

Detection of charge inhomogeneity in cuprates by NQR

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Outline

- Motivation.
- Magnetic resonance for spin $3/2$ nuclei.
- The YBCO compound.
- Three experimental methods and their results.
- Summary and conclusions.

Motivation

- The parent compounds of the cuprates superconductors are AFM insulators. Superconductivity is achieved by chemical doping.
- For some of these compounds there are evidence of phase separation in the CuO planes.
- Some theoretical work predict charge inhomogeneity as a natural consequence of an impurity independent Hamiltonian.

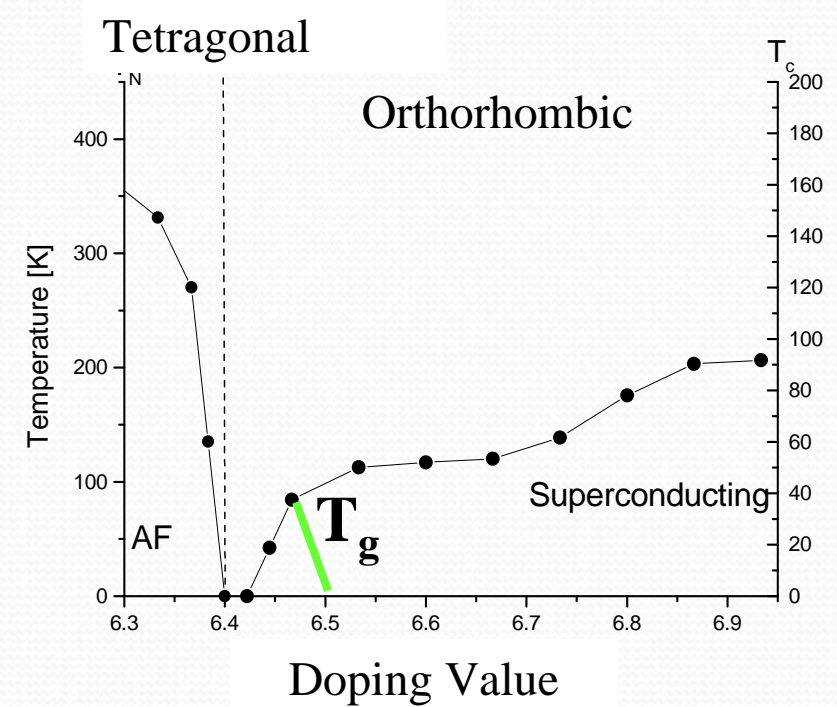
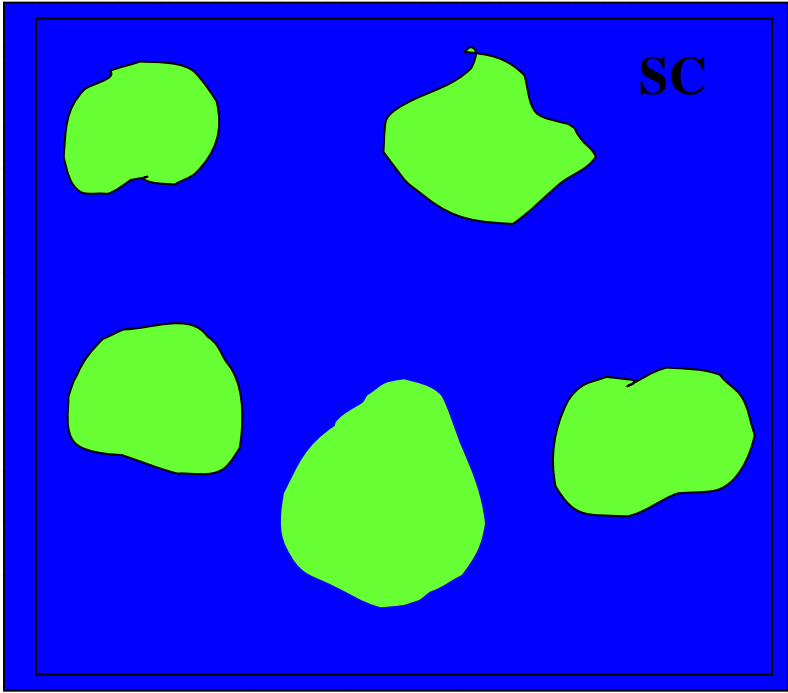
- Key question:

Is this phase separation an intrinsic property of the CuO planes and is it an essential part of the mechanism of HTSC? or is it a result of the chemical doping?

Evidence of inhomogeneity

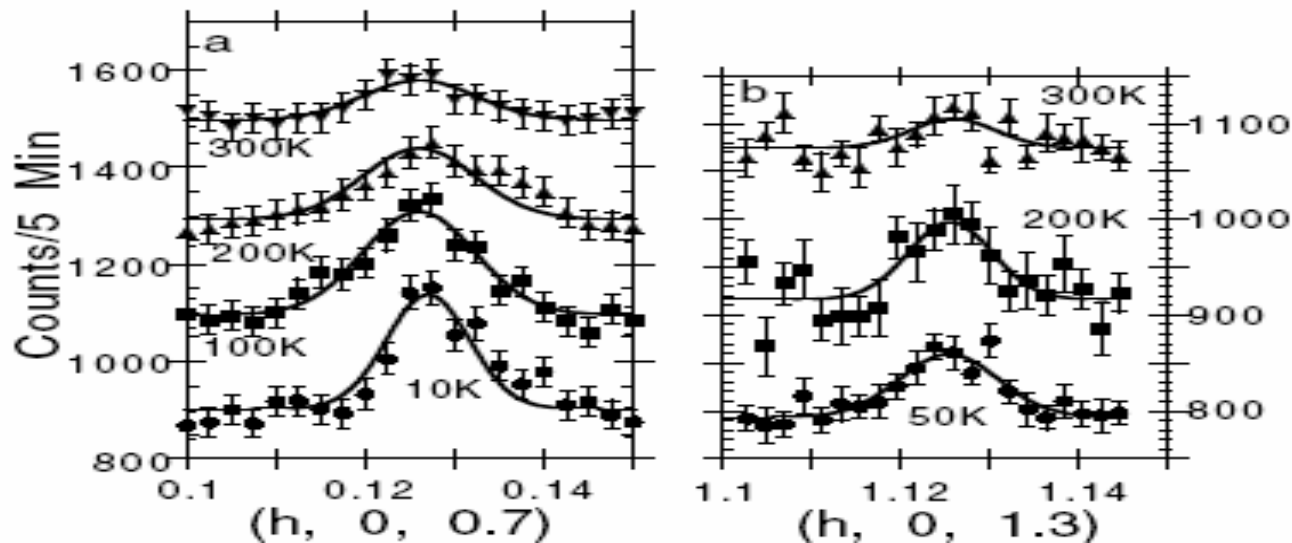
Low doping

μ SR



- This result supports the presence of some magnetic structure.
- Increasing the doping decreases the inhomogeneity.
- It seems that the structure is a remainder of the AF phase.

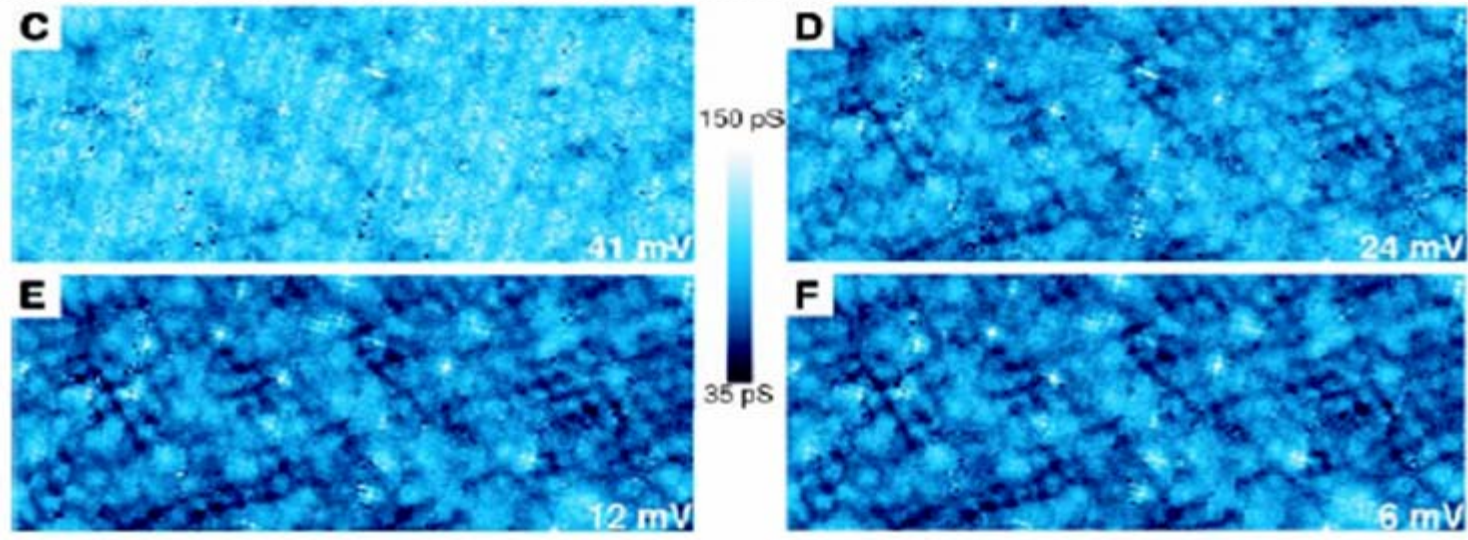
inhomogeneity with neutron scattering



Neutron scattering on YBCO_{6.35}

The charge distribution is measured indirectly by atoms that move in response to the charge.

