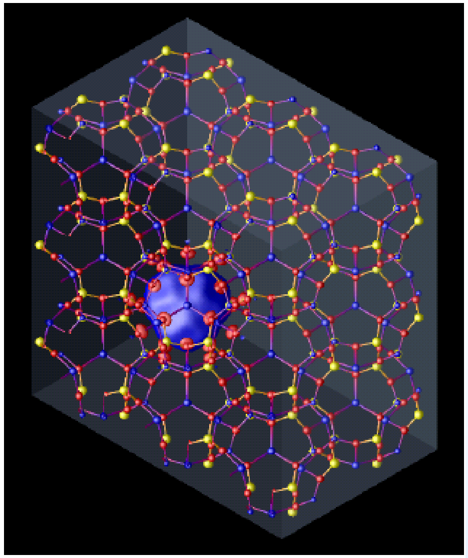
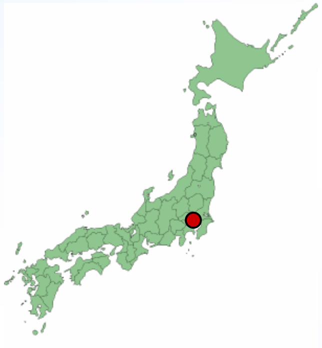
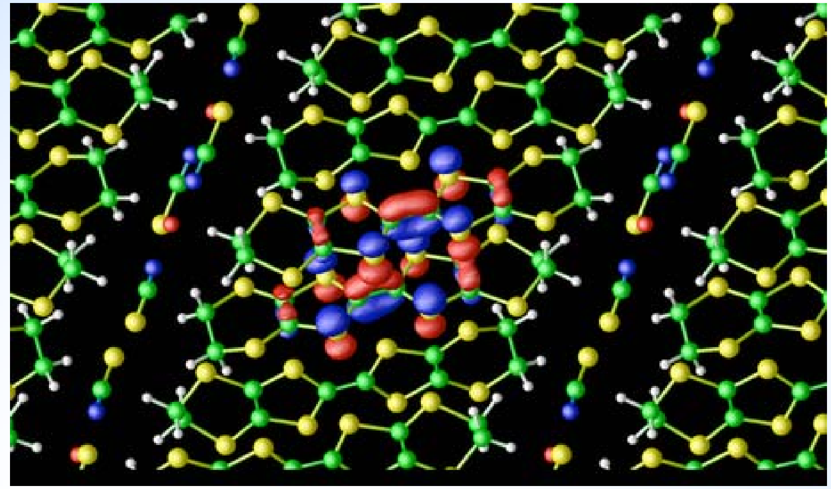
# Toward “tailor-made correlations” in zeolites





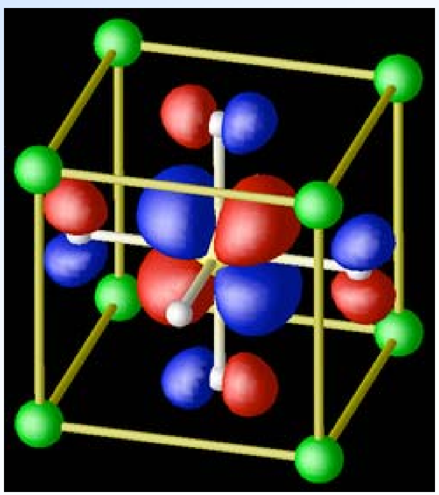
Ryotaro ARITA
Department of Applied Physics, University of Tokyo

# Strongly correlated electron systems

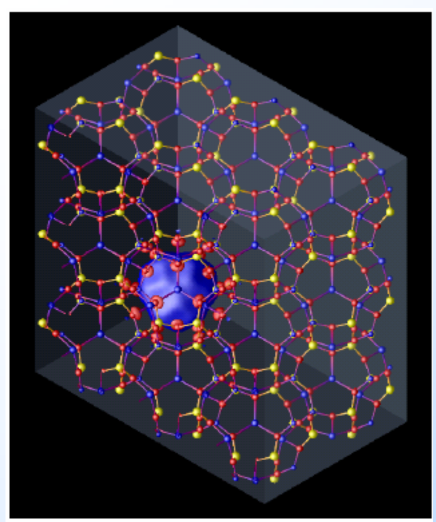


d electron system
(Transition metal oxides)

f electron system
(Heavy electron systems)



Correlated p electron system
(organic compounds, e.g., BEDT-TTF)



Zeolite =
Correlated s electron system

# Collaborators

- Yoshiro Nohara (Dept. Phys., Univ. Tokyo)

- Kazuma Nakamura (Dept. Appl. Phys., Univ. Tokyo)

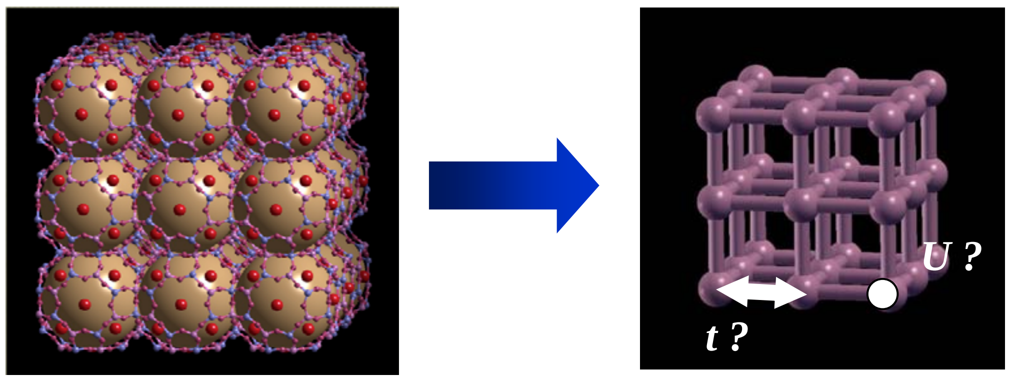
- Takashi Koretsune (Dept. Phys., Tokyo Inst. Tech.)

- References:
  - Phys. Rev. B 80, 220410(R) (2009)
  - Phys. Rev. B 80, 174420 (2009)

# Outline

- Introduction to zeolite
  - nanoporous aluminosilicates + cluster of alkali atoms
  - Family of huge members, rich variety of physical/chemical properties
  - Strongly correlated electron system made from Al, Si, O, K (Na, Rb)

- Ferromagnetism in zeolite LTA
  - Ferromagnet comprising only non-magnetic elements
    - Mechanism of spin polarization: described by the multi-orbital Hubbard model



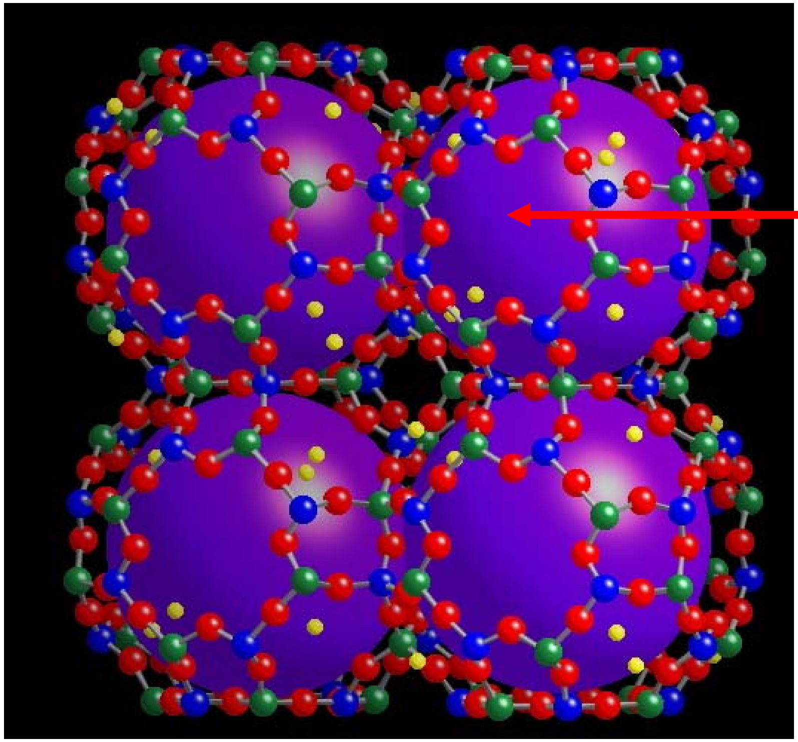

Supercrystal of superatom

    - “superatom” picture: materials design in terms of superatom ?
    - Design of correlation effect (Taylor-made correlation)

- How large is *U* of superatom ?
  - Estimate of interaction parameters by cRPA

# What is zeolite ?

**Host**

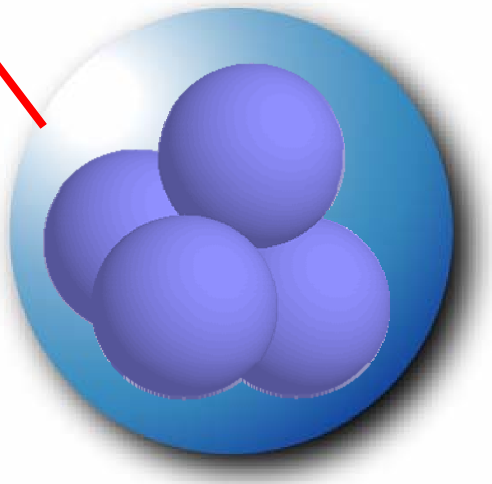


: Al : O :Si

cage made of aluminosilicate

\+

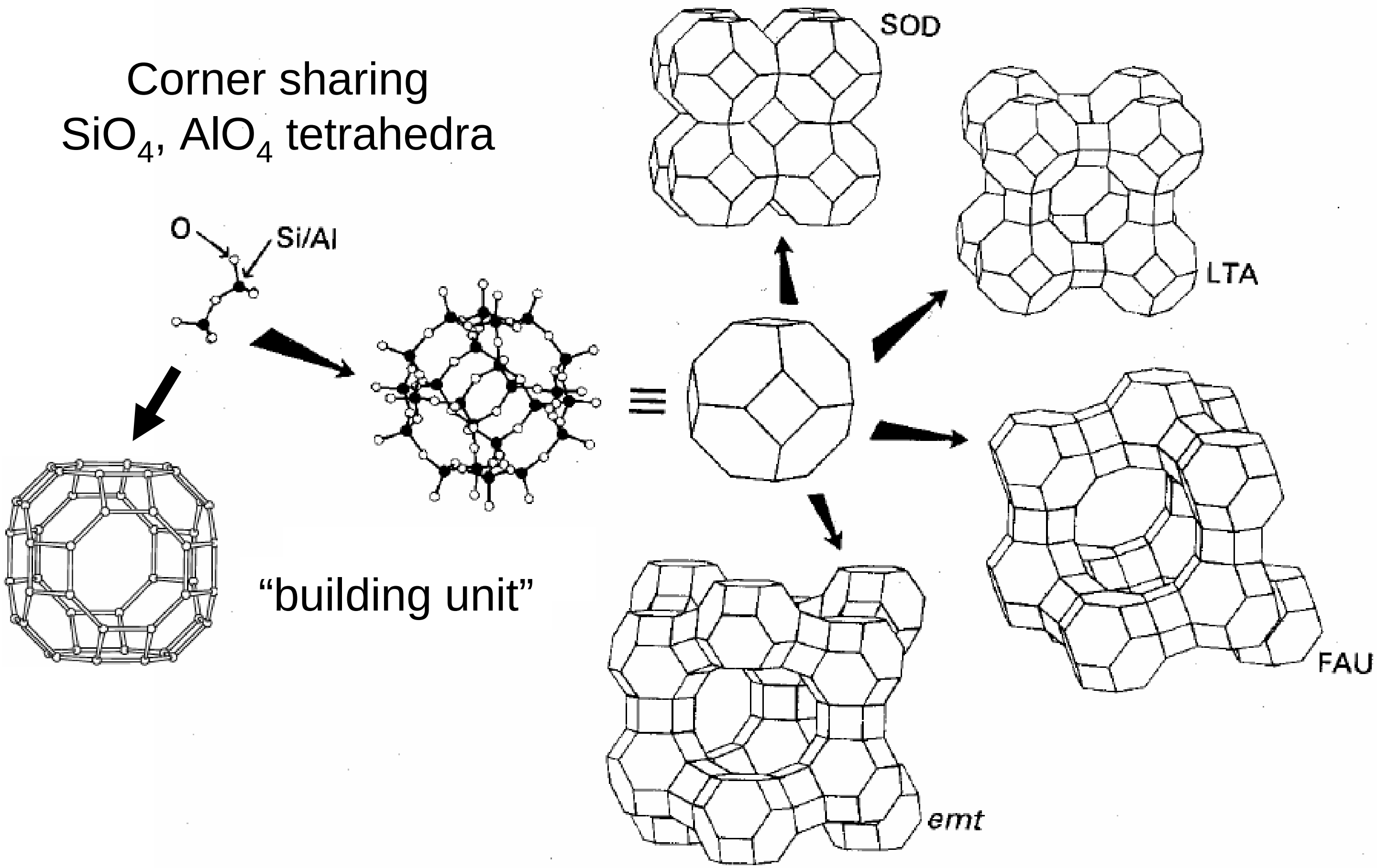
**Guest**



alkali cluster
(K, Na, Rb, etc.)

# What is zeolite ? : rich variety of host-cage structures

Corner sharing
$SiO_4$, $AlO_4$ tetrahedra




“building unit”

various host-cage structure

# What is zeolite ? : rich variety of host-cage structures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| ABW | ACO | AEI | AEL | AEN | AET | AFG | AFI | AFN | AFO | AFR | AFS |
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~200 kinds of structures

http://www.iza-structure.org/databases/

# What is zeolite ? : rich variety of host-cage structures



Database of Zeolite Structures

IZA-SC | Framework Type | References | Powder Patterns | Building Schemes | Disordered Structures | Other Links

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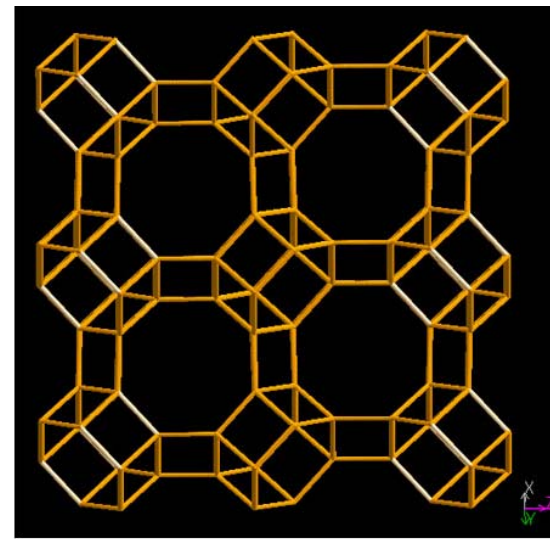

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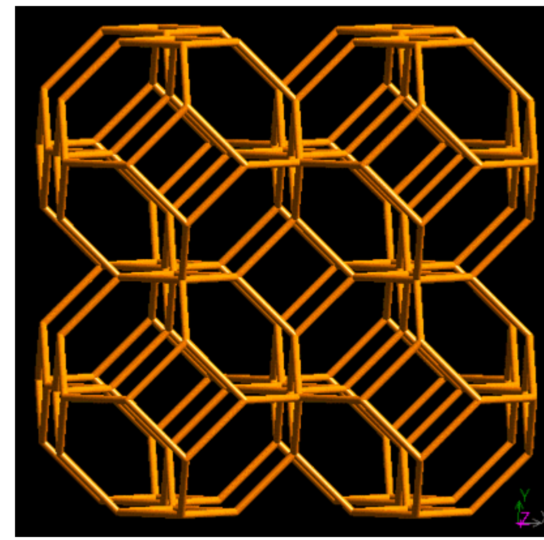

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# What is zeolite ? : rich variety of host-cage structures


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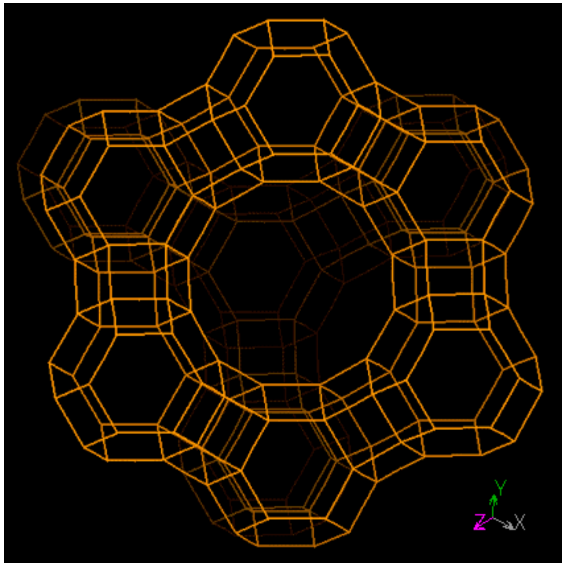


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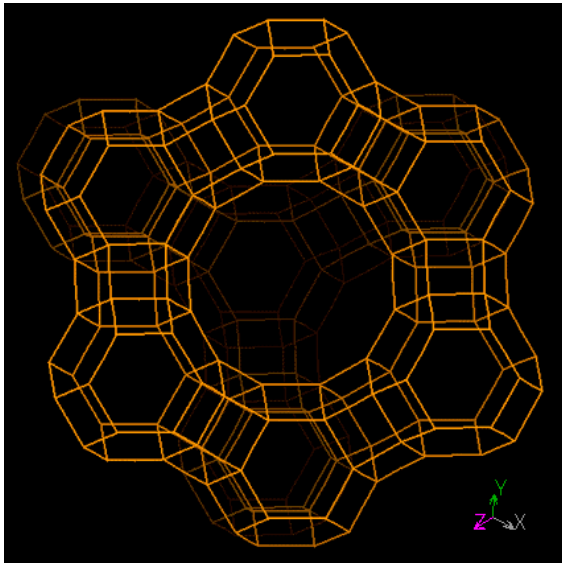


