



12th European Conference
on Applied Superconductivity

6th - 10th September 2015

Lyon - France

MgB₂ and the Iron-based superconductors



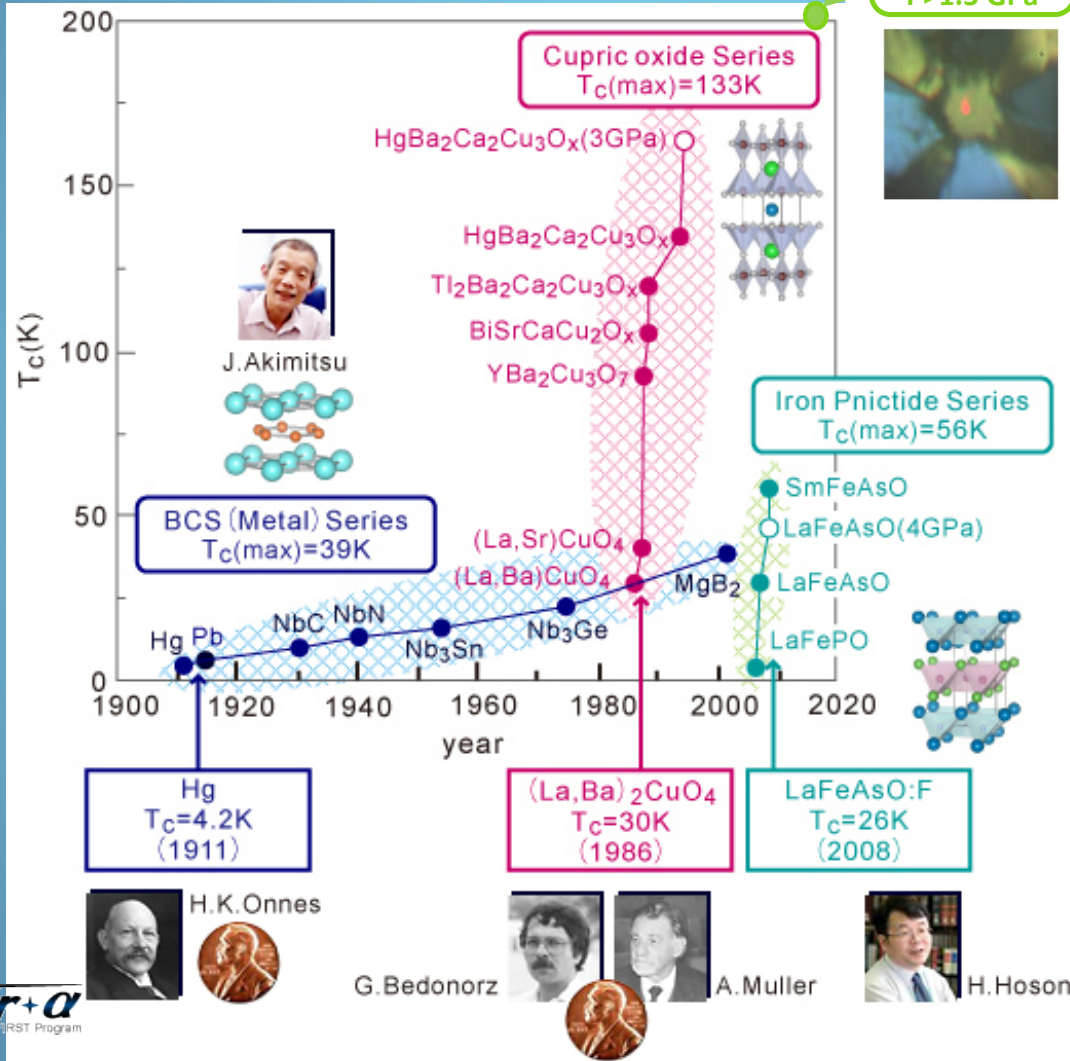
Marina Putti

University of Genova and CNR-SPIN



UNIVERSITÀ
DEGLI STUDI
DI GENOVA

STORY of SUPERCONDUCTIVITY



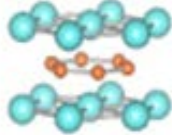
Ermet's group

THE STORY of LAST 15 YEARS

MgB₂



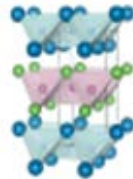
J. Akimitsu



BCS (Metal) Series
 $T_c(\text{max})=39\text{K}$

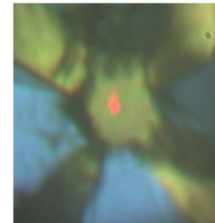


H. Hosono



Iron-based
superconductors
 $T_c(\text{max})=58\text{K}$

H₃S
 $T_c=203\text{K}$
 $P>1,5\text{GPa}$



Ermets's group

Magnesium diboride

NATURE | VOL. 410 | 1 MARCH 2001

Superconductivity at 39 K in magnesium diboride

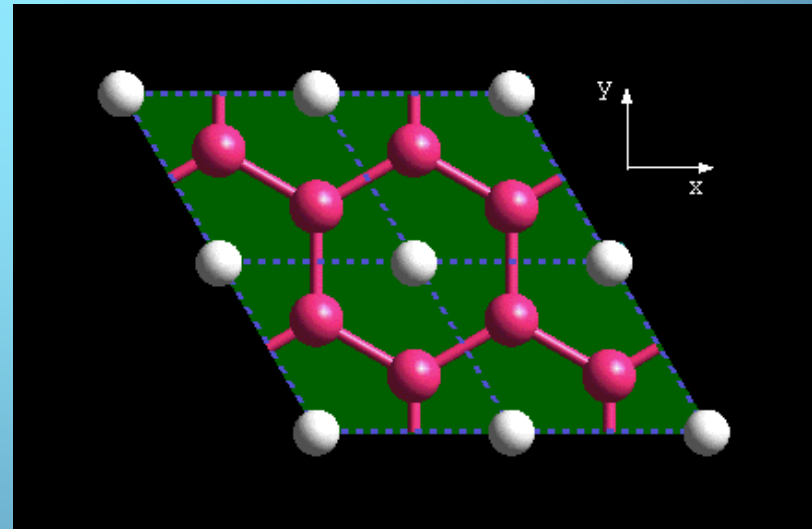
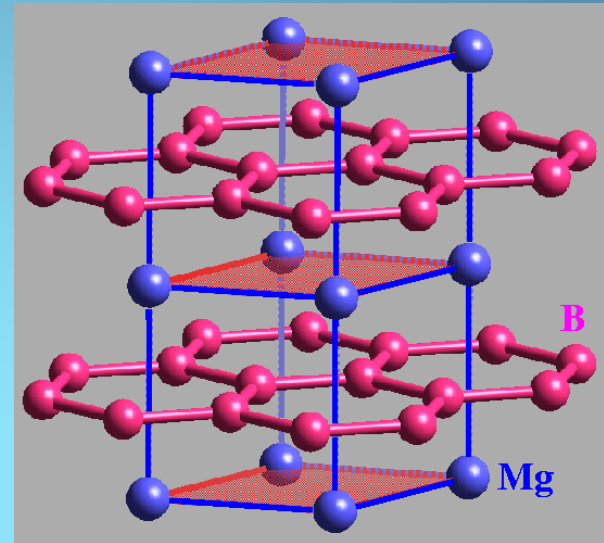
Jun Nagamatsu*, Norimasa Nakagawa*, Takahiro Muranaka*,
Yuji Zenitani* & Jun Akimitsu*†

* Department of Physics, Aoyama-Gakuin University, Chitosedai, Setagaya-ku,
Tokyo 157-8572, Japan

† CREST, Japan Science and Technology Corporation, Kawaguchi, Saitama 332-
0012, Japan

- Strong covalent bonds between the boron atoms.
- Coupling of electron with the optical vibration mode of boron atoms (mode E_{2g}).

$T_c = 39$ K, close to the
maximum value predicted
by BCS theory



MgB₂ first example of two-gap superconductor

VOLUME 87, NUMBER 4

PHYSICAL REVIEW LETTERS

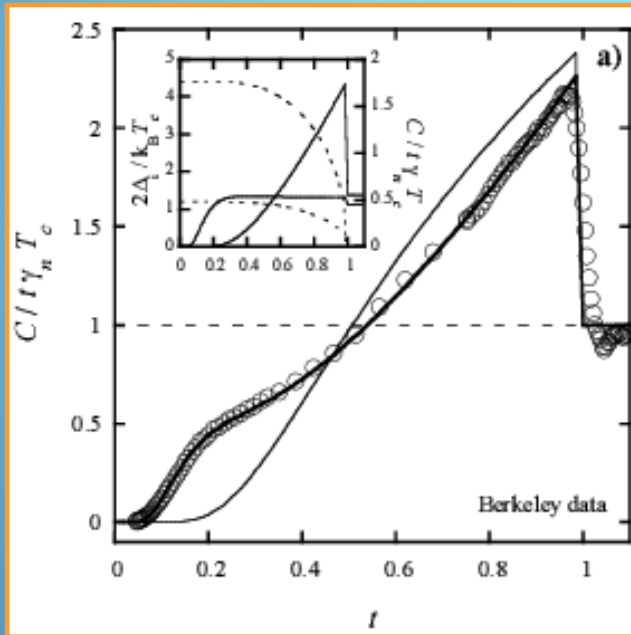
23 JULY 2001

Specific Heat of Mg¹¹B₂: Evidence for a Second Energy Gap

F. Bouquet,¹ R. A. Fisher,¹ N. E. Phillips,¹ D. G. Hinks,² and J. D. Jorgensen²

¹Lawrence Berkeley National Laboratory and Department of Chemistry, University of California, Berkeley, California 94720

²Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
 (Received 26 March 2001; published 5 July 2001)



$$\Delta_{\pi}(0) \sim 2 \text{ meV} ; \Delta_{\sigma}(0) \sim 7 \text{ meV}$$

VOLUME 89, NUMBER 24

PHYSICAL REVIEW LETTERS

9 DECEMBER 2002

Direct Evidence for Two-Band Superconductivity in MgB₂ Single Crystals from Directional Point-Contact Spectroscopy in Magnetic Fields

R. S. Gonnelli,^{*} D. Daghero, and G. A. Ummarino

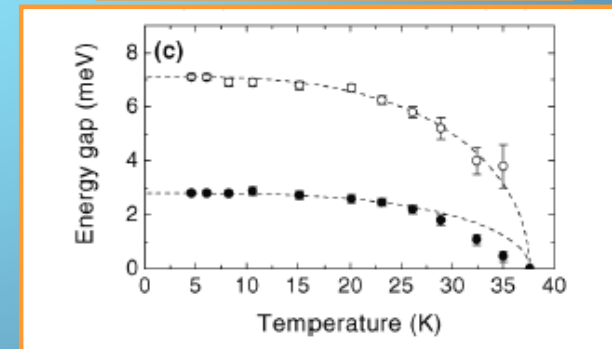
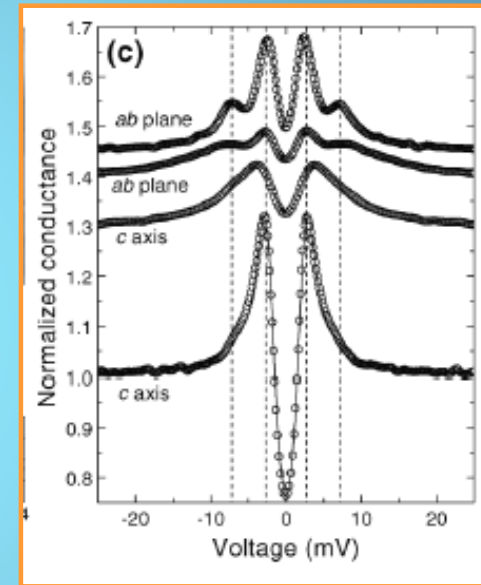
INFN-Dipartimento di Fisica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

V. A. Stepanov

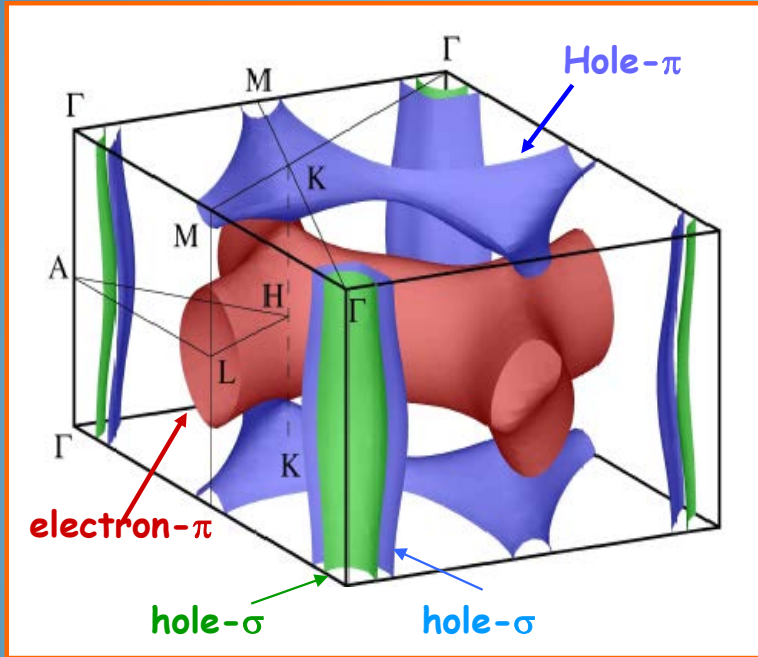
P.N. Lebedev Physical Institute, Russian Academy of Sciences, Leninsky Prospekt 53, 119991 Moscow, Russia

J. Jun, S. M. Kazakov, and J. Karpinski

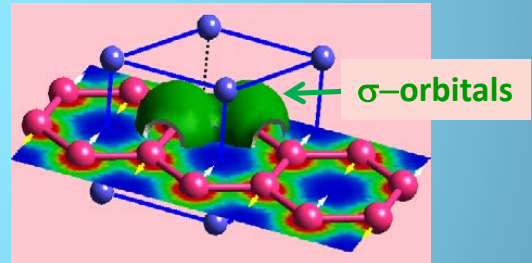
Solid State Physics Laboratory, Swiss Federal Institute of Technology (ETH), CH-8093 Zürich, Switzerland
 (Received 2 August 2002; published 25 November 2002)



