JOURNAL OF MATERIALS SCIENCE 17 (1982) 843–848

Magnetic ordering in Cu–Zn ferrite

R. G. KULKARNI
Department of Physics, Saurashtra University, Rajkot, 360 005, India

V. U. PATIL
Department of Physics, Marathawada University, Aurangabad, 431 004, India

The variation of magnetization with temperature of the $Zn_xCu_{1-x}Fe_2O_4$ system has been obtained between 300 K and the Néel temperature at a constant magnetic field of 5.57×10^5 A m^{-1} for $x = 0$ to 0.8. The observations indicate the existence of a Yafet–Kittel (Y–K) type of magnetic ordering in the mixed ferrites. A molecular field analysis of the Y–K spin-ordering using a three-sublattice model is shown to explain the experimental data satisfactorily. For the sake of verification, Néel temperatures of Cu–Zn ferrites were also determined from Mössbauer studies.

1. Introduction

Ferrites have gained importance because they possess the combined properties of magnetic materials and insulators [1]. It has been shown by a number of workers [2–4] that a variety of substitutional ferrites can be prepared with a fairly large range of saturation magnetization and Néel temperature values. These materials are also of considerable theoretical interest, as they are ideal for the study of the various types of spin arrangement and exchange interactions. To prepare ferrites with specified properties, it is necessary to know various magnetic and electrical properties, such as the saturation magnetization, $4\pi M_s$, Néel temperature, T_N, resistivity, ρ, dielectric constant, ϵ, permeability, μ, etc.

Practically no information about the magnetic properties of Cu–Zn ferrites exists in the literature, except for our recent short communication [5]. This reported Mössbauer parameters such as hyperfine fields, isomer shifts and quadrupole splitting of Cu–Zn ferrite obtained at room temperature.

The present paper reports a magnetization and Mössbauer study of Cu–Zn ferrites with different zinc concentrations. The magnetization measurements of Cu–Zn ferrites up to the Néel temperature were undertaken for the following three reasons. First to study the variation of the saturation magnetization with zinc concentration and temperature, second to determine the Néel temperatures of Cu–Zn ferrites at different zinc concentrations, and third to gain information about the Yafat–Kittel (Y–K) angles in the system. The variation of the magneton number, n_B, with zinc concentration in this system is similar in nature to that in the Ni–Zn ferrite system and the existence of Y–K angles on the B-site, observed in the latter case [6], is strongly suspected. A molecular field analysis of the Y–K spin-ordering using a three-sublattice model is shown to explain the experimental data satisfactorily.

In order to verify the Néel temperatures obtained from magnetization measurements, the Néel temperatures for samples with $x = 0.0$, 0.2, 0.4 and 0.5 were also found from Mössbauer spectroscopic methods.

2. Experimental details

Seven samples with $x = 0.0$, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0 were prepared by the ceramic method, from pure Fe_2O_3, CuO and ZnO powders. The oxides were mixed in the desired proportions, fired at 1100° C for 48 h in a furnace 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 CuKα radiation and are presented in Table I. In addition to X-ray

0022–2461/82/030843–06$03.22/0

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

x (calculated)	x (chemical analysis)	Lattice constant (nm)
0.00	0.00	0.8225 ± 0.0002
0.20	0.20	0.8267 ± 0.0002
0.40	0.42	0.8303 ± 0.0002
0.50	0.51	0.8328 ± 0.0002
0.60	0.60	0.8352 ± 0.0002
0.80	0.79	0.8378 ± 0.0002
1.00	1.00	0.8421 ± 0.0002

analysis, chemical analysis was also performed for the determination of weight per cent of copper and zinc in the Cu–Zn ferrite. These results are also given in Table I.

The variation of the magnetization with the temperature of the Cu–Zn ferrite system has been measured between 300 K and the Néel temperatures at a constant magnetic field of 5.57×10^5 A m^{-1} for $x = 0$ to 0.8; the results are shown in Fig. 1. Temperatures were measured with a chromel–alumel thermocouple with an accuracy of ± 1 K. The thermocouple was calibrated using well-known temperature baths: ice, steam, sulphur bath, etc. 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. These results are in broad agreement with those of Somlenskij [7], but there are some differences.

The Mössbauer absorber was prepared by pressing a powdered sample between two very thin aluminium foils; the thickness of the absorber was 10 to 20 mg cm^{-2}. The Mössbauer spectrometer was equipped with a source of 4.5 mCi ^{57}Co (Cu). The experimental set-up has been described elsewhere [8]. The Mössbauer spectra of $Zn_xCu_{1-x}Fe_2O_4$ for $x = 0.0$, 0.2, 0.4 and 0.5 were obtained at different temperatures between room temperature and the Néel temperature.

