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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY
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SMR/481 - 6

EXPERIMENTAL WORKSHOP ON
HIGH TEMPERATURE SUPERCONDUCTORS AND RELATED MATERIALS
(ADVANCED ACTIVITIES)

(26 November - 14 December 1990)

" On the nature of low energy excitations in high T_C superconductors "

presented by:

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Consiglio Nazionale delle Ricerche
Istituto Spettroscopia Molecolare
Via de' Castagnoli 1
40126 Bologna
Italy

ON THE NATURE OF LOW ENERGY EXCITATIONS IN HIGH TC SUPERCONDUCTORS

C. Taliani , Institute of Molec. Spectroscopy. CNR, Bologna,Italy

a) Optical properties of the semiconducting parent of the HTSC when it is doped by light.

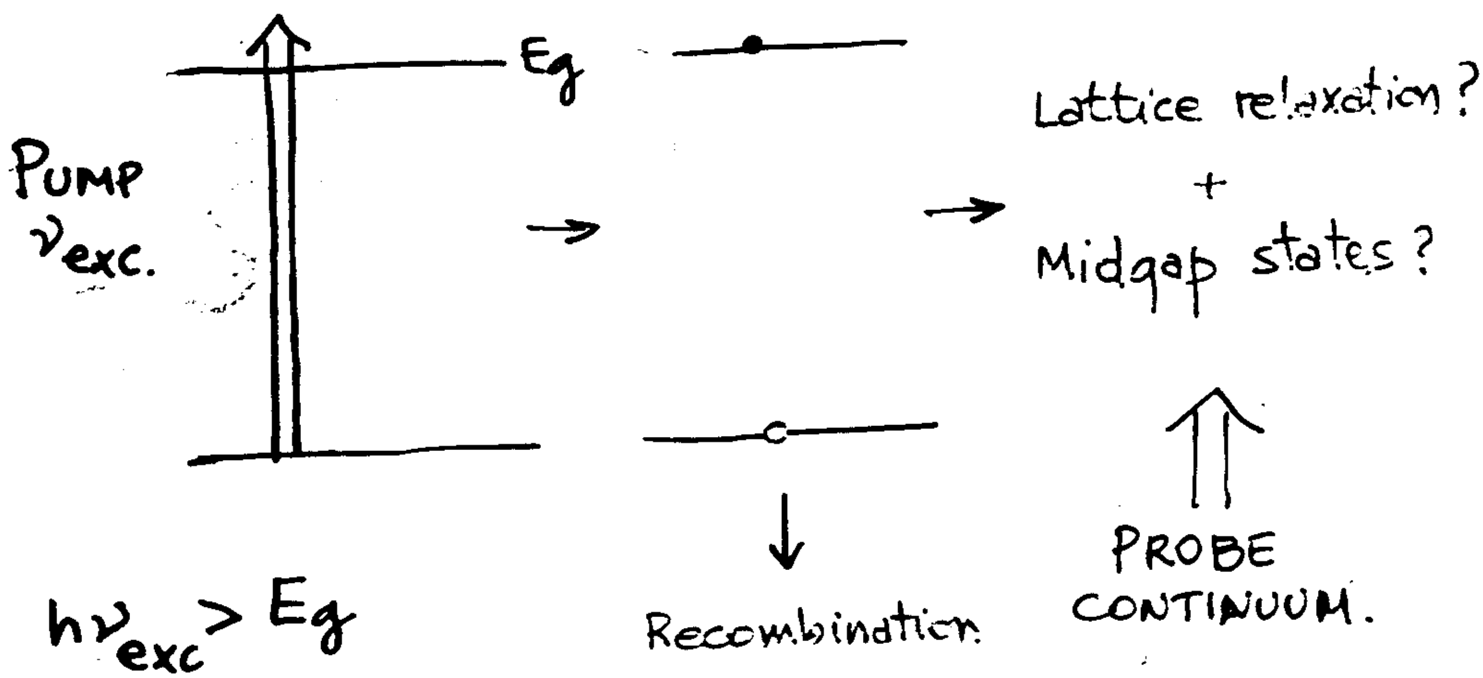
Photoinduced optical absorption and photomodulation spectroscopy on:
$YBa_2Cu_3O_6$, La_2CuO_4 and $BaBiO_3$
Evidence of lattice distortions associated with charge excitations in the gap.

comparison of PA in the semiconducting and optical conductivity spectrum of the normal state in $YBa_2Cu_3O_6$.

General features of layered and non-layered HTSC.

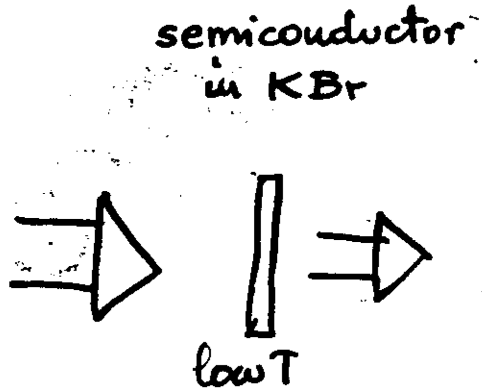
b) Low energy localized states in $YBa_2Cu_3O_6$ by IR excited Raman spectroscopy

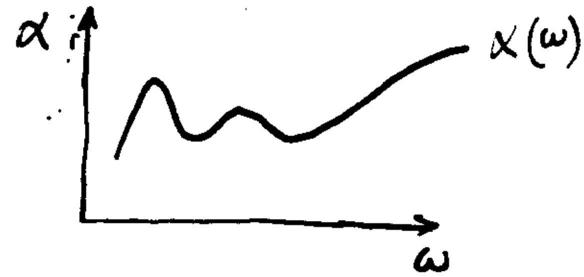
Mechanism of Photoinduced Abs.

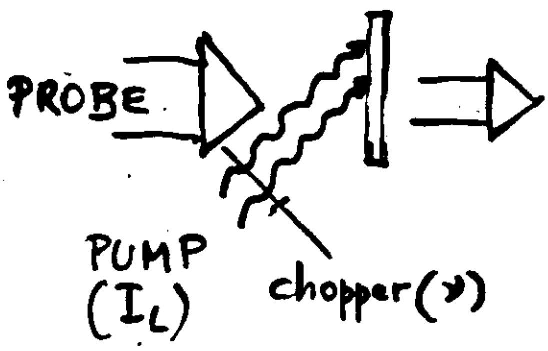


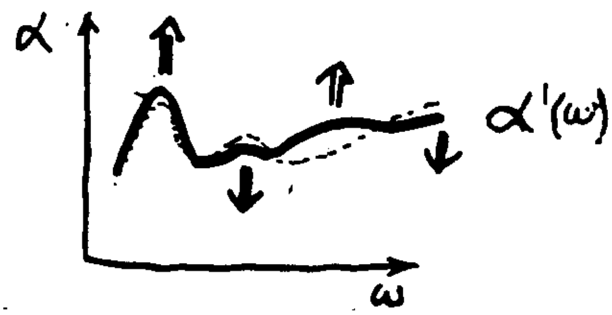
PHOTOINDUCED ABSORPTION

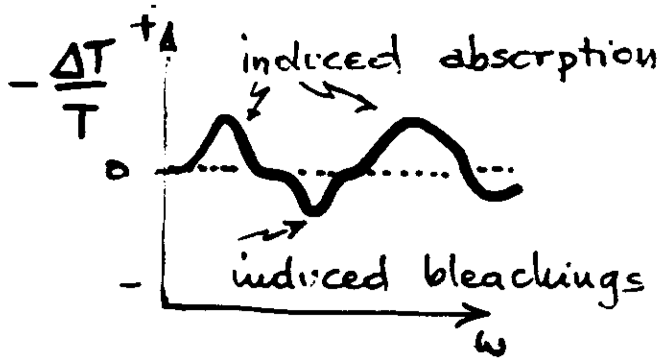
Study of the optical properties induced by photoinjected charge carriers at <u>low doping</u>











Dependences:

I_L	recombination processes
T	"

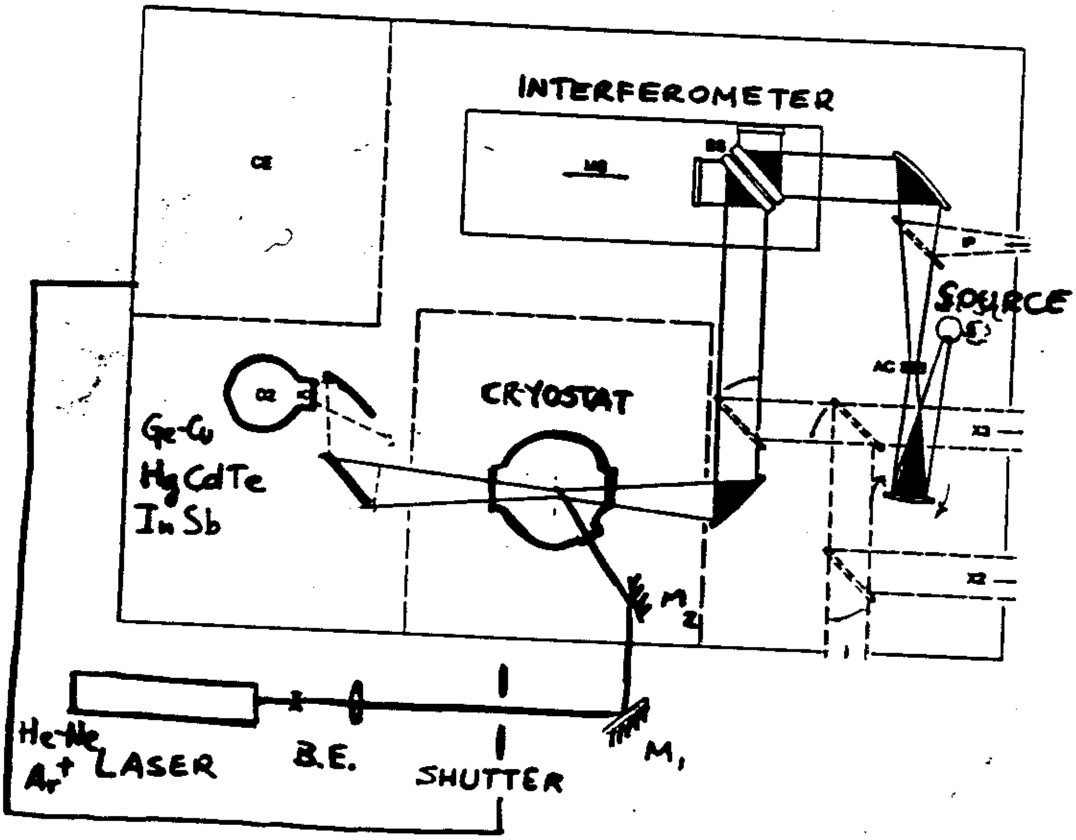
Doping level:

A) from the photon flux → (quantum yield)

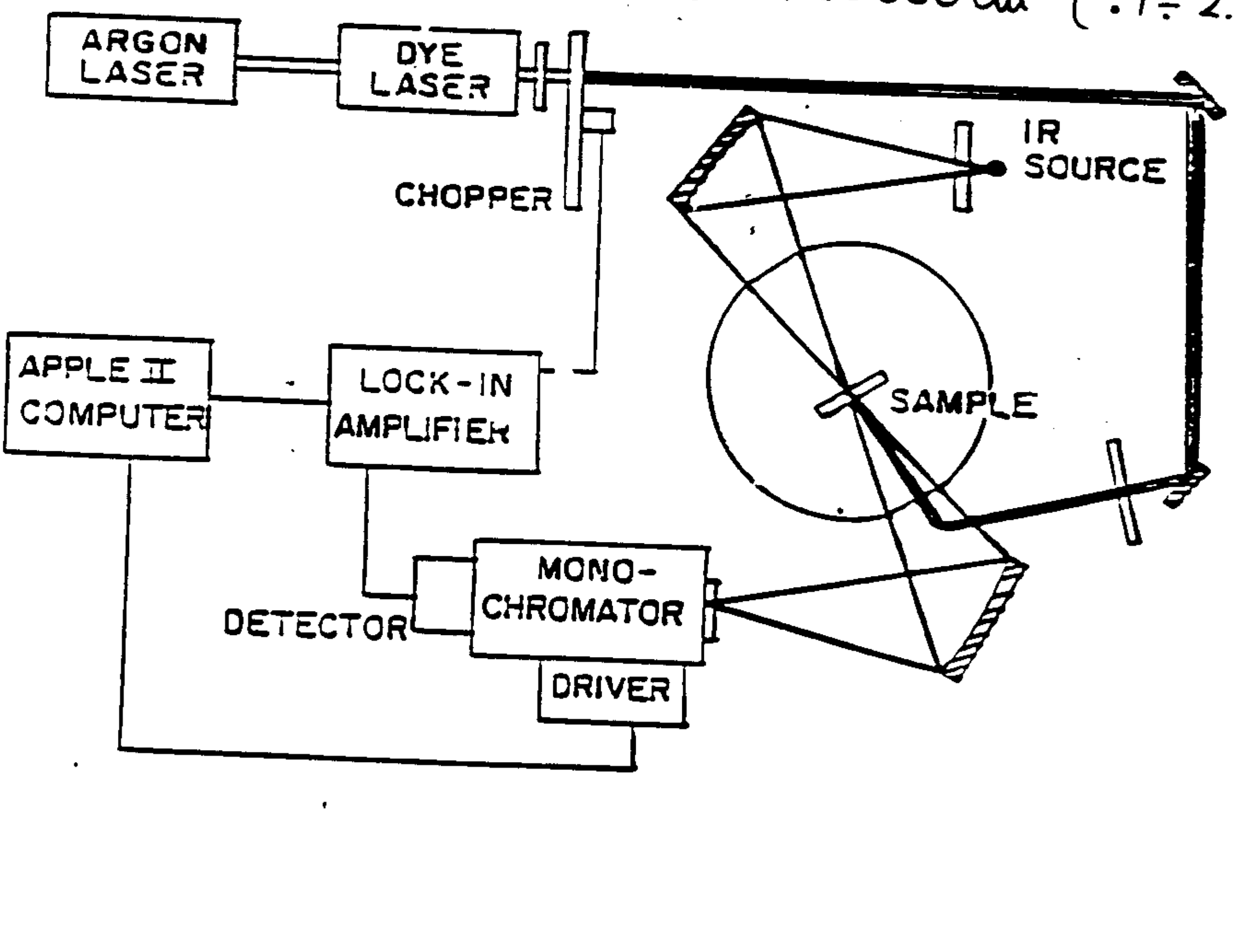
B) from $\Delta\alpha$ → ($\Delta\alpha$ vs doping) → $\sim 10^{18}$ carriers/cm^3

PHOTOINDUCED ABSORPTION EXP. SET UP.

A) LOW ENERGY RANGE: 200 ÷ 8000 cm^{-1} (.05 ÷ 1 eV)

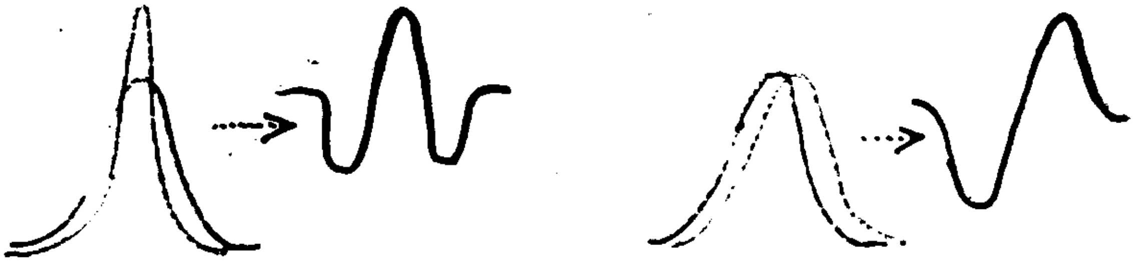


B) HIGHER ENERGY RANGE: 800 ÷ 20'000 cm^{-1} (.1 ÷ 2.5 eV)

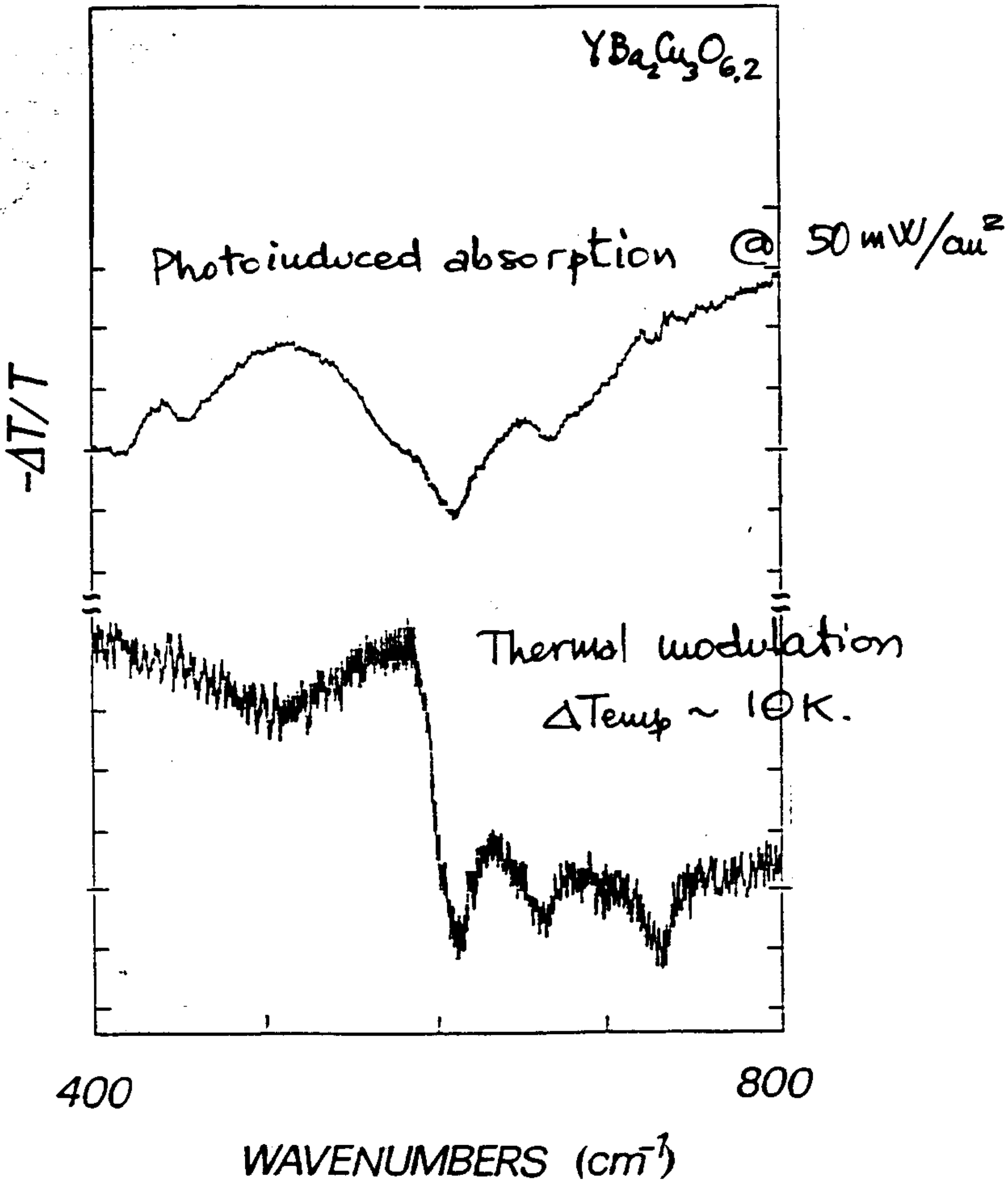


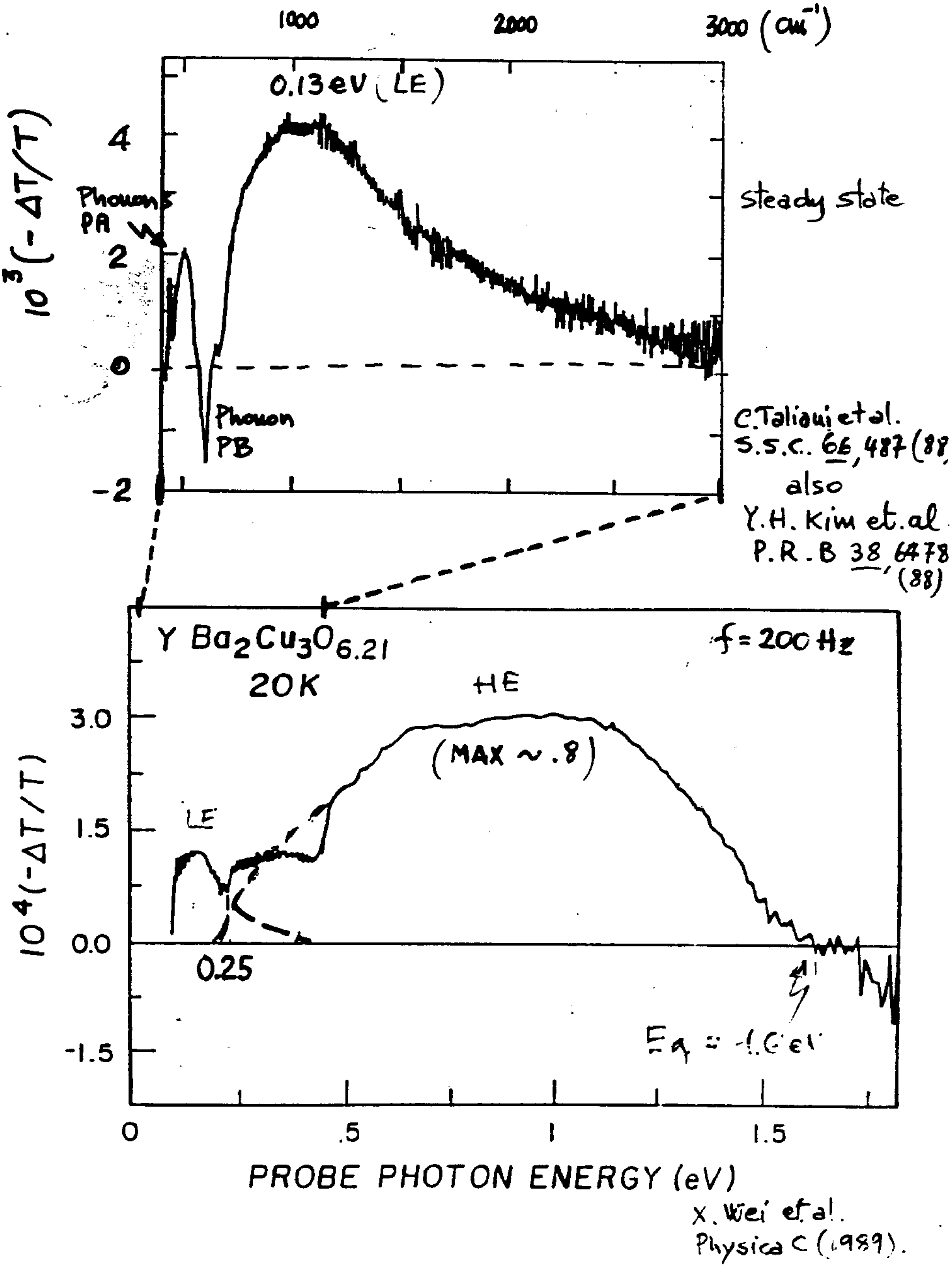
heating artifacts:

1) shape



2) linear effects with heating (i.e. $\propto I_{LASER}$).





