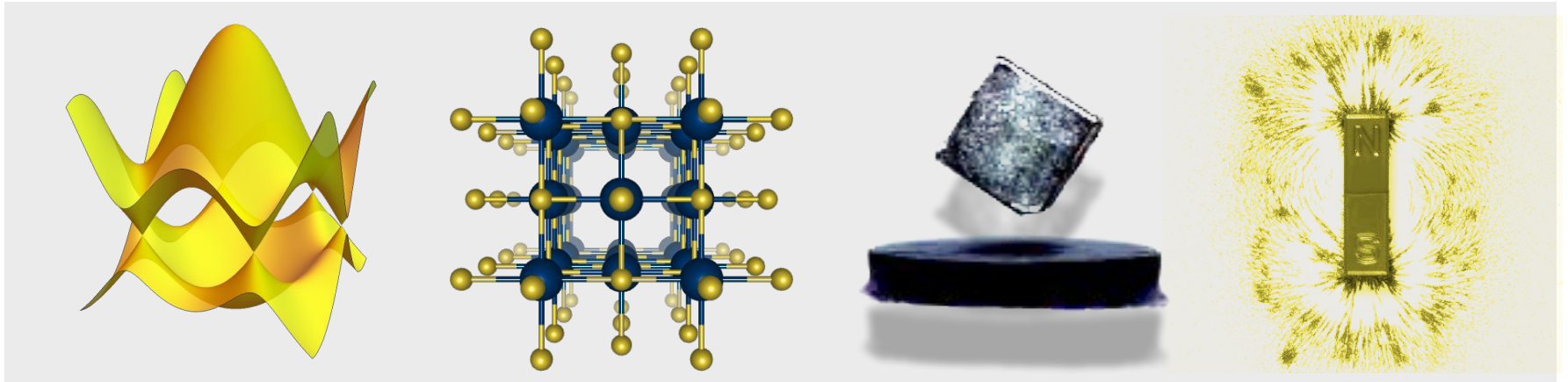# ESCOLA SÉRGIO MASCARENHAS DE FÍSICA DA MATÉRIA CONDENSADA

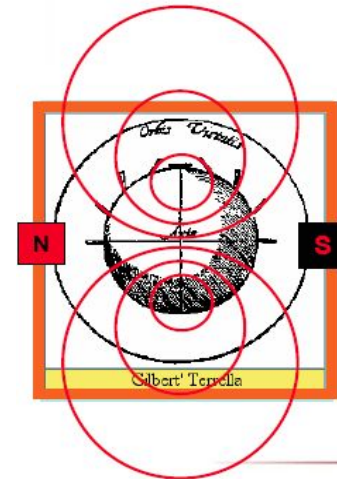Aula 4 – 18 de Julho

Propriedades Magnéticas

História

- O termo surge da antiga cidade grega de Magnésia, onde muitos magnetos naturais eram achados. Hoje nos referimos a esses materiais como ímãs, que contém magnetita, um ferromagneto natural (Fe_3O_4).

- Plínio, o velho (23-79 DC) descreveu uma montanha próxima ao Rio Indu que era inteiramente feita de uma pedra que atraía o ferro.

- Os chineses, já em 121 DC sabiam que uma haste de ferro aproximada desses magnetos naturais adquiriria e reteria as propriedades magnéticas… e que essa haste, ao ser suspensa por um fio, se alinharia na direção norte-sul.

Primórdios...

- Lodestone: rocha magnetizada
  - Rica em magnetita (Fe_3O_4)
  - "lead stone" indicar o caminho"
  - Chineses e europeus 800AC

- 1600 *De Magnete*, de William Gilbert:
  - Primeiro tratado científico de magnetismo.
  - Observação do campo de dipolo para diferentes formas de ímã.
  - A terra é um grande ímã

Curiosidades...

Mesmer - 1780

Kenko Patto Travesseiro

Indicações: dores nos ombros, cabeça, nuca, braços, queda de cabelo, problemas faciais e que transpiram muito na cabeça.

• Sob o travesseiro de uma "esposa infiel" levaria à confissão do crime durante o sono.

• Magnetismo animal: poder de curar...

• Dr. James Graham: "Royal Patagonian Magnetic Bed"
                    (50 guinés/noite)

"O campo magnético proporciona o equilíbrio energético"

CUIDADO!!!!
Efeito interrompido por
ALHO ou CEBOLA

Rabatan com imãs e photon

Prof. Knobel-UNICAMP

Magnetoterapia

- **O que é o Magnetismo:**
  :: O magnetismo é uma força gravitacional emitida do centro do globo terrestre. Alguns físicos propõem que existe um gigantesco magneto permanente no centro da Terra ou uma corrente elétrica que é responsável pelo campo magnético da Terra, transformando-a num imenso imã, energia esta chamada de geomagnetismo, que atua sobre todos os seres vivos trazendo grandes benefícios para saúde. (Magnetoterapia pág. 37/1999).
  www.unimagcolchoes.com.br/m

- Travesseiros Terapêuticos ZiFF - Proporcionam um sono profundo e revitalizador, respeitando a
  anatomia da cabeça, dos ombros e, principalmente, sem forçar a coluna, ajudando a prevenir uma série de problemas à sua saúde, pela melhor posição circulação. http://www.ziff.com.br/

Capa Magnética

Magnetoterapia

- **"Magnetismo Humano Sutil"**

- Ministrado pelo autor, ininterruptamente desde 1973, com material integralmente elaborado por ele, inclusive 42 slides.

- **www.portaluz.com.br/curso_magnetismo.htm**

Sabia-se que os fenômenos existiam e foram desenvolvidas aplicações interessantes.

Mas ninguém os entendia!

Finalmente, a Ciência!

- Somente em 1819 é que foi encontrada uma conexão entre os fenômenos elétricos e magnéticos. O Cientista Danês Hans Christian Oersted observou que uma agulha de uma bússola na vizinhança de um fio que transportava corrente elétrica era defletida.

- Em 1831, Michael Faraday descobriy que uma corrente momentânea aparecia em um circuito quando a corrente em um circuito próximo era iniciada ou parada.

- Logo depois, ele descobriu que o movimento de um ímã em direção a ou saindo de um circuito podia produzir o mesmo efeito. Aparentemente, Joseph Henry havia descoberto esses fenômenos antes, mas não conseguiu publicá-los.

A conexão foi estabelecida

Oersted mostrou que efeitos magnéticos podiam ser produzido ao mover cargas elétricas; Faraday e Henry mostraram que as correntes elétricas podiam ser produzidas por ímãs em movimento.

Então.....

Todos os fenômenos magnéticos resultam de forças entre cargas elétricas em movimento!

Olhando com mais detalhe

- Ampère foi o primeiro a sugerir em 1820 que as propriedades da matéria eram devidas a minúsculas correntes atômicas.

- Todos os átomos exibem fenômenos magnéticos

- O meio no qual as cargas se movem tem efeito profundo nas forças magnéticas observadas.

O que podemos aprender sobre magnetismo?

1. Há pólos norte e pólos sul.

2. Pólos iguais se repelem, e pólos opostos se atraem.

3. Forças magnéticas atraem somente materiais magnéticos.

4. Forças magnéticas atuam a distância.

5. Enquanto estão magnetizados, os magnetos temporários atuam como magnetos permanentes.

6. Uma espira com uma corrente elétrica fluindo através dela torna-se um magneto.

7. Colocar ferro dentro de uma bobina com corrente aumenta a força do eletroímã.

8. Um campo magnético variável induz uma corrente elétrica em um condutor.

9. Uma partícula carregada não sente a força magnética quando se movimenta paralelamente a um campo magnético, mas quando se move perpendicular a esse campo ela sente uma força que é perpendicular tanto ao campo quanto à direção de movimento.

10. Um fio condutor de corrente em um campo magnético perpendicular sente uma força na direção perpendicular tanto ao fio quanto ao campo.
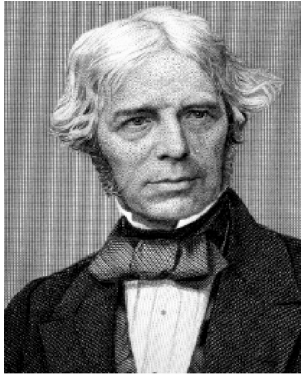
Michael Faraday

- 1820 Oersted: efeito magnético das correntes

- 1820-21 Ampère:
  - atribui o magnetismo da matéria a "correntes moleculares"

- 1831 Faraday: campo variável induz corrente elétrica em um circuito

- 1864 Maxwell: teoria eletromagnética:
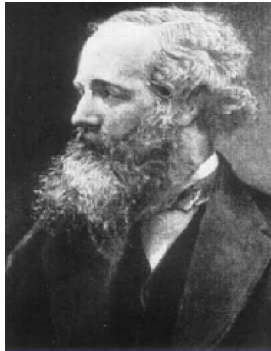
$$\nabla \cdot \vec{B} = 0 \, ,$$
$$\nabla \times \vec{E} + \partial \vec{B}/\partial t = 0 \, ,$$
$$\nabla \cdot \vec{D} = \rho \, ,$$
$$\nabla \times \vec{H} - \partial \vec{D}/\partial t = \vec{J} \, .$$

- 1897 descoberta do elétron

- Sec XX : Teoria Quântica (1925-1930)
  (Heisenberg, Dirac, Schrödinger, Pauli)

James Clerk Maxwell

Andre-Marie Ampere

Diamagnetismo
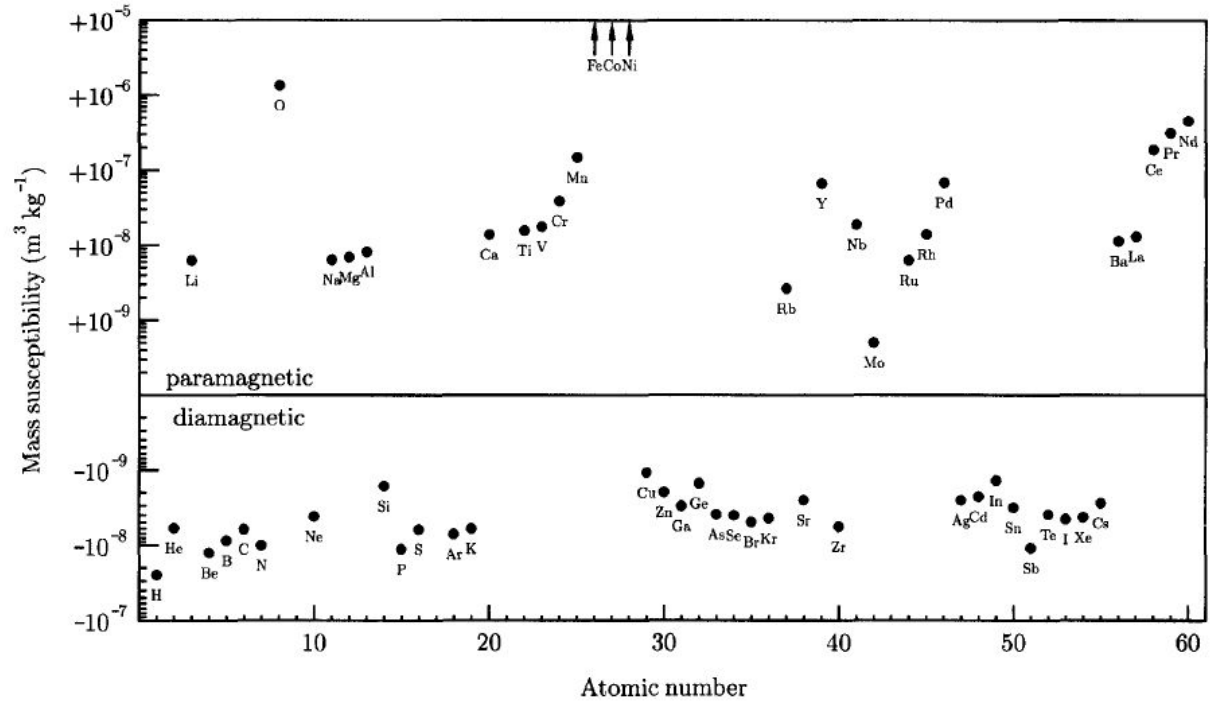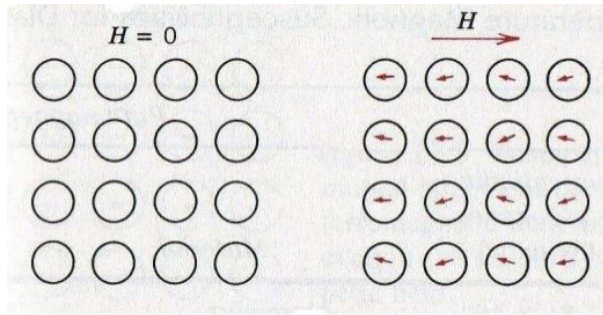
$$\sum_{i=1}^{Z_{\text{eff}}} \langle r_i^2 \rangle \approx Z_{\text{eff}} r^2$$
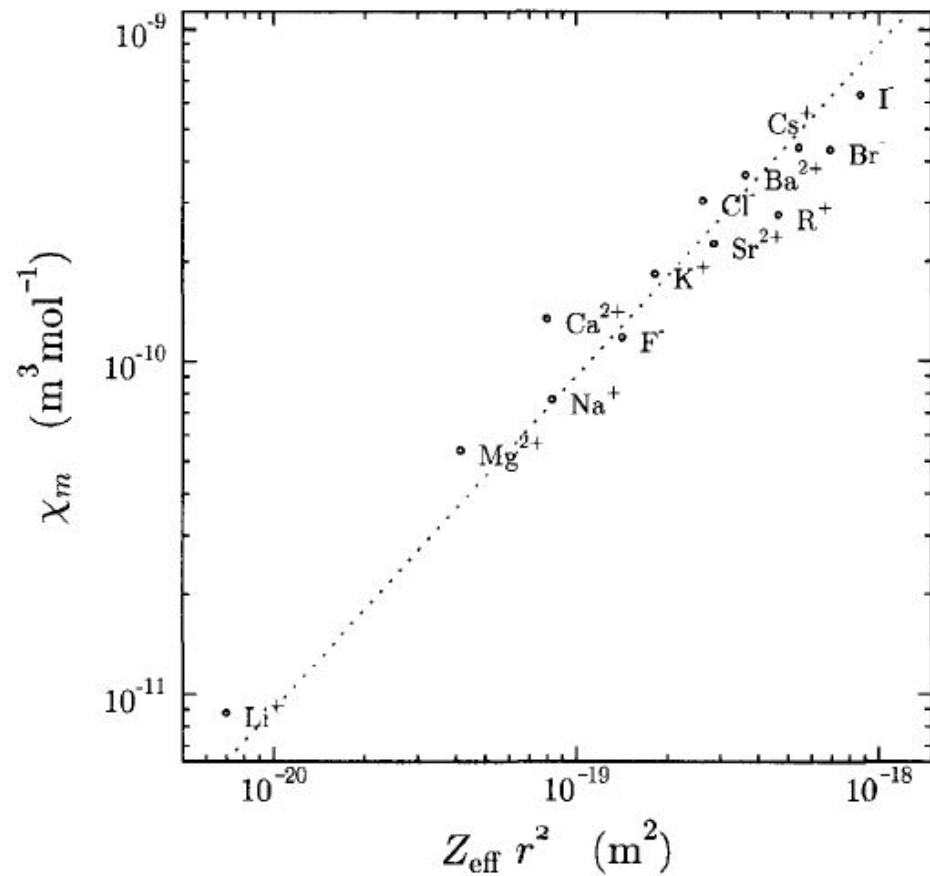
Grafito pirolitico

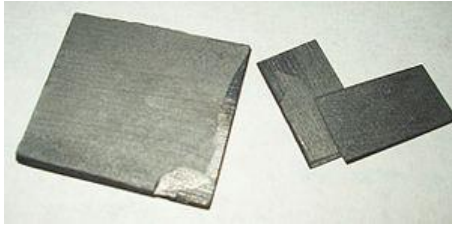## Diamagnetic Susceptibility of Pyrolytic Graphite*

D. B. FISCHBACH
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California
(Received April 12, 1961)
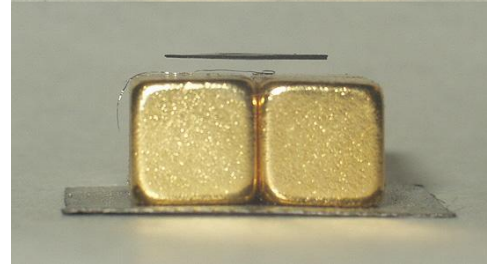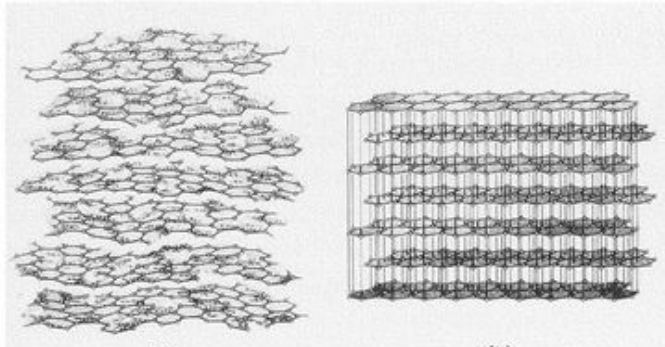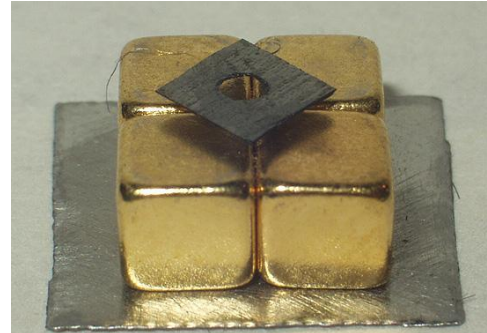
Magnetic and transport properties of i-*R*-Cd icosahedral quasicrystals (*R*=Y, Gd-Tm)

Tai Kong,[1] Sergey L. Bud'ko,[1] Anton Jesche,[1] John McArthur,[2] Andreas Kreyssig,[1]
Alan I. Goldman,[1] and Paul C. Canfield[1,*]

[1]*Ames Laboratory, US DOE, and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[2]*Quantum Design Japan, 1-11-16 Takamatsu, Toshima ku, Tokyo 171-0042, Japan*
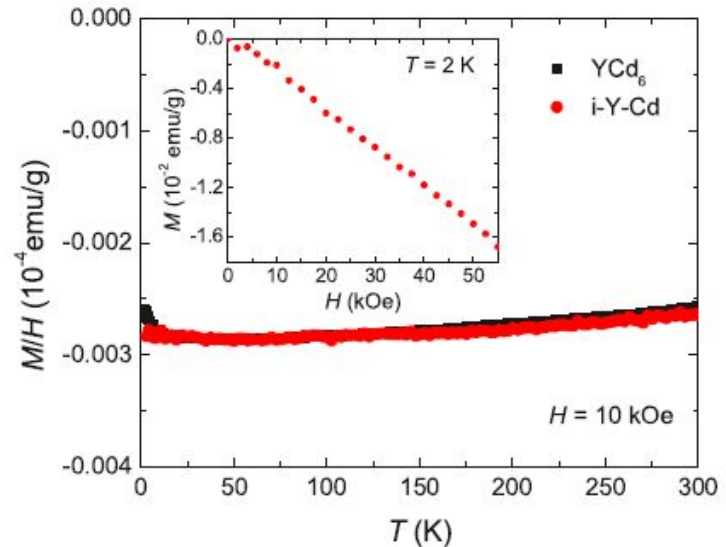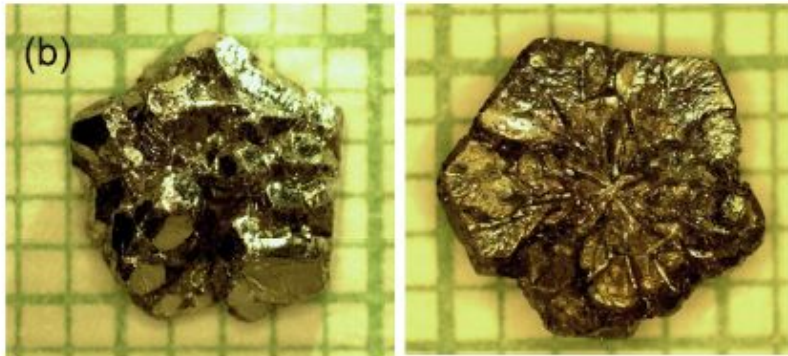
Unusual evolution from a superconducting to an antiferromagnetic ground state in $Y_{1-x}Gd_xPb_3$ ($0 \leqslant x \leqslant 1$)

M. Cabrera-Baez,[1,*] V. C. Denis,[2] L. Mendonça-Ferreira,[2] M. Carlone,[3] P. A. Venegas,[4] M. A. Avila,[2] and C. Rettori[1,2]

[1]*Instituto de Física "Gleb Wataghin," UNICAMP, Campinas, São Paulo 13083-859, Brazil*

[2]*CCNH, Universidade Federal do ABC, Santo André, São Paulo 09210-580, Brazil*

[3]*Programa de Pós-Graduação em Ciência e Tecnologia de Materiais, Faculdade de Ciências, Universidade Estadual Paulista - UNESP, Bauru, São Paulo 17033-360, Brazil*

[4]*Departamento de Física, Faculdade de Ciências, Universidade Estadual Paulista, Bauru, São Paulo 17033-360, Brazil*
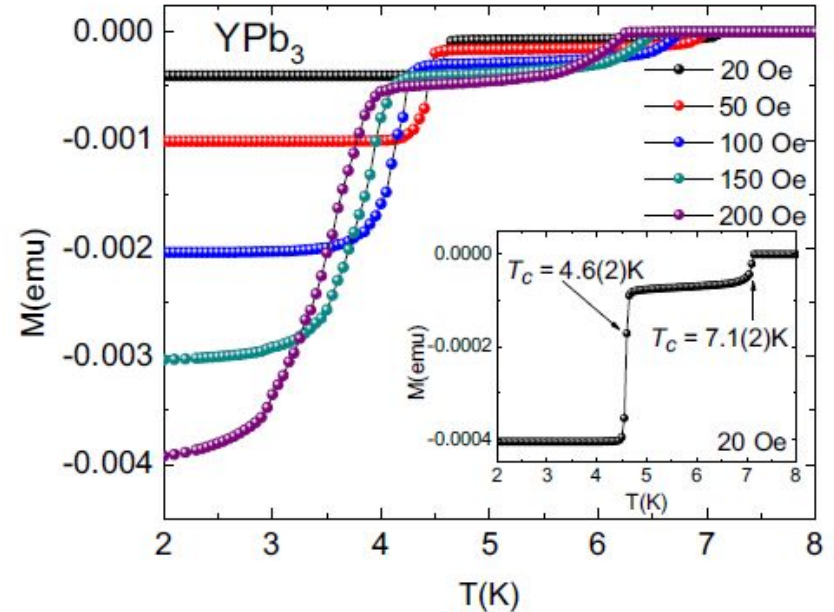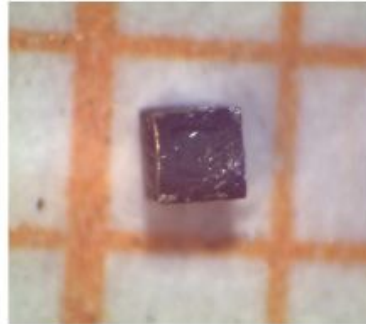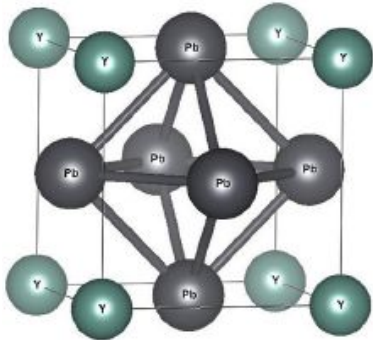
Susceptibilidade em escala
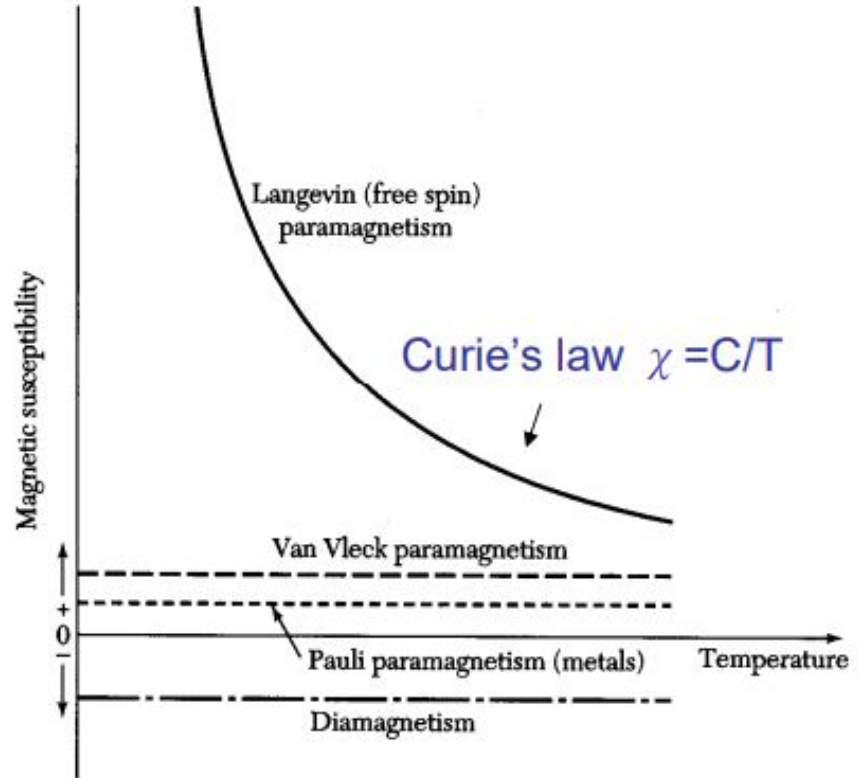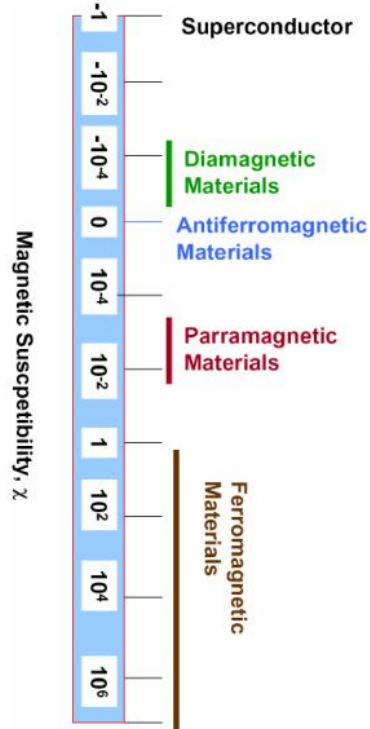
Atomic susceptibility

$$H = \sum_i \left(\frac{p_i^2}{2m} + V_i \right) + \mu_B \left(\vec{L} + g\vec{S} \right) \cdot \vec{H} + \frac{e^2}{2mc} \sum_i A_i^2, \quad \mu_B = \frac{e\hbar}{2mc}$$

$$= H_0 + \Delta H$$

Order of magnitude

- $$\mu_B \left(\vec{L} + g\vec{S} \right) \cdot \vec{H} \approx \mu_B H \approx \hbar \omega_c$$

$$\approx 10^{-4} eV \quad \text{when } H = 1\,\text{T}$$

- $$\vec{A}_i = \frac{H}{2}(-y_i, x_i, 0)$$

$$\frac{e^2}{2mc} \sum_i A_i^2 \approx \left(\frac{eH}{mc} \right)^2 ma_0^2, \quad a_0 \equiv \frac{\hbar^2}{me^2}$$

$$\approx \frac{(\hbar \omega_c)^2}{e^2 / a_0} \approx 10^{-5} \text{ of the linear term at } H=1\,\text{T}$$

$J = 6$ $^7F_6$ ———— $E_6 = 21\lambda$

$J = 5$ $^7F_5$ ———— $E_5 = 15\lambda$

$J = 4$ $^7F_4$ ———— $E_4 = 10\lambda$

$J = 3$ $^7F_3$ ———— $E_3 = 6\lambda$

$J = 2$ $^7F_2$ ———— $E_2 = 3\lambda$

$J = 1$ $^7F_1$ ———— $E_1 = \lambda$
$J = 0$ $^7F_0$ ———— $E_0 = 0$
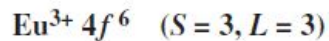
Eu^{3+} $4f^6$ $(S = 3, L = 3)$

