



Magnetic properties of materials



Lecture 11



The interaction of radiation with matter

Name	Differential form	Integral form
Gauss' law:	$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$	$\oint_S \mathbf{E} \cdot d\mathbf{A} = \frac{Q_S}{\epsilon_0}$
Gauss' law for magnetism (absence of magnetic monopoles):	$\nabla \cdot \mathbf{B} = 0$	$\oint_S \mathbf{B} \cdot d\mathbf{A} = 0$
Faraday's law of induction:	$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$	$\oint_{\partial S} \mathbf{E} \cdot d\mathbf{l} = -\frac{d\Phi_{B,S}}{dt}$
Ampère's Circuital Law (with Maxwell's correction):	$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}$	$\oint_{\partial S} \mathbf{B} \cdot d\mathbf{l} = \mu_0 \mathbf{I}_S + \mu_0 \epsilon_0 \frac{d\Phi_{E,S}}{dt}$

$$\nabla = \mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z}$$

$$\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}$$

$$\mathbf{M} = \chi_m \mathbf{H}$$

and the  $\mathbf{D}$  and  $\mathbf{B}$  fields are related to  $\mathbf{E}$  and  $\mathbf{H}$  by:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = (1 + \chi_e) \epsilon_0 \mathbf{E} = \epsilon \mathbf{E}$$

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = (1 + \chi_m) \mu_0 \mathbf{H} = \mu \mathbf{H}$$

$$\vec{D} = \hat{\epsilon}(\omega) \vec{E}$$

$$c = \frac{c_0}{n} = \frac{1}{\sqrt{\mu \epsilon}}$$

where

$$n = \sqrt{\frac{\mu \epsilon}{\mu_0 \epsilon_0}}$$

$$\vec{j} = \hat{\sigma}(\omega) \vec{E}$$

$\chi_e$  is the electrical susceptibility of the material,

$\chi_m$  is the magnetic susceptibility of the material,

$\epsilon$  is the electrical permittivity of the material, and

$\mu$  is the magnetic permeability of the material

Symbol	Name	Numerical Value	SI Unit of Measure
$c$	Speed of light in vacuum	$2.99792458 \times 10^8$	meters per second
$\epsilon_0$	electric constant	$8.85419 \times 10^{-12}$	farads per meter
$\mu_0$	magnetic constant	$4\pi \times 10^{-7}$	henries per meter

For your references:

Symbol	Meaning (first term is the most common)	SI Unit of Measure
$\nabla \cdot$	the divergence operator	per meter (factor contributed by applying vector operator)
$\nabla \times$	the curl operator	per second (factor contributed by applying the operator)
$\frac{\partial}{\partial t}$	partial derivative with respect to time	per second (factor contributed by applying the operator)
$\mathbf{E}$	electric field also called the electric flux density	volt per meter or, equivalently, newton per coulomb
$\mathbf{B}$	Magnetic field also called the magnetic induction also called the magnetic field density also called the magnetic flux density	tesla, or equivalently, weber per square meter
$\rho$	electric charge density	coulomb per cubic meter
$\epsilon_0$	Permittivity of free space, a universal constant	farads per meter
$\oint_S \mathbf{E} \cdot d\mathbf{A}$	The flux of the electric field over any closed Gaussian surface S	joule-meter per coulomb
$Q_S$	net unbalanced electric charge enclosed by the Gaussian surface S, including so-called bound charges	coulombs
$\oint_S \mathbf{B} \cdot d\mathbf{A}$	The flux of the magnetic field over any closed surface S	Tesla meter-squared or weber
$\oint_{\partial S} \mathbf{E} \cdot d\mathbf{l}$	line integral of the electric field along the boundary (therefore necessarily a closed curve) of the surface S	Joule per coulomb
$\Phi_{B,S} = \int_S \mathbf{B} \cdot d\mathbf{A}$	magnetic flux over any surface S (not necessarily closed)	weber
$\mu_0$	magnetic permeability of free space, a universal constant	henries per meter, or newtons per ampere squared
$\mathbf{J}$	current density	ampere per square meter
$\oint_{\partial S} \mathbf{B} \cdot d\mathbf{l}$	line integral of the magnetic field over the closed boundary of the surface S	tesla-meter
$\mathbf{I}_S = \int_S \mathbf{J} \cdot d\mathbf{A}$	net electrical current passing through the surface S	amperes
$\Phi_{E,S} = \int_S \mathbf{E} \cdot d\mathbf{A}$	Electric flux over any surface S, not necessarily closed	
$d\mathbf{A}$	differential vector element of surface area A, with infinitesimally small magnitude and direction normal to surface S	square meters
$d\mathbf{l}$	differential vector element of path length tangential to contour	meters

The interaction of radiation with matter

Decoupled form of MaxEq. in vacuum:

$$\frac{\partial^2 \mathbf{E}}{\partial t^2} - c^2 \cdot \nabla^2 \mathbf{E} = 0$$

$$\frac{\partial^2 \mathbf{B}}{\partial t^2} - c^2 \cdot \nabla^2 \mathbf{B} = 0$$

Same in material medium (solid state) [SI]

$$\nabla^2 \vec{E} = \epsilon \mu \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma \mu \frac{\partial \vec{E}}{\partial t}$$

$$\nabla^2 \vec{H} = \epsilon \mu \frac{\partial^2 \vec{H}}{\partial t^2} + \sigma \mu \frac{\partial \vec{H}}{\partial t}$$

[CGS]

$$\nabla^2 \vec{E} = \frac{\epsilon \mu}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi \sigma \mu}{c^2} \frac{\partial \vec{E}}{\partial t}$$

$$\nabla^2 \vec{H} = \frac{\epsilon \mu}{c^2} \frac{\partial^2 \vec{H}}{\partial t^2} + \frac{4\pi \sigma \mu}{c^2} \frac{\partial \vec{H}}{\partial t}$$

Solution:

Plane EM wave (light)

$$\vec{E} = \vec{E}_0 e^{i(\vec{K} \cdot \vec{r} - \omega t)}$$

## Definition of fundamental quantities

In vacuum,  $\mathbf{B} = \mu_0 \mathbf{H}$ ;  $\mu_0 = 4\pi \times 10^{-7}$  (SI units:  $\text{N}\cdot\text{A}^{-2}$ );

$\mathbf{B}$  – magnetic induction;  $\mathbf{H}$  – magnetic field intensity

When a material medium is placed in a magnetic field, the medium is magnetized. This is described by the *magnetization vector*  $\mathbf{M}$  - the magnetic dipole moment per unit volume.

$$\mathbf{B} = \mu_0 \mathbf{H} + \mu_0 \mathbf{M}$$

Magnetization is induced by the field  $\Rightarrow$  assume that  $\mathbf{M}$  is proportional to  $\mathbf{H}$ :

$$\mathbf{M} = \chi \mathbf{H} \rightarrow \mathbf{B} = \mu_0(1 + \chi)\mathbf{H} \quad \text{or} \quad \mathbf{B} = \mu \mathbf{H}; \quad \mu = \mu_0(1 + \chi); \quad \mu_r = 1 + \chi$$

$\chi$  - *magnetic susceptibility* of the medium (no physical relationship to the electric susceptibility).

Real crystals are anisotropic, and the susceptibility is represented by a second-rank tensor.

For simplicity, we shall ignore anisotropic effects.

We assumed that  $\mathbf{M}$  is proportional to  $\mathbf{H}$ , the external field - ignored such things as demagnetization field, which were included in the electric case.

This is justifiable in the case of paramagnetic and diamagnetic materials because  $\mathbf{M}$  is very small compared to  $\mathbf{H}$  (typically  $\chi = \mathbf{M}/\mathbf{H} \sim 10^{-5}$ ), unlike the electric case, in which  $\chi \sim 1$ .

But when we deal with ferromagnetic materials, where  $\mathbf{M}$  is quite large, the above effects must be included.

Note also that  $\chi$  can be dependent on the applied magnetic field.

In this case, we can define the magnetic susceptibility as follows:

$$\chi = \frac{\partial \mathbf{M}}{\partial \mathbf{H}}$$

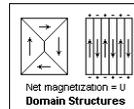
The magnetization can be defined as  $\mathbf{M} = -\frac{\partial E}{\partial \mathbf{H}}$

where  $E$  is the total energy of the system. These definitions are more general.

