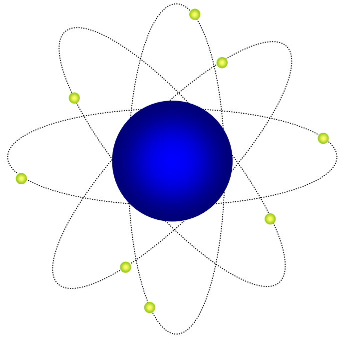
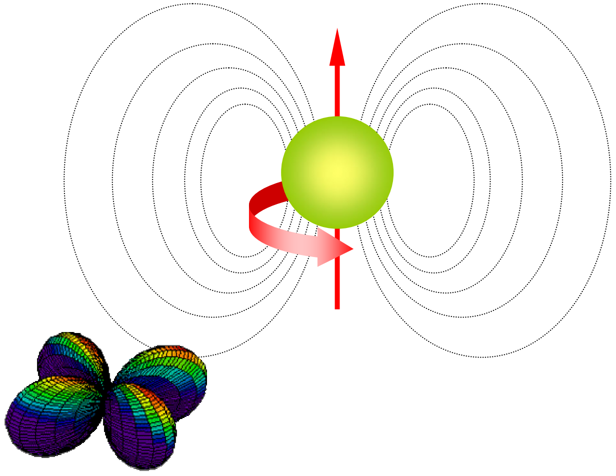
Kap. 12
Magnetic solids

What is magnetism?

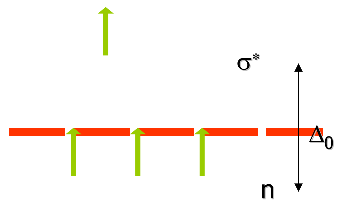


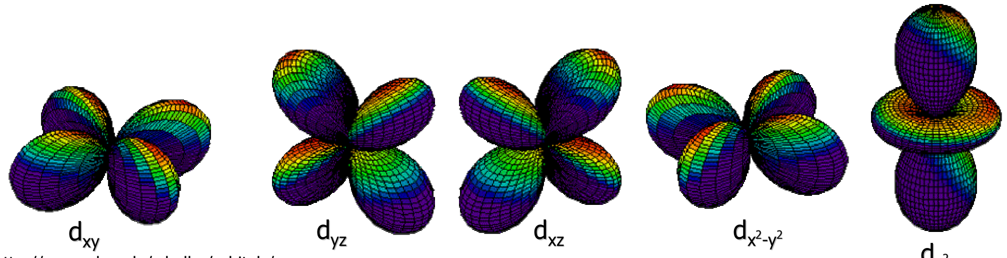
What is magnetism?



What is magnetism?

