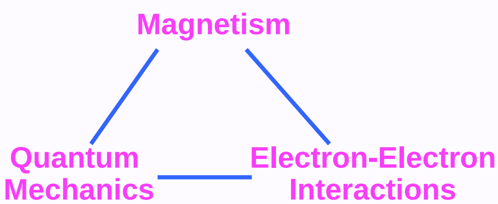
Lecture 24 - Magnetism

Lecture 24: Magnetism
(Kittel Ch. 11-12)



Outline

- Magnetism is a purely quantum phenomenon!
  Totally at variance with the laws of classical physics
  (Bohr, 1911)
- Diamagnetism
- Spin paramagnetism – (Pauli paramagnetism)
- Effects of electron-electron interactions
  - Hund's rules for atoms – examples: Mn, Fe
  - Atoms in a magnetic field – Curie Law
  - Atomic-like local moments in solids
  - Explains magnetism in transition metals, rare earths
- Magnetic order and cooperative effects in solids
  - Transition temperature Tc
  - Curie-Weiss law
- Magnetism: example of an "order parameter"
- (Kittel Ch. 11-12 – only selected parts)

Magnetism and Quantum Mechanics

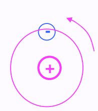
- **Why is magnetism a quantum effect?**
- In classical physics the change in energy of a particle per unit time is **F** · **v** (**F** = force, **v** = velocity **vectors**).
- In a magnetic field the force is always perpendicular to velocity - therefore the energy of a system of particles cannot change in a magnetic field **B**
- Similarly the equilibrium free energy cannot change with applied **B** field
- Since the change in energy is d**B** · **M** , there must be no total magnetic moment **M** !

Definitions

- **B** = μ_0 (**H** + **M**)
  (μ_0 is the permeability of free space,
  B is the field that causes forces on particles)
- If the magnetization is proportional to field,
  M = χ **H** and **B** = μ **H** , $\mu = \mu_0 (1 + \chi)$
- Diamagnetic material: $\chi < 0$; $\mu < \mu_0$
- Paramagnetic material: $\chi > 0$; $\mu > \mu_0$
- Ferromagnetic material: **M** $\neq 0$ even if **H** $= 0$

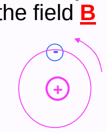
Diamagnetism

- Consider a single "closed shell" atom in a magnetic field
  (In a closed shell atom, spins are paired and the electrons are distributed spherically around the atom - there is no total angular momentum.)
- Diamagnetism results from current set up in atom due to magnetic field
- Like Lenz's law - current acts to oppose the external field and "shield" the inside of the atom from the field (like a dielectric)



"Classical" Theory of Diamagnetism

- If the field **B** is small compared to the quantum energy level separation, the closed shell atom may be considered to rotate rigidly due to the field **B**
- This is like a classical current - BUT it occurs only because the atom is in a quantized state



- The entire electron system rotates together with the frequency $\omega = eB/2m$
- Like Lenz's law - the current acts to oppose the external field

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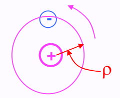
"Classical" Theory of Diamagnetism

- Total current = charge/time = $I = (-Ze)\ (1/2\pi)(eB/2m)$
- Magnetic moment = current times area = $I \times \pi\langle\rho^2\rangle$
  $= \mu = (-Ze^2B/4m)\ \langle\rho^2\rangle$
  (ρ = distance from axis)



- Susceptibility =

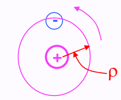
  $\chi = \mu_0\ M/B = -\ \mu_0 NZe^2/4m\ \langle\rho^2\rangle = -\ \mu_0 NZe^2/6m\ \langle r^2\rangle$

  where $M = N\mu$, N = density of atoms, and for a spherical atom $\langle r^2\rangle = 2/3\ \langle\rho^2\rangle$, where r is the radius in 3 dimensions

