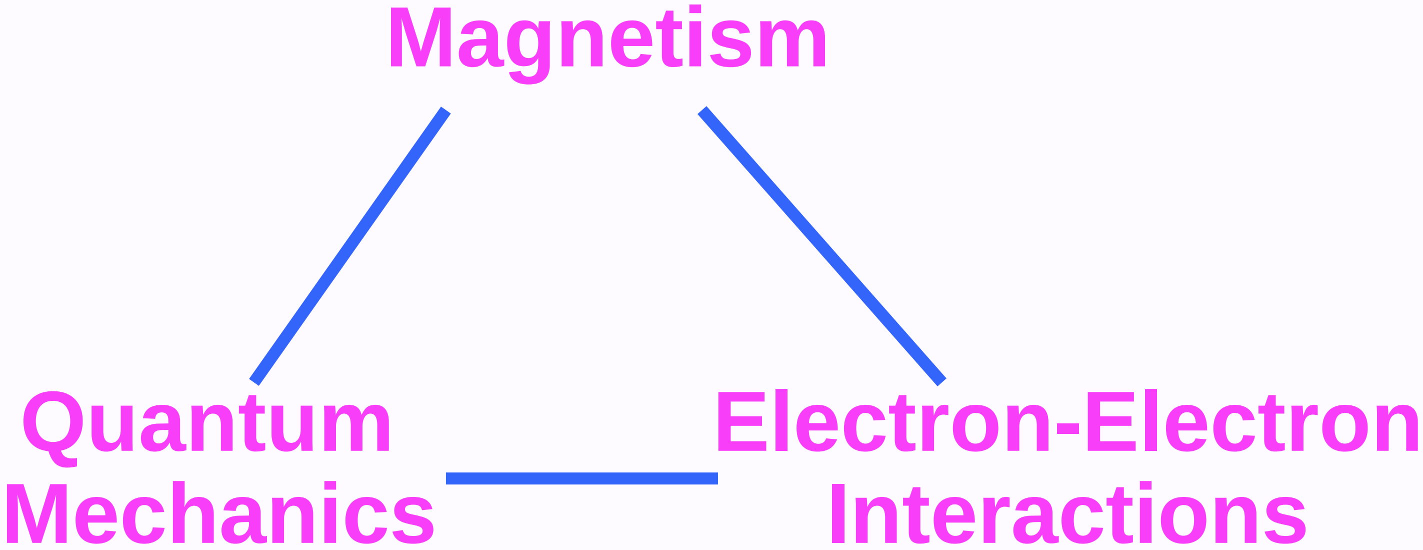
Lecture 24: Magnetism

(Kittel Ch. 11-12)



Magnetism

Quantum Mechanics

Electron-Electron Interactions

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

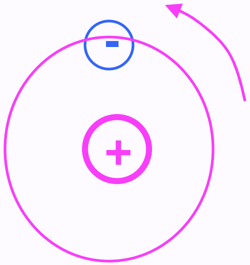
- $\underline{\mathbf{B}} = \mu_0 (\underline{\mathbf{H}} + \underline{\mathbf{M}})$
  (μ_0 is the permeability of free space,
  B is the field that causes forces on particles)
- If the magnetization is proportional to field,
  $\underline{\mathbf{M}} = \chi \underline{\mathbf{H}}$ and $\underline{\mathbf{B}}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

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.)

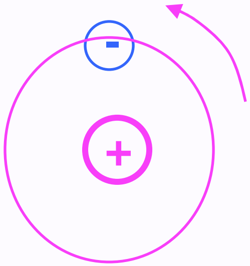
- Diamagnetism results from current set up in atom due to magnetic field

- 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**



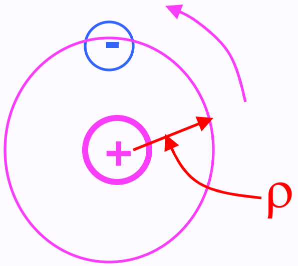
- This is like a classical current - BUT it occurs only because the atom is in a quantized state

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

“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)



Average value

- Susceptibility =

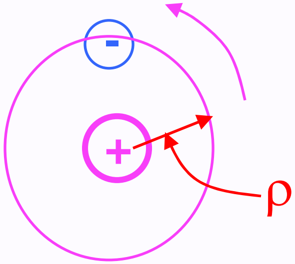
$$\chi = \mu_0\, M/B = -\,\mu_0 NZe^2/4m\,\langle\rho^2\rangle = -\,\mu_0 NZe^2/6m\,\langle r^2\rangle$$

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

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



- 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

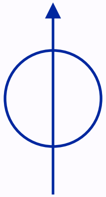
Spin Paramagnetism

- What about spin?

- Unpaired spins are affected by magnetic field!
- The energy in a field is given by

