Magnetic properties and electronic structures of rare-earth-transition metal compounds

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1. Exchange enhanced paramagnets
2. Magnetic ordered compounds
    2.1 Exchange interactions
    2.2 Induced cobalt moments
    2.3 Magnetism and pressure effects
        Transition metals:
        2.3.1 Strong ferromagnetism, RCo_5 compounds
        2.3.2 Weak ferromagnetism, RCo_2 compounds
        2.3.3 Intermediate degree of localization
            RCo_4X (X = B, Si), R-Co-B

3. Conclusions

Methods

Crystal structures

Magnetic properties

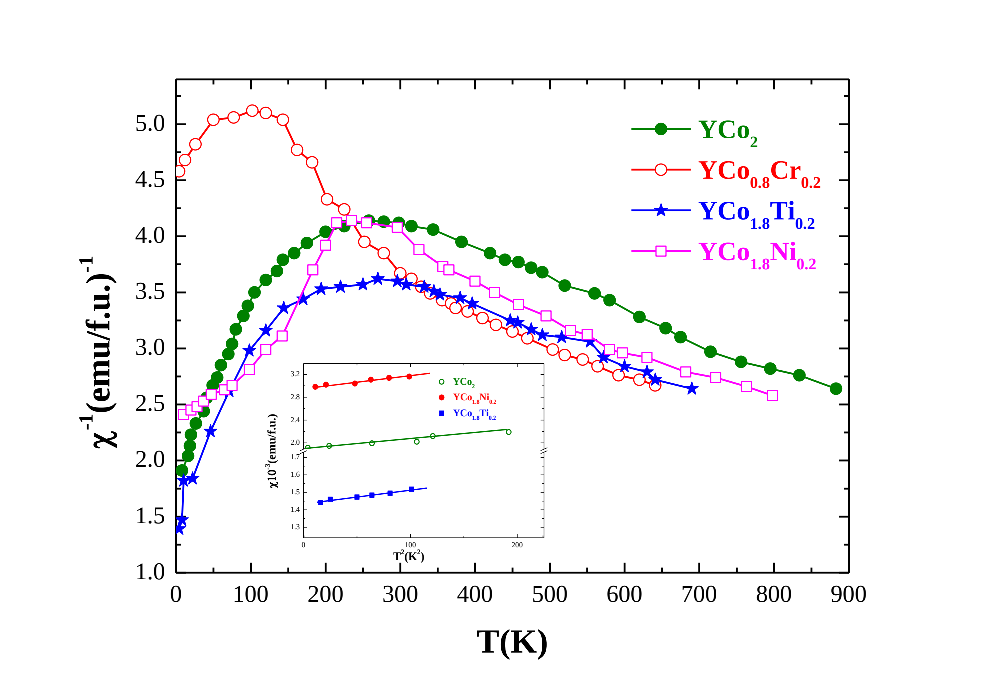
Magnetocaloric effect

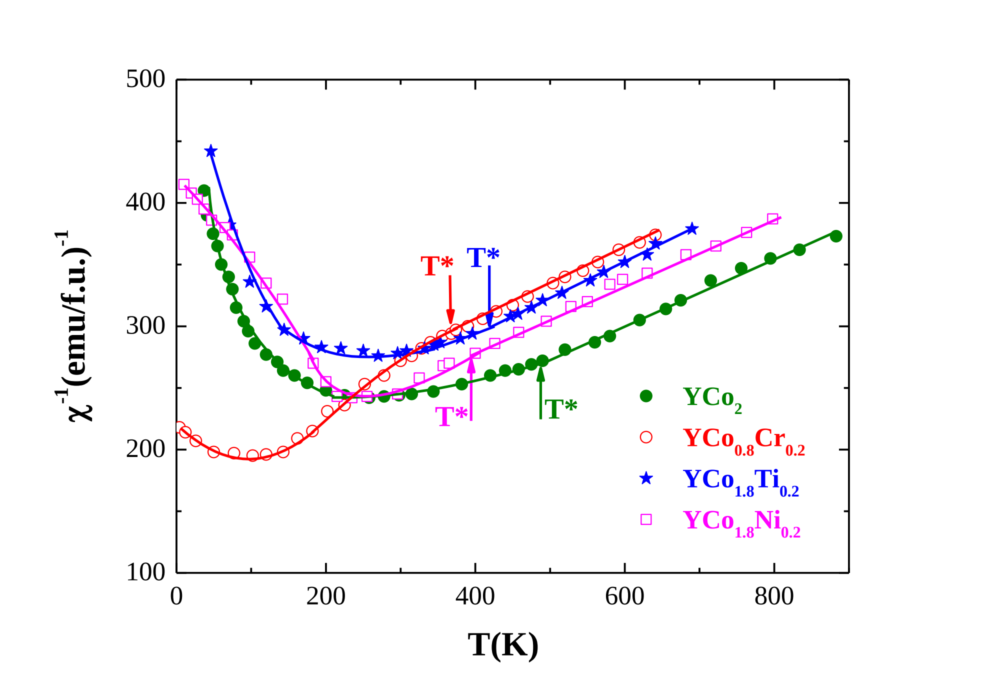
Band structure calculations

LMTO-ASA

LDA+U

1. Exchange enhanced paramagnets





Low temperature $\chi = \chi_0(1+aT^2)$

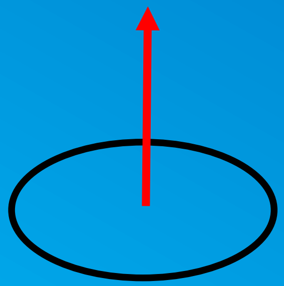
High temperature $T > T^*$ $\chi = C(T-\theta)^{-1}$

$\theta < 0$

Self consistent theory of spin fluctuations

Wave number dependent susceptibility, χ_q, for a nearly ferromagnetic alloy has a large enhancement for small q values

$$\chi_q = \frac{\bar{\chi}_q}{1 - J\bar{\chi}_q(\mu_0 \mu_B^2)}$$



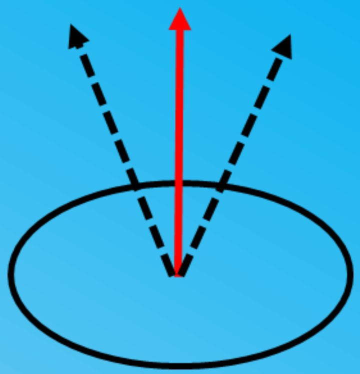
Frequency of longitudinal spin fluctuations $\omega^* \propto \frac{1}{\tau}$

τ-lifetime of LSF

Low temperature

$\omega^* > \frac{k_B T}{\hbar}$ thermal fluctuations (transversal) slow

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



Approximation for nonmagnetic state

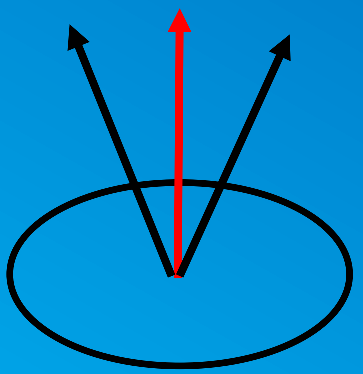
$\chi \propto T^2$ $\chi(T)\nearrow$ as $T\nearrow$

$\eta'' > 0$ (necessary condition, not sufficient)

High temperature

Average mean amplitude of LSF is temperature dependent

$$\left\langle S_{loc}^{2} \right\rangle = 3k_B T \sum_q \chi_q \qquad \omega^* < \frac{k_B T}{\hbar}$$

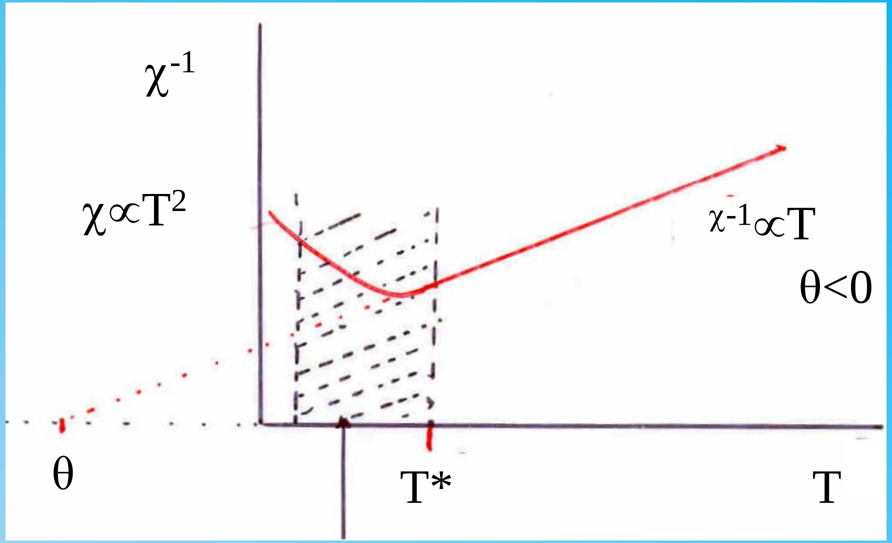


S_{loc}↗ as T ↗ up to T* (S_{loc})

S_{loc} determined by charge neutrality condition

The system behaves as having local moments for temperatures T > T* where the frequency of thermal fluctuations is higher than of logitudinal.

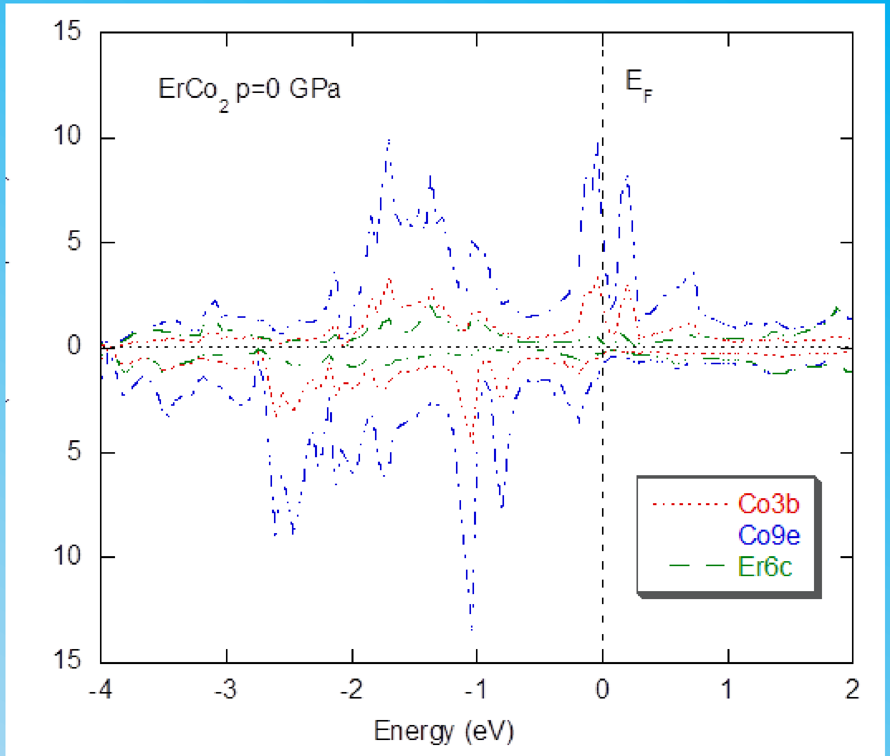
Transition from exchange enhanced paramagnetism to Curie-Weiss type behaviour.



