# Solid-state NMR investigations of porous carbons, manganites and Mg-based organometallics

Jair C. C. Freitas

# Outline

- **Porous carbons:**
  - Structure, interest, preparation, surface groups.
  - **$^{13}C$, $^{23}Na$, $^{31}P$ NMR.**
- **Manganites:**
  - Structure, applications, physical properties.
  - **$^{139}La$ NMR.**
- **Mg-based organometallics:**
  - Motivation, choice of samples and methods.
  - **$^{25}Mg$, $^{23}Na$ NMR.**
- **Conclusion.**

# Carbon Materials

**Laboratory of Carbon and Ceramic Materials (LMC)**

**Federal University of Espírito Santo, Vitória, Brazil**

http://www.cce.ufes.br/dfis/lmc.htm

**Some materials of interest:**

- ✓ Chars produced from natural resources (peat, rice hulls, coconuts, etc).
- ✓ Carbon blacks produced by plasma pyrolysis of natural gas.
- ✓ Plasma modified vacuum residues of oil refinement.
- ✓ Activated carbons.
- ✓ Composites of porous carbons and magnetic nanoparticles.

**Some characterization techniques:**

- ✓ XRD, SEM, NMR ($^{13}C$, $^{29}Si$, etc), Mössbauer spectroscopy, TG, DSC, CHNSO analysis, etc.
- ✓ Textural properties (BET surface area, pore size distribution, true density, etc).
- ✓ Physical properties (electrical resistivity, magnetic susceptibility, etc).

# Structure of disordered carbons

Graphite-like crystallites

Cross-links

Pores

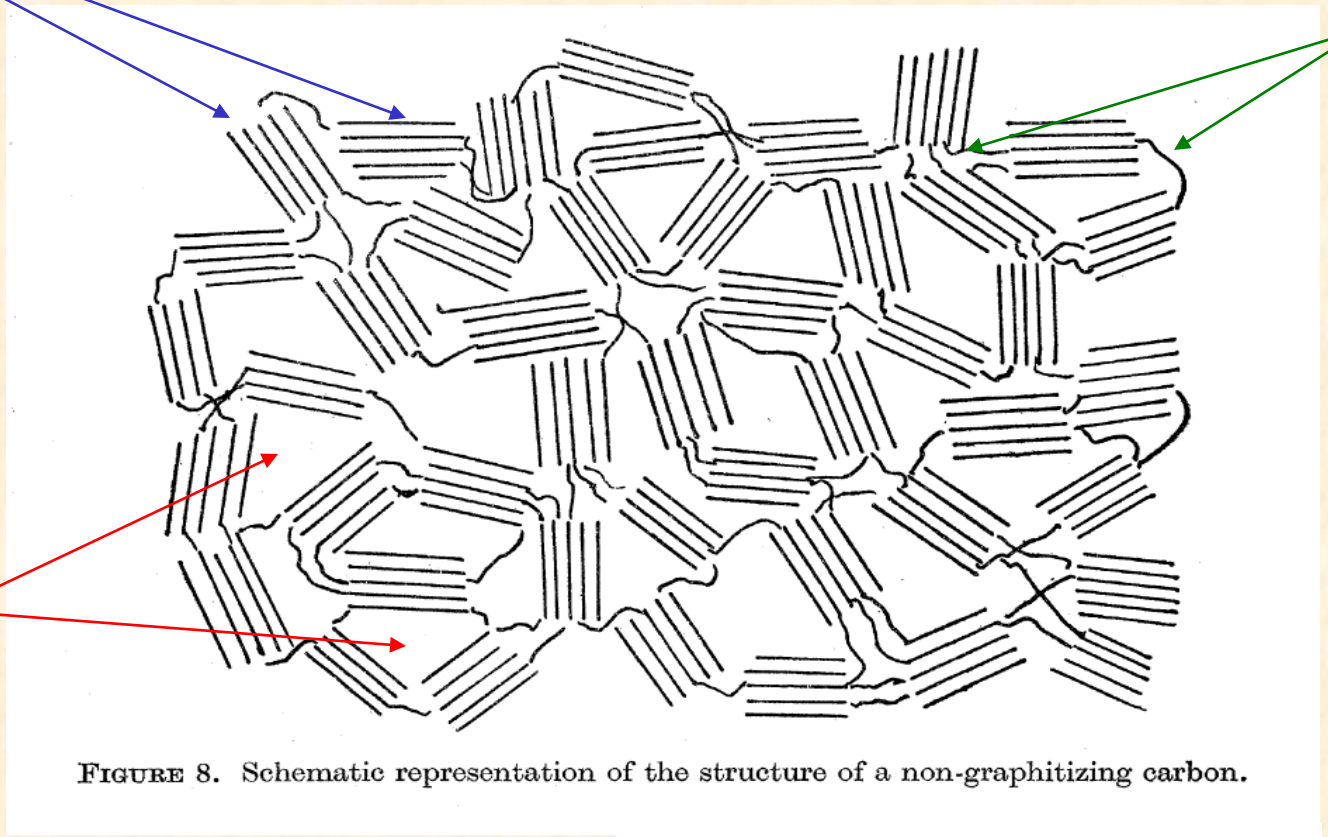


FIGURE 8. Schematic representation of the structure of a non-graphitizing carbon.

R. E. Franklin, *Proc. Roy. Soc. London A* 209 (1951) 196

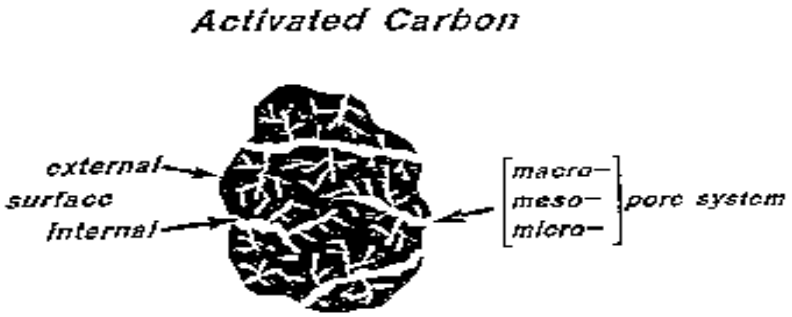
Composition: C, H, O (major), N, S, ashes,...

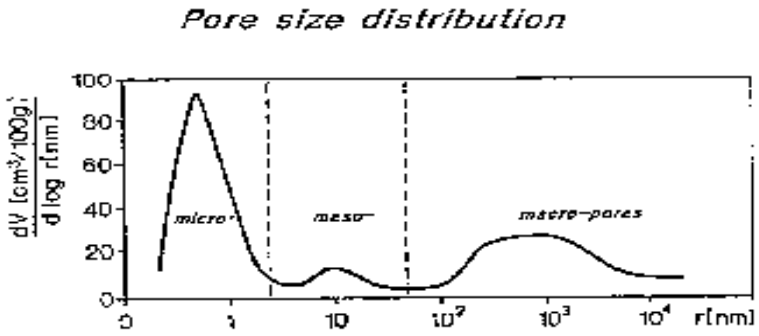
# Activated carbons

- Large internal surface area.
- Controlled pore-size distribution.
- Use as adsorbents, filters, catalysts, supporting material, etc.
- Manufacture:
  - Physical activation: steam, air, $CO_2$,…
  - Chemical activation: $H_3PO_4$, NaOH, KOH, $CaCl_2$, …
  - Precursors: coal, anthracite, chars, lignocellulosic materials, …
  - Heat-treatments, purification, drying, …

# Activated carbons

Pore sizes and distribution:




Surface groups:

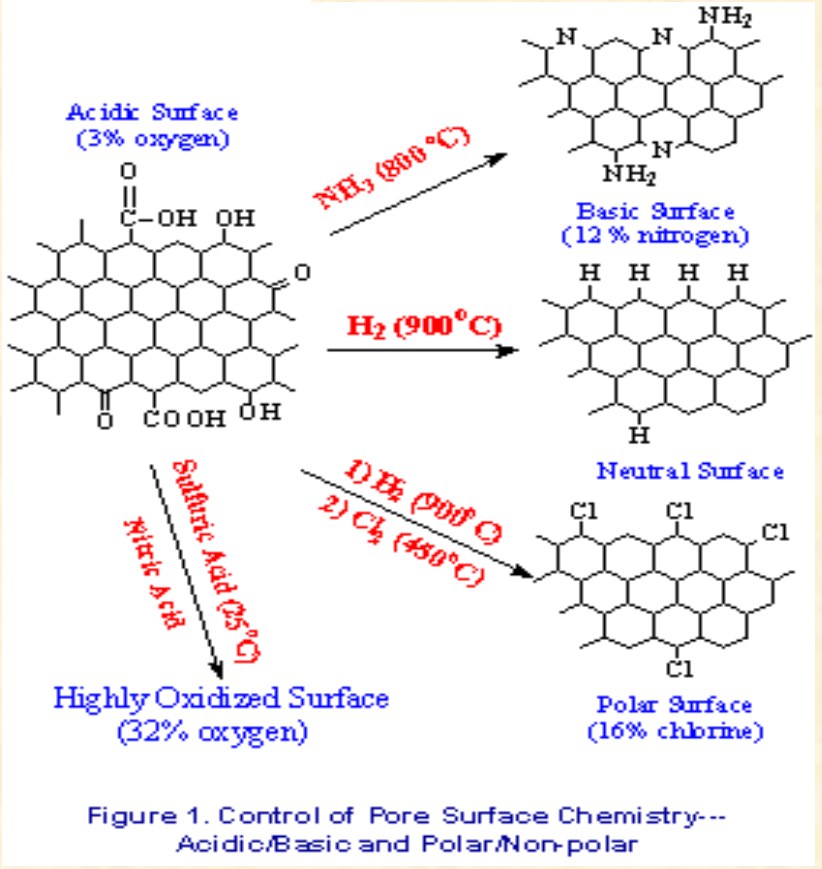
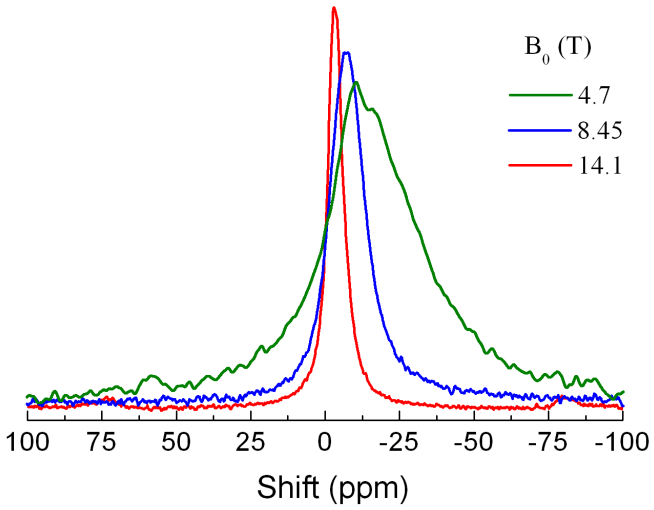
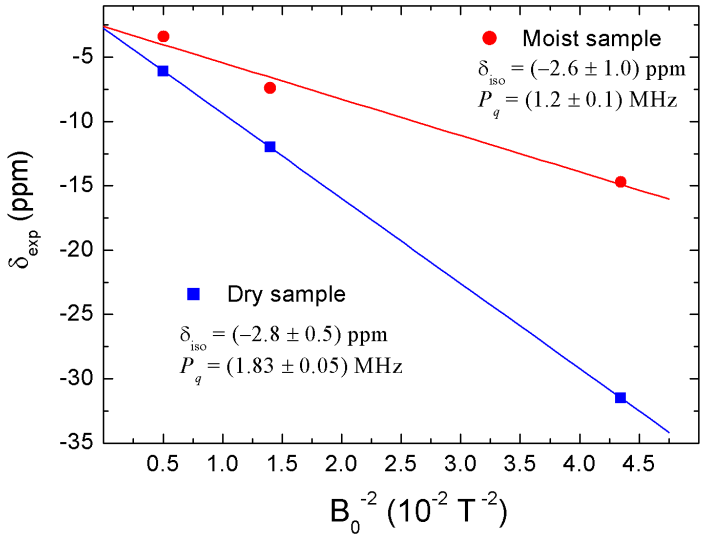



