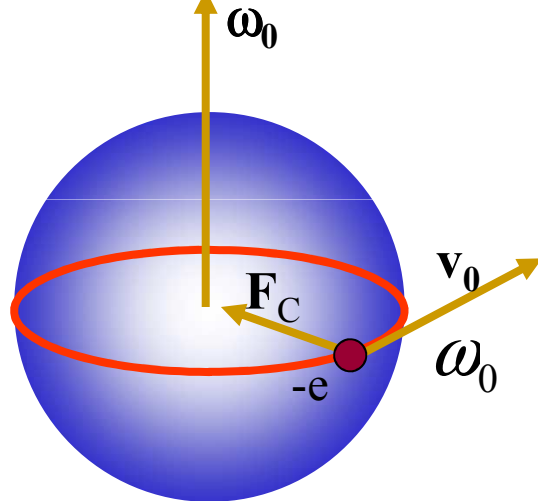


Diamagnetismo y paramagnetismo

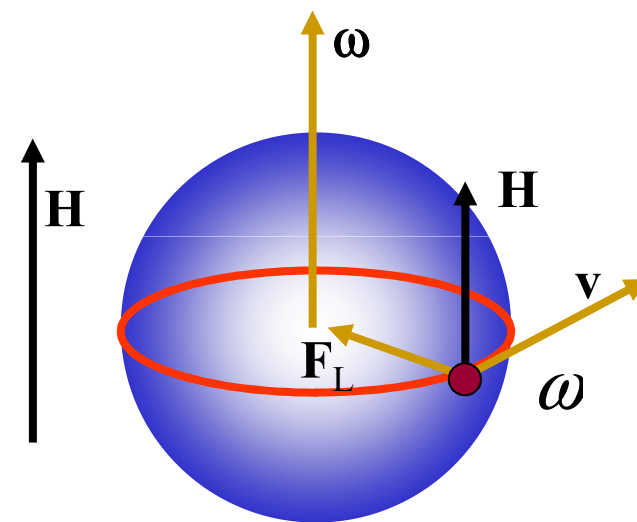
Diamagnetismo – enfoque clásico

En ausencia de campo magnético



$$F_C = F_e = eE(r)$$

En presencia de campo magnético

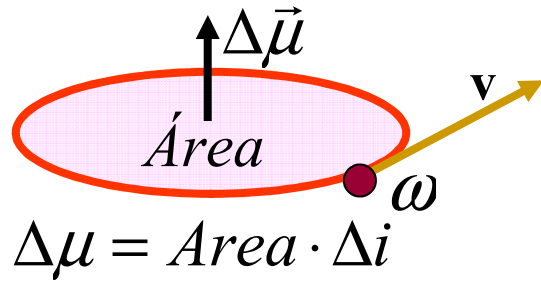


$$\vec{F}_L = -e\vec{v} \times \vec{B} \Rightarrow F_L = -\mu_0 evH$$

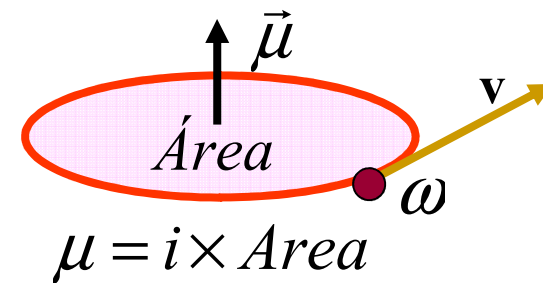
$$\vec{F}_C = \vec{F}_e + \vec{F}_L$$

Diamagnetismo – enfoque clásico

Frecuencia ω , período $2\pi/\omega$



Frecuencia ω , período $2\pi/\omega$



$$\Delta\chi = \frac{\Delta M}{H} = N \frac{\Delta\mu}{H}$$

Para un ión con Z electrones

$$\chi_{dia} = -\frac{N\mu_0 e^2}{6m} \sum_{i=1}^z \overline{r_i^2}$$

Diamagnetismo de Langevin

Diamagnetismo

Ejemplo: susceptibilidad diamagnética del carbono

$$N = \frac{N_{Av}}{V_{mol}} = N_{Av} \frac{\rho}{\mathcal{M}_{at}} \quad \text{átomos por unidad de volumen}$$

$$\chi_{dia} = -\frac{\mu_0 e^2 N_{Av} \rho}{6m \mathcal{M}_{at}} \sum_{i=1}^Z \langle r_i^2 \rangle$$

Estimación teórica

$$\rho = 2.22 \times 10^3 \text{ kg / m}^3$$

$$\mathcal{M}_{at} = 1.2 \times 10^{-2} \text{ kg / mol}$$

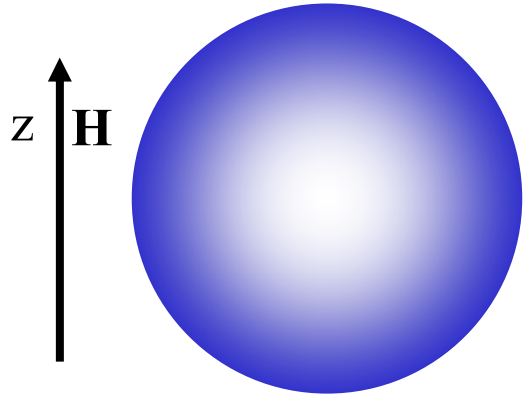
$$\sum_{i=1}^Z \langle r_i^2 \rangle \approx (0.7 \times 10^{-10} \text{ m})^2$$

$$\chi_{dia} = -18.9 \times 10^{-6}$$



$$\chi_{exp} = -13.8 \times 10^{-6}$$

Diamagnetismo y Paramagnetismo – enfoque cuántico



$$\chi = \underbrace{-\frac{eN\hbar}{2m} g \frac{\partial \langle J_z \rangle}{\partial H}}_{\text{paramagnetismo}} \overset{\text{momento angular}}{\downarrow} - \underbrace{\frac{\mu_0 e^2 N}{6m} \sum_{i=1}^Z \langle r^2 \rangle_i}_{\text{diamagnetismo}}$$

Poco dependiente de T

Magnetón de Bohr

$$\mu_B = -\frac{e\hbar}{2m}$$



$$\chi = -Ng\mu_B \frac{\partial \langle J_z \rangle}{\partial H} + \chi_{dia}$$

↓

$$\chi_{para} = -Ng\mu_B \frac{\partial \langle \vec{J}_z \rangle}{\partial H}$$

Paramagnetismo

Momento permanente

$$\langle \mu_z \rangle = -\mu_B g \sum_{i=1}^Z \langle j_z \rangle = -\mu_B g \langle J_z \rangle \longrightarrow \vec{\mu} = -\mu_B g \vec{J}$$

$$\vec{\mu} = -g \mu_B \vec{J}$$

Factor de Landé

$$\vec{J} = \vec{L} \Rightarrow g = 1$$

$$\vec{J} = \vec{S} \Rightarrow g = 2$$

$$\vec{J} = \vec{L} + \vec{S} \Leftrightarrow g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Paramagnetismo