Compound	$\chi_{exp} \cdot 10^{-3}$ at 2 K (emu/f.u.)	$\chi_{calc} \cdot 10^{-3}$ at 2 K (emu/f.u.)	T_{max} (K)	T* (K)	$a \cdot 10^{-3}$		M_{eff}Co μ_B/atom
					exp.	theor.	
$LuCo_2$	1.82	1.92	370	550	0.764	0.91	4.10
YCo_2	1.95	2.25	260	485	1.64	1.81	3.86
$YCo_{1.8}Ni_{0.2}$	2.9	3.02	215	408	1.24	1.36	3.84
$YCo_{0.9}Ti_{0.1}$	1.271		275	450	1.068		3.95
$YCo_{1.875}T_{0.125}$		1.796				0.9961	
$YCo_{1.8}Ti_{0.2}$	1.442		250	420	0.908		3.90
$YC_{1.75}Ti_{0.25}$		2.046				0.8945	
$YCo_{0.8}Cr_{0.2}$	4.58		180	370			

2. Magnetic ordered compounds

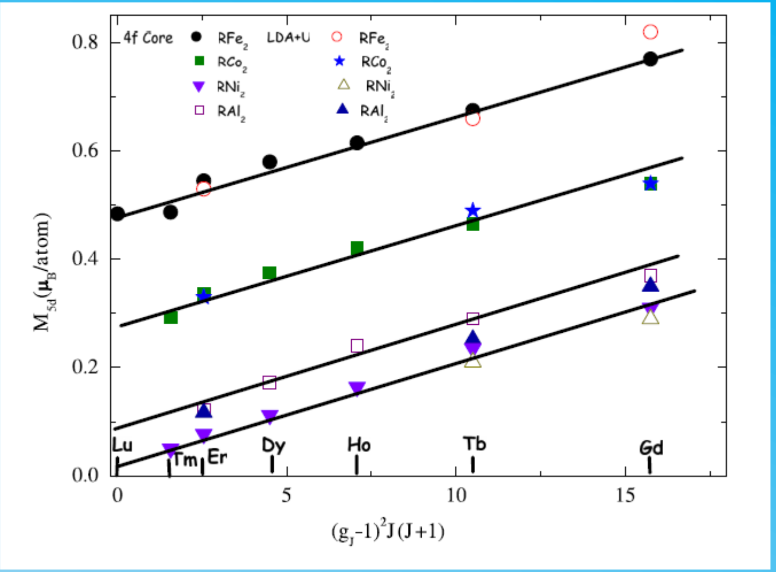
2.1 Exchange interactions RCo_2 compounds

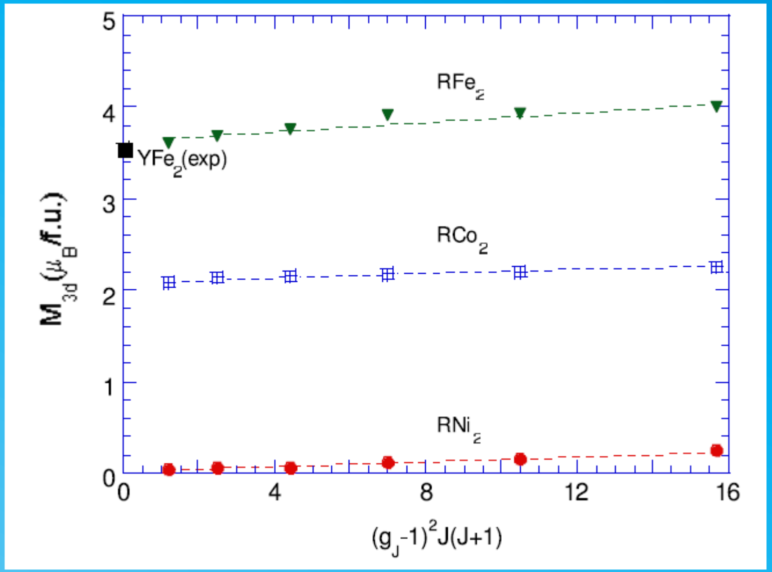


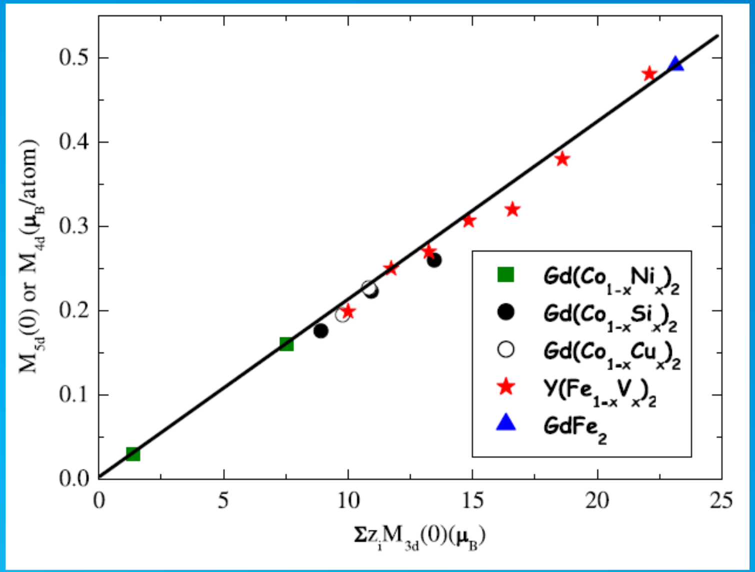
Strong hybridization Co3d bands at site Co3b and Co9e with Er5d one

4f-5d-3d model Campbell 1972

Burzo et al, J. Phys. Cond. Matter. 23, 1026001 (2011)







$M_{5d}=M_{5d}(0)+\alpha G \quad G=(g_J-1)^2J(J+1)$

4f-5d

$$J_{4f-5d} = \int g(\rho(r))\phi_{4f}^2(r)\phi_{5d}^2 dr$$

$M_M = M(0)+\alpha G$

5d-3d short range exchange interactions

$$H = -2J_{3d-5d}S_{5d}(0)\sum_i S_{3d_i}$$

$\downarrow$

$M_{5d}(0) \propto \sum z_i M_i \quad \frac{M_{5d}(0)}{\sum z_i M_i} = 2 \cdot 10^{-2}$

$M_{5d}(0) = 0.03\ \mu_B\ RNi_2$

$= 0.29\ \mu_B\ RCo_2$

$= 0.49\ \mu_B\ RFe_2$

Parimagnetism, Griffits phase

$T > T_c$

The 5d-3d coupling exist at $T > T_c$

H_{ext} align M_R moments

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$J_{5d\text{-}3d}$ coupling

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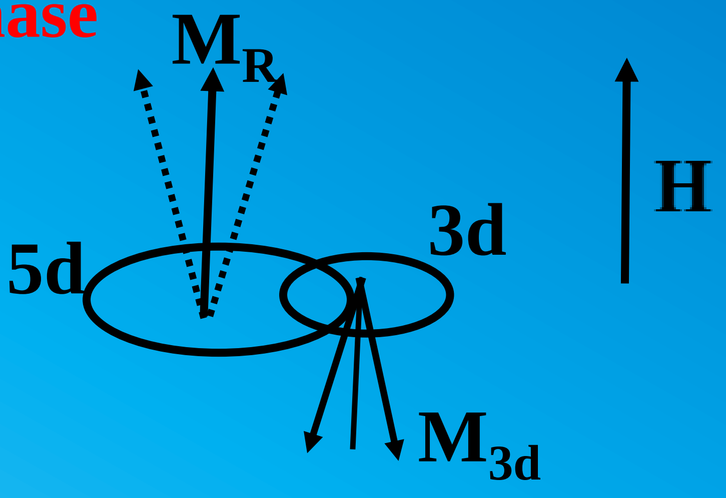
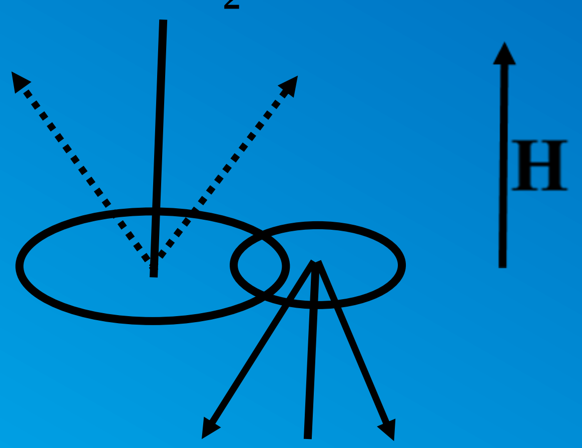
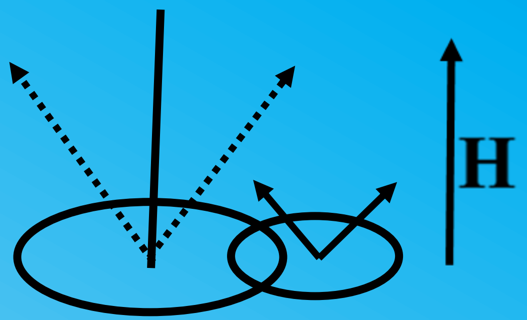
Antiparallel oriented Co moment

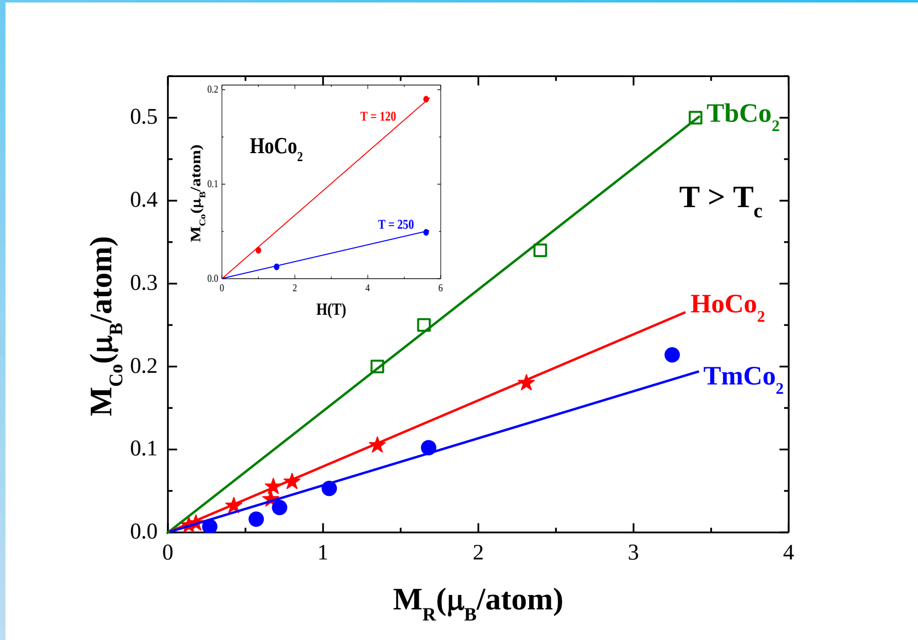


T < T_2



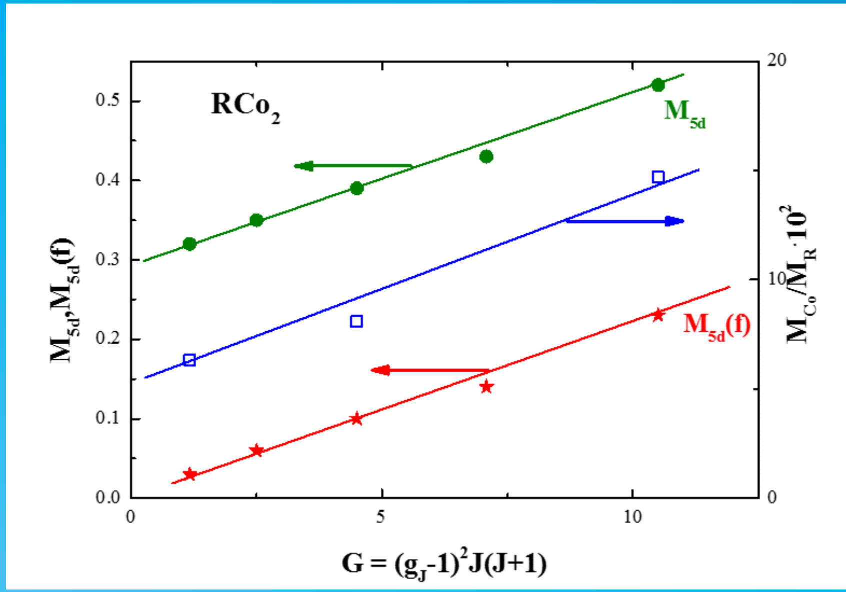
T > T_2





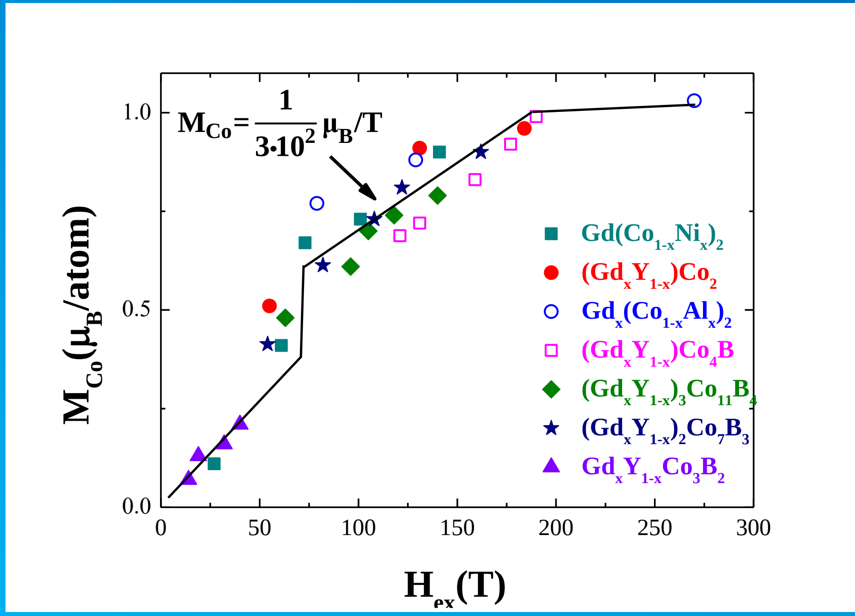
$J_{4f\text{-}5d} \propto G$; $G = (g_J-1)^2 J(J+1)$