## Classification of materials

All magnetic materials may be grouped into three magnetic classes, depending on the magnetic ordering and the sign and magnitude of the magnetic susceptibility:

- **diamagnetics**: the magnetic susceptibility is negative - the magnetization is opposite to the applied magnetic field. Usually its magnitude is  $\sim -10^{-6}$  to  $-10^{-5}$ . In diamagnetic materials the susceptibility nearly has a constant value independent of temperature. Example: Ionic crystals and inert gases.
- **paramagnetics**:  $\chi$  is positive, i.e.  $\mathbf{M}$  is parallel to  $\mathbf{H}$ . The susceptibility is also very small:  $10^{-4}$  to  $10^{-5}$ . The best-known examples of paramagnetic materials are the ions of transition and rare-earth ions.
- **ferromagnetics**: very large positive  $\chi$  (e.g.  $10^5$ ), spontaneous magnetization below a certain temperature. Will discuss later, as well as *antiferromagnetics* and *ferrimagnetics*



## Magnetism of a free atom

1. spins of electrons  $\mathbf{S}$
2. orbital momentum of electrons around the nucleus  $\mathbf{L}$
3. A change of the orbital momentum caused by the external magnetic field

**paramagnetism**: 1 and 2 (positive contribution)

**diamagnetics**: 3 (negative contribution)



## Classical consideration: diamagnetism

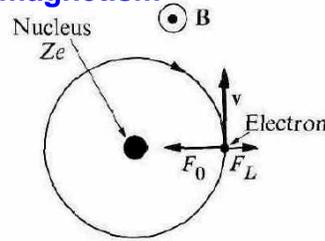
Can obtain the same formula classically:

Consider an electron rotating about the nucleus in a circular orbit; let a magnetic field be applied.

Before this field is applied, we have, according to Newton's second law,

$$F_0 = m\omega_0^2 r$$

$F_0$  is the attractive Coulomb force between the nucleus and the electron, and  $\omega_0$  is the angular velocity.



Applied field  $\rightarrow$  an additional force: the Lorentz force  $F_L = -e(\mathbf{v} \times \mathbf{B})$

$$F_L = -eB\omega r \Rightarrow F_0 - eB\omega r = m\omega^2 r \quad \omega = \omega_0 - \frac{eB}{2m}$$

Reduction in frequency  $\rightarrow$  corresponding change in the magnetic moment.

The change in the frequency of rotation is equivalent to the change in the current around the nucleus:  $\Delta I = (\text{charge}) \times (\text{revolutions per unit time})$

$$\Delta I = -Ze \frac{1}{2\pi} \frac{eB}{2m}$$

The magnetic moment of a circular current is given by the product (current)  $\times$  (area of orbit)

$$\Delta \mu = -e \frac{1}{2\pi} \frac{eB}{2m} \pi \langle r_{xy}^2 \rangle = -\frac{e^2 \langle r_{xy}^2 \rangle}{4m} B$$

Here  $\langle r_{xy}^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$ . The mean square distance of the electrons from the nucleus is  $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$ .

For a spherically symmetrical charge distribution  $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \langle r^2 \rangle / 3$

$$\Rightarrow \langle r_{xy}^2 \rangle = \frac{2}{3} \langle r^2 \rangle \Rightarrow \Delta \mu = -\frac{e^2 \langle r^2 \rangle}{6m} B \Rightarrow \chi = -\frac{\mu_0 e^2 N Z \langle r^2 \rangle}{6m}$$

Diamagnetism in ionic crystals and crystals composed of inert gas atoms: they have atoms or ions with complete electronic shells.

Another class of diamagnetics is noble metals, which will be discussed later.

$$\chi^{\text{molar}} = -Z_i N_A \frac{e^2}{6mc^2} \langle r^2 \rangle = -Z_i \left( \frac{e^2}{\hbar c} \right)^2 \frac{N_A a_0^3}{6} \langle (r/a_0)^2 \rangle.$$

Since  $a_0 = 0.529 \text{ \AA}$ ,  $e^2/\hbar c = 1/137$ , and  $N_A = 0.6022 \times 10^{24}$ ,

$$\chi^{\text{molar}} = -0.79 Z_i \times 10^{-6} \langle (r/a_0)^2 \rangle \text{ cm}^3/\text{mole}.$$

The quantity  $\langle (r/a_0)^2 \rangle$  is of order unity, as is the number of moles per cubic centimeter (by which the molar susceptibility must be multiplied to get the dimensionless susceptibility). We conclude that diamagnetic susceptibilities are typically of order  $10^{-5}$ ; i.e.,  $M$  is minute compared with  $H$ .

### MOLAR SUSCEPTIBILITIES OF NOBLE GAS ATOMS AND ALKALI HALIDE IONS<sup>a</sup>

ELEMENT	SUSCEPTIBILITY	ELEMENT	SUSCEPTIBILITY	ELEMENT	SUSCEPTIBILITY
F <sup>-</sup>	-9.4	He	-1.9	Li <sup>+</sup>	-0.7
Cl <sup>-</sup>	-24.2	Ne	-7.2	Na <sup>+</sup>	-6.1
Br <sup>-</sup>	-34.5	A	-19.4	K <sup>+</sup>	-14.6
I <sup>-</sup>	-50.6	Kr	-28	Rb <sup>+</sup>	-22.0
		Xe	-43	Cs <sup>+</sup>	-35.1

<sup>a</sup> In units of  $10^{-6} \text{ cm}^3/\text{mole}$ . Ions in each row have the same electronic configuration. Source: R. Kubo and T. Nagamiya, eds., *Solid State Physics*, McGraw-Hill, New York, 1969, p. 439.

## Quantum-mechanical calculation of atomic susceptibilities

In the presence of a uniform magnetic field the Hamiltonian of an ion (atom) is modified in the two major ways:

- 1) In the total kinetic energy term the electron momentum is replaced:  $\mathbf{p} \rightarrow \mathbf{p} + e\mathbf{A}$ , where  $\mathbf{A}$  is the vector potential associated with the magnetic field:  $\mathbf{B} = \nabla \times \mathbf{A}$ .

We assume that the applied field is uniform so that  $\mathbf{A} = -\frac{1}{2} \mathbf{r} \times \mathbf{B}$

- 2) The interaction energy of the field with each electron spin must be added to the Hamiltonian:  $H_{\text{spin}} = 2\mu_B \mathbf{B} \cdot \mathbf{S}$  where  $\mu_B$  is the Bohr magneton  $\mu_B = \frac{e\hbar}{2m_0}$   $\mathbf{S}$  – spin momentum

As the result the total energy of electrons will have a form:

$$H = \frac{1}{2m} \sum_i \left( \mathbf{p}_i - \frac{e}{2} \mathbf{r}_i \times \mathbf{B} \right)^2 + 2\mu_B \mathbf{B} \cdot \mathbf{S}$$

Have 
$$H = \frac{1}{2m} \sum_i \left( \mathbf{p}_i - \frac{e}{2} \mathbf{r}_i \times \mathbf{B} \right)^2 + 2\mu_B \mathbf{B} \mathbf{S}$$

Let  $T_0$  - the kinetic energy in the absence of the applied field:  $T_0 = \frac{1}{2m} \sum_i \mathbf{p}_i^2$

The cross term in the brackets can be rewritten taking into account that  $\mathbf{p}_i \cdot (\mathbf{r}_i \times \mathbf{B}) = -\mathbf{B} \cdot (\mathbf{r}_i \times \mathbf{p}_i)$

Note that although  $\mathbf{r}$  and  $\mathbf{p}$  are quantum-mechanical operators, here we can work with them as with classical variables because only non-diagonal components enter this product (i.e. there are no terms which contain, e.g.,  $x$  components of both  $\mathbf{r}$  and  $\mathbf{p}$  which do not commute).

