Collocvium tasks: Magnetism.

1.1 What types of magnetic materials do we have?

      Diamagnetic
      Paramagnetic
      Ferromagnetic
      Antiferromagnetic
      Ferrimagnetic

1.2 Write the Curie-Weiss law and explain how the constant (θ) varies for the different types of magnetisms.

$$\chi = \frac{C}{T - \theta}$$

Paramagnetic: $\theta = 0$
Ferromagnetic: $\theta > 0$
Antiferomagnetic: $\theta < 0$

1.3 Calculate the magnetic dipolemoment for the ions: V^{3+}, Cr^{3+}, Mn^{3+} (HS), Ni^{2+}.

Using the approximate formula: $m = g_J[S(S+1)]^{\frac{1}{2}} \mu_B$

$g_J = 2$
$\mu_B = 9.274\ 009\ 49 \times 10^{-24}$ J·T^{-1}, but this does not matter since we are going to report the moment using the unit μ_B.

Since these are transition metals we can assume that the orbital moment is quenched and that only the spin contributes.

V^{3+}, d^2, $S = 1 \rightarrow m = 2.83\ \mu_B$.
Cr^{3+}, d^3, $S = 3/2 \rightarrow m = 3.87\ \mu_B$.
Mn^{3+}, d^4, $S = 2 \rightarrow m = 4.9\ \mu_B$.
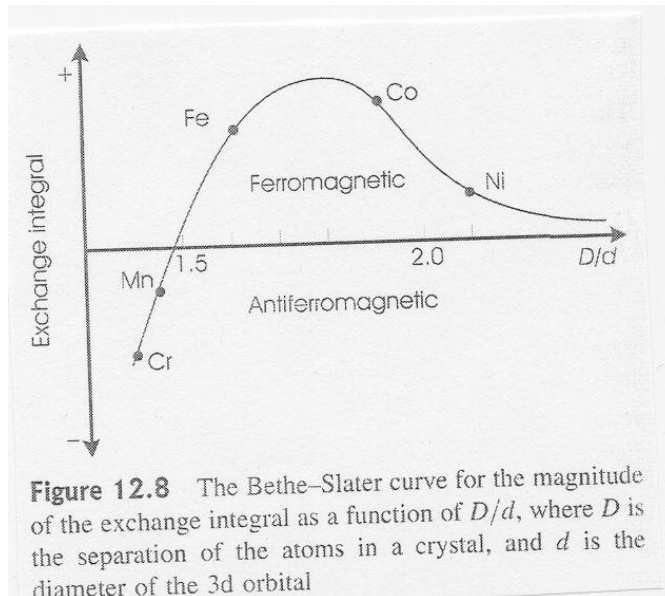Ni^{2+}, d^8, $S = 1 \rightarrow m = 2.83\ \mu_B$.

1.4 Why is Fe a ferromagnetic metal and Cu not?

Only Ni, Fe, Co and some lanthanides are ferromagnetic compounds. One way to explain this is to look at the different opposing mechanisms.
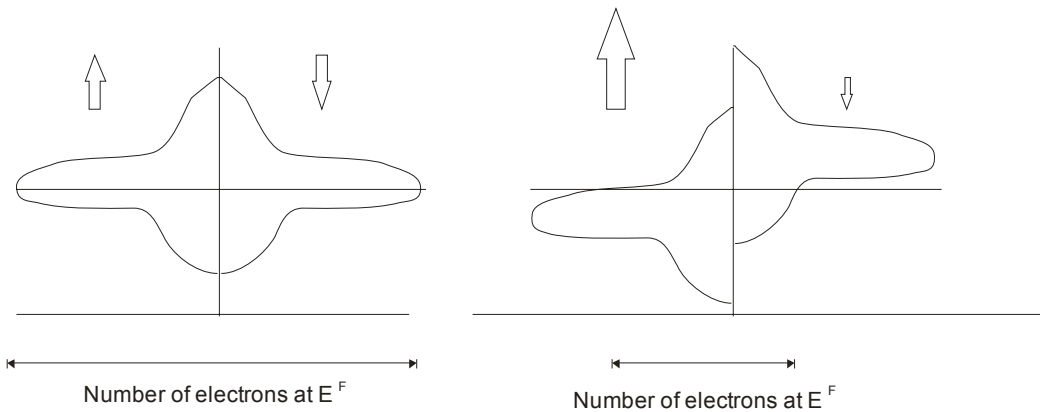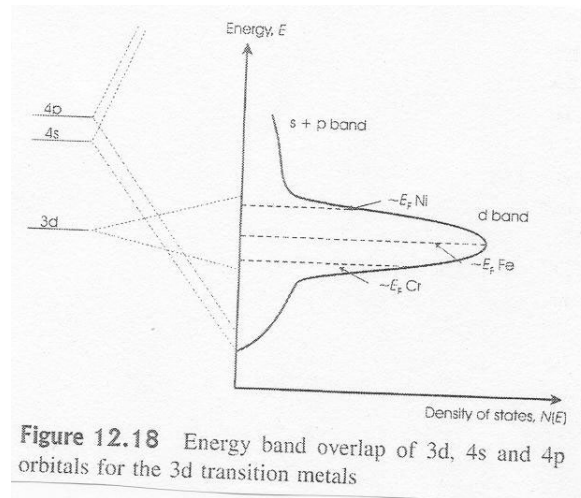
An isolated atom will fill its orbitals according to Hunds rule, viz. as many unpaired electrons as possible, divided among as many orbitals as possible. The

reason for this is that there is a positive exchange energy between electrons of parallel orientation.

