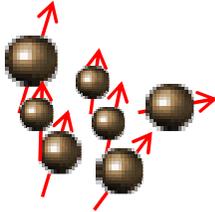


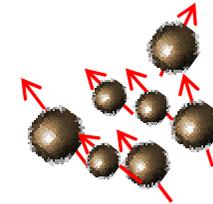
Nanomateriales Magnéticos

Fundamentos y Aplicaciones



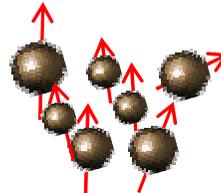
Francisco H Sánchez

2013



Departamento de Física – UNLP

IFLP - CONICET



<http://www.fisica.unlp.edu.ar/Members/sanchez/curso>

Presentación

Francisco H. Sánchez

Prof. UNLP

Investigador CONICET

Director G3M

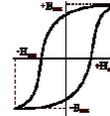
Proyectos

Materiales magnéticos nanocompuestos
Materiales para la biomedicina



Programa

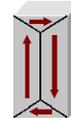
Introducción - definiciones



Intercambio: dia-para-ferro-ferri (etc)-magnetismo

Anisotropías: cristalina-forma-elástica-interfaz-intercambio

Energía magnetostática: dominios



Partículas nanométricas: estado monodominio-relajación-interacciones

Aplicaciones

Bibliografía

***Introduction to Magnetic Materials* B.D. Cullity,
(Massachusetts, Addison-Wesley, 1972).**

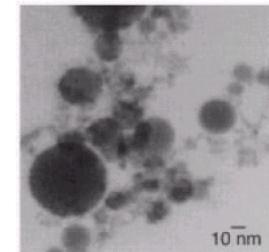
Introduction to the Theory of Ferromagnetism, Amikam
Aharoni, Oxford Science Publications, 1998.

Modern Magnetic Materials, Robert C. O'Handley, John
Wiley & Sons, 1999

Introduction to Magnetism and Magnetic Materials,
David Jiles, Chapman & Hall 1996.

**Nanomedicine: design and applications of magnetic
nanomaterials, nanosensors and nanosystems
Vijay K. Varadan, Linfeng Chen, Jining Xie, 2008
John Wiley & Sons, Ltd**

Artículos seleccionados



Introducción

Materiales magnéticos

¿Cómo es un material magnético?

Cantidades Magnéticas de interés práctico

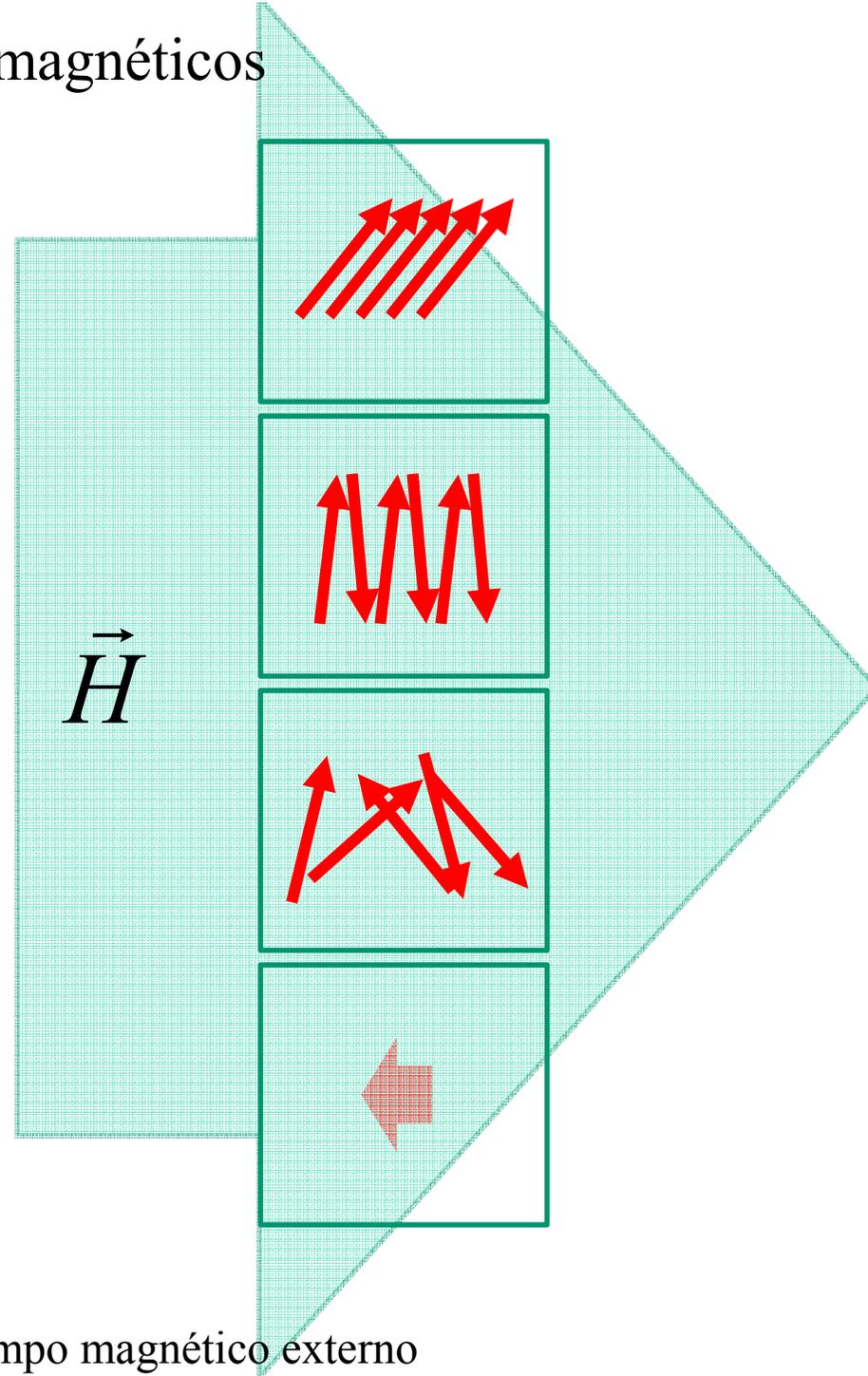
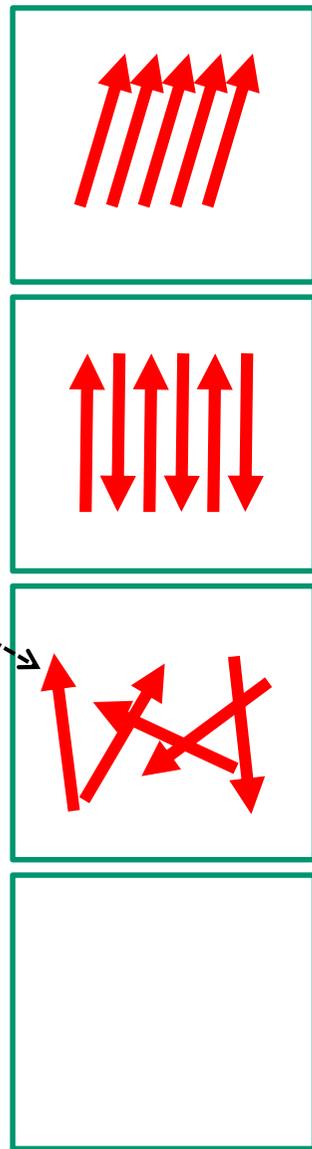
Interacciones Magnéticas

Dominios

Pequeñas partículas

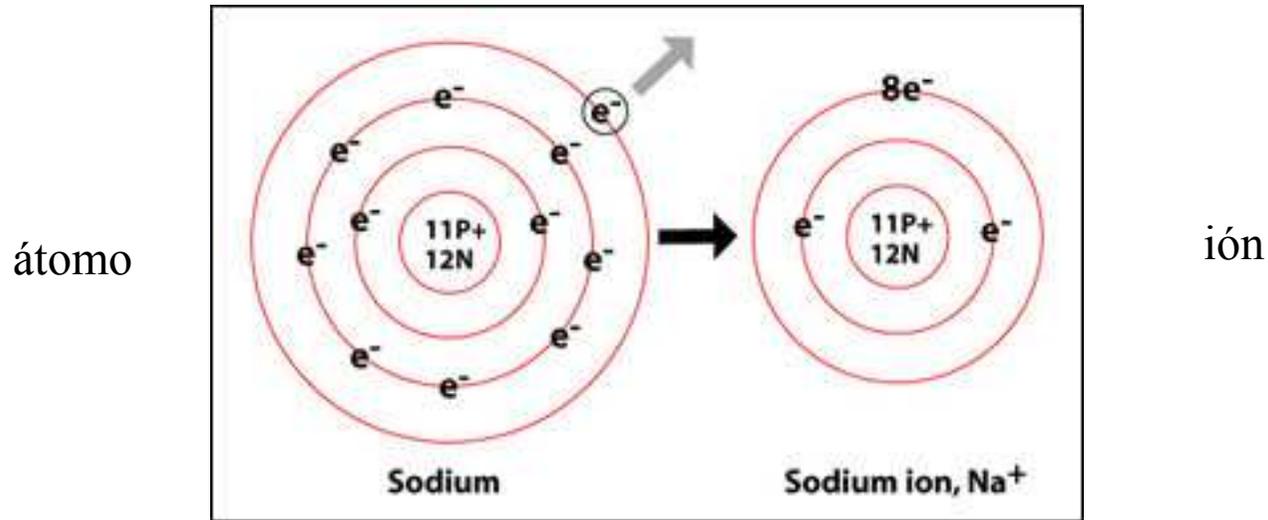
Materiales magnéticos

Momento magnético

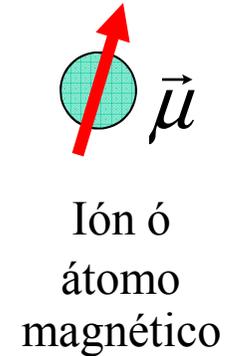
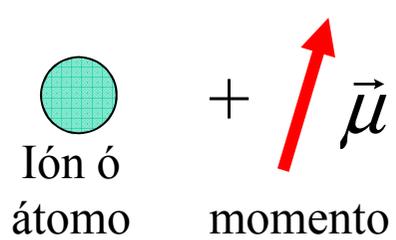


Respuesta a un campo magnético externo

Origen del momento magnético



Momento magnético atómico permanente μ



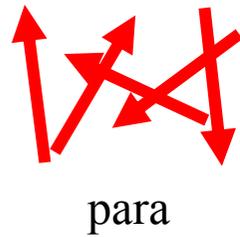
$$\vec{\mu} \propto \vec{J}$$

Momento angular atómico

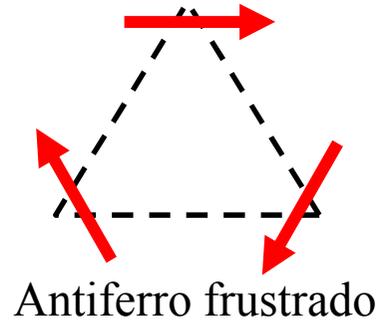
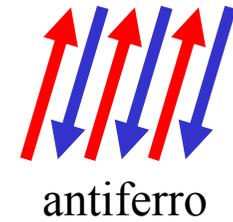
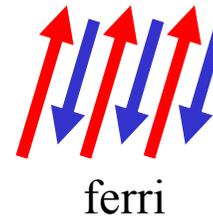
El momento magnético depende del estado electrónico del átomo

¿Cómo es un material magnético?

Desorden $\forall T$
No hay interacción entre momentos



Orden para $T < T_c$
Interacciones entre momentos



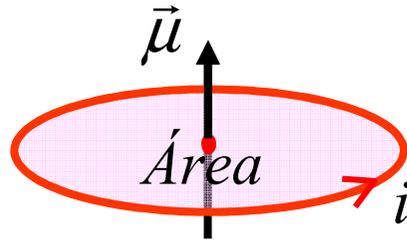
The periodic table of the elements

	1A	2A	3A	4A	5A	6A	7A	8	1B	2B	3B	4B	5B	6B	7B	8		
1	H															He		
2	Li	Be									B	C	N	O	F	Ne		
3	Na	Mg									Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	A															
	L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

- Metals
- Metalloids
- Non-metals
- Transition Metals
- Gases

Cantidades Físicas

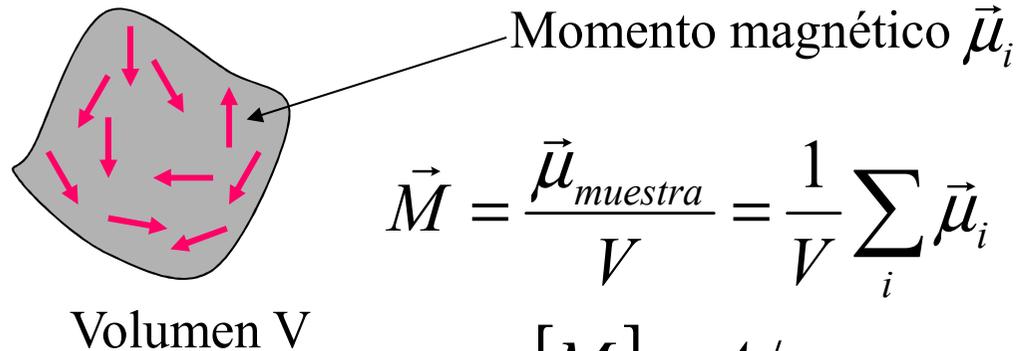
Momento Magnético $\vec{\mu}$



$$\mu = \text{Área} \times i \quad [\mu] = \text{Am}^2$$

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

Magnetización \vec{M}

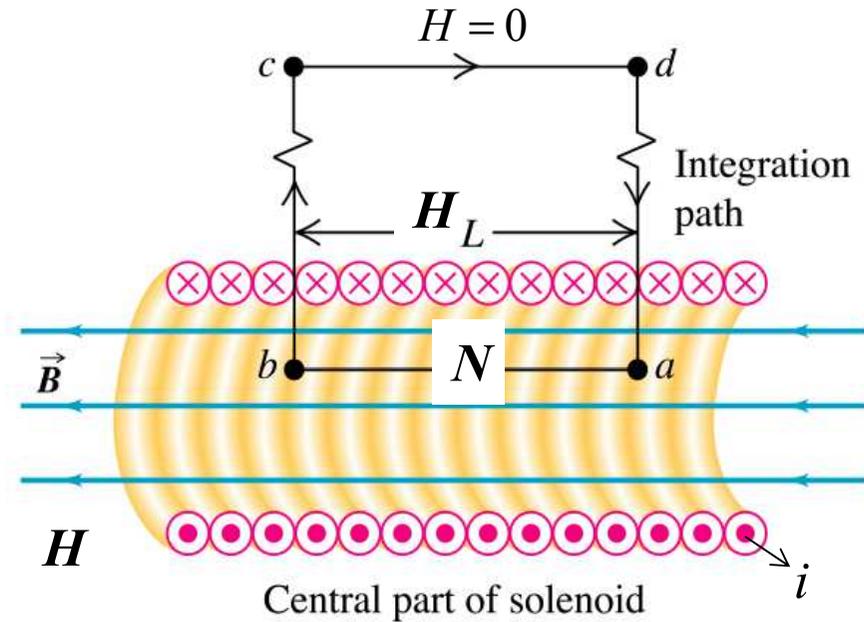
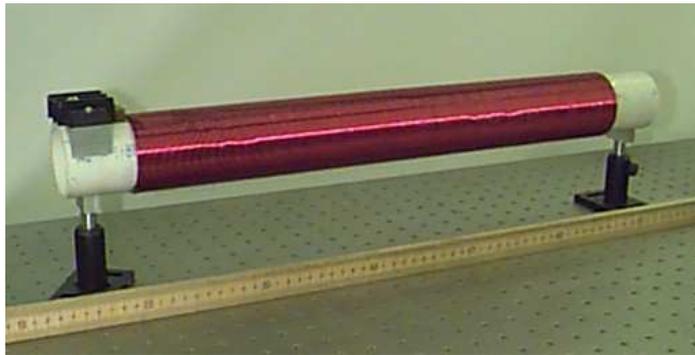


$$\vec{M} = \frac{\vec{\mu}_{\text{muestra}}}{V} = \frac{1}{V} \sum_i \vec{\mu}_i$$

$$[M] = \text{A} / \text{m}$$

Campo Magnético \vec{H}

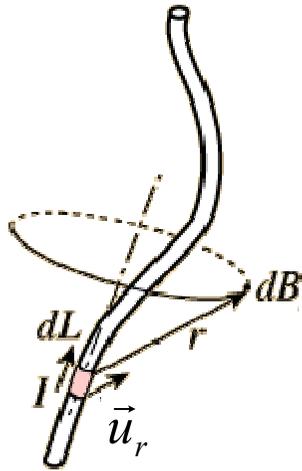
Solenoid largo



Ley de ampere

$$\oint \vec{H} \cdot d\vec{l} = I_{tot} \Rightarrow H = Ni / L \Rightarrow [H] = A / m$$

