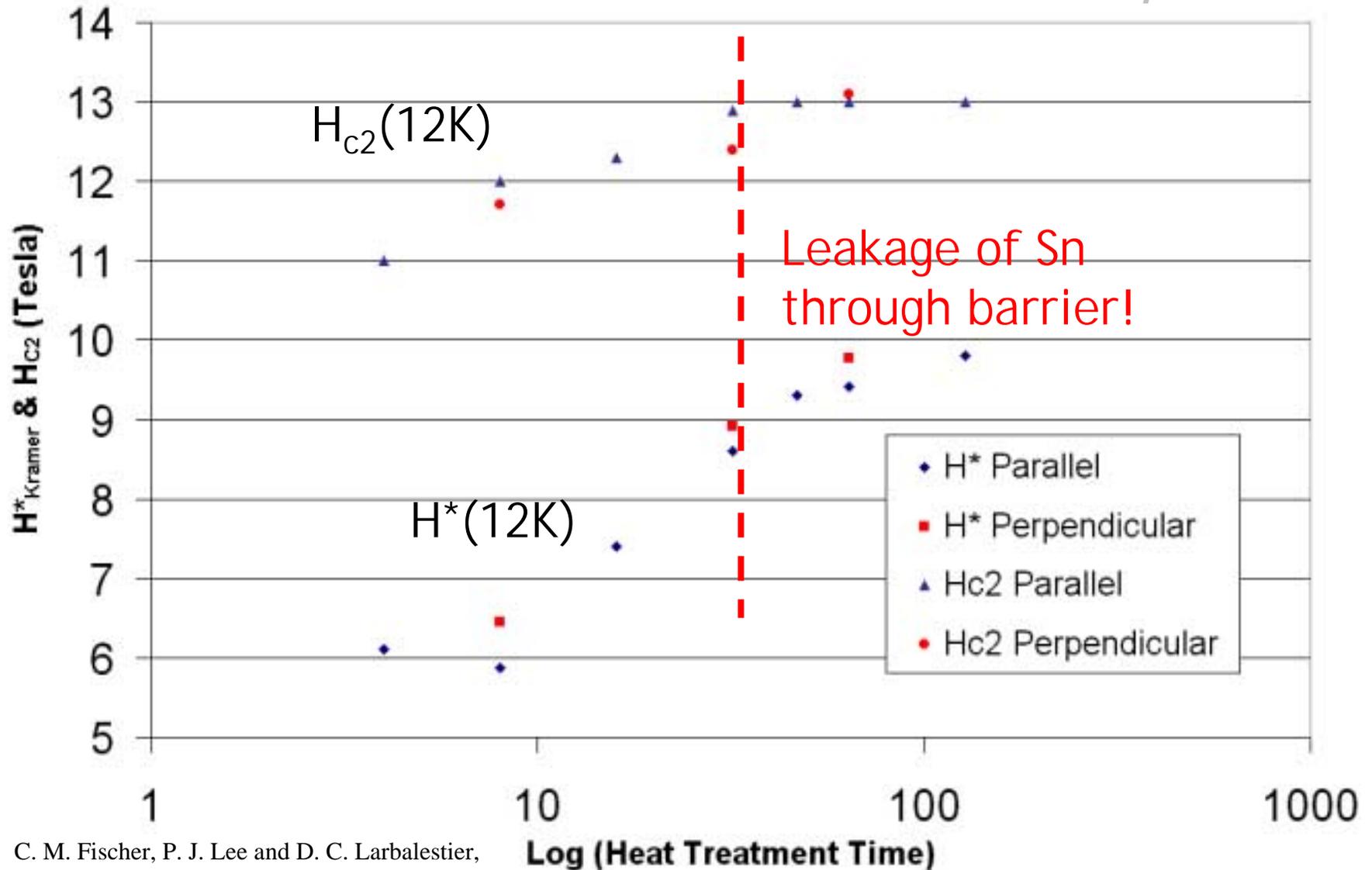


Increasing HT time at 675 C results in:
Sharper transition.
Increase in max T_c .
Increase in the amount of Nb_3Sn .

