NANOFABRICATION APPROACHES IN SUPERCONDUCTIVITY FOR ENERGY APPLICATIONS

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Nanofabrication: concepts, techniques and applications in Nanotechnology
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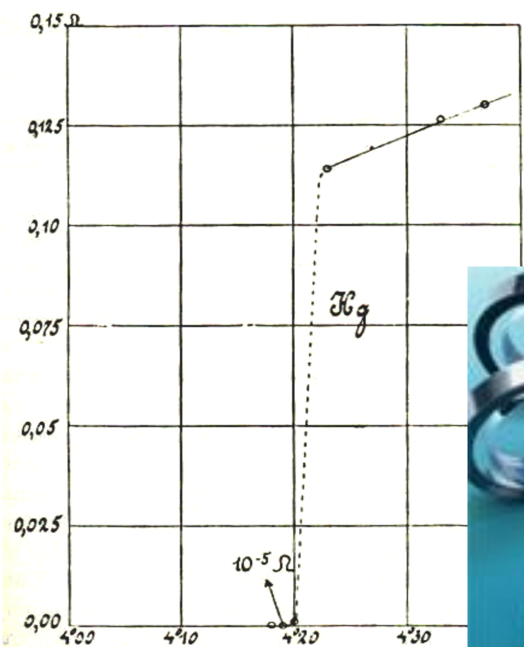
OUTLINE

- Basic properties of a superconductor
- Applications of superconductors
- Importance of the nanotechnology in superconductivity
    - Improve vortex pinning in CC
    - Manipulate and gather knowledge on vortex motion in model systems
- Summary

Superconducting Materials

THE PERFECT CONDUCTOR

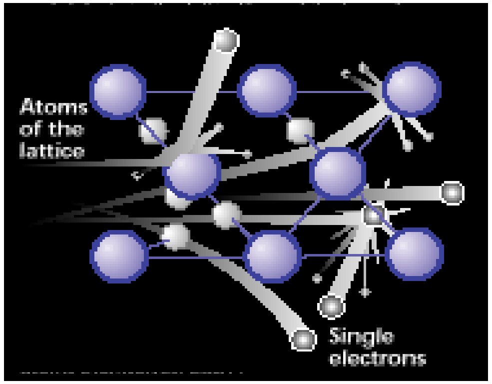
Current flows without resistance below critical temperature, T_c



1911
Kamerlingh Onnes

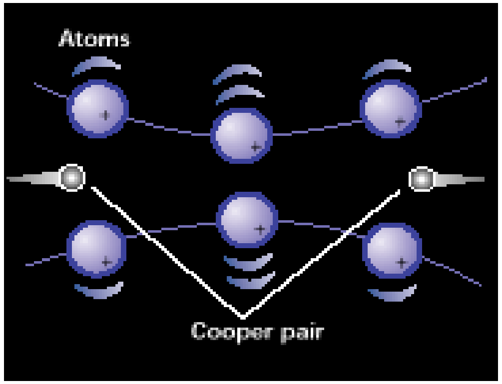
Superconducting wire → current without dissipation

"normal" State



Electrical resistance due to collisions of electrons → energy losses

Superconducting State



Electrons are bounded in pairs and cannot be scattered at impurities → **NO** energy losses

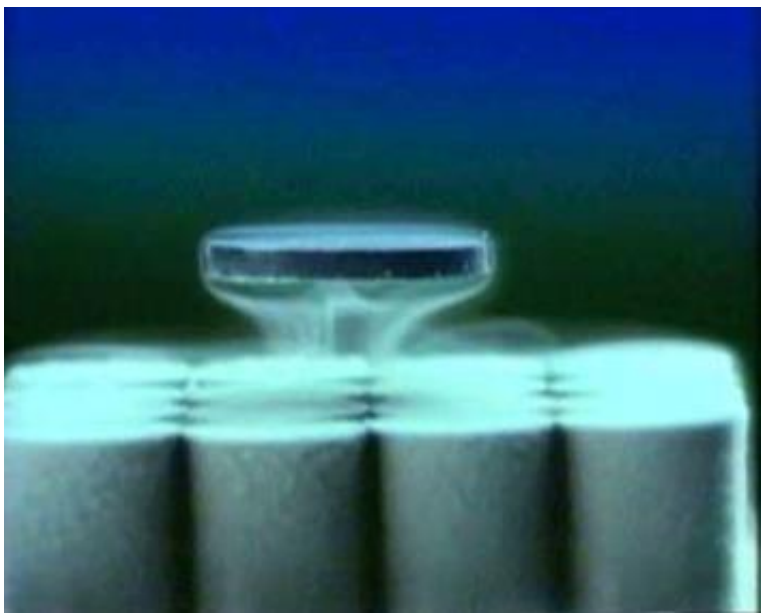
Superconducting Materials

THE PERFECT DIAMAGNET

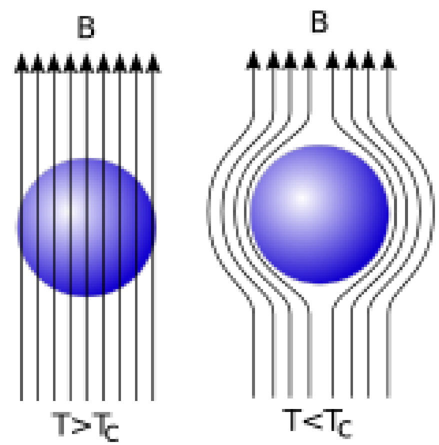
The unusual magnetic properties of superconductors

1933
Meissner & Ochsenfeld
Berlin

Meissner effect: Magnetic field expulsion



Superconductor Levitation

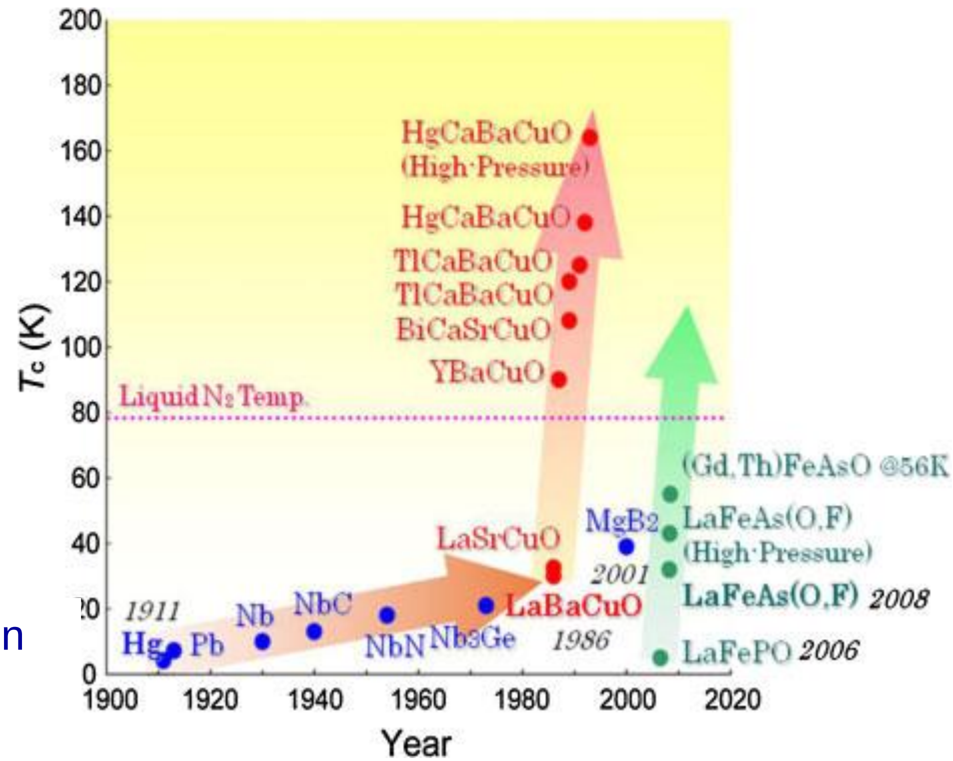


superconductors were more than just perfect conductors !

High temperature superconductors

A revolution for material science

1986: The discovery of copper oxide SCs
J.G. Bednoz and K.A. Müller
1987: Nobel prize

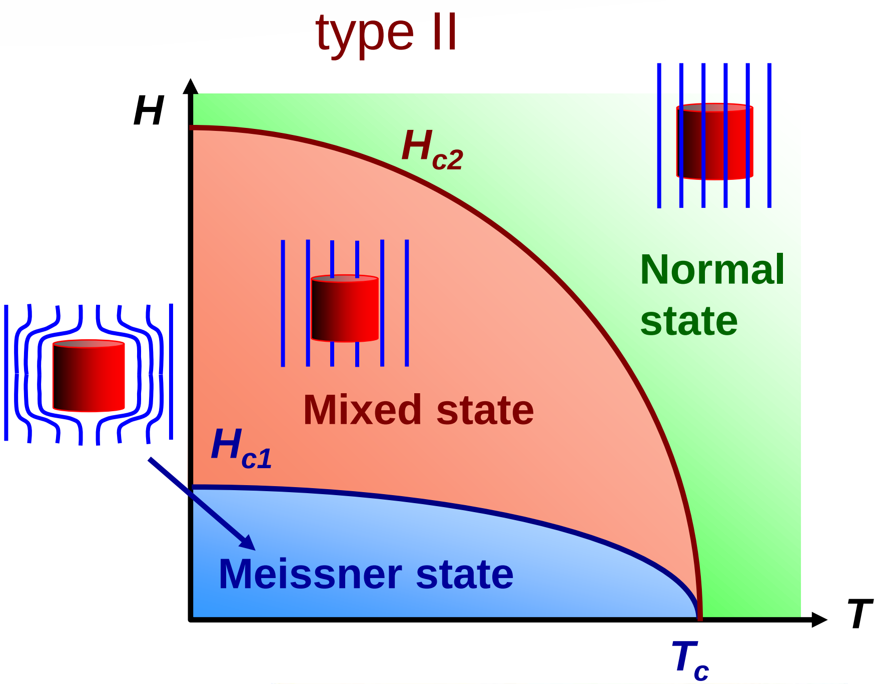


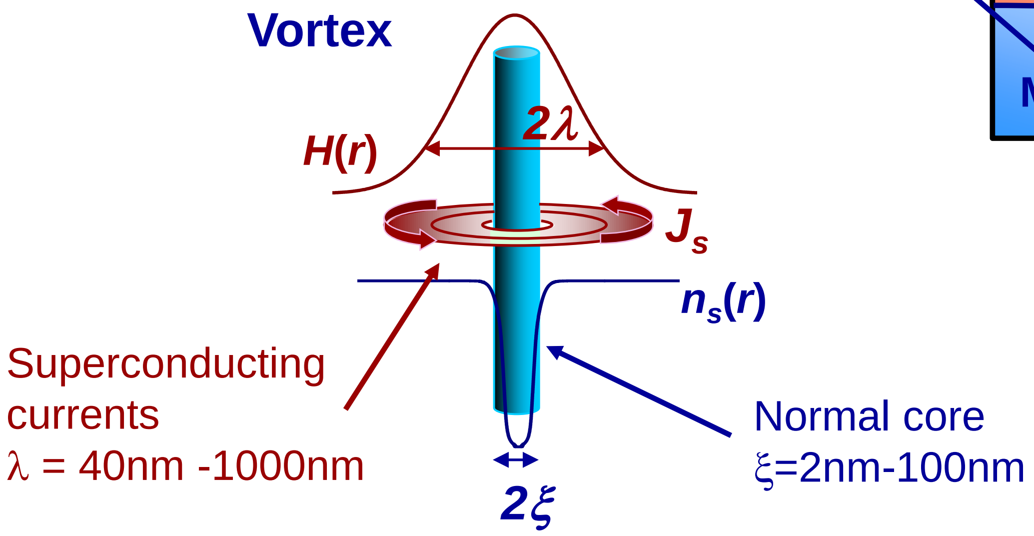
cooling with inexpensive liquid nitrogen or mechanical cryocoolers.

Reducing refrigeration costs for superconducting applications
Nano-engineering has been necessary to be able to exploit their applications

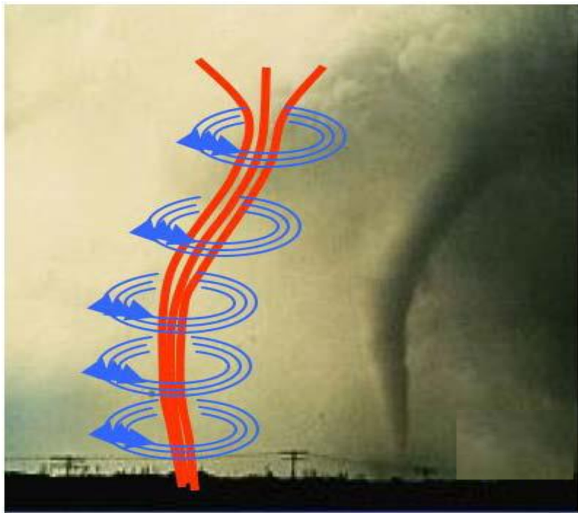
Mixed state in type II superconductors: vortices

Mixed state → Magnetic field penetration as quantum flux lines

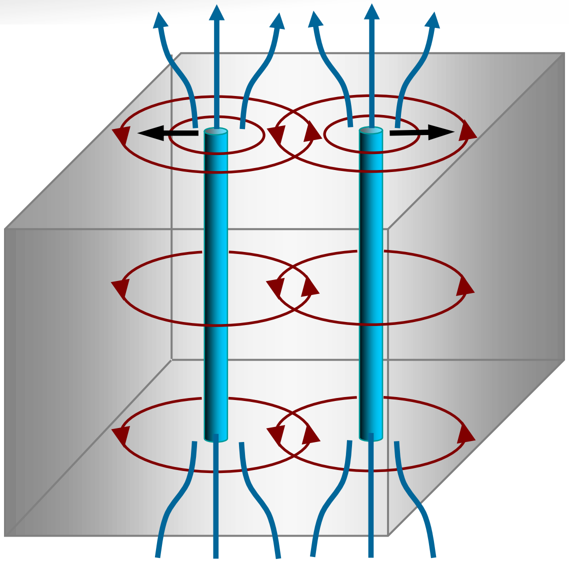




$\Phi_0 = 2.07 \cdot 10^{-15}$ Tm^2



Vortex state: The Abrikosov lattice

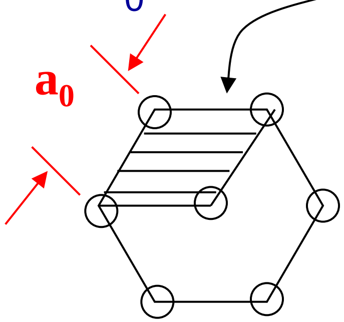


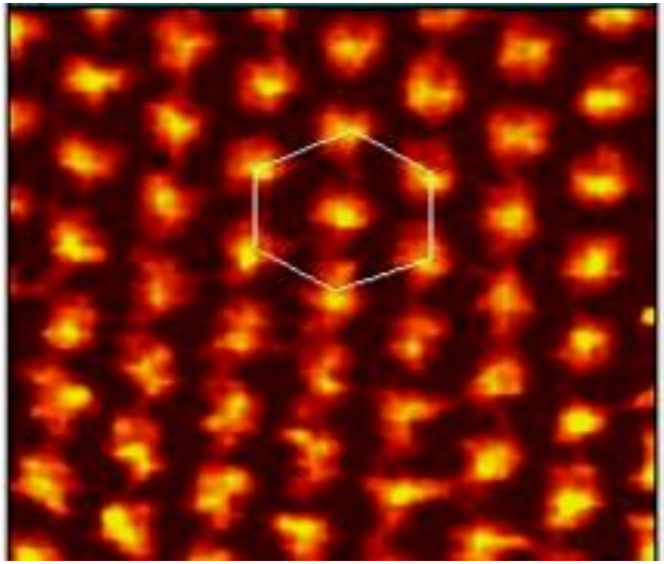
vortices repel each other forming an ordered lattice:
The Abrikosov lattice

$B = n\,\Phi_0$ and $n \sim 1/a_0^2$

$a_0 = \sqrt{\Phi_0/B}$

Φ_0

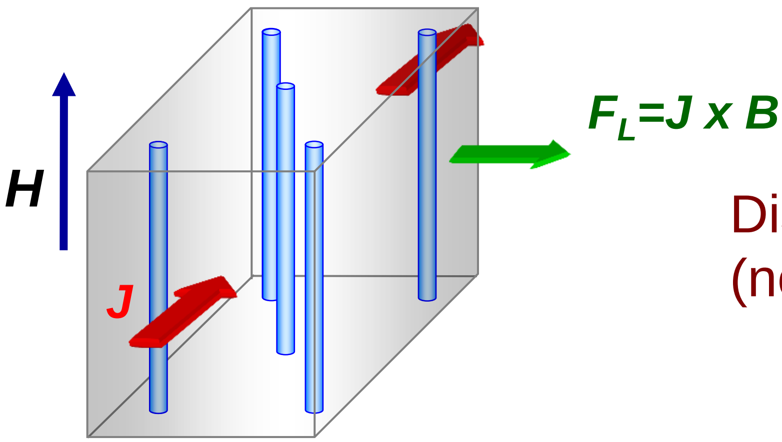




STM

B ↑ a_0 ↓

Vortex motion: Dissipation



Dissipation due to vortex motion (normal core)

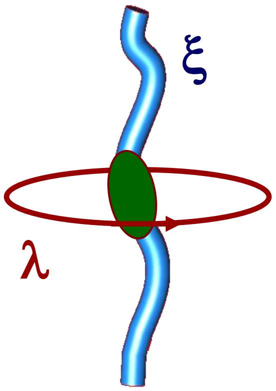
We need to trap vortices in the material

Non superconducting regions in the material → Vortex core pinning

Core pinning energy: energy required to drive normal electrons in the core away from the pinning center

