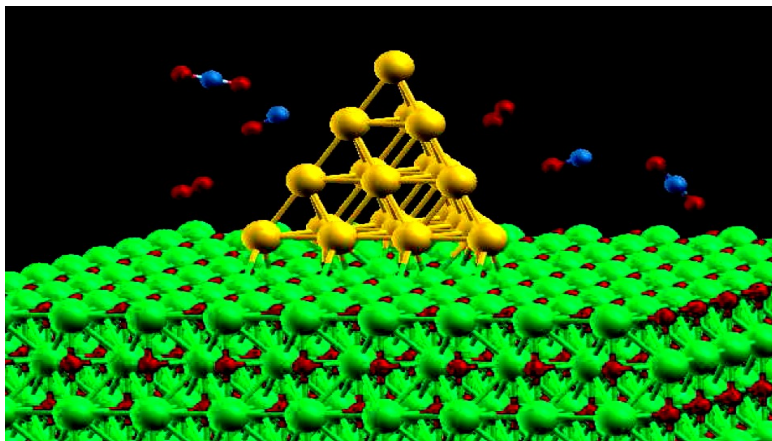


# **A few projects with Quantum ESPRESSO a personal selection**

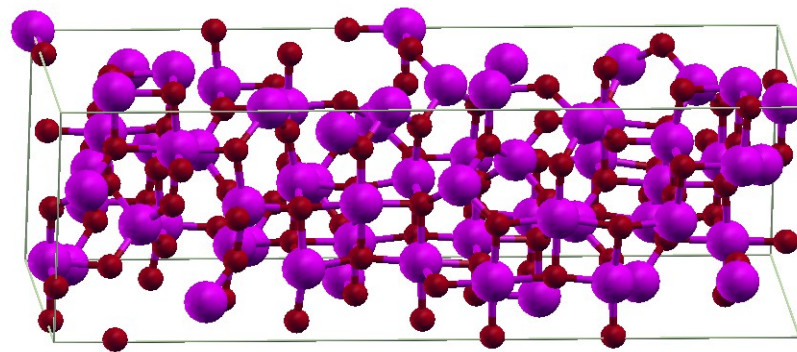
Stefano de Gironcoli

SISSA and CNR-IOM DEMOCRITOS

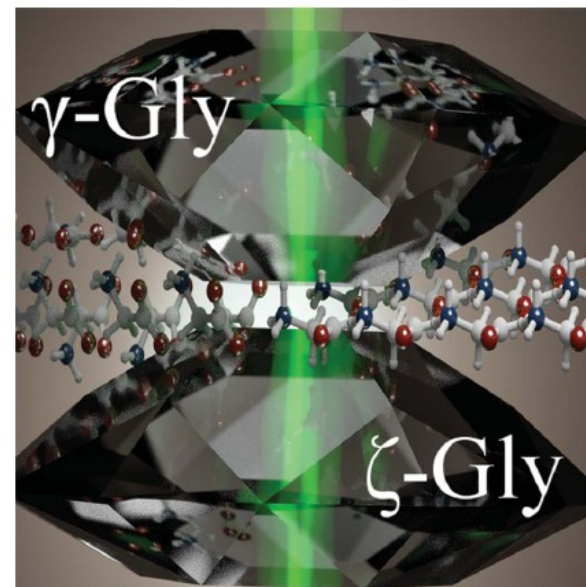
## Controlling morphology of Au<sub>20</sub>-clusters by substrate doping



## <sup>27</sup>Al NMR shifts of Alumina and its precursors



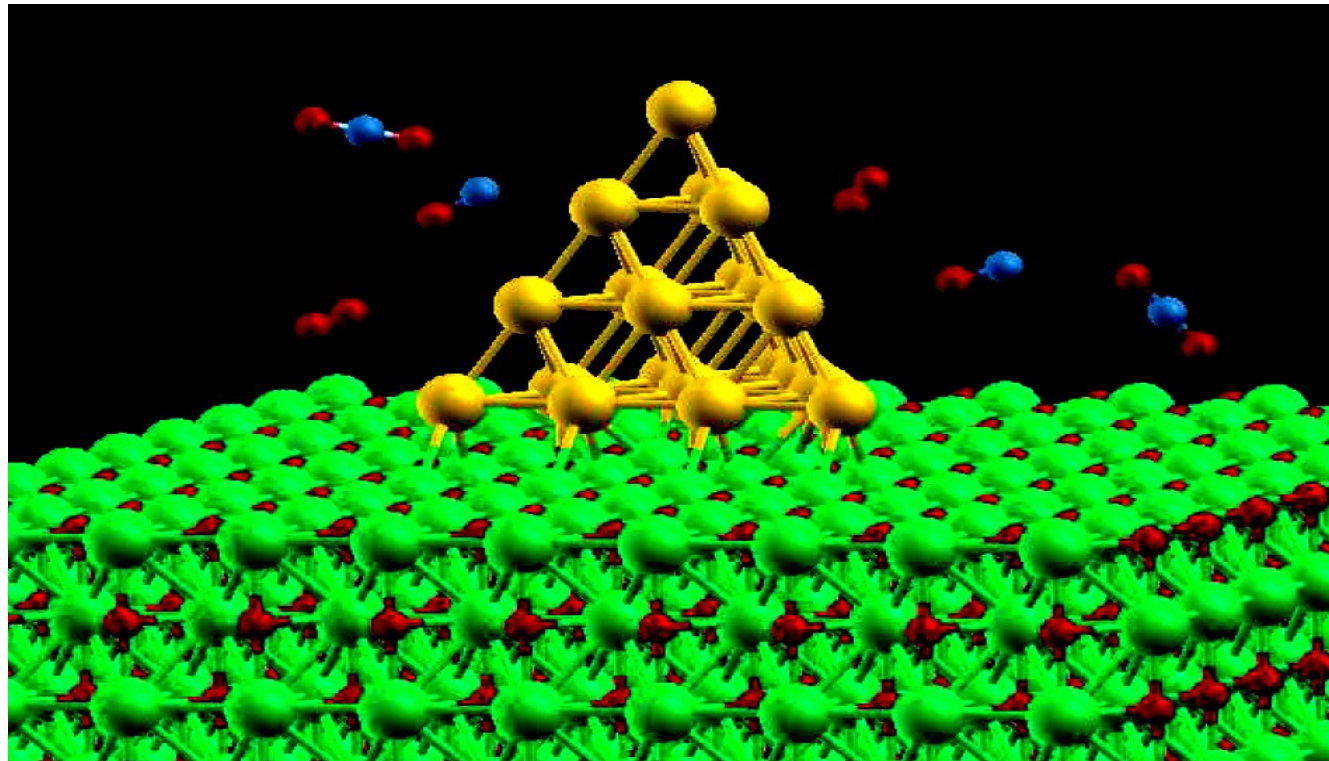
## ζ-Glycine: Insight into the mechanism of a polymorphic phase transition



## Complete <sup>13</sup>C Chemical Shift Assignment for Cholesterol Crystal



# Controlling morphology of $\text{Au}_{20}$ – clusters by substrate doping



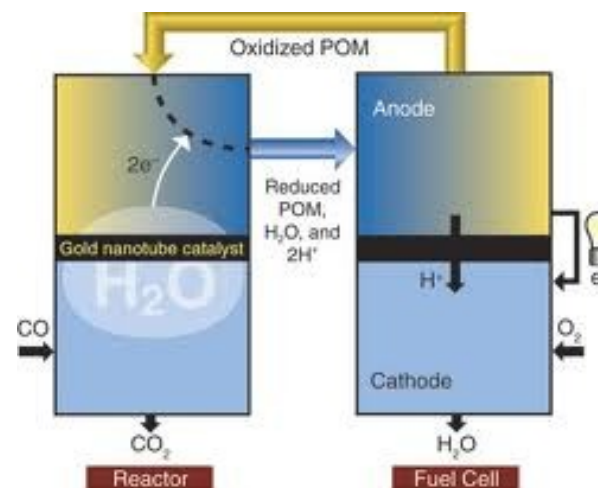
# Catalytic Activity of Gold

- Bulk gold → inert;
- nanoclusters → good catalysts
- Most important reaction: CO oxidation to CO<sub>2</sub>
  - In automobile exhaust
  - Prevent CO poisoning in fuel cells
- negatively charged cluster showed excellent CO conversion yields and rates<sup>1</sup>
- conversion rate dependent on size and shape of cluster
- Au<sub>20</sub> - extremely robust<sup>2</sup> to distortions when supported over an MgO surface, keeping its tetrahedral structure



Vehicle exhaust emissions

<http://saferenvironment.wordpress.com>

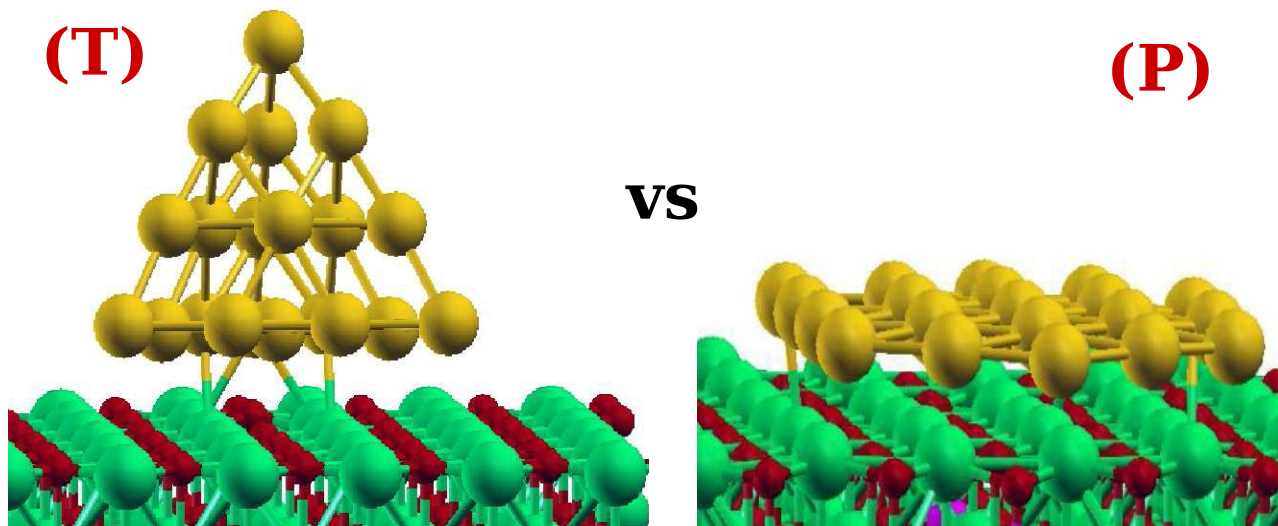


[http://comdig.unam.mx/index.php?id\\_issue=2004.35](http://comdig.unam.mx/index.php?id_issue=2004.35)

1. B. Yoon, et al . Science 307 (2005) 403
2. J. Li, Xi Li, H. Zhai, L. Wang, Science 299 (2003)



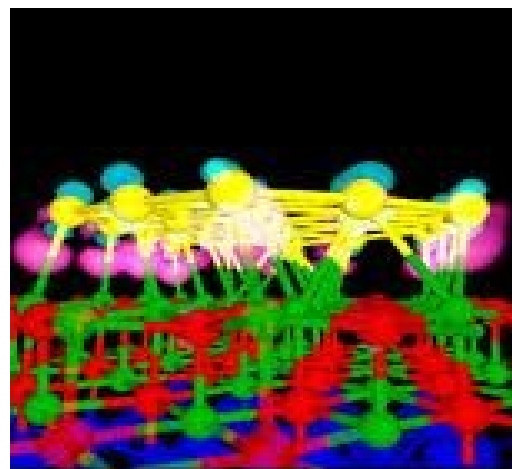
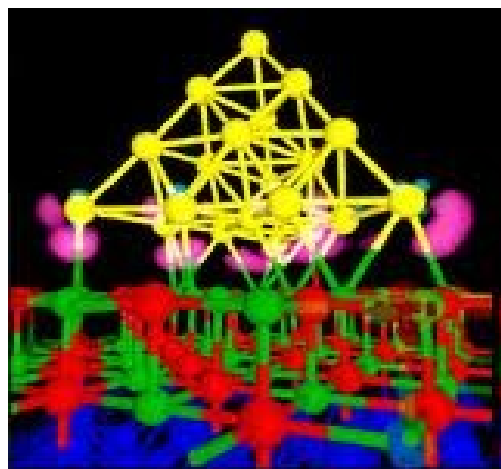
# Problem and Motivation



## **Why Au(P) desirable over Au(T)?**

- (1) more charge absorbed from substrate
- (2) more surface area
- (3) more sites of high charge accumulation → more active sites for reaction
- (4) better catalytic activity for oxidation reactions

# Possible Methods



## How to favor (P) over (T) ?

- MgO support? No
  - F-center defect rich MgO?<sup>1</sup> No
  - Thin oxide layer over metal support?<sup>2</sup> Yes!
  - Placing system in high electric field?<sup>3</sup> Yes!
- } Impractical for applications

**Look for better solution ...**

1. Z. Yan, D. W. Goodman, JACS 127 (2005), 1604.
2. C. Harding, U. Landman, J. Am. Chem. Soc. 131 (2009) 538.
3. B. Yoon, U Landman, PRL 100 (2008) 056102.

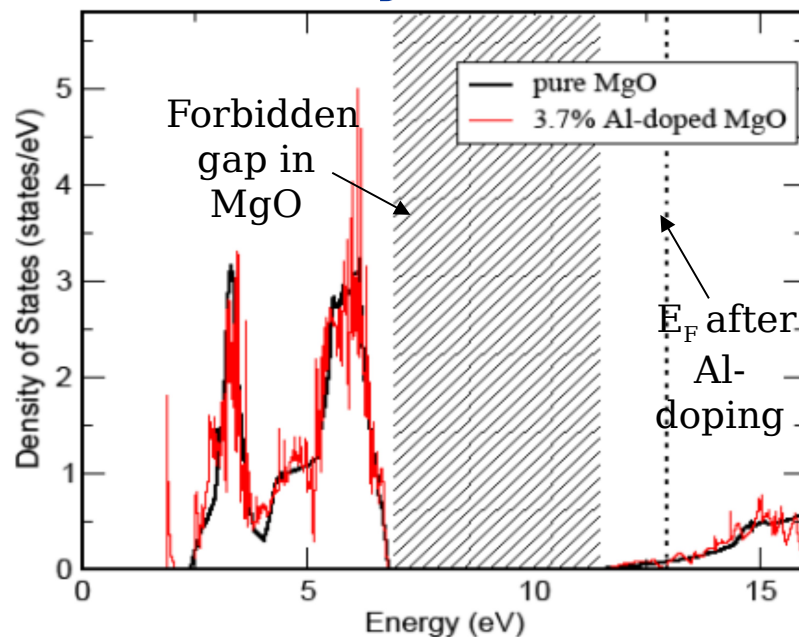
# Technical Details

- Quantum ESPRESSO package used
- Plane wave energy cut-off 30 Ry, charge density cut-off 240 Ry
- Exchange-correlation functional – GGA
- Ultrasoft pseudopotentials used, scalar relativistic pseudopotentials used for Au
- Smearing – Marzari-Vanderbilt
- Bulk calculations on MgO and Al-doped MgO –  $3 \times 3 \times 3$  cells used
- Slab calculations on MgO, Al-doped MgO, substrate supported Au clusters –  $6 \times 6$  cell with 4 layers of substrate and 14 Å vacuum considered
- k-point sampling at gamma point

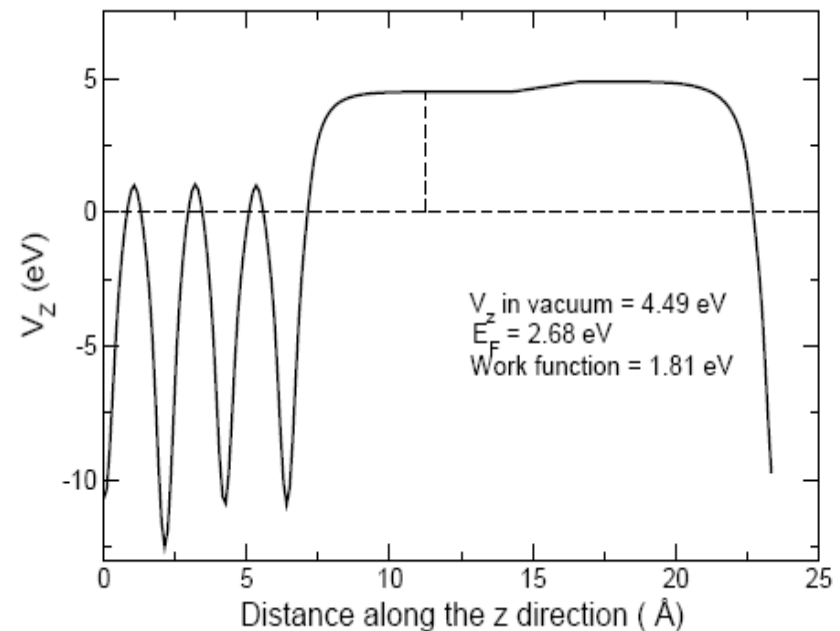
# Our proposed solution

- Mg [Ne] 3s<sup>2</sup>
- Al [Ne] 3s<sup>2</sup>, 3p<sup>1</sup>
- Doping of MgO with Al → extra electron of Al delocalized in MgO → charge transfer to Au cluster → **(P) favored ??**

## Density of States



## Work Function

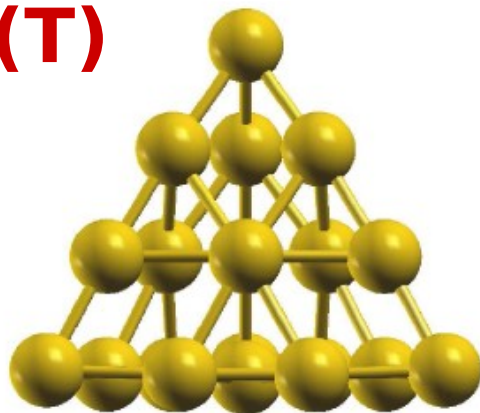


- Shift of the Fermi level into the conduction band on doping
- Work function on doping (conc. 2.78%) = 1.81 eV.



# Results on Au<sub>20</sub> free clusters

**(T)**

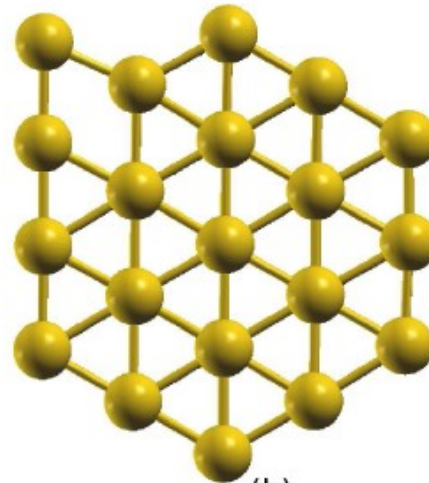


(a)

Binding energy  
= 1.14 eV/atom

Shortest NN bond  
dist = 2.69 Å

**(P)**



(b)

Binding energy  
= 1.06 eV/atom

Shortest NN bond  
dist = 2.70 Å

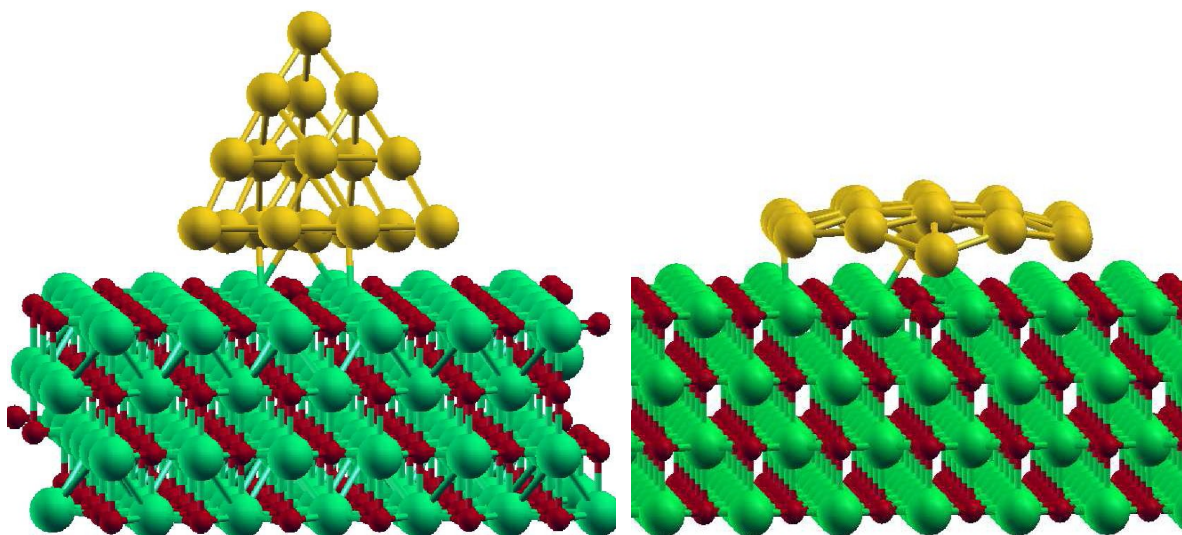
**Tetrahedral (T) structure favored over planar (P) structure in vacuum by 1.52 eV**

