

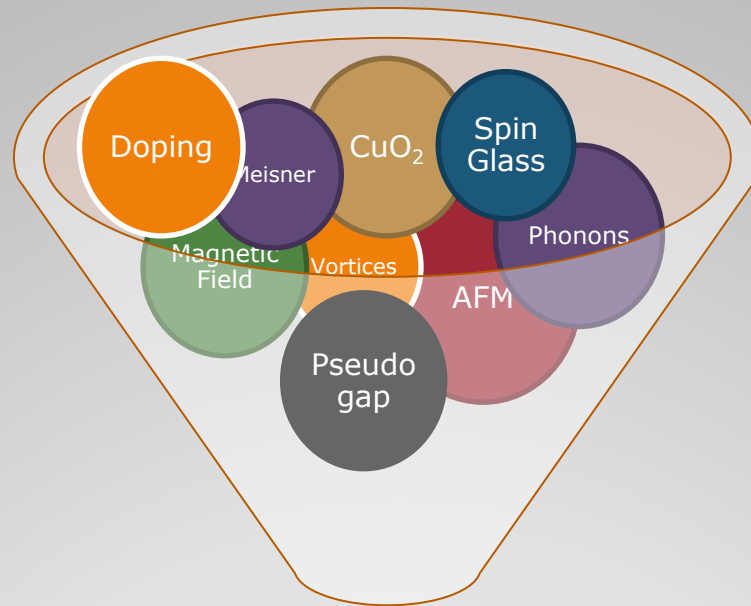
# Investigating the mechanism of High Temperature Superconductivity by Oxygen Isotope Substitution

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Superconductivity

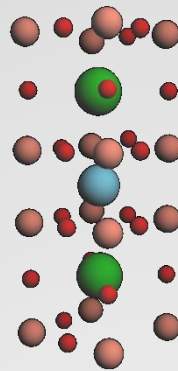
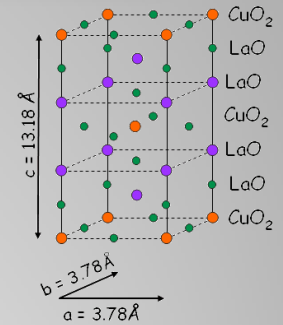
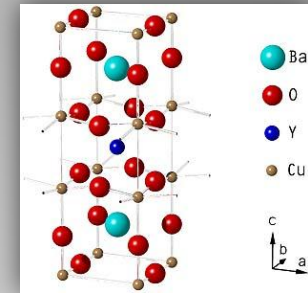
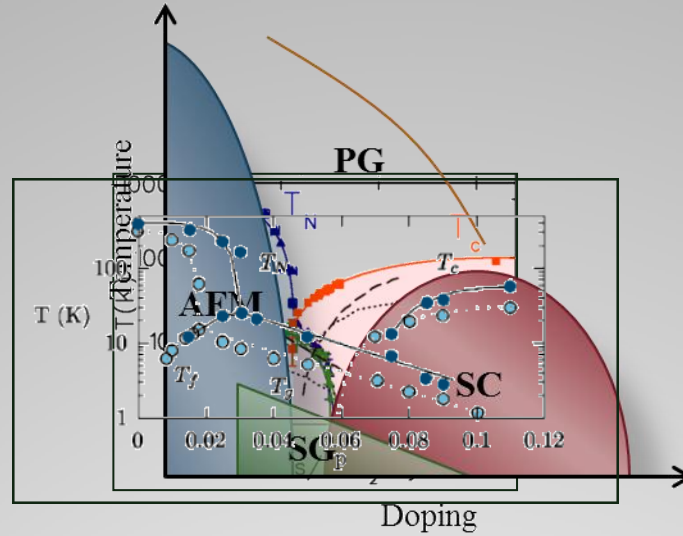
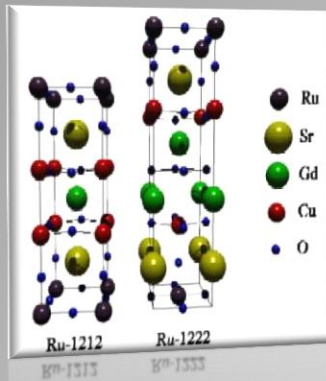
**How can we study a complex system?**

Apply a perturbation and check what happens.

# Outline:

- Cuprates- a complicated system...
- What is the source of critical doping variations?
  - CLBLCO
  - NMR
  - Results
  - Conclusions
- Oxygen Isotope Effect on the Néel temperature.
  - The Isotope Effect
  - $\mu$ SR
  - Results
  - Conclusions
- CLBLCO: is it all about disorder?
  - Impurities in CLBLCO

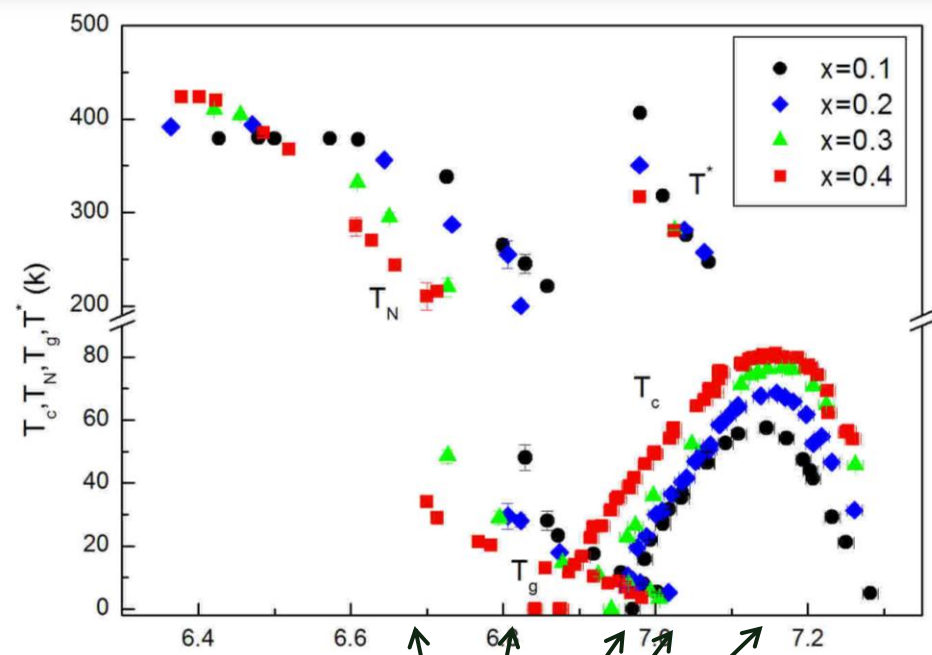
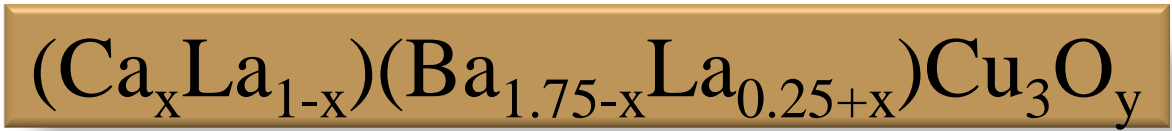
# Cuprates



<http://www.fis.unipr.it/~derenzi>

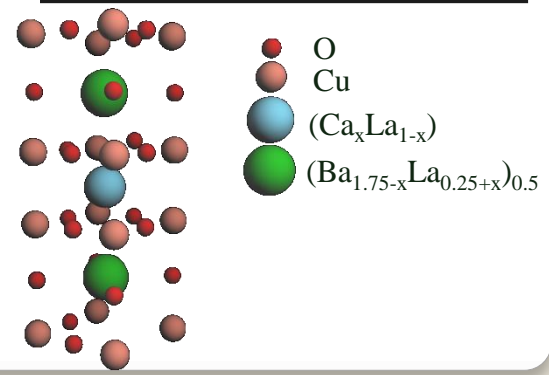
S. Chakravarty *et al.* PRB **63**, 094503

# The CLBLCO Compound

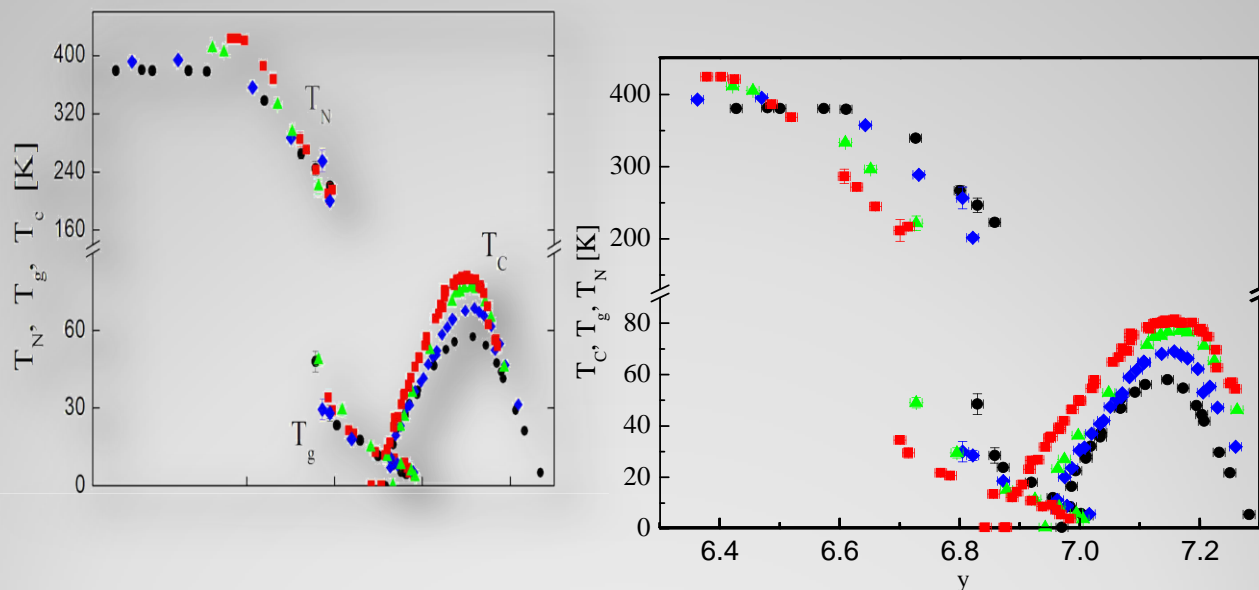


Critical Doping levels  $x=0.1$  (black)

- $y$  controls the total charge (doping).
- $x$  controls the charge location.
- The total cation charge does not change with  $x$ .
- There's a 30% difference in  $T_c^{\max}$  between the families.



# The CLBLCO Compound

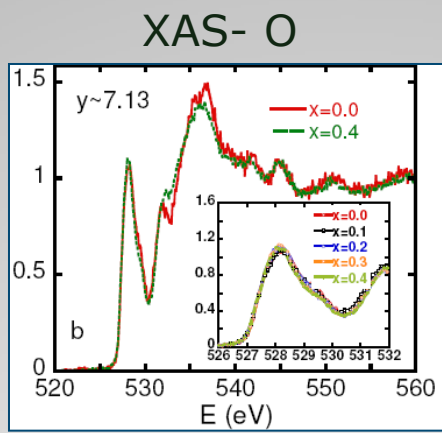
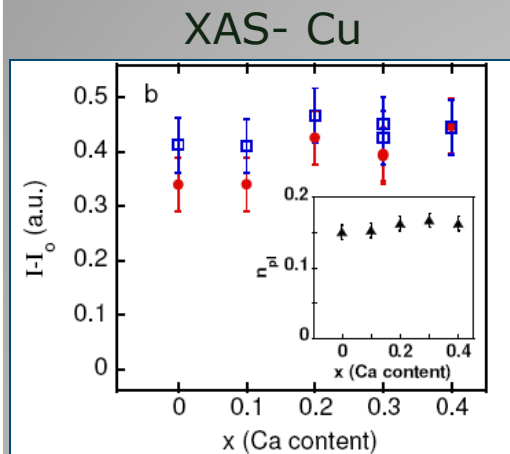


- Stretching each family data by a factor of  $K(x)$  creates identical critical doping levels.

