

# HTS-Materialien - Grundlagen -

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- „Need to know“ über Supraleitung
- HTS-Materialklassen
- Materialeigenschaften
- Herstellungstechnologien

# Leibniz Institute for Solid State and Materials Research Dresden

- ▶ Budget: about 20 Mio. € per year (50 % Federal Government, 50% State of Saxony)
- ▶ Additional project funding from public and industrial sources: about 6.5 Mio. € per year
- ▶ staff: 400, including 130 scientists, 70 PhD students



*Institute's Mission :*  
*Fundamental and applied research and development*  
*in the fields of solid state and materials research*

## Superconductivity & superconductors

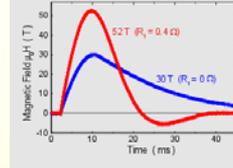


Fermisurface mapping reveals electronic structure of high-temperature superconductors

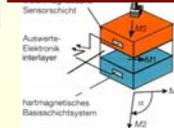


World record 2001: 16 Tesla in superconducting permanent magnets

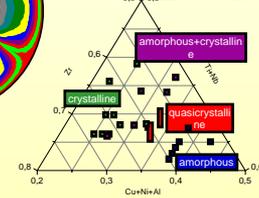
Measurements in high magnetic fields



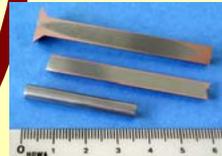
## Magnetisms & Magnetic Materials



Phase diagram of the system Zr-Ti-Nb-Cu-Ni-Al.

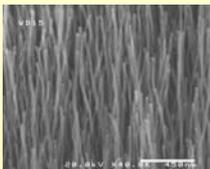


## Metastable Alloys

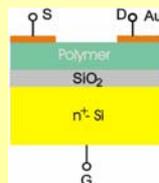
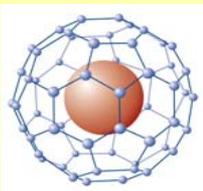


Extruded powder samples encapsulated in Cu-cans

## Conjugated Carbon Systems



Aligned carbon nanotubes for applications in displays

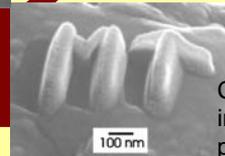
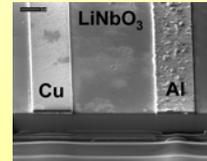


Organic field effect-transistors



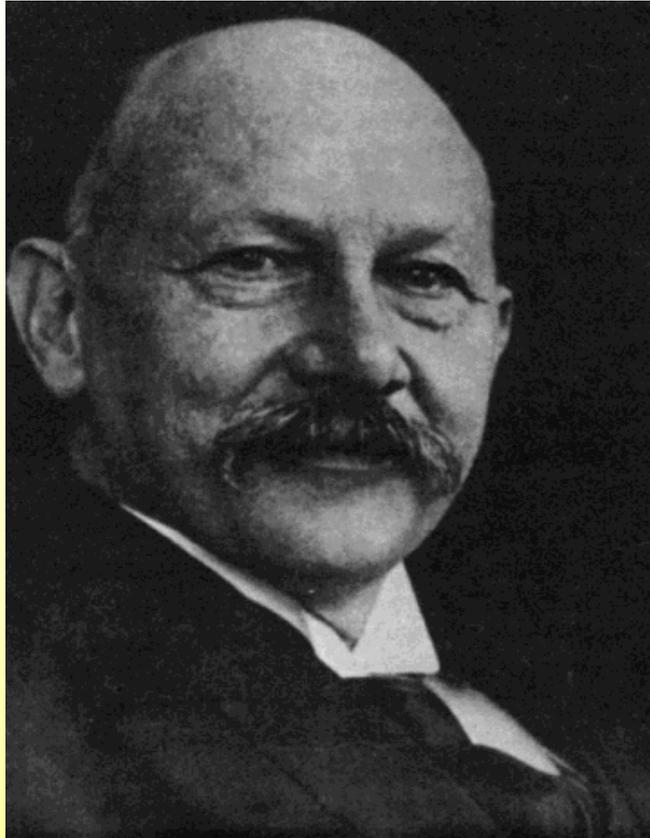
## Thin Film Systems for Electronics

Cu-technology for SAW components

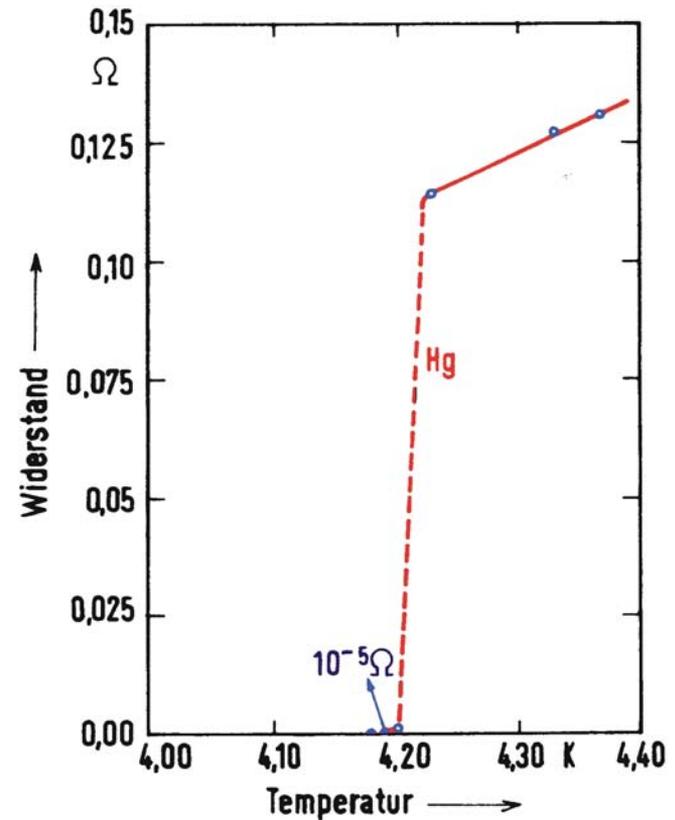


Conducting imprint stamp for parallel nanolithography

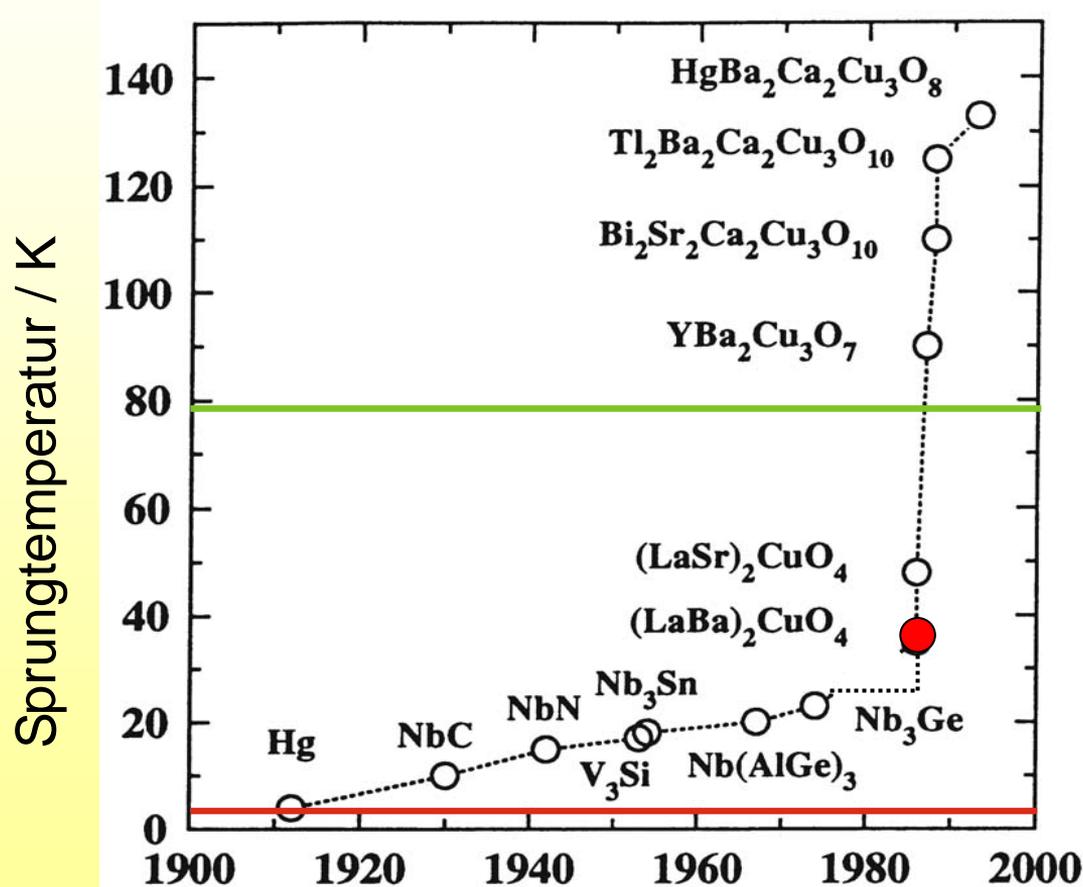
- $R = 0$
- Cooper Paare
- Idealer Diamagnetismus (Meissner-Ochsenfeld)
- Typ I - TypII Supraleiter
- Pinning



