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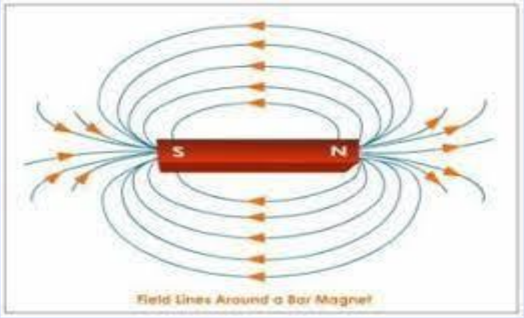
PG DEPARTMENT OF CHEMISTRY

LEARNING RESOURCES

MAGNETIC PROPERTIES



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MAGNETIC PROPERTIES OF

LANTHANIDES AND ACTINIDES

Magnetic properties of lanthanides

The La $^{3+}$, Lu^{3+}, Ce $^{4+}$ and Yb $^{2+}$ ions which have 4f or 4f electronic configurations are diamagnetic .

The rest of the tri valent lanthanides ions which contains unpaired electrons in the 4f orbital are Para magnetic .

The magnetic properties of the lanthanides are different from those of the transition elements.

The magnetic moment arise from two types of motion of electron.

The spin motion of electron around its own axis produces magnetic moment called spin magnetic moment.

While the orbital motion of electron around the nucleus produces magnetic moment called orbital magnetic moment .

The observed magnetic properties of a substances are the result of both the spin magnetic moment and the orbital magnetic moment .

In the case of compounds of transition elements.(d-block elements).

The d electrons of the metal ions interacts strongly with the electron of the ligands surrounding the metal ion.

Due the electric field of the ligands the orbital motion of the electrons gets restricted and there by the orbital magnetic moments of these electrons gets almost quenched.

The magnetic moment of d block elements thus arises mainly from the contribution of spin motion of the electrons.

- The simple relationship based on the contribution of the electron, viz,.

Where n is the number of unpaired electron roughly accounts for the magnetic properties of d block elements .

The above relationship is not valid in the case of f block elements.

In these f block elements the 4forbitals are well shielded from the surroundings by the overlying 5s and 5p sub shells.

As a result , the electric field of the ligands surrounding the ion doesn't restrict the orbital motion of the electrons.

- Thus , orbital contribution which was ignored in the case of d block elements. The magnetic moment in such a cases is given by the relationship.

- Where J is the total “angular momentum quantum number

”• The few values of magnetic moment calculated by the above expression are seen to be in good agreement with the experimental value.

- The experimental magnetic moments of tripositive lanthanides ions are plotted in figure against their respective atomic numbers.
- La^{3+} ion is diamagnetic because of its f^0 configuration . the value increases upto Nd^{3+} ion and then drop to 1.47 for Sm^{3+} ion.
- It starts rising again becoming maximum for Dy^{3+} ion. When it is about 11. it again starts dropping becomes zero for Lu^{3+} (f^{14}configuration) which is diamagnetic.

MAGNETIC PROPERTIES OF ACTINIDES:

- In the 5f series, $Pu^{3+}$and Am^{3+} ions show the analogous behavior as noted for $Sm^{+}$and Eu^{3+} ions in 4f series.
- The magnetic properties of the actinide ions are considerably more difficult to explain than those of the lanthanide ions.

- The values of magnetic moments found experimentally are usually lower than those calculated using Russell-Saunders coupling scheme.

- This due to perhaps to the inadequacy of the Russell-Saunders coupling scheme for 5f ions and also to more subtle ligand field effects which involve 5f-orbitals to a greater extent than the 4f-orbitals are involved in bonding in the lanthanide complexes.

- An equation used for the calculation of molar susceptibility, χ is given by,

$$\chi_{M} = \qquad\qquad + N\alpha$$

Where

N = Avogadro's number, g

= Lande splitting factor

which is given by :

β = Bohr Magneton = eh/2πmc =$9.27*10^{-21}$ erg/gauss

J=Total angular momentum of atom = |L+S|,

K=Boltzmann constant ,

T=absolute temperature,

α= small,temperature independent term due to second order Zeeman effect.

- Strictly speaking the above equation can be applied only to gaseous ions in which the multiplet intervals are larger compared with kT and the value of J to be used in it is taken from the ground state symbols of ions.
- A comparison of the plots of molar magnetic susceptibilities of tripositive lanthanide and actinide ions against the number of 4f- or 5f- electrons(fig 1)reveals that there are remarkable similarities between the two plots .1

- The plot of lanthanide ions has two humps while that of actinide ions has only one.
- In both the cases the first hump is, however, at the identical place.

- . The moments of the lanthanide ions agree closely with theoretical predictions but those of the transuranic ions are somewhat lower than expected. Fig(b).
- This is because the 5f-electrons of the transuranic ions are less effectively screened from the crystal field, which quenches orbital contribution, than

are the 4f-electrons of the lanthanide ions.