

4. SOLUTIONS

4.1. a) $\text{Fe}^{2+} 3d^6, 4\mu_B, \text{Fe}^{3+} 3d^5, 5\mu_B, \text{Mn}^{2+} 3d^5, 5\mu_B, \text{and Zn}^{2+} 3d^{10}, 0\mu_B$

b) Mn^{2+} prefers the A sites even more than Fe^{3+} does, so unlike the other transition metal ferrites, Mn occupies A site and 2Fe^{3+} occupy B sites. However, this makes no difference to the moment per FU because Mn^{2+} and Fe^{3+} have the same moment. Net moment is $5\mu_B$ per FU.

c) As Zn replaces Mn, there is no change in iron B-site occupation but the reduction of the moment on the A sublattice, $\text{Mn}_{1-x} + \text{Zn}_x$, allows the net moment to increase linearly because a smaller A-site moment is subtracted from the 10 Bohr magnetons on the B sublattice. At some value of x , the weaker moment on the A sites will allow the antiferromagnetic interaction between the two moments on B sites to take precedence. Beyond this Zn concentration, the net moment decreases as the moment on the B sites decreases rapidly from 10 Bohr magnetons.

4.2 Substitution of Zn for Ni in Fe_2NiO_4 . Ni^{2+} has less tetrahedral (A) preference than Fe^{3+} so site distribution is as indicated in table. But Zn^{2+} has stronger A preference than Fe^{3+} so while it substitutes for Ni, it displaces Fe^{3+} from A sites to B sites.

	A	B
Fe_2NiO_4	Fe^{3+}	$\text{Fe}^{3+} \text{Ni}^{2+}$
$\text{Fe}_2\text{Ni}_{1-x}\text{Zn}_x\text{O}_4$	$(1-x)\text{Fe}^{3+} \quad x \text{Zn}^{2+}$	$(1+x)\text{Fe}^{3+} \quad (1-x)\text{Ni}^{2+}$
Moment	$-(1-x)5 - 0x$	$+(1+x)5 + (1-x)2$
	$\mu_m = [2 + 8x] \mu_B$	

This is the initial linear increase shown in Fig.4.15.

4.3 a) There are two Ni atoms per unit cell so $C = N_v \mu_o \mu m^2 / k_B \approx 0.48$. Hence, for $T_C = 630\text{K}$, $\lambda = T_C / C = 1300$.

b) Use $\chi = C / (T - T_C)$. For $T = 730$ and 930K , $\chi \approx 3.3 \times 10^{-3}$ and 1.1×10^{-3} , respectively. Thus, $C = 0.99$ and 0.11 respectively and $\lambda = 5730$ and 636 , respectively.