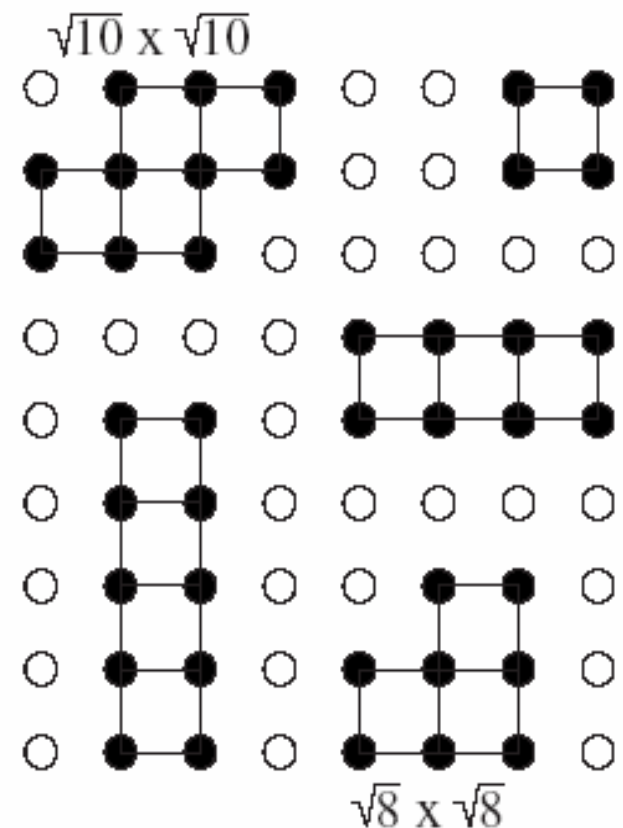
Evidence of inhomogeneity with STM



Real-space conductance maps of underdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ at 100K (pseudogap phase), showing the spatial dependence of the density of states.

Theoretical work

- A model for phase separation in 2D Hubbard model.
- For strong U : The doping driven transition from microscopic coexistence of AFM and SC to pure SC phase is accompanied by phase separation.



The problem

There is no clear correlation or anti-correlation between the dopant atoms and charge inhomogeneity.

Plan of operation

- Magnetic resonance experiment:
charge distribution in the bulk and not just on the surface.
- NQR measurements on the Cu nuclei,
the charge distribution in the Cu-O planes.
- The YBCO compound:
narrow NQR resonance lines,
distinguish between the different Cu resonance lines.

Nuclear Magnetic Resonance

- A nucleus under magnetic field $H_0 \hat{z}$

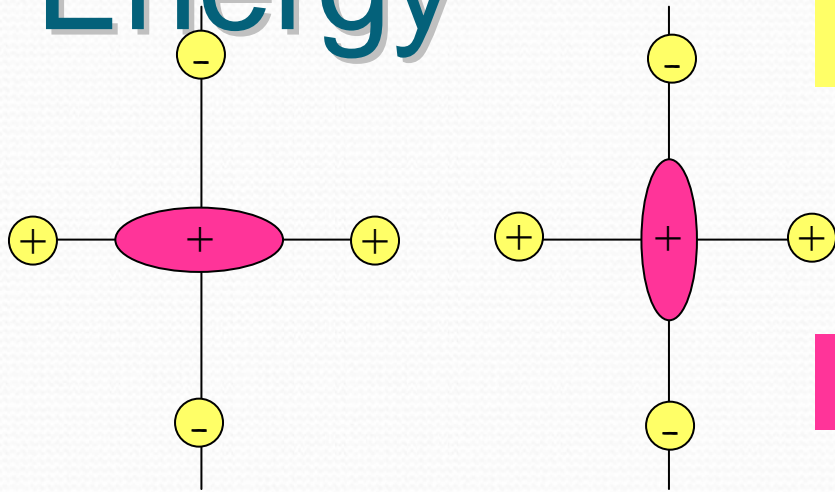
$$\mathcal{H} = -\vec{\mu} \cdot \vec{H}_0 = -\gamma \hbar H_0 I_z$$

- Energy levels: $E = -\gamma \hbar H_0 m$ $m = I, I-1, \dots, -I$

$$\omega_0 = \gamma H_0$$

- Transitions between the levels are forced by a rf magnetic field perpendicular to the static field.
- A nucleus in solid \rightarrow additional interactions \rightarrow shift the energy levels.
- We will focus on the **quadrupole interaction**.

The Quadrupole Energy



From the environment:

The EFG (Electric Field Gradient):

$$V(r) \Rightarrow \frac{\partial V}{\partial x_i \partial x_j} \equiv V_{ij} \quad i, j = x, y, z$$

From the nucleus:

I_x, I_y, I_z - The spin of the nucleus

The quadrupole Hamiltonian:

$$\mathcal{H} = \frac{\hbar v_q}{6} \left[3I_z^2 - I^2 + \eta \left(I_x^2 - I_y^2 \right) \right]$$

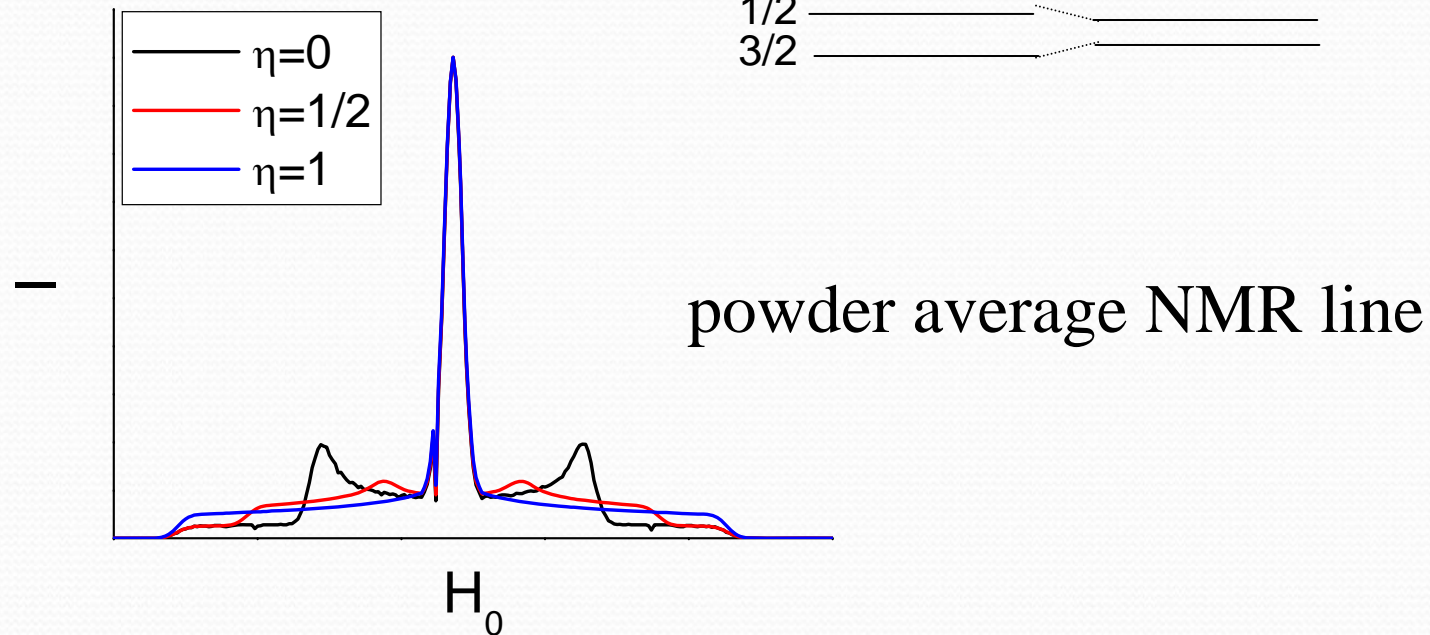
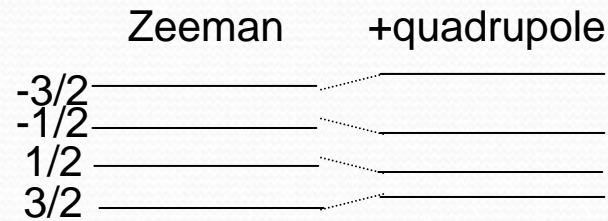
$$v_q \propto V_{zz} \quad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

η is a measure of charge inhomogeneity.

