MAGNETIC PROPERTIES OF Fe, Co AND Ni IN LAVES PHASE BASED COMPOUNDS

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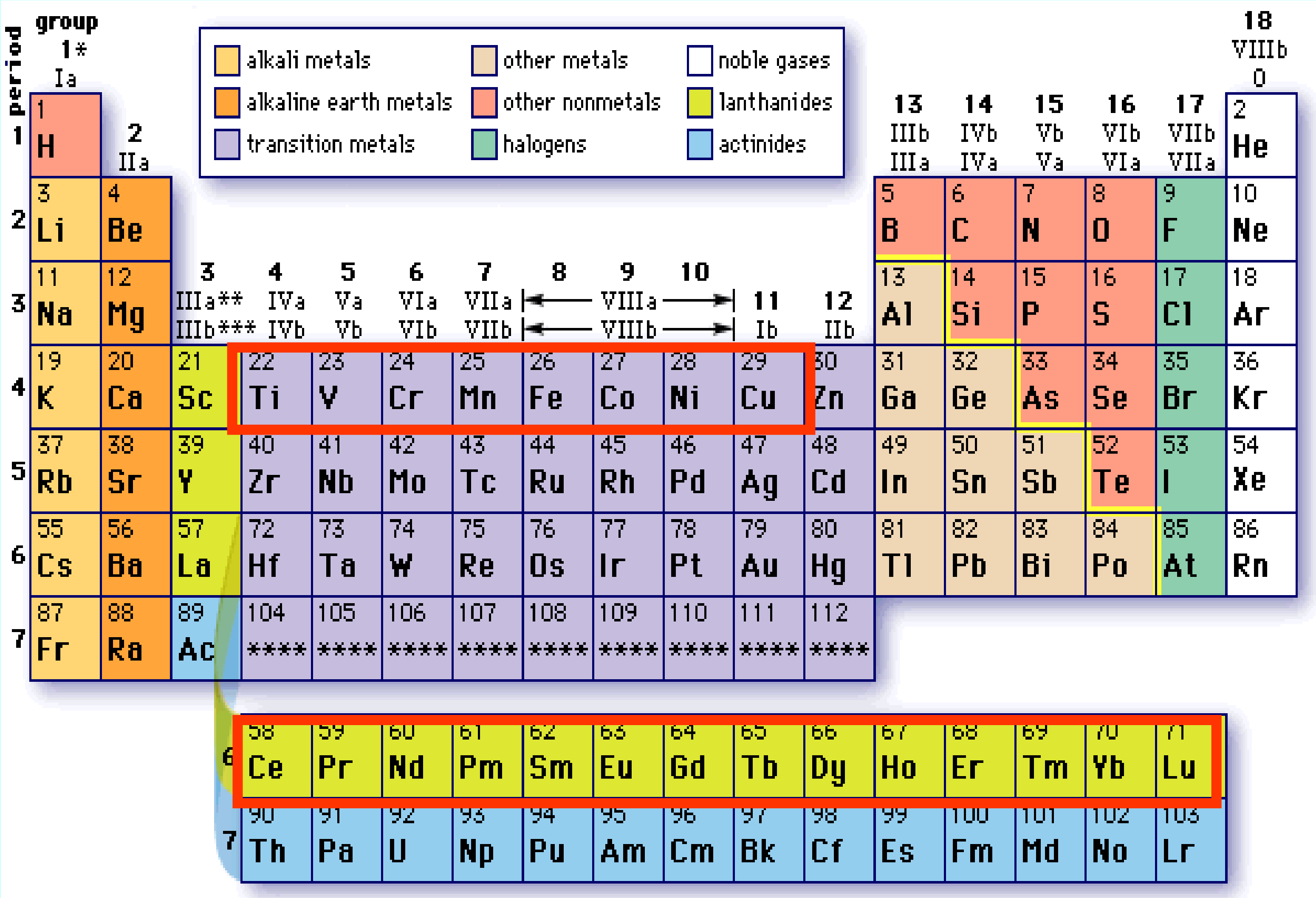
Overview:

1. Introduction
2. Itinerant electron magnetism
3. Laves phases
4. Magnetic properties
5. Conclusions



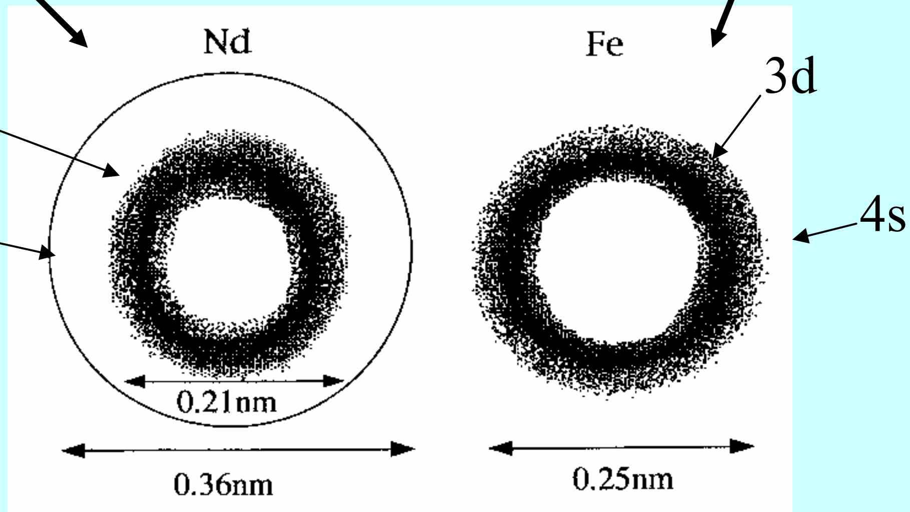
79 out of the 103 first elements are magnetic in their ground state

A few of them only are magnetic in the solid state

The 2 main series of magnetic elements

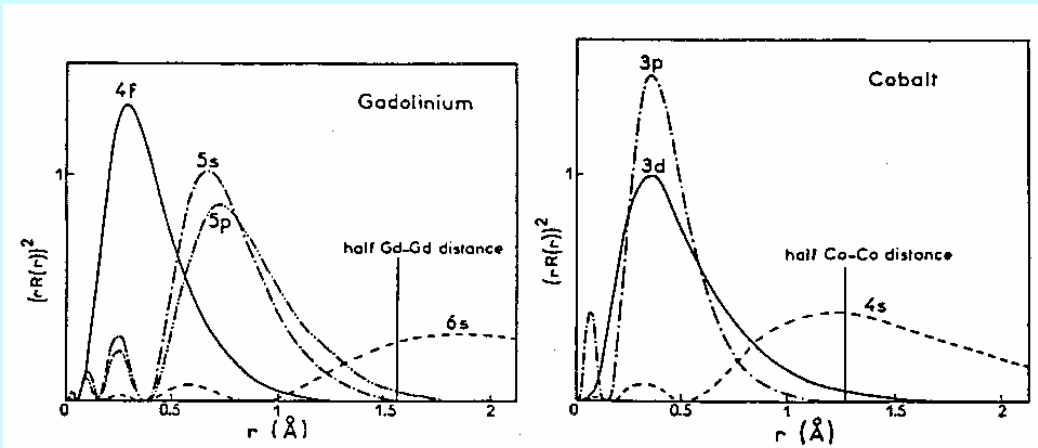
Rare-earth element

Transition-metal element

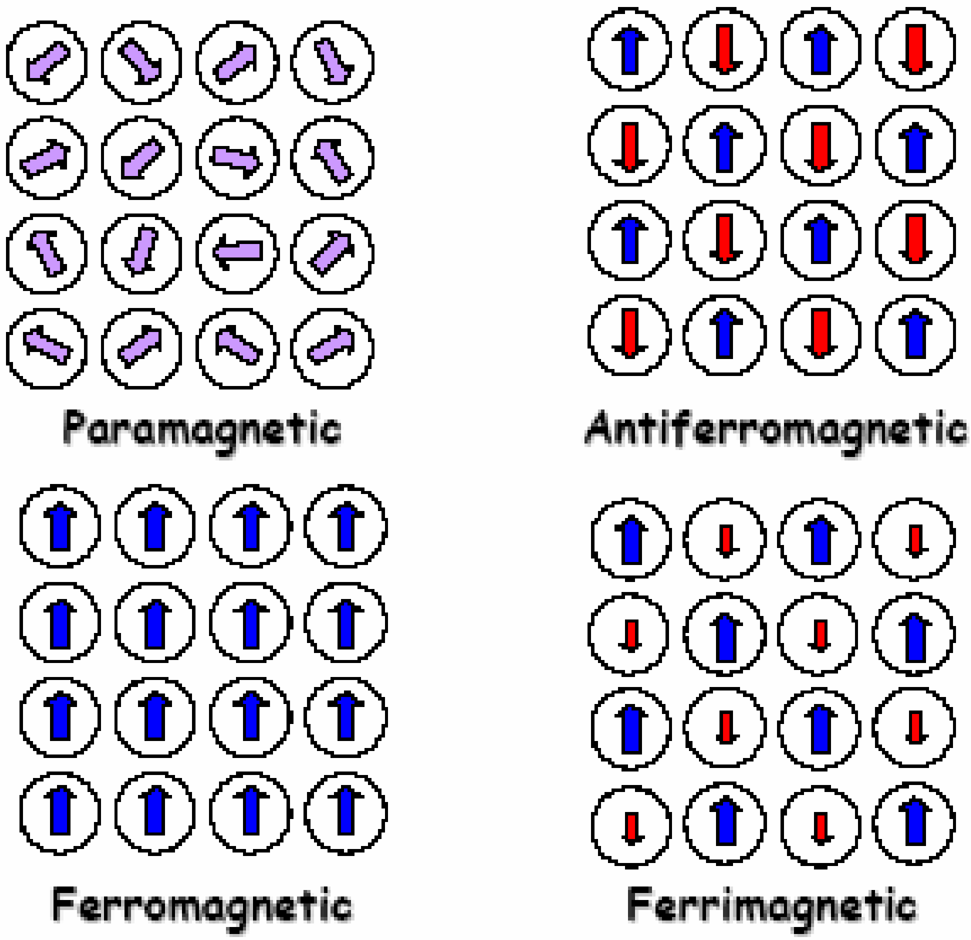


4f electrons : inner shell
3d electrons : outer shell

leads to very different behaviours



Magnetic Ordering



Rare-earth (R)-transition metal (M) compounds

Intrinsec R-M properties:

- **exchange interactions** (between all unpaired spins)
- **magnetocrystalline anisotropies**

Rare-earth (R)-transition metal (M) compounds

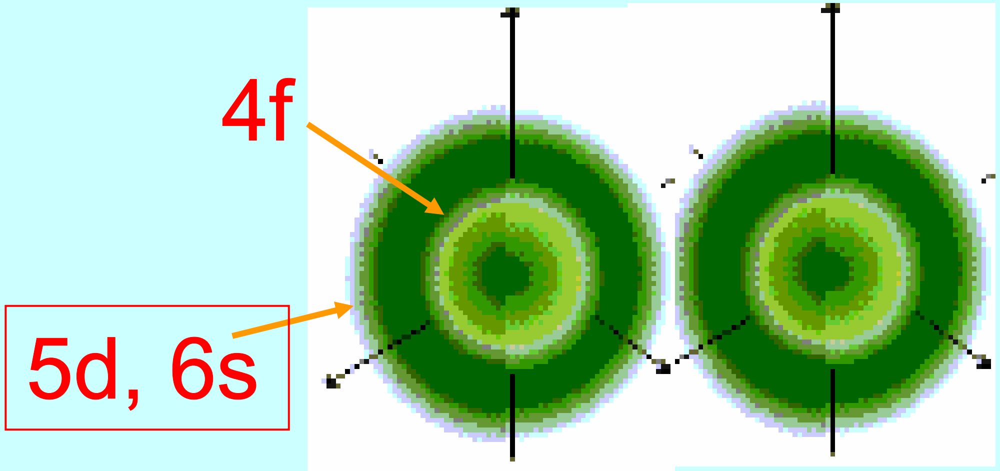
Intrinsec R-M properties:

- **exchange interactions** (between all unpaired spins)
- **magnetocrystalline anisotropies**

Interactions:

- R-R (it's the weakest, RKKY type)
- M-M (it's the strongest)
- R-M

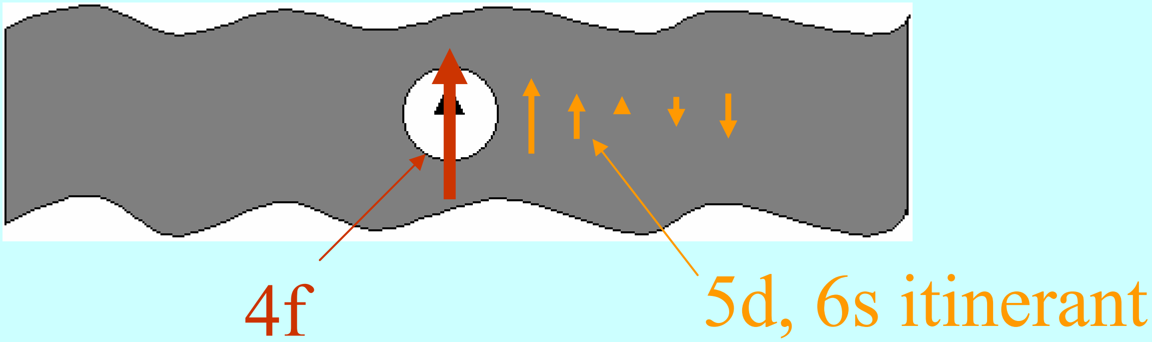
Exchange interactions in rare-earth metals



