

中國科學院物理研究所

Institute of Physics, Chinese Academy of Sciences



超导基础理论和实验技术讲座

National Lab for Superconductivity Lecture Series

【第95期】

高温超导涂层导体及其磁通钉扎的人工调控



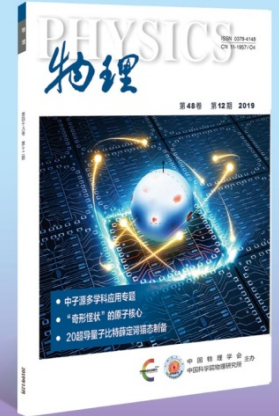
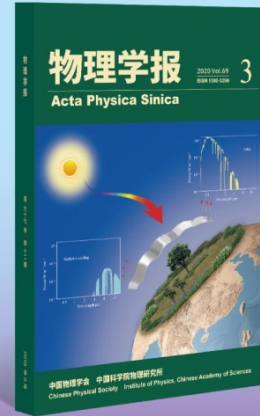
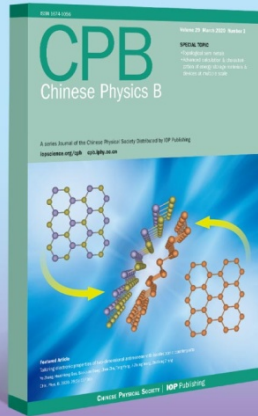
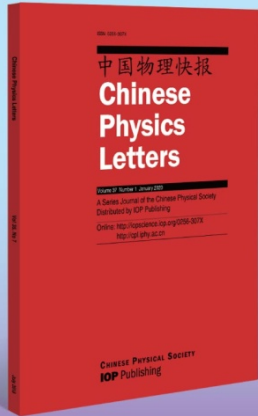
蔡传兵

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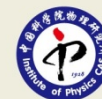
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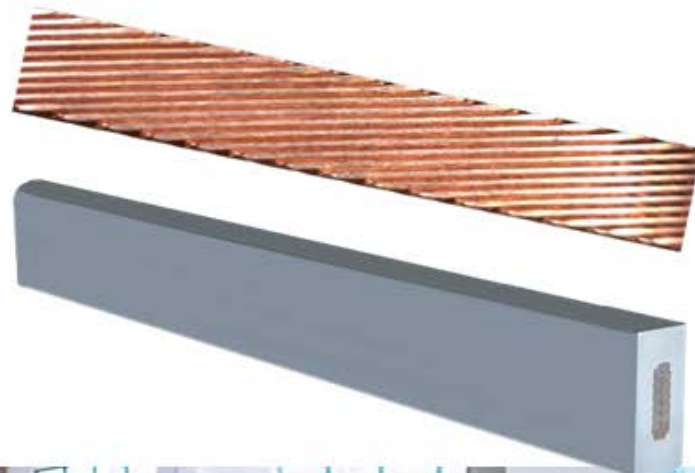
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蔡传兵，上海大学理学院物理系教授，上海市高温超导重点实验室主任。长期从事氧化物超导材料及其薄膜异质结功能器件研究。

先后在中科院上海冶金所（现微系统所）、日本大阪大学、日本铁道综合技术研究所、英国伯明翰大学、德国莱布尼茨固体材料所学习和工作。

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高温超导涂层导体 及其磁通钉扎的人工调制

蔡传兵

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@上海大学理学院物理系、高温超导重点实验室
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- 赵跃、洪志勇等 @上海超导科技股份有限公司
- 熊旭明、蔡渊等 @苏州新材料研究所
- 张喜泽、宗曦华等 @上海电缆研究所/上海国际超导科技有限公司
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一

实用超导材料概况

二

高温超导涂层导体技术演变和发展现状

三

高温超导涂层导体磁通钉扎及其人工调制

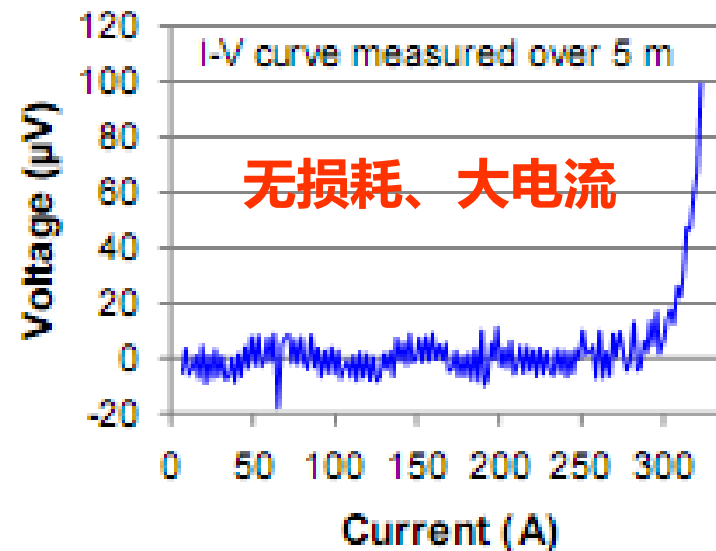
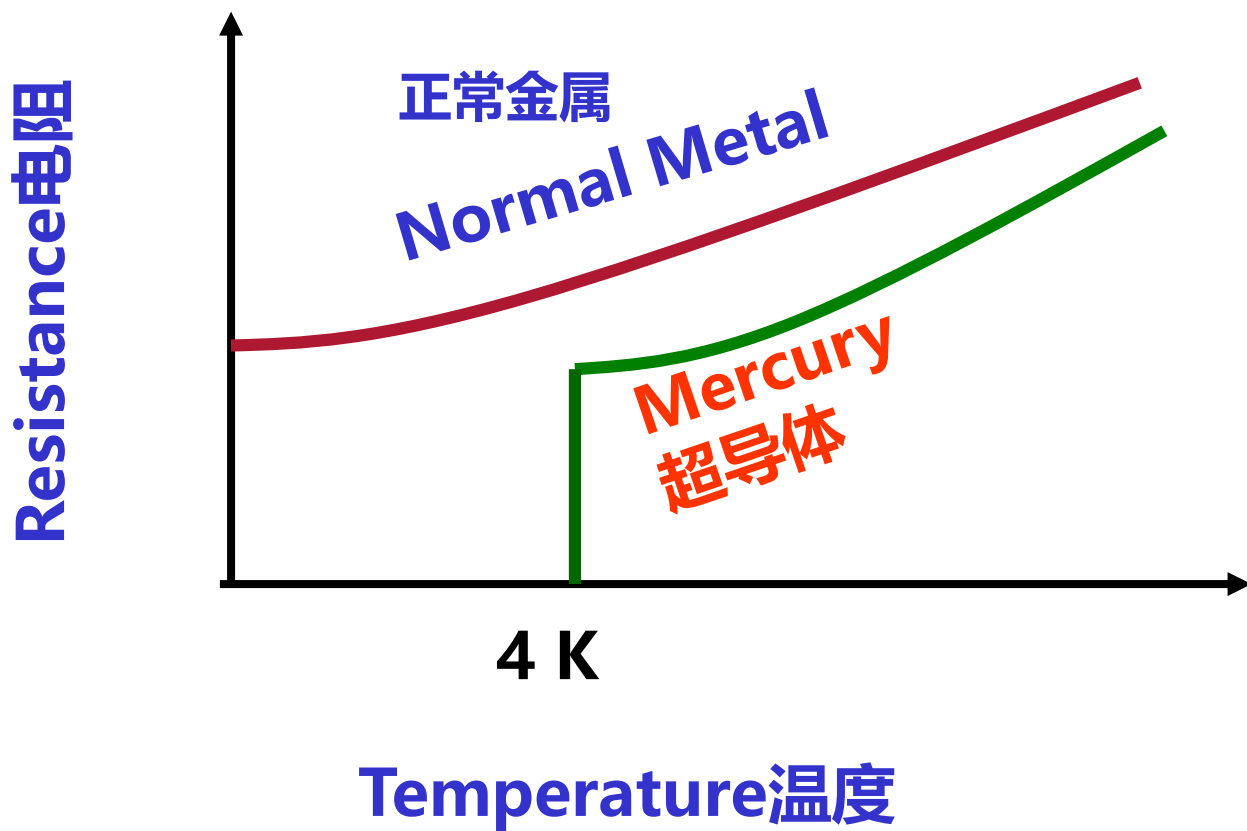
四

若干应用发展和挑战

前言: 超导的发现

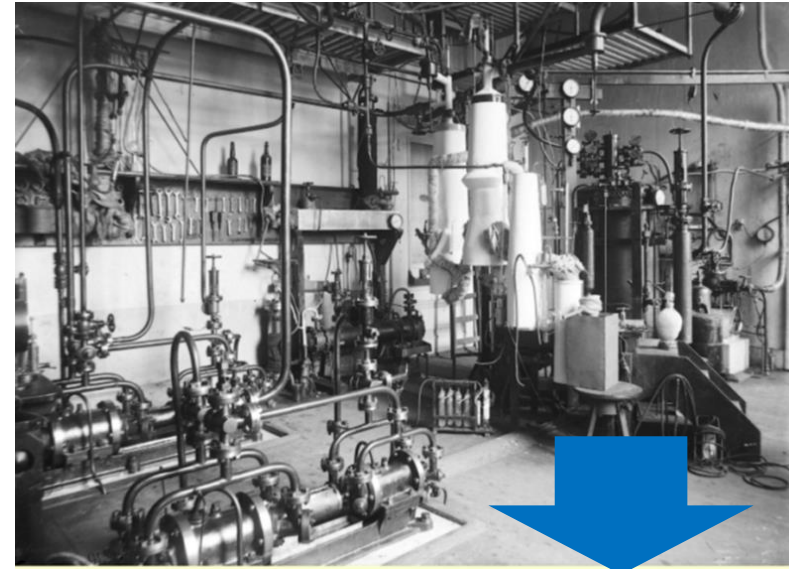
Resistance of Mercury

Onnes (1911/4/8) 荷兰Leiden大学教授(1913Nobel)



百年前发现、商业应用已半个世纪、大规模应用not yet

超导圣地Leiden: a typical university city, the oldest university (1575) in NL



20世纪初
难题:

永久气体
He的液化



@2011
After 100th
Anniversary



Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

A. P. Drozdov^{1*}, M. I. Erements^{1*}, I. A. Troyan¹, V. Ksenofontov² & S. I. Shylin²

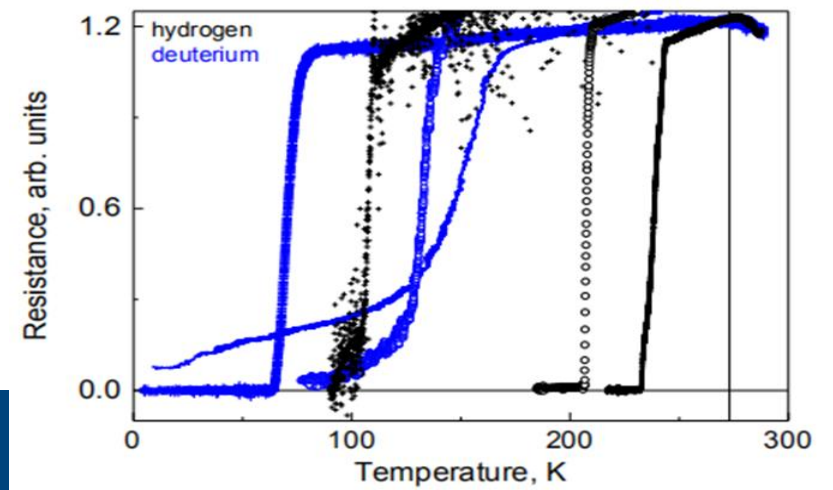
Nature 525(2015 Sept.)

$$T_c \approx \tilde{\Omega} \exp\left(-\frac{1}{\lambda - \mu^*}\right)$$

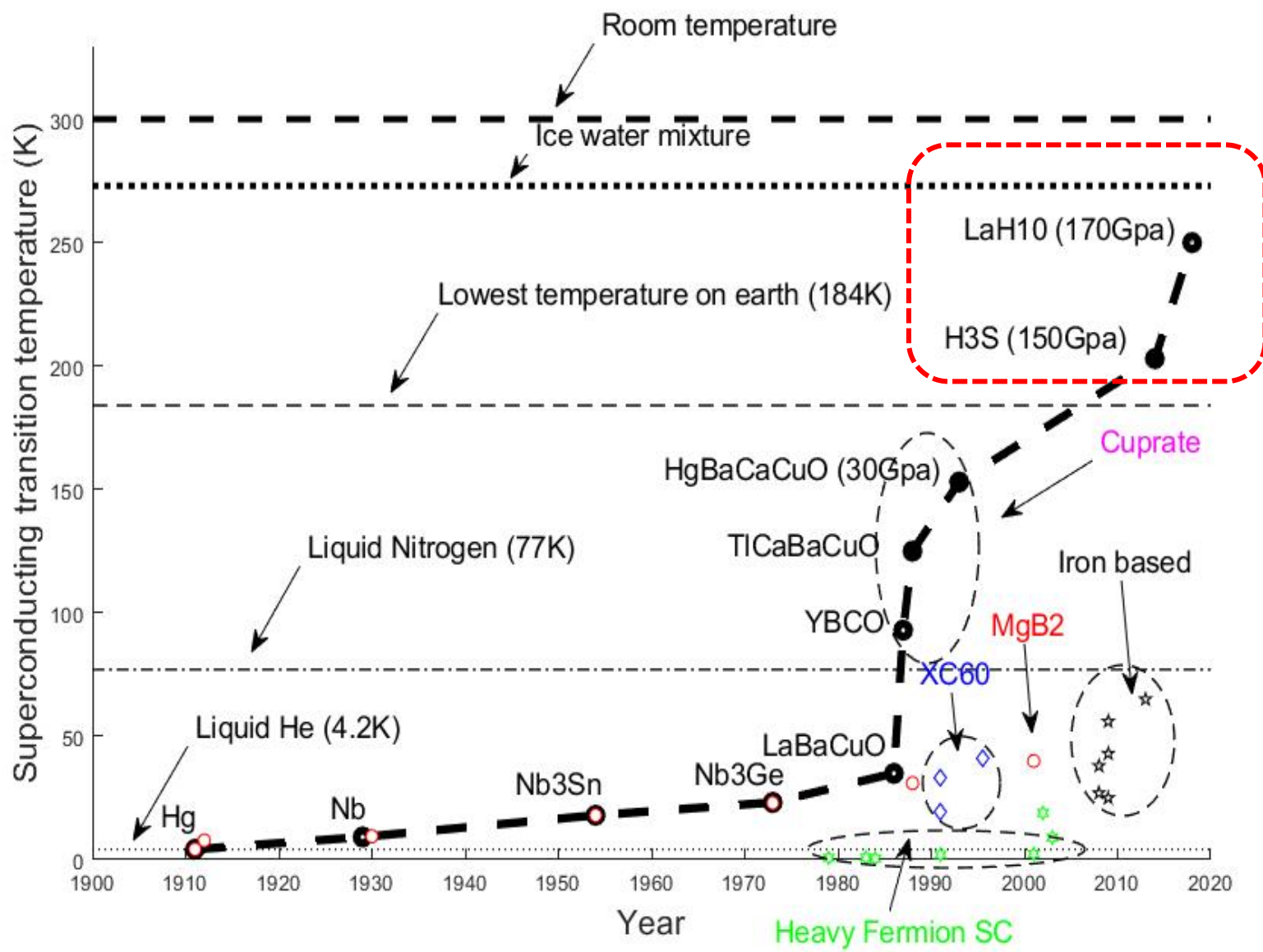
BCS和Migdal-Eliashberg

Superconductivity at 250 K in lanthanum hydride under high pressures

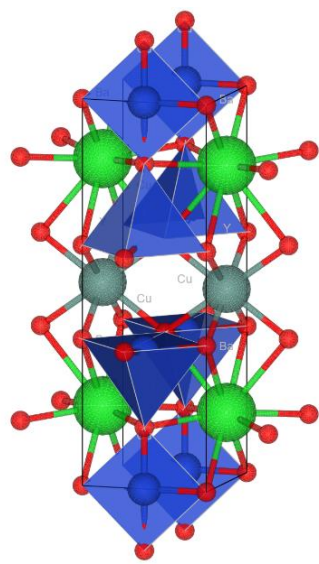
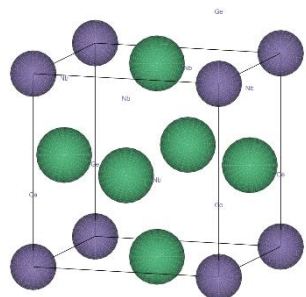
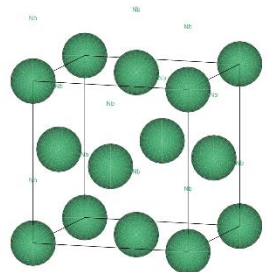
A. P. Drozdov¹, P. P. Kong¹, V. S. Minkov¹, S. P. Besedin¹, M. A. Kuzovnikov^{1,6}, S. Mozaffari², L. Balicas², F. Balakirev³, D. Graf², V. B. Prakapenka⁴, E. Greenberg⁴, D. A. Knyazev¹, M. Tkacz⁵, and M. I. Erements¹



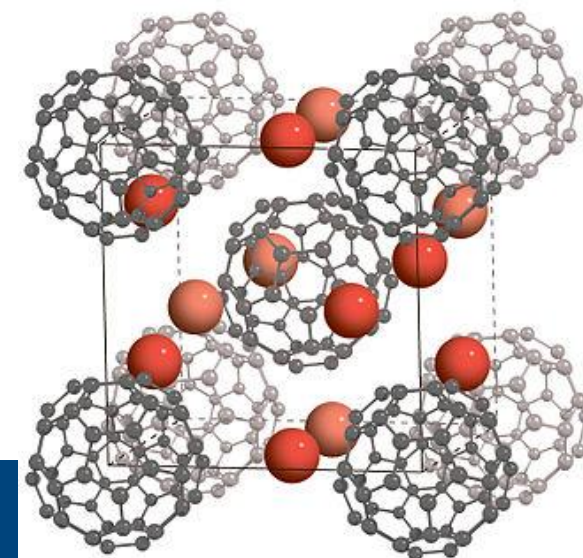
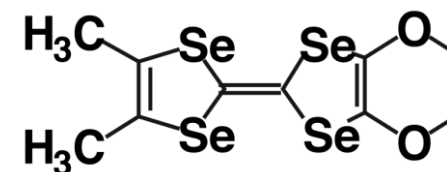
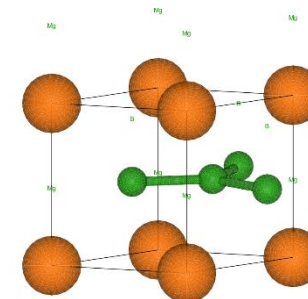
Superconducting Material Family: Old and Young !



Superconductor family- from single element to macromolecule



Type	Name	Tc
Simple metals	Nb	9K
Alloys	Nb ₃ Ge	23K
Organic SC	MgB ₂	39K
	DMEDO-TSeF	4.8K
Molecular SC	M ₃ C ₆₀ (M = Na, K, Rb)	42K
Oxy-pnictides	SmFeAs(O,F)	55K
Cuprate	YBa ₂ Cu ₃ O _x	90K
	HgBa ₂ Ca ₂ Cu ₃ O _x	135K



唯象的单胞原子数 vs. Tc (高压效应除外)

HTS材料实用化的基本要素

▶ 本征特性

- ◆ 特定运行温度下的不可逆场
- ◆ 临界电流密度及其磁场依赖性
- ◆ 各向异性

▶ 晶界连接

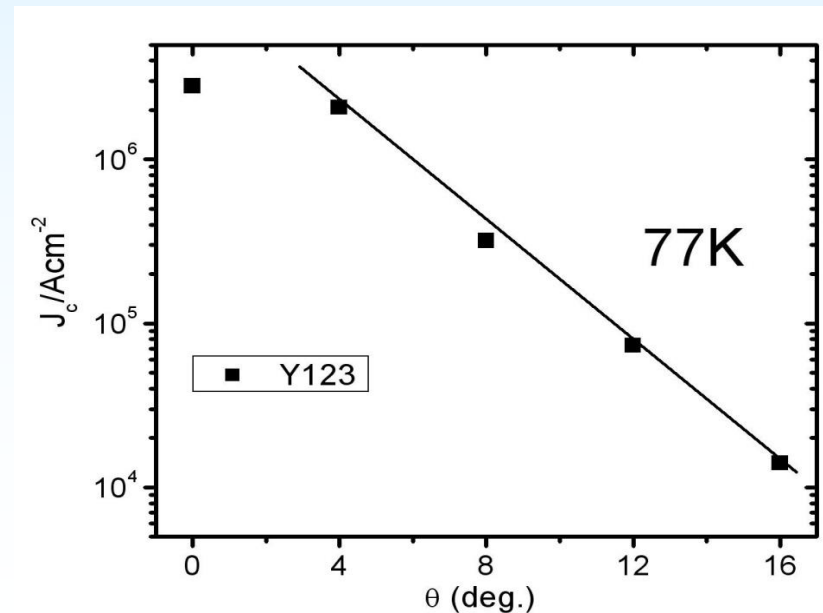
- ◆ 晶界和晶内载流能力
- ◆ 晶界弱连接情况

$$J_c(\theta) = J_c(0), \quad \theta < 4^\circ$$

$$J_c(\theta) = J_c(0) \exp[-(\theta - \theta_0) / \theta_1], \quad \theta > 4^\circ$$

▶ 可控制备和机械性

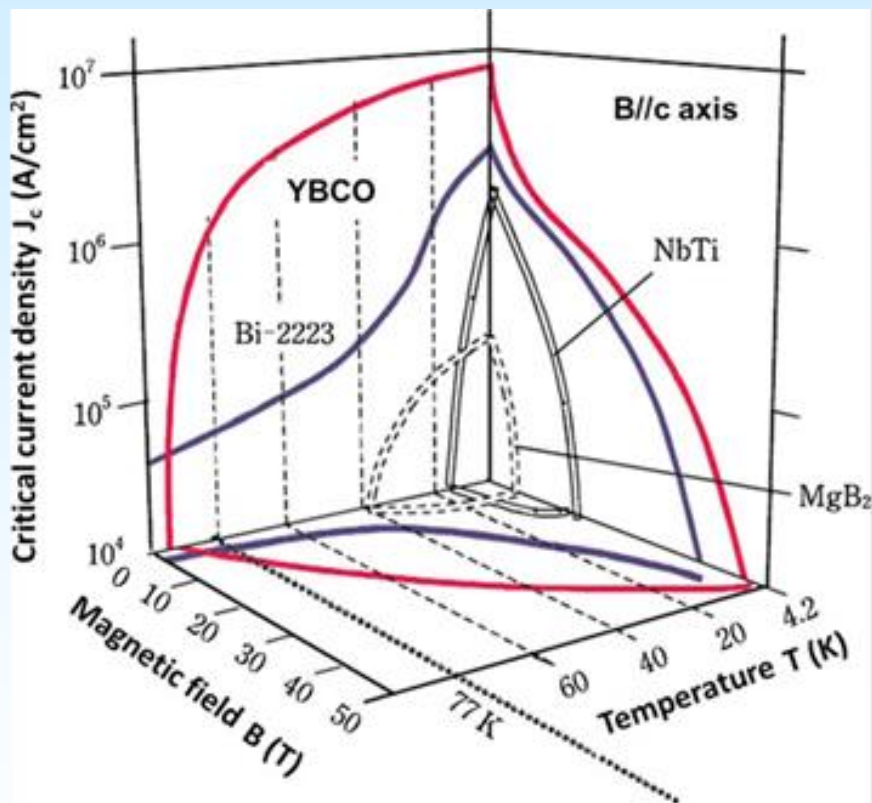
- ◆ 柔韧性和致密化
- ◆ 材料和工艺成本
- ◆ 高密度可控的缺陷或无序 (适度“脏”)

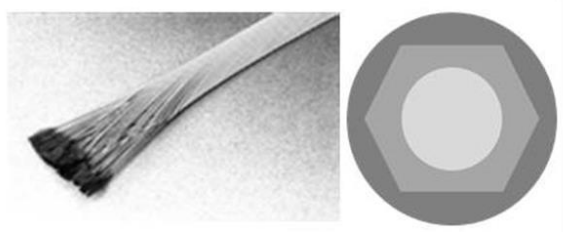

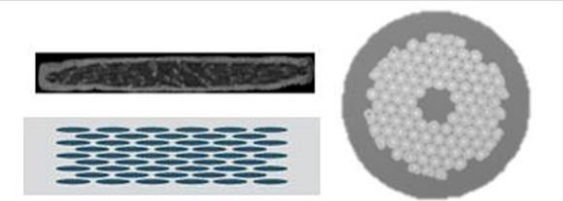
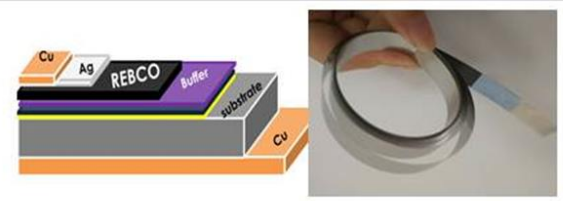


▶ 环境友好性

主要实用超导材料一览：三维相图及外观形貌

(包括NbTi、MgB₂、Bi2223、RE123等)的临界温度 T_c (B , J)、上临界磁场 B_{c2} (T , J)和临界电流密度 J_c (T , H) 三维图。可见RE123在较大温度、磁场范围获得较高的临界电流密度 (红色)

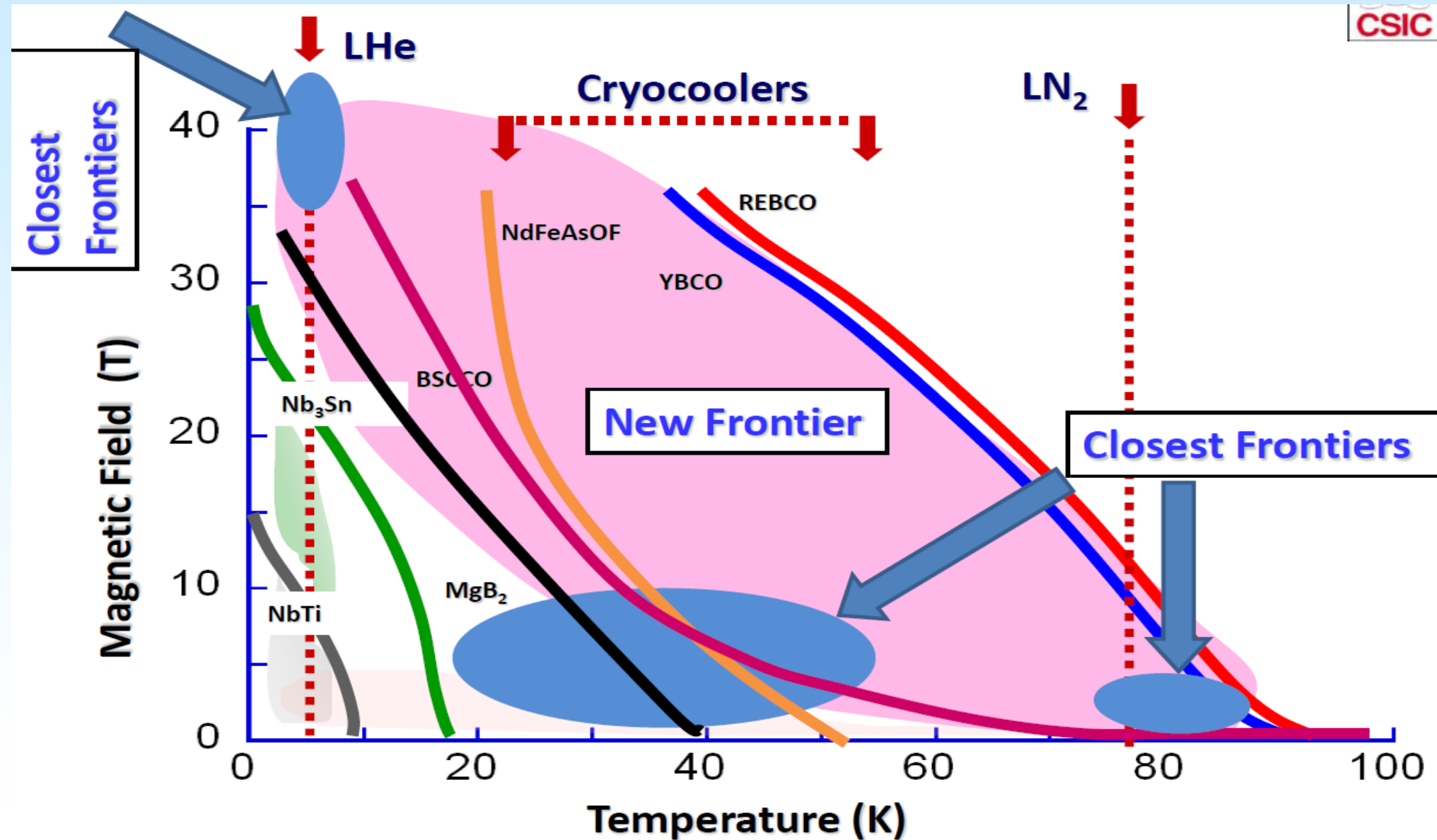


<p>低温超导线材/商业化成熟 金属 NbTi (Nb₃Sn etc.)</p> 	<p>中温超导线材/商业化探索 化合物 MgB₂/Fe-based</p> 
<p>1G高温超导带材/商业化中期 氧化物 Bi2223/Bi2212</p> 	<p>2G高温超导带材/商业化初期 氧化物 REBCO</p> 

Crisan, Vortices and Nanostructured Superconductors, Springer Series in Materials Science 261, 2017

常用实用化超导材料的外观形貌及截面图

Practical SC Materials vs. Operating Temperatures

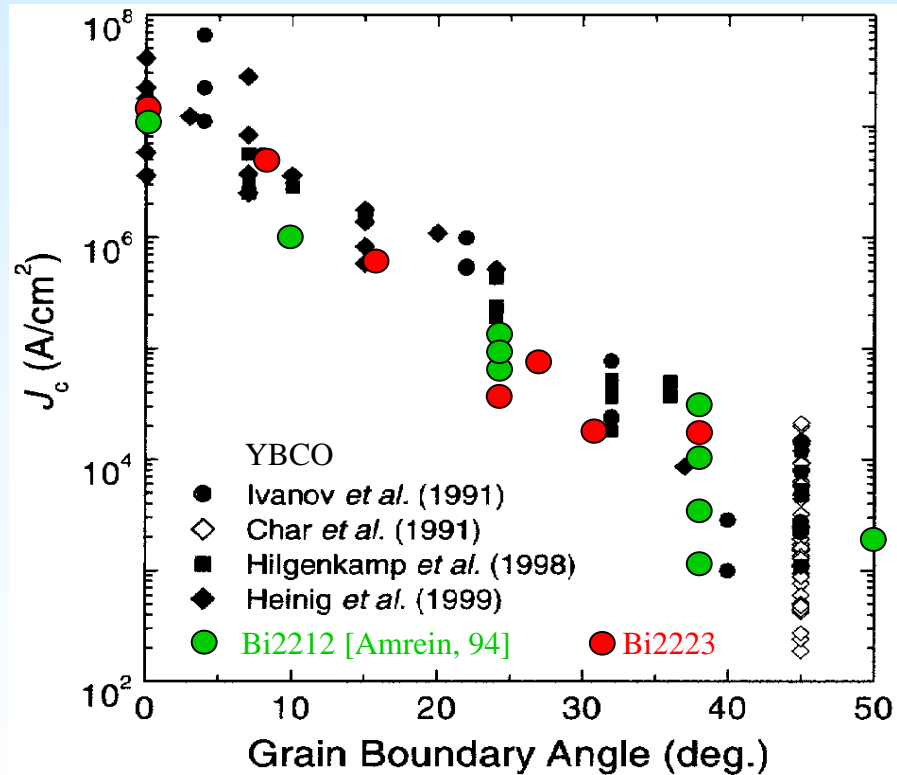


Adapted from M. Matsumoto

Fundamental Challenges of Cuprate HTS Application

J_c limited by weak link@GBs

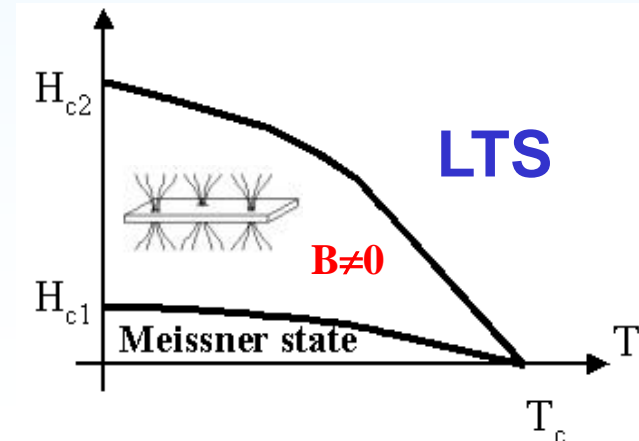
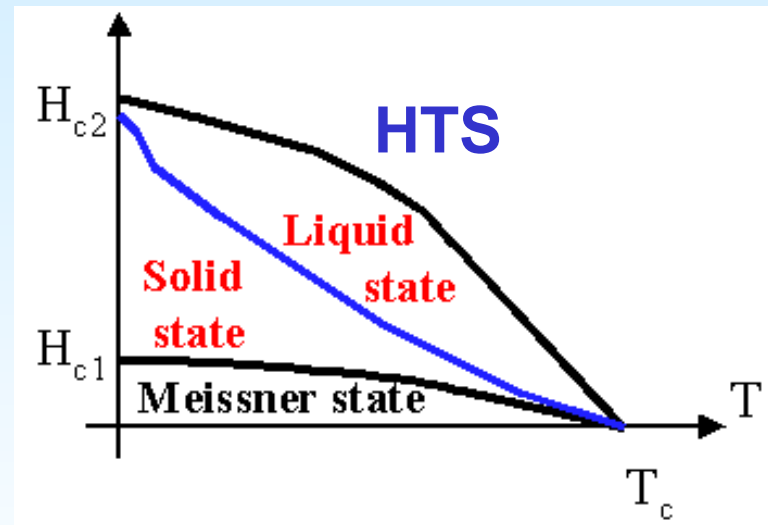
- Layered structure
- $\xi_{ab} = 1.3-3.5\text{nm}$; $\xi_c = 0.2-1\text{nm}$