$$U = - \underline{\mu} \cdot \underline{\mathbf{B}} = - m\, g\, \mu_B\, B$$

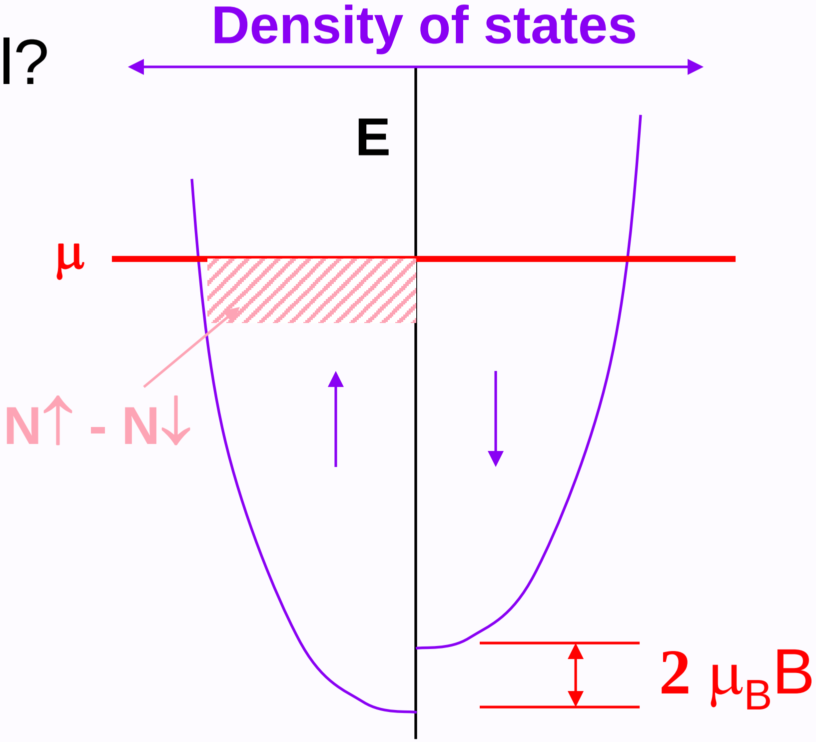
where m = component of spin = ±1/2,
g = "g factor" = 2,
and μ_B = Bohr magneton = $e\hbar/2m$



- 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
  $M = \mu_B (N\uparrow - N\downarrow)$
  $= \mu_B (1/2) D(E_F)\, 2 \mu_B B = \mu_B^2 D(E_F) B$

Density of states for both spins

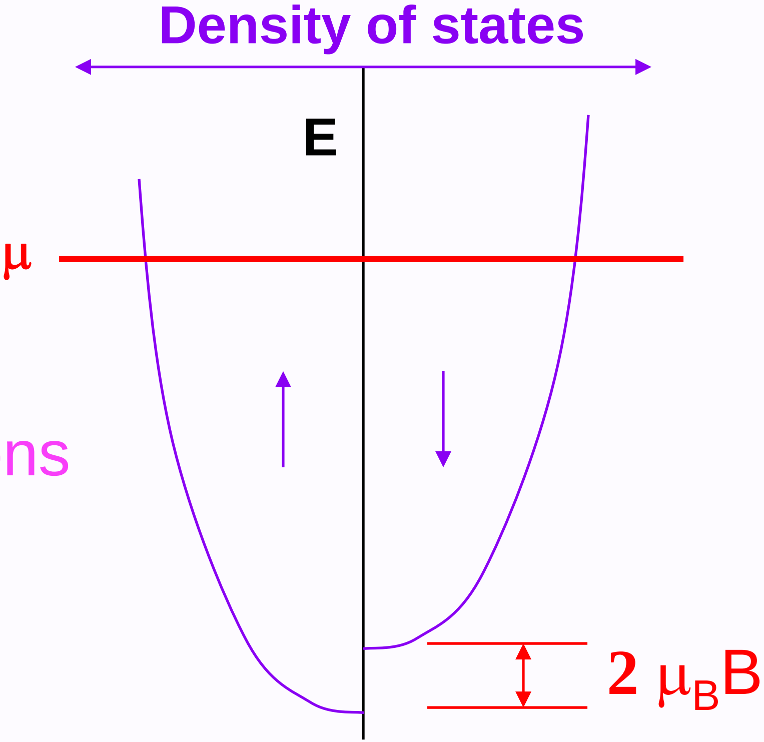
- Free electron gas (see previous notes + Kittel)
  $M = (3/2) N \mu_B^2 B/(k_B T_F)$

Spin Paramagnetism in a metal

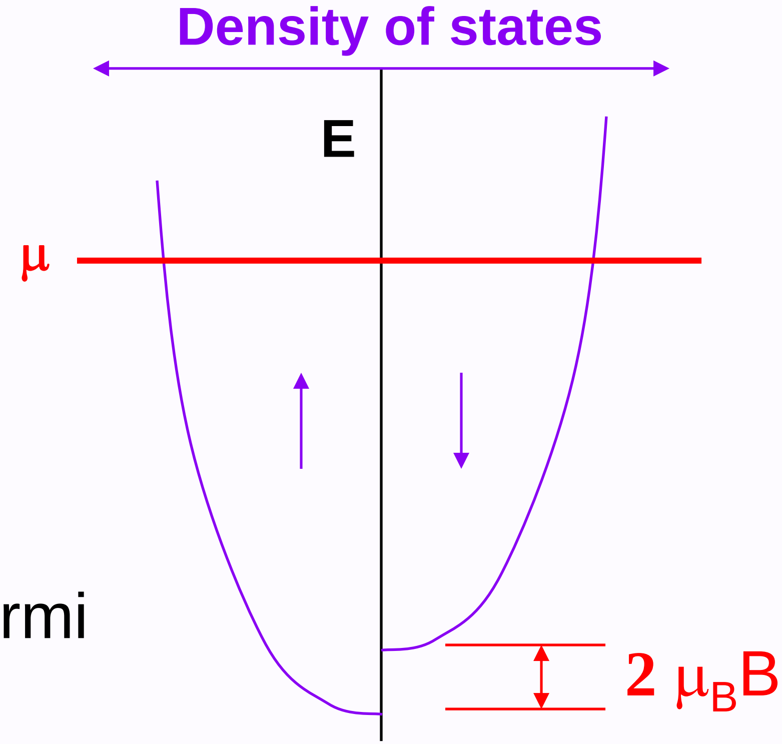
- Result for a metal:
- $M = \mu_B^2 D(E_F) B$ or
  $\chi = \mu_B^2 D(E_F)$
- This is a way to measure the density of states!
  (Note: There are corrections from the electron-electron interactions.)