1000
2000
3000 (cm⁻¹)
0.13 eV (LE)
Phonons PA
Phonon PB
steady state
$10^3(-\Delta T/T)$
4
2
0
-2
C. Taliani et al. S.S.C. 66, 487 (88)
also
Y.H. Kim et. al P.R.B 38, 6478 (88)
Y Ba$_2$Cu$_3$O$_{6.21}$
20K
f = 200 Hz
HE
(MAX ~ .8)
LE
0.25
E_g = 1.6 eV
$10^4(-\Delta T/T)$
3.0
1.5
0.0
-1.5
0
.5
1
1.5
PROBE PHOTON ENERGY (eV)
X. Wei et al. Physica C (1989).

Solid State Communications, Vol.66, No.5, pp.487-490, 1988.
Printed in Great Britain.

0038-1098/88 $3.00 + .00
Pergamon Press plc

INFRARED PHOTOINDUCED ABSORPTION IN THE $YBa_2Cu_3O_{7-y}$ HIGH T_c SUPERCONDUCTING SYSTEM

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F.C.Matacotta
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(received February 8, 1988 by M. Cardona)

like behaviour in the PA. We believe that the bleach at 600 cm^{-1} is at least partially due to a PA effect.

Having proved that the PA spectrum is indeed due to a genuine PA process we may comment on it.

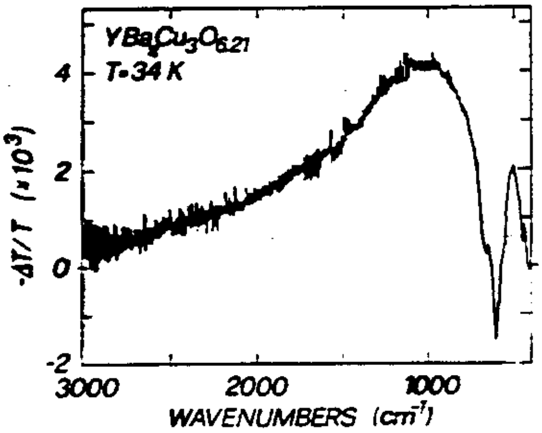

Fig.1 Photoinduced absorption spectrum of $YBa_2Cu_3O_{7-y}$ (y = 0.79) at 34K.

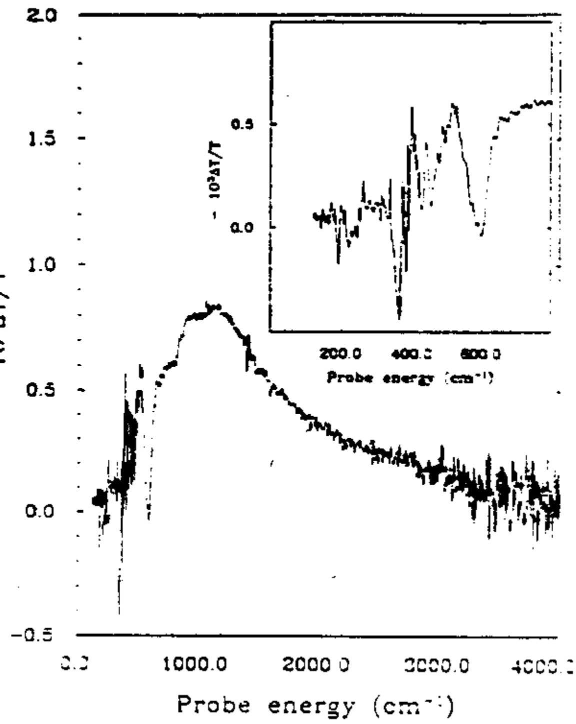

FIG. 1. Photoinduced absorption spectrum of $Y_1Ba_2Cu_3O_{7-\delta}$ (δ=0.75) at 15 K (2.7-eV pump at 30 mW/cm^2); inset shows detailed IRAV features.

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Photoinduced self-localized structural distortions in $YBa_2Cu_3O_{7-\delta}$

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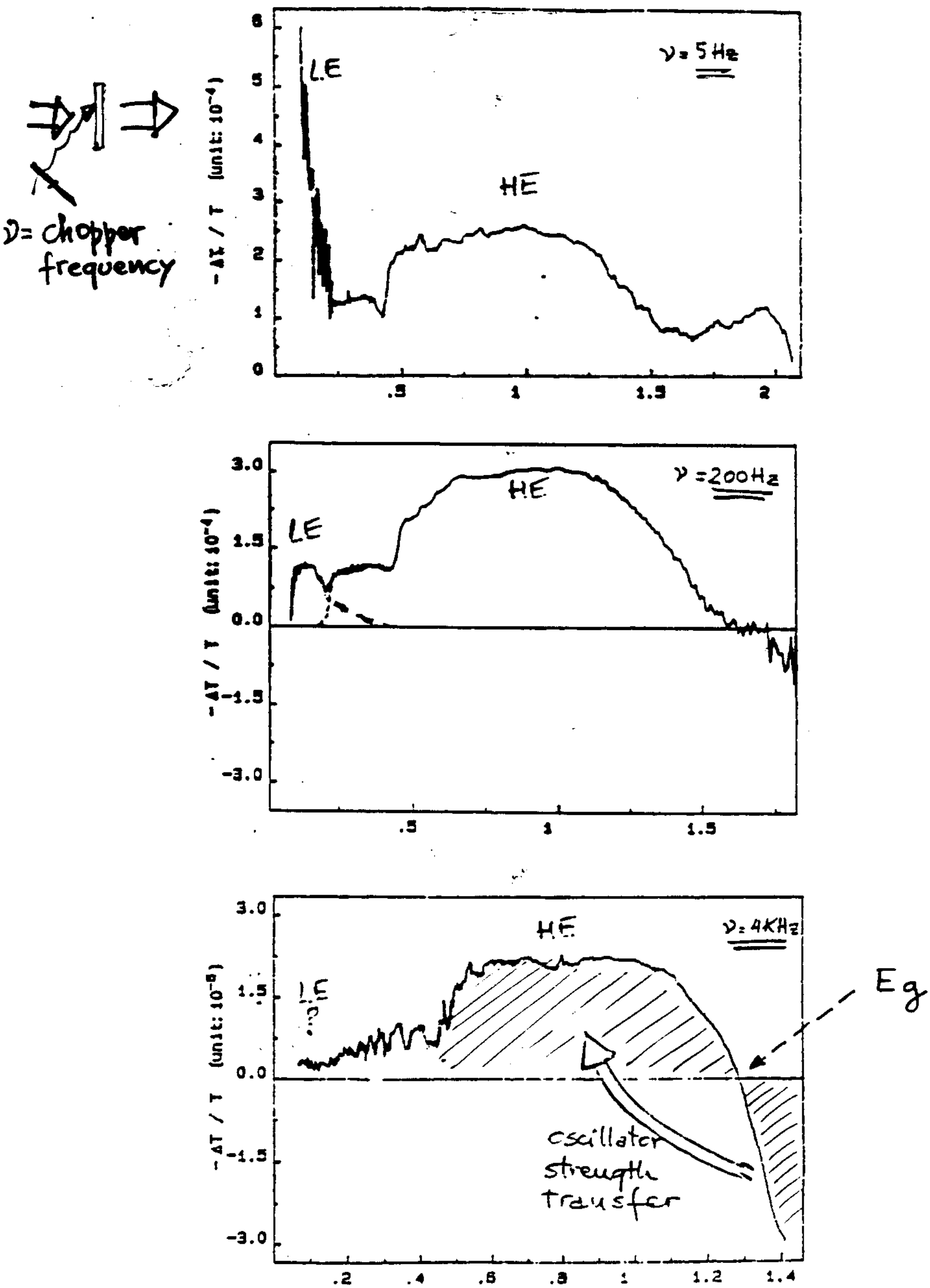
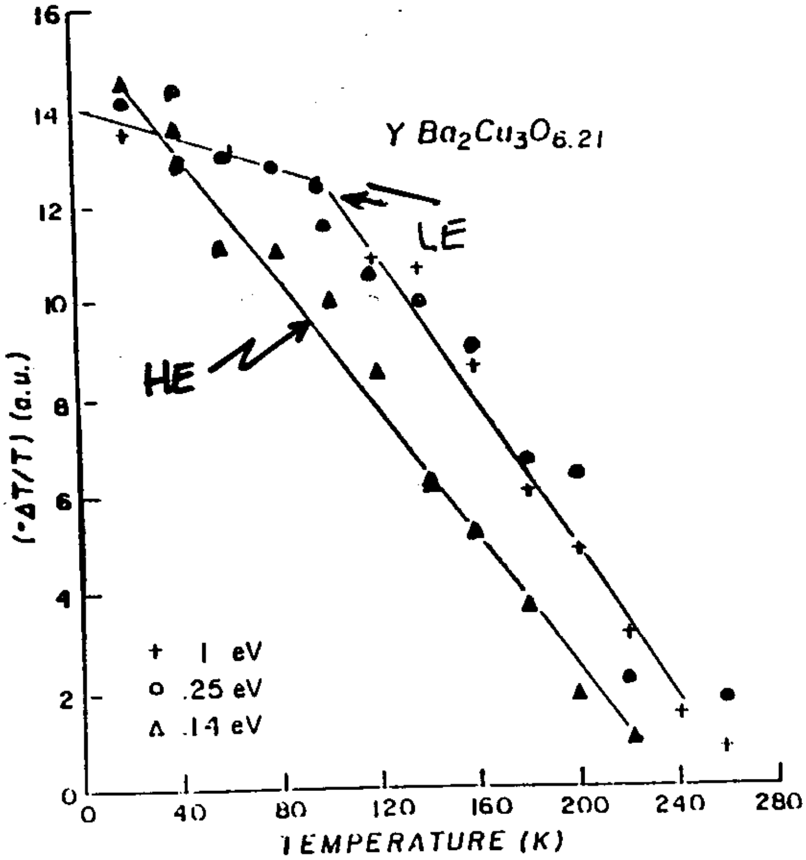
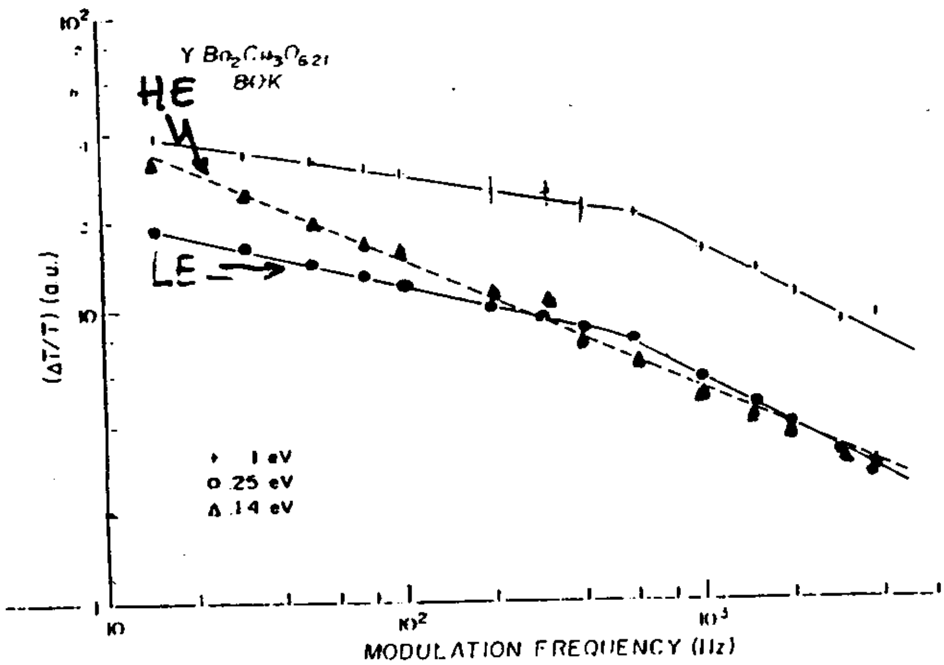
S. Cox and G. Stucky
Department of Chemistry, Institute for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, California 93106
(Received 15 March 1988; revised manuscript received 25 July 1988)



ν = chopper frequency
ν = 5 Hz
LE
HE
-ΔT / T (unit: 10^-4)
.5
1
1.5
2
ν = 200 Hz
LE
HE
-ΔT / T (unit: 10^-4)
3.0
1.5
0.0
-1.5
-3.0
ν = 4 KHz
HE
LE ?
-ΔT / T (unit: 10^-5)
Eg
oscillator strength transfer
.2
.4
.6
.8
1
1.2
1.4
PHOTON ENERGY (eV)

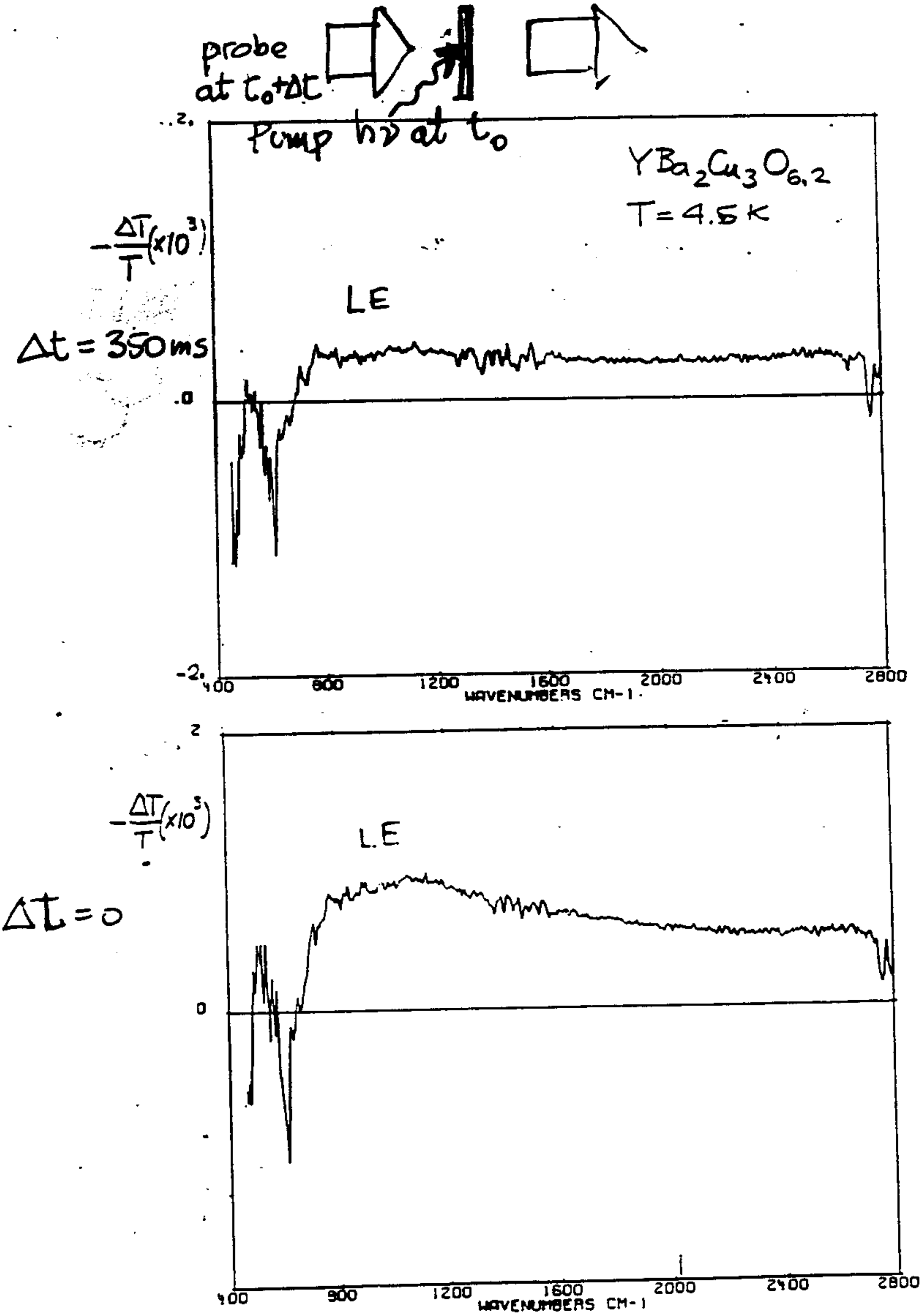


Y $Ba_2Cu_3O_{6.21}$
LE
HE
(-ΔT/T) (a.u.)
+ 1 eV
o .25 eV
Δ .14 eV
TEMPERATURE (K)

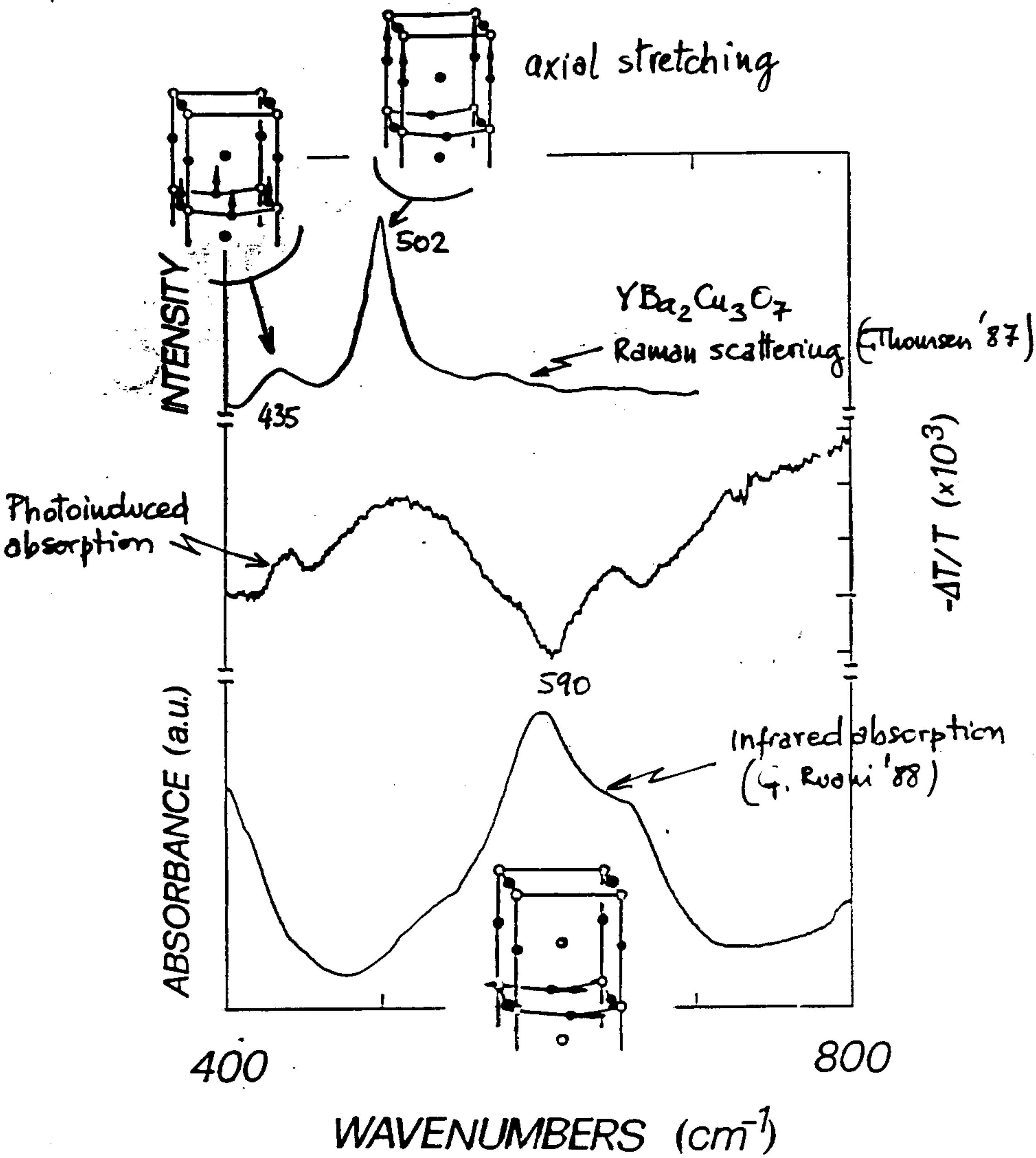


Y $Ba_2Cu_3O_{6.21}$
80K
HE
LE
(ΔT/T) (a.u.)
+ 1 eV
o .25 eV
Δ .14 eV
MODULATION FREQUENCY (Hz)