NMR

- Strong H_0 \rightarrow the quadrupole term is treated as a perturbation.

- For spin $3/2$ nuclei:



- η and ν_q can be extracted from the line shape.

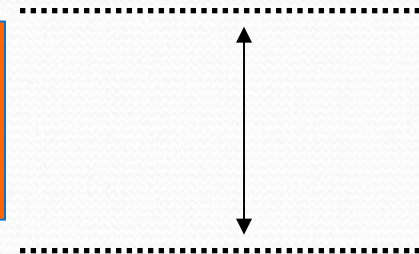
Pure NQR

- No permanent magnetic field

$$\mathcal{H} = \frac{\hbar\nu_q}{6} \left[3I_z^2 - I^2 + \eta \left(I_x^2 - I_y^2 \right) \right]$$

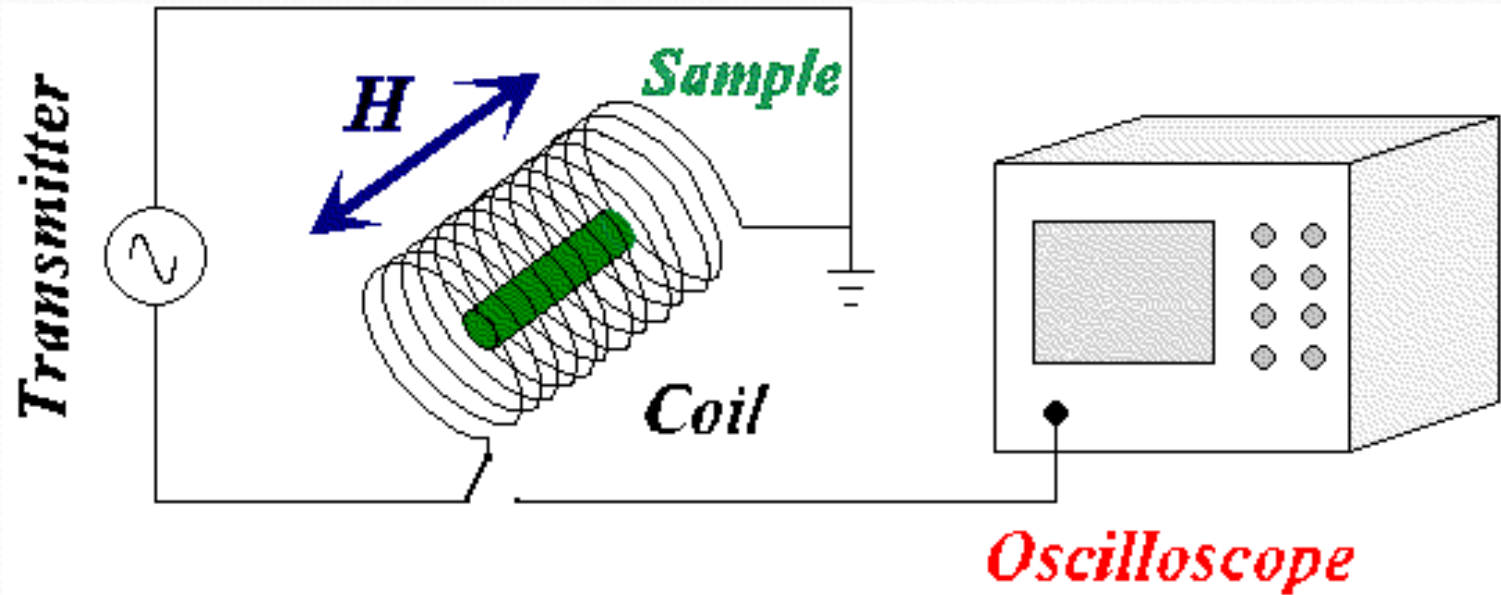
For a spin 3/2 nucleus:

$$f_{NQR} = \hbar\nu_q \sqrt{1 + \frac{\eta^2}{3}}$$



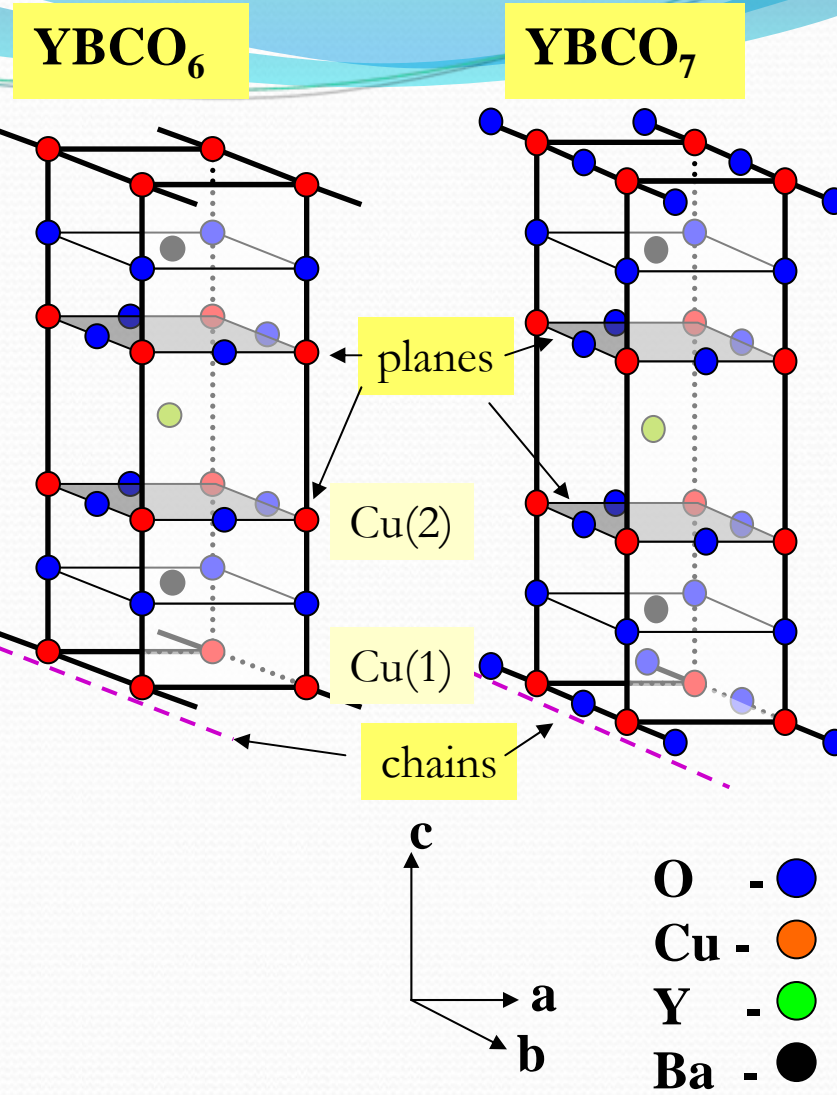
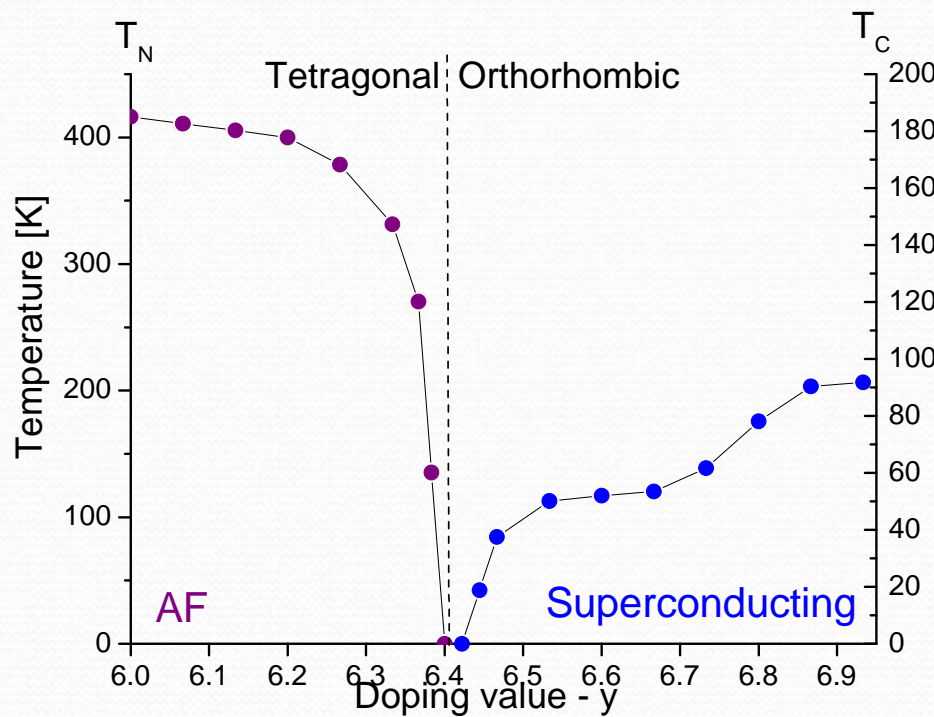
ν_q and η cannot be determined separately.