- **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

  $$\mu_B B/(k_B T_F)$$

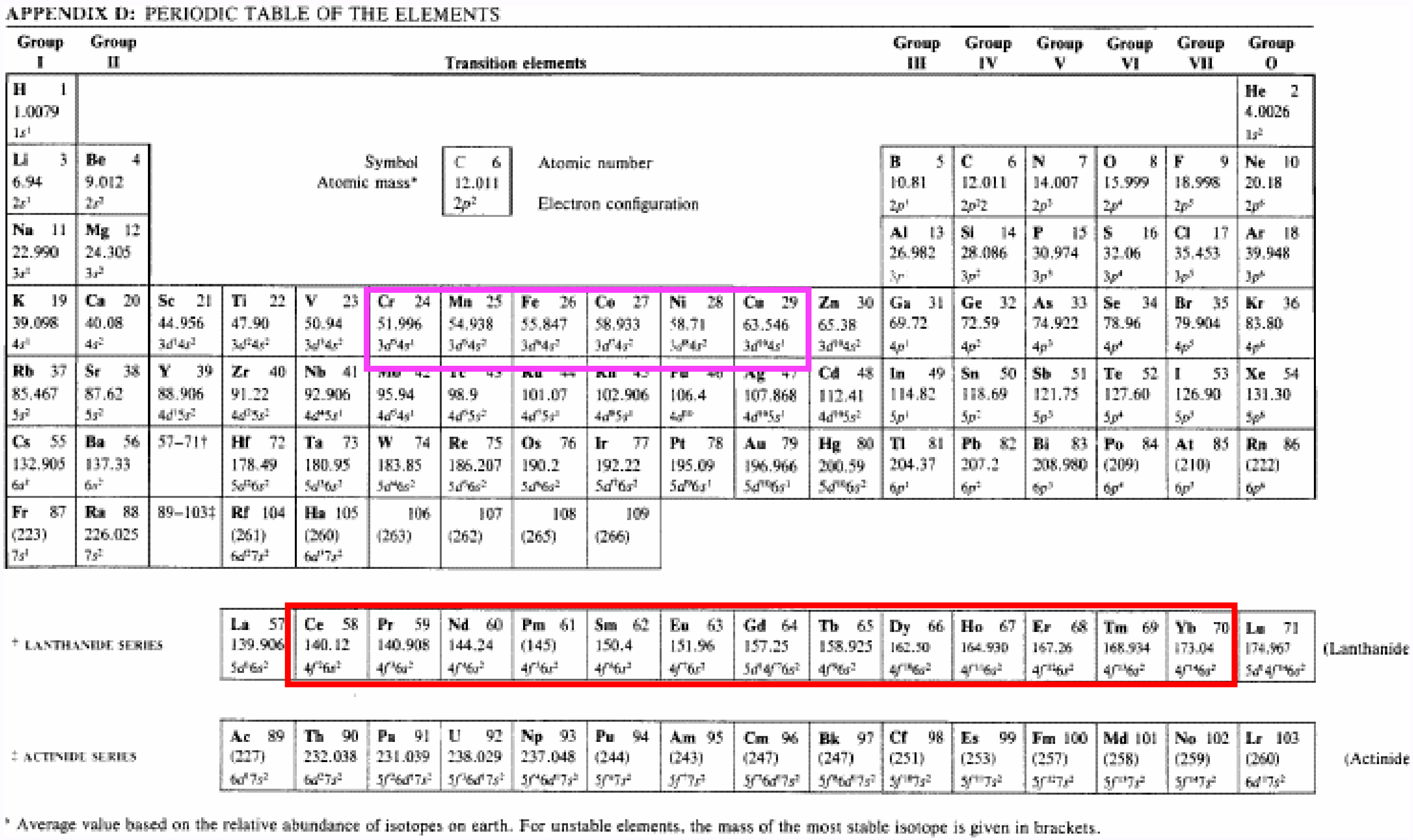
  due to the fact that the Fermi energy $E_F = k_B T_F >> \mu_B B$ for any reasonable B
- The same reason that the heat capacity is very small compared to the classical result

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**



APPENDIX D: PERIODIC TABLE OF THE ELEMENTS

Symbol / Atomic mass* — C 6 / 12.011 / $2p^2$ — Atomic number / Electron configuration

