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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

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SMR/481 - 2

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

(26 November - 14 December 1990)

" Investigation of Electron-Phonon Coupling in High-T_C Oxides "

presented by:

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INVESTIGATION OF ELECTRON-PHONON COUPLING IN HIGH-Tc OXIDES

D.Mihailovič
ICTP Advanced workshop, Dec. 1990

Typical energy scales for the relevant interactions in high-Tc materials are given by:

$$E_F \sim 0.1 \text{ eV (from photoemission)}$$

$$\hbar\omega_{phonon} \sim 0.06 \text{ eV } (500 \text{ cm}^{-1})$$

$$J_{exchange} \sim 0.1 \text{ eV (in insulator precursor materials)}$$

The magnetic and electron-phonon interactions are of the same order of magnitude and therefore we cannot easily ignore either one (although the size of J in the doped case is not clear).

An equivalent stetement is:

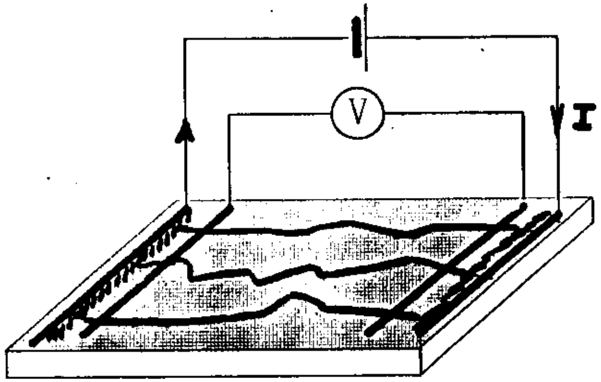
$$v_F \sim v_s$$

where v_s is the velocity of sound, and v_F is the Fermi velocity. A carrier will thus carry with it a polarization cloud: normally this is called a polaron.

The main subject of this presentation is an investigation of electron-phonon coupling. We show a number of electron-phonon coupling- induced lattice effects (anharmonicity, polar structure) and suggest that a polaron model of superconductivity which includes apex O anharmonicities should be investigated further. The presence of a polar structure casts some doubt on the interpretation of circular birefringence measurements being evidence of anyon or flux-phase superconductivity.

INTERACTION BETWEEN SUPERCONDUCTING CURRENT & THE LATTICE:

$YBa_2Cu_3O_7$ THIN FILM



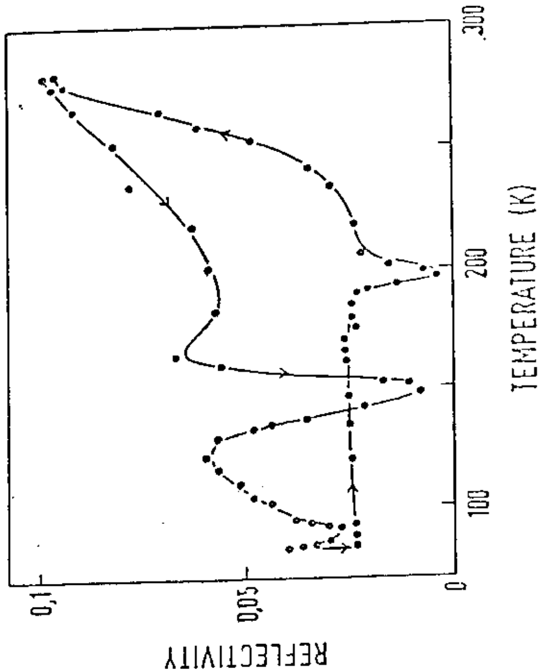
THE TWO ARE UNDENYABLY COUPLED !!

I=45 mA at 4.2K (for 166h)

Prokhorov et al, JETP Lett. 51, 149 (1990)

Changes in morphology of the superconducting film under the influence of a <u>supercurrent</u> strongly suggests the lattice is coupled to it!

Evidence for structural instability was available very early. Reflectivity from single crystals or ceramics shows that O reordering is taking place on the surface (i.e. ~0.06 μm) even at very low T. Note hysteresis.



Mihailovic et al (1927)

Figure 1 White light TE polarization <u>reflectivity</u> as a function of temperature. Data were taken in a single temperature cycle.

An anomaly in the lattice constants is seen above T_c in X-ray diffraction

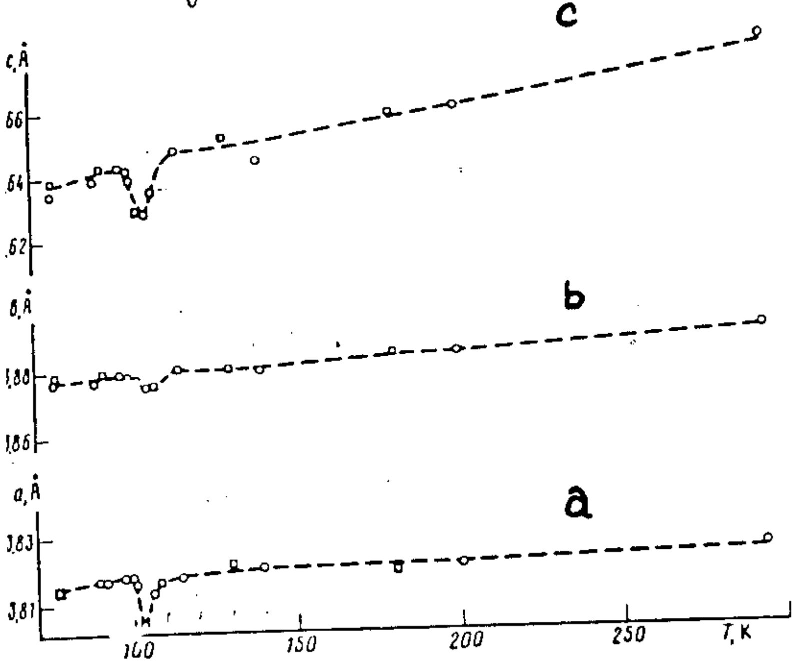
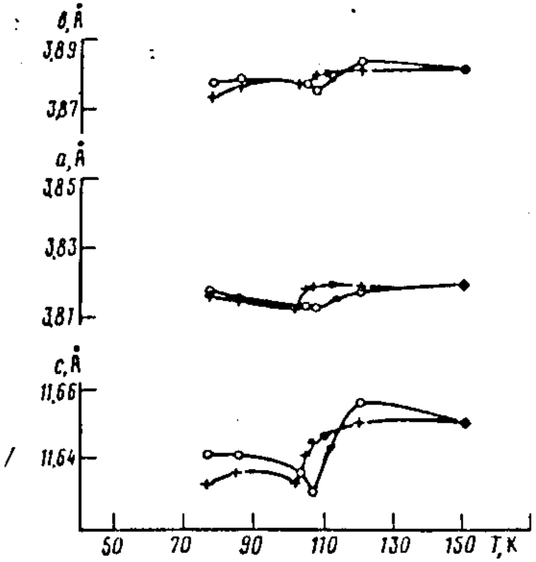


FIG. 1. Temperature dependences of the orthorhombic lattice constants a, b, and c of the ceramic $YBa_2Cu_3O_7$.

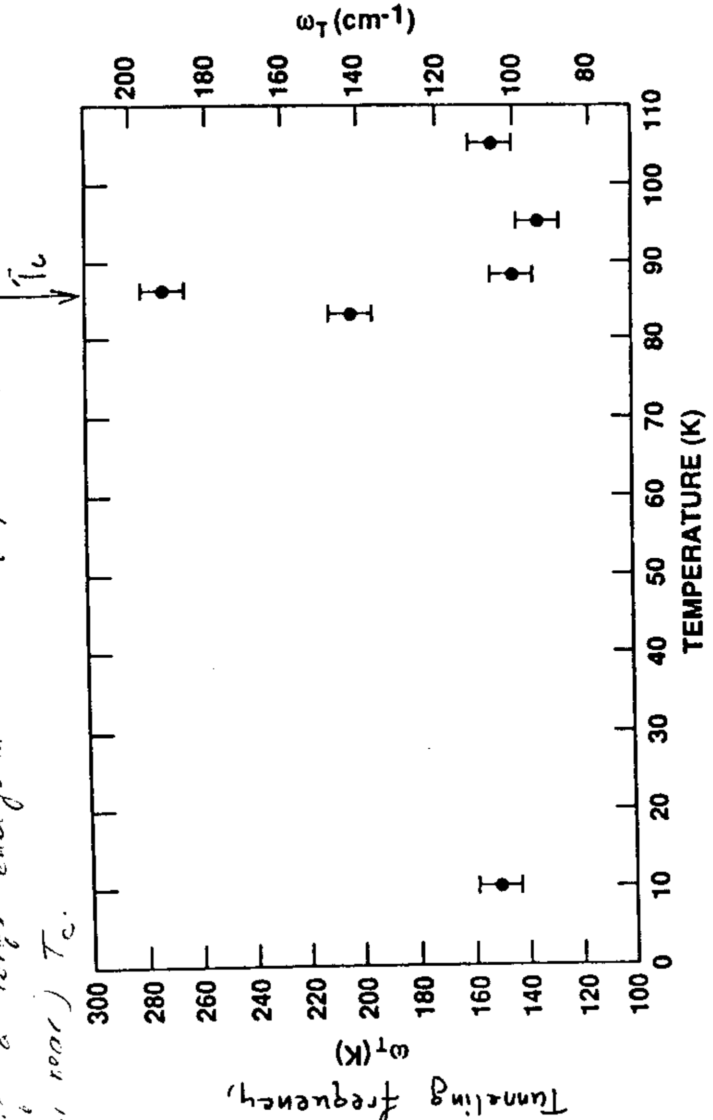


Golovashkin *et al.*

JETP Lett., Vol. 46, No. 8, 25 October 1987

The anomaly shows hysteretic behavior, suggesting the involvement of defects.

Analysis of T-dep. of XANES data shows an anomaly suggesting a large change in tunneling frequency of apex O atom at (or near) T_c.



This interpretation presupposes a double-well potential for the apex O.

J. Mustre de Leon et al
PRL (1990)

The Pyroelectric Effect in $YBa_2Cu_3O_7$, (H[illegible], SSC, [illegible])

1. Primary pyroelectricity at constant volume

$$\left(\frac{\partial D}{\partial T}\right)_\sigma = \left(\frac{\partial D}{\partial T}\right)_\varepsilon$$

2. Secondary pyroelecricity arises due to strains arising from ΔT.

$$\left(\frac{\partial D}{\partial T}\right)_\sigma = \left(\frac{\partial D}{\partial \varepsilon}\right)_T \left(\frac{\partial \varepsilon}{\partial T}\right)_\sigma$$

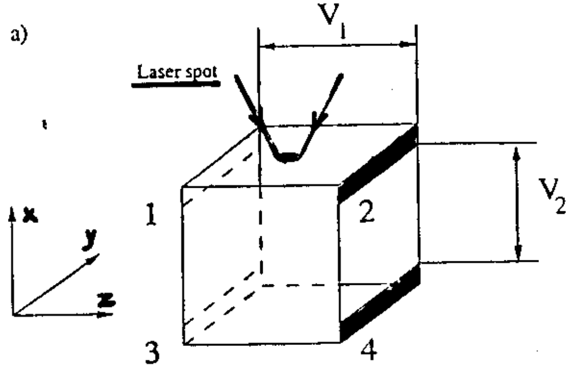
where
σ = STRESS
ε = STRAIN

3. Tertiary pyroelectricity arises due to strains arising from non-uniform ΔT. (an artifact)

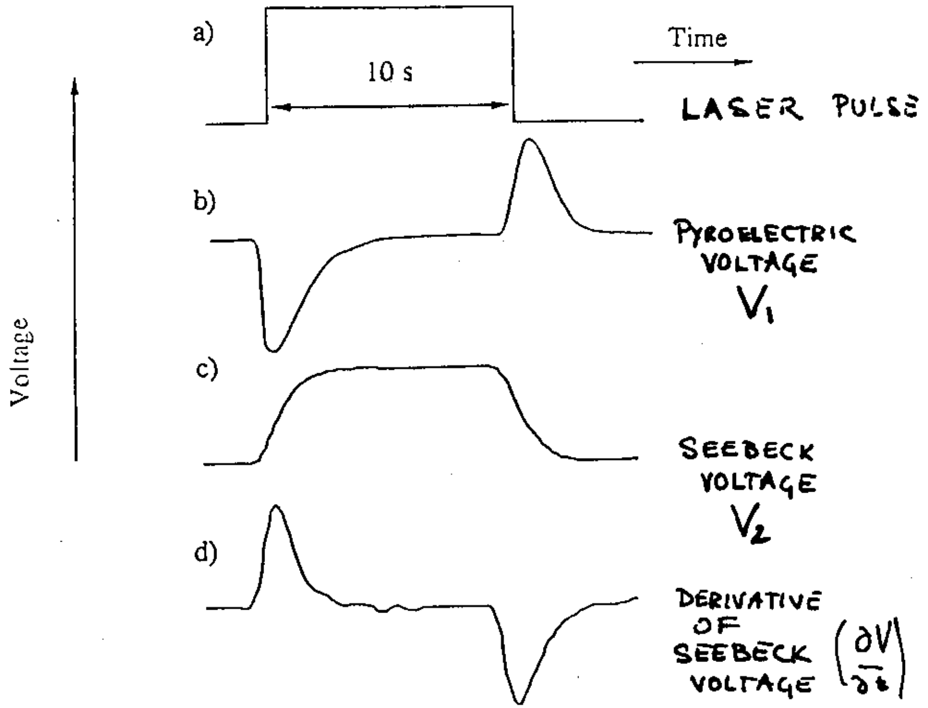
The appearance of pyroelectricity implies the existance of MACROSCOPIC POLAR regions (and NO CENTRE OF INVERSION).