~200 kinds of structures
+ Al/Si ratio (controls acidity)
+ size/species (Na, K, Rb) of guest clusters

= Family of huge members / various physical & chemical properties

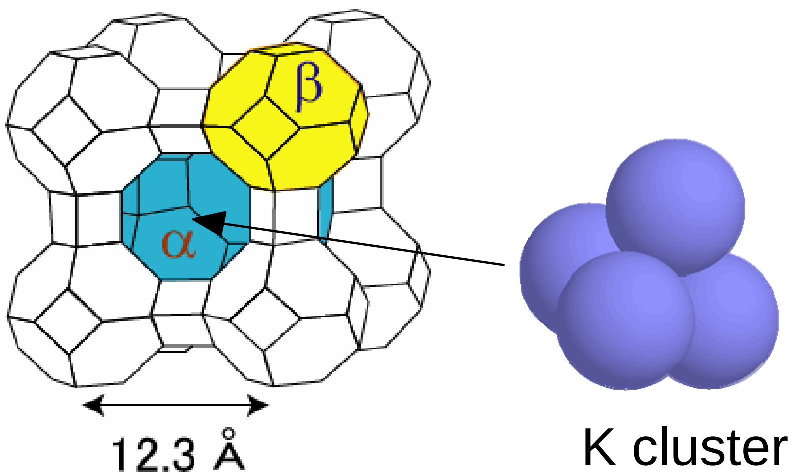
# What is zeolites ?: many applications

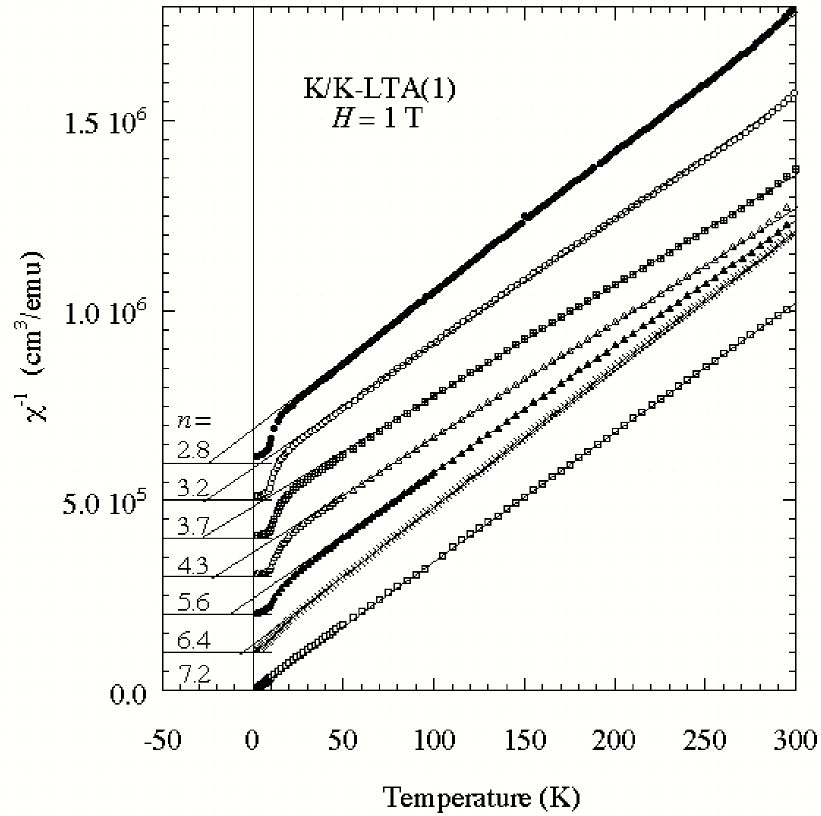
- Detergents: taking advantage of iron-exchange capability
  - Cations in the host-cage such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ etc., are rather loosely held so that they can readily be exchanged for others in a contact solution
- Molecular sieves: takeing advantage of regular pore structure of molecular dimensions
  - Zeolites can selectively sort molecules in a size-exclusion process. (Molecules small enough to pass through the pores are absorbed while larger molecules are not.)
- Catalysis: taking advantage of high surface area and acidity
- …

# What is zeolite ?

Strongly correlated electron system made from Al, Si, O, K (Na, Rb)

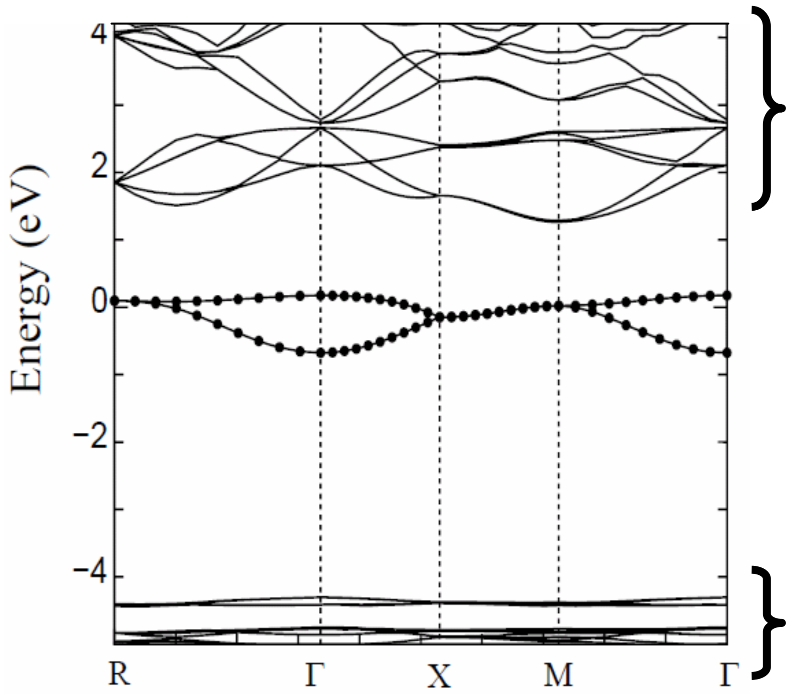
LTA

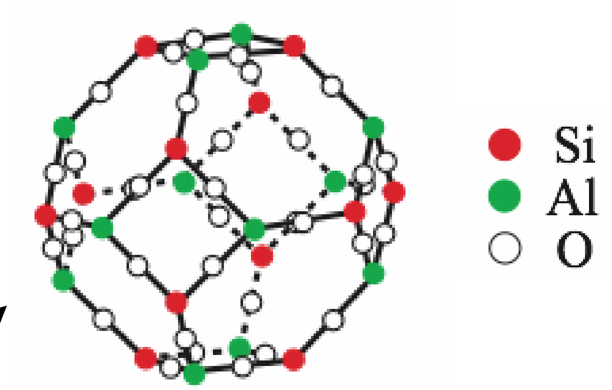



Ferromagnetism in a system comprising only non-magnetic elements (Nozue et al., 92)

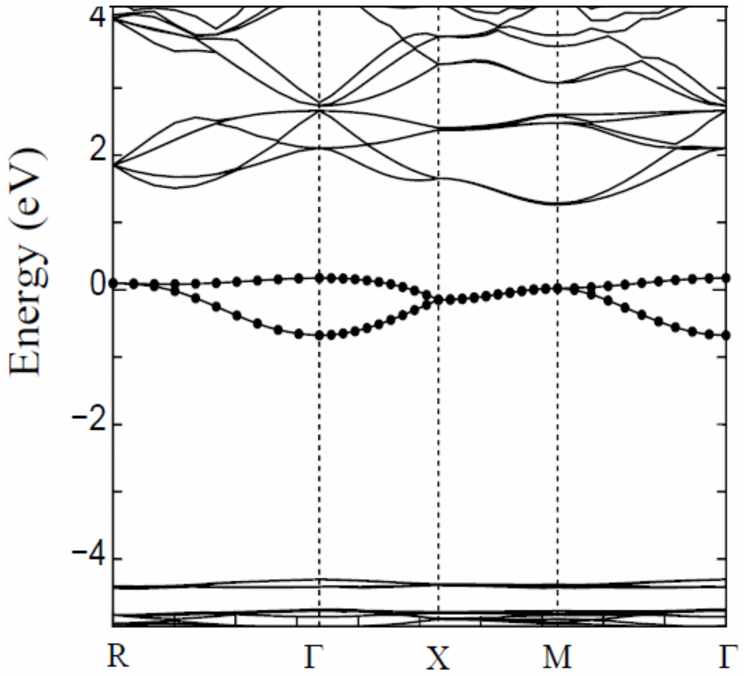
# Electronic structure of zeolite

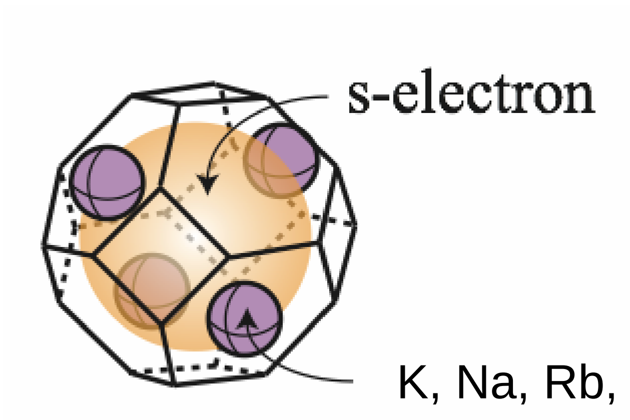



“host” (= aluminosilicate) cage forms a gap ~6eV

# Electronic structure of zeolite

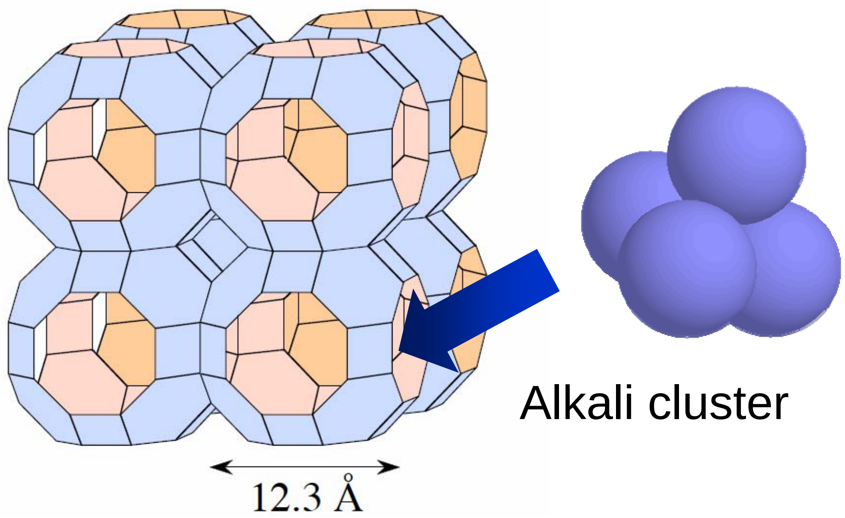


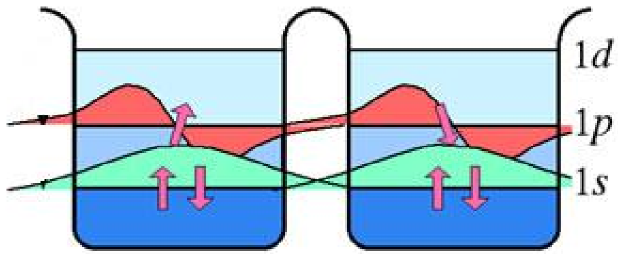




“guest” (= alkali cluster) makes states inside the gap

# Electronic structure of zeolite: superatom picture

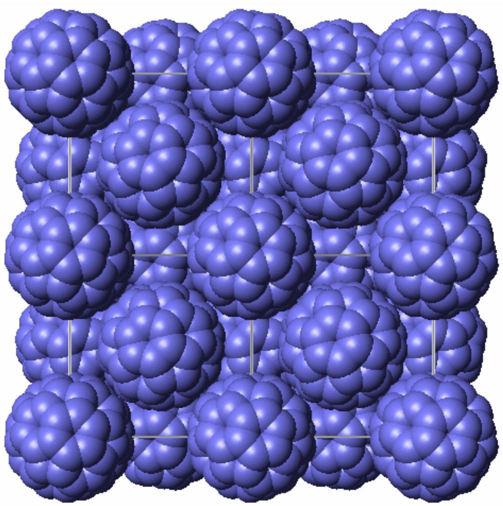
- potential formed by cages = atomic potential of superatom
- s-electron systems of alkali cluster = valence electrons of superatom

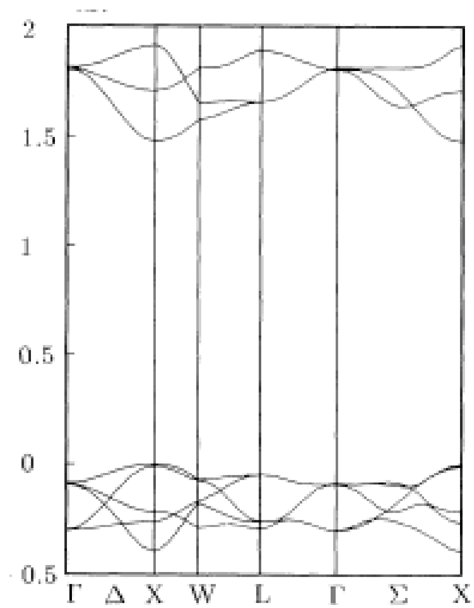


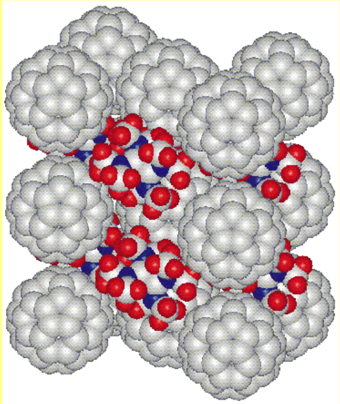

Correlation effects explained in terms of “superatom” ?
Materials design in terms of “superatom” ?