$$\vec{\mu} = -g\mu_B\vec{J}$$

$$\mu^2 \Leftrightarrow J^2$$

$$\mu_z \Leftrightarrow J_z$$

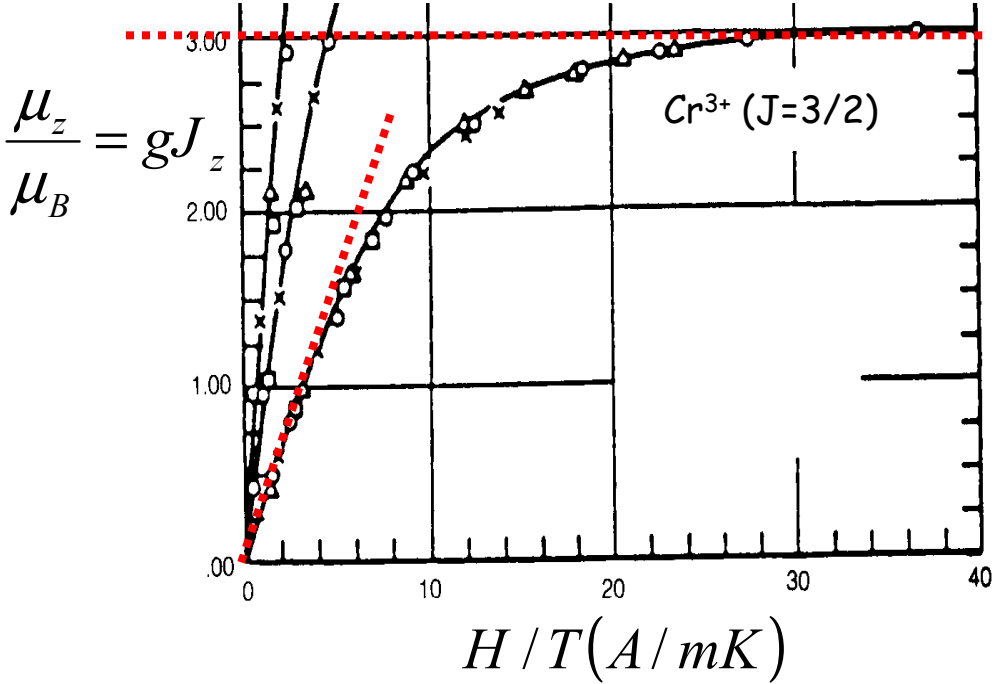
$$\mu = g[J(J+1)]^{1/2} \mu_B$$

Medidas de magnetización de saturación

$$\mu_z = gJ_z \mu_B$$

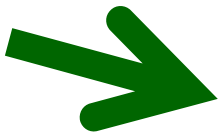
$$\mu_z^{m\acute{a}x} = gJ \mu_B$$

Medidas de susceptibilidad

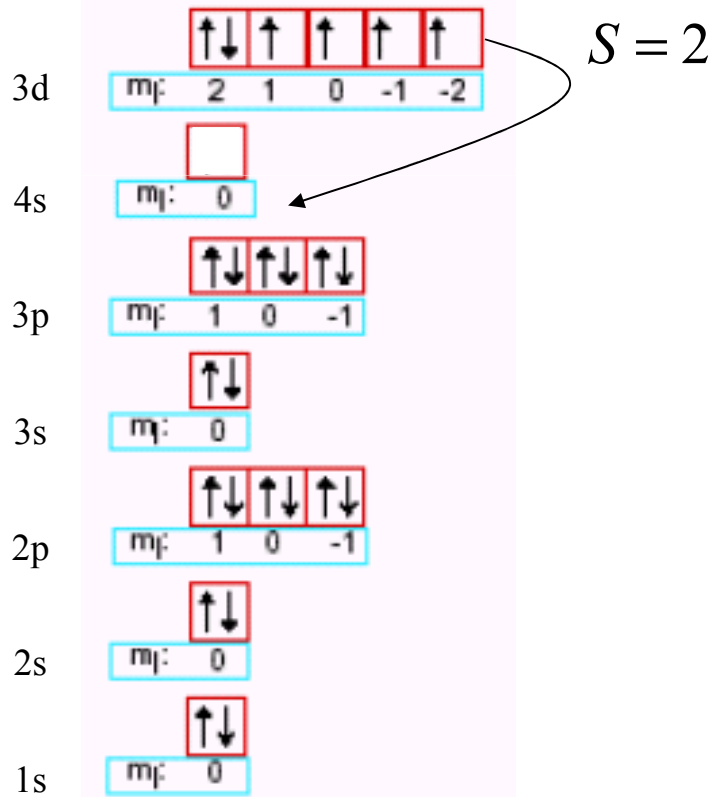
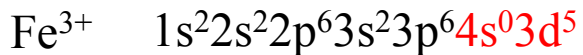
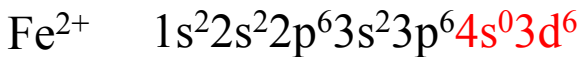
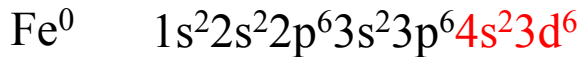