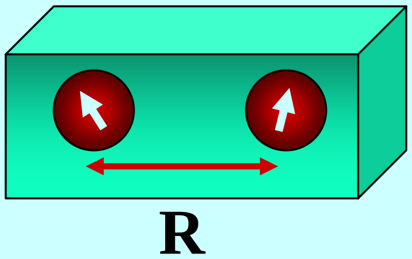
Magnetic 4f electrons localised
5d, 6s itinerant

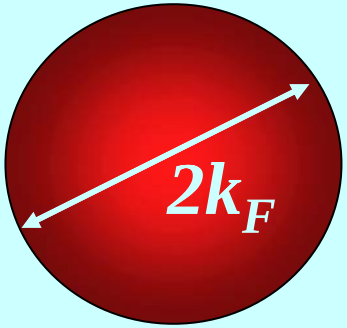
4f moments coupled via
indirect RKKY interactions

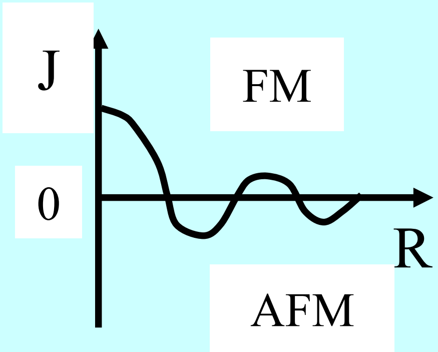
RKKY interactions



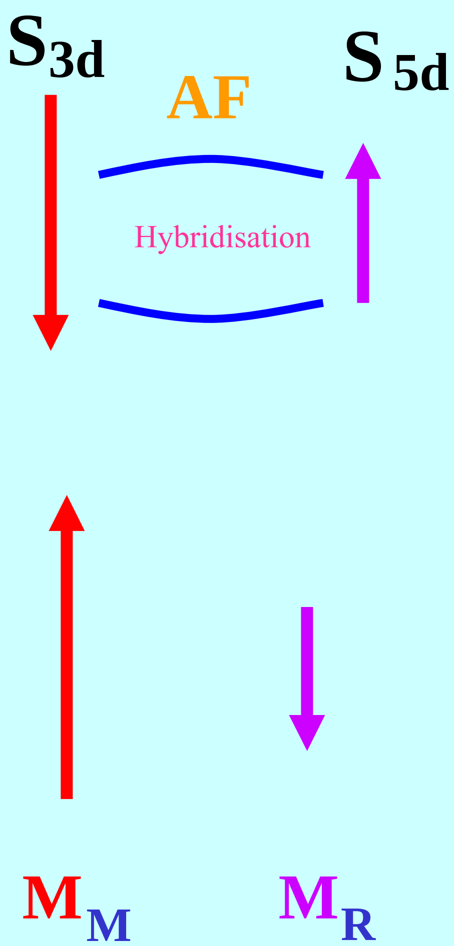
$$J_{RKKY}(R) \propto \frac{\cos(2k_F R)}{(2k_F R)^3} \propto \frac{1}{R^3}$$





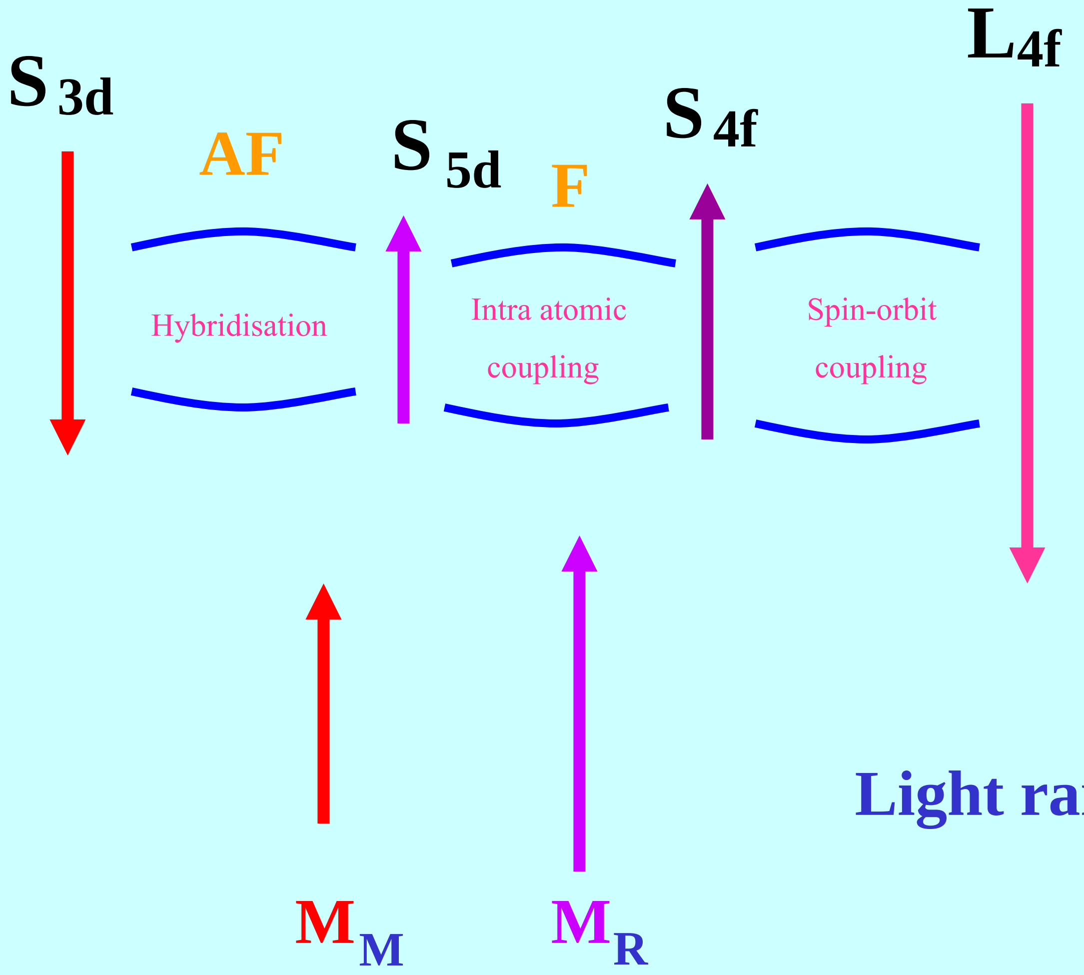


Interaction between magnetic moments in R-M intermetallics



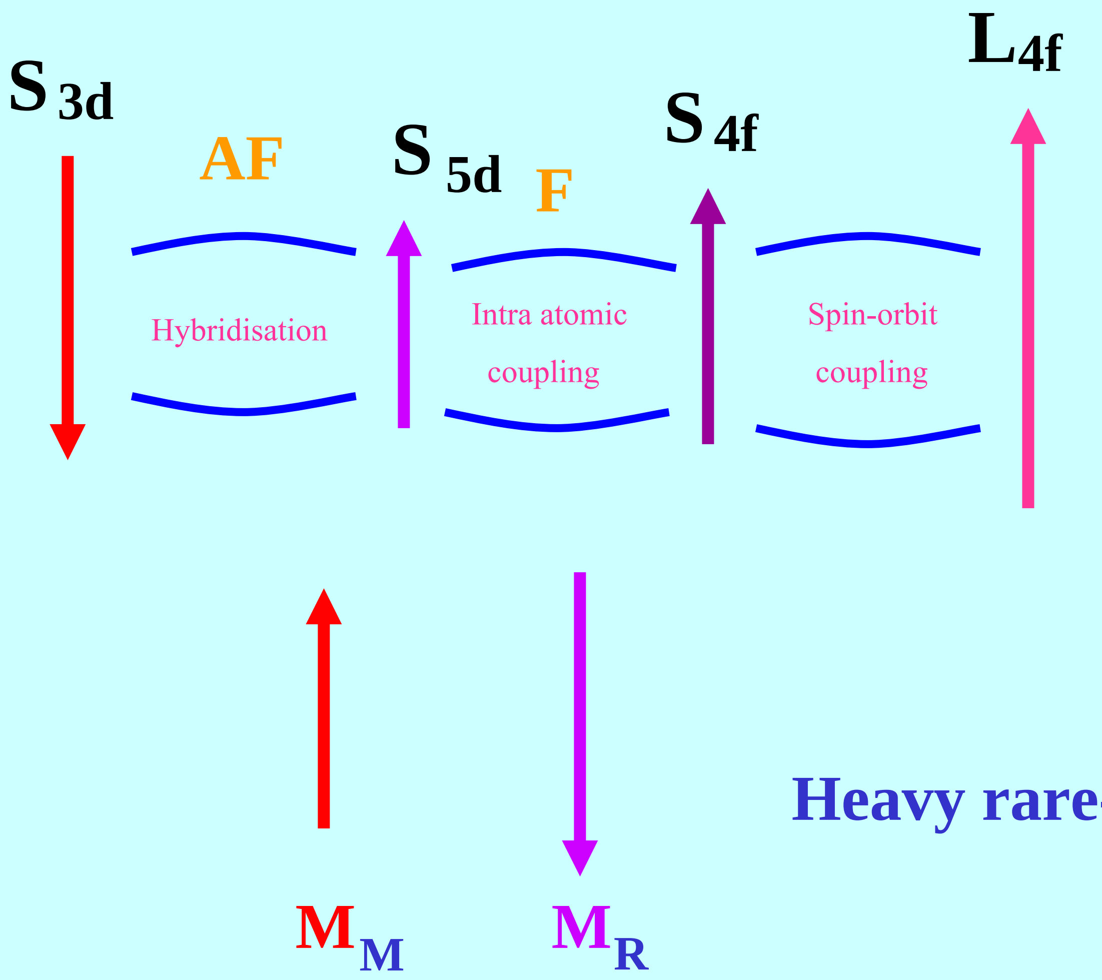
Non - 4f moment

Interaction between magnetic moments in R-M intermetallics



Light rare-earth

Interaction between magnetic moments in R-M intermetallics



Heavy rare-earth

Itinerant-Electron Magnetism

Ex: Metallic systems based on 3d transition elements

-3d electrons are responsible for magnetic properties

- we assume that the 3d bands are rectangular

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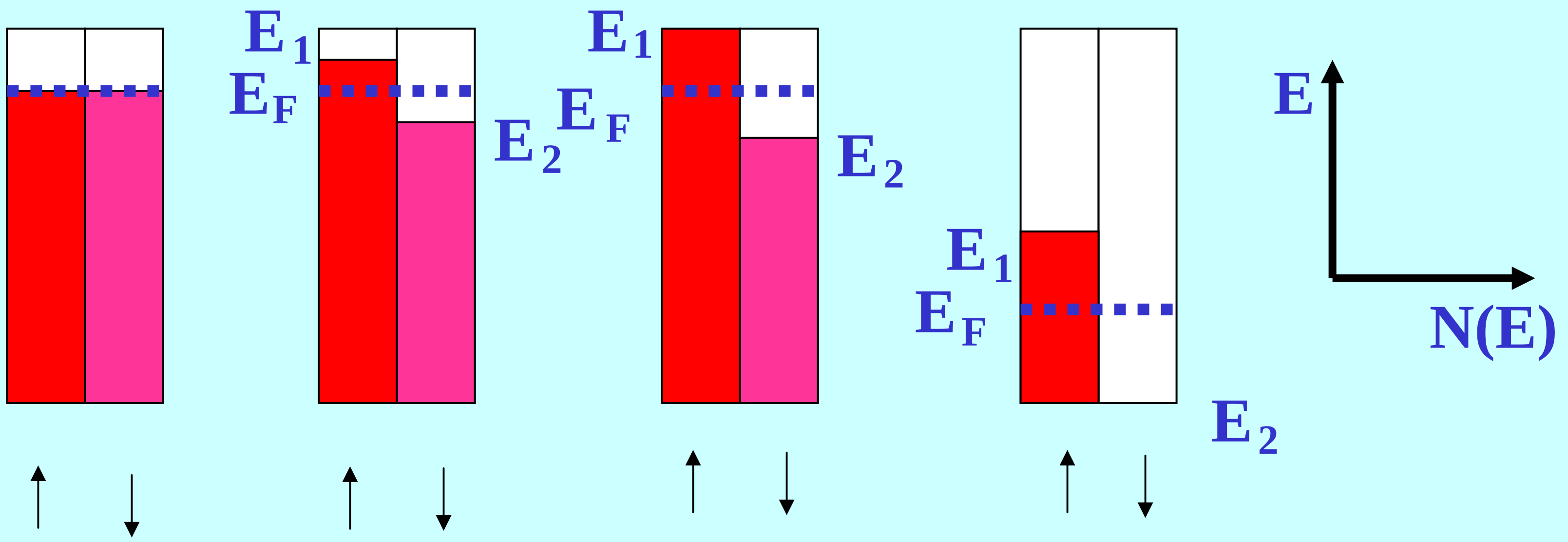
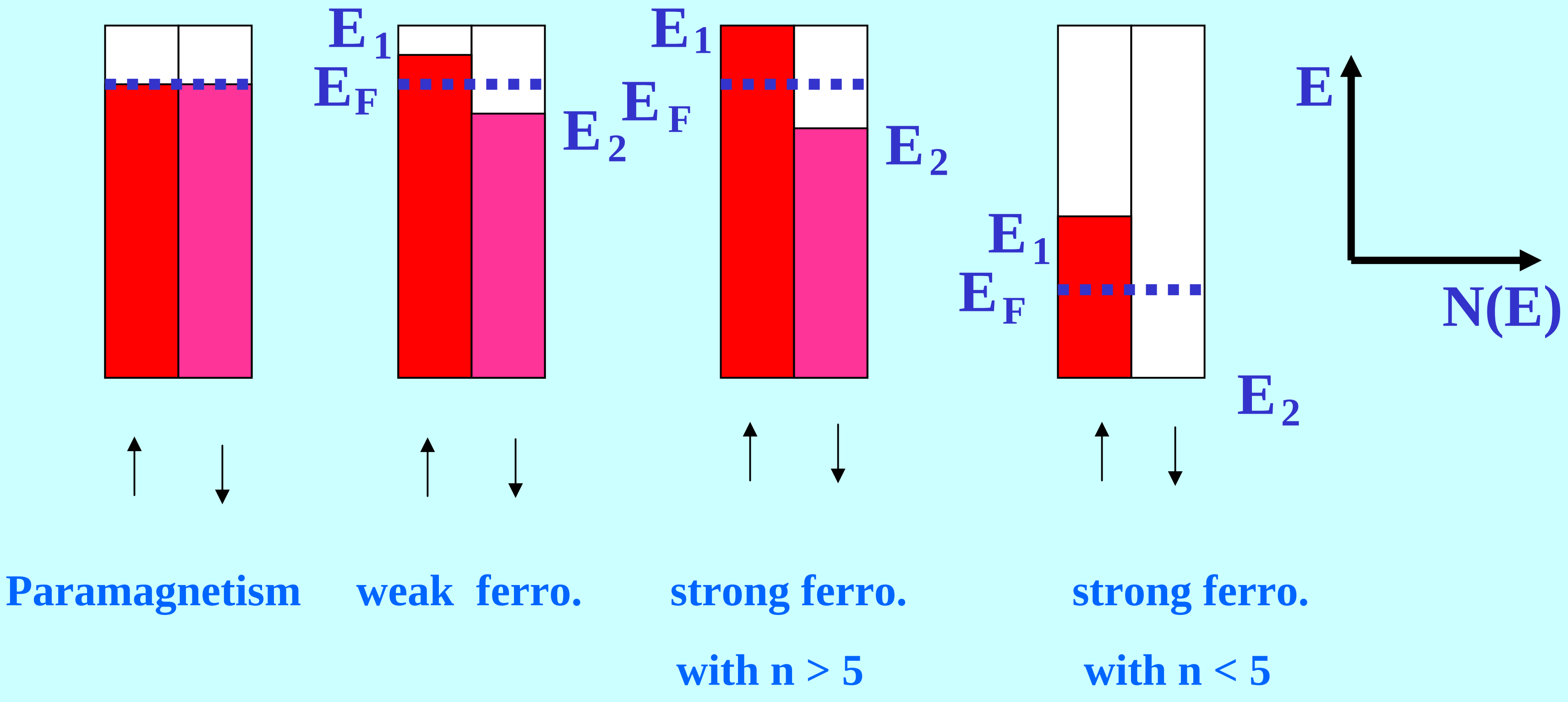
N(E) remain constant over the whole energy range spanned by the bandwidth W