Fig. 1. Energy levels of the lowest multiplet ^7F_J of trivalent Eu^{3+} ions in the absence of the external field. These separations are caused by the spin–orbit interaction $\lambda\mathbf{L}\cdot\mathbf{S}$. The magnitude of λ indicates the energy difference between the ground state and the first excited state.
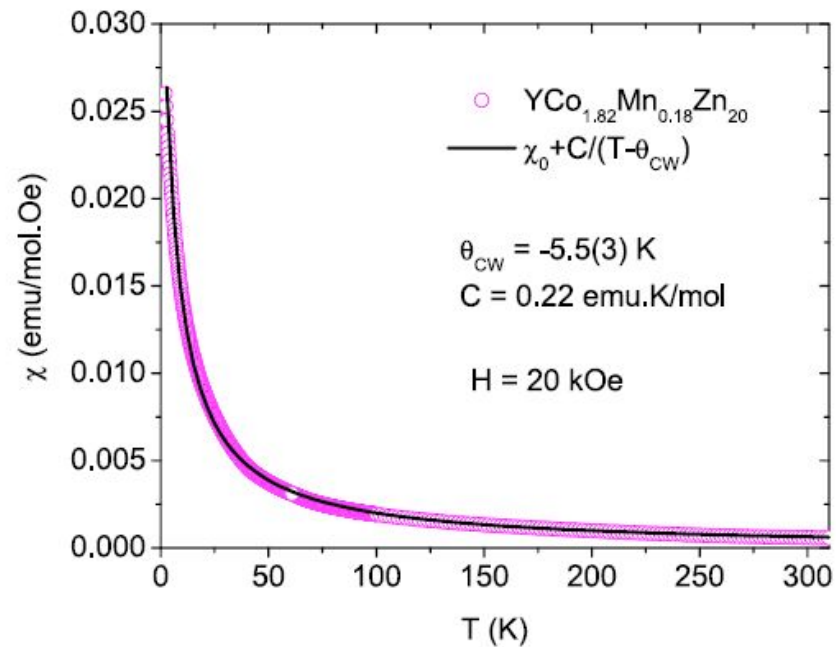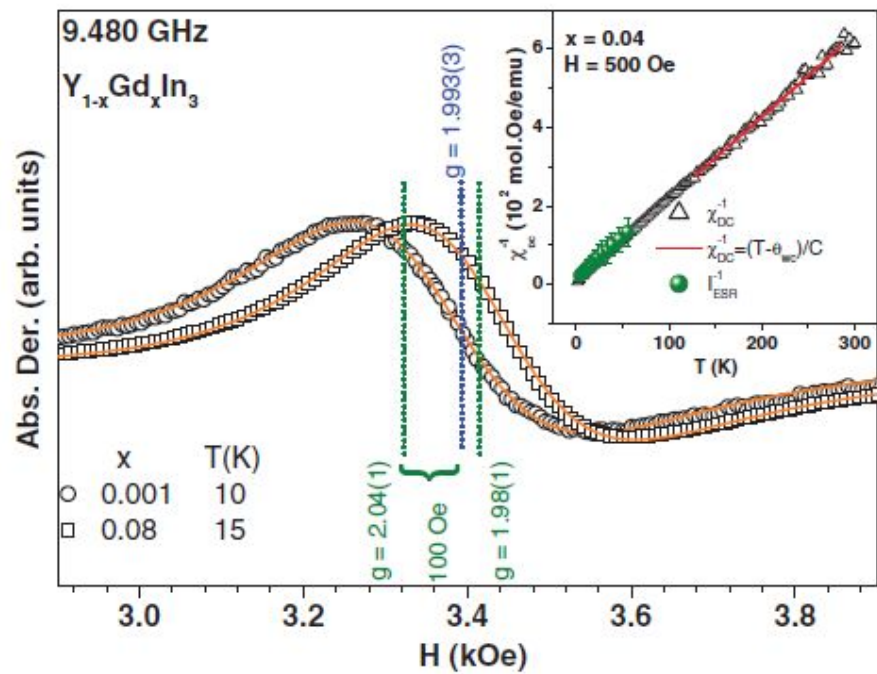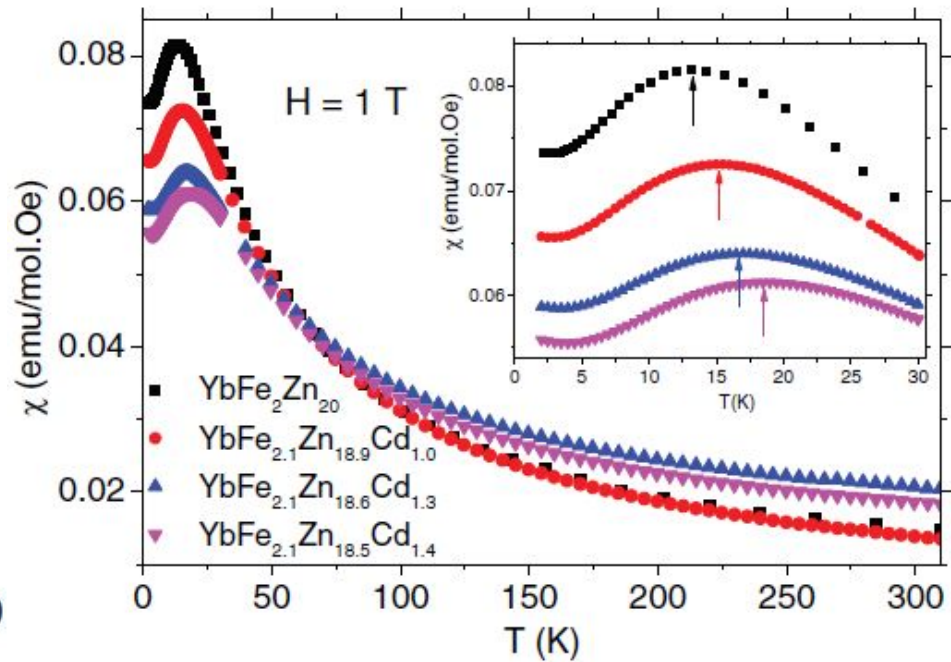
λ (K)
a 200
b 300
c 400
d 500
e 600
f 700
g 800
h 900
i 1000
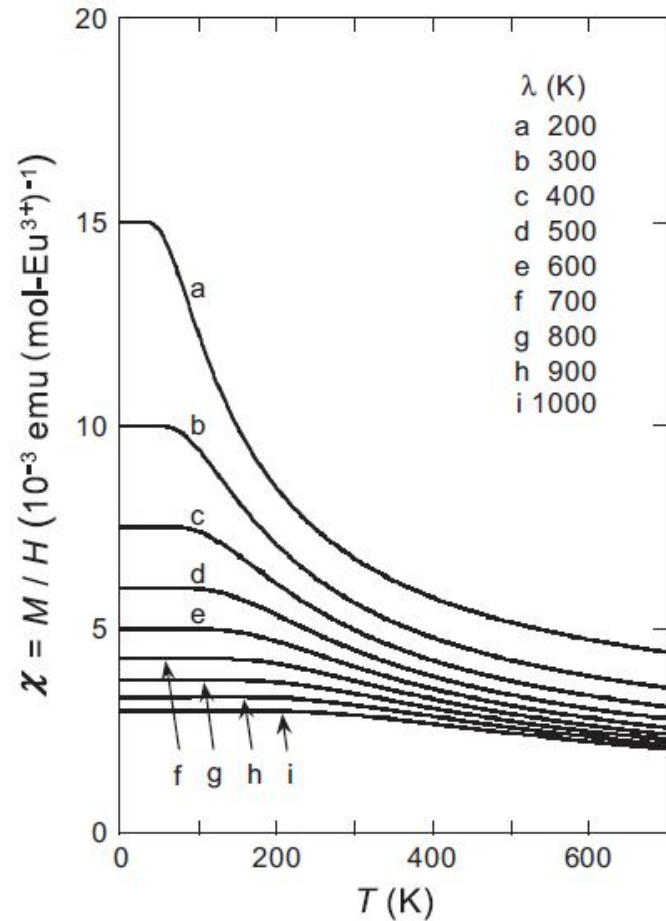
Table 4.6. The $4f$ ions. The paramagnetic moment m_{eff} and the saturation moment m_0 are in units of μ_B

$4f^n$		S	L	J	g	$m_0 = gJ$	$m_{eff} = g\sqrt{J(J+1)}$	m_{eff}^{exp}
1	Ce^{3+}	$\frac{1}{2}$	3	$\frac{5}{2}$	$\frac{6}{7}$	2.14	2.54	2.5
2	Pr^{3+}	1	5	4	$\frac{4}{5}$	3.20	3.58	3.5
3	Nd^{3+}	$\frac{3}{2}$	6	$\frac{9}{2}$	$\frac{8}{11}$	3.27	3.52	3.4
4	Pm^{3+}	2	6	4	$\frac{3}{5}$	2.40	2.68	
5	Sm^{3+}	$\frac{5}{2}$	5	$\frac{5}{2}$	$\frac{2}{7}$	0.71	0.85	1.7
6	Eu^{3+}	3	3	0	0	0	0	3.4
7	Gd^{3+}	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.0	7.94	8.9
8	Tb^{3+}	3	3	6	$\frac{3}{2}$	9.0	9.72	9.8
9	Dy^{3+}	$\frac{5}{2}$	5	$\frac{15}{2}$	$\frac{4}{3}$	10.0	10.65	10.6
10	Ho^{3+}	2	6	8	$\frac{5}{4}$	10.0	10.61	10.4
11	Er^{3+}	$\frac{3}{2}$	6	$\frac{15}{2}$	$\frac{6}{5}$	9.0	9.58	9.5
12	Tm^{3+}	1	5	6	$\frac{7}{6}$	7.0	7.56	7.6
13	Yb^{3+}	$\frac{1}{2}$	3	$\frac{7}{2}$	$\frac{8}{7}$	4.0	4.53	4.5

9.480 GHz

$Y_{1-x}Gd_xIn_3$

Abs. Der. (arb. units)

g = 1.993(3)

g = 2.04(1)

100 Oe

g = 1.98(1)

x	T(K)
0.001	10
0.08	15

H (kOe)

Inset:
x = 0.04
H = 500 Oe

χ_{ac}^{-1} (10^2 mol.Oe/emu)

△ χ_{DC}^{-1}
— $\chi_{DC}^{-1}=(T-\theta_{wc})/C$
● I_{ESR}^{-1}

T (K)

χ (emu/mol.Oe)

○ $YCo_{1.82}Mn_{0.18}Zn_{20}$
— $\chi_0 + C/(T-\theta_{CW})$

$\theta_{CW} = -5.5(3)$ K
C = 0.22 emu.K/mol

H = 20 kOe

T (K)
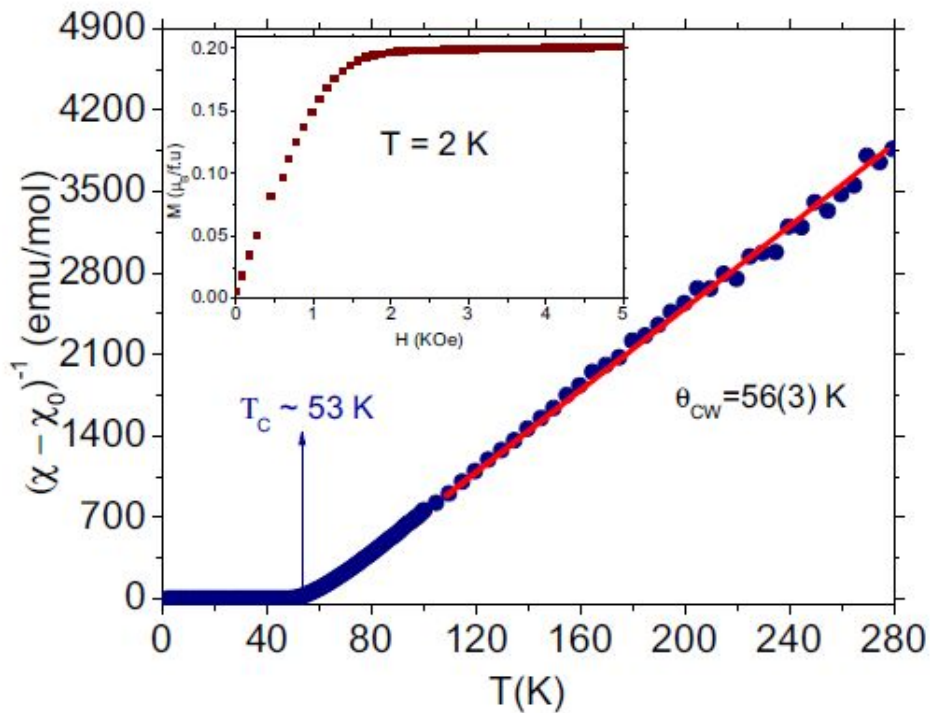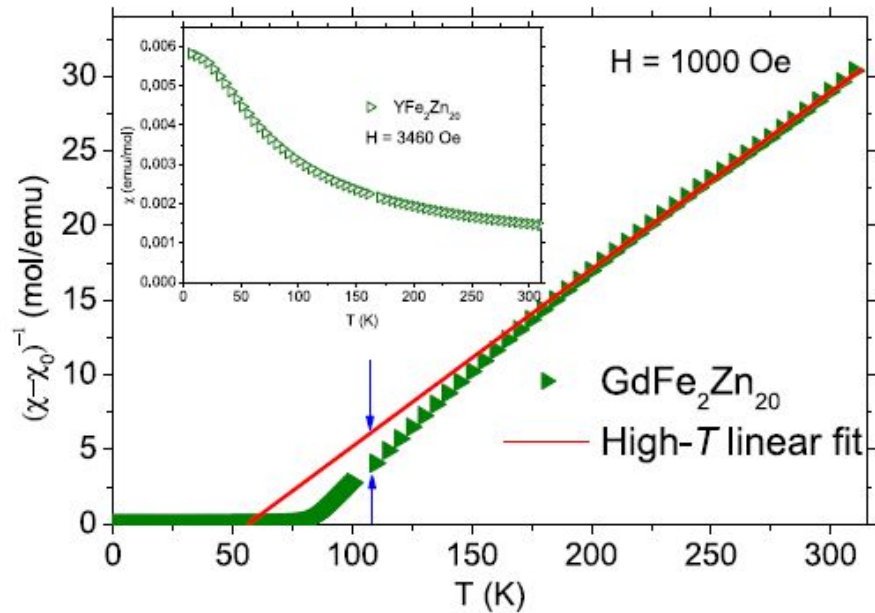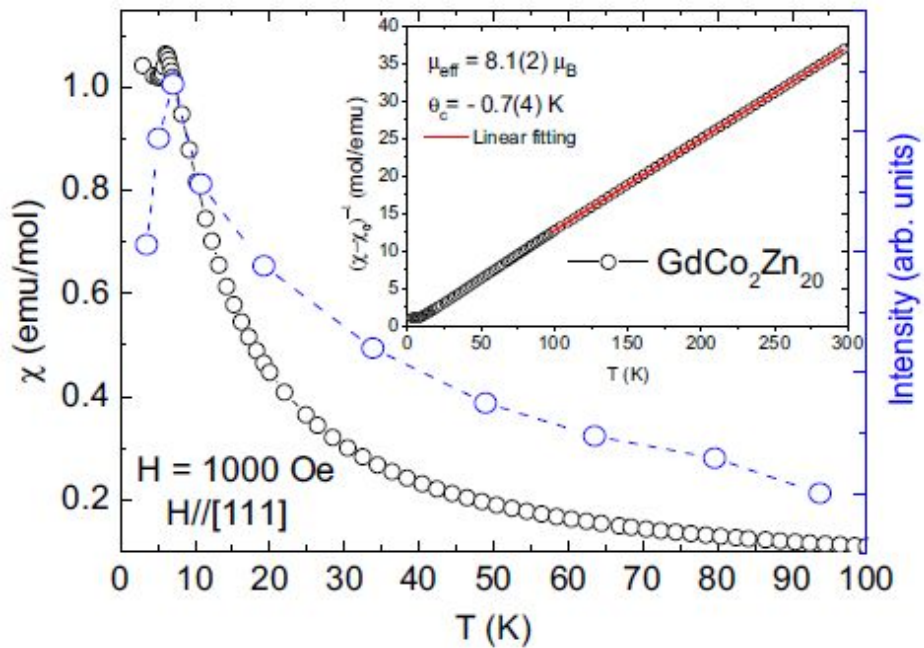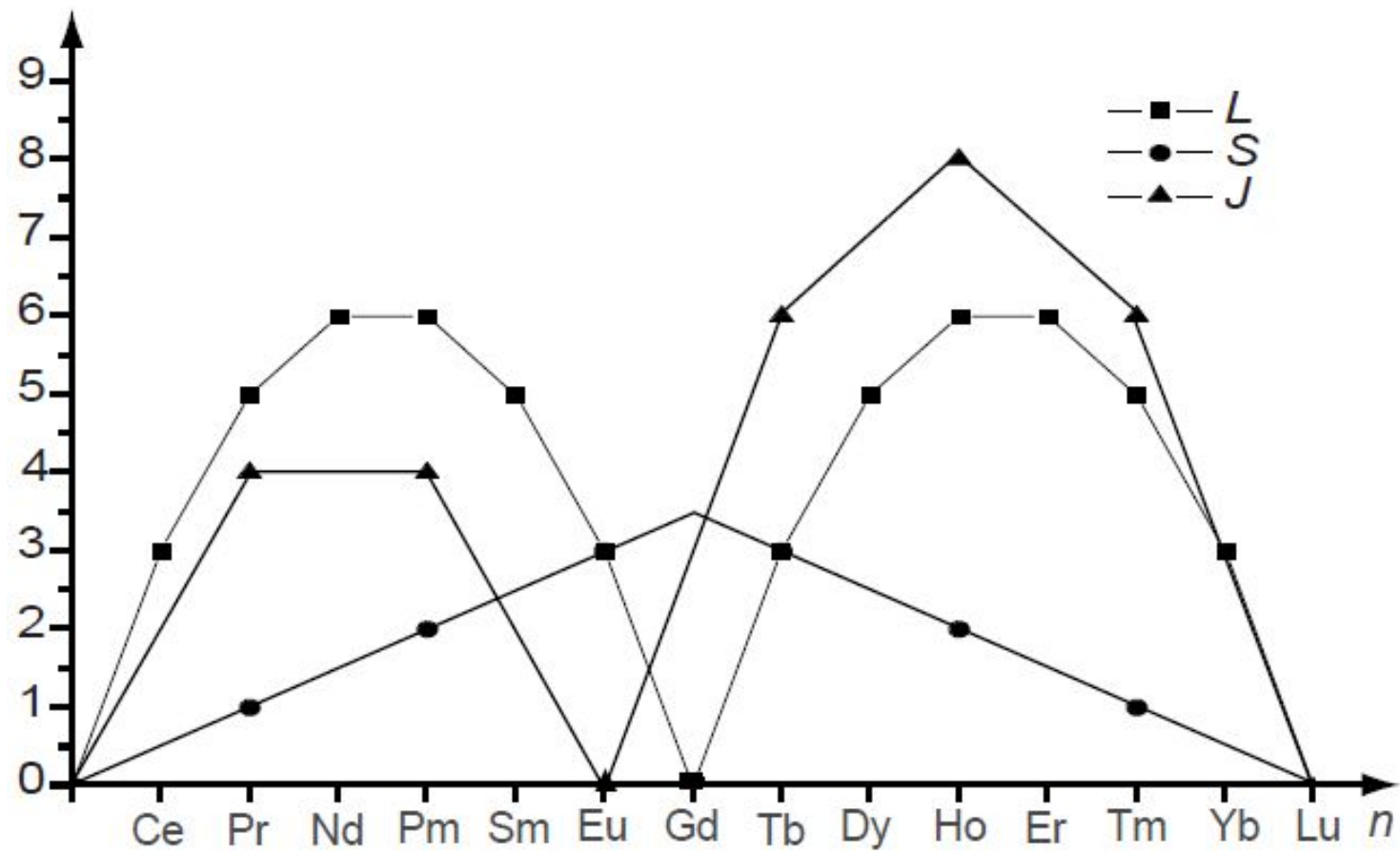
Table 4.7. The $3d$ ions. $\mathfrak{m}_{eff}$ is in units of μ_B

$3d^n$		S	L	J	g	$\mathfrak{m}_{eff} = g\sqrt{J(J+1)}$	$\mathfrak{m}_{eff} = g\sqrt{S(S+1)}$	$\mathfrak{m}_{eff}^{exp}$
1	Ti^{3+}, V^{4+}	$\frac{1}{2}$	2	$\frac{3}{2}$	$\frac{4}{5}$	1.55	1.73	1.7
2	Ti^{2+}, V^{3+}	1	3	2	$\frac{2}{3}$	1.63	2.83	2.8
3	V^{2+}, Cr^{3+}	$\frac{3}{2}$	3	$\frac{3}{2}$	$\frac{2}{5}$	0.78	3.87	3.8
4	Cr^{2+}, Mn^{3+}	2	2	0			4.90	4.9
5	Mn^{2+}, Fe^{3+}	$\frac{5}{2}$	0	$\frac{5}{2}$	2	5.92	5.92	5.9
6	Fe^{2+}, Co^{3+}	2	2	4	$\frac{3}{2}$	6.71	4.90	5.4
7	Co^{2+}, Ni^{3+}	$\frac{3}{2}$	3	$\frac{9}{2}$	$\frac{4}{3}$	6.63	3.87	4.8
8	Ni^{3+}	1	3	4	$\frac{5}{4}$	5.59	2.83	3.2
9	Cu^{2+}	$\frac{1}{2}$	2	$\frac{5}{2}$	$\frac{6}{5}$	3.55	1.73	1.9

Table 4.5. Spin-orbit coupling constants for ions in the $3d$ and $4f$ series, in kelvin. $\Delta\varepsilon$ is the energy of the first excited multiplet

	Ion	λ	Λ	$\Delta\varepsilon$
$3d^1$	Sc^{2+}	124	124	310
$3d^2$	Ti^{2+}	176	88	264
$3d^3$	V^{2+}	246	82	205
$3d^4$	Cr^{2+}	340	85	85
$3d^6$	Fe^{2+}	656	-164	656
$3d^7$	Co^{2+}	818	-272	1224
$3d^8$	Ni^{2+}	987	-494	3948
$4f^1$	Ce^{3+}	920	920	3220
$4f^2$	Pr^{3+}	1080	540	2700
$4f^3$	Nd^{3+}	1290	430	2365
$4f^4$	Pm^{3+}	1540	380	1900
$4f^5$	Sm^{3+}	1730	350	1225
$4f^6$	Eu^{3+}	1950	330	330
$4f^8$	Tb^{3+}	2450	-410	2460
$4f^9$	Dy^{3+}	2730	-550	4125
$4f^{10}$	Ho^{3+}	3110	-780	6240
$4f^{11}$	Er^{3+}	3510	-1170	8775
$4f^{12}$	Tm^{3+}	3800	-1900	11400
$4f^{13}$	Yb^{3+}	4140	-4140	14490

s

p_x

p_y

p_z

d_{z^2}

$d_{x^2-y^2}$

$\left.\begin{array}{c} \\ \\ \end{array}\right\}e_g$

d_{xy}

d_{xz}

d_{yz}

$\left.\begin{array}{c} \\ \\ \end{array}\right\}t_{2g}$

(a)

(a)

d_{xy}

(b)

$d_{x^2-y^2}$

y

x

e_g

$3\Delta/5$

Δ

free
ion

$2\Delta/5$

t_{2g}
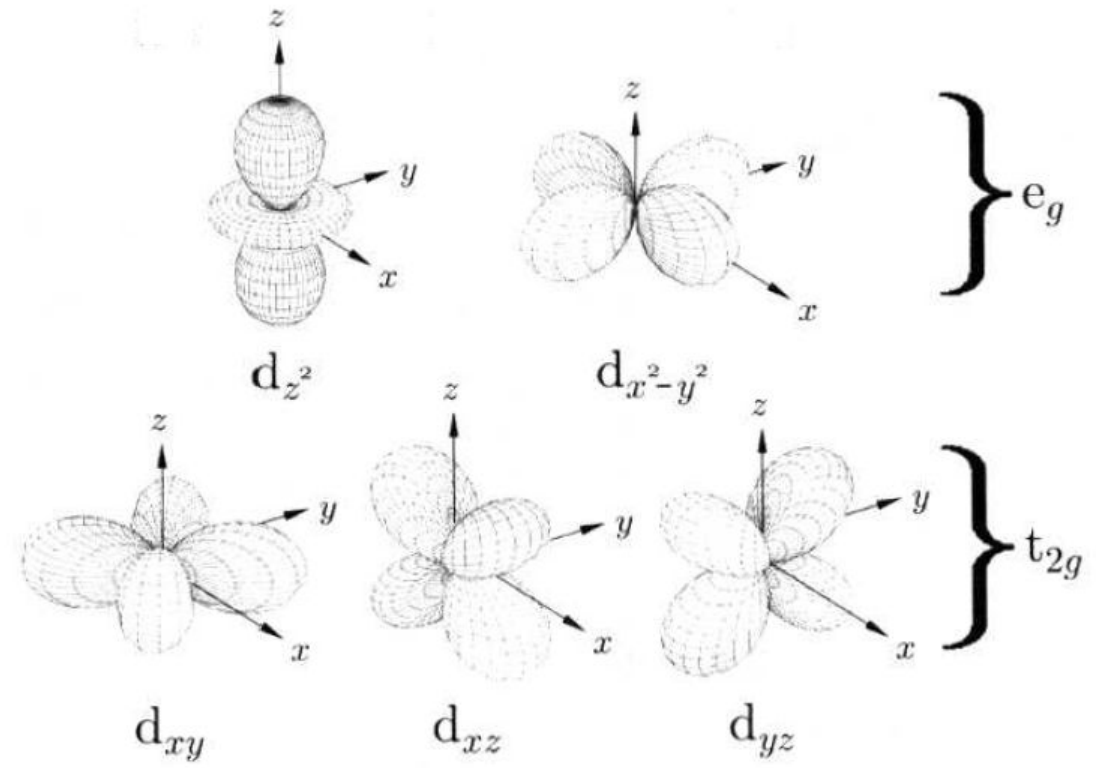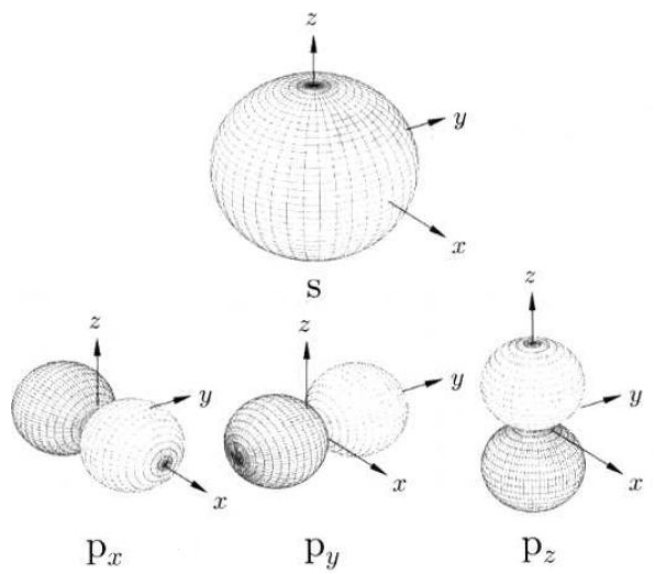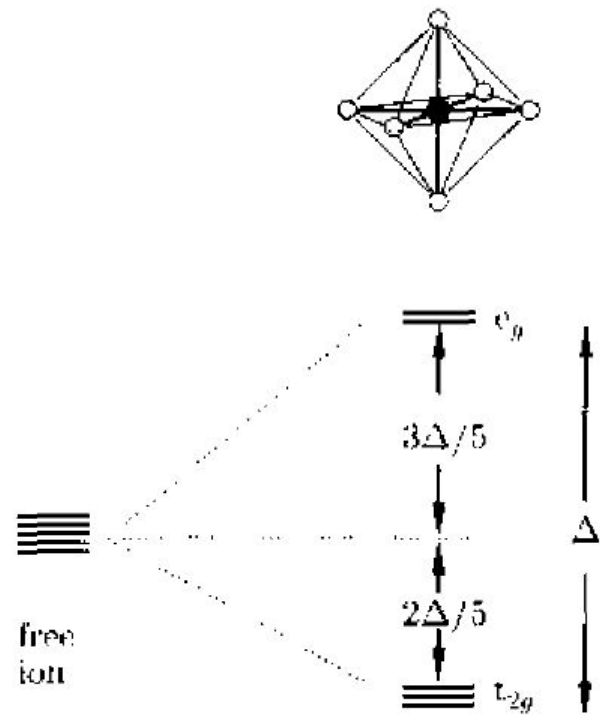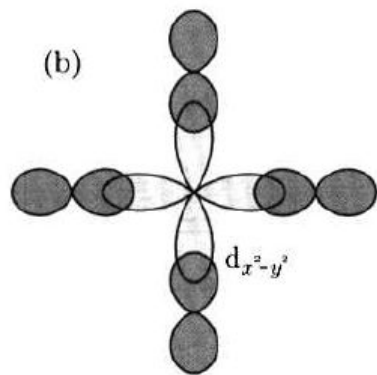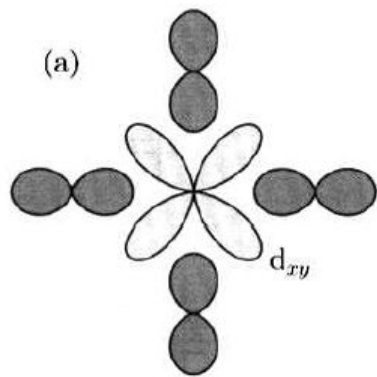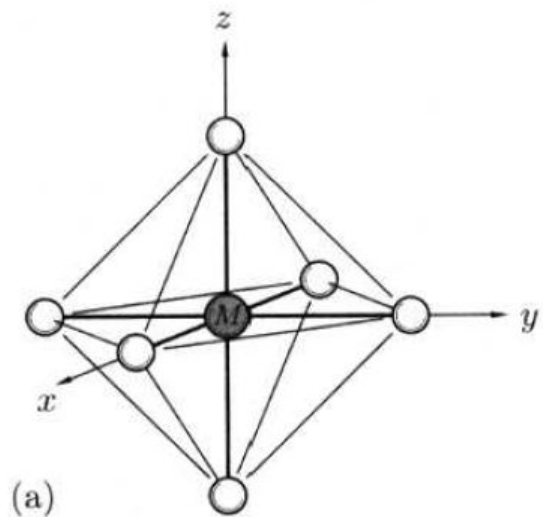
Table 4.9. The splitting of the one-electron levels in different symmetry