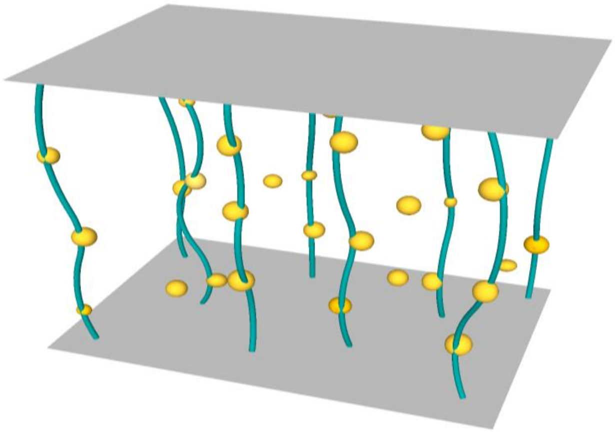
Condensation energy of cooper pairs in the vortex core volume

$$U_{CP} \sim (H_c^2/8\pi)\ (\pi\ \xi^{\ 2}) \sim (\phi_0/\lambda_L)^2$$



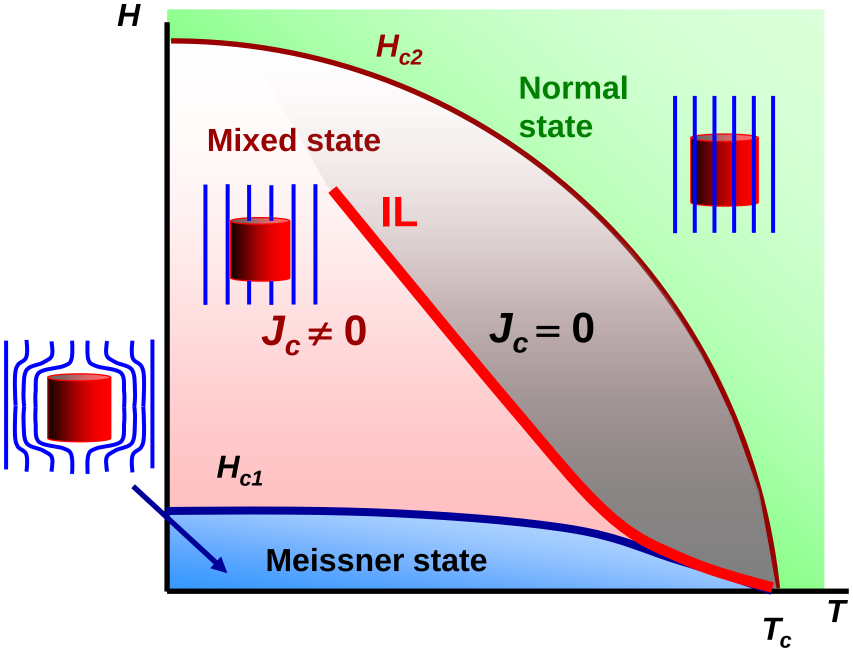
Vortex motion: Dissipation

High current density: $J \times B = F_L > F_P$ $\rightarrow$ vortex motion $\rightarrow$ $J_c = 0$



$F_L = J_c \times B = F_p$ $\longrightarrow$ Current without dissipation

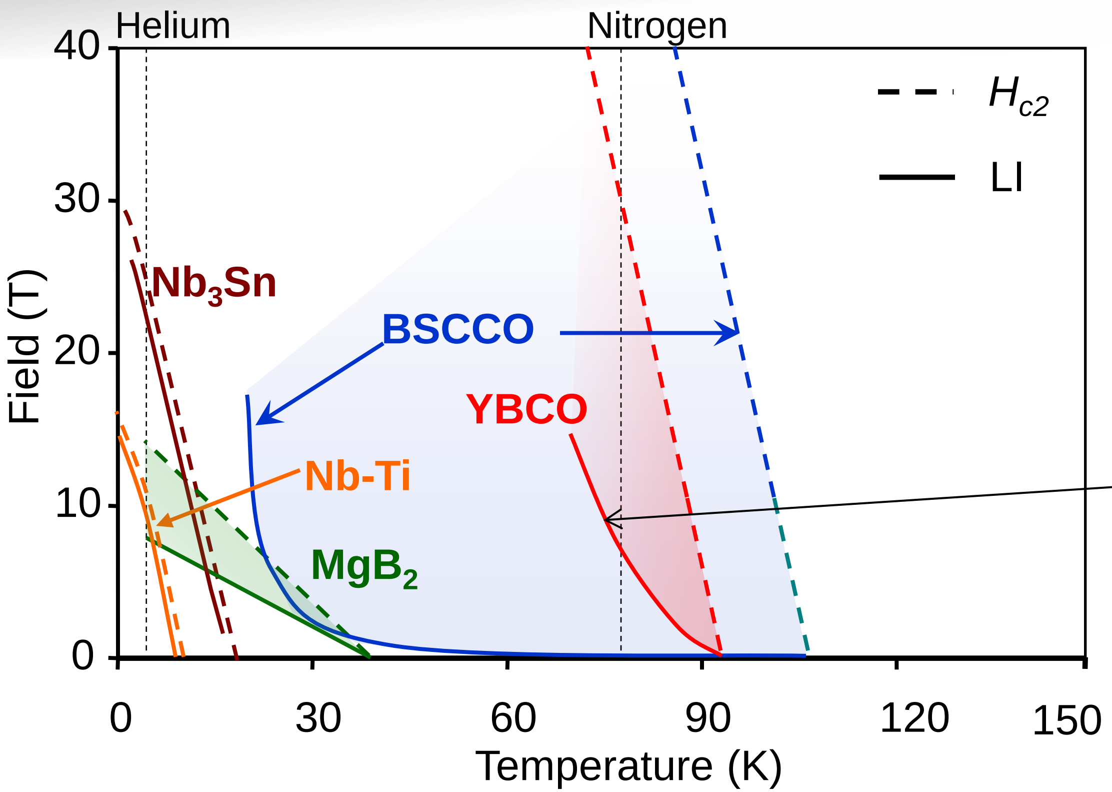
Critical current: maximum current that can flow in the superconductor without dissipation

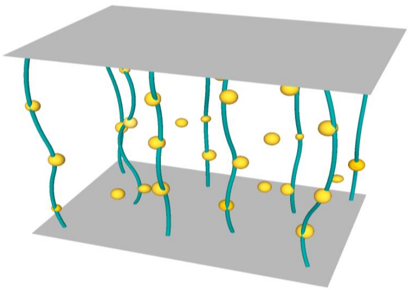


Any kind of defect will be able to pin vortices??

Control of vortex motion $\rightarrow$ Nanometric defects $\sim \xi$ (nm)

The irreversibility line





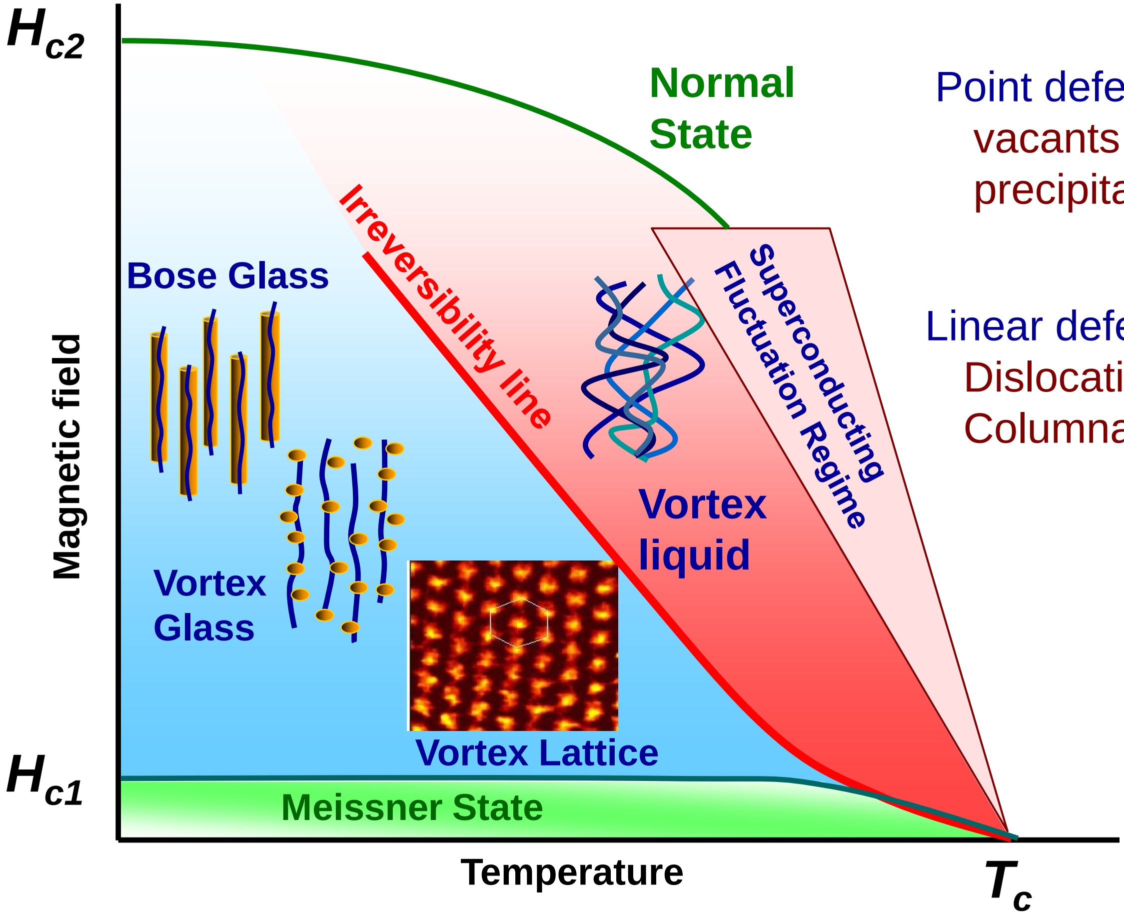
Pinning centres in the material → enhancement IL

LTSC → $H_{c2}(T)$ very close to IL

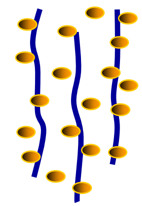
Applications at high fields and high temperatures → $YBa_2Cu_3O_{7-d}$ (YBCO)

Magnetic phase diagram in a HTS

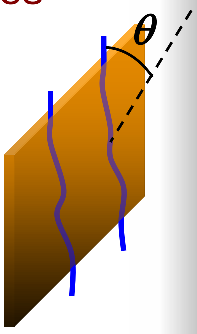
Great variety of pinning sites→ complex vortex matter



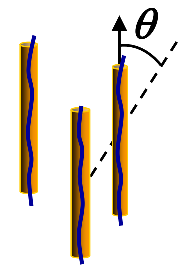
Point defects
vacants
precipitates



Planar defects
Twin boundaries
Stacking faults
CuO_2 planes



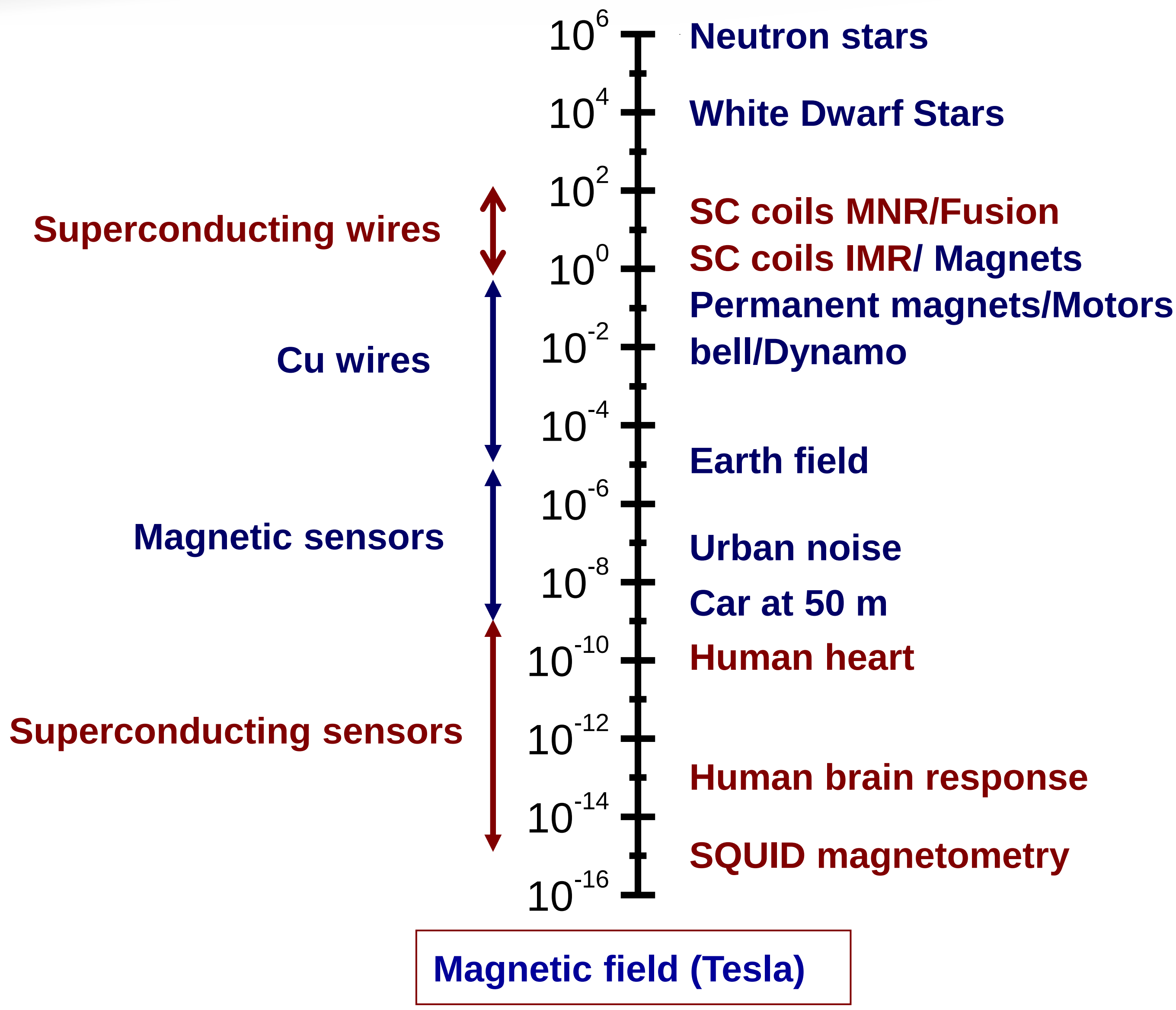
Linear defects
Dislocations
Columnar deffects



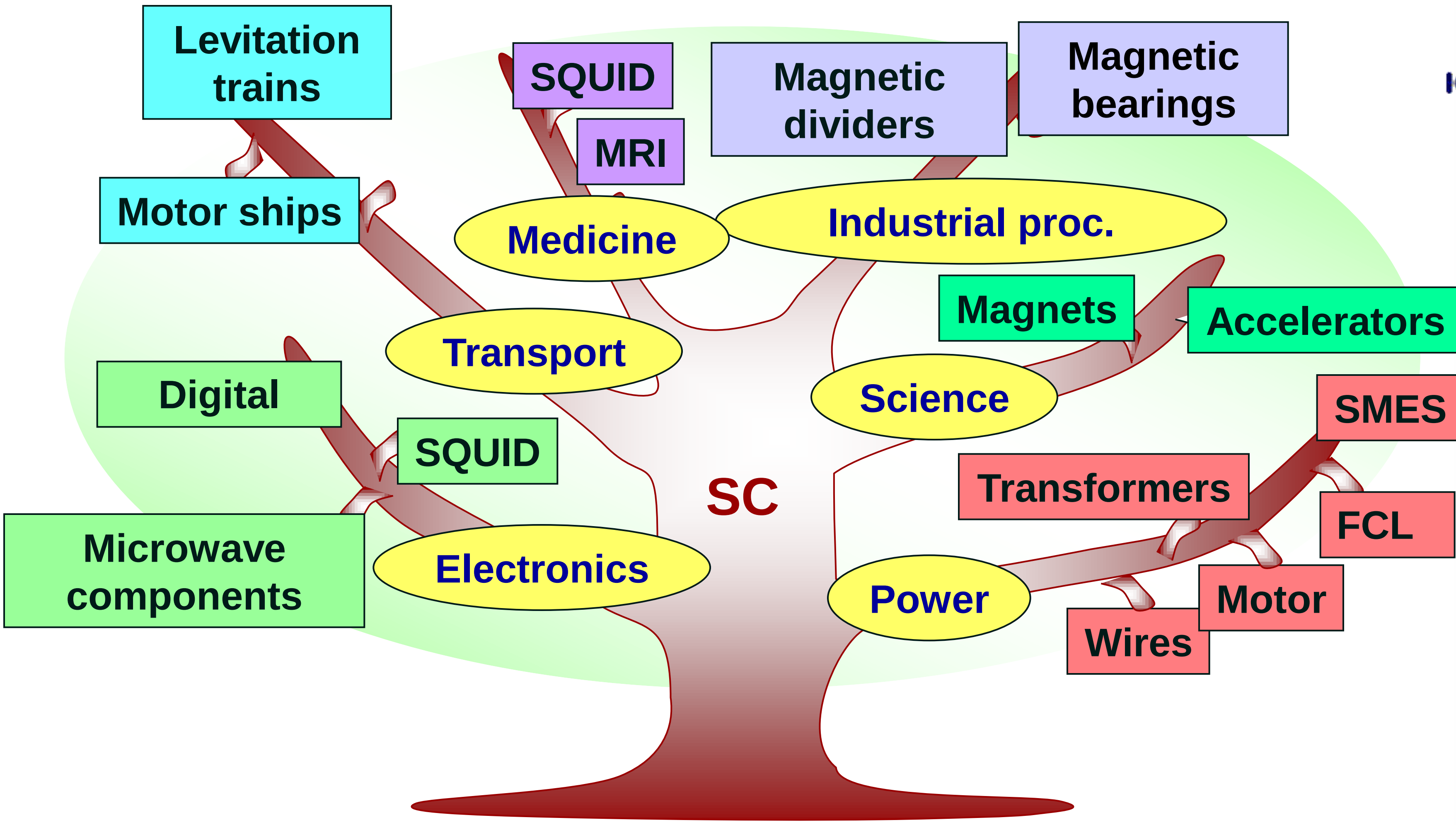
Four competing energies

Interaction → Ordered lattice
Pinning → glass
Elastic → 3D vortex
Thermal → liquid

Magnetic field range for applications



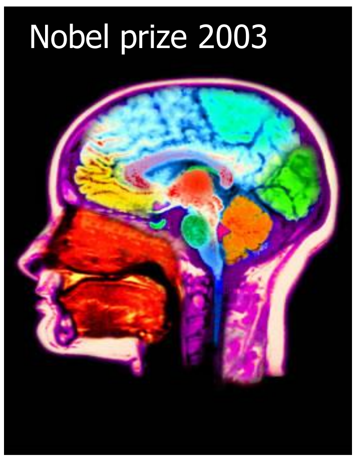
Superconducting applications



Superconducting applications which are now a reality

Strong magnets that exploit their zero resistance

Medicine : Magnetic resonance imaging, MRI



non-invasive technique to produce high quality images of the inside of the human body

Persistent current SC magnets surround the human body with a strong and stable magnetic field

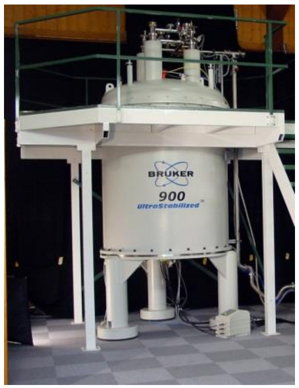
Open gap MRI
MgB_2

Superconducting applications which are now a reality

Strong magnets that exploit their zero resistance

Research:

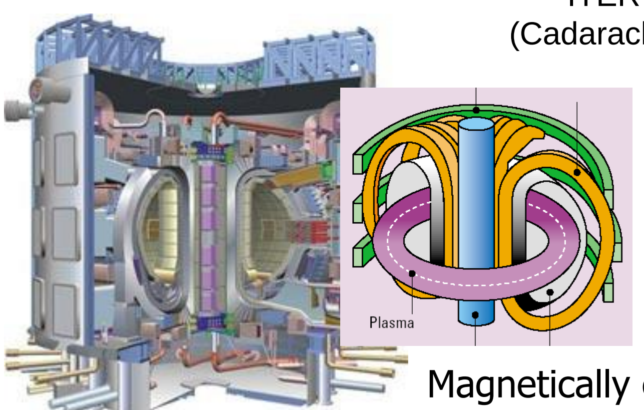
Magnets for high field magnetic resonance , NMR



Very high magnetic fields combining first and second generation wires (>23 T 1 GHz)
Molecular biology, Chemistry, Physics..

