

HIGH SATURATION MAGNETIZATION AND SPIN CANTING IN COBALT-CADMIUM FERRITES SYNTHESIZED BY SOL-GEL METHOD**T.R.K.Pydiraju¹, P.Apparao², K.Srinivasrao³, M.ChaitanyaVarma⁴ and K.H.Rao⁵**^{1,2}*Dadi Institute of Engineering & Technology, Anakapalle, Visakhapatnam, India*³*PBN Degree College, Ponnuru, India*⁴*GITAM University, Visakhapatnam, India*⁵*RGUKT, Nuzuvidu, India.*

Abstract- A high value of room temperature specific saturation magnetization, 104.54 emu/gm has been obtained in $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ($x=0.07$) synthesized by sol-gel method. A reasonable cation distribution has been proposed using experimental data collected from Vibration Sample Magnetometer, X-ray diffraction. VSM and Mossbauer measurements at room temperature show the existence of A-B exchange interaction in all the samples.

I. INTRODUCTION

Ferrites have the joint properties of magnetic materials and insulators [1]. The important structural, electrical and magnetic properties of these spinels responsible for their applications in various fields are found to depend on the magnetic interaction and the distribution of cations among the two sublattices, tetrahedral (a) and octahedral (b) sites. Among various spinel ferrites, cobalt ferrite based composites have received interest because of their high magnetostriction, high sensitivity of magnetic induction to applied stress, chemical stability and low-cost [2-6]. Such properties make these materials more attractive for use in magneto-elastic sensors, actuators and more recently composite multiferroics. CoFe_2O_4 possesses a partially inverse spinel structure [7] and the degree of inversion depends upon heat treatment, synthesis method and substitution of metal ions [8]. The partial replacement of cobalt with diamagnetic ions (e.g. Zinc or cadmium) may weaken the exchange interactions between A- and B-sites and result in decrease of the magnetic hyperfine field as well as the Curie temperature [9].

Very few studies have been reported on mixed Co-Cd systems. Non-collinear spin structure has been observed by Ghani and Sattar [10] in $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$) from high field magnetization study in the temperature range 4.2 to 300K. For low concentration of Cd^{2+} ($x \leq 0.25$) Neel's two-sublattice model was observed by Vasambekar et al. [8], where for higher concentrations canted spin model existed for which they calculated Yafet-Kittel (Y-K) angles. Nikumbh et al. [11] prepared $\text{Cd}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1) by the tartrate coprecipitation technique and attempted to find the effect of cadmium ferrite spinel formation and the role of cobalt content on its structural, magnetic and electrical properties. However, there is no reported work in the literature on Co-Cd ferrites synthesized by the sol-gel method of mixed metal nitrates with PVA as chelating agent. So in the present study Co-Cd ferrites have been synthesized through the sol-gel method [12] using PVA as chelating agent and aimed to understand the effect of cadmium ions on structural and magnetic properties of cobalt ferrite spinel by X-ray diffraction (XRD), VSM and Mossbauer measurements at room temperature.

II. RESULTS AND DISCUSSION**XRD Studies**

From X-ray diffraction patterns of all the compositions shown in Fig. 1, it is clearly observed

that with increase in cadmium concentration, splitting of peaks into two as well as widening happens. This may be due to volatilization of cadmium at the selected sintering temperatures and occurrence of defect phase in the lattice.

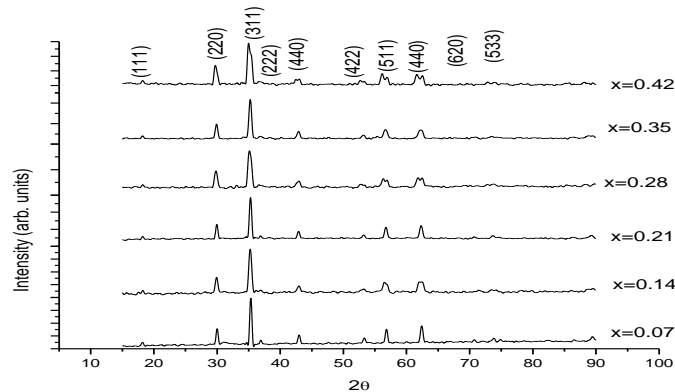


Figure 1: variation of intensity with 2θ for all samples with increasing cadmium content.