Paramagnetismo

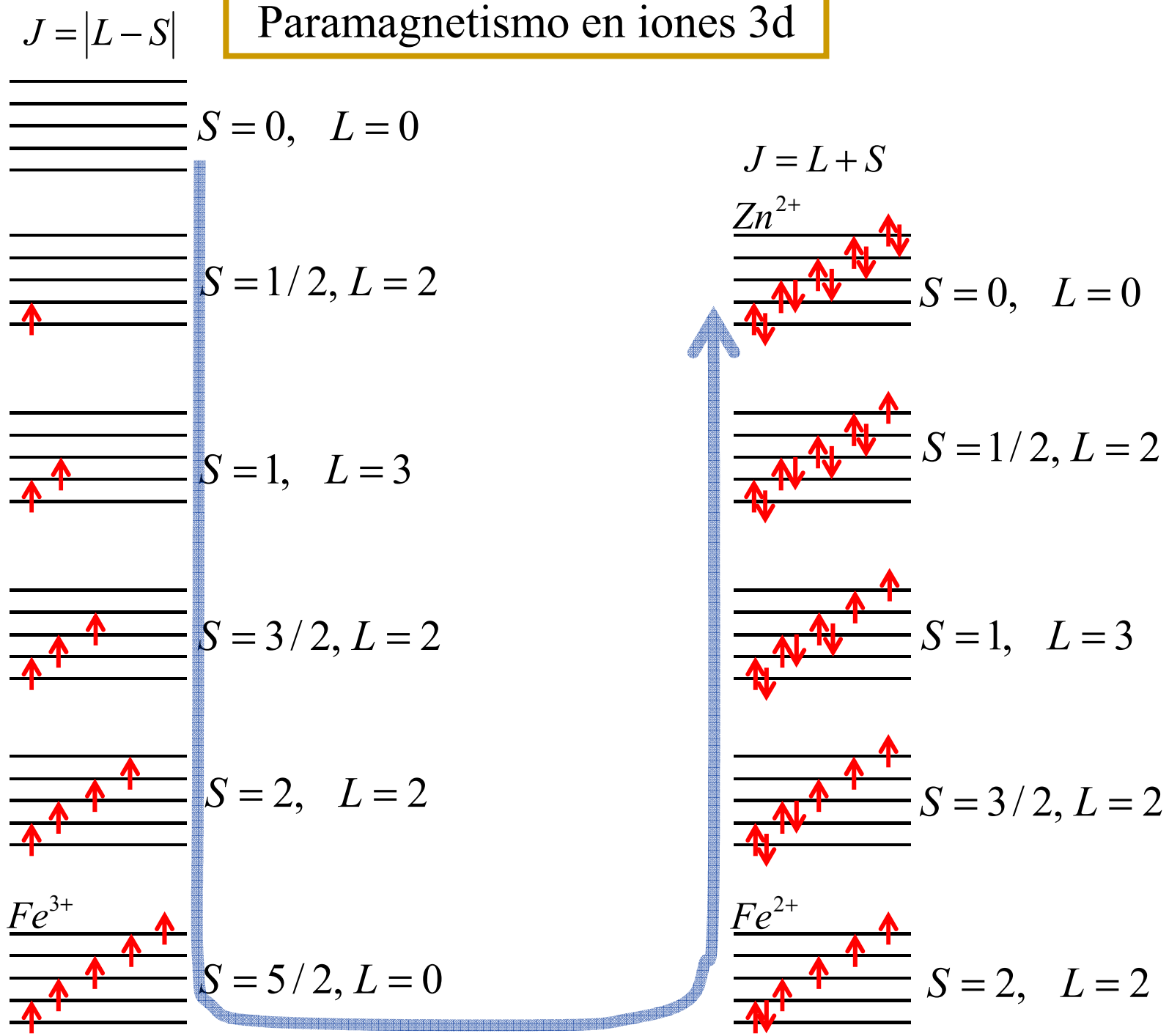
Configuración electrónica



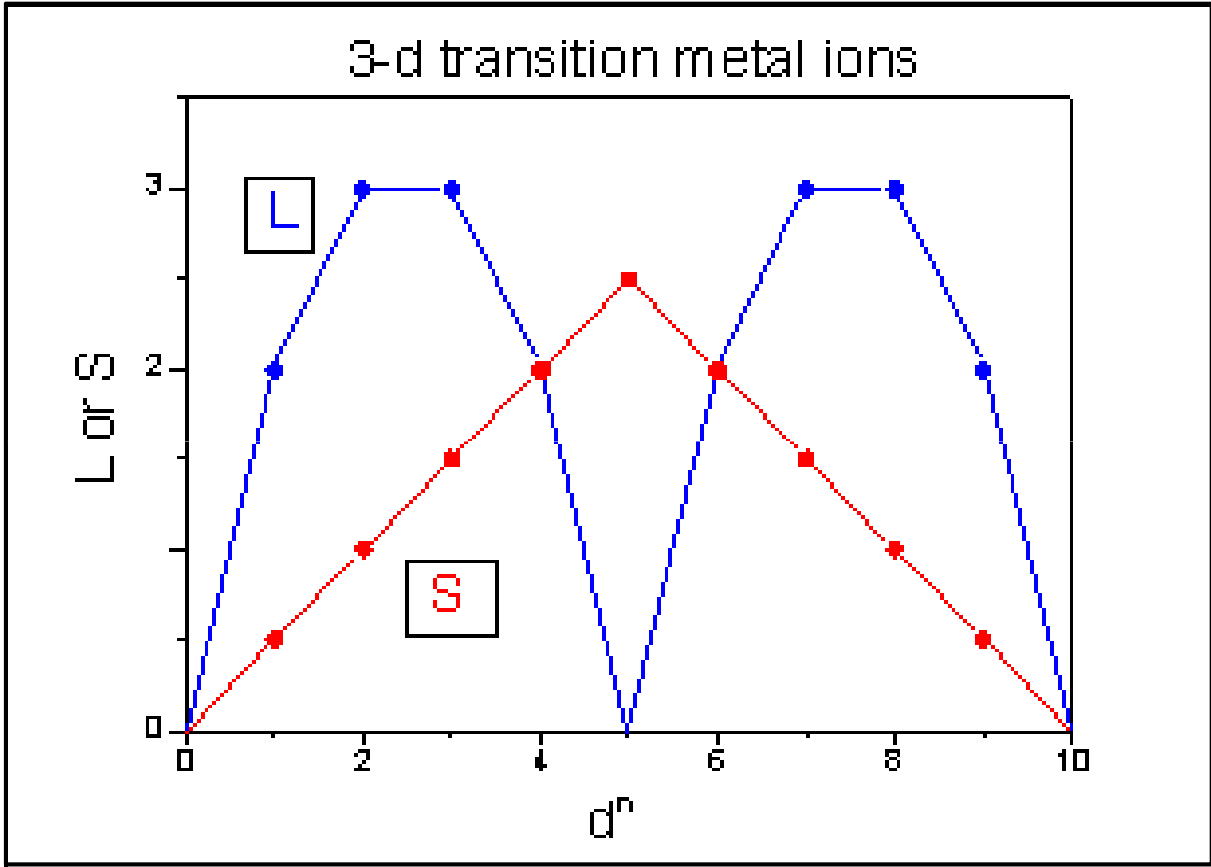
Fe²⁺



Paramagnetismo en iones 3d



Paramagnetismo en iones 3d



21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
39	40	41	42	43	44	45	46	47	48

Átomos neutros

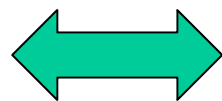
Paramagnetismo en iones 3d

$$\vec{\mu} = -g\mu_B \vec{J}$$

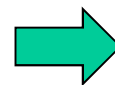
$$\vec{J} = \vec{L} + \vec{S}$$

$$\mu = g\mu_B [J(J+1)]^{1/2}$$

Iones 3d:
“quenching” del
momento
angular orbital



$$\langle \vec{L} \rangle = 0$$



$$\vec{\mu} = -g\mu_B \vec{S}$$
$$\mu = g\mu_B [S(S+1)]^{1/2}$$

Paramagnetismo en iones 3d

Momento magnético en magnetones de Bohr

ión	Configuración	g[j(j+1)] ^{0.5} Calc.	g[s(s+1)] ^{0.5} Calc.	medido
Ti ³⁺ , V ⁴⁺	3d ¹	1.55	1.73	1.8
V ³⁺	3d ²	1.63	2.83	2.8
Cr ³⁺ , V ³⁺	3d ³	0.77	3.87	3.8
Mn ³⁺ , Cr ³⁺	3d ⁴	0	4.90	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	5.92	5.92	5.9
Fe ²⁺	3d ⁶	6.70	4.90	5.4
Co ²⁺	3d ⁷	6.63	3.87	4.8
Ni ²⁺	3d ⁸	5.59	2.83	3.2
Cu ²⁺	3d ⁹	3.55	1.73	1.9

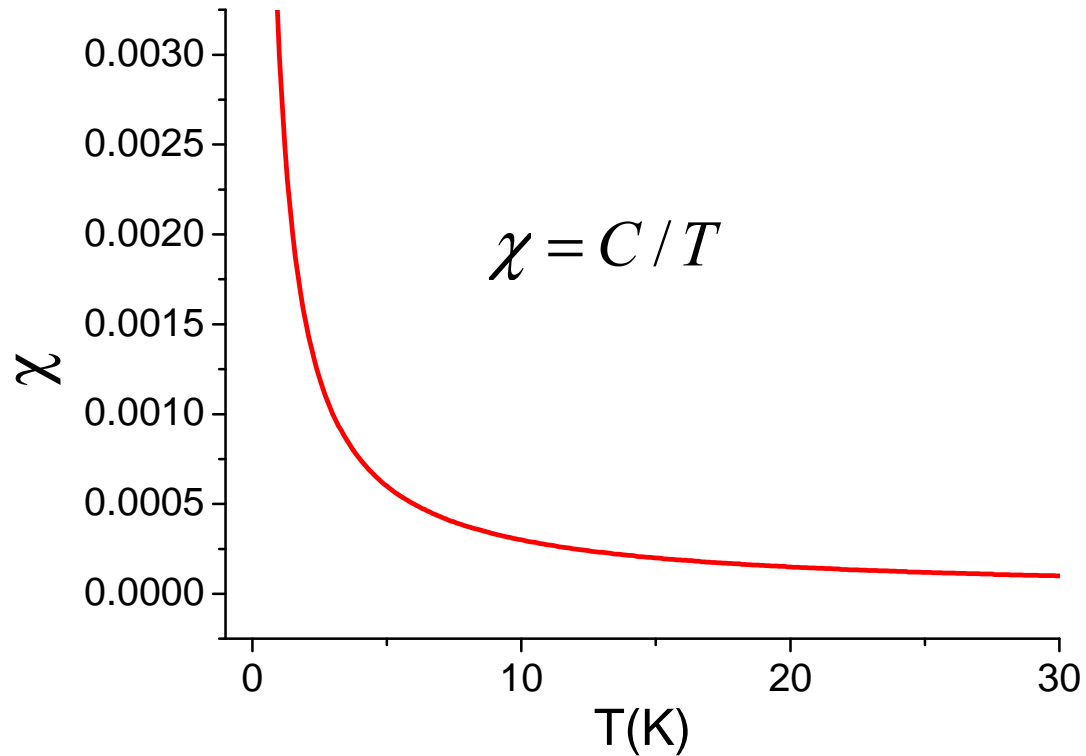
Paramagnetismo en iones 4f

Momento magnético en magnetones de Bohr

ión	configuración	$g[j(j+1)]^{0.5}$	medido
Ce ³⁺	4f ¹ 5s ² 5p ⁶	2.54	2.4
Pr ³⁺	4f ² 5s ² 5p ⁶	3.58	3.5
Nd ³⁺	4f ³ 5s ² 5p ⁶	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² 5p ⁶	2.68	-
Sm ³⁺	4f ⁵ 5s ² 5p ⁶	0.84	1.5
Eu ³⁺	4f ⁶ 5s ² 5p ⁶	0	3.4
Gd ³⁺	4f ⁷ 5s ² 5p ⁶	7.94	8.0
Tb ³⁺	4f ⁸ 5s ² 5p ⁶	9.72	9.5
Dy ³⁺	4f ⁹ 5s ² 5p ⁶	10.63	10.6
Ho ³⁺	4f ¹⁰ 5s ² 5p ⁶	10.60	10.4
Er ³⁺	4f ¹¹ 5s ² 5p ⁶	9.59	9.5
Tm ³⁺	4f ¹² 5s ² 5p ⁶	7.57	7.3
Yb ³⁺	4f ¹³ 5s ² 5p ⁶	4.54	4.5