Magnetic confinement

ITER Fusion
(Cadarache, France)

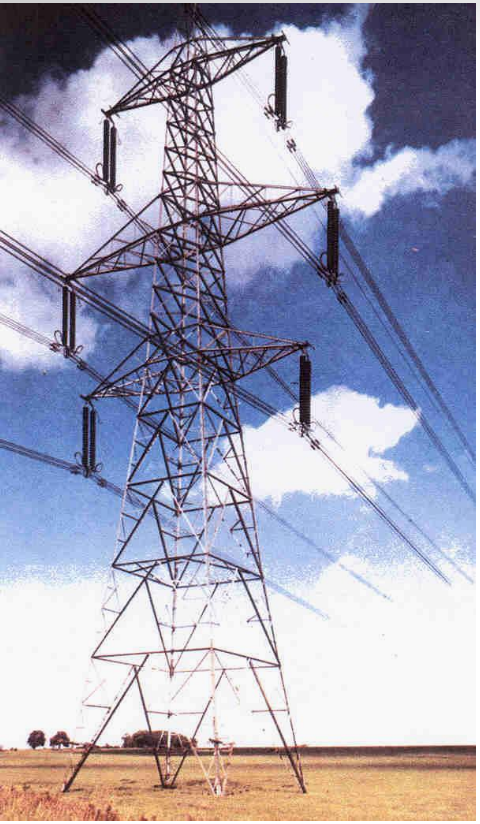


Magnetically confined plasma

High field accelerator magnets

Fermilab (Chicago)

Superconducting wires: Promising applications



power transmission cables to replace the actual Cu wires

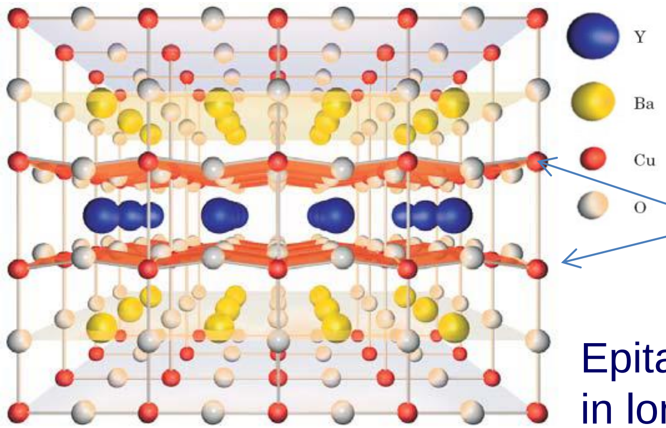
- very high current without electrical losses
- Reduction weight/volume $\rightarrow$ higher power density
- Cooling with N_2 instead of flammable oils
- Clean and efficient electricity

LIPA Project
Long Island
High tension transmission line (345KV) I=2000A,
600m Bi-2223

SuperPower
(Albany, NY,USA)
13kV, I=0.8kA
300m1G +30 m 2G

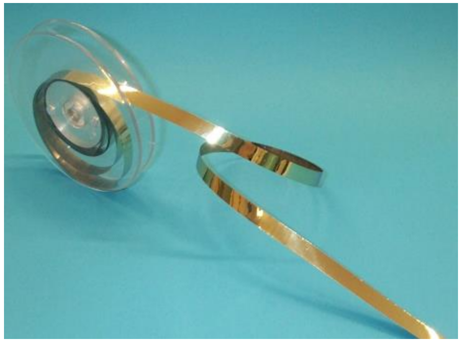
Novare-ENDESA award (Nov 2010)
Technology design, demonstration and
testing . 25 kV, 3200 A (139 MVA) 30 m

Second generation superconducting tapes: $YBa_2Cu_3O_{7-d}$ Coated conductors



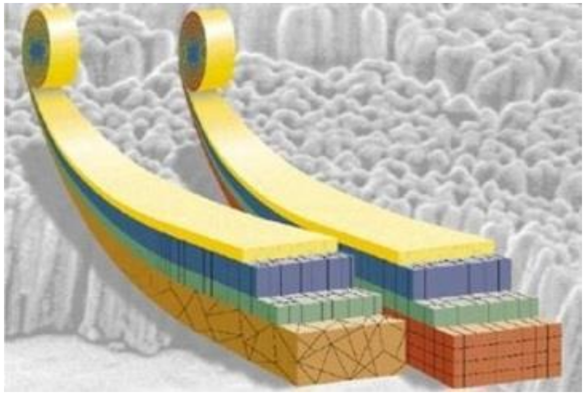
Ceramic materials: Fragile, difficult to fabricate, anisotropic

SC planes

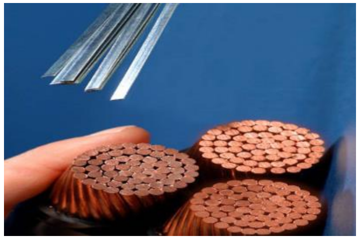


Epitaxial materials (at atomic scale) in long lengths (Km)

Coated Conductor architecture



Km length epitaxial multilayer carrying more than 150 times higher current density than Cu



Reduction weight/volume → higher power density

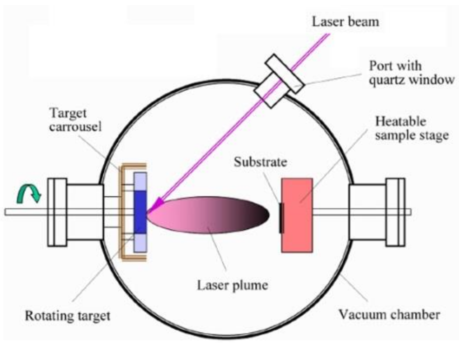
Challenges:

- Develop simple conductor architectures cost-effective and scalable keeping performance
- Implement existing CC into power systems with best engineering designs to demonstrate reliability

Growing epitaxial flexible YBCO Coated Conductors

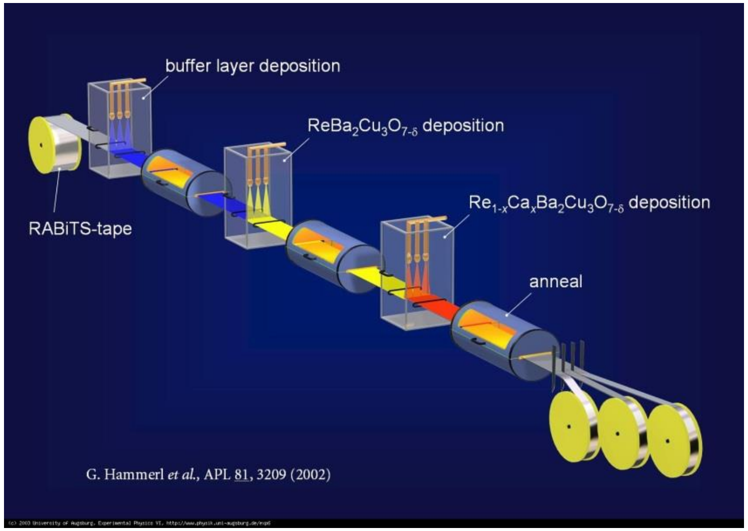
Physical methods

- Pulsed laser deposition
- Sputtering
- Thermal evaporation



Chemical methods

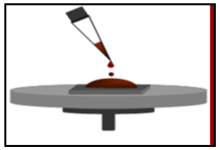
- Metal-organic decomposition
- Chemical vapor deposition



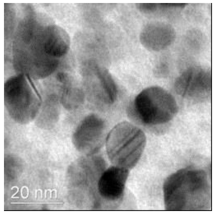
… a versatile, scalable and low cost methodology for growing nanostructured epitaxial films

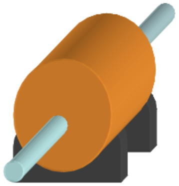
Precursor solution synthesis → Y, Ba,Cu metal-organic precursors

Solution deposition → Spin-coating, Ink-jet

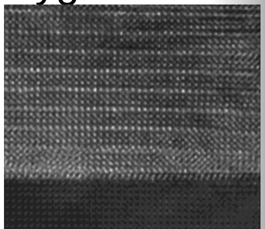


Pyrolysis → Removal organic precursors



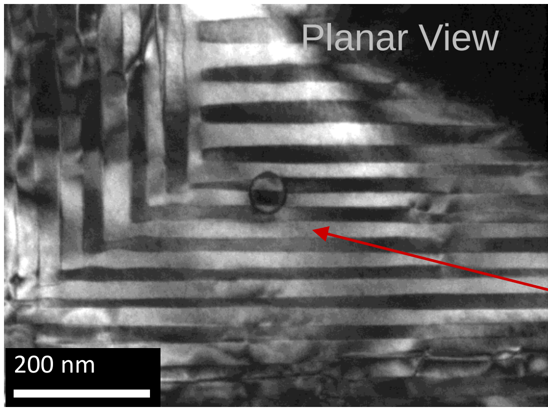


Ex-situ Growth → Nucleation, crystallization and oxygenation

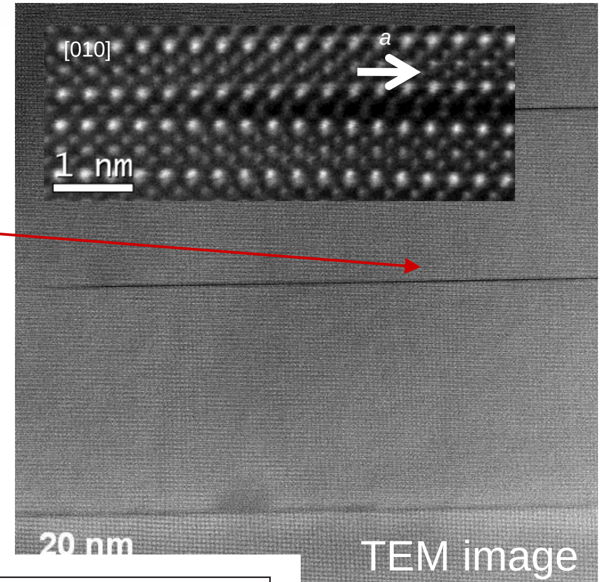


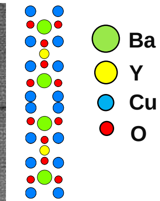
Natural defects of YBCO thin films

YBCO films → Natural defects at nanometric scale



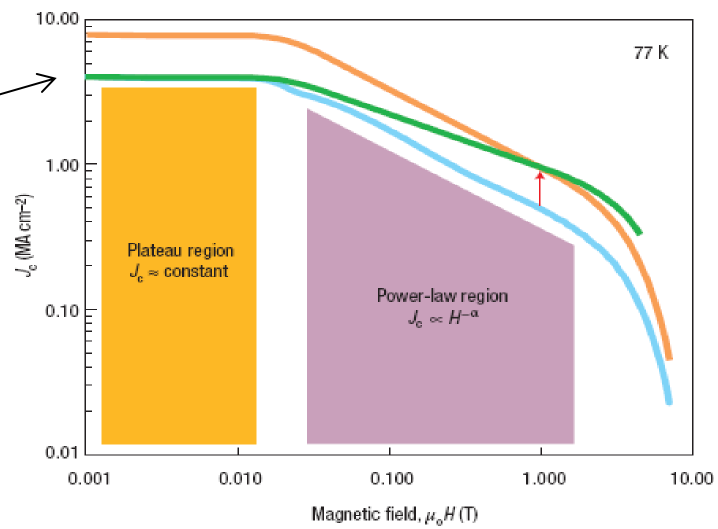
Natural defects
- Stacking faults
- dislocations
- vacancies
- Low angle GBs
- Twin boundaries
- precipitates





Very good performances at low magnetic fields

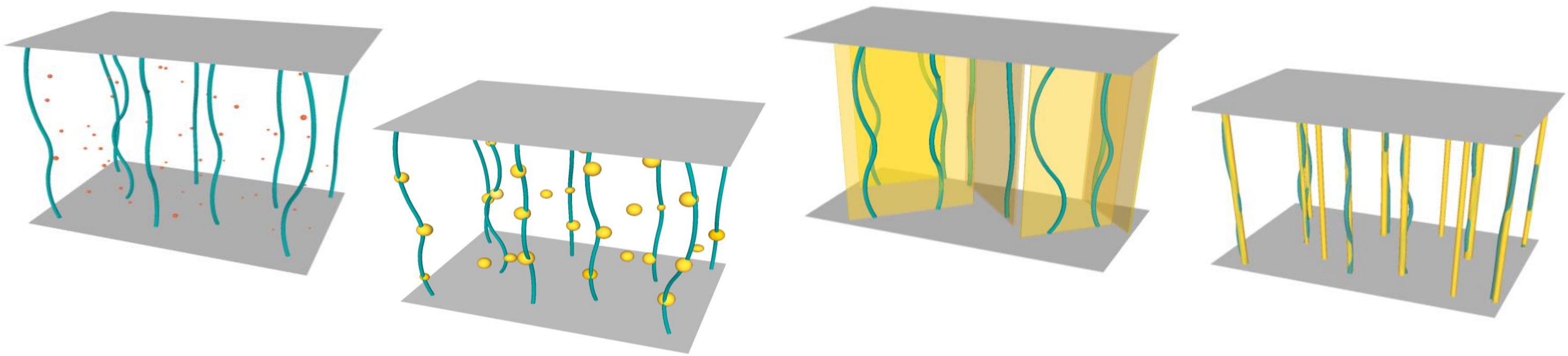
J_c(77 K)= 3-5 MA/cm^2



Nanotechnology: Essential tool for superconducting applications → Introduce artificial vortex pinning defects to improve J_c at high fields

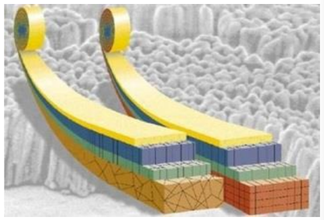
Practical applications: Engineered nanostructures

The study of vortex dynamics and methods for enhancing vortex pinning is of major importance when considering technological applications

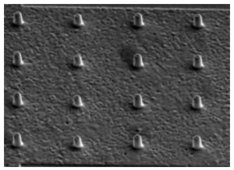


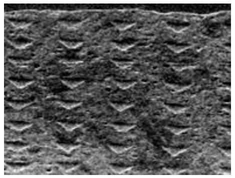
Tune size, shape, dimensionality, distribution, density of artificial pinning sites….

- Improve vortex pinning in CC → Power Applications at high fields



- Manipulate and gather knowledge on vortex motion in model systems → Fundamental studies / Electronic devices

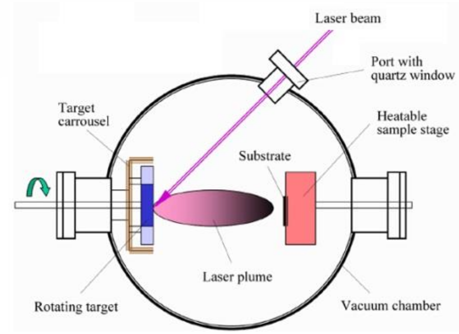


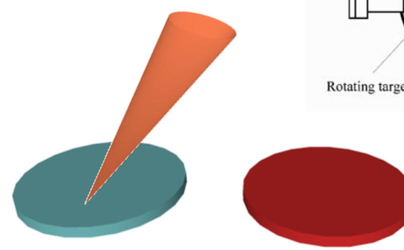


Self assembling nanoparticles in films grown by PLD

Addition of nanoparticle dispersions to enhance flux pinning of YBCO SC

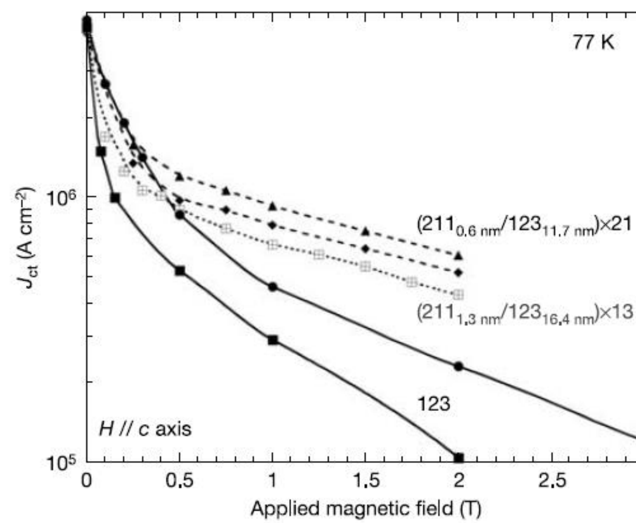
Growth of ultra thin films: PLD with 2 targets





$(211_{\sim 0.9nm}/123_{\sim 10.4nm})$x200

$YBa_2Cu_3O_7$ (123) alternating ultra-thin films of Y_2BaCuO_5 (211) (non superconductor)

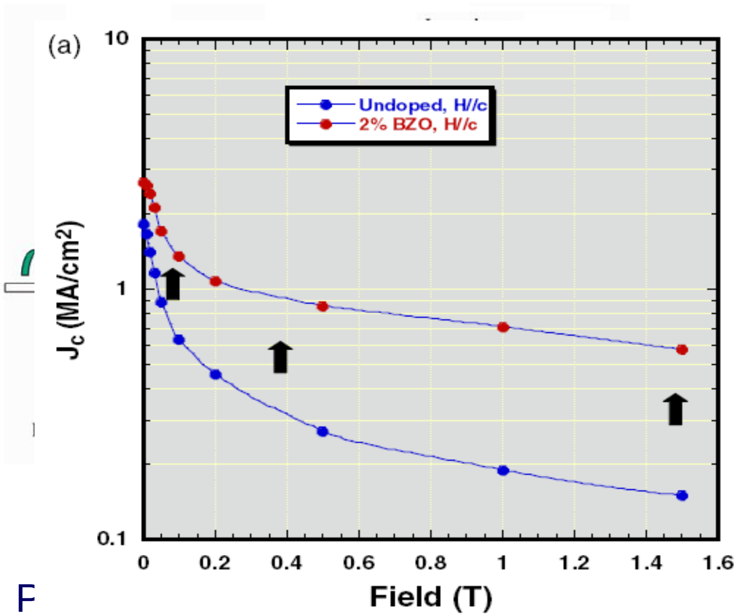


J_c(H) improvement at high magentic fields

Haugan et al. Nature 430 (2004)