Campo de inducción B



Ley de Biot Savart (SI)

$$d\vec{B} = \frac{\mu_0 I d\vec{L} \times \vec{u}_r}{4\pi r^2}$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ J} / \text{A}^2 \text{m}$$

$$[B] = \text{J} / \text{Am}^2 = \text{Tesla}$$

unidades

<i>SI</i>	<i>cgs</i>
$[\mu] = Am^2$	$[\mu] = emu$
$[M] = A/m$	$[M] = emu/cm^3$
$[H] = A/m$	$[H] = Oe$
$[B] = Tesla$	$[B] = Gauss$

SI

$$[MB] = \text{Joule} / m^3; [MB] = A\text{Tesla} / m \Rightarrow \boxed{\text{Tesla} = \text{Joule} / Am^2}$$

$$\mu_0 = 4\pi \times 10^{-7} J / A^2 m$$

unidades

<i>SI</i>	<i>cgs</i>
$\vec{\sigma} = \sum_i \vec{\mu}_i / m$	$\vec{\sigma} = \sum_i \vec{\mu}_i / m$
$[\sigma] = Am^2 / kg$	$[\sigma] = emu / g$

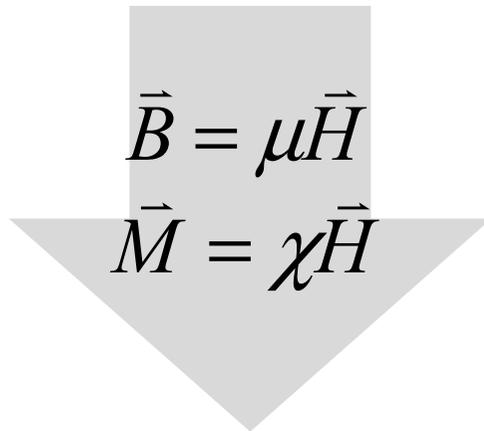
Momento específico o magnetización másica

m = masa de la muestra

Relaciones entre **B**, **H**, **M**

<i>SI</i>	<i>cgs</i>
$\vec{B} = \mu_0(\vec{H} + \vec{M})$	$\vec{B} = \vec{H} + 4\pi\vec{M}$
$\vec{B} = \mu\vec{H}$ $\vec{M} = \chi\vec{H}$	$\vec{B} = \mu\vec{H}$ $\vec{M} = \chi\vec{H}$
aproximadas	
$[\mu] = mTesla / A$ χ <i>adimensional</i>	$[\mu]$ <i>adimensional</i> χ <i>adimensional</i>

$$\vec{B} = \mu_0 (\vec{H} + \vec{M})$$


$$\vec{B} = \mu \vec{H}$$
$$\vec{M} = \chi \vec{H}$$

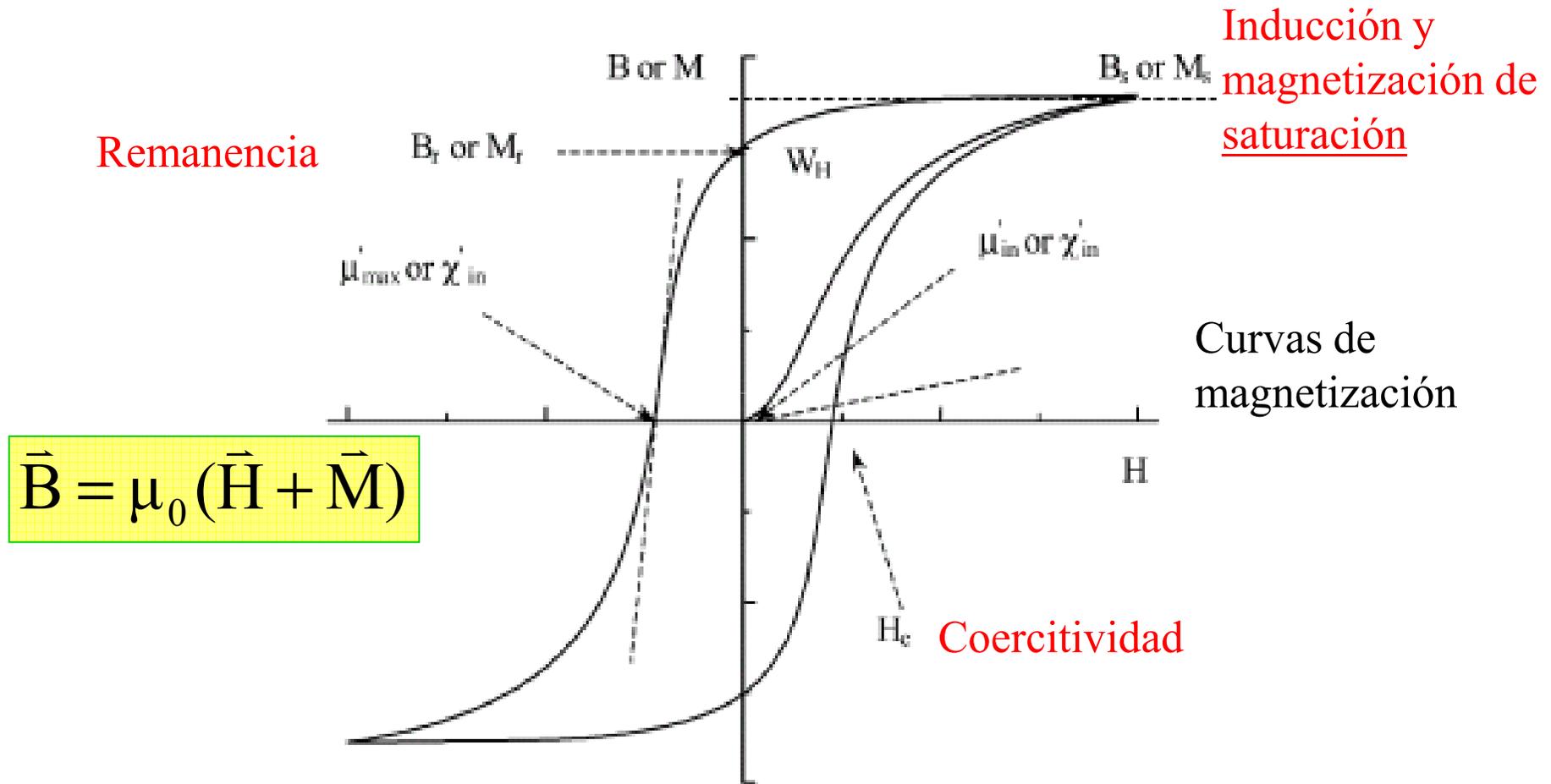
$$\mu = \mu_0 (1 + \chi) \quad \mu_R = \frac{\mu}{\mu_0} = 1 + \chi \quad \begin{array}{l} \text{permeabilidad} \\ \text{relativa al} \\ \text{vacío} \end{array}$$

Diamagnetos $\mu_R < 1 \Rightarrow \chi < 0 \quad \chi \approx -10^{-6} \text{ a } -10^{-5}$

Paramagnetos $\mu_R > 1 \Rightarrow \chi > 0 \quad \chi \approx 10^{-5} - 10^{-4}$

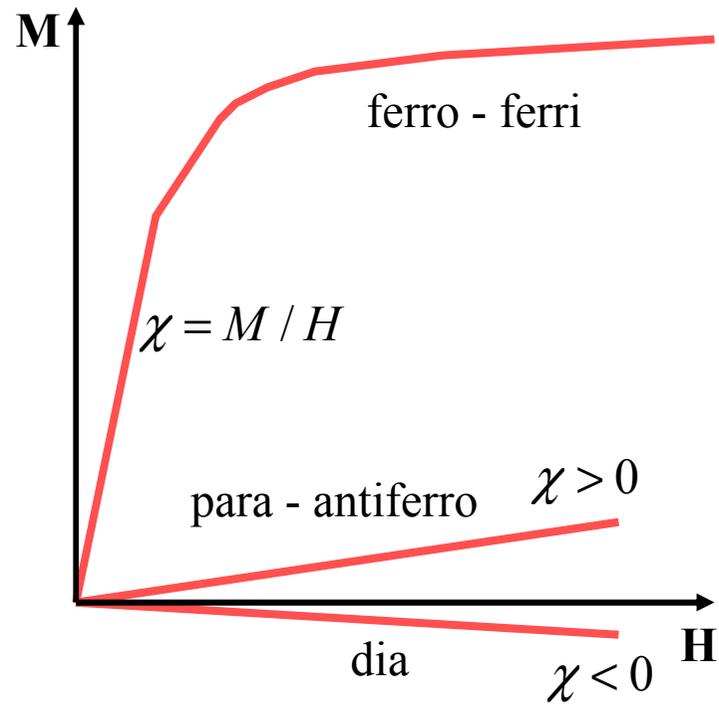
Ferromagnetos $\mu_R \gg 1 \Rightarrow \chi \approx \mu_R \gg 0 \quad \chi \approx 10 - 10^5$

Relaciones entre \mathbf{B} , \mathbf{H} , \mathbf{M}

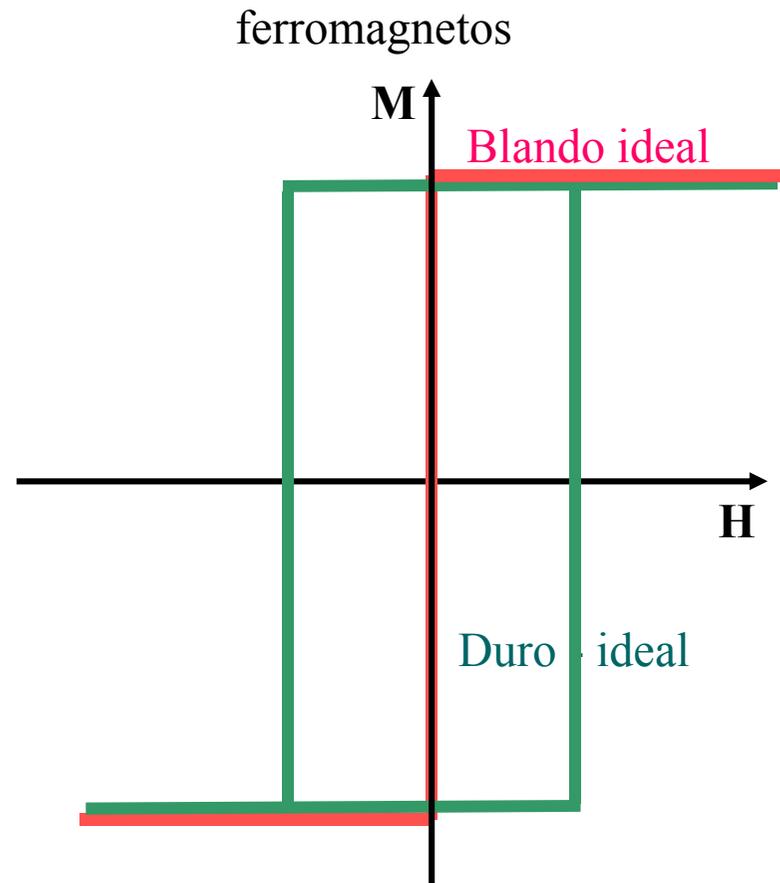
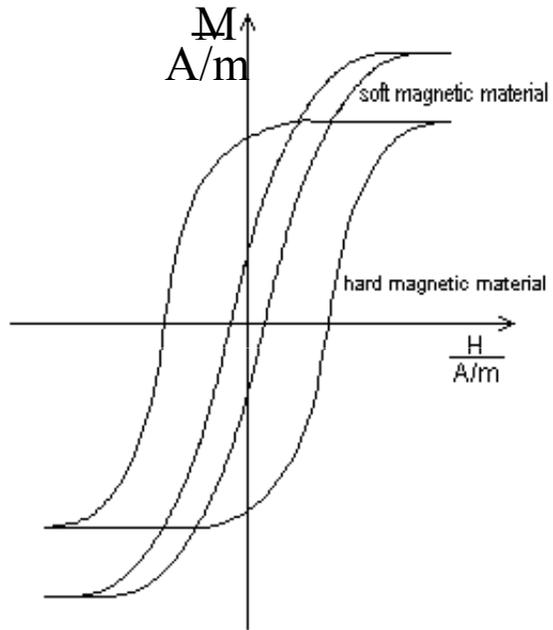


