**Course Name:** Chemistry of d-and f-block elements

**Paper Number: 201
Section:B
Course Instructor: Dhanraj T. Masram
Study Material (name of topic/chapter): Magnetism**

**Magnetism**

The primary measurement in magnetochemistry is magnetic susceptibility. This measures the strength of interaction on placing the substance in a magnetic field.

The **magnetic susceptibility** is a measure of how much a material will become magnetized in an applied magnetic field. Mathematically, it is the ratio of [magnetization](https://en.wikipedia.org/wiki/Magnetization) **M** (magnetic moment per unit volume) to the applied magnetizing field intensity **H**. This allows a simple classification of most materials' response to an applied magnetic field into two categories: an alignment with the magnetic field, *χ* > 0, called paramagnetism or an alignment against the field, *χ* < 0, called diamagnetism

### Volume susceptibility

The *volume magnetic susceptibility*, represented by the symbol *χv* (often simply *χ*, sometimes *χm* - magnetic, is defined in the [International System of Units](https://en.wikipedia.org/wiki/International_System_of_Units) - in other systems there may be additional constants- by the following relationship: {\displaystyle \mathbf {M} =\chi \_{v}\mathbf {H} .}$Mm$

**M**  = *χv* . **H**

**M** is the [magnetization](https://en.wikipedia.org/wiki/Magnetization) of the material (the [magnetic dipole moment](https://en.wikipedia.org/wiki/Magnetic_dipole_moment) per unit volume), measured in [amperes](https://en.wikipedia.org/wiki/Ampere) per meter, and

**H** is the [magnetic field strength](https://en.wikipedia.org/wiki/Effective_magnetic_field), also measured in amperes per meter.

*χv* is therefore a [dimensionless quantity](https://en.wikipedia.org/wiki/Dimensionless_quantity).

Using [SI units](https://en.wikipedia.org/wiki/SI_electromagnetism_units), the [magnetic induction](https://en.wikipedia.org/wiki/Magnetic_field) **B** is related to **H** by the relationship

**B=** *μ*0(H+M)= *μ*0(1 + *χv*)H = *μ* H

{\displaystyle \mathbf {B} \ =\ \mu \_{0}\left(\mathbf {H} +\mathbf {M} \right)\ =\ \mu \_{0}\left(1+\chi \_{v}\right)\mathbf {H} \ =\ \mu \mathbf {H} }where, *μ*0 is the [vacuum permeability](https://en.wikipedia.org/wiki/Vacuum_permeability) (see table of [physical constants](https://en.wikipedia.org/wiki/Physical_constant)), and (1 + *χv*) is the [relative permeability](https://en.wikipedia.org/wiki/Permeability_%28electromagnetism%29#Relative_permeability_and_magnetic_susceptibility) of the material. Thus the *volume magnetic susceptibility* *χv* and the [magnetic permeability](https://en.wikipedia.org/wiki/Magnetic_permeability) *μ* are related by the following formula: *μ*= *μ*0 (1 + *χv*)

{\displaystyle \mu =\mu \_{0}\left(1+\chi \_{v}\right).}Sometimes an auxiliary quantity called *intensity of magnetization* **I** (also referred to as *magnetic polarisation* **J**) and measured in [teslas](https://en.wikipedia.org/wiki/Tesla_%28unit%29), is defined as **I=** *μ*0M

{\displaystyle \mathbf {I} =\mu \_{0}\mathbf {M} .}This allows an alternative description of all magnetization phenomena in terms of the quantities **I** and **B**, as opposed to the commonly used **M** and **H**.

