IEEE/CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), October 2015.
Plenary presentation PL7 given at EUCAS 2015; Lyon, France, September 6 – 10, 2015.
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Nanocomposite Coated Conductors

Towards optimal vortex pinning for high field applications

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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

European Research Council Executive Agency

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ICMAB-CSIC: X. Obradors, A. Palau, S. Ricart, M. Coll, J, Gázquez, E. Bartolomé, X. Granados, C. Pop, M. Tristany , P. Cayado, V. Rouco, R. Guzman, F. Vallès, B. Mundet, P. Garcés, H. Chen, L. Soler, B. Villarejo

EUROTAPES: J. Driscoll, R. Hühne, P. Pahlke, B. Holzapfel, J. Hänisch, G.Celentano, F. Rizzo, I. Van Driessche, K. Keukeleere, G. Van Tendeloo, A. Meledin, M. Eisterer, M. Lao

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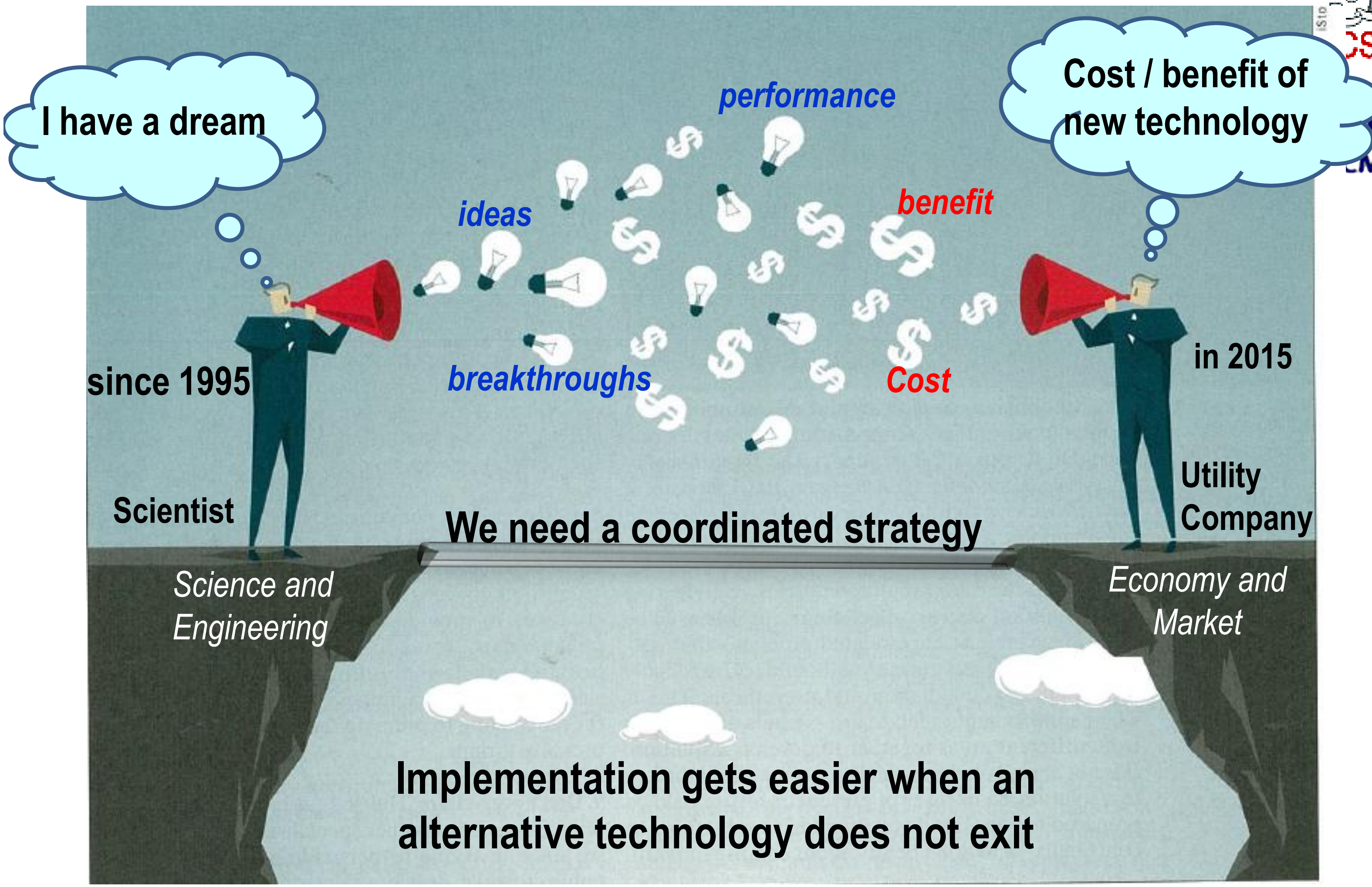
The World of Coated Conductors



Adapted from Physcs World August 2015

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The history of Coated Conductors

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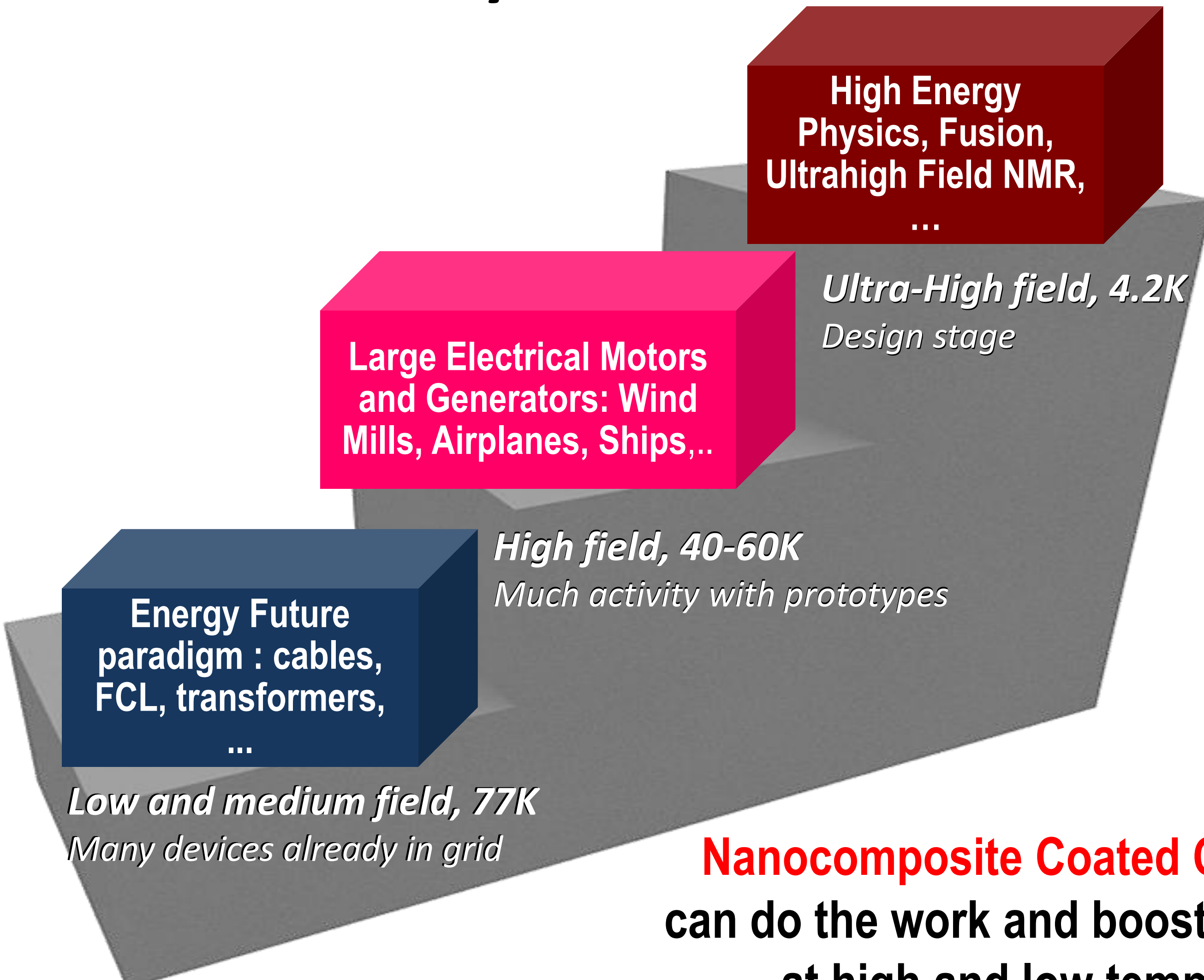

Nanocomposite Coated Conductors
can do the work and boost applications at high and low temperature

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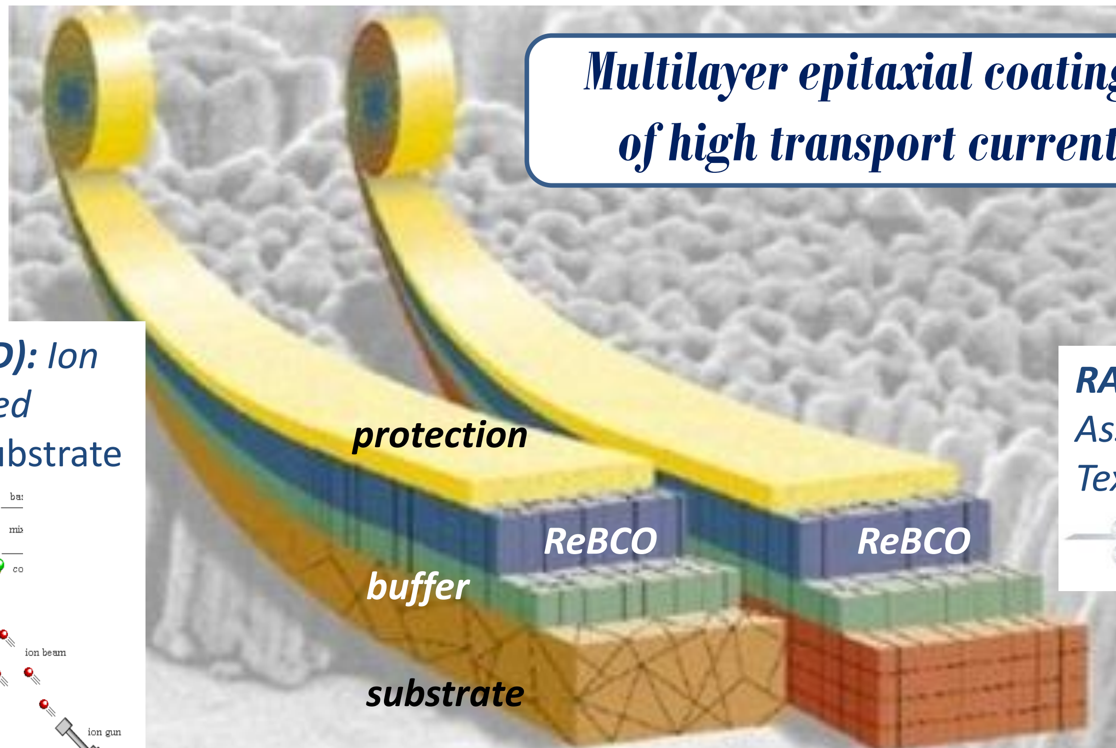
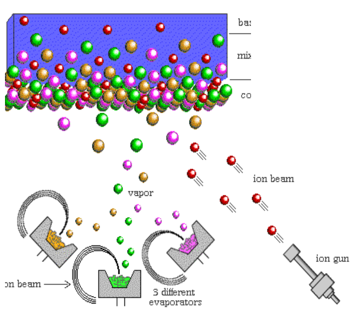
Coated Conductors are a revolution in materials science and engineering

started 15 years ago



IBADs (ABAD): *Ion Beam Assisted Deposited* substrate



RABiTs: *Rolling Assisted Biaxially Textured* substrate

… scalable technology for growing km-length epitaxial (RE)$Ba_2Cu_3O_7$ films on flexible metallic substrates

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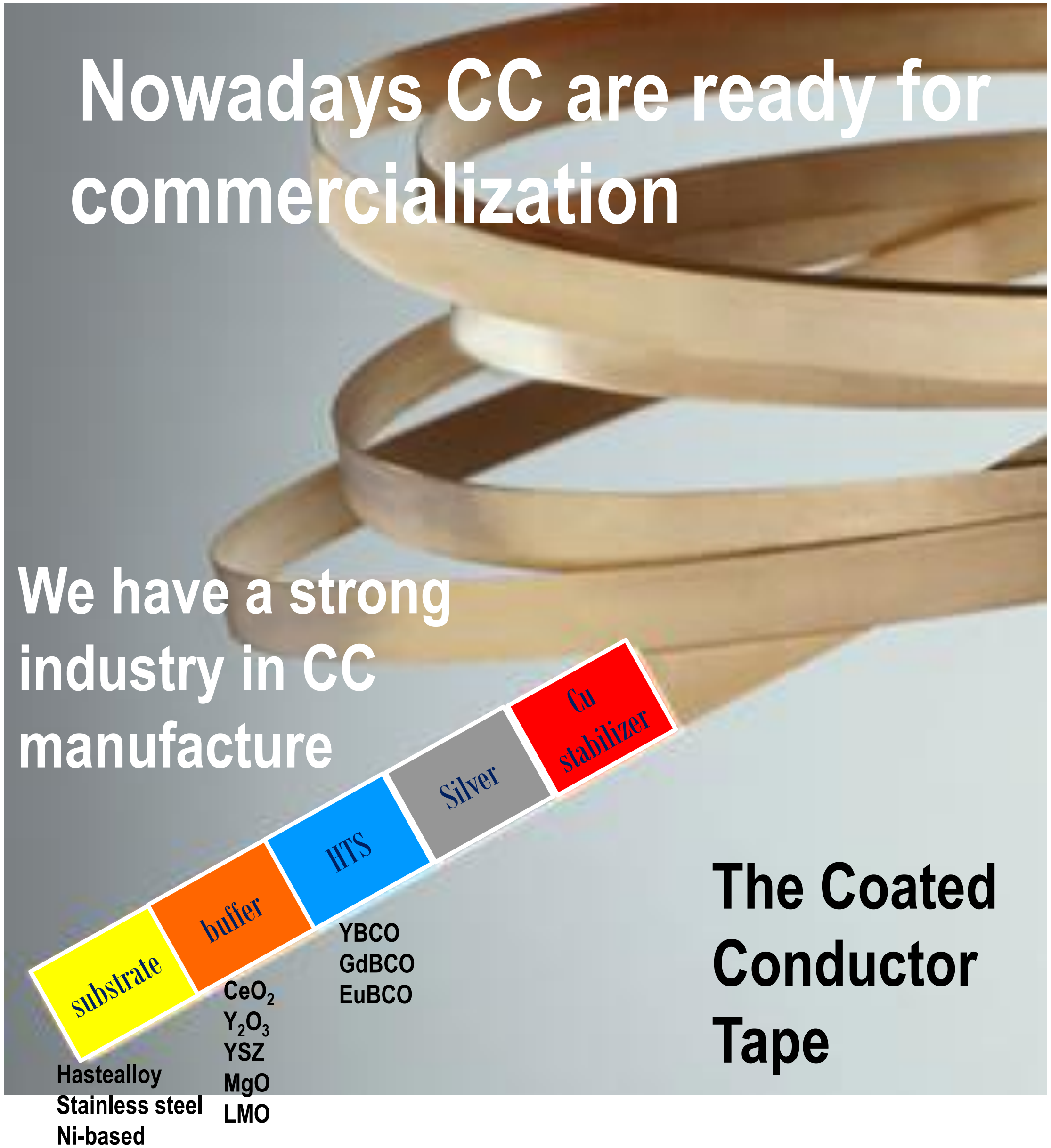

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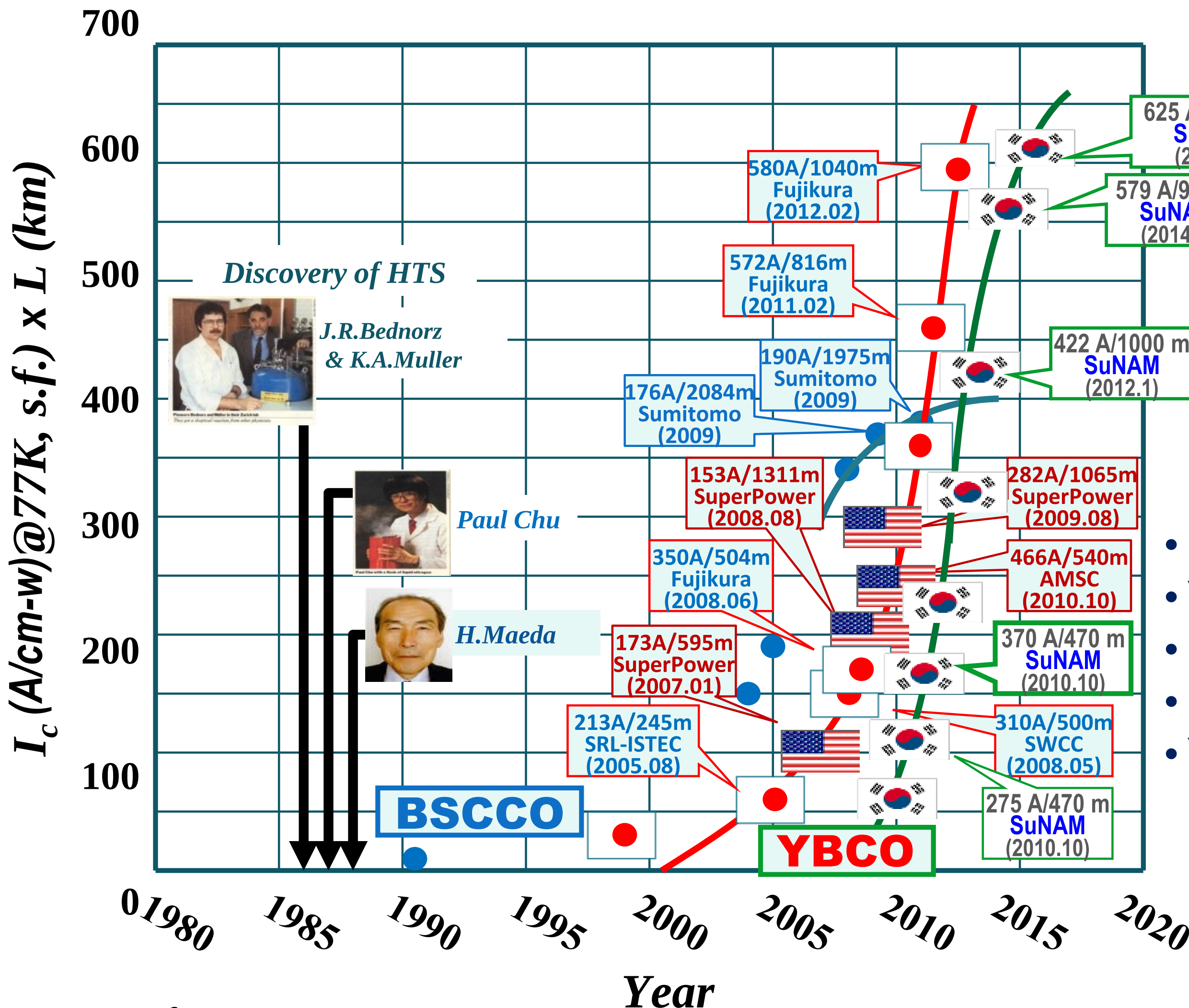
The huge progress of CC in the last 10 years



$I_c \times L = J_c \times t \times L$

- Current density (J_c)
- YBCO Thickness (t)
- Length (L)
- Homogeneity
- Yield

Courtesy of Dr. T. izumi

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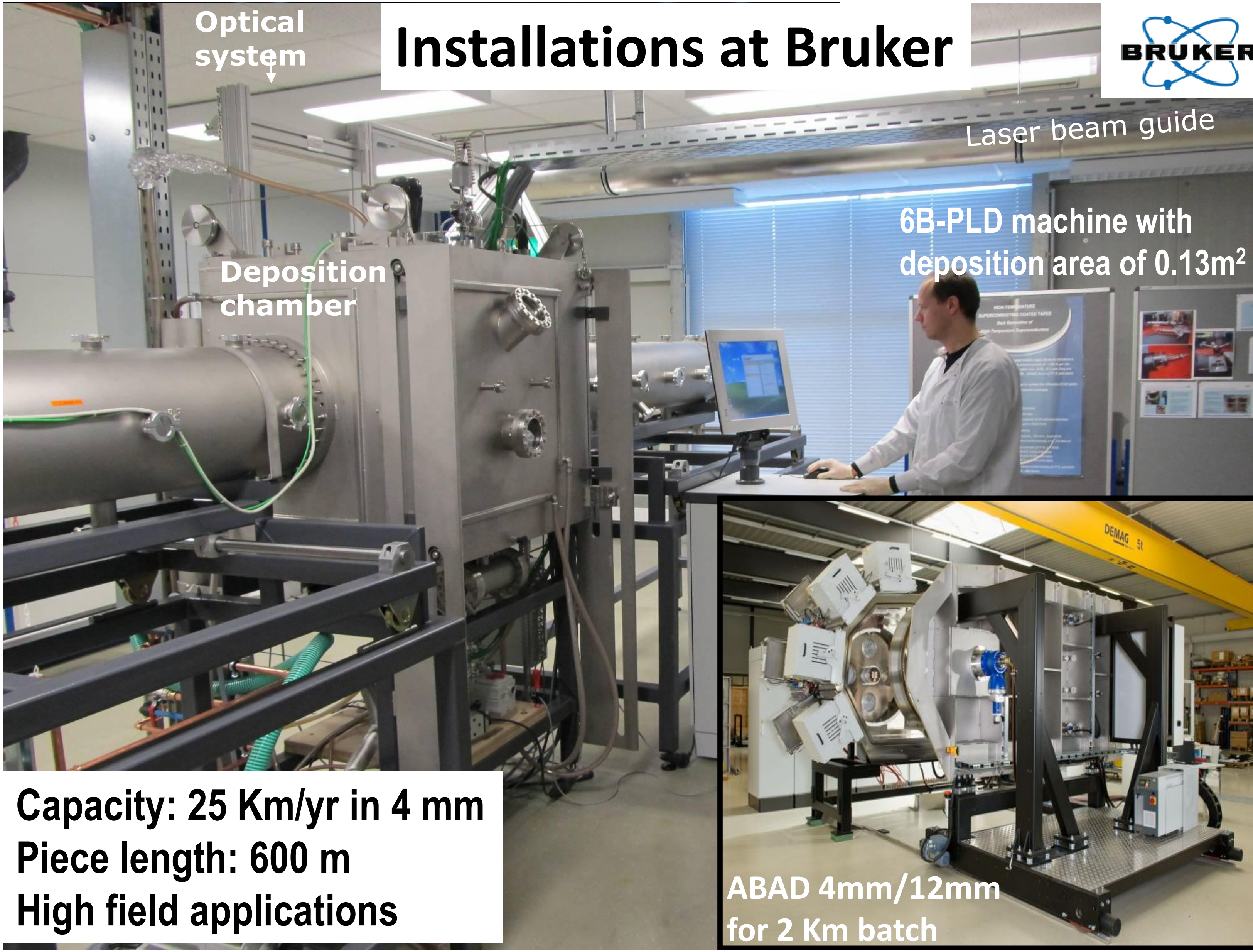
Installations at Bruker
BRUKER
Optical system
Laser beam guide
Deposition chamber
6B-PLD machine with deposition area of 0.13m^2
Capacity: 25 Km/yr in 4 mm
Piece length: 600 m
High field applications
ABAD 4mm/12mm
for 2 Km batch

