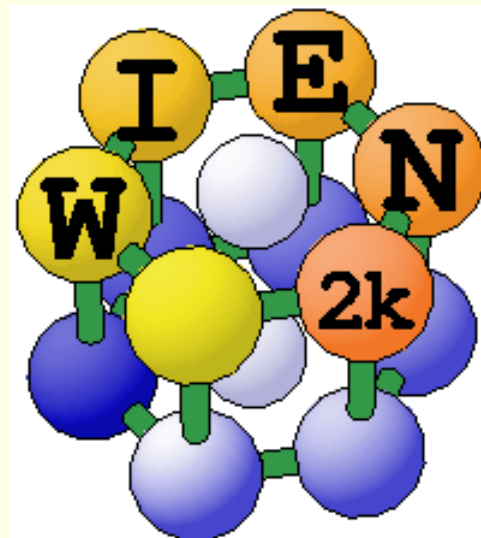


Magnetism (FM, AFM, FSM)

Karlheinz Schwarz

Institute of Materials Chemistry

TU Wien





Localized vs. itinerant systems



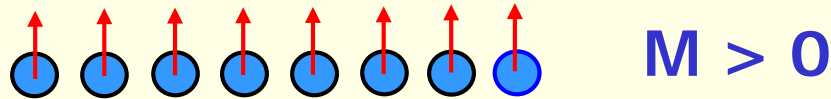
- In **localized** systems (e.g. some rare earth) the magnetism is mainly governed by the atom (Hund's rule)
- In **itinerant (delocalized)** systems (many transition metals) magnetism comes from partial occupation of states, which differ between spin-up and spin-down.
- **Boarderline** cases (some f-electron systems)
details of the structure (e.g. lattice spacing) determine whether or not some electrons are localized or itinerant.



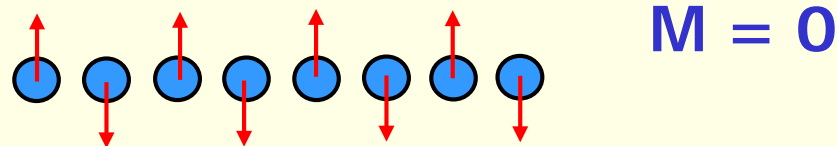
Ferro-, antiferro-, or ferri-magnetic



- Ferromagnetic (FM) (e.g. bcc Fe)

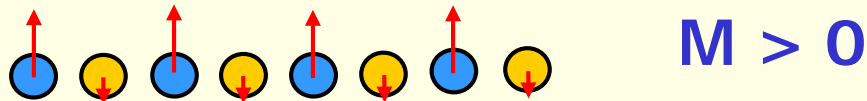


- Antiferromagnetic (AFM) (e.g. Cr)



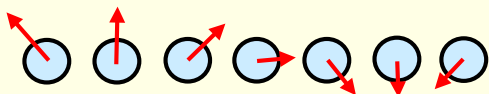
- Ferrimagnetic cases

the moments at different atoms are antiparallel but of different magnitude



- Non-collinear magnetism (NCM)

the magnetic moments are not lined up parallel.





Experimental facts:

	σ [emu/g]	σ [μ_B]	T_c [K]	ρ at 298K [g/cm^3]
Fe (bcc)	221.7	2.22	1044	7.875
Co (fcc)	166.1	1.75	1388	8.793
Co (hcp)	163.1	1.72	1360	8.804
Ni (fcc)	58.6	0.62	627	8.912



Curie
temperature



1. The carriers of magnetism are the unsaturated spins in the d-band.
2. Effects of exchange are treated with a molecular field term.
3. One must conform to Fermi statistics.

Stoner, 1936



Stoner model for itinerant electrons

In a

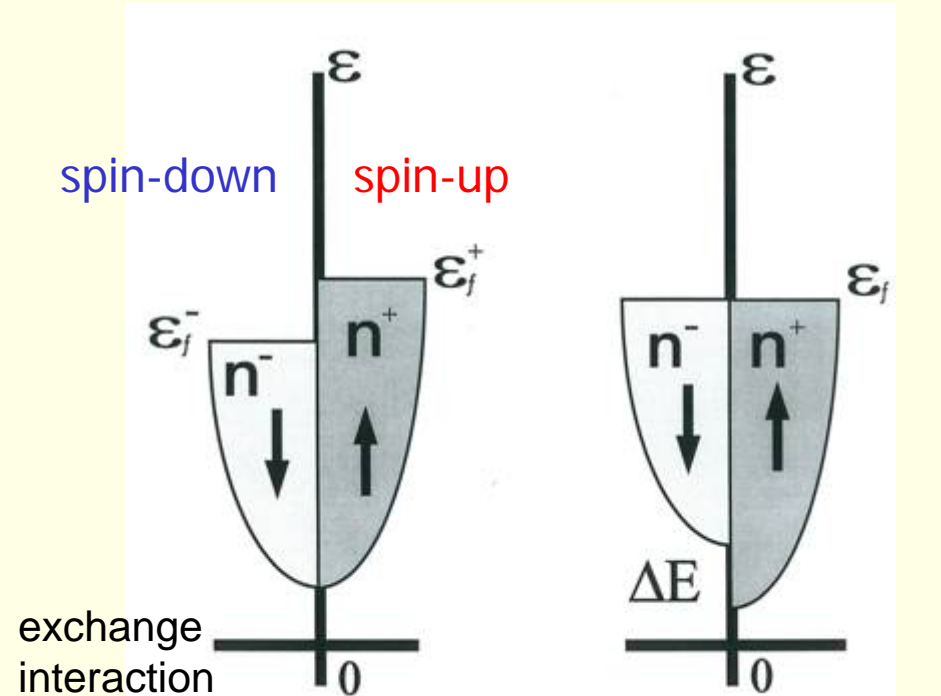
- **non magnetic (NM) case**
 $N_{\uparrow} = N_{\downarrow}$ (spin-up and spin-down)

- **ferromagnetic (FM) case**
 $N_{\uparrow} > N_{\downarrow}$ (majority and minority spin)
 the moments at all sites are parallel (collinear)

- **the (spin) magnetic moment m**
 - $m = N_{\uparrow} - N_{\downarrow}$
 - its orientation with respect to the crystal axes is only defined by **spin orbit coupling.**

- **there can also be an orbital moment**
 it is often suppressed in 3d transition metals

Exchange splitting



$$E_b = \int_0^{\epsilon_F} \epsilon \mathcal{N}(\epsilon) d\epsilon - \int_{\epsilon^-}^{\epsilon_F} \epsilon \mathcal{N}(\epsilon) d\epsilon + \int_0^{\epsilon_F} \epsilon \mathcal{N}(\epsilon) d\epsilon + \int_{\epsilon_F}^{\epsilon^+} \epsilon \mathcal{N}(\epsilon) d\epsilon - \frac{I_s M^2}{2}$$

$$\chi = \frac{\chi_P}{1 - 2\mu_B^2 I_s \mathcal{N}(\epsilon_F)} = \chi_P S$$

Stoner criterion

$$2\mu_B^2 I_s \mathcal{N}(\epsilon_F) > 1$$



Stoner model for itinerant electrons

- The existence of **ferromagnetism (FM)** is governed by the

- **Stoner criterion**

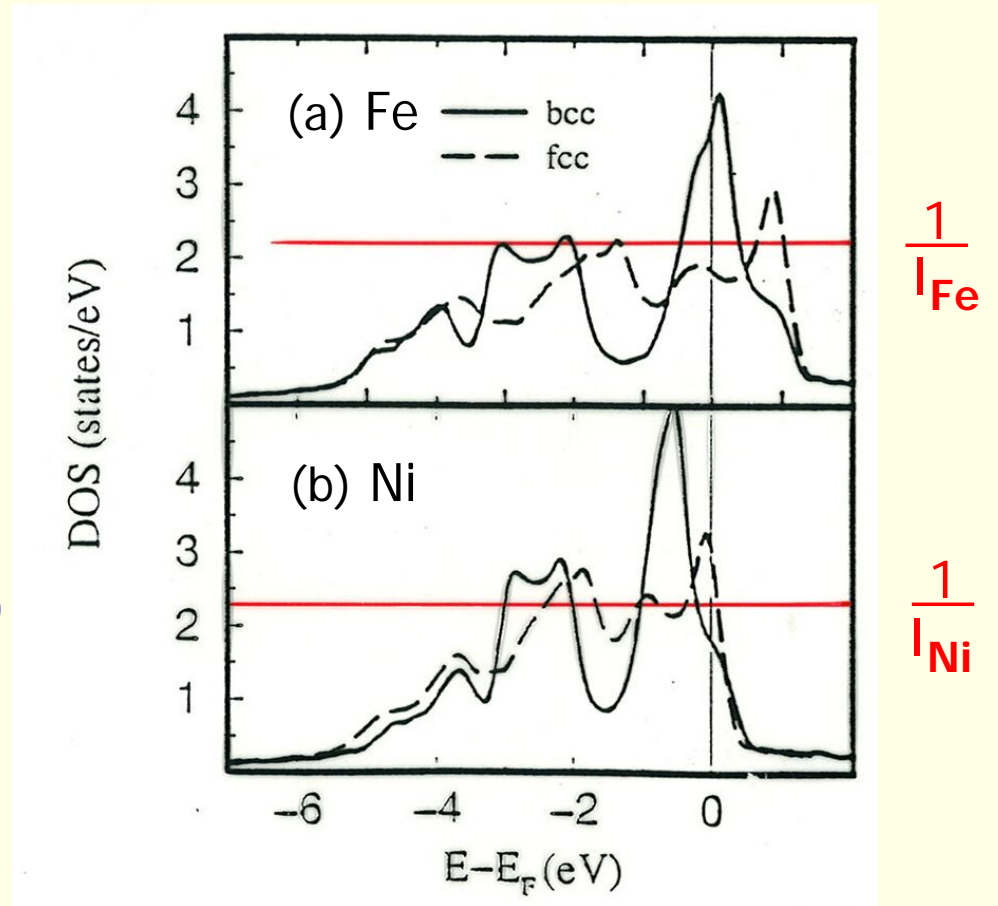
$$I \cdot N(E_F) > 1$$

$N(E_F)$ DOS at E_F (of NM case)

I Stoner parameter

~ independent of structure

- **Ferromagnetism** appears when the **gain** in exchange energy is larger than the **loss** in kinetic energy