Figure 1. Control of Pore Surface Chemistry---Acidic/Basic and Polar/Non-polar

# $^{23}$Na NMR results

## NaOH activated carbon:




Freitas, Wong, Smith et al., *SSNMR* 2007 (in press)

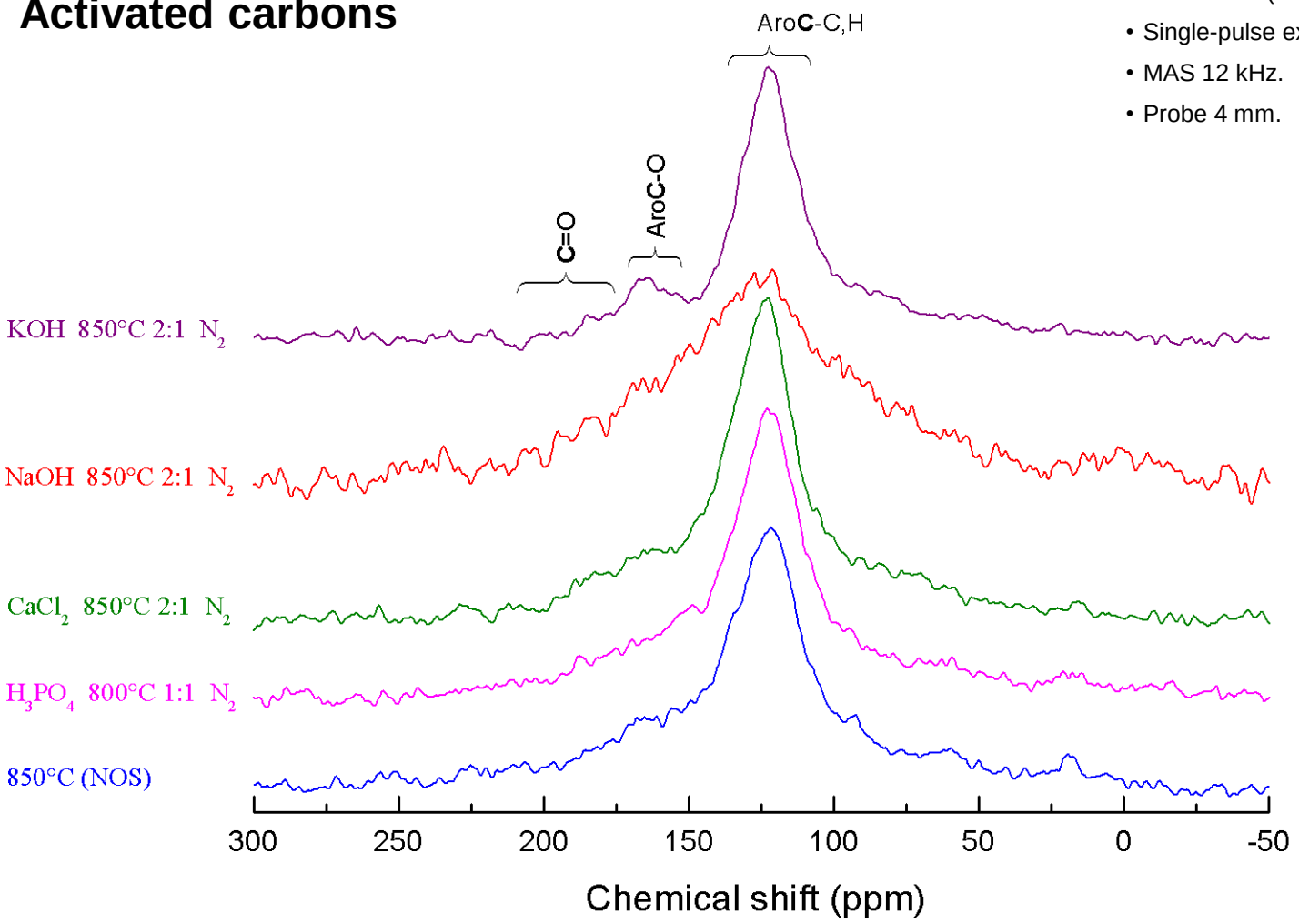
- ✓ Disordered materials – no quadrupolar features directly observed.
- ✓ Evidences of motion affecting the lineshapes.
- ✓ Chemical shift pointing to oxygenated Na groups.
- ✓ Possible existence of surface groups containing Na-O-C bonds at the edges of aromatic lamellae.
- ✓ Strong effect of hydration on quadrupolar coupling.

- Single-pulse or spin-echo.
- MAS at 12 kHz or static experiments.
- Probes 4 mm.

# $^{13}C$ NMR results

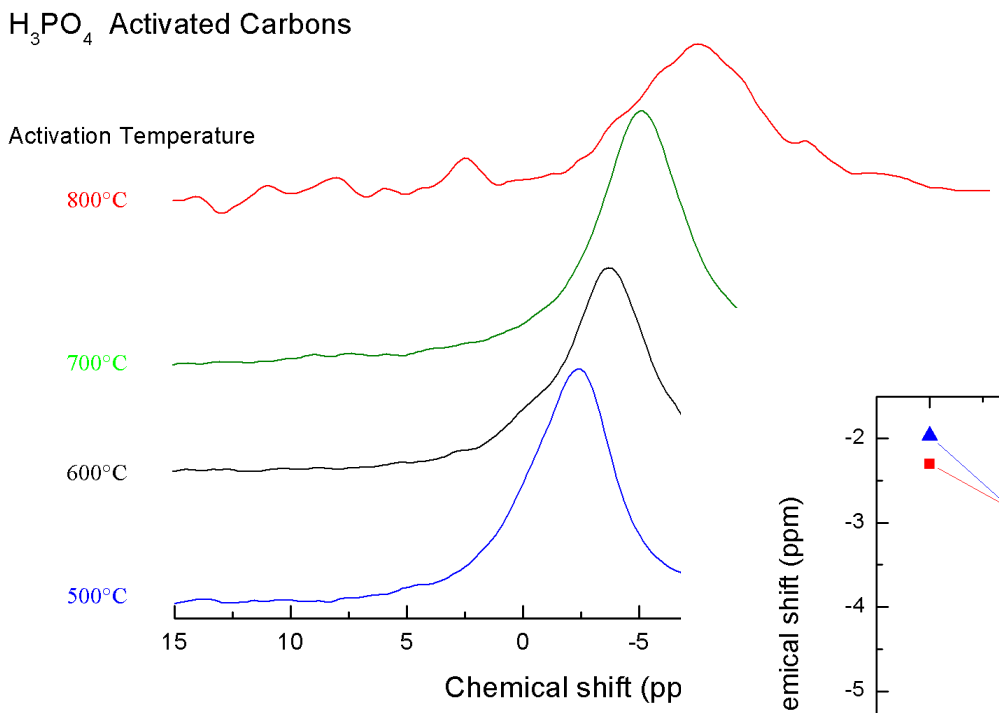
## Activated carbons

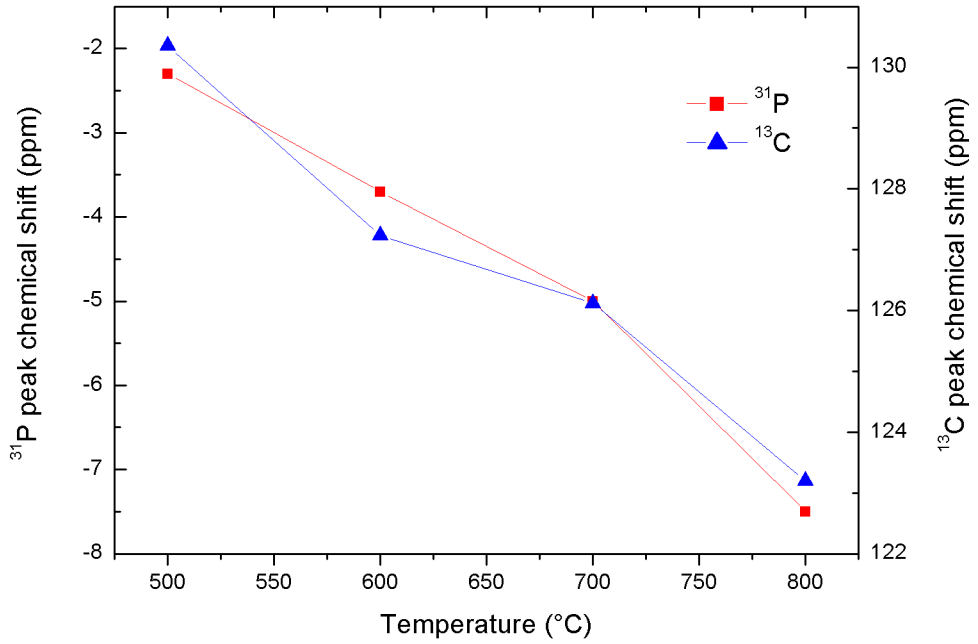
- 51.38 MHz (CM 200).
- Single-pulse experiments.
- MAS 12 kHz.
- Probe 4 mm.