There are two other measures of susceptibility, the *mass magnetic susceptibility* (*χ*mass or *χ*g, sometimes *χm*), measured in m3/kg (SI) and the [*molar*](https://en.wikipedia.org/wiki/Mole_%28unit%29)*magnetic susceptibility* (*χ*mol) measured in m3/mol that are defined below, where *ρ* is the [density](https://en.wikipedia.org/wiki/Density) in kg/m3 and *M* is [molar mass](https://en.wikipedia.org/wiki/Molar_mass) in kg/mol:

*χ*mass= *χv*/ *ρ* ; {\displaystyle \chi \_{\text{mass}}={\frac {\chi \_{v}}{\rho }}}{\displaystyle \chi \_{\text{mol}}=M\chi \_{\text{mass}}={\frac {M\chi \_{v}}{\rho }}}

*χ*mol= **M** *χ*mass = **M** *χv/ ρ*  {\displaystyle \mathbf {B} ^{\text{cgs}}\ =\ \mathbf {H} ^{\text{cgs}}+4\pi \mathbf {M} ^{\text{cgs}}\ =\ \left(1+4\pi \chi \_{v}^{\text{cgs}}\right)\mathbf {H} ^{\text{cgs}}}

Diamagnetism-When placed in a magnetic field the atom becomes magnetically polarized, that is, it develops an induced magnetic moment. The force of the interaction tends to push the atom out of the magnetic field. By convention diamagnetic susceptibility is given a negative sign. Very frequently diamagnetic atoms have no unpaired electrons *ie* each electron is paired with another electron in the same [atomic orbital](https://en.wikipedia.org/wiki/Atomic_orbital). The moments of the two electrons cancel each other out, so the atom has no net magnetic moment. However, for the ion Eu3+ which has six unpaired electrons, the orbital angular momentum cancels out the electron angular momentum, and this ion is diamagnetic at zero Kelvin.

Paramagnetism. At least one electron is not paired with another. The atom has a permanent magnetic moment. When placed into a magnetic field, the atom is attracted into the field. By convention paramagnetic susceptibility is given a positive sign.

When the atom is present in a [chemical compound](https://en.wikipedia.org/wiki/Chemical_compound) its magnetic behavior is modified by its chemical environment. Measurement of the magnetic moment can give useful chemical information.

In certain crystalline materials individual magnetic moments may be aligned with each other (magnetic moment has both magnitude and direction). This gives rise to [ferromagnetism](https://en.wikipedia.org/wiki/Ferromagnetism), [antiferromagnetism](https://en.wikipedia.org/wiki/Antiferromagnetism%22%20%5Co%20%22Antiferromagnetism) or [ferrimagnetism](https://en.wikipedia.org/wiki/Ferrimagnetism%22%20%5Co%20%22Ferrimagnetism). These are properties of the crystal as a whole, of little bearing on chemical properties.

If *χ* is positive, a material can be [paramagnetic](https://en.wikipedia.org/wiki/Paramagnetic). In this case, the magnetic field in the material is strengthened by the induced magnetization. Alternatively, if *χ* is negative, the material is [diamagnetic](https://en.wikipedia.org/wiki/Diamagnetic). In this case, the magnetic field in the material is weakened by the induced magnetization. Generally, nonmagnetic materials are said to be para- or diamagnetic because they do not possess permanent magnetization without external magnetic field. [Ferromagnetic](https://en.wikipedia.org/wiki/Ferromagnetic), [ferrimagnetic](https://en.wikipedia.org/wiki/Ferrimagnetism%22%20%5Co%20%22Ferrimagnetism), or [antiferromagnetic](https://en.wikipedia.org/wiki/Antiferromagnetic%22%20%5Co%20%22Antiferromagnetic) materials possess permanent magnetization even without external magnetic field and do not have a well defined zero-field susceptibility.

Exchange interactions occur when the substance is not magnetically dilute and there are interactions between individual magnetic centres. One of the simplest systems to exhibit the result of exchange interactions is crystalline [copper(II)acetate](https://en.wikipedia.org/wiki/Copper%28II%29_acetate), Cu2(OAc)4(H2O)2. As the formula indicates, it contains two copper(II) ions. The Cu2+ ions are held together by four acetate ligands, each of which binds to both copper ions. Each Cu2+ ion has a d9 electronic configuration, and so should have one unpaired electron. If there were a covalent bond between the copper ions, the electrons would pair up and the compound would be diamagnetic. Instead, there is an exchange interaction in which the spins of the unpaired electrons become partially aligned to each other. In fact two states are created, one with spins parallel and the other with spins opposed. The energy difference between the two states is so small their populations vary significantly with temperature. In consequence the magnetic moment varies with temperature in a [sigmoidal](https://en.wikipedia.org/wiki/Sigmoid_function%22%20%5Co%20%22Sigmoid%20function) pattern. The state with spins opposed has lower energy, so the interaction can be classed as antiferromagnetic in this case. It is believed that this is an example of [superexchange](https://en.wikipedia.org/wiki/Superexchange%22%20%5Co%20%22Superexchange), mediated by the oxygen and carbon atoms of the acetate ligands. Other dimers and clusters exhibit exchange behaviour.