	ℓ	Cubic	Tetragonal	Trigonal	Rhombohedral
s	0	1	1	1	1
p	1	3	1, 2	1, 2	1, 1, 1
d	2	2, 3	1, 1, 1, 2	1, 2, 2	1, 1, 1, 1, 1
f	3	1, 3, 3	1, 1, 1, 2, 2	1, 1, 1, 2, 2	1, 1, 1, 1, 1, 1, 1

Figure 4.13

The effect of a tetragonal distortion of octahedral symmetry on the one-electron energy levels.
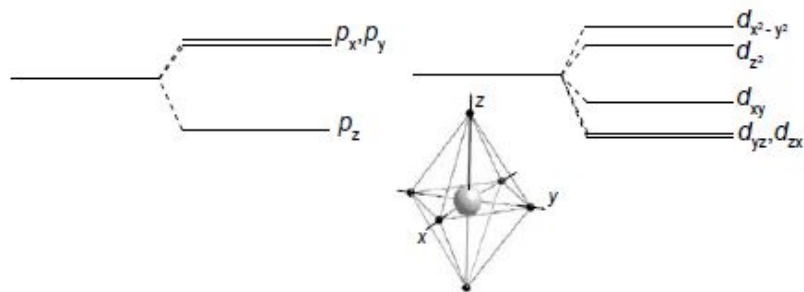
Figure 4.14

Jahn–Teller distortion of an octahedral site containing a d^1 ion.
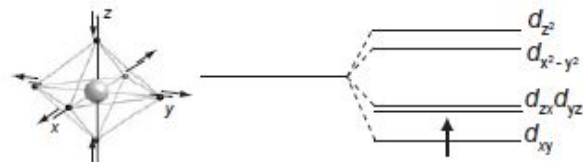
Classificação

- Origem dos momentos magnéticos
- Tipo de interação entre os momentos

  - Magnetismo Fraco
    - Diamagnetos
    - Paramagnetos

  - Magnetismo Forte
    - Materiais Ordenados:
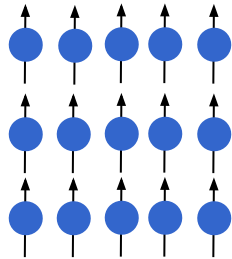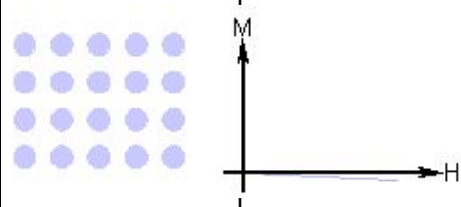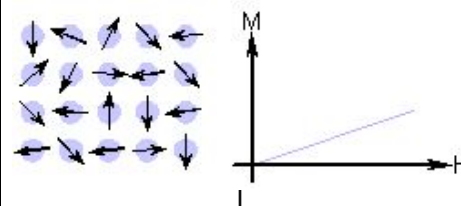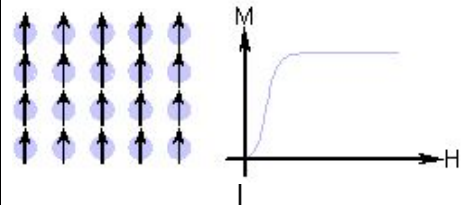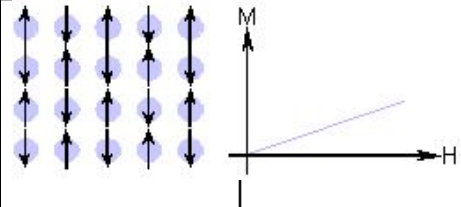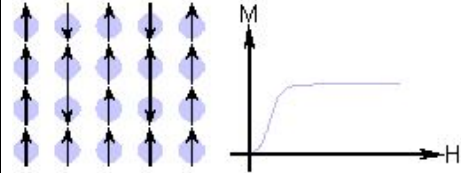
  - **Ferromagnetos**   - **Ferrimagnetos**   - **Antiferromagnetos**
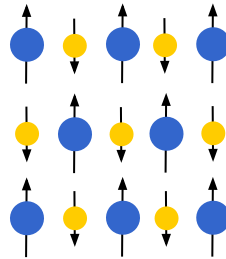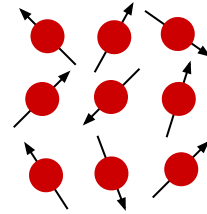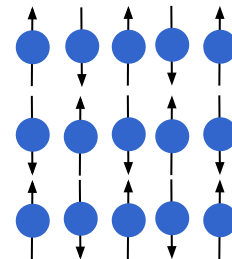
Type of Magnetism	Susceptibility	Atomic / Magnetic Behaviour		Example / Susceptibility
Diamagnetism	Small & negative.	Atoms have no magnetic moment		-2.74×10^{-6} -0.77×10^{-6}
Paramagnetism	Small & positive.	Atoms have randomly oriented magnetic moments		0.19×10^{-6} 21.04×10^{-6} 66.10×10^{-6}
Ferromagnetism	Large & positive, function of applied field, microstructure dependent.	Atoms have parallel aligned magnetic moments		~100,000
Antiferromagnetism	Small & positive.	Atoms have mixed parallel and anti-parallel aligned magnetic moments		3.6×10^{-6}
Ferrimagnetism	Large & positive, function of applied field, microstructure dependent	Atoms have anti-parallel aligned magnetic moments		~3

Diamagnetos

• Não possuem momento permanente

    • Origem: variação do momento orbital dos elétrons

<mark>(*Lei de Lenz*)</mark> duzida pela ação de um campo magnético

    • Resposta se opõe ao campo $\longrightarrow$

$$\chi = \frac{M}{H} \; (\approx 10^{-6})$$

μ
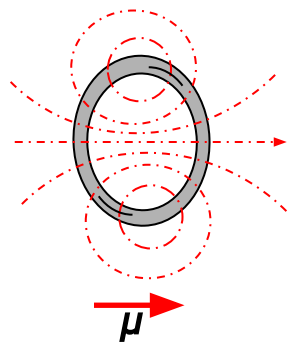
• Todo material apresenta diamagnetismo
• Resulta do efeito de um campo VARIÁVEL sobre os elétrons
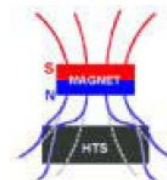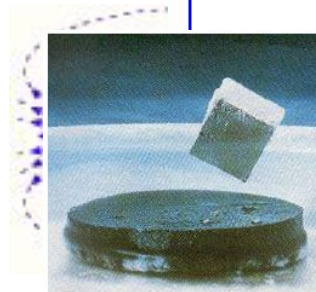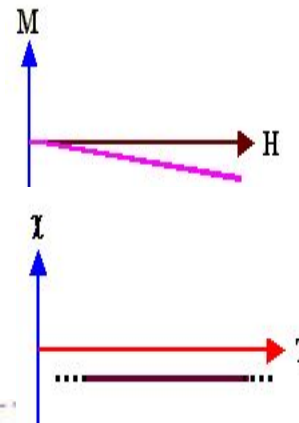
Paramagnetismo

- Possuem momento magnético permanente
- Não há interação entre momentos
- χ>0 porém pequena (10^{-5} - 10^{-3}) (tende a alinhar com o campo)

Temperatura
x
Campo Magnético

H=0, M=0   H≠0
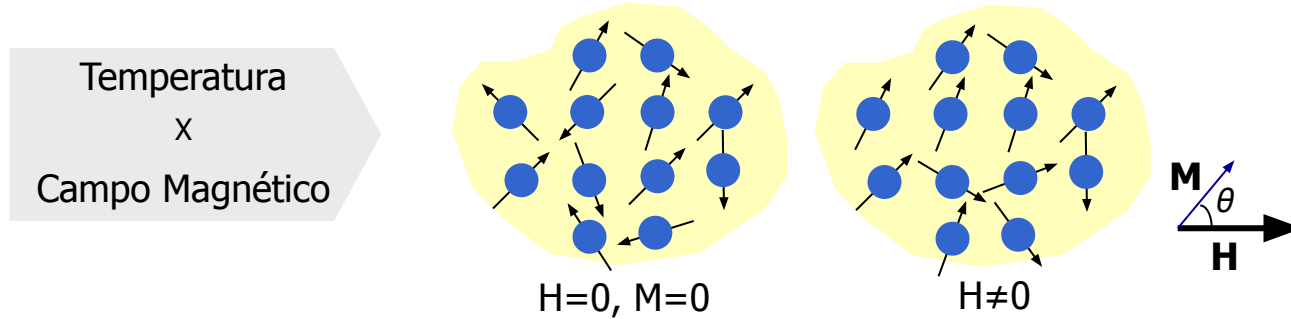
- Langevin (Clássica): momentos idênticos que não interagem e apontam em qualquer direção

Campo
Magnético

$$E = -\underline{\boldsymbol{\mu}} \cdot \underline{\boldsymbol{B}}$$

$$= -\mu \cos\theta \, B$$

Projeção do momento na direção de B

- E^{min}: momentos alinhados com **B**

- Competição com agitação térmica

Paramagnetismo Quântico

Campo Magnético
x
Temperatura

N : alta densidade de mom. mag.

μ : momento orbital
momento de spin

Clássico

B=0   B≠0

B

θ contínuo

$< \cos\theta >= 0$ $< \cos\theta >\neq 0$

$+\mu$
B
E
$-\mu$
B

Quântico

B=0   B≠0

B

θ discreto

$N_\downarrow$
$N_\uparrow$
E
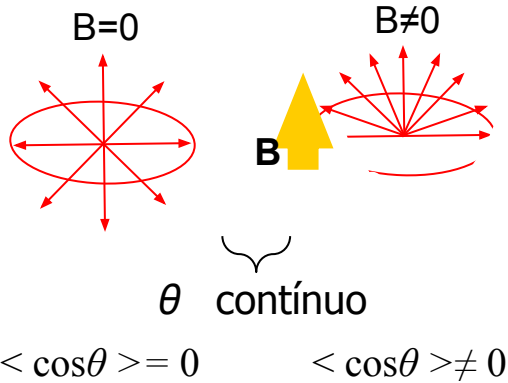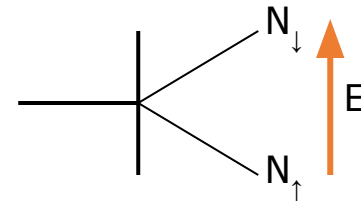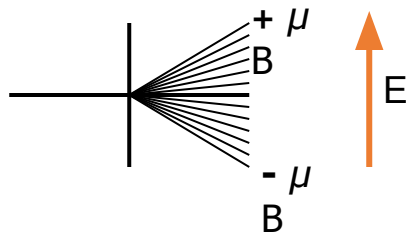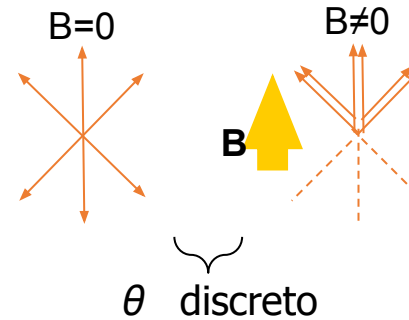
- Quantização do mom. angular:

$E = -\underline{\mu} \cdot \underline{B}$

$\underline{\mu} = -g\,\mu_B\,\underline{J}$

$= g\,\mu_B\,J^z\,B$

B

μ

$J^z : J,$
$\quad\quad J-1,$
$\quad\quad J-2,$
J $\quad\quad \dots -J$

$J^z = \pm 1/2$

angular: $J=1/2$ e g=2

$E = \pm\mu B$

$N_\downarrow$ 2 $+\mu_B B$

$B = 0$

$N_\uparrow$ 1 $-\mu_B B$

$B \neq 0$
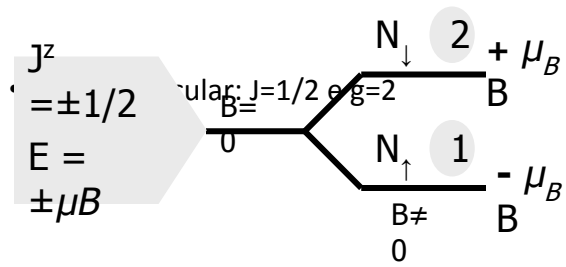
- População $\;N_T = N_1 + N_2$

$$n_1 = N_1/N_T = e^{-E_1/kT}\Big/\left(e^{-E_1/kT} + e^{-E_2/kT}\right)$$

$$n_2 = N_2/N_T = e^{-E_2/kT}\Big/\left(e^{-E_1/kT} + e^{-E_2/kT}\right)$$

- Magnetização resultante:

$$M = \mu\left(N_1 - N_2\right)/V = N\mu\frac{e^x - e^{-x}}{e^x + e^{-x}}$$

$$x = \frac{\mu B}{kT}$$

$\tanh(x)$

- Para qualquer J:

$$M = g\,\mu_B\,J\,N\,B_J(x)$$

Função de Brillouin

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

- Para $x = \dfrac{\mu B}{kT} \ll 1$ temos:

$$\coth x = \frac{1}{x} + \frac{x}{3} \boxtimes$$

$$B_J(x) \xrightarrow{x \ll 1} \frac{J(J+1)}{3J^2} x$$

- Logo:

$$M = \frac{NJ(J+1)g^2\mu_B^2 B}{3kT} = \frac{C}{T} B$$
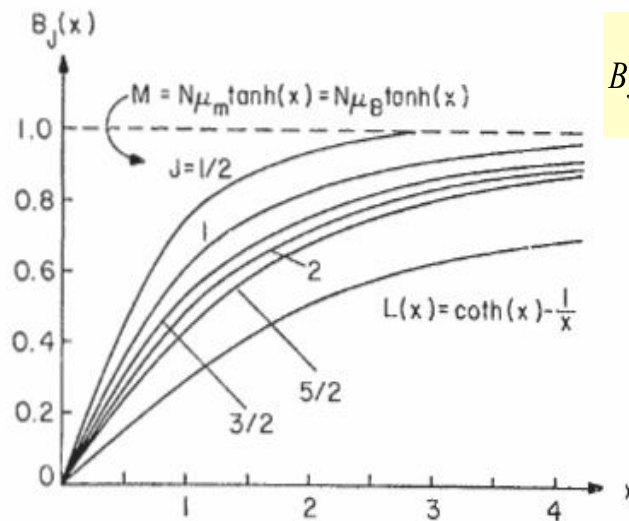
$$\chi = \frac{M}{H} = \mu_0 \frac{Ng^2\mu_B^2 J(J+1)}{3J^2 kT}$$

- No limite de *J muito grande:*

$$B_J(x) \xrightarrow{J \to \infty} L(x)$$

Limite Clássico!!

Ferromagnetismo

momento
dipolo magnético

Paramagnetismo

?
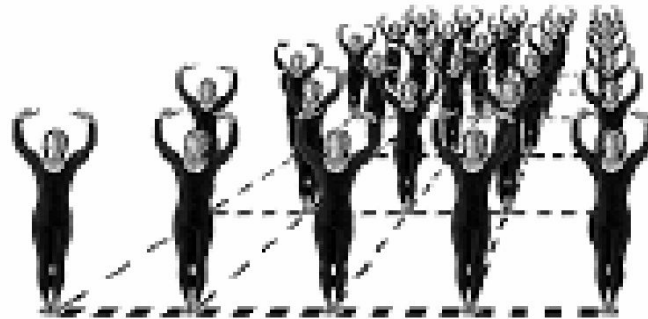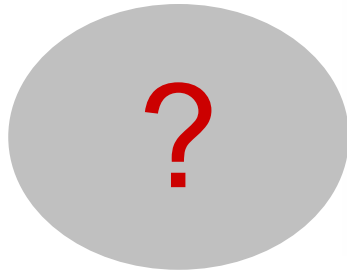
Ferromagnetismo

Ferromagnetismo : Campo Molecular

Hipótese de Weiss

- Cada momento de dipolo magnético sofre a ação de um campo magnético efetivo criado pelos vizinhos

- Campo molecular médio → Magnetização espontânea (M_s)

$$H_e = \lambda M$$

$$H_{tot} = H_a + H_e = H + \lambda M$$

$$M = \chi H = (C/T)H \quad ou \quad M = (C/T)(H + \lambda M)$$

$$\chi = \frac{M}{H} = \frac{C}{T - T_c} \quad onde \quad T_C = \lambda C$$

Lei de Curie-Weiss
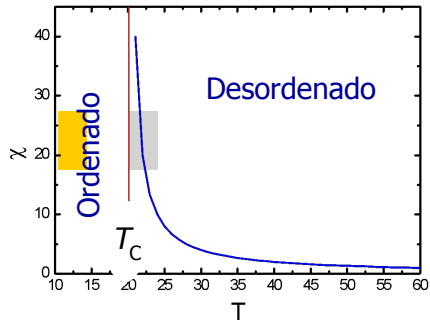
Soluções : origem e ponto P (estável)

- Origem: M=0 (instável)
  - distribuição aleatória de mom. magn.
  - λM=0
  - aparecimento de um alinhamento local
  - P' – desloca em direção a P (estável)

$M=M_0B_J(x)$

$H=\lambda M$

Estado desmagnetizado??
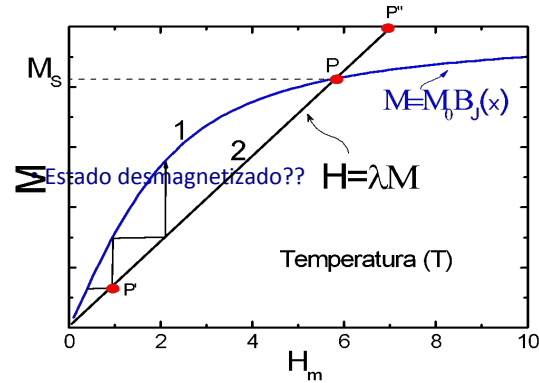
- Domínios magnéticos
- Processo de magnetização:
  multidomínios ⇒ monodomínios

Ferromagnetismo : Teoria de Weiss

M x T para o Ni
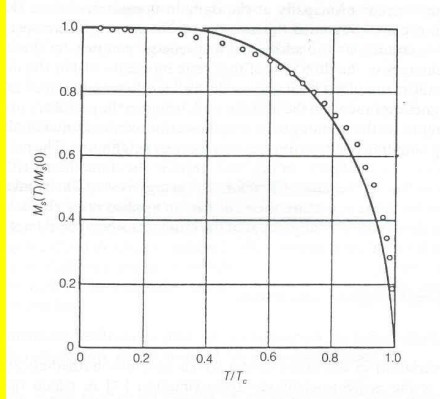
$$\chi = \frac{C}{T - \theta}$$

Lei de Curie-Weiss

- Temperatura de Curie T_C :
  - indicação de λ
  - intensidade do campo molecular

$$\lambda = \frac{3kT_C}{N\mu^2}$$

- Para o Fe: μ = 2.2μ_B
    N = 8.54x10^{28} m^{-3}
  T_C= 1063 K

$$\lambda = 7.8 \times 10^8$$

$$H_m = \lambda M$$

$$H_m = \lambda N \mu_B$$

$$H_m = 1.7 \times 10^8 \, A/m = 2.1 \times 10^7 \, Oe$$

Ferromagnetismo : origem do campo molecular
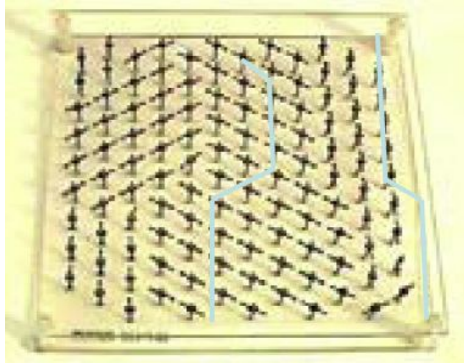
$$E_{i\leftrightarrow j}\left(\vec{r}=\vec{r}_i-\vec{r}_j\right)=\frac{\vec{m}_i\cdot\vec{m}_j}{r^3}-3\frac{(\vec{r}\cdot\vec{m}_i)(\vec{r}\cdot\vec{m}_j)}{r^5}$$

- Interação dipolar leva à formação de domínios magnéticos PORÉM é muito fraca para explicar a presença de um estado ordenado em temperatura ambiente

- **INTERAÇÃO DE TROCA**

- **Interação QUÂNTICA**

$$H=-2J\sum_{i,j}\mathbf{s}_i\cdot\mathbf{s}_j$$

J > 0 : Ferromagnetismo ↑↑↑↑↑↑

J < 0 : Antiferromagnetismo ↑↓↑↓↑↓↑

Table 5.2 The g-factors for 4f ions using Hund's rules.

ion	shell	S	L	J	g_J	$g_J - 1$	$(g_J - 1)^2 J(J+1)$
Ce^{3+}	$4f^1$	$\frac{1}{2}$	3	$\frac{5}{2}$	$\frac{6}{7}$	$-\frac{1}{7}$	0.18
Pr^{3+}	$4f^2$	1	5	4	$\frac{4}{5}$	$-\frac{1}{5}$	0.80
Nd^{3+}	$4f^3$	$\frac{3}{2}$	6	$\frac{9}{2}$	$\frac{72}{99}$	$-\frac{27}{99}$	1.84
Pm^{3+}	$4f^4$	2	6	4	$\frac{3}{5}$	$-\frac{2}{5}$	3.20
Sm^{3+}	$4f^5$	$\frac{5}{2}$	5	$\frac{5}{2}$	$\frac{2}{7}$	$-\frac{5}{7}$	4.46
Eu^{3+}	$4f^6$	3	3	0	–	–	–
Gd^{3+}	$4f^7$	$\frac{7}{2}$	0	$\frac{7}{2}$	2	1	15.75
Tb^{3+}	$4f^8$	3	3	6	$\frac{3}{2}$	$\frac{1}{2}$	10.50
Dy^{3+}	$4f^9$	$\frac{5}{2}$	5	$\frac{15}{2}$	$\frac{4}{3}$	$\frac{1}{3}$	7.08
Ho^{3+}	$4f^{10}$	2	6	8	$\frac{5}{4}$	$\frac{1}{4}$	4.50
Er^{3+}	$4f^{11}$	$\frac{3}{2}$	6	$\frac{15}{2}$	$\frac{6}{5}$	$\frac{1}{5}$	2.55
Tm^{3+}	$4f^{12}$	1	5	6	$\frac{7}{6}$	$\frac{1}{6}$	1.17
Yb^{3+}	$4f^{13}$	$\frac{1}{2}$	3	$\frac{7}{2}$	$\frac{8}{7}$	$\frac{1}{7}$	0.32
Lu^{3+}	$4f^{14}$	0	0	0	–	–	–

a)

H = 1000 Oe

Legend:
- □ GdCo$_2$Zn$_{20}$
- ○ Gd(Co$_{0.9}$Fe$_{0.1}$)$_2$Zn$_{20}$
- △ Gd(Co$_{0.8}$Fe$_{0.2}$)$_2$Zn$_{20}$
- ▽ Gd(Co$_{0.7}$Fe$_{0.3}$)$_2$Zn$_{20}$
- ◆ Gd(Co$_{0.4}$Fe$_{0.6}$)$_2$Zn$_{20}$
- ◀ Gd(Co$_{0.2}$Fe$_{0.8}$)$_2$Zn$_{20}$
- ▶ GdFe$_2$Zn$_{20}$

Y-axis: χ(emu/mol)

X-axis: T(K)

b)

Legend:
- $T_N = 5.3$ K
- $T_c = 5.3$ K
- $T_c = 11.3$ K
- $T_c = 15.8$ K
- $T_c = 24.8$ K
- $T_c = 43.7$ K
- $T_c = 83.7$ K

y-axis: $(\chi - \chi_0)^{-1}$ (mol/emu)

x-axis: T(K)

Inset text:

$\mu_{eff} = 8.1(2)\mu_B$

$\theta_c = -0.7(4)$ K

Linear fitting

$(\chi - \chi_0)^{-1}$ (mol/emu)

GdCo$_2$Zn$_{20}$

T (K)

Main plot labels:

χ(emu/mol)

Intensity (arb. units)

H = 1000 Oe
H//[111]