# $^{31}$P NMR results

- 145.77 MHz (CM 360).
- Single-pulse experiments.
- MAS 10 kHz.
- Probe 4 mm.



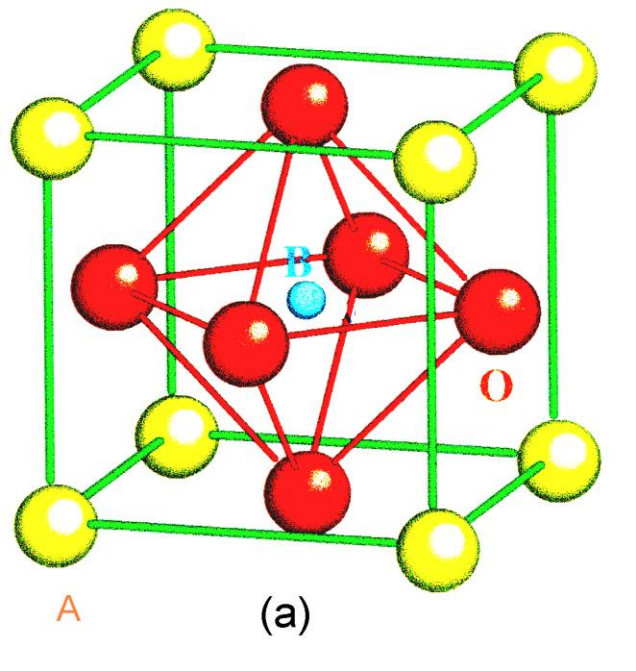
# Summary – Activated Carbons

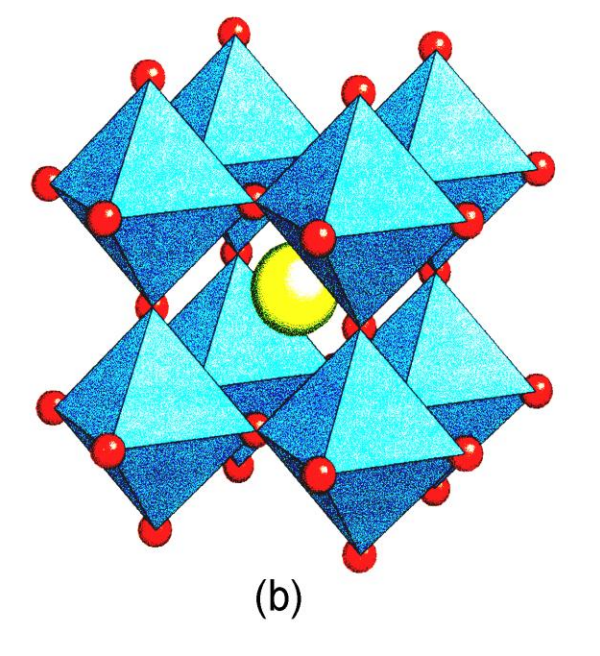
- **NMR results:**
  - Detection of NMR signals for heteroelements ($^{23}$Na, $^{39}$K, $^{31}$P).
  - Detection of oxygenated groups by $^{13}$C NMR.
  - Characterization of quadrupolar coupling for $^{23}$Na.
  - Similar trends for $^{13}$C and $^{31}$P chemical shifts.

- **To be done – compare NMR results with:**
  - Elemental analysis data (O/C ratio, heteroelements contents).
  - Textural and structural data (surface area, crystallite size, etc).
  - Methods of production (temperature, washing, etc).

# Manganites - Perovskite structure

$ABO_3$

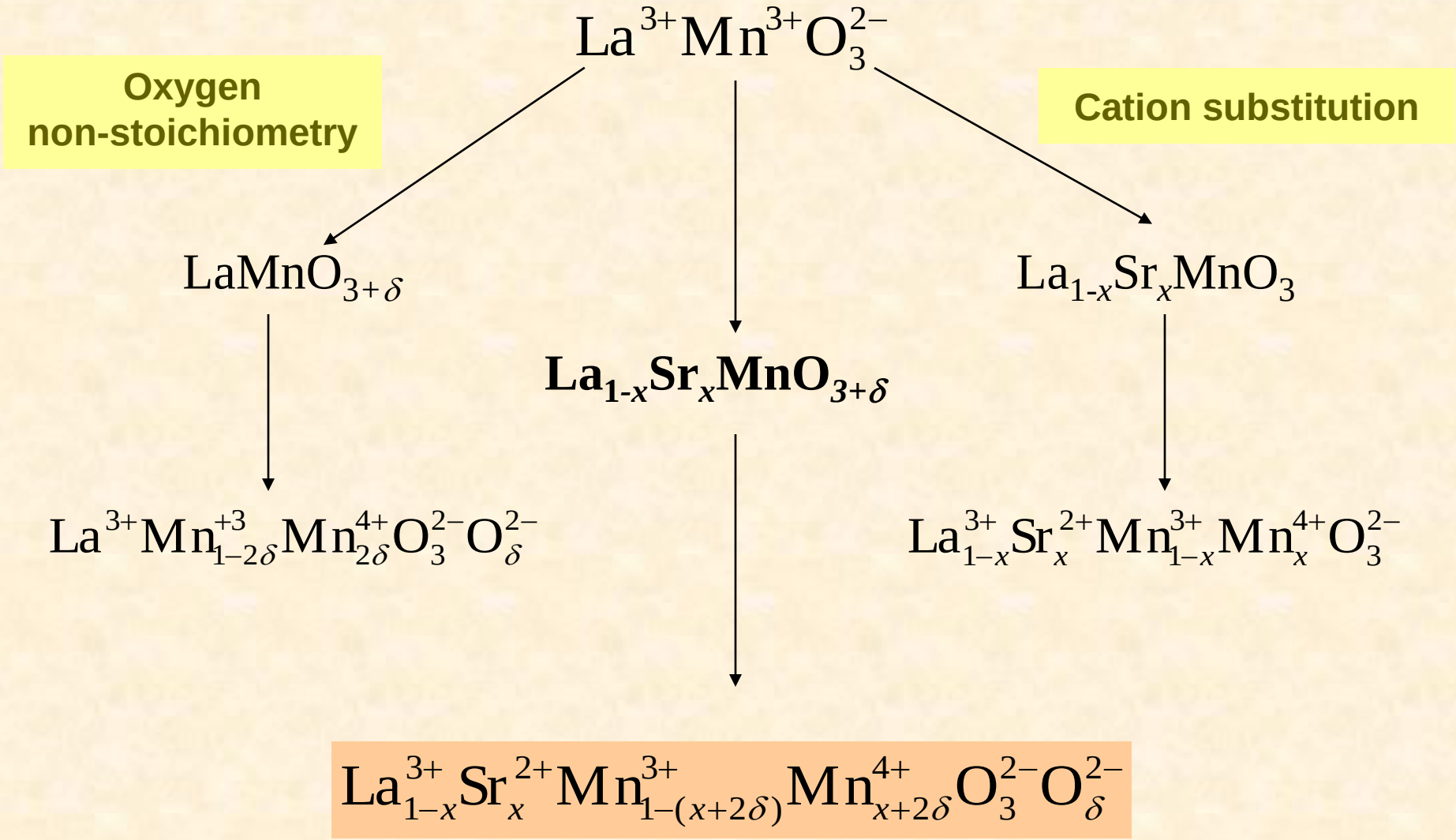



***A*** = trivalent (**$La^{3+}$**, $Pr^{3+}$) or divalent element ($Ca^{2+}$, **$Sr^{2+}$**).
***B*** = transition metal (**Mn**, Ti, Fe).