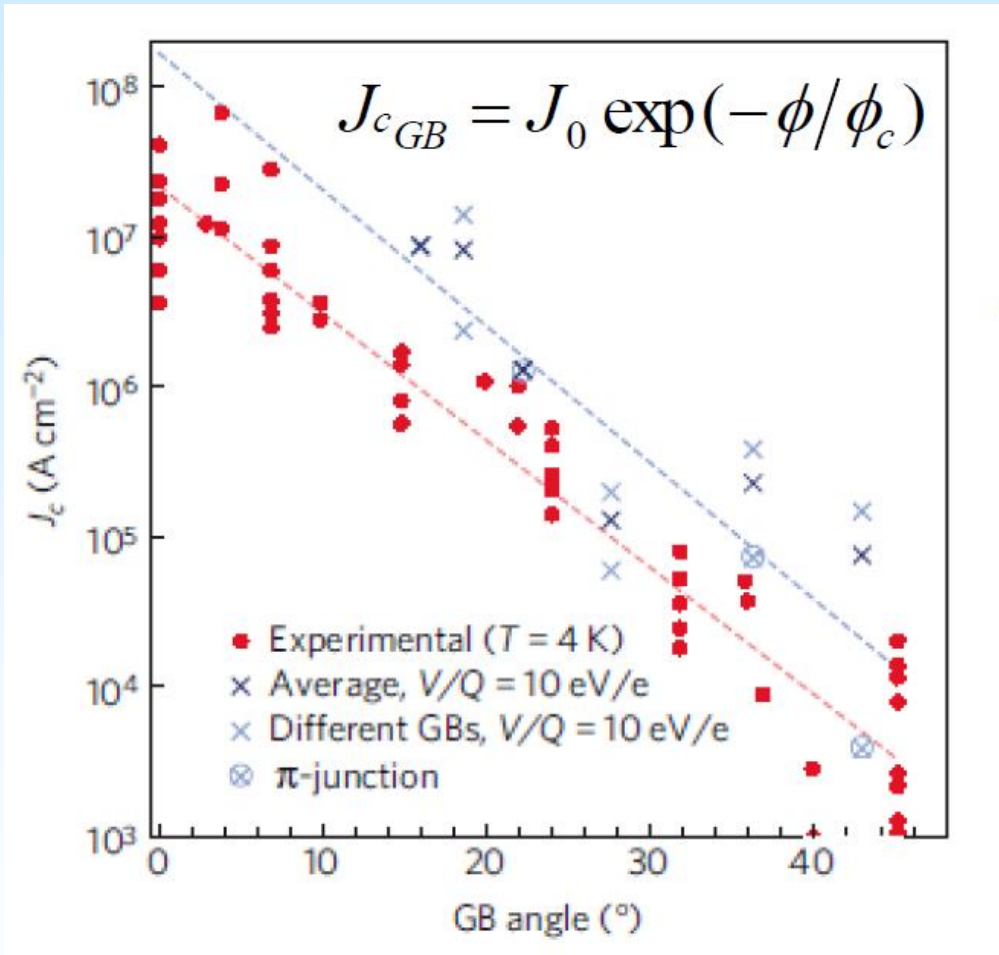
$$J_c(\vartheta) = J_c^0 * \exp(-(\vartheta - 4^\circ) / 2.4^\circ) \text{ for } \vartheta > 4^\circ$$

Giant flux motion by thermal fluctuation

- high running temperature
- Low pinning potential of single vortex ($\sim \xi^n$)

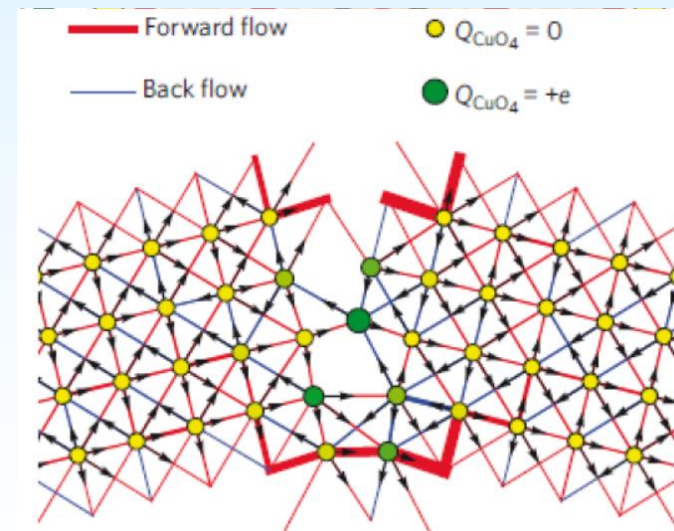
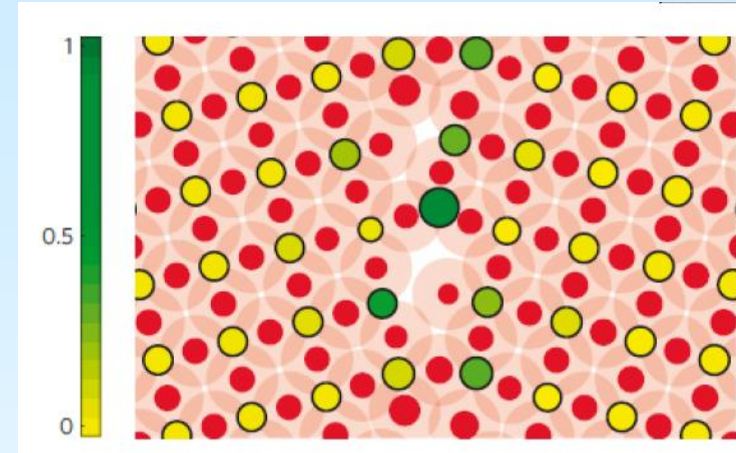


HTS实用化基础问题(1): 晶界弱连接



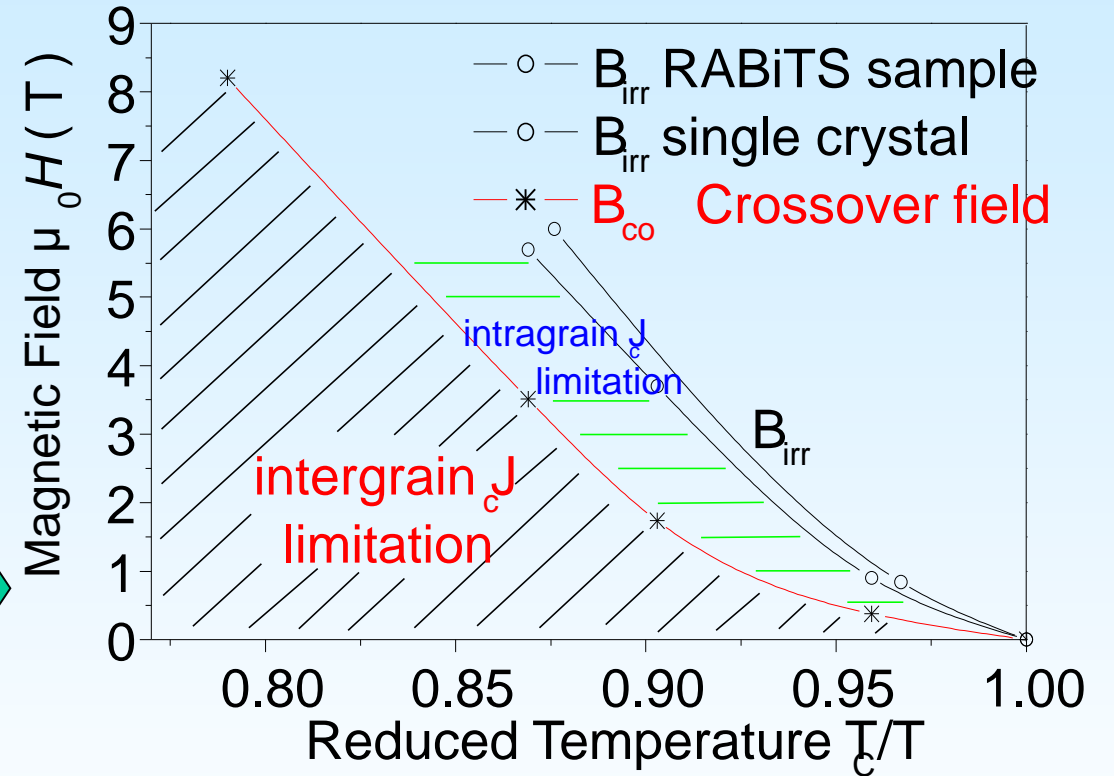
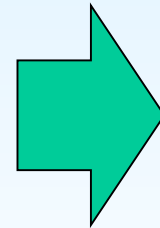
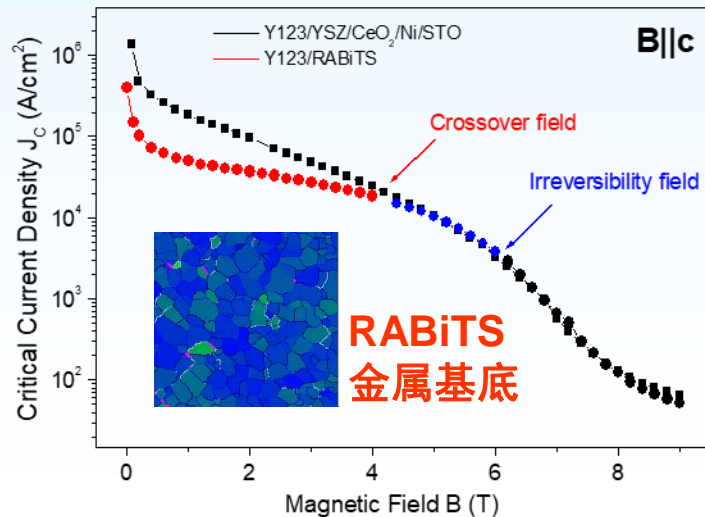
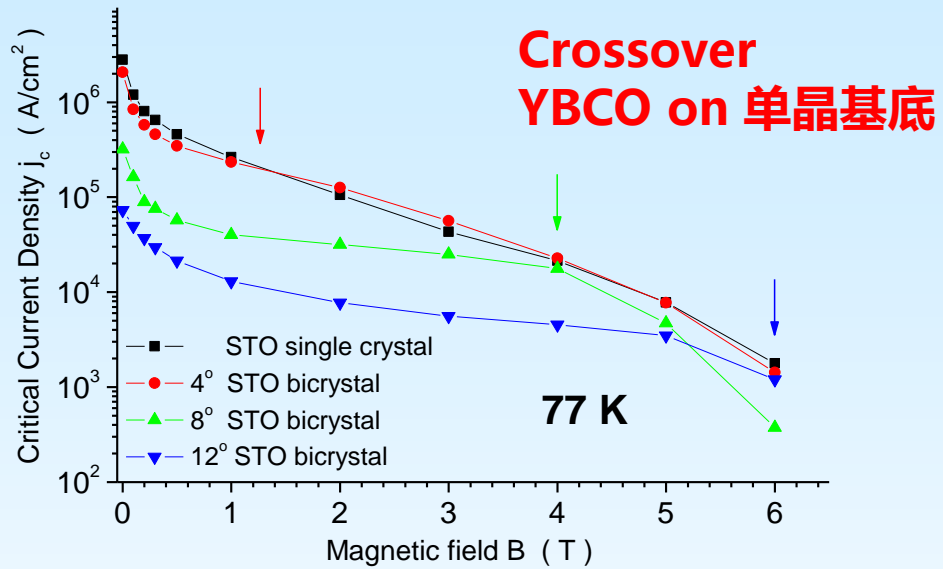
Charging of CuO_4 quares: screening $L \sim$ Interatomic d

Graser, Nature Phys 6 (2010) 609
Wolf, PRL, 108 (2012) 117002



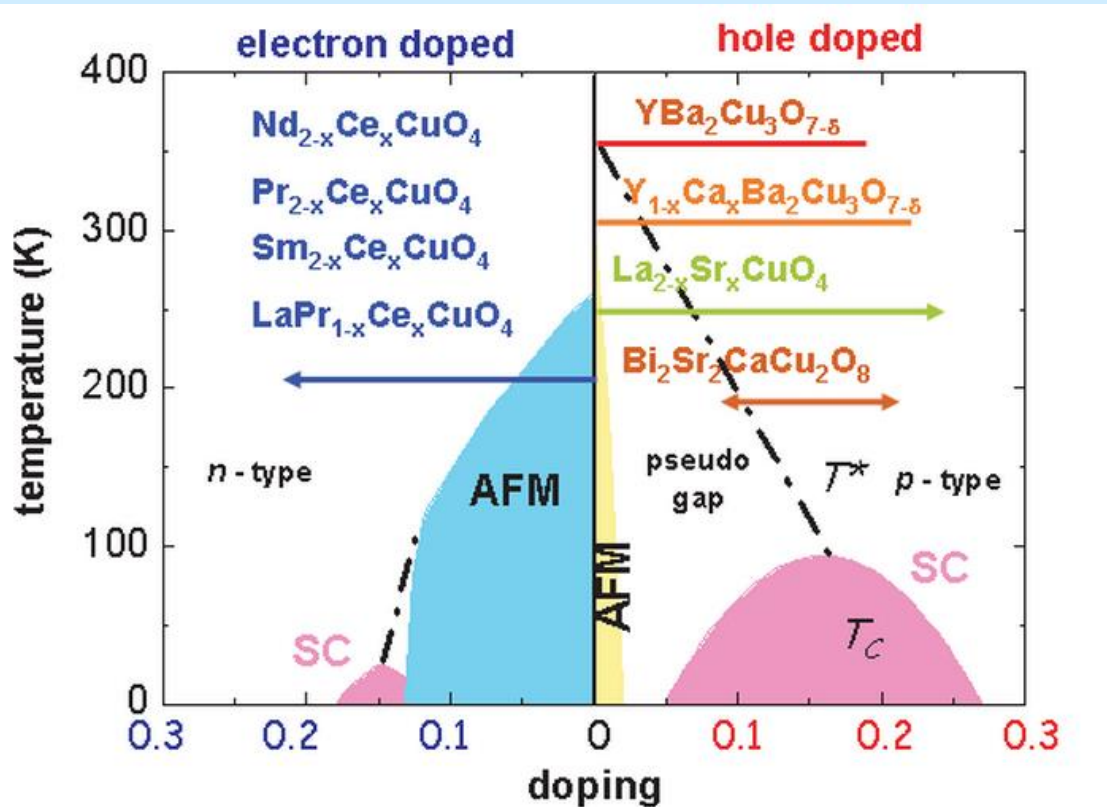
Charge imbalance at the GB depresses J_c at the interface ($t-J$ model calculations)

HTS实用化基础问题(1): 晶界弱连接



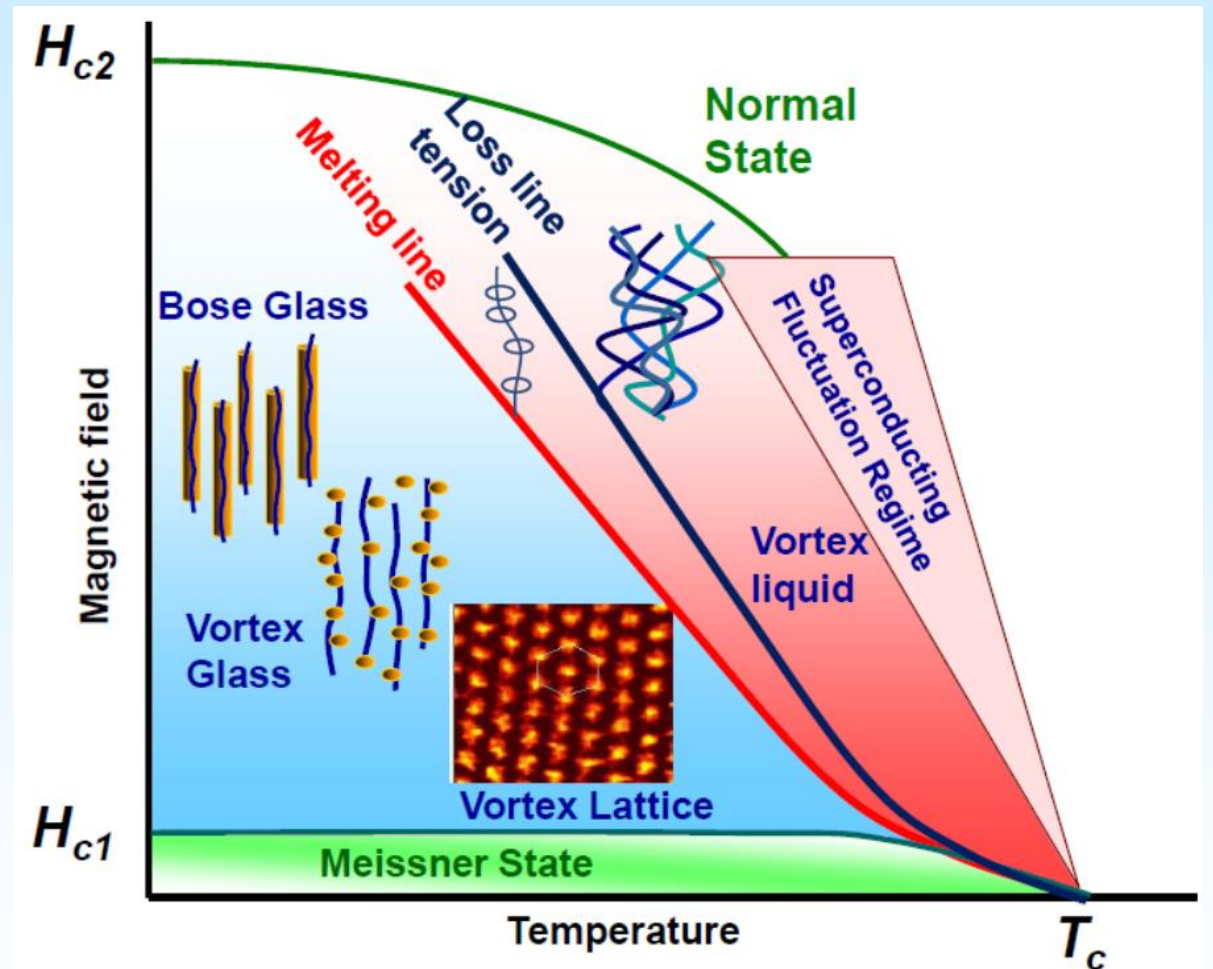
Besides the **irreversibility field**, there is the **crossover field**, both recognisable in the I(V) characteristics.

HTS实用化基础问题(2): 复杂的磁热相和磁通运动



Electronic State Diagram for Cuprates

<http://for538.wmi.badw-muenchen.de/>



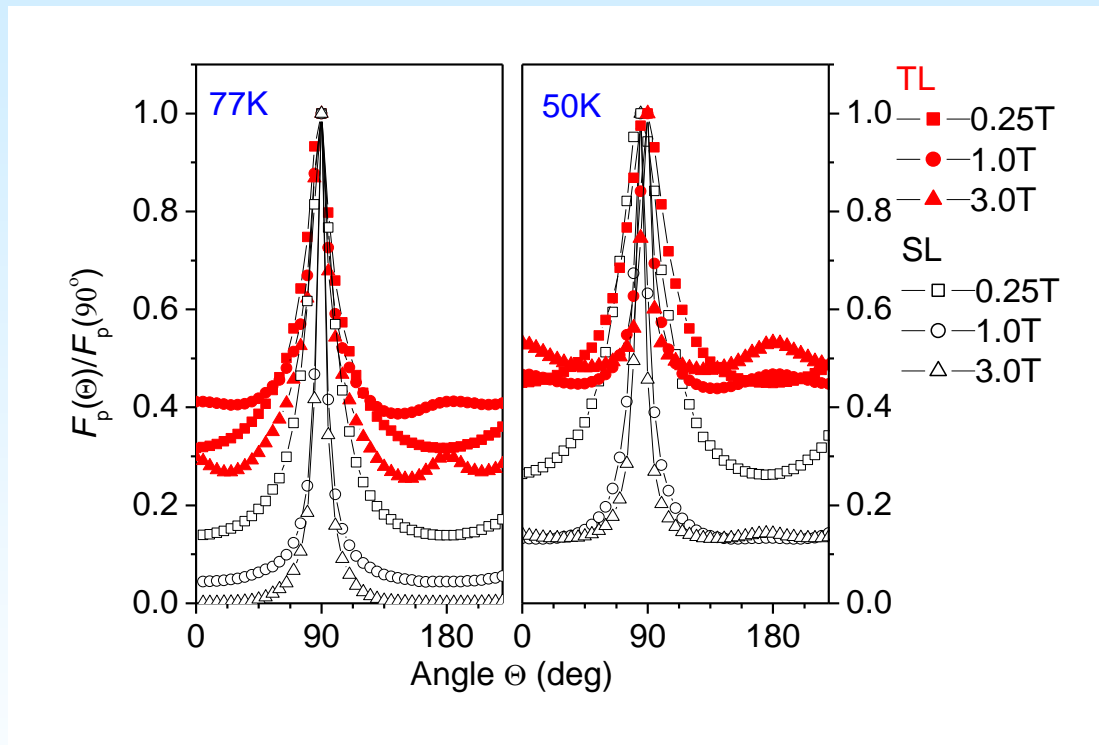
Magneto-thermal Phases for Cuprates

Leggett, Nature Phys., 2 (2006)134

Obradors, SuST, 27(2014)044003

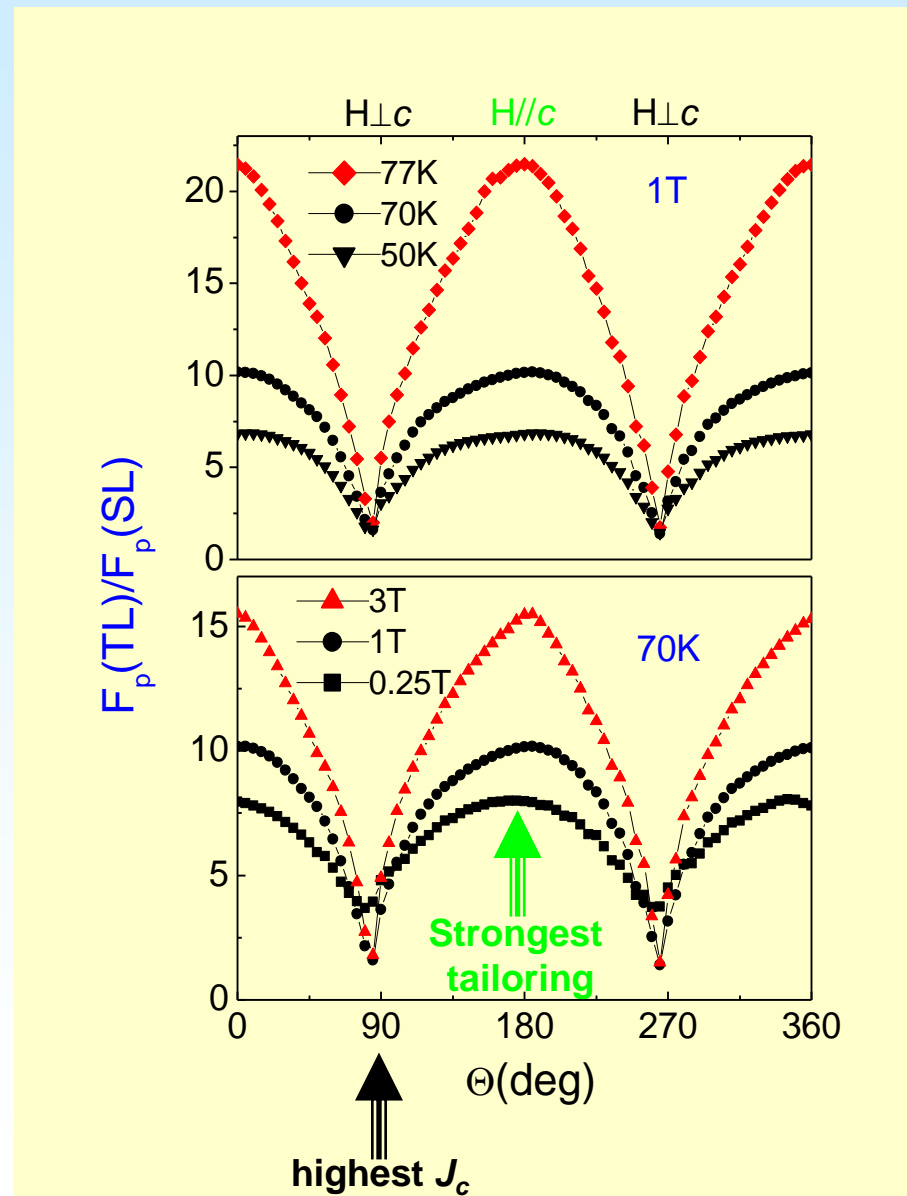
HTS实用化基础问题(3): 磁传输各向异性

➤ Anisotropy of flux pinning decreased in TL



C. Cai et al., *Phys. Rev. B.* 70, 064504(2004):
Phys. Rev. B. 70, 212501(2004)

➤ Strongest tailoring of flux pinning occurs at $H//c$, while the highest J_c at $H\perp c$



一

实用超导材料概况

二

高温超导涂层导体技术演变和发展现状

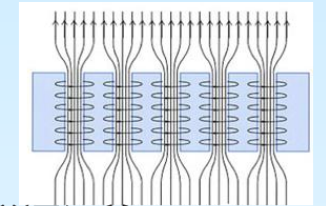
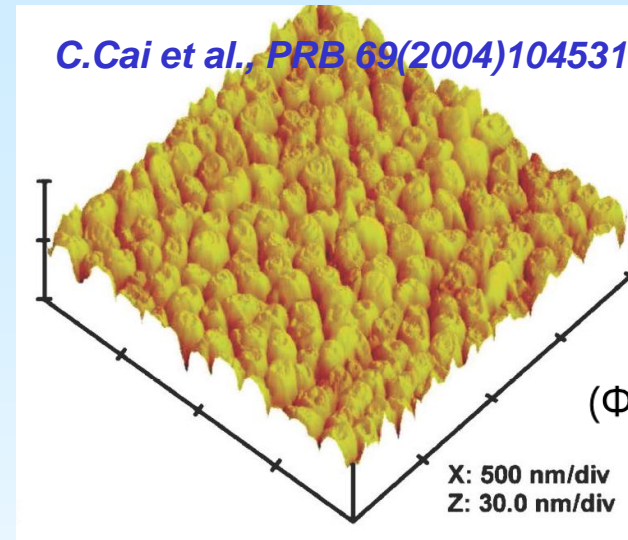
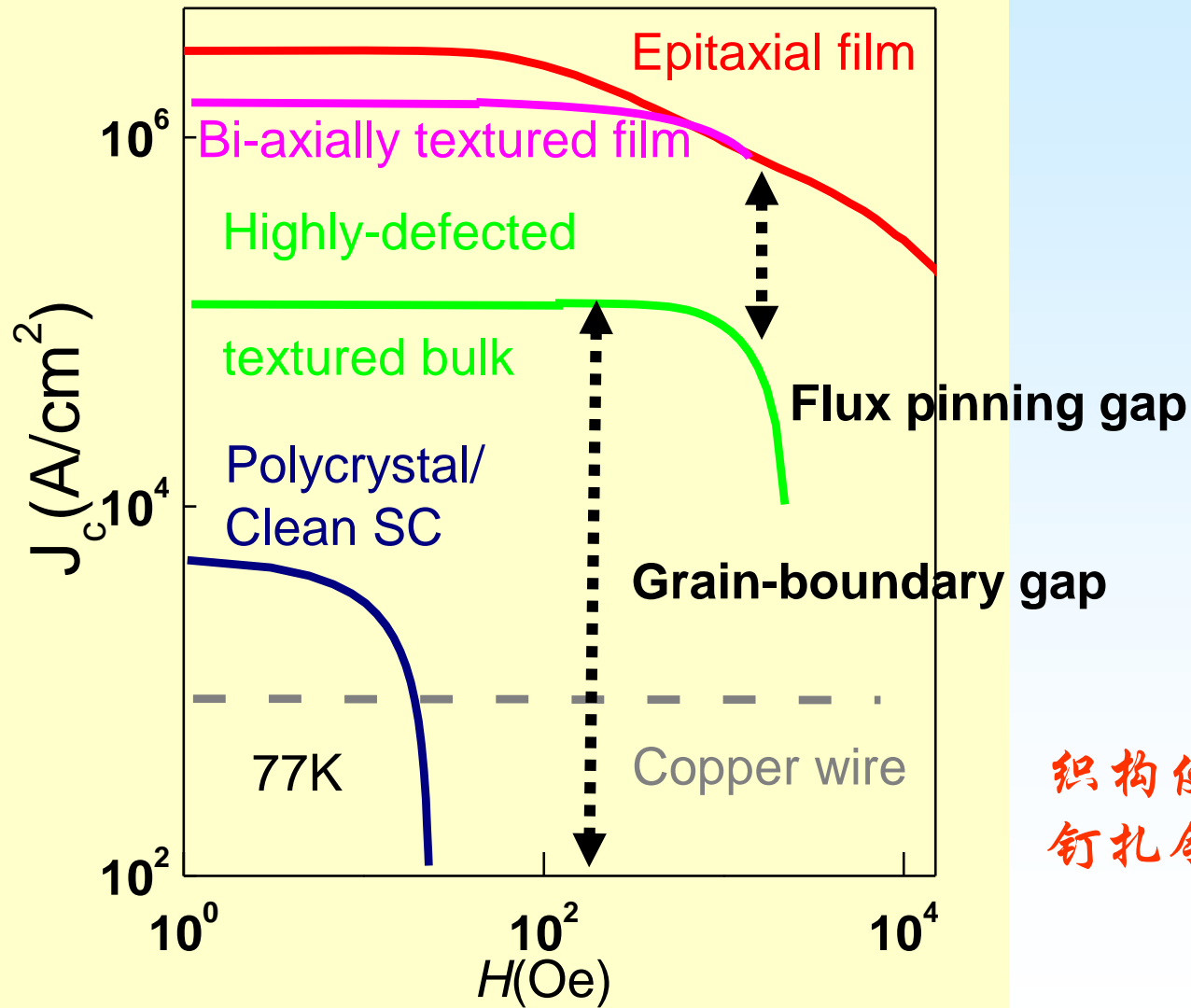
三

高温超导涂层导体磁通钉扎及其人工调制

四

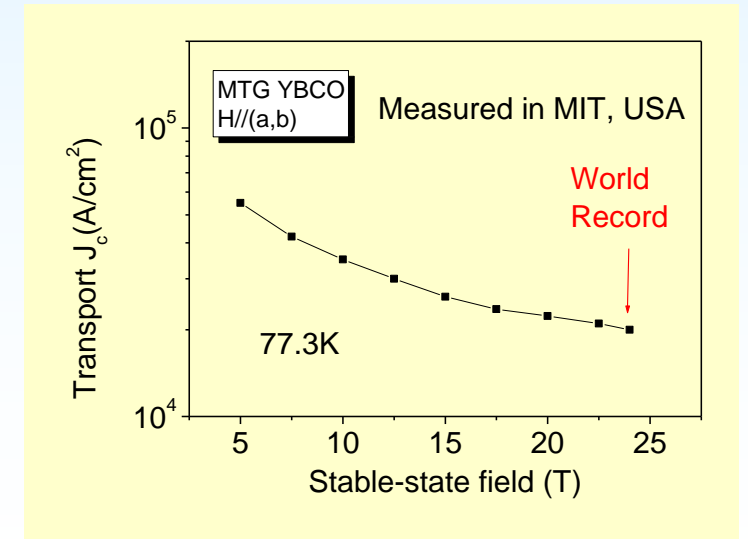
若干应用发展和挑战

HTS实用化基本应对措施：晶界减小和高密度钉扎中心



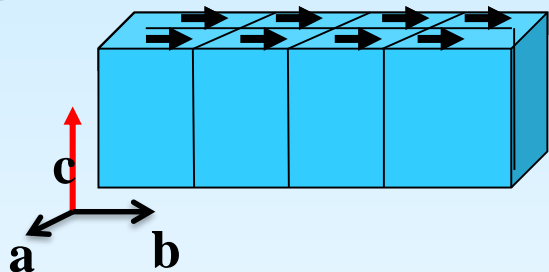
磁通涡旋 (vortex)
($\Phi_0 = h/2e = 2.068 \times 10^{-15}$ Wb)

织构使它进步!
钉扎令它强壮!

