Calculations of Hyperfine parameters in solids based on DFT and using WIEN2k

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Hyperfine parameters:

- Isomer shift: $\delta = \alpha \, (\rho_0^{Sample} - \rho_0^{Reference})$;
  - *it is proportional to the electron density ρ_0 at the nucleus*
  - *the constant α is proportional to the change of nuclear radii during the transition (we use $\alpha = -.291 \, au^3 mm \, s^{-1}$)*

- Magnetic Hyperfine fields: $B_{tot} = B_{contact} + B_{orb} + B_{dip}$
  - *these fields are proportional to the spin-density at the nucleus and the orbital moment of the probed atom as well as the spin moment distribution in the crystal*

- **Quadrupole splitting**: $\Delta \sim e \, Q \, V_{zz}$
  - *given by the product of the nuclear quadrupole moment Q times the electric field gradient V_{zz}. The EFG is proportional to an integral over the non-spherical charge density (weighted by $1/r^3$)*

Schrödinger equation

- From the previous slide it is obvious, that we need an accurate knowledge of the electron (and magnetization) density, which in principle can be obtained from the solution of the many-body Schrödinger equation for the corresponding solid.

$$H \, \Psi = E \, \Psi$$

- However, a many-body problem with $\sim 10^{23}$ particles is not solvable at all and we must create models for the real material and rely on an approximate solution of the Schrödinger equation. (This will be briefly discussed in the next slides and my preferred options are marked in red.)

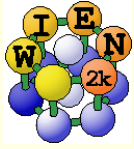$$\left[-\frac{1}{2}\nabla^2 + V(r) \right]\varphi_i^k = \varepsilon_i^k \varphi_i^k$$

- **Representation of the solid:**
  - cluster model: approximate solid by a finite cluster
  - periodic model: approximate "real" solid by infinite ideal solid (supercells !)

BaSnO$_3$
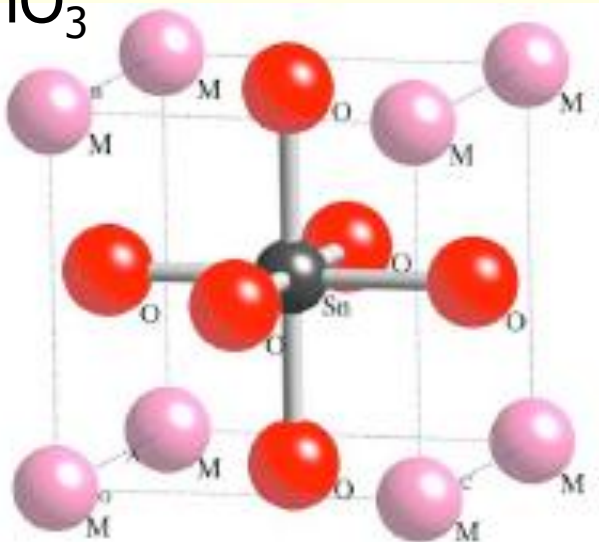
If calculations disagree with experiment:
the **structural model** could be wrong

$$\left[-\frac{1}{2} \nabla^2 + V(r) \right] \varphi_i^k = \varepsilon_i^k \varphi_i^k$$

- **Exchange and correlation:**
  - Hartree-Fock (exact exchange, no correlation)
    - correlation: MP2, CC, ...
  - Density functional theory: **approximate** exchange + correlation
    - LDA: local density approximation, "free electron gas"
    - GGA: generalized gradient approximation, various functionals
    - hybrid-DFT: mixing of HF + GGA, various functionals
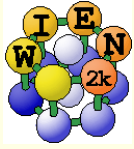   - LDA+U, DMFT: explicit (heuristic) inclusion of correlations

If calculations disagree with experiment:
the **DFT approximation** could be too crude

$$\left[-\frac{1}{2}\nabla^2 + V(r) \right] \varphi_i^k = \varepsilon_i^k \varphi_i^k$$

- **basis set for wavefunctions:**
  - "quantum chemistry": LCAO methods
    - Gauss functions (large "experience", wrong asymptotics, ...)
    - Slater orbitals (correct r~0 and r~∞ asymptotics, expensive)
    - numerical atomic orbitals
  - "physics": plane wave based methods
    - plane waves (+ pseudopotential approximation)
    - augmented plane wave methods (APW)
      - combination of PW (unbiased+flexible in interstitial regions)
   - + numerical basis functions (accurate in atomic regions, cusp)

$$\left[-\frac{1}{2}\nabla^2 + V(r) \right]\varphi_i^k = \varepsilon_i^k \varphi_i^k$$
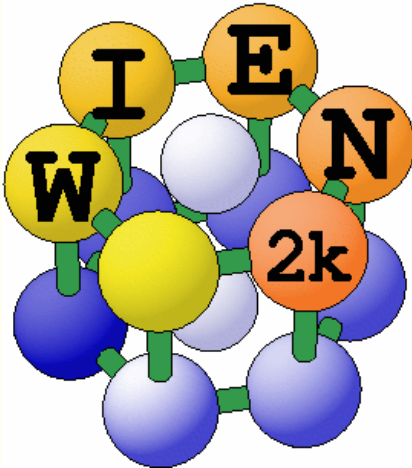
- **Computational approximations:**
  - relativistic treatment:
    - non-, scalar-, fully-relativistic treatment
  - treatment of spin, magnetic order
  - approximations to the form of the potential
    - shape approximations (ASA)
    - pseudopotential (nodeless valence orbitals)
    - "full potential"
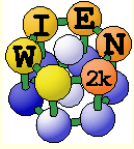
• in many cases, the experimental knowledge about a certain system is very limited and also the exact atomic positions may not be known accurately (powder samples, impurities, surfaces, ...)

• Thus we need a theoretical method which can not only calculate HFF-parameters, but can also model the system:

- total energies + forces on the atoms:
    - perform structure optimization for "real" systems
    - calculate phonons (+ partial phonon-DOS)
    - investigate various magnetic structures, exchange interactions
- electronic structure:
    - bandstructure + DOS
    - compare with ARPES, XANES, XES, EELS, ...
- hyperfine parameters
    - isomer shifts, hyperfine fields, electric field gradients
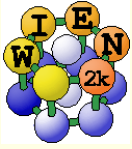
WIEN2k software package

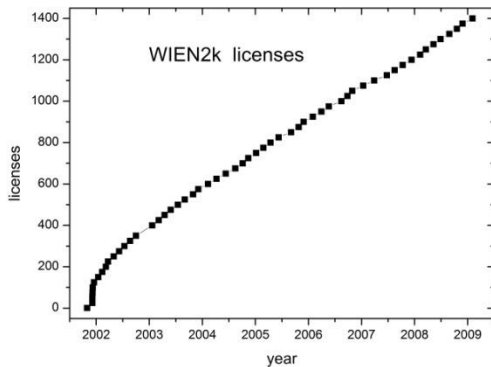WIEN2k: ~1700 groups
mailinglist: 1800 users

**An Augmented Plane Wave Plus Local Orbital
Program for Calculating Crystal Properties**

**Peter Blaha
Karlheinz Schwarz
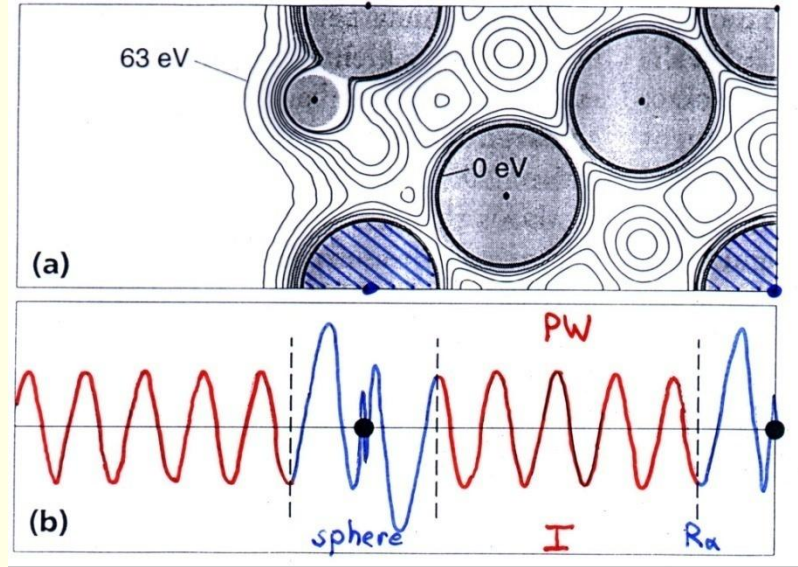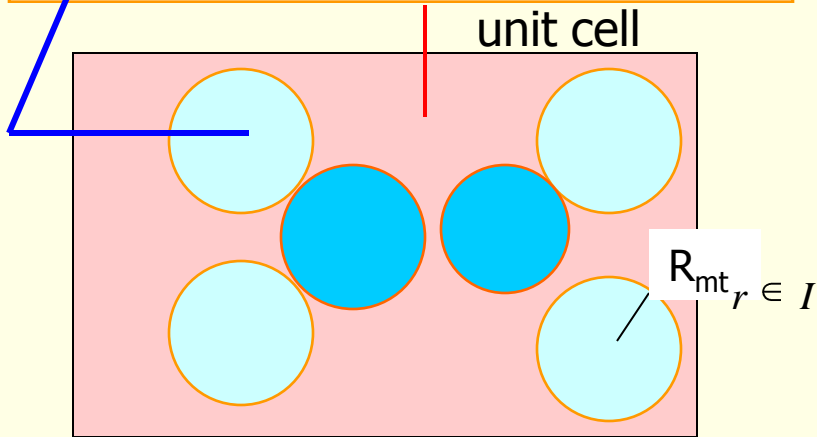Georg Madsen
Dieter Kvasnicka
Joachim Luitz**

November 2001
Vienna, AUSTRIA
Vienna University of Technology

http://www.wien2k.at

APW Augmented Plane Wave method

The unit cell is partitioned into:
   atomic spheres
   Interstitial region

unit cell

R_{mt} $r \in I$

63 eV

0 eV

(a)

(b)   PW

sphere   I R_a
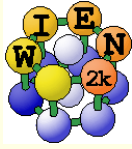
Basisset:

PW: $e^{i(\vec{k}+\vec{K}).\vec{r}}$

Atomic partial waves

$$\sum_{\ell m} A_{\ell m}^{K} u_{\ell}(r', \varepsilon) Y_{\ell m}(\hat{r}')$$

join

$u_l(r,\varepsilon)$ are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy ε

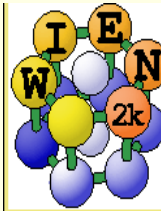A_{lm}^{K} coefficients for matching the PW

"Exact" solution for given (spherical) potential!

w2web GUI (graphical user interface)

- Structure generator
  - *spacegroup selection*
  - *import cif file*
- step by step initialization
  - *symmetry detection*
  - *automatic input generation*
- SCF calculations
  - *Magnetism (spin-polarization)*
  - *Spin-orbit coupling*
  - *Forces (automatic geometry optimization)*
- Guided Tasks
  - *Energy band structure*
  - *DOS*
  - *Electron density*
  - *X-ray spectra*
  - *Optics*

Session: **TiC**
/area51/pblaha/lapw/2005-june/TiC

StructGen™

You have to click "Save Structure" for changes to take effect!

[Save Structure]

Execution >>
StructGen™
initialize calc.
run SCF
single prog.
optimize(V,c/a)
mini. positions

Utils. >>

Tasks >>

Files >>
struct file(s)
input files
output files
SCF files

Session Mgmt. >>
change session
change dir
change info

Configuration

Usersguide
html-Version
pdf-Version

Idea and realization
by

Title: TiC
Lattice:
Type: F

P
F
B
CXY
CYZ
CXZ
R
H
1_P1

Spacegroups from
Bilbao Cryst Server

Lattice parameters in Å
a= 4.328000038 b= 4.328000038 c= 4.328000038
α= 90.000000 β= 90.000000 γ= 90.000000

Inequivalent Atoms: 2
Atom 1: Ti   Z= 22.0 RMT= 2.0000   remove atom

Pos 1: x= 0.00000000 y= 0.00000000 z= 0.00000000   remove
add position

Atom 2: C   Z= 6.0   RMT= 1.9000   remove atom

Pos 1: x= 0.50000000 y= 0.50000000 z= 0.50000000   remove
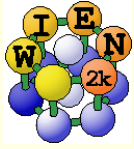add position

theoretical EFG calculations

- The coulomb potential V_c is a central quantity in any theoretical calculation (part of the Hamiltonian) and is obtained from all charges ρ (electronic + nuclear) in the system.

$$V_c(r) = \int \frac{\rho(r')}{r-r'} dr' = \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r})$$

- The EFG is a tensor of second derivatives of V_C at the nucleus:

$$V_{ij} = \frac{\partial^2 V(0)}{\partial x_i \partial x_j}; \qquad V_{zz} \propto \int \frac{\rho(r) Y_{20}}{r^3} dr$$

- Since we use an "all-electron" method, we have the full charge distribution of all electrons+nuclei and can obtain the EFG without further approximations

- The spherical harmonics Y_{20} projects out the **non-spherical** (and non-cubic) part of ρ. The EFG is proportional to the differences in orbital occupations (eg. p_z vs. p_x, p_y)

- We do not need any "Sternheimer factors"
  (these shielding effects are included in the self-consistent charge density)
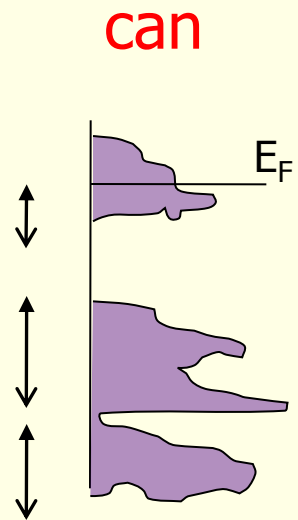
theoretical EFG calculations

- The charge density ρ in the integral $\quad V_{zz} \propto \int \dfrac{\rho(r)Y_{20}}{r^3}\, dr \quad$ can be decomposed in various ways for analysis:

  - *according to energy (into various valence or semi-core contributions)*

  - *according to angular momentum l and m (orbitals)*
  - *spatial decomposition into "atomic spheres" and the "rest" (interstital)*

- Due to the $1/r^3$ factor, contributions near the nucleus dominate.

