PHOTOSYNTHESIS OF SUPERCONDUCTIVITY

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LET THERE BE LIGHT

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AFOSR, NSF, DOE

Philosophy 1

- **It is the speakers responsibility to prove that (s)he is correct**
- **It is not the audience's responsibility to prove that (s)he is wrong**

ASK QUESTIONS

Synthesis is purposeful execution of chemical reactions in order to get a product, or several products. This happens by physical and chemical manipulations usually involving one or more reactions.

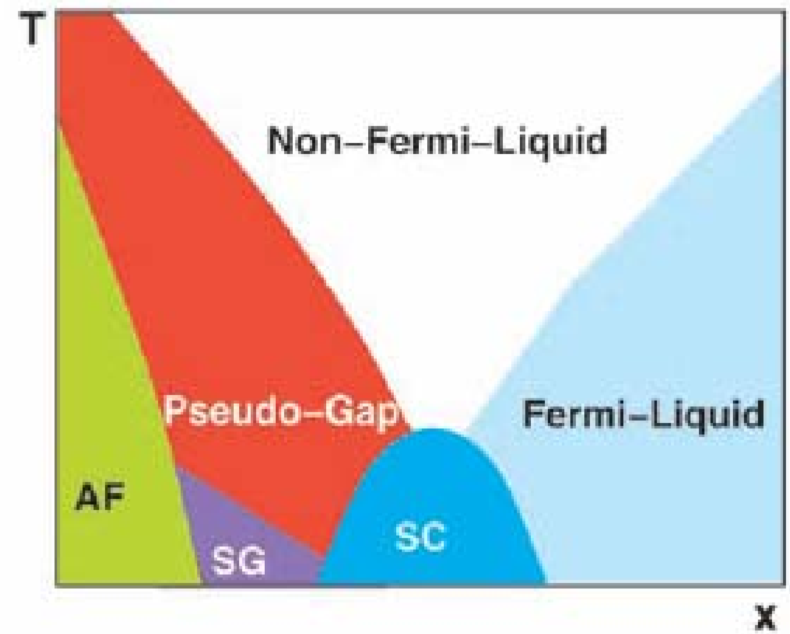
WIKIPEDIA

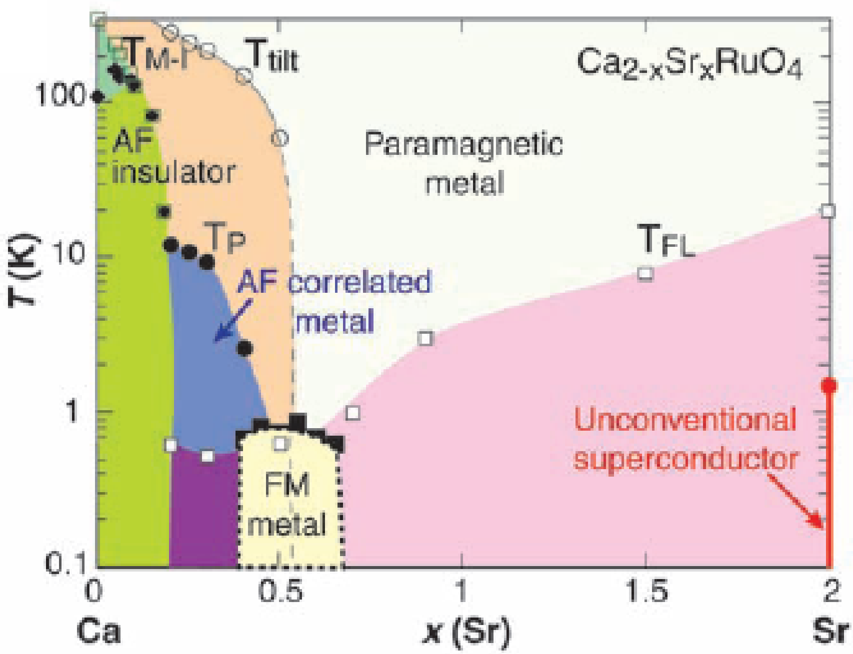
Photosynthesis is the process of converting light energy to chemical energy and storing it in the bonds of sugar.

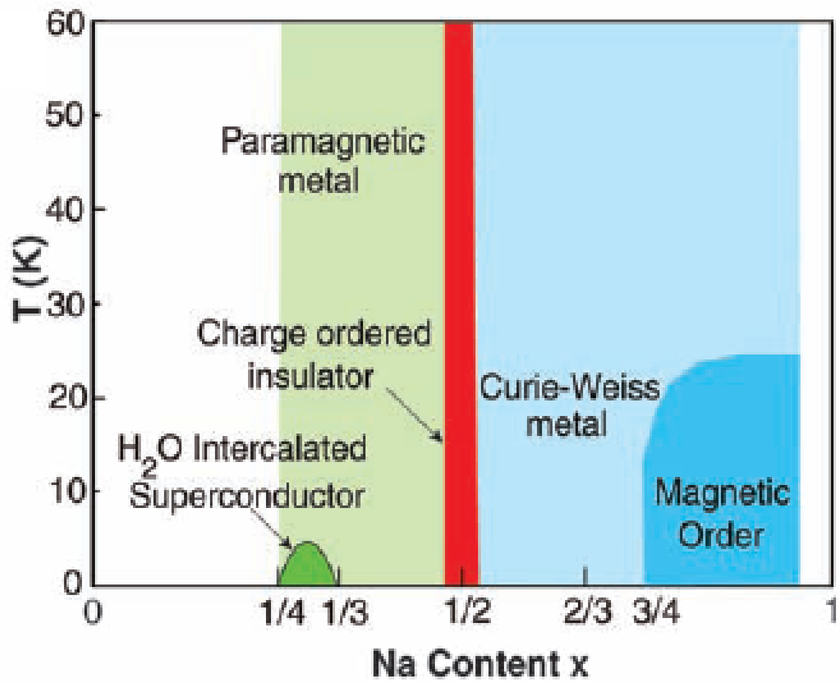
My high-school Biology Prof.

Unconventional Superconductors

Doping is the Crucial Parameter







MOTIVATION
Superconductors

- **Conventional**
  - *** Nonequilibrium**
  - *** Relaxation Properties**
  - *** New Properties**

- **Unconventional**
  - *** Nonequilibrium**
  - *** Relaxation Properties**
  - *** Doping**

NORTHWESTERN UNIVERSITY

PHOTOEXCITATION IN SUPERCONDUCTORS

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

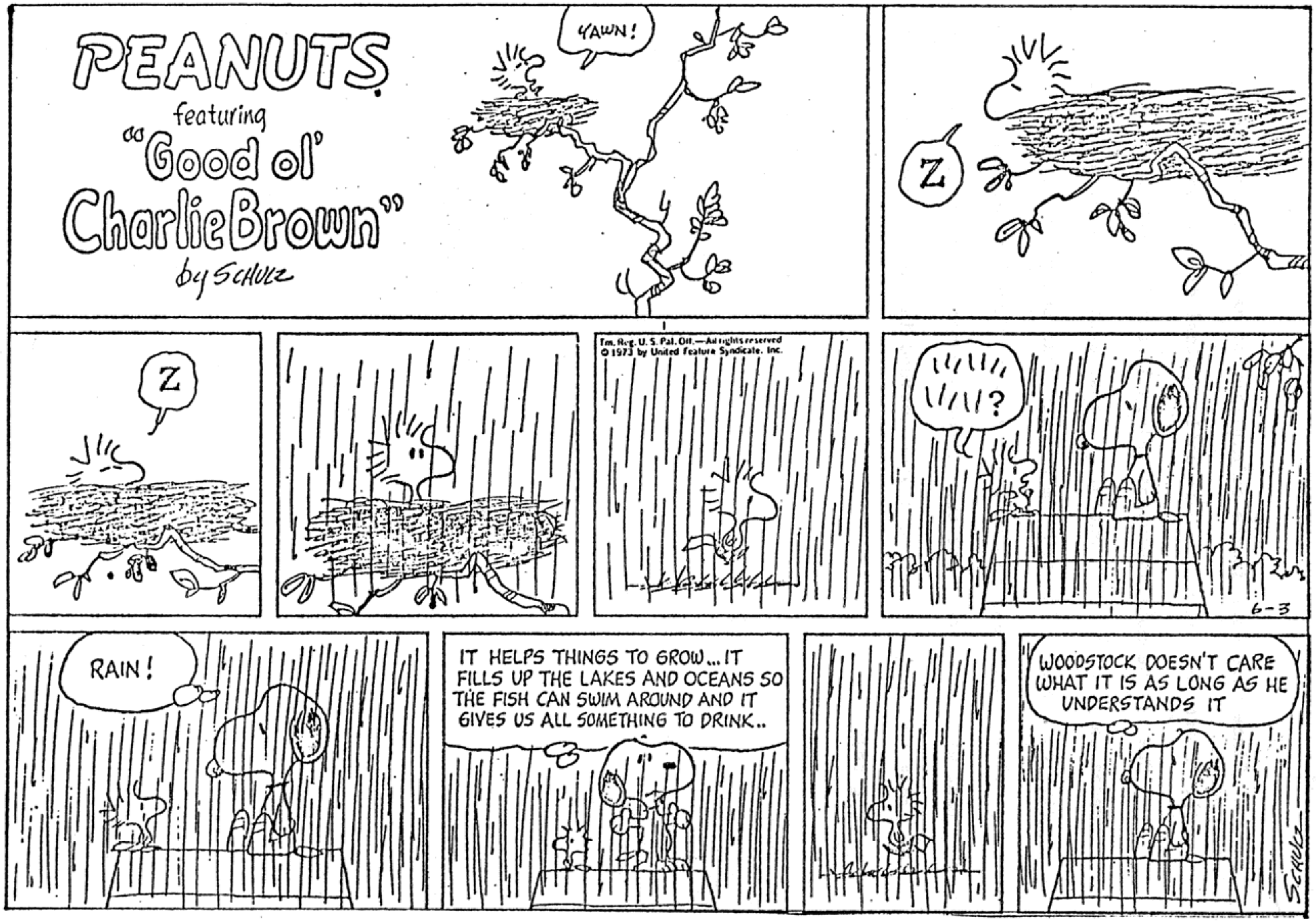
Field of Physics

By

IVAN SCHULLER

Evanston, Illinois

June 1976



Basic Research=Surprises

CONVENTIONAL SUPERCONDUCTORS

Resistivity

- Follows the light
- Similar to heating

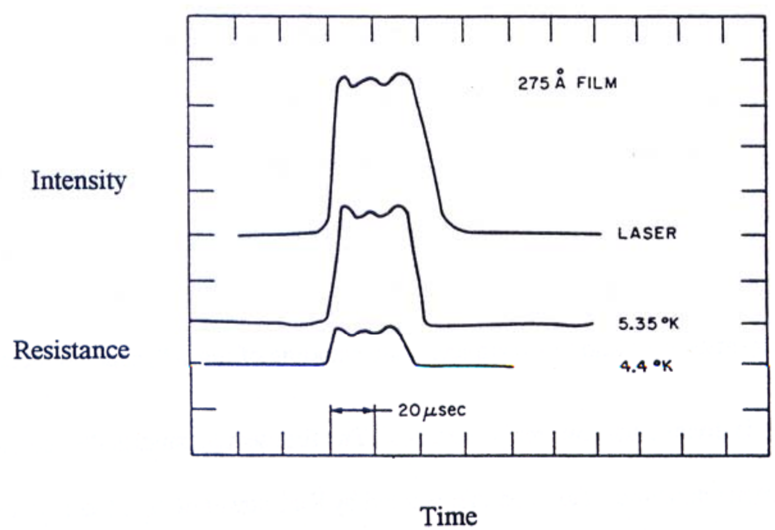
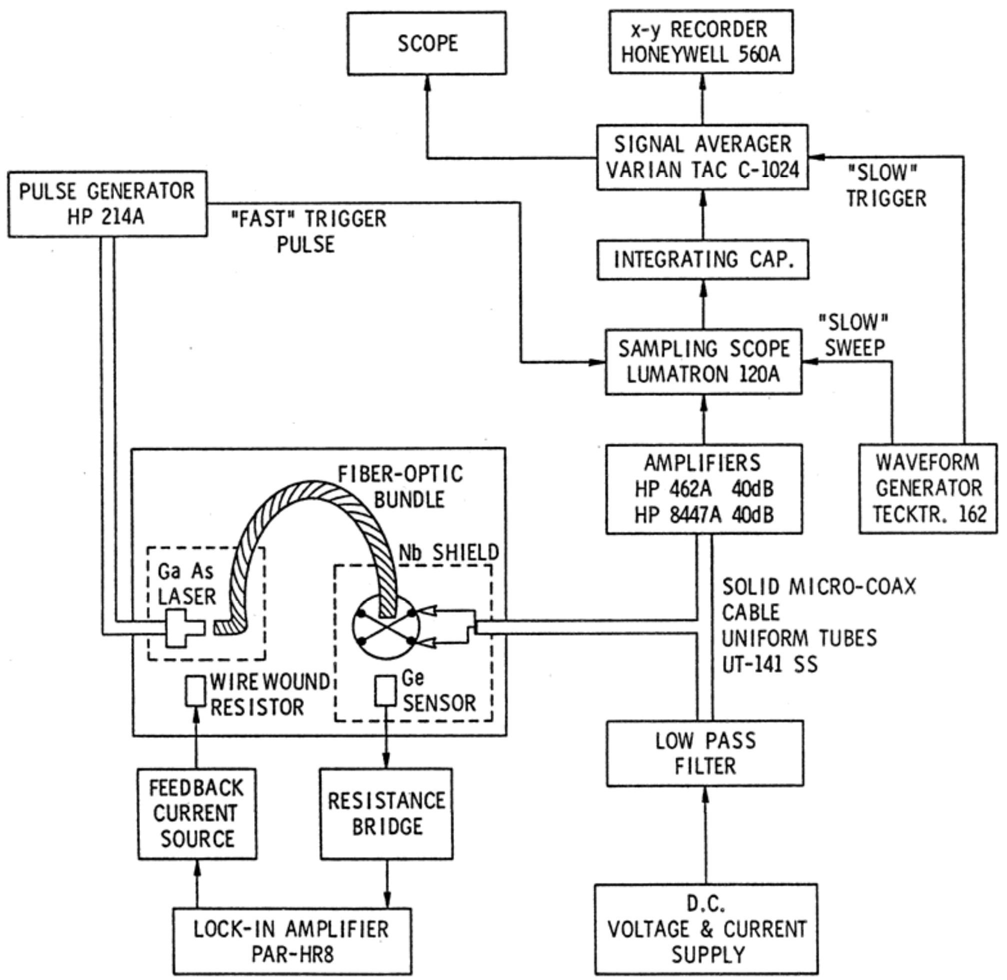
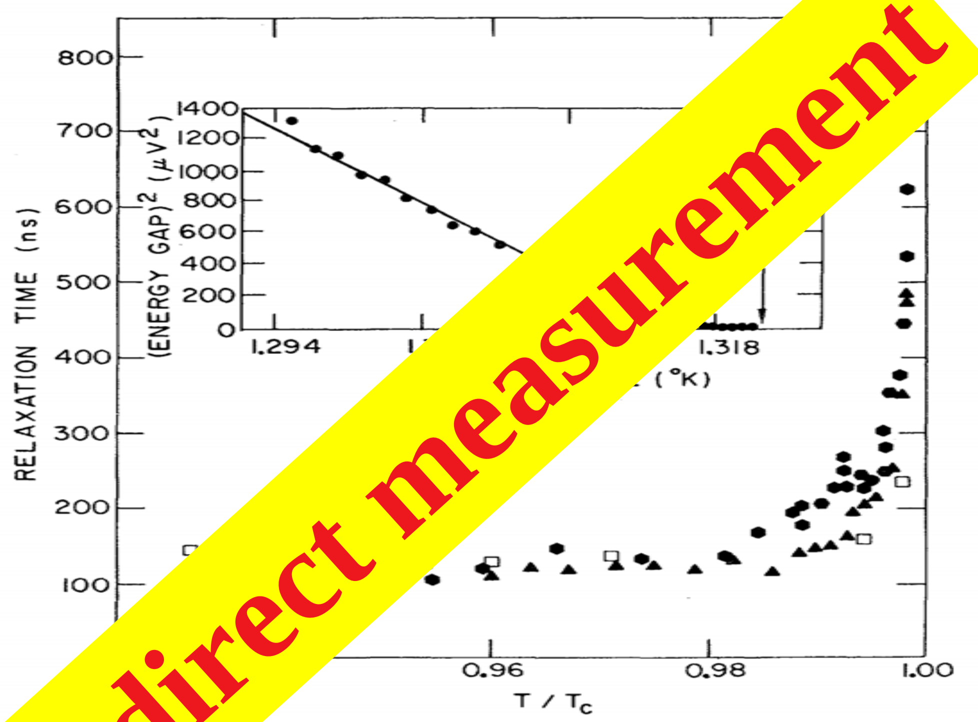


Figure I-1 Laser output (upper curve) and sample resistance at two temperatures (lower curves) as a function of time for a lead (Pb) film.[3]

Relaxation Time -Measurement



CRITICAL SLOWING DOWN



First direct measurement

...axation time τ versus the reduced temper-
... solid data points are the relaxation times
... in two different samples. The open squares
... quasiparticle lifetimes which are scaled as ex-
...d in the text. The inset shows the temperature
...ndence of the equilbrium energy gap and the solid
...e is the BCS prediction.

I. K. Schuller and K. E. Gray, PRL36, 429(1976)

NEW (?) **PROPERTIES**

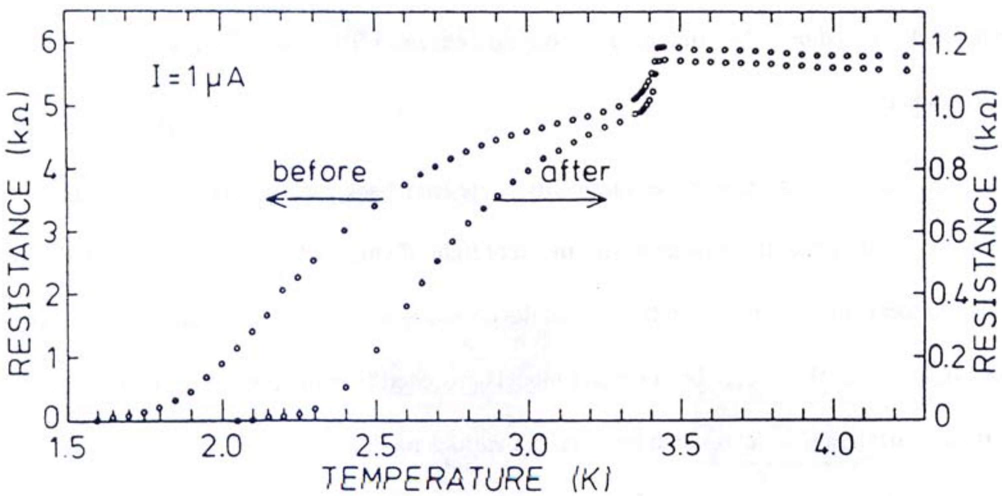


Figure I-6 Resistivity as a function of temperature before and after illumination for a CdS-In film.[7]

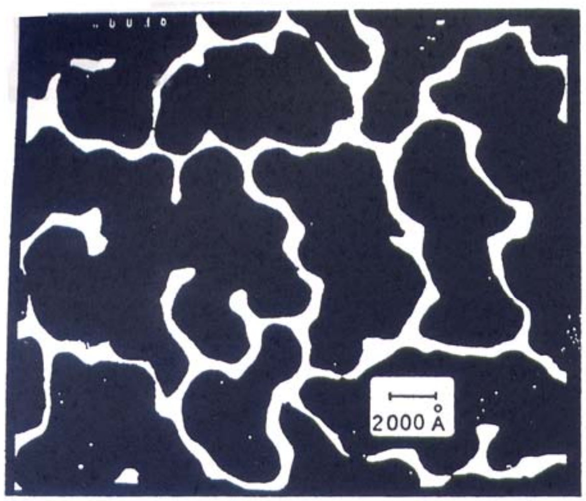


Figure I-5 Electron microscope picture of an In layer deposited on a CdS layer. Notice the small inter-island spacing between the grains of In.[7]

Easily Understood

G. Deutcher, A. Barone 1970s

Philosophy 2

- It is your responsibility to search the literature

- Nothing resembles as much a new effect as a mistake

PREVIOUS WORK

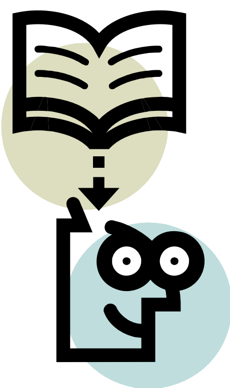
EFFECT OF LIGHT

Conventional Superconductors

•Enhanced Coupling of Grains

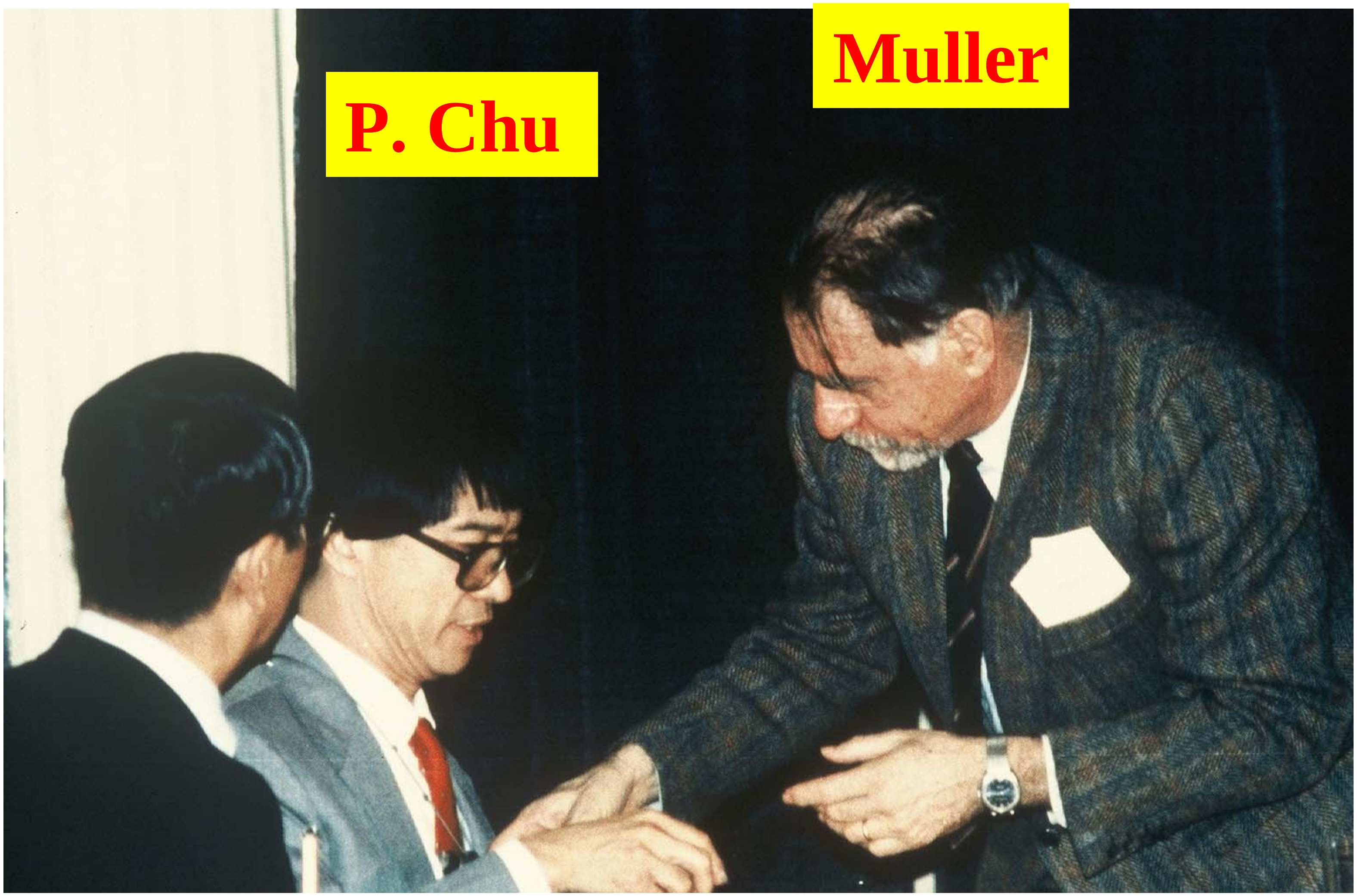
• “Heating”

Ceramic Superconductors



AHA !!!!!!

