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Study of canted spin structure in Cu–Cd ferrites*

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The variation of magnetization with cadmium concentration of the $Cd_xCu_{1-x}Fe_2O_4$ system has been obtained at a constant magnetic field of $5.57 \times 10^5 A m^{-1}$ for $x = 0.0$ to 0.8 at room temperature (300 K). The observations indicate the existence of a Yafet–Kittel (YK) type of magnetic ordering in the mixed ferrites. A molecular field analysis of the YK spin ordering using a three-sublattice model is shown to explain the experimental data satisfactorily.

1. Introduction

Most of the zinc substituted mixed ferrites like Ni–Zn [1], Fe–Zn [2] and Cu–Zn [3] show canted spin arrangement on the octahedral or B site. The canting of the spins gives rise to Yafet–Kittel angles (YK), which suggests that A–B and B–B superexchange interactions are comparable in strength.

As zinc and cadmium are both divalent, it would be interesting to investigate similar effects in cadmium-substituted mixed ferrites like Cu–Cd and Ni–Cd. Practically no information about the magnetic properties of the $Cd_xCu_{1-x}Fe_2O_4$ ferrite system exists in the literature, except for our recent Mössbauer study [4]. Mössbauer spectra for $x = 0.0$ to 0.6 exhibit well defined Zeeman patterns. A ferromagnetic relaxation is observed for $x = 0.7$ and for $x \geqslant 0.8$ it shows paramagnetic doublets. There is a striking resemblance between the observed Mössbauer spectra of the cadmium-substituted $CuFe_2O_4$ [4] and those of zinc-substituted $CuFe_2O_4$ [3]. Both Zn^{2+} and Cd^{2+} ions are nonmagnetic and they occupy tetrahedral sites when substituted in $CuFe_2O_4$. Furthermore, the general nature of the Mössbauer spectra of $Cd_xCu_{1-x}Fe_2O_4$ and $Zn_xCu_{1-x}Fe_2O_4$ as a function of x are found to be nearly the same. It is known that the $Zn_xCu_{1-x}Fe_2O_4$ system shows a canted configuration of spins for $x < 0.5$. Hence we think that the canted spin arrangement may be present in $Cd_xCu_{1-x}Fe_2O_4$ also for $x < 0.5$, mainly because of the above mentioned similarities between the two systems.

The present paper reports the magnetization measurements of $Cd_xCu_{1-x}Fe_2O_4$ ferrite system which were undertaken primarily to study the variation of the saturation magnetization with cadmium concentration and to gain information about the YK angles in the system. The variation of the magneton number, n_B, with cadmium concentration in this system is similar in nature to that of zinc-substituted ferrite systems like Ni–Zn [1], Fe–Zn [2], and Cu–Zn [3]. A molecular field analysis of the YK spin ordering using the three-sublattice model is shown to explain the experimental data satisfactorily.

2. Experimental details

Eleven samples with $x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0, were prepared by the ceramic method from analytical reagent grade Fe_2O_3 (Robert and Johnson), CuO (BDH) and CdO (USSR). The oxides were mixed in the desired proportions, fired at 1100° C for 50 h and slowly cooled to room temperature. All the samples were found to be single-phase spinel by X-ray powder diffractometry. The lattice constants were determined with Cu$K\alpha$ radiation and are presented in Table I.

The variation of magnetization with cadmium-

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TABLE I Results of X-ray analysis for $Cd_xCu_{1-x}Fe_2O_4$ ferrites

X	Lattice constant (nm)
0.0	0.8220 ± 0.0002
0.2	0.8289 ± 0.0002
0.4	0.8369 ± 0.0002
0.6	0.8369 ± 0.0002
0.8	0.8508 ± 0.0002
1.0	0.8598 ± 0.0002

concentration of the Cu–Cd ferrite system has been measured at a constant magnetic field of $5.57 \times 10^5 \mathrm{A\,m^{-1}}$ at room temperature (300 K). The magnetization method used here depends on the well known method of Weiss and Forres. The values of the magnetization per kg at 300 K are given in Table II.

3. Results and discussion

3.1. Lattice constant

The lattice constant increases linearly from $CuFe_2O_4$ to $CdFe_2O_4$. The increase in lattice constant with x is similar in nature to that of Ni–Zn [1] and Cu–Zn [3] systems, and is due to the larger ionic crystal radius of Cd^{2+} (0.097 nm) which, when substituted for the divalent metal ion in the lattice, replaces the smaller Fe^{3+} ion (0.060 nm) in the A site. No measurements of lattice constants of Cu–Cd ferrites at different values of cadmium content and have been reported previously.

