Magnetism and Magnetic Materials

Chemistry 754
Solid State Chemistry
Lecture #23
May 23, 2003

Magnetic Moment of an Electron

Magnetism in solids originates in the magnetic properties of an electron.

\[ \mu_s = g[S(S+1)]^{1/2} \left[ \frac{e\hbar}{4\pi m_e} \right] \]
\[ \mu_B = \frac{e\hbar}{4\pi m_e} \]
\[ \mu_s = g[S(S+1)]^{1/2} \mu_B \]

- \( S = \frac{1}{2} \), the spin quantum number
- \( g \sim 2 \), the gyromagnetic ratio
- \( \mu_B = 9.2742 \times 10^{-24} \text{ J/T} \), the Bohr magneton

So that for a free electron
\[ \mu_s = 1.73 \mu_B \]
Magnetic Moments of Atoms & Ions

Almost all atoms have multiple electrons, but most of the electrons are paired up in orbitals with another electron of the opposite spin. When all of the electrons on an atom are paired the atom is said to be diamagnetic. Atoms/ions with unpaired electrons are paramagnetic.

Diamagnetic Ions = There is a very small magnetic moment associated with an electron traveling in a closed path around the nucleus.

Paramagnetic Ions = The moment of an atom with unpaired electrons is given by the spin, S, and orbital angular, L and total momentum, J, quantum numbers.

\[ \mu_{\text{eff}} = g_s[J(J+1)]^{1/2} \mu_b \] Full treatment: Accurate for Lanthanides

\[ \mu_{\text{eff}} = [4S(S+1)+L(L+1)]^{1/2} \mu_b \] Neglecting spin-orbit coupling

\[ \mu_{\text{eff}} = 2[5(S+1)]^{1/2} \mu_b \] Spin only value

Atomic Moments in Compounds

Unpaired electrons and paramagnetism are usually associated with the presence of either transition metal or lanthanide (actinide) ions. In many transition metal compounds the surrounding anions/ligands quench the orbital angular momentum and one needs only to take into account the spin only moment. Consider the following examples:

<table>
<thead>
<tr>
<th>Ion</th>
<th>e⁻ Config.</th>
<th>S</th>
<th>( \mu_S(\mu_B) )</th>
<th>( \mu_{S-L}(\mu_B) )</th>
<th>( \mu_{\text{obs}}(\mu_B) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti⁴⁺</td>
<td>d¹</td>
<td>1/2</td>
<td>1.73</td>
<td>3.01</td>
<td>1.7-1.8</td>
</tr>
<tr>
<td>V²⁺</td>
<td>d²</td>
<td>1</td>
<td>2.83</td>
<td>4.49</td>
<td>2.8-3.1</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>d³</td>
<td>3/2</td>
<td>3.87</td>
<td>5.21</td>
<td>3.7-3.9</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>d⁶ (HS)</td>
<td>5/2</td>
<td>5.92</td>
<td>5.92</td>
<td>5.7-6.0</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>d⁶ (HS)</td>
<td>1</td>
<td>2.83</td>
<td>4.49</td>
<td>2.9-3.9</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>d⁹</td>
<td>1/2</td>
<td>1.73</td>
<td>3.01</td>
<td>1.9-2.1</td>
</tr>
</tbody>
</table>

Deviations from the spin-only value can occur for the following reasons:

- Orbital (L) Contribution
  - Can arise for partially filled (not ½ full) t²g orbitals

- Spin-orbit Coupling
  - Increases the moment for d⁶, d⁷, d⁸, d⁹
  - Decreases the moment for d¹, d², d³, d⁴
Magnetic Ordering

- Paramagnetic
- Antiferromagnetic
- Ferromagnetic
- Ferrimagnetic

Interaction between an Applied Magnetic Field and a Magnetic Material

The interaction between an external magnetic field ($H$) and a material depends upon its magnetic properties.