March Meeting 1987-Woodstock



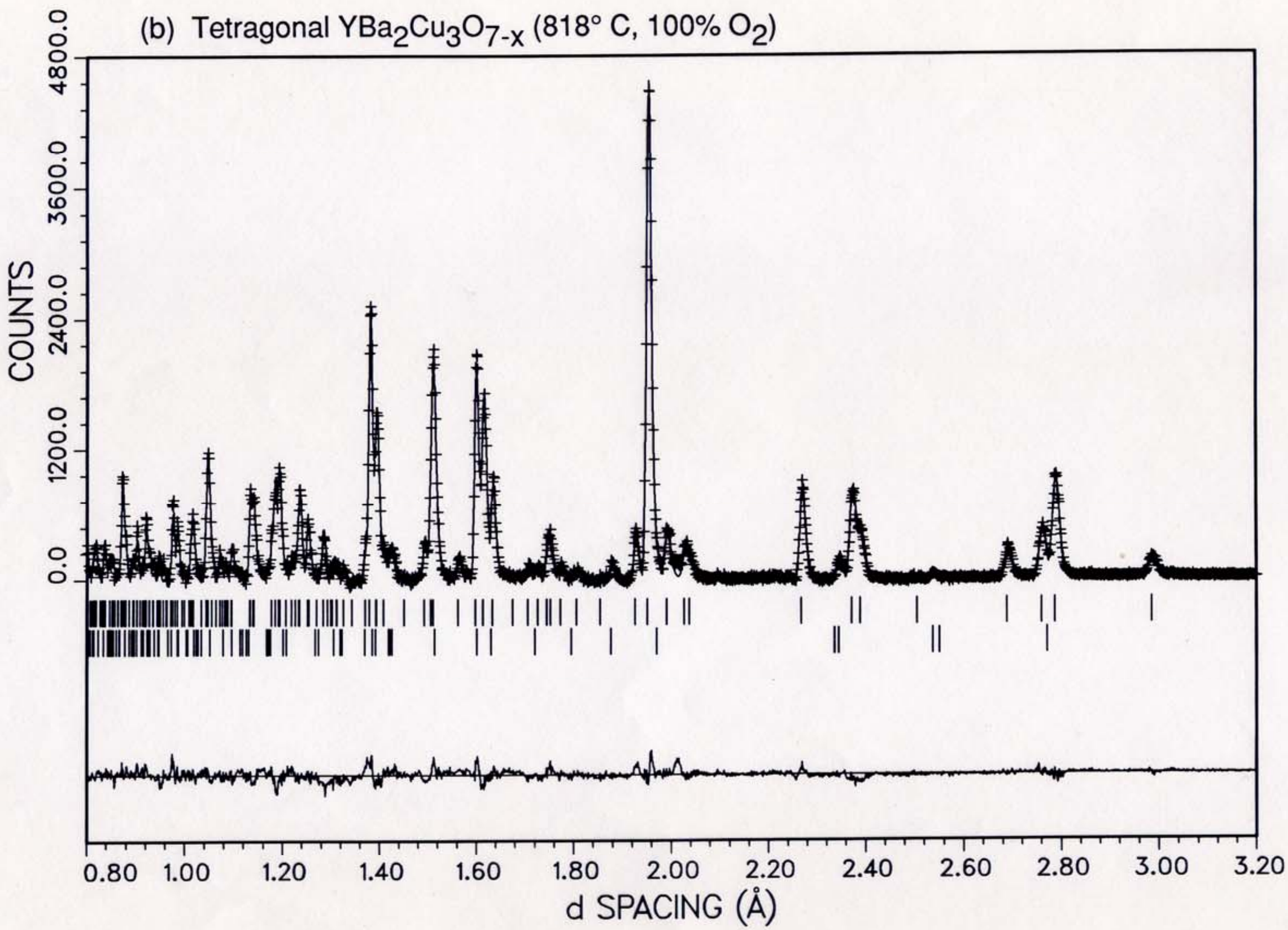
WHERE ARE THE ATOMS?

OXYGENS ARE PRESENT ⟹

NEED NEUTRON DIFFRACTION

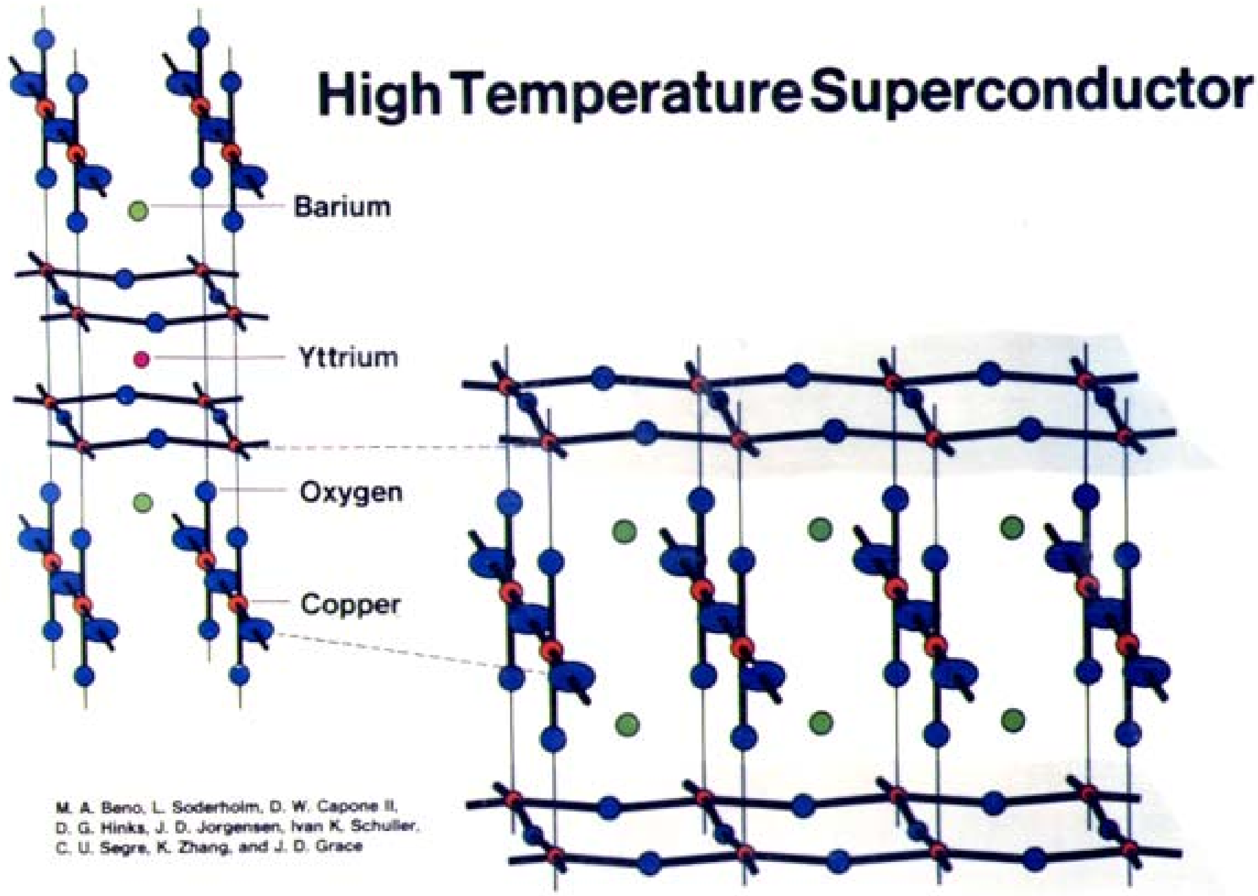
- MEASURE 567 REFLECTIONS
- USE 27 ADJUSTABLE PARAMETERS
- RIETVELD REFINEMENT

POWDER SAMPLE



(b) Tetragonal $YBa_2Cu_3O_{7-x}$ (818° C, 100% O_2)
COUNTS
0.0
1200.0
2400.0
3600.0
4800.0
0.80
1.00
1.20
1.40
1.60
1.80
2.00
2.20
2.40
2.60
2.80
3.00
3.20
d SPACING (Å)

Finished
March 3, 1986



Beno, Soderholm, Capone, Hinks, Jorgensen, IKS, Segre, Zheng, Grace

- APL 51,57 (1987),
- Nature 327, 310 (1987)

1ST submitted, 1st published

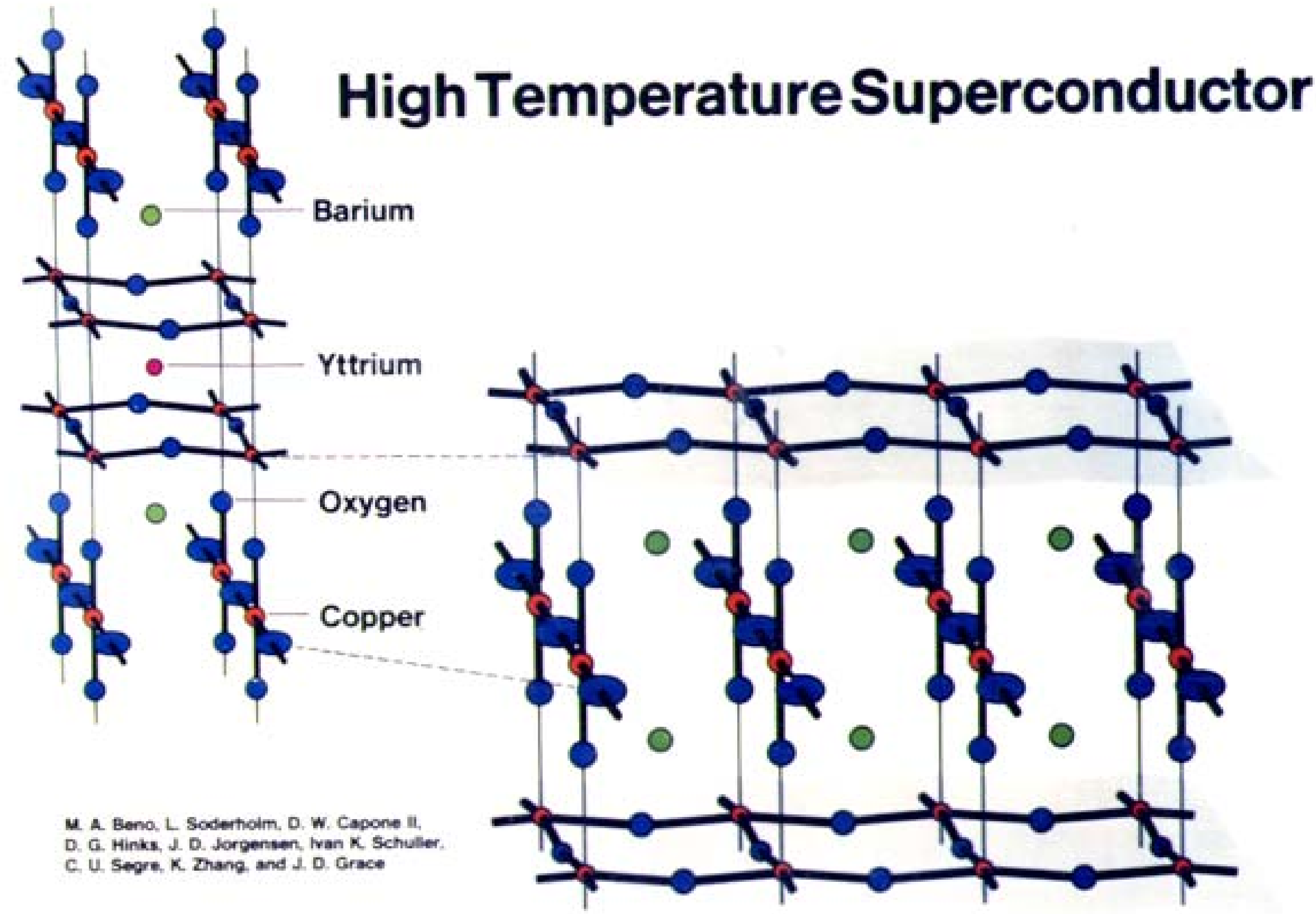
Doping Controls Superconductivity

Two Distinct Regions

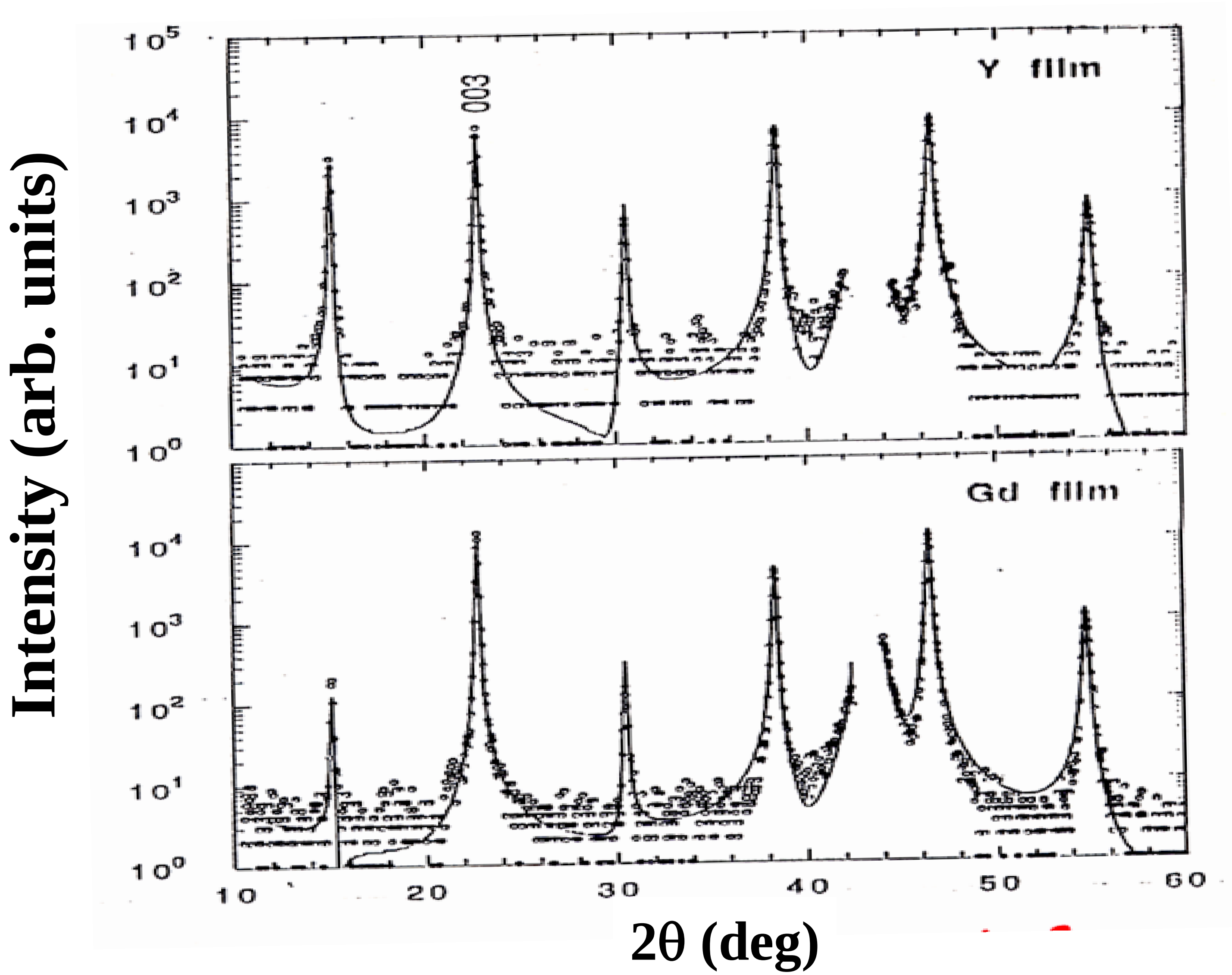
FILMS ARE REQUIRED

- Sharp Transitions
- Variable Oxygen Content

FILMS


High Temperature Superconductor
Barium
Yttrium
Oxygen
Copper
M. A. Beno, L. Soderholm, D. W. Capone II,
D. G. Hinks, J. D. Jorgensen, Ivan K. Schuller,
C. U. Segre, K. Zhang, and J. D. Grace

$YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ Sputtered Films



E. Fullerton, et al. APL

REFINEMENT

AGREES WITH

BULK
STRUCTURE

TO .03 Å

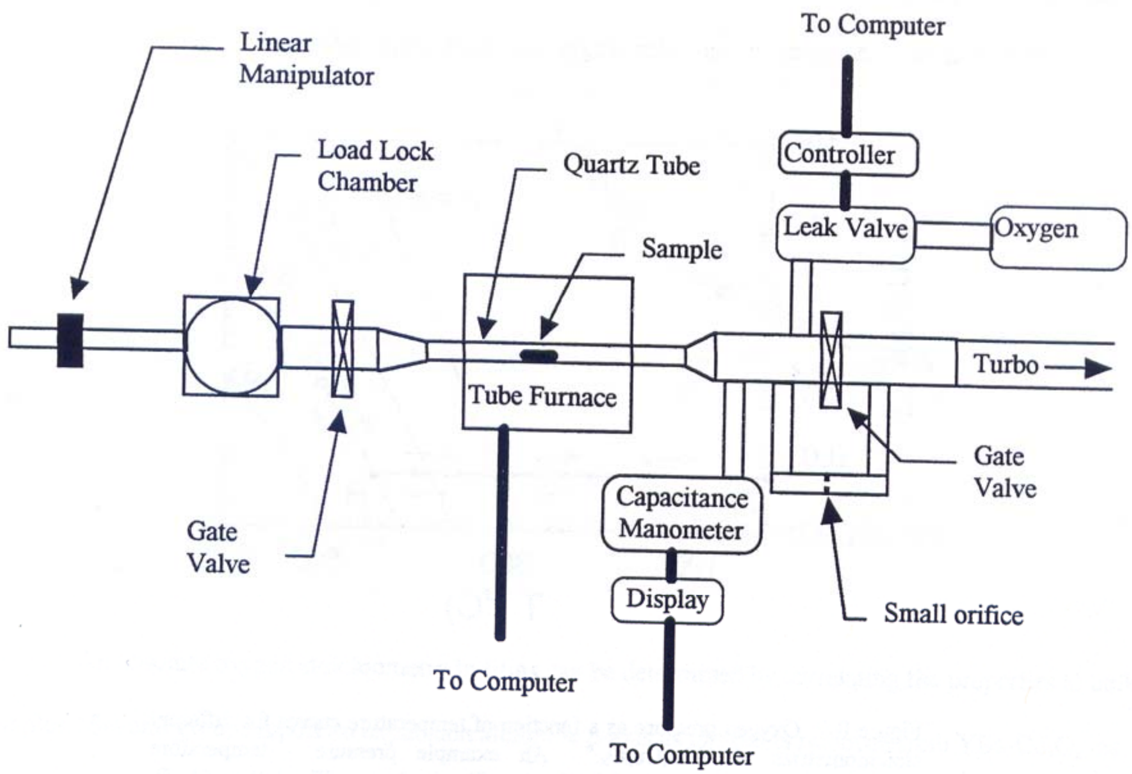


Figure II-6 Gas evolution system used to deplete oxygen from $RBa_2Cu_3O_x$.

Very Reproducible

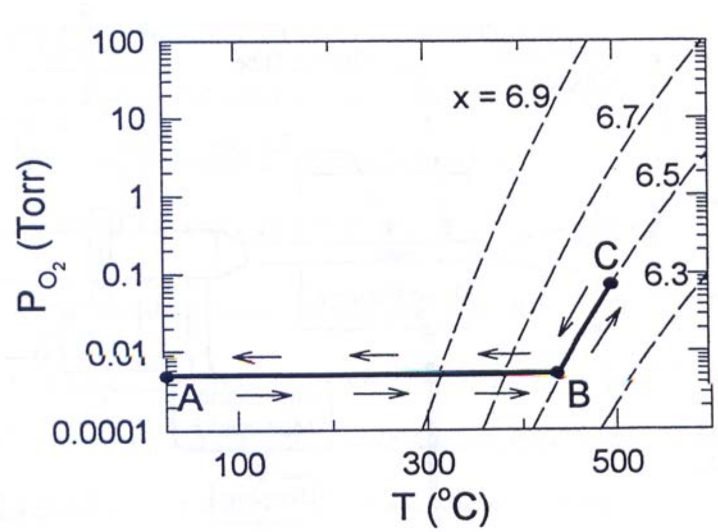


Figure II-7 Oxygen pressure as a function of temperature curves for different stoichiometries of $YBa_2Cu_3O_x$.[6] An example pressure - temperature processing path for making a $RBa_2Cu_3O_{6.5}$ film is shown. The letters (A, B, and C) denote stages during the processing treatment.