Observation of PE is further evidence for a role of the e-p interaction in cuprates.

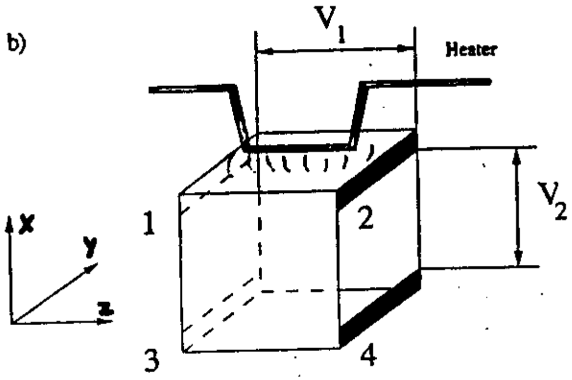
Geometry for PE experiment

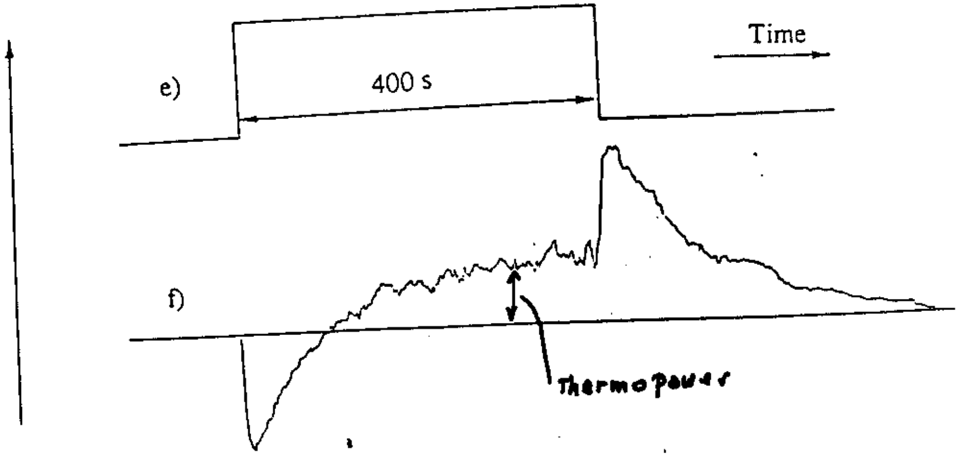


$YBa_2Cu_3O_{6.9}$ SINGLE CRYSTAL, ~ 1mm^3, SOURCE: COLLIN



Possible photovoltaic effects are eliminated by replacing the heating source :





D. Mihailović. Sol. Stat Comm. 75, 319 (1990)

Given that the measured $p_i = (0,0,p)$

From Nye, only possible groups with

$(0,0,p)$

are :

<u>tetragonal</u>: 4 (C_4), 4mm (C_{4v})

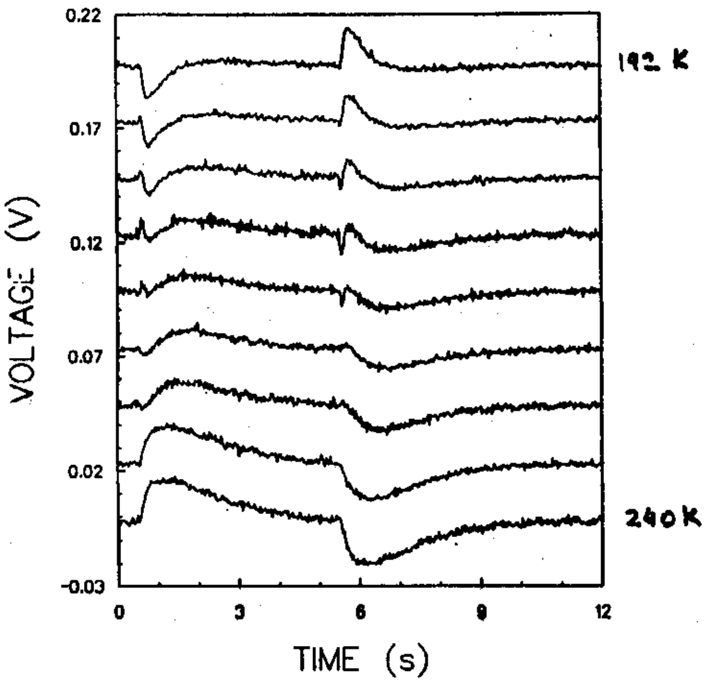
for $YBa_2Cu_3O_7$: <u>orthorhombic; mm2 (C_{2v})</u>

(+<u>monoclinic</u> m (C_s) & 1 (C_1) group)

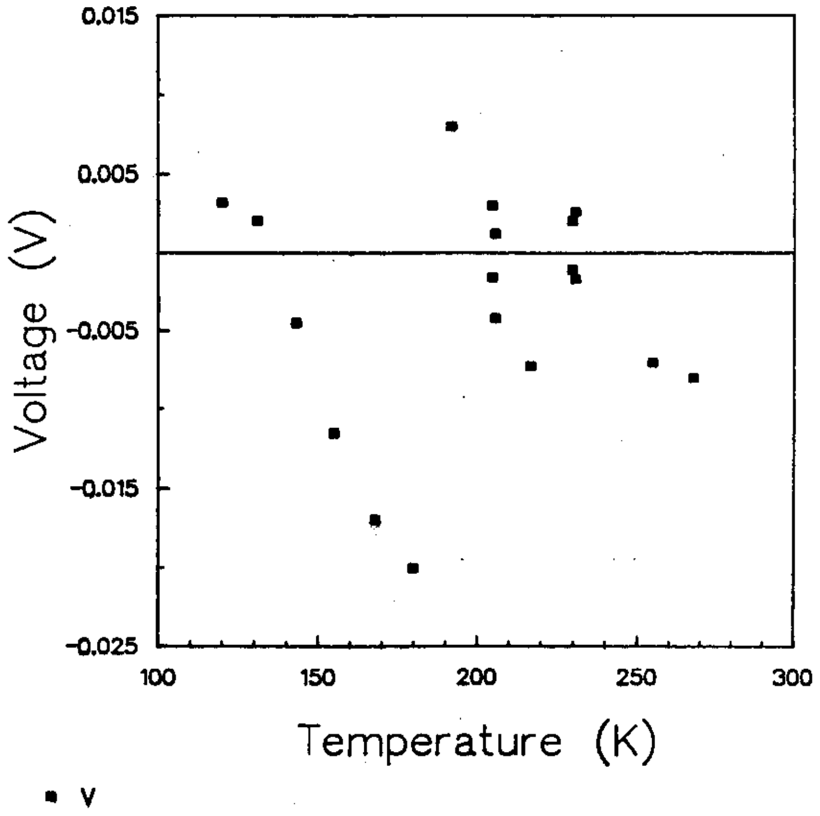
Incidentally,

The unambiguous appearance of polar structure costs doubt on recent experiments of optical circular birefringence upon reflection from the material surface as evidence for anyon or flux-phase superconductivity. Circular birefringes naturally arises in a polar structure!

POLARIZATION REVERSAL WITH TEMPERATURE IN $YBa_2Cu_3O_{6.9}$ SINGLE CRYSTAL



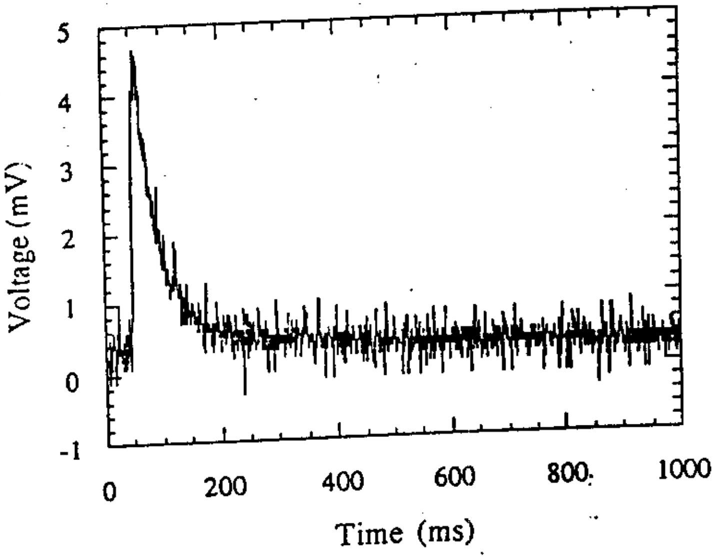
VARIATION OF PYROELECTRIC VOLTAGE WITH TEMPERATURE

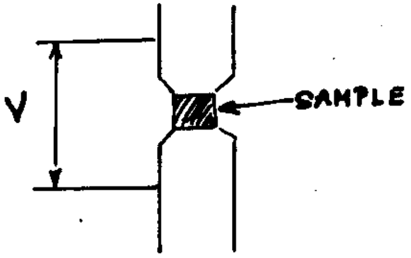


PE Voltage shows polarization reversal which is a sign of shifting domains with temperature

Similar evidence is seen in ultrasonic measurements

PIEZOELECTRIC VOLTAGE
IN
$YBa_2Cu_3O_7$





Confirms polar structural regions in material.

ORTS 38

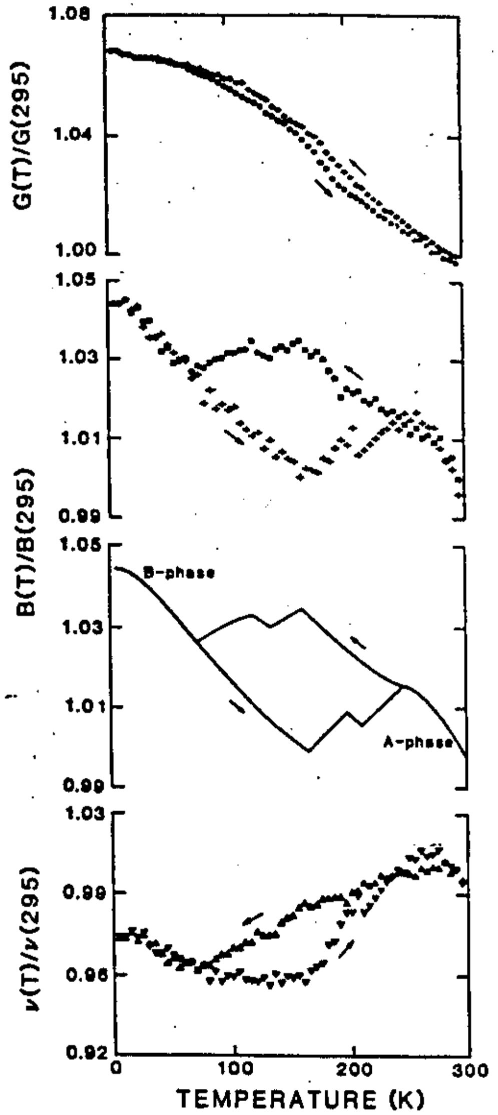


FIG. 2. For $Y_1Ba_2Cu_3O_{7-x}$, temperature variation of G=shear modulus, B=bulk modulus, and ν=Poisson ratio.

Ledbetter & Kim (1988)

Raman Scattering in High-Tc materials

Summary of information that can be gained:

1) Phonons:

   - anomalies related to possible electron - phonon mechanisms can be seen at T_c in the phonon spectra.
   - show the effect of doping on (electronic) structure.

2) Raman Scattering from Impurities and Defects

3) Resonant Raman Scattering

   - resonance condition gives information about symmetry and structure (energy) of electronic states (bands)

4) Electronic Raman Scattering

   - gives low energy part of the excitation spectrum !