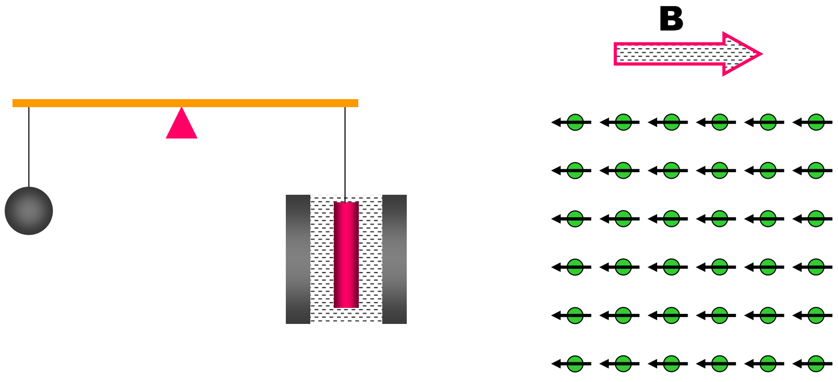
Cr	Mn	Fe	Co	Ni





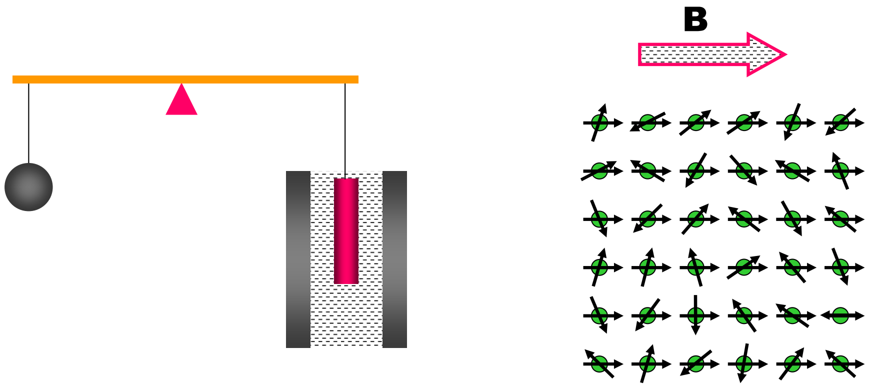
http://www.uky.edu/~holler/orbitals/

Diamagnetism



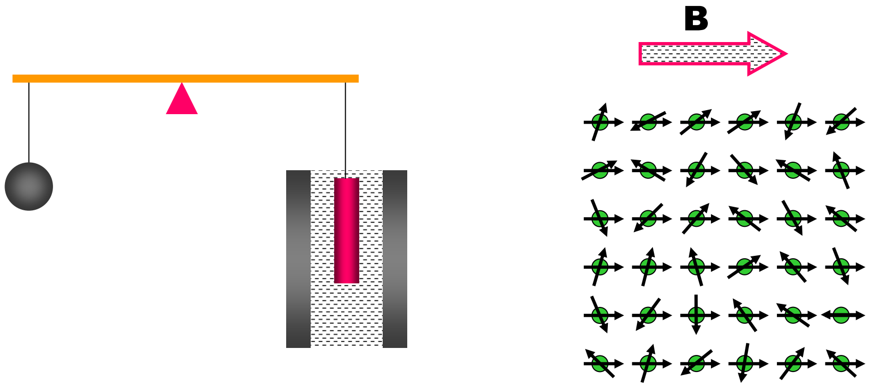
Diamagnetism occurs in materials with no unpaired electrons. Al_2O_3, MgO etc.

Paramagnetism



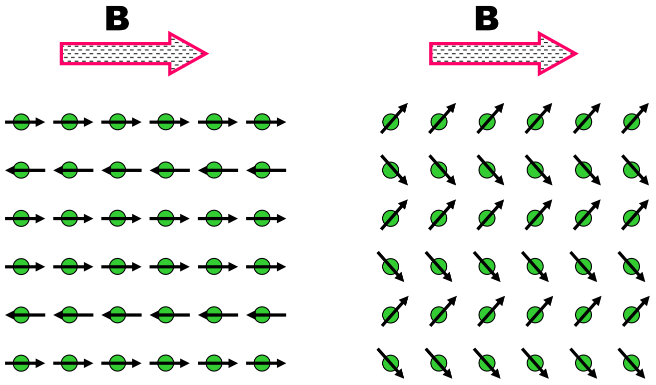
Paramagnetism occurs in materials with unpaired electrons but insufficient long range interaction between their magnetic moment. Typical phenomena at high temperatures.

Ferromagnetism



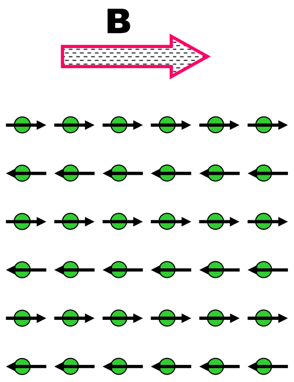
Ferromagnetism occurs in materials that has an exchange mechanism which ensures parallel orientation between the magnetic moments.

