



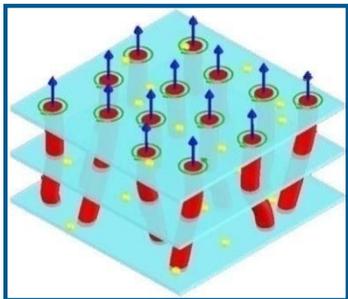
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FACULTÉ DES SCIENCES

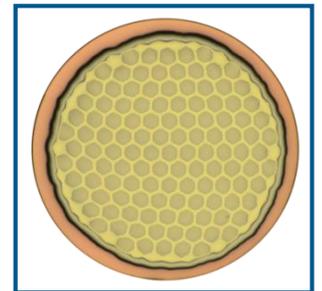
DOMP
<http://supra.unige.ch>

Superconductivity and its applications

Lecture 8



Carmine SENATORE

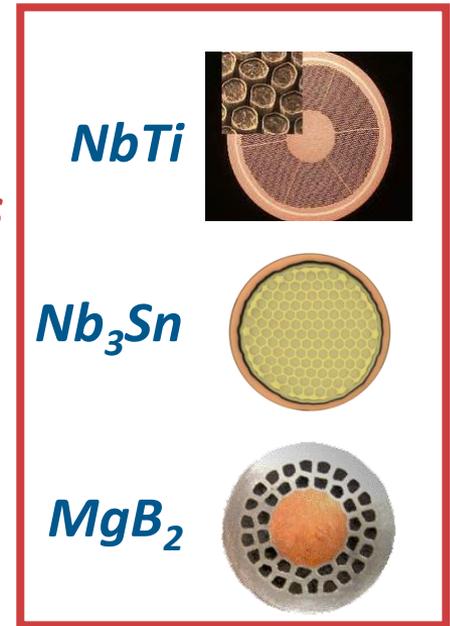
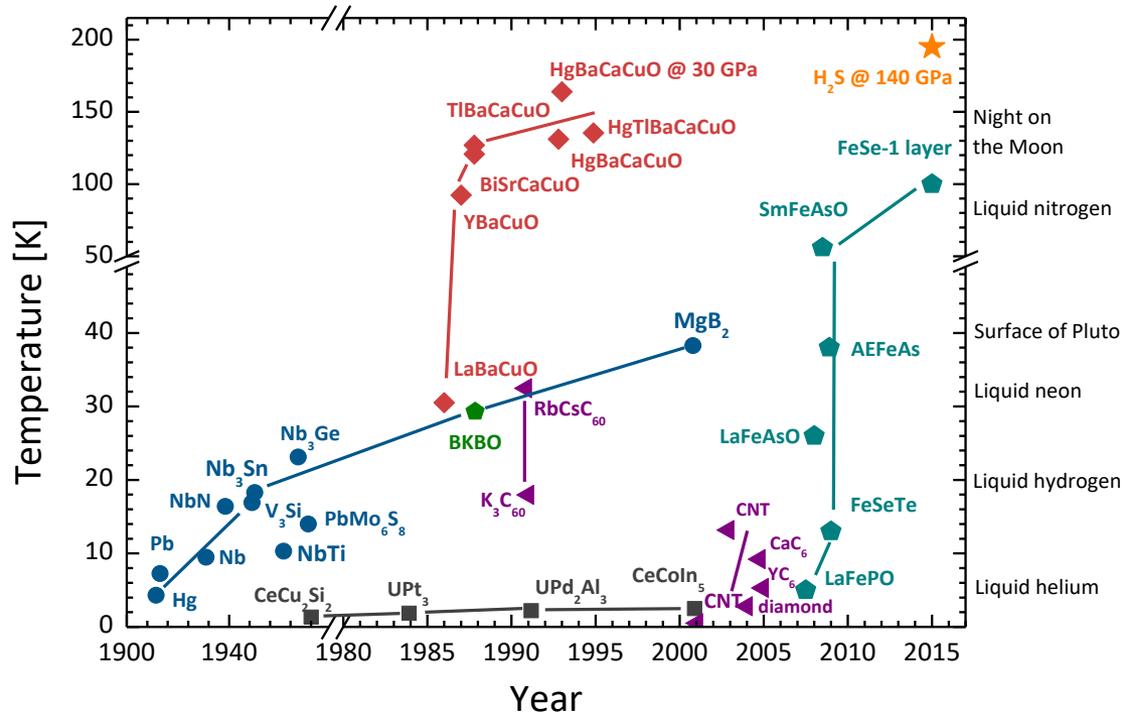


*Group of Applied Superconductivity
Department of Quantum Matter Physics
University of Geneva, Switzerland*

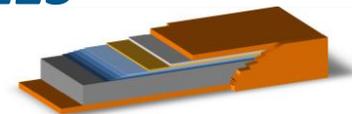
Previously, in lecture 7

From superconducting materials...

...to technical superconductors



Y123



1. Superconducting ? 10'000
2. $T_c > 4.2K$ & $B_{c2} > 10T$? 100
3. $J_c > 1000 A/mm^2$? ~10

Previously, in lecture 7

	T_c [K]	B_{c2} [T]	
NbTi	9.8	10.5	Alloy Easy to produce in multifilamentary wires Wires does not need reaction heat treatment
Nb₃Sn	18.0	30+	
MgB₂	39.0	10-60	Intermetallic compounds Three different fabrication technologies Wires must be reacted after fabrication

Key parameter for J_c optimization

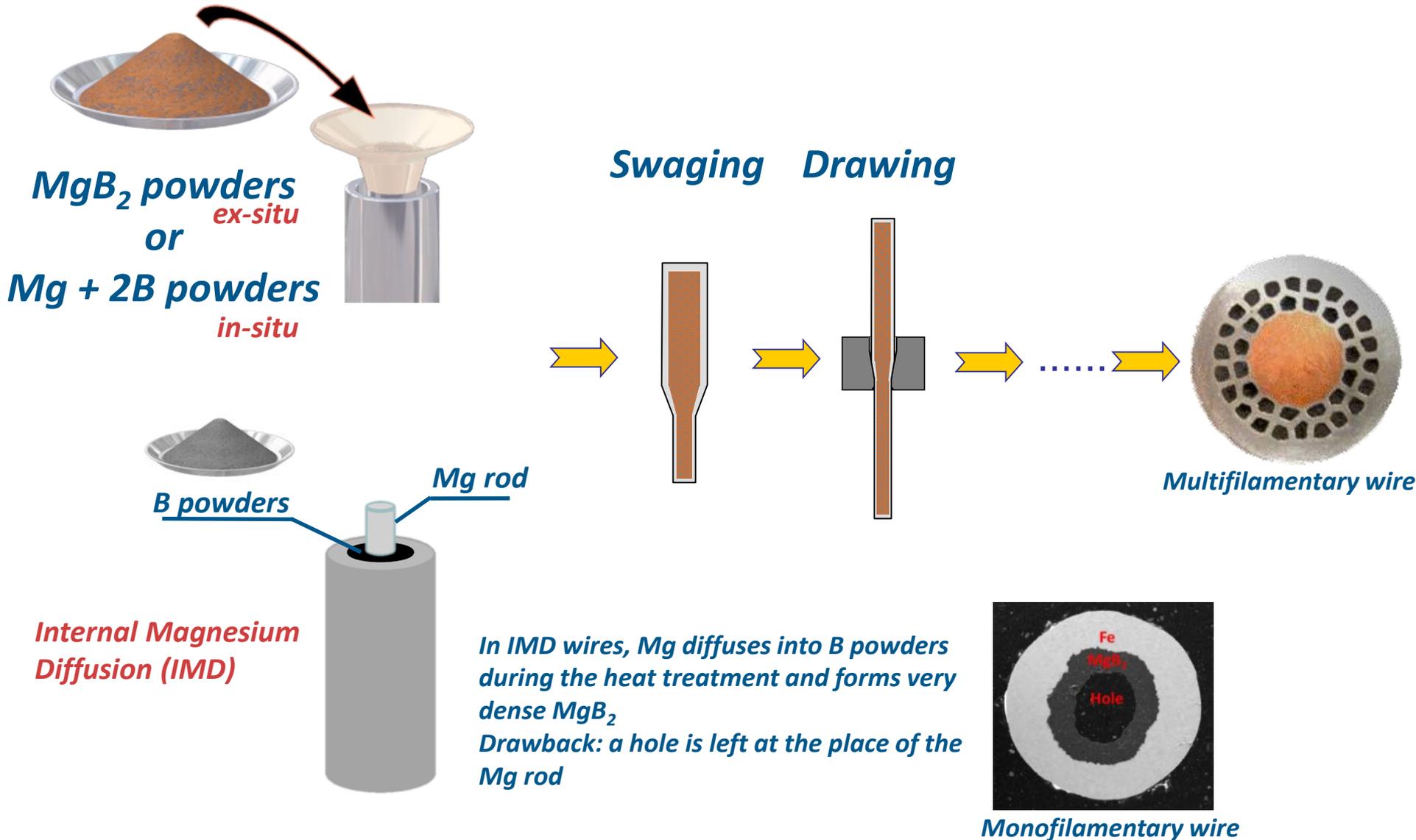
NbTi → α -Ti precipitates acts as pinning centers

Nb₃Sn → Grain morphology (pinning) and composition/doping (B_{c2})

MgB₂ → Doping (B_{c2}) and connectivity (densification)