Technical aspects of NMR\NQR





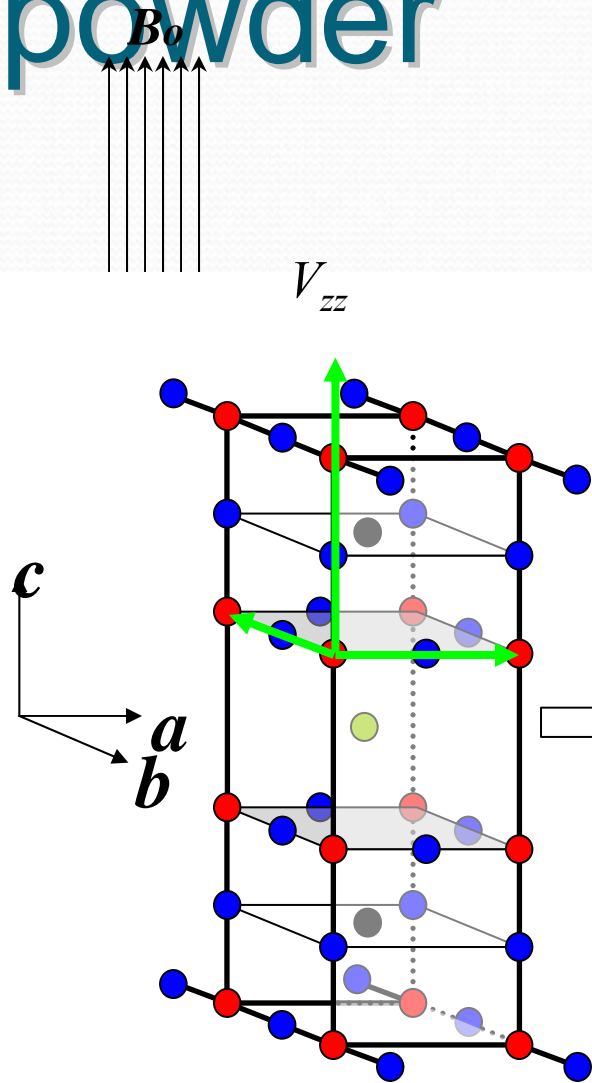
Phase diagram



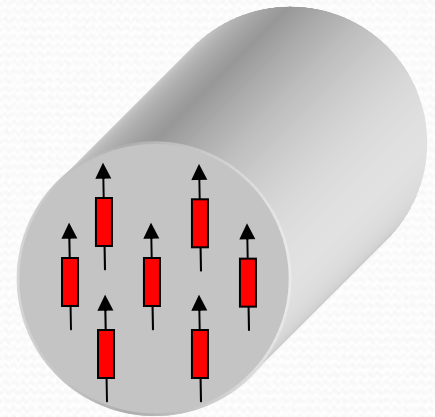
Unit cell

Our samples are unique in that they contain a single Cu^{63} isotope and not two.

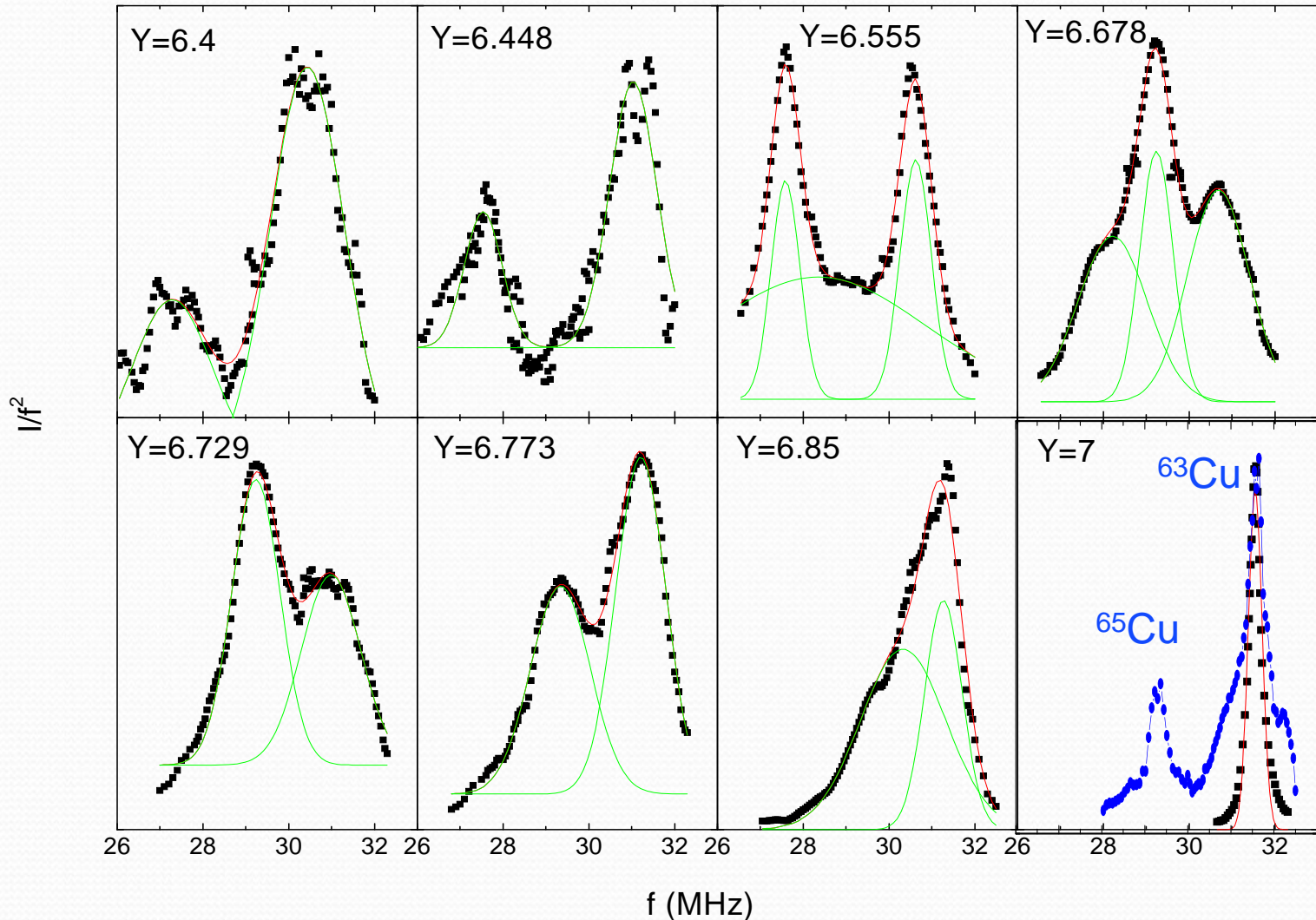
Orientation of the YBCO powder



- In YBCO₇ V_{zz} is in the c direction.
- η is a measure of charge homogeneity in the CuO₂ planes.