E_F

theoretical EFG calculations

We write the charge density and the potential inside the atomic spheres in an lattice-harmonics expansion

$$\rho(r) = \sum_{LM} \rho_{LM}(\bar{r}) Y_{LM}(\hat{r}) \qquad V(r) = \sum_{LM} v_{LM}(\bar{r}) Y_{LM}(\hat{r})$$

spatial decomposit ion :

$$V_{zz} \propto \int \frac{\rho(r) Y_{20}}{r^3} d^3 r = \int_{sphere} \frac{\sum_{LM} \rho_{LM}(r) Y_{LM} Y_{20}}{r^3} d^3 r + \int_{int\ erstital} \frac{\rho(r) Y_{20}}{r^3} d^3 r$$

$$V_{zz} \propto = \int_{sphere} \frac{\rho_{20}(r)}{r^3} dr + interstiti\ al$$

orbital decomposit ion :

$$\rho_{20}(r) = \int \sum_{k,n.l,l',m,m'} \phi_{lm}^{nk\ *} \phi_{l'm'}^{nk} Y_{20}\ d\hat{r} \quad \Rightarrow \quad p-p; d-d;(s-d)\ contr.$$

$$V_{zz} = V_{zz}^{pp} + V_{zz}^{dd} + \ldots.. + interstiti\ al$$

theoretical EFG calculations

$$V_{zz} = V_{zz}^{pp} + V_{zz}^{dd} + ... + \textit{interstitial}$$

$$V_{zz}^{pp} \propto \left\langle \frac{1}{r^3} \right\rangle_p \left| \frac{1}{2}(p_x + p_y) - p_z \right|$$

$$V_{zz}^{dd} \propto \left\langle \frac{1}{r^3} \right\rangle_d \left| d_{xy} + d_{x^2-y^2} - \frac{1}{2}(d_{xz} + d_{yz}) - d_{z^2} \right|$$

- EFG is **proportial** to **differences of orbital occupations ,** e.g. between p_x, p_y and p_z.
- if these occupancies are the same by symmetry (cubic): **$V_{zz}=0$**
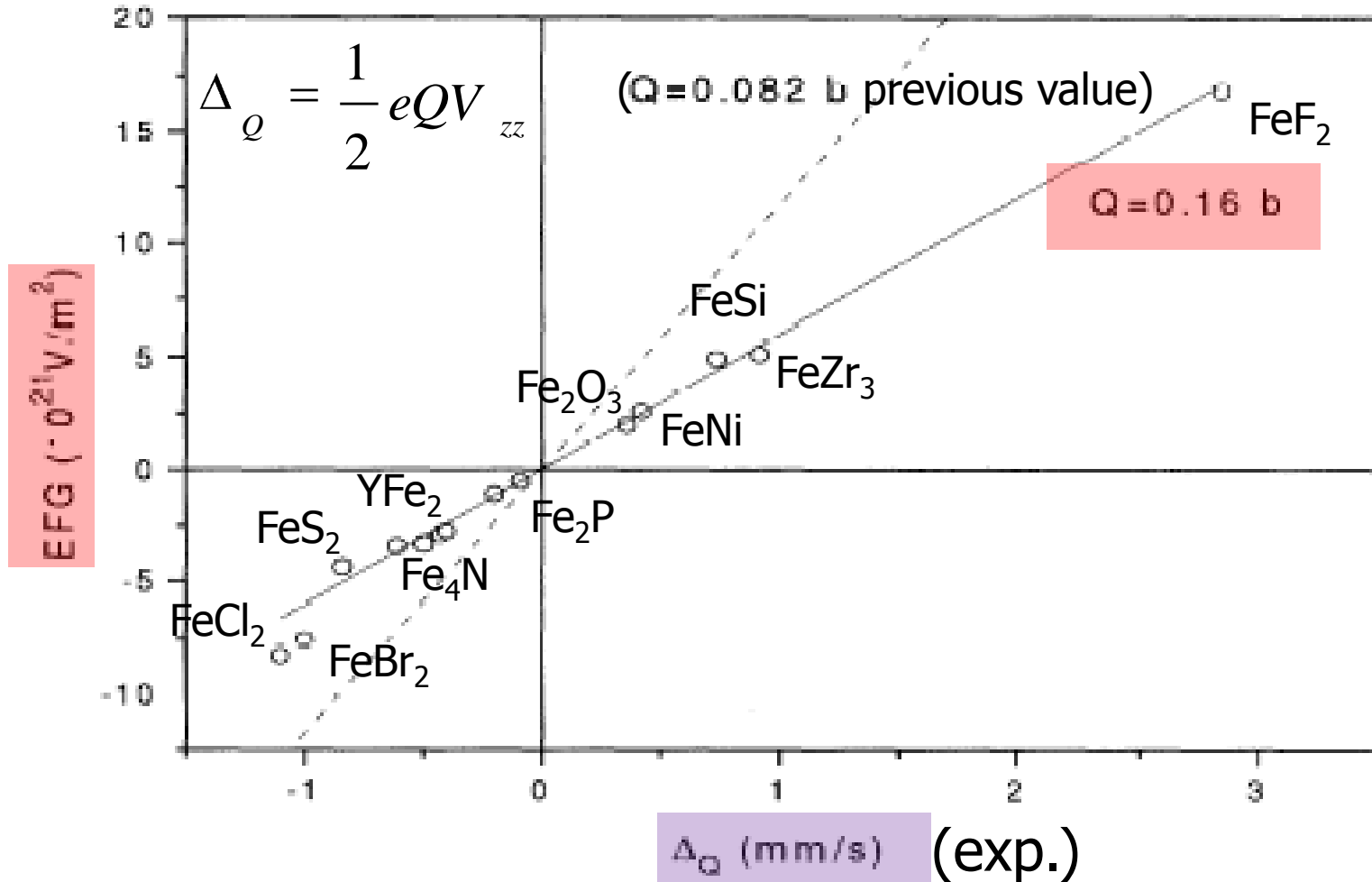- with "axial" (hexagonal, tetragonal) symmetry ($p_x=p_y$): η**=0**

In the following various examples will be presented.

Determination of the Nuclear Quadrupole Moment of ^{57}Fe
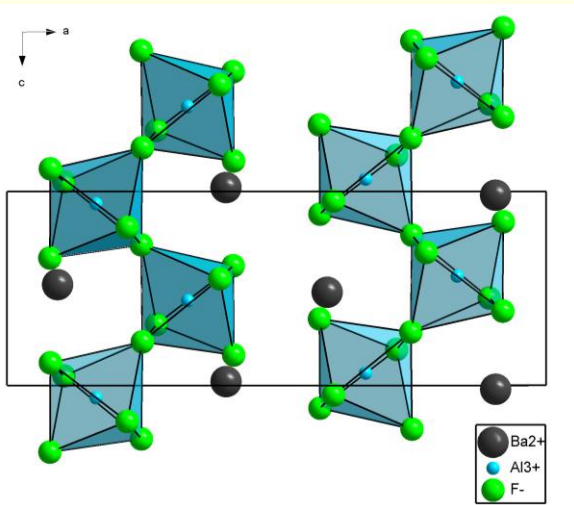
Philipp Dufek, Peter Blaha, and Karlheinz Schwarz

Compare theoretical and experimental EFGs ⟹ **Q**

$$\Delta_Q = \frac{1}{2} eQV_{zz}$$

(Q=0.082 b previous value)

FeF$_2$

Q=0.16 b

FeSi

FeZr$_3$

Fe$_2$O$_3$

FeNi

YFe$_2$

Fe$_2$P

FeS$_2$

Fe$_4$N

FeCl$_2$

FeBr$_2$

EFG ($\cdot 10^{21}$ V/m^2)

Δ_Q (mm/s) (exp.)

F - EFGs in fluoroaluminates

10 different phases of known structures from CaF_2-AlF_3, BaF_2-AlF_3 binary systems and CaF_2-BaF_2-AlF_3 ternary system

Isolated chains of octahedra linked by corners

Isolated octahedra

Rings formed by four octahedra sharing corners

α-BaAlF$_5$

α-CaAlF$_5$, β-CaAlF$_5$, β-BaAlF$_5$, γ-BaAlF$_5$
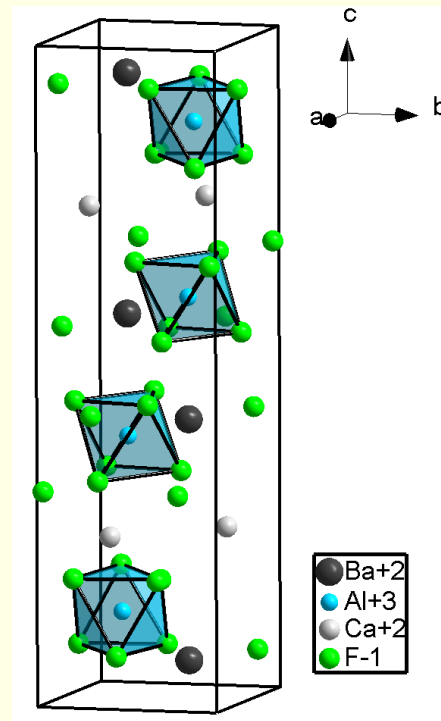
α-BaCaAlF$_7$

Ca$_2$AlF$_7$, Ba$_3$AlF$_9$-Ib, β-Ba$_3$AlF$_9$
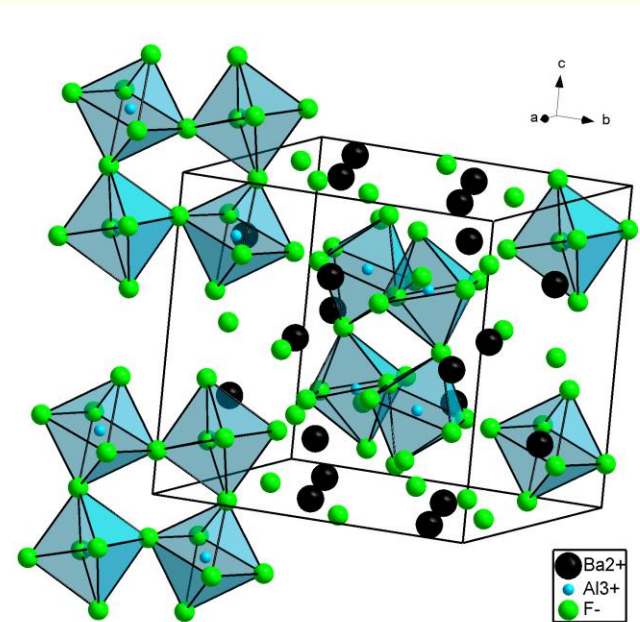
Ba$_3$Al$_2$F$_{12}$

ν_Q and η_Q calculations **using XRD data**

$\eta_{Q,exp} = 0,803\ \eta_{Q,cal}$
$R^2 = 0,38$

$\nu_Q = 4,712.10^{-16}\ |V_{zz}|$ with $R^2 = 0,77$
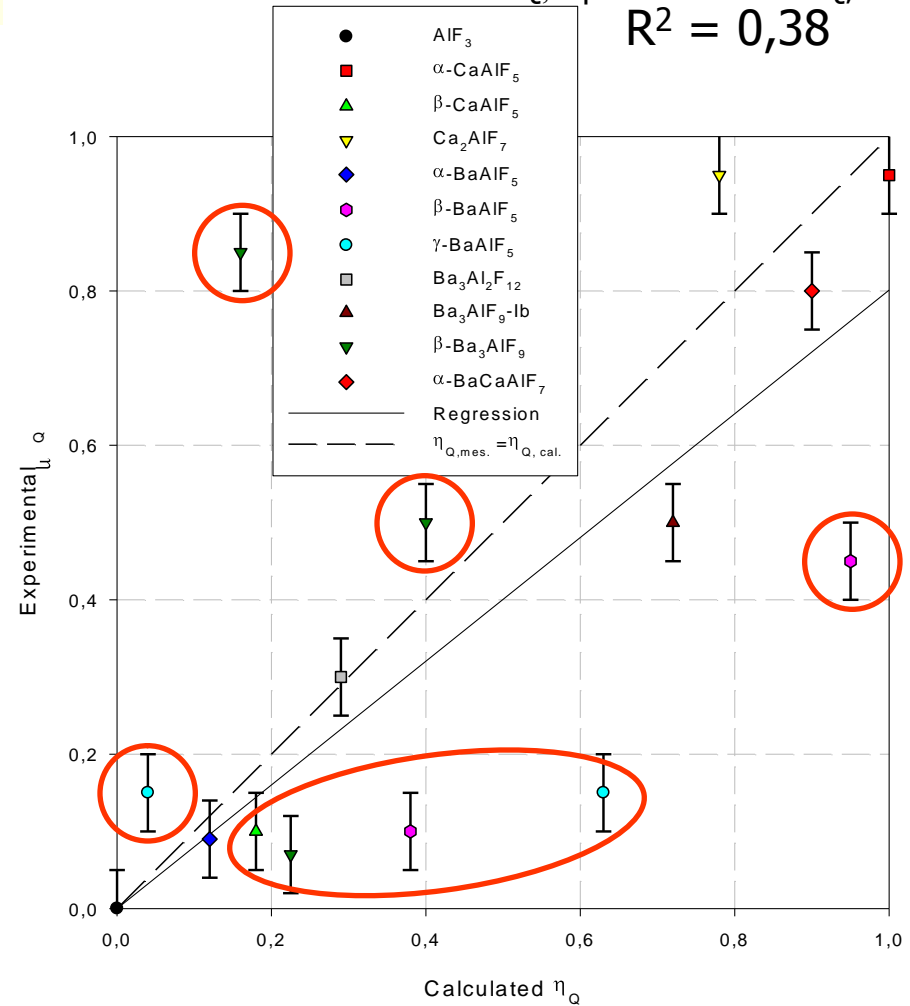
Important discrepancies when structures are used which were determined from X-ray powder diffraction data

