

Magnetic ordering in a Zn-substituted Co-Mn-Fe-O ferrite system

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Abstract : The structural and bulk magnetic properties of Zn-substituted $\text{Co}_{1-x}\text{Zn}_x\text{Mn}_0.5\text{FeO}_4$ ($x = 0.0 - 0.6$) ferrite system are studied using X-ray diffraction, magnetization and a.c. susceptibility measurements. The X-ray intensity calculations indicate that Mn^{4+} , Co^{2+} occupy only B-sites, Zn^{2+} have strong preference for A-site and Fe^{3+} ions distributed among A and B-sites. The magnetization measurements exhibits a significant canting on the B-site which is satisfactorily explained on the basis of the non-collinear spin model of uniform canting. The a.c. susceptibility indicates that system orders into a cluster spin glass state with the magnetic moment of the cluster randomly frozen.

Keywords : Ferrite, a.c. susceptibility, magnetization, canting angle

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1. Introduction

The appearance of various magnetic structure caused due to change in concentration of non-magnetic ions in different sub-lattices, make ferrites a very interesting material [1-4]. Among these, systems with spinel structure seem to be particularly attractive, as they allow a variety of magnetic disorders and frustration to be introduced. Recently, a tentative phase diagram has been proposed [1] to classify the different substituted ferrite compounds. In addition to these, the presence of Mn^{4+} , Co^{2+} and Fe^{3+} in the ferrite system, introduce additional factors *i.e.* uniaxial random anisotropy [5], which increases the possible magnetic structure and changes the above mentioned phase diagram [1].

A large number of investigators have studied Ti - substituted spinels in order to understand their magnetic properties. Brand *et al* [6] have found in the case of $\text{Mg}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ that on increasing dilution x , the collinear ferrimagnetic phase breaks down before reaching the ferrimagnetic percolation threshold and for higher concentration of Ti system approaches towards spin glass. Dormann *et al* [7] have also studied the magnetization measurements of Ti^{4+} - substituted lithium ferrite using different techniques and suggested the possibility of canted spin arrangement to explain the magnetization measurements.

In order to understand the influence of magnetic ion Mn^{4+} in place of nonmagnetic Ti^{4+} , we have carried out structural and magnetic measurements on Zn-substituted $\text{Co}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ system.

Our results on $\text{Co}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ system show that Mn^{4+} and Co^{2+} ions occupy B-sites while A-site is mainly occupied by Fe^{3+} ions. The magnetization results show collinear spin arrangement for $0 \leq x \leq 0.3$. The temperature dependent a.c. susceptibility measurements [$\chi_{ac}(T)$] results of $\text{Co}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ system display two peaks, one sharp near $T_N \sim 605$ K and another broad peak at much lower temperature $T_f \sim 450$ K. The $\chi_{ac}(T)$ behaviour observed in this system, can be explained using the magnetic phase diagram proposed for the disordered spinel system [8] and according to which the existence of two peaks up to $x < 0.5$ indicate that the system undergoes a para to unstable ferromagnetic transition (T_N) followed by cluster spin glass ordering (T_f). We have modified the ferromagnetic phase of $\text{Co}_{1.5}\text{Mn}_{0.5}\text{FeO}_4$ ($x = 0.5$) by substituting magnetic Co^{2+} (3mB) ions with non-magnetic Zn^{2+} ions with non-magnetic Zn^{2+} ions in the system. Thus, the magnetic ion concentration of the A sub-lattice reduces, which may lead to frustration in the sub system. In view of this, bulk magnetic properties of the $\text{Co}_{1.5-x}\text{Zn}_x\text{Mn}_{0.5}\text{FeO}_4$ system have been investigated for $x \leq 0.6$. Here we report the results of X-ray

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diffraction, magnetization and a.c. susceptibility measurements on the above spinel system.

2. Experimental

Seven samples of the spinel series $\text{Co}_{1.5-x}\text{Zn}_x\text{Mn}_{0.5}\text{FeO}_4$ with $x = 0.0$ to 0.6 were prepared by the usual double sintering ceramic process. The starting materials were analytical reagent grade oxides, Fe_2O_3 , ZnO , MnO_2 and CoO . These oxides were mixed in proper proportions and pre-sintered at 900°C for 12 hours. In the final sintering process, the material was held at 1100°C for 12 hours for complete ferritization and then slowly cooled at room temperature at the rate of $2^\circ\text{C}/\text{minute}$. The X-ray diffractograms were recorded using $\text{CuK}\alpha$ radiation on a Philips X-ray diffractometer (PW 1700). The diffraction pattern showed sharp lines corresponding to a single-phase spinel structure for all samples (Figure 1).