When these atoms are bonded to other atoms, they must share some orbitals. Orbitals can only be shared if the electrons they share have anti parallel spins, thus promoting an anti-ferromagnetic coupling. Promotion of ferromagnetic compounds occurs when the inter-atom orbital overlap is small enough so that the exchange mechanism prevails.

Figure 12.8 The Bethe–Slater curve for the magnitude of the exchange integral as a function of D/d, where D is the separation of the atoms in a crystal, and d is the diameter of the 3d orbital

An alternative mechanism to explain the observation is to examine the shape of s, p, and d orbitals of the desired metals. The s and p orbitals are broad in energy and do not give a large density of electrons at the Fermi level. The d-orbital, on the other hand, is narrow in energy and correspondingly wide when it comes to population of electrons. The narrowness is in fact related to the degree of orbital overlap between atoms, large overlap gives broad orbitals in term of energy, small overlap gives narrow bands. For Fe, Co and Ni a situation arises with many electrons at the Fermi level, which is energetically unfavorable. It is desired to reduce the amount of electrons at the Fermi level. One way to do this is to raise and lower orbitals with up and down spins respectively. One may then encounter the situation of reduced number of electrons at the Fermi level with respect to the equal energy state. The situation is then a ferromagnetic compound, also with an energy contribution from exchange energy.

Figure 12.18 Energy band overlap of 3d, 4s and 4p orbitals for the 3d transition metals

Number of electrons at E^F

Number of electrons at E^F

1.5   What is the superexchange mechanism?

The superexchange mechanism is a mechanism that explains why two metals that are separated by an oxygen should have oppositely aligned spins.

The shape of one oxygen p-orbital consists of two lobes. When this orbital is occupied by two electrons, then the electron spin on opposite sides of the oxygen must be anti parallel. The orientation of these spins affects the orientation of the partly occupied d-orbitals in the metal atom, which then must be anti parallel as well.

The effect is weakened when the M-O-M angle deviates from 180°.

Figure 12.9 Superexchange leading to antiferromagnetic alignment of spins on cations
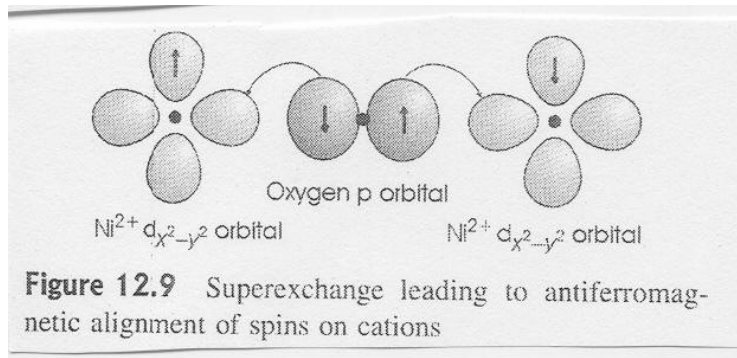
How does this explain that MnO, FeO, CoO and NiO (all adopt the NaCl-type structure) are antiferromagnets?

The NaCl-type of structure is built of MO_6 octahedra that are connected by sharing edges or corners. The edge sharing octahedra has M-O-M angles of 90° and does not transfer much spin orientation information. The corner sharing octahedra, on the other hand, does have M-O-M angles of 180° and makes the metal atoms in corner neighbours anti parallel.

Why does the T_N increase in temperature for the series MnO → NiO?

The extent of the super exchange mechanism depends on orbital overlap. Orbital overlap is also a measure of bond strength. Thus the metal oxides that has the strongest bonds should also remain anti ferromagnetic to the highest temperatures. The melting point of these oxides increase in the order MnO → NiO.

1.6   What is the double exchange mechanism?

The double exchange mechanism can take part when there is a distribution of one metal in more than one oxidation state. Conduction can then take place if one electron can jump from one metal atom to the other. In oxides, this can be done by using an intervening oxygen atom. However this oxygen atom can not end up in a situation with a lack of electrons. There must therefore be a simultaneous jump of one electron from one metal atom at the same time at one electron jumps from the oxygen to the other metal atom. For this to be possible, both electrons have to be parallel aligned. The fact that these electrons can jump around will after some jumping promote the metal atoms to be parallel aligned.