D.C. Jiles / Acta Materialia 51 (2003) 5907–5939

Tipos de materiales magnéticos

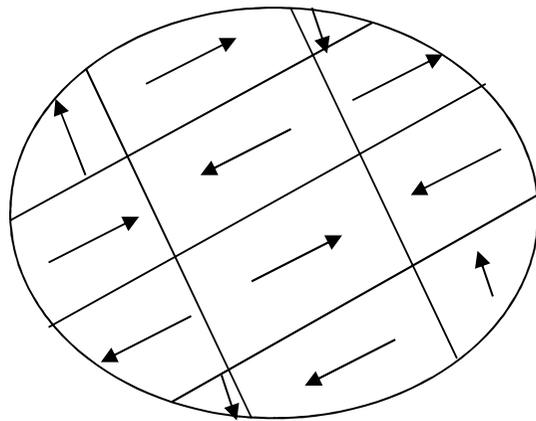


Tipos de materiales magnéticos

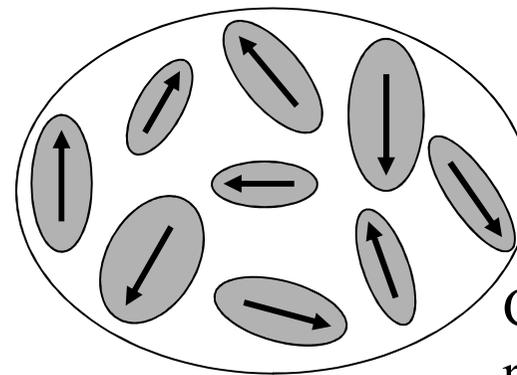


Ejemplos de materiales ferromagnéticos

Dominio: región donde todos los momentos están alineados



Monocristal “grande”
multidominio

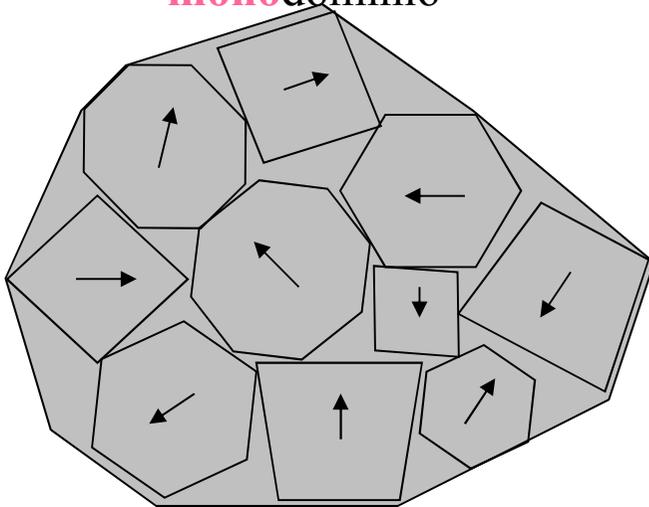


Conjunto de
partículas
cristalinas
monodominio

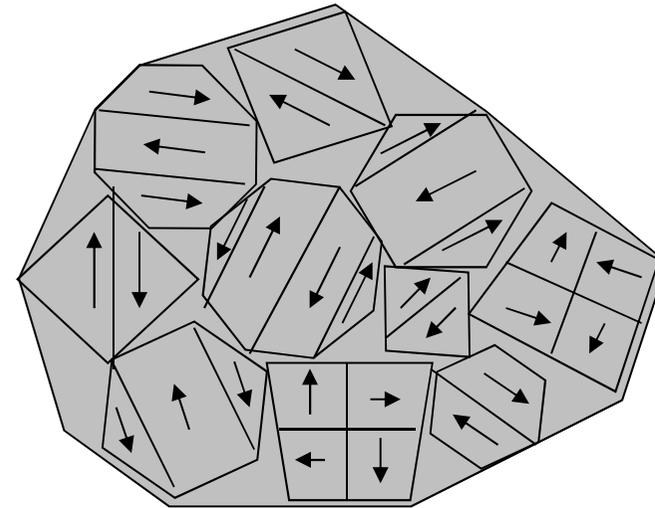
Ejemplos de **materiales ferromagnéticos**

Dominio: región donde todos los momentos están alineados

Policristal.
Conjunto de
cristales
monodominio

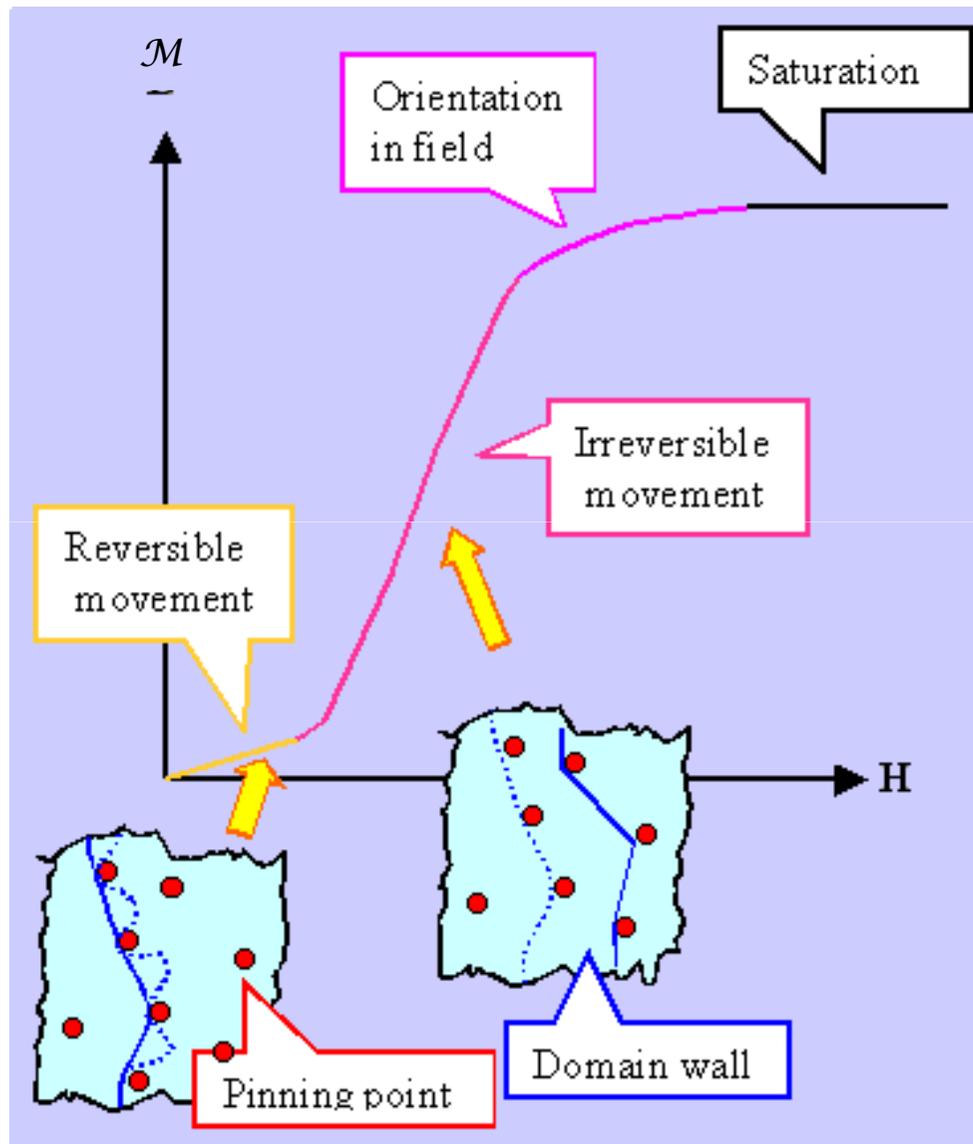


Policristal.
Conjunto de
cristales
multidominio



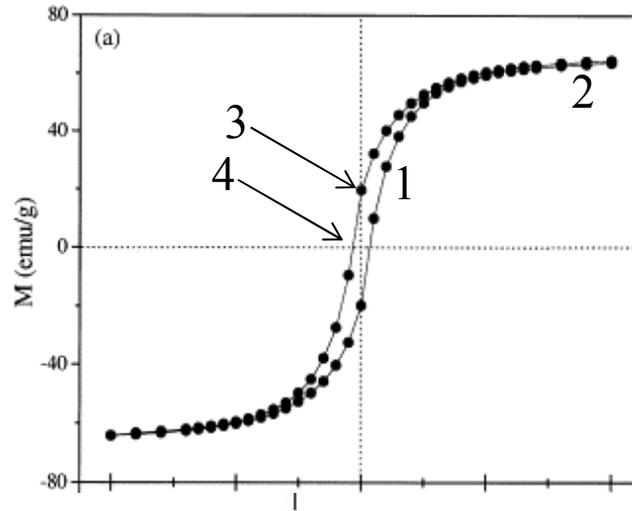
Procesos de magnetización

Materiales 'bulk'

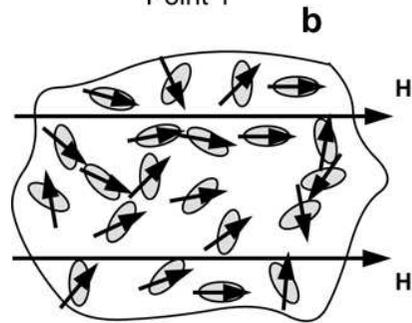


Procesos de magnetización

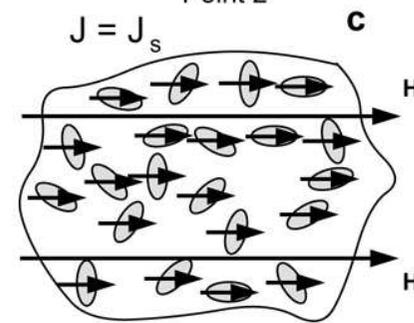
Nanopartículas
monodominio
anisotrópicas



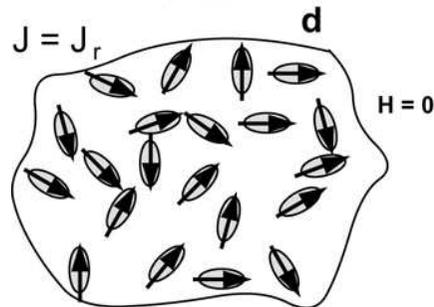
Point 1



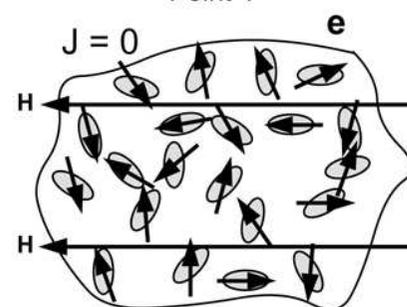
Point 2



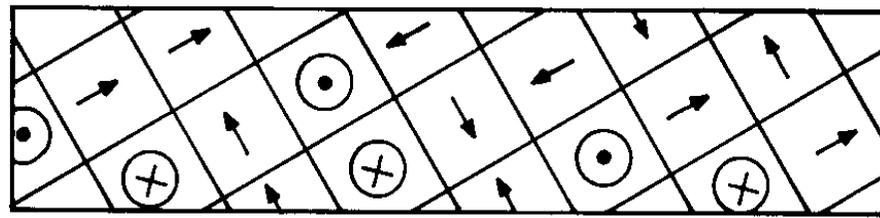
Point 3



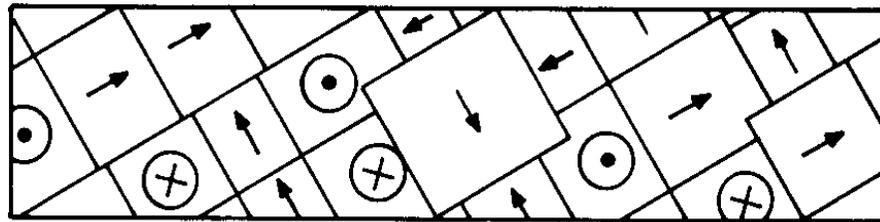
Point 4



Procesos de magnetización en un monocristal multidominio



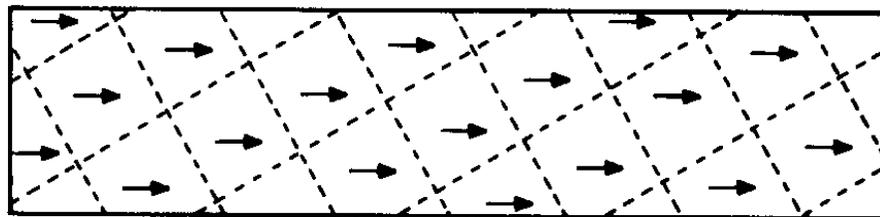
(a)



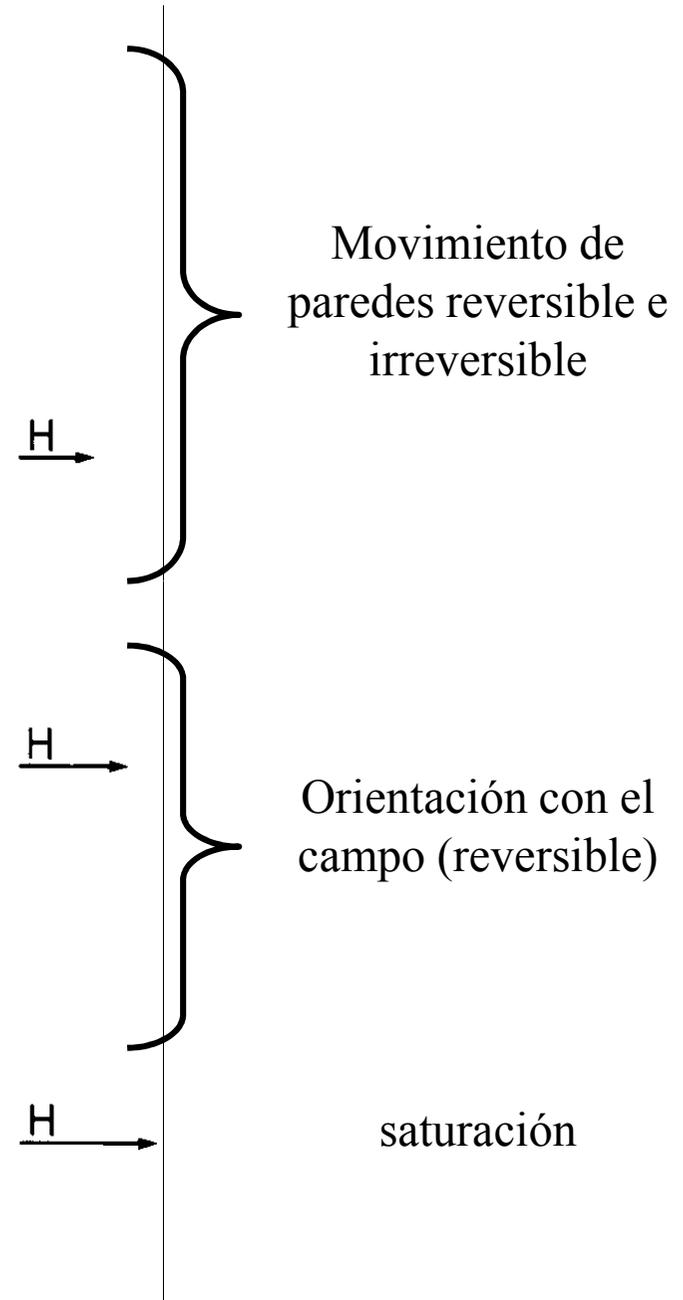
(b)



(c)