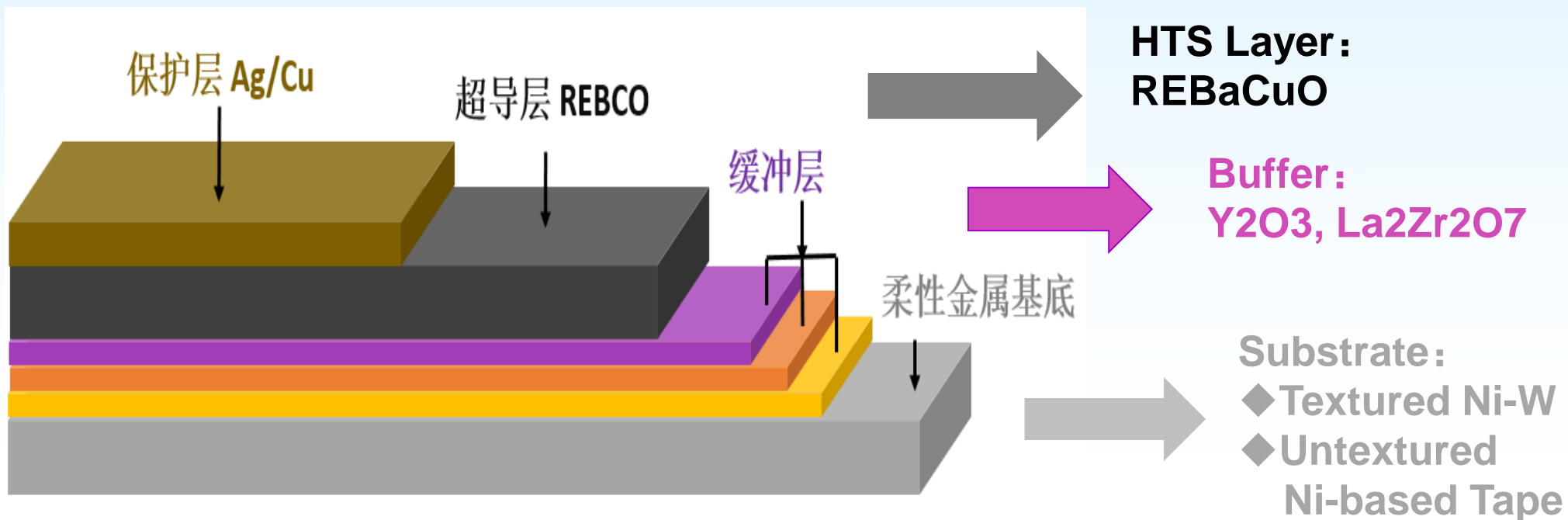
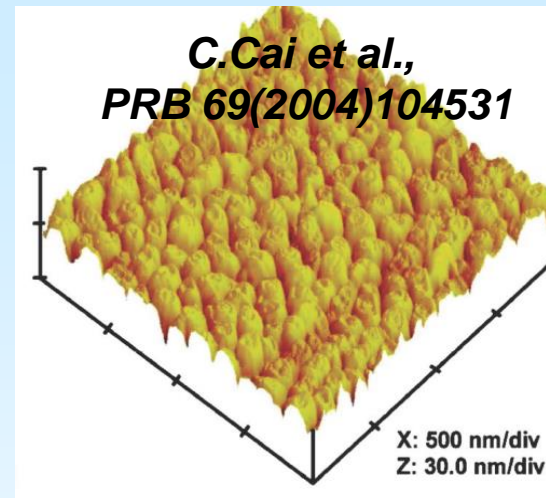


Architectures for HTS Coated Conductors

Key issues (1):
biaxial texture and
epitaxial growth

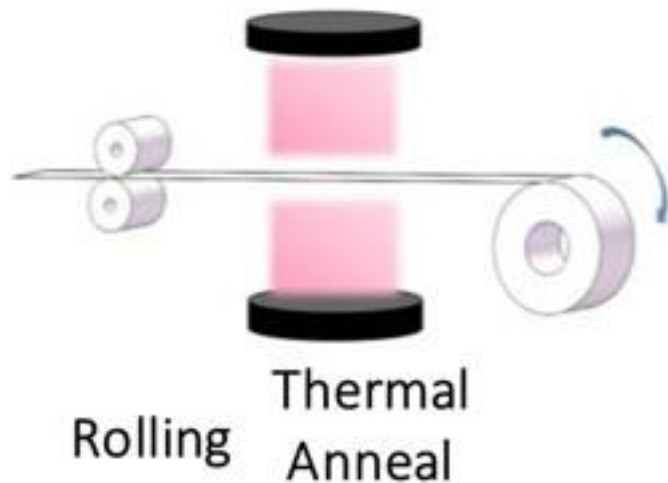


Key issues (2):
High-density
flux pinning
centers



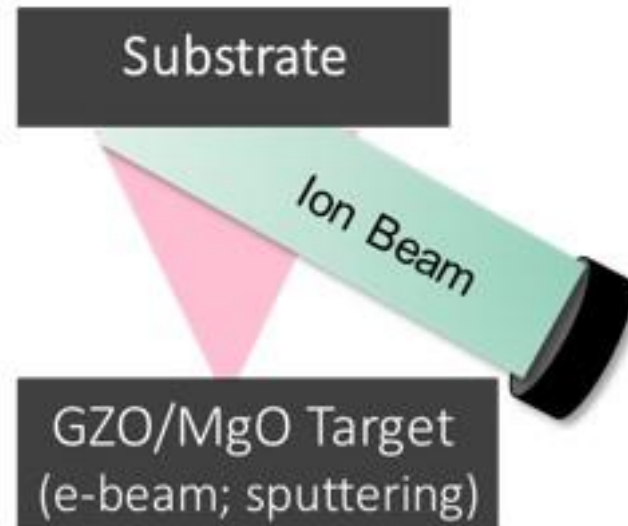
技术路线之：按缓冲层织构的建立途径

RABiTS工艺



CeO ₂
YSZ
Y ₂ O ₃
Texture NiW

IBAD工艺



LaMnO ₃ or CeO ₂
Homo-epi MgO
IBAD-MgO
Untextured Metal

ISD工艺

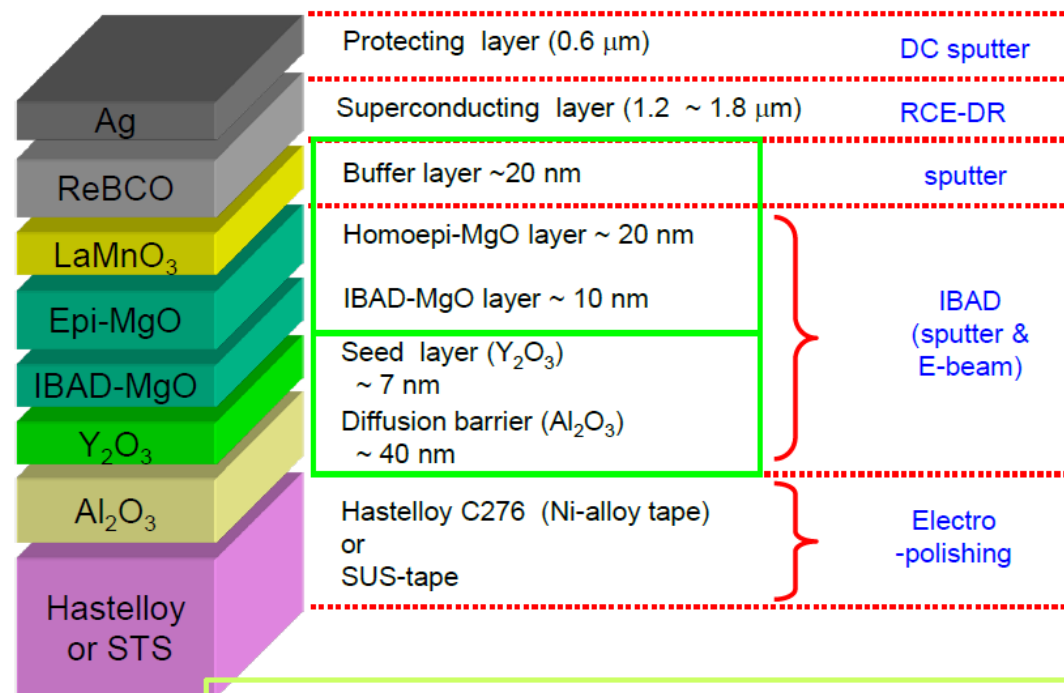


CeO ₂
Homo-epi MgO
ISD MgO
Untextured Metal

◆ Cai et al, *Progress in Physics (Chinese)*, 4(2007)467: Cai et al, *Advance in China Materials*, 30(2010)1

典型的组份结构和沉积速率 (以SuNAM为例)

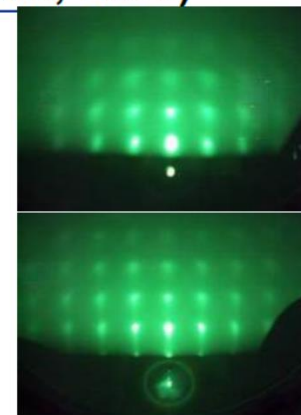
SuNAM's 2G Wire Architecture



(Not to scale)

Typical $I_c \sim 600 \text{ A}/12 \text{ mm}$ at 77 K self-field ($J_c \sim > 4 \text{ MA}/\text{cm}^2$)

Barrier, Seed, IBAD& Buffer (D&M, 2009)



IBAD-MgO

Homo-epi MgO



Process Speed

Each Step	R&D system ('08)	Pilot system('09)
Al ₂ O ₃	210 m/hr	600 m/hr
Y ₂ O ₃	500 m/hr	(1 system)
IBAD-MgO	600 m/hr	360 m/hr
Homo-epi MgO	~ 70 m/hr	(1 system)
LMO buffer	~50 m/hr	Buffer layer limits the speed.

* 4 mm width equivalent.

2G高温超导带材产业化的关键问题

目标	材料和制造 成本低	薄膜沉积 速率高	单位宽 临界电流密度高	自主研发 动态连续化装备
<ul style="list-style-type: none">● 规模化生产● 低制造成本● 先进装备	<ul style="list-style-type: none">➢ 低成本制备缓冲层和超导层➢ 新基带、新工艺降低双基带成本	<ul style="list-style-type: none">➢ 提高超导层、缓冲层生长速率➢ 发展适于快速制备的缓冲层和超导层工艺与结构	<ul style="list-style-type: none">➢ 通过增加膜厚提高超导传输能力➢ 增加有效的磁通钉扎中心密度、提高临界电流	<ul style="list-style-type: none">➢ 设计和建立拥有自主知识产权的薄膜动态沉积系统➢ 提高系统研发和合成水平

参见：《上海市第二代高温超导带材及其应用发展战略研究（2010-2020）》（2010/02）

HTS Coated Conductors

@Shanghai Jiaotong University & Spinning-off Company, SSTC

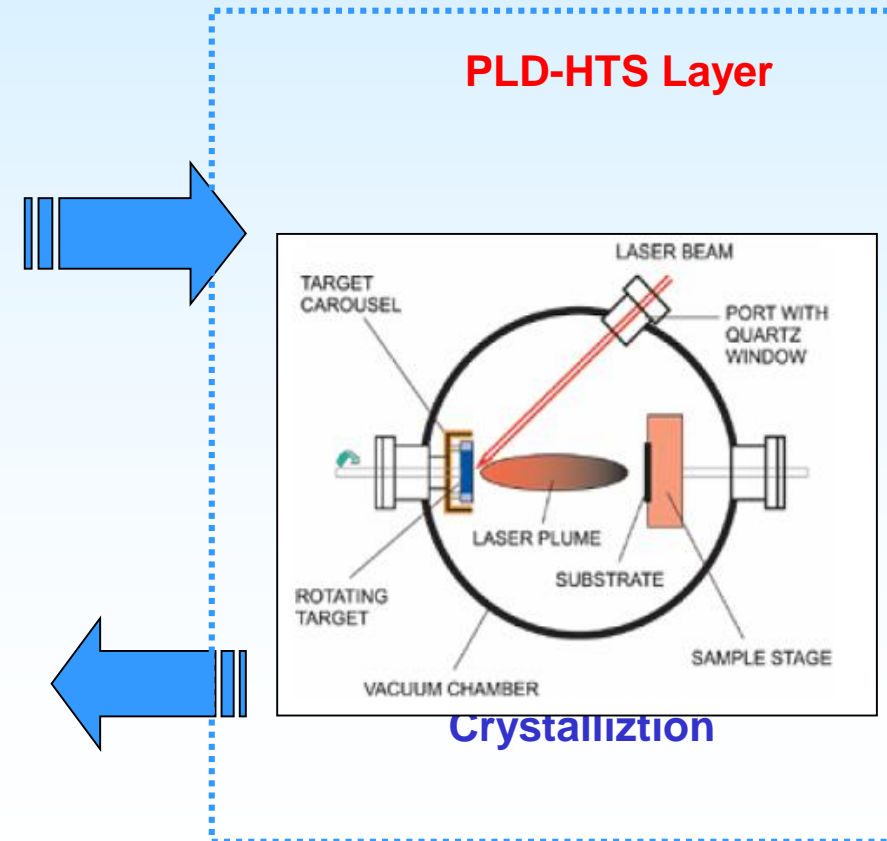
- ◆ Textured Oxide Buffers on Textured metallic tape **via IBAD**
- ◆ Epitaxial HTS Films on Textured Oxide Buffer **via PLD**



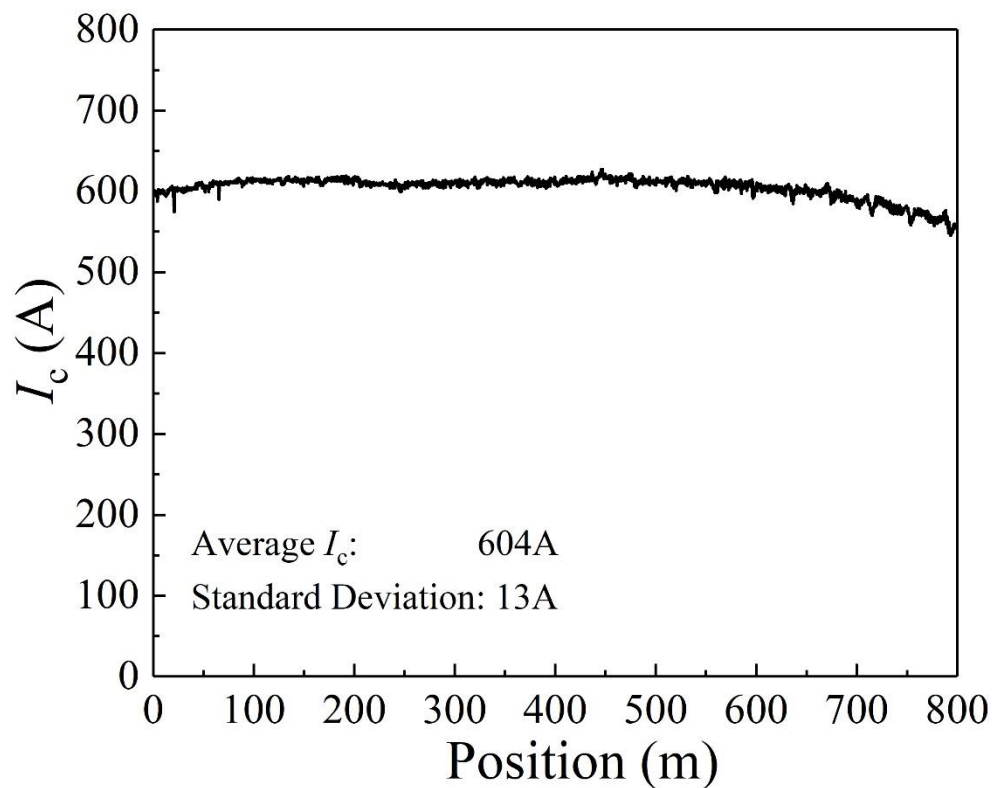
CeO ₂ : 200 nm
LaMnO ₃ : 30-50 nm
IBAD-MgO: 5 nm
Y ₂ O ₃ : 20 nm
Al ₂ O ₃ : 80 nm
哈斯勒合金 ~30 / 50 μm

One way for Oxide Buffer on
Textured Hastelloy

Protection and stabilization

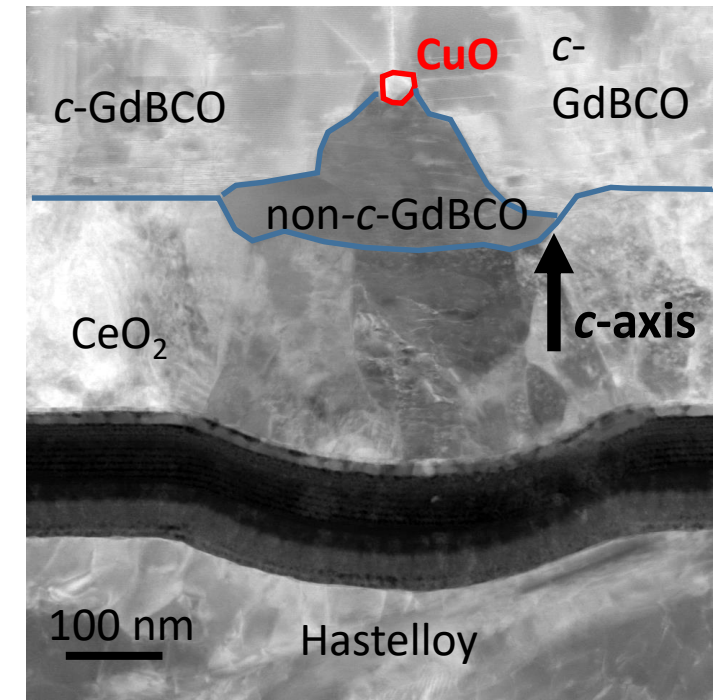


High performance GdBCO films with "robust" structure



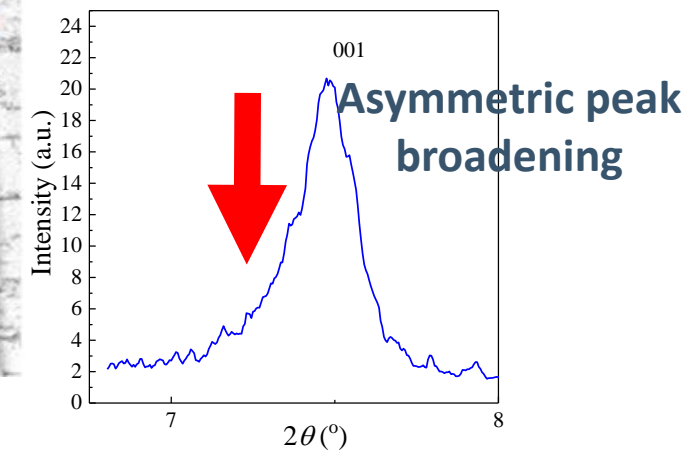
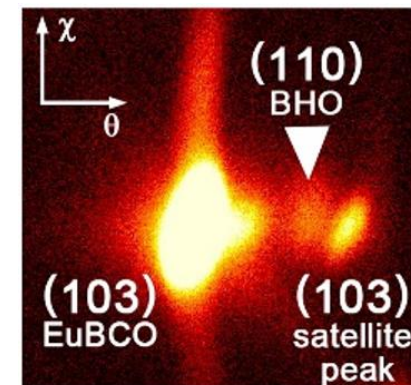
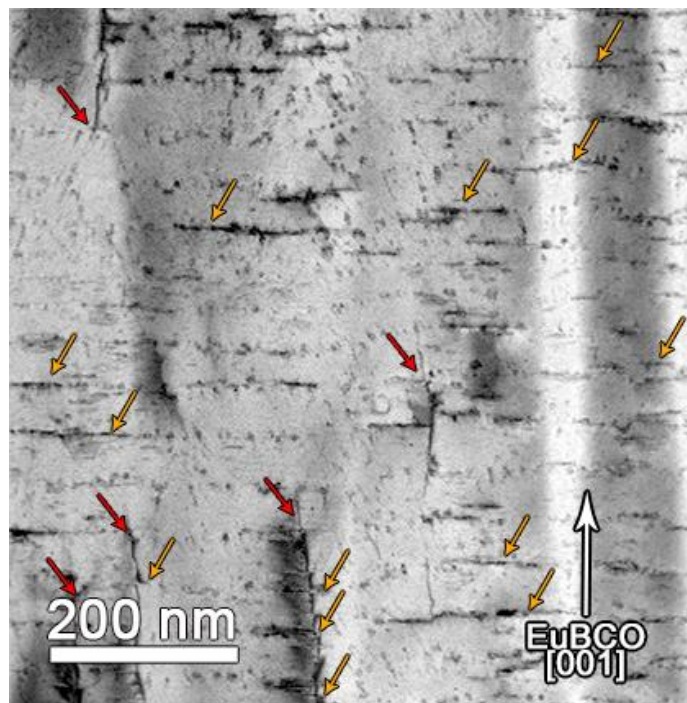
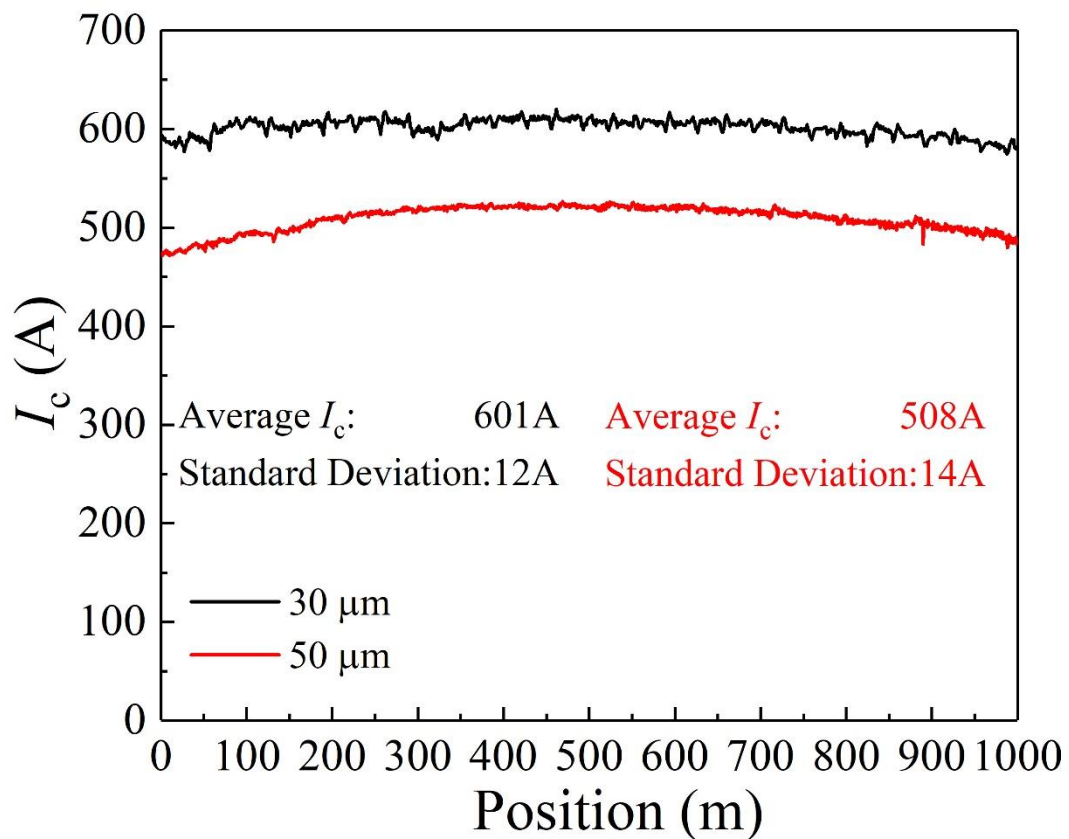
Annual production for a 300W PLD:
>150 km*500 A

Defective region



High quality GdBCO film grown
under "overgrowth" mechanism

Mixed-landscape pinning centers in “fast grown” EuBCO films



KM-Long EuBCO tapes with high I_c achieved on 30 and 50 μm substrates

Inclined nano-rods and high density of stacking faults co-exist throughout the film

HTS Coated Conductors

@Suzhou Advanced Materials Institute

- ◆ Textured Oxide Buffers on Textured metallic tape **via IBAD**
- ◆ Epitaxial HTS Films on Textured Oxide Buffer **via MOCVD**



Oxide Buffer on
Textured Hastelloy

LaMnO ₃ : 100-120 nm
外延-MgO: 30-50 nm
IBAD-MgO: 10 nm
Y ₂ O ₃ : 8-10 nm
Al ₂ O ₃ : 80 nm
哈斯勒合金 ~60 μm

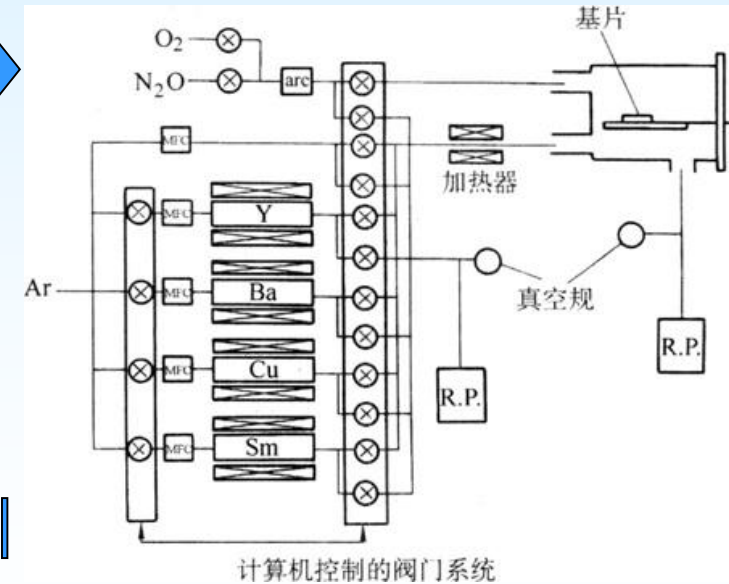


Protection and stabilization



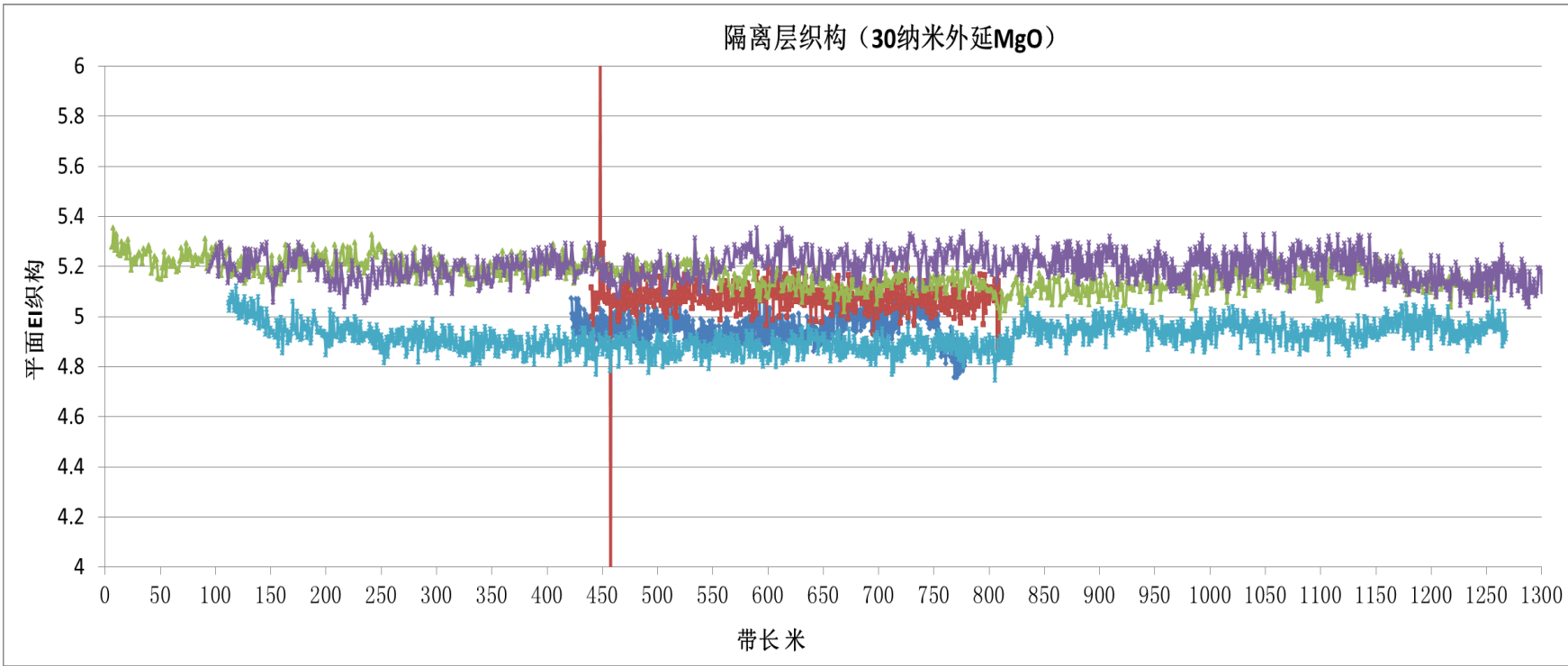
苏州新材料研究所

MOCVD-HTS Layer



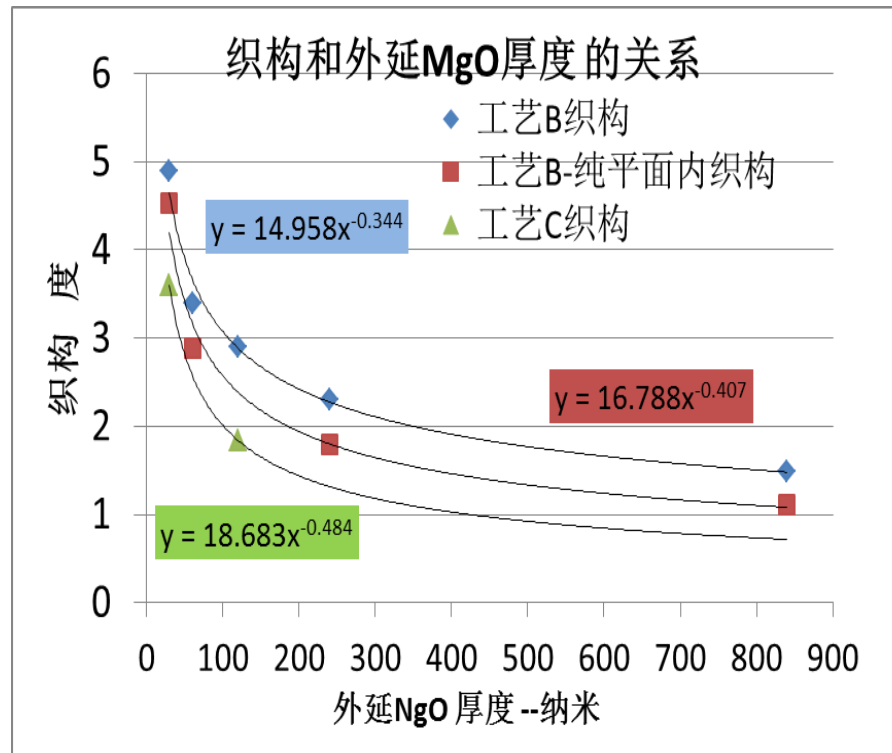
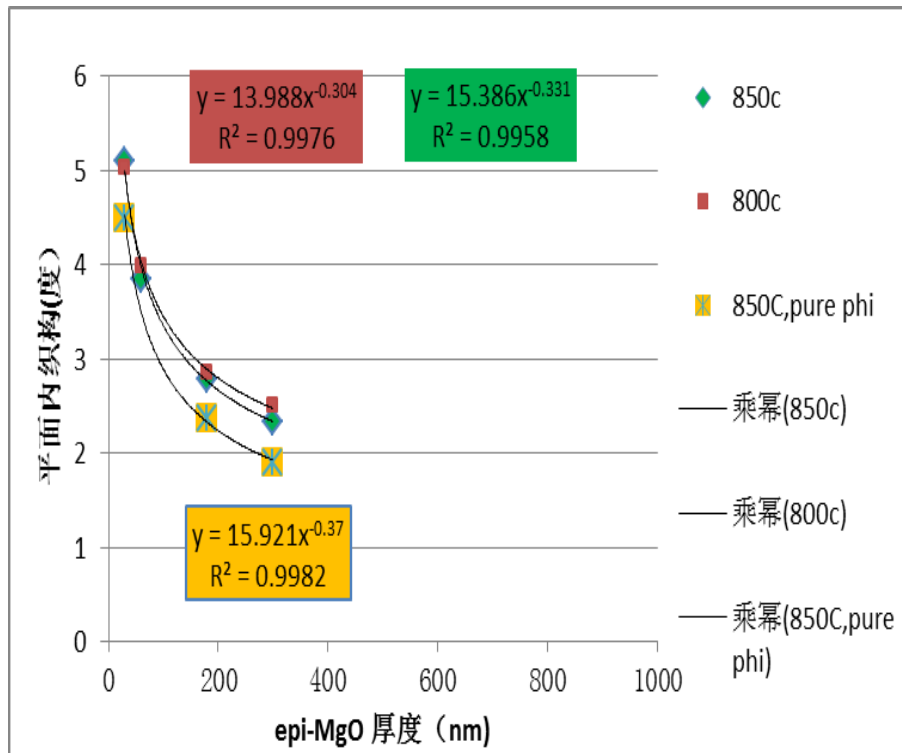
- ◆ IBAD-MgO长带生产速率达到220m/h，平面内织构（30纳米MgO） $<5.5^\circ$ 的良率大于90%。
- ◆ 4mm年产能600公里，（5天/周，50周/年）。1.4公里带子沉积时间仅6.3小时，准备时间38小时，有很大的提升空间

90nm LMO
30nm MgO
7nm IBAD MgO
7nm Y2O3
70nm Al2O3
基带



可以为铁基超导长带的产业化提供准单晶织构的千米长带

平面内织构和外延MgO的关系



现在长带生产的工艺A

外推到2000nm MgO，纯平面外织构~1度

工艺B，840nm，纯平面外织构1度

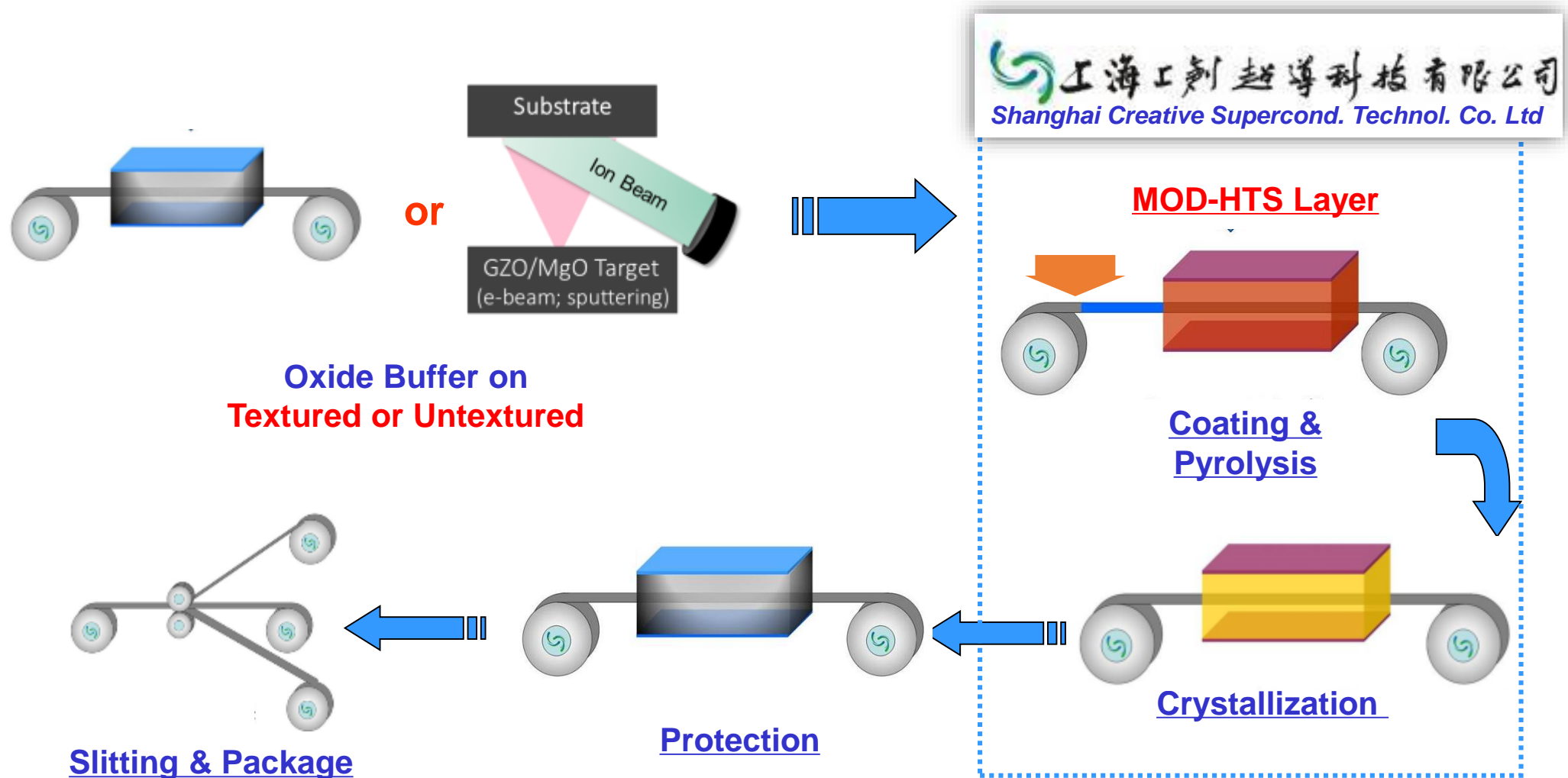
工艺C，400nm，平面外织构< 1度。

30nm MgO，织构~5.2度

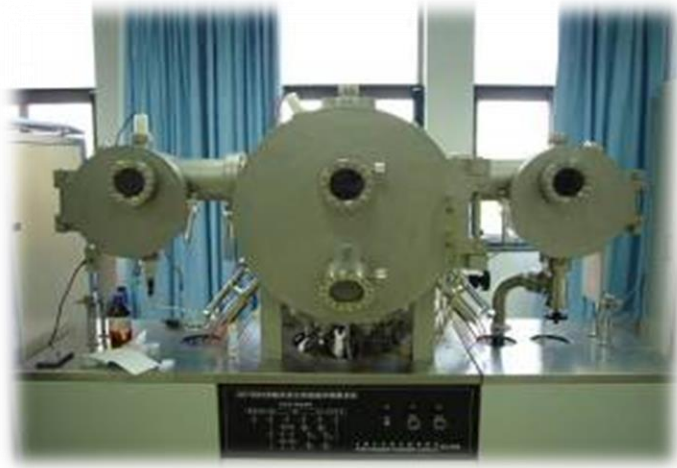


30nm MgO，织构3.6度

- ◆ Textured Oxide Buffers on Textured or Untextured Tape via RABiTS or IBAD
- ◆ Epitaxial HTS Films on Textured Oxide Buffer via MOD



Reel-to-Reel System Development in Past Ten Years



Research Level R2R Sputtering System

Industry-level Sputtering Production Line

NSFC、MOST-863/973 Project



STCSM-Key Project



Shanghai Municipal Key Project



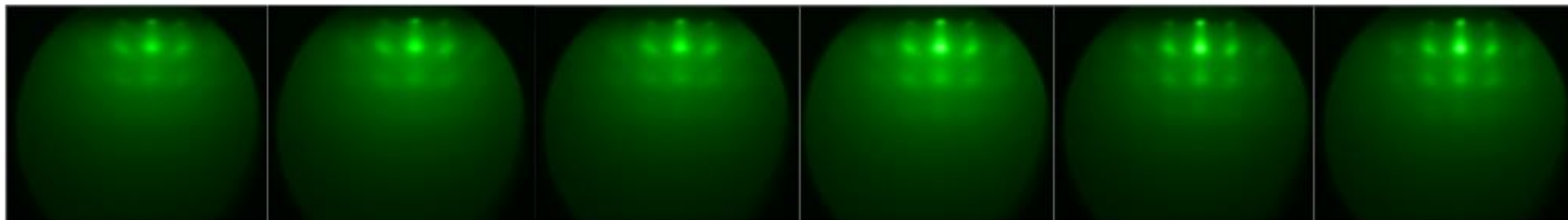
Research Level R2R Solution Coating System