Schematic representation of a partially depleted 3d band



Paramagnetism | weak ferro. | strong ferro. with n > 5 | strong ferro. with n < 5

Schematic representation of a partially depleted 3d band



$U_{eff}\,N(E_F) > 1$ **Stoner criterion**

Susceptibility enhancement

$$\chi = \frac{\chi_{\mathbf{o}}}{\mathbf{1\text{-}U_{eff}\,N(E_F)}}$$

$[1\text{-}U_{eff}\,N(E_F)]^{-1}$ very high

Strong interaction between electrons

and/or

N(E_F) high

Susceptibility enhancement

$$\chi = \frac{\chi_{\mathbf{o}}}{\mathbf{1\text{-}U_{eff}\,N(E_F)}}$$

$$\mathbf{[1\text{-}U_{eff}\,N(E_F)]^{-1}} \xrightarrow[\text{high}]{\text{very}}$$

N(E_F) high

metallic systems close to magnetic instability

LAVES PHASE COMPOUNDS

- YCo_2 exchange enhanced paramagnetism
- YFe_2 ferromagnetic
- YNi_2 paramagnetic
- $YFe_{2-x}V_x$ ferromagnetic
- $YCo_{2-x}A_x$; (A=Cr, Ti, V) exchange enhanced paramagnetism
- RM_2 ; (R=heavy rare earth, M=Fe, Co, Ni) ferrimagnetic
- $GdCo_{2-x}A_X$; (A=Si, Cu) ferrimagnetic

Laves phases

⇓

tetrahedrally close-packed alloys

3 types

$MgCu_2$ $MgZn_2$ $MgNi_2$

Laves phases

tetrahedrally close-packed alloys

3 types

$MgCu_2$ $MgZn_2$ $MgNi_2$

fcc – C15

Laves phases

tetrahedrally close-packed alloys

3 types

$MgCu_2$ — fcc – C15

$MgZn_2$ — hexagonal-C14

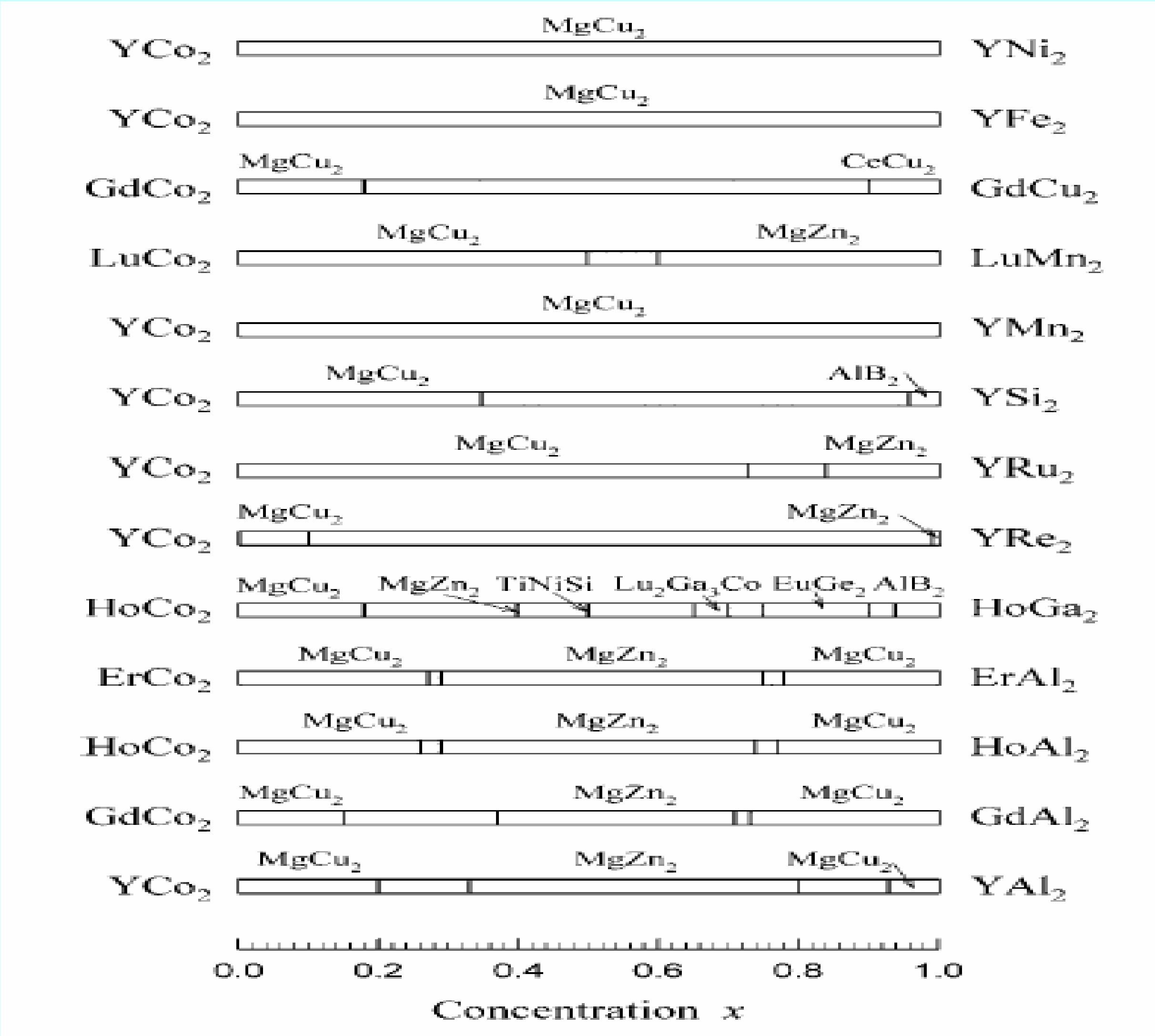
$MgNi_2$

Laves phases

tetrahedrally close-packed alloys

3 types

$MgCu_2$	$MgZn_2$	$MgNi_2$
fcc – C15	hexagonal-C14	hexagonal C36



E. Gratz, et, al., J.Phys.: Condens. Matter, 2001

The RM_2 Cubic Laves Structure (C15)

History: more than 20 years

Very interesting properties:

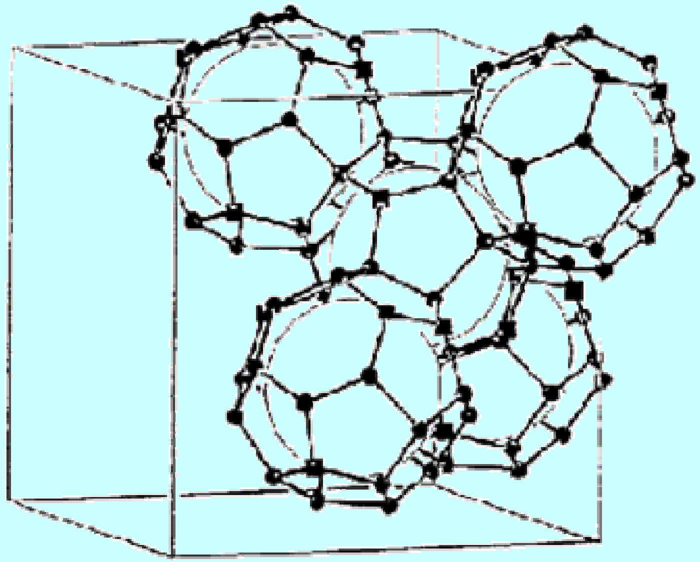
- variable moment on the M atom
- first order magnetic transition
- applied or molecular field induced metamagnetic transition

Interest:

- fundamental (simple crystal structure and intriguing characteristics –ideal for checking physical theories of magnetism)
- technical (hydrogen storage, refrigeration…)

Hidrogen storage

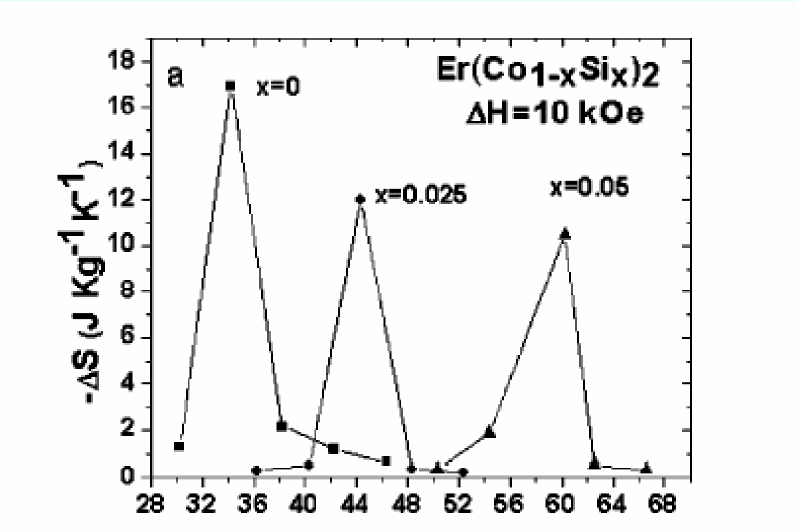
The arrangement of hydrogen sites in C15 Laves phase compounds. The g and e sites are shown as circles and squares, respectively.

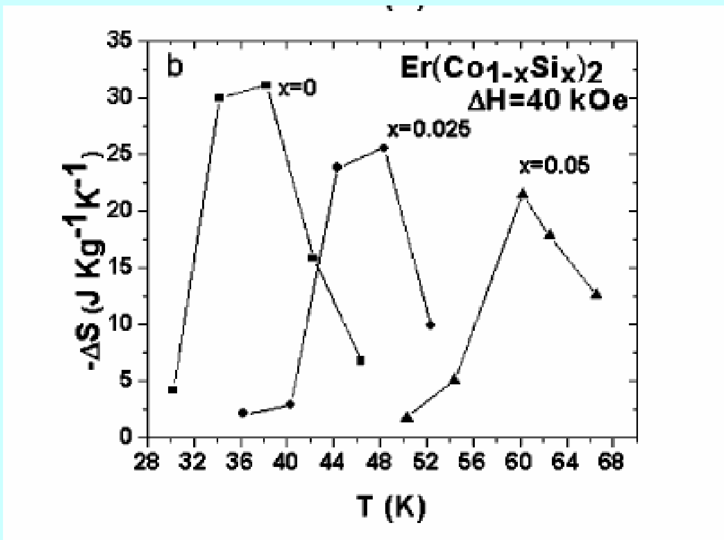


- At low hydrogen content, only the lowest energy sites (g sites) are occupied. These sites form a network of interpenetrating hexagons .

- As the hydrogen content is increased, the higher energy sites (e sites) also become occupied.