P. James, O. Eriksson, B. Johansson,
I. A. Abrikosov,
Phys. Rev. B **58**, ... (1998)

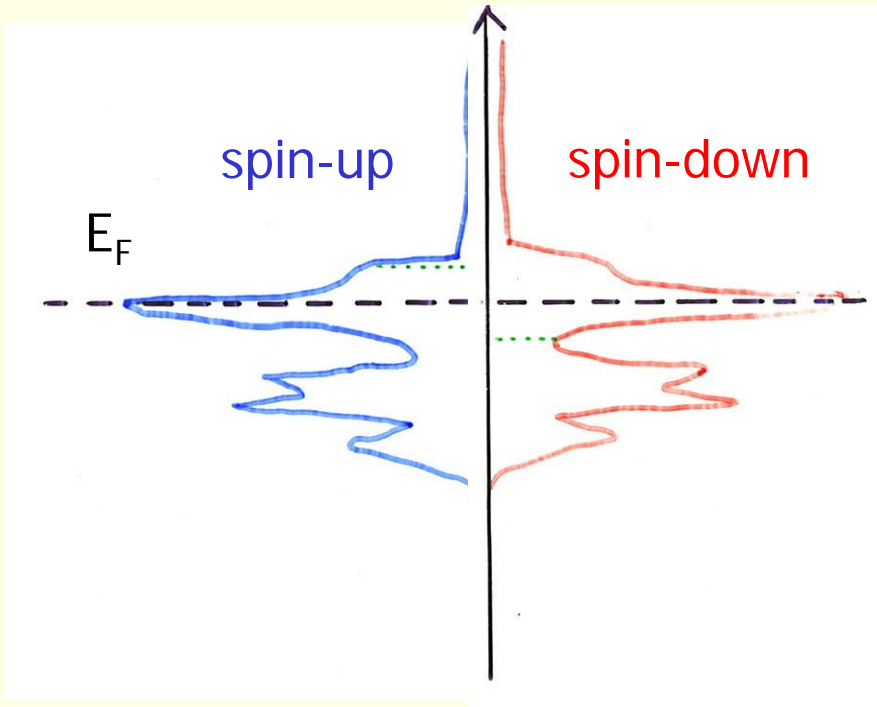


bcc Fe

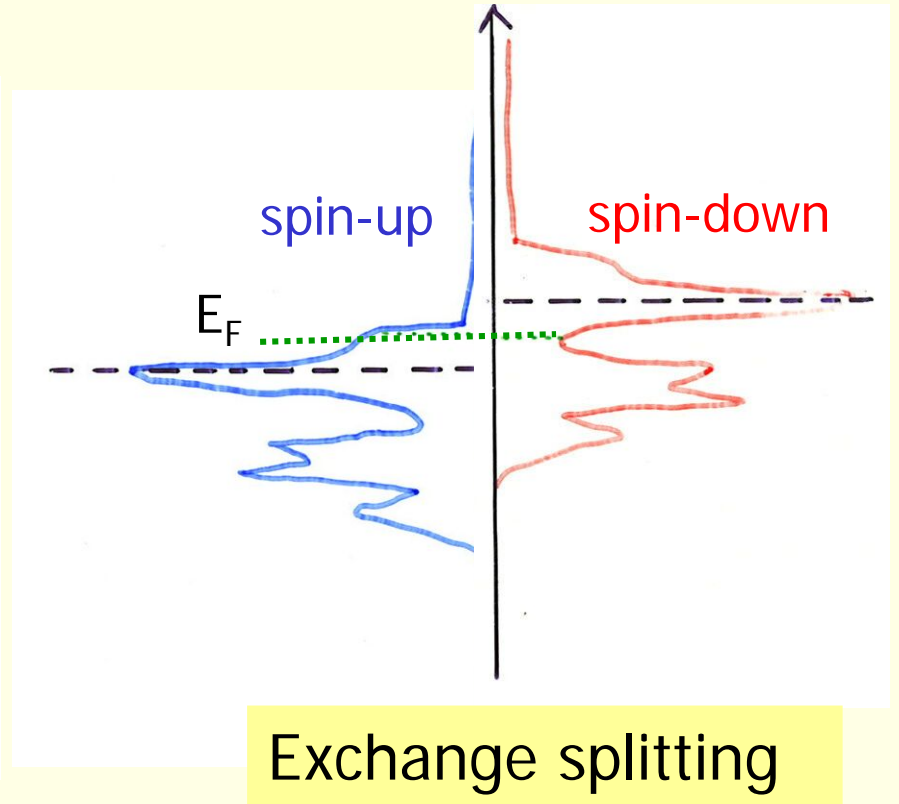


ferromagnetic case

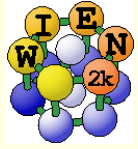
■ Non magnetic case



E_F at high DOS



Exchange splitting

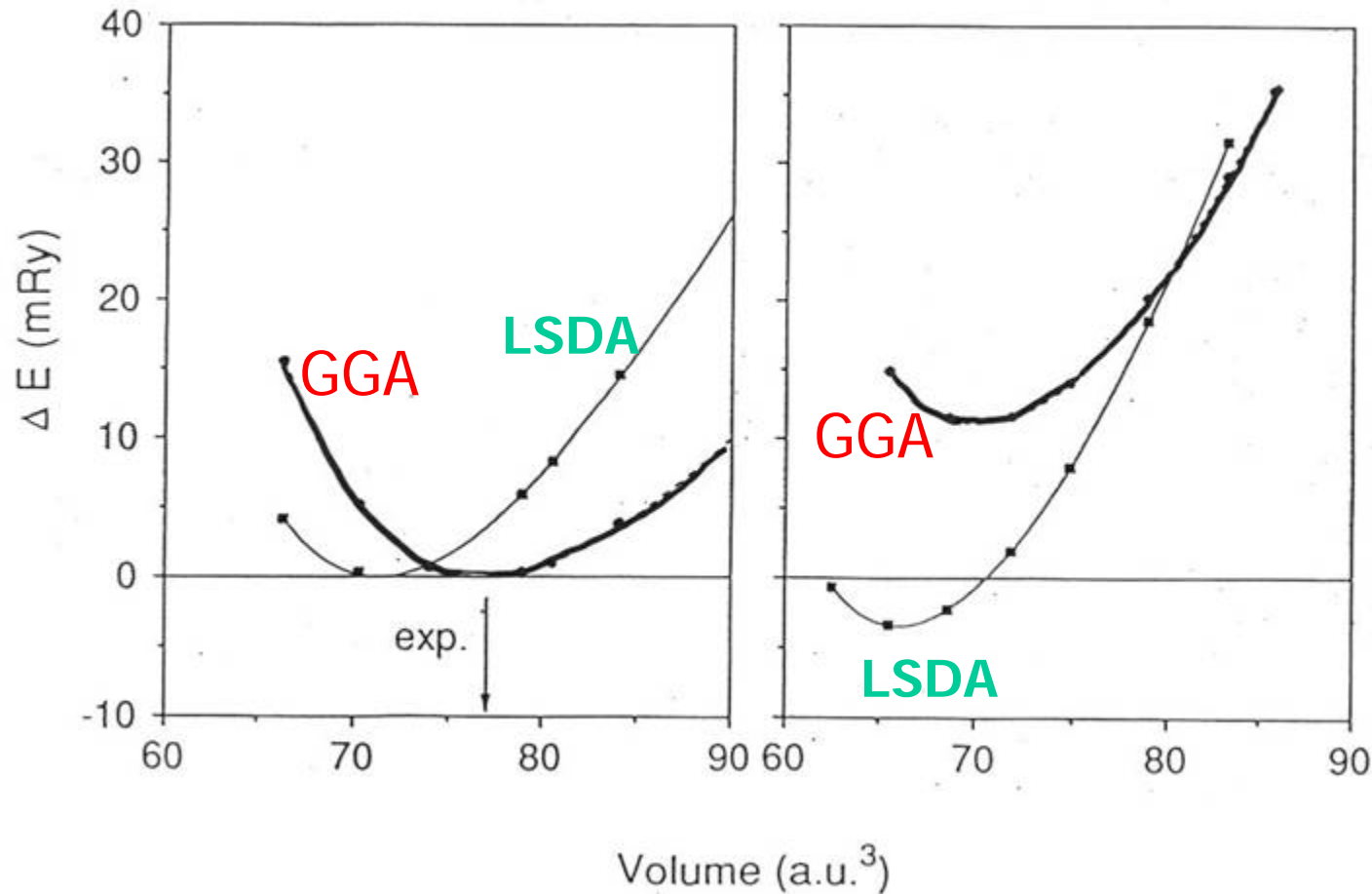


DFT ground state of iron



bcc Fe

fcc Fe



LSDA

- NM
- fcc
- in contrast to experiment

GGA

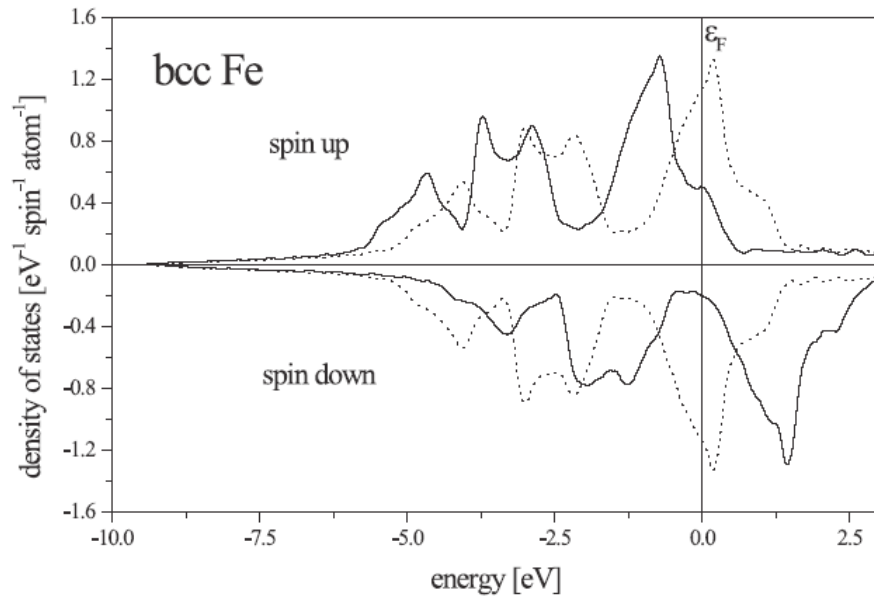
- FM
- bcc
- Correct lattice constant

Experiment

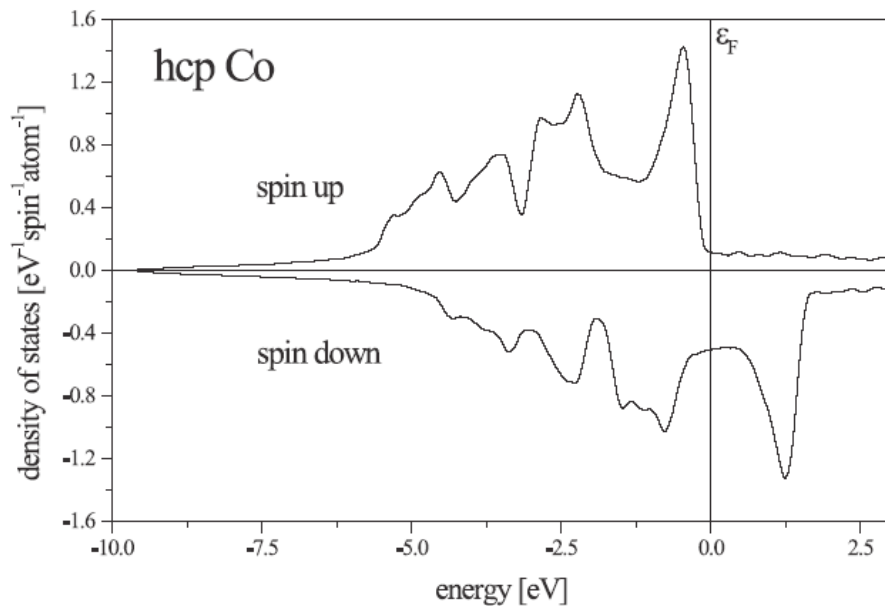
- FM
- bcc



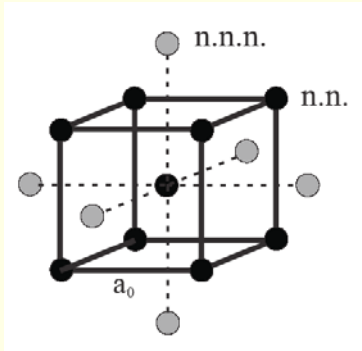
Iron and its alloys



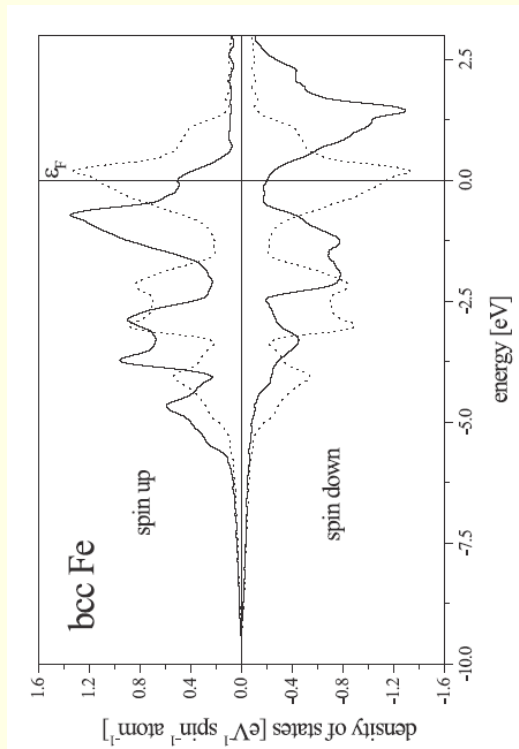
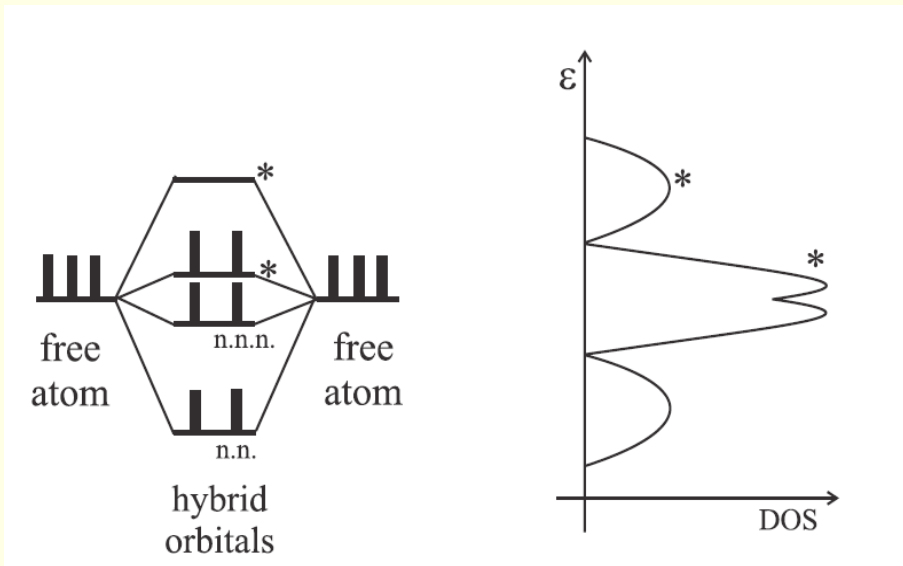
Fe: weak ferromagnet
(almost)



Co: strong ferromagnet



V. Heine: „metals are systems with unsaturated covalent bonds“



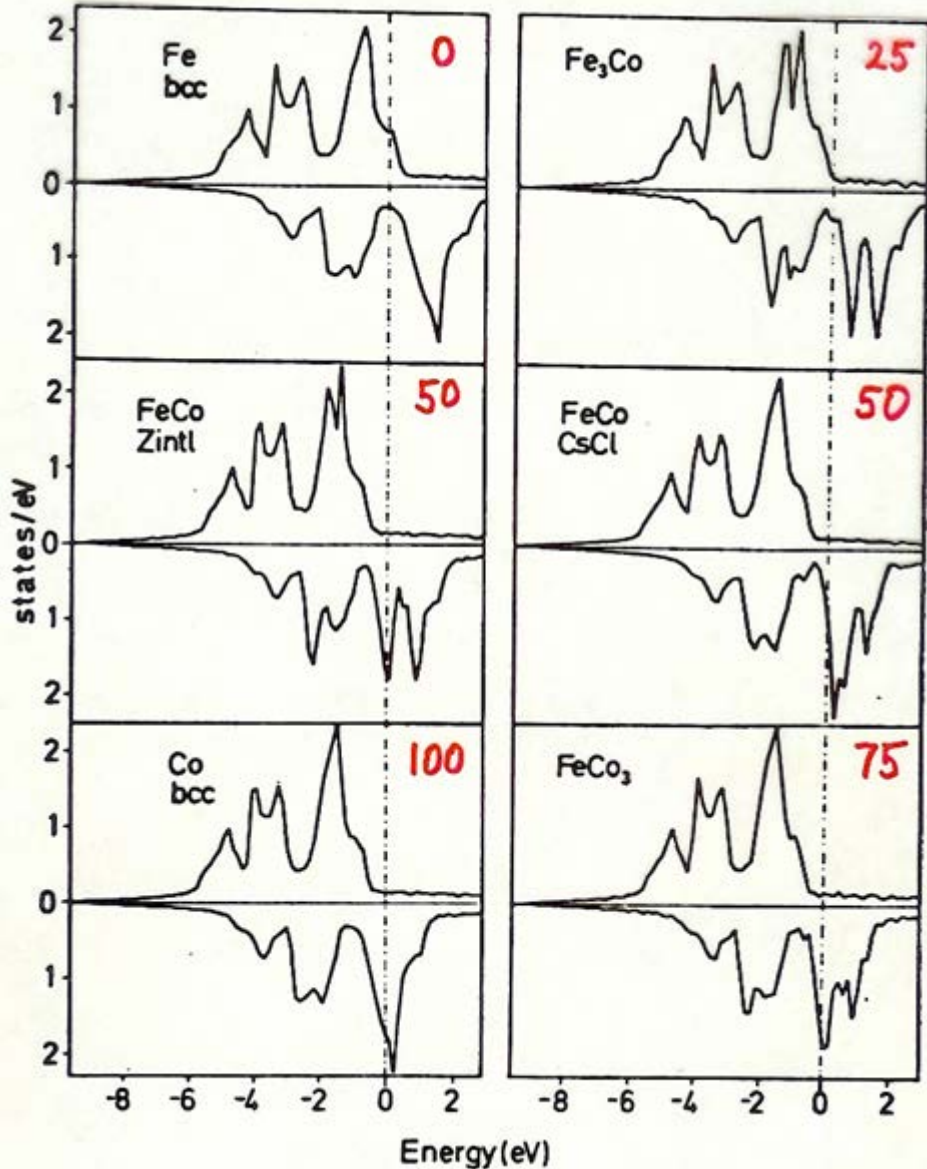


Covalent magnetism Fe-Co alloys



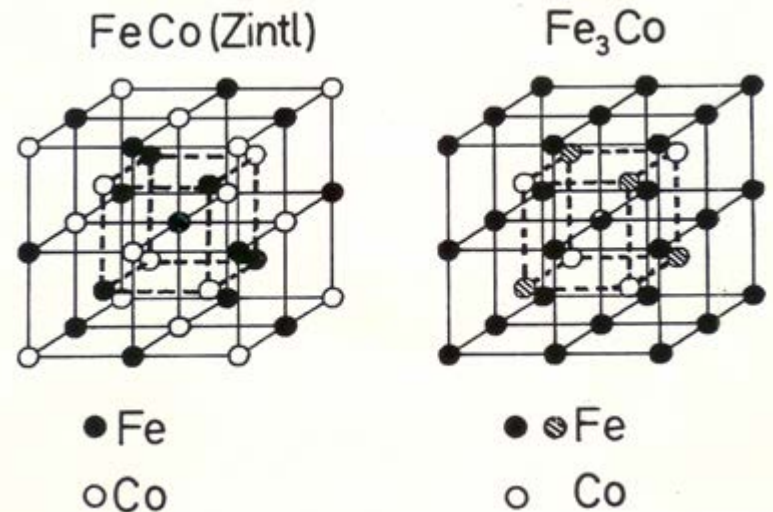
- e.g. Fe-Co alloys
- Wigner delay times

% Co

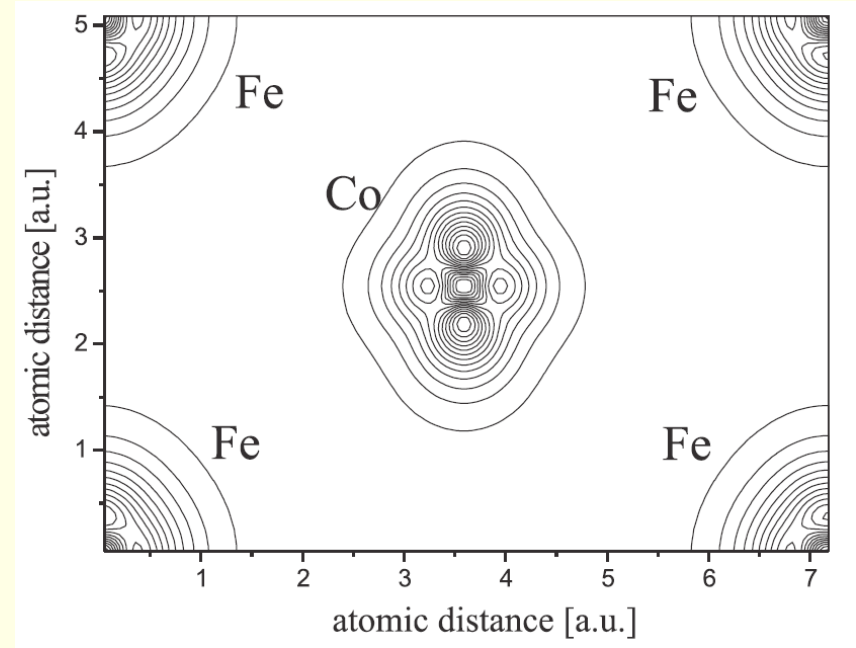
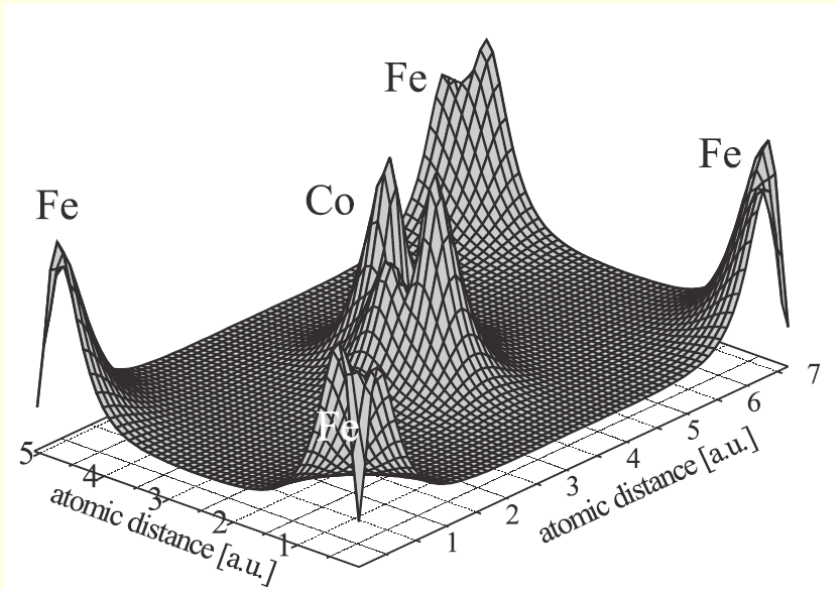


■ The alloy is represented by **ordered structures**

- Fe_3Co and $FeCo_3$ (Heusler)
- $FeCo$ Zintl or CsCl
- Fe, Co bcc



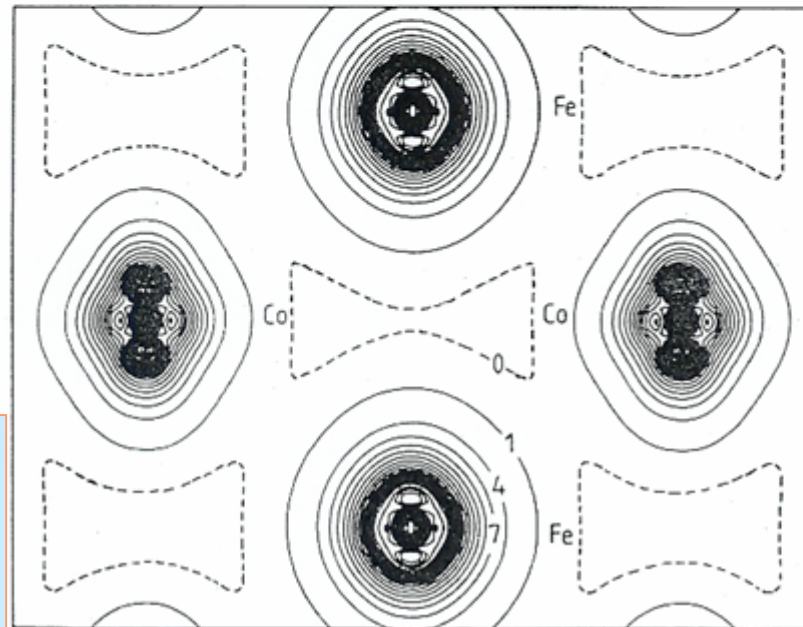
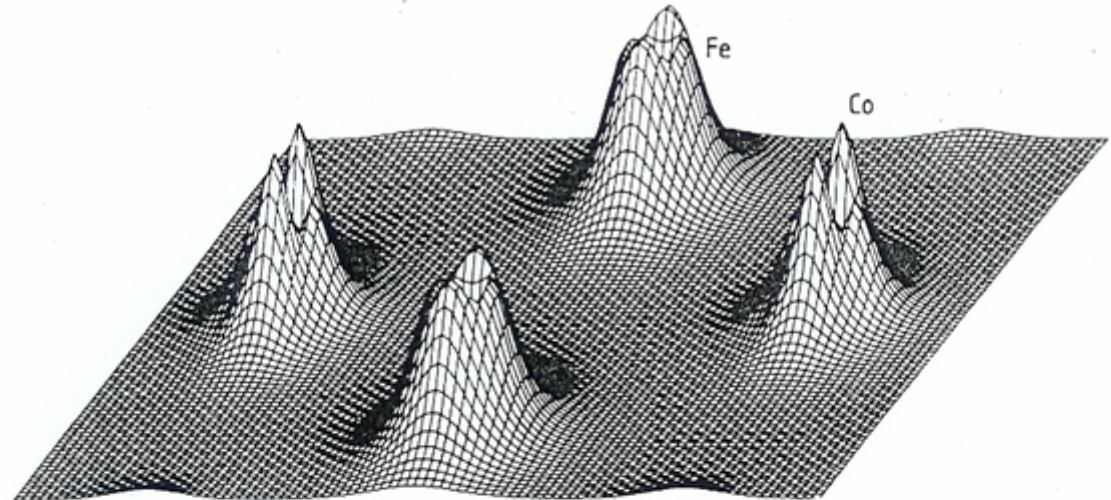
Itinerant or localized?