The experimentally observed d - spacing values and relative intensities were compared with those reported in literature [13]. The lattice parameter for each composition was then calculated using Nelson- Riley Function [14] and shown in TABLE:1. The variation of lattice parameter “a” as a function of cadmium addition X in $Co_{1-x}Cd_xFe_2O_4$ is represented in Fig. 2. Wolska *et al.* [15,16] showed that the intensity ratios of (220) and (422) of X-ray peaks depend on the cations present at A-sites and (222) peak intensity depends on cations present at B-site. Since these ratios are very sensitive to presence of various cations in the present system they give valuable information on distribution of Cd^{2+} ions in the lattice. Figure.3 shows that the intensity ratios linearly increase as Cd^{2+} ions concentration increases.

III. CATION DISTRIBUTION

The relative concentration of Co^{2+} and Cd^{2+} in the ferrite structure not only influences the lattice constant but also causes deviation in cation distribution. The resulting cation distribution in the present study can be due to two competing processes: (a) the strong chemical affinity of certain cations to specific sites viz. A- or B-sites and (b) the metastable cation distribution. The case becomes complex when the stoichiometric changes [17] and this may arise when ions with larger ionic radii replace ions having smaller ionic as given by cation distribution.

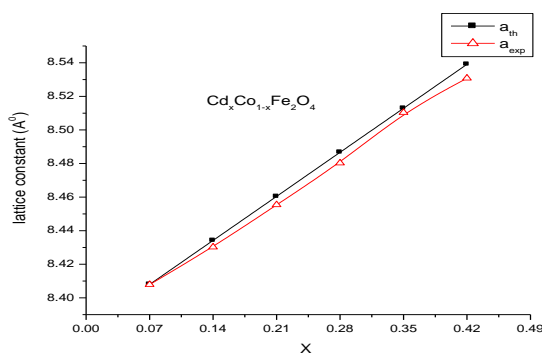


Figure 2: Variation of lattice constant with Cd. Conc.

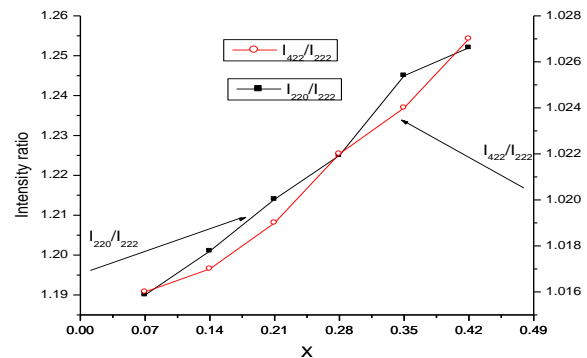


Figure 3: Variation of intensity ratios at A-site & B-site with increasing Cd conc.(x)

The above cation distribution formula is assumed in predicting lattice parameters and explaining the variations in magnetization with increasing cadmium content. Lattice constant has been calculated by varying the distribution of cations at A and B–sites using radius of tetrahedral and octahedral sites as given by formulae.

$$a_{th} = \frac{8}{3\sqrt{3}} [(r_A + 1.32) + \sqrt{3}(r_B + 1.32)]$$

A-site ionic radius has been observed to increase whereas that of B-site reduced with increasing cadmium content. Based on the earlier reports we assume that substituting cadmium ions in place of cobalt ions transfers Fe³⁺ ions from the tetrahedral site to octahedral site. Since Cd²⁺ ions have larger ionic radius compared to Fe³⁺ ions, and Cd²⁺ ions occupy A-sites, this leads to increase in A-site radius as well as lattice constant.

Even though there is an agreement in lattice constants and bond lengths between experimental and those, calculated based on predicted cation distribution but still it is observed in XRD pattern that one of the peak values of the peaks are becoming into two peaks as their diffraction angles are very closely spaced. But the effect of splitting of peaks, actually shows the presence of defect structure or other phases which can be clearly observed using Mossbauer spectra.