Self assembling nanoparticles in films grown by PLD c

Nanocolumns give YBCO wires a big boost



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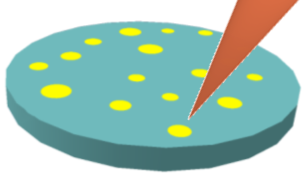
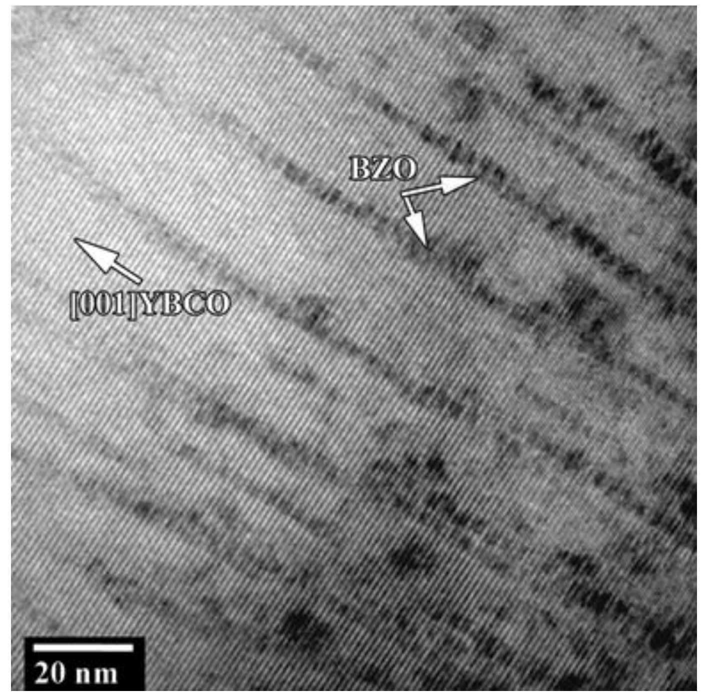
BZO nanoparticles

Nano-composite → pinning enhancement (specially effective when H is oriented along nanodots)





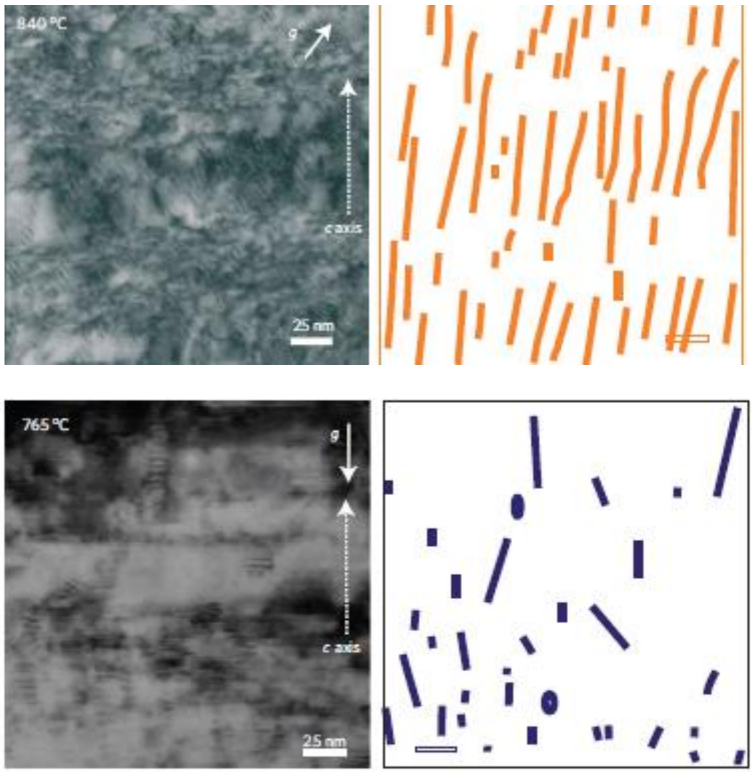
Self aligned nanodots of BZO during the growth due to elastic tensions

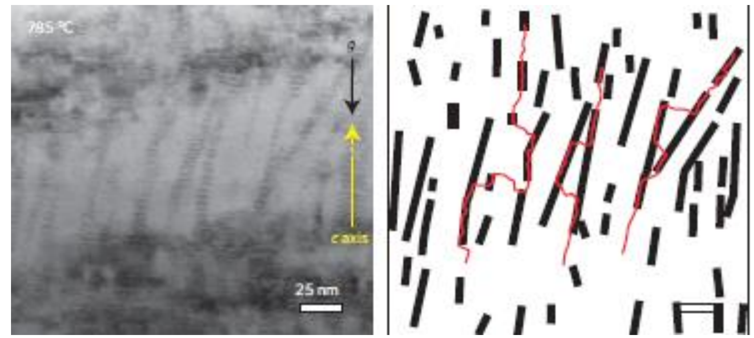
Interfaces and associated strains, defects, … can be tuned and maximized to optimize vortex pinning properties

Kang et al. Science 311 (2006)

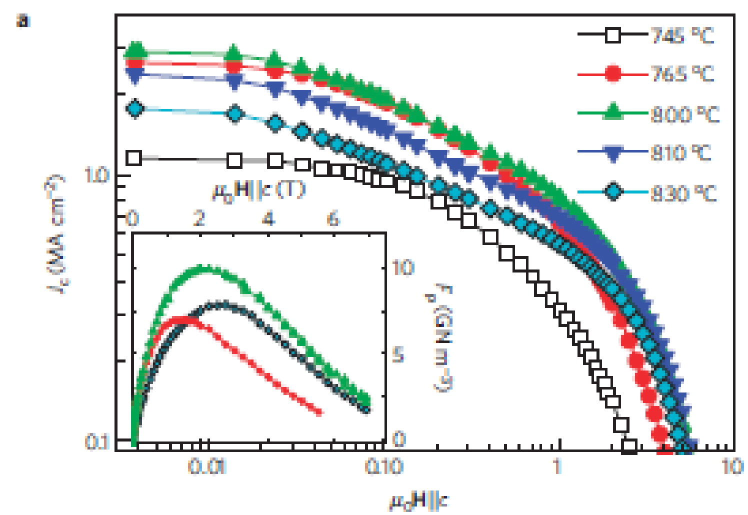
Self assembling nanoparticles in films grown by PLD c

Tuning the temperature and growth rate during PLD deposition of BZO doped YBCO → nanoparticles or self-assembled columnar defects





Synergetic combination of different types of defect to optimize pinning landscape



Maiorov et al. Nature Mat. 8(2009)

CSD YBCO Nanocomposites

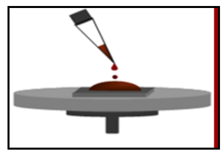
… a versatile, scalable and low cost methodology for growing nanostructured epitaxial films

Precursor solution synthesis

Y, Ba,Cu metal-organic precursors

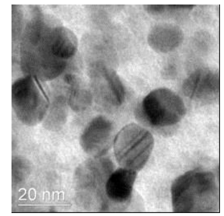
Solution deposition

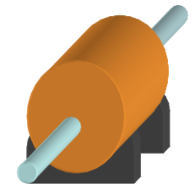
Spin-coating
Ink-jet



Pyrolysis

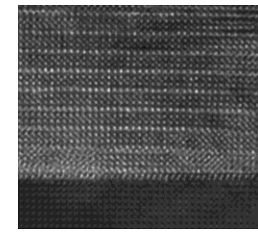
Removal organic precursors





Ex-situ Growth

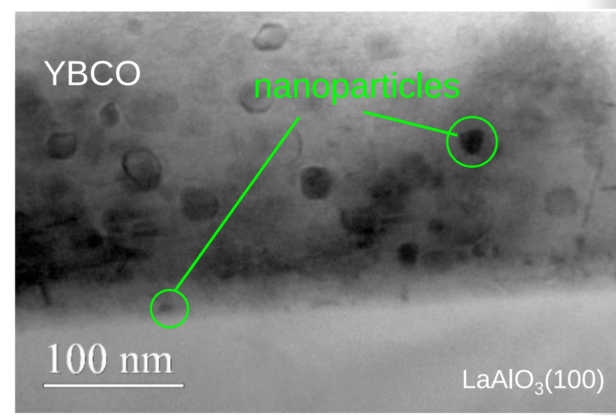
Nucleation, crystallization and oxygenation



Addition of metal-organic salts (Zr, Ce, Ta,…) in the YBCO precursor solution

Spontaneous Np segregation : Y_2O_3, $BaZrO_3$, Ba_2YTaO_6, $BaCeO_3$, …

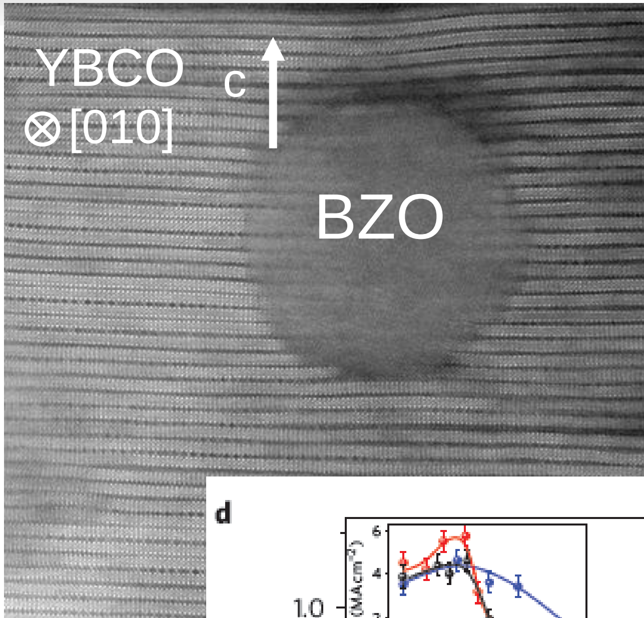
- *Nanoparticles size, shape, concentration, orientation, strain…. and consequently properties can be tuned*
- *Interfaces are the key issue for the performances achieved*

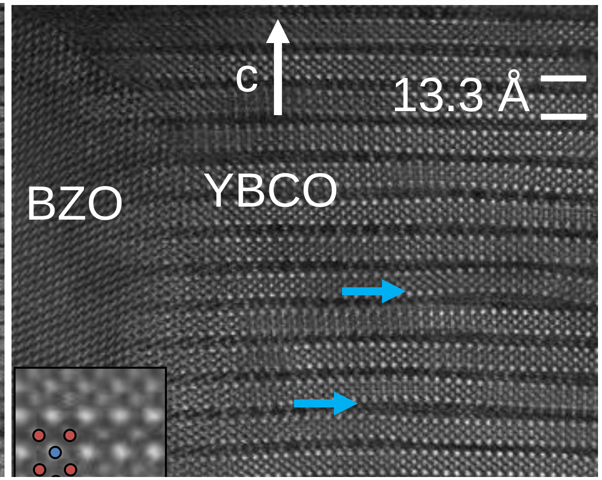


Llordés, Palau et al. Nature Materials 11 (2012)
Gutierrez, Llordés et al. Nature Materials 6 (2007)

CSD YBCO Nanocomposites

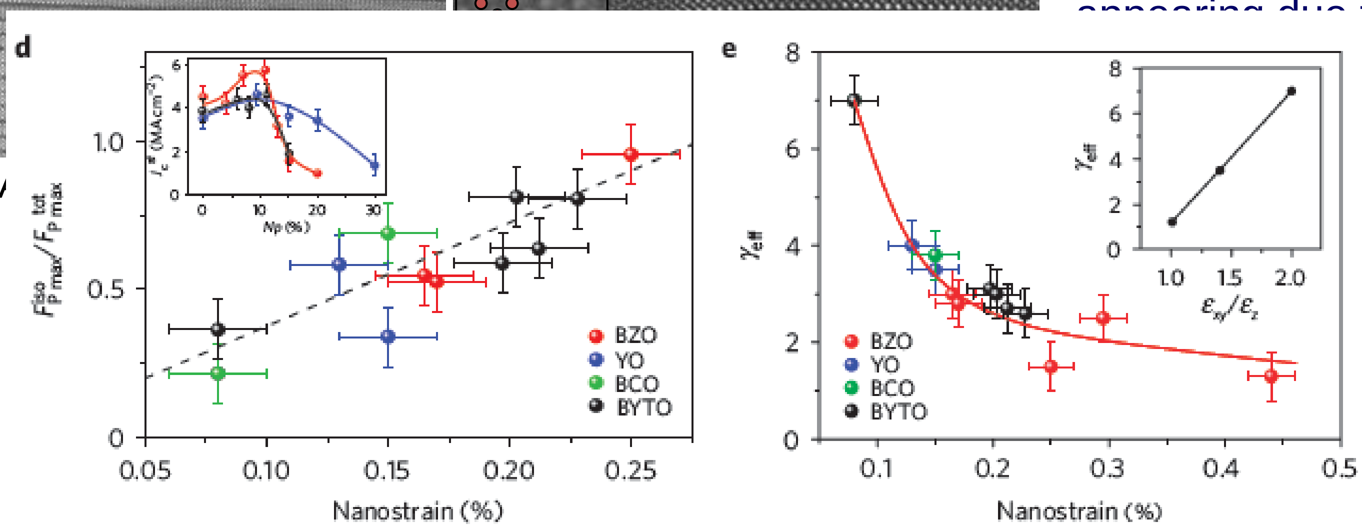
Interfaces are the key issue for the performances achieved





STEM-HA

- High density of intergrowths: Double (Y248) and triple (Y125) Cu-O chains
- Strong strains should be appearing due to the intergrowths

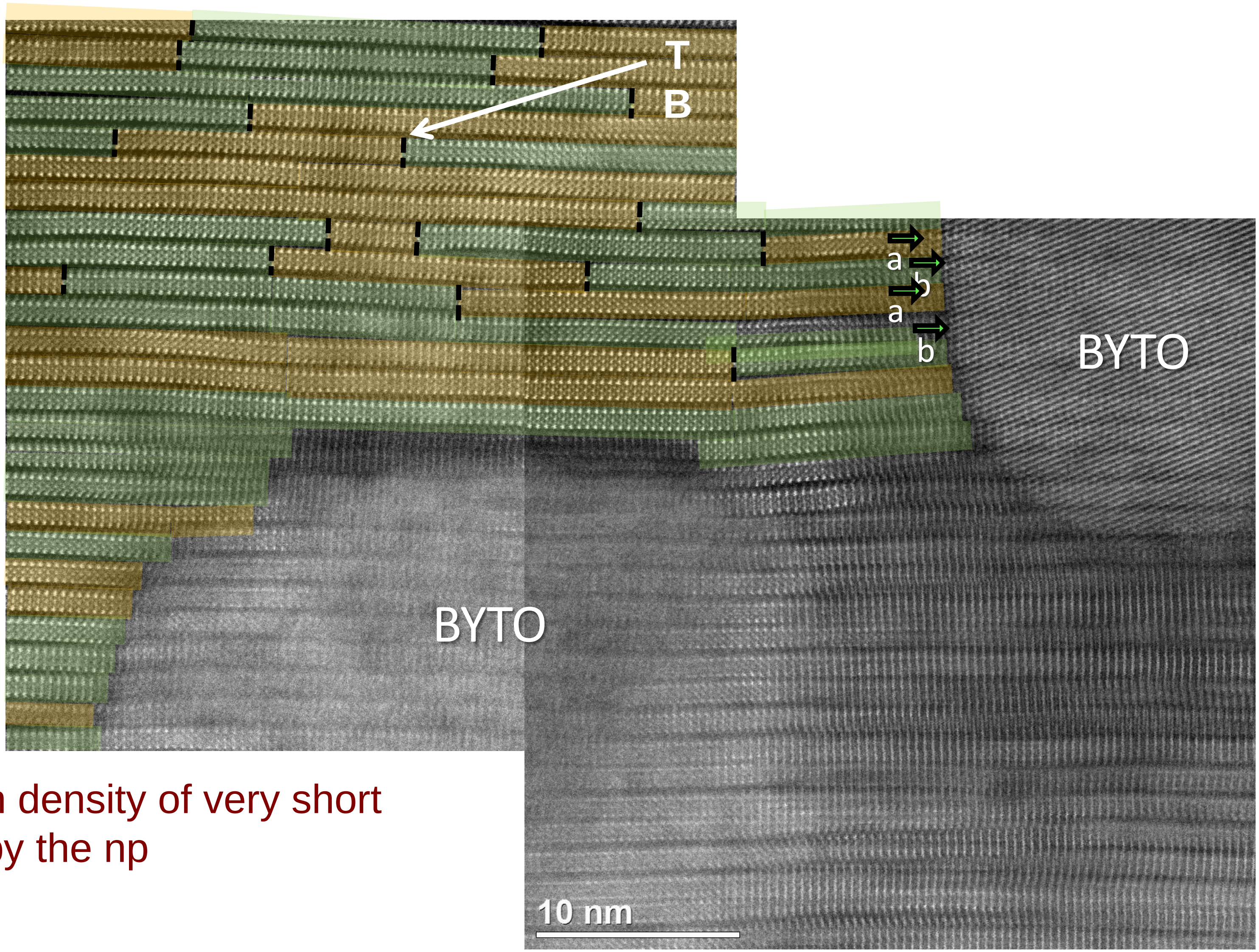


Local lattice strain produce a huge improvement in superconducting performances of CSD-YBCO nanocomposites

Llordés, Palau et al. Nature Materials 11 (2012)
Gutierrez, Llordés et al. Nature Materials 6 (2007)

CSD YBCO Nanocomposites

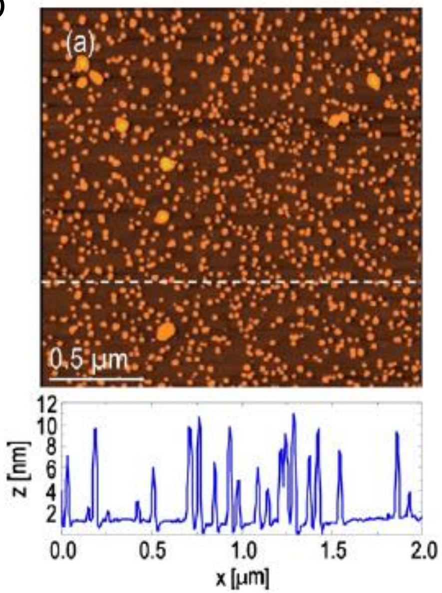
NP completely change the pinning landscape → Interaction between natural and artificial defects