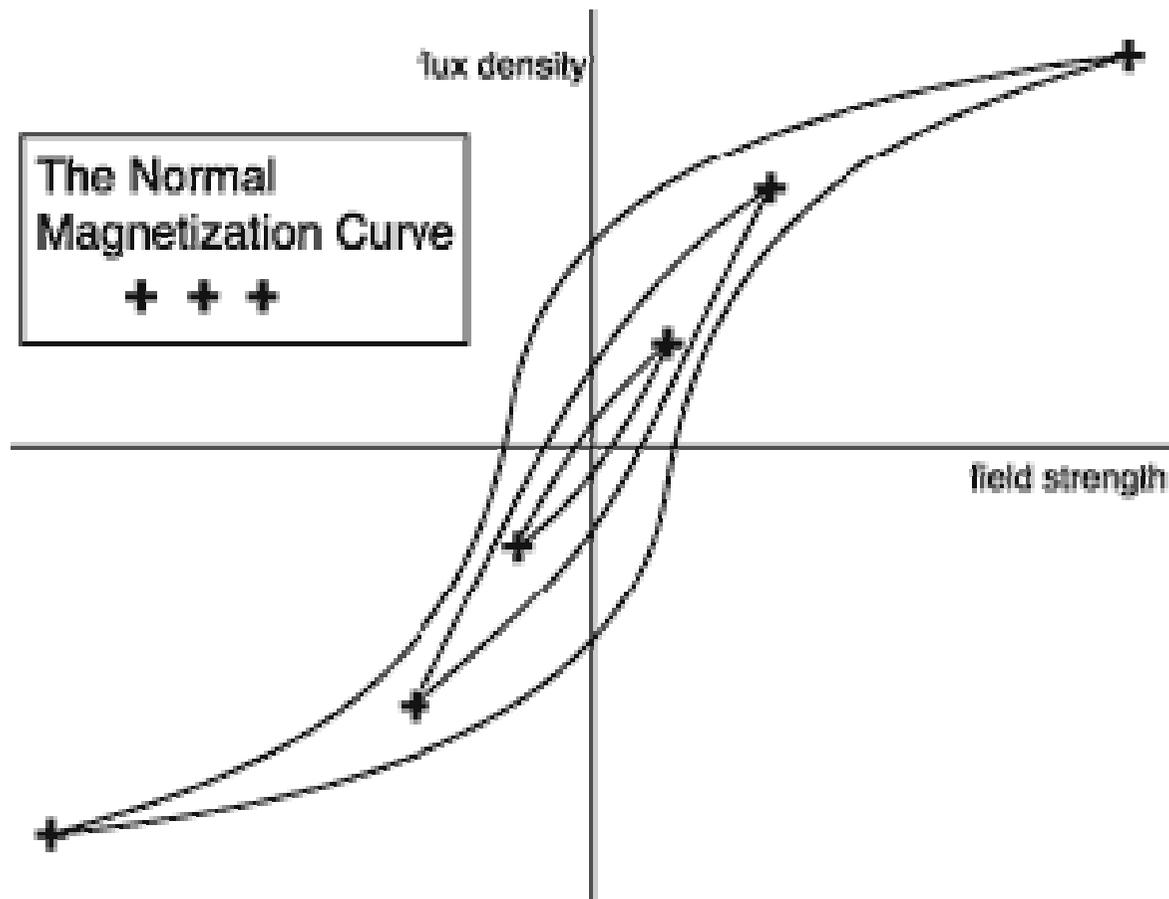


(d)

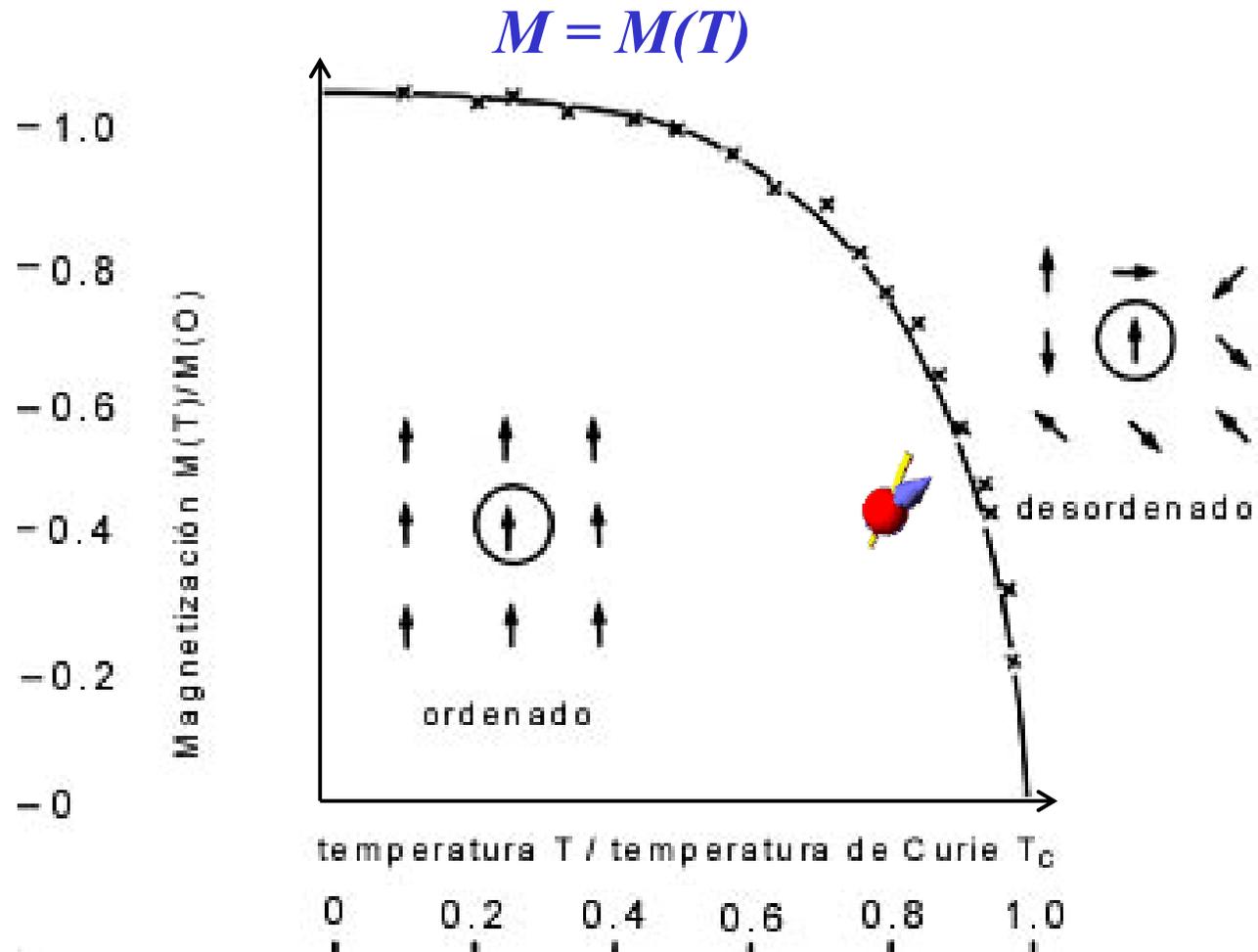


Procesos de magnetización

Ciclos menores



Magnetización vs temperatura



Ferro y ferrimagnetos

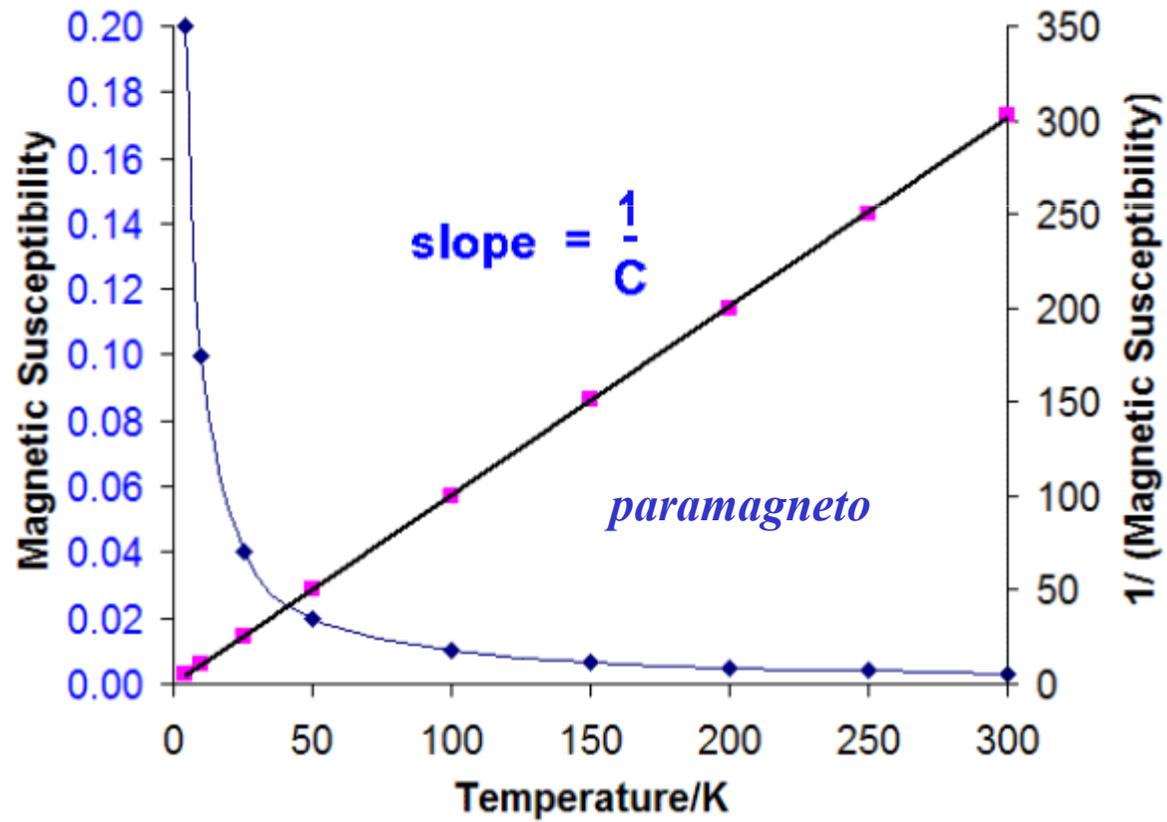
Magnetización vs temperatura

$$\chi = M/H$$

$$\chi(T) = \alpha/T$$

(Curie)

Curie Law Plots



Interacciones Magnéticas

Interacción Zeeman

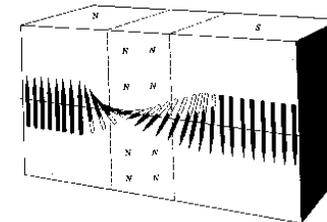
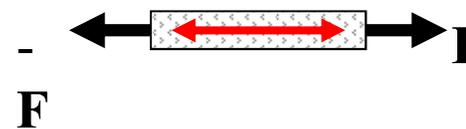
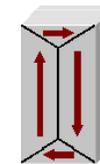
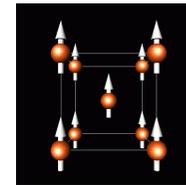
Interacción de Intercambio

Anisotropía Magnetocristalina

Energía Magnetostática

Energía Magnetoelástica

Energía de pared de Dominio



Interacción Zeeman

En presencia de un campo magnético externo \mathbf{H} cada momento sólo experimenta la interacción Zeeman.

$$E_i = -\vec{\mu}_i \cdot \vec{B} = -\mu_0 \vec{\mu}_i \cdot \vec{H}$$

$\mu_0 = 4 \pi \times 10^{-7}$ (unidades SI): permeabilidad del vacío

Si no hay interacción entre los momentos magnéticos: **paramagneto**

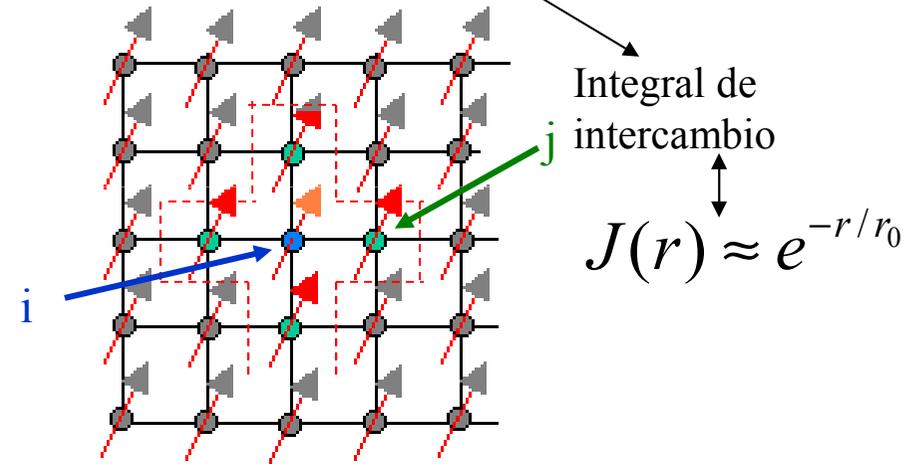
Interacciones Magnéticas

Intercambio: interacción de corto alcance

solamente interacción entre vecinos.

Un fenómeno **MC** conducente a ordenamiento ferro, ferri, antiferro, etc.,

$$E_J = -2 \sum_i^N \sum_j^z J_{i,j} \vec{S}_i \cdot \vec{S}_j$$



N átomos/iones en el sistema

Z primeros vecinos

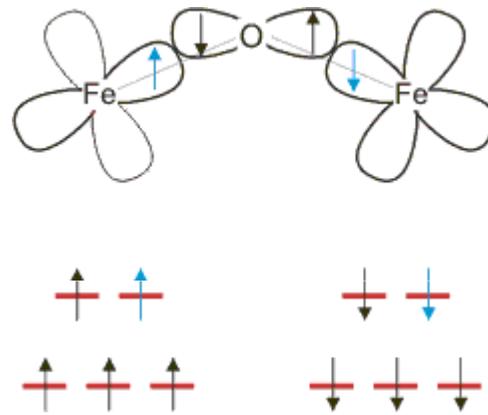
Interacción de Intercambio

$$E_J = -2 \sum_i^N \sum_j^z J_{i,j} \vec{S}_i \cdot \vec{S}_j$$



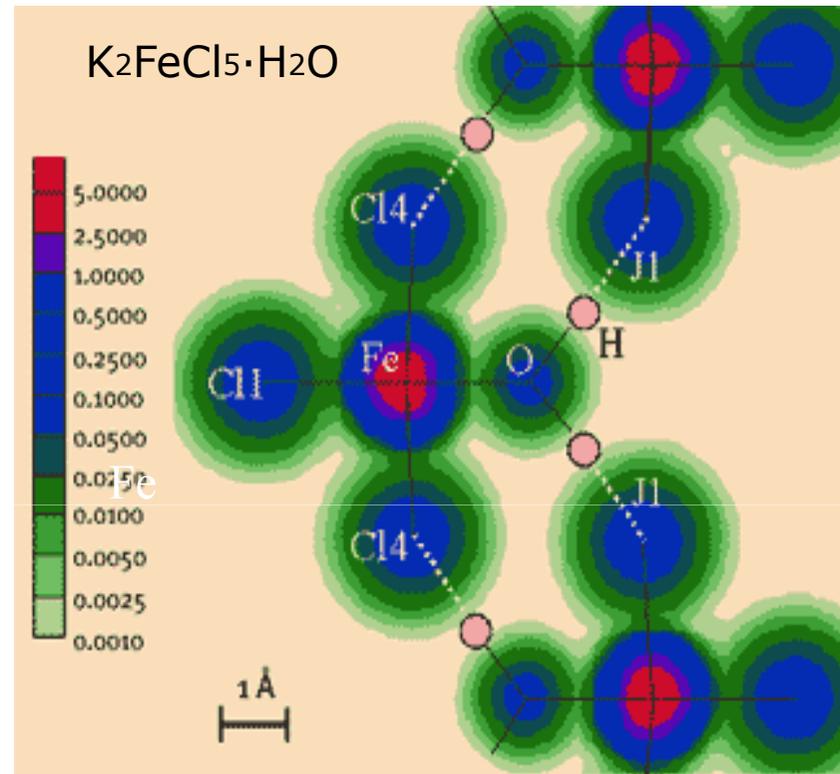
overlap of electrons
causes spin-spin coupling

Interacción de Superintercambio



Acoplamiento entre espines del Fe
mediada por oxígenos

Interacción de Superintercambio



Densidad de spin en el plano que contiene el camino de super intercambio $FeCl_1 \cdots (H)OFe$. Normalizada a $5 \mu_B$ por octaedro.