TABLE: 1—Variation of experimental (exp) and theoretical (th) lattice constant, bond-length, lattice edge ionic radius and X-ray Intensities ratio with increasing Cd conc.

Cd Conc	Lattice Constant a(A ⁰)		Bond length at A-site d _{AX} (A ⁰)		Bond length at B-site d _{BX} (A ⁰)		Lattice Edge at A-site (A ⁰)		Lattice Edge at B-site (A ⁰)		Ionic radius at B-site (A ⁰)		X-ray Intensities ratio	
	exp	Th	exp	th	exp	th	exp	th	exp	th	r _A	r _B	A-site	B-site
0.07	8.408	8.408	1.820	1.820	2.102	2.102	3.641	3.641	2.973	2.973	0.683	0.677	1.190	1.016
0.14	8.430	8.434	1.825	1.826	2.108	2.109	3.650	3.652	2.981	2.982	0.706	0.673	1.201	1.017
0.21	8.455	8.460	1.831	1.832	2.114	2.115	3.661	3.663	2.989	2.991	0.729	0.670	1.214	1.019
0.28	8.480	8.487	1.836	1.837	2.120	2.122	3.672	3.675	2.998	3.000	0.752	0.666	1.225	1.022
0.35	8.510	8.513	1.843	1.843	2.128	2.128	3.685	3.686	3.009	3.010	0.776	0.663	1.245	1.024
0.42	8.531	8.539	1.847	1.849	2.133	2.135	3.694	3.698	3.016	3.019	0.799	0.659	1.252	1.027

Magnetic Studies

Magnetic hysteresis curves for the system Co_{1-x}Cd_xFe₂O₄ of were obtained by Vibrating sample magnetometer at a field intensity of 5T. The magnetic parameters like the coercive field H_C, saturation magnetization M_S, ratio of remanence to saturation magnetization M_R/M_S, magnetic moment n_B and Y-K angles α_{YK} values are listed in TABLE.2. Magnetic moment n_B, H_C, M_S, and M_R/M_S have been observed to decrease with increasing Cd²⁺ content as shown in the Fig.4. and these variations can be understood from the strong preference of Cd²⁺ and Co²⁺ ions to A and B sites respectively [11].

Cation distribution has been proposed as (Cd_xCo_yFe_{1-x-y})_A [Co_{1-x-y} Fe_{1+x+y}]_B and magnetic moment can be calculated using [3(1-x-y)+5(1+x+y)]-[3y+5(1-x-y)] by considering the magnetic moment of Co²⁺ ions as 3μ_B and that of Fe³⁺ ions as 5μ_B. The substitution of diamagnetic Cd²⁺ ions at A-

site may cause some Fe⁺³ ions to migrate to B-sites. Due to dilution of A-sites by Cd²⁺ ions, magnetic moment at this site decreases and one may expect an increase in net magnetic moment ($n_{net} = n_B - n_A$). With the substitution of cadmium, A-site ionic radius and lattice edges at A, B-sites have been observed to increase which leads to decrease in net A-B indirect exchange interaction and this gives rise to B-B interaction which makes B spins no longer parallel to each other[10] and so net magnetic moment decreases. This behavior has been observed by many workers in different ferrite systems [3,4,5,8] and such a variation in magnetic moment is attributed to the presence of super-magnetic clusters of paramagnetic centers [5], preparation techniques employed. Since in the present system we observed a decrease net magnetic moment, we expect the presence of canting between spins of A and B sites and this can be estimated using the formula α_{YK} for the proposed cation distribution [20-22].

$$\alpha_{YK} = \cos^{-1} \left[\frac{n_B + 3y + 5(1-x-y)}{3(1-x-y) + 5(1+x+y)} \right]$$

The major factors which caused the decrease in magnetization with cadmium concentration in the present system are decrease in magnetic moment at A-site, increase in bond lengths and canting between spins of A and B-sites. The decrease in coercivity in the present samples has been due to decrease in cobalt content which has large magnetic anisotropy, whereas the substituting ion Cd²⁺ has zero magnetic anisotropy.

