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

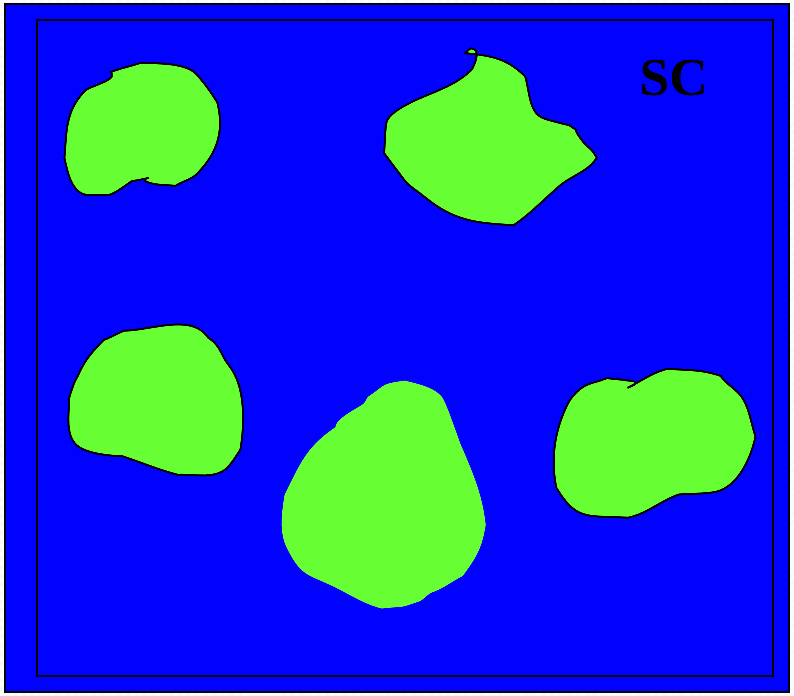
- The parent compounds of the cuprates superconductors are AFM insulators. Superconductivity is achieved by chemical doping.
- For some of these compounds there are evidence of phase separation in the CuO planes.
- Some theoretical work predict charge inhomogeneity as a natural consequence of an impurity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

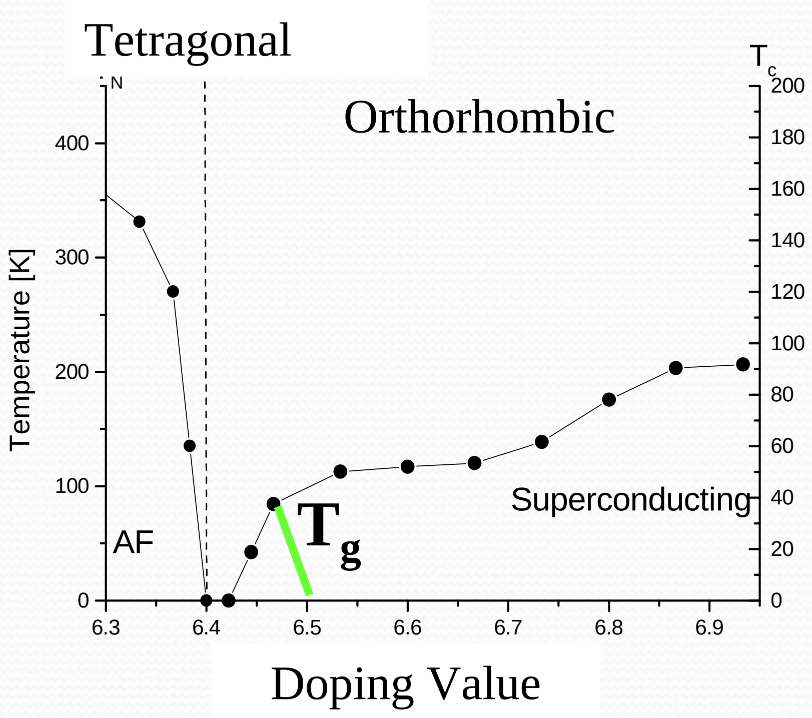
  Is this phase separation an intrinsic property of the CuO planes and is it an essential part of the mechanism of HTSC? or is it a result of the chemical doping?

Evidence of inhomogeneity

Low doping

μSR

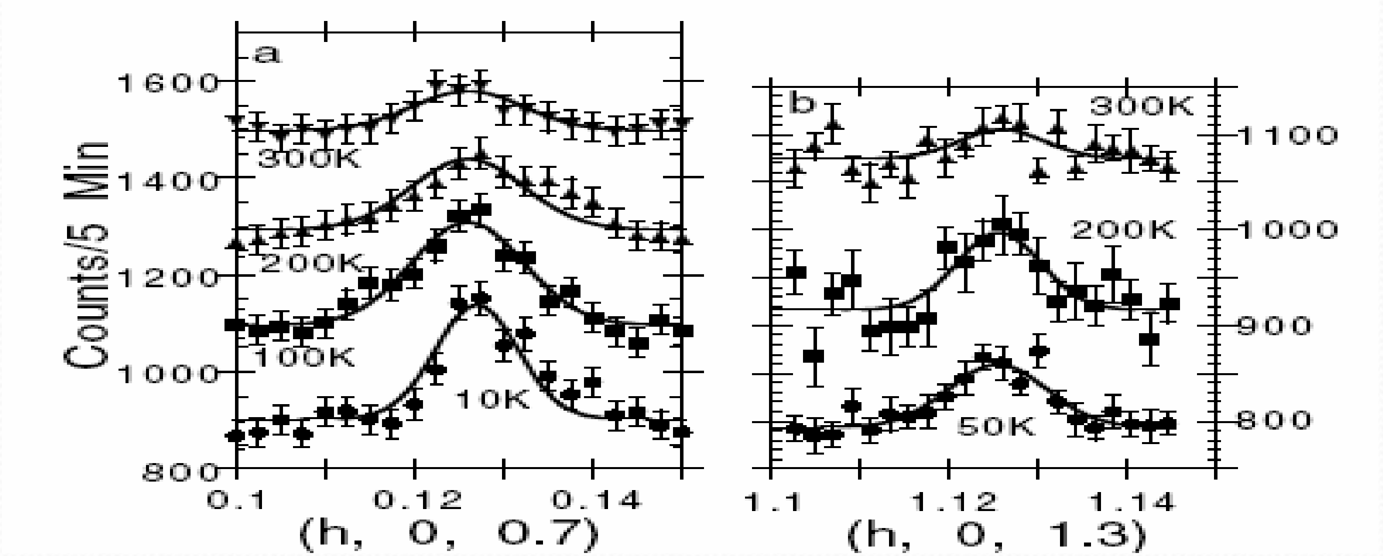




- This result supports the presence of some magnetic structure.
- Increasing the doping decreases the inhomogeneity.
- It seems that the structure is a remainder of the AF phase.