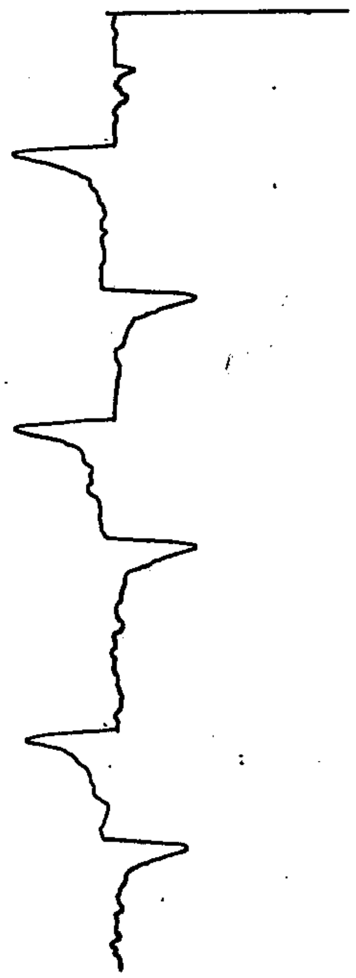
5) Magnetic Raman Scattering

   - two magnon spectra (together with neutron scattering) are the best evidence for the existence of spin-waves in high-T_c cuprates

$La_2CuO_{4+\delta}$

PYROELECTRIC VOLTAGE

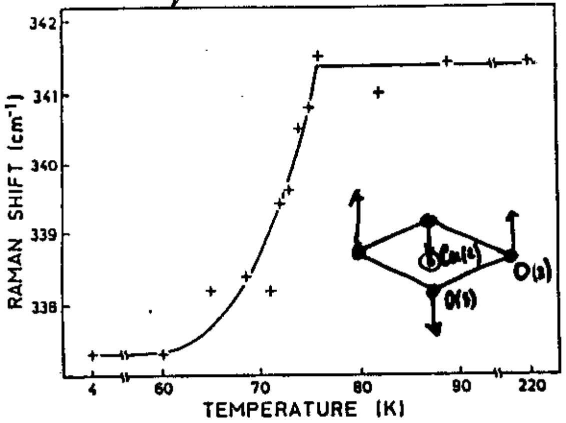
$\Delta V \parallel c$ axis



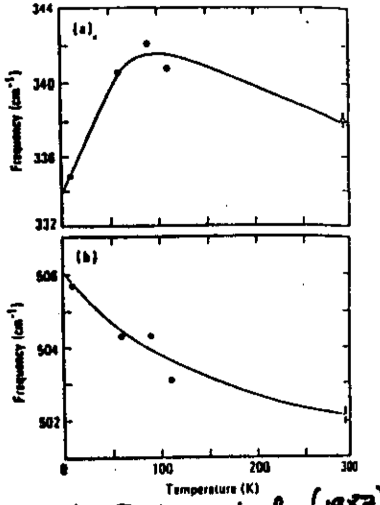
SAMPLE: La_2CuO_4, SOURCE: P.CANFIELD, LANL #PC062

The effect is also observed in $La_2CuO_{4+\delta}$, single crystals, and is not limited to $YBa_2Cu_3O_7$.

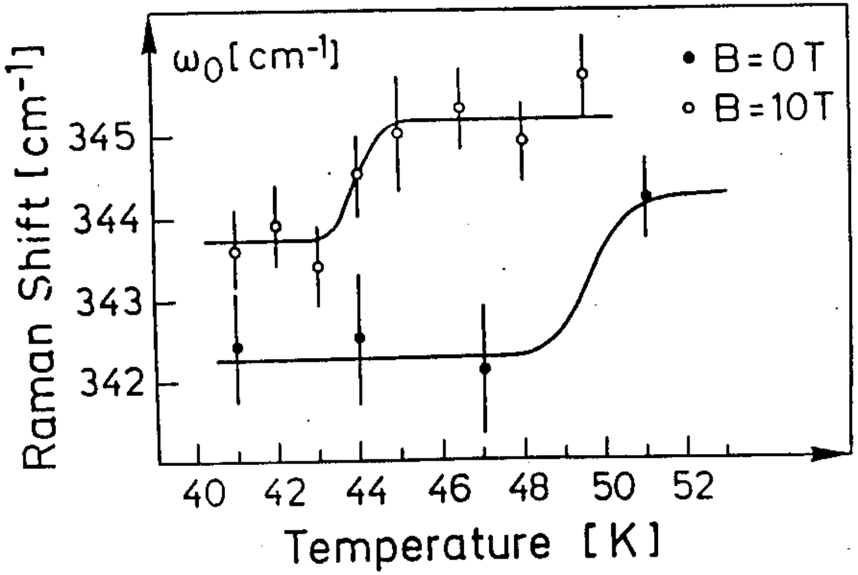
Phonon anomalies at T_c are well known from Raman spectra:



Thomsen et al (1988)



MacFarlane et al (1987)

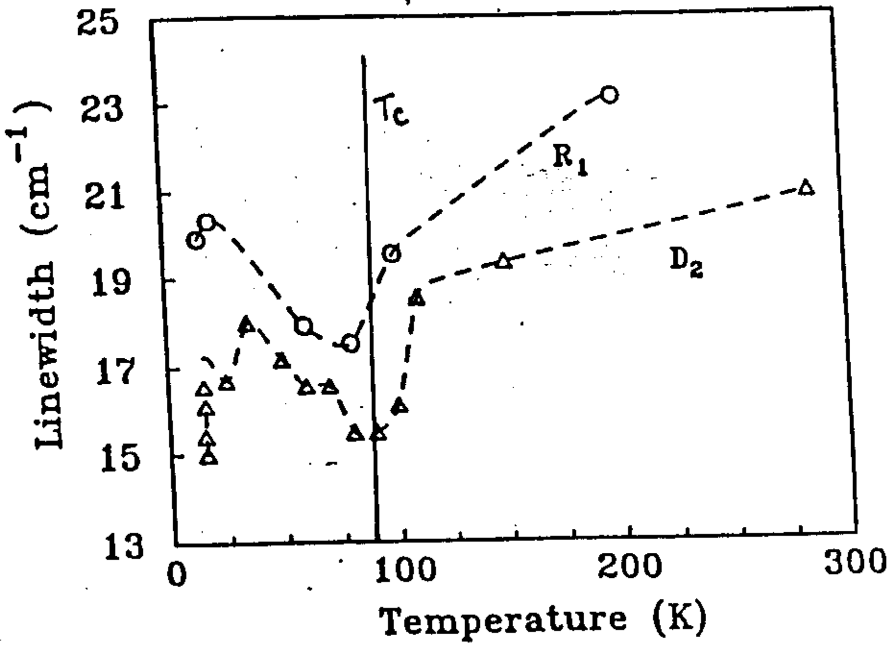


Ruf et al (1988)

Phonon anomaly of 340 cm^{-1} mode in Raman

but an anomaly of the apex O, whose frequency lies well above $2\Delta = 5kT_c$ has been observed only very recently:

ANOMALY OF Apex O(4) VIBRATION LINEWIDTH AT ? NEAR ? T_c



Altendorf et al, SSC 76, 591 (1990)

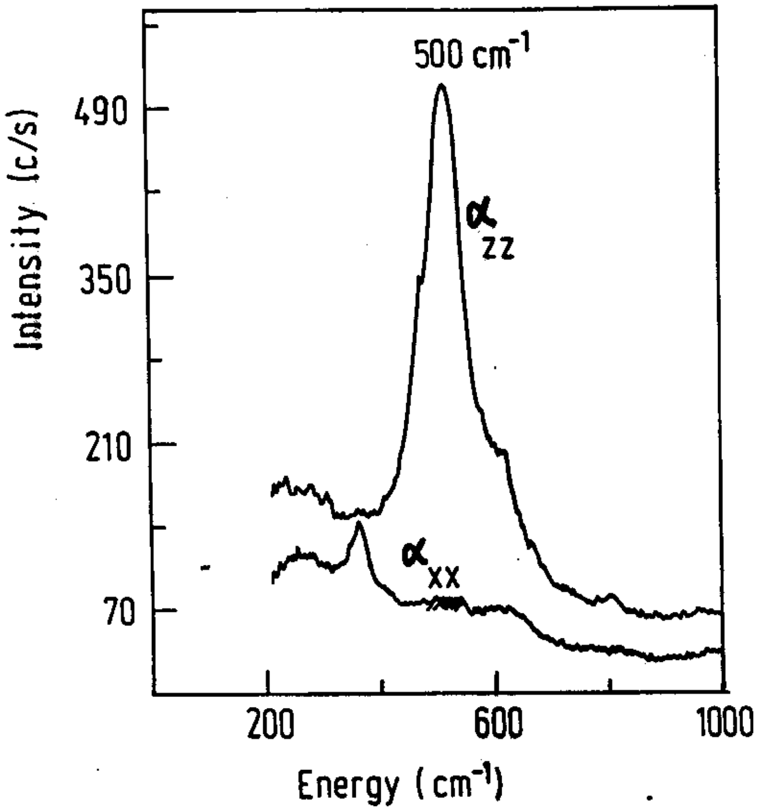
It is precisely this mode (or one involving O(4)) which may lead to the polar symmetry in $YBa_2Cu_3O_7$.

The reason for looking at Raman spectra:

Raman intensity $\propto \chi^{nl}$

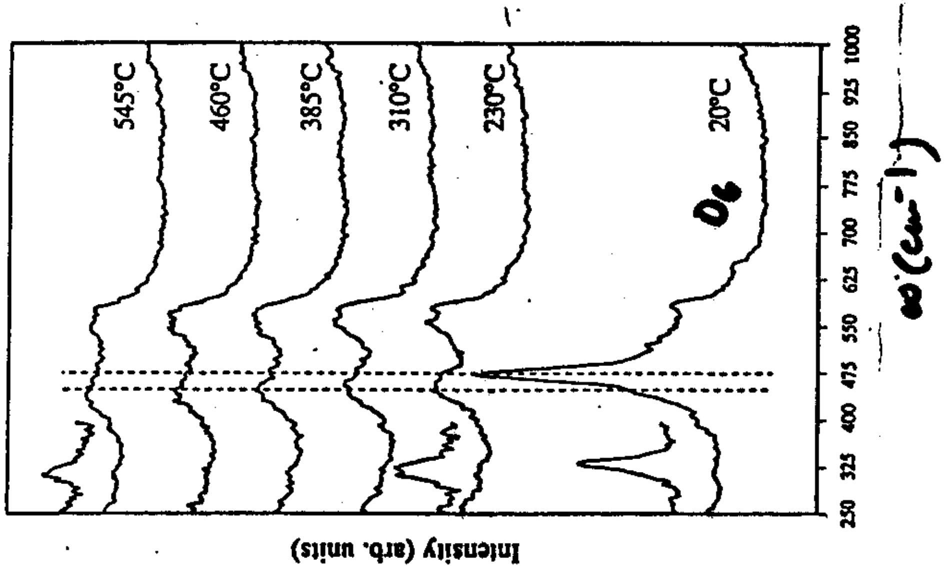
For apex O vibration,

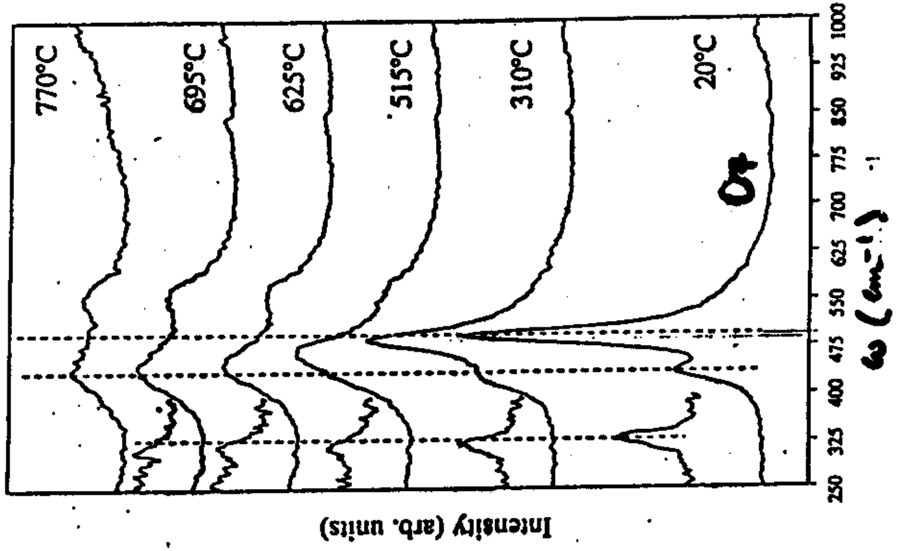
$$\chi^{nl} \propto \begin{bmatrix} \alpha_{xx} & & \\ & \alpha_{yy} & \\ & & \alpha_{zz} \end{bmatrix}$$



Mihailović & Brničević (1987)

χ_{nl} is also a quantity that can be related superconductivity mechanisms.

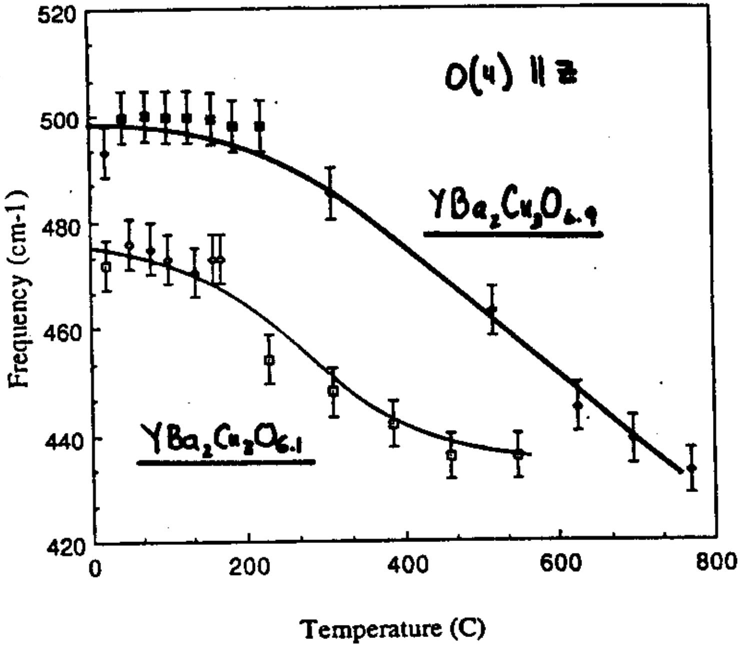


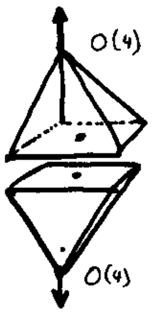


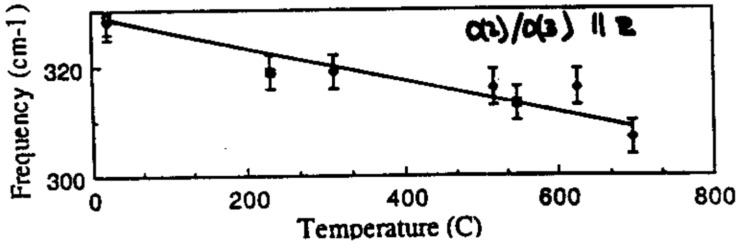
MacCarthy et al (1988)

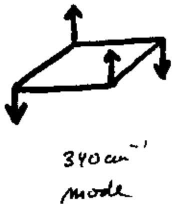
High-temperature phonon softening. Note the apex O(4)

High temperature data on apex O mode shows signs of some anharmonicity or hopping of O!

