

Site Preference for Spinel and Inverse Spinel

Question: **Why does some AB_2O_4 compounds having transition elements as A and /or B prefer the inverse Spinel structure and some others normal Spinel structure?**



O^{2-} = a weak field ligand

$Mn^{2+} = d^5$ HS : CFSE = 0

$Mn^{3+} = d^4$ HS : CFSE = $-0.6 \Delta_o$

Mn^{2+} by exchanging positions with Mn^{3+} in an octahedral hole is **not going to gain** any extra crystal field stabilization energy.

While Mn^{3+} by being in the octahedral hole will have CFSE.

Therefore Mn_3O_4 will be **Normal Spinel**



$Fe^{2+} = d^6$ HS : CFSE = $-0.4 \Delta_o$

$Fe^{3+} = d^5$ HS: CFSE = 0

Fe^{2+} by exchanging positions with Fe^{3+} to an octahedral hole is going to gain extra crystal field stabilization energy. While Fe^{3+} by being in the octahedral hole will not have any CFSE.

Therefore Fe_3O_4 will be **Inverse Spinel**

- Based on CFSE values, it is possible to predict the type of compounds having the formula AB_2O_4 whether it belongs to normal spinels or Inverse Spinel

Merits of crystal Field Theory

- Predict most favorable geometry of a complex
- Accounts for four coordinated complexes (tetrahedral and square planar)
- Explains the ligands forming outer / inner orbital complexes (high spin / low spin)
- Interprets magnetic properties taking in to consideration the orbital contributions also
- Interprets color of transition metal complexes
- Explains spectral properties of many transition metal complexes
- Predict site selection in spinel and antispinel structures

Limitations of CFT

- CFT considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals such as s-, p-orbitals and the ligand π -orbitals. Therefore, to explain all the properties of the complexes dependent on the π -ligand orbitals will be outside the scope of CFT. This does not consider the formation of **π -bonding in complexes**.
- Less accurate when **covalent bonding increases or partly covalent nature of the metal-ligand bonds** (As ligand orbital and electrons become more important). Bonding strength and chemical properties cannot be explained in some complexes based on only electrostatic interactions (purely ionic) as assumed by the theory
- CFT is unable to account satisfactorily for the **relative strengths of ligands**, e.g. it gives no explanation as to why H_2O appears in the spectrochemical series as a stronger ligand than OH^-

Preparation of Complex Compounds

➤ Complexes are prepared by the following types of reactions:

➤ **Connection Reactions:**



➤ **Substitution Reactions:**



➤ **Exchange Reactions:**



➤ **Redox Reactions:**