3.2. Magnetization

The magneton number, i.e. the saturation magnetization per formula unit in Bohr magnetons, n_B, at room temperature (300 K), initially increases as x is increased.

A similar variation of n_B with x has been observed also [5] in zinc-substituted ferrites like Ni–Zn, Co–Zn and Mn–Zn. This variation in Ni–Zn ferrite was earlier thought to arise due to the presence of superparamagnetic clusters or paramagnetic centres formed due to insufficient magnetic linkages. The neutron diffraction measurements of Satyamurthy *et al.* [6] and low temperature Mössbauer studies of Leung *et al.* [7] do not support this proposal. The recent Mössbauer studies of Fe–Zn ferrite by Srivastava *et al.* [8] and Cu–Zn ferrite by Patil and Kulkarni [9] have also ruled out the possibility of the existence of paramagnetic clusters.

TABLE II Results of magnetization measurement for $Cd_xCu_{1-x}Fe_2O_4$

X	Magnetization	
	σ ($\mathrm{Am^{-1}}$) at 300 K	n_B (Bohr magneton)
0.0	27.57	1.18
0.1	40.09	1.75
0.2	44.48	1.98
0.3	47.98	2.18
0.4	51.35	2.33
0.5	53.19	2.51
0.6	52.19	2.51
0.7	29.92	1.46
0.8	03.16	0.16

It is now believed that the change in magnetization on zinc substitution occurs due to the presence of Yafet–Kittel angles in the spin system on B sites. This was proposed by Satyamurthy *et al.* [6] on the basis of their neutron diffraction studies of Ni–Zn ferrites and later confirmed by a number of other workers [1, 7]. By making a similar assumption, Kulkarni and Patil [3] and Srivastava *et al.* [2] have found the existence of Yafet–Kittel angles in Cu–Zn and Fe–Zn ferrites, respectively. On account of similarities between Cu–Zn and Cu–Cd systems, it is reasonable to assume that Yafet–Kittel angles are also present in the latter system.

An indirect check for the presence of a canted spin structure follows from the apparent proportionality between average nuclear hyperfine field $|H|$ and the average sublattice magnetization. It can be shown that

$$\mu(x) = \frac{|H_B(x)|}{|H_B(0)|}\Big[(1+x)\mu(\mathrm{Fe}^{3+}) + (1-x)\mu(\mathrm{Cu}^{2+})\Big] - \frac{|H_A(x)|}{|H_A(0)|}\,[(1-x)\mu(\mathrm{Fe}^{3+})] \tag{1}$$

where $\mu(x)$ is the magnetic moment per formula unit $(Cd_x^{2+}Fe_{1-x}^{3+})^A\,[Cu_{1-x}^{2+}Fe_{1+x}^{3+}]^B O_4^{2-}$, $\mu(Fe^{3+})$ and $\mu(Cu^{2+})$ are the ionic moments of Fe^{3+} and Cu^{2+}, and $|H_B(x)|$ and $|H_A(x)|$ are the magnitudes of average nuclear magnetic fields for the octahedral (B) and tetrahedral (A) Fe^{3+} ions respectively. It is assumed that the relative magnetization $\sigma(x)/\sigma(0)$ as a function of x were evaluated from Equation 1 using the values of nuclear magnetic fields obtained at room temperature from Mössbauer studies (Table III) of Panicker *et al.* [4] and the same are shown in Fig. 1 as dots with circles. The crosses in Fig. 1 represent the values of $\sigma(x)/\sigma(0)$ at 300 K

TABLE III The average sublattice magnetization obtained from Mössbauer data [4]

X	Hyperfine field (KOe)		$\sigma(x)/\sigma\ (x=0)$
	$H_{\mathrm{hf}}(\mathrm{B})$	$H_{\mathrm{hf}}(\mathrm{A})$	
0.0	503 ± 3	482 ± 3	1.00
0.1	502 ± 3	450 ± 3	2.19
0.2	470 ± 3	445 ± 3	2.66
0.3	458 ± 3	408 ± 3	3.59
0.4	450 ± 3	408 ± 3	4.26
0.5	450 ± 3	392 ± 3	5.12
0.6	425 ± 3	359 ± 3	5.61

for magnetization measurements. The agreement between the values of $\sigma(x)/\sigma(0)$ obtained from Mössbauer data and from magnetization measurements is quite satisfactory, for $x < 0.1$, but it becomes increasingly worse as x increases above 0.1. This behaviour can be interpreted as indirect evidence for the presence of canted spin structure because the Mössbauer effect measures the magnitude of $\langle S_z \rangle$ parallel to the external field. Thus the discrepancy between the magnetization measurements and Mössbauer data can be taken as indirect evidence for the presence of Yafet–Kittel angles.