**(in agreement with earlier results)**

# Main Result

## Au<sub>20</sub> on pure MgO

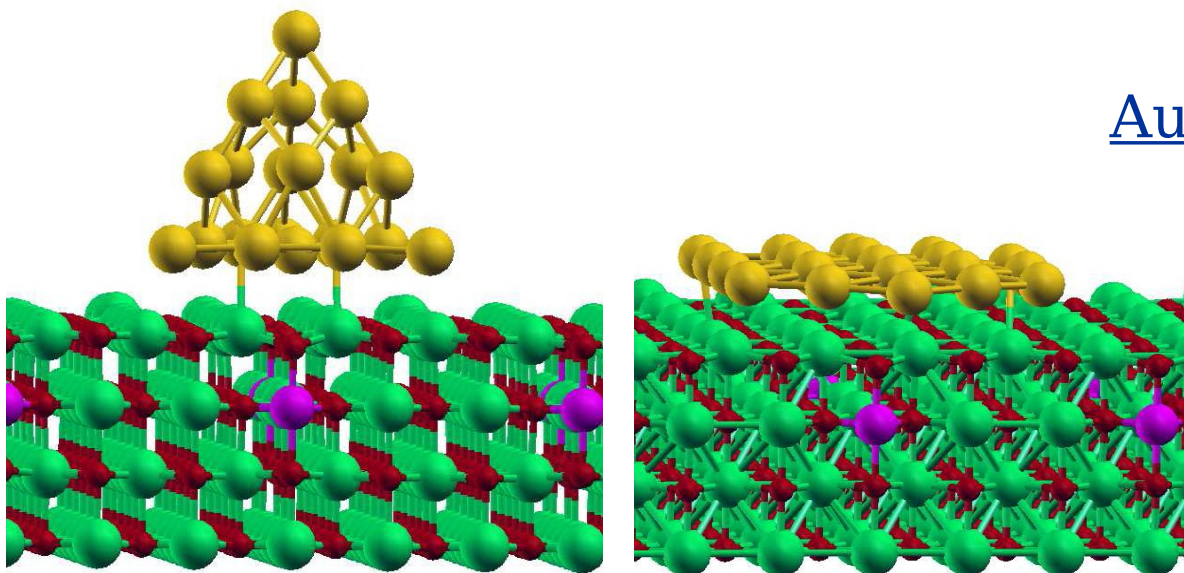
Au(T) favored  
over Au(P) by  
0.60 eV



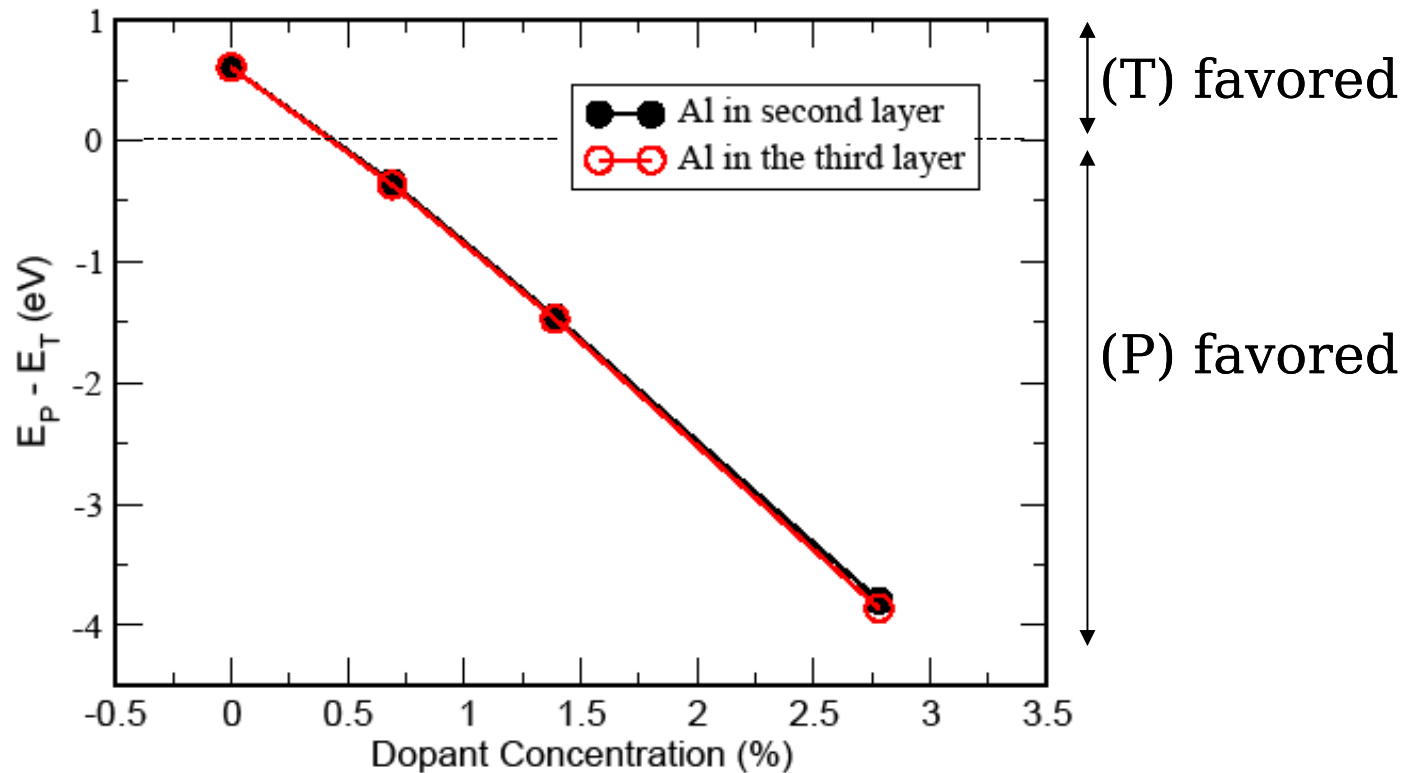
## Au<sub>20</sub> on Al-doped MgO

Various conc.s studied

Au(P) favored  
over Au(T) by  
value dependent  
on conc.

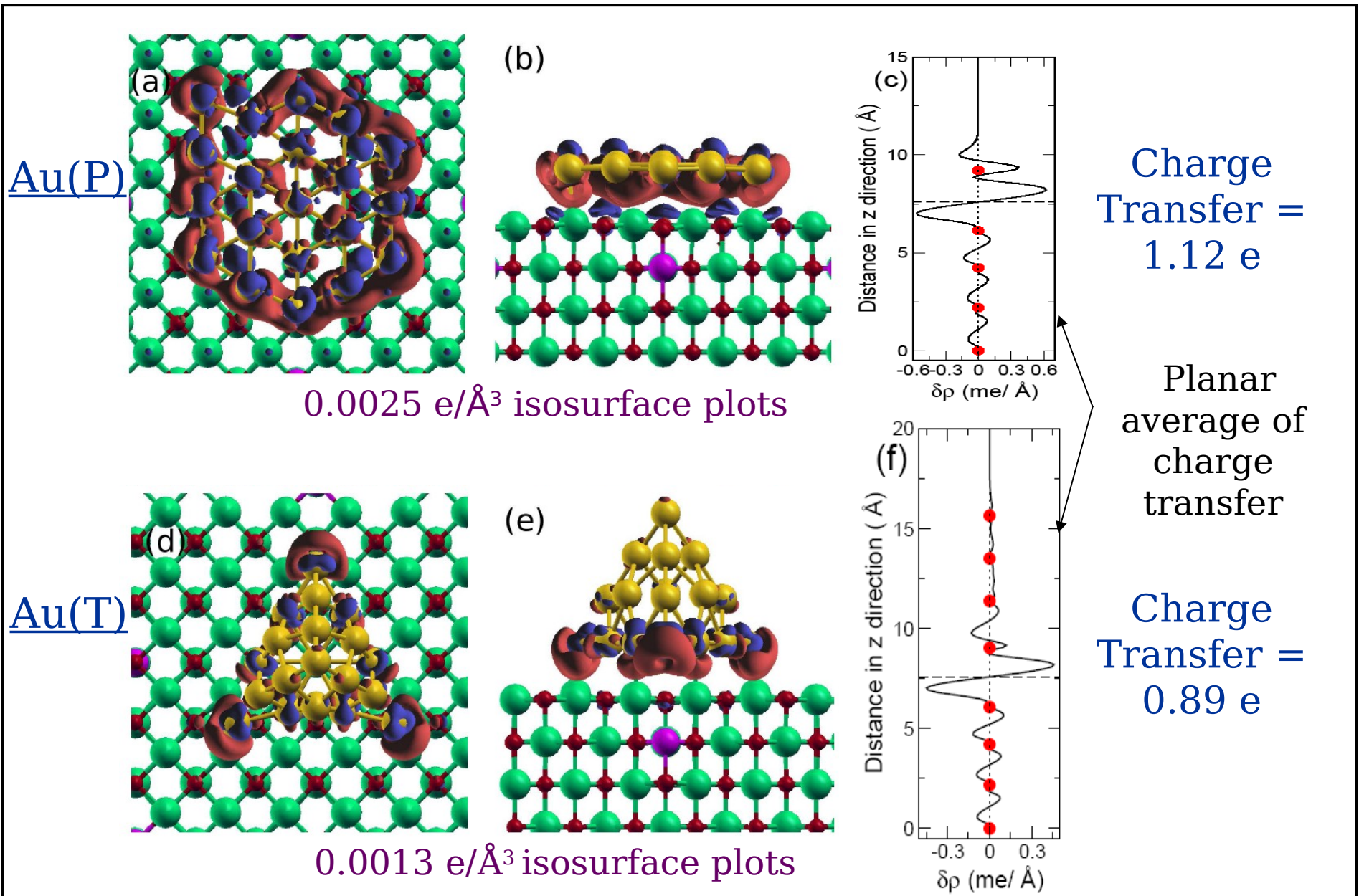


# Au clusters on Al-doped MgO



- ~ **Linear relationship** between **dopant concentration** and **stability of (P) structure over (T)** obtained.
- Results not very sensitive to position of Al atoms
- **Minimum conc. of Al** required to **flip geometry** of Au cluster = **0.4 %**

# Charge transfer from substrate to cluster





# Conclusions

- Doping of MgO results in dimensionality crossover of Au<sub>20</sub> cluster from (T) to (P)
- Linear relation between dopant concentration and energy difference between (P) and (T) observed.
- Why our method?
  - (1) preparation of metal-supported MgO difficult
  - (2) electric field applied (1 V/nm) too high
  - (3) Al dopant atoms may act as anchor sites for Au clusters

## Credits

**Nisha Mariam Mammen**

**Shobhana Narasimhan**

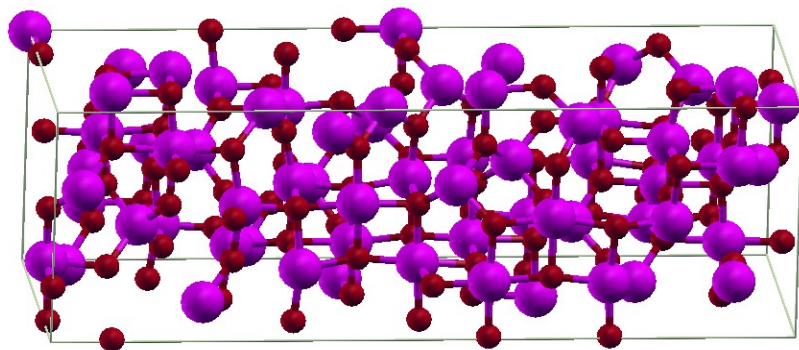


**TSU-JNCASR, Bangalore**



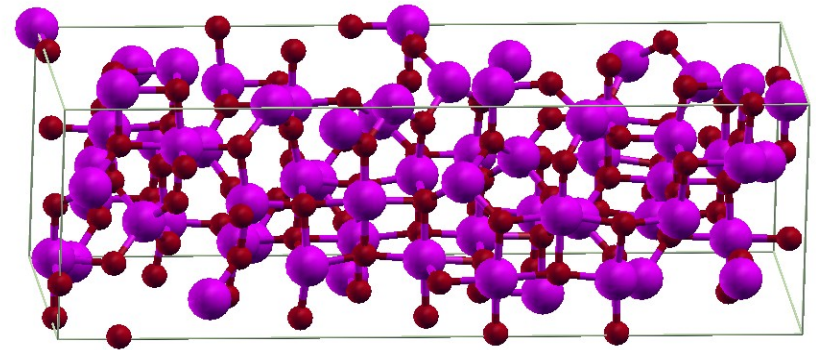


# NMR properties of Materials from Density Functional Perturbation Theory



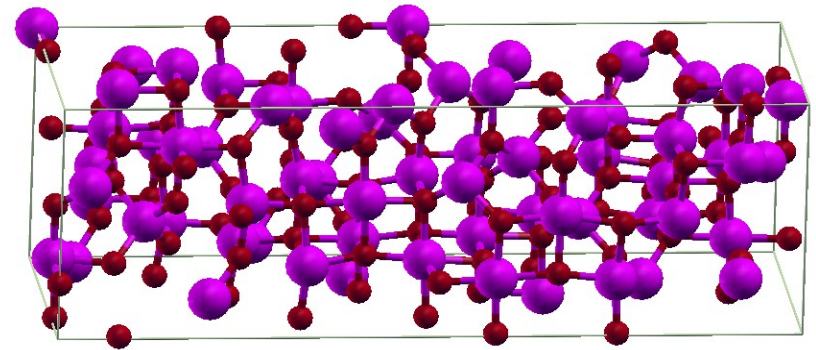
# Outline

- Theory (GIPAW + PAW)
- $^{27}\text{Al}$  NMR shifts of alumina and its precursors
- $^{13}\text{C}$  NMR of Cholesterol Crystals

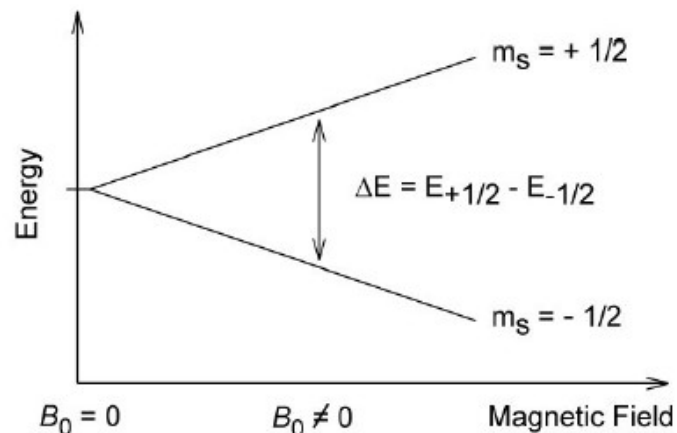


# Outline

- Theory (GIPAW + PAW)
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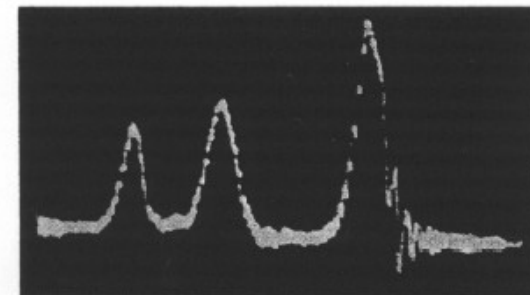


# Theory : NMR Chemical Shifts

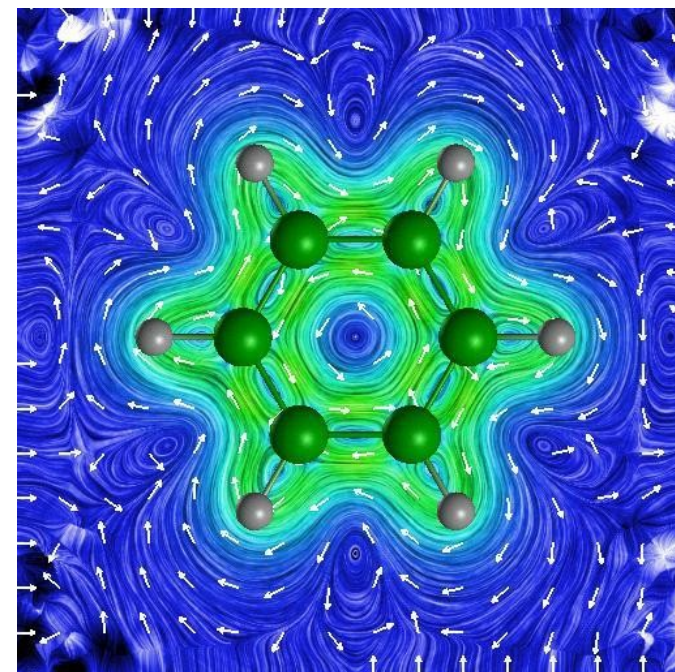


$$\Delta E = \hbar \gamma B_{\text{tot}} \Delta m_s = \hbar \omega$$

$$B_{\text{tot}} = B_{\text{ext}} + B_{\text{ind}} + B_{\text{other}}$$

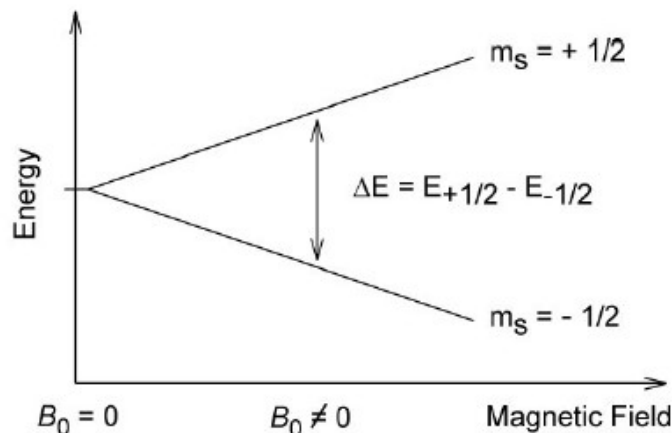


Arnold,  
Dhamatti  
Packard,  
JCP **19**,  
507 (1951)



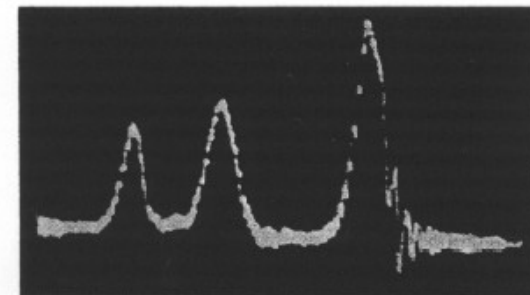


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Arnold,  
Dhamatti  
Packard,  
JCP **19**,  
507 (1951)

## shielding tensor

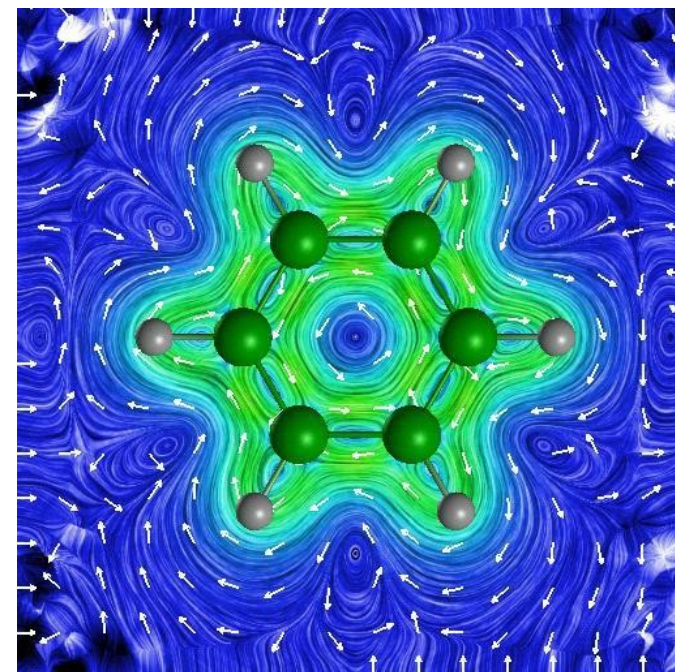
$$B_{\text{eff}} = B_{\text{ext}}(1 - \vec{\sigma})$$

- independent of magnetic field
- usually  $\ll 1$
- measured in ppm (1 ppm =  $10^{-6}$ )

## chemical shift

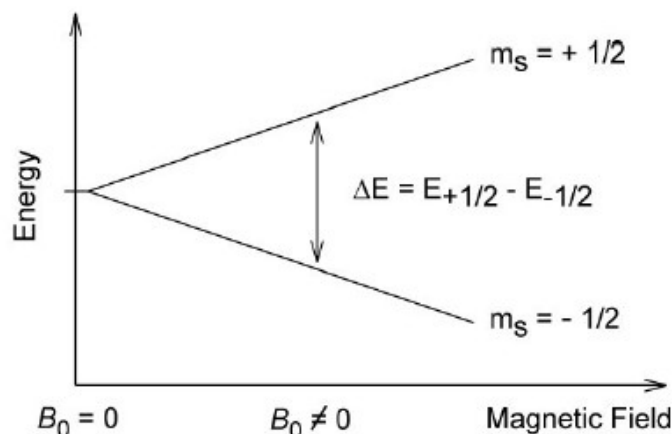
$$\delta = -(\sigma - \sigma_{\text{ref}})$$

- given as deviation from a reference
- TMS( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ )
- measured in ppm (1 ppm =  $10^{-6}$ )



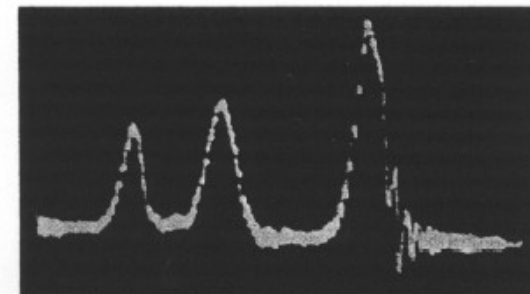


# Theory : NMR Chemical Shifts



$$\Delta E = \hbar \gamma B_{\text{tot}} \Delta m_s = \hbar \omega$$

$$B_{\text{tot}} = B_{\text{ext}} + B_{\text{ind}} + B_{\text{other}}$$



Arnold,  
Dhamatti  
Packard,  
JCP **19**,  
507 (1951)

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$$B_{\text{eff}} = B_{\text{ext}}(1 - \vec{\sigma})$$

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- usually  $\ll 1$
- measured in ppm (1 ppm =  $10^{-6}$ )

## chemical shift

$$\delta = -(\sigma - \sigma_{\text{ref}})$$

- given as deviation from a reference
- TMS( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ )
- measured in ppm (1 ppm =  $10^{-6}$ )

## Other NMR interactions

Dipolar magnetic coupling  
Indirect magnetic coupling (J coupling)  
Quadrupolar interactions

## All-electron magnetic response with pseudopotentials: NMR chemical shifts

Chris J. Pickard\*

*Institut für Geowissenschaften, Universität Kiel, Olshausenstrasse 40 D-24098 Kiel, Germany*

Francesco Mauri

*Laboratoire de Minéralogie-Cristallographie de Paris, Université Pierre et Marie Curie, 4 Place Jussieu, 75252, Paris, Cedex 05, France*

(Received 17 November 2000; published 10 May 2001)

### ◆ Density Functional Perturbation Theory :

$$\left| \phi_n^{(0)} \right\rangle \longrightarrow \left| \phi_n^{(1)} \right\rangle \longrightarrow \mathbf{j}_{\text{ind}}(\mathbf{r}) \longrightarrow \mathbf{B}_{\text{ind}}(\mathbf{r})$$

$$\mathbf{B}_{\text{ind}}(\mathbf{r}) = \frac{1}{c} \int d^3\mathbf{r}' \frac{\mathbf{j}_{\text{ind}}(\mathbf{r}') \times (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}$$

$$\mathbf{B}_{\text{ind}} = -\bar{\bar{\sigma}} \mathbf{B}_{\text{ext}}$$

# ◆ Gauge-Including Projector-Augmented Wave

Bloch, PRB50, 17953 (1994)