Paramagnetismo: experimentos

Dependencia de M con H y con T

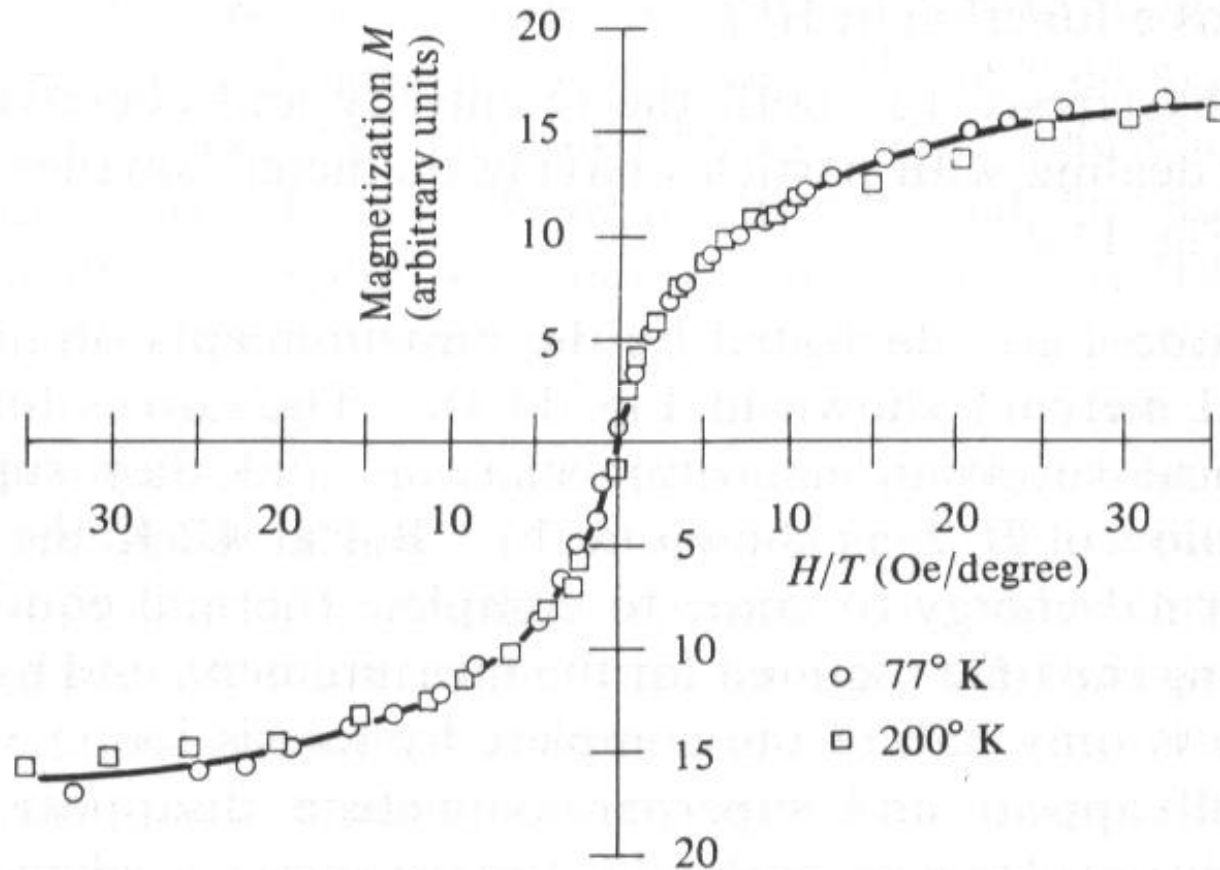


Susceptibilidad de un paramagneto bajo
pequeños campos

$$\chi = \lim_{H \rightarrow 0} \frac{\partial M}{\partial H}$$

Paramagnetismo: experimentos

Dependencia de M con H y con T



Función universal de H/T

Dependencia de \mathbf{M} con \mathbf{H} y con T . Modelo estadístico

Paramagneto (Curie):

Ausencia de interacciones entre
espines

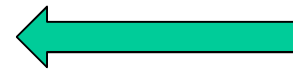
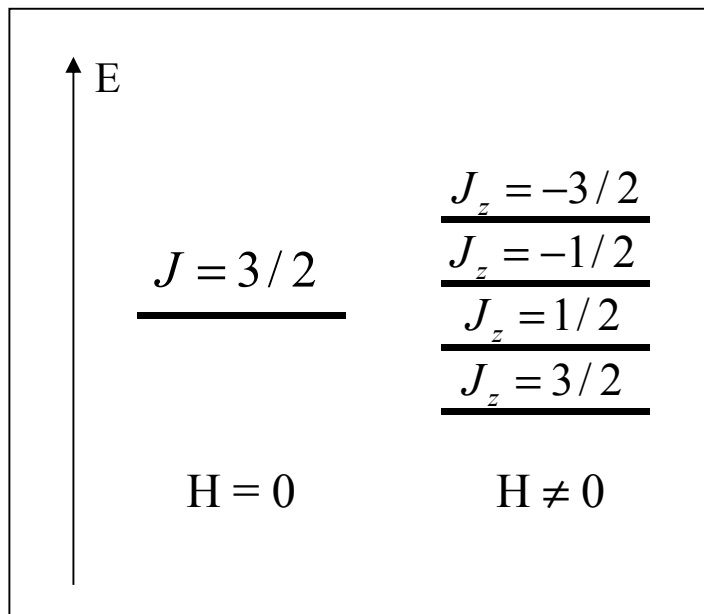
Momento permanente localizado

$$\vec{\mu} = -g\mu_B\vec{J}$$

$$E_B = -\vec{\mu} \cdot \vec{B} = -\mu_0\vec{\mu} \cdot \vec{H} = -\mu_0g\mu_BJ_zH$$



Ejemplo: $J = 3/2$



Suponemos que la probabilidad de ocupación de los subniveles de energía es proporcional a los factores de Boltzmann:

$$e^{-E_z/kT} = e^{-\mu_0g\mu_BJ_zH/kT}$$

$$\mu_z = -g\mu_BJ_z$$

$$x = \mu_0g\mu_BJH/kT$$

solución

$$\frac{\langle \mu_z \rangle}{\mu} = \frac{\langle J_z \rangle}{J} = B_J(x) \quad x = \frac{\mu_0 g \mu_B J H}{kT}$$