Heike Kamerlingh Onnes  
Physik-Nobelpreis 1913



# Entwicklung der Sprungtemperatur

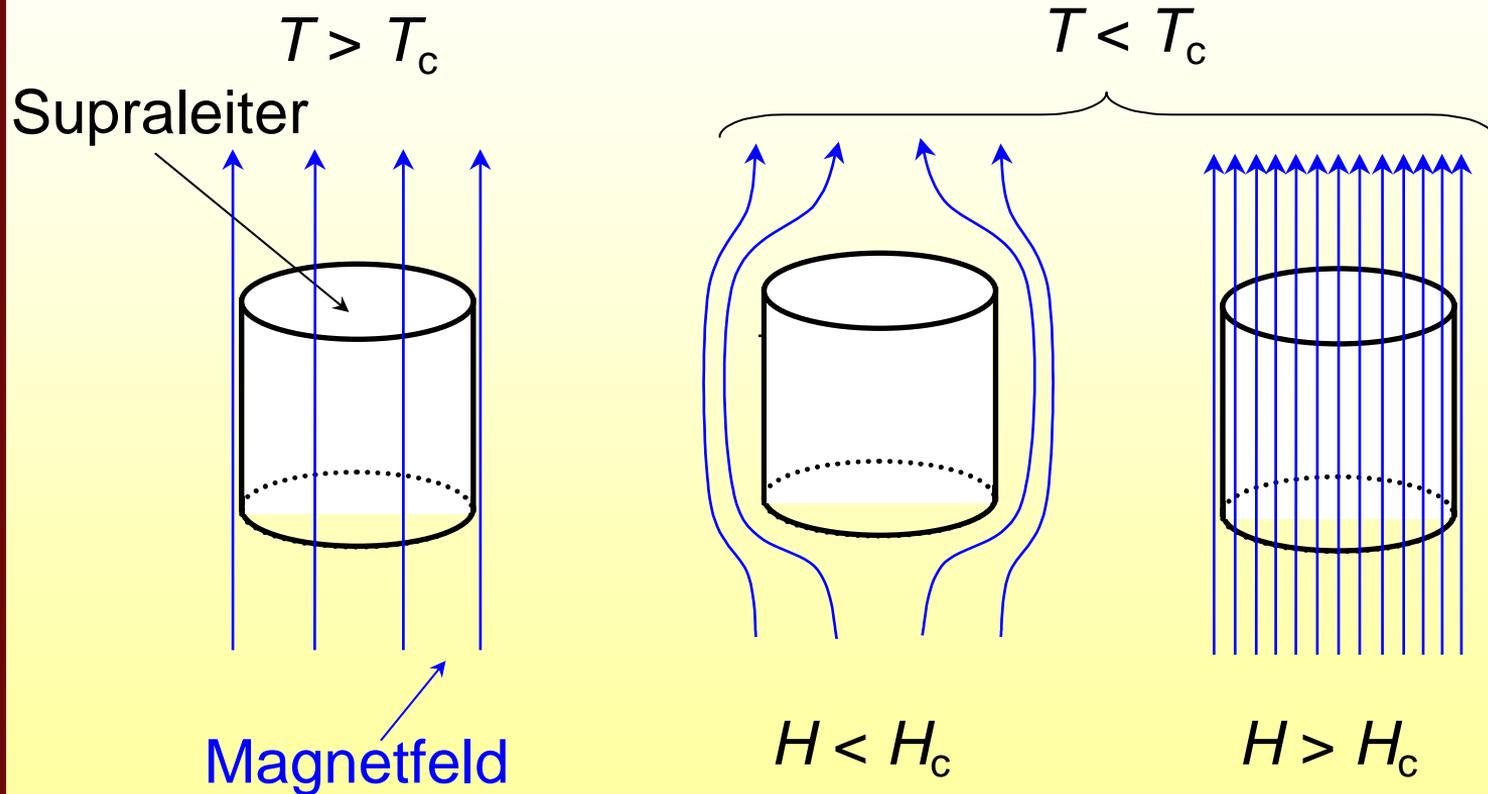


**N<sub>2</sub>: 77 K**

1. Hochtemperatur-Supraleiter 1986  
(Bednorz und Müller)  
➔ Nobelpreis 1987

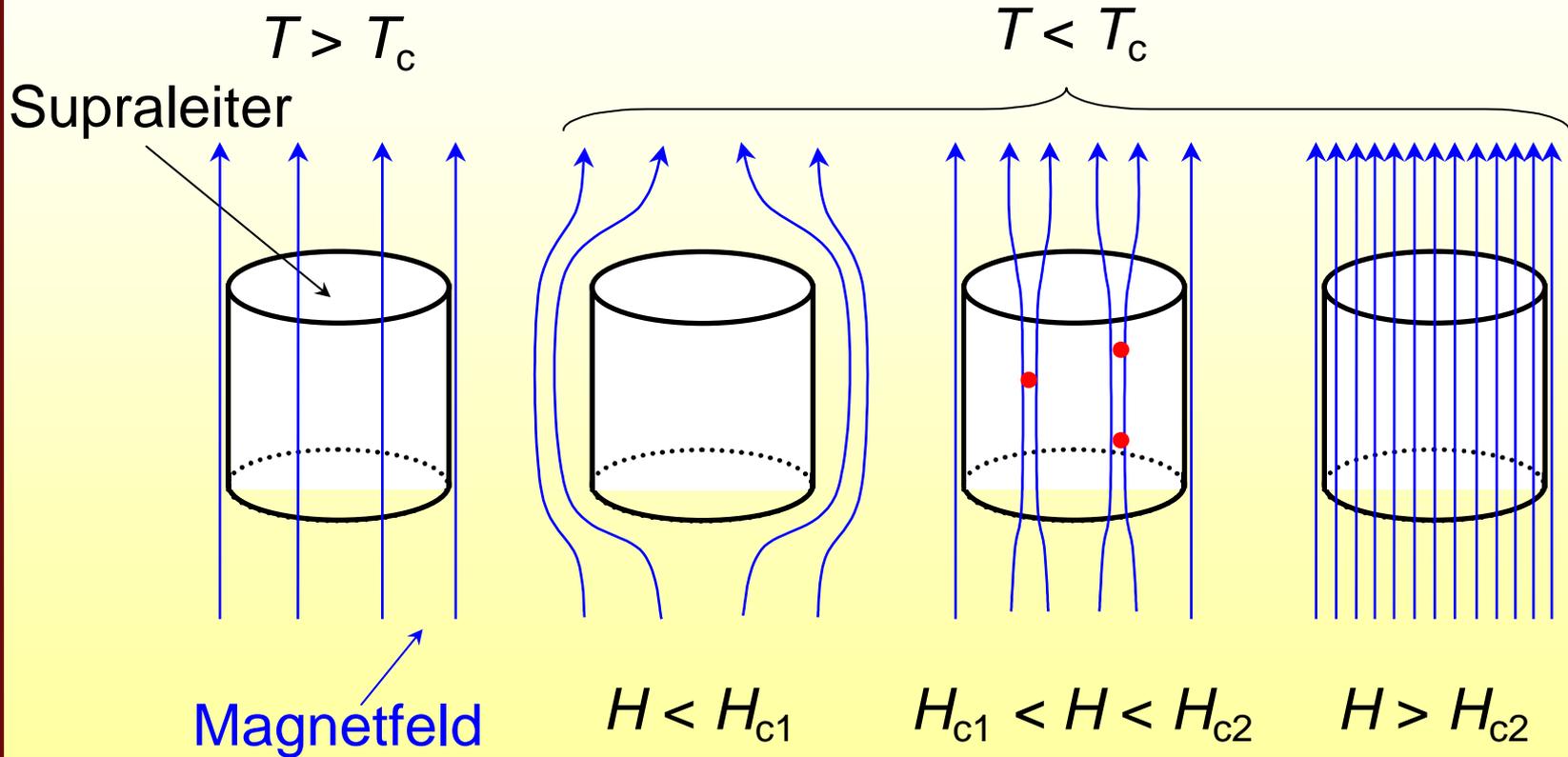
**He: 4.2 K**

- ***Elektrischer Widerstand:***  
Streuung der Elektronen am Atomgitter  
(Umbesetzung der Quantenzustände)
- ***Widerstandsfreier Ladungstransport (Supraleitung)***  
Energieaustausch der Elektronen mit dem Gitter über Streuung verhindern!  
(obwohl freie Quantenzustände vorhanden sind)  
Voraussetzung: Elektronen in gebundenen Zustand bringen
- ***Wechselwirkung zwischen Elektronen über Gitterschwingungen***  
„Cooper-Paare“



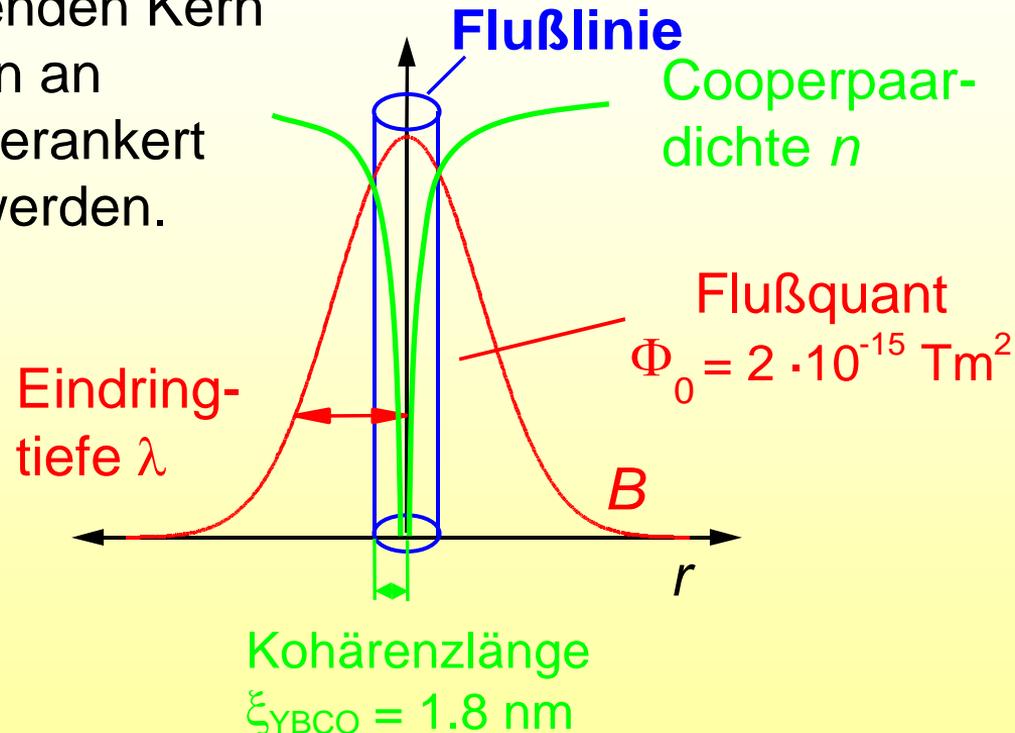
Meissner-Ochsenfeld Effekt

# Typ-II Supraleiter im Magnetfeld



# Der harte Typ-II Supraleiter im Magnetfeld

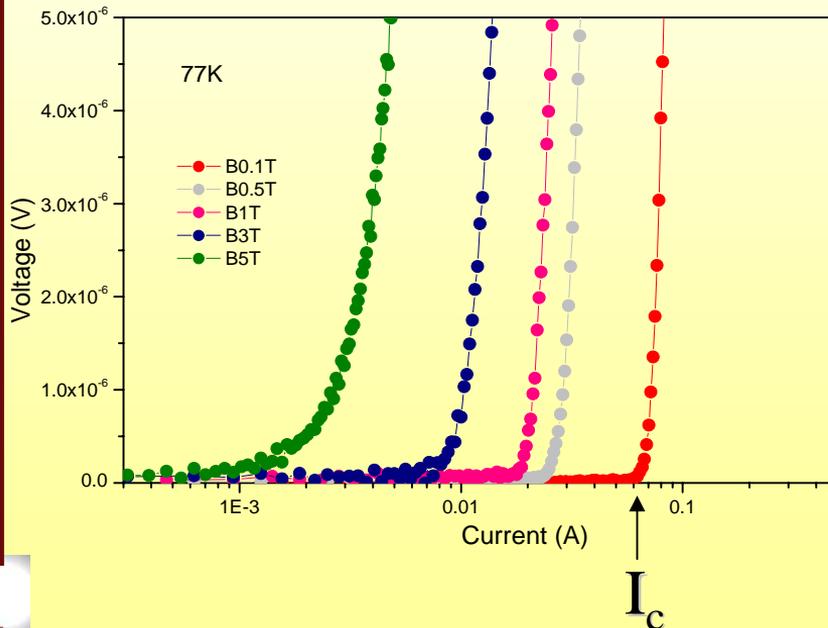
- Flußlinien besitzen normaleleitenden Kern und können an Defekten verankert (gepinnt) werden.



$$J_e = I_c / (A^{SL} + A^{NL}) \left\{ \begin{array}{l} A^{SL} \\ A^{NL} \end{array} \right\} J_c = I_c / A^{SL}$$

$J_c$  : Kritische Stromdichte

$J_e$  : Gesamtstromdichte



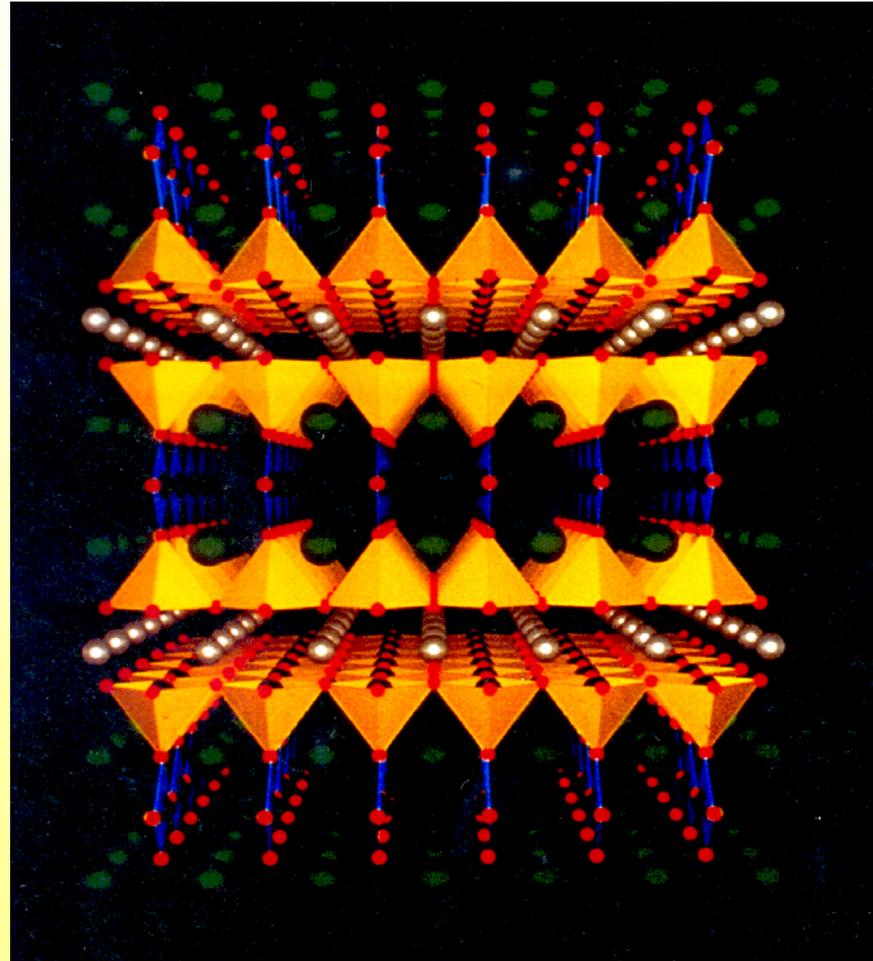
↪  $J_c$  ist magnetfeld- und temperaturabhängig :  $J_c(B,T)$

- $R=0$  für  $T < T_c$
- $B < B_{c1}$ : Abschirmung eines äußeren Magnetfeldes  
(Meissner-Ochsenfeld Effekt)
- $B_{c1} < B < B_{c2}$ : Eindringen des Magnetfeldes in Form von Flußfäden  
(Typ II-Supraleiter)
- Pinning von Flußfäden an Defekten
- Verlustfreier Stromtransport ( $I_c, J_c, I_e$ ) nur bei Pinning

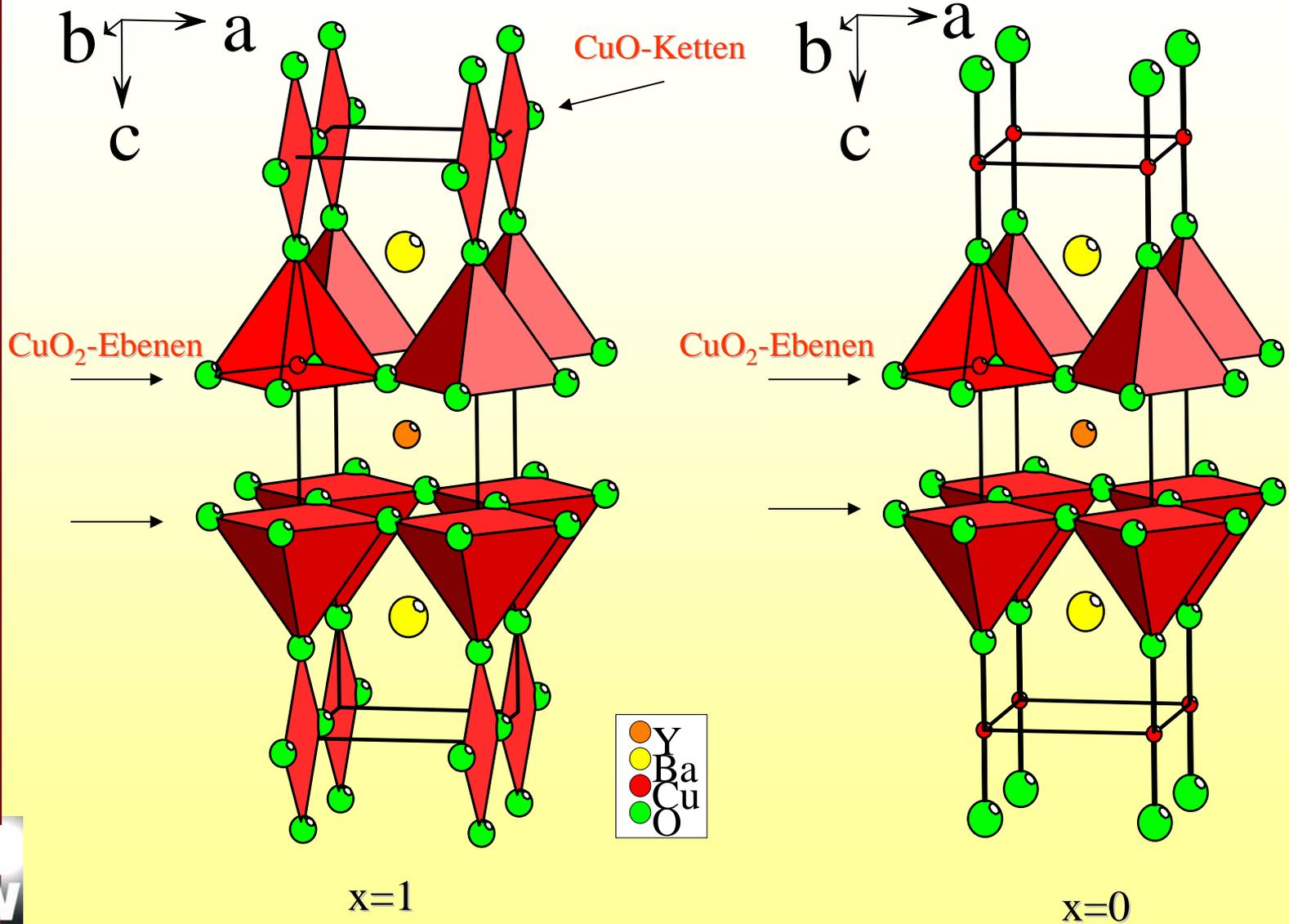
HTS Materialklassen

Materialeigenschaften

Herstellungstechnologien



# Die $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Kristallstruktur

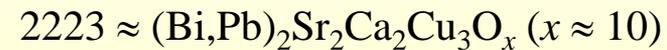
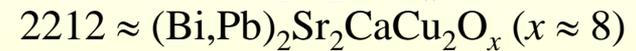
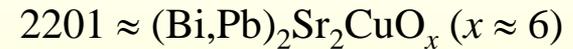
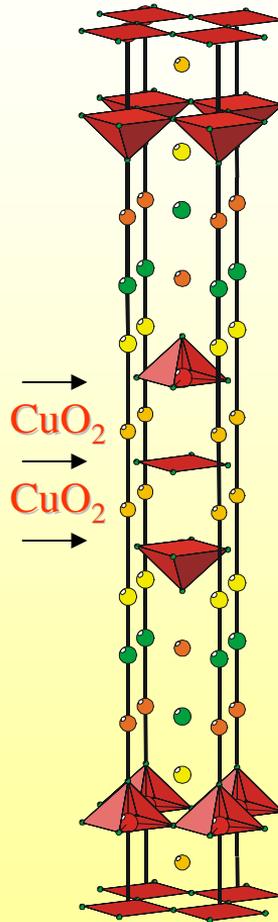
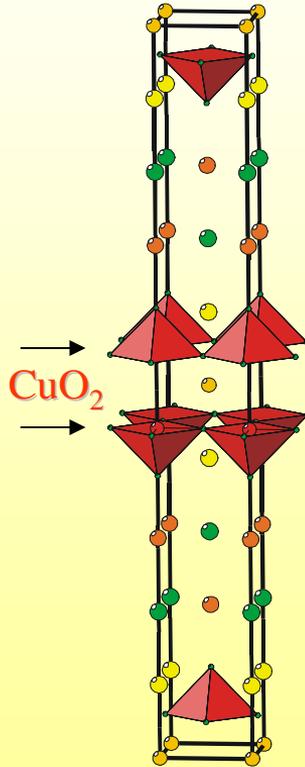
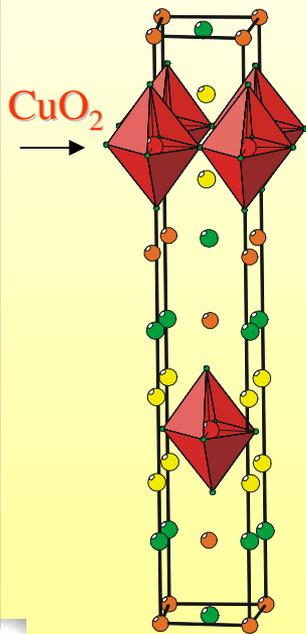