$M_{5d}(f) = \alpha G$, $\alpha = 2.1 \cdot 10^{-2}\ \mu_B$

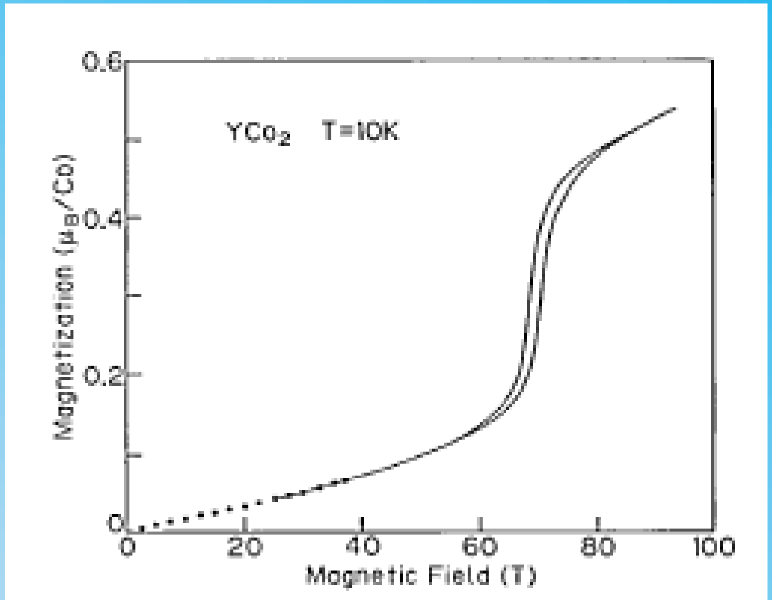


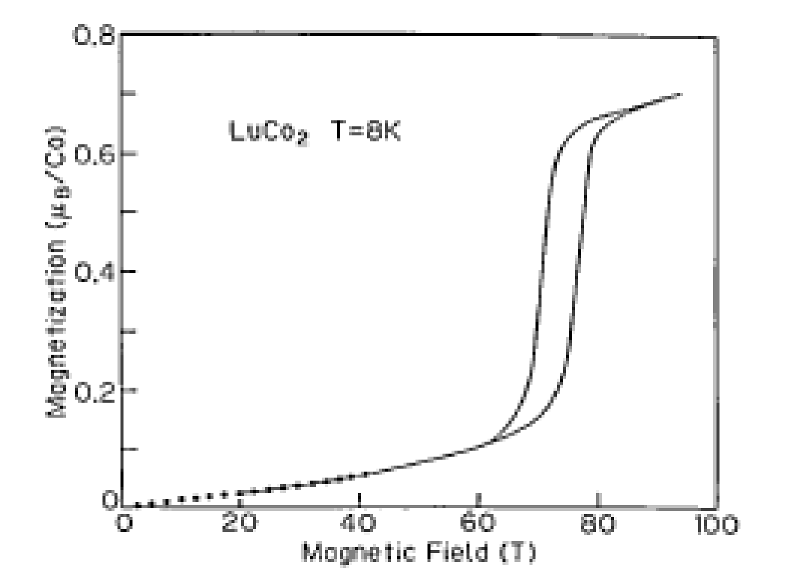
2.2 Induced cobalt moments

Critical field for inducing cobalt ordered moment



- Itinerant electron metamagnetism: conditions for a paramagnetic substance to become ferromagnetic by application and subsequent removal of strong magnetic field (Wholfarth-Rhodes, 1962).
- Induced magnetism (epamagnetism): shift of the spin-up and spin down bands under the action of exchange of external field (Burzo 1977).





RCo_4M, M = Ga, Si, Al

M_{Co} strongly dependent on composition

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exchange interactions

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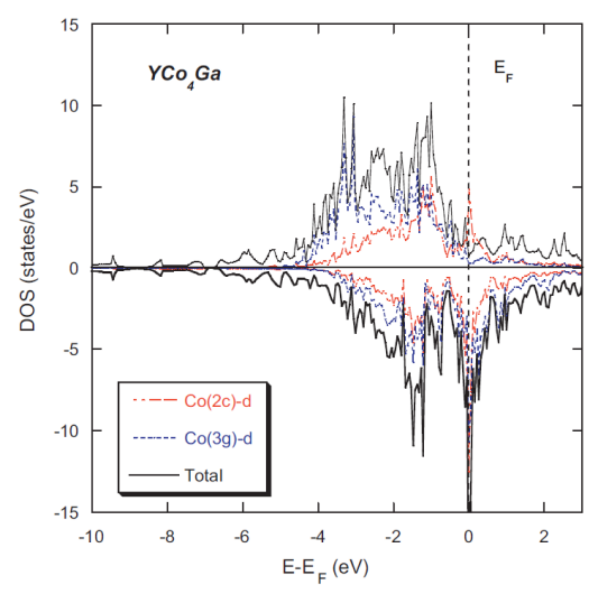
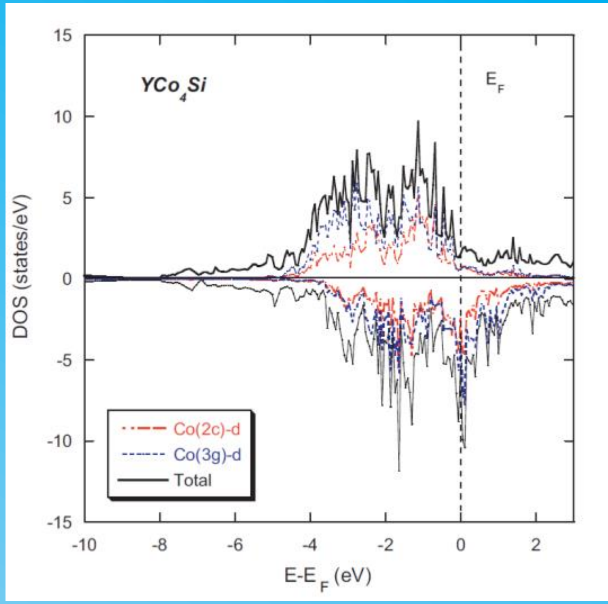
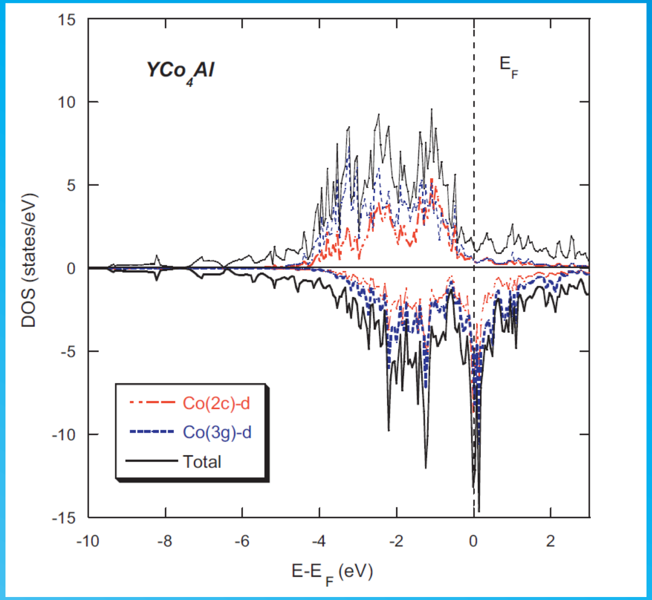
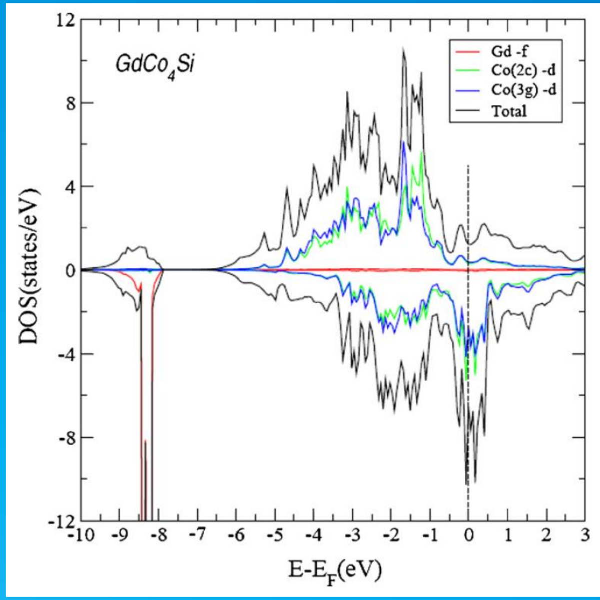
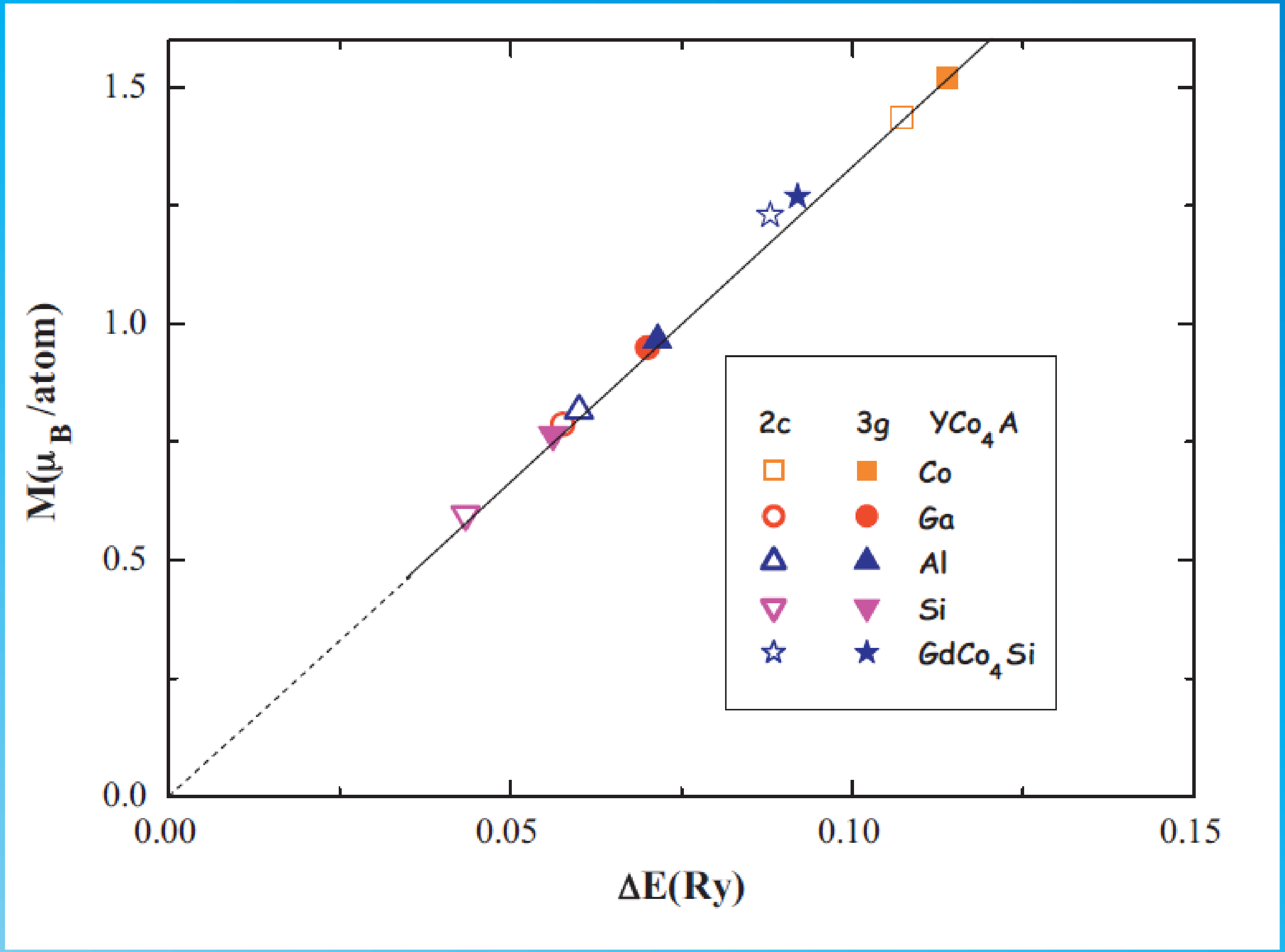
splitting on 3d bands