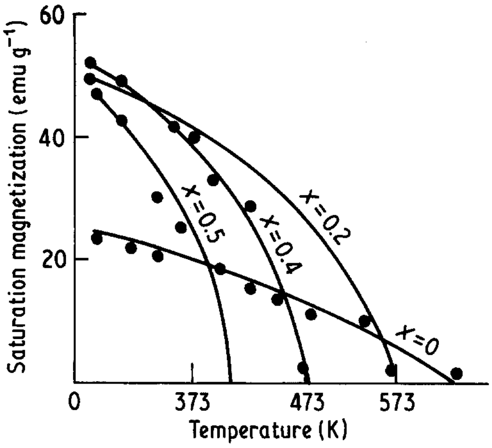

Figure 1 Saturation magnetization as a function of temperature for $Zn_xCu_{1-x}Fe_2O_4$ for $x = 0$, 0.2, 0.4 and 0.5.

3. Analysis and discussion

By means of Mössbauer results [5], X-ray diffraction and chemical analysis of Cu–Zn ferrite, the cationic distribution has been found to be $(Zn^{2+}_x Fe^{3+}_{1-x})^A [Cu^{2+}_{1-x} Fe^{3+}_{1+x}]^B O^{2-}_4$, where the ions enclosed by round brackets correspond to tetrahedral, or A sites, and the ions enclosed by square brackets correspond to octahedral, or B, sites.

3.1. Lattice constant

The variation of the lattice constant with zinc content is shown in Fig. 2. The increase in lattice constant with x is similar in nature to that in the Ni–Zn system [6] and is due to the larger ionic crystal radius of Zn^{2+} ($r_i = 0.074$ nm) which, when substituted for the divalent metal ion in the lattice, replaces the smaller Fe^{3+} ($r_i = 0.06$ nm) ion on the A-site. No previous measurements of lattice constants exist in the literautre for Cu–Zn ferrites at different values of zinc content.

TABLE II The magnetization per kg, σ, at 300 K and the Néel temperature for $Zn_xCu_{1-x}Fe_2O_4$. For comparison the values of T_N obtained from Somlenskij *et al.* [7] are also given

x	σ (A m^{-1}) at 300 K	T_N (K) (present work)		T_N (K) (from Somlenskij, [7])
		Magnetization	Mössbauer	
0.0	25	635	642	703
0.2	50	530	536	628
0.4	52	475	480	533
0.5	48	383	390	483
0.6	23	-	-	-
0.8	3	-	-	-

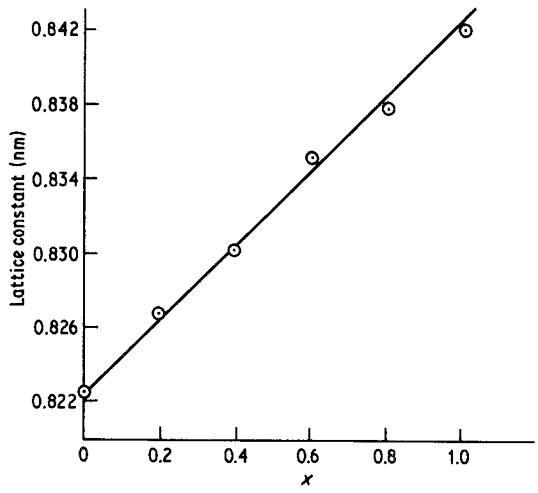

Figure 2 Variation of the lattice constant of the $Zn_xCu_{1-x}Fe_2O_4$ system as a function of x.

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 and then decreases as x is increased. This behaviour of n_B against x is shown in Fig. 3. The critical temperature for the $x = 0.0$, 0.2, 0.4 and 0.5 samples, as found from Mössbauer measurements, agrees with the magnetization measurements within a 2% error, whereas the values of T_c obtained by Somlenskij [7] are significantly higher than that of the present values. It is rather difficult to explain the discrepancy between the present measurements and Somlenskij's values for critical temperature, as it is not exactly known what constant magnetic field they used and what their method of preparation of samples was.

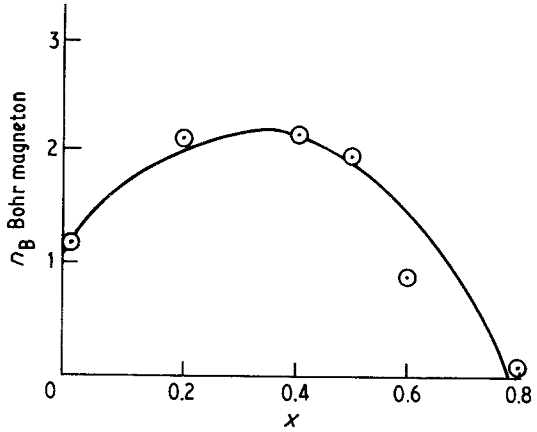

Figure 3 Variation of n_B (Bohr magneton) with zinc concentration (x).