Assume that  $\mathbf{B}$  is along  $z$  direction  $\rightarrow$  can rewrite  $(\mathbf{r}_i \times \mathbf{B})^2 = B^2 (x_i^2 + y_i^2)$

Finally we find for the field-dependent correction to the total Hamiltonian:

$$\Delta H = H - T_0 = \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m} B^2 \sum_i (x_i^2 + y_i^2)$$

where  $\mathbf{L}$  is the total orbital momentum:  $\hbar \mathbf{L} = \sum_i (\mathbf{r}_i \times \mathbf{p}_i)$

$$\Delta H = H - T_0 = \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m} B^2 \sum_i (x_i^2 + y_i^2)$$

This equation is the basis for theories of the magnetic susceptibility of individual atoms, ions, or molecules.

First term: paramagnetism, second term: diamagnetism

The energy correction due to the applied field is small compared to electron energies;  $\mu_B = 5.8 \times 10^{-5} \text{ eV/T}$ .  $\rightarrow$  for  $B = 1 \text{ T}$   $\mu_B B = 5.8 \times 10^{-5} \text{ eV}$ .

$\Rightarrow$  can compute the changes in the energy levels induced by the field with ordinary perturbation theory.

### Langevin diamagnetism

Let us now apply the obtained results to a solid composed of ions or atoms with all electronic shells filled.

Such atoms have zero spin and orbital angular momentum in its ground state:

$$\langle 0 | \mathbf{S} | 0 \rangle = \langle 0 | \mathbf{L} | 0 \rangle = 0$$

$\Rightarrow$  only last term of  $\Delta H$  contributes to the field-induced shift in the ground state energy:

$$E = \langle 0 | H | 0 \rangle = \frac{e^2}{8m} B^2 \langle 0 | \sum_i (x_i^2 + y_i^2) | 0 \rangle = \frac{e^2}{12m} B^2 \langle 0 | \sum_i r_i^2 | 0 \rangle$$

This follows from the spherical symmetry of the closed-shell ion:

$$\langle 0 | \sum_i x_i^2 | 0 \rangle = \langle 0 | \sum_i y_i^2 | 0 \rangle = \langle 0 | \sum_i z_i^2 | 0 \rangle = \frac{1}{3} \langle 0 | \sum_i r_i^2 | 0 \rangle$$

It is conventional to define a mean square ionic radius by

$$\langle r^2 \rangle = \frac{1}{Z} \langle 0 | \sum_i r_i^2 | 0 \rangle$$

where  $Z$  is the total number of electrons in an ion.

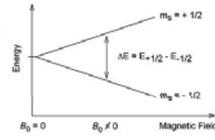
We obtain then for the magnetization induced by the applied magnetic field:

$$E = \frac{e^2}{12m} NZ \langle r^2 \rangle B^2 \quad \mathbf{M} = -\frac{\partial E}{\partial H} = -\mu_0 \frac{\partial E}{\partial B} = -\frac{\mu_0 e^2 NZ \langle r^2 \rangle B}{6m}$$

where  $N$  is the number of atoms per unit volume.

$\Rightarrow$  a negative magnetic susceptibility:  $\chi = -\frac{\mu_0 e^2 NZ \langle r^2 \rangle}{6m}$

## Quantum theory of paramagnetism



$$\Delta H = H - T_0 = \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} + \frac{e}{8m} B^2 \sum_i (x_i^2 + y_i^2)$$

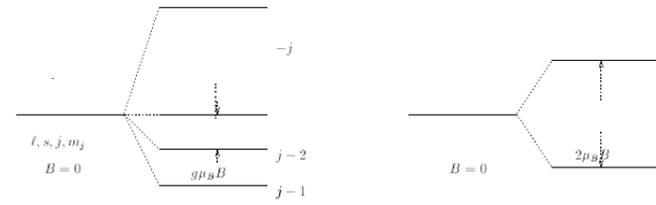
CGS:

$$\mathcal{H}'_{\text{para}} = \sum_i - \left( \frac{e}{2mc} \right) (\vec{L}_i + 2\vec{S}_i) \cdot \vec{B} = -\vec{\mu}_{\text{para}} \cdot \vec{B}$$

$$\vec{\mu}_{\text{para}} = \frac{e}{2mc} \sum_i (\vec{L}_i + 2\vec{S}_i).$$

1. determination of the moment  $\vec{\mu}_{\text{para}}$
2. a statistical calculation of the average of  $\vec{\mu}_{\text{para}}$

## Quantum theory of paramagnetism



- (a) Equally spaced levels for different  $m_j$  values  $-j \leq m_j \leq j$  in a magnetic field where the Zeeman splitting between adjacent levels is  $g\mu_B B$  where  $g$  is the Landé  $g$ -factor.  
 (b) For a 2-level, spin up and spin down system, the Zeeman splitting is  $2\mu_B B$ .

1. determination of the moment  $\vec{\mu}_{\text{para}}$
2. a statistical calculation of the average of  $\vec{\mu}_{\text{para}}$

## Quantum theory of paramagnetism

If atoms in a solid have non-filled electronic shells than we have to take into account the first term in the Hamiltonian.

Its contribution is much larger than the contribution from the second term  
 → can ignore it.

Consider the effect of the first term on an ion in a ground state which can be described by quantum numbers  $L, S, J$  and  $J_z$ , where  $\mathbf{J}$  is the total angular momentum,  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ ; and  $J_z$  is the projection of this momentum into a quantization axis.

It can be shown that  $\langle LSJ J_z | \mathbf{L} + 2\mathbf{S} | LSJ J_z' \rangle = g \langle LSJ J_z | \mathbf{J} | LSJ J_z' \rangle$   
 $\mathbf{L} + g_0 \mathbf{S} = g(JLS)\mathbf{J}$ .

where  $g$  is the  $g$ -factor, given by  $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

This relation is valid only within the  $(2J+1)$ -dimensional set of states that make up the degenerate atomic ground state in zero field, i.e. only for matrix elements taken between states that are diagonal in  $J, L$ , and  $S$ .

If the splitting between the zero-field atomic ground state multiplet and the first excited multiplet is large compared with  $k_B T$  (as is frequently the case), then only the  $(2J+1)$  states in the ground-state multiplet will contribute appreciably to the energy.

In that case the first term in the Hamiltonian leads to the energy  $E = -\boldsymbol{\mu} \cdot \mathbf{B}$

Magnetic moment of an ion is proportional to the total angular momentum of the ion:

$$\boldsymbol{\mu} = -g(JLS)\mu_B \mathbf{J}$$

The applied magnetic field lifts degeneracy of the ground state multiplet and splits it into  $2J+1$  equidistant levels - *Zeeman splitting*.

The energies of these levels are given by  $E_{J_z} = g\mu_B B J_z$

$J_z$  is a quantized and has values from  $-J$  to  $J$ .

If thermal energy is less or comparable with the Zeeman splitting, these levels will be populated differently and give a different contribution to the magnetic moment of the ion.

Magnetization is determined by the average value of the magnetic moment:

$\mathbf{M} = N\langle\boldsymbol{\mu}\rangle$ , where  $N$  is the concentration of ions in the solid;

$\langle\boldsymbol{\mu}\rangle$  - value of magnetic moment averaged over the Boltzmann distribution:

$$\mathbf{M} = N\langle\boldsymbol{\mu}\rangle = -N g \mu_B \frac{\sum_{J_z=-J}^J J_z e^{\frac{g \mu_B B J_z}{k_B T}}}{\sum_{J_z=-J}^J e^{\frac{g \mu_B B J_z}{k_B T}}}$$

The summation can be done using the geometric progression formula.