- Diamagnetic $\rightarrow$ Repulsive
- Paramagnetic $\rightarrow$ Attractive

$$B = H + 4\pi I$$

- $B$ = Magnetic Induction (field strength within the sample)
- $H$ = Applied magnetic field (field coming from external source)
- $I$ = Magnetization Intensity (field originating from the sample)
**Magnetic Susceptibility**

\[ B = H + 4\pi I \]

The permeability, \( P \), is obtained by dividing the magnetic induction, \( B \) (total field in the sample), by the applied field, \( H \).

\[ P = \frac{B}{H} = 1 + 4\pi I/H = 1 + 4\pi \chi \]

Where \( \chi \) is the volume susceptibility (extrinsic property). To obtain the intrinsic material property, \( \chi_m \), molar susceptibility we multiply by the Formula weight, \( FW \), and divide by the density, \( \rho \).

\[ \chi_m = \chi(FW)/\rho \]

Typical molar susceptibilities are:
- **Paramagnetic Comp.** ~ +0.01 \( \mu_B \)
- **Diamagnetic Comp.** ~ -1x10^-6 \( \mu_B \)
- **Ferromagnetic Comp.** ~ +0.01-10 \( \mu_B \)
- **Superconducting Comp.** ~ Strongly negative, repels fields completely in some instances (Meisner effect)

**Superexchange**

In order for a material to be magnetically ordered, the spins on one atom must couple with the spins on neighboring atoms. The most common mechanism for this coupling (particularly in insulators) is through the semicovalent superexchange interaction. The spin information is transferred through covalent interactions with the intervening ligand (say oxygen).

The covalent interaction through the O 2p orbital stabilizes antiferromagnetic coupling.

Here the oxygen based electron will spend some time on Cr\(^{3+}\) and due to Hund's rule polarize the \( t_{2g} \) \( e^- \) leading to ferromagnetic coupling.
**Magnetic Susceptibility vs. Temperature**

Paramagnetic substances with localized, weakly interacting electrons obey the Curie-Weiss law.

\[ \chi_m = C/(T+\theta) \]

- \( \chi_m \) = Molar magnetic susceptibility
- \( C \) = Curie constant
- \( \theta \) = Weiss constant

A Curie-Weiss plot is a plot of \( 1/\chi_m \) vs. temperature. Ideally it should give a straight line if the C-W law is obeyed. From such a plot we can then extract the Curie constant from the inverse of the slope and the Weiss constant from the x-intercept.

\[ 1/\chi_m = (T+\theta)/C = (1/C)T + \theta/C \]

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**Curie-Weiss Plot**

The Curie constant is equal to the inverse of the slope. It gives us the size of the moment per formula unit.

\[ C = (N_A/3k)\mu^2 \]

\[ \mu = (3kC/N_A)^{1/2} = 2.84 \text{ } C^{1/2} \]

- \( N_A \) = Avogadro's Number
- \( k \) = Boltzmann's constant

The Weiss constant is equal to the x-intercept. It's sign tells us about the short range magnetic interactions.

- \( \theta = 0 \rightarrow \text{Paramagnetic} \)  
  Spins independent of each other
- \( \theta > 0 \rightarrow \text{Ferromagnetic} \)  
  Spins tending to align parallel
- \( \theta < 0 \rightarrow \text{Antiferromagnetic} \)  
  Spins tending to align antiparallel
**Ferromagnets & Antiferromagnets**

**Ferromagnet**
- The susceptibility increases dramatically at the Curie temp. As the T decreases further the magnetic ordering and the susceptibility increase.

**Antiferromagnet**
- The susceptibility begins decreasing at the Neel temp. As the T decreases further the magnetic ordering increases and the susceptibility decreases.

The Curie-Weiss Law characteristic of a pure paramagnet is typically only obeyed when \( T \geq 3T_C \) in a ferromagnet. Deviations also occur in AFM systems above \( T_N \).

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**Other Classes of Magnetism**

**Spin Glass** - A random orientation of frozen spin orientations (in a paramagnet the spin orientations are fluctuating.) Can occur when the concentrations of magnetic ions are dilute or the magnetic exchange interactions are frustrated.

**Cluster Glass** - The spin orientations lock in with magnetic order in small clusters, but no order between the clusters (similar to a spin glass).

**Metamagnet** - There is a field-induced magnetic transition from a state of low magnetization to one of relatively high magnetization. Typically the external field causes a transition from an antiferromagnetic state to a different type (such as a ferromagnet).

**Superparamagnet** - A ferromagnet whose particle size is too small to sustain the multidomain structure. Thus the particle behaves as one large paramagnetic ion.
Magnetic Ordering in Rock Salt Oxides

In the rock salt structure the primary mechanism for magnetic exchange is the linear M-O-M superexchange interaction. In all of the compounds below the $e_g$ orbitals are $\frac{1}{2}$ filled, so the exchange interaction is AFM and overall magnetic structure is AFM as shown below.