Ferri magnetism



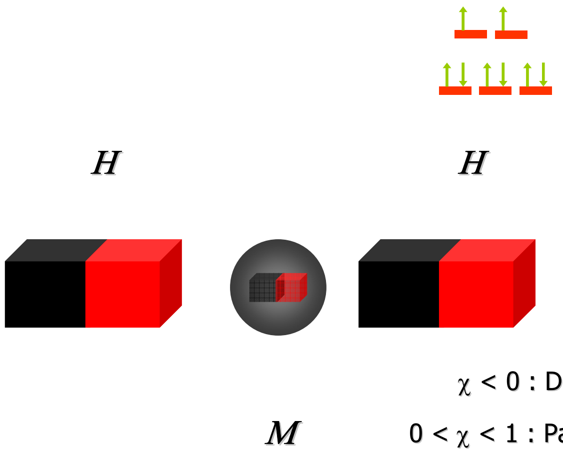
Ferrimagnetism occurs in materials that has an exchange mechanism which ensures a net orientation between the magnetic moments.

Anti-ferro magnetism



Anti ferromagnetism occurs in materials that has an exchange mechanism which ensures anti-parallel orientation between the magnetic moments.

What to measure?



$\chi < 0$: Diamagnetic

$0 < \chi < 1$: Paramagnetic

$\chi > 1$: Ferromagnetic

$$M = \chi x H$$

Magnetic susceptibility

What to measure?

$$\chi = \frac{C}{T}$$

$$\chi = \frac{C}{T-\theta}$$

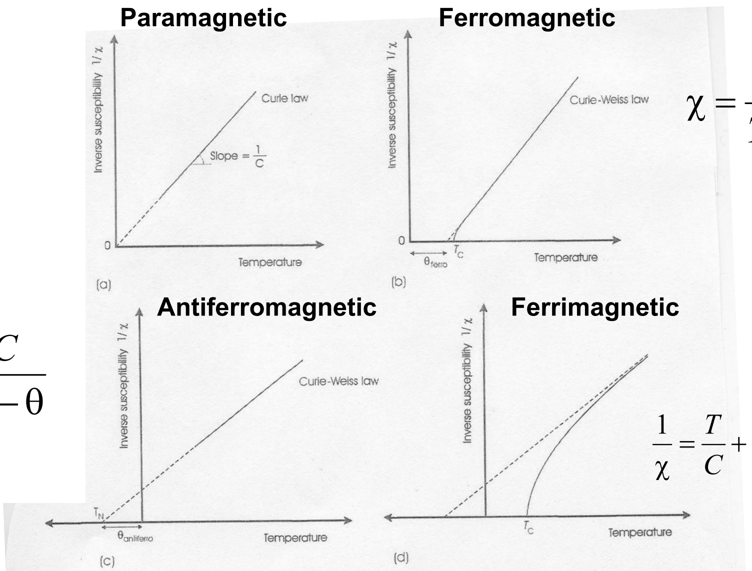
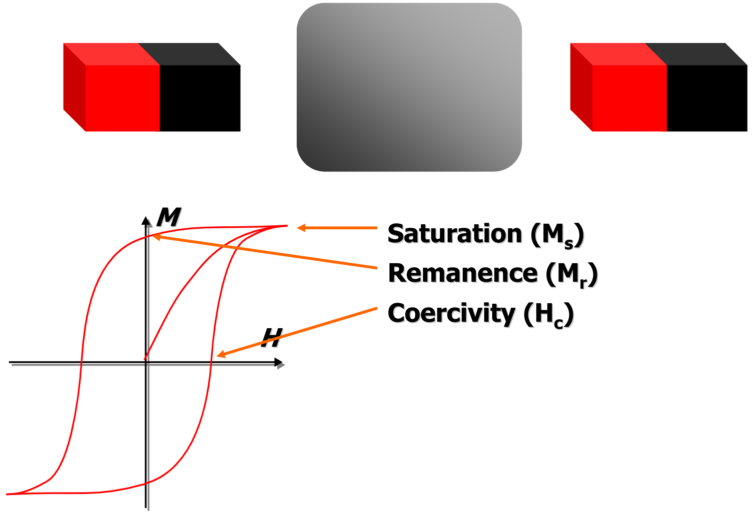


Figure 12.4 The temperature dependence of the reciprocal magnetic susceptibility: (a) Curie law behaviour of a paramagnetic solid; (b) Curie–Weiss law behaviour of a ferromagnetic solid above the Curie temperature, in the paramagnetic state; (c) Curie–Weiss law behaviour of an antiferromagnetic solid; and (d) behaviour of a ferrimagnetic solid

$$\chi = \frac{C}{T-\theta}$$

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} + \frac{\xi}{T-\theta}$$

What to measure?