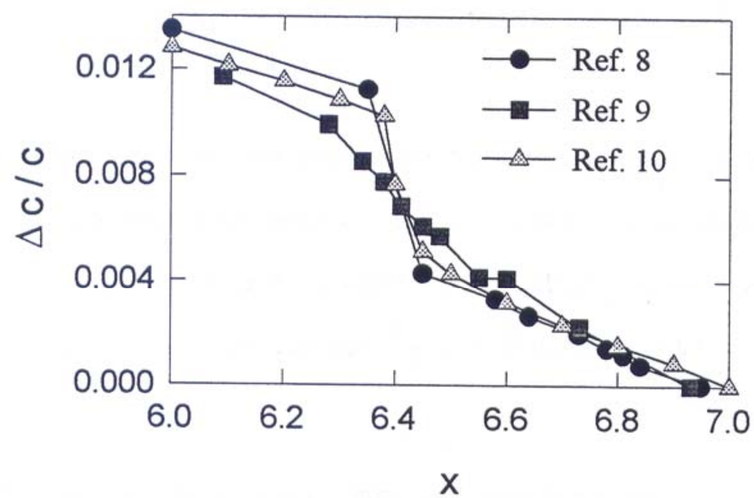
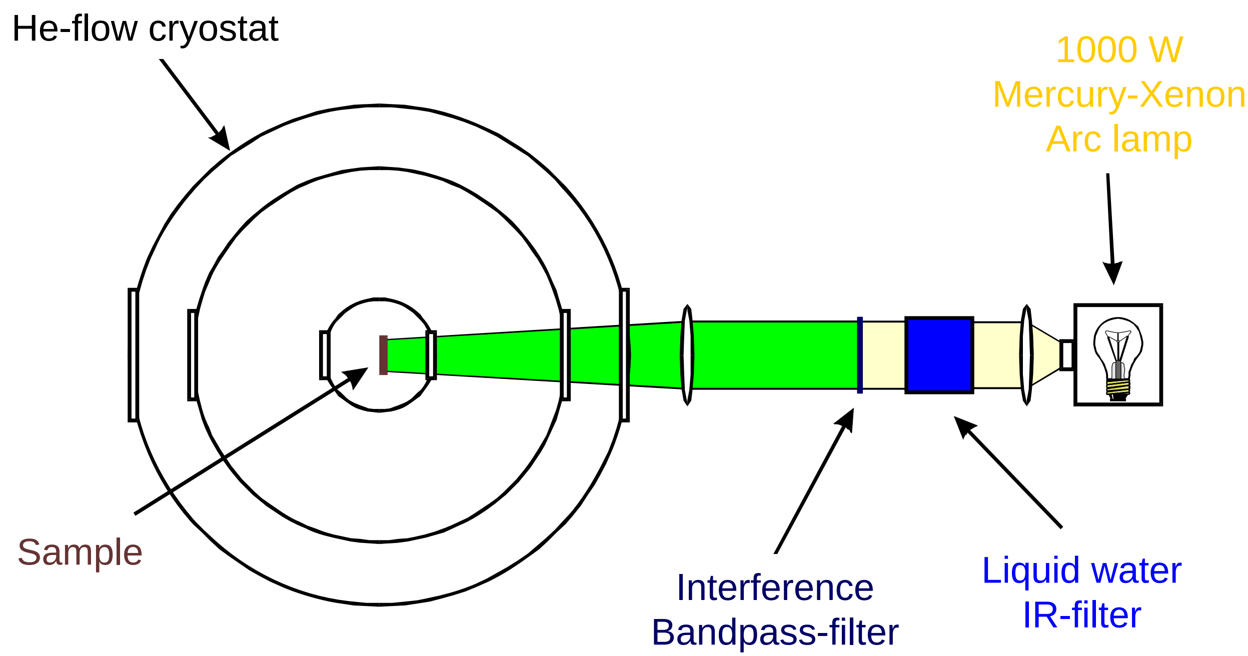


Figure II-8 Fractional change in *c*-axis, $\Delta c\ /\ c$, as a function of oxygen stoichiometry, x.[8, 9, 10]

Experimental Setup



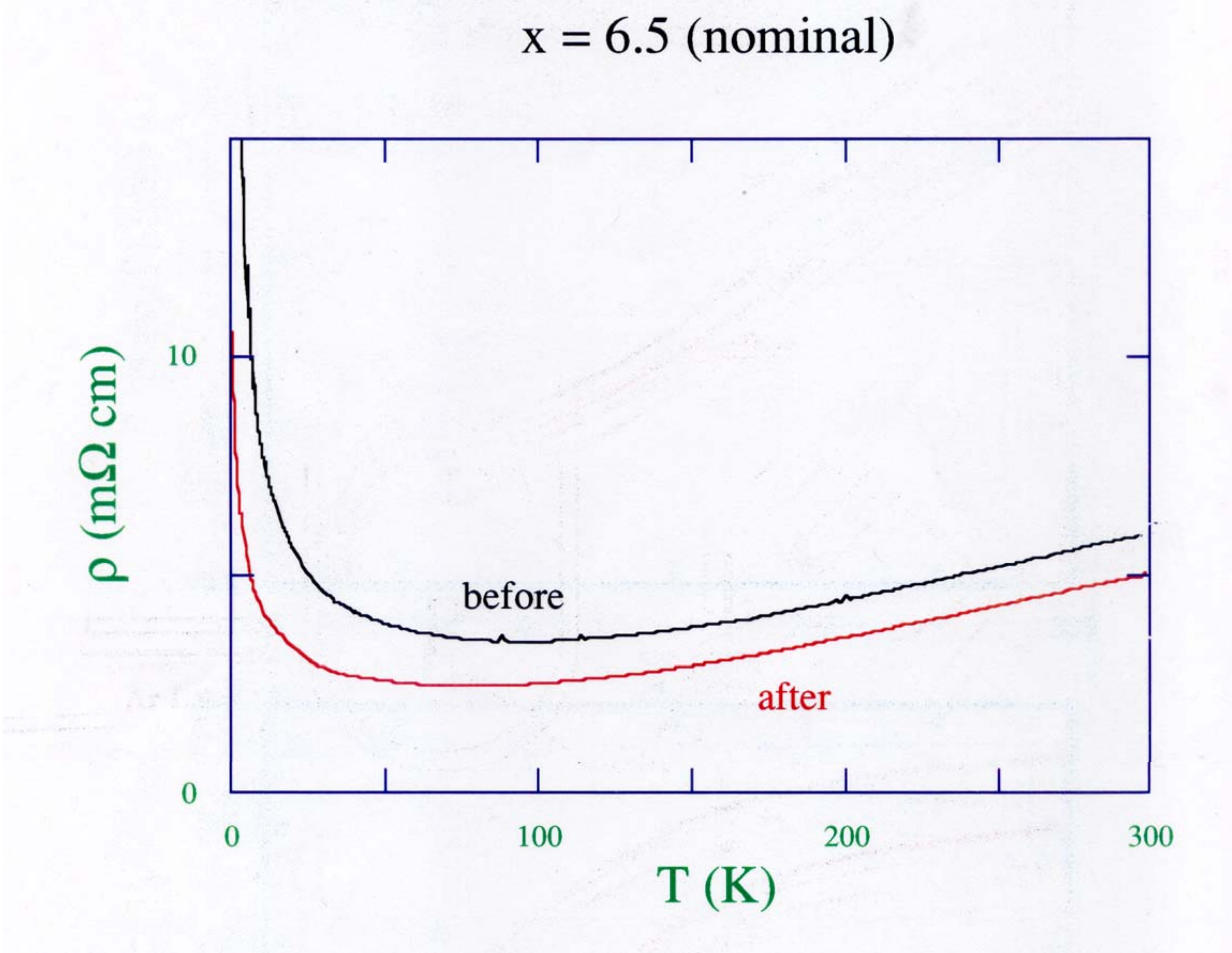
Optical Setup

Bandpass Filters:	250-900 nm (4.8-1.4 eV)
	10 nm Bandwidth
Intensity at Sample:	0.04-5 mW/cm^2

Transport Measurements

4-point resistance, Hall measurements

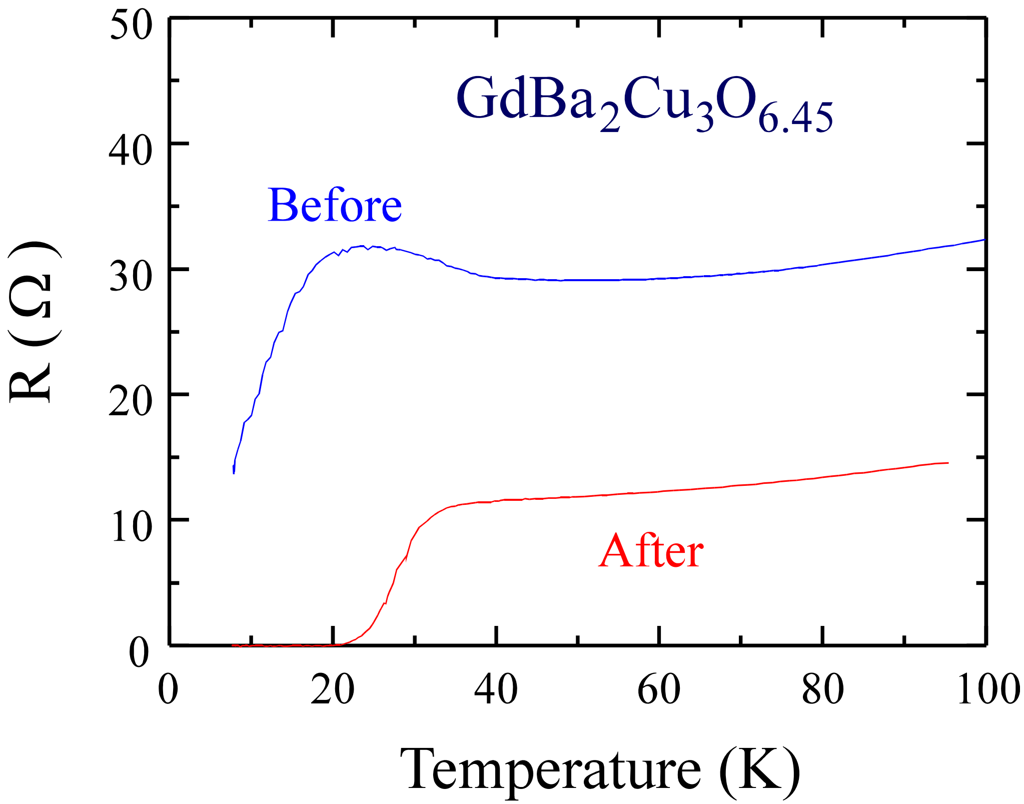
$GdBa_2Cu_3O_{7-\delta}$: **SURPRISE**



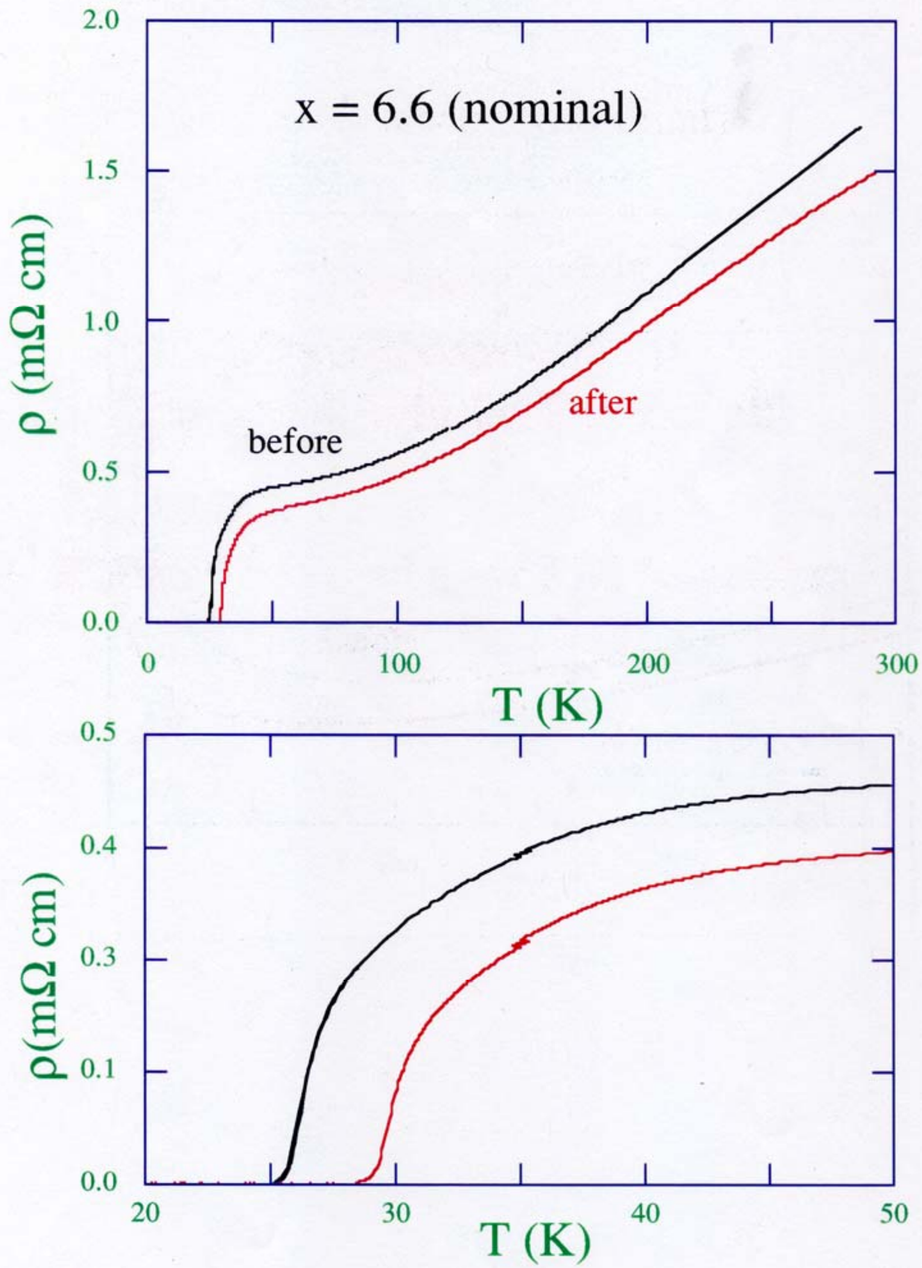
V. Kudinov, 1994 ?

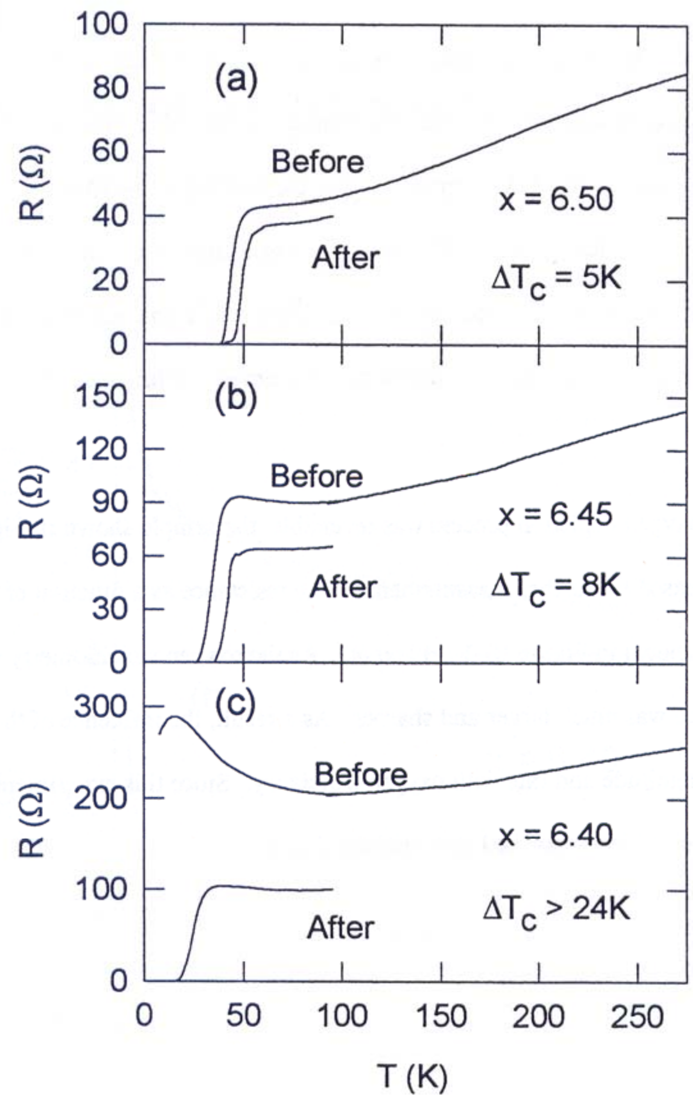
BASIC EFFECT

Opposite from Conventional Superconductors



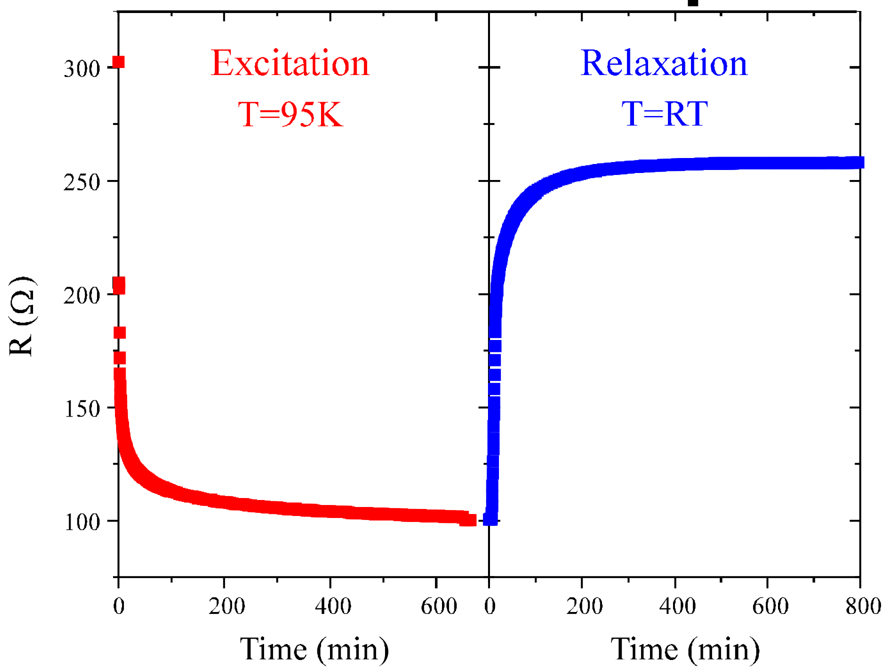
G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt,B. Wuyts, Y. Bruynseraede, M.B. Maple, and I.K. Schuller, Appl. Phys. Lett. 60, 2159 (1992)


x = 6.6 (nominal)
before
after
ρ (mΩ cm)
T (K)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
ρ(mΩ cm)
0.5
0.4
0.3
0.1
0.0
20
30
40
50
T (K)



Is it permanent ?