***Manganite = manganese perovskite***

# Mixed-valence manganites

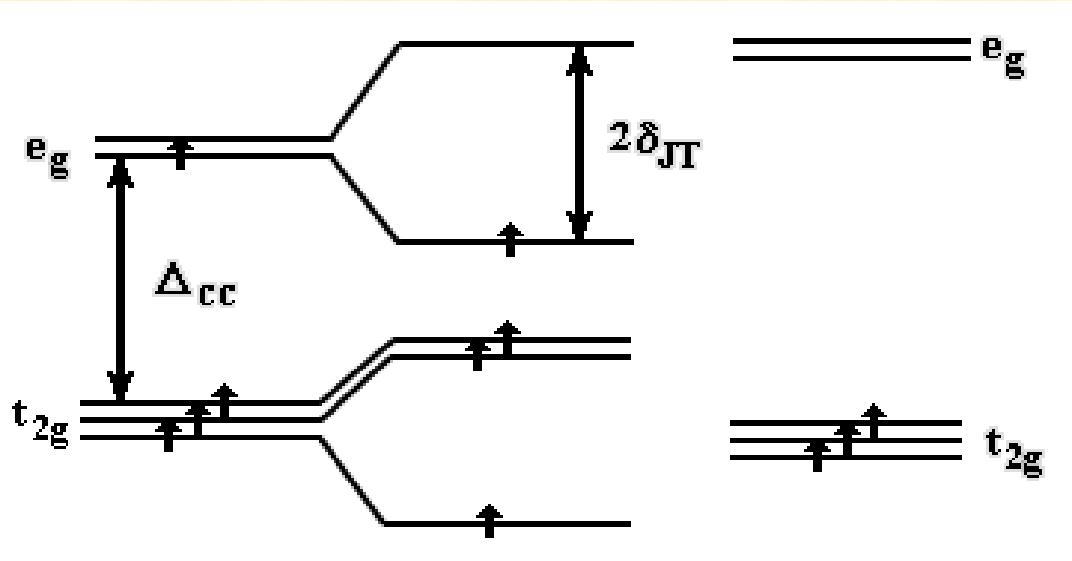


# Mixed-valence manganites

$Mn^{3+}$

$[Ar]3d^4$

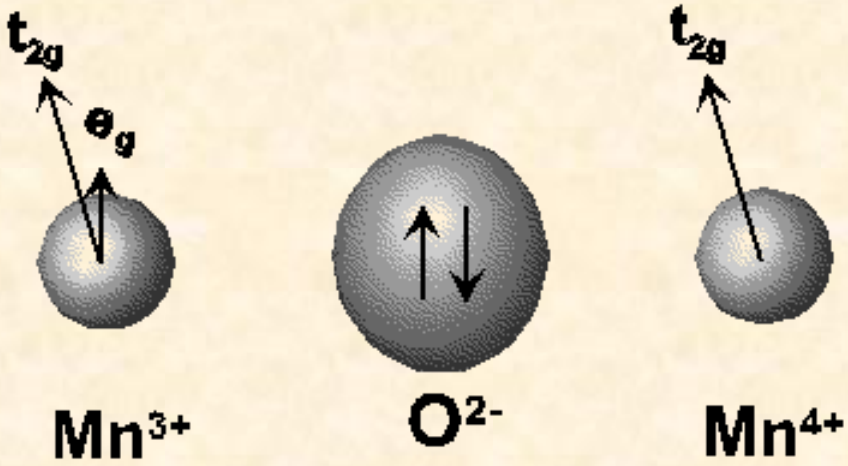
$S = 2$




$Mn^{4+}$

$[Ar]3d^3$

$S = 3/2$




**Carrier mobility**

***Double-exchange* (DE) *model: FM + metallic conductivity***

# Mixed-valence manganites

- **$Mn^{3+}/Mn^{4+}$ pairs:**
  - Electron / hole mobility.
  - Electrical conductivity.
  - Ferromagnetism (FM) $\times$ antiferromagnetism (AFM).
  - Colossal magneto-resistance (CMR).
  - Interplay between charge, spin, orbital, and structural degrees of freedom.
  - Charge ordering, orbital ordering.
  - Nanoscale phase separation.

# NMR in manganites

- Zero-field NMR in magnetically ordered systems.
- Measurement of the hyperfine magnetic field.
- Most studied nuclei in manganites:
  - $^{139}$La ($I$ = 7/2)
  - $^{55}$Mn ($I$ = 5/2)
- Dipolar and contact contributions.
- Quadrupolar interaction: EFG in non-perfect cubic environment.

# $^{139}$La NMR in manganites

$$\mathbf{B}_{loc} = \underbrace{\frac{2\pi}{^{139}\gamma} g\mu_B \sum_j A_j \mathbf{S}_j}_{} + \mathbf{B}_{appl} + \cancel{\mathbf{B}_{dip}}$$