$$\nu_Q = 5,85.10^{-16}\ V_{zz}$$
$$R^2 = 0,993$$

$$\eta_{Q,\ exp} = 0,972\ \eta_{Q,cal}$$
$$R^2 = 0,983$$
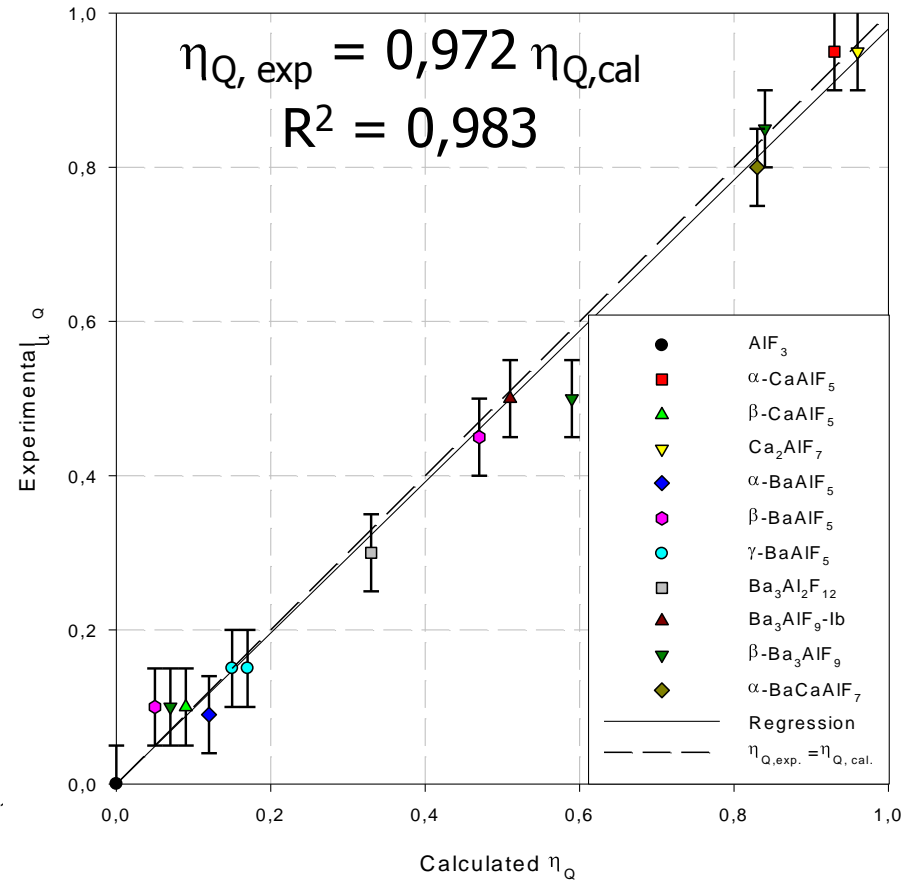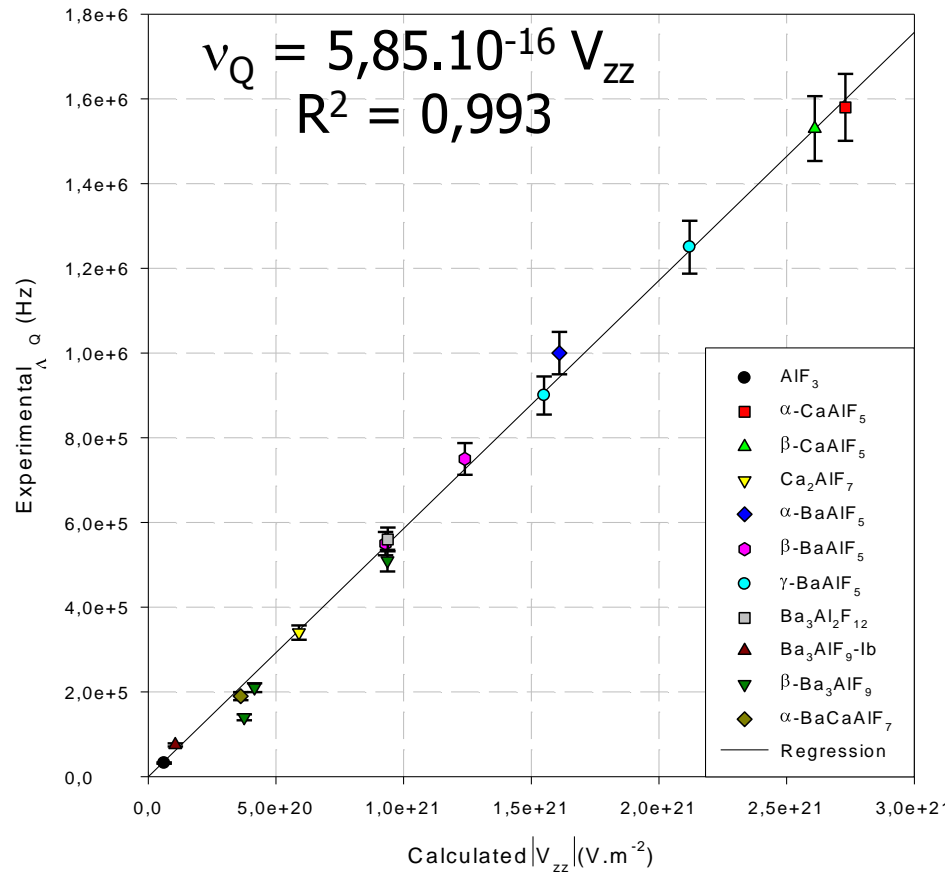
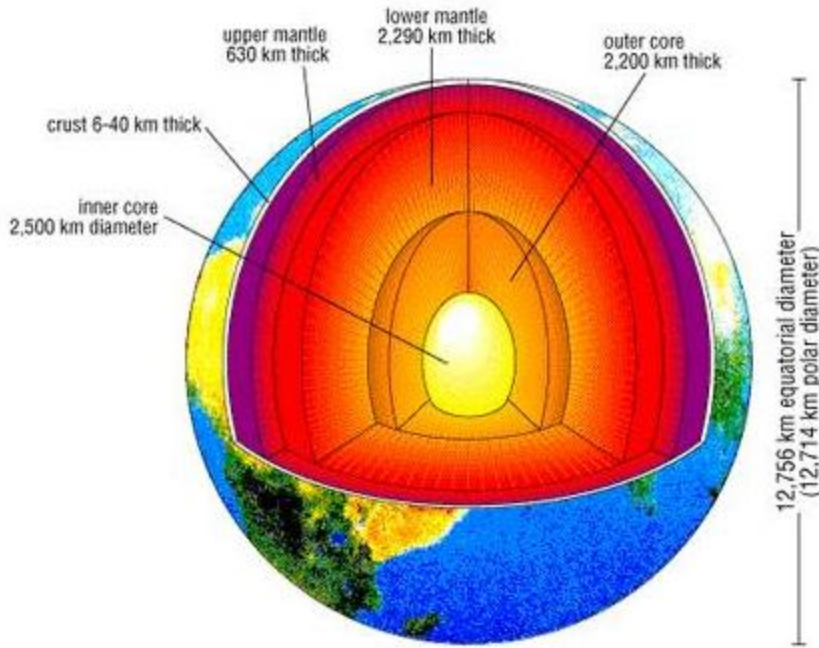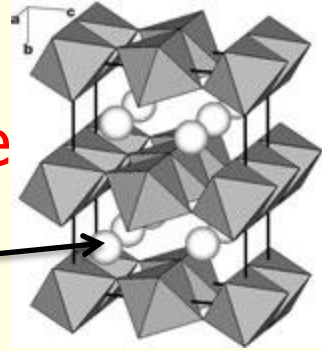Very fine agreement between experimental and calculated values

M.Body, et al., *J.Phys.Chem. A 2007, 111, 11873* (Univ. LeMans)

■ The earth lower mantle consists of (Mg,Fe)O and
$(Mg_{1-x}Fe_x)SiO_3$ perovskite

(Mg,Fe)

upper mantle 630 km thick
lower mantle 2,290 km thick
crust 6-40 km thick
outer core 2,200 km thick
inner core 2,500 km diameter
12,756 km equatorial diameter (12,714 km polar diameter)

Mössbauer under pressure (McCammon)

QS: 2.4 mm/s

5 GPa
17 GPa
27 GPa
37 GPa
43 GPa
44 GPa
48 GPa
55 GPa
60 GPa
64 GPa

Relative transmission

Velocity (mm/s)

QS: 3.5 mm/s
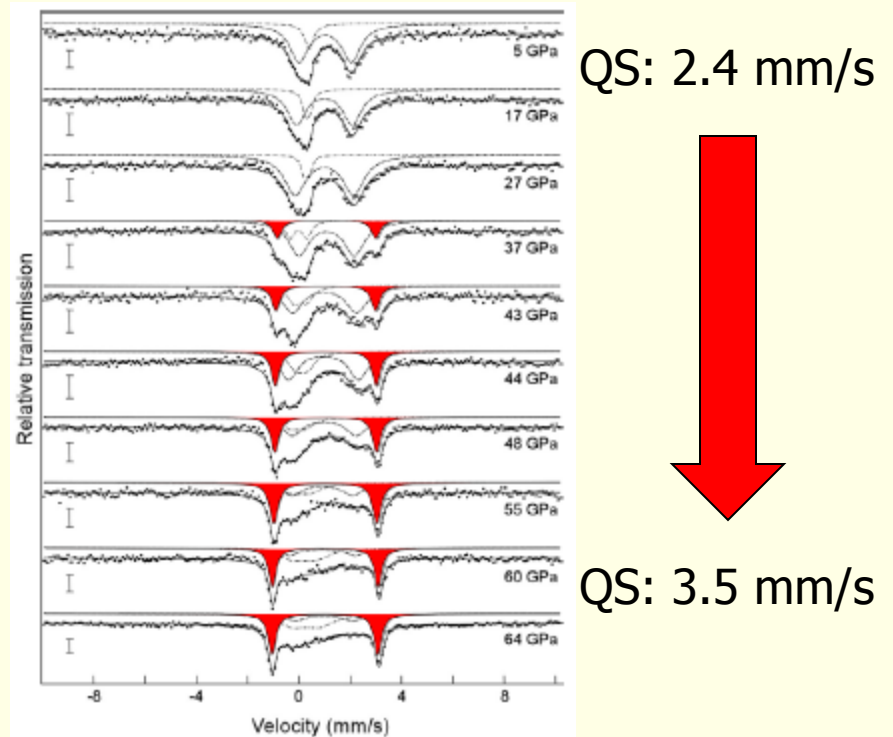
interpretation:
**high-spin → intermediate spin
transition**

spin states of Fe^{2+} (3d^6)

HS (M=4u$_B$)   IS (M=2u$_B$)   LS (M=0)

e_g
t_{2g}

e_g
t_{2g}
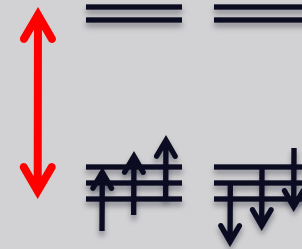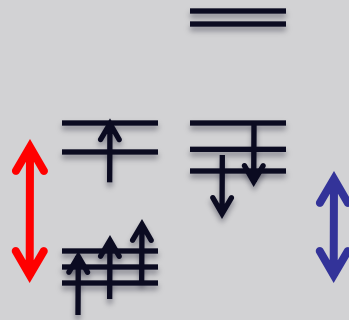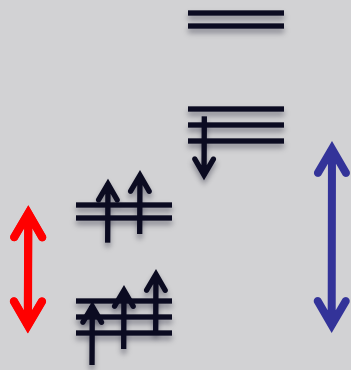
crystal field: small   intermediate   large
spin splitting: large   intermediate   zero

t$_{2g}$
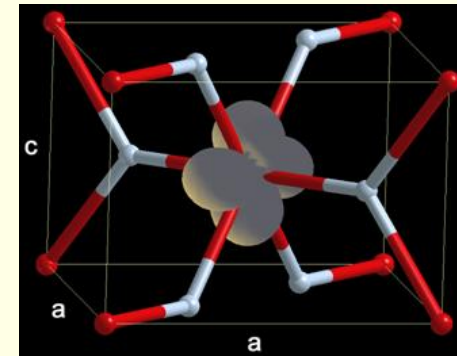
•**extensive structure optimizations** (including soft phonons) of various possible spin states at different pressures and with different orbital occupations:
• leading to several (meta-) stable phases:
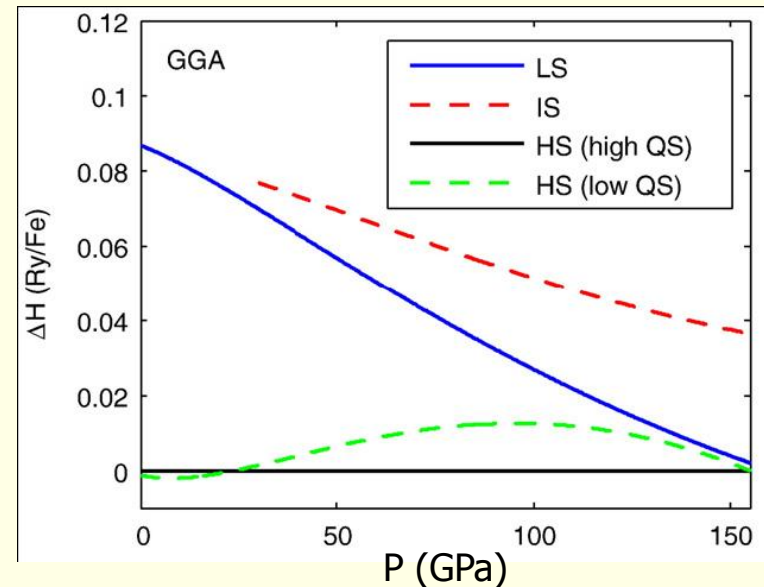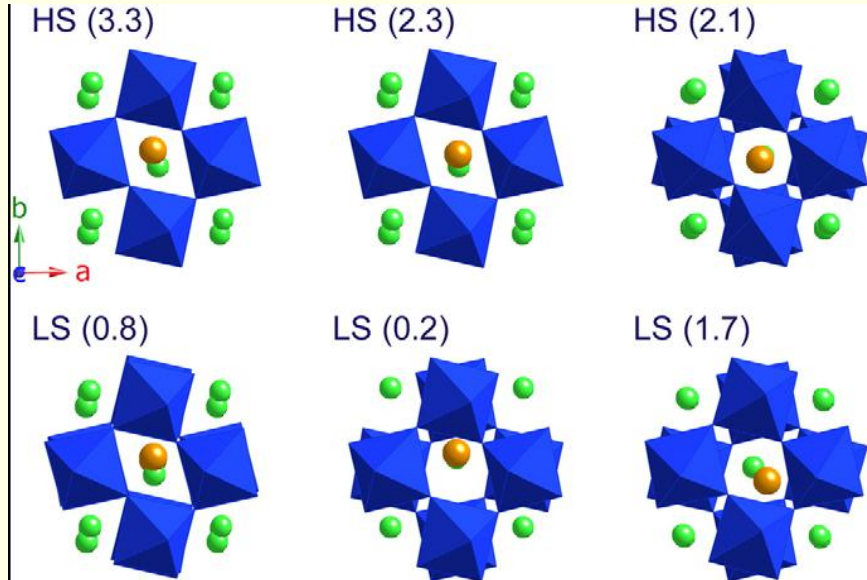
• two different HS states compete with each other
• IS state never the ground state
• LS state not stable at relevant pressures