Previously, in lecture 7

MgB₂ wires: fabrication by powder metallurgy



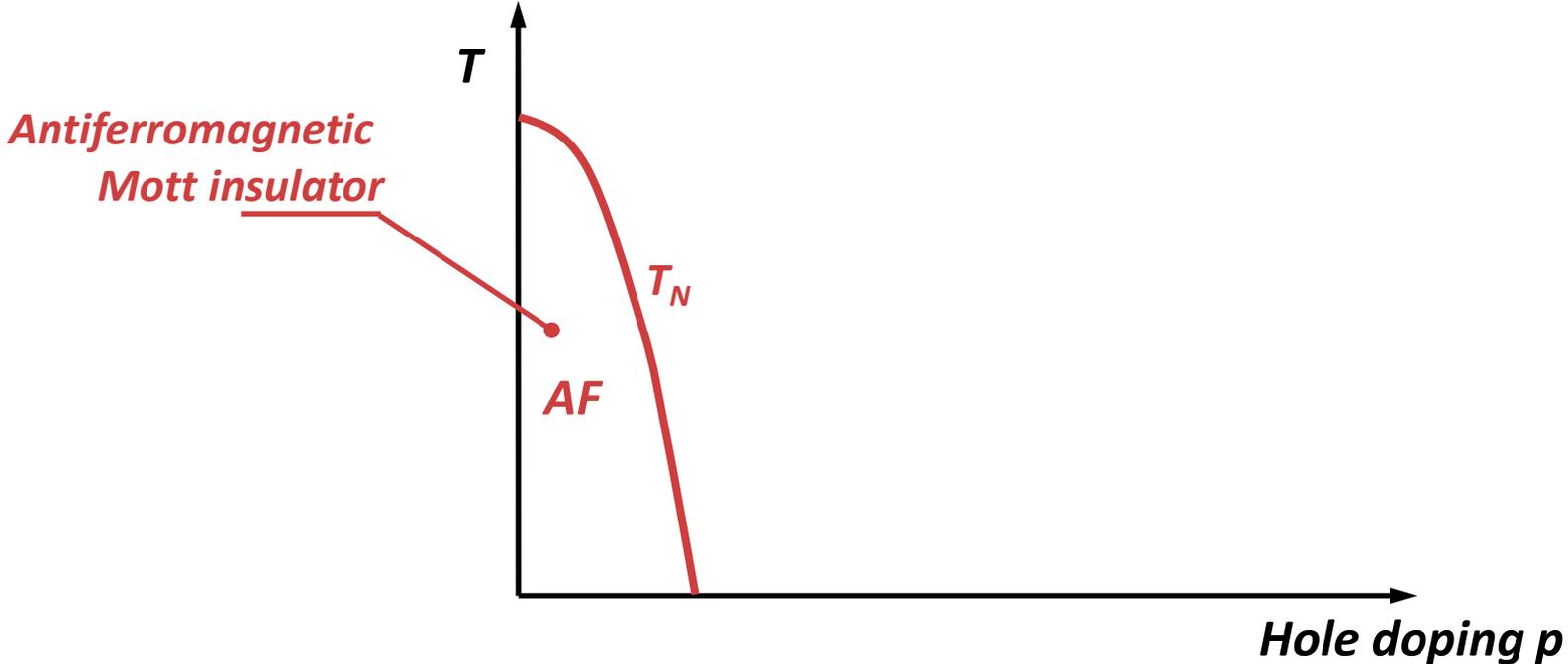
Previously, in lecture 7

Relevant HTS families

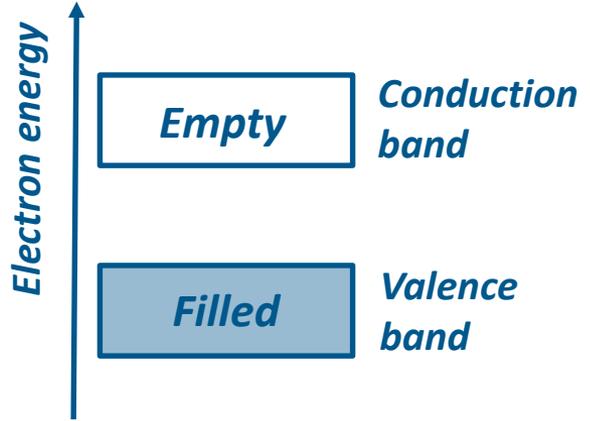
	Compound	T_c [K]	Short name		
hole-doped	REBCO	La _{1.85} Sr _{0.15} CuO ₄	39	LaSCO	
		YBa ₂ Cu ₃ O ₇	92	Y123 or YBCO	
	Bi family		Bi ₂ Sr ₂ CuO ₆	15	Bi2201
			Bi ₂ Sr ₂ CaCu ₂ O ₈	91	Bi2212
			Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀	110	Bi2223 or BSCCO
	Tl families		Tl ₂ Ba ₂ CuO ₆	90	
			Tl ₂ Ba ₂ CaCu ₂ O ₈	110	
			Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	125	Tl2223 or TBCCO
			TlBa ₂ CaCu ₂ O ₇	91	
			TlBa ₂ Ca ₂ Cu ₃ O ₉	116	
			TlBa ₂ Ca ₃ Cu ₄ O ₁₁	122	
	Hg family		HgBa ₂ CuO ₄	95	
			HgBa ₂ CaCu ₂ O ₆	122	
			HgBa ₂ Ca ₂ Cu ₃ O ₈	133	Hg1223
electron-doped		Nd _{1.85} Ce _{0.15} CuO ₄	25	NCCO	

Record T_c of ~165 K under high pressure

A quick introduction to the HTS phase diagram

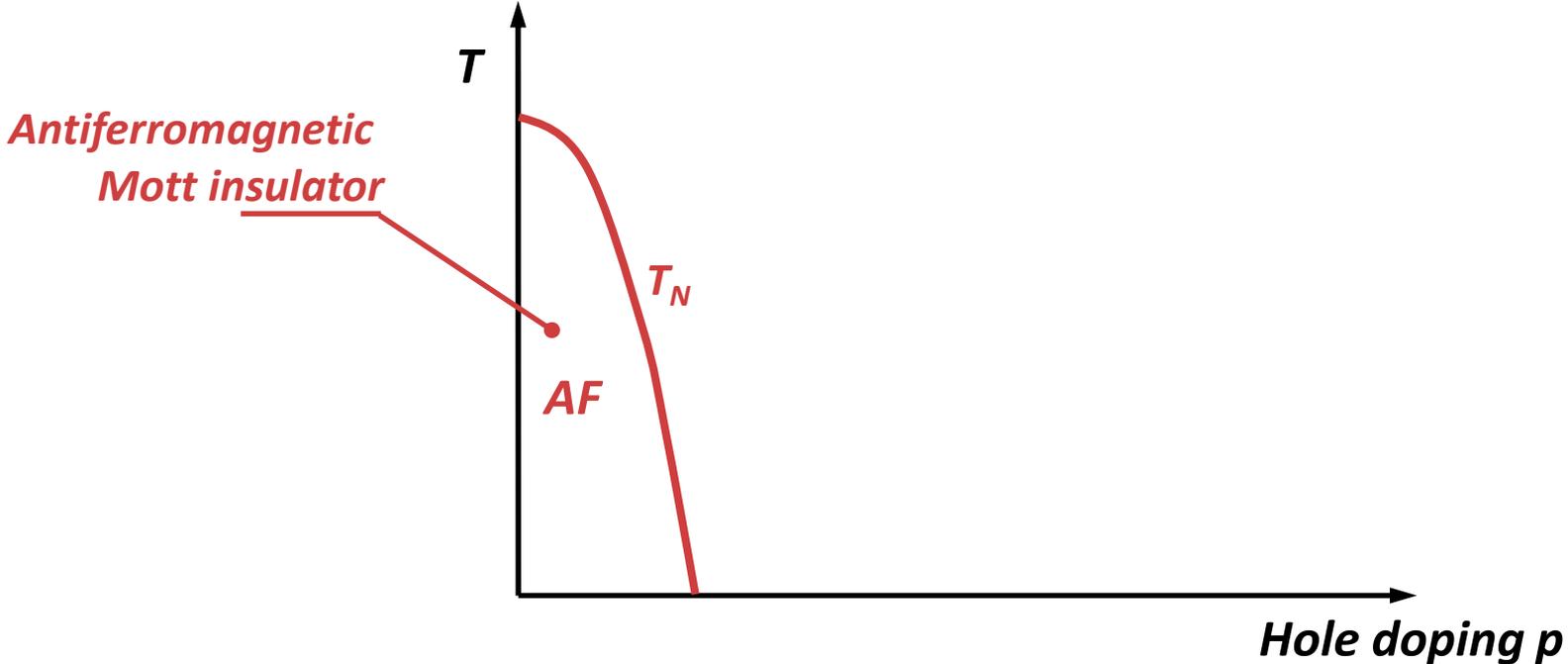


Band (Bloch-Wilson) insulator

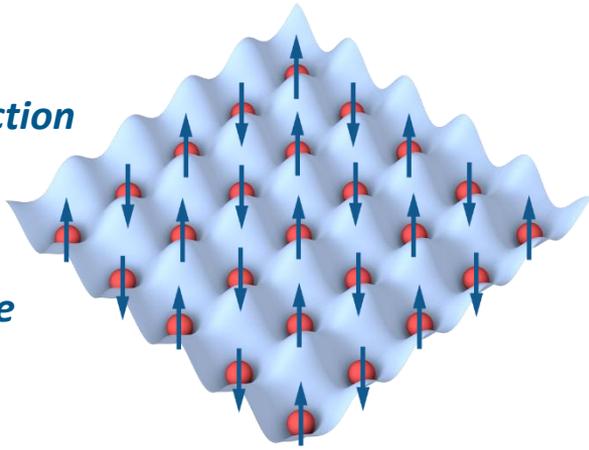
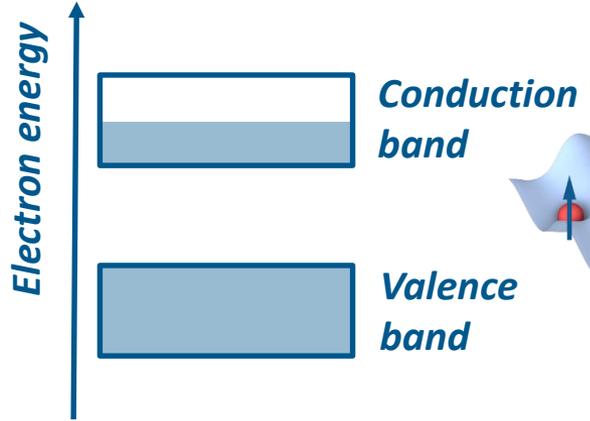


HTS are copper oxides
The undoped parent compounds are antiferromagnetic Mott insulators