The condition for YK angles to occur in the Ni–Zn system has been investigated in the molecular field approximation by Satyamurthy *et al.* [6] using a noncollinear, three-sublattice model. In this model, the molecular fields acting on various ions in the Cu–Cd ferrites are given by

$$\begin{bmatrix} H_{\mathrm{A}}(\mathrm{Fe}^{3+}) \\ H_{\mathrm{B}}(\mathrm{Cu}^{2+}) \\ H_{\mathrm{B}_1}(\mathrm{Fe}^{3+}) \\ H_{\mathrm{B}_2}(\mathrm{Cu}^{2+}) \\ H_{\mathrm{B}_2}(\mathrm{Fe}^{3+}) \end{bmatrix} = \begin{bmatrix} \lambda_{\mathrm{AA}} & \alpha & \beta & \alpha & \beta \\ \alpha & \gamma' & \epsilon' & \gamma & \epsilon \\ \beta & \epsilon' & \delta' & \epsilon & \delta \\ \alpha & \gamma & \epsilon & \gamma' & \epsilon' \\ \beta & \epsilon & \delta & \epsilon' & \delta' \end{bmatrix} \begin{bmatrix} (1-x)m_{\mathrm{A}}\ \ (\mathrm{Fe}^{3+}) \\ \frac{1}{2}(1-x)m_{\mathrm{B}_1}(\mathrm{Cu}^{2+}) \\ \frac{1}{2}(1+x)m_{\mathrm{B}_1}(\mathrm{Fe}^{3+}) \\ \frac{1}{2}(1-x)m_{\mathrm{B}_2}(\mathrm{Cu}^{2+}) \\ \frac{1}{2}(1+x)m_{\mathrm{B}_2}(\mathrm{Fe}^{3+}) \end{bmatrix} \tag{2}$$

where $H_{\mathrm{A}}(\mathrm{Fe}^{3+})$ is the molecular field acting on the Fe^{3+} ion at the A site due to all other ions, etc, and

$$|m_{\mathrm{A}}(\mathrm{Fe}^{3+})| = |m_{\mathrm{B}_1}(\mathrm{Fe}^{3+})| = |m_{\mathrm{B}_2}(\mathrm{Fe}^{3+})| = \left(\frac{N_{\mathrm{A}}d}{M}\right)(5\mu_{\mathrm{B}})$$

$$|m_{\mathrm{B}_1}(\mathrm{Cu}^{2+})| = |m_{\mathrm{B}_2}(\mathrm{Cu}^{2+})| = \left(\frac{N_{\mathrm{A}}d}{M}\right)(1\mu_{\mathrm{B}})$$

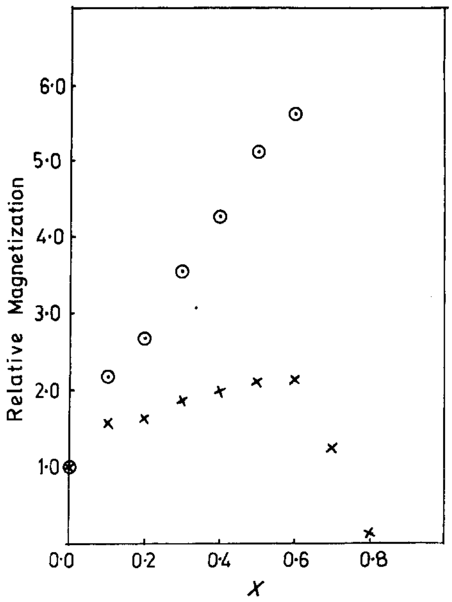

Figure 1 The relative magnetization per formula unit against cadmium content (x) at 300 K. The dots with circles represent the relative magnetization obtained from Mössbauer data and the cross represent data from magnetization measurements.