electronic HS - HS transition

HS (2.3)
2.461
2.055
2.554
2.179
2.554
1.985
2.554
2.055
2.461

HS (3.3)
2.484
2.088
2.295
2.140
2.295
2.106
2.088
2.484
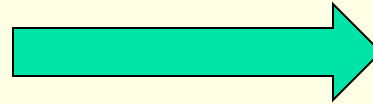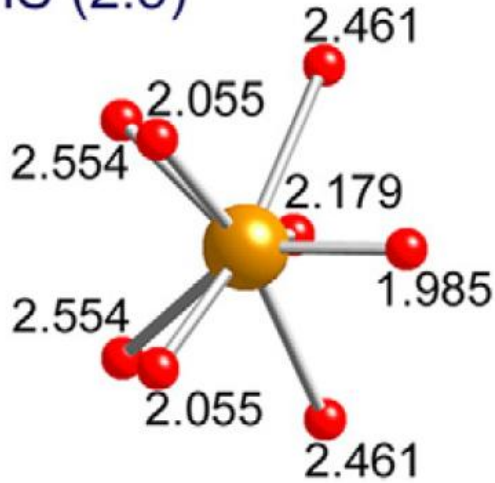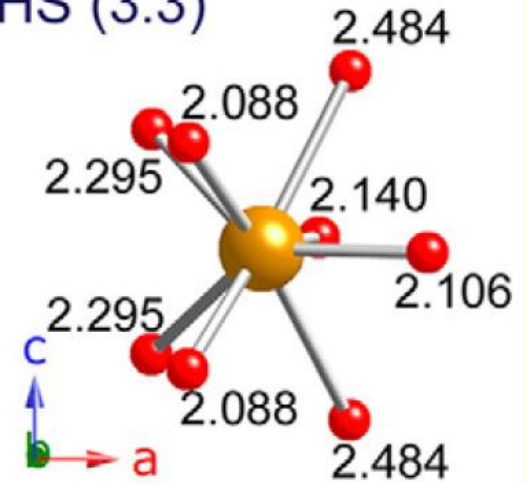
spin-dn e⁻: d_{yz}
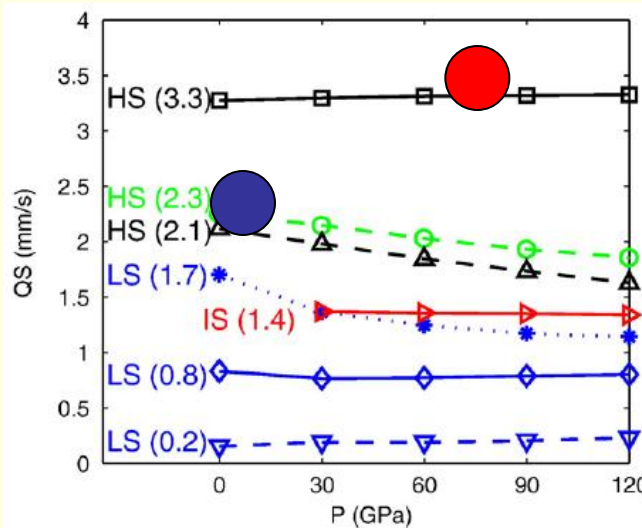
$d_{xy}+d_{x2-y2}$

$$V_{zz}^{dd} \propto \left\langle \frac{1}{r^3} \right\rangle_d \left[d_{xy} + d_{x^2-y^2} - \frac{1}{2}(d_{xz} + d_{yz}) - d_{z^2} \right]$$

H. Hsu et al., Earth and Planetary Science Letters 294 (2010) 19–26

The Verwey transition in $RBaFe_2O_5$

(temperature induced PT between charge-ordered and mixed valence state)

$$2\ Fe^{2.5+} \rightarrow Fe^{2+} + Fe^{3+}$$
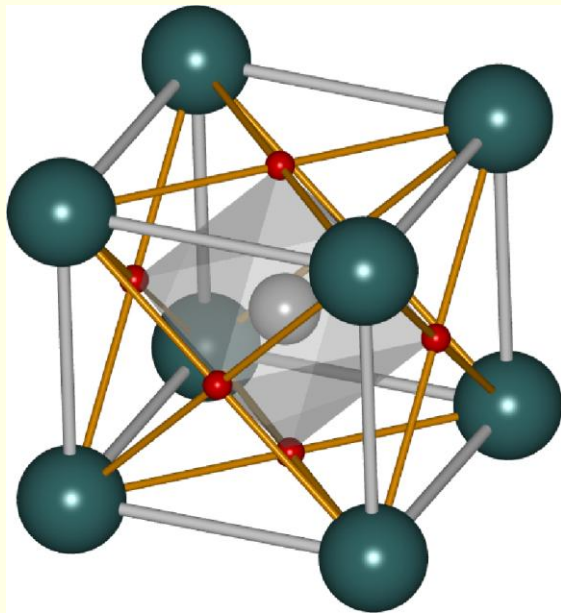
ABO_3 O-deficient double-perovskite

Ba

Y (R)

square pyramidal coordination
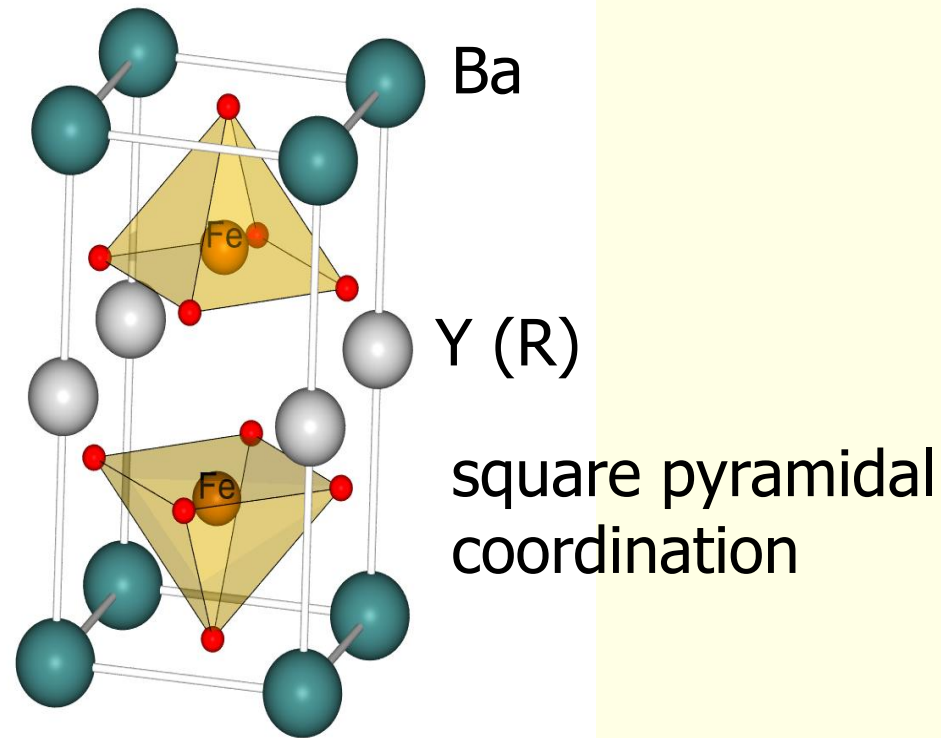
Antiferromagnet with a 2 step Verwey transition around 300 K

Woodward&Karen, Inorganic Chemistry 42, 1121 (2003)

structural changes

CO structure: Pmma
a:b:c=2.09:1:1.96 (20K)
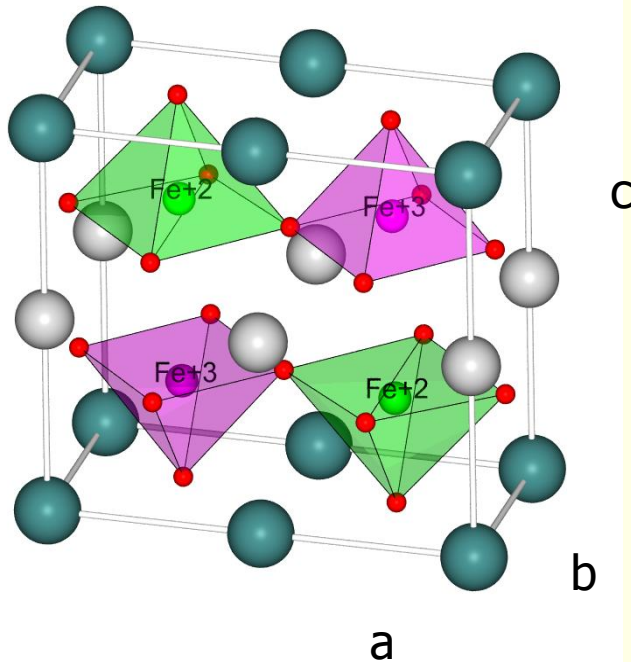
VM structure: Pmmm
a:b:c=1.003:1:1.93 (340K)
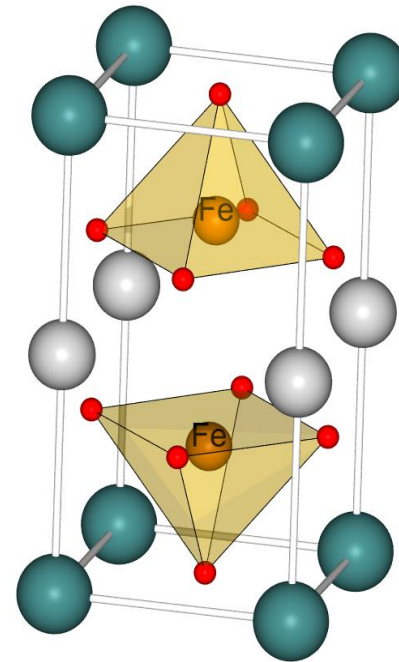
- Fe^{2+} and Fe^{3+} chains along b
- contradicts Anderson charge-ordering conditions with minimal electrostatic repulsion (checkerboard like pattern)
- has to be compensated by orbital ordering and e^--lattice coupling

- *Metallic behaviour/No bandgap*
  - Fe-dn t_{2g} states not splitted at E_F
  - overestimated covalency between O-p and Fe-e_g
- *Magnetic moments too small*
  - Experiment:
    - CO: 4.15/3.65 (for Tb), 3.82 (av. for Y)
    - VM: ~3.90
  - Calculation:
    - CO: 3.37/3.02
    - VM: 3.34
- *no significant charge order*
  - charges of Fe^{2+} and Fe^{3+} sites nearly identical
- *CO phase less stable than VM*

- ***LDA/GGA NOT suited for this compound!***
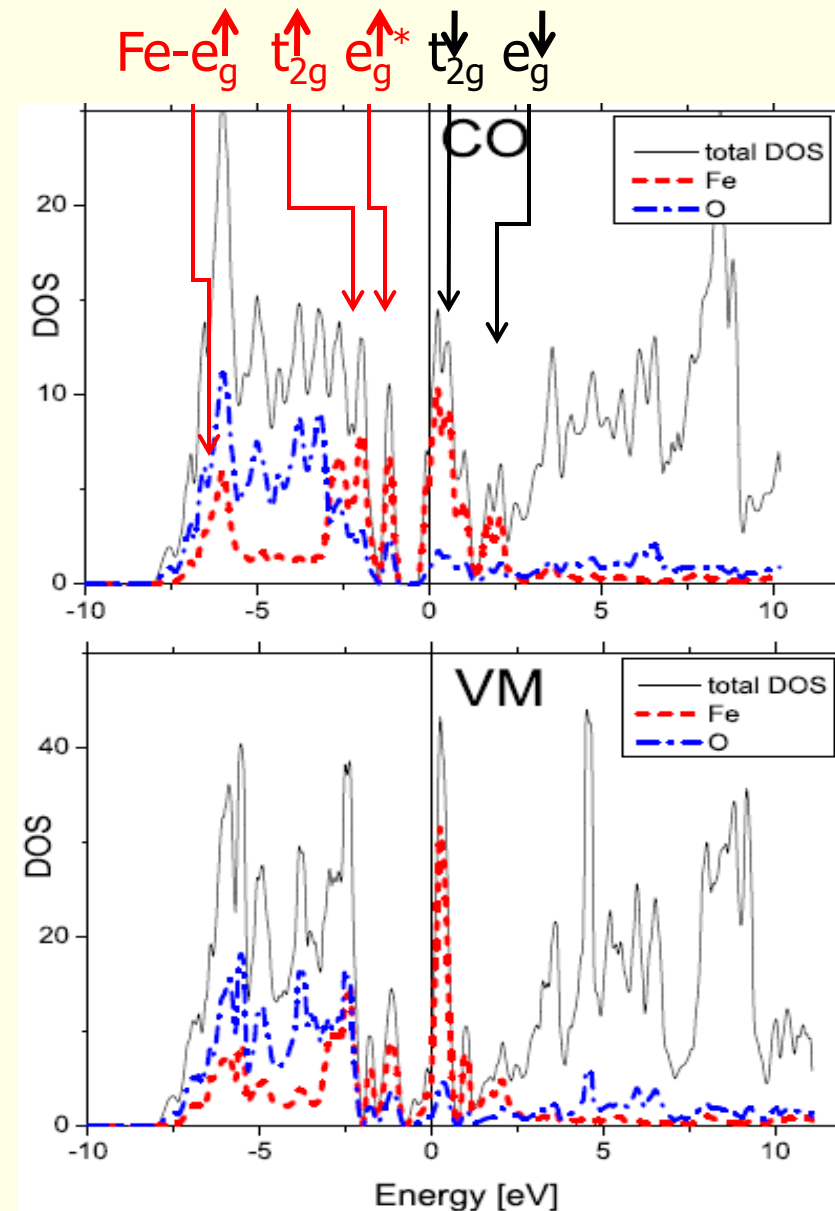
"Localized electrons": GGA+U