MgB₂ two-band superconductor



σ bands	π bands
2D	3D
hole-like	nearly electron-like
strongly coupled with E _{2g} mode	weakly coupled with E _{2g} mode
Different parity	
Interband scattering is negligible	



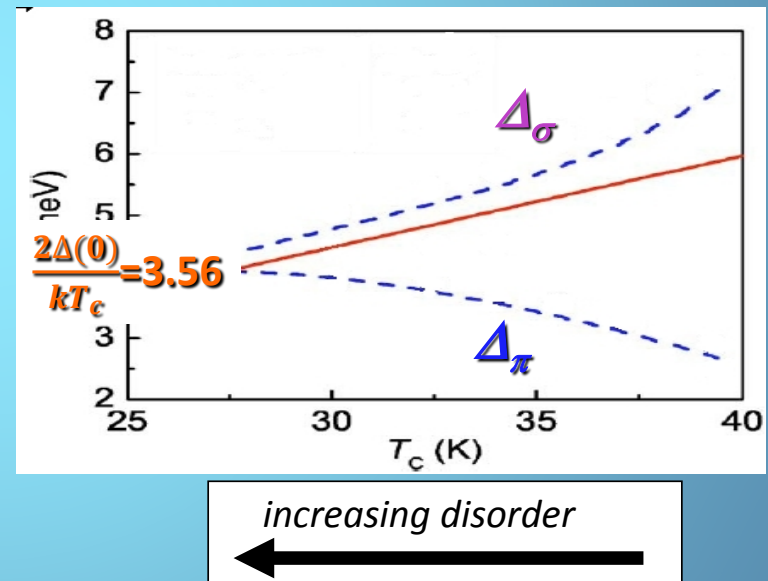
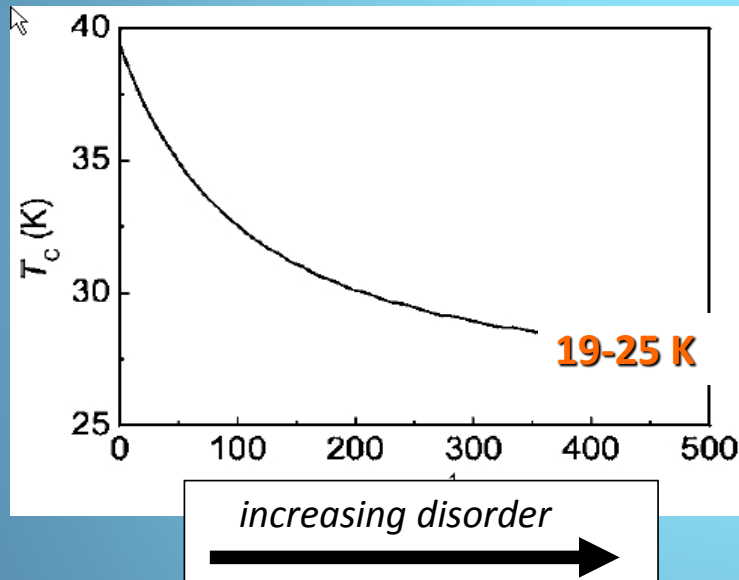
	$\Delta(0)$, meV	v_{Fab} (m/s)	v_{Fab}/v_{Fc}	$\xi_{ab}(0)$ (nm)	$\lambda_{ab}(0)$ (nm)	$\kappa = \lambda/\xi$	
σ	7	4.40×10^5	5–6	13	49	4	Type II
π	2.2	5.35×10^5	~1	51	34	0.7	Type I

T_c is amplified (by a factor 2) by the occurrence of two decoupled bands

Role of disorder

In a two-band s/c interband scattering mixes strong σ -pairs with weak π -pairs and causes pair breaking.

A.A.Golubov and I.I.Mazin, PRB 55 (1977)

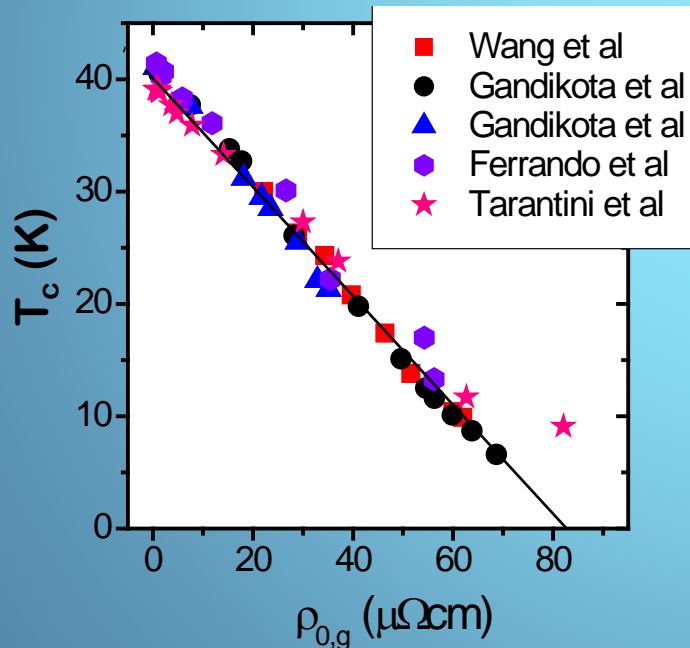


O.V. Dolgov *et al.* PRB 72, 024504 (2005)

Substitutional impurities:

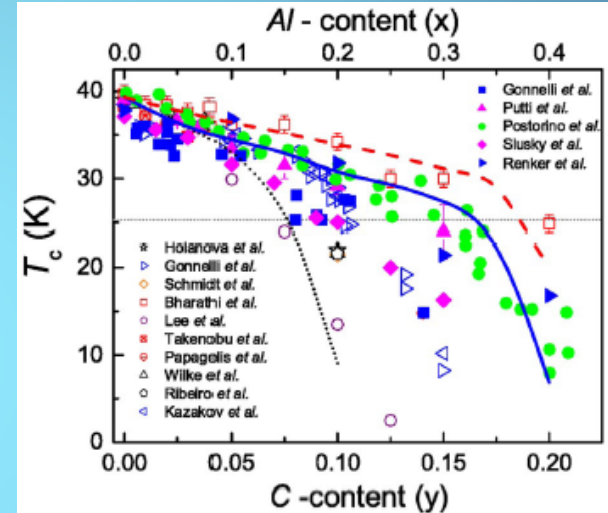
Artificial defects:

- Neutron irradiation
- α -particle irradiation



Putti et al SUST **21** (2008) 043001

- C in the B site: $\text{Mg}(\text{B}_{1-y}\text{C}_y)_2$
- Al in the Mg site: $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$



J. Kortus et al. PRL **94**, 027002 (2005)

Electron doping

⇒ emptying of the σ -bands

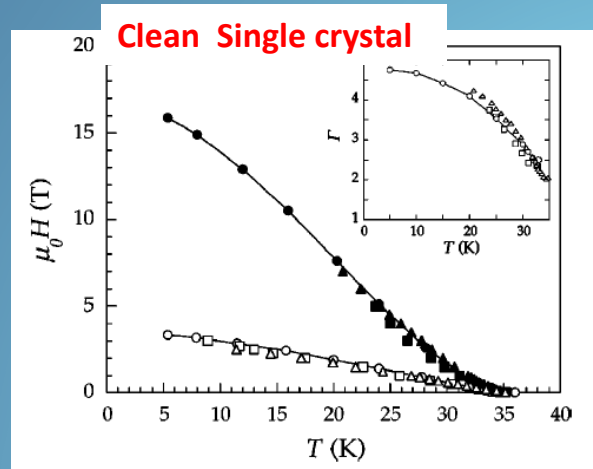
Interband scattering

⇒ merging of the gaps

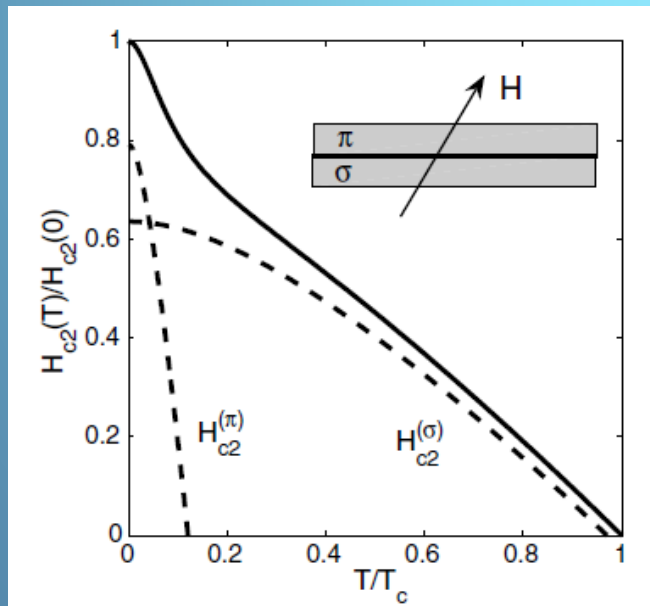
Intraband scattering

⇒ smearing of the DOSs

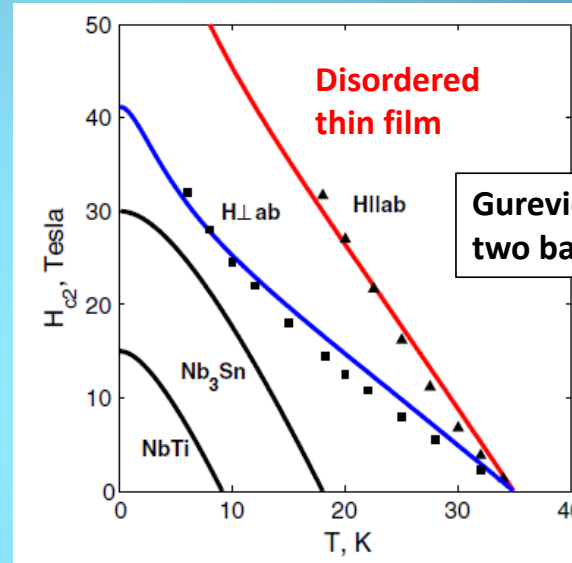
$T_c \rightarrow 0$



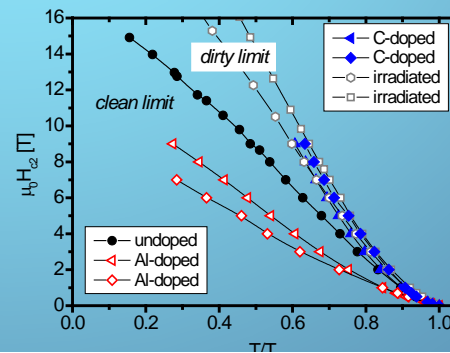
Lyard et al., PRB **66**, 180502(R) 2002



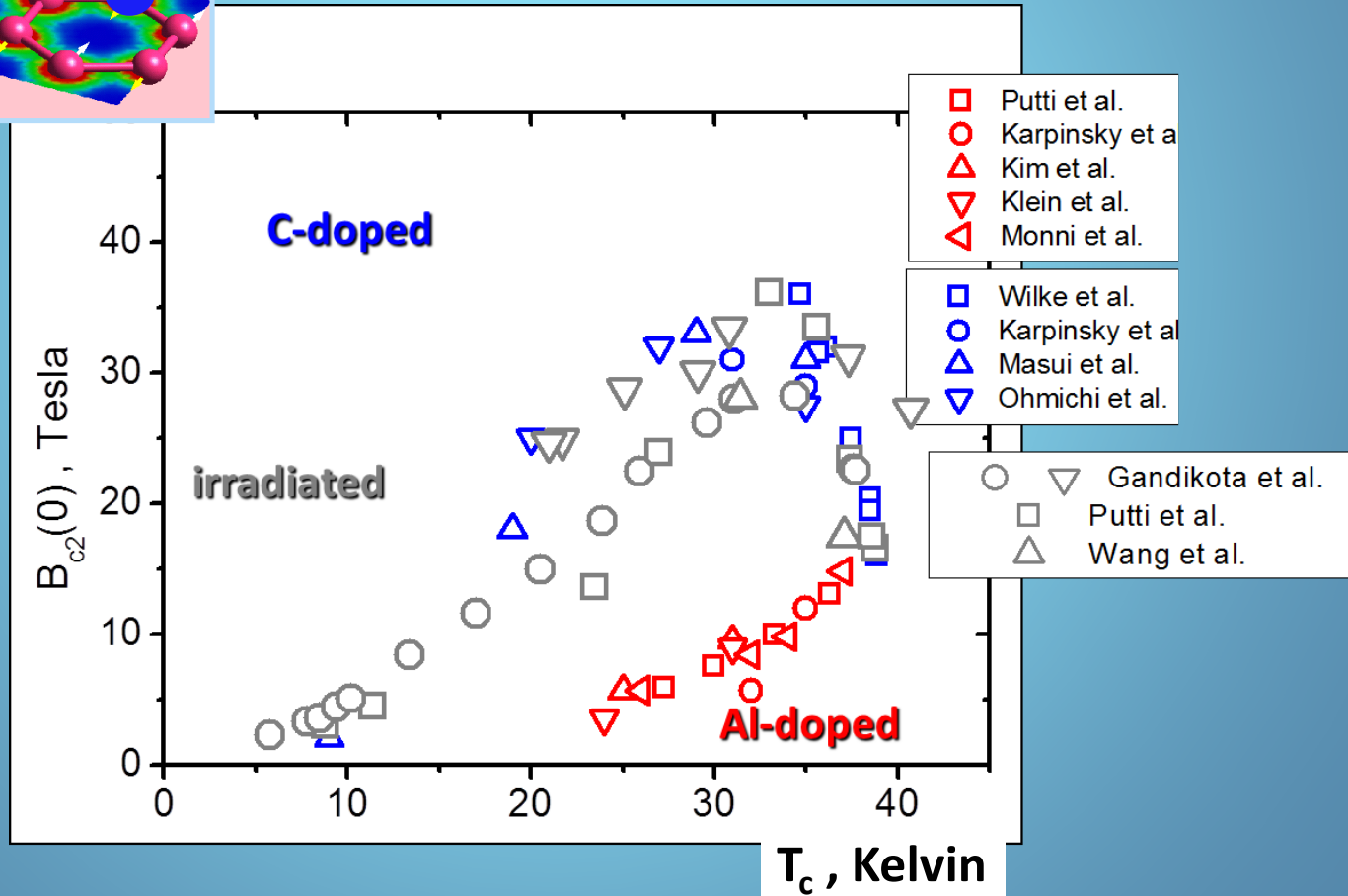
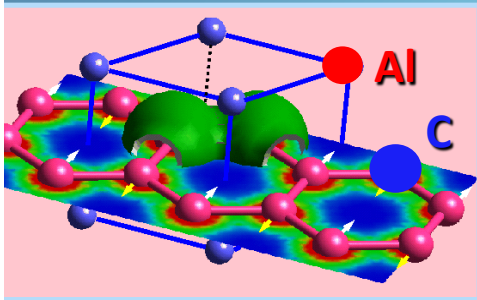
Upper critical field



