

Study of Origins of Magnetic Behaviour and types of Magnetism

Amika, Guest Faculty as Assistant Professor, Mahila Mahavidyalaya, Jhojhu Kalan, Charkhi Dadri

Introduction: Magneto chemistry is the study of the magnetic properties of materials. By "magnetic properties" we mean not only whether a material will make a good bar magnet, but whether it will be attracted or repelled by a magnet. This includes synthesis, analysis and understanding. This paper is meant to give a basic understanding about Magnetic Properties of

Materials. Magnetism arises from moving charges, such as an electric current in a coil of wire. In a material which does not have a current

present, there are still magnetic interactions. Atoms are made of charged particles (protons and electrons) which are moving constantly.

The processes which create magnetic fields in an atom are

1. Nuclear spin. Some nuclei, such as a hydrogen atom, have a net spin, which creates a magnetic field.

2. Electron spin. An electron has two intrinsic spin states (similar to a top spinning) which we call up and down or alpha and beta.

3. Electron orbital motion. There is a magnetic field due to the electron moving around the nucleus. Each of these magnetic fields interact with one another and with external magnetic fields.

Key Words : Magnetic Fields, Paramagnetism, Ferromagnetism

Origins of Magnetic Behaviour

The magnetic properties of materials can be very useful in understanding their chemistry. It should be noted that although the origins of magnetism are based in single magnetic centres, unlike the other techniques we have studied, the interaction of these centres gives rise to bulk properties which can be measured.

Let us consider what happens when a substance is placed in an external magnetic field of strength H - a magnetic field of strength B is induced in the material given by the following expression:

$$\mathbf{B} = \mathbf{H} + 4\pi I$$

where *I* is the intensity of magnetisation. Traditionally, magnetism is discussed in terms of susceptibilities which may be defined as follows:

Volume susceptibility $\kappa = I / H$





Gram susceptibility, $\chi = \kappa / \rho$ (where ρ = density)

Molar susceptibility, $\chi_M = \chi \cdot M.Wt$.

 $\chi_{\rm M}$ is also defined by the Lande equation, such that

$$\chi_M = \frac{N_A \mu^2}{3kT}$$

Where N_A = Avagadro's number, μ = magnetic moment, k = Boltzmann constant and T = temperature. Rearranging this equation gives:

$$\mu = \sqrt{\left(\frac{3kT}{N_A}\right) \cdot \chi_M}$$

 μ is usually referred to as the effective magnetic moment, and by enumerating the constants the

$$\mu_{eff} = 2.83 \sqrt{\chi_M.T}$$

equation becomes

There are two major types of behaviour when a substance is placed in a magnetic field:

If B < H the substance is said to be diamagnetic. It is repelled by the field and χ is negative. Diamagnetism occurs as a result of electrons in closed shells circulating under the influence of the external magnetic field to generate a local field which is in opposition to the external field.

If B > H the substance is said to be paramagnetic. It is attracted by the field and χ is positive. Paramagnetism arises from the interaction of the spin and angular momentum of unpaired electrons with the external field. (If the spins are paired the spin and angular momentum cancel each other out). Note that paramagnetism is roughly 3 orders of magnitude greater than diamagnetism – hence, although paramagnetic species will have a diamagnetic contribution to the magnetic moment due to the core electrons in closed shells, the magnitude of this effect is relatively small (*ca* 1 – 5 %).

Types of Magnetism



Paramagnetism

Paramagnetic species can display a number of subclasses of magnetic behaviour. In simple paramagnetic materials the magnetic centres are separated by diamagnetic species and are said to be magnetically dilute. This means that the individual magnetic centres do not interact with one another. In such species the magnetic moment is given by the expression

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

Where S is the total spin (ie the sum of values of m_s) and L is the total orbital angular momentum (ie the sum of the values of m_l).

For many compounds the sum of the orbital angular momentum is zero, so we can use the spin-

$$\mu_{spinonly} = \sqrt{4S(S+1)}$$

only formula as a good approximation to the magnetic moment as given by:

This can also be expressed in terms of the number of unpaired electrons, n (since n = 2S)

$$\mu_{spinonly} = \sqrt{n(n+2)}$$

Ferromagnetism and Antiferromagnetism

There are, however, many compounds in which the neighbouring magnetic centres can interact (or couple) with each other, leading to magnetic ordering of the bulk material. This can take two main forms, ferromagnetism and antiferromagnetism (you will also discuss a third form, ferrimagnetism, in Dr Kennedy's Solid State Chemistry course).

If the magnetic moments all line up in parallel (as shown below), then the species is said to be ferromagnetic.

In ferromagnetic compounds μ_{eff} is generally much greater than $\mu_{spin-only}$ due to the cooperative effect of the spins coupling in parallel which reinforces the bulk magnetic moment. The most



common ferromagnetic materials are metals such as iron and cobalt and their alloys. CrO_2 is a rare example of a binary compound which is ferromagnetic at room temperature.

If the magnetic moments line up antiparallel with respect to one another (as shown below) then the substance in said to be antiferromagnetic.

 $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$

In antiferromagnetic compounds μ_{eff} tends to be somewhat less than $\mu_{spin-only}$ since the coupling of the spins into an anti-parallel arrangement results in the individual magnetic moments cancelling one another out. Antiferromagnetic materials are much more common than ferromagnetic materials.

The coupling of the magnetic moments arises via a mechanism known as super-exchange, in which the ligands help to order the spins on the metal centres.



Antiferromagetic

Ferromagnetic

Ferromagnetic and antiferromagnetic coupling is not restricted to ionic lattice type compounds, but can also be observed in polymetallic molecular compounds. So simple dimers and larger clusters can have the magnetic moments from neighbouring metal ions coupled via bridging ligands giving rise to discrete magnetic molecular entities which exhibit a degree of magnetic ordering.

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