**Is there a physical explanation?**

# Previous Results- CLBLCO

The hole density of Copper is  $x$  invariant: "Two Fluids"



## BVS calculations - Cu

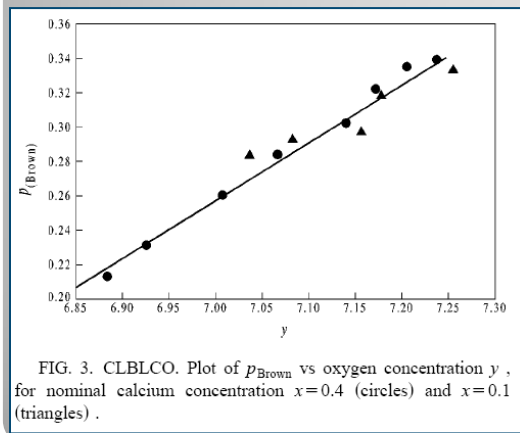
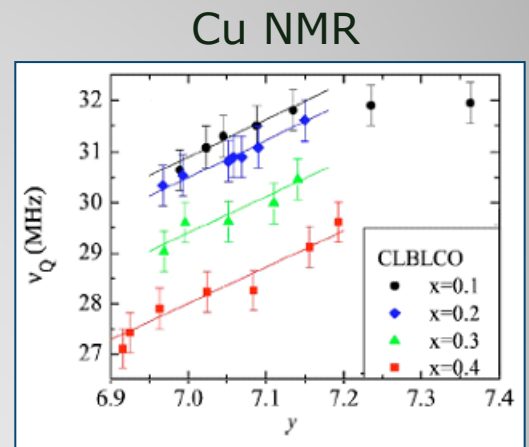


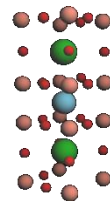
FIG. 3. CLBLCO. Plot of  $p_{\text{Brown}}$  vs oxygen concentration  $y$ , for nominal calcium concentration  $x=0.4$  (circles) and  $x=0.1$  (triangles).



S. Sanna *et al.* EPL **86**, 67007 (2009)

O. Chmaissem, Y. Eckstein and C. G. Kuper, PRB **63**, 174510 (2001)

A. Keren, A. Kanigel and G. Bazalitsky, PRB **74**, 172506 (2006)

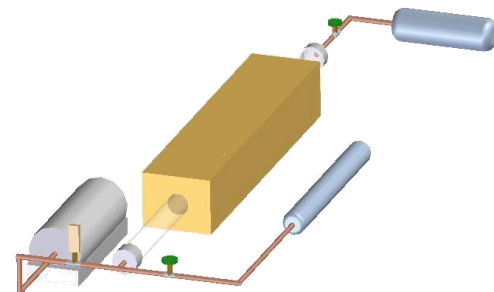


# Oxygen 17 NMR

- $^{17}\text{O}$  nucleus has a quadrupole moment. It is sensitive to both electric and magnetic field distributions.

$$H = H_{\text{Zeeman}} + H_{\text{Quadrupole}}(\text{EFG})$$

- In the doping process holes are induced in the planar oxygen orbitals.
- $^{17}\text{O}$  has a relatively small spectral width.

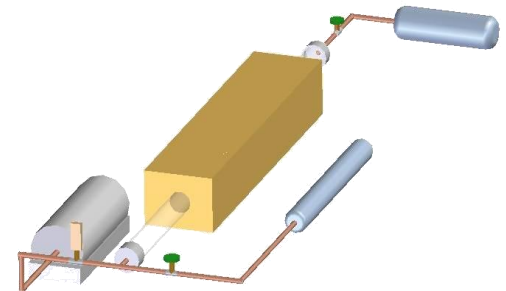
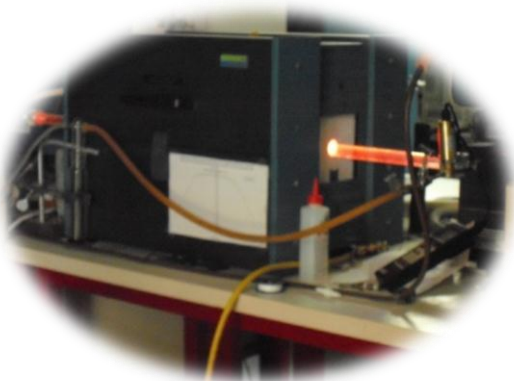




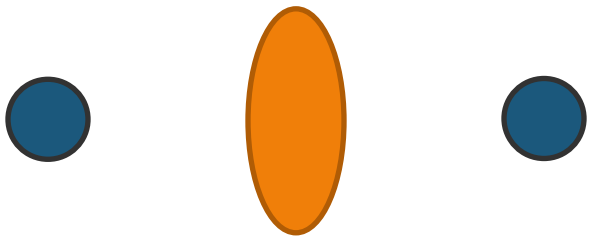
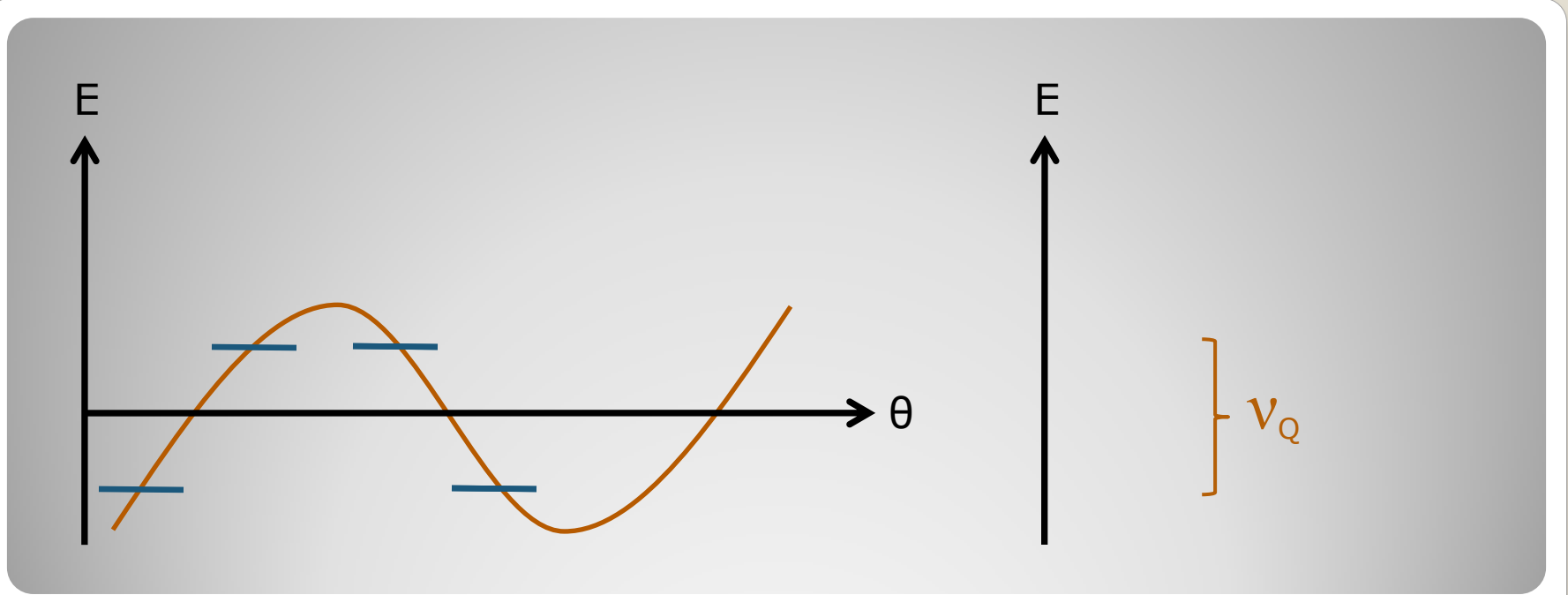
## The Enrichment process:

- Samples are put in the furnace.
- The furnace is sealed and vacuumed.
- Gas containing the desired isotope - either  $^{18}\text{O}$  or  $^{17}\text{O}$  - is released into the tube with the sample.
- The furnace is heated to allow the isotope to diffuse into the sample.

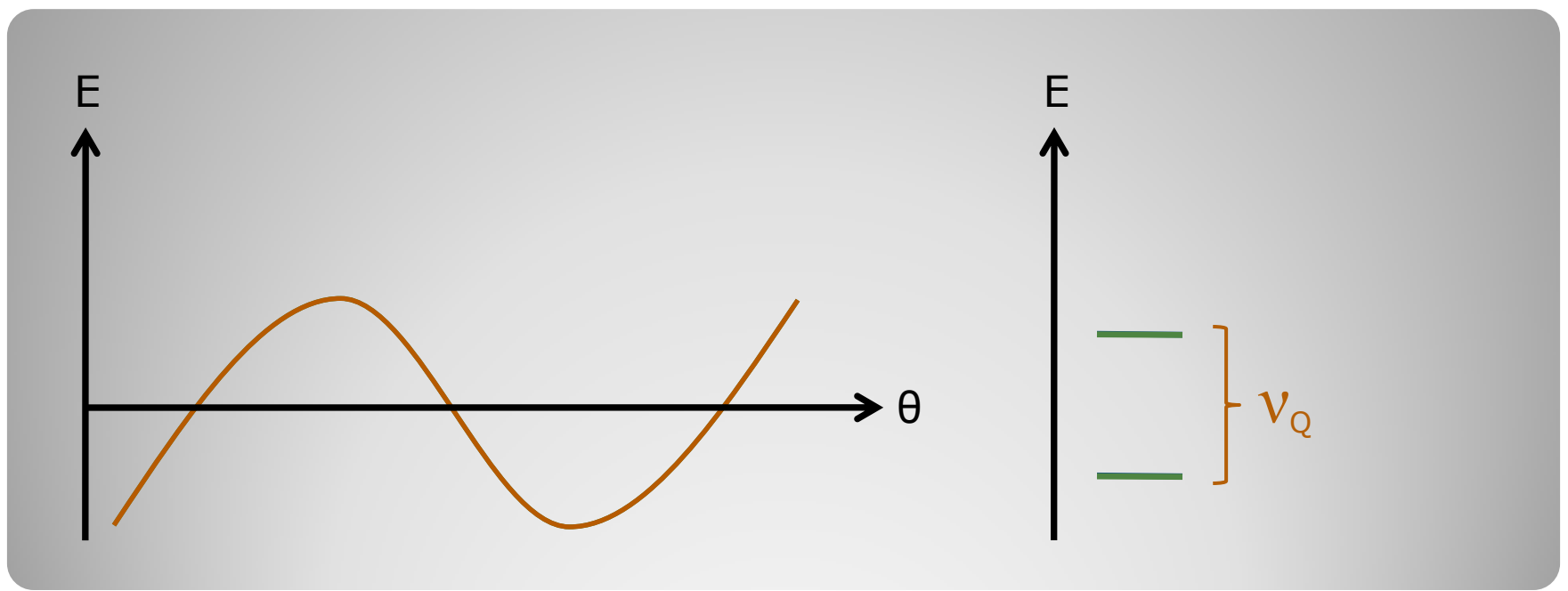
<u>Isotope</u>	<u>Natural abundance</u>
$^{16}\text{O}$	99.76%
$^{17}\text{O}$	0.038%
$^{18}\text{O}$	0.21%