A. Gurevich Physica C 456 (2007) 160–169



Upper critical field



Upper critical field

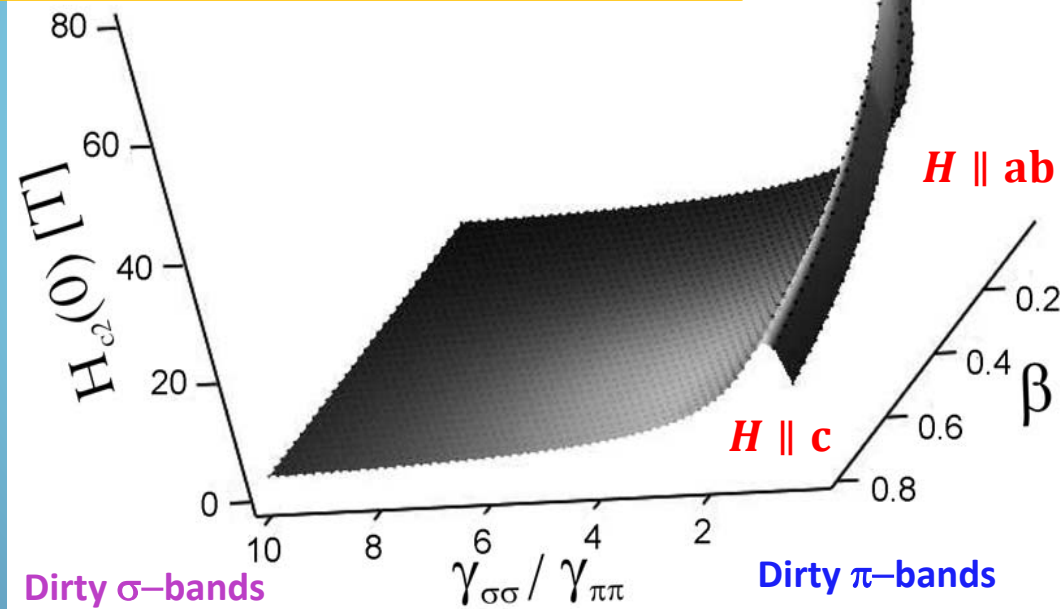
Ab-initio model predicts :

$$\mu_0 H_{c2} \parallel ab \sim 80T$$

$$\mu_0 H_{c2} \parallel c \sim 30T$$

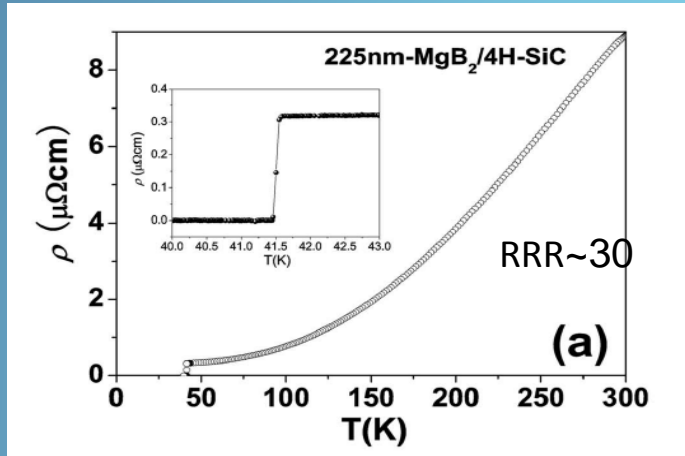
In extremely dirty π bands

⇒ smearing of π -DOS does not affect T_c

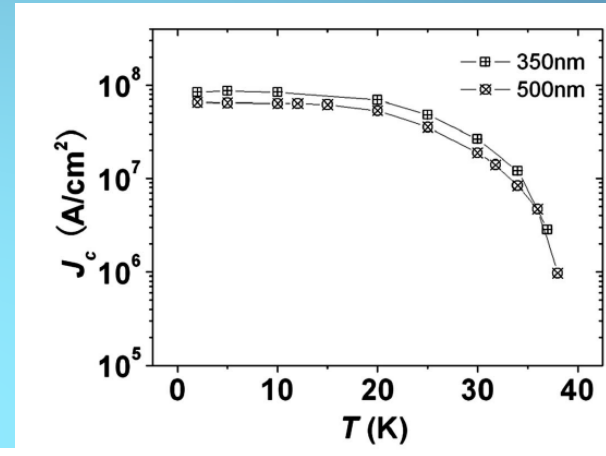


Brotto et al., PRB **82**, 134512 (2010)

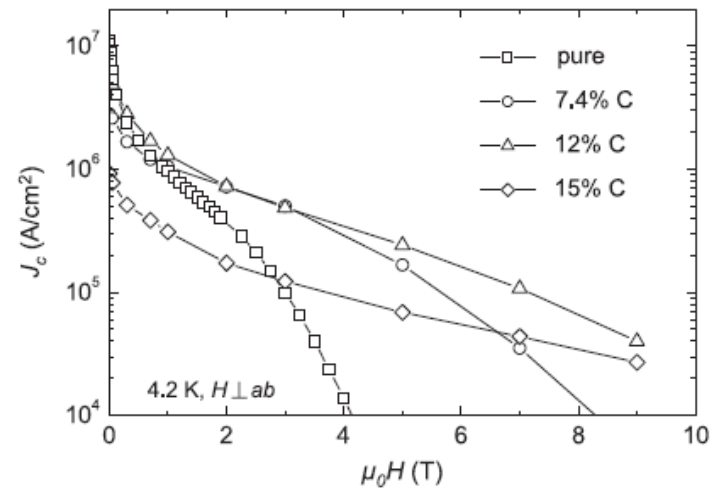
Jc of thin films



J. Appl. Phys. 104, 013924 (2008)



Chen J, PRB 74 174511 (2006)

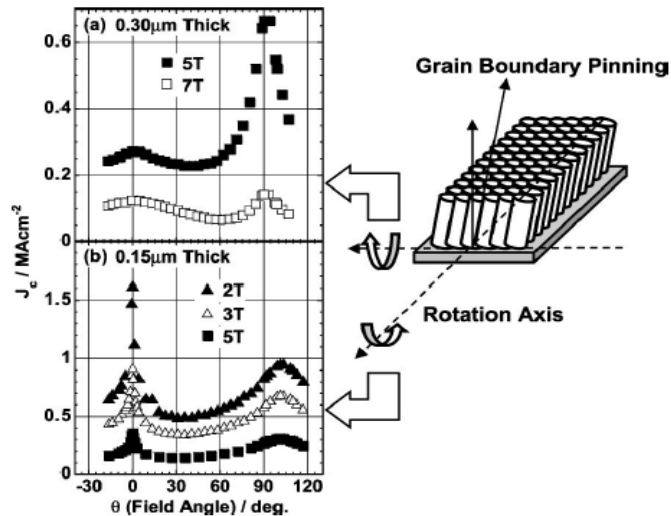


Thin films produced by hybrid physical–chemical vapor deposition (HPCVD) (X X Xi group)

- ⇒ Extremely clean ($\rho_0 < 1 \mu\Omega\text{cm}$)
- ⇒ Enhanced T_c ($T_c > 40 \text{ K}$)
- ⇒ Huge $J_c(0)$ ($\sim 10^8 \text{ A}/\text{cm}^2$)
- ⇒ C-doping substantially improves $J_c(H)$

J_c of thin films

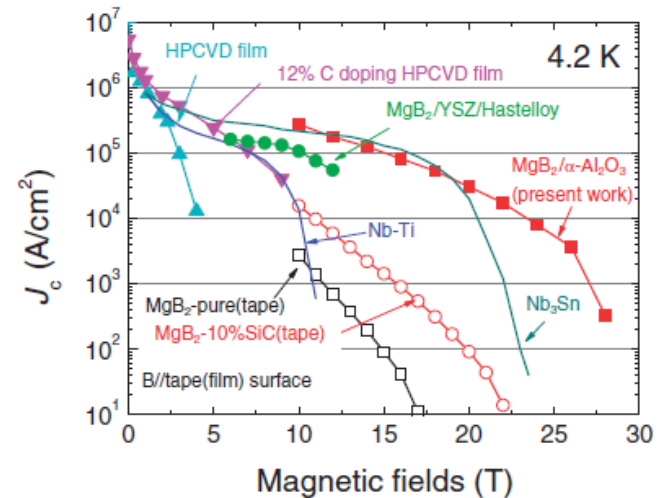
Electron Beam evaporation



Kitaguchi et al | APL 85, 2842 (2004)

Nanometer-sized columnar-grain structure can produce $J_c(B)$ exceeding 10^6 A/cm²

PLD + post-annealing process



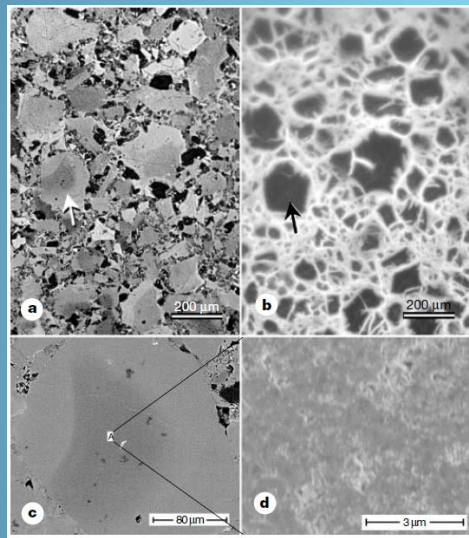
A. Matsumoto: APEX 1, 021702 (2008)

J_c enhancements in fields up to 26 T above Nb₃Sn performance in nanostructured thin films

In thin films J_c is enhanced by grain boundary pinning

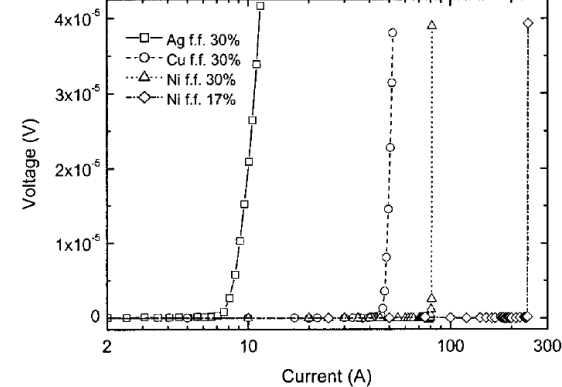
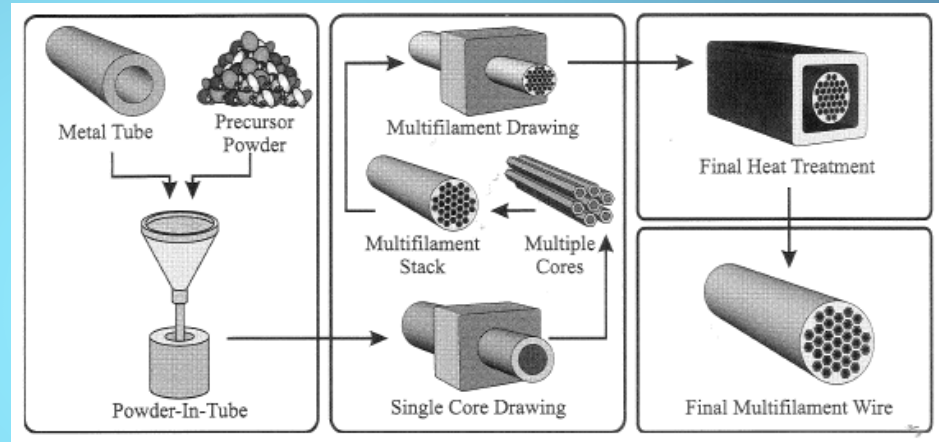
- ➔ High T_c , B_{c2} and J_c
- ➔ No evidence of “weak link”

Fast development of Powder in Tube (PIT) technique



D.C.Larbalestier et al., *Nature* **410**, 186 (2001)

Coherence length
 $\xi \sim 10$ nm



G.Grasso et .al. 2001 APL 72, number 9

Role of anisotropies in Polycrystals

Current Percolation and B_{c2} Anisotropy.