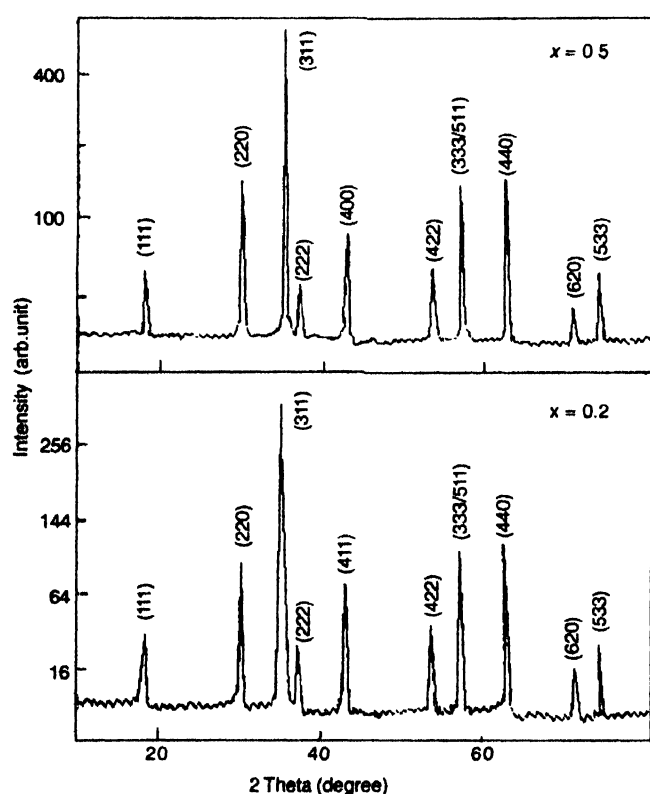


Figure 1. Typical X-ray diffraction pattern of Co-Mn-Fe-O ferrite.

Room temperature (300K) magnetization measurements were performed using high field hysteresis loop technique [9]. Low field a.c. susceptibility measurements were carried out using a double coil set up as described elsewhere [10] in the temperature range of 77 to 600 K. The applied field was 0.5 Oe.

3. Results and discussion

Figure 1 depicts typical X-ray diffraction patterns for $x = 0.2$ and $x = 0.5$. The lattice constant ' a ' (\AA) of the series $\text{Co}_{1.5-x}\text{Zn}_x\text{Mn}_{0.5}\text{FeO}_4$ plotted as a function of ' x ' is shown in Figure 2. It is observed from Figure 2, that the lattice constant ' a '

(\AA) increases with Zn content ' x '. The variation of lattice constant ' a ' (\AA) with Zn content ' x ' can be explained on the basis of difference in ionic radii of constituent ions. The increase in lattice constant ' a ' with ' x ' is due to the fact that the larger Zn^{2+} (0.74\AA) ions replace smaller Co^{2+} (0.71\AA) ions in the spinel

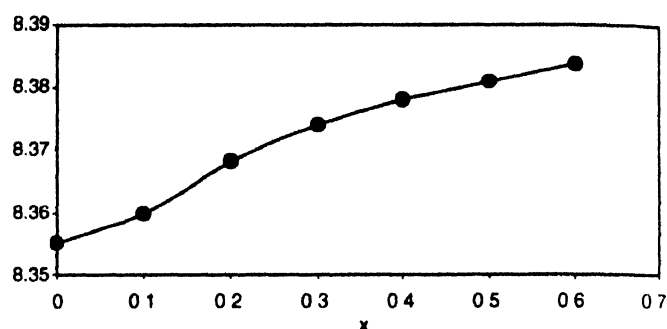


Figure 2. Variation of lattice constant with x .