# Electronic structure of $C_{60}$



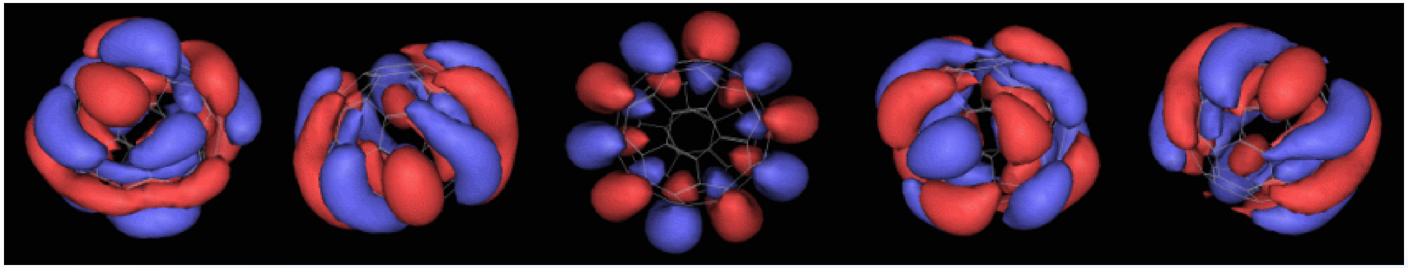



Ferromagnet
made from C, H, N
$C_{60}$-TDAE

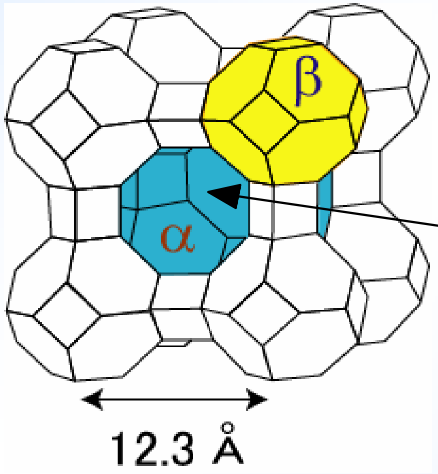


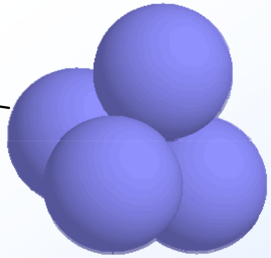
$T_c$~16K

$C_{60}$ HOMO



# Ferromagnetism in potassium-loaded zeolite LTA



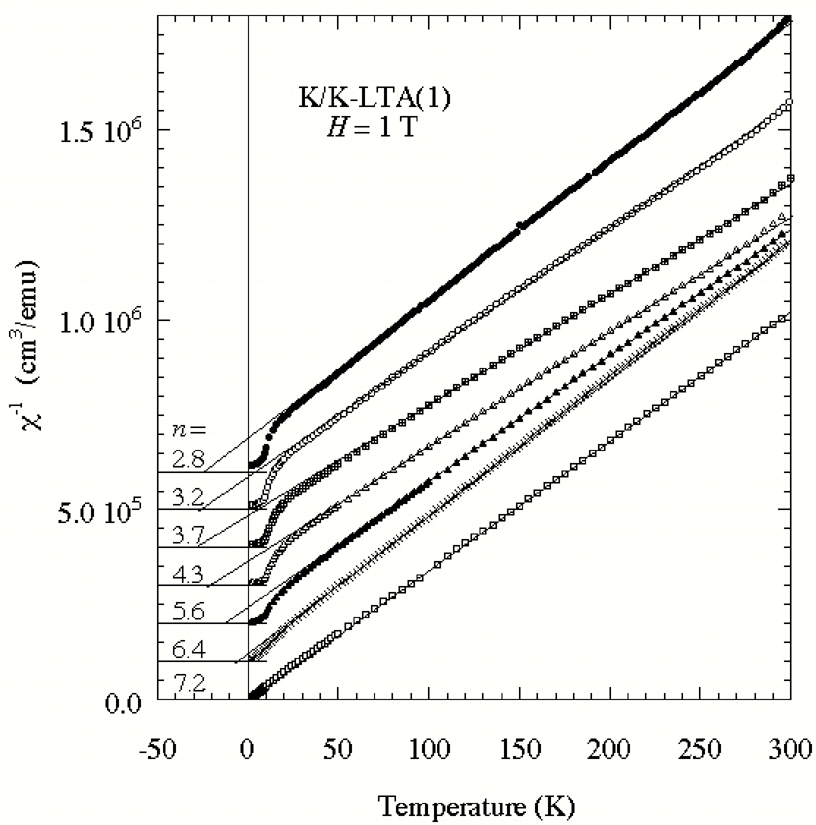
**K cluster**

Y. Nohara, K. Nakamura & RA
PRB 80 220410(R) (2009)

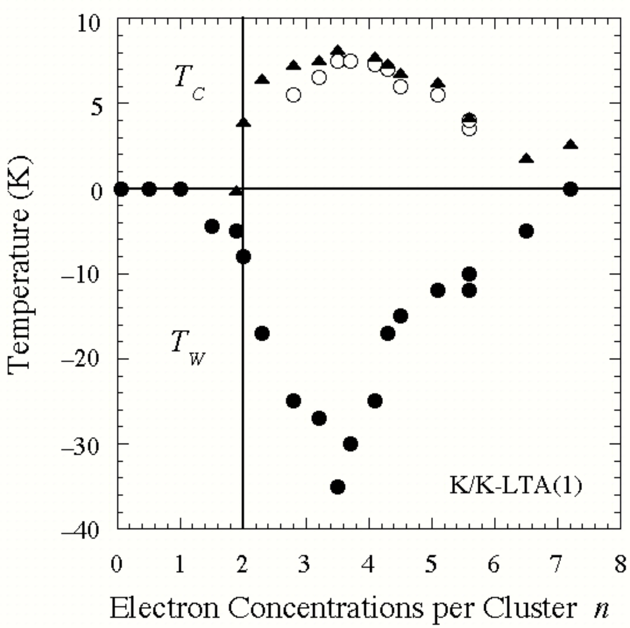
# K-loaded zeolite LTA $(K_n + K_{12}Al_{12}Si_{12}O_{48})$

Ground state = ferromagnetic

Nozue et al, PRL68 3789(1992)




Curie temperature &
Weiss temperature

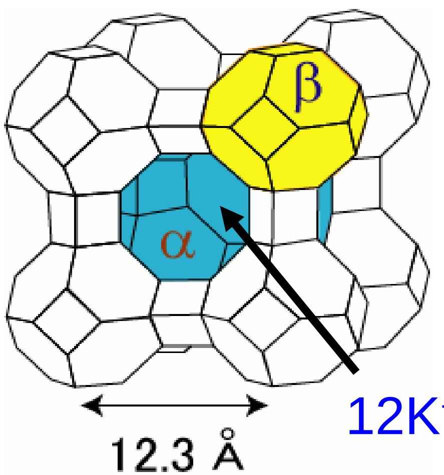



(Nozue *et al*, 1992,

Nakano *et al*, 2002)

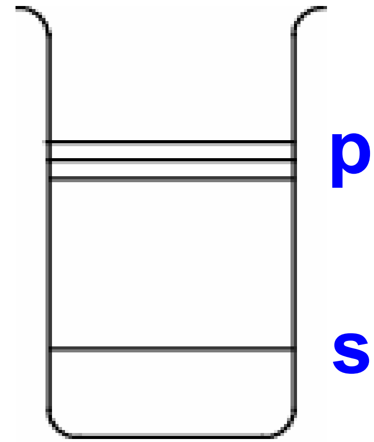
# Description of magnetism in terms of “superatom”

$(Al_{12}Si_{12}O_{48})^{12-}$

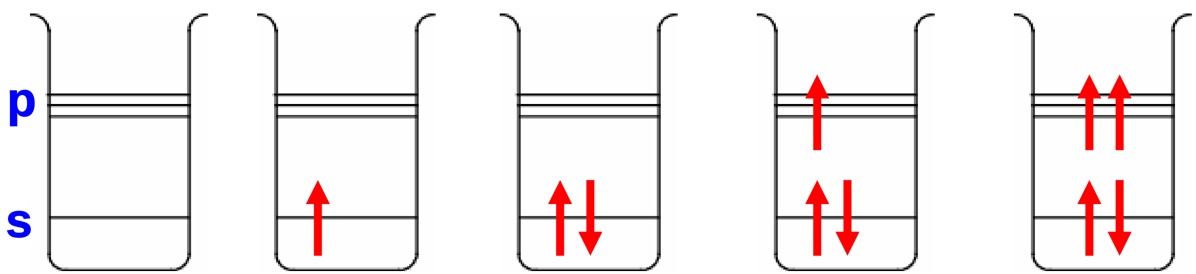



$12K^{+}+n\ (K^{+}+e^{-})$

$(K_{12+n}Al_{12}Si_{12}O_{48})^{n+}$




n=0 n=1 n=2 n=3 n=4




Nozue et al.

F appears

Highest $T_c$

# Mechanism of spin polarization?

Ab initio study for zeolite LTA has been limited, because

- Position of K not determined
  - Detailed Neutron scattering measurement

    T. Ikeda et al, Chem. Phys. Lett. 318, 93 (2000)

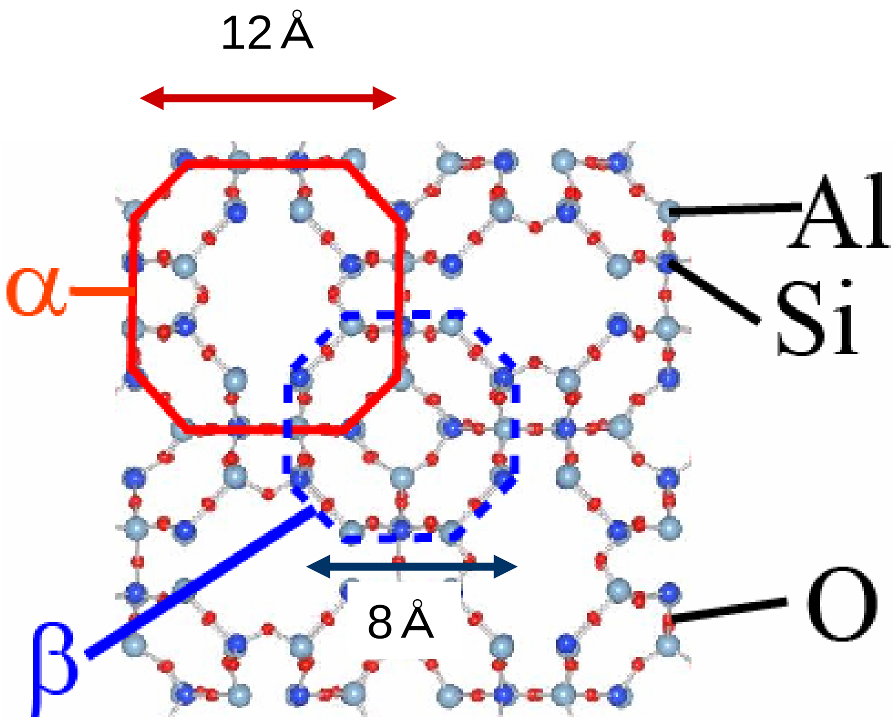
- Large unit cell: ~200 atoms in the unit cell
  - LDA for a “simplified” unit cell with < 100 atoms

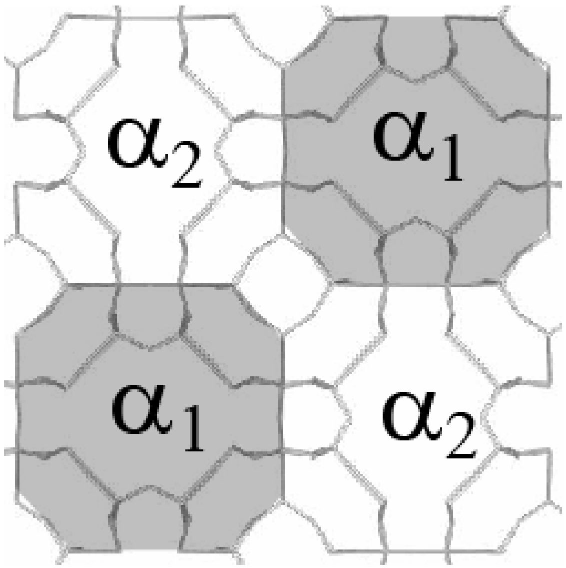
    RA et al, Phys. Rev. B. 69, 195106 (2004)

- LSDA calculation for LTA (n=4)
  - Ferromagnetic ground state ?

Nohara, Nakamura, RA 09

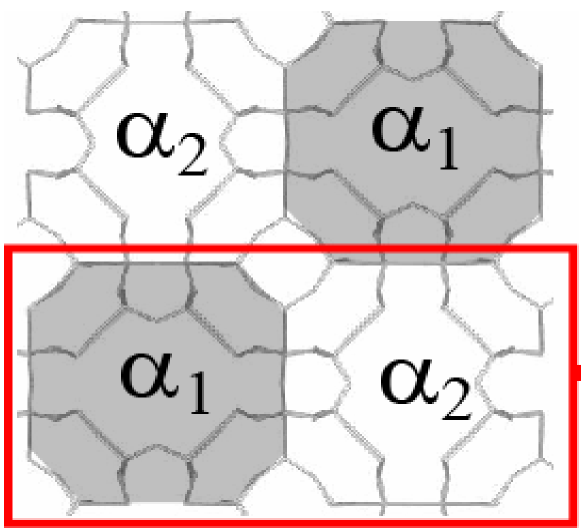
# Atomic configuration: host cage

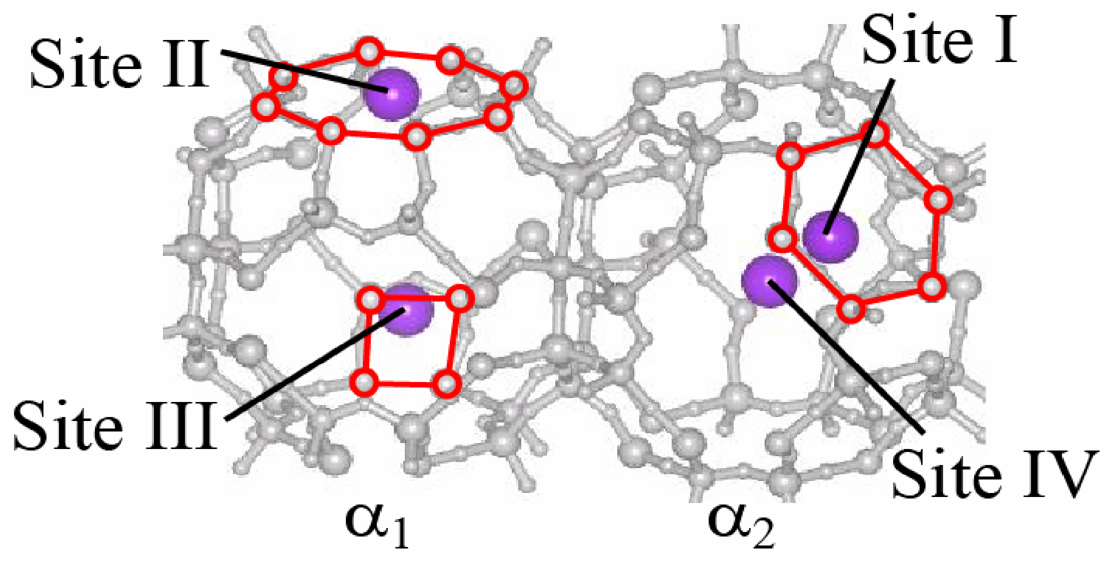


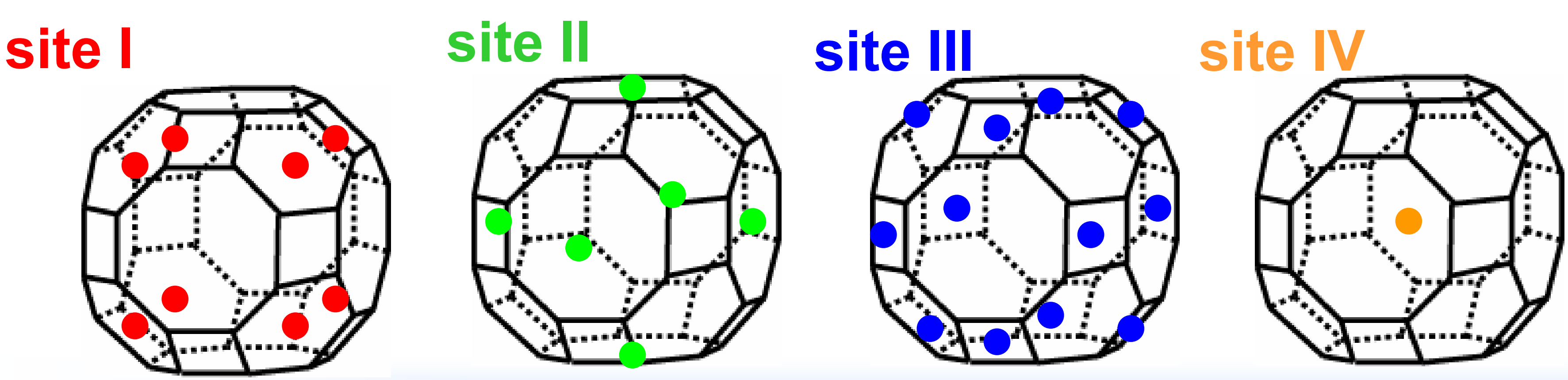



# Atomic configuration: positions of K

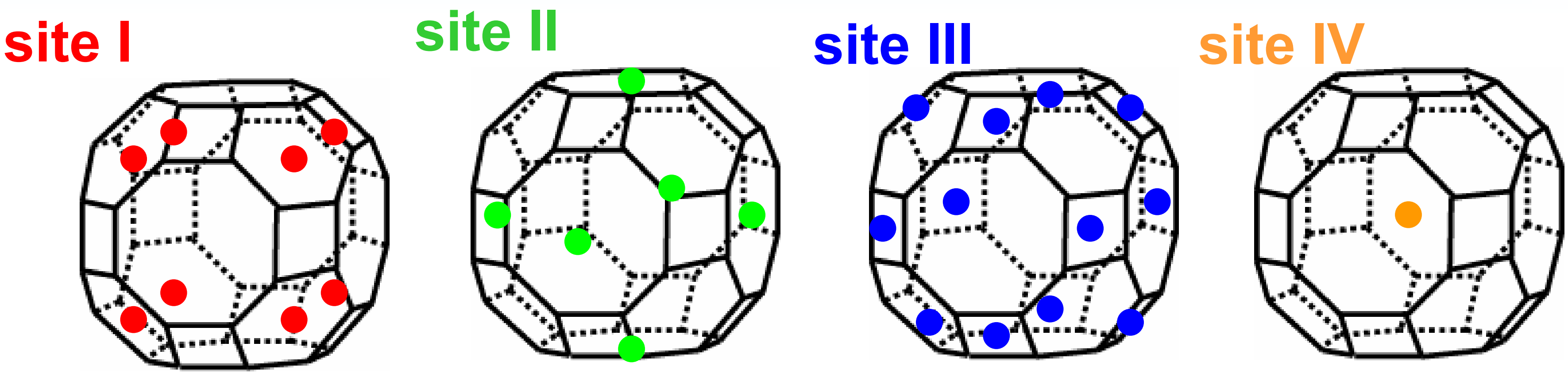
K are in α, not β (Ikeda et al, 2000)