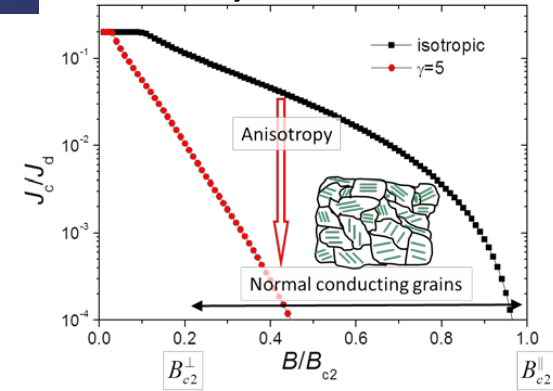
Eisterer, et al., PRL **90**, 247002 2003

⇒ $J_c(B)$ is function of the B_{c2} anisotropy

$$B_{c2}(\theta) = \frac{B_{c2}^{\parallel}}{\sqrt{\gamma^2 \cos(\theta)^2 + \sin(\theta)^2}}$$

$$\gamma = \frac{B_{c2}^{\parallel}}{B_{c2}^{\perp}} \sim 5 - 6 \text{ (clean limit)}$$

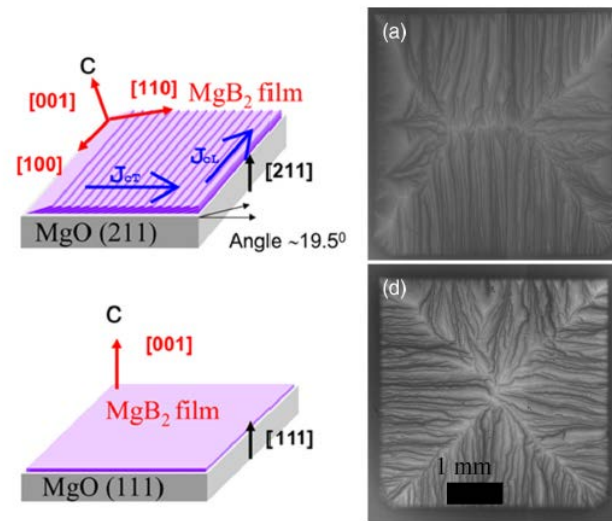
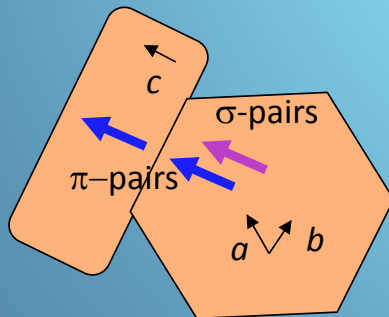
Courtesy of M. Eisterer



λ anisotropy and pairbreaking effects

Polyanskii et al., PRB **90**, 214509 (2014)

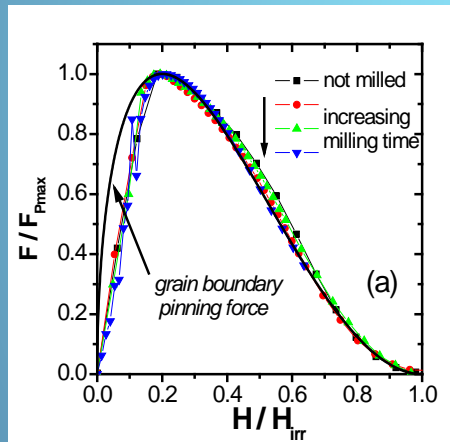
⇒ $J_c(B=0)$ is function of the λ anisotropy



How to enhance pinning strength in polycrystals

- ⇒ Increasing H_{c2} with C doping
- ⇒ Introducing pinning centers with nanoparticle addition

Carbon in elemental form (microspheres, nanotubes, nanodiamond, graphene)
C-containing compounds such as SiC, TiC, B_4C ,
Organic compounds: -malic acid, toluene, benzene, naphthalene, thiophene, pyrene

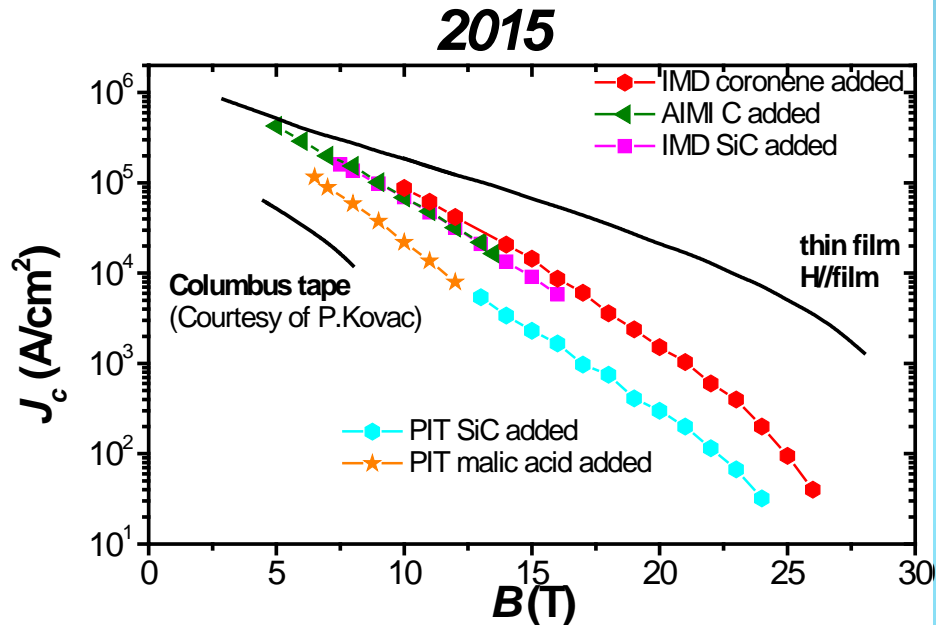


V Braccini, INFM, Italy
E W Collings, The Ohio State University, US
S X Dou, University of Wollongong, Australia
R Flukiger, DPMC, University of Geneva; Switzerland
W Goldacker, KIT, Germany
H Kumakura, NIMS, Japan
Y Ma, et al Chinese Academy of Sciences, China
.....

Despite many attempts at nanoparticle additions, the principal pinning defects in MgB_2 are grain boundaries.

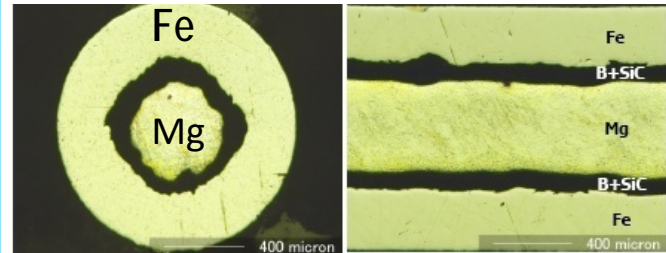
Fine grains in C additioned MgB_2

Critical current density

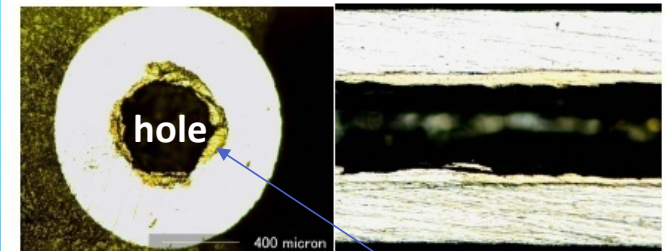


➔ **Moving from 1stG (PIT) to 2^oG (IMD) wires**
 (Giunchi G, et.al 2003 SUST 16 285)

a) Before reaction



(b) After reaction



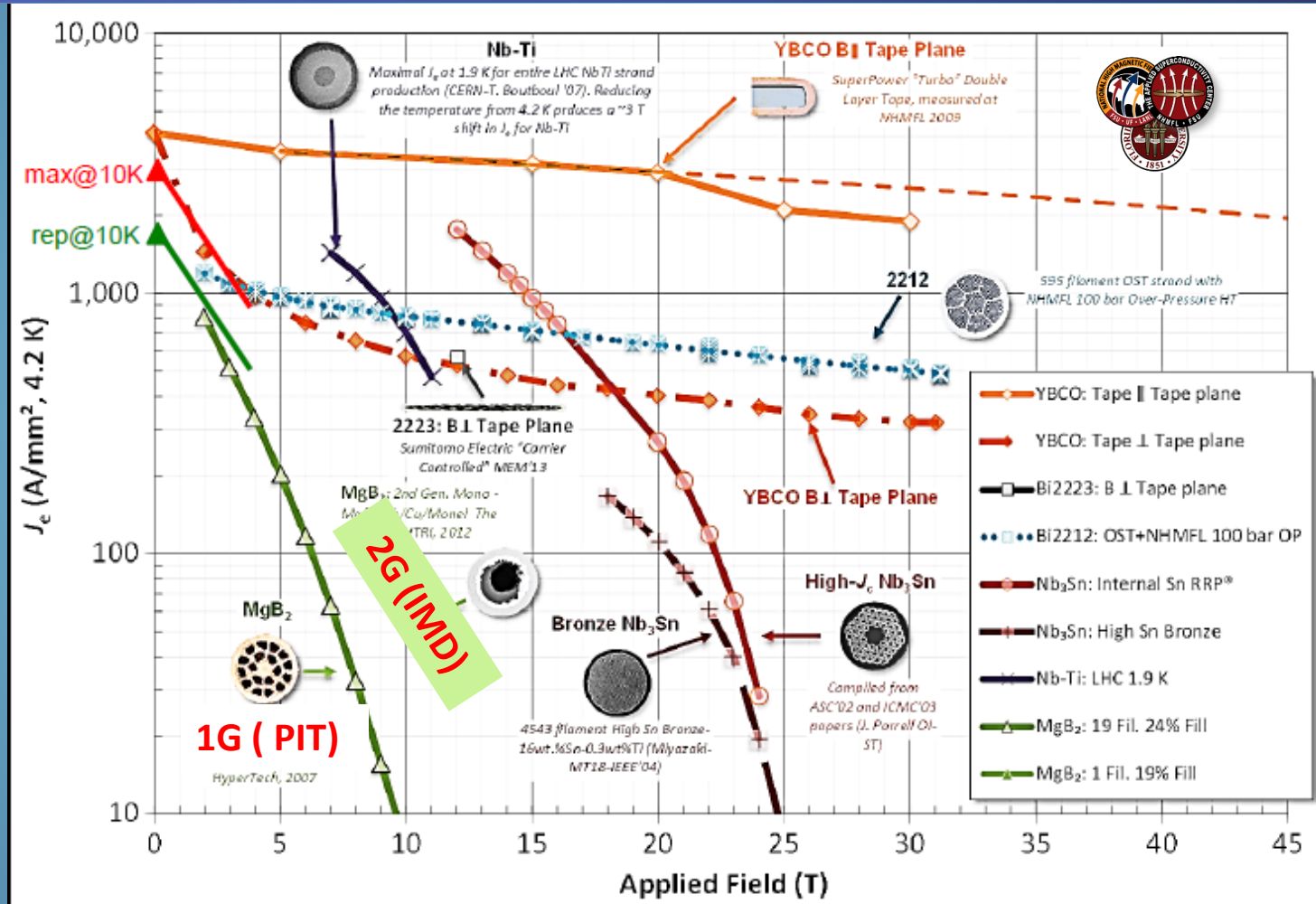
MgB₂

Courtesy: H. Kumakura, NIMS

K Togano, et al., SUST **22** (2009) 015003
 J.H. Kim, et al., SUST **23** (2010) 075014
 G Z Li et al. SUST **26** (2013) 095007
 Shu Jun Ye, et al., SUST **27** (2014) 085012

M. Putti and G.Grasso MRS BULLETIN **36**, 608

Engineering critical current



Wire manufacturing companies



Ready for industrial production
2 different manufacturing process
ex-situ and in-situ technique



Interested in commercial production
of wires or wires+magnet

*Early stage New York based company,
granted as SME partner by UK for R&D activities on MgB₂
They plan to start commercial production in early 2014.*

*MgB₂ wires for Cryo-free MRI
Summer 2015 for MRI magnet 1.5T-3T magnet*

Interested in the MgB₂ technology



*1000 m of MgB₂ wire
already demonstrated
in collaboration with IFW Dresden*

*Patents on MgB₂ wires
Several R&D activities*



Courtesy of 

MgB₂ on the market: MRI application



First commercial systems using MgB₂ installed in hospital in EU and North America

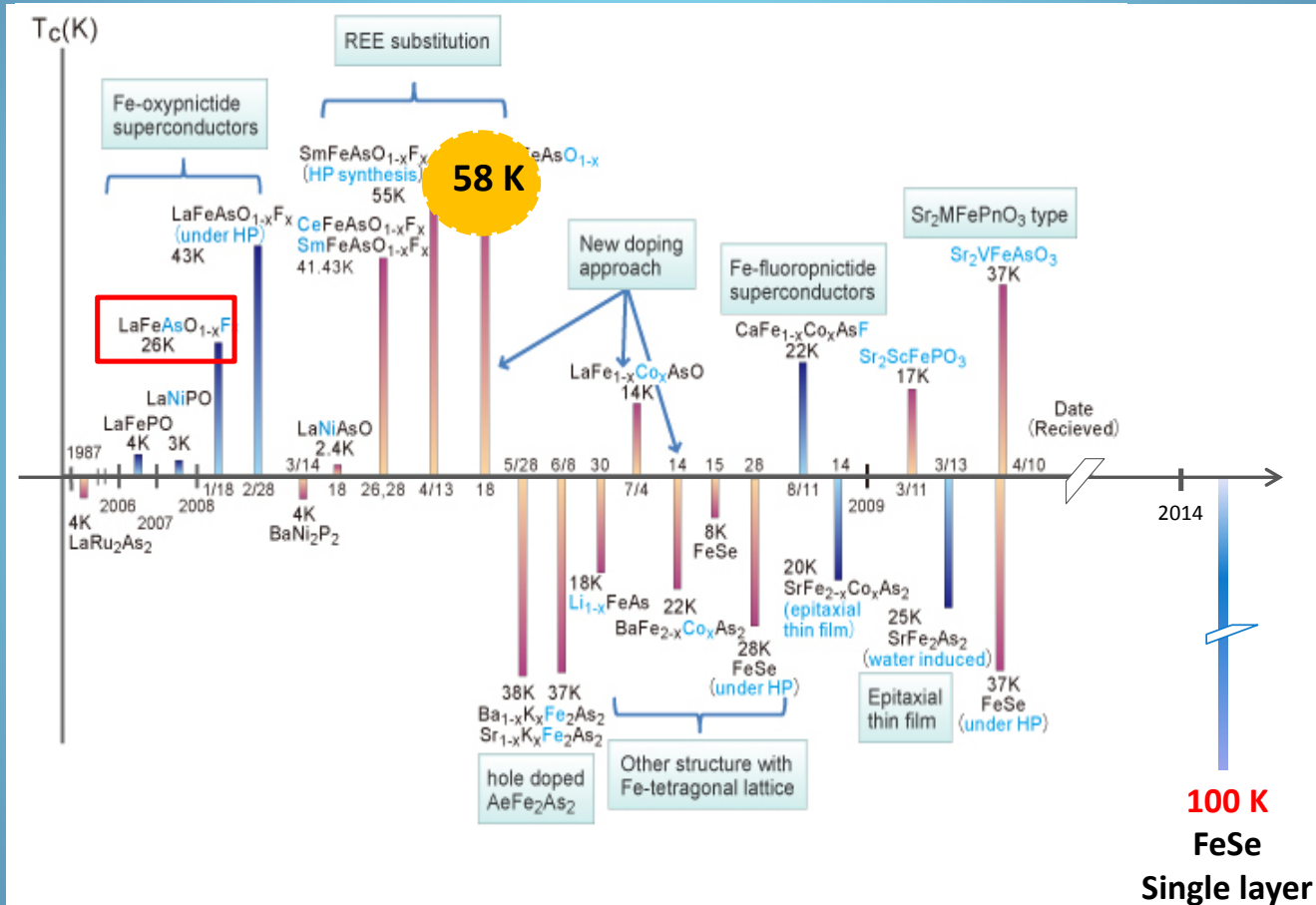
Operating T=20K

26 magnet systems produced so far

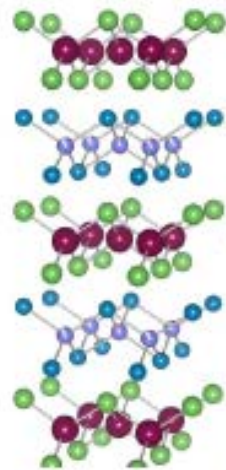
Courtesy of  Columbus Superconductors

This demonstrates that 14th years since its discovery MgB₂ is a reality, but it needs a breakthrough to become a high field conductor