Saturation (M_s)

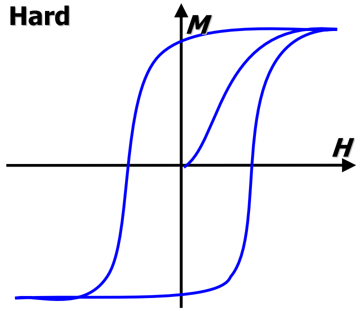
Remanence (M_r)

Coercivity (H_c)

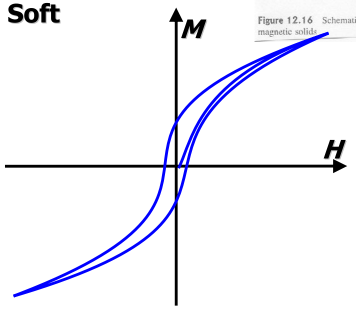
What to measure?

What to measure?

Hard



Soft



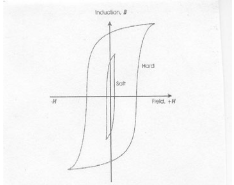


Figure 12.16 Schematic B–H loops for soft and hard magnetic solids

Hard to to magnetize and demagnetize
Very large remanence
Can be made into permanent magnerts
High coercivity

Easy to magnetize and demagnetize
Minimal remanence
Low coercivity

Weak magneitc materials

Diamagnetic materials: No magnetic dipoles in the material. The material responds to external magnetic fields according to Lenz's Law.

Paramagnetic materials: The magnetic moment of the material is dependent on the quantunm numbers S, L, J. The magnetic moment for transition materisl can be approximated by its spin-only angular momenta:

$$m = g_J\left[S(S+1)\right]^{1/2}\mu_B$$

where: $g_J = 2$
S = number of unpaired electrons * ½
μ_B = Bohr magnetron, magnetic moment of one electron

