

## Quadrant II – Transcript and Related Materials

**Programme: Bachelor of Science (Second Year)**

**Subject: Chemistry**

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**Paper Title: PHYSICAL CHEMISTRY AND INORGANIC CHEMISTRY**

**Unit: I**

**Module Name: Colour, Magnetic properties of Lanthanoids**

**Module No: 08**

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### Notes:

- Lanthanide ions can have electrons in the  $f$ -orbital and also empty  $f$  orbitals like the d-block elements. When a frequency of light is absorbed, the light transmitted exhibits a colour complementary to the frequency absorbed. Inner transition element ions can absorb the frequency in the visible region to use it for  $f$ - $f$  electron transition and produce visible colour.
- Most lanthanoid ions are only weakly coloured because their absorptions in the visible region of the spectrum are commonly  $f$ - $f$  transitions which are symmetry forbidden
- The spectra of their complexes generally show much narrower and more distinct absorption bands than those of d-metal complexes.
- Many of the lanthanoid metals are silvery-white. The lanthanoid ions with +3 oxidation state are coloured in aqueous solution
- The colour of a cation depends on the number of unpaired  $f$  electrons. Lanthanides, with  $xf$  electrons, have the same colour as of  $(14-x)f$  electron elements.
- The  $4f$  orbitals are deeply embedded inside the atom and well shielded by  $5s$  and  $5p$  electrons therefore, the  $f$  electrons are practically

unaffected by complex formation, hence colour remains almost constant for a particular ion regardless of the ligands

### Magnetic Properties:

The Lanthanides belongs to the inner transition series. These elements are generally trivalent, The paramagnetism in these elements arises from the 4f electrons. These electrons are effectively shielded from external influence (surrounding coordinating ligand) by filled 5s and 5p sub-shells.

The magnetic moment  $\mu$  of many d-metal ions can be calculated by using the spin-only approximation because the strong ligand field quenches the orbital contribution. For the lanthanoids, where the spin-orbital coupling is strong, the orbital angular momentum contributes to the magnetic moment, and the ions behave like almost free atoms. Therefore, the magnetic moment must be expressed in terms of the total angular momentum quantum number  $J$ :

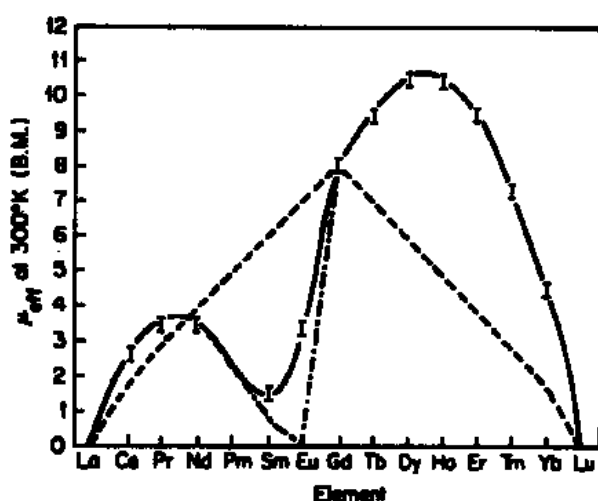
$J = L - S$  when the orbital is less than half filled

$J = L + S$  when the orbital is more than half filled

For lanthanides  $\mu = g \sqrt{J(J + 1)}$

$g$  is the Lande splitting factor and is given by

$$g = 1.5 + \frac{S(S + 1) - L(L + 1)}{2J(J+1)}$$



Magnetic moment values of lanthanides vary depending upon the atomic number.  $\text{La}^{3+}$  is diamagnetic ( $f^0$ ) and the value of magnetic moment increases attaining maximum value at Neodymium. It then suddenly drops to 1.47 for Samarium. It increases again reaching maximum value for Dysprosium and Holmium. Thereafter, it falls again touching zero at Lutetium which is diamagnetic ( $f^{14}$ ).

The unusual shape of the curve arises because the spin and orbital magnetic moments work in opposite directions when the  $f$  – subshell is less than half full. But they, supplement each other when  $f$ - subshell is more than half full.