"Classical" Theory of Diamagnetism

- From previous slide - for closed shell atoms

  $\chi = \mu_0\ M/B = -\ \mu_0 NZe^2/6m)\ \langle r^2\rangle$



- Results: VERY small diamagnetism!
  For rare gasses in a solid, magnetic susceptibility is only VERY slightly less than in vacuum

- Similar results are found for typical "closed shell" insulators -- like Si, diamond, NaCl, SiO_2, …. because they have paired spins and filled bands like a closed shell atom -- VERY weak diamagnetism

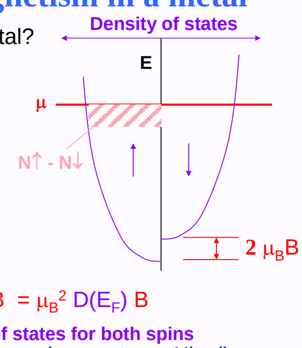
Spin Paramagnetism

- What about spin?
- Unpaired spins are affected by magnetic field!
- The energy in a field is given by
  $U = -\ \underline{\mu} \cdot \underline{B} = -\ m\ g\ \mu_B\ B$
  where m = component of spin = ±1/2,
  g = "g factor" = 2,
  and μ_B = Bohr magneton = $e\hbar/2m$

- Any atom with an unpaired spin (e.g. and odd number of spins) must have this effect
- At temperature = 0, the spin will line up with the field in a paramagnetic way - i.e. to increase the field

Spin Paramagnetism in a metal

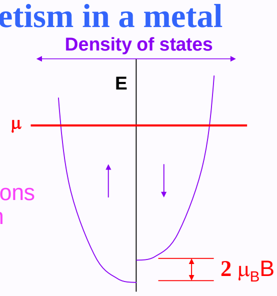
- What happens in a metal?
- Spin up electrons (parallel to field) are shifted opposite to spin down electrons (antiparallel to field)
- Energies shift by
  $\Delta E = \pm\ \mu_B\ B$
- Magnetization
  $M = \mu_B\ (N\uparrow - N\downarrow)$
  $= \mu_B\ (1/2)\ D(E_F)\ 2\ \mu_B\ B\ = \mu_B^2\ D(E_F)\ B$



- Free electron gas (see previous notes + Kittel)
  $M = (3/2)\ N\ \mu_B^2\ B/(k_B T_F)$

Spin Paramagnetism in a metal

- Result for a metal:
- $M = \mu_B^2\ D(E_F)\ B$ or
  $\chi = \mu_B^2\ D(E_F)$
- This is a way to measure the density of states!
  (Note: There are corrections from the electron-electron interactions.)

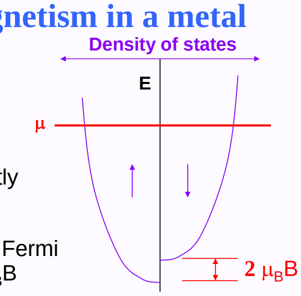


- **Paramagnetic**

  Tends to align with the field to increase the magnetization

Spin Paramagnetism in a metal

- Early success of quantum mechanics
- Explained by Pauli



- The magnitude is greatly reduced by the factor
  $\mu_B B/(k_B T_F)$
  due to the fact that the Fermi energy $E_F = k_B T_F \gg \mu_B B$ for any reasonable B
- The same reason that the heat capacity is very small compared to the classical result

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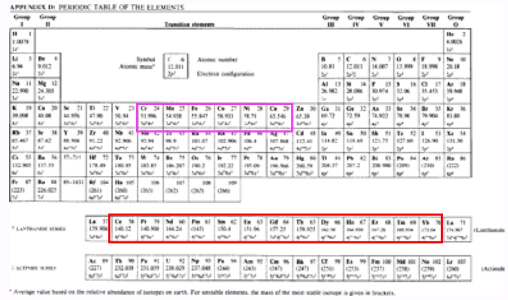
Magnetic materials

- What causes some materials (e.g. Fe) to be ferromagnetic?
- Others like Cr are antiferromagnetic (what is this?)
- Magnetic materials tend to be in particular places in the periodic table: transition metals, rare earths Why?
- Starting point for understanding: the fact that open shell atoms have moments. Why?
- Leads us to a re-analysis of our picture of electron bands in materials. The band picture is not the whole story!