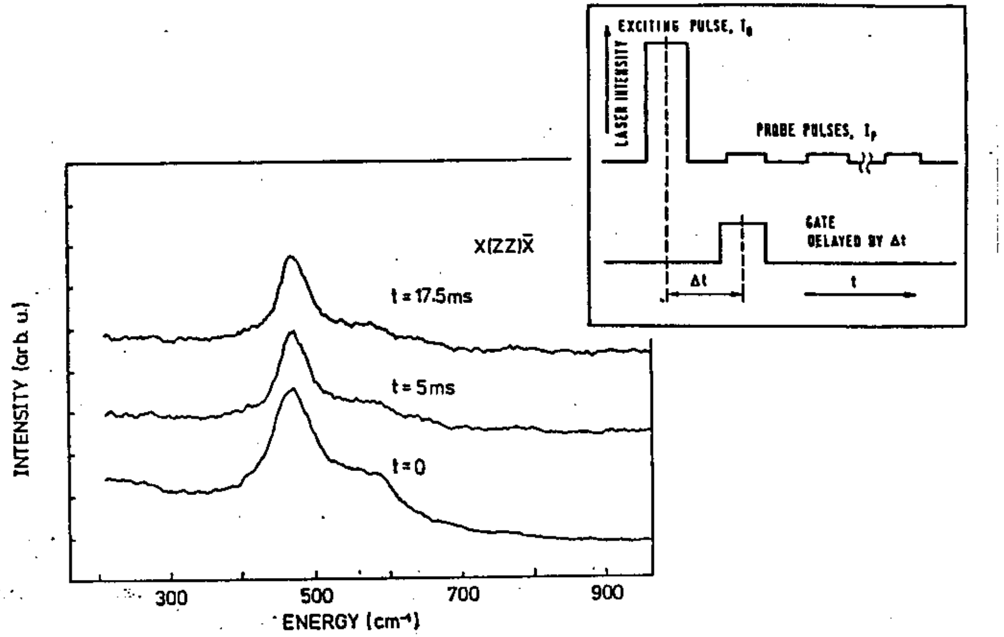


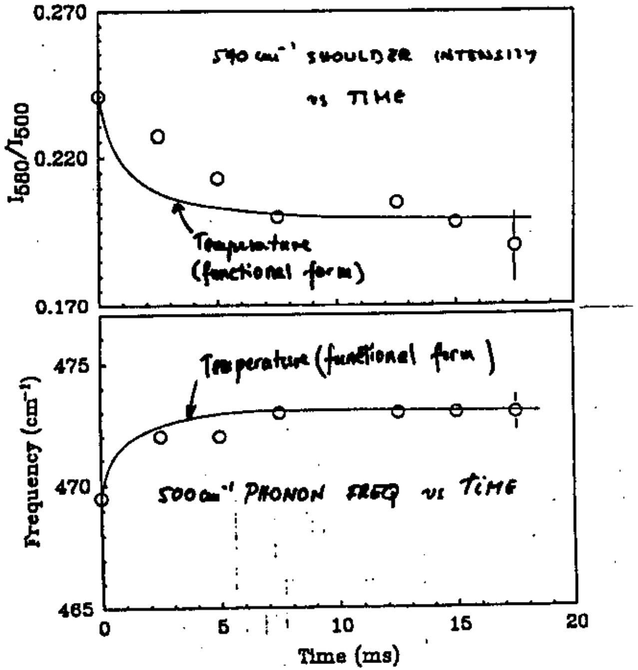






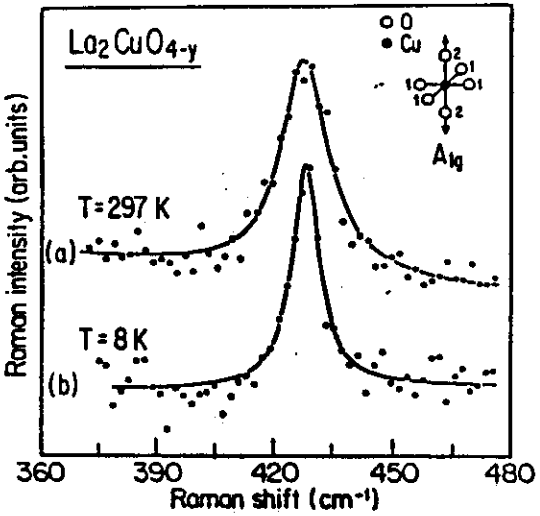
D. Mihailovic & Foster, SSC (1990)
FIGURE 2

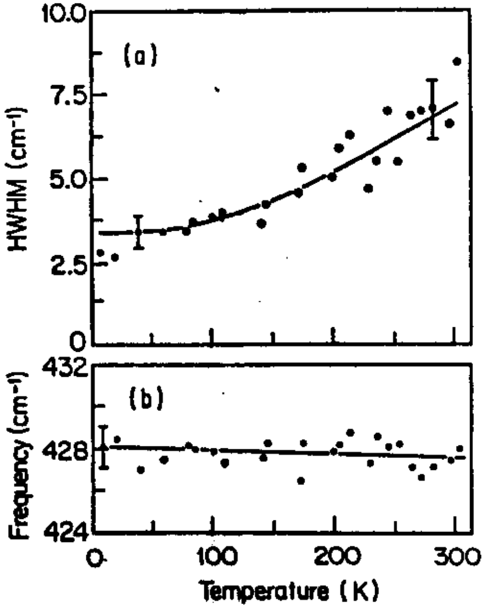




I. Poberaj et al (1990) Phys. Rev. B

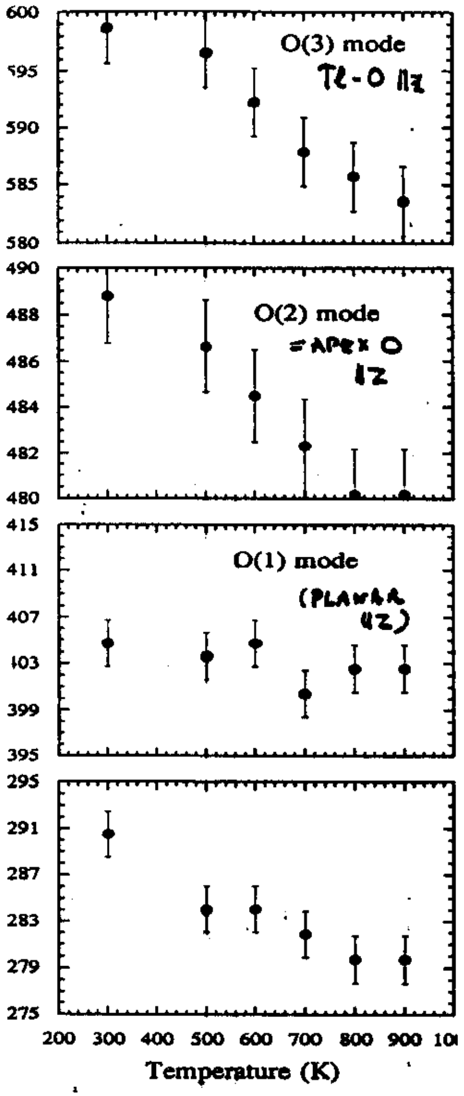
it is reversible and

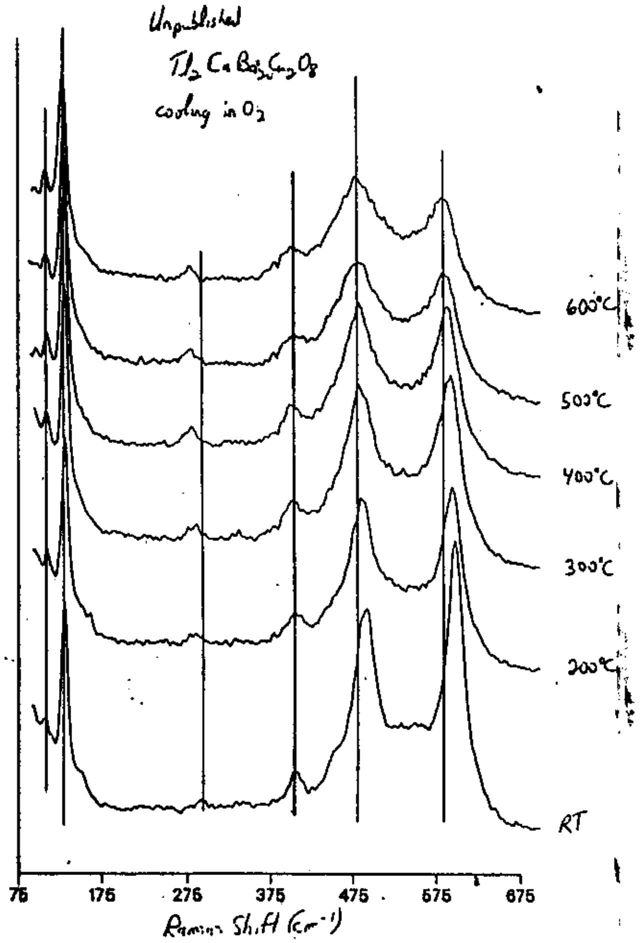




O'Kane et al (1989)

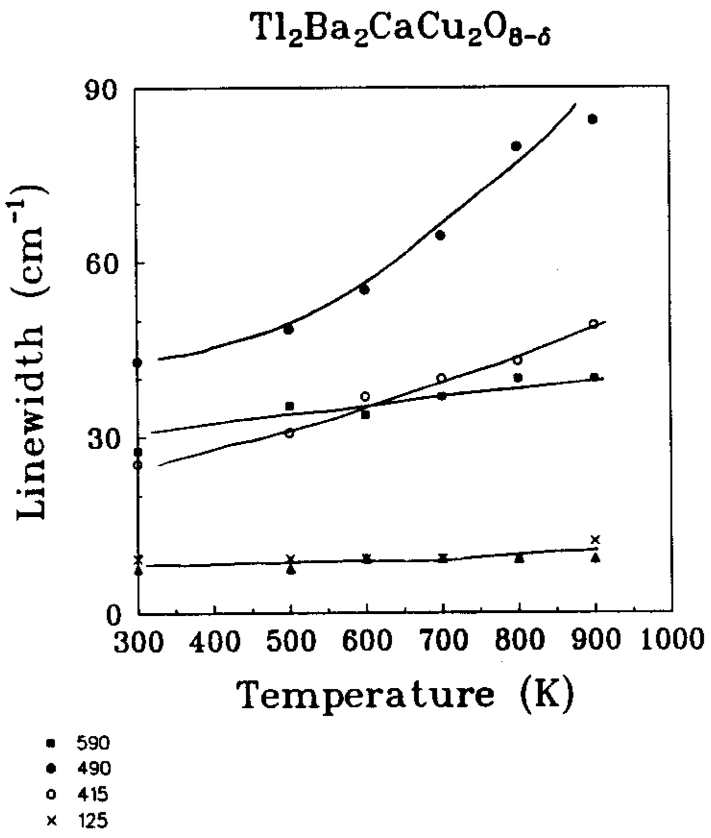
Anharmonic apex O vibration is also seen in La_2CuO_{4-y}