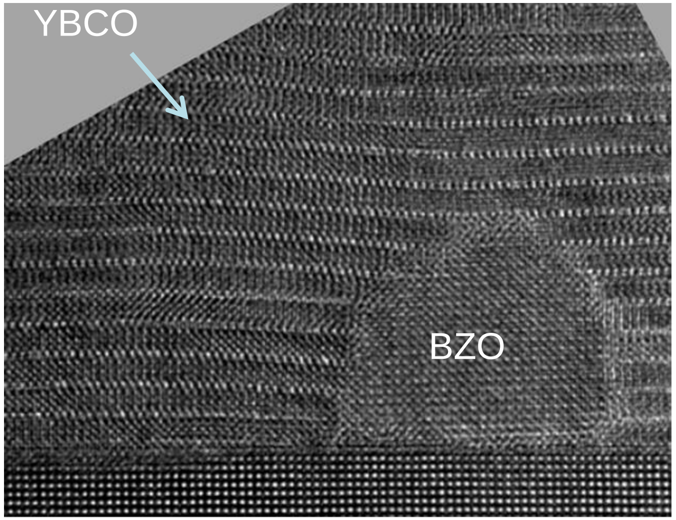


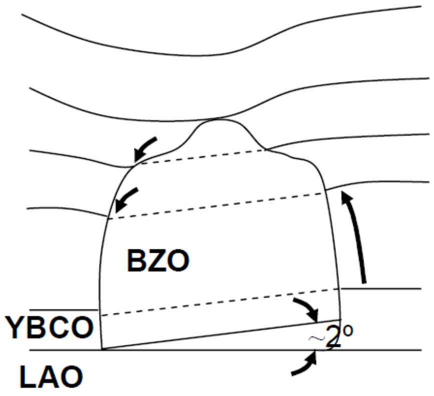
Very high density of very short TB nearby the np

Interfacial templates : Substrate decoration

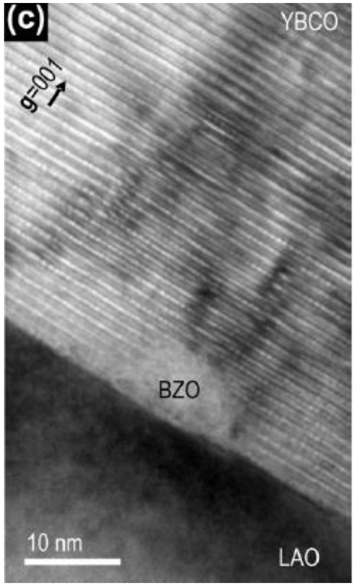
BZO nanodot template grown by CSD



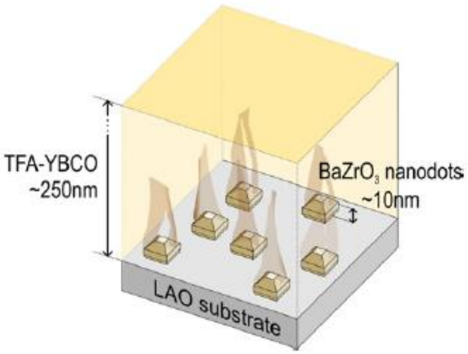


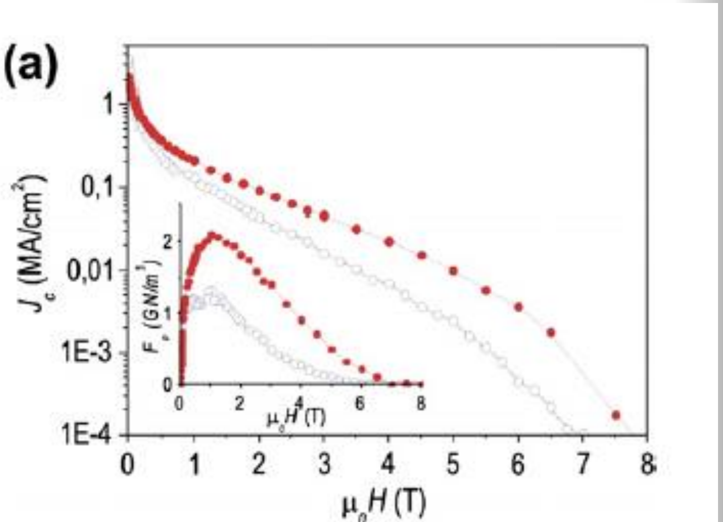


decorated substrates → perturb the nucleation stage of the films modifying the final microstructure



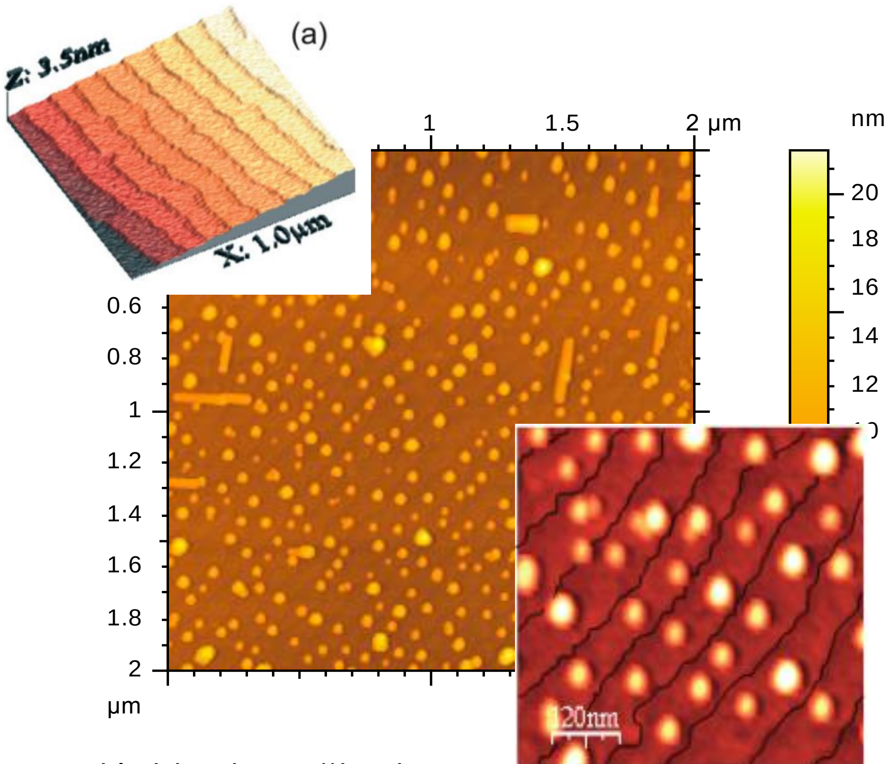
strained regions within the matrix
→ enhanced pinning force





Self-Organization of nanostructures grown by CSD

LAO vicinal single crystal substrate thermal treated to form atomically flat terraces

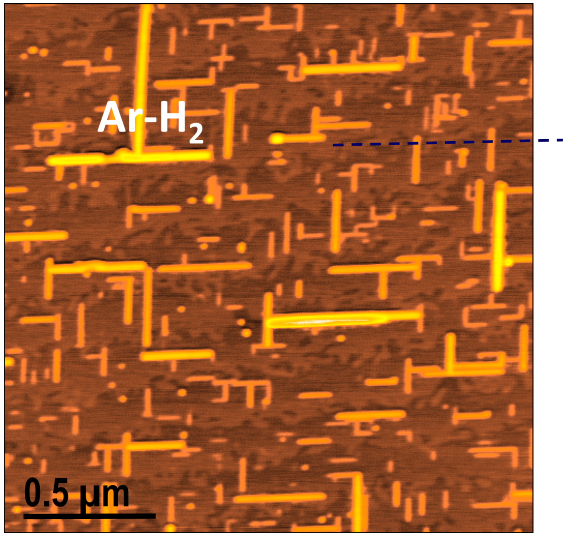


Self-assembled (001)CGO//(001)LAO

interfacial energy is the driving force to form quasi one-dimensional arrays of nanodots confined within the terraces rows

Tuning of growth conditions → nucleation (001) or (011) orientations

systems with different equilibrium shapes and kinetics



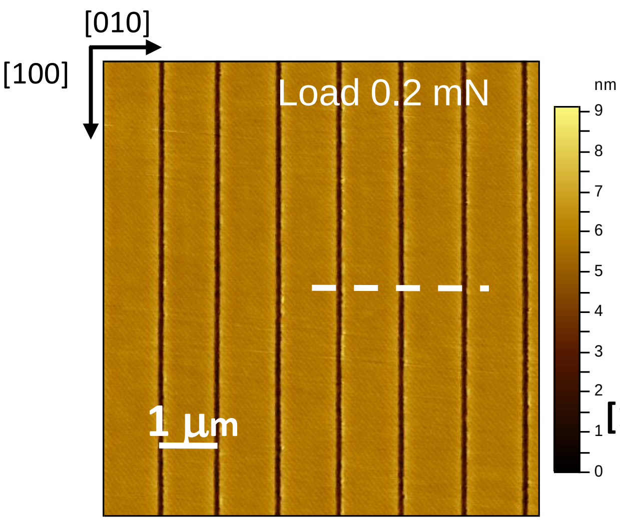
(011)CGO//(001)LAO leads to highly elongated nanowires

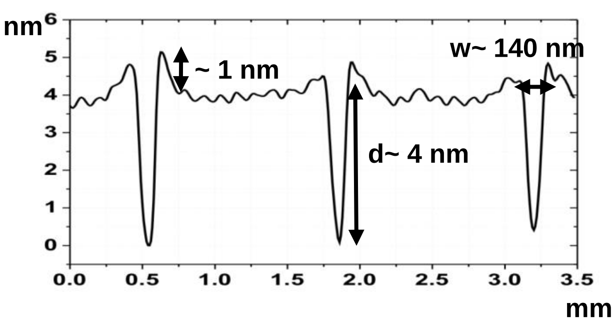
tuning of a nanodot-to-nanowire ratio through kinetic control

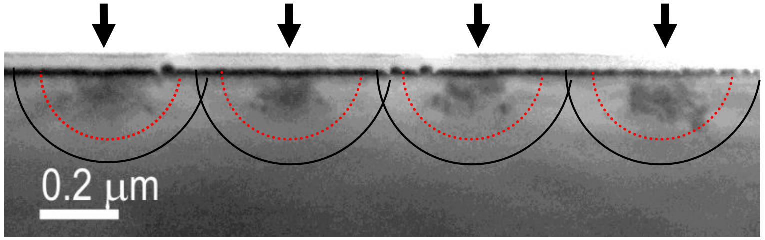
Gibert et al. Adv. Mater. 19 (2007)

Gibert et al. CrystEngComm. 13 (2011)

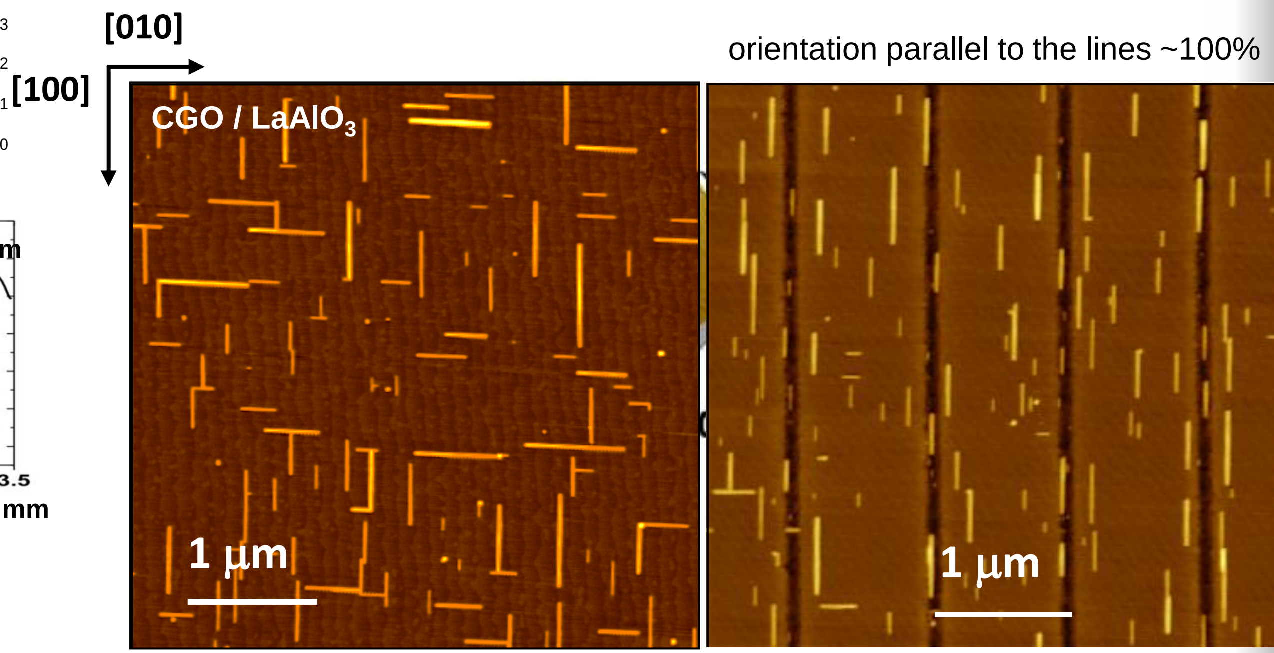
Guided self-organization of oxide nanoestructures by nanoindentation







Local anisotropic strain in the zones beneath the indentation lines

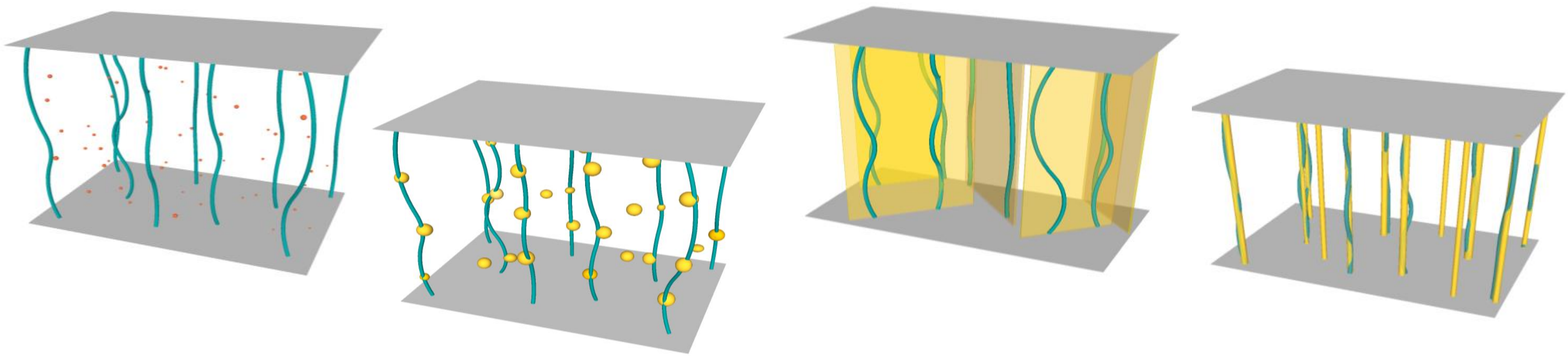


local anisotropic strain → breaking of the pre-existing orientation degeneracy

J. Zabaleta et al. Nanotechnology 21 (2010)

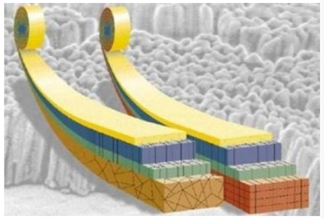
Control of artificial defects at nanometric scale

The study of vortex dynamics and methods for enhancing vortex pinning is of major importance when considering technological applications

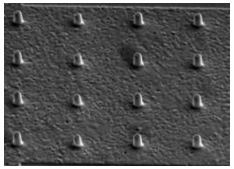


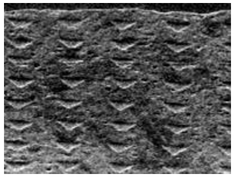
Tune size, shape, dimensionality, distribution, density of artificial pinning sites….

- Improve vortex pinning in CC → Power Applications at high fields



- Manipulate and gather knowledge on vortex motion in model systems → Fundamental studies / Electronic devices

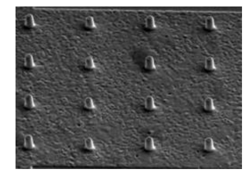


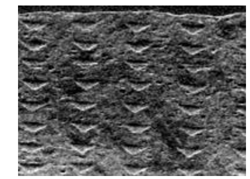


vortex dynamics in model systems

Engineering the energy landscape for vortices via the introduction of ordered distributions of nanometric structures

Model systems → flux dynamics on controlled energy landscapes with special geometries

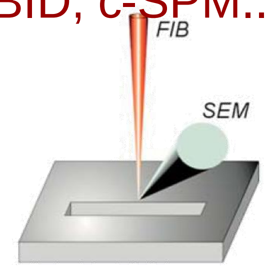


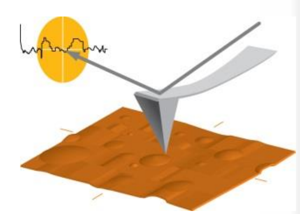


- study vortex pinning mechanisms to optimize J_c performances for particular applications
- manipulate vortices (vortex confinement, vortex guidance) → novel computing applications

High resolution lithography techniques: FIB, EBL, FEBID, c-SPM..