2G superconducting tape by PVD

THEVA

PILOT PRODUCTION LINE

GdBCO evaporation on ISD-MgO tape

Min. processing speed: 30+ m/h

fully automated

inline quality inspection

reel-to-reel & air-to-air tape transfer

Piece length: 1 km

Capacity: 150 km/yr in 12 mm-width

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deutsche nanoschicht

Expanded pilot line

All CSD approach on RABiTs

- Construction in 2015

(Start sampling for customer projects in 2015/2016)

- **Planned capacity > 200 km/yr**
- **Present Length: 20 -100 m**

I_c(77K,0T)/w = 294 ± 5 A/cm
I_c(30K,1T)/w = 853 ± 5 A/cm
HTS layer thickness d = 1 μm

Lab processing

Expanded Pilot Line

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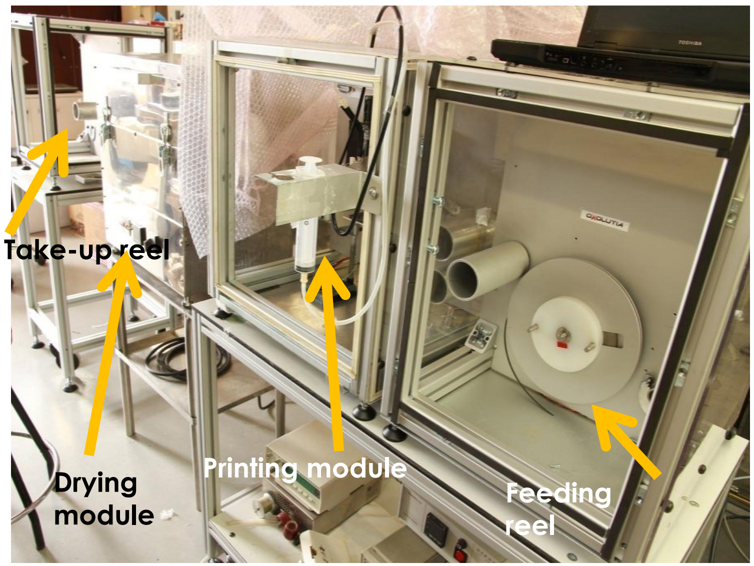
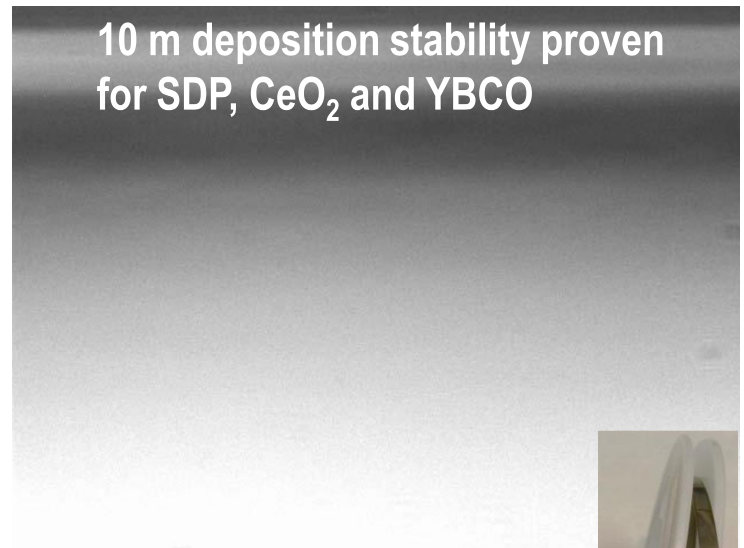
Chemical Solution Deposition scalability processes at Oxolutia

OXOLUTIA

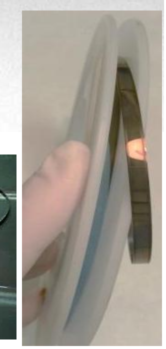
eurotapes CSIC ICMAB

Reel-to-reel Ink Jet Printing pilot plant for all CSD on ABAD Bruker subtrates





10 m CeO_2 buffer @ 28 m/h



1 m YBCO

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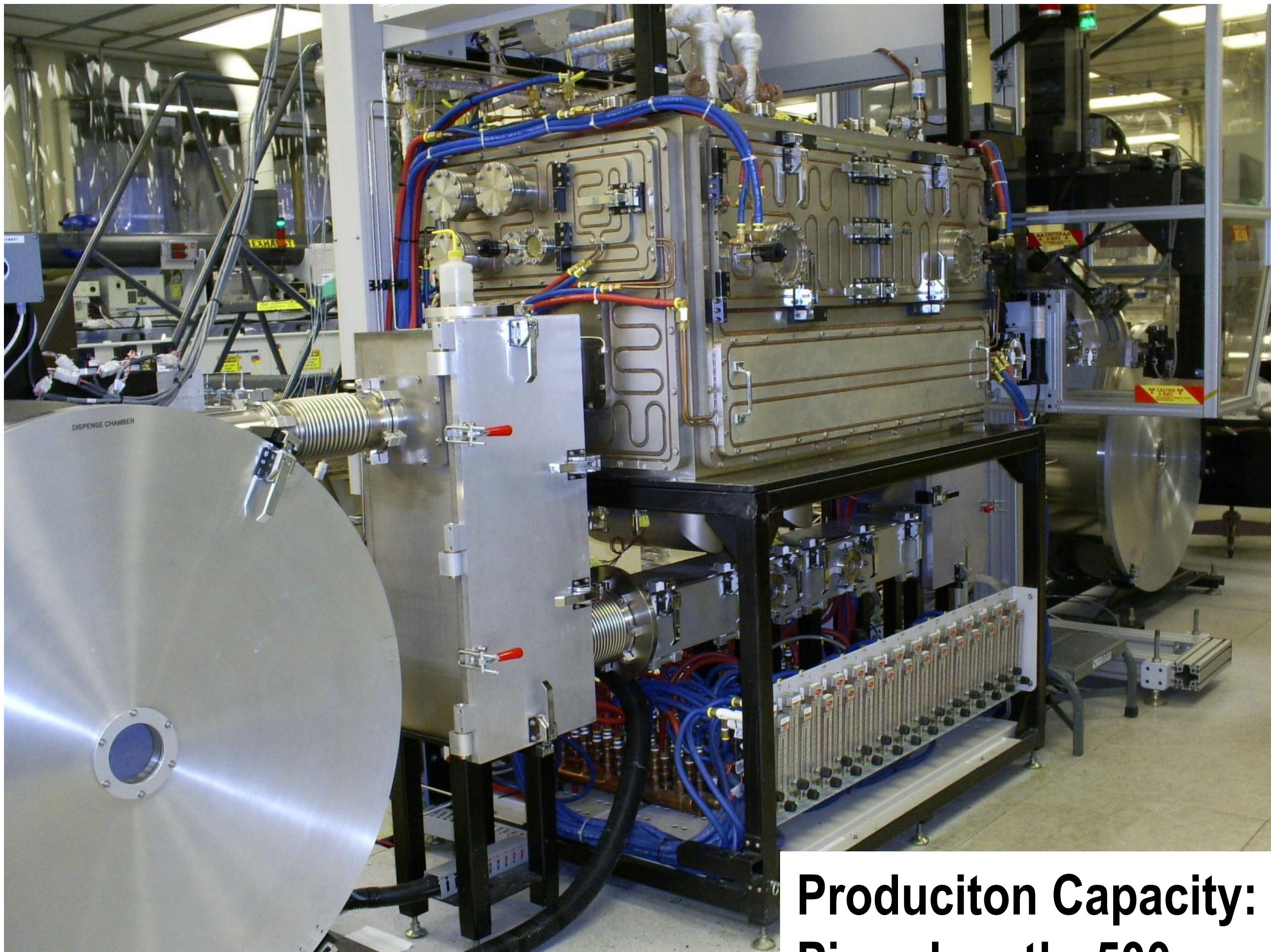
MOCVD approach on IBAD

SuperPower Inc.



Produciton Capacity: 1000 Km/yr
Piece length: 500 m

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Installations at Fujikura

"Tsunagu" Technology
Fujikura

Installations at Showa

Batch furnace for TFA-CSD / IBAD

Production capacity : 20 Km/yr
Piece length: 125 m

SWCC GROUP

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SuNAM (Korea): Production Facilities

RCE-DR on IBAD

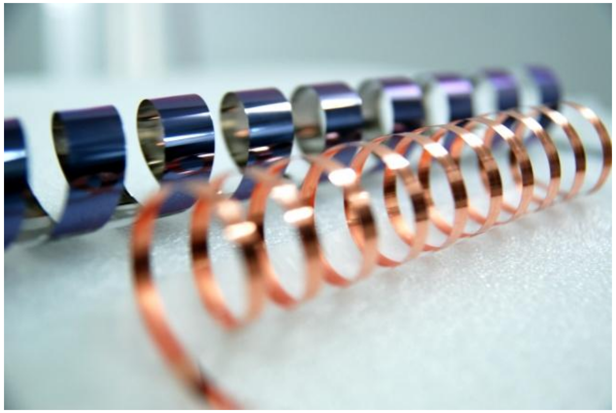
IBAD facility: ~17 m long

System for Al_2O_3 barrier & Y_2O_3 seed

System for IBAD, homo-epi & buffer

Production capacity: ~ 1000 km/yr. Piece length : 1 km

Reactive Co-Evaporation Deposition and Reaction



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HTS at all magnetic fields

Cost/Performance

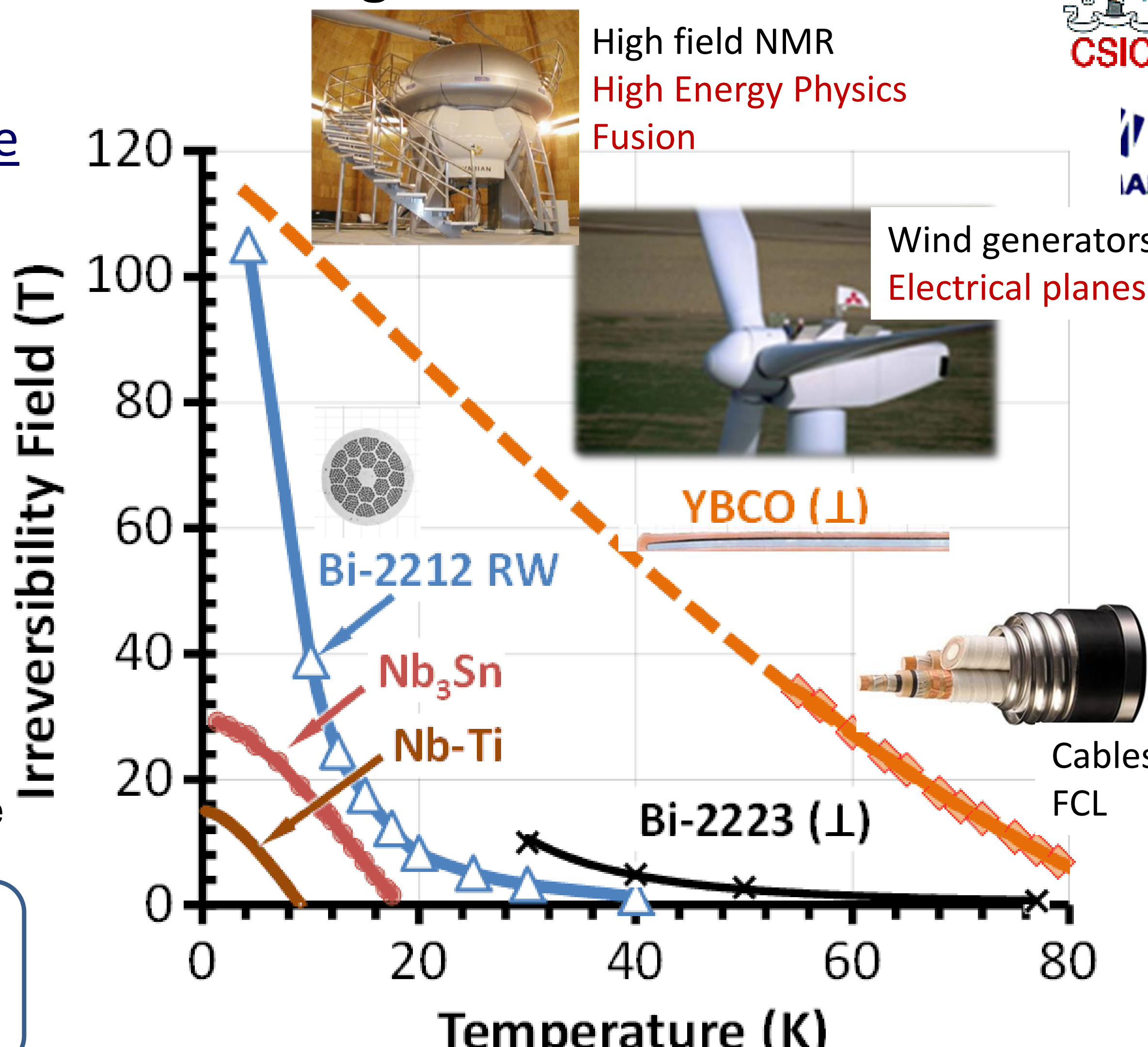
Figure of merit:
€/kAm at specific T and H

Present:
~200 €/kAm (77K, SF)
(I_c= 400 A)

~100 €/kAm (30 K, 3T)
(I_c= 800 A)

Further nano-structuration and production scalability expects a factor 4 decrease

Estimated Market by 2030: ~15.000 km/yr



D. Larbalestier, Nature Materials (2014)

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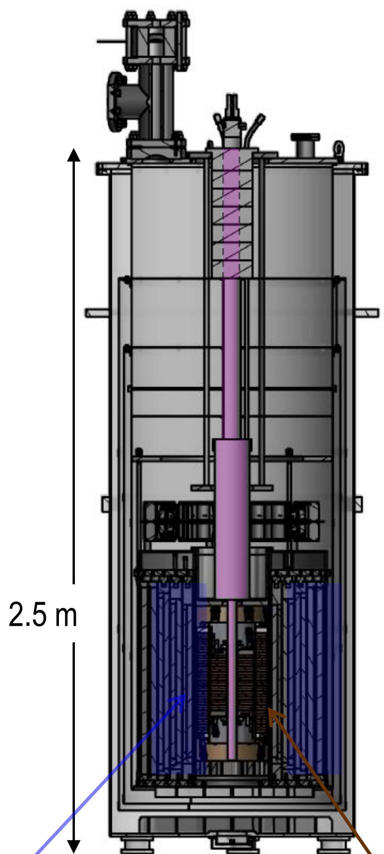
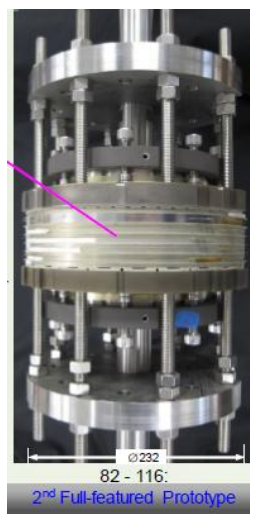
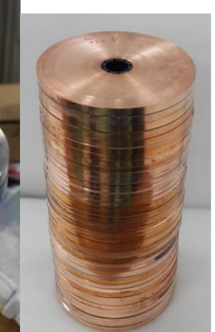
32 T LTS-HTS Magnet





26.4 T HTS Magnet

With Multi-Width and No-Insulation REBCO Wire



26 Double Pancake Coils Stacking

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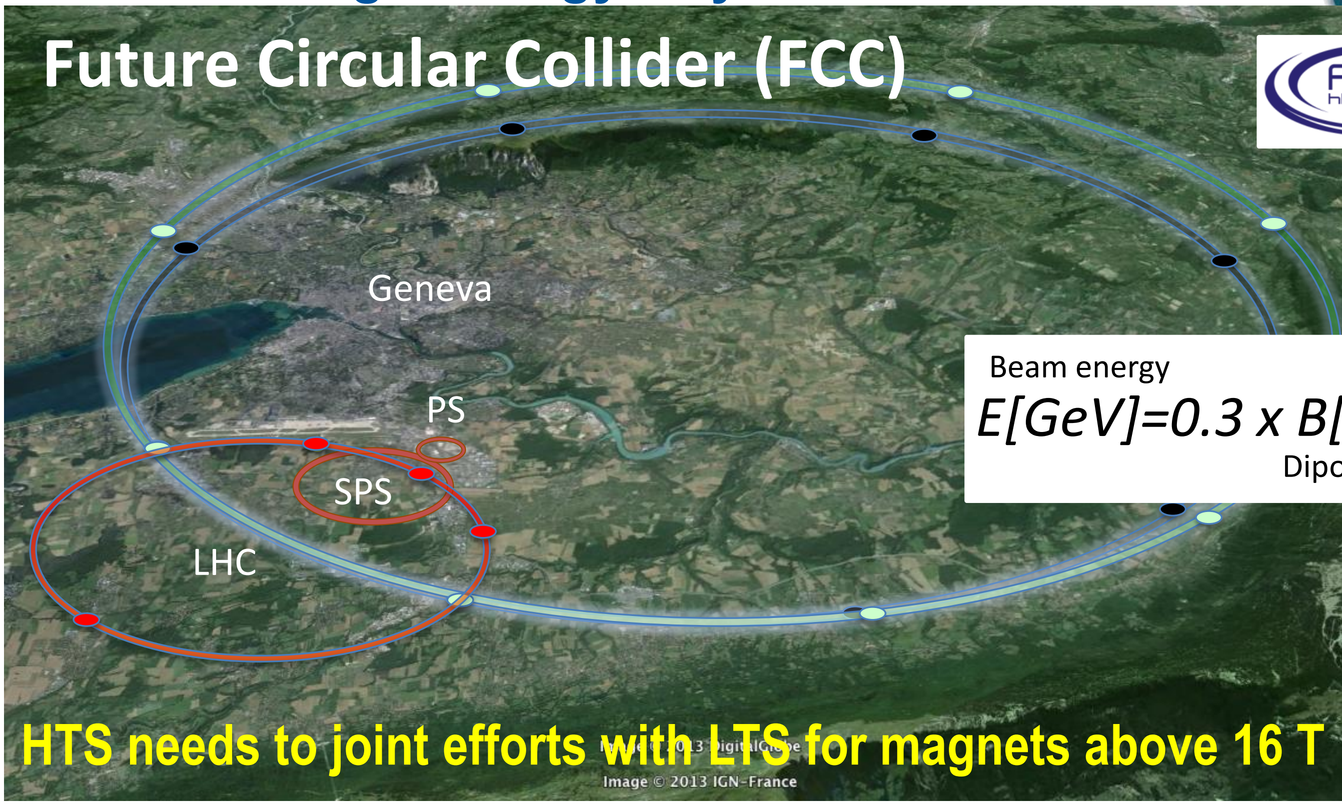
The Call of High Energy Physics: LTS and HTS



Beam energy — Bending radius

$$E[GeV]=0.3 \times B[T] \times \rho[m]$$

Dipole field

LHC	HE-LHC (2025)	FCC-hh (2035)	FCC-hh (2035)
27 km, 8.33 T	27 km, 20 T	80 km, 20 T	100 km, 16 T
14 TeV (c.o.m.)	33 TeV (c.o.m.)	100 TeV (c.o.m.)	100 TeV (c.o.m.)
1300 tons NbTi	3000 tons LTS	9000 tons LTS	6000 tons Nb_3Sn
	700 tons HTS	2000 tons HTS	3000 tons Nb-Ti

Luca.Bottura@cern.ch

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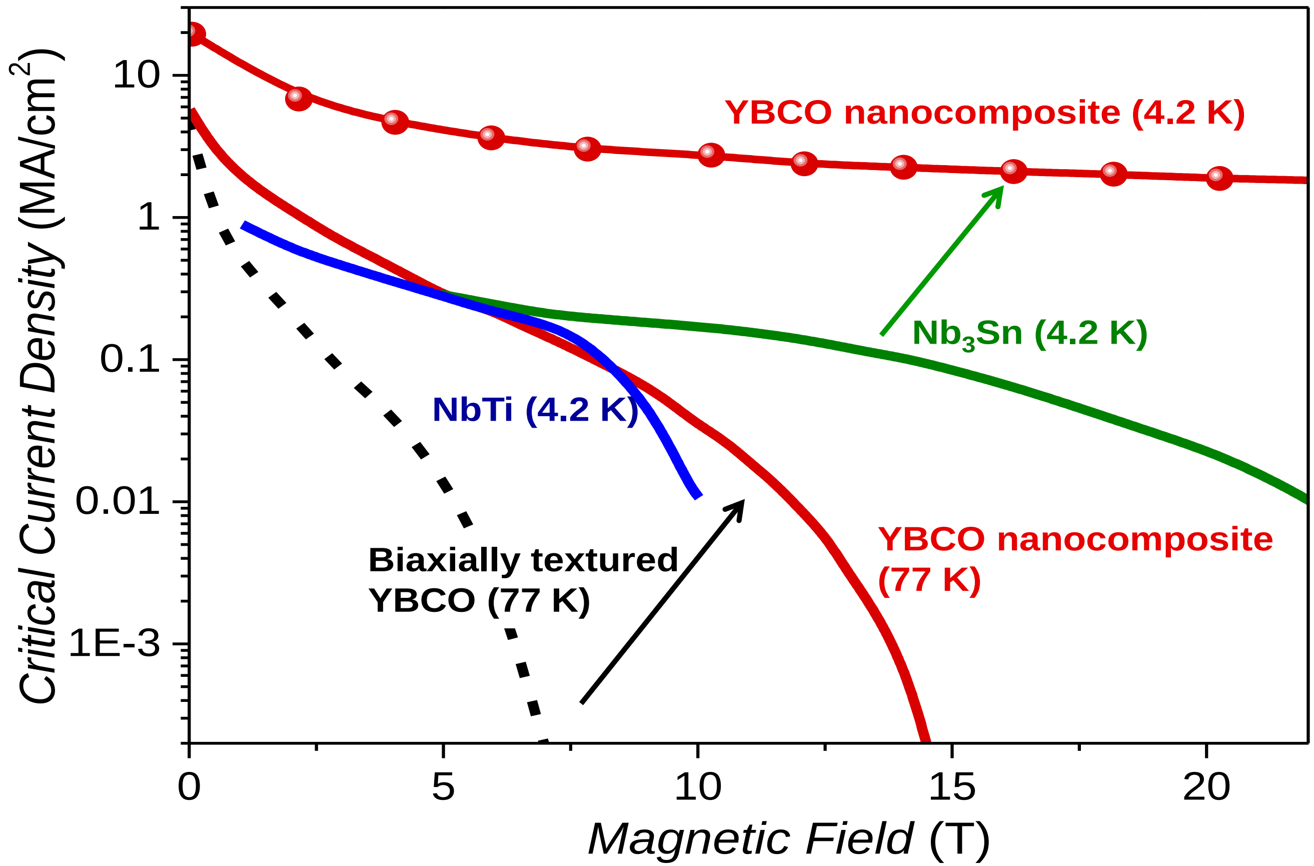
Nanotechnology engineering enables YBCO to improve at all regions