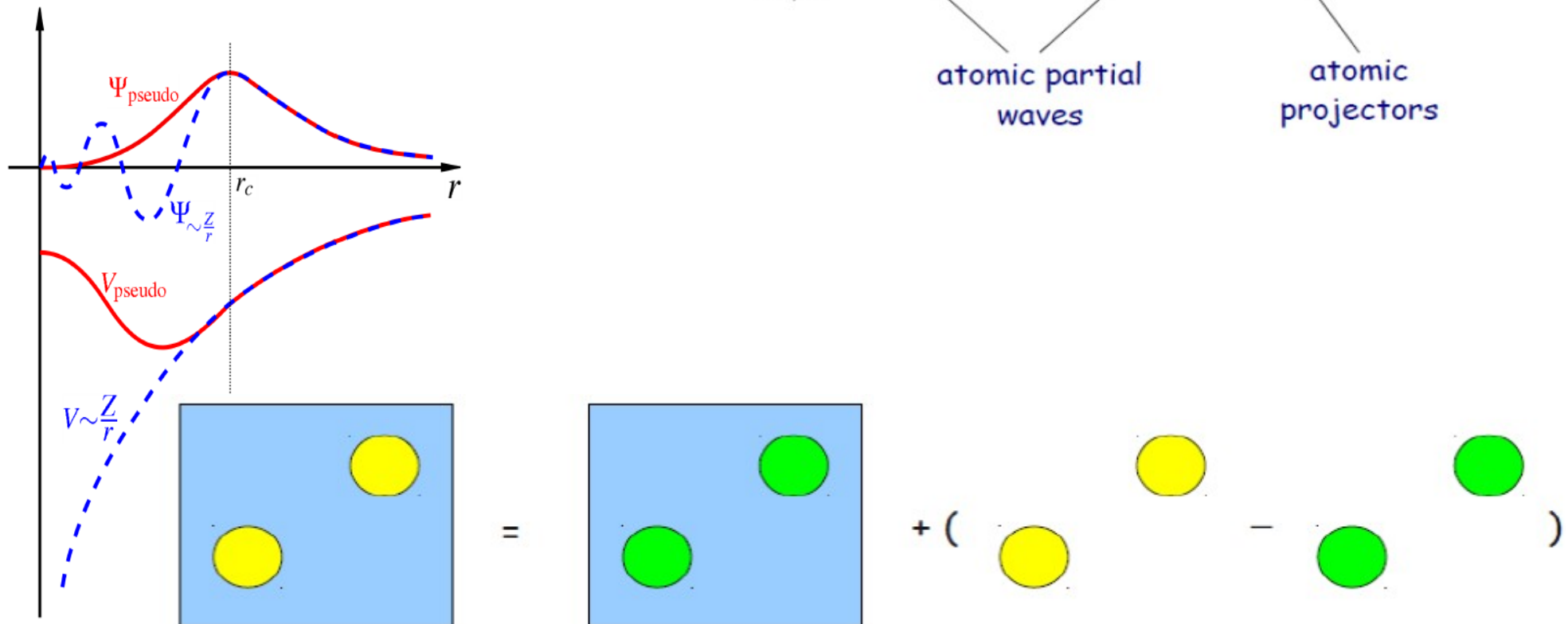
$$|\Psi\rangle = \mathcal{T}|\tilde{\Psi}\rangle$$

$$|\psi^{\text{AE}}\rangle = |\psi^{\text{PS}}\rangle + \sum_{R,n} (|\phi_{r,n}^{\text{AE}}\rangle - |\phi_{R,n}^{\text{PS}}\rangle) \langle p_{R,n} | \psi^{\text{PS}} \rangle$$

valence wfcs

atomic partial  
waves

atomic  
projectors



# gauge origin problem

Under uniform magnetic field  $B$  , one center

$$H = \frac{1}{2} \left( \mathbf{p} + \frac{1}{c} \mathbf{A}(\mathbf{r}) \right)^2 + V(\mathbf{r}) \quad \mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{d})$$

$$H = \frac{1}{2} \mathbf{p}^2 + V(\mathbf{r}) + \frac{1}{2c} \mathbf{L} \cdot \mathbf{B} + \frac{1}{8c^2} (\mathbf{B} \times \mathbf{r})^2$$

$$\tilde{O} = O + \sum_{ij} |\tilde{p}_i\rangle [\langle \phi_i | O | \phi_j \rangle - \langle \tilde{\phi}_i | O | \tilde{\phi}_j \rangle] \langle \tilde{p}_j |$$

More than one center

$$H' = \frac{1}{2} \left( \mathbf{p} + \frac{1}{c} \mathbf{A}(\mathbf{r}) \right)^2 + V(\mathbf{r} - \mathbf{t}) \quad \Psi'(\mathbf{r}) = e^{(i/2c) \mathbf{r} \cdot \mathbf{t} \times \mathbf{B}} \Psi(\mathbf{r})$$

Gauge Including PAW

$$\mathcal{T} = 1 + \sum_{\mathbf{R}, n} (|\phi_{\mathbf{R}, n}\rangle - |\tilde{\phi}_{\mathbf{R}, n}\rangle) \langle \tilde{p}_n |$$

$$\mathcal{T}_{\mathbf{B}} = 1 + \sum_{\mathbf{R}, n} e^{(i/2c) \mathbf{r} \cdot \mathbf{R} \times \mathbf{B}} [|\phi_{\mathbf{R}, n}\rangle - |\tilde{\phi}_{\mathbf{R}, n}\rangle] \langle \tilde{p}_{\mathbf{R}, n} | e^{-(i/2c) \mathbf{r} \cdot \mathbf{R} \times \mathbf{B}}$$

## GIPAW developments

Originally implemented by Pickard and Mauri [Phys. Rev. B 63, 245101 (2001)] for Norm-Conserving PseudoPotentials only.

Extended to UltraSoft PseudoPotentials by Yates, Pickard and Mauri [Phys. Rev. B 76, 024401 (2007)]

Ported to Quantum ESPRESSO and extended to PAW by Emine Kucukbenli.

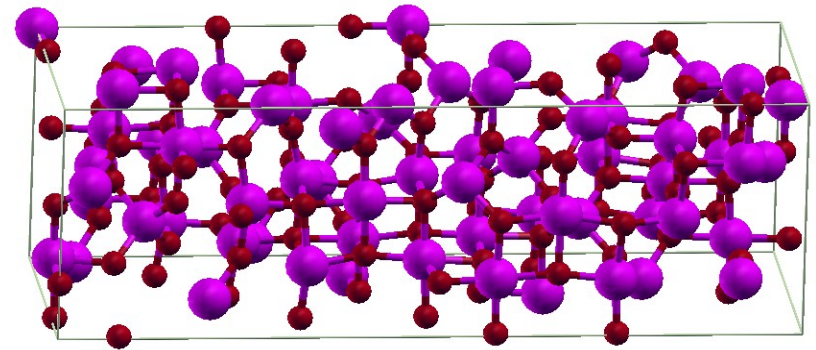
All-electron quality calculations are now possible, no extra generation needed w.r.t. PAW datasets used in the scf cycle





# Outline

- Theory (GIPAW + PAW)
- $^{27}\text{Al}$  NMR shifts of alumina and its precursors
- $^{13}\text{C}$  NMR of Cholesterol Crystals



# Alumina and its calcination precursors

Aluminium oxide ( $\text{Al}_2\text{O}_3$ ), also known as alumina, is one of the most important oxides because of its many industrial applications.

Corundum ( $\alpha\text{-Al}_2\text{O}_3$ ), the most stable crystalline form of alumina, is the final product of the calcination of hydroxides or oxyhydroxides of aluminium at elevated temperature.

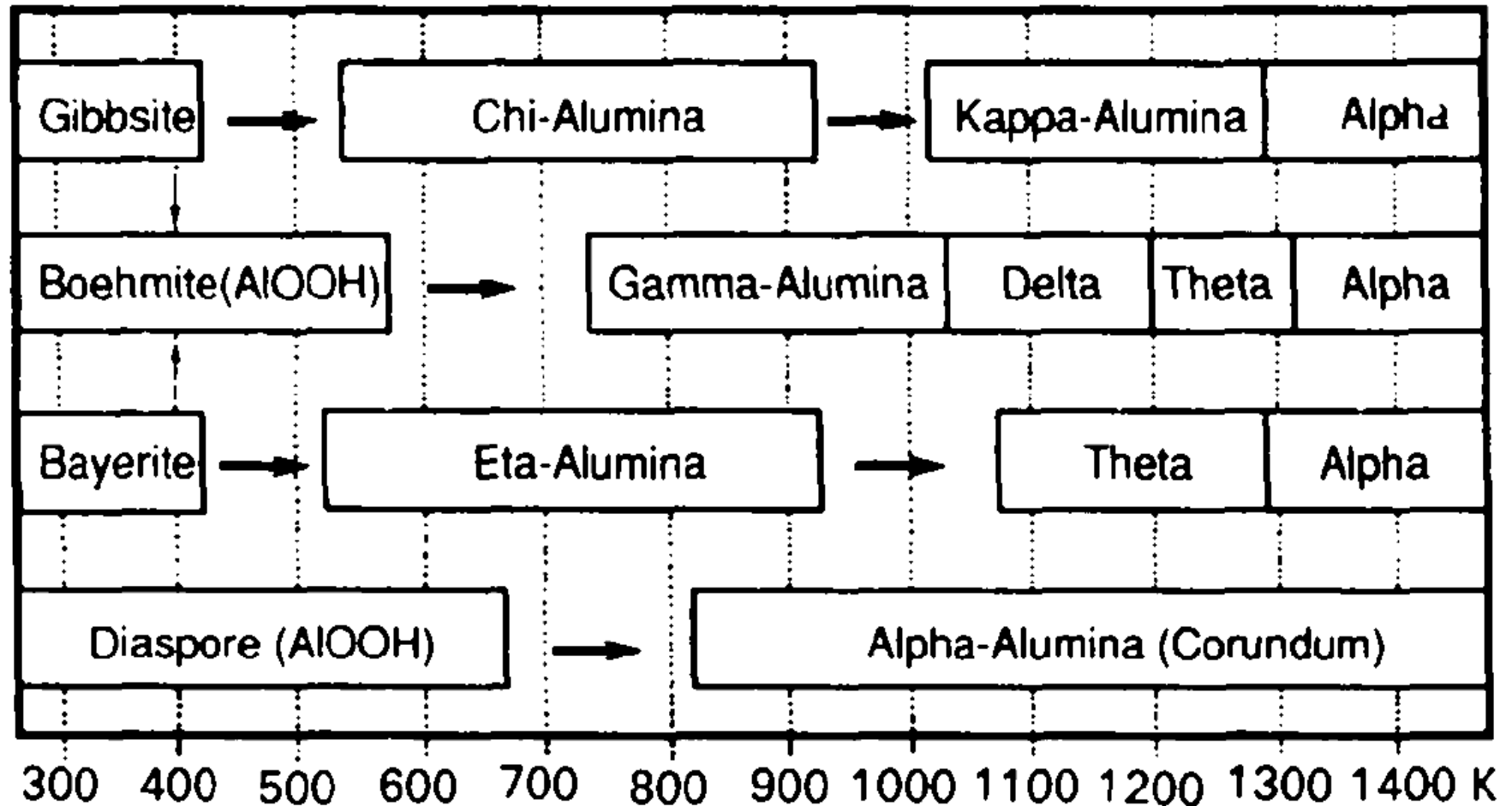
The transformation from aluminium hydrates to the final oxide involves a variety of relatively stable transitional intermediate phases.

$\gamma\text{-Al}_2\text{O}_3$  is particularly valued for its applications as catalyst and catalyst support in petrochemical applications.

Its crystal structure is still poorly known

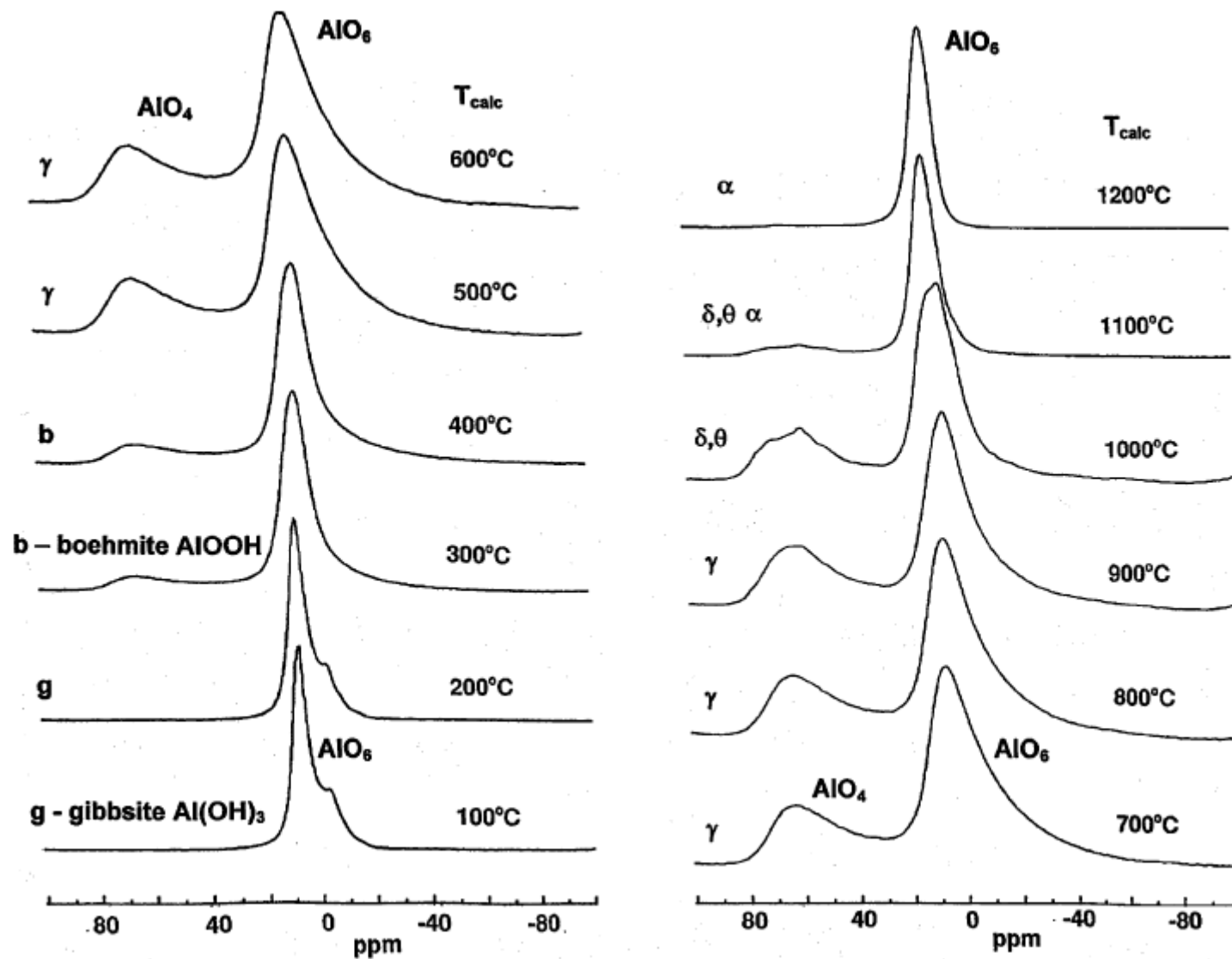


# Alumina and its calcination precursors



Thermal diagram of transition alumina (after Wefers & Misra, 1987)

# NMR Spectra during Alumina calcination



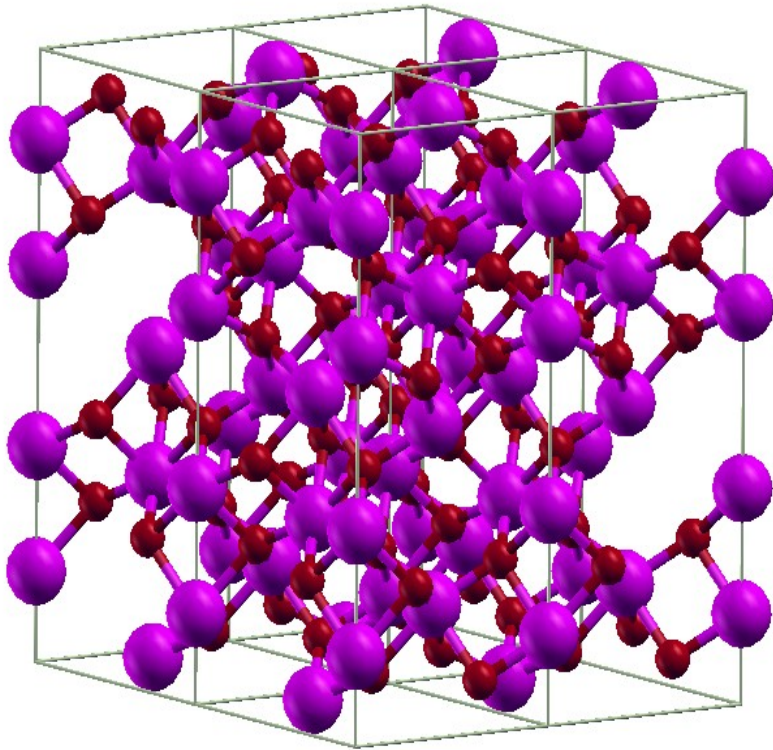
Hill et al Chem. Mater 19, 2877 (2007)



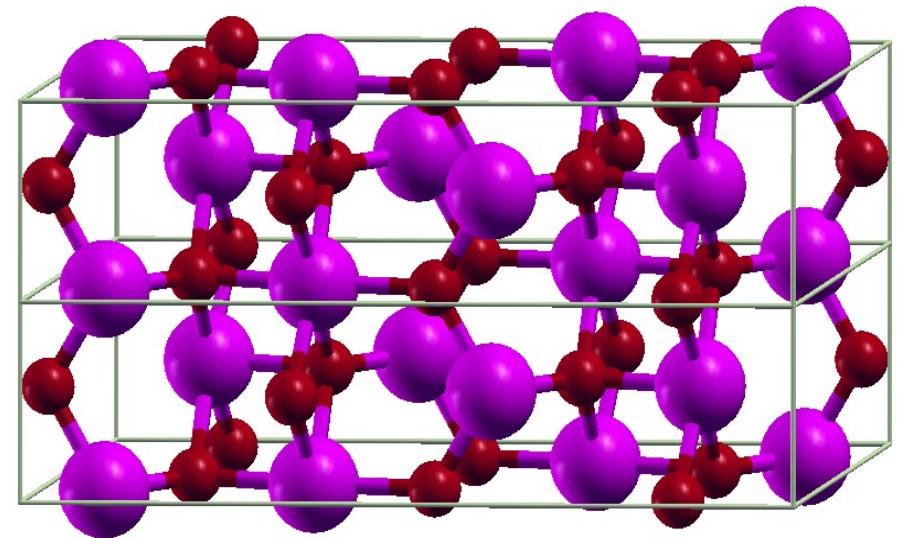
- Structures are fully relaxed
- PAW datasets with 45 Ry cutoff  
(1 mRyd/atom, 0.5 ppm in NMR chemical shifts)
- XC considered: PBE / revPBE86 / vdW-DF
- including Quadrupolar Coupling (EFG)
- spectra obtained using QuadFit code