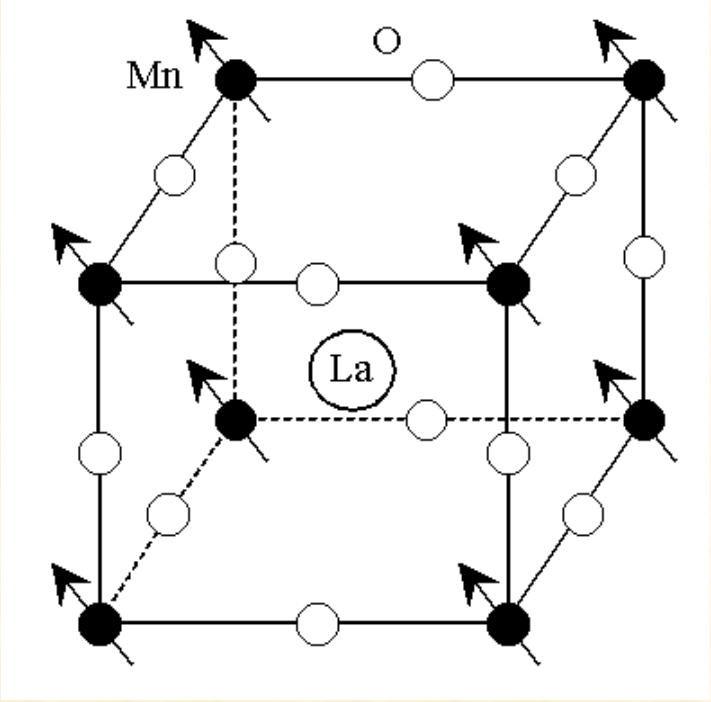
8 Mn ions

Transferred hyperfine field

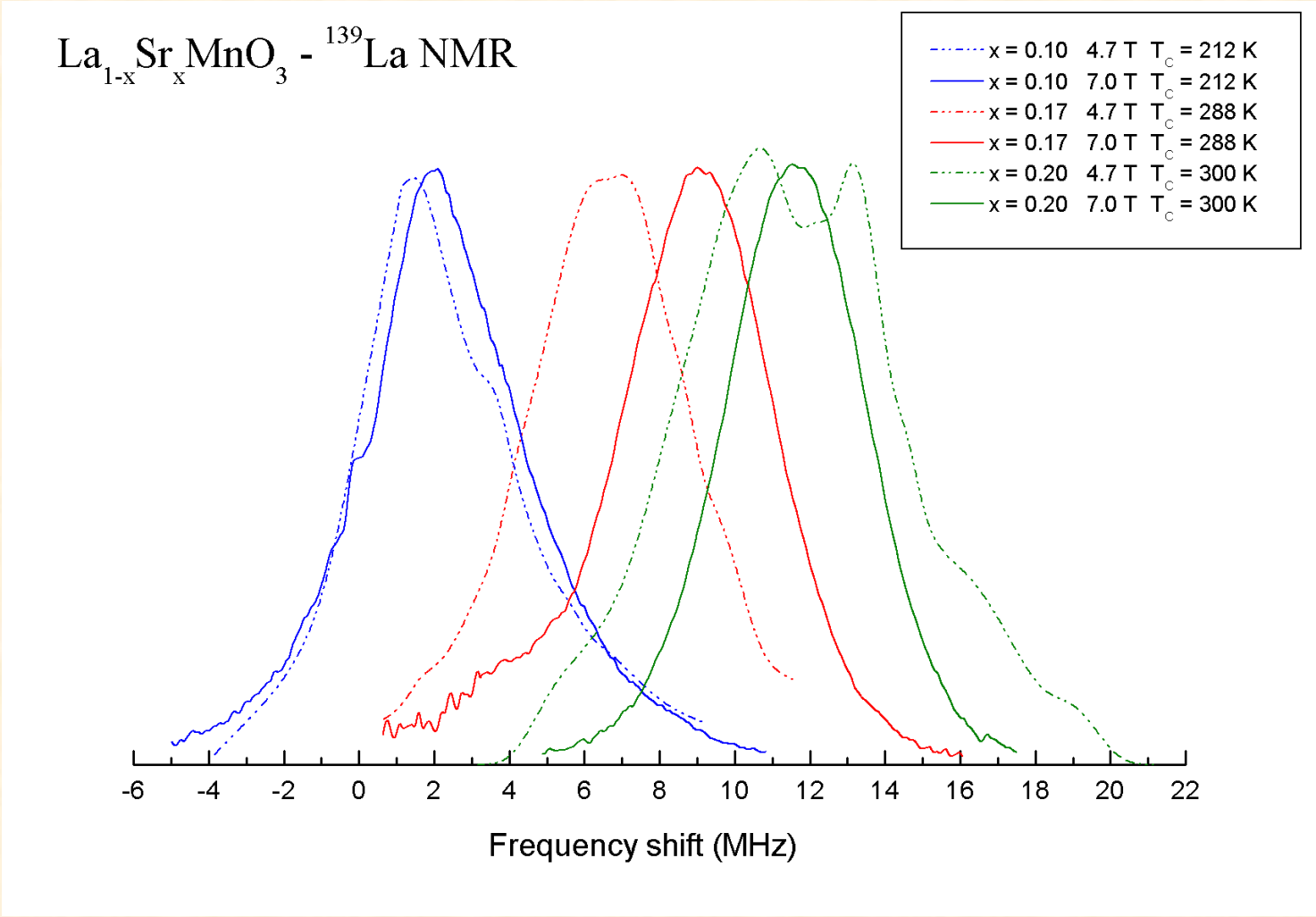
$$B_{hf} = A\langle S \rangle$$

Generally: $B_{hf} \propto M_{loc}$

$$\nu_{\mathrm{NMR}} = {}^{139}\gamma(B_{hf} + B_{appl})$$

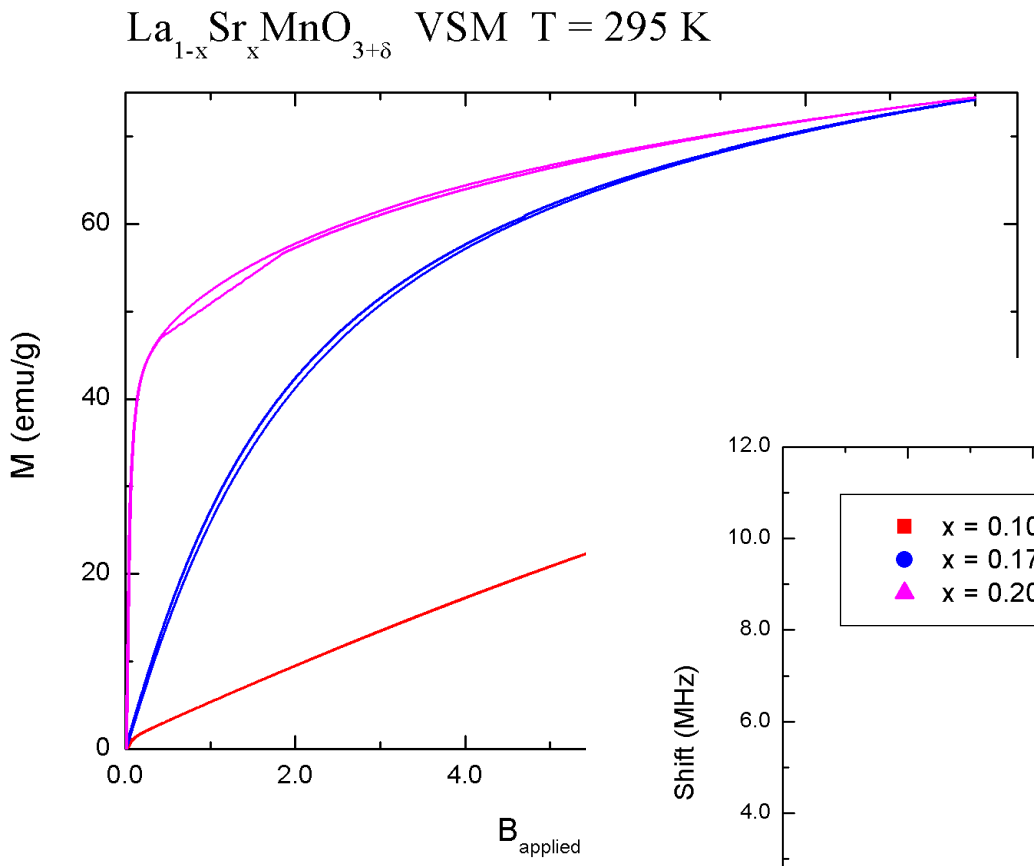


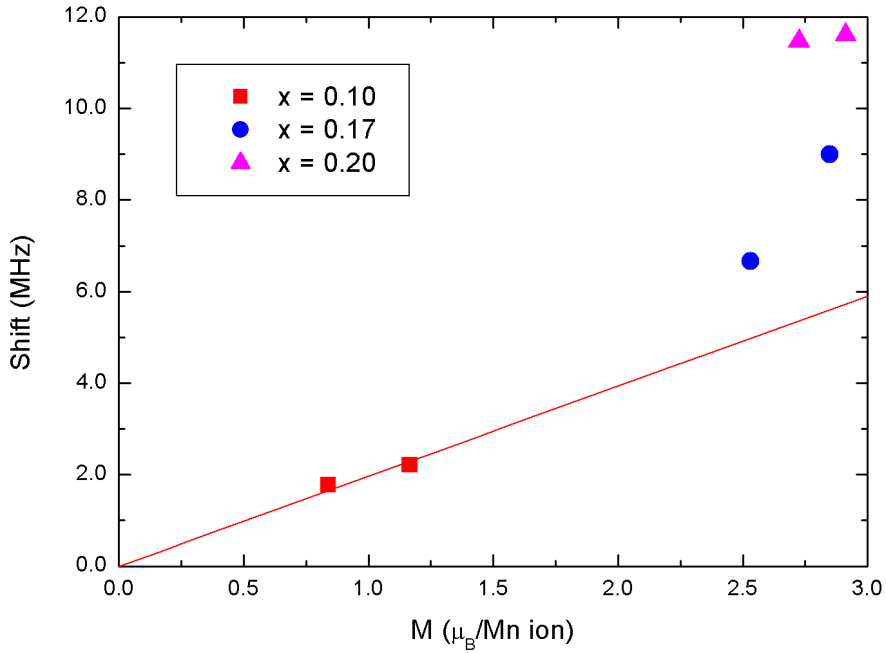
# $^{139}$La NMR in manganites



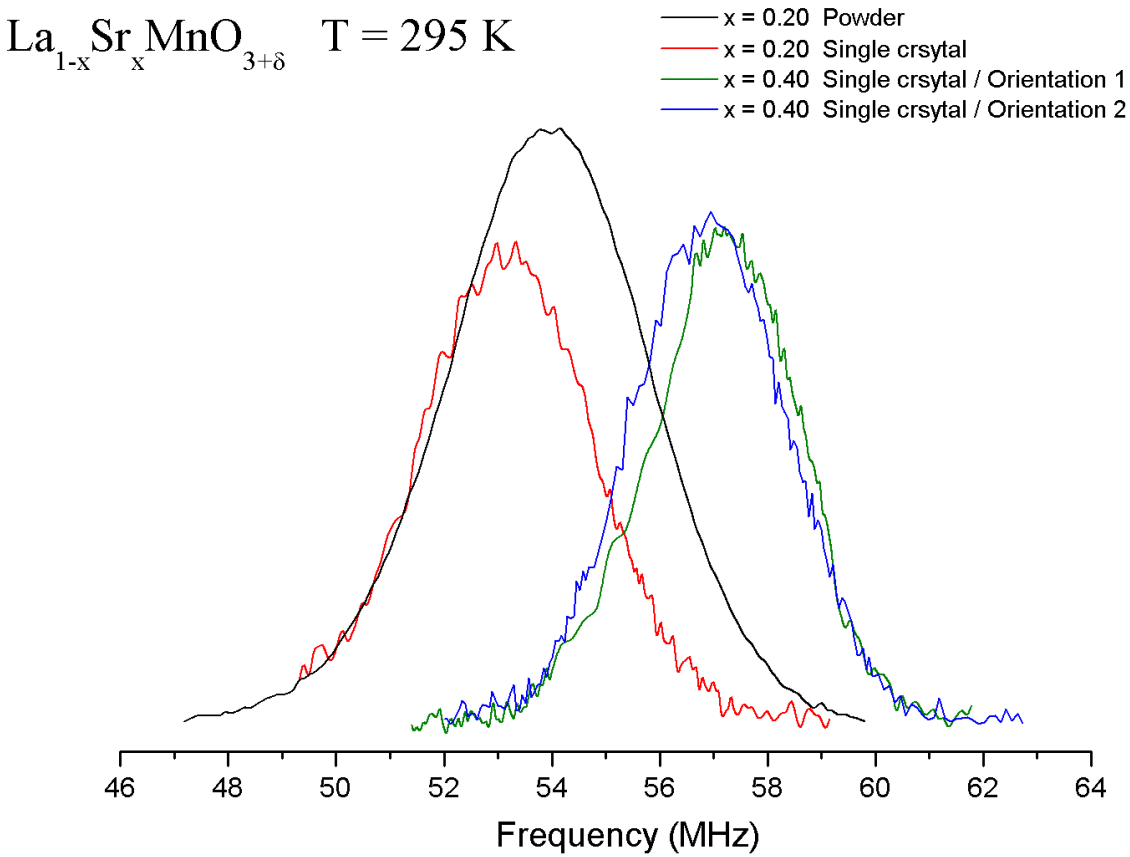

- Room temperature.
- Spin-echo, point by point.
- Shifts with respect to $LaCl_3$.

# Magnetic characterization



# $^{139}$La NMR in manganites




- Room temperature.
- Spin-echo, point by point.
- Field sweep + Frequency stepping .

# $^{139}$La NMR in manganites

| x | $B_0$ (T) | *$B_0$ ratio* | M (emu/g) | *M ratio* | Shift (MHz) | *Shift ratio* | Linewidth (MHz) | *Linewidth ratio* |
|---|---|---|---|---|---|---|---|---|
| 0.10 | 4.7 | | 19.8 | | 1.8 | | 4.4 | |
| 0.10 | 7.0 | *1.5* | 27.5 | *1.4* | 2.2 | *1.2* | 4.9 | *1.1* |
| 0.17 | 4.7 | | 60.6 | | 6.7 | | 5.5 | |
| 0.17 | 7.0 | *1.5* | 68.2 | *1.1* | 9.0 | *1.3* | 4.7 | *0.9* |
| 0.20 | 4.7 | | 65.7 | | 11.5 | | 8.6 | |
| 0.20 | 7.0 | *1.5* | 70.2 | *1.1* | 11.6 | *1.0* | 4.8 | *0.6* |

# Summary – Manganites

- **$^{139}$La NMR results:**
  - Detection of broad and downfield shifted lines in all cases.
  - Broadening caused by quadrupolar effects superimposed to magnetic shifts distribution.
  - Indication of ferromagnetic correlations above $T_C$.

- **To be done:**
  - Zero-field $^{139}$La and $^{55}$Mn NMR above $T_C$.
  - Extract quadrupolar information from time-domain NMR data (nutation, quadrupole oscillations, ...).

# $^{25}$Mg NMR spectroscopy

- Magnesium is an essential element in biological systems, with importance in processes including the activity of metalloproteins and enzymes, cellular metabolism, photosynthesis, etc.
- $Mg^{2+}$ ion has closed electronic structure, which makes it little sensitive to many spectroscopic methods.
- Solid-state NMR appears as a promising useful tool, but...

**Problems:**

– Low natural abundance (10.0 %) of NMR active nuclide ($^{25}$Mg).

– Quadrupolar nucleus: $I$ = 5/2, $Q$ = 0.20 barn.

– Low *gamma* nucleus: $^{25}\gamma/2\pi = -2.608$ MHz/T.

36.735 MHz @ 600 MHz

# Purpose

- Combination of strategies (signal-enhancement methods, high-magnetic field spectrometers, large volume probes) to make natural abundance $^{25}$Mg NMR spectroscopy a practical method for studies of solid samples.
- Analysis of Mg-containing organic compounds to investigate the correlation between structural features and NMR derived parameters ($C_q$, $\eta_q$, $\delta_{iso}$).

# Signal-enhancement methods

Multiple pulse methods:

- ✓QCPMG.
- ✓QCPMG variations.

Methods based on population transfer:

- ✓RAPT / FSG.
- ✓DFS.
- ✓Adiabatic inversion pulses.

