

Lecture 24

Origins of Magnetization

(A number of illustrations in this lecture were generously provided by Prof. Geoffrey Beach)

Today

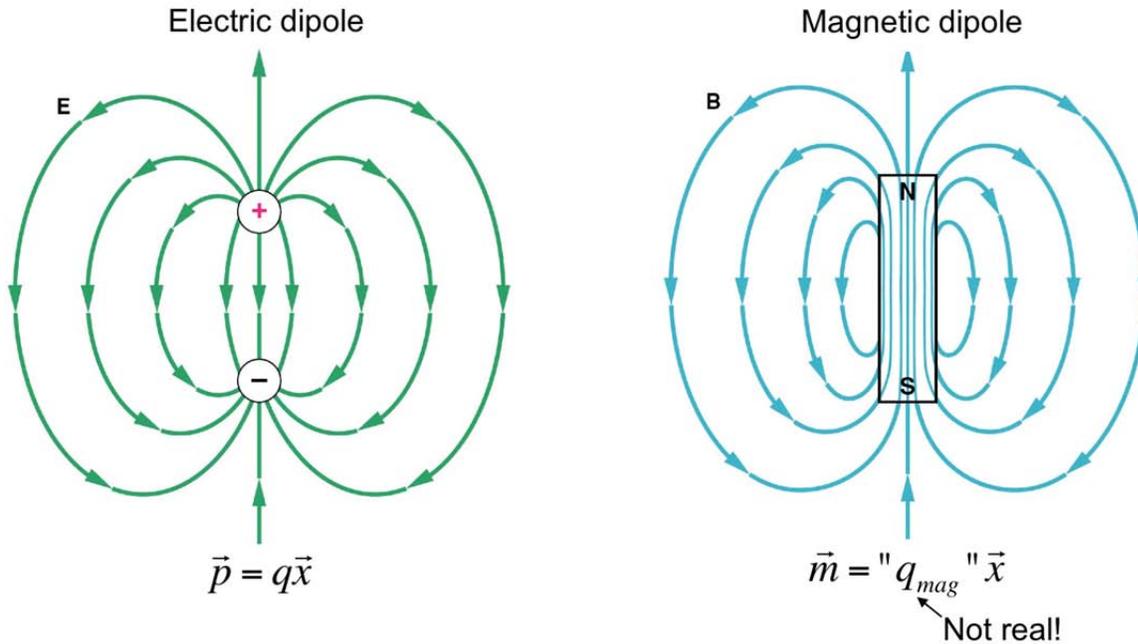
1. Magnetic dipoles.
2. Orbital and spin angular momenta.
3. Non-interacting magnetic dipoles: paramagnetism
4. Exchange interaction: ferromagnetism, anti-ferromagnetism, ferrimagnetism.
5. Curie and Néel temperatures.

Questions you should be able to answer by the end of today's lecture

1. What is the origin of magnetic dipoles?
2. How does magnetic dipole relates to the orbital angular momentum and spin?
3. What is saturation magnetization?
4. What is the physical origin of the exchange interaction?
5. What is the form of magnetic interaction Hamiltonian?
6. How to classify materials with respect to exchange integral?
What are the differences between ferromagnetic, anti-ferromagnetic and ferromagnetic materials?
7. At what temperature do materials loose their ferro-, anti-ferro- and ferromagnetic properties?

Recall our discussion of the origins of polarization and its implications on the optical properties of materials. Similar logic can be applied to the discussion of magnetization.

We can describe the material as a collection of magnetic dipoles \vec{m} :



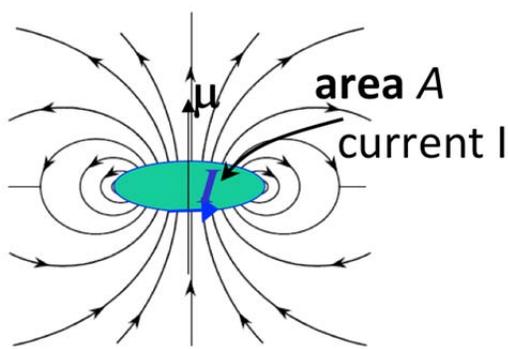
Then we can draw an analogy between the polarization and magnetization:

$$\left. \begin{aligned} \vec{P} &= N\vec{p} = \epsilon_0 \chi \vec{E} \\ \vec{D} &= \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 (1 + \chi) \vec{E} \end{aligned} \right\} \rightarrow \left\{ \begin{aligned} \vec{M} &= N\vec{\mu} = \mu_0 \chi_m \vec{H} \\ \vec{B} &= \epsilon_0 \vec{H} + \vec{M} = \mu_0 (1 + \chi_m) \vec{H} \end{aligned} \right.$$

Obviously, magnetic monopoles have not yet been found and likely do not exist. So what is the origin of magnetic dipoles inside a material?