## $\alpha$ -alumina and $\theta$ -alumina

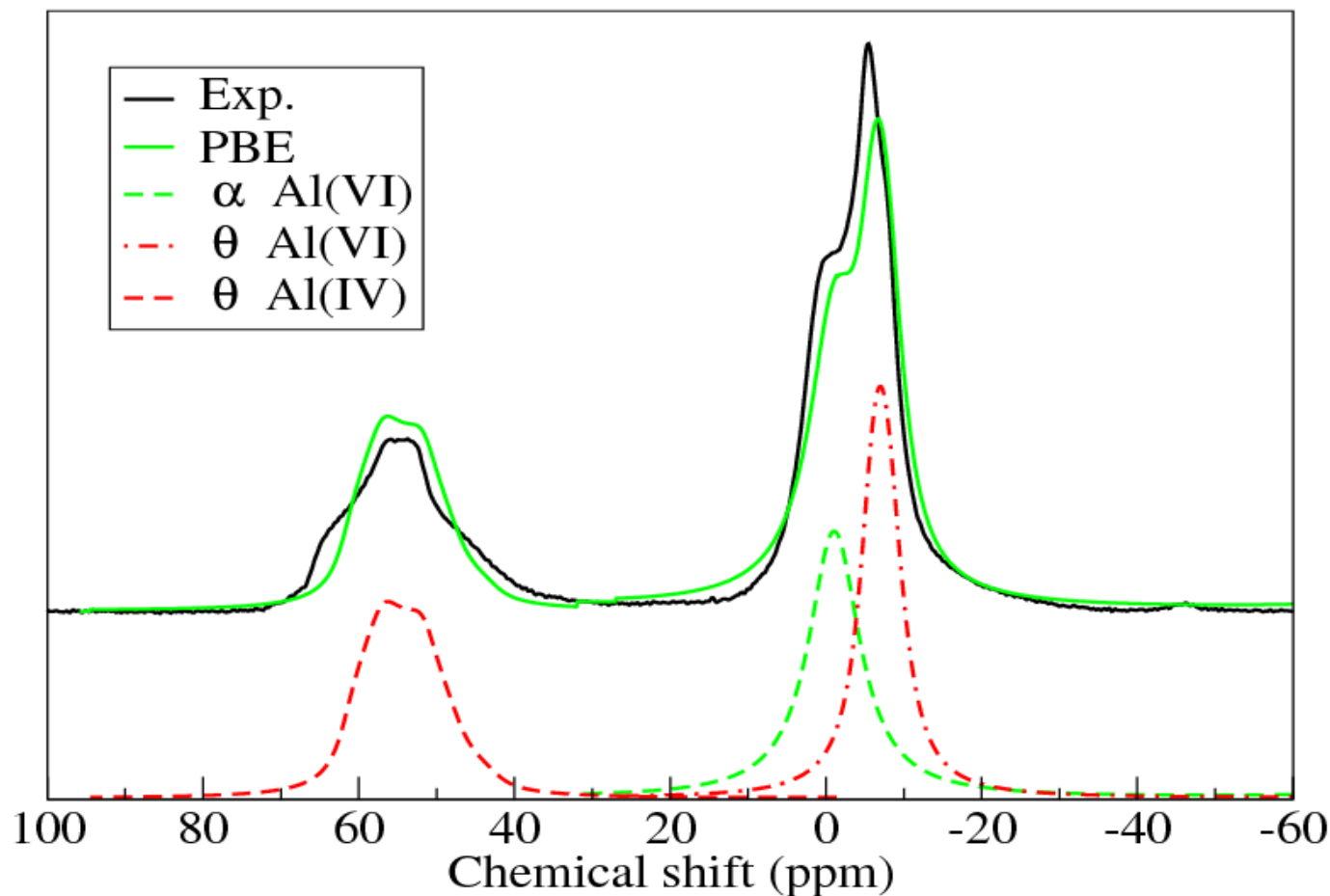


Octahedrally  
coordinated Al sites



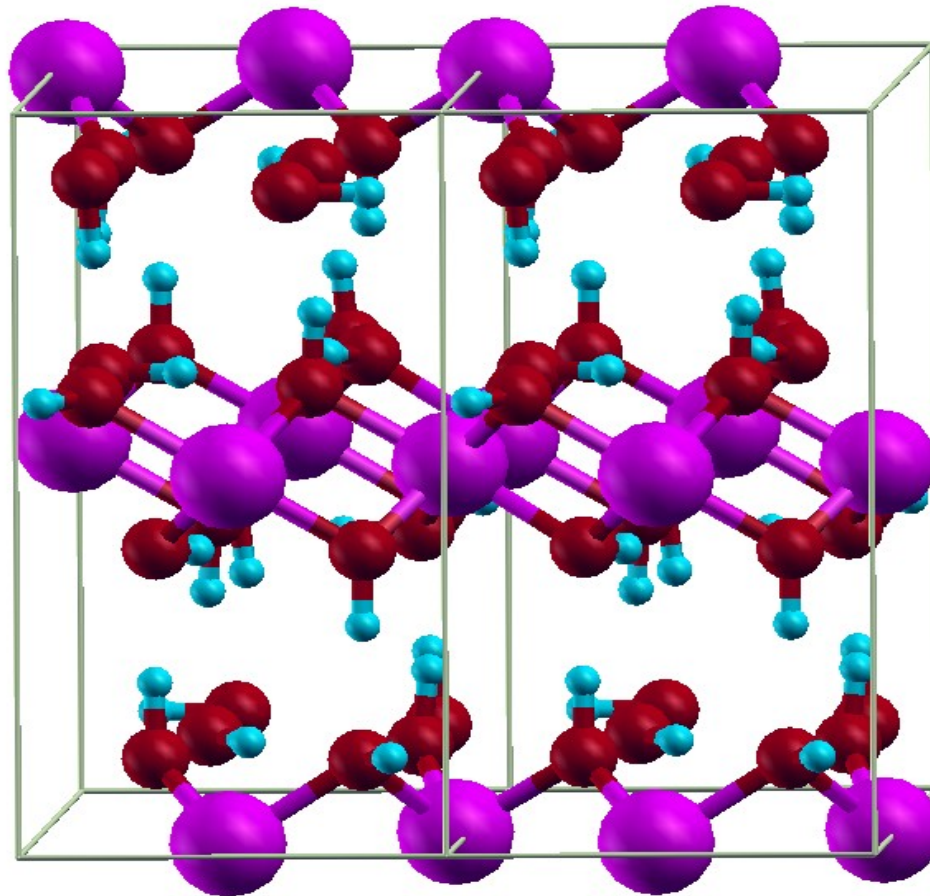
Octahedrally and Tetrahedrally  
coordinated Al sites

## $\alpha$ - and $\theta$ -alumina NMR spectra



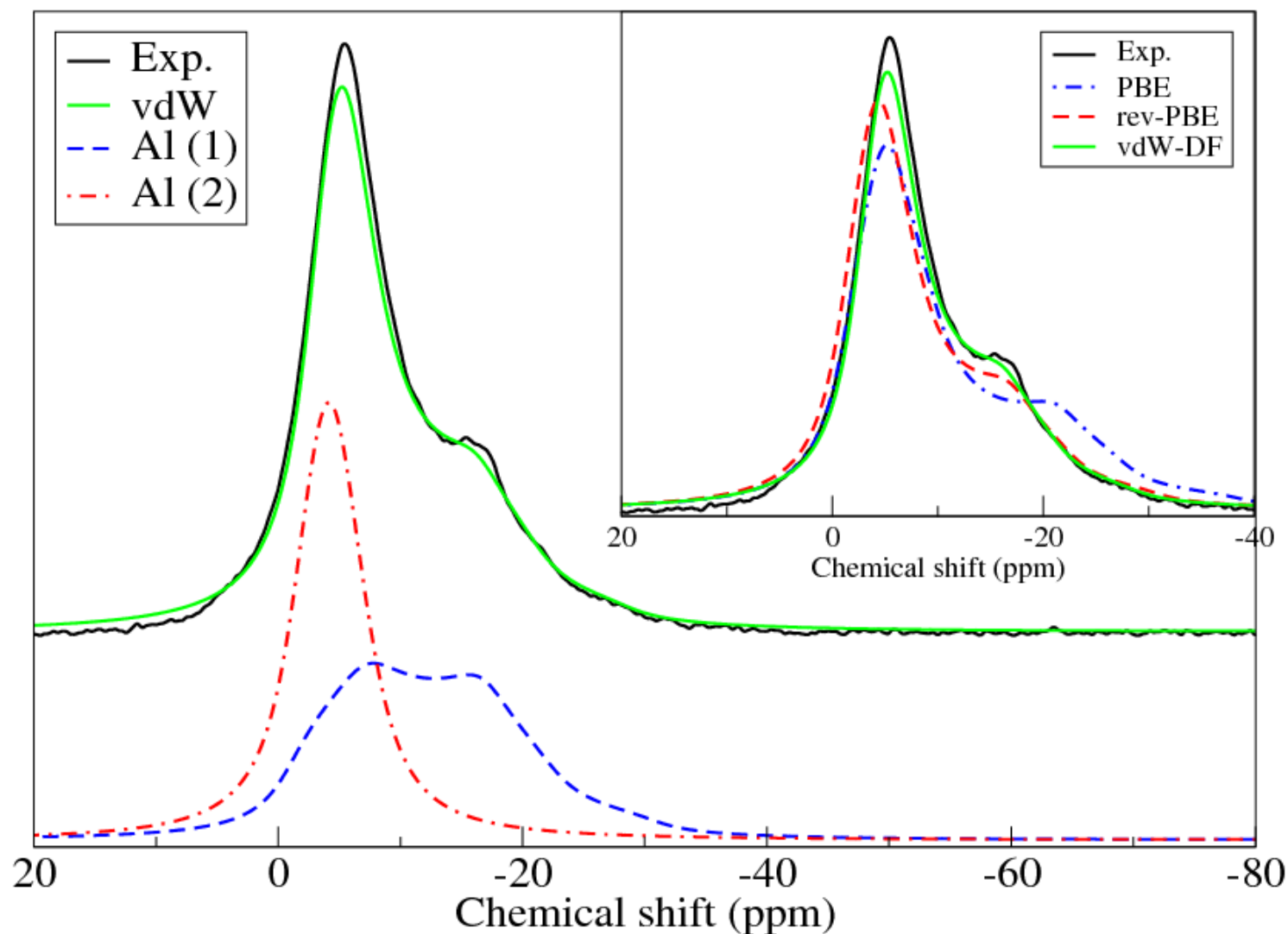
Exp: O'Dell, Savin, Chadwick, and Smith,  
Solid State Nucl. Magn. Reson. **31**, 169 (2007)

## Gibbsite [ $\gamma$ -Al(OH) $_3$ ]



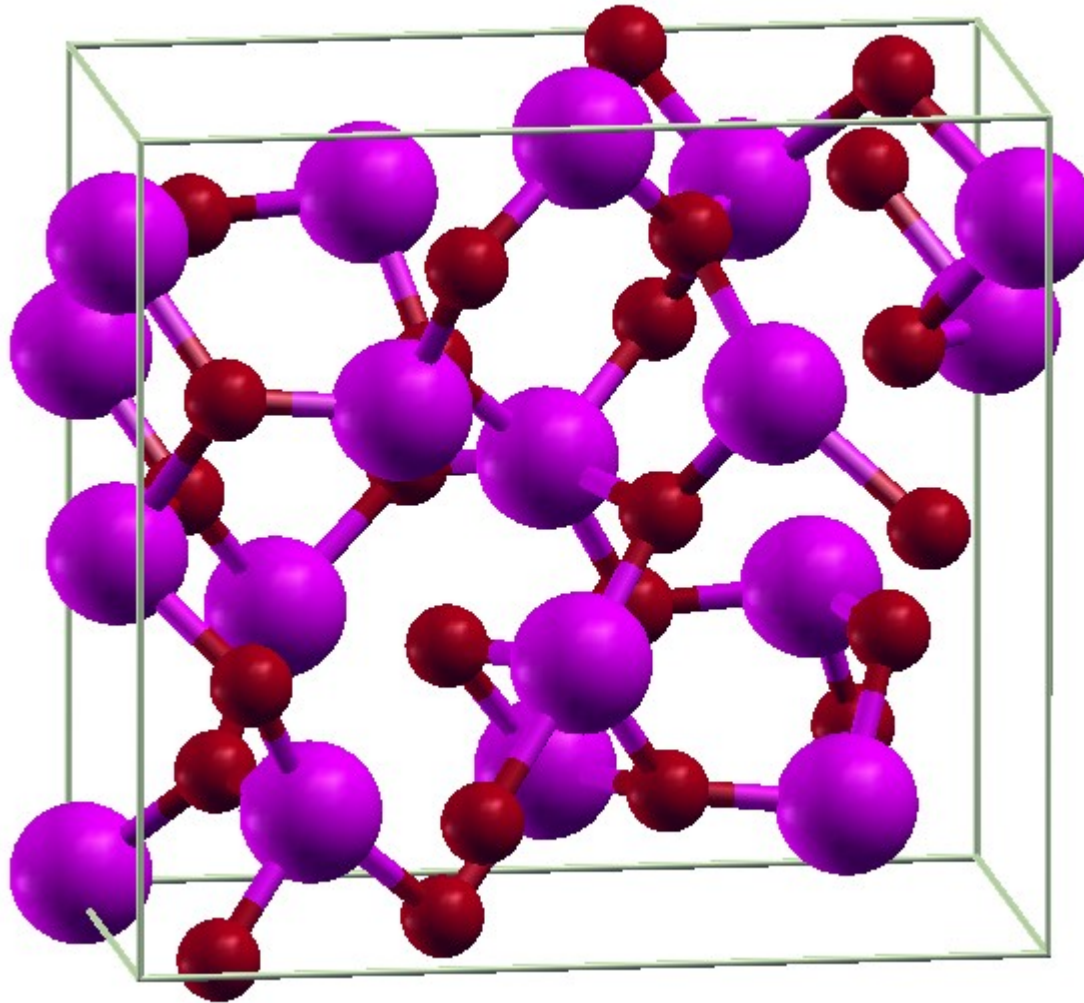
Octahedrally coordinated Al sites

# Gibbsite [ $\gamma$ -Al(OH) $_3$ ] NMR spectrum



Octahedrally coordinated Al: **two different H-bond networks**

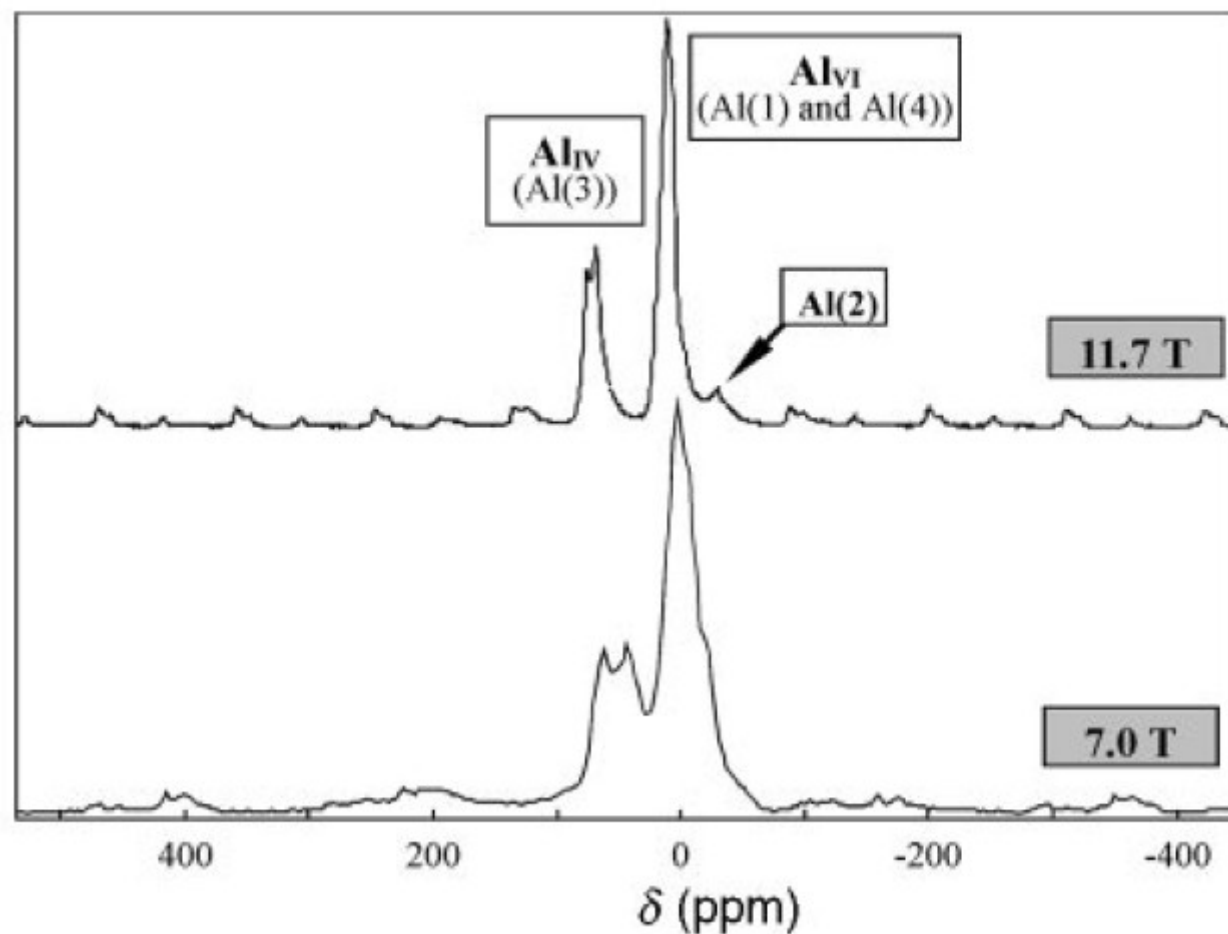
## $\kappa$ -alumina structure



3 Octahedrally coordinated Al sites  
1 Tetrahedrally coordinated Al site

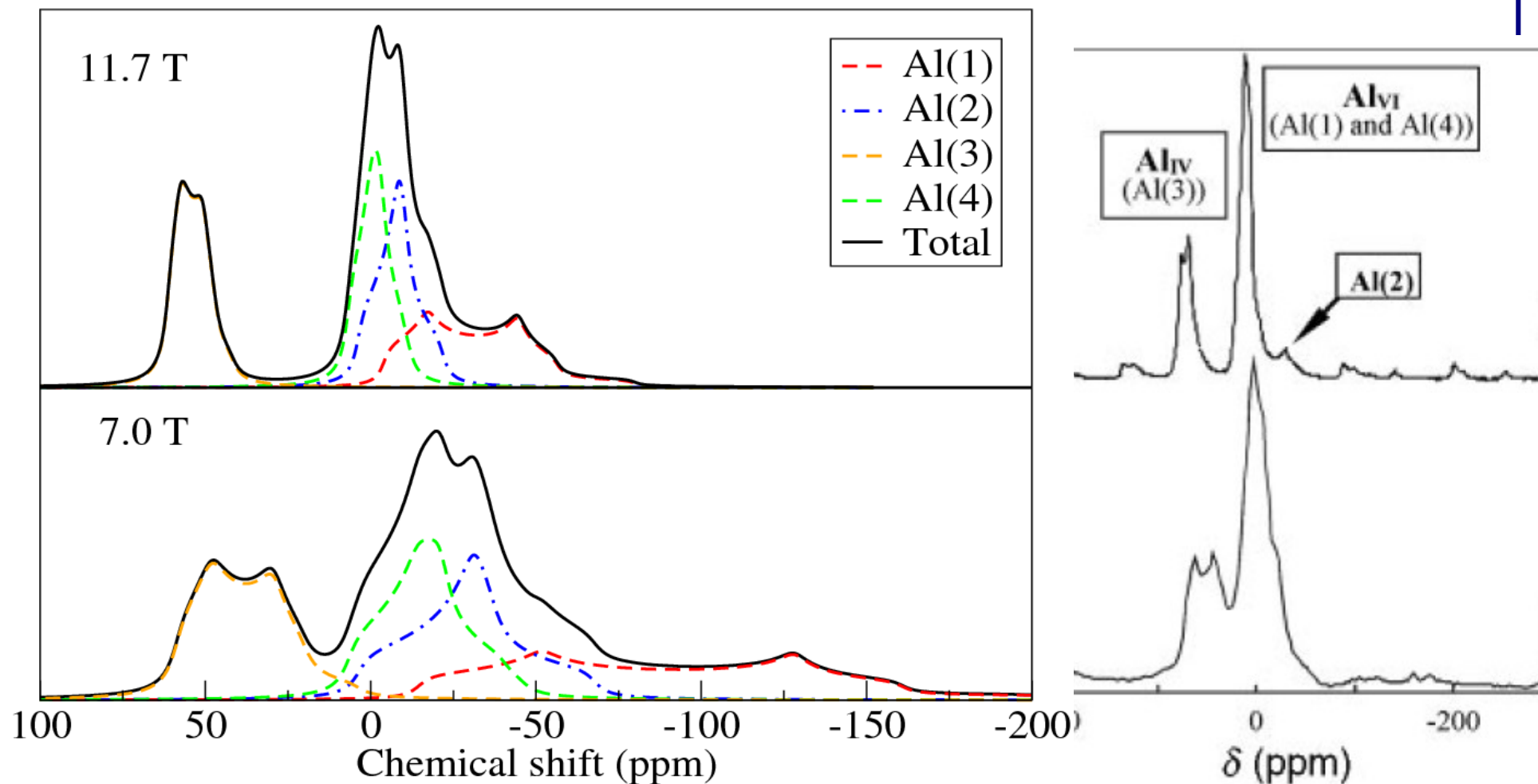


## $\kappa$ -alumina NMR spectra



Exp: Ollivier et al. J. Mater. Chem. 7, 1049 (1997)

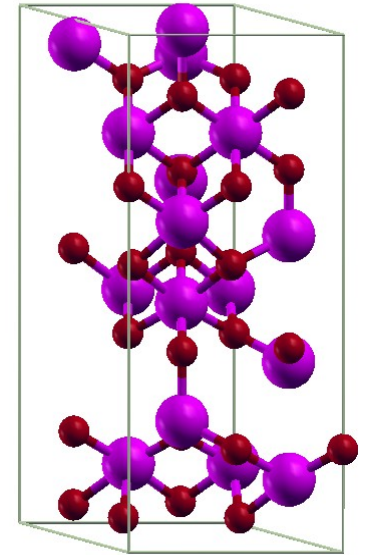
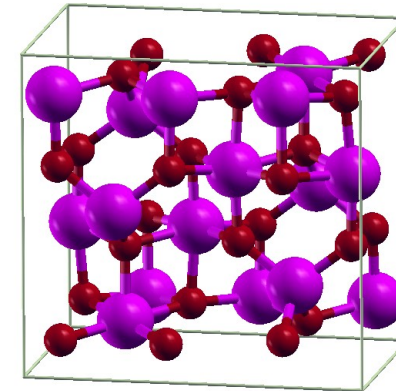
# $\kappa$ -alumina NMR spectra



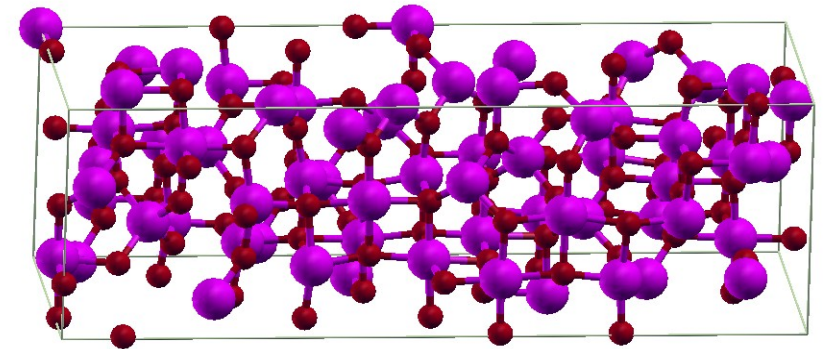
Exp: Ollivier et al. J. Mater. Chem. 7, 1049 (1997)

# $\gamma$ -alumina models (based on powder XRD)

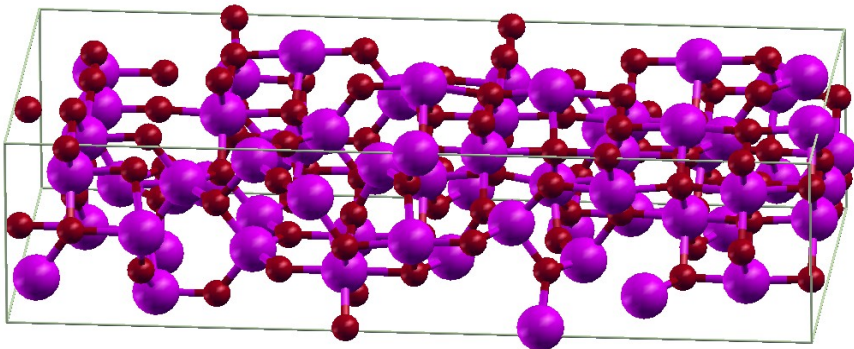
A) Gutierrez *et al.* defective spinel model  
(40 atoms - 8 formula units)



B) Krokidis *et al.* Non-spinel model  
(40 atoms - 8 formula units)