and postulate for low T applications



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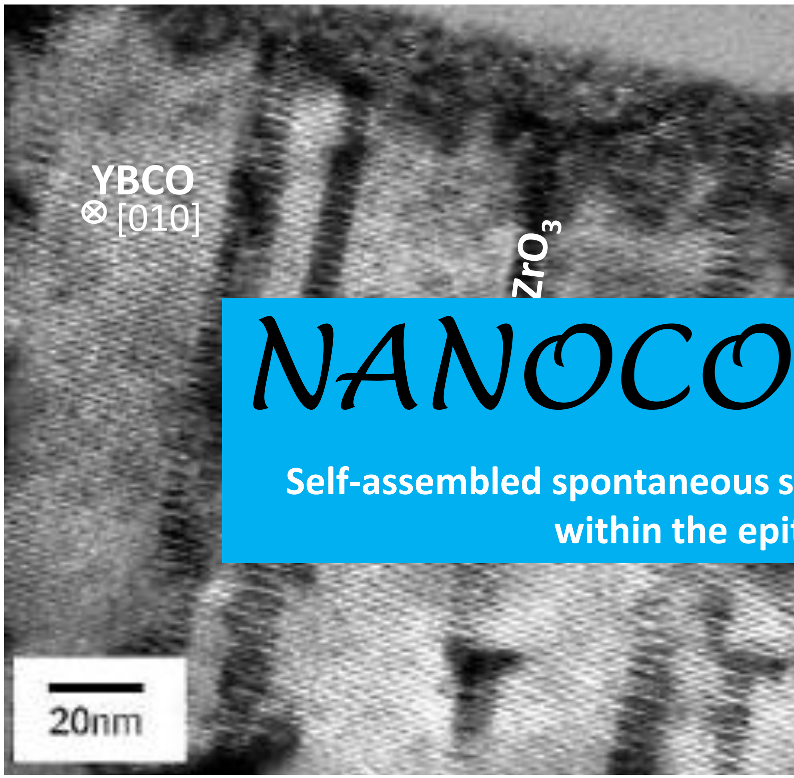
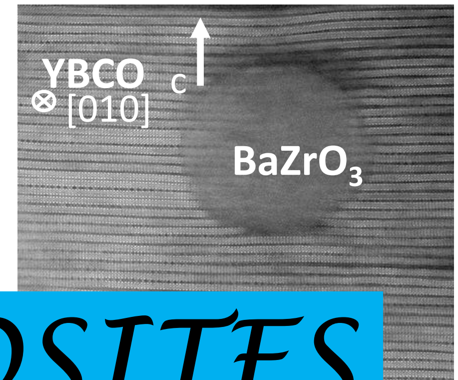
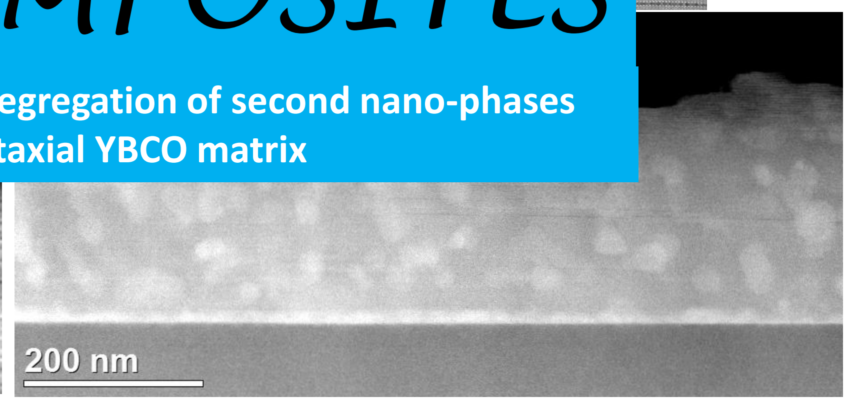
The outstanding push towards scalable Artificial Pinning Centers

By Pulsed Laser Deposition (also by MOCVD)



By Chemical Solution Deposition





NANOCOMPOSITES

Self-assembled spontaneous segregation of second nano-phases within the epitaxial YBCO matrix

J. Driscoll, Nat. Mat. 3(2004);T. Haugan, Nature 430(2004)
Y. Yamada, APL 87(2005); S. Kang, Science 311 (2006)
B. Maiorov, Nat Mat 8 (2009);A Kiessling, SUST 24 (2011)

J. Guiterrez, Nat Mat 11 (2007)
A. Llordés, Nat Mat 6 (2012)
M. Miura, SUST 26 (2013), M. Miura, SUST 23(2010)
S. Engel, APL 90 (2007)

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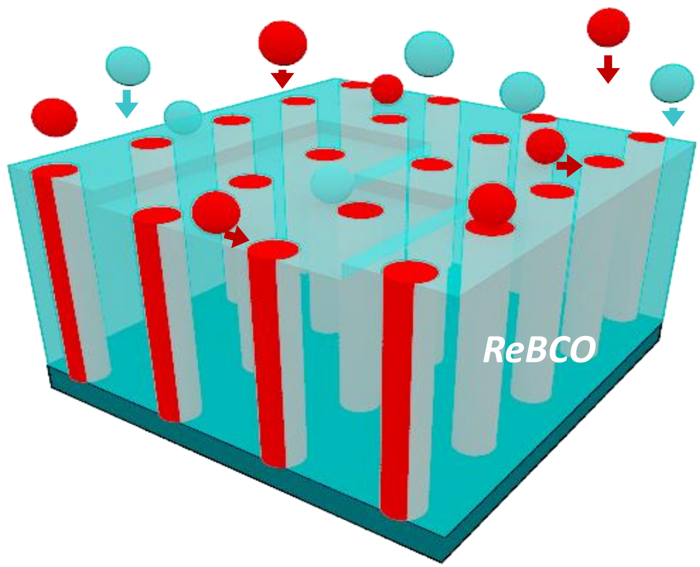
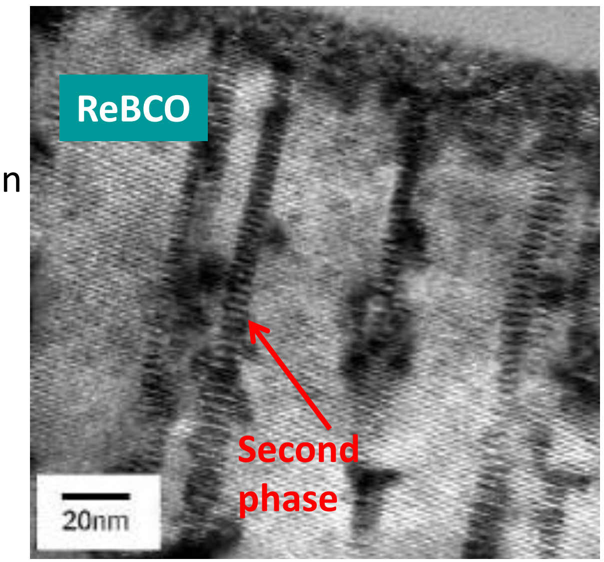
Growth of ReBCO Nanocomposites

Simultaneous deposition and growth

(Case PLD, MOCVD and HLPE)



Deposition
Absorption
Surface diffusion
Self-assembly



- Epitaxial nanorods form with YBCO simultaneously
- Semicoherent interfaces between nanorods and YBCO induce localized strain

Pulsed Laser Deposition (PLD): Physical vapor deposition

Metalorganic chemical vapor deposition (MOCVD): Chemical vapor deposition

Hybrid liquid phase epitaxy (HLPE): Physical deposition with solid-liquid reaction

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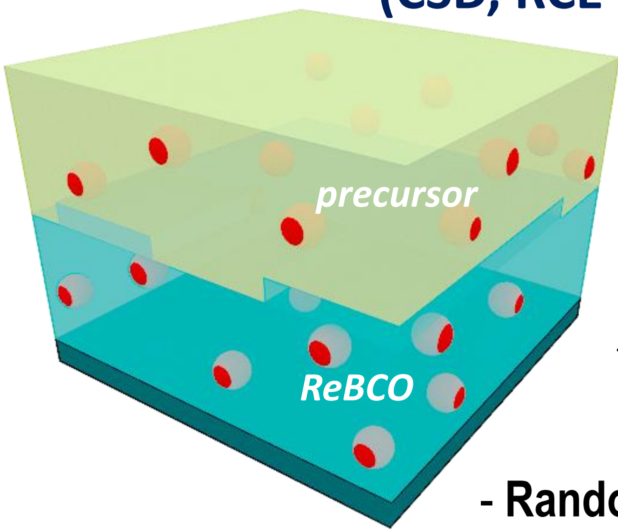
Growth of ReBCO Nanocomposites

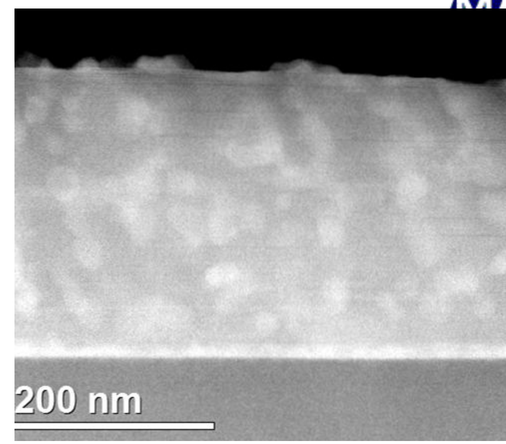
Sequential deposition and growth

(CSD, RCE-DR and CSD-TLAG cases)

CSIC



Precursor deposition
Nanoparticles formation
ReBCO conversion and
trapping of nanoparticles



- Random oriented nanoparticles form prior to YBCO
- A heavily long range isotropic nanostrained matrix

Chemical Solution Deposition of metalorganics (MOD-CSD)
Chemical gas-solid conversion

Reactive co-evaporation by deposition and reaction (RCE-DR)
Physical co-evaporation and fast conversion from a liquid

European Research Council
Executive Agency

CSD- Transient Liquid Assisted Growth (CSD-TLAG)
Fast liquid-solid reaction from CSD precursors

CSD -Transient Liquid Assisted Growth

Chemical Solution Deposition

Liquid-Assisted growth

✓ Low cost

✓Very fast growth rate

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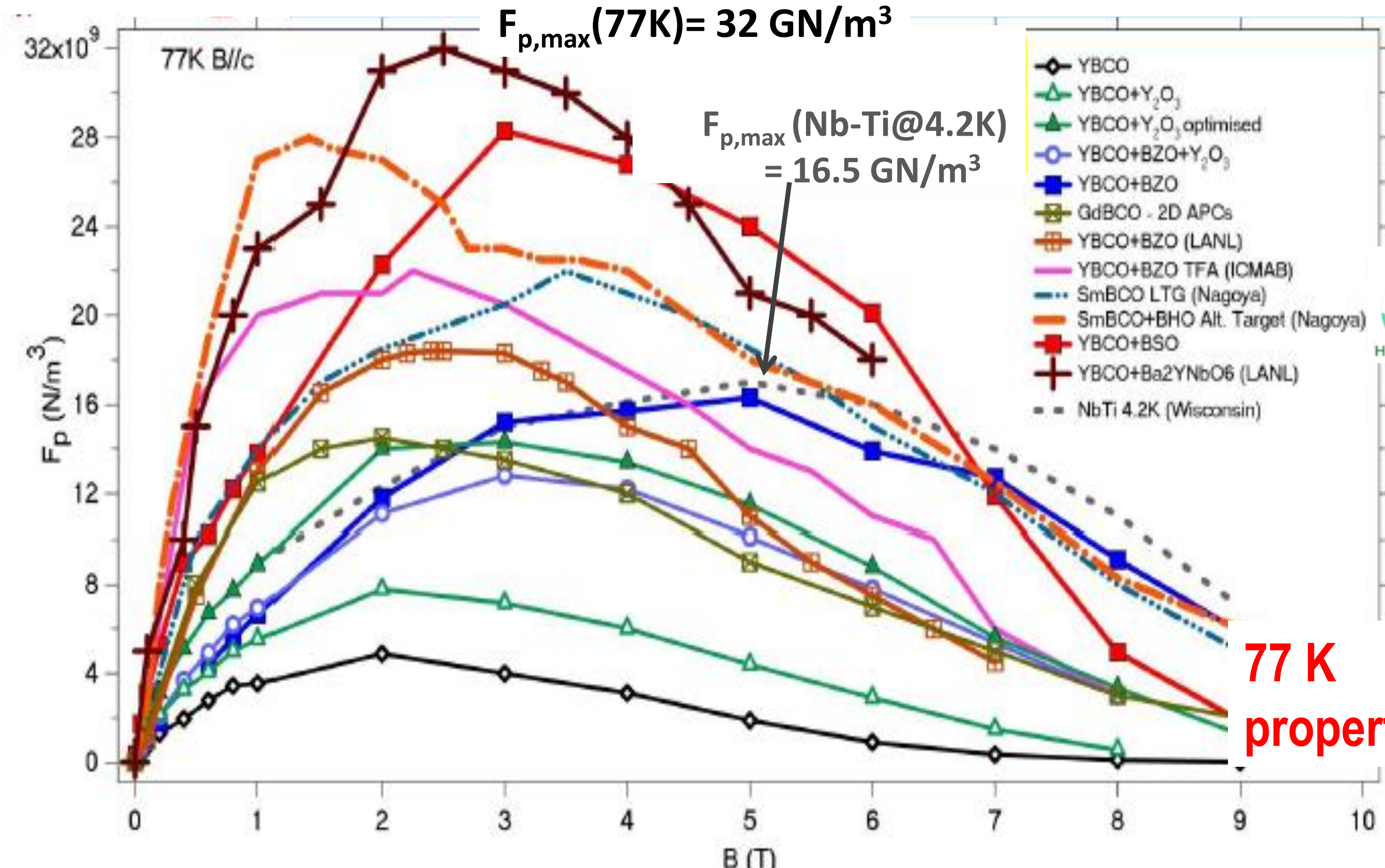
Strong increase of Pinning Force ($F_p=J_c x B$) by Nanocomposites



X.Obradors, T. Puig, A. Palau, F. Sandiumenge, P. Mele, K. Matsumoto – "Nanostructured Superconductors with efficent vortex pinning" in Comprehensive nanoscience and nanotechnogly, AP, Vol 3 (2011) 303-349 [added with YBCO+Ba2YNbO6 and SmBCO+BHO]

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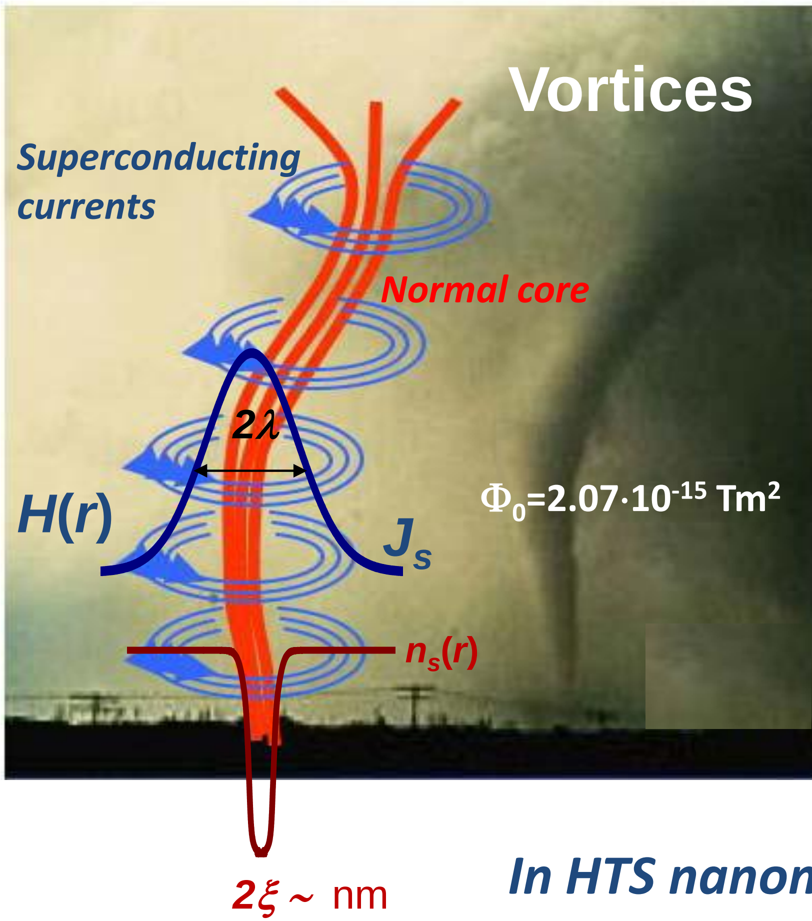
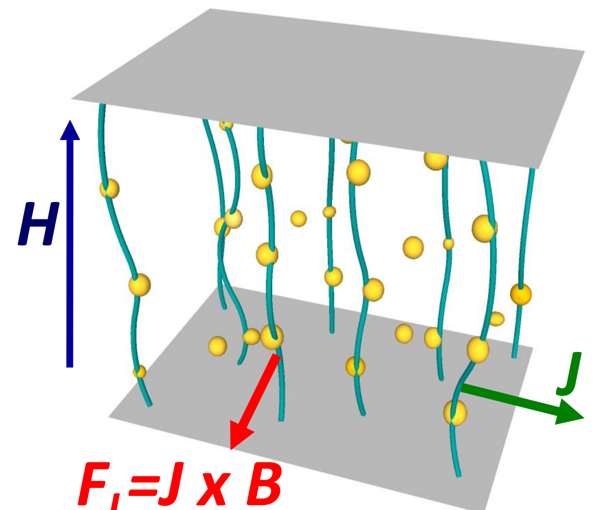
It is all about Vortices … quantized flux lines



Their motion and the role of pinning centers



$U_p \sim (H_c^2/8\pi)\ (\pi\ \xi^2) \sim (\phi_0/\lambda_L)^2$

(core) pinning

In HTS nanometer defects get into the game

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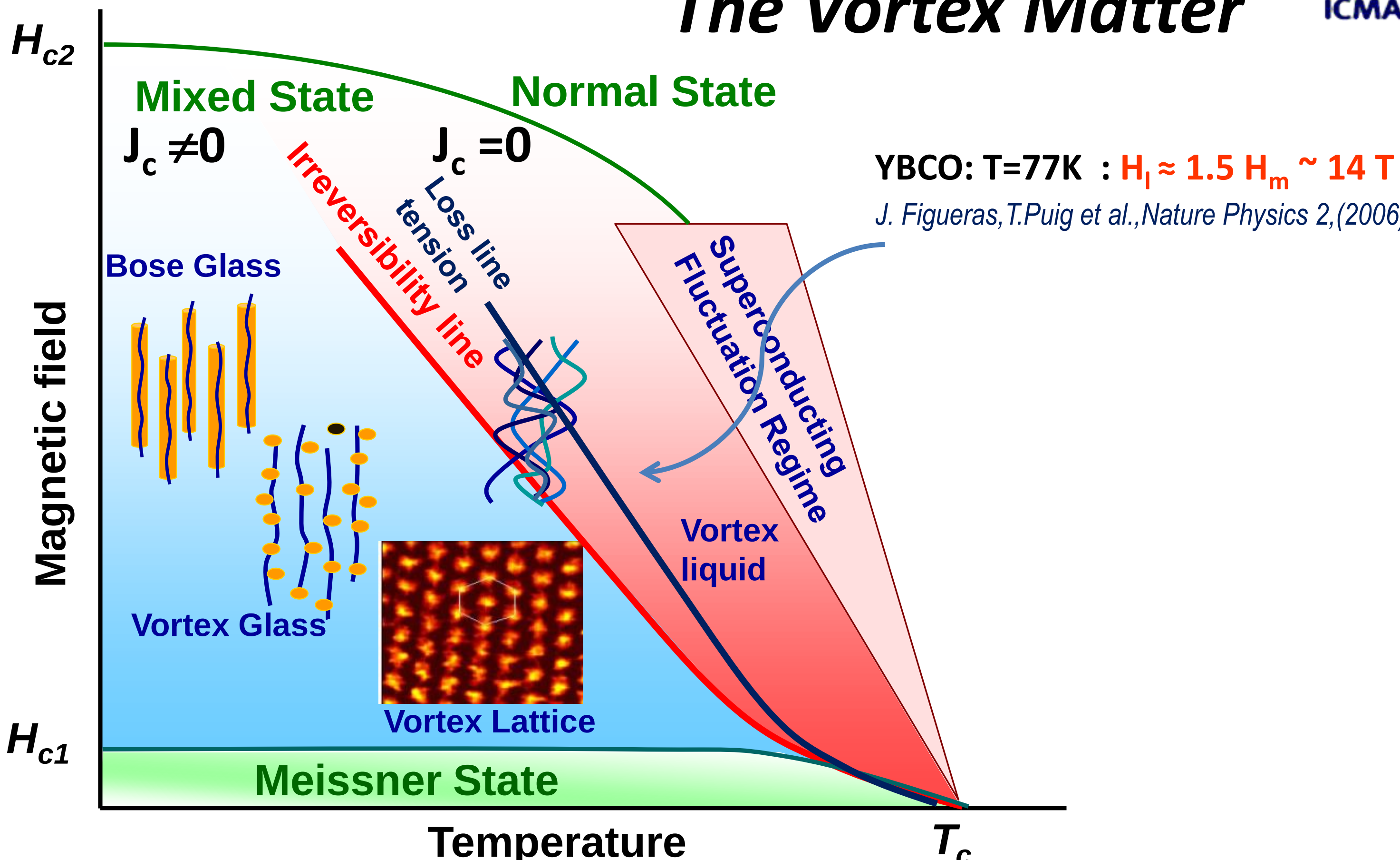
Abrikosov Vortices in HTS

Thermal fluctuations, elastic energy, pinning energy and vortex-vortex repulsion play relevant roles

The Vortex Matter



G.W. Crabtree et al, Phys. Today 50 (1997)

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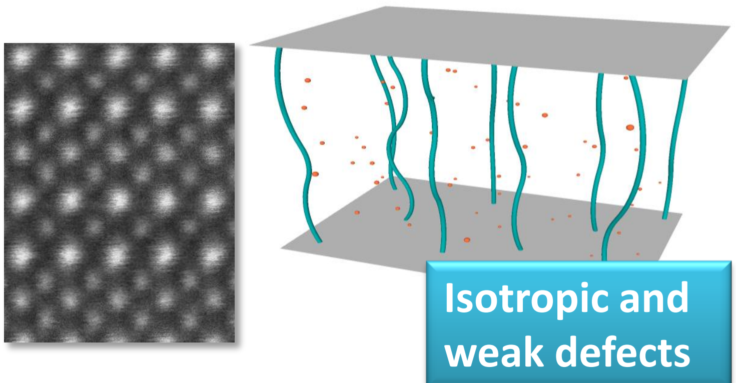
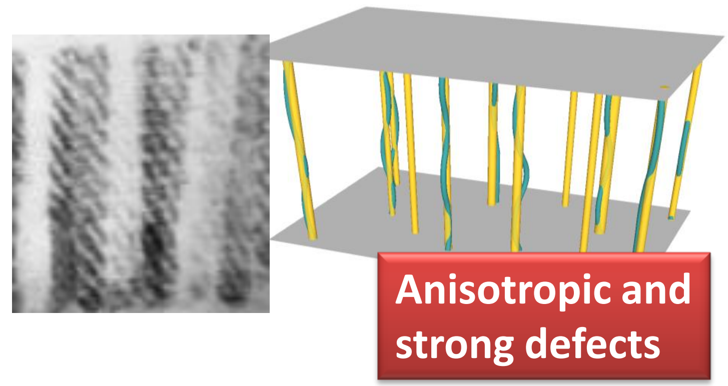
Vortex Pinning Centers in HTS