Exchange interactions can act over infinite chains in one dimension, planes in two dimensions or over a whole crystal in three dimensions. These are examples of long-range magnetic ordering. They give rise to [ferromagnetism](https://en.wikipedia.org/wiki/Ferromagnetism), [antiferromagnetism](https://en.wikipedia.org/wiki/Antiferromagnetism%22%20%5Co%20%22Antiferromagnetism) or [ferrimagnetism](https://en.wikipedia.org/wiki/Ferrimagnetism%22%20%5Co%20%22Ferrimagnetism), depending on the nature and relative orientations of the individual spins.

Compounds at temperatures below the Curie temperature exhibit long-range magnetic order in the form of ferromagnetism. Another critical temperature is the [Néel temperature](https://en.wikipedia.org/wiki/N%C3%A9el_temperature%22%20%5Co%20%22N%C3%A9el%20temperature), below which antiferromagnetism occurs.

The magnetic properties of the lanthanides are due to the electrons in the partial filled 4*f*shell. The magnetic properties of the first-row transition metals are due to the electrons in the partial filled 3*d*shell. There are two important differences between the 3*d*shell and the 4*f* shell.

The first difference is that *d* electrons have much greater overlap with their neighboring atoms than *f*electrons do. This means that *d* bands are not as localized as *f* bands are.

The second difference is that the spin-orbit coupling is much stronger in the lanthanides than in the 3*d* transition metals. For the lanthanides we use the *JJ-*coupling approximation, but for the 3*d* transition metals we use Hund’s rule, which are a result of the *LS*-coupling approximation.

**Lanthanides-**

The elements in which the last electron enters in (n-2)f orbitals are called  f-block elements . In these elements last electron is added to the (third to the outer most shell) ante penultimate shell. They are also called inner transition elements. The valence shell electronic configuration of these elements can be represented as , (n-2) f 0,2-14, (n-1) d 0,1,2,ns2

They consist of two series of elements & are placed at the bottom of periodic table are 4f & 5f.

**Lanthanides or Rare Earth elements or 4f – series -**When last electron enters in 4f orbital, then series of elements is 4f or lanthanide series. The Lanthanide series include 14 elements i- e. 58Ce – 71Lu.

**Magnetic property -** Ions which contain  all  paired  electrons  are diamagnetic  while those containing unpaired electrons are paramagnetic . Among the lanthanides, La3+ [4f 0] & Lu3+ [4f 14] are diamagnetic. All trivalent lanthanide ions are paramagnetic due to unpaired electrons.

**Basic character of hydroxides -**All the lanthanides form hydroxides of the formula Ln(OH)3. These are ionic & basic. Since the ionic size decreases from La3+ to Lu3+ , the basicity of hydroxides decreases . La(OH)3 is strongest base while Lu(OH)3 is weakest base.

**Atomic & ionic radius (Lanthanide Contraction)-** As we move along the lanthanide series, there is a decrease in atomic & ionic radii. This steady decrease in the atomic & ionic radii is called Lanthanide contraction.

**Cause of Lanthanide Contraction -** In the lanthanide series, as we move from one element to another , the nuclear  charge increases by one unit & one electron is added. The new electrons are added to the same inner 4f subshell. So 4f electrons shield each other from the nuclear charge quite poorly because of very diffused shapes of the f orbitals. Hence with increasing atomic number & nuclear charge, the effective nuclear charge experienced by each 4f electrons increases. So whole of 4f electron shell contracts at each successive element, so decrease is very small.