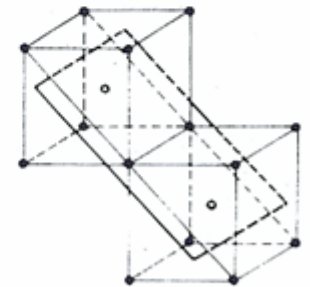
- Magnetization density difference between
 - Majority spin
 - Minority spin

$$m(r) = \rho^\uparrow(r) - \rho^\downarrow(r)$$

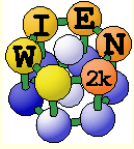
- Localized around
 - Fe and Co
 - slightly negative between the atoms
- Itinerant electrons



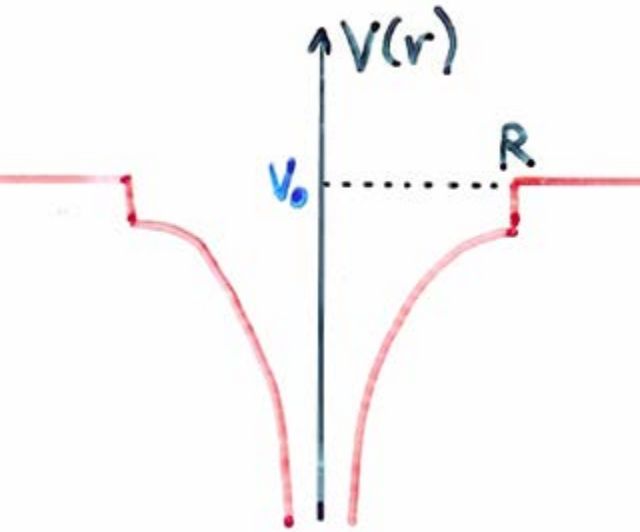
CsCl structure



K.Schwarz, P.Mohn, P.Blaha, J.Kübler,
*Electronic and magnetic structure of
 bcc Fe-Co alloys from band theory*,
 J.Phys.F:Met.Phys. **14**, 2659 (1984)



Bonding by Wigner delay time



$$V(r) = \begin{cases} V(r) & r \leq b, \\ 0 & r > b. \end{cases} \quad (1)$$

Inside such a sphere of radius b the radial Schrödinger equation (in Rydberg atomic units)

$$\left[-\frac{d^2}{dr^2} - \frac{2}{r} \frac{d}{dr} + \frac{l(l+1)}{r^2} + V(r) - \varepsilon \right] R_l(\varepsilon, r) = 0, \quad (2)$$

single scatterer (Friedel)

$V(r)=0$ solution:

$$S_l(r) = A_l [\overset{\text{Bessel}}{\downarrow} j_l(kr) \cos \eta_l(\varepsilon) - \overset{\text{Neumann}}{\downarrow} n_l(kr) \sin \eta_l(\varepsilon)], \quad (3)$$

R_l joined in value and slope defines phase shift :

$$\tan \eta_l(\varepsilon) = \frac{R_l(\varepsilon, b) j'_l(kb) - j_l(kb) R'_l(\varepsilon, b)}{R_l(\varepsilon, b) n'_l(kb) - n_l(kb) R'_l(\varepsilon, b)}, \quad (4)$$

Friedel sum

$$N(\varepsilon) = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \eta_l(\varepsilon),$$

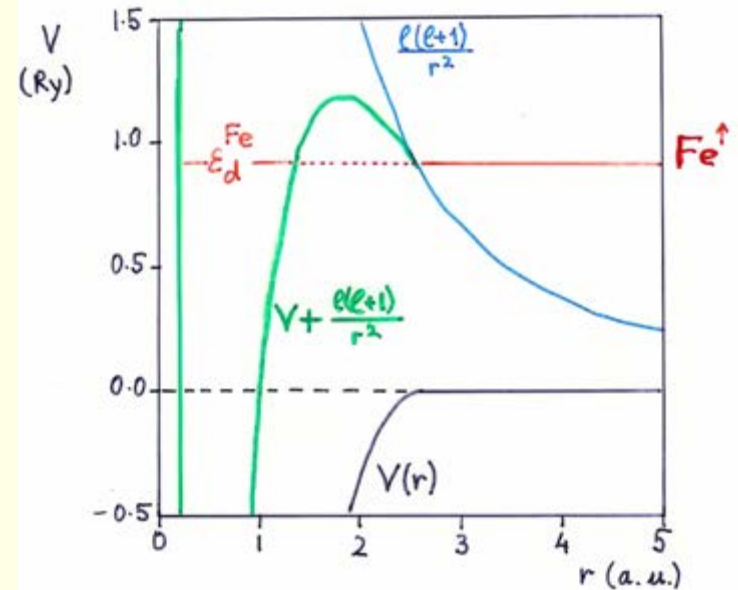
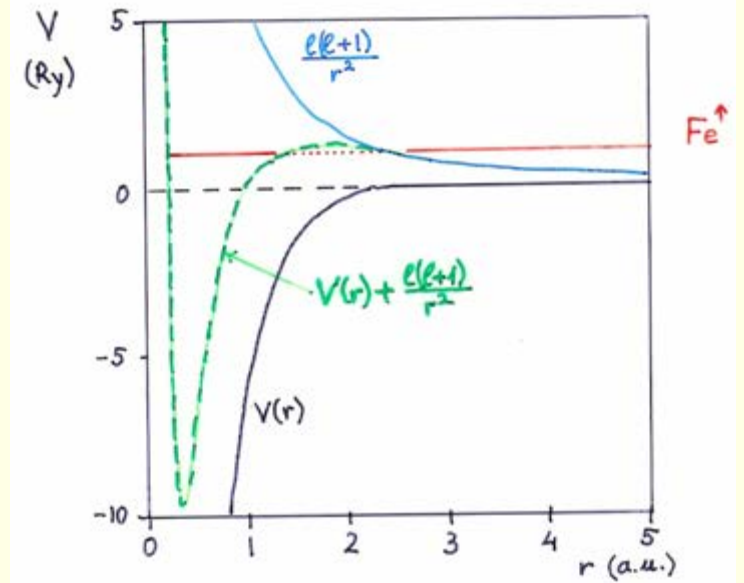
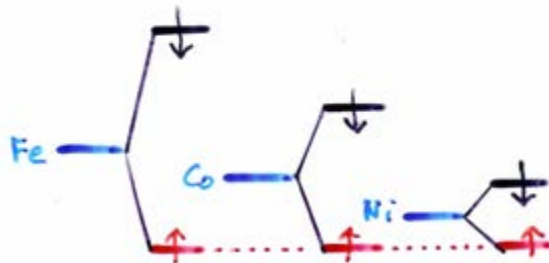
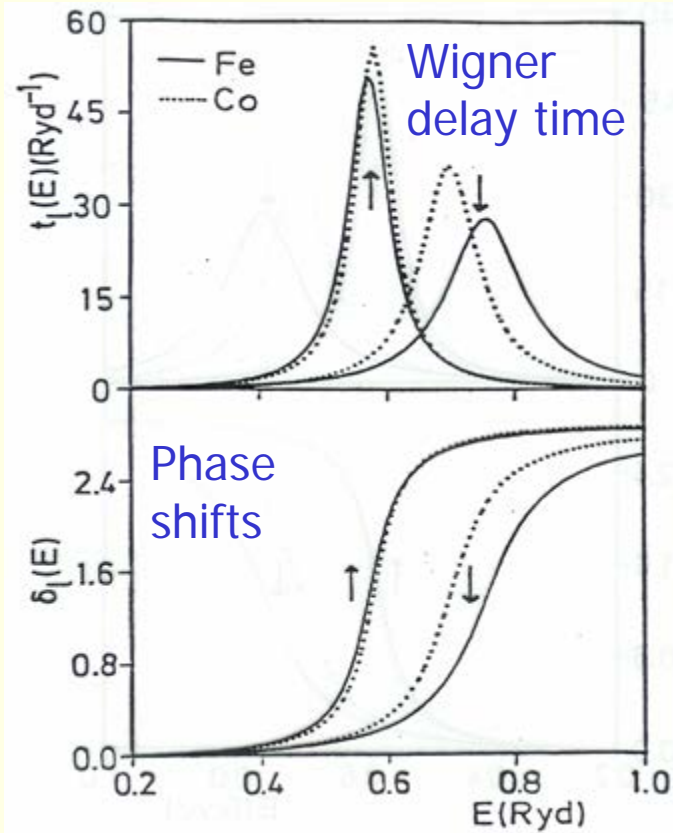
Wigner delay time

$$n(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon} = \frac{1}{\pi} \sum_{l=0}^{\infty} (2l+1) t_l^D(\varepsilon). \quad (6)$$



Phase shifts, Wigner delay times of Fe, Co, Ni

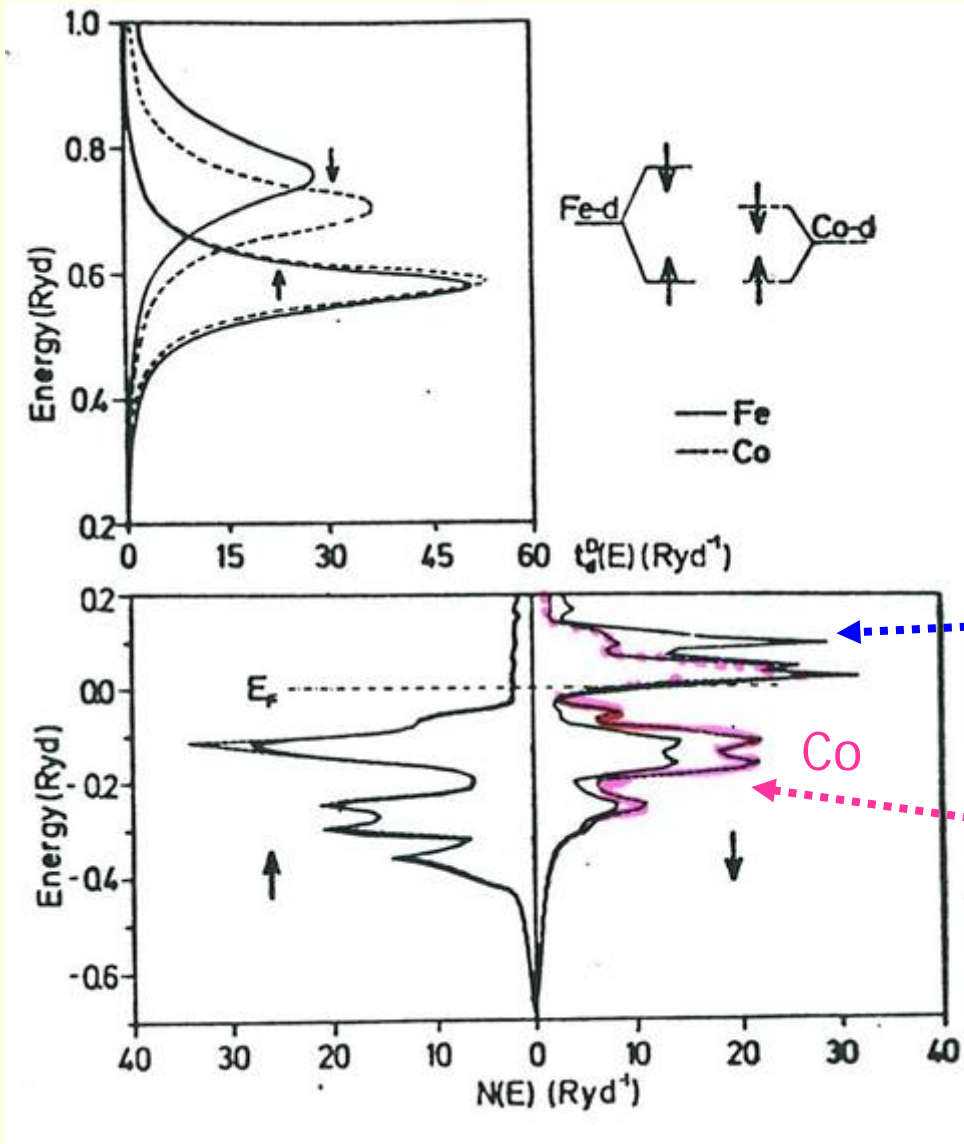
resonance states





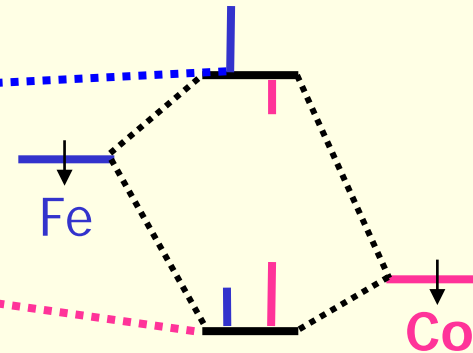
Covalent magnetism in FeCo

Wigner delay time



- For spin up
 - *Fe and Co equivalent*
 - *partial DOS similar*
 - *typical bcc DOS*
- For spin down
 - *Fe higher than Co*

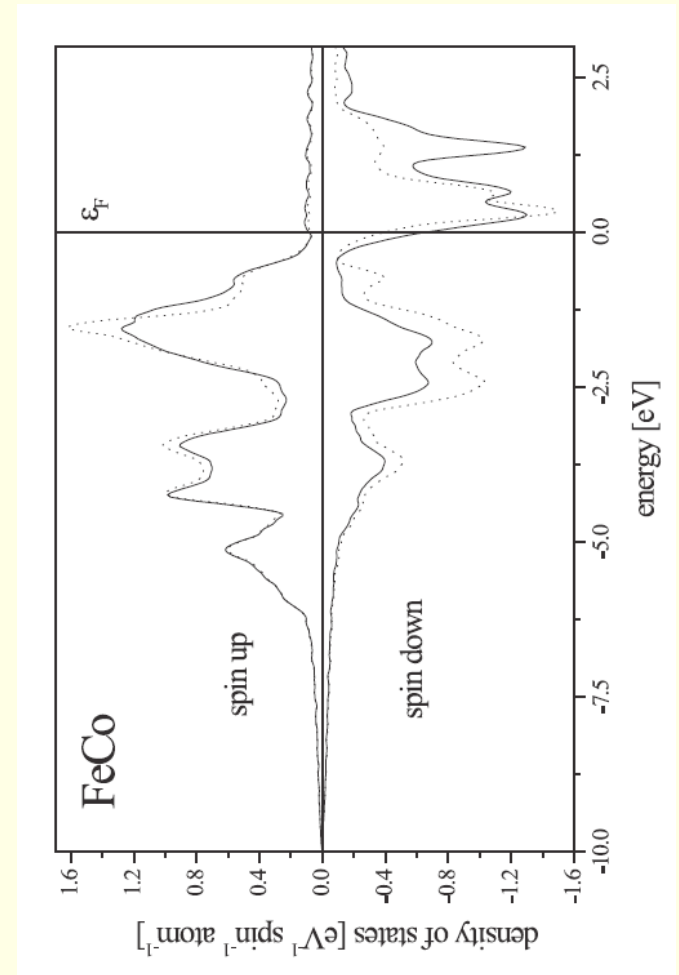
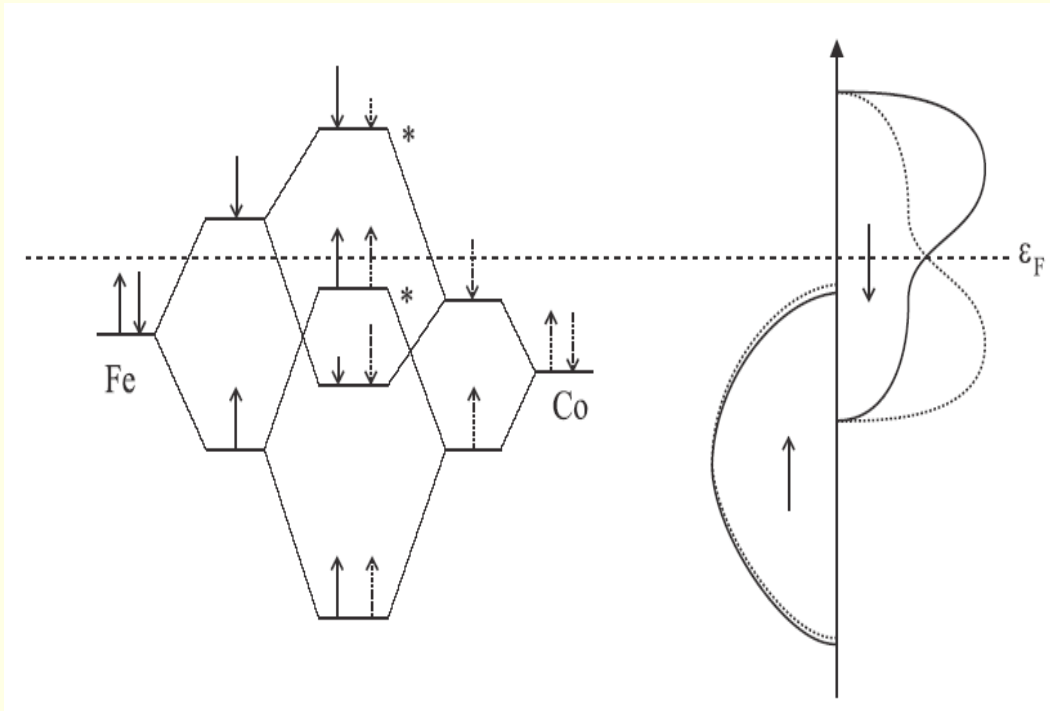
antibonding