Great variety of pinning sites and complex vortex matter

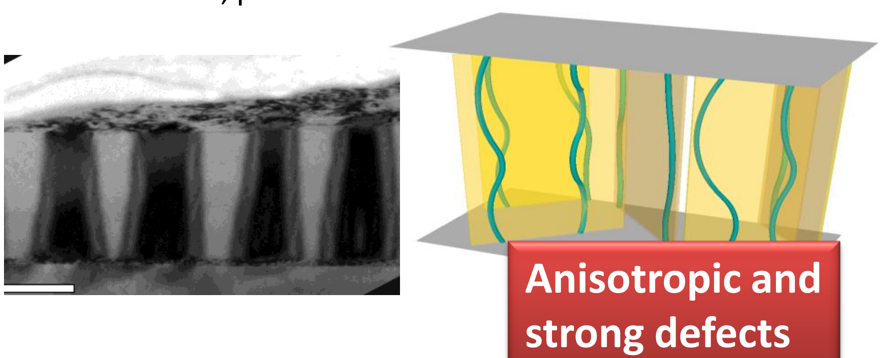
0D-PC: Oxygen vacancies, element substitutions, **point defects**



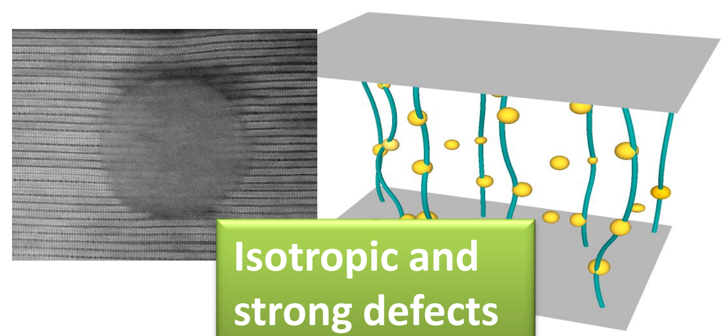
1D-PC: Dislocations, **columnar defects**



2D-PC: Grain boundaries, **twin boundaries**, planar defects



3D-PC: **Precipitates,** secondary phases, local strain



Nanoengineering is the path towards control of vortex pinning and enhace performances. Interaction with natural defects to be considered

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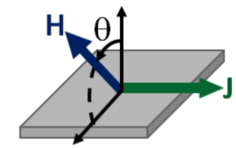
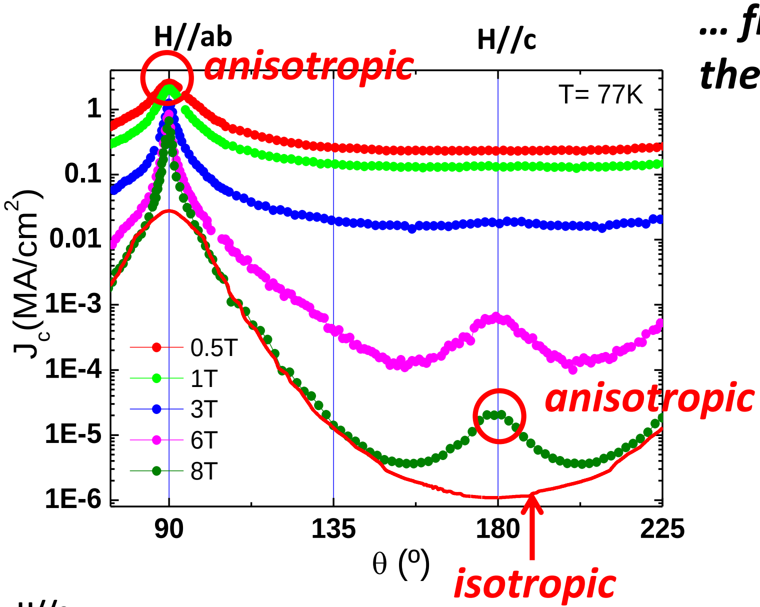
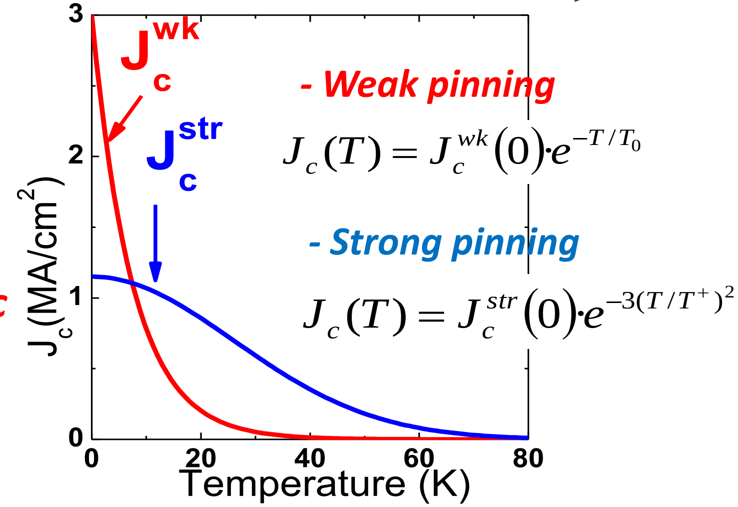
Pinning strength diagrams

... from $J_c(H,T,\theta)$ we separate the different components





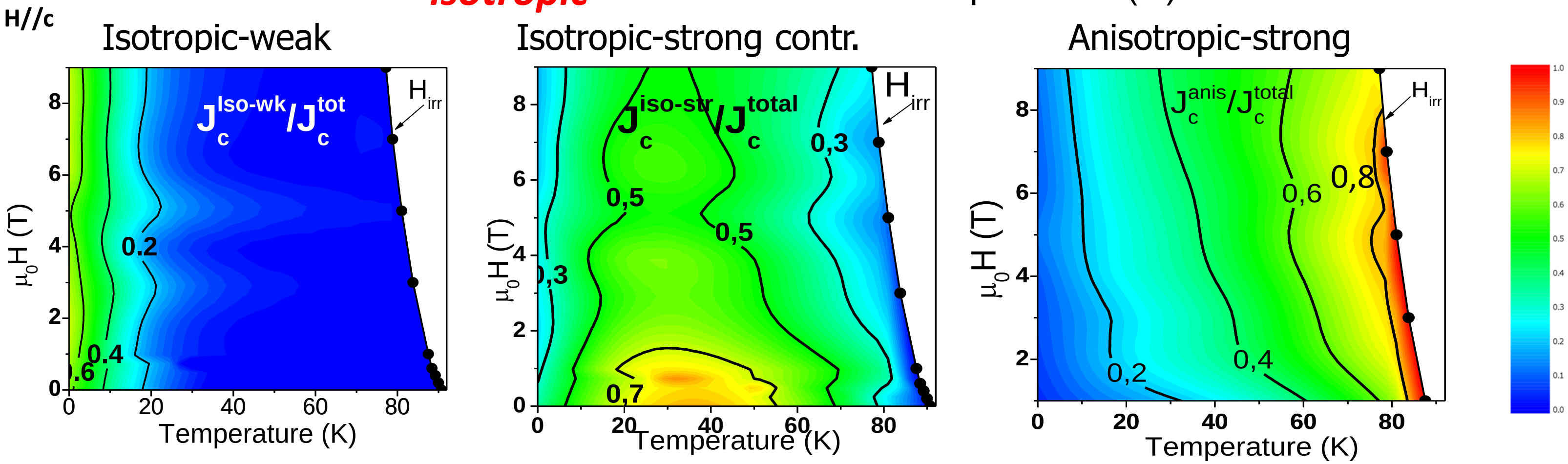


- Weak pinning

$$J_c(T) = J_c^{wk}(0) \cdot e^{-T/T_0}$$

- Strong pinning

$$J_c(T) = J_c^{str}(0) \cdot e^{-3(T/T^+)^2}$$



T.Puig et al., SUST 21, 034008 (2008); J. Plain et al, PRB 65, 104526 (2002); J.Gutierrez et al., Appl. Phys. Lett. 90 (2007)

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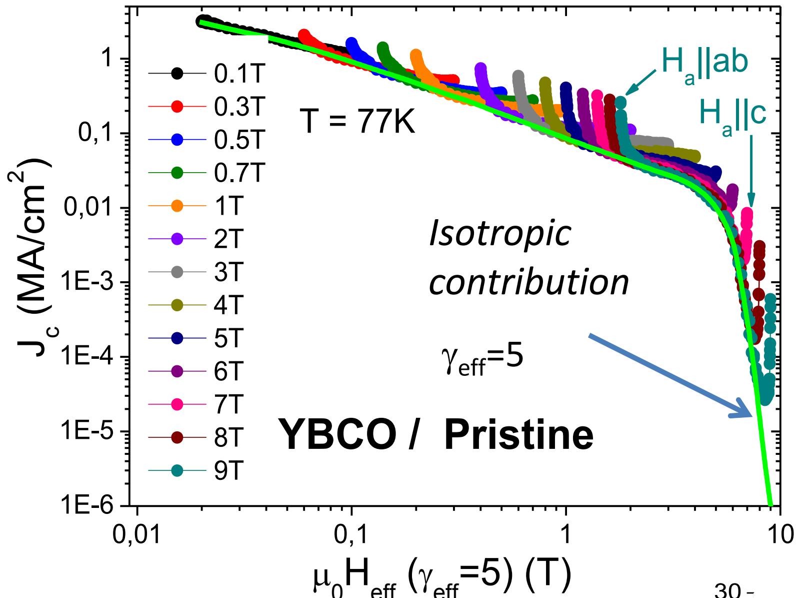
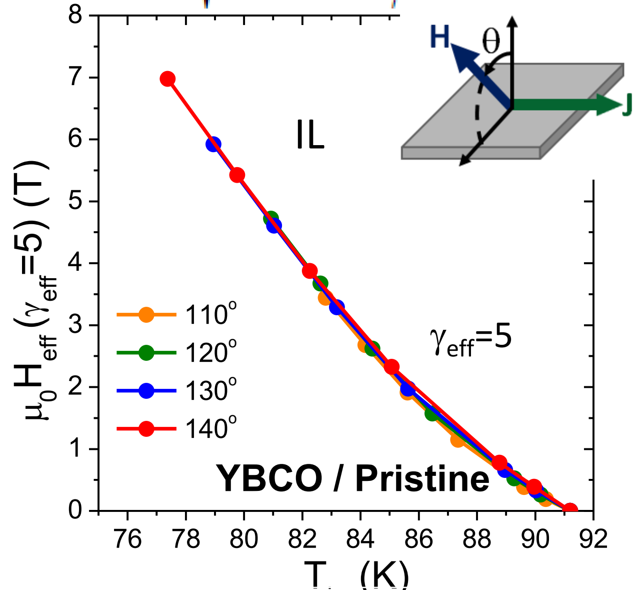
Anisotropy of Critical Currents , IL and H_{c2}

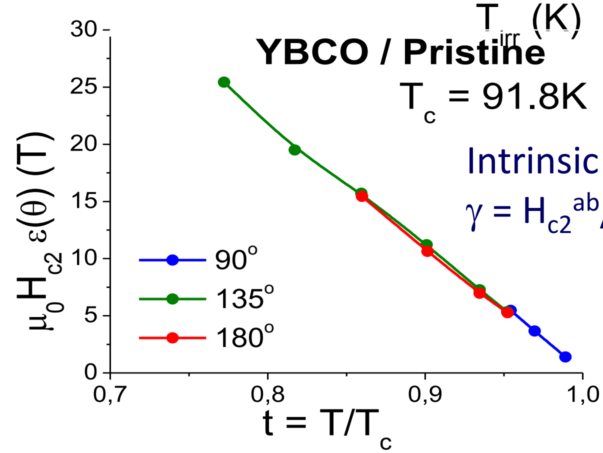
Blatter scaling approach

$$H_{eff} = H_a\varepsilon(\theta) = H_a\sqrt{cos^2\theta + \frac{1}{\gamma^2}sin^2\theta}$$





Pinning Anisotropy (J_c, IL)= γ_{eff}



Intrinsic mass anisotropy,
$\gamma = H_{c2}^{ab}/H_{c2}^{c} = \xi_0^{ab} / \xi_0^{c} = 5$

γ_{eff} =γ in YBCO films and most nanocomposites
γ_{eff} < γ specialy in CSD nanocomposites

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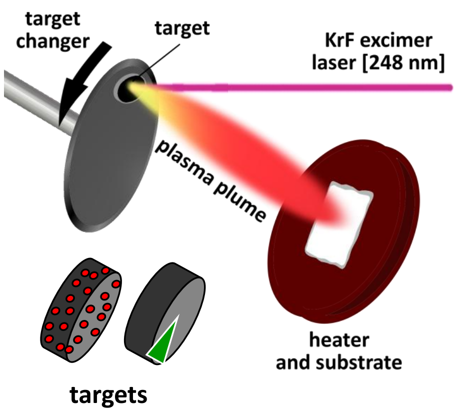
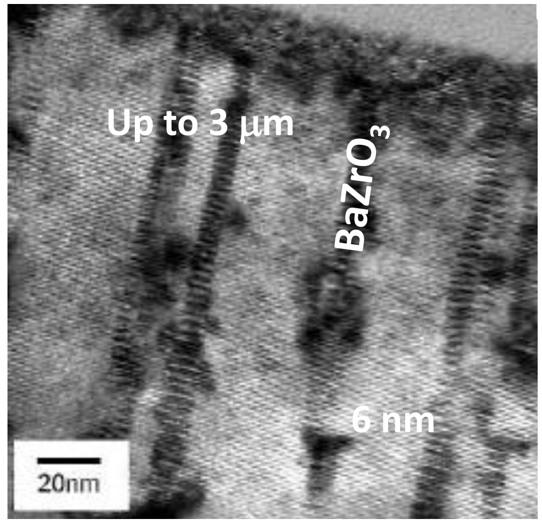
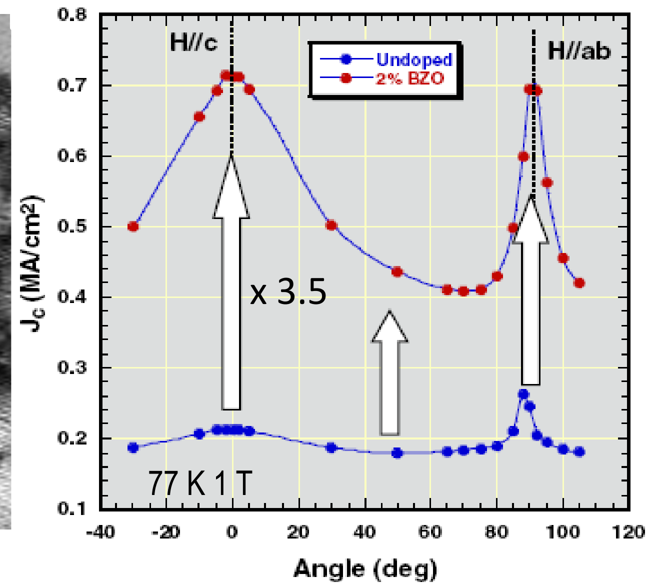
The Breakthroughs of Nanocomposites by PLD

A physical vapor phase growth method giving rise to a self-assembly process of nanocolumns through spontaneous phase segregation







Anisotropic increase of perfomance with $BaZrO_3$ nanorods

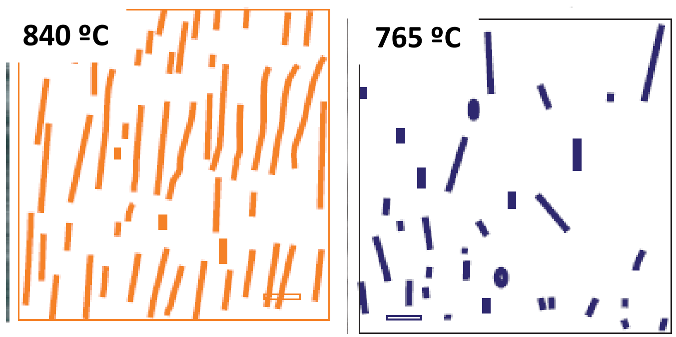
First demonstration of 3D epitaxial self-assembly in complex functional oxides

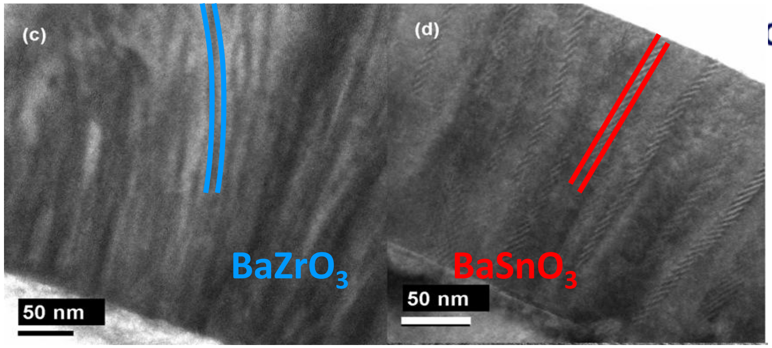
Anisotropic (correlated) pinning

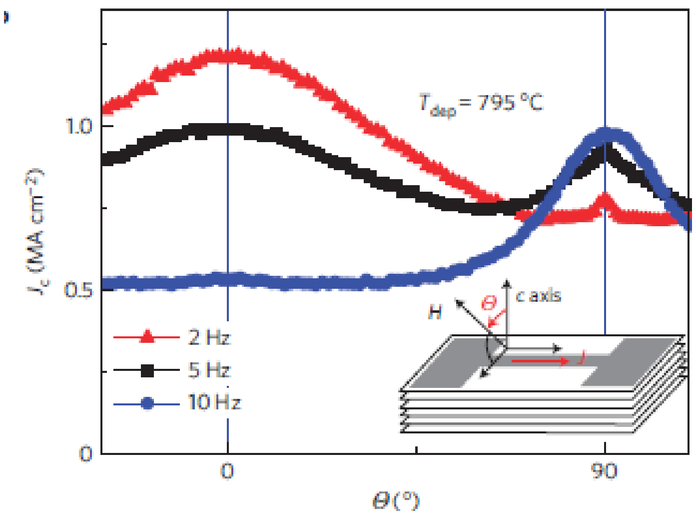
Yamada et al, APL 87(2005), A. Goyal, et al, SUST 18 (2005), Maiorov et al. Nature Mat. 8(2009)

Tunability of Nanocomposites by PLD

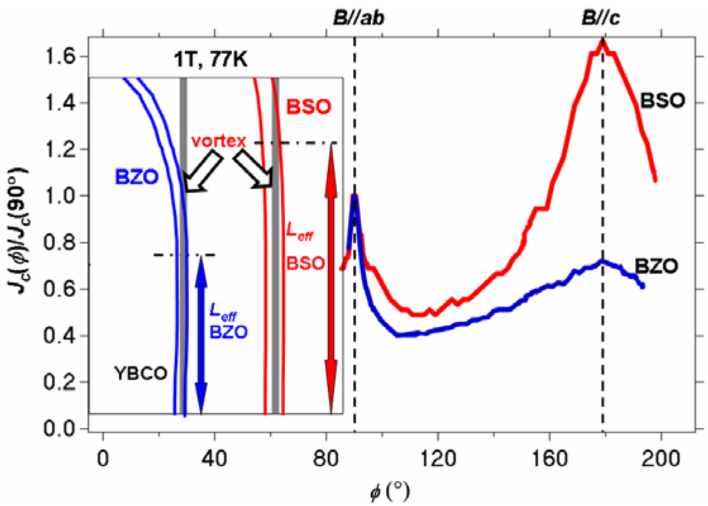
Growth temperature, growth rate, second phase composition determine self-assembling with direct consecuences on J_c







Maiorov et al. Nature Mat. 8(2009)



P. Mele et al, Supercond. Sci. Technol. 21 (2008)

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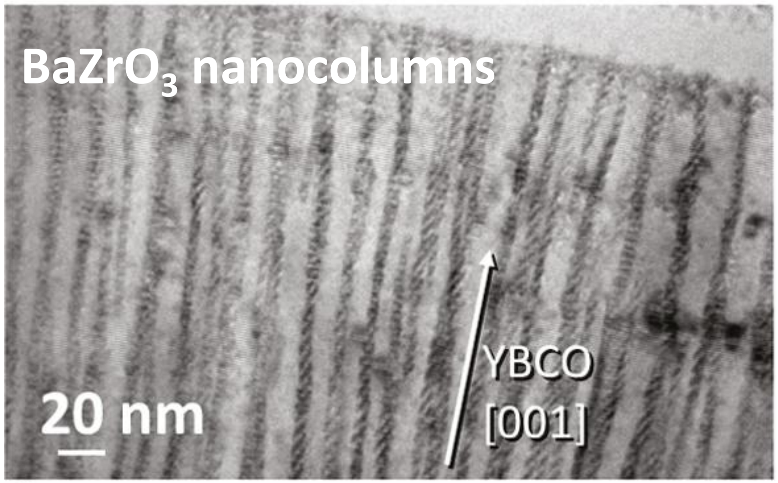
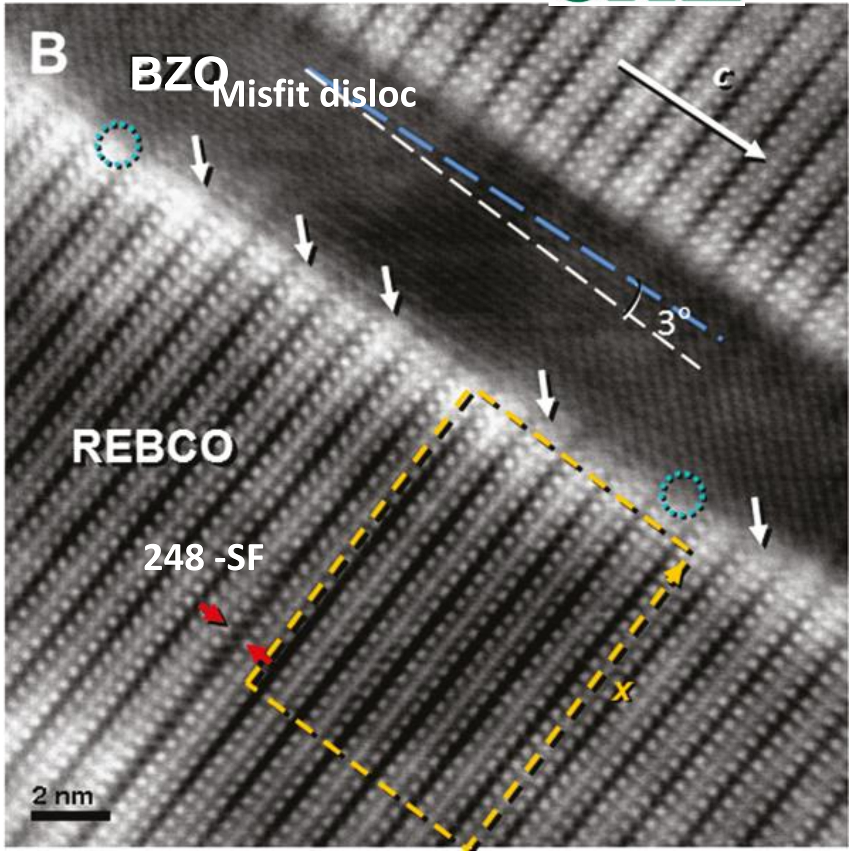
Self-assembly in PLD Nanocomposites

Strain field develope around the nanocolumns to reduce boundary energy inducing self-assembly



Misfit dislocations form at the YBCO/ BZO interface giving rise to a semicoherent strained boundary

Nanocolumns are pinning centers, but associated strain may also induce isotropic pinning at low T



C. Cantoni et al , ACSNano 2011

T. Puig -EUCAS 2015

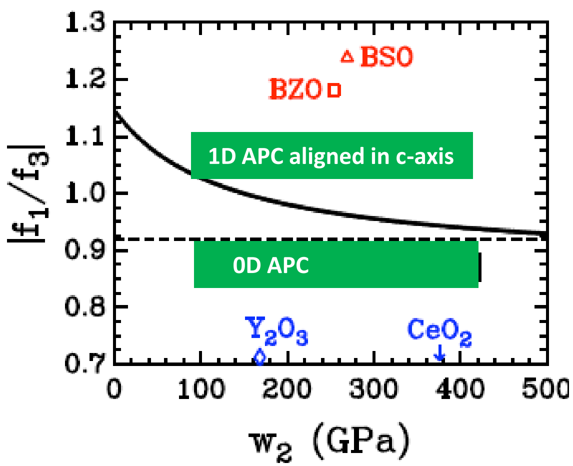
IEEE/CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), October 2015.
Plenary presentation PL7 given at EUCAS 2015; Lyon, France, September 6 – 10, 2015.
Not submitted to IEEE Trans. Appl. Supercond.