Evidence of charge inhomogeneity with neutron scattering

Low doping



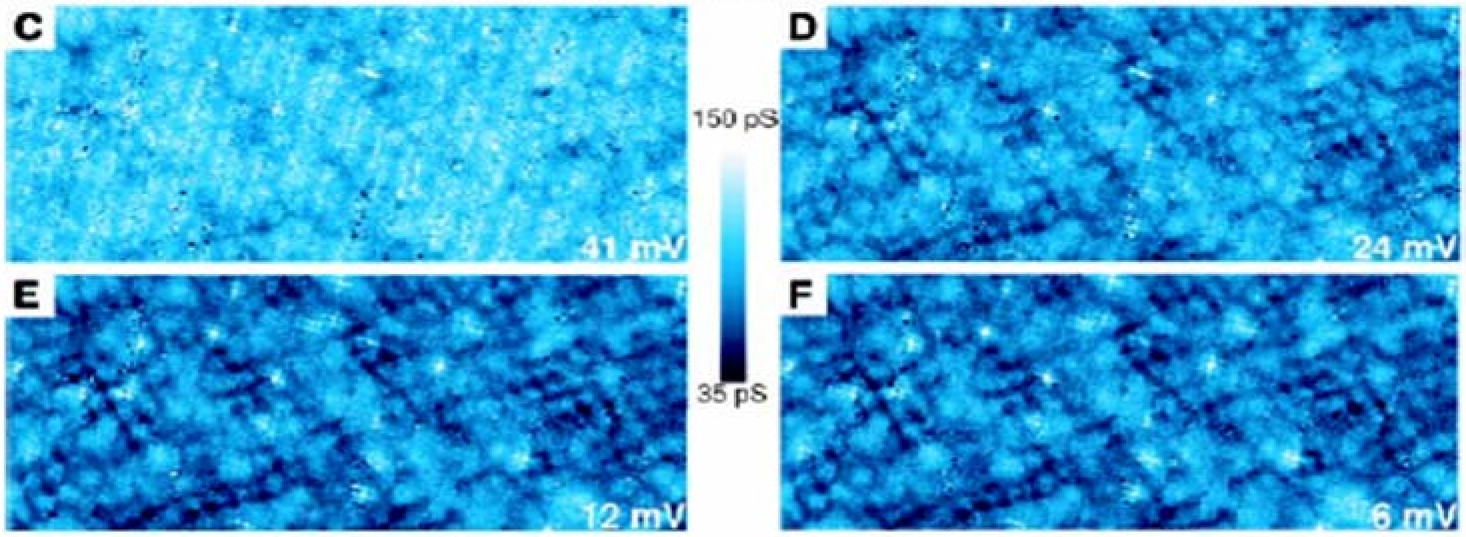
Neutron scattering on $YBCO_{6.35}$

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

H. A. Mook *et al,* Phys. Rev. Lett., **88**, 097004 (2002)

Evidence of inhomogeneity with STM

Surface

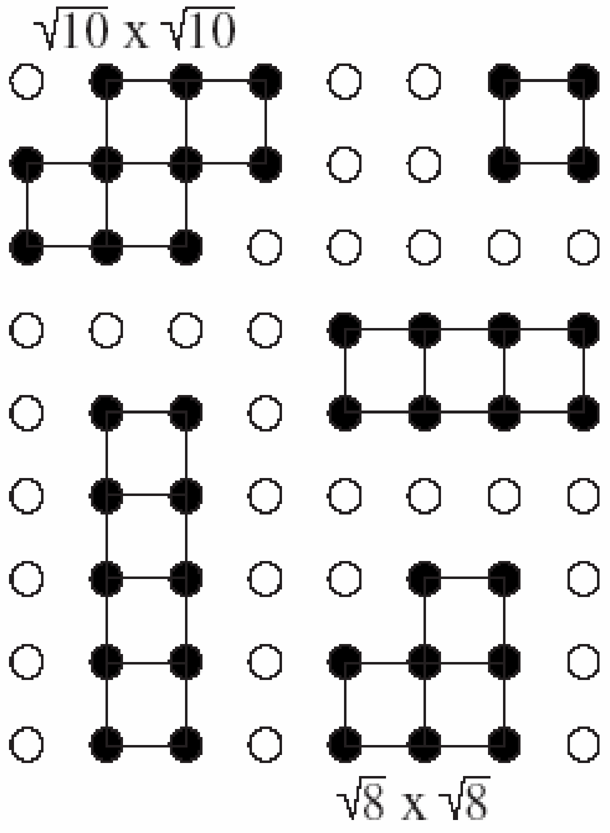


Real-space conductance maps of underdoped $Bi_2Sr_2CaCu_2O_y$ at 100K (pseudogap phase), showing the spatial dependence of the density of states.

M. Vershinin *et al,* Science, **303**, 1995 (2004)

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.



M. Aichhorn *et al,* Phys. Rev. B, **76**, 224509 (2007)

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 $H_0\hat{z}$

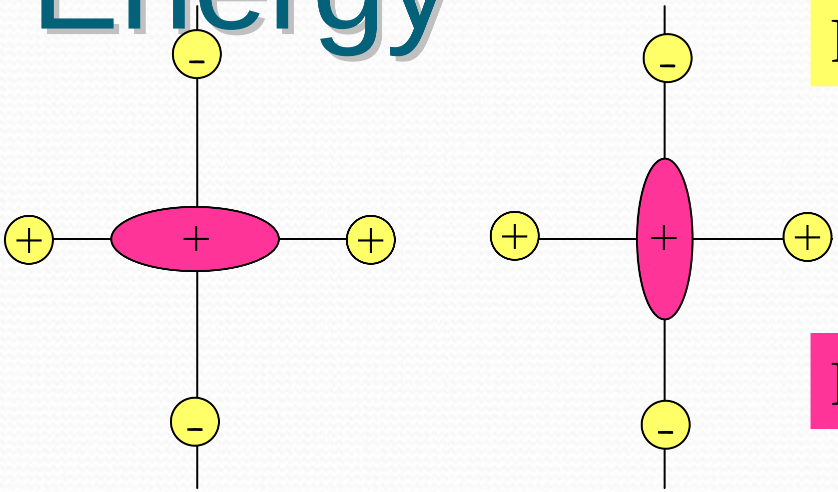
$$\mathcal{H} = -\vec{\mu}\cdot\vec{H}_0 = -\gamma\hbar H_0 I_z$$

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

$$\omega_0 = \gamma H_0$$

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

The Quadrupole Energy



From the environment:

The EFG (Electric Field Gradient):

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

From the nucleus:

I_x, I_y, I_z - The spin of the nucleus

The quadrupole Hamiltonian:

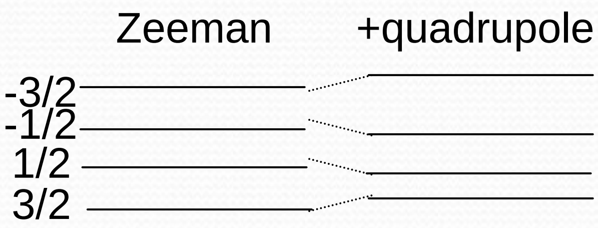
$$\mathcal{H} = \frac{\hbar \upsilon_q}{6}\left[3I_z^2 - I^2 + \eta\left(I_x^2 - I_y^2\right)\right]$$

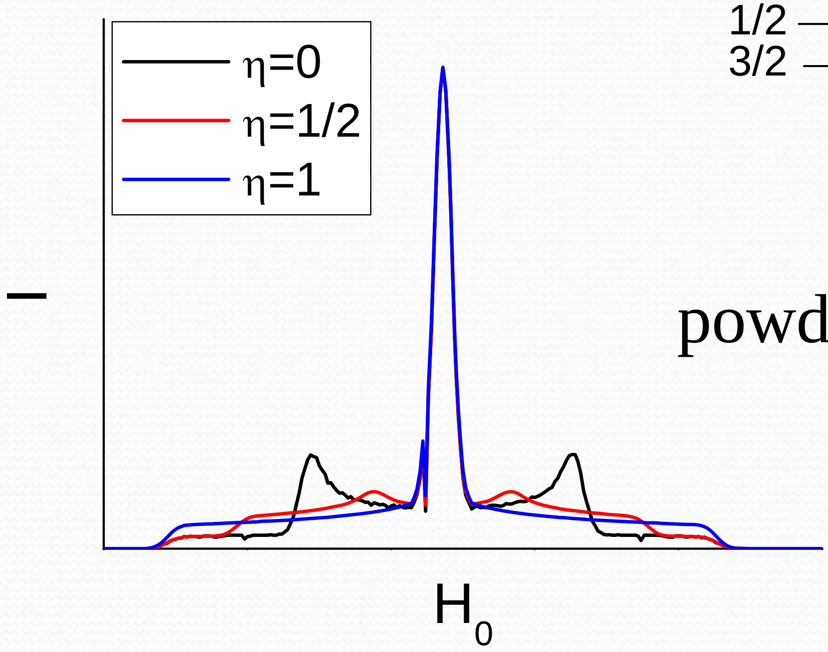
$$\nu_q \propto V_{zz} \qquad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

η is a measure of charge inhomogeneity.