Magnetocalloric effect





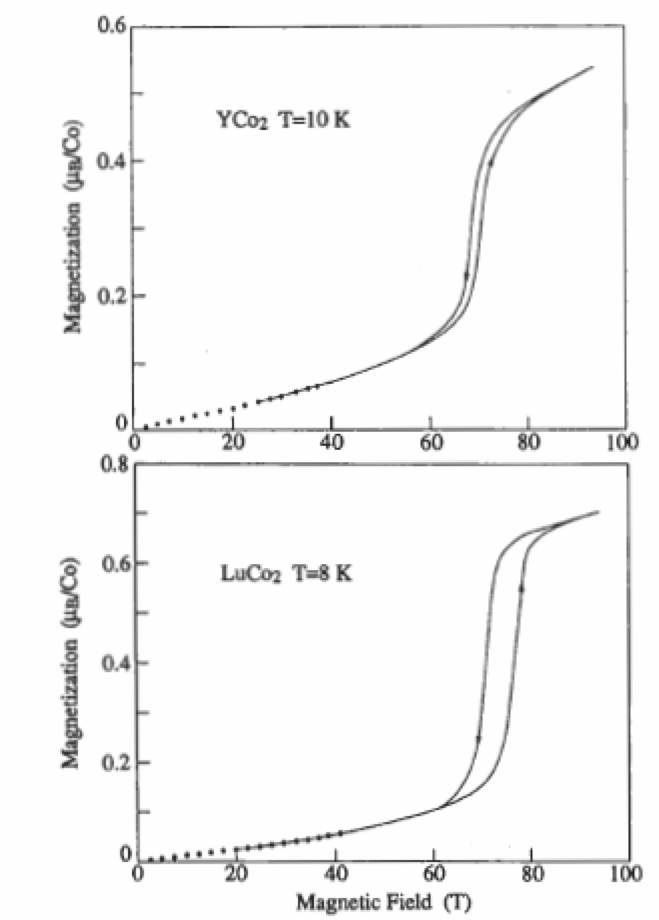
J.K.Singh et.al., J. Appl. Phys, 2004

-the magnetic entropy show maxima around Tc

-decrease with the increase of the Si content

-soft magnetically around Tc (magnetic hysteresis very small)

Metamagnetic transition



T. Goto et. Al., Physica B, 2001

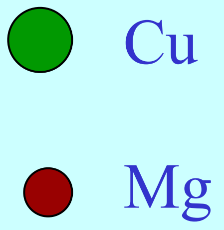
-magnetization not completly saturated

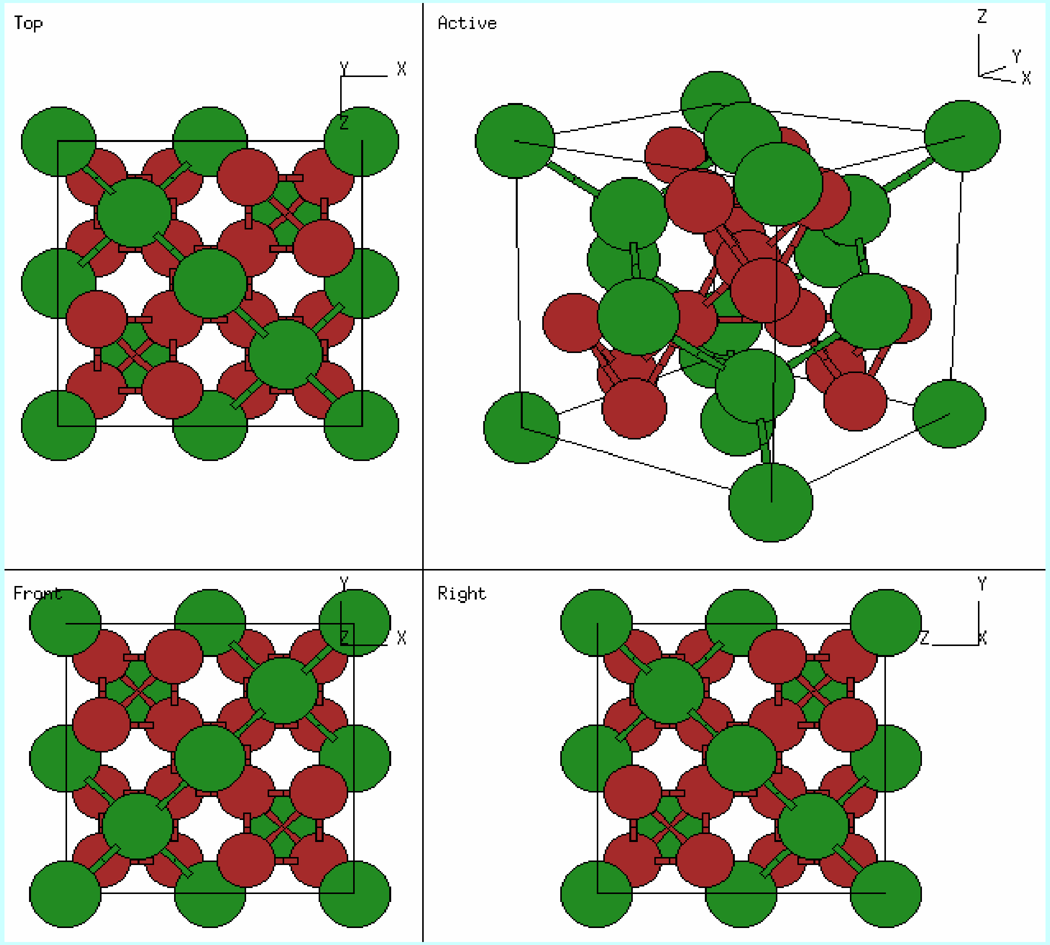
-with the increase of B the Fermi level of the minority band approaches the peak of the DOS and FM state occurs

-the metamagnetic transition is affected by spin fluctuations

-probably, MT affect the electronic structure of the d electron system

The $MgCu_2$ Cubic Laves Structure (C15)





Sample preparation

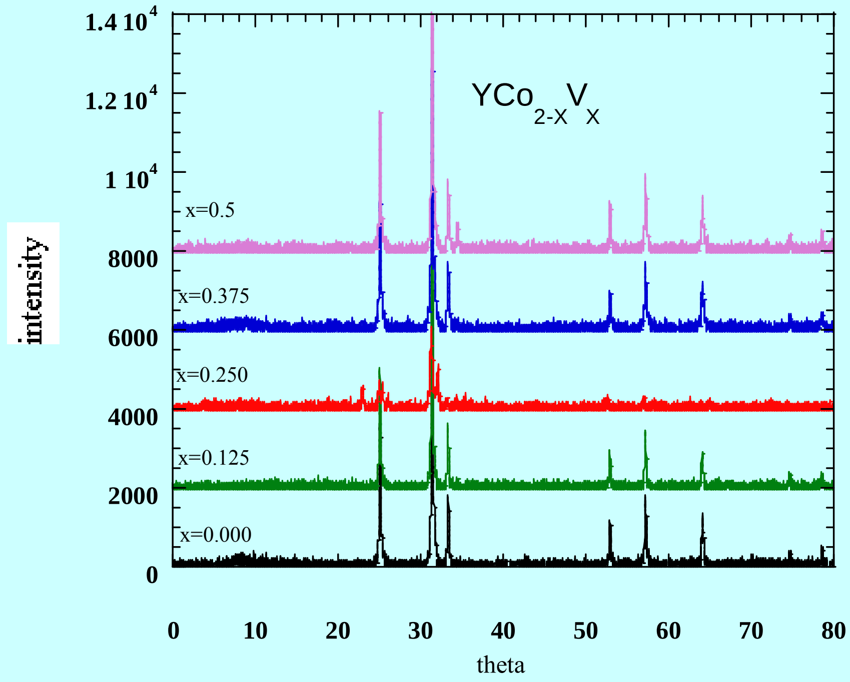
1. - arc melting

   -induction furnance

   - high purity ingots (better than 99.9 %)
   - small excess of Y or rare earth

2. -thermally treatment

   - several days
   - temperatures between 850-1000 ^{o}C



Compound	Crystal structure	R=Fe (Å)	R=Co (Å)	R=Ni (Å)
GdM_2	$MgCu_2$	7,396	7,256	7,204
TbM_2	$MgCu_2$	7,347	7,206	7,160
DyM_2	$MgCu_2$	7,325	7,188	7,148
HoM_2	$MgCu_2$	7,304	7,164	7,136
ErM_2	$MgCu_2$	7,283	7,144	7,125
TmM_2	$MgCu_2$	7,247	7,121	7,088
LuM_2	$MgCu_2$	7,222	7,122	7,085
YM_2	$MgCu_2$	7,363	7,216	7,182

MAGNETIC PROPERTIES

- temperature range 4.2-1000 K
- external magnetic fields up to 9 T

Spontaneous magnetizations:

$$M = M_s\left(1 - \frac{a}{H}\right) + \chi_o H$$

Paramagnetic region

$$\chi = \chi_p + \frac{cM_s'}{H}$$

Band structure calculation

- TB-LMTO-ASA (O.K.Anderson, O.Jepsen...)

Local density approximation:

Total electronic potential = sum of external, Coulomb and exchange correlation potentials (R.O.Jones, O.Gunnarson)

Functional form of the exchange-correlation energy:

Free electron gas parameterization (von Barth and Hedin)

Supercells used:

8 times greater than the unitary cell

-strong hybridization between 3d states (M) and

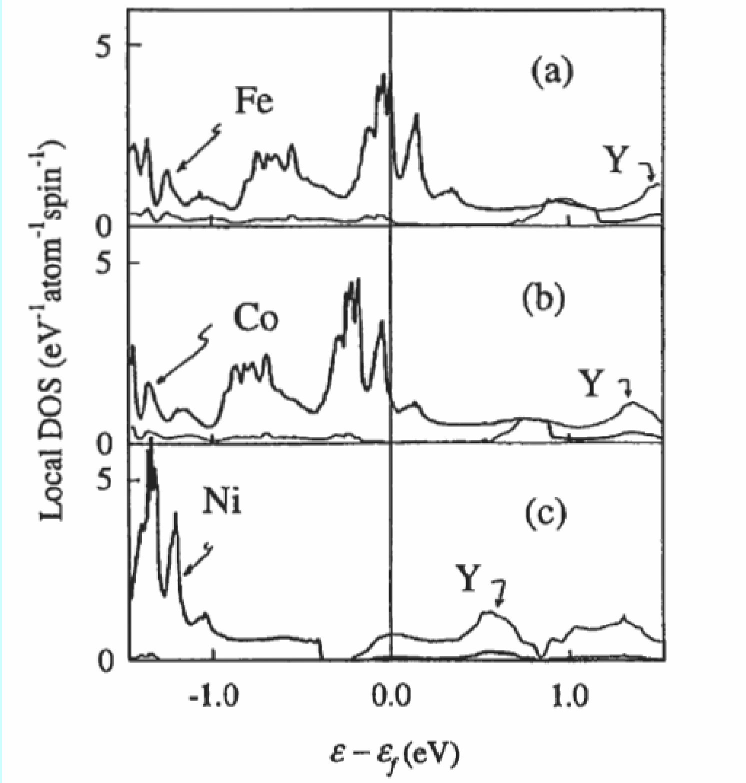
5d (4d) states of Y or R

-similarities in shape

-Ueff $N(E_F)$ =0.21 in YNi_2 (nonmagnetic)

- = 2.6 in YFe_2 (strong itinerant ferromagnet)

- =0.9 in in YCo_2 (exchange enhanced paramagnet)



H.Yamada, Phys. Rev.B., 1993

MODELS

- Buschow ´71

  - R-M interactions RKKY-type

- Campbell `72

  - 4f electrons of R polarize their 5d band
  - direct 5d-3d exchange interactions with M
  - 4f-5d (4d) exchange interactions are positive

- Brooks et.al. `89, 91, 93

  - describe the 4f-5d exchange interactions by:

$$\boldsymbol{H}_{4f-5d} = -2\boldsymbol{J}_{4f-5d}\boldsymbol{S}_{4f}\boldsymbol{S}_{5d}$$

-Li et.al. `91

- consider in addition J_{4f-6s} and J_{4f-6p}

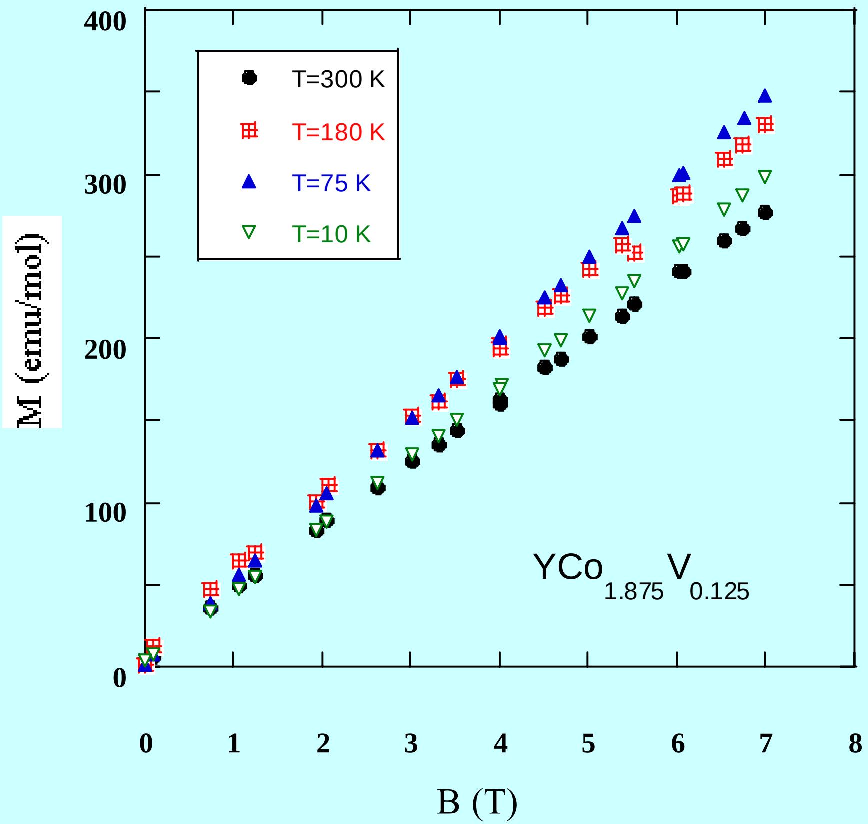
- Belorizky et.al. `87

- the decrease of J_{4f-5d} is related to the radii variation of 5d and 4f shells