Interacción Zeeman + intercambio

En presencia de un campo magnético externo \mathbf{H} cada momento interactúa con los vecinos vía intercambio y con el campo externo vía la interacción Zeeman.

$$E_i = -\vec{\mu}_i \cdot \vec{B}_{ef} = -\mu_0 \vec{\mu}_i \cdot \vec{H} - 2 \sum_j J \vec{s}_i \cdot \vec{s}_j$$

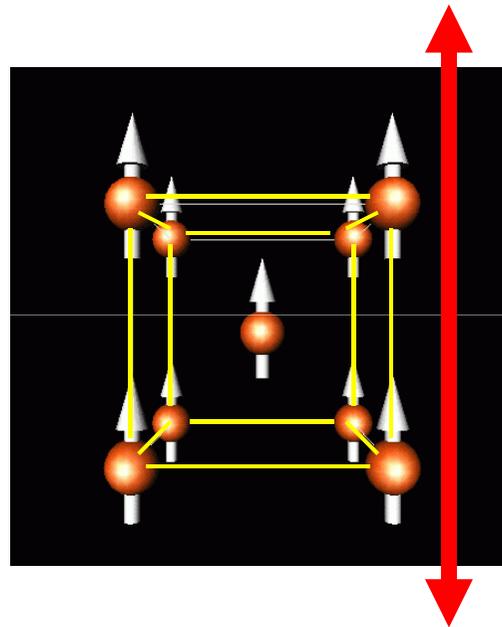
$$\vec{\mu} = -g \vec{s} \mu_B$$

$$E_i = -\vec{\mu}_i \cdot \vec{B}_{ef} = \mu_0 \mu_B g \vec{s}_i \cdot \vec{H} - 2 \sum_j J \vec{s}_i \cdot \vec{s}_j$$

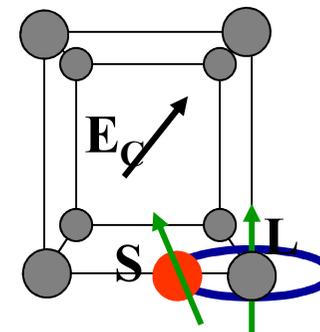
Interacciones Magnéticas

Anisotropía magnetocrystalina

Fe



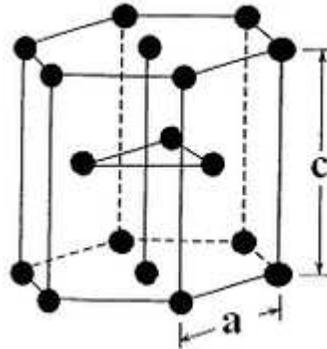
interacciones
Spin – órbita +
campo cristalino



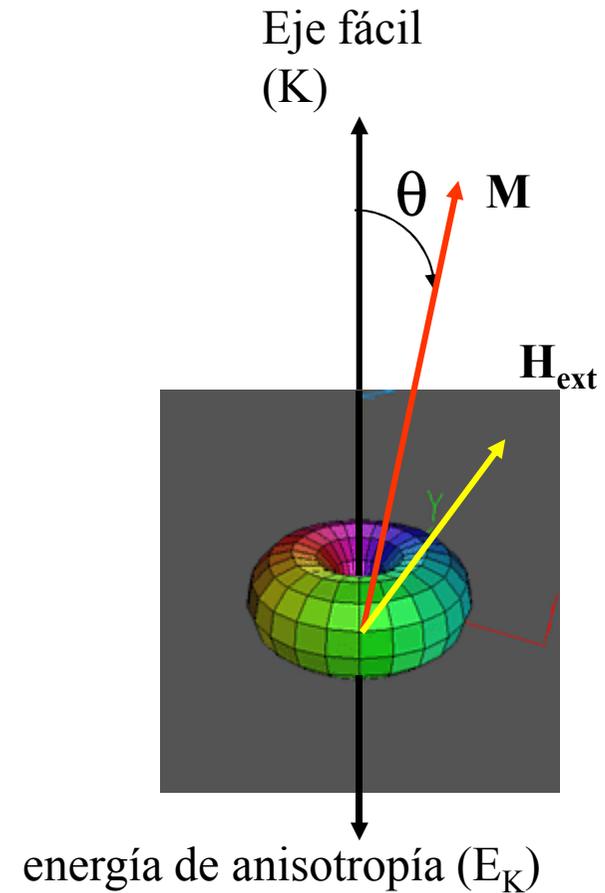
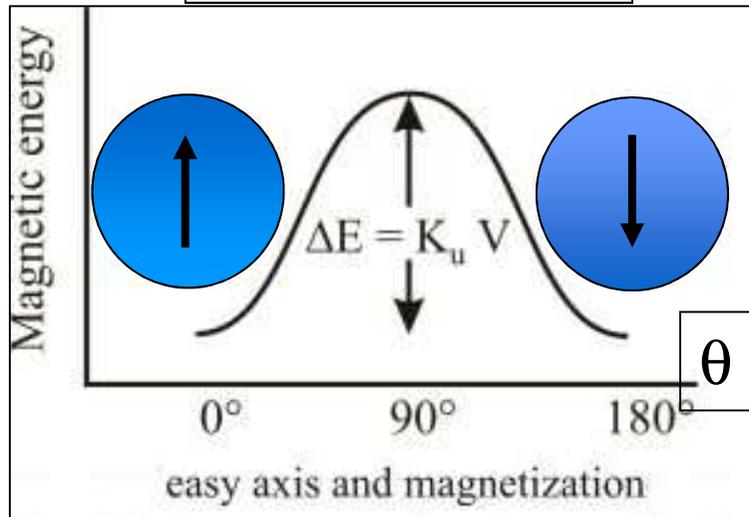
Estructura cristalina :
anisotropía
magnetocrystalina

Energía de anisotropía Magnetocrystalina

situación uniaxial; ejemplo: Co hcp

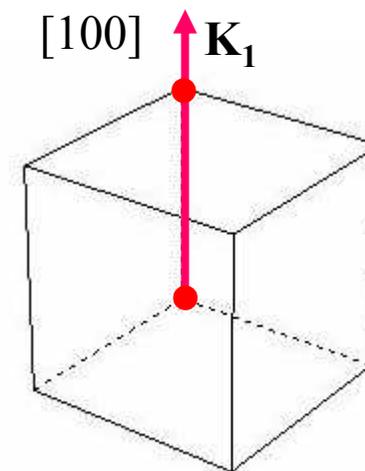
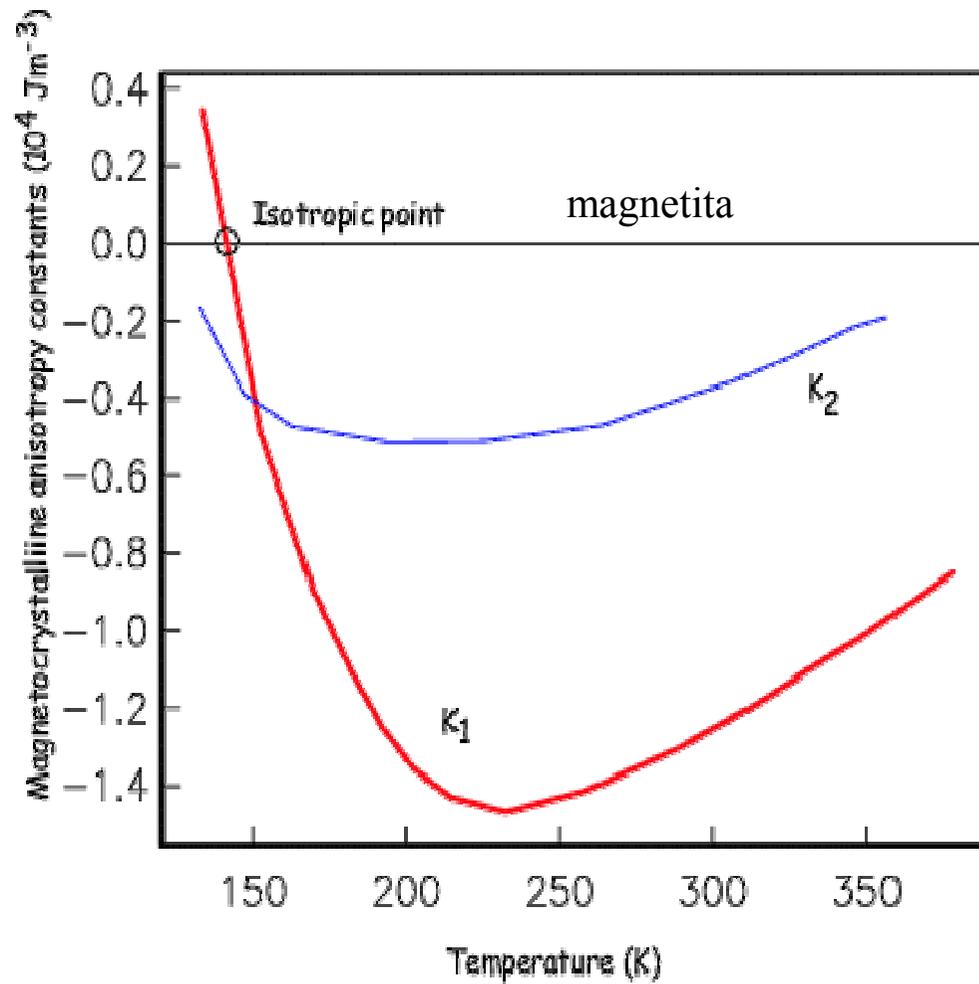


$$E_K = KV \sin^2 \theta$$



Energía de anisotropía Magnetocristalina

situación cúbica; ejemplo: Fe_3O_4



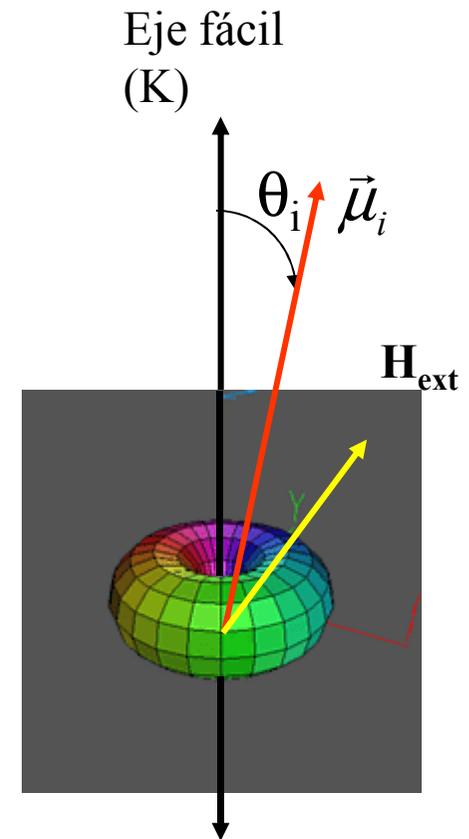
Interacción Zeeman + intercambio + anisotropía

$$E_i = -\vec{\mu}_i \cdot \vec{B}_{ef} = \mu_0 \mu_B g \vec{s}_i \cdot \vec{H} - 2 \sum_j J \vec{s}_i \cdot \vec{s}_j + KV_i \sin^2 \theta_i$$

$$\sin^2 \theta_i = 1 - \cos^2 \theta_i$$

$$\cos \theta_i = \hat{e}_K \cdot \hat{e}_{\mu_i}$$

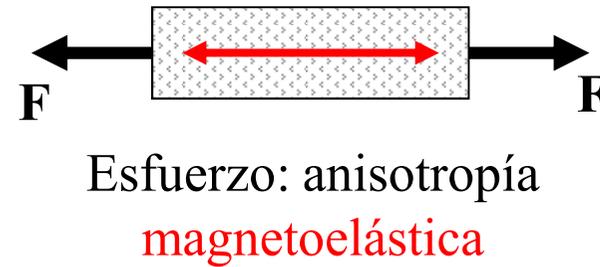
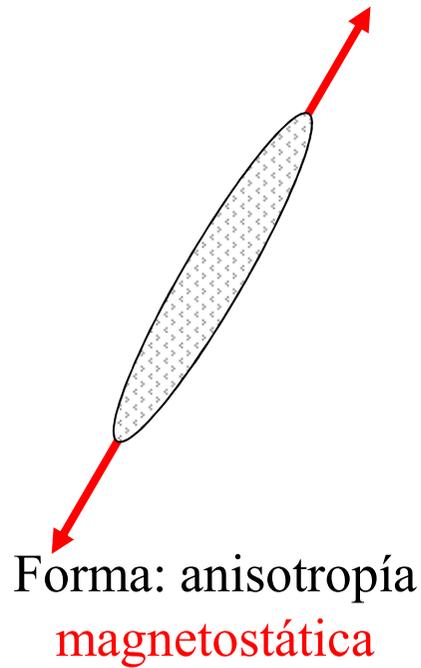
$$\sin^2 \theta_i = 1 - \frac{(\vec{e}_K \cdot \vec{s}_i)^2}{s_i^2}$$



$$E_i = -\vec{\mu}_i \cdot \vec{B}_{ef} = \mu_0 \mu_B g \vec{s}_i \cdot \vec{H} - 2 \sum_j J \vec{s}_i \cdot \vec{s}_j - KV_i \frac{(\vec{e}_K \cdot \vec{s}_i)^2}{s_i^2}$$