Let's take a closer look at a simplistic classical representation of the Hydrogen atom: electron spinning around the proton nucleus.

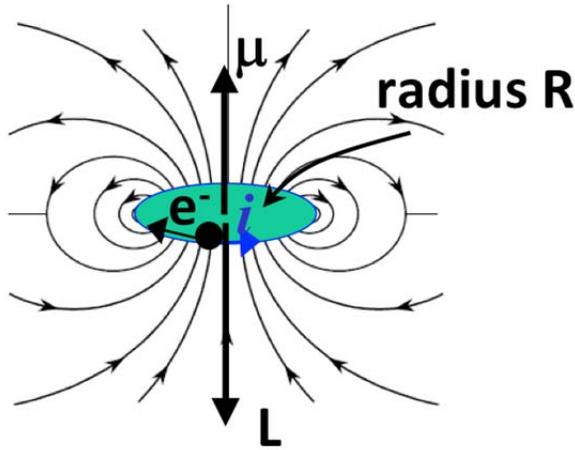
From Maxwell's equation we know that in the absence of alternating electric field magnetic field is produced by currents:



$$\left. \begin{aligned} \nabla \times \vec{H} - \frac{\partial \vec{D}}{\partial t} &= \vec{J} \\ \frac{\partial \vec{D}}{\partial t} &= \vec{0} \end{aligned} \right\} \Rightarrow \nabla \times \vec{H} = \vec{J}$$

If we approximate the atom with a current loop, then the magnetic dipole moment can be related to the current simply as: $|\vec{\mu}| = I \cdot A$, where A is the area of the current loop and I is current in the loop.

If the radius of the Hydrogen atom (approximated by the current loop) is R and electron charge is e , then the current corresponding to the electron rotation around the nucleus is:



$$I = \frac{ev}{2\pi R}$$

Then the magnetic dipole is:

$$|\vec{\mu}| = I \cdot A = \frac{ev}{2\pi R} \pi R^2 = \frac{1}{2} evR$$

The expression above looks very similar to the one for the orbital angular momentum:

$$\vec{L} = m\vec{v} \times \vec{r} \Rightarrow |\vec{L}| = mvR$$

Hence we can relate the magnetic dipole to the orbital angular momentum:

$$|\vec{\mu}| = \frac{e}{2m_e} |\vec{L}| = \gamma |\vec{L}|, \text{ where } \gamma = \frac{e}{2m_e} \text{ is the gyromagnetic ratio.}$$

While our naive classical view of the spinning electron is helpful in gaining the intuition about the connection between the orbital angular momentum and the magnetic dipole, it is not completely correct.

As you remember from our discussion of the Hydrogen atom, the orbital angular momentum can be described by the operators \hat{L}^2 , \hat{L}_z :

$$\hat{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi)$$

$$\hat{L}_z Y_l^m(\theta, \varphi) = \hbar m Y_l^m(\theta, \varphi)$$

From the first equation we can conclude that the length of the orbital angular momentum is:

$$|\vec{L}| = \sqrt{\hat{L}^2} = \hbar \sqrt{l(l+1)}, \text{ then } \mu_l = \gamma |\vec{L}| = \gamma \hbar \sqrt{l(l+1)}$$

However, this is still not a complete picture – we need to include another part of the angular momentum: spin!

Recall, that spin is described similar to the orbital angular momentum:

$$\hat{S}^2 \chi = \hbar^2 s(s+1) \chi, \text{ then } \mu_s = \gamma |\vec{S}| = \gamma \hbar \sqrt{s(s+1)}$$

$$\hat{S}_z \chi = \hbar s \chi$$

The value: $\mu_B = \gamma \hbar = \frac{e\hbar}{2m_e}$ is generally referred to as **Bohr magneton**.