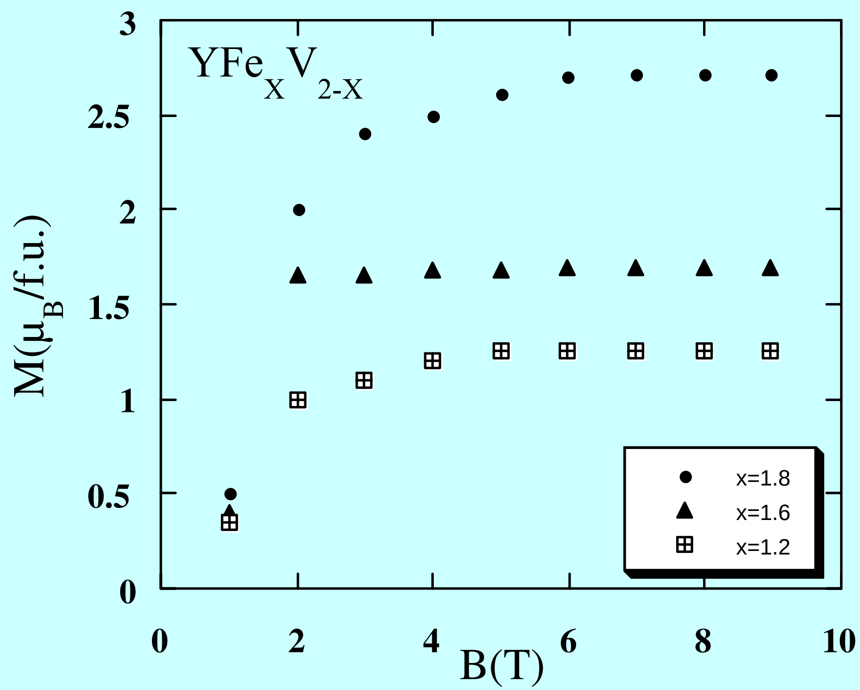
- Fähnle et.al. `93

- J_{4f-5d} is important

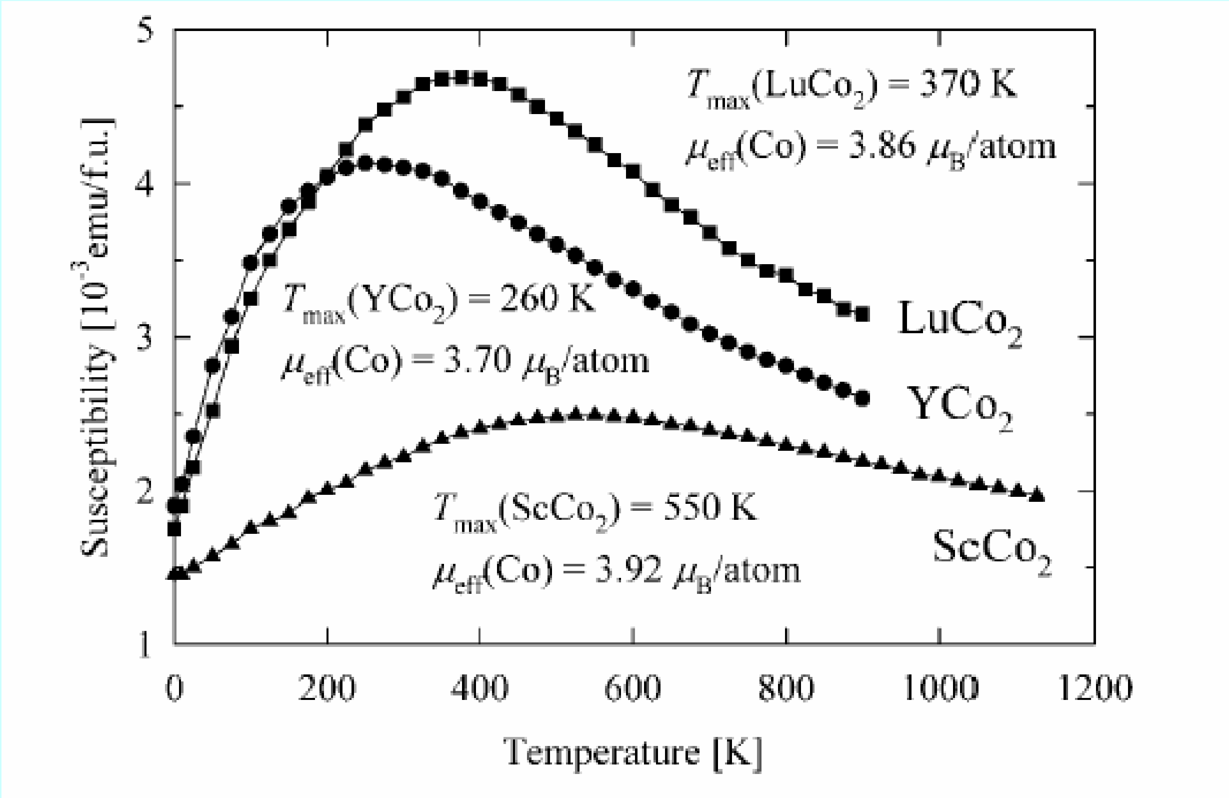
- no major contribution from J_{3d-5d}



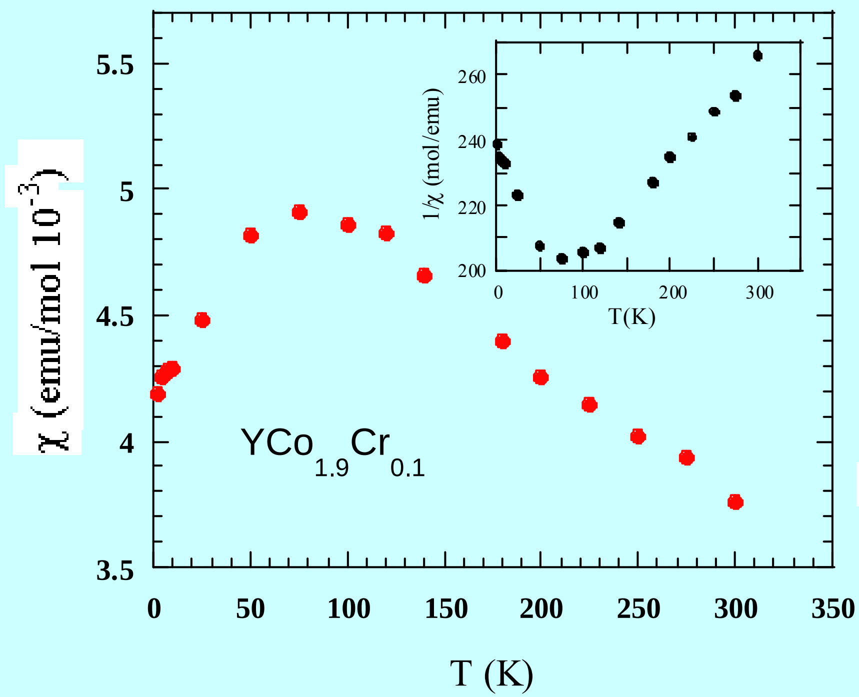
T=300 K
T=180 K
T=75 K
T=10 K
YCo1.875V0.125
M (emu/mol)
B (T)

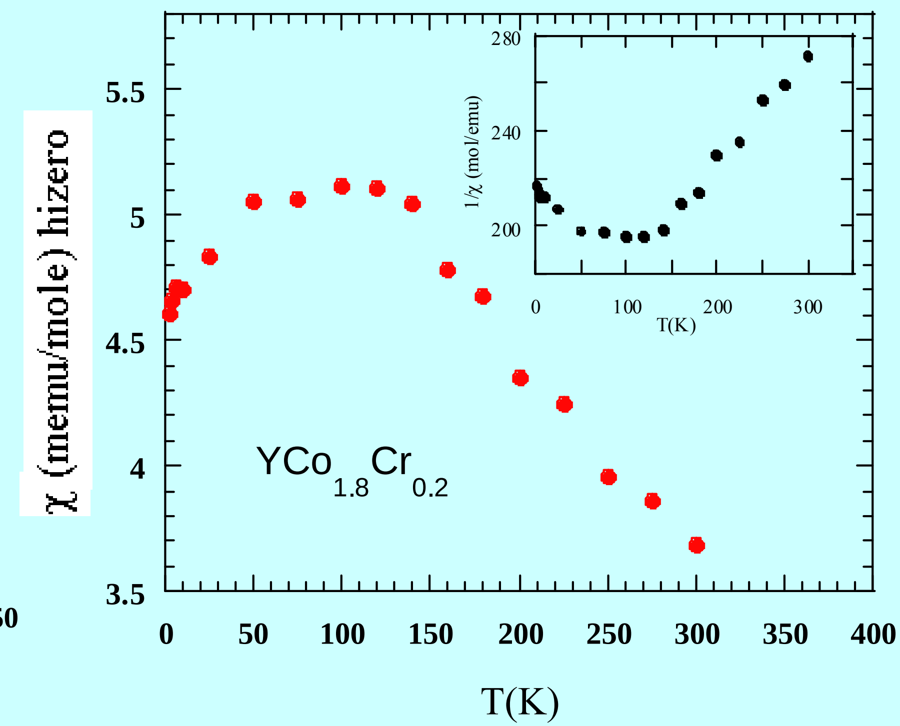


YFeXV2-X
x=1.8
x=1.6
x=1.2
M(μB/f.u.)
B(T)



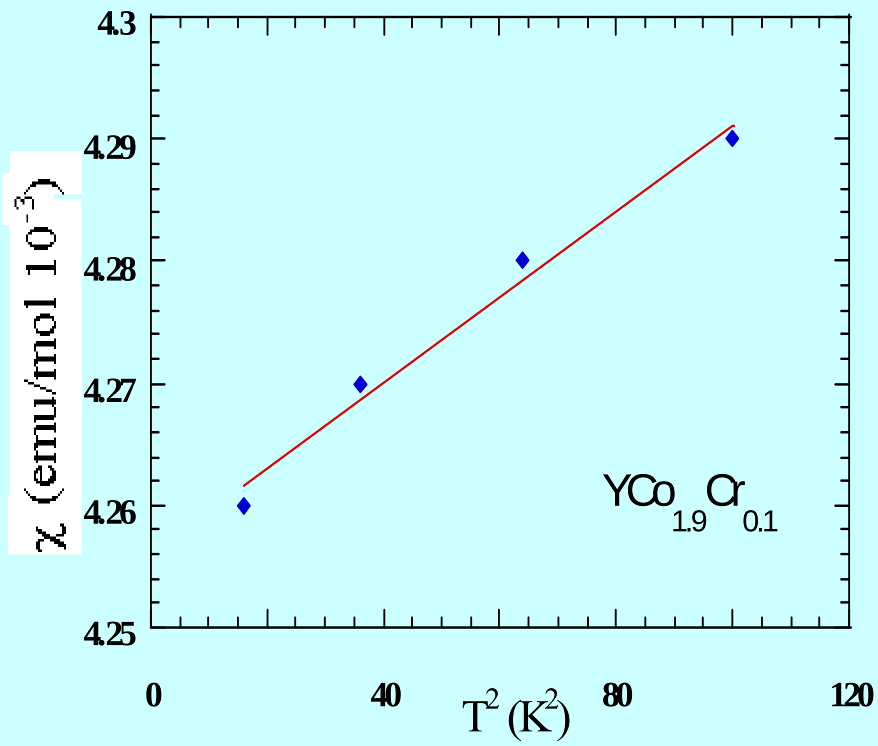
Ê.Burzo et. al., J. .Magn. Magn. Mater., 1993