T(K)
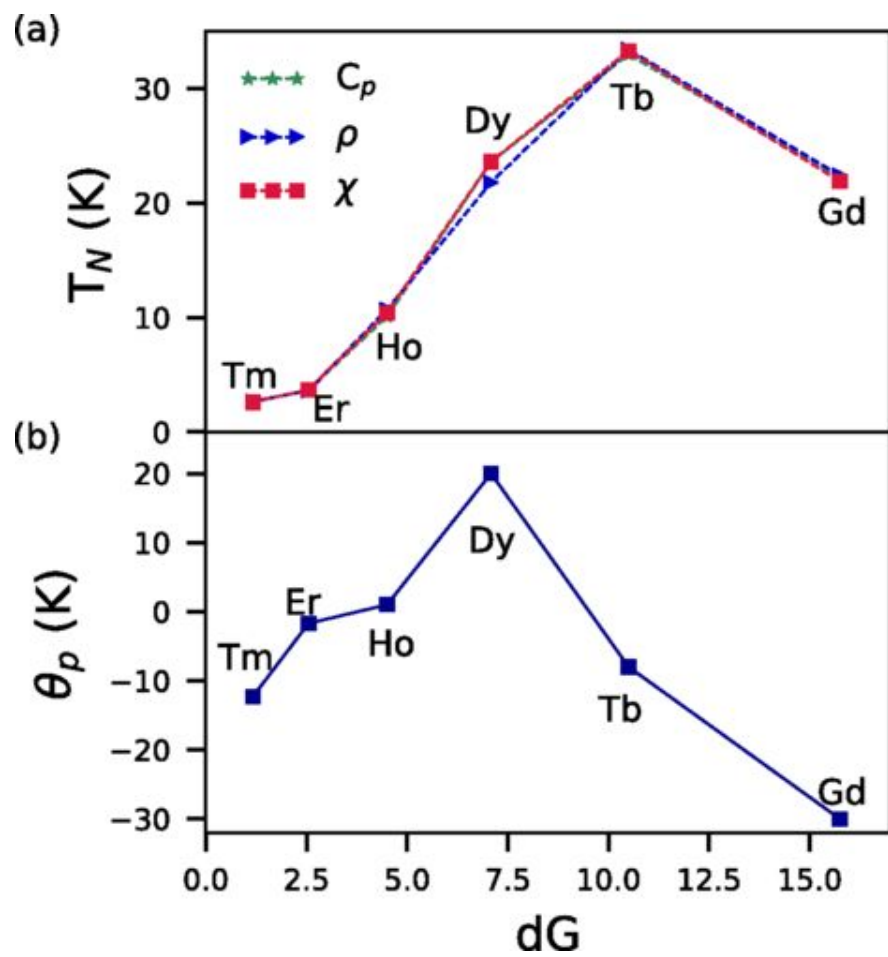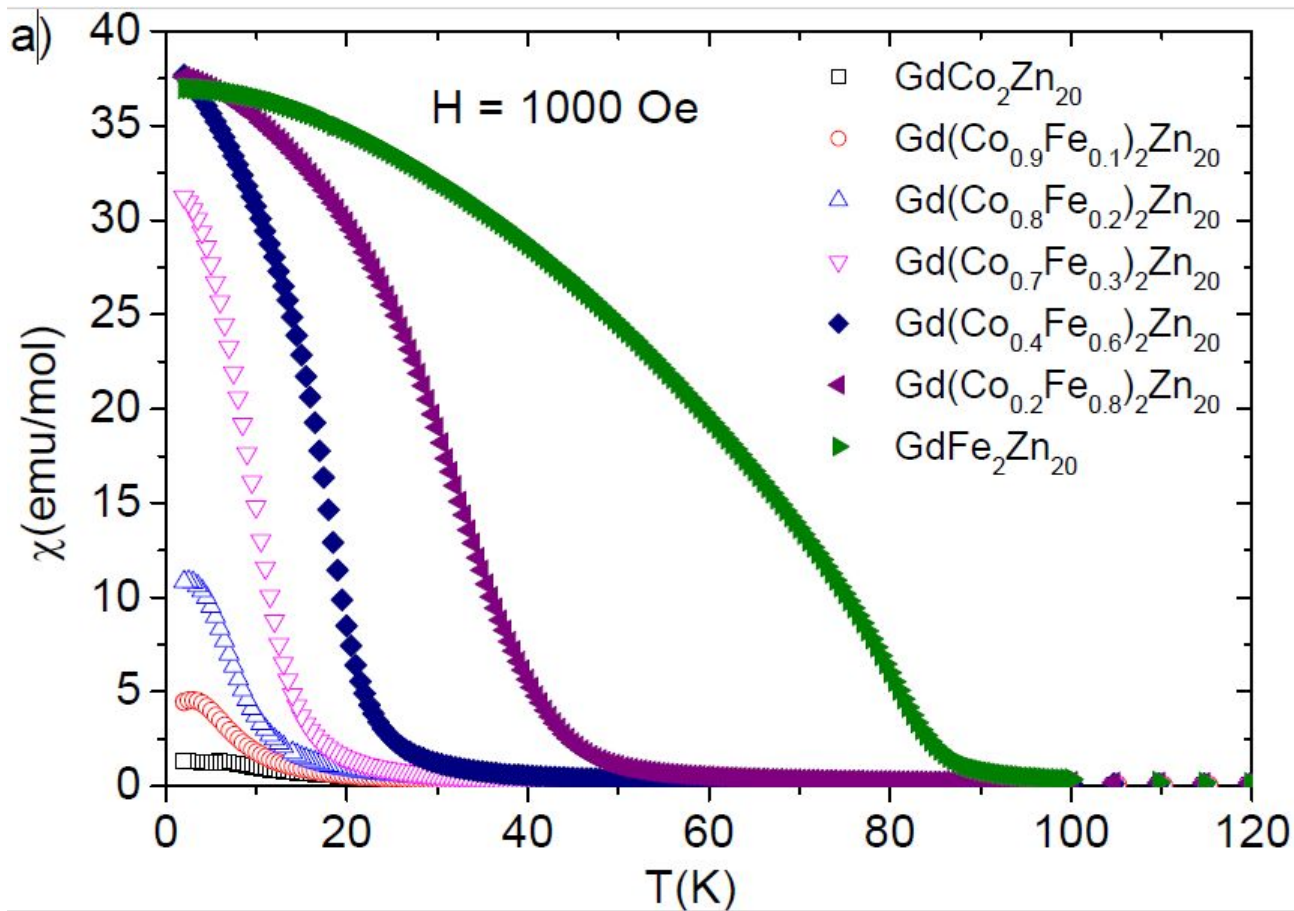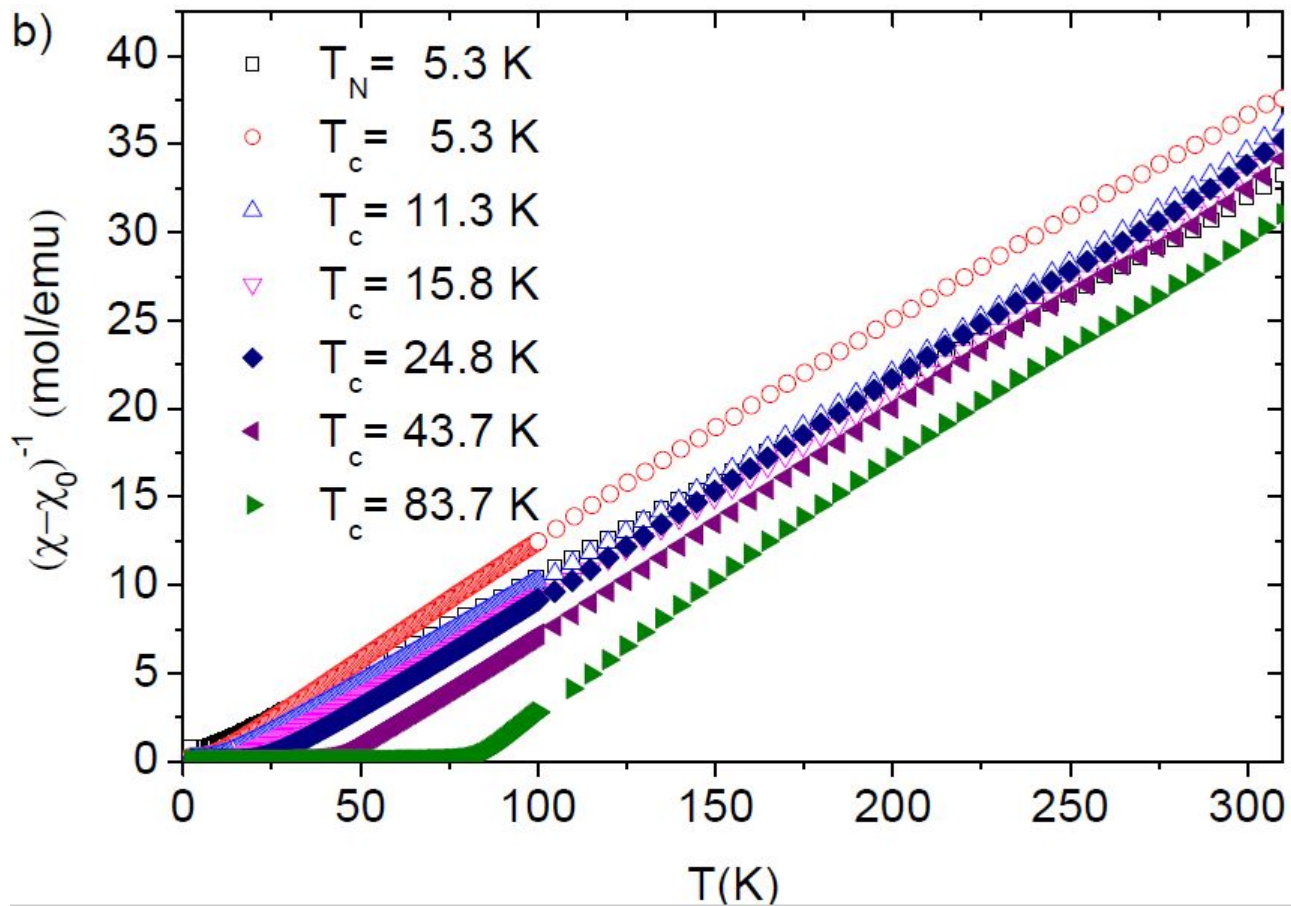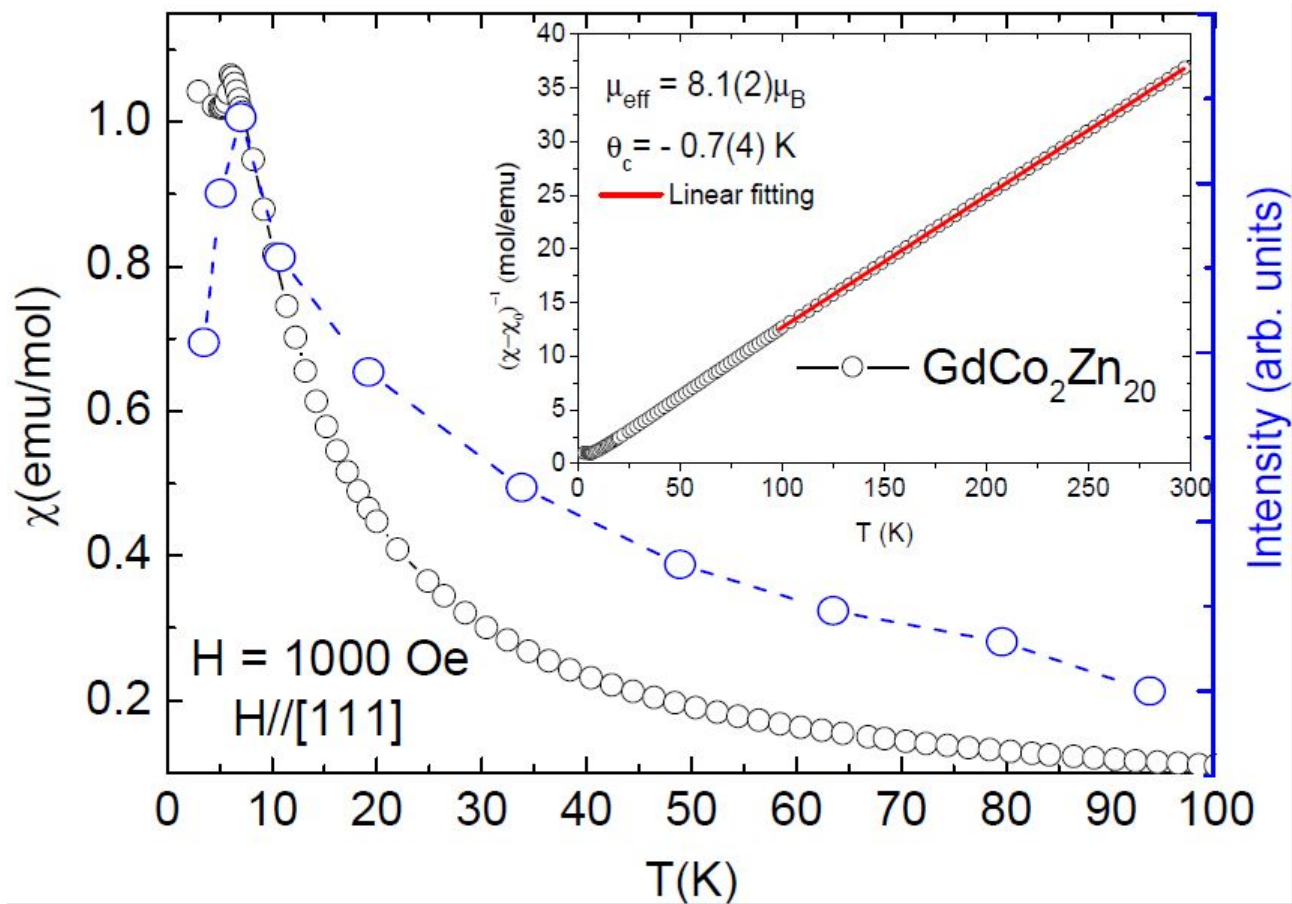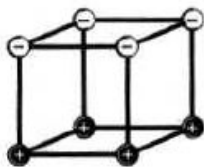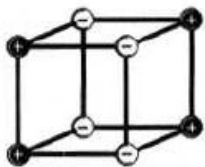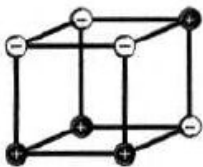
(a) type A (b) type C (c) type E (d) type G

(a)

(b)

(c)

Spinel AB$_2$O$_4$

Legend: O, Al, Mg
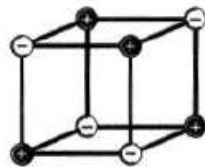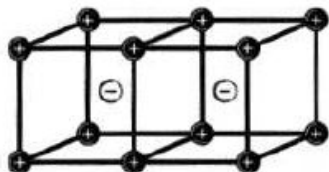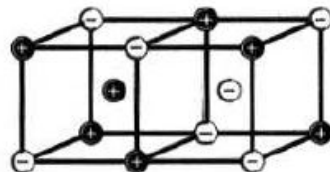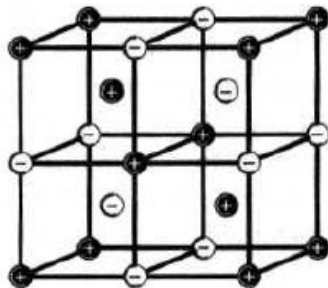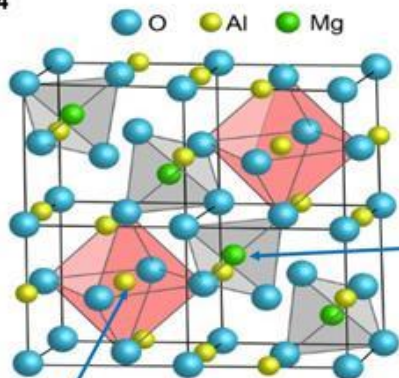
A Site – one metal with four nearest-neighbor oxygens. **Tetrahedral site**

B site – one metal with six nearest-neighbor oxygens. **Octahedral site**

Y₃Fe₅O₁₂

- Y³⁺ dodecahedral
- Fe³⁺ octahedral
- Fe³⁺ tetrahedral
- O²⁻

tetrahedral

dodecahedral

octahedral

Y³⁺

O²⁻

Fe³⁺

Y$_3$Fe$_5$O$_{12}$
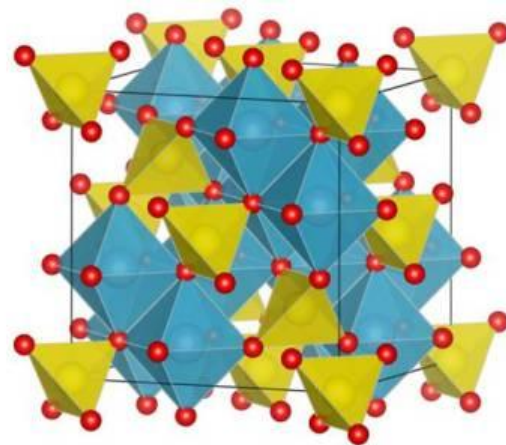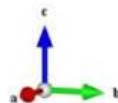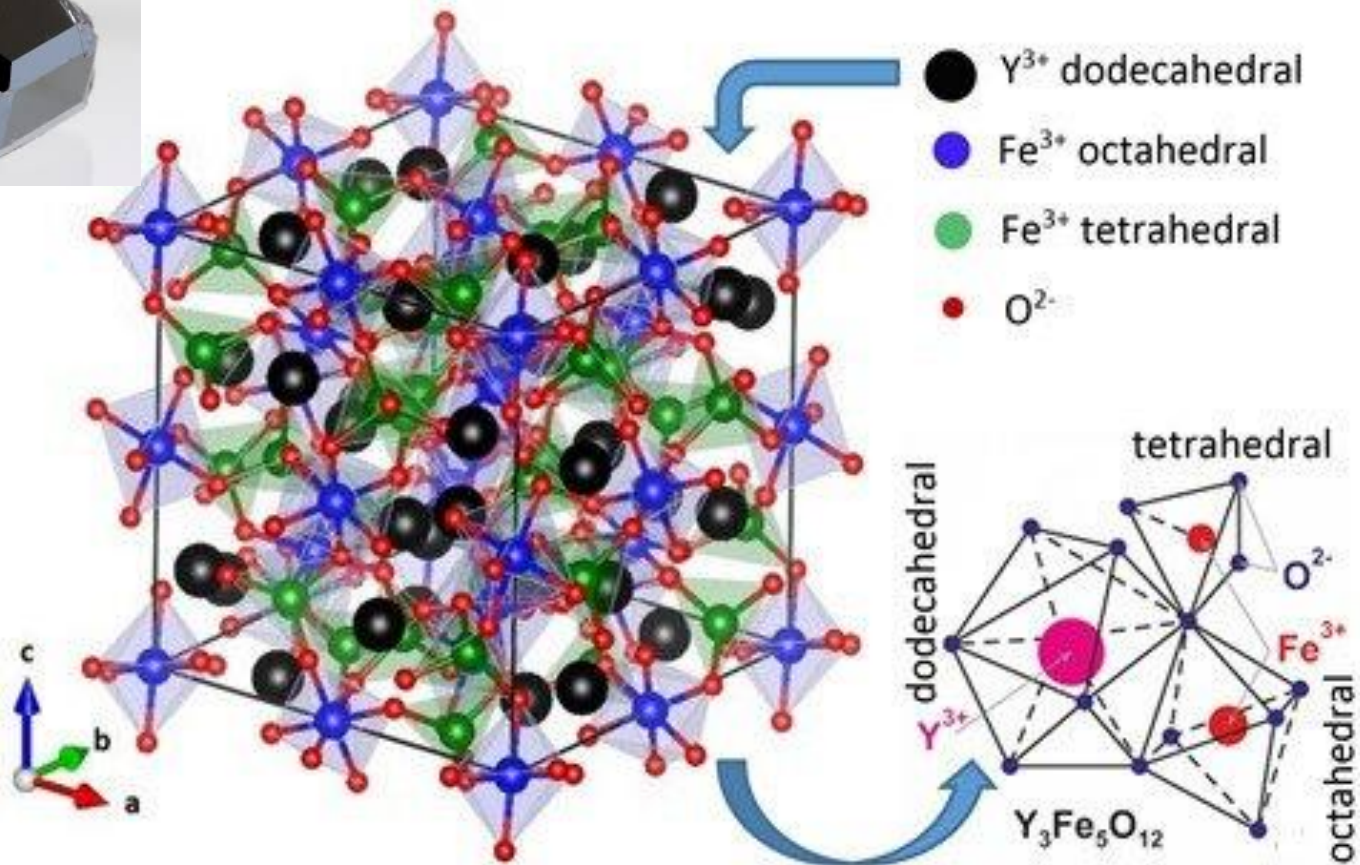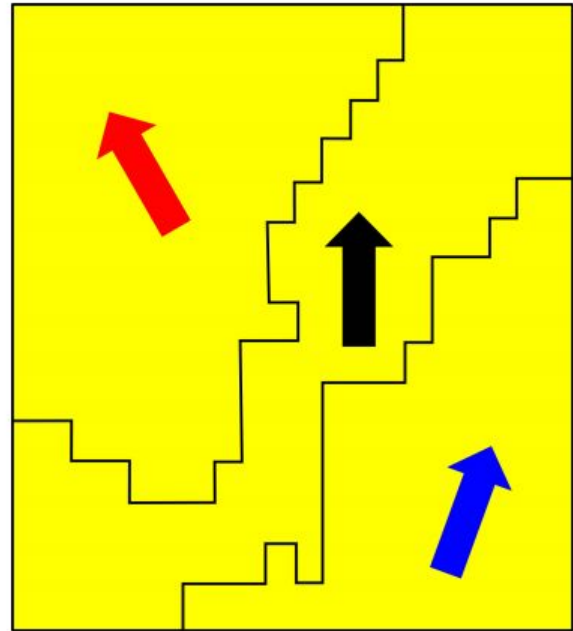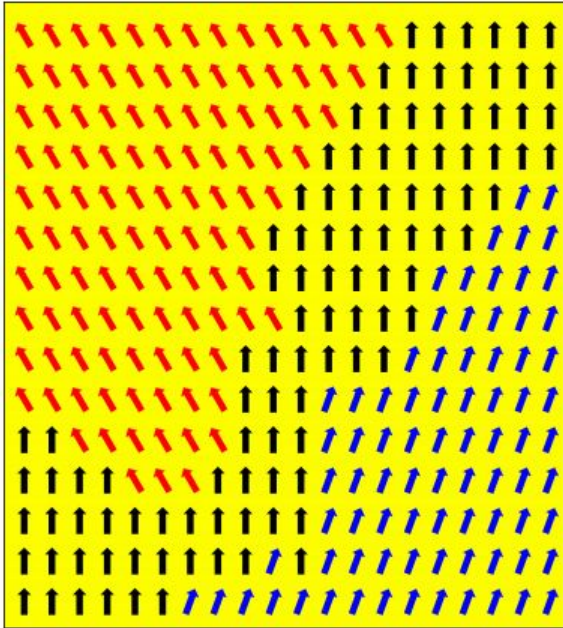
Results

- Y-GdCo$_2$Zn$_{20}$
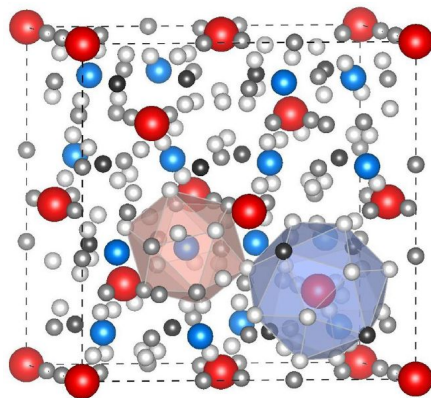
- Features
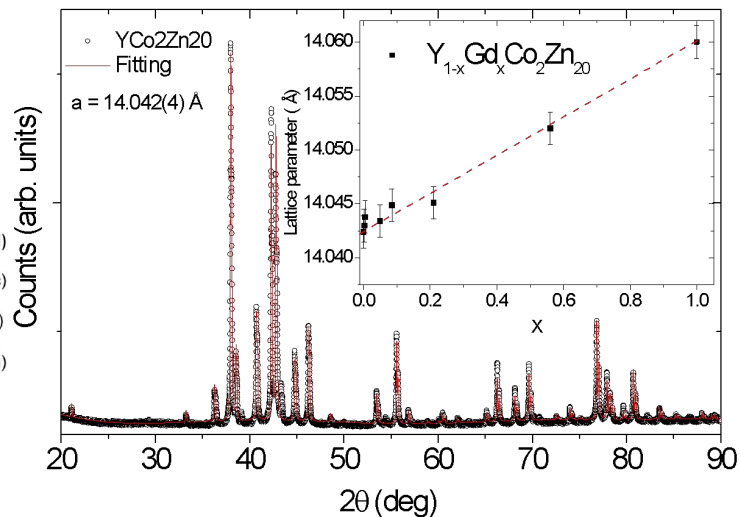
- Cubic (space group No. 227 CeCr$_2$Al$_{20}$-type)

- a = 14.042(4) A

13

Results

Cp vs T^2

3.8(8)

$$C_v = \frac{2}{3} k_B^2 \pi^2 D(E_F)T = \gamma T$$

YCo$_2$Zn$_{20}$

γ = 18(3) mJ/mol.K^2

β = 0.9(5) mJ/mol.K^4

4.8(9)
States/eV.fu.spin
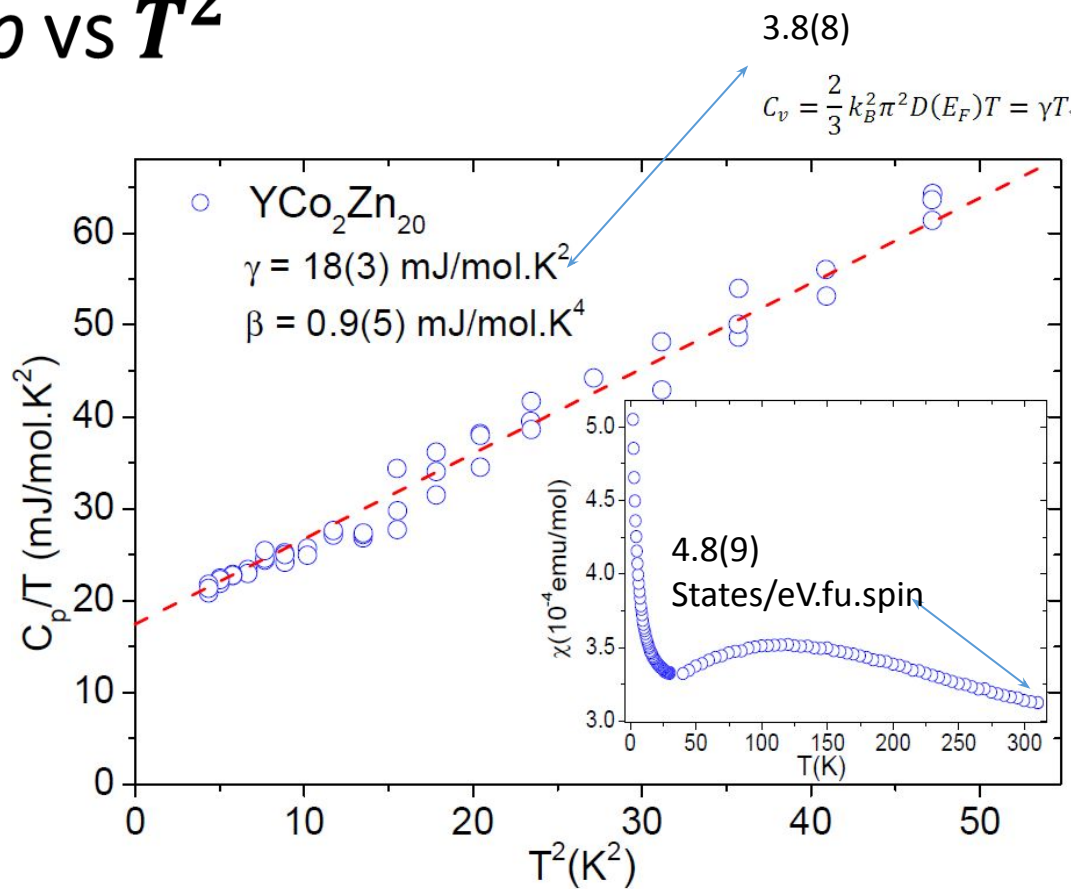
Partial density of states (DFT)

3.01(1)
States/eV.fu.spin
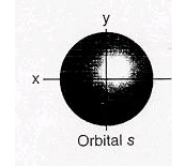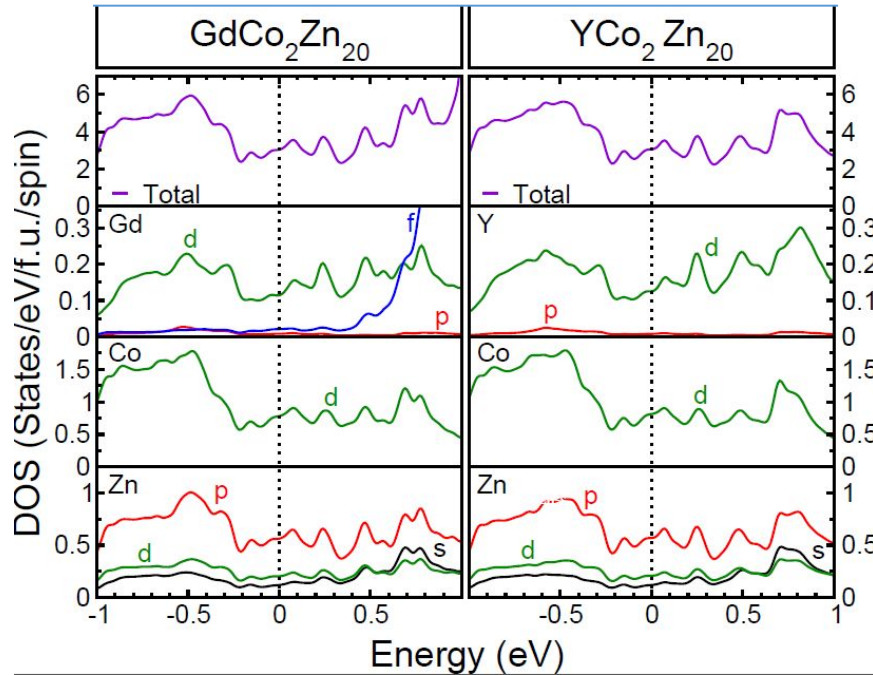
Type s 0.13(1)
States/eV.fu.spin
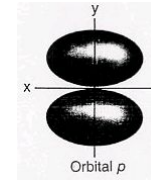
Type p 0.59(1)
States/eV.fu.spin
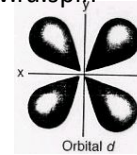
Type d 1.09(1)
States/eV.fu.spin

15

Prof. Dr. Jorge Osorio and Andrés

Table 3.6. Summary of localized and delocalized magnetism

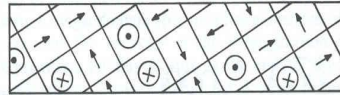| Localized magnetism	Delocalized magnetism
Integral number of $3d$ or $4f$ electrons	Nonintegral number of unpaired spins on the ion core
Integral number of unpaired spins per atom	
Discrete energy levels	Spin polarized energy bands with strong correlations
Ni^{2+} $3d^8$ $m = 2\,\mu_B$	Ni $3d^{9.4}4s^{0.6}$ $m = 0.6\,\mu_B$
$\Psi \approx \exp(-r/a_0)$	$\Psi \approx \exp(-i\boldsymbol{k} \cdot \boldsymbol{r})$
Boltzmann statistics	Fermi–Dirac statistics
$4f$ metals and compounds; some $3d$ compounds	$3d$ metals; some $3d$ compounds
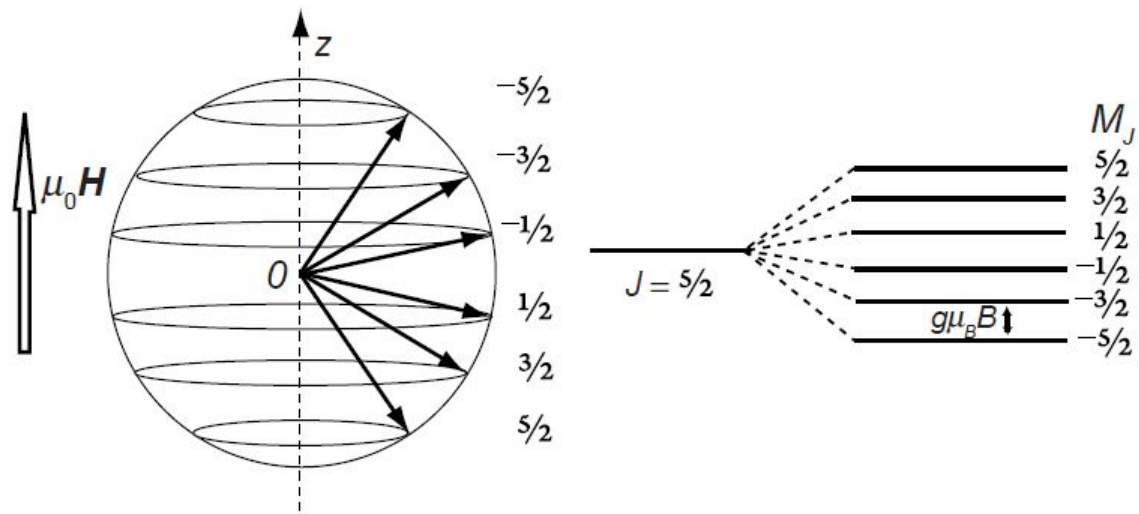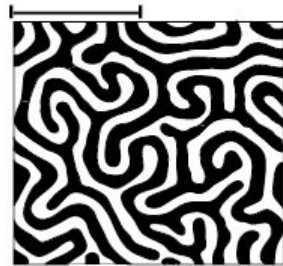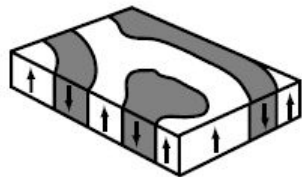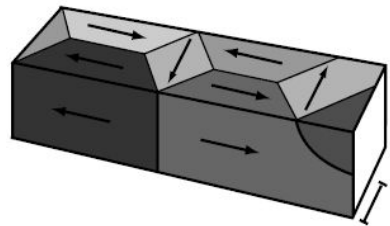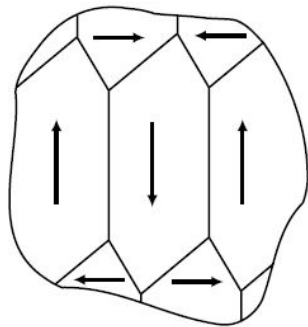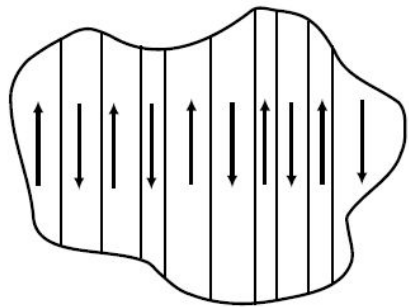
Domínios