RETARDED PHOTOINDUCED ABSORPTION

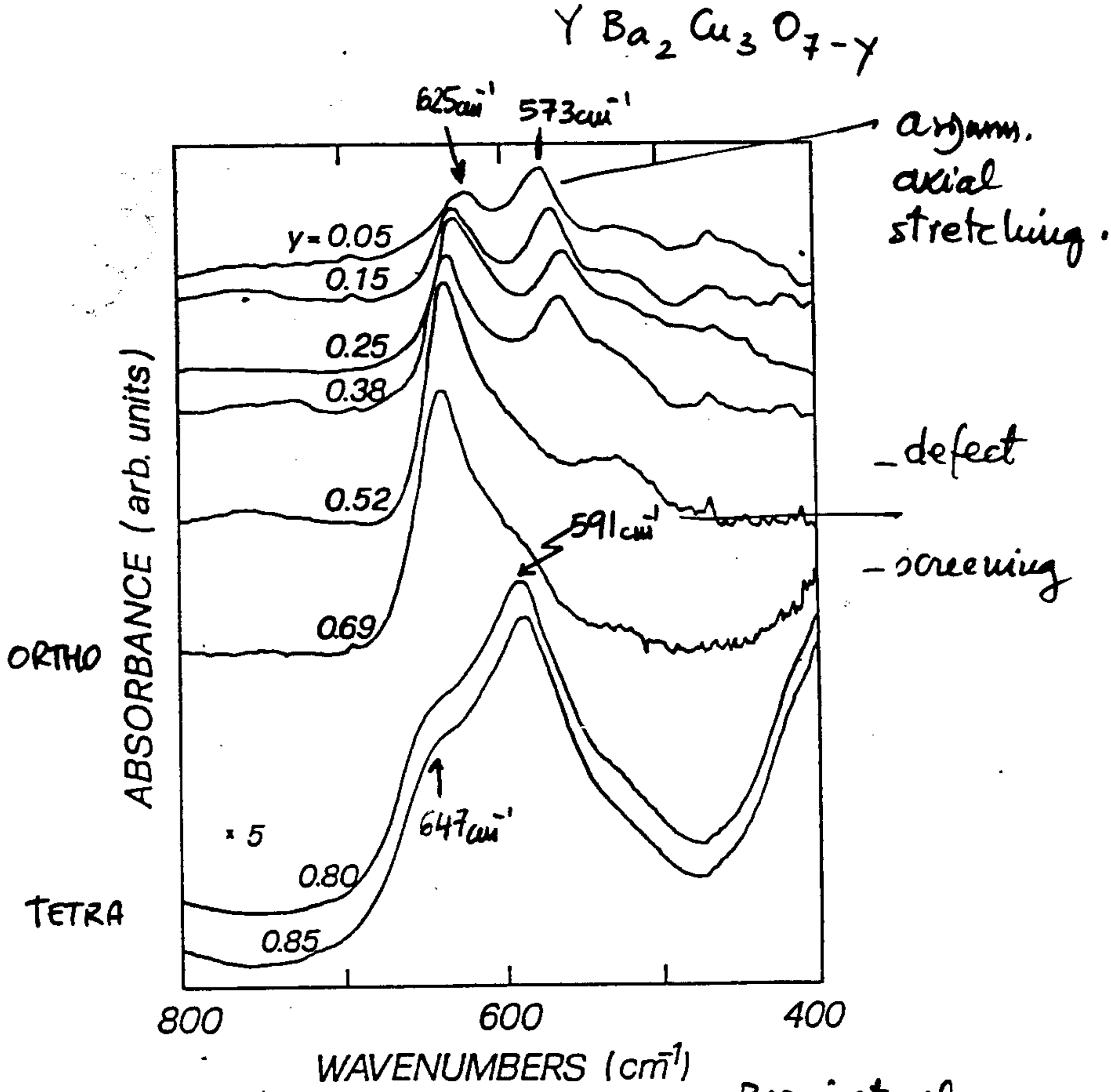


LE long lived photoinduced charge excitation (defect?)

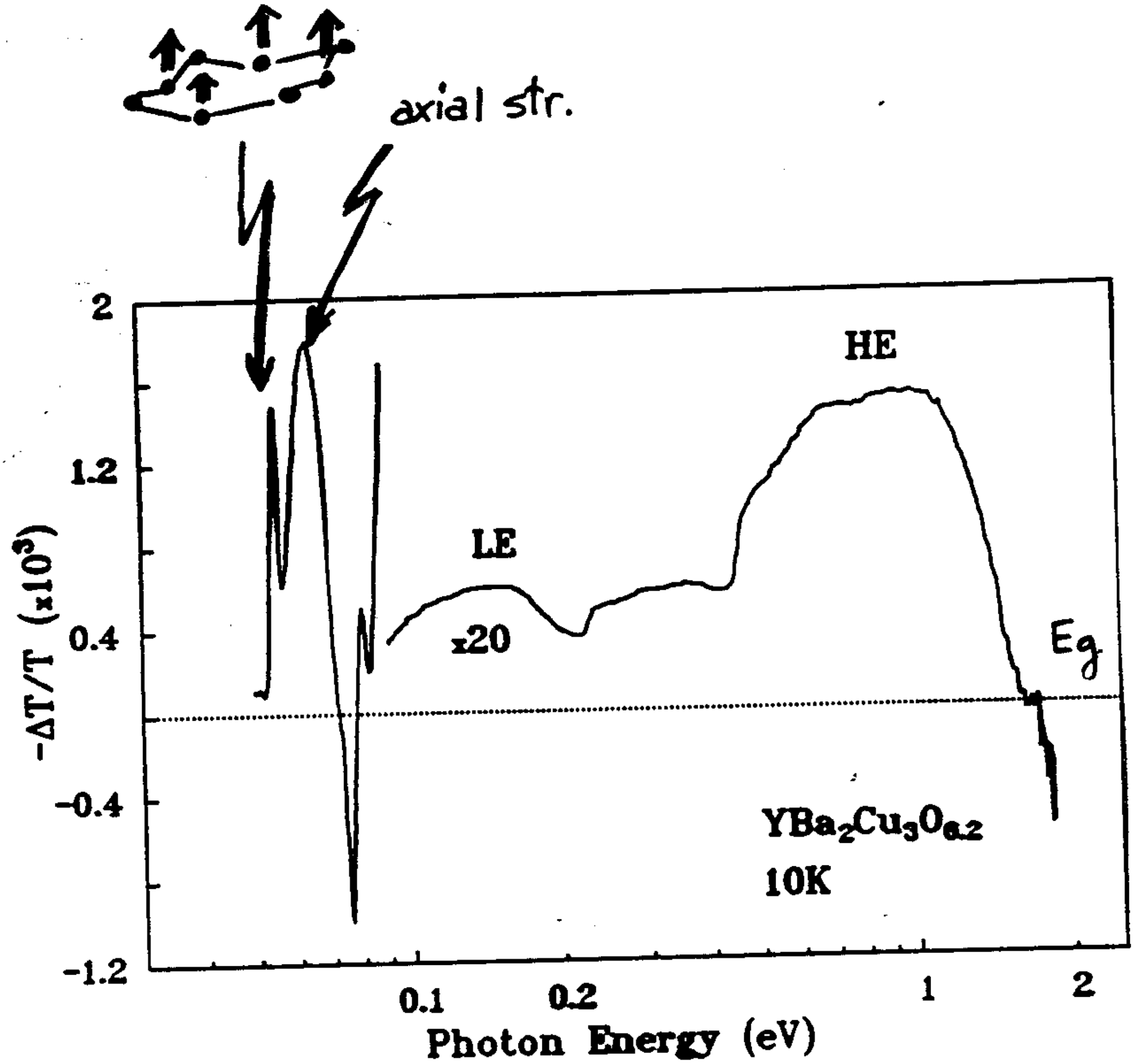


axial stretching
502
435
$YBa_2Cu_3O_7$
Raman scattering (Thomsen '87)
INTENSITY
Photoinduced absorption
$-\Delta T/T$ ($\times 10^3$)
590
ABSORBANCE (a.u.)
Infrared absorption (G. Ruani '88)
400
800
WAVENUMBERS (cm^{-1})

IR vs Oxygen content in gettered annealed $YBa_2Cu_3O_{7-y}$ samples.



Ruani et. al.
(JOSA B 89)



– v2 phonon spectrum   PA ≡ Abs. vs doping

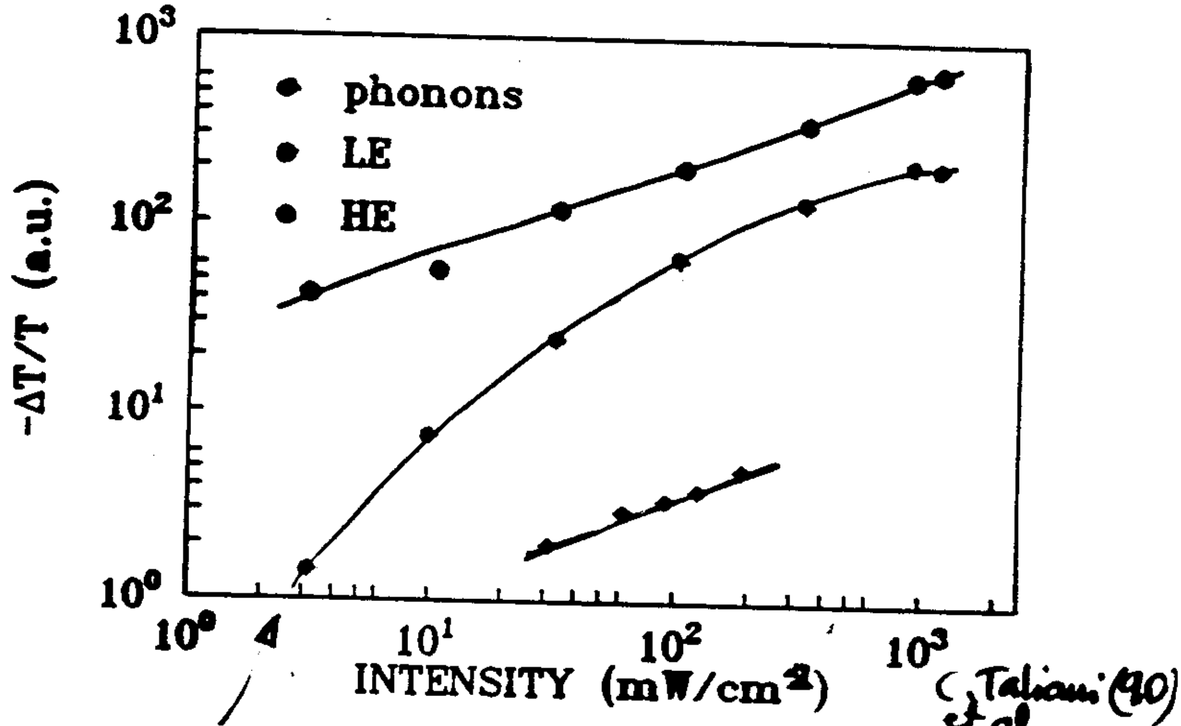
LE → defect

HE → intrnsic charge excitatien associated with lattice distrortion

bimclecular recombination

$YBa_2Cu_3O_{7-\delta}$ ($\delta = 0.8$)

Photoinduced Absorption vs Laser Intensity



defect state (gives rise to saturation)

n_{ps} = n° of photoexcited species

$$\frac{d n_{ps}}{dt} = \alpha I_{Laser} - \beta n_{ps}^2 = c \text{ (steady state)}$$

$$n_{ps} = \frac{\alpha}{\beta} I_{Laser}^{1/2}$$

HE + phonons ← fingerprints of the same photoex. species

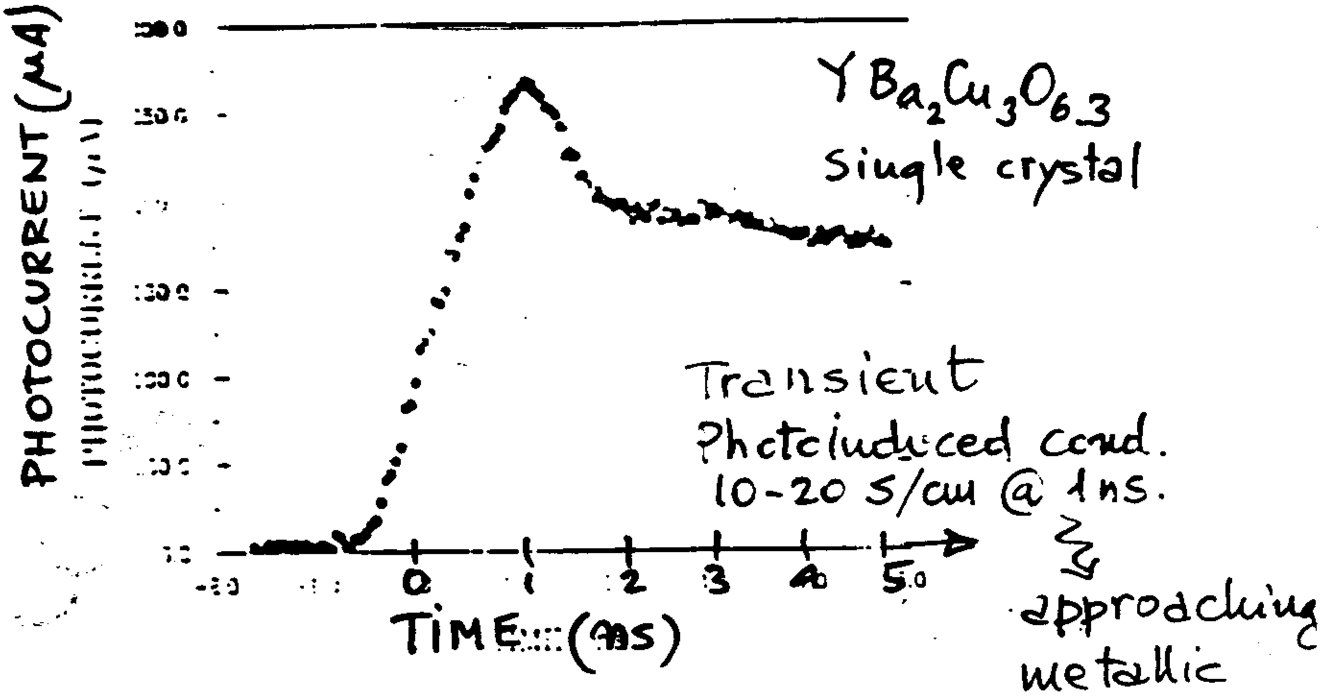


Figure 1: The time resolved photocurrent of the $YBa_2Cu_3O_{6.3}$ single crystal sample at room temperature; the bias is 5 volts; the photon flux is 1.5×10^{16} cm^{-2}. The photocurrent is proportional to the applied bias voltage. The transient response was checked with 300 ps and 450 ps instrumental resolution with no difference in the time delay.

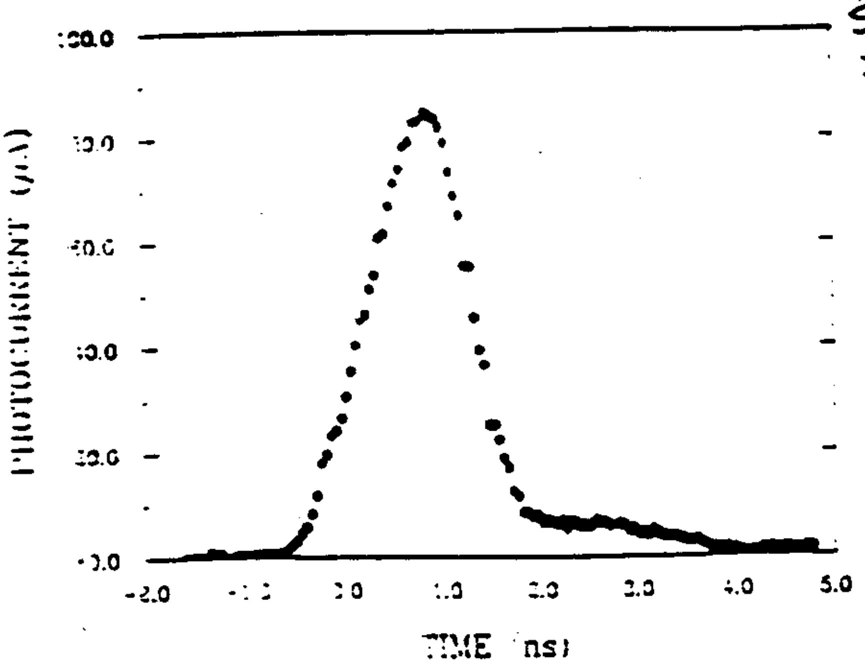


Figure 3: The time resolved photocurrent of the $YBa_2Cu_3O_{6.3}$ single crystal sample at 81.5K.; the bias is 10V; the photon flux is 1.5×10^{16} cm^{-2}. The photocurrent is proportional to the applied bias voltage.

Femtosecond Optical Detection of Quasi-Particle Dynamics in High T_c $YBa_2Cu_3O_{7-\delta}$ Superconducting Thin Films

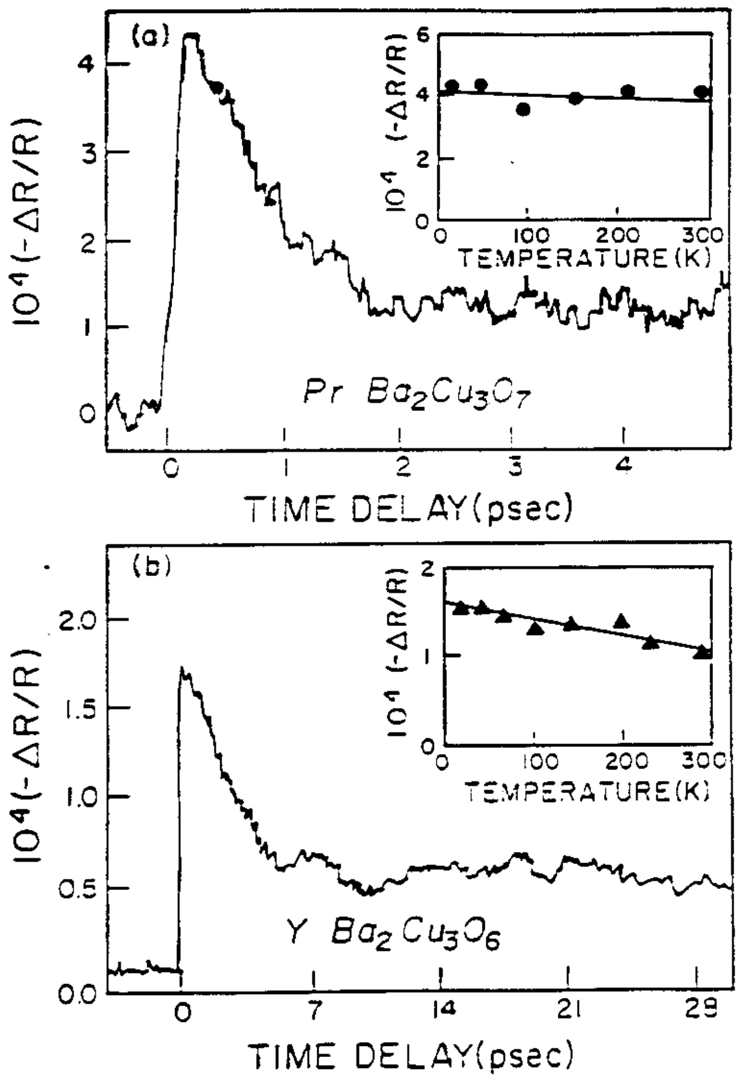
S.G. Han, Z.V. Vardeny, K.S. Wong and O.G. Symko
Department of Physics, University of Utah, Salt Lake City, UT 84112