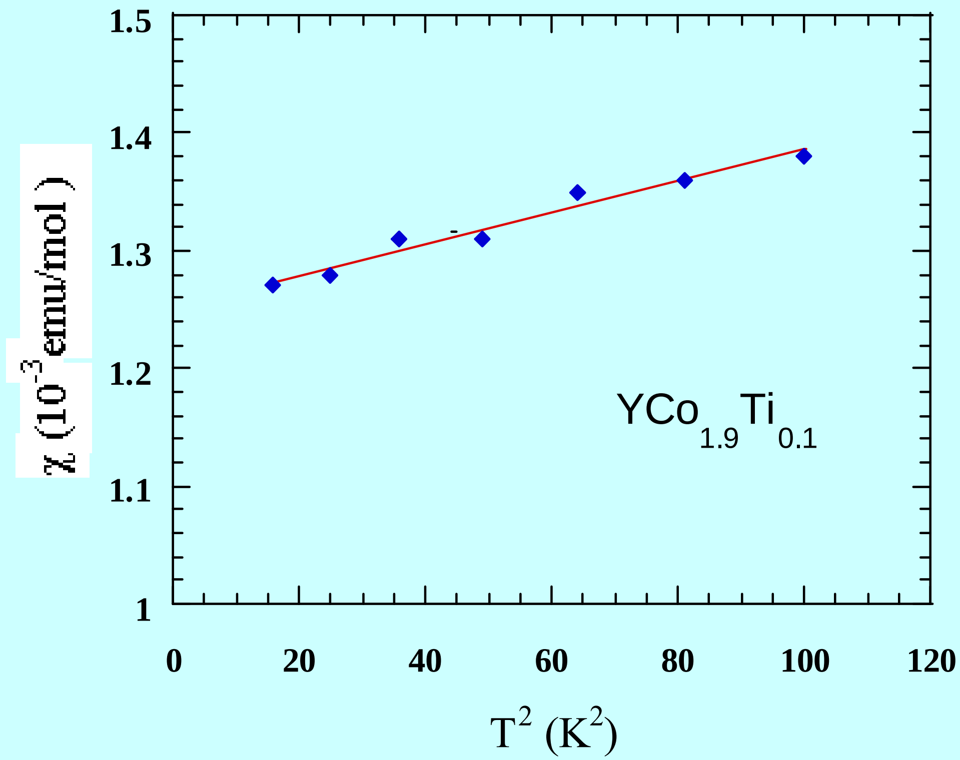


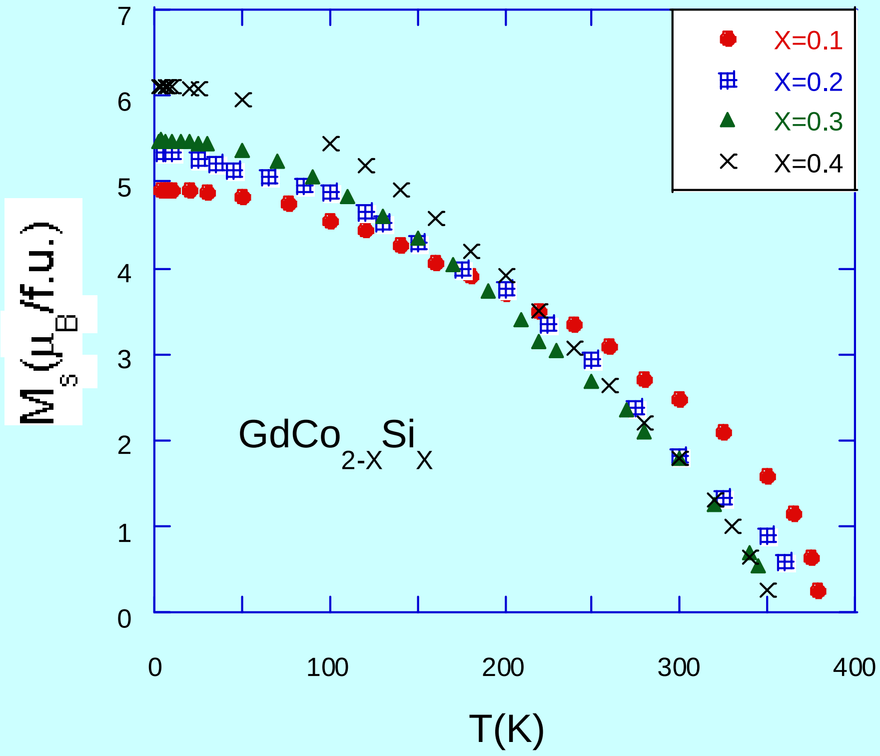


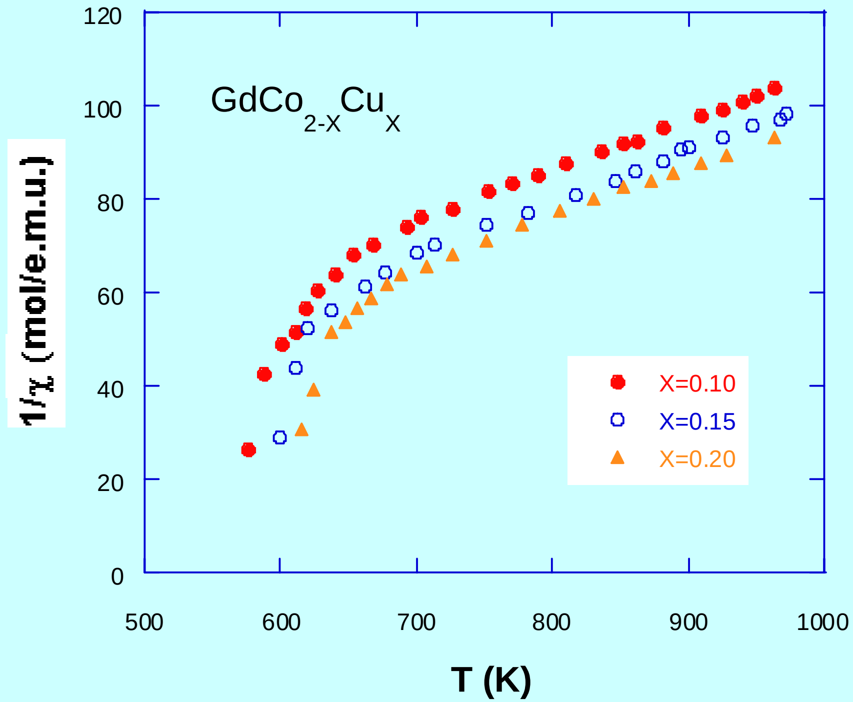
R. Tetean et.al., Mat. Sci. Forum, 2001

$$\chi = s\chi_p\left[1+\frac{\pi^2}{6}\left(2\frac{N''}{N}-1.2\frac{N'^2}{N^2}\right)_{E_F} s^2T^2\right]$$



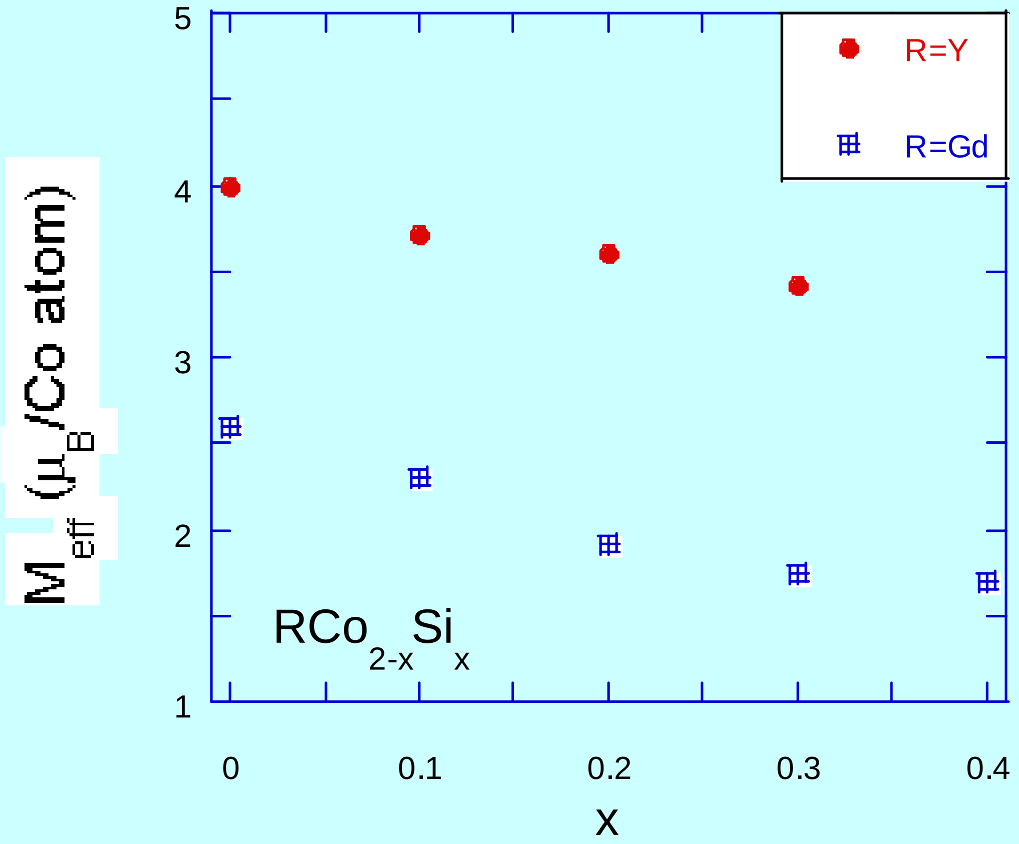




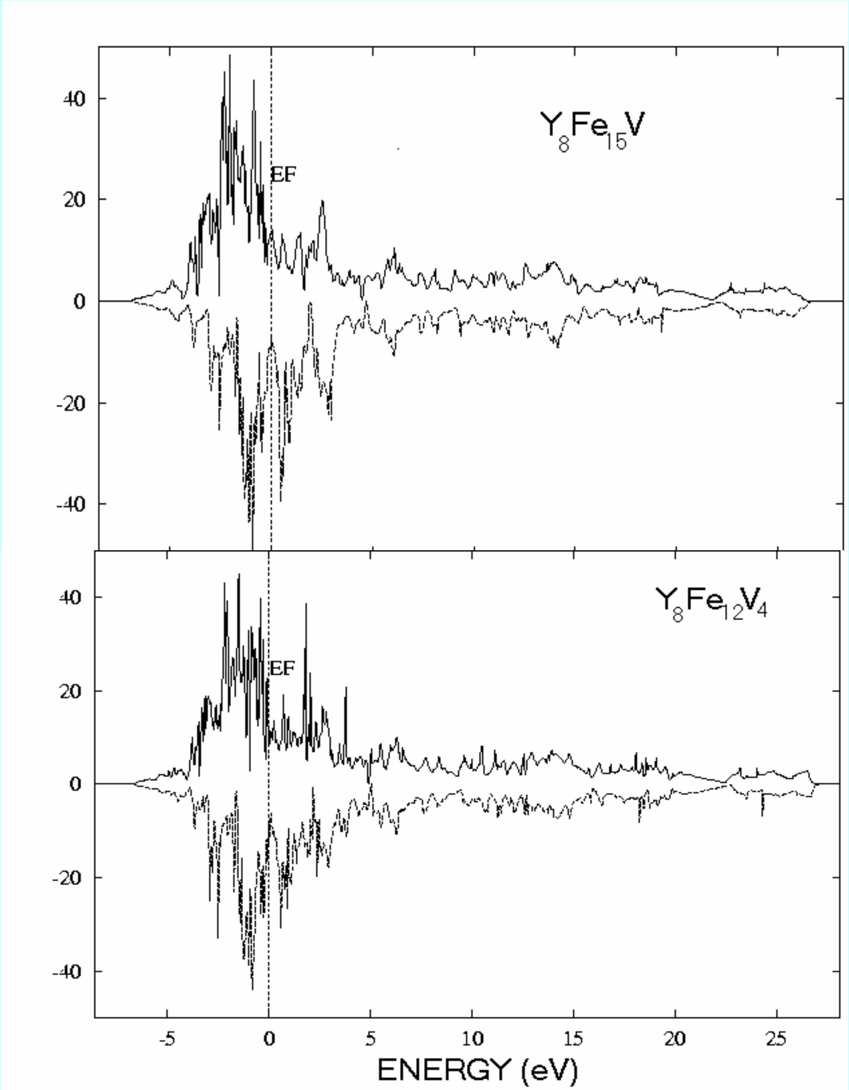


E.Burzo, R.Tetean et al., J. Alloys. and Comp., 2001

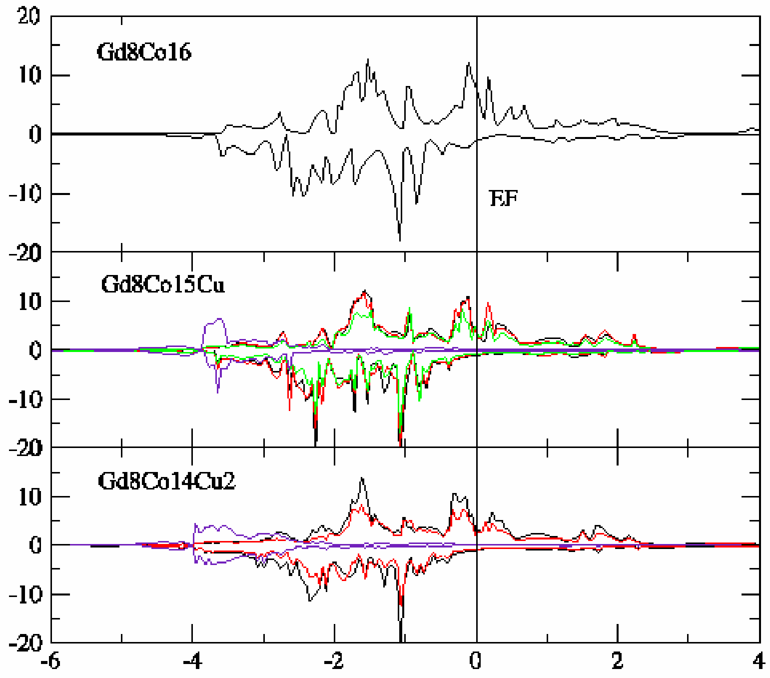
R.Tetean et. al., Phys. Stat. Sol. (a), (2003



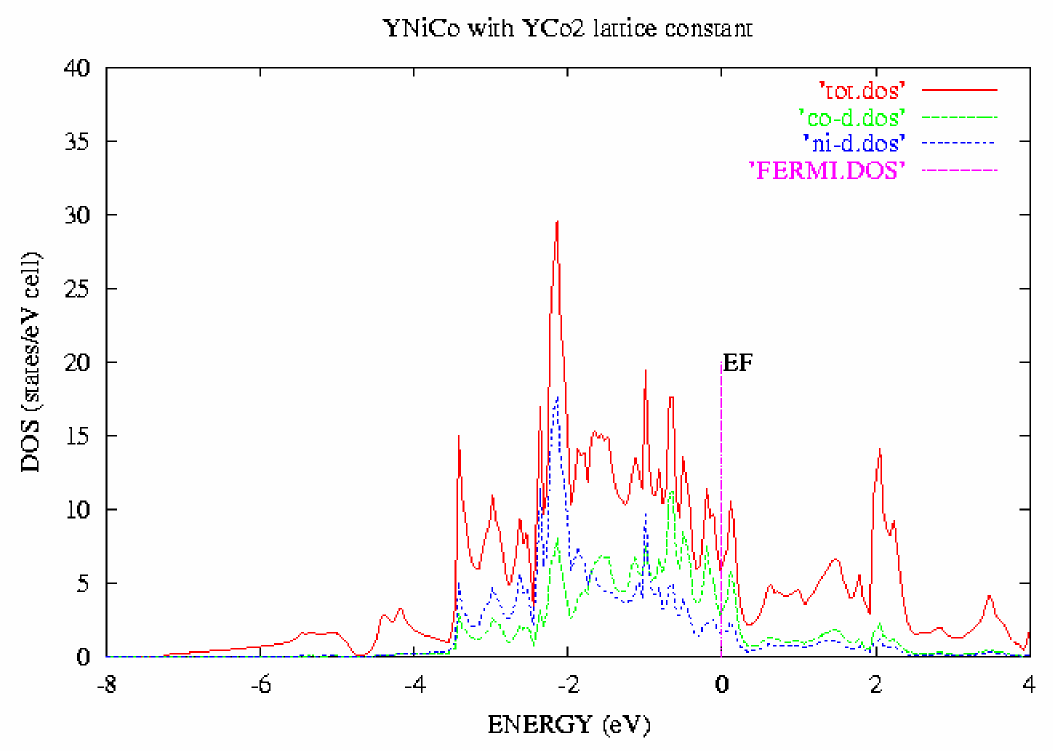
R.Tetean, et. al., J. Alloys and Comp., 2001