Group I	Group II	Transition elements										Group III	Group IV	Group V	Group VI	Group VII	Group 0
H 1 1.0079 $1s^1$																	**He** 2 4.0026 $1s^2$
Li 3 6.94 $2s^1$	**Be** 4 9.012 $2s^2$											**B** 5 10.81 $2p^1$	**C** 6 12.011 $2p^2$	**N** 7 14.007 $2p^3$	**O** 8 15.999 $2p^4$	**F** 9 18.998 $2p^5$	**Ne** 10 20.18 $2p^6$
Na 11 22.990 $3s^1$	**Mg** 12 24.305 $3s^2$											**Al** 13 26.982 $3p^1$	**Si** 14 28.086 $3p^2$	**P** 15 30.974 $3p^3$	**S** 16 32.06 $3p^4$	**Cl** 17 35.453 $3p^5$	**Ar** 18 39.948 $3p^6$
K 19 39.098 $4s^1$	**Ca** 20 40.08 $4s^2$	**Sc** 21 44.956 $3d^14s^2$	**Ti** 22 47.90 $3d^24s^2$	**V** 23 50.94 $3d^34s^2$	**Cr** 24 51.996 $3d^54s^1$	**Mn** 25 54.938 $3d^54s^2$	**Fe** 26 55.847 $3d^64s^2$	**Co** 27 58.933 $3d^74s^2$	**Ni** 28 58.71 $3d^84s^2$	**Cu** 29 63.546 $3d^{10}4s^1$	**Zn** 30 65.38 $3d^{10}4s^2$	**Ga** 31 69.72 $4p^1$	**Ge** 32 72.59 $4p^2$	**As** 33 74.922 $4p^3$	**Se** 34 78.96 $4p^4$	**Br** 35 79.904 $4p^5$	**Kr** 36 83.80 $4p^6$
Rb 37 85.467 $5s^1$	**Sr** 38 87.62 $5s^2$	**Y** 39 88.906 $4d^15s^2$	**Zr** 40 91.22 $4d^25s^2$	**Nb** 41 92.906 $4d^45s^1$	**Mo** 42 95.94 $4d^54s^1$	**Tc** 43 98.9 $4d^55s^2$	**Ru** 44 101.07 $4d^75s^1$	**Rh** 45 102.906 $4d^85s^1$	**Pd** 46 106.4 $4d^{10}$	**Ag** 47 107.868 $4d^{10}5s^1$	**Cd** 48 112.41 $4d^{10}5s^2$	**In** 49 114.82 $5p^1$	**Sn** 50 118.69 $5p^2$	**Sb** 51 121.75 $5p^3$	**Te** 52 127.60 $5p^4$	**I** 53 126.90 $5p^5$	**Xe** 54 131.30 $5p^6$
Cs 55 132.905 $6s^1$	**Ba** 56 137.33 $6s^2$	57–71†	**Hf** 72 178.49 $5d^26s^2$	**Ta** 73 180.95 $5d^36s^2$	**W** 74 183.85 $5d^46s^2$	**Re** 75 186.207 $5d^56s^2$	**Os** 76 190.2 $5d^66s^2$	**Ir** 77 192.22 $5d^76s^2$	**Pt** 78 195.09 $5d^96s^1$	**Au** 79 196.966 $5d^{10}6s^1$	**Hg** 80 200.59 $5d^{10}6s^2$	**Tl** 81 204.37 $6p^1$	**Pb** 82 207.2 $6p^2$	**Bi** 83 208.980 $6p^3$	**Po** 84 (209) $6p^4$	**At** 85 (210) $6p^5$	**Rn** 86 (222) $6p^6$
Fr 87 (223) $7s^1$	**Ra** 88 226.025 $7s^2$	89–103‡	**Rf** 104 (261) $6d^27s^2$	**Ha** 105 (260) $6d^37s^2$	106 (263)	107 (262)	108 (265)	109 (266)									

† LANTHANIDE SERIES	**La** 57 139.906 $5d^16s^2$	**Ce** 58 140.12 $4f^26s^2$	**Pr** 59 140.908 $4f^36s^2$	**Nd** 60 144.24 $4f^46s^2$	**Pm** 61 (145) $4f^56s^2$	**Sm** 62 150.4 $4f^66s^2$	**Eu** 63 151.96 $4f^76s^2$	**Gd** 64 157.25 $5d^14f^76s^2$	**Tb** 65 158.925 $4f^96s^2$	**Dy** 66 162.50 $4f^{10}6s^2$	**Ho** 67 164.930 $4f^{11}6s^2$	**Er** 68 167.26 $4f^{12}6s^2$	**Tm** 69 168.934 $4f^{13}6s^2$	**Yb** 70 173.04 $4f^{14}6s^2$	**Lu** 71 174.967 $5d^14f^{14}6s^2$	(Lanthanide
‡ ACTINIDE SERIES	**Ac** 89 (227) $6d^17s^2$	**Th** 90 232.038 $6d^27s^2$	**Pa** 91 231.039 $5f^26d^17s^2$	**U** 92 238.029 $5f^36d^17s^2$	**Np** 93 237.048 $5f^46d^17s^2$	**Pu** 94 (244) $5f^67s^2$	**Am** 95 (243) $5f^77s^2$	**Cm** 96 (247) $5f^76d^17s^2$	**Bk** 97 (247) $5f^86d^17s^2$	**Cf** 98 (251) $5f^{10}7s^2$	**Es** 99 (253) $5f^{11}7s^2$	**Fm** 100 (257) $5f^{12}7s^2$	**Md** 101 (258) $5f^{13}7s^2$	**No** 102 (259) $5f^{14}7s^2$	**Lr** 103 (260) $6d^17s^2$	(Actinide

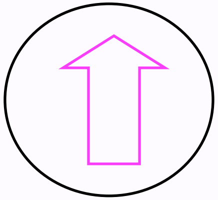
* Average value based on the relative abundance of isotopes on earth. For unstable elements, the mass of the most stable isotope is given in brackets.