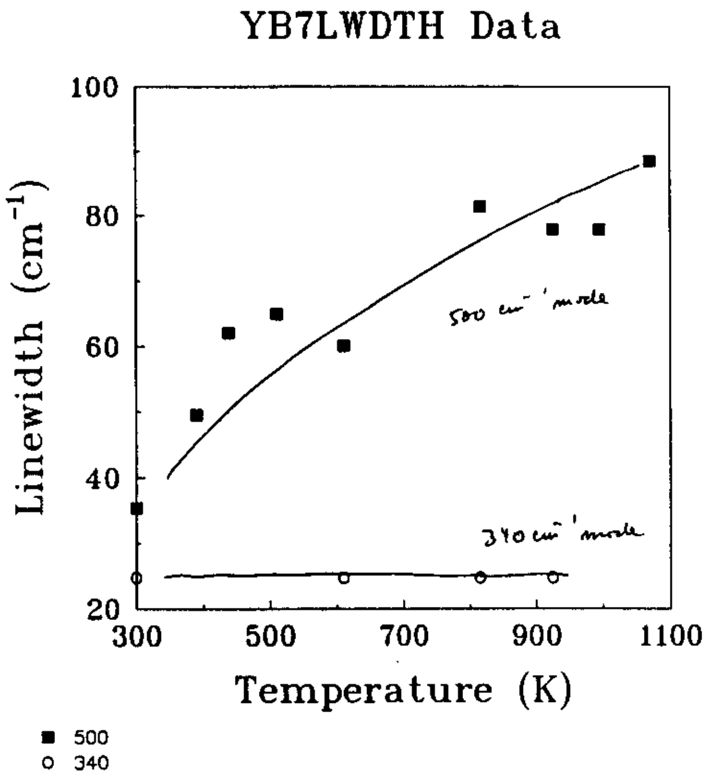


K. McCarty (unpublished)

As well as in $Tl_2CaBa_2Cu_2O_{8-\delta}$,



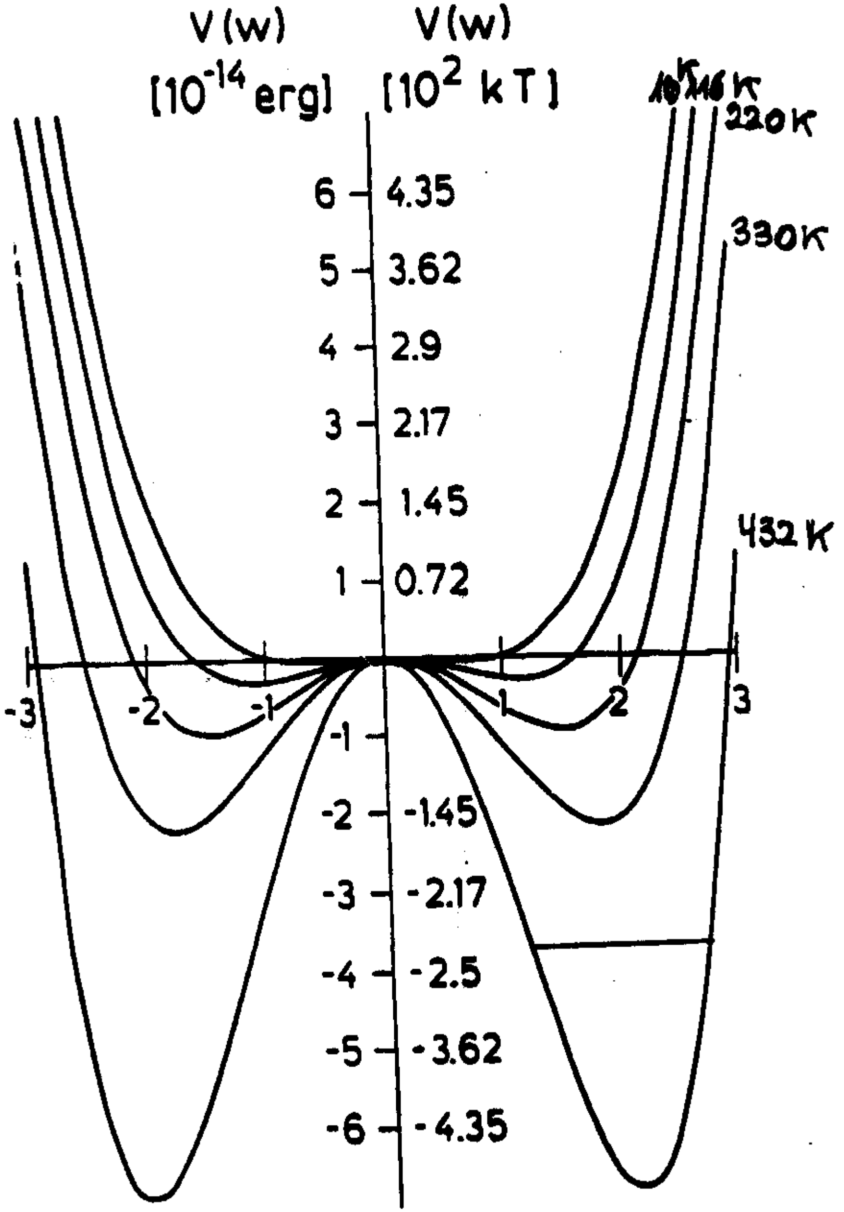
Linewidth of O modes is strongly T-dependent, but ONLY for apex Oxygen and Tl-O plane vibrations.



Width of apex O vibration vs T.

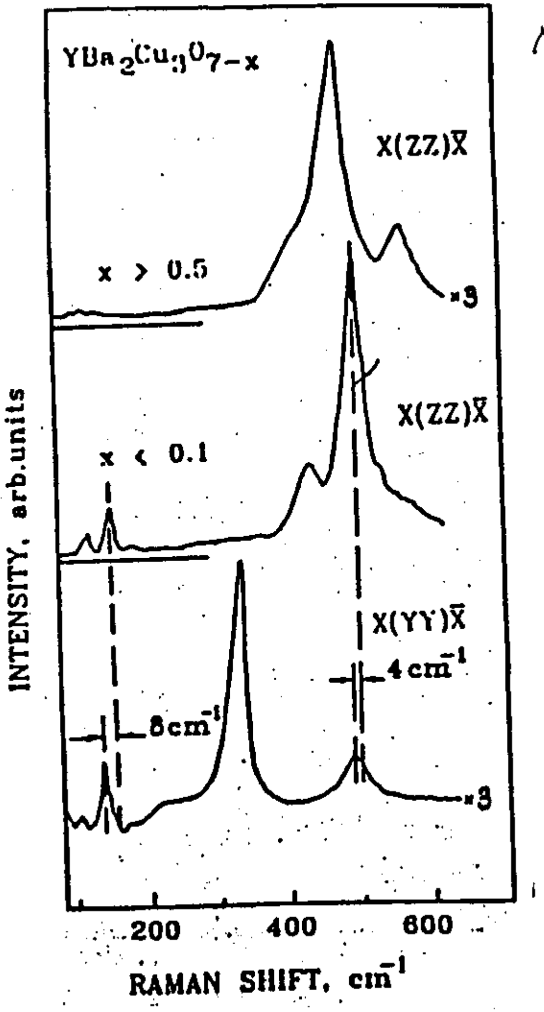
Note the 340 cm^{-1} mode shows no broadening.

T_s =



A.B-Holder, (unpublished)

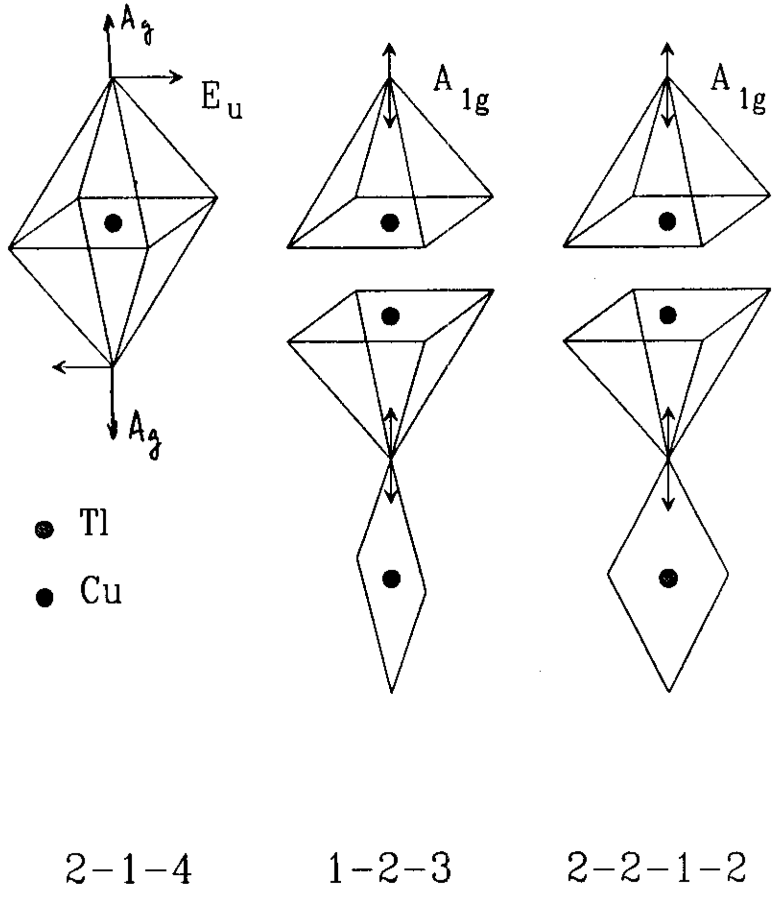
A model potential for the apex O vibration following the XANES & RAMAN



Miaochko et al
Stanford proceedings
(1989)
Physica C

An important observation is that the phonon frequencies for apex O and Cu vibrations are different in xx and in zz!

Some Anharmonic modes



In summary: some anharmonic modes in high-T_c superconductors, related to CT fluctuations.

Raman Scattering from Magnons

Well characterized in K_2NiF_4, a prototype 2D antiferromagnet.

and $J \sim 100\ cm^{-1}$,

Both lineshape and symmetry of observed Raman scattering spectum is in good quantitative agreement with theory.

In cuprates, J is much larger (0.1 eV or 800 cm^{-1}).

But,

- lineshape not in agreement with simple theory
- observed lineshape may be explained including next-nearest-neighbour interactions J' (J.P.Singh, 1990)
- symmetry of observed scattering is not in agreement with theoretical predicitions for a 2D AF.
- significant spin-lattice interaction is seen in temperature dependence of the 2-magnon peak (Knoll et al 1990)

UPON DOPING:

- scattering intensity drops dramatically, (and dissappears ?)
- peak in spectrum shifts to lower energy,

But what is the spectrum that remains in the superconducting phase?

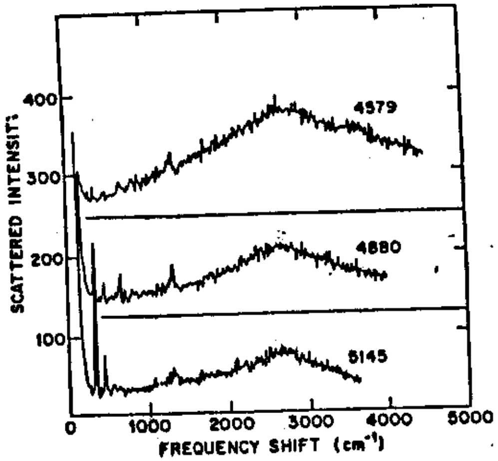


Figure 1

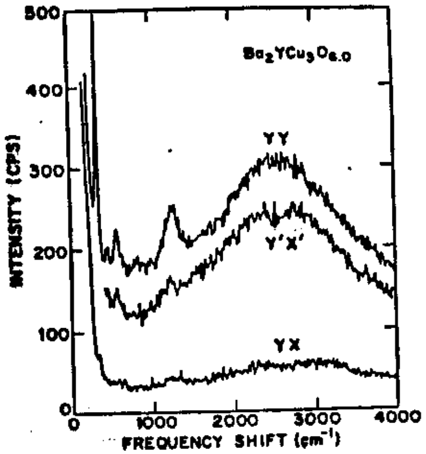


Figure 2a

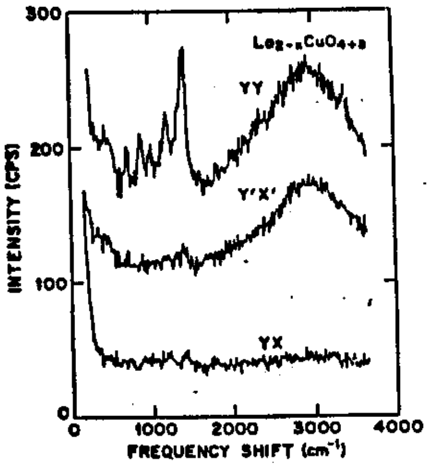


Figure 2b

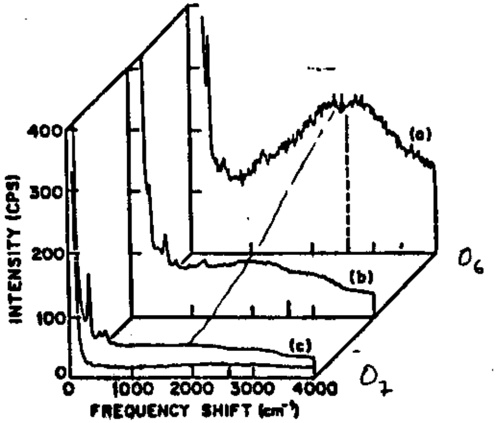
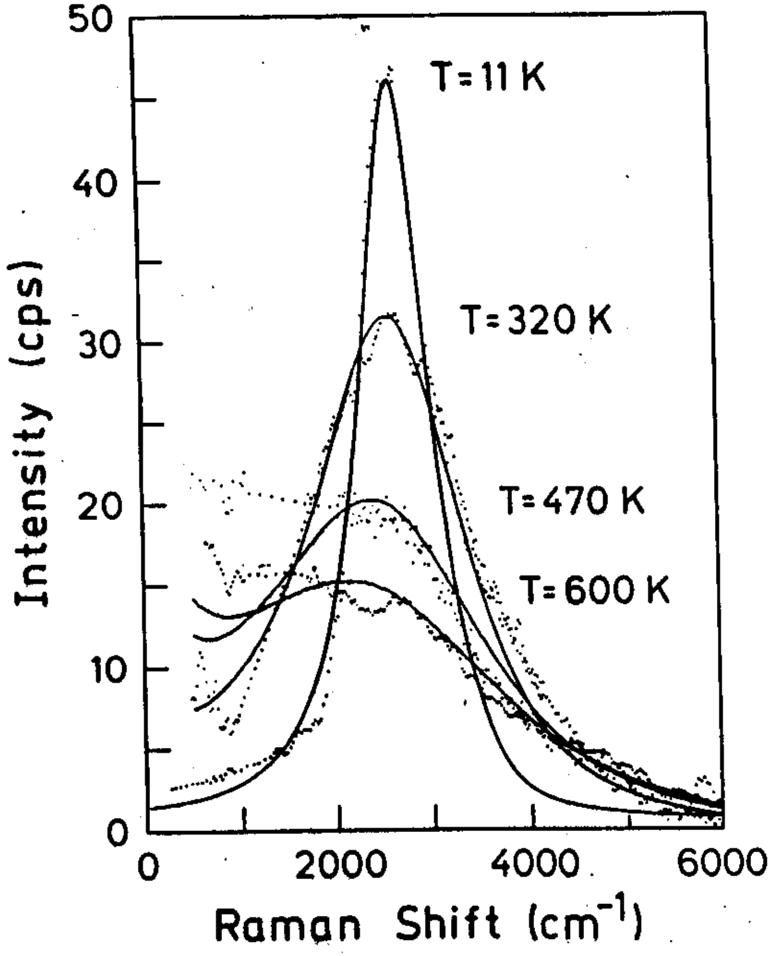


