Non-colinear spin structure in Ni–Cd ferrite system*

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Though several investigators [1–3] have reported Mössbauer studies of the Ni–Cd ferrite system, they have concentrated mainly on investigations of the variation of quadrupole splitting (QS) with cadmium concentration. To date there is no information concerning the variation of the hyperfine field with cadmium concentrations and the existence of Yafet–Kittel (YK) angles in the system. The present paper reports the magnetization and Mössbauer study of the $Cd_xNi_{1-x}Fe_2O_4$ ferrite system at different cadmium concentrations.

Eleven samples with $0 \leqslant X \leqslant 1$ were prepared by the ceramic method, from analytical reagent grade Fe_2O_3 (Robert Johnson), NiO (BDH) and CdO (USSR). The oxides were mixed in the desired proportions, fired at 1100° C for 50 h in a furnace and slowly cooled to room temperature. All the samples were found by X-ray powder diffractometry to be single phase spinel. The magnetization measurements were done at a constant magnetic field of 7 kOe at 300 K.

The variation of lattice constant with the cadmium concentration is shown in Fig. 1. It is clear from Fig. 1 that the variation of lattice constant with cadmium concentration is nonlinear and a quadratic fit by the method of least squares gives the following equation:

$$a_x = 8.2871 - 0.1231X + 0.4651X^2 \quad (1)$$

where a is expressed in 10^{-1} nm.

The increase in lattice constant with X 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+} (0.060 nm) ion on the tetrahedral (A) site. Previous measurements [3] of lattice constant with X show linear behaviour because of the lack of accuracy.

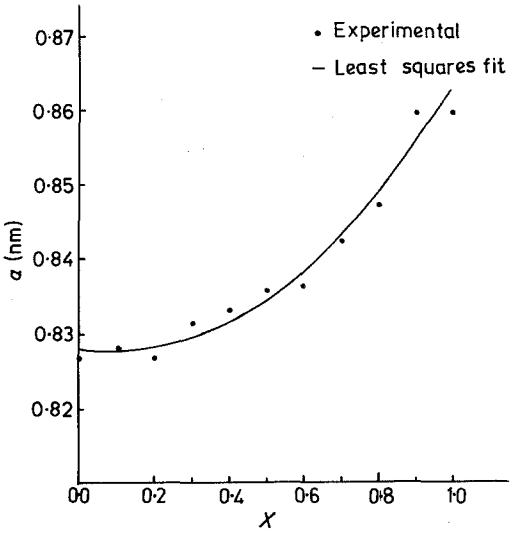

Figure 1 Variation of lattice parameters of the $Cd_xNi_{1-x}Fe_2O_4$ system as a function of X.

The change in magnetization on zinc substitution occurs due to the presence of Yafet–Kittel angles in the spin system on the B-site which was proposed by Satyamurthy *et al.* [4] on the basis of their neutron diffraction studies of Ni–Zn ferrites. On account of the similarities between the Ni–Zn and Ni–Cd systems, it is reasonable to assume that the Yafet–Kittel angles are present in the later system also. On a similar assumption, Kulkarni and Patil [5] and Srivastava *et al.* [6] have found the existence of Yafet–Kittel angles in Cu–Zn and Fe–Zn ferrites respectively.

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

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$$\mu(X) = \frac{|H_B(X)|}{|H_B(0)|}\,[(1+X)\mu(Fe^{3+}) + (1-X)\mu(Ni^{2+})] - \frac{|H_A(X)|}{|H_A(0)|}\,[(1-X)\mu(Fe^{3+})] \quad (2)$$

where $\mu(X)$ is the magnetic moment per formula unit $(Cd_x^{2+}Fe_{1-x}^{3+})^A\ [Ni_{1-x}^{2+}Fe_{1+x}^{3+}]^B O_4^{2-}$, $\mu(Fe^{3+})$ and $\mu(Ni^{2+})$ are the ionic magnetic moments of Fe^{3+} and Ni^{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 was assumed that the relative magnetization $\sigma(X)/\sigma(0)$ at room temperature is $\mu(X)/\mu(X=0)$. The values of $\sigma(X)/\sigma(0)$ were evaluated using the values of nuclear fields obtained at room temperature from Mössbauer studies (Table I), 5 and 2 Bohr magnetons for $\mu(Fe^{3+})$ and $\mu(Ni^{2+})$, respectively, and the same are shown in Fig. 2. The agreement between $\sigma(X)/\sigma(0)$ as calculated from Equation 1 and as measured from magnetization measurements at 300 K 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. 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 the existence of YK angles in the Ni–Zn system has been investigated in the molecular field approximation by Satyamurthy *et al.* [4] using a noncolinear three-sublattice model. On a similar basis we can write the interaction energy involving the YK angles for the Ni–Cd system as:

TABLE I The average sublattice magnetization obtained from Mössbauer data

X	Hyperfine field (kOe)		$\sigma(X)/\sigma(X=0)$
	$H_{hf}(B)$	$H_{hf}(A)$	
0.0	519 ± 5	507 ± 5	1.00
0.1	515 ± 5	478 ± 5	1.50
0.2	511 ± 5	462 ± 5	1.92
0.3	511 ± 5	458 ± 5	2.31
0.4	493 ± 5	446 ± 5	2.58
0.5	482 ± 5	392 ± 5	2.98

*Data to be published in a separate paper.