The first step in understanding magnetic materials

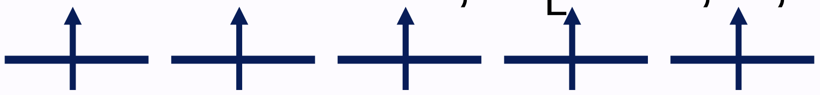
- Magnetic moments of atoms
- In most magnetic materials (Fe, Ni, ….) the first step in understanding magnetism is the consider the material as a collection of atoms
- Of course the atoms change in the solid, but this gives a good starting point – qualitatively correct

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



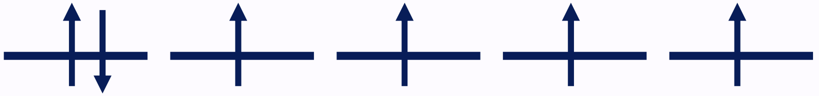
- Example: Mn^{2+} - 5 d electrons
  A d shell has L=2, m_L = -2,-1,0,1,2



m_L = -2 -1 0 1 2

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

- Fe^{2+} - 6 d electrons



m_L = -2 -1 0 1 2

S_{total} = 4/2, L_{total} = 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

$$M = \mu (N_1 - N_2) = \mu N \tanh(x), \quad x = \mu B/k_BT$$

Magnetic atoms in free space

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

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

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

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

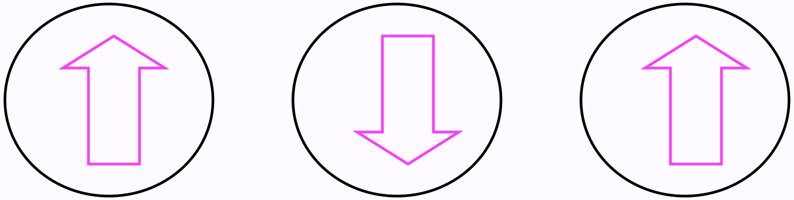
Curie Law

$\chi = M/B = C/T$, 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?

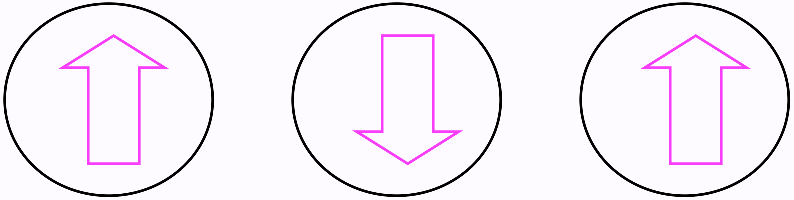
- Which atoms are most likely to keep their atomic like properties in a solid?

  Transition metals and rare earths

  Why?

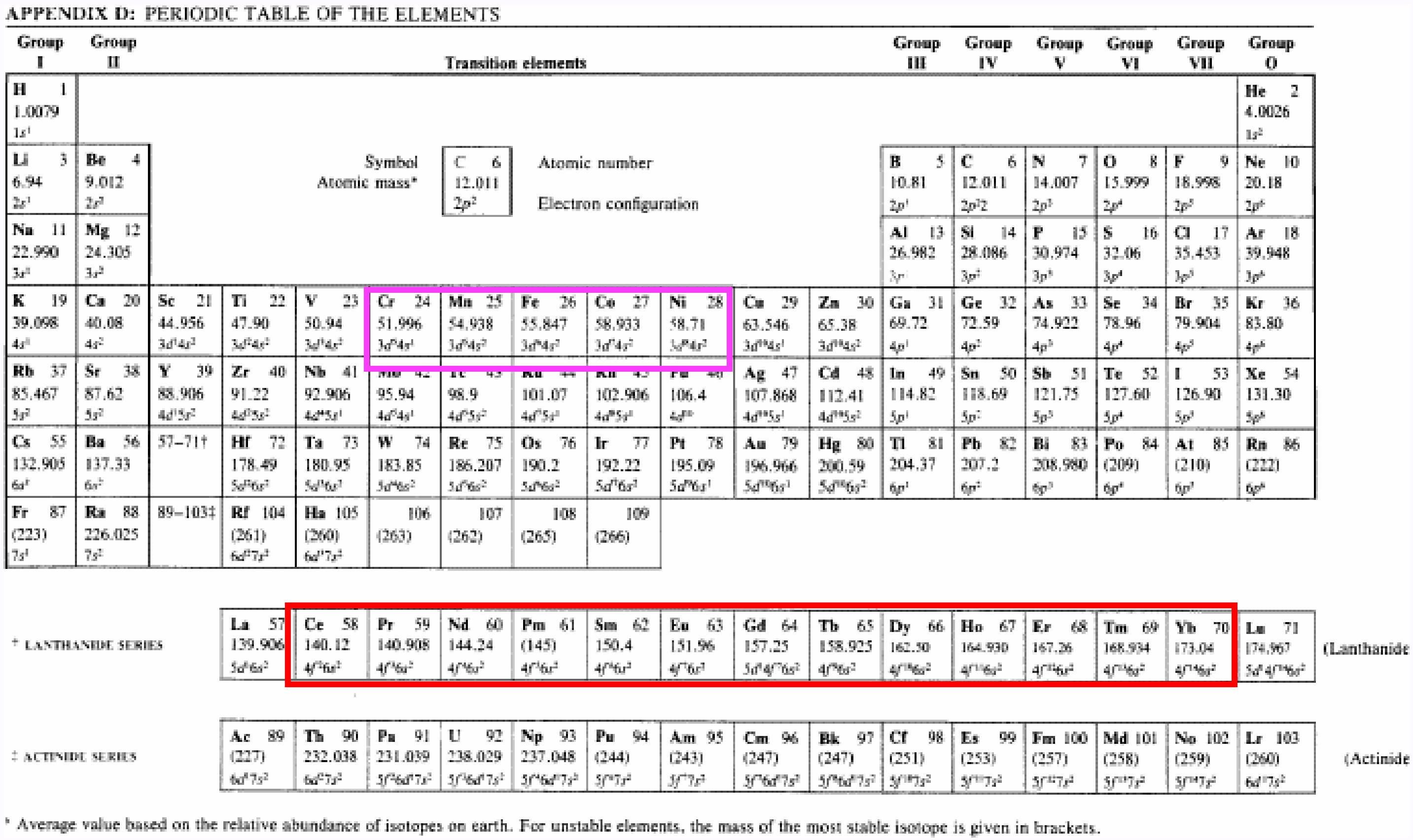
  Because the electrons act like they have partially filled shells even in the solid!