Iron based superconductors (IBS)

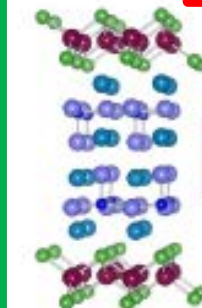
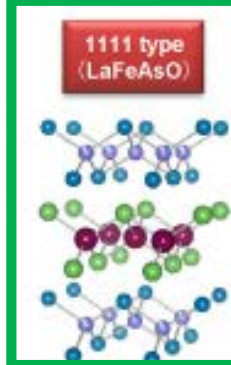
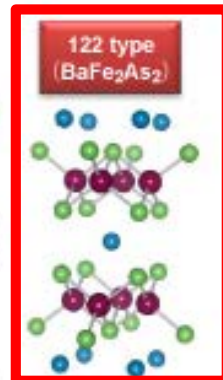
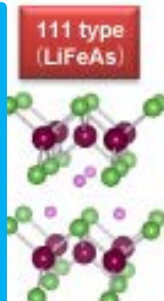
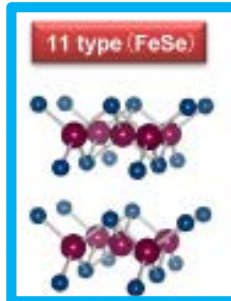
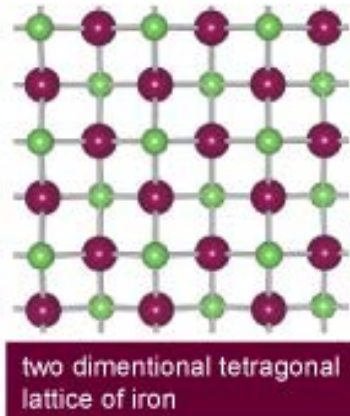


IBS families



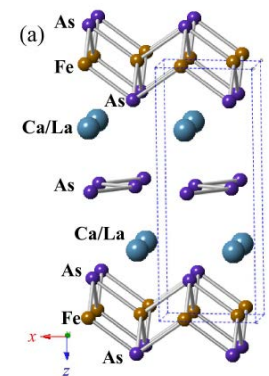
FeAs
conducting
layer

LaO(F)
blocking
layer

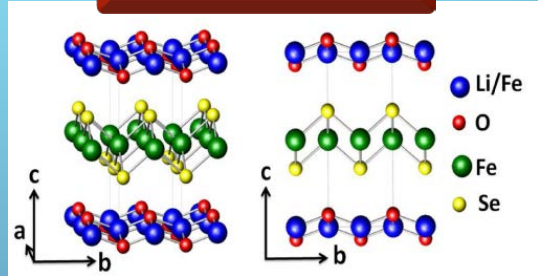


21113 type (Sr₂VFeAsO₃)

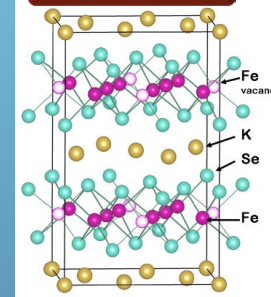
112 type (CaFeAs₂)



Intercalated FeSe-11

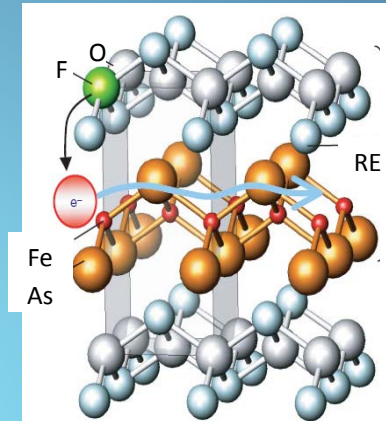
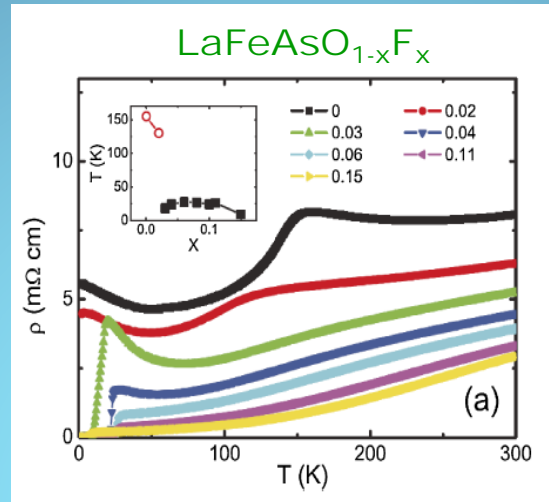


122 (KFe₂Se₂)

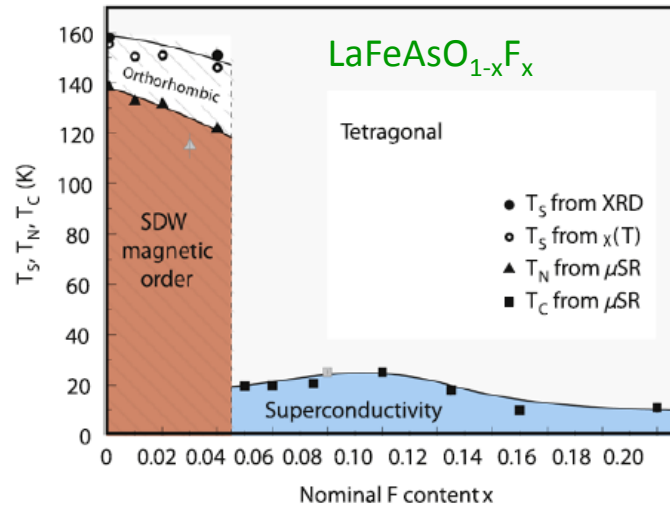


Phase diagrams:

1111

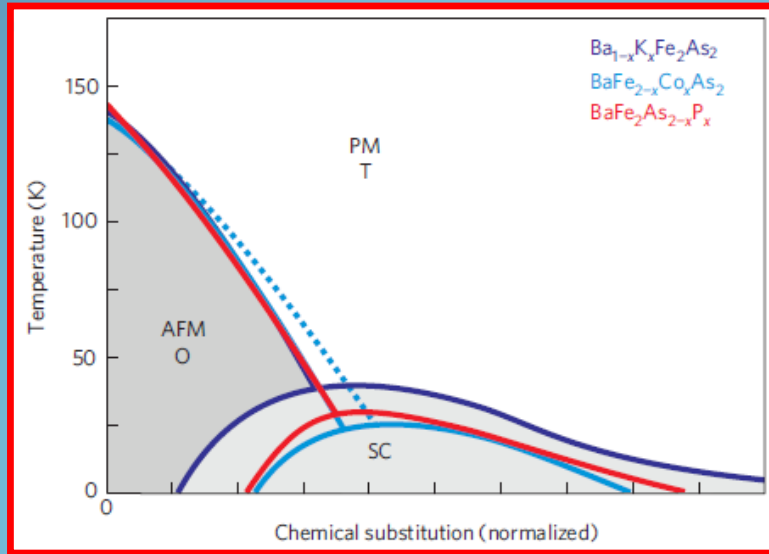


(a) Luetkens et al., Nature Materials, **8**, 305–309, 2009.

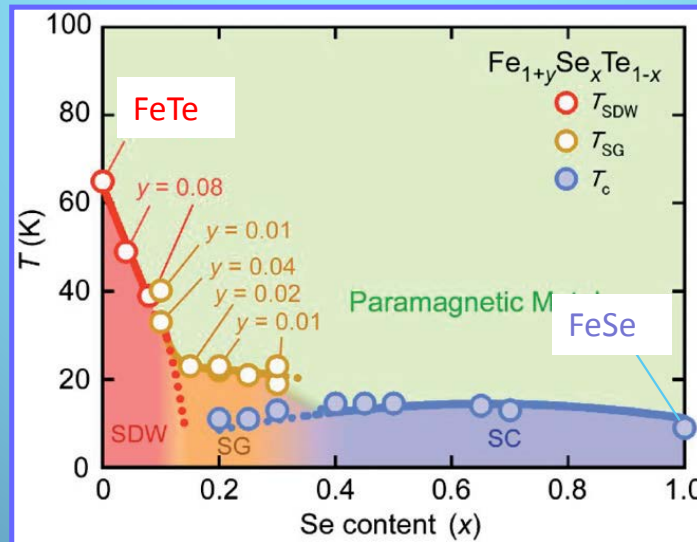




Phase diagrams :

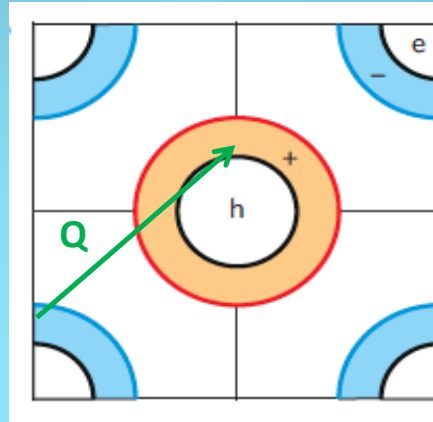
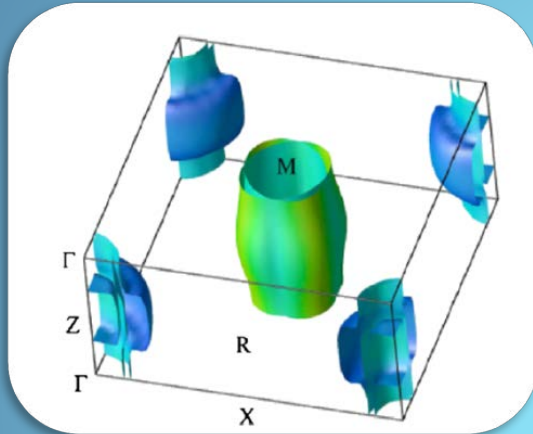


122



11

Band structure



Superconductivity promoted by AFM fluctuations which couple e- and h-bands

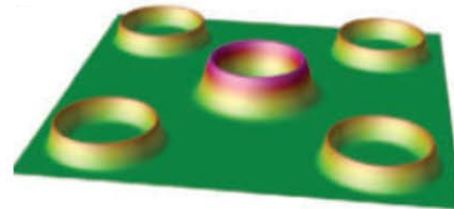
D. J. Singh and M.-H. Du: Phys. Rev. Lett. 100 (2008)

Igor I. Mazin, Nature 464 (2011) 183

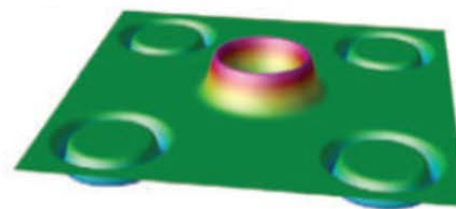
Superconducting order parameter:

- ⇒ MgB_2 : two-band s wave with the same sign
- ⇒ IBS : two-band s_{\pm} wave

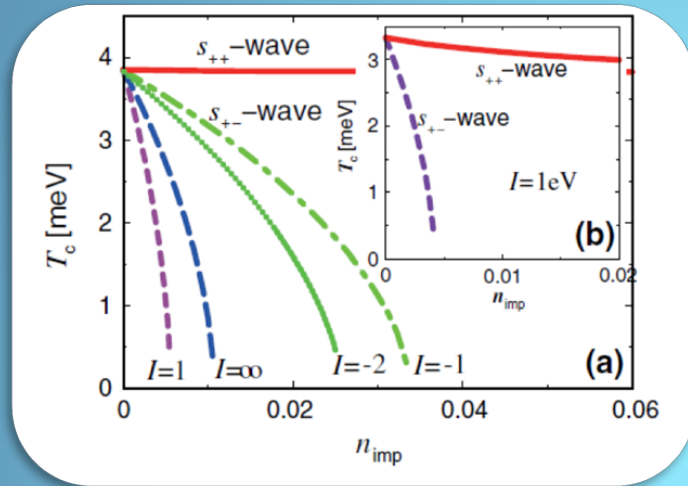
MgB_2



IBS



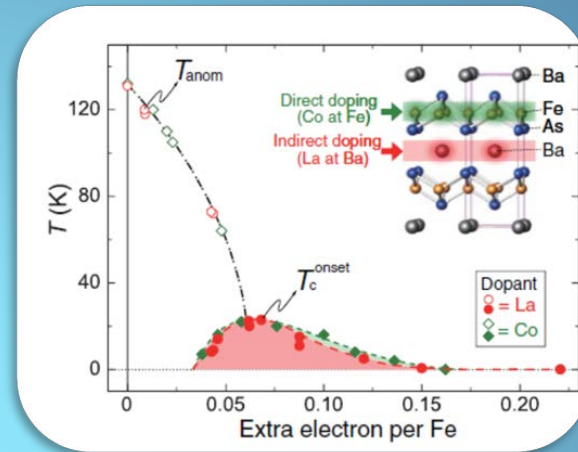
T_c vs impurities



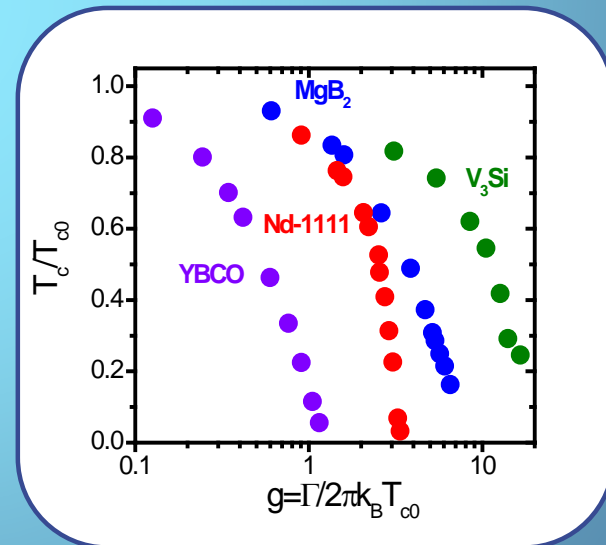
S Onari et al., PRL 103, 177001 (2009)]