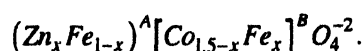
lattice. This behaviour is similar to the Zn^{2+} substituted Co-Ge [11], and Co-Ti [8] system, in which lattice constant ' a ' (\AA) increases with concentration ' x '. Comparing the site preference energies of the constituent ions [12] and from the earlier results [13], the cation distribution for $x = 0.0$ was found to be



In order to determine the cation distribution for the substituted system, the X-ray intensity calculations were made using the formula suggested by Burger [14]

$$I_{hkl} = |F_{hkl}|^2 \cdot P \cdot L_p,$$

where, F_{hkl} is the structure factor, P is the multiplicity factor and L_p is the Lorentz polarization factor. It is known [15] that the intensity ratio of planes $I(220)/I(400)$, $I(220)/I(440)$ and $I(400)/I(422)$ are considered to be sensitive to the cation distribution parameter (x); therefore, these ratios are used in estimating the cation distribution. As Zn^{2+} ions have strong preference for A-site, cation distribution for the present system can be written as



Finally, the cation distribution for these compounds is estimated from magnetization (300 K) and X-ray intensity calculations. Table 1 gives the results of X-ray intensity calculation for the best-fit cation distribution for $x = 0.1, 0.2, 0.3,$ and 0.5 samples.

The saturation magnetization (σ_s) and the magneton number (n_B) (the saturation magnetization per formula unit in Bohr magneton) at 300 K obtained from magnetization data for all the samples up to $x = 0.4$ are summarized in Table 2. Figure 3 shows the variation of n_B with Zn-content (x). It is evident from Figure 3 that n_B increases upto $x < 0.3$ and then decreases. From eq. (2), it is clear that as Zn replaces the magnetic ions from A-site, the

Table 1. Comparison of X-ray intensity ratios for $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$

Content x	A-site cation	B-site cation	$I_{(220)}/I_{(440)}$		$I_{(220)}/I_{(400)}$		$I_{(400)}/I_{(422)}$	
			Obs	Cal	Obs.	Cal.	Obs	Cal
0.1	$(Zn^{2+}_{0.1}Fe^{3+}_{0.9})$	$(Co^{2+}_{1.4}Mn^{4+}_{0.5}Fe_{0.1})$	0.660	0.631	1.260	1.164	1.920	2.500
0.2	$(Zn^{2+}_{0.2}Fe^{3+}_{0.8})$	$(Co^{2+}_{1.3}Mn^{4+}_{0.5}Fe_{0.2})$	0.800	0.602	1.190	1.400	2.460	2.050
0.3	$(Zn^{2+}_{0.3}Fe^{3+}_{0.7})$	$(Co^{2+}_{1.2}Mn^{4+}_{0.5}Fe_{0.3})$	0.730	0.661	2.000	1.340	1.720	2.150
0.5	$(Zn^{2+}_{0.5}Fe^{3+}_{0.5})$	$(Co^{2+}_{1.0}Mn^{4+}_{0.5}Fe_{0.5})$	1.050	0.691	2.150	1.700	1.430	1.670

Table 2. Saturation magnetization (σ_s), magneton number (n_B), Yafet-Kittel angle (α_{YK}) and Curie temperature (T_c) for the $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$ system [17].

The exchange constants used in calculating α_{YK} are

$$J_\alpha = -15 \text{ K}, J_\beta = -5 \text{ K}, J_\gamma = -14 \text{ K}, J_\delta = -9 \text{ K}, J_\epsilon = -4 \text{ K},$$

$$J_\xi = -7.5 \text{ K}, J_\sigma = -7.5 \text{ K}, J_\psi = -12 \text{ K}, J_\mu = -4.5 \text{ K}$$

Zn-Content	σ_s (emu/gm) 300 K	n_B (μ_B)	α_{YK} (Obs) In degrees	α_{YK} (Cal)	T_c (K) ($\pm 5K$)
0.0	33.60	1.41	-	-	458
0.1	34.07	1.44	-	-	428
0.2	40.06	1.70	34.30	41.46	403
0.3	34.25	1.45	45.80	42.09	383
0.4	22.89	0.97	57.05	59.97	360
0.5	-	-	-	-	318
0.6	-	-	-	-	300

magnitude of the A-site moment decreases but the difference between A-site and B-site moments increases; as a result, the n_B increases. Therefore, the initial increase in n_B with x can be explained with eq. (2); but the decrease in n_B after $x > 0.3$ indicates the possibility of a non-collinear spin structure in the system. On account of the similarities between the present system and the other Zn-substituted system [11], it is reasonable to assume Yafet-Kittel (Y-K) [16] type magnetic ordering in the present system.