s = 0.95 eV/μ_B general characteristic

No presence of itinerant electron metamagnetism

2.3 Magnetism and pressure effects

Magnetic behaviour of RCo_5 under pressure

RCo_5 compounds

Crystal structure $CaCu_5$

Co 2c, 3g R1a

R = Pr, Nd, Sm, Y ferromagnetic

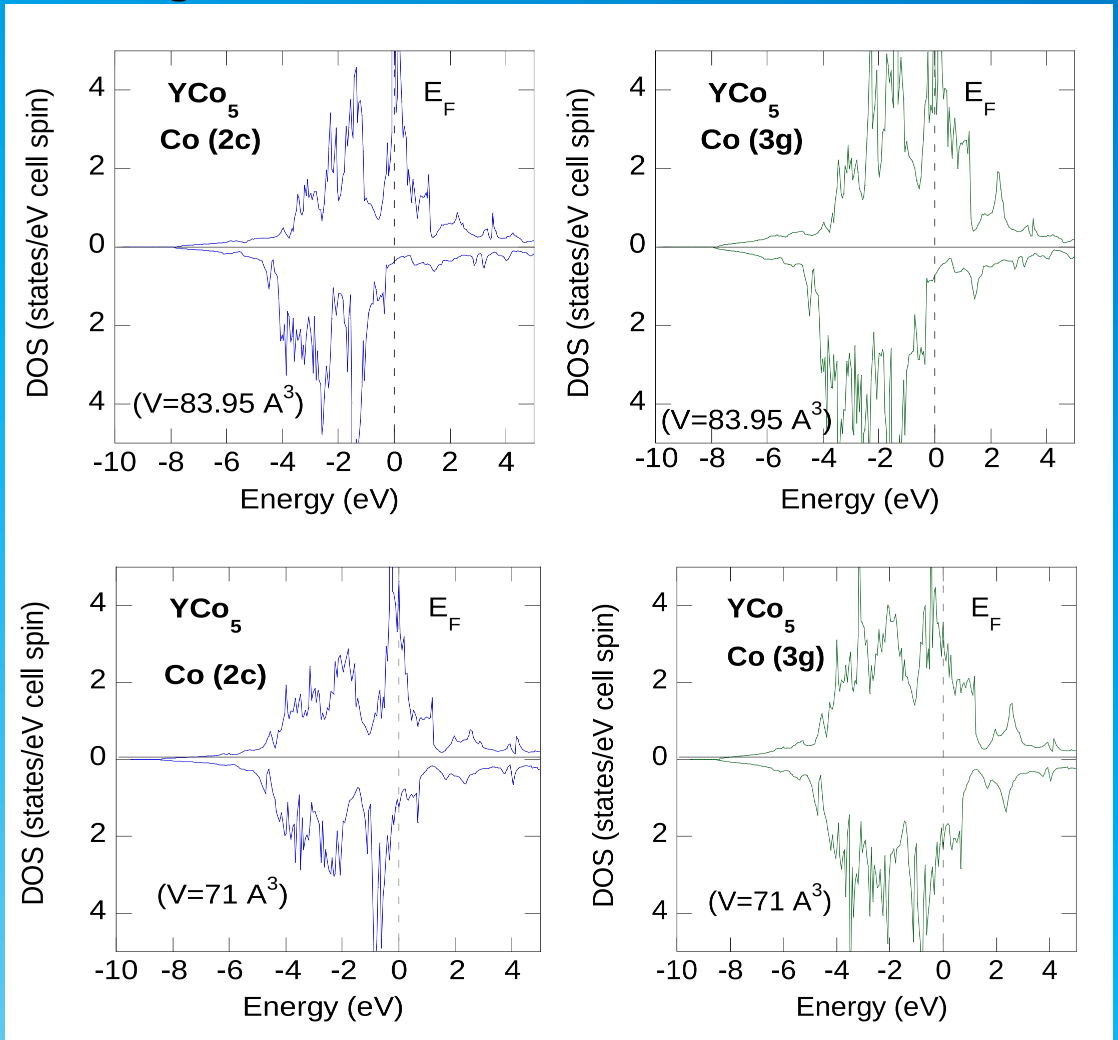
R = Gd, Tb, Dy, Ho, Er ferrimagnetic

YCo_5, $GdCo_5$

Cobalt shows strong ferromagnetism

YCo_5

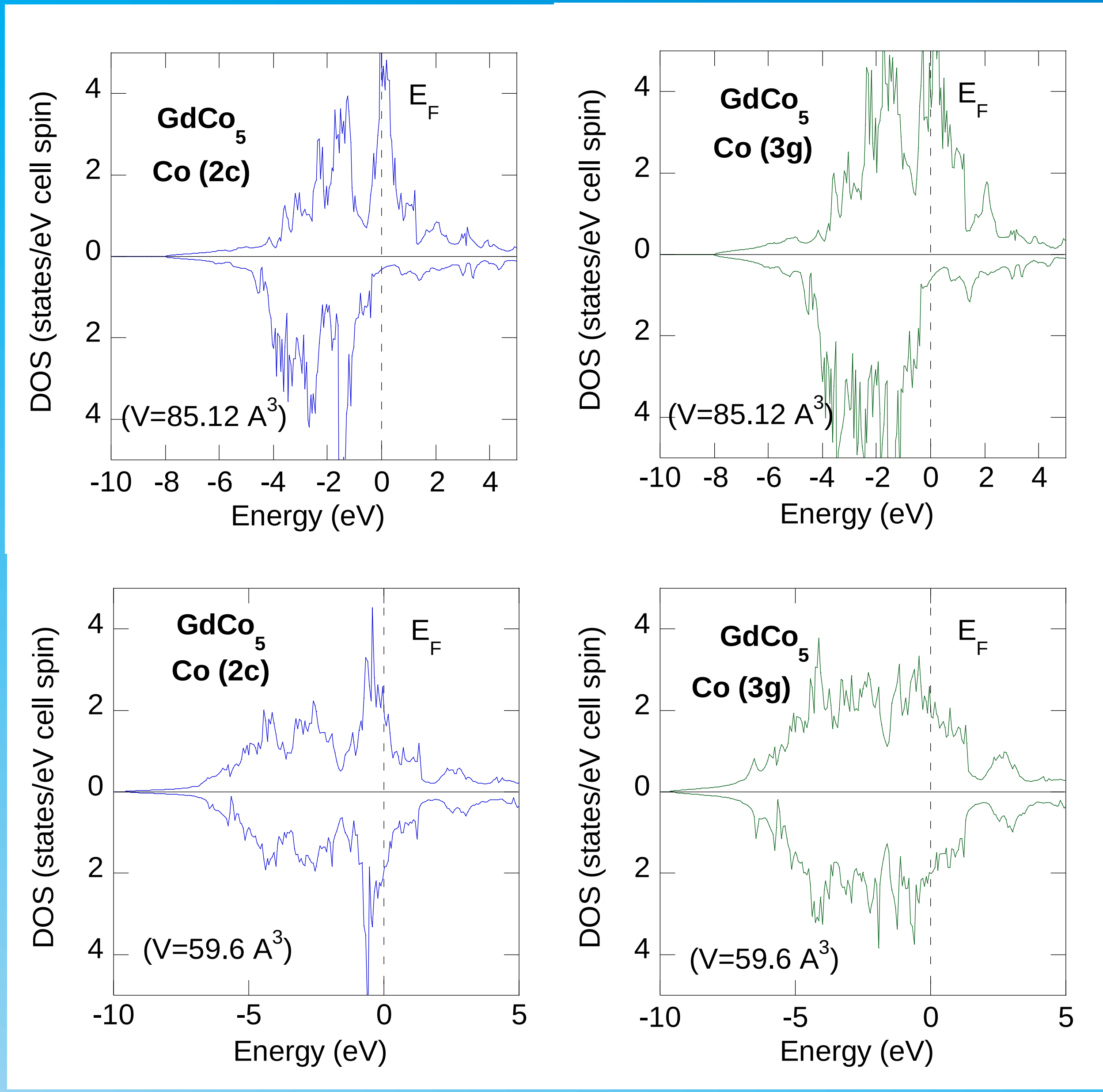
H_a = 18 T at 4 K, T_c = 1000 K



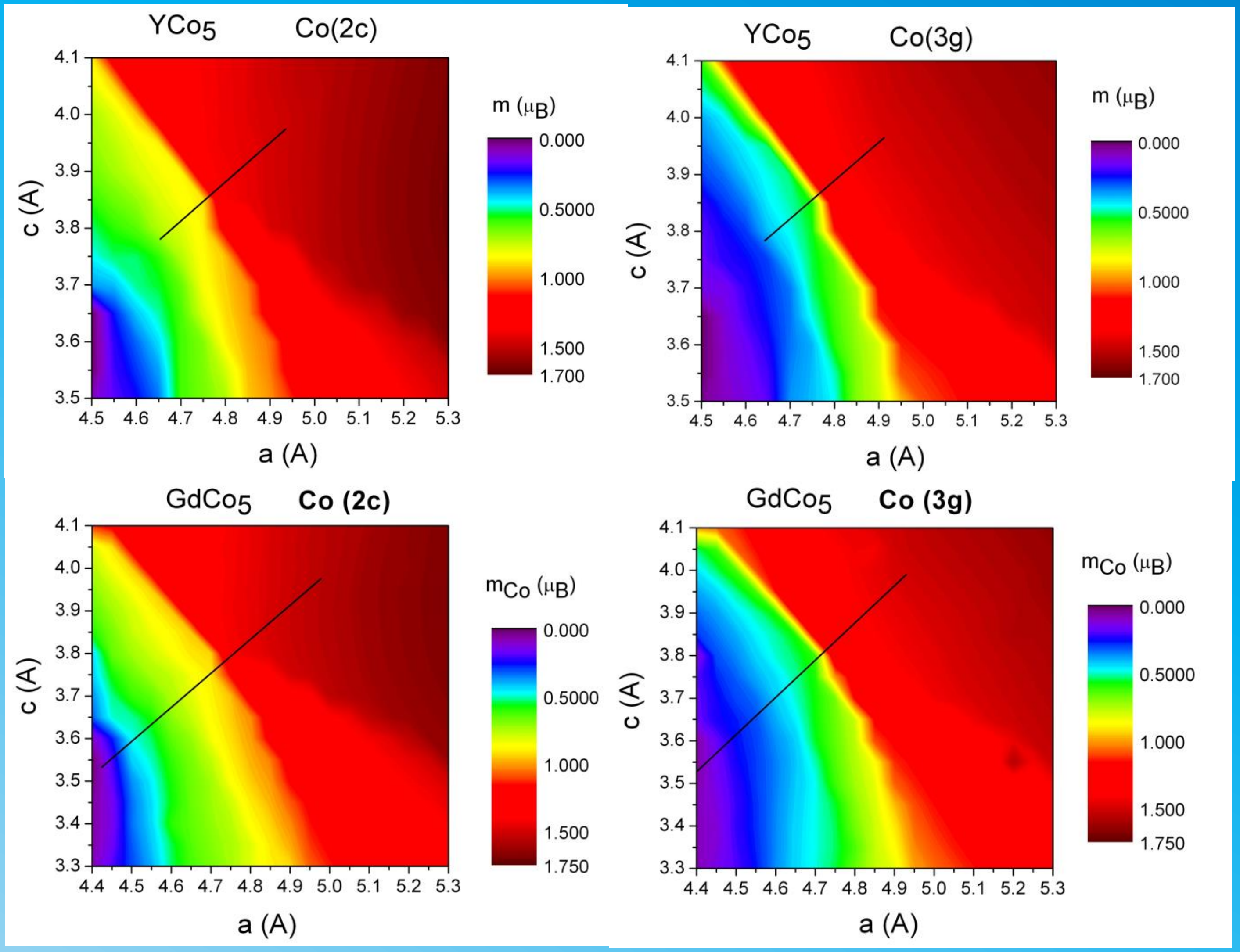
spin-up sub-band → shift to lower energies
spin-down sub-band → shift to higher energies