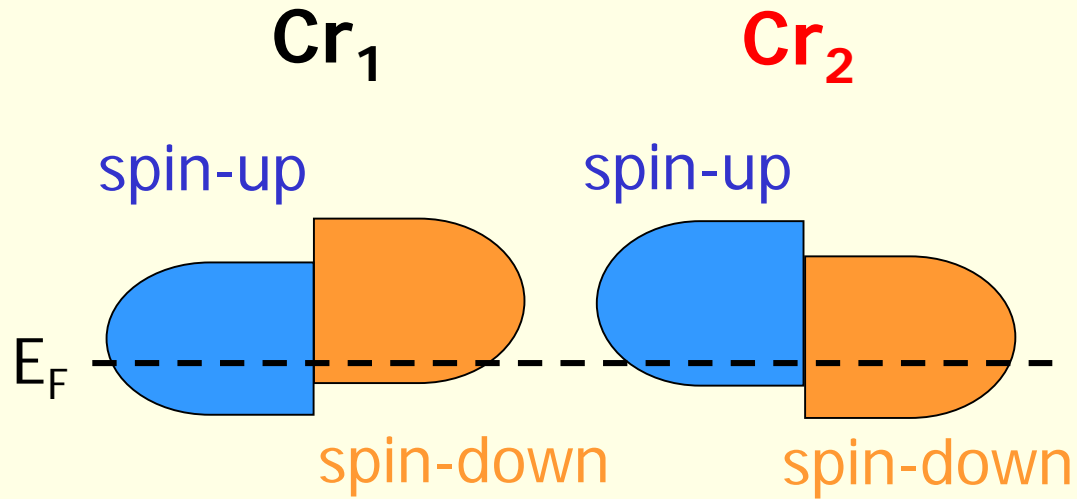
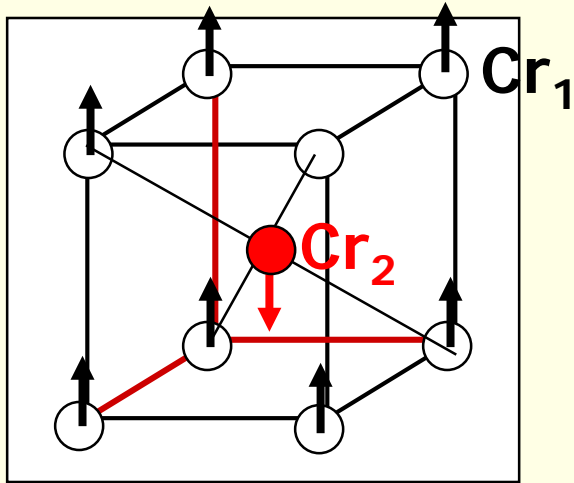
bonding

No charge transfer between Fe and Co

Covalent magnetism, FeCo:



- Cr has AFM bcc structure

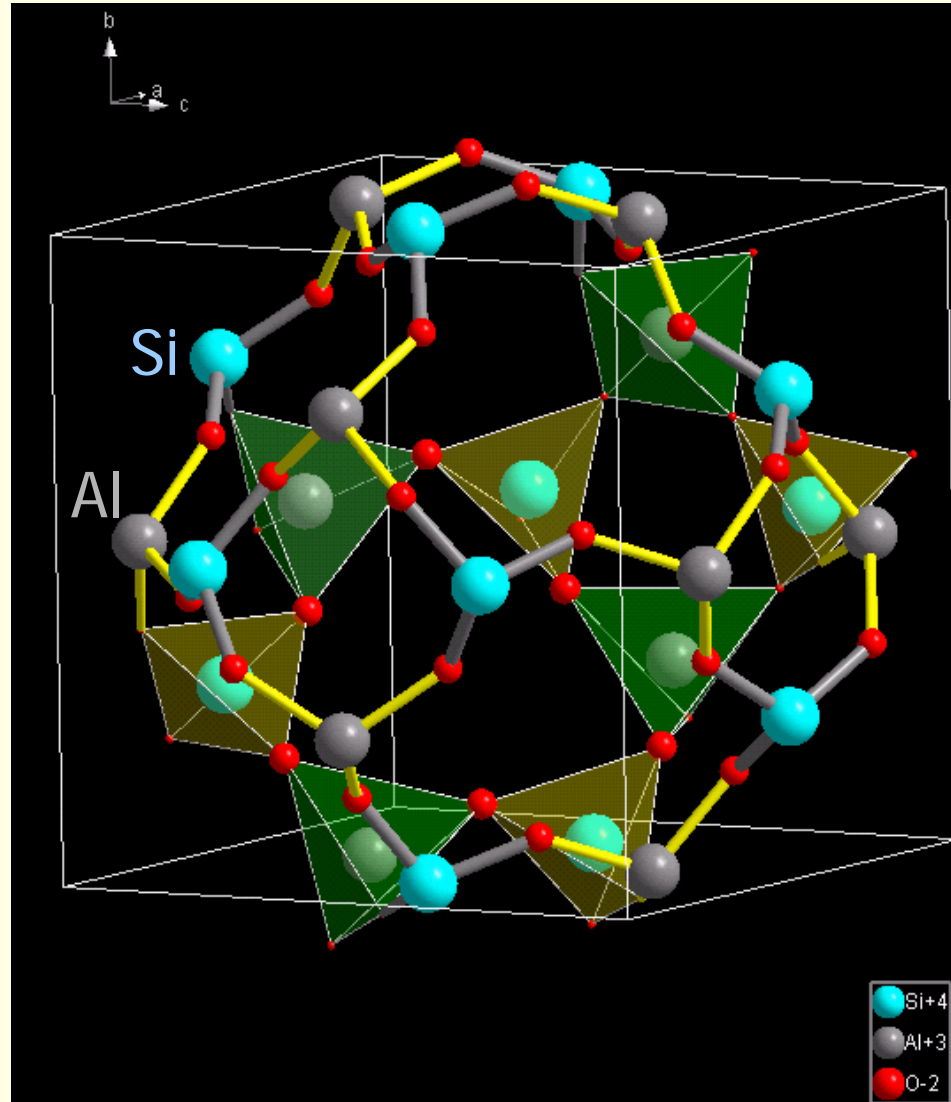


- There is a symmetry
it is enough to do the spin-up
calculation
spin-down can be copied

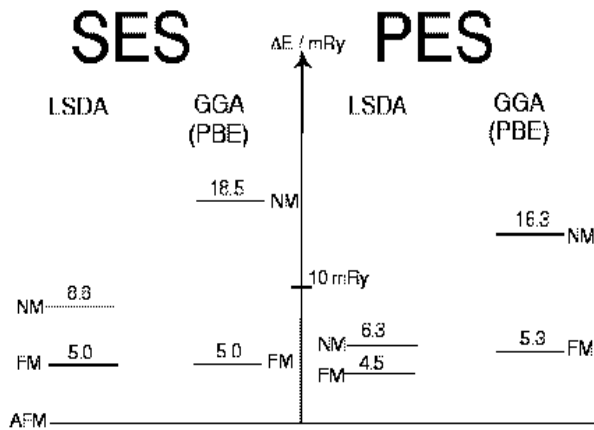
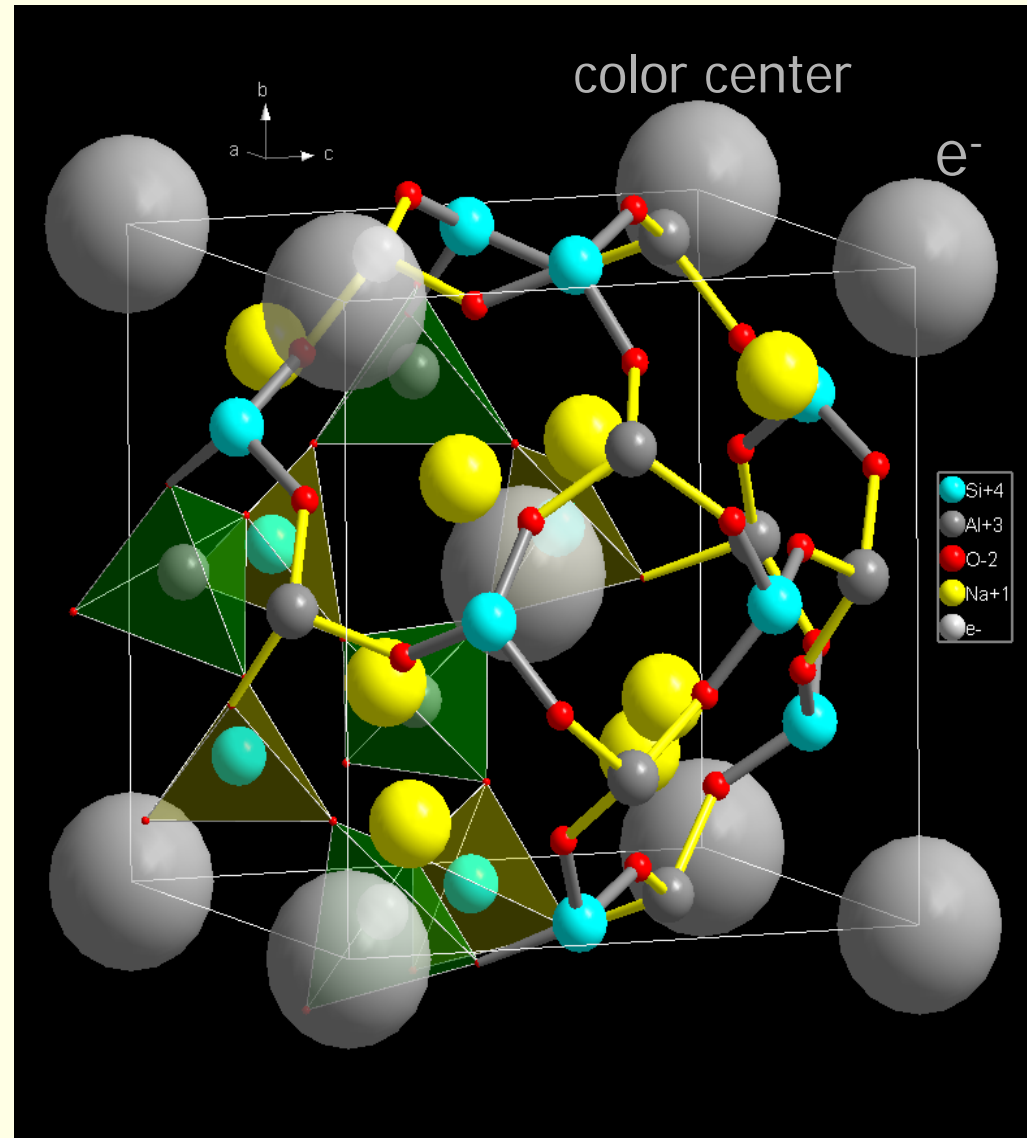
$$\text{Cr}_1 \downarrow = \text{Cr}_2 \uparrow$$

$$\text{Cr}_2 \downarrow = \text{Cr}_1 \uparrow$$

- Al-silicate
- corner shared
 - SiO_4 tetrahedra
 - AlO_4 tetrahedra
- β cage
- Al / Si ratio 1
- alternating
- ordered (cubic)
- 3 e⁻ per cage



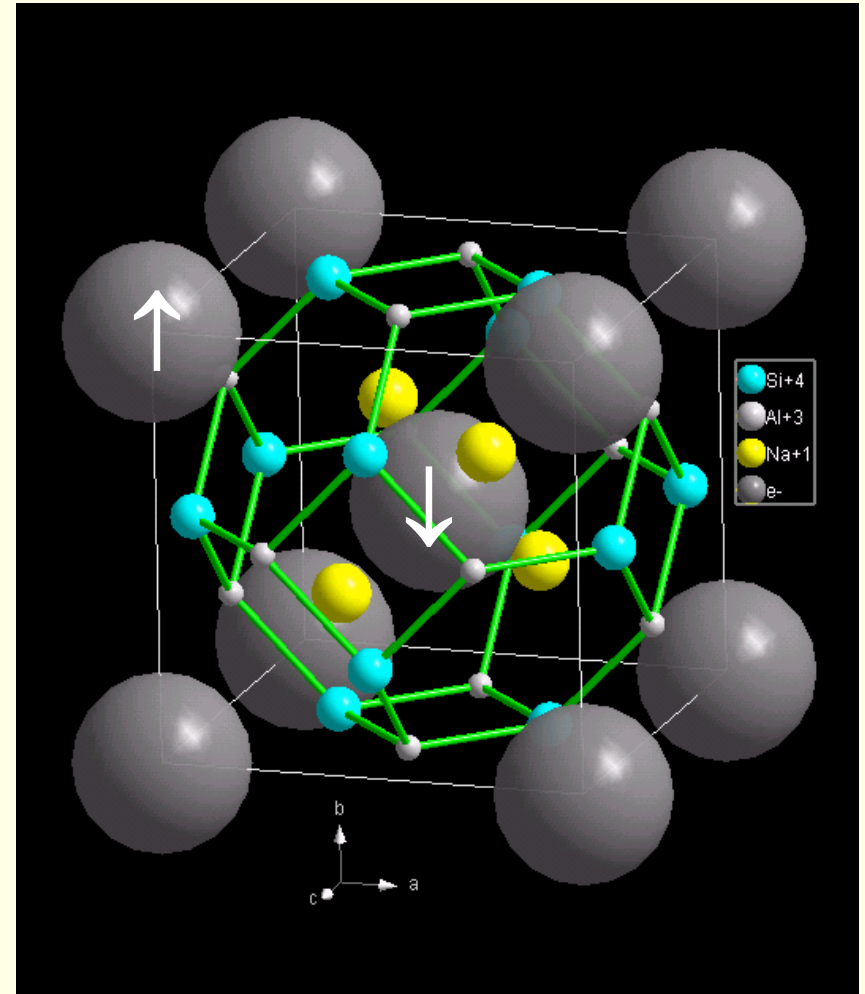
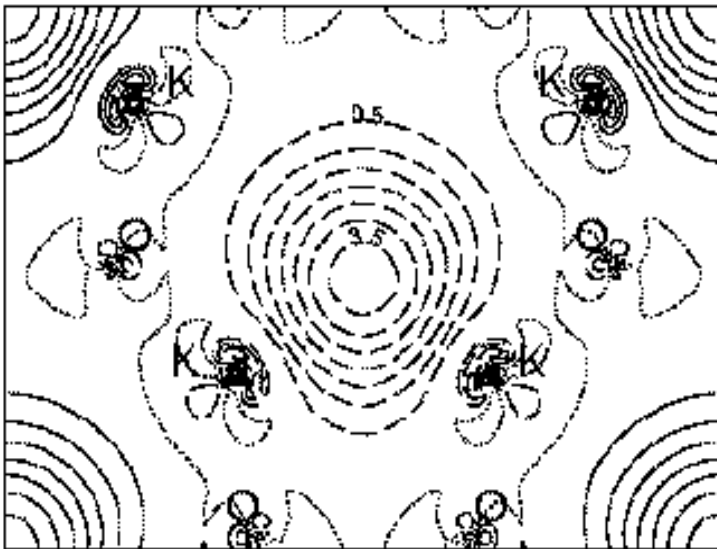
- **Si-Al zeolite (sodalite)**
 - *Formed by corner-shared SiO_4 and AlO_4 tetrahedra*
- **Charge compensated by doping with**
 - *4 Na^+*
 - *one e^- (color center)*
- **antiferromagnetic (AFM) order of e^-**



Energy (relative stability)

AFM order between
color centers (e^-)