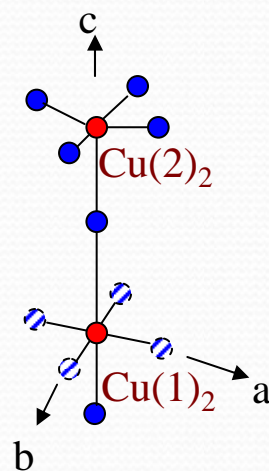
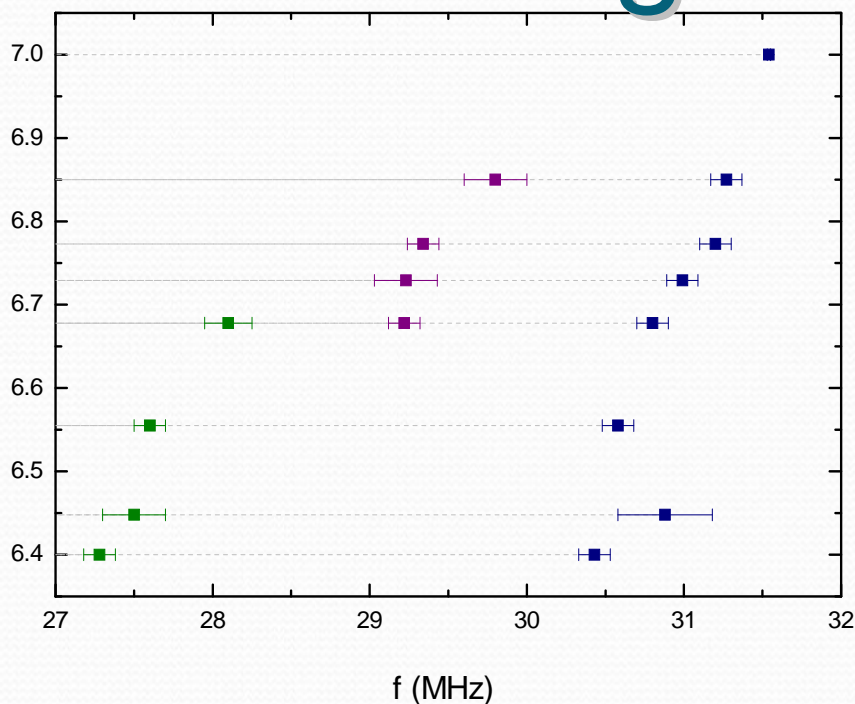


NQR lines for YBCO

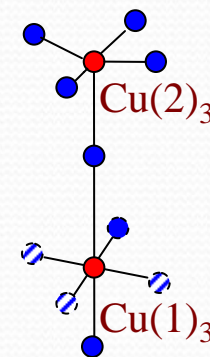


One can see the importance of enrichment, without it lines would overlap.

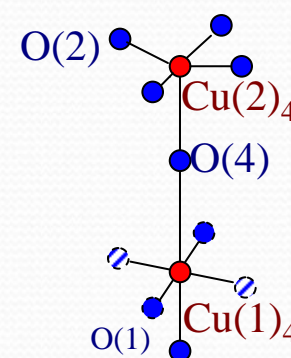
Site assignment






$Y=6$



$Y=6.5$



$Y=7$

Oxygen atom 
 Oxygen vacancy 
 Copper atom 

3 different $\text{Cu}(2)$ lines, for the 3 different ionic environments:

- 31MHz: $\text{Cu}(2)$ with full chain.
- 29MHz: $\text{Cu}(2)$ with chain half full, $\text{Cu}(1)$ with coordination 3.
- 27.5MHz: conducting $\text{Cu}(2)$ with empty chains.

Our Main motivation; finding

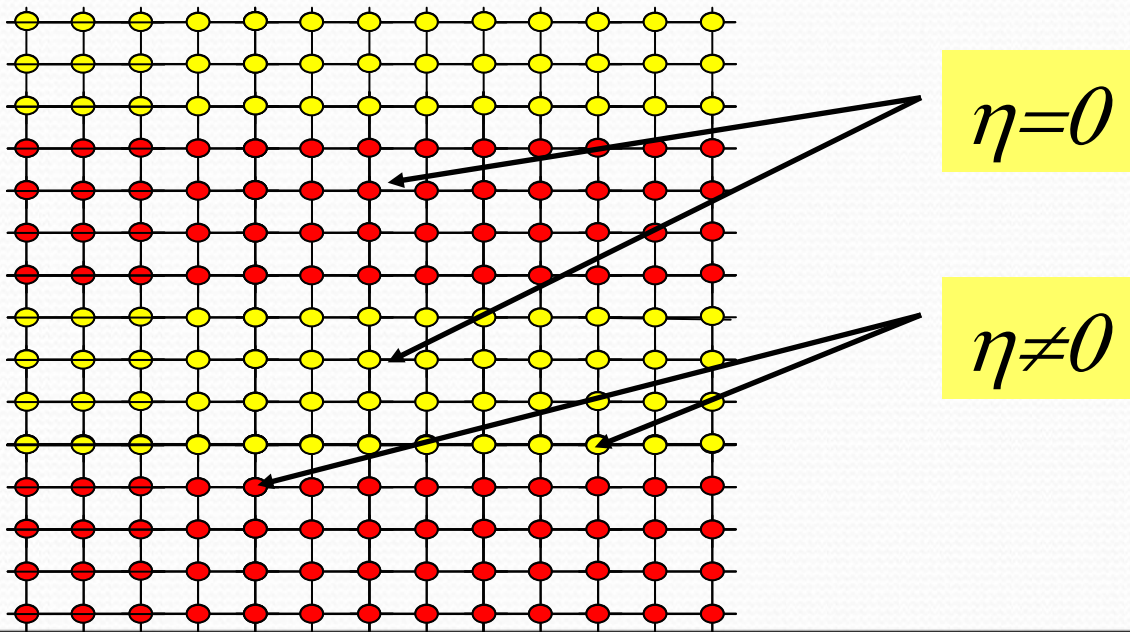
η

$$f_{NQR} = \hbar v_q \sqrt{1 + \frac{\eta^2}{3}}$$

$$v_q \propto V_{zz} \quad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

For YBCO_7 V_{zz} is in the c direction of the lattice. \rightarrow

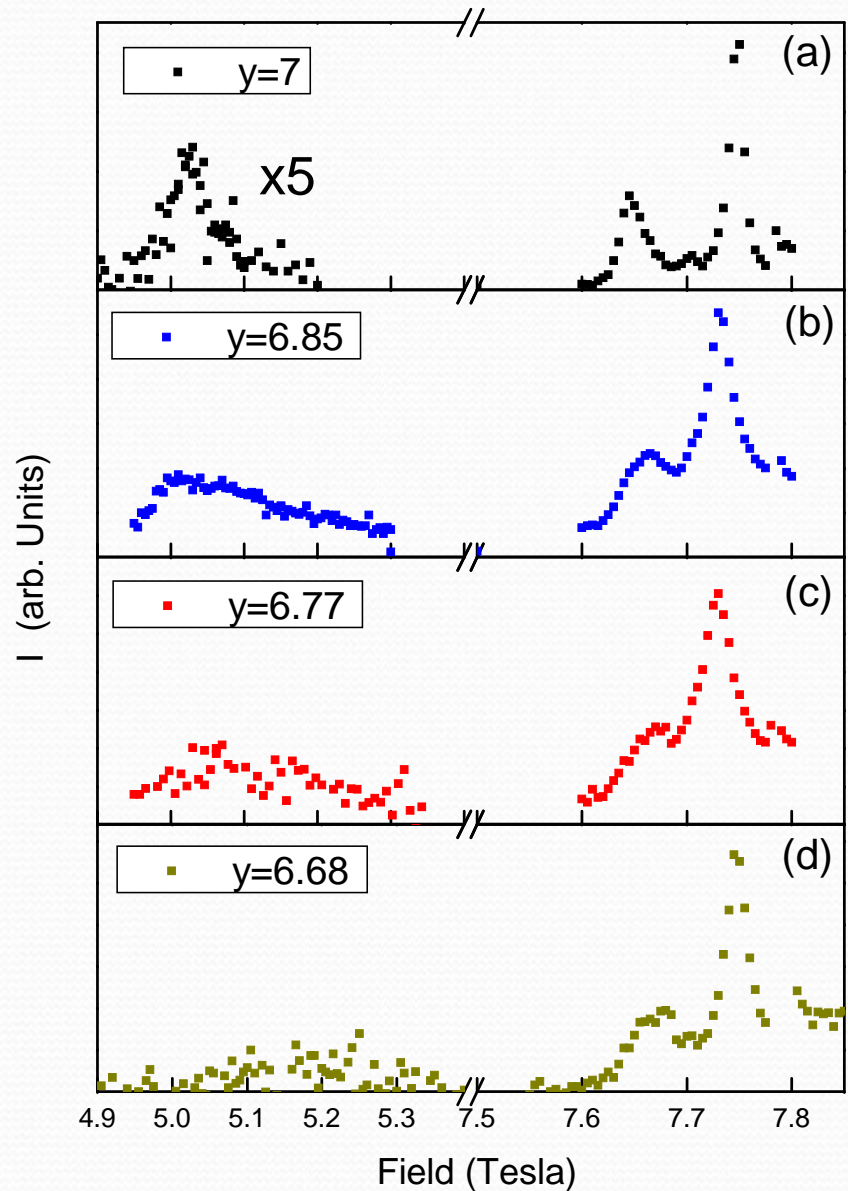
η determines the homogeneity of the charge distribution in the CuO planes:



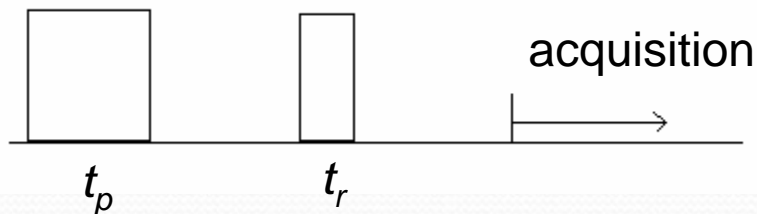
NMR Results

- For lower doping levels, the satellites disappear

→ η cannot be extracted.