A quick introduction to the HTS phase diagram



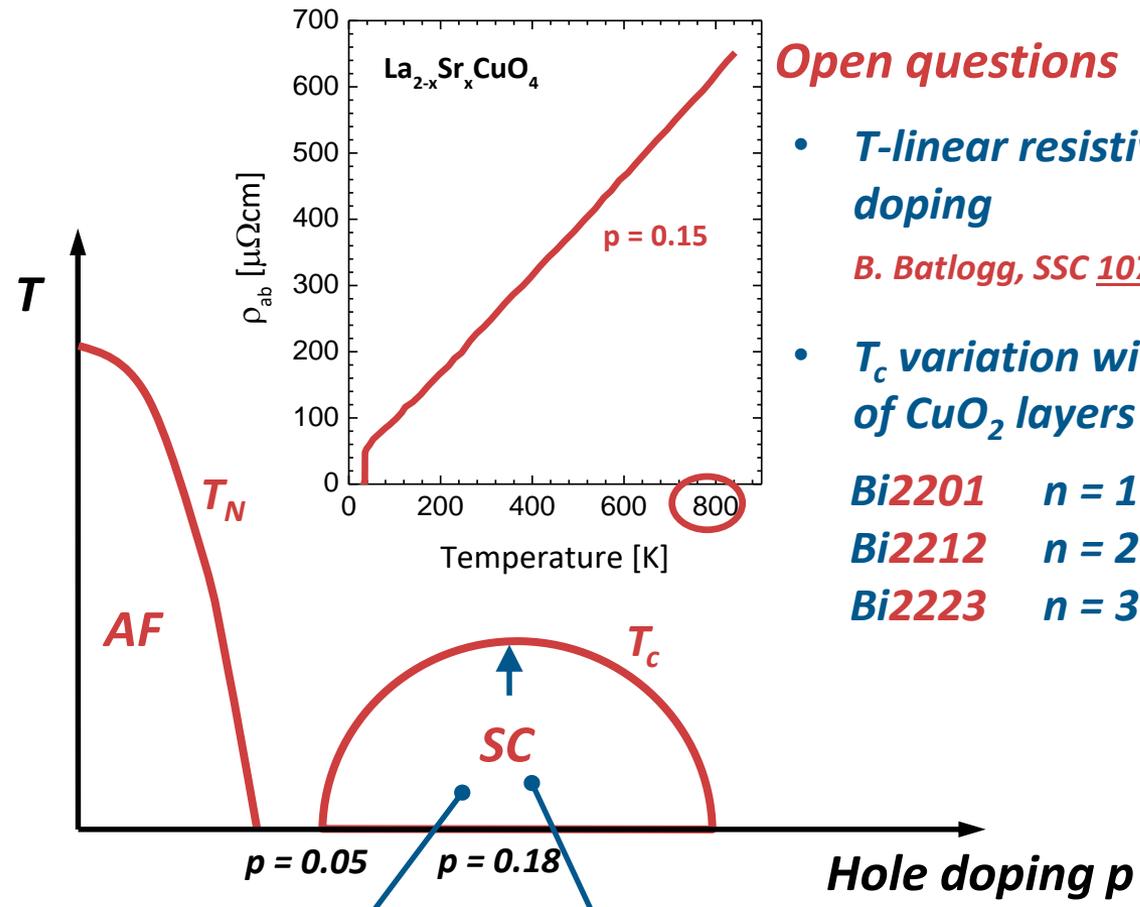
Mott insulator



Only one electron per site but the strong Coulomb repulsion between the electrons impedes their flow

On the top of that the antiferromagnetic interaction

A quick introduction to the HTS phase diagram



Open questions

- *T-linear resistivity at optimal doping*
B. Batlogg, SSC 107 (1998) 639
- *T_c variation with the number of CuO_2 layers*

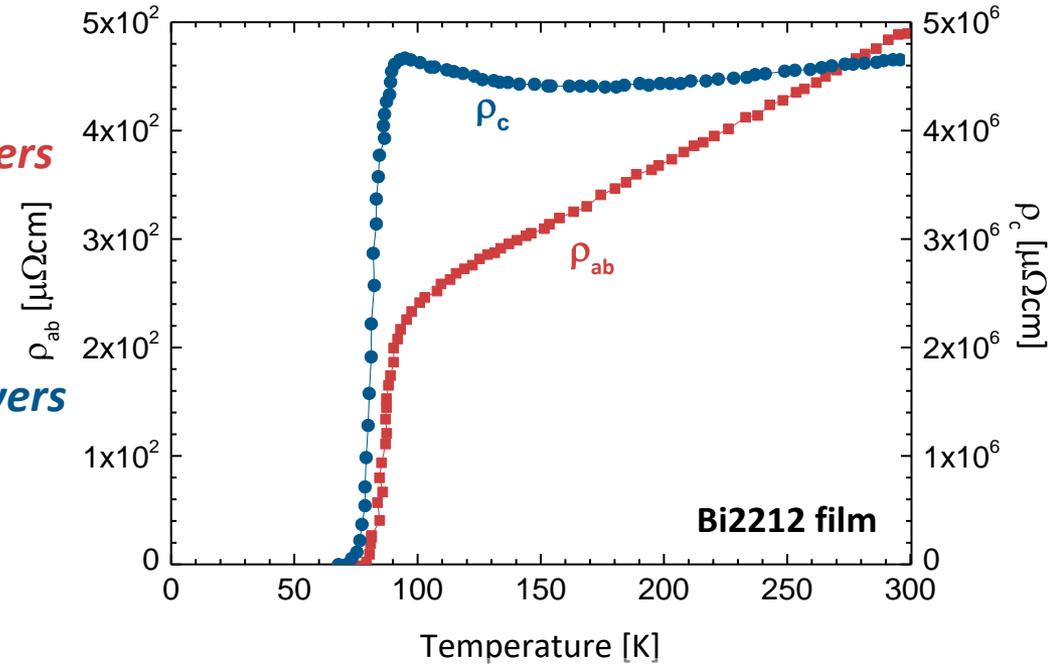
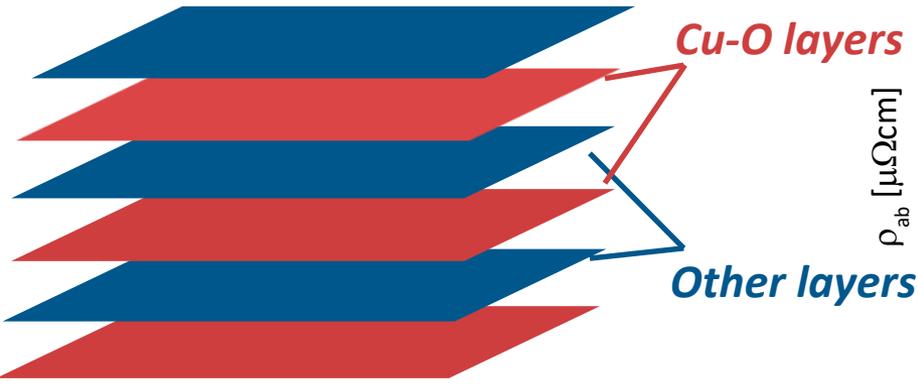
Bi2201	$n = 1$	$T_c = 15 \text{ K}$
Bi2212	$n = 2$	$T_c = 91 \text{ K}$
Bi2223	$n = 3$	$T_c = 110 \text{ K}$

Superconductivity arises in the CuO_2 planes

Macroscopic Ginzburg-Landau describes the electromagnetic properties

$$\rho = \frac{m}{ne^2\tau}$$

Layered structure and Anisotropy



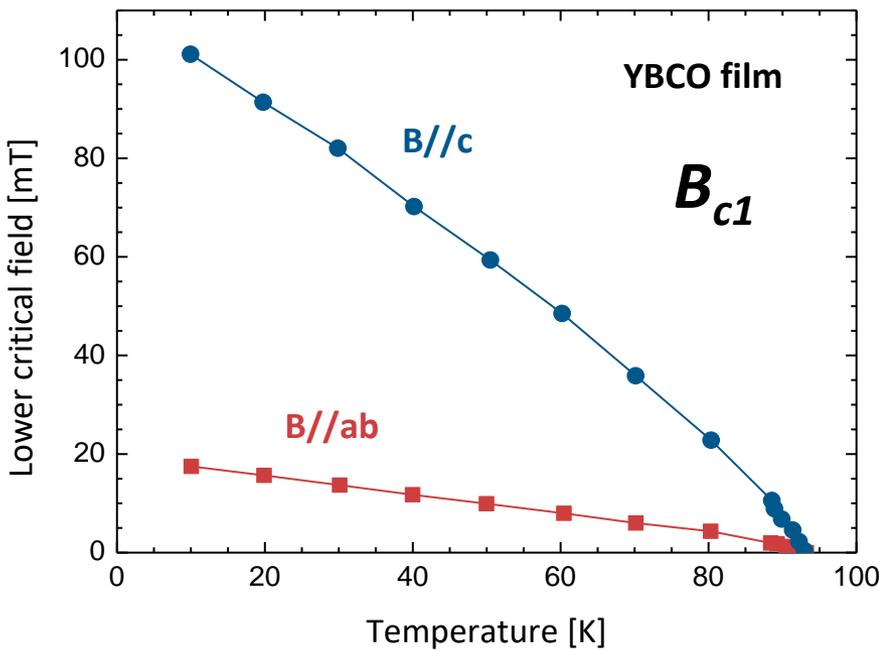
Raffy et al., Physica C 460-462 (2007) 851

Charge carriers have effective masses that depend on the crystallographic orientation

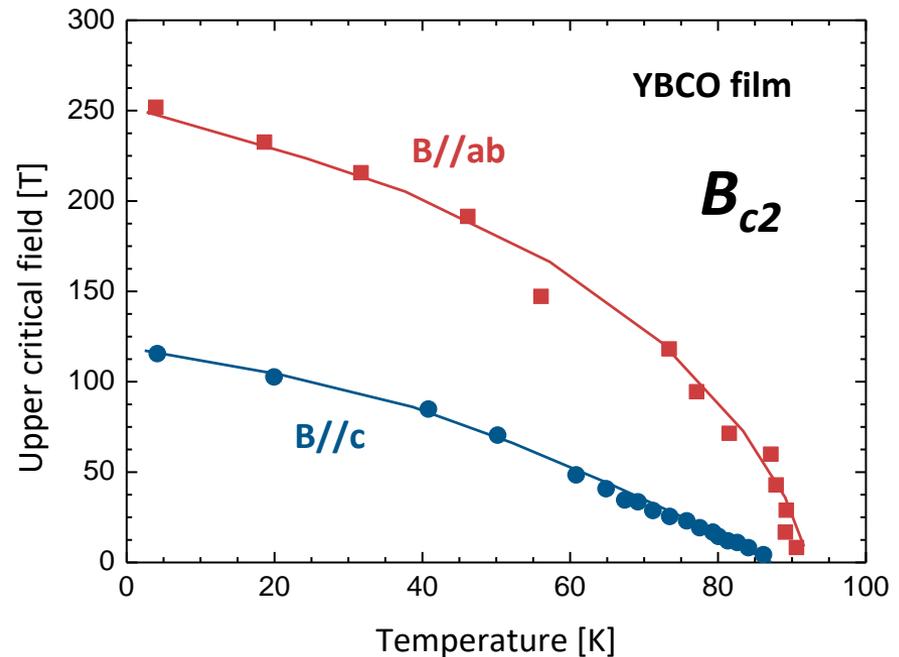
$\frac{m_c}{m_{ab}}$ ranges between 50 and 10'000 in cuprates