Then the atom is described by the magnetic dipoles originating from both orbital and spin angular momenta:

$$\mu_l = \mu_B \sqrt{l(l+1)}$$

$$\mu_s = \mu_B \sqrt{s(s+1)}$$

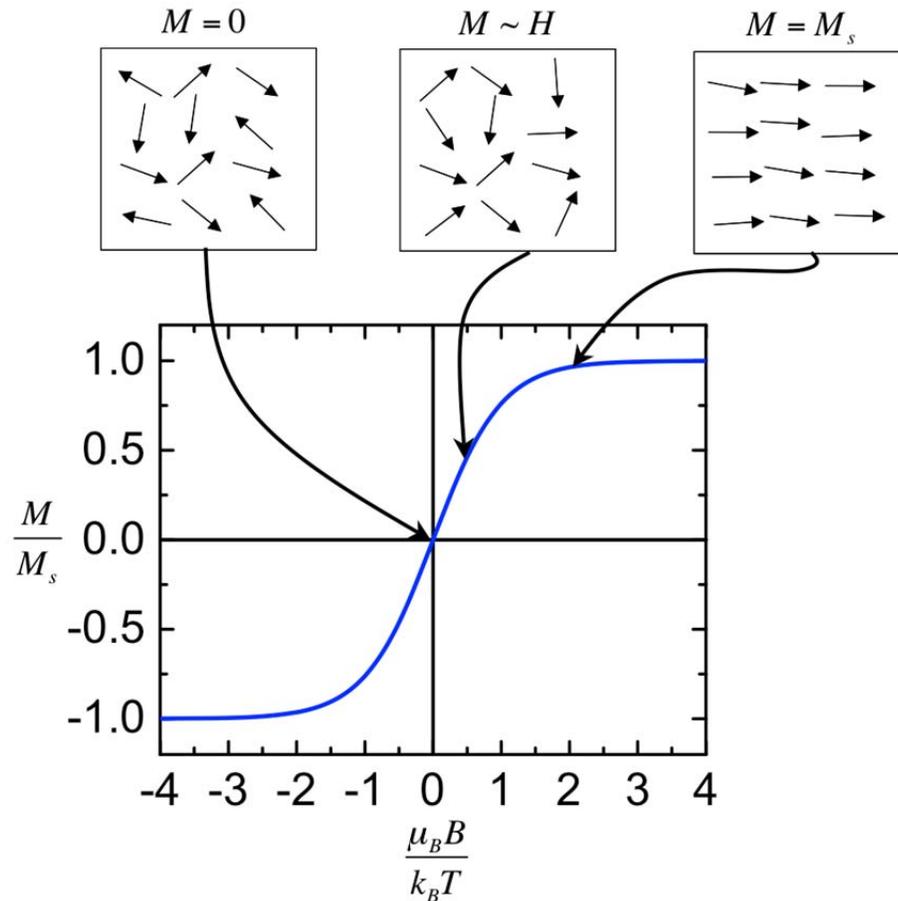
In reality the magnetic dipole is correctly described by the combined angular momentum:

$\vec{J} = \vec{L} + \vec{S}$, which obeys the same formalism as the orbital and spin angular momenta:

$$\hat{J}^2 \psi = \hbar^2 j(j+1) \psi \Rightarrow |\vec{J}| = \hbar \sqrt{j(j+1)} \Rightarrow |\vec{\mu}| = \mu_B \sqrt{j(j+1)}$$

Now that we have established the origins of the magnetic dipoles inside the material, we can investigate the behavior of the material in the magnetic field. Let's start with the simplest material, in which we can approximate all the magnetic dipoles as independent and non-interacting with each other. These materials are called "*paramagnetic*".

Paramagnetism



When the magnetic dipoles do not interact with each other, **at room temperature in the absence of the external magnetic field** they will be oriented randomly with respect to each other and hence the **magnetization** of the sample as a whole **is zero**.

When sufficiently large external magnetic field is applied, the magnetic dipoles will start to orient parallel to the field. Eventually when all magnetic dipoles are oriented parallel to the field the magnetization of the material reaches its maximum value referred to as a “saturation magnetization” M_s .

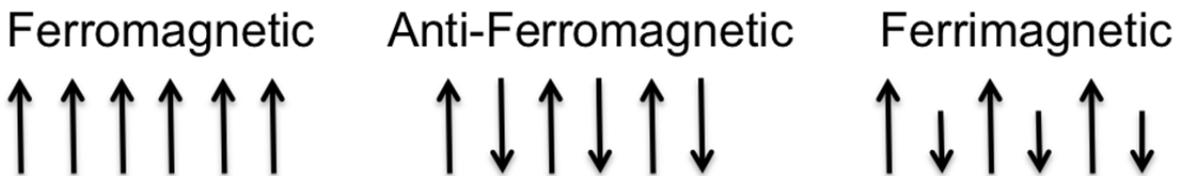
Note, that in order to get to saturation magnetization in a paramagnetic material one needs extremely high magnetic fields on the order of ~ 100 T (T=Tesla). However the largest magnets that have been experimentally achieved provide fields on the order of 10s of Tesla. Consequently, paramagnets never achieve saturation magnetization experimentally.