# Atomic configuration: positions of K



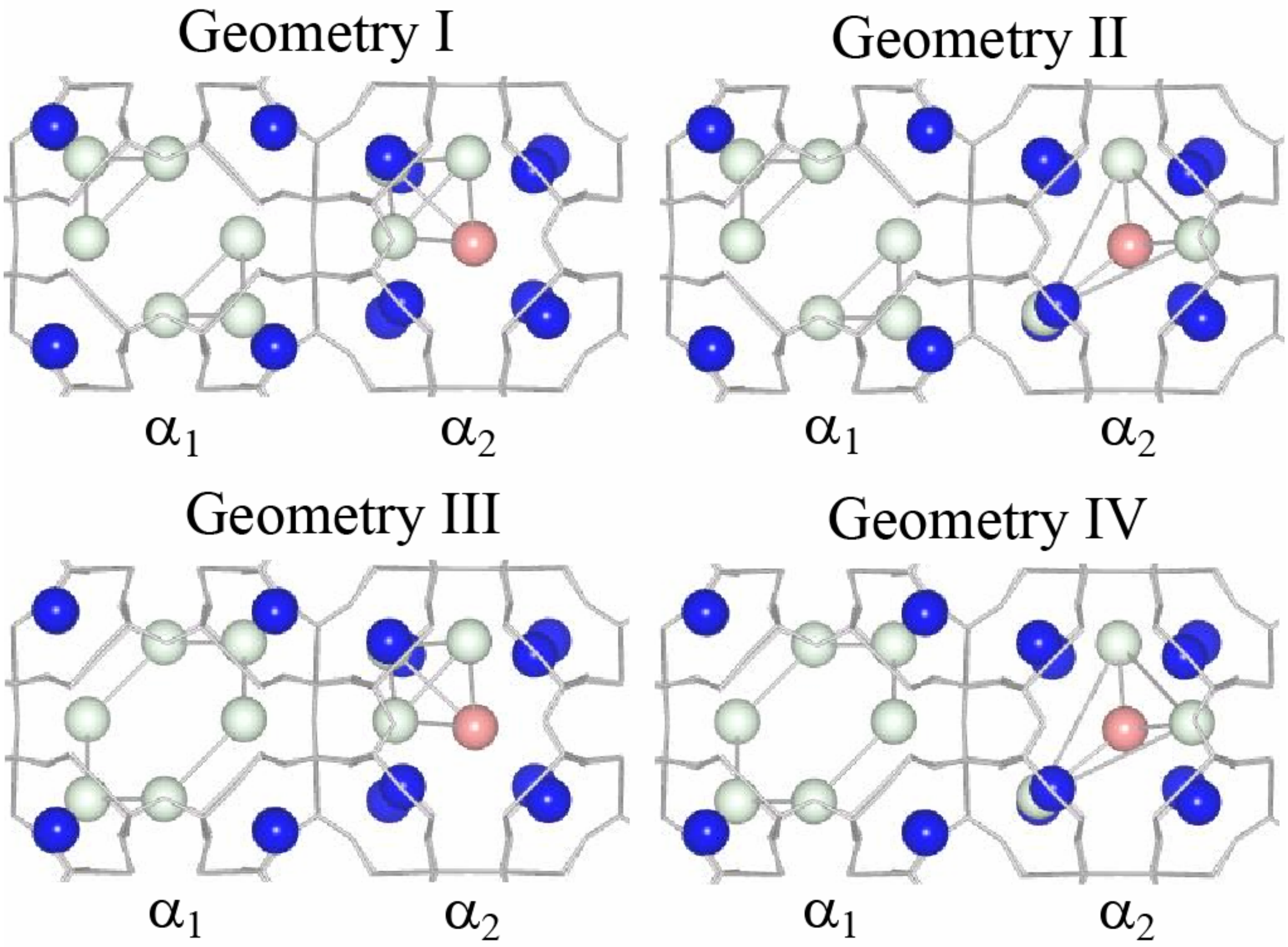

Occupancies ($K_4$+$K_{12}Al_{12}Si_{12}O_{48}$)   Ikeda et al, 2000

| | I(α1) | I(α2) | II | III(α1) | III(α2) | IV(α1) | IV(α2) | |
|---|---|---|---|---|---|---|---|---|
| # of sites | 8 | 8 | 6 | 12 | 12 | 1 | 1 | |
| Expt | 8 | 8 | 6.4 | 5.9 | 3.5 | 0 | 0.5 | (Ikeda et al, 2000) |
| Our model | 8 | 8 | 6 | 6 | 3 | 0 | 1 | |

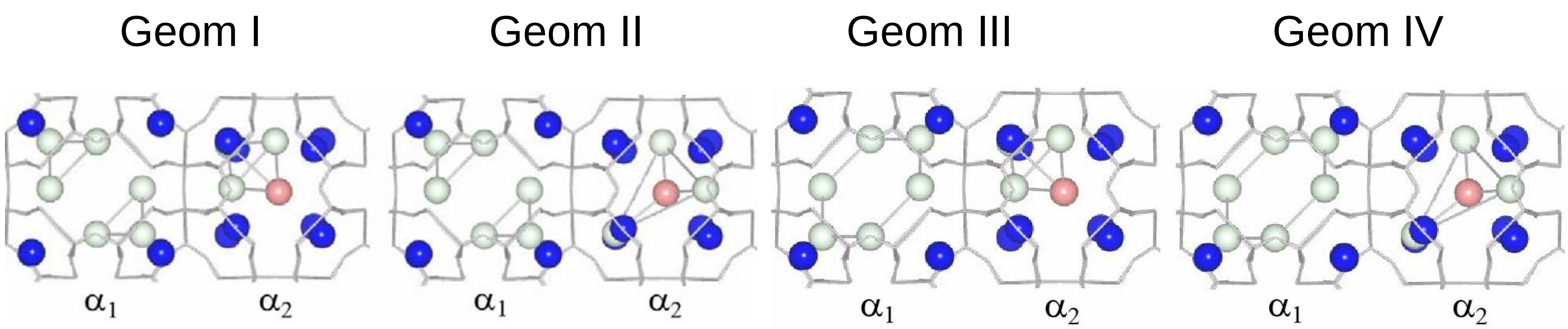
Partially filled:

Many possible configurations=${}_{12}C_6$ x ${}_{12}C_3$

# Configurations with trigonal symmetry



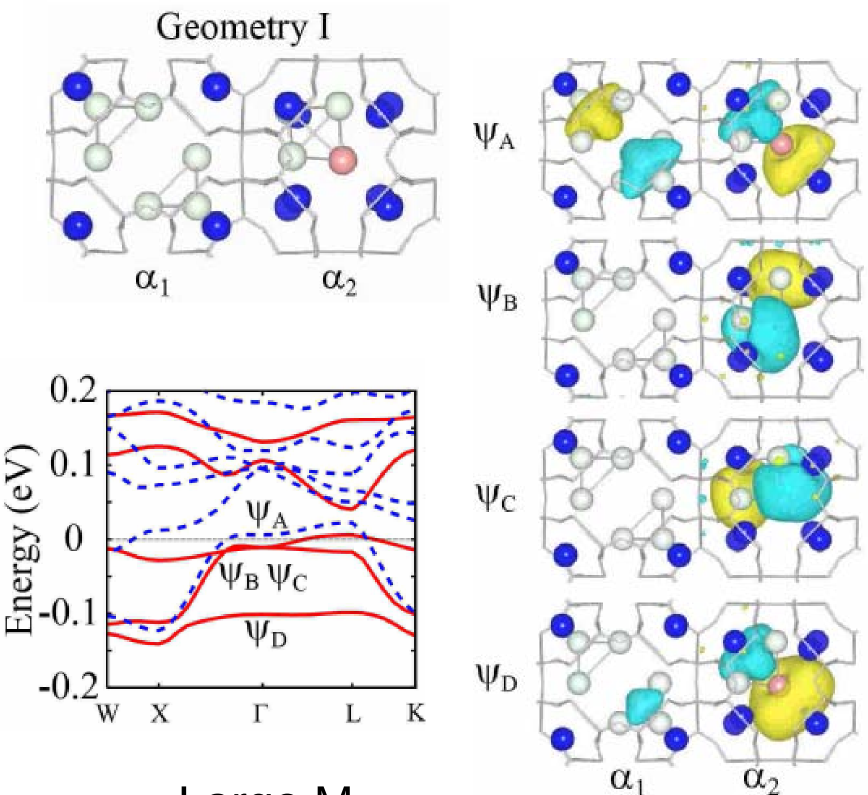
# Total energy & magnetic moment



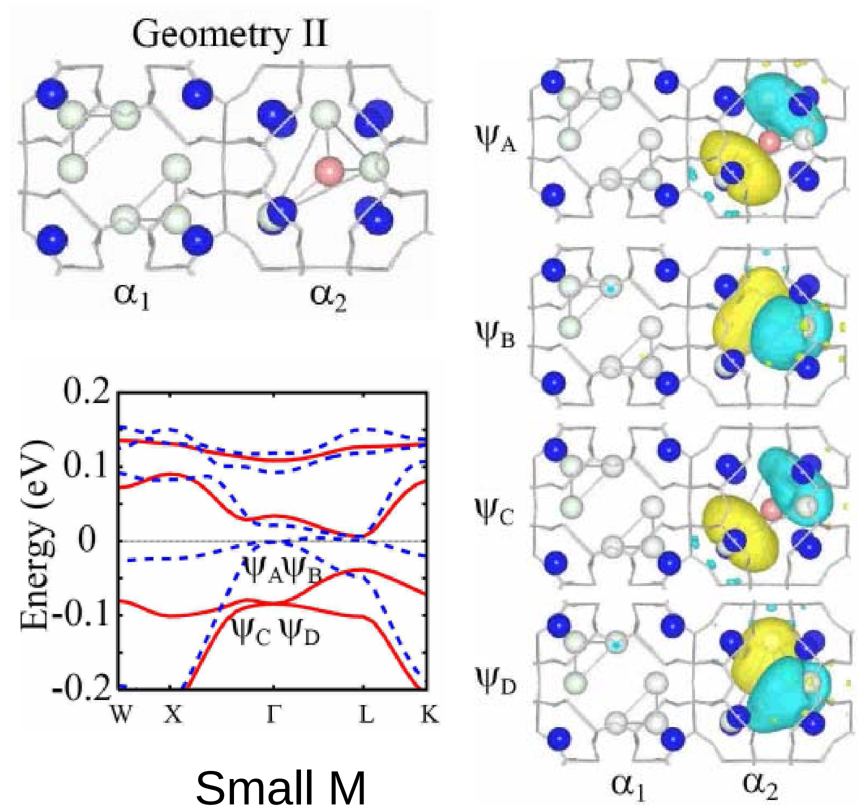

| | Geom I | Geom II | Geom III | Geom IV |
|---|---|---|---|---|
| $\Delta E_{\mathrm{tot}}(\mathrm{eV})$ | 0 | 1.02 | 1.49 | 0.12 |
| $M_1(\mu_B)$ | $-0.02$ | $-0.20$ | 0.06 | $-0.16$ |
| $M_2(\mu_B)$ | 1.92 | 0.33 | 1.36 | 1.00 |

LSDA gives finite magnetic moment

# Band dispersion & wave function



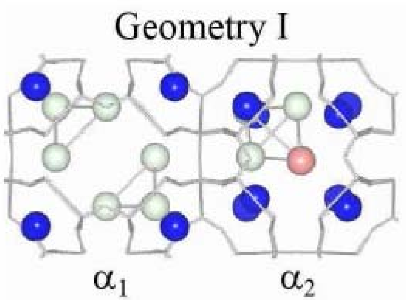

Large M

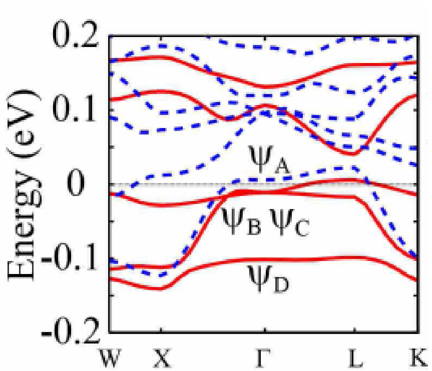



Small M

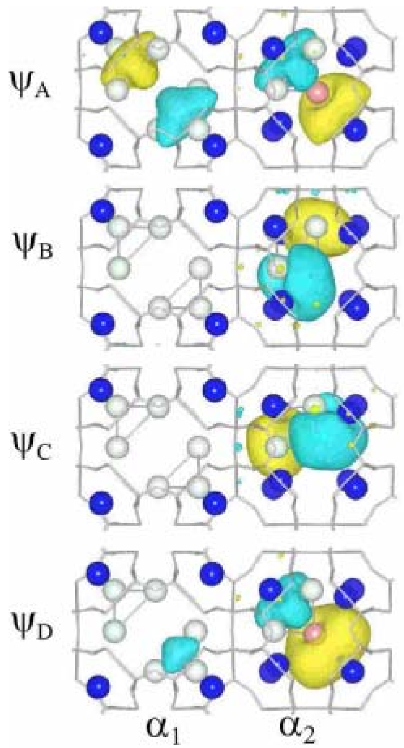
“p-states” are responsible for magnetism