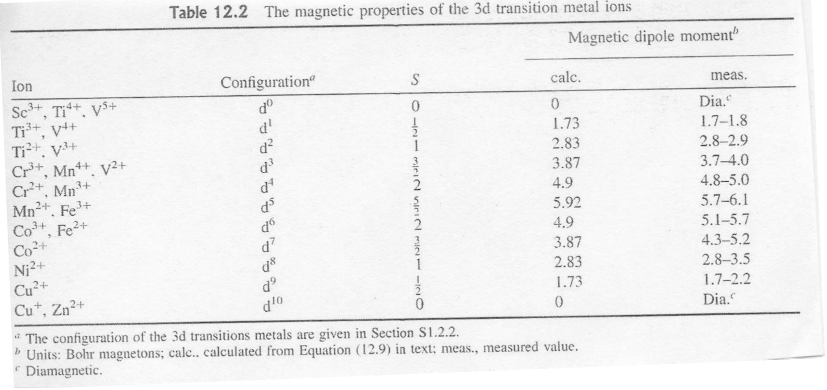


Table 12.2 The magnetic properties of the 3d transition metal ions

Ion	Configuration[a]	S	Magnetic dipole moment[b] calc.	meas.
Sc^{3+}, Ti^{4+}, V^{5+}	d^0	0	0	Dia.[c]
Ti^{3+}, V^{4+}	d^1	$\frac{1}{2}$	1.73	1.7–1.8
Ti^{2+}, V^{3+}	d^2	1	2.83	2.8–2.9
Cr^{3+}, Mn^{4+}, V^{2+}	d^3	$\frac{3}{2}$	3.87	3.7–4.0
Cr^{2+}, Mn^{3+}	d^4	2	4.9	4.8–5.0
Mn^{2+}, Fe^{3+}	d^5	$\frac{5}{2}$	5.92	5.7–6.1
Co^{3+}, Fe^{2+}	d^6	2	4.9	5.1–5.7
Co^{2+}	d^7	$\frac{3}{2}$	3.87	4.3–5.2
Ni^{2+}	d^8	1	2.83	2.8–3.5
Cu^{2+}	d^9	$\frac{1}{2}$	1.73	1.7–2.2
Cu^{+}, Zn^{2+}	d^{10}	0	0	Dia.[c]

[a] The configuration of the 3d transitions metals are given in Section S1.2.2.

[b] Units: Bohr magnetons; calc., calculated from Equation (12.9) in text; meas., measured value.

[c] Diamagnetic.

Ferromagnetic materials

Ferromagnetic materials are claimed to have an internal magnetic field.

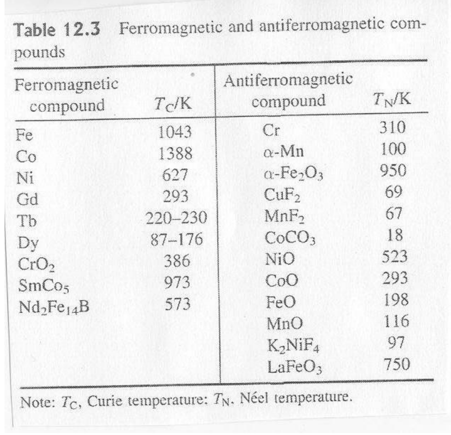


Table 12.3 Ferromagnetic and antiferromagnetic compounds

Ferromagnetic compound	T_C/K	Antiferromagnetic compound	T_N/K
Fe	1043	Cr	310
Co	1388	α-Mn	100
Ni	627	α-Fe_2O_3	950
Gd	293	CuF_2	69
Tb	220–230	MnF_2	67
Dy	87–176	$CoCO_3$	18
CrO_2	386	NiO	523
$SmCo_5$	973	CoO	293
$Nd_2Fe_{14}B$	573	FeO	198
		MnO	116
		K_2NiF_4	97
		$LaFeO_3$	750

Note: T_C, Curie temperature; T_N, Néel temperature.

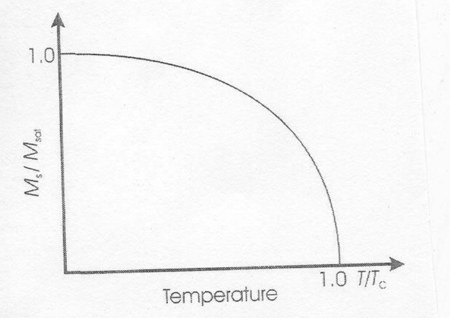


Figure 12.7 Variation of the relative spontaneous magnetisation, M_s/M_{sat}, as a function of relative temperature, T/T_C. When $T = 0$ the magnetisation is equal to the saturation magnetisation, M_{sat}. When $T = T_C$, the Curie temperature, the spontaneous magnetisation is zero

Ferromagnetic materials, Exchange energy

The exchange energy, j, favours parallel spin as far apart as possible. -> Hunds rule

Chemical bonding favours pairing of electrons, giving no magnetic moment.

Ferromagnetic materials can be obtained when the electrons are so far apart that they can be parallel (viz. a weak bond), but still so close that they can interact magnetically.

This gives in general weak bonding.