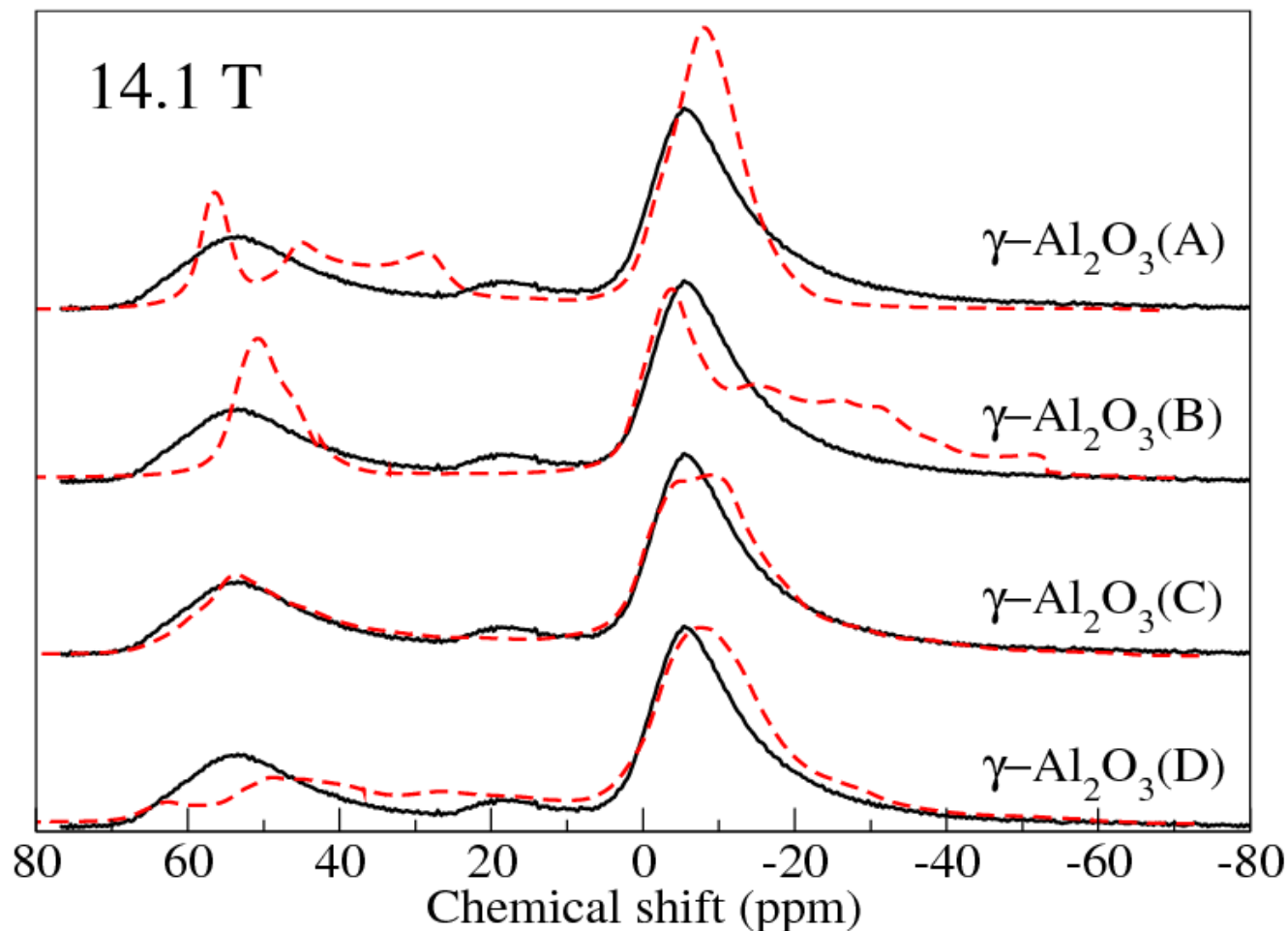


C) Paglia model Fd3m sym.  
(160 atoms - 32 formula units)



D) Paglia model I41/amd sym.  
(160 atoms - 32 formula units)

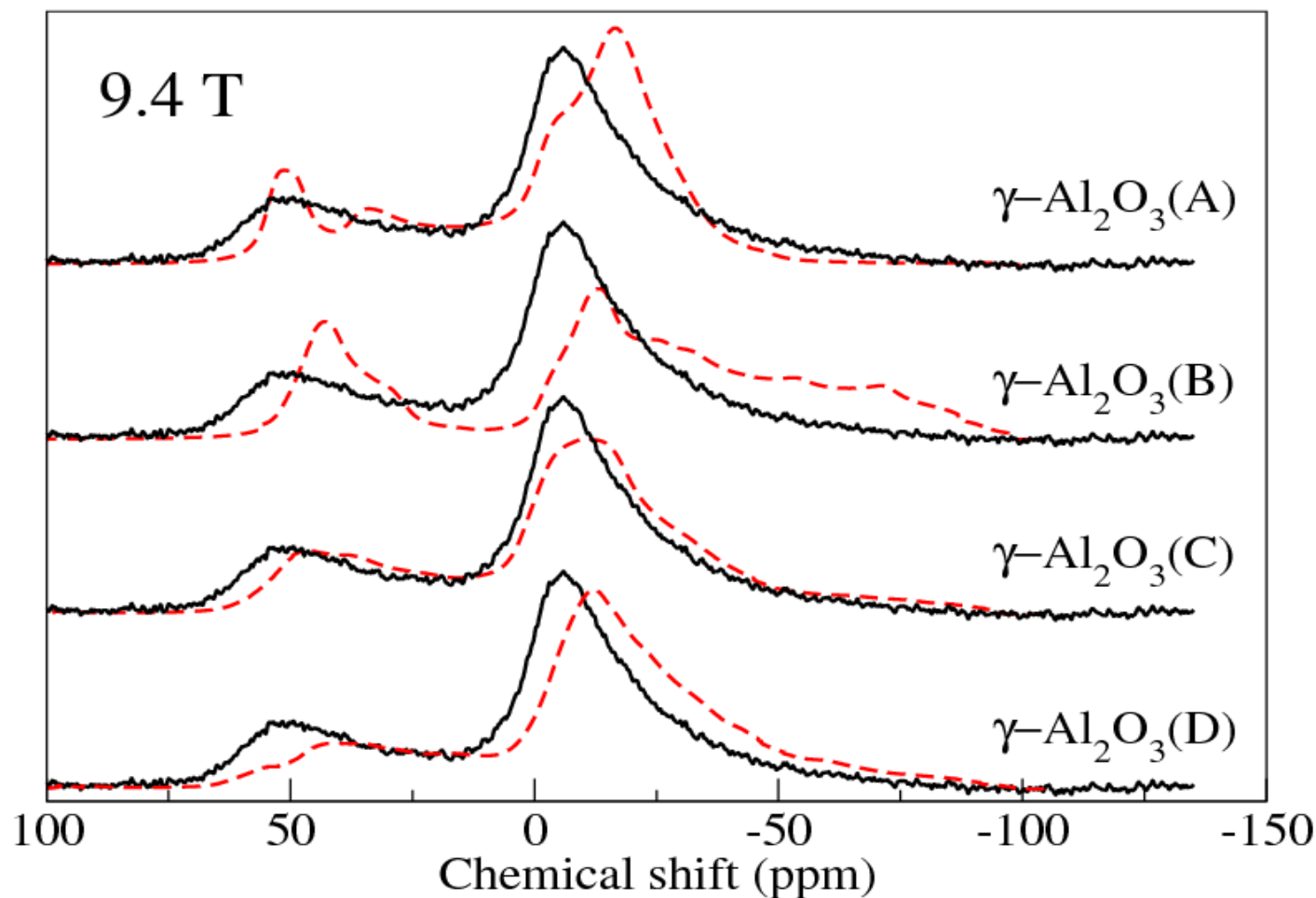
# gamma-alumina NMR spectra



Comparison with O'Dell, Savin, Chadwick, and Smith,  
Solid State Nucl. Magn. Reson. **31**, 169 (2007)



# gamma-alumina NMR spectra

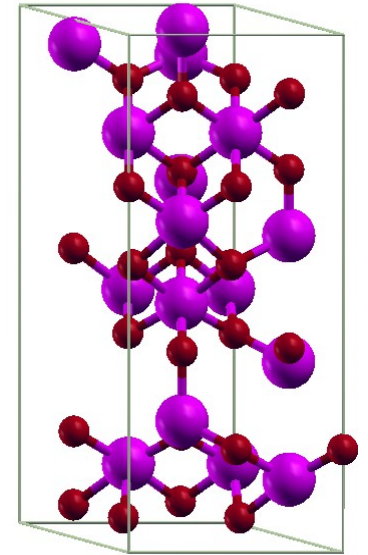
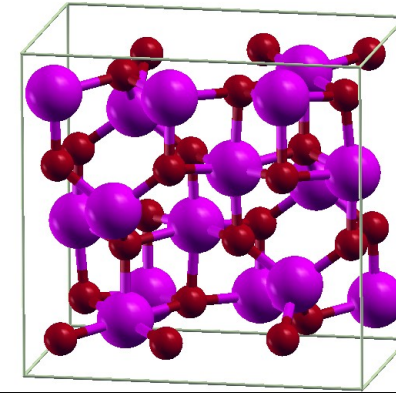


Comparison with Hill, Bastow, Celotto, and Hill,  
Chem. Mater. **19**, 2877 (2007).



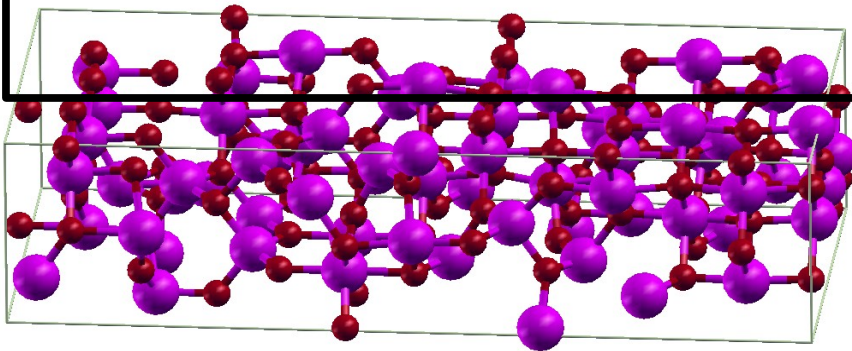
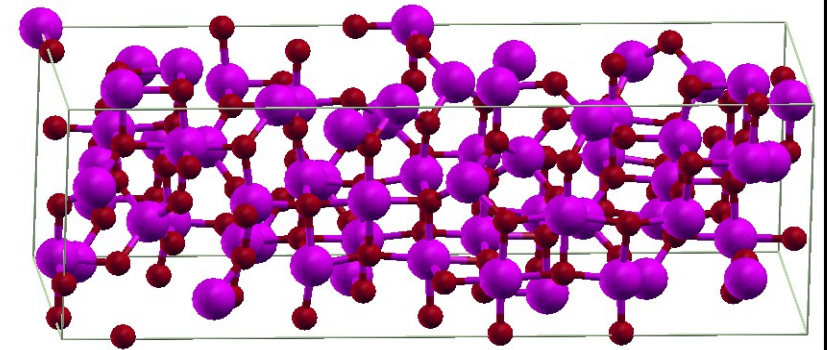
# $\gamma$ -alumina models (based on powder XRD)

A) Gutierrez *et al.* defective spinel model  
(40 atoms - 8 formula units)



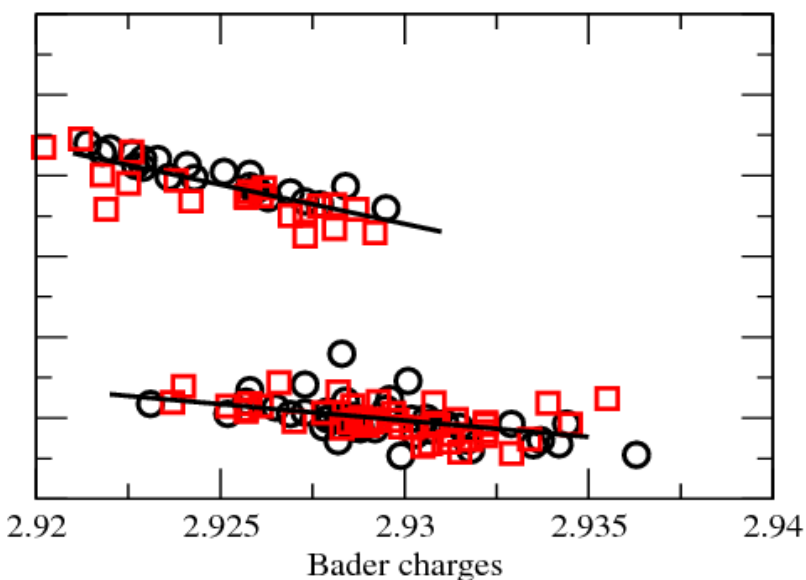
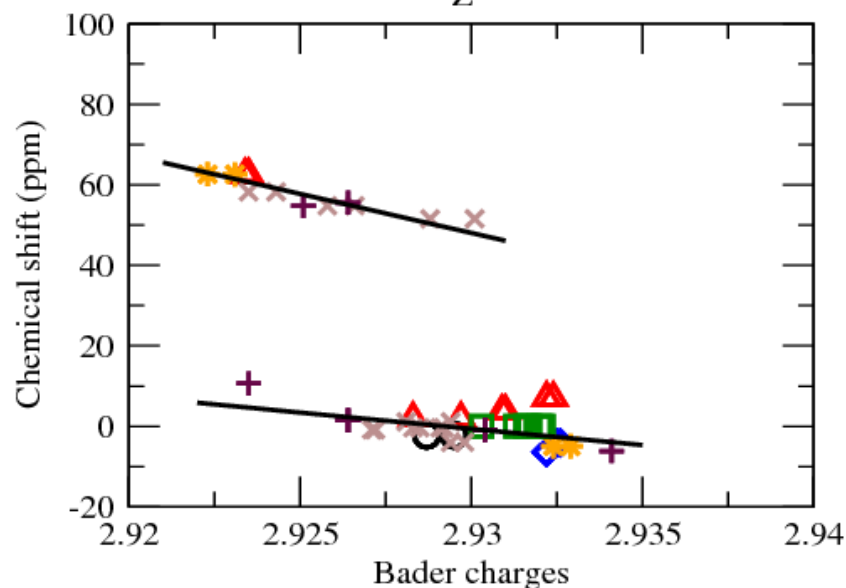
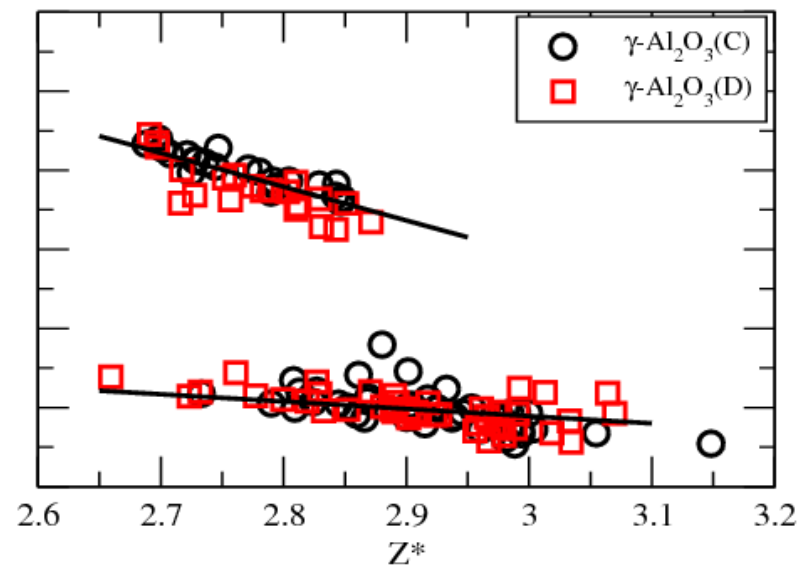
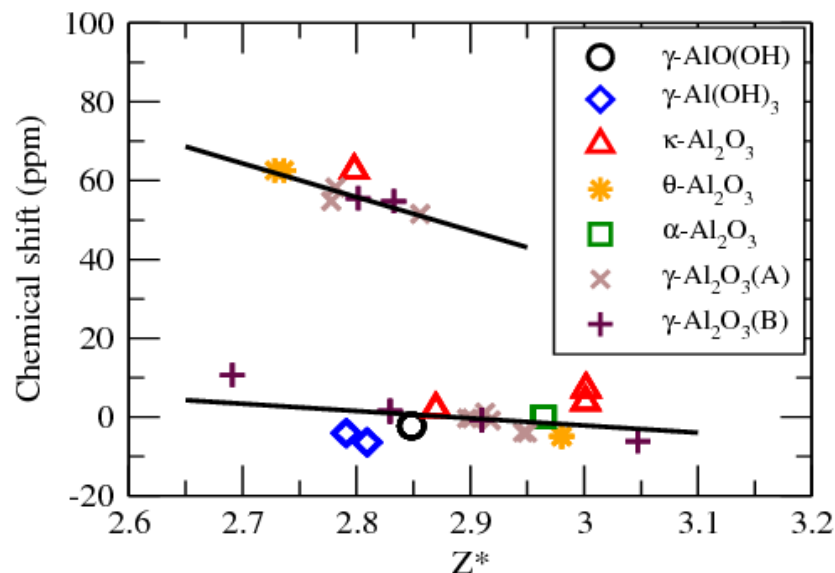
B) Krokidis *et al.* Non-spinel model  
(40 atoms - 8 formula units)

C) Paglia model Fd3m sym.  
(160 atoms - 32 formula units)



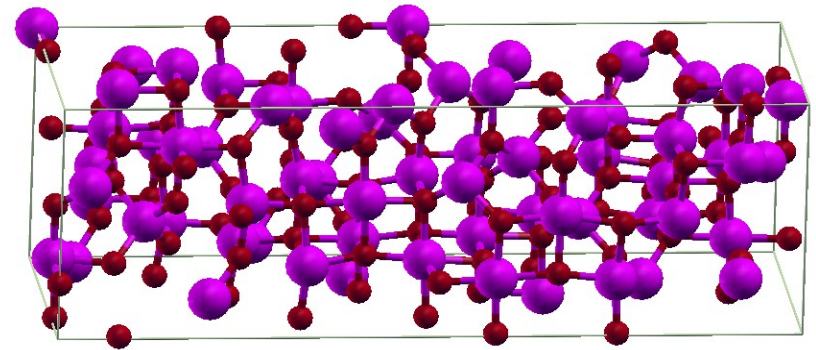
D) Paglia model I41/amd sym.  
(160 atoms - 32 formula units)

# Correlation of NMR chemical shifts with local Electronic Structure indicators

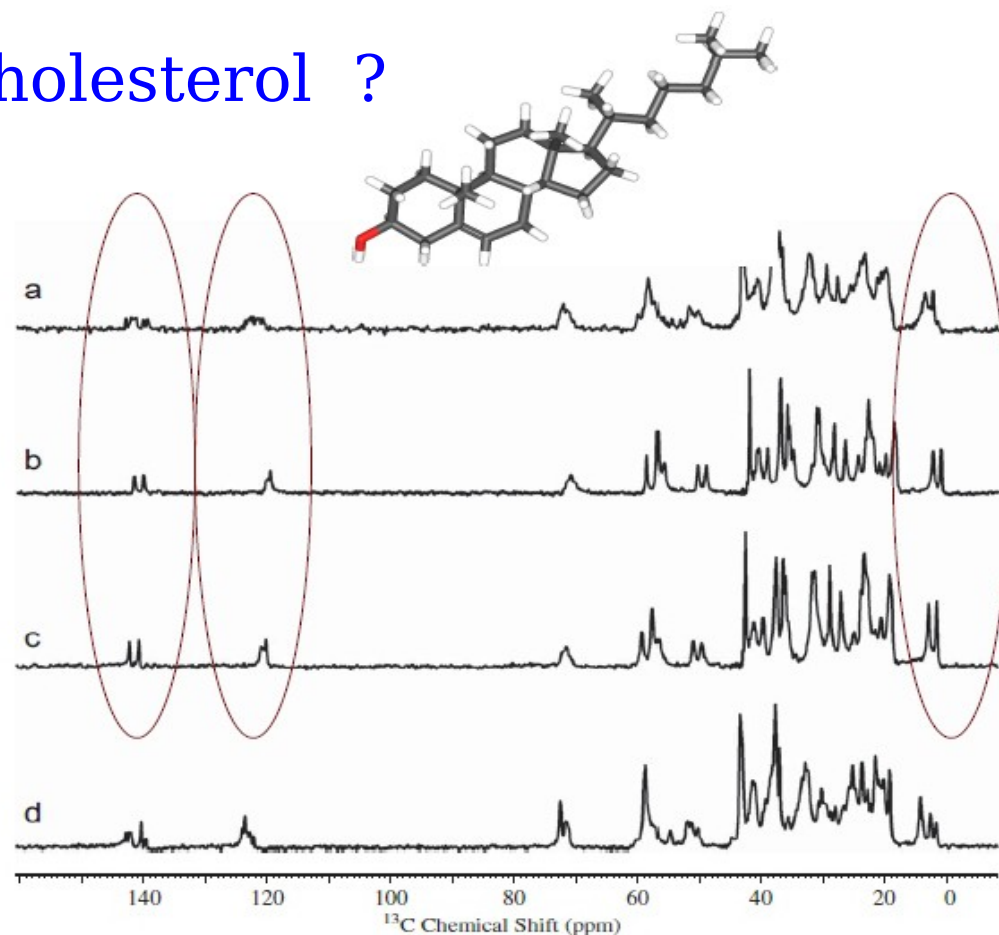
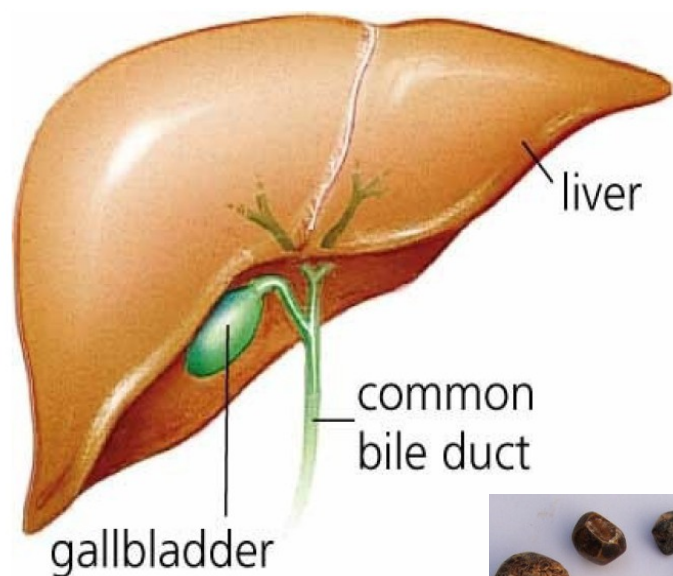