Función de Brillouin

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

$$M = N \langle \mu_z \rangle = NgJ\mu_B B_J(x)$$

$$\leftarrow M = M(H/T)$$

Número de momentos por unidad de volumen

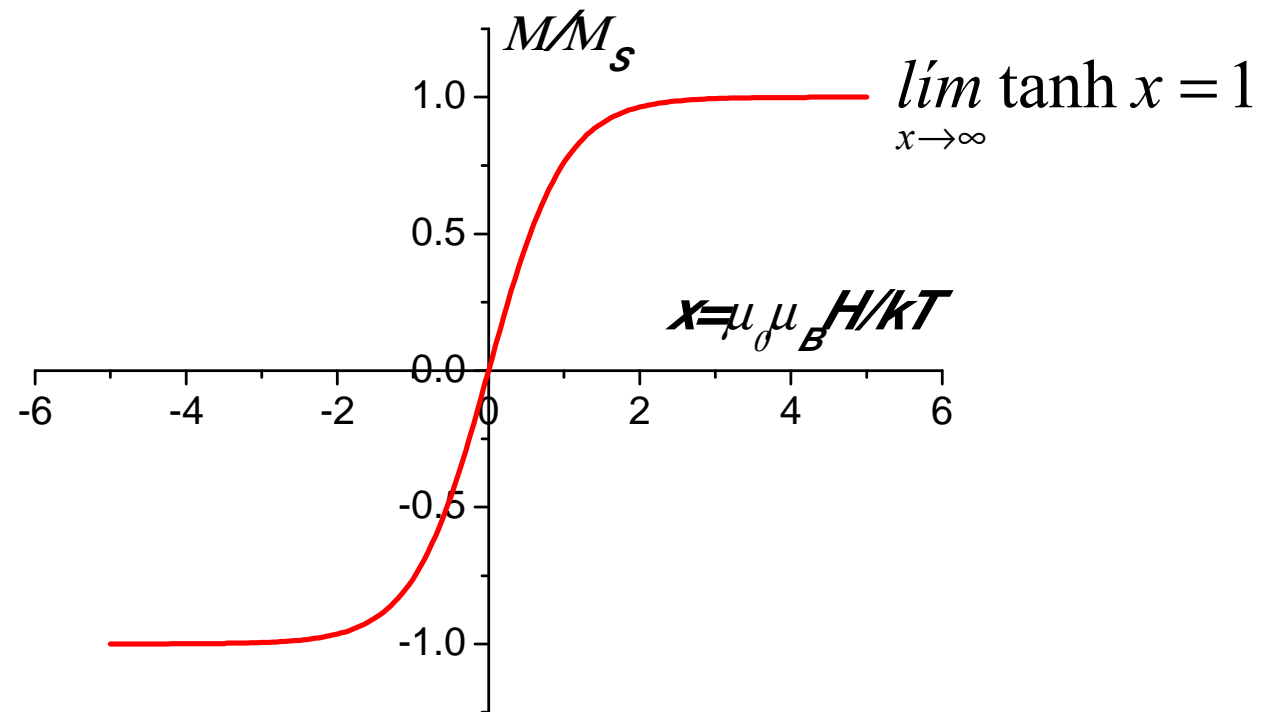
$$J = 1/2$$

$$si \ g = 2$$

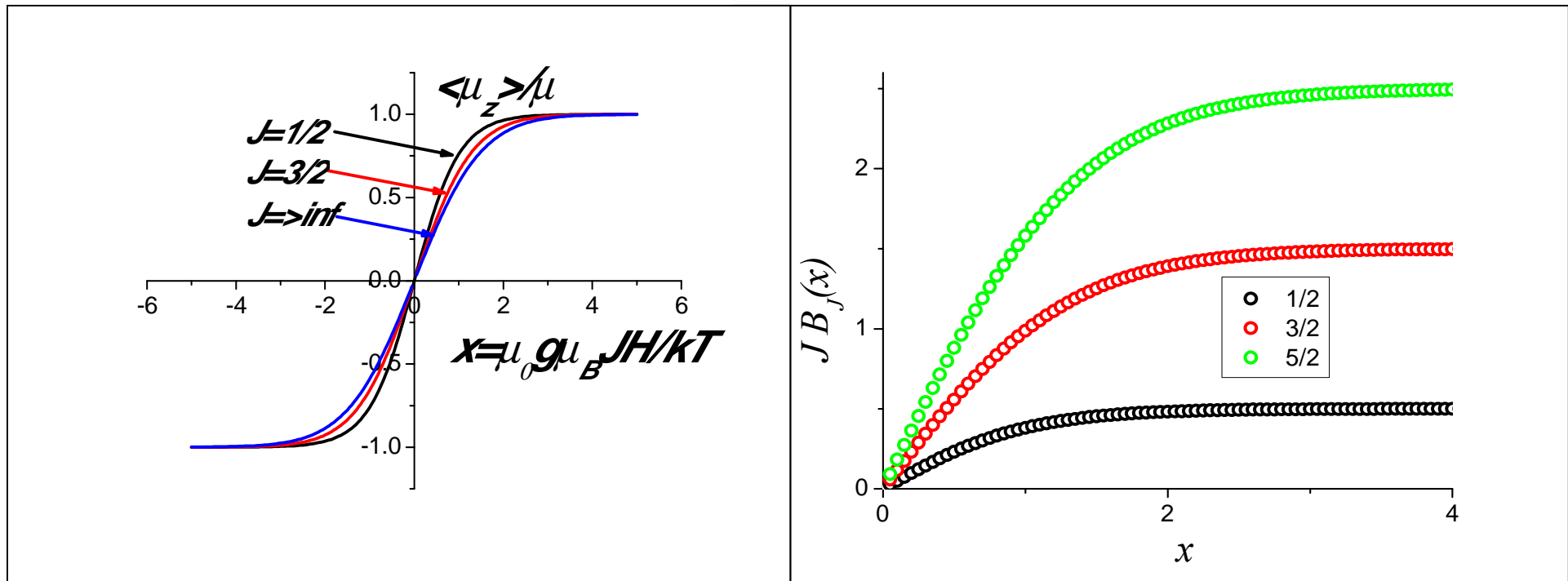
$$B_J(x) = \tanh x$$

$$M(x) = NgJ\mu_B \tanh x = N\mu_B \tanh x$$

$$M_S(x) = NgJ\mu_B$$



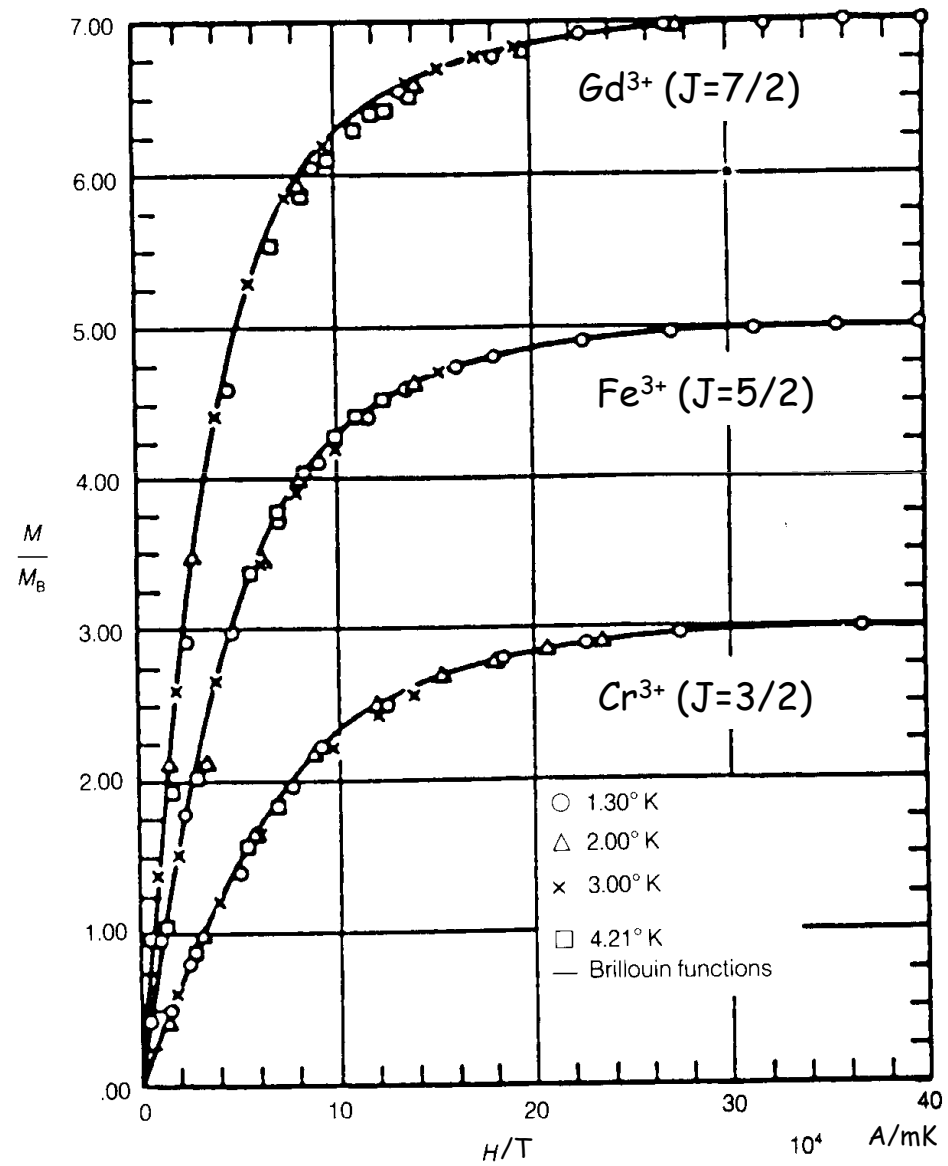
$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$



La función “satura” para $x \geq 4$

Sales
paramagnéticas
de:

Cr^{3+} ($J=3/2$) Fe^{3+}
($J=5/2$) Gd^{3+}
($J=7/2$)



Buen acuerdo de la
teoría con los
resultados
experimentales

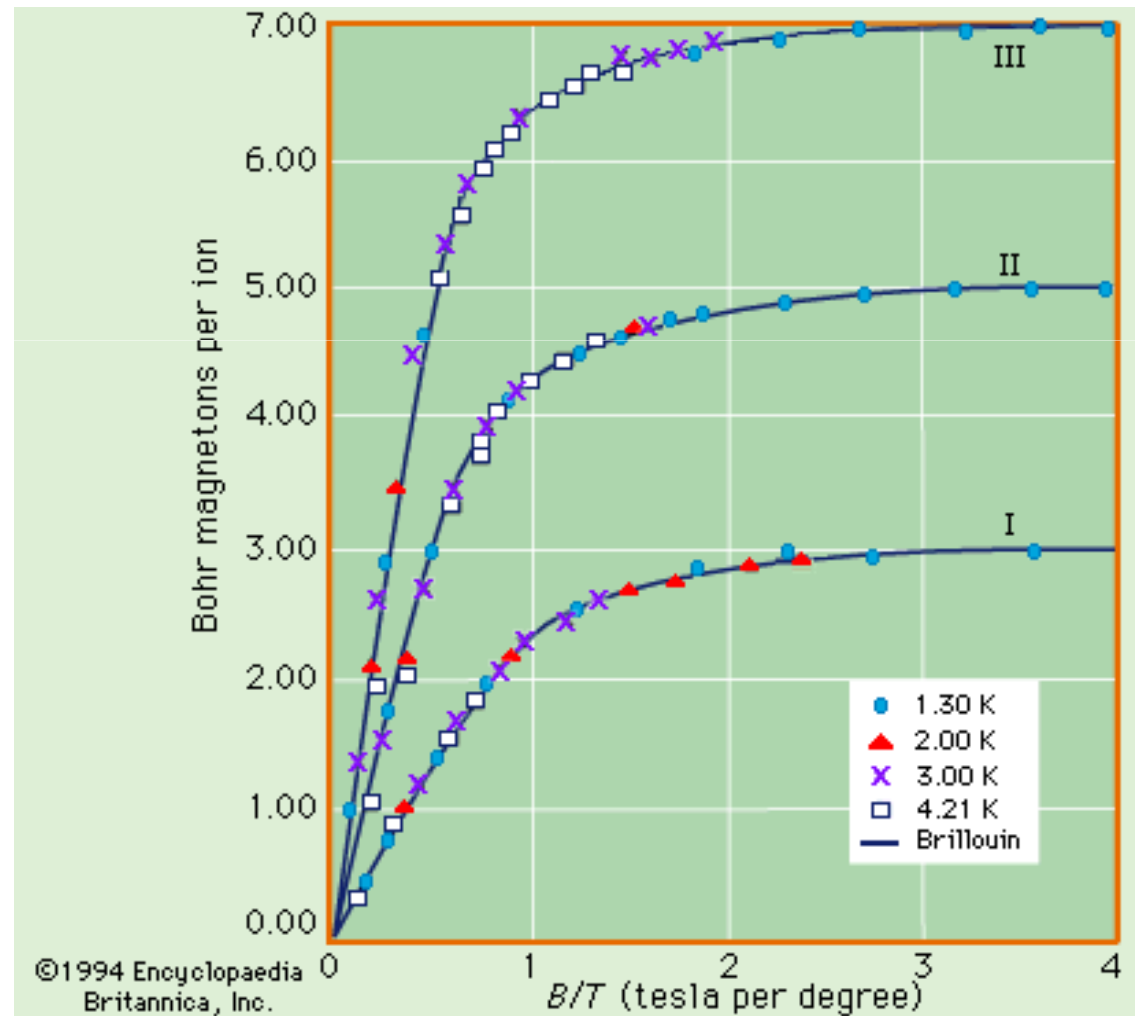
Comportamientos límites

Saturación

$$x \rightarrow \infty \quad B_J(x) \rightarrow 1$$

$$M = M_S = NgJ\mu_B B_J(x) \rightarrow NgJ\mu_B = N\mu$$

De la medida de M_S se obtiene el valor de la proyección máxima del momento en la dirección del campo



Campo necesario para saturar un paramagneto

$$x = \frac{\mu_0 g \mu_B J H}{k T}$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ (SI)}$$

$$\mu_B = 9.27 \times 10^{-24} \text{ (SI)}$$

$$k = 1.38 \times 10^{-23} \text{ (SI)}$$

$$g = 2; J = 1/2$$

$$x = 8.44 \times 10^{-6} \frac{H(A/m)}{T(K)}$$

$$x = 5$$

$$T = 1K \Rightarrow H_s \geq 5.92 \times 10^5 A/m \Rightarrow B_s \geq 0.74 T$$

$$T = 300K \Rightarrow H_s \geq 1.78 \times 10^8 A/m \Rightarrow B_s \geq 222 T \quad !!!!!$$

Que corriente se necesita?