In case of $s \pm$ wave pairing a rapid suppression of T_c with impurities has been predicted

Superconductivity in IBS is quite **robust against disorder**



T Katase et al., PRB 85, 140516(R) (2012)

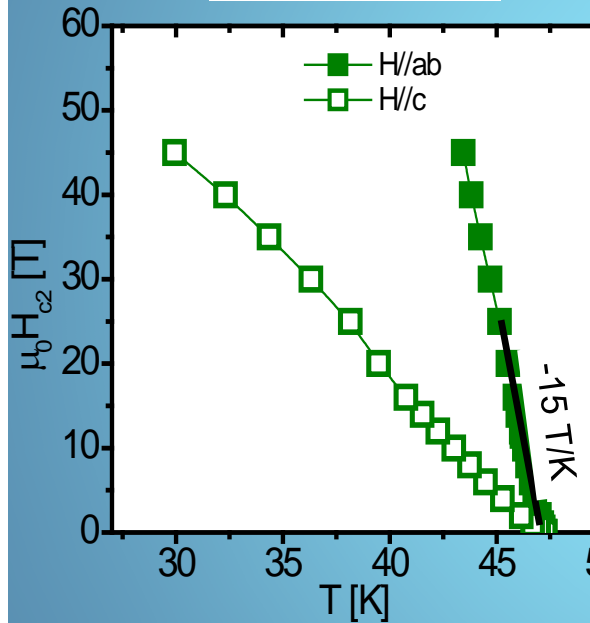


C Tarantini et al., PRL 104, 087002 (2010)

Upper critical fields

1111

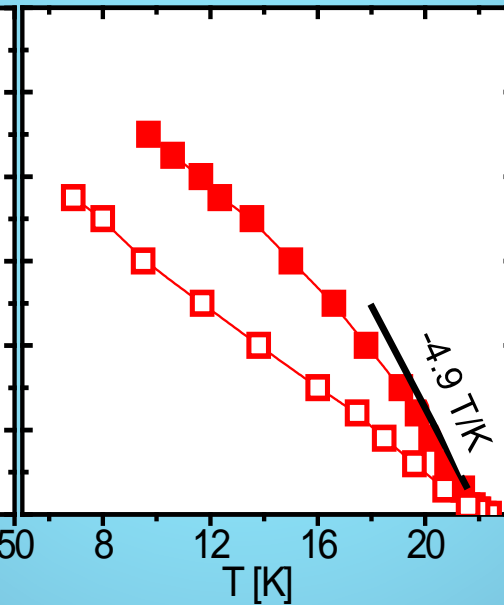
NdFeAs(OF)



- ✓ Slope -15 T/K
- ✓ Anisotropy is 5

122

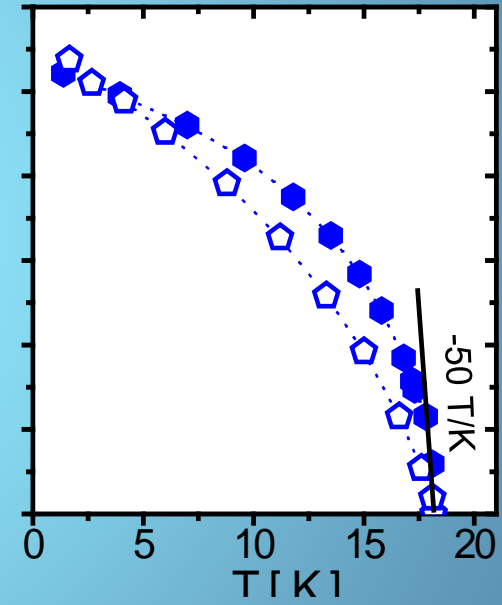
Ba(FeCo)₂As₂



- ✓ Slope -4.9 T/K
- ✓ Anisotropy is 2-1.5

11

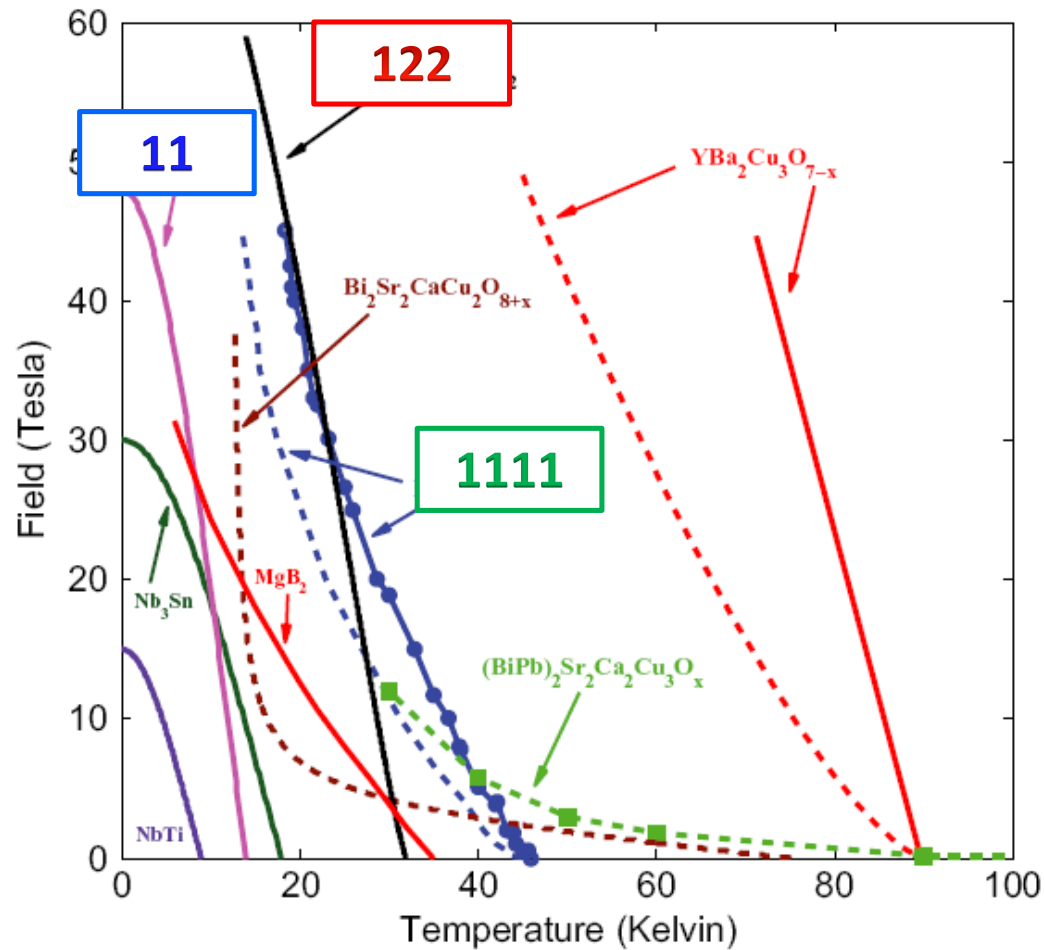
Fe(TeSe)



- ✓ Slope -50 T/K
- ✓ Anisotropy 3-1

Putti et al. SUST 23 034003 (2010)

Upper critical Fields



C. Tarantini et al., PRB 84, 184522 (2011)

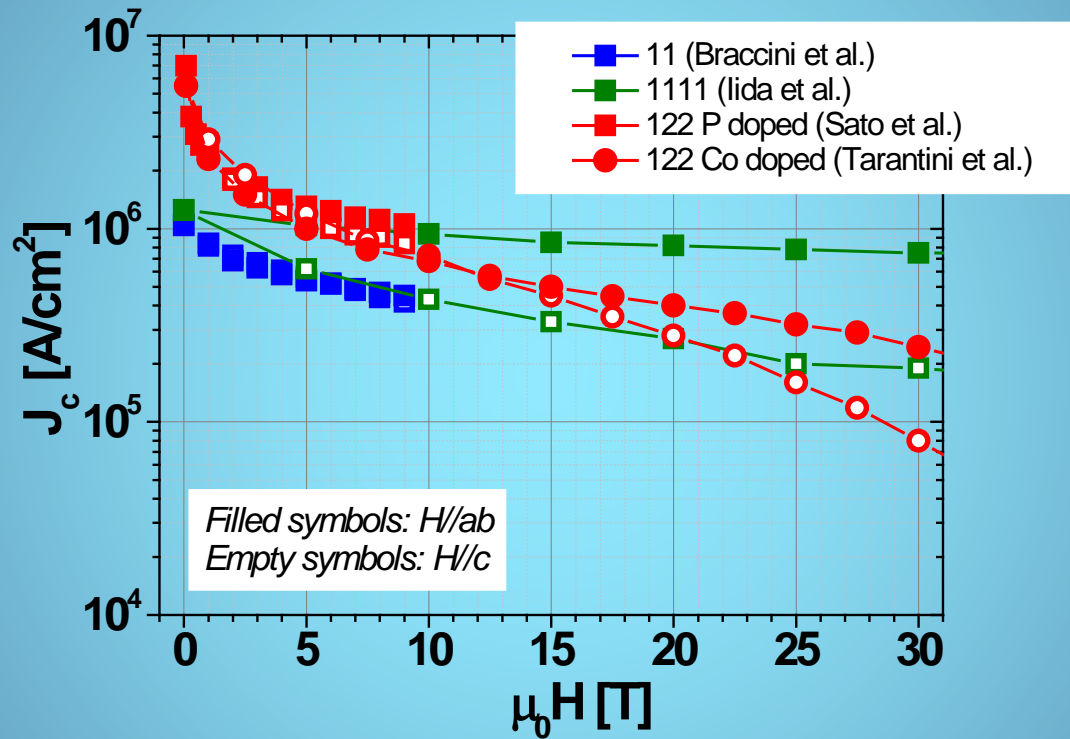
Superconducting parameters

	1111	122	11	YBCO	MgB ₂
T _c [K]	55	38	16	93	39
B _{c2} (0) [T]	>50	60	55	>50	20-30
ξ _{ab} [nm]	2.5	3	1.5	2.2	10
γ _H	5	2	2-3	4-14	3-5
λ _{ab} (nm)	200	200	490	180	50-100
Ginzburg number G _i	4·10 ⁻⁴	2·10 ⁻⁵	1·10 ⁻³	>10 ⁻³	<10 ⁻⁵
pairing	Not BCS	Not BCS	Not BCS	Not BCS	BCS

Several similarities with HTS :

High H_{c2}, small coherence length, unconventional pairing
 but, *lower anisotropy*

Critical current of thin films



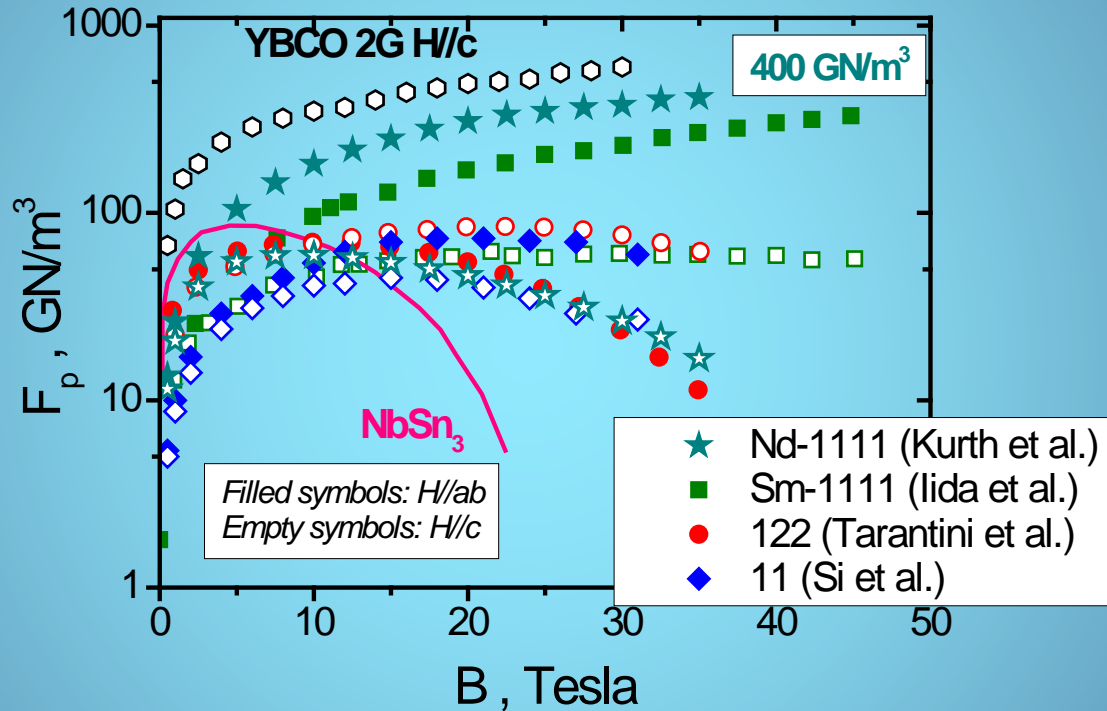
V. Braccini, *APL* 103, 172601 (2013)

Iida, *Sci. Rep.* 3:2139 (2013)

Tarantini et al., *Sci. Rep.* 4, (2014).