Figure 12.10 Double exchange, possible only with ferromagnetic alignment of spins on cations
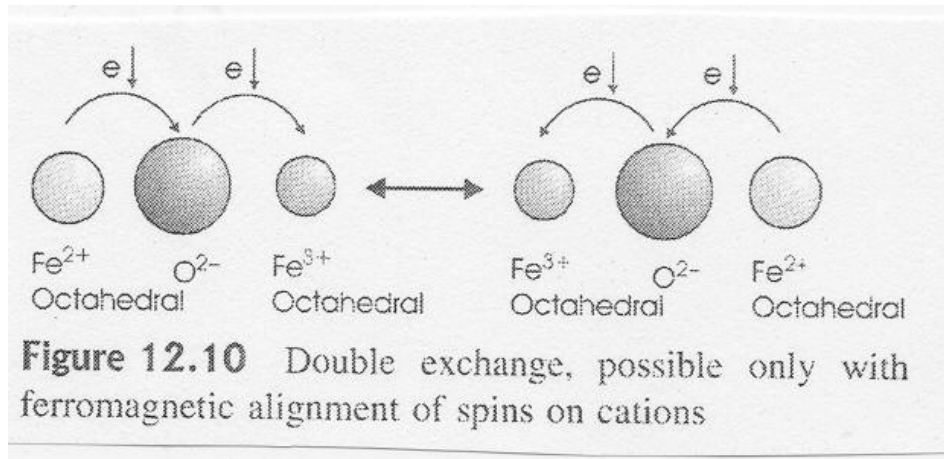
How does this explain that $(La_{0.67}Ca_{0.33})MnO_3$ is a ferromagnet?
The compound adopts a slightly distorted perovskite ABO_3 structure where Mn occupies the B positions (octahedral environment). These octahedra are connected by their corners in the same type as in the ReO_3 structure.

In $(La_{0.67}Ca_{0.33})MnO_3$ the oxidation state of Mn is 2.33 meaning a collection of 1/3 Mn^{4+} and 2/3 Mn^{3+}. There is then a distribution of Mn in two oxidation states. The perovskite structure is constructed of MO_6 octahedra connected through corners and promotes them to be parallel aligned.

Will the ferromagnetism increase or decrease of the octahedrons were rotated with respect to each other?

As with super exchange, double exchange also depends on orbital overlap. Therefore any deviation from a M-O-M angle of 180° will decrease the exchange mechanism.

1.7   What is Pauli paramagnetism?
Or; why are most metals paramagnetic and not diamagnetic?

Metals have natively an equal amount of spins in both directions. It should therefore be treated as a diamagnetic material. However, when an external magnetic field is applied the situation changes in the way that those electrons with a parallel spin increases in energy and population. The number of these electrons are generally not enough to ensure a ferromagnetic coupling between them, and the material becomes then paramagnetic.
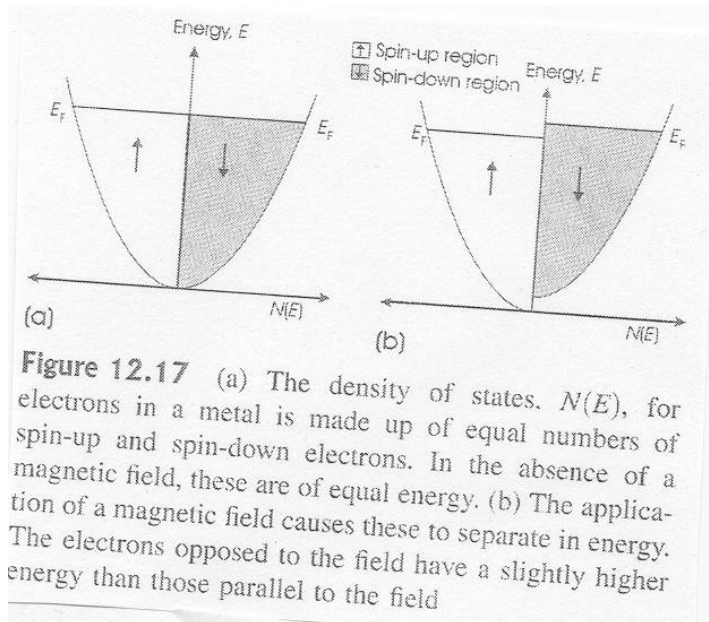
Figure 12.17 (a) The density of states, $N(E)$, for electrons in a metal is made up of equal numbers of spin-up and spin-down electrons. In the absence of a magnetic field, these are of equal energy. (b) The application of a magnetic field causes these to separate in energy. The electrons opposed to the field have a slightly higher energy than those parallel to the field

1.8 What is superparamagnetism?
Or; why can't they make hard disks of 10 TB?

In order for a ferromagnetic material to be ferromagnetic is it has to be of a certain size so that the exchange mechanism does work. If the particle size becomes too small then there will not be enough parallel spins to maintain them parallel when the external magnetic field is removed. Temperature, and thus increase in entropy becomes a more important effect than the ferromagnetic coupling.

One of the major problems in decreasing the storage density on magnetic recording media is that they now become so small that the magnetic domains become unstable. You can no longer be sure that the data you store is going to be there after one year.