Result for the magnetization:  $M = N g J \mu_B B_J(x)$  where  $x = \frac{g \mu_B J B}{k T}$

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

- the Brillouin function

Magnetization for three different ions as a function of applied magnetic field

At relatively low fields and not too low temperatures we can expand the  $\coth(x)$  assuming that  $x \ll 1$ :

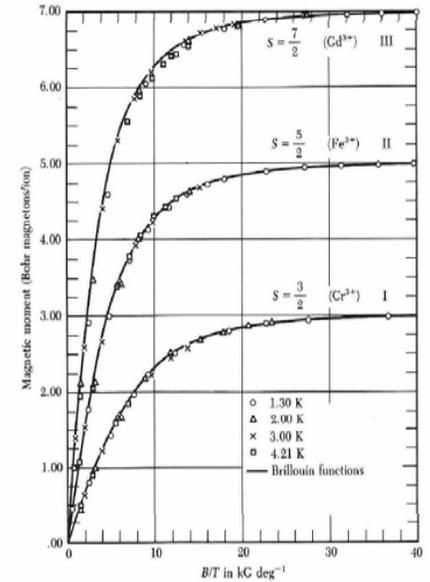
$$\coth(x) \approx \frac{1}{x} + \frac{x}{3}$$

Get for the susceptibility:

$$\chi = \mu_0 \frac{M}{B} = \frac{N J (J+1) g^2 \mu_B^2}{3 k_B T} = \frac{\mu_0 N p^2 \mu_B^2}{3 k_B T} = \frac{C}{T} \quad \text{Curie Law}$$

where  $p$  is the effective number of Bohr magnetons, defined as  $p = g[J(J+1)]^{1/2}$

$C$  is the Curie constant



$$\chi = \frac{N (g \mu_B)^2 J(J+1)}{V 3 k_B T}, \quad (k_B T \gg g \mu_B H),$$

$$\chi^{\text{molar}} = N_A \frac{(g \mu_B)^2 J(J+1)}{3 k_B T}, \quad p = g[J(J+1)]^{1/2}$$

CALCULATED AND MEASURED EFFECTIVE MAGNETON NUMBERS  $p$  FOR THE IRON (3d) GROUP IONS\*

ELEMENT (AND IONIZATION)	BASIC ELECTRON CONFIGURATION	GROUND-STATE TERM	CALCULATED <sup>b</sup> $p$		MEASURED <sup>c</sup> $p$
			$(J = S)$	$(J =  L \pm S )$	
Ti <sup>3+</sup>	3d <sup>1</sup>	<sup>2</sup> D <sub>3/2</sub>	1.73	1.55	—
V <sup>4+</sup>	3d <sup>1</sup>	<sup>2</sup> D <sub>3/2</sub>	1.73	1.55	1.8
V <sup>3+</sup>	3d <sup>2</sup>	<sup>3</sup> F <sub>3</sub>	2.83	1.63	2.8
V <sup>2+</sup>	3d <sup>3</sup>	<sup>4</sup> F <sub>3/2</sub>	3.87	0.77	3.8
Cr <sup>3+</sup>	3d <sup>3</sup>	<sup>4</sup> F <sub>3/2</sub>	3.87	0.77	3.7
Mn <sup>4+</sup>	3d <sup>2</sup>	<sup>4</sup> F <sub>3/2</sub>	3.87	0.77	4.0
Cr <sup>2+</sup>	3d <sup>4</sup>	<sup>3</sup> D <sub>0</sub>	4.90	0	4.8
Mn <sup>3+</sup>	3d <sup>4</sup>	<sup>3</sup> D <sub>0</sub>	4.90	0	5.0
Mn <sup>2+</sup>	3d <sup>5</sup>	<sup>6</sup> S <sub>5/2</sub>	5.92	5.92	5.9
Fe <sup>3+</sup>	3d <sup>5</sup>	<sup>6</sup> S <sub>5/2</sub>	5.92	5.92	5.9
Fe <sup>2+</sup>	3d <sup>6</sup>	<sup>5</sup> D <sub>4</sub>	4.90	6.70	5.4
Co <sup>2+</sup>	3d <sup>7</sup>	<sup>4</sup> F <sub>3/2</sub>	3.87	6.54	4.8
Ni <sup>2+</sup>	3d <sup>8</sup>	<sup>3</sup> F <sub>4</sub>	2.83	5.59	3.2
Cu <sup>2+</sup>	3d <sup>9</sup>	<sup>2</sup> D <sub>3/2</sub>	1.73	3.55	1.9

\* Because of quenching, much better theoretical values are obtained by taking  $J$  equal to  $S$ , the total spin, than by taking the value  $J = |L \pm S|$  appropriate to the free ion.

<sup>b</sup> Equation (31.50). In the case  $J = S$ , one takes  $L = 0$ .

<sup>c</sup> Equation (31.49).

Source: J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, 1952, p. 285; R. Kubo and T. Nagamiya, eds., *Solid State Physics*, McGraw-Hill, New York, 1969, p. 453.

## Hund Rules

Used to determine  $L$ ,  $J$ , and  $S$  for an atom with known number of electrons in the incomplete shell.

The Hund rules as applied to atoms and ions affirm that electrons will occupy orbitals in such a way that the ground state is characterized by the following:

- 1) The maximum value of the total spin  $S$  allowed by the exclusion principle;
- 2) The maximum value of the orbital angular momentum  $L$  consistent with this value of  $S$ ;
- 3) The value of the total angular momentum  $J$  is equal to  $|L-S|$  when the shell is less than half full and to  $L+S$  when the shell is more than half full.

This is due to the spin-orbit interaction the constant of which has opposite sign depending on whether is less than half full or more than half full.

When the shell is just half full, the application of the first rule gives  $L = 0$ , so that  $J = S$ .

Example: carbon. Two electrons in the  $2p$  shell ( $L = 1$ ). Rule #1  $\Rightarrow S = 1$ ;

Maximum  $L = 1$ . Shell is less than half-full  $\Rightarrow J = |L-S| = 0$ . No paramagnetism.

## Iron-group ions

iron-group ions behave magnetically as if  $J = S$ , that is, only the spin moment can contribute to magnetization.

The magnetic properties of this group of elements are due to the electron in the incomplete  $3d$  shell. Since electrons in this outermost shell interact strongly with neighboring ions, the orbital motion is essentially destroyed, or *quenched*, leaving only the spin moment to contribute to the magnetization.

In other words, in these ions, the strength of the crystal field is much greater than the strength of the spin-orbit interaction, just the reverse of the situation in rare-earth ions.

Sc	21
Ti	22
V	23
Cr	24
Mn	25
Fe	26
Co	27
Ni	28
Cu	29
Zn	30

## Hund Rules

the hallowed spectroscopic code:

$$L = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6$$

$$X = S \ P \ D \ F \ G \ H \ I$$

The spin is specified by affixing the number  $2S + 1$  (known as the multiplicity) to the letter as a superprefix, and only  $J$  is given as the number  $J$ , affixed as a right subscript. Thus the lowest lying  $J$ -multiplet is described by the symbol:  $(2S+1)X_J$ .

### GROUND STATES OF IONS WITH PARTIALLY FILLED $d$ - OR $f$ -SHELLS, AS CONSTRUCTED FROM HUND'S RULES<sup>a</sup>

$d$ -shell ( $l = 2$ )						$S$	$L =  \sum l_z $	$J$	SYMBOL	
$n$	$l_z = 2,$	$1,$	$0,$	$-1,$	$-2$					
1	↓					1/2	2	3/2	$J =  L - S $	$^2D_{3/2}$
2	↓	↓				1	3	2		$^3F_2$
3	↓	↓	↓			3/2	3	3/2	$^4F_{3/2}$	
4	↓	↓	↓	↓		2	2	0	$^5D_0$	
5	↓	↓	↓	↓	↓	5/2	0	5/2	$^6S_{5/2}$	
6	↑↓	↑	↑	↑	↑	2	2	4	$J = L + S$	$^3D_4$
7	↑↓	↑↓	↑	↑	↑	3/2	3	9/2		$^4F_{9/2}$
8	↑↓	↑↓	↑↓	↑	↑	1	3	4	$^3F_4$	
9	↑↓	↑↓	↑↓	↑↓	↑	1/2	2	5/2	$^2D_{5/2}$	
10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	$^1S_0$	

## Rare-earth ions

Rare-earth ions in crystals obey the Curie law, with an effective number of magnetons in agreement with the theory of spin-orbit interaction.

In these ions, the angular momenta  $L$  and  $S$  are strongly coupled, and the moment of the ion can respond freely to the external field.

In these ions - from La to Lu - the only incomplete shell is the  $4f$  shell. The outer  $5p$  shell is completely filled, while the  $5d$  and  $6s$  shells are stripped of their electrons to form the ionic crystal.

⇒ Thus the  $4f$  shell is the one in which the magnetic behavior occurs.

Since electrons in this shell lie deep within the ion, screened by the outer  $5p$  and  $5d$  shells, they are not appreciably affected by other ions in the crystal. Magnetically their behavior is much like that of a free ion.