$GdBa_2Cu_3O_{7-\delta}$: Time Dependence



Excitation

- **τ ∝ Intensity of light**
- **τ depends on wavelength**

Relaxation

- **No relaxation below ~100 K**
- **Thermally activated at RT (E = 0.9±0.1 eV)**
- **Partial (up to 5%) IR quenching at low T**

J.Hasen, PhD thesis, University of California, San Diego, 1995.

$$R(t) = R(t=\infty) + \Delta R_{\max} e^{-\left(\frac{t}{\tau}\right)^{\beta}}$$

PERSISTENT

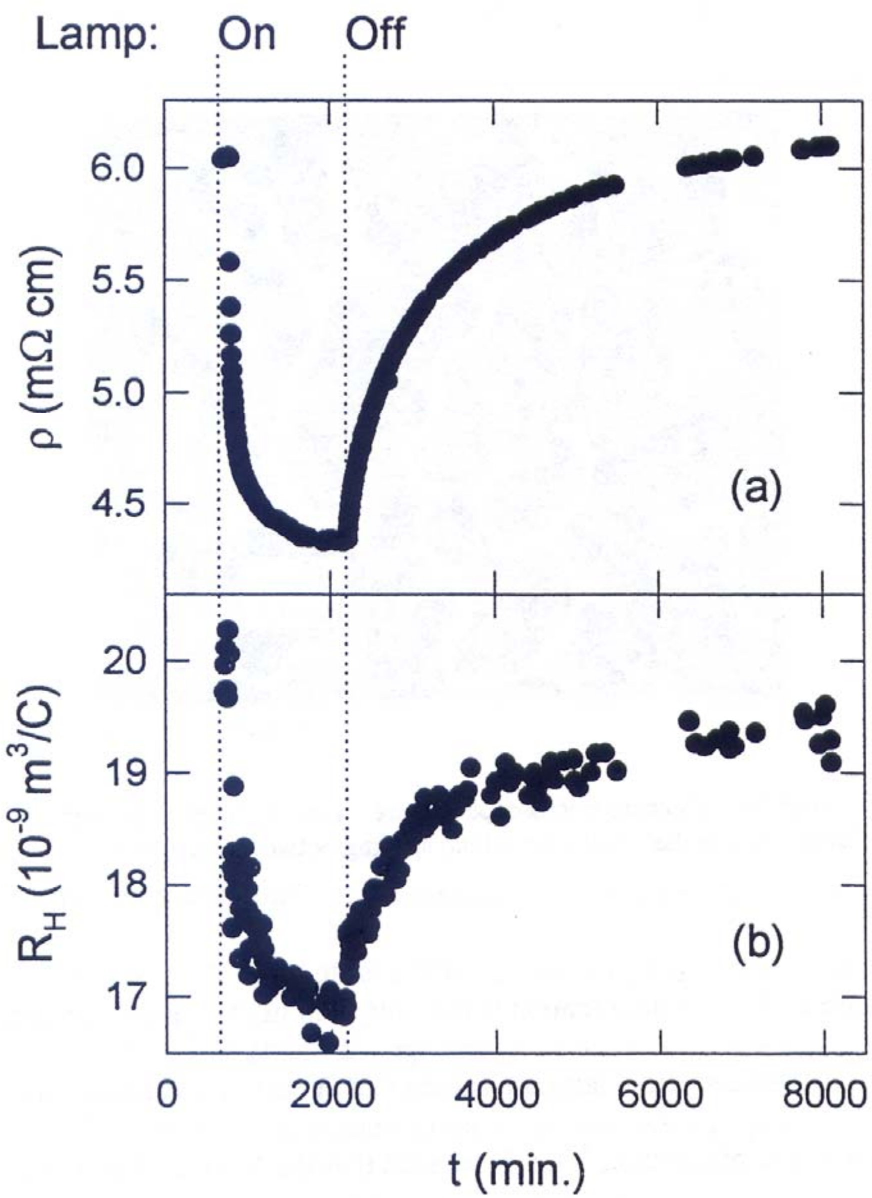


Figure I-4 Resistivity (a) and Hall coefficient (b) as a function of time during and after illumination of a $YBa_2Cu_3O_{6.5}$ film at 300 K.[6]

RESISTIVITY

Enhanced conductivity

HALL EFFECT

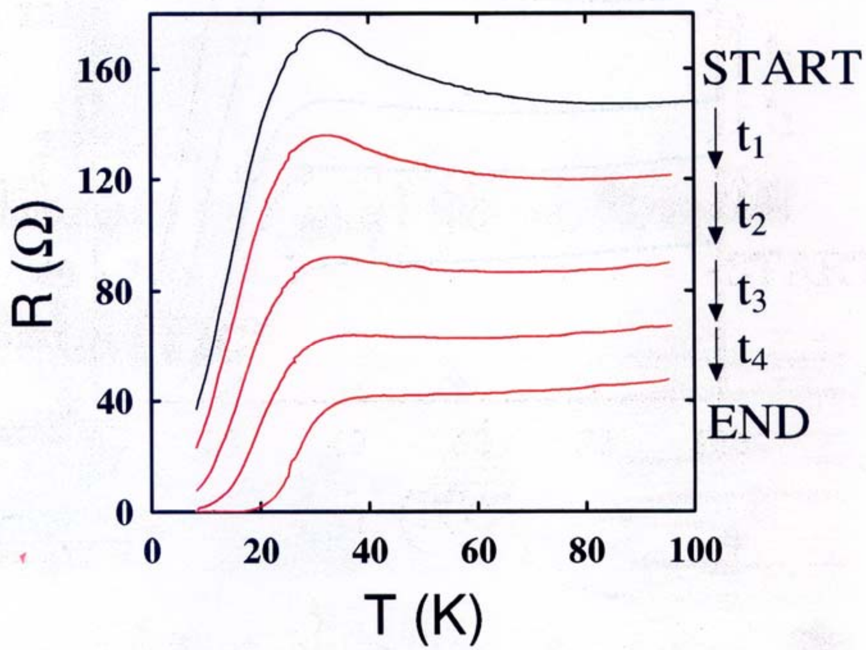
Increased doping n

HYSTERESIS EXPERIMENT

What happens in between full saturation and relaxation?

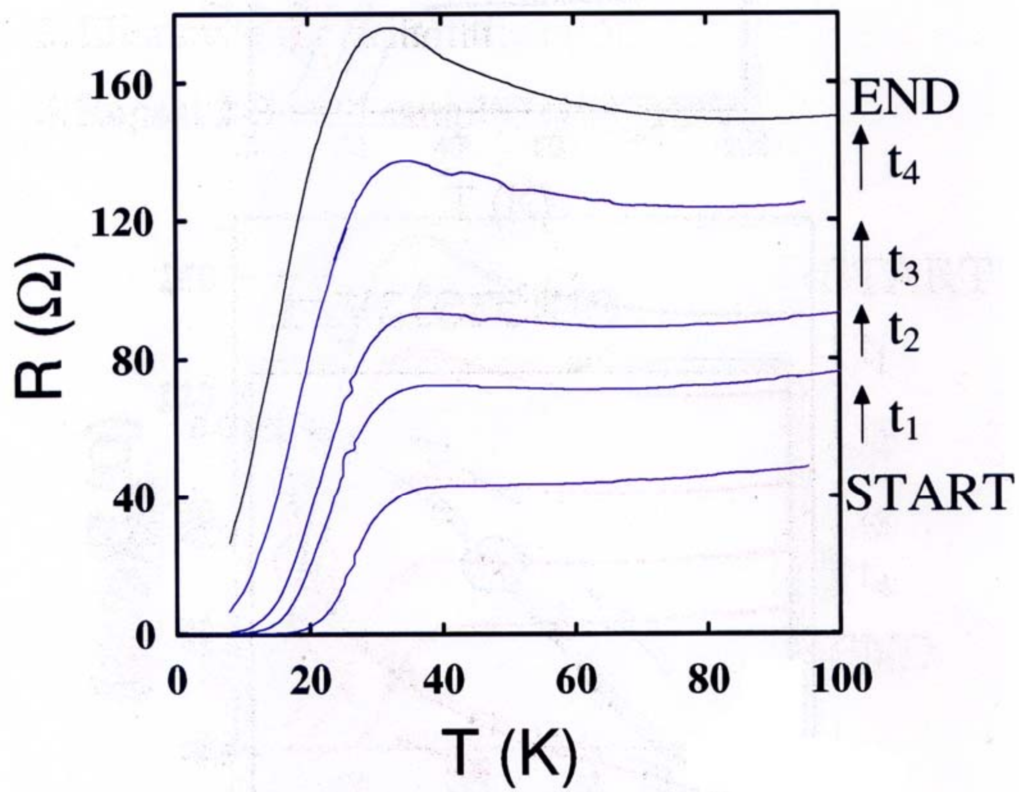
I. Excitation

1. Cool to 95K.
2. Measure R(T).
3. Illuminate for a short time (t_i).
4. Repeat 2-3 until sample is saturated.

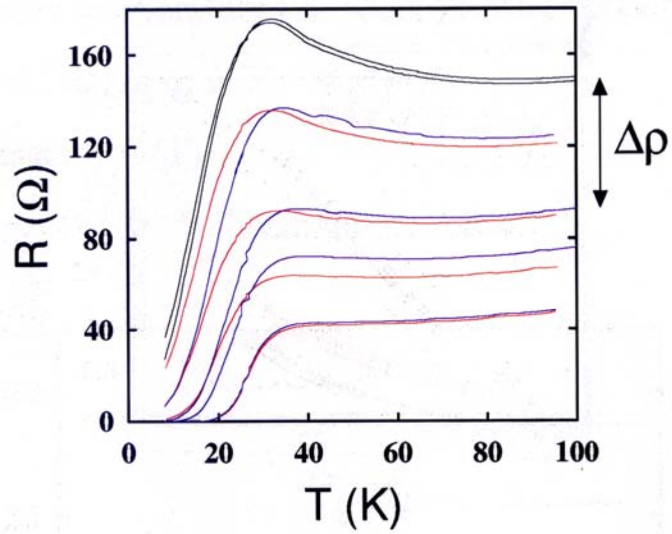


II. Relaxation

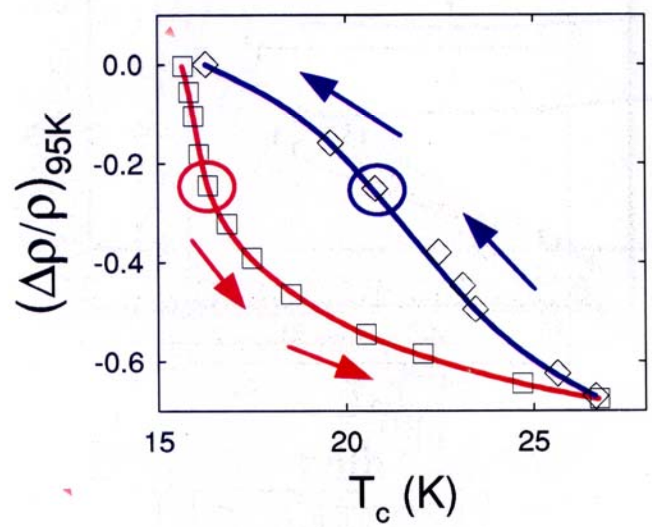
1. Raise temperature (≤ 300K) for a short time (t_i).
2. Cool down to 95K.
3. Measure R(T).
4. Repeat 1-3 until sample is relaxed.



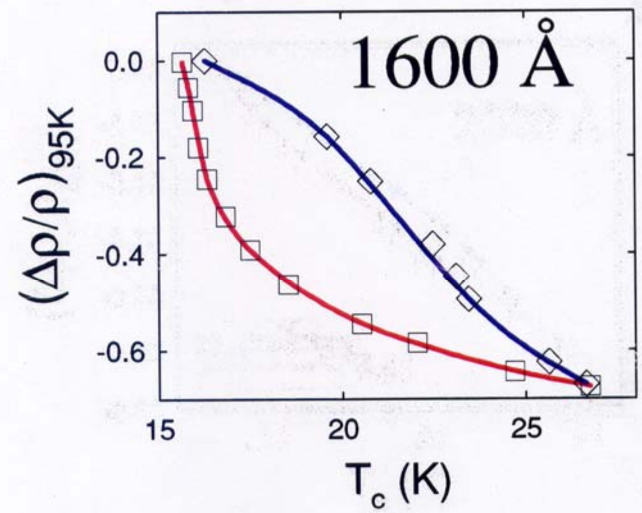
Excitation ≠ Relaxation

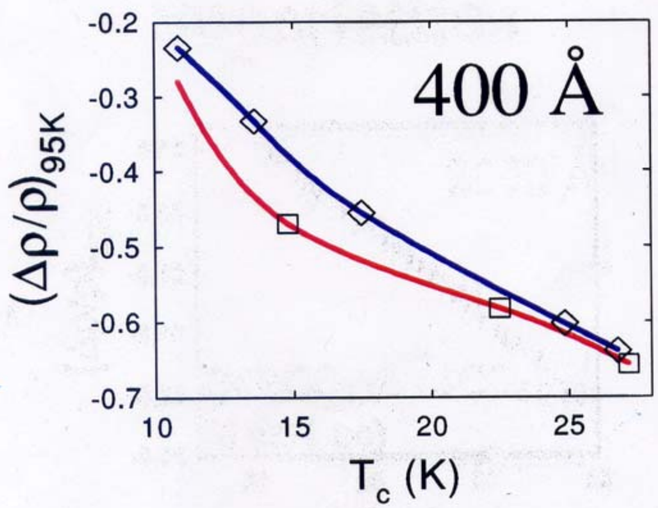


Hysteresis



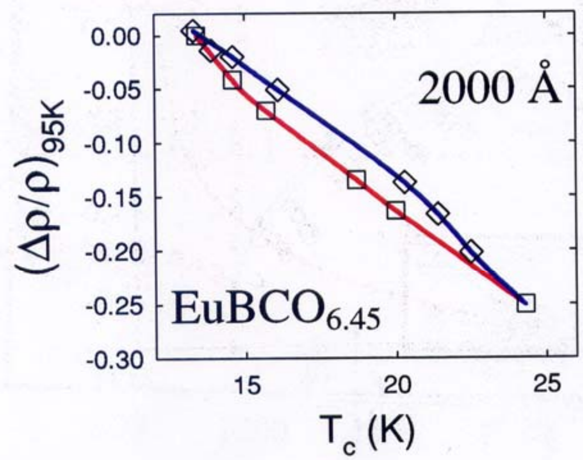
Thickness Dependence



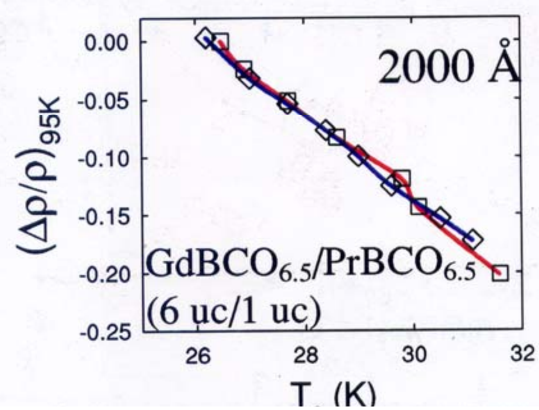


Decreases with thickness

a-axis Films



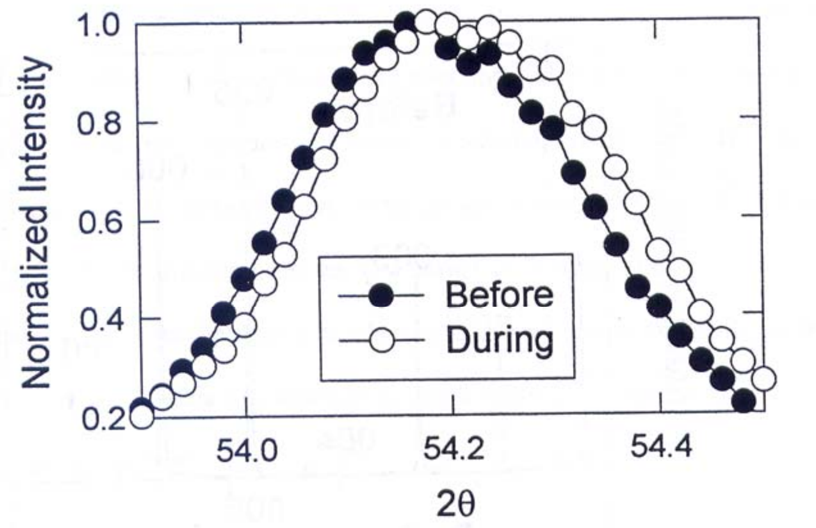
Superlattice



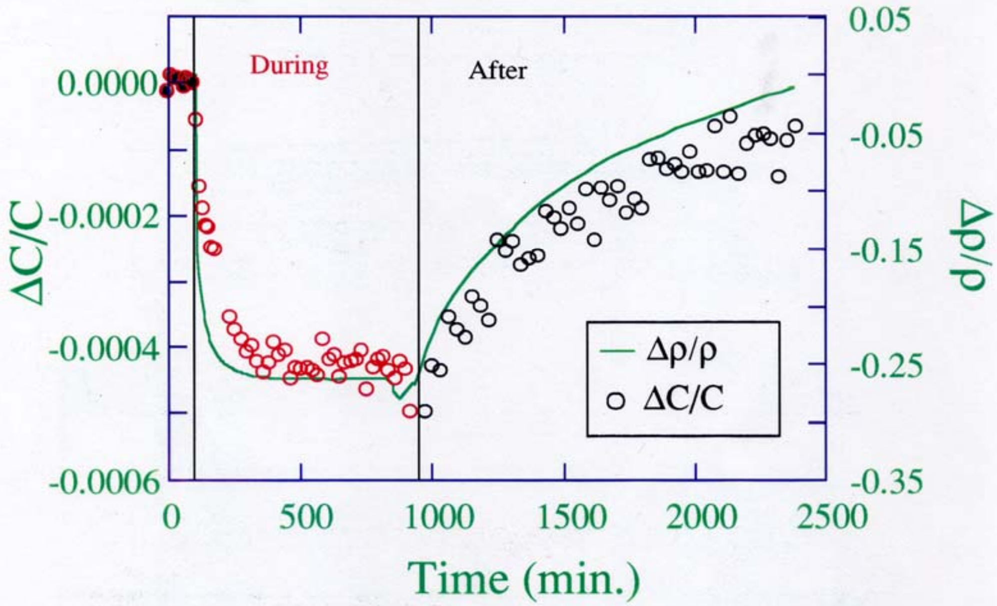
No Hysteresis

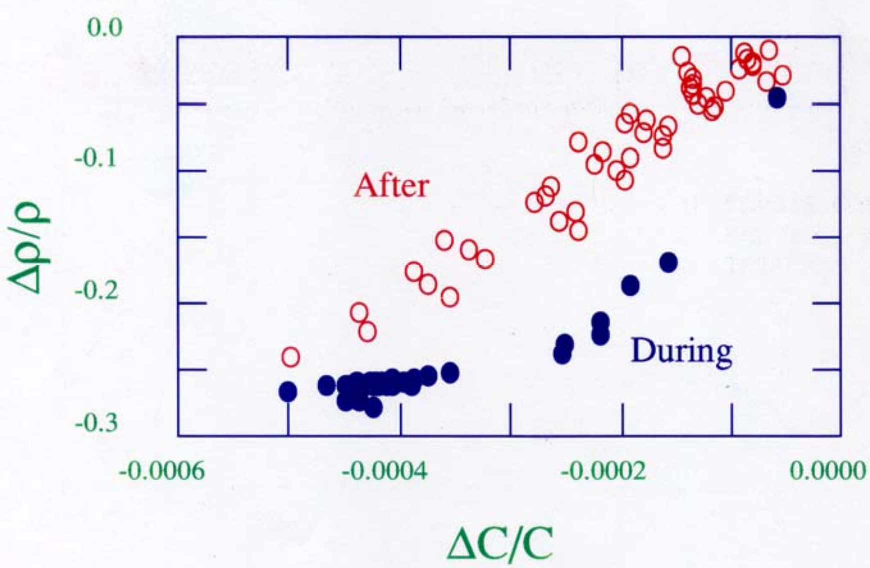
STRUCTURE

007 Peak



Extremely Challenging


During
After
0.0000
-0.0002
-0.0004
-0.0006
ΔC/C
0.05
-0.05
-0.15
-0.25
-0.35
Δρ/ρ
0
500
1000
1500
2000
2500
Time (min.)
Δρ/ρ
ΔC/C


0.0
-0.1
-0.2
-0.3
Δρ/ρ
After
During
-0.0006
-0.0004
-0.0002
0.0000
ΔC/C

RESULTS

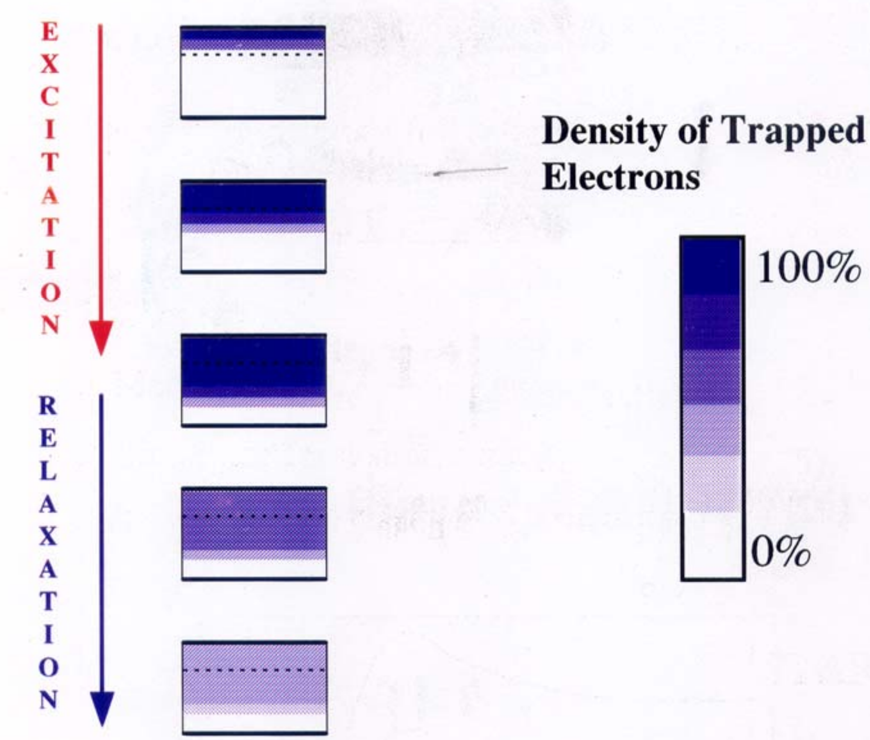
Excitation ≠ Relaxation

c-axis → large effect (decreases with thickness)

a-axis → small effect

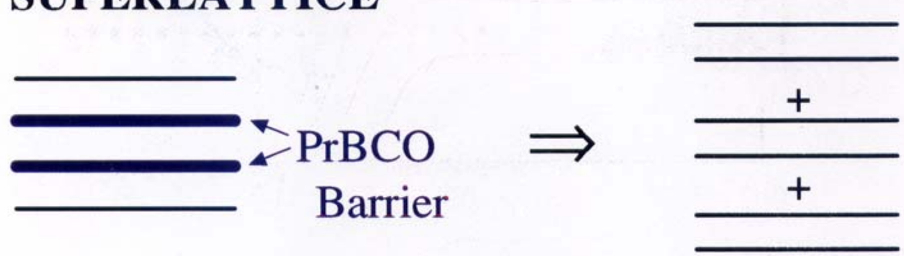
superlattice → no effect

structure → large effect
(D. Lederman et al., APL **64**, 652 (94))