Spin density $\rho^\uparrow - \rho^\downarrow$



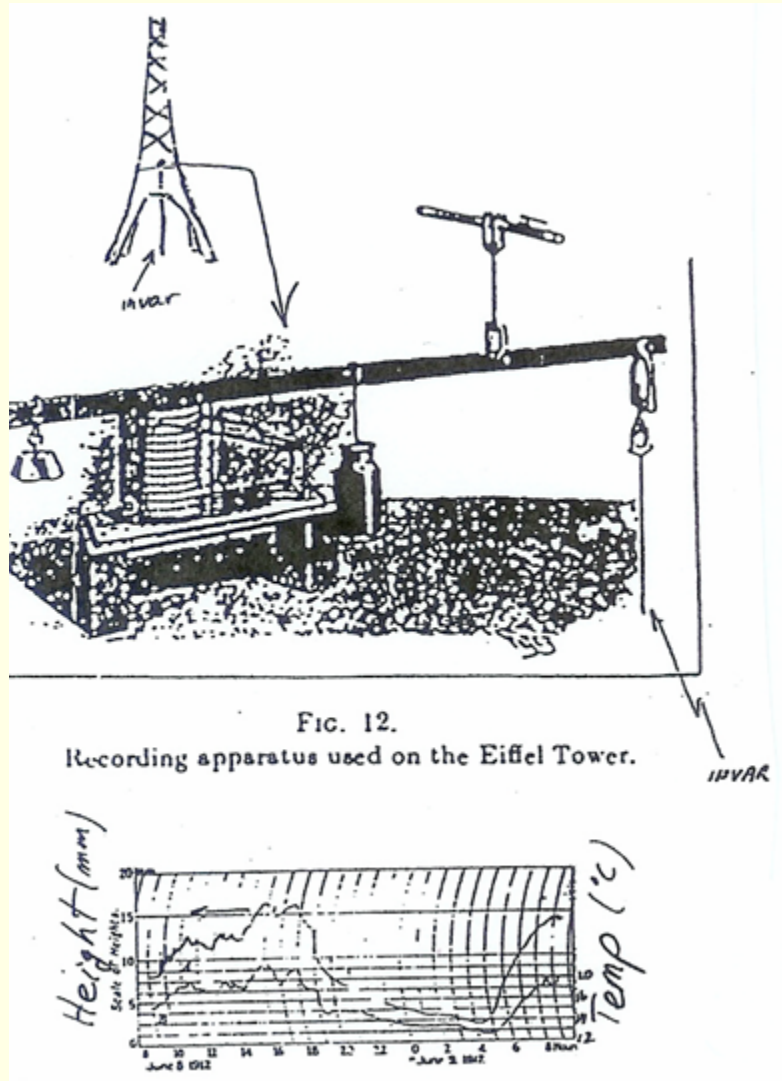
*G.K.H. Madsen, Bo B. Iversen, P. Blaha, K. Schwarz,
Phys. Rev. B 64, 195102 (2001)*



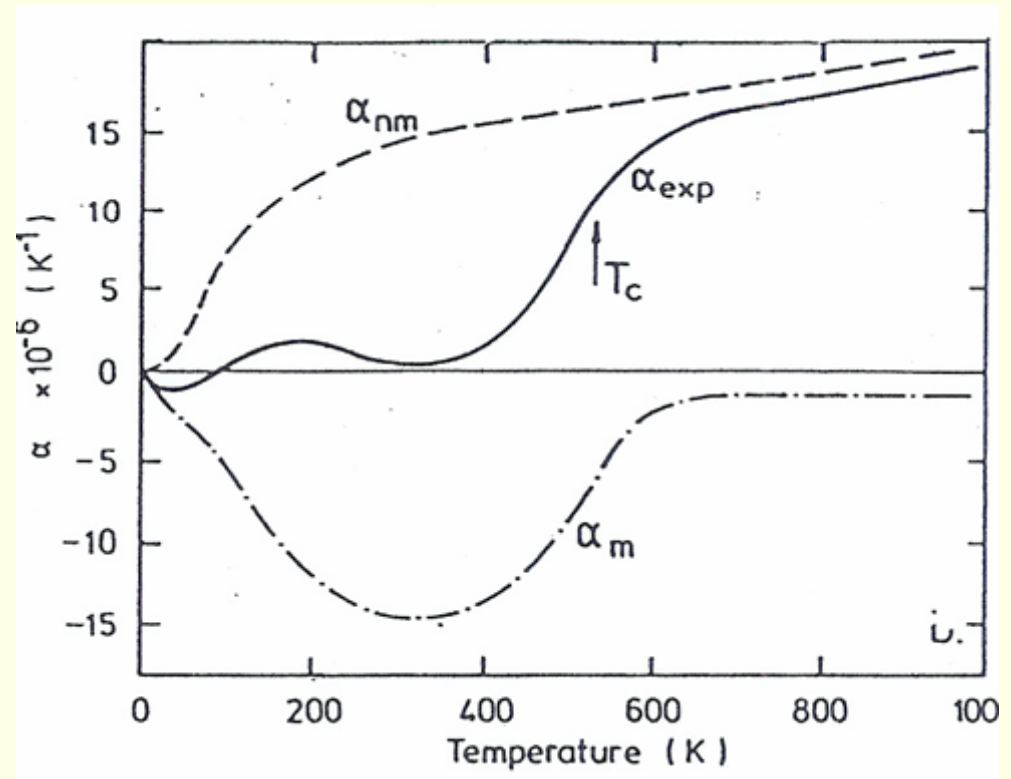
INVAR alloys (invariant)



- e.g. Fe-Ni
- Such systems essentially show **no thermal expansion** around room temperature



- The thermal expansion of the Eiffel tower
- Measured with a rigid Fe-Ni INVAR wire
- The length of the tower correlates with the temperature
- **Fe₆₅Ni₃₅** alloy has vanishing thermal expansion around room temperature

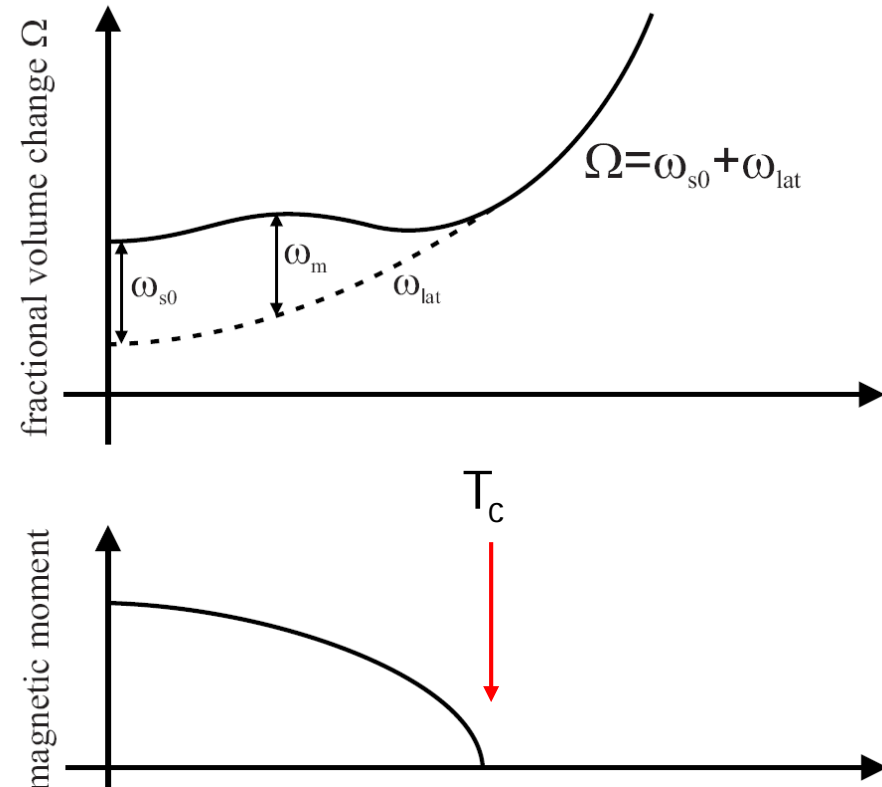


Ch.E.Guillaume (1897)

What is magnetostriction?

Magnetostriction ω_{s0} is the difference in volume between the volume in the magnetic ground state and the volume in a hypothetical non-magnetic state.

Above the Curie temperature the magnetic contribution ω_m vanishes.

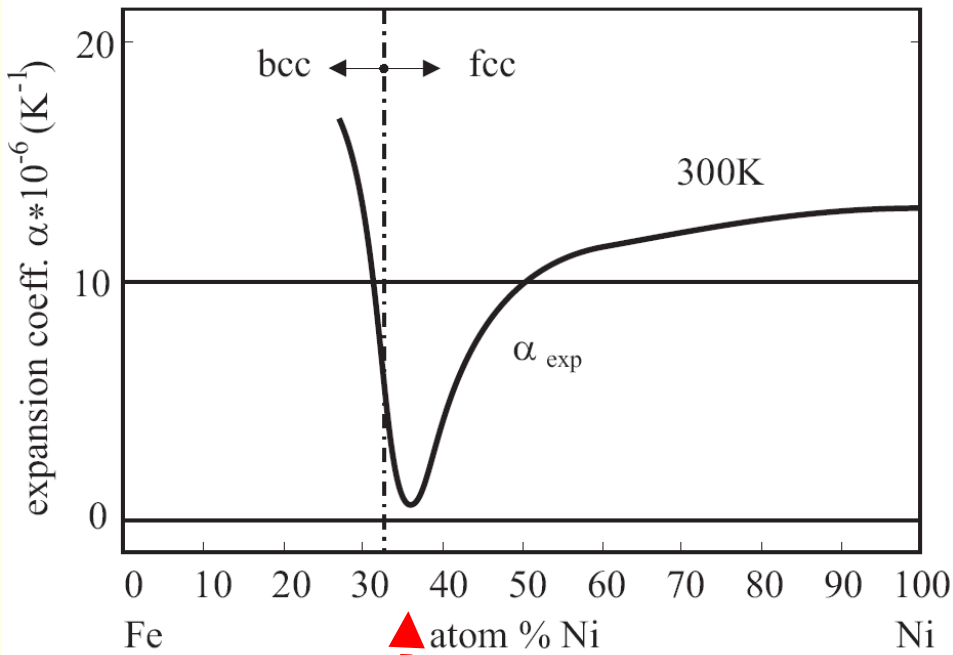




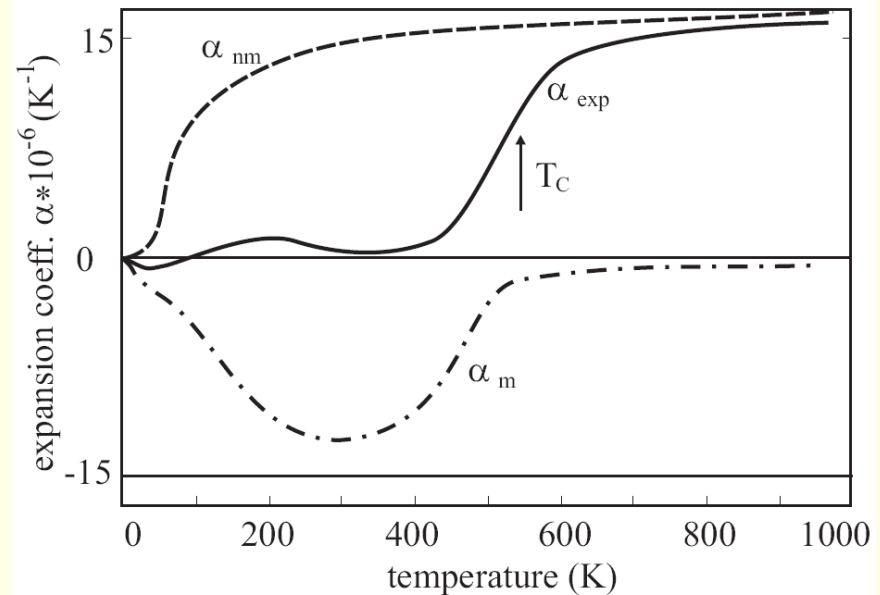
Fe-Ni Invar alloys



„classical“ Fe-Ni Invar



- **Fe₆₅Ni₃₅** alloy has vanishing thermal expansion around room temperature





Early explanations of INVAR

R.J.Weiss
Proc.Roy.Phys.Soc (London) **32**, 281 (1963)

fcc Fe

low spin

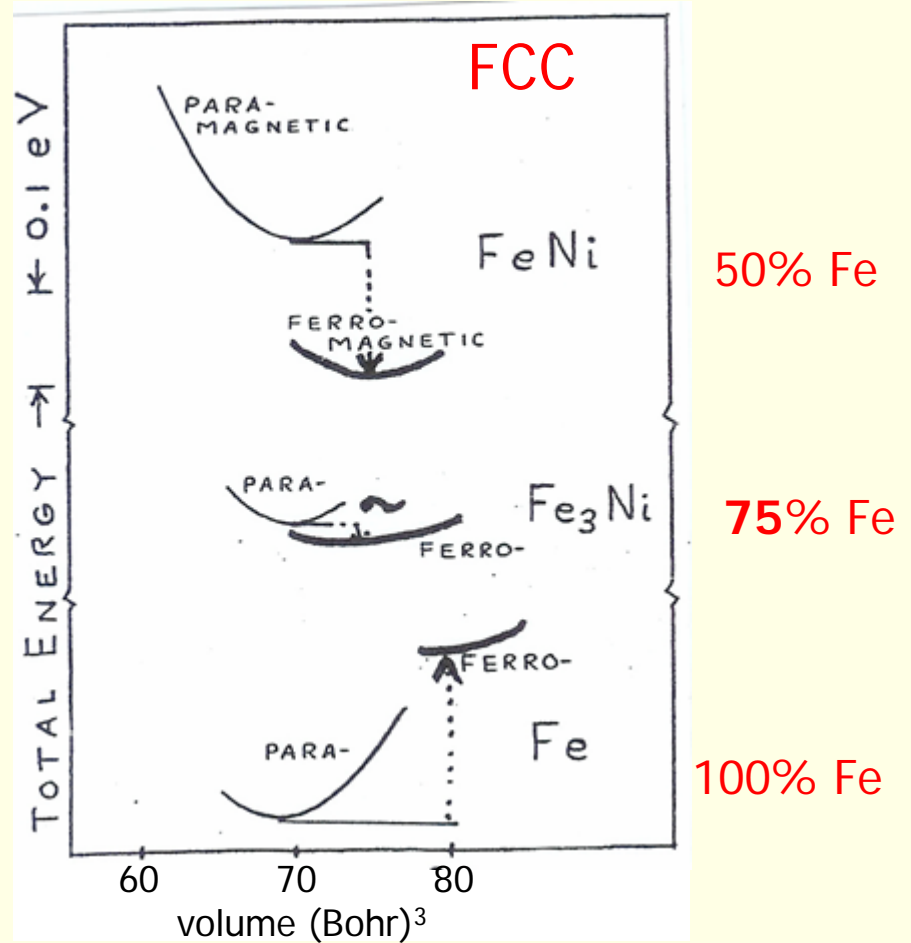
$m=0.5 \mu_B$ AF
 $a = 3.57 \text{ \AA}$