Another reason why the free-ion treatment applies to the rare-earth ions is that the spin-orbit interaction is strong in these substances, because this interaction is proportional to  $Z$ , the atomic number of the element concerned, and all the rare-earth ions have large  $Z$ 's.

$5s^2 p^6$

La	57
Ce	58
Pr	59
Nd	60
Pm	61
Sm	62
Eu	63
Gd	64
Tb	65
Dy	66
Ho	67
Er	68
Tm	69
Yb	70

## Hund Rules

### GROUND STATES OF IONS WITH PARTIALLY FILLED $d$ - OR $f$ -SHELLS, AS CONSTRUCTED FROM HUND'S RULES<sup>a</sup>

$f$ -shell ( $l = 3$ )						$S$	$L =  \sum l_z $	$J$	SYMBOL	
$n$	$l_z = 3,$	$2,$	$1,$	$0,-1,-2,-3$						
1	↓					1/2	3	5/2	$J =  L - S $	$^2F_{5/2}$
2	↓	↓				1	5	4		$^3H_4$
3	↓	↓	↓			3/2	6	9/2	$^4I_{9/2}$	
4	↓	↓	↓	↓		2	6	4	$^5I_4$	
5	↓	↓	↓	↓	↓	5/2	5	5/2	$^6H_{5/2}$	
6	↓	↓	↓	↓	↓	3	3	0	$^7F_0$	
7	↓	↓	↓	↓	↓	7/2	0	7/2	$^8S_{7/2}$	
8	↑↓	↑	↑	↑	↑	3	3	6	$J = L + S$	$^7F_6$
9	↑↓	↑↓	↑	↑	↑	5/2	5	15/2		$^6H_{15/2}$
10	↑↓	↑↓	↑↓	↑	↑	2	6	8	$^5I_8$	
11	↑↓	↑↓	↑↓	↑↓	↑	3/2	6	15/2	$^4I_{15/2}$	
12	↑↓	↑↓	↑↓	↑↓	↑	1	5	6	$^3H_6$	
13	↑↓	↑↓	↑↓	↑↓	↑	1/2	3	7/2	$^2F_{7/2}$	
14	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	$^1S_0$	

<sup>a</sup> ↑ = spin  $\frac{1}{2}$ ; ↓ = spin  $-\frac{1}{2}$ .

## Pauli Spin paramagnetism in metals

Arises from the fact that each conduction electron carries a spin magnetic moment which tends to align with the field.

An electron has spin  $1/2$  - might expect a Curie-type paramagnetic contribution to the magnetization of the metal :

$$j = s = 1/2 \text{ and } g = 2. \quad g^2 j(j+1) = 2^2 \left(\frac{1}{2}\right) \left(\frac{3}{2}\right) = 3. \quad \chi = \frac{\mu_0 N \mu_B^2}{k_B T}$$

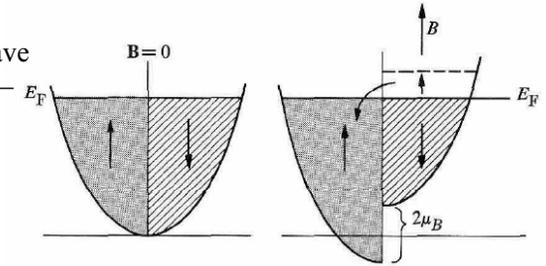
However, experiments show, that spin susceptibilities in metals are essentially **independent of temperature**, and the observed values are also considerably smaller.

Source of this discrepancy:

the above formula was derived on the basis of localized electrons obeying the Boltzmann distribution, whereas the conduction electrons are delocalized and satisfy the Fermi distribution.

The proper treatment must taking this into account.

No field: half the electrons have spins along  $+z$ , the other half - spins along  $-z$  direction  $\Rightarrow$  vanishing net magnetization.



Field is applied along the  $z$ -direction:

the energy of the spins  $\parallel \mathbf{B}$  is lowered by the amount  $\mu_B B$ ;  
the energy of spins opposite to  $\mathbf{B}$  is raised by the same amount.

$\Rightarrow$  some electrons near the Fermi level begin to transfer from the opposite-spin half to the parallel-spin one, leading to a net magnetization.

Note that only relatively few electrons near the Fermi level are able to flip their spins and align with the field. The other electrons, lying deep within the Fermi distribution, are prevented from doing so by the exclusion principle.

We can now estimate the magnetic susceptibility.

The electrons participating in the spin flip occupy an energy interval  $\sim \mu_B B$

$\Rightarrow$  their concentration is  $N_{eff} = \frac{1}{2} D(E_F) \mu_B B$ ,

where  $D(E_F)$  - the density of states at the Fermi energy level

Each spin flip increases the magnetization by  $2\mu_B$  (from  $-\mu_B$  to  $+\mu_B$ )

$\Rightarrow$  the net magnetization  $M = N_{eff} 2\mu_B = \mu_B^2 D(E_F) B$

leading to a paramagnetic susceptibility  $\chi = \mu_B^2 D(E_F) \mu_0$

$\Rightarrow$  susceptibility is determined by the density of states at the Fermi level.

$\Rightarrow \chi$  is essentially independent of temperature. (Temperature has only a small effect on the Fermi-Dirac distribution of the electrons)

$\Rightarrow$  the derivation remains valid.

If we apply the results for free electrons:  $D(E_F) = 3N/2E_F = 3N/2k_B T_F$ ,

then  $\chi = \frac{3N\mu_B^2}{2k_B T_F}$   $T_F$  - Fermi temperature ( $E_F = k_B T_F$ ).  
 $T_F$  is very large (often 30,000°K or higher),  $\Rightarrow \chi$  is smaller by factor of  $\sim 10^2$  - in agreement with experiment.

## Landau diamagnetism

Conduction electrons also exhibit diamagnetism on account of the cyclotron motion they execute in the presence of the magnetic field.

Each electron loop is equivalent to a dipole moment whose direction is opposite to that of the applied field.

Classical treatment shows that the total diamagnetic contribution of all electrons is zero.

Quantum treatment however shows that for free electrons this causes a diamagnetic moment equal to  $-1/3$  of the Pauli paramagnetic moment.

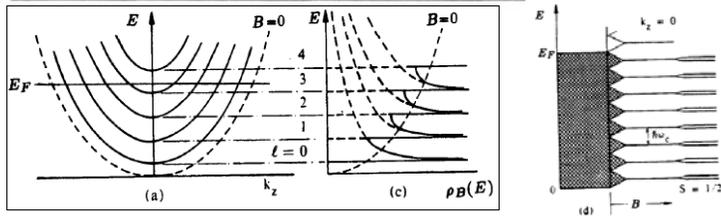
$\Rightarrow$  the total susceptibility of a free electrons gas is  $\chi = \frac{N\mu_B^2}{k_B T_F}$

The net response is therefore paramagnetic.

In comparing theoretical results with experiment, one must also include the diamagnetic effect of the ion cores (Langevin diamagnetism).