Elastic Strain Model

Understanding & controlling self-assembly of Artificial Pinning Centers

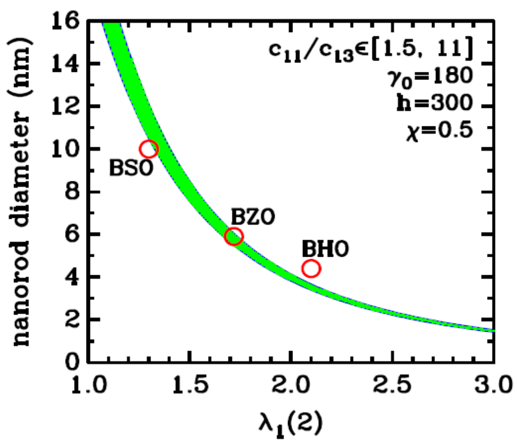
Univ. Kansas

Dimensionality of APC depend on elastic properties and lattice constants



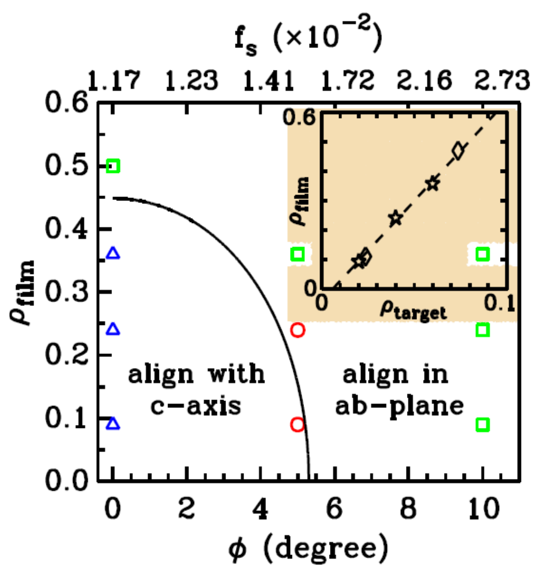
J. Shi and J.Z. Wu, *Philosophic Magazine* 92, 2911 (2012); *92, 4205* (2012).

Nanorod diameter depends on the inverse strain decay length $\lambda_1(2)$



J. Wu, et al, *SUST* 27, (2014); Shi and Wu, submitted

APC alignment direction depends on APC concentration and strain



F.J. Baca, et al, Advanced Functional Materials 23, (2013); J. Wu, et al, *IEEE TAS* 25 (2015); Wu et al, submitted

T. Puig-EUCAS2015

Advanced APC structures by PLD

Opportunities to tune Isotropic / anisotropic performances

Hiroshima University

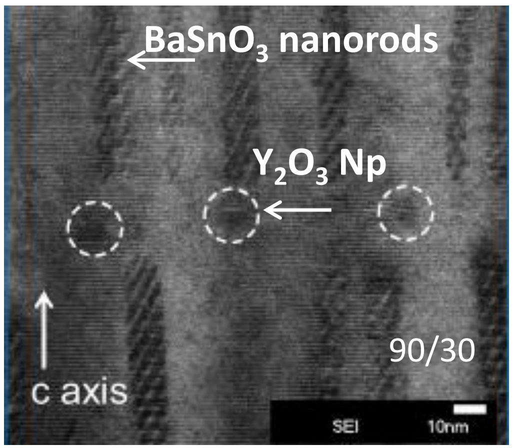
TOHOKU UNIVERSITY

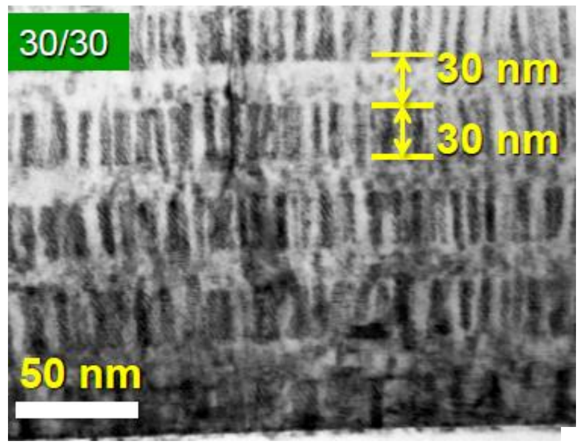
KYUSHU INSTITUTE OF TECHNOLOGY 1907

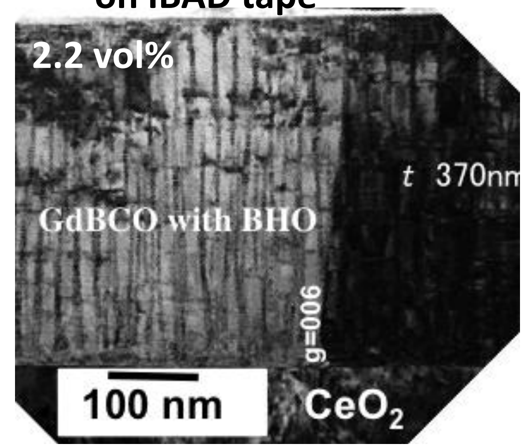
Hybrid multilayers

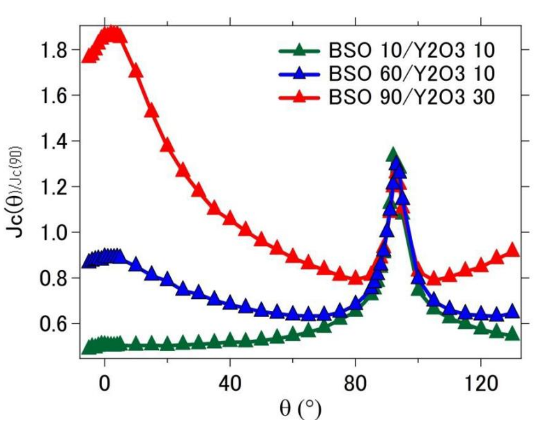
Segmented $BaSnO_3$ nanorods

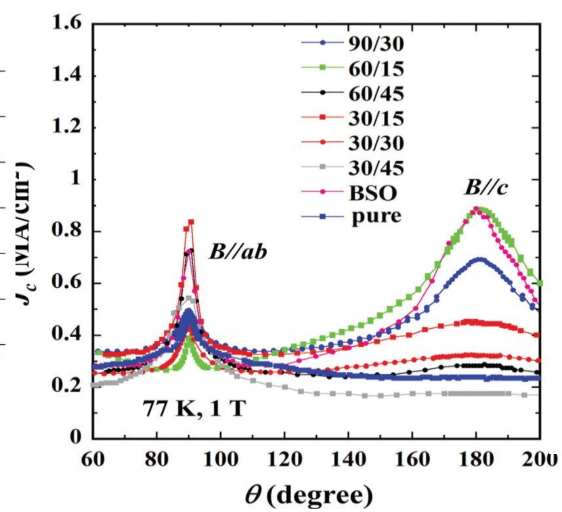
$GdBa_2Cu_3O_7$-$BaHfO_3$ on IBAD tape

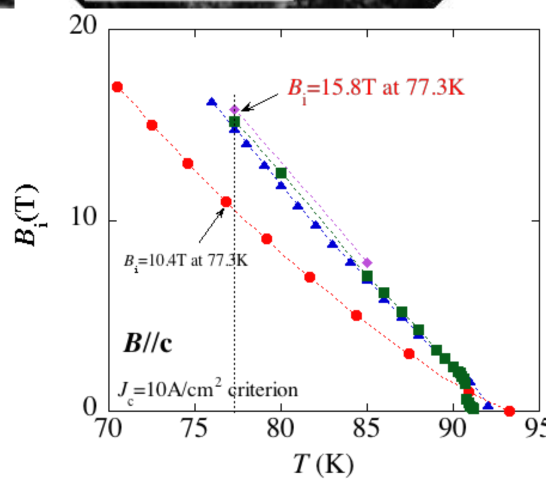












K. Matsumoto et al, 116 (2014)

S. Awaji et al, APEX 8 (2015)

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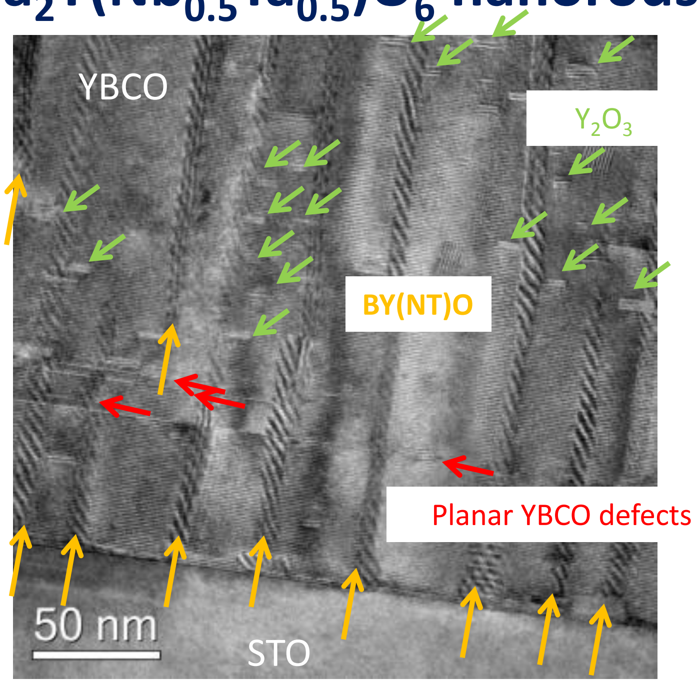
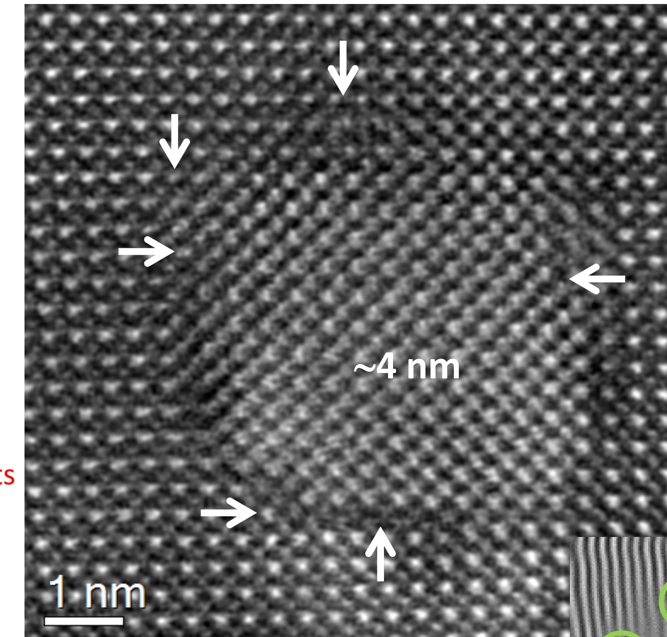
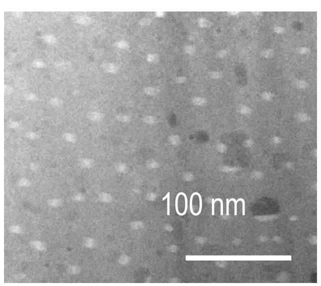
Mixed double perovskite nanocomposites

$Ba_2Y(Nb_{0.5}Ta_{0.5})O_6$ nanorods and Y_2O_3 nanoparticles

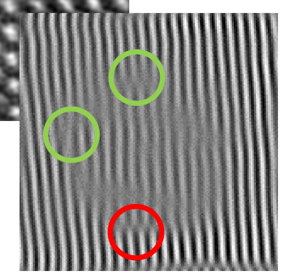






1 column / 30 nm
→ B_m = 2.2 T

10% cell parameter difference between YBCO and BYNTO causes the presence of misfit dislocations

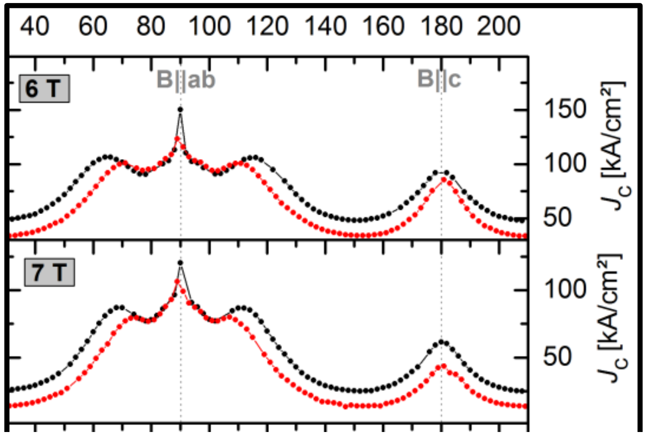


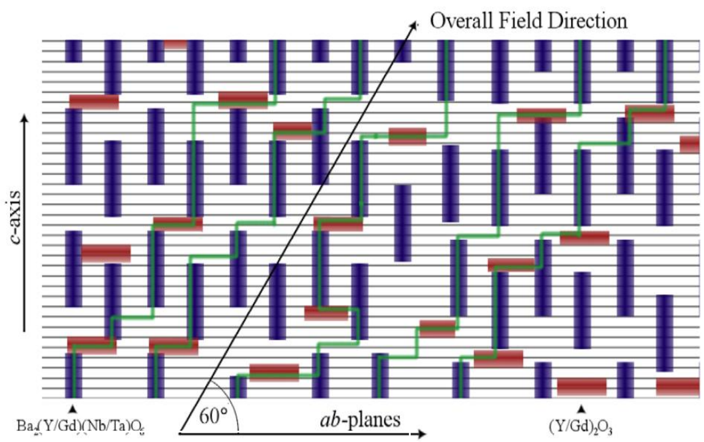
Rich pinning landscape → Complex J_c dependencies expected

G. Ercolano et al, SUST 24 (2011), Opherden et al,to be published

T. Puig -EUCAS 2015

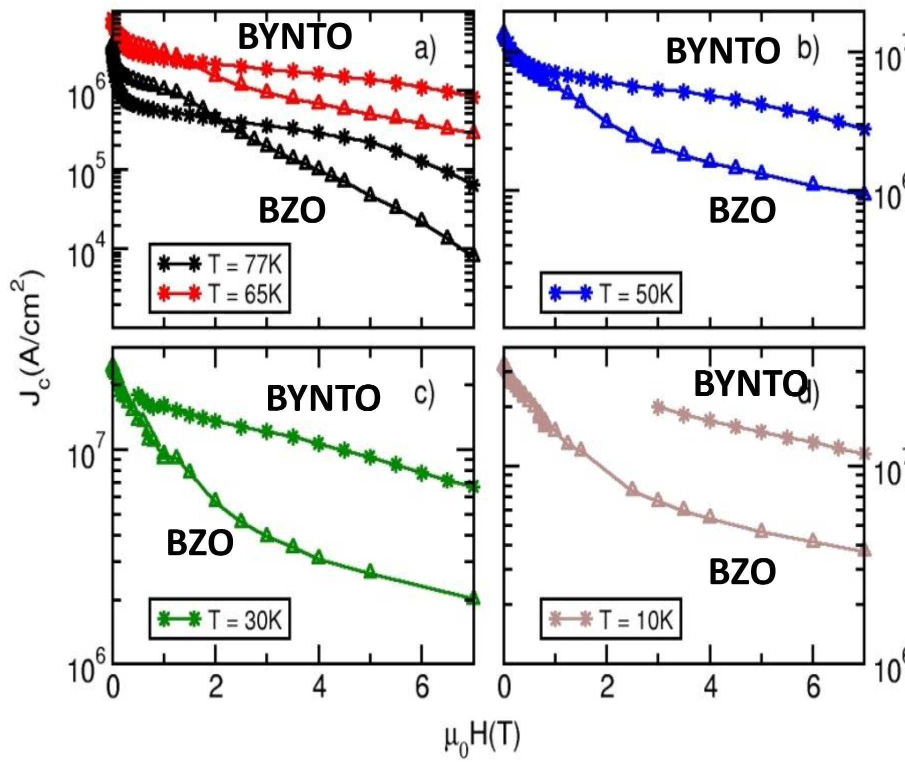
High pinning properties by mixed double perovskites





G. Ercolano et al, SUST 24 (2011)

Vortices accommodate simultaneously to nanorod-segments and nanoplatelets



F_{pmax} = 25 GN/m³ at 77 K
F_{pmax} = 750 GN/m³ at 10 K
among the highest values in literature

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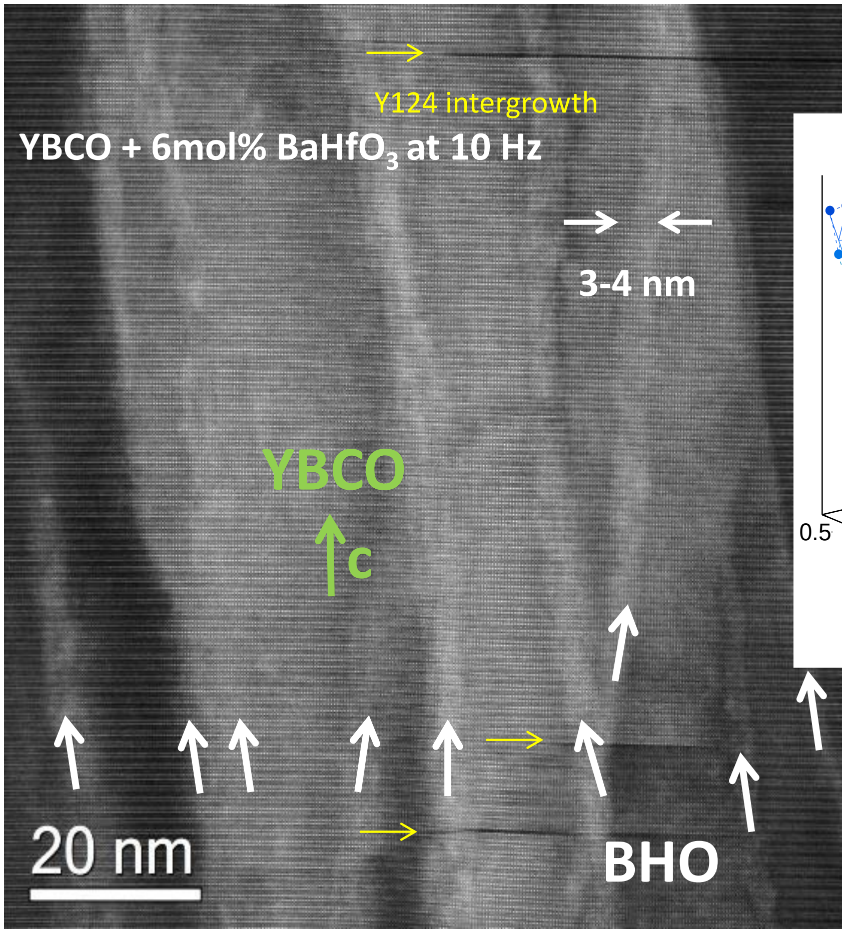
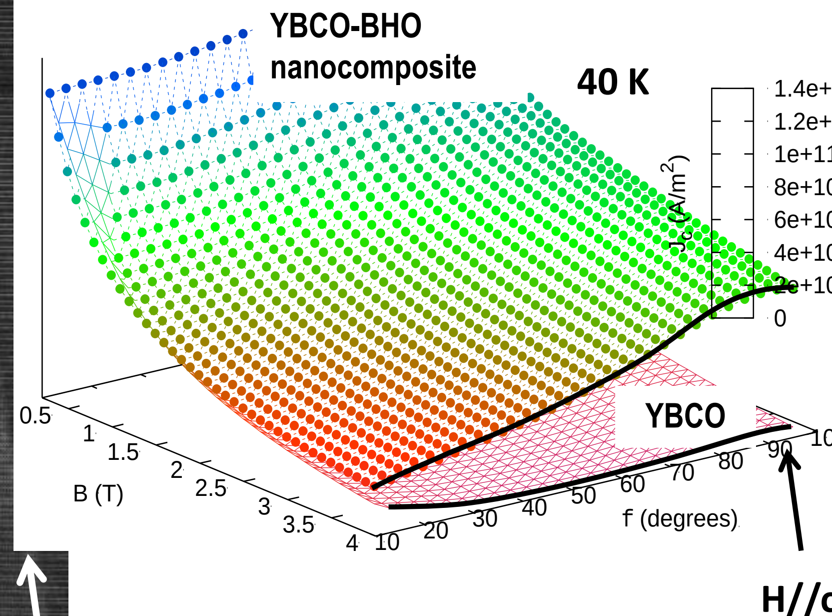
Fan-shaped $BaHfO_3$ nanorods by High Rate PLD on YSZ^{ABAD} substrates