# Die $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ -Supraleiterfamilie

Bi(Pb)-2201

Bi(Pb)-2212

Bi(Pb)-2223



Oder auch schlicht

**BSCCO(2223) : 3-Schichten**

**BSCCO(2212) : 2-Schichten**

**BSCCO(2201) : 1-Schichten**



„Need to know“ über Supraleitung

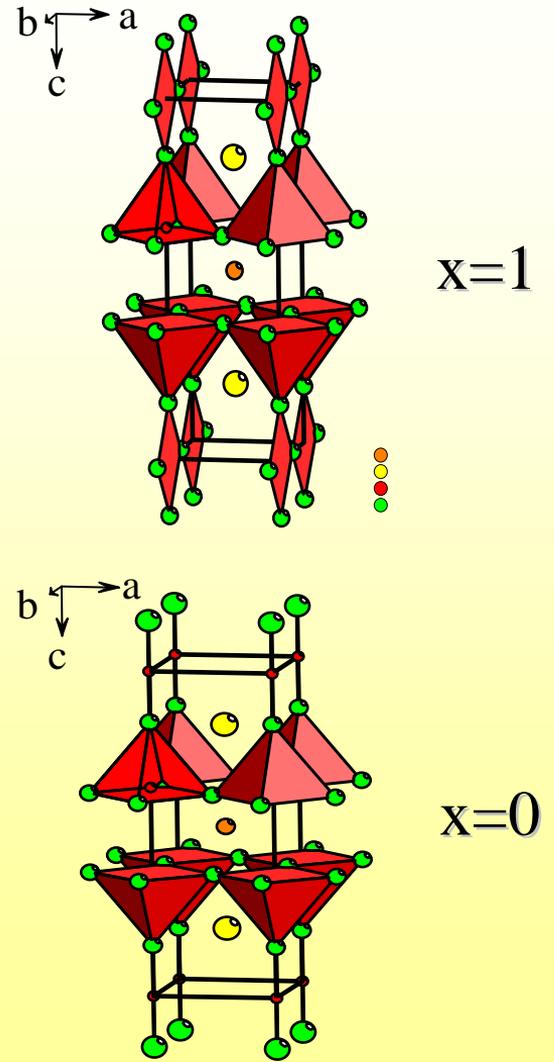
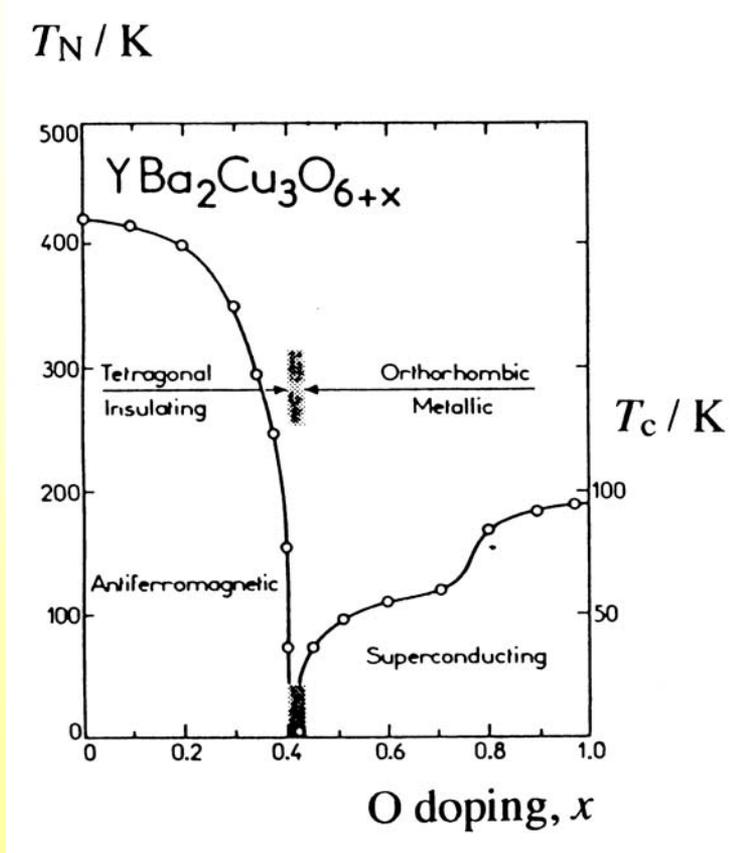
HTS Materialklassen

- $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  bzw.  $\text{REBa}_3\text{Cu}_3\text{O}_{7-\delta}$
- $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$  (BSCCO-2201, -2212, -2223)
- Supraleitung getragen durch  $\text{CuO}_2$ -Ebenen
- Schichtstruktur

Materialeigenschaften

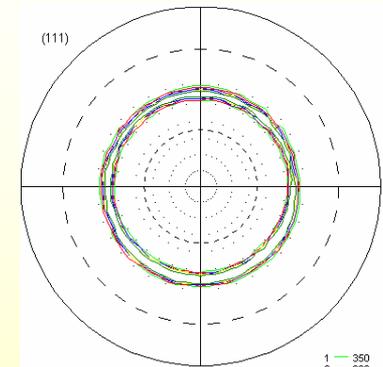
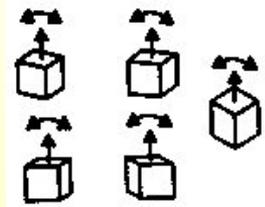
Herstellungstechnologien

# O-Dotierungsabhängigkeit von $T_c$

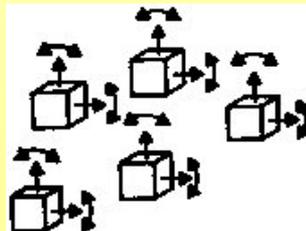


A) Untexturiert : zufällige Orientierung der einzelnen Kristallite

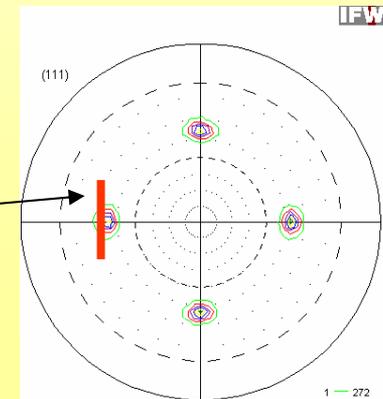
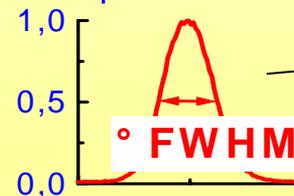
B) Fasertextur : eine kristallographische Richtung  
z.B. (100), aller Kristallite gleich orientiert  
Texturschärfe: c-Achsen-Orientierung



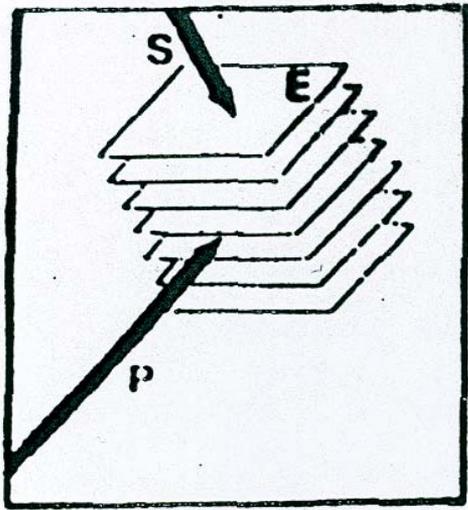
C) Biaxiale Textur : bevorzugte Orientierung der Kristallite  
in allen 3 Raumrichtungen festgelegt  
Texturschärfe: in-plane Orientierung



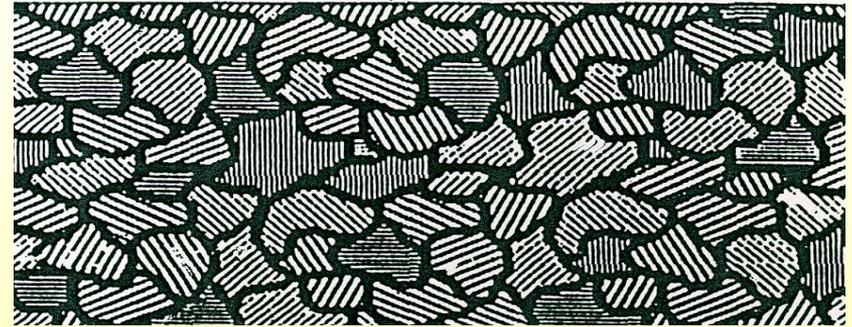
in-plane Textur



# Bedingungen für makroskopischen Stromtransport

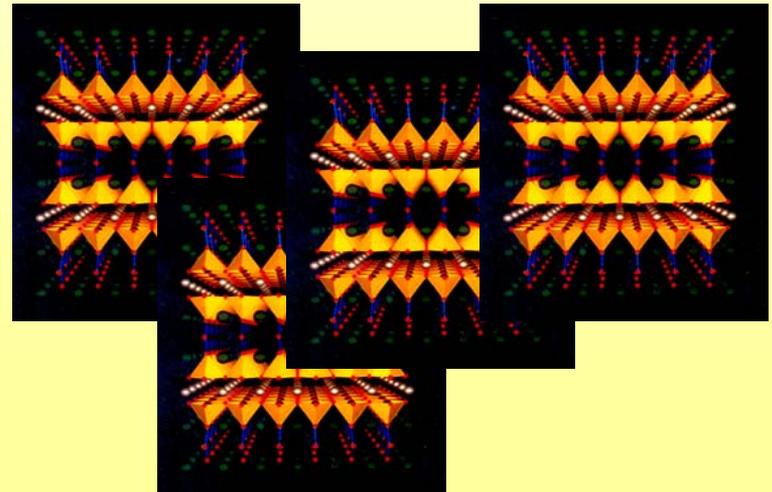


polykristallin, nicht-texturiert:

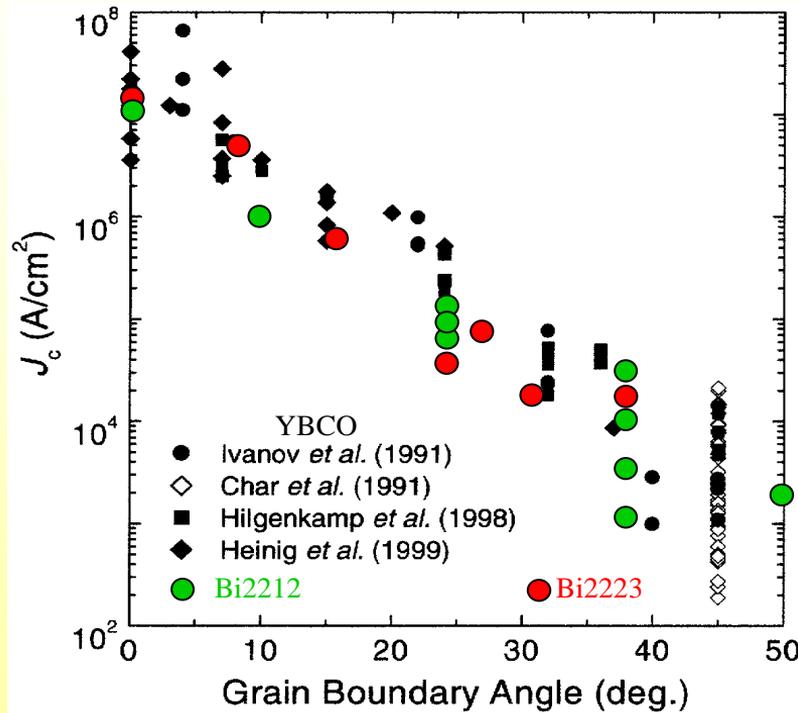


- E: CuO Ebenen
- P: Strom in der Ebene
- S: Strom senkrecht zur Ebene

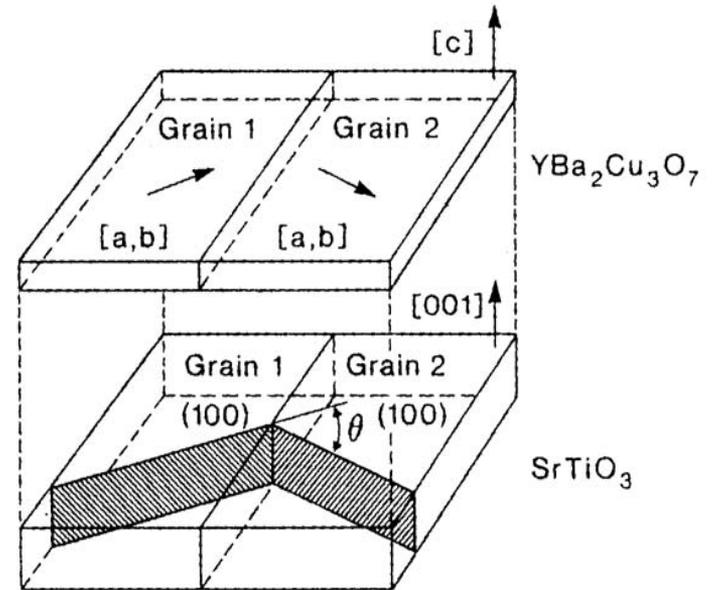
Strom P leichter als S



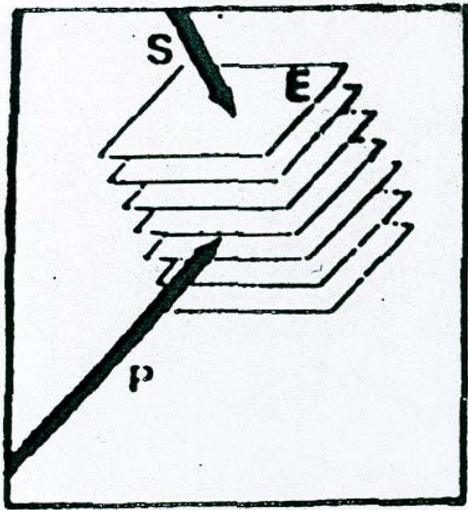
→ **c-Achsen-Textur**



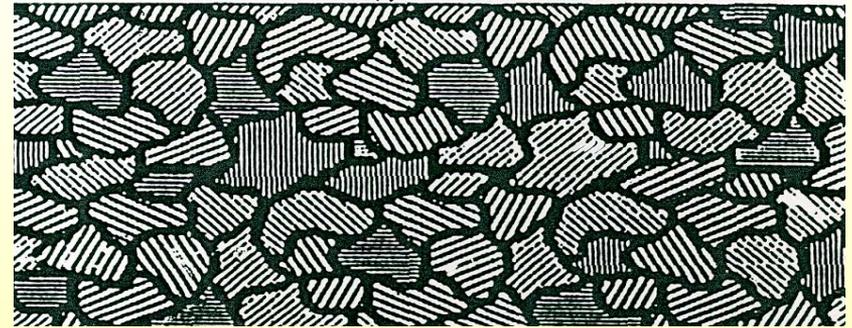
## Bikristallgeometrie



# Bedingungen für makroskopischen Stromtransport

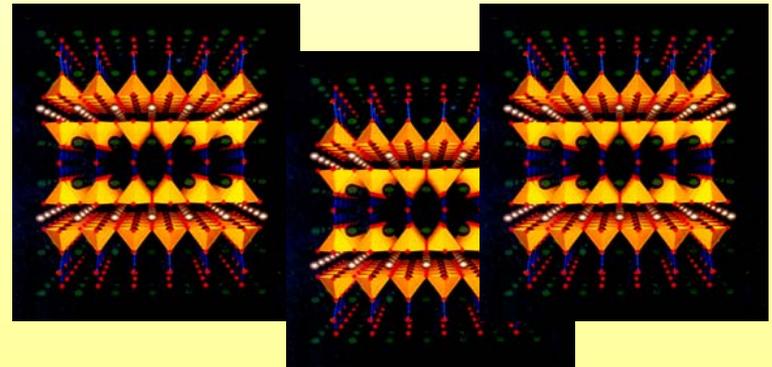


polykristallin, nicht-texturiert:



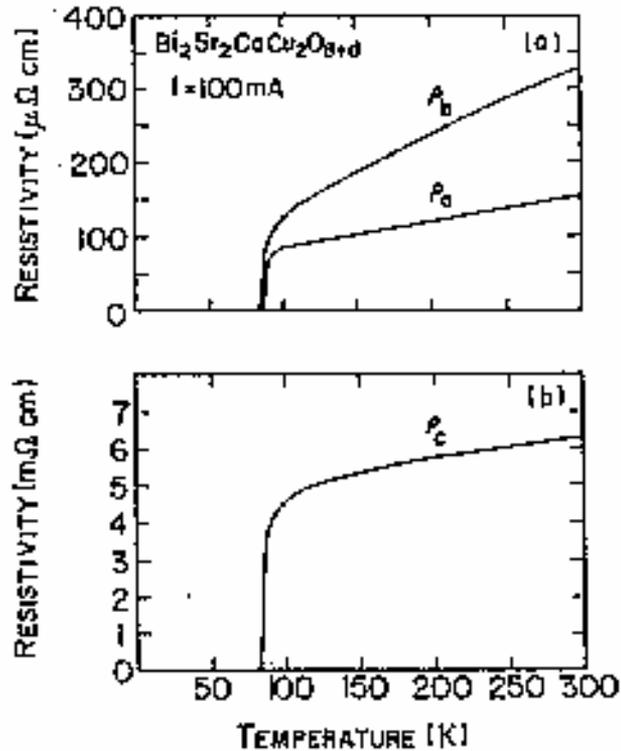
- E: CuO Ebenen
- P: Strom in der Ebene
- S: Strom senkrecht zur Ebene

Strom P leichter als S

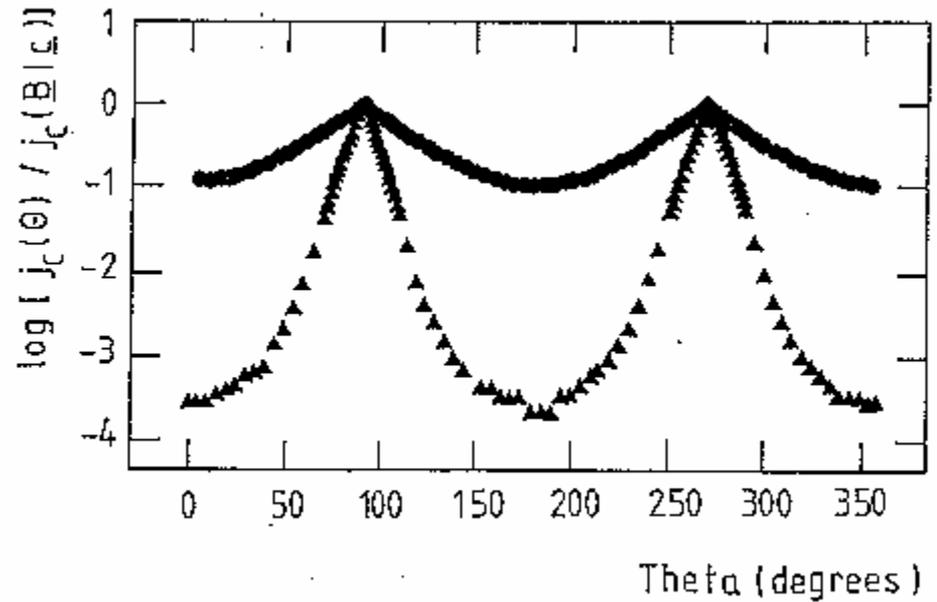


→ **c-Achsen-Textur + in-plane Textur notwendig**

## Widerstand



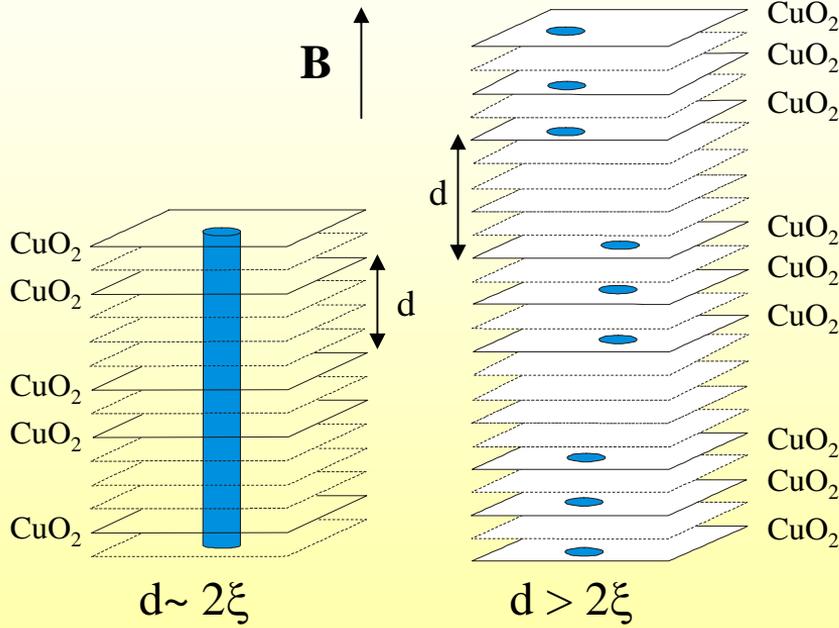
## Kritische Stromdichte



YBCO

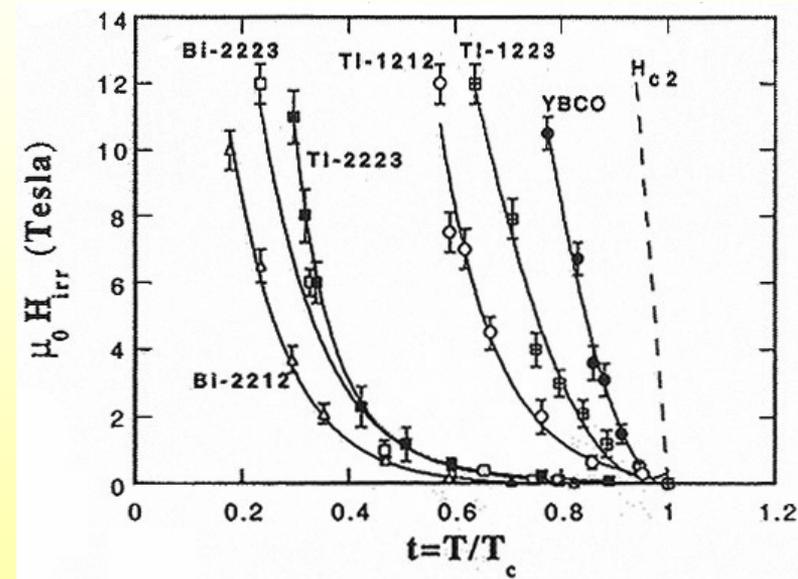
BSCCO-2223

Irreversibilitätsfelder



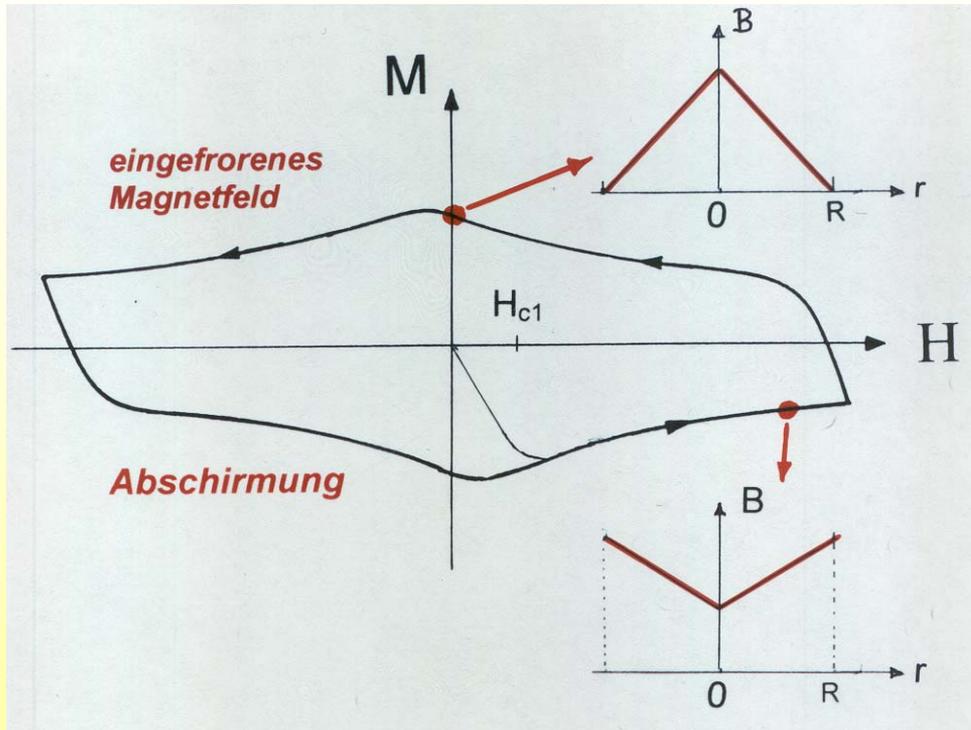
3D Flusslinie

2D *pancake* vortizes



# Typ II Supraleiter im Magnetfeld

## Magnetisierung und Feldprofil

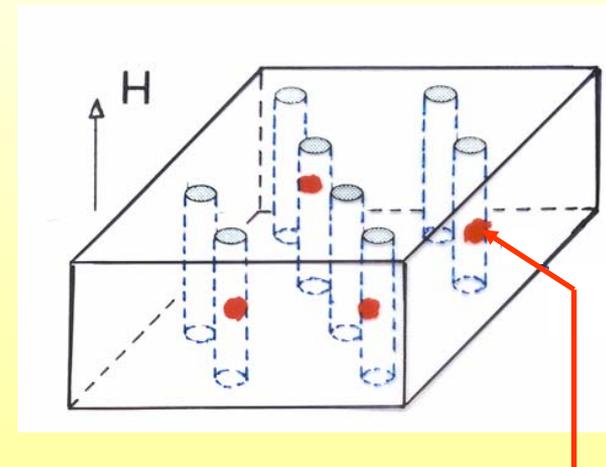


## Flußschläuche und ihre Verankerung

$H > H_{c1}$ :  $\Rightarrow$  Eindringen von Flußschläuchen

$$\Phi_0 = 215 \cdot 10^{-15} \text{ Tm}^2$$

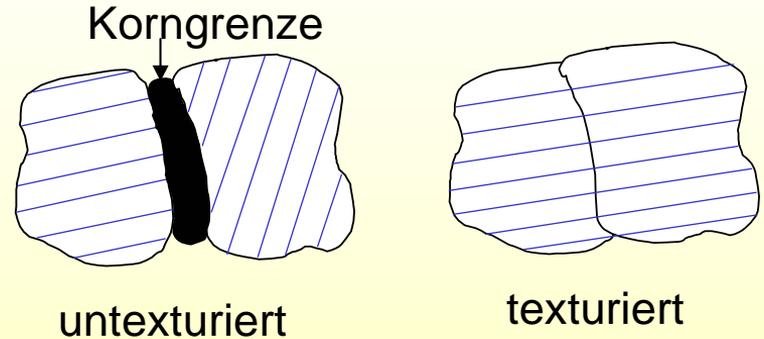
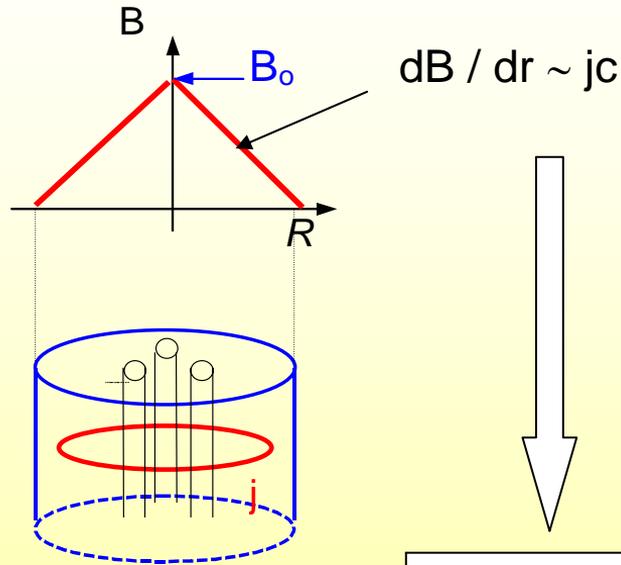
$$\xi = 1,8 \text{ nm}$$



Verankerung der Flußschläuche an Defekten (Pinningzentren)