## Susceptibilities of some monovalent and divalent metals $\times 10^6$ (Room T)

Element	$\chi_{\text{total}}$ (expt)	Experimental		Theoretical
		$\chi_{\text{core}}$	$\chi_{\text{electron}} = \chi_{\text{total}} - \chi_{\text{core}}$	$\chi_{\text{electron}} = \chi_{\text{spin}} + \chi_{\text{orbit}}$
K	0.47	-0.31	0.76	0.35
Rb	0.33	-0.46	0.79	0.33
Cu	-0.76	-2.0	1.24	0.65
Ag	-2.1	-3.0	0.9	0.60
Au	-2.9	-4.3	1.4	0.60
Mg	0.95	-0.22	1.2	0.65
Ca	1.7	-0.43	2.1	0.5



## Summary

- When a material medium is placed in a magnetic field, the medium is magnetized. Magnetisation is proportional to the magnetic field:

$$\mathbf{M} = \chi \mathbf{H}; \quad \chi - \text{magnetic susceptibility of the medium}$$

$$\text{magnetic permittivity } \mu = \mu_0(1 + \chi); \quad \mu_r = 1 + \chi$$

- Langevin diamagnetism - ions or atoms with all electronic shells filled

$$\text{negative magnetic susceptibility: } \chi = -\frac{\mu_0 e^2 N Z \langle r^2 \rangle}{6m}$$

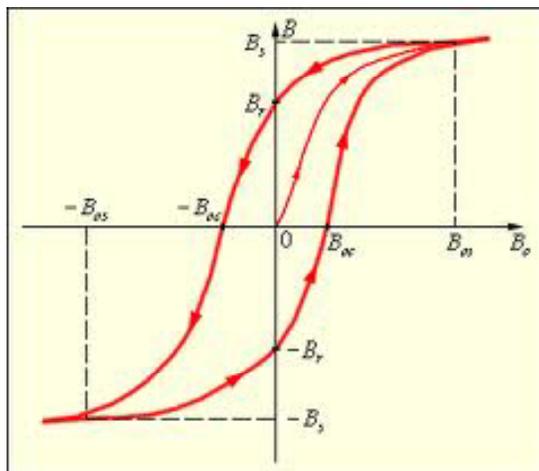
- Langevin paramagnetism: if an atom has moment  $\mu$ , then classical paramagnetic susceptibility

$$\chi = \frac{\mu_0 N \mu^2}{3k_B T}$$

quantum treatment  $\rightarrow$  same result for  $\mu = g[J(J+1)]^{1/2} \mu_B$

- In metals, conduction electrons make a spin paramagnetic contribution:  $\chi = \mu_B^2 D(E_F) \mu_0$  - independent on T
- Conduction electrons also exhibit diamagnetism due to the cyclotron motion, which is equal to 1/3 of the spin paramagnetic contribution.
- Ion core effect must also be taken into account

## Ferromagnetism



## Magnetism / Magnetic Order

↑↑↑ ferromagnet

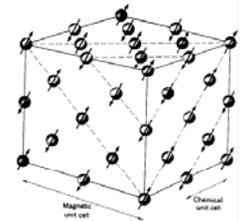
ferromagnet - the magnetic moments (spins) all line up parallel to one another, and

↑↓↑↓ antiferromagnet

antiferromagnet - equal magnetic moments (spins) on nearest neighbor sites which tend to line up antiparallel.

More complicated arrangements are possible like a

↑↓↑↑ ferrimagnet



Ordered arrangements of spins of the  $\text{Mn}^{2+}$  ions in  $\text{MnO}$ , as determined by neutron diffraction. The lattice for  $\text{MnO}$  is a NaCl structure, though the  $\text{O}^{2-}$  ions are not shown in the figure. The chemical and magnetic unit cells are indicated in the figure.

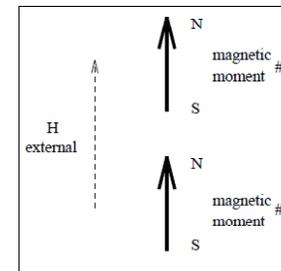


Table 7.1: Magnetic parameters for a number of ferromagnetic materials. Here  $n_B$  is the number of Bohr magnetons per atom and  $M_S$  is the spontaneous magnetization in units of gauss.

material	$M_S(300K)$	$M_S(0K)$	$n_B(0K)$	$T_c$ (K)
Fe	1707	1740	2.22	1043
Co	1400	1446	1.72	1400
Ni	485	510	0.606	631
Gd	-	2010	7.10	292
Dy	-	2920	10.0	85
$\text{Cu}_2\text{MnAl}$	500	(550)	(4.0)	710
MnAs	670	870	3.4	318
MnBi	620	680	3.52	630
$\text{Mn}_4\text{N}$	183	-	1.0	743
MnSb	710	-	3.5	587
MnB	152	163	1.92	578

## Ferromagnetism

- *Ferromagnetism* is the phenomenon of spontaneous magnetization – the magnetization exists in a material in the absence of applied magnetic field.
- The best-known examples - transition metals Fe, Co, and Ni. Also, other elements and alloys involving transition or rare-earth elements, such as the rare-earth metals Gd, Dy, and the insulating transition metal oxides (CrO<sub>2</sub>).
- The phenomenon is restricted to transition and rare-earth elements ⇒ it is related to the unfilled 3*d* and 4*f* shells in these substances.
- Ferromagnetism involves the alignment of a significant fraction of the molecular magnetic moments in some favorable direction in the crystal.
- Ferromagnetism appears only below a certain temperature, which is known as the *ferromagnetic transition temperature* or simply as the *Curie temperature* (depends on the substance).

## Curie-Weiss law

Above the Curie temperature, the moments are oriented randomly, resulting in a zero net magnetization.

In this region the substance is paramagnetic, and its susceptibility is given by

$$\chi = \frac{C}{T - T_C} \quad \begin{array}{l} \text{- Curie-Weiss law.} \\ C \text{ - Curie constant} \\ T_C \text{ - Curie temperature} \end{array}$$

The Curie-Weiss law can be derived using arguments (Weiss):

In the ferromagnetics the moments are magnetized spontaneously, which implies the presence of an internal field to produce this magnetization.

The field is assumed that this field is proportional to the magnetization:

$$H_E = \lambda M \quad \lambda \text{ is the Weiss constant}$$

Weiss called this field the molecular field.

In reality, the origin of this field is the *exchange interaction*.

## Exchange interaction

- The exchange interaction is the consequence of the Pauli exclusion principle and the Coulomb interaction between electrons.
- Consider for example the system of two electrons. Two possible arrangements for the spins of the electrons: either parallel or antiparallel.

If they are parallel - electrons remain far apart (exclusion principle).

If spins are antiparallel, the electrons may come closer together and their wave functions overlap considerably.

- These two arrangements have different energies because, when the electrons are close together, the energy rises as a result of the large Coulomb repulsion (an explanation of the first Hund rule).

→ the electrostatic energy of an electron system depends on the relative orientation of the spins: the difference in energy defines the exchange energy.

- The exchange interaction is short-ranged ⇒ only nearest neighbor atoms are responsible for producing the exchange field.

The magnitude of the exchange field is very large – of the order of 10<sup>3</sup> T

Consider the paramagnetic phase: an applied magnetic field  $H_0$  causes a finite magnetization. This in turn causes a finite exchange field  $H_E$ .

If  $\chi_p$  is the paramagnetic susceptibility, the induced magnetization is given by

$$M = \chi_p (H_0 + H_E) = \chi_p (H_0 + \lambda M)$$

Note that  $M = \chi H$ , where  $\chi$  - constant holds only if the fractional alignment of magnetic moments is small: this is where the assumption is used that the sample is in the paramagnetic phase.

Solve the above equation for the magnitude of the magnetization  $M$ :

$$M = \frac{\chi_p H_0}{1 - \chi_p \lambda}$$

The paramagnetic susceptibility  $\chi_p$  is given by the Curie law  $\chi_p = C/T$ , where  $C$  is the Curie constant.

Then the susceptibility of the ferromagnetic material is  $\chi = \frac{M}{H_0} = \frac{C}{T - C\lambda} = \frac{C}{T - T_C}$

- Curie-Weiss law;  $T_C = C\lambda$

The susceptibility (5) has a singularity at  $T_C$ .  
 At this temperature (and below)  $\rightarrow$  a spontaneous magnetization  
 ( $\chi$  is infinite  $\Rightarrow$  can have a finite  $M$  for zero  $B_0$ )

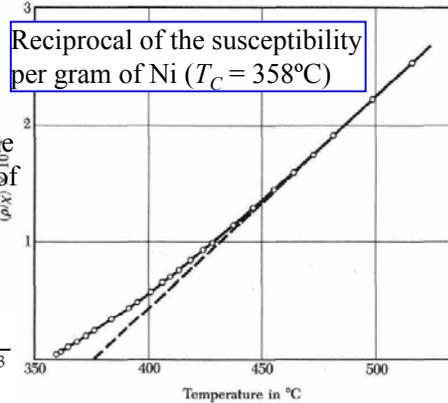
Last time, we obtained for  $C$ :  $C = \frac{\mu_0 N p^2 \mu_B^2}{3k_B}$  where  $p = g[J(J+1)]^{1/2}$

Then the Curie temperature is given by

$$T_C = \frac{\mu_0 N p^2 \mu_B^2 \lambda}{3k_B}$$

Deviations from Curie-Weiss only in the vicinity of the  $T_C$  - strong fluctuations of the magnetic moments close to the  $T_C$  can not be described by the mean field theory.