Sato et al., *Applied Physics Letters* 104, 182603 (2014);

Pinning Force



Kurth et al., EUCAS 2015

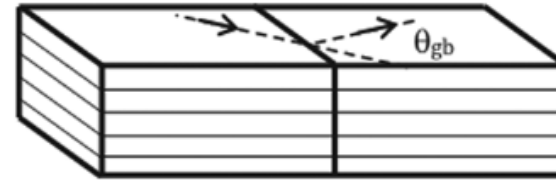
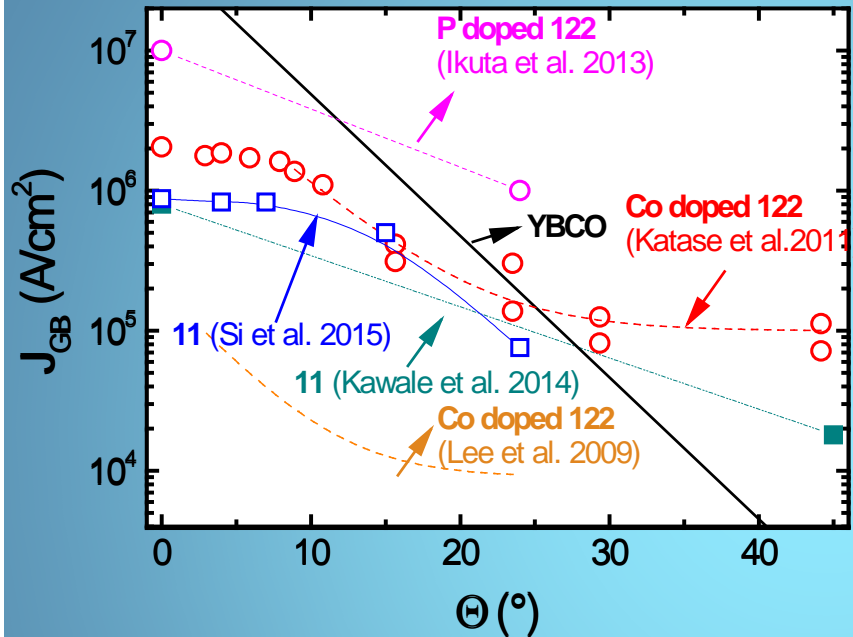
Iida, Sci. Rep. 3:2139 (2013)

Tarantini et al., Sci. Rep. 4, (2014).

Sato et al., Applied Physics Letters **104**, 182603 (2014)

Si, W. et al. Nat. Commun. 4:1347 (2013).

Dependence of J_c on the misalignment angle



122 bicrystals

Lee et al., *Appl. Phys. Lett.* 95, 212505 (2009).
Katase et al., *Nat. Commun.* 2, 409 (2011)
Sagakami et al., *Physica C* 494 (2013) 181–184

11 bicrystals

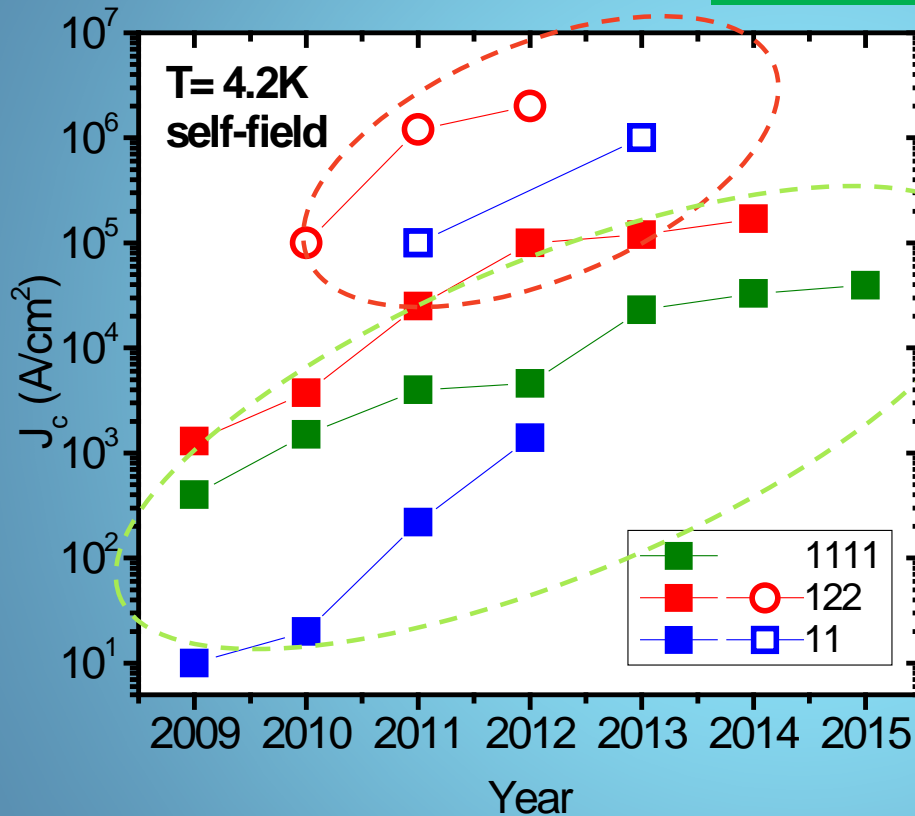
Kawale et al., *ASC* 2014
Si et al., *Appl. Phys. Lett.* **106** 032602 (2015)

In HTS J_c decreases exponentially with GB angle

IBS Advantageous GB over HTS

J_c of technical conductors

Coated Conductors

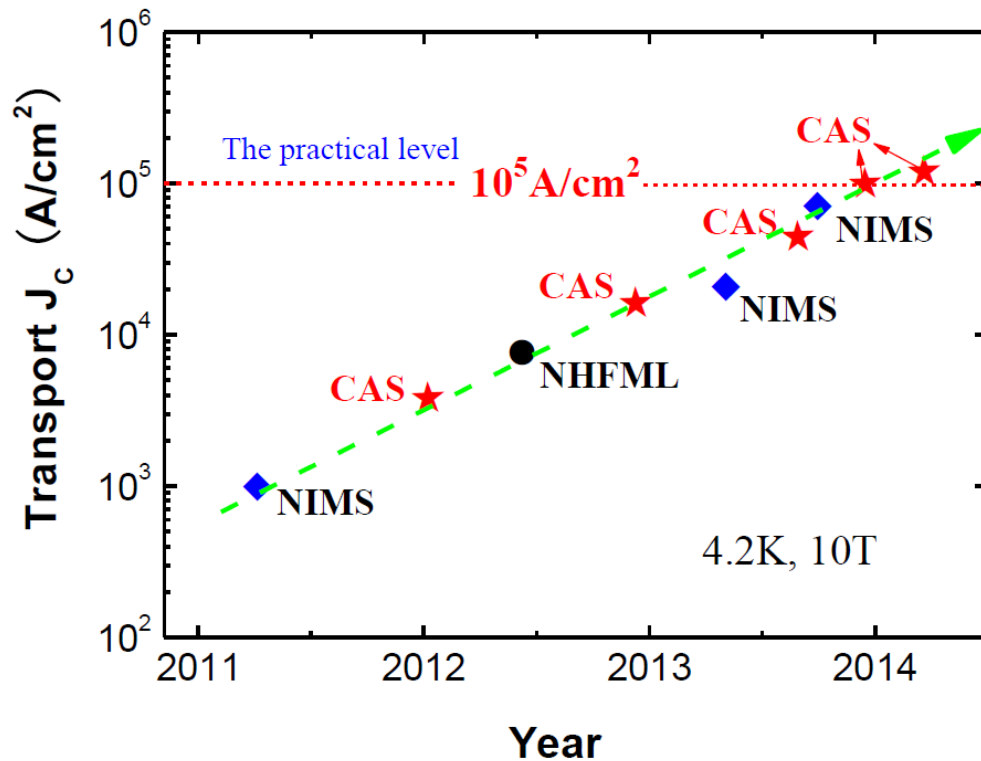


PIT Wires&Tapes

- ➔ Improving the phase purity
- ➔ Controlling the mechanical processes
- ➔ Increasing the density by HP

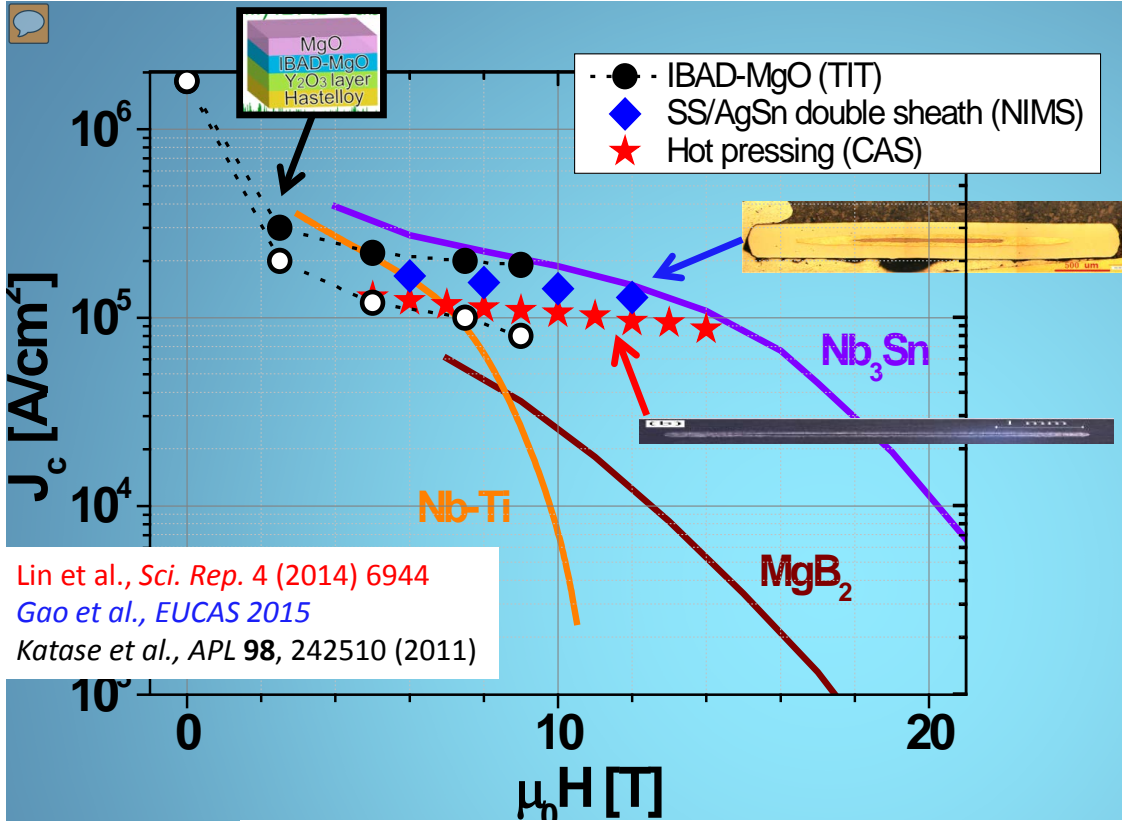
I.Pallecchi et al, SUST (2015) 28

PIT processed 122 wires & tapes



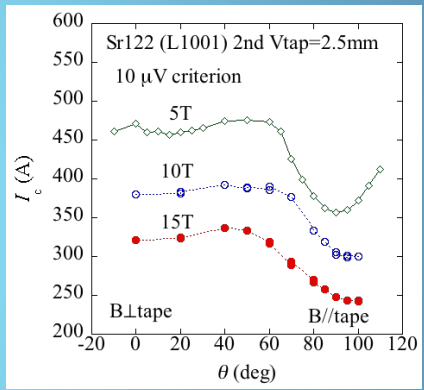
2015
◆ $1.4 \times 10^5 A/cm^2$
NIMS

Y. Ma, Physica C 516 (2015) 17-26



122 tapes

Jc anisotropy
 Awaji EUCAS2015



Lin et al., *Sci. Rep.* 4 (2014) 6944
 Gao et al., *EUCAS 2015*
 Katase et al., *APL* 98, 242510 (2011)

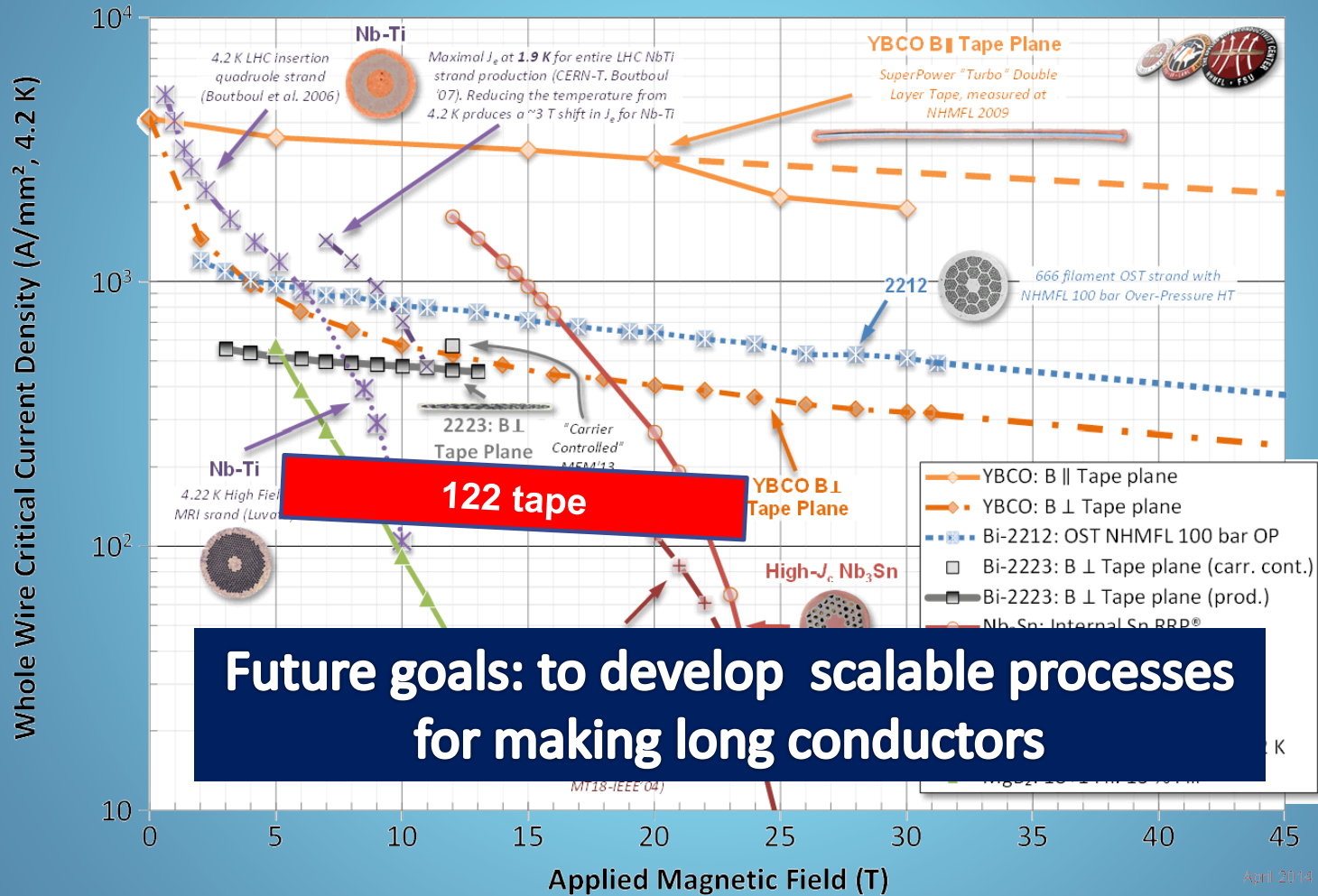
Courtesy: Y.Ma CAS

Effect of strain

11 m tape

2x10⁴ A/cm²

Engineering critical current



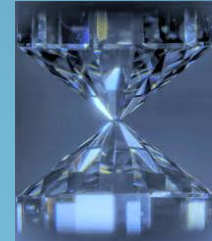
Sulfur hydride systems-brief story

Always Hydrogen has been the best candidate **for room temperature superconductivity** but it need extremely high pressure to become **metallic**.