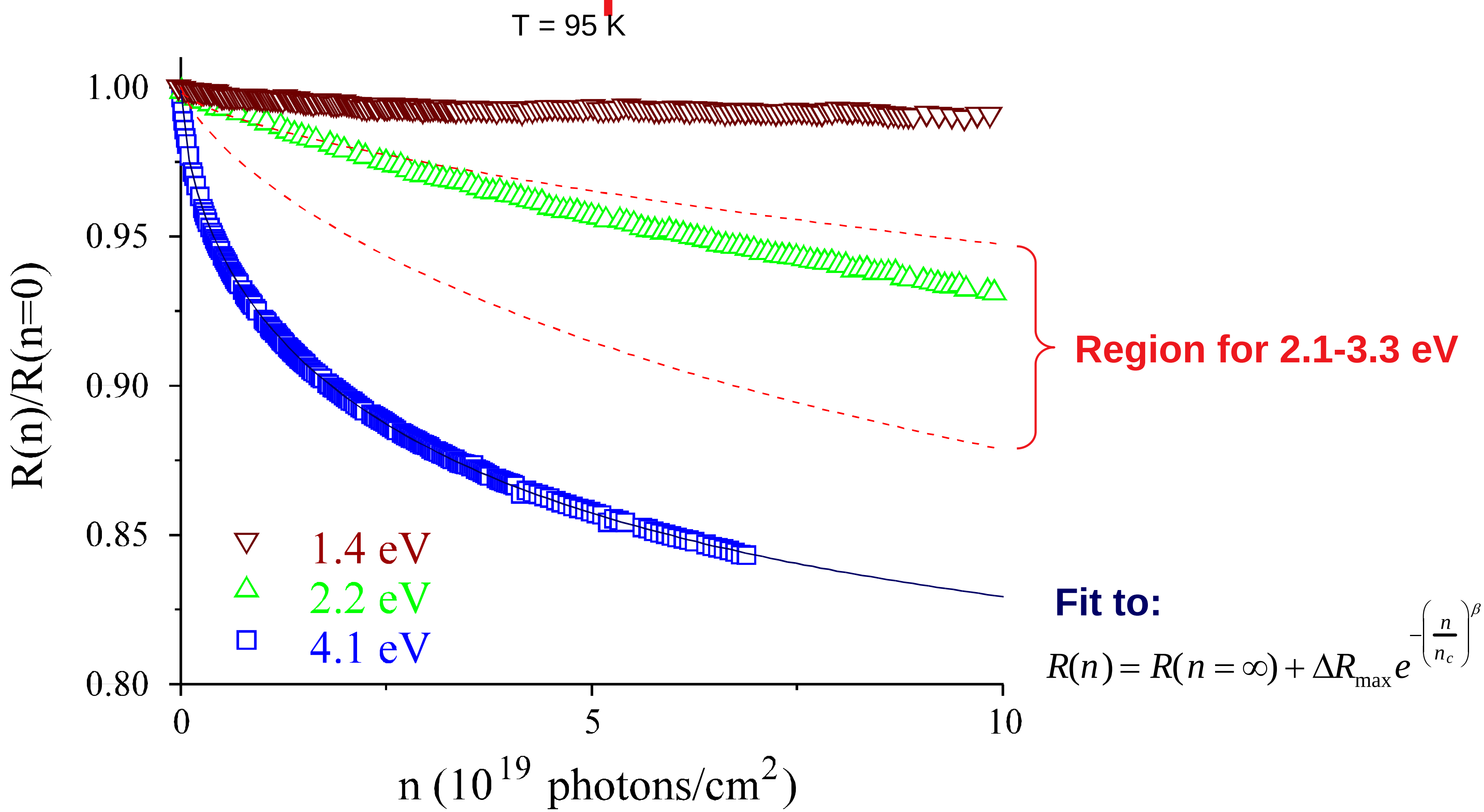
Film Thickness > Penetration Depth → **Hysteresis**

SUPERLATTICE



Independent set of thin films → **No Effect**

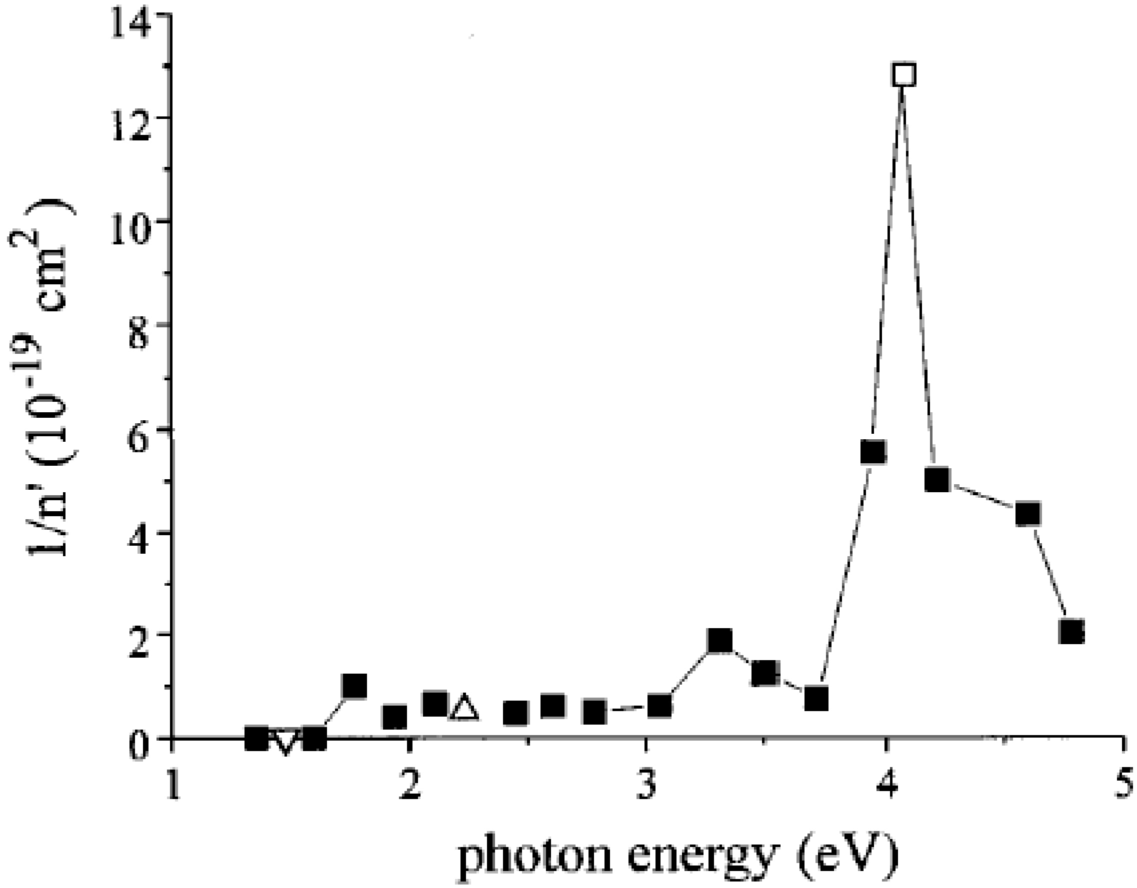
$GdBa_2Cu_3O_{6.3}$: Spectral Dependence



T. Endo, A. Hoffmann, J. Santamaría, and I.K. Schuller, Phys. Rev. B, 54 3750 (1996).

$GdBa_2Cu_3O_{6.3}$: Spectral Dependence

T = 95 K



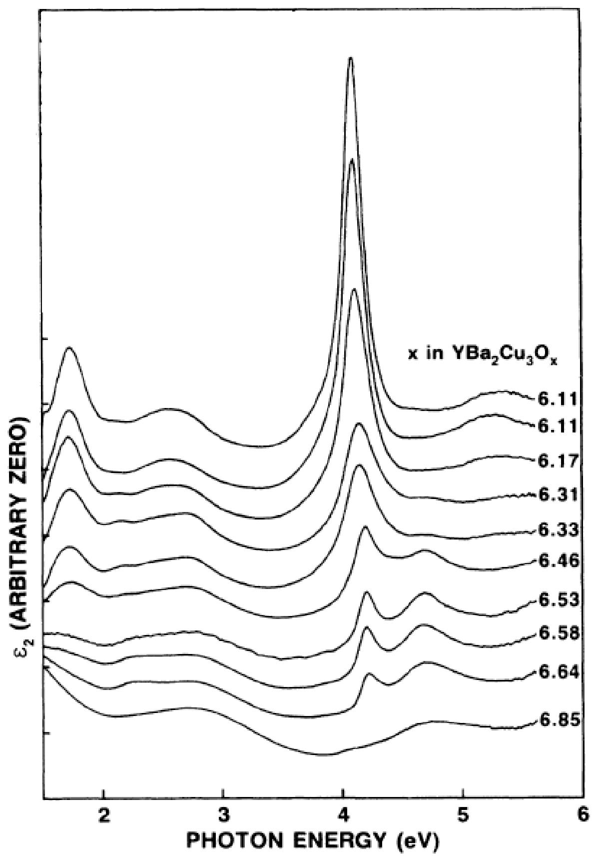
n': 2% decrease of resistance

- Onset at 1.6 eV
- Enhancement at 4.1 eV

T. Endo, A. Hoffmann, J. Santamaría, and I.K. Schuller, Phys. Rev. B, 54 3750 (1996).

Other Optical Measurements

Dielectric Function

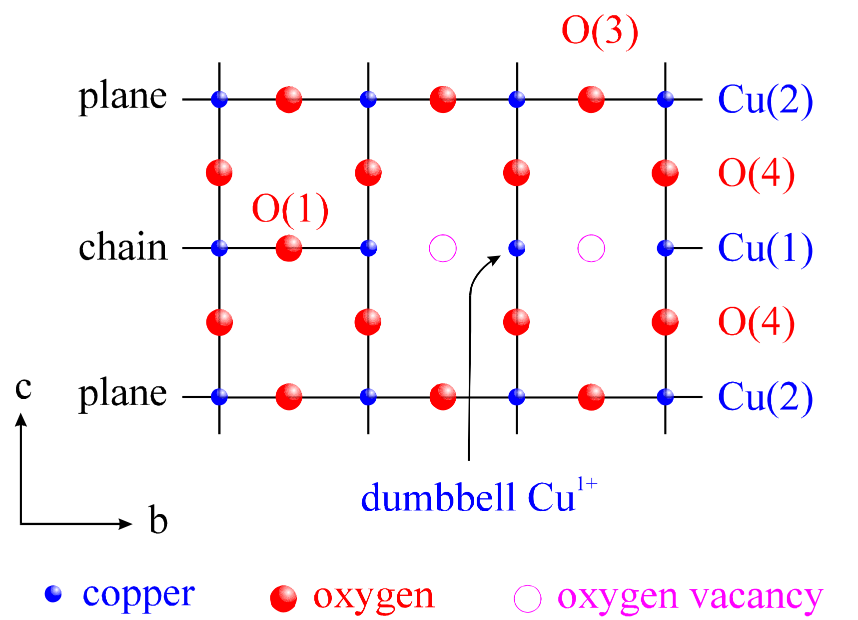


M. K. Kelley, *et al.*, Phys. Rev. B, 38 870 (1989).

< 1.6 eV:
Charge Transfer Gap CuO_2 plane

1.6 - 3.2 eV:
CuO_2-plane: Cu^{2+} 3d + O^{2-} $2p_{x,y} \rightarrow Cu^{2+}\ 3d_{x^2-y^2}$

4.1 eV:
CuO-chain: $Cu^{1+}\ 3d_{z^2-1} \rightarrow Cu^{1+}\ 4p_{x,y}$



ReBCO (123 Compounds)

- Resistance *R* ↘
- T_c ↗
- Hall coefficient R_H ↘
- Hall mobility μ ↗
- *c*-axis ↘

Penetration of light

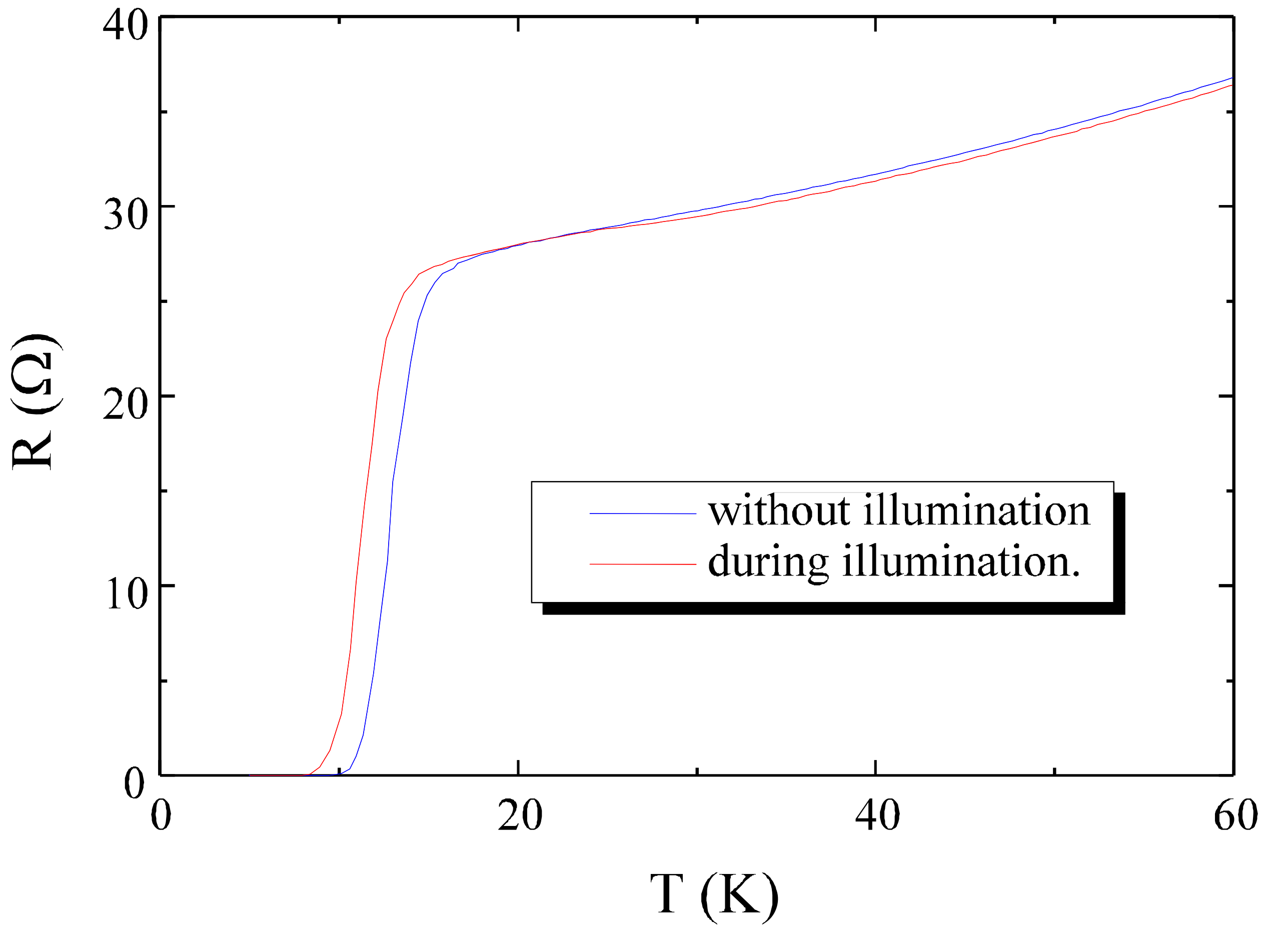
Only 123 ???

Oxygen deficiency or depressed superconductivity ???

$Tl_2Ba_2CuO_{6+\delta}$

- Simple Structure
  - Tetragonal
  - One CuO_2 plane / unit cell
  - No CuO-chains
- T_c: 0-90 K
  - By Vacuum or Oxygen annealing
  - Overdoped

$Tl_2Ba_2CuO_{6+\delta}$: Basic Effect



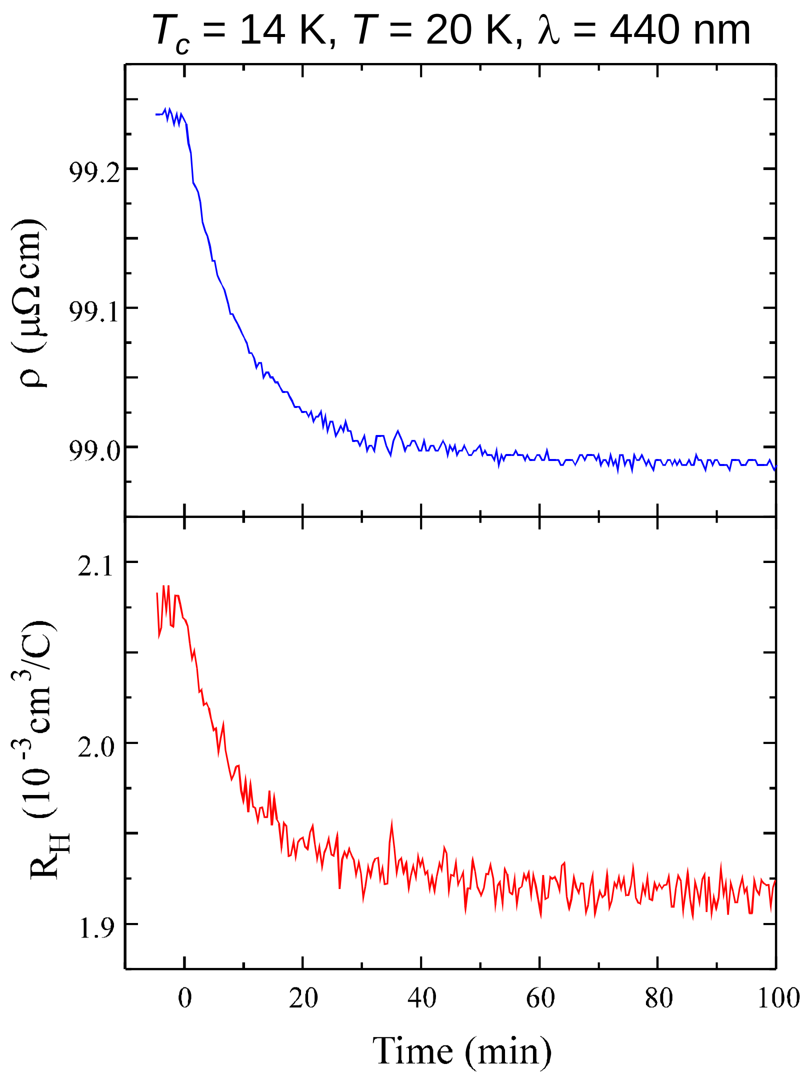
ΔR much smaller!

Overdoped

$\Downarrow$

R ↘, T_c ↘

$Tl_2Ba_2CuO_{6+\delta}$



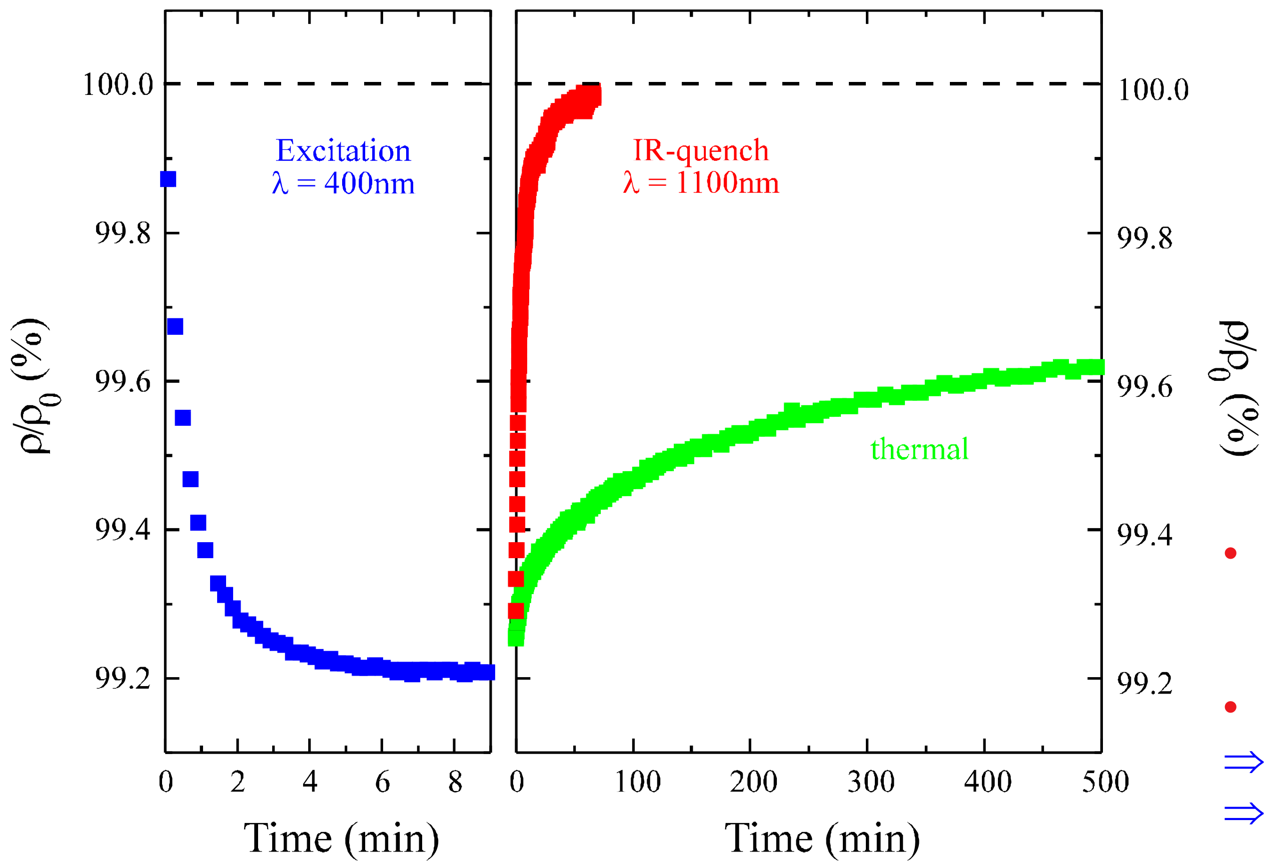
RESISTIVITY

HALL EFFECT

Increased n

$Tl_2Ba_2CuO_{6+\delta}$: t Dependence

T_c = 14 K, T = 30 K



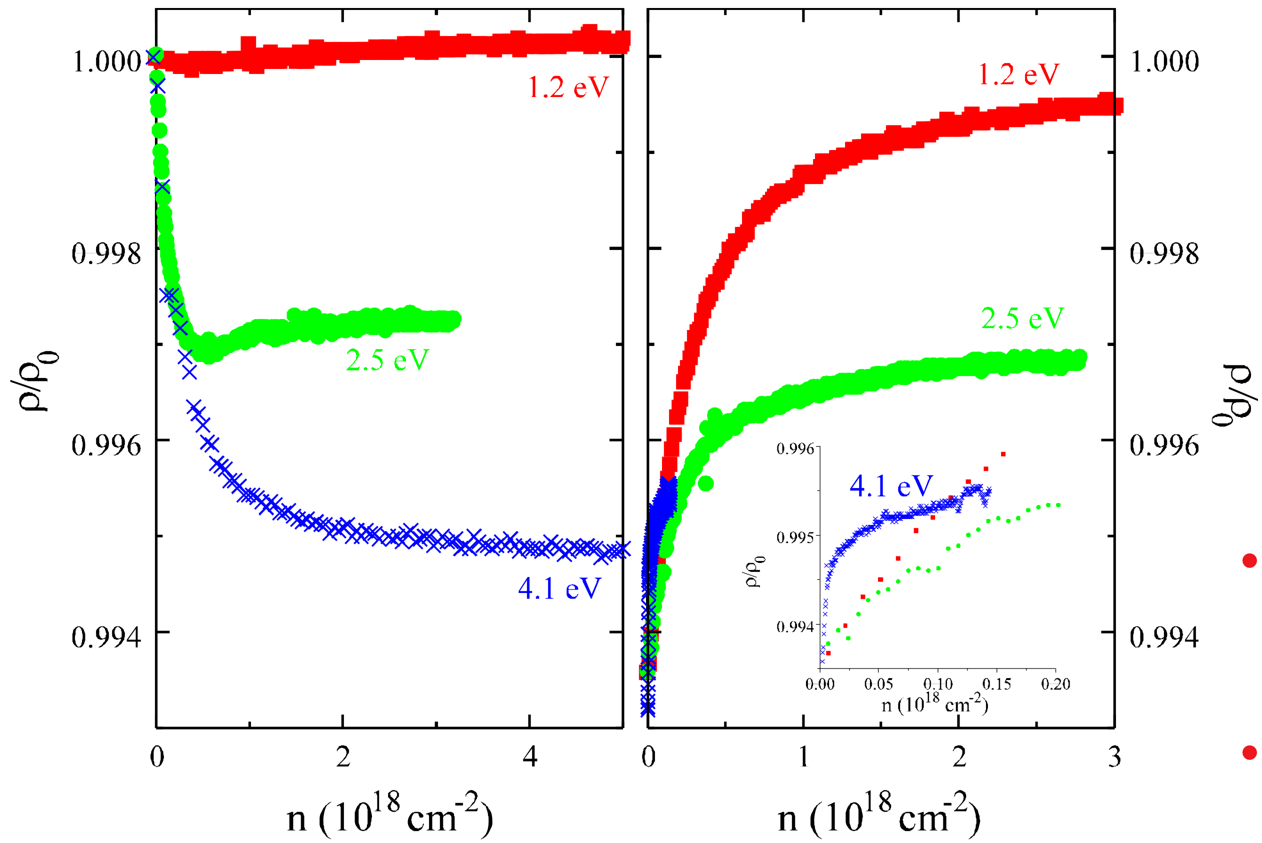
- Slow thermal relaxation at low *T*
- Complete IR-quenching!