high spin

$m=2.8 \mu_B$ FM
 $a = 3.64 \text{ \AA}$

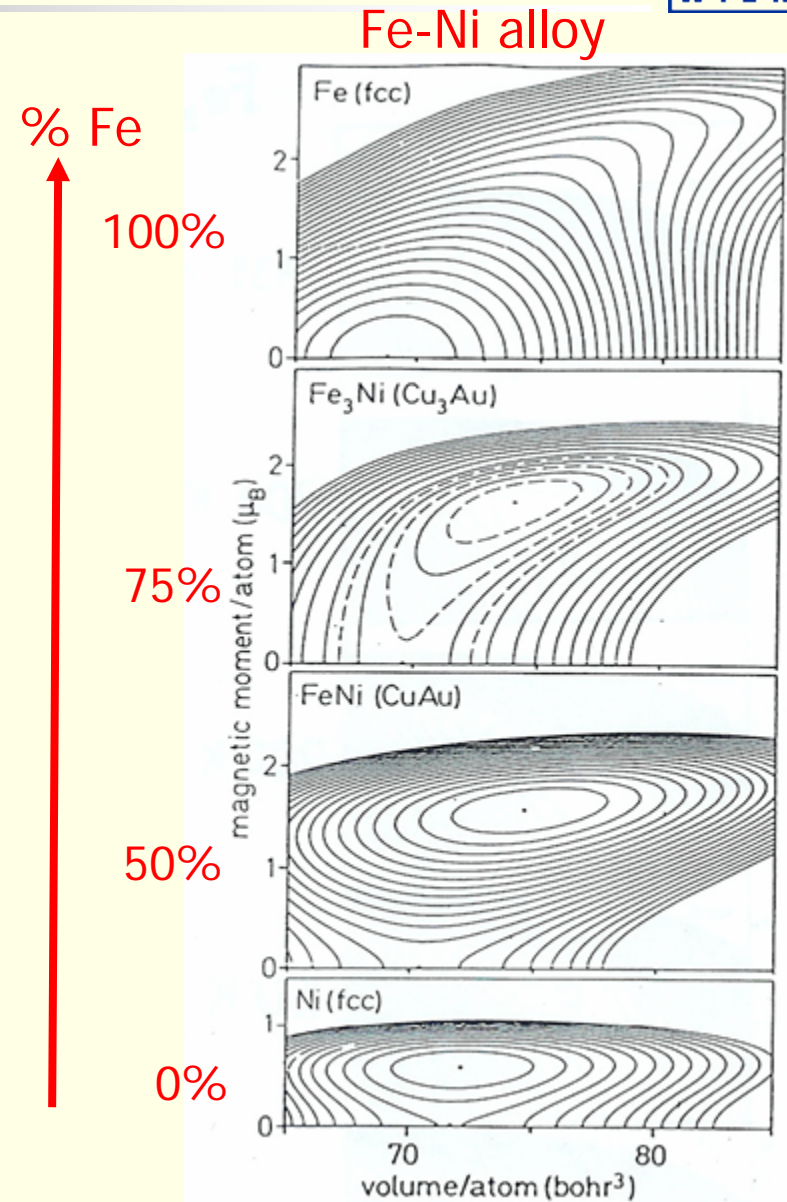
small moment
small volume Y_1 AF

kT high moment
large volume Y_2 FM



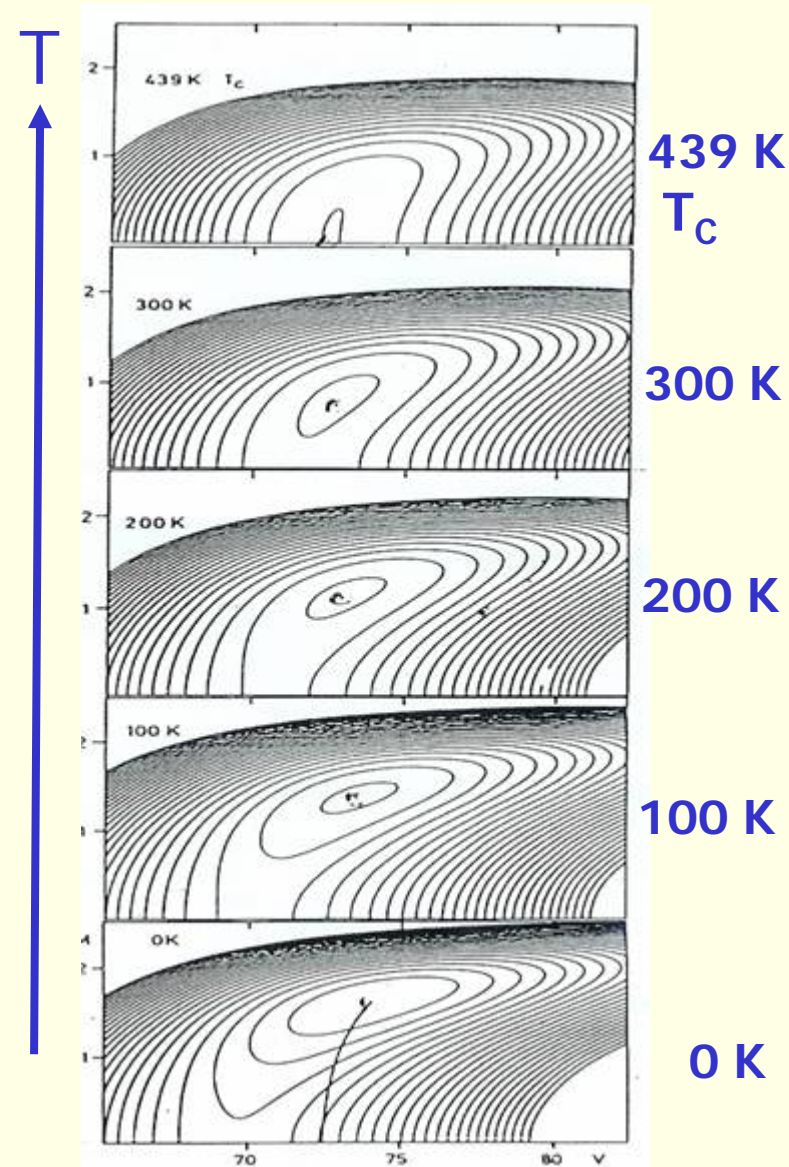
A.R.Williams, V.L.Moruzzi, G.D.Gelatt Jr., J.Kübler, K.Schwarz,
Aspects of transition metal magnetism,
J.Appl.Phys. **53**, 2019 (1982)

- This fcc structure
 - from *non magnetic Fe (fcc)*
 - to *ferromagnetic Ni*
 - as the composition changes
- At the INVAR composition
 - There is a flat energy surface
 - as function of volume and moment



- Energy surface at $T=0$ (DFT)
 - as a function of volume and moment
 - using fixed spin moment (FSM) calculations
- Finite temperature
 - Spin and volume fluctuations
 - Ginzburg-Landau model

$$H = V^{-1} \int d^3r (E(\mathbf{M} + \underline{\mathbf{m}}(\mathbf{r})), V + \underline{v}(\mathbf{r})) + \frac{C}{2} \sum_{ij} (\underline{\nabla}_j \mathbf{m}_i)^2 + \frac{D}{2} (\underline{\nabla} v(\mathbf{r}))^2$$





- fixed spin moment (FSM)
e.g. **Fe-Ni alloy**
- allows to explore **energy surface** $E(V, M)$
as function of
 - *volume* V
 - *magnetic moment* M



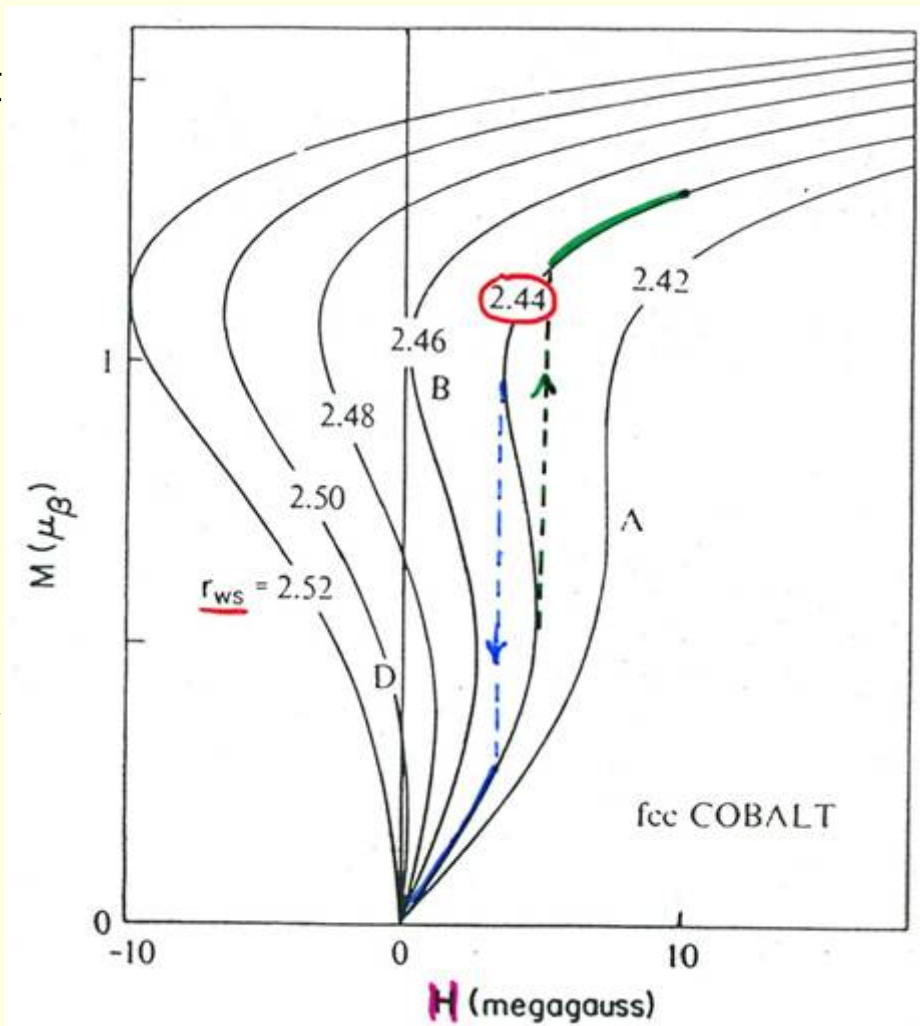
Fixed spin moment (FSM) method

- There are systems (e.g. like fcc Fe or fcc Co), for which the magnetization shows a **hysteresis**, when a magnetic field is applied (at a volume V).
- The volume of the unit cell defines the Wigner-Seitz radius r_{ws}

$$V = \frac{4\pi r_{ws}^3}{3}$$

- The **hysteresis** causes numerical difficulties, since there are several solutions (in the present case 3 for a certain field H).
- In order to solve this problem the **FSM method** was invented

Hysteresis





Fixed spin moment (FSM) method

Conventional scheme

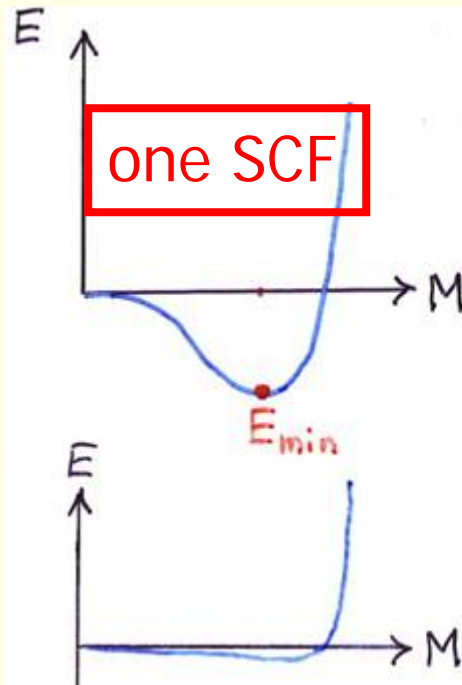
$$E_F^\uparrow = E_F^\downarrow$$

$$Z_v = N^\uparrow + N^\downarrow$$

output

$$M = N^\uparrow - N^\downarrow$$

Simple case:
bcc Fe



difficult case:
 Fe_3Ni

poor convergence

constrained (FSM) method

$$E_F^\uparrow \neq E_F^\downarrow$$

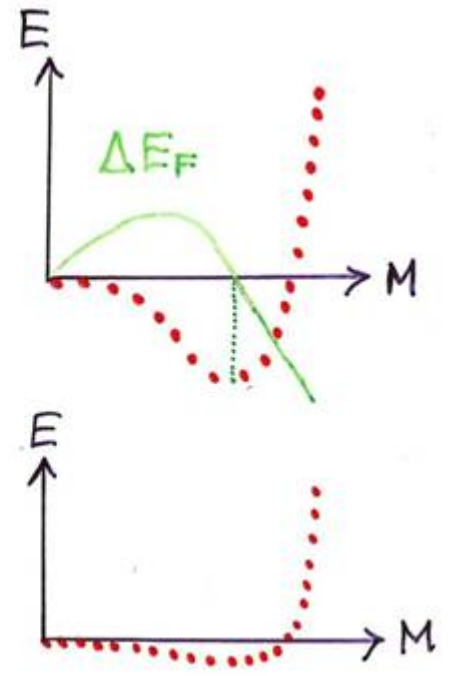
$$Z_v = N^\uparrow + N^\downarrow$$

output

$$M = N^\uparrow - N^\downarrow$$

input

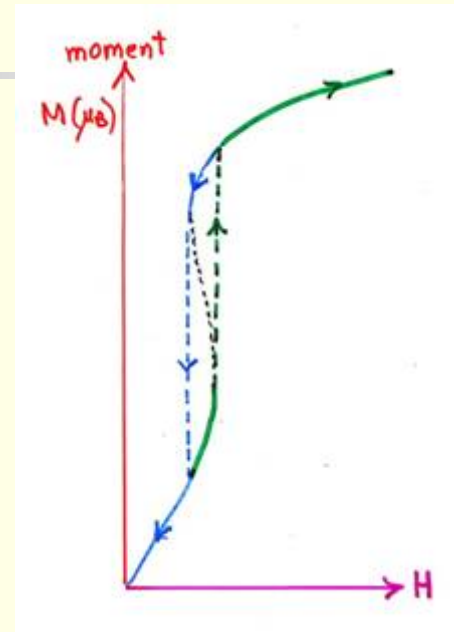
many
calculations



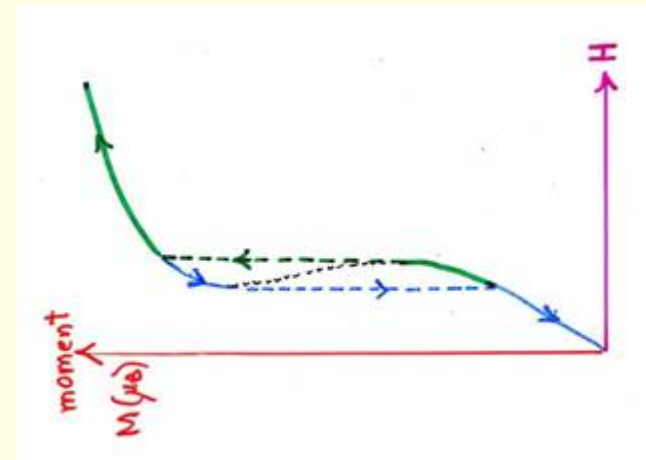
good convergence



- **Physical situation:**
 - *One applies a field H and obtains M*
 - *but this functions can be multivalued*



- **Computational trick (unphysical):**
 - *One interchanges the dependent and independent variable*
 - *this function is single valued (unique)*
 - *i.e. one chooses M and calculates H afterwards*





FSM key references



A.R.Williams, V.L.Moruzzi, J.Kübler, K.Schwarz,
Bull.Am.Phys.Soc. **29**, 278 (1984)

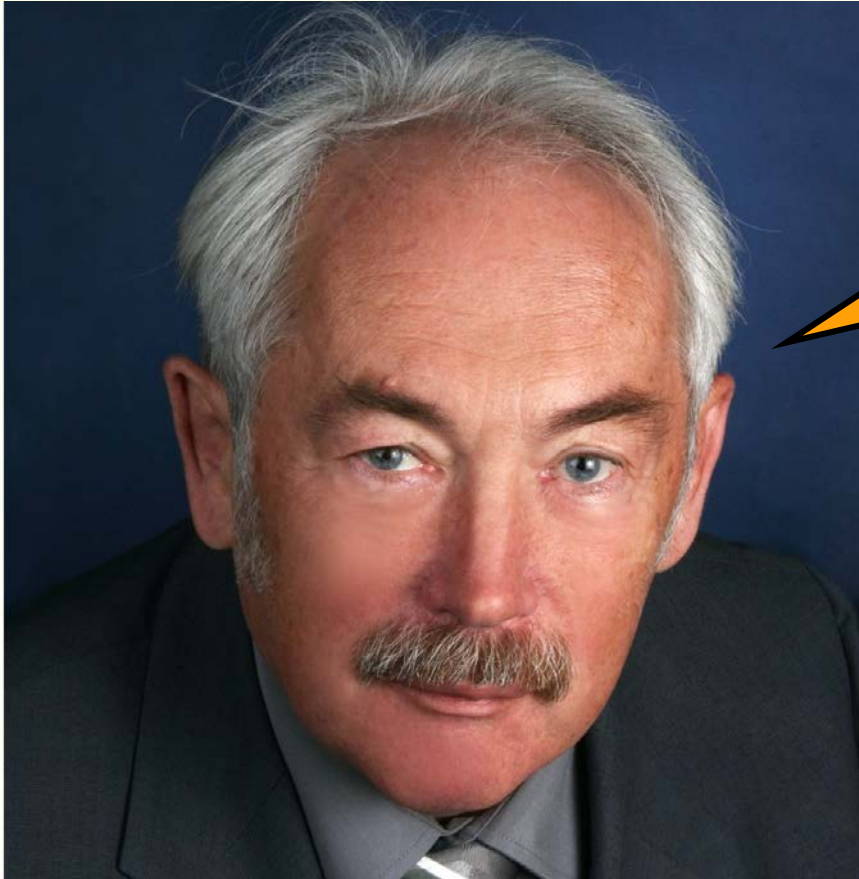
K.Schwarz, P.Mohn
J.Phys.F **14**, L129 (1984)

P.H.Dederichs, S.Blügel, R.Zoller, H.Akai,
Phys. Rev, Lett. **53**,2512 (1984)



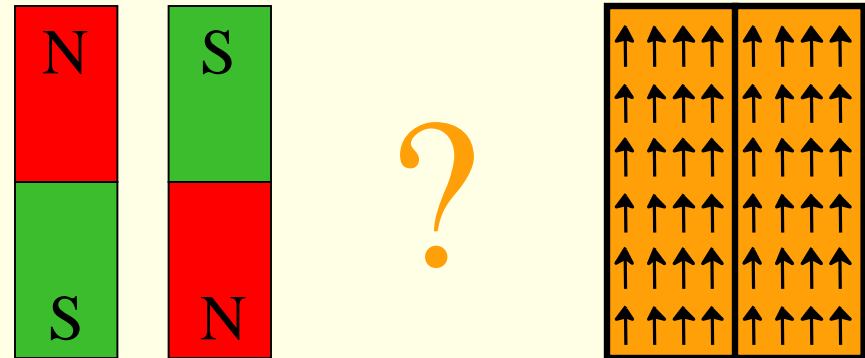
- GMR (Giant Magneto Resistance)
- half-metallic systems
e.g. CrO_2
- important for **spintronics**

Once upon a time, in the early 1980's ...



Peter Grünberg

“What happens if I bring two ferromagnets close –I mean *really* close– together?”