Influence of Reaction on H^*



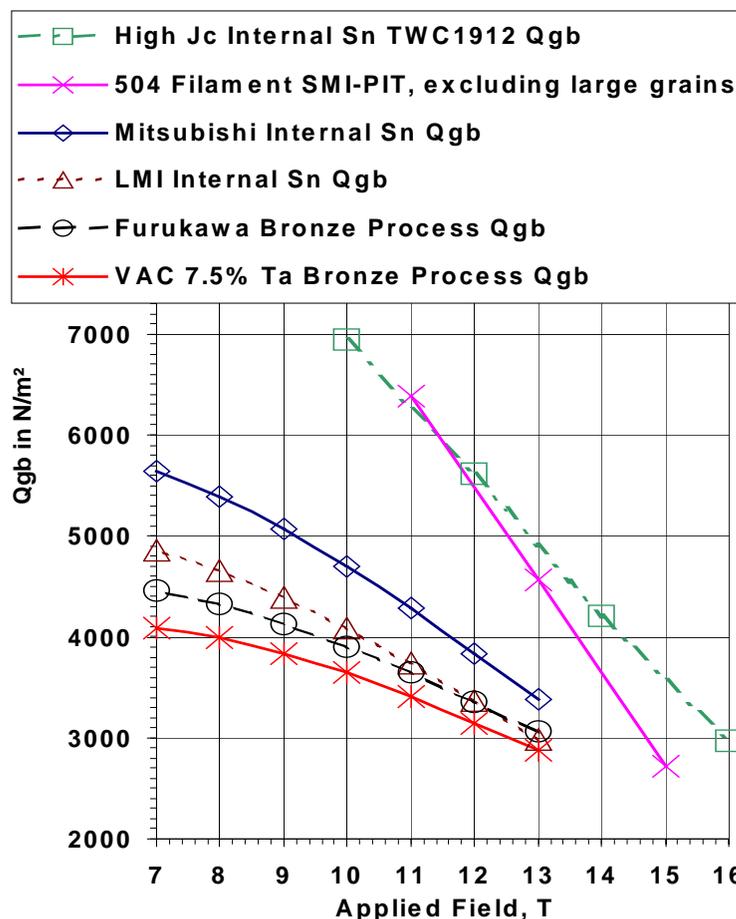
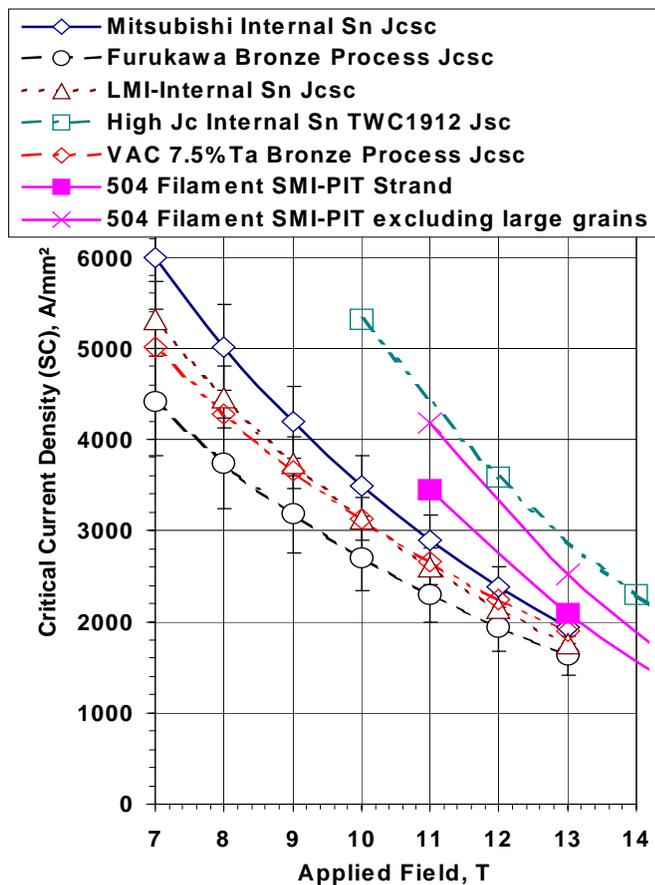
Influence of Reaction on H^* , H_{c2}



C. M. Fischer, P. J. Lee and D. C. Larbalestier,
“ H^* and J_c as a function of heat treatment
time and temperature for powder-in-tube
 Nb_3Sn conductors”, ICMC 2001