Industry-level Solution Coating System



上创超导
Shanghai Creative Superconductor

On-line Check for Texture of Kilometer's Oxide Buffer on Untextured Metallic Tapes



10m

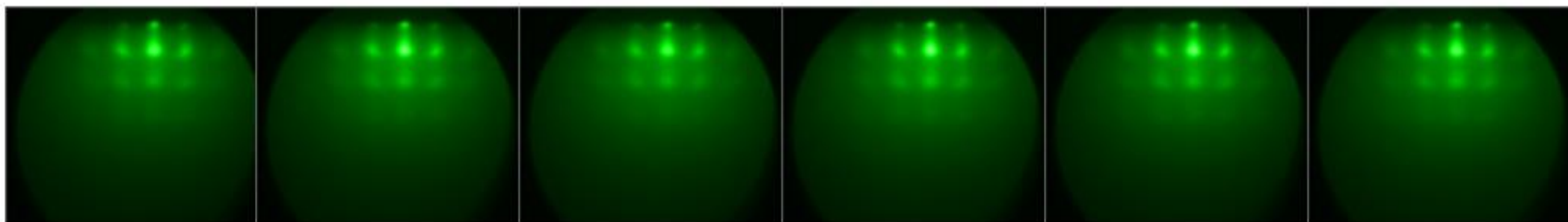
50m

100m

200m

300m

400m



500m

600m

700m

800m

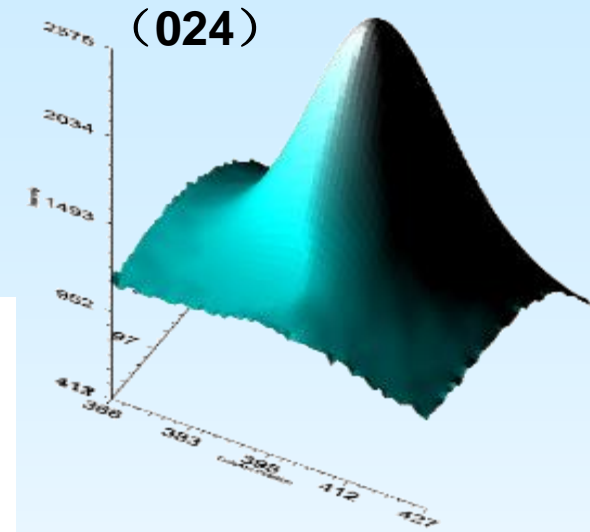
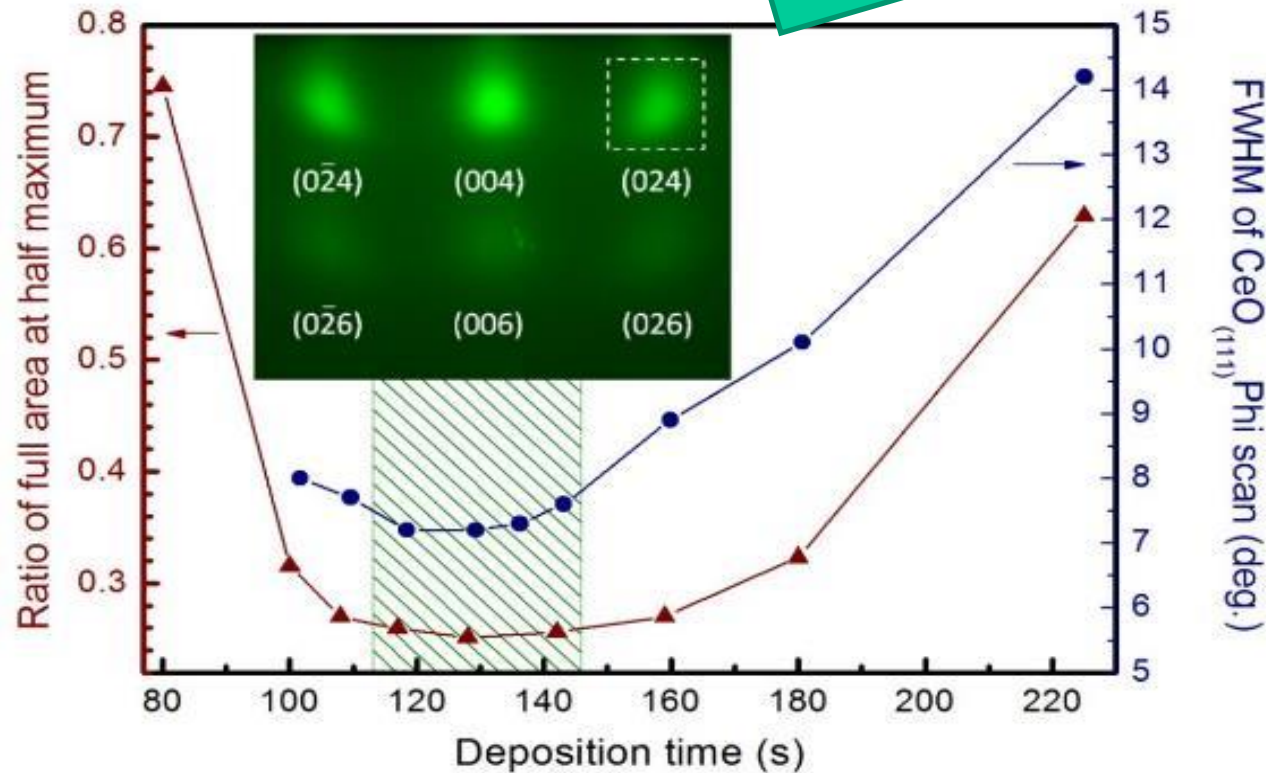
900m

1050m



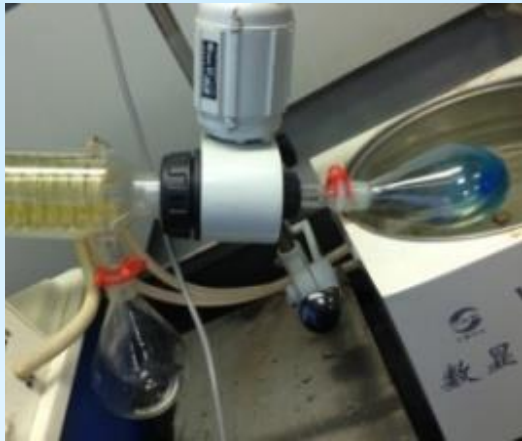
Evaluation Method Developed for Texture of Oxide Buffer

- Direct comparison of time dependence of In-situ RHEED pattern and ex-situ x-ray Phi scanning

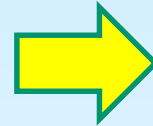


- Characteristic Method Developed For in-situ Check of Texture

Industrial Process for MOD-RBaCuO Coated Conductors



Solution Preparation



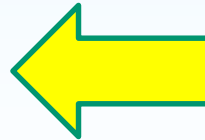
Coating + Low temperature Pyrolysis



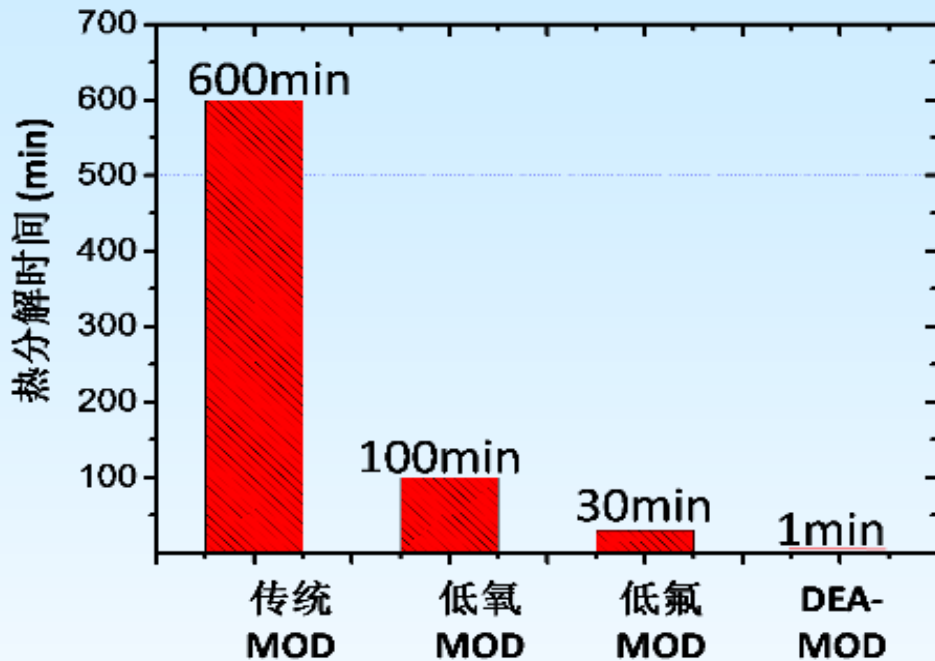
High-temperature Crystallization



Oxygenation



Dramatic Reduction For Pyrolysis Time of MOD



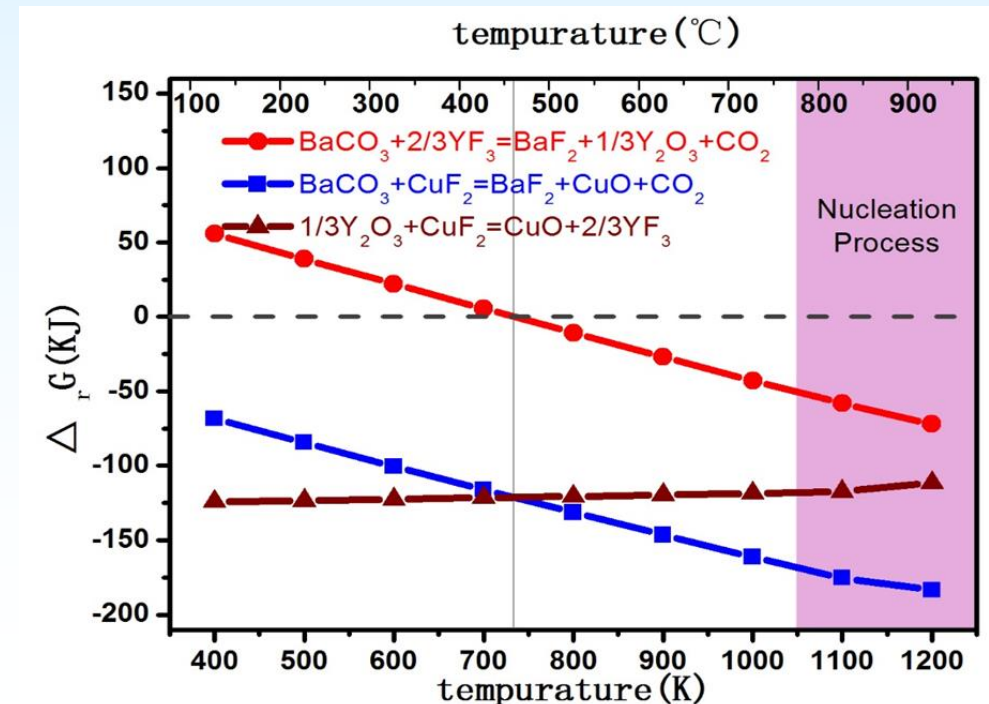
$\Delta G < 0$, Possible reaction

$\Delta G = 0$, Balanced reaction

$\Delta G > 0$, Impossible reaction

$$\Delta G_T^\theta = \sum v \Delta G_{f,T}^\theta(\text{products}) - \sum v \Delta G_{f,T}^\theta(\text{reactants})$$

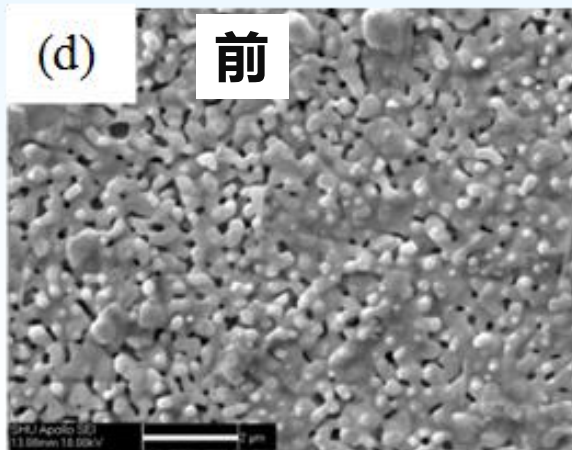
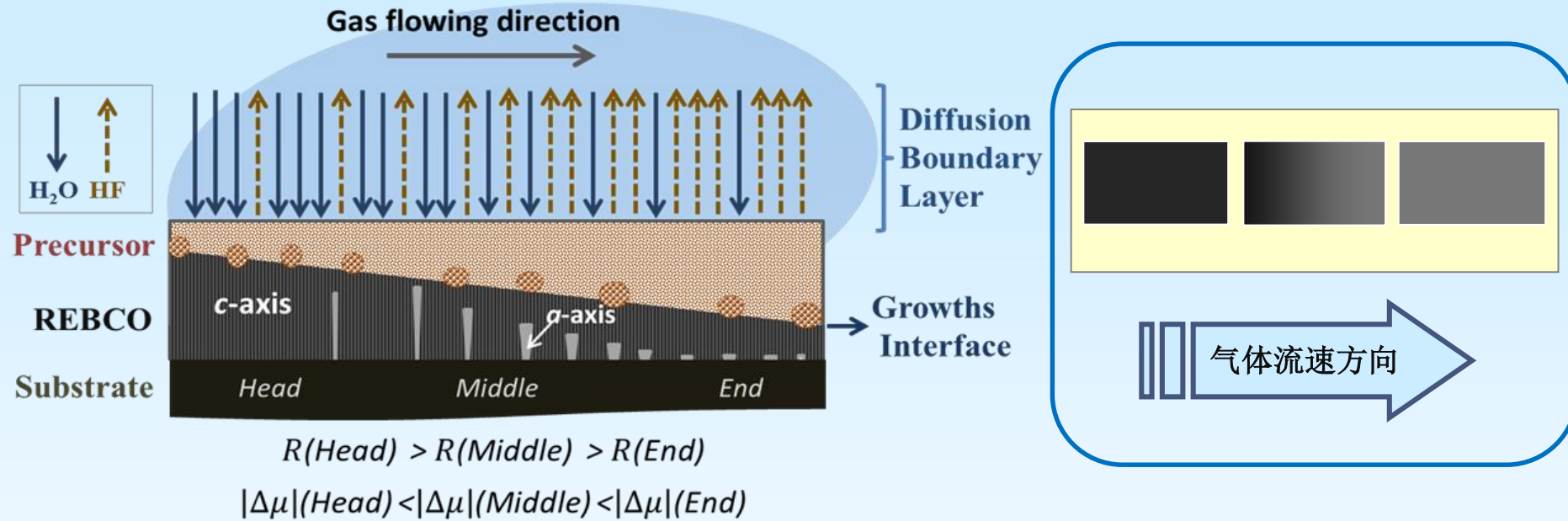
- ◆ Pyrolysis time reduced to be as short as one minute using extremely low F-content solutions
- ◆ Smooth and dense films obtained at a pyrolysis rate as high as 25 K/min



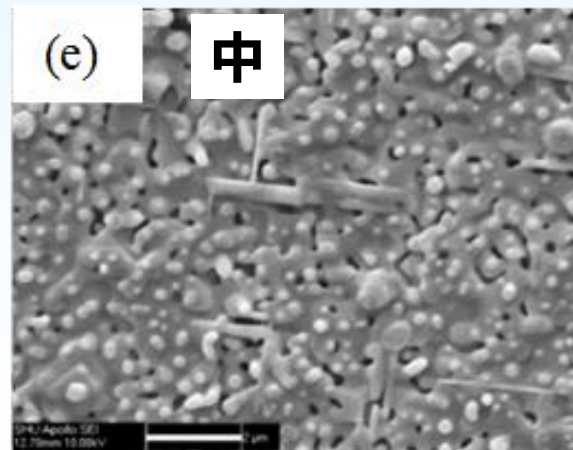
Li *et al.*, *Physica C*, 537(2017), 29–33.

Lu *et al.*, *IEEE Trans. Supercond.* 29(2019)6602805

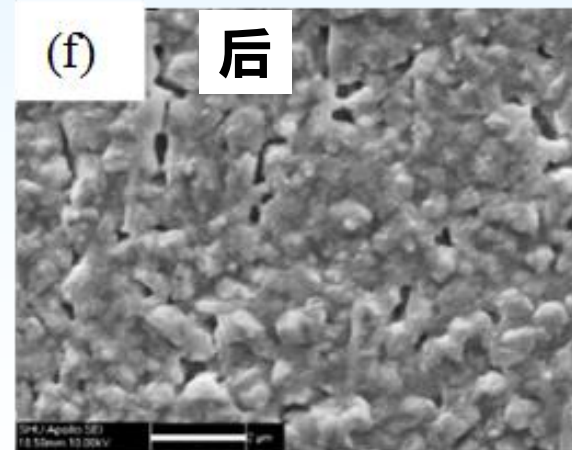
Phase Formation, nucleation and growth of MOD-derived YBCO



生长速率快
a轴取向少



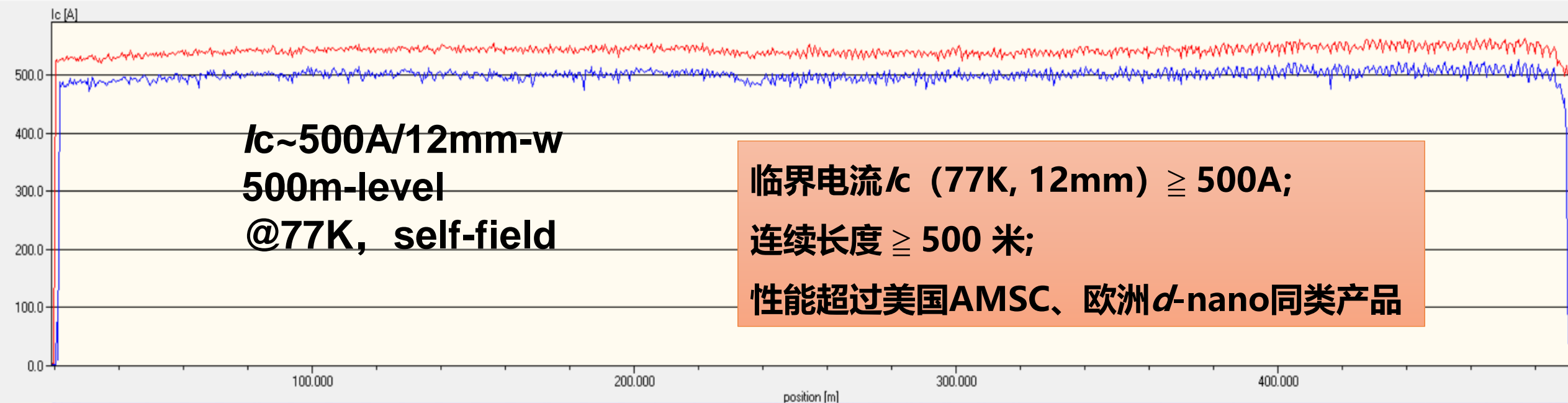
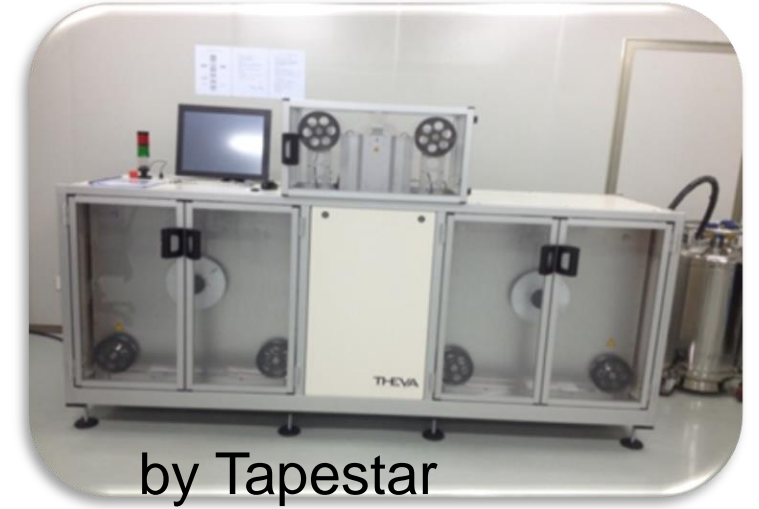
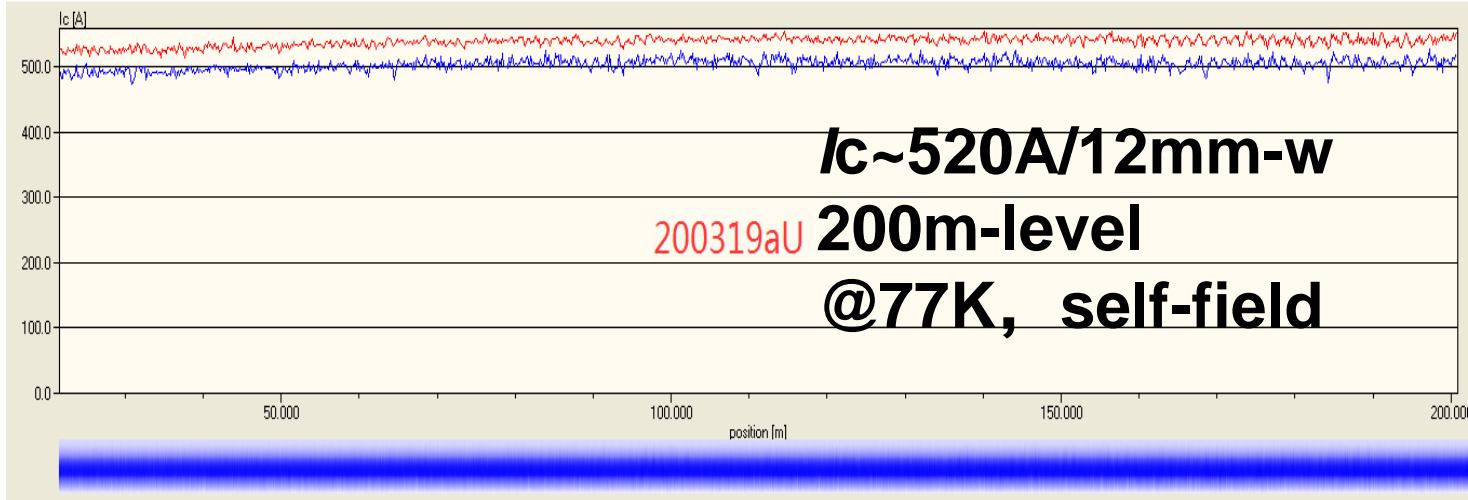
生长速率略慢
a轴取向多



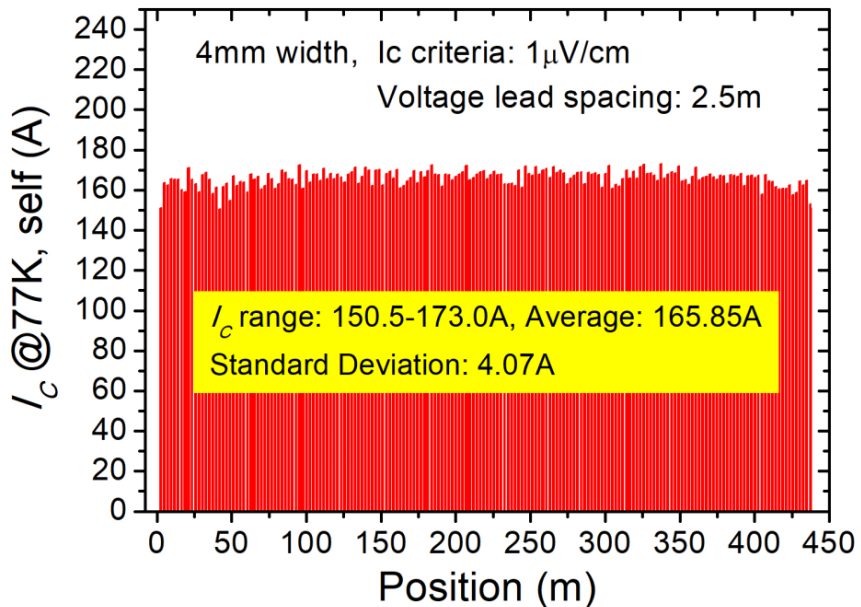
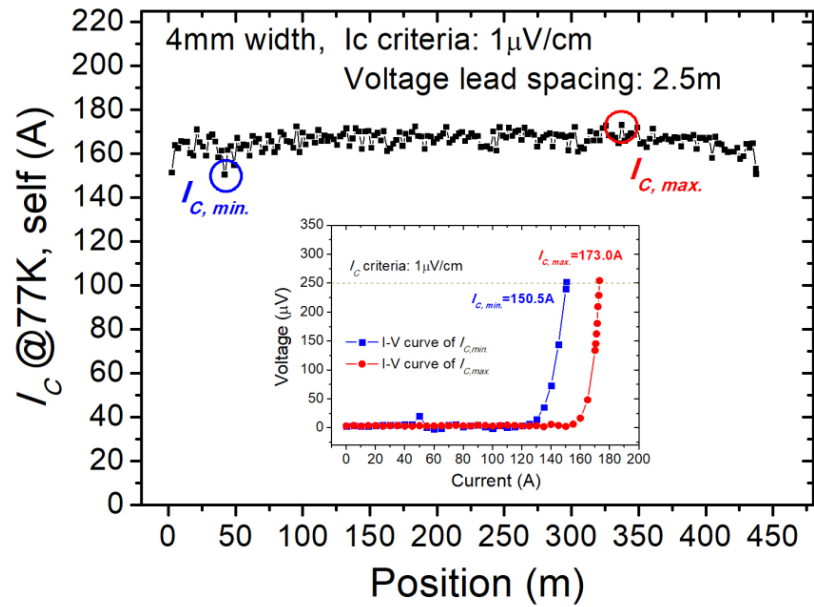
整体生长速率极慢 **R小**
a轴取向成核多但生长也慢

Li *et al.*, *Physica C*,
537(2017), 29–33.
Lu *et al.*, *IEEE Trans.*
Supercond.
29(2019)6602805

Critical Current for Typical MOD-HTS Tapes at SCSC



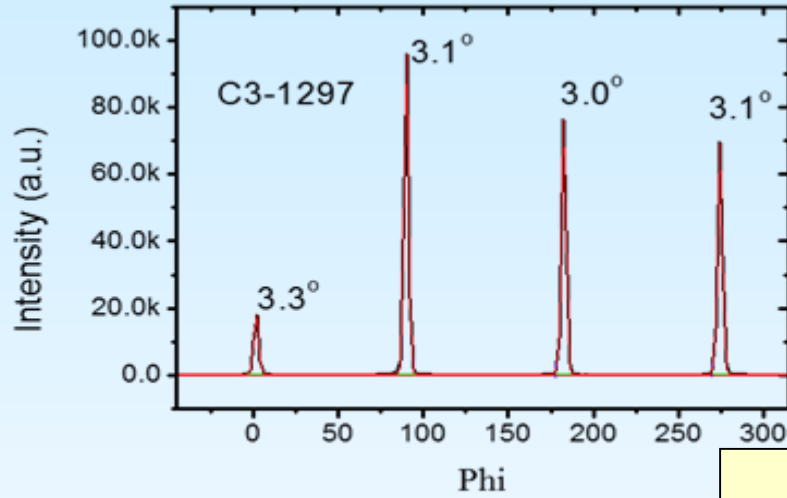
Latest 4mm-wide products tested by R2R transport I_c measurement



R2R system developed for continuous I_c measurement of HTS tapes as long as 1 km with a higher running rate

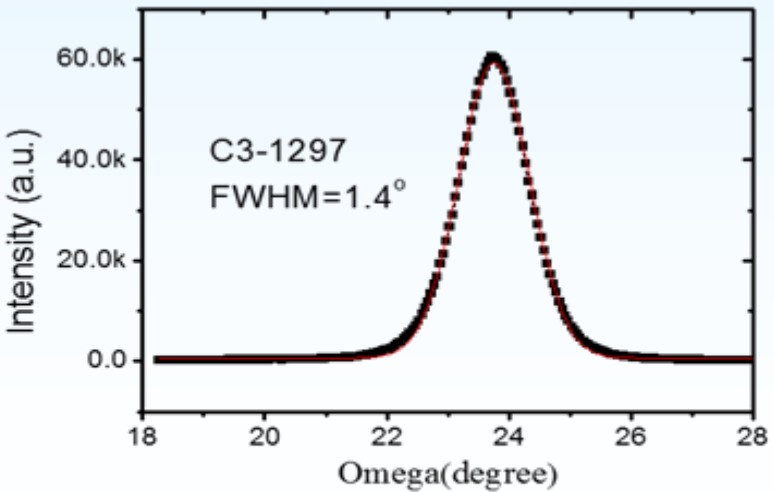
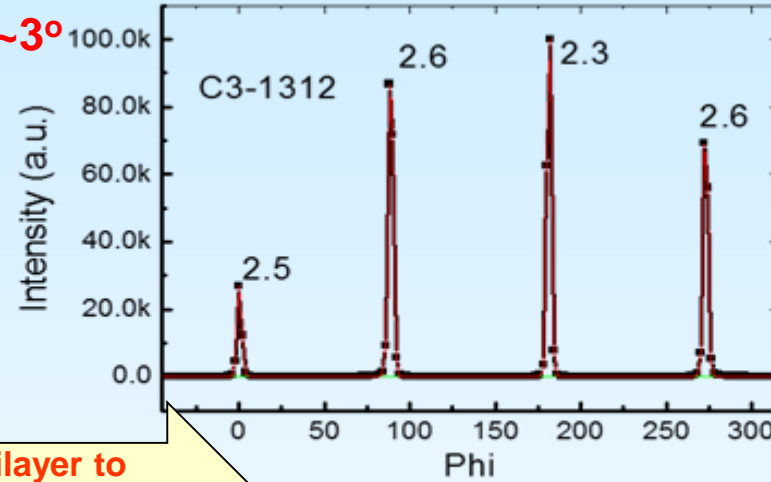


Texture Properties for MOD HTS Layers

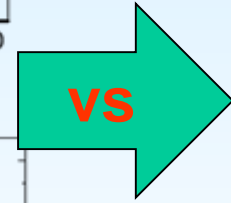
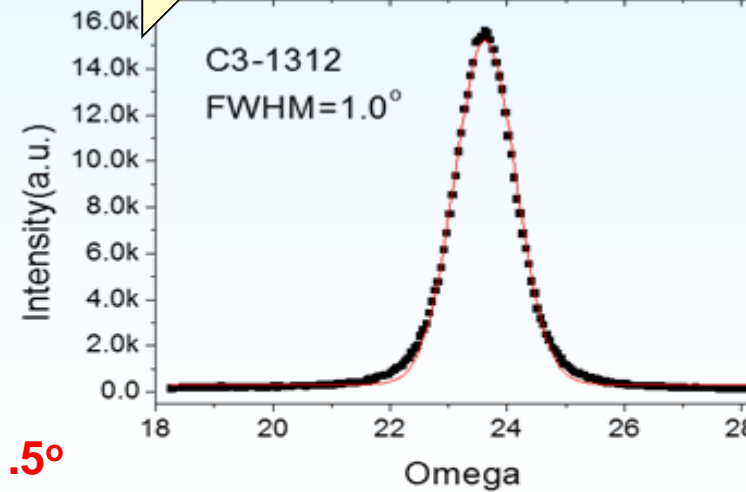


In-plane texture

2~3°



From bilayer to triple HTS layers



General Level

In-plane

~4°

Out-of-plane

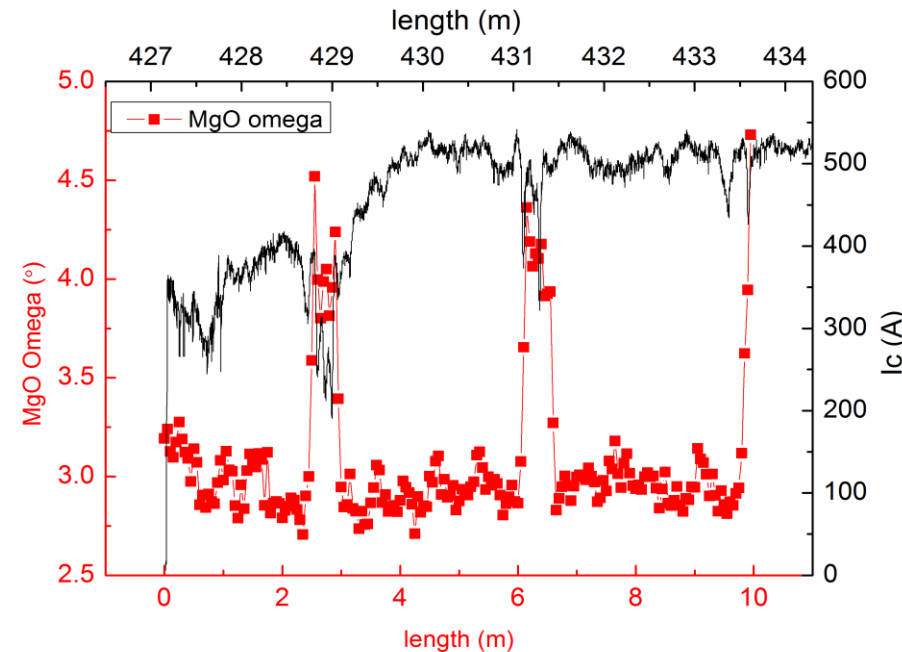
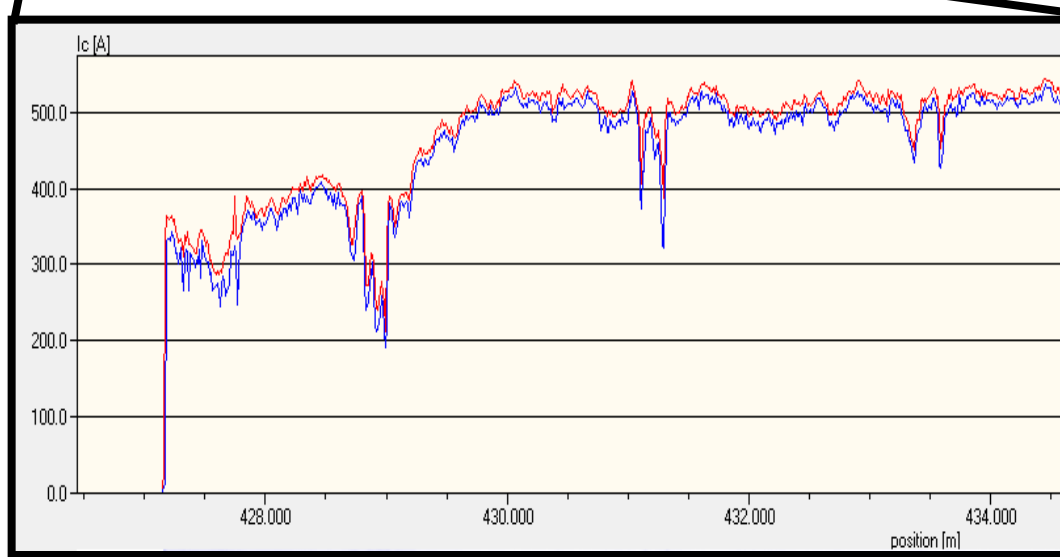
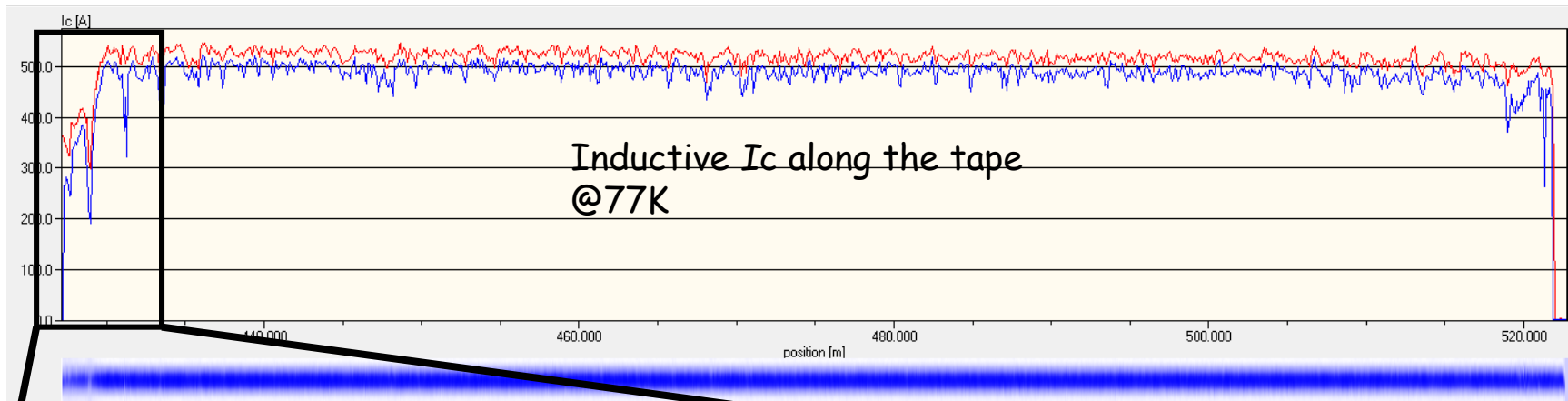
~2°