Accurate calculations:  $\chi \propto \frac{C}{(T - T_C)^{1.33}}$



One can also use the mean field approximation below the  $T_C$  to find the magnetization as a function of temperature.

Proceed as before but instead of the Curie law for paramagnetics (valid for not too high magnetic fields and not too low temperatures) can use the complete Brillouin function.

Omit the applied magnetic field and replace  $H$  by the exchange field  $E_E = \lambda M$

Get  $M = NgJ\mu_B B_J \left( \frac{\mu_0 g J \mu_B \lambda M}{k_B T} \right)$  where  $B_J(x)$  is the Brillouin function.

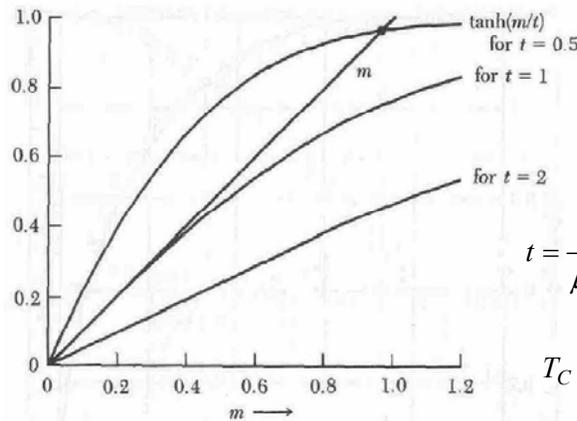
For  $J = s = 1/2$ , it has the form  $M = Ng\mu_B \tanh \left( \frac{\mu_0 g \mu_B \lambda M}{k_B T} \right)$

This is a transcendental equation in  $M$ , which can be solved numerically.

Write it the form  $M = Ng\mu_B \tanh x$  where  $x = \frac{\mu_0 g \mu_B \lambda}{k_B T} M$

or  $m = \tanh \frac{m}{t}$  where  $m = \frac{M}{Ng\mu_B}$   $t = \frac{k_B T}{\mu_0 Ng^2 \mu_B^2 \lambda}$

Graphical solution of  $m = \tanh \frac{m}{t}$



$$m = \frac{M}{Ng\mu_B}$$

$$t = \frac{k_B T}{\mu_0 Ng^2 \mu_B^2 \lambda} = \frac{T}{T_C}$$

$$T_C = \frac{\mu_0 N (g\mu_B)^2 \lambda}{k_B}$$

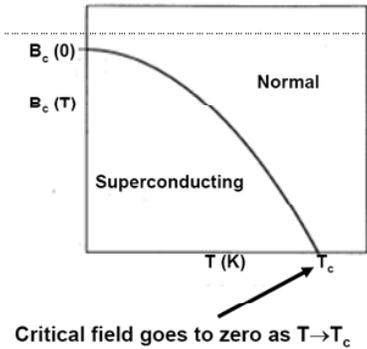
The curve for  $t = 1$  (or  $T = T_C$ ) is tangent to the straight line  $m$  at the origin; this temperature marks the onset of ferromagnetism.

As  $t \rightarrow 0$  the intercept moves up to  $m = 1 \Rightarrow$  all magnetic moments are aligned at  $T = 0$ . Maximum magnetization:  $m = 1 \Rightarrow M = Ng\mu_B$

Graphical solution of the equation for the Curie-Weiss model. The left-hand side of Eq. 7.14 is plotted as a straight line  $m$  with unit slope. The right-hand side of Eq. 7.14 involves the function  $\tanh(m/t)$  which is plotted vs  $m$  where the reduced magnetization  $m$  is given by  $m = M/(Ng\mu_B)$ . In the figure, plots are given for three different values of the reduced temperature  $t = k_B T / N \mu_B^2 \lambda M = T/T_C'$  for  $s = 1/2$  and  $g = 2$ . The three curves correspond to the temperatures  $2T_C'$ ,  $T_C'$ , and  $0.5T_C'$ . The curve for  $t = 2$  intersects the straight line  $m$  only at  $m = 0$ , as appropriate for the paramagnetic region (where the solution corresponds to zero external applied magnetic field). The curve for  $t = 1$  (or  $T = T_C'$ ) is tangent to the straight line  $m$  at the origin; this temperature marks the onset of ferromagnetism. The curve for  $t = 0.5$  is in the ferromagnetic region and intersects the straight line  $m$  at about  $m = 0.94N\mu_B$ . As  $t \rightarrow 0$  the intercept moves up to  $m = 1$ , so that all magnetic moments are lined up at absolute zero.

## SUPERCONDUCTORS

### B-T phase diagram



## FERROMAGNETS

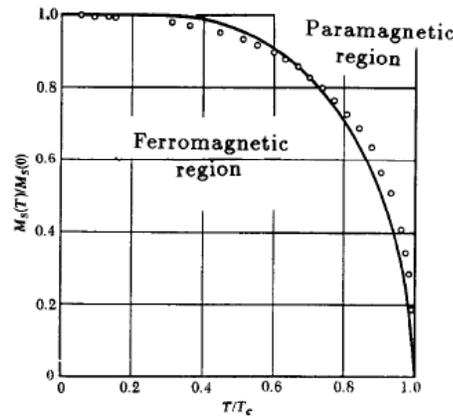


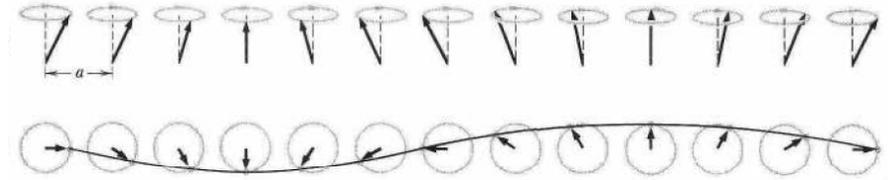
Figure 7.3: Phase diagram for a ferromagnetic system showing magnetization vs.  $T$ . The points are for Ni and the line is from mean field theory for  $S = 1/2$ .

## Spin waves

In ferromagnetic materials the lowest energy of the system occurs when all spins are parallel to each other in the direction of magnetization.

When one of the spins is tilted or disturbed, however, it begins to precess – due to the field from the other spins.

Due to the exchange interaction between nearest neighbors the disturbance propagates as a wave through the system:



Lattice waves – phonons - atoms oscillate around their equilibrium positions, their displacements are correlated through lattice forces.

In spin waves – *magnons* - the spins precess around the equilibrium magnetization and their precessions are correlated through exchange forces.

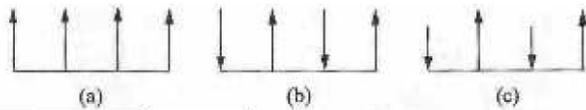
## Ferrimagnetism

The exchange interaction model leads to ferromagnetism, if the constant  $J$  is positive: the parallel-aligned state has a lower energy than the antiparallel.

The negative constant  $J$  leads to antiferromagnetism or ferrimagnetism.

**Antiferromagnetic** arrangement: the dipoles have equal moments, but adjacent dipoles point in opposite directions  $\Rightarrow$  zero net magnetization.

**Ferrimagnetic** arrangement: pattern: neighboring dipoles point in opposite directions, but the moments are unequal  $\Rightarrow$  a finite net magnetization.



Magnetic arrangements: (a) ferromagnetic, (b) antiferromagnetic, (c) ferrimagnetic.

A typical example of a ferrimagnetic material is magnetite,  $\text{Fe}_3\text{O}_4$ .

More explicitly,  $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \rightarrow$  two types of iron ions:  $\text{Fe}^{2+}$  (ferrous) and  $\text{Fe}^{3+}$  (ferric).

Spinel structure ( $\text{AB}_2\text{O}_4$ ):

The unit cell contains 56 ions, 24 – iron; the rest - oxygen.