# Outline

- Theory (GIPAW + PAW)
- $^{27}\text{Al}$  NMR shifts of alumina and its precursors
- $^{13}\text{C}$  NMR of Cholesterol Crystals



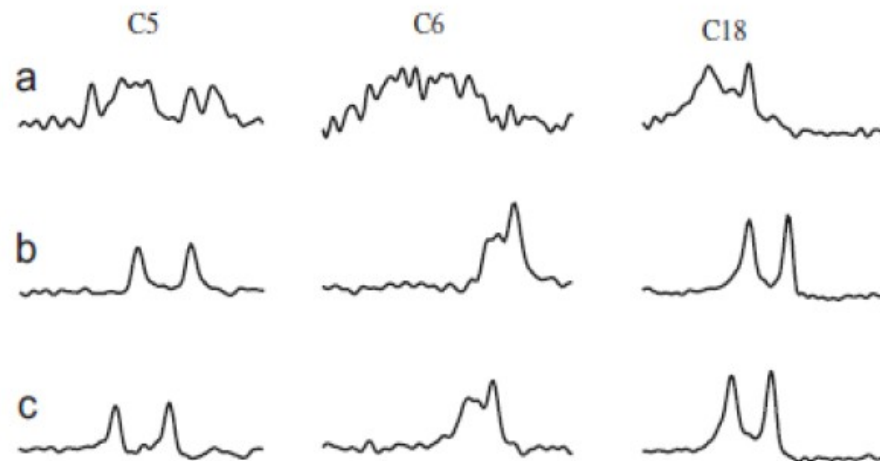
# Why Cholesterol ?



a) Gallbladder Cancer

b) Chronic Cholecystitis

c) Xantho-Granulomatous Cholecystitis

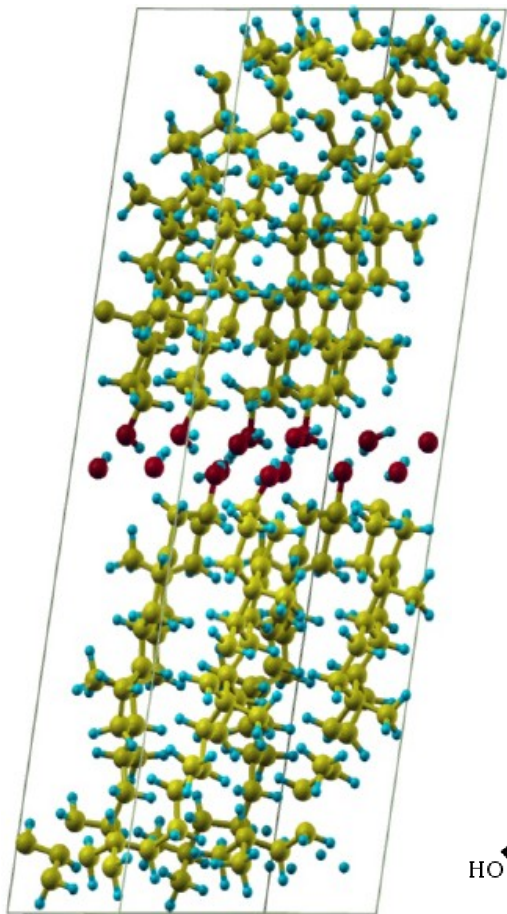


Gall stones associated to different pathologies have distinct NMR spectra.

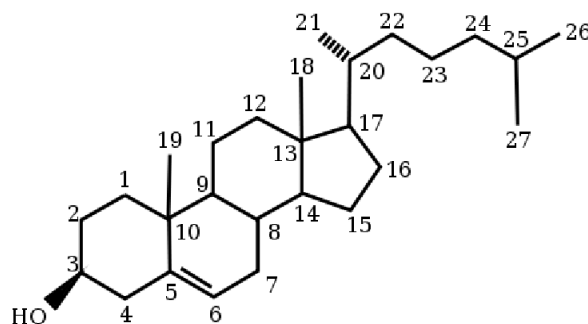
It would be important to understand the structural differences between these stones and the underlying reasons.

Can we distinguish the NMR spectra of different Cholesterol crystalline polymorphs ?

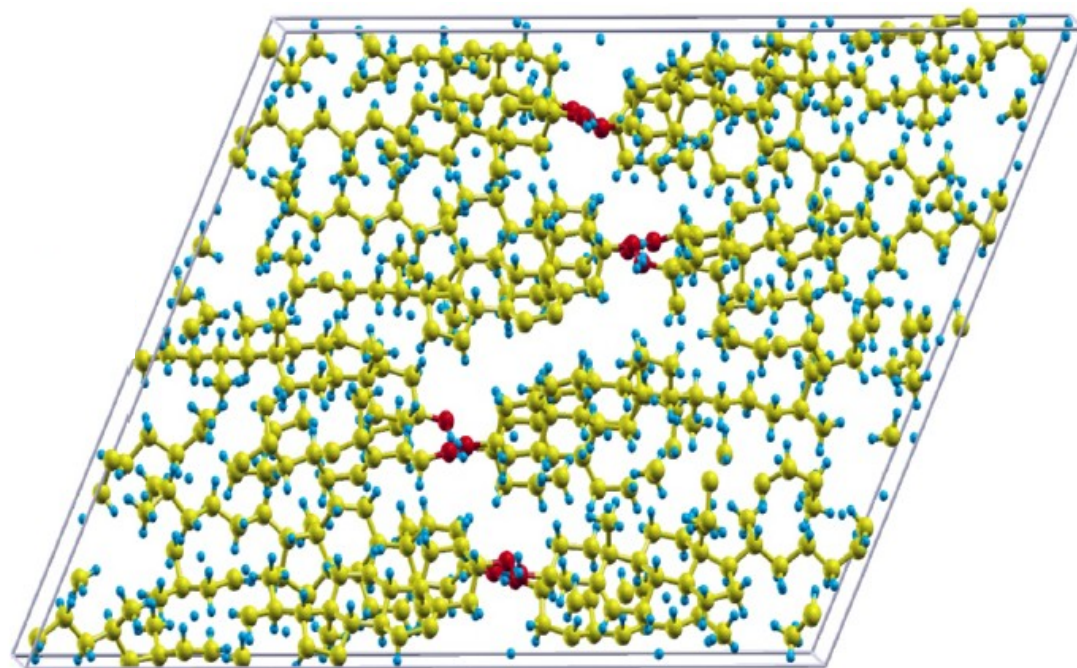




**Monohydrate Cholesterol (ChM)**  
 8 CLR + 8 w molecules - 616 atoms



**High temperature Anhydrous Cholesterol (ChAh)**  
 16 CLR mol - 1184 atoms

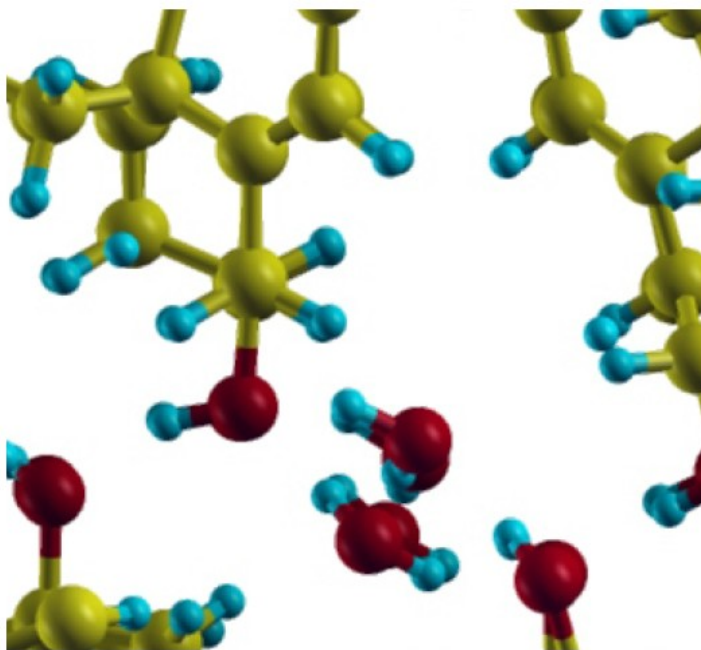


**Low temperature Anhydrous Cholesterol (ChAl)**  
 8 CLR mol - 592 atoms

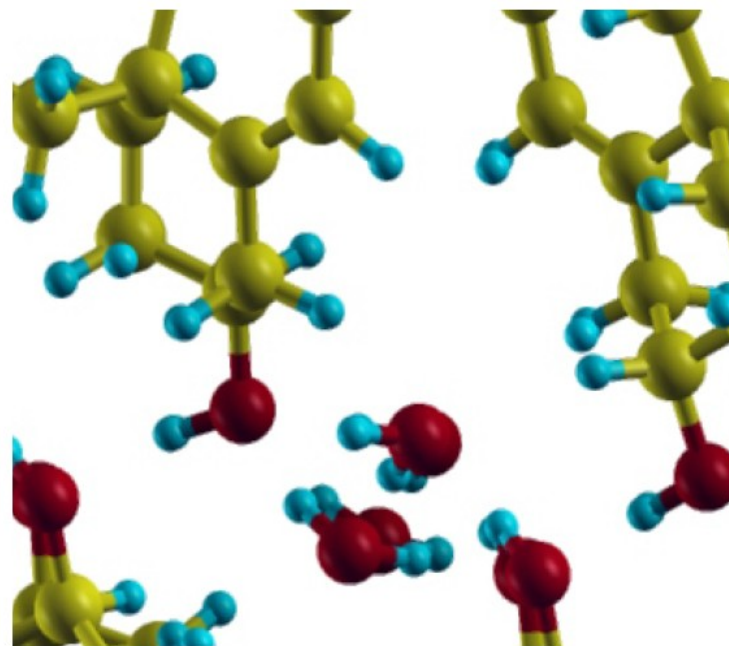
(not shown)

- Structures are fully relaxed
- PAW datasets with 45 Ry cutoff  
(1 mRyd/atom, 0.5 ppm in NMR chemical shifts)
- XC considered: vdW-DF
- As GIPAW tends to over(under)-estimate the high(low)-ppm resonances with respect to Experiment for a better comparison we propose to add an environment-dependent correction:  
CH0: -4.5 ppm, CH: -1.5 ppm, CH2:0.0 ppm, CH3=+2.0 ppm

# Importance of accurate structural relaxation (ChM)



First principles

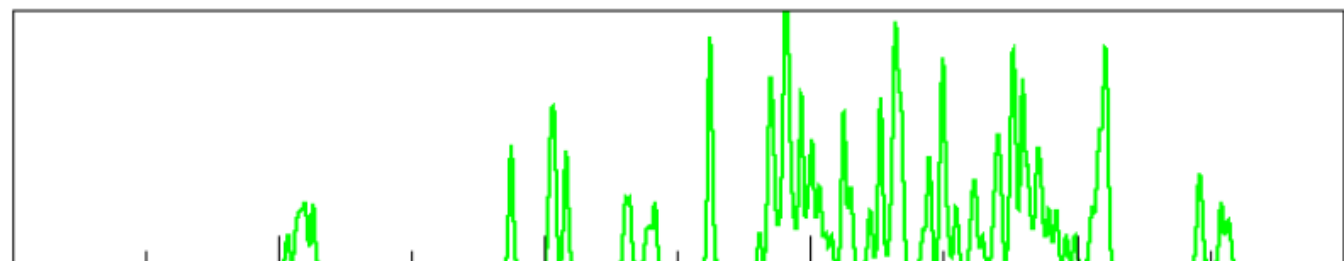
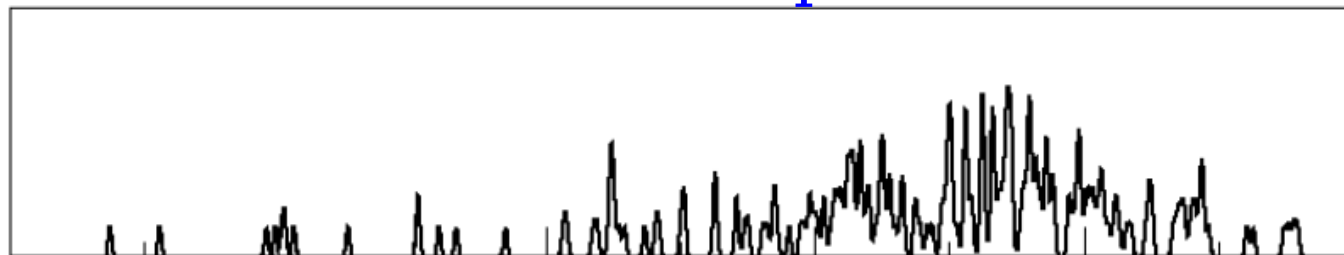
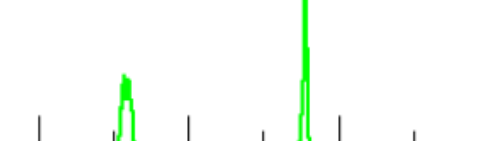


Exp + FF

Exp + FF

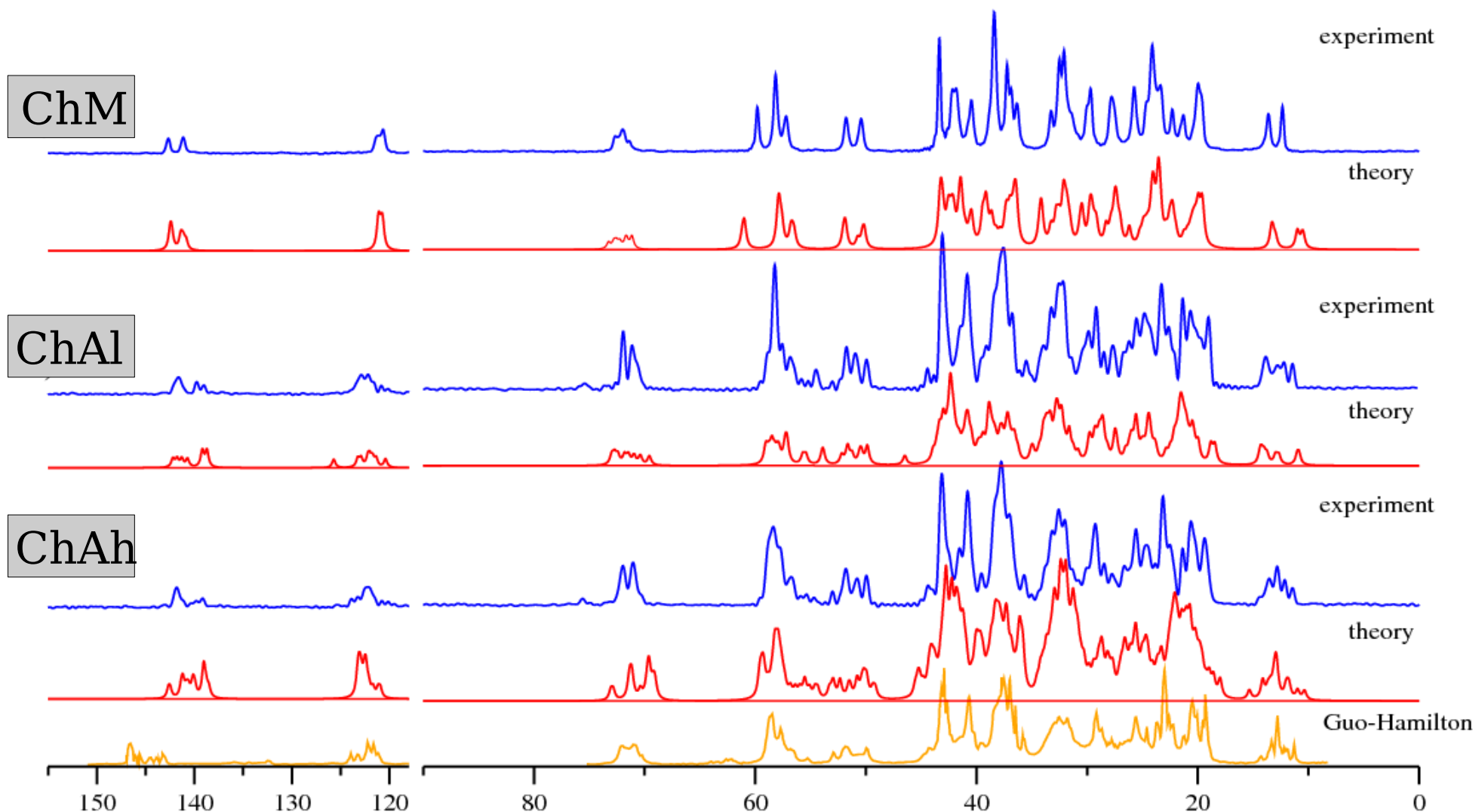


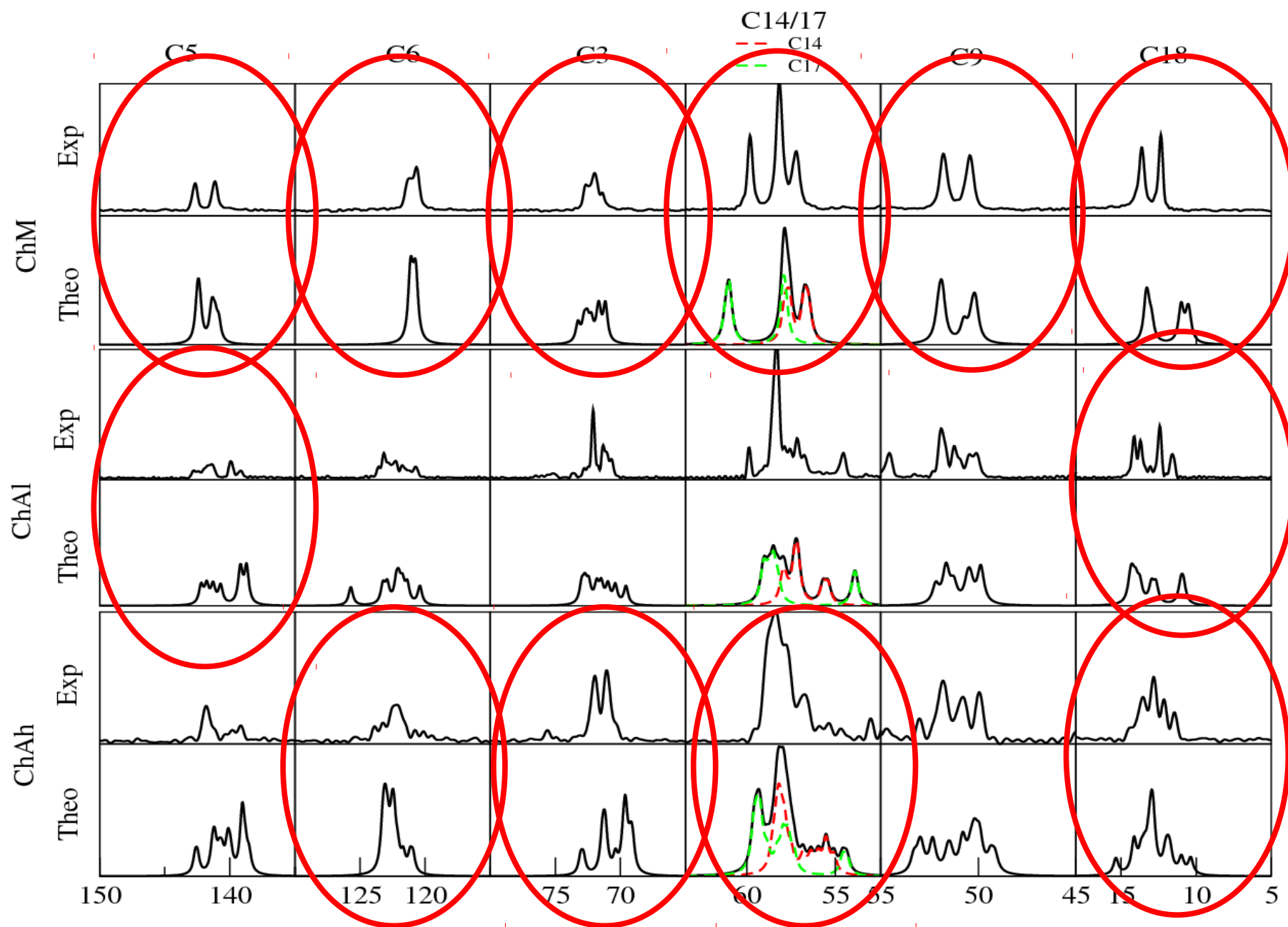
First principles



# Comparison with Experimental Spectra

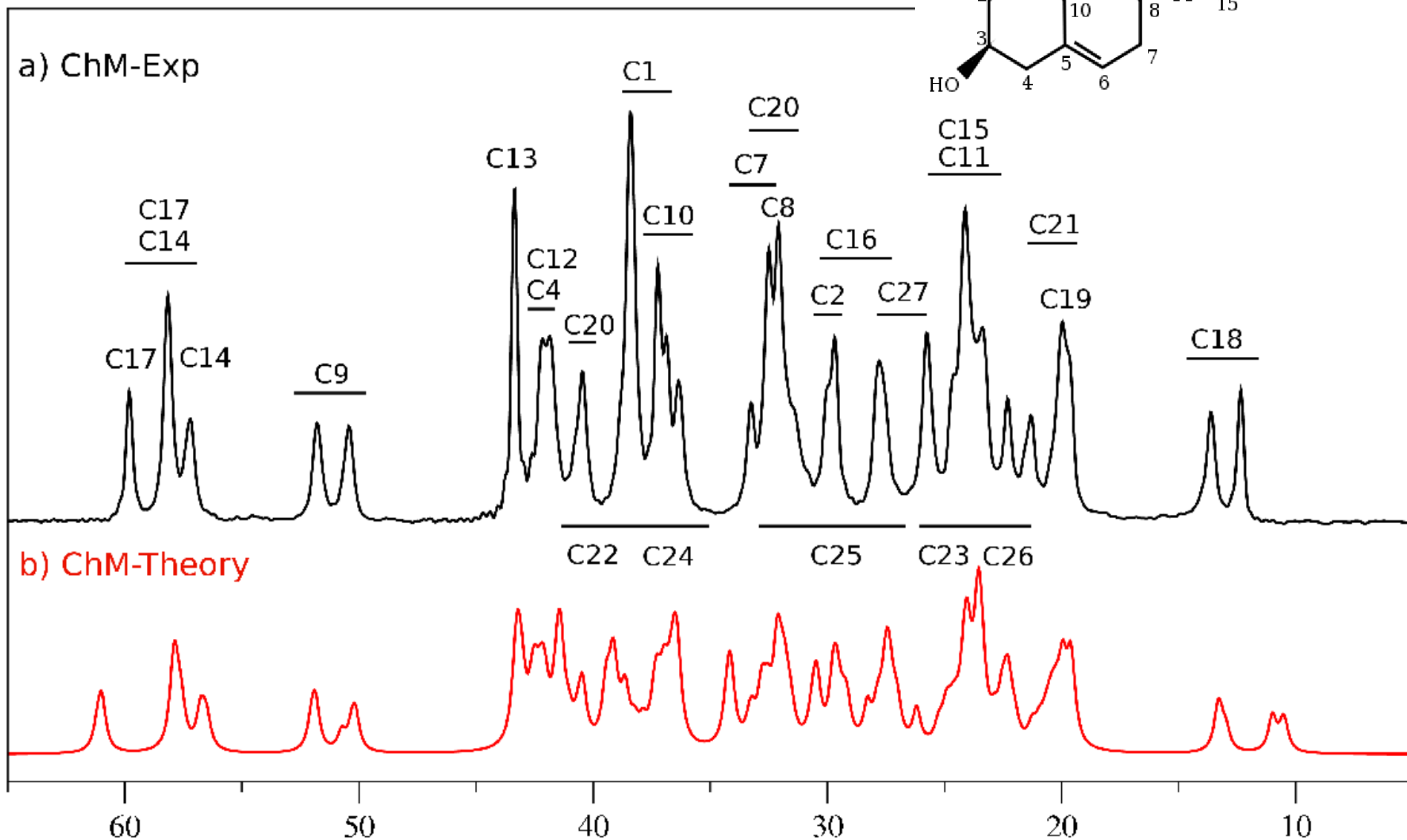
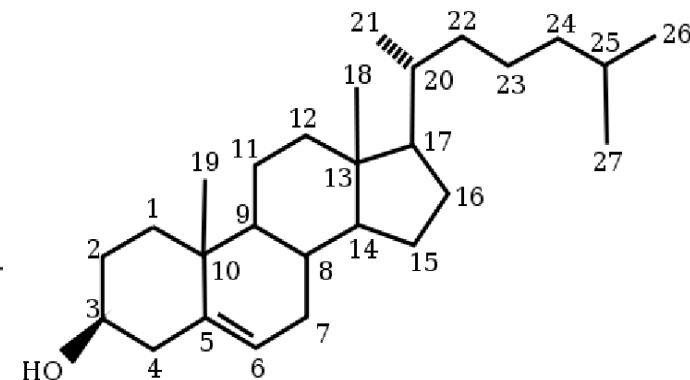
(E.Kucukbenli, K.Sonkar, N. Shina, SdG, JPCA 2012)



