Study Notes on Spinels

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Spinels

Structure of spinels:

Spinels have the general chemical formula AB_2X_4. Here,

A^{II}- a divalent cation like Mn, Cr, Fe, Co, Ni

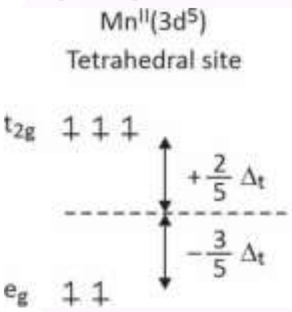
B^{III}- a trivalent cation like Ga, Al, Cr, Mn, Fe

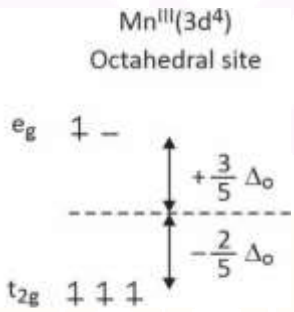
Mixed metal oxides having the composition $A^{II}B_2^{III}$ O_4 are called spinels. A and B may be different metals or the same metal in different oxidation states. Spinels are classified into two types: normal spinels, $A^{II}[B_2^{III}]O_4$ inverse spinels, $B^{III}[A^{II}\ B^{III}]O_4$. In normal spinels, A occupies tetrahedral interstices, while B occupies octahedral interstices. The compound $NiAl_2O_4$ is an example of normal spinel. In inverse spinels, half B's occupy tetrahedral sites and half B's octahedral sites, while A is in octahedral interstices. An example of an inverse spinel is Fe_3O_4, when it may be represented as, $Fe^{III}[Fe^{II}Fe^{III}]O_4$.

For transition metal oxide spinels, the choice of the normal and inverse spinels is generally driven by the CFSE of ions in the tetrahedral and octahedral sites. For spinels containing 3d elements like Mn, Fe, Cr and Co, the electronic configuration is typically high spin because O^{2-} is a weak field ligand.

Whether a particular spinel will acquire normal structure or inverse structure largely depends on CFSE. That structure prevails which has a greater negative value of CFSE. For example, consider the mixed manganese oxide, Mn_3O_4. If it is a normal spinel, its CFSE may be calculated as follows:

$Mn^{II}[Mn_2^{III}]O_4$





$$\text{CFSE} = 2\left(-\frac{3}{5}\Delta_t\right)+3\left(+\frac{2}{5}\Delta_t\right) = 0$$

$$\text{CFSE} = 3\left(-\frac{2}{5}\Delta_o\right)+1\left(+\frac{3}{5}\Delta_o\right)$$

$$=\left(-\frac{3}{5}\Delta_o\right)$$

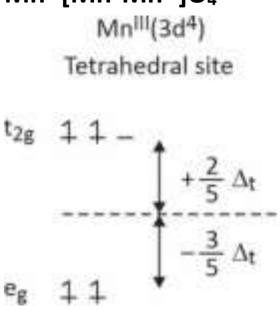
$$=\left(-\frac{3}{5}\Delta_o\right)\times 2=-\frac{6}{5}\Delta_o$$

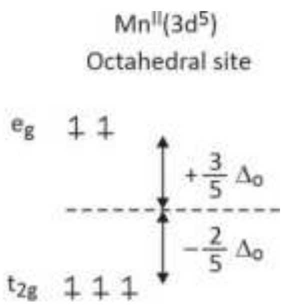
(Since there are two Mn^{III} ions)

$$\text{Total CFSE} = -\frac{6}{5}\Delta_o$$

If it is an inverse spinel, the crystal field stabilization energy may be calculated as follows:

$Mn^{III}[Mn^{II}Mn^{III}]O_4$





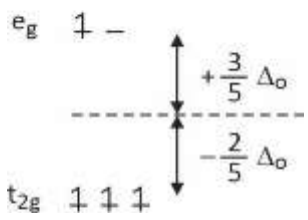
$$\text{CFSE} = 2\left(-\frac{3}{5}\Delta_t\right)+2\left(+\frac{2}{5}\Delta_t\right) \qquad \text{CFSE} = 3\left(-\frac{2}{5}\Delta_o\right)+2\left(+\frac{3}{5}\Delta_o\right)$$

$$= -\frac{2}{5}\Delta_t \qquad\qquad = 0$$

$$= -\frac{1}{5}\Delta_0 \ (\text{Since } \Delta_t \approx \frac{1}{5}\Delta_o)$$

$Mn^{III}(3d^4)$

Octahedral site



$$\text{CFSE} = 3\left(-\frac{2}{5}\Delta_o\right)+1\left(+\frac{3}{5}\Delta_o\right)$$

$$= -\frac{3}{5}\Delta_o$$

$$\text{Total CFSE} = -\frac{1}{5}\Delta_o + 0 + \left(-\frac{3}{5}\Delta_o\right) = -\frac{4}{5}\Delta_o$$

The normal spinel has a greater negative CFSE and hence this structure prevails.

(II) (III)

$Co_3O_4 \longrightarrow CoCo_2O_4$

Co^{3+} is low spin in the field produced by oxide ions.

Octahedral	**Tetrahedral**
$Co^{3+}(d^6)\, t_{2g}^6\, e_g^0$	$e_g^3\, t_{2g}^3$
CFSE = $[-0.6 \times 4 + 0.6 \times 0]\Delta_o$	CFSE = $[-0.27 \times 3 + 0.18 \times 3]\Delta_o$
$= -2.4\ \Delta_o$	$= -0.27\ \Delta_o$
$Co^{2+}(d^7)\, t_{2g}^5\, e_g^2$	$e_g^4\, t_{2g}^2$
CFSE = $[-0.4 \times 5 + 0.6 \times 2]\Delta_o$	CFSE = $[-0.27 \times 4 + 0.18 \times 3]\Delta_o$
$= 0.8\ \Delta_o$	$= 0.54\ \Delta_o$

Since CFSE for Co^{3+} is highest in octahedral field.

Therefore, Co^{3+} will occupy octahedral and Co^{2+} will occupy tetrahedral voids. Hence Co_3O_4 is a normal spinel.