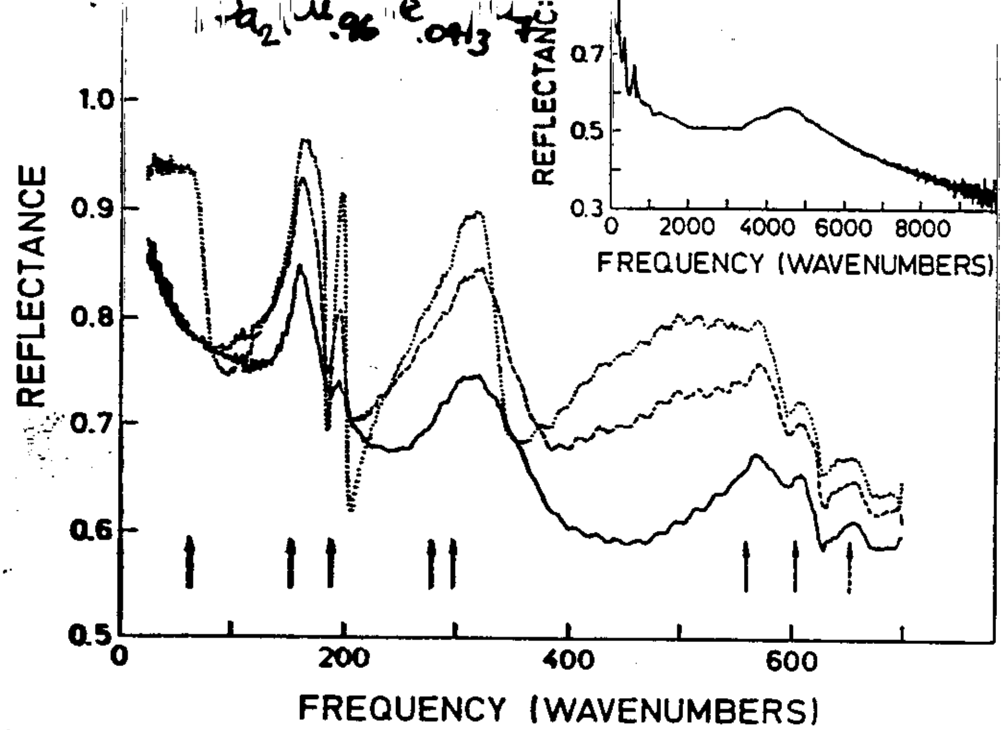
and

Gad Koren
Department of Physics, Technion, Haifa, 32000, Israel

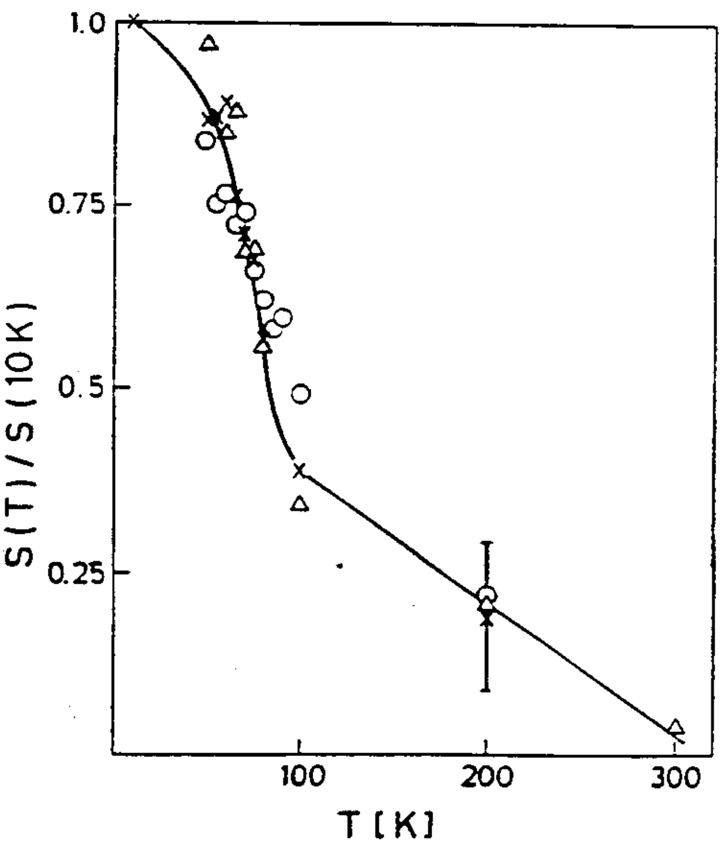
Abstract

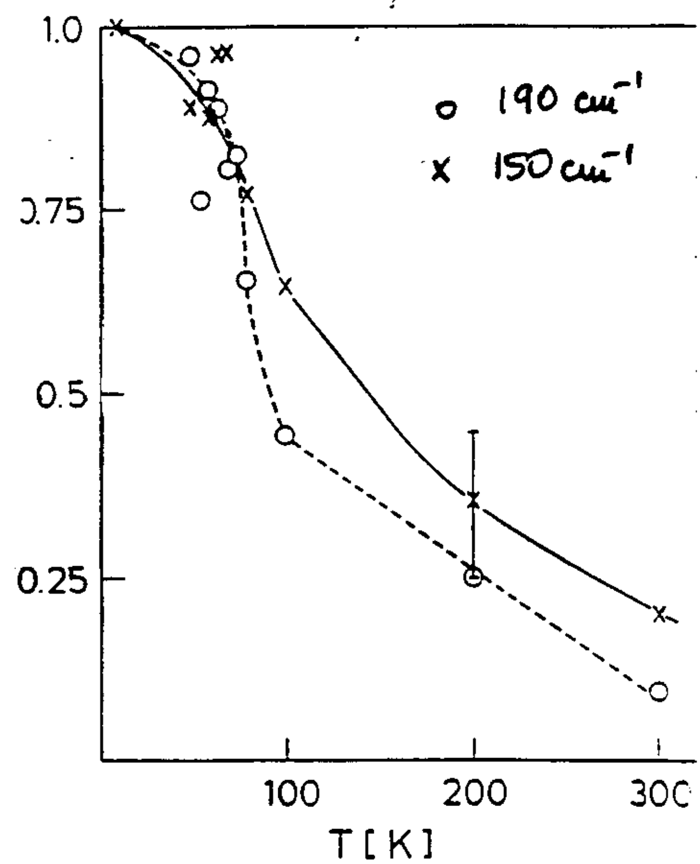
Femtosecond dynamics of photogenerated quasi-particles in $YBa_2Cu_3O_{7-\delta}$ superconducting thin films shows at $T \leq T_c$ two main electronic processes: (i) quasi-particles avalanche production during hot carrier thermalization, which takes about 300 fsec; (ii) recombination of quasi-particles to form Cooper-pairs which is completed within 5 psec. In contrast, nonsuperconducting ceramic films such as $PrBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ show regular picosecond electronic response.





Genzel et. al.
preliminary





Softening of the 335 cm⁻¹ B_{1g} mode

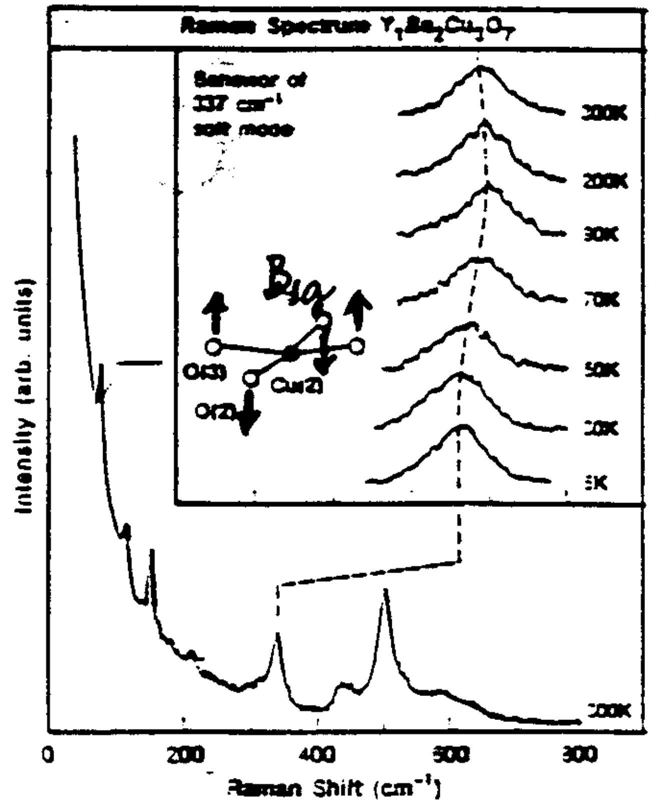


FIG. 1. First-order Raman spectrum of $YBa_2Cu_3O_{7.00}$ showing characteristic peaks with room-temperature positions at 155, 337, 433, and 502 cm⁻¹ (the features at 79 and 117 cm⁻¹ are due to plasma lines). The inset shows the temperature dependence and normal-mode displacements [only for one Cu(2)-O(2,3) plane] of the 337-cm⁻¹ mode.

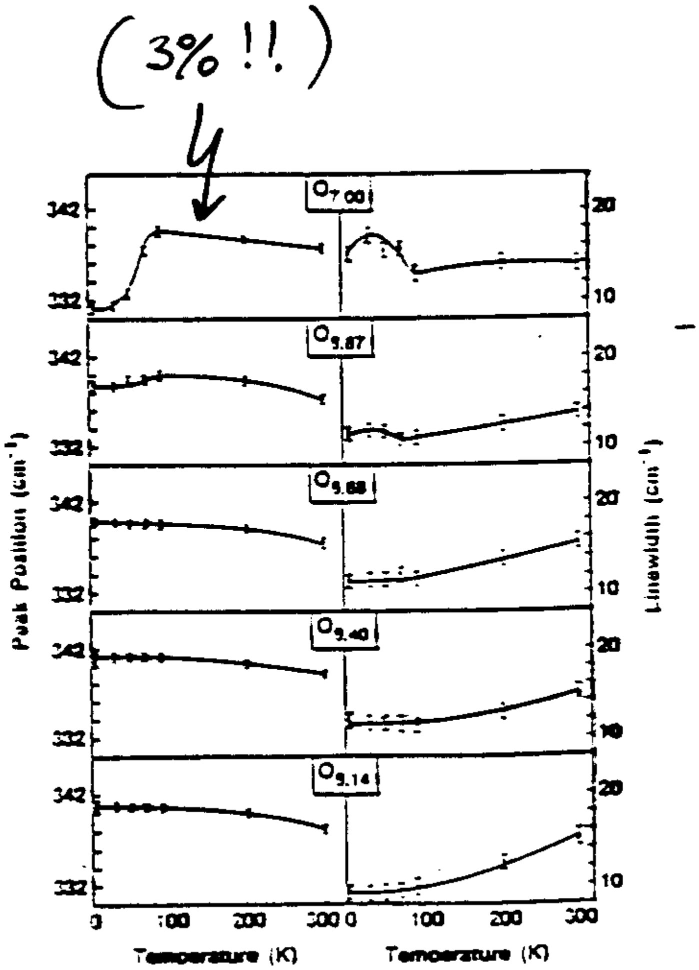


FIG. 2. Temperature-dependent peak positions and linewidths (full width at half maximum) of the 337-cm⁻¹ mode in $YBa_2Cu_3O_x$ displayed for oxygen stoichiometries $x=7.00$, 6.87, 6.68 with respective superconducting transition temperatures of 92, 84, and 51 K and semiconducting samples with $x=6.40$ and 6.14.

M. Krantz et. al. PRB 38, 4992 (88).

This paper has been submitted to Phys. Lett. A.

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Institute for Physical Problems
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Telefax: 7-095-938-20-30.

PHOTOINDUCED SUPERCONDUCTIVITY IN YBaCuO FILMS.

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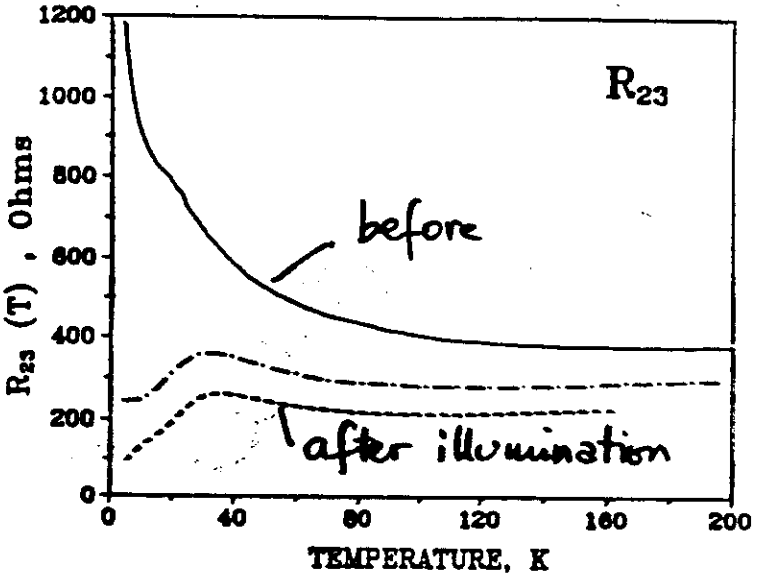
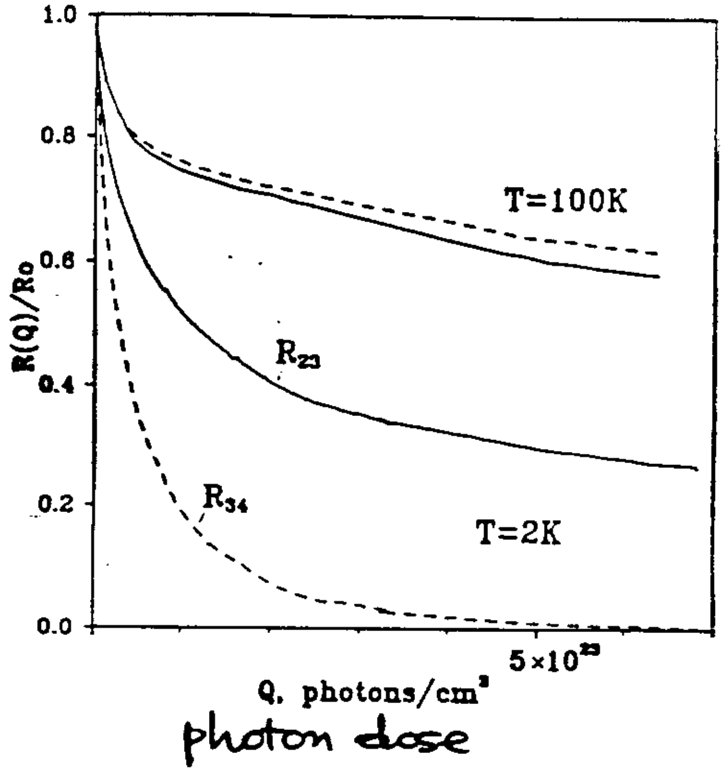
Institute for Physical Problems. Academy of Sciences. GSP-1, ul. Kosygina 2. Moscow 117973, USSR.
R. Laiho, E. Lahderanta.
Wihuri Physical Laboratory, University of Turku, 20500 Turku SC, Finland.

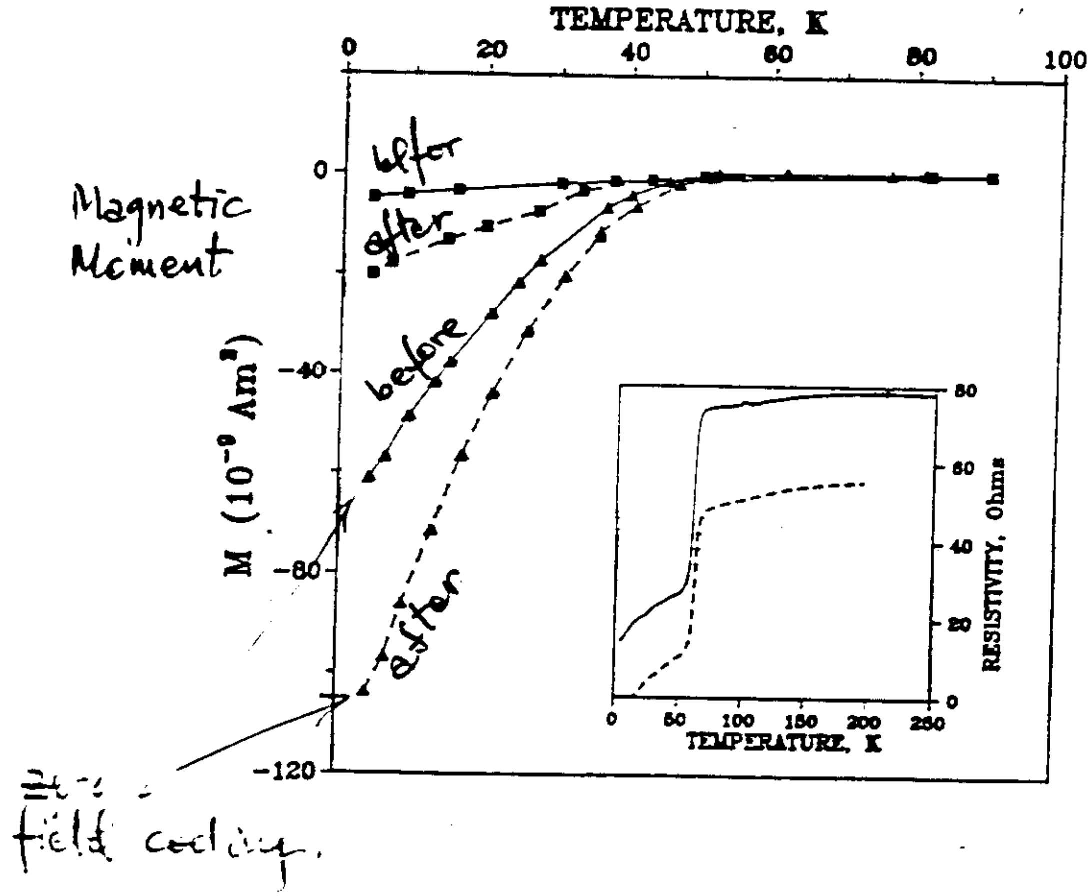
The phenomenon of persistent photoconductivity in $YBa_2Cu_3O_{6+x}$ (x=0.4) films near semiconductor-metal transition has been studied. Transport and magnetic measurements of the illuminated films were performed. Transition to metallic state and photoinduced superconductivity has been observed. The mechanism of persistent photoconductivity in reduced $YBa_2Cu_3O_{6+x}$ films is also discussed.

$YBa_2Cu_3O_{6.6}$ film on $SrTiO_3$

λ_{exc} = 647 nm 100-300 mW







photoinduced self-localization of charges at very low doping regime is a strong indication of the presence of polarons

still the question is open if the mechanism of s.c. is polaronic!

Some references

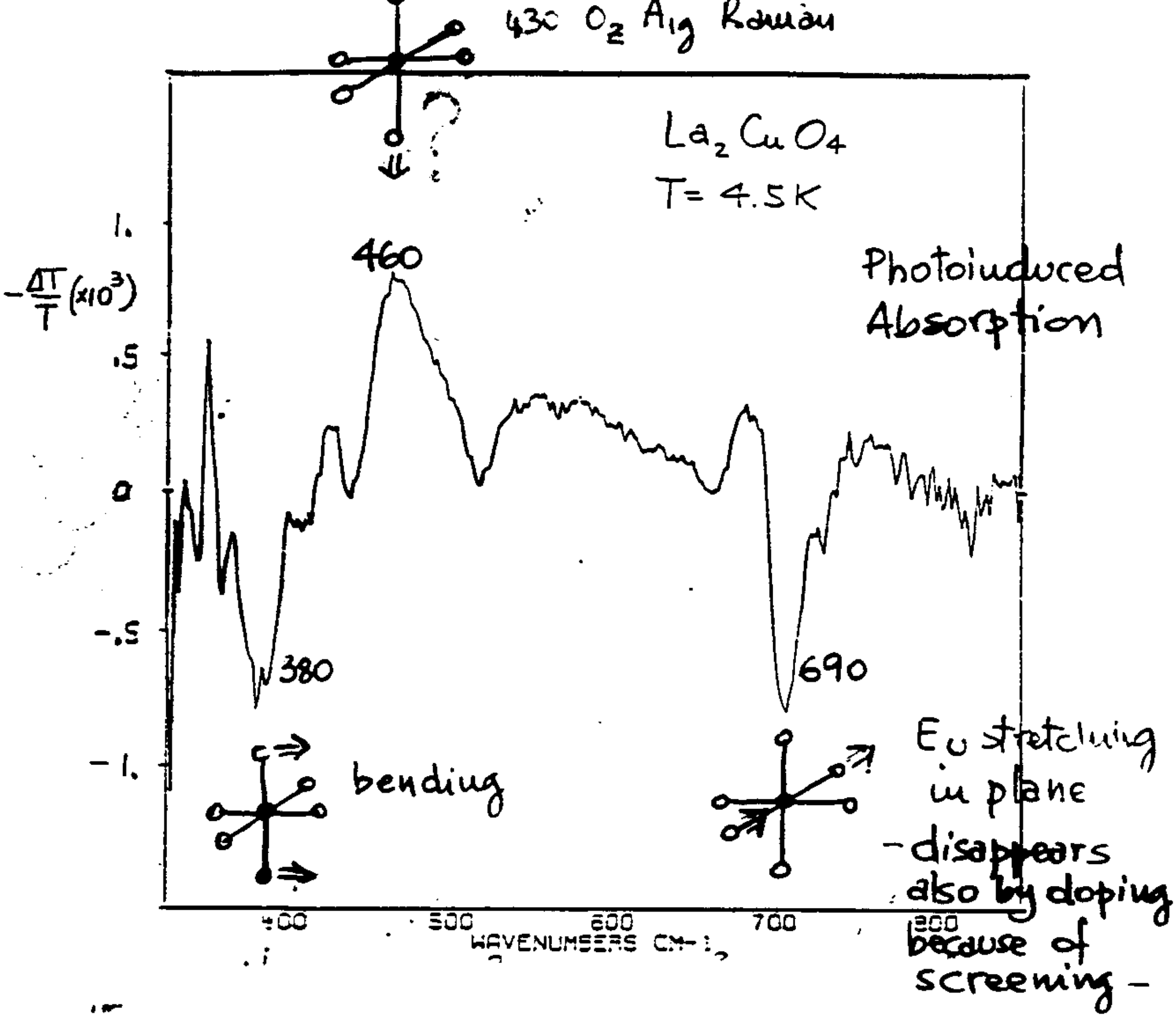
A.S.Alexandrov and J.Ranninger (1981), J.Ranninger (1990)

K.Nasu (1988)