Questions for understanding materials:

- **Why are most magnetic materials composed of the 3d transition and 4f rare earth elements**

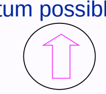


The first step in understanding magnetic materials

- Magnetic moments of atoms
- In most magnetic materials (Fe, Ni, ….) the first step in understanding magnetism is the consider the material as a collection of atoms
- Of course the atoms change in the solid, but this gives a good starting point – qualitatively correct

When are atoms magnetic?

- An atom MUST have a magnetic moment if there are and odd number of electrons – spin ½ (at least)
- "Open shell" atoms have moments – Hund's rules –
  1st rule: maximum spin for electrons in a given shell
  2nd rule: maximum angular momentum possible for the given spin orientation



- Example: Mn^{2+} - 5 d electrons
  A d shell has L=2, m_L = -2,-1,0,1,2

  ↑ ↑ ↑ ↑ ↑ **S_{total} = 5/2, L_{total} = 0**

  m_L = -2 -1 0 1 2

- Fe^{2+} - 6 d electrons

  ↑↓ ↑ ↑ ↑ ↑ **S_{total} = 4/2, L_{total} = 2**

  m_L = -2 -1 0 1 2

Hund's Rules & Electron Interactions

Hund's rules –

1st rule: maximum spin for electrons in a given shell

Reason – parallel-spin electrons are kept apart because they must obey the exclusion principle – thus the repulsive interaction between electrons is reduced for parallel spins!

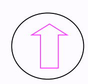
2nd rule: maximum angular momentum possible for the given spin orientation

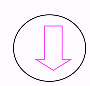
Reason – maximum angulat momentum means electrons are going the same direction around the nucleus – stay apart – lower energy!

Electron-Electron Interactions!

Magnetic atoms in free space

- **Curie Law** (Kittel p 305)
- Consider N isolated atoms, each with two states (spin 1/2) that have the same energy with no magnetic field, but are split in a field into $E_1 = -\mu B$, $E_2 = \mu B$





- In the field B, the populations are:
  $N_1 / N = \exp(\mu B/k_BT) / [\exp(-\mu B/k_BT) + \exp(\mu B/k_BT)]$
  $N_2 / N = \exp(-\mu B/k_BT) / [\exp(-\mu B/k_BT) + \exp(\mu B/k_BT)]$
- So the magnetization M is
  $M = \mu (N_1 - N_2) = \mu N \tanh(x)$, $x = \mu B/k_BT$

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Magnetic atoms in free space

- **Curie Law** -- continued
- Similar laws hold for any spin

$M = gJ\mu_B N B_J(x)$, $x = gJ\mu_B B / k_B T$

where $B_J(x)$ = Brillouin Function (Kittel p 304)

- Key point: For small x (small B or large T) the susceptibility has the form

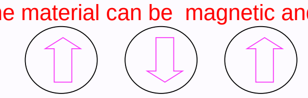
Curie Law

$\chi = M/B = C/T$, where C = Curie constant

- For large x (large B or T small compared to $gJ\mu_B B / k_B$) M saturates and $\chi \to$ constant

When do solids act like an array of magnetic moments?

- Consider a solid made from atoms with magnetic moments
- If the atoms are widely spaced, they retain their atomic character -- insulators because electron-electron interactions prevent electrons from moving freely
- Thus the material can be magnetic and insulating!



- OPPOSITE to what we said before! Real materials can be metallic and non-magnetic (like Na) or magnetic insulators (see later)

When are atoms magnetic?