$$\begin{aligned} \mathbf{m}_{\mathrm{B}_1}\cdot\mathbf{m}_{\mathrm{A}} &= \sim|\mathbf{m}_{\mathrm{B}_1}|\,|\mathbf{m}_{\mathrm{A}}|\cos\alpha_{\mathrm{YK}'} \\ \mathbf{m}_{\mathrm{B}_2}\cdot\mathbf{m}_{\mathrm{A}} &= -|\mathbf{m}_{\mathrm{B}_2}|\,|\mathbf{m}_{\mathrm{A}}|\cos\alpha_{\mathrm{YK}'} \\ \mathbf{m}_{\mathrm{B}_1}\cdot\mathbf{m}_{\mathrm{B}_2} &= |\mathbf{m}_{\mathrm{B}_1}|\,|\mathbf{m}_{\mathrm{B}_2}|\cos 2\alpha_{\mathrm{YK}'}. \end{aligned} \tag{3}$$

Here N_{A} is Avagadro's number, M and d are the molecular weight and density of $\mathrm{Cd}_x\mathrm{Cu}_{1-x}\mathrm{Fe}_2\mathrm{O}_4$, respectively. The molecular field constants relate to the following exchange interactions:

λ AA: $\mathrm{A}(\mathrm{Fe}^{3+}) \rightarrow \mathrm{A}(\mathrm{Fe}^{3+})$
α : $\mathrm{A}(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_i(\mathrm{Cu}^{2+})$
β : $\mathrm{A}(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_i(\mathrm{Fe}^{3+})$
ν : $\mathrm{B}_1(\mathrm{Cu}^{2+}) \rightarrow \mathrm{B}_2(\mathrm{Cu}^{2+})$
ν' : $\mathrm{B}_i(\mathrm{Cu}^{2+}) \rightarrow \mathrm{B}_i(\mathrm{Cu}^{2+})$
δ : $\mathrm{B}_1(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_2(\mathrm{Fe}^{3+})$

δ' : $B_i(Fe^{3+}) \rightarrow B_i(Fe^{3+})$

ϵ : $B_1(Fe^{3+}) \rightarrow B_2(Cu^{2+})$

ϵ' : $B_i(Fe^{3+}) \rightarrow B_i(Cu^{2+})$

where $i = 1, 2$.

The part of the interaction energy involving YK angles can be written as $\gamma = \gamma'$, $\delta = \delta'$ and $\epsilon = \epsilon'$.

$$\begin{aligned} E(\mathrm{YK}) = {} & [|m_{\mathrm{A}}(\mathrm{Fe}^{3+})|\,|m_{\mathrm{B}_1}(\mathrm{Cu}^{2+})|\,(1-x)^2\alpha \\ & + |m_{\mathrm{A}}(\mathrm{Fe}^{3+})|\,|m_{\mathrm{B}_1}(\mathrm{Fe}^{3+})| \\ & \times (1-x^2)\beta] \cos\alpha_{\mathrm{YK}} \\ & - \tfrac{1}{4}[|m_{\mathrm{B}_1}(\mathrm{Cu}^{2+})|\,|m_{\mathrm{B}_2}(\mathrm{Cu}^{2+})| \\ & \times (1-x)^2\gamma + |m_{\mathrm{B}_1}(\mathrm{Fe}^{3+})| \\ & \times |m_{\mathrm{B}_2}(\mathrm{Fe}^{3+})|\,(1+x)^2\delta \\ & + 2|m_{\mathrm{B}_1}(\mathrm{Fe}^{3+})|\,|m_{\mathrm{B}_2}(\mathrm{Cu}^{2+})| \\ & \times (1-x^2)\epsilon] \cos 2\alpha_{\mathrm{YK}'} \end{aligned} \tag{4}$$

If Fe^{3+} and Cu^{2+} have moments $5\mu_B$ and $1\mu_B$ respectively, then E(YK) becomes

$$\begin{aligned} E(\mathrm{YK}) = {} & [5(1-x)^2\alpha + 25(1-x^2)\beta] \cos\alpha_{\mathrm{YK}'} \\ & - \tfrac{1}{4}[(1-x^2)\gamma + 25(1+x)^2\delta \\ & + 10(1-x^2)\epsilon] \cos 2\alpha_{\mathrm{YK}}. \end{aligned} \tag{5}$$