- Balanço Energético
- um único domínio - mono domínio
  - alta energia magnetostática
- Divisão em estruturas
  - fechamento do fluxo magnético
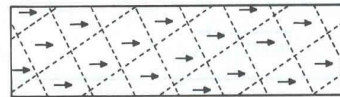 - minimiza energia
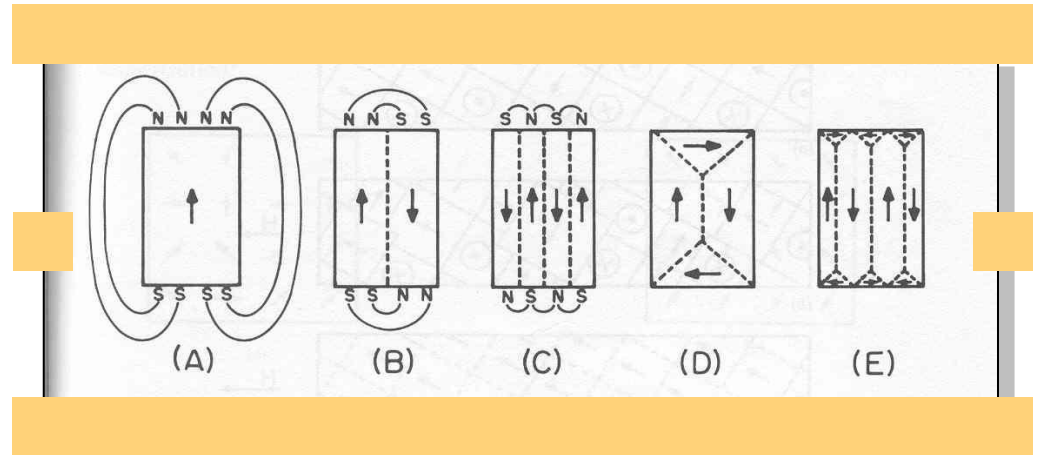
Histerese e Processos de Magnetização

M$_r$: remanência
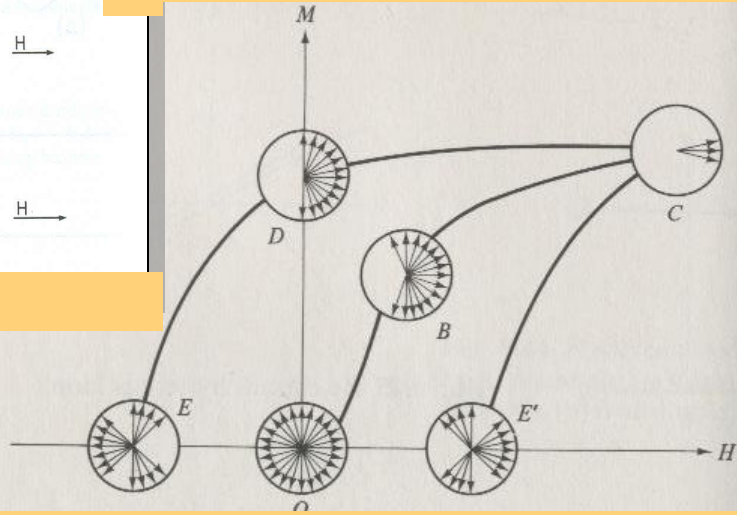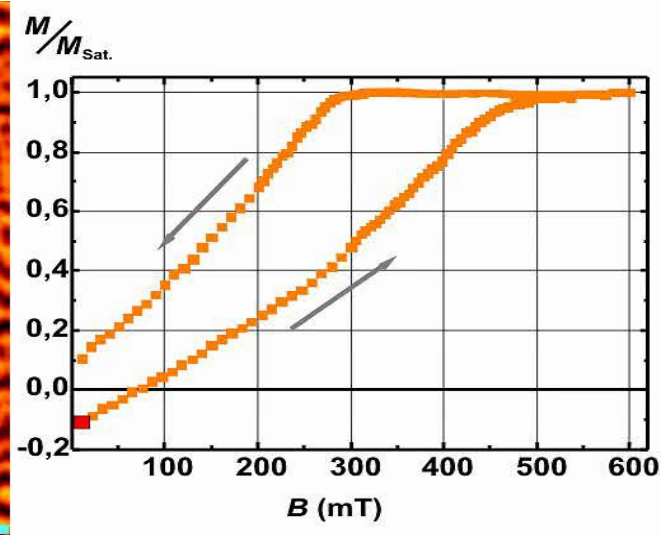Magnetização resultante quando o campo é retirado após saturação

M$_S$
Magnetização de Saturação

Ferromagneto Macio

H$_c$: coercividade
Campo reverso que reduz a magnetização a zero

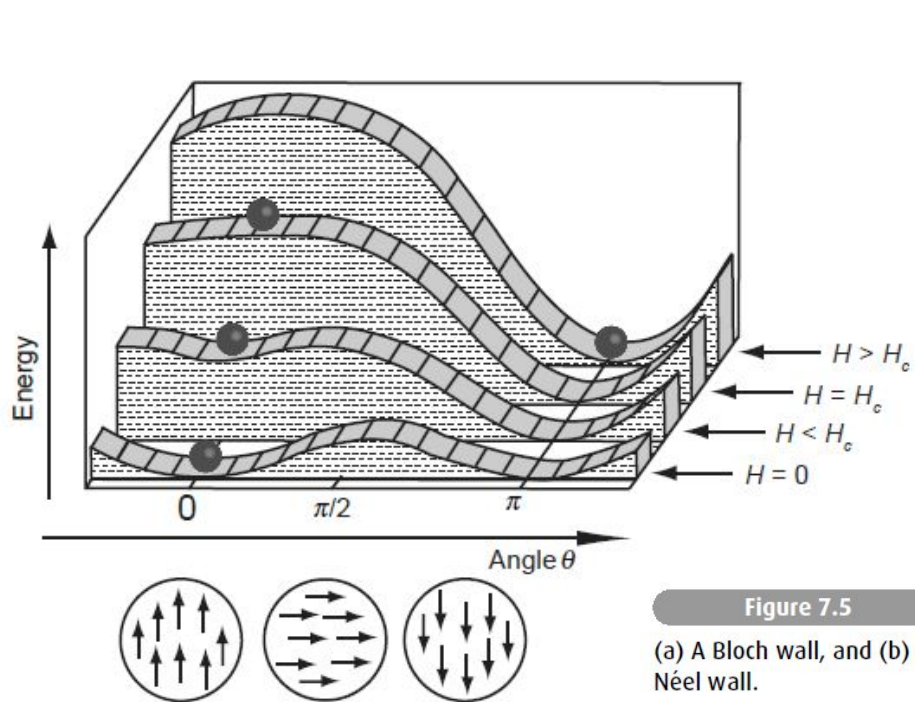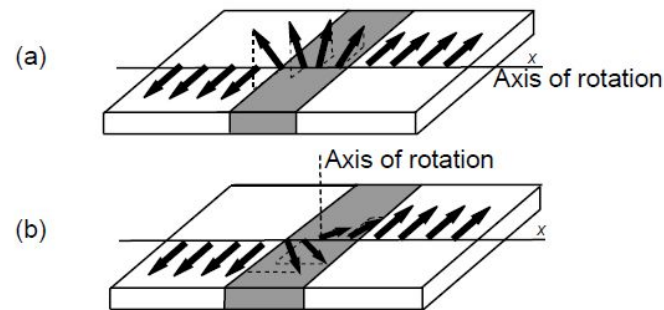Ferromagneto Duro
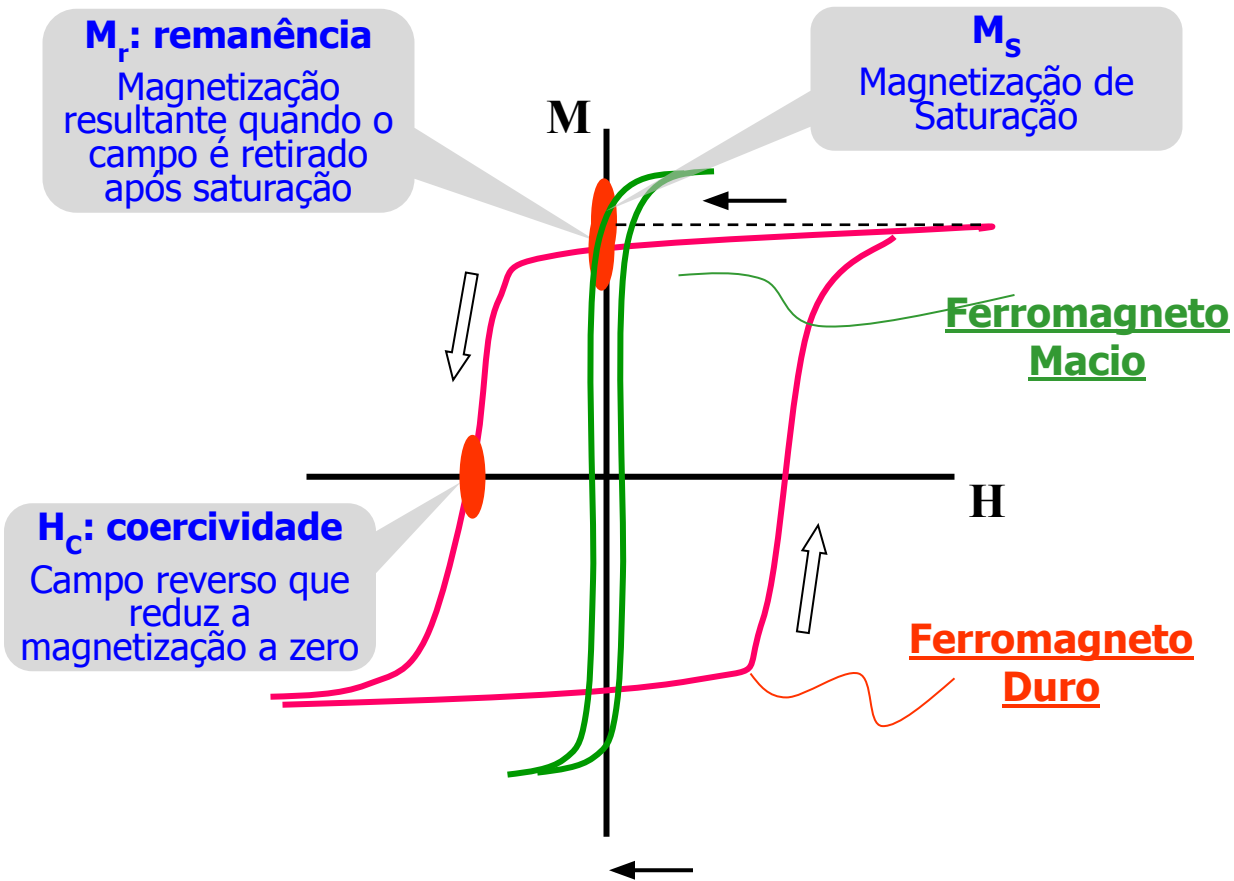
Domínios

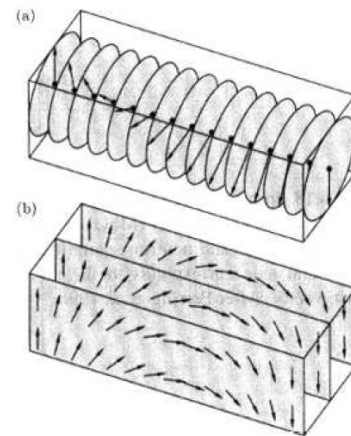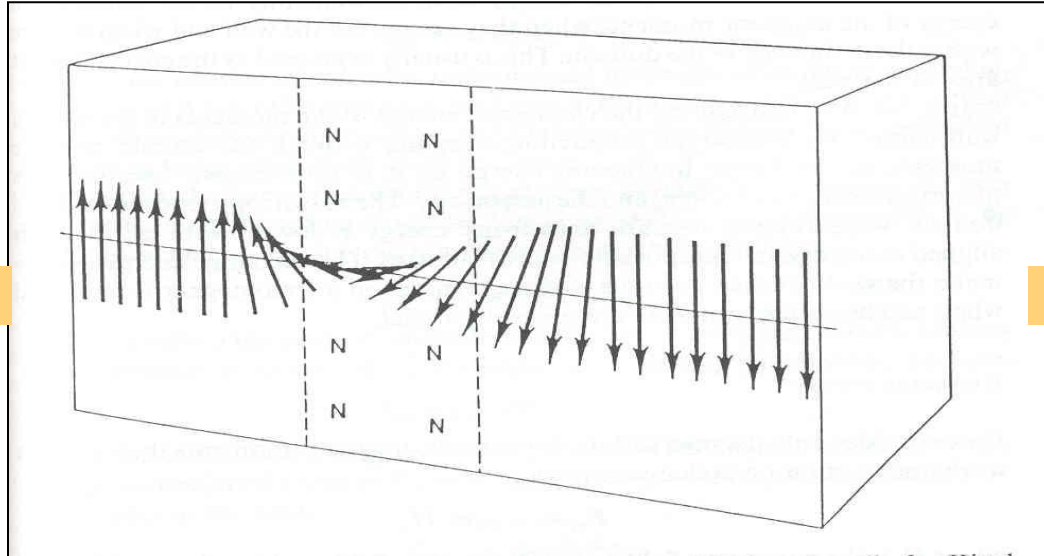# Movimento de Paredes de Domínio
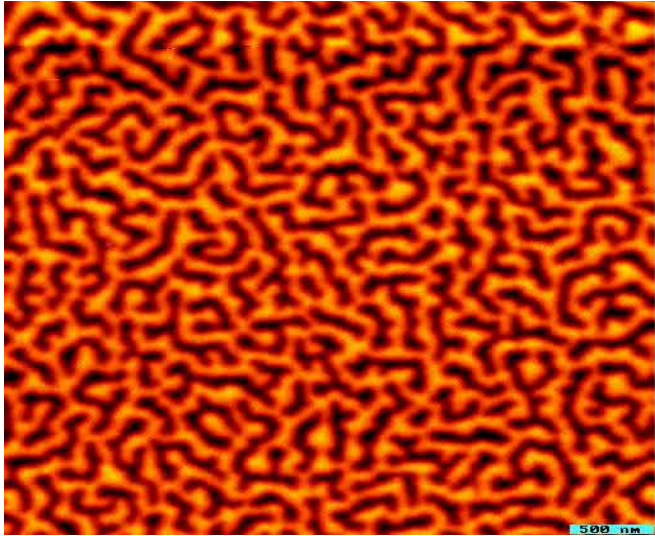
Figure 7.5

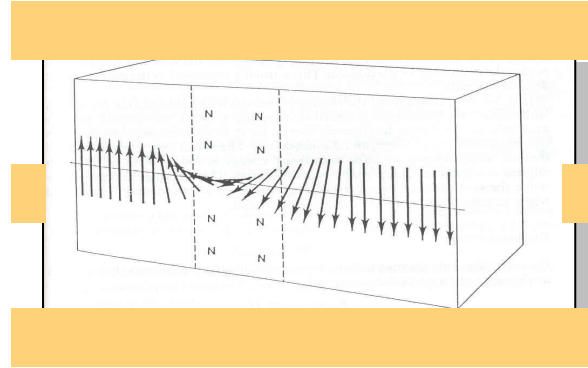(a) A Bloch wall, and (b) a Néel wall.

Parede de domínio

- Qual é o custo de energia?
- Qual é a largura?

- Definição:
  - Diferença de energia dos momentos
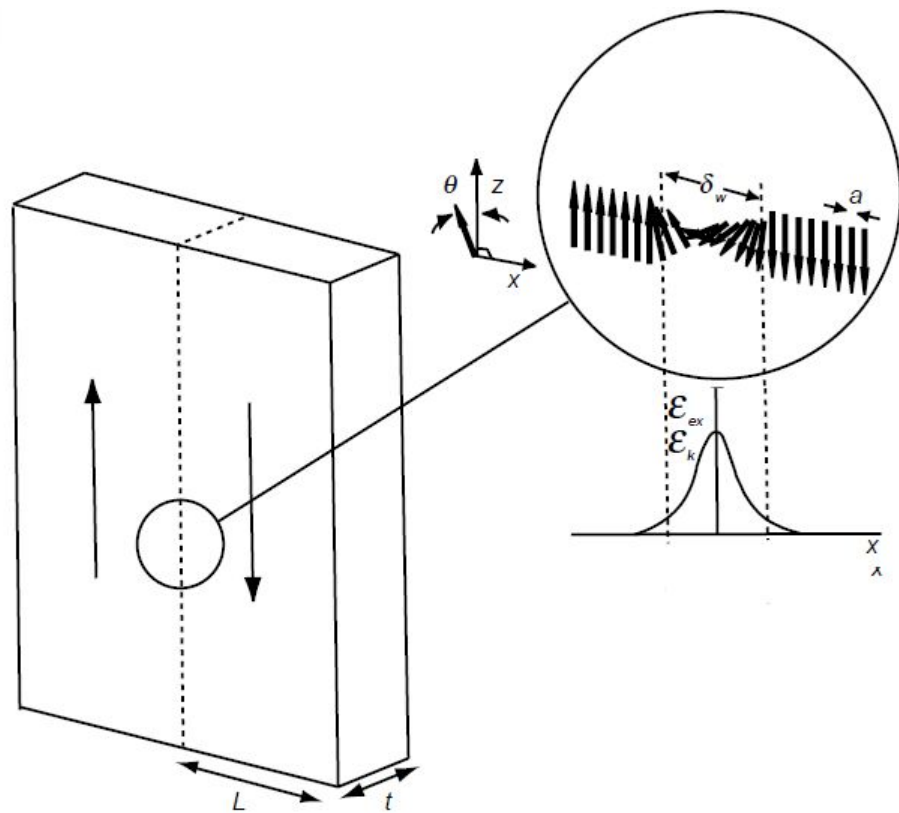   - dentro da parede
    - dentro do domínio

- Dois termos
  - Energia de troca
    - momentos paralelos
  - Anisotropia
    - momento em uma direção

$$\delta_{wall} \approx \pi \left(\frac{A}{K_u} \right)^{1/2} \quad \text{Fe: 30 nm}$$

$$\sigma_{wall} \approx a \left(A K_u \right)^{1/2} \quad \text{Fe: 0.7mJ/m}^2$$

Figure 7.6
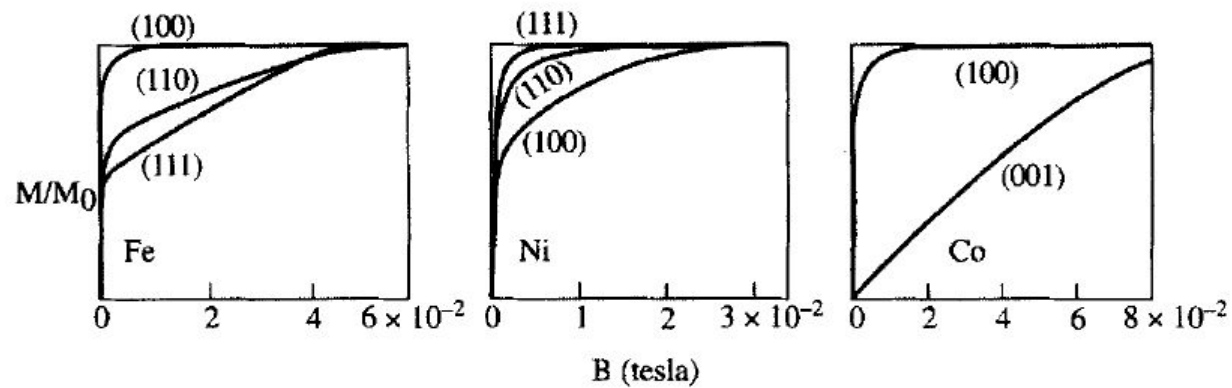
Detail of the 180° Bloch wall.

Fig. 6.22 Magnetization in Fe, Co and Ni for applied fields in different directions showing anisotropy. After Honda and Kaya 1926, Kaya 1928.
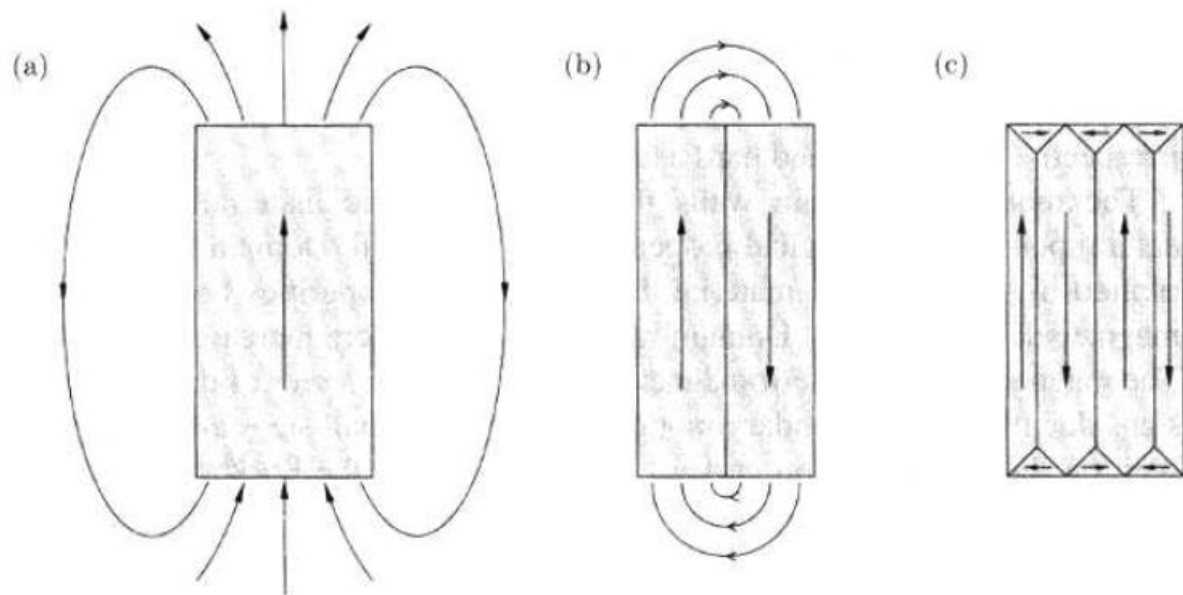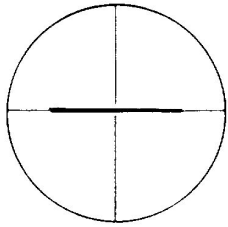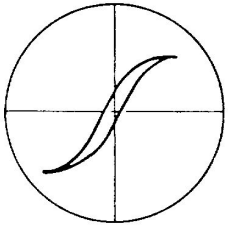
Fig. 6.23 A sample which is (a) uniformly magnetized, (b) divided into two domains, and (c) with a simple closure domain structure.
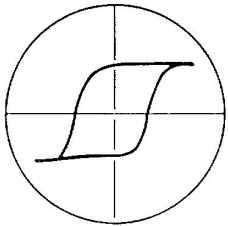
Ferromagnetos - Classificação

Paramagnético

- Os materiais ferromagnéticos podem ser separados basicamente em três classes, dependendo de sua resposta ao campo magnético aplicado (curva de histerese):

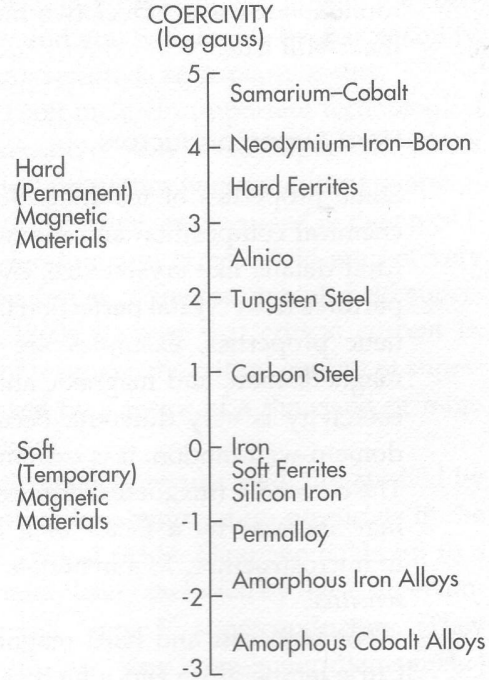   - Ferromagnetos Moles, ou doces
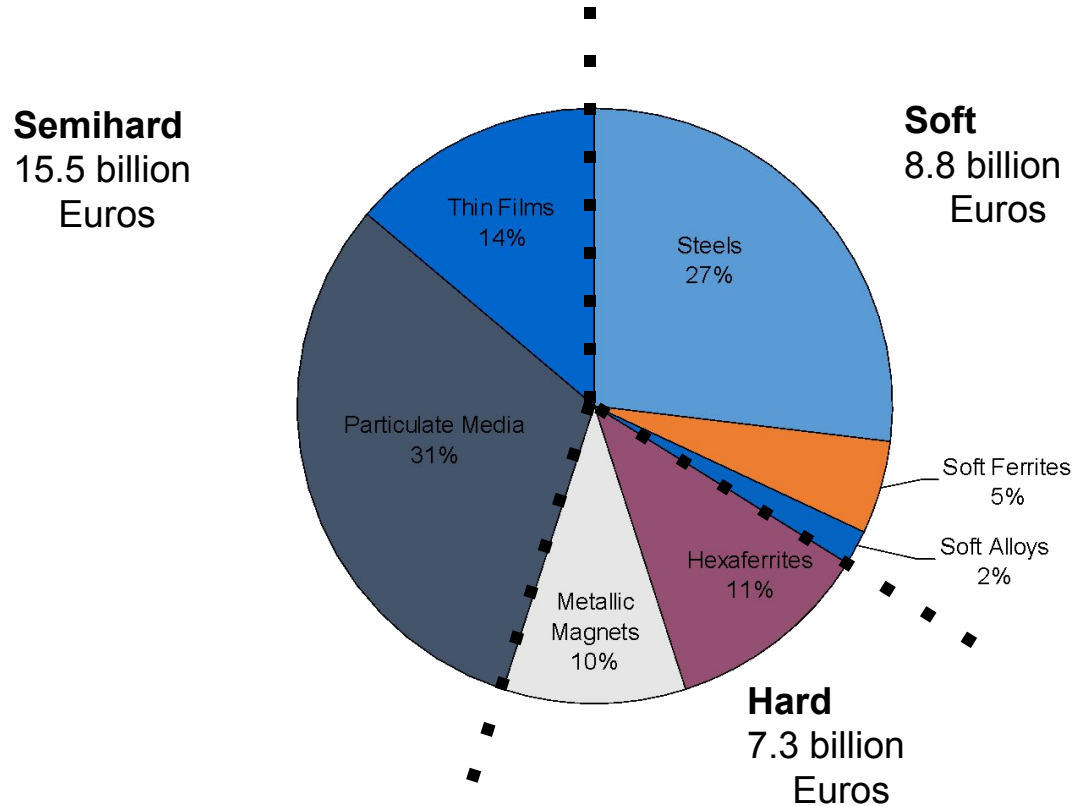
    - Ferromagnetos Duros
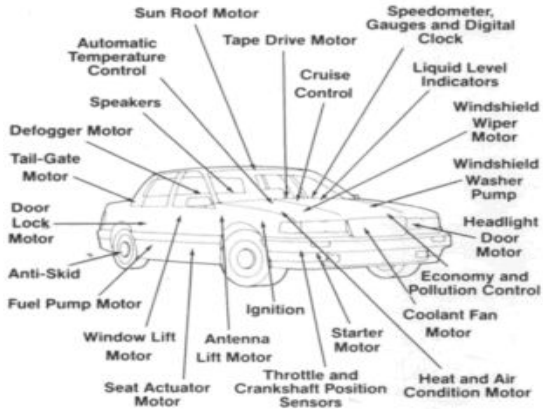
    - Ferromagnetos intermediários

Ferromagnetos

Figure 6.5 The coercivity—the strength of an applied field needed to demagnetize a magnetic material—of various hard and soft magnets, on a logarithmic scale. Amorphous metals (see Chapter 8) may be demagnetized by a field of a milligauss (10^{-3} gauss), whereas rare-earth permanent magnets (see Chapter 4) require fields of tens of kilogauss (10^4 gauss and more) to be demagnetized.