The superconductor lengths depend on the carrier mass: $\xi \propto \frac{1}{\sqrt{m}}$ and $\lambda \propto \sqrt{m}$

Anisotropy of the critical fields B_{c1} and B_{c2}



Liang et al., PRB 50 (1994) 4212



Nagakawa et al., JPCM 10 (1998) 11571

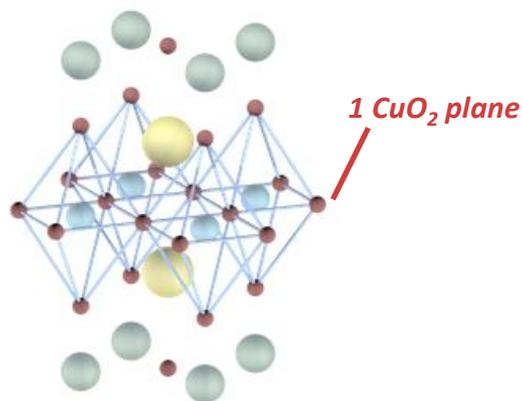
Sekitani et al., NJP 9 (2007) 47

The superconductor anisotropy parameter

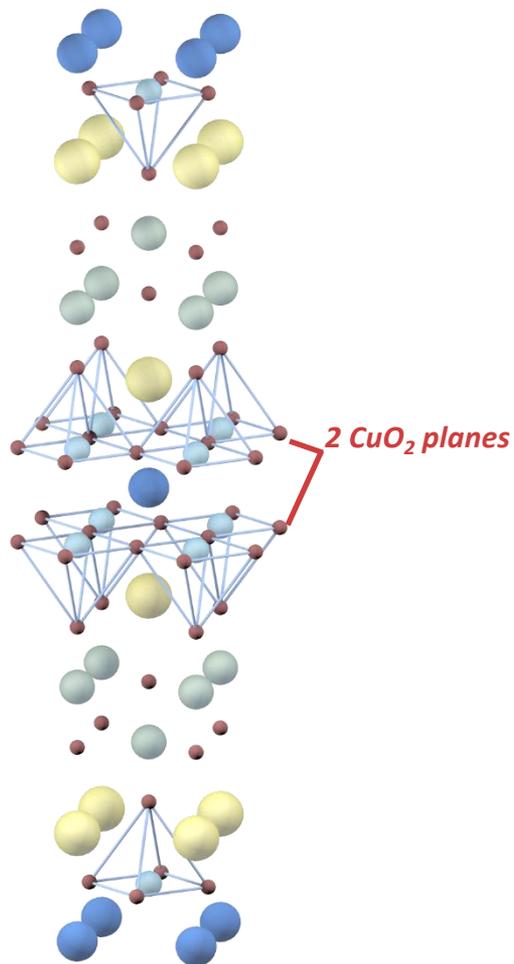
$$\gamma = \sqrt{\frac{m_c}{m_{ab}}} = \frac{\lambda_c}{\lambda_{ab}} = \frac{\xi_{ab}}{\xi_c}$$

	Bi2212	Bi2223	Y123
γ	~150	~30	~7

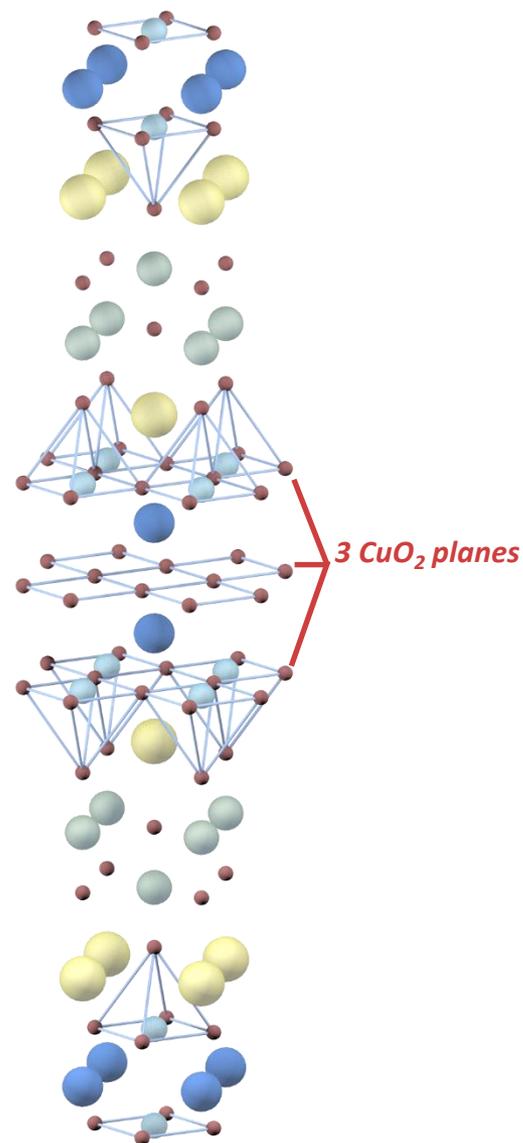
The BiSrCaCuO (BSCCO) family



Bi2201
 $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$



Bi2212
 $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$

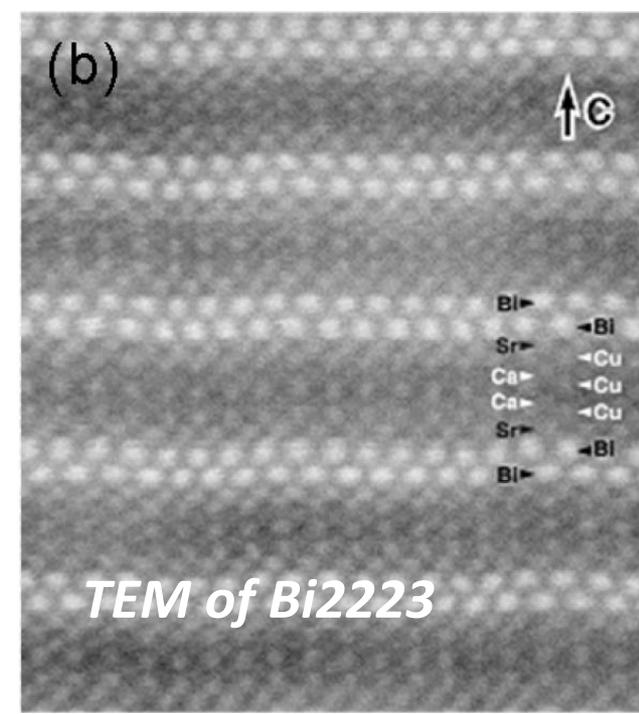


Bi2223
 $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$

- O
- Ca
- Cu
- Sr
- Bi

The BiSrCaCuO (BSCCO) family

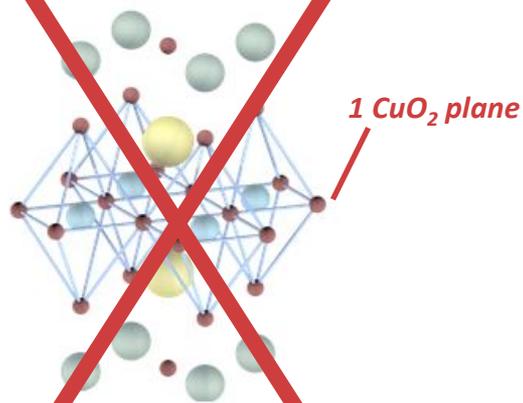
	<i>Bi2201</i>	<i>Bi2212</i>	<i>Bi2223</i>
a [Å]	5.362	5.415	5.413
b [Å]	5.374	5.421	5.421
c [Å]	24.622	30.880	37.010
# of adjacent CuO ₂ planes	1	2	3
T_c [K]	15	91	110
$B_{c2} // ab$ [T]	15-20	>100	>100
Anisotropy γ	>150	150	30



These 2 parameters are correlated

$$\gamma = \sqrt{\frac{m_c}{m_{ab}}} = \frac{B_{c1}^{ab}}{B_{c1}^c} = \frac{B_{c2}^c}{B_{c2}^{ab}}$$