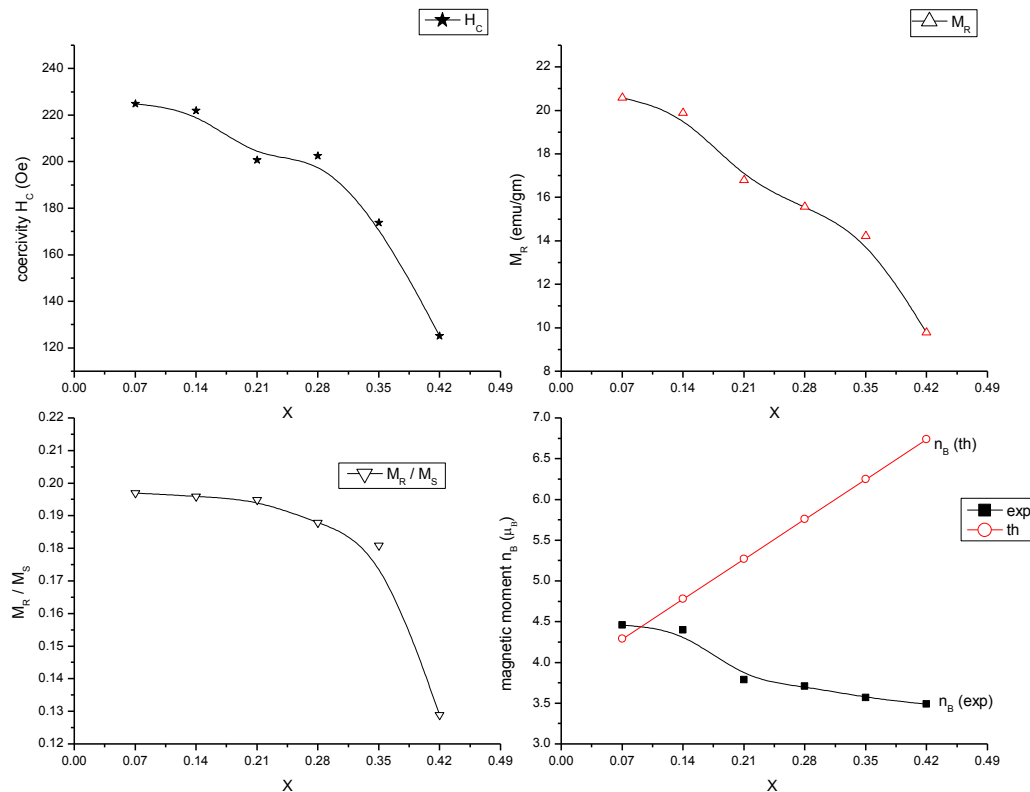


Figure 4: Variation of H_C, M_R, M_R/M_S, magnetic moment(n_B) experimental and theoretical with Cd. Conc. (x).

The magnetic anisotropy contribution due to Fe³⁺ ions is small both at A and B-sites. The decrease in coercivity can also be attributed to increase in grain size which allows the presence of multi-domain behavior [23] and it is also confirmed by considerable decrease (TABLE.2) in the ratio of remanence to saturation magnetization (M_R/M_S) at room temperature.

The most important observation from the above table is the best agreement in experimental and calculated magnetic moments/saturation magnetization with varying cadmium content. This shows that the sol-gel method employed in the present study played an important role not only in controlling the particle size and shape but also in the variation of cation distribution at A and B-sites in the lattice.

IV. MOSSBAUER STUDIES

The representative Mossbauer spectra for Co–Cd ferrites at room temperature are shown in Fig.5. The spectra were fitted with Lorentzian-shaped lines by the method of least squares. The observed increase in the broadness of the spectra with increasing cadmium content is due to the increase in bond lengths of both tetrahedral and octahedral sites as given in TABLE 1. This increase in bond lengths decreases the exchange interactions between various lattice sites and the same will be exhibited in Mossbauer spectra. Such a variation in bond lengths along with dilution of A-site spins with increase in Cd²⁺ ions makes the analysis of Mossbauer spectra more complex.