Comportamientos límite

Magnetización inicial

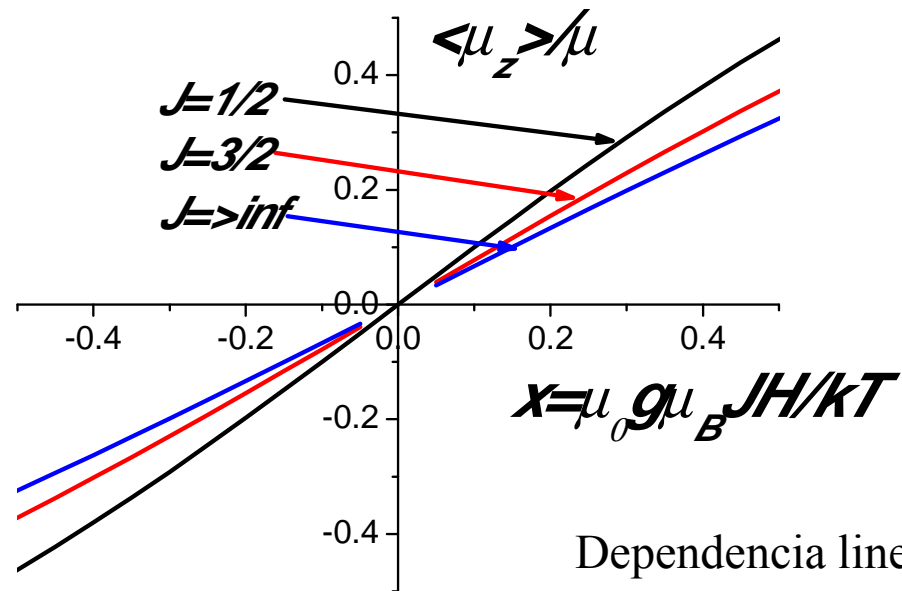
$x \rightarrow 0$ ($x \ll 1$)

$$\coth(x) \approx \frac{1}{x} + \frac{x}{3} + O(x^3)$$

$$B_J(x) \approx \frac{J+1}{3J} x + \cancel{O(x^3)}$$

$$\langle \mu_z \rangle = gJ\mu_B B_J(x) \approx g\mu_B J \frac{J+1}{3J} x = g\mu_B \frac{J+1}{3} x$$

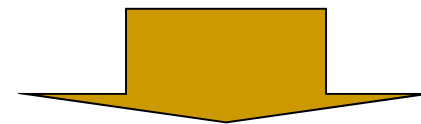
$$M = N \langle \mu_z \rangle \approx \frac{N \mu_0 \overbrace{g^2 \mu_B^2}^{\mu^2} J(J+1) H}{3kT} = \frac{N \mu_0 \mu^2 H}{3kT}$$



Dependencia lineal con H,

$$x \leq 0.2$$

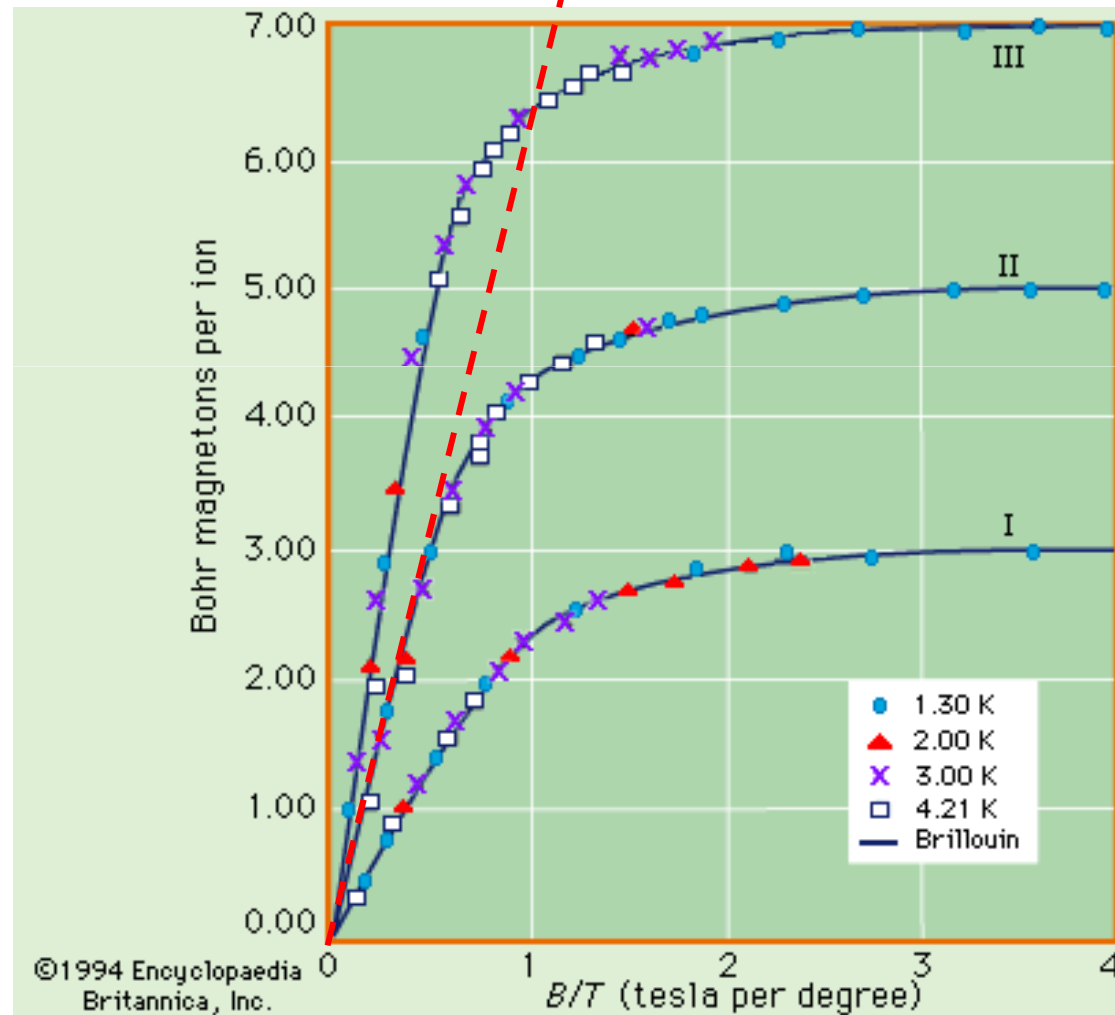
$$T = 300 \text{ K}$$



$$H_i \leq 2.4 \times 10^4 \text{ A/m} \approx 300 \text{ Oe} \Rightarrow B_i \leq 30 \text{ mT}$$

$$\chi_{inic} = \frac{M_{inic}}{H} \approx \frac{N\mu_0 g^2 \mu_B^2 J(J+1)}{3kT}$$