The BiSrCaCuO (BSCCO) family

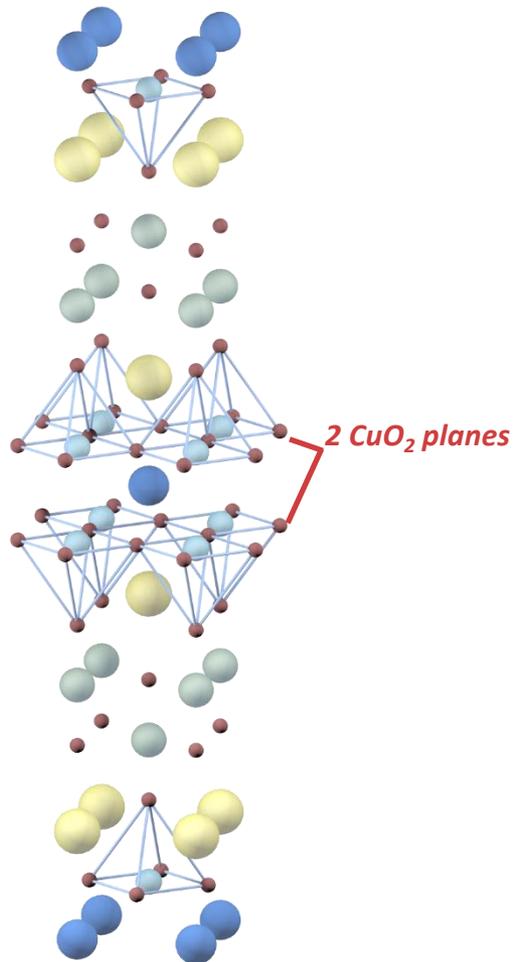


1 CuO₂ plane

Bi2201

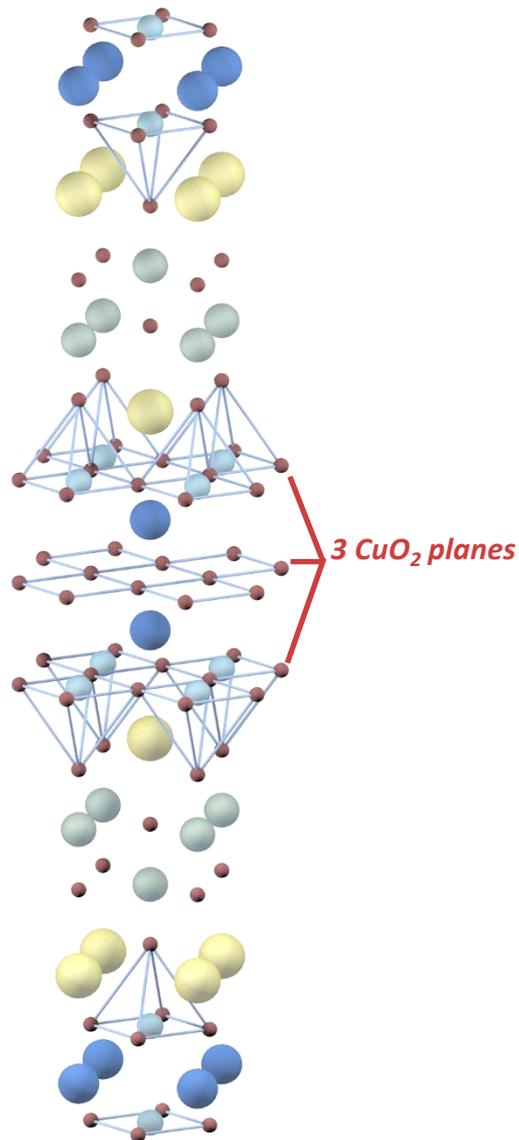


-  O
-  Ca
-  Cu
-  Sr
-  Bi



2 CuO₂ planes

Bi2212



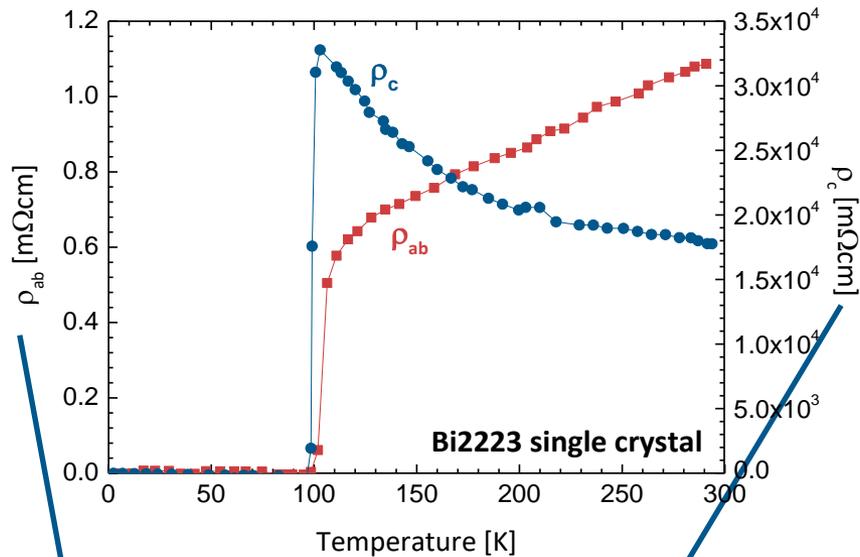
3 CuO₂ planes

Bi2223



$$\rho = \frac{m}{ne^2\tau}$$

Bi2223: anisotropy of the electrical properties

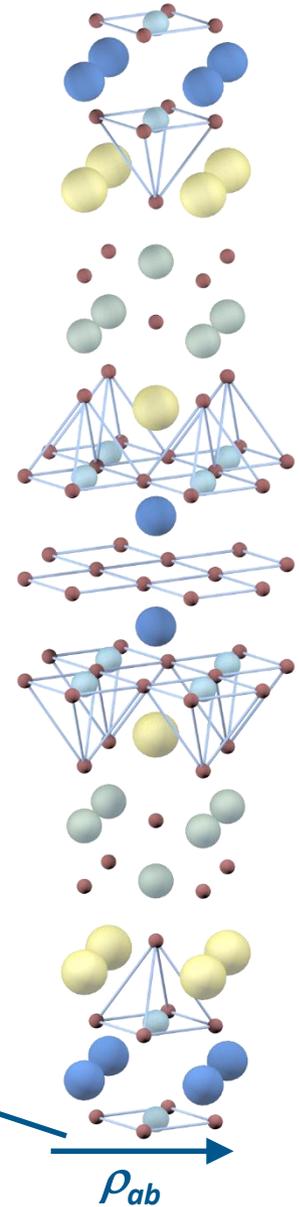


Liang et al., Physica C 383 (2002) 75

**High resistivity when current flows along c
Low $J_c // c$ in the superconducting state**

**Low resistivity when current flows in the ab plane
High $J_c // ab$ in the superconducting state**

Grains in the Bi2223 conductors must have defined orientation !!



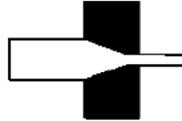
Bi2223 conductor technology

Powder-in-Tube fabrication process (PIT)

Hikata et al., *Jap. J. App. Phys.* **28** (1989) 82



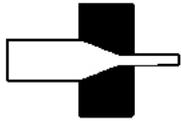
1 - Oxide precursor powder packed into Ag tube



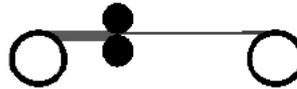
2 - Ag/oxide composite drawn to wire



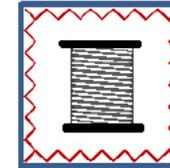
3 - Ag/oxide wire cut and re-bundled into Ag tube



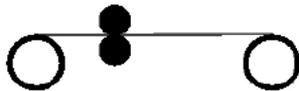
4 - Multi-filamentary composite drawn to wire



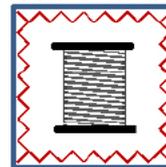
5 - Round wire deformed to tape



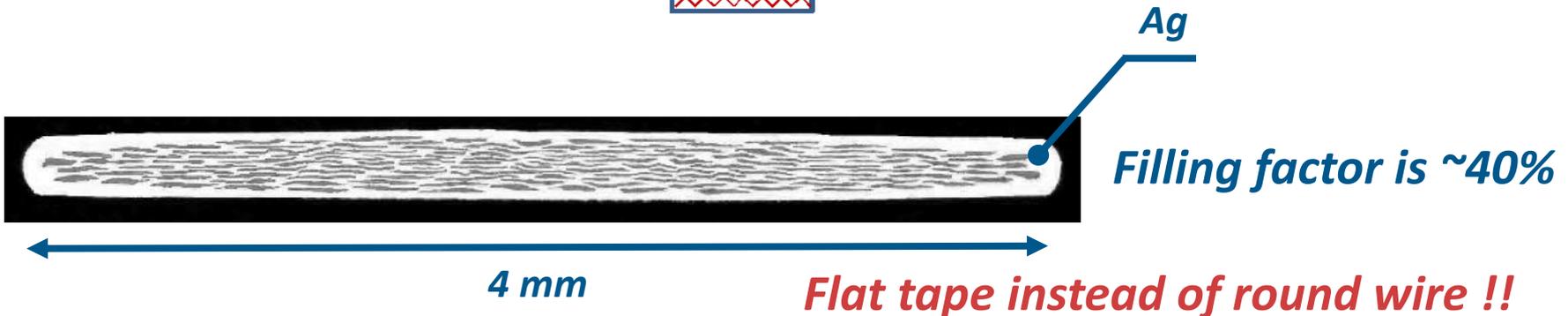
6 - Thermal process forms HTS phase



7 - Deformation process densifies ceramic core



8 - Thermal process completes conversion to HTS phase



Bi2223 conductor technology

Precursor powders preparation

- 1. Mixture of $\text{CuC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$, $\text{Bi}_2(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$, PbC_2O_4 , $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$***
- 2. Repeated calcinations to decompose oxalates and eliminate carbon and water (thermal treatment in air at 300-500°C for 1 to 5 hours)***
- 3. Multiple steps of hand grinding and reaction at 700-800°C in air***

1, 2 and 3 are necessary to eliminate the carbon impurities, obtain Bi2212 (!) as main phase and limit the grain size to about 2-5 μm

The result is a mixture of Bi2212 (75-80%), Bi2201 (~5%), Ca_2PbO_4 (10%) and CuO

Overall composition close to $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

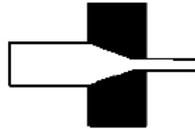
Bi2223 conductor technology

Ag is permeable to O₂

Bi2212 (75-80%), Bi2201 (~5%), Ca₂PbO₄ (10%) and CuO in a Ag tube



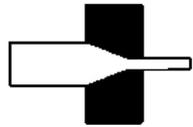
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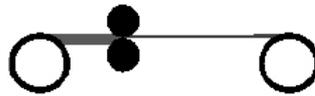
2 - Ag/oxide composite drawn to wire



3 - Ag/oxide wire cut and re-bundled into Ag tube

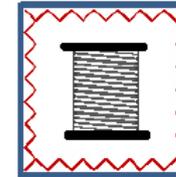


4 - Multi-filamentary composite drawn to wire



5 - Round wire deformed to tape

Bi2223 FORMATION

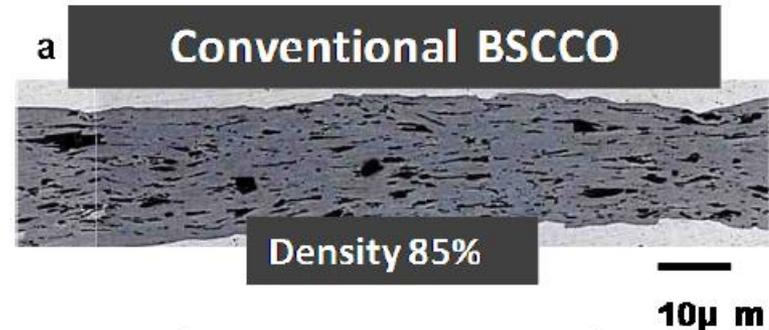


6 - Thermal process forms HTS phase

Reaction @830-850°C in ~7.5%O₂

Platelet-like Bi2212 grains are aligned with parallel c-axis (texturing) during the wire-to-tape (rolling) deformation

Reaction also leads to the CO₂ formation in the filaments ⇒ bubbles ⇒ de-densification



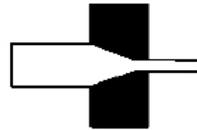
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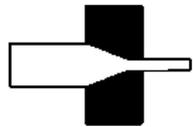
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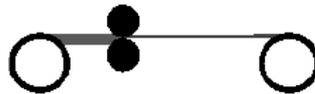
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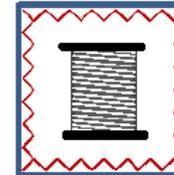
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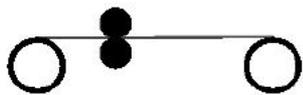
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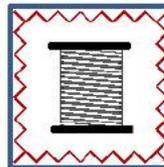
Bi2223 FORMATION