Laser Frequency = 1-50 Hz



Pahlke et al., IEEE Trans. Appl. Supercond., to be published



Very effective at intermediate T

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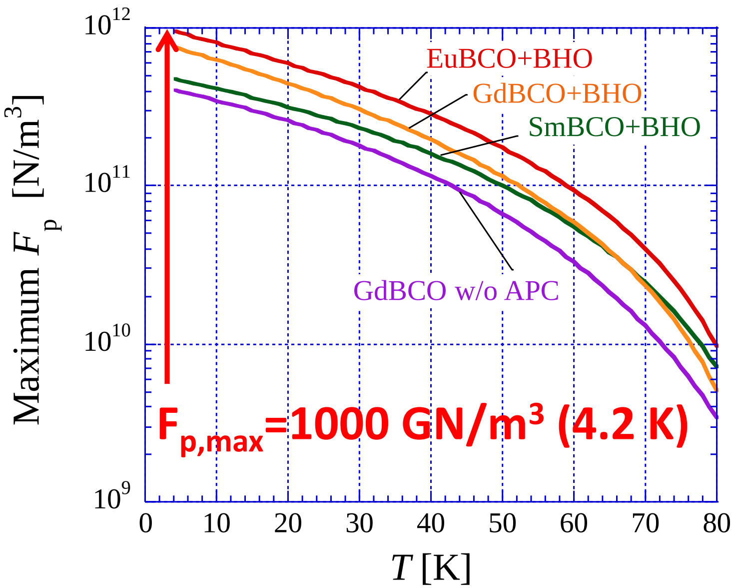
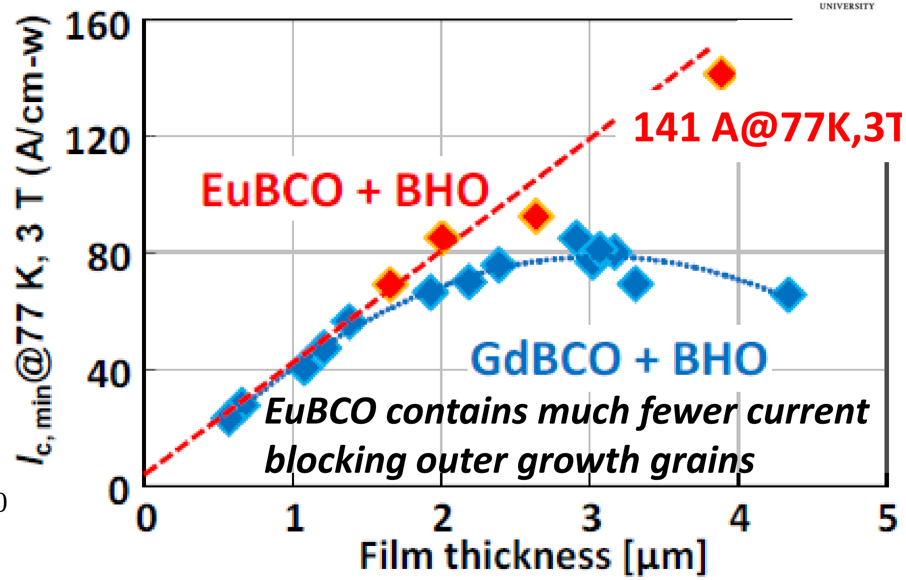
$EuBa_2Cu_3O_7$ + $BaHfO_3$ by PLD has superior properties and it is scalable

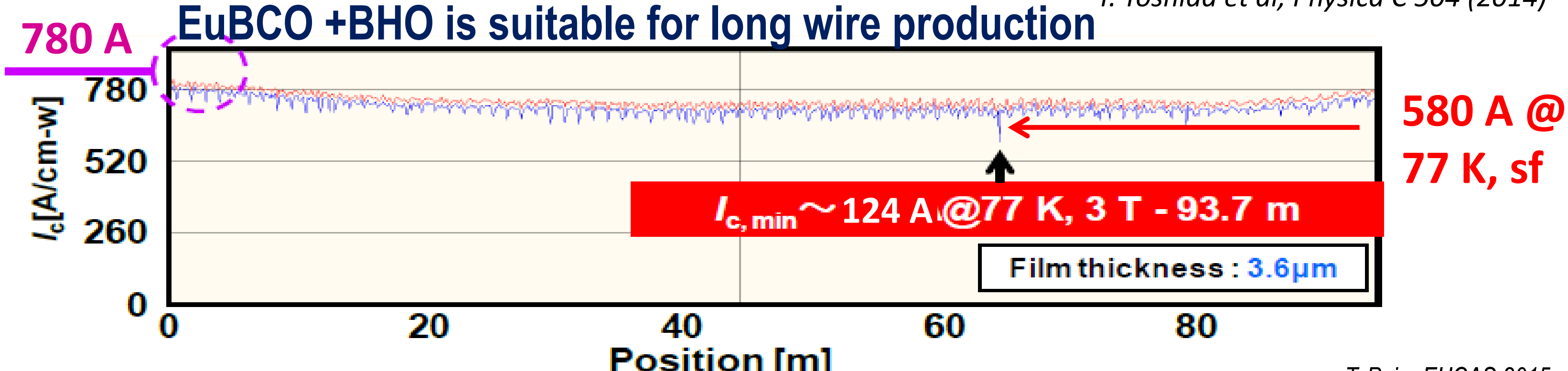
ISTEC iSTERA KYUSHU UNIVERSITY





T. Yoshida et al, Physica C 504 (2014)

EuBCO +BHO is suitable for long wire production



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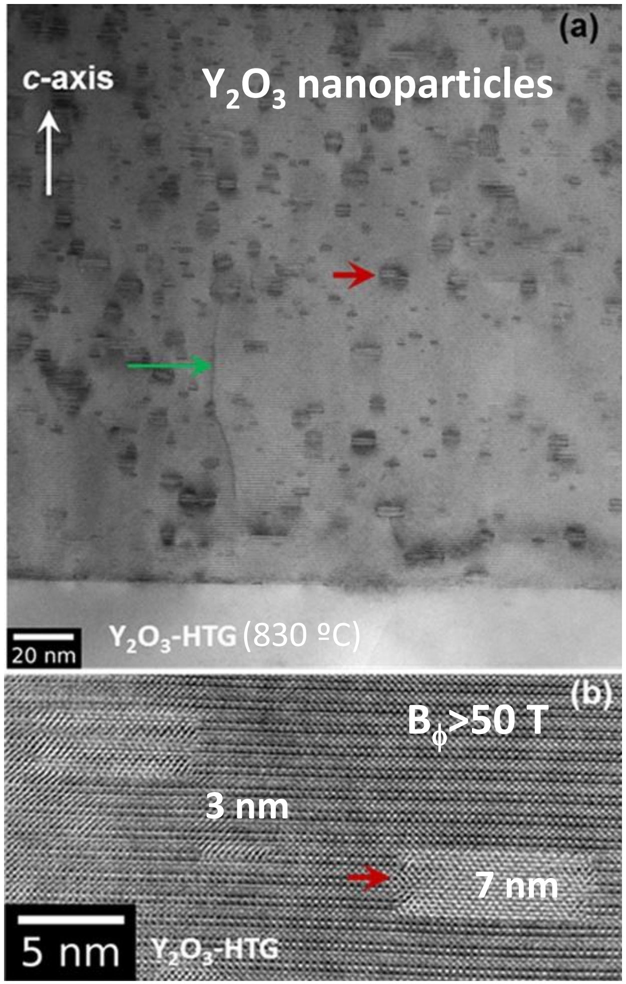
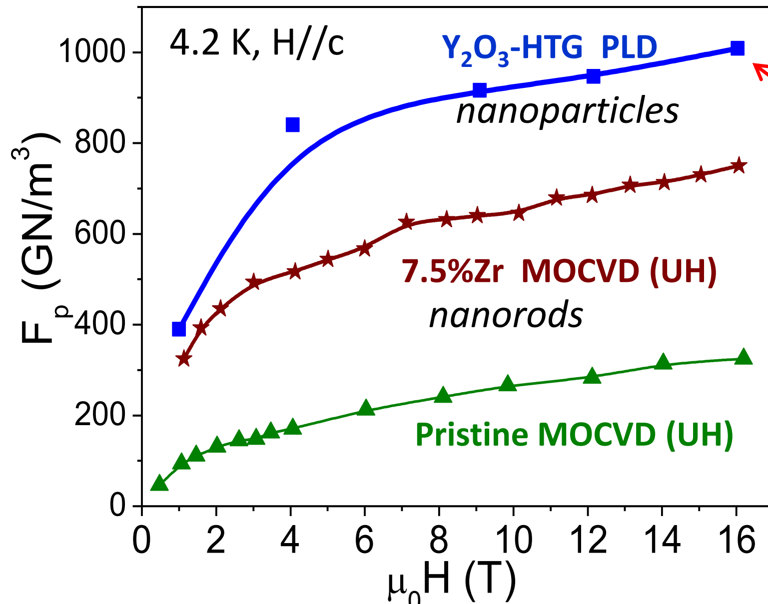
High F_p in YBCO PLD with Y_2O_3 nanoparticles

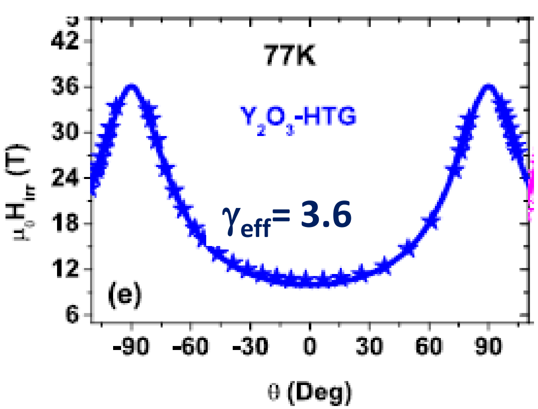
NHMFL
Tallahasse





F_p = 1000 GN/m³ is reached at 4.2 K, 16 T

(Ni-Ti at 16.5 GN/m³)



Isotropic strain pinning induced at low T

Reduced pinning anisotropy but $\gamma=H_{c2}^{ab}/H_{c2}^{c}$ = 5-7

A. Xu et al, Appl. Phys. Lett. 106 (2015)

T. Puig -EUCAS 2015

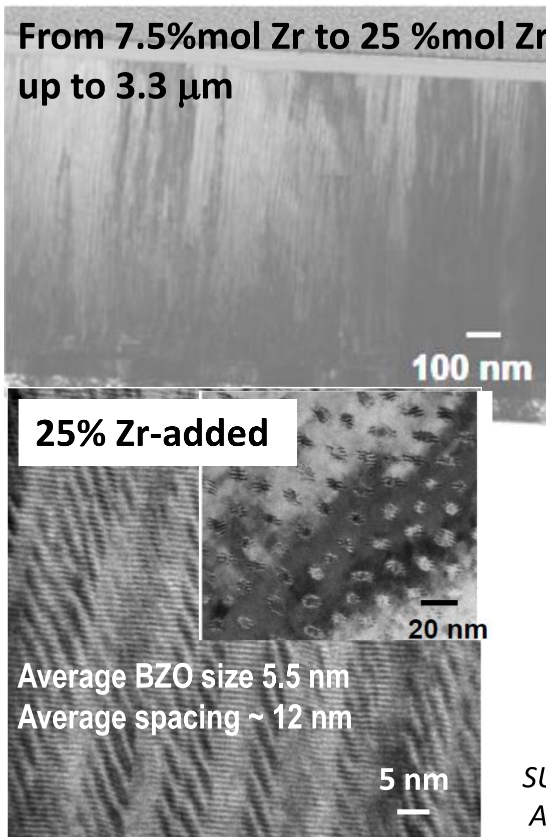
The Breakthroughs of Nanocomposites by MOCVD

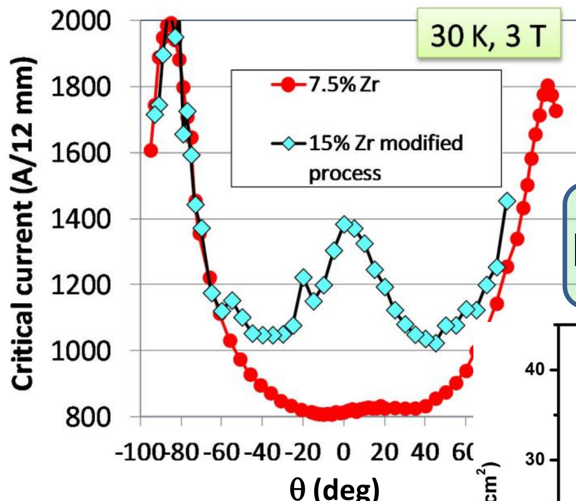
UNIVERSITY of HOUSTON

NHMFL Tallahassee

A **chemical vapor phase growth method** giving rise to a self-assembly process of **nanocolumns** through spontaneous phase segregation

(Y,Gd)BCO –BZO with extrem high density of BZO nanorods

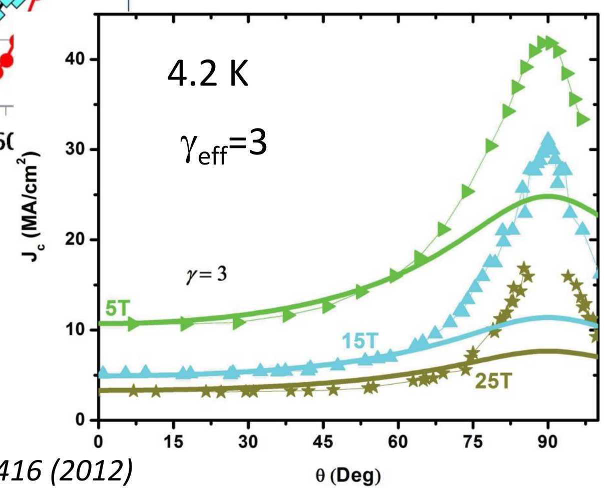




Anisotropic pinning from BZO nanorods dominates J_c *down to 30 K*

F_p=1650 GN/m^3 @4.2 K,30 T

Weak Isotropic pinning strain field around BZO nanorods dominates J_c *at low T*



SUST, 26, 035006 (2013), PRB 86, 115416 (2012)
APL MAT. 2, 046111 (2014)

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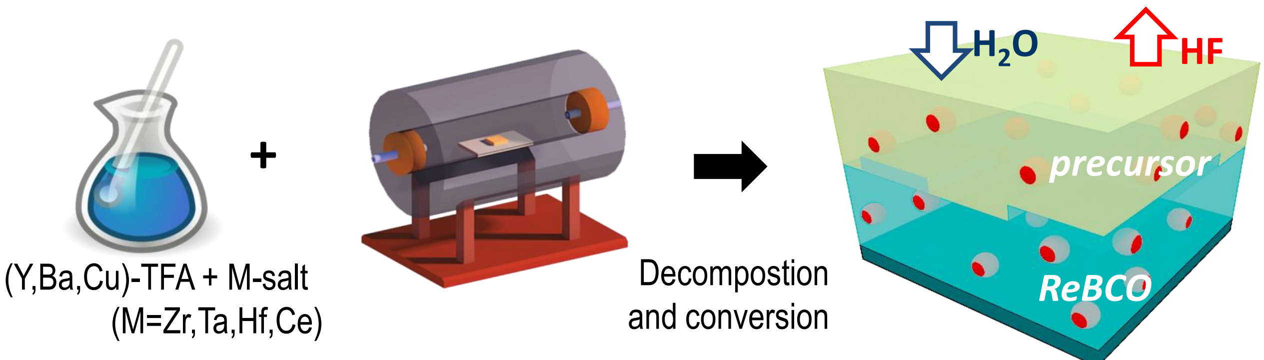
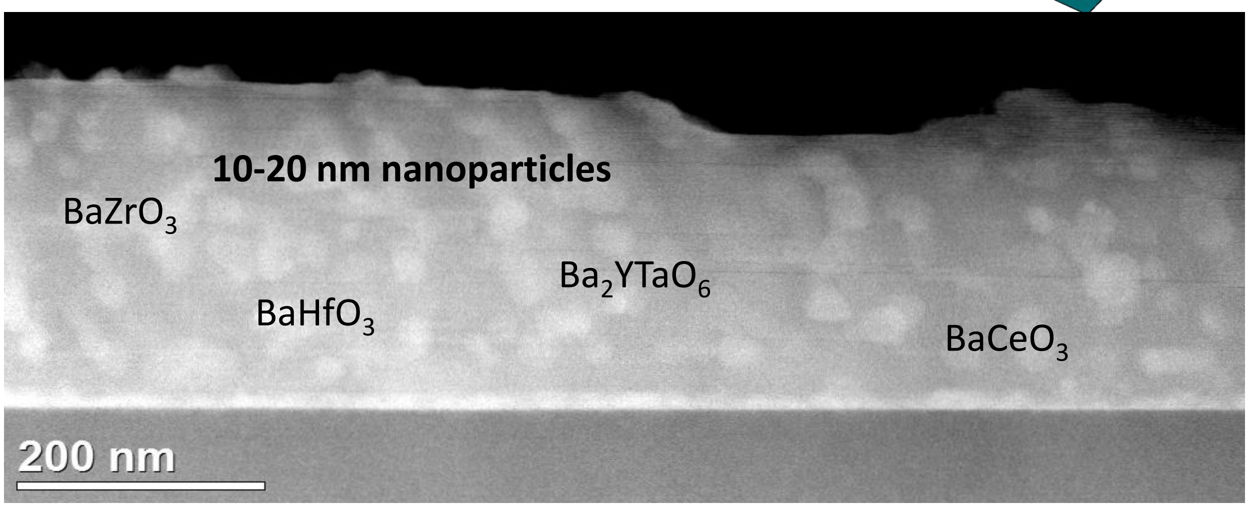
The Breakthroughs of Nanocomposites by Chemical Solution Deposition

A **chemical gas-solid reaction growth** method giving rise to a self-assembly process of **nanoparticles** through spontaneous phase segregation



TFA-route
- T
- Heating rate
- PO_2
- PH_2O
- Gas velocity
- P_{total}



Randomly oriented nanoparticles are segregated from the YBCO matrix

A. Llordés, et al. Nat. Mater , 11, 329 (2012), J. Gutierrez et al, Nat. Mater. 6, 367 (2007)

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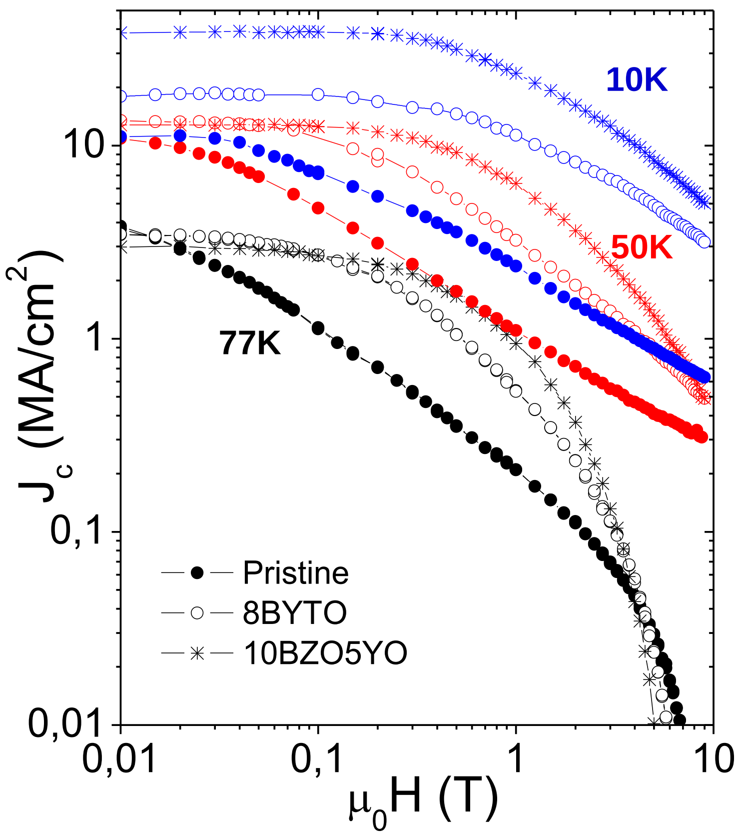
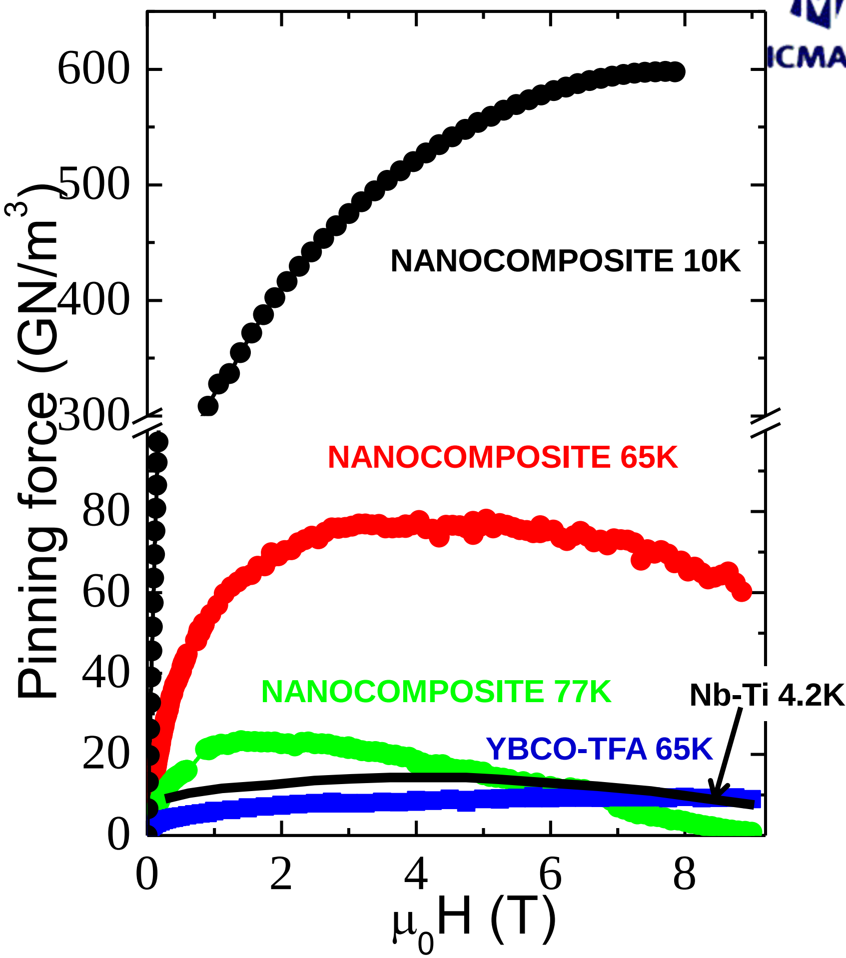
High performance of CSD-YBCO Nanocomposites

High performance at all temperatures

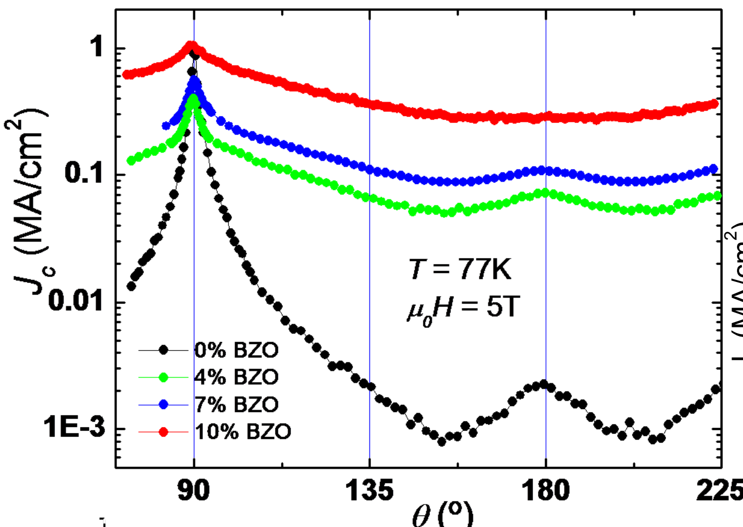


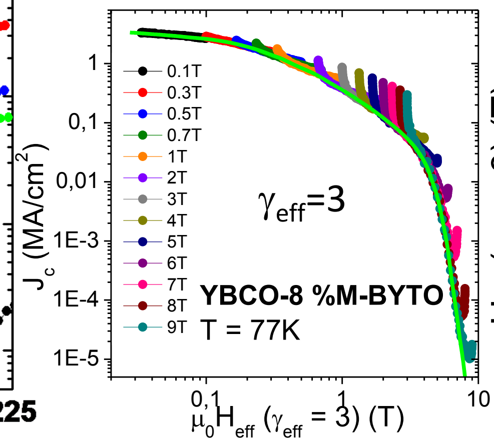


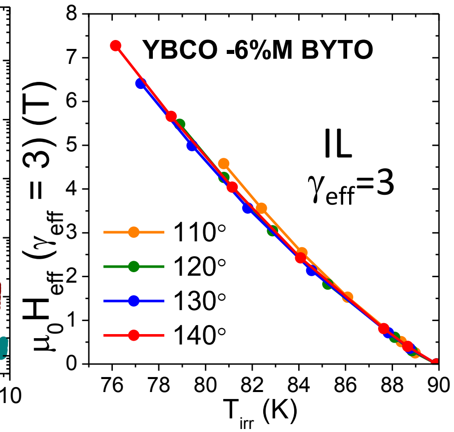
A. Llordés, et al. Nat. Mater , 11, 329 (2012),
J. Gutierrez et al, Nat. Mater. 6, 367 (2007)