# Grundlagen hoher Remanenzfelder in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO)

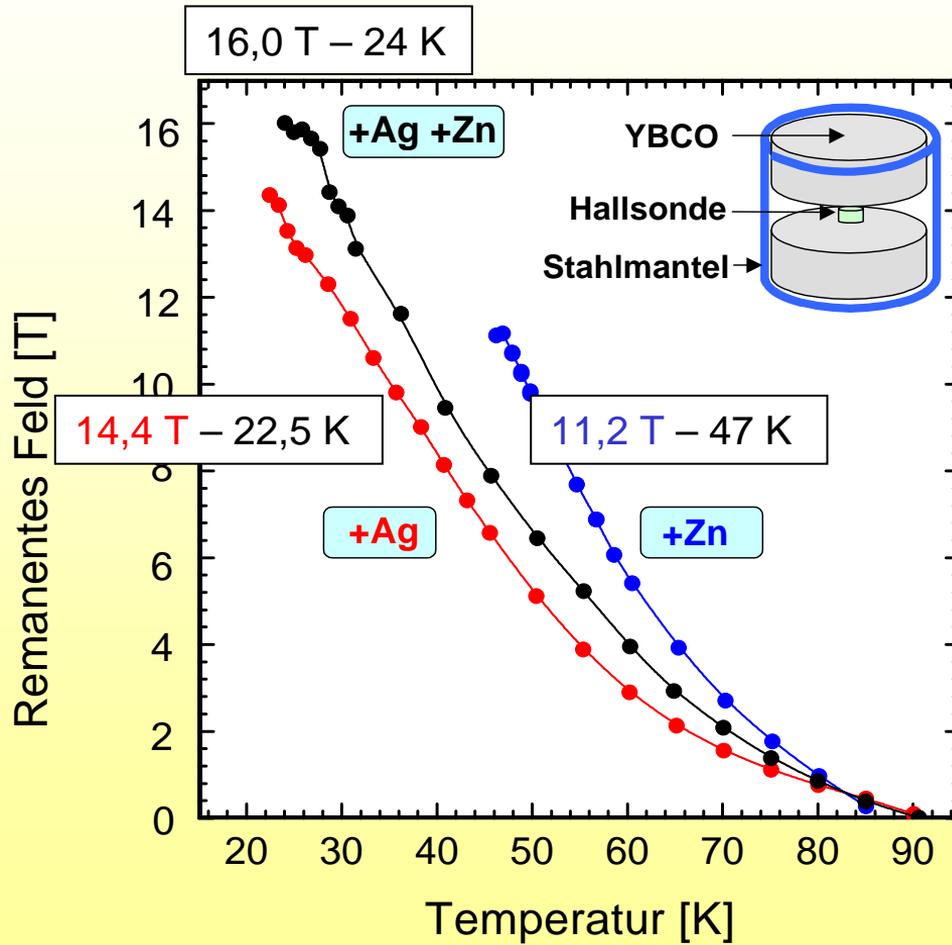
Feldprofil für in Supraleiter eingefrorenes Magnetfeld



$$B_0 \sim j_c R$$

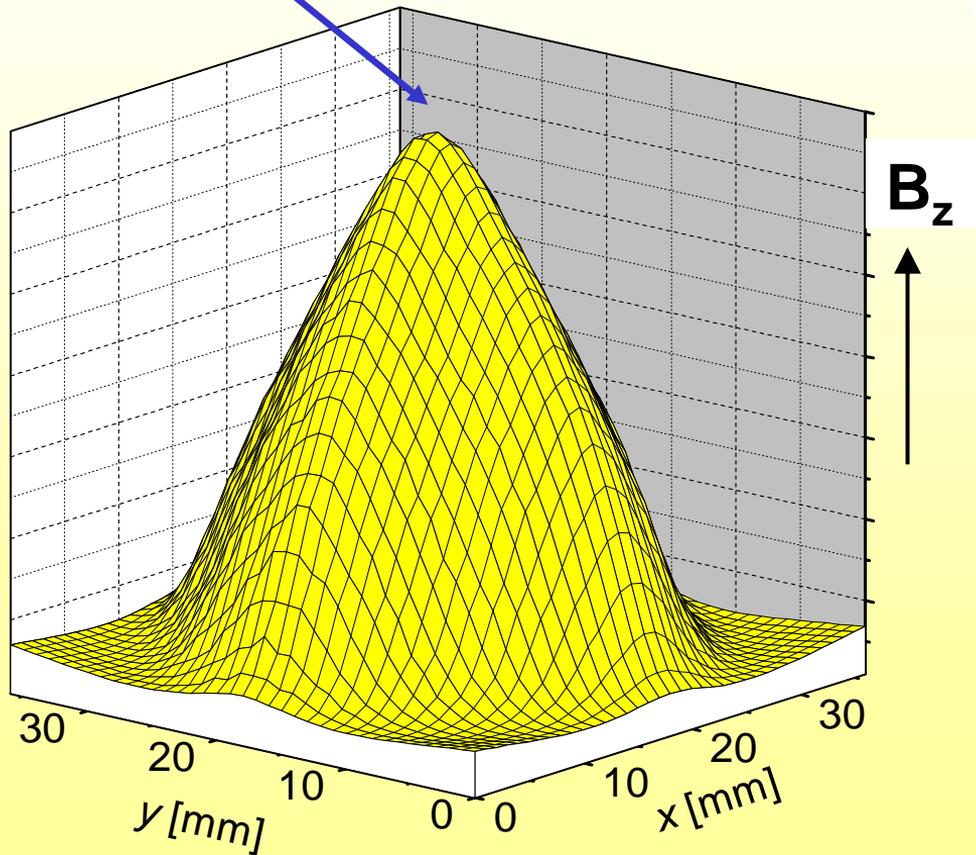
Große Stromschleifen durch c-Achsen-Textur  
(→ Schmelztexturierung)

Pinningwirksame Defektstruktur

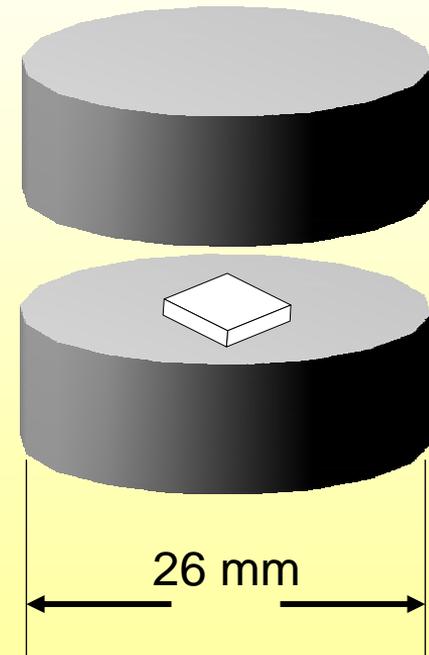


## Eingefrorenes Magnetfeld in YBCO

$B_0 = 16 \text{ T}$  (bei 24K)



*Probengeometrie*





„Need to know“ über Supraleitung

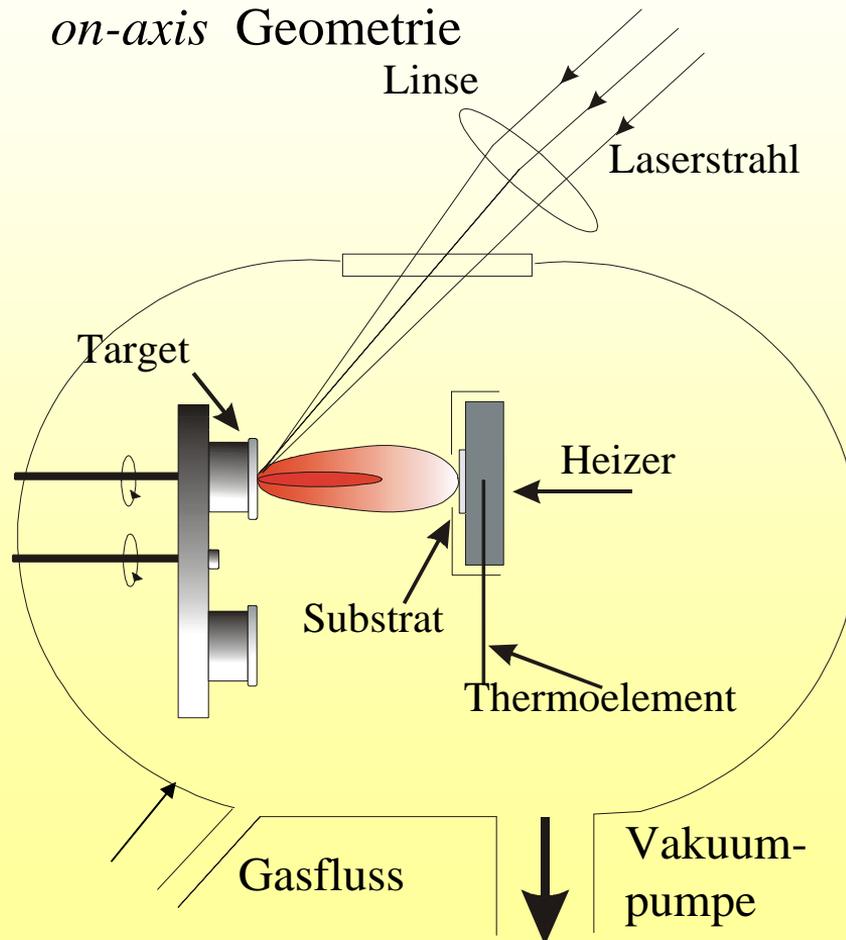
HTS Materialklassen

Material Eigenschaften

- Sauerstoffgehalt bestimmt  $T_c$
- Starke Reduktion der kritischen Stromdichte über Korngrenzen
- Für Hochstromanwendungen nur Kleinwinkelkorngrenzen tolerabel
- BSCCO für Magnetfeldanwendungen bei 77K nicht geeignet
- Durch Pinning werden supraleitende Permanentmagnete möglich

Herstellungstechnologien

z.B. mittels gepulster Laserdeposition  
(PLD)



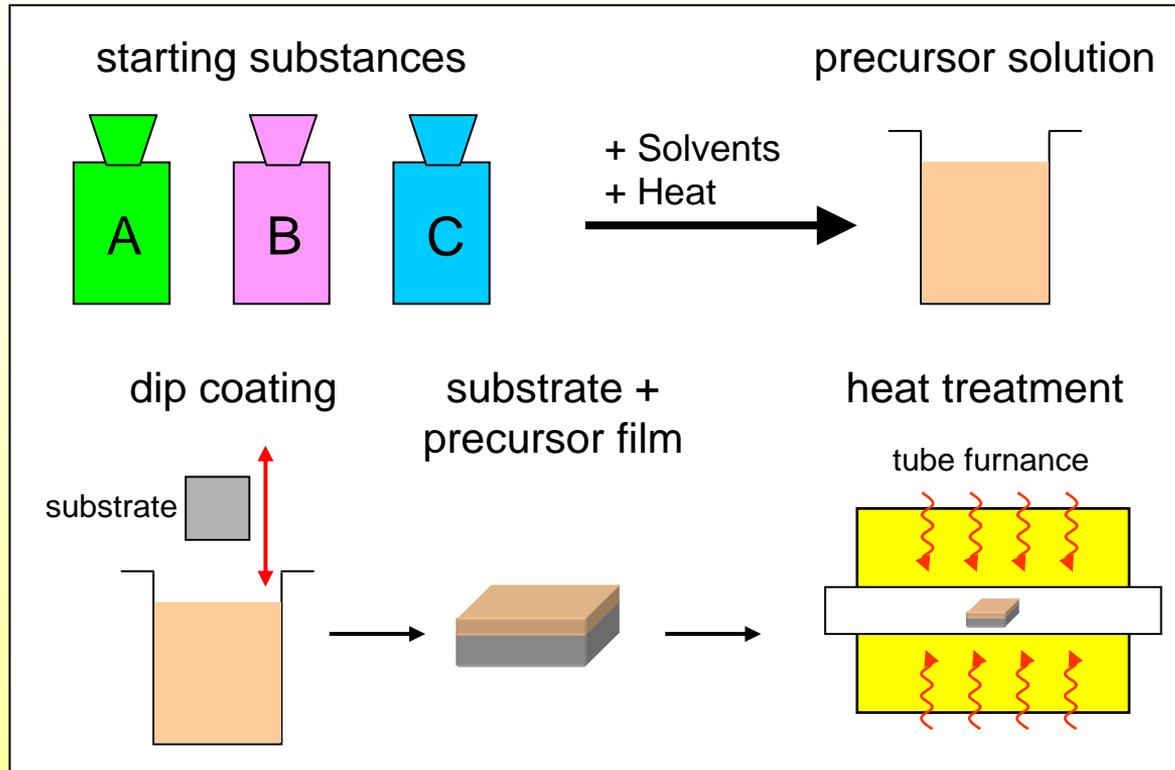
## Depositionsparameter

YBCO-Schicht

200 nm Schichtdicke bei

**0.3 mbar O<sub>2</sub>, 770°C, 2 J/cm<sup>2</sup>**

## Overview of the preparation of CSD samples



### **Solvents:**

e.g. methanol  
ethanol  
toluol

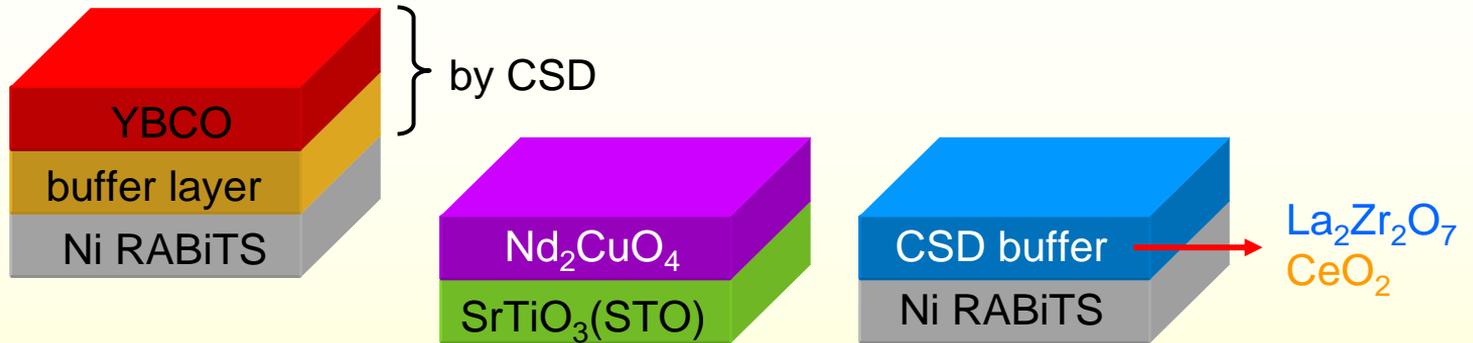
### **Precursor solutions:**

real solution  
**Sol-Gel**

### **Coating methods:**

**dip coating**  
**spin coating**  
spray coating  
roll coating

**Aim:**



## Why *Chemical Solution Deposition*?

- ⇒ low-cost and non-vacuum deposition method (simple, inexpensive equipment)
- ⇒ excellent control of the stoichiometry of precursor solutions
- ⇒ ease of compositional modifications
- ⇒ possibility of coating deposition on large-area substrates

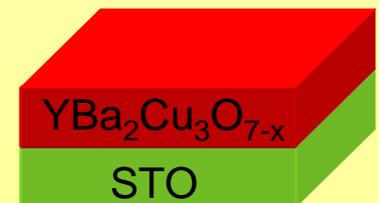
→ many advantages for future commercial production