Interacciones Magnéticas

Anisotropía – otras fuentes

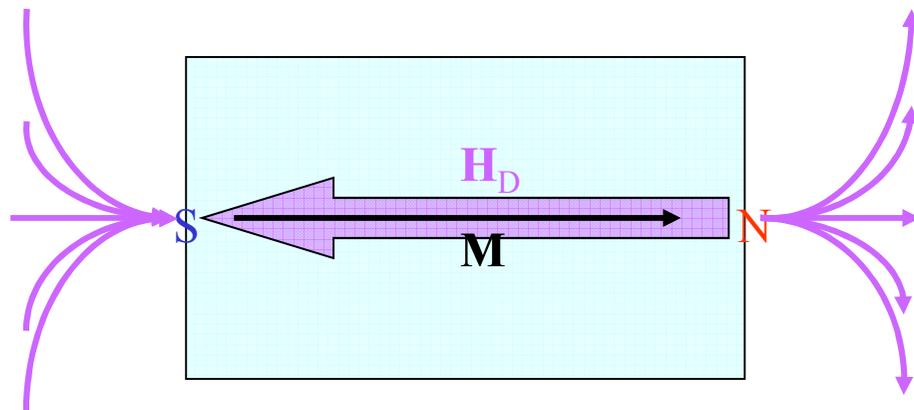
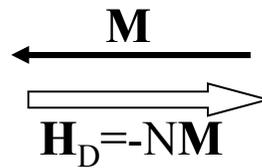


energía magnetostática

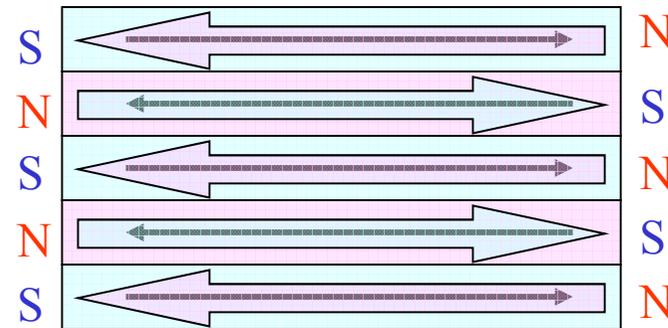
$$E_M = -\frac{\mu_0}{2} \int \vec{M} \cdot \vec{H}_D dV = \alpha(N_i) V \mu_0 M_S^2$$

Campo demagnetizante

Número y estructura de dominios



mono dominio

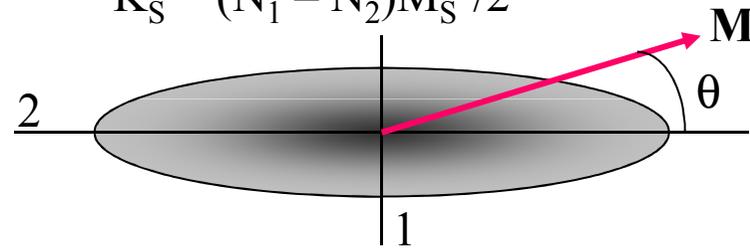


Multidominio

energía magnetostática

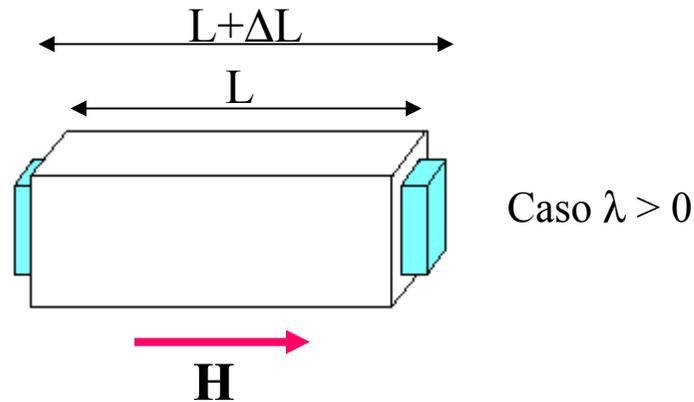
Anisotropía de **forma**

$$K_S = (N_1 - N_2)M_S^2/2$$

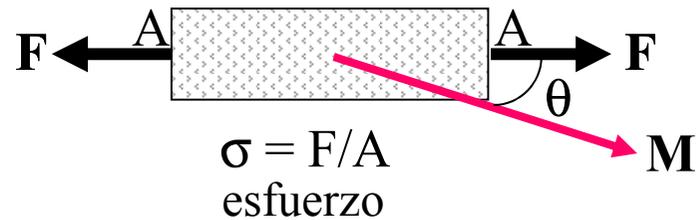


$$E_S = K_S V \sin^2 \theta$$

anisotropía magnetoelástica



$$\lambda_s = \Delta L / L \text{ (magnetostricción)}$$



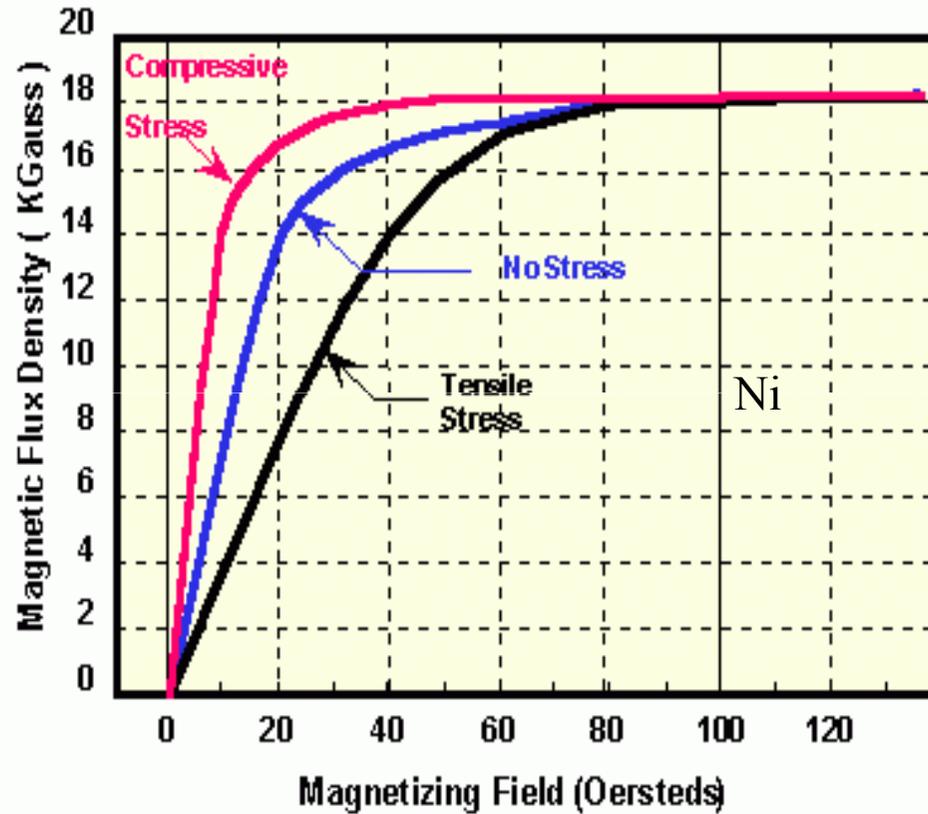
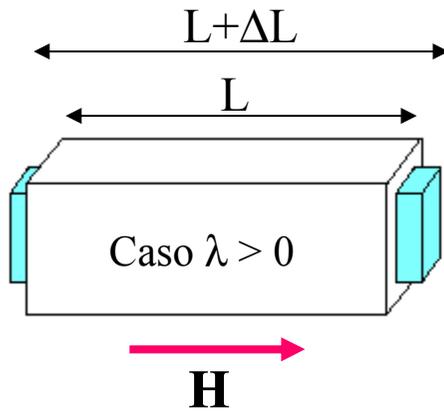
$$e_\sigma = K_\sigma V \sin^2 \theta$$

densidad de energía magnetoelástica

$$K_\sigma = (3/2) \lambda \sigma$$

Constante de anisotropía magnetoelástica

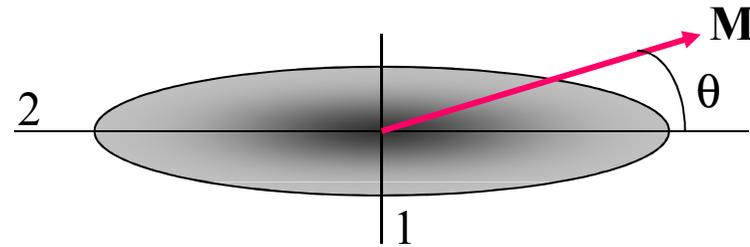
anisotropía magnetoelástica



$$e_{\sigma} = (3/2) \lambda \sigma \sin^2 \theta$$

densidad de energía magnetoelástica

anisotropía efectiva



$$E_{K_{ef}} = K_{ef} V \sin^2 \theta$$

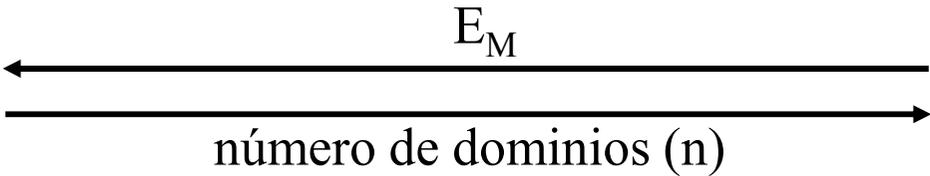
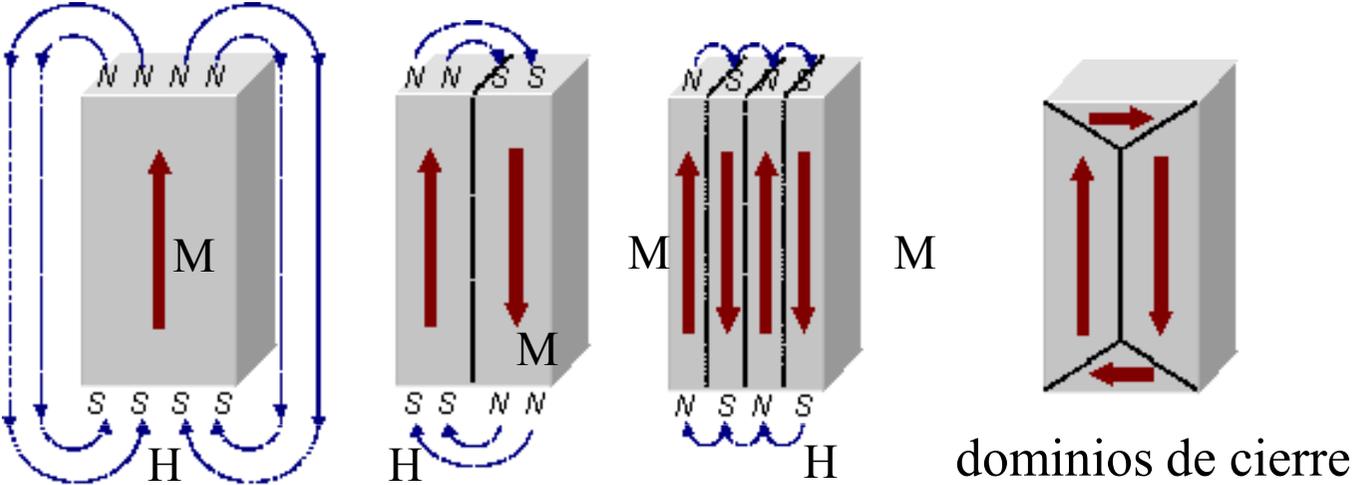
$$K_{ef} = K_C + K_S + K_\sigma + \dots$$

← cristalina

↓ forma

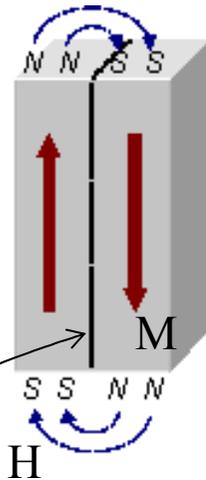
→ elástica

energías magnetostática + pared de dominio

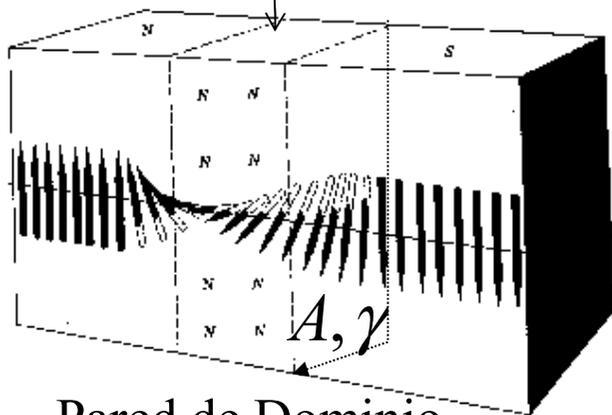


$$E_M \approx \frac{\alpha V \mu_0 M_S^2}{n} \quad \alpha < 1$$

energías magnetostática + pared de dominio

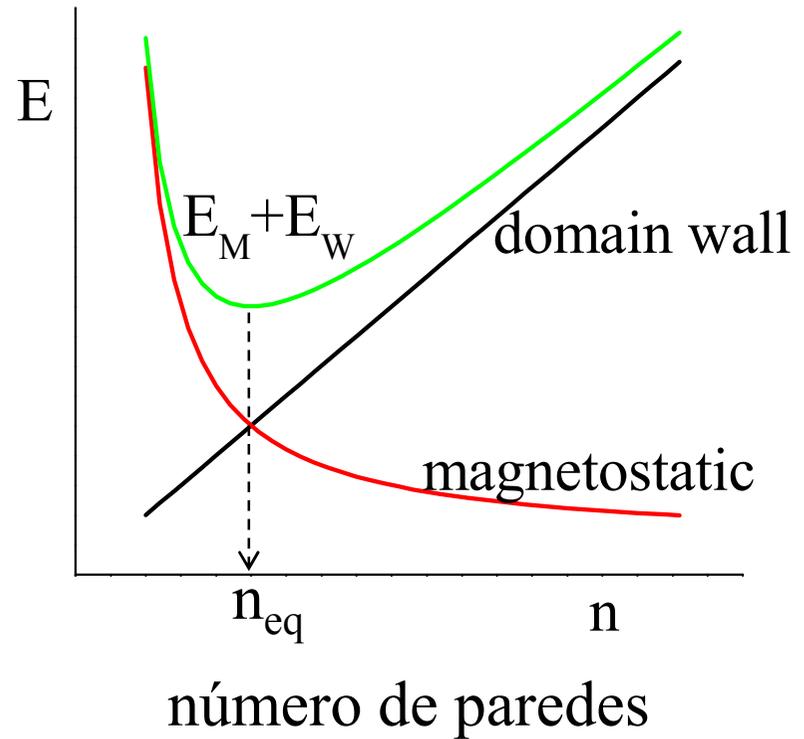


$$E_M \approx \frac{\alpha V \mu_0 M_S^2}{n}$$



$$E_W \approx n A \gamma$$

Pared de Dominio
(Bloch)

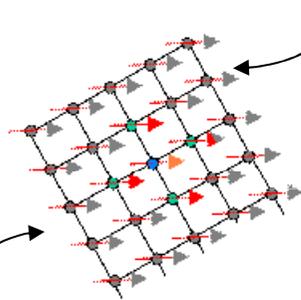
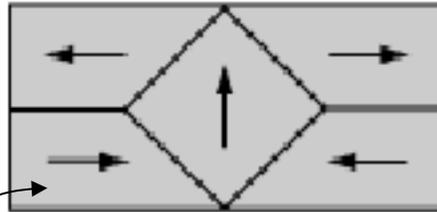


número de paredes

dominios magnéticos en un ferromagneto; pequeñas partículas

bulk Cristal $>10^{15}$ átomos

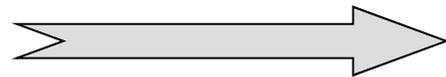
$>10\ \mu\text{m}$



dominio:

1-10 μm (10^{12}
a 10^{15} átomos)

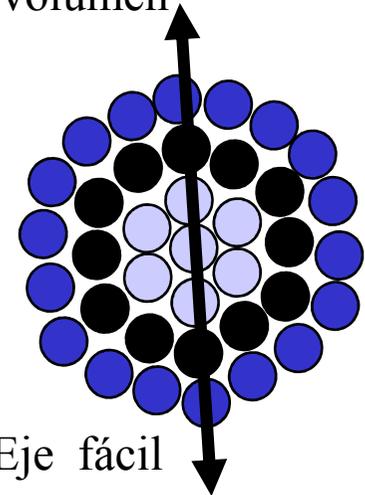
partícula submicrométrica:
($< 10^{12}$ átomos)



monodominio



Alta relación
superficie/volumen



superparamagneto

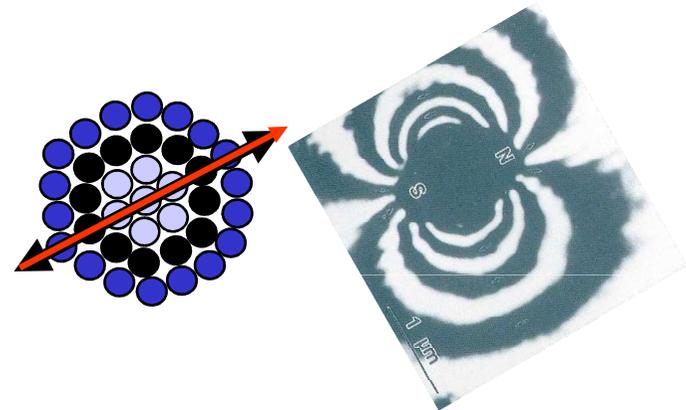
Partículas magnéticas monodominio que no interactúan entre sí. La partícula tiene un momento total igual a la suma vectorial de sus momentos atómicos (supermomento). Poseen anisotropía (eje fácil).

$$\vec{\mu}_p = \sum_i \vec{\mu}_i^{at}$$

$$\vec{\mu}_p = N\vec{\mu}_i^{at}$$

En el caso más simple:

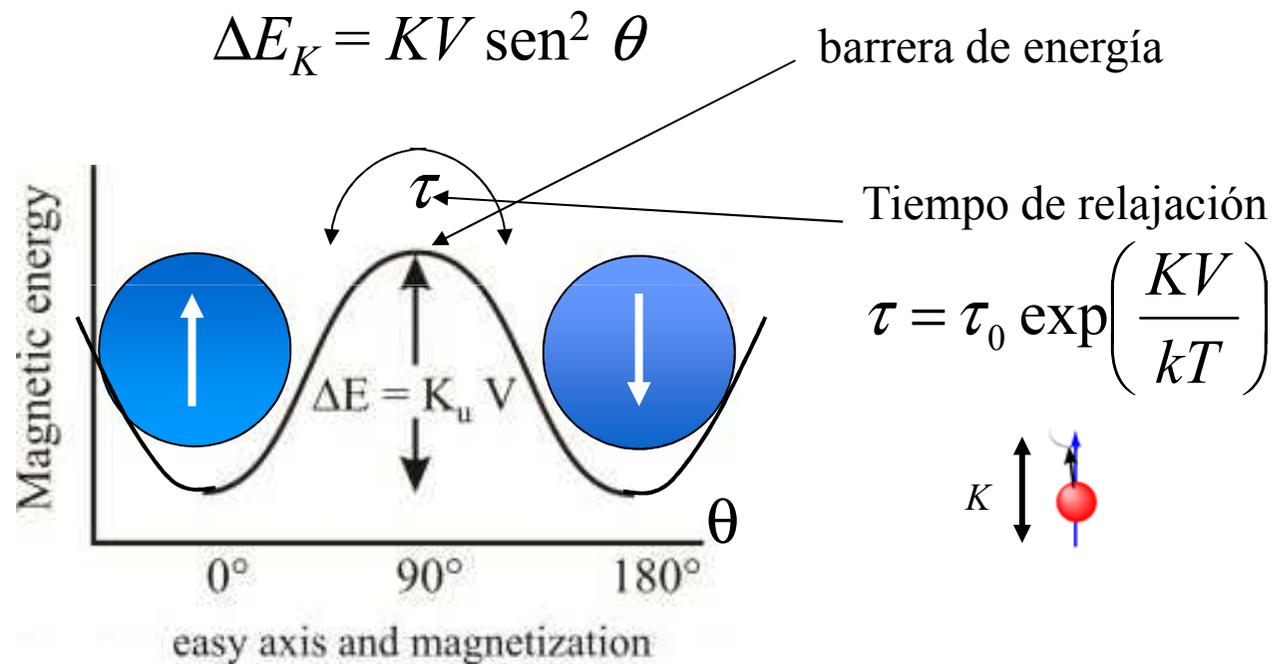
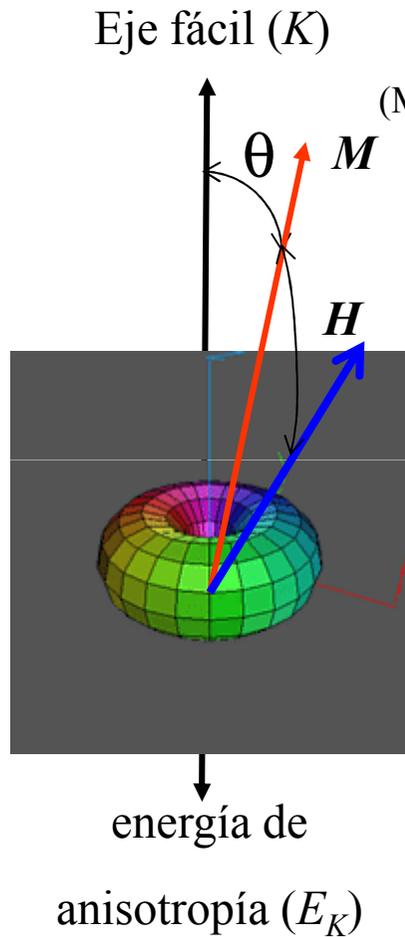
K



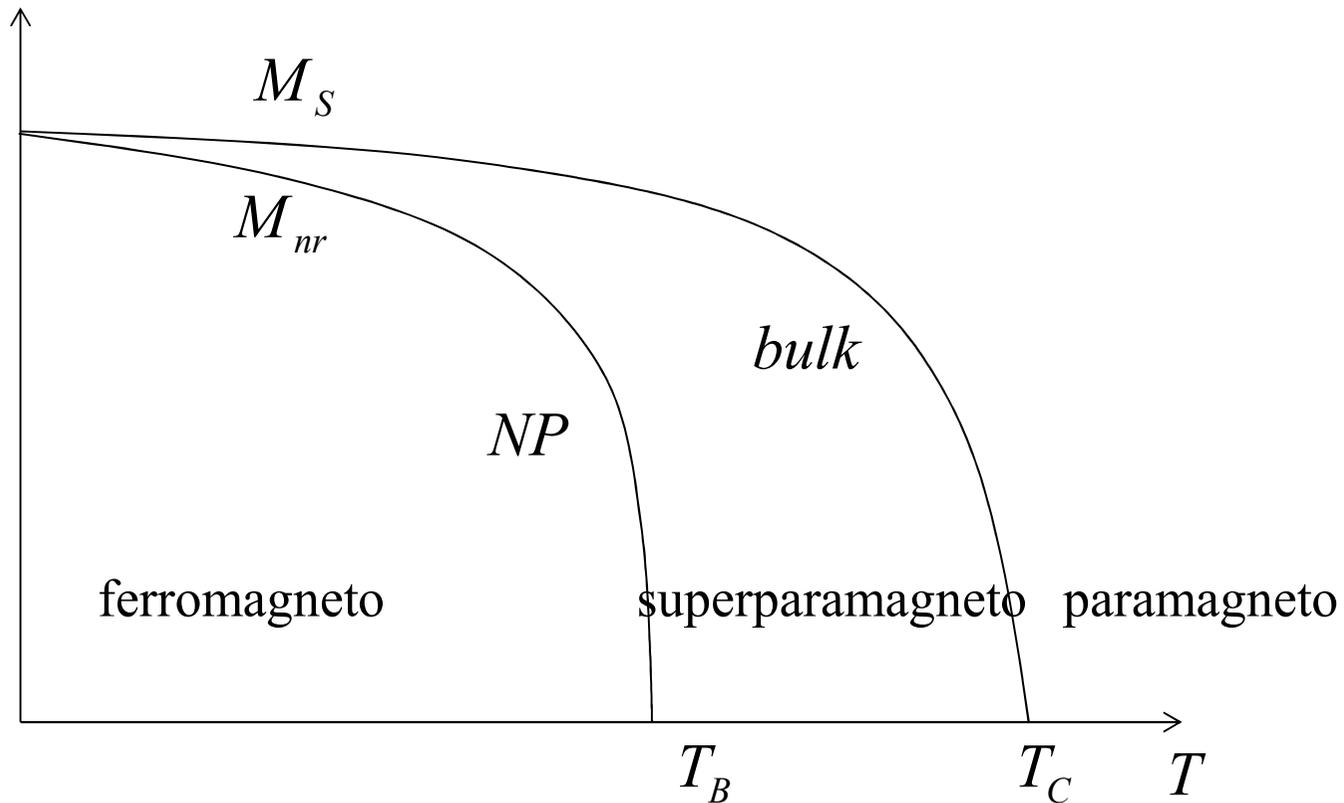
A temperaturas altas, en presencia de un campo magnético externo \mathbf{H} sólo se observa la interacción Zeeman de la partícula con el campo.

$$E_p = -\mu_0 \vec{\mu}_p \cdot \vec{H}$$

Propiedades magnéticas de partículas **pequeñas, monodominio,** Efecto de la temperatura: **régimen superparamagnético**



Efecto de la anisotropía y la temperatura en partículas pequeñas

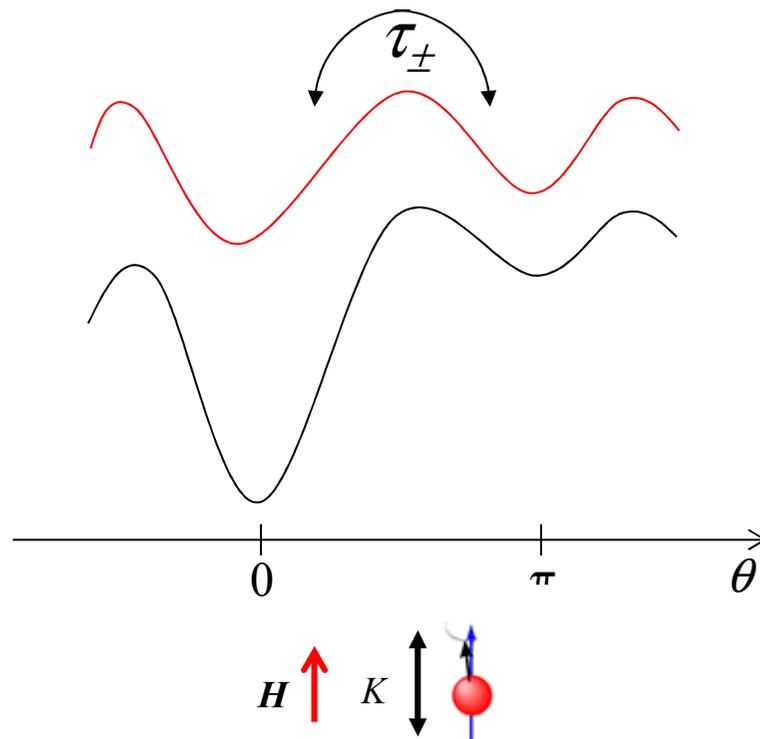


$$\vec{M}_{nr}(T) = \langle \vec{M}_S \rangle_T \approx \vec{M}_S(0)(1 - \alpha T) \quad (BT)$$

$$\alpha = \frac{kT}{KV}$$

Propiedades magnéticas de partículas **pequeñas, monodominio,**
 Efecto de la temperatura: **régimen superparamagnético**

$$\Delta E_K = KV \text{sen}^2 \theta - \mu_0 \mu H \cos \theta$$



Tiempo de relajación

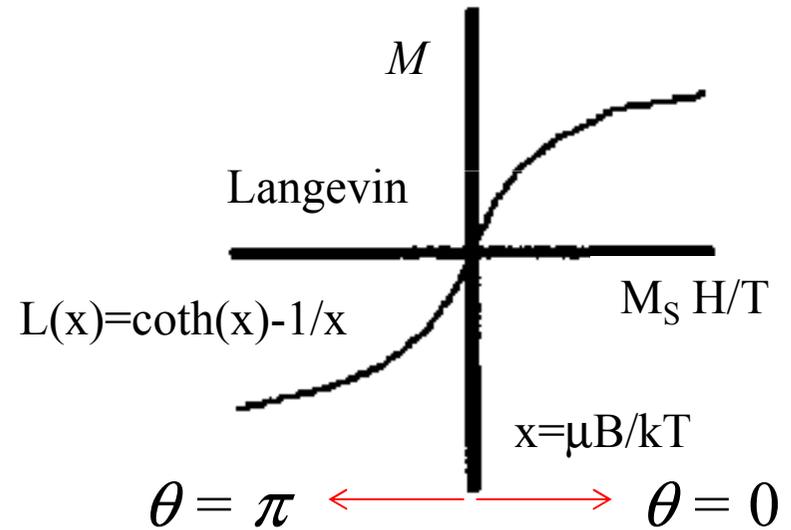
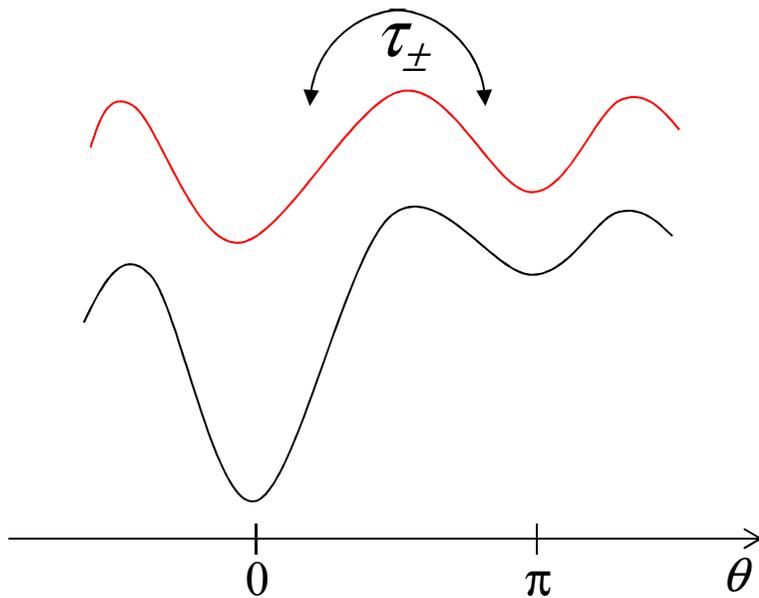
$$\tau = \tau_0 \exp\left(\frac{KV}{kT} \left(1 + \frac{H}{H_K}\right)^2\right)$$