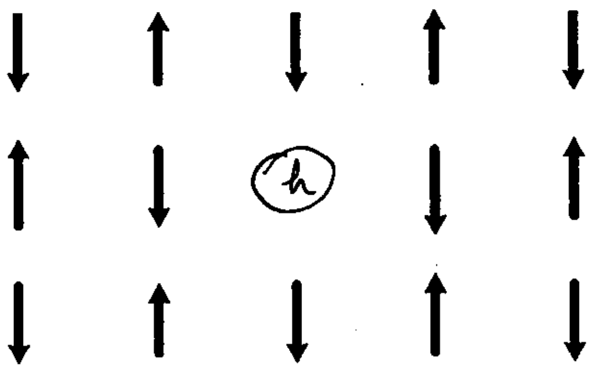
Figure 3

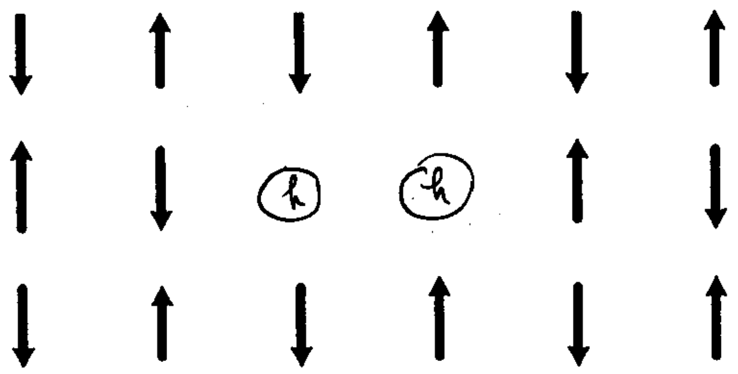
K.B. Lyons et al ;



Linewidth of 2-magnon peak is strongly temperature dependent, suggesting a very sharp spin-lattice interaction.

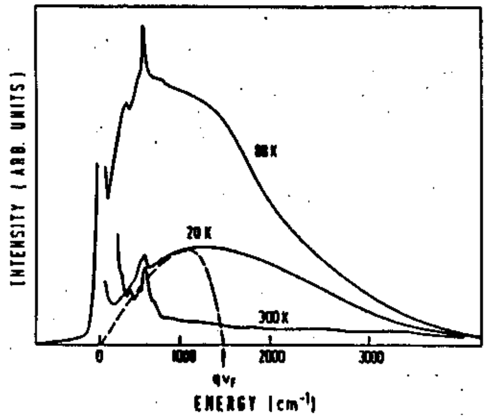
P. Knoll et al. 1990

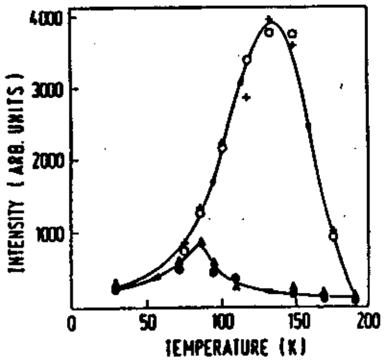




Electronic Raman Scattering

Originally observed in ceramic $YBa_2Cu_3O_7$.(1987)

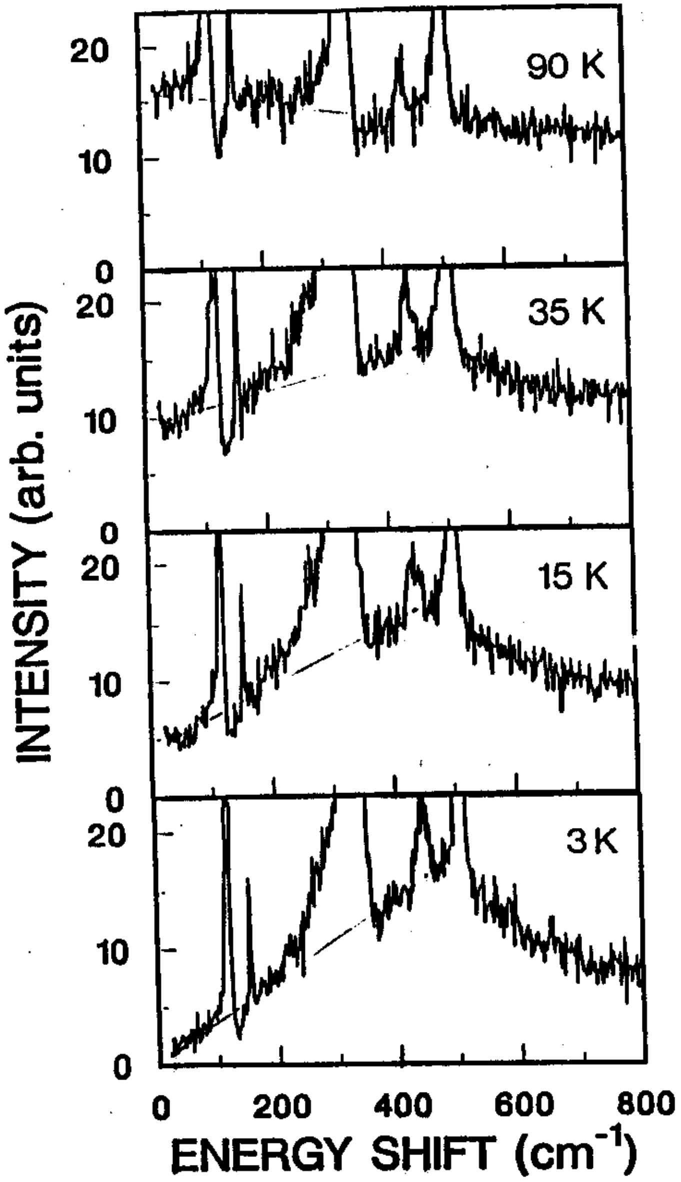




Behaved rather unexpectedly:

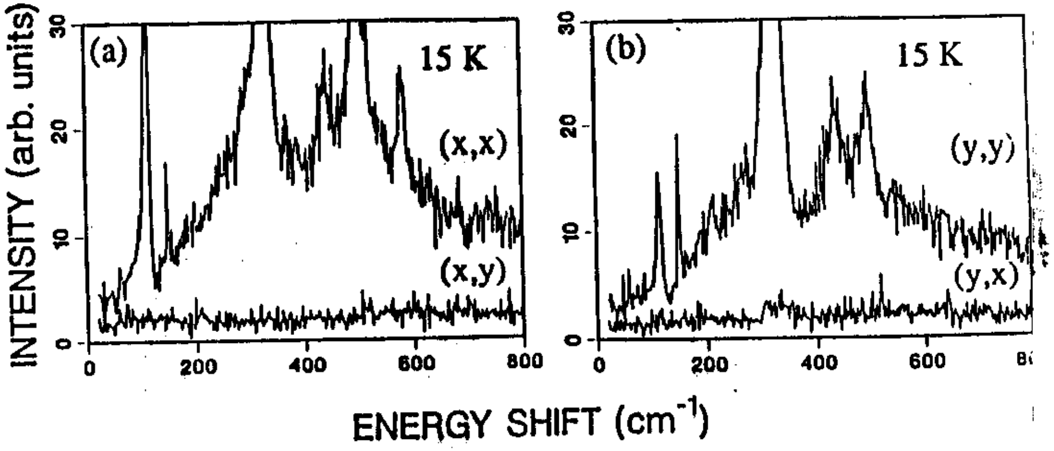
- redistribution of states was seen above Tc

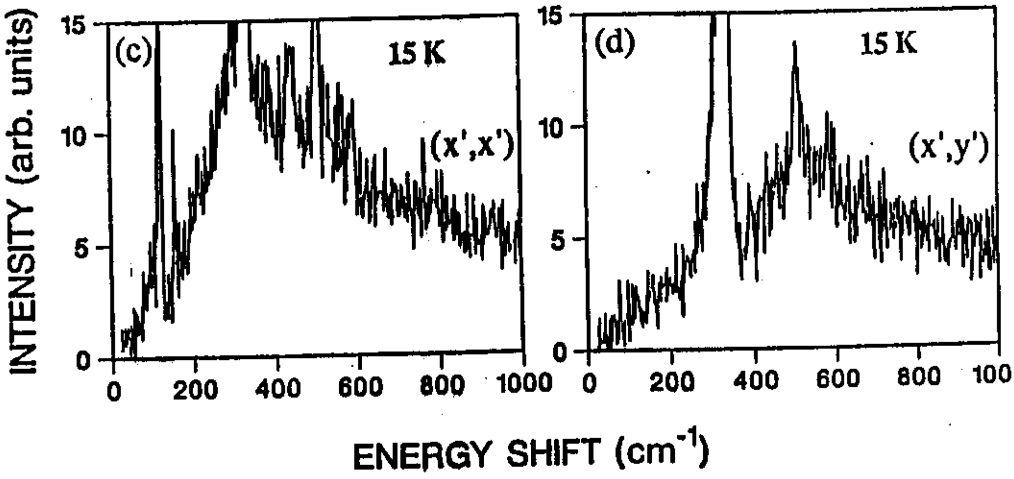
Further work on $YBa_2Cu_3O_7$ single crystals with Tc > 90K showed a clear redistribution of states below 90K (e.g. Cooper et al, 1988)



More recent results on $YBa_2Cu_3O_{7-\delta}$ with Tc = 60K show different components of the scattering (Slakey et al, 1990) behaving differently:

Part of the spectrum (Ag symmetry) shows a redistribution of states above Tc (similar to the original suggestions on ceramic material) (Slakey et al, 1990)





Ag component of the scattering intensity at 500 cm^{-1} (at ~ 8 k_BT_c) shows a clear maximum just above Tc, with similar behaviour at 150 cm^{-1} (within the gap)

T_c = 60 K !