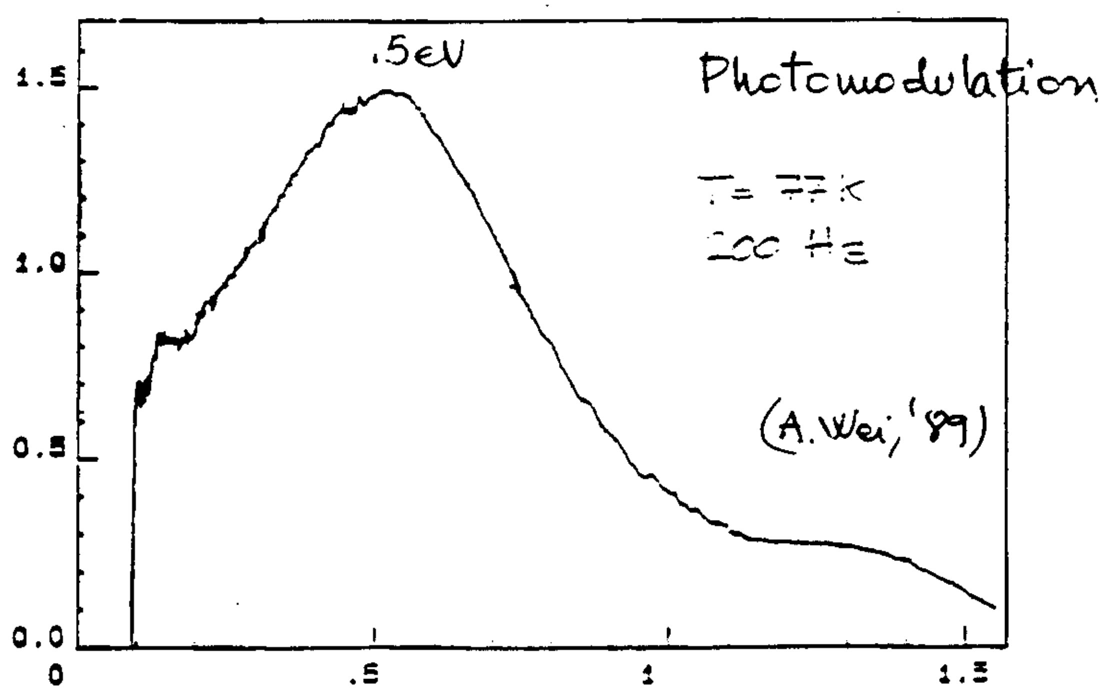
L.J.DeJong (1988)

D.Emin (1989)

J. Lorenzana, J.Lu (preprint)



430 O_z A_{1g} Raman
?
La_2CuO_4
T= 4.5K
1.
$-\frac{\Delta T}{T}$ ($\times 10^3$)
.5
0
-.5
-1.
460
Photoinduced Absorption
380
690
bending
E_u stretching in plane
- disappears also by doping because of screening -
400
500
600
700
800
WAVENUMBERS CM-1



.5eV
Photomodulation
T= 77K
200 Hz
(A. Wei, '89)
1.5
1.0
0.5
0.0
0
.5
1
1.5

Direct evidence of the importance of electron-phonon coupling in La_2CuO_4: Photoinduced ir-active vibrational modes

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Department of Physics, University of California, Santa Barbara, Santa Barbara, California 93106

L. Acedo and G. Stucky
Department of Chemistry, University of California, Santa Barbara, Santa Barabara, California 93106

F. Wudl
Department of Physics and Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

(Received 20 July 1987; revised manuscript received 24 August 1987)

We present direct evidence of the importance of the electron-phonon interaction in pure La_2CuO_4. Photoinduced ir-active vibrational modes (IRAV) and associated bleaching of the La_2CuO_4 phonon modes are observed in the spectral range below 700 cm^{-1}. The observation of photoinduced IRAV modes implies the existence of structural deformation around the photoexcited carriers, indicative of coupling of the photoexcitations to the lattice. We find, in addition, a broad photoinduced absorption which peaks at ≈ 0.5 eV, indicating an electronic transition deep within the energy gap.

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identificati
the high T_c
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volved. Re
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tronically
consistent
YBa_2Cu_3
ported[4] fo
high T_c is
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phonon int
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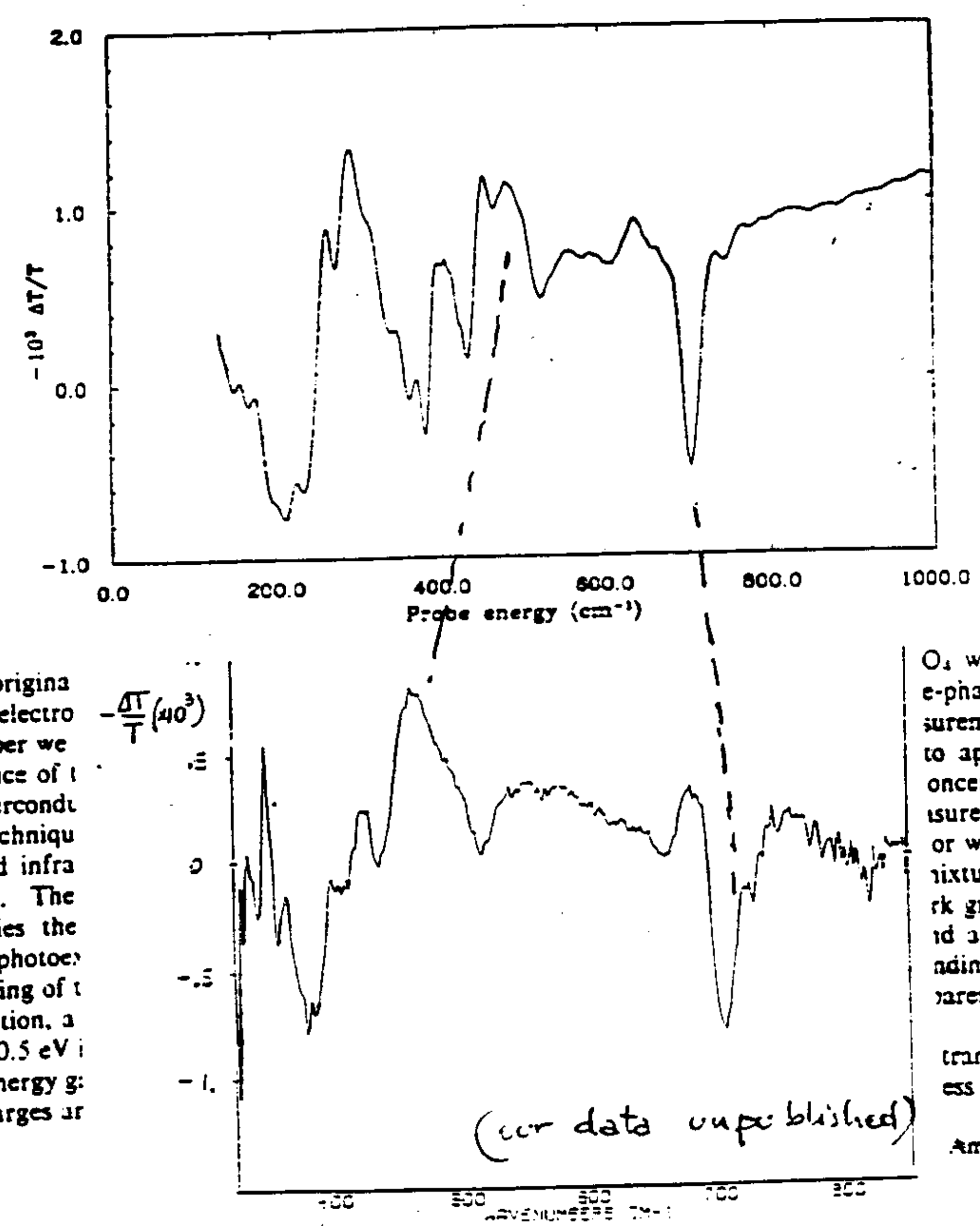
In this paper we
the importance of t
class of supercondu
excitation techniqu
photoinduced infra
in La_2CuO_4. The
modes implies the
around the photoe
strong coupling of t
find, in addition, a
peaks at ≈ 0.5 eV i
within the energy g
When charges ar



ptical pumping
disrupt the per-
create charged
of a degenerate
ton pairs) when
d.[7] These non-
itions and allow
al modes to be-
ced or photoin-
charge-induced
e self-localized
doping-induced
$\omega < E_g$ (the to-
single induced
pirit, we initiat-
CuO_4 in search
nstrate whether
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O_4 was characterized by
e-phase material. For the
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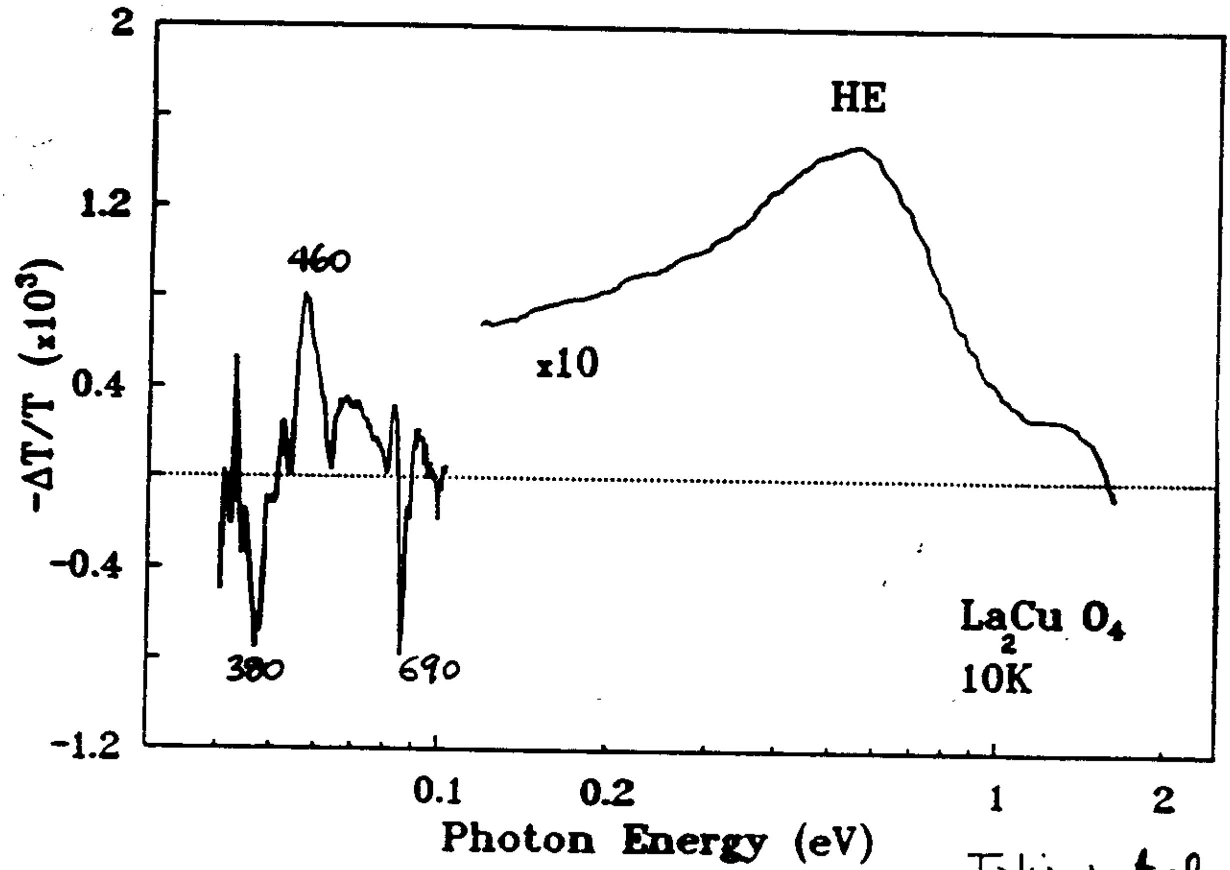
to approximately micron
oncentration of 1–2 wt.%
asurements in the spectral
or with CsI powder (120
mixtures were then com-
rk grey thin pellets. The
nd and then repressed to
nding-pressing cycle was
parency and homogeneity

transform infrared inter-
ess for the external laser



Taliani et al.
to appear.

- suppression of 690 screening in plane
- self trapping of polarons (phonon PA + charge exc. PA
  I_{LASER} dependence
- absence of any LE → ~ defect excitation
  (contrary to $YBa_2Cu_3O_{6.2}$)
  ↕ oxygen disorder in chains!!

$BaBiO_3$

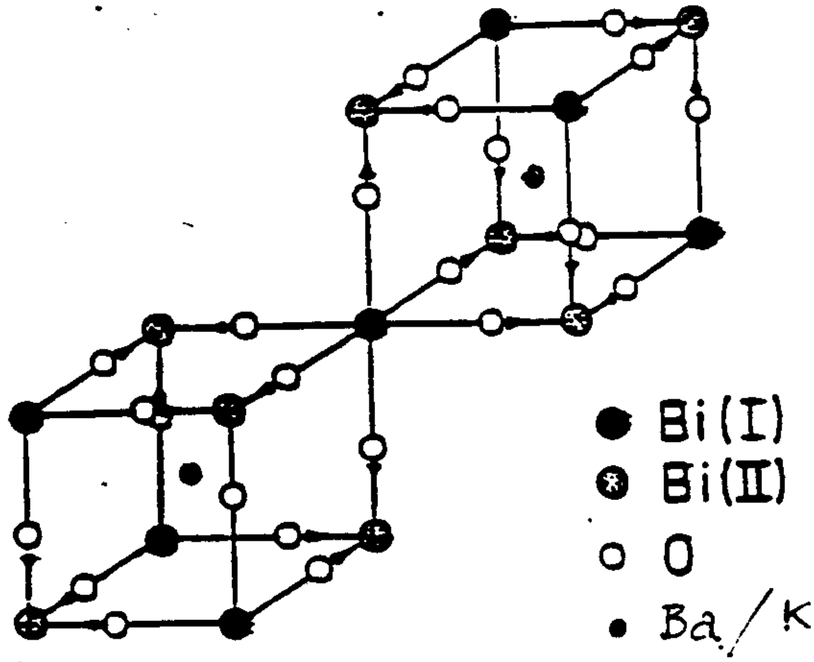
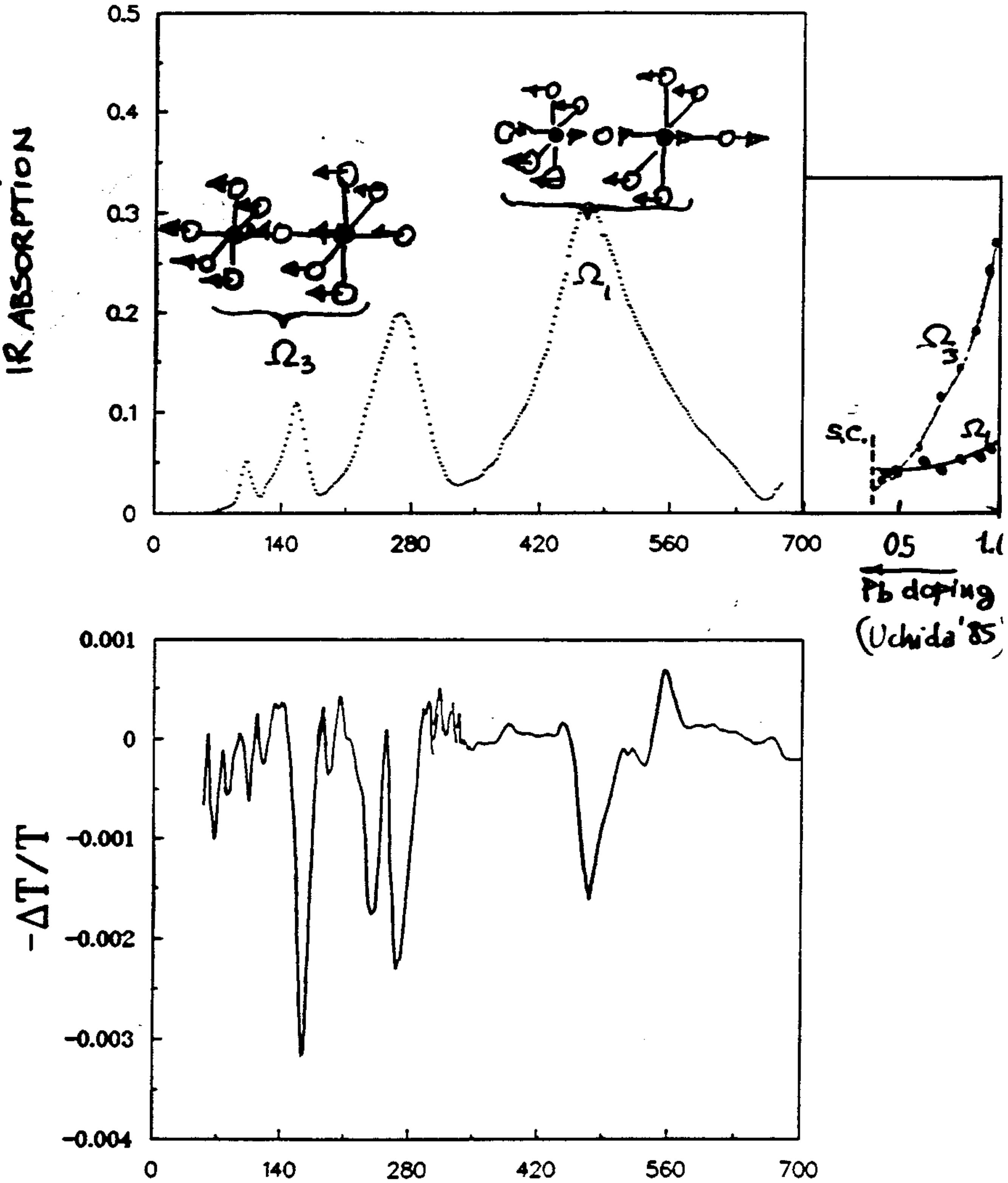


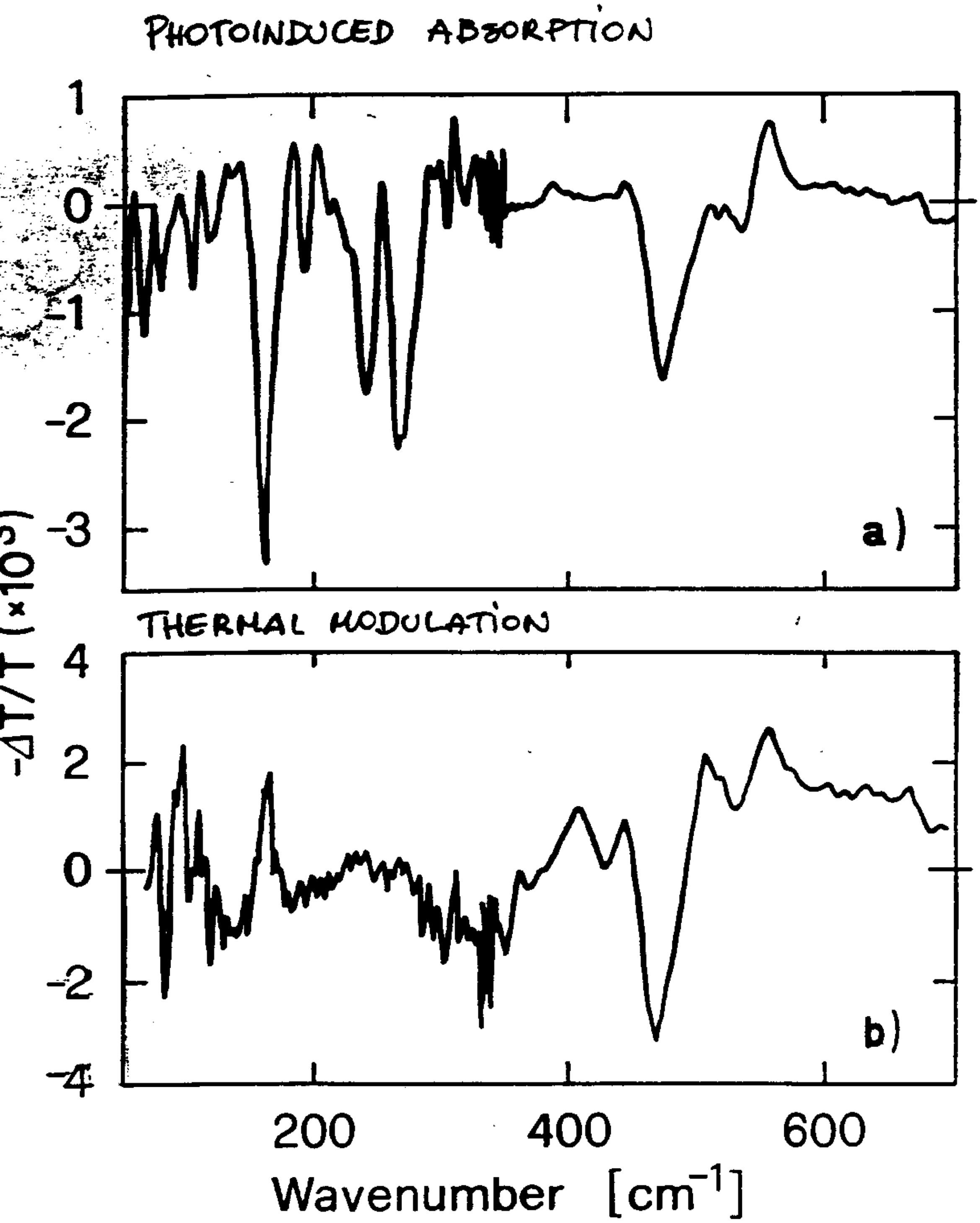
Fig. 4. Bi(I)–Bi(II) NaCl lattice. The breathing-mode distortions of the O atoms are exaggerated.