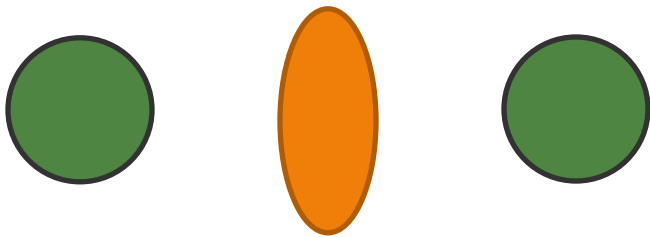
# Nuclear Quadrupole Resonance



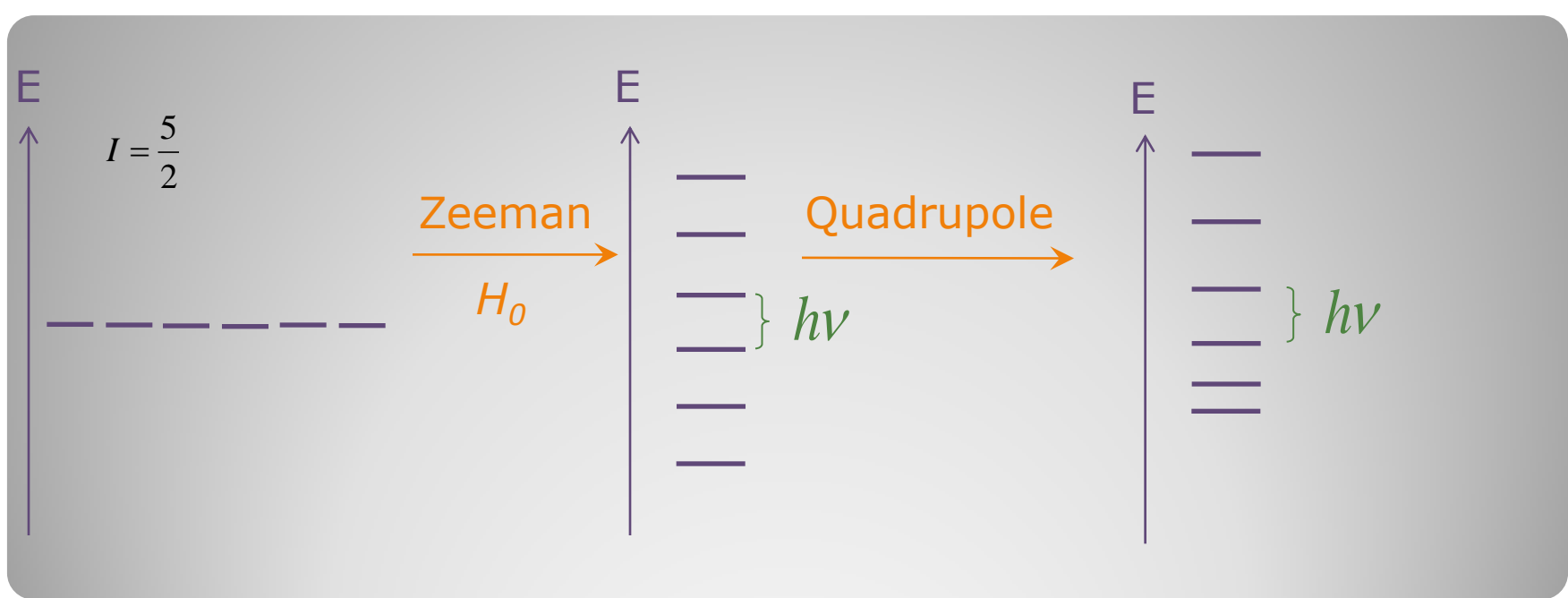
# Nuclear Quadrupole Resonance



- The Quadrupole Frequency measures the Charge Distribution around the nucleus



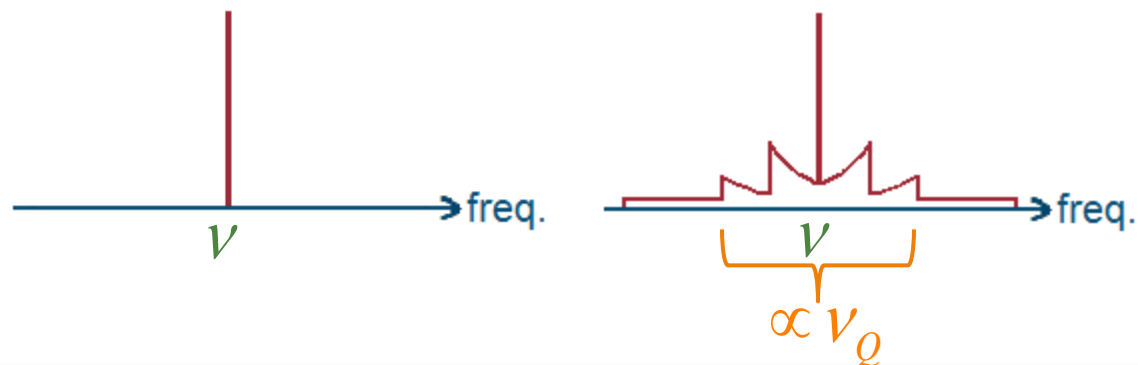
# Nuclear Magnetic Resonance



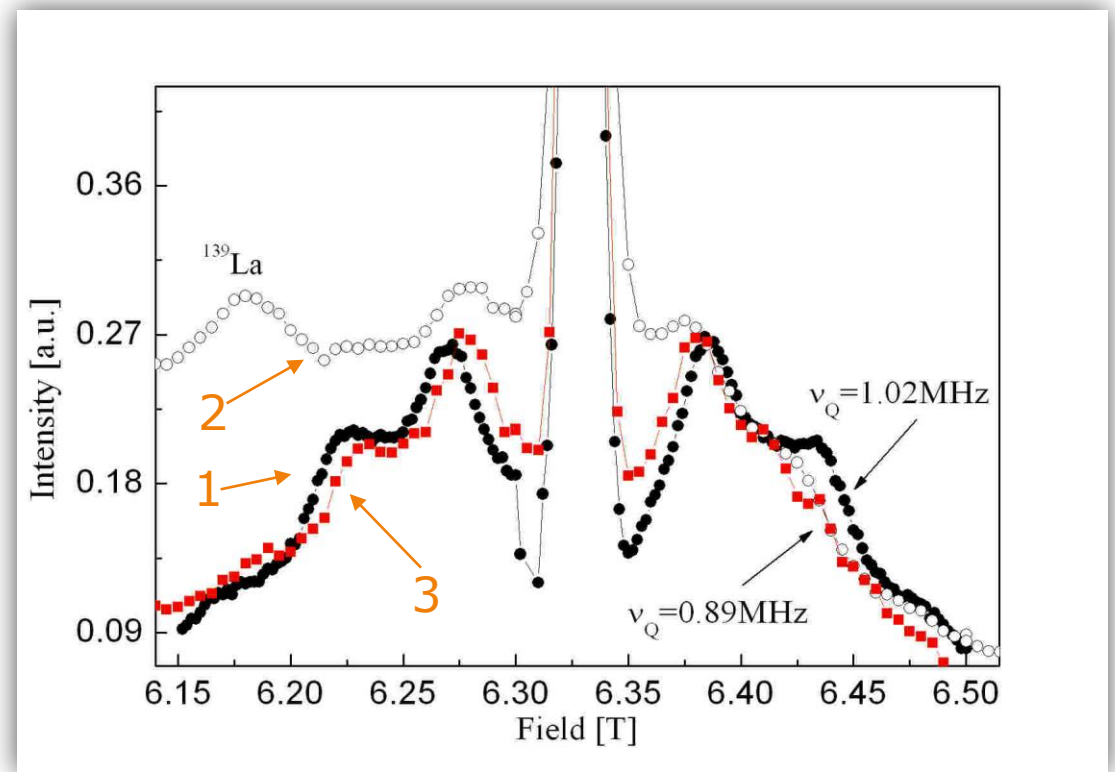
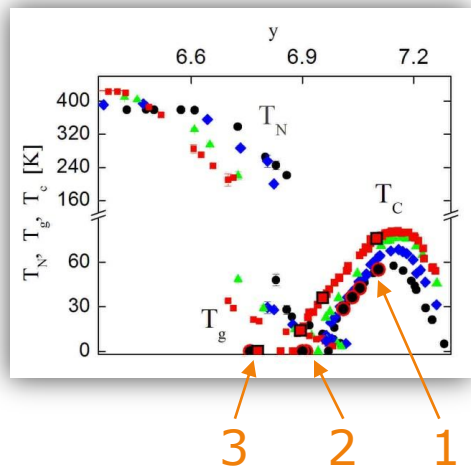
$$H = -\gamma\hbar H_0 (1 + \sigma) I + \frac{1}{6} \nu_Q \left[ 3I_z^2 - I^2 + \eta (I_x^2 - I_y^2) \right]$$

$H_{Zeeman}$   $H_{Quadrupole}$

NMR Spectrum:



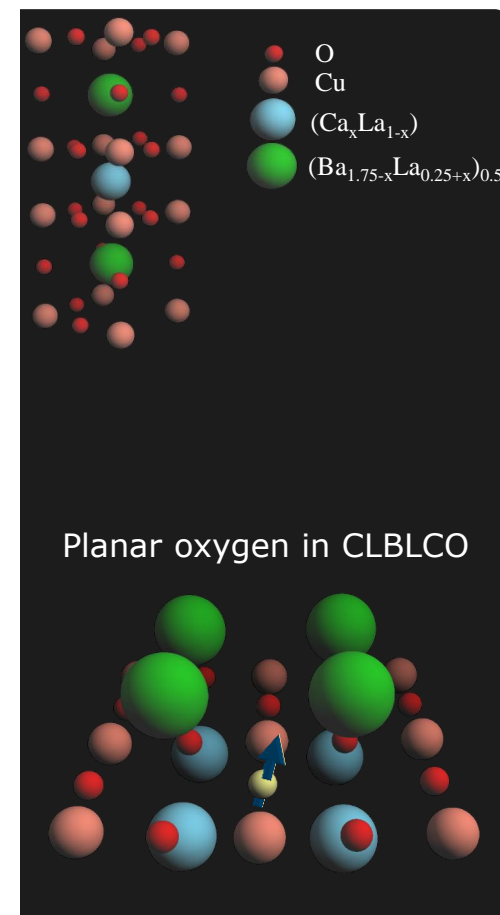
# $^{17}\text{O}$ NMR of CLBLCO- Raw Data



**The parameters  $x$  and  $y$  change the quadrupole frequency**

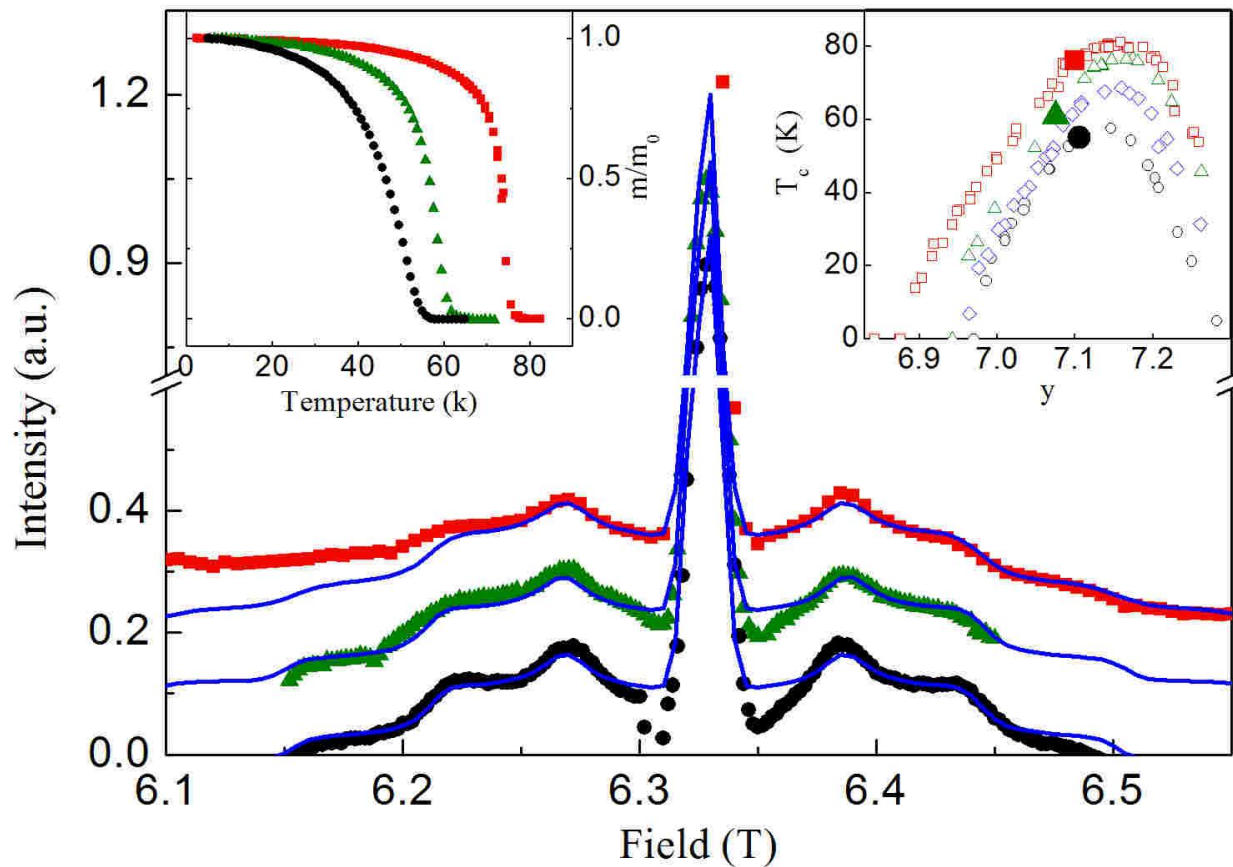
The contributions to the planar oxygen  $\nu_Q$ :

