8.3.2: Magnetism

Movement of an electrical charge (which is the basis of electric currents) generates a magnetic field in a material. Magnetism is therefore a characteristic property of all materials that contain electrically charged particles and for most purposes can be considered to be entirely of electronic origin.

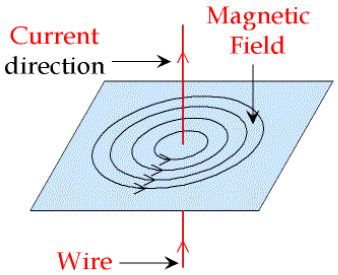

Figure 8.3.2.1: The Right Hand Rule for an induced magnetic field

In an atom, the magnetic field is due to the coupled spin and orbital magnetic moments associated with the motion of electrons. The spin magnetic moment is due to the precession of the electrons about their own axes whereas the orbital magnetic moment is due to the motion of electrons around the nucleus. The resultant combination of the spin and orbital magnetic moments of the constituent atoms of a material gives rise to the observed magnetic properties.

Historically, magnetism has been recognized for thousands of years. An account, that is probably apochryphal, tells of a shepherd called Magnes in Crete who around 900 B.C discovered the naturally occurring magnet lodestone (a form of the the spinel magnetite, Fe_3O_4) in a region later named Magnesia. Supposedly while he was walking over a deposit, the lodestone pulled the nails out of his sandals and the metal tip from his staff.

The Classical Theory of Magnetism

The classical theory of magnetism was well developed before quantum mechanics. Lenz's Law states that when a substance is placed within a magnetic field, H, the field within the substance, B, differs from H by the induced field, $4\pi I$, which is proportional to the intensity of magnetization, I. That is;

$$B = H + 4\pi I \tag{8.3.2.1}$$

where B is the magnetic field within the substance and H is the applied magnetic field and I is the intensity of magnetization

Lenz's Law (1834)

Lenz's Law can also be written as

$$\frac{B}{H} = 1 + \frac{4\pi I}{H} \tag{8.3.2.2}$$

or

$$\frac{B}{H} = 1 + 4\pi\kappa \tag{8.3.2.3}$$

where

- B/H is called the magnetic permeability of the material and
- κ is the magnetic susceptibility per unit volume, (I/H)

By definition, κ in a vacuum is zero, so under those conditions the equation would reduce to $B = H$. It is usually more convenient to measure mass than volume and the mass susceptibility, χ_g, is related to the volume susceptibility, κ, through the density.

$$\chi_g = \frac{\kappa}{\rho} \tag{8.3.2.4}$$

where ρ is the density.

Finally to get our measured quantity on a basis that can be related to atomic properties, we convert to molar susceptibility

$$\chi_m = \chi_g \times RMM \tag{8.3.2.5}$$

Since this value includes the underlying diamagnetism of paired electrons, it is necessary to correct for the diamagnetic portion of χ_m to get a corrected paramagnetic susceptibility.

$$\chi'_m = \chi_m + \chi_{dia} \tag{8.3.2.6}$$

Examples of these corrections are tabulated below.

Table 8.3.2.1: Table of Diamagnetic Corrections (Pascal's constants, 10^{-6} c.g.s. units)

Ion	DC	Ion	DC
Na^+	6.8	Co^{2+}	12.8
K^+	14.9	Co^{3+}	12.8
NH_4^+	13.3	Ni^{2+}	12.8
Hg^{2+}	40	VO^{2+}	12.5
Fe^{2+}	12.8	Mn^{3+}	12.5
Fe^{3+}	12.8	Cr^{3+}	12.5
Cu^{2+}	12.8	Cl^-	23.4
Br^-	34.6	SO_4^{2-}	40.1
I^-	50.6	OH^-	12
NO_3^-	18.9	$C_2O_4^{2-}$	34
ClO_4^-	32	OAc^-	31.5
IO_4^-	51.9	pyr	49.2
CN^-	13	Me-pyr	60
NCS^-	26.2	$Acac^-$	62.5
H_2O	13	en	46.3
$EDTA^{4-}$	~150	urea	33.4

these can be converted to S.I units of $m^3\ mol^{-1}$ by multiplying by $4\ \pi$ x 10^{-7}

There are numerous methods for measuring magnetic susceptibilities, including, the **Gouy, Evans and Faraday methods**. These all depend on measuring the force exerted upon a sample when it is placed in a magnetic field. The more paramagnetic the sample, the more strongly it will be drawn toward the more intense part of the field.

Determination of Magnetic Susceptibility

- **The Gouy Method:** The underlying theory of the Gouy method is described here and a form for calculating the magnetic moment from the collected data is available as well.
- **The Evans method:** The Evans balance measures the change in current required to keep a pair of suspended magnets in place or balanced after the interaction of the magnetic field with the sample. The Evans balance differs from that of the Gouy in that, in the former the permanent magnets are suspended and the position of the sample is kept constant while in the latter the position of the magnet is constant and the sample is suspended between the magnets.

Orbital contribution to magnetic moments

From a quantum mechanics viewpoint, the magnetic moment is dependent on both spin and orbital angular momentum contributions. The spin-only formula used last year was given as:

$$\mu_{s.o.} = \sqrt{4S(S+1)} \tag{8.3.2.7}$$

and this can be modified to include the orbital angular momentum

$$\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)} \tag{8.3.2.8}$$

An orbital angular momentum contribution is expected when the ground term is triply degenerate (i.e. a triplet state). These show temperature dependence as well.

In order for an electron to contribute to the orbital angular momentum the orbital in which it resides must be able to transform into an exactly identical and degenerate orbital by a simple rotation (it is the rotation of the electrons that induces the orbital contribution). For example, in an octahedral complex the degenerate t_{2g} set of orbitals (d_{xz},d_{yx},d_{yz}) can be interconverted by a 90^o rotation. However the orbitals in the e_g subset (d_{z^2},$d_{x^2\text{-}y^2}$) cannot be interconverted by rotation about any axis as the orbital shapes are different; therefore an electron in the e_g set does not contribute to the orbital angular momentum and is said to be quenched. In the free ion case the electrons can be transformed between any of the orbitals as they are all degenerate, but there will still be partial orbital quenching as the orbitals are not identical.

Electrons in the t_{2g} set do not always contribute to the orbital angular moment. For example in the d^3, t_{2g}^3 case, an electron in the d_{xz} orbital cannot by rotation be placed in the d_{yz} orbital as the orbital already has an electron of the same spin. This process is also called quenching.

Tetrahedral complexes can be treated in a similar way with the exception that we fill the e orbitals first, and the electrons in these do not contribute to the orbital angular momentum. The tables in the links below give a list of all d^1 to d^9 configurations including high and low spin complexes and a statement of whether or not a direct orbital contribution is expected.

- Octahedral complexes
- Tetrahedral complexes

Contributors and Attributions

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