Nutation Spectroscopy



- Measuring the NQR signal as a function of t_p .
- The intensity of the signal after a time t :

$$I(t_p, \theta, \phi, \eta) \propto \lambda(\theta, \phi) \sin \left(\frac{\lambda(\theta, \phi)}{2\sqrt{3 + \eta^2}} \gamma H_1 t_p \right) \sin^2 \left(\frac{\lambda(\theta, \phi)}{\sqrt{3 + \eta^2}} \gamma H_1 t_r \right) \sin(\omega_Q t)$$

- where: $\lambda(\theta, \phi) = \sqrt{(9 + \eta^2 + 6\eta \cos(2\phi)) \sin^2 \theta + 4\eta^2 \cos^2 \theta}$
- Fourier transform over t_p gives the frequency:

$$\omega_p(\theta, \phi) = \frac{\lambda(\theta, \phi)}{2\sqrt{3 + \eta^2}} \gamma H_1$$

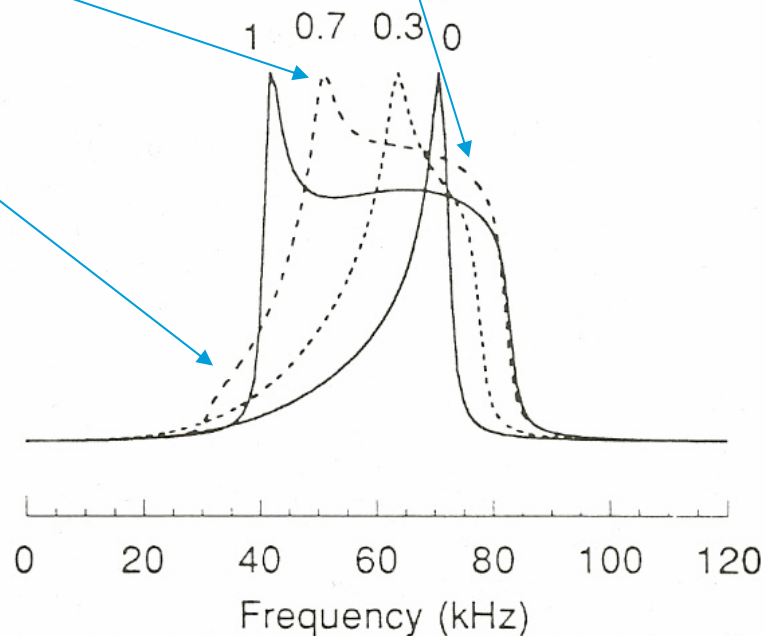
Nutation Spectroscopy

- Three singularities:

$$\frac{2\eta}{2\sqrt{3+\eta^2}}\gamma H_1, \quad \frac{3-\eta}{2\sqrt{3+\eta^2}}\gamma H_1, \quad \frac{3+\eta}{2\sqrt{3+\eta^2}}\gamma H_1$$

- Theoretical $I(\omega_p)$
for different η :

The location of the singularities is independent of the EFG orientation.



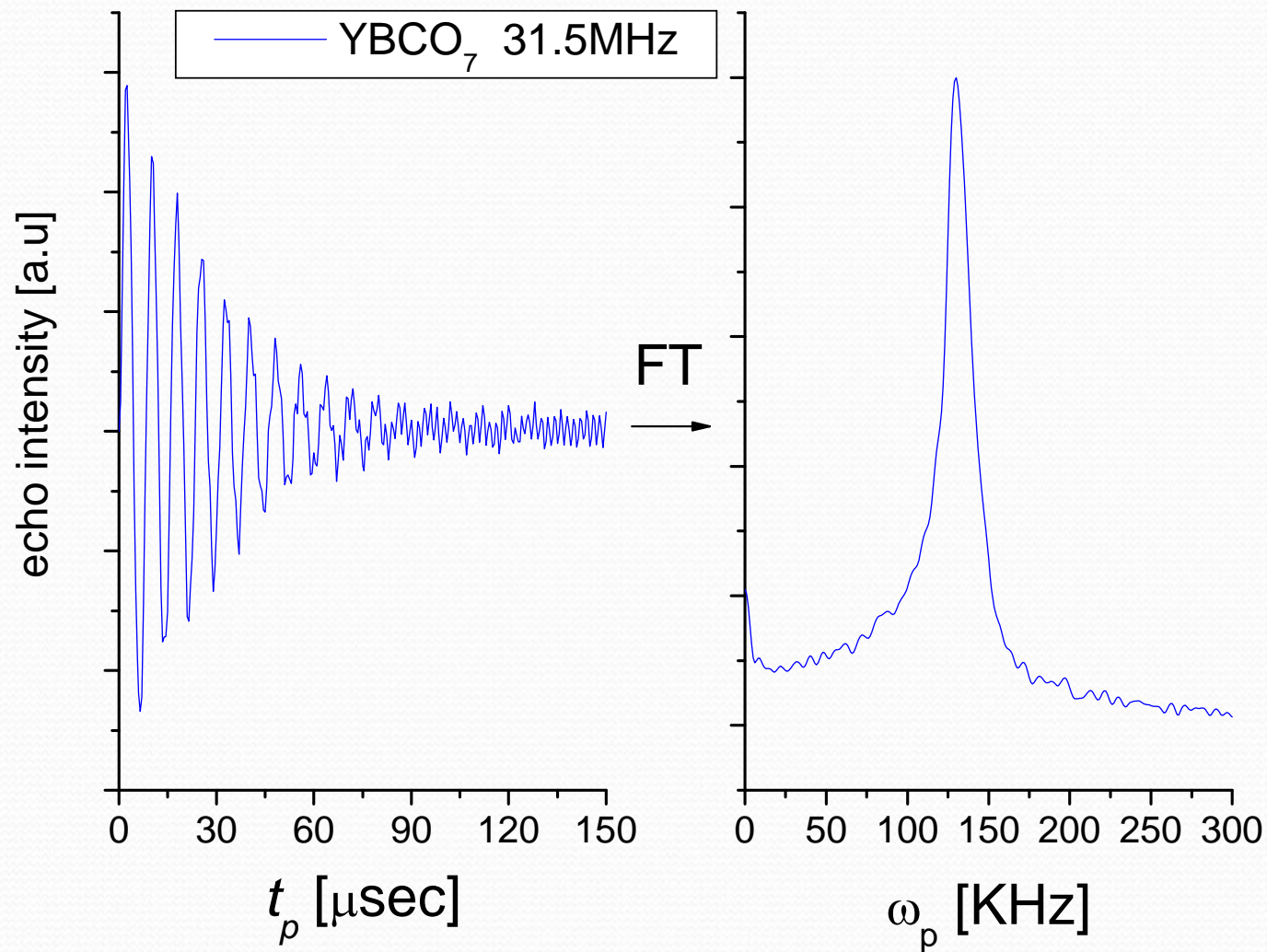
The nutation probe

- Small sample in a long coil to improve the homogeneity H_1 .
- A current monitor - perform all measurements with the same H_1 .



$$\omega_p(\theta, \phi) = \frac{\lambda(\theta, \phi)}{2\sqrt{3 + \eta^2}} \gamma H_1$$