1. Holes in the oxygen  $2p_\sigma$  orbital
2. Holes in copper orbitals
3. Surrounding atoms (La, Ba, Ca)

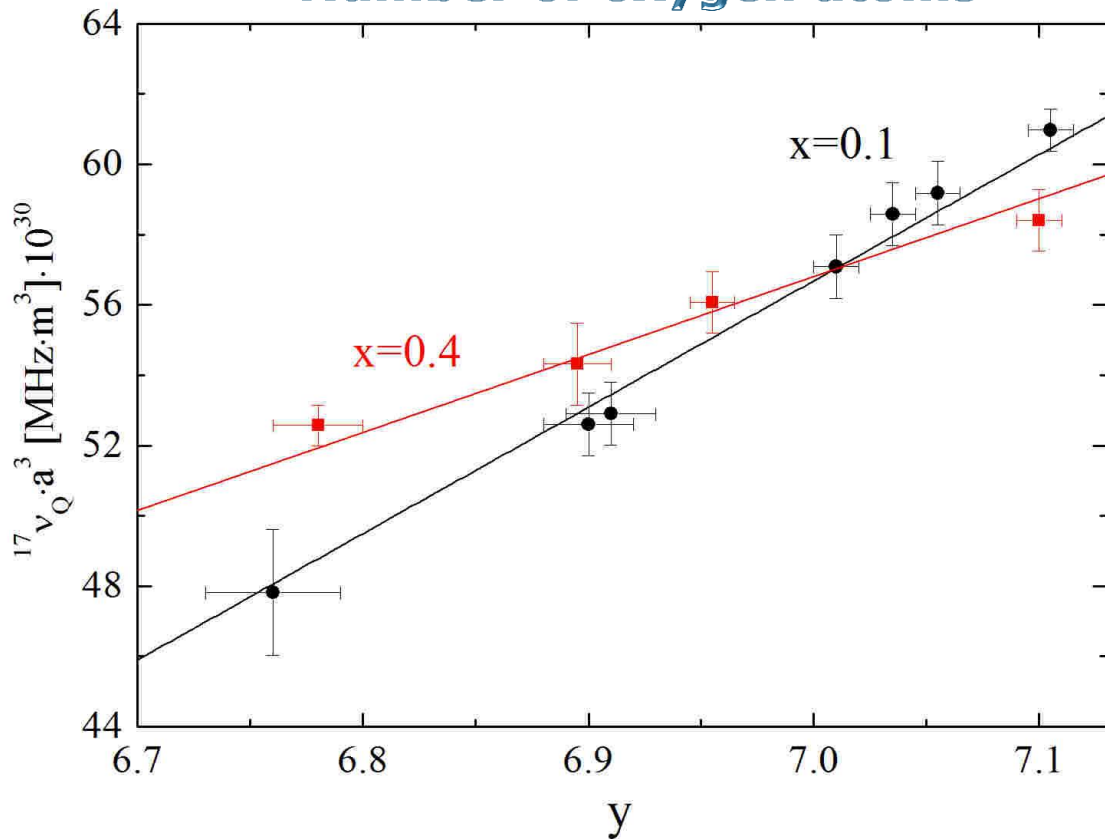
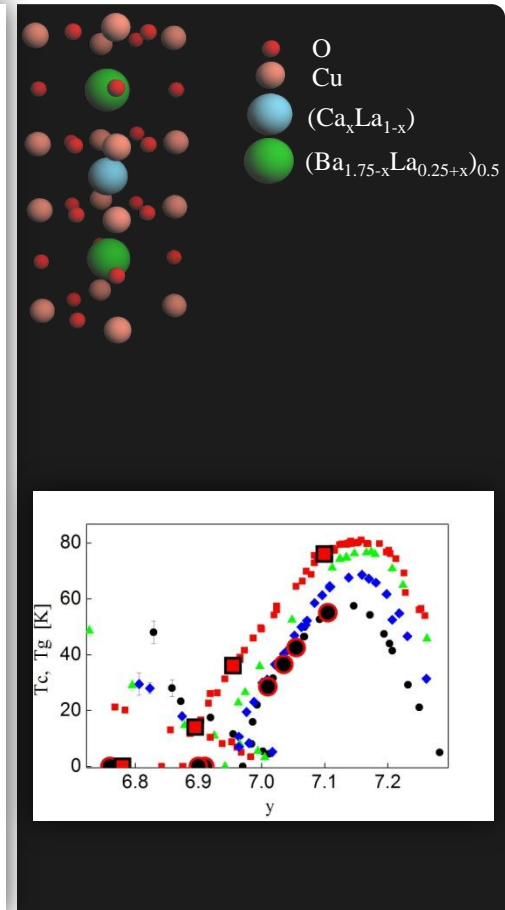


- We compare samples with different doping levels.

**$\nu_Q$  measures the number of planar oxygen  $2p_\sigma$  holes**

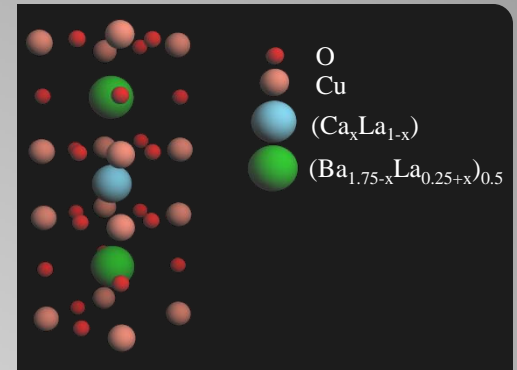
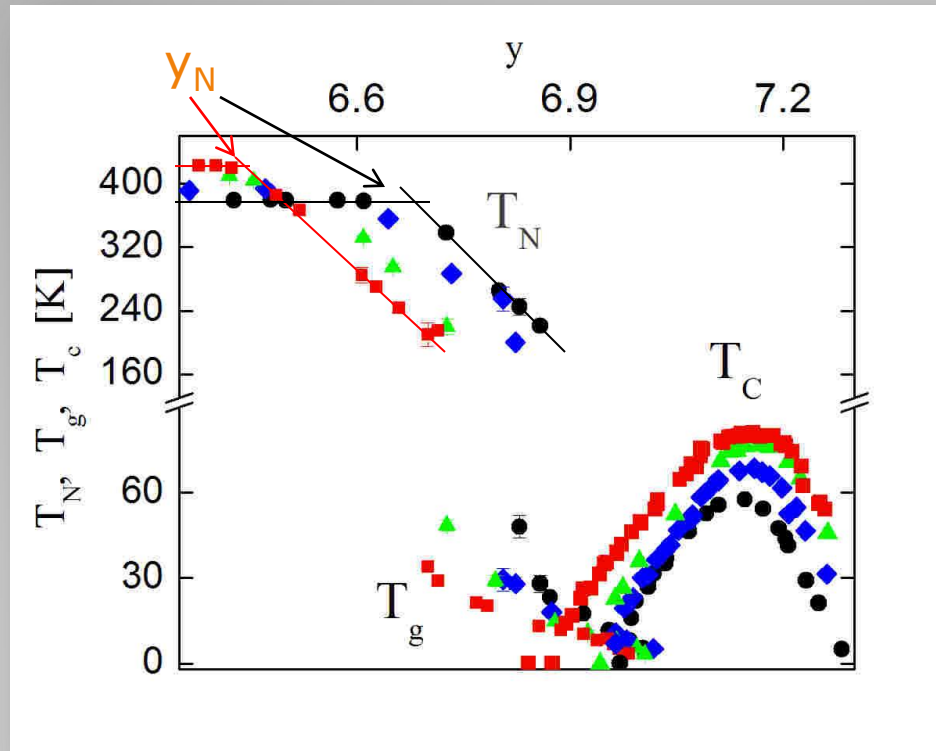


## Number of oxygen atoms

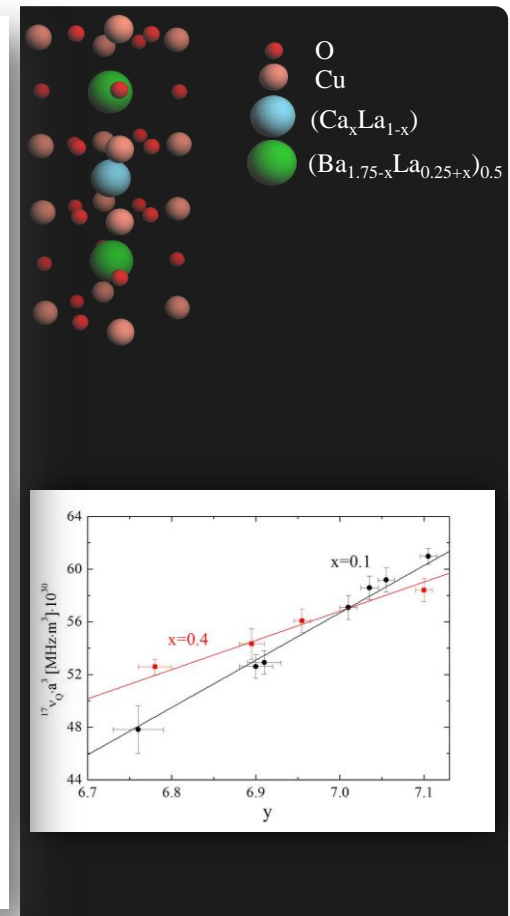
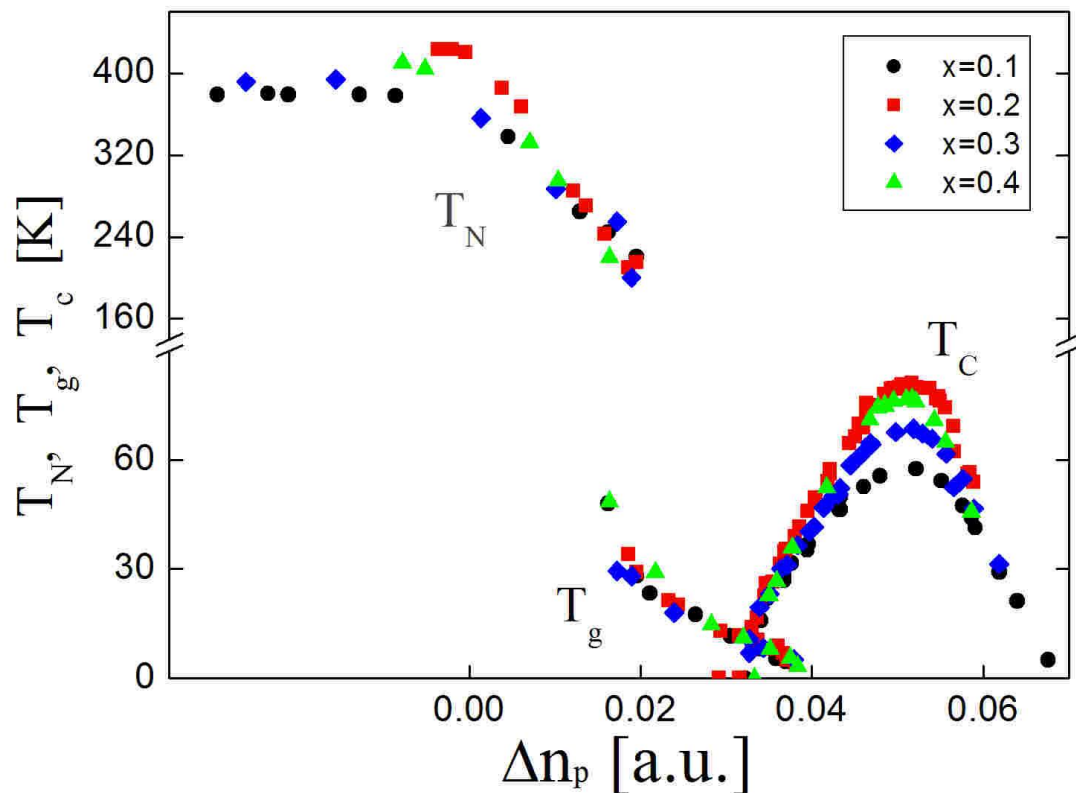
Change in  $2p_{\sigma}$  holes

The ratio between the slopes is equal to  $K(x=0.1)$  over  $K(x=0.4)$





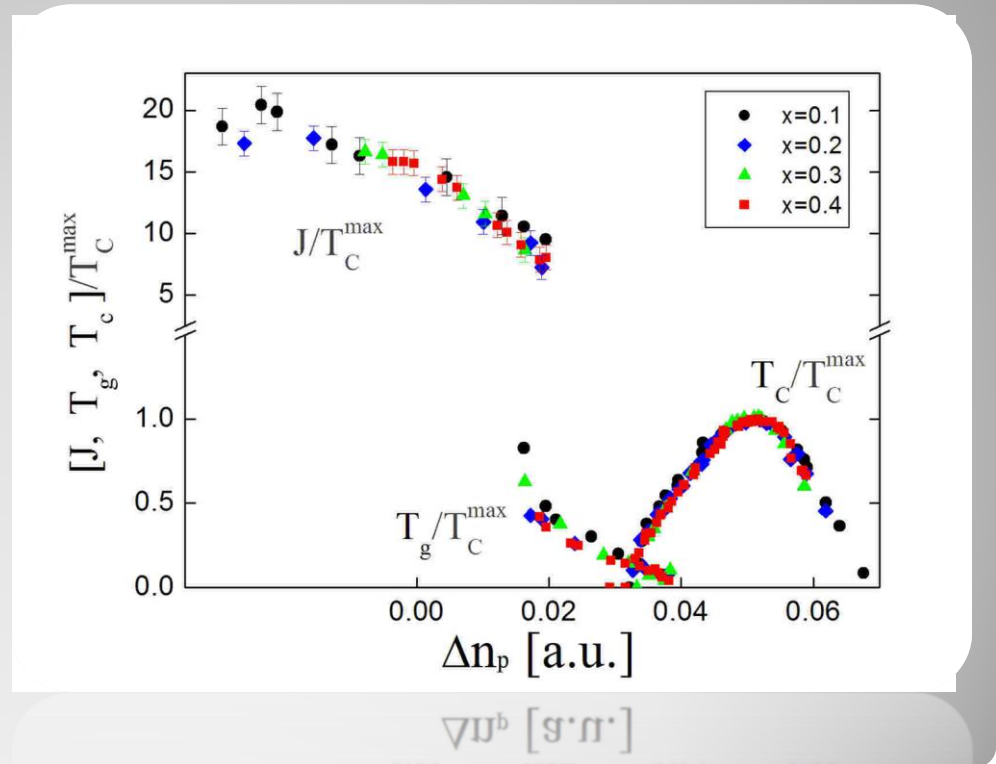
For  $y < y_N$  the number of planar O  $2p_\sigma$  holes does not change



The critical doping values are global and depend only on the number of  $2p_\sigma$  holes created by doping.