NMR

- Strong H_0 ⟹ the quadrupole term is treated as a perturbation.
- For spin 3/2 nuclei:





powder average NMR line

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

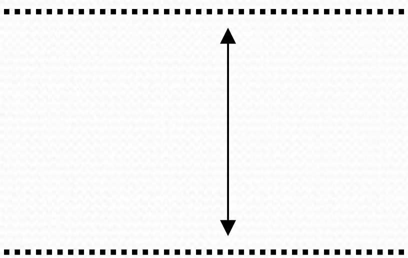
Pure NQR

- No permanent magnetic field

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

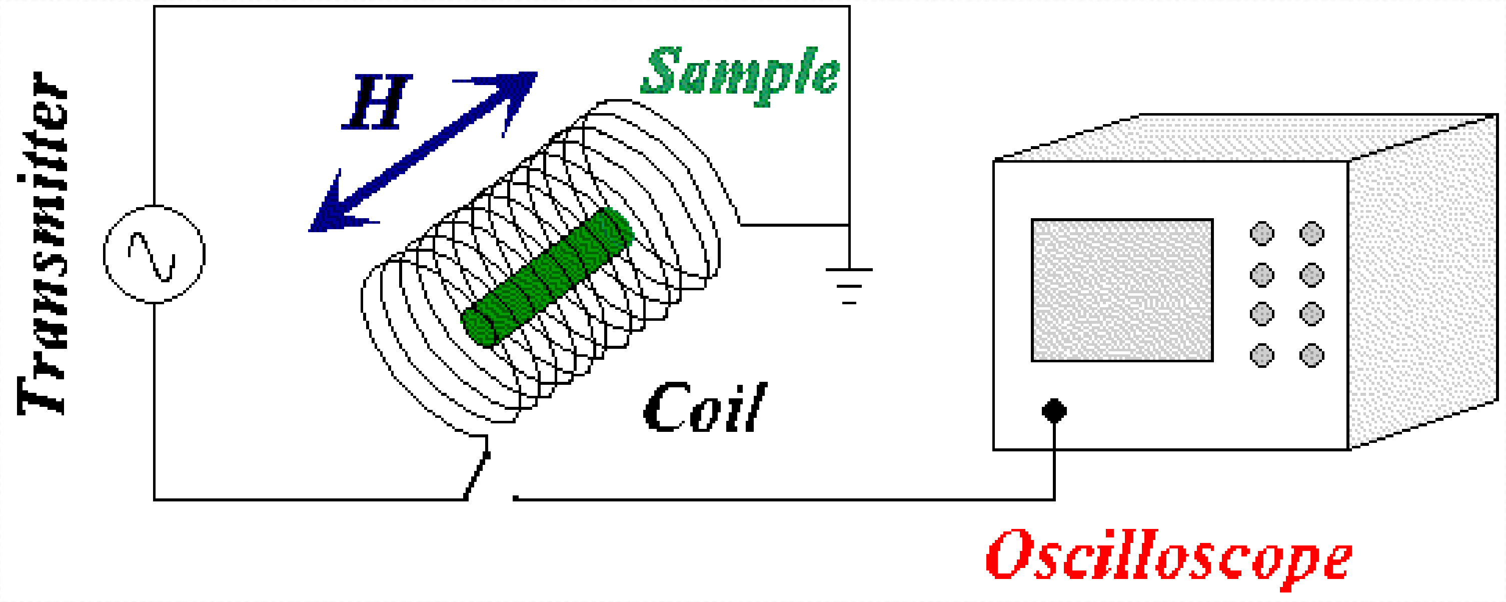
For a spin 3/2 nucleus:

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



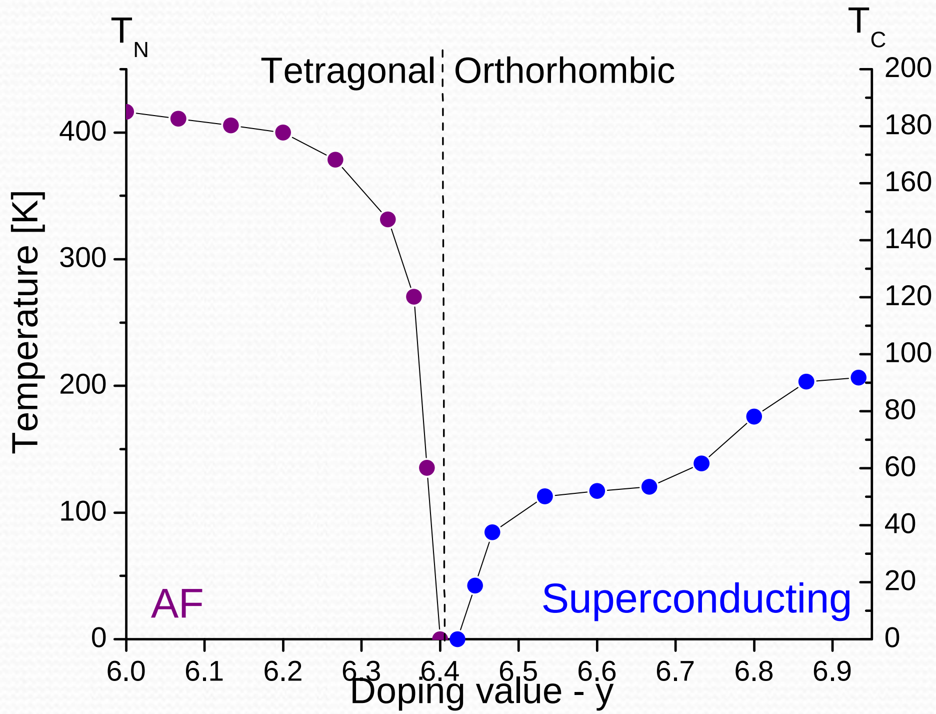
ν_q and η cannot be determined separately.