## Best result of a CSD YBCO film on STO

→  $T_c = 89,9 \text{ K} ; \Delta T_c = 0,7 \text{ K}$

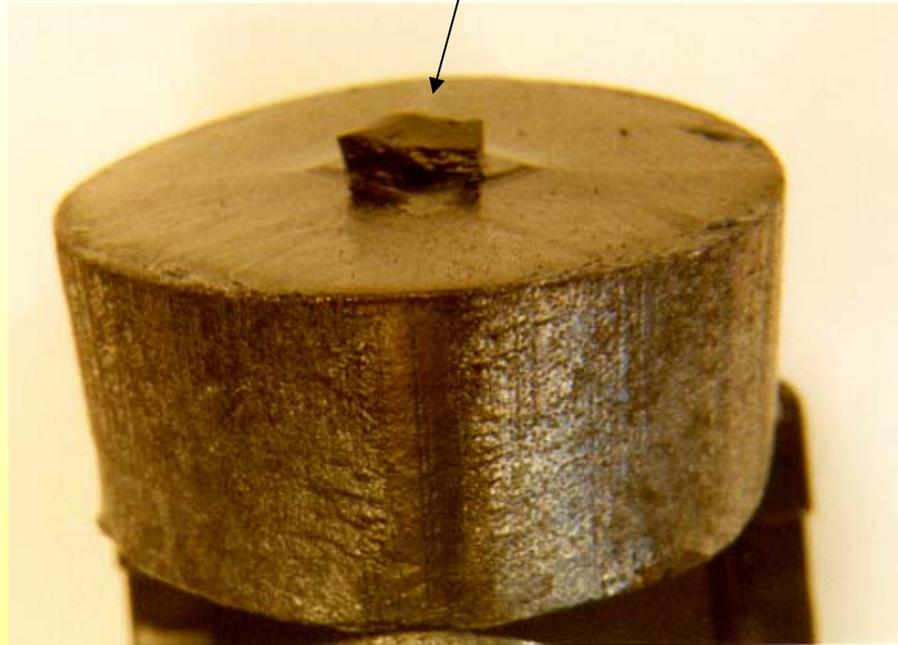
$J_c = 4 \text{ MA/cm}^2 (B = 0 \text{ T}, T = 77 \text{ K})$

M. Falter et al, Physica C, 372-376, 46-49, 2002



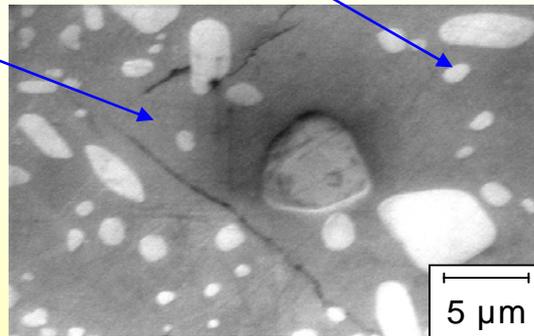
# Schmelztexturiertes Y123 Massivmaterial

Keimkristall

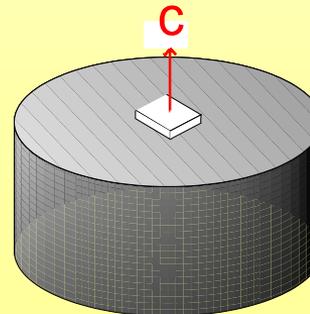
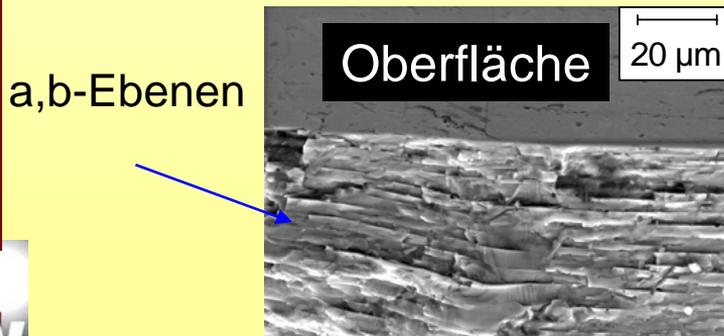


# Modifizierte Schmelztexturierung

- Pulver ( $\text{YBCO} + \text{Y}_2\text{O}_3 + \text{Pt}$ ) wird gepreßt und hitzebehandelt
- Peritektische Reaktion:  
 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \leftrightarrow \text{Y}_2\text{BaCuO}_5 \text{ (Y-211)} + \text{flüssige Phase} + n \text{ O}_2$



- Orientierung der Körner unter Verwendung von  $\text{SmBa}_2\text{Cu}_3\text{O}_7$  Keimkristallen



## Precursor

Mixture of  
Bi, Pb, Sr, Ca and Cu  
Compounds



- Sol-gel methods
- Co-precipitation
- Spray freeze drying
- Spray pyrolysis



Calcination

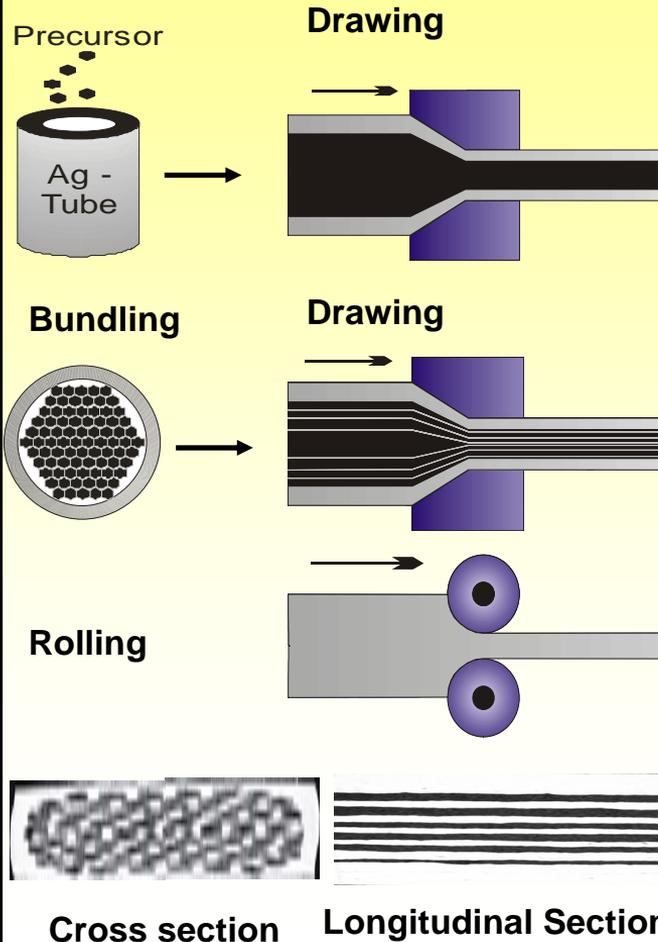


Bi-Pb-Sr-Ca-Cu-O  
powder

with Bi-2223  
composition

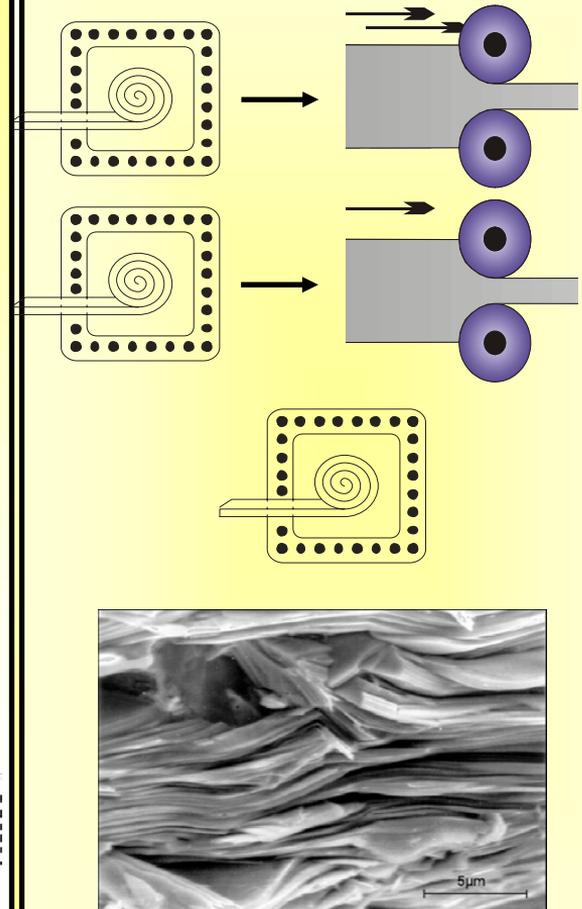
but phase assemblage  
Bi-2212 + other phases

## Deformation



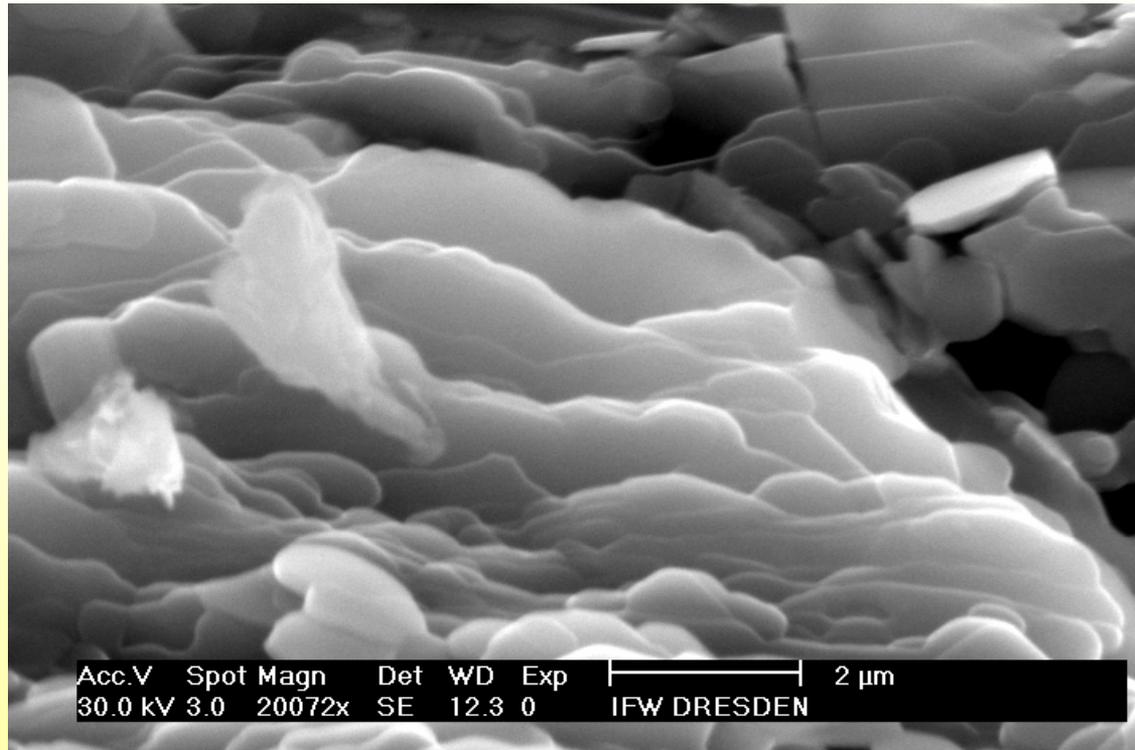
## Thermomechanical Treatment

800-850°C / 10-100h / N<sub>2</sub>+8%O<sub>2</sub>



# Microstructure of superconducting core

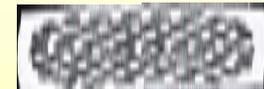
- SEM image of a longitudinal fracture surface:



- Core consists of platelike „colonies“ (ensemble of grains with common c-axis orientation but random a, b orientation with typical dimensions of 20 μm x 20 μm x 0.5 μm)
- Colonies are stacked upon each other along the c-axis (normal to the tape plane)

550m IFW BSCCO(2223) PIT-tape

**HT<sub>c</sub>-tapes for power/magnet applications  
like transformers, cables, motors, NMR magnets**



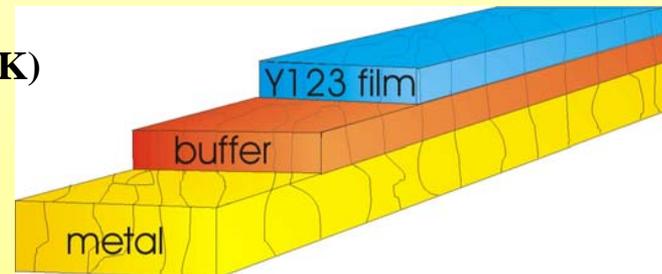
**tape cross section**

**Today : BiPbSrCaCuO (2223) PIT-tapes**

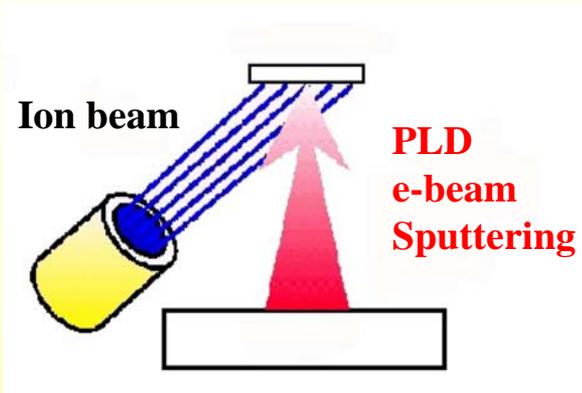
- ✎ Available in long length
- ✎ Moderate performance ( $J_c < 60\text{kA/cm}^2$ )  
Can not be used in magnetic fields at 77K  
Too expensive (Ag)

**Future : Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Coated Conductor**

- ✎ High performance ( $J_c > 1\text{MA/cm}^2$  @ 77K)  
Can be used in magnetic fields at 77K  
Can be cheap
- ✎ Not available in long length

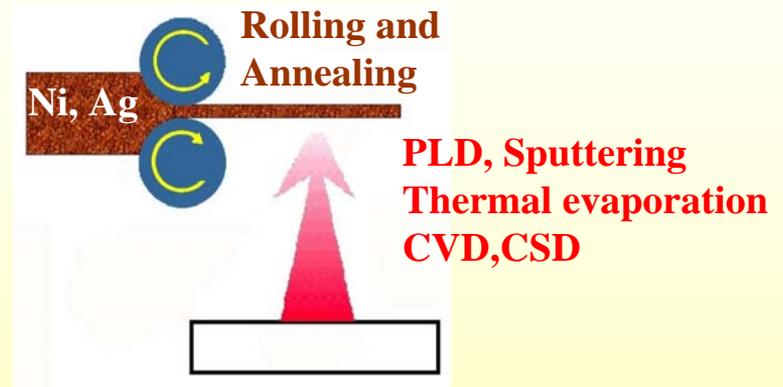


## Ion Beam Assisted Deposition (IBAD)



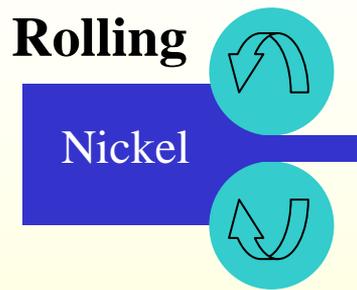
**Biaxially textured buffer layers**

## Rolling Assisted Biaxially Textured Substrates (RABiTS)



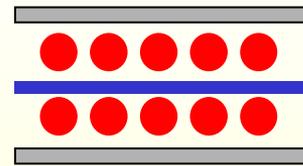
**Biaxially textured substrates**

(Rolling Assisted Biaxially Textured Substrates (RABiTS))