## Scaling:

- Dividing by  $T_C^{\max}(x)$
- Replacing  $T_N$  with  $J$

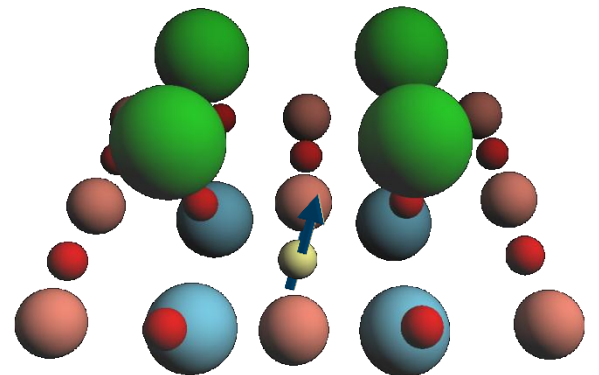


The CLBLCO phase diagram is scaled with no adjustable parameter.

The maximum  $T_C$  is defined by the AFM coupling  $J$

## Summary: Critical doping variations

- We compared the number of  $2p_{\sigma}$  holes of CLBLCO samples with different  $x$  and  $y$  values using  $^{17}\text{O}$  NMR.
- The critical doping values are global and depend only on the number of  $2p_{\sigma}$  holes created by doping.
- The CLBLCO phase diagram (with  $T_C^{\text{max}}$  difference of 30%) is scaled with no adjustable parameter.
- The maximum  $T_C$  is defined by the AFM coupling  $J$ .



*“THE main facts which a theory of superconductivity must explain are (1) a second-order phase transition at the critical temperature,  $T_c$ , ... (5) the dependence of  $T_c$  on isotopic mass,  $T_c \sqrt{M} = \text{const}$ . We present here a theory which accounts for all of these...”*

*J. Bardeen, L. N. Cooper, and J. R. Schrieffer,  
Phys. Rev. 108, 1175–1204 (1957).*

The Isotope Effect was one of the key experimental findings in the path to understanding conventional superconductivity

## The Isotope Definition

The Isotope Effect is the change in the critical temperature due to isotopic substitution:

$$\alpha \equiv -\frac{d \ln T_q}{dm} \quad \leftrightarrow \quad T_q \propto m^{-\alpha}$$

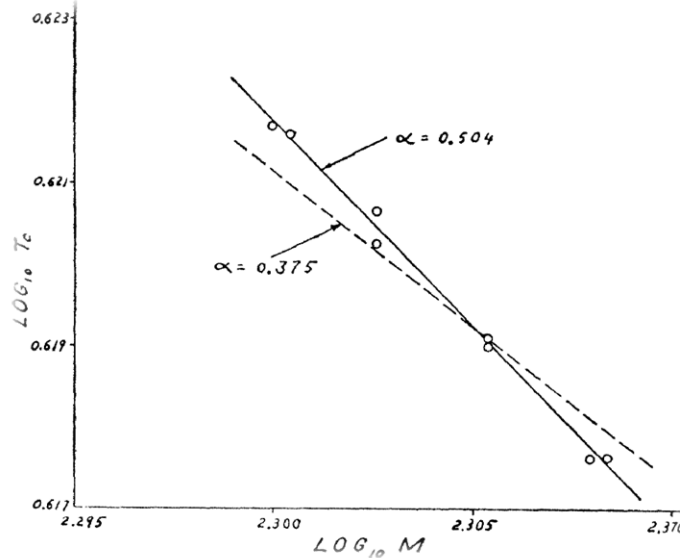
For a small effect:

$$\alpha = -\frac{\Delta T_q}{T_q} \frac{m}{\Delta m}$$

$T_q$  - the critical temperature.

$m$  - the element's mass.

$\Delta$  - the change caused by substitution.



For most conventional superconductors

$$\alpha = 0.5,$$

as explained by BCS theory:

$$T_C \approx 1.13 \Omega e^{-\frac{1}{N(0)V}}.$$

The Cooper pairs are phonons mediated.

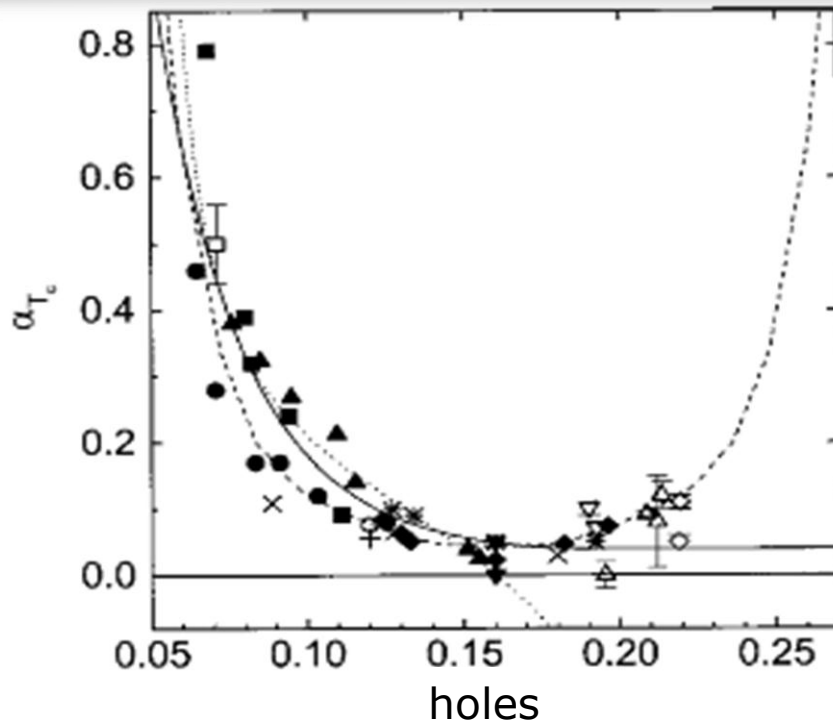
The IE:

$$T_q \propto m^{-\alpha}$$

Spring frequency:

$$\Omega = \sqrt{\frac{K}{m}}$$

# Isotope Effect in Cuprates



- △  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$
- ◇  $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$
- ▽  $\text{Y}_{0.84}\text{Ca}_{0.16}\text{Ba}_2\text{Cu}_3\text{O}_7$
- $\text{Y}_{0.84}\text{Ca}_{0.16}\text{Ba}_2\text{Cu}_3\text{O}_6$
- $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$
- ▲  $\text{Y}(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_7$
- $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_7$
- ▼  $\text{YBa}_2\text{Cu}_3\text{O}_7$
- $\text{YBa}_2\text{Cu}_4\text{O}_8$
- †  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$
- ◆  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_2\text{Cu}_4\text{O}_8$
- \*  $\text{Y}_{0.8-y}\text{Pr}_{0.2}\text{Ca}_y\text{Ba}_2\text{Cu}_3\text{O}_7$

Why is there IE in Cuprates?



- Phonons

BCS (1957), A. Bill (1996).

- Zero point motion

D. S. Fisher (1988).

- Polarons

R. Khasanov (2008).

- Normal doping

V. Z. Kresin (1994).

- Superfluid density

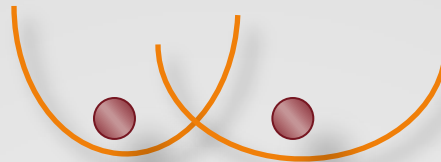
M. Serbyn (2010).

$$T_C = 1.13 \Omega e^{\frac{1}{N(\rho^*)V}} \quad \mu^* = \frac{\mu}{1 + \mu \ln\left(\frac{E_F}{\Omega}\right)}$$

t changes:

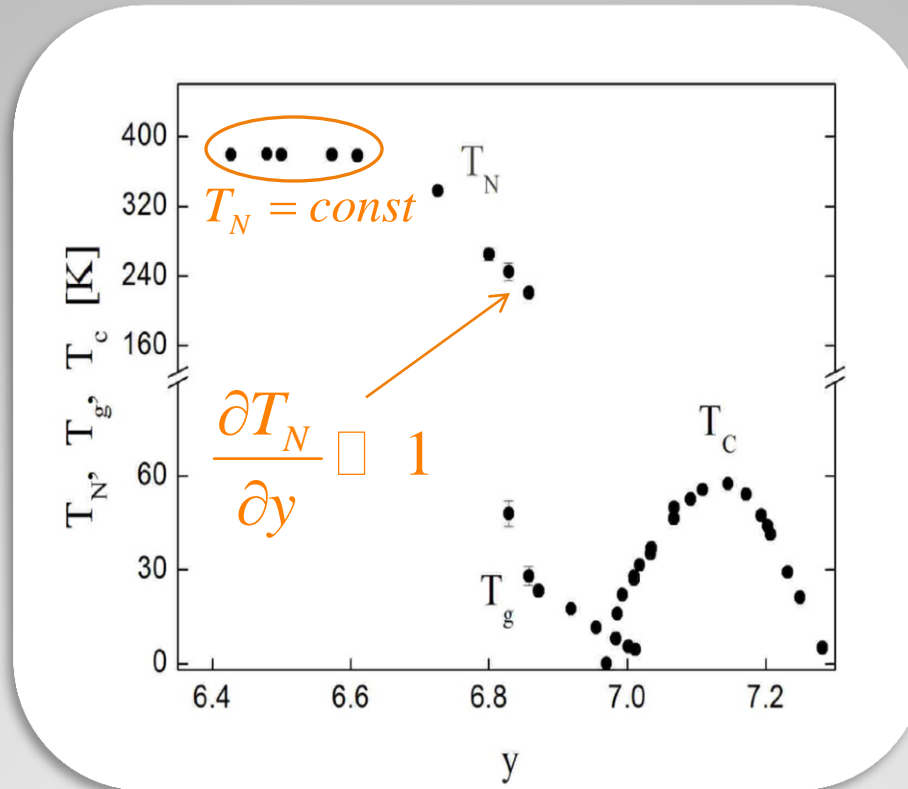
$$m^* = m_e e^{\frac{A}{\omega}}$$

*Do the isotope effect experiments prove that  $T_C$  is not related to J?*



Exploring the AFM phase may improve our understanding of the SC phase.

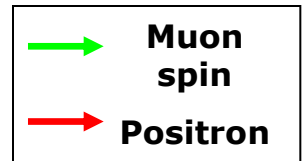
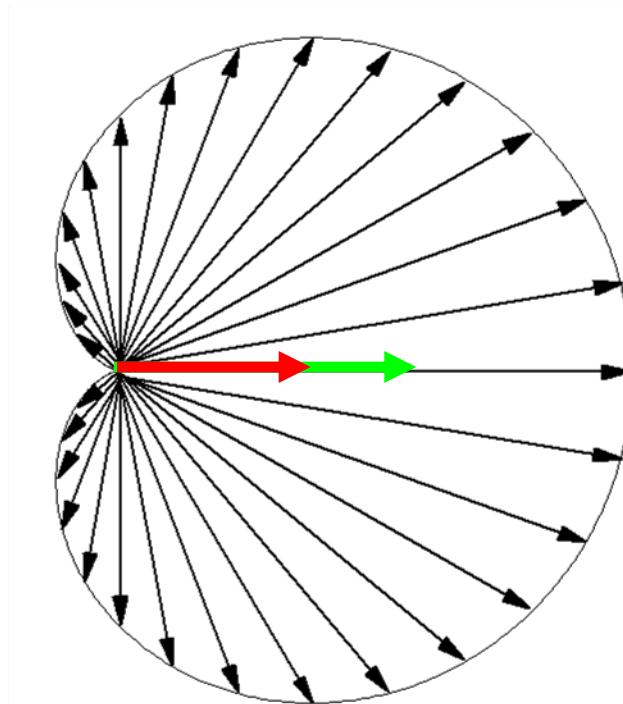
More accurate measurements can be performed.