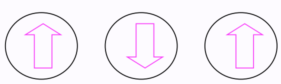
- Which atoms are most likely to keep their atomic like properties in a solid?

Transition metals and rare earths

Why?

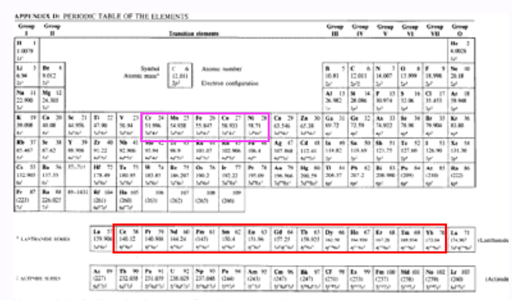
Because the electrons act like they have partially filled shells even in the solid!

This is why they have a special place in the periodic table - the elements in the transition series have similar chemical properties as the electrons fill the 3d or 4f shell



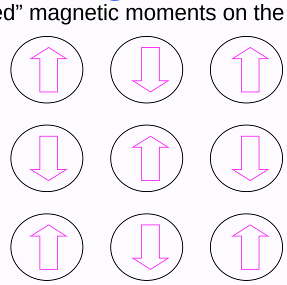
Questions for understanding materials:

3d transition 4f rare earth



Magnetic solid

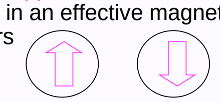
- "Localized" magnetic moments on the atoms



- How do the atoms decide to order?

How do magnetic atoms affect each other?

- Curie-Weiss Law (Kittel p 324)
- The simplest approximation is to assume each atom acts like it is in an effective magnetic field $\underline{\mathbf{B}}_E$ due to the neighbors



- One expects $\underline{\mathbf{B}}_E = \lambda \underline{\mathbf{M}}$ where λ is some factor - see next slide
- At high temperature we do not expect any net order, i.e., $\underline{\mathbf{B}}_E = 0$ and $\underline{\mathbf{M}} = 0$ unless one applies an external field $\underline{\mathbf{B}}_A$.
- What happens as the temperature is lowered?

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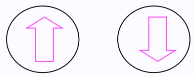
How do magnetic atoms affect each other?

- Note: The "effective magnetic field $\mathbf{B}_E$" is NOT really a "magnetic field" as in Maxwell's Equations



- The "effective magnetic field $\mathbf{B}_E$" is due to the exclusion principle and electron-electron interactions that depend upon the relative spin of nearby electrons
- The "effective magnetic field $\mathbf{B}_E$" can favor parallel spins or antiparallel spins - depends upon many details - simplest approximation is $\mathbf{B}_E = \lambda\, \mathbf{M}$

Curie-Weiss Law

- At high temperature we have
  $\mathbf{M} = \chi\, (\mathbf{B}_E + \mathbf{B}_A)$ or $\mathbf{M}\,(1-\lambda\chi) = \chi\, \mathbf{B}_A$
  or $\mathbf{M} = \mathbf{B}_A\, \chi / (1-\lambda\chi)$

Approximate form valid at high T - sufficient for present purposes

- Using the form of $\chi = C/T$,

  $\chi / (1-\lambda\chi) = 1/(T/C - \lambda)$

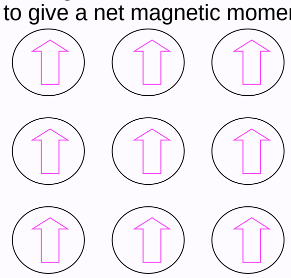
Diverges as T is reduced to $T = T_c = \lambda C$

  or
  $\chi_{eff} = \chi / (1-\lambda\chi) = C/(T - T_c)$, $T_c = C\,\lambda$

- What does this mean? The magnetic moments all allign to make a ferromagnet without any external field below a critical temperature T_c

Ferromagnetic solid

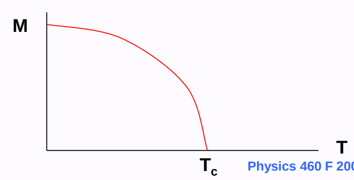
- "Localized" magnetic moments on the atoms aligned together to give a net magnetic moment



- Although there is some thermal disorder, there is a net moment at finite temperature.