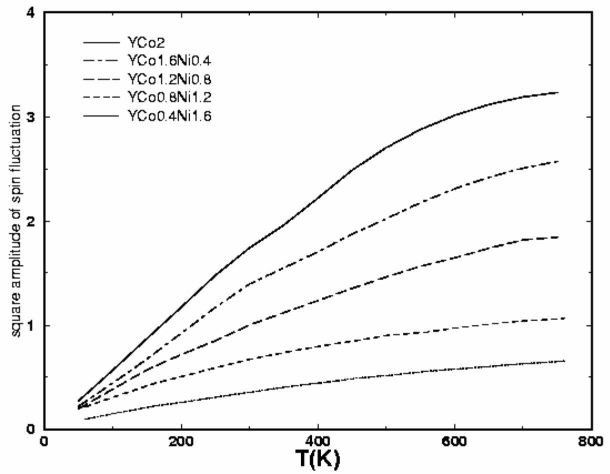
R.Tetean et.al., J.Magn. Magn. Mater., 2002

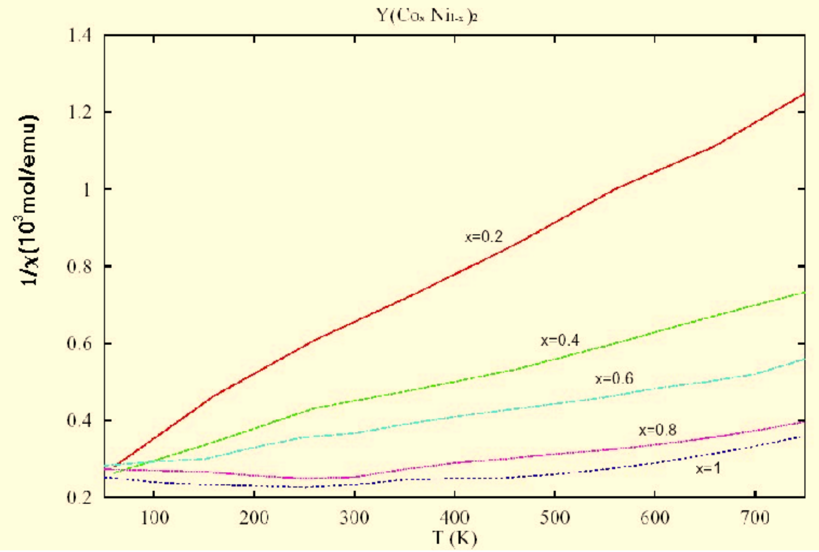


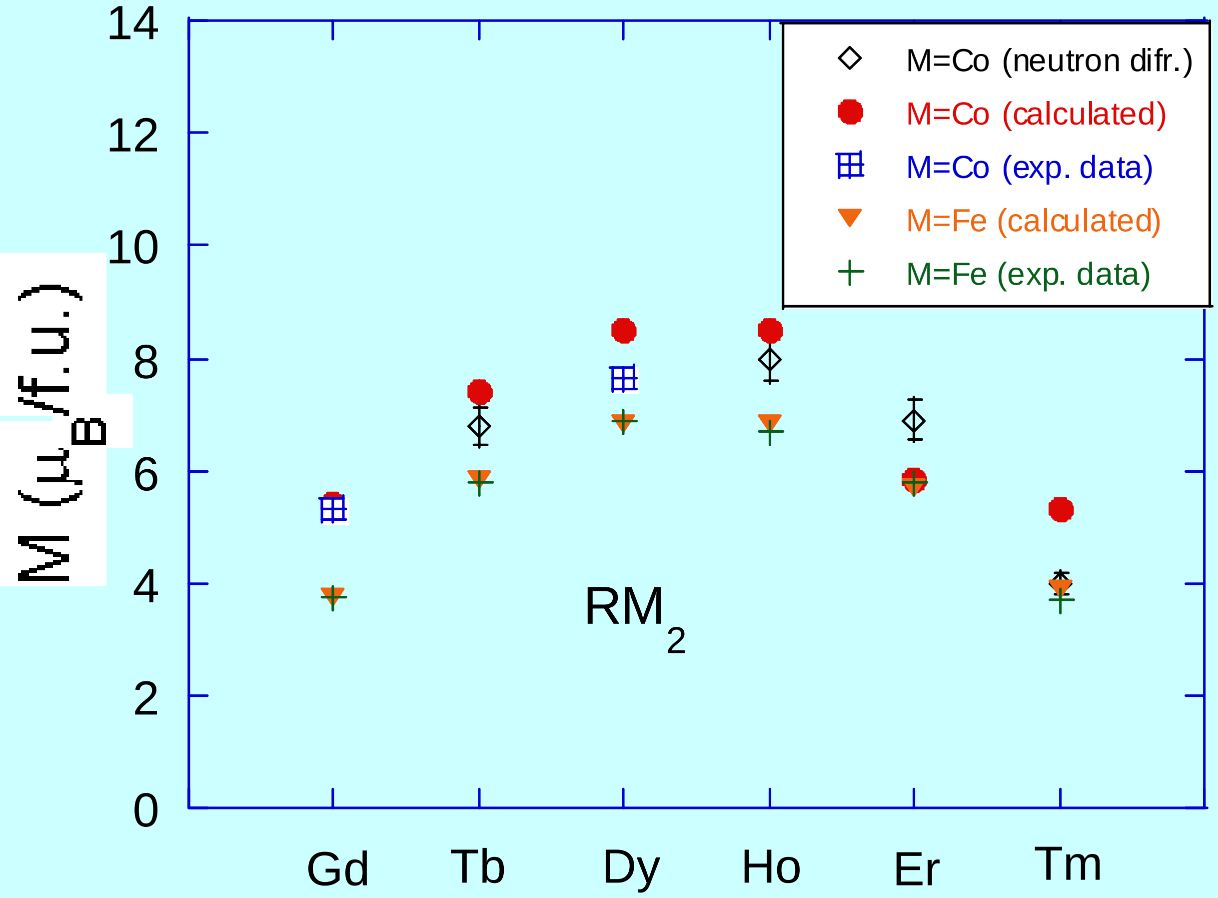
R.Tetean et. al., Phys. Stat. Sol. (a), (2003



L. Chioncel et.al., Mol. Cryst. Liquid Crystals (2004)


YCo2
YCo1.6Ni0.4
YCo1.2Ni0.8
YCo0.8Ni1.2
YCo0.4Ni1.6
square amplitude of spin fluctuation
T(K)


Y(Cox Ni1-x)2
1/χ(10^3 mol/emu)
T (K)
x=0.2
x=0.4
x=0.6
x=0.8
x=1

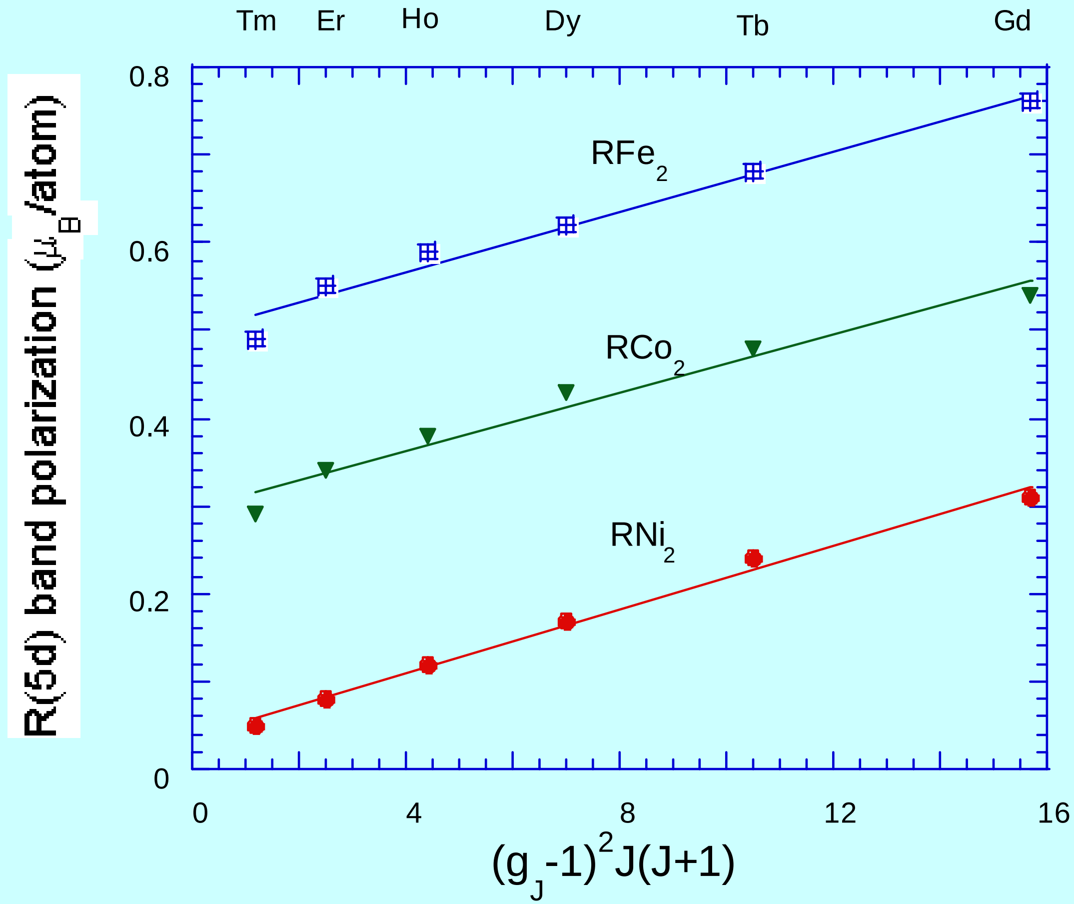


$M_{Fe} \approx 1.80 \mu_B/atom$

$M_{Co} \approx 1.00 \mu_B/atom$

$M_{Ni} \approx 0.00 \mu_B/atom$

R. Tetean et.al., Intermetallics, in press


Tm
Er
Ho
Dy
Tb
Gd
RFe2
RCo2
RNi2
0.8
0.6
0.4
0.2
0
0
4
8
12
16
R(5d) band polarization (μB/atom)
(gJ-1)2J(J+1)

$$M_{5d} = M_{5d}(O) + aG$$

$$M_{5d} = M_{5d}(O) + aG$$

$a = 2.1 \cdot 10^{-2}\mu_B$ independent on M

$$M_{5d}(0) = \begin{cases} 0.02\mu_B & M = Ni \\ 0.27\mu_B & M = Co \\ 0.49\mu_B & M = Fe \end{cases}$$

Two contributions:

- local 4f-5d exchange (the same for three series)
- ***$M_{5d}(0)$*** is dependent on M magnetic contribution (was attributed to the 5d band polarization as result of 5d-3d hybridization)

$$M_{5d} = M_{5d}(O) + aG$$

M=Ni

R5d polarization only 4f-5d exchange

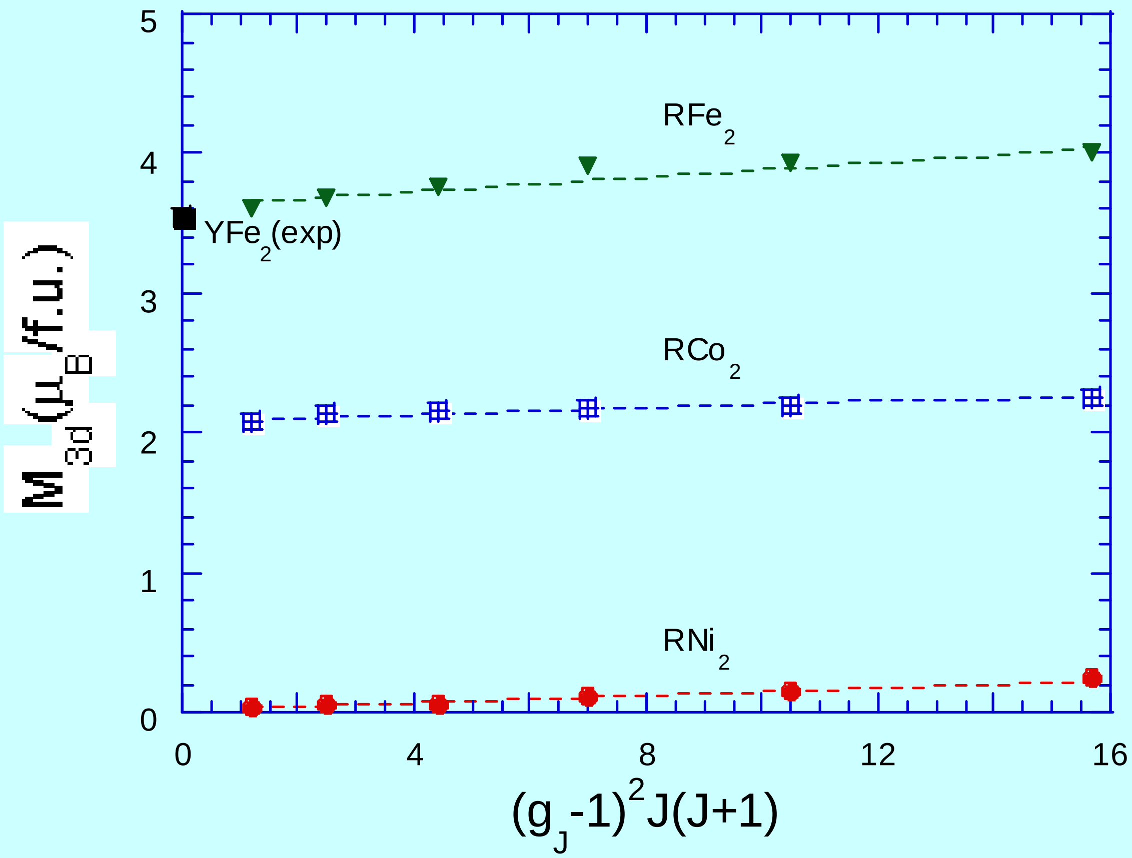
! is the same for a given **R**, independent on **M**