A similar variation of n_B with x has also been observed in other zinc-substituted ferrites, such as Ni–Zn, Co–Zn and Mn–Zn [9]. This variation in Ni–Zn ferrite was earlier thought to arise because of the presence of superparamagnetic clusters or paramagnetic centres formed due to insufficient magnetic linkages. The neutron diffraction measurements of Satya Murthy *et al.* [6] and the low-temperature Mössbauer studies of Leung *et al.* [10] do not support this proposal. In the neutron diffraction studies it would be expected that the background paramagnetic scattering intensity would increase with increasing zinc concentration. This is because the statistical model predicts a rapid increase in the number of paramagnetic centres for $x > 0.5$. Satya Murthy *et al.* [6] looked for such an effect in their neutron diffraction studies of the Ni–Zn system but failed to observe it. The recent Mössbauer study of ferrous zinc ferrite by Srivastava *et al.* [11] has also ruled out the possibility of the existence of paramagnetic clusters.

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 Satya Murthy *et al.* [6] on the basis of their neutron diffraction studies of Ni–Zn ferrites and later confirmed by a number of other workers [10, 12]. Because of the similarities between the Ni–Zn and Cu–Zn systems it is reasonable to assume that Yafet–Kittel angles are also present in the latter system. By making a similar assumption, Srivastava *et al.* [13] have found the existence of Yafet–Kittel angles in Fe–Zn ferrites.

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

$$\begin{aligned}\mu(x) = {} & \frac{|H_{nB}(x)|}{|H_{nB}(0)|}[(1+x)\mu(\mathrm{Fe}^{3+}) \\ & + (1-x)\mu(\mathrm{Cu}^{2+})] \\ & - \frac{|H_{nA}(x)|}{|H_{nA}(0)|}[(1-x)\mu(\mathrm{Fe}^{3+})], \qquad (1)\end{aligned}$$

where $\mu(x)$ is the magnetic moment per formula unit $Zn_xFe^{3+}_{1-x}[Cu^{2+}_{1-x}Fe^{3+}_{1+x}]O^{4-}_2$, $\mu(Fe^{3+})$ and $\mu(Cu^{2+})$ are the ionic magnetic moments of Fe^{3+} and Cu^{2+}, and $|H_{nB}(x)|$ and $|H_{nA}(x)|$ are the magnitudes of the average nuclear magnetic fields for the octahedral and tetrahedral Fe^{3+} ions, respectively. It is assumed that the relative

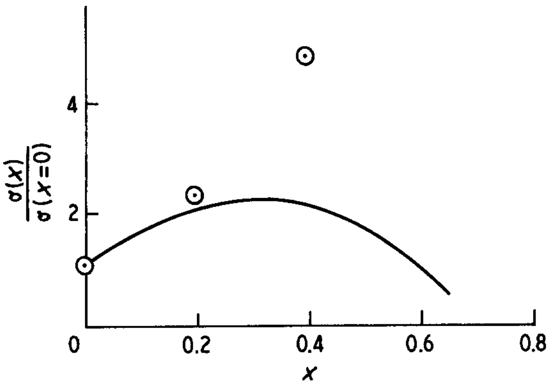

Figure 4 The relative saturation magnetization per formula unit at 300 K for Cu–Zn ferrites. The full line represents the data from magnetization and the circles with dots are the data from Mössbauer studies.

magnetization $\sigma(x)/\sigma(x-0)$ at room temperature is $\mu(x)/\mu(x=0)$. The values of relative magnetization $\sigma(x)/\sigma(x=0)$ as a function of x were determined from Equation 1 using the values of nuclear magnetic fields obtained at room temperature from the Mössbauer studies of Patil and Kulkarni [5]. These are shown in Fig. 4 as dots with circles. The full line in Fig. 4 represents the values of $\sigma(x)/\sigma(x=0)$ at 300 K for magnetization measurements. The agreement between the values of $\sigma(x)/\sigma(x=0)$ obtained from Mössbauer data and from magnetization measurements is quite good for $x < 0.2$, but it becomes increasingly poorer as x increases above 0.2. This behaviour can be interpreted as indirect evidence for the presence of a 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 (Y–K) angles.

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

$$\begin{bmatrix} H_