**Why is  $(\text{Ca}_{0.1}\text{La}_{0.9})(\text{Ba}_{1.65}\text{La}_{0.35})\text{Cu}_3\text{O}_y$  ideal for this experiment?**

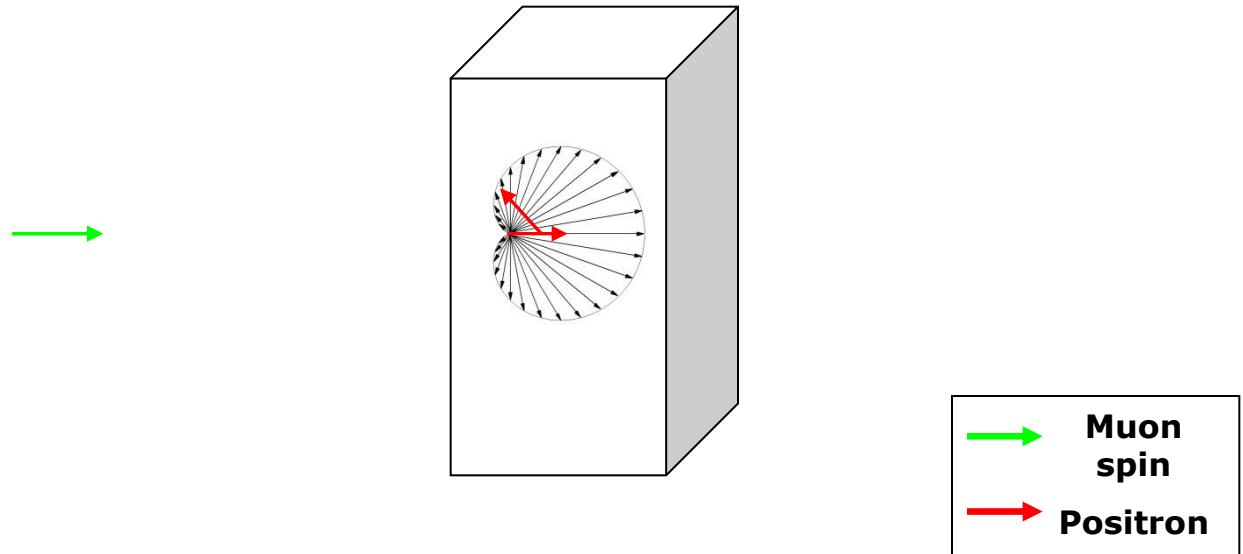
**Muon**- A Lepton with a mass of 105.7 MeV,  
The charge is identical to a positron (or an electron).  
Spin- $\frac{1}{2}$ , Life time-2.2 micro-seconds.  
Gyromagnetic ratio-  $135.5 \cdot 10^6$  Hz/T.  
Decays into a positron (+ neutrino and anti-neutrino).

The direction of the emitted positron:

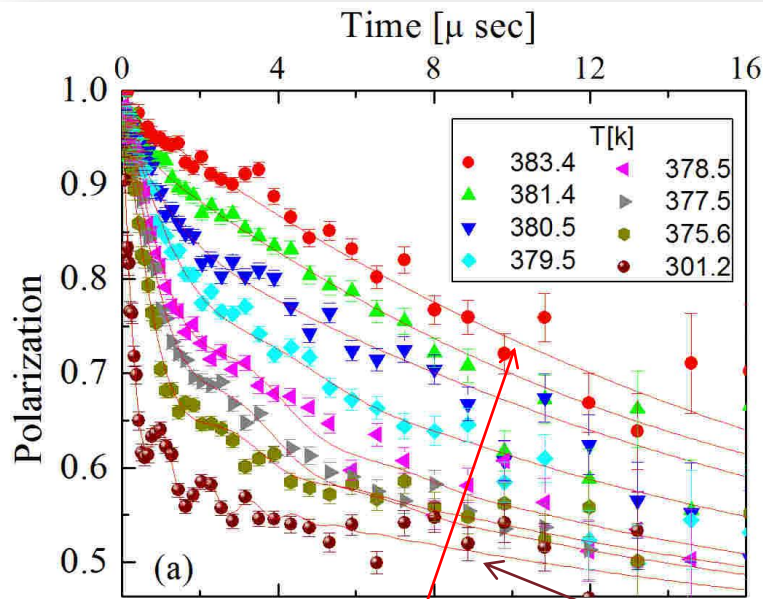


# Muon Spin Rotation

A beam of polarized muons hits the sample.  
Each muon rotates and decays into a positron.



# Muon Spin Rotation



$t$	Time
$P_n$	Normal fraction
$P_m$	Magnetic fraction
$\Delta$	Normal decay ( $t_2$ )
$a \approx \frac{2}{3}$	
$\lambda_1$	Normal decay
$\lambda_2$	Magnetic decay

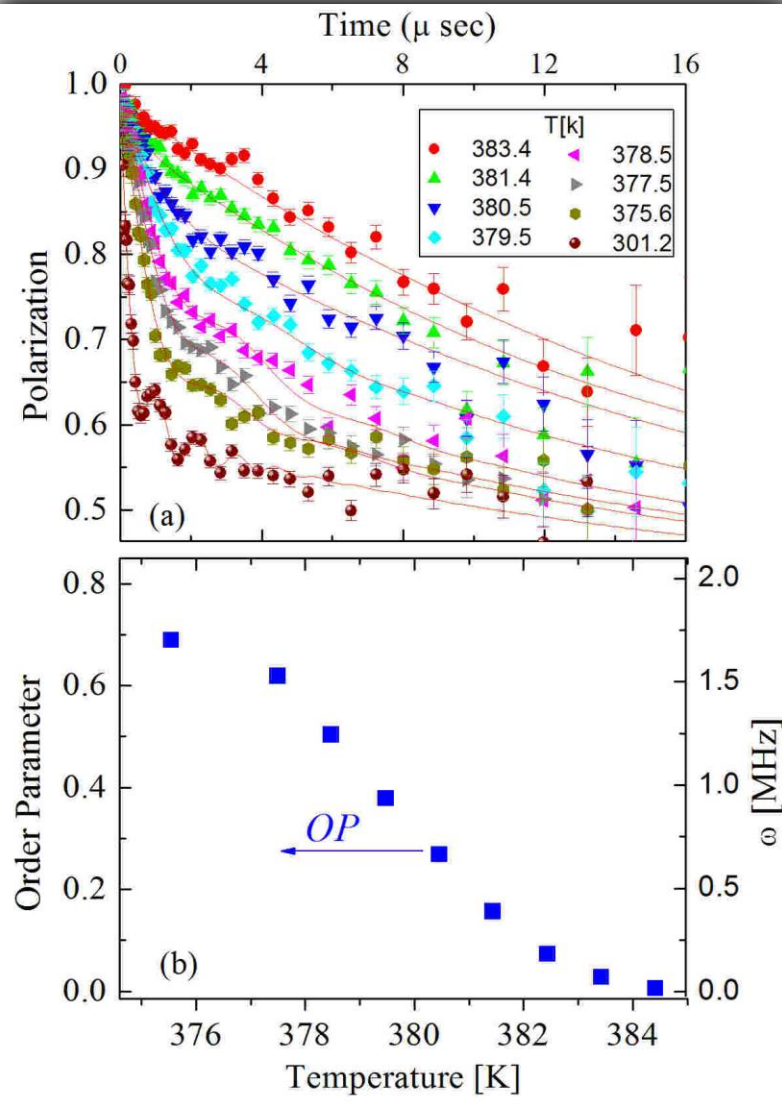
Non-magnetic phase (high T)

Magnetic phase (low T)  
Oscillations at the Larmor frequency  $\omega$

The muons polarization is:

$$P_z(t) = P_n e^{-\Delta t} + P_m (a e^{-\lambda_1 t} + (1-a) e^{-\lambda_2 t} \cos(\omega t))$$

# Choosing Order Parameter



$\omega$  Larmor Frequency

$P_n$  Normal fraction

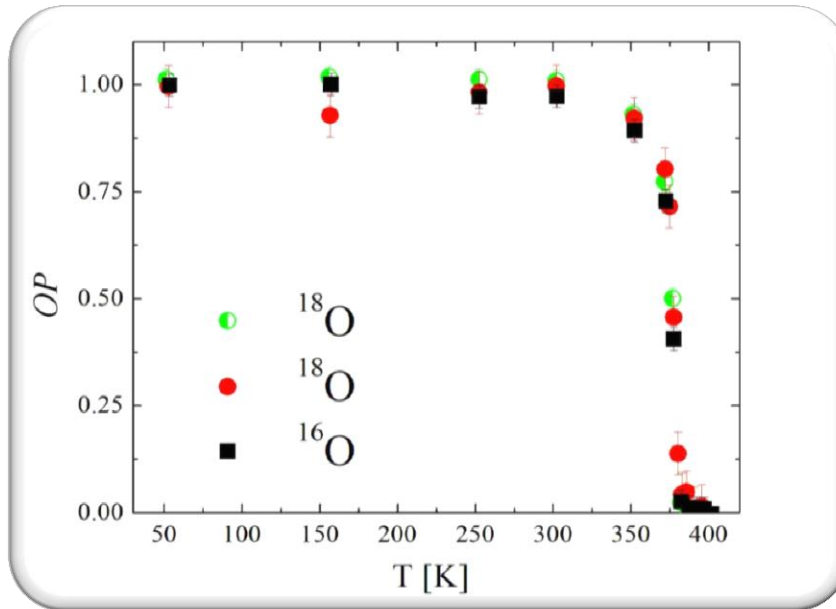
$P_m$  Magnetic fraction

In order to increase the sensitivity we defined a new order parameter:

$$OP(T) \equiv \frac{\langle P_{inf} \rangle - \langle P(T) \rangle}{\langle P_{inf} \rangle - \langle P(0) \rangle}$$

$$P_z(t) = P_n e^{-\Delta t} + P_m (a e^{-\lambda_1 t} + (1-a) e^{-\lambda_2 t} \cos(\omega t))$$

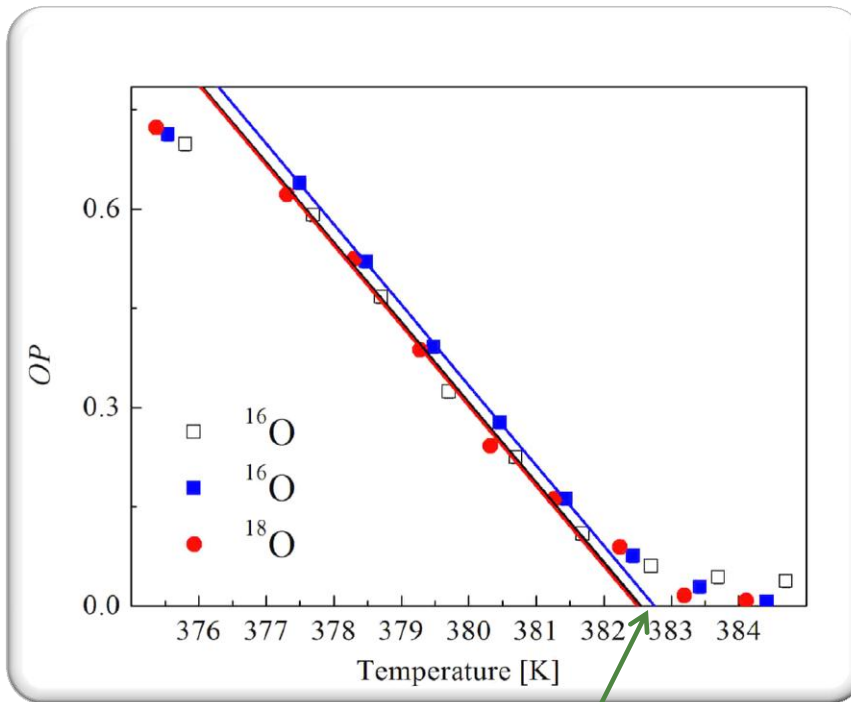
# Results



$$\text{OP}(T) \equiv \frac{\langle P_{inf} \rangle - \langle P(T) \rangle}{\langle P_{inf} \rangle - \langle P(0) \rangle}$$

$$P_z(t) = P_n e^{-\Delta t} + P_m (a e^{-\lambda_1 t} + (1-a) e^{-\lambda_2 t} \cos(\omega t))$$