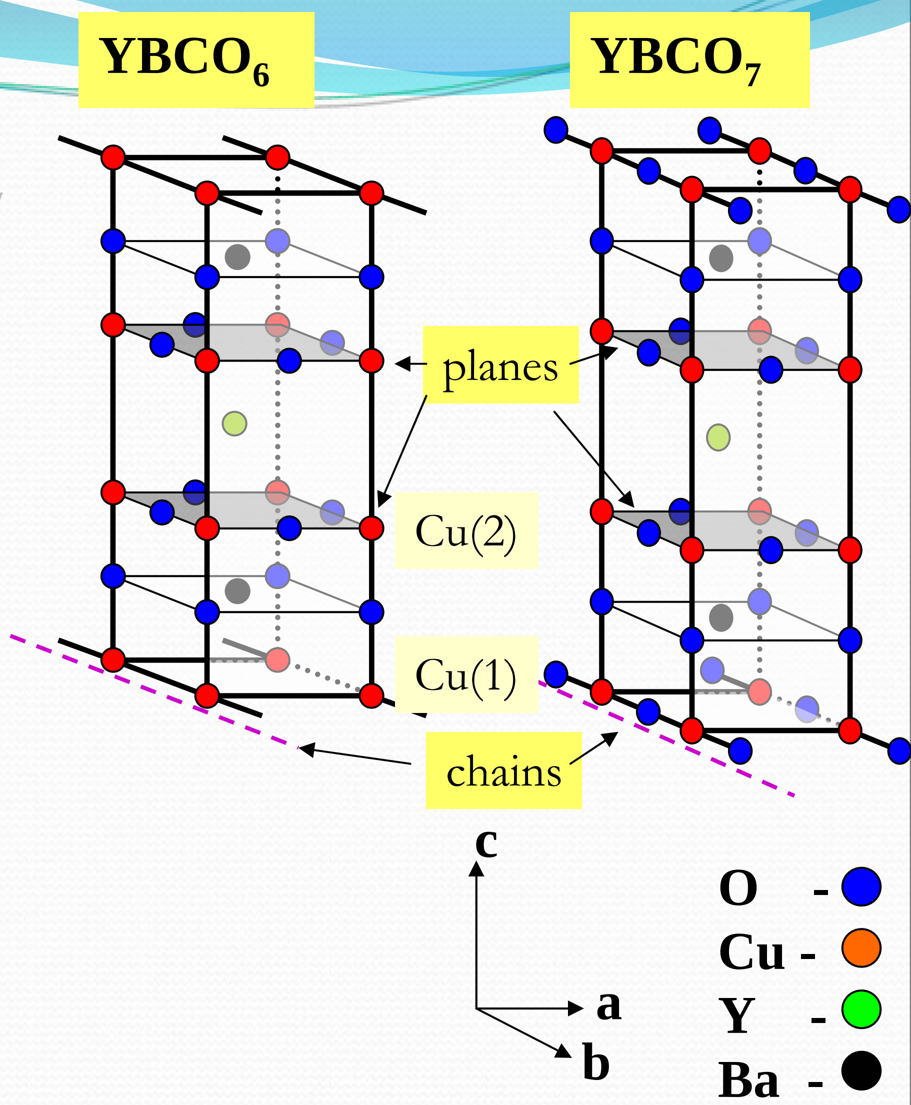
Technical aspects of NMR\NQR



$Y_1Ba_2Cu_3O_y$

Phase diagram

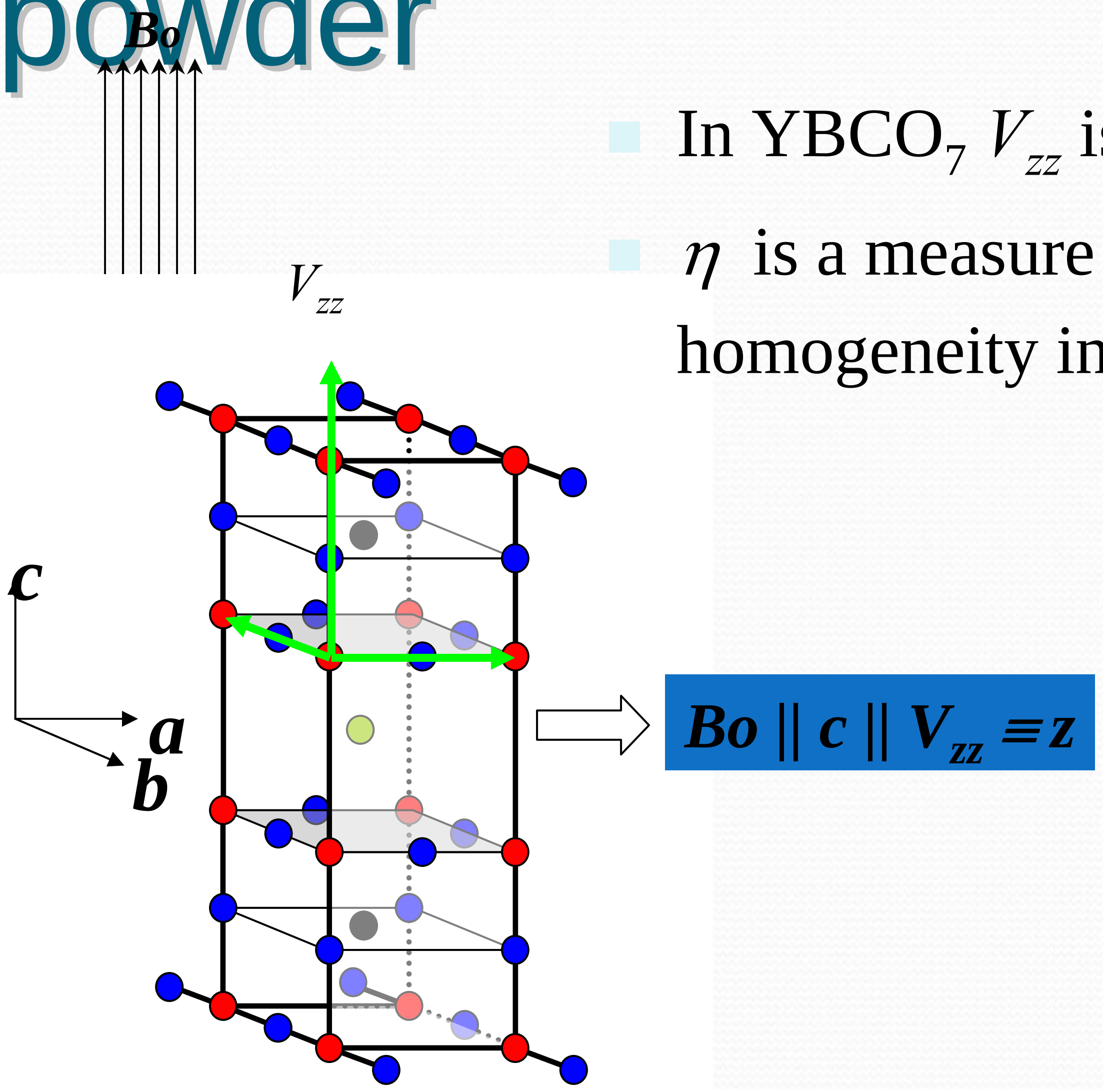




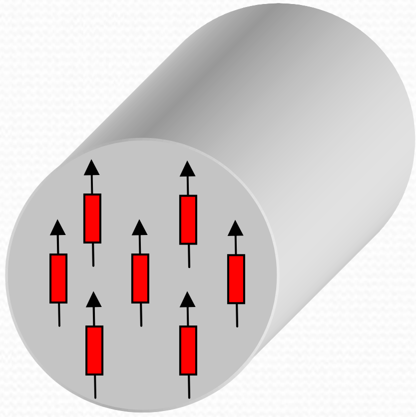
Unit cell

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

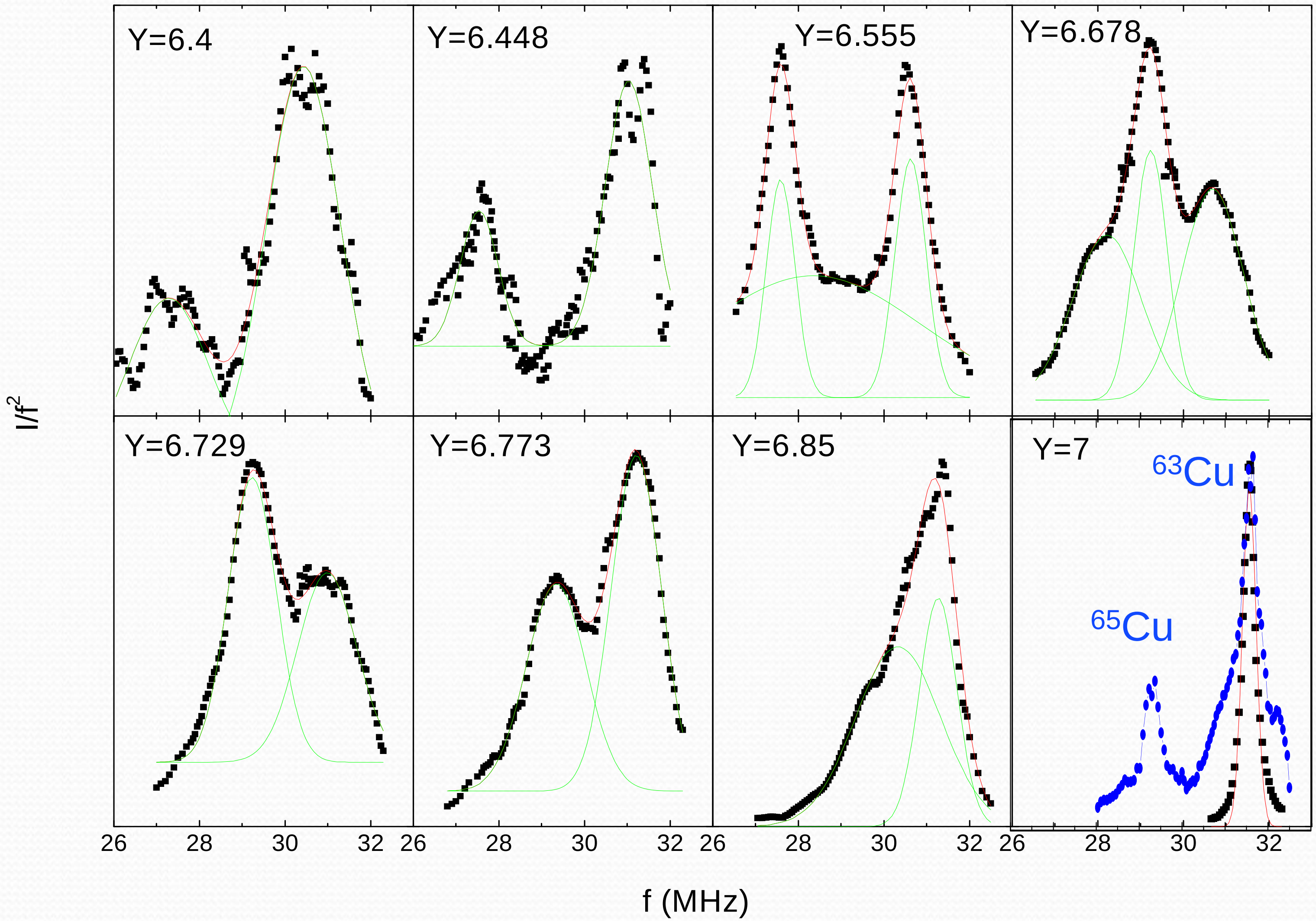
Orientation of the YBCO powder



- In $YBCO_7$ V_{zz} is in the c direction.
- η is a measure of charge homogeneity in the CuO_2 planes.