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Reaction @830-850°C in ~7.5%O₂



7 - Deformation process densifies ceramic core

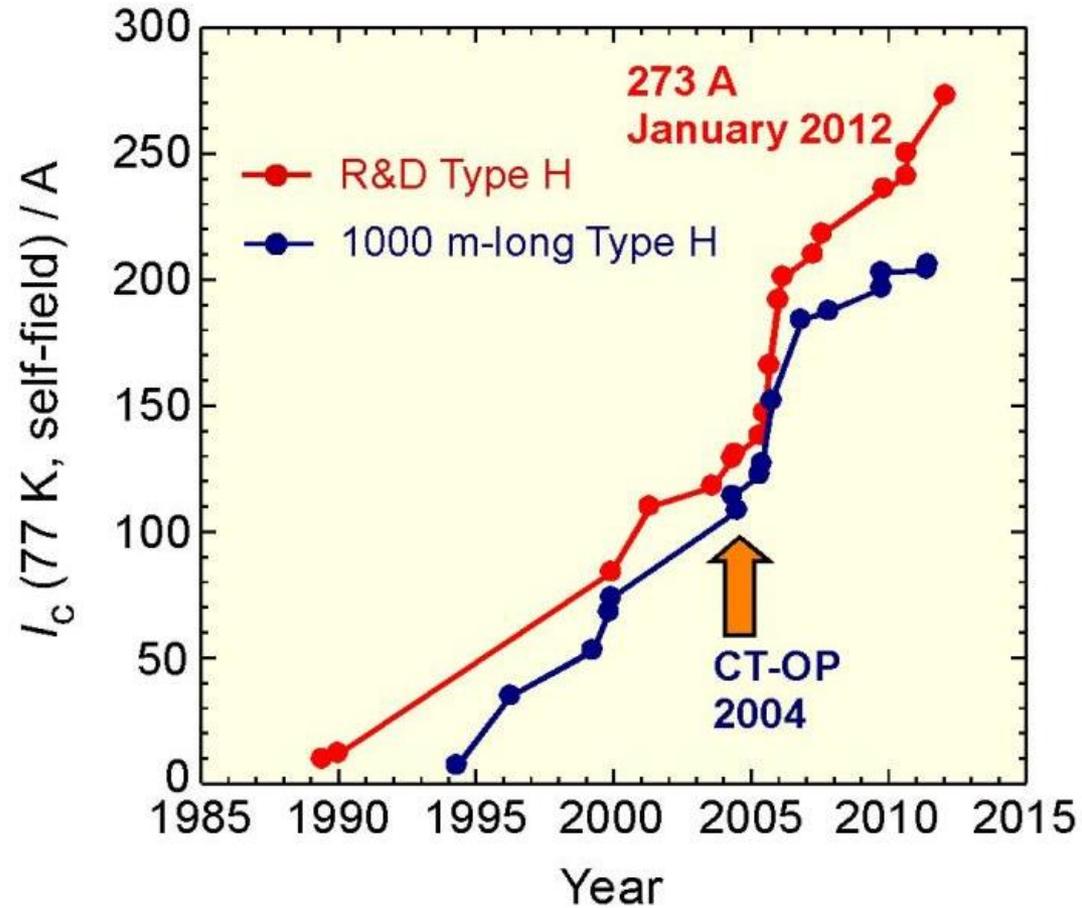
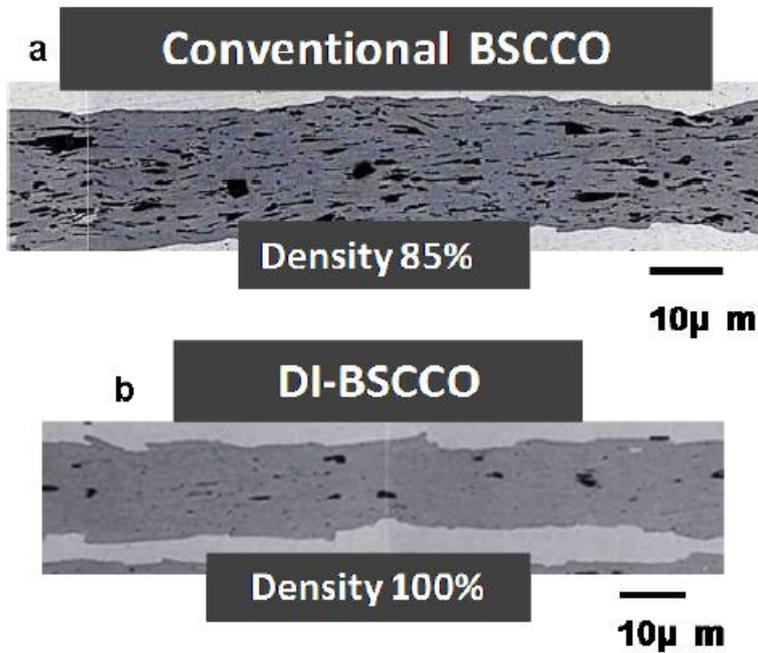


8 - Thermal process completes conversion to HTS phase

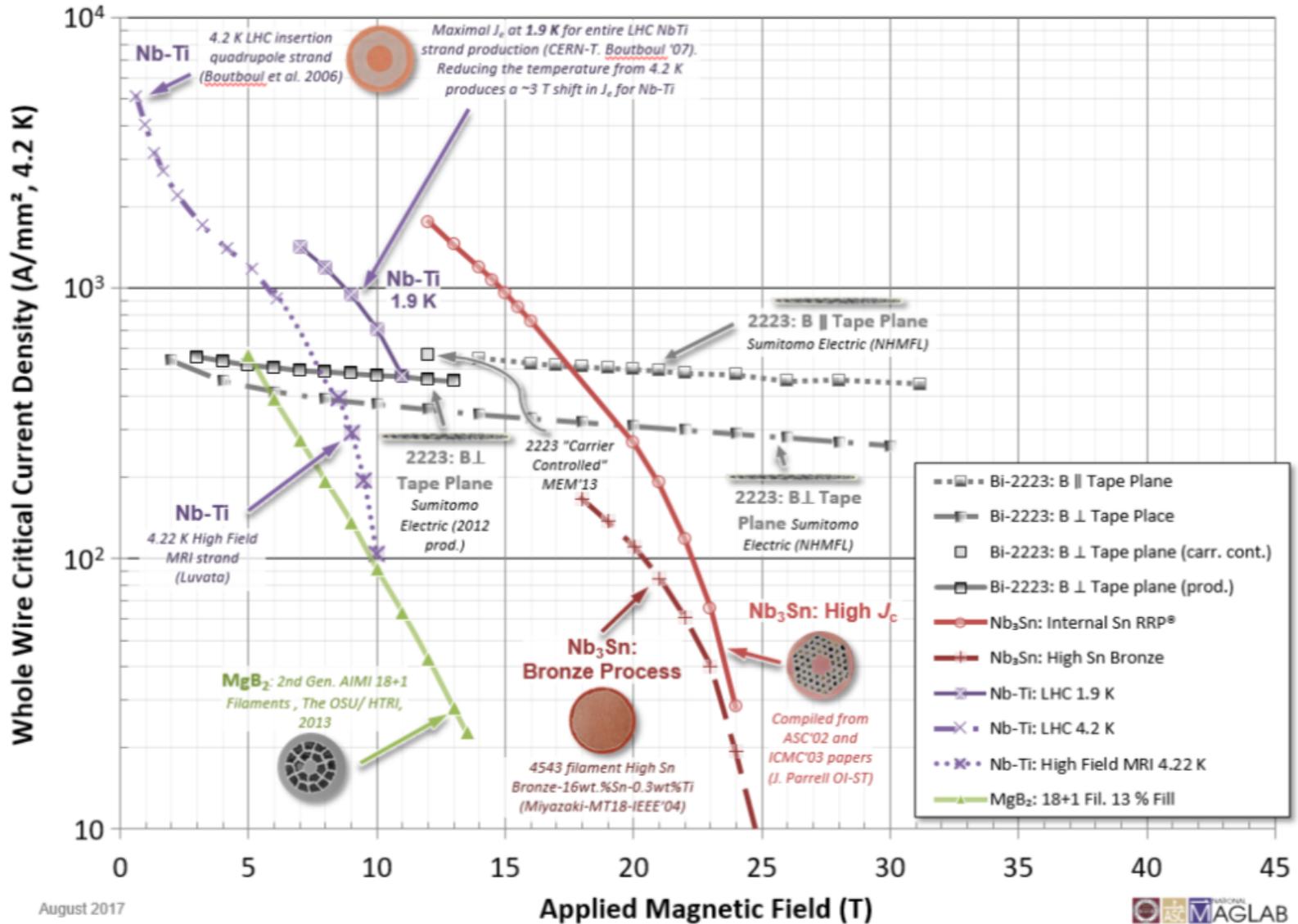
DENSIFICATION

Overpressure processing: heat treatment in high pressure, up to 30MPa, to remove voids

Bi2223 tapes: evolution of I_c vs. year (77K, self-field)



Bi2223 tapes: engineering critical current density J_e



August 2017



Bi2212 conductor technology

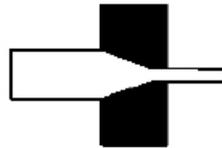
Heine et al., APL 55 (1989) 2441

Enomoto et al., Jap. J. App. Phys. 29 (1990) L447

Bi2212 powders in a Ag tube *Ag is permeable to O₂*



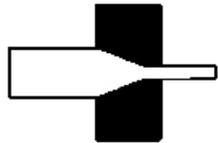
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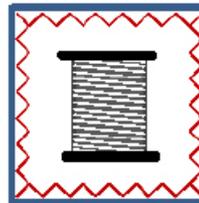
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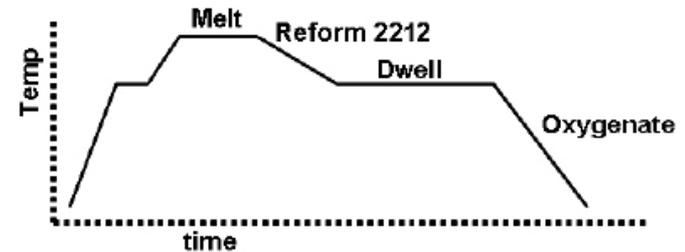
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5 - Thermal process forms HTS phase