If paramagnetism does not allow us to create large permanent magnets, then what does?

Can magnetic dipoles inside the material get oriented spontaneously?

When magnetic dipoles inside the material interact with each other, it causes them to orient themselves in particular arrangements that minimize the total energy of the material.

Based on the respective orientation of the neighboring magnetic dipoles, the materials are classified into ferromagnetic, anti-ferromagnetic and ferrimagnetic.



What is the origin of the interaction that causes the neighboring magnetic dipoles to take on a particular orientation with respect to each other?

To address this question let’s consider a simple material consisting of the Hydrogen-like atoms with a single electron on the outer most orbital. Now let’s consider two of such atoms brought into each other’s immediate vicinity. Recall that electrons are fermions and when we bring two of them into our system we need to build an anti-symmetric wavefunction for that system (see Lecture 12).

Wavefunction for the 2-electron system can be build simply as a multiplication of the spacial and spin parts:

$$\Psi(1,2) = \psi(\vec{r}_1, \vec{r}_2) \chi(1,2)$$

Where $\psi(\vec{r}_1, \vec{r}_2)$ is the spacial wavefunction and $\chi(1,2)$ is the spin wavefunction.

Since electrons are Fermions $\Psi(1,2) = -\Psi(2,1)$, either $\psi(\vec{r}_1, \vec{r}_2)$ or $\chi(1,2)$ need to be anti-symmetric with respect to the electron exchange.

From Lecture 12 you remember that the spacial function can have the following form:

$$\text{Symmetric: } \psi_s(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)]$$

$$\text{Anti-symmetric: } \psi_a(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)]$$

Here $\varphi_1(\vec{r}_1)$ and $\varphi_2(\vec{r}_2)$ are the single electron wavefunctions.

Similar logic applies to the spin wavefunctions. Taking into account that spin wavefunctions only carry the information about spin being “up” or “down”, the 2-electron wavefunctions can have the following forms:

$$\chi_s(1, 2) = \begin{cases} \chi_{\uparrow}(1)\chi_{\uparrow}(2) \\ \chi_{\downarrow}(1)\chi_{\downarrow}(2) \\ \frac{1}{\sqrt{2}}[\chi_{\uparrow}(1)\chi_{\downarrow}(2) + \chi_{\downarrow}(1)\chi_{\uparrow}(2)] \end{cases} = \text{triplet state}$$

$$\chi_a(1, 2) = \frac{1}{\sqrt{2}} [\chi_{\uparrow}(1)\chi_{\downarrow}(2) - \chi_{\downarrow}(1)\chi_{\uparrow}(2)] = \text{singlet state}$$

Consequently, the total 2-electron wavefunction can take the following forms:

$$\Psi(1, 2) = \begin{cases} \psi_s(\vec{r}_1, \vec{r}_2)\chi_a(1, 2) \\ \psi_a(\vec{r}_1, \vec{r}_2)\chi_s(1, 2) \end{cases}$$

How would we describe the Hamiltonian that imposes the rules for interaction between the two electrons? The total Hamiltonian for this 2-electron system can be written as follows:

$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{ex}$, where \hat{H}_1 , \hat{H}_2 are the single electron Hamiltonians and \hat{H}_{ex} is the Hamiltonian for the exchange interaction.

$\hat{H}_{ex} = -2J_{ex}\hat{S}_1\hat{S}_2$, where \hat{S}_1 , \hat{S}_2 are the spin operators for the electrons 1 and 2 and J_{ex} is the “**exchange integral**” or “**overlap integral**”, which basically informs us about the relative proximity of the electrons to each other:

$$J_{12} = \iint \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\hat{H}_{ex}\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)d^3\vec{r}_1d^3\vec{r}_2$$

Exchange interaction is very strong, but exponentially decays with distance. This interaction is sufficient to spontaneously orient neighboring magnetic dipoles at room temperature.