双层 (1.0~1.1微米)

1~1.5°
Out-plane texture

三层 (1.5~1.6微米)

Latest developed Reel-to-Reel XRD: Defect and performance analysis tool

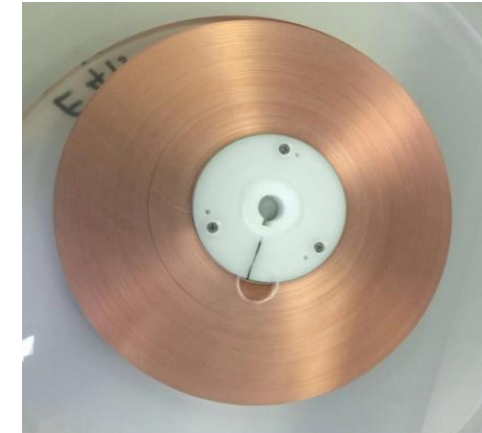
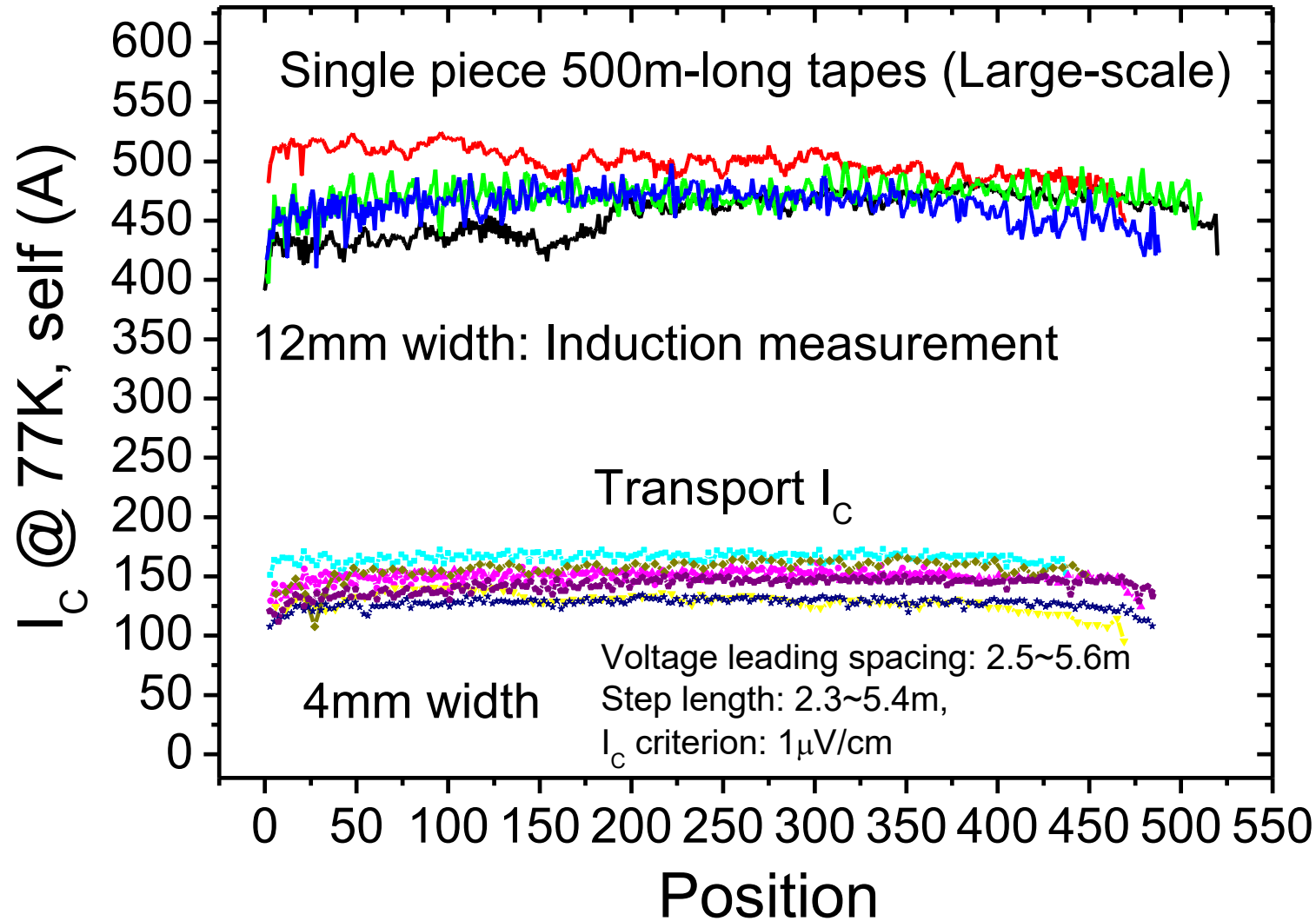


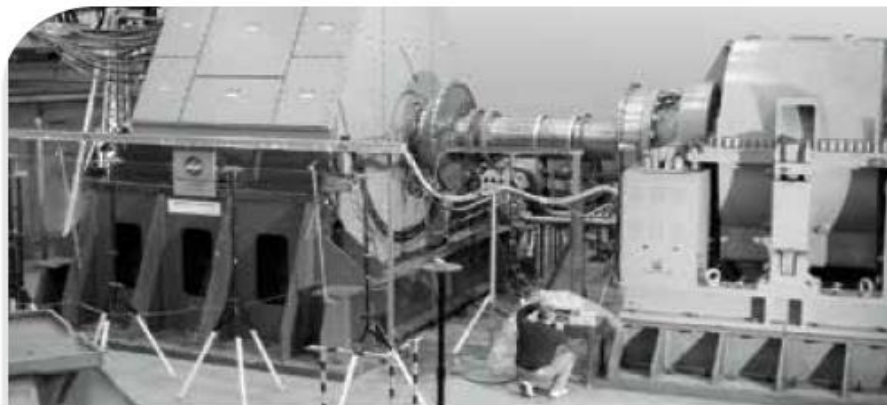
— I_c along several hundreds of long tapes reaching 110-150 A/4mm-w (77K, self field),

—evidencing the cost-effective MOD technique promising.



Typical performances for 12mm/4mm-wide products





AMSC 36.5 MW, 120 rpm ship propulsion motor

Second generation HTS wire
for power dense coil
applications

Type 8501 and 8502

□ 中国在MOD化学法
2G超导带材领域

□ 超过AMSC和德国
同类企业

MECHANICAL PROPERTIES	Type 8501 (4.8 mm)	Type 8502 (12 mm)
Average thickness:	0.17 mm - 0.21 mm	0.18 mm - 0.22 mm
Minimum width:	4.70 mm	11.9 mm
Maximum width:	4.95 mm	12.3 mm
Minimum double bend diameter (RT):	30 mm ⁱ	30 mm ⁱ
Minimum double bend diameter for spliced wire (RT):	100 mm ⁱ	100 mm ⁱ
Maximum rated tensile stress (RT):	150 MPa ⁱ	150 MPa ⁱ
Maximum rated wire tension (RT):	12 kg ^j	30 kg ^j
Maximum rated tensile strain (77K):	0.25% ⁱ	0.3% ⁱ
Maximum rated C-Axis stress:	20 MPa ⁱ	20 MPa ⁱ

ELECTRICAL PROPERTIES	Type 8501 (4.8 mm)	Type 8502 (12 mm)
Minimum amperage (I _c) ⁱⁱ	Average Engineering current density - J _e (A/cm ²) ⁱⁱⁱ	Average Engineering current density - J _e (A/cm ²) ⁱⁱⁱ
80 A	8,700 A/cm ²	—
90 A	9,800 A/cm ²	—
100 A	10,900 A/cm ²	—
250 A	—	10,300 A/cm ²
275 A	—	11,330 A/cm ²
300 A	—	12,360 A/cm ²

Spliced wire available in long lengths

Insulation options: Contact factory

一

实用超导材料概况

二

高温超导涂层导体技术演变和发展现状

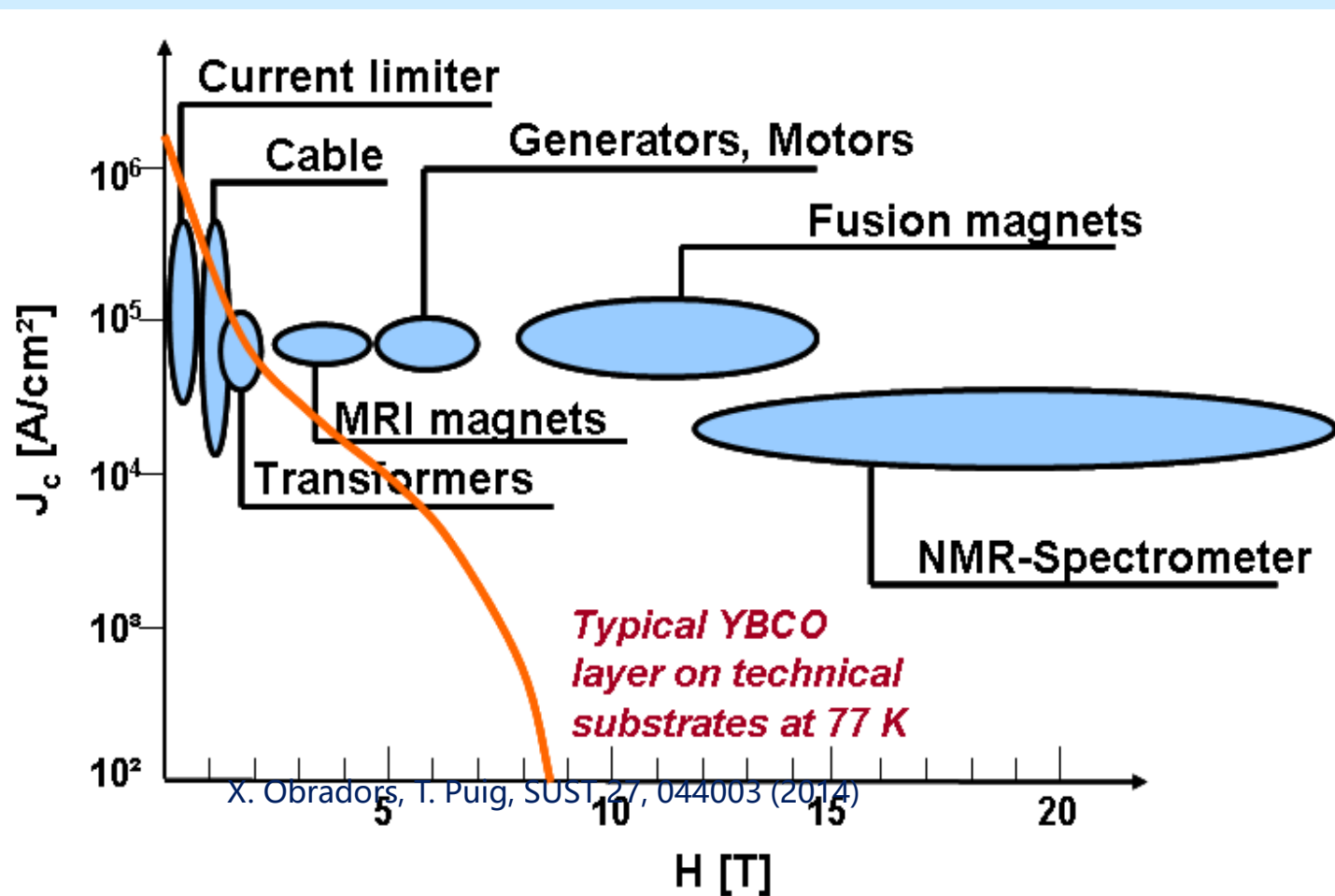
三

高温超导涂层导体磁通钉扎及其人工调制

四

若干应用发展和挑战

HTS薄膜及涂层导体的人工钉扎



◆ 要求其在液氮温区较高的 J_c 和 H_{irr}

◆ 可通过提高磁通钉扎提高 J_c , 要求缺陷具有与 ξ 相近的尺度 (纳米量级)

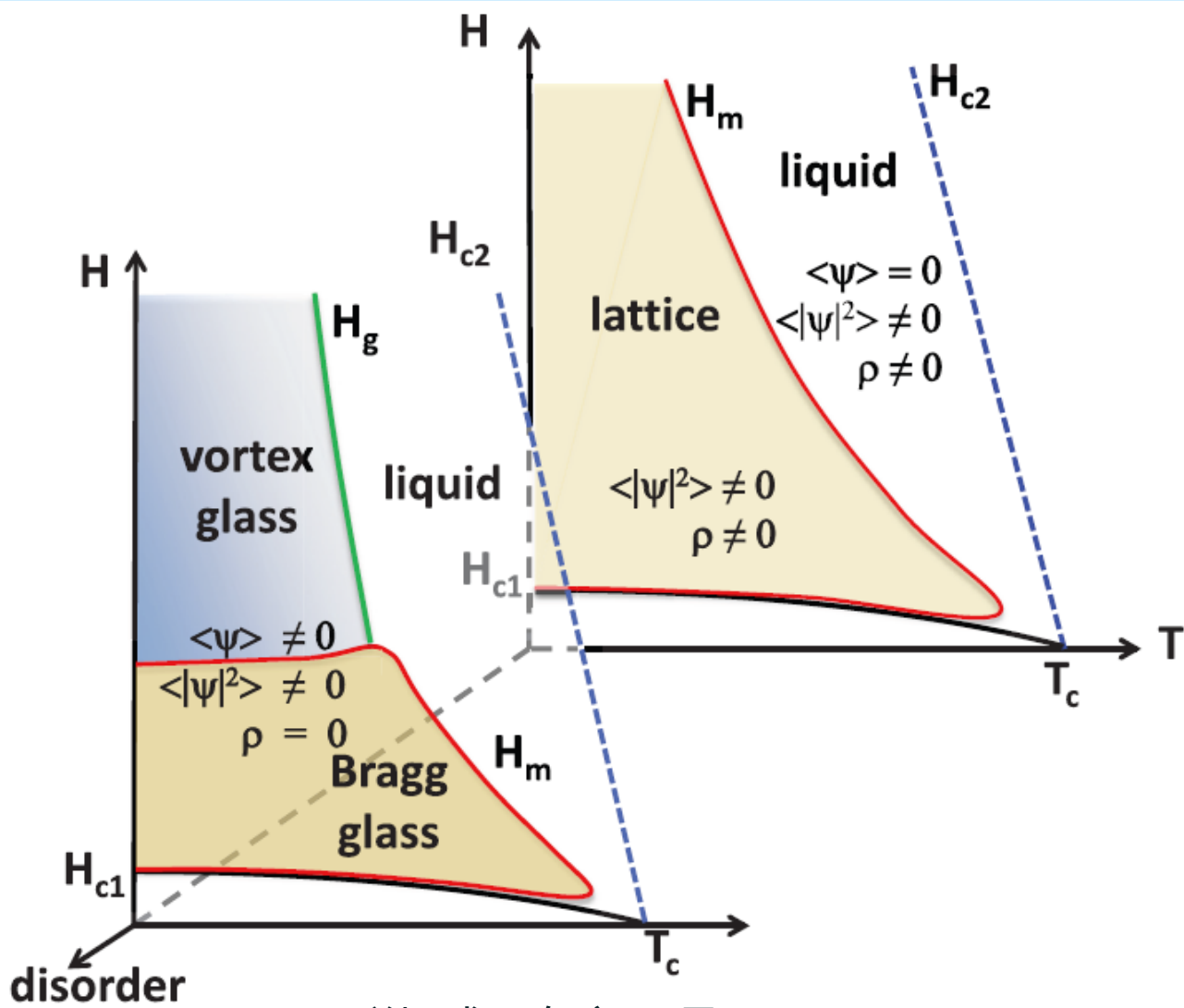
◆ 在外延高温超导薄膜本征缺陷密度能达到 10^9cm^{-2} , 临界电流密度达 10^6Acm^{-2}

◆ 库伯对拆对电流密度 $J_{dp} \sim 10^8\text{A/cm}^2$

要进一步提高 J_c , 增加缺陷密度, 即引入人工强钉扎中心

临界电流密度仍存在一定的提升空间!

涂层导体磁场应用挑战：复杂的磁热相和磁通运动



弱磁场或弱有序下是 BG
无序性增加或磁场增加是 VG

强烈无序性或热涨落将破坏涡旋点阵，

$$T_m \approx 0.1 \epsilon_0 a / \gamma \quad H_{c1} \ll B \ll H_{c2}$$

1st order melting line H_m

$$H_m < H_{c2} \quad \text{HTSs}$$

$$H_m \sim H_{c2} \quad \text{Low-Tc Sc}$$

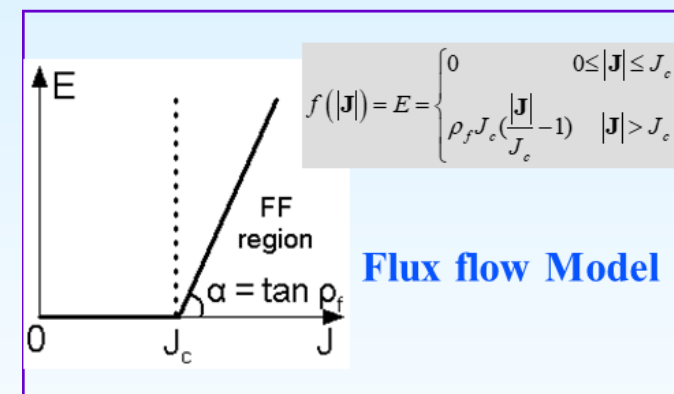
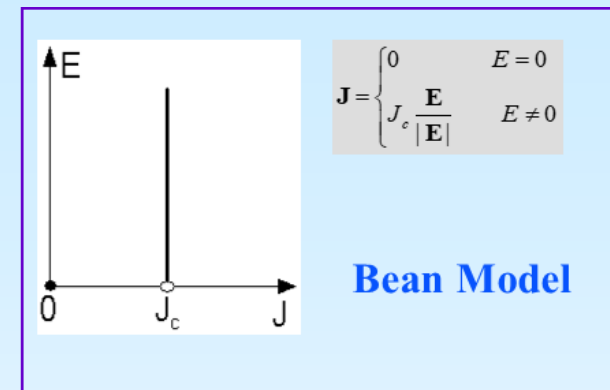
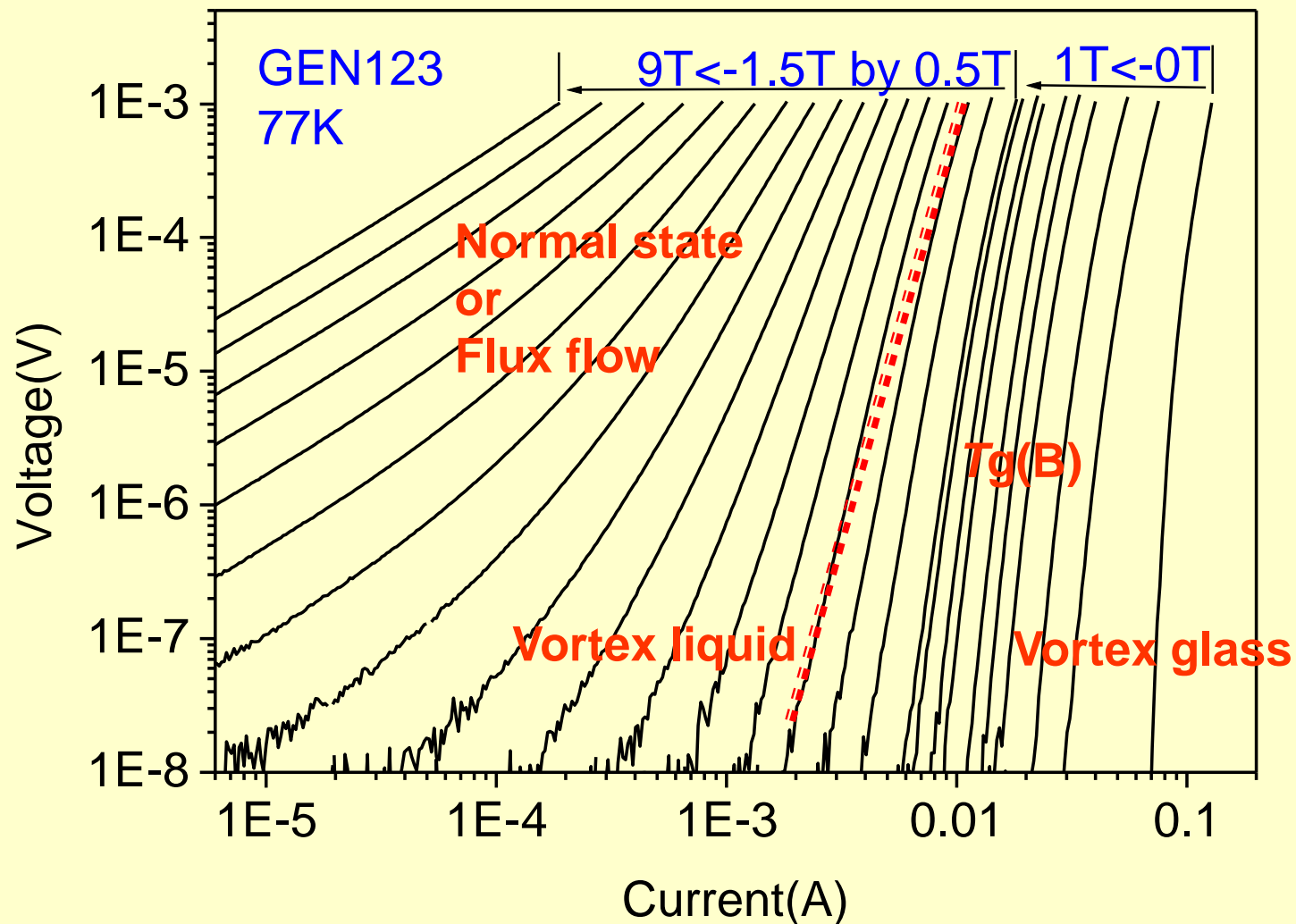
BG: vanishing of the linear resistivity $\rho=0$

BG-VG: emergence of a hysteretic magnetization

With finite disorder, the Abrikosov lattice gives way to

- vortex glass at high fields
- Bragg glass at low fields

涂层导体磁场应用挑战：复杂的磁热相和磁通运动



Vortex Glass Model:

$$J_{sc} \propto (T - T_g)^{\nu(z-1)}$$

钉扎类型及可能机制

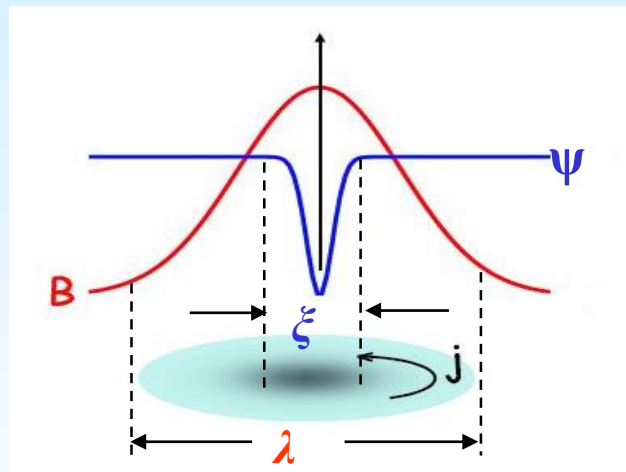
$$G_s = G_n + \int_V \left\{ \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{4m} \left| -i\hbar \nabla \psi - \frac{2e}{c} A \psi \right|^2 \right\} dV + \int_V \left\{ \frac{B^2}{8\pi} - \vec{B} \cdot \vec{M} - \frac{\vec{B} \cdot \vec{H}_{ex}}{4\pi} \right\} dV$$

Ψ 调制 (芯钉扎)

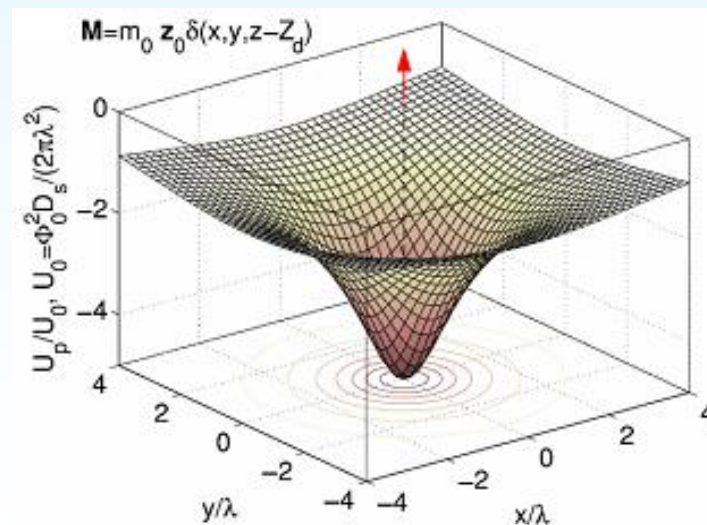
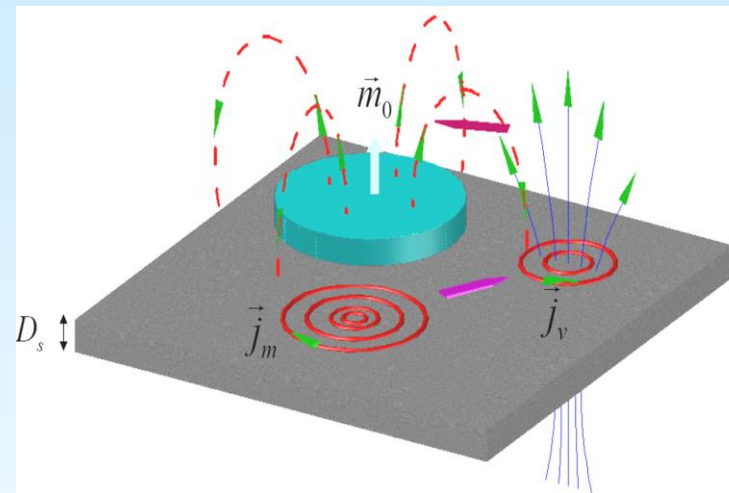
B 调制 (磁钉扎)

$$U_{mp} = -\vec{m}_0 \cdot \vec{B}_{v,i}(\vec{R}_d)$$

$$U_{mp}(r) = -\int_{V_f} \vec{M}(\vec{r}') \cdot \vec{B}_v(\vec{r} - \vec{r}') d^3r'$$



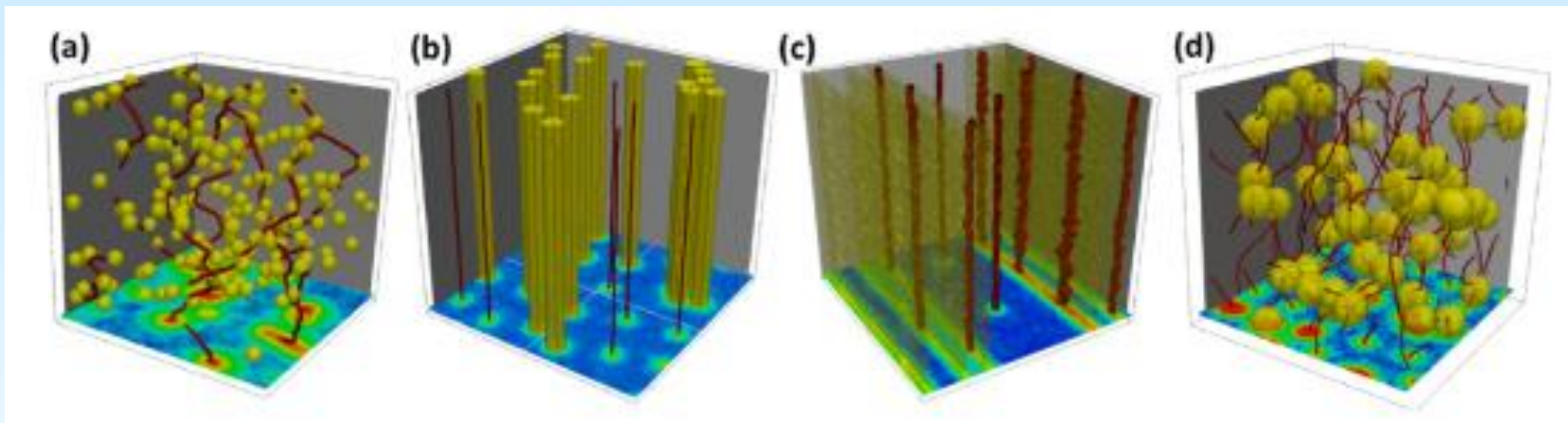
磁点偶极距的磁钉扎势分布



	芯钉扎	磁钉扎
起源	ψ 空间调制	B 空间调制
特征尺度	相干长度 ξ	穿透深度 λ
钉扎对象	涡旋芯	涡旋整体
钉扎能温度依赖关系	正比于 $1-T/T_c$	几乎独立于 T
钉扎中心灵活性	预先固定	受外场调制

PRB 69, 214504 (2004)

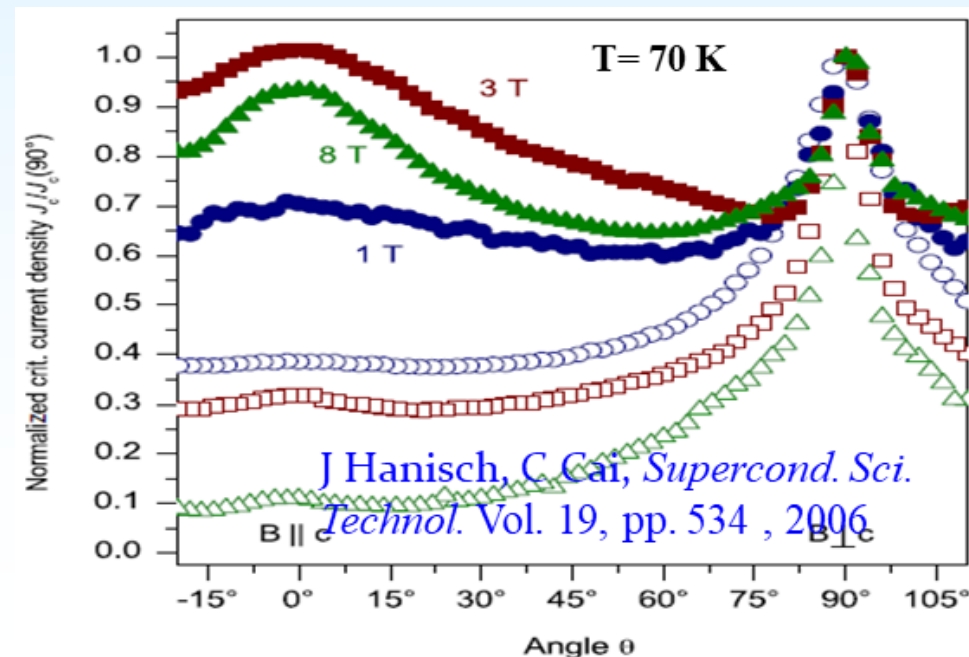
不同维度钉扎中心vs 磁传输各向异性



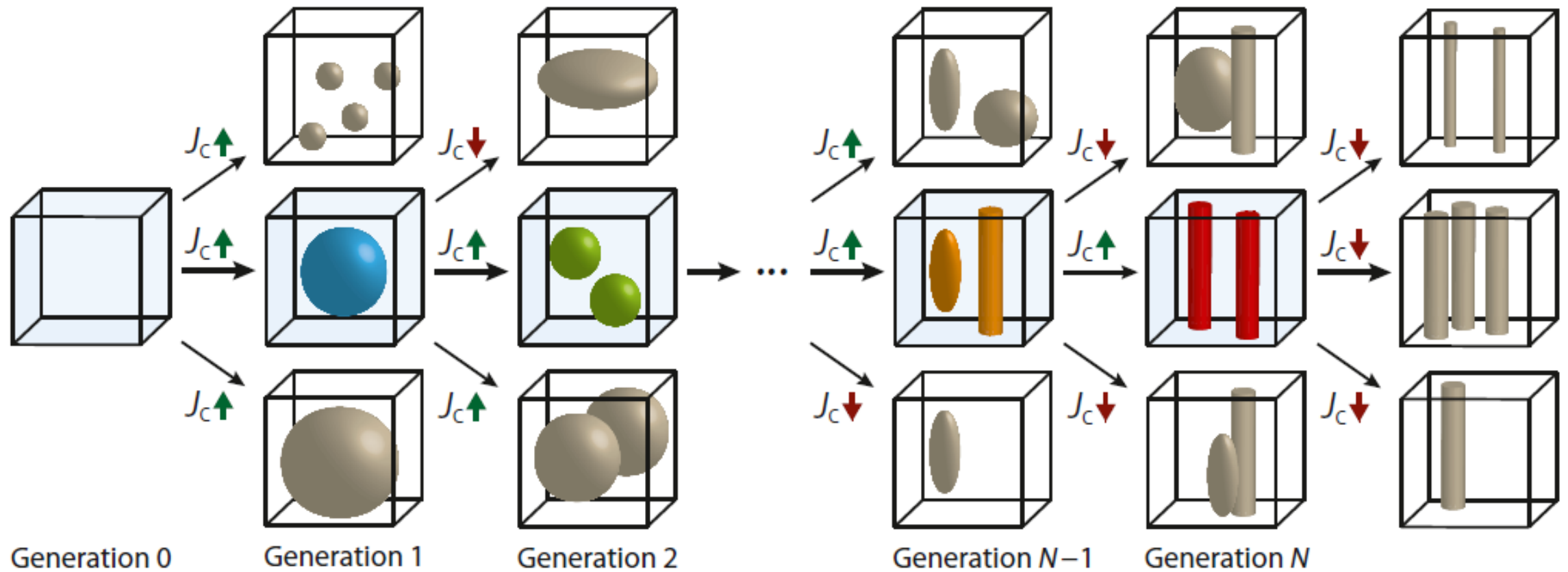
- a) 0D随机分布的原子级点状缺陷；
- b) 1D缺陷（包括位错、自组装纳米棒、辐照柱状缺陷等）；
- c) 2D平面缺陷（包括孪晶界、堆积层错和本征层状结构等）；