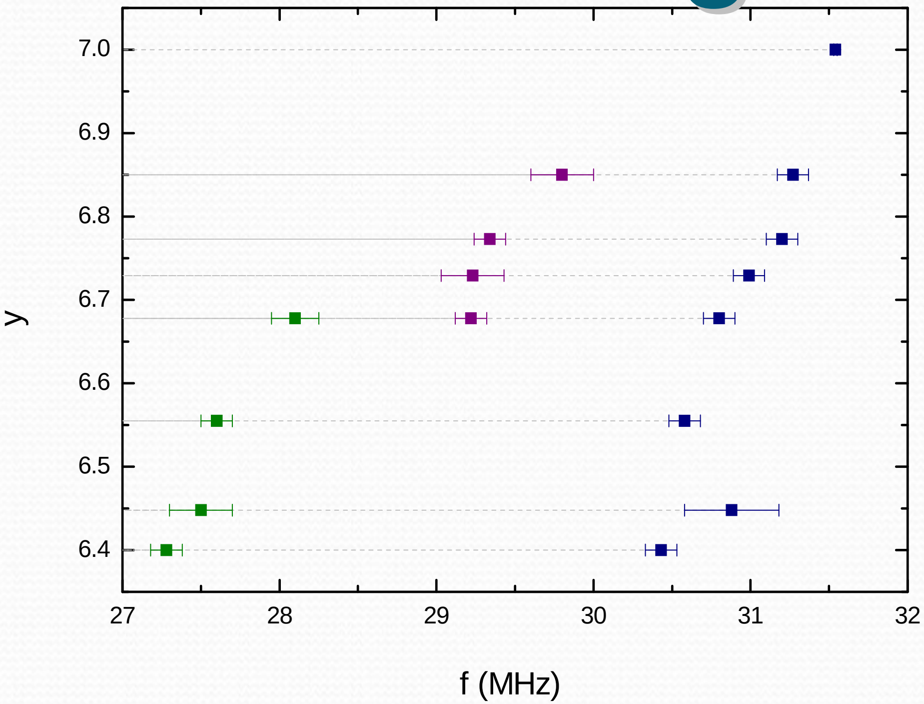


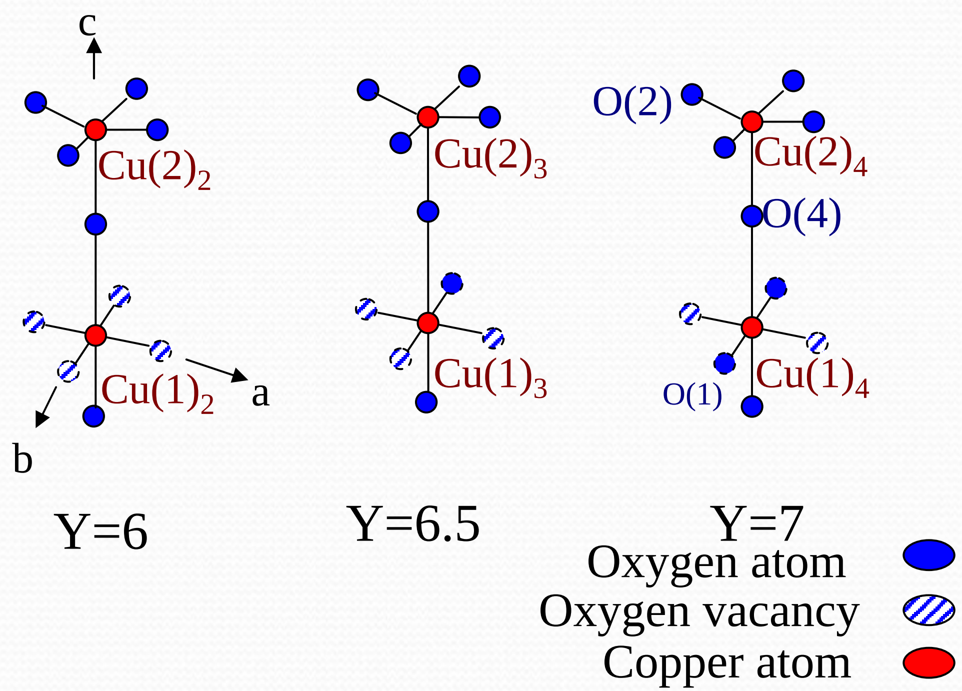
NQR lines for YBCO



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

Site assignment





3 different Cu(2) lines, for the 3 different ionic environments:

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

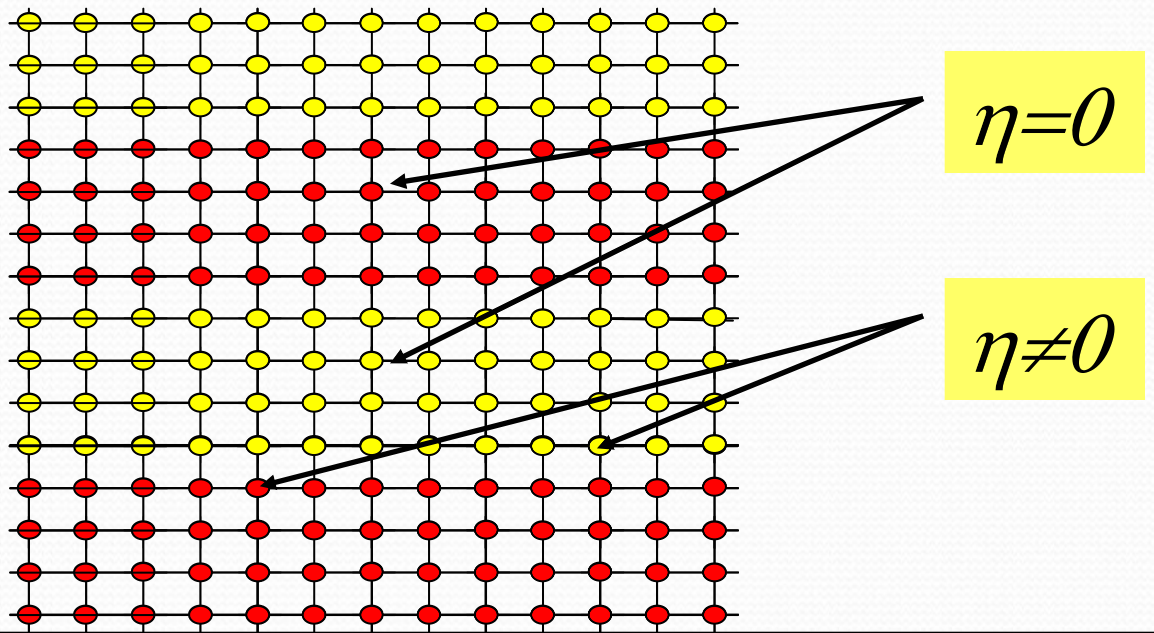
Our Main motivation; finding η

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

$$\nu_q \propto V_{zz} \qquad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

For $YBCO_7$ V_{zz} is in the *c* direction of the lattice.