There is no IE on  $T_N$ :  $\alpha_N = 0.005 \pm 0.011$



$$T_N \propto m^{-\alpha_N}$$

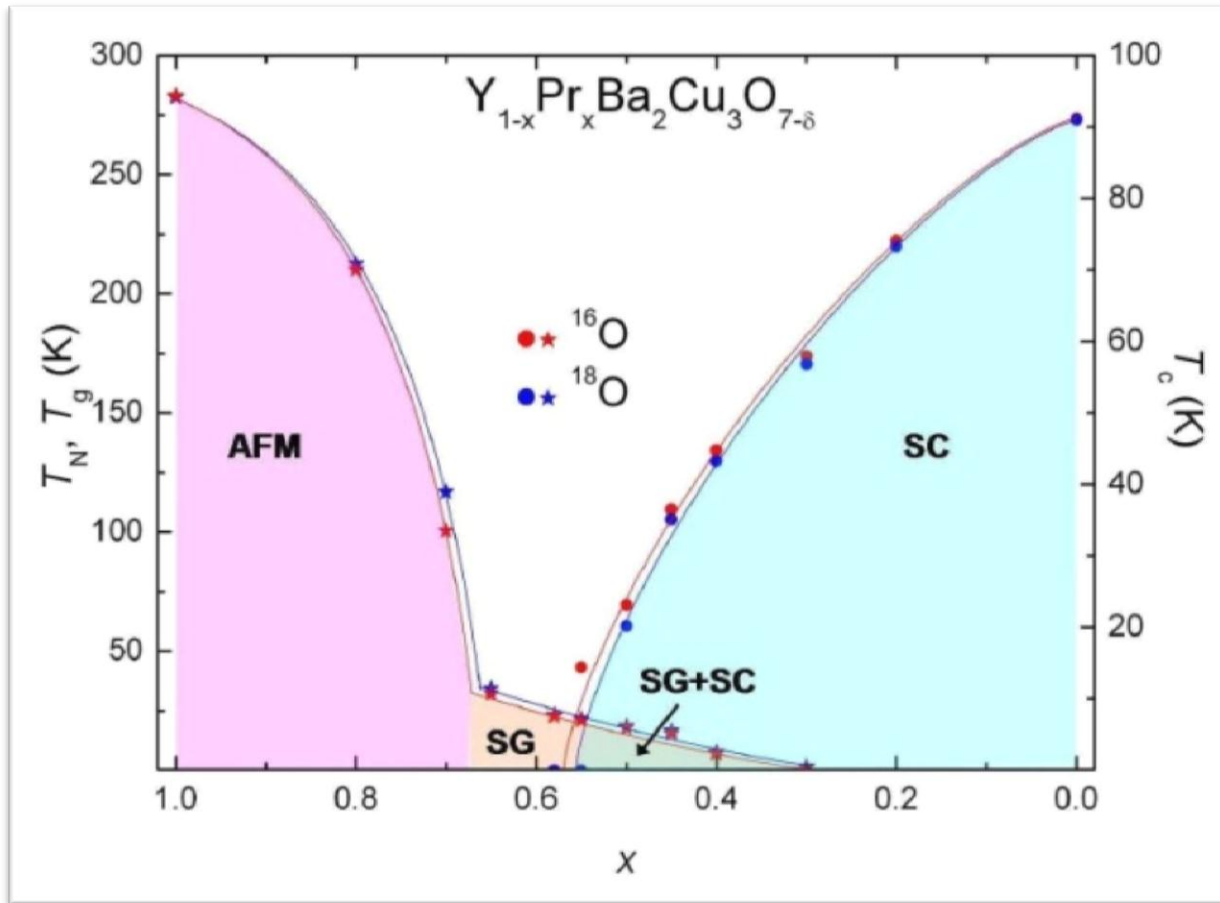
$$\text{OP}(T) \equiv \frac{\langle P_{inf} \rangle - \langle P(T) \rangle}{\langle P_{inf} \rangle - \langle P(0) \rangle}$$

$$P_z(t) = P_n e^{-\Delta t} + P_m (a e^{-\lambda_1 t} + (1-a) e^{-\lambda_2 t} \cos(\omega t))$$



# OIE in Cuprates

But maybe its because we should use the physical parameter..



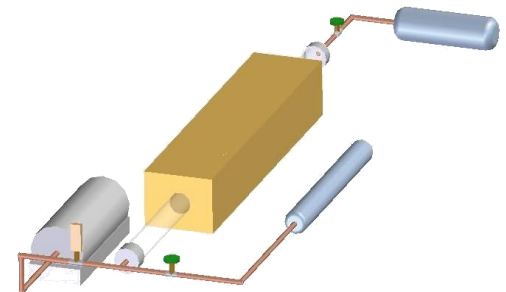
The oxygen isotope effect changes with sample's doping:  
In the SC phase  $\alpha > 0$ ;  
In the AFM phase  $\alpha < 0$   
In the SC phase  $\Delta n < 0$ ;  
In the AFM phase  $\Delta n < 0$

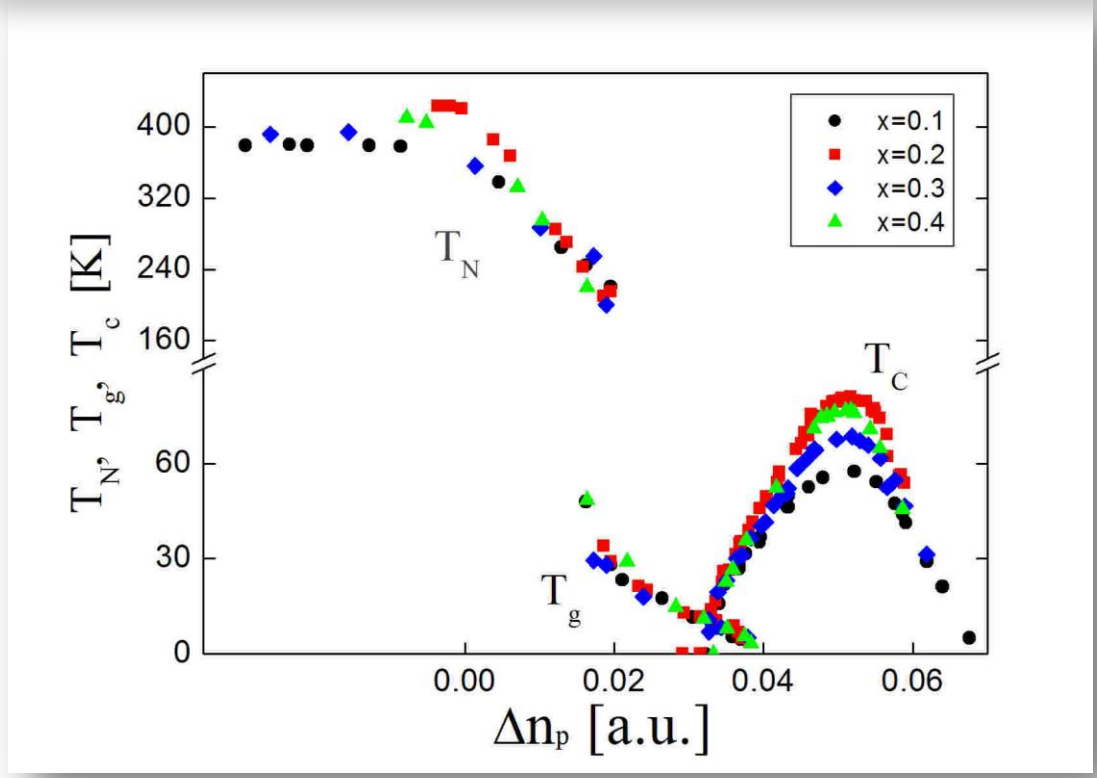
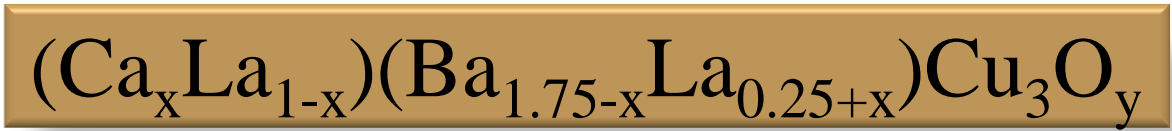
R. Khasanov *et al.*, PRL  
**101**, 077001 (2008)

A change of about 1% in the number of planar holes between the isotopes may explain the effect.

## Summary: The Isotope Effect in Cuprates

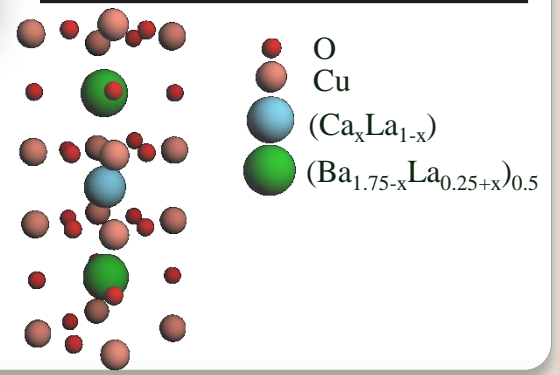
- We compared the Néel temperature of samples with  $^{16}\text{O}$  and  $^{18}\text{O}$  using  $\mu\text{SR}$ .
- The isotope coefficient was found to be  $\alpha_N = 0.005 \pm 0.011$
- Isotope substitution does not change the magnetic excitations.
- The isotope effect in cuprates can be explained by a change in the doping efficiency.
- In order to use isotope experiments to understand the mechanism of superconductivity, precise measurements should be performed on materials where  $T_C$  does not depend on doping.

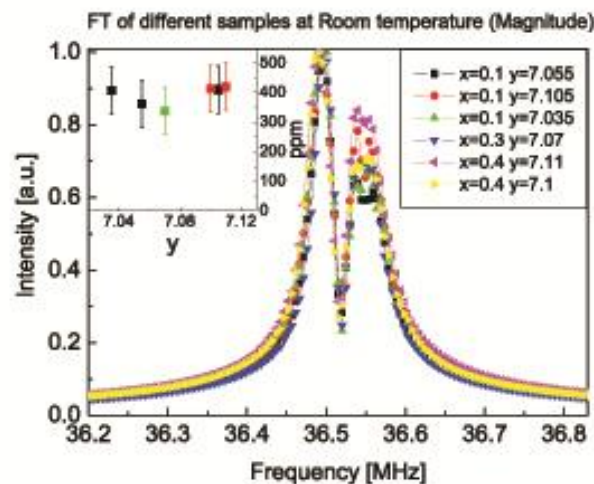
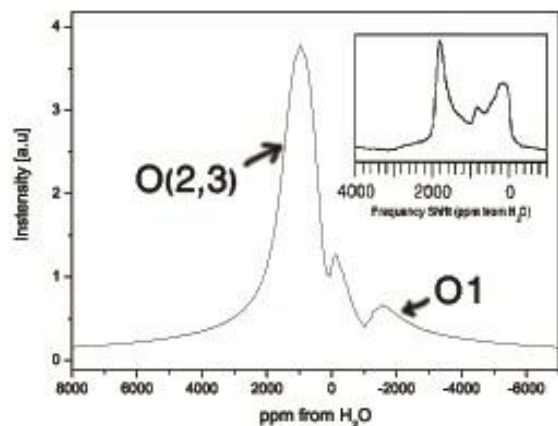
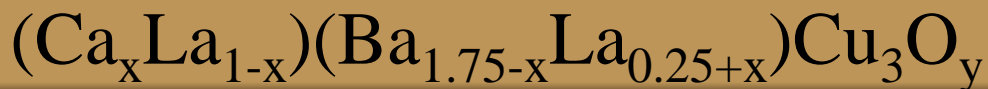




- y controls the total charge (doping).
- x controls the charge location.
- The total cation charge does not change with x.
- There's a 30% difference in  $T_c^{\max}$  between the families.

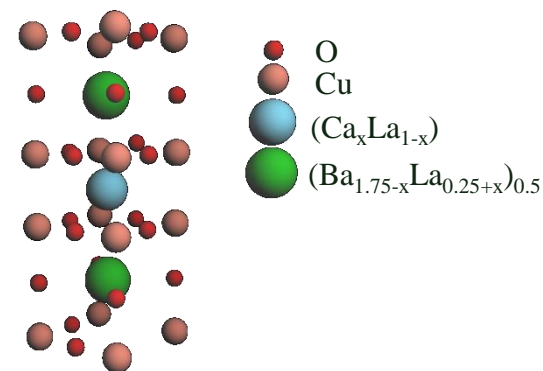
Could it be that it's all about impurities?