The energy is a minimum for (a) $\sin\alpha_{\mathrm{YK}} = 0$, which corresponds to the Néel configuration, or for (b)

$$\cos\alpha_{\mathrm{YK}} = \frac{5(1-x)^2\alpha + 25(1-x^2)\beta}{(1-x)^2\gamma + 25(1+x^2)\delta + 10(1-x^2)\epsilon} \tag{6}$$

which respresent the situation where the YK ordering is feasible. Here, for example,

$$\alpha = \frac{2\,Z_{\mathrm{AB}}\,J_\alpha(\mathrm{Fe}^{3+} - \mathrm{Cu}^{2+})}{N_{\mathrm{B}_i} g_{\mathrm{A}}\, g_{\mathrm{B}_i} \mu_{\mathrm{B}}^2} \tag{7}$$

where J_α is the interaction between $A(Fe^{3+})$ and $B_i(Cu^{2+})$. Z_{AB_i} is the B_i nearest neighbour to A. N_{B_i} is the number of ions per unit volume, μ_B is Bohr magneton and g denotes Lande's splitting factor. On physical grounds, it is expected that $J_{\gamma'}$, $J_{\delta'}$, $J_{\epsilon'}$ will be close to J_γ, J_δ and J_ϵ respectively.

The molecular field constants can be obtained from the observed variation of the saturation magnetization with cadmium concentration. The exchange constants so obtained should be consistent with the existing data on similar ferrimagnetic systems. Adopting the procedure of Kulkarni and Patil [3] the following values: $J_\alpha = -5.25$ K, $J_\beta = -14.8$ K and $J_\delta = -10.0$ K, have been accepted for $Cd_xCu_{1-x}Fe_2O_4$. Finally, we estimated the values of γ and ϵ from the best fit for the variation of saturation magnetization with cadmium concentration using the relation

$$n_{\mathrm{B}} = (6+x)\cos\alpha_{\mathrm{YK}} - 5\,(1-x) \tag{8}$$

where n_B has been expressed in units of Bohr magnetons. We obtained $J_\gamma = -329.45$ K and $J_\epsilon = -21.31$ K. As $J_\gamma = J_{\gamma'}$ and $J_\epsilon = J_{\epsilon'}$, it is assumed that the primed values are the same as the unprimed values.

TABLE IV Saturation magnetization per formula unit at 300 K and the value of exchange constant used to calculate α_{YK} are: $J_\alpha = -5.25$ K; $J_\beta = -14.8$ K; $J_\gamma = -329.45$ K; $J_\delta = -10$ K; $J_\epsilon = -21.31$ K

X	n_B (Bohr magneton)	Yafet–Kittel angle, α_{YK} Calculated	Yafet–Kittel angle, α_{YK} Experimental
0.0	1.18	0°0′	0°0′
0.1	1.75	6°36′	6°34′
0.2	1.98	16°22′	24°32′
0.3	2.18	26°00′	31°52′
0.4	2.33	35°35′	38°46′
0.5	2.51	45°05′	45°34′
0.6	2.51	54°27′	51°15′
0.7	1.46	63°38′	65°51′
0.8	0.16	72°38′	80°20′

The values of the exchange constants used in calculating Yafet–Kittel angles, α_{YK}, from Equation 6 are listed in Table IV along with α_{YK} values. The experimental values of α_{YK} have been obtained from the observed variation of n_B with x using Equation 8. These values are also given in Table IV. There is a satisfactory agreement between the experimental and theoretical values of α_{YK}. Thus the observed variation of the saturation magnetization with cadmium concentration has been explained on the basis of the existence of Yafet–Kittel angles on the B site spins. This suggests that A–B and B–B superexchange interactions are comparable in strength.

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References

1. J. M. DANIELS and A. ROSENWAIG, *Can. J. Phys.* **48** (1970) 381.
2. C. M. SRIVASTAVA, S. N. SHRINGI, R. G. SRIVASTAVA and N. G. NANDIKAR, *Phys. Rev.* **B14** (1976) 2032.
3. R. G. KULKARNI and V. U. PATIL, *J. Mater. Sci.* **17** (1982) 843.
4. V. G. PANICKER, S. N. RAO and R. G. KULKARNI, *Solid State Commun.* **43** (1982) 647.
5. J. SMIT and H. P. J. WIJN, "Ferrites" (John Wiley, New York, 1959).
6. N. S. SATYAMURTHY, M. G. NATERA, S. I. YOUSEFF, R. J. BEGUM and C. M. SRIVASTAVA, *Phys. Rev.* **181** (1969) 969.
7. L. K. LEUNG, B. J. EVANS and A. H. MORRISH, *ibid.* **B8** (1973) 29.
8. C. M. SRIVASTAVA, S. N. SHRINGI and R. G. SRIVASTAVA, *ibid.* **B14** (1976) 2041.
9. V. U. PATIL and R. G. KULKARNI, *Solid State Commun.* **31** (1979) 551.

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