# Band dispersion & wave function




Large M

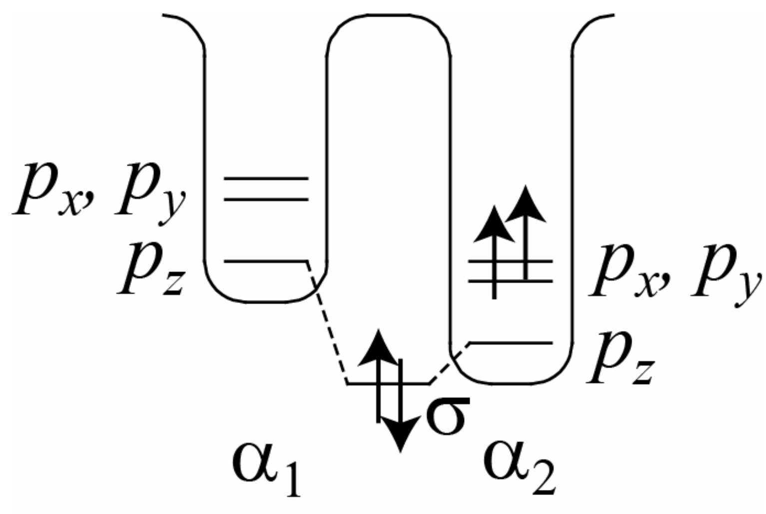



Pz ↓

Px ↑

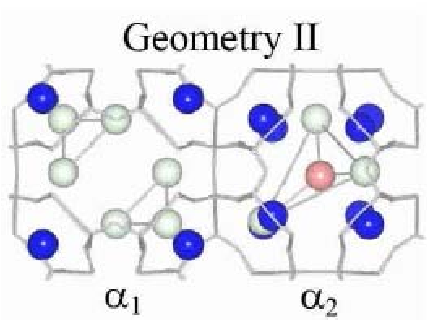
Py ↑

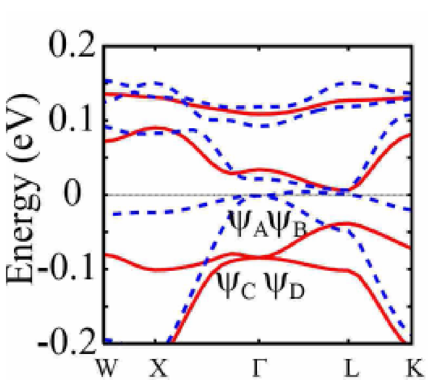
Pz ↑



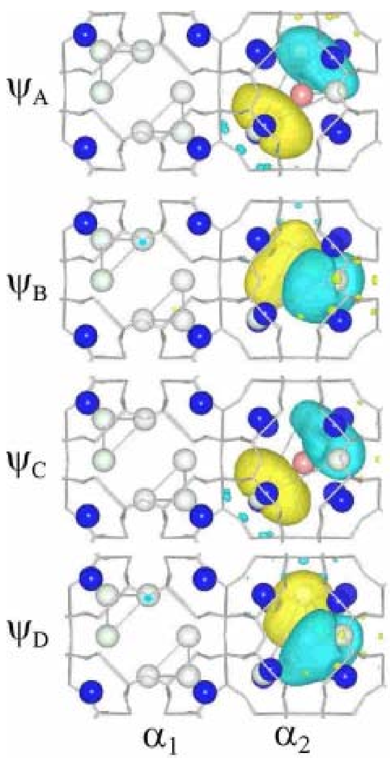

“p-states” are responsible for magnetism

# Band dispersion & wave function




Small M

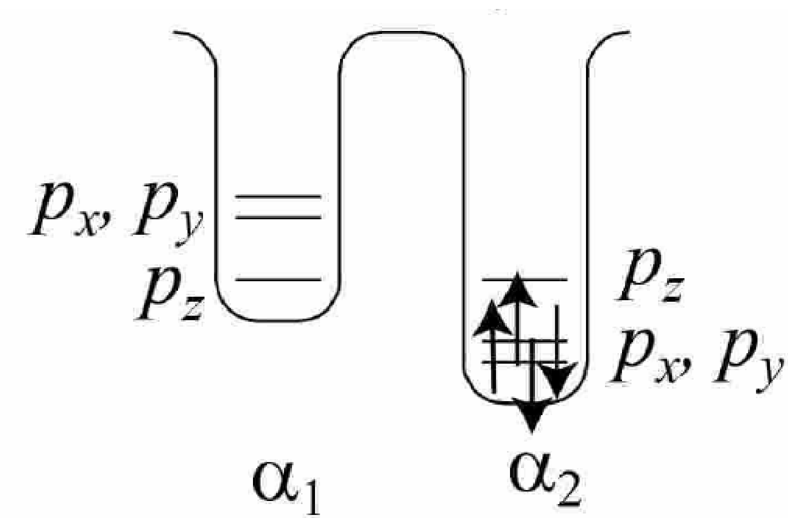



Py ↓

Px ↓

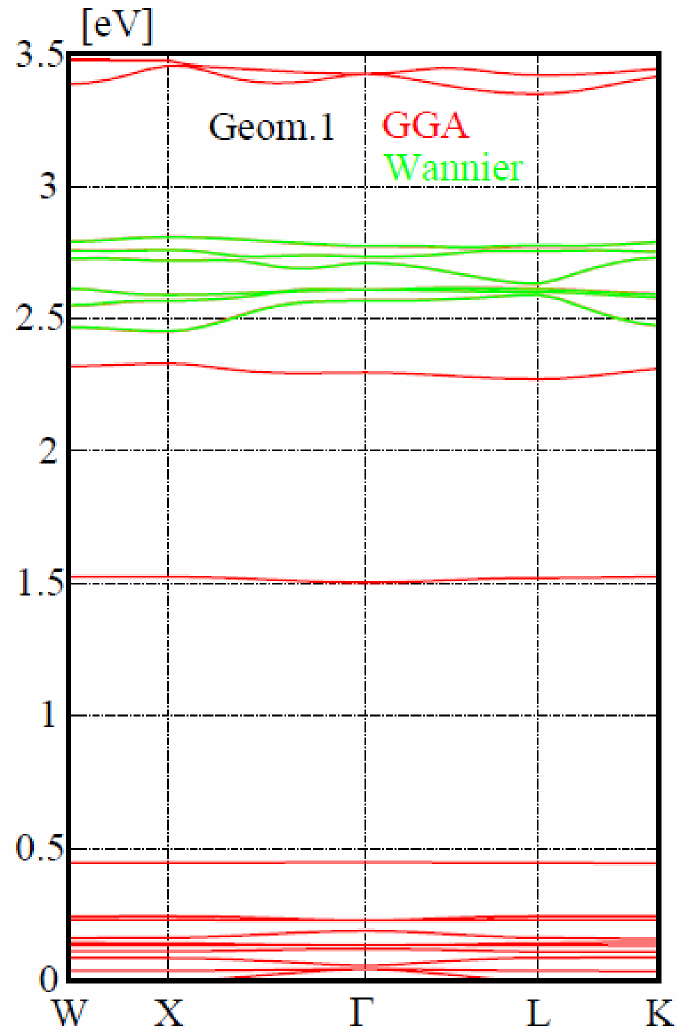
Py ↑

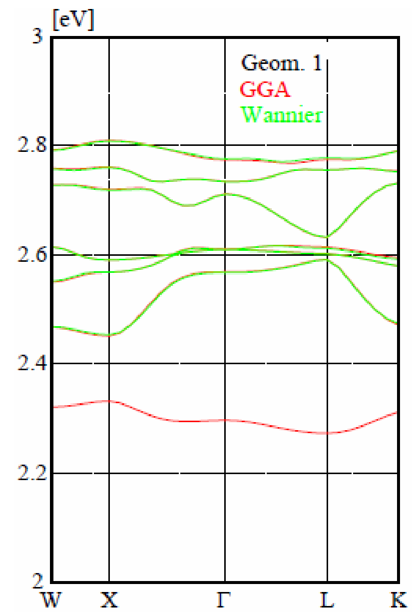
Px ↑



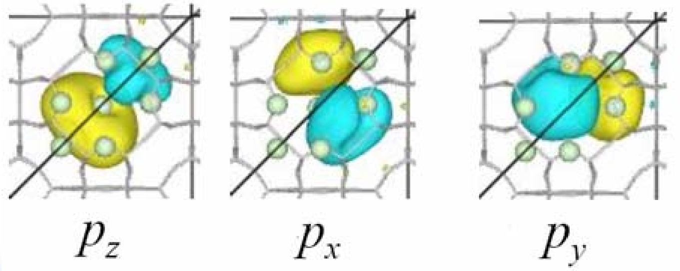

“p-states” are responsible for magnetism

# Effective low-energy model



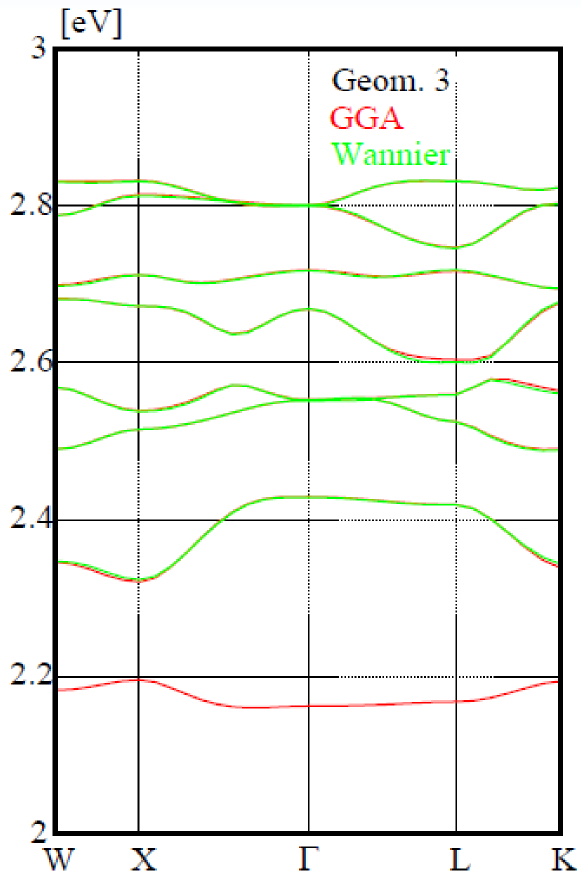



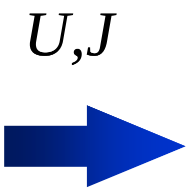

Maximally localized Wannier fn.

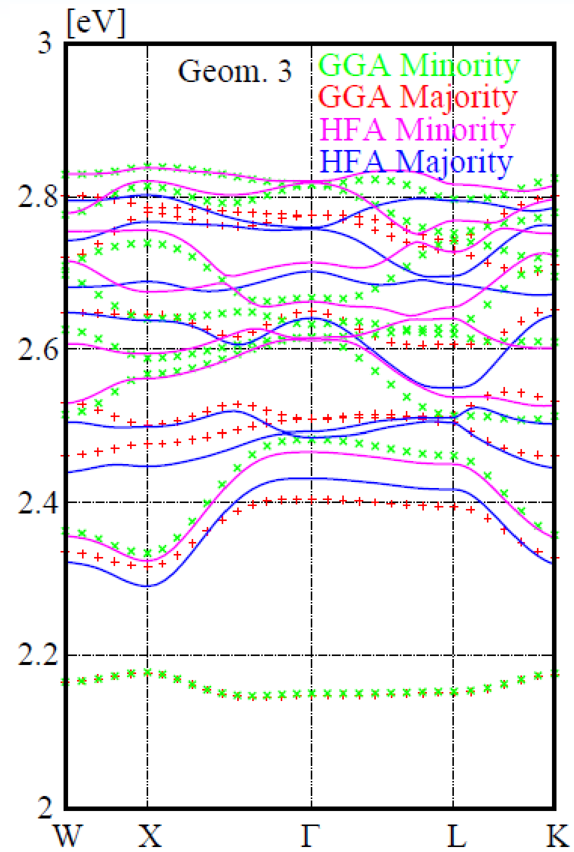



R.Arita

# Hartree-Fock calculation for the effective model



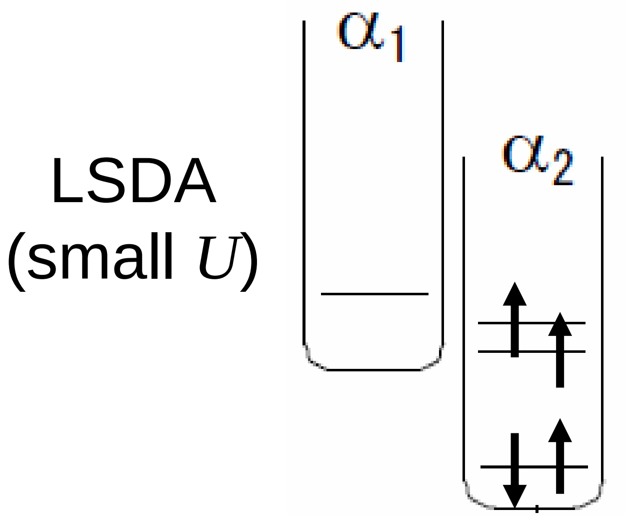



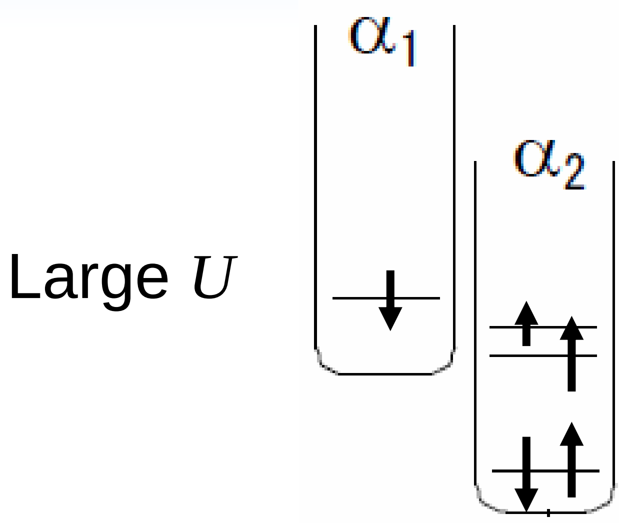




Multi-orbital Hubbard model for superatom *p* states describes the magnetism

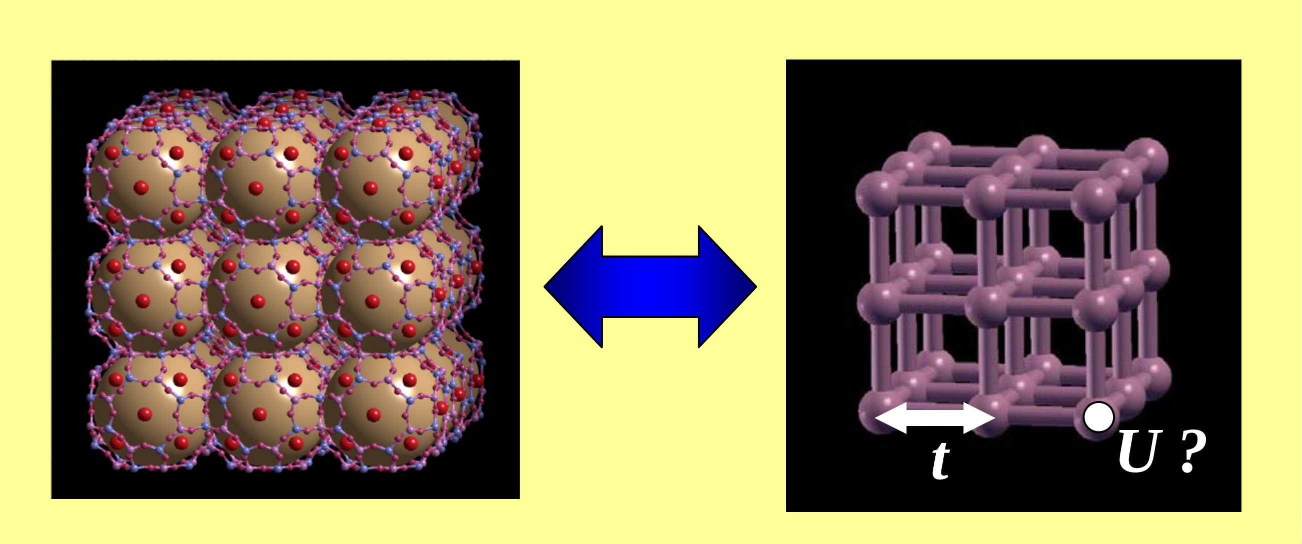
# How large is $U$ ?





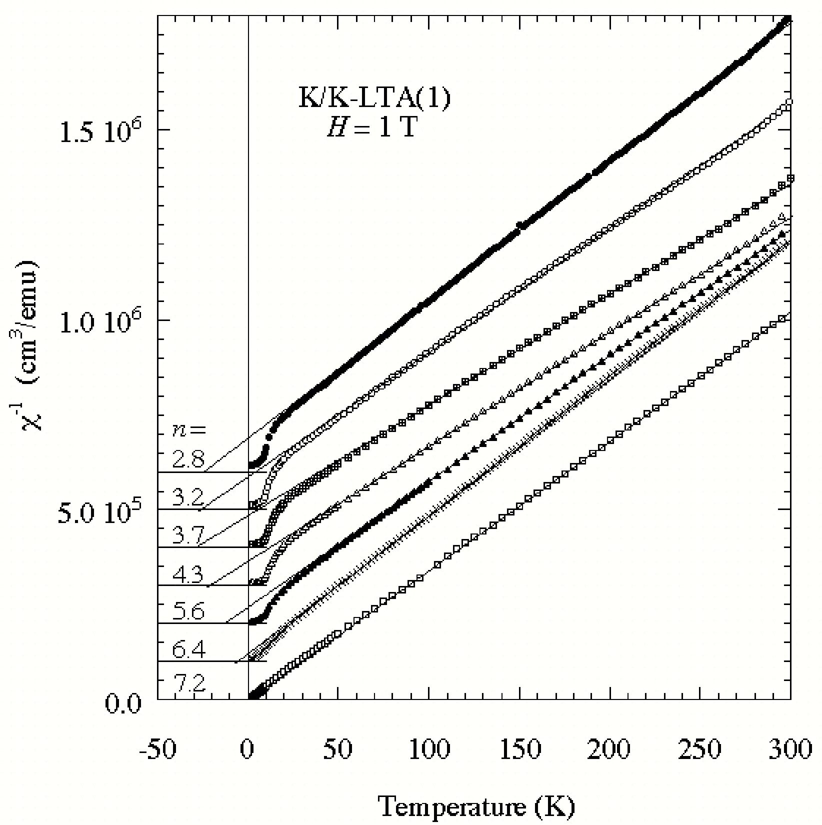

Ferrimagnetic GS



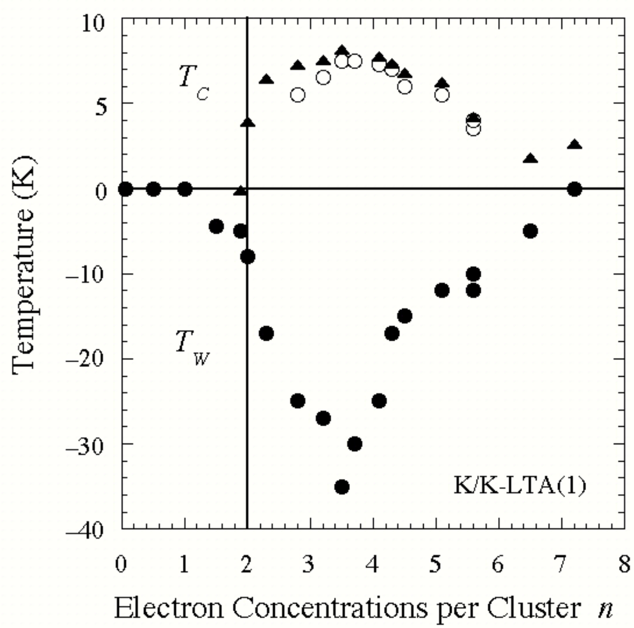
# K-loaded zeolite LTA (K$_n$+ $K_{12}Al_{12}Si_{12}O_{48}$)

Ground state = ferromagnetic

Nozue et al, PRL68 3789(1992)




Curie temperature &
Weiss temperature

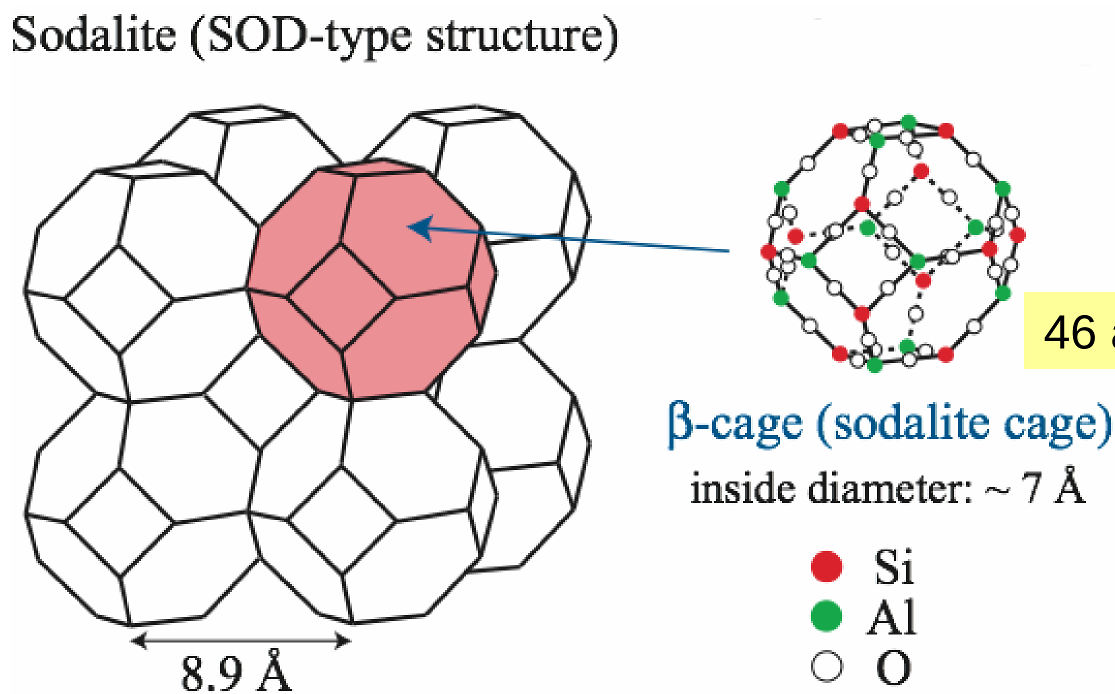



(Nozue *et al*, 1992,

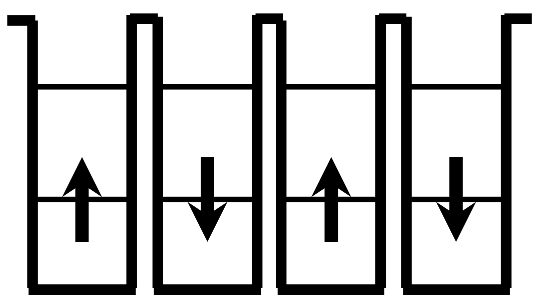
Nakano *et al*, 2002)

R.Arita

# Hydrogen superatom in zeolite



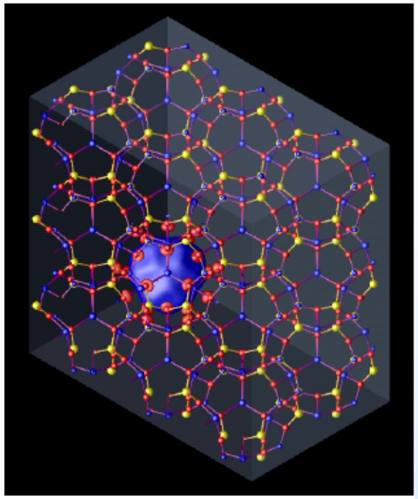

46 atoms / unit cell



1 electron in 1s state

*U* of 1s ?