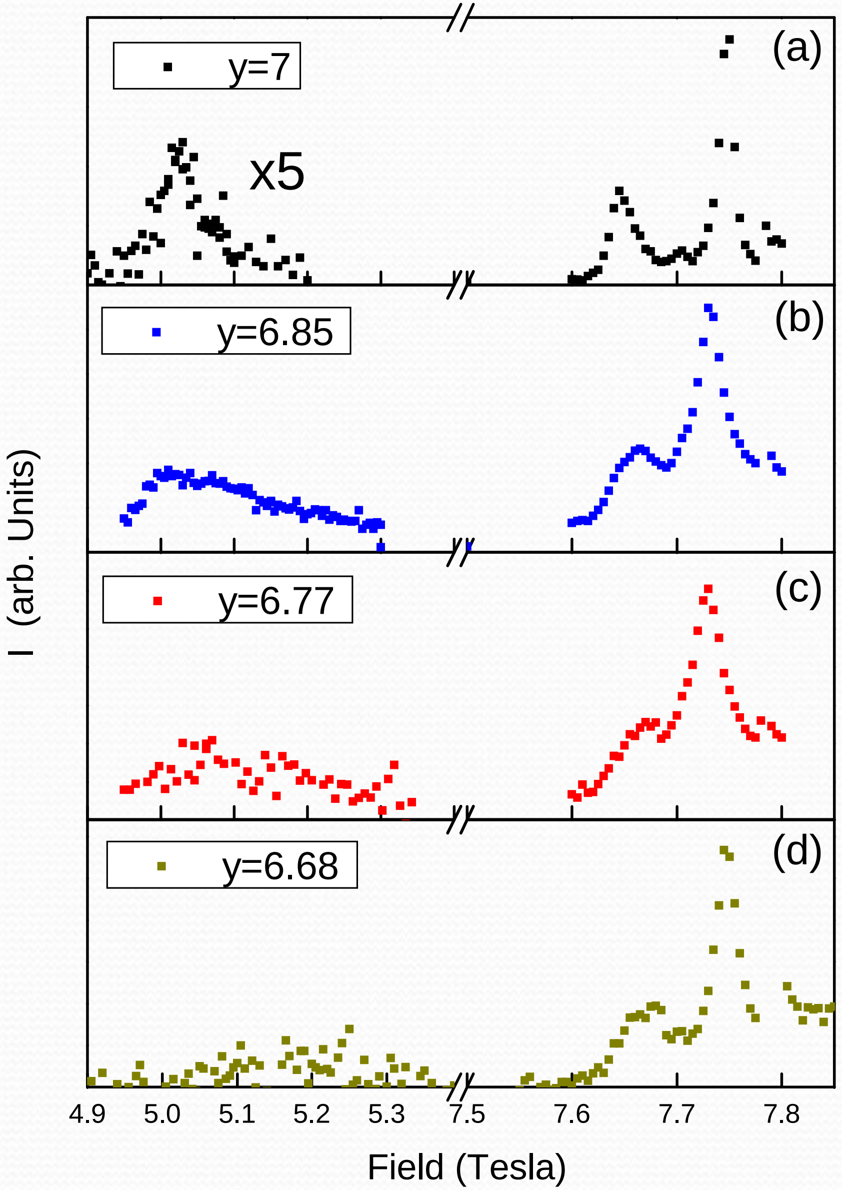
η determines the homogeneity of the charge distribution in the CuO planes:



NMR Results

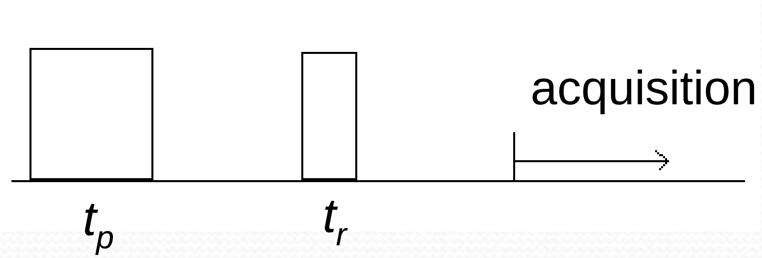
- For lower doping levels, the satellites disappear

⇒ η cannot be extracted.



G. S. Harbison *et al.* , Z. Naturforch. **45A**, 575 (1990).

Nutation Spectroscopy



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

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

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

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

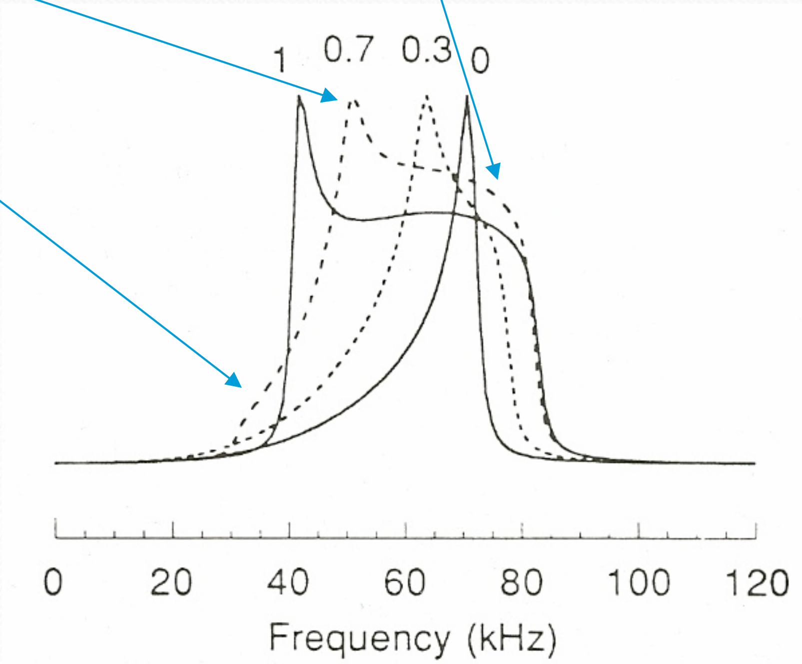
Nutation Spectroscopy

- Three singularities:

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

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

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



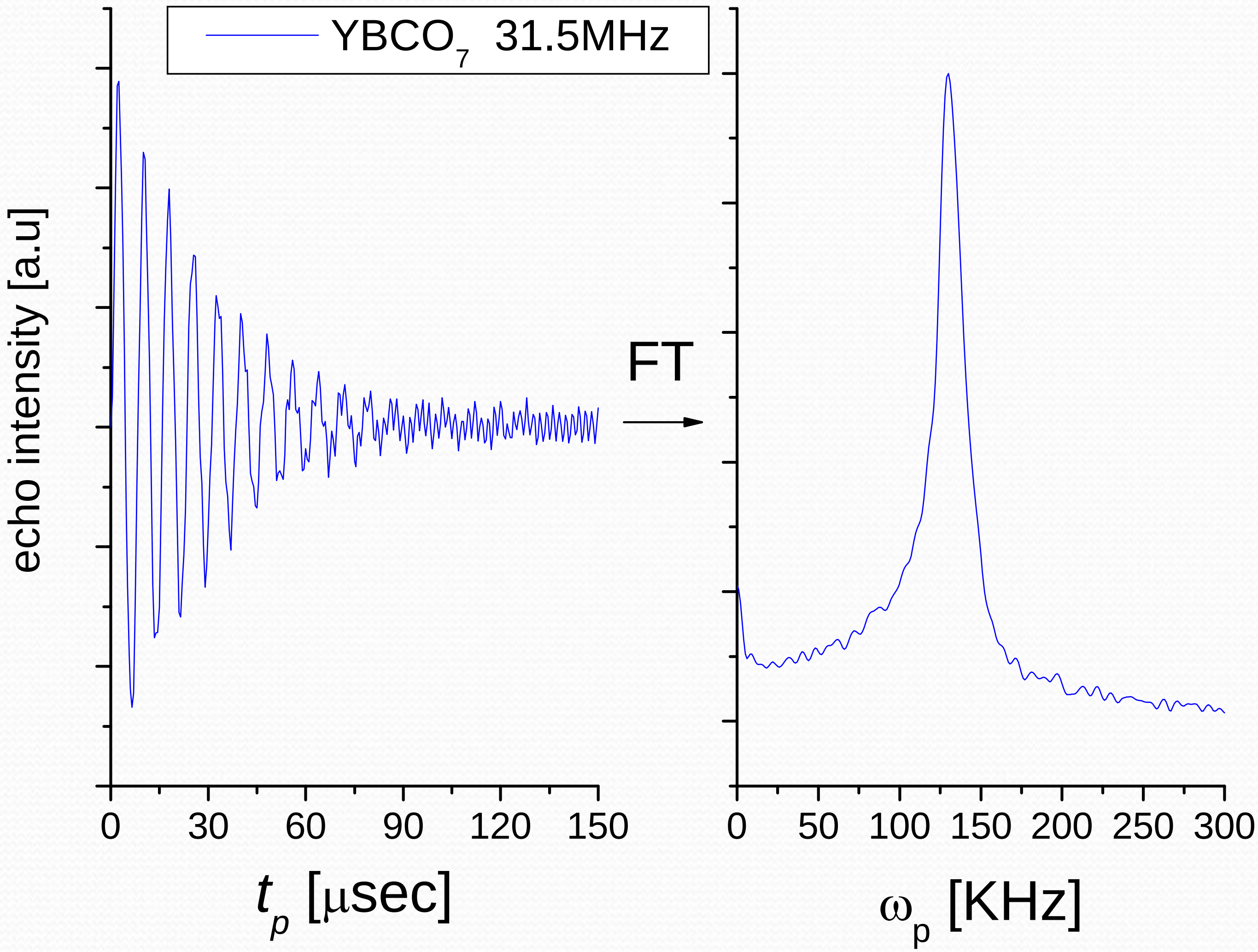
A. J. Vega, Israel Journal of Chemistry 32, 195 (1992)

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.

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

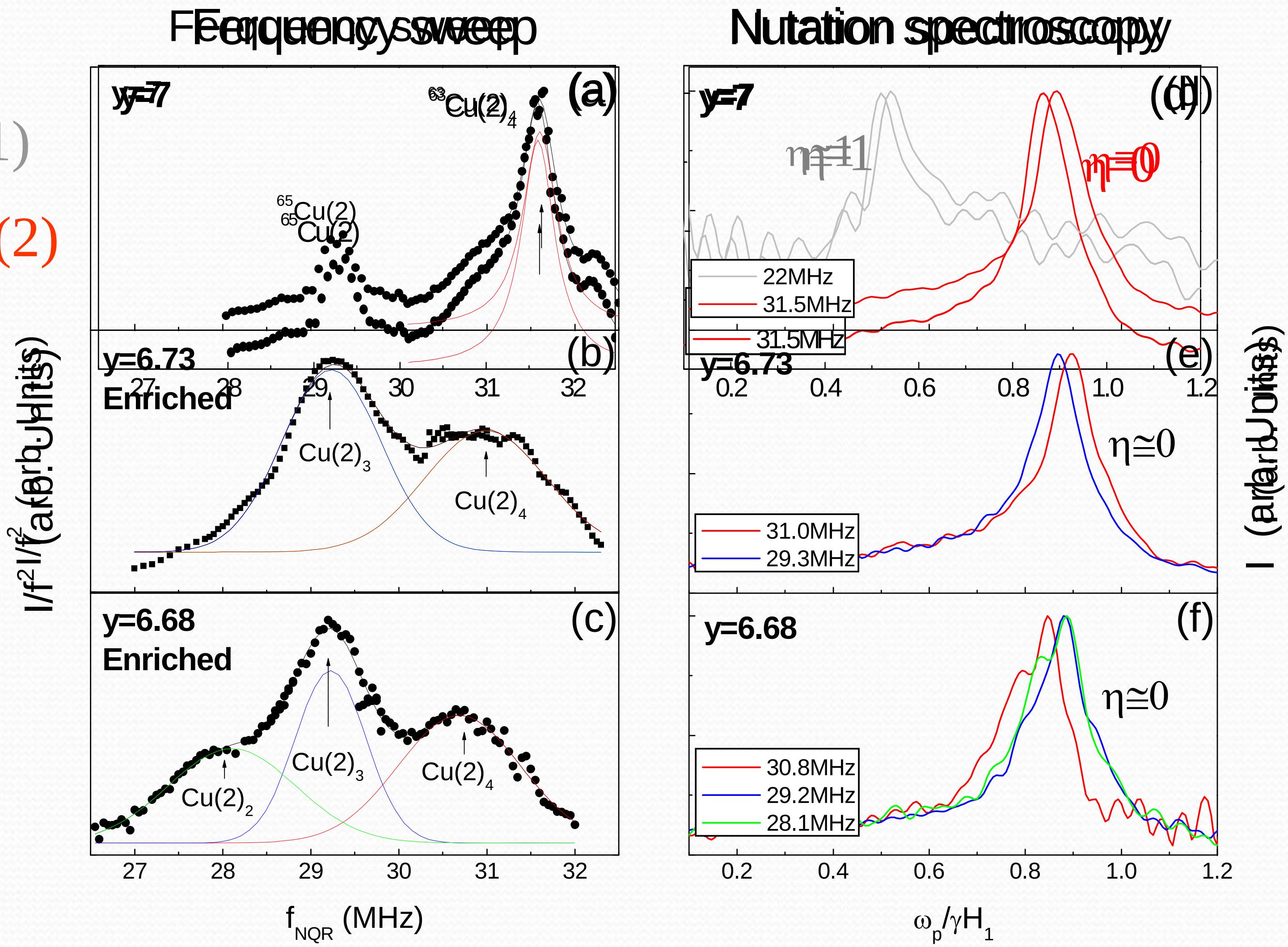
Nutation raw data



Nutation Results

22 MHz - Cu(1)

31.5MHz - Cu(2)



Nutation Results

- For $YBCO_7$: Cu(2) $\eta=0$

  Cu(1) $\eta=1$

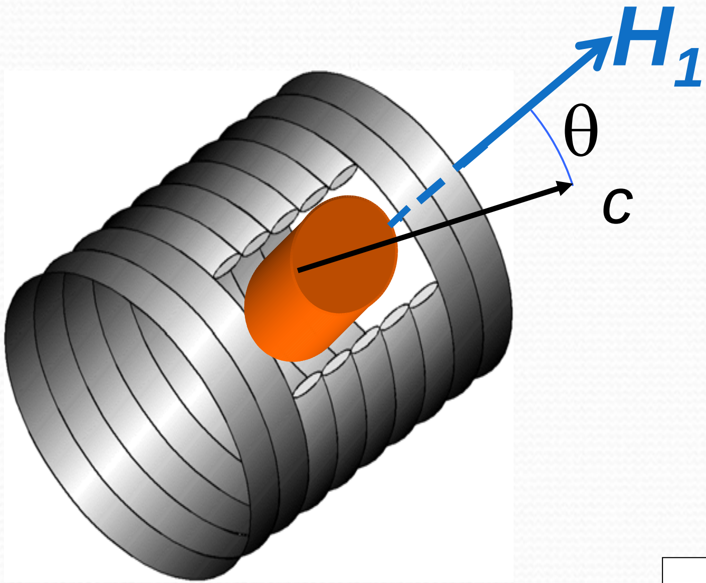
- For lower doping:

  $\eta \approx 0$ for all different Cu(2) environments.

- Not sensitive to the EFG orientation.

S. Levy and A. Keren, Journal of Magnetic Resonance **167**, 317 (2004)

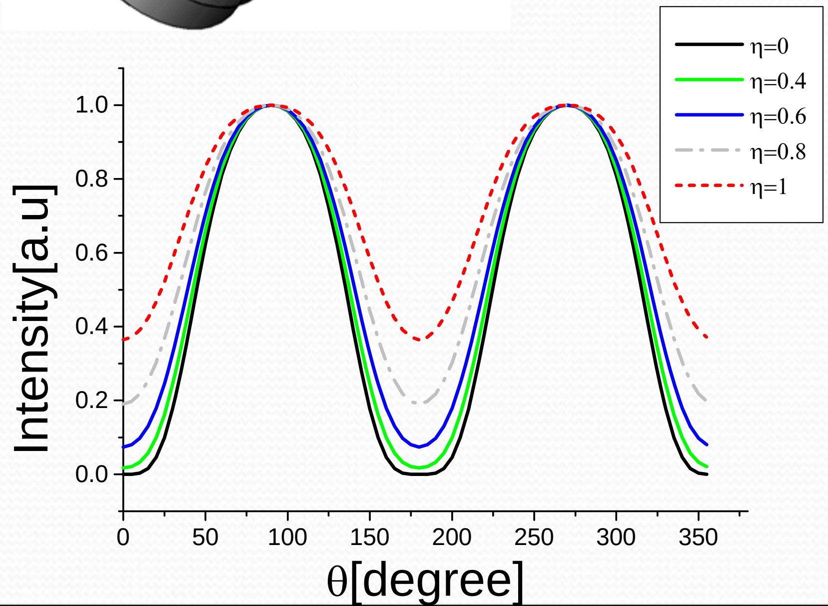
Angle dependant NQR



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

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

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



- For *η=0, θ=0*

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

  ⟹ no spin transitions.

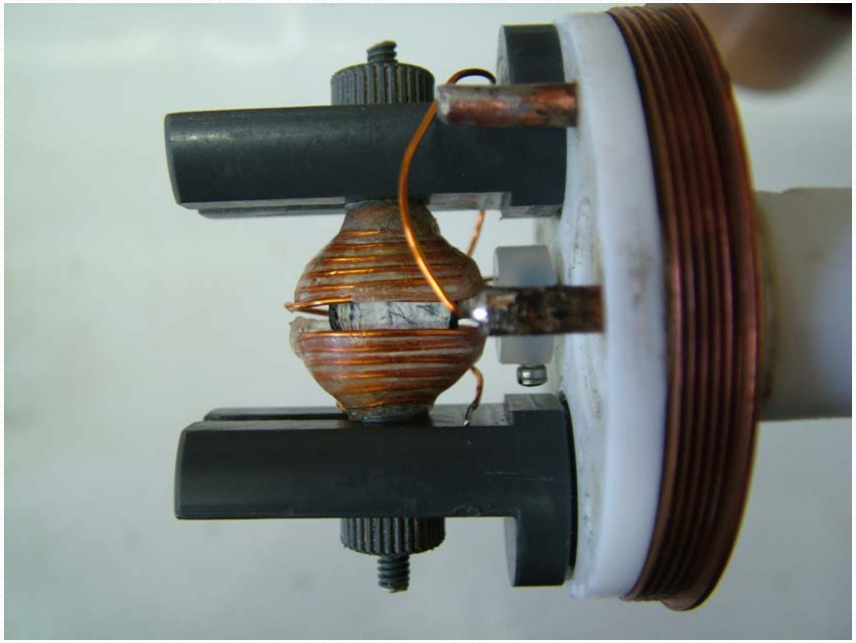
- For *η>0*,

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

  ⟹ signal even for *θ=0*.

The ADNQR probe

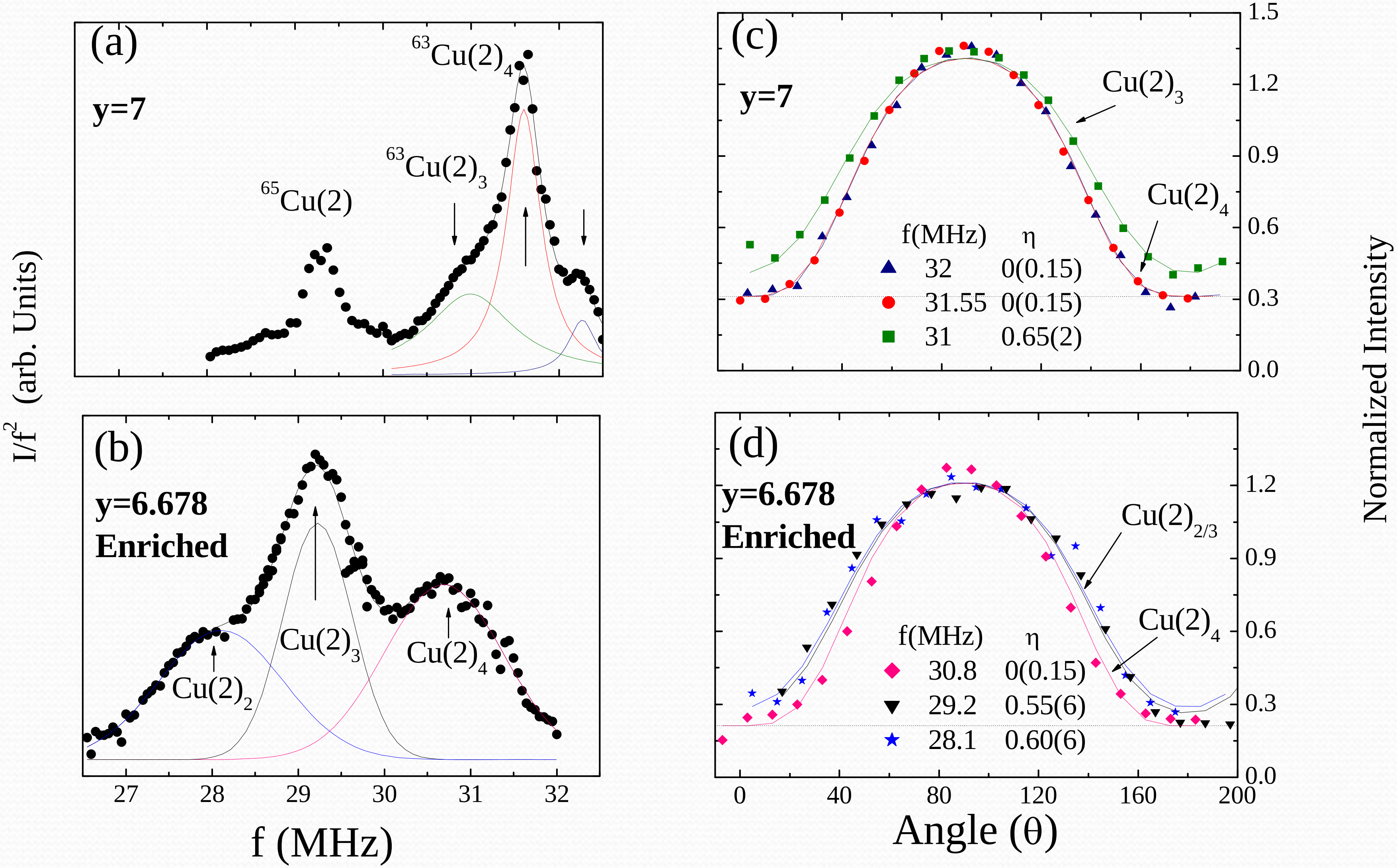
- Spherical coil to improve the homogeneity of the rf field.
- Connection to a motor for an automated rotation of the sample. (ability to measure at low temperatures).



ADNQR results

Ferquency sweep

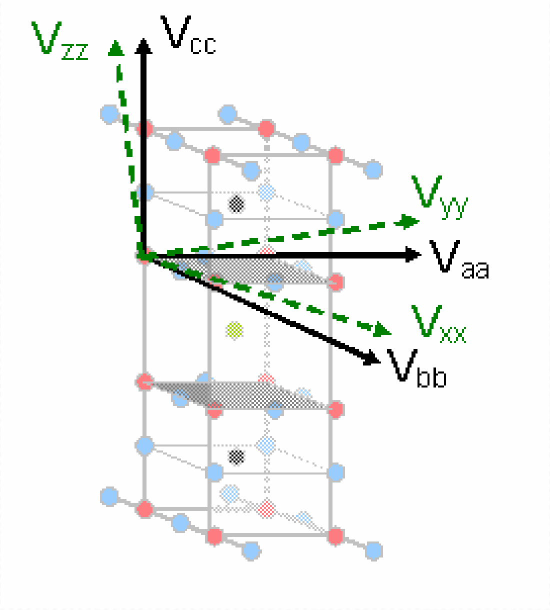
ADNQR



Interpretation

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

  Rotation of V_{zz} from the c direction:



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

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

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

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

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