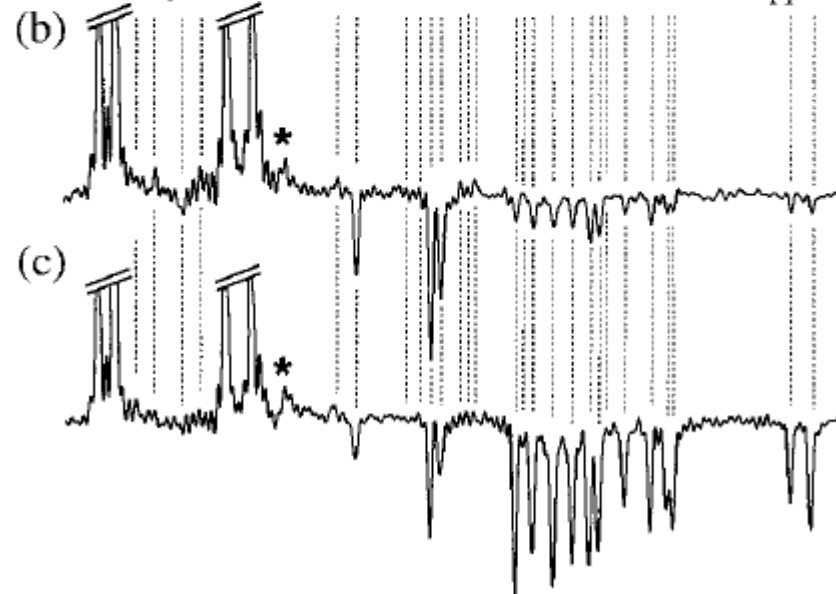
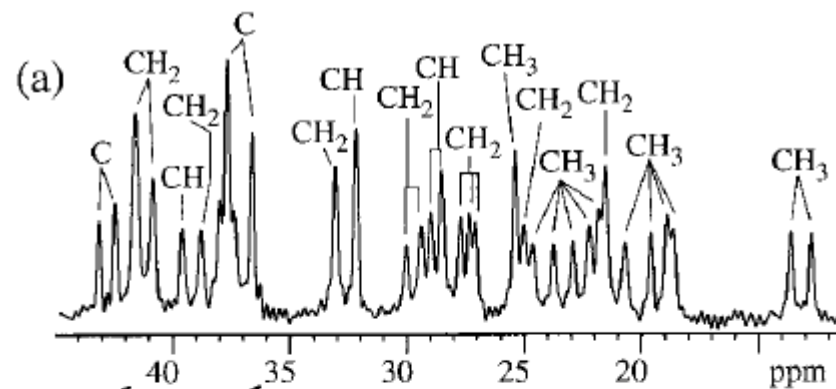
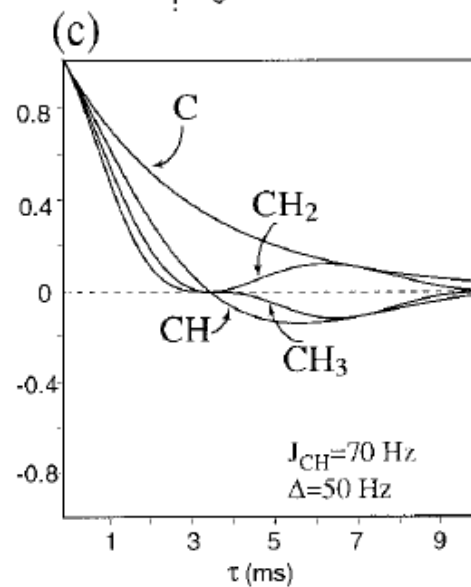
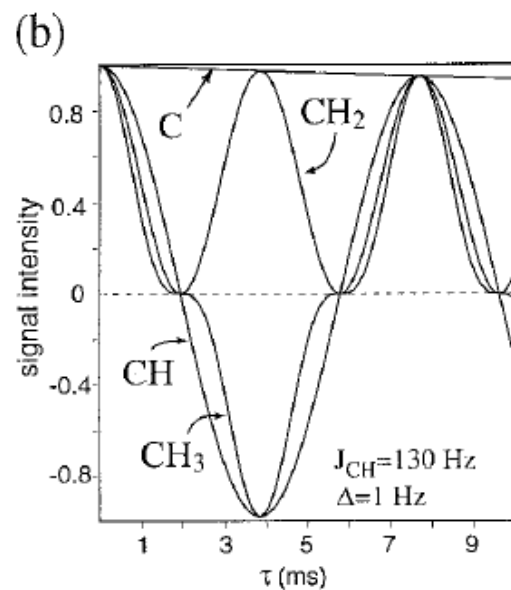
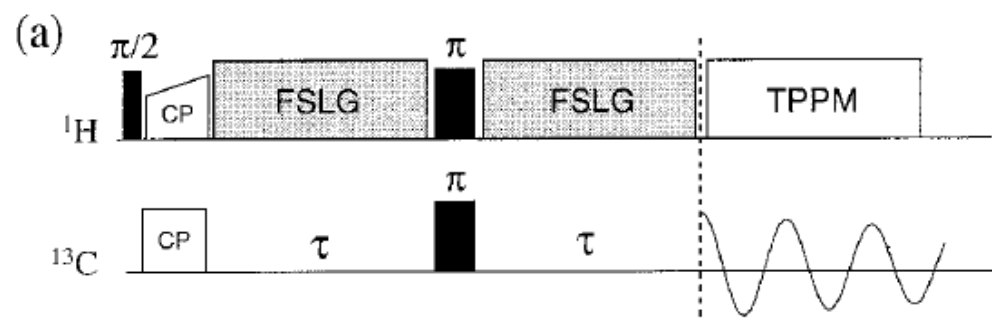




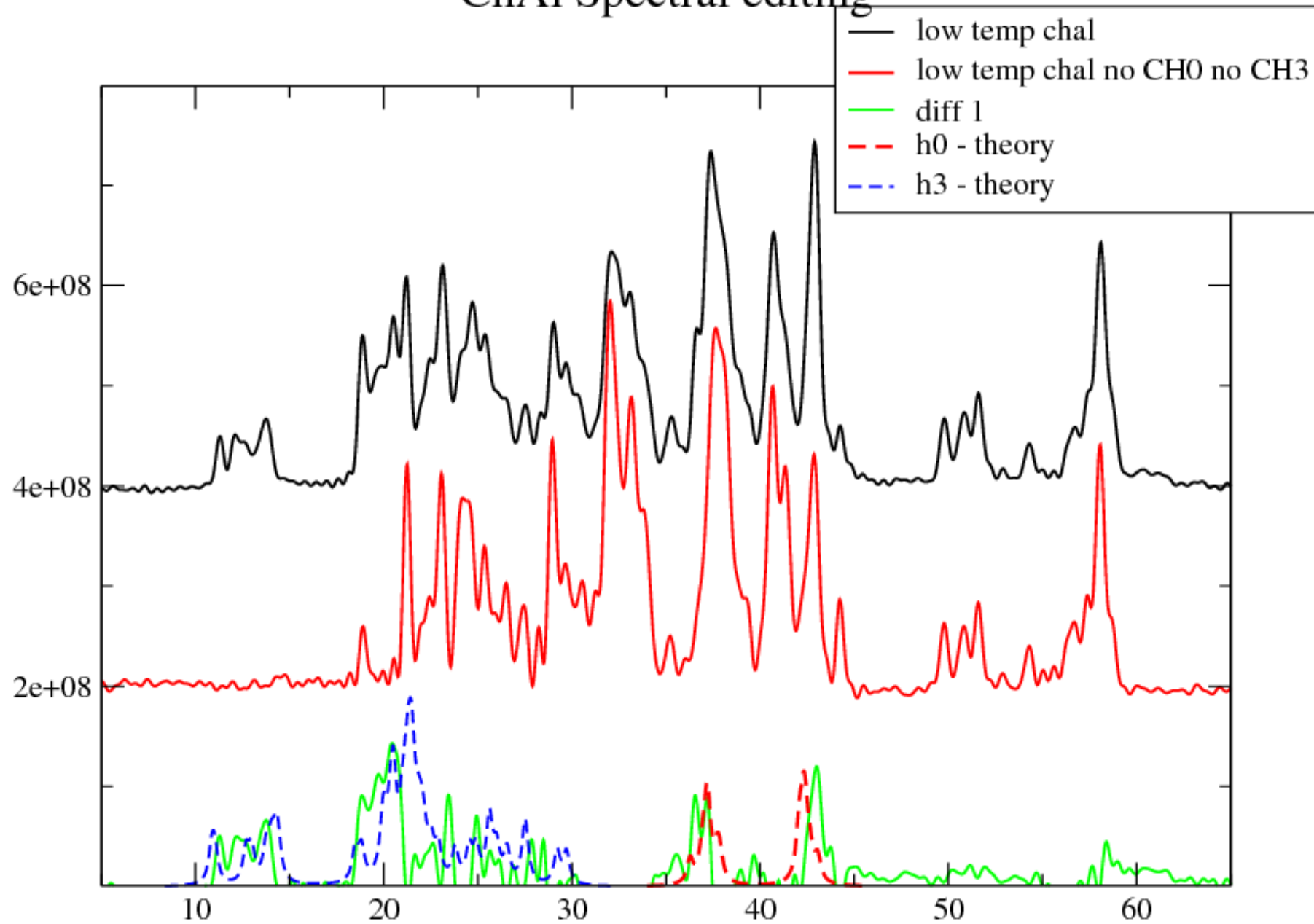
# Peak assignement in ChM



# Spectral editing

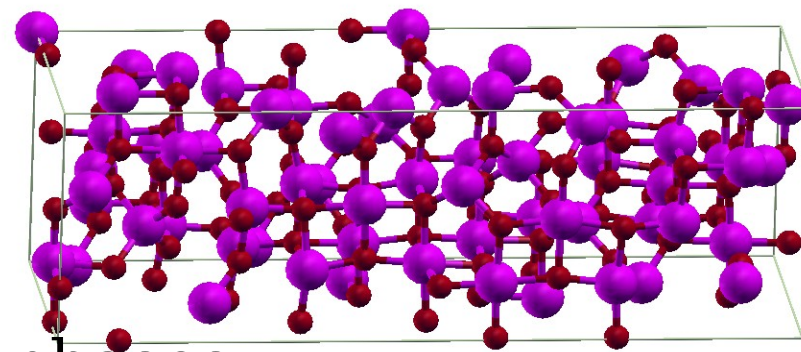


# ChAl Spectral editing



# Summary

- Theory:  
GIPAW + PAW fully implemented
- $^{27}\text{Al}$  NMR shifts of alumina  
and its precursors



Good agreement for well known phases  
Calculations support Paglia's  $Fd\bar{3}m$  model for  $\gamma$ -alumina

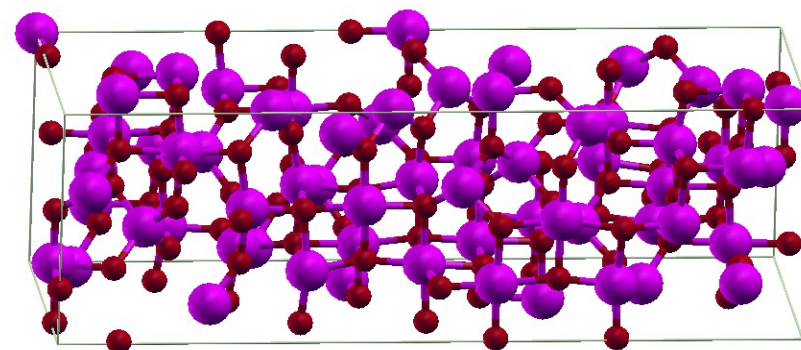
- $^{13}\text{C}$  NMR of Cholesterol Crystals  
Calculations reproduce the main  
features of the spectra and are able  
to distinguish different polymorphs  
It is possible to provide a complete  
peak assignment, confirmed with  
spectral editing exp.



# Credits

- Theory (GIPAW + PAW)

Emine Kucukbenli



- $^{27}\text{Al}$  NMR shifts of alumina and its precursors

Ary Ferreira, Emine Kucukbenli, Alexandre Leitao

UFJF Brasil -  **PETROBRAS**

- $^{13}\text{C}$  NMR of Cholesterol Crystals

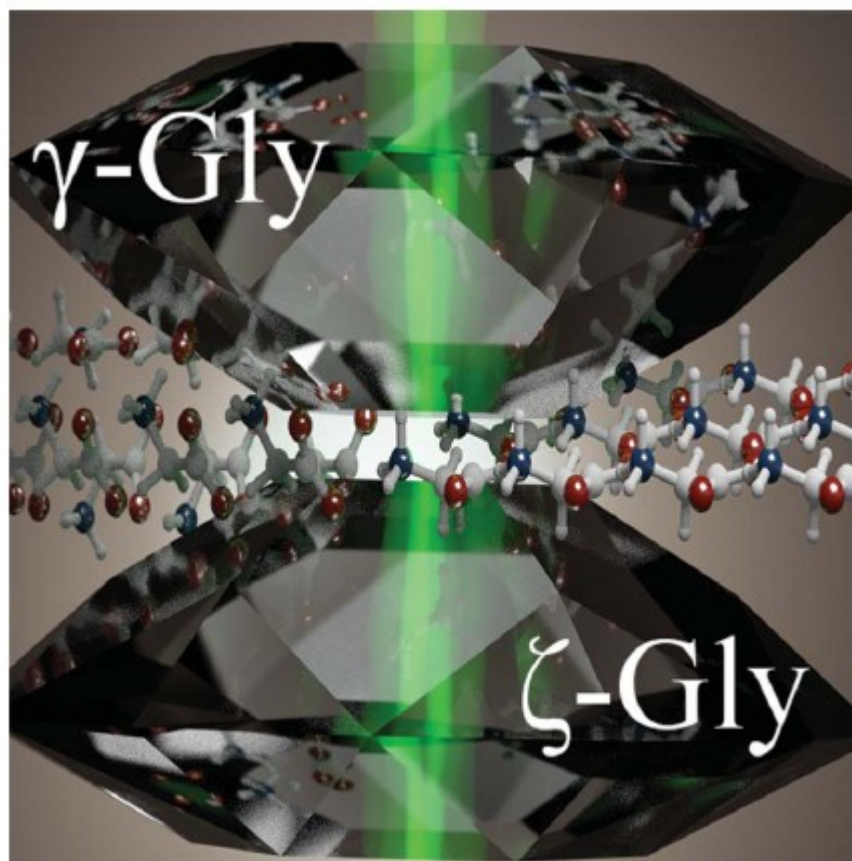
Emine Kucukbenli, Kanchan Sonkar,  
Neeraj Shina

Centre of Biomedical Magn. Resonance,  
Lucknow, India

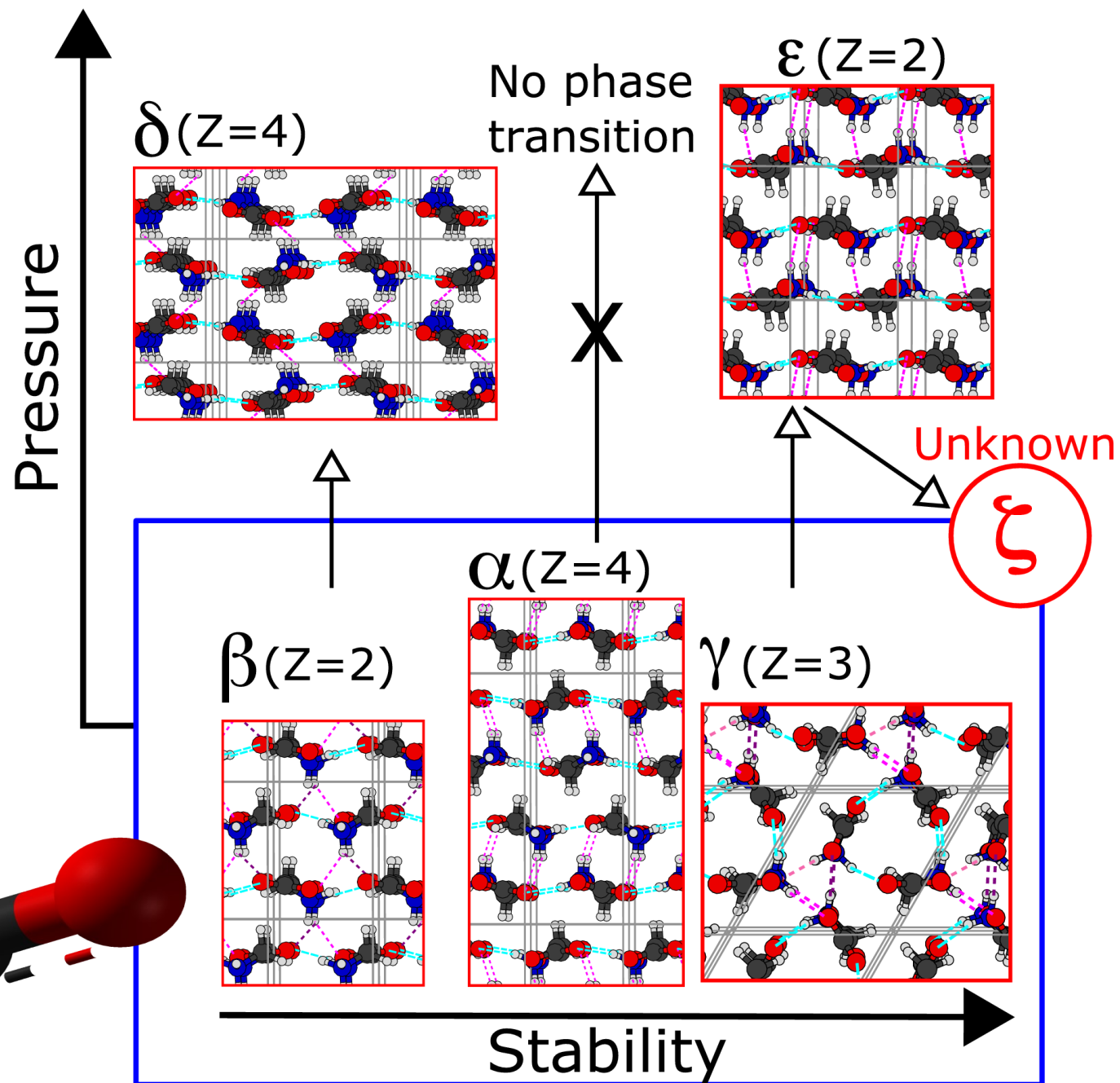
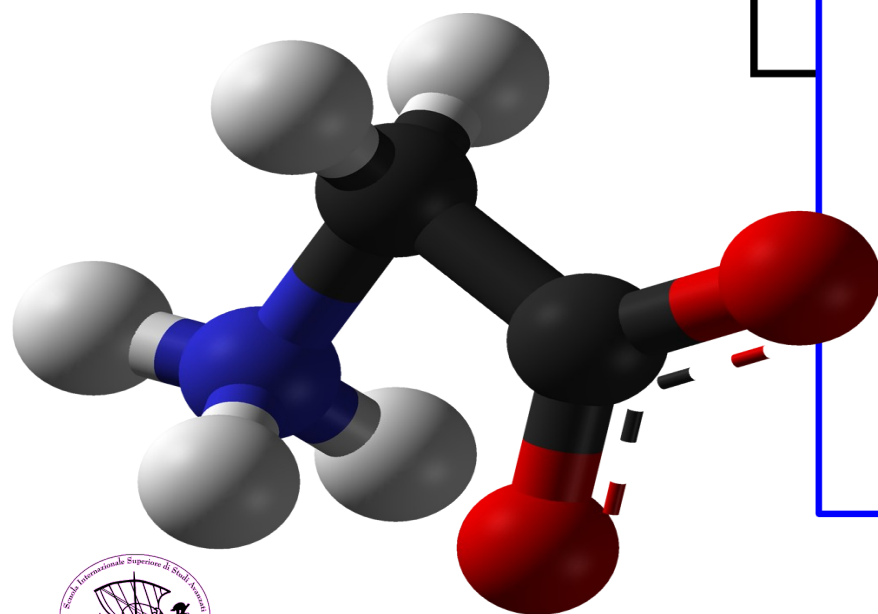