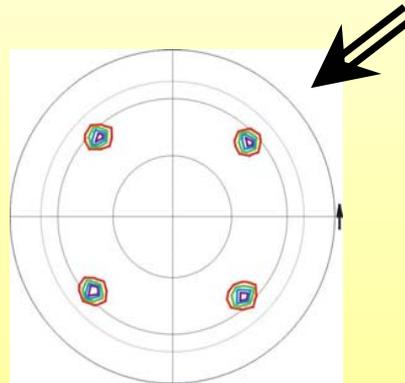


- Cold deformation >95%
- Pure Ni
- Microalloyed Ni :  
Ni-0.1at%Mn
- Alloyed Ni :  
Ni-5at%W  
Ni-9at%V  
Ni-13at%Cr

## Recrystallization

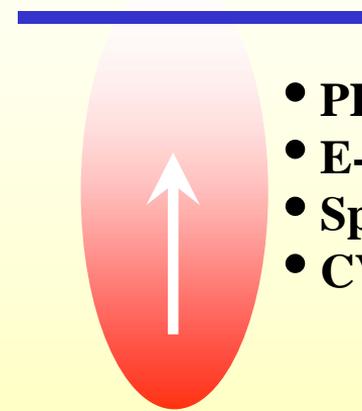


- Typical 900°C/1h
- H<sub>2</sub>-atmosphere



(111)-Ni

## Epitaxial Film Deposition



- PLD
- E-beam
- Sputtering
- CVD, CSD



# Results - CSD YBCO on Ni/Cryoelectra buffer

## properties of the buffer system

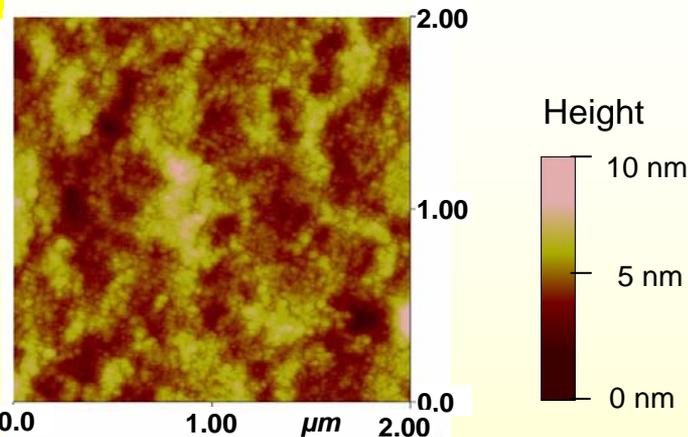
~200 nm YBCO
75 nm CeO <sub>2</sub>
600 nm YSZ
75 nm CeO <sub>2</sub>
Ni-RABiTS

CSD (TFA-process) IFW

HF-sputtering Cryoelectra GmbH

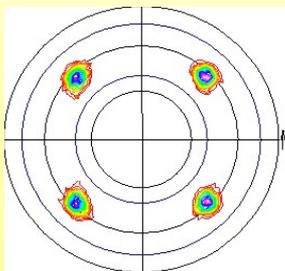
reaktive evaporation

IFW



AFM picture of the CeO<sub>2</sub> surface

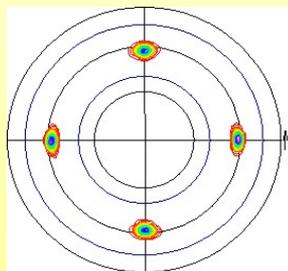
(200) Ni



FWHM = 9,39°

FWHM = 9,27°

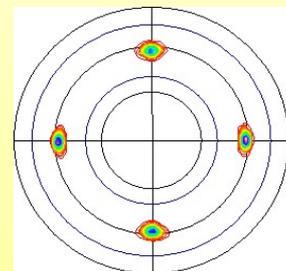
(111) YSZ



FWHM = 7,11°

FWHM = 5,72°

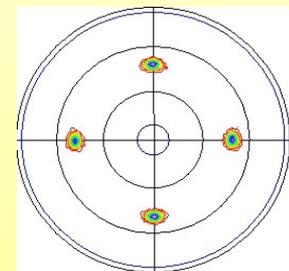
(111) CeO<sub>2</sub>



FWHM = 7,05°

FWHM = 5,64°

(103) YBCO



FWHM = 7,07°

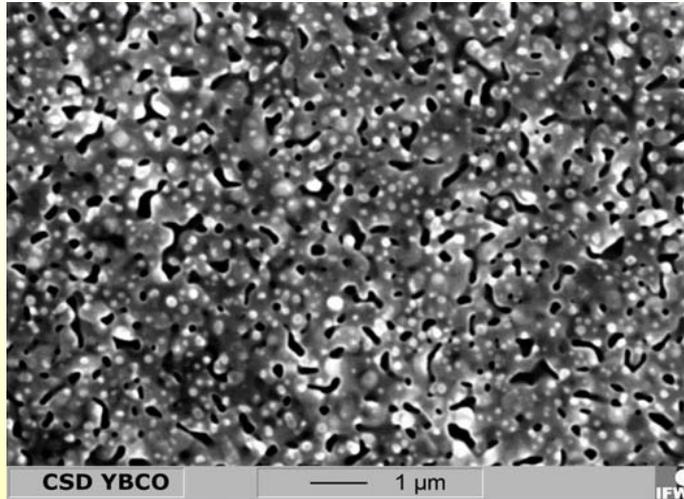
FWHM = 3,56°

in-plane orientation

out-of-plane orientation

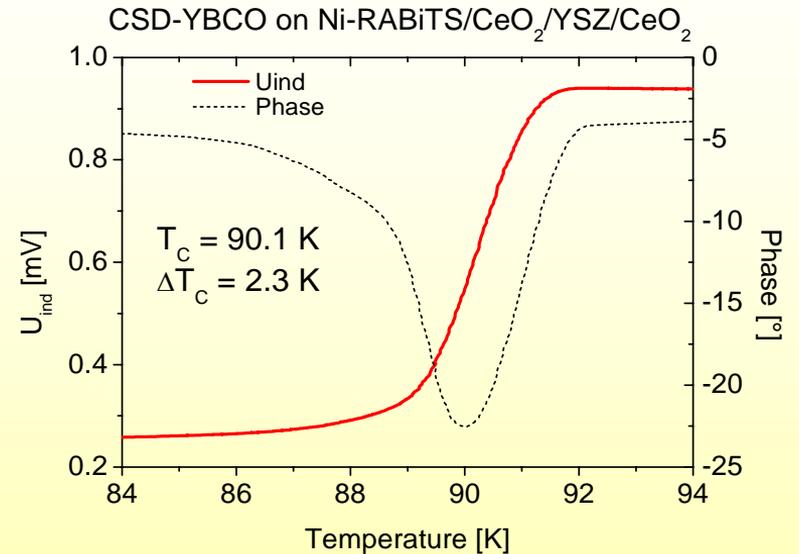
# Results - CSD YBCO on Ni/ Cryoelectra buffer

## properties of the CSD YBCO film



REM picture of a typical TFA-YBCO film on Ni/Cryoelectra buffer

### Inductive measurement of $T_c$



### Critical current density of a TFA YBCO film

inductive measurement:  $J_C = 0.85 \text{ MA/cm}^2$

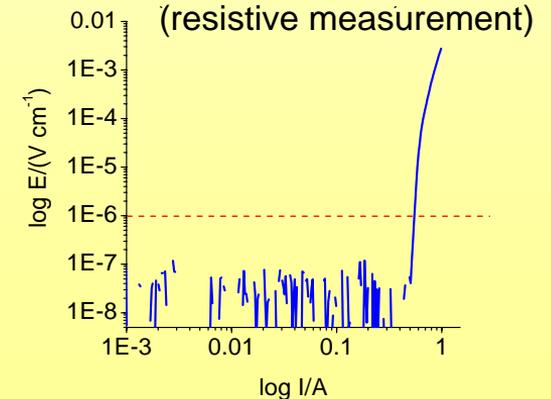
resistive measurement:  $J_C = 0.83 \text{ MA/cm}^2$

(measured on a 10x10 mm<sup>2</sup> sample;  $d_{YBCO} \sim 200 \text{ nm}$ )

criteria:  $E_C = 1 \mu\text{V/cm}$

### I-V curve

(resistive measurement)



„Need to know“ über Supraleitung

HTS Materialklassen

Materialeigenschaften

Herstellungstechnologien

➤ **Dünnschichten mittels**

Physikalischen Schichtdepositionsmethoden

(PLD, thermisches Verdampfen, Sputtern)

Chemischen Depositionsmethoden

(MOCVD, CSD)

➤ **Massivmaterial mittels Schmelztexturierung**

➤ **Bandleiter mittels :**

Powder-in-tube (BSCCO,  $\text{MgB}_2$ )

Coated Conductor (RE123)

## Induction furnace



## Hot rolling



## Intermediate Ni bars

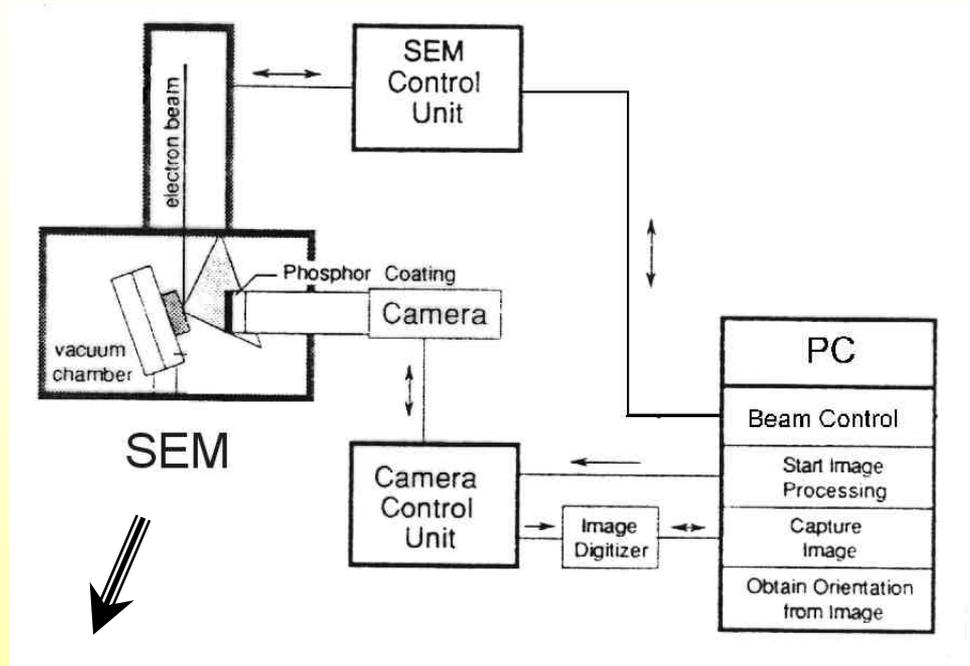
Special 4-high mill



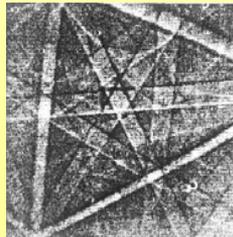
Final tape (up to 70m)



## Electron Back Scattering Diffraction

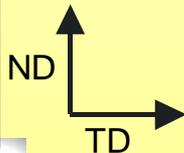
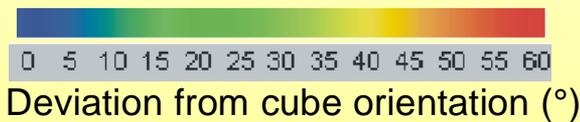
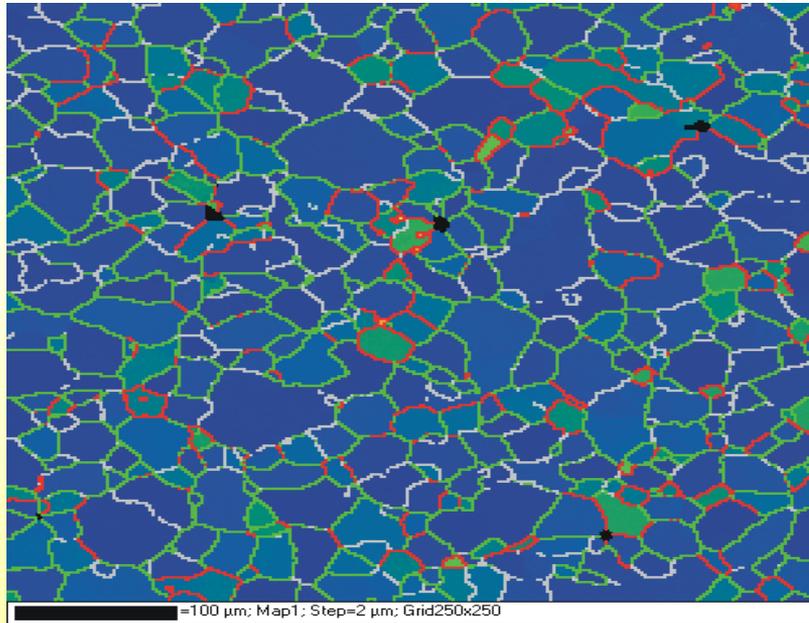


„Kikuchi pattern“



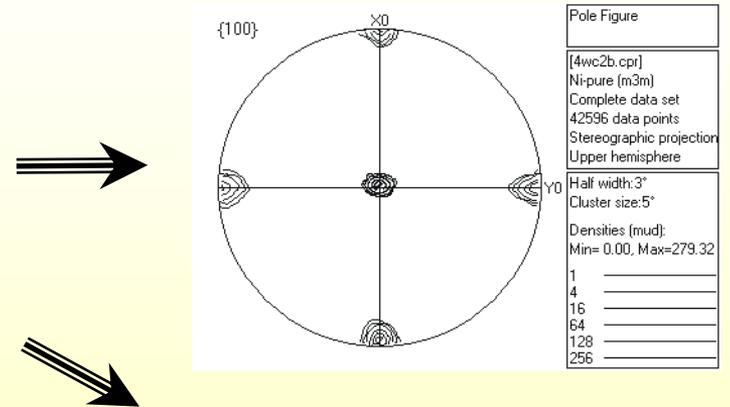
Local texture information  
„Texture maps“

## EBSD Texture Map

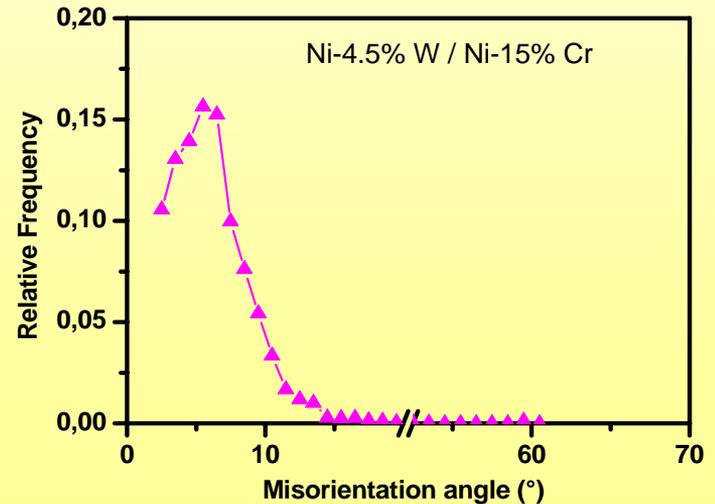


- Misorientation angle < 5°
- Misorientation angle < 10°
- Misorientation angle > 10°