- multilayers
- holes (antidots / blind antidots)
- nano-particles (insulating, magnetic…)
- Nano-regions with suppressed SC



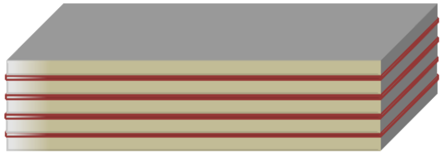


Nanofabrication techniques for High temperature superconductors

- SC properties highly dependent on oxygen content
- Ga+ implantation can easily damage the material
- Strong intrinsic pinning → weaker impact of the artificial defects

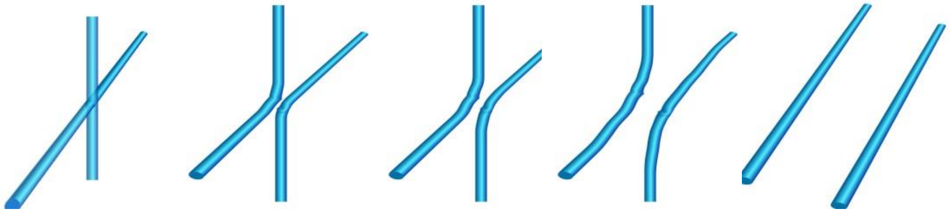
3D vortex dynamics in non homogeneous superconducting systems

Heteroestructures

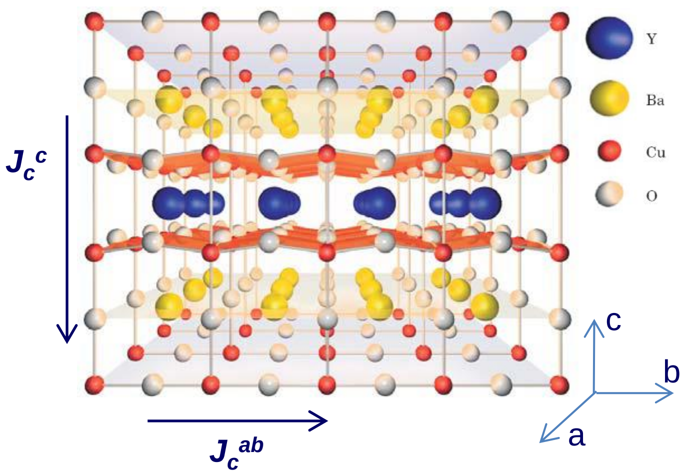


Multilayers with different pinning behaviour

Technological superconductors: inhomogeneous pinning → Vortex entanglement, crossing of lattices



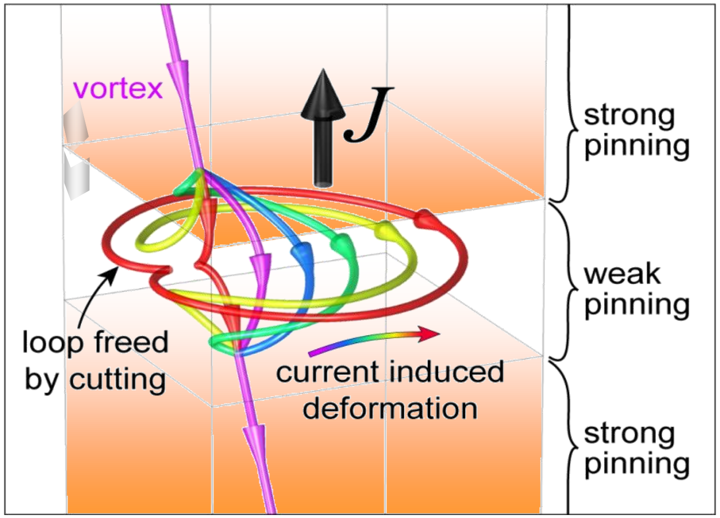
Anisotropic superconductors



$J_c^c \sim J_c^{ab}/\gamma$ YBCO : γ = 5-8

ab-planes: low vortex pinning channels

Flux flow within a **non homogeneous** superconductor with strong and weak pinning regions



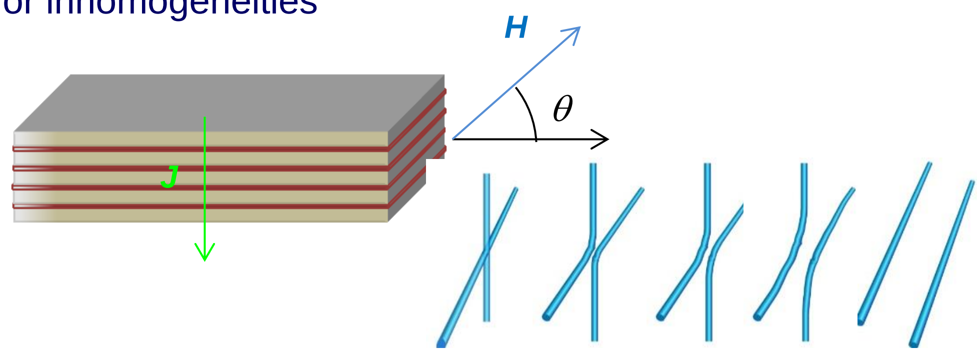
vortex cutting and channelling

3D nano-patterned devices for vertical transport measurements

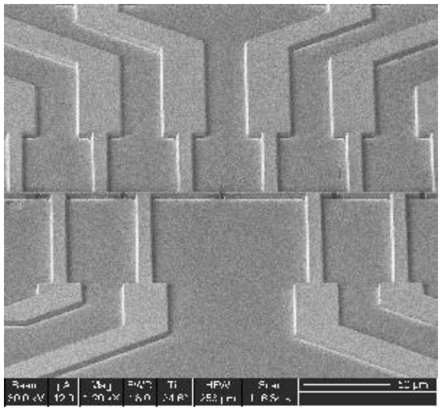
CSIC

ICMAB

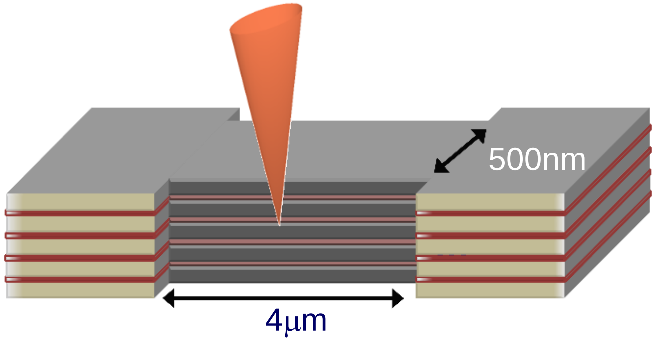
transport properties through different heterostructres or inhomogeneities



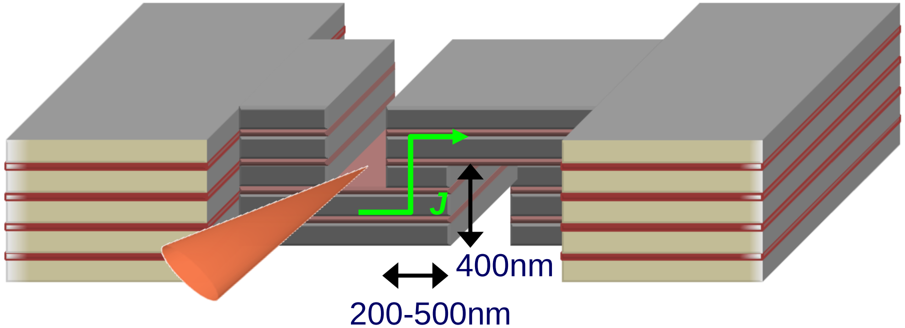
6μ - 10μ wide current tracks defined by standard photolithography



Current track narrowed from above with FIB to ~ 500nm



Lateral cuts performed by FIB to force current flow through the weak pinning layer.

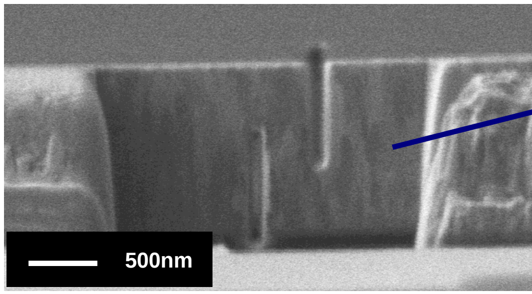


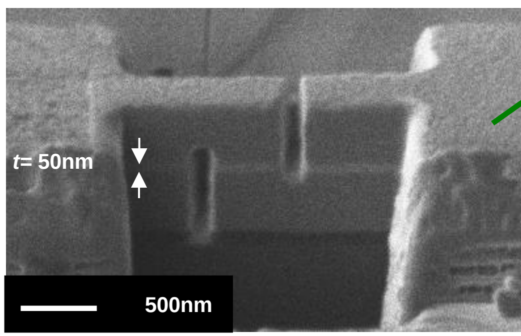
Nano-devices with dimensions in the range 100-500nm in which the current is constrained to flow along the *vertical* axis → transport properties in very confined areas

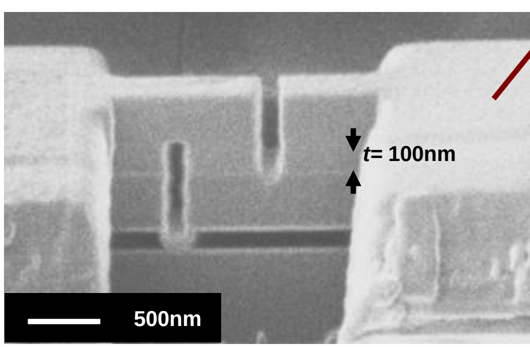
Vortex Breaking and Cutting in Type II Superconductors

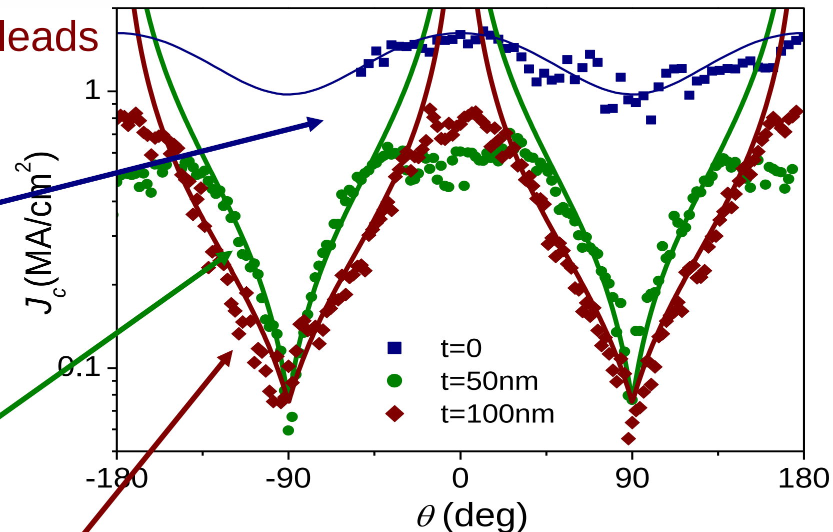
Structures in which a weak pinning layer is sandwiched between two strongly pinning leads

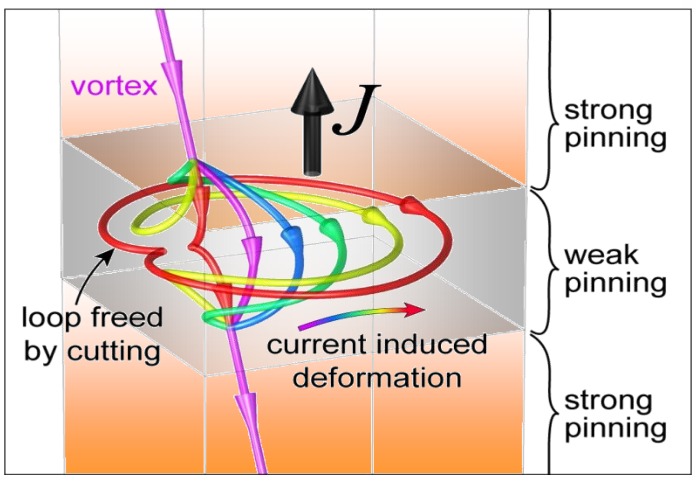
Nb/MoSi/Nb









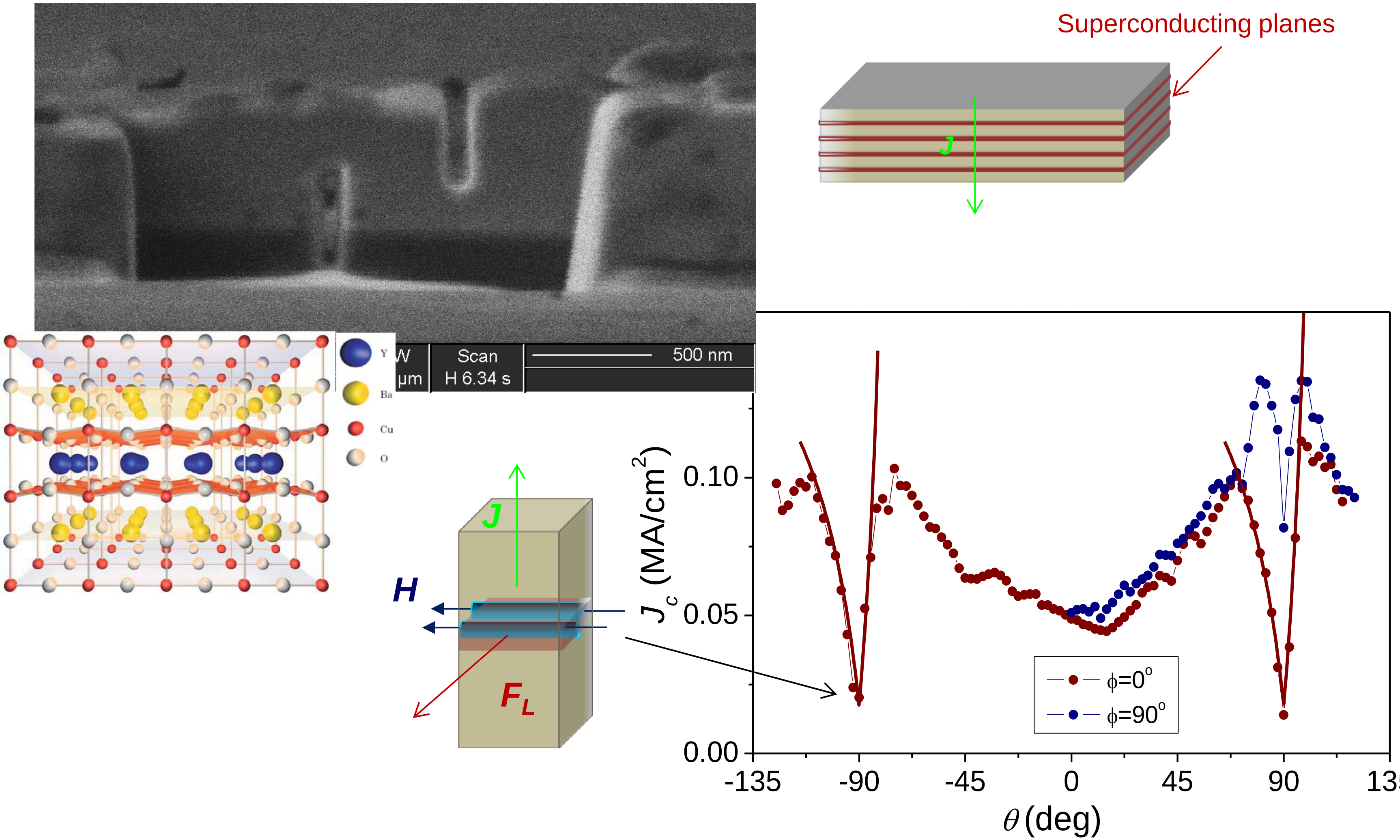


well controlled weak pinning channels →
Quantitative analysis of flux cutting and channeling

Palau et al. PRL 101 (2008)

Vortex Breaking and Cutting in Type II Superconductors

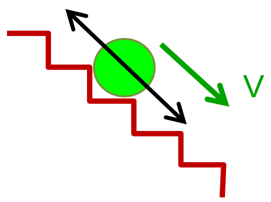
YBCO Devices with natural channels (*ab* planes)



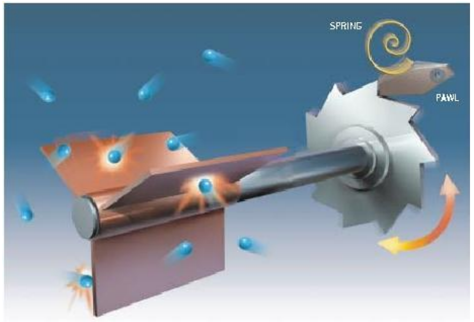
Easy vortex flow along the *ab* – planes→ vortex cutting and channeling

Asymmetric pinning potentials

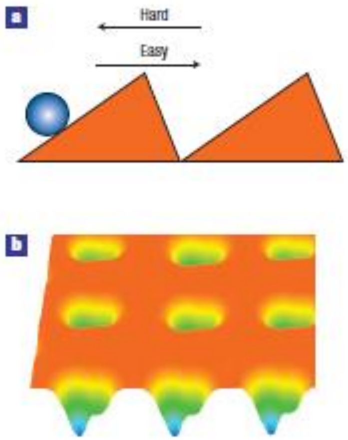
Asymmetric pinning potentials → the vortex lattice acquires a net velocity out of an unbiased (zero time-averaged) alternate drive.



"ratchet effect"



Controlled vortex motion → Net transport of matter at the nanoscale



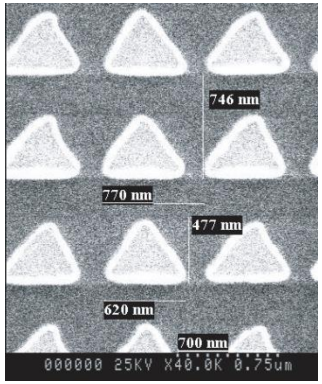
Electronic devices in superconductors:

rectify ac driving forces

field dependence reversible vortex diodes

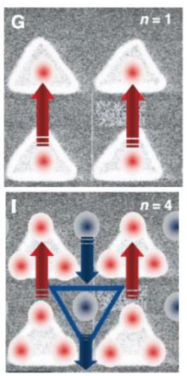
Asymmetric pinning potentials in LTS

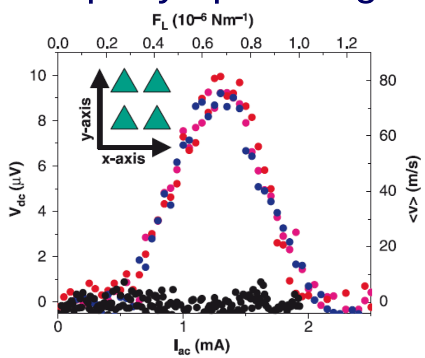
Array of Ni triangles fabricated with EBL on on Si(100) substrates.