} exchange splitting diminishes

$GdCo_5$: shift of sub-bands as in YCo_5



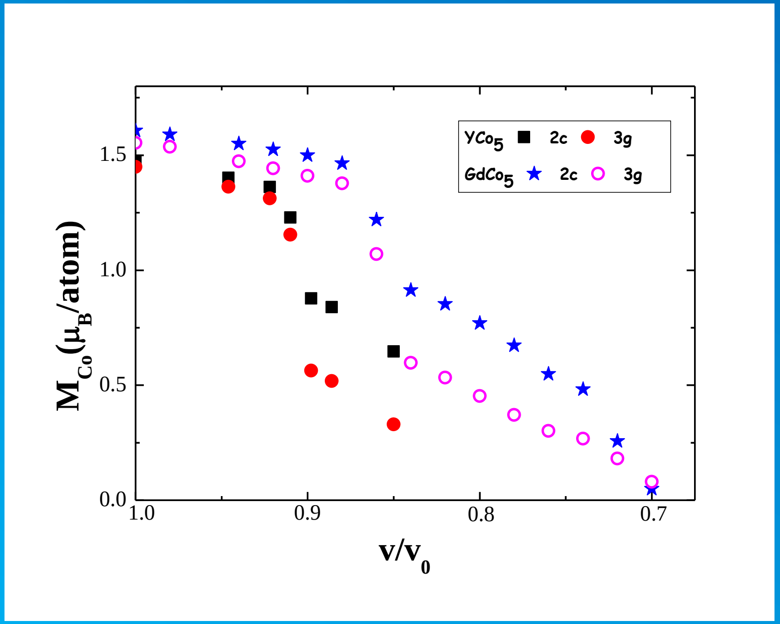
Dependence of cobalt moment on lattice parameters



Transition from high spin state (HS) to low spin state (LS)

YCo_5 $v/v_0 = 0.90$

$GdCo_5$ $v/v_0 = 0.86$



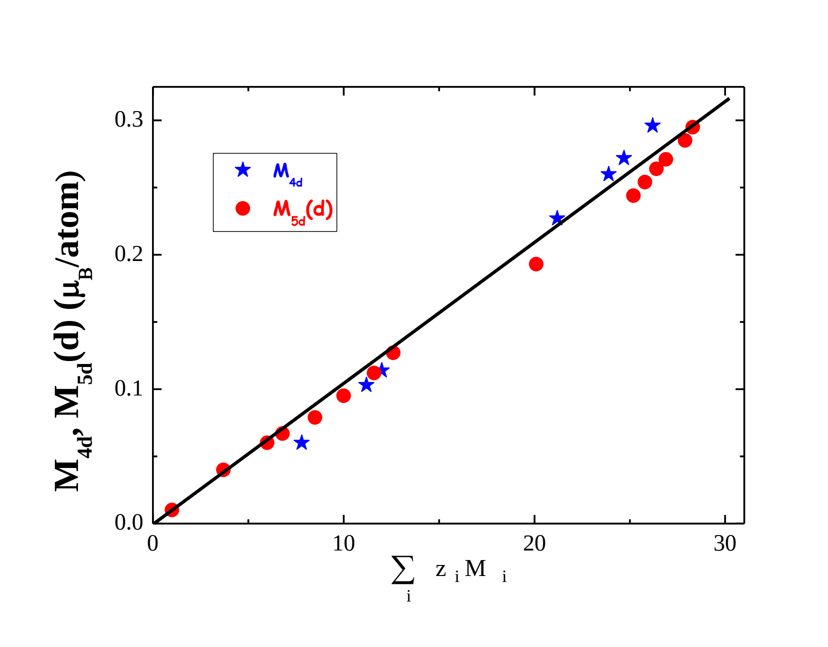
R-Co 4f-5d-3d exchange interactions

Y-Co 4d-3d exchange interactions

$$M_{5d} = M_{5d}(0) + M_{5d}(f)$$

$$M_{5d}(0) \propto \sum z_i M_{Co_i};\ M_{4d} \propto \sum z_i M_{Co_i}$$

The same behaviour for $M_{5d}(0)$ and M_{4d}



Pressure effects

Co strong ferromagnet:

- high hydrostatic pressure destroys the strong ferromagnetism
- the transformation proceeds in a stepwise fashion concomitant with isomorphic lattice charge
- there is a shift of the bands

  spin up to lower energies

  spin down to lower energies

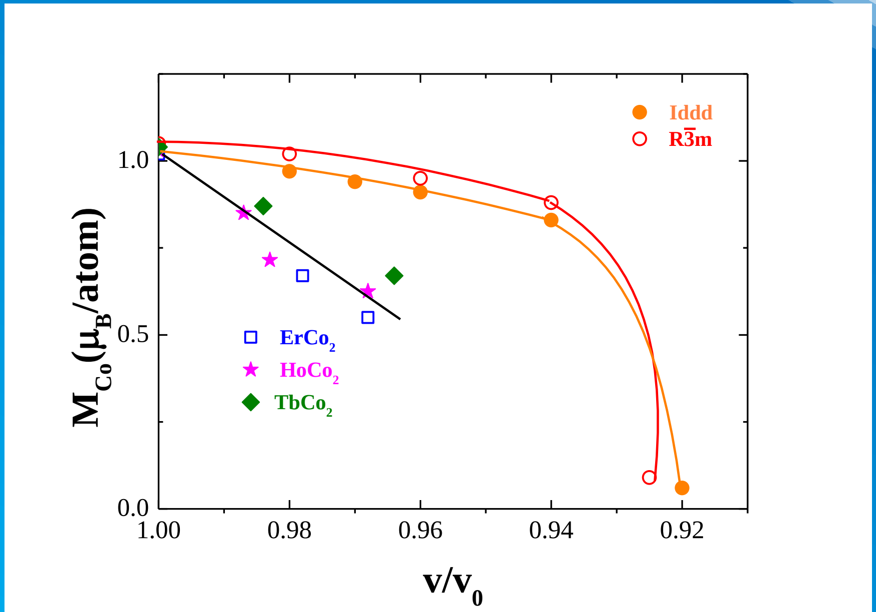
Unstable thermodynamic state

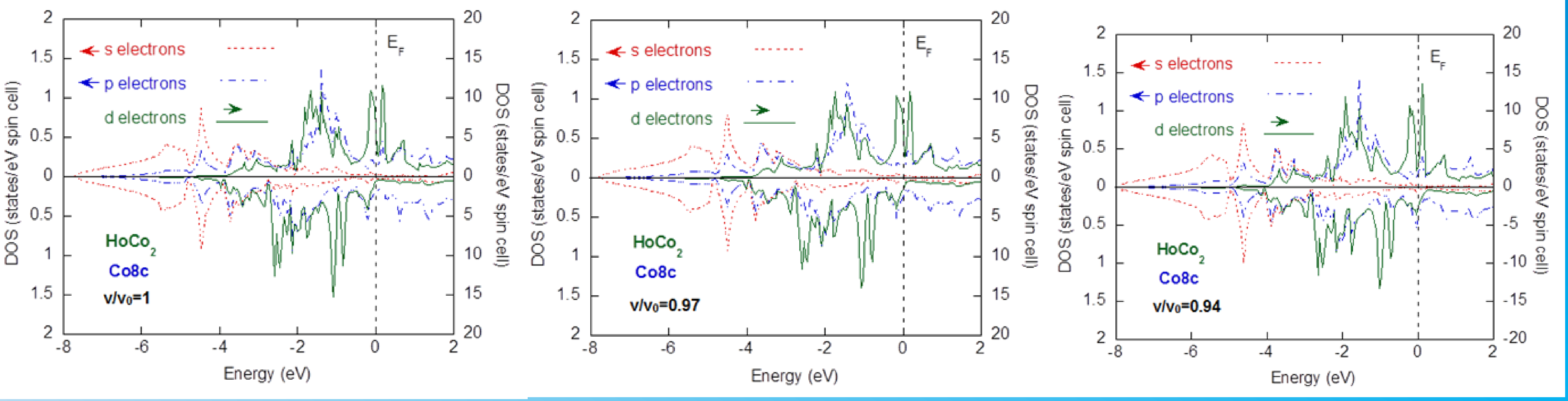
rather high DOS at both spin up and spin down bands

2.3.2 Weak ferromagnetism Pressure effects

$HoCo_2$

T < T_c = 85 K Crystal structure: tetragonal $I4_1/amd$





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J. Alloys Comp. 584, 393 (2014)

Magnetovolume effects

RCo_2

$$\Gamma = \frac{1}{k_B T_C}\frac{dT_C}{dp} = \frac{d\ln T_C}{d\ln v}$$

$$\Gamma = \frac{5}{3} + BT_c^{-2}$$ band model

$$B = \frac{5}{6}\frac{I}{I_b}\bar{I}T_F^2, \; T_c = T_F(\bar{I}-1)^{-1}$$

I effective intra-atomic exchange integral reduced from its bare value I_b,

$$\bar{I} = I\eta(E_F)$$

$B = 3.5 \cdot 10^4 T_c^{-2}$, $T_F = 240$ K

$I/I_b = 0.85$

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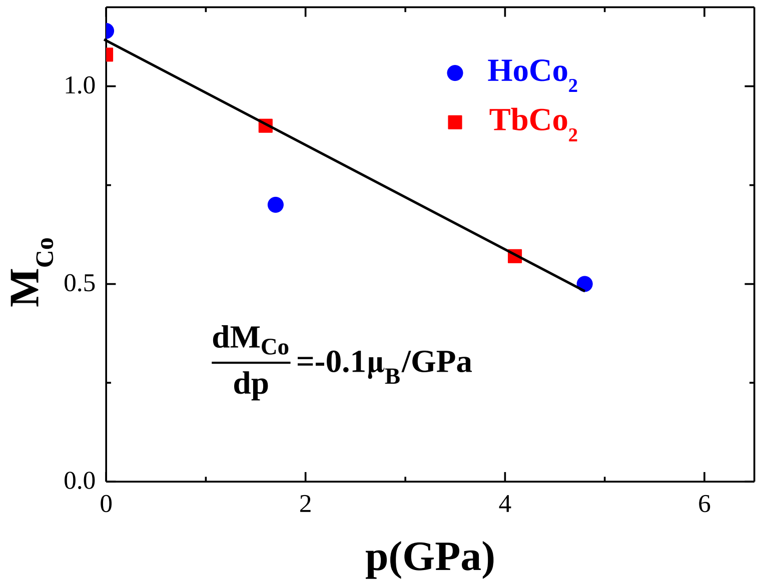
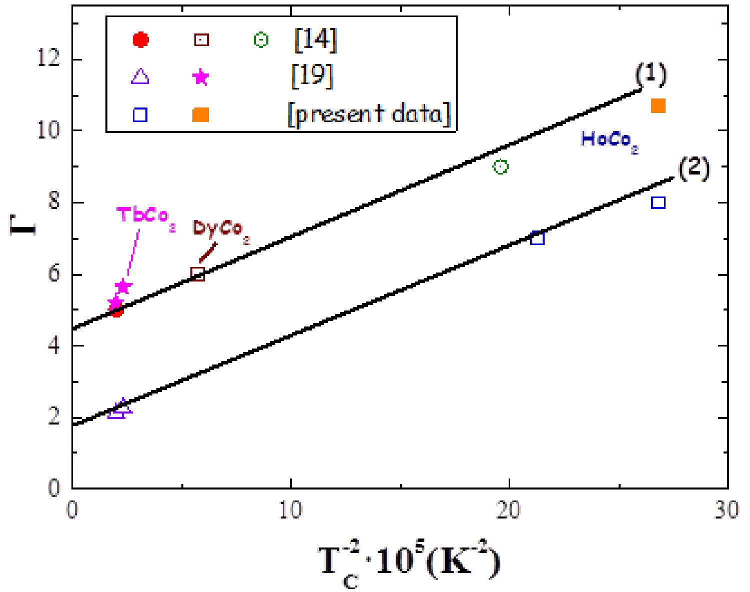
important correlation between 3d electrons