- ## Hybrid-DFT
  - $E_{xc}^{PBE0}[\rho] = E_{xc}^{PBE}[\rho] + \alpha (E_x^{HF}[\Phi_{sel}] - E_x^{PBE}[\rho_{sel}])$

- ## LDA+U, GGA+U
  - $E^{LDA+U}(\rho,n) = E^{LDA}(\rho) + E^{orb}(n) - E^{DCC}(\rho)$
    - separate electrons into "itinerant" (LDA) and localized e⁻ (TM-3d, RE 4f e⁻)
    - treat them with "approximate screened Hartree-Fock"
    - correct for "double counting"

  $$E^{orb}(\hat{n}) = \frac{U}{2} \sum_{m,m',\sigma} \hat{n}_{m\sigma}\hat{n}_{m'-\sigma} + \frac{U-J}{2} \sum_{m\neq m',\sigma} \hat{n}_{m\sigma}\hat{n}_{m'\sigma}$$

  - Hubbard-U describes coulomb energy for 2e⁻ at the same site

  - orbital dependent potential

  $$V_{m,m',\sigma} = (U - J)\left(\frac{1}{2} - n_{m,m',\sigma}\right)$$
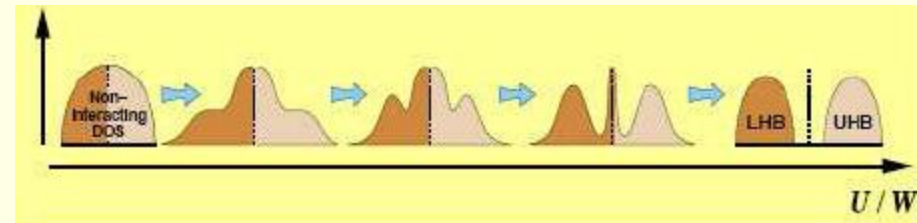
DOS: GGA+U vs. GGA

GGA+U   GGA

single lower Hubbard-band in VM splits in CO with Fe^{3+} states lower than Fe^{2+}
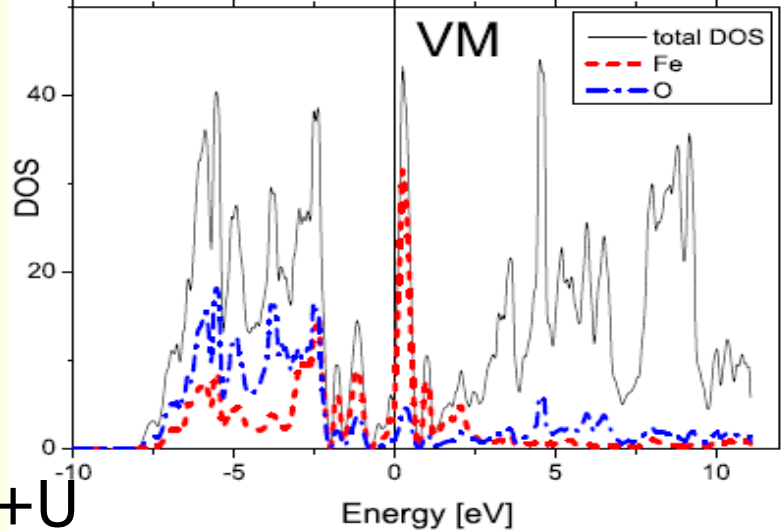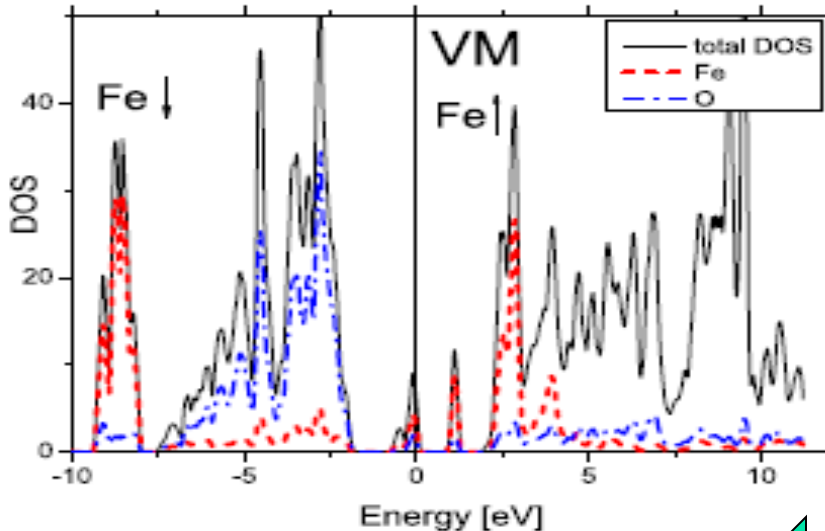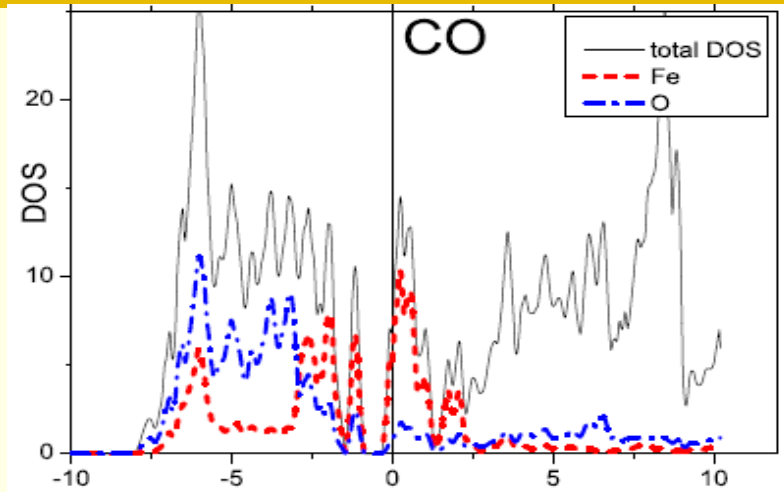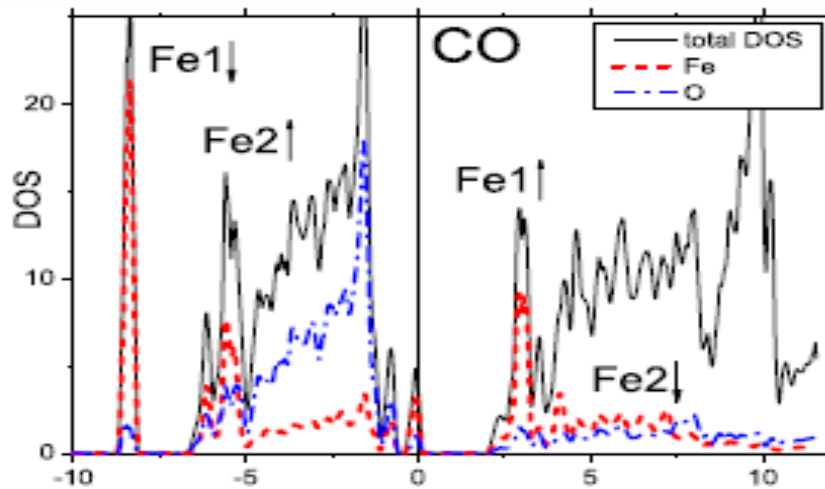
GGA+U

insulator   metal
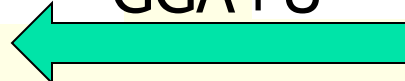
- Fe^{2+} $(3d^6)$ CO Fe^{3+} $(3d^5)$ VM $Fe^{2.5+}$ $(3d^{5.5})$

- **majority-spin fully occupied**
- strong covalency effects   very localized states at lower energy than Fe^{2+}
  in e_g and d-xz orbitals

- **minority-spin states**
- d-xz fully occupied (localized)   empty   d-z^2 partly occupied
- ⇒ short bond in y   short bond in z (one O missing)   FM Fe-Fe; distances in z ??
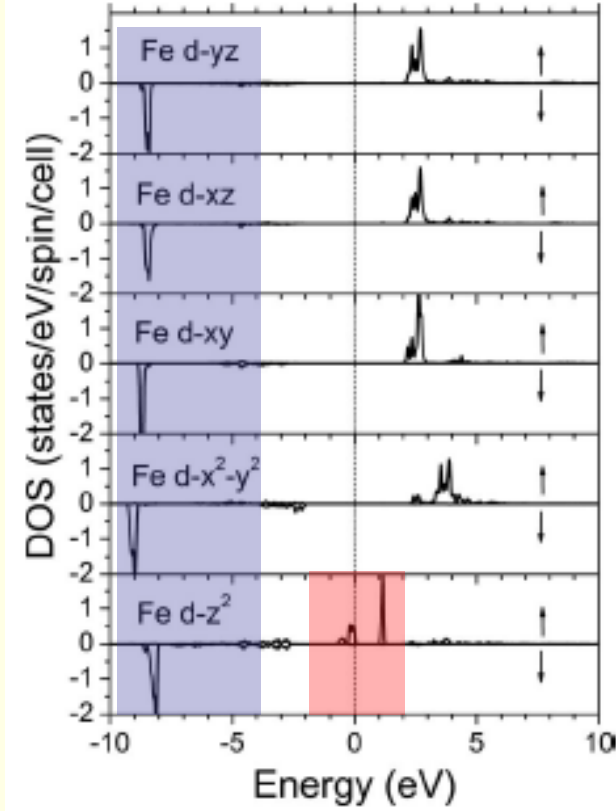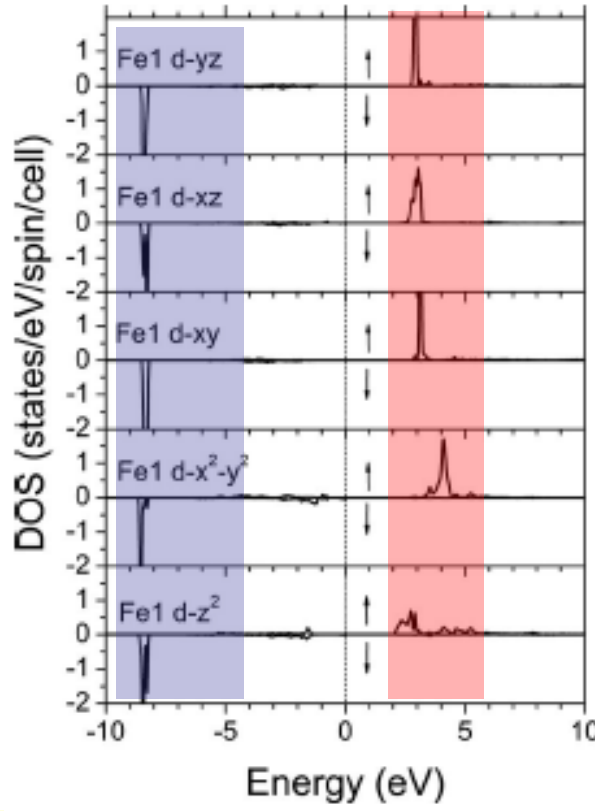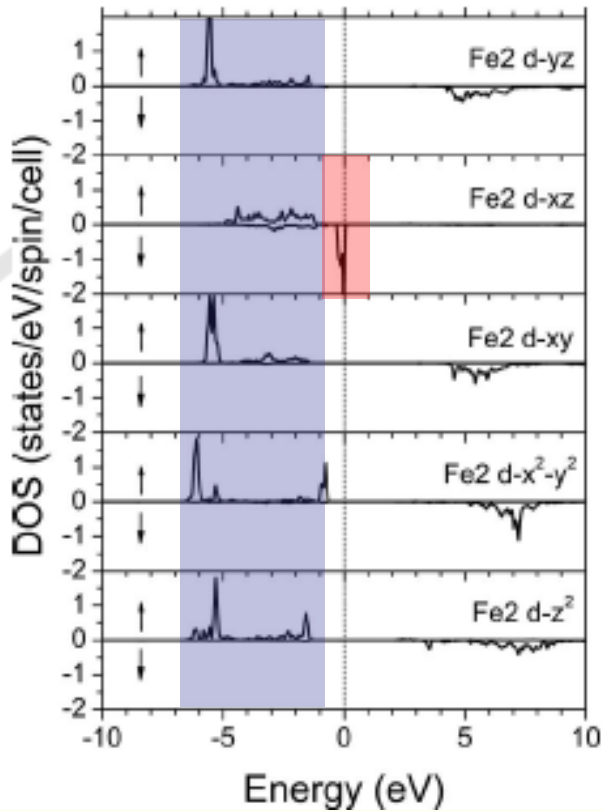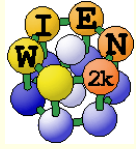
Difference densities $\Delta\rho = \rho_{cryst} - \rho_{at}^{sup}$

