# A Shiver down the Spine-l

Elementary Problem 6 - 10 points

Deadline: September $7^{th}$ at 8:30 PM IST

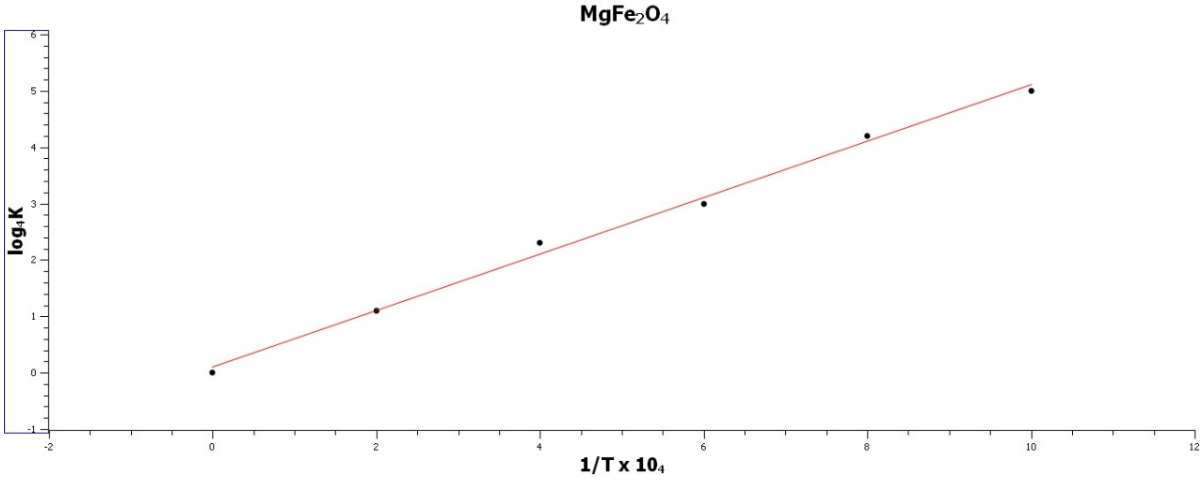
1. Let A and B be two divalent cations and C be a trivalent cation and $0 < d < 1$. $A_{1-d}B_dO.C_2O_3$ forms a normal spinel structure. For each unit, there is one tetrahedral site and two octahedral sites. Consider $v$ molecules of this compound. Let there be two parameters $x$ and $y$ which define the distribution of $A^{2+}$ and $B^{2+}$ ions in tetrahedral sites, such that there are $xv$ $A^{2+}$ ions in tetrahedral sites and $yv$ $B^{2+}$ ions in tetrahedral sites. Write the distribution of each cation in both tetrahedral and octahedral sites and find the number of ways such a distribution ($A_{1-d}B_dO.C_2O_3$) can be achieved (denote that with w).

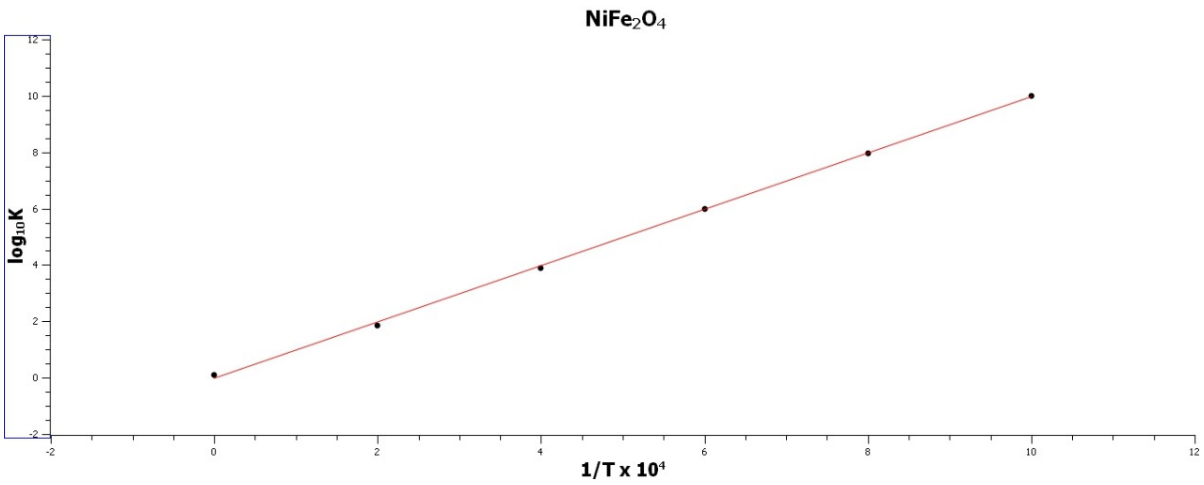
2. Consider a compound $A_{1-x}B_x(A_xB_{2-x})O_4$ where $x$ is the fraction of tetrahedral sites occupied by $B^{2+}$ ions. Initially, the compound exists as a normal spinel. Consider the inversion of the structure:

$$A + (B) \rightleftharpoons (A) + B$$

   a. Write the equilibrium constant (K) in terms of $x$.

   b. From the plots deduce the entropy due to non-configuration changes ($\Delta S^\circ$). (T denotes the absolute temperature)






c. Derive the expression for configurational entropy (-$R$ ln$w$) for this compound and plot its variation with $x$. (Hint: try using the same method as in Part 1)

3. Which structure will $Co_3O_4$ adopt and why?