- $Ba_{0.6}K_{0.4}BiO_3$ $T_c \sim 30$ K → HTSC
- no magnetic ions
- 3 Dimensional
- static charge density wave (CDW)



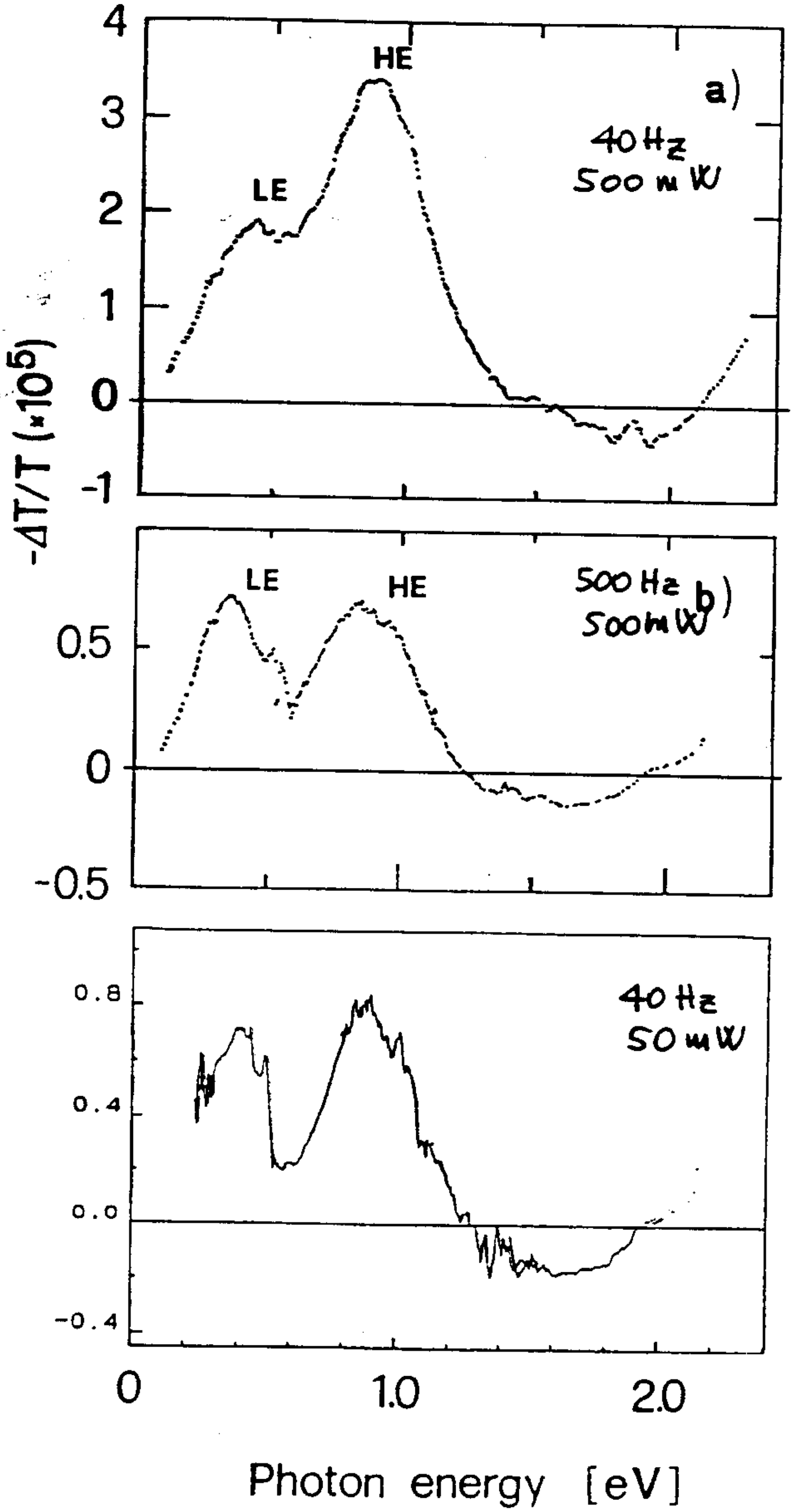
IR ABSORPTION
Ω3
Ω1
S.C.
Pb doping
(Uchida '85)
-ΔT/T

BaBiO3



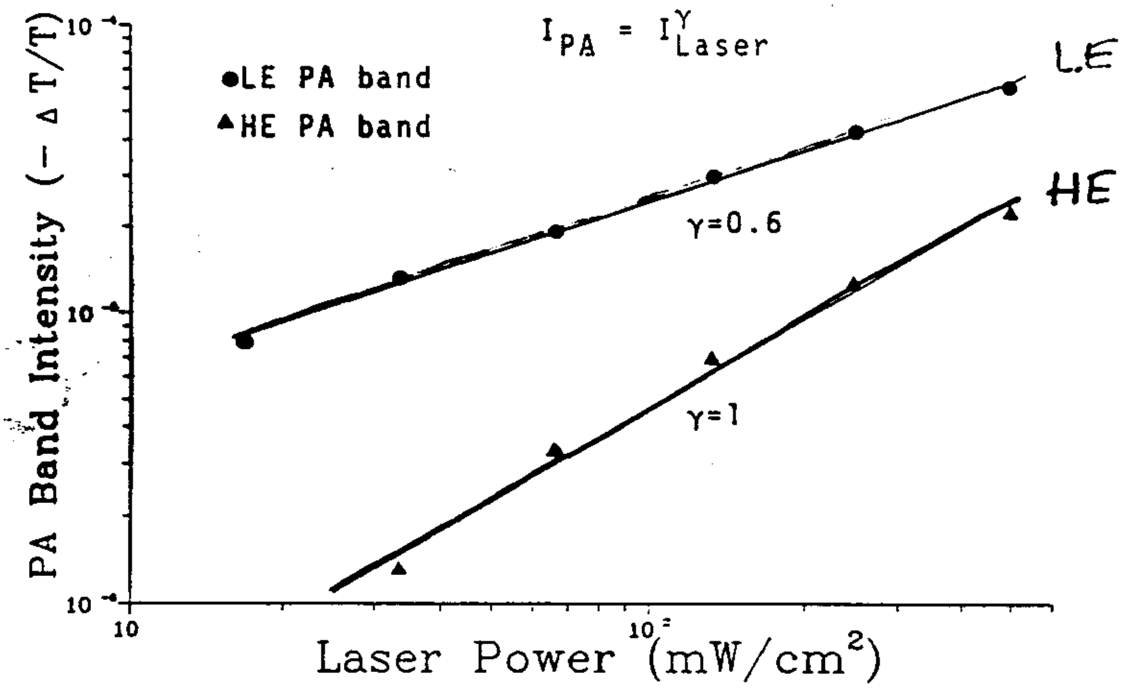
PHOTOINDUCED ABSORPTION
1
0
-1
-2
-3
a)
-ΔT/T (×10³)
THERMAL MODULATION
4
2
0
-2
-4
b)
200
400
600
Wavenumber [cm⁻¹]

$BaBiO_3$

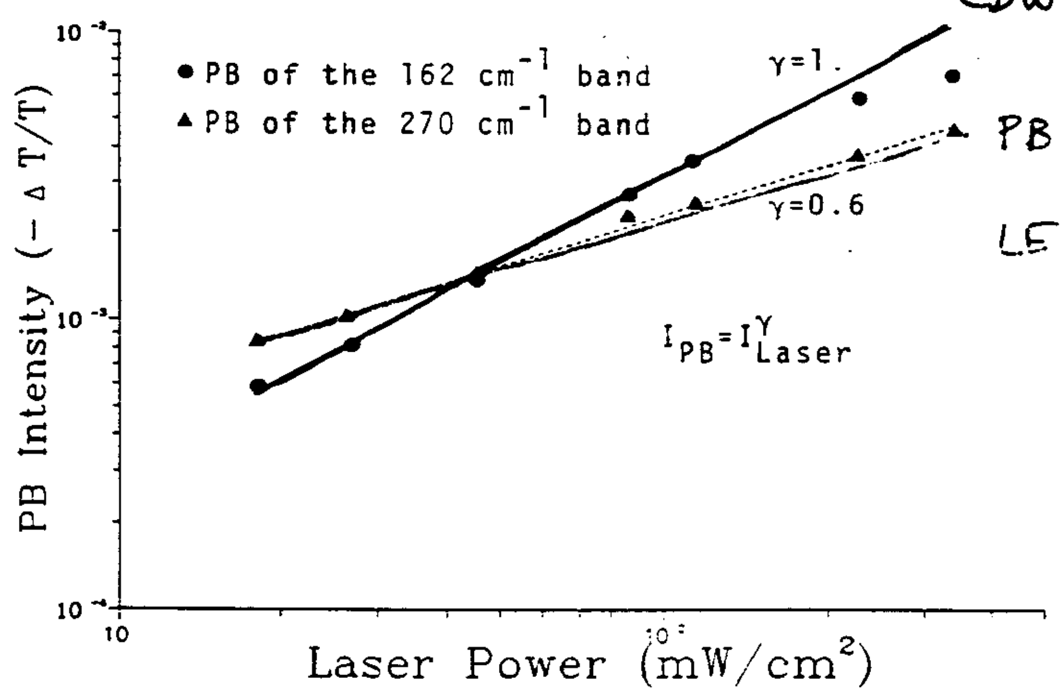


$\tau_{HE} > \tau_{LE}$

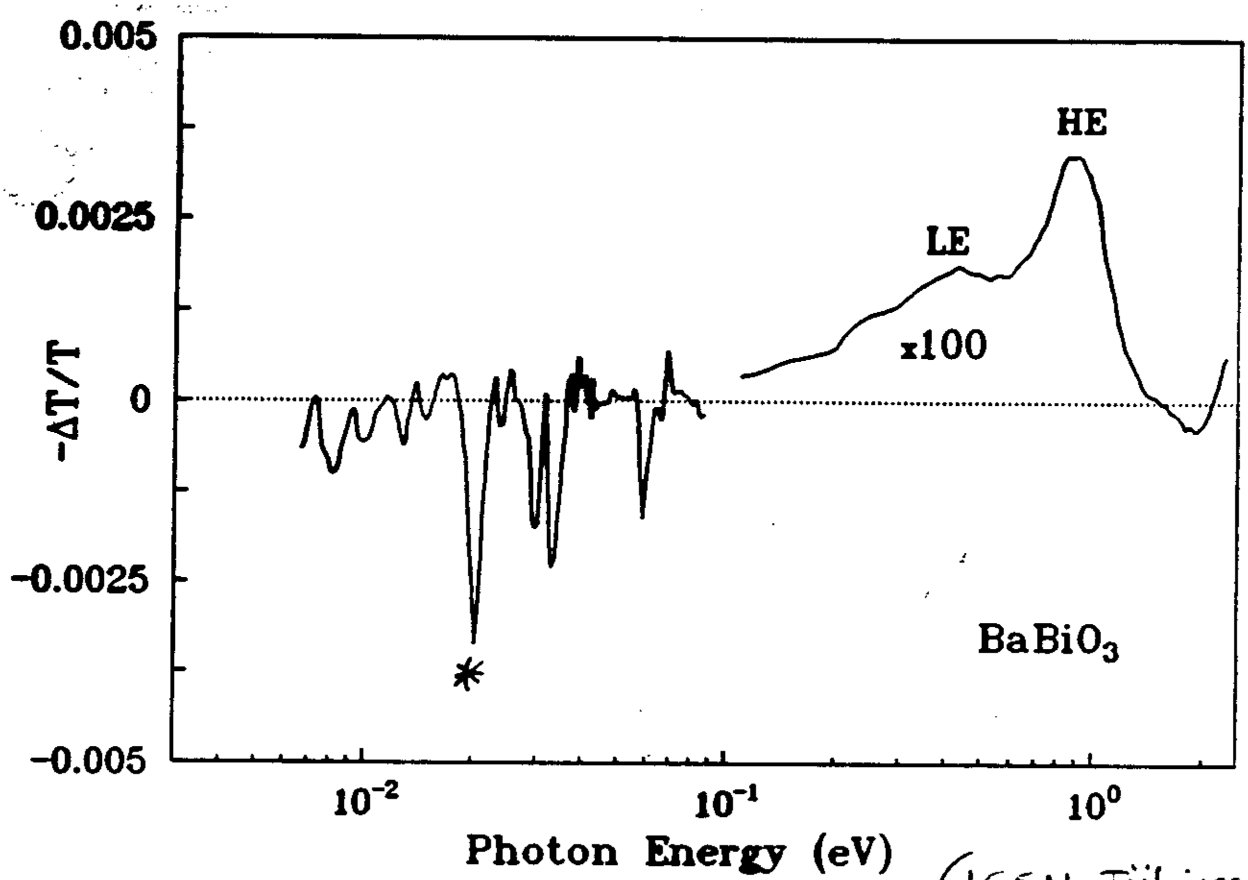
$BaBiO_3$



suppression of CDW ≡ HE

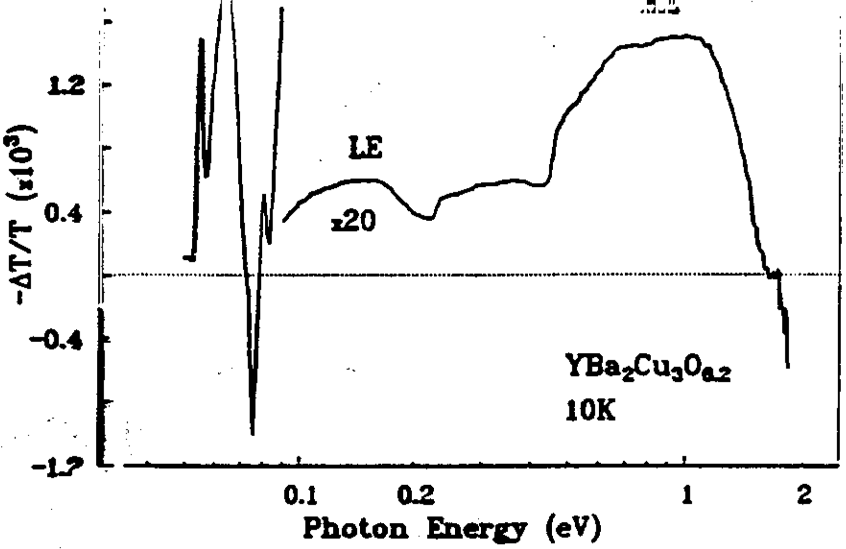


PB @ 270 cm^{-1} ≡ LE band

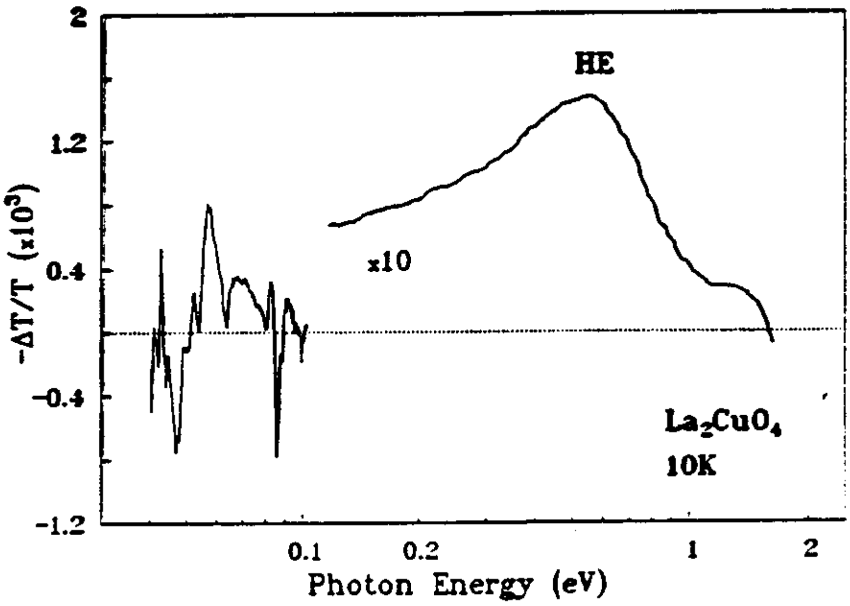


(ICSM Tübingen 9x proceedings)

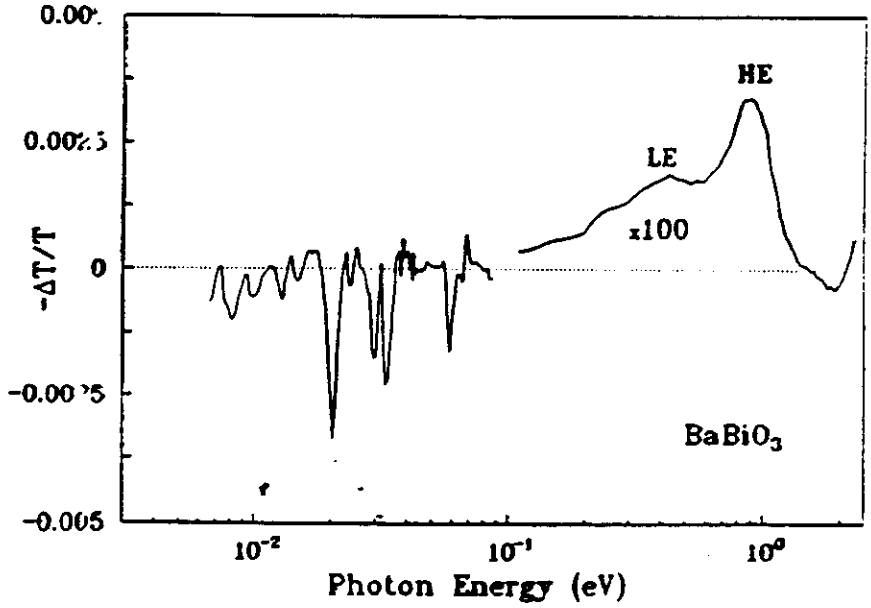
- charge density wave suppression *
- self trapping of polarons (PB + LE charge etc.)
- polarons ---> bipolarons I_{LASER} dependence



1.2
0.4
-0.4
-1.2
-ΔT/T (x10³)
LE
x20
YBa₂Cu₃O₆.₂
10K
0.1
0.2
1
2
Photon Energy (eV)



2
1.2
0.4
-0.4
-1.2
-ΔT/T (x10³)
HE
x10
La₂CuO₄
10K
0.1
0.2
1
2
Photon Energy (eV)



0
-0.005
-ΔT/T
HE
LE
x100
BaBiO₃
10⁻²
10⁻¹
10⁰
Photon Energy (eV)

mid-IR

LOW DOPING IN	CHARGE EXCITATION (eV) ONSET	MAX	ASSOCIATED with LATTICE DISTORTION	
$YBa_2Cu_3O_{6.2}$	~.25	.7	YES	
($Tl_2Ba_2Ca_{1-x}Gd Cu_2O_8$			YES) (Heeger '89)	
La_2CuO_4	~.3	.5	YES	$460 cm^{-1}$ (?)
$BaBiO_3$	~.3	.45	YES	suppression of CDW

- charged excitations → paired recombination
  ↓
  coupled with phonons → strong e-ph coupling, self localization.

- <u>COMMON</u> CHARACTERISTIC OF HTSC (2D and 3D)

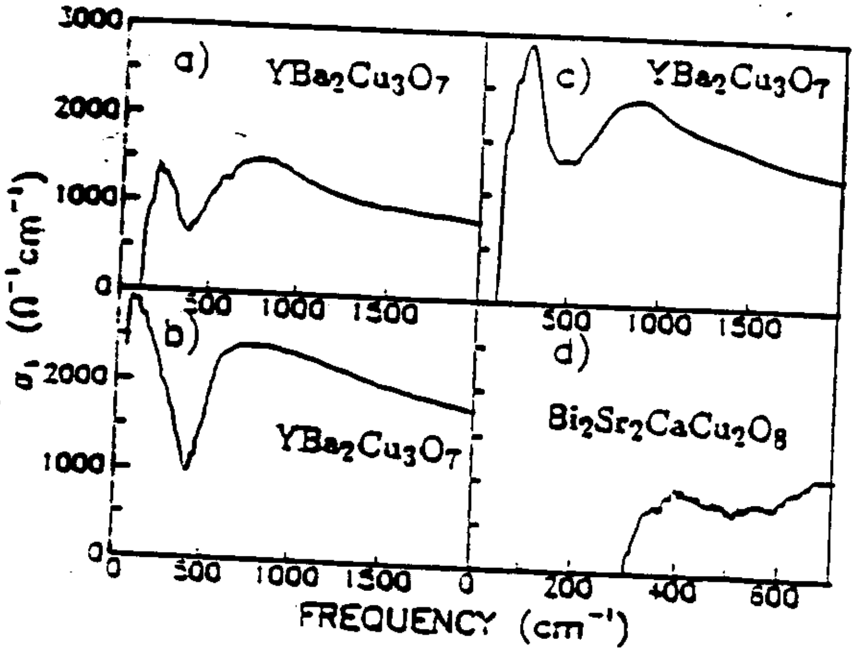
- mid-IR indipendent on Cu → no spin excitation!
  ↓
  polaron in the oxygen sublattice!

Regensburg Univ.

AT&T Lab.

Bellcore + Florida Univ.

Mc Master Univ.