--- 有效改善磁场//c-axis的磁通钉扎

- d) 3D较大尺寸的随机分布缺陷（包括稀土氧化物颗粒、二次相颗粒、缺陷团簇和孔(SuST 31 (2018) 034004)

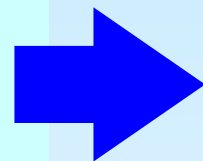


不同维度钉扎中心的演变及其对 J_c 影响

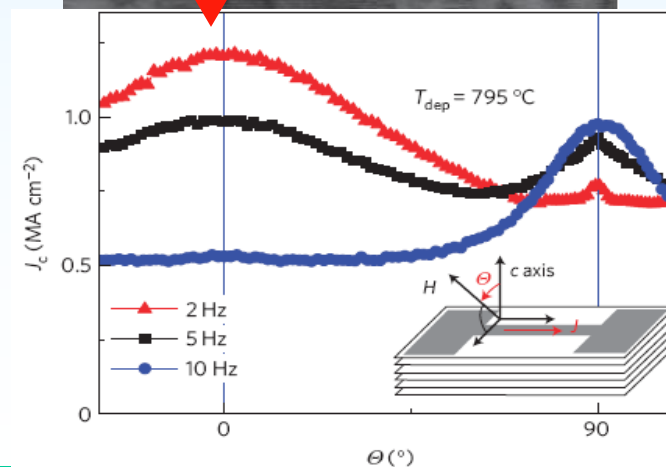
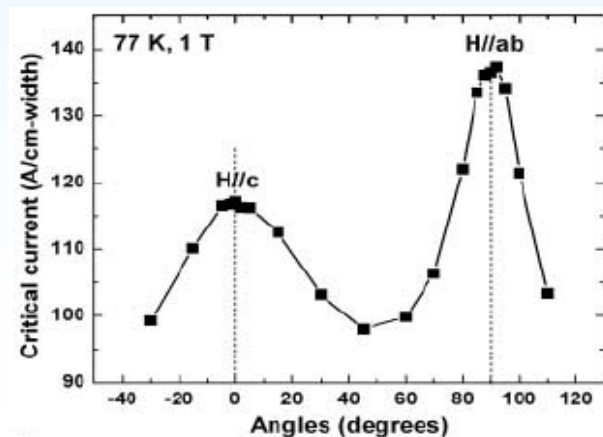
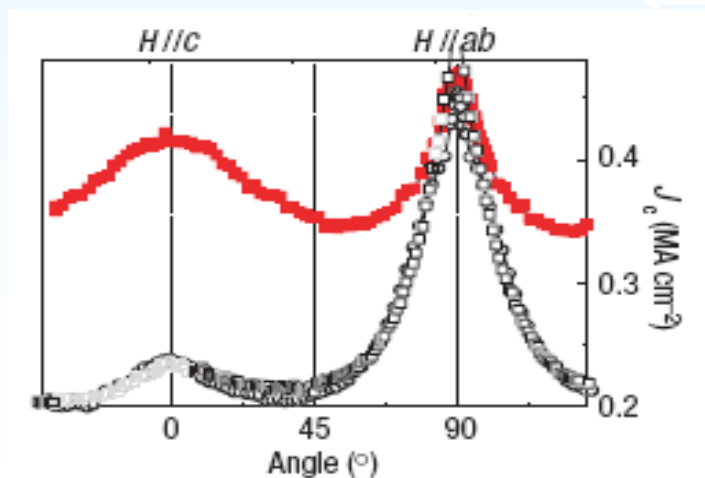
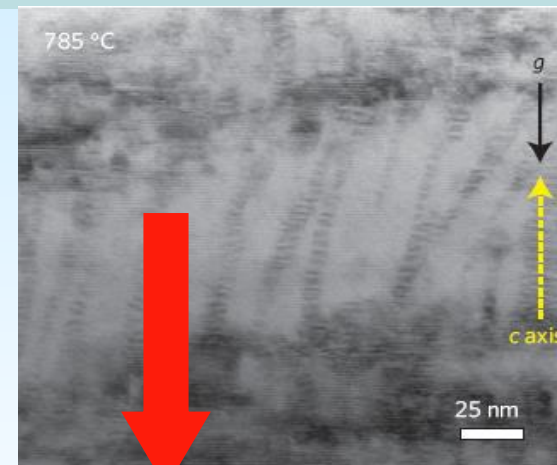
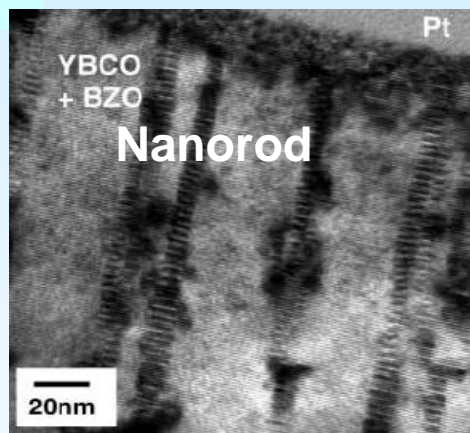
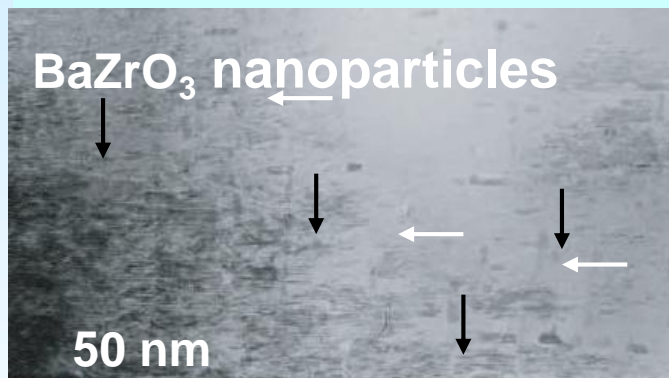


不同维度磁通钉扎中心 vs. 磁传输各向异性调制

Defects v.s Vortex Lines



- ❖ Emerged defects as: Much desired !!!
- High density: $(H/2) \times 10^{11} \text{cm}^{-2}$ (in T)
- Low Dimension: 1D, 2D
- Anisotropic: c-axis correlated

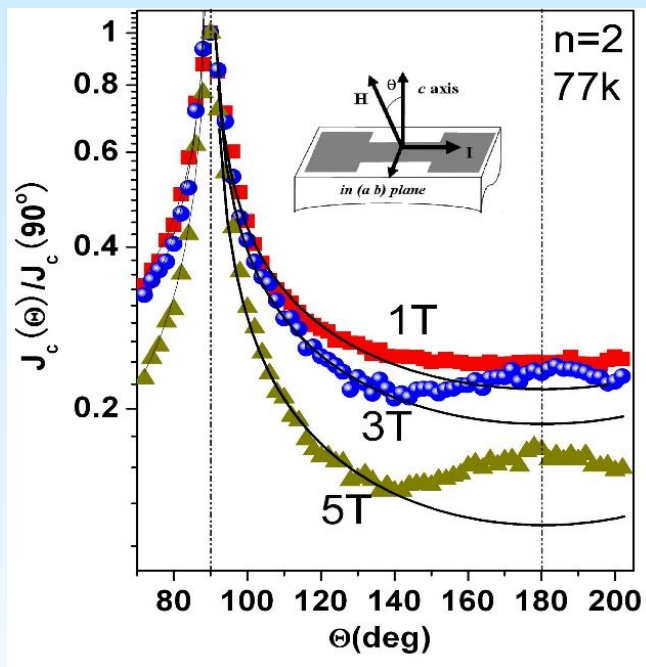


Nature Materials 3, 439 (2004)

Science 311,1911 (2006)

Nature Materials 8, 398 (2009)

不同维度磁通钉扎中心 vs. 磁传输各向异性调制

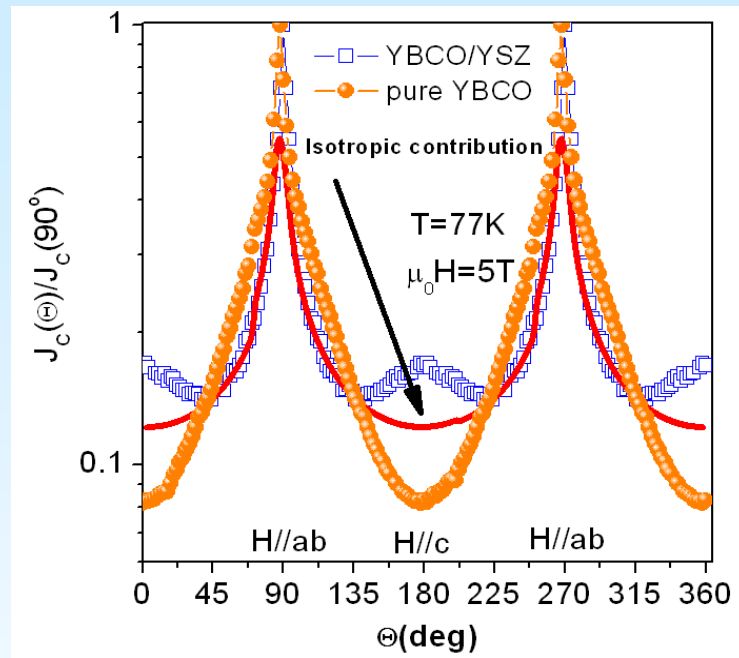


临界电流密度

$$J_c^{is}(H, \Theta) = J_c^{is}(\tilde{H}_{eff})$$

$$\tilde{H}_{eff} = H\varepsilon(\Theta)$$

$$\varepsilon(\Theta) = (\cos^2 \Theta + \gamma^{-2} \sin^2 \Theta)^{1/2}$$



L. Peng, C. Cai, *et al*,
 J. Appl. Phys. 104, (2008) 033920:
 J. Phys. D:Appl. Phys. 41, (2008) 155403

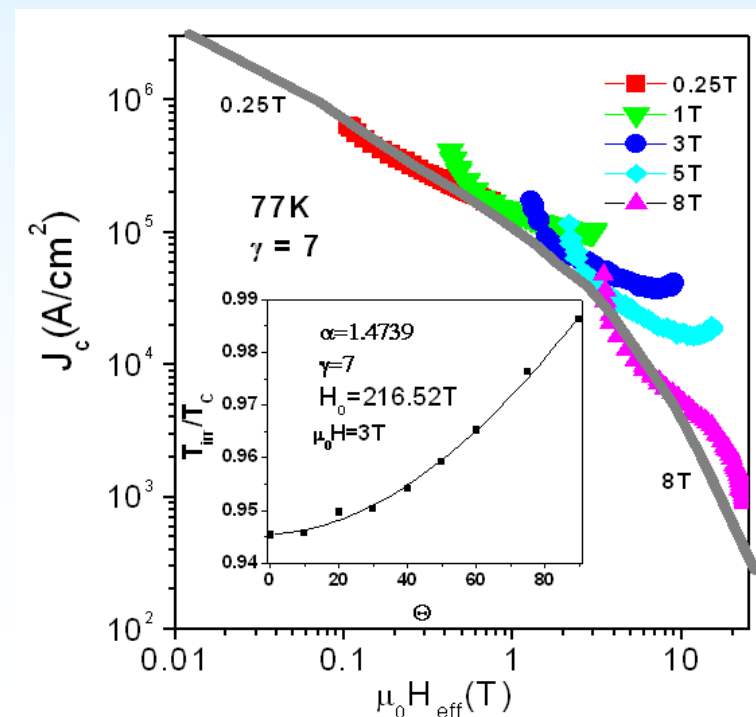
$J_c(H, \Theta)$ 的标度行为 (定性的说明)

◆ 各向同性缺钉扎结果 $J_c(H, \Theta)$ 可仅通过一有效场来描述其对临界电流密度的贡献将塌陷成一条曲线。

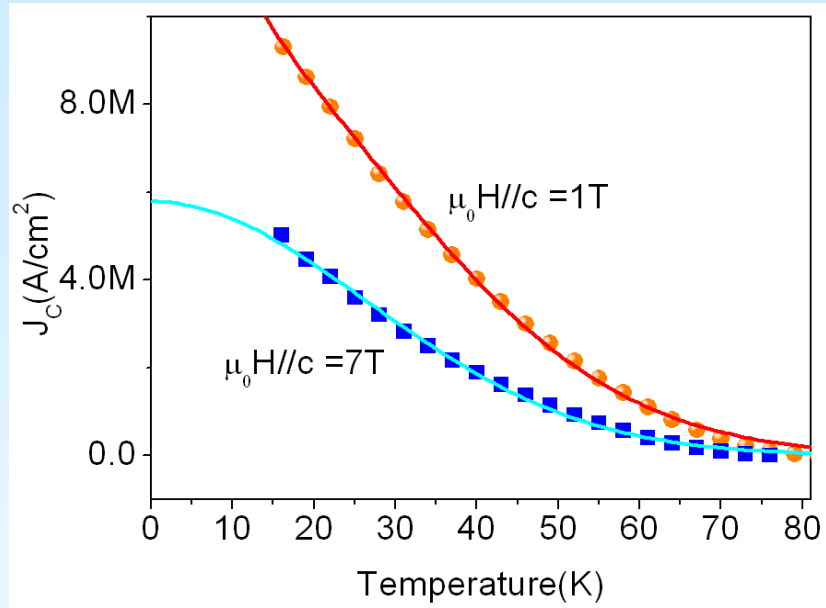
Tachiki-Takahashi
 本征钉扎模型：

$$J_c(\Theta) = J_c(0) |\cos \Theta|^{-0.5}$$

◆ 二次峰的出现很可能由各向异性缺陷 (c轴关联) 对磁通钉扎的结果。



各向同性和各向异性缺陷对临界电流的贡献



弱的各向同性钉扎:

$$J_c^{WP}(T) = J_c^{WP}(0) \times e^{-T/T_0}$$

随温度呈较快下降趋势

强的各向异性钉扎:

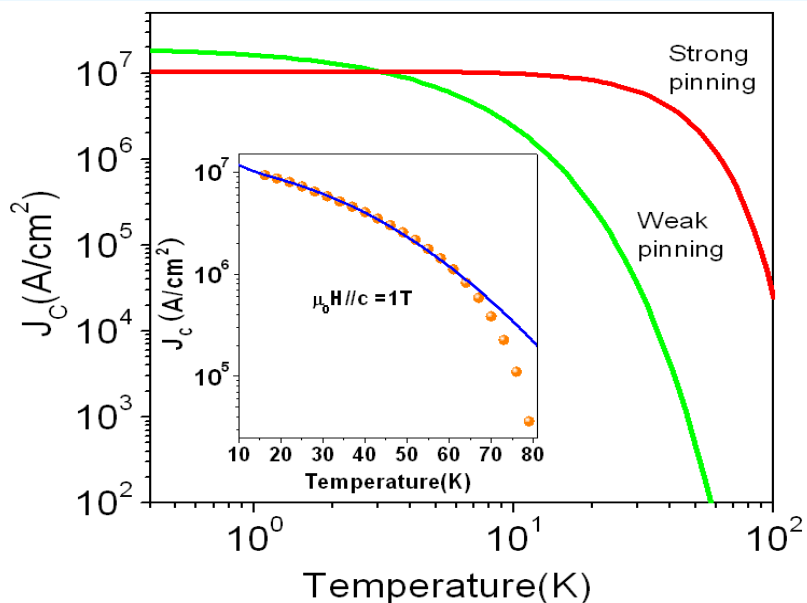
$$J_c^{SP}(T) = J_c^{SP}(0) \times e^{-3(T/T^*)^2}$$

随温度呈缓慢下降趋势

各向同性、各向异性共同钉扎:

$$J_c^{MP}(T) = J_c^{WP}(0) \times e^{-T/T_0} + J_c^{SP}(0) \times e^{-3(T/T^*)^2}$$

- ◆ 低温下，各向同性缺陷钉扎占重要地位
- ◆ 随着温度的增加，各向异性缺陷起主导作用，各向同性缺陷钉扎作用迅速减弱至消失



准多层二次相掺杂：制备

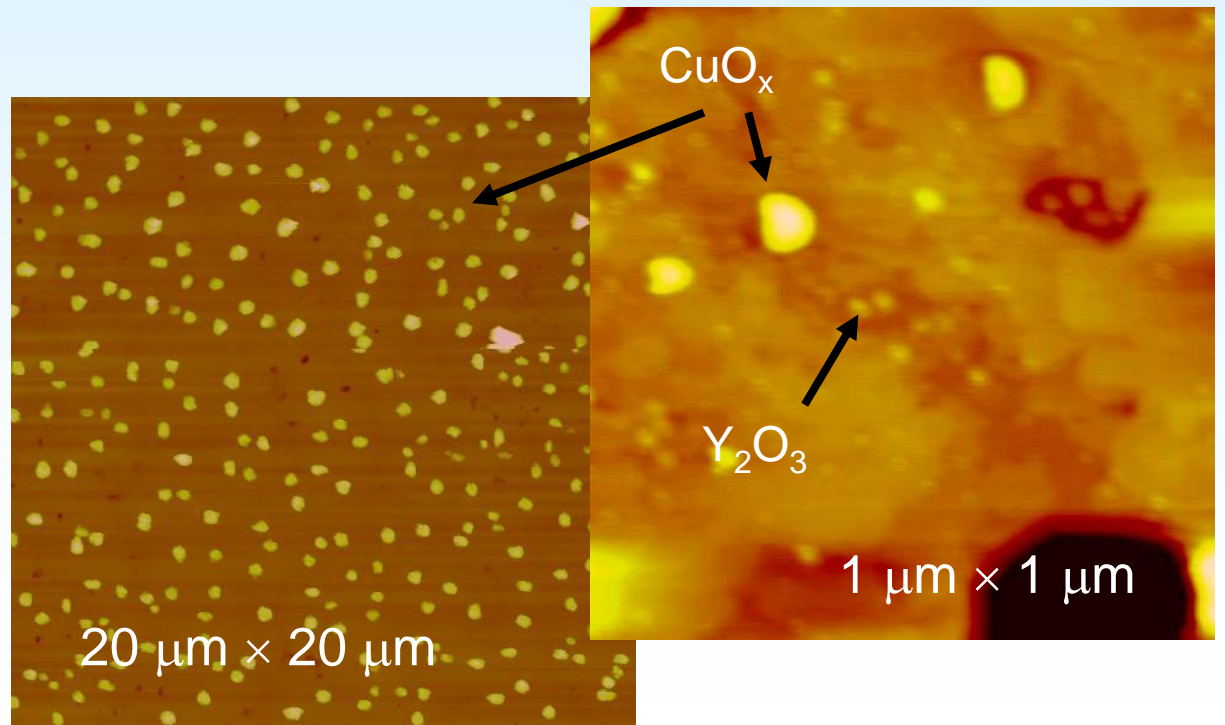
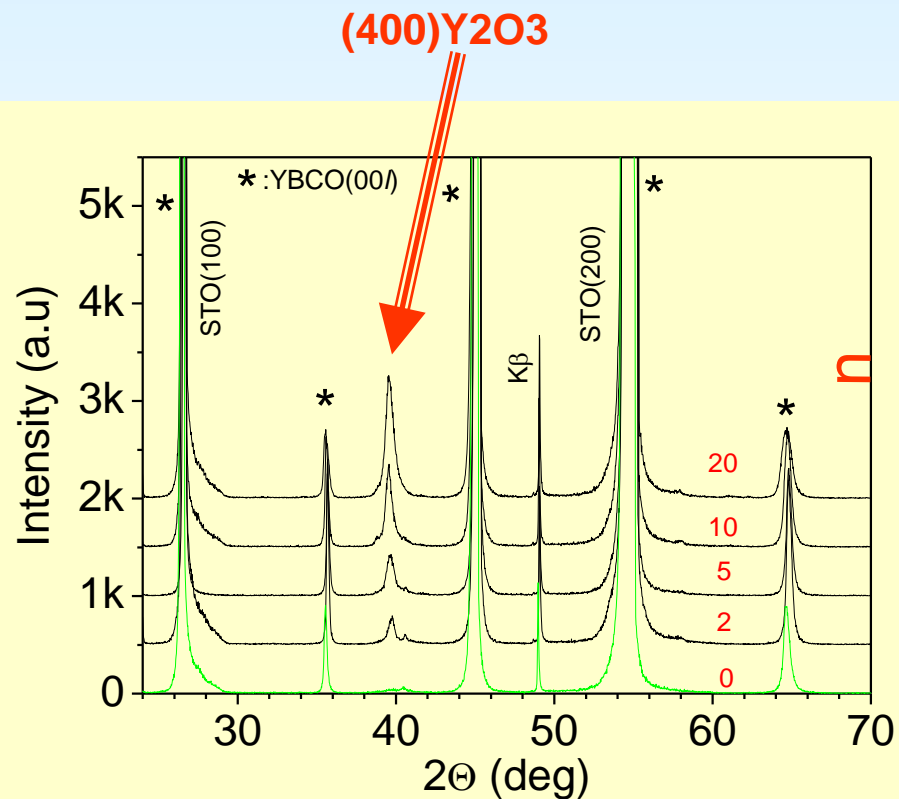
Y123/Y₂O₃ quasi-multilayer ~ 280 nm

70 x (m Y123/ n Y₂O₃)

m ≡ 40 p.s ⇒ 3.4 u.c

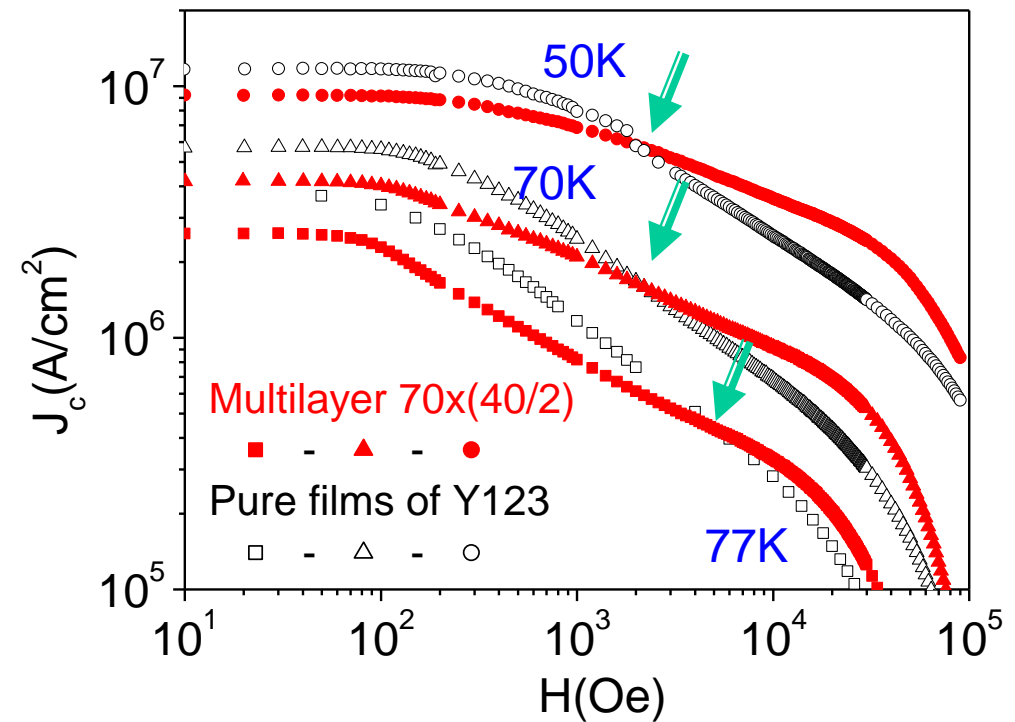
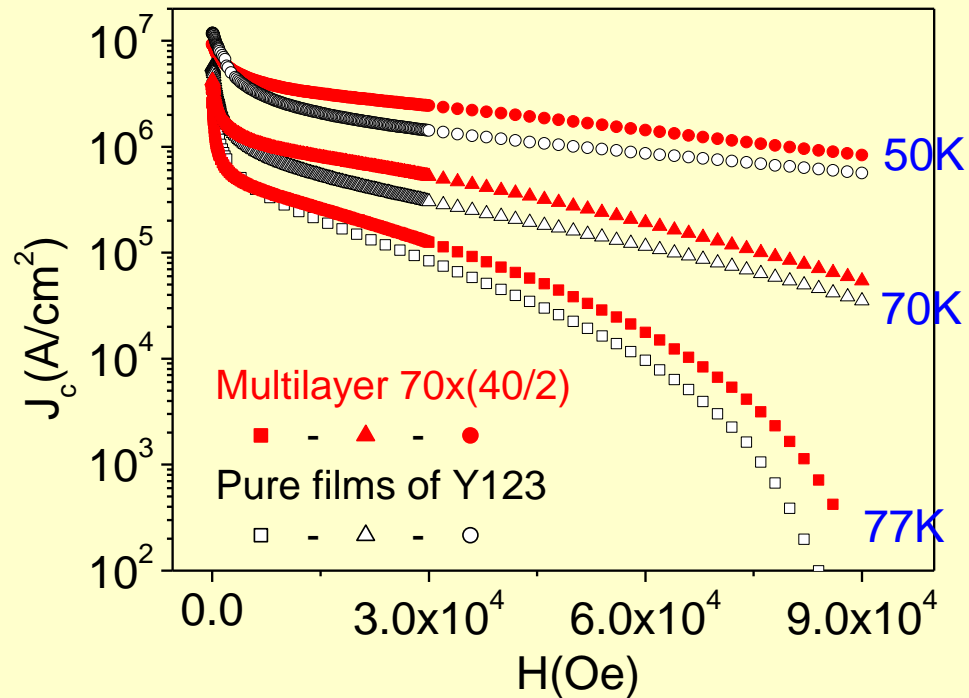
n = 2, 5, 10, 20 p.s ⇒ 0.075 - 0.75 u.c

incomplete layer!!



准多层二次相掺杂：磁传输

- ❖ Enhanced flux pinning: at high fields
- ❖ Crossover behavior: **temperature dependent**



Crossover field: 2000 Oe at 50K
6200 Oe at 77K

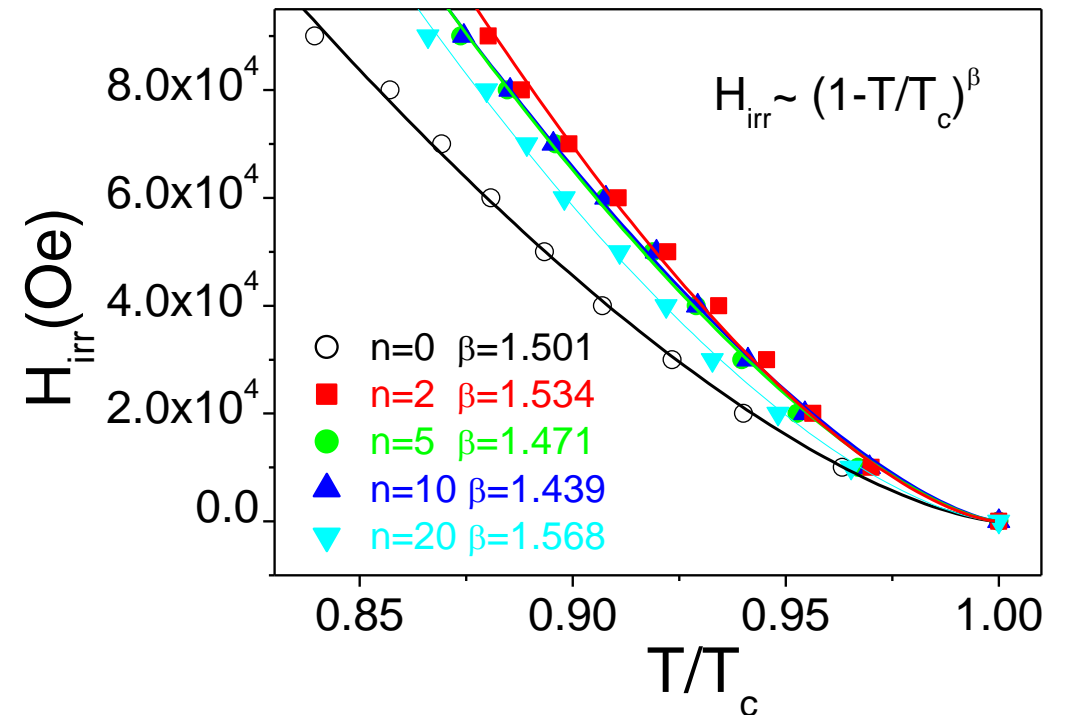
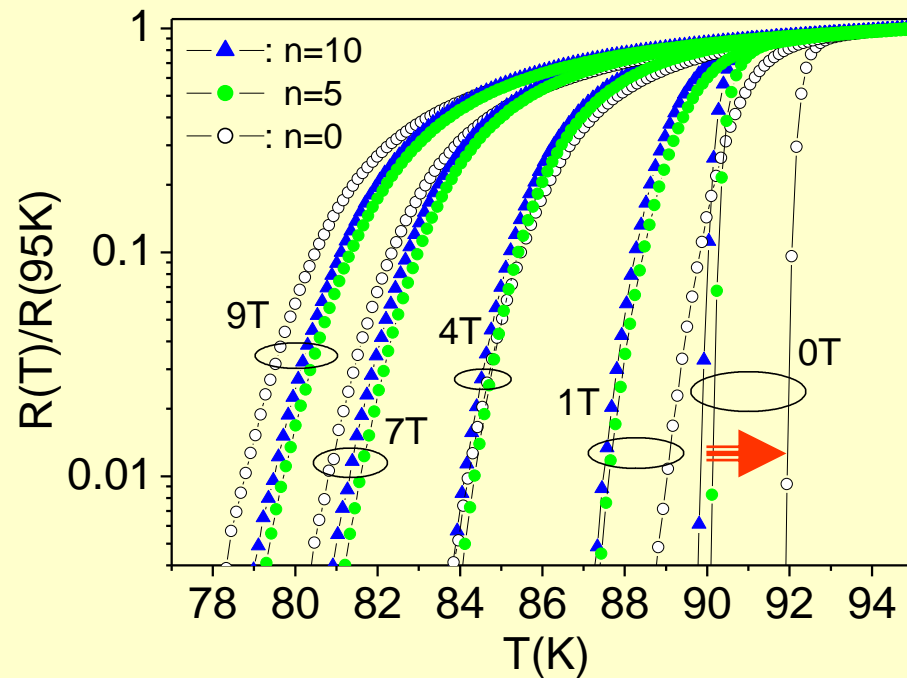
准多层二次相掺杂：不可逆场

❖ Magneto-resistance further evidences

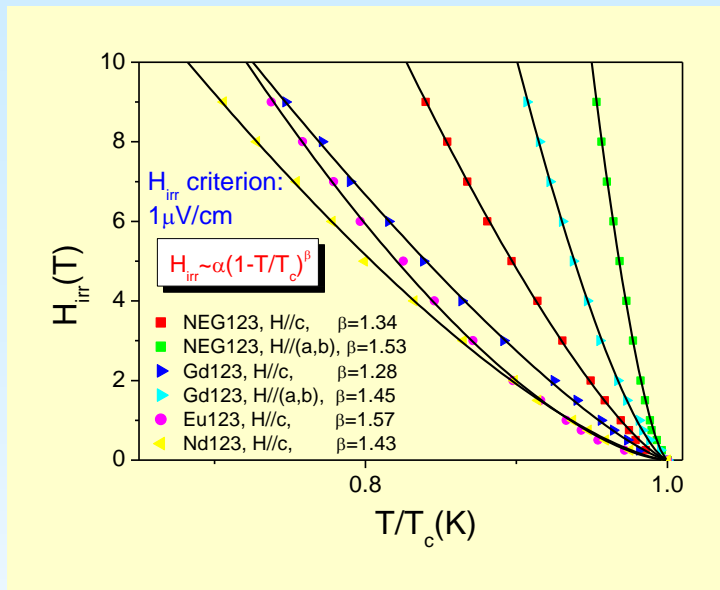
enhanced flux pinning at high fields

❖ IRL line shifted upwards, the lower T, the larger gap \Rightarrow

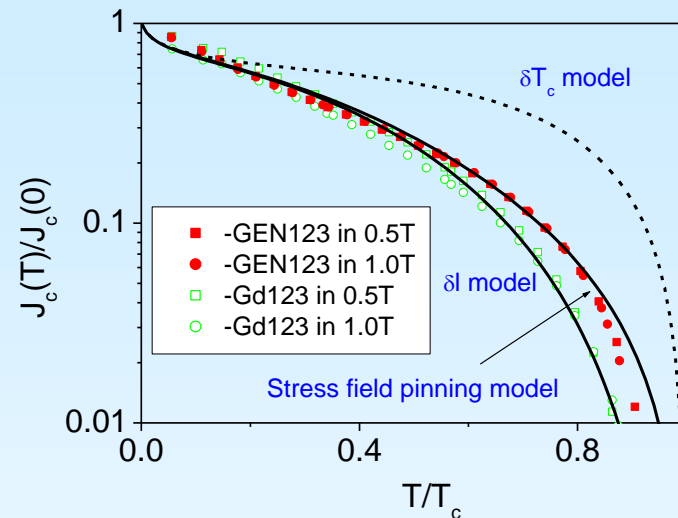
temperature dependence of crossover behavior



多元/多层HTS薄膜：磁传输和磁热相图的调制

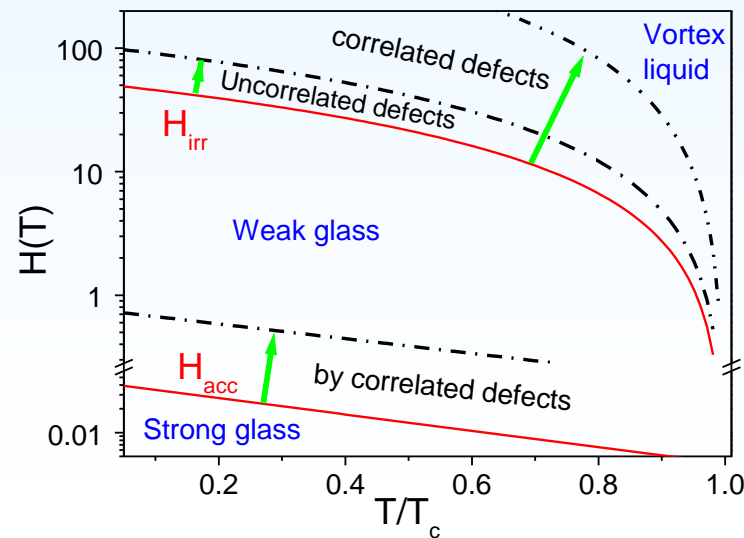
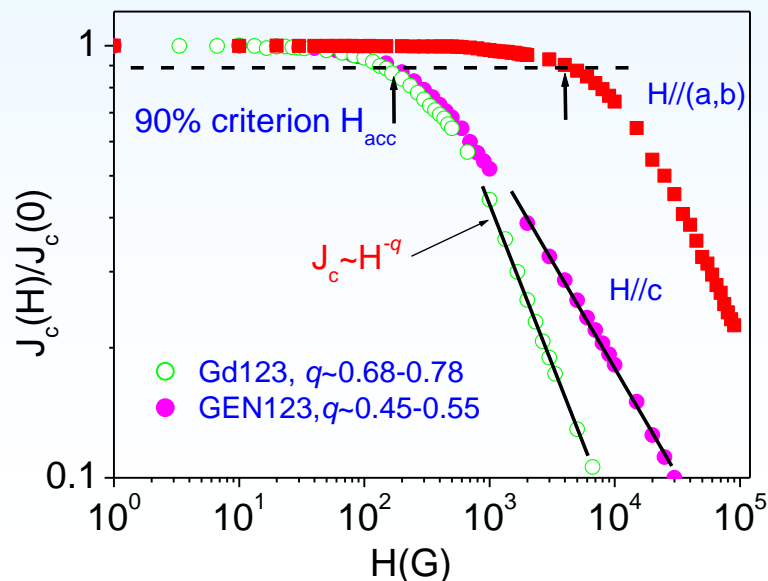