- **CO phase**   **VM phase**
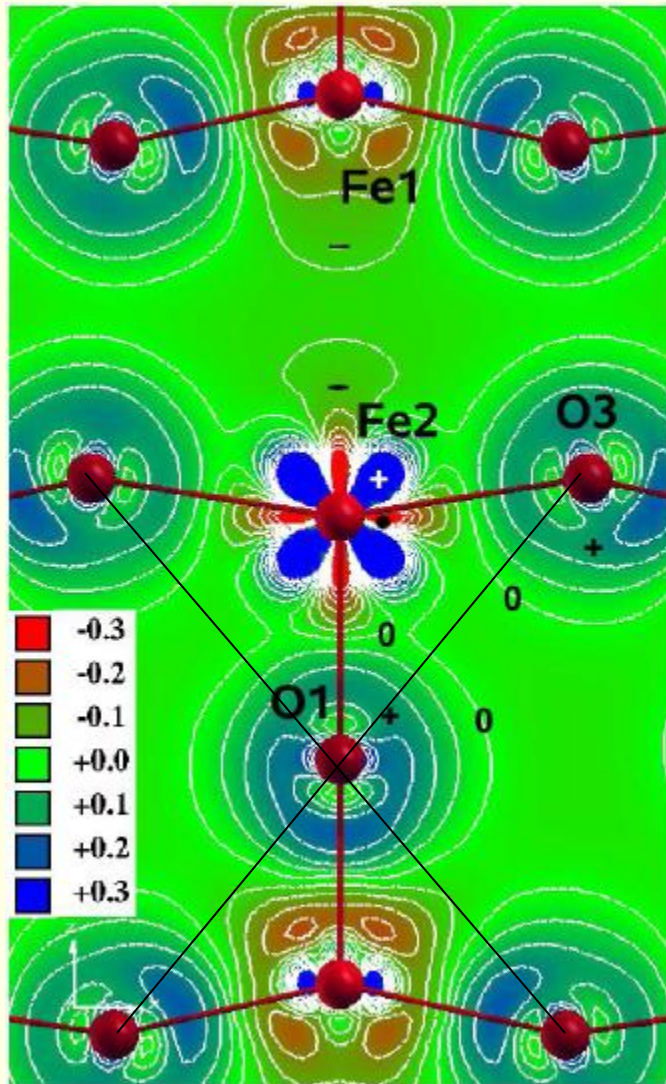
Fe^{2+}: d-xz
Fe^{3+}: d-x^2
O1 and O3: polarized
                toward Fe^{3+}

Fe: d-z^2 Fe-Fe interaction
O: symmetric

-0.3	
-0.2	
-0.1	
+0.0	
+0.1	
+0.2	
+0.3	
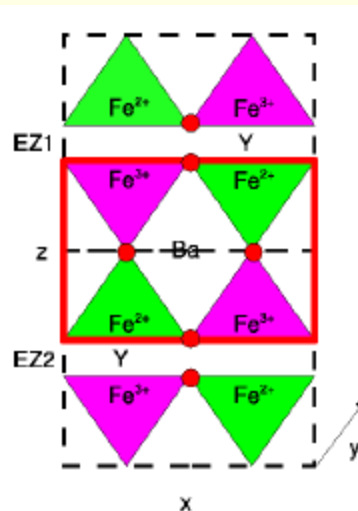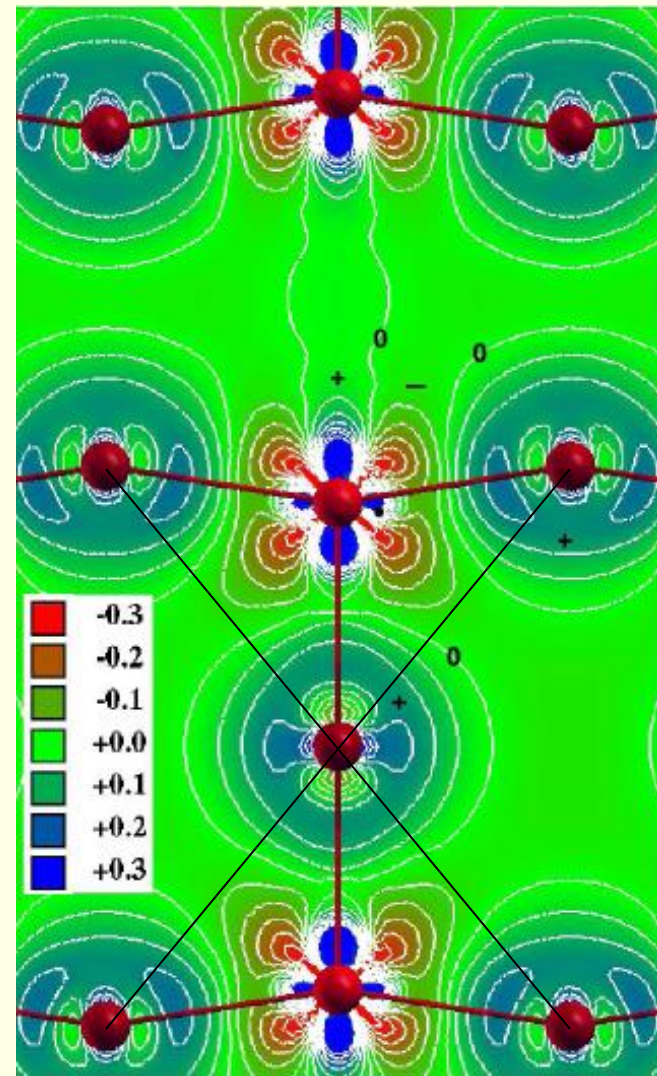
d_{xz} spin density (ρ_{up}-ρ_{dn}) of CO phase
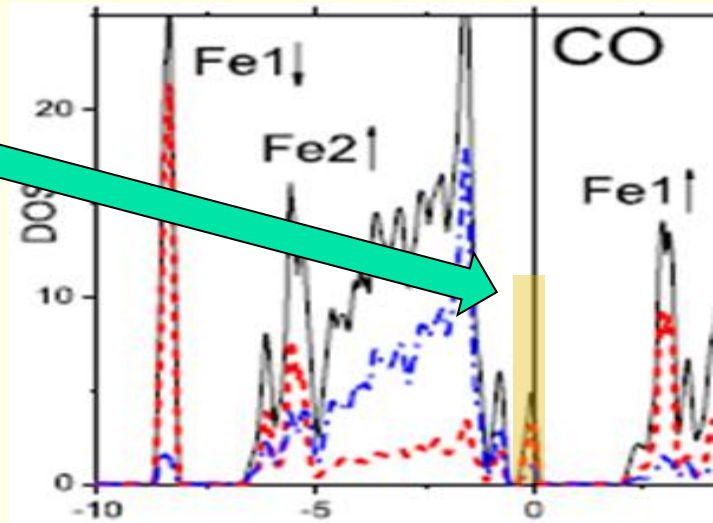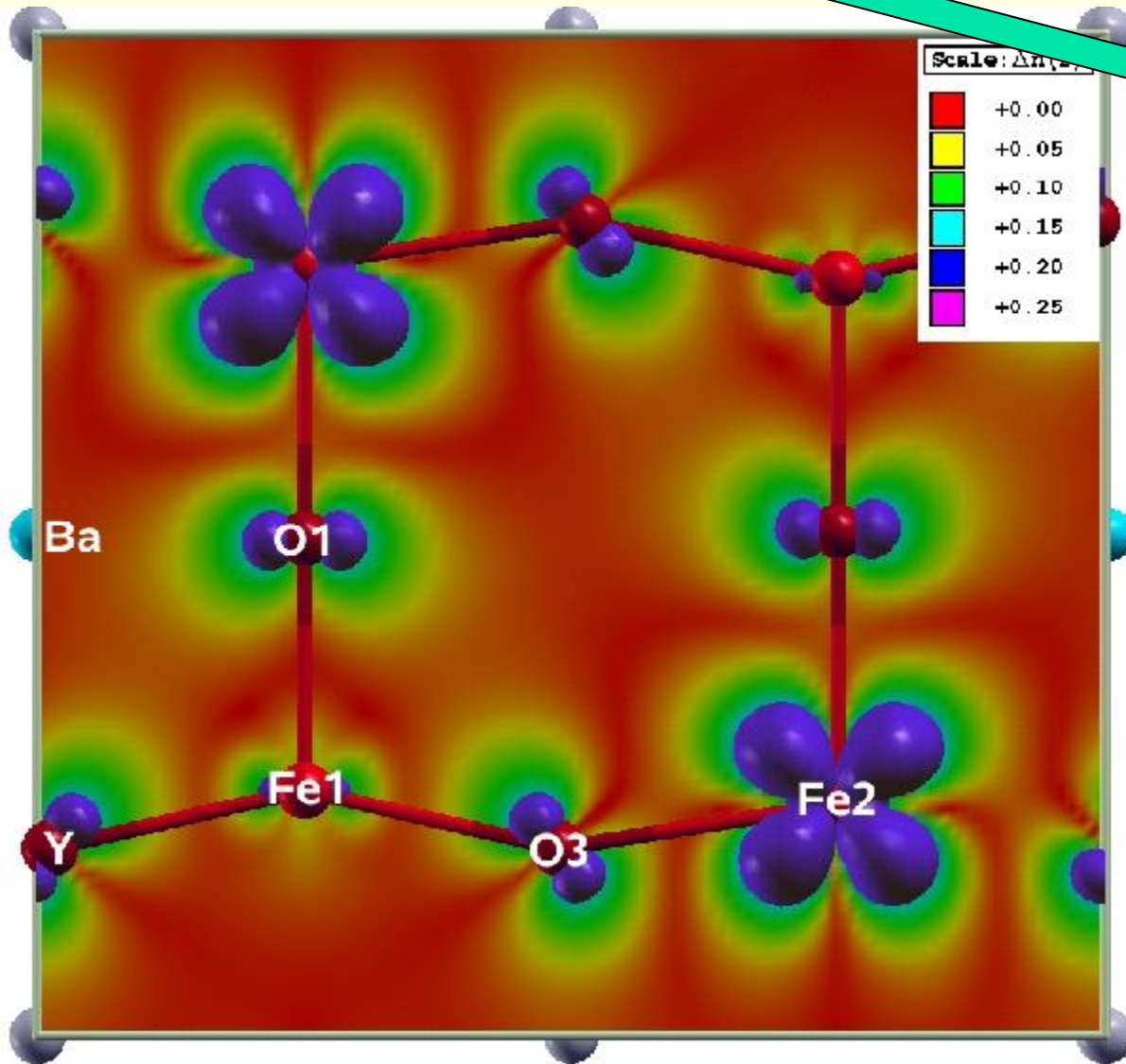
Fe^{3+}: no contribution
Fe^{2+}: d_{xz}
  weak π-bond with O
  tilting of O3 π-orbital

Mössbauer spectroscopy:

- **Isomer shift:** $\delta = \alpha\ (\rho_0^{Sample} - \rho_0^{Reference})$; α=-.291 au^{3}mm s^{-1}
  - *proportional to the electron density ρ at the nucleus*

- **Magnetic Hyperfine fields:** $B_{tot} = B_{contact} + B_{orb} + B_{dip}$

  - *$B_{contact}$ = 8π/3 μ_B[ρ_{up}(0) − ρ_{dn}(0)]   ...   spin-density at the nucleus*

$$\vec{B}_{orb} = 2\mu_B \langle \Phi | \frac{S(r)}{r^3} \vec{l} | \Phi \rangle$$ ...   *orbital-moment*

$$\vec{B}_{dip} = 2\mu_B \langle \Phi | \frac{S(r)}{r^3} \left[3(\vec{s}\,\vec{\hat{r}})\,\vec{\hat{r}} - \vec{s} \right] | \Phi \rangle$$ *... spin-moment*

S(r) is reciprocal of the relativistic mass enhancement $S(r) = \left[1 + \frac{\epsilon - V(r)}{2mc^2} \right]^{-1}$
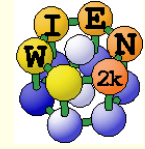
TABLE VIII: Hyperfine fields B (in Tesla), isomer shifts δ (mm/s) and quadrupole coupling constants eQV_{zz} (mm/s) for the CO phase for various exchange and correlation potentials and experiment[8–10].

CO

	U_{eff} [eV]	exp. ——	GGA+U 5	6	7	8	LDA ——	GGA ——
$Fe2^{2+}$	B_{dip}	—	-16.29	-16.49	-16.66	-16.83	-6.68	-12.67
	B_{orb}	—	-6.73	-6.90	-8.26	-7.65	-9.57	-6.34
	$B_{contact}$	—	32.25	32.23	32.58	32.60	32.21	31.58
	B_{tot}	~ 8	9.23	8.83	7.66	8.13	15.96	12.57
	δ	~ 1	0.92	0.94	0.96	0.99	0.74	0.79
	eQV_{zz}	$3.6 - 4^a$	3.66	3.74	3.81	3.89	-0.82	2.60
$Fe1^{3+}$	B_{dip}	—	-0.67	-0.60	-0.52	-0.45	1.29	0.39
	B_{orb}	—	-0.52	-0.45	-0.37	-0.28	-7.96	-2.65
	$B_{contact}$	—	37.65	38.28	38.15	37.86	29.64	31.63
	B_{tot}	~ 50	36.46	37.24	37.26	37.12	22.97	29.37
	δ	~ 0.4	0.33	0.30	0.28	0.25	0.50	0.47
	eQV_{zz}	$1 - 1.5^a$	1.46	1.50	1.51	1.52	1.04	-0.30

^{a}depending on rare earth ion

VM

	U_{eff} [eV]	exp. ——	GGA+U 5	6	7	8	LDA ——	GGA ——
$Fe^{2.5+}$	B_{dip}	—	-3.00	-2.98	-2.95	-2.87	-2.13	-2.83
	B_{orb}	—	-3.11	-2.99	-2.84	-2.74	-5.47	-4.56
	$B_{contact}$	—	41.17	40.96	41.45	41.17	33.10	36.36
	B_{tot}	~ 30	35.06	34.98	35.67	35.56	25.50	28.98
	δ	~ 0.5	0.53	0.52	0.51	0.49	0.60	0.60
	eQV_{zz}	~ 0.1	0.12	0.13	0.13	0.13	0.19	-0.27

2k

Summary

- **EFGs can routinely be calculated for all kinds of solids.**
  - *"semi-core" contribution large for "left"-atoms of the periodic table*
  - *p-p contribution always large (on-site (eg. O-2p) vs. off-site (Fe-4p))*
  - *d-d (f-f) contributions for TM (lanthanide/actinide) compounds*
  - *EFG stems from different orbital occupations due to covalency or crystal field effects*
- **EFG is very sensitive to**
  - *correct structural data (internal atomic positions)*
  - *correct theoretical description of the electronic structure*
    - "highly correlated" transition metal compounds (oxides, halides)
    - 4f and 5f compounds
    - "beyond" LDA (LDA+U, Hybrid-DFT, …)