# *Ab initio* estimate of Hubbard $U$ in zeolites

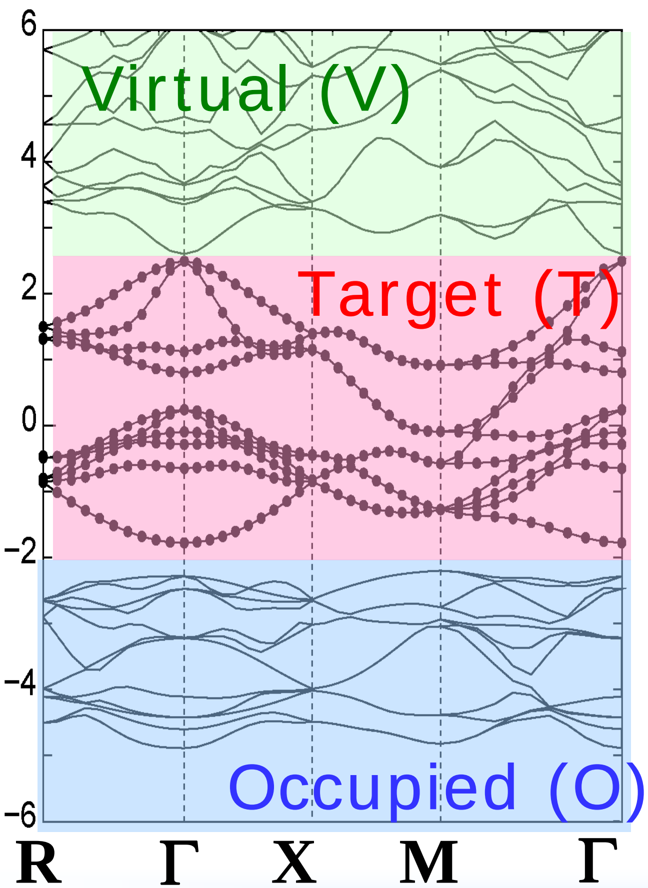


K. Nakamura, T. Koretsune & R. Arita
PRB 80 174420 (2009)

# Estimate of interaction parameters by constrained RPA

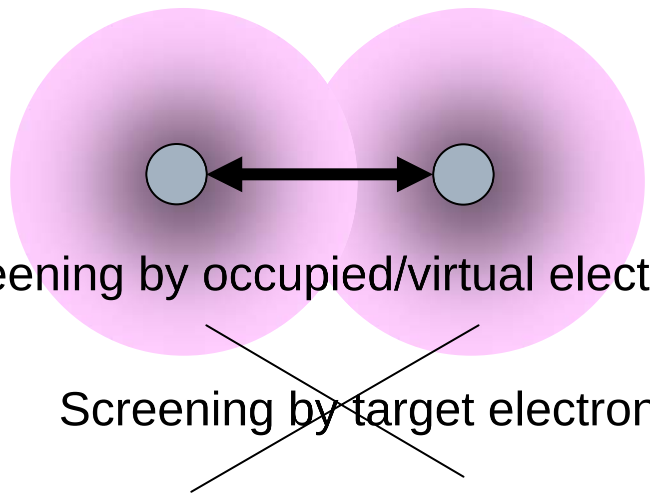
Aryasetiawan et al, PRB 70, 195104 (2004)
Solovyev-Imada, PRB 71, 045103 (2005)

$$W = (1 - v\chi)^{-1} v$$



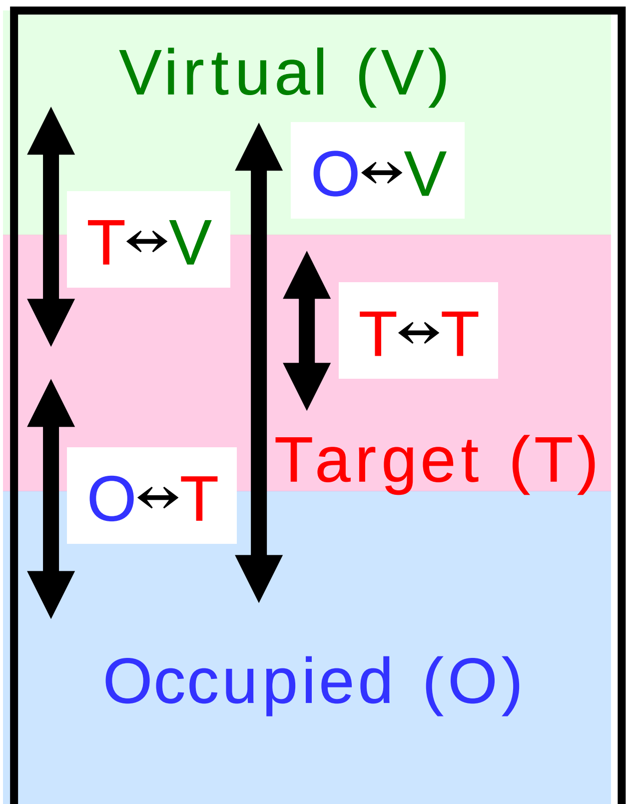

Full RPA polarizability:

$$\chi = \sum_i^{occ} \sum_j^{unocc} \frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega - \varepsilon_j + \varepsilon_i \pm i\delta}$$



# Estimate of interaction parameters by constrained RPA

$$W=(1-v\chi)^{-1}v$$




Full RPA polarizability:

$$\chi=\sum_i^{occ}\sum_j^{unocc}\frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega-\varepsilon_j+\varepsilon_i\pm i\delta}$$

$$\chi=\sum_{O\leftrightarrow T}+\sum_{T\leftrightarrow V}+\sum_{O\leftrightarrow V}+\sum_{T\leftrightarrow T}$$

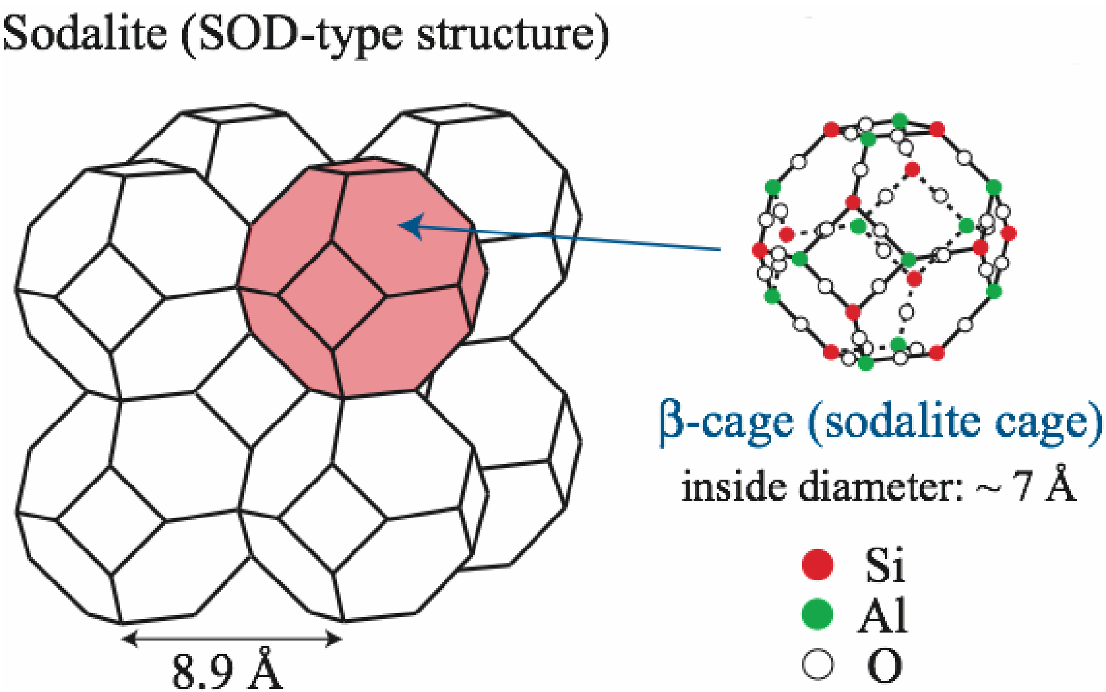
$$\chi_{\mathrm{r}}=\sum_{O\leftrightarrow T}+\sum_{T\leftrightarrow V}+\sum_{O\leftrightarrow V}\qquad \chi_{\mathrm{d}}=\sum_{T\leftrightarrow T}$$

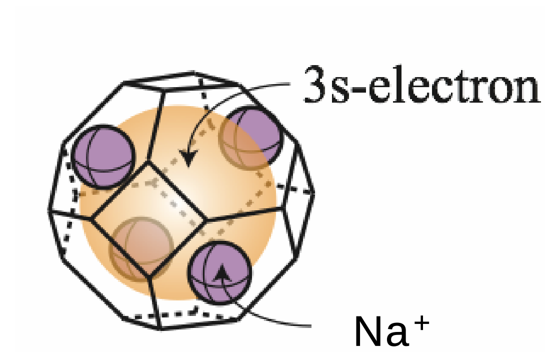
$$W_{eff}=(1-v\chi_{\mathrm{r}})^{-1}v$$

$$W=\frac{v}{1-v\chi}=\frac{W_{eff}}{1-W_{eff}\chi_d}$$

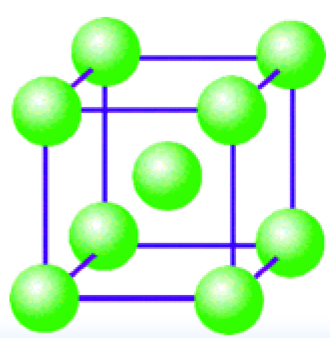
$$U_{\mathbf{R}}=\left\langle w_{\mu\mathbf{0}}w_{\mu\mathbf{0}}\middle|W_{eff}\middle|w_{\nu\mathbf{R}}w_{\nu\mathbf{R}}\right\rangle$$

# Sodalite



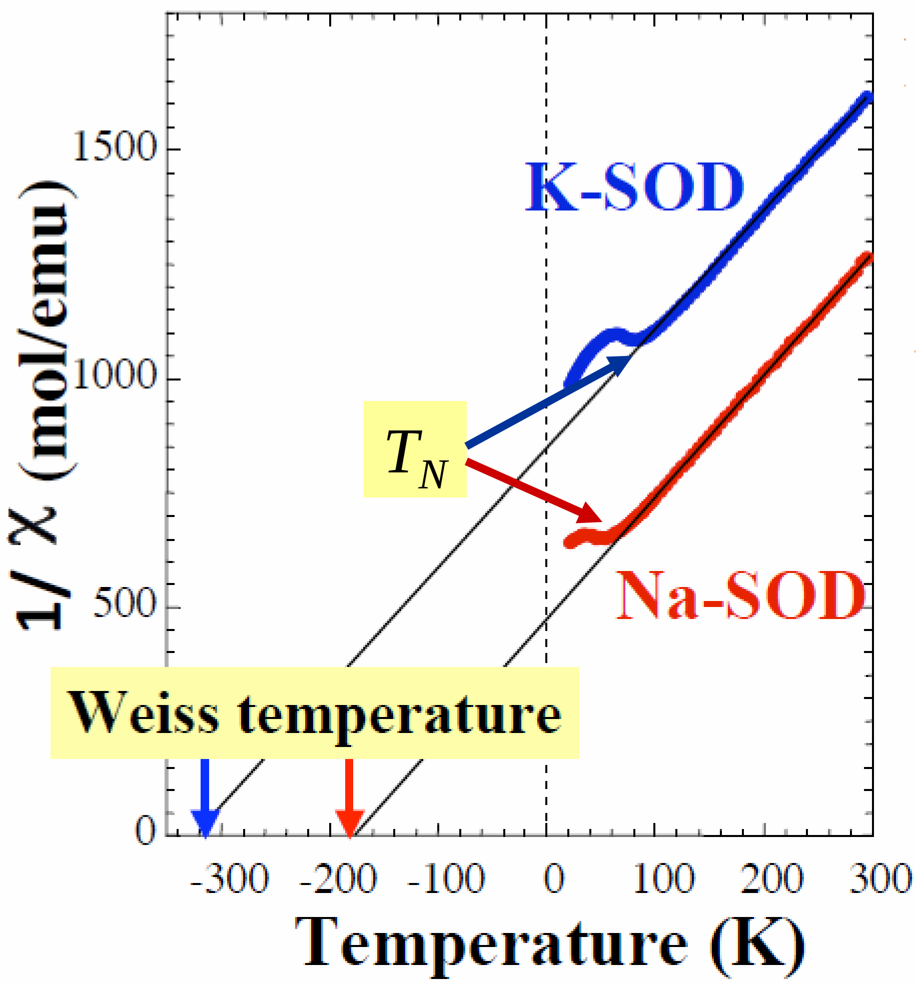




$Na^+$
$K^+$
$Rb^+$

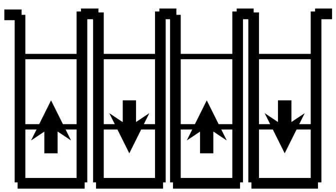


“BCC lattice” of β-cage

# Black sodalite: spin susceptibility




Nozue et al.



Slope of $1/\chi$ ➡ s = 1/2 spins in each cage

/$T_N$<1: frustrated $J_1$-$J_2$ Heisenberg model on BCC lattice

# High temperature expansion for $\chi$

S=1/2 Heisenberg model $\quad H=\sum_{\langle kl\rangle} J_{kl} S_k \cdot S_l = \sum_{\langle kl\rangle} h_{kl}$

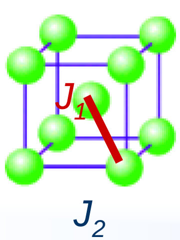
Power series expansion around $\beta=1/k_BT=0$

$$\langle S_i^z \cdot S_j^z \rangle = \frac{\mathrm{Tr}\, e^{-\beta H} S_i^z \cdot S_j^z}{\mathrm{Tr}\, e^{-\beta H}}$$

$$= \langle S_i^z \cdot S_j^z \rangle_c - \beta\left(\sum_{kl} \langle S_i^z \cdot S_j^z h_{kl} \rangle_c\right) + \frac{\beta^2}{2}\left(\sum_{klmn} \langle S_i^z \cdot S_j^z h_{kl} h_{mn} \rangle_c\right) + \cdots$$

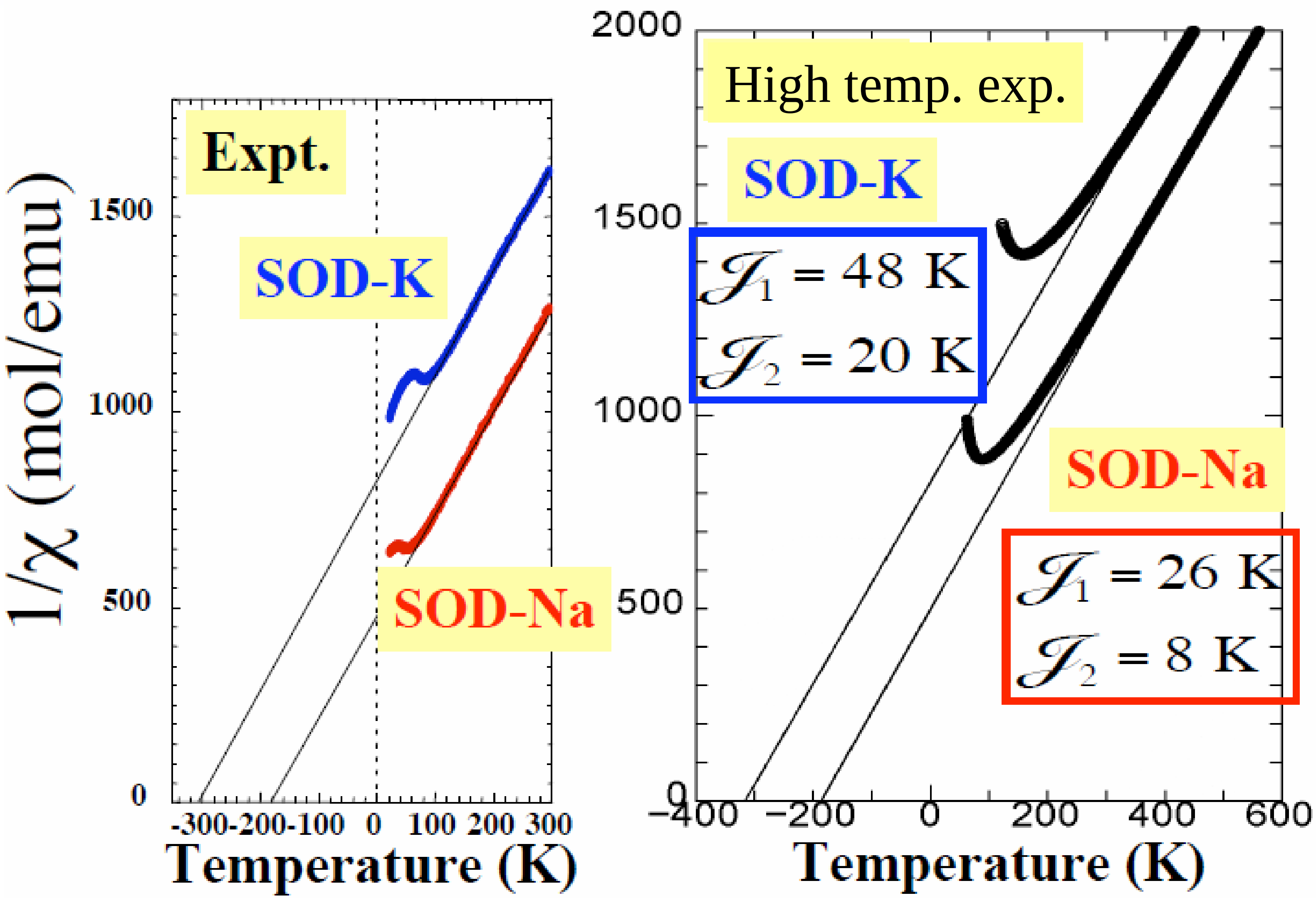
- Computer-aided analytical method
- Calculation for thermodynamic limit (Free from finite-size effect)