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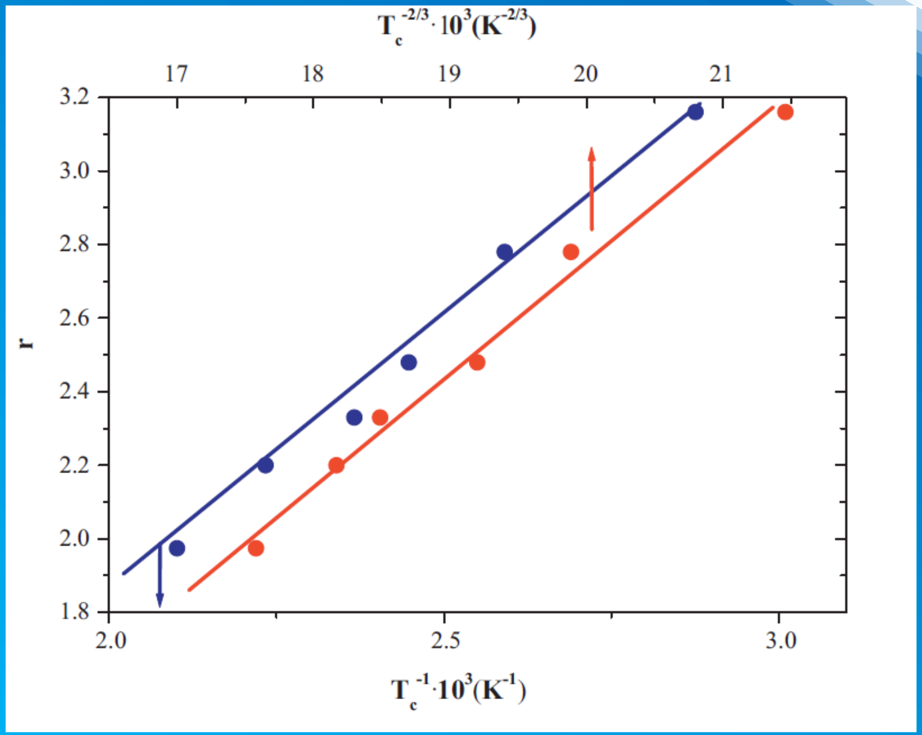
RCo_2 compounds

Behaviour: spin fluctuations

continuous change of the degree of localization of the cobalt moment



$r = S_p/S_0$

$\mu_{eff} = g\sqrt{S_p(S_p+1)}$

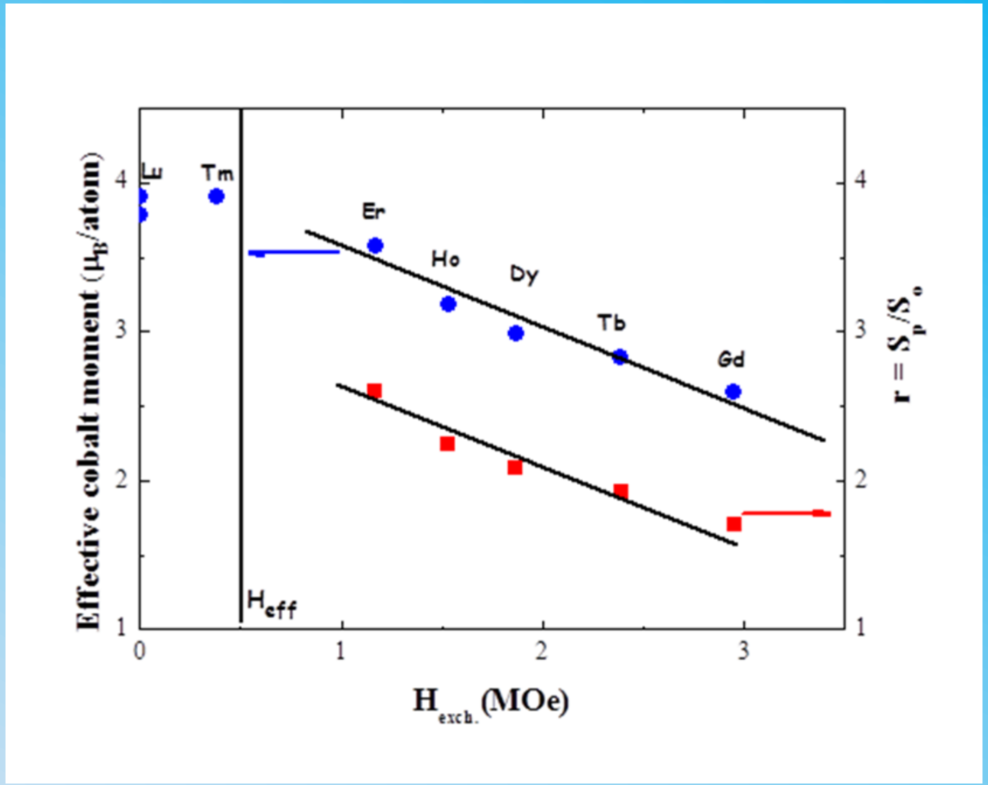
$\mu_0 = gS_0$

$r \propto T_c^{-2/3}$ spin fluctuations

$r \propto T_c^{-1}$ band model

r = 1 localized model

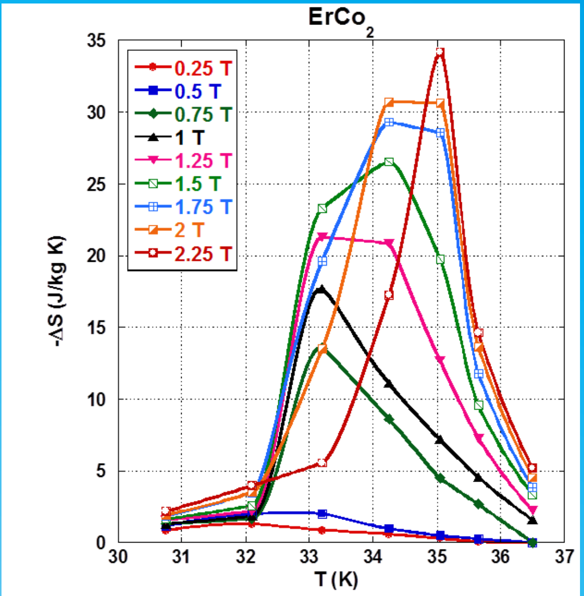
$r \rightarrow \infty$ band model

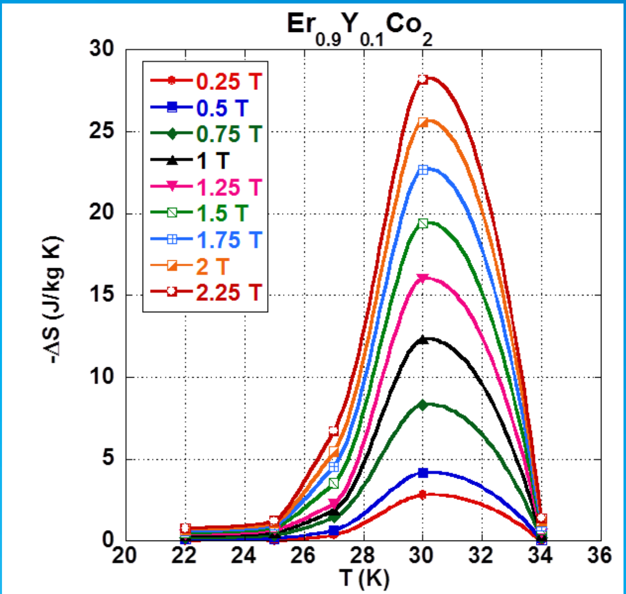


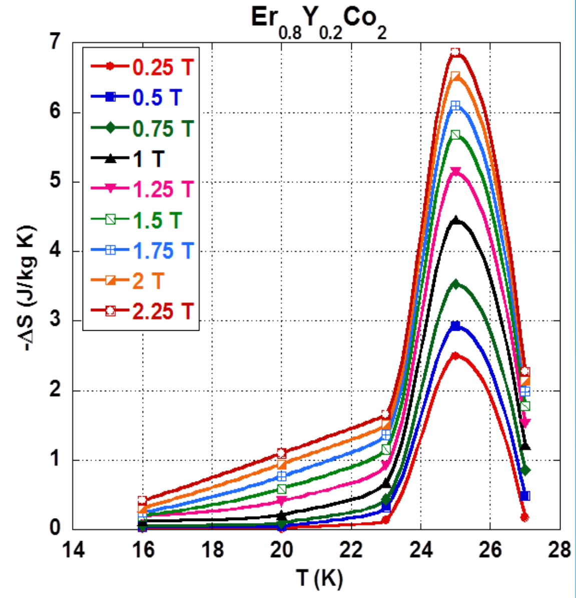
The degree of localization increase with H_{exch}