Snowmass July 5, 2001

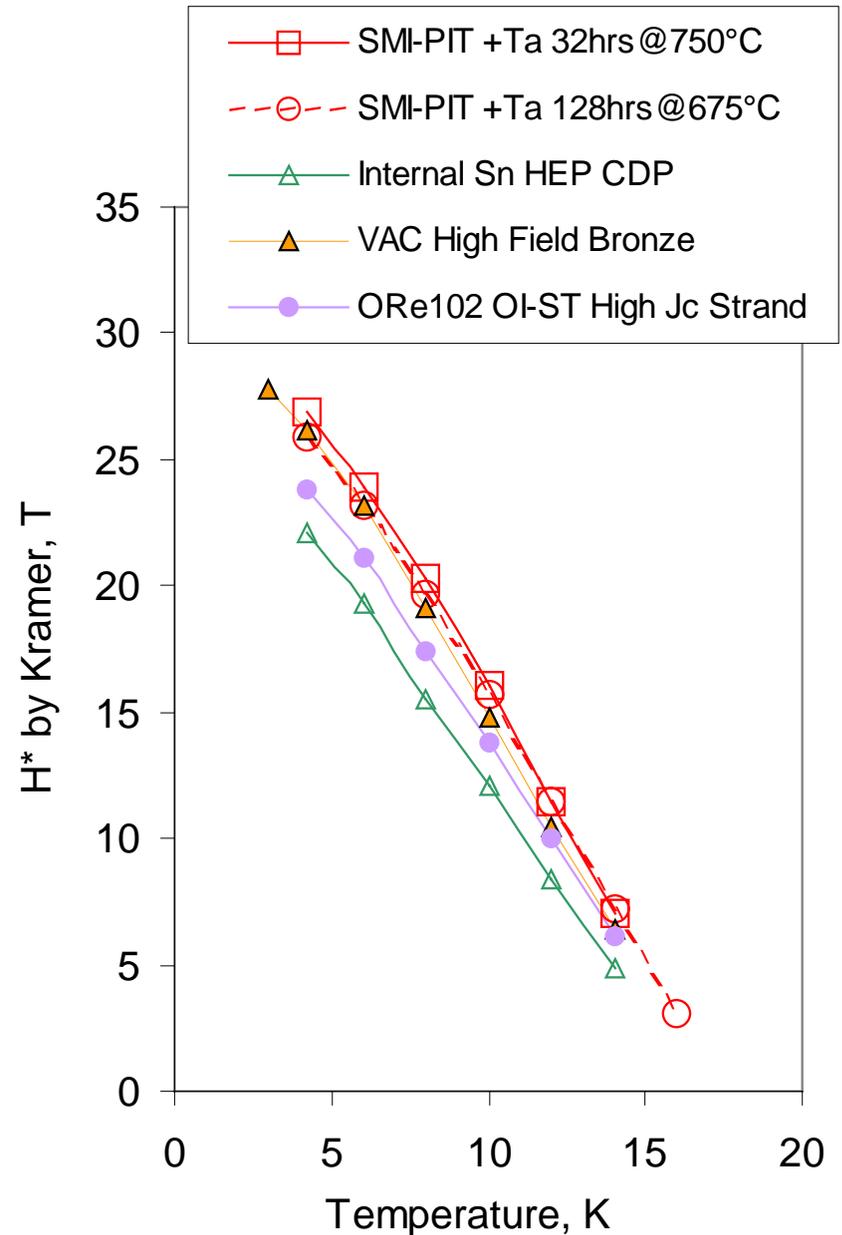
Jc in the A15 layer and its flux pinning strength



No common
 H^* behavior
yet for
 Nb_3Sn !

Highest $J_c(12T)$ have
lowest H^* !

Problem of composite
design



Nb₃Sn: The summary

- Big improvements are occurring in magnets and conductor
 - Industry-magnet builder-fundamental feedback loop
- Fundamental side has benefited enormously from nanoscale structural and electromagnetic tools

The End of the Beginning

- MgB_2 - an anisotropic 39K superconductor
 - no GB problem
 - BUT texturing and/or alloying needed
 - Mg and B are very cheap!
 - Maybe more boride superconductors!
- Nb_3Sn - an existing 18K superconductor
 - GB no problem, nor is need for texture
 - J_c , H^* , H_{c2} limits being probed now
- Choices!