Nutation raw data

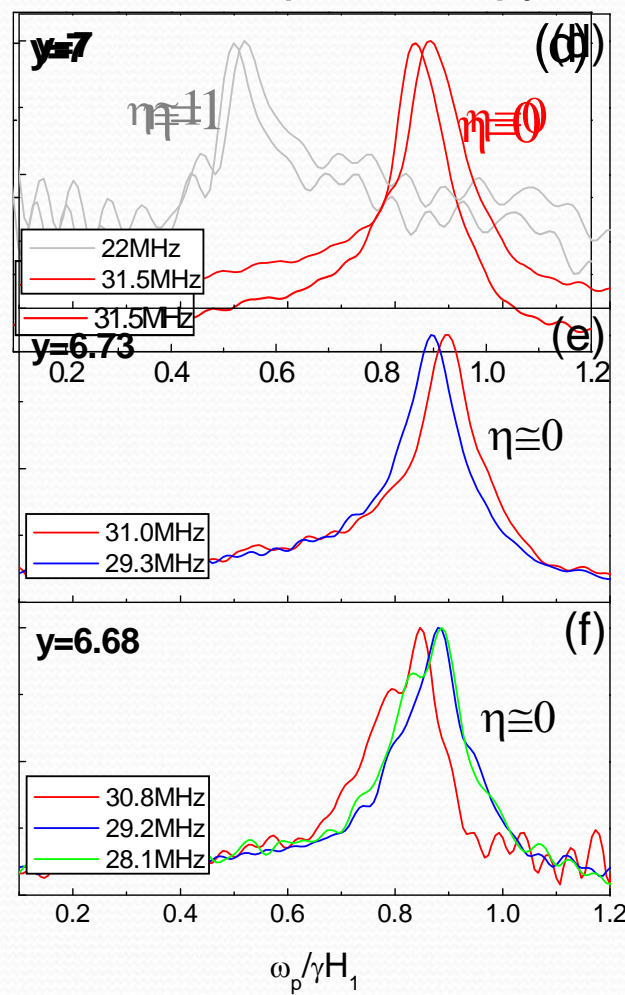
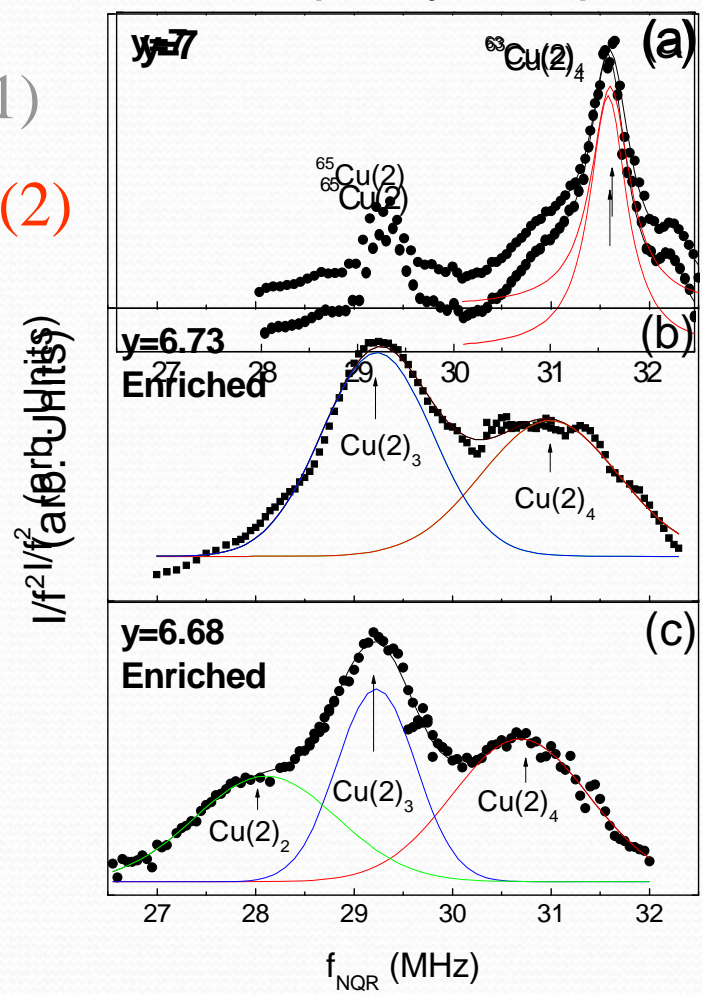


Nutation Results

Frequency sweep

Nutation spectroscopy

22 MHz - Cu(1)
31.5 MHz - Cu(2)

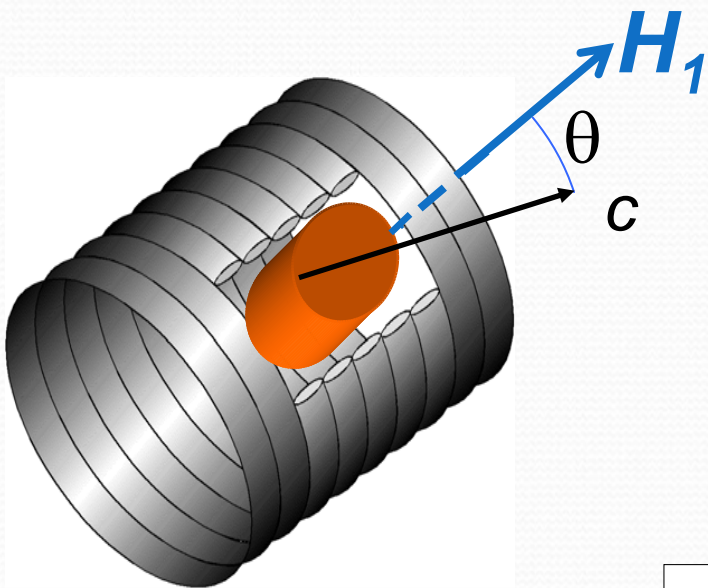


I (arb. units)

Nutation Results

- For YBCO_7 :
Cu(2) $\eta=0$
Cu(1) $\eta=1$
- For lower doping:
 $\eta \approx 0$ for all different Cu(2) environments.
- Not sensitive to the EFG orientation.

Angle dependant NQR



$$\mathcal{H}_{NQR} = \frac{\hbar\nu_q}{6} \left[3I_z^2 - I^2 + \eta \left(I_x^2 - I_y^2 \right) \right]$$

$$\mathcal{H}_{rf} = \hbar\gamma \vec{H}_1 \cdot \vec{I} \cos(\omega t)$$

$$\vec{H}_1 = H_1 \left[\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta \right]$$

- For $\eta=0, \theta=0$

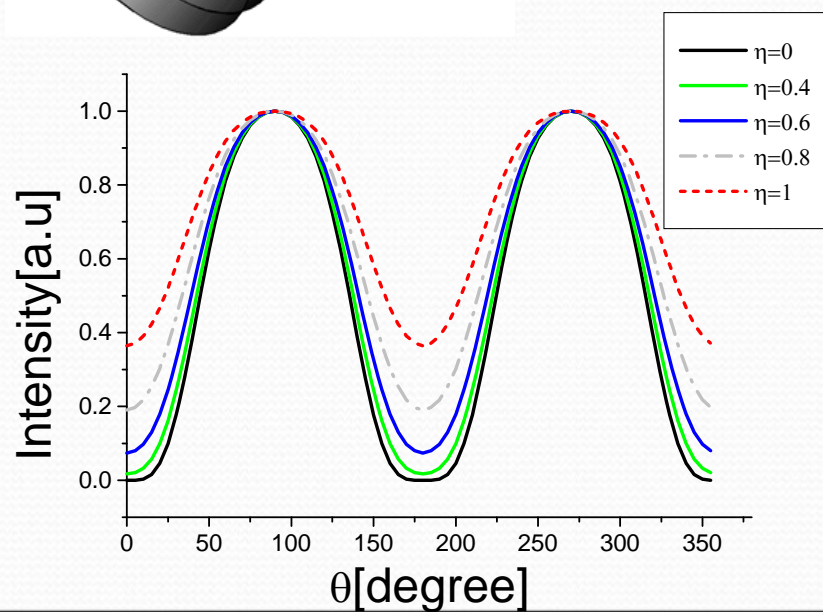
\mathcal{H}_{NQR} and \mathcal{H}_{rf} commute

➡ no spin transitions.

- For $\eta>0,$

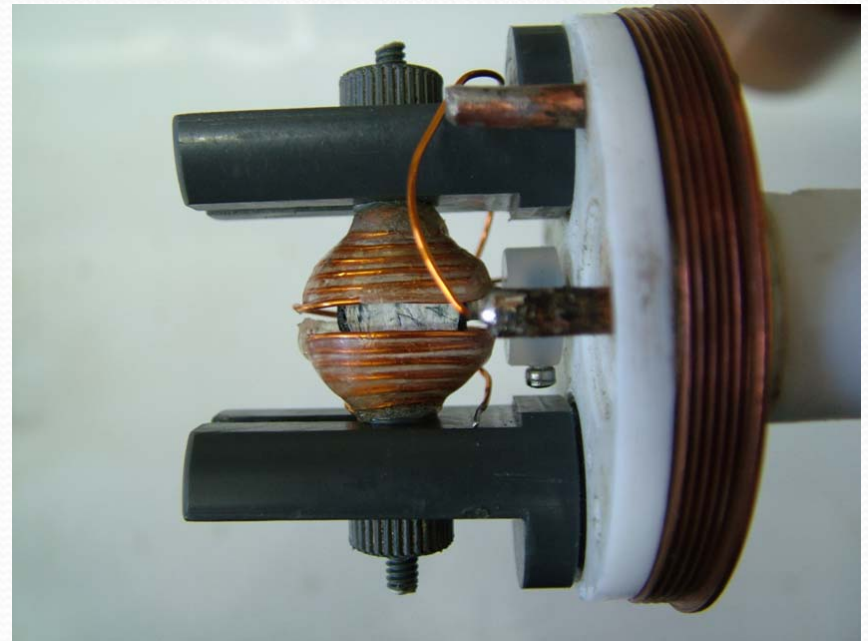
\mathcal{H}_{NQR} and \mathcal{H}_{rf} do not commute even for $\theta=0$