Información sobre
N, g, J, T



Susceptibilidad inicial

$$\mu^2 = g^2 \mu_B^2 J(J+1)$$

$$\chi = \frac{M}{H} \approx \frac{N\mu_0 \mu^2}{3kT} = \frac{C}{T}$$

Constante de Curie

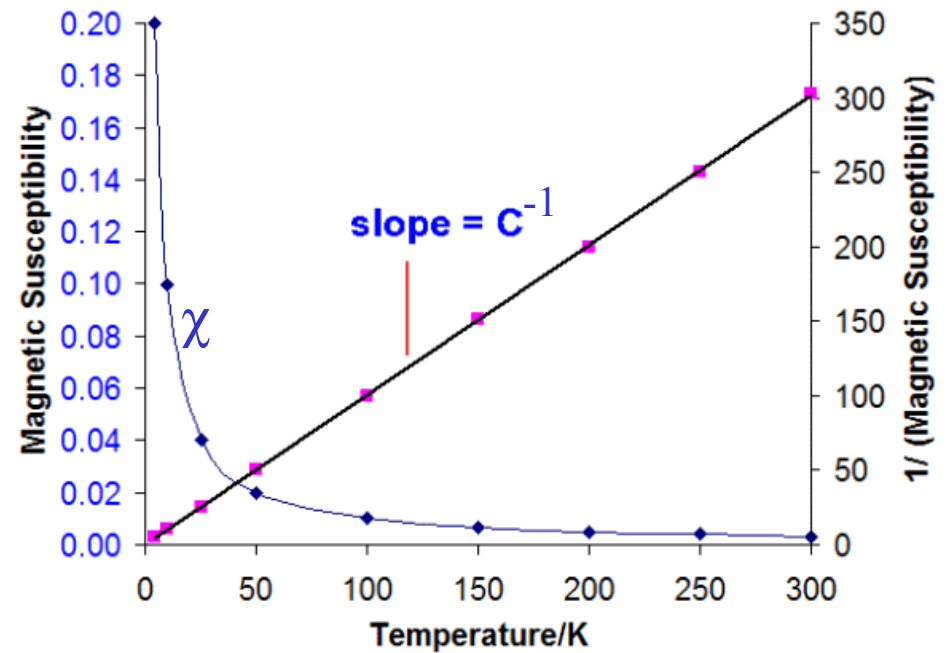
$$\chi^{-1} = \frac{T}{C}$$

Ley de Curie

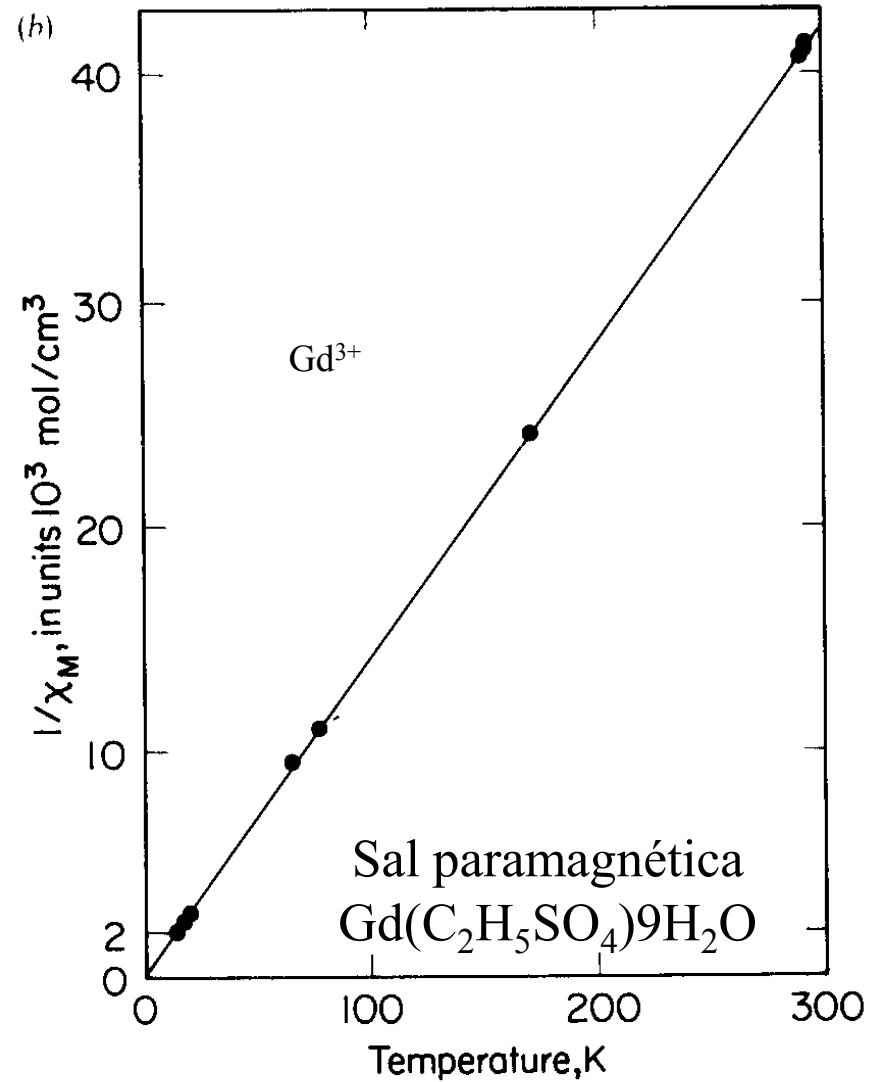
Pierre Curie
(1859-1906)



Curie Law Plots



Susceptibilidad inicial



Límite clásico ($J \rightarrow \infty$)

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

Cuando $J \rightarrow \infty$

$$(2J+1)/2J \rightarrow 1$$

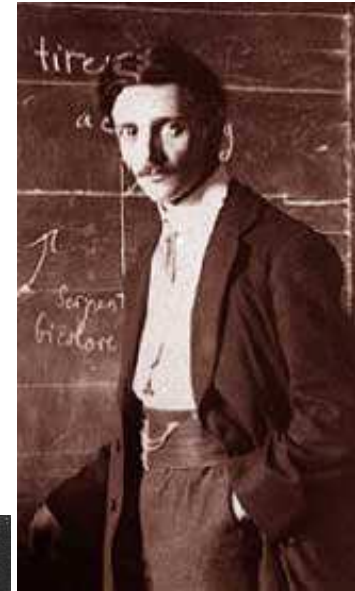
$$\coth(x/2J) \rightarrow 2J/x$$



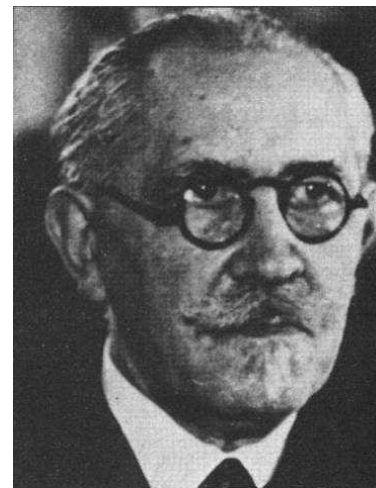
$$B_J(x) \rightarrow L(x) = \coth(x) - \frac{1}{x}$$

Función de
Langevin

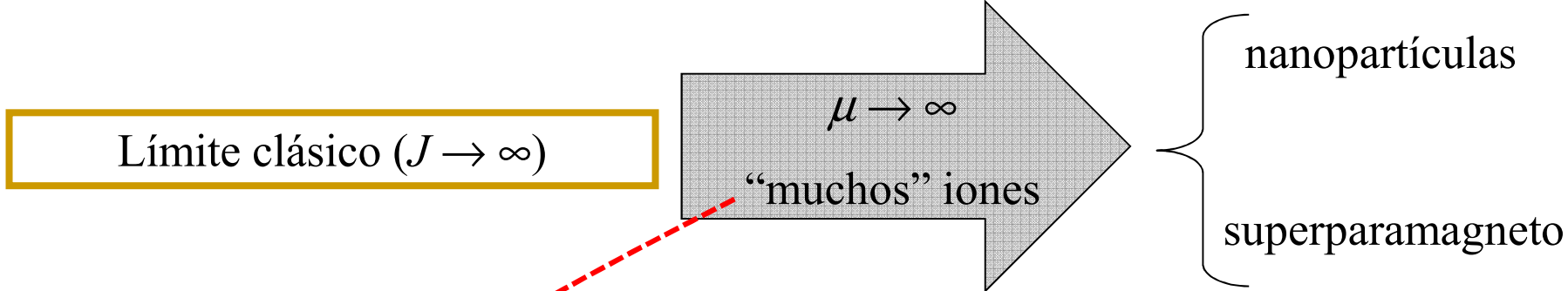
Función de
Brillouin



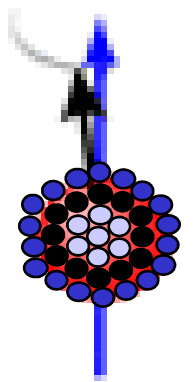
Léon Brillouin
(1889-1969)



Paul Langevin
(1872-1946)