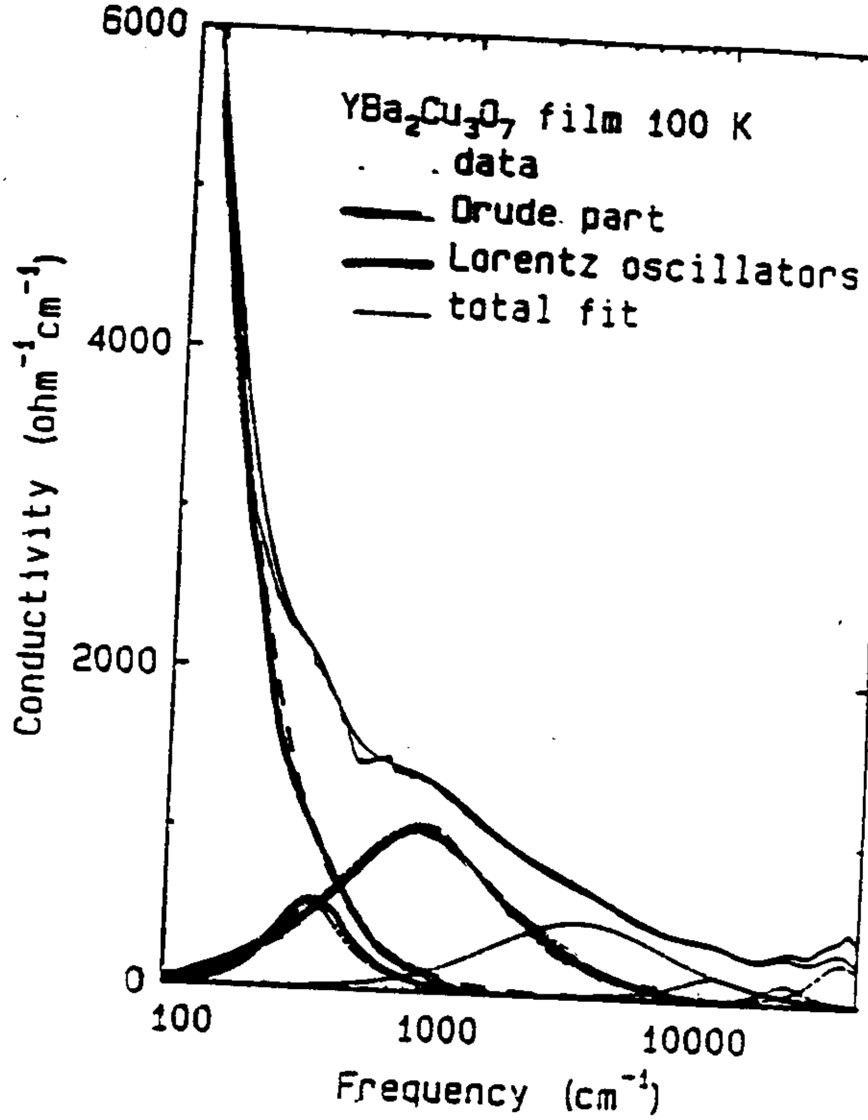
(2

Figure 1

The midinfrared band, data from four groups. a) Thin film produced by laser ablation by the Siemens/Regensburg group. b) Another laser processed film from the Bellcore/Florida collaboration. c) A single crystal of $YBa_2Cu_3O_7$ from AT&T. d) $Bi_2Sr_2CaCu_2O_8$ crystal from McMaster. In all cases there is temperature independent absorption in the midinfrared of the order of 1500 $(\Omega\ cm)^{-1}$ in amplitude. The gap-like onset of the absorption has the superficial appearance of a superconducting gap but the gap is also present in the normal state.

from: T. Timusk et al.
Physica C 162-164, 841 (89)

+ Genzel group, MPI Stuttgart.

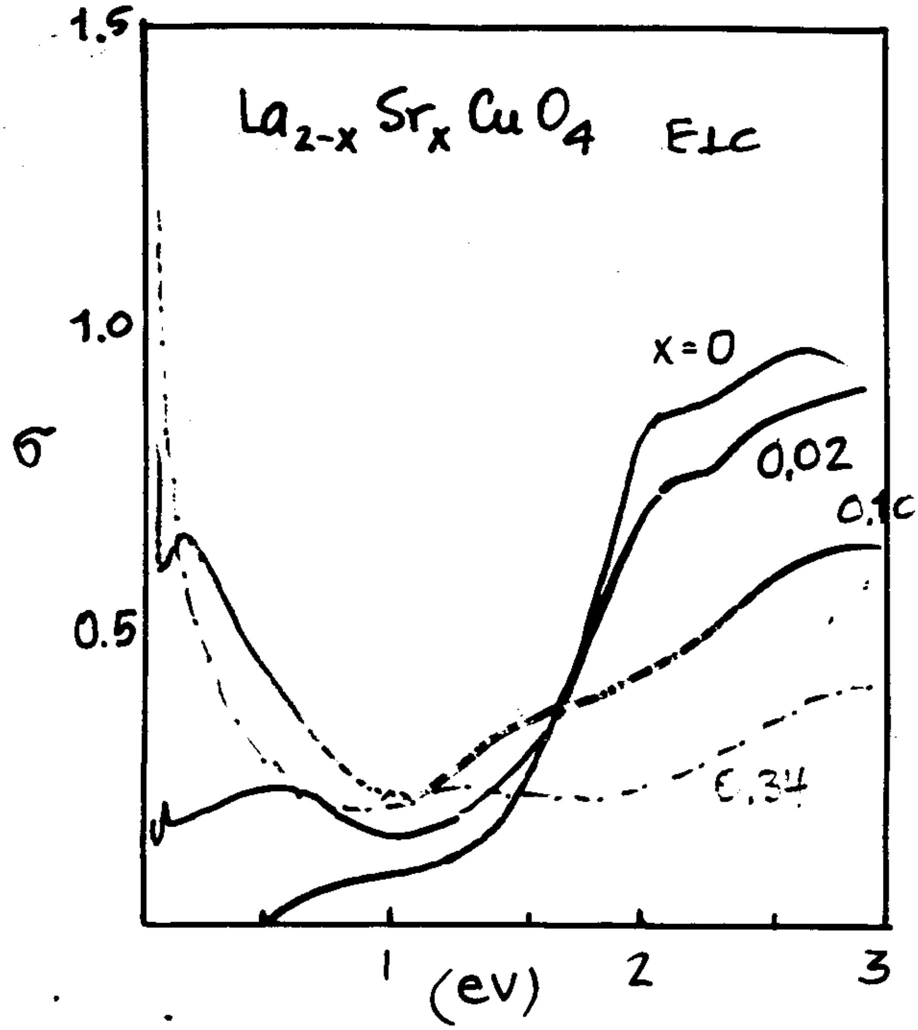


K. Kamaras et al. (90)

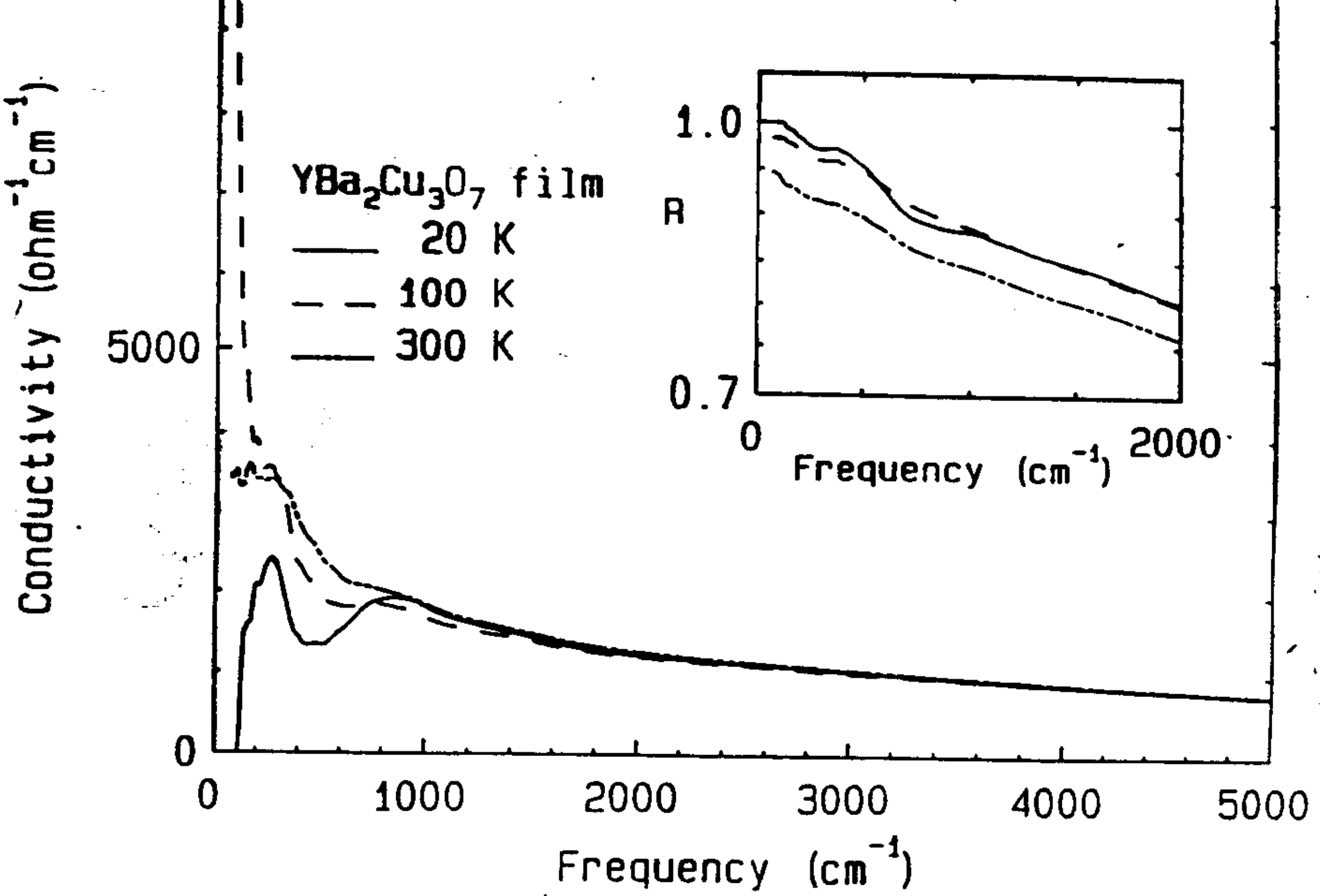
$$\epsilon(\omega) = \frac{\omega_p^2 D}{\omega^2 + i\omega/\tau} + \frac{\omega_{pe}^2}{\omega_e^2 - \omega^2 - i\omega\gamma_e} + \sum_{J=1,N} \frac{S_J \omega_J^2}{\omega_J^2 - \omega^2 - i\omega\gamma_J} + \epsilon(\infty)$$

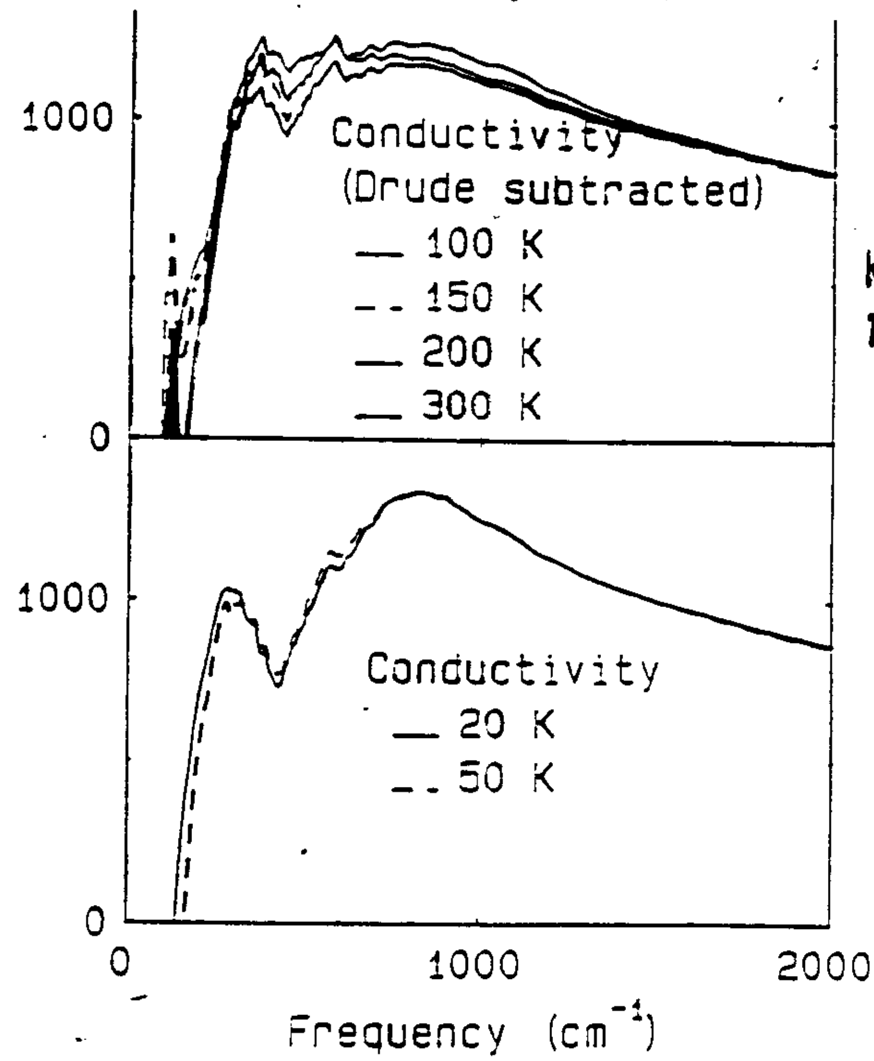
DRUDE MID-IR PHONONS

$\omega_p = .7 \rightarrow 1.4\,eV$ $\omega_e \sim .26\,eV$

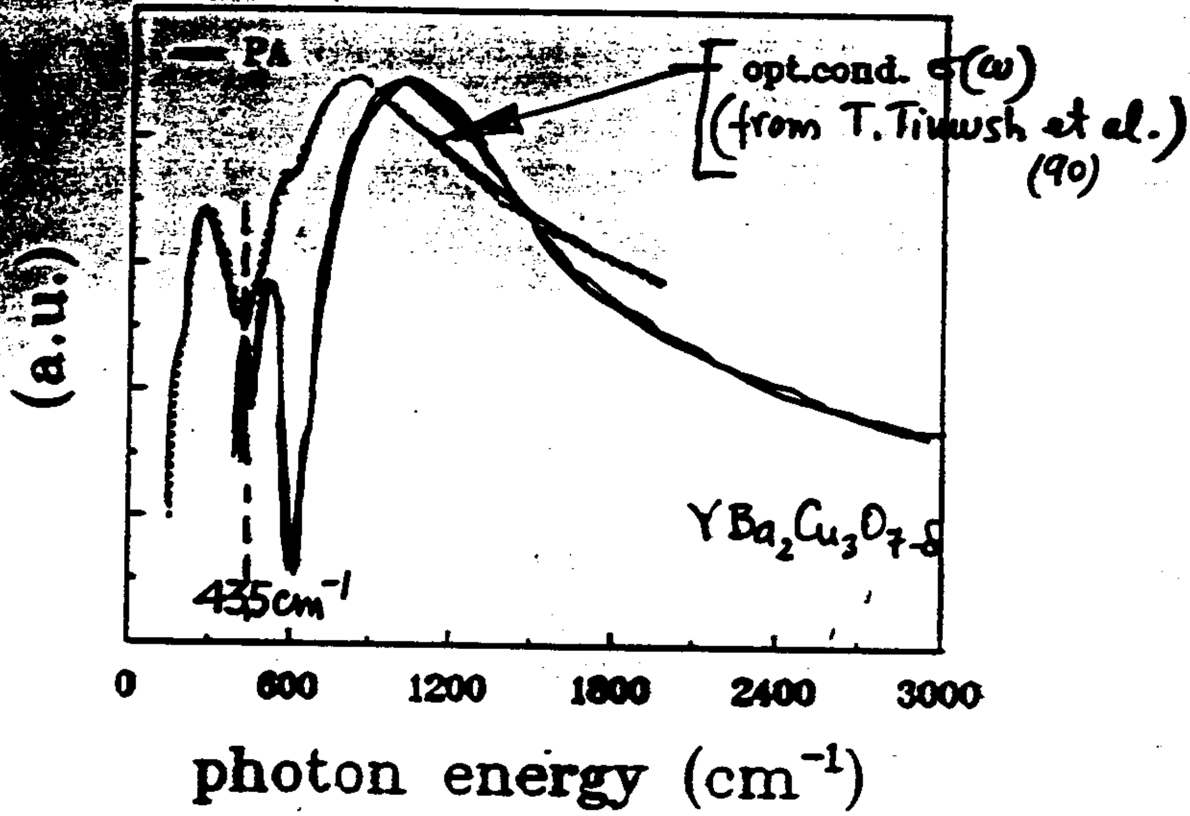


Tajima et al. (1990)





K. Kamaras et al
PRL 64, 84 (90)



435 cm^{-1} 

→ antiresonance in $\sigma(\omega)$

→ lattice self localization (PA).

→ softening (neutron diffr) (Rietschel '89

linked

LE defect state

HE onset ~ 0.3 eV

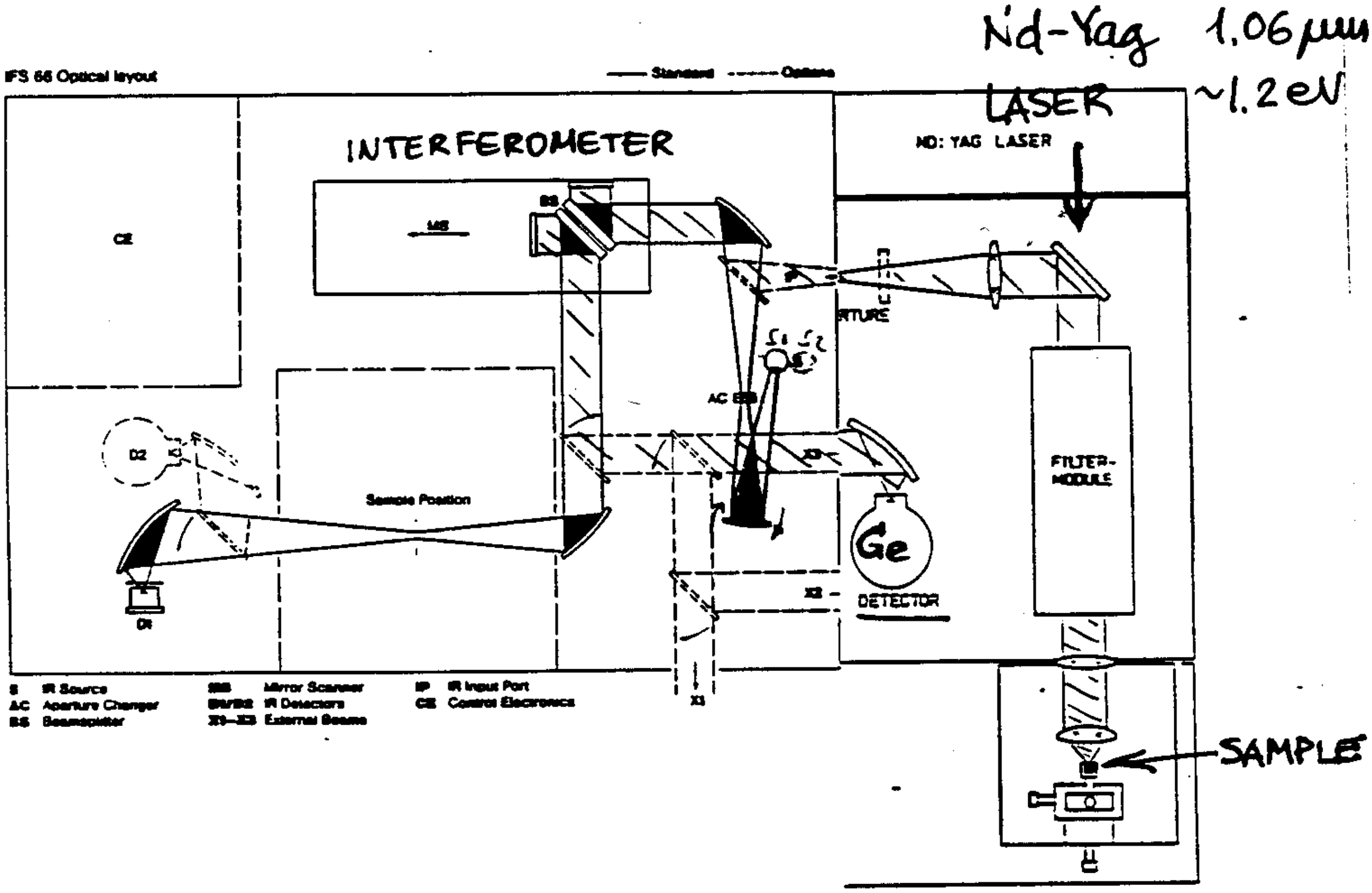
common to La_2CuO_4 and $BaBiO_3$

⇓

charge excitation in the oxygen network?