  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**



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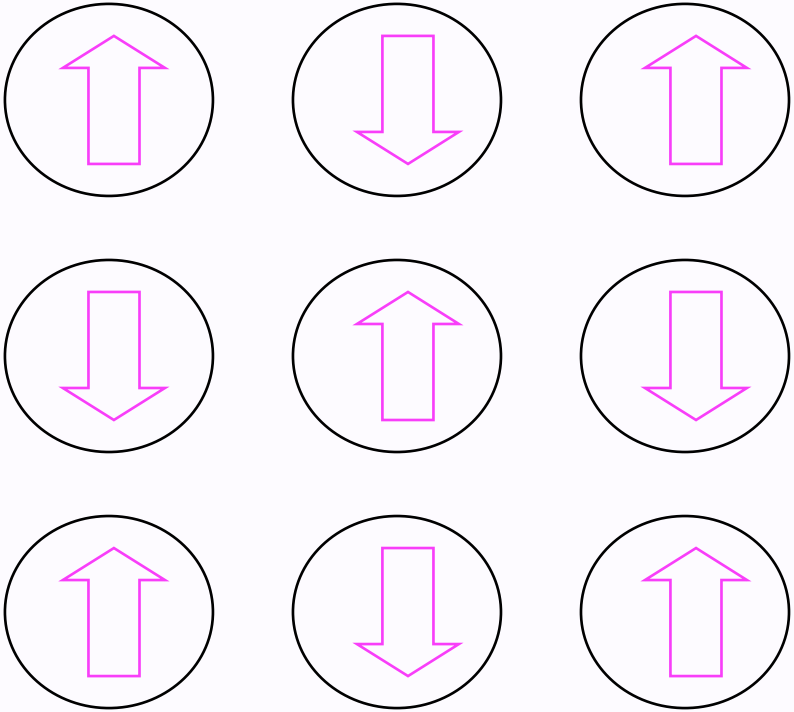
Fr 87 (223) $7s^1$	**Ra** 88 226.025 $7s^2$	89–103‡	**Rf** 104 (261) $6d^27s^2$	**Ha** 105 (260) $6d^37s^2$	106 (263)	107 (262)	108 (265)	109 (266)									

† LANTHANIDE SERIES	**La** 57 139.906 $5d^16s^2$	**Ce** 58 140.12 $4f^26s^2$	**Pr** 59 140.908 $4f^36s^2$	**Nd** 60 144.24 $4f^46s^2$	**Pm** 61 (145) $4f^56s^2$	**Sm** 62 150.4 $4f^66s^2$	**Eu** 63 151.96 $4f^76s^2$	**Gd** 64 157.25 $5d^14f^76s^2$	**Tb** 65 158.925 $4f^96s^2$	**Dy** 66 162.50 $4f^{10}6s^2$	**Ho** 67 164.930 $4f^{11}6s^2$	**Er** 68 167.26 $4f^{12}6s^2$	**Tm** 69 168.934 $4f^{13}6s^2$	**Yb** 70 173.04 $4f^{14}6s^2$	**Lu** 71 174.967 $5d^14f^{14}6s^2$	(Lanthanide
‡ ACTINIDE SERIES	**Ac** 89 (227) $6d^17s^2$	**Th** 90 232.038 $6d^27s^2$	**Pa** 91 231.039 $5f^26d^17s^2$	**U** 92 238.029 $5f^36d^17s^2$	**Np** 93 237.048 $5f^46d^17s^2$	**Pu** 94 (244) $5f^67s^2$	**Am** 95 (243) $5f^77s^2$	**Cm** 96 (247) $5f^76d^17s^2$	**Bk** 97 (247) $5f^86d^17s^2$	**Cf** 98 (251) $5f^{10}7s^2$	**Es** 99 (253) $5f^{11}7s^2$	**Fm** 100 (257) $5f^{12}7s^2$	**Md** 101 (258) $5f^{13}7s^2$	**No** 102 (259) $5f^{14}7s^2$	**Lr** 103 (260) $6d^17s^2$	(Actinide

* Average value based on the relative abundance of isotopes on earth. For unstable elements, the mass of the most stable isotope is given in brackets.

Magnetic solid

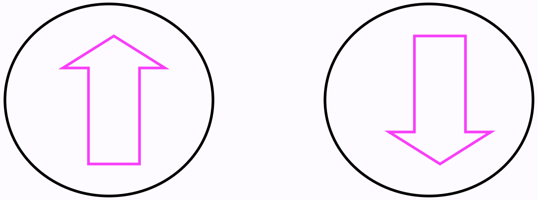
- “Localized” magnetic moments on the atoms



- How do the atoms decide to order?

How do magnetic atoms affect each other?