HEATING



AEC

CF

COOLING

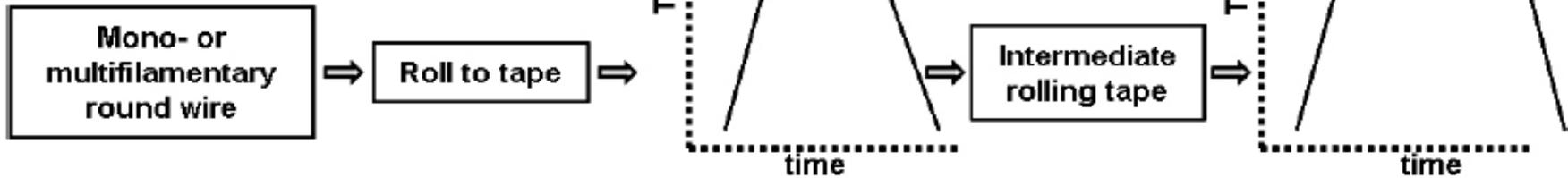
Bi2212 conductor technology

Heine et al., *APL* **55** (1989) 2441

Enomoto et al., *Jap. J. App. Phys.* **29** (1990) L447

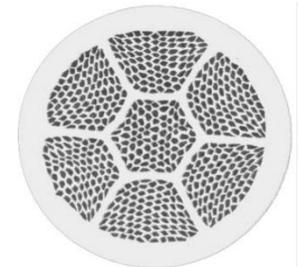
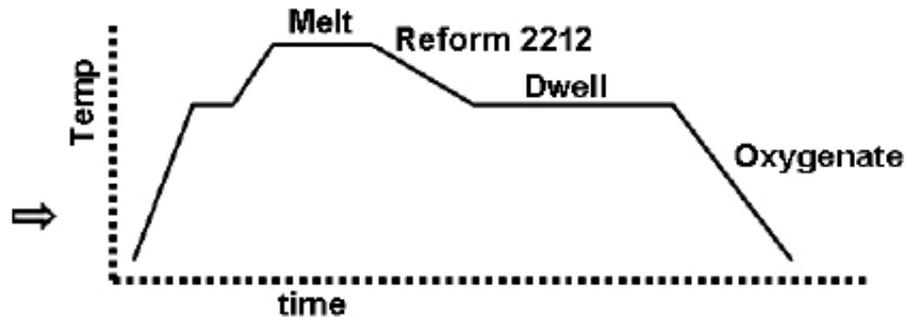
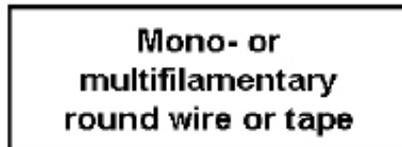
Bi2223 route

2223 processing route



Bi2212 route

2212 processing route

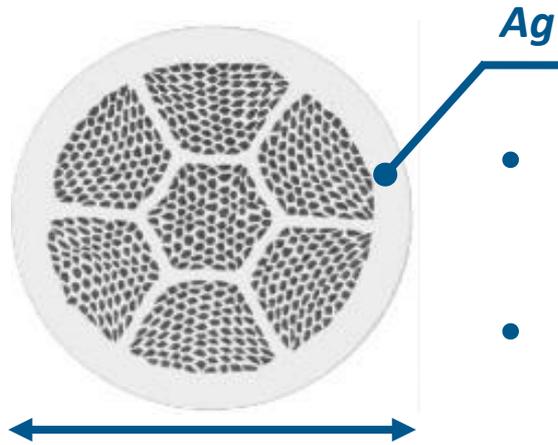
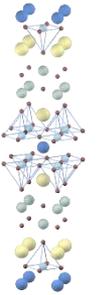


Bi2212 conductors are multifilamentary round wires

Bi2212 Powder-In-Tube round wires: Some facts

Heine et al., APL 55 (1989) 2441

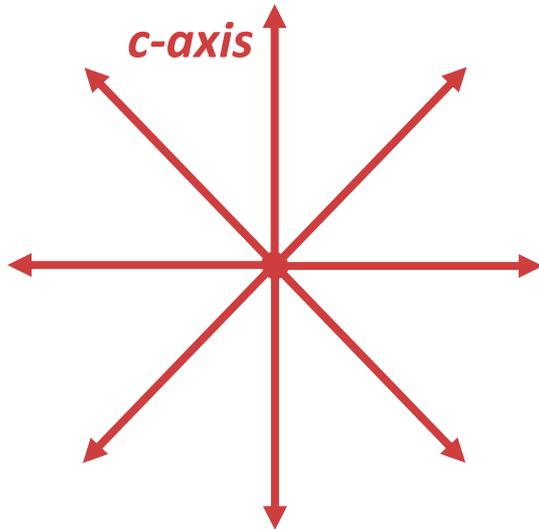
Enomoto et al., Jap. J. App. Phys. 29 (1990) L447



0.8 mm

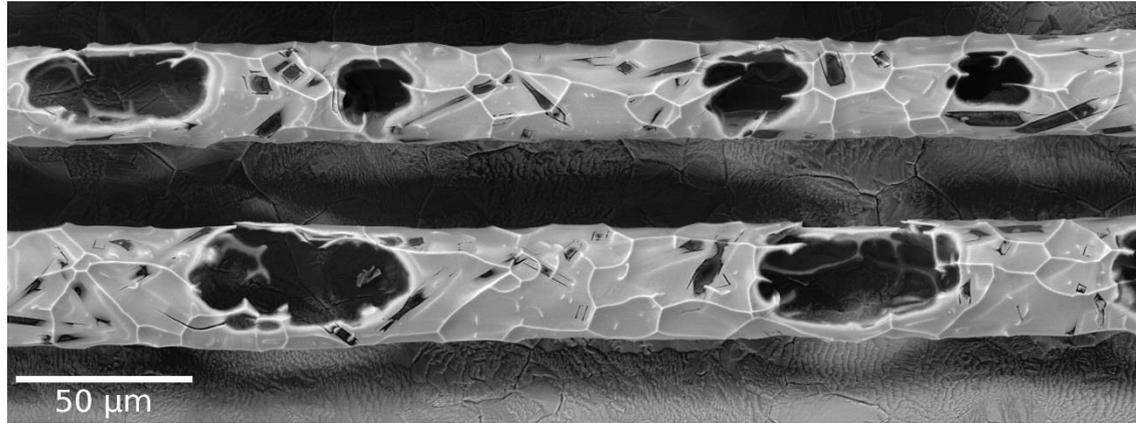
Filling factor is ~25-30%

- The intrinsic anisotropy of Bi2212 is higher compared to Bi2223
- However, it is not necessary to deform the Bi2212 conductors to flat tapes in order to get high J_c
- Melting and recrystallization during the heat treatment determines a gradual **rotation of the c-axis** of grains around the wire axis
- The **advantage** is that Bi2212 conductors **do not have preferential orientation** with respect to the magnetic field
- The **disadvantage** is that Bi2212 **can usefully operate only up to ~20K**, while Bi2223 can operate at 77K, s.f.

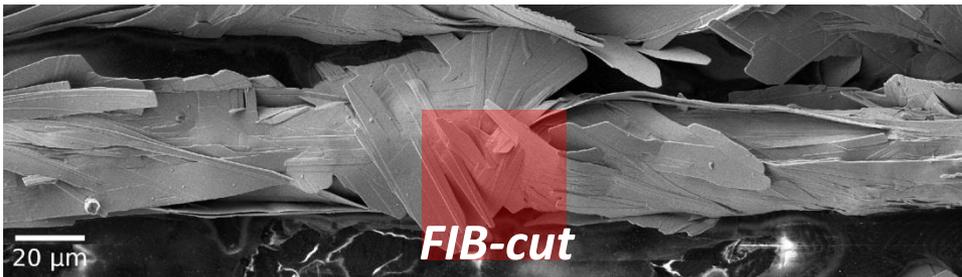


Bi2212: Powder-In-Tube round wires

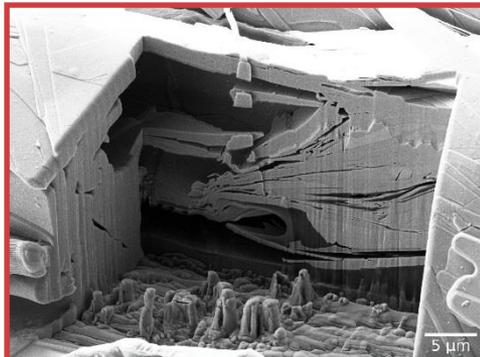
Filament structure



Large bubbles form on melting and holding at T_{max} during the heat treatment



Bubbles can be partially filled on resolidification and Bi2212 reformation, but many voids remain



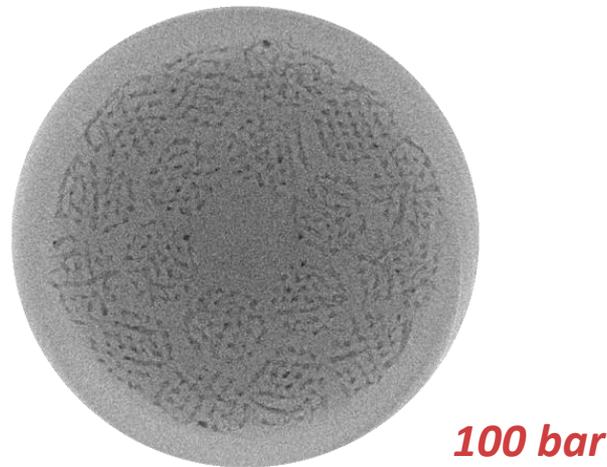
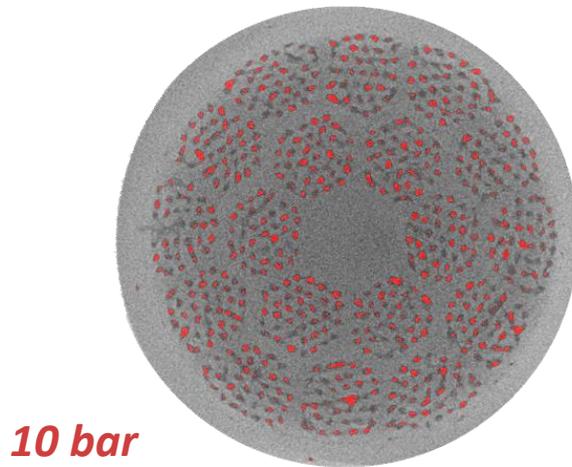
How do we get high J_c in Bi2212 wires ?

