INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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EXPERIMENTAL WORKSHOP ON
"HIGH TEMPERATURE SUPERCONDUCTORS"
(30 March - 14 April 1989)

INTRODUCTION TO EXPERIMENTAL ACTIVITY: MATERIALS CHARACTERIZATION
(Parts I & II)

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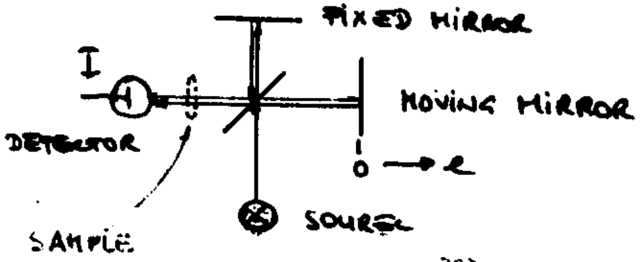
INFRARED SPECTROSCOPY

BASIC PRINCIPLE OF IR-SPECTROMETER

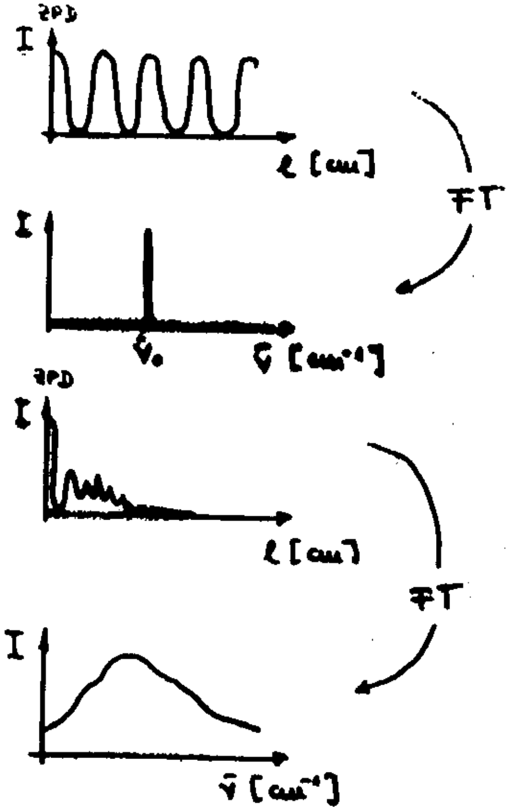
- DISPERSIVE
- FTIR



MICHELSON INTERFEROMETER

MONOCHROMATIC LIGHT SOURCE

POLYCHROMATIC LIGHT SOURCE



I-SAMPLE SPECTRUM IS TAKEN IMMEDIATELY AFTER I_0-BACKGROUND SPECTRUM

$$\text{TRANSMISSION} = \frac{I(\tilde{\nu})}{I_0(\tilde{\nu})}$$

SINCE SINGLE BEAM MEASUREMENT ABSORPTIONS FROM H_2O, CO_2

CO_2 : $\nu_{as} = 2350\ cm^{-1}$
$\nu_{def} = 666\ cm^{-1}$

H_2O : $\nu_{sym}, \nu_{asym.} \sim 3700\ cm^{-1}$
$\nu_{def} \sim 1500\ cm^{-1}$

BROAD DISTRIBUTION OF NARROW LINES ⇒ ROTATIONAL SPLITTING

BELOW ~ $400\ cm^{-1}$
PURE ROTATION BAND OF H_2O

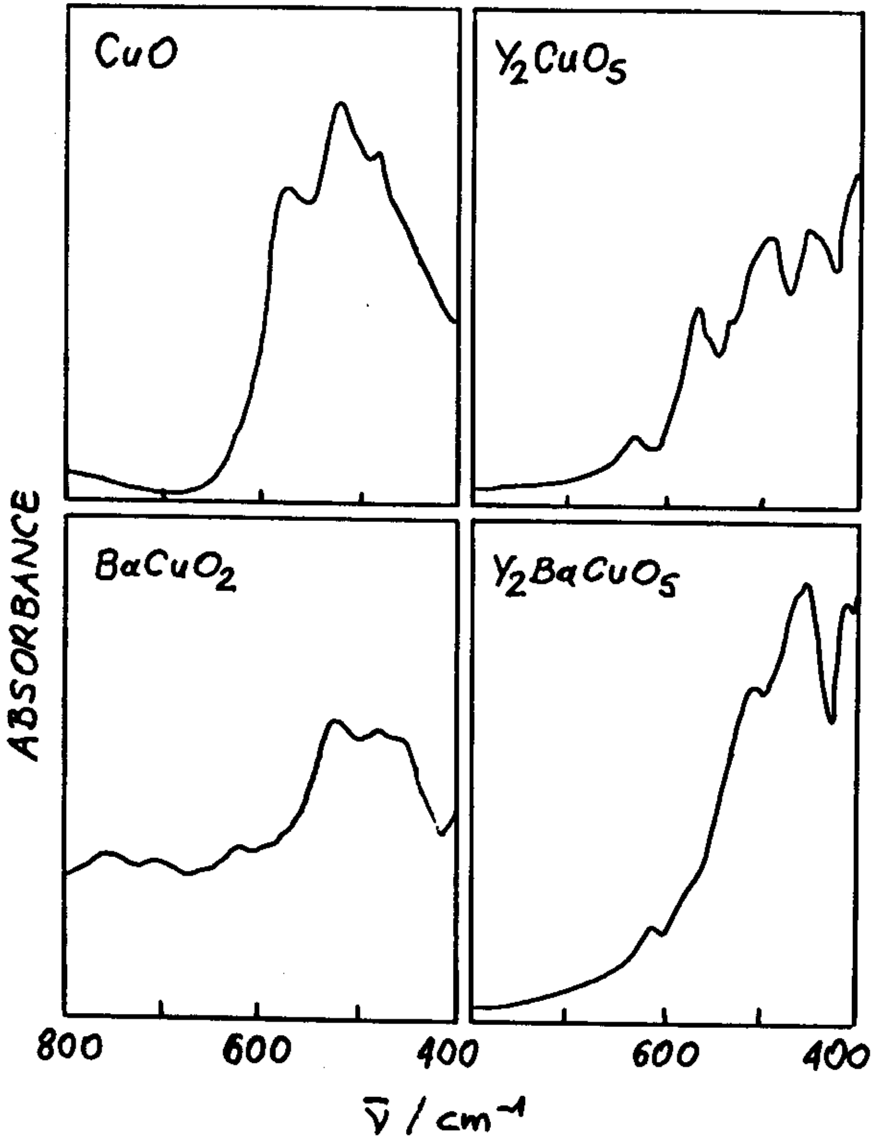
⇒ INSTRUMENT PURGED BY N_2 FLOW

PELLET MATERIALS FOR TRANSMISSION

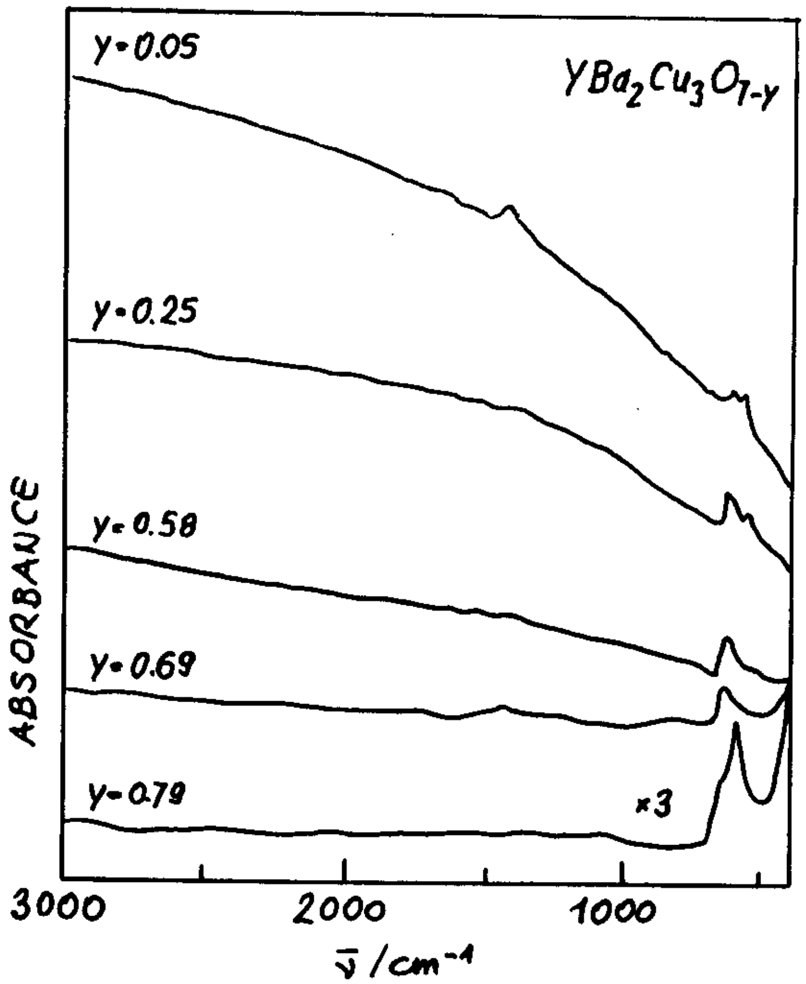
KBr $\nu_{min} \sim 400\ cm^{-1}$

CsJ $\nu_{min} \sim 200\ cm^{-1}$

CAUTION: DIFFUSE SCATTERING IF NOT CAREFULLY PREPARED



FROM C.TALIANI et.al.



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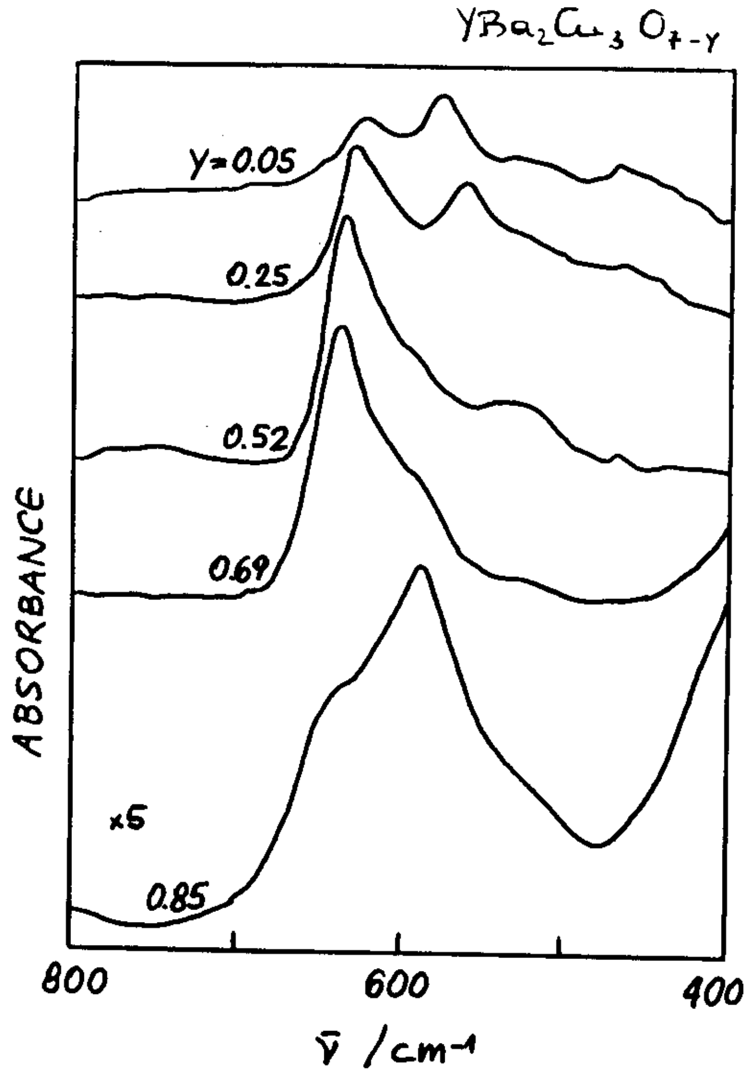
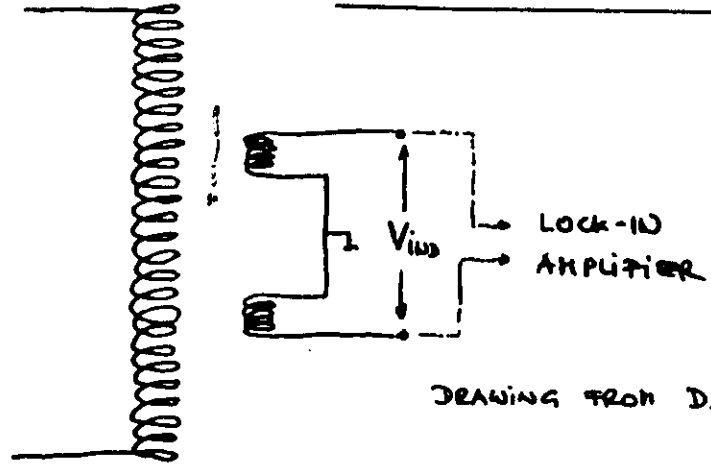


FROM. C. TALIANI et al.

MAGNETIC PROPERTIES



DRAWING FROM D. DROBAC

AC - SUSCEPTIBILITY
SET UP

A_s: CROSS SECTIONAL AREA OF THE PICK-UP COIL

N_s: NUMBER OF TURNS

F: FILLING FACTOR

$$V_{IND} = -\frac{d\phi}{dt} \propto -\frac{d}{dt}\left[N_s A_s \left(\cancel{\mu_0} H + \mu_0 F H\right) - N_s \cancel{A_s} \mu_0 H\right]$$

$$= -\mu_0 \cdot N_s \cdot F \cdot A_s \frac{dH}{dt} = -\mu_0 \cdot N_s \cdot F \cdot A_s \frac{dH}{dH} \cdot \frac{dH}{dt}$$

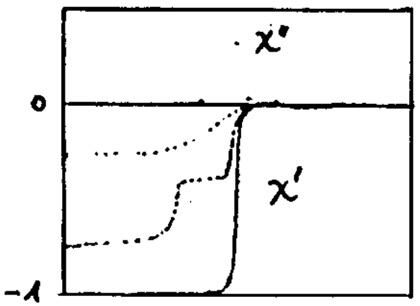
$$H = H_0 \cdot e^{i\omega t}$$

$$V_{IND} = -i\, \mu_0 \cdot \omega \cdot H \cdot N_s \cdot F \cdot A_s \cdot \frac{dH}{dH}$$

$$V_{IND} \sim \chi$$

$\chi = \chi' + i\,\chi''$

LOCK-IN TECHNIQUE: BY DETECTING THE INPHASE AND OUT-OF PHASE COMPONENT ⇒ GIVING THE REAL PART AND IMAGINARY PART OF χ



-1: CORRESPONDS TO A COMPLETE FIELD EXPULSION PERFECT DIAMAGNETISM

FOR ABSOLUTE MEASUREMENT, CALIBRATION TO A KNOWN REFERENCE HAS TO BE DONE.

OTHER FACTORS: SAMPLE DENSITY, POROSITY ABSOLUTE FILLING FACTOR, SAMPLE GEOMETRY

INFORMATION:

- PERCENTAGE OF SUPERCONDUCTING VOLUME
- DISTRIBUTION OF SUPERCONDUCTING TRANSITION TEMPERATURES
- DETECT SUPERCONDUCTING PHASES OF LOW PERCENTAGE (NOT SEEN IN RESISTIVITY) ⇒ CAUTION: PHASE TRANSITIONS
- SEPARATING INTERGRAIN AND INTRAGRAIN CONTRIBUTIONS

GOOD SAMPLE OF $YBa_2Cu_3O_7$ SHOWS TWO PEAKS IN $\chi''(T)$

INTERGRAIN (B)

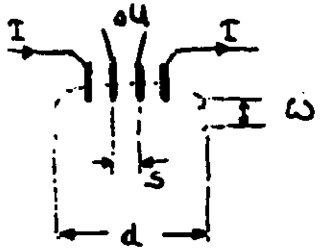
INTRAGRAIN (A)

WHERE (B) DEPENDS MORE STRONGLY ON THE APPLIED FIELD (AC, DC) THAN (A)

IN AVERAGE QUALITY SAMPLES ONLY (B) IS SEEN

TRANSPORT PROPERTIES

ELECTRICAL RESISTIVITY :
CONVENTIONAL 4-PROBE ARRANGEMENT
FOR CHARACTERIZING CERAMIC SAMPLES



IF $s \ll w, d$

$$\Rightarrow \boxed{\rho = 2\pi s \cdot \frac{U}{I}}$$

IF $s \ll w, d$ DOES NOT HOLD $\Rightarrow$

CORRECTIONS

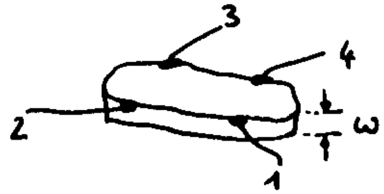
w/s	K
0.4	0.9995
0.7	0.9798

THE CORRECTIONS IN CASE OF d ARE MORE DIFFICULT TO TAKE INTO ACCOUNT

BUT

WITH OUR CONTACT ARRANGEMENT AND SAMPLE SIZE WE CAN HOLD $s < d$.

VAN DER PAUW - GEOMETRY



$R_1 = U_{12} / I_{34}$

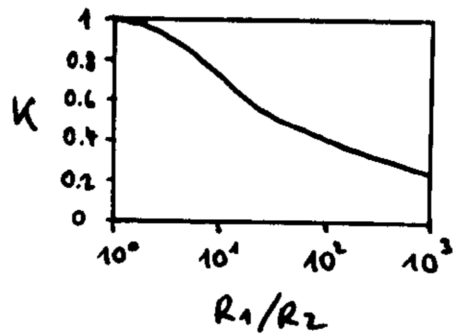
$R_2 = U_{14} / I_{23}$

- HOMOGENEOUS SAMPLE AND THICKNESS
- NO HOLES

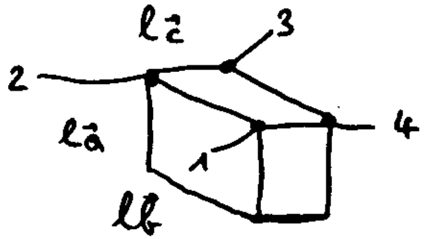
THEN

$$\boxed{\rho = \frac{\pi \cdot w}{\ln 2} \; \frac{R_1 + R_2}{2} \cdot K}$$

CORRECTION FACTOR FOR RESISTIVITY RATIOS:



ANISOTROPIC SAMPLES, SINGLE CRYSTALS FOR THE DETERMINATION OF THE CONDUCTIVITY TENSOR



CONTACTS WITH SILVER PAINT
→ ANNEALED IN O_2 / 400°C

VAN DER PAUW ARRANGEMENT

- l_a, l_b, l_c HAVE TO BE MEASURED ACCURATELY
- CONTACTS NOT TOO LARGE !

$$R_c = U_{14} / I_{23}$$
$$R_b = U_{12} / I_{34}$$

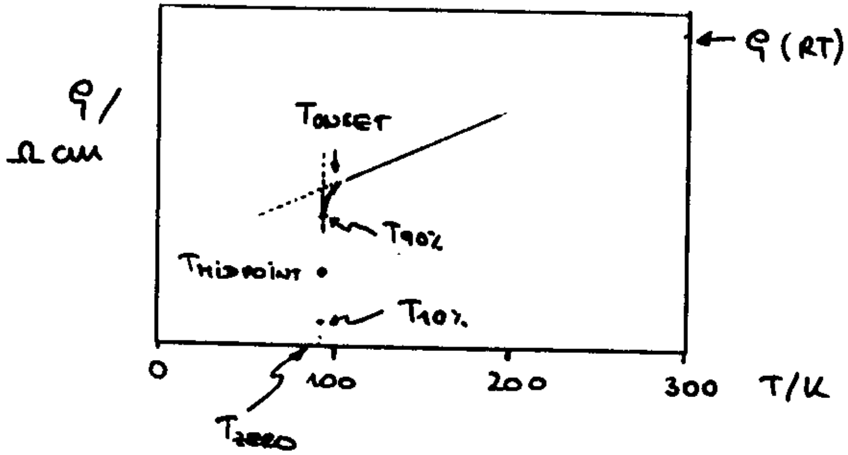
WITH R_c, R_b, l_a, l_b, l_c IN GRAPHS OF

REF: H.C. MONTGOMERY
J. APPL. PHYS. 42 (1971) 2971

⇓

ρ_a, ρ_b

CHARACTERIZATION OF RESISTIVITY BEHAVIOUR



DESIRED VALUES:

RESISTIVITY AT ROOM TEMPERATURE

$$\rho_{RT} \lesssim 1 \text{ m}\Omega\text{cm}$$

RESISTIVITY RATIO BETWEEN RT AND T_{ONSET}

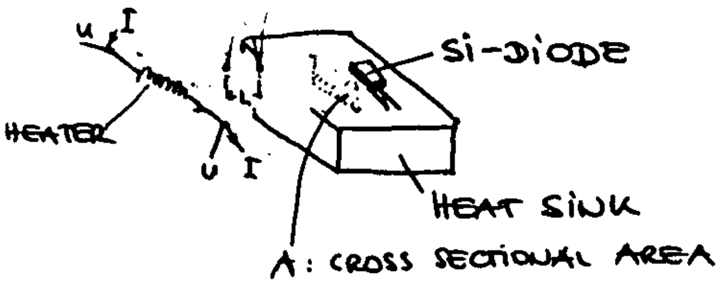
$$\rho(RT) / \rho(T_{onset}) \gtrsim 3$$

WIDTH OF THE TRANSITION

$$T_{90\%} - T_{10\%} = \Delta T \lesssim 1 \text{ K}$$

THERMAL CONDUCTIVITY
(STEADY - STATE METHOD)

ΔT .



P : FOUR PROBE MEASUREMENT TO ACCOUNT FOR RESISTIVITY CHANGES OF HEATER

$P = U \cdot I$

$$\Rightarrow \quad \boxed{K = \frac{P}{\Delta T} \cdot \frac{L}{A}} \qquad W\,cm^{-1}K^{-1}$$

FOR POOR THERMAL CONDUCTORS : POSSIBLE ERRORS WITH MEASUREMENTS AT HIGH TEMPERATURES (>200K) DUE TO RADIATION LOSSES

INFORMATION FROM THERMAL CONDUCTIVITY
- CONTRIBUTION OF CHARGE CARRIERS
- — " — OF PHONONS
- — " — OF ELECTRON-PHONON INTERACTION

$$K = K_{CARRIERS} + K_{PHONONS}$$

ASSUMING ELASTIC SCATTERING OF CARRIERS

ESTIMATE OF $K_{CARRIERS}$ FROM THE WIEDEMANN - FRANZ LAW

$$K_{CARRIERS} = \frac{1}{\rho} L_0 \cdot T$$

$L_0 = 2.45 \cdot 10^{-8}\ W\Omega K^{-1}$ LORENZ NUMBER

IF SIGNIFICANT INELASTIC SCATTERING

$$L_{EFFECTIVE} < L_0$$

UPPER LIMIT FOR $K_{CARRIERS}$

$K_c(100K) < 2.5 \cdot 10^{-4}\ W cm^{-1} K^{-1}$ $\quad (\rho(100K) = 10\,m\Omega\,cm)^*$

$K_c(100K) < 2.5 \cdot 10^{-2}\ W cm^{-1} K^{-1}$ $\quad (\rho(100K) = 100\,\mu\Omega\,cm)$

* FROM: MORELLI et al Phys. Rev. B 36 (1987) 3917

THERMOPOWER – SEEBECK COEFFICIENT, S (T)

THE SAME EXPERIMENTAL ARRANGEMENT AS FOR THERMAL CONDUCTIVITY

INFORMATION:

- SIGN OF MAJORITY CARRIERS
- VALUE OF S: • BETWEEN 100 – 1000 μV/K FOR SEMICONDUCTORS
  - • LESS THAN 100 μV/K DOWN TO A FEW μV/K FOR METALS
  - • ZERO IN THE SUPERCONDUCTING STATE
- CARRIER SCATTERING ON CARRIERS AND PHONONS

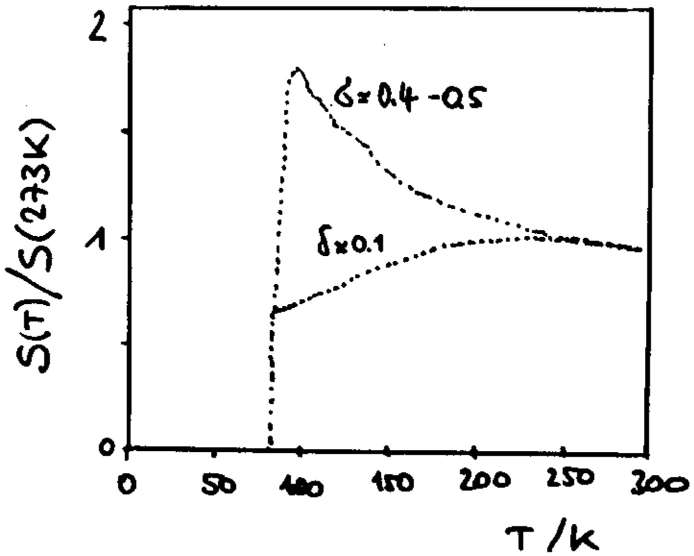
SIMPLE MODEL ASSUMING NEARLY-FILLED BAND METALLIC SYSTEM AND ENERGY INDEPENDENT SCATTERING

$$S(T) = \frac{\pi^2}{3} \cdot \frac{k_B}{e} \cdot T \cdot \eta(e_F)$$

$\eta(e_F)$: DENSITY OF STATES PER CARRIER AT THE FERMI LEVEL

OBSERVED BEHAVIOUR:

$YBa_2Cu_3O_{7-\delta}$



KANG et al
Phys. Rev. B
39 (1989) 2763

MORE REALISTIC:

ENERGY DEPENDENT SCATTERING

$$S(T) = \frac{\pi^2 k_B}{3e} \cdot T \cdot \frac{d \ln \sigma(E)}{dE_F}$$

THERMOGRAVIMETRY

$YBa_2Cu_3O_{7-\delta}$

IF ALL Cu IS IN Cu^{2+} OR $(Cu{-}O)^{0}$

THEN $YBa_2Cu_3O_{6.5}$ $\delta = 0.5$

IF $\delta < 0.5$

THEN SOME $(Cu-O)^{+} = 2(0.5-\delta)$

THIS CAN BE EVALUATED BY

- O_2 EVOLUTION
- IODOMETRY
- TGA

O_2-EVOLUTION:

$$YBa_2Cu_3O_{7-\delta} + H^{+} \rightleftarrows \left(\frac{0.5-\delta}{2}\right) O_2$$

EVOLVED O_2 MEASURED

IODOMETRY:

$$YBa_2Cu_3O_{7-\delta} + K^{+}I^{-} + H_2O + H^{+} \leftrightharpoons I_2$$

I_2 AMOUNT DETERMINED BY TITRATION WITH $Na_2S_2O_3$

TGA:

$$YBa_2Cu_3O_{7-\delta} \equiv \underset{\uparrow}{YBa_2O_{3.5}} + Cu_3O_{3.5-\delta}$$

THIS SPECIES CANNOT BE FURTHER REDUCED

DOING TGA UNDER H_2 ATMOSPHERE WILL REDUCE

$Cu_3O_{3.5-\delta}$ TO $3Cu + (3.5-\delta)H_2O$

FROM WEIGHT LOSS $\Rightarrow \delta$

AND CHECKING WITH IODOMETRIC RESULT

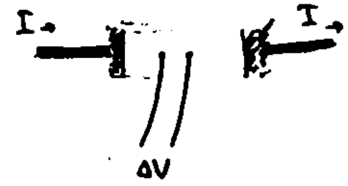
PRINCIPLE - IODOMETRY

$$x\,(\text{HOLES}) + x\,I^- \rightleftharpoons \frac{x}{2} I_2$$

$$\frac{x}{2} I_2 + 2\,Na_2S_2O_3 \rightleftharpoons Na_2S_4O_6 + 2\,NaI$$

CRITICAL CURRENT

ARRANGEMENT :

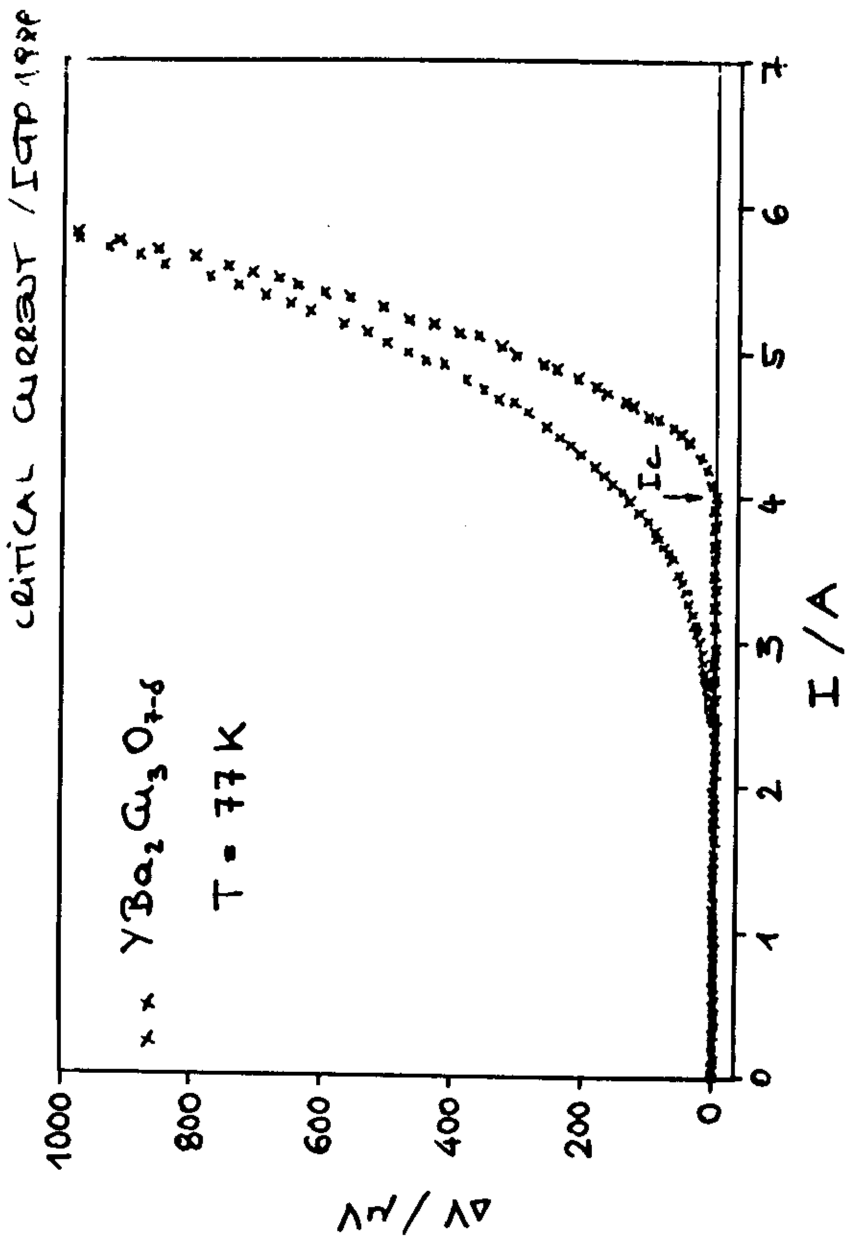


- IMPORTANT • GOOD THERMAL CONTACT OF SAMPLE TO THE HEAT SINK ⇒ THEREFORE SAMPLE IMMERSED IN LIQUID NITROGEN FOR GOOD THERMAL CONTACT
  • VERY GOOD CURRENT CONTACTS (LOW CONTACT RESISTANCE) POSSIBLE CONTACT MATERIALS FOR $YBa_2Cu_3O_{7-\delta}$ - In SOLDERED TO SAMPLE OR AG PAINT CONTACTS ANNEALED UNDER O_2 / 400°C FOR SEVERAL HOURS.

MEASUREMENT : COMPUTER CONTROLLED SWEEPS AUTOMATICALLY THE CURRENT

FIT TO $\Delta V = A_o \exp(I - I_c)$

BASIC IDEA: PERCOLATION PROCESS INVOLVED FOR DESCRIBING THE DISTRIBUTION OF NORMAL DRIVEN WEAK LINKS.



CRITICAL CURRENT VALUES : J_c ($YBa_2Cu_3O_{7-\delta}$)

INTRAGRAIN $\geq 10^6$ A/cm^2
INTERGRAIN ~ 200 A/cm^2

⇒ CRITICAL CURRENT VALUES OF CERAMICS ARE DETERMINED BY THE INTERGRAIN J_c

SOME POSSIBLE REASONS FOR THE OCCURENCE OF THE WEAK LINK JUNCTIONS AT THE GRAIN BOUNDARIES:

- THE SMALL COHERENCE LENGTH (~ 10Å)
- MISALIGNMENT OF NEIGHBOURING GRAINS (LARGE ANISOTROPY OF SC PROPERTIES)
- DISTURBANCE OF THE STRUCTURE AT THE GRAIN BOUNDARY
- FOREIGN PHASES OR JUNK IN THE GRAIN BOUNDARY

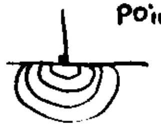
CONCLUSION: J_c MEASUREMENT IS A TEST FOR THE INTERGRAIN CONTACT SO FOR THE QUALITY OF THE SAMPLE.

IDEAS : GRAIN BOUNDARY DOPING

⋮

APPLICATIONS

4-PROBE RESISTIVITY
IN LINE CONTACTS



POINT CURRENT CONTACT GIVES
(SPHERICAL POTENTIAL DISTRIBUTION ASSUMED)
FOR THE CURRENT DENSITY : $S = \dfrac{I}{2\pi r^2}$

WITH OHM'S LAW: $\vec{S} \cdot \rho = \vec{E}$ IT GIVES $\Rightarrow$

$$E = \frac{I}{2\pi r^2}\rho$$

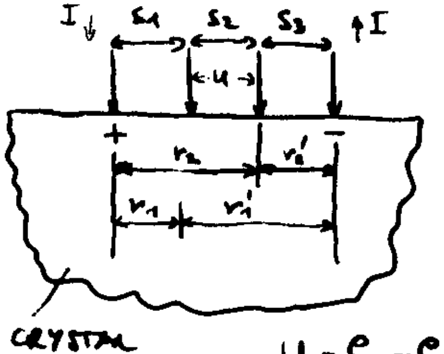
THE POTENTIAL DIFFERENZ BETWEEN TWO POINTS

$$U = -\int_{P_1}^{P_2} E\,dr = -\frac{I}{2\pi}\rho\int_{r_1}^{r_2}\frac{1}{r^2}dr = \frac{I}{2\pi}\rho\left(\frac{1}{r_1}-\frac{1}{r_2}\right)$$

THE APPROXIMATION FOR EXAMPLE P_2 WITH $r_2 \to \infty$

$\Rightarrow$ POTENTIAL $\varphi = \dfrac{I}{2\pi}\rho\dfrac{1}{r}$

WITH THE ARRANGEMENT :



$$\varphi_1 = \frac{I}{2\pi}\rho\left(\frac{1}{r_1}-\frac{1}{r_1'}\right)$$

$$\varphi_2 = \frac{I}{2\pi}\rho\left(\frac{1}{r_2}-\frac{1}{r_2'}\right)$$

$$U = \varphi_1 - \varphi_2 = \frac{I}{2\pi}\rho\left(\frac{1}{r_1}-\frac{1}{r_1'}-\frac{1}{r_2}+\frac{1}{r_2'}\right)$$

EXPRESSING r_n BY S $\Rightarrow$

$$U = \frac{I}{2\pi}\rho\left(\frac{1}{s_1}-\frac{1}{s_2+s_3}-\frac{1}{s_1+s_2}+\frac{1}{s_3}\right)$$

FOR EQUAL CONTACT DISTANCE

$$s_1 = s_2 = s_3 = s$$

$$\Rightarrow \boxed{\rho = 2\pi s\frac{U}{I}}$$

WE DID NOT TAKE INTO ACCOUNT THE SAMPLE BOUNDARY SO THE ABOVE IS ONLY VALID FOR $d \gg s$ AND $w \gg s$