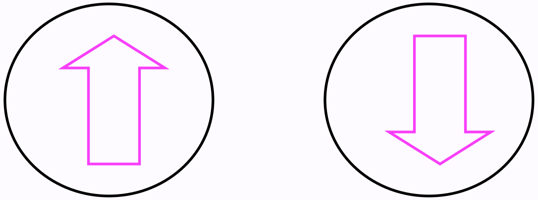
- Curie-Weiss Law (Kittel p 324)
- The simplest approximation is to assume each atom acts like it is in an effective magnetic field $\underline{\mathbf{B}}_E$ due to the neighbors



- 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?

How do magnetic atoms affect each other?

- Note: The “effective magnetic field $\mathbf{\underline{B}}_E$” is NOT really a “magnetic field” as in Maxwell’s Equations



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

Curie-Weiss Law

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

Approximate form valid at high T - sufficient for present purposes

- Using the form of χ = C/T,

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

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

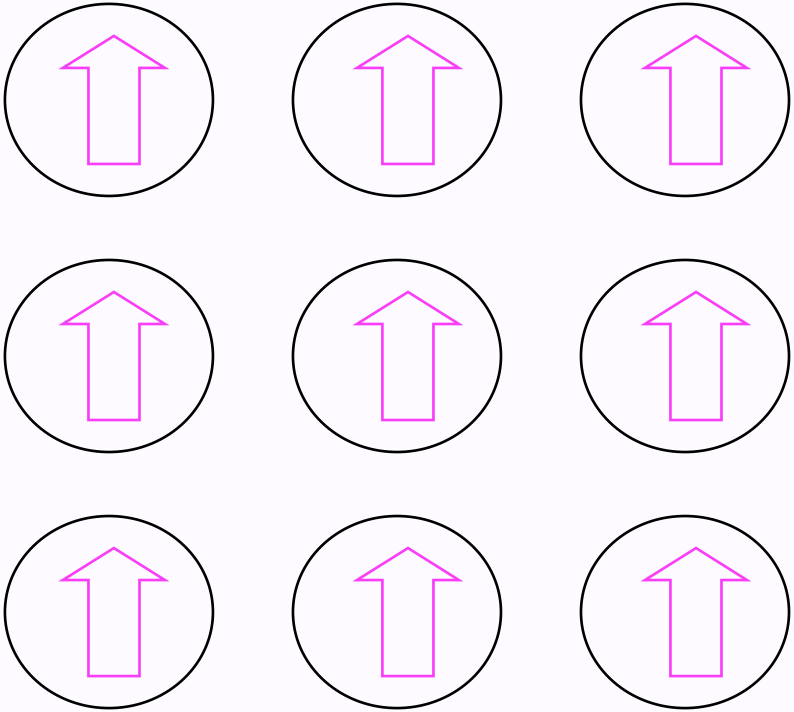
or

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

- 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

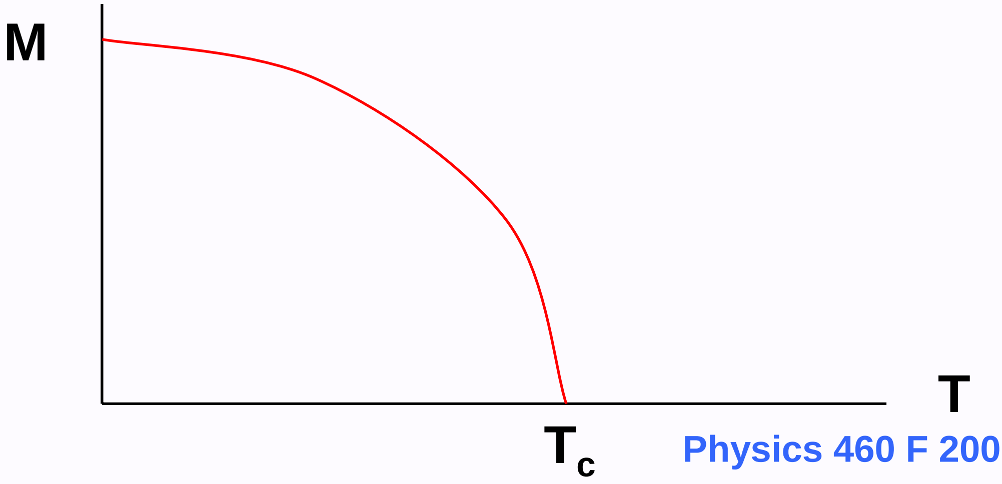
- “Localized” magnetic moments on the atoms aligned together to give a net magnetic moment