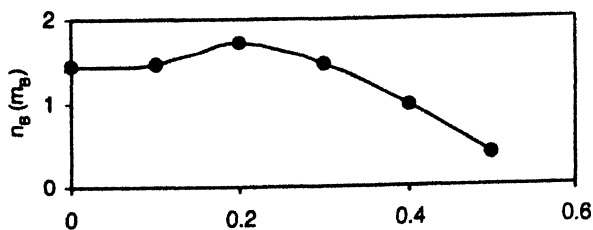


Figure 3. Variation of a. c. susceptibility with x .

Adopting the procedure of Satyamurthy *et al* [2], the condition for the existence of a Y-K angle can be found for

$x \geq 0.2$. Using this model [2], the part of interaction energy 's' involving Y-K angle may be written as

$$E(YK) = [15(1-x)(1.5-x)\alpha + 25(1-x)x\beta + 20(1-x)(0.5)\gamma] \times \cos(\alpha_{YK})^{-1/4} [9(1.5-x)^2\delta + 30(1-x)(1.5-x)\epsilon + 25x^2\xi + 40x(0.5)\sigma + 24(1.5-x)(0.5)\psi - 16(0.5)2\mu] \cos(2\alpha_{YK}),$$

where $\alpha, \beta, \gamma, \delta, \epsilon, \xi, \sigma, \psi$ and μ are the molecular field constants related to the following sets of interactions:

$$\alpha : A(Fe^{3+}) - B_1(Co^{2+}),$$

$$\beta : A(Fe^{3+}) - B_1(Fe^{3+}),$$

$$\gamma : A(Fe^{3+}) - B_1(Mn^{4+}),$$

$$\delta : B_1(Fe^{3+}) - B_2(Co^{2+}),$$

$$\epsilon : B_1(Fe^{3+}) - B_2(Co^{2+}),$$

$$\xi : B_1(Fe^{3+}) - B_2(Fe^{3+}),$$

$$\sigma : B_1(Mn^{4+}) - B_2(Fe^{3+}),$$

$$\psi : B_1(Co^{2+}) - B_2(Mn^{4+}),$$

$$\mu : B_1(Mn^{4+}) - B_2(Mn^{4+}).$$

The energy is minimum for either

(a) $\sin(\alpha_{YK}) = 0.0$ which corresponding to Neel's configuration,

or

$$(b) \cos(\alpha_{YK}) = \frac{[15(1-x)(1.5-x)\alpha + 25(1-x)x\beta + 20(1-x)(0.5)\gamma]}{[9(1.5-x)^2\delta + 30(1-x)(1.5-x)\epsilon + 25x^2\xi + 40x(0.5)\sigma + 24(1.5-x)(0.5)\psi - 16(0.5)2\mu]} \quad (1)$$

which corresponds to the situation where the Y-K angle is feasible. The molecular constants can be obtained from the variation of saturation magnetization with Zn content. The

experimental values of α_{YK} can be obtained from the observed variation of n_B with x using the relation [16]

$$n_B = M_B \cos(\alpha_{YK}) - M_A \quad (2)$$

where M_B and M_A are the magnetic moments of B-sites and A-sites respectively. Table 2 contains the values of α_{YK} obtained using eqs. (3) and (4). The experimental values of α_{YK} agree nearly well with those obtained theoretically. This suggests that in this system, AB and BB super-exchange interactions are complete in strength.

Figure 4 shows the plots of thermal variation of a.c. susceptibility (χ_T/χ_{RT}), for all the samples, which exhibit normal ferrimagnetic behaviour. It can be seen from Figure 4 that all the samples, only one peak is observed and on increasing Zn concentration x , the peak shifts towards lower temperature. The intensity of this peak decreases with increase in Zn concentration x .