TABLE 2—Mol.Wt, magnetic measurement values obtained from VSM & proposed cation distribution for various samples with Cd conc.

Cd Conc. X	Proposed cation distribution for Co _{1-x} Cd _x Fe ₂ O ₄	Mol. Wt. of the sample (gm)	Experimental values obtained from VSM						Theoretical values obtained from proposed cation distribution		
			M _S (emu/g)	M _R (emu/g)	H _c (Oe)	M _R /M _S	nB(μB)	MS (emu/g)	nB(μB)	αYK	
0.07	(Cd _{0.07} Co _{0.2} Fe _{0.73}) [Co _{0.73} Fe _{0.73}]	238.37	104.54	20.58	224.89	0.197	4.46	100.52	4.29	11.39	
0.14	(Cd _{0.14} Co _{0.2} Fe _{0.66}) [Co _{0.66} Fe _{0.66}]	242.11	101.39	19.89	221.93	0.196	4.40	110.27	4.78	17.12	
0.21	(Cd _{0.21} Co _{0.2} Fe _{0.59}) [Co _{0.59} Fe _{0.59}]	245.85	86.16	16.80	200.68	0.195	3.79	119.72	5.27	33.64	
0.28	(Cd _{0.28} Co _{0.2} Fe _{0.52}) [Co _{0.52} Fe _{0.52}]	249.60	82.91	15.56	202.50	0.188	3.71	128.89	5.76	39.59	
0.35	(Cd _{0.35} Co _{0.2} Fe _{0.45}) [Co _{0.45} Fe _{0.45}]	253.34	78.69	14.23	173.82	0.181	3.57	137.78	6.25	45.14	
0.42	(Cd _{0.42} Co _{0.2} Fe _{0.38}) [Co _{0.38} Fe _{0.38}]	257.08	75.78	9.77	125.15	0.129	3.49	146.42	6.74	49.60	

The spectra showed that the lines of the B-site patterns are broadened and appear to be composite, so, B-site pattern has been fitted into two components to obtain the B-site sub patterns. The Mossbauer spectral data, including isomer shift (IS), quadrupole splitting (QS), line width (I) and hyperfine magnetic field (H_{hf}), are summarized in TABLE 3. The isomer shift (IS) is a physical parameter for probing the valence state of the Mossbauer atom.

The Fe⁺² ions have lesser s-electron density at the nucleus due to the greater screening of the d-electron. This produces a positive isomer shift in Fe⁺² ions greater than in Fe⁺³. The reported isomer shift values for Fe⁺² and Fe⁺³ ions [2,10,11] lies in the range 0.6 – 1.7 mm/s and 0.1 - 0.5mm/s respectively. This difference in isomer shift can also attribute to the difference in Fe⁺³ – O⁻² distance for the two sites A and B. By comparing our results in TABLE.3, it is known that the IS value indicates that the resolved sextets in studied samples are due to Fe⁺³ ions only. The observed decrease in hyperfine fields obtained

at different sites with increasing Cd^{+2} ions content in $\text{Cd}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ demonstrate a reduction in ferrimagnetic behavior.

It is also apparent from the TABLE.3 that compounds with higher cadmium content show high values of quadrupole splitting, while compounds with $x \leq 0.21$ have practically very small or negligible quadrupole splitting, which suggests the coexistence of chemical disorder and overall cubic symmetry causes no net quadrupole splitting. CoFe_2O_4 is a partially inverse spinel with Co^{+2} ions (80%) on the octahedral site and it is well known that Cd^{+2} ions have a strong tetrahedral site preference [11], Cd^{+2} will cause some migration of Fe^{+3} ions from tetrahedral to octahedral sites, so the cation distribution formula can be used to describe the system is $(\text{Cd}_x\text{Co}_y\text{Fe}_{1-x-y})[\text{Co}_{1-x-y}\text{Fe}_{1+x+y}]\text{O}_4$, where X denotes the cadmium content and Y denotes the normalcy of cobalt ions.