COERCIVITY (log gauss)

Hard (Permanent) Magnetic Materials

- 5 — Samarium–Cobalt
- 4 — Neodymium–Iron–Boron
- Hard Ferrites
- 3 —
- Alnico
- 2 — Tungsten Steel
- 1 — Carbon Steel

Soft (Temporary) Magnetic Materials

- 0 — Iron
- Soft Ferrites
- Silicon Iron
- -1 — Permalloy
- Amorphous Iron Alloys
- -2 —
- Amorphous Cobalt Alloys
- -3 —

Materiais Magnéticos no mercado Mundial

Semihard
15.5 billion Euros

Soft
8.8 billion Euros

Hard
7.3 billion Euros

Thin Films 14%

Steels 27%

Particulate Media 31%

Soft Ferrites 5%

Soft Alloys 2%

Metallic Magnets 10%

Hexaferrites 11%

Sun Roof Motor

Automatic Temperature Control

Tape Drive Motor

Speedometer, Gauges and Digital Clock

Cruise Control

Liquid Level Indicators

Speakers

Windshield Wiper Motor

Defogger Motor

Windshield Washer Pump

Tail-Gate Motor

Door Lock Motor

Headlight Door Motor

Anti-Skid

Economy and Pollution Control

Fuel Pump Motor

Ignition

Coolant Fan Motor

Window Lift Motor

Antenna Lift Motor

Starter Motor

Seat Actuator Motor

Throttle and Crankshaft Position Sensors

Heat and Air Condition Motor

Electric Shaver

Audio tape deck & Speakers

Washer & Dryer

Toys

Garage Door Opener

Refrigerator

Lawn Mower

Weed Trimmer

Telephone(s)

Hand-held Vacuum Cleaners & Rechargable Tools

Personal Computer

Furnace

Television Video Cassette Recorder

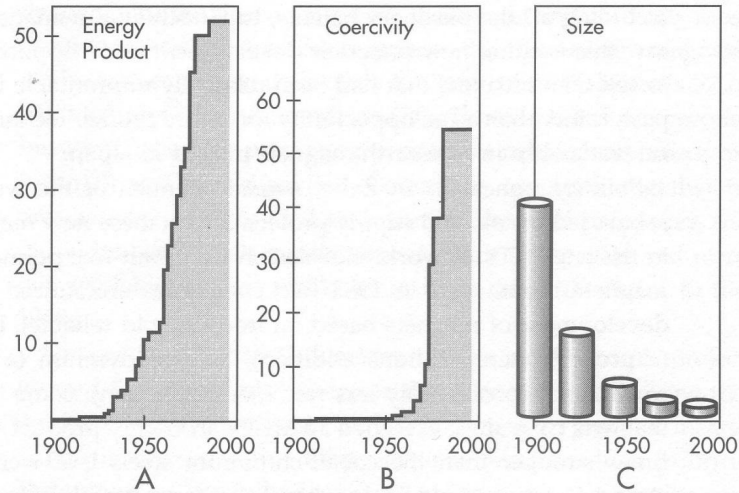Air Conditioner

Ferromagnetos Duros

Figure 4.1 The remarkable increases in (A) energy product (in megagauss-oersted) and (B) coercivity (in kilogauss) of permanent-magnet materials in this century. As magnets became more powerful, the size and length of a magnet required for a specific application (C) decreased.

Brass bound lodestone, ferrite block and NdFeB magnet: each store the same magnetic energy (~0.4J) & contain ~70% iron by weight, yet the mass has decreased a thousand fold.

Ferromagnetos - Aplicações

Driving Force: The Natural Magic of Magnets
by James D. Livingston
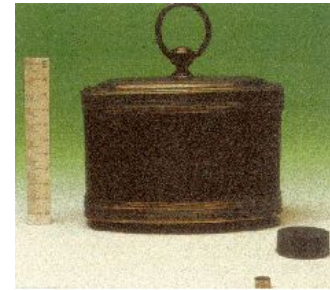
Automotive:
Starter motors, Anti-lock braking systems (ABS), Motor drives for wipers, Injection pumps, Fans and controls for windows, seats etc, Loudspeakers, Eddy current brakes, Alternators.

Telecommunications:
Loudspeakers, Microphones, Telephone ringers, Electro-acoustic pick-ups, Switches and relays.

Data Processing:
Disc drives and actuators, Stepping motors, Printers.

Consumer Electronics:
DC motors for showers, Washing machines, Drills, Low voltage DC drives for cordless appliances, Loudspeakers for TV and Audio, TV beam correction and focusing device, Compact-disc drives, Home computers, Video Recorders, Clocks.

Electronic and Instrumentation:
Sensors, Contactless switches, NMR spectrometer, Energy meter disc, Electro-mechanical transducers, Crossed field tubes, Flux-transfer trip device, Dampers.

Industrial:
DC motors for magnetic tools, Robotics, Magnetic separators for extracting metals and ores, Magnetic bearings, Servo-motor drives, Lifting apparatus, Brakes and clutches, Meters and measuring equipment.

Astro and Aerospace:
Frictionless bearings, Stepping motors, Couplings, Instrumentation, Travelling wave tubes, Auto-compass.

Biosurgical:
Dentures, Orthodontics, Orthopaedics, Wound closures, Stomach seals, Repulsion collars, Ferromagnetic probes, Cancer cell separators, Magnetomotive artificial hearts, NMR / MRI body scanner.

http://www.aacg.bham.ac.uk/magnetic_materials/hard_magnets.htm

Ferromagnetos Doces

- Transformadores

- Cabeçotes de leitura e gravação

- Sensores (Fluxgate)
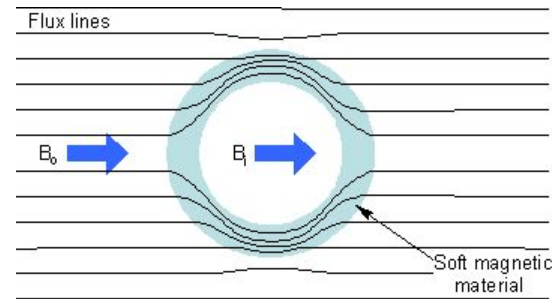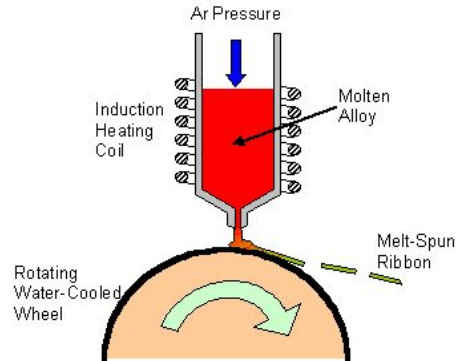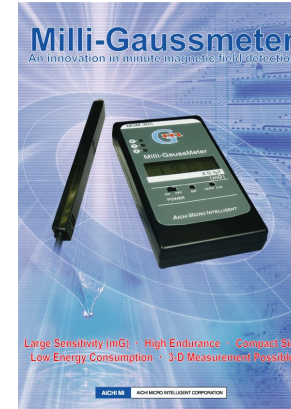
http://www.aacg.bham.ac.uk/magnetic_materials/soft_magnets.htm

Ferromagnetos – Outras Aplicações

- Magnetoresistência gigante
- Magnetostrição gigante
- Efeito Hall extraordinário
- Refrigeração magnética
- Magnetos moleculares
- Ressonância magnética

http://electronics.howstuffworks.com/mri.htm
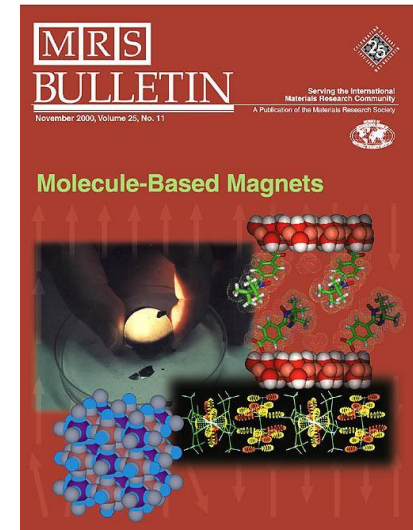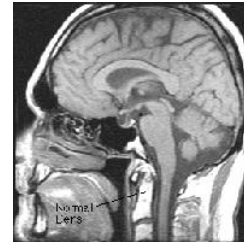
- Refinamento do grão
  - ↑ interação de troca
  - ↑ remanência

- Propriedades magnéticas
  - tamanho de grão
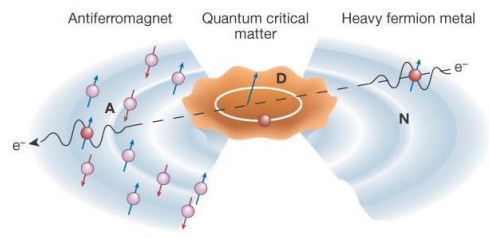 - fração volumétrica das fase

Nanocompósitos de NdFeB (ímãs nanoestruturados)

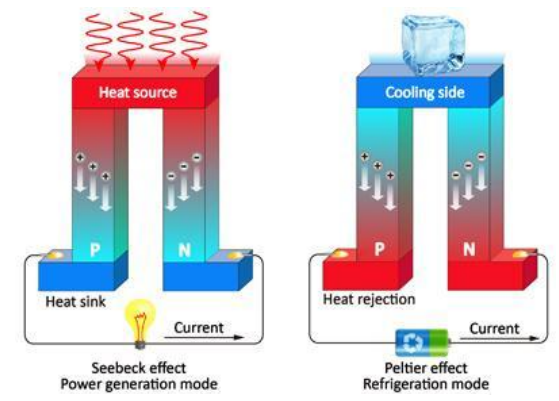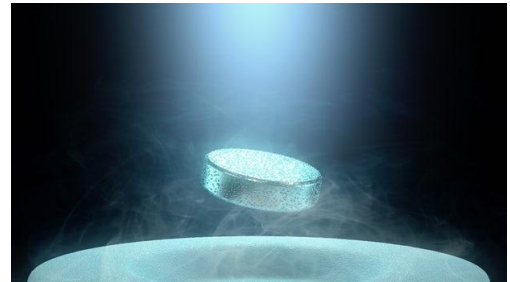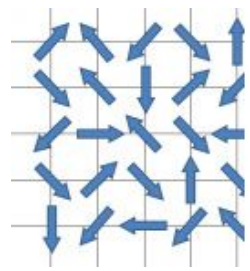Acoplamento de troca

Aumento da remanência
$M_r \approx 0.8M_S$

$Nd_4Fe_{78}B_{18}$

$Nd_2Fe_{14}B$
ISOTRÓPICO

d☐20nm

$Nd_2Fe_{14}B + \alpha\text{-Fe}$

$Nd_{15}Fe_{77}B_8$

M (10^2 emu/g)

$Nd_4Fe_{78}B_{18}$
$Nd_2Fe_{14}B$
$Nd_{15}Fe_{77}B_8$

Field (kOe)

Interactions

Electron → Heavy fermion

Heat source
Heat sink
Seebeck effect
Power generation mode

Cooling side
Heat rejection
Peltier effect
Refrigeration mode

Antiferromagnet   Quantum critical matter   Heavy fermion metal

https://chem.au.dk/forskning/forskningscentre/center-for-materials-crystallography/research/energy-materials/thermoelectrics/
https://www.nature.com/articles/nature032
79

Tabela Periódica dos Elementos

Original interface

Product Layer

Solid State Reactions

• Diffusion controlled: Fick's 1st Law

$$J=-D(dc/dx)$$

• Small particle sizes that are well mixed are needed to maximize the surface contact area.

• Tamman's Rule suggests a temperature of about two-thirds of the melting point (K) of the lower melting reactant is needed to have reaction to occur in a reasonable time.
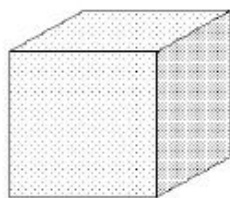
$A=6cm^2$
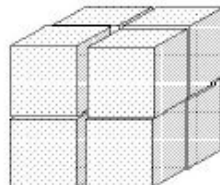
Pieces half the original size. Twice the surface area

$A=12cm^2$
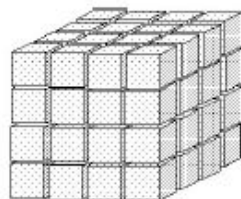
Pieces one quarter the original size. Four times the surface area

$A=24cm^2$
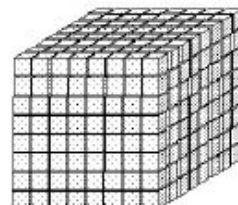
Pieces one eighth the original size. Eight times the surface area

$A=48cm^2$

•Thorough grinding is necessary to achieve a homogenous mixture of reactants.

•The number of crystallites in contact may be increased by pelletizing the powders using a hydraulic press.

•The reaction mixture is typically removed and reground to bring fresh surfaces in contact, which speeds up the reaction.

•Reaction times are sometimes hours, but may range into several days or weeks for a complete reaction, with intermediate grinding.

•Sample purity is typically examined using powder X-ray diffraction.

$$-\!\!\!\bigvee\!\!\!\bigvee\!\!\!\bigvee\!\!-$$
$$R$$

•Furnaces use resistance heating with metal, SiC, or $MoSi_2$ heating elements.

•Conversion of electrical energy into heat (to 2300 K). An electrical arc directed at the sample may achieve 3300 K. A CO_2 laser can give temperatures up to 4300 K.

•Containers for the reaction (crucibles) must be able to withstand high temperatures and be sufficiently inert to the reactants. Common crucibles are silica (to 1430 K), alumina (to 2200 K), zirconia (to 2300 K), or magnesia (2700 K). Platinum (m.p. 2045 K) and silver (m.p. 1235 K) are also used for some reactions.
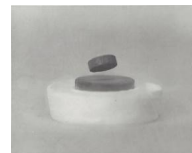
Synthesis of some compounds must be carried out under a special atmosphere.

• an noble gas, argon, may be used to prevent oxidation to higher oxidation state.

• an oxidizing gas, oxygen, might be used to form a high oxidation state.

• a reducing gas, hydrogen, might be used to form a low oxidation state.

Reactions usually take place in a small boat crucible placed in a tube in a horizontal tube furnace.

• Gas is passed of a period of time to expel all air from the apparatus, then continues to flow during the heating and cooling cycle. A bubbler is used to ensure positive pressure is maintained.
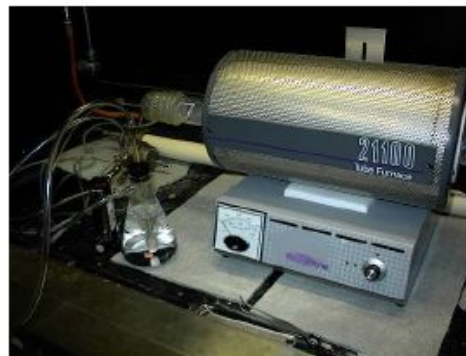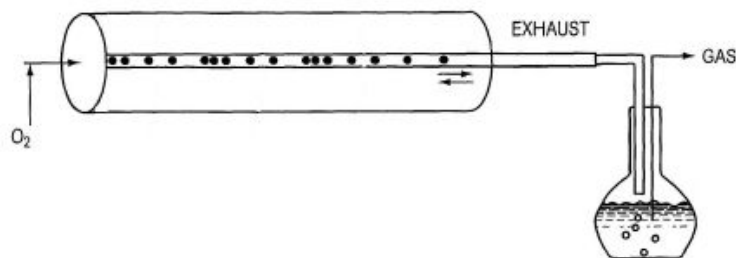
Microwave Synthesis

In a liquid or solid, the molecules of ions are not free to rotate.

The alternating electric field of the radiation:

1. If charged particles are present, these move under the influence of the field and produce an oscillating electric current. Resistance to the movement causes energy to be transferred to the surroundings as heat, known as conduction heating.

2. If no particles are present that can move freely, but molecules or units with dipole moments are present, then the electric field acts to align the dipole moments. This is dielectric heating. This is the type of heating that acts on water molecules in food.

The electric field of the microwave radiation is oscillating at the frequency of the radiation, but the electric dipoles in solids do not change their alignment instantaneously, but with a characteristic time, τ.

The oscillating electric field changes its direction rapidly so that the time between changes is much smaller than τ, then the dipoles cannot respond fast enough and do not realign (lags behind).

The solid absorbs some of the microwave radiation and the energy is converted to heat.

Depends on the dielectric constant and the dielectric loss.

To use microwave heating, at least one component of the reaction mixture must absorb microwave radiation.
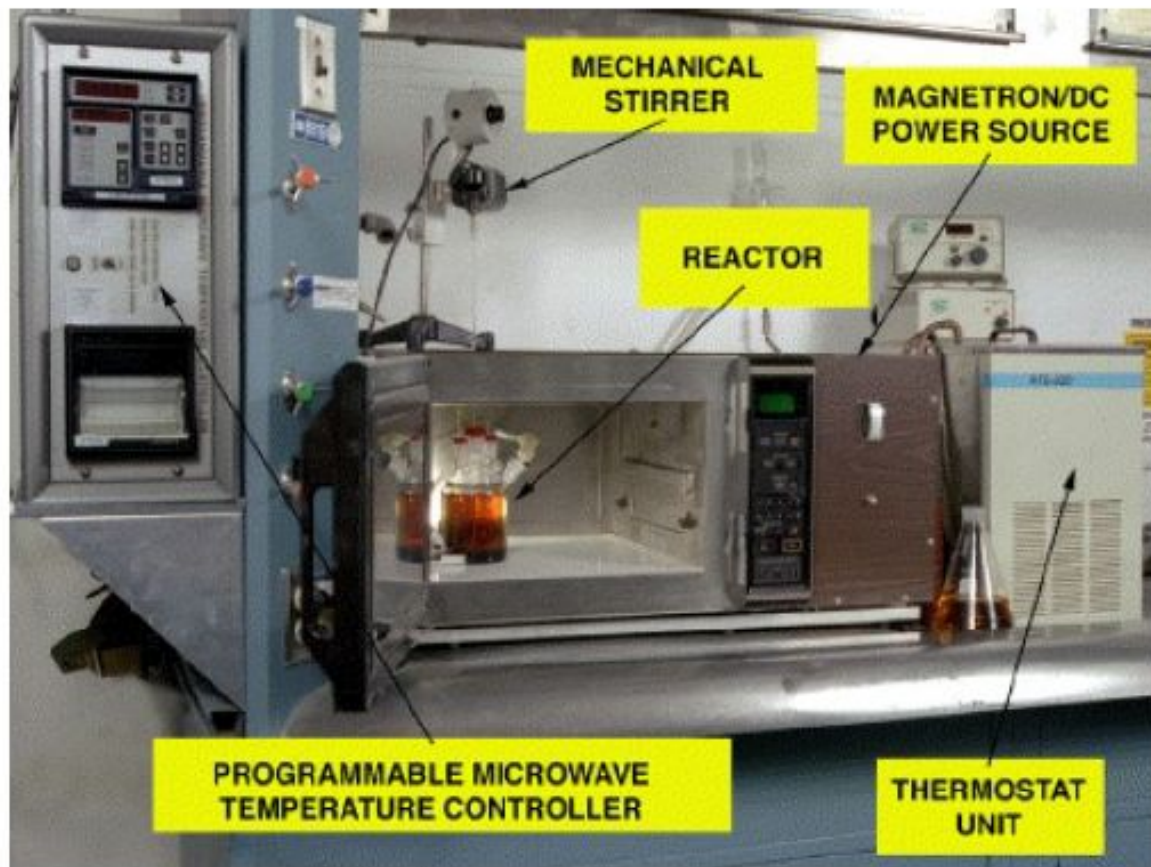
High Temperature Superconductor YBa$_2$Cu$_3$O$_{7-x}$

Conventional method takes about 24 hours to complete, whereas it takes approximately 2 hours using microwave synthesis.

• A stoichiometric mixture of CuO, Ba(NO$_3$)$_2$, Y$_2$O$_3$ are placed in a modified microwave oven that allows the safe removal of nitrogen oxides formed during the reaction.

• The reaction mixture is treated with 500 watts of microwave radiation for five minutes, then reground and exposed to microwave radiation between 130-500 watts for 15 minutes. The reaction mixture is ground again and exposed to microwave radiation for 25 minutes.

Microwave irradiation raises the temperature of the whole volume simultaneously (i.e. bulk heating).

b   Microwave   Oil bath
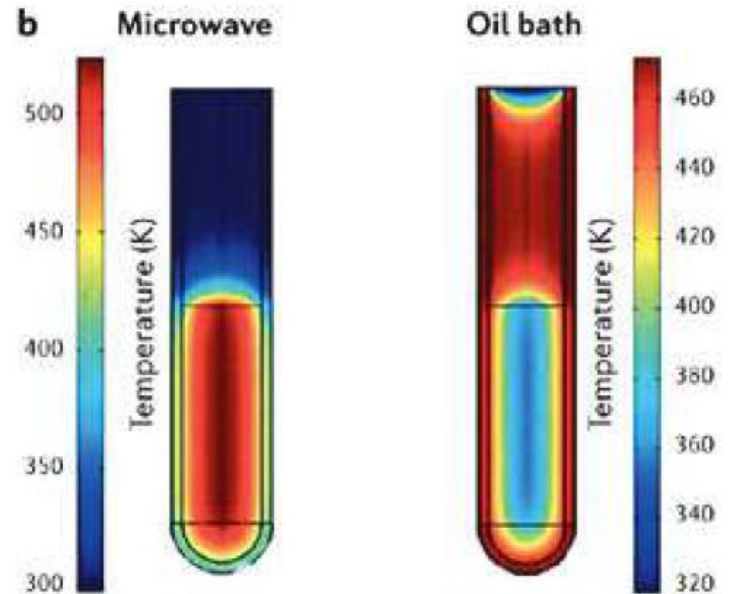
In CVT, a solid or solids interact with a volatile compound and a solid product is deposited in different part of the apparatus.

Powdered magnetite

Crystal

HCl gas

1270 K

1020 K
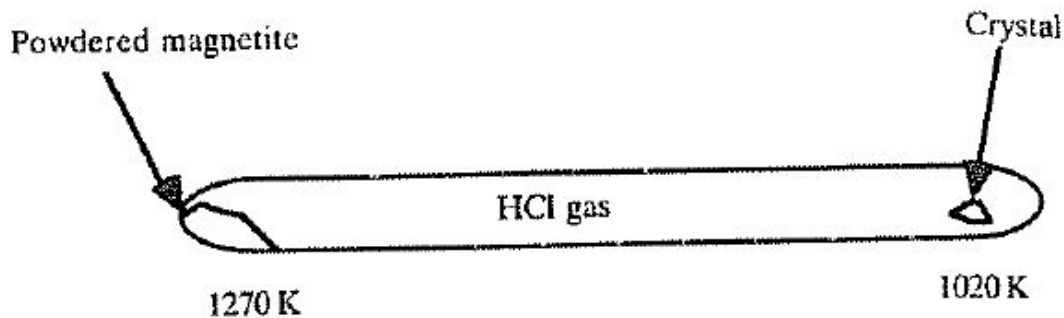
Growth of magnetite crystals using chemical vapour transport

$$Fe_3O_4(s) + 8HCl(g) \rightarrow FeCl_2(g) + 2FeCl_3(g) + 4H_2O(g)$$
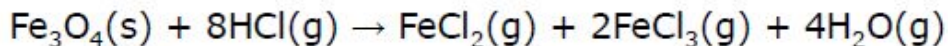
The reaction is endothermic, so the equilibrium moves to the right as the temperature is raised. A the cooler end of the tube, the equilibrium shifts to the left and magnetite is deposited.

Silicon for the electronics industry has to have low levels of impurities, less than one impurity atom in 10^{10} Si.

$SiHCl_3$ is highly volatile and distilled and decomposed as polycrystalline material onto rods of high purity silicon at 1300 K.

Large single crystals are made by the Czochralski process.

• The silicon is melted in an atmosphere of Ar, then a single crystal seed rod is used as a seed which is dipped into the melt.

• The crystal is slowly withdrawn, pulling an ever lengthening single crystal in the same orientation as the original seed.
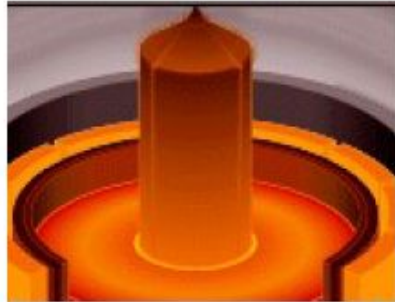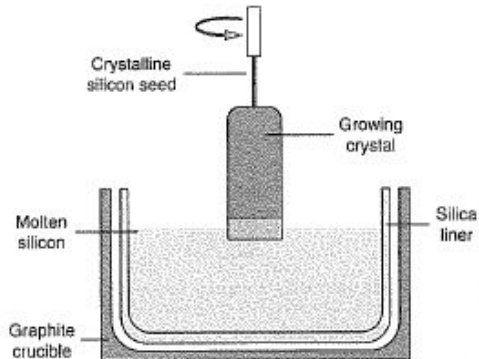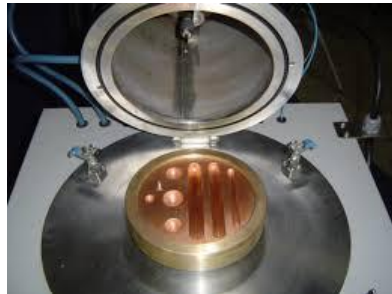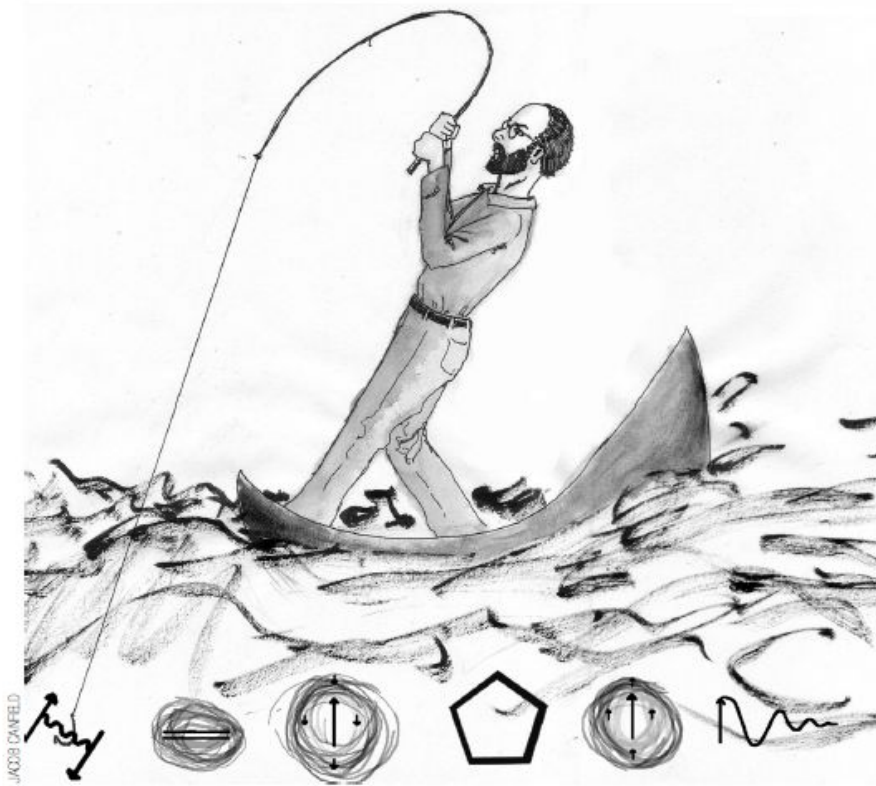
Growth of single crystals from metallic fluxes

By P. C. CANFIELD and Z. FISK

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Los Alamos, New Mexico 87545, USA

ABSTRACT

Our experience with the growth of a wide variety of intermetallic compounds from molten fluxes is reviewed. Common problems associated with this method of sample growth are discussed, as are problems and advantages of particular fluxes.

Desenhar e criar o sistema
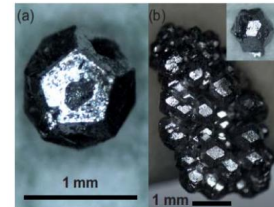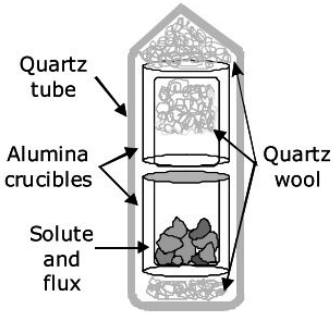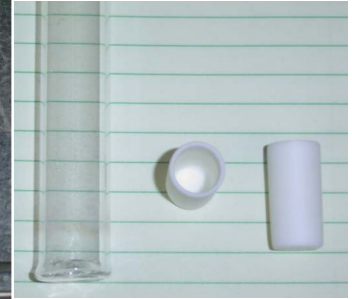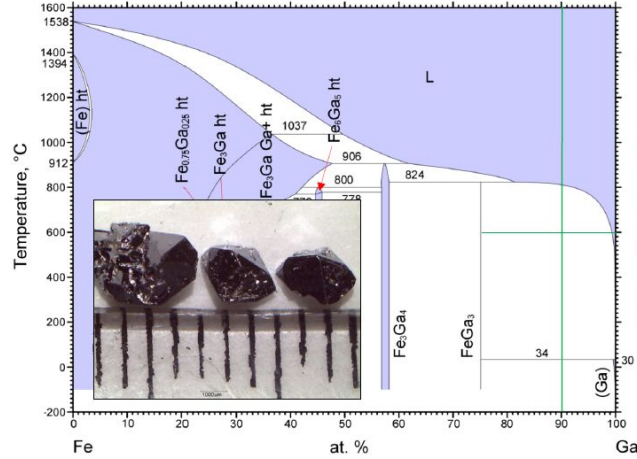
Zc-Zn
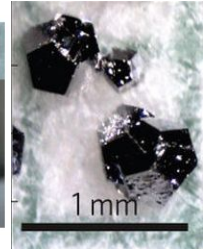
Gd-Cd

TbFe$_2$Ge$_2$ *

FeGa$_3$
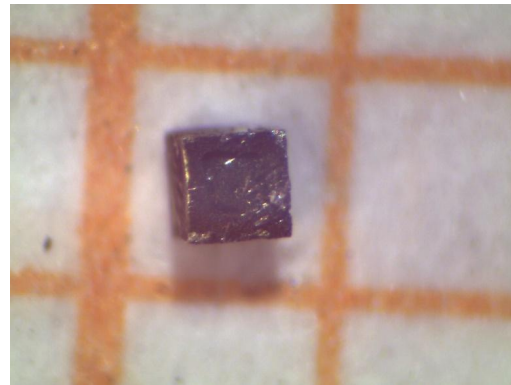
GdPb$_3$
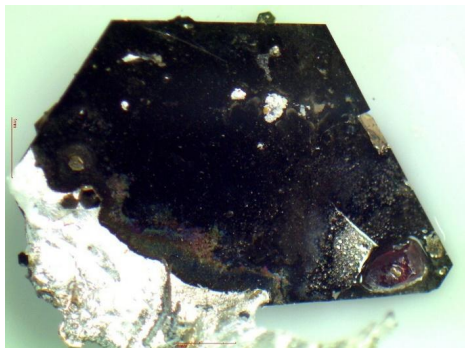
AlB$_2$
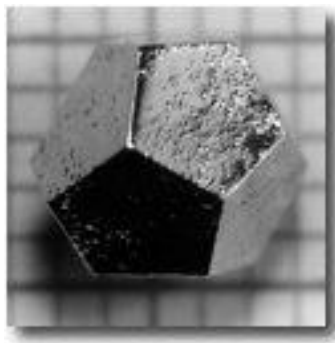
Ho-Mg-Zn *
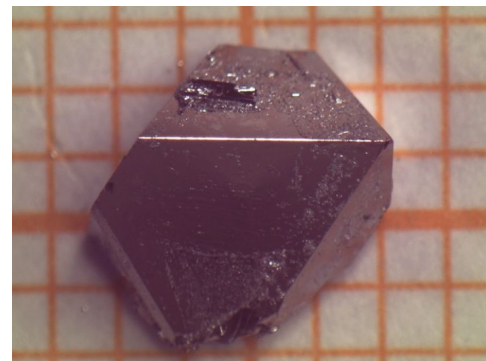
YbFe$_2$Zn$_{20}$

* Canfield´s

Rudolf L. MÖSSBAUER

discovers the "Recoilless Nuclear Resonance Absorption of γ-Radiation" in1958
and receives the Nobel Prize in 1961

R.L. Mössbauer made his first observation of recoilless nuclear resonant absorption in ^{191}Ir!