<u>For frustrated BCC lattice:</u>




$$\chi = \frac{N(g\mu_B)^2\beta}{4}(1+(4J_1+3J_2)\beta+(12J_1^2+24J_1J_2+6J_2^2)\beta^2+$$
$$\left(\frac{104}{3}J_1^3+105J_1^2J_2+84J_1J_2^2+11J_2^3\right)\beta^4\cdots)$$

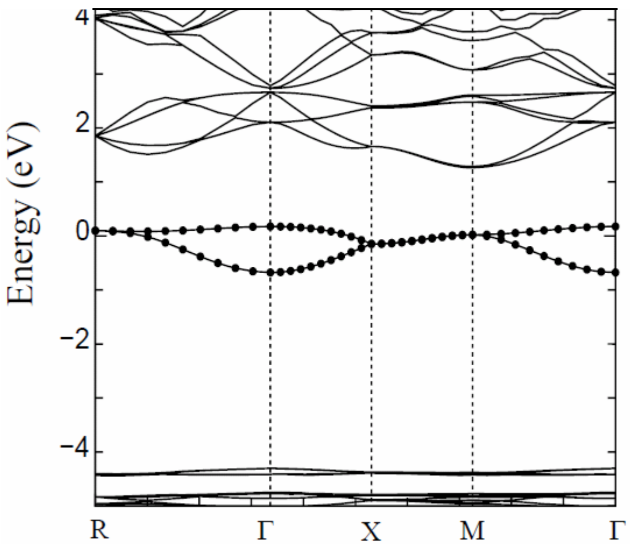
# Estimate of $J_{exp}$

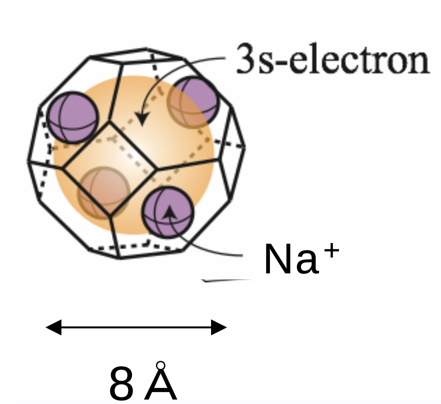



**Comparison between $J_{exp}$ and $J_{theory}$**

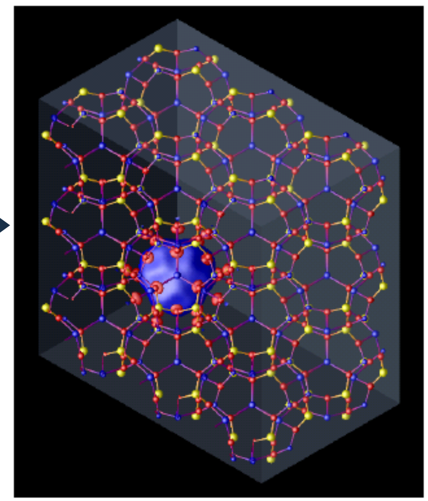
# Procedure of downfolding

LDA




Maximally localized Wannier functions



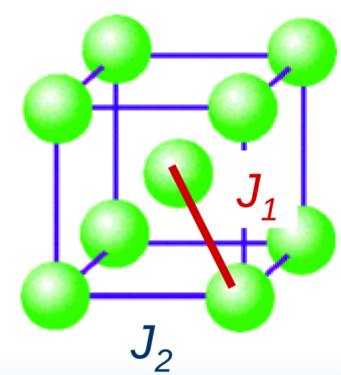
cRPA

Estimate of int. parameters by cRPA

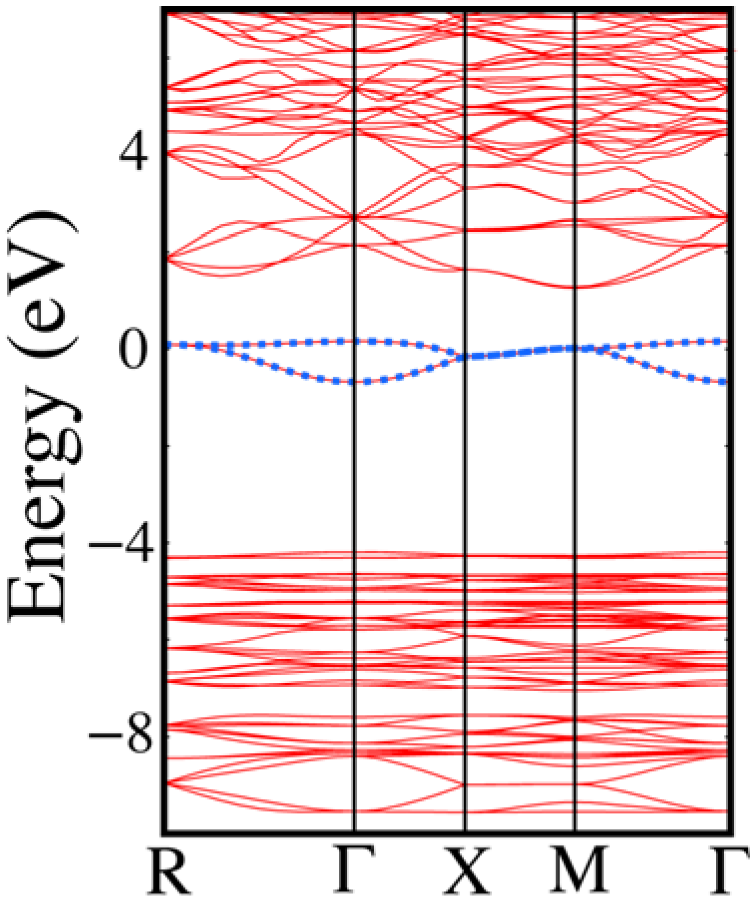
Extended Hubbard model

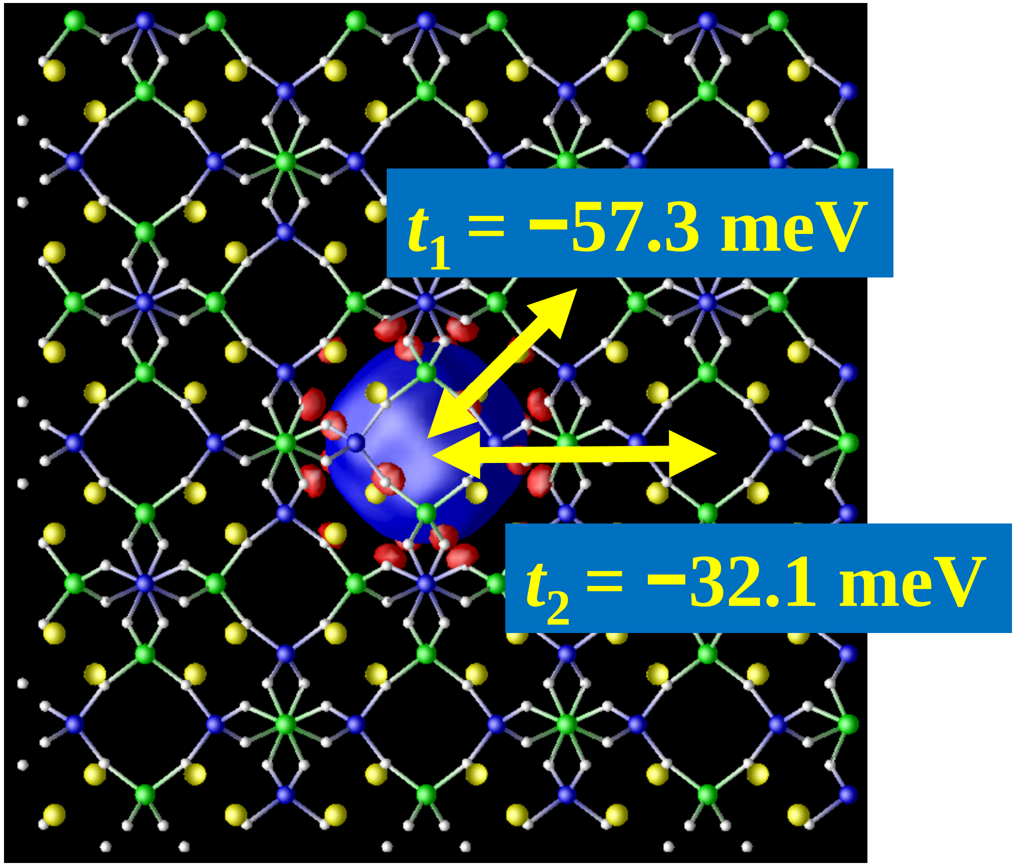
$$\mathscr{H} = \sum_{ij\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \frac{1}{2}\sum_{ij\sigma\tau} V_{ij} c^{\dagger}_{i\sigma} c^{\dagger}_{j\tau} c_{j\tau} c_{i\sigma} + \frac{1}{2}\sum_{ij\sigma\tau} J_{ij} c^{\dagger}_{i\sigma} c^{\dagger}_{j\tau} c_{i\tau} c_{j\sigma}$$

Heisenberg model



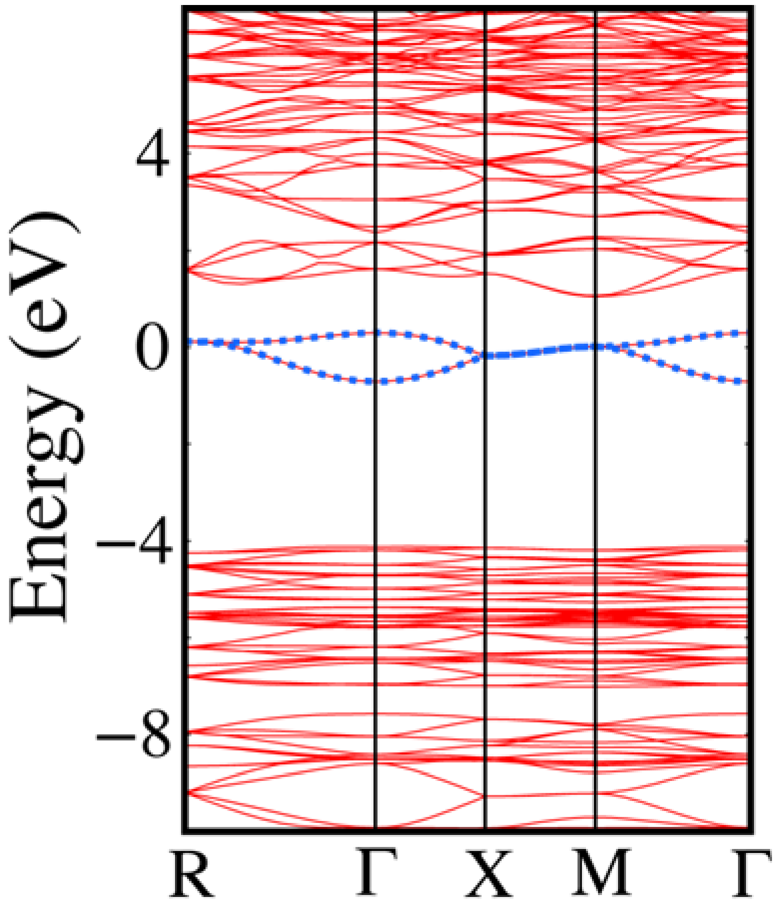
# Downfolding (1) MaxLoc of Na-SOD

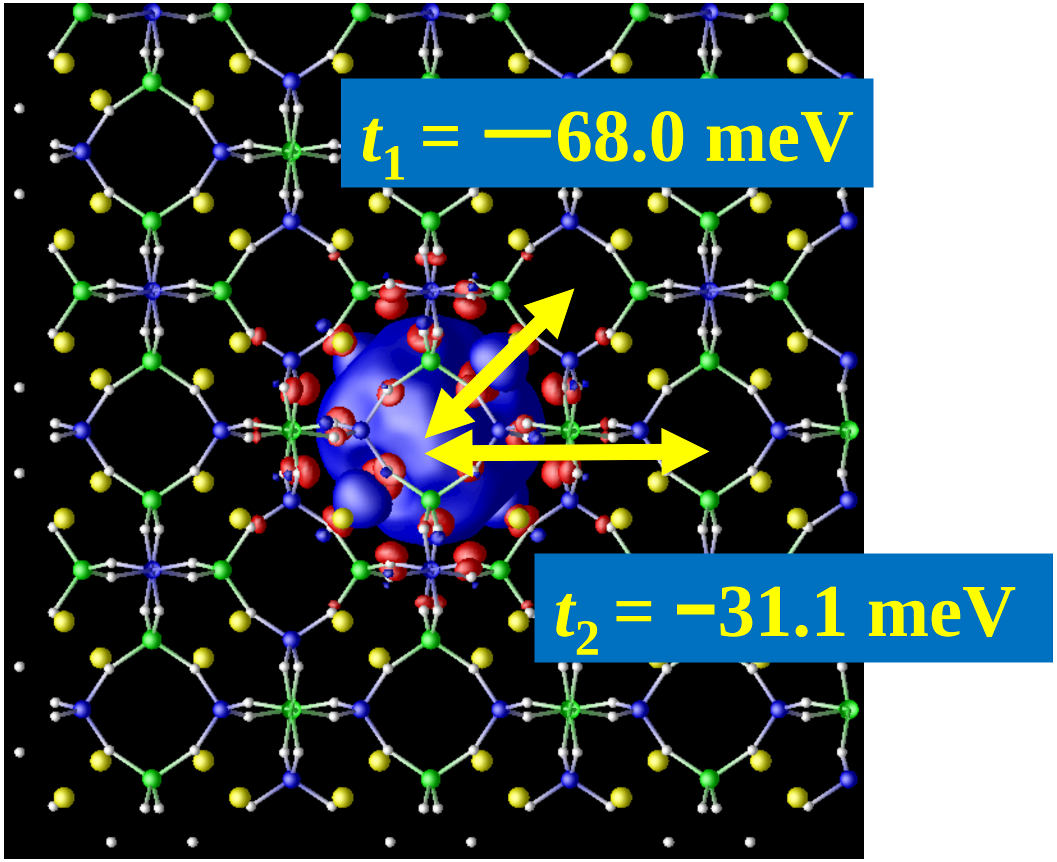



Superatom s state

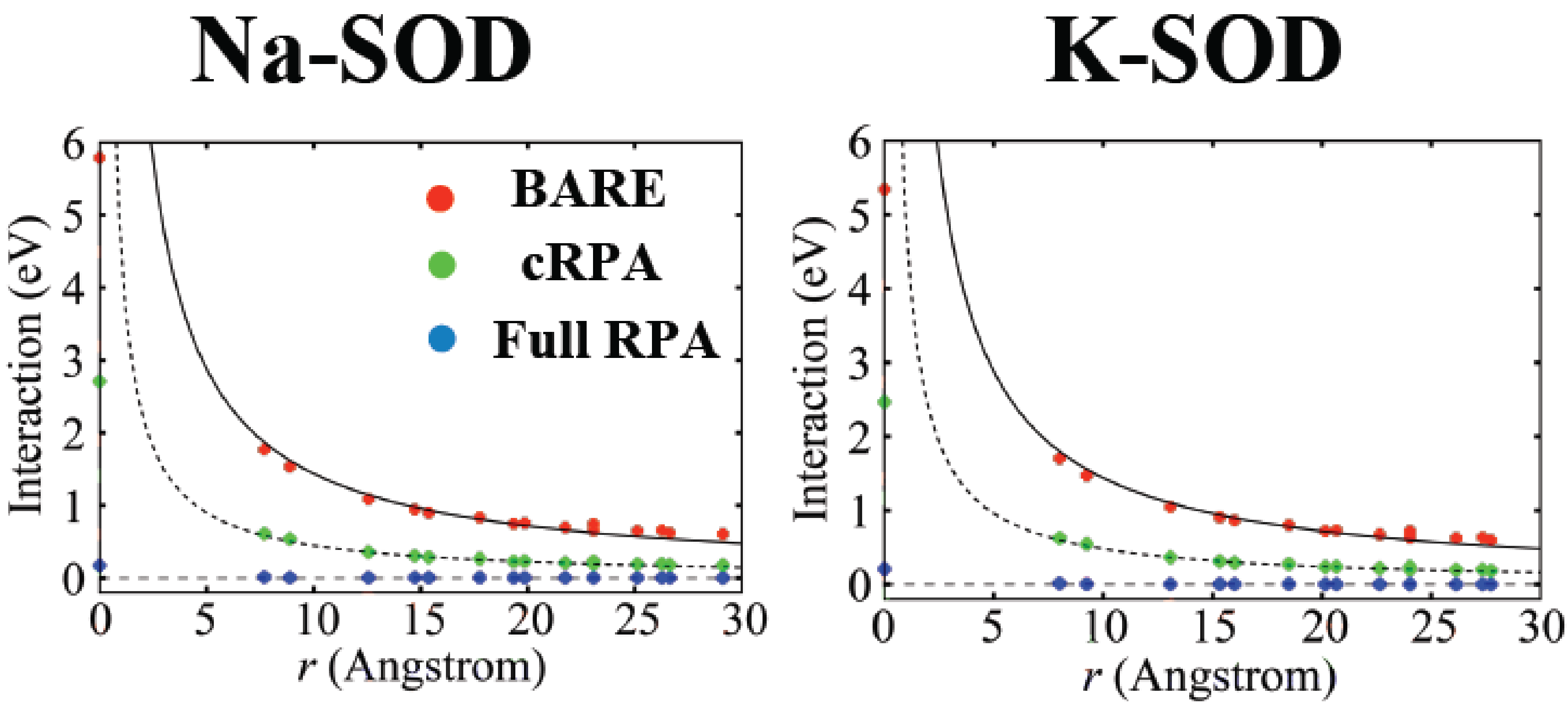
# Downfolding (1) MaxLoc of K-SOD




Superatom s state

# Downfolding (2): cRPA

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# Downfolding (2): cRPA

| | sodium electrosodalite | | | potassium electrosodalite | | |
|---|---|---|---|---|---|---|
| | bare | cRPA | RPA | bare | cRPA | RPA |
| $U$ | 5.79 | 2.71 | 0.17 | 5.34 | 2.47 | 0.21 |
| $V_1$ | 1.77 | 0.61 | 0.01 | 1.70 | 0.63 | 0.01 |
| $V_2$ | 1.54 | 0.54 | 0.00 | 1.47 | 0.54 | 0.00 |
| $J_1$ | 56.9 | 27.0 | 22.4 | 97.2 | 44.5 | 34.8 |
| $J_2$ | 22.4 | 10.6 | 8.8 | 20.9 | 9.9 | 8.3 |
| $K_1$ | 18.9 | 36.3 | 476.1 | 29.4 | 58.2 | 535.6 |
| $K_2$ | 5.6 | 11.0 | 143.7 | 5.8 | 11.7 | 109.2 |