K.Schwarz, C.Spiel, R.Laskowski, TU Vienna

Han Hsu, R. Wentzcovitch, Univ. Minnesota (perovskite)

M.Body, G.Silly, Univ. Le Mans (Al-fluorides)

Thank you for your attention !

structural changes in YBaFe$_2$O$_5$

- above T$_N$ (~430 K): tetragonal (P4/mmm)

- 430K: slight orthorhombic distortion (Pmmm) due to AFM

  all Fe in class-III mixed valence state +2.5;

- ~334K: dynamic charge order transition into class-II MV state,

  visible in calorimetry and Mössbauer, but not with X-rays

- 308K: complete charge order into

  class-I MV state (Fe^{2+} + Fe^{3+})

  large structural changes (Pmma)

  due to Jahn-Teller distortion;

  change of magnetic ordering:

  direct AFM Fe-Fe coupling vs. FM Fe-Fe exchange above T$_V$
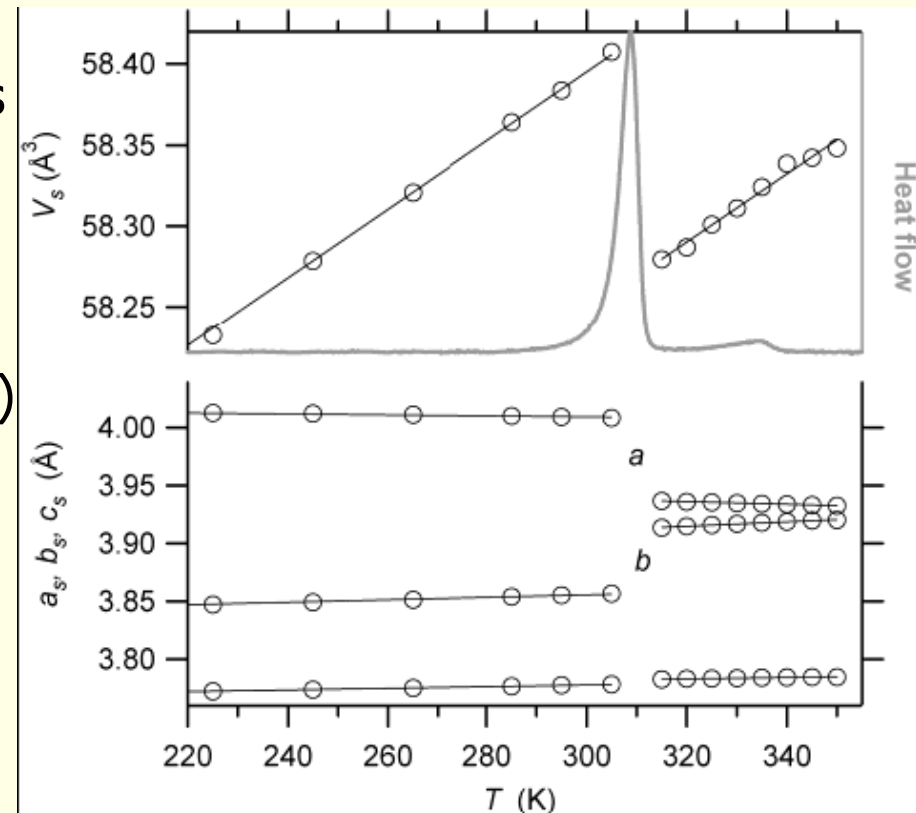
antiferromagnetic structure

CO phase: G-type AFM

- AFM arrangement in all directions, also across Y-layer
- Fe moments in b-direction
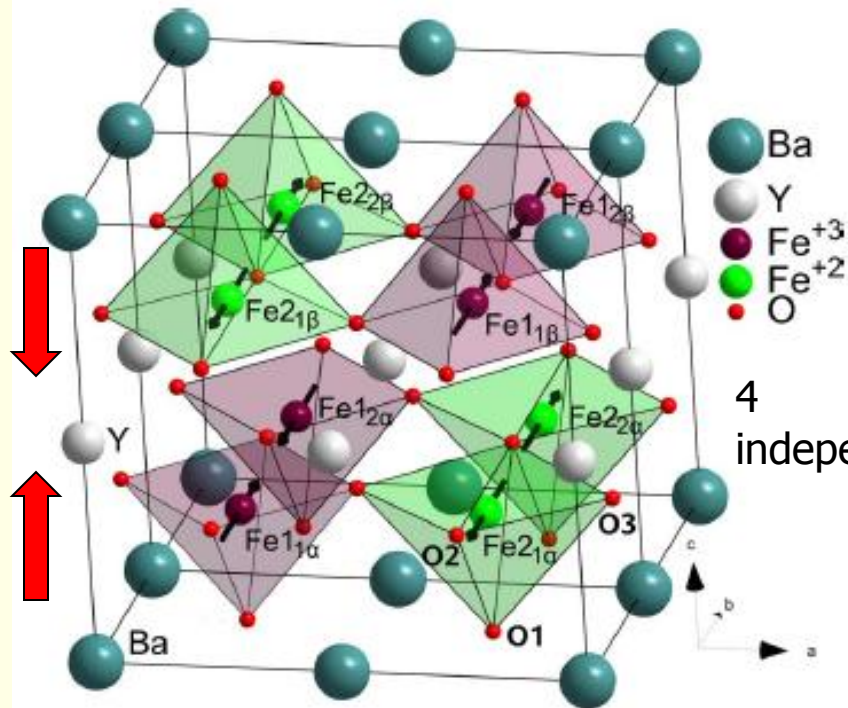
VM phase:

AFM for all Fe-O-Fe superexchange paths
FM across Y-layer (direct Fe-Fe exchange)

4 independent Fe atoms

FIG. 1. (Color online) The magnetic $1 \times 2 \times 1$ CO supercell. The arrows depict the direction of the magnetic moments.

8 independent Fe atoms
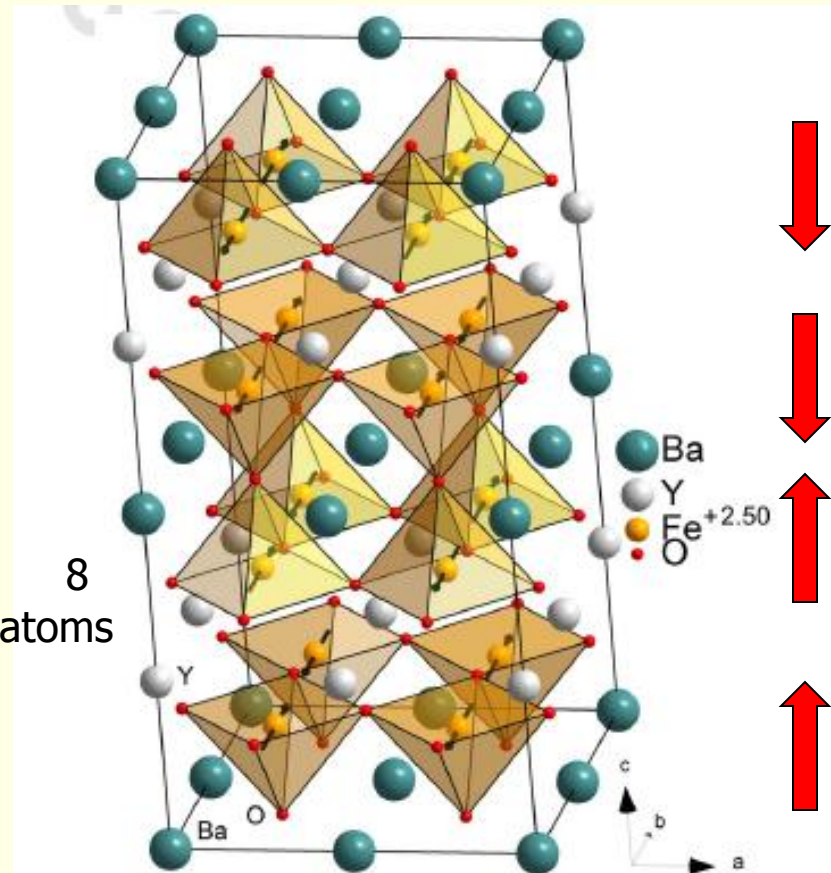
FIG. 2. (Color online) The magnetic $2 \times 2 \times 2$ VM supercell. The arrows depict the direction of the magnetic moments.

magnetic moments and band gap

TABLE V: Dependence of the band gap (in eV), the orbital μ_{orb}, spin μ_S and total moments μ_{tot} (in μ_B) on U_{eff} for the CO and VM phases. Experimental values are taken from ref.[7].

| | CO | | | | | VM | | | | |
| | exp. | U_{eff} [eV] | | | | exp. | U_{eff} [eV] | | | |
	—	5	6	7	8	—	5	6	7	8
μ_{orb} Fe1^{3+}	—	0.01	0.01	0.01	0.01	—	0.05	0.05	0.04	0.04
μ_{orb} Fe2^{2+}	—	0.10	0.10	0.12	0.11					
μ_S Fe1^{3+}	—	3.95	4.02	4.07	4.14	—	3.81	3.87	3.92	3.97
μ_S Fe2^{2+}	—	3.34	3.38	3.42	3.45					
μ_{tot} Fe1^{3+}	4.15	3.96	4.03	4.08	4.14	3.90[a]	3.86	3.91	3.96	4.01
μ_{tot} Fe2^{2+}	3.65	3.44	3.49	3.54	3.56					
band gap	—	1.8	2.1	2.4	2.7	—	0.9	1.0	1.0	1.1

- **magnetic moments in very good agreement with exp.**
  - **LDA/GGA:** CO: 3.37/3.02   VM: 3.34 μ_B
  - orbital moments small (but significant for Fe^{2+})
- **band gap: smaller for VM than for CO phase**
  - exp: semiconductor (like Ge); VM phase has increased conductivity
  - **LDA/GGA:** metallic

Charge transfer (in GGA+U)

- **Charges according to Baders "Atoms in Molecules" theory**
  - *Define an "atom" as region within a zero flux surface* $\vec{\nabla}\rho \cdot \vec{n} = 0$
  - *Integrate charge inside this region*

Atom	CO		VM	
	Multiplicity	Charge	Multiplicity	Charge
Ba	4	+1.51	8	+1.52
Y	4	+2.17	8	+2.15
$Fe1^{3+}$	4	+1.84		
$Fe2^{2+}$	4	+1.36	16	+1.62
O1	4	−1.36	8	−1.36
O 2a	4	−1.40		
O 2b	4	−1.36	16	−1.39
O3	8	−1.38	16	−1.39

Structure optimization (GGA+U)

- **CO phase:**
  - *Fe^{2+} : shortest bond in y (O2b)*
  - *Fe^{3+} : shortest bond in z (O1)*

- **VM phase:**
  - *all Fe-O distances similar*
  - *theory deviates along z !!*
    - Fe-Fe interaction
    - different U ??
    - finite temp. ??
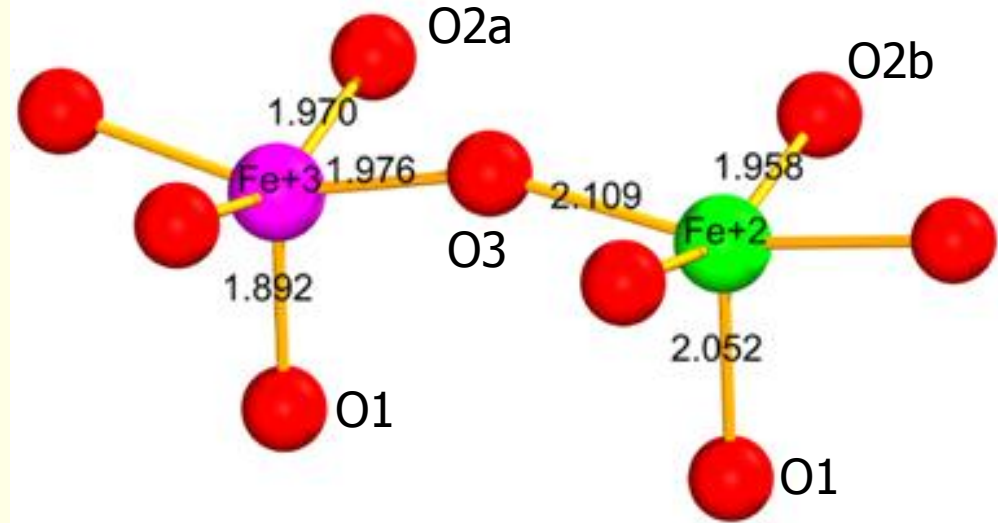
Bond	Direction	CO		VM	
		exp.	theory	exp.	theory
$Fe1^{3+}$ - O1	z	1.892	1.899	1.999	2.056
$Fe2^{2+}$ - O1		2.052	2.057		
$Fe1^{3+}$ - O2b	y	1.970	1.968	1.995	1.983
$Fe2^{2+}$ - O2a		1.958	1.965		
$Fe1^{3+}$ - O3	x	1.976	1.957	2.000	1.989
$Fe2^{2+}$ - O3		2.109	2.128		
$Fe1^{3+}$ - $Fe2^{2+}$	z	3.587	3.576	3.571	3.456

- Take U_{eff} as "empirical" parameter (fit to experiment)
- Estimate U_{eff} from constraint LDA calculations
  - *constrain the occupation of certain states (add/subtract e⁻)*
  - *switch off any hybridization of these states ("core"-states)*
  - *calculate the resulting E_{tot}*

$$F_0^{\text{eff}} = \varepsilon_{3d\uparrow}\left(+\frac{1}{2}e\right) - \varepsilon_{3d\uparrow}\left(-\frac{1}{2}e\right) - \varepsilon_F\left(+\frac{1}{2}e\right) + \varepsilon_F\left(-\frac{1}{2}e\right)$$

Phase	CO		VM
Ion	$Fe1^{3+}$	$Fe2^{2+}$	$Fe^{2.5+}$
U_{eff}	7.52	7.22	6.58

  - *we used U_{eff}=7eV for all calculations*

magnetic interactions

CO phase:

- *magneto-crystalline anisotropy: moments point into y-direction in agreement with exp.*

Richtung [hkl]	Energie [Ry]
[100]	-115578,24026
[010]	-115578,24065
[001]	-115578,24024

- *experimental G-type AFM structure (AFM direct Fe-Fe exchange) is 8.6 meV/f.u. more stable than magnetic order of VM phase (direct FM)*

VM phase:

- *experimental "FM across Y-layer" AFM structure (FM direct Fe-Fe exchange) is 24 meV/f.u. more stable than magnetic order of CO phase (G-type AFM)*

FIG. 1. (Color online) The magnetic $1 \times 2 \times 1$ CO supercell. The arrows depict the direction of the magnetic moments.