R.L. Mössbauer,
Z. Physik, 1958, 151, 124.
R.L. Mössbauer,
Naturwissenschaften, 1958, 45, 538

Mössbauer effect:

"Recoilless nuclear resonance absorption of γ-rays"

similar to

Acoustic resonance between two tuning forks with

same frequency $f_s = f_r$

f_S

f_E

Acoustic wave

$$f_s = f_r$$
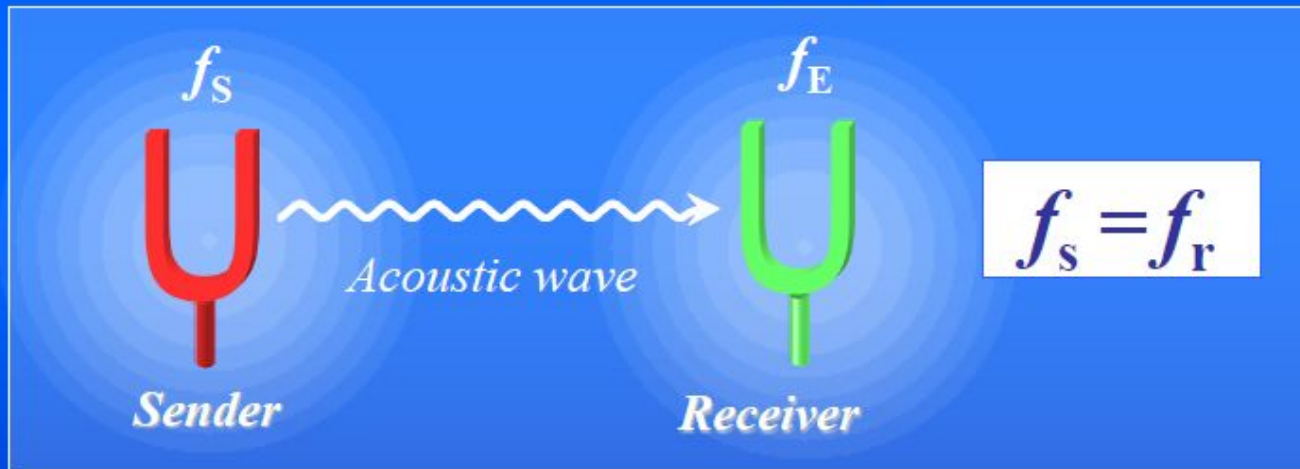
Sender

Receiver

Mössbauer effect: Atomic nuclei instead of tuning forks
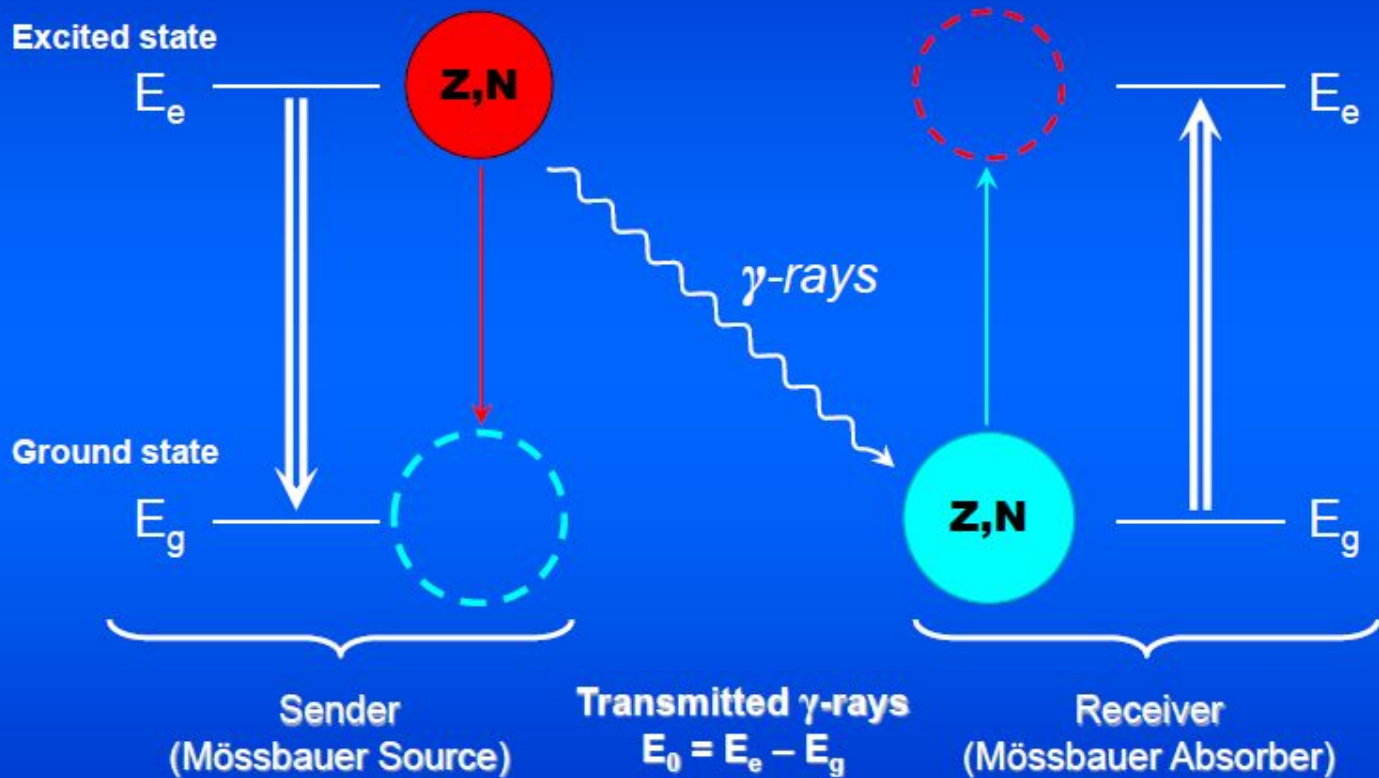
Important:
Elimination of recoil effect
upon emission and absorption of γ-rays!

E_R ✕ ← **Z, N** ∿∿∿∿∿∿→ **Z, N** ✕ → E_R

γ-rays

emitting atom

absorber atom

$$E_R = E_\gamma^2/2mc^2$$
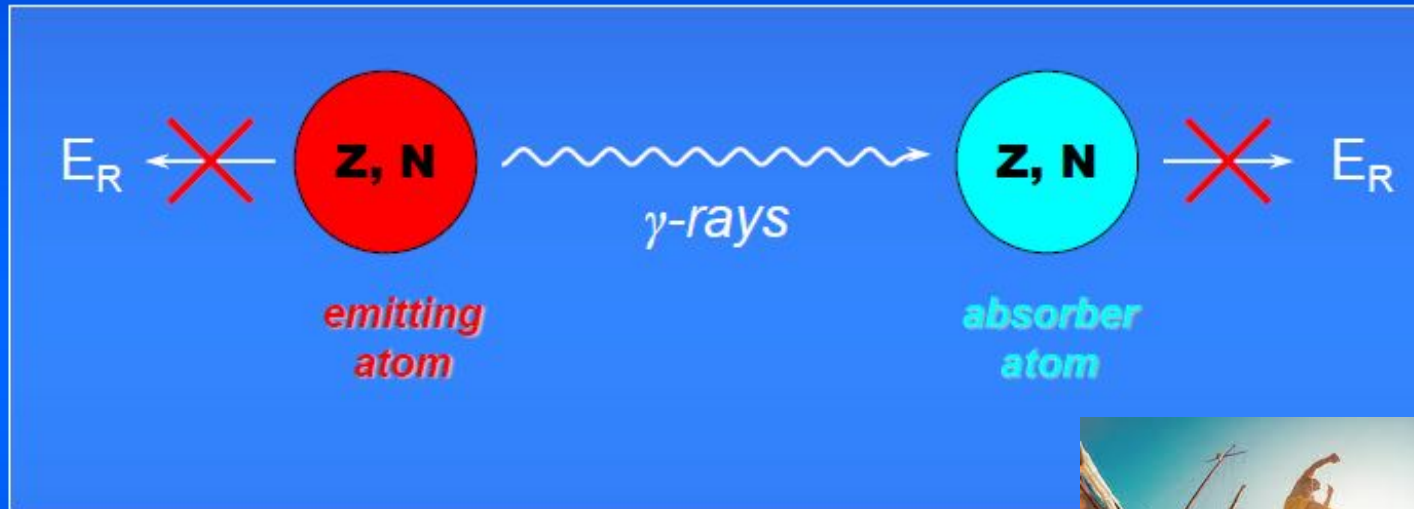
shutterstock.com · 701551372

Recoilless Nuclear Resonance Absorption and Fluorescence of γ-Radiation

Nucleus in Excited State

Nucleus in Ground State

Conversion electron

E_e

E_g

γ

e^- γ

γ-Emission

Resonance Absorption

Resonance Fluorescence
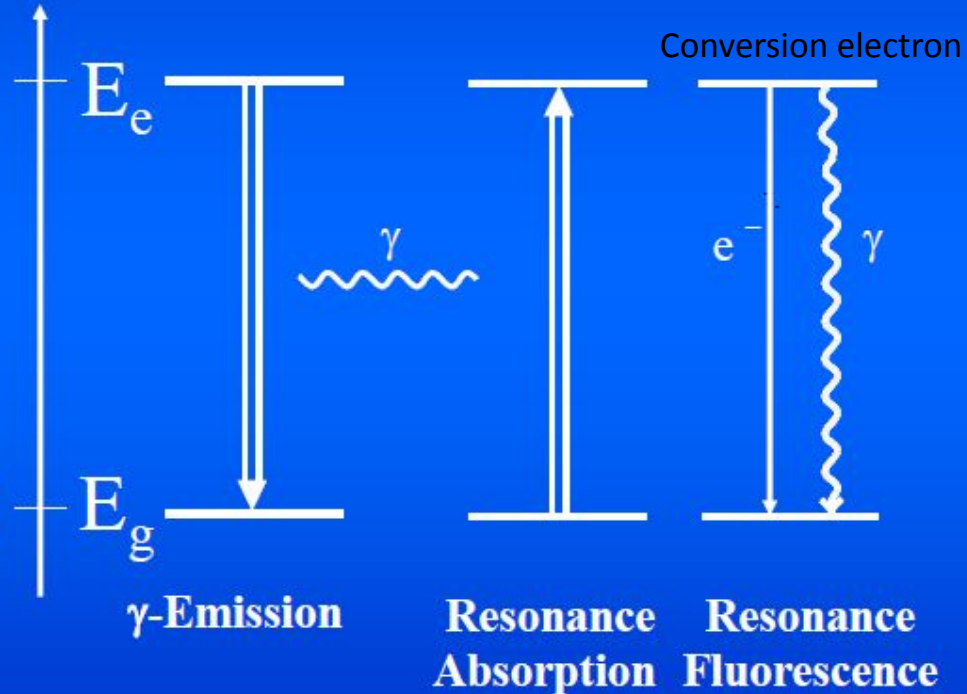
The preparation of narrow-line Mössbauer sources of ^{57}Co in metallic matrices

G. LONGWORTH and B. WINDOW

Materials Physics Division, AERE, Harwell, Berks

Abstract.   The merits of various cubic matrices for the preparation of high-activity small-area sources of ^{57}Co are discussed.   The useful areal density of activity is limited to about $150 \, \mathrm{mCi \, cm^{-2}}$ for all matrices owing to resonance broadening, and the thickness of the source foil is determined by self absorption and the generation of fluorescence x rays.   Electrostatic broadening and the change of isomer shift with age are shown to be relatively unimportant for sources of the above density of activity on chromium, rhodium and palladium.   Rhodium is the best choice for a strong, unsplit source for use at $4 \cdot 2 \, \mathrm{K}$.   Methods of preparation which give linewidths close to natural linewidths are discussed.
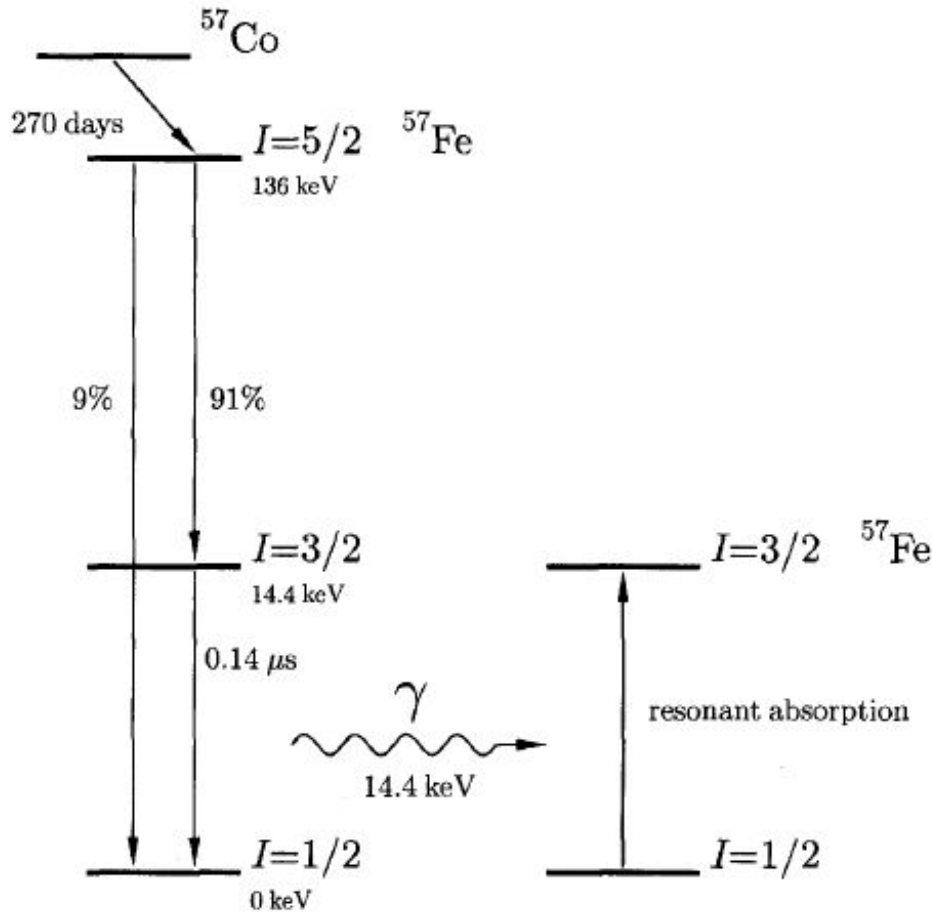
Radioactive 57Co with 270 days halflife, which may be generated in a cyclotron and diffused into a noble metal like rhodium, serves as the gamma radiation source for 57Fe Mössbauer spectroscopy. 57Co decays by electron capture (EC from K-shell, thereby reducing the proton number, from 27 to 26 corresponding to 57Fe) and initially populates the 136 keV nuclear level of 57Fe with nuclear spin quantum number I = 5/2. This excited state decays after ca. 10 ns and populates, with 85 % probability the 14.4 keV level by emitting 122 keV gamma quanta, with 15 % probability the 136 keV level decays directly to the ground state of 57Fe. The 14.4 keV nuclear state has a halflife of ca. 100 ns. Both the halflife and the emitted gamma quanta of 14.4 keV energy are ideally suited for 57Fe Mössbauer spectroscopy.

Nuclear parameters for selected Mössbauer isotopes

Isotope	E_γ/keV	Γ_r/(mm s^{-1}) = 2 Γ_{nat}	I_g	I_e	α	Natural abundance %	Nuclear decay*
^{57}Fe	14.41	0.192	1/2−	3/2−	8.17	2.17	^{57}Co(EC 270 d)
^{61}Ni	67.40	0.78	3/2−	5/2−	0.12	1.25	^{61}Co(β−99 m)
^{119}Sn	23.87	0.626	1/2+	3/2+	5.12	8.58	^{119m}Sn(IT 50 d)
^{121}Sb	37.15	2.1	5/2+	7/2+	~10	57.25	^{121m}Sn(β−76 y)
^{125}Te	35.48	5.02	1/2+	3/2+	12.7	6.99	^{125}I(EC 60d)
^{127}I	57.60	2.54	5/2+	7/2+	3.70	100	^{127m}Te (β−109 d)
^{129}I	27.72	0.59	7/2+	5/2+	5.3	nil	^{129m}Te (β−33 d)
^{149}Sm	22.5	1.60	7/2−	5/2−	~12	13.9	^{149}Eu(EC 106 d)
^{151}Eu	21.6	1.44	5/2+	7/2+	29	47.8	^{151}Gd(EC 120 d)
^{161}Dy	25.65	0.37	5/2+	5/2−	~2.5	18.88	^{161}Tb(β−6.9 d)
^{193}Ir	73.0	0.60	3/2+	1/2+	~6	61.5	^{193}Os(β−31 h)
^{197}Au	77.34	1.87	3/2+	1/2+	4.0	100	^{197}Pt(β−18 h)
^{237}Np	59.54	0.067	5/2+	5/2−	1.06	nil	^{241}Am(α458 y)

*EC = electron capture, β− = beta-decay, IT = isomeric transition, α − alpha-decay

Mean lifetime τ of excited state and natural line width Γ

An excited state (nuclear or electronic) of mean lifetime τ can never be assigned a sharp energy value, but only a value within the energy range ΔE, which correlates with the uncertainty in time Δt via the **Heisenberg Uncertainty Principle:** $\Delta E \Delta t \geq \hbar$. Weisskopf and Wigner have shown that in general $\Gamma \cdot \tau = \hbar$.

$$\Gamma = \hbar/\tau = \textbf{natural line width,}\ \hbar = h/2\pi\ \text{Planck's constant}$$
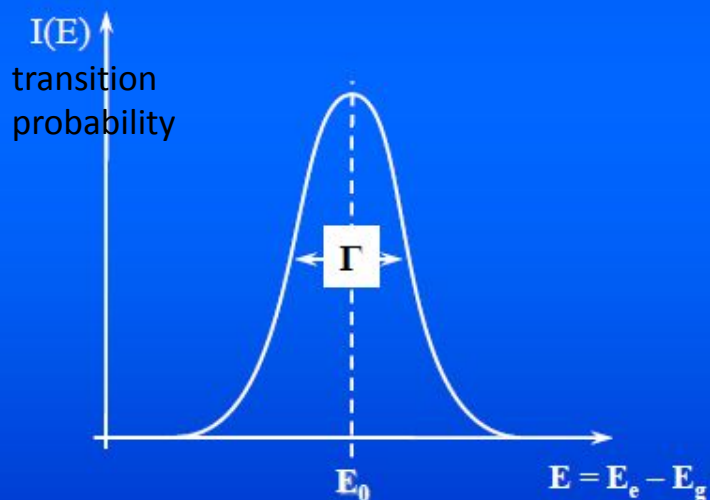
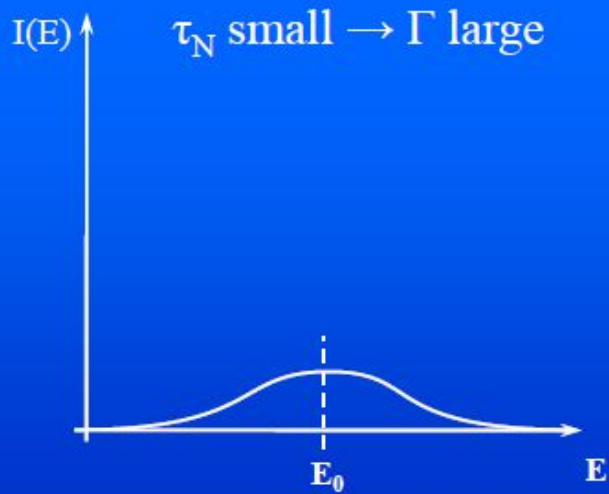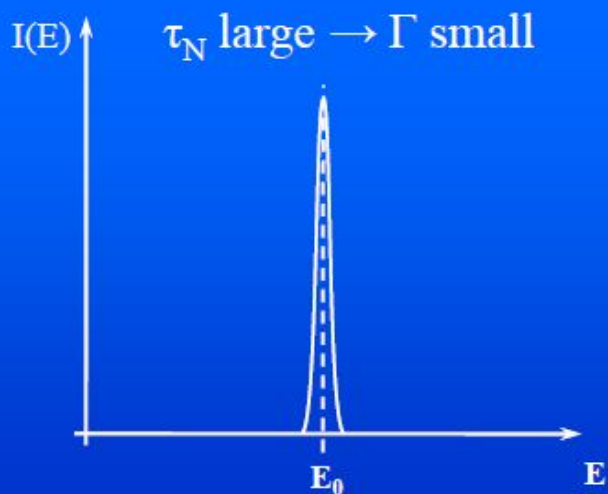Intensity as function of transition energy E of nuclear (or optical) transitions.
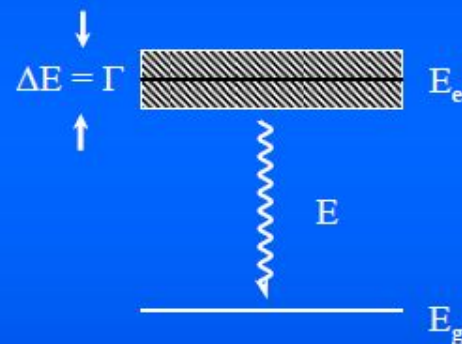
Transitions from an excited state (e) to the ground state (g) or vice versa involve all possible energies within the range of ΔE. The transition probability or intensity as a function of E yields a spectral line centered around the most probable transition energy E_0.

According to Weisskopf and Wigner the distribution of energies about the energy E_0 (= transition probability as function of transition energy E) is given by the **Breit-Wigner (or Lorentzian) formula**:

$$I(E) = \frac{(\Gamma/2)^2}{(E - E_0)^2 + (\Gamma/2)^2}$$

The mean lifetime τ determines the width of the resonance lines ($\Gamma \cdot \tau = \hbar$).
The mean lifetime τ is related to the halflife $t_{1/2}$ by the relation $\tau = \ln 2 \cdot t_{1/2}$.

$I(E)$ τ_N large $\rightarrow \Gamma$ small E_0 E

$I(E)$ τ_N small $\rightarrow \Gamma$ large E_0 E
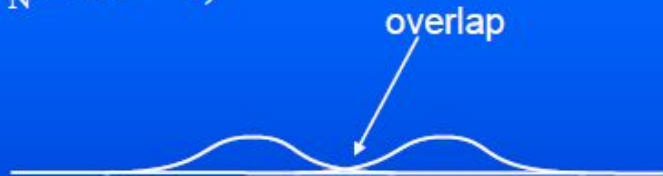
Resonance absorption is observable only if the emission and absorption lines **overlap sufficiently**. This is not the case when the lines are:

- too narrow ($\tau_N \geq 10^{-6}$ s)

overlap

- too broad ($\tau_N \leq 10^{-11}$ s)

overlap
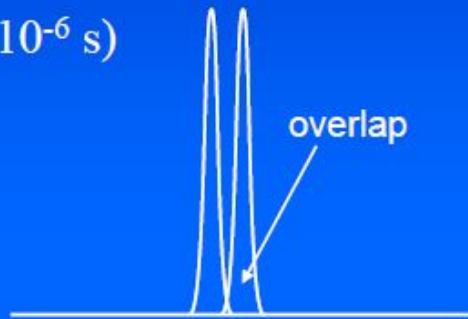
Resonance absorption is "hidden in the noise"

Suitable for Mössbauer spectroscopy: 10^{-6} s $\geq \tau_N \geq 10^{-11}$ s

Recoil Effect

By emission or absorption of γ-quanta with energy E_γ in a **free atom or molecule** (gas, liquid) the atom (molecule) of mass **m** suffers a recoil effect with energy E_R given by the equation

$$E_R = E_\gamma^2/2mc^2$$

which is much larger (5-6 orders of magnitude) than the natural line width $\Gamma \rightarrow$ <u>no resonance possible between free atoms or molecules</u>

Freely emitting atom of mass m
(at rest)

recoil

γ-quantum

$E_R = E_\gamma^2/2mc^2$

$E_\gamma = E_0 - E_R$
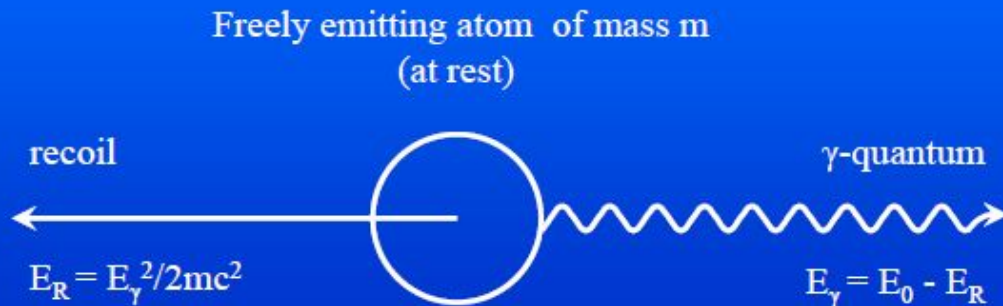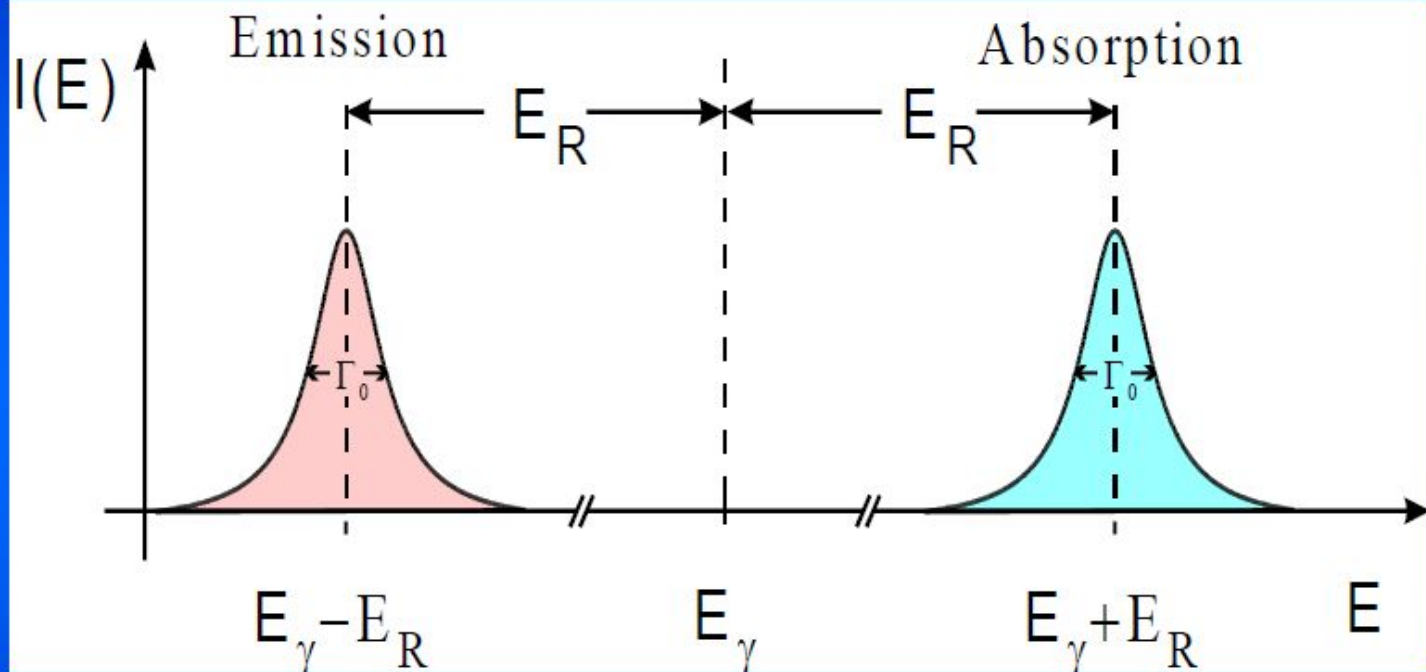
Free-atom Recoil and Thermal Broadening

We consider the emission of a γ-quantum of initial energy E_0 from an atom with mass m moving with velocity v_N in the direction of the γ-ray propagation.