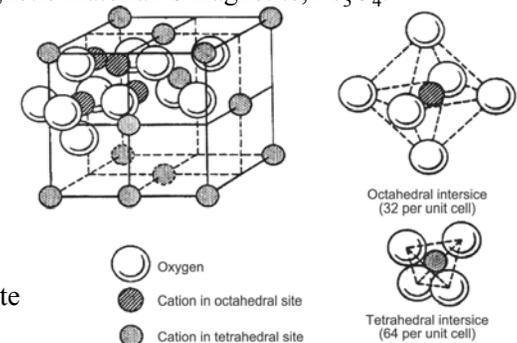
Fe ions - two different coordinate environments: a tetrahedral and octahedral (surrounded by 4 and 6 oxygen ions)

8 of the 16  $\text{Fe}^{3+}$  ions in the unit cell are in each type of position

The tetrahedral structure has moments oriented opposite to those of the octahedral one  $\rightarrow$  complete cancellation of the contribution of the  $\text{Fe}^{3+}$  ions.

$\Rightarrow$  the net moment is entirely due to the 8  $\text{Fe}^{2+}$  ions (octahedral sites)

Each of these ions has six 3d electrons, whose spin orientations are  $\uparrow\uparrow\uparrow\uparrow\downarrow$ .  
 $\Rightarrow$  each ion carries a moment equal to  $4\mu_B$ .



## Antiferromagnetism

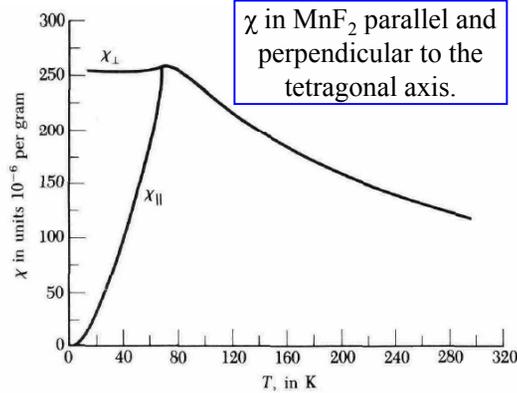
An antiferromagnet – like a ferrimagnet with both sublattices having equal magnetizations.

In an antiferromagnet the spins are ordered in an antiparallel arrangement with zero net moment at temperatures below the ordering temperature which is called the *Néel temperature* ( $T_N$ ).

Above the  $T_N$

$$\chi = \frac{C}{T + T_N'}$$

below the Néel temperature,  $\chi$  depends strongly on the orientation of magnetic field.



## Ferromagnetism in metals

Model discussed – for insulators (localized electrons)

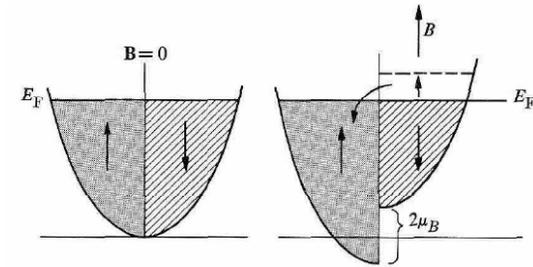
In metals, the electrons are delocalized

In the non-magnetic state, the two subbands are equally populated.

Now, assume there is an exchange interaction → tends to align spins ↑↑

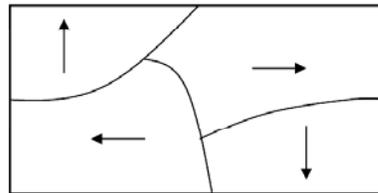
⇒ electrons flip their spins from ↓ to ↑ - subbands are no longer equal

⇒ net magnetization appears

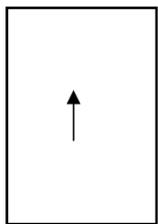


## Domains

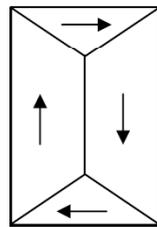
Spin in a material with long range magnetic ordering (ferromagnetic, antiferromagnetic etc.) form domains.



Reason for domain formation:



Higher energy



Lower energy

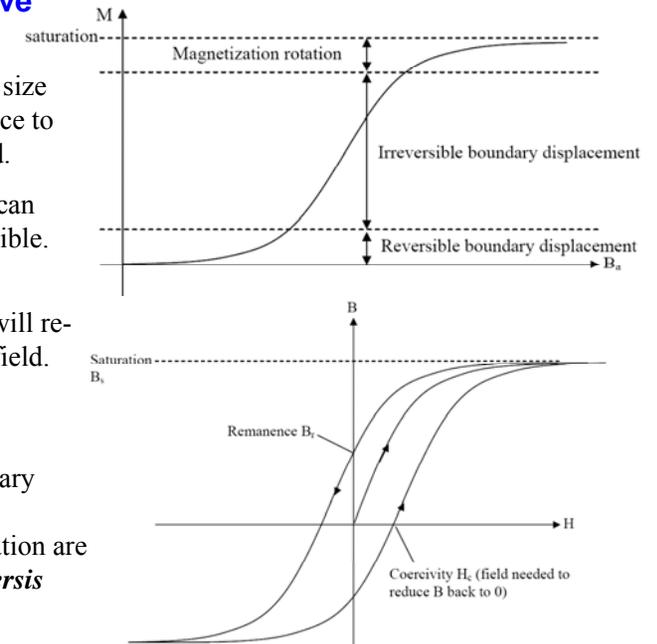
## Magnetization curve

For small field, domain size will change in accordance to the direction of the field.

Change in domain size can be reversible or irreversible.

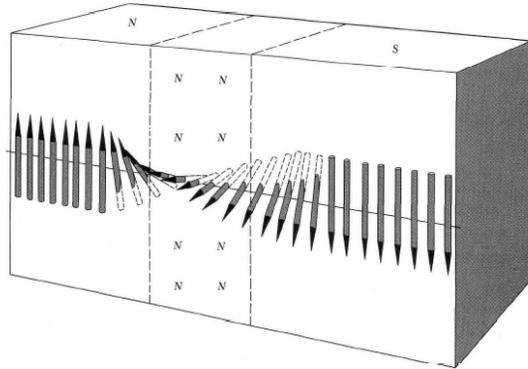
For large field, domain magnetization will realign with the external field.

Irreversible boundary displacement and magnetization rotation are the causes of *hysteresis*



## Domain walls

The boundary regions between neighboring domains



The typical size of the domains is 1-100  $\mu\text{m}$ ;  
the width of the domain walls is much smaller:  $\sim 100$  nm.

→ the domain structure consists of uniformly magnetized domains separated by narrow boundaries.

## Summary

- ❖ Ferromagnetic material exhibits spontaneous magnetization below the Curie temperature ( $T_C$ ).  
Above the  $T_C$  – paramagnetic; Curie-Weiss Law:  $\chi = \frac{C}{T - T_C}$
  - ❖ Cause for ferromagnetism: - exchange interaction
  - ❖ Due to the exchange interaction, a spin disturbance propagates through a material as a spin wave. Their quanta - magnons
  - ❖ When a magnetic field is applied to a material, the dipole moments of the atoms precess around it with a frequency  $\omega_0 = \gamma B_0$ ;  
 $\gamma = ge/2m$  – gyromagnetic ratio. When an electromagnetic wave of frequency  $\omega = \omega_0$  passes through material, it is absorbed by the dipoles. This is called **electron paramagnetic resonance**
- Nuclear magnetic resonance** – the same phenomenon caused by nuclear magnetic moments
- Ferromagnetic resonance** – the same as EPR, but strong internal magnetic field has to be taken into account

Knowing the  $T_C$  (measured experimentally)  
one can determine the Weiss constant  $\lambda$ :

$$\lambda = \frac{k_B T_C}{\mu_0 N (g \mu_B)^2}$$

The Weiss constant  $\lambda$  is related to the exchange constant.

The interaction between two spins may be written as  $V_{ex} = J \mathbf{s}_1 \cdot \mathbf{s}_2$

$J$  must be positive (parallel spins:  $V_{ex}$  negative)

If we assume exchange interaction is with the nearest neighbors only,  
the total exchange energy for the dipole is  $-zJ's^2$

This is equivalent to an exchange field  $H_E$ :  $\mu_0 H_E g s \mu_B = -zJ's^2$

Maximum value of  $H_E$