FOURIER TRANSFORM { RAMAN / PHOTOLUMINESCENCE

EXPERIMENTAL SET-UP



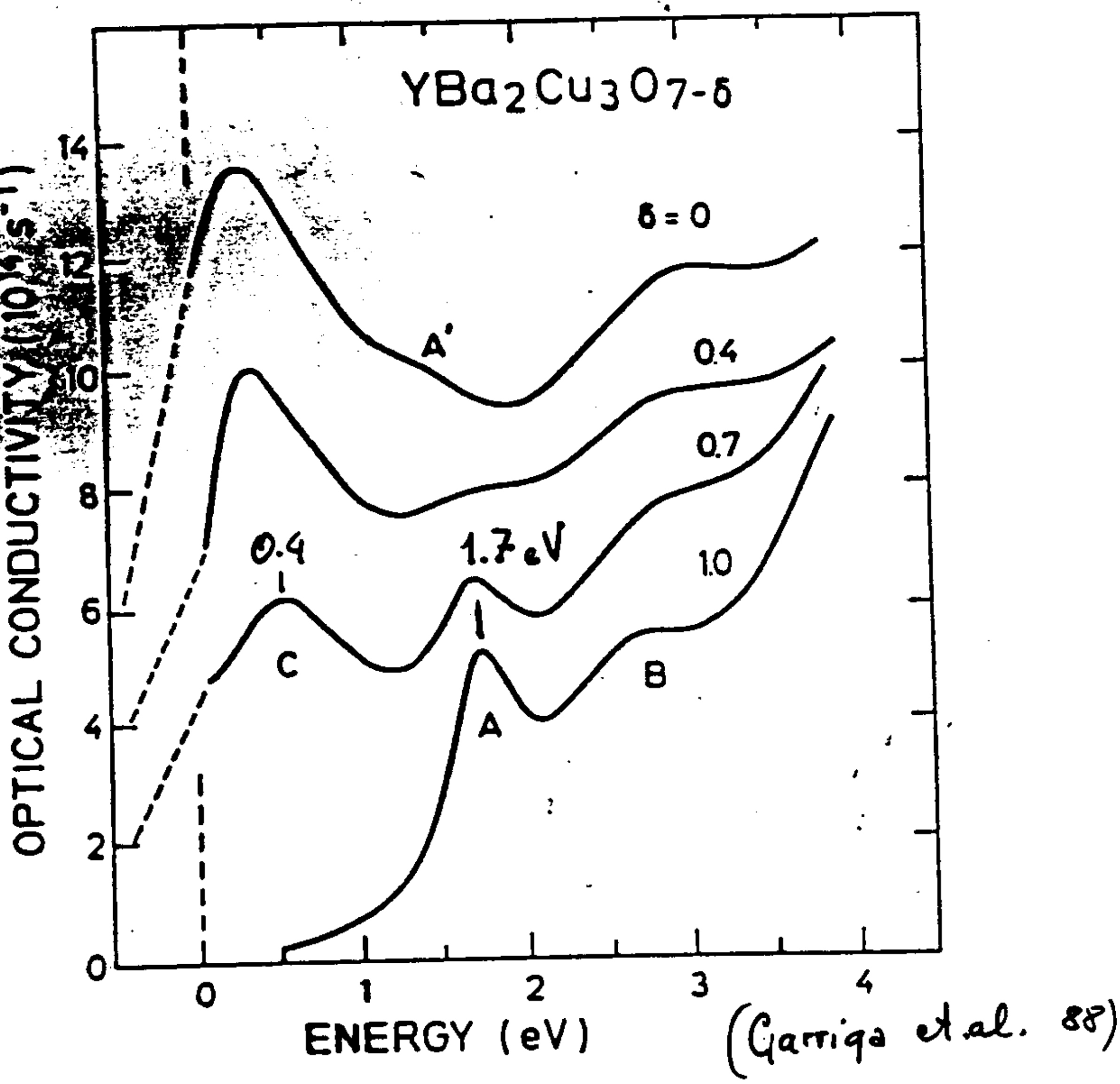
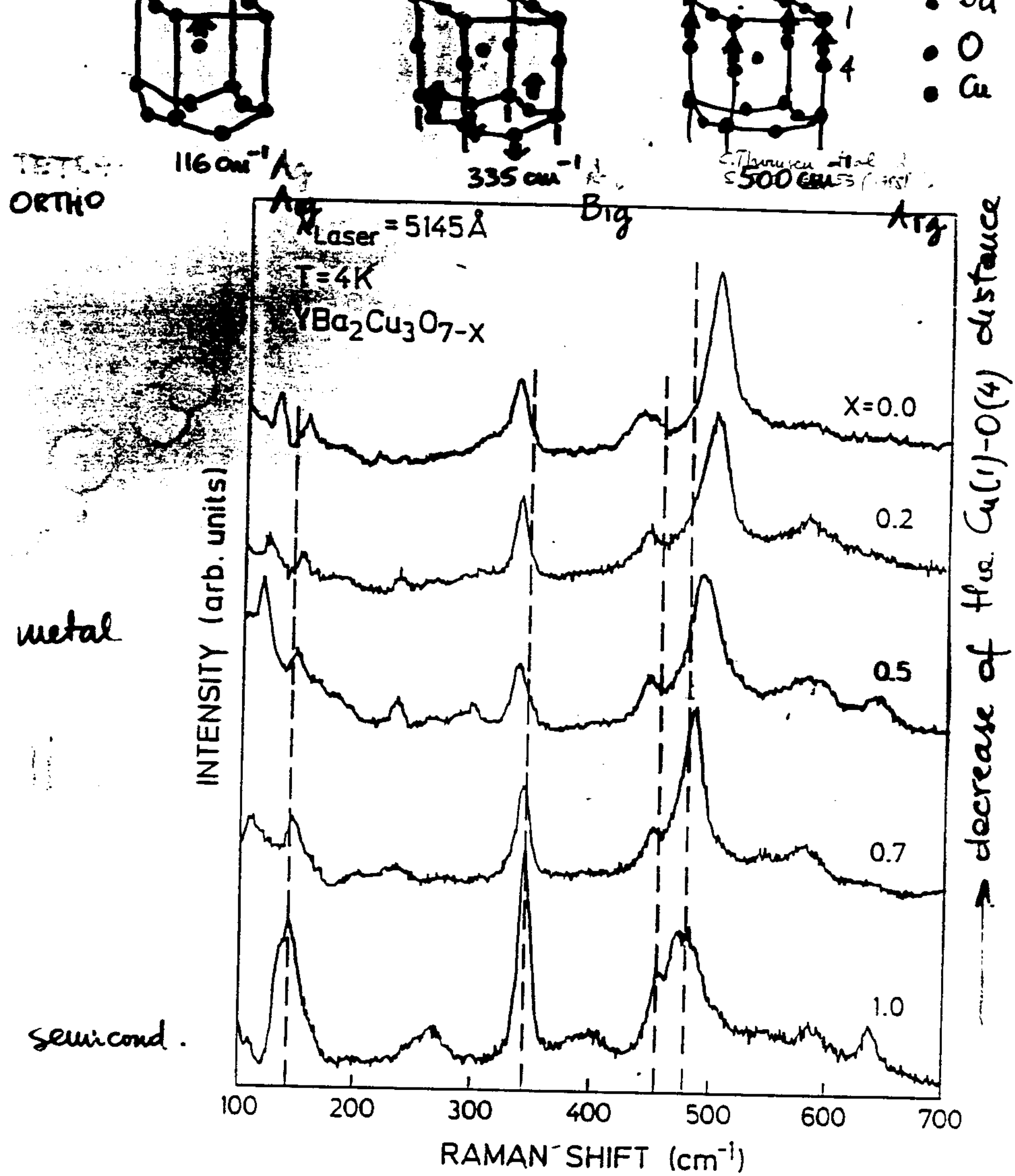


FIGURE 2

Optical conductivity of ceramic $YBa_2Cu_3O_{7-\delta}$ for different oxygen content.



C. Thomsen et al.
S.S. Commun. 65, 55 (88)

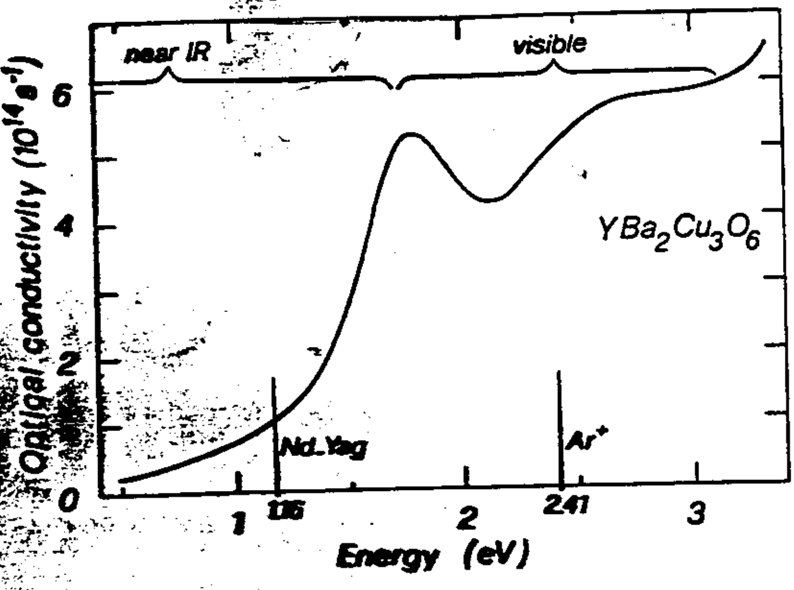


Fig.4-The optical conductivity spectrum of $YBa_2Cu_3O_6$ (from Ref. 1). Nd-Yag and Ar^+ laser photon energies are shown for comparison. → (Gamiqa 88)

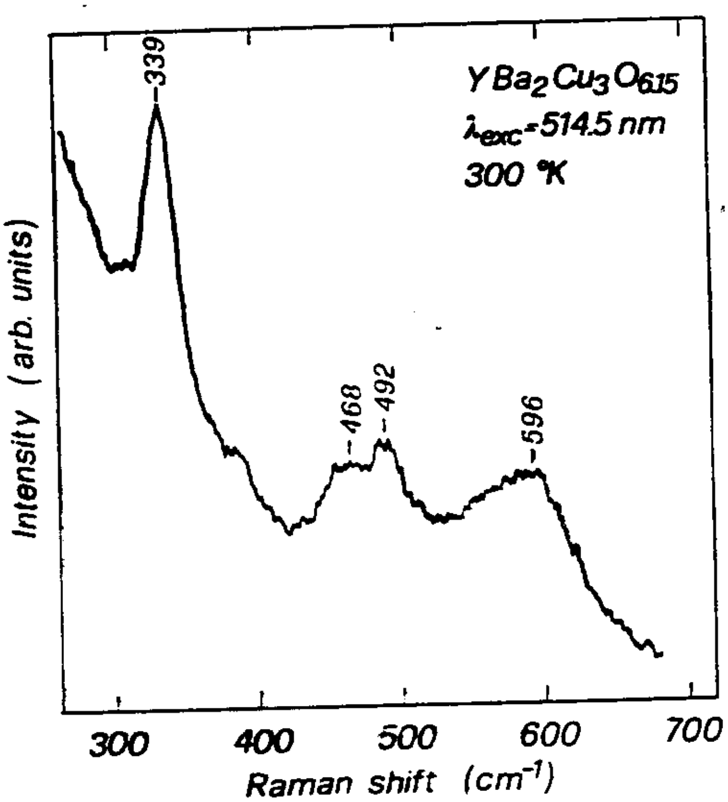


Fig.3-The standard Raman scattering spectrum of $YBa_2Cu_3O_{6.15}$ excited with a visible Ar^+ laser line at 514.5 nm. Note that the 640 cm^{-1} band due to impurities is absent.

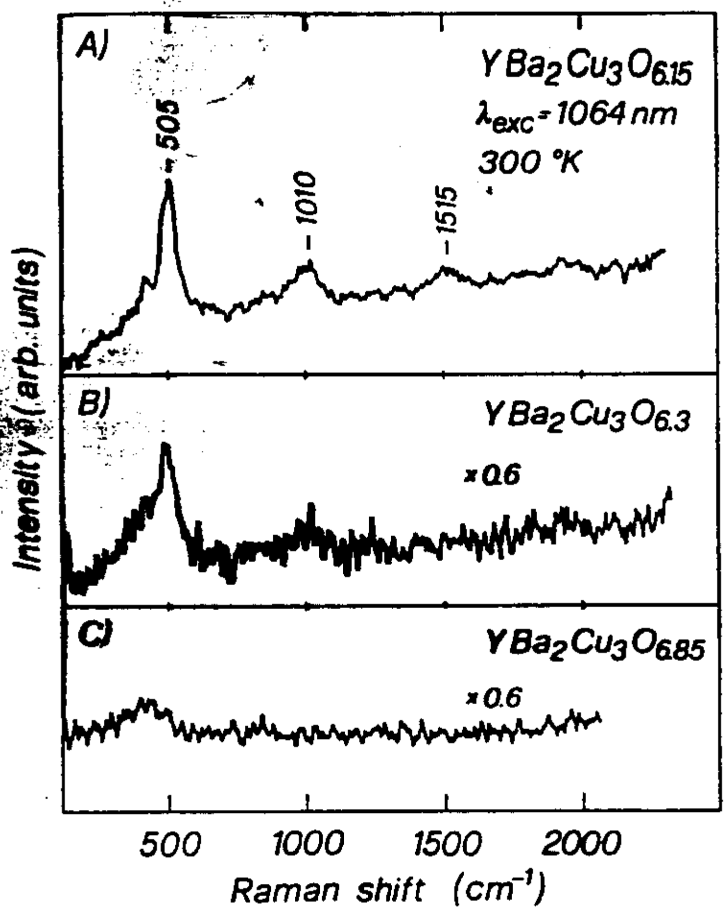


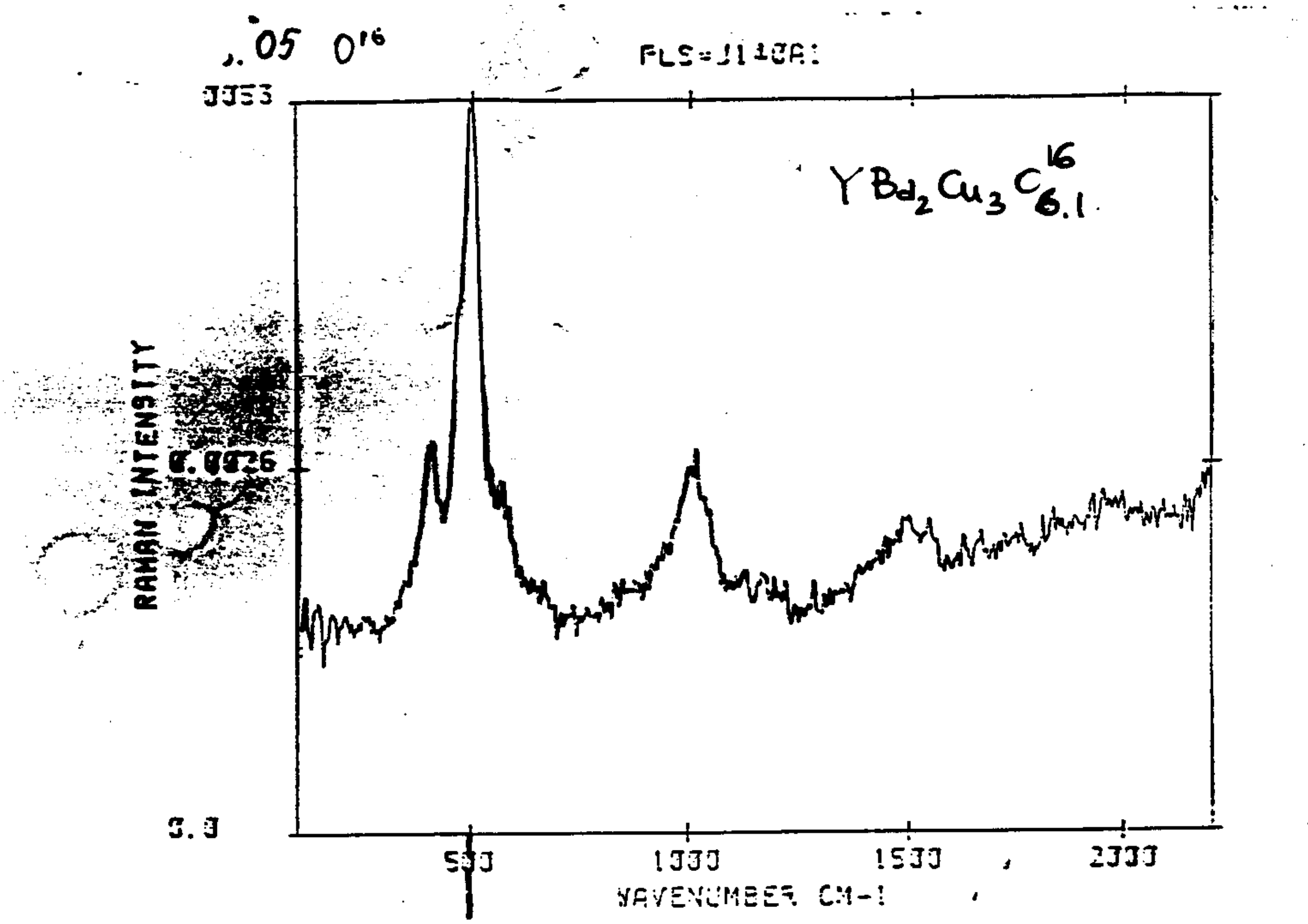
Fig.1-The Fourier-transform Raman spectra of the $YBa_2Cu_3O_{7-y}$ superconducting system excited with an infrared Nd-Yag laser source at 1064 nm (1.16eV) at three different oxygen stoichiometries: A) $O_{6.15}$, B) $O_{6.3}$ and C) $O_{6.85}$.

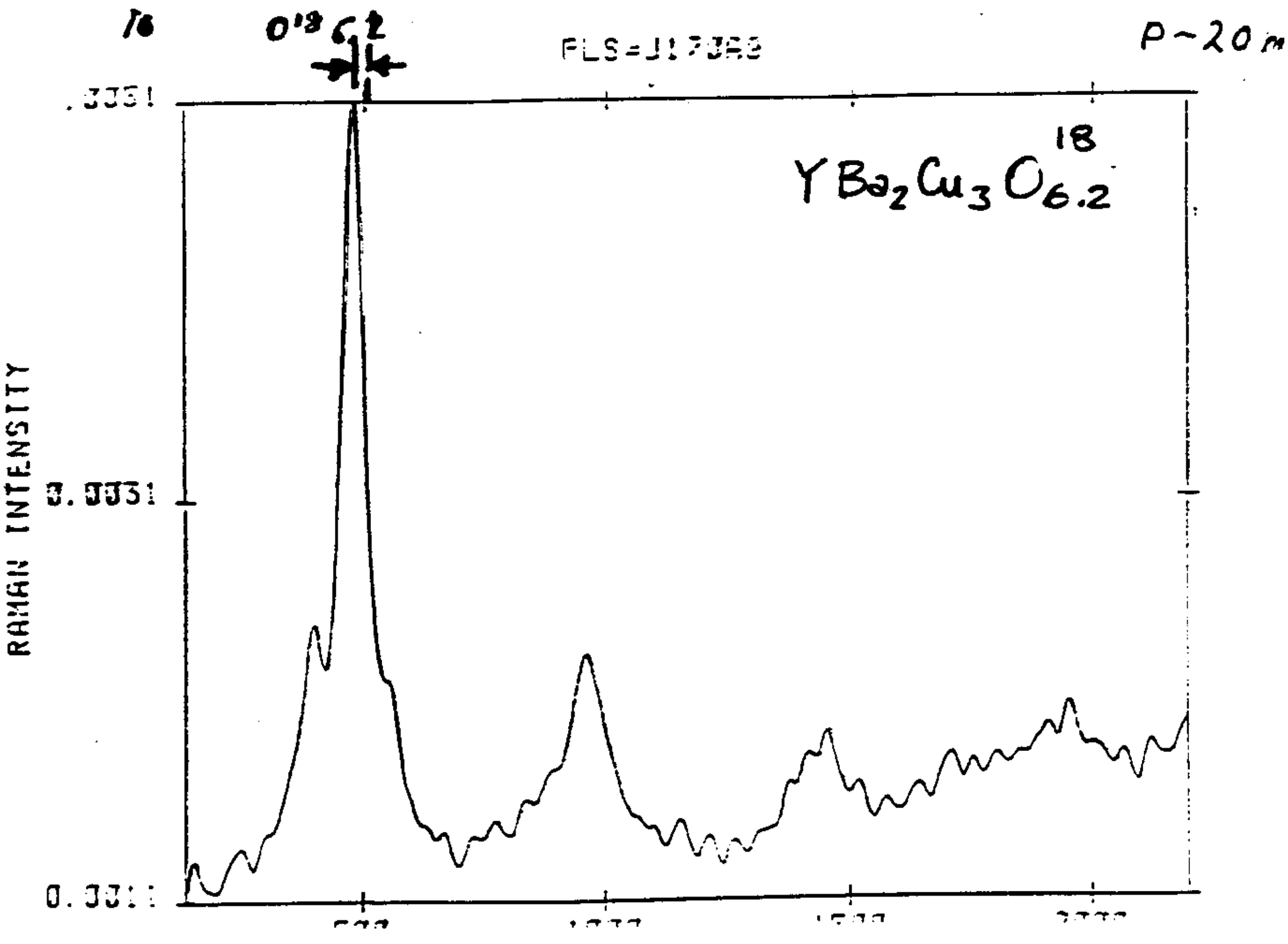
$$\alpha = \langle A \rangle + \langle B \rangle + NRT$$

where the first term is given by the expression:

$$A = \sum_i M_{i0}(R_0) \times M_{i0}(R_0) \cdot \sum_{n_i} \langle n_f | n_i \rangle \langle n_i | n_0 \rangle \frac{1}{\omega_{i,n_i} - \omega_{0,n_0} - \omega_L}$$

in which ω_L is the excitation frequency, ω_{i,n_i} is the vibrational frequency of the n_i th vibrational state in the i th electronic state, n_o, n_i and n_f are the vibrational wavefunctions of the ground, intermediate and final states respectively and $M_{i0}(R_0)$ is the dipole matrix element between states i and j calculated at the equi-


.05 O16
FLS=J140A1
YBa2Cu3O6.1 16
RAMAN INTENSITY
WAVENUMBER CM-1
500
1000
1500
2000


16
O18 62
FLS=J170A3
P~20m
YBa2Cu3O6.2 18
RAMAN INTENSITY

6) CONCLUSIONS

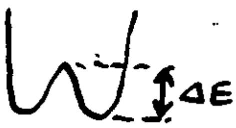
1) Warning! Raman scattering in HTSC is always a Resonance Raman scattering!

2) multiphonon scattering @ $\lambda_{exc} = 1.06\,\mu$. in $YBa_2Cu_3O_{6.15}$ of apex oxygen stretching(ω)

$\updownarrow$

resonance with localized states in the gap

3) <u>If</u> the apex O is in



$\tilde{\omega} \gg \Delta E \gg \omega$ in $YBa_2Cu_3O_{6.1}$

4) local states in the gap – absent in O_6
– develop with [O].