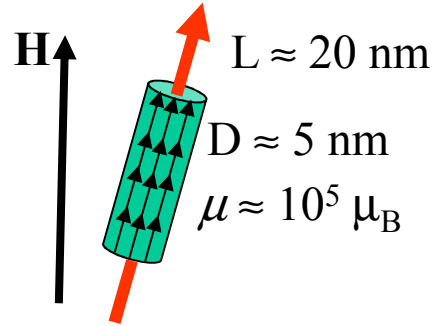


$\mu \gg \mu_{\text{át}} \approx \mu_B$



$\tau < \tau_{\text{obs}}$

Superparamagneto: NP con $\mu \leq 10^6 \mu_B$

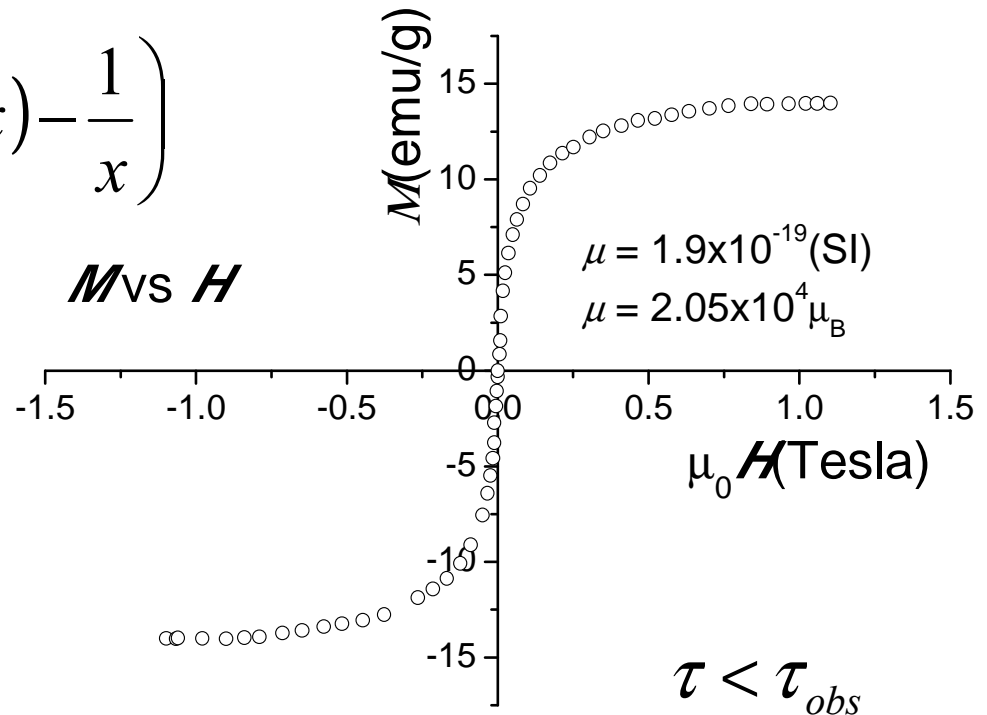


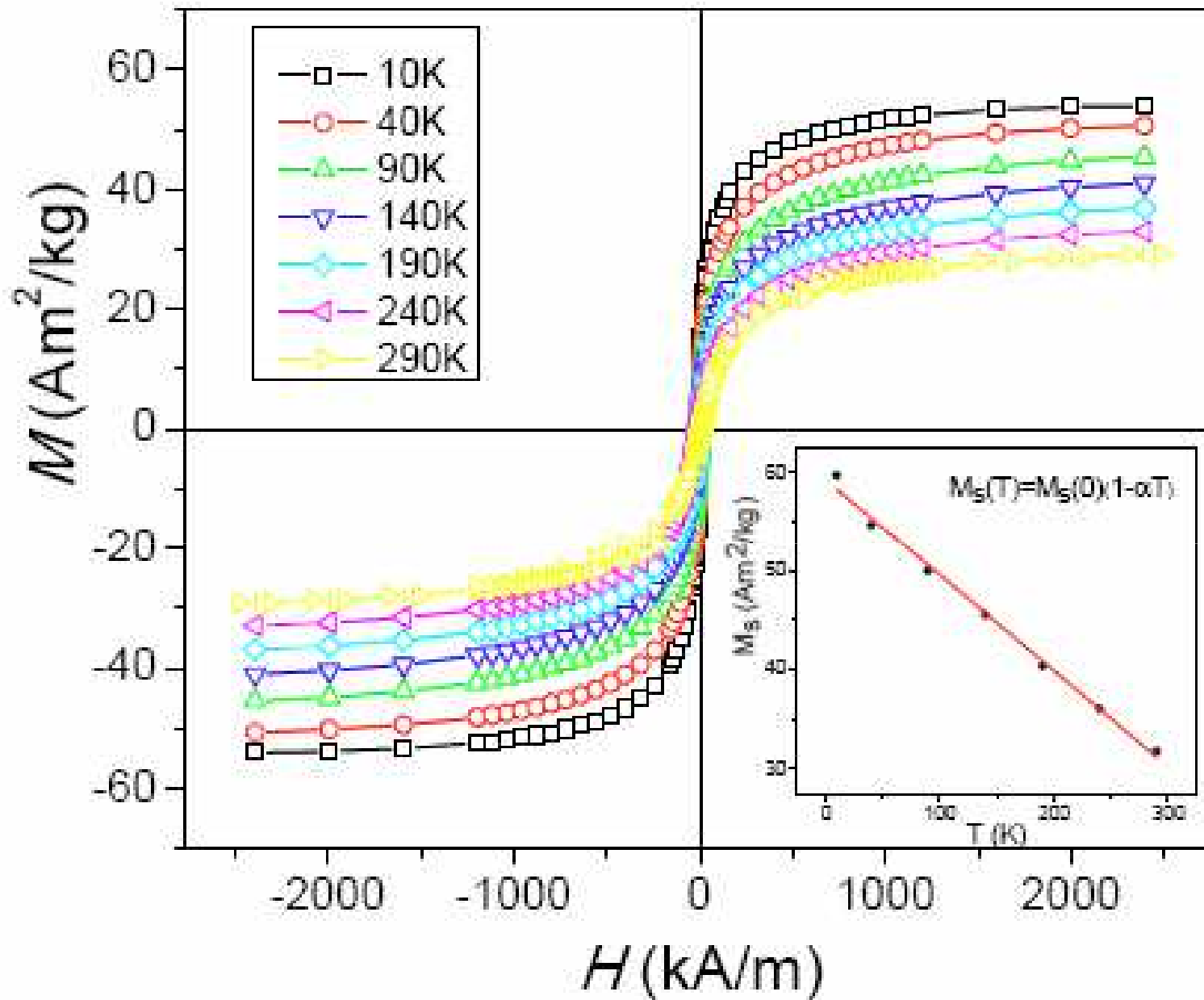
Aerogel de sílica con partículas de maghemita ($\sim 5 \times 20 \text{ nm}$)

$$\langle \mu \rangle_H = \mu L(x) = \mu \left(\coth(x) - \frac{1}{x} \right)$$

$$x = \frac{\mu_0 \mu H}{kT}$$

RT





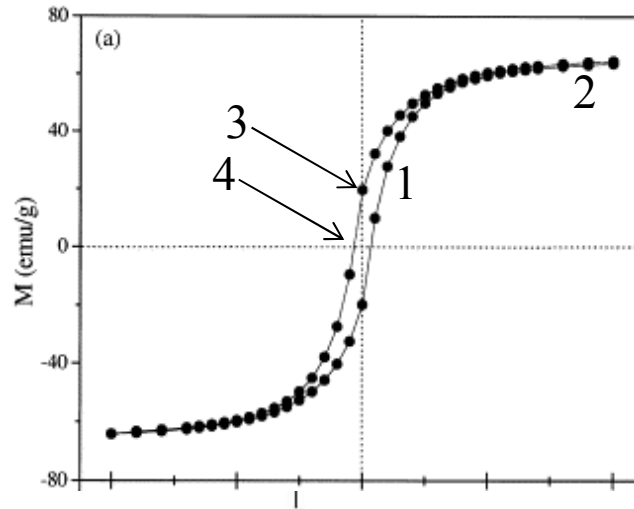
$$\alpha \approx \frac{k}{8KV}$$

$$\tau < \tau_{obs}$$

Comportamiento superparamagnético de NP de magnetita (4 nm) dispersas en un hidrogel de PVA (ferrogel).

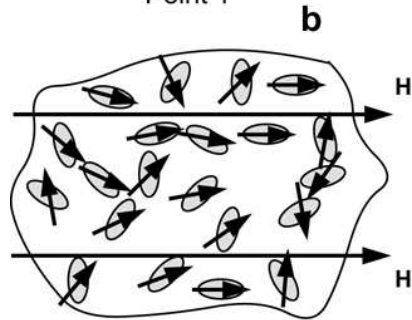
Proceso diferente de:

Nanopartículas monodominio

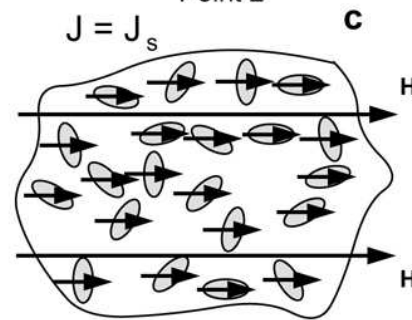


$$\tau > \tau_{obs}$$

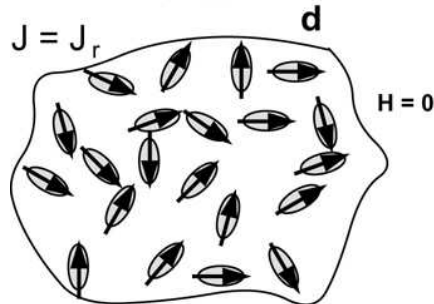
Point 1



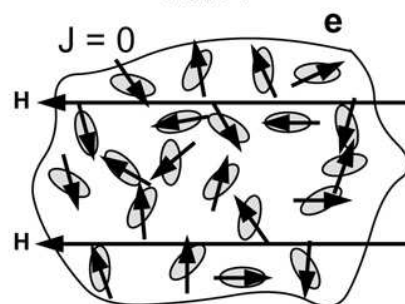
Point 2



Point 3



Point 4





Fin módulo