Giant magnetoresistance (GMR)



Ferromagnet
Metal
Ferromagnet

Electrical
resistance:

R_P

<(>)

R_{AP}

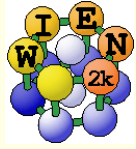
The electrical resistance depends on the **relative magnetic alignment** of the ferromagnetic layers

$$\text{GMR} = \frac{R_{AP} - R_P}{R_P}$$

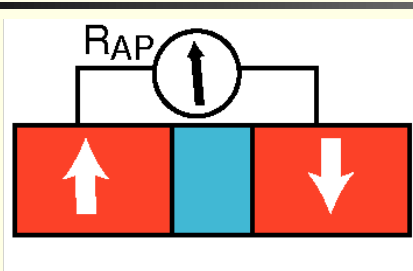
19% for trilayers @RT

80% for multilayers @ RT

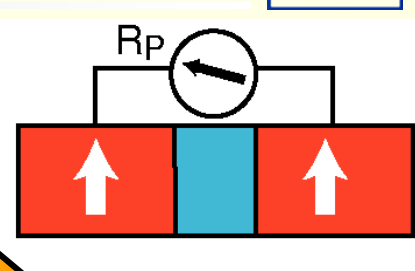
GMR is much **larger than the anisotropic magnetoresistance (AMR)**



1988: ... simultaneously, but independent ...



“Does the electrical resistance depend on the magnetization alignment?”



Albert Fert



Peter Grünberg



KUNGL.
VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES



The Nobel Prize in Physics 2007



This year's Nobel Prize in Physics is awarded to Albert Fert and Peter Grünberg for their discovery of Giant Magnetoresistance. Applications of this phenomenon have revolutionized techniques for retrieving data from hard disks.

Scientific Background on the Nobel Prize in Physics 2007

<http://www.kva.se/>

Scientific background

The Discovery of Giant Magnetoresistance

compiled by the Class for Physics of the Royal Swedish Academy of Sciences

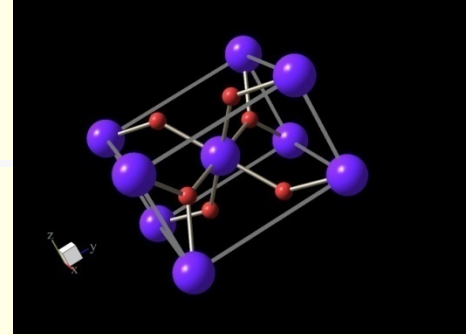
4. Half-metals

Since magnetoresistance deals with electrical conductivity it is obvious that it is the behaviour of the electrons at the Fermi surface (defined by the Fermi energy) which is of primary interest. The more spin-polarized the density of states (DOS) at the Fermi energy, i.e., the more $N_{\uparrow}(E_F)$ deviates from $N_{\downarrow}(E_F)$, the more pronounced one expects the efficiency of the magnetoelectronic effects to be. In this respect a very interesting class of materials consists of what are called half-metals, a concept introduced by de Groot and co-workers (23). Such a property was then predicted theoretically for CrO_2 by Schwarz in 1986 (24). The name half-metal originates from the particular feature that the spin down band is metallic while the spin up band is an insulator.

24. K. Schwarz, "CrO₂ predicted as a half-metallic ferromagnet", J. Phys. F, **16**, L211 (1986).



CrO₂ half-metallic ferromagnet

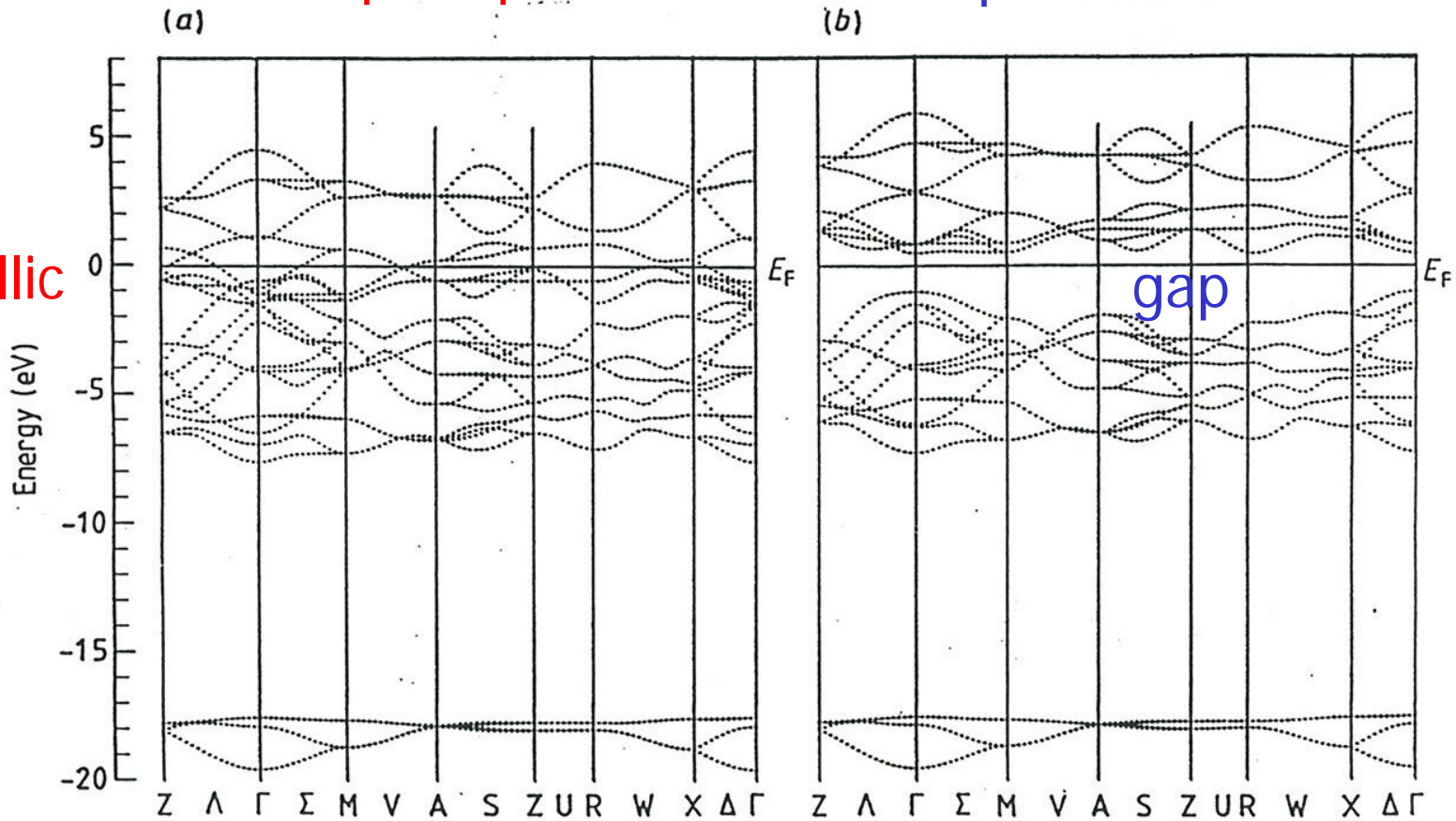


- CrO₂ (rutile structure)

spin-up

spin-down

metallic



important for spintronics



CrO₂ DOS

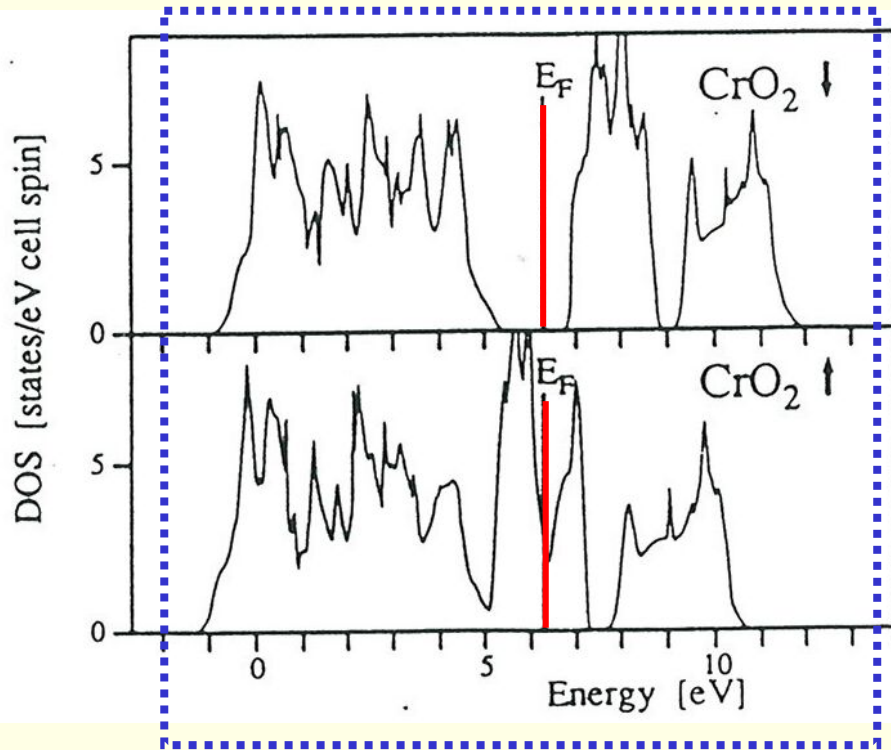


K.Schwarz,
*CrO₂ predicted as a
half-metallic ferromagnet,*
J.Phys.F:Met.Phys. **16**, L211 (1986)

The DOS features of CrO₂ are qualitatively like

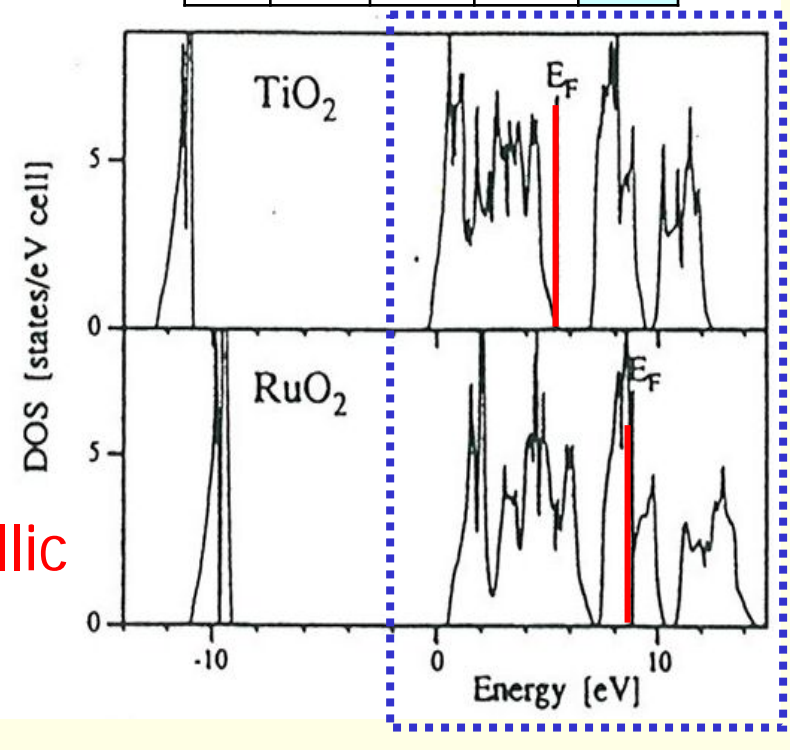
- TiO₂ (for spin-down)
- RuO₂ (for spin-up)

	4	5	6	7	8
spin ↓	Ti	V	Cr	Mn	Fe
spin ↑	Zr	Nb	Mo	Tc	Ru



gap

metallic



all three compound crystallize in the rutile structure

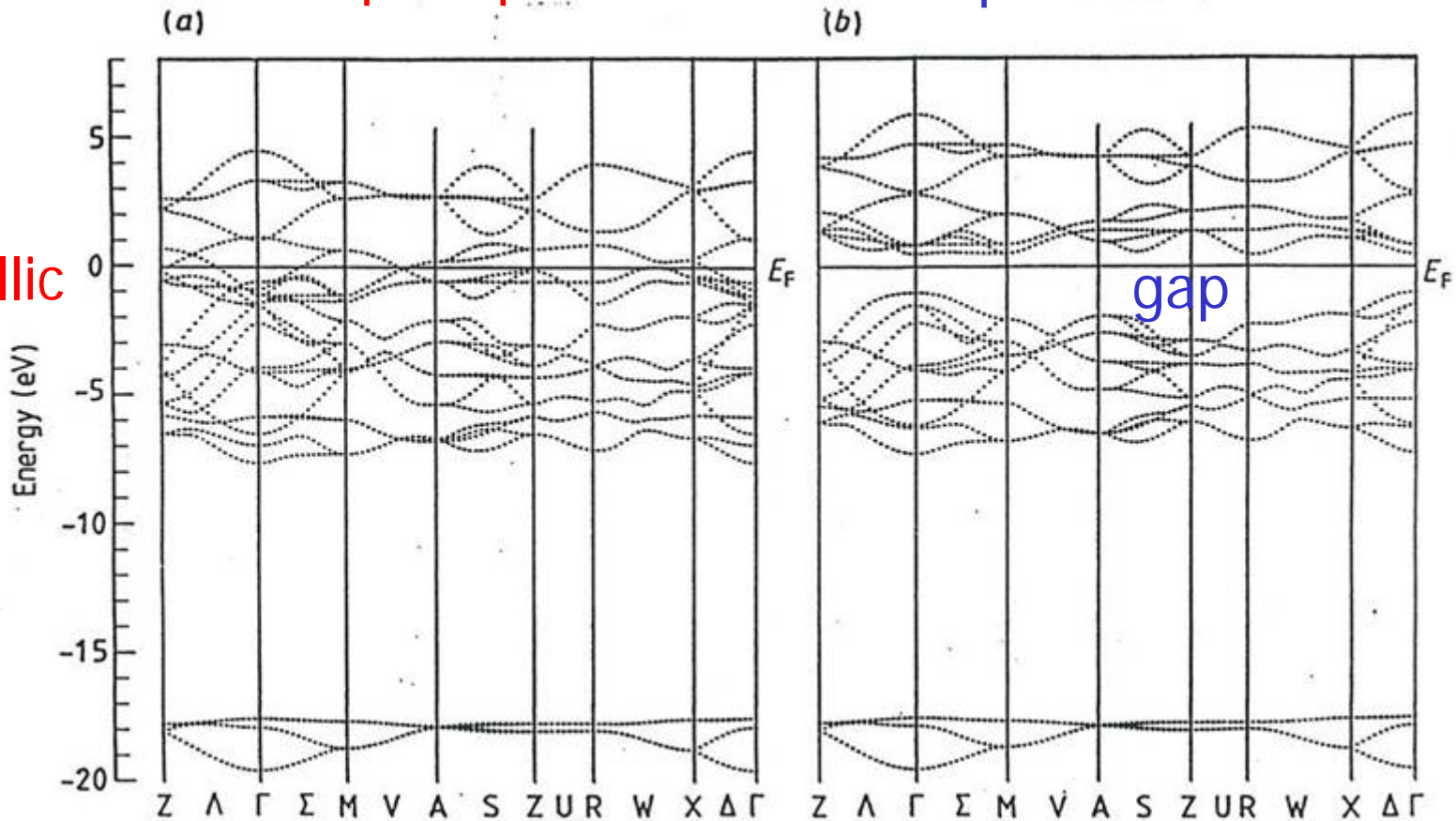
- CrO₂ (rutile structure)

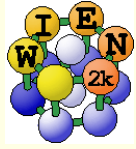
spin-up

spin-down

metallic

gap





CrO₂ spin-down (TiO₂) spin-up (RuO₂)



Atomic number

Symbol

Atomic weight

Metal
 Semimetal
 Nonmetal

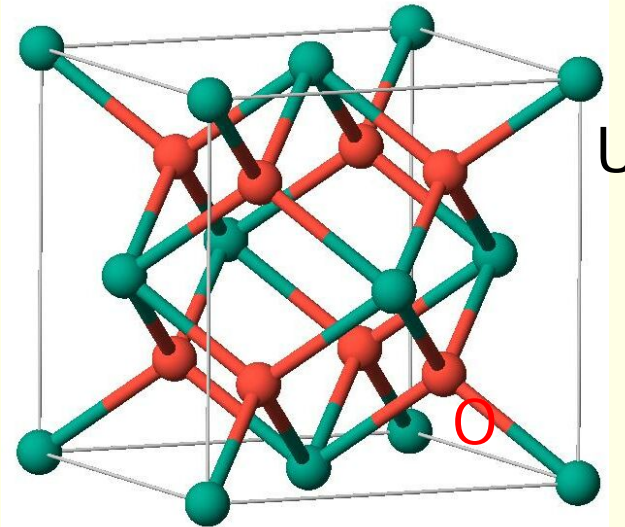
1	2											13	14	15	16	17	18
1 H 1.008												5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3 Li 6.941	4 Be 9.012											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn 222.0
55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	113 Uut	114 Uuq 289	115 Uup	116 Uuh 289	117 Uus	118 Uuo 293
87 Fr 223.0	88 Ra 226.0	103 Lr 262.1	104 Rf 261.1	105 Db 262.1	106 Sg 263.1	107 Bh 264.1	108 Hs 265.1	109 Mt 268	110 Uun 269	111 Uuu 272	112 Uub 277						
		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0		
		89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 251.1	99 Es 252.0	100 Fm 257.1	101 Md 258.1	102 No 259.1		

- R.Laskowski
- G.K.H.Madsen
- P.Blaha
- K.Schwarz



■ topics

- *non-collinear magnetism*
- *spin-orbit coupling*
- *LDA+U (correlation of U-5f electrons)*
- *Structure relaxations*
- *electric field gradient (EFG)*