$$H_K = \frac{2K}{\mu_0 M_S}$$

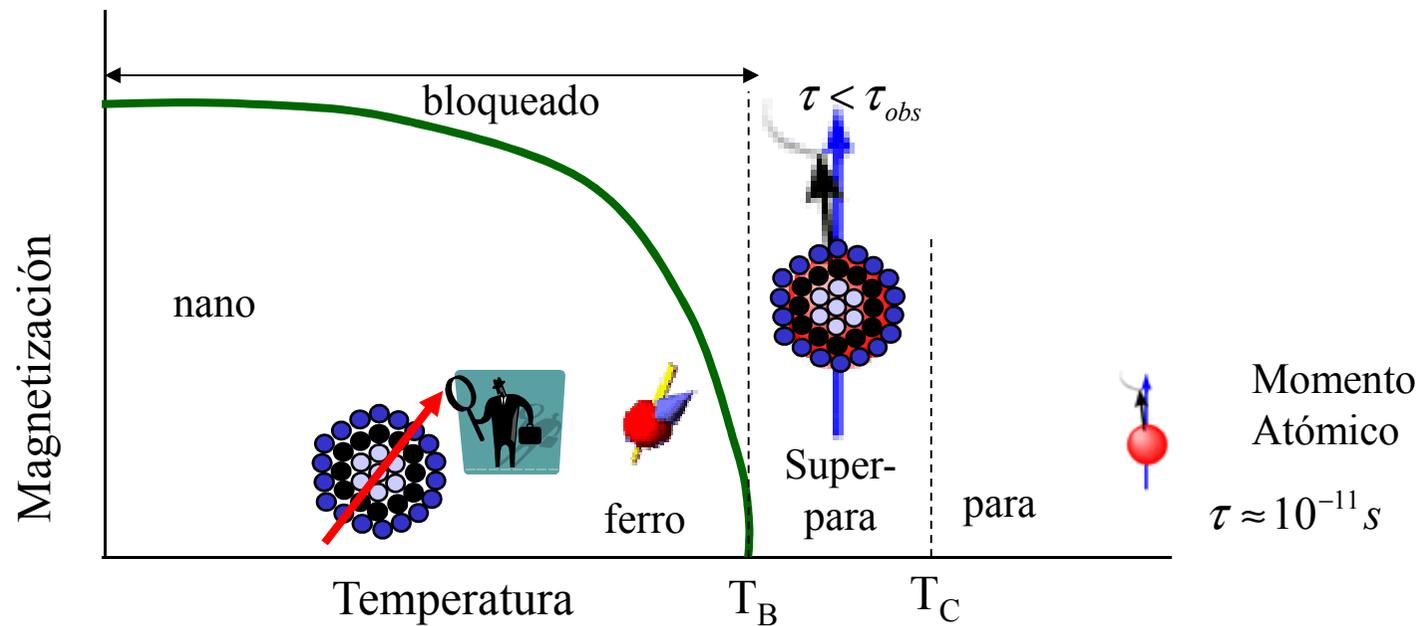
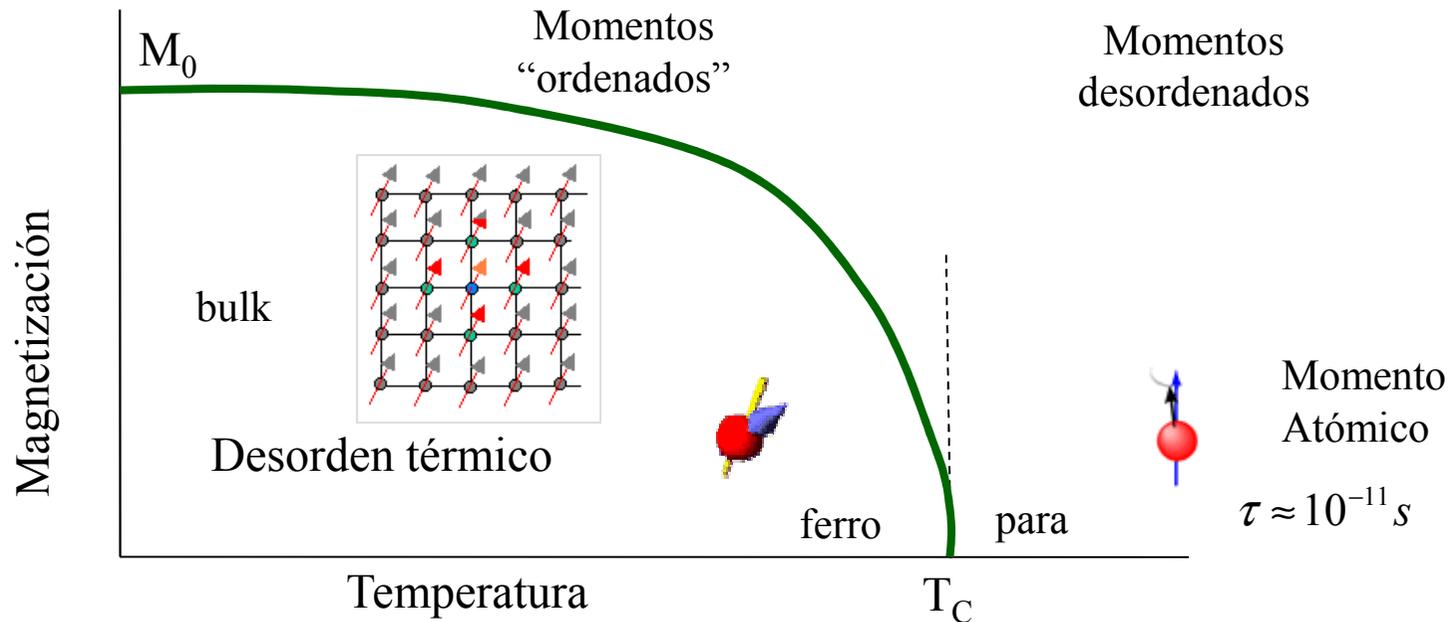
Propiedades magnéticas de partículas **pequeñas, monodominio,**
 Efecto de la temperatura: **régimen superparamagnético**

$$\Delta E_K = KV \text{sen}^2 \theta - \mu_0 \mu H \cos \theta$$

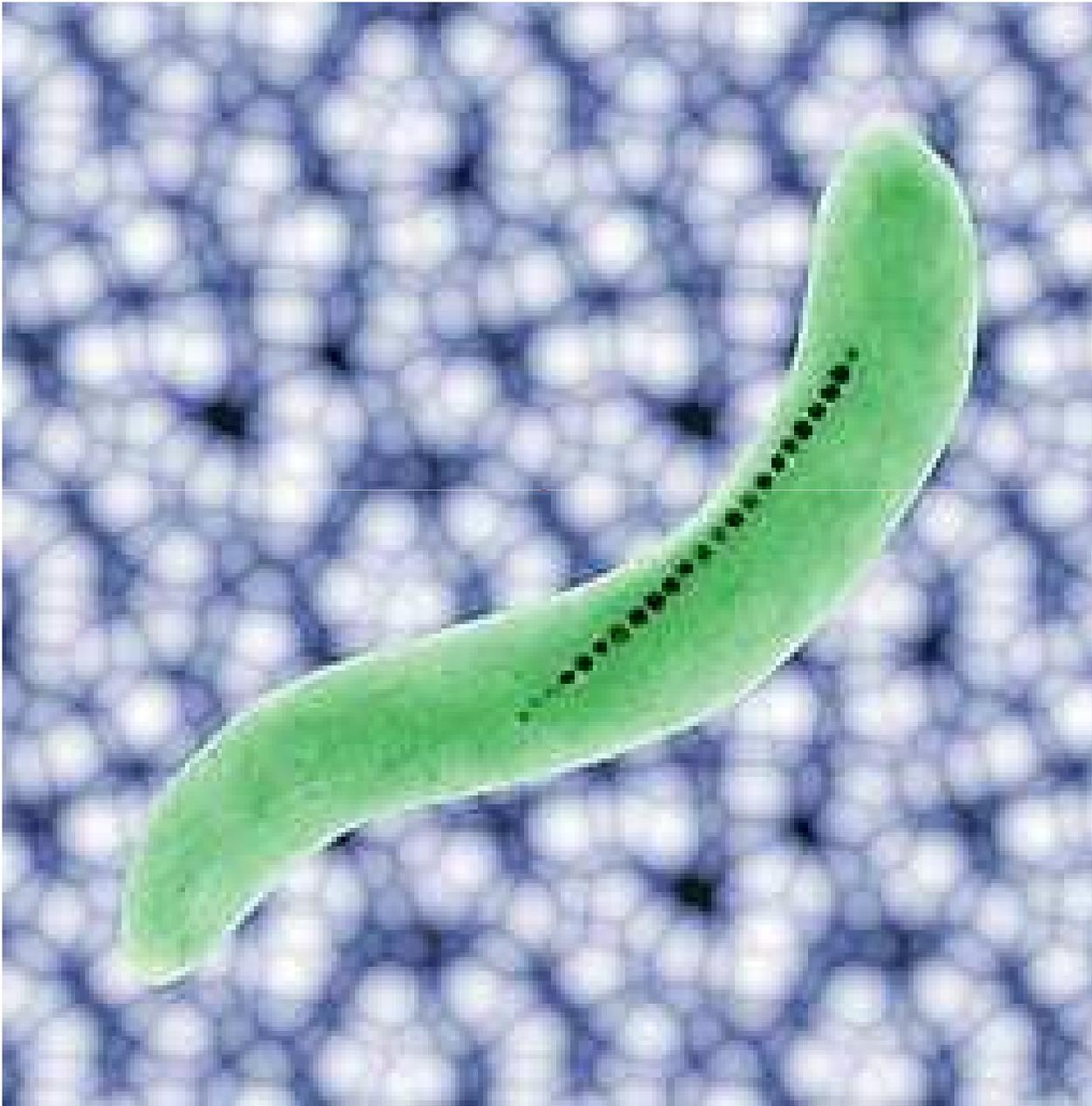
Teniendo en cuenta efectos térmicos



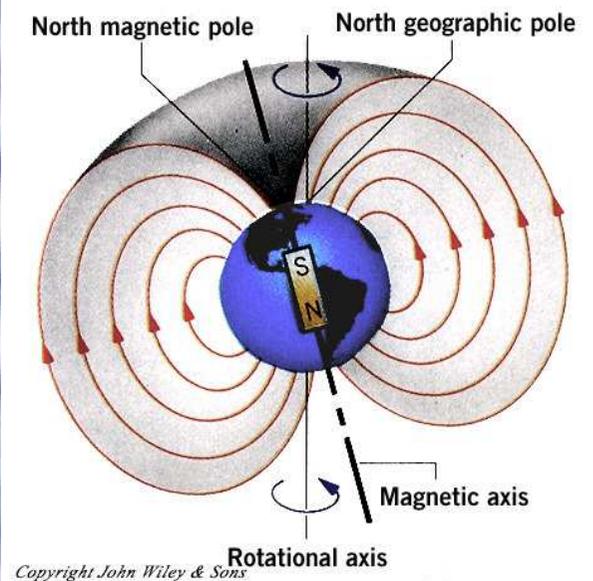
Propiedades magnéticas de partículas **pequeñas, monodominio,**



Propiedades magnéticas de partículas **pequeñas, monodominio,**

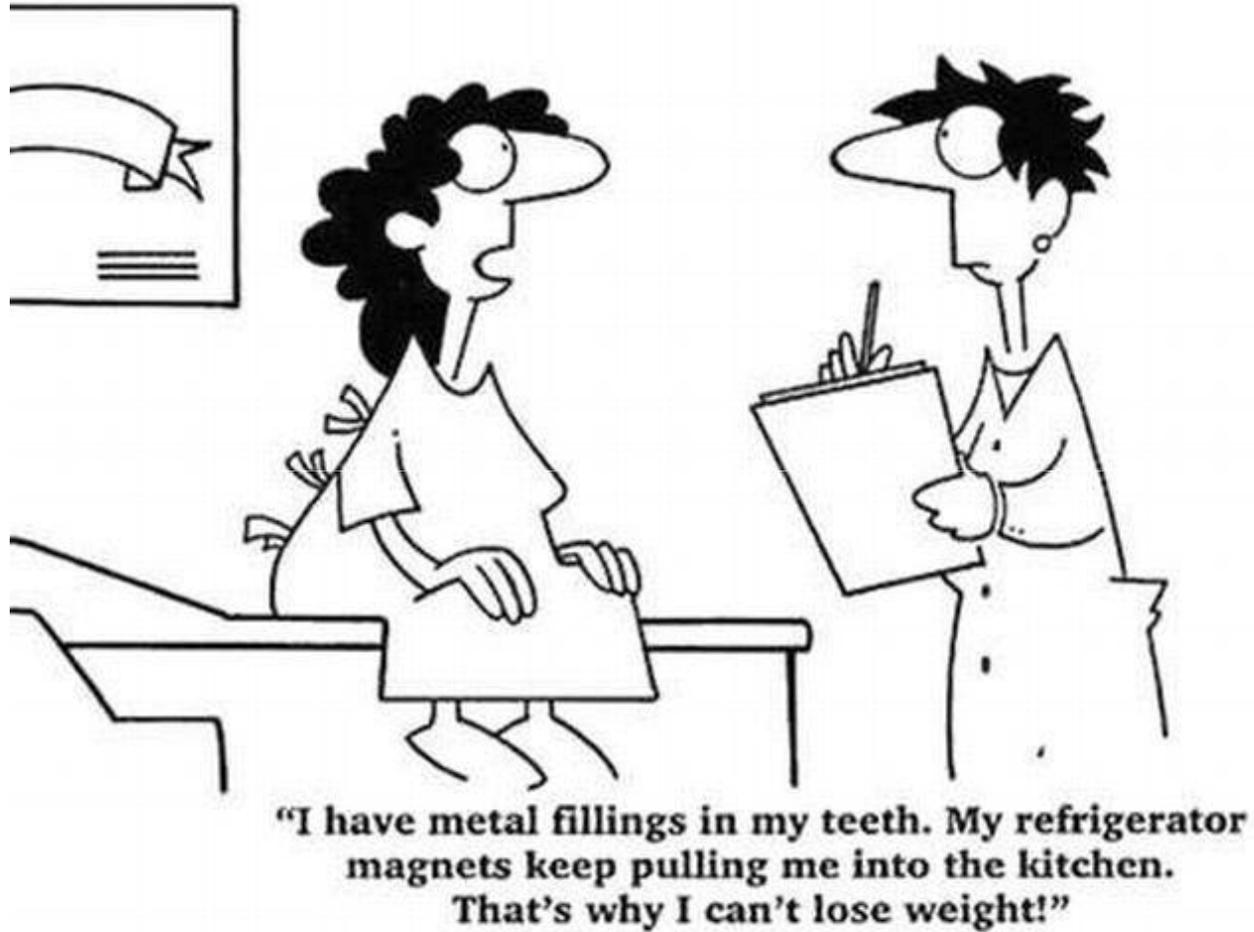


Magnetic or
“magnetotactic”
bacteria



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La dieta y los materiales magnéticos...



Fin módulo