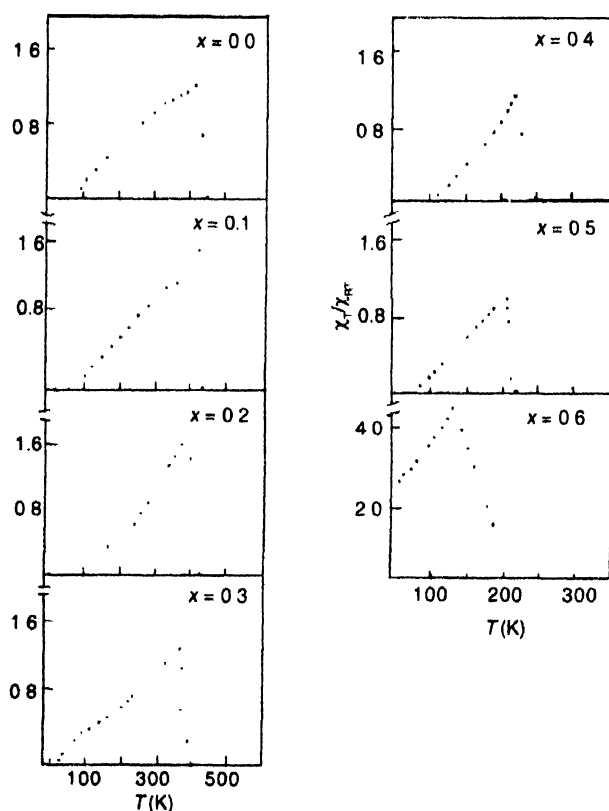


Figure 4. Thermal variation of a. c. susceptibility.

The values of Curie temperature (T_c) deduced from χ_T/χ_{RT} plots are summarized in Table 2. According to Neel's model, A-B interaction is most dominant in ferrites; therefore, Curie temperature of the ferrites are determined from the overall strength of A-B interaction. The strength of A-B interaction is a function of the number of $\text{FeA}^+ - \text{O}^{2-} - \text{FeB}^{3+}$ linkages, which in turn, depends upon the number of Fe^{3+} ions in the

formula unit and their distribution amongst tetrahedral (A) and octahedral [B] sites. In the present system, Co^{2+} ions ($3\mu_B$) are replaced by Zn^{2+} ions ($0\mu_B$). This results in decreasing the A-B interaction which lead to decrease in Curie temperature (T_c)

4. Conclusion

In conclusion, our X-ray diffraction, magnetization and a.c. susceptibility measurement on the disordered spinel system $\text{Co}_{1.5-x}\text{Zn}_x\text{Mn}_{0.5}\text{FeO}_4$ show that

- (i) Mn^{4+} and Co^{2+} ions occupy B-site only, Zn^{2+} have strong A-site preference and Fe^{3+} ions distributed among A- and B-sites.
- (ii) Magnetization results exhibits a significant canting on the B-site which is satisfactorily explained on the basis of uniform canting model.
- (iii) a.c. susceptibility data indicates that T_c decreases with increasing concentration x .

References

- [1] J L Dormann and M Nognes *J Phys. Condens. Matter* **2** 1223 (1990)
- [2] N S Satyamurthy, M G Natera, S I Yousof, R J Begum and C M Srivastava *Phys. Rev.* **181** 4412 (1969)
- [3] D Fiorani, S Viticoli, J L Dormann, J L Tholence and A P Murani *Phys. Rev.* **B30** 2776 (1984)
- [4] K Murlidharan, J K Srivastava, V R Maratna and R Vijayraghavan *J. Phys.* **C18** 5897 (1985)
- [5] J B Goodenough *Magnetism of the Chemical Bond* (New York Wiley) (1963)
- [6] R A Brand, Georges H Gilbert, H Hubsch and J A Hellel *J Phys* **F15** 1887 (1985)
- [7] J L Dormann, M El Harfaoui, M Nognes and J Love *J Phys* **C20** L161 (1987)
- [8] R V Upadhyaya, R B Jotania and R G Kulkarni *Physica* **B190** 183 (1993)
- [9] C Radhakrishna Murthy, S D Likhate and S Sastry *Phil. Mag* **23** 803 (1971)
- [10] C Radhakrishna Murthy, S D Likhate and P W Sahastrabudhic *Proc. Indian. Acad. Sci.* **87** A245 (1978)
- [11] R B Jotania, R V Upadhyaya and R G Kulkarni *IEEE Trans Magn.* **28** 1889 (1992)
- [12] D Fiorani and S Viticoli *Solid State Commun.* **29** 1363 (1978)
- [13] D R Shengule, *Ph. D. Thesis* (Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India) (1999)
- [14] M J Burger *J. Crystal Structure Analysis* (New York : John Wiley) (1960)
- [15] H Ohnishi and T Teranijhi *J. Phys. Soc. Jpn.* **16** 36 (1961)
- [16] Y Yafat and C Kittel *Phys. Rev.* **87** 290 (1952)
- [17] F Scholl and K Binder *Z. Phys.* **B39** 239 (1980)
- [18] C M Shrivastava, S N Shringri, R G Shrivastava and N G Nanandikar *Phys. Rev.* **B14** 2032 (1976)