- Heisenberg model: $H = \Sigma_{i,j} \; J_{ij} \, \boldsymbol{S}_i \cdot \boldsymbol{S}_j$

- 4 different super-exchange interactions (Fe-Fe exchange interaction mediated by an O atom)

  - J_{22}^{b} : Fe^{2+}-Fe^{2+} along b
  - J_{33}^{b} : Fe^{3+}-Fe^{3+} along b
  - J_{23}^{c} : Fe^{2+}-Fe^{3+} along c
  - J_{23}^{a} : Fe^{2+}-Fe^{3+} along a

- 1 direct Fe-Fe interaction

  - J_{direct}: Fe^{2+}-Fe^{3+} along c

  - J_{direct} negative (AFM) in CO phase
  - J_{direct} positive (FM) in VM phase
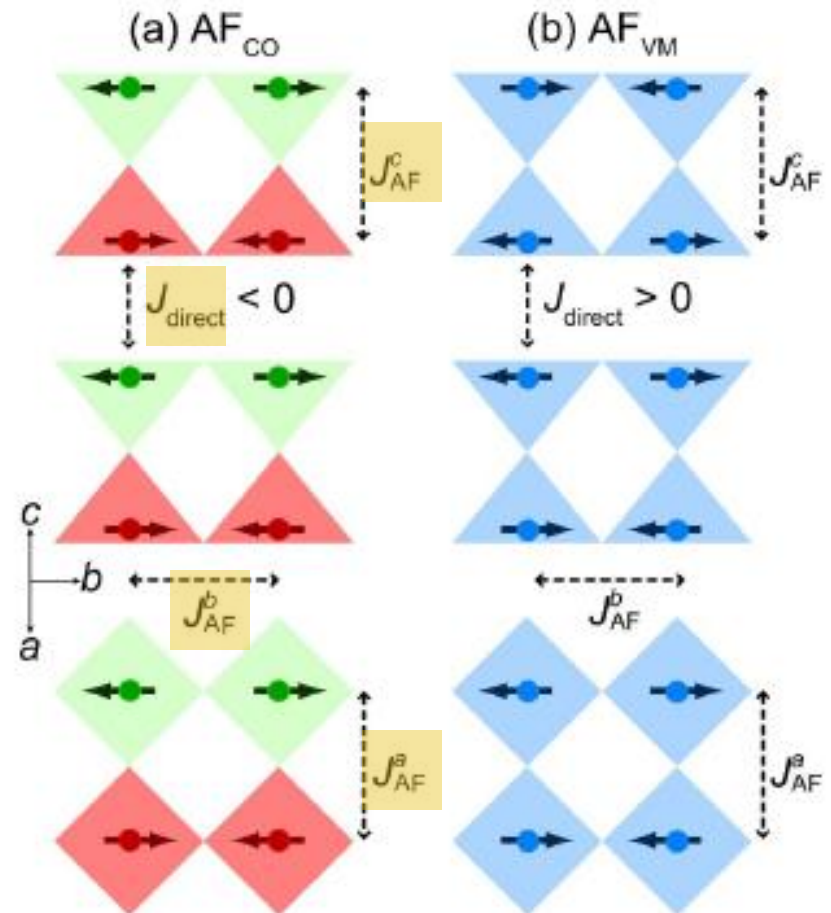
Inelastic neutron scattering

- S.Chang etal., PRL 99, 037202 (2007)

- $J_{33}^b = 5.9\ meV$
- $J_{22}^b = 3.4\ meV$
- $J_{23} = 6.0\ meV$
  - $J_{23} = (2J_{23}^a + J_{23}^c)/3$
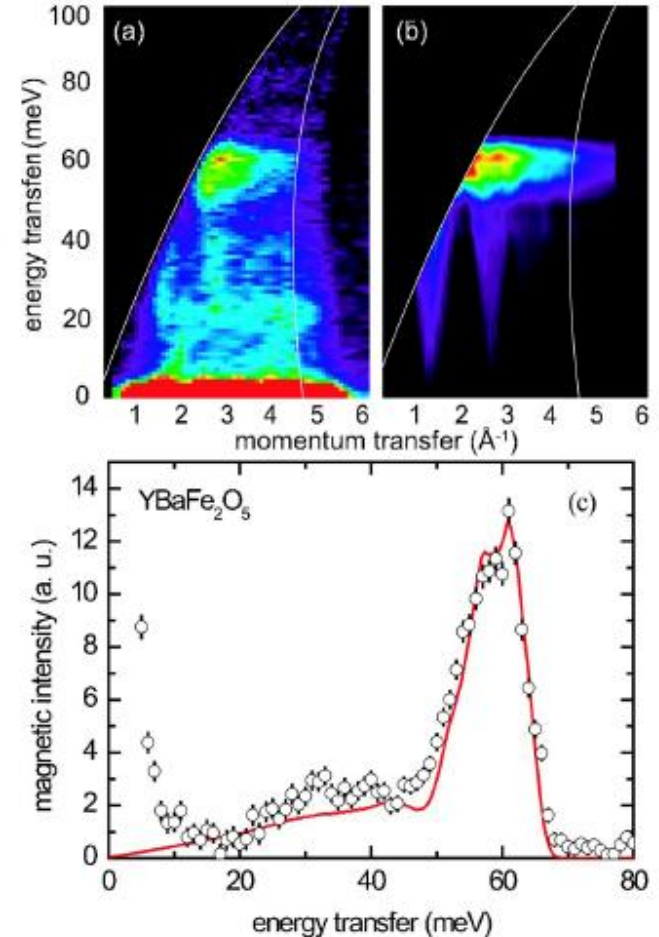
FIG. 2 (color online). (a) Inelastic neutron scattering intensity $S(Q, E)$ for $YBaFe_2O_5$ at $T = 6$ K. White lines are loci of constant angles in (Q, E) space that denote limits of the angle summation $2\theta = 1°–35°$. (b) Calculation of $S(Q, E)$ for $YBaFe_2O_5$ at $T = 6$ K using a Heisenberg model with $J_{33} = 5.9$ meV, $J_{22} = 3.4$ meV, and $J_{23} = 6.0$ meV. (c) Comparison of angle-summed magnetic scattering data (open symbols) with Heisenberg model calculation (line).

Theoretical calculations of J_{ij}

- **Total energy of a certain magnetic configuration given by:**

$$E_{ex} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i=1}^{N} n_i z_{ij} J_{ij} S_i S_j \sigma_i^{(\alpha)} \sigma_j^{(\alpha)}$$

n_i ... number of atoms i

z_{ij} ... number of atoms j which are neighbors of i

$S_i = 5/2$ (Fe^{3+}); 2 (Fe^{2+})

$\sigma_i = \pm 1$

- **Calculate E-diff when a spin on atom i (Δ_i) or on two atoms i,j (Δ_{ij}) are flipped**

$$J_{ij} = \frac{\Delta_{ij} - \Delta_i - \Delta_j}{S_i S_j n_i z_{ij} \sigma_i^{(0)} \sigma_j^{(0)}}$$

- **Calculate a series of magnetic configurations and determine J_{ij} by least-squares fit**

Investigated magnetic configurations

(a) AFM - Typ G

(b) AFM - Typ A

(c) AFM - FM xz

(d) AFM - FM yz

(e) AFM - FM x

(f) Ferrimagnetisch

(g) AFM - Typ C

(h) AFM - Typ F

(i) Ferromagnetisch
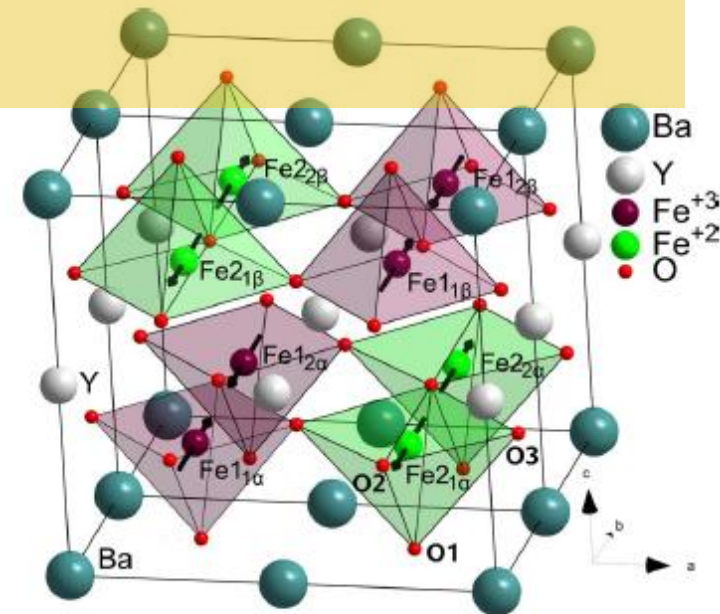
FIG. 1. (Color online) The magnetic $1\times2\times1$ CO supercell. The arrows depict the direction of the magnetic moments.

| Arrangement	$1_{1\alpha}$	$1_{1\beta}$	$1_{2\alpha}$	$1_{2\beta}$	$2_{1\alpha}$	$2_{1\beta}$	$2_{2\alpha}$	$2_{2\beta}$
AFM-Type G	+	+	−	−	−	−	+	+
AFM-FM in x	+	−	−	+	+	−	−	+
AFM-Type C	+	−	−	+	−	+	+	−
ferrimagnetic	+	+	+	+	−	−	−	−
AFM-FM in xz	+	+	−	−	+	+	−	−
AFM-Type F	+	−	+	−	+	+	−	−
AFM-Type A	+	−	+	−	+	−	+	−
AFM-FM in yz	+	−	+	−	−	+	−	+
ferromagnetic	+	+	+	+	+	+	+	+

TABLE XI: Energy differences per formula unit (meV) of different magnetic arrangements with respect to the most stable AFM-Type G structure of the CO phase. ΔE^{DFT} from direct DFT calculations (column 2), $\Delta E^{J_{calc}}$ using the calculated J values from table XII (column 4) and $\Delta E^{J_{lsf}}$ from J values obtained by least square fit (column 5). Contributions of J values in column 3.

Arrangement	ΔE^{DFT}	Contribution	$\Delta E^{J_{calc}}$	$\Delta E^{J_{lsf}}$
AFM-Type G (exp.)	0	—	0	0
AFM-FM in x	36.7	J_{23}^a	41.4	44.7
AFM-Type C	46.7	J_{23}^c	55.9	52.4
ferrimagnetic	69.6	$\frac{J_{33}^b + J_{22}^b}{2}$	79.1	81.1
AFM-FM in xz	89.9	$J_{23}^a + J_{23}^c$	97.3	97.1
AFM-Type F	107.1	$\frac{J_{23}^a + J_{23}^c + J_{33}^b}{2}$	110.8	107.1
AFM-Type A	124.4	$J_{23}^a + \frac{J_{22}^b + J_{33}^b}{2}$	120.5	125.8
AFM-FM in yz	129.8	$J_{23}^c + \frac{J_{22}^b + J_{33}^b}{2}$	135.0	133.5
ferromagnetic	194.9	$J_{23}^a + J_{23}^c + \frac{J_{22}^b + J_{33}^b}{2}$	176.4	178.1
CO phase with VM arrangement	8.6	—	—	—

TABLE XII: Calculated exchange interactions J using equation 5 (column 6) and by least square fit to the energies given in table XI (column 7, together with estimated error). Experimental values[31] in column 8. Difference energies Δ per formula unit and exchange parameters J in meV.

Interaction	Iron atoms	Δ_i	Δ_j	Δ_{ij}	Theory (Equ. 5)	Theory (least square fit)	Exp.
J_{33}^b	$Fe1_{1\alpha}^{3+}$ - $Fe1_{2\alpha}^{3+}$	53.3	53.3	44.5	10.0	9.4(2.0)	5.9
J_{22}^b	$Fe2_{1\alpha}^{2+}$ - $Fe2_{2\alpha}^{2+}$	29.5	29.5	42.0	4.3	5.7(3.3)	3.4
J_{23}^a	$Fe1_{1\alpha}^{3+}$ - $Fe2_{1\alpha}^{2+}$	53.3	29.5	62.1	4.2	4.5(0.7)	6.0^a
J_{23}^c	$Fe1_{1\alpha}^{3+}$ - $Fe2_{1\beta}^{2+}$	53.3	29.5	54.8	5.6	5.2(0.7)	

^{a}experimentally averaged as $J_{23} = \frac{2J_{23}^a + J_{23}^c}{3}$

Summary

- **Standard LDA/GGA methods cannot explain YBaFe$_2$O$_5$**
  - *metallic, no charge order (Fe^{2+}-Fe^{3+}), too small moments*
- **Needs proper description of the Fe 3d electrons (GGA+U, …)**
- **CO-phase:** Fe^{2+}: high-spin d^6, occupation of a single spin-dn orbital (d$_{xz}$)
  - *Fe^{2+}/Fe^{3+} ordered in chains along b, cooperative Jahn-Teller distortion and strong e$^-$-lattice coupling which dominates simple Coulomb arguments (checkerboard structure of Fe^{2+}/Fe^{3+})*
- **VM phase:** small orthorhombic distortion (AFM order, moments along b)
  - *Fe d-z^2 spin-dn orbital partly occupied (top of the valence bands)*
    leads to direct Fe-Fe exchange across Y-layer and thus to ferromagnetic order (AFM in CO phase).
- **Quantitative interpretation of the Mössbauer data**
- **Calculated exchange parameters J$_{ij}$ in reasonable agreement with exp.**