C. Cai et al., APL. 84(2004)377

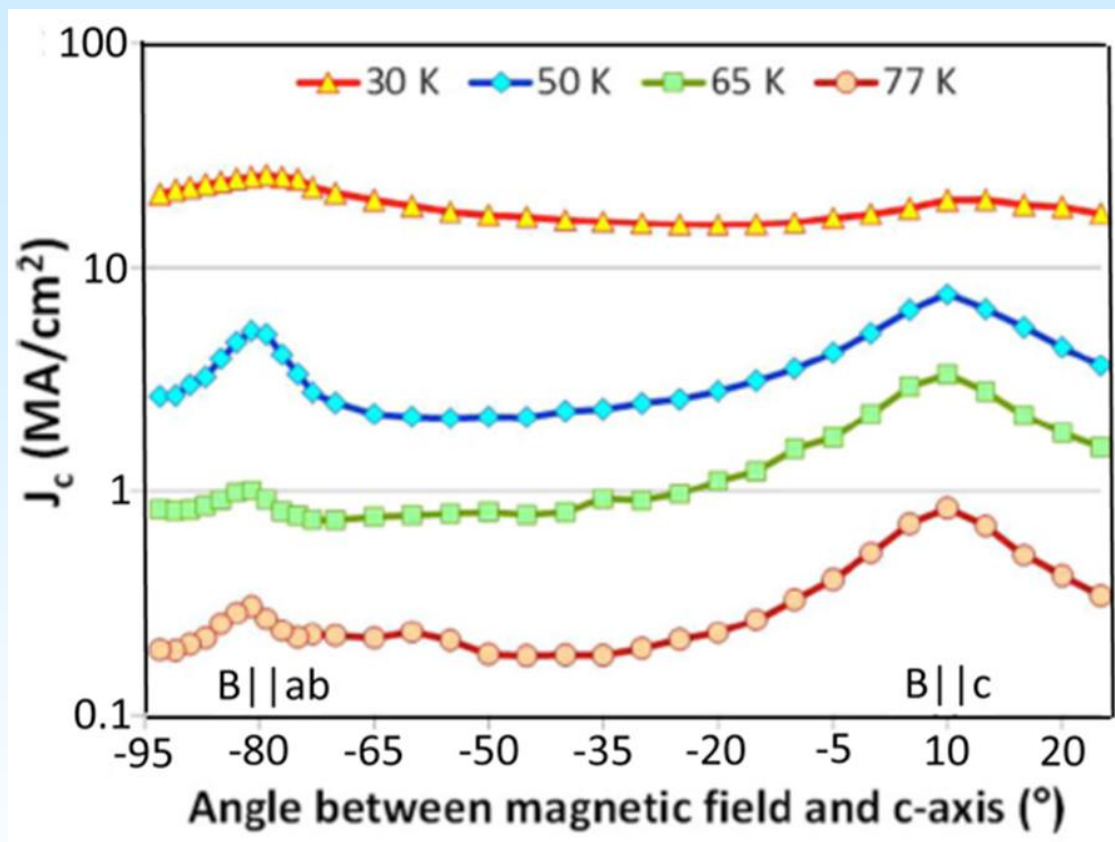


C. Cai et al.,
PRB. 69,
(2004) 104531

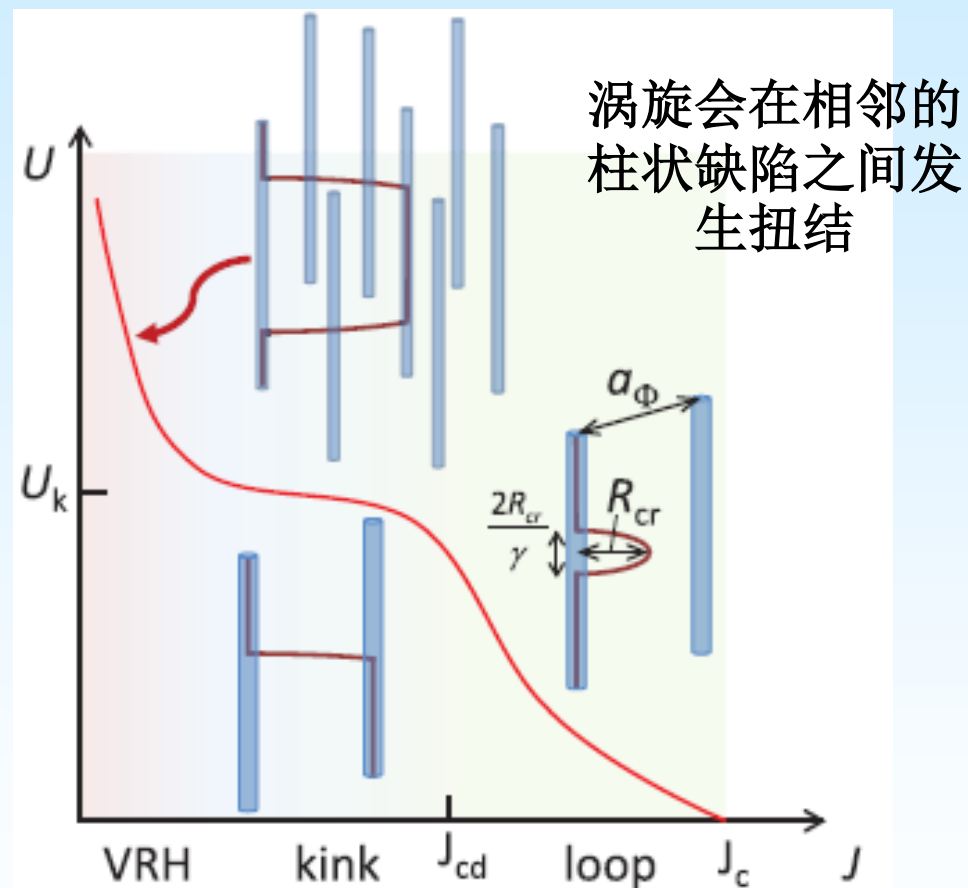
$$J_c(T)/J_s(0) = f(t) / [(1 + \mu k_B S T_c t / g(t))]^{1/\mu}$$



低维柱状缺陷或无序的高效钉扎



(SuST 31 (2018) 034004)

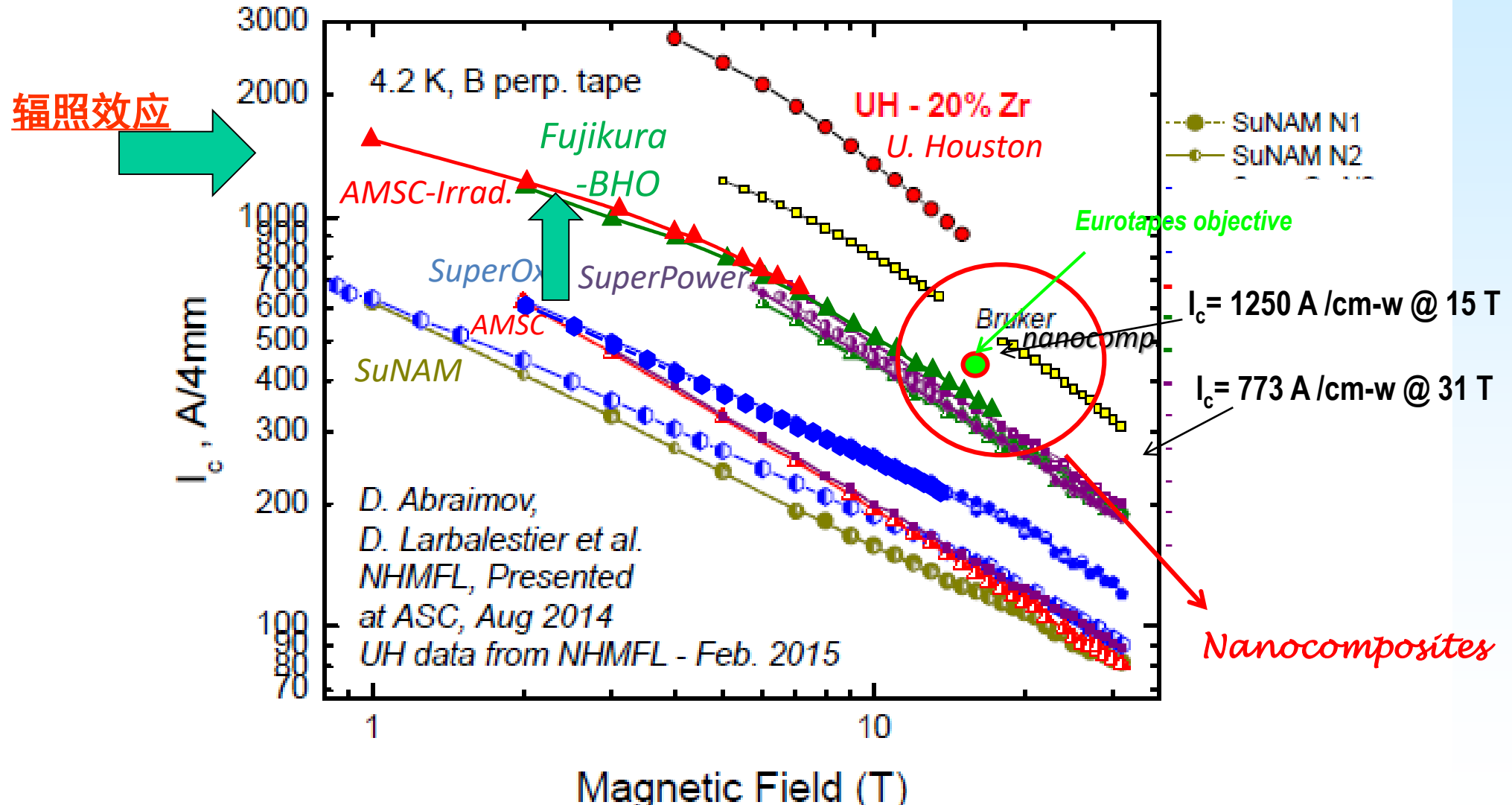


- ◆ 高浓度Zr掺杂后的1D缺陷 vs. 磁场各向异性 J_c ,
- ◆ 大温度范围高于本征钉扎的磁场平行c-axis的 J_c
- ◆ 随温度降低磁各向异性得到大大抑制

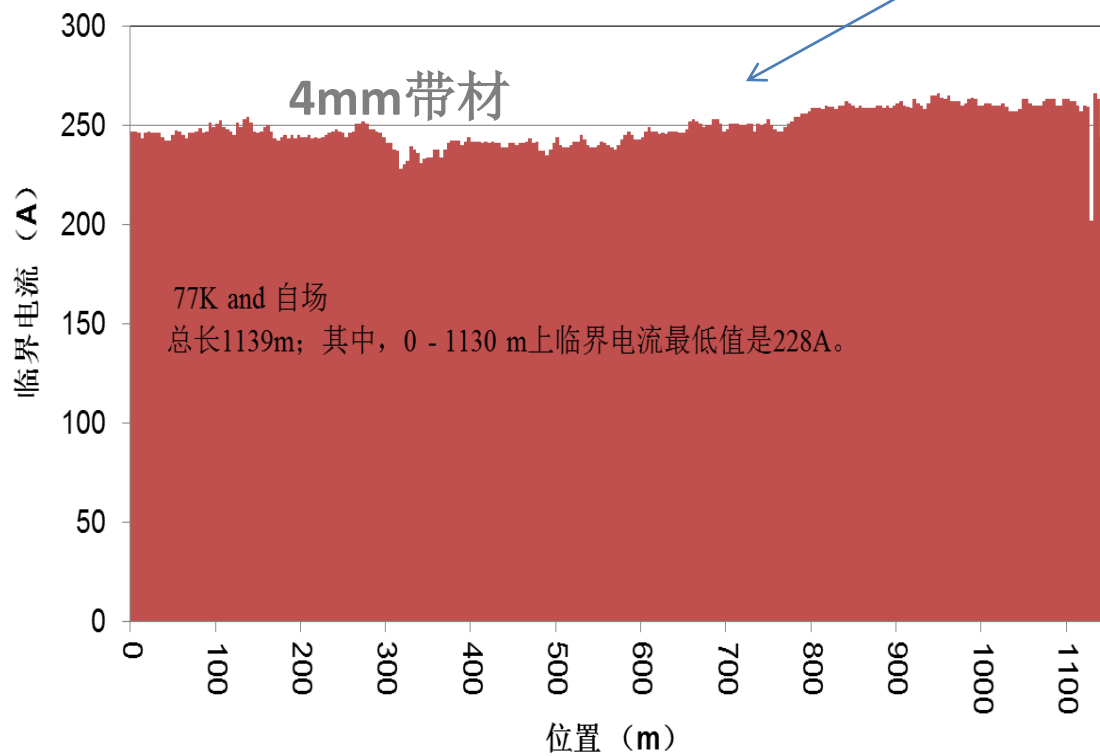
$$U_k \approx \frac{\epsilon_0 a_\Phi}{\gamma} \ln \frac{a_\Phi}{\xi}$$

Nanocomposite Coated Conductors

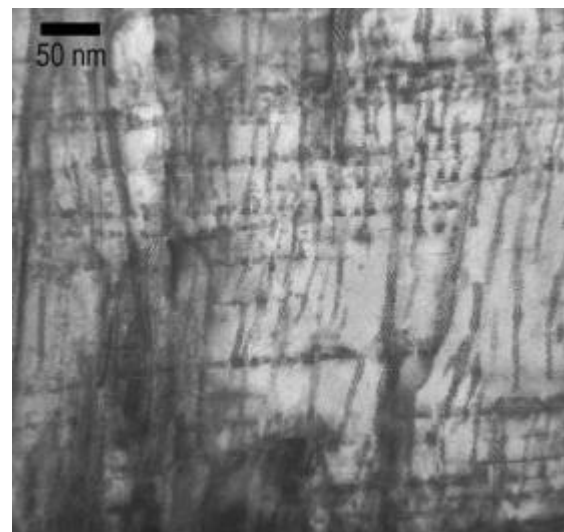
A reality and yet continuously improving and breakout



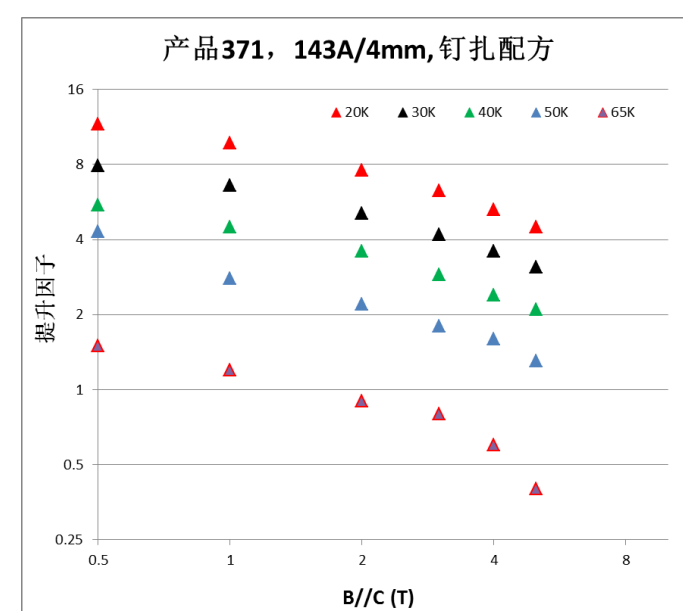
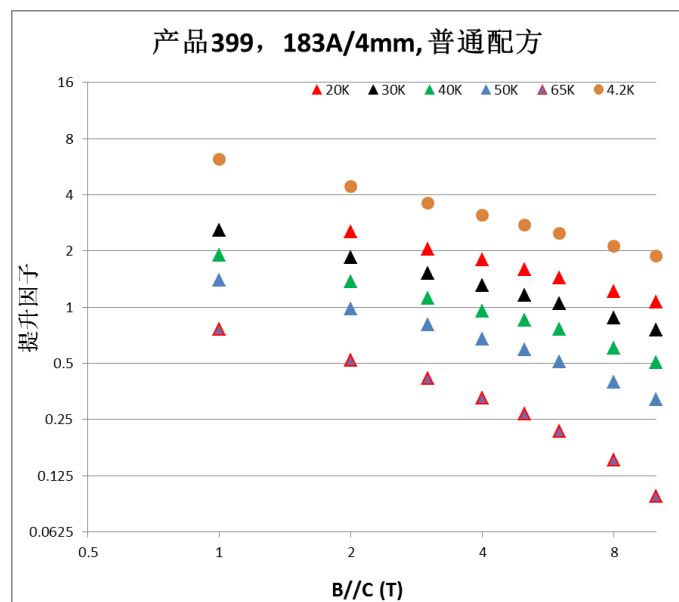
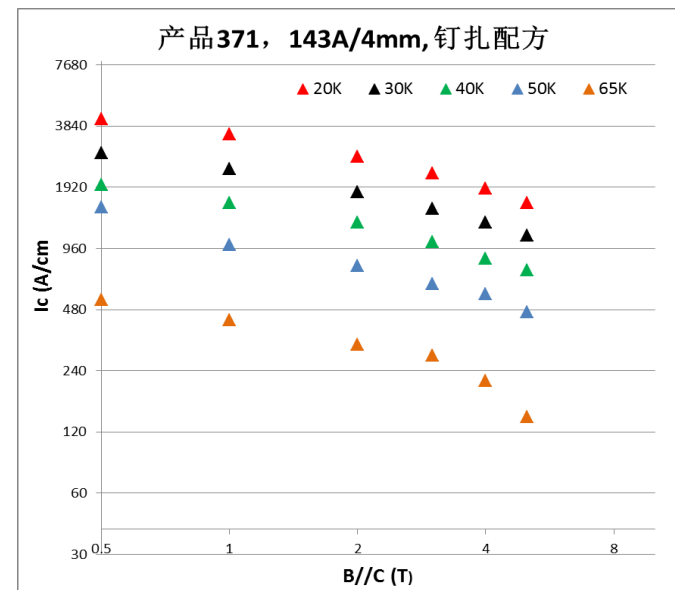
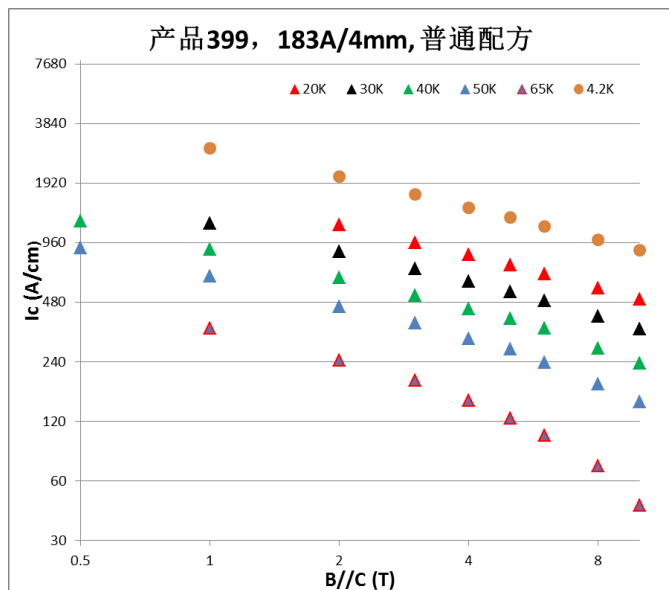
- ◆ 日常长带生产，电流在400-540A / 12mm。
- ◆ 量产的2种产品
 - ◆ 普通配方---电力电缆应用，77K自场，4mm产品， $I_c=100A-160A$ 。
 - ◆ 最好的长带 I_c *长度，为228A×1130米
 - ◆ 钉扎配方---高磁场应用，BZO柱状钉扎4mm带材，垂直场下
30K, 3T, I_c 在440-600A---世界最好水平
 4.2K, 10T, I_c 在350-650A



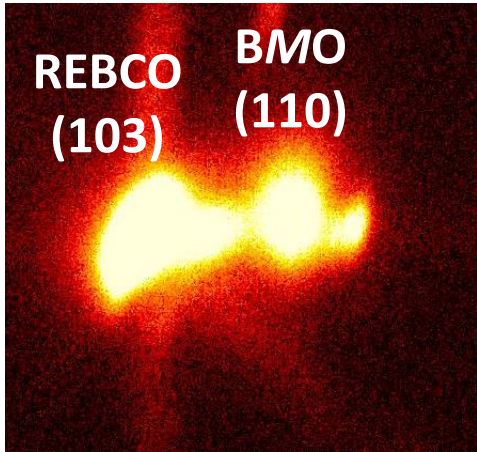
BZO柱状钉扎



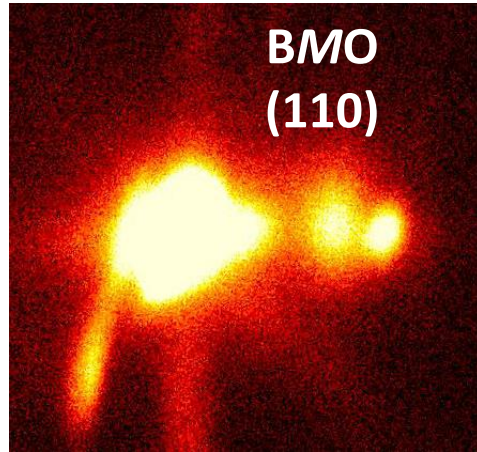
柱状钉扎大幅度提升 磁场性能



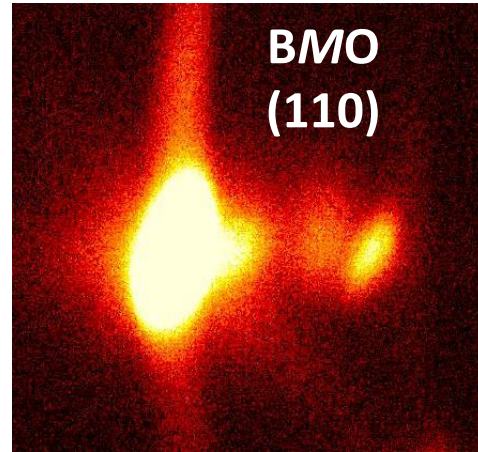
Various composition for enhanced pinning properties



Composition A



Composition B

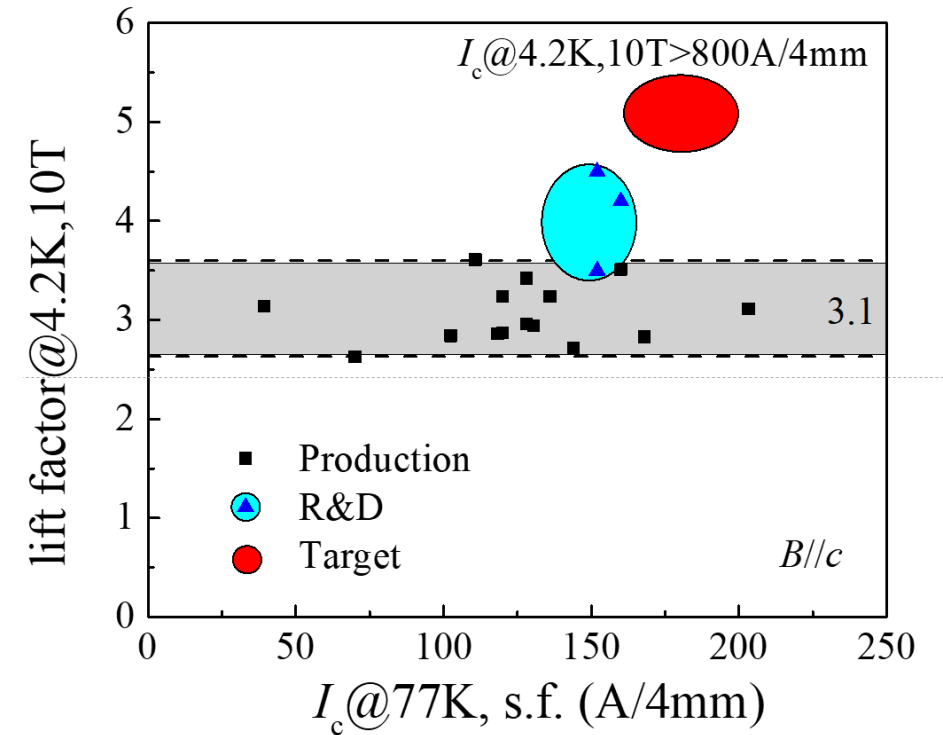


Composition C

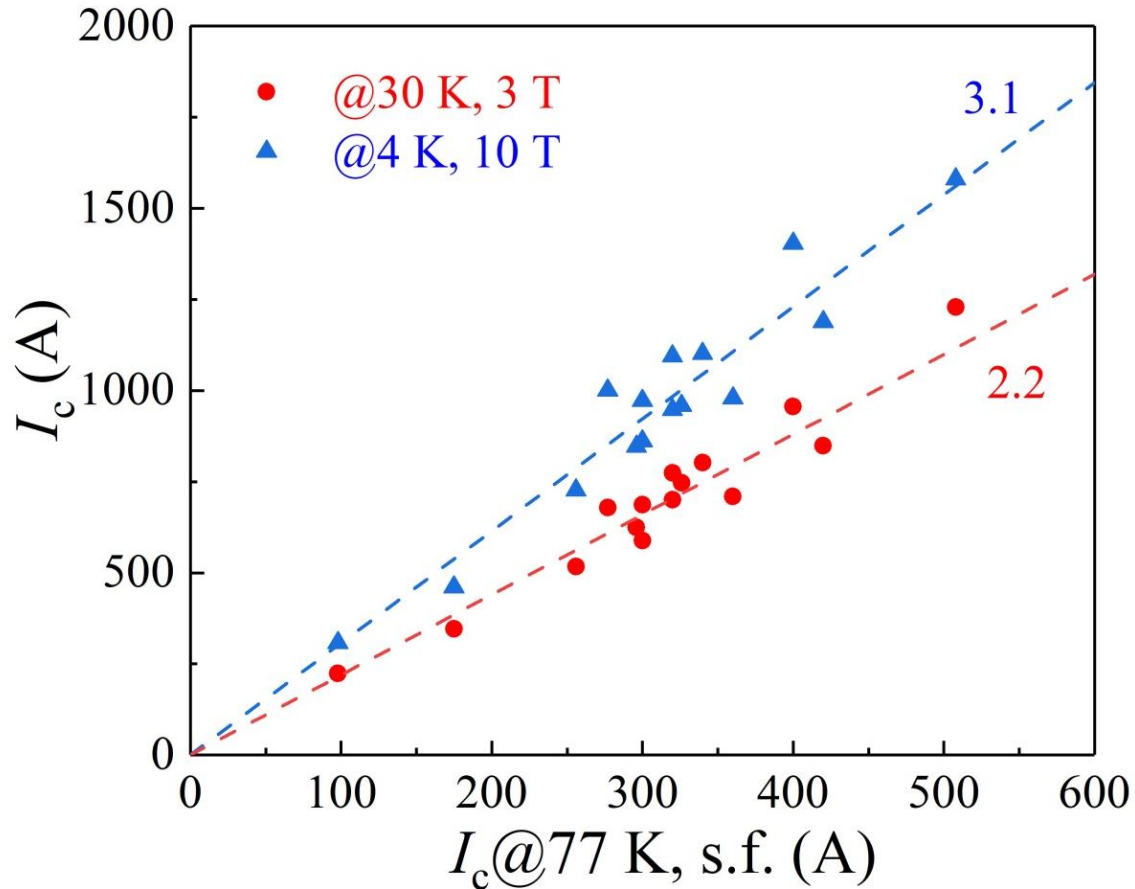
Tunable defect landscapes under high growth rates:
from strongly correlated pins to random ones

At 30 K 1 T, LF increases from 3.0 to 3.5

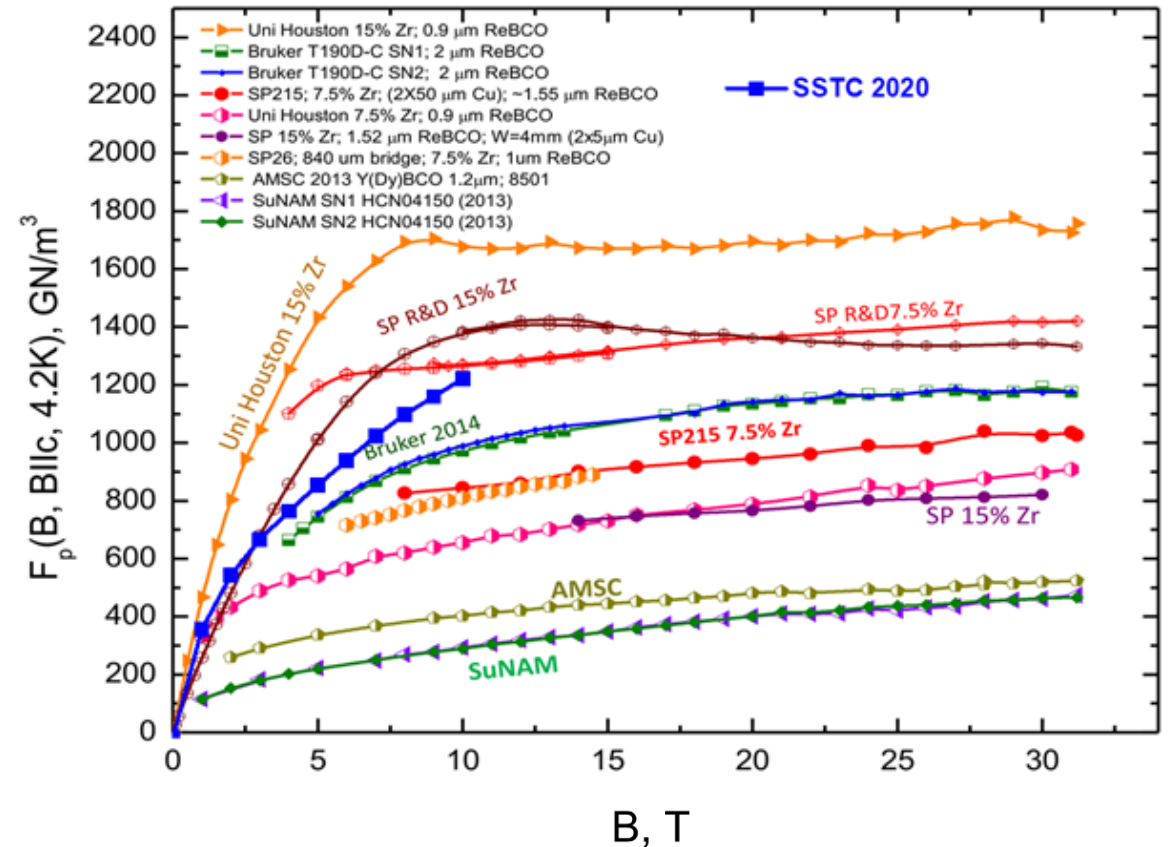
At 4.2 K, 10 T, LF increased from 3.1 to 4.5



Pinning behaviors of APCs EuBCO films (mass product)



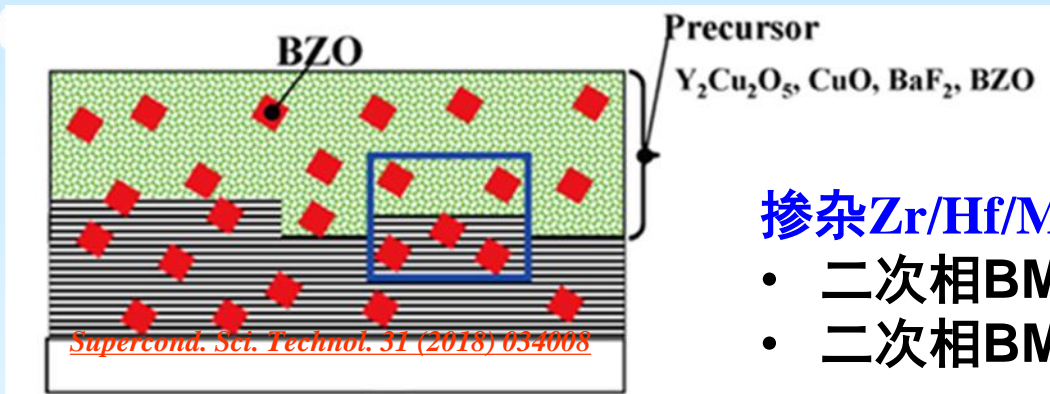
- ✓ High consistency of lift factor among different batches



- ✓ High pinning force at 4.2 K, high magnetic fields.
- ✓ Radom Pinning machinimas is dominated.