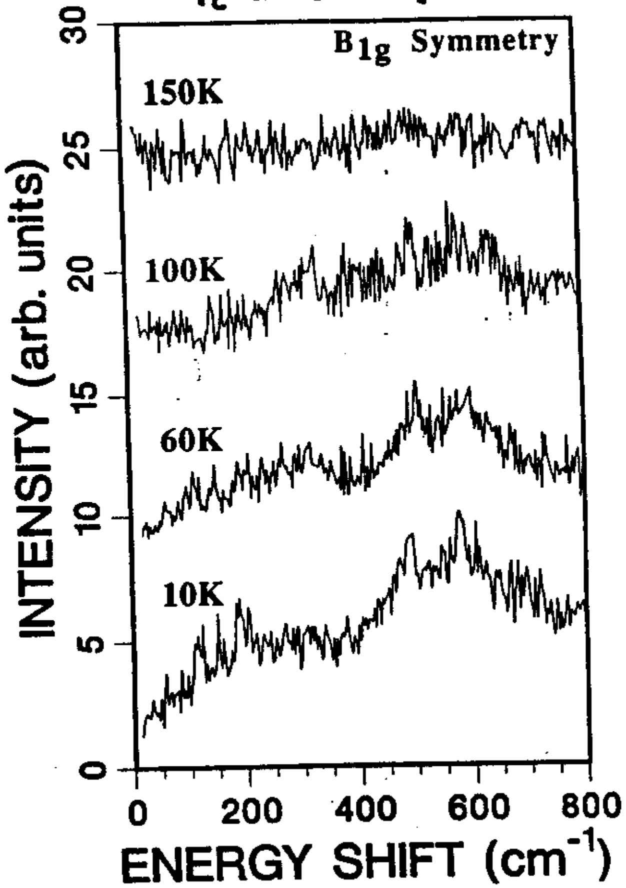
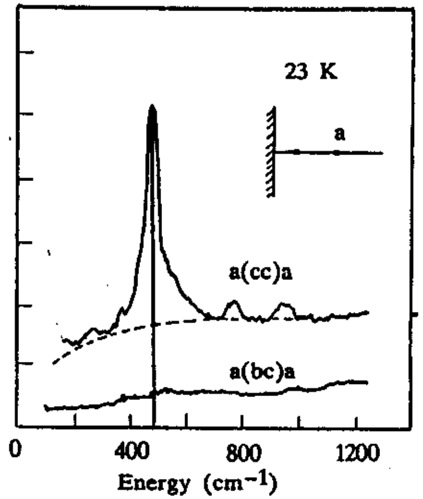
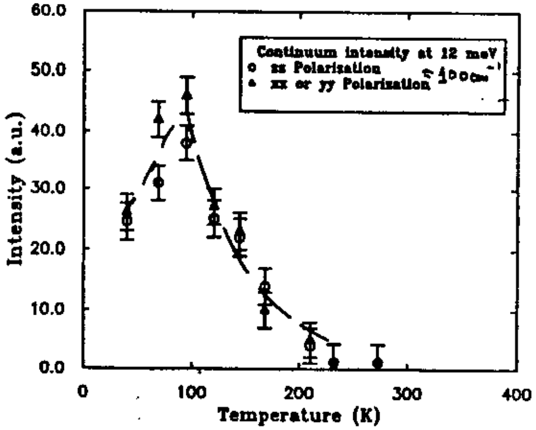


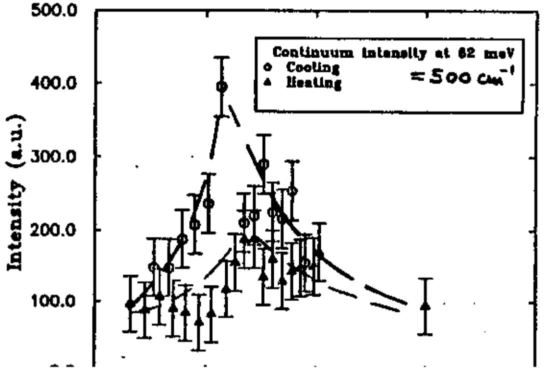
Fig 5

Energy "gap" shows up __above__ T_c – Results are from Slakey et al (1990), for YBaCuO sample with T_c ~ 60 K. The redistribution



ZZ SCATTERING !

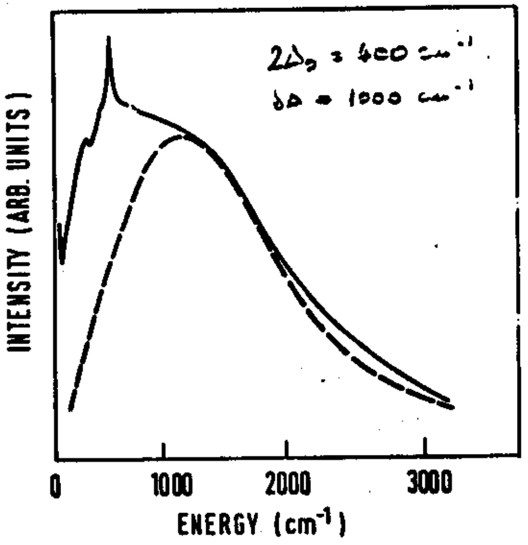




CT fluctuations!

normalized continuum intensity at 12 and 62 meV in $YBa_2Cu_3O_{6.9}$ shows a peak near T_c (is hysteretic)

Electronic RS: Conclusions



FIT: BCS WITH GAP ANISOTROPY

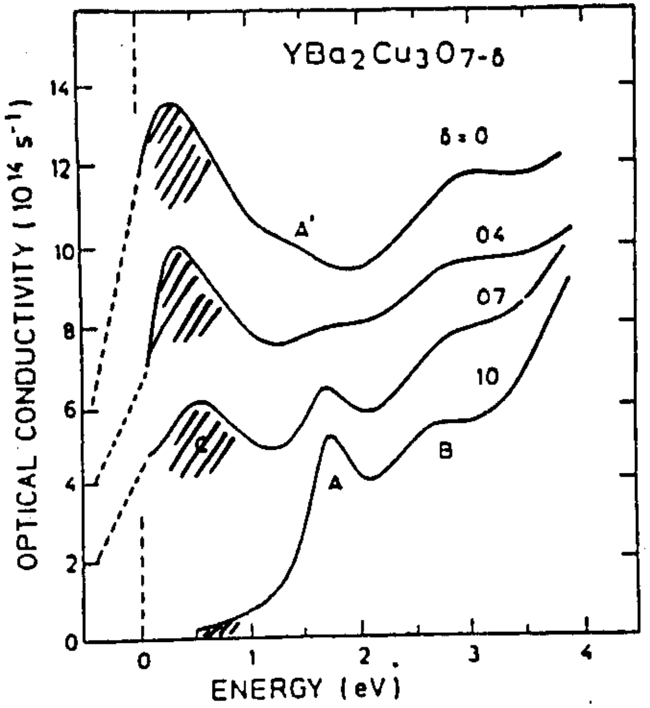
a) The shape of the spectrum can be fitted using a

- BCS model,
- marginal Fermi Liquid (Ruvalds et al, 1989)
- Mott-Hubbard model (Shriram et al 1990).

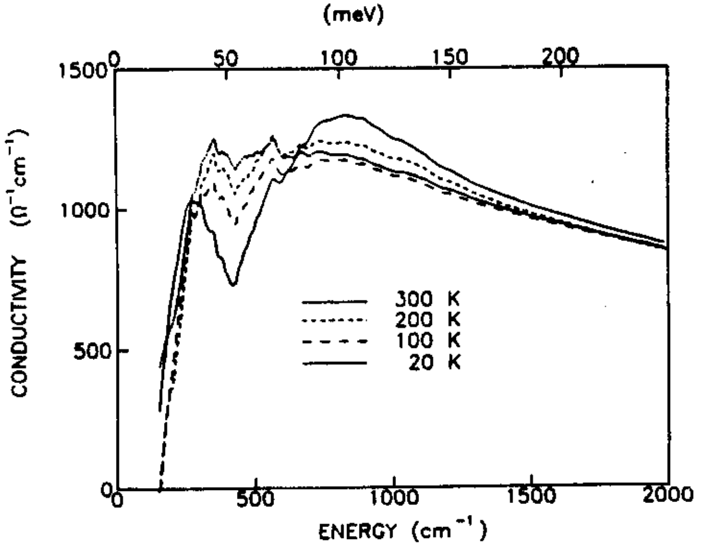
b) The symmetry of the scattering can possibly be used for a more unambiguous determination of the origin of the scattering.

c) Hysteresis in Ag spectra suggests also the presence of hot luminescence or scattering associated with O defects

d) The effects of changing resonance condition with T (due to band edge shift) have not yet been properly taken into account.



GARRIGA et al (1988)



KAMARÁS et al (1990)

Fig 1

MID-IR peak upon doping :

Polaron model for mid-IR peak:

$$H = H_e + H_L + H_{e\text{-}L}$$

where

$$H_e = \Sigma_{i,j,\sigma}\ t_{ij}\ c^+_{i\sigma}c_{j\sigma} + U\,\Sigma_i\ n_{i\uparrow}\,n_{i\downarrow}$$

$$H_L = \Sigma_k\ \omega_k\ a_{\,k}a_k$$

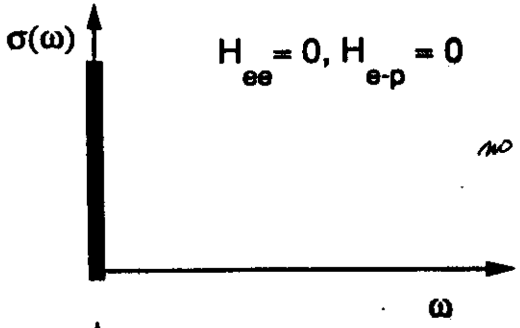
$$H_{e\text{-}L} = \Sigma_{k,i,\sigma}\ \omega_k\ \alpha_k\ e^{-ikR_i}\,(a_k + a_{\,-k})\ n_{i\sigma}$$

↑ Holstein Linear chain model

via Kubo's formula, we can calculate the frequency dependent conductivity,

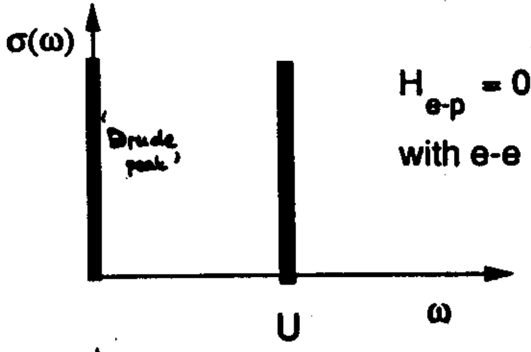
$$\sigma(\omega) = \sqrt{2\pi}\,\frac{J^2e^2N}{\hbar^3\omega_0^{\,2}}\ e^{-\eta}\left\{\frac{\omega_0}{\omega}\right\}^{\left(\frac{\omega}{\omega_0}+\frac{3}{2}\right)}\ e^{\left(\frac{\omega}{\omega_0}\right)}\,\eta^{\left(\frac{\omega_0}{\omega}\right)}$$

e.g. Reik et al, (1963)

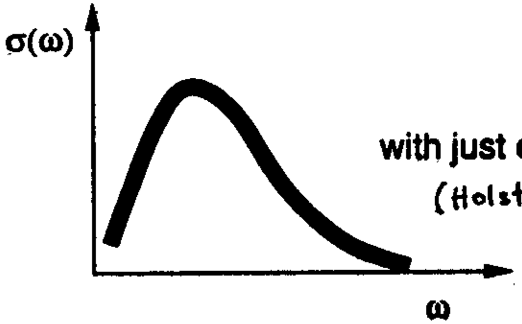


$H_{ee} = 0, H_{e-p} = 0$

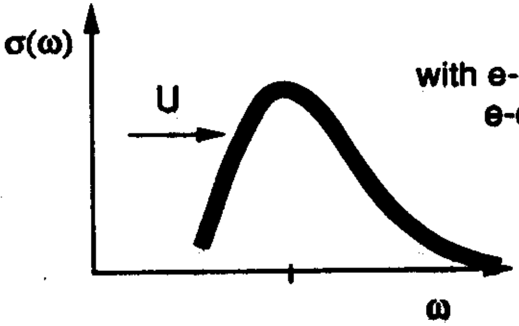
no ee or e-p interactions



$H_{e-p} = 0$
with e-e interaction



with just e-p interaction
(Holstein model)



with e-p and
e-e interaction

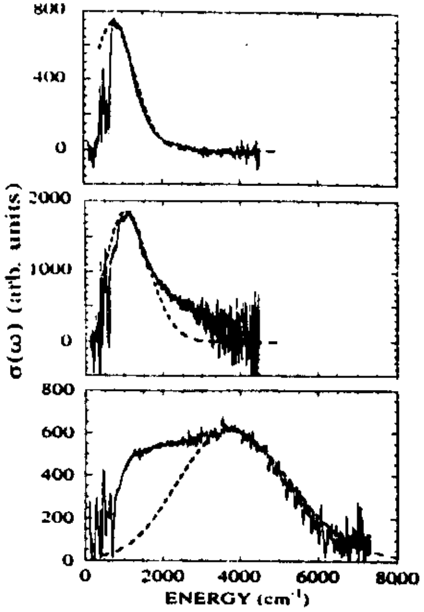


FIG. 1. The photoinduced infrared conductivity $\sigma_p(\omega)$ (solid lines) in the insulator precursors for $Tl_2Ba_2CaCu_2O_8$ (top), $YBa_2Cu_3O_7$ (middle), and $La_{2-x}Sr_xCuO_4$ (bottom) compared with fits to polaron-transport theory $\sigma_{PT}(\omega)$ as calculated using Eq. (1) (dashed lines).

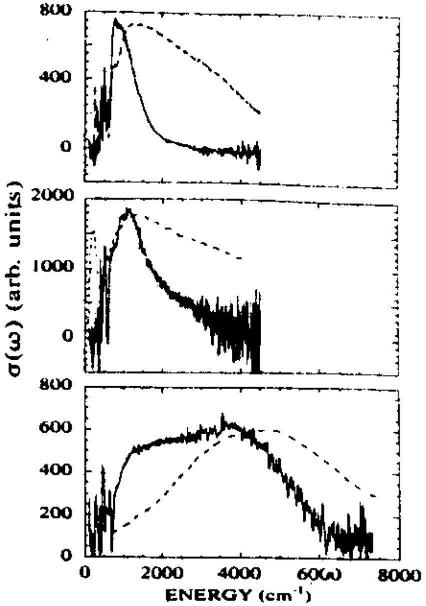


FIG. 2. The infrared conductivity $\sigma(\omega)$ (dashed lines) for $Tl_2Ba_2CaCu_2O_8$ (top), $YBa_2Cu_3O_7$ (middle), and $La_{2-x}Sr_xCuO_4$ (bottom) compared with the photoinduced infrared conductivity $\sigma_p(\omega)$ (solid lines) in their respective insulator precursors.