⇒ Not oxygen ordering

⇒ Electronic mechanism

$Tl_2Ba_2CuO_{6+\delta}$: Spectral Dependence

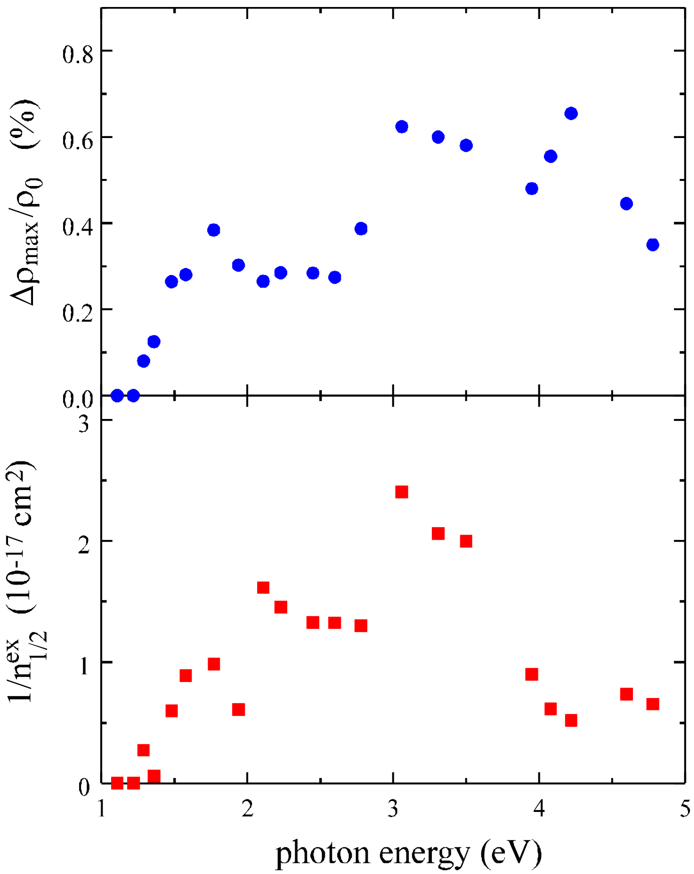
T_c = 14 K, T = 30 K



- **$\Delta\rho$ depends on photon energy**
- **Final ρ independent of initial ρ**

$Tl_2Ba_2CuO_{6+\delta}$: Spectral Dependence

T_c = 14 K, T = 30 K



- Onset at 1.3 eV
- Two different levels for $\Delta\rho$

$\Rightarrow$ Two different kinds of localized states

- Potential Candidates
  - Cu for Tl substitution
  - Interstitial Oxygen

A. Hoffmann, I.K. Schuller, Z.F. Ren, Y.Y. Lao, and J.H. Wang, Phys. Rev. B, 54 3750 (1996).

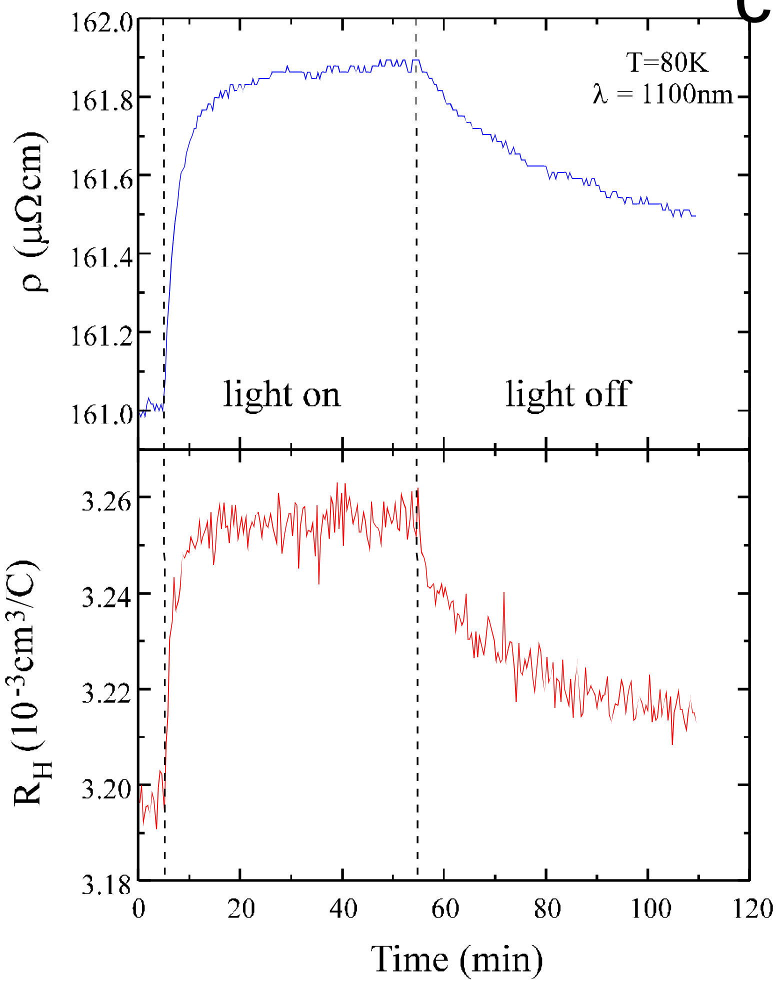
Conclusion

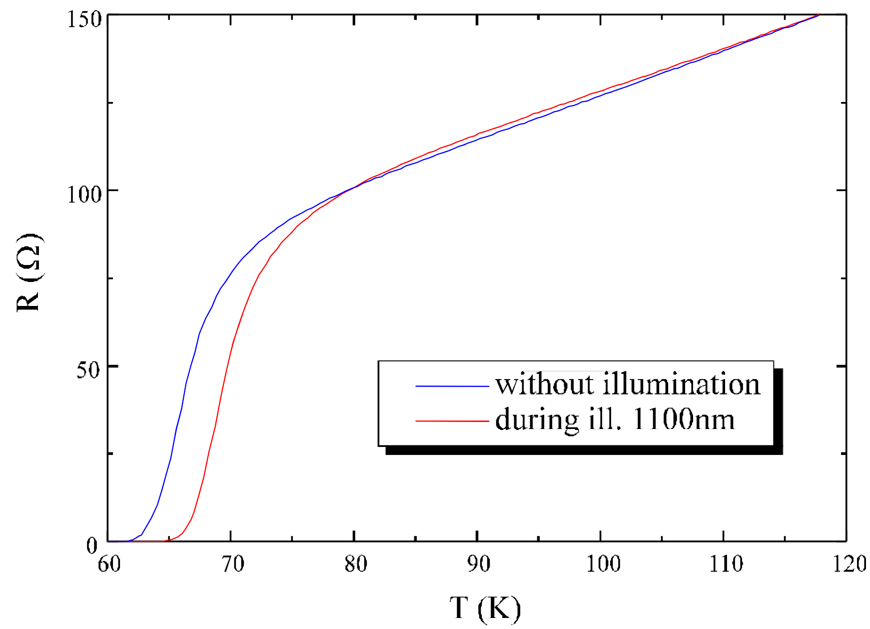
- $GdBa_2Cu_3O_{7-\delta}$
  - **Illumination: increases carrier density**
  - **Photoinduced Effects are persistent at low *T***
  - **Spectral Dependence shows Enhancement at 4.1 eV**

  Electron trapping at oxygen vacancy in CuO chain
- $Tl_2Ba_2CuO_{6+\delta}$
  - **Illumination: increase or decrease carrier density**
  - **Reversible with IR-quenching even at low *T***
  - **Persistent Photoconductivity without CuO chains**

  Mechanism is purely electronic

$Tl_2Ba_2CuO_{6+\delta}$: Low Doping, High T_c (66 K)

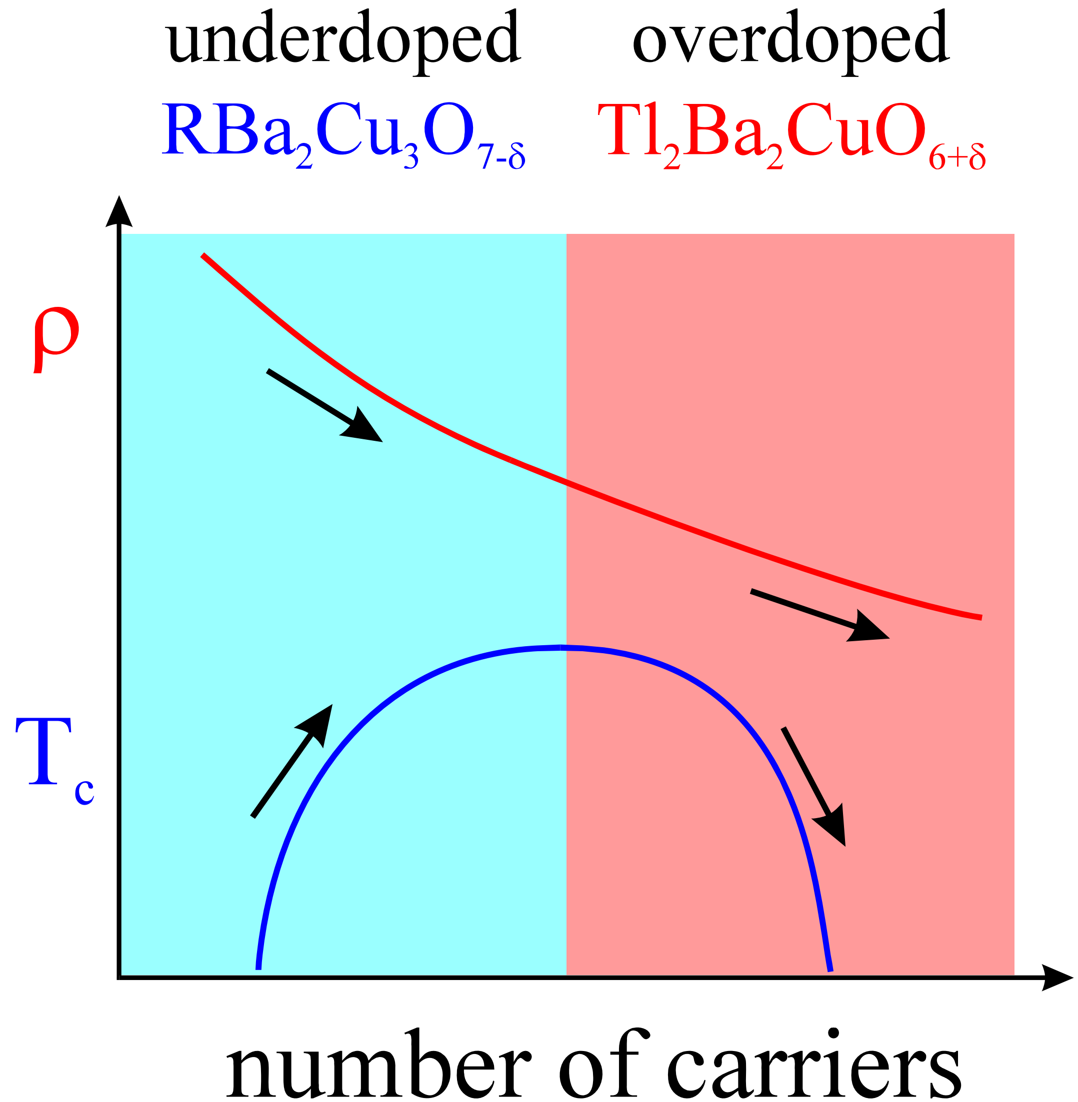




IR Illumination:

- **Increase in ρ, R_H, and T_c**

⇒ **Localized states are below Fermi level**



underdoped
overdoped
$RBa_2Cu_3O_{7-\delta}$
$Tl_2Ba_2CuO_{6+\delta}$
ρ
T_c
number of carriers

Is it the Oxygen deficiency

or

the reduced T_c ?

Pr doping

All on the same substrate

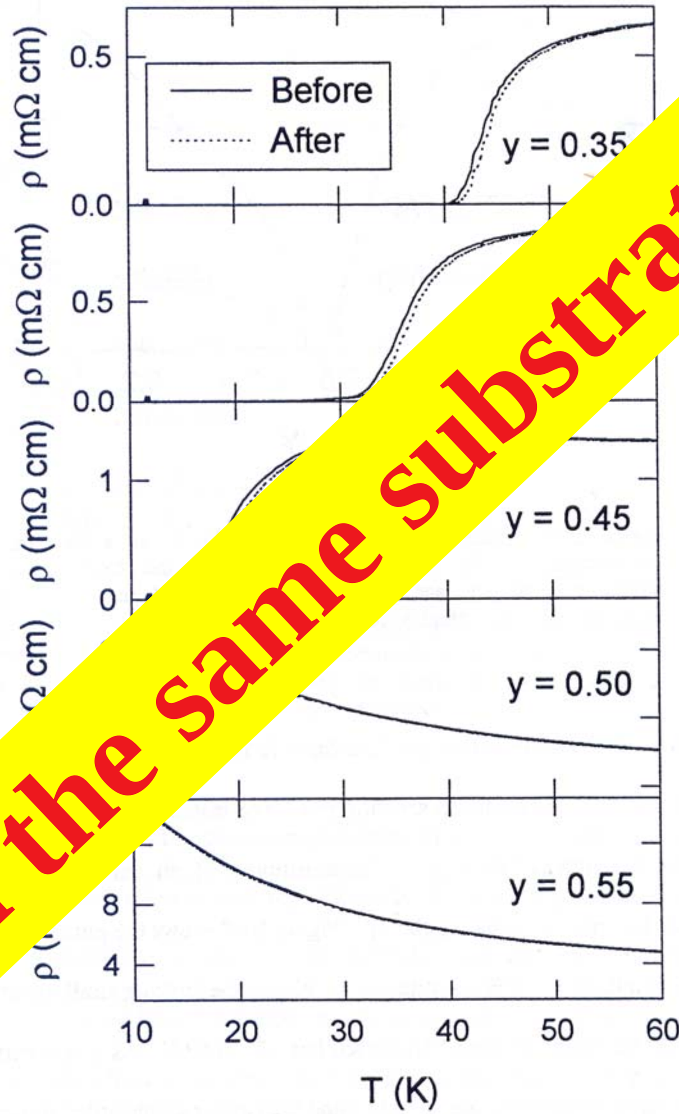


Figure III-8 Resistivity as a function of temperature for several strips of $Pr_yY_{1-y}Ba_2Cu_3O_7$ with varying Pr substitution, before and after illumination.

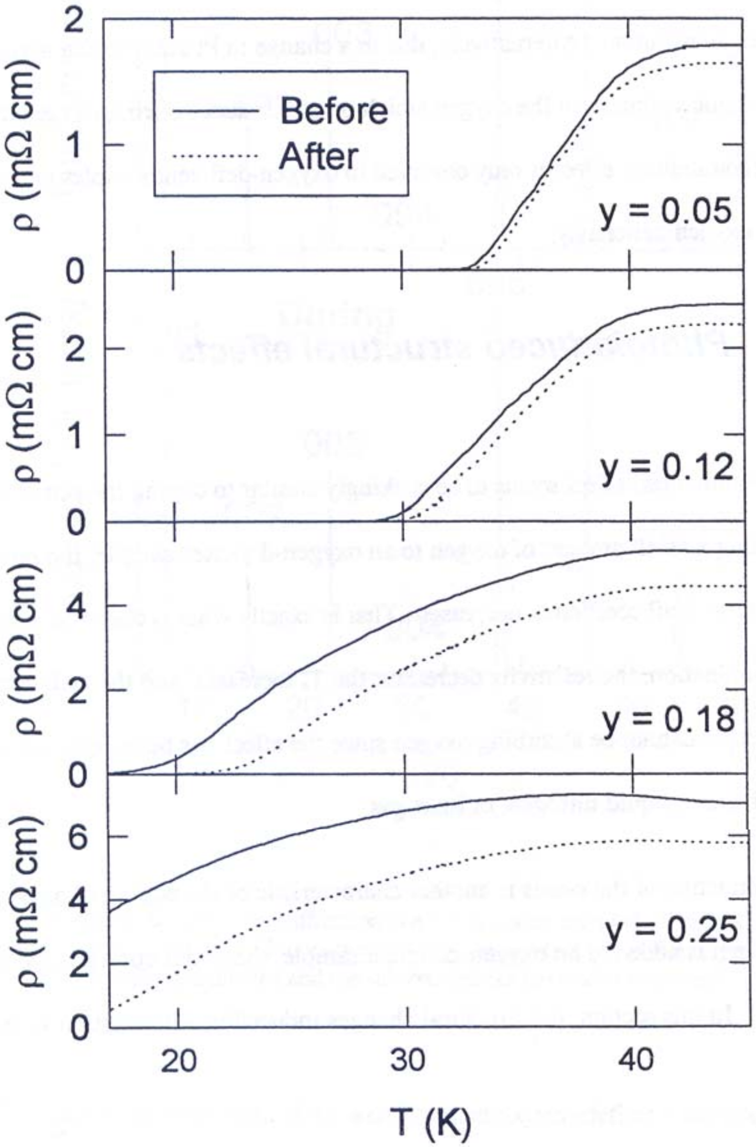
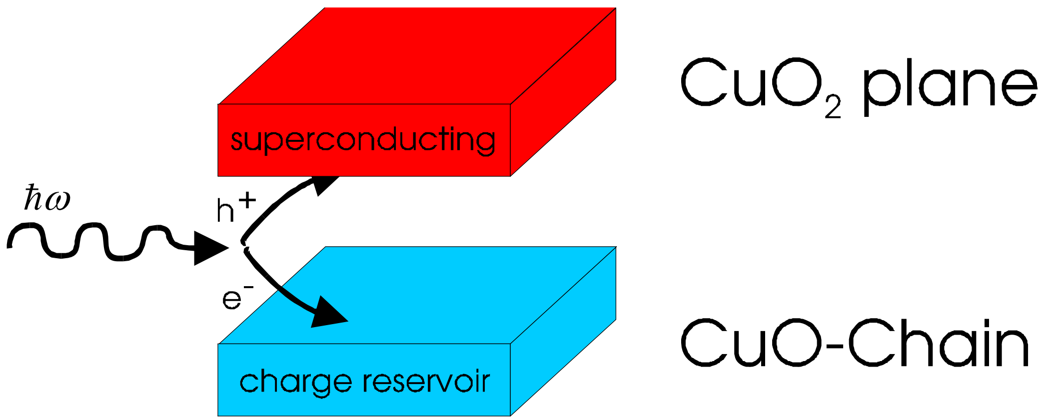


Figure III-9 Resistivity as a function of temperature for several strips of $Pr_yY_{1-y}Ba_2Cu_3O_{6.7}$ with varying Pr substitution, before and after illumination.[6]