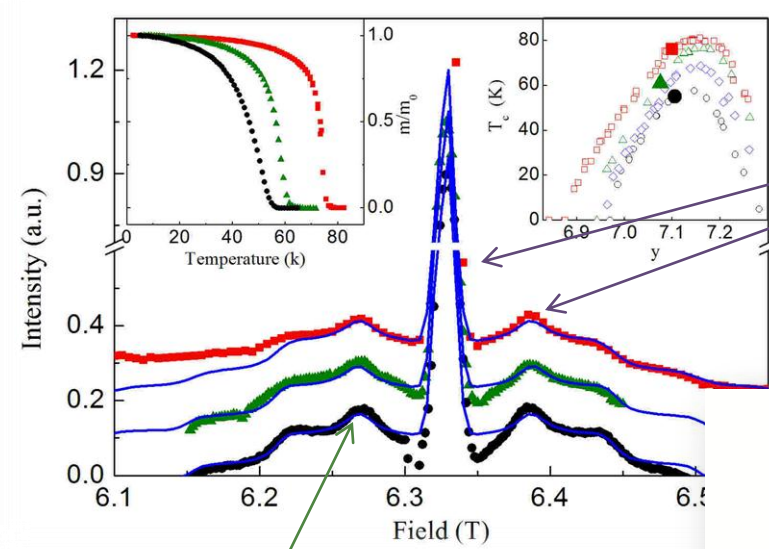
There are three oxygen sites in CLBLCO:

- Planar oxygen-  $\text{O}_{2,3}$
- Bridging oxygen-  $\text{O}_1$
- "Chain" oxygen-  $\text{O}_4$   
- has a wider peak



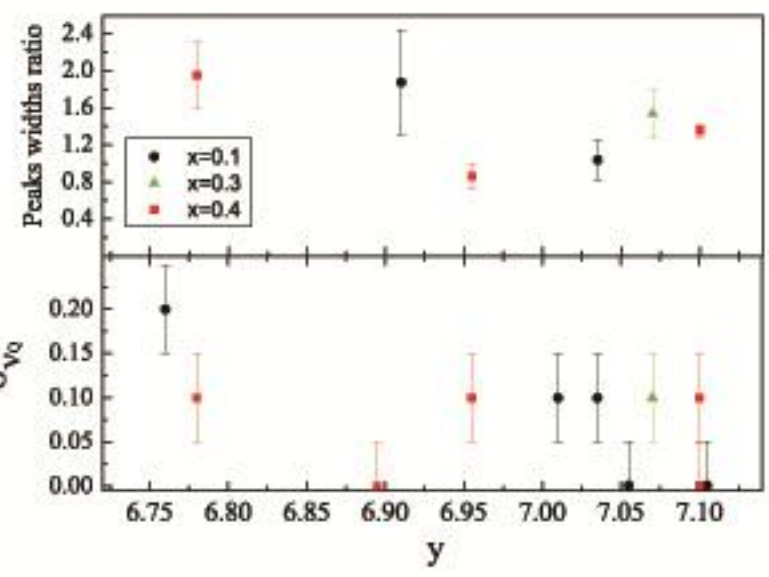
The widths of NMR signals are similar for all families.

# Quadrupole frequency as inhomogeneity measurement



Ratio of peaks width

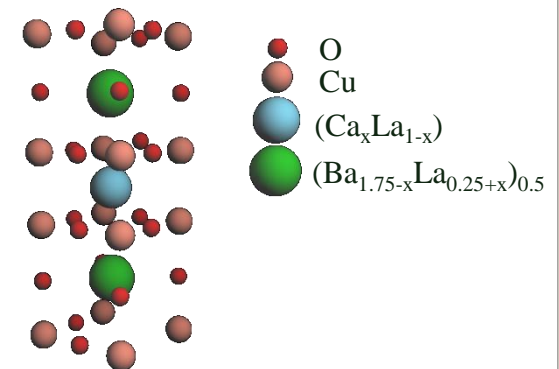
Charge inhomogeneity  
The quadrupole frequency distribution



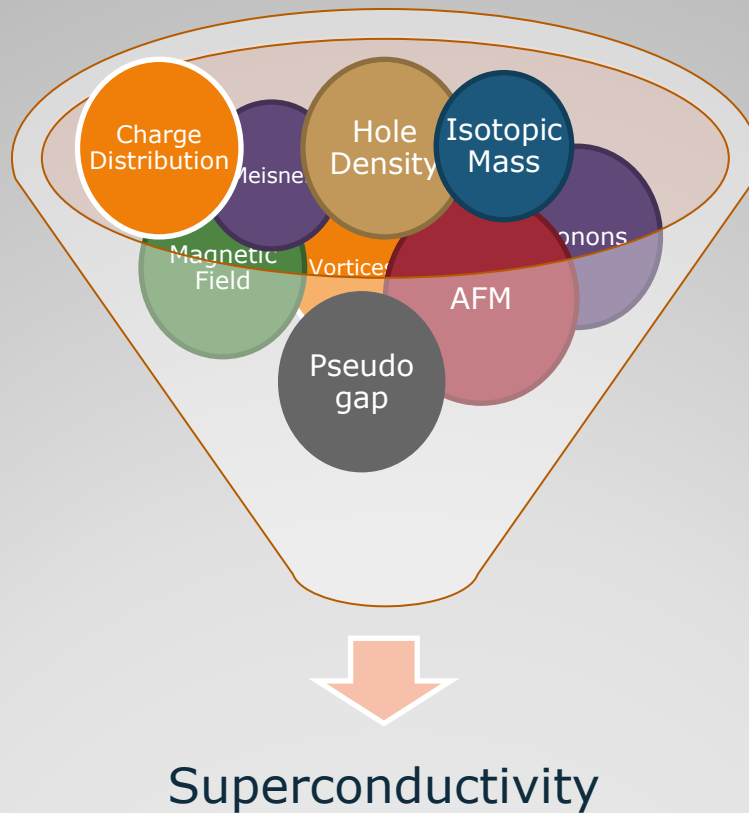
The widths of NMR signals are similar for all families.

# Quadrupole frequency as inhomogeneity measurement

- NMR does not show any difference in crystal quality of the different CLBLCO families.
- Impurities cannot explain the big difference in  $T_c^{\max}$  of the families.



# Summary: Small Effects in the Cuprates Phase Diagram



**The "hole" effect can be misinterpreted as some more exotic mechanism...**

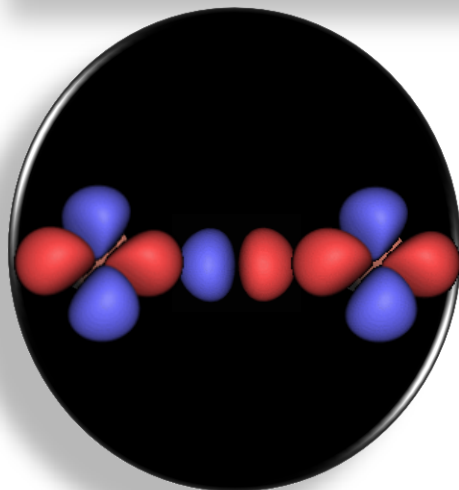
Thank you..





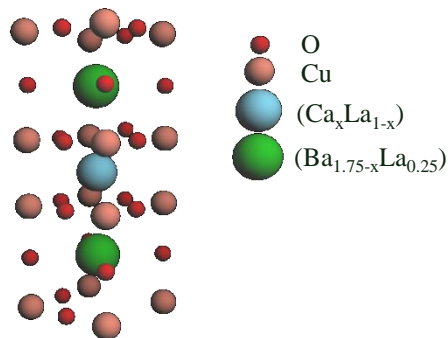
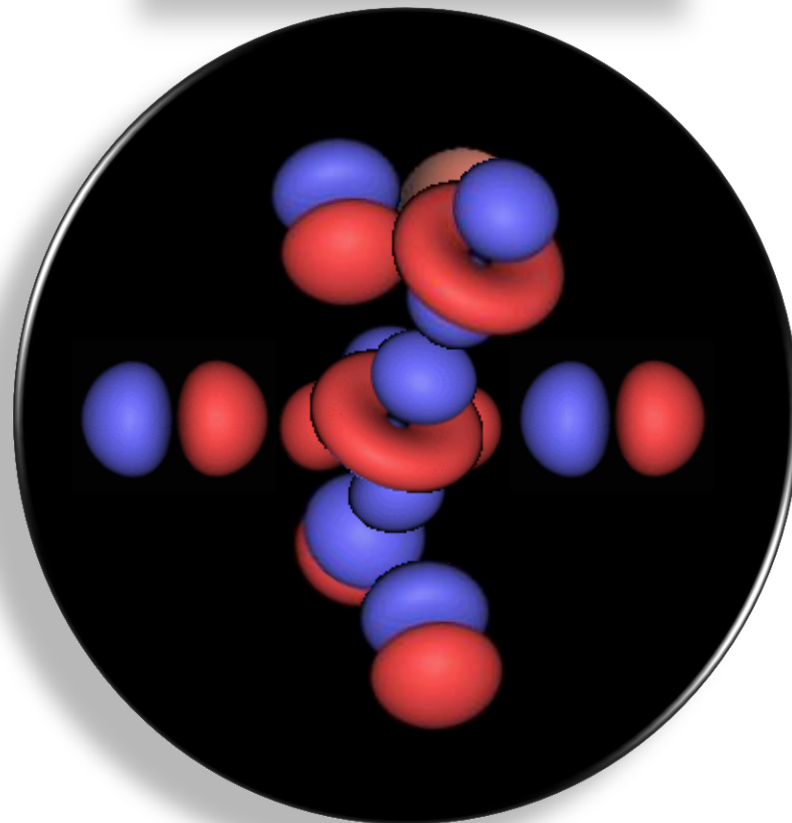
- It is very difficult to distinguish between the different contributions.

## Planar Oxygen



- $Cu\ 3d_{x^2-y^2}$
- $O\ 2p_{\sigma}$
- $Cu\ 3d_{z^2}$
- $O\ 2p_z$
- $Cu_{II}$
- $Cu\ 4s$

## Planar Copper



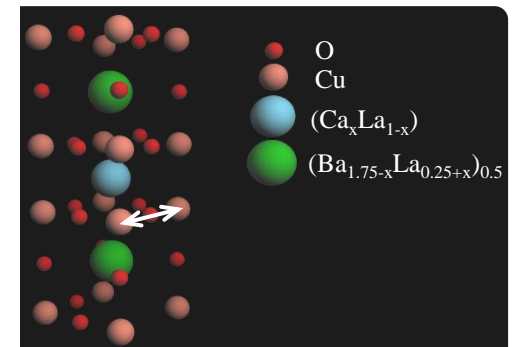
### Comparing samples of different families:

The typical length changes, but the symmetries of the electronic wavefunctions do not change.

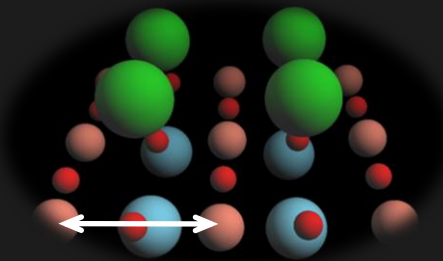


$$\Delta \nu_Q Ca_x^3 = \Delta n_p$$


**$\nu_Q$  measures the number of planar oxygen  $2p_\sigma$  holes**



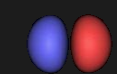
Planar oxygen in CLBLCO



Cu  $3d_{x^2-y^2}$



O  $2p_\sigma$



We measure at a constant frequency and change the external magnetic field.

For each field we integrate the real part of the spectrum.

The theoretical line is:

$$S(H, f) = \sum_{m=-\frac{3}{2}}^{\frac{5}{2}} W(m) \int_{\nu=0}^{\infty} d\sigma'_{iso} e^{-\frac{1}{2} \left( \frac{\sigma'_{iso} - \sigma_{iso}}{\Delta\sigma'_{iso}} \right)^2} \int_{\nu=0}^{\infty} d\nu'_Q e^{-\frac{1}{2} \left( \frac{\nu'_Q - \nu_Q}{\Delta\nu'_Q} \right)^2} \cdot \int_{\theta=0}^{\pi} \cos(\theta) d\theta \int_{\phi=0}^{2\pi} d\phi \delta \left( f(H, m, \sigma'_{iso}, \nu'_Q, \eta, \theta, \phi) - f \right)$$

$$f(H, m, \sigma, \nu_Q, \eta, \theta, \phi) = \gamma H [1 - \sigma_{iso}] + \nu_q \left[ \frac{1}{2} (3 \cos^2(\theta) - 1) - \frac{1}{2} \eta \sin^2(\theta) \cos(2\phi) \right] \left( m - \frac{1}{2} \right)$$

where  $S(H, f)$  is the intensity at external field  $H$  and frequency  $f$ .