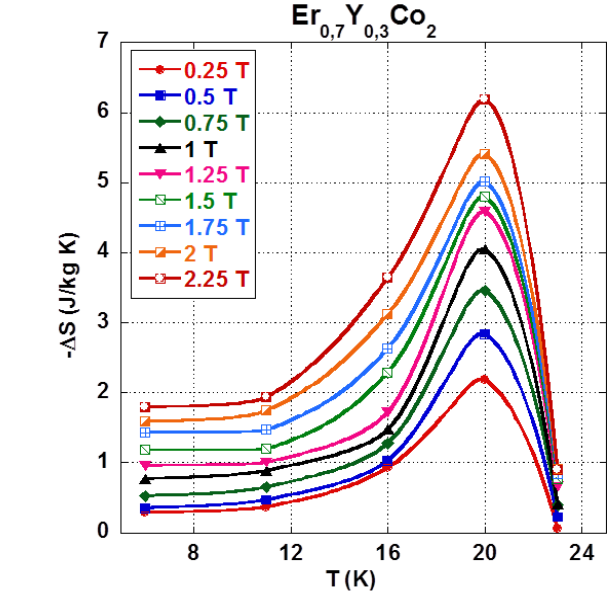
Magnetocaloric effect

$Er_{1-x}Y_xCo_2$





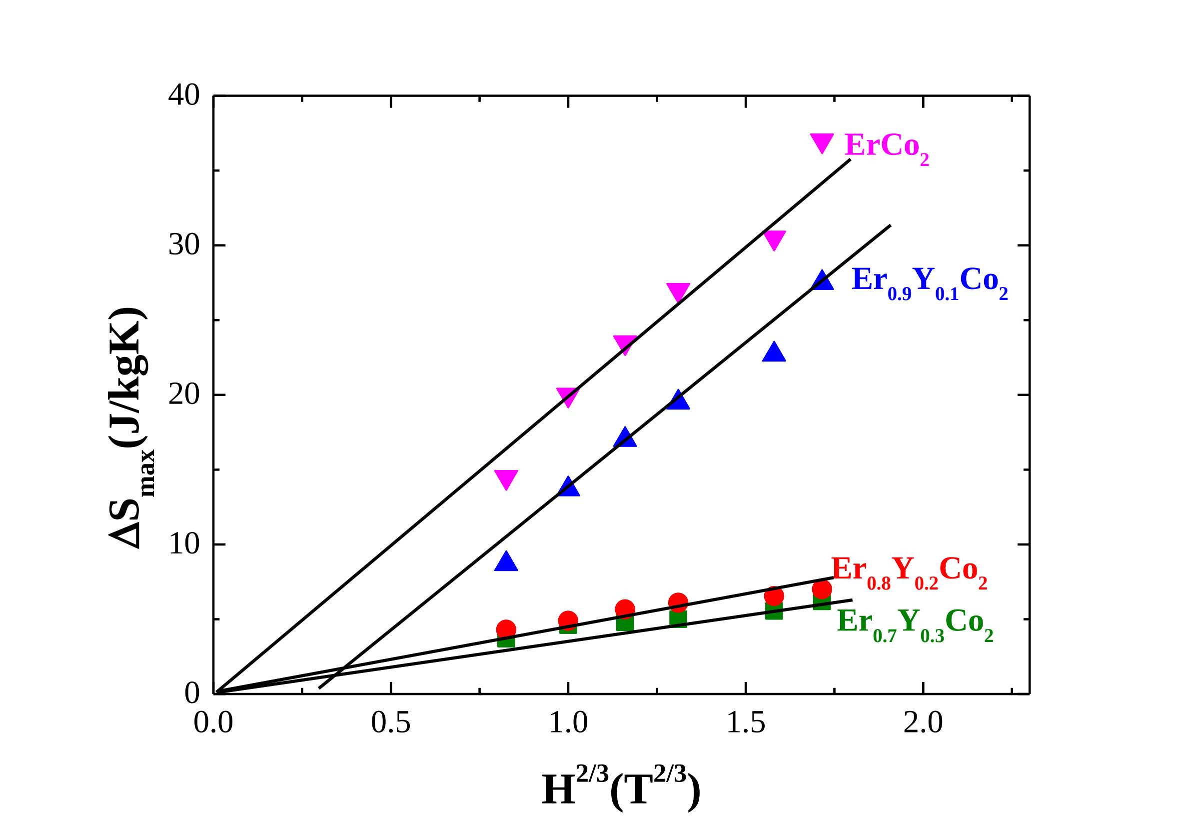




$Er_{1-x}Y_xCo_2$

High magnetocaloric effect: first order transition x = 0, x = 0.1

Low magnetocaloric effect: second order transition x = 0.2, x = 0.3

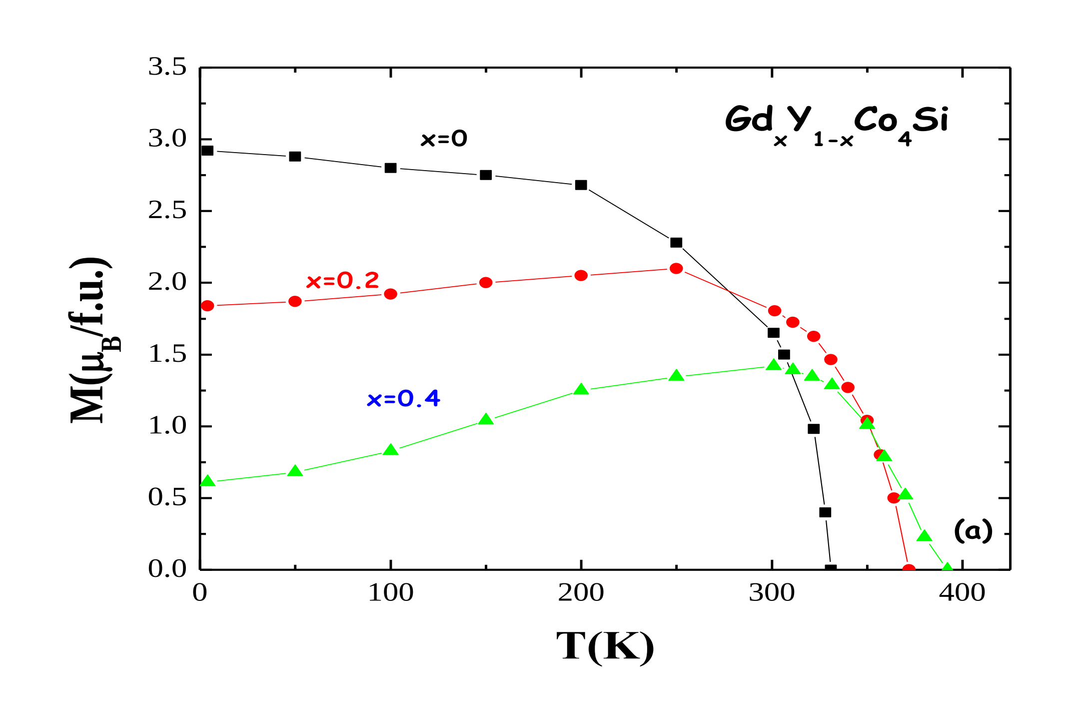


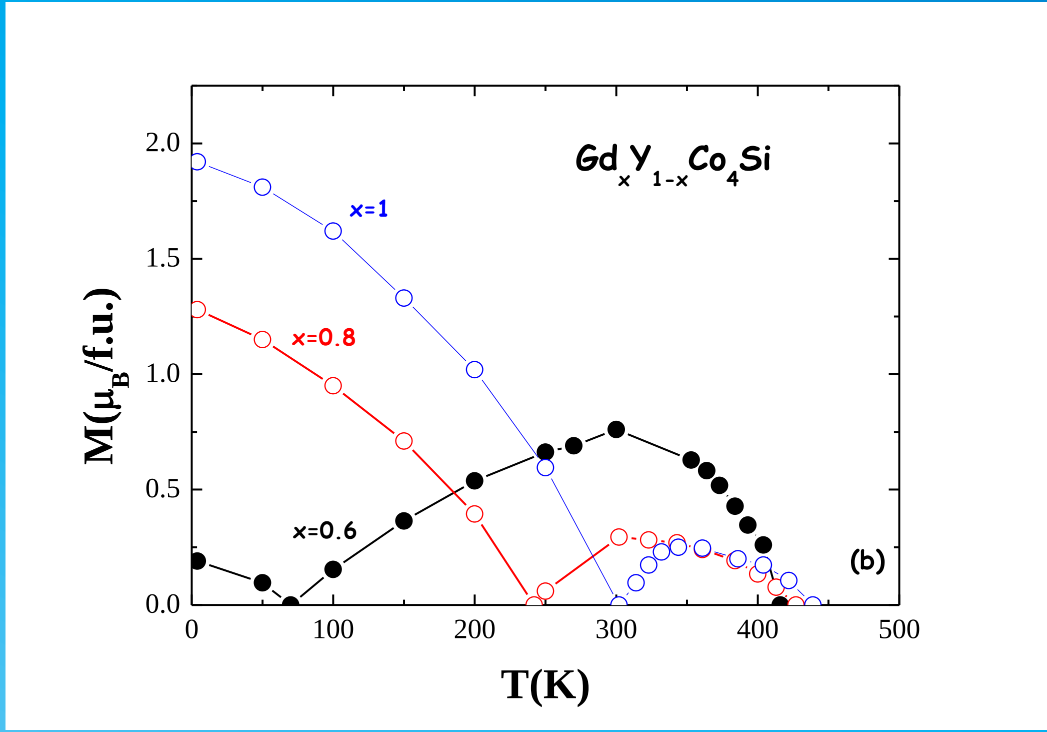
$\Delta S \propto H^{2/3}$

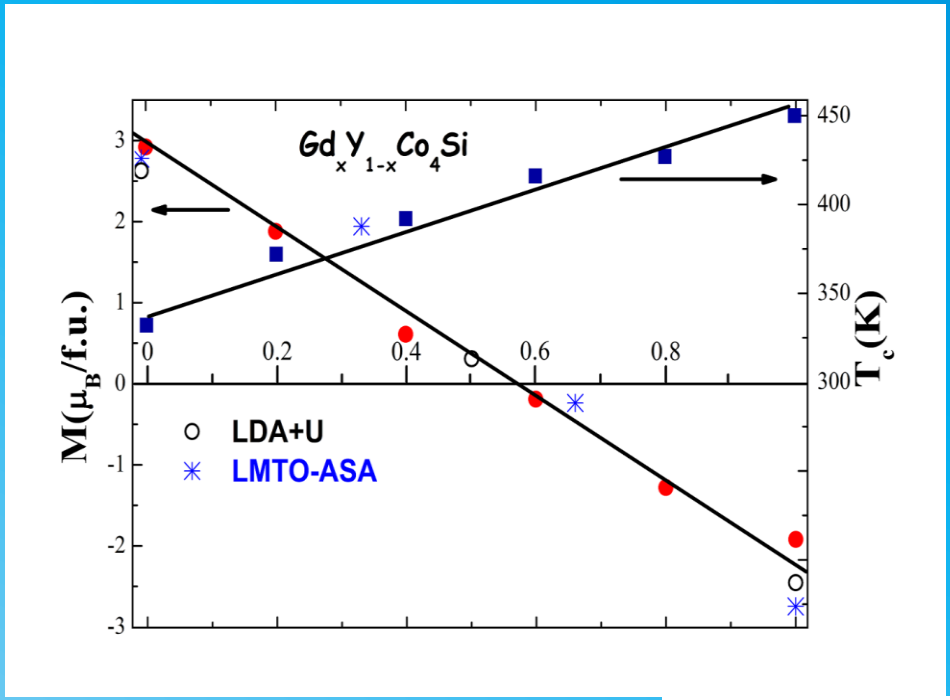
2.4 Weak to strong ferromagnetism

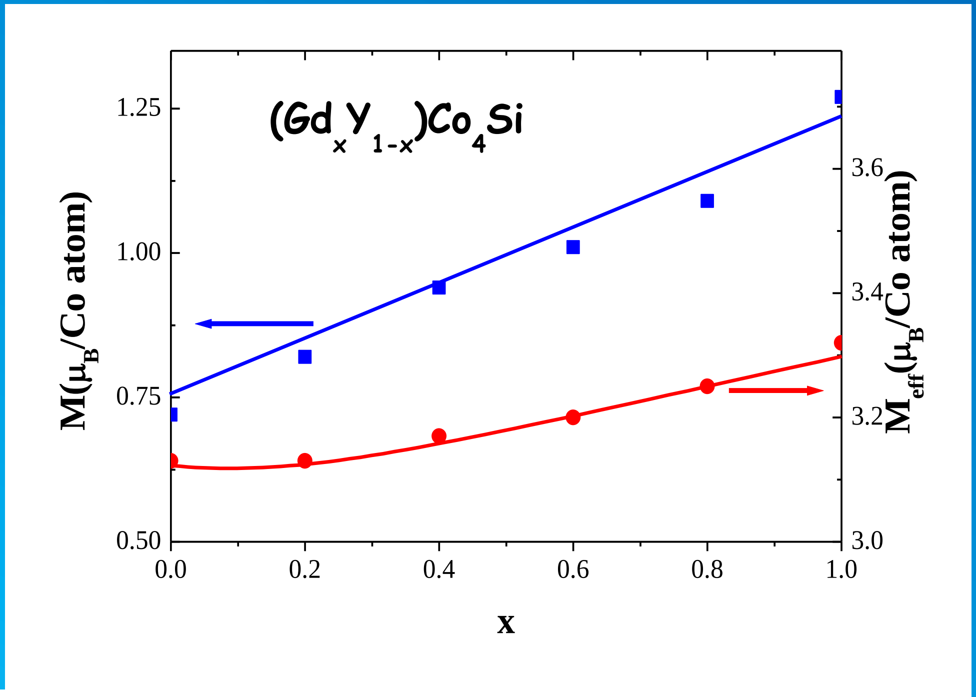
$Gd_xY_{1-x}Co_4Si$, Gd-Co-B

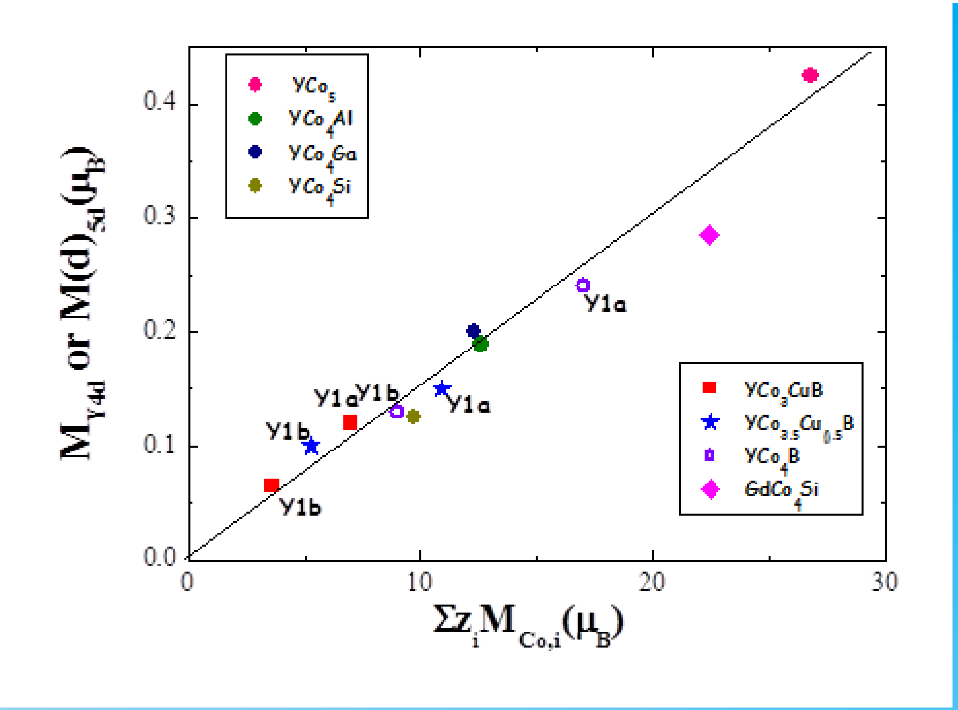
Transition from strong ferromagnetism to weak ferromagnetism. Example $Gd_xY_{1-x}Co_4Si$.











$M_{5d}(0)$ or $M_{5d} \propto \sum_i z_i M_{Co_i}$

RCo_4B, R = Ce, Y, Gd, $R_2Fe_{17}C_2$

Pressure effects

Localized model $\Gamma = a - bT_c$

$$a = -\frac{5}{3} + \frac{d\ln J_{eff}}{d\ln v}$$

$$b = \frac{5}{8}\frac{k_B N_0 g^2 I^2}{S(S+1)J_{eff}^2 I_b}$$

I effective intra-atomic exchange integral reduced from bare value I_b

RCo_4B a = 13.4 b = -0.022 K^{-1}

$R_2Fe_{17}C_2$ a = 37.5 b = -0.0063 K^{-1}

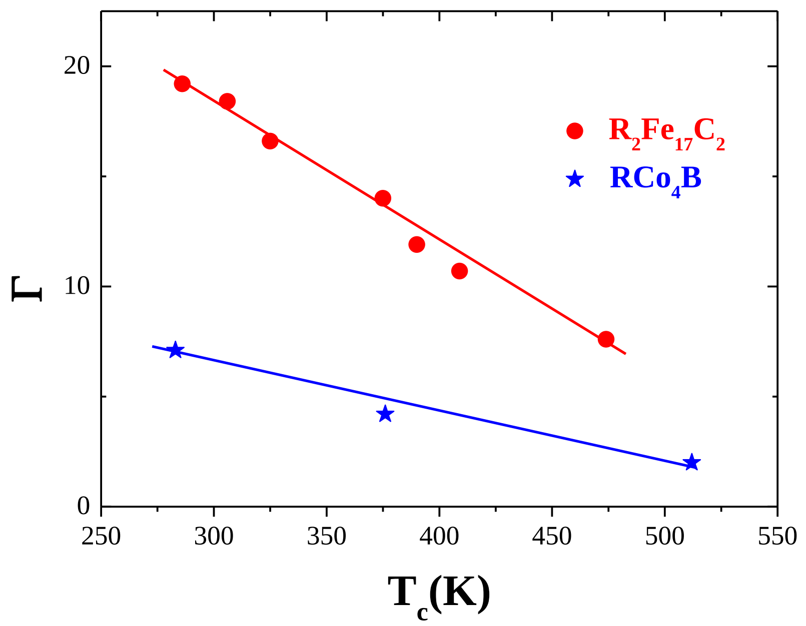
$$\frac{d\ln J_{eff}}{d\ln v}$$ → 6 for RCo_4B; → 11 for $R_2Fe_{17}C_2$

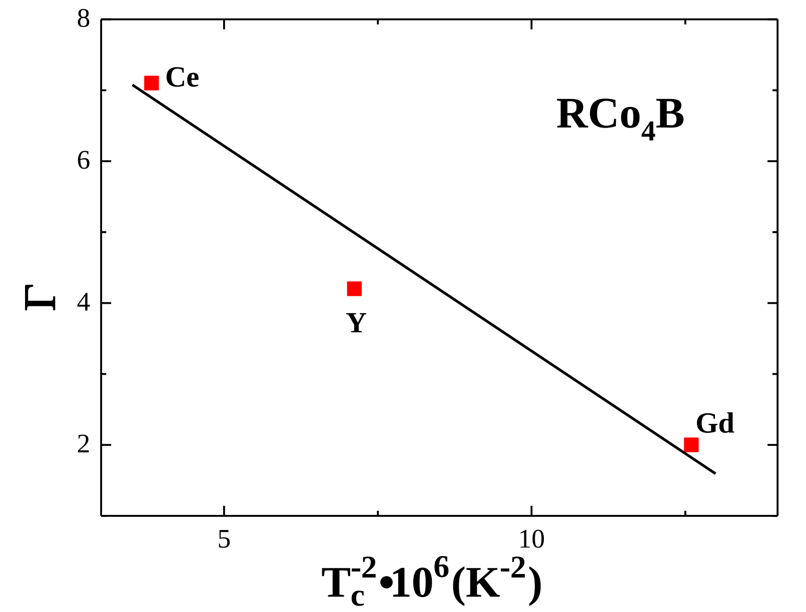