The “secret” of its recent success

OVERPRESSURE (up to 100 bar) during the heat treatment prevents the formation of bubbles

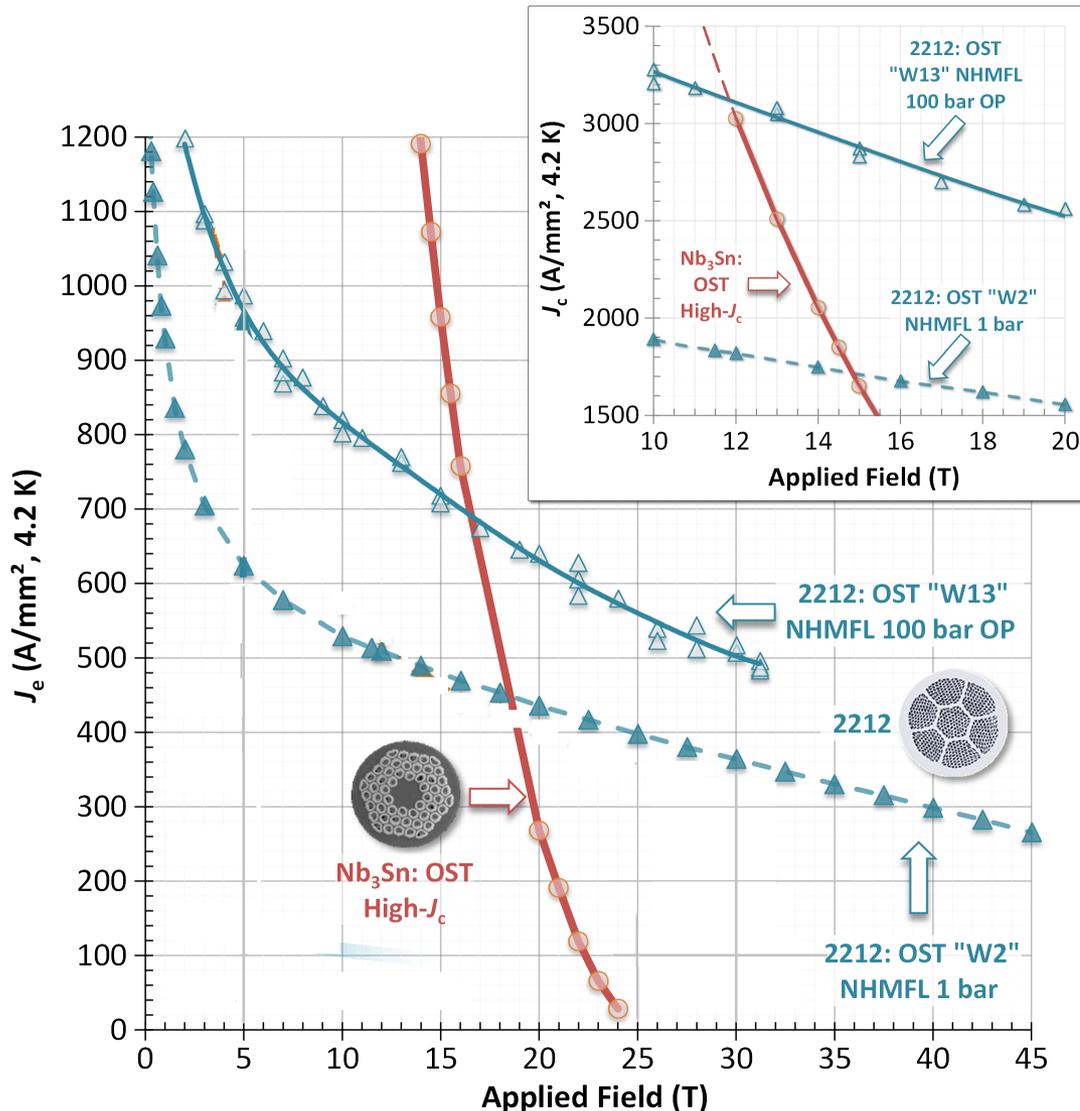
To increase the current carrying cross section

Larbalestier et al., Nat. Mat. 13 (2014) 375



Bi2212: reaction in overpressure (OP)

Enhancement of J_c : 2500 A/mm² at 20 T and 4.2 K



Reaction in OP is very effective to reduce porosity and thus raise J_c

Related papers:

D. Larbalestier et al., *Nat. Mat.* **13** (2014) 375

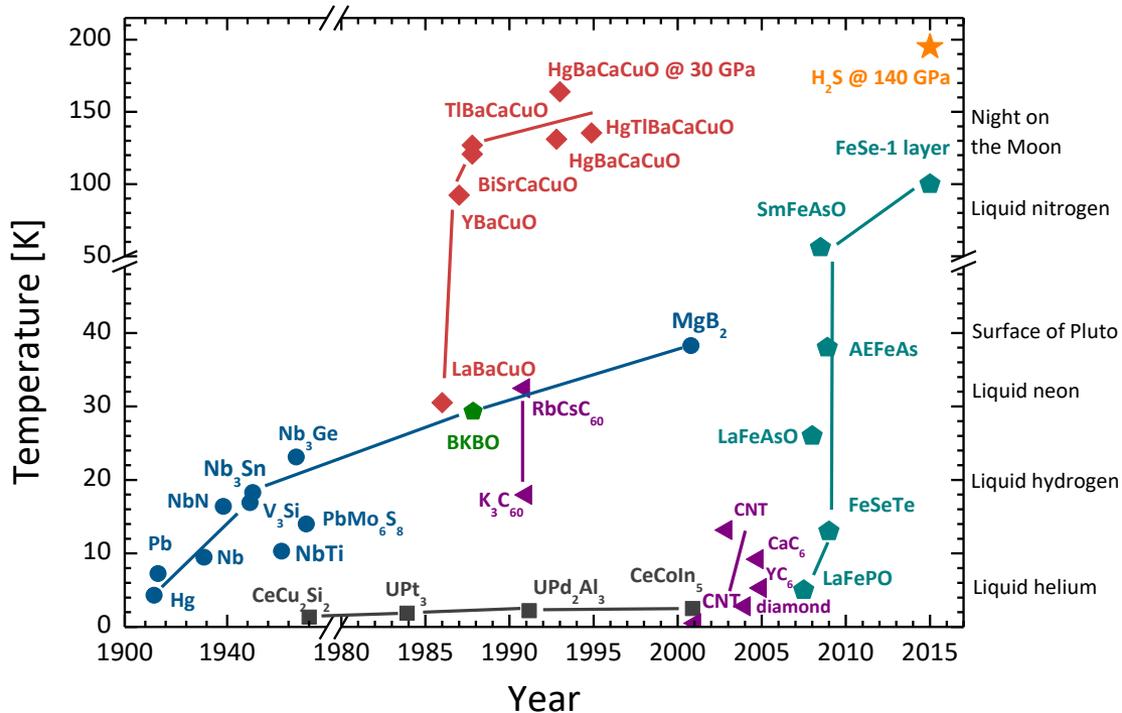
J. Jiang et al., *IEEE TAS* **23** (2013) 6400206

J. Jiang et al., *SuST* **24** (2011) 082001

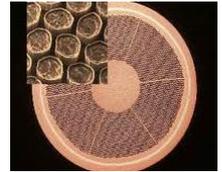
Previously, in lecture 7

From superconducting materials...

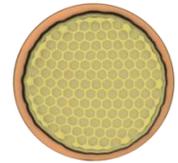
...to technical superconductors



NbTi



Nb₃Sn



MgB₂



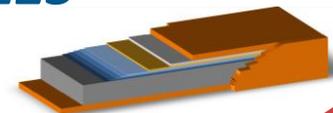
Bi2223



Bi2212

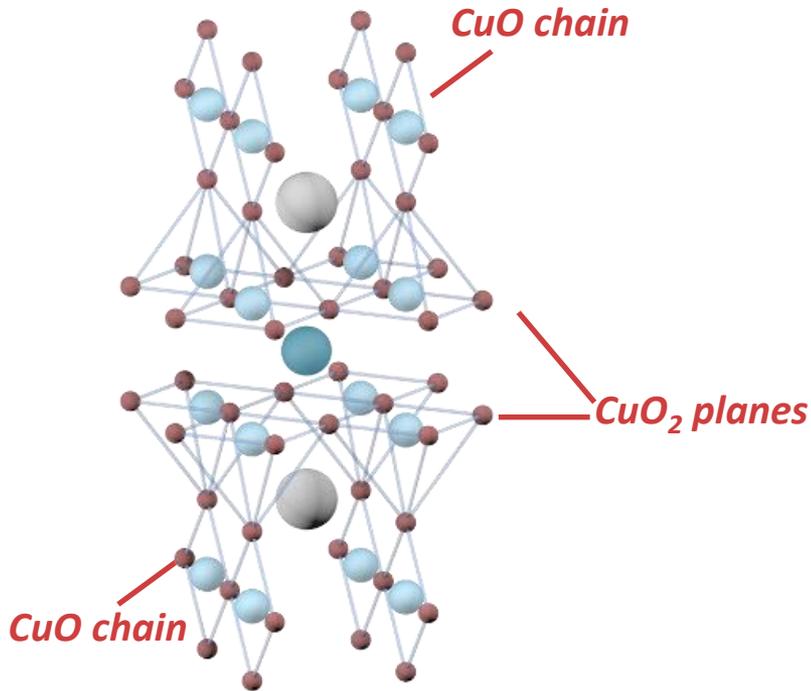


Y123



1. Superconducting ? 10'000
2. $T_c > 4.2K$ & $B_{c2} > 10T$? 100
3. $J_c > 1000 A/mm^2$? ~10

YBCO – Y123 – $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: Some facts



- Discovered by C. P. Chu soon after Bednorz&Müller LaBaCuO
- 1st material with $T_c > 77\text{K}$
- SC @ 92K not only with Y, but with many RE

	Y123
a [Å]	3.8227
b [Å]	3.8872
c [Å]	11.680
# of adjacent CuO_2 planes	2
T_c [K]	92
$B_{c2}^{//ab}$ [T]	>100
anisotropy γ	7-8

$$\gamma = \sqrt{\frac{m_c}{m_{ab}}} = \frac{B_{c1}^{ab}}{B_{c1}^c} = \frac{B_{c2}^c}{B_{c2}^{ab}}$$

$\frac{b}{a} \approx 1.001$ in BSCCO, whereas $\frac{b}{a} \approx 1.02$ in YBCO

Bibliography

Rogalla & Kes

100 Years of Superconductivity

Chapter 11 Section 4 (Bi2223 & Bi2212)

Fosshein & Sudbø

Superconductivity: Physics and Applications

Chapter 2

Papers cited in the slides