1) Improvement of diamond anvil cells (DAC) which today allows to reach 600 Gpa exceeding the pressure in the Earth's inner core (360 GPa).

Several new elements superconducting under pressure discovered in the last 15 years: **Sulfur (17 K)**, **Oxygen 0.6 K** , Iron (1.2 K) , **Boron (11 K)**, **Lithium (20 K)**, Europium (2.5 K).

Dense **hydrogen has been made conductive** at around 300 Gpa.



2) Discovery of MgB₂ which clarifies that high T_c superconductivity is promoted by covalent bonds which assure strong electron–phonon coupling.

These conditions can be fulfilled for covalent compounds dominated by hydrogen
N.W. Ashcroft (Hydrogen Dominant Metallic Alloys: High Temperature Superconductors? *Phys. Rev. Lett.* 92, 187002 (2004).

Ashcroft's idea was supported in numerous calculations predicting high values of T_c for many hydrides. So far only T_c ~17 K has been observed experimentally **in silane under pressure**.

The discovery of superconductivity **190 K in H₂S** has been posted on [arXiv.org](https://arxiv.org) in December 2014 by the Eremet's group. **They have done the giant leap**.

Conventional superconductivity at 203 Kelvin at high pressure in the sulfur hydride

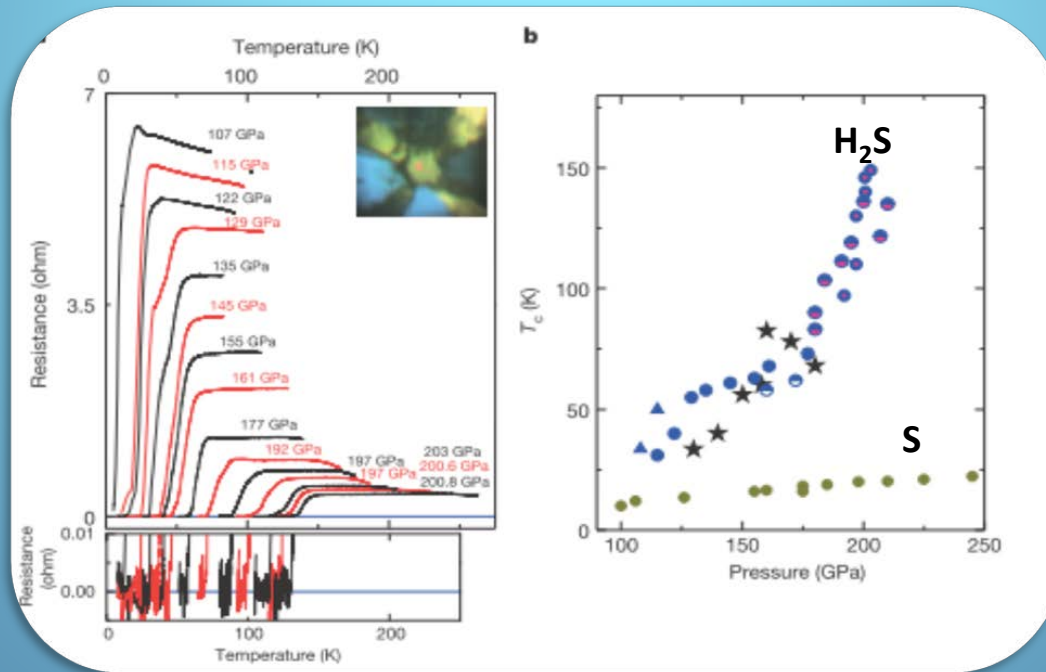
A.P. Drozdov, M.I. Erements I. A. Troyan, V. Ksenofontov, S. I. Shylin
Nature published 17 August 2015, doi: 10.138/Nature 14964

H₂S: relatively easy to handle and predicted to transform to a metal and a superconductor at a low pressure $P < 100$ GPa with a high $T_c < 80$ K

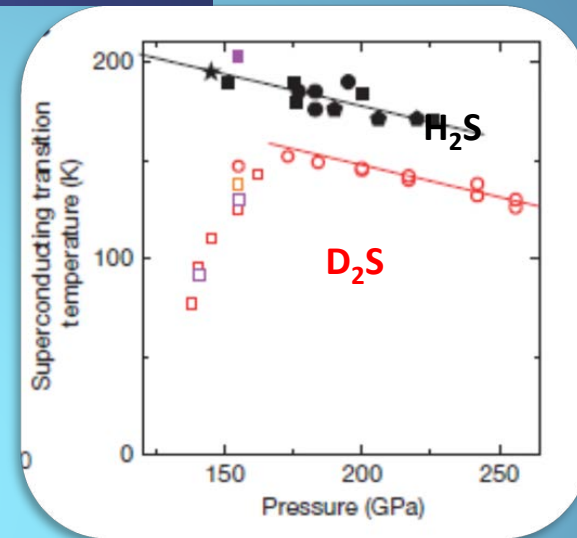
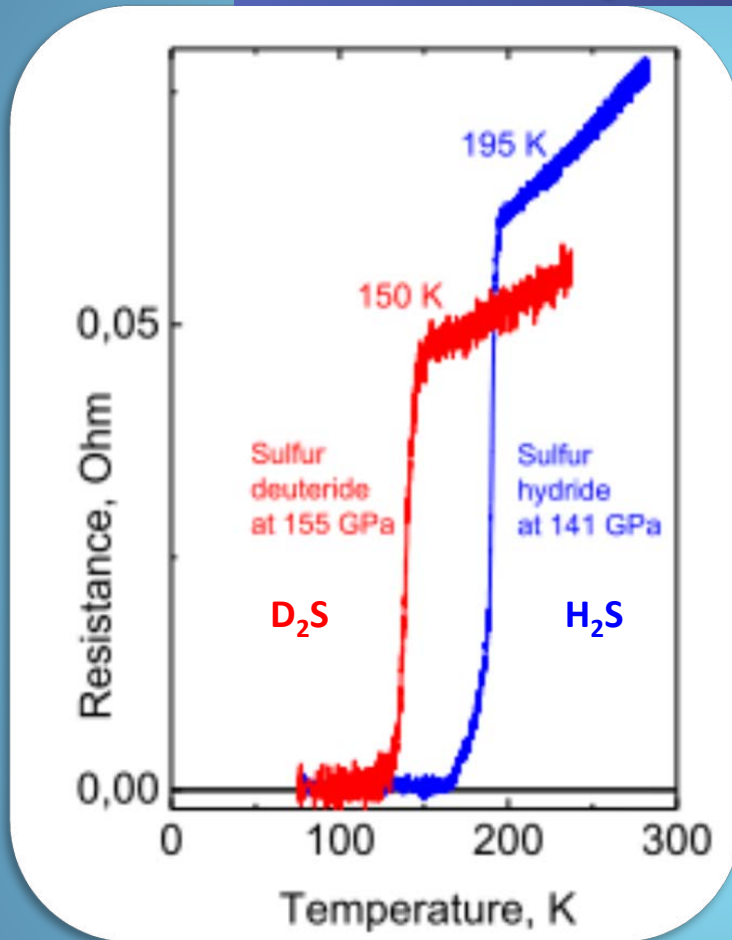
Li et al, J. Chem. Phys. 140, 174712 (2014).

Further investigations has indicated that at experimentally relevant pressures H₂S is unstable, decomposing into **H₃S** and **S**.

PRB 91, 060511(R) (2015)].



Isotopic effect



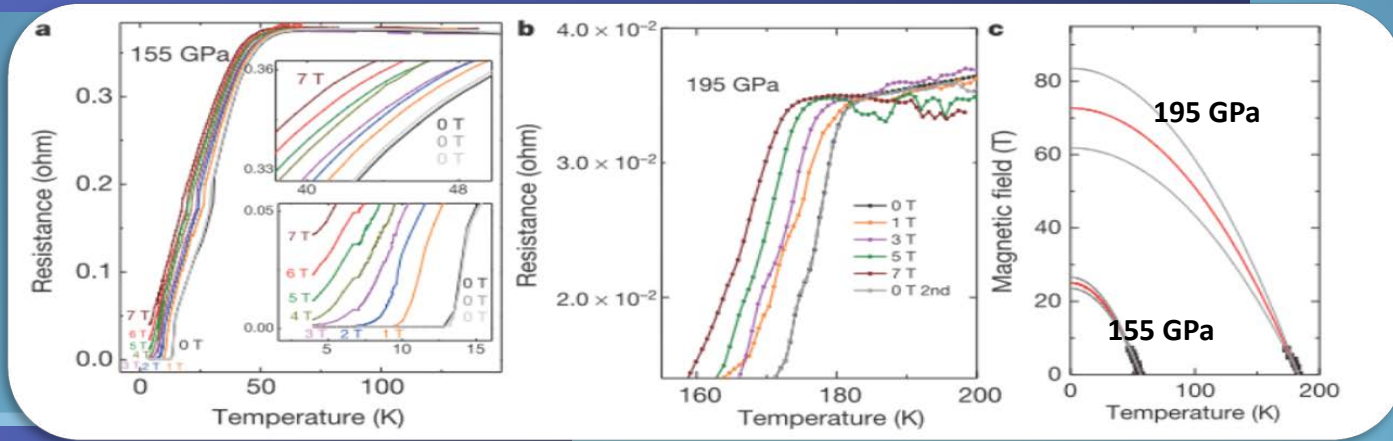
$$T_c \propto M^{-\alpha}$$



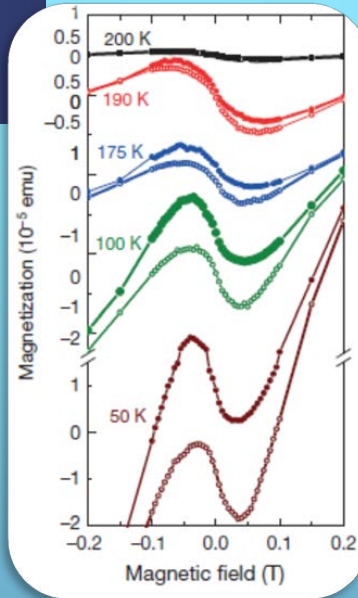
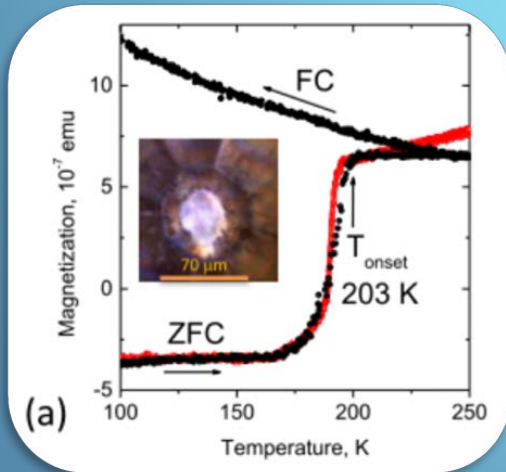
$$\alpha \sim 0.3$$

BCS superconductor

Electrical characterization



Magnetic characterization



**Type II
superconductor**

$B_{c2}(0) \sim 70 \text{ T}$

$B_{c1}(0) \sim 30 \text{ mT}$

Superconducting parameters

	H₃S	IBS-122	YBCO	MgB₂
T_c [K]	200	38	93	39
B_{c2} (0) [T]	70	60	>50	20-30
ξ [nm]	2.5	3	2.2	10
B_{c1} (0) [mT]	30	40	20	100
λ_{ab} (nm)	125	200	180	50-100
Ginzburg number G_i	10⁻³	2·10⁻⁵	>10⁻³	<10⁻⁵
pairing	BCS	Not BCS	Not BCS	BCS

Conclusion

- ◆ Another step towards achieving superconductivity at room temperature has been done.
- ◆ The myth that BCS superconductors can not be a high temperature superconductor has been debunked.
- ◆ There are many hydrogen-containing materials with strong covalent bonding (such as organics) but typically they are insulators.
- ◆ In principle, they could be tuned to a metallic state by doping or gating. High power available ab-initio calculation method could facilitate exploration for the desired High T_c materials.

Many thanks to all the colleagues and friends who helped me in the present talk

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12th European Conference
on Applied Superconductivity
6th - 10th September 2015 Lyon - France

Thank you for your attention