RCo_4B can also be described by

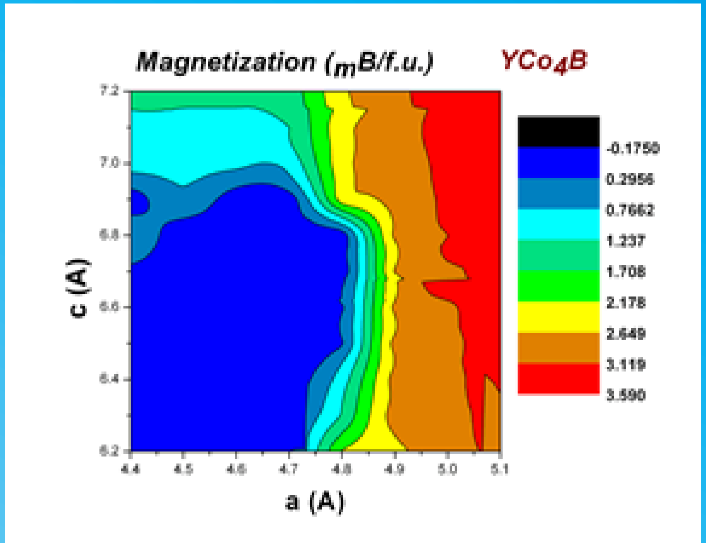
$$\Gamma = a_1 + BT_c^{-2}$$

Weak → strong ferromagnetim

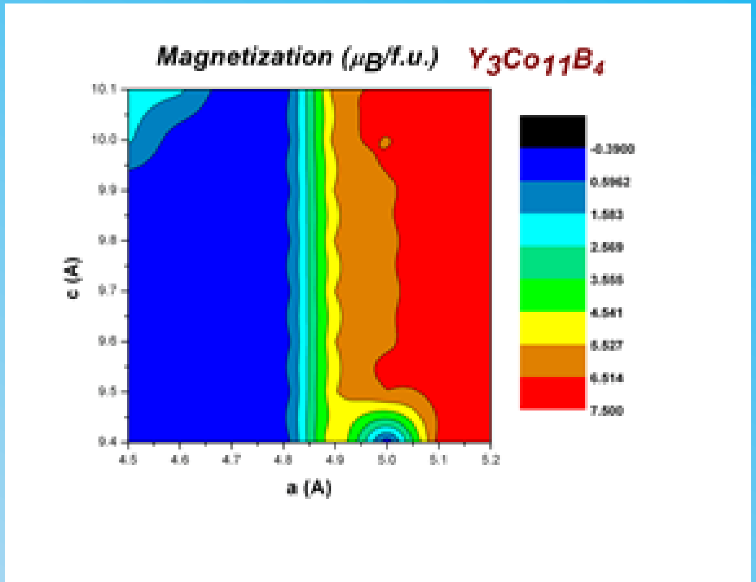
SF model



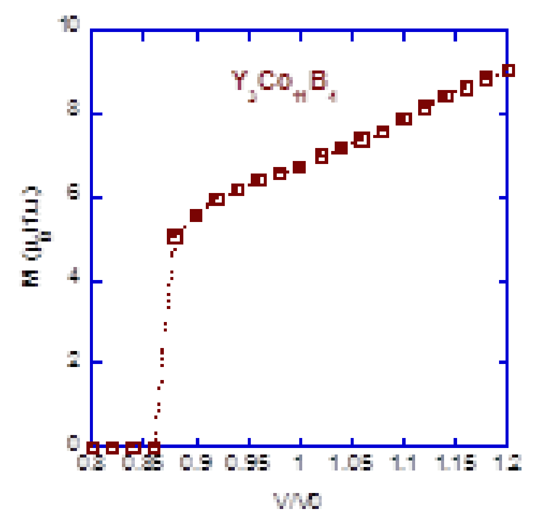




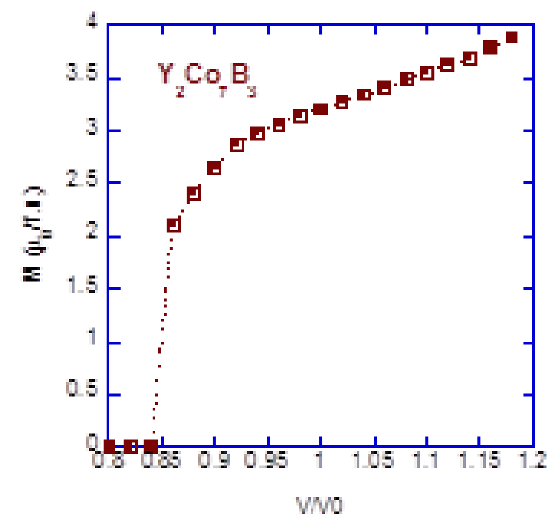
Magnetization (mB/f.u.)
YCo_4B
c (A)
a (A)
-0.1750
0.2956
0.7662
1.237
1.708
2.178
2.649
3.119
3.590



Magnetization (μ_B/f.u.)
$Y_3Co_{11}B_4$
c (A)
a (A)



$Y_3Co_{11}B_4$
M (μ_B/f.u.)
V/V0



$Y_2Co_7B_3$
M (μ_B/f.u.)
V/V0

Conclusions

Exchange enhanced paramagnets

induced temperature moments

$\chi \propto T^2 \rightarrow \chi \propto T^{-1}$

Exchange interactions 4f-5d-3d model

$M_{5d} = M_{5d}(0)+M5d(f)$

$M_{5d}(0) \propto \sum z_i M_i$ $M_{5d}(f) \propto (g_J-1)^2 J(J+1)$

Induced cobalt moment

$H_{ex} = H_{cr} \cong 70$ T

$H > H_{cr}$ $M_{co} = aH_{exch}$ $a = (3\cdot 10^{-2})\mu_B/T$

At $T>T_c$: induced moments by alignment of M_R by external field due to 5d-3d coupling.

High magnetocaloric effect: compounds showing first order magnetic transition

Pressure effect:

weak ferromagnet:direct collapse of M_{Co}

strong ferromagnet: sequential collapse of M_{Co} with at least one step

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Thank you very much for your attention