# Adiabatic Inversion Pulses

HS: Hyperbolic Secant inversion pulse

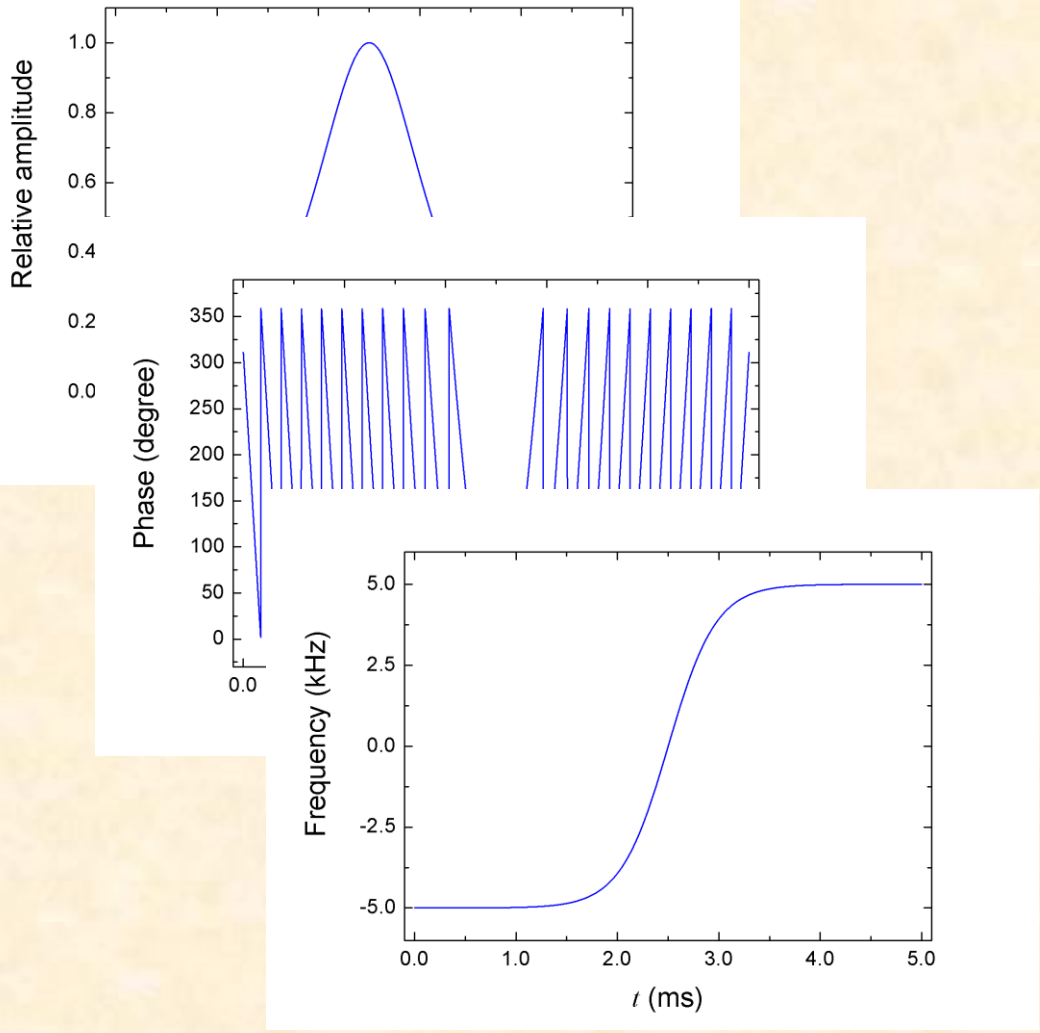
$T_P$ = 5.0 ms
λ= 5.0 kHz
β = 5.3

**RF amplitude and phase modulation:**
$T_P$ = Pulse duration
β = truncation factor
λ = bandwidth / 2
$\Delta\omega_0$ = offset

$$\omega_1(t) = \gamma B_1^{amp}(t) = \omega_1^{\max} \operatorname{sech}\left[\beta\left(1-\frac{2t}{T_P}\right)\right]$$

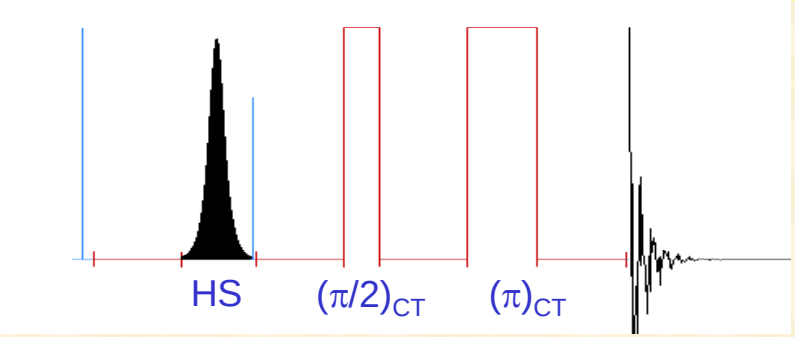
$$\phi(t) = \Delta\omega_0 t + \left(\frac{\lambda}{\beta}\right)\frac{T_P}{2}\ln\left\{\operatorname{sech}\left[\beta\left(1-\frac{2t}{T_P}\right)\right]\right\}$$

$$\Delta\omega(t) = \frac{d\phi}{dt} = \Delta\omega_0 + \lambda\tanh\left[\beta\left(1-\frac{2t}{T_P}\right)\right]$$



# Adiabatic Inversion Pulses

## HS pulse + Spin echo sequence




**Cosine amplitude modulation:**

✓ Satellites at offsets = $\pm\Delta\omega_{off}$

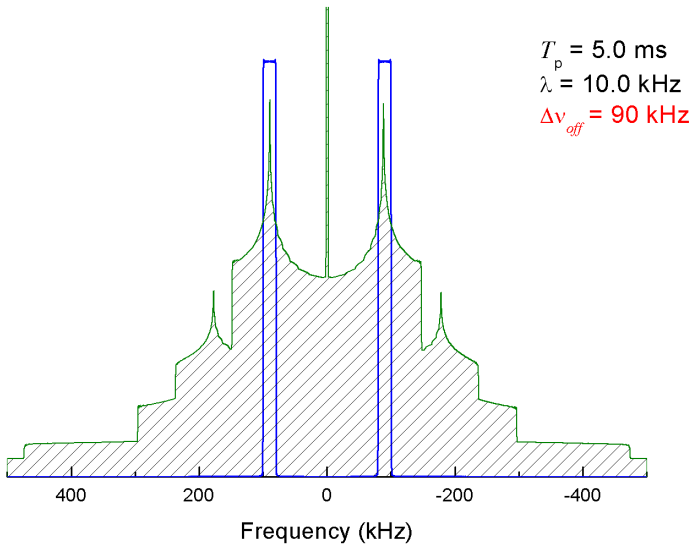
$$\omega_1^{max} = \omega_1^0 \cos(\Delta\omega_{off} t)$$

**Optimal settings for MAS experiments:**

- ✓ Offsets should be placed around the peaks of the static powder pattern and bandwidth must be set close to the spinning frequency (only one spinning sideband is then inverted).
- ✓ Sweep direction should be chosen to first invert ST2, then ST1, without hitting CT.
- ✓ When properly optimised, the method can give enhancement factors close to ST inversion limit.
- ✓ Distortions in the spectral lineshape can occur, depending on offsets and bandwidth values.
- ✓ Short $T_1$ values restrict the efficiency of the method in many cases.

Wasylishen et al., *J. Magn. Res.* 184 (2007) 85

FFT spectrum of waveform:

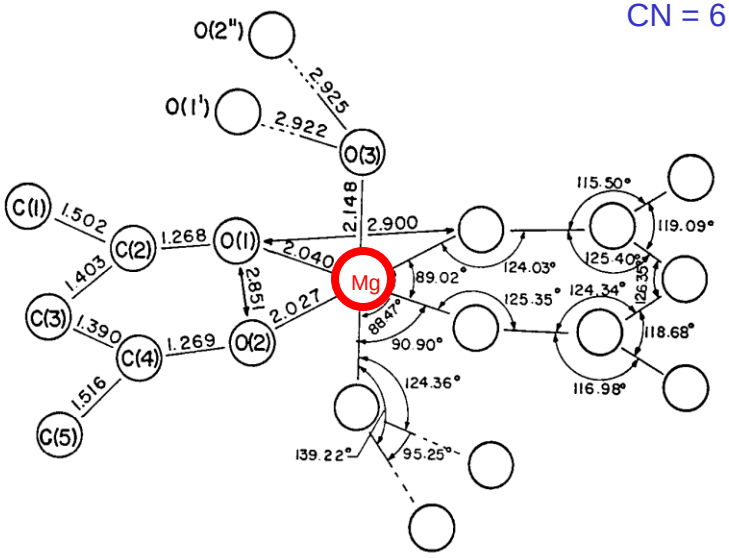


# Materials

**$Mg(Acac)_2 \cdot 2H_2O$**

**$Na_2MgEDTA \cdot xH_2O$**

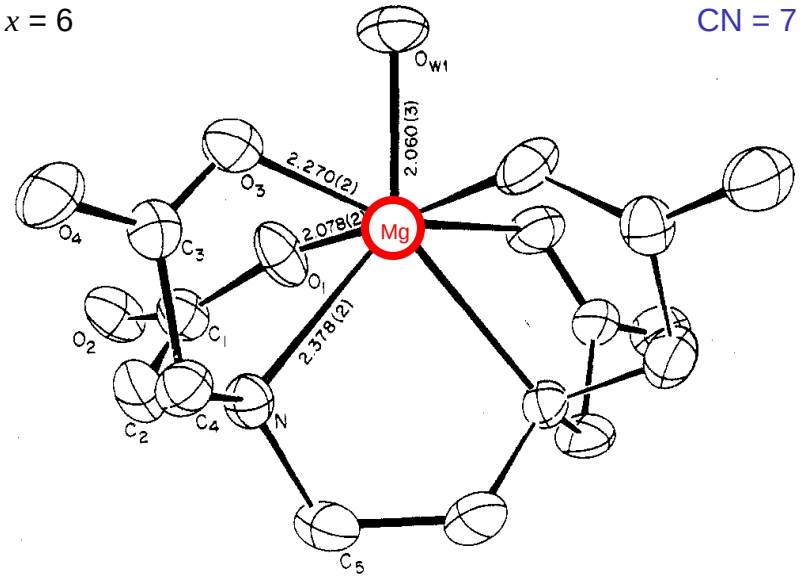
CN = 6




Morosin, *Acta Cryst.* 22 (1967) 316

$x$ = 6

CN = 7

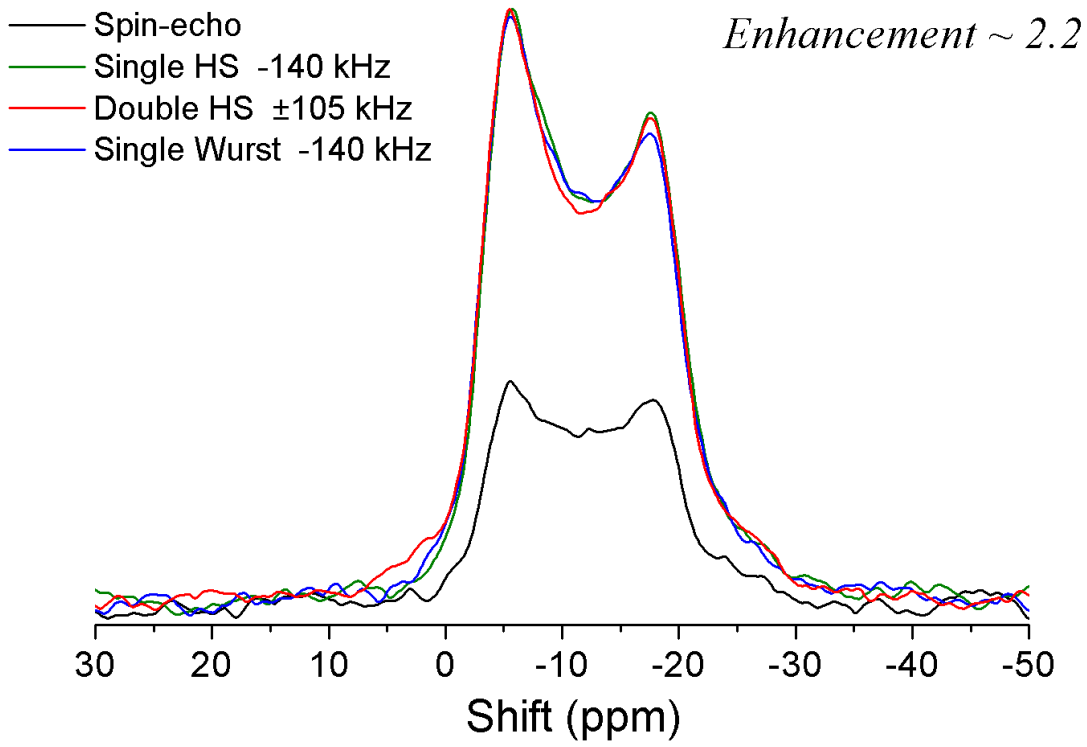



Stezowski et al., *Inorg. Chem.* 12 (1973) 1749

- Natural abundance materials.
- Commercial samples (Aldrich), used as received.
- Structure and hydration level checked by XRD and TG: $x = 4$

# $^{25}$Mg NMR results

**$Na_2MgEDTA \cdot 4H_2O$**




- MAS - 3.5 kHz.
- Probe 9.5 mm.
- $\omega_1/2\pi$ = 14 kHz
- 1000 scans.
- $T_P$ = 2 ms
- BW = 10 kHz

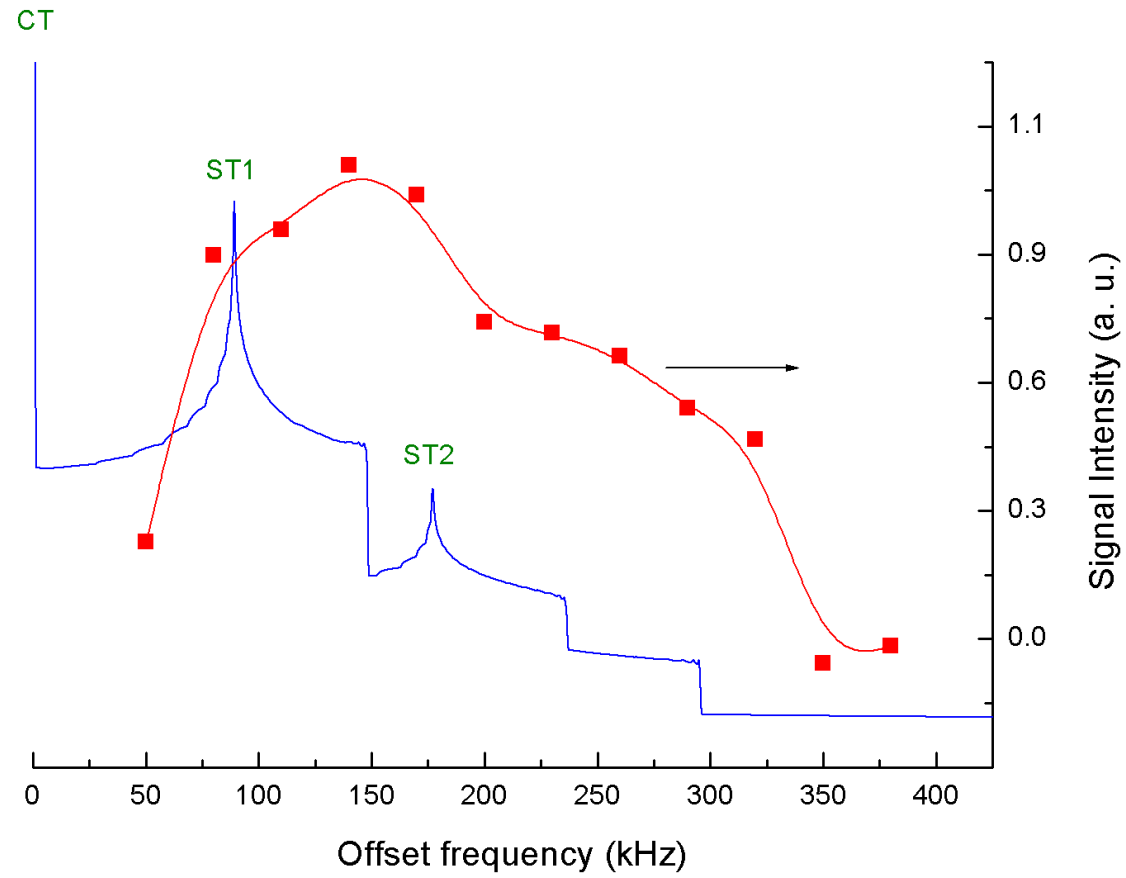
$$T_1^{CT} \lesssim 10\,\text{ms}$$

Short $T_1$ is a limiting factor for signal-enhancement in this material.

# $^{25}$Mg NMR results

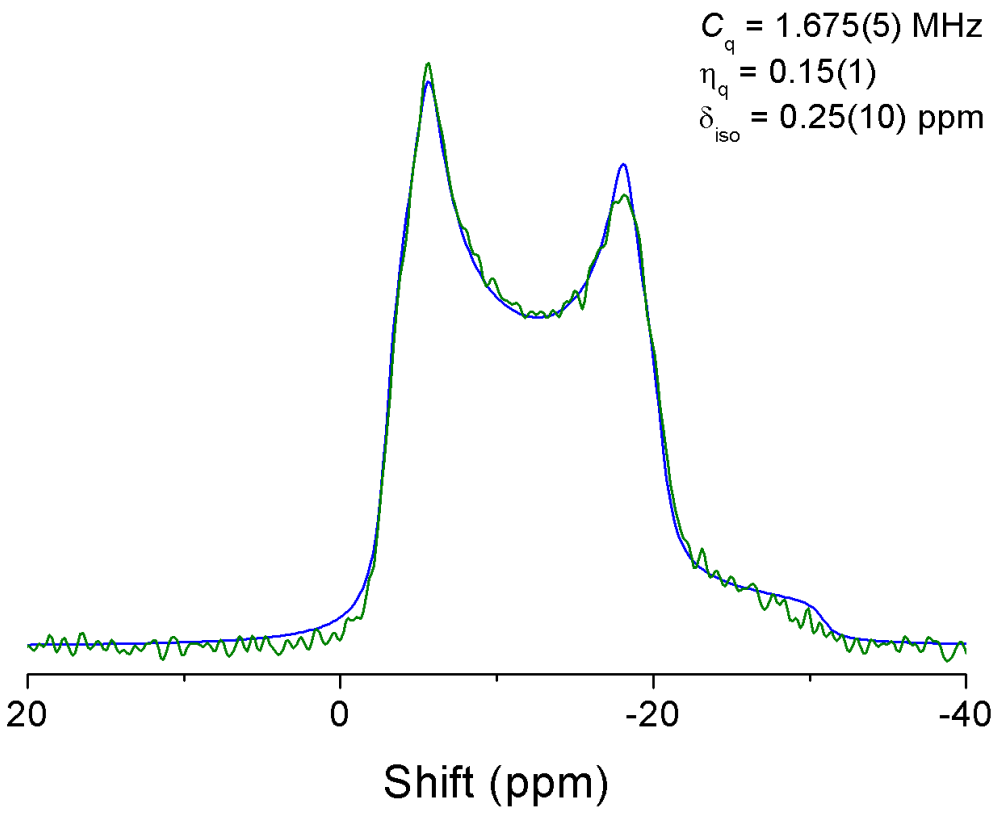
**$Na_2MgEDTA \cdot 4H_2O$**

- Single HS + spin-echo
- MAS - 7.0 kHz.
- Probe 7 mm.
- 1000 scans.