➡ signal even for $\theta=0.$



The ADNQR probe

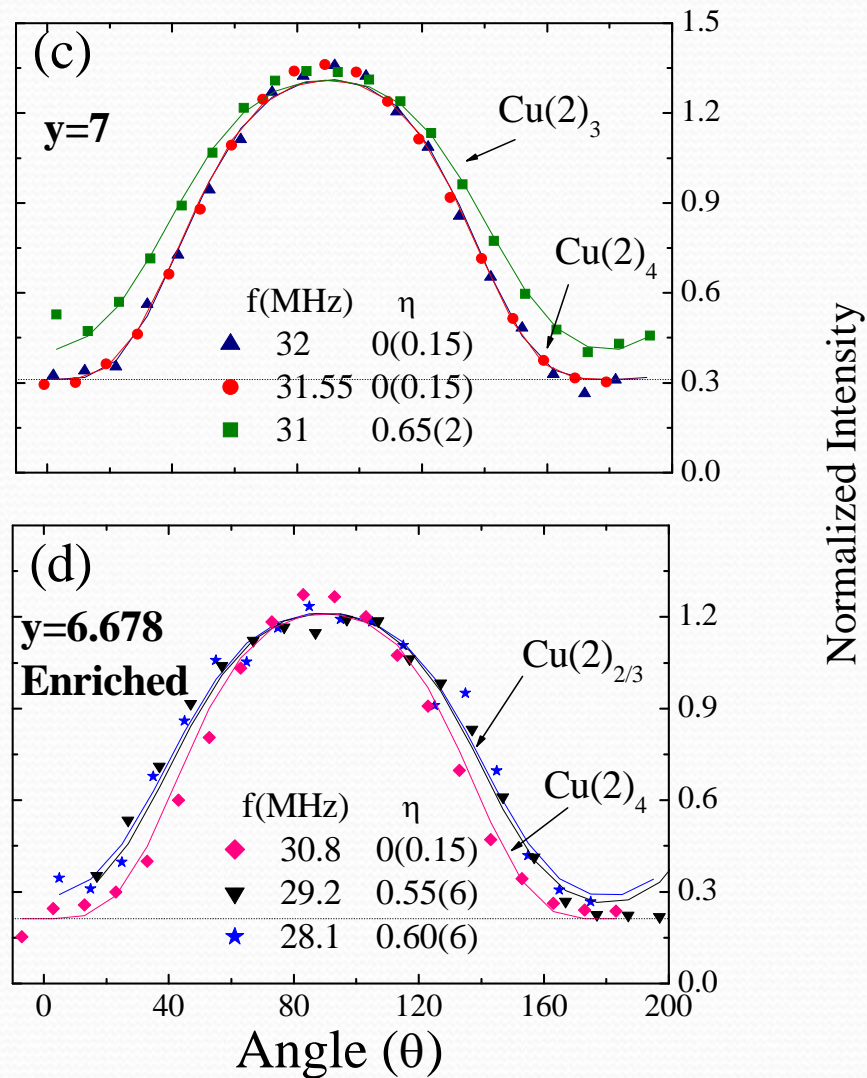
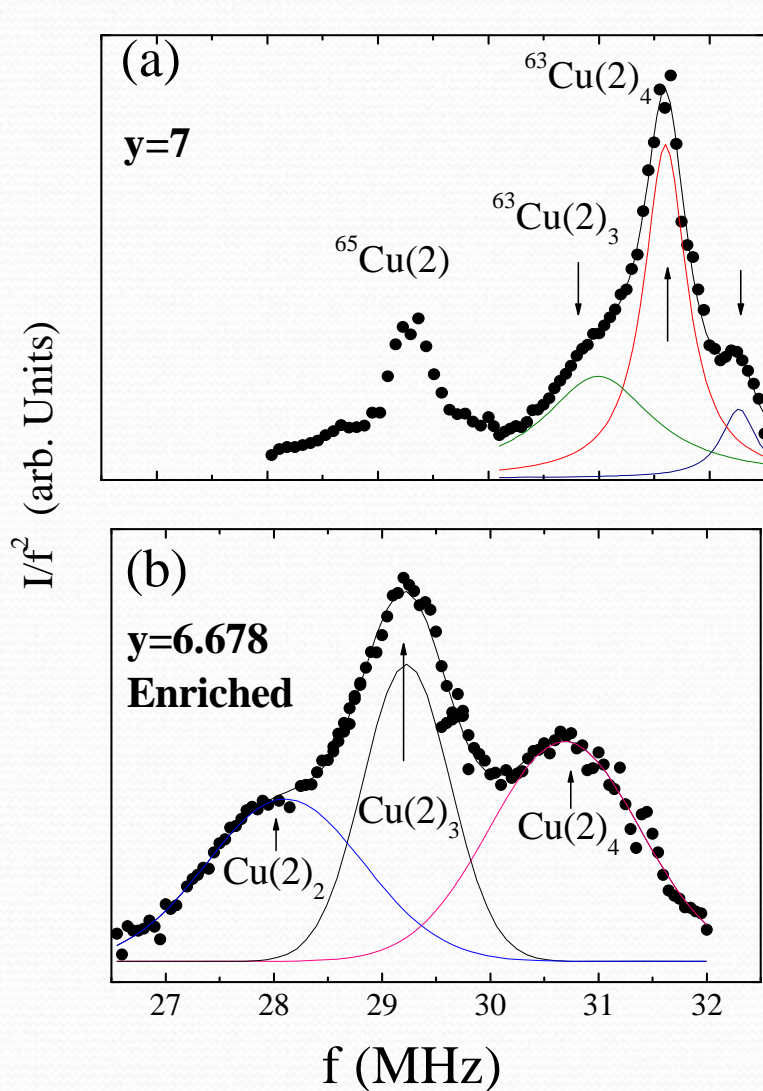
- Spherical coil to improve the homogeneity of the rf field.
- Connection to a motor for an automated rotation of the sample. (ability to measure at low temperatures).



ADNQR results

Frequency sweep

ADNQR



Interpretation

- The ADNQR assumes $V_{zz} \parallel c$.
- This is true for YBCO_7 , what about lower doping?
- An alternative explanation for the $\text{YBCO}_{6.68}$ with oxygen deficiency in the chain:

Rotation of V_{zz} from the c direction:

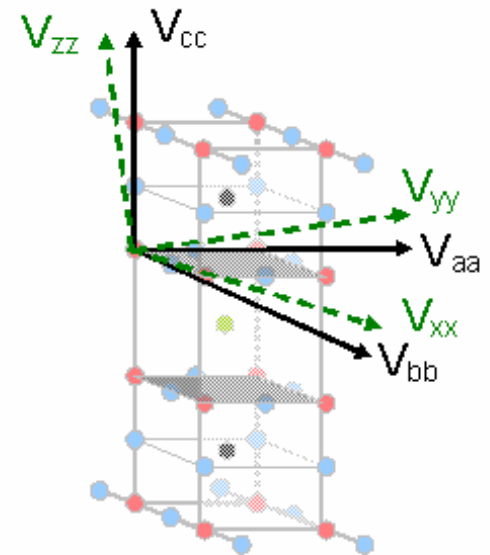
- When $V_{zz} \perp c$:

$$\mathcal{H}_{NQR} = \frac{\hbar v_q}{6} \left[3I_z^2 - I^2 + \eta \left(I_x^2 - I_y^2 \right) \right]$$

$$\mathcal{H}_{rf} = \hbar \gamma \vec{H}_1 \cdot \vec{I} \cos(\omega t)$$

$$\vec{H}_1 = H_1 \left[\sin \theta \cos \phi, \cos \theta, \sin \theta \sin \phi \right]$$

\mathcal{K}_{NQR} and \mathcal{K}_{rf} do not commute even for $\eta=0$.



Summary

- YBCO_7 - $\eta=0$, the CuO_2 plane is charge homogeneous.
- For lower doping:
 - **NMR** – η cannot be determined
 - **Nutation** – $\eta=0$ for all different Cu(2) environments.

Not sensitive to the EFG orientation.

- **ADNQR:** – For Cu(2) neighboring a full chain - $\eta=0$

For Cu(2) next to an oxygen deficiency in the chain –there is a rotation of V_{zz} from the c direction.

Conclusion

- Any charge inhomogeneity in the CuO_2 planes is found only in conjunction with oxygen deficiency in the chains.

In other words,

if there is a phase separation in the planes in the YBCO compound, it is correlated with the O dopant atoms.

END