Some data are from D. Abraimov et.al, "Comparison of in-field transport I_c , J_c , and F_p for R&D and production ReBCO tapes", EUCAS 2017, Geneva, 2017

■ 异位法MOD薄膜的二次掺杂

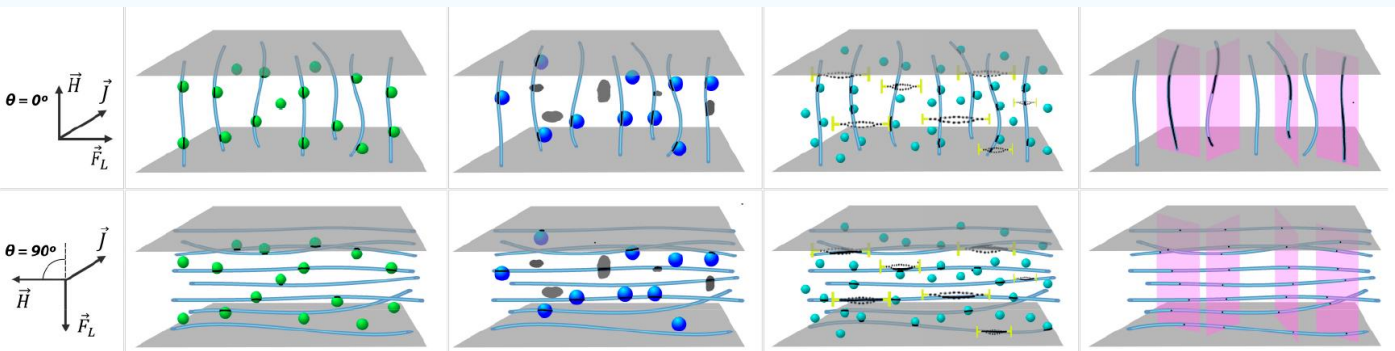
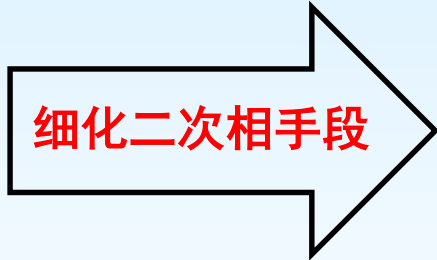


掺杂Zr/Hf/Mn/Sn等元素：

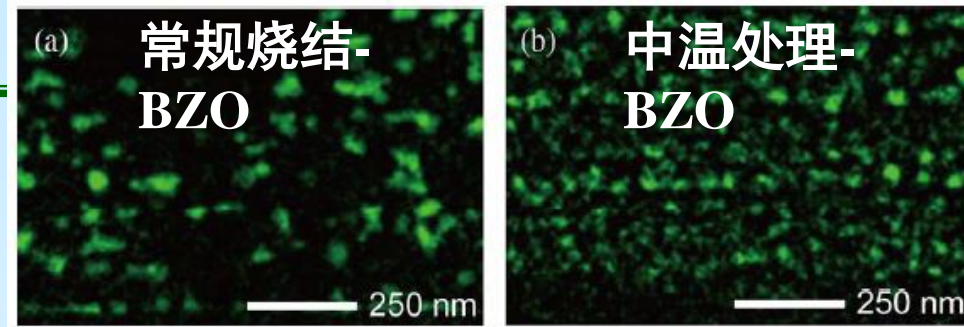
- 二次相BMO尺寸分布大
- 二次相BMO分布不均匀

磁通钉扎方式：

- 离散分布的二次相会与薄膜中其他缺陷（Y2O3、孪晶晶界、面堆叠位错等）起协同钉扎作用
- 属于三维钉扎方式

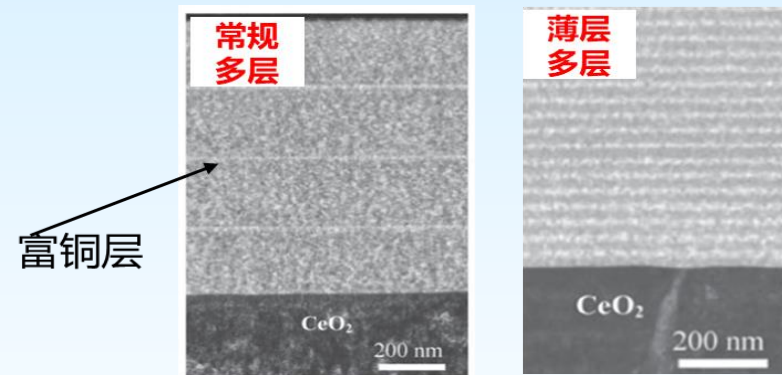


1. 高温晶化前增加中温处理



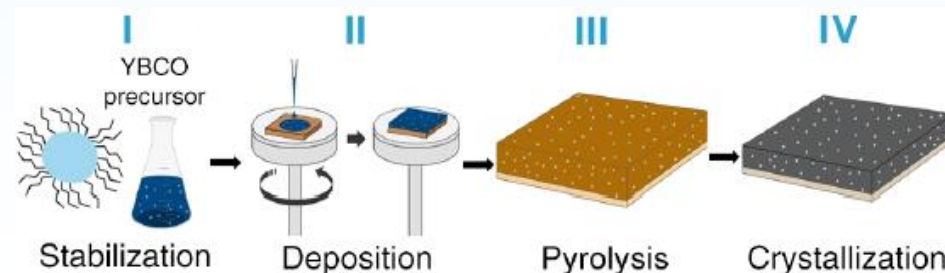
IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY 2016

2. 薄层手段：细化二次相颗粒



Supercond. Sci. Technol. 30 (2017) 055008

3. 添加预成型的纳米颗粒



离子辐照对超导材料磁传输及各向异性的影响



Ref: APPLIED PHYSICS LETTERS 101, 232601 (2012)

离子辐照

- 易于控制缺陷
- 可形成c轴缺陷

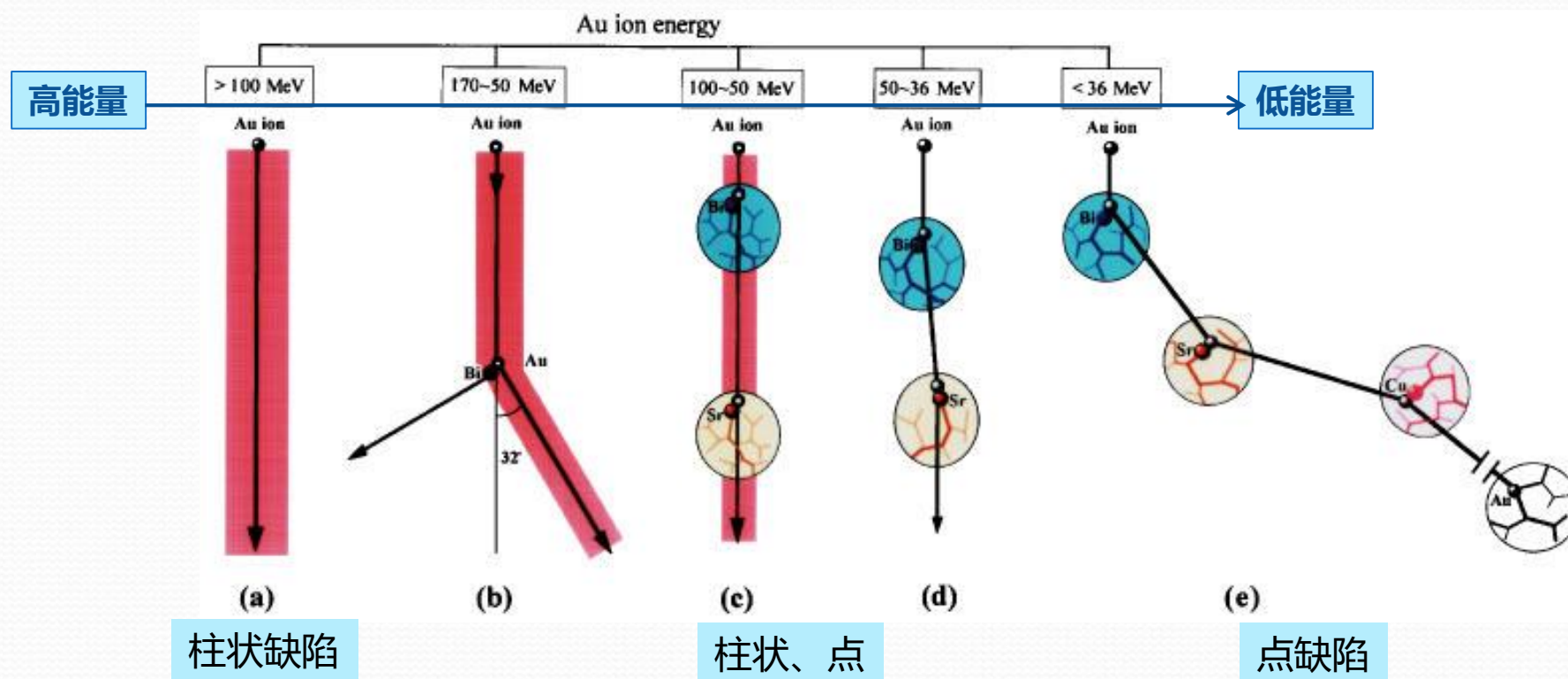
E_i , 离子能量
 M_i , 离子质量
 Φ , 剂量
 θ , 入射角度



缺陷大小
缺陷形状
缺陷密度
缺陷取向

离子辐照作用机理

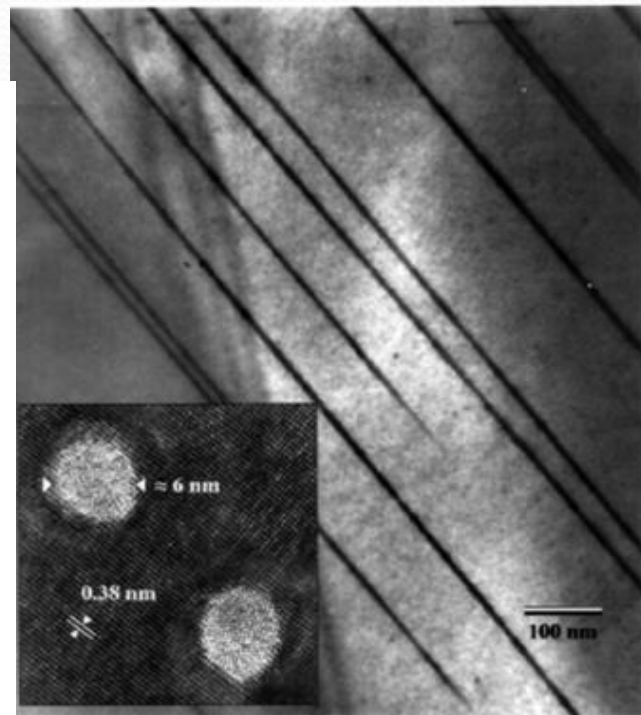
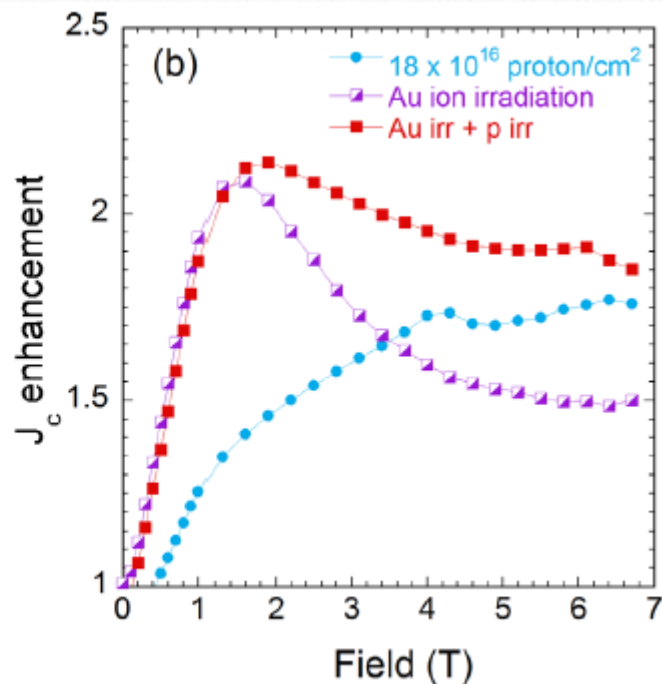
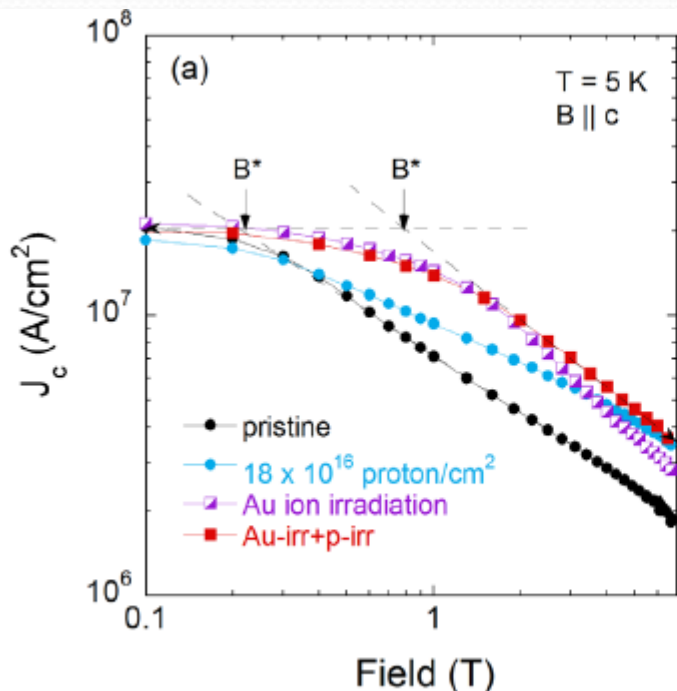
以 230 MeV Au-irradiated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ 为例



离子辐照 对超导膜磁传输及各向异性的影响

离子辐照

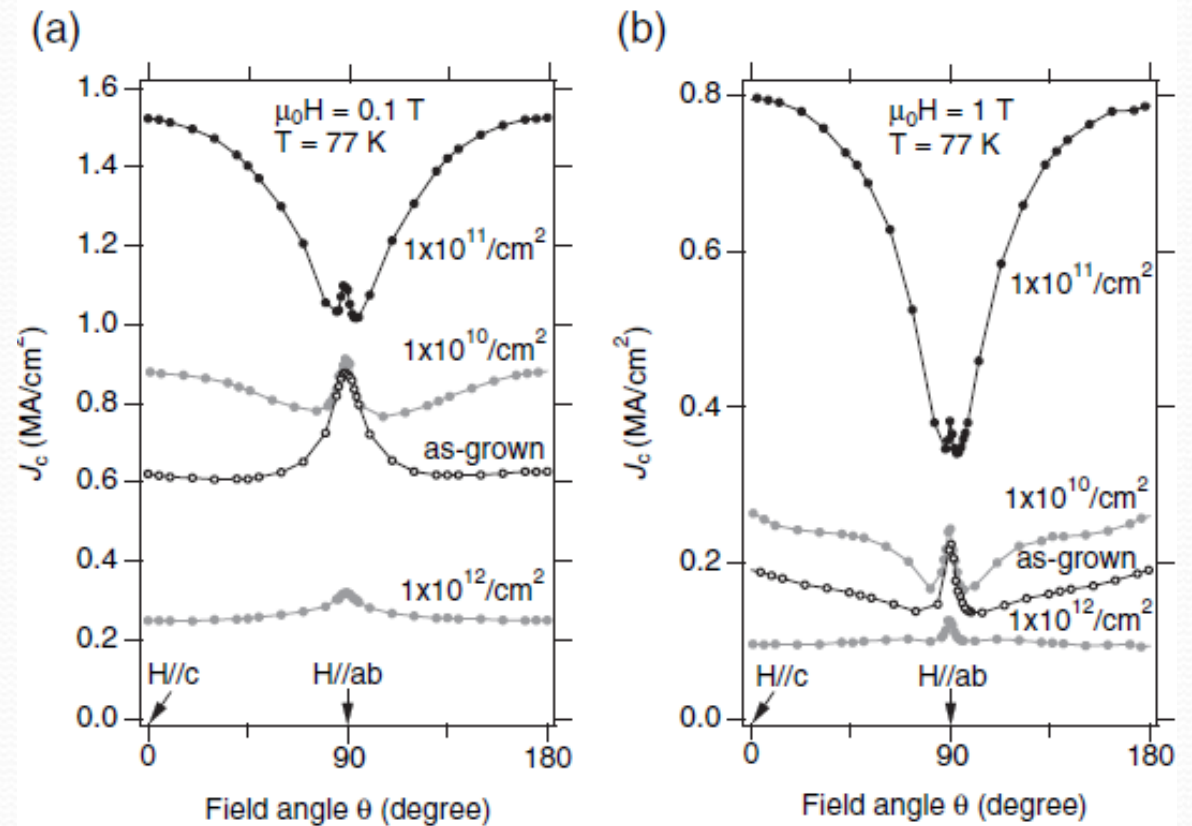
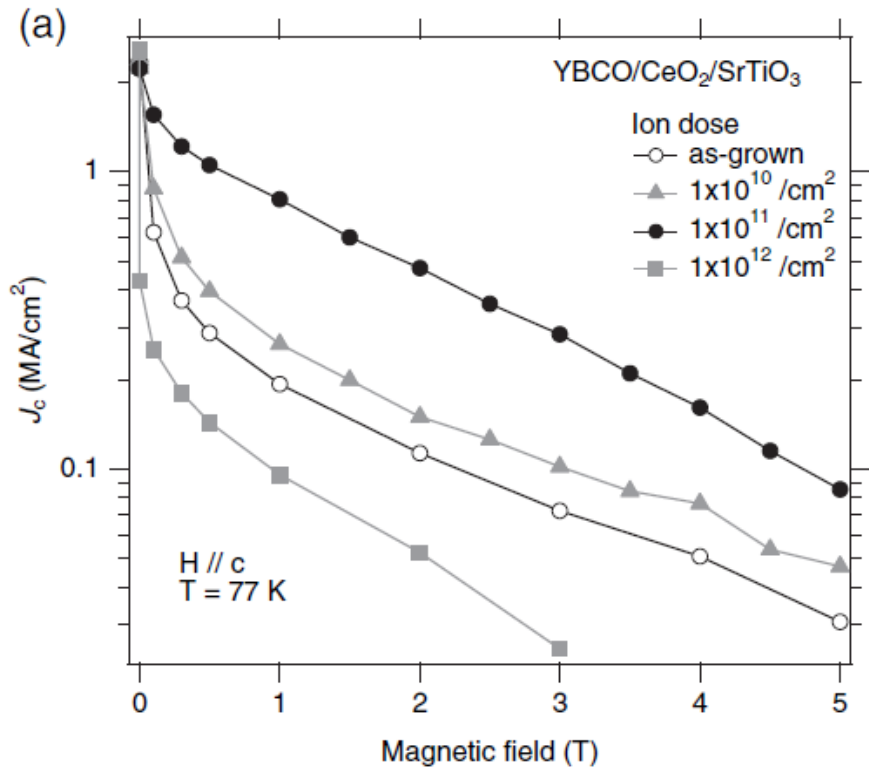
- 尤其对溶液法长带REBCO适用
- 易于控制缺陷



- **density** can be controlled via the **irradiation dose**
- **morphology of the defect** (points, cascades and their size, linear tracks) can be controlled by **the choice of the incoming particle**.

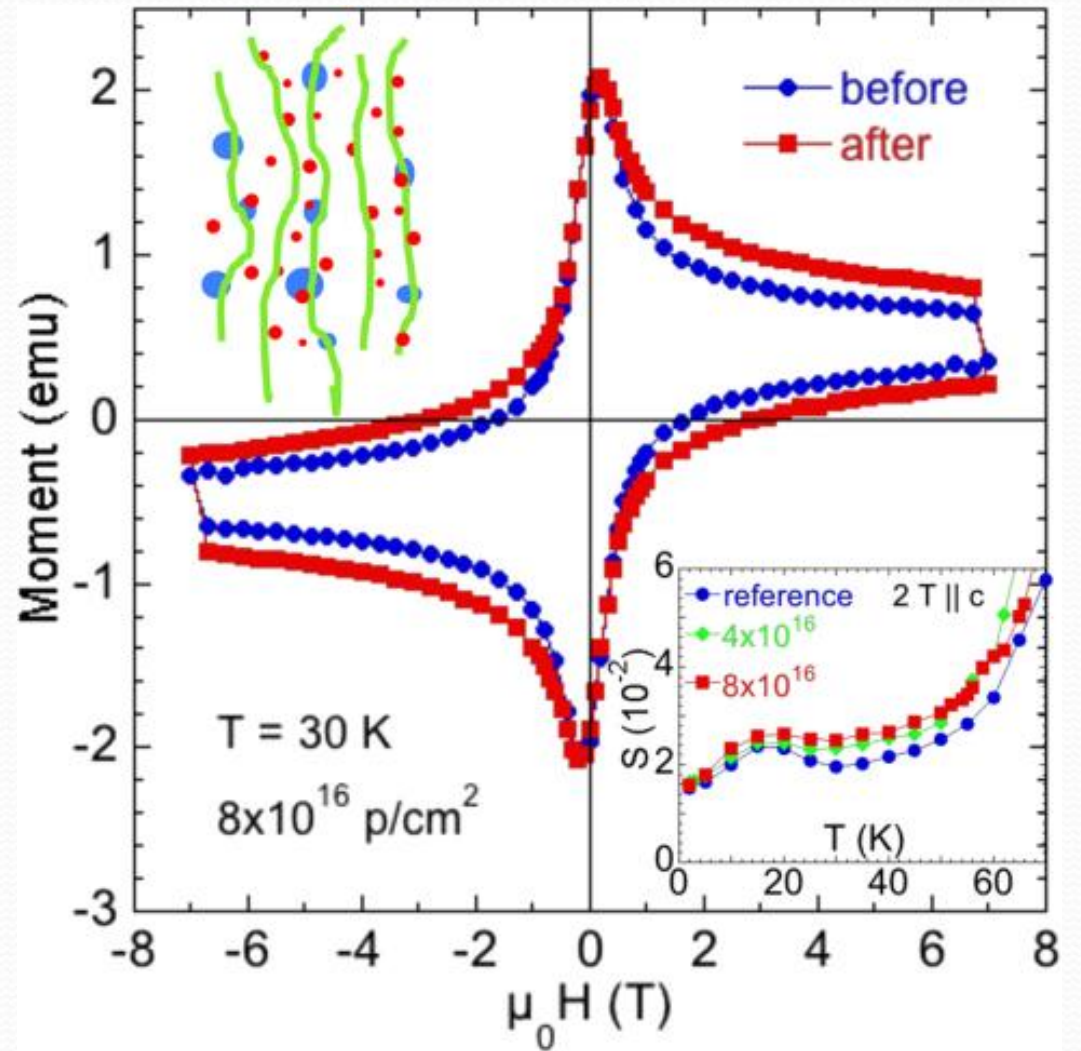
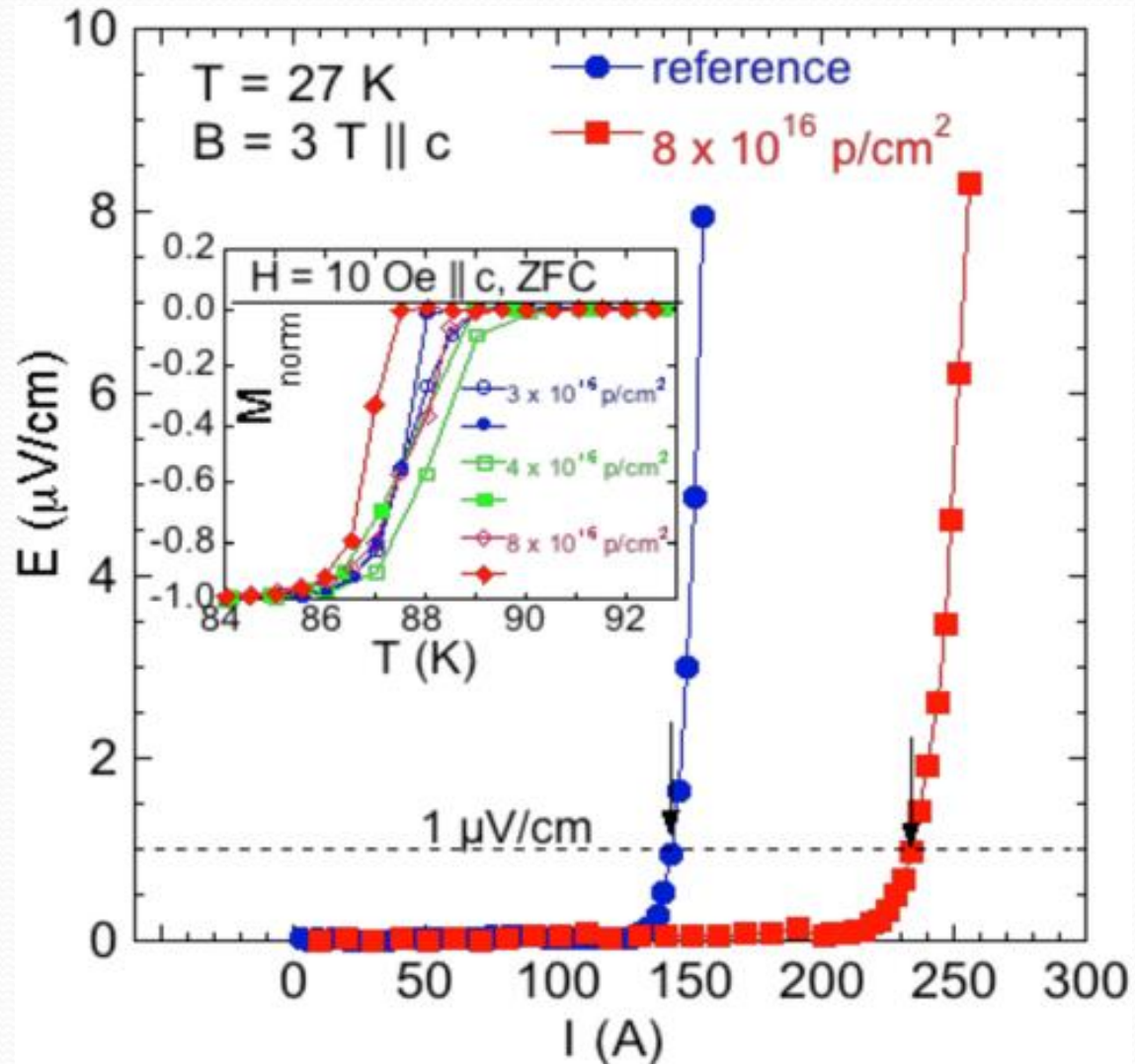
较低能量离子的辐照情况:

3MeV-Au



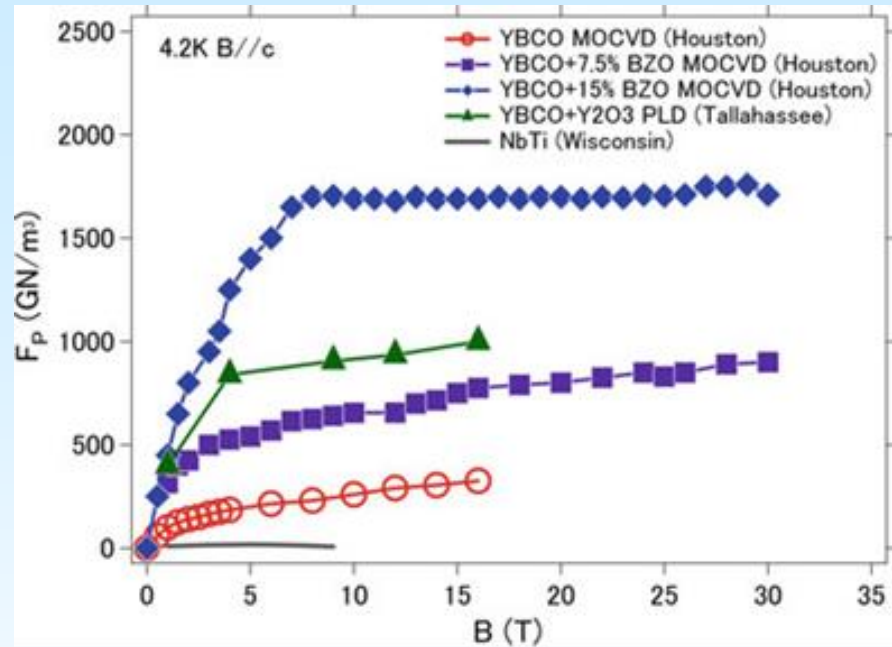
较低能量离子的辐照情况:

4-MeV protons



RE123薄膜及涂层导体液氮温区和平行c-axis下

不可逆磁场和磁通钉扎力密度的人工调控



高密度BZO掺杂RE123薄膜液氮温区
平行c轴下的 F_p 达到1700 GN/m³。

科学通报

强磁场用第二代高温超导带材研究进展与挑战

蔡传兵, 池长鑫, 李敏娟, 刘志勇, 鲁玉明, 郭艳群, 白传易, 陆齐 and 豆文芝

Citation: 科学通报; doi: 10.1360/N972018-00687

View online: <http://engine.scichina.com/doi/10.1360/N972018-00687>

Published by the 《中国科学》杂志社

超导与 二次相组份	不可逆磁场 B_{irr} (77K)	磁通钉扎力密度 F_p^{max} (B//c) GN/m ³	参考 与备注
Y123	11	28.3 (3 T, 77 K)	PLD
+BaSnO ₃			
(Y,Gd)123	14.8	14 (5 T, 77 K); 1700 (4.2 K)	MOCVD
+15%Zr			
Sm123	15	28 (77 K)	LTG-PLD
+BaHfO ₃			
Gd123	15.8	23.5 (77 K)	PLD
+BaHfO ₃			
Y123	8-11	12-16 (77 K)	PLD
+BaZrO ₃		700 (4.2 K)	
Y123	NA	32.3 (75.5 K)	PLD
+Ba ₂ YNbO ₆		122 (65 K).	
Sm123	12	23 (77 K)	MOD
+BaZrO ₃			
Y123+GBs	NA	15 (77 K)	GB 尺寸从 196 nm 降到 92 n m
Y123	NA	14.3 (77 K)	MOD
+Y ₂ O ₃		1000 (4.2 K)	颗粒细化
纯 Y123	5-7	~4 (77 K)	常规薄膜
纯 Bi2223	0.2	NA	1G-HTS 线
低温超导 NbTi	11 (4.2K)	16 (4.2 K)	LTS 线材

一

实用超导材料概况

二

高温超导涂层导体技术演变和发展现状

三

高温超导涂层导体磁通钉扎及其人工调制

四

若干应用发展和挑战

若干应用及共性问题

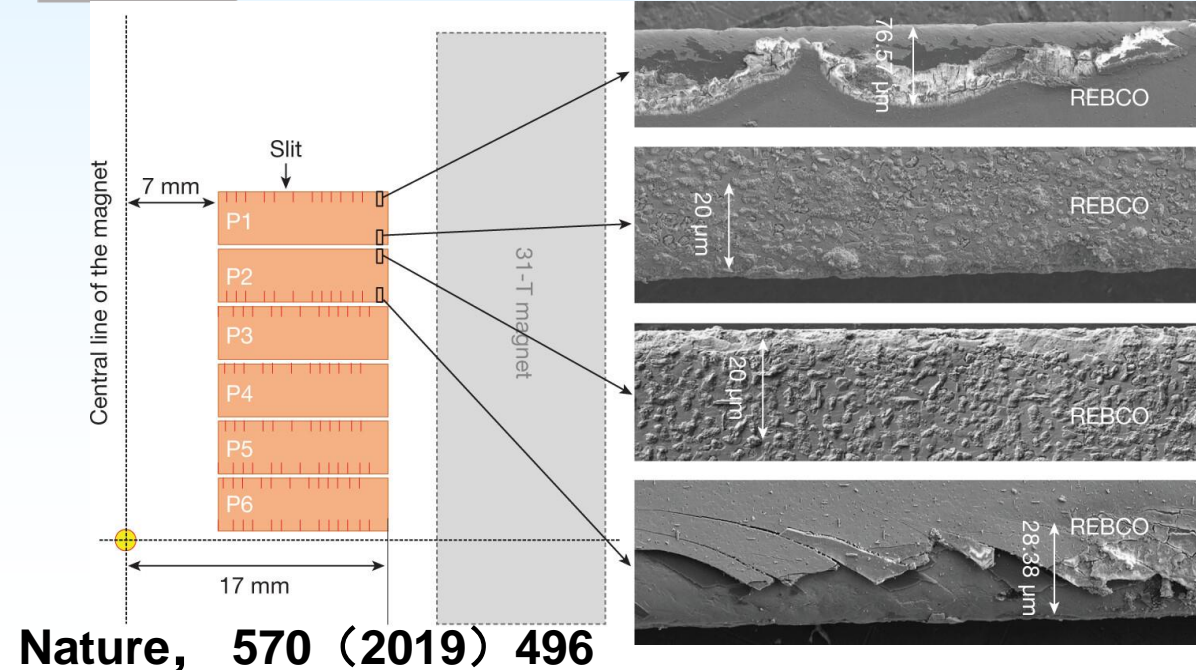
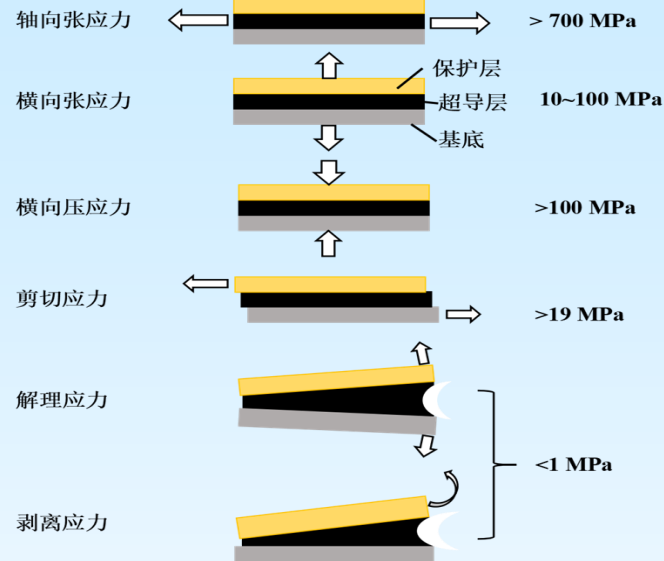
➤ 机械性能 Various stresses in service state;

- Electromagnetic force
- Thermal induced stress
- Bending induced stress
- ...

➤ 成型导体 Application handling - round, isotropic shape wanted

➤ 无阻焊接 Resistance-free Joint technology

➤ 性价比 Marketing vs. Price-Performance

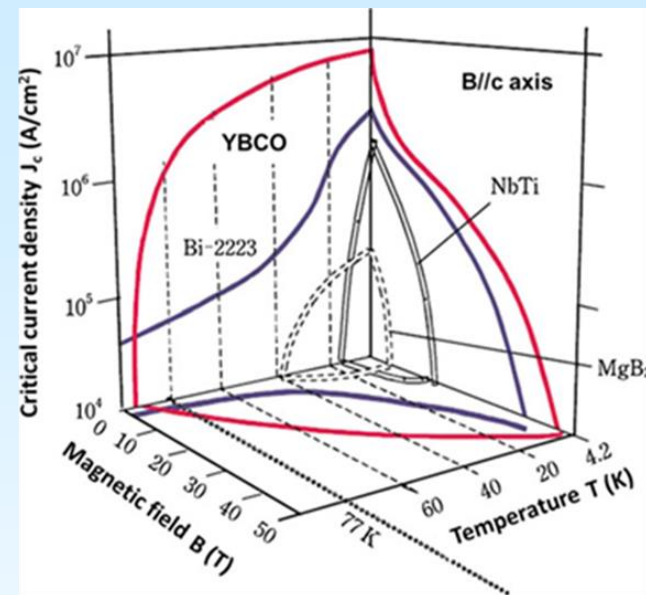


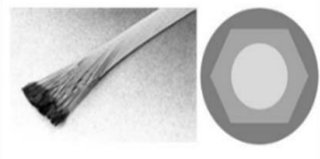

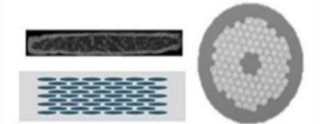
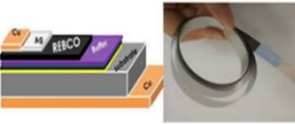
Metric	Today	Customer requirement
Price	\$ 400/kA-m	< \$ 100/kA-m* For commercial market entry (small market)
		< \$ 50/kA-m* For medium commercial market
		< \$ 25/kA-m* For large commercial market

Four to 15-fold improvement in wire price-performance needed !

小结

- ◆ 新型超导体或超导现象发现层出不穷，可实用化HTS材料屈指可数，传统的LTS-NbTi/Nb₃Sn仍是当前市场应用的主流，冷却介质和运行成本问题使人们对HTS渴望；
- ◆ 2G-HTS带材基于半导体外延技术发展起来，结构和工艺复杂、难度大。磁传输性能和各向异性可通过人工钉扎有效改善，仍然是目前液氮温区及低温强磁场下性能最优、最值得期待的实用化HTS材料；
- ◆ 各类基于2G-HTS带材的强电应用示范逐步增多，其服役行为、磁热稳定性需要加强研究。广泛推广存在可能，但需要大幅度提高其成材效率和性价比



低温超导线材/商业化成熟 金属 NbTi (Nb ₃ Sn etc.)	中温超导线材/商业化探索 化合物 MgB ₂ /Fe-based
	
1G高温超导带材/商业化中期 氧化物 Bi2223/Bi2212	2G高温超导带材/商业化初期 氧化物 REBCO
	

Thank you for your attention

Welcome young people to visit or join our group
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