**Unit: eV** ($U$, $V_1$, $V_2$)

**Unit: K** ($J_1$, $J_2$, $K_1$, $K_2$)

$$K_{ij} = \frac{2t_{ij}^2}{U - V_{ij}}$$

# Comparison with experiments

$$\mathscr{H}_{ex} = \sum_{\langle NN \rangle} \mathscr{J}_1 \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \sum_{\langle NNN \rangle} \mathscr{J}_2 \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

$$\mathscr{J}_{ij} = K_{ij} - J_{ij}$$

$$K_{ij} = \frac{2t_{ij}^2}{U - V_{ij}}$$

$\mathcal{J}_1$ $\mathcal{J}_2$ : Result of subtle balance between J & K

Unit: $K$

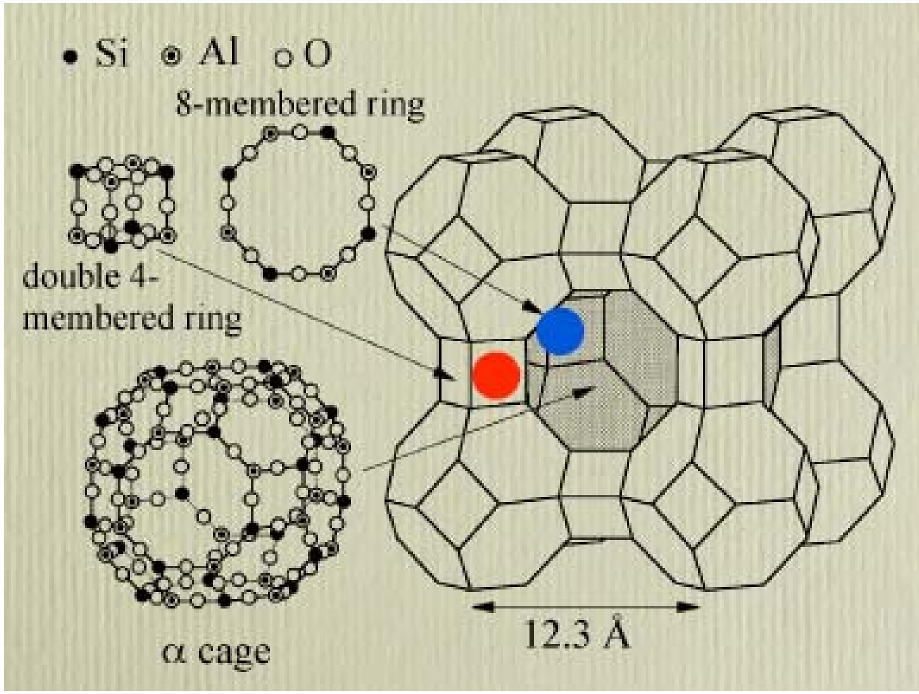
| | sodium electrosodalite | | | | potassium electrosodalite | | | |
|---|---|---|---|---|---|---|---|---|
| | bare | cRPA | RPA | Expt. | bare | cRPA | RPA | Expt. |
| $\mathcal{J}_1$ | −37.9 | 9.3 | 453.7 | 26 | −67.8 | 13.8 | 500.8 | 48 |
| $\mathcal{J}_2$ | −16.8 | 0.4 | 134.9 | 8 | −15.1 | 1.8 | 100.9 | 20 |

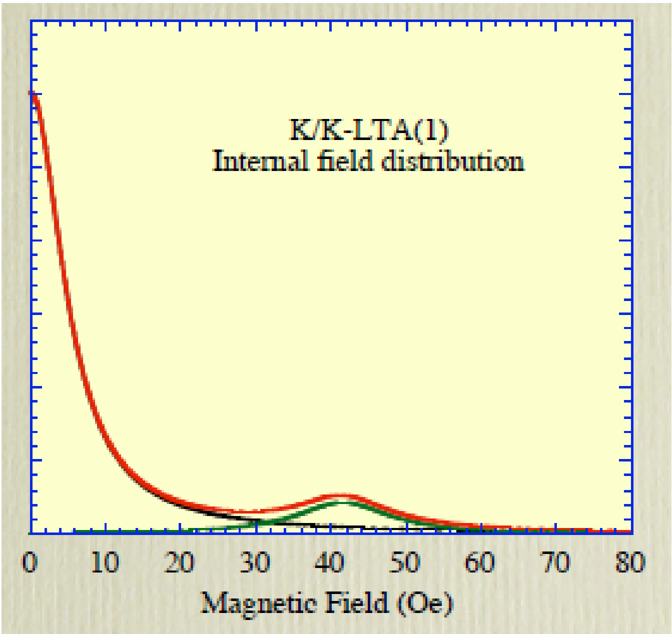
# Summary

- Ferromagnetism in zeolite LTA
  - Magnetism described by “superatom” picture

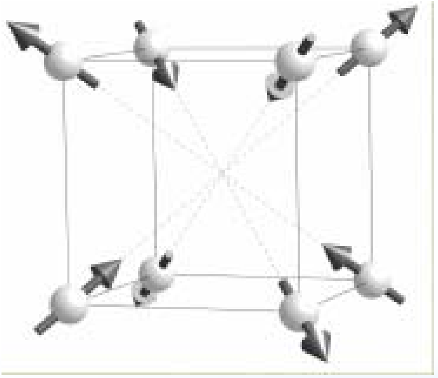
- *ab initio* derivation of low-energy model
  - Estimate of interaction parameters by cRPA
  - First step to “taylor-made correlation”

# Future problem: relativistic effect in zeolite




Nozue et al.

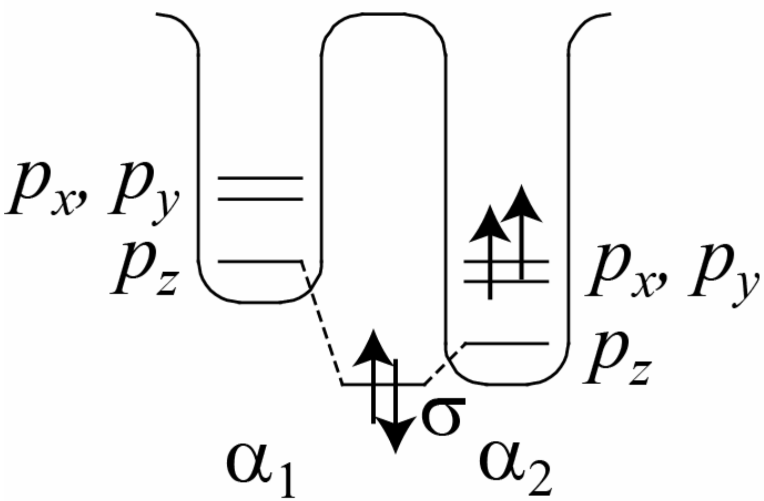


Canted AF due to the Dzyaloshinskii-Moriya int. ?

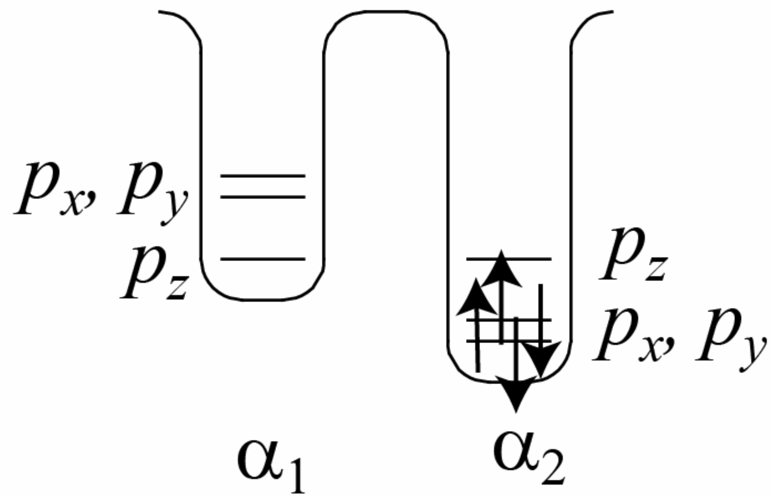
Large LS coupling ?

Relativistic effect in materials of light elements

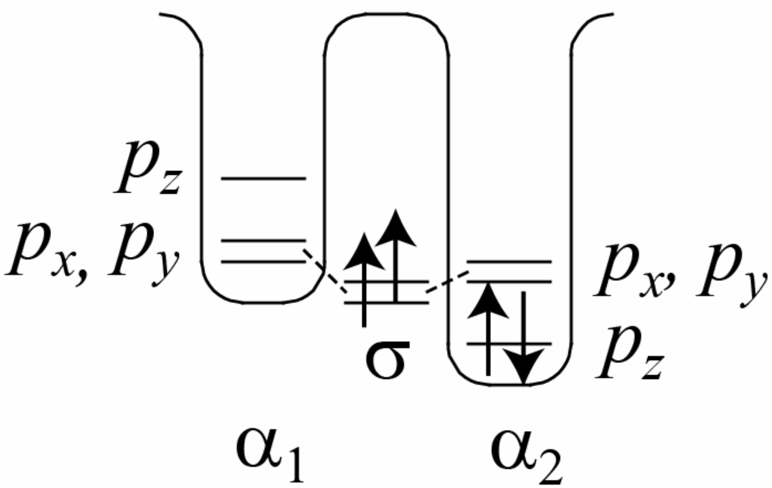
## Geometry I



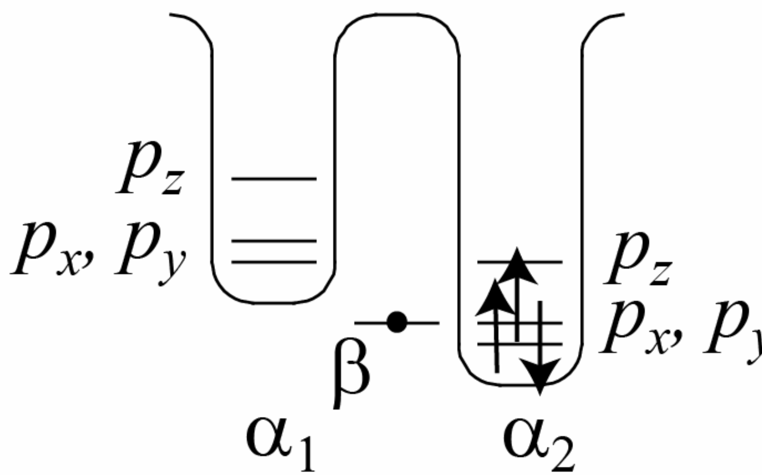

## Geometry II



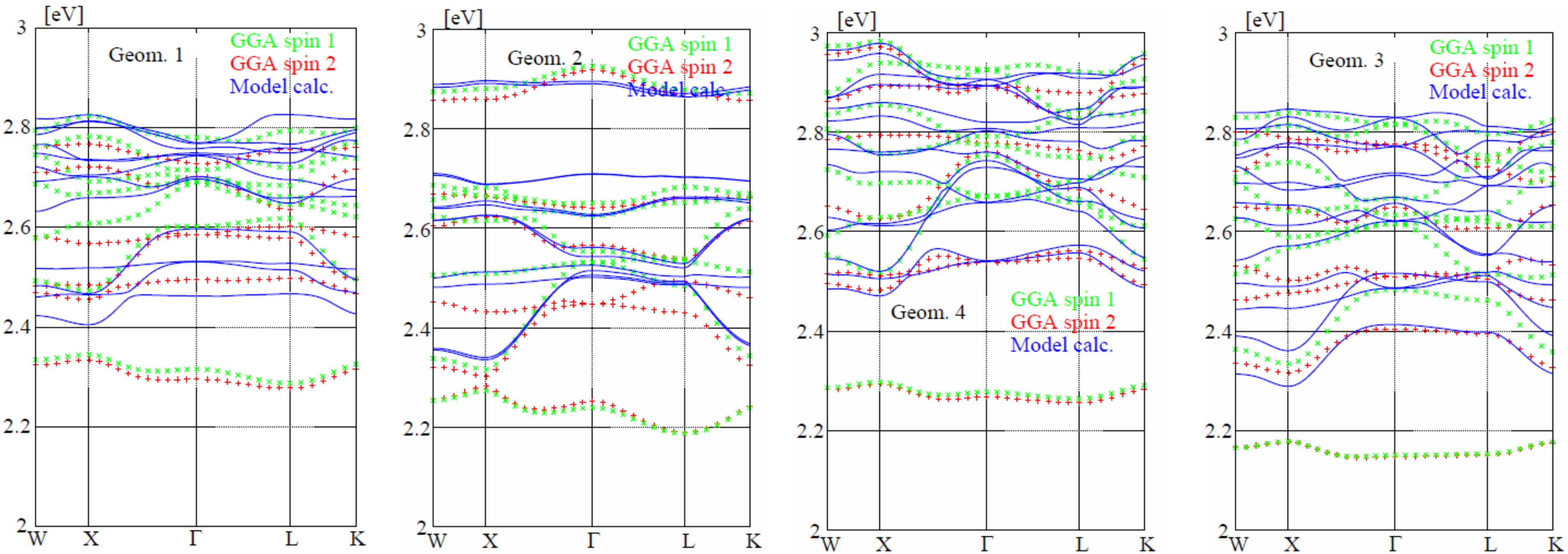

## Geometry III




## Geometry IV

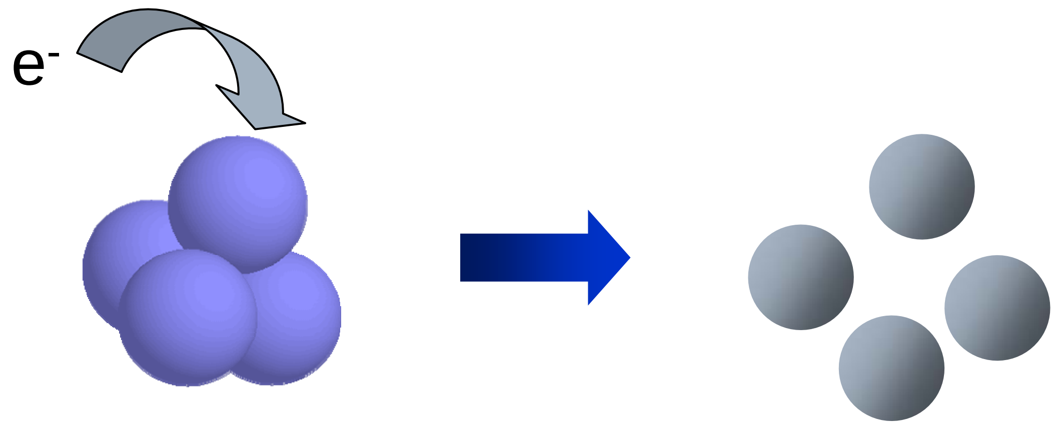


# Mean Field calculation for the effective model



# Attractive interaction due to ele-phonon coupling

Onsite Coulomb is overestimated ?




$U_{\mathrm{eff}}$ = *U-S (S: attractive int. due to ele-ph)*

*S* can be as large as *0.2~0.4 eV*
$\rightarrow J_1$ can be ~ *20 K*