Before emission:
$$E_0 + \frac{1}{2} m v_N^2$$

After emission:
$$E_\gamma + \frac{1}{2} m (v_N + v_R)^2 \qquad v_R = \text{velocity due to recoil}$$
$$\text{(opposite to } v_N)$$

Conservation of energy:
$$E_0 + \frac{1}{2} m v_N^2 = E_\gamma + \frac{1}{2} m (v_N + v_R)^2$$

Difference between nuclear transition energies before and after emission:
$$\delta E = E_0 - E_\gamma = \underbrace{\frac{1}{2} m v_R^2}_{\substack{\text{Recoil} \\ \text{energy } E_R}} + \underbrace{m v_N v_R}_{\substack{\text{Doppler} \\ \text{energy } E_D}}$$

Mössbauer-Experiment
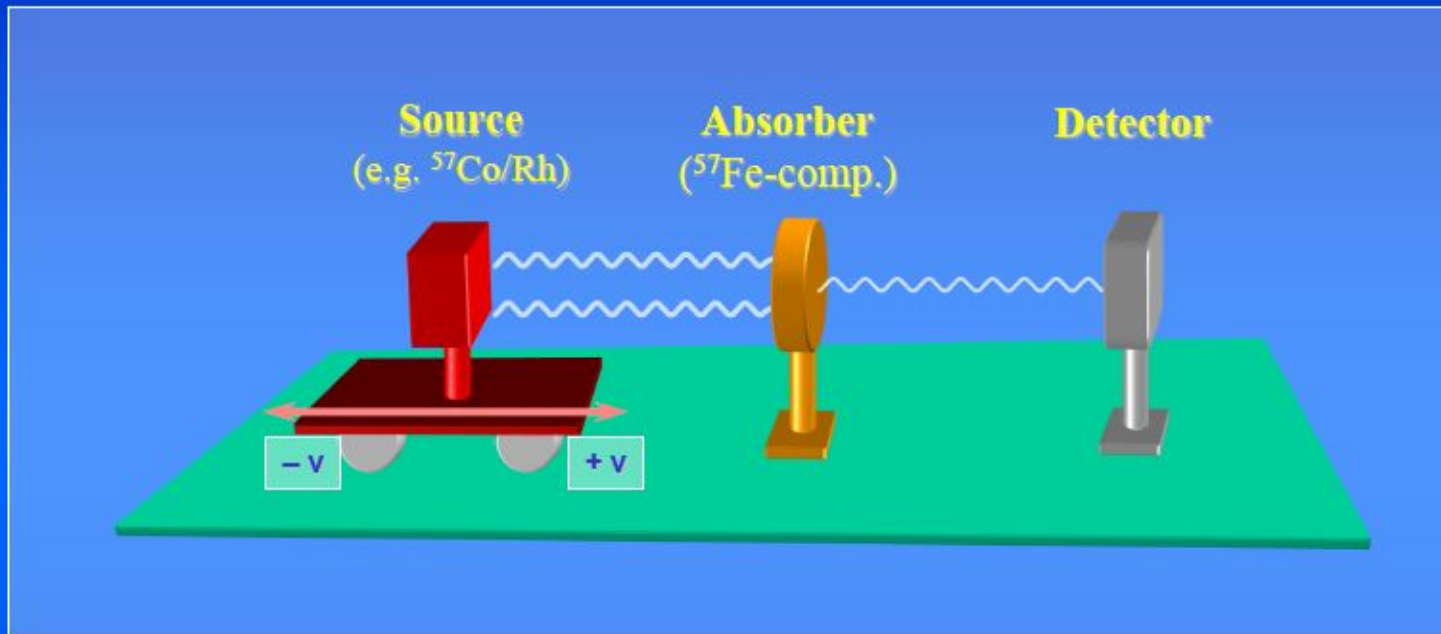
Source and absorber are moved relative to each other with

Doppler velocity $v = c \, (\Gamma_0/E_\gamma)$

c = velocity of light

^{57}Fe : $\Gamma_0 = 4.7 \cdot 10^{-9}$ eV, $E_\gamma = 14400$ eV, $v = 0.096$ mm s^{-1}

Hyperfine Interactions between Nuclei and Electrons and Mössbauer Parameters

— **Electric Monopole Interaction**

$\Rightarrow$ **Isomer Shift δ**

— **Electric Quadrupole Interaction**

$\Rightarrow$ **Quadrupole Splitting ΔE_Q**

— **Magnetic Dipole Interaction**

$\Rightarrow$ **Magnetic Splitting ΔE_M**

Hyperfine Interactions and Mössbauer Parameters

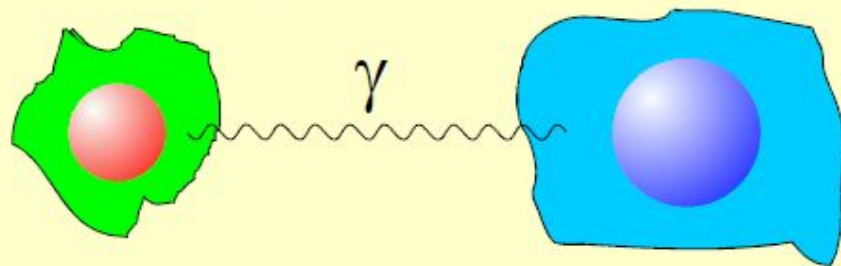| Mössbauer Parameter	Type of Interaction	Information for Chemistry
Isomer Shift δ (mm/sec)	Electric Monopole (Coulombic) interaction between nucleus (protons) and electrons	Oxidation state Electronegativity of ligands Character of bonds Spin state (HS, IS, LS)
Quadruple splitting ΔE_Q (mm/sec)	Electric quadrupole interaction between nuclear qudrupole moment and inhomogeneous electric field	Molecular symmetry Oxidation state Character of bonds Spin state (HS, IS, LS)
Magnetic splitting ΔE_M (mm/sec)	Magnetic dipole interaction between nuclear magnetic dipole moment and magnetic field	Magnetic interactions e.g. ferromagnetism, antiferromagnetism

Conditions for Hyperfine Interactions

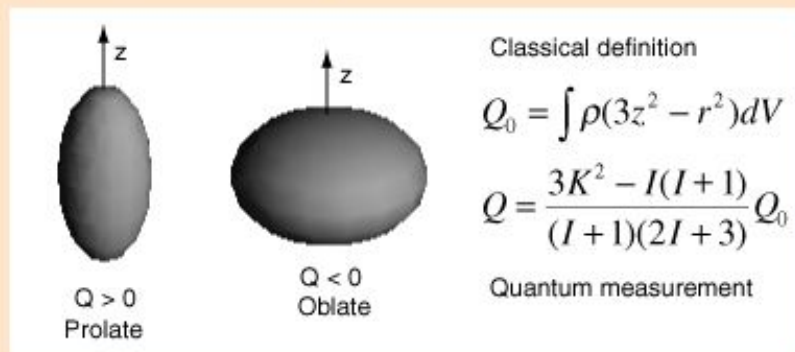| Type of Interaction	Nuclear Condition	Electronic Condition	Consequence
Electric Monopole interaction	$R_e^2 \neq R_g^2$	$\|\Psi(0)\|_A^2 \neq \|\Psi(0)\|_S^2$	Different shift of nuclear levels $\Rightarrow$ **Isomer shift δ**
Electric Quadrupole interaction	Electric quadrupole moment $eQ \neq 0$ $(I > \frac{1}{2})$	$EFG \neq 0$	Nuclear states split into $I + \frac{1}{2}$ substates $\|I, \pm m_I>$ (twofold degenerate) $\Rightarrow$ **Quadrupole Splitting ΔE_Q**
Magnetic dipole interaction	Magn. dipole moment $\mu \neq 0$ $(I > 0)$	$H \neq 0$	Nuclear states $\|I>$ split into $2I+1$ substates $\|I, m_I>$ with $m_I = +I, +I-1, \ldots, -I$ $\Rightarrow$ **Magnetic dipole splitting ΔE_M**

$E_A - E_S = \delta$

Oxidation state
Spin state
Bond properties
Covalency
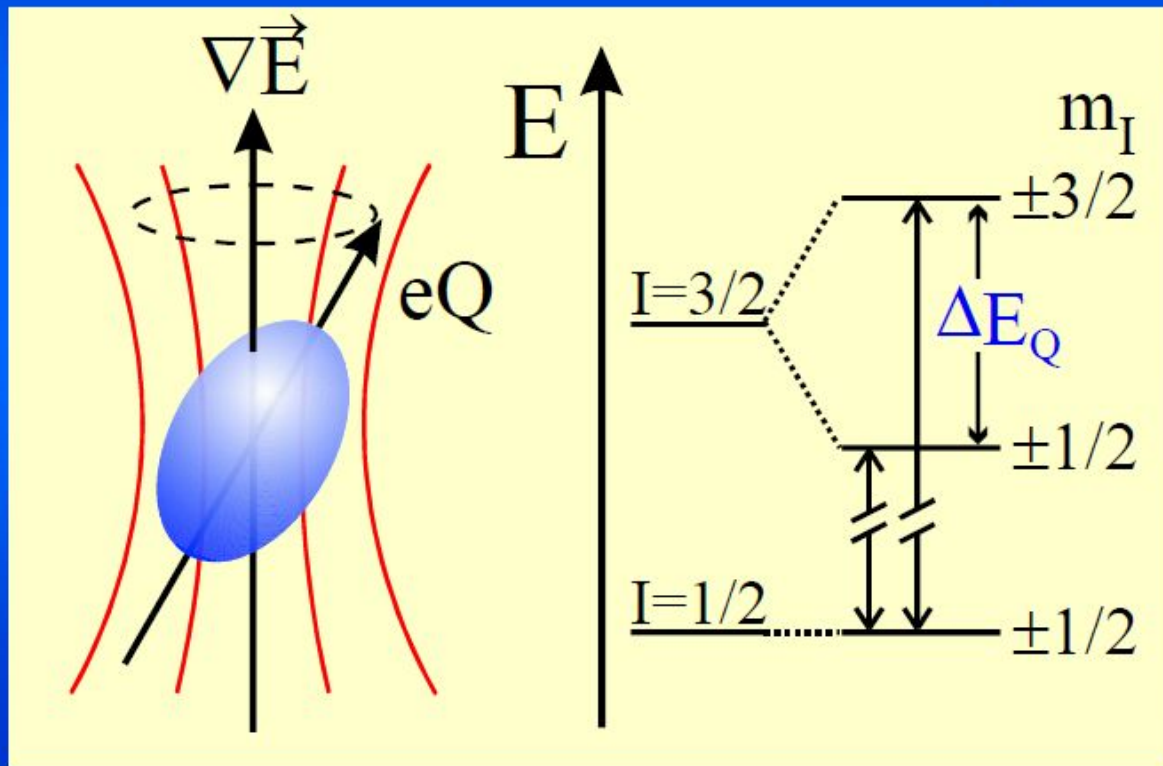**Electronegativity**

Electric Quadrupole Moments of Nuclei

The nuclear electric quadrupole moment is a parameter which describes the effective shape of the ellipsoid of nuclear charge distribution. A non-zero quadrupole moment Q indicates that the charge distribution is not spherically symmetric. By convention, the value of Q is taken to be positive if the ellipsoid is prolate and negative if it is oblate.

Classical definition

$$Q_0 = \int \rho(3z^2 - r^2)dV$$

$$Q = \frac{3K^2 - I(I+1)}{(I+1)(2I+3)}Q_0$$

Quantum measurement

Q > 0
Prolate

Q < 0
Oblate

The quantity Q_0 is the classical form of the calculation represents the departure from spherical symmetry in the rest frame of the nucleus. The expression for Q is the quantum mechanical form which takes takes into account the nuclear spin I and the projection K in the z-direction.
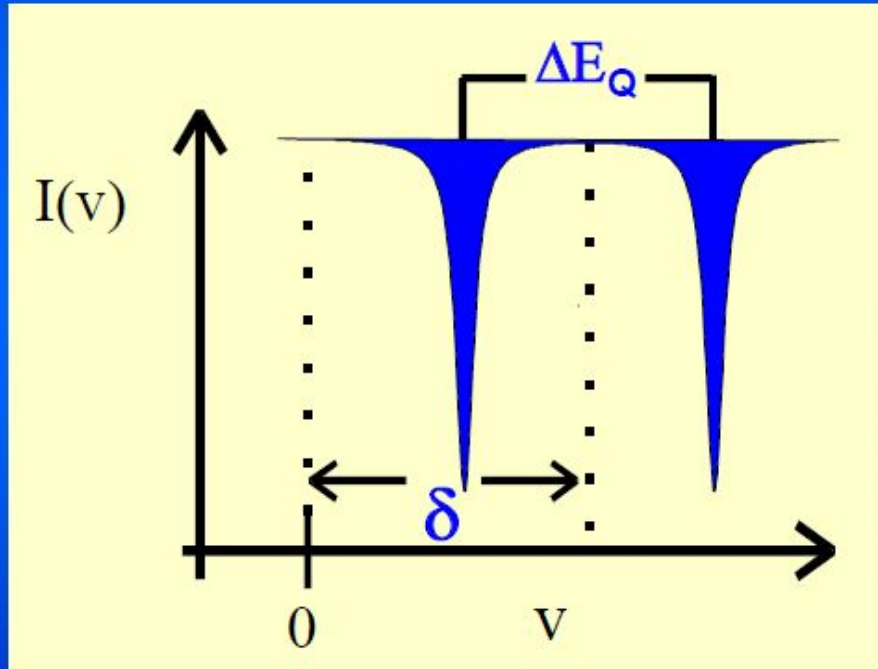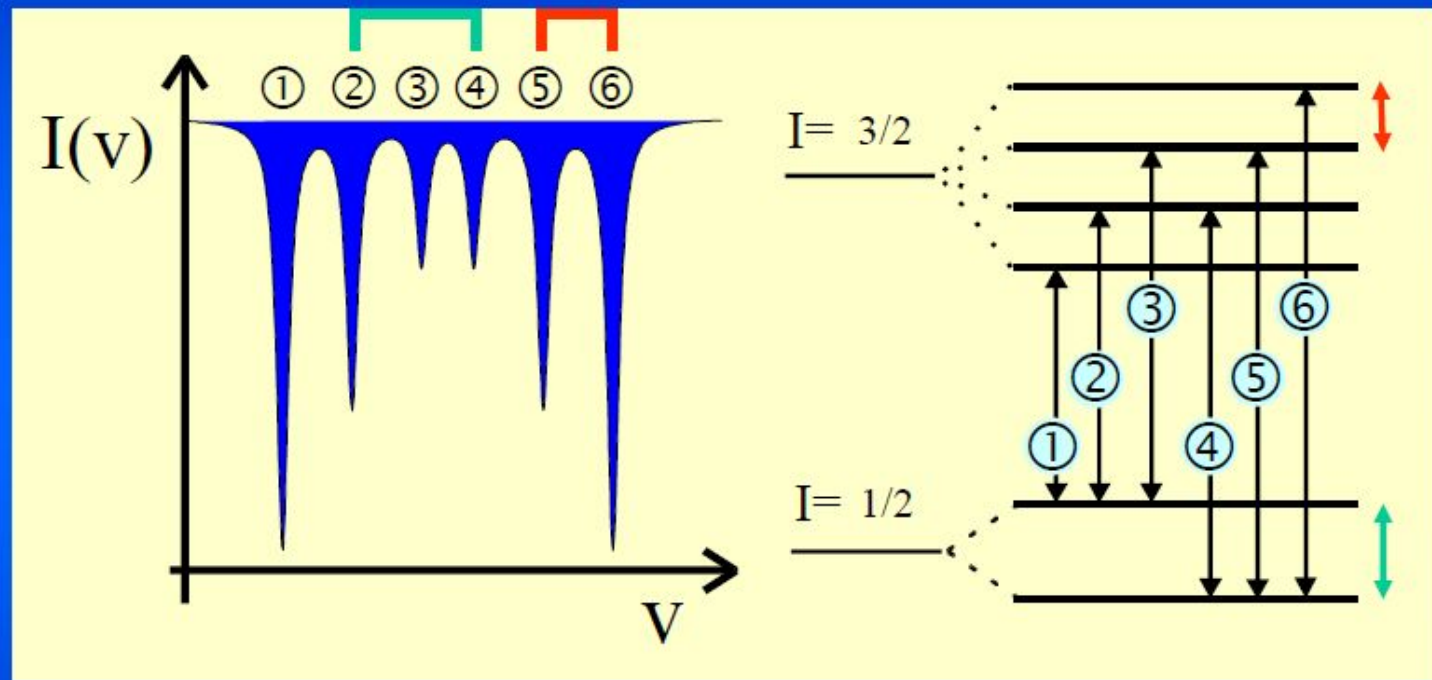
Electric Quadrupole Interaction
Quadrupole Splitting ΔE_Q

$$E_M(m_I) = -\mu H m_I / I$$

Ferro-, Antiferro-, Ferri -magnetism

Pure magnetic dipole interaction

Magnetic dipole interaction (Zeeman effect) is described by the Hamiltonian

$$\hat{H}_M = -\hat{\vec{\mu}} \cdot \hat{\vec{H}} = -g_N \beta_N \hat{\vec{I}} \cdot \vec{H}$$

g_N: nuclear Landé-factor

$\beta_N = e\hbar/2Mc$ nuclear Bohr magneton

If $\vec{H} \parallel \vec{z}$:

$$\hat{H}_M = -g_N \beta_N H \hat{I}_z$$

First order perturbation theory yields the matrix (elements) equations:

$$\left\| \left\langle I, m'_I \left| \hat{H}_M \right| I, m_I \right\rangle - E_M \delta m'_I m_I \right\| = 0 \quad \text{with eigenvalues} \quad \mathbf{E_M(I, m_I) = - g_N \beta_N H m_I}$$
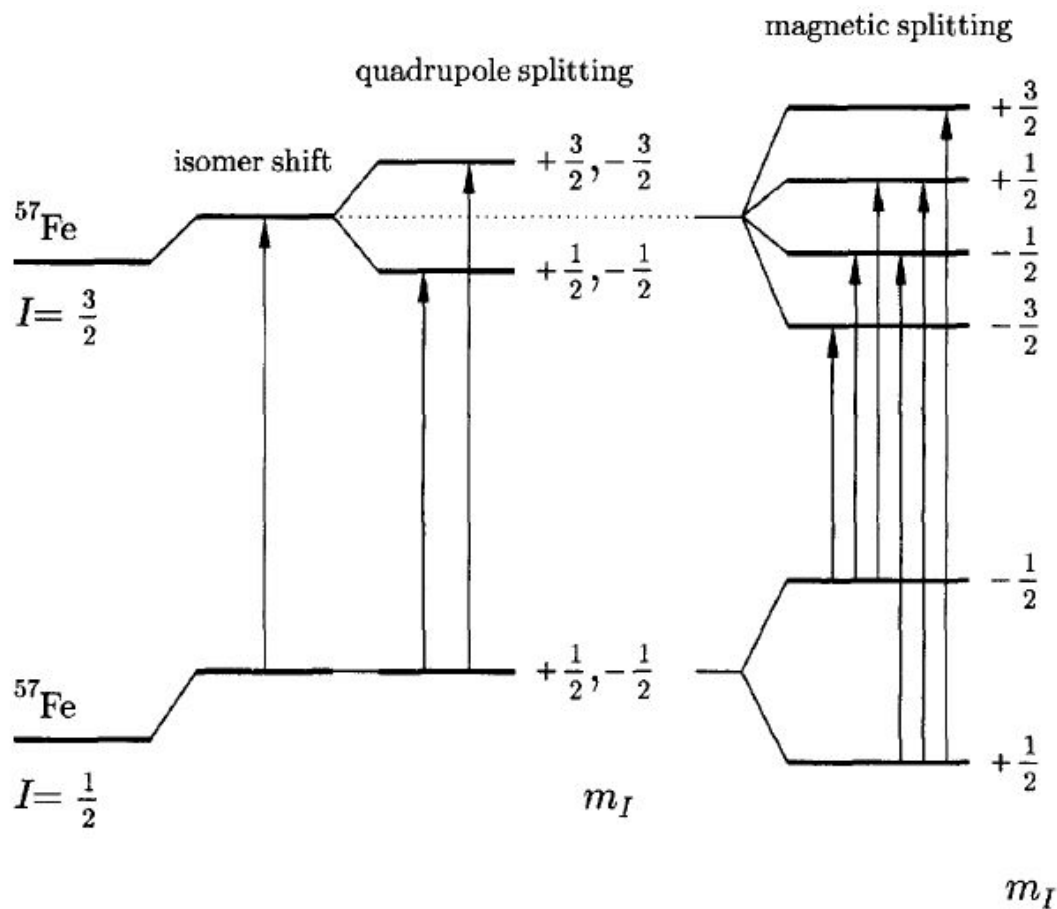
Fig. 3.20 The effects of chemical shift, quadrupole splitting and magnetic splitting on the nuclear energy levels of ^{57}Fe. The arrows show the Mössbauer absorption transitions. The difference in the size of the transitions is greatly exaggerated; in reality they typically differ from each other by less than 1 part in 10^{11}.
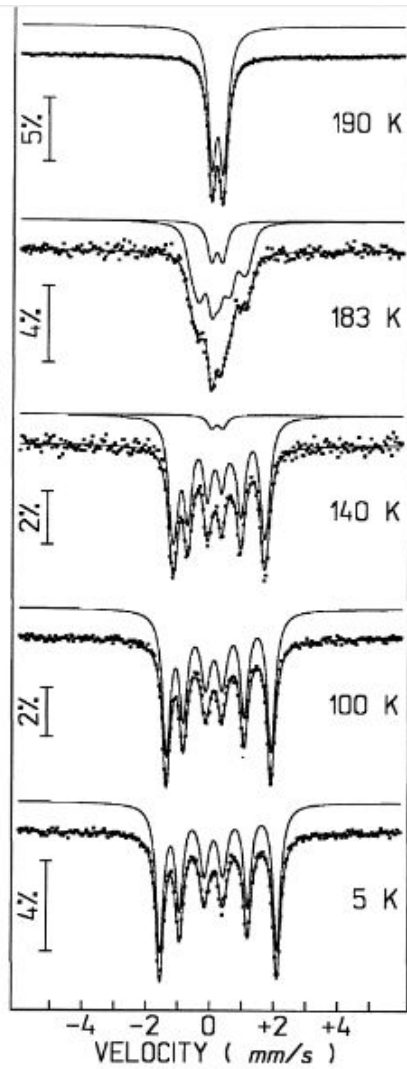
^{57}Fe Mössbauer spectroscopy study of the AFe$_x$Al$_{12-x}$ intermetallics (A=Y, Tm, Lu and U, $4 \leq x \leq 4.3$)

J.C. Waerenborgh[a],*, P. Salamakha[a], O. Sologub[a], A.P. Gonçalves[a], S. Sério[b], M. Godinho[b], M. Almeida[a]

[a]Departamento de Química, Instituto Tecnológico e Nuclear, P-2686-953 Sacavém, Portugal
[b]Departamento de Física, Faculdade de Ciências da Universidade de Lisboa, P-1749-016 Lisboa, Portugal

MB

The Mössbauer Spectrometer on the Mars Exploration Rovers, Spirit and Opportunity, is known as MB. The MB determines the makeup and quantities of iron-bearing minerals in geological samples studied by the rover. MB can be placed right up to rock and soil samples for close-up study, and it also examines magnetic dust samples
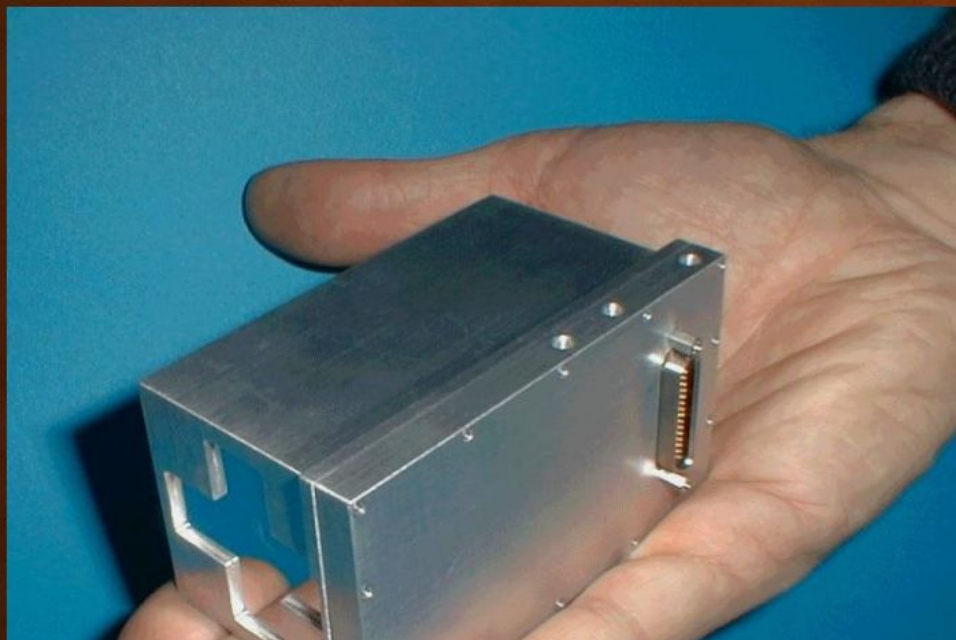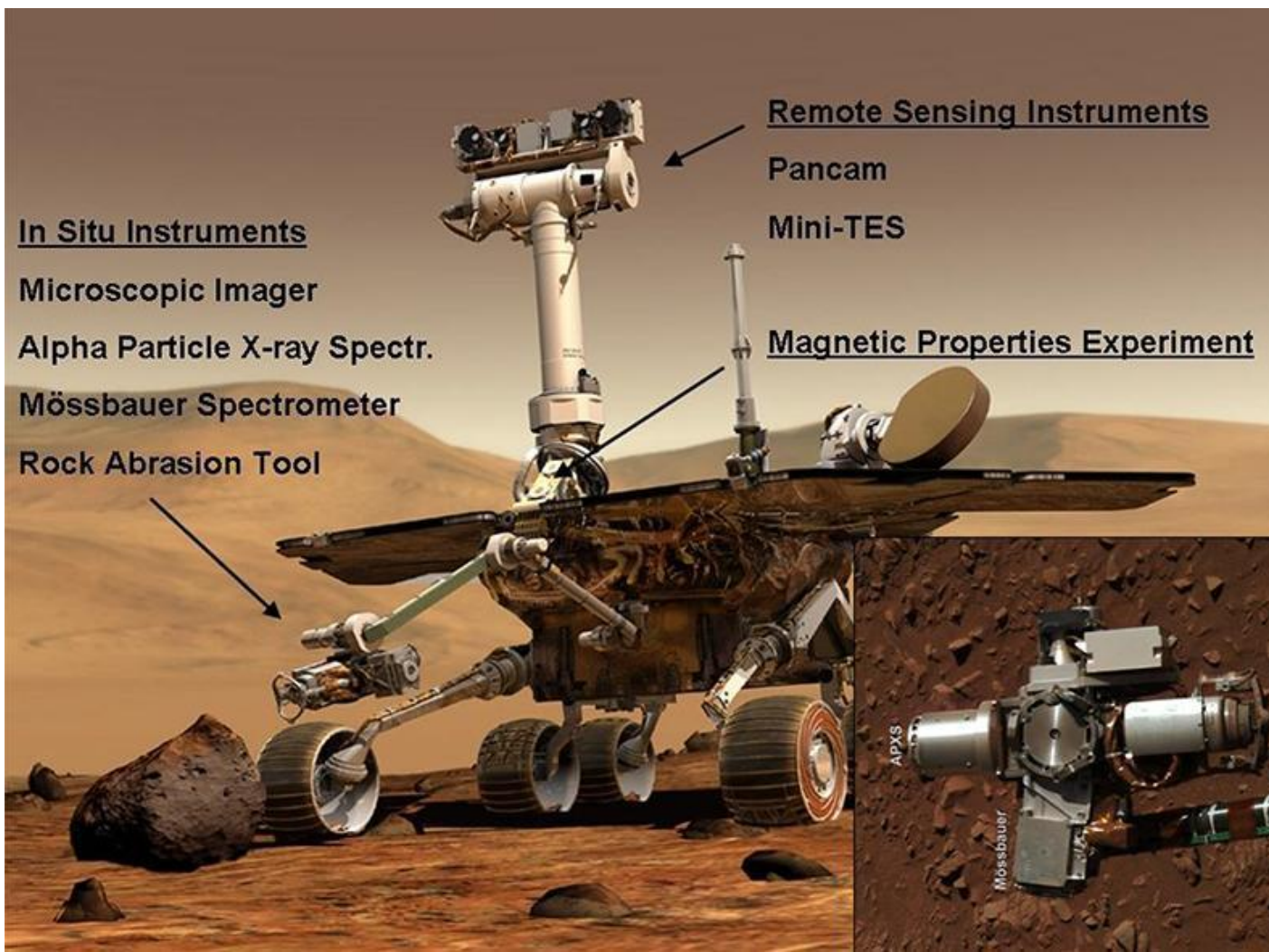
Propriedades Magnéticas

Propriedades Magnéticas