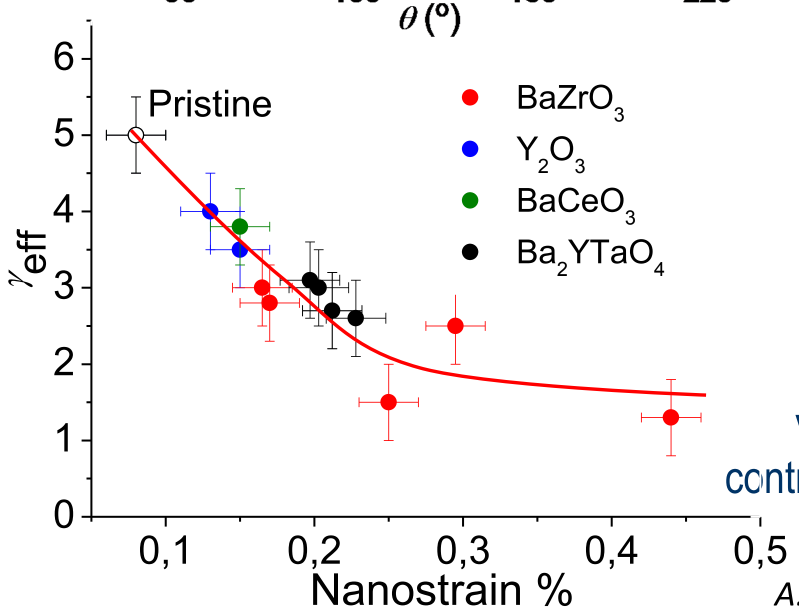
T. Puig -EUCAS 2015

Anisotropy in CSD Nanocomposites

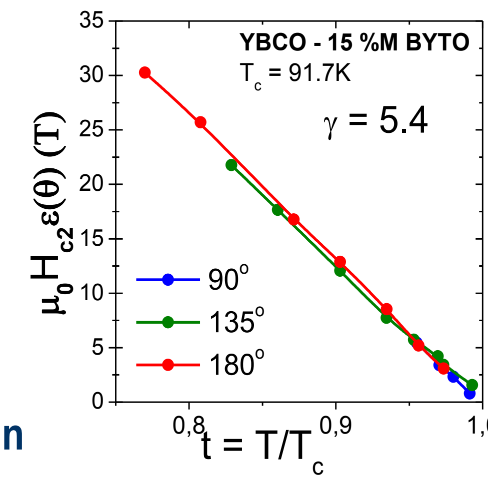








γ_{eff} reduction is
controlled by **nanostrain**

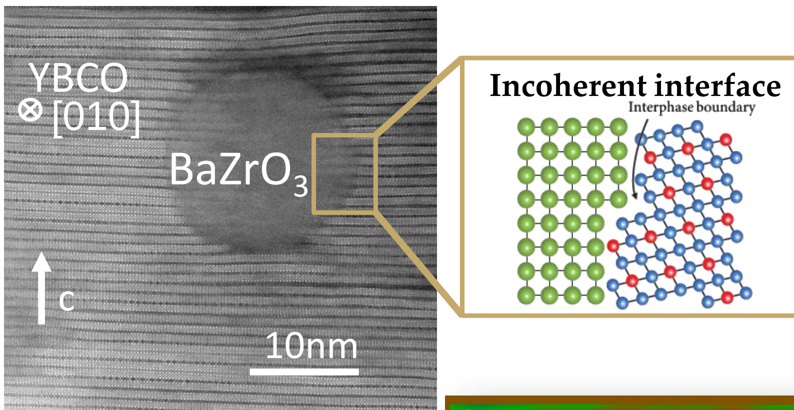


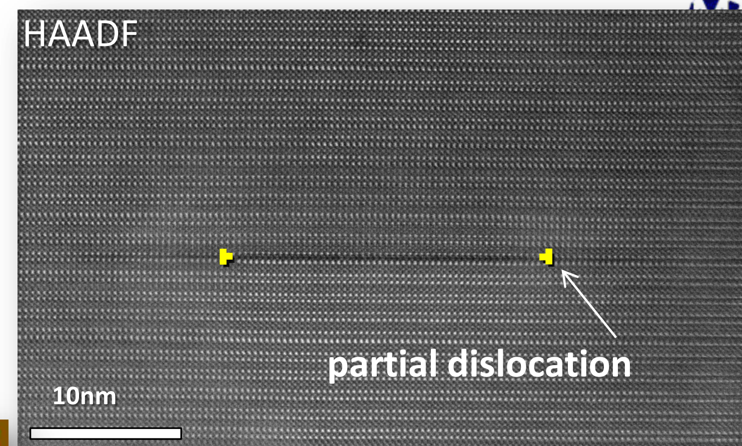
A. Llordés .T Puig., Nat Mat, 11 (2012)

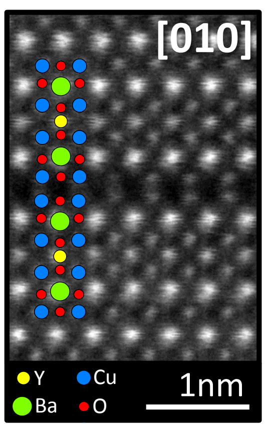
T. Puig -EUCAS 2015

Incoherent YBCO-$BaZrO_3$ interfaces give rise to high density of Y248 intergrowths and associated nanostrain

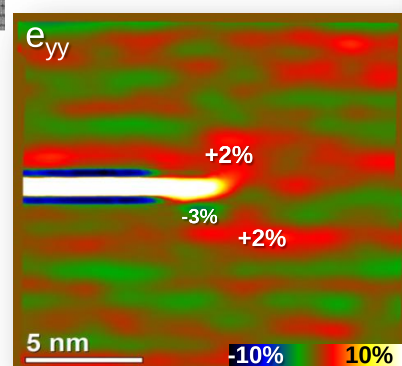
CSIC

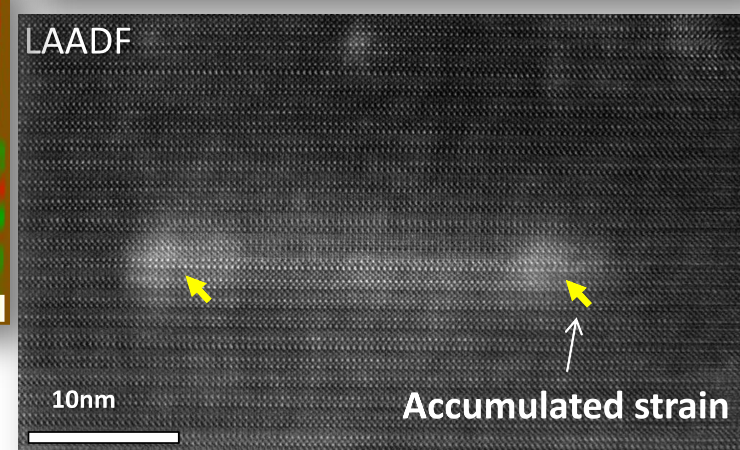






CuO double chain





APC (strain) is embeded in the YBCO matrix

A. Llordés, et al. Nat. Mater , 11, 329 (2012), J. Gutierrez et al, Nat. Mater. 6, 367 (2007)

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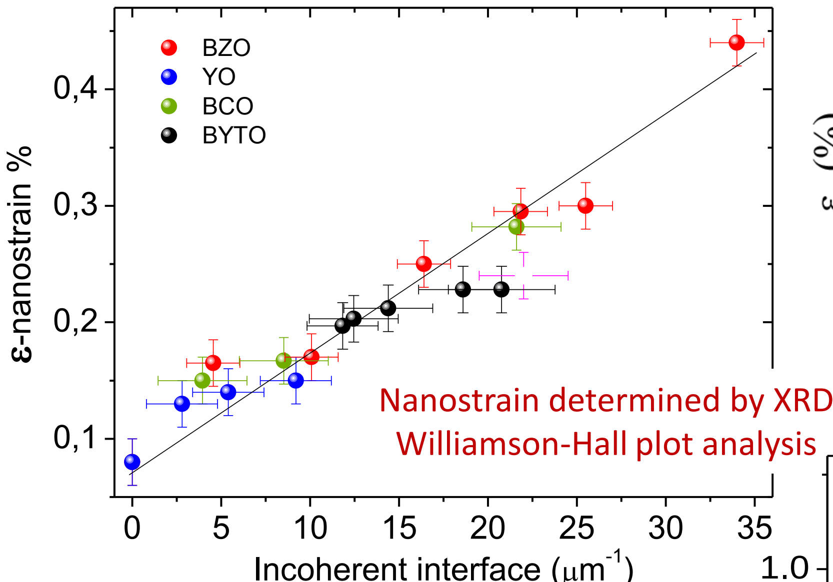
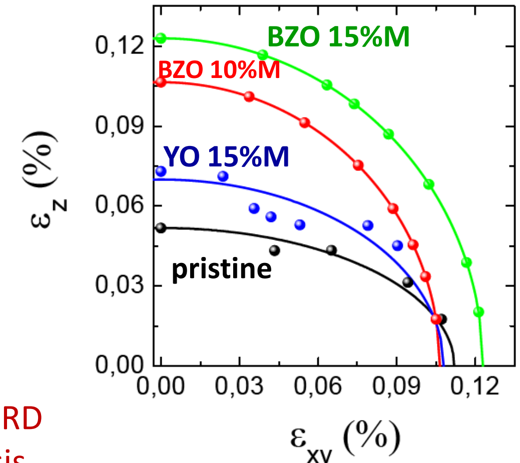
Local lattice strains control the **isotropic pinning** landscape of CSD-nanocomposites

CSIC

ICMAB

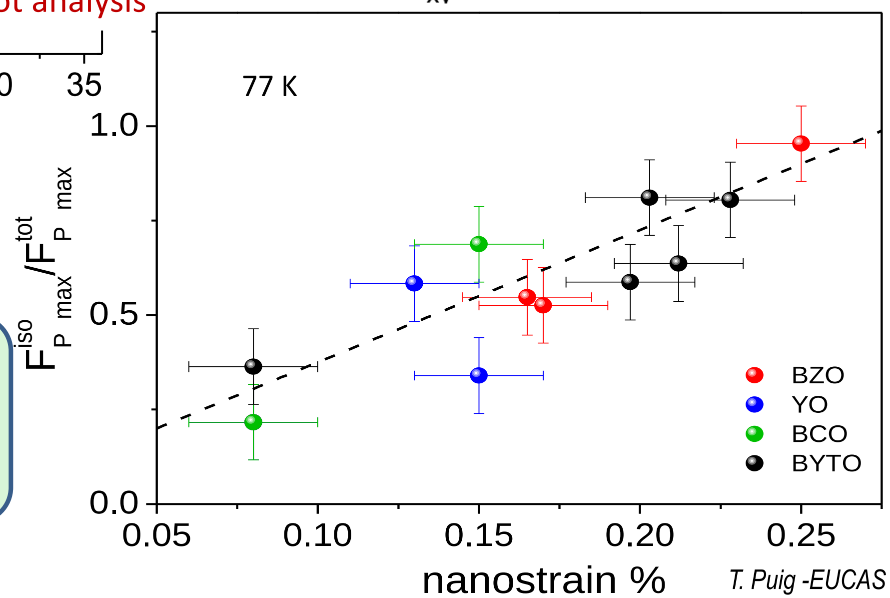




Random nanoparticles induce isotropic nanostrain

Nanostrain is controlled by random nanoparticles

The highest isotropic performance ever found in any superconducting material



A. Llordés et al., Nat Mat, 11, 329 (2012)

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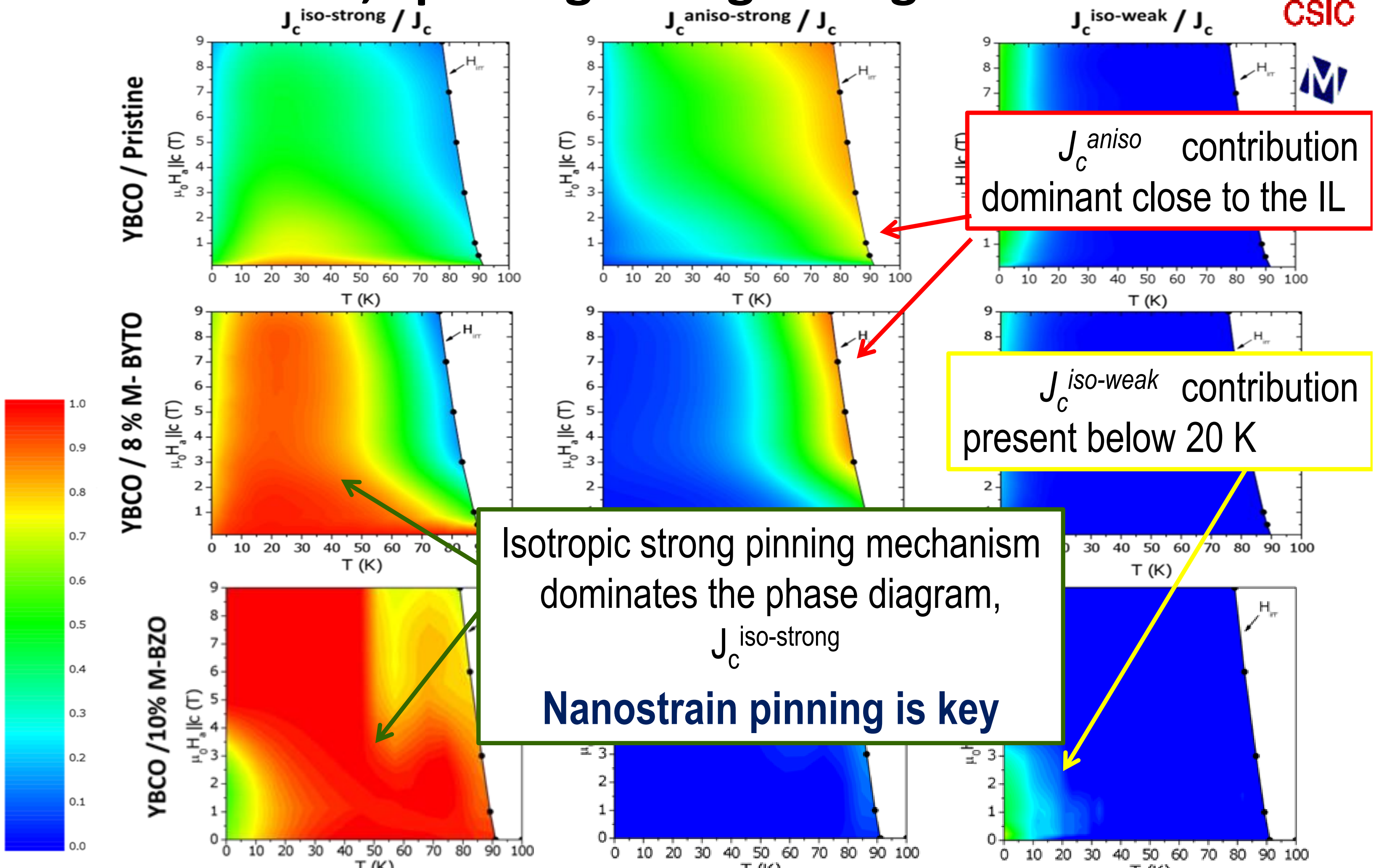
Pinning properties of CSD YBCO nanocomposites
H,T pinning strength diagrams



T.Puig et al., SUST 21 (2008); J. Plain et al, PRB 65, (2002); J.Gutierrez et al., Appl. Phys. Lett. 90 (2007)

T. Puig -EUCAS 2015

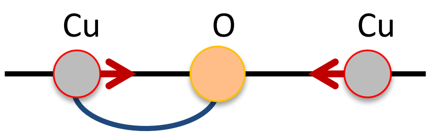
New vortex pinning mechanism based on strain induced Cooper-pair suppression

CSIC

ICMAB

Nanostrain leads to unpaired nanoscale regions

Bond
Contraction
Pairing :



G. Deutscher, APL (2010)
Llordes et al., Nat. Mater 2012

Pair breaking energy:

$$2\Delta = 4\frac{(t_{CuO})^2}{U} - 8t_0$$

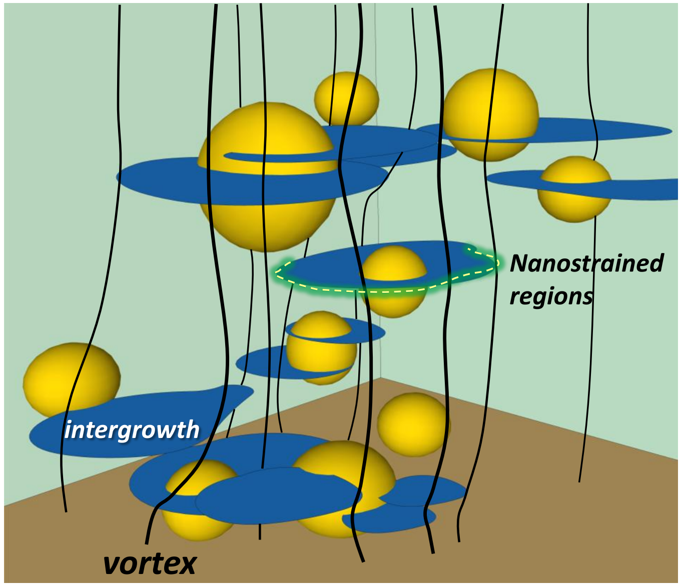
t_{CuO} ($\propto 1/d_{CuO}^5$)

- t_{CuO} : transfer integral between Cu *d* and O *p* orbitals
- U : on-site Coulomb repulsion
- t_0 : half bandwidth

Tensile strain quenches pair formation

Vortex bending accommodates to a ***3D* ramified network** of localized isotropic nano-strained regions

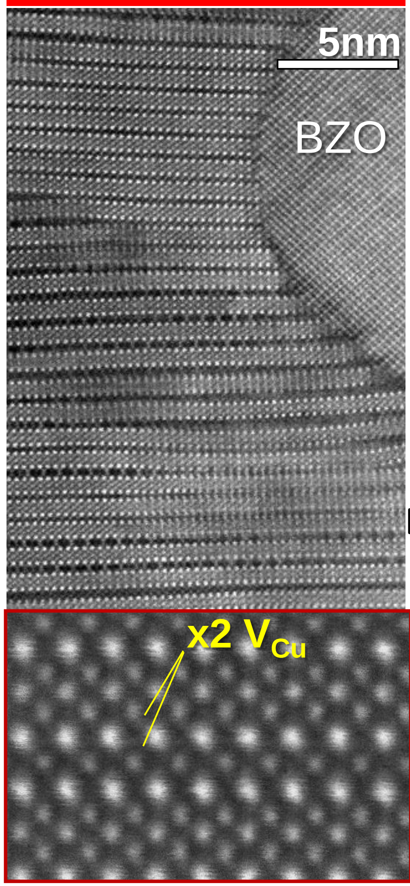
Isotropic Strong pinning occurs by saving vortex line tension energy in a significant fraction of their length