Calculated fit to mid IR in 3 materials
(Mihailovic et al
(Phys Rev B, 1990)

m^*, coupling constants

	m^*/m_e	η	ω_0 (cm^{-1})
$La_{2-x}Sr_xCuO_4$	23	10	450
$YBa_2Cu_3O_7$	13	7	200
$Tl_2Ba_2CaCu_2O_8$	11	5.6	200

PEAK IN $\sigma(\omega)$ OF VARIOUS PEROVSKITES

	T_c (K)	Mid-IR peak (eV)
$SrTiO_3$	0.3^8	$>1^8$
$Ba_{1-x}Pb_xBiO_3$	13^6	1.2^6
La_2CuO_4	34	0.5
$YBa_2Cu_3O_7$	93	0.13
$Tl_2Ba_2CaCu_2O_8$	110	0.09

The mid-IR peak is present in all perovskite superconductors! Is it "just a defect"?

Conclusions

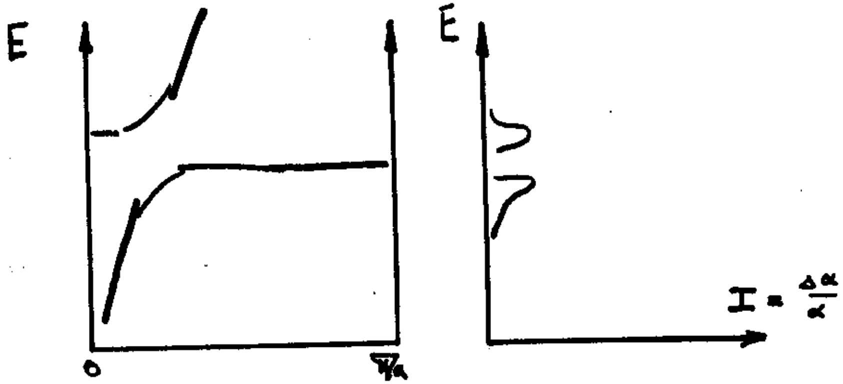
The e-p interaction in High-Tc materials manifests itself in a number of ways:

- Anaharmonicity of apex O modes
- Pyroelectricity, incipient ferroelectricity
- Anomalous T-dependences in Raman spectra
- Local distortions suggest apex oxygen involvement in vibronic interaction
- Polaron hopping gives $\sigma(\omega)$ in mid-IR
- Phonon (structural) anomalies at Tc (or just above T_c)

Conclude: whatever the effect of other interactions, e-p coupling has clearly been shown to be important in describing the normal properties of the superconducting perovskites.

Photoinduced Local Mode Spectroscopy (PLMS)

No *q* =*0* selection rule!

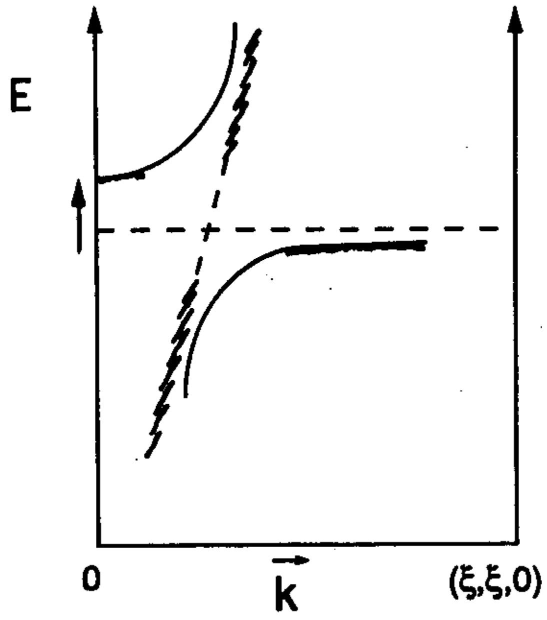


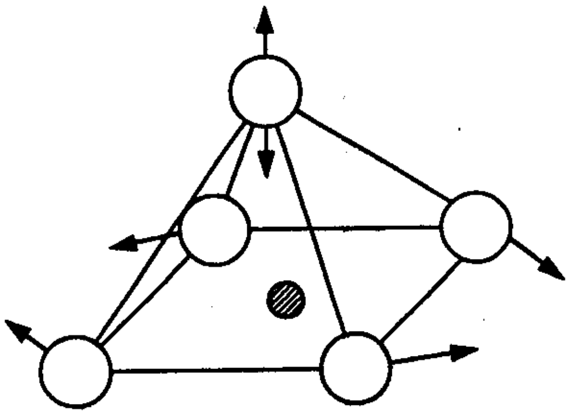
Photoinduced absorption spectroscopy

$$\Delta\alpha(\omega)/\alpha(\omega) = \Delta\sigma(\omega)/\sigma(\omega)$$

where $\Delta\alpha(\omega)$ is due to the effect of optically excited carriers (electrons and holes).

Neutron data: results of elastic scattering.





"Scissor mode"

Reichardt et al. (1990)

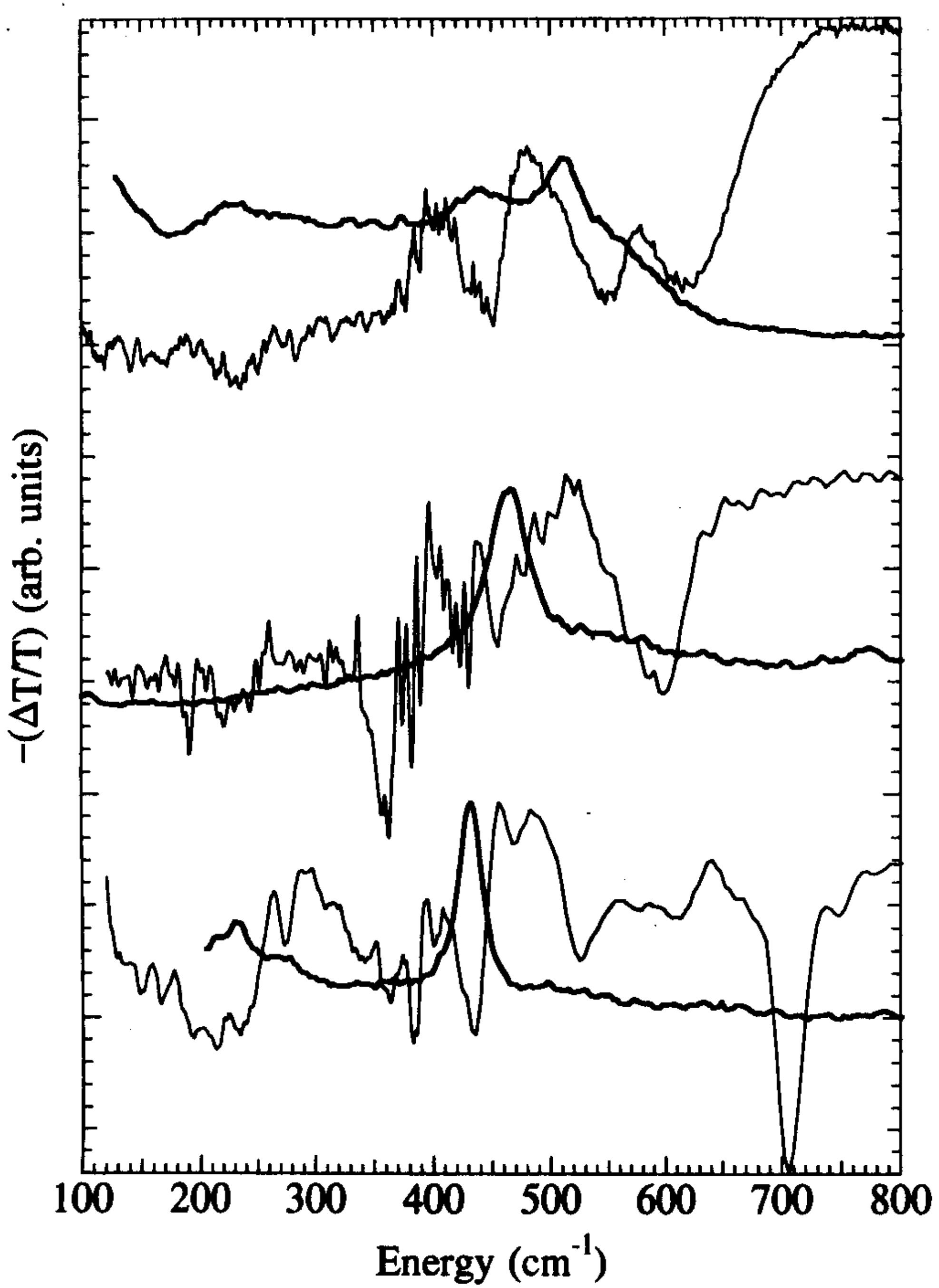


FIG. 1. Photoinduced local vibrational modes (PILMs) (thin lines) in La_2CuO_4, $YBa_2Cu_3O_{6.3}$

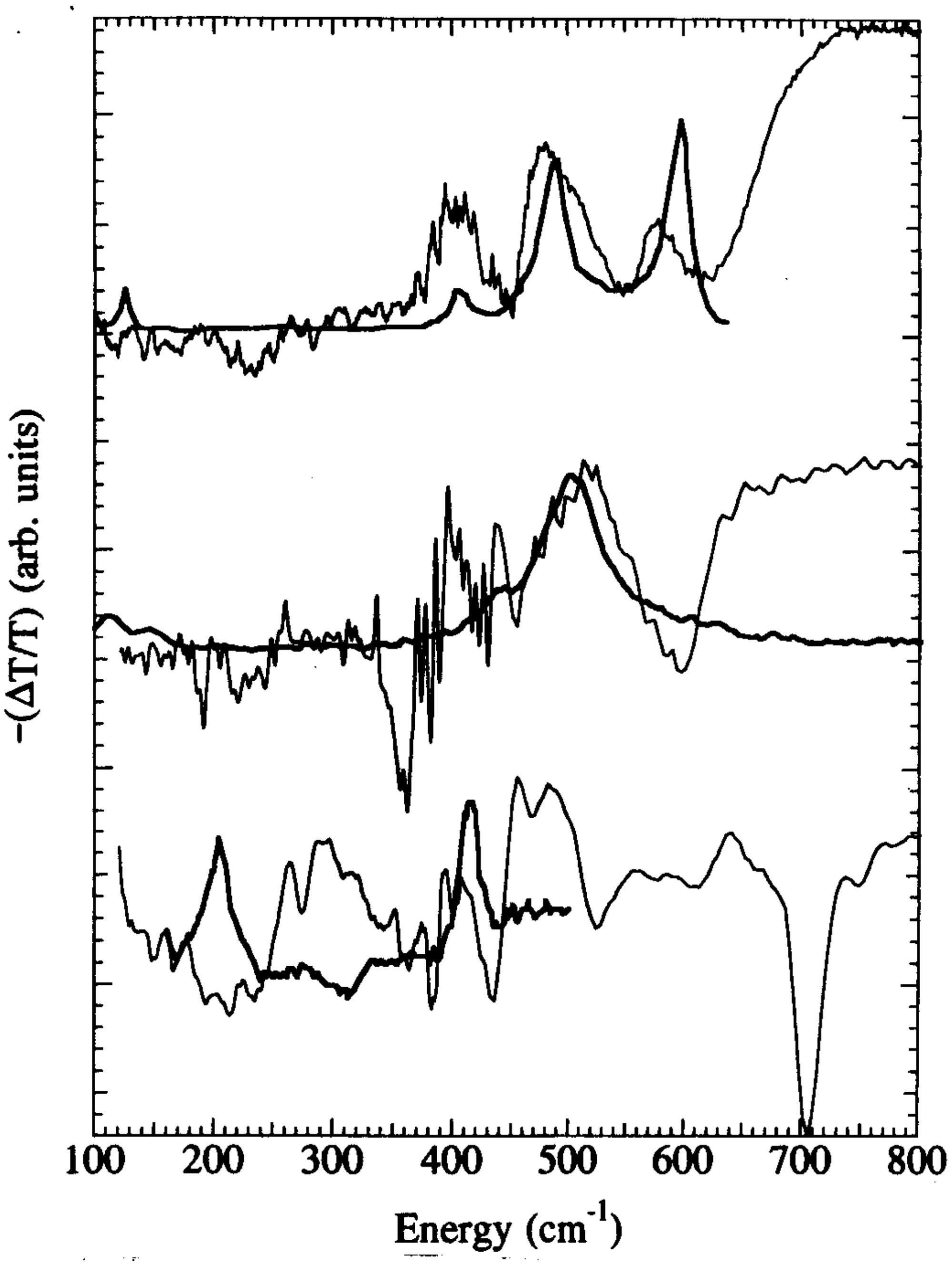


FIG. 2. Photoinduced local vibrational modes (PILMs) (thin lines) in La_2CuO_4, $YBa_2Cu_3O_{6.3}$ and $Tl_2Ba_2Ca_{1-x}Gd_xCu_2O_8$ are compared with Raman spectra (thick lines) of metallic

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