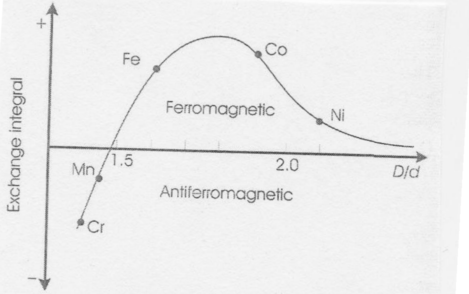
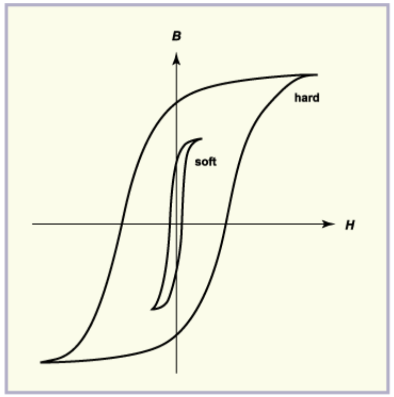


Figure 12.8 The Bethe–Slater curve for the magnitude of the exchange integral as a function of D/d, where D is the separation of the atoms in a crystal, and d is the diameter of the 3d orbital

Soft and hard magnets
Easy and hard axis



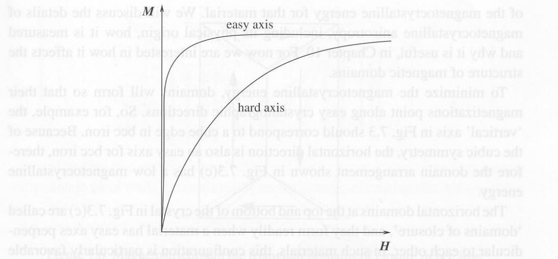


Figure 7.4 Schematic magnetization curves for a ferromagnet with the field oriented along the hard and easy directions.

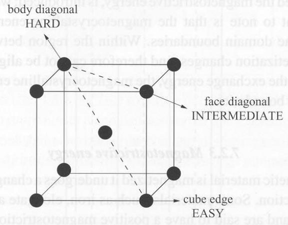


Figure 7.5 Easy, medium and hard directions of magnetization in a unit cell of bcc iron.

Anti-ferromagnetic Superexchange

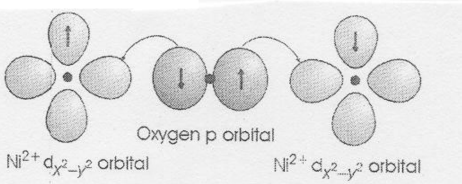


Figure 12.9 Superexchange leading to antiferromagnetic alignment of spins on cations

Superexchange occurs when an intermittent atom (Oxygen) transfers orbital information so that the metallic neighbours must be anti-parallel in orbital moment.

Without this exchange the material would be paramagnetic.

Typical mechanism for anti-ferromagnetic oxides with NaCl-type structure.

T_N increases with covalency: MnO, FeO, CoO, NiO
and is dependent on orbital overlap, viz. M-O-M angle

Ferrimagnetic materials, Doubleexchange

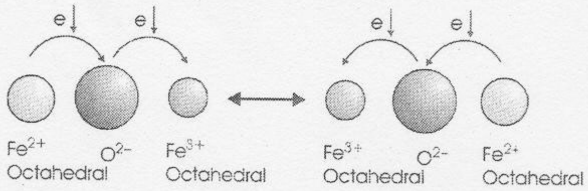


Figure 12.10 Double exchange, possible only with ferromagnetic alignment of spins on cations

Doubleexchange occurs when electrons can jump between metal atoms using an intermediate oxygen as bridge. Both electrons jump simultaneously. This produces parallel spin on the metal atoms.

This mechanism is frequent in inverse spinels (Fe_3O_4, ($Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ etc.) giving ferrimagnetic materials.

Domains

Ferromagnetic material produce a microstructure of magnetic domains "Weiss domains". These reduce the reduce the magnetostatic energy.