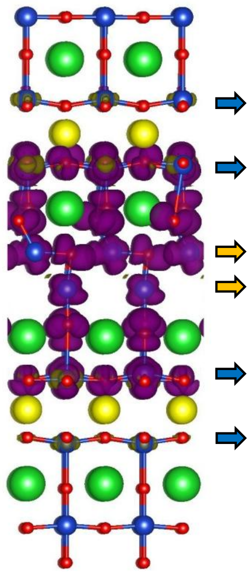
T. Puig -EUCAS 2015

Vacancies in Y248 intergrowth avoid Stoichiometry Catastrophe

YBCO + $BaZrO_3$

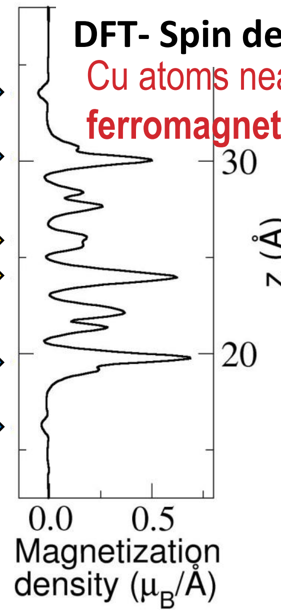


J. Gázquez et al, (submitted)

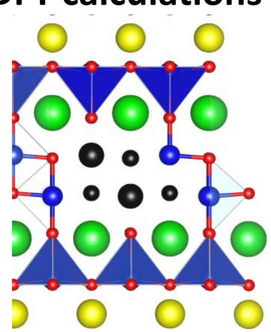


DFT- Spin density isosurface

Cu atoms near the vacancy align **ferromagnetically,** V_{Cu} ~ **1.1μ_B**



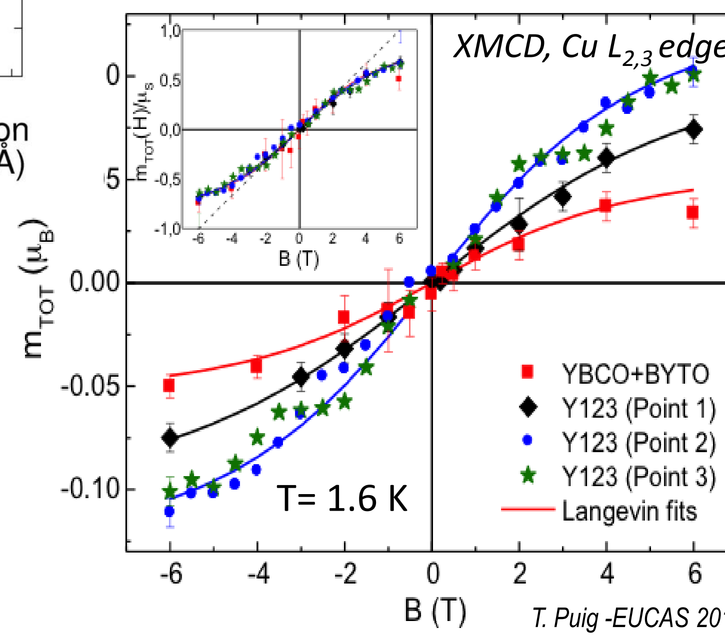
DFT calculations



2 V_{Cu} + 3 V_O

E/Cu=1.1 eV

This clusters induce dilute ferromagnetism in YBCO nanocomposites



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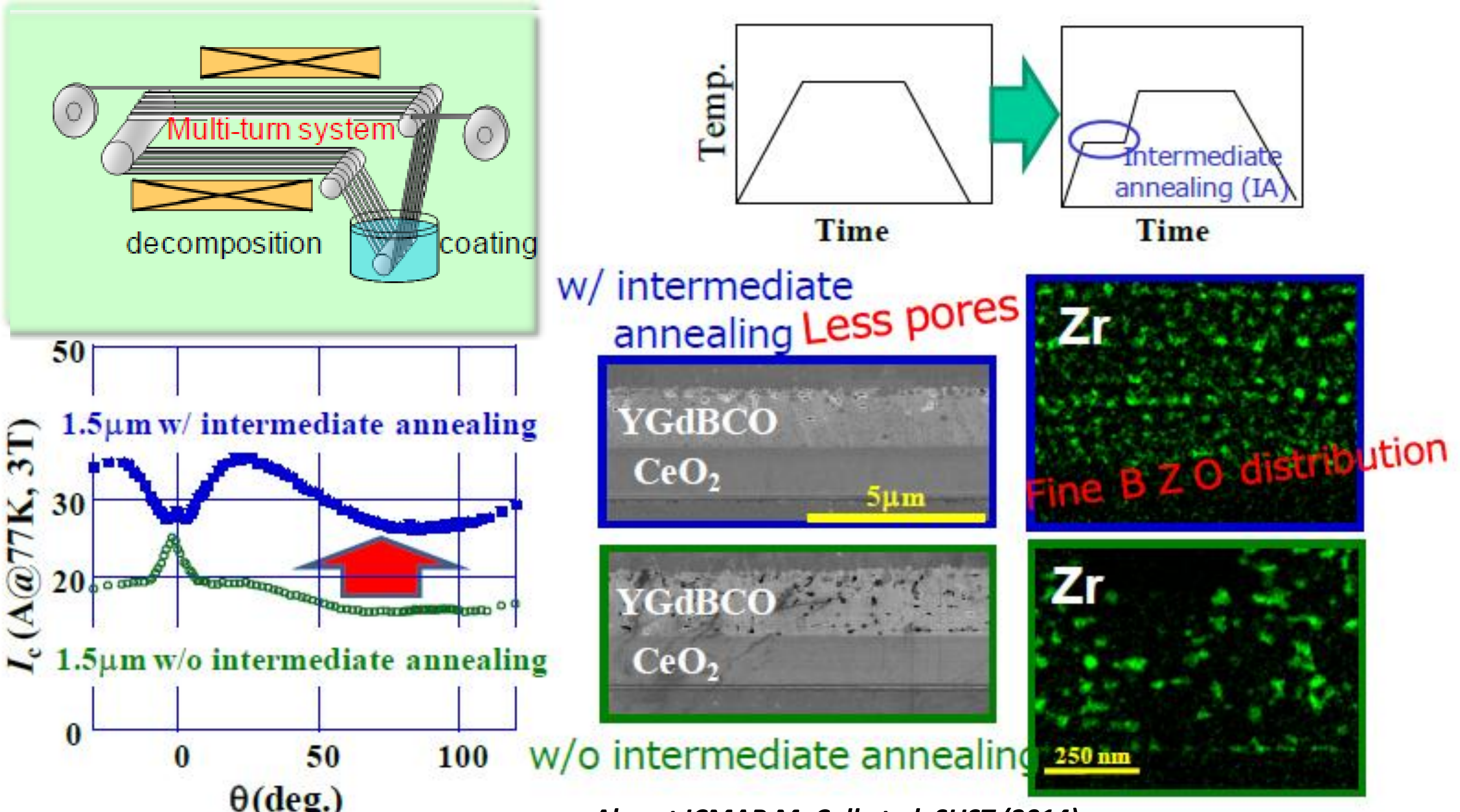
Nanocomposites by Chemical Solution Deposition : (Y,Gd)BCO+BZO

Improving in-field performance by limiting coarsening and avoiding porosity **in thick films** by an **interim processes**



Also at ICMAB M. Coll et al, SUST (2014)

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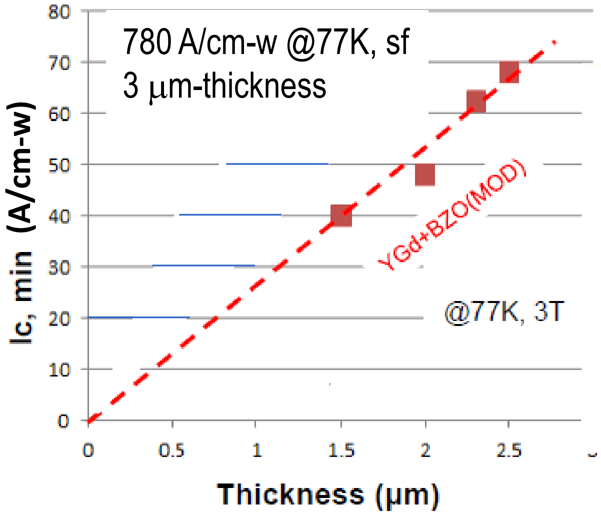
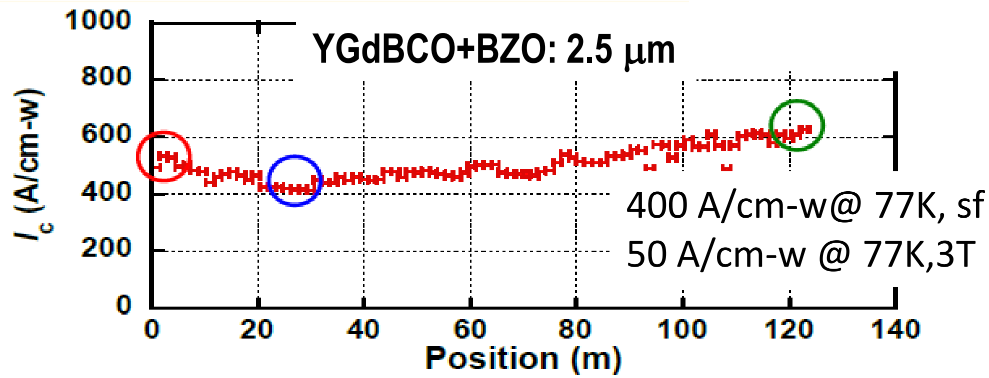
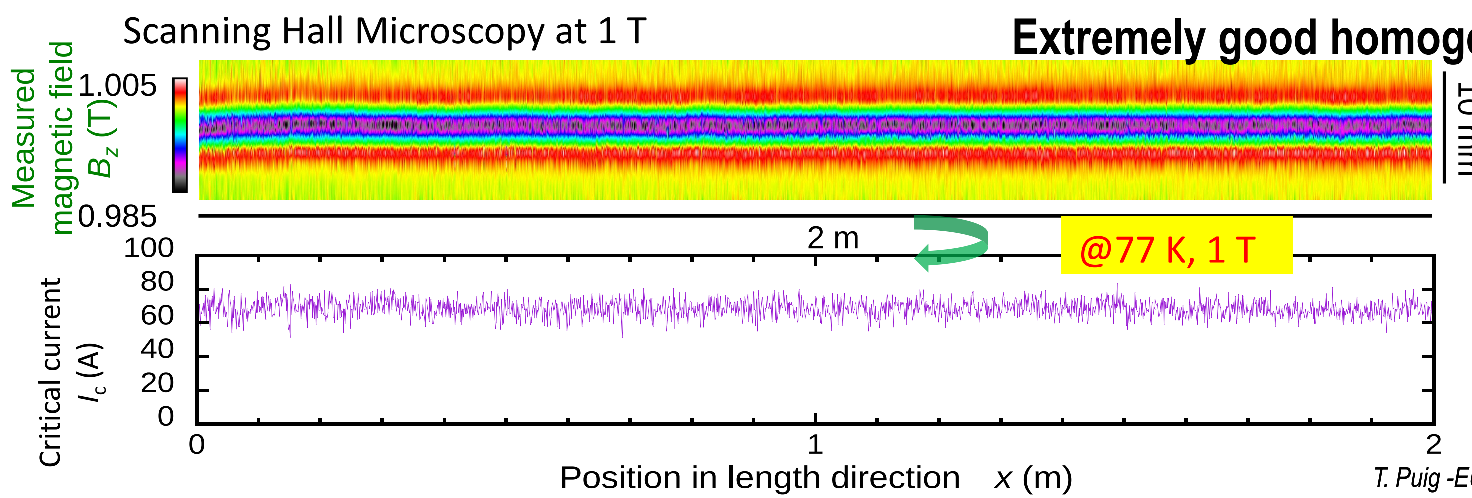
In-Field and Temperature dependence of (Y,Gd)BCO+BZO





CSD nanocomposites are scalable

Extremely good homogeneity



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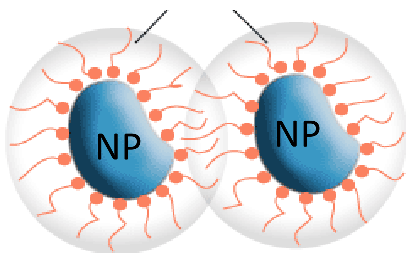
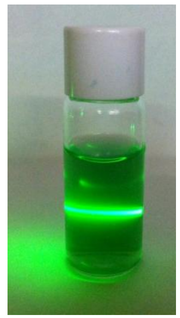
Nanocomposites by Chemical Solution Deposition with preformed nanoparticles

Stabilizing compound

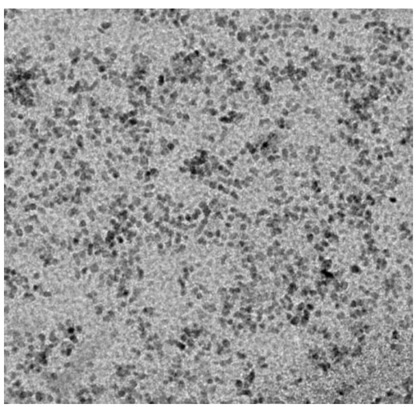




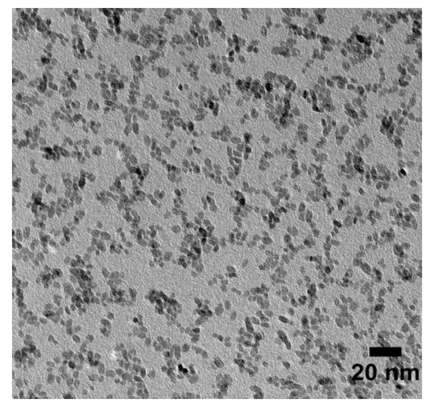
YBCO-TFA+ZrO_2 Np

Thermal and microwave-assisted solvothermal synthesis of nanoparticles

ZrO_2 Np(8x2 nm) in YBCO-TFA solution



CeO_2 Np(2 ±0.4 nm) in YBCO-TFA solution

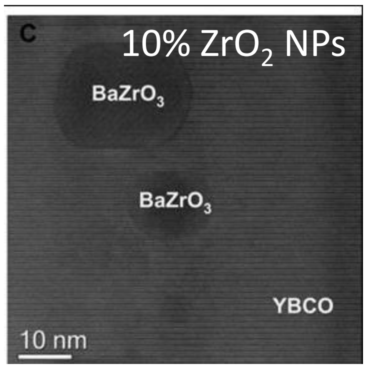


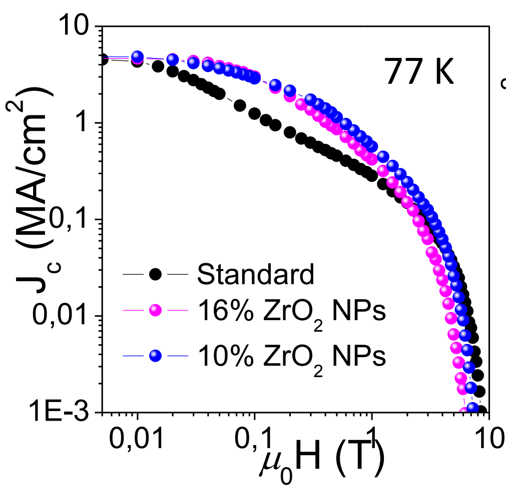
Several **oxide nanoparticles** could to be **stabilized in alcoholic and ionic environment** of YBCO precursor solution **at high concentrations**

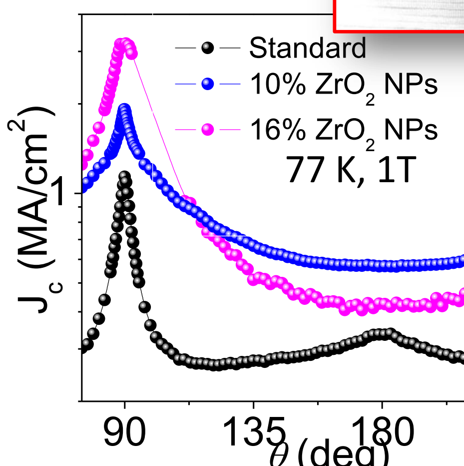
P. Cayado, K De Keukeleere, et al SUST (submitted), F. Martinez-Julian, T.Puig et al. J. Nanosc.&Nanotech. 11 (2011)
I. Bretos et al, J. Mat. Chem. C 3 (2015), K. De Keukeleere et al, Inorg. Chem. 54 (2015)

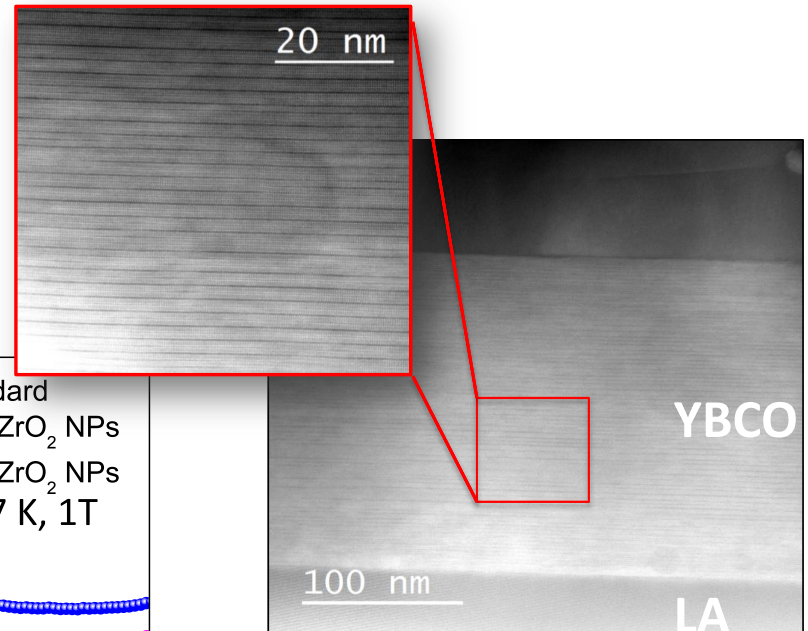
CSD growth of Nanocomposites with preformed nanoparticles

Growth of **colloidal solutions** tend to induce **nanoparticles reactivity, pushing, coarsening** or **accumulation** at the substrate interface, but performance starts to show up









γ_{eff} ~2.4- 3

An opportunity to further enhance CSD performance

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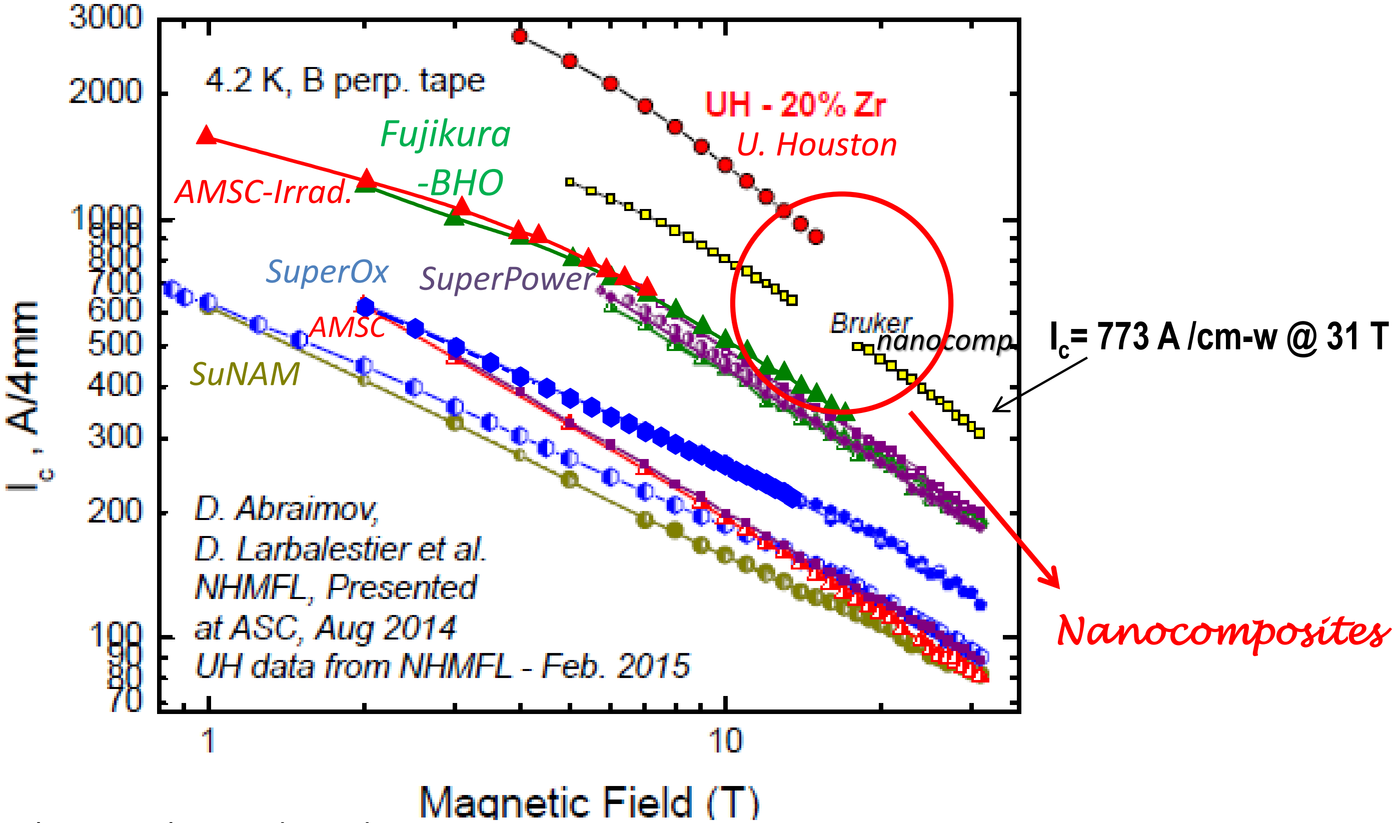
Nanocomposite Coated Conductors

A reality and yet continuously improving

Now, strong interest for low temperature properties and ultrahigh magnetic fields



Courtesy of V. Selvamanickam -adapted

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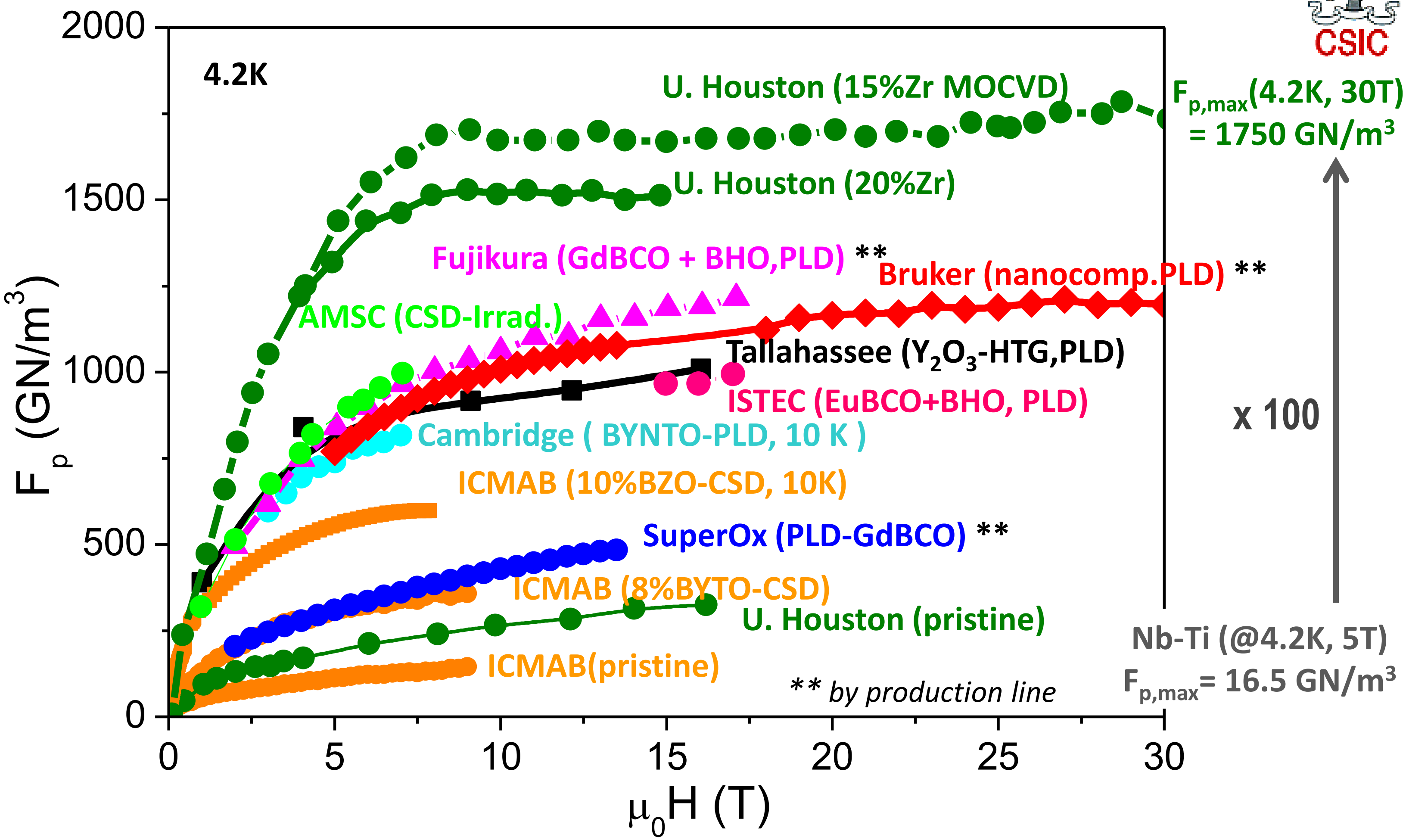
Extraordinary future for ultra-high field applications

CSIC



Isotropic (random) strain seems to be a common feature for increasing properties at low temperature and reach ultrahigh fields with nanocomposites

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CONCLUSIONS

CSIC

ICMAB

- **We are ready for HIGH FIELD CONDUCTORS development and optimization based on Nanocomposite Coated conductors (NCCs)**
- We should concentrate effort on **vortex pinning at 4.2 K**
- **HTS must join LTS efforts**
- NCCs are **scalable based on “react and wind”**
- Reinforce **fast and low cost growth** methods
- **Expanding manufacturing capabilities will decrease cost (Figure of merit €/kA-m @ H,T)**
- **R&D in technology issues beyond Critical Current:** Compactness, transposition, quench detection, protection, joints, insulation, mechanical strength, …

A winning story of joint efforts

Materials **E**ngineers, **P**hysicists, **C**hemists, **E**lectrical **E**ngineers, **M**anufacturers: **The Superconducting Community**

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