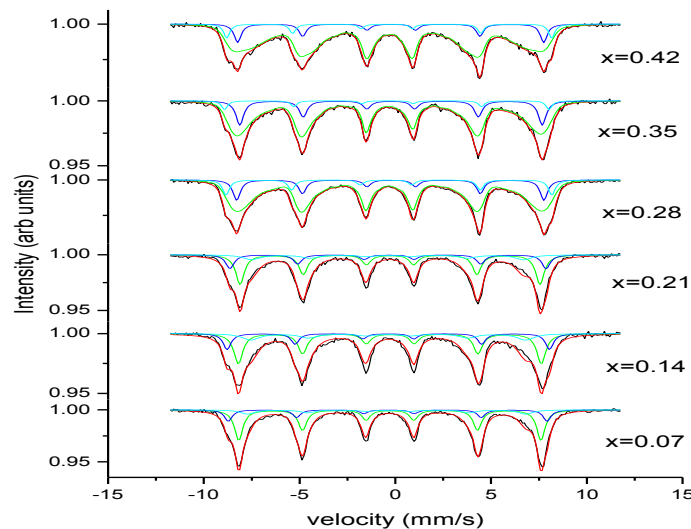


Figure 5: Mossbauer spectra for Co–Cd ferrite samples at room temperature.

The cation distributions estimated from Mossbauer experiments in table:2 shows that Cd^{+2} at A-site, forces the Fe^{+3} ions into B-site with increasing of the Cd^{+2} content. Therefore, because of the radius of $\text{Cd}^{+2}(0.97\text{Å})$ is larger than that $\text{Co}^{+2}(0.74\text{Å})$ and $\text{Fe}^{+3}(0.64\text{Å})$ [24], the radius of tetrahedral becomes larger and that of the octahedral slightly changed with the content

TABLE.3—Isomer shift(IS), Quadrupole splitting(QS), Hyperfine field (H_{hf}), Line width (Γ) for various samples with Cd conc.

x	IS (mm/s)			QS (mm/s)			H_{hf} (T)			Line width (Γ)			Fractional Area		
	A-site	B ₁ -site	B ₂ -site	A-site	B ₁ -site	B ₂ -site	A-site	B ₁ -site	B ₂ -site	A-site	B ₁ -site	B ₂ -site	A-site	B ₁ -site	B ₂ -site
0.07	0.28	0.36	0.42	0.01	0.06	0.07	48.94	51.63	45.08	0.52	0.49	0.91	57.5	18.8	23.7
0.14	0.28	0.36	0.38	0.01	-0.01	0.01	49.05	52.19	44.52	0.57	0.51	1.11	45.2	18.7	36.1
0.21	0.28	0.35	0.38	0.01	-0.06	-0.05	48.57	51.19	44.02	0.55	0.52	1.08	48.3	20.8	30.9
0.28	0.31	0.24	0.41	0.02	-0.06	0.16	43.7	49.75	52.77	0.45	0.46	0.43	74.5	15.1	10.4
0.35	0.34	0.23	0.41	0.02	0.01	-0.05	44.3	48.98	52.54	0.45	0.49	0.36	76.1	18.9	5.0
0.42	0.34	0.23	0.39	0.02	-0.03	0.13	40.7	49.56	52.63	0.45	0.44	0.39	80.5	11.6	7.9

V. CONCLUSIONS

The present systems showed a definite hysteresis loop. A high value of saturation magnetization (104.54emu/gm) is observed for $\text{Cd}_{0.07}\text{Co}_{0.93}\text{Fe}_2\text{O}_4$. The coercive force, saturation magnetization and the ratio of remanance to saturation magnetization decrease as cadmium content increases. Increase in lattice constant and dilution of A-site magnetic moment has been the main cause for the observed decrease in saturation magnetization and canted spin structure.

VI. ACKNOWLEDGEMENTS

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