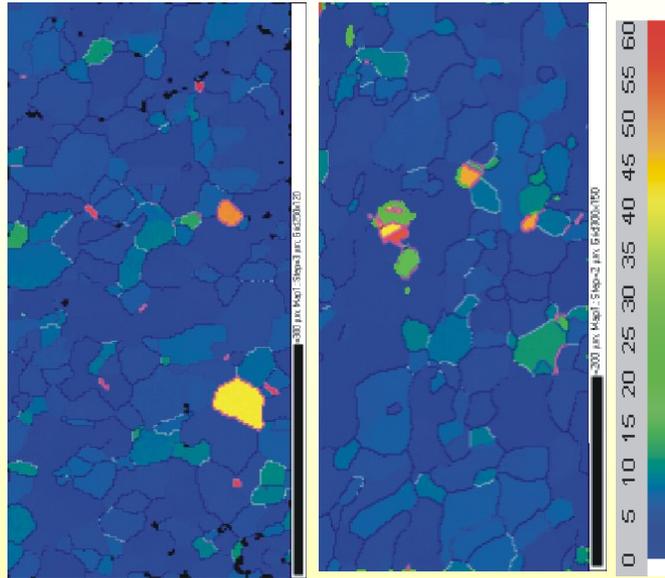
## Pole Figure



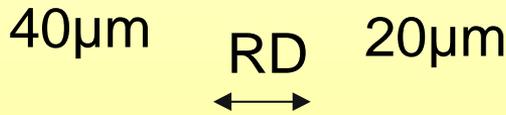
## GB Misorientation



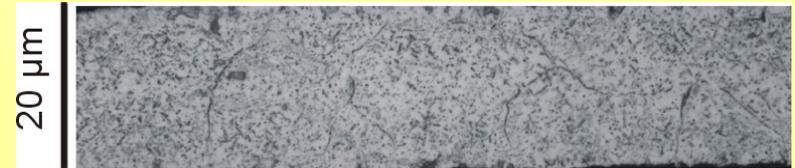
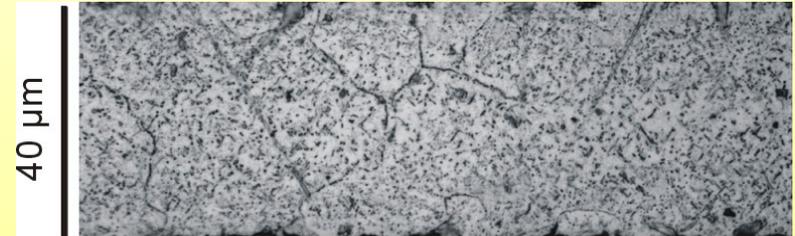
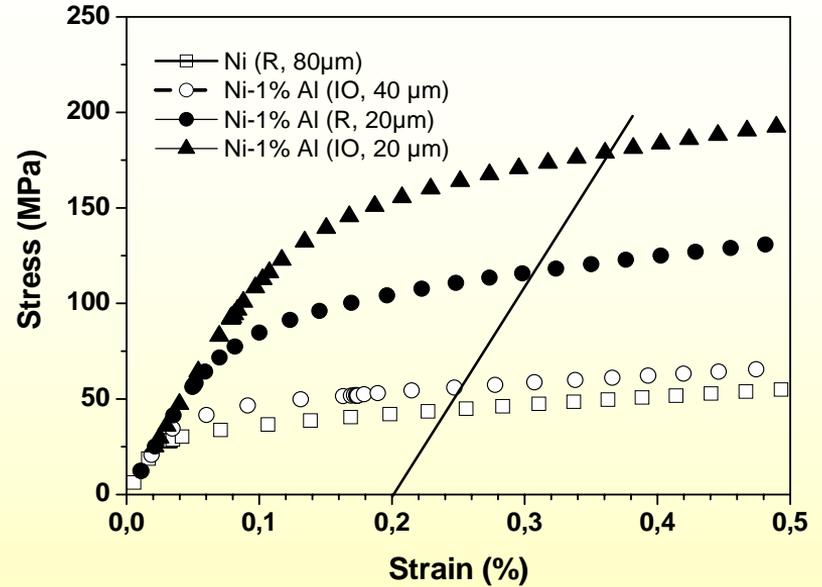
Ni - 1 % Al, Rex 900°C



Deviation from cube texture

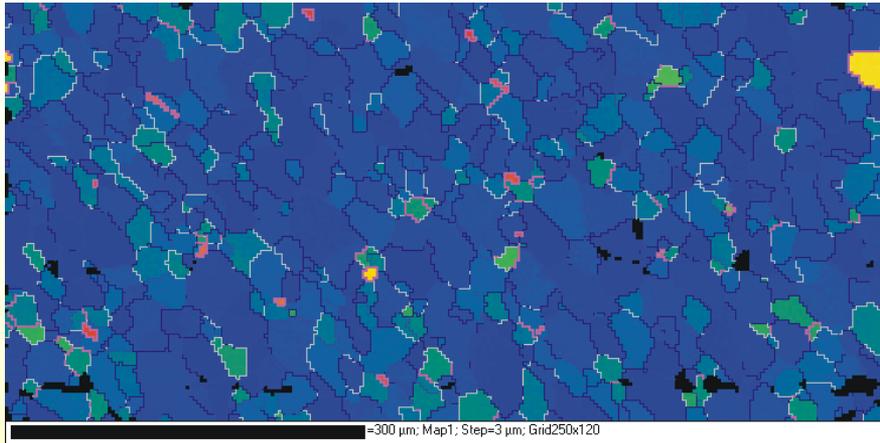


Yield Strength	
Pure Ni :	44 MPa
Ni-1%Al (40μm, recr.) :	56 MPa
Ni-1%Al (40μm, io) :	117 MPa
Ni-1%Al (20μm, io) :	179 MPa

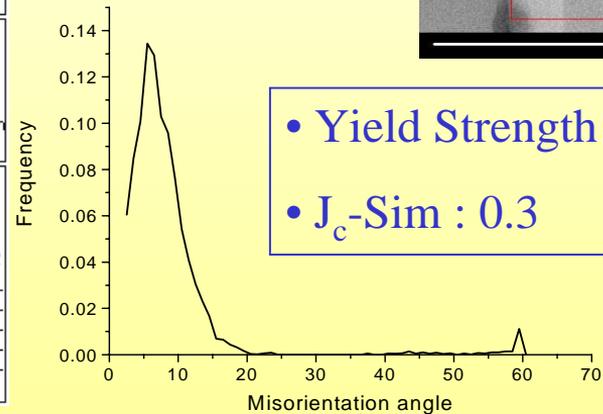
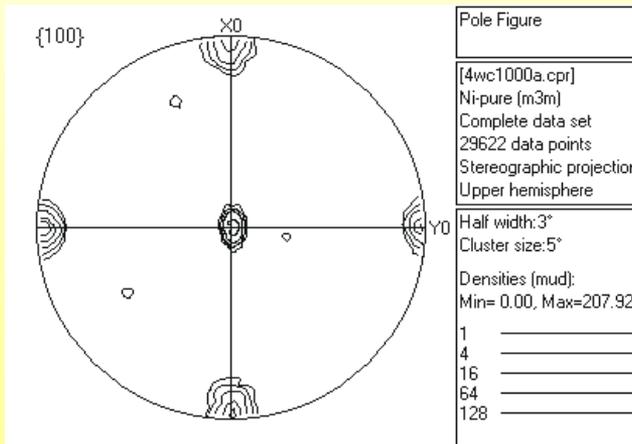
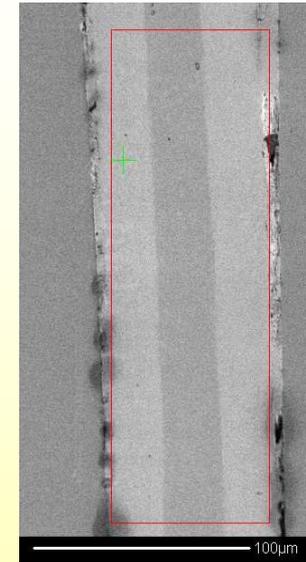


# Ni-4at%W / Ni-15at%Cr Komposite

EBSD



SEM



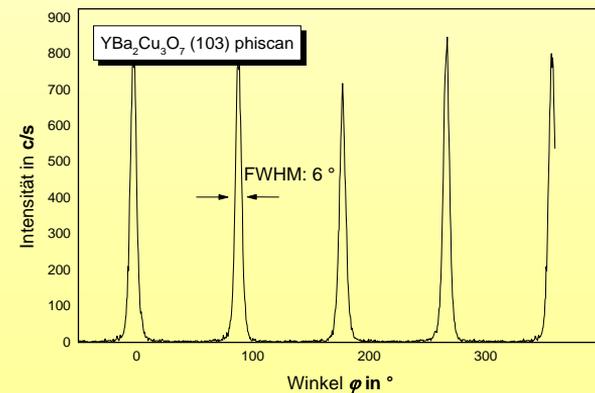
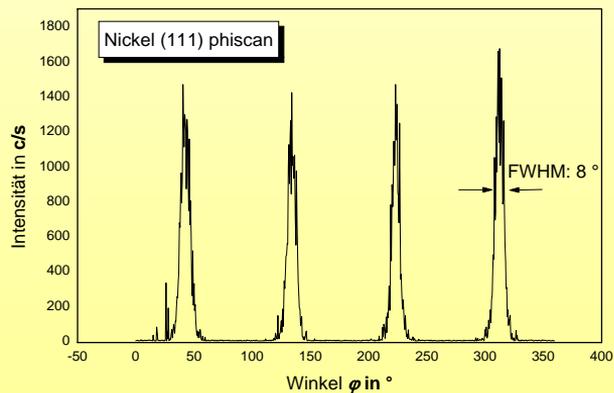
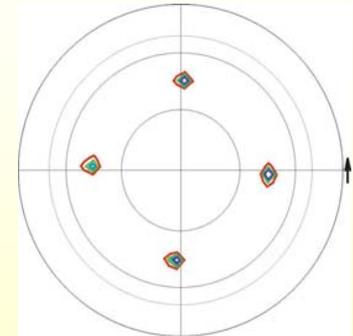
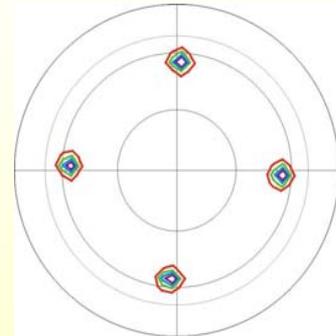
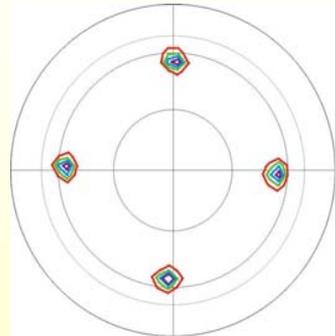
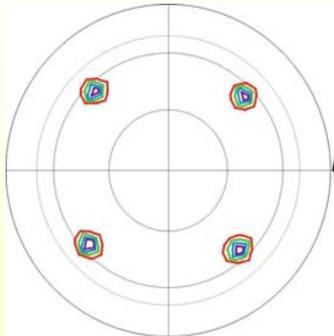
- Yield Strength : 197 MPa
- $J_c$ -Sim : 0.3

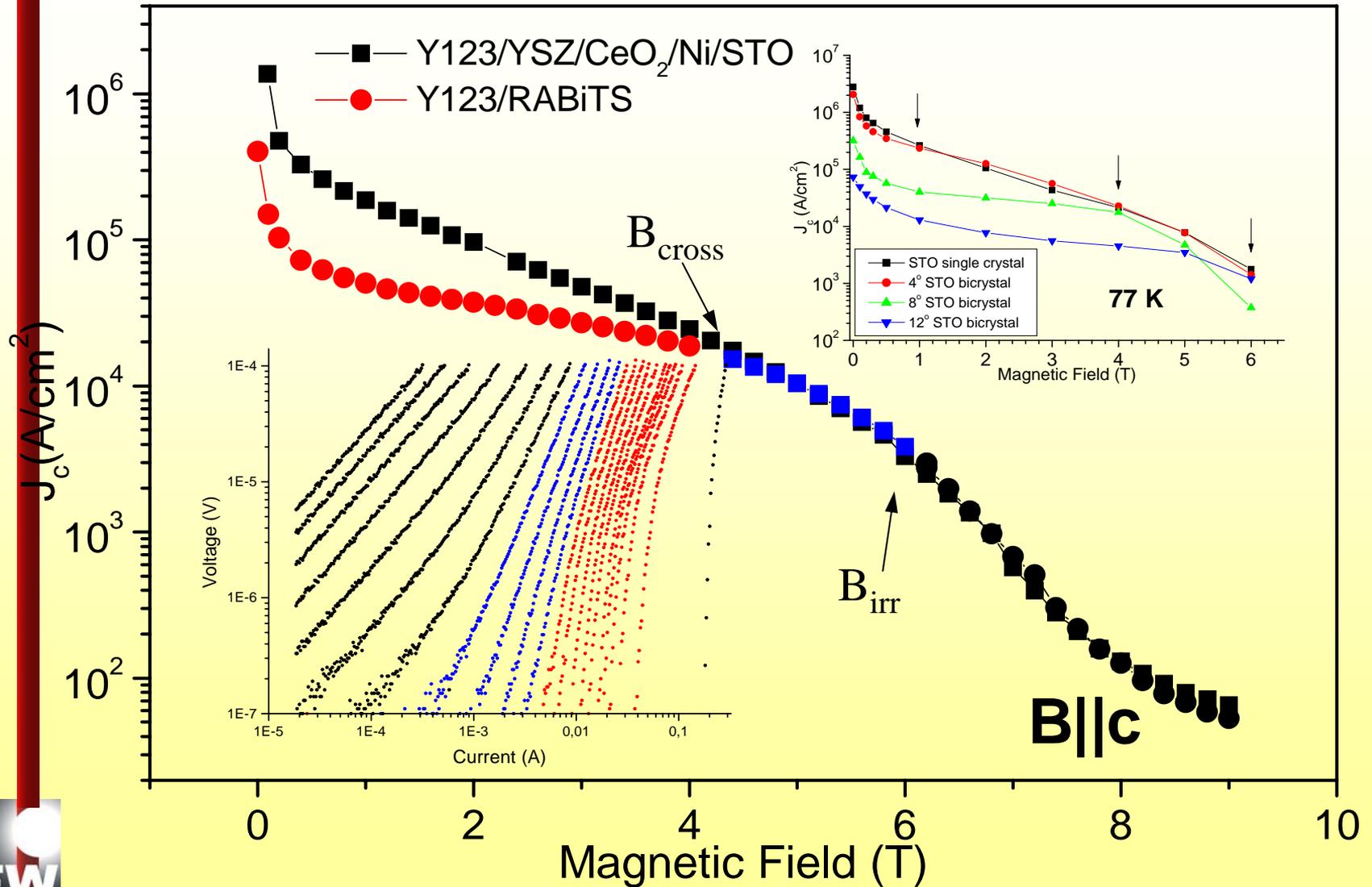
(111) Ni-0.1at%Mn

(111)-CeO<sub>2</sub>

(111)-YSZ

(103)-Y123





# $J_c$ -Limitation „Phase“-Diagramm