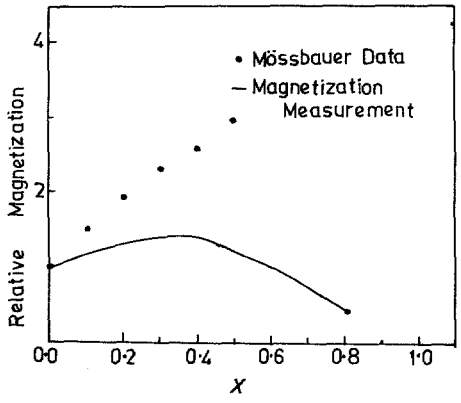

Figure 2 The relative magnetization per formula unit against cadmium content (X) at 300 K.

$$E(YK) = [10(1-X)^2\alpha + 25(1-X^2)\beta]\cos\alpha_{YK} - 1/4\,[4(1-X)^2\gamma + 25(1+X)^2\delta + 20(1-X^2)\epsilon]\cos 2\alpha_{YK} \quad (3)$$

The term α, β, γ, δ and ϵ are the molecular field constants related to the following exchange interactions:

$$\alpha = A(Fe^{3+}) - B_i(Ni^{2+}) \quad (4)$$

$$\beta = A(Fe^{3+}) - B_i(Fe^{3+}) \quad (5)$$

$$\gamma = B_i(Ni^{2+}) - B_2(Ni^{2+}) \quad (6)$$

$$\delta = B_1(Fe^{3+}) - B_2(Fe^{3+}) \quad (7)$$

$$\epsilon = B_1(Fe^{3+}) - B_2(Ni^{2+}) \quad (8)$$

where $i = 1,2$.

The energy is minimum for

$$\sin\alpha_{YK} = 0 \quad (9)$$

which corresponds to Néel's configuration, or for

$$\cos\alpha_{YK} = \frac{10(1-X)^2\alpha + 25(1-X^2)\beta}{4(1-X)^2\gamma + 25(1+X)^2\delta + 20(1-X^2)\epsilon} \quad (10)$$

which represents the situation where Y–K ordering is feasible. Here for example,

$$\alpha = \frac{2Z_{ABi}J_\alpha(Fe^{3+} - Ni^{2+})}{N_{B_i}g_A g_{B_i}\mu_B^2} \quad (11)$$

where J_α is the interaction between $A(Fe^{3+})$ and $B_i(Ni^{2+})$, Z_{AB_i} is the number of B_i nearest neighbours to A, N_{B_i} is the number of ions per

TABLE II Magnetization σ (e.m.u. gram^{-1}), saturation magnetization per formula unit in Bohr magneton 300 K and the value of exchange constant used to calculate α_{YK} are: $J_\alpha = -10.0$ K, $J_\beta = -14.8$ K, $J_\gamma = -10.0$ K, $J_\delta = -118.9$ K and $J_\epsilon = -10.7$ K

X	σ (e.m.u. gram^{-1})	n_B(300 K)	α_{YK} (experimental)	α_{YK} (calculated)
0.0	50.00	2.00	0°	0°
0.1	53.10	2.28	17° 14′	6° 16′
0.2	58.65	2.58	24° 1′	15° 33′
0.3	60.91	2.74	31° 21′	24° 56′
0.4	61.06	2.80	38° 23′	34° 28′
0.5	54.04	2.53	47° 52′	44° 5′
0.6	40.99	1.96	58° 34′	53° 40′
0.7	31.32	1.53	66° 51′	63° 7′
0.8	15.76	0.78	77° 18′	72° 22′

unit volume, μ_B is the Bohr magneton, and g denotes Lande's splitting factor.

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 [5] the following values of $J_\alpha = -10.0$ K, $J_\beta = -14.8$ K and $J_\delta = -10.0$ K have been accepted for $Cd_xNi_{1-x}Fe_2O_4$. Finally we have estimated the values of γ and ϵ from the best fit for the variation of saturation magnetization with cadmium concentration using the relation:

$$n_B = (7 + X)\cos\alpha_{YK} - 5(1 - X) \qquad (12)$$

where n_B has been expressed in units of Bohr magnetons. We have obtained $J_\gamma = -118.9$ K and $J_\epsilon = -10.7$ K.

The values of exchange constants used in calculating Yafet–Kittel angles α_{YK} from Equation 3 are listed in Table II 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 5. These values have also been given in Table II. There is a satisfactory agreement between the experimental and calculated 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 super-exchange interactions are comparable in strength.

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References

1. O. A. BAYUKOV, V. P. IKONNIKOV, G. N. ILINOVA and G. P. POPOV, *Sov. Phys. Solid State* **14** (1973) 2040.
2. N. A. EISSA, A. A. BHAGAT and M. K. FAYEK, *J. Phys.* F7 (1977) 2209.
3. P. MUTHUKUMARASMAY, T. NAGARAJAN and A. NARAYANASAMY, *Phys. Status Solidi* **a64** (1981) 747.
4. N. S. SATYAMURTHY, M. G. NATREA, S. I. YOUSSEF, R. J. BEGUM and C. M. SRIVASTAVA, *Phys. Rev.* **181** (1969) 969.
5. R. G. KULKARNI and V. U. PATIL, *J. Mater. Sci.* **17** (1982) 843.
6. C. M. SRIVASTAVA, S. N. SHRINGI, R. G. SRIVASTAVA and N. G. NANDIKAR, *Phys. Rev.* **B14** (1976) 2032.

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