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| **Lanthanide Magnetism** |
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| --- | --- | --- | --- | --- | --- | --- |
|  | **config.** | **Ground** | **No. of** |  |  | **Observed** |
| **Ln** | **Ln3+** | **State** | **unpaired e-** | **Colour** | https://www.radiochemistry.org/periodictable/la_series/images/gjjj+1.gif | **meff/mB** |
| **La** | 4f0 | 1S0 | 0 | *colourless* | 0 | 0 |
| **Ce** | 4f1 | 2F5/2 | 1 | *colourless* | 2.54 | 2.3 - 2.5 |
| **Pr** | 4f2 | 3H4 | 2 | *green* | 3.58 | 3.4 - 3.6 |
| **Nd** | 4f3 | 4I9/2 | 3 | *lilac* | 3.62 | 3.5 - 3.6 |
| **Pm** | 4f4 | 5I4 | 4 | *pink* | 2.68 | - |
| **Sm** | 4f5 | 6H5/2 | 5 | *yellow* | 0.85 | 1.4 - 1.7 |
| **Eu** | 4f6 | 7F0 | 6 | *pale pink* | 0 | 3.3 - 3.5 |
| **Gd** | 4f7 | 8S7/2 | 7 | *colourless* | 7.94 | 7.9 - 8.0 |
| **Tb** | 4f8 | 7F6 | 6 | *pale pink* | 9.72 | 9.5 - 9.8 |
| **Dy** | 4f9 | 6H15/2 | 5 | *yellow* | 10.65 | 10.4 - 10.6 |
| **Ho** | 4f10 | 5I8 | 4 | *yellow* | 10.6 | 10.4 - 10.7 |
| **Er** | 4f11 | 4I15/2 | 3 | *rose-pink* | 9.58 | 9.4 - 9.6 |
| **Tm** | 4f12 | 3H6 | 2 | *pale green* | 7.56 | 7.1 - 7.6 |
| **Yb** | 4f13 | 2F7/2 | 1 | *colourless* | 4.54 | 4.3 - 4.9 |
| **Lu** | 4f14 | 1S0 | 0 | *colourless* | 0 | 0 |

Magnetic Properties* Magnetic properties have **spin & orbit contributions**(contrast "*spin-only"* of transition metals)
* Magnetic moments of Ln3+ ions are generally well-described from the coupling of spin and orbital angular momenta ~ **Russell-Saunders Coupling** Scheme
* **spin orbit coupling** constants are typically **large** (ca. 1000 cm-1)
* **ligand field** effects are very **small** (ca. 100 cm-1)

Þ only ground J-state is populatedÞ spin-orbit coupling >> ligand field splittingsÞ magnetism is essentially **independent of environment*** Magnetic moment of a J-state is expressed by the **Landé formula**

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|  |
| --- |
| **Sample Landè Calculation*****e.g*** **Pr3+ [Xe]4f2*** Find Ground State from Hund's Rules
	+ **Maximum Multiplicity** **S** = 1/2 + 1/2 = 1 https://www.radiochemistry.org/periodictable/la_series/images/blank.gif**Þ 2S + 1 = 3**
	+ **Maximum Orbital Angular Momentum** **L** = 3 + 2 = 5https://www.radiochemistry.org/periodictable/la_series/images/blank.gif **Þ H state**
	+ **Total Angular Momentum** **J** = (L + S), (L + S) - 1, ÁL - SÁ = 6 , 5, 4
		- Less than half-filled sub-shell **Þ** Minimum J https://www.radiochemistry.org/periodictable/la_series/images/blank.gif**Þ J = 4** *{Greater than half-filled sub-shell***Þ***Maximum J}*
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https://www.radiochemistry.org/periodictable/la_series/images/lnmagcom.gif |

##### Ln3+ Magnetic Moments compared with Theory

Experimental \_\_\_\_\_****Landé Formula -•-•-****Spin-Only Formula - - -

**Landé formula fits well** with observed magnetic moments for all but **SmIII** and **EuIII,**

Moments of **SmIII** and **EuIII** are altered from the Landé expression by **temperature-dependent population of low-lying excited J-state(s)**