! $\mathbf{J_{4f\text{-}5d}}$ little dependent on **R**

M=Co or Fe

! $\boldsymbol{M_{5d}(0)}$) increase as **M** moment increase

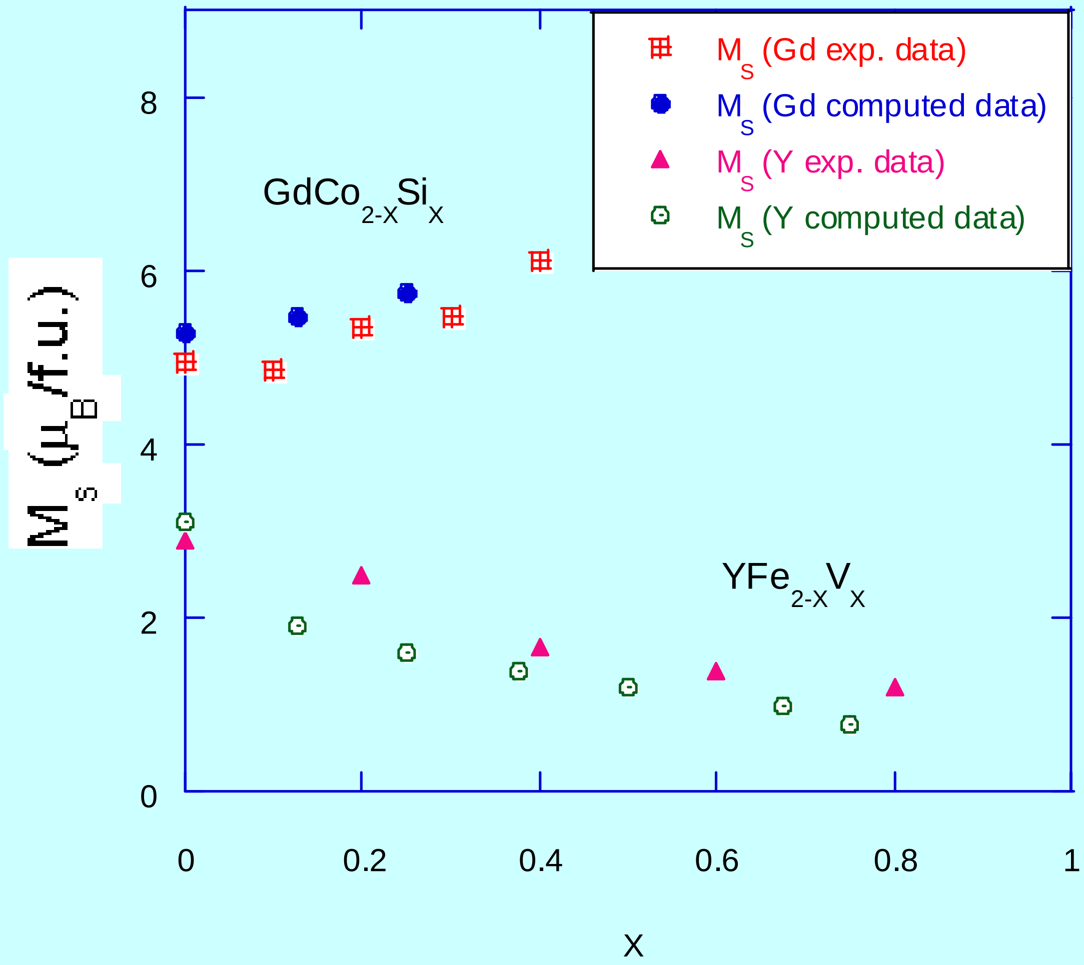
$$M_{3d} = M_{3d}(O) + bG$$



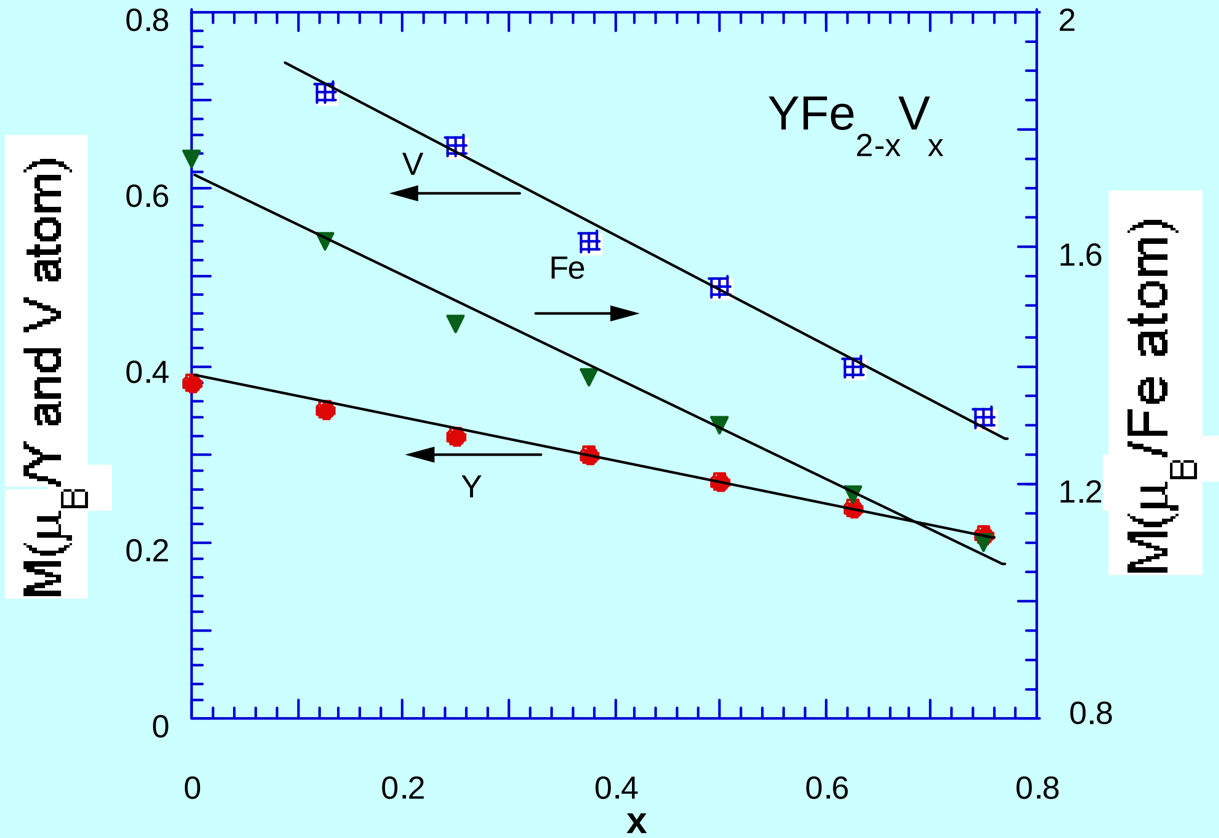
$$M_{3d} = M_{3d}(O) + bG$$

$$b = \begin{cases} 1.20 \cdot 10^{-2}\mu_B & M = Ni \\ 1.90 \cdot 10^{-2}\mu_B & M = Co \\ 2.00 \cdot 10^{-2}\mu_B & M = Fe \end{cases}$$

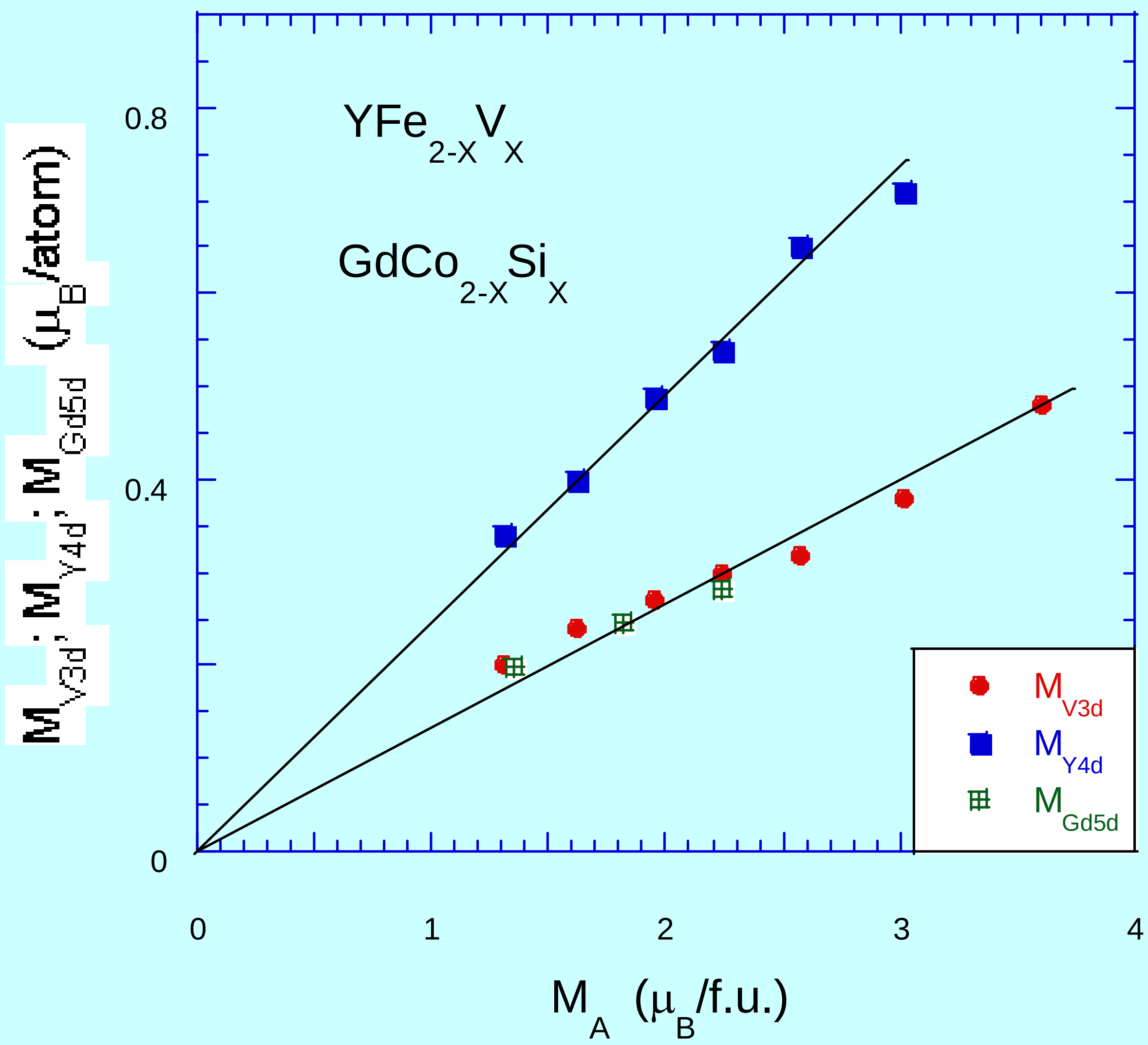
$$M_{3d}(0) = \begin{cases} 0.02\mu_B & M = Ni \\ 2.00\mu_B & M = Co \\ 3.60\mu_B & M = Fe \end{cases}$$



GdCo2-xSix
YFe2-xVx
Ms (Gd exp. data)
Ms (Gd computed data)
Ms (Y exp. data)
Ms (Y computed data)
Ms (μB/f.u.)
x
0
2
4
6
8
0.2
0.4
0.6
0.8
1



R. Tetean et.al., J. Magn. Magn. Mat., 2002



0.8
0.4
0
0
1
2
3
4
YFe2-XVX
GdCo2-XSiX
MV3d; MY4d; MGd5d (μB/atom)
MA (μB/f.u.)
MV3d
MY4d
MGd5d

CONCLUSIONS

• the exchange interaction parameters J_{5d-3d} and for a given type of structure are nearly constant

•an identical ratio $M_{5d}(0)/M_{3d}(0)=0.12+(-)0.01$ in RCo_2 and RFe_2 series was shown. This suggest that the additional polarization is induced by 5d-3d short range exchange interactions

•the 5d-3d exchange interaction act like an internal field and increase the 5d band polarization

•the internal field quenched the spin fluctuation

FUTURE PROSPECTS

- ultra high magnetic field measurements
- measurements under high pressure
- electrical measurements
- consideration of 4f-6s, 4f.5d and 5d-5d interactions

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