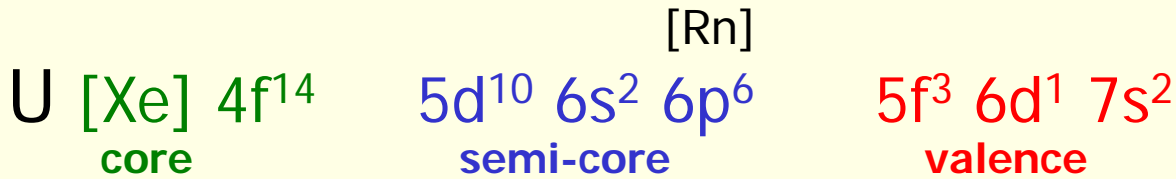


R.Laskowski, G.K.H.Madsen, P.Blaha, K.Schwarz:

Magnetic structure and electric-field gradients of uranium dioxide: An ab initio study
 Phys.Rev.B **69**, 140408-1-4 (2004)



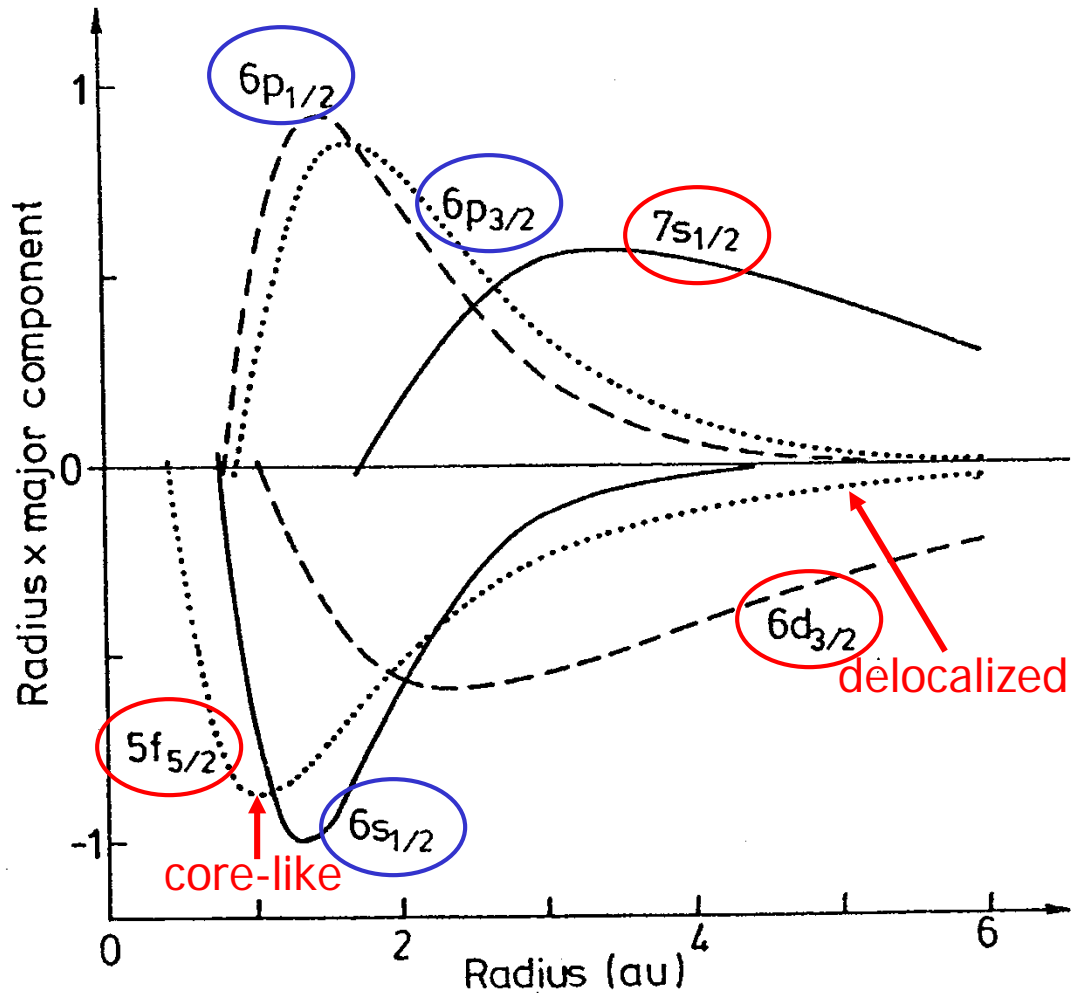
Atomic configuration of uranium (Z=92)



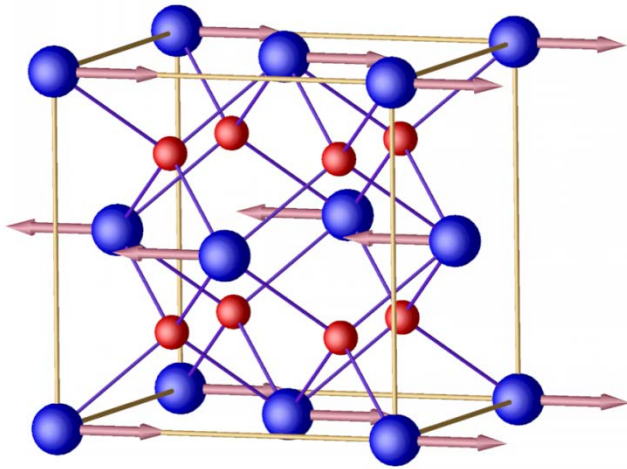
[Rn]

E_j (Ryd)

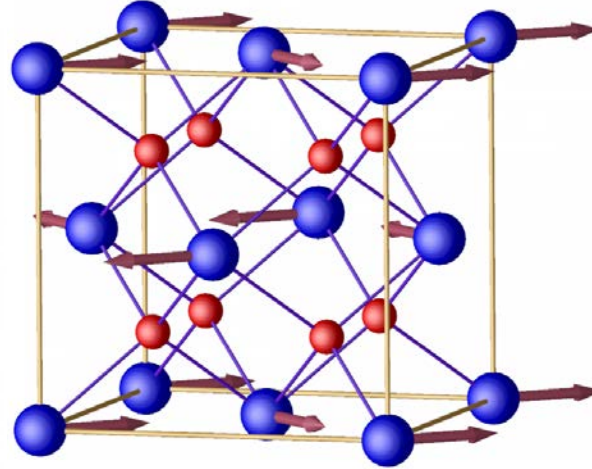
n l	j (relativ.)	
	l-s	l+s
7s		-0.25
6d	-0.29	-0.25
5f	-0.17	-0.11
6p	-1.46	-2.10
6s	-3.40	
5d	-7.48	-6.89
5p	-18.05	-14.06
5s		-22.57
4f	-27.58	-26.77
...		
1s		-8513.38



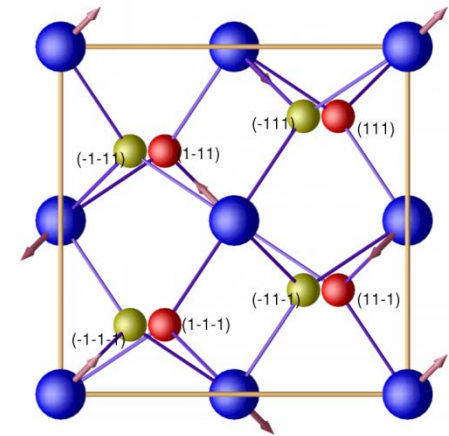
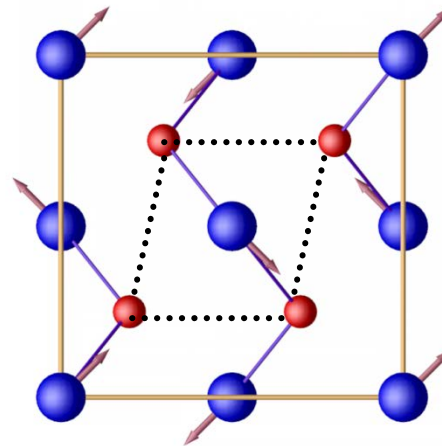
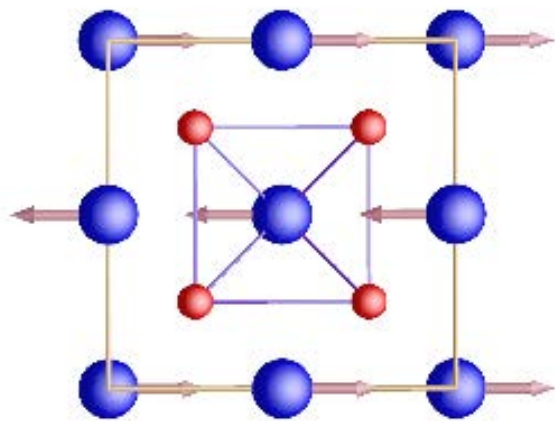
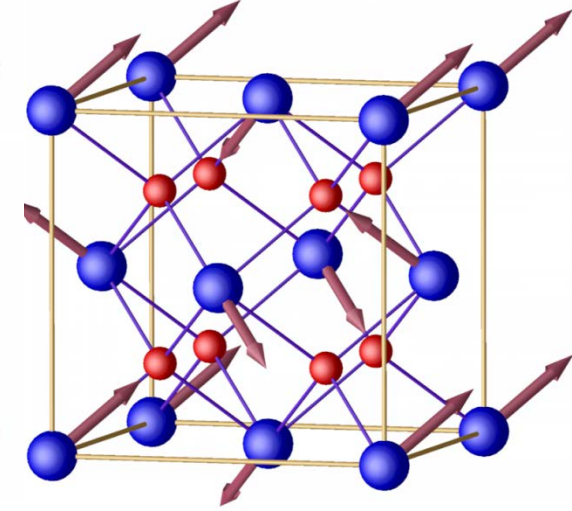
collinear 1k-

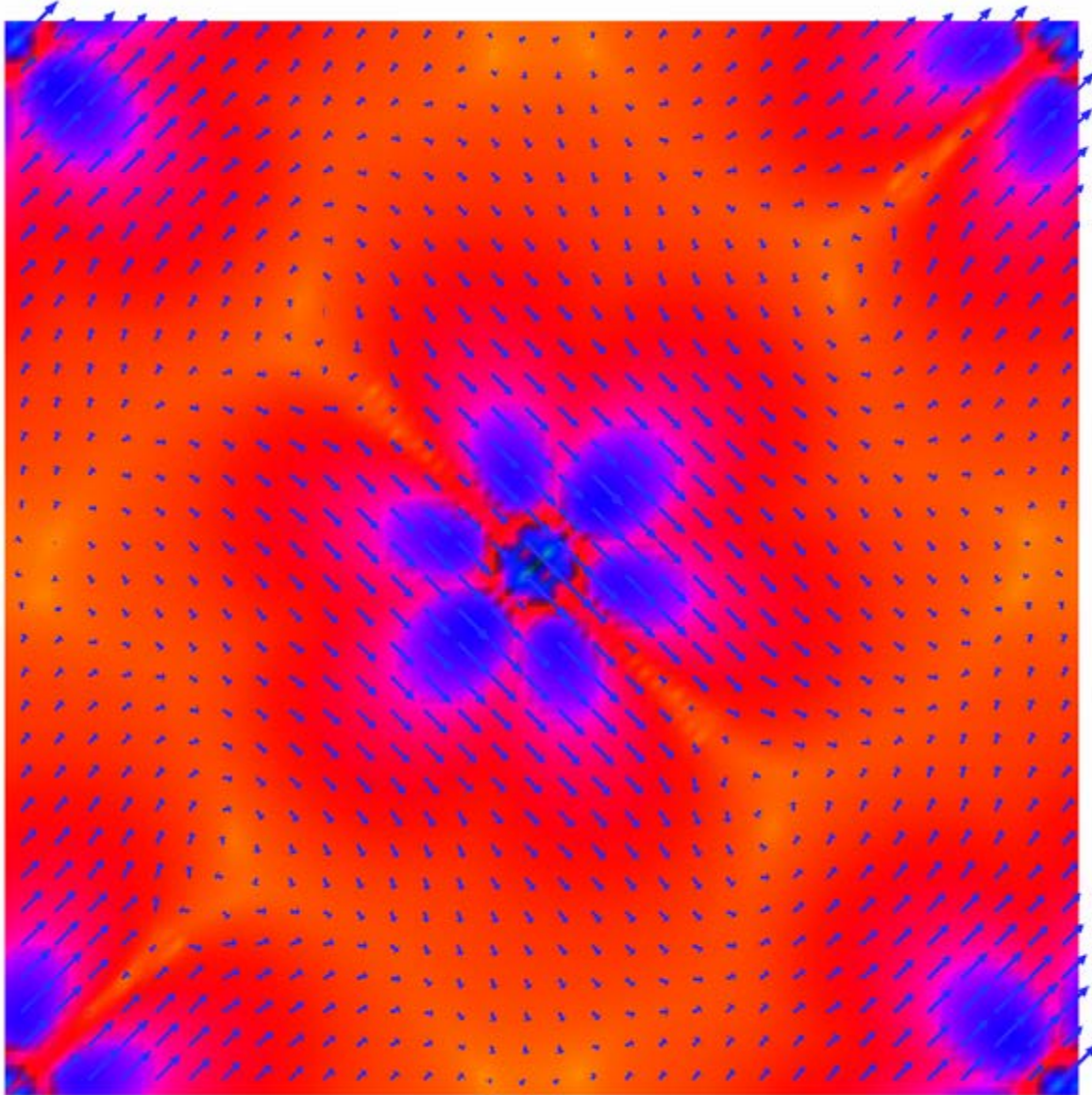


non-collinear 2k-

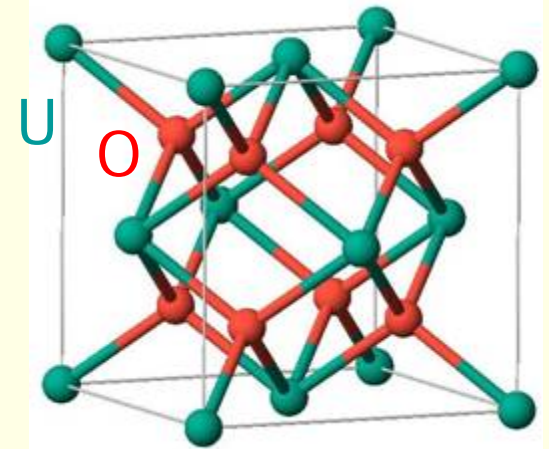


or 3k-structure





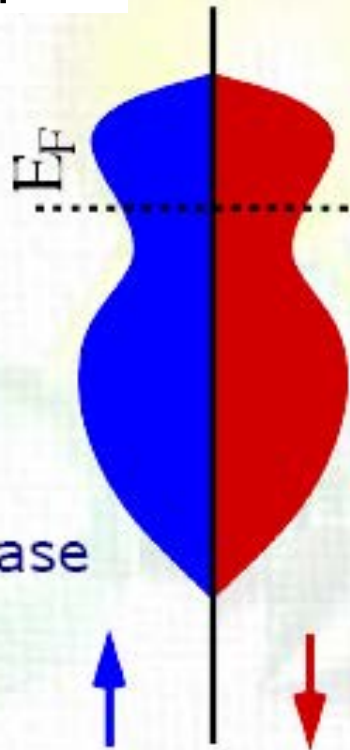
- Magnetisation direction perpendicular at the two U sites (arrows)
- Magnetisation density (color)



- Wien2k can only handle collinear or non-magnetic cases

run_lapw script: DOS

```
x lapw0
x lapw1
x lapw2
x lcore
x mixer
```

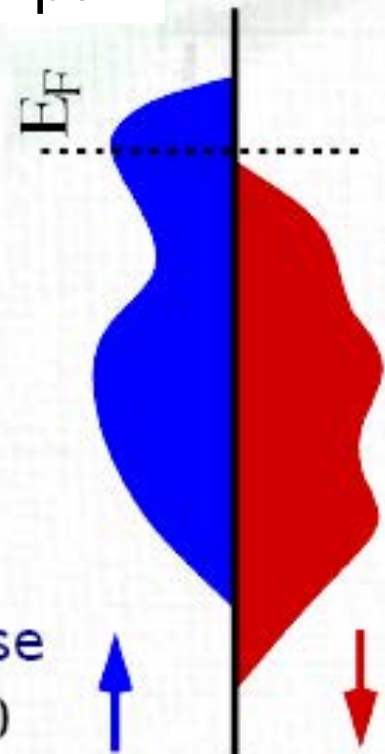


non-magnetic case

$$m = n_{\uparrow} - n_{\downarrow} = 0$$

runsp_lapw script: DOS

```
x lapw0
x lapw1 -up
x lapw1 -dn
x lapw2 -up
x lapw2 -dn
x lcore -up
x lcore -dn
x mixer
```



magnetic case

$$m = n_{\uparrow} - n_{\downarrow} \neq 0$$



- *runsp_lapw* script (unconstrained magnetic calc.)
 - runs lapw1/2 for both spins **independently**
 - case.scf contains extra information:
 - `grep :MMT case.scf` (for total moment)
 - `grep :MMI case.scf` (for atomic moments)
 - `grep :HFF case.scf` (for hyperfine fields)



- *runsp_lapw* script (unconstrained magnetic calc.)
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 - `grep :MMT case.scf` (for total moment)
 - `grep :MMI case.scf` (for atomic moments)
 - `grep :HFF case.scf` (for hyperfine fields)
- *runfsm_lapw -m value* (constrained moment calc.)
 - for difficult to converge magnetic cases or simply to constrain a moment (\rightarrow 2 Fermi-energies \rightarrow external magnetic field)
- *runafm_lapw* (anti-ferromagnetic calculation)
 - calculates only spin-up, uses symmetry to generate spin-dn



- *runsp_lapw* script (unconstrained magnetic calc.)
- *runfsm_lapw -m value* (constrained moment calc.)
- *runafm_lapw* (anti-ferromagnetic calculation)

- spin-orbit coupling can be included in second variational step
- **never mix polarized and non-polarized calculations in one case directory !!!**



Thank you for your attention



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