# $\zeta$ -Glycine: Insight into the mechanism of a polymorphic phase transition



# Glycine



# Is CSP a formidable problem?

- CSP problem: Name a chemical or stoichiometric formula; find the (local) minima of the free energy landscape under given thermodynamic conditions (often at certain T,P)
- “What is the most stable structure of glycine at ambient conditions?” “What is the carbon structure that is stable at very high pressures”
- Challenges:
  - A very vast space of possibilities.
  - Free energy landscape is very expensive to obtain accurately

# How to tackle CSP?

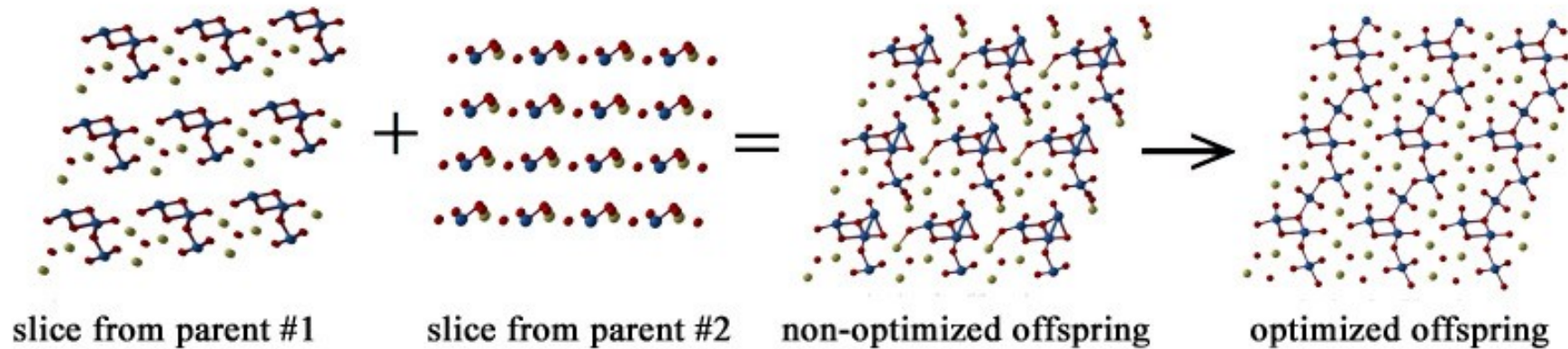
Explore: Use smart algorithms to explore as much of the landscape as possible

Molecular dynamics / Monte Carlo walkers

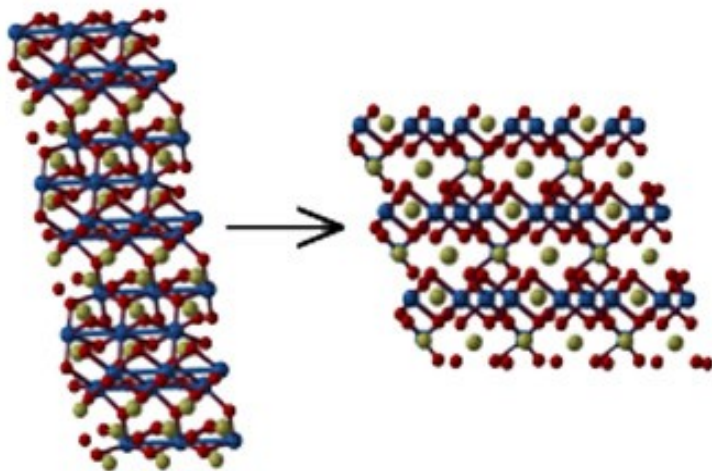
- Simulated annealing
- Metadynamics
- Basin hopping
- Minima hopping
- Genetic algorithm

# Genetic algorithm

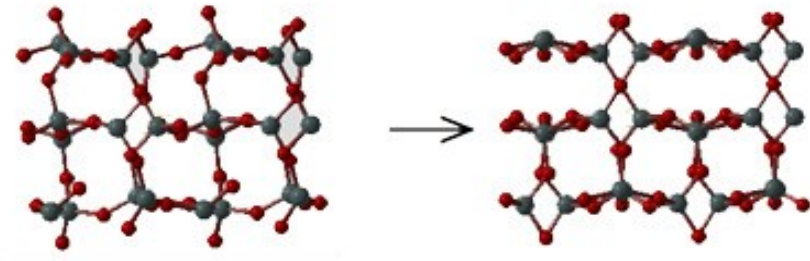
(a) heredity



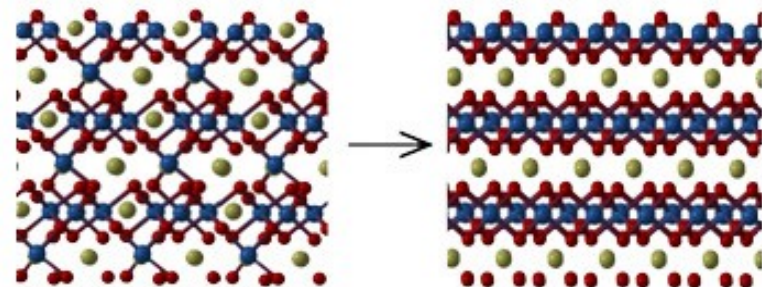
(b) lattice mutation



(c) softmode mutation



(d) permutation



USPEX operations





+

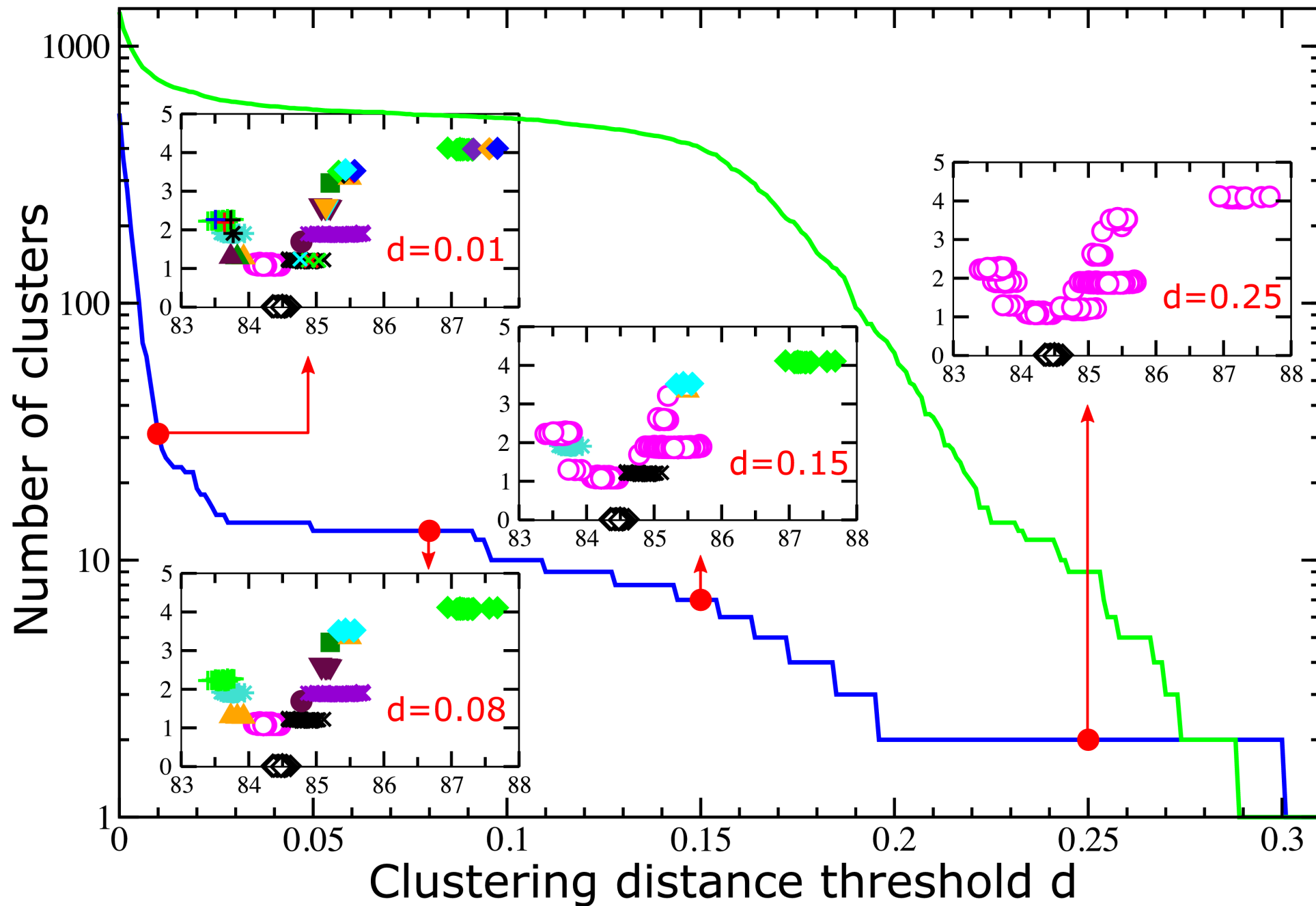


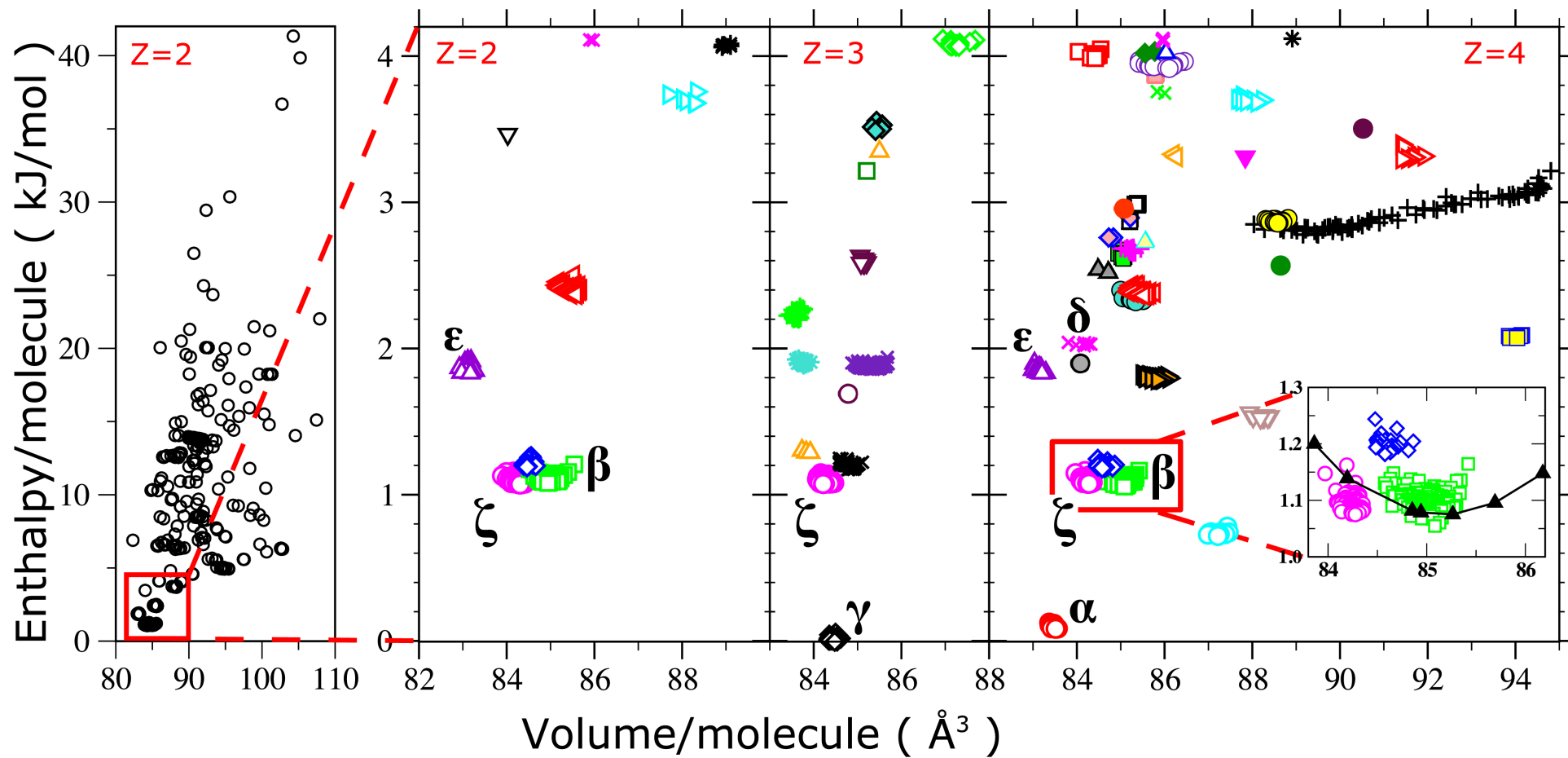


+



+ vdWDF + clustering





# $\zeta$ -phase

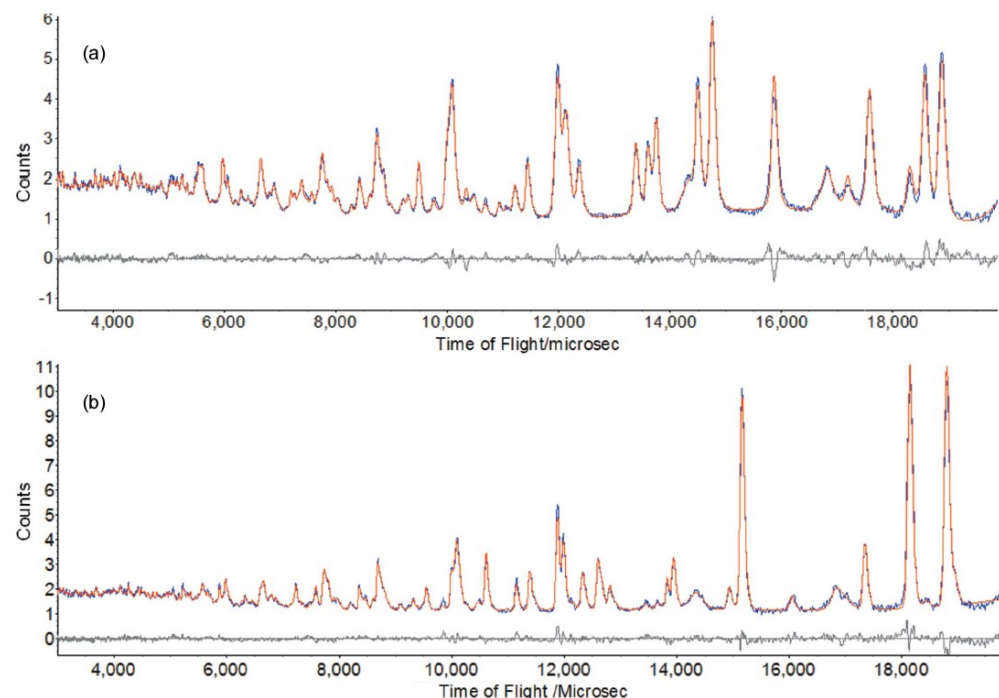


Figure 2

(a) Rietveld fit of the neutron powder diffraction pattern of  $\zeta$ -glycine at 100 K (blue = observed, red = calculated). In addition to the peak  $\zeta$ -glycine, the pattern also shows the presence of residual  $\varepsilon$ - and a trace of  $\gamma$ -glycine. Other peaks arise from the sample environment, namely the pressure marker and the  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  components of the anvils of the pressure cell. (b) Rietveld fit of the neutron powder diffraction pattern of  $\beta$ -glycine (contaminated with  $\zeta$ - and a trace of  $\gamma$ -glycine) at 290 K. A 1 Å  $d$  spacing approximates to 4837  $\mu\text{s}$  in time-of-flight.

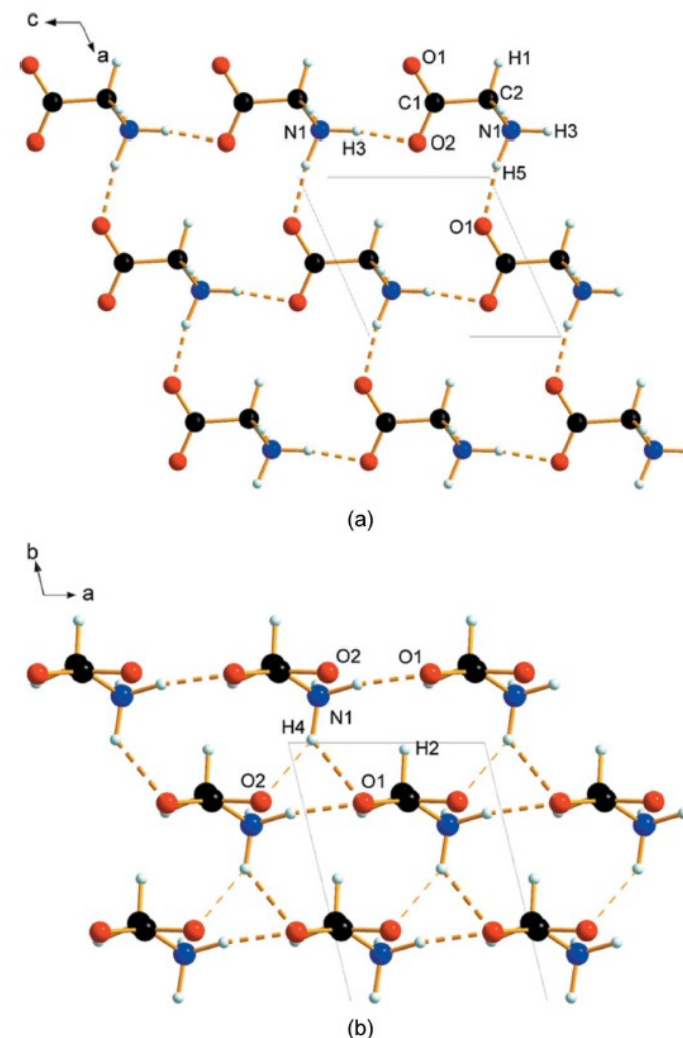


Figure 3

Intermolecular interactions in  $\zeta$ -glycine. (a) Layers formed in the  $ac$  plane, viewed along  $b$ . (b) Stacking of the layers, viewed along  $c$ .

E Kucukbenli, CH Pham, SdG,  
C Bull, G Flowitt-Hill, HY Playford, M Tucker, S Parsons  
Int Union Crist J **4**, 569–574 (2017)





# Credits



- Theory and Calculations

Emine Kucukbenli, Cong Huy Pham



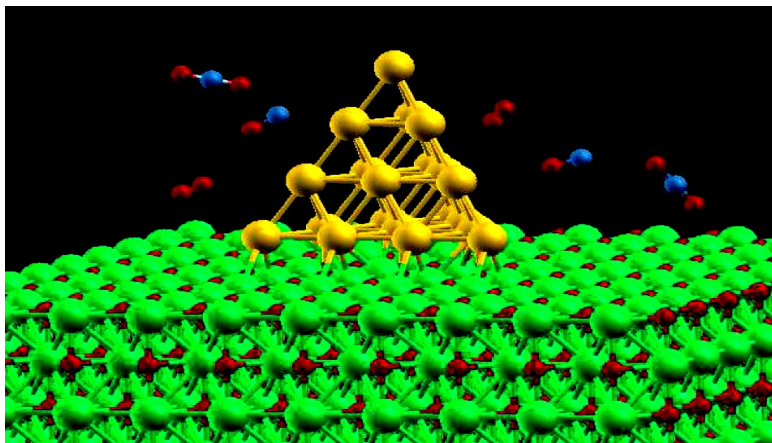
- Experiments

C Bull, G Flowitt-Hill, HY Playford, M Tucker, S Parsons

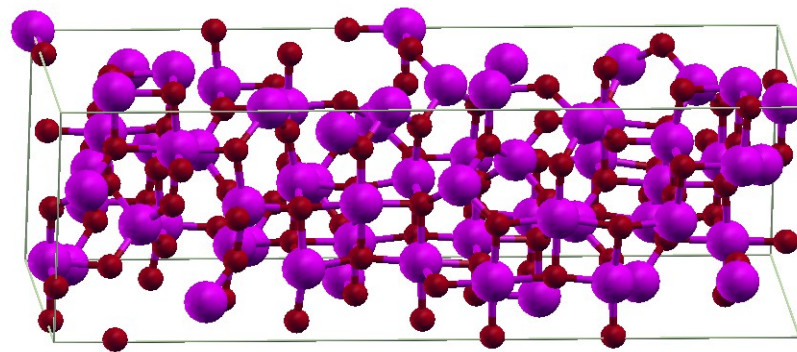
- Networking

Qiang Zhu

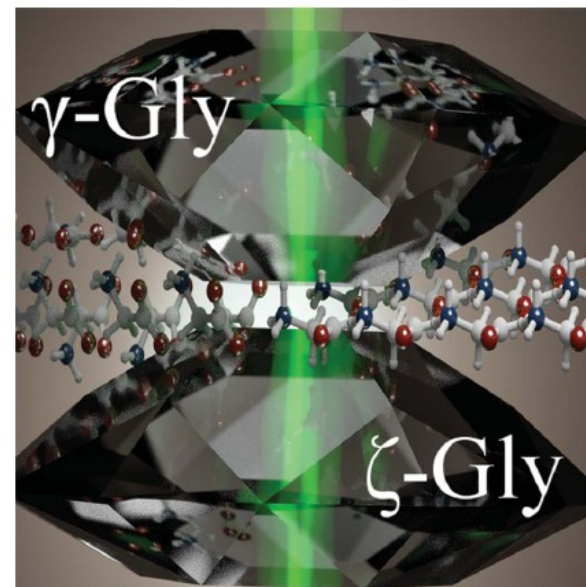
## Controlling morphology of Au<sub>20</sub>-clusters by substrate doping



## <sup>27</sup>Al NMR shifts of Alumina and its precursors



## ζ-Glycine: Insight into the mechanism of a polymorphic phase transition



## Complete <sup>13</sup>C Chemical Shift Assignment for Cholesterol Crystal



Thank you for your attention