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

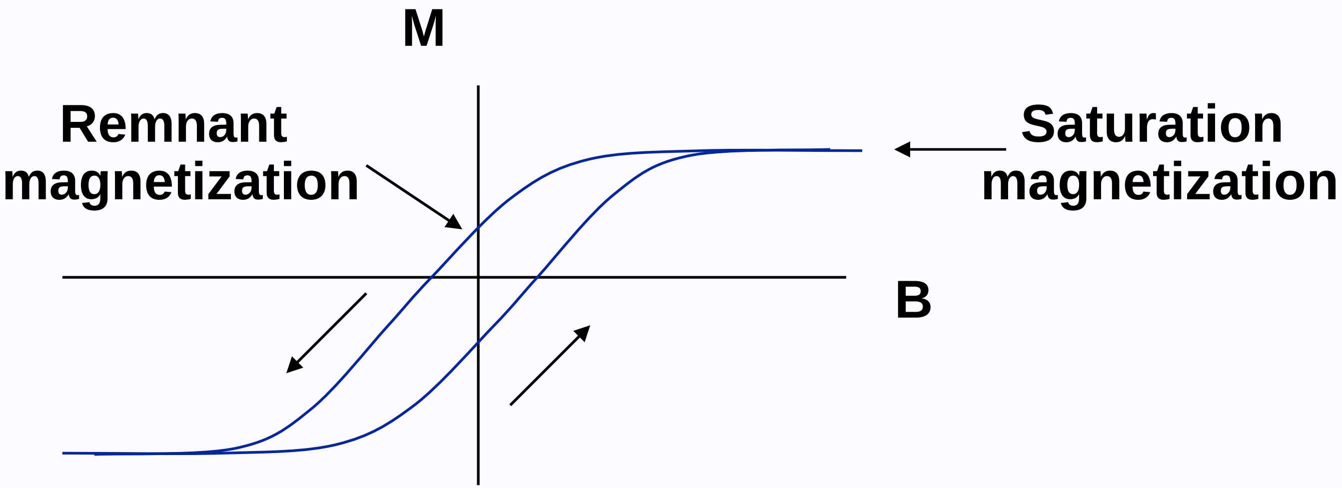
Example of a phase transition to a state of new order

- 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



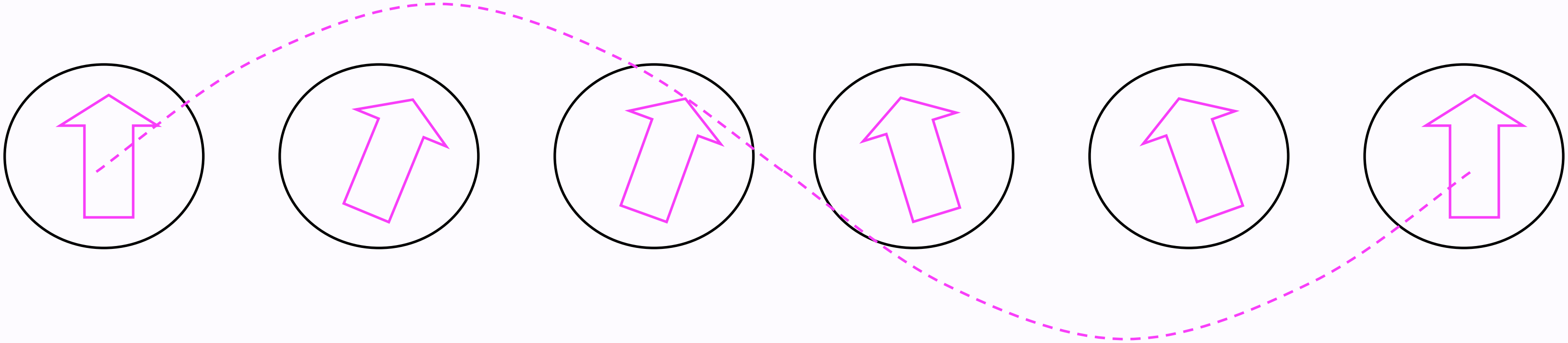
Real Magnetic materials

- 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

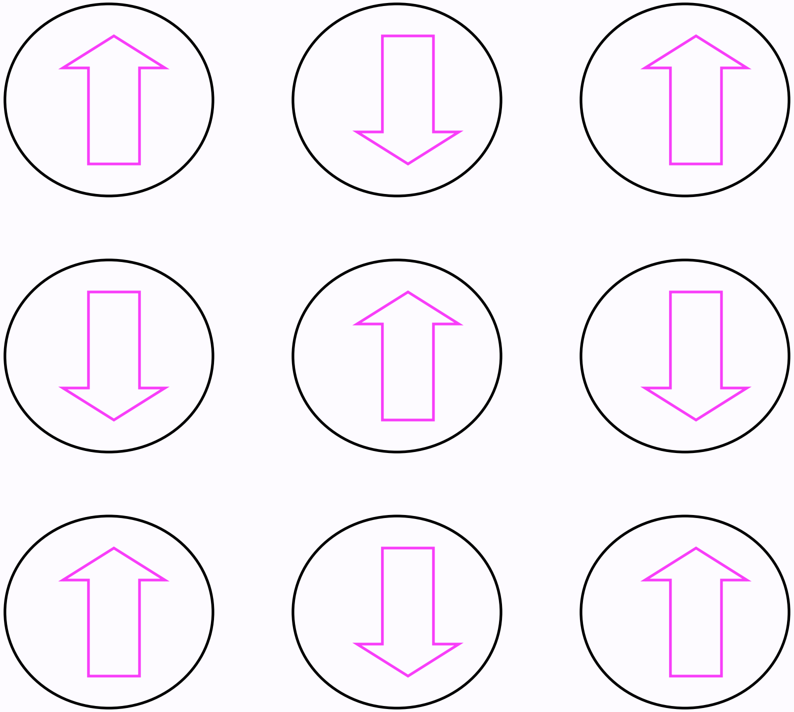
- Whenever there is an order, there can be variations in the order as function of position
- “Magnons” are quanta of magnetic vibrations very much like “phonons”



- Can be observed directly by neutron scattering

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** - $\underline{\mathbf{M}}$ opposite to $\underline{\mathbf{H}}$
  - **Closed shell atoms**
  - **Insulators like Si, NaCl, ...**
  - **Very weak**
- **Spin paramagnetism** - $\underline{\mathbf{M}}$ adds to $\underline{\mathbf{H}}$
  - **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)**