# $^{25}$Mg NMR results

**$Na_2MgEDTA \cdot 4H_2O$**



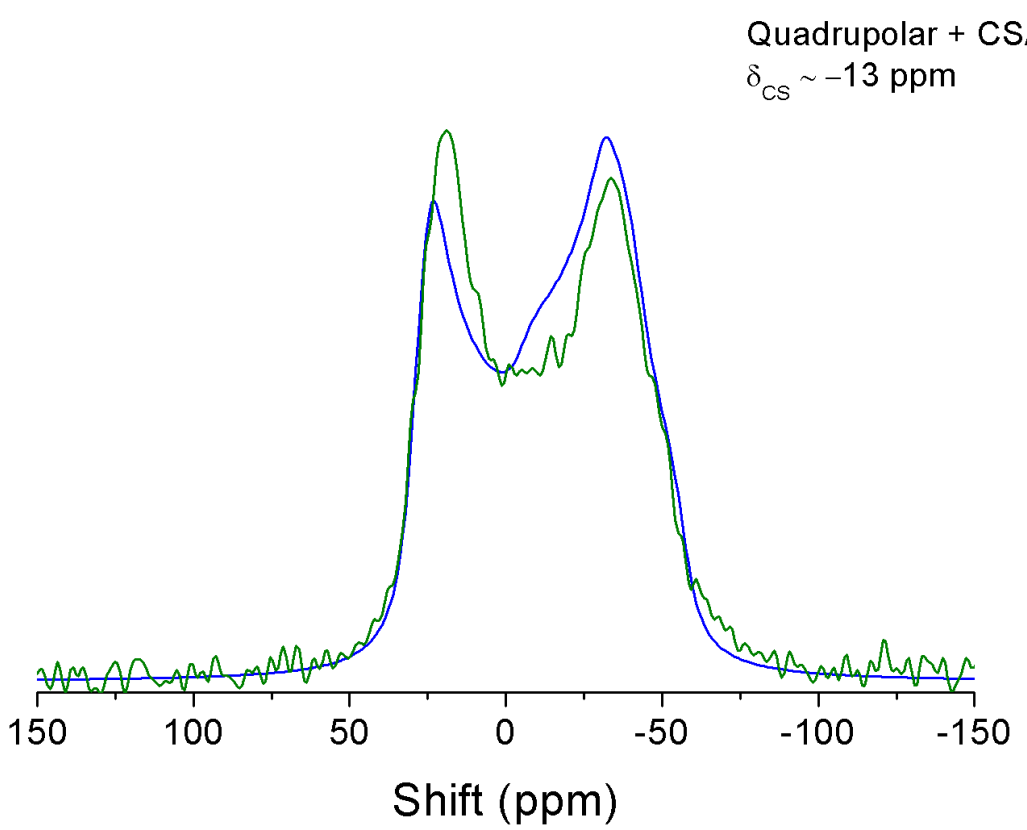

- Spin-echo sequence.
- MAS - 3.5 kHz.
- Probe 9.5 mm.
- $\omega_1/2\pi$ = 14 kHz
- 20000 scans.

Fitted using DMFIT - Massiot et al., *Magn. Res. Chem.* 40 (2002) 70

# $^{25}$Mg NMR results

**$Na_2MgEDTA \cdot 4H_2O$**

- Spin-echo sequence.
- Static.
- Probe 9.5 mm.
- $\omega_1/2\pi$ = 17 kHz
- 774000 scans.

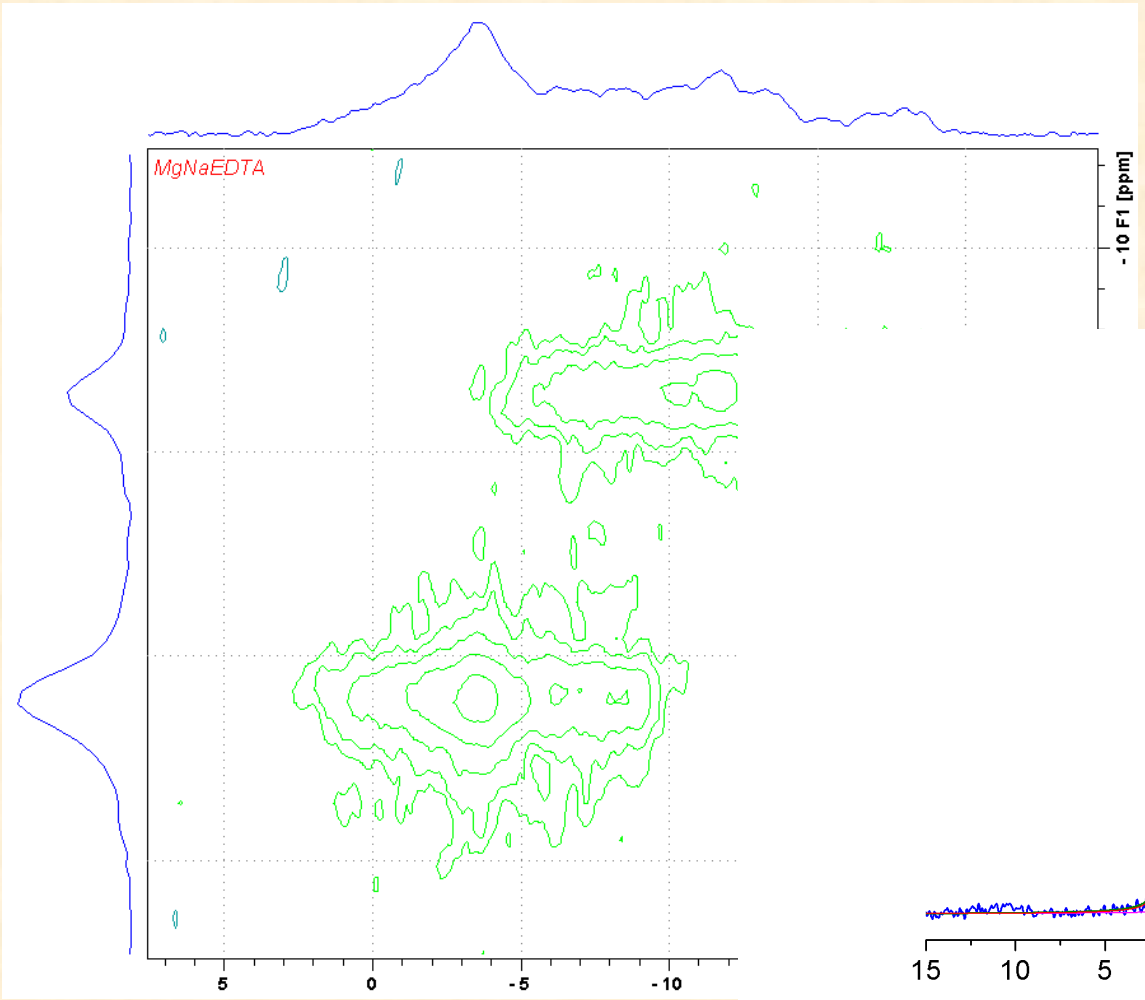


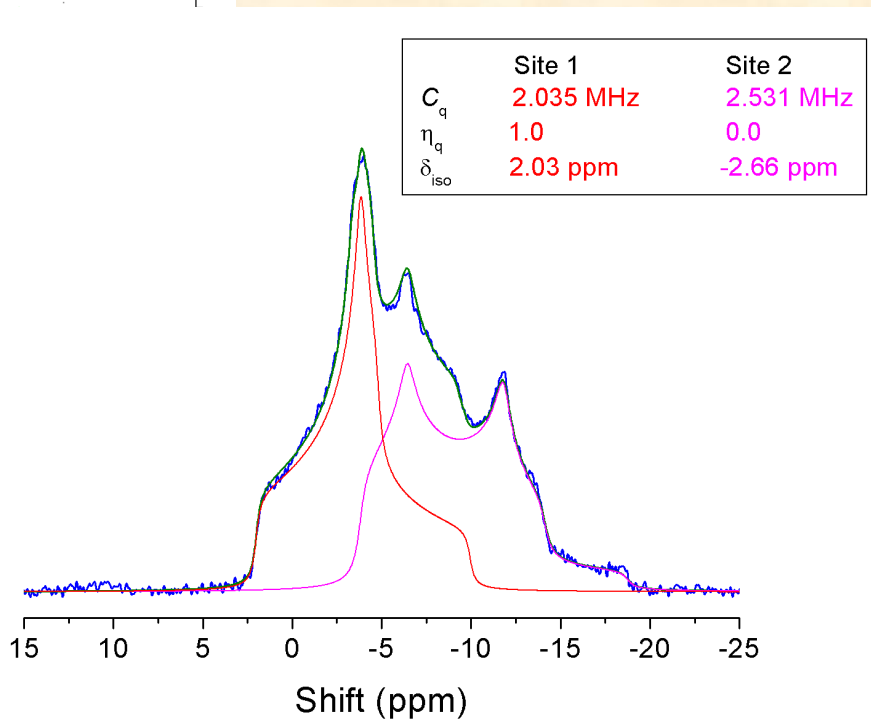

Fitted using DMFIT - Massiot et al., *Magn. Res. Chem.* 40 (2002) 70

# $^{23}$Na NMR – MQ/MAS

**$Na_2MgEDTA \cdot 4H_2O$**

- $t_1$-split method.
- Amplitude modulation.
- MAS at 10 kHz.
- Probe 2.5 mm.
- 6200 scans.



# Comparisons

| Sample | Ref. | $C_q$ (MHz) | $\eta$ | $\delta_{iso}$ (ppm) | CN | Structure | Comments |
|---|---|---|---|---|---|---|---|
| Mg Methylmalonate Hydrate | Sham & Wu *Inorg. Chem. 2*000;39:4 | 1.95 | 0.80 | 12 | 6 | Distorted octahedral $Mg(H_2O)_4(MetMal)_2$ | $^{25}$Mg Enriched |
| Mg Acetate Hydrate | Sham & Wu *Inorg. Chem. 2*000;39:4 | 1.90 | 0.82 | 27 | 6 | Distorted octahedral $Mg(H_2O)_4(OAc)_2$ | $^{25}$Mg Enriched |
| Mg Orotate Hydrate | Sham & Wu *Inorg. Chem. 2*000;39:4 | 2.56 | 0.15 | 6 | 6 | Distorded octahedral Asymmetrycal ligands 5 N 1 O | $^{25}$Mg Enriched |
| Mg Phtalocyanine Hydrate Pyridine | Wong et al. *JPCA* 2006;110:10084 | 13.0 | 0.00 | nd | 5 | Square pyramidal $Mg(H_2O)_1(N)_4$ | $^{25}$Mg Enriched |
| **$Mg(Acac)_2.2H_2O$** | **This work** | **7.1** | **1.0** | **–1.0** | **6** | **Distorted Octahedral $Mg(O)_6$** | **Natural abundance** |
| **$Na_2MgEDTA\ .\ 4H_2O$** | **This work** | **1.675** | **0.15** | **0.25** | **7** | **$Mg(O)_4(Ow)_1(N)_2$** | **Natural abundance** |

# Summary – Mg organometallics

- Work in progress...
- More representative samples are needed.
- $Na_2MgEDTA \cdot 4H_2O$ is a good setup sample for $^{25}Mg$ NMR.
  - ✓ Chemical shift reference.
  - ✓ Moderate quadrupolar coupling.
  - ✓ Short $T_1$.
  - ✓ Setup of signal-enhancement methods for $^{25}Mg$ NMR (DFS, RAPT, HS pulses, etc).

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Welcome to Vitória (anytime...)