When external magnetic field is applied the total Hamiltonian for the system will have the following form:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{ex} + \hat{H}_{1,field} + \hat{H}_{2,field} = \hat{H}_1 + \hat{H}_2 - J_{12}\hat{S}_1\hat{S}_2 + \vec{B} \cdot \hat{\mu}_1 + \vec{B} \cdot \hat{\mu}_2$$

For simplicity we can write: $\hat{\mu}_{1,2} = \gamma \hat{S}_{1,2} = \frac{\mu_B}{\hbar} \hat{S}_{1,2}$

Then the magnetic portion of the Hamiltonian can be written as:

$$\hat{H}_{magnetic} = -J_{12} \hat{S}_1 \hat{S}_2 + \frac{\mu_B}{\hbar} \vec{B} \hat{S}_1 + \frac{\mu_B}{\hbar} \vec{B} \hat{S}_2$$

When we have a magnetic field applied to a large collection of magnetic dipoles originating from electron spins, the magnetic Hamiltonian will have a form:

$$\hat{H}_{magnetic} = -\sum_{i,j} J_{ij} \hat{S}_i \hat{S}_j + \frac{\mu_B}{\hbar} \sum_i \vec{B} \hat{S}_i = \sum_i \left[\sum_j J_{ij} \hat{S}_j + \frac{\mu_B}{\hbar} \vec{B} \right] \cdot \hat{S}_i$$

Rather than considering exchange interactions between each pair of magnetic dipoles inside the material it is simpler to think of a mean magnetic field originating from a collection of neighboring magnetic dipoles and its actions on the individual magnetic dipole:

$$-\sum_j J_{ij} \hat{S}_j \rightarrow \frac{\mu_B}{\hbar} \vec{B}_{ex}, \text{ where } \vec{B}_{ex} \text{ is referred to molecular exchange field.}$$

Then the magnetic Hamiltonian is simply a combination of the effects of the exchange and the applied magnetic field:

$$\hat{H}_{magnetic} = \frac{\mu_B}{\hbar} \sum_i \left[\vec{B}_{ex} + \vec{B}_{applied} \right] \cdot \hat{S}_i$$

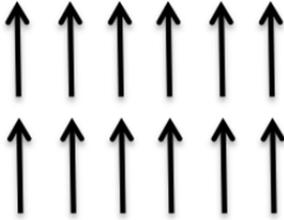
The mean exchange field is responsible for spontaneous ordering of the magnetic dipole in the absence of the applied magnetic field.

Obviously spontaneous ordering of magnetic moments minimizes the entropy and consequently it cannot happen just at any temperature. At certain temperature the thermal energy $k_B T$ becomes greater than the exchange energy E_{ex} and the material becomes disordered (entropy wins) and behaves as paramagnetic.

The temperature at which the material undergoes the transition from disordered to ordered is referred to as Curie temperature T_C for ferromagnetic materials and Neél temperature T_N for anti-ferromagnetic and ferrimagnetic materials.

Material	Curie temperature, K
Iron (Fe)	1043
Cobalt (Co)	1388
Nickel (Ni)	627
Gadolinium (Gd)	293
Dysprosium (Dy)	85
Iron Oxide (Fe ₂ O ₃)	895

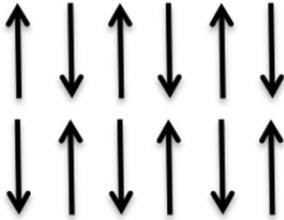
Based on the sign of the exchange integral we can classify materials as:



Ferromagnetic:

$J_{ex} > 0 \Rightarrow$ exchange energy is minimized when $\hat{S}_i \uparrow \uparrow \hat{S}_j$

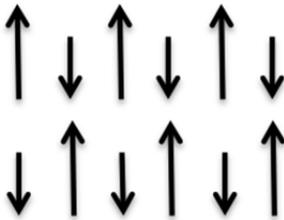
Large spontaneous magnetization at $T < T_C$



Anti-ferromagnetic:

$J_{ex} < 0 \Rightarrow$ exchange energy is minimized when $\hat{S}_i \uparrow \downarrow \hat{S}_j$

No net magnetization, but ordering at $T < T_N$



Ferrimagnetic:

$J_{ex} < 0 \Rightarrow$ exchange energy is minimized when $\hat{S}_i \uparrow \downarrow \hat{S}_j$

Reduced net magnetization (as compared to ferromagnetic materials),
spontaneous ordering at $T < T_N$

All materials become paramagnetic at temperatures above T_C or T_N .

MIT OpenCourseWare
<http://ocw.mit.edu>

3.024 Electronic, Optical and Magnetic Properties of Materials
Spring 2013

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.