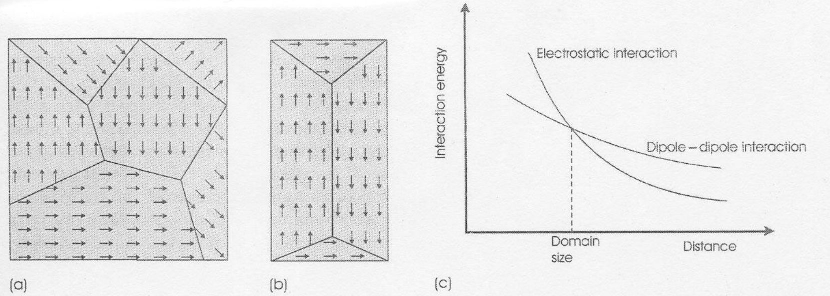
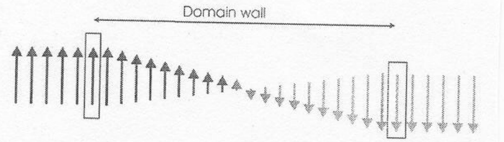


Figure 12.12 (a) Representation of Weiss domains; the magnetic dipoles are represented by arrows; (b) Domain closure; and (c) graph of interaction energy as a function of distance. The dipole–dipole interactions in the solid tend to produce antiparallel alignment of magnetic dipoles, and the electrostatic interactions a parallel alignment of magnetic dipoles. The domain size is a reflection of the point where these interactions balance



Bloch wall

Domains

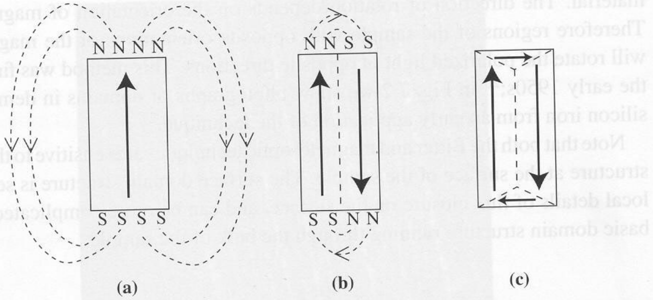


Figure 7.3 Reduction of the magnetostatic energy by domain formation in a ferromagnet.

Pauli paramagnetism

Paramagnetic metals do not show a Curie Weiss relationship. $\chi = \frac{C}{T}$

By applying an external field the density of states for the up and down spin states shifts differently.

The suceptibility becomes dependent on the applied field, but not temperature.

$$\chi = \frac{\mu_0 \mu_B^2 N}{E_F}$$

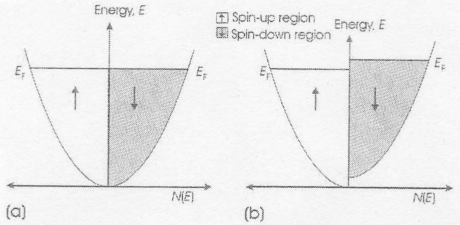


Figure 12.17 (a) The density of states. $N(E)$, for electrons in a metal is made up of equal numbers of spin-up and spin-down electrons. In the absence of a magnetic field, these are of equal energy. (b) The application of a magnetic field causes these to separate in energy. The electrons opposed to the field have a slightly higher energy than those parallel to the field

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Superparamagnetism

When particles of a magnetic solid are below the domain size, the electrostatic interactions dominate. The magnetic dipoles tend to align parallel to each other and a superparamagnetic state results.

Domain closure in thin films

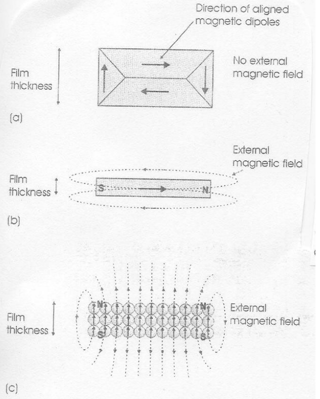

Figure 12.19 (a) Domain closure in a bulk film prevents magnetic flux from escaping. (b) A film less than a domain wide has magnetic dipoles aligned, so the flux escapes longitudinally; acicular crystals in magnetic recording media are ideally in this form. (c) A thin film of the order of one atomic thickness has elementary dipoles aligned perpendicular to the film, allowing flux to escape normal to the film