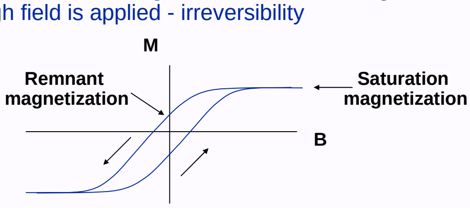
Example of a phase transition to a state of new order

- At high temperature, the material is paramagnetic
  Magnetic moments on each atom are disordered
- At a critical temperature T_c the moments order
  Total magnetization M is an "Order Parameter"
- Transition temperatures:
  T_c = 1043 K in Fe, 627 K in Ni, 292 K in Gd



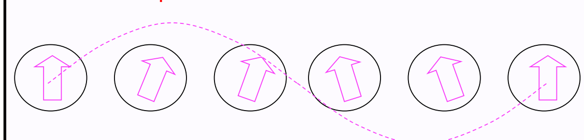
Real Magnetic materials

- Domains and Hysteresis
- A magnet usual breaks up into domains unless it is "poled" - an external field applied to allign the domains
- A real magnet has "hysteresis" - it does not change the direction of its magnetization unless a large enough field is applied - irreversibility



Magnons

- Whenever there is an order, there can be variations in the order as function of position
- "Magnons" are quanta of magnetic vibrations very much like "phonons"



- Can be observed directly by neutron scattering

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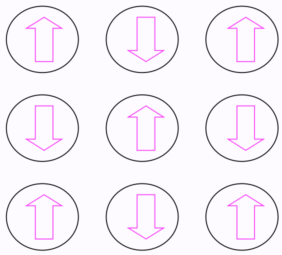
Antiferromagnetic solid

- Magnetic moments can also order to give no net moment - antiferromagnet



- Transition temperature $T_{transition} = T_{Neel}$ (named for Louis Neel)

Summary

- **Magnetism is a purely quantum phenomenon!** **Totally at variance with the laws of classical physics - (Bohr, 1911)**
- $\underline{\mathbf{B}} = \mu_0 (\underline{\mathbf{H}} + \underline{\mathbf{M}})$, $\underline{\mathbf{M}} = \chi \underline{\mathbf{H}}$ and $\underline{\mathbf{B}} = \mu \underline{\mathbf{H}}$
- **Diamagnetism - M** opposite to **H**
  - **Closed shell atoms**
  - **Insulators like Si, NaCl, ...**
  - **Very weak**
- **Spin paramagnetism - M** adds to **H**
  - **Example of metal - measures density of states**
- **How does ferromagnetism happen? Other forms of magnetism?**
- **Why does magnetism occur in transition metals, rare earths?**

Summary

- **Open shell atoms have magnetic moments**
  - **Controlled by electron-electron interactions**
  - **Hund's Rules**
- **Curie Law for atoms in a magnetic field**
- **Atomic-like effects (local magnetic moments) can occur in solids – transition metals, rare earths**
- **Magnetism is cooperative phenomenon whereby all the moments together go through a phase transition to form an ordered state**
  - **Curie-Weiss Law**
  - **Ferromagnetism**
  - **Antiferromagnetism**
  - **Magnetism as an "order parameter"**
  - **Magnons**
  - **Domains, irreversibility**

  (Only mentioned briefly)
- **(Kittel - parts of Ch 11-12)**

Next time

- **Special presentation – Raffi Budakian Magnetic Resonance Force Spectroscopy**
  - **– see Kittel, p. 356**
- **Start Surfaces and Scanning Tunneling Microsope (STM)**