<table>
<thead>
<tr>
<th></th>
<th>M-O Distance</th>
<th>$T_N$ (K)</th>
<th>Moment (µB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>d$^5$</td>
<td>2.22 Å</td>
<td>120</td>
</tr>
<tr>
<td>FeO</td>
<td>d$^6$</td>
<td>2.15 Å</td>
<td>198</td>
</tr>
<tr>
<td>CoO</td>
<td>d$^7$</td>
<td>2.13 Å</td>
<td>291</td>
</tr>
<tr>
<td>NiO</td>
<td>d$^8$</td>
<td>2.09 Å</td>
<td>530</td>
</tr>
</tbody>
</table>

$(M-O$ distance $\downarrow) \rightarrow (Covalency \uparrow) \rightarrow (Superexchange \uparrow) \rightarrow (T_N \uparrow)$

The moments given in this table (and the ones that follow) were measured at low temperature using neutron diffraction. Under such circumstances the moment should roughly be equal to the number of unpaired electrons.

AFM Magnetic Ordering in Perovskites

The perovskite structure has even simpler magnetic interactions (in rock salt there is a competing interaction across the shared octahedral edge). Some magnetic data and the most common AFM structure for perovskite is shown below. The coloring of the magnetic structure is analogous to the crystal structure of NaCl. It is called the $G$-type magnetic structure.

<table>
<thead>
<tr>
<th></th>
<th>M-X Distance</th>
<th>$T_N$ (K)</th>
<th>Moment (µB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO$_3$</td>
<td>d$^3$</td>
<td>1.97 Å</td>
<td>282</td>
</tr>
<tr>
<td>CaMnO$_3$</td>
<td>d$^3$</td>
<td>1.90 Å</td>
<td>110</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>d$^5$</td>
<td>1.99 Å</td>
<td>750</td>
</tr>
<tr>
<td>KNiF$_3$</td>
<td>d$^8$</td>
<td>2.00 Å</td>
<td>275</td>
</tr>
</tbody>
</table>

Note that the superexchange that involves $\frac{1}{2}$ filled $e_g$ orbitals (LaFeO$_3$) is much stronger than the corresponding interaction of $\frac{1}{2}$ filled $t_{2g}$ orbitals. Also upon going from oxide (LaFeO$_3$) to fluoride (KNiF$_3$) the covalency decreases, which weakens the superexchange and lowers $T_N$. 
Magnetic Ordering in LaMnO$_3$

An interesting example that shows where the superexchange rules do not always lead to an AFM structure, with ferromagnetic nearest neighbor interactions is the magnetic structure of LaMnO$_3$. Which contains HS Mn$^{3+}$, a d$^4$ ion with one electron in the e$_g$ orbitals.

This structure is called the A-type AFM structure.

Overlap of $\frac{1}{2}$ filled and empty e$_g$ orbitals gives FM coupling and stabilizes FM layers.

Double Exchange in Fe$_3$O$_4$

Fe$_3$O$_4$ is an inverse spinel, with Fe$^{3+}$ on the tetrahedral sites and a 1:1 mixture of Fe$^{2+}$/Fe$^{3+}$ on the octahedral sites. It is ferrimagnetic, with the octahedral sites and the tetrahedral sites aligned in different directions. The ferromagnetic alignment of the octahedral sites is necessary for delocalized carrier transport of the minority spin t$_{2g}$ electron. This mechanism is called double exchange.
Summary

Magnetic Ordering in Solids
- **Diamagnetism**: No unpaired e⁻
- **Paramagnetism**: Unpaired e⁻, disordered and fluctuating
- **Ferromagnetism**: All unpaired e⁻ spins aligned parallel
- **Antiferromagnetism**: Unpaired e⁻ aligned antiparallel
- **Ferrimagnetism**: Unpaired e⁻ aligned antiparallel but don’t fully cancel out

Magnetic Superexchange
- Unpaired electron spins couple through covalent interactions with intervening ligand
- ½ filled metal orbital - ½ filled metal orbital, AFM SE
- ½ filled metal orbital - empty metal orbital, FM SE
- Strength of superexchange interaction increases as covalency increases

Double Exchange
- Spins on neighboring atoms must be aligned in a certain manner (usually ferromagnetically) in order to allow carrier delocalization
- Magnetism and electrical transport are intimately linked