Asymmetric pinning centres

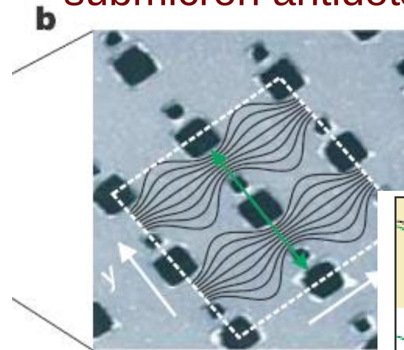
100-nm-thick Nb film on top by sputtering



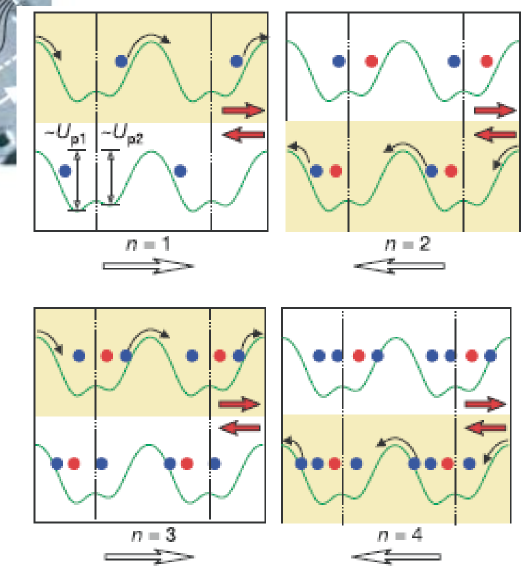


Villegas et al. Science, 302 (2003)

Al films patterned with square arrays of submicron antidots by EBL



Double antidot array → asymmetric pinning potential



Clecio et al, Nature 440 (2006)

- Net motion of vortices versus the ac Lorentz force → ratchet effect
- Direction of the vortex drift does undergo multiple reversals as the vortex density is increased

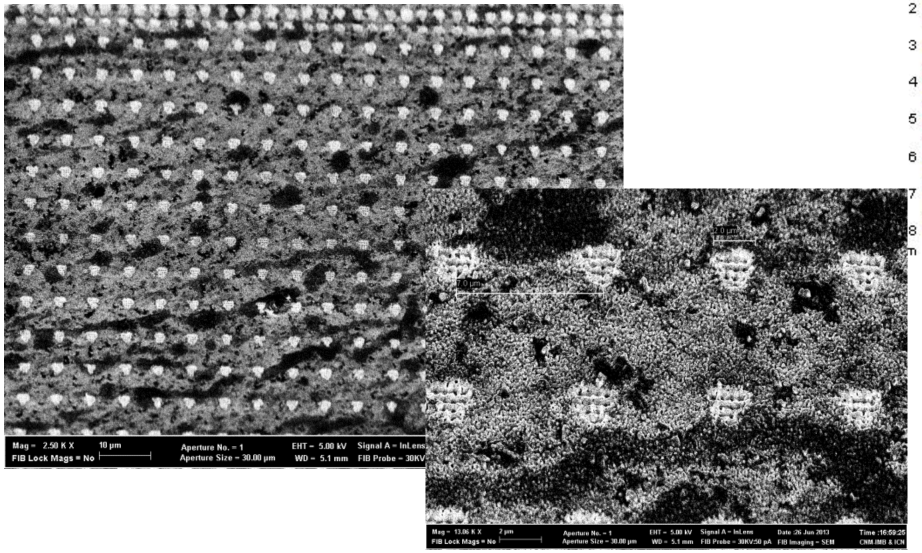
Model systems for understanding similar ratchet phenomena in biological systems

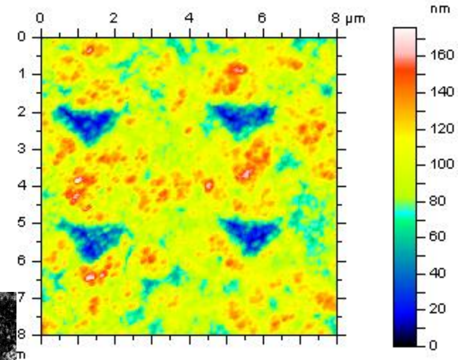
(biomembranes in two drift regimes: diluted (single particles) and concentrated (interacting particles)

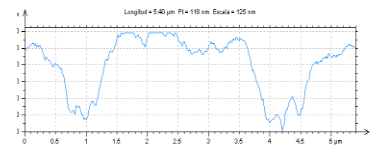
Asymmetric pinning potentials in HTS

HTS: strong intrinsic pinning → highly efficient artificial pinning centers

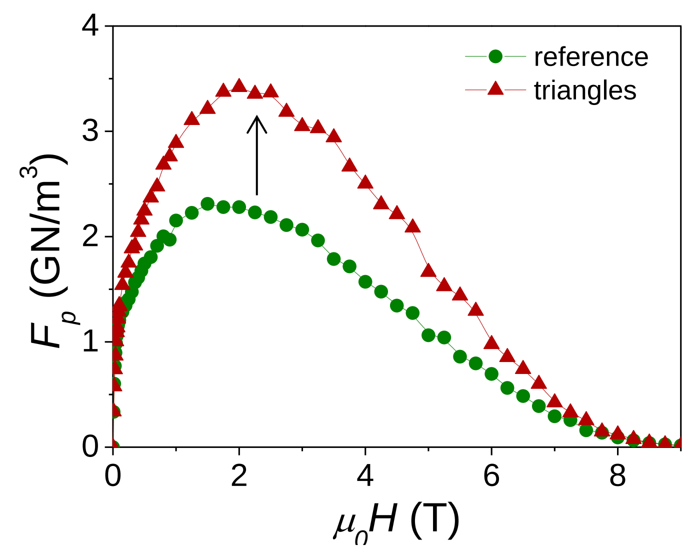
Triangular array of blind antidots fabricated by FIB







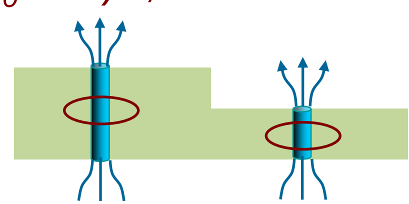
Size ~ 0.5-5 µm
depth ~ 50-150 nm
Shape



Vortex pinning assigned to the local spatial thickness modulation → Reduction of the vortex line free energy

$E_l = \varepsilon_0\, t\, ln(\lambda/\zeta)$

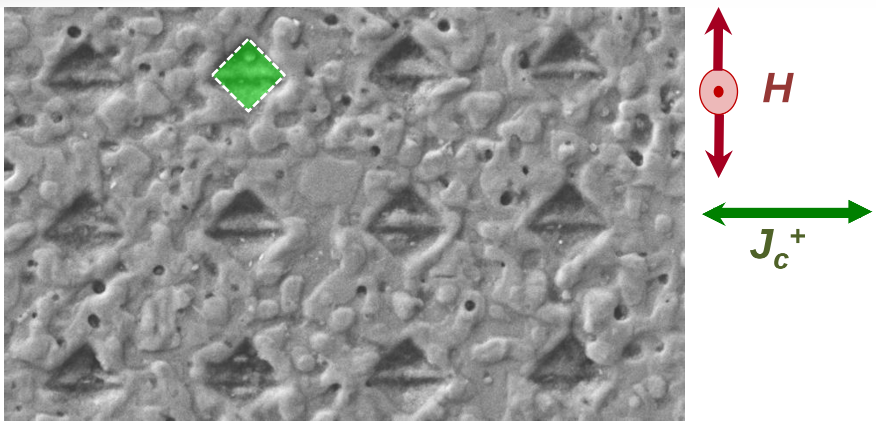
$\varepsilon_0 = (\phi_0/4\pi\lambda)^2$, vortex self energy



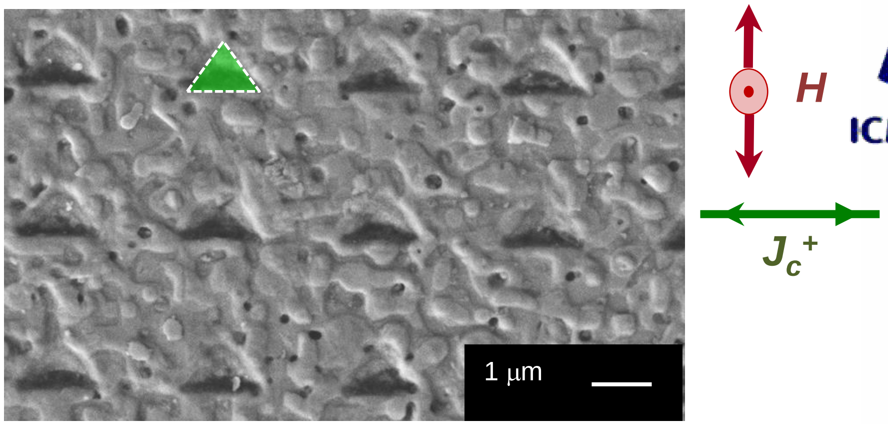
Blind antidots act as effective pinning sites →
F_p> Pinning natural defects

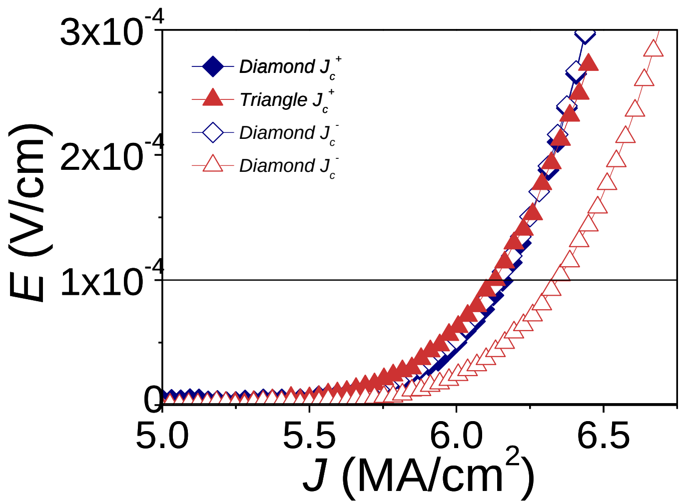
Asymmetries in the critical current density

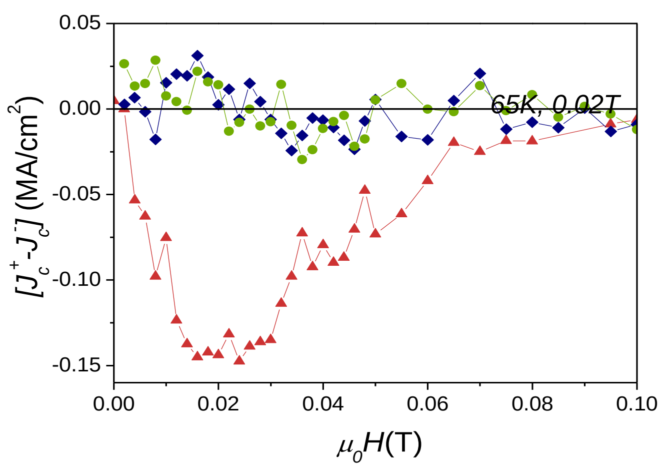
Symmetric (diamond)



asymmetric (triangular)







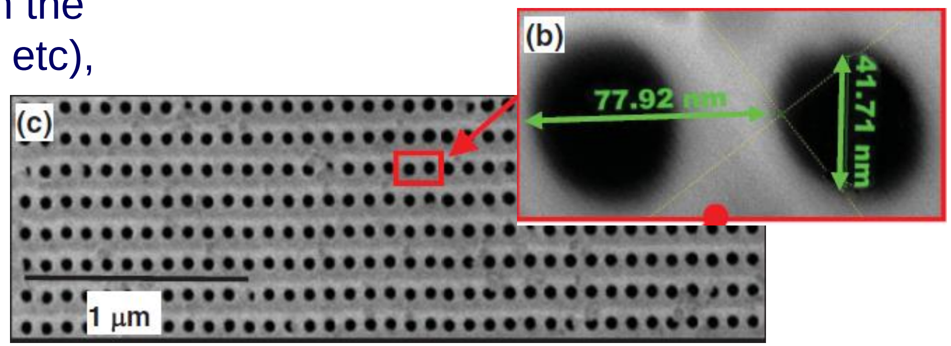
Ratchet at high fields → collective ratchet effect dominated by vortex-vortex interactions

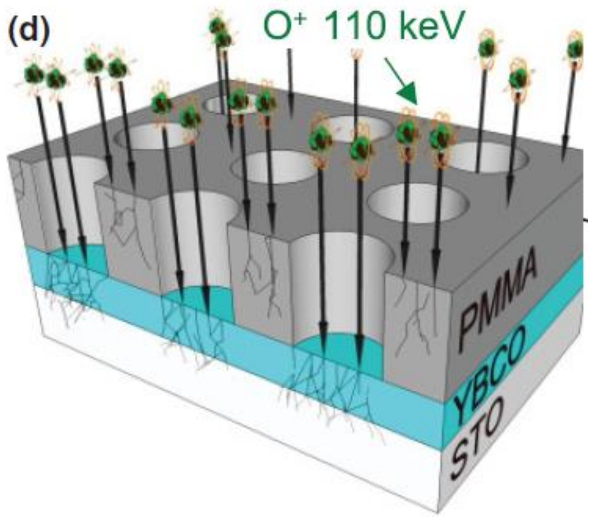
anisotropy in J_c for opposite current directions in the track with anisotropic pinning centers

Palau et al. Physical Rev. B 85 (2002)

Vortex energy landscapes engineered via masked ion irradiation

EBL: periodic hole arrays in PMMA with the desired geometry (square, rectangular, etc),



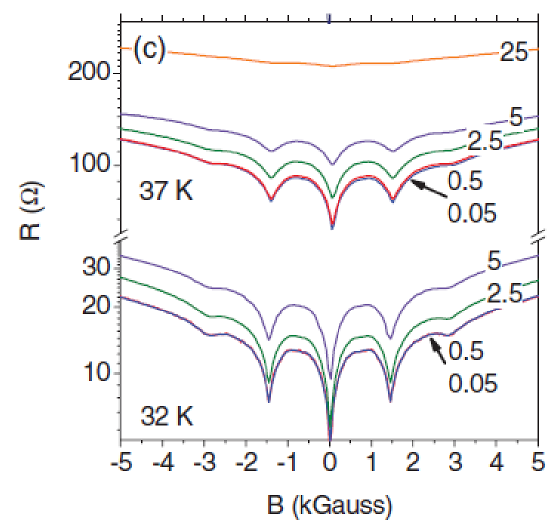


nanoperforated PMMA layer used as a mask through which O+ ions are irradiated

The O+ ion bombardment does not change the YBCO surface morphology but creates point defects

Nanometric resolution→ vortex manipulation in very high magnetic fields (up to two orders of magnitude higher than with other techniques)

Study of matching fields at much higher fields and temperatures than LTS

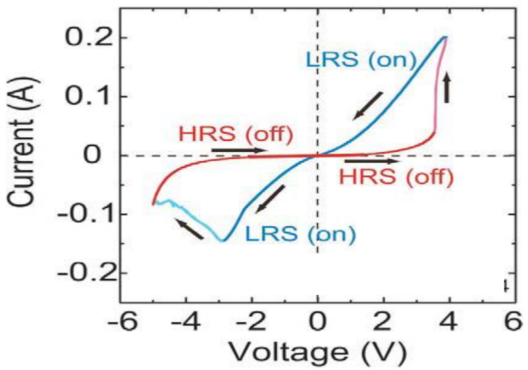


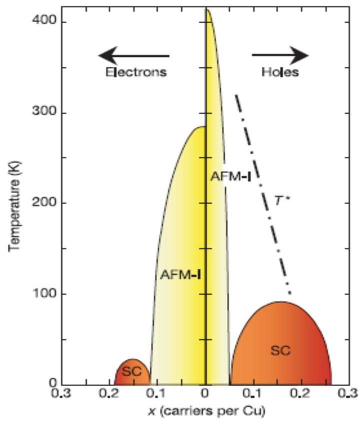
Minima →One vortex at each defect

Reconfigurable pinning sites: Resistive switching effect

Resistive switching fenomena: two reversible resistance states (ON/OFF) induced upon an application of an electric field

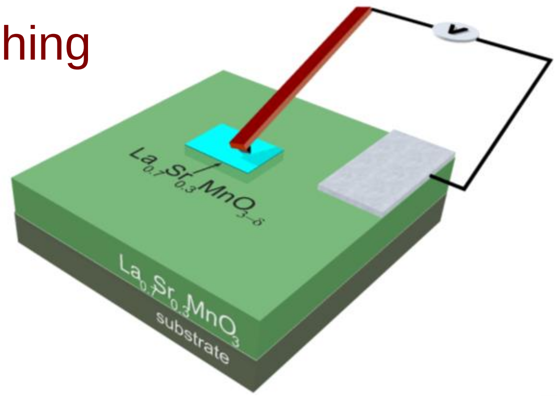
Observed in complex oxides with a metal insulator transition that can be controlled by doping





Phase diagram of the HTS

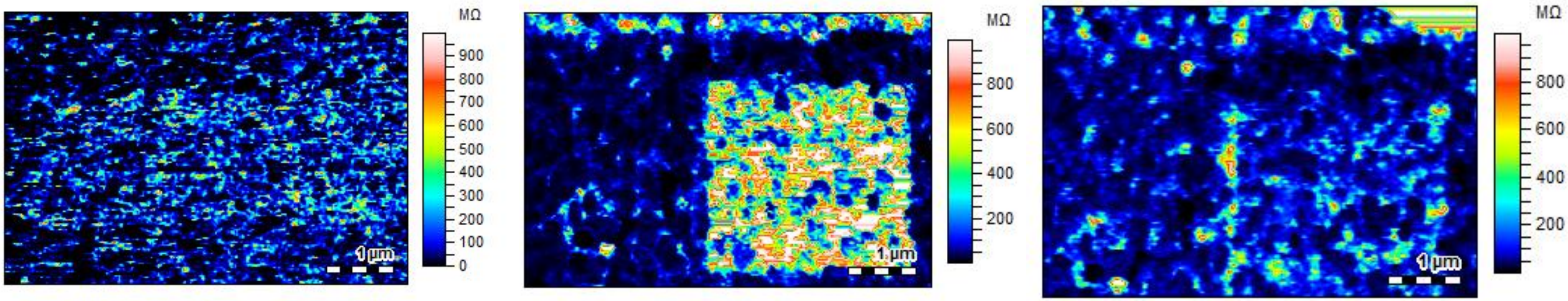
current –SPM to apply large local Electric fields → Switching reversible Metal / Insulator transitions at the nanoscale

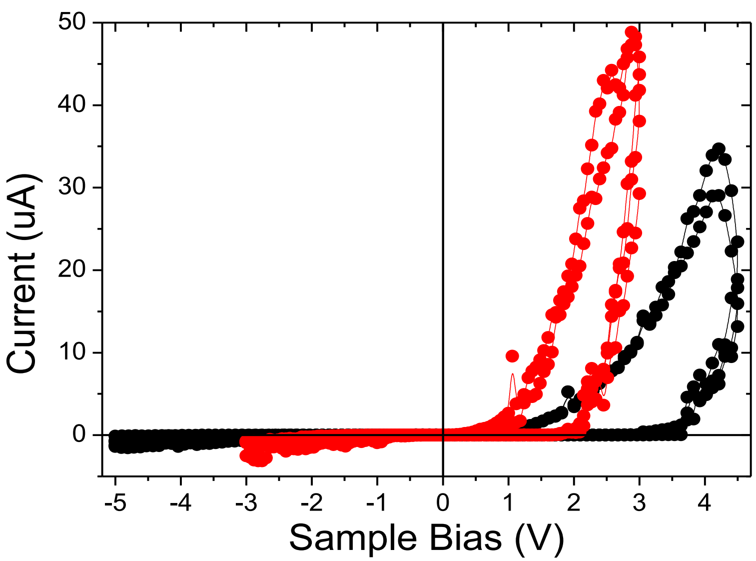


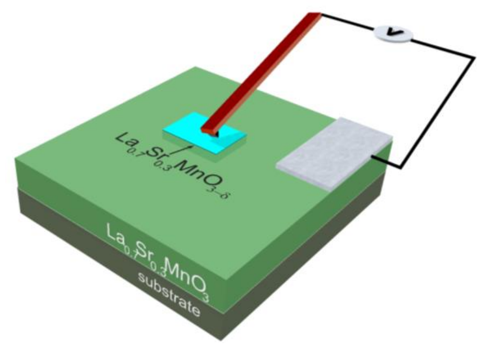
Induce nanometric reversible non SC regions in SC films → reconfigurable pinning sites

Resistive Switching phenomena in YBCO thin films

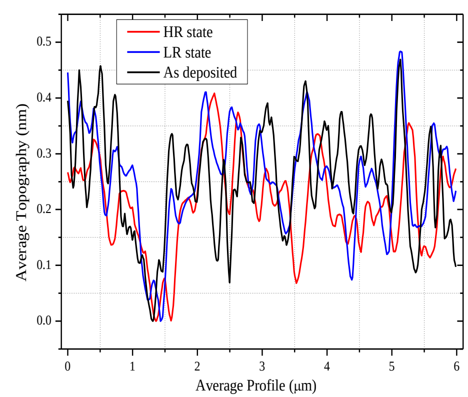
WRITE (HR) -3.5V **ERASE (LR)** 3.5V



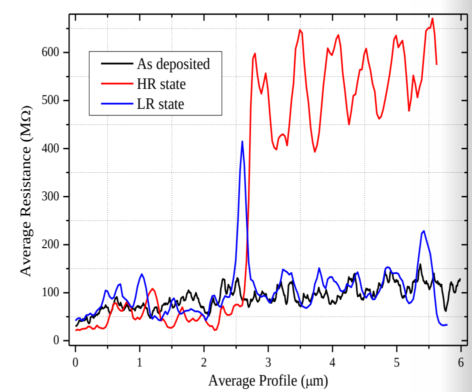




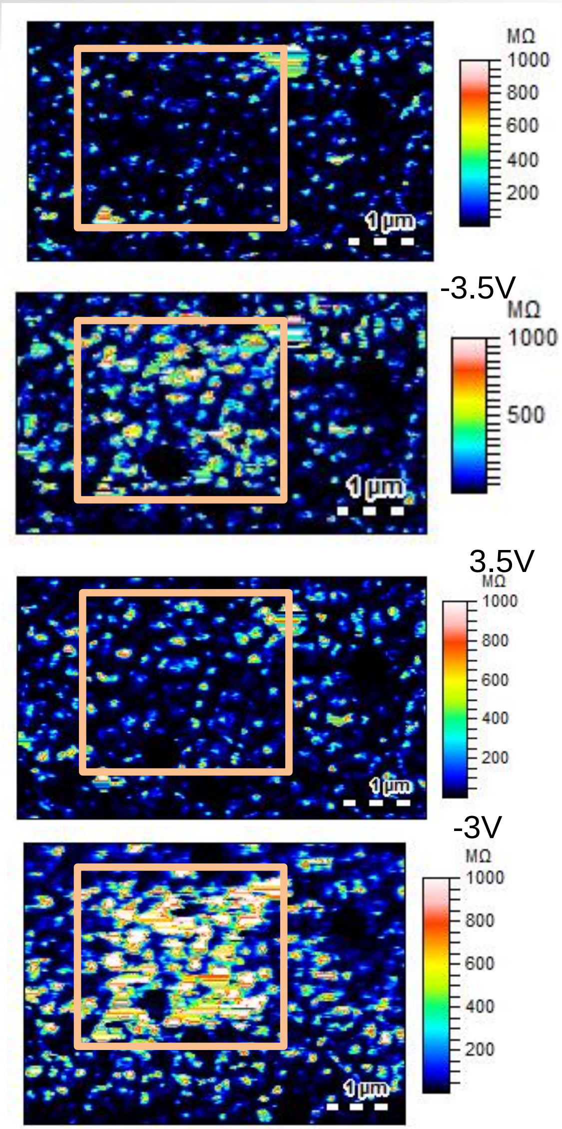
No surface modification

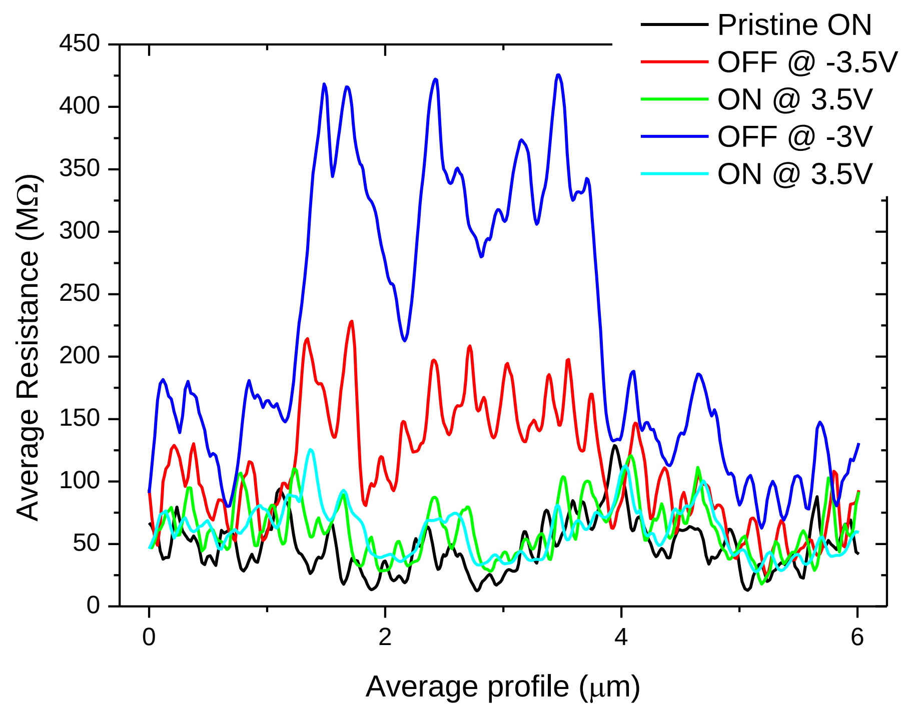


Resistance modulation



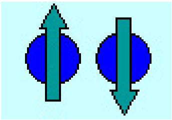
Different resistance states can be induced

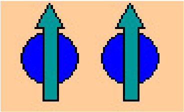




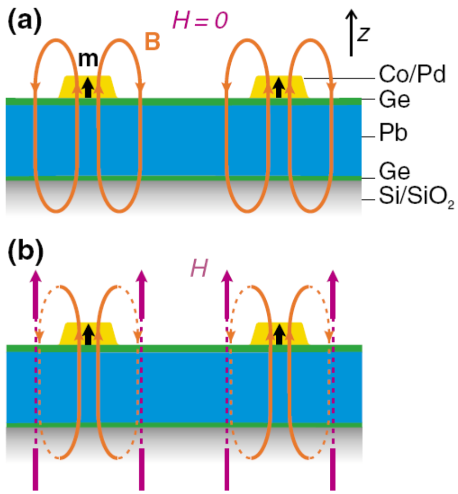
Hybrid systems: Ferromagnetic/Superconductor interactions

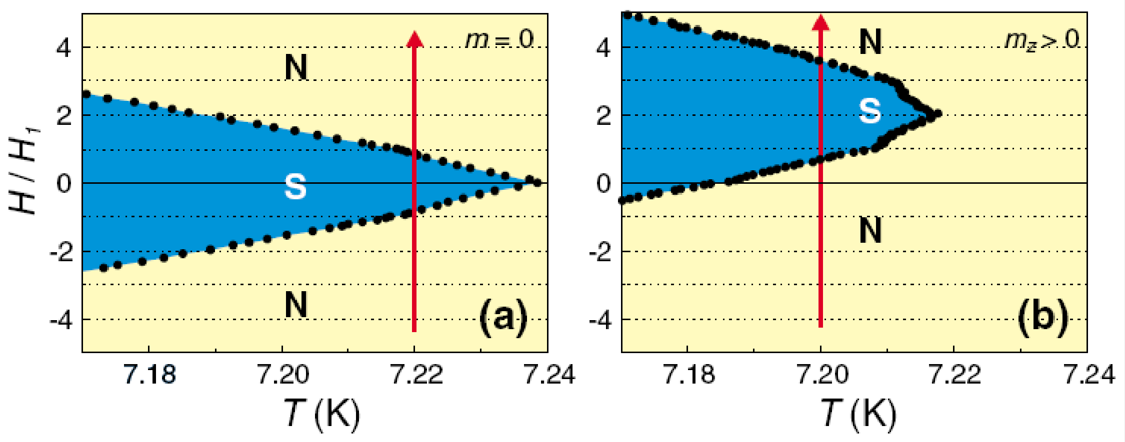
Antagonic phenomena

Cooper pairs in a superconductor (SC) $\rightarrow$ e^- with opposite spin 

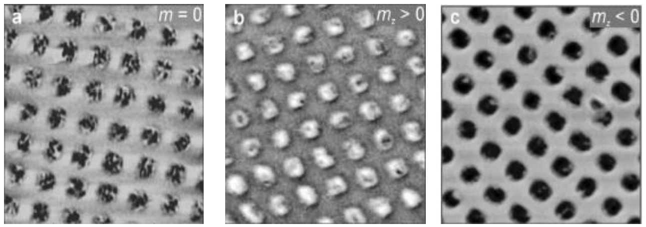
Ferromagnetic (FM) $\rightarrow$ aligned spins 

LTS with FM nanodots fabricated by EBL





Magnetic-field-induced superconductivity due to the compensation of the applied field by the stray field of the dipoles.



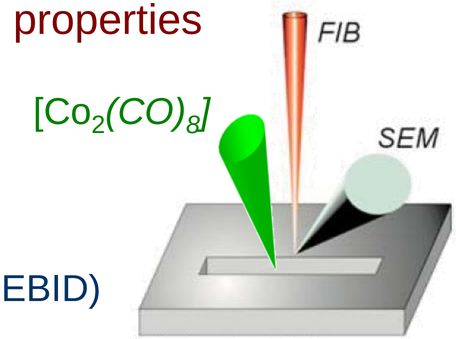
MFM images

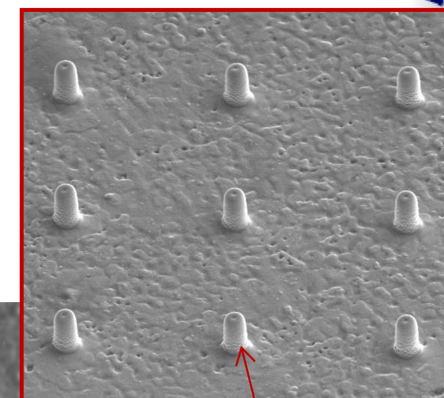
switching between different magnetic states of nanodots the SC and Normal states can be effectively controlled

M. Lange et al., PRL 90 (2003)

Hybrid SC/FM systems with HTSC

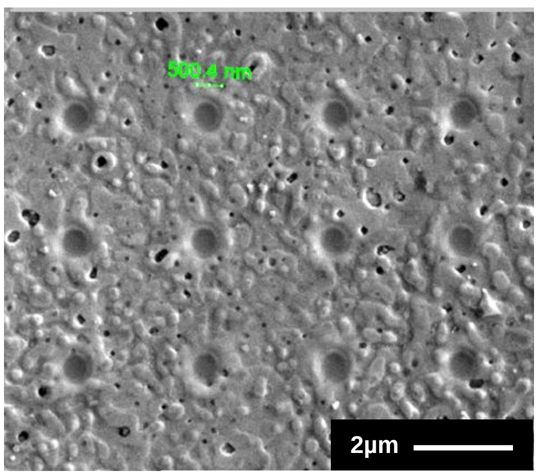
Difficult to fine nanofabrication techniques to combine FM nanostructures in HTS without damaging de SC properties



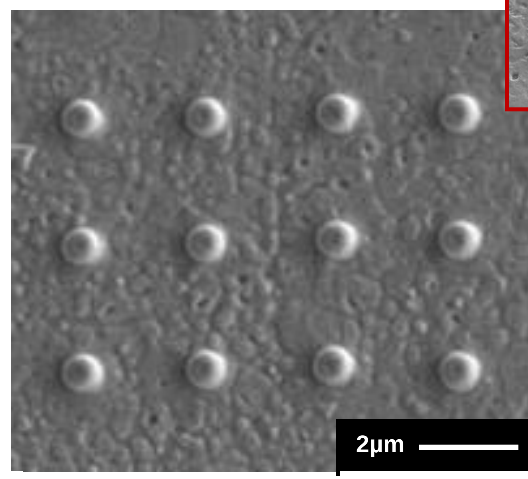


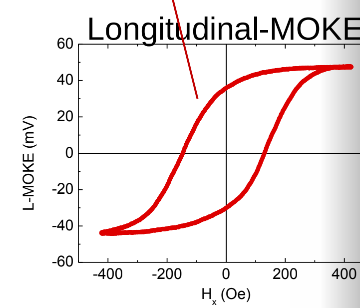
Focused Ion Miling (FIB) +
Focused Electron Beam Induced Deposition (FEBID)

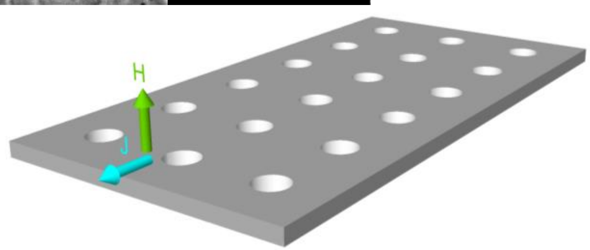
Antidots

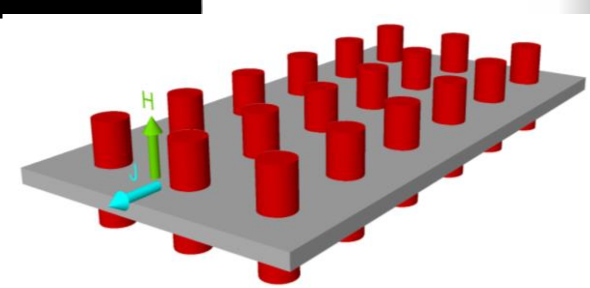


Co rods









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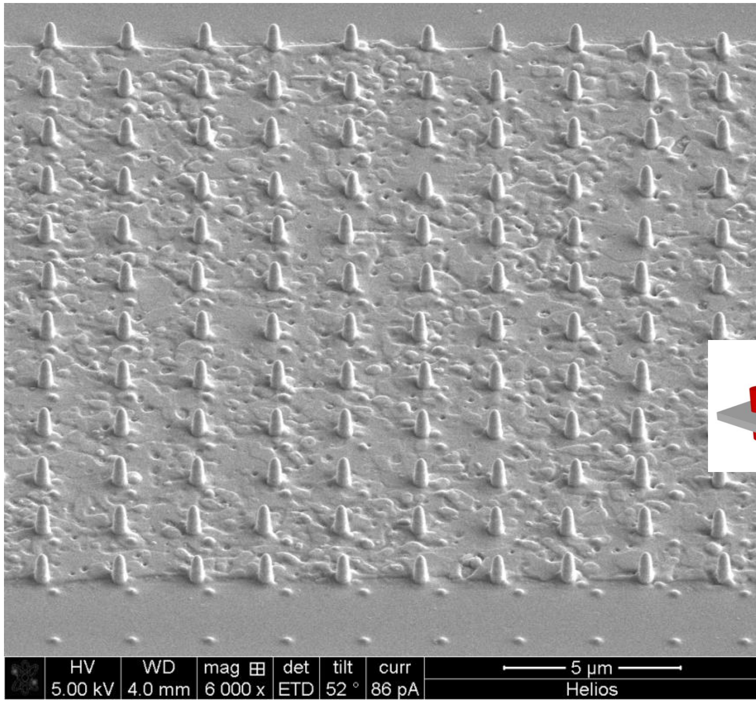
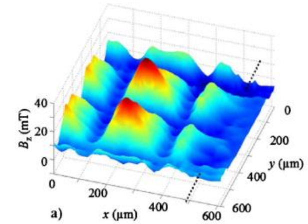
Focalized deposition → No damage of the SC properties

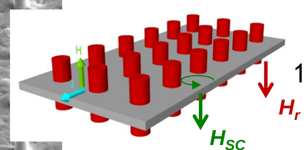
YBCO thin film pierced by ferromagnetic Co rods

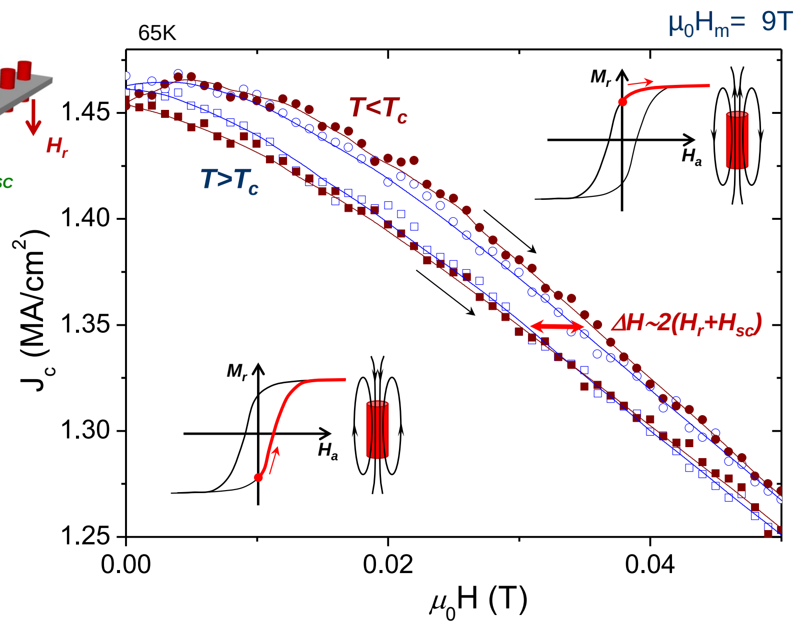
model HTS hybrid system



YBCO high intrinsic pinning → trapped magnetic fields in the SC may interact with FM nanostructures







explore novel interactions which do not appear in other wider studied systems based on conventional LTS

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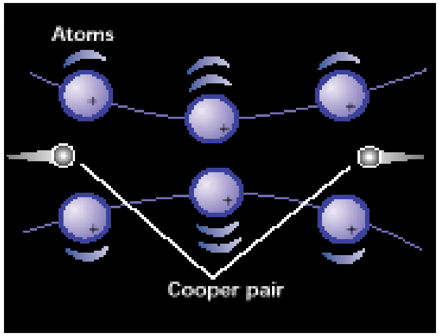
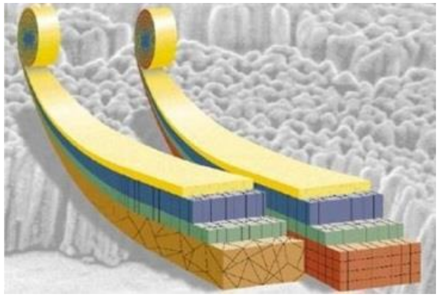
Rouco et al. in prep.

SUMMARY

- The superconductivity is a quantum phenomena which have already improved our lives and present a lot of new applications (supercurrent wires)



- High-temperature cuprate superconductors are among the most complex materials ever explored for practical application



- Nanotechnology in superconductors is essential for high magnetic field applications