Theoretical Model

Electron Trapping



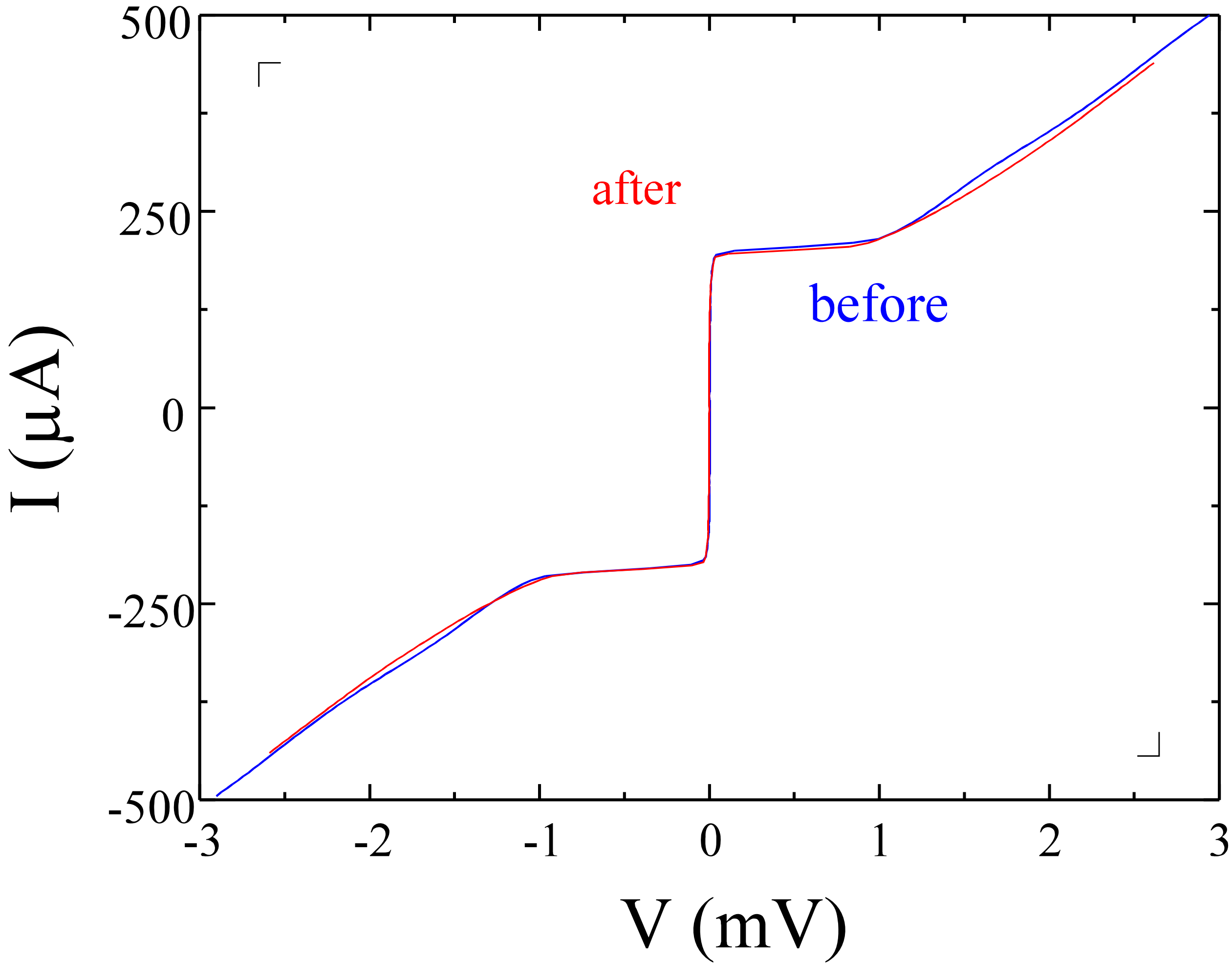
Illumination $\Rightarrow$ **electron-hole pair**
$\Rightarrow$ **electron trapped at oxygen vacancy**
$\Rightarrow$ **hole increases conductivity**

☺ **Consistent with ALL observed persistent photoinduced effects**

A. Gilabert, A. Hoffmann, M.G. Medici, and I.K. Schuller,
J. Super. 13, **1 (2000)**

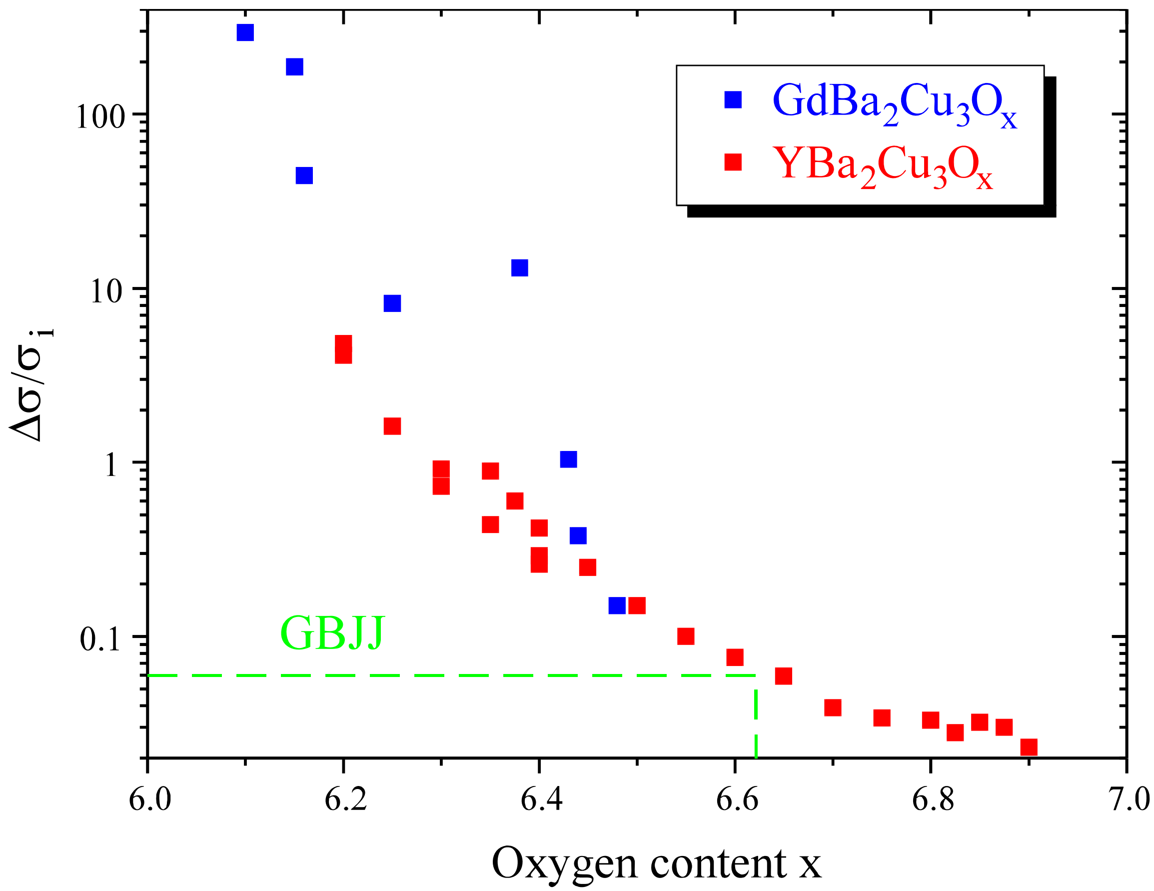
Josephson Effect

$YBa_2Cu_3O_7$, T = 12K



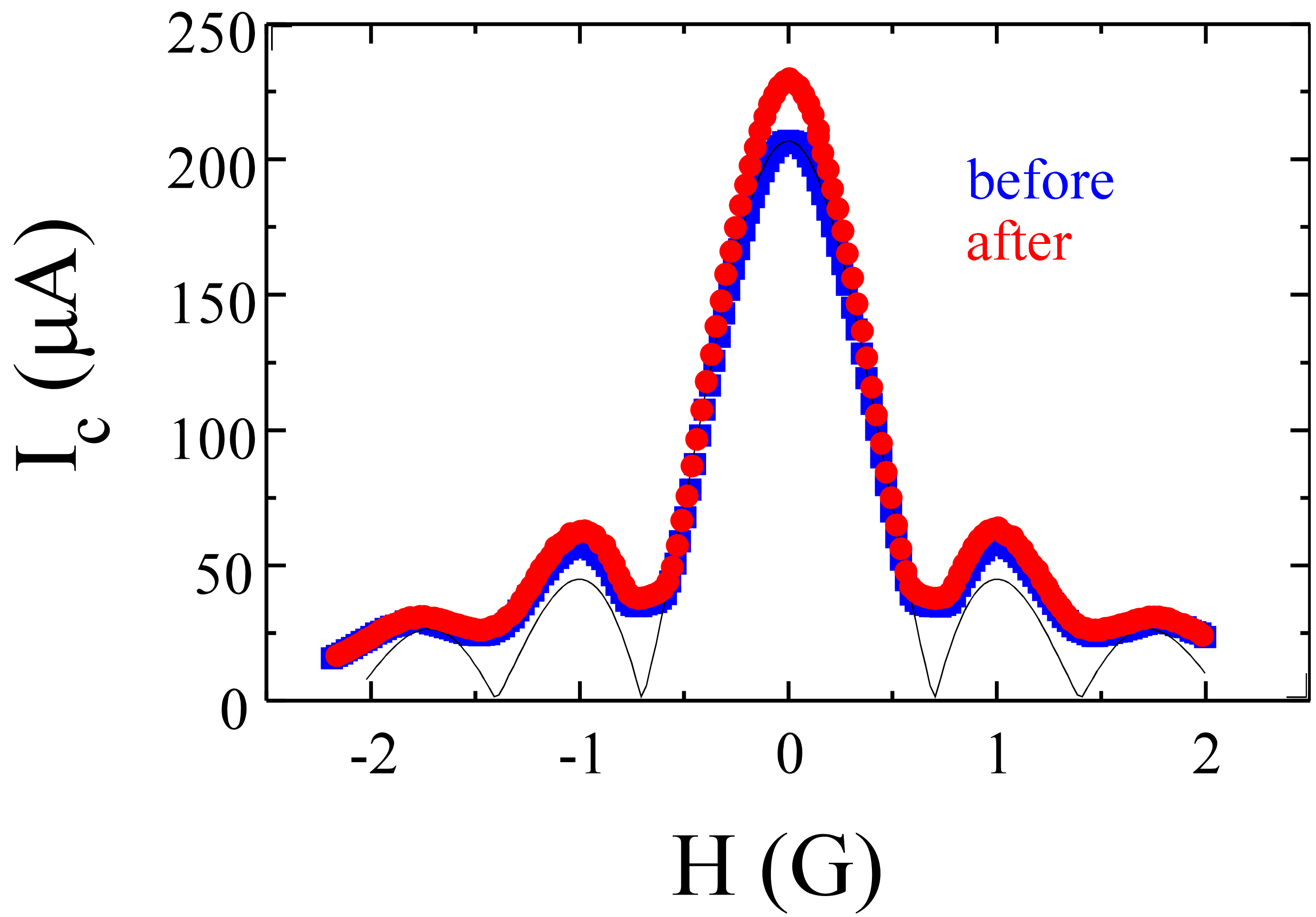
Doping Dependence

GBJJ: $\Delta\sigma/\sigma_i$ = 6% $\Rightarrow$ x = 6.6±0.1

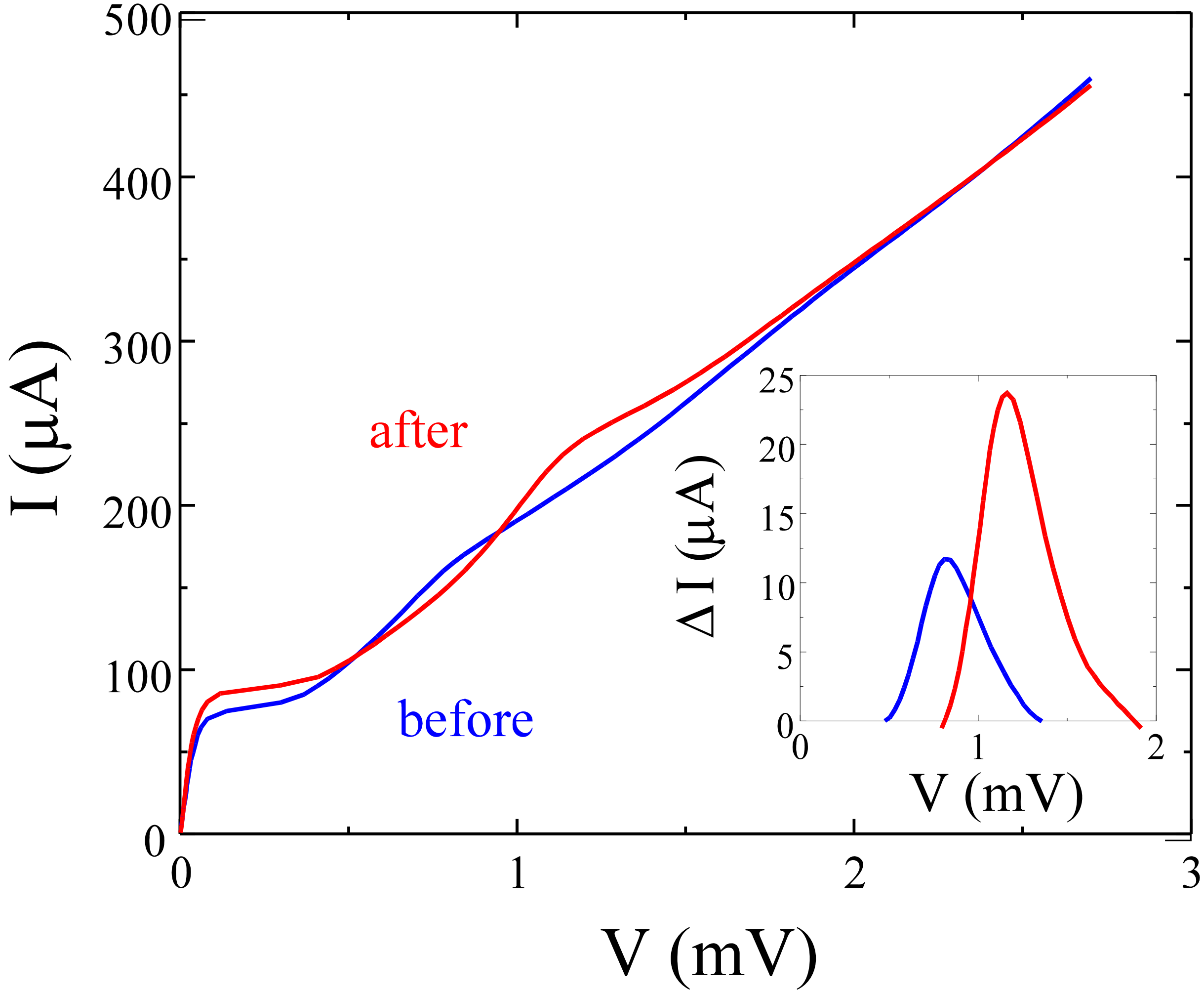


J. Hasen, D. Lederman, I.K. Schuller, V. Kudinov, M. Maenhoudt, and Y. Bruynseraede, Phys. Rev B **51**, 1342 (1995)

Fraunhofer Pattern



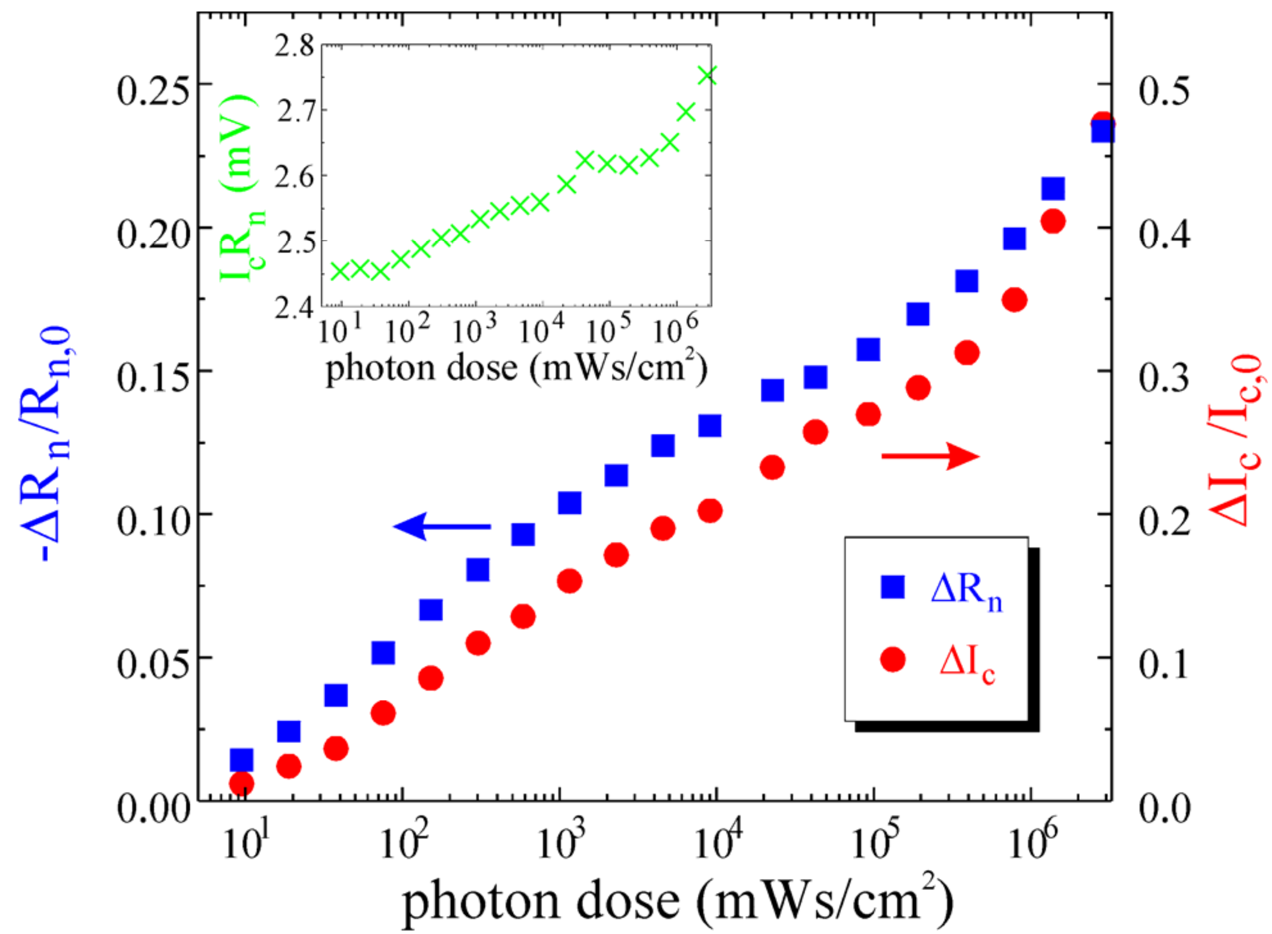
Fiske Resonances
H = 0.56G



ΔI and V increase ⇒ ε of barrier ↘ by factor 2

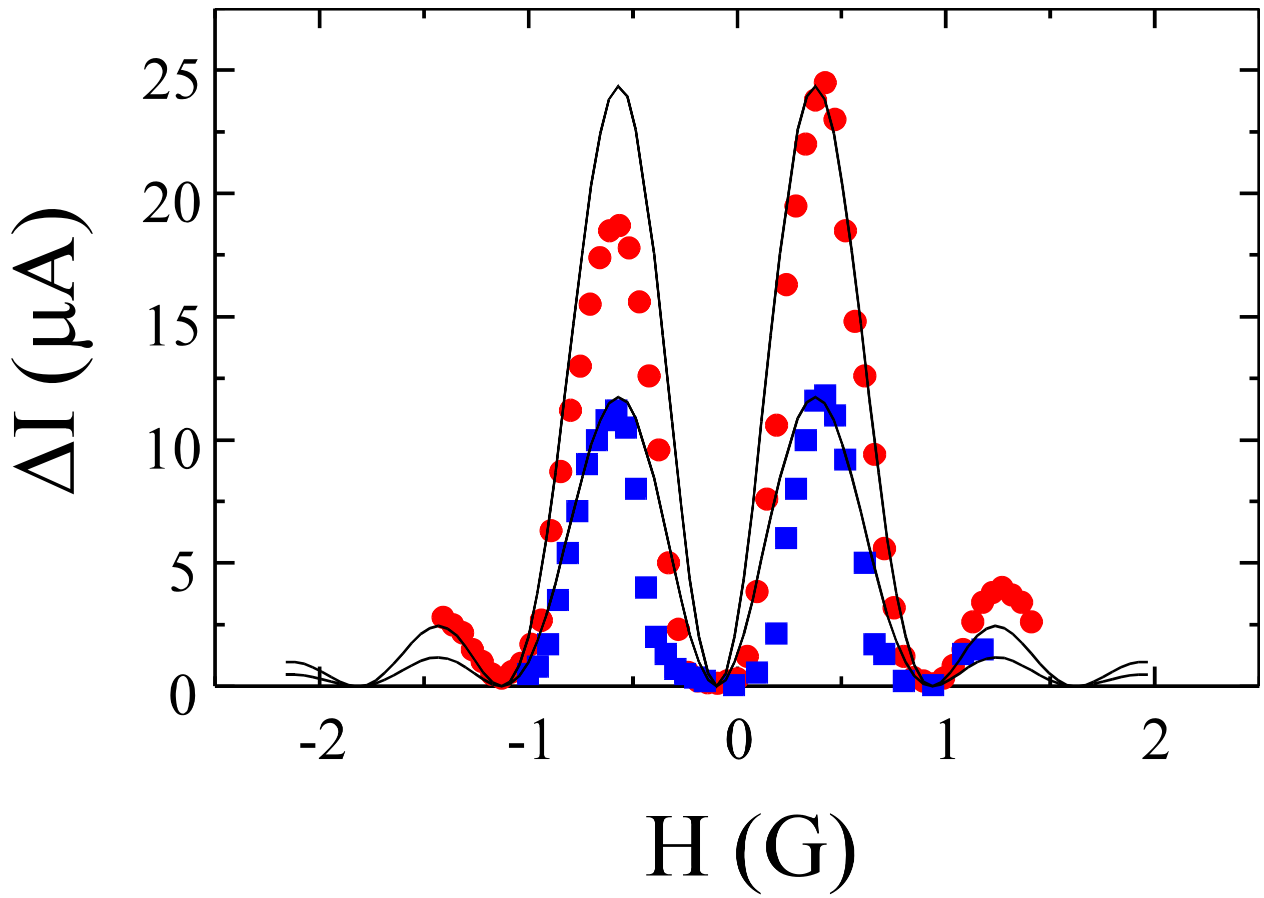
Photon Dose Dependence T = 5K

IcRn increases⇒ weak link more superconducting

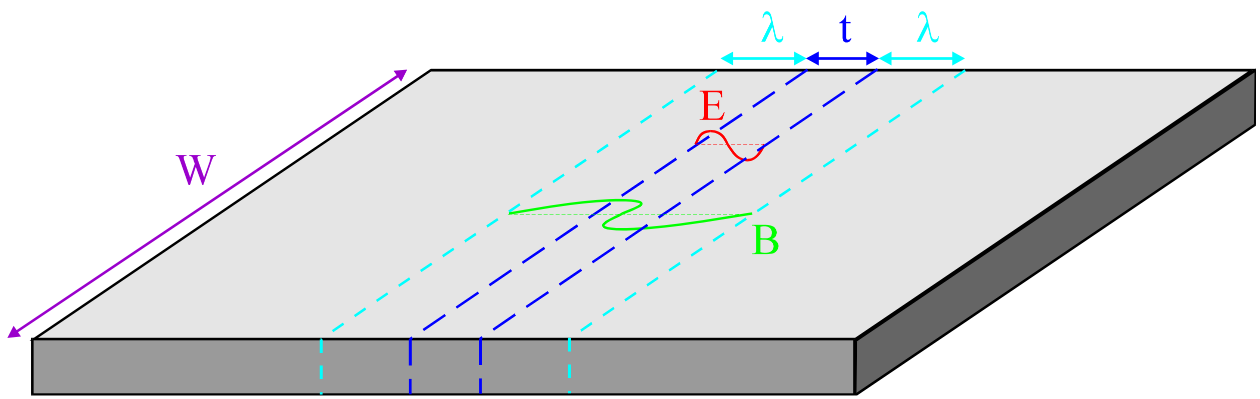


IcRn tunable with photon dose

Fiske Resonance



Fiske Resonance Theoretical Model



Fiske resonance: $$V = \Phi_0 \frac{c}{2W}$$ with

$$c = c_0 \sqrt{\frac{t}{\varepsilon(2\lambda + t)}}$$

(Swihart velocity) ⇒

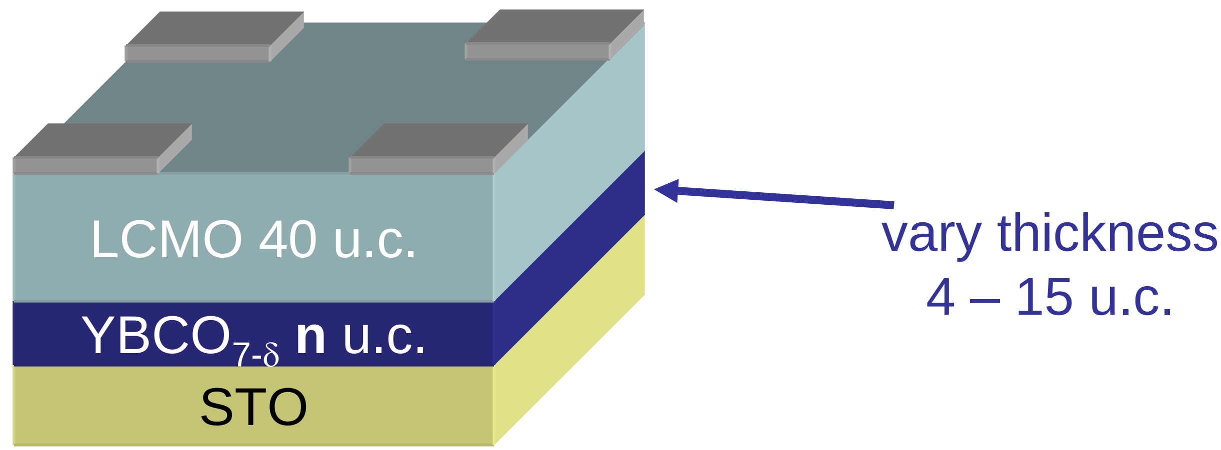
$$\frac{\varepsilon}{\varepsilon_L} = \left(\frac{V_L}{V}\right)^2 \approx 2$$

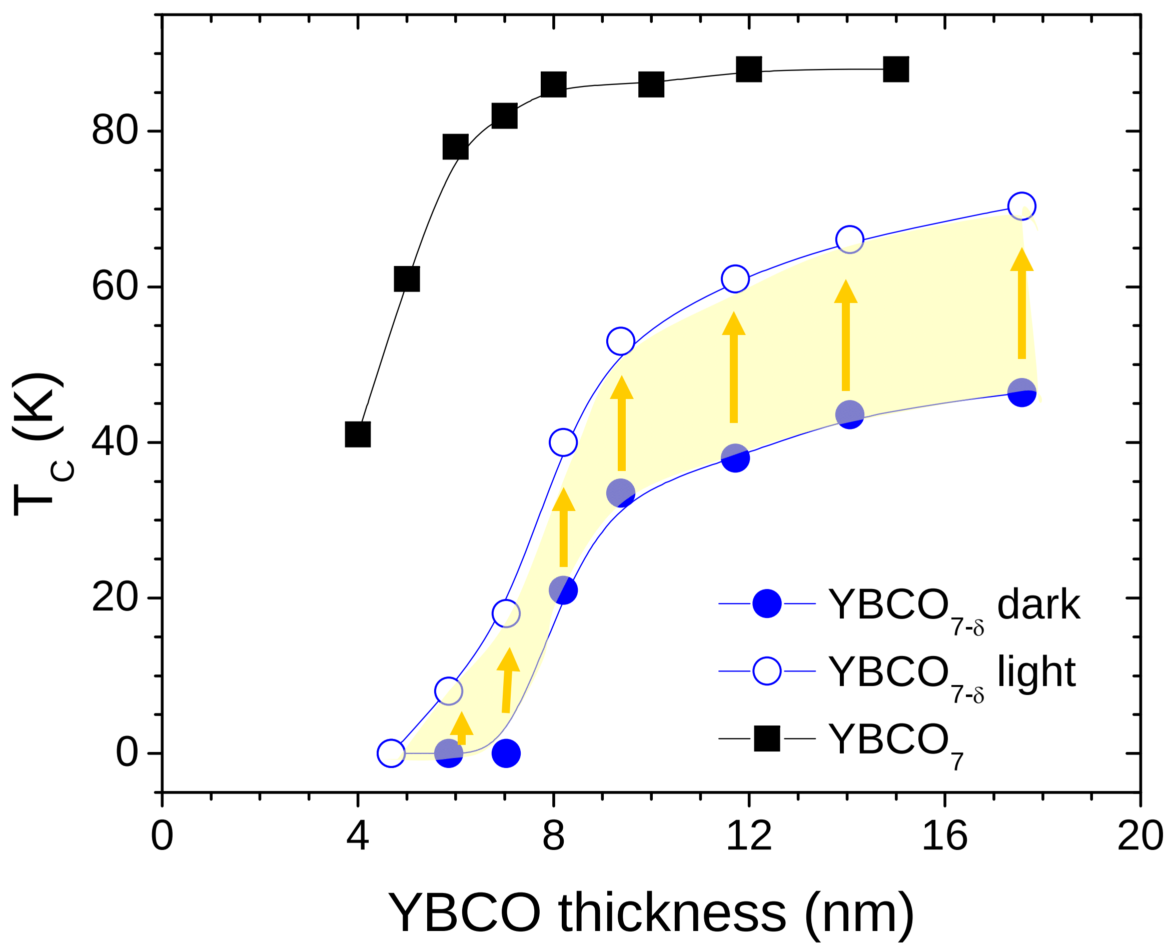
Interfacially Controlled Transient Photoinduced Superconductivity in Magnetic-Superconducting Hybrids

Vanessa Peña, Thomas Gredig,
Ivan K. Schuller, Jacobo Santamaría

PRL 2007

MAGNETIC-SUPERCONDUCTING
HYBRID

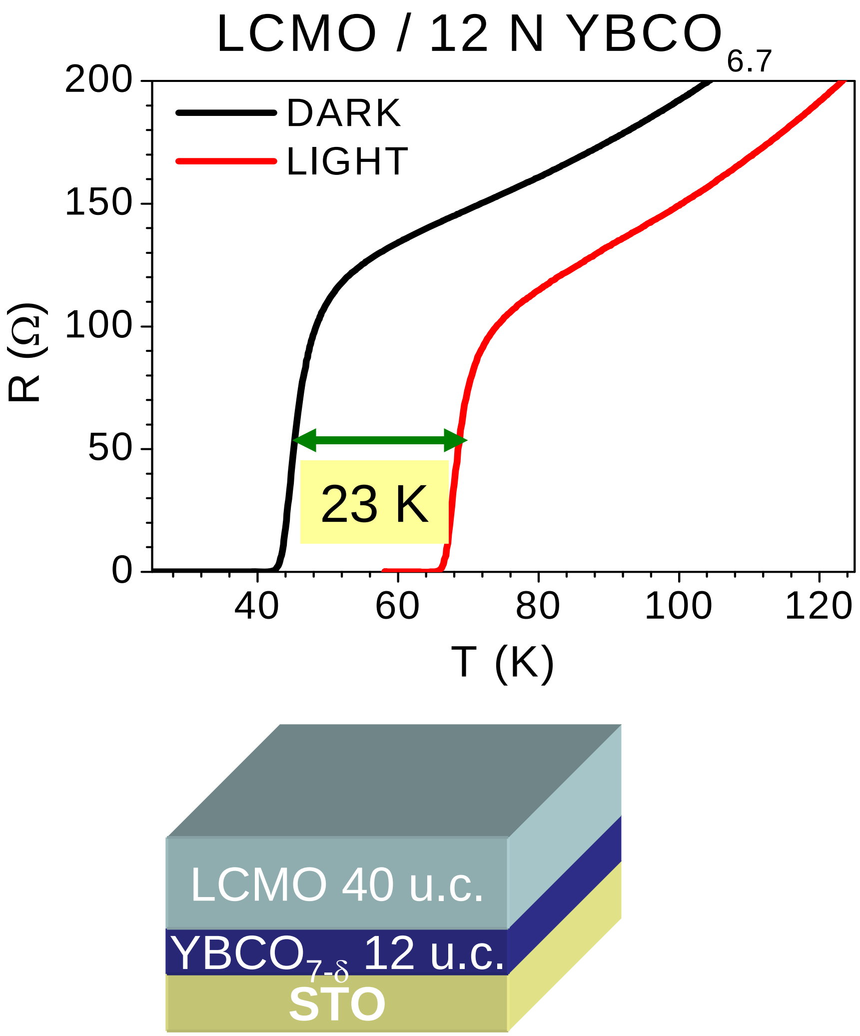


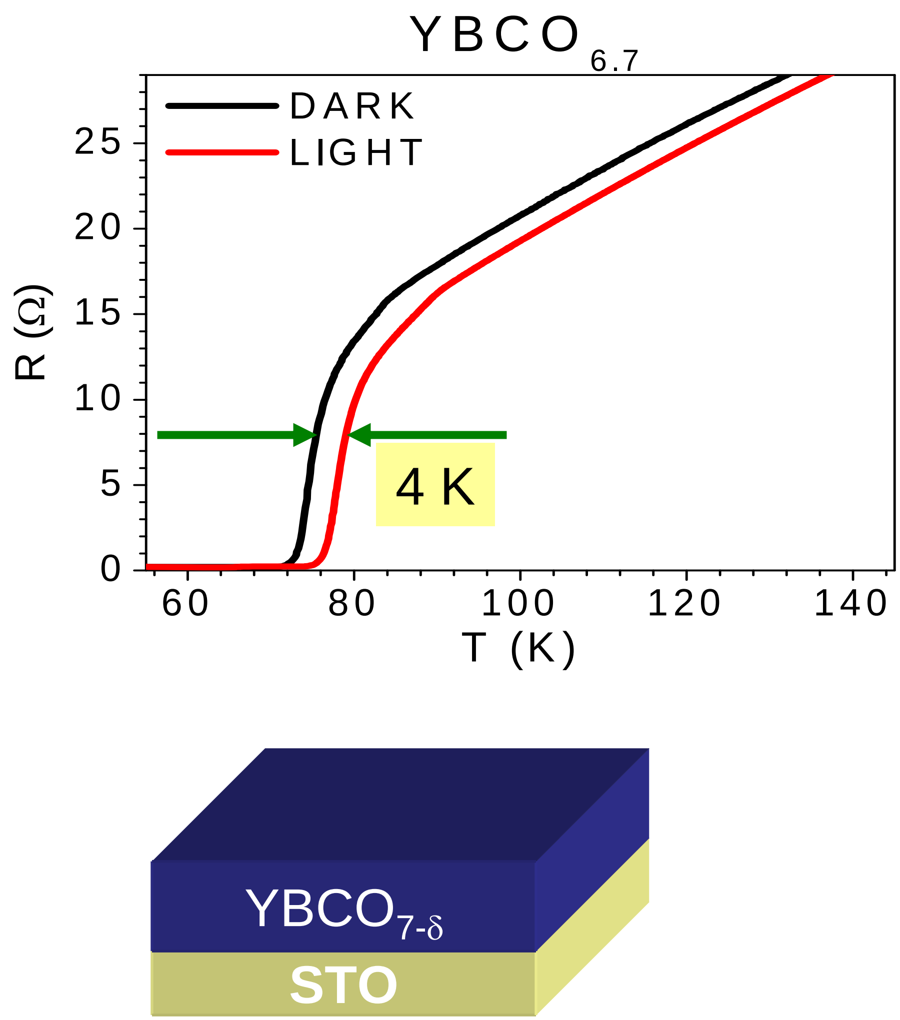


Black: fully oxygenated YBCO

Blue: deoxygenated YBCO

Effect of LCMO

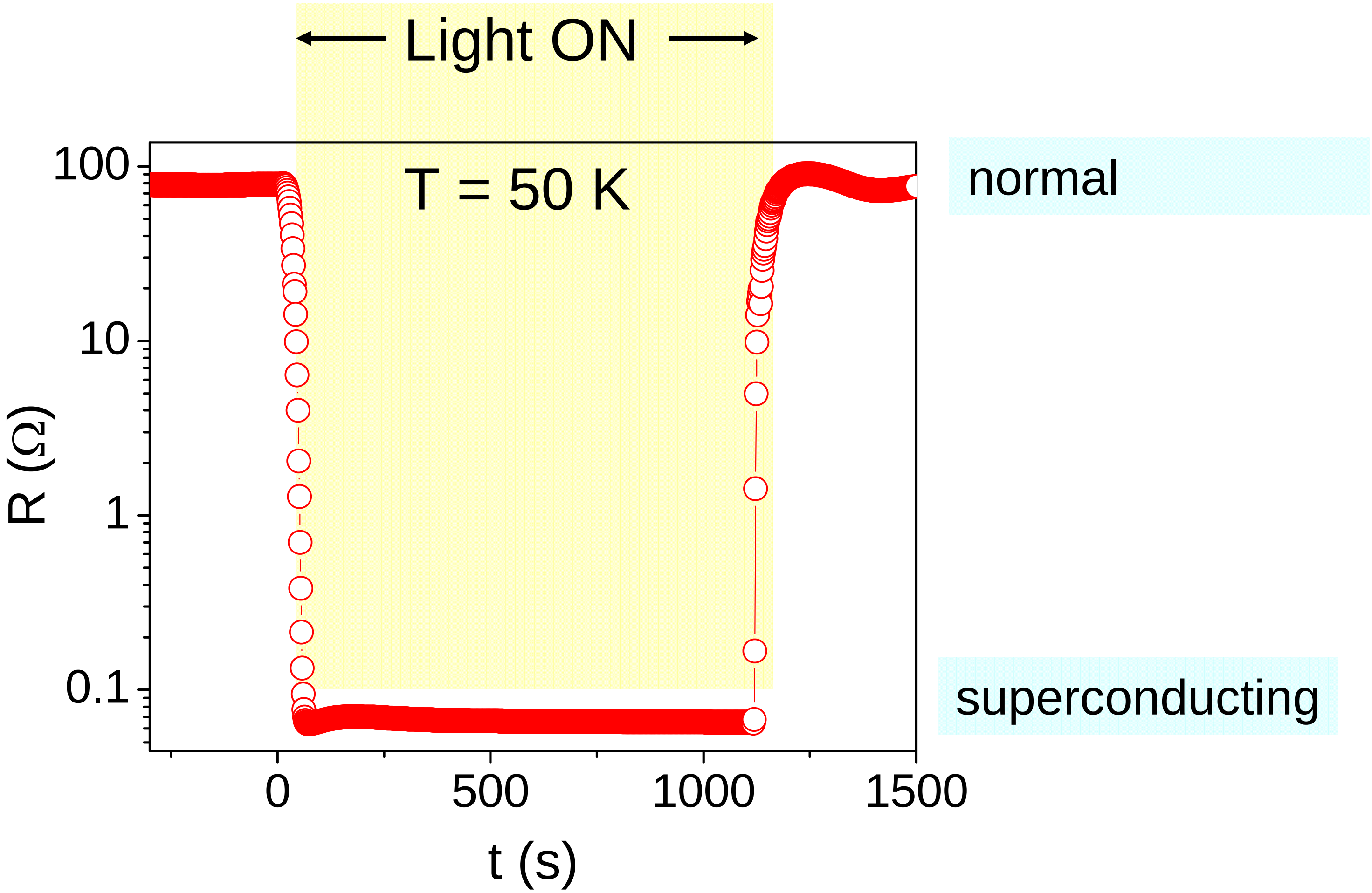




Time Dependence

"FAST"

LCMO / $YBCO_{6.7}$ 12 u.c./STO



CONCLUSIONS

- **Photodoping-**

Convenient way to tune doping !

- **Photodoping-**

General feature of Complex Oxides **!**

- **Spatial Separation at the Nanoscale**

Superconducting-Nonsuperconducting

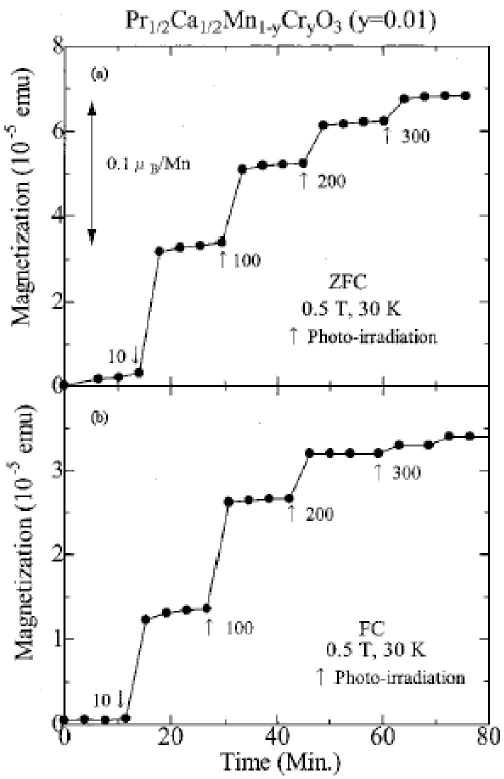
- **Transport controlled by Cuprate**

  Relaxation time controlled by Manganite

Outlook

Future looks bright for Persistent Photodoping in Oxides!

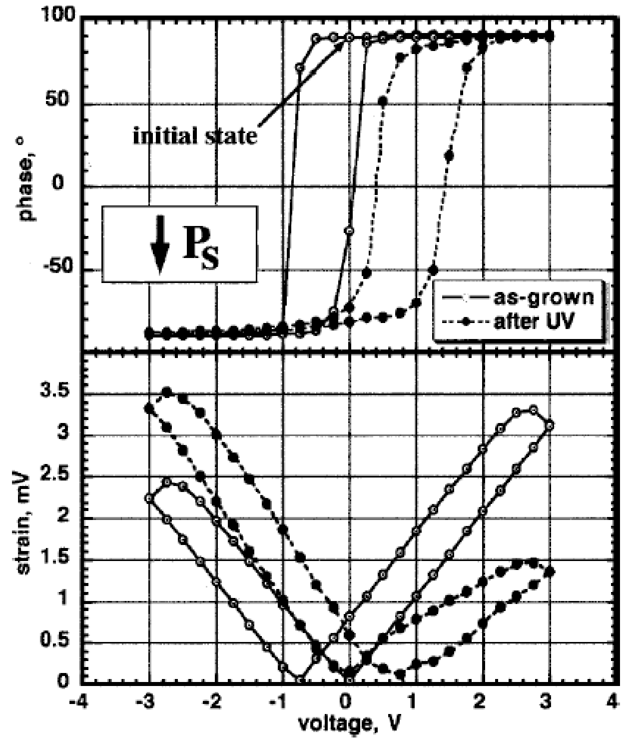
Ferromagnets



Y. Okimoto, *et al.*,
Appl. Phys. Lett. **80**, 1031 (2002)

Ferroelectrics

PbTiO3

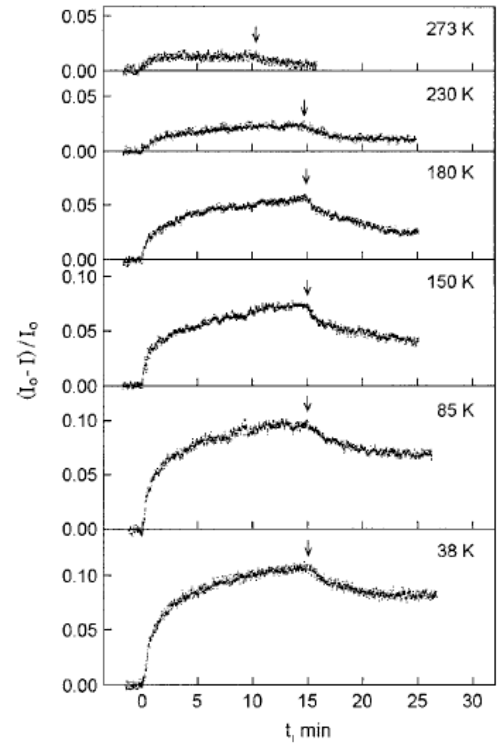


Gruverman, *et al.*,
J. Appl. Phys. **92**, 2734 (2002)

$Ca_3Ga_2Ge_3O_{12}$-Mn garnet

Other

Optical Absorption



V.V. Eremenko, *et al.*,
Appl. Phys. Lett. **79**, 734 (2001)

POLITICALLY INCORRECT

- What is on firm footing that everybody agrees ?
- How to judge the “correct experiments” ?
- How to judge the correct theory ? (Predictions, least number of assumptions,…
- Are inhomogeneities present at short length scales, even in “very good” samples ?
- Is d-wave well established ?
- Is 2-dimensionality needed ?
- Are there more than one mechanisms possible ?
- Are they real ?
- a) WOx   high Tc
- b) RuSr2(Gd, Eu, Sm)Cu2O8, F-S at 58 K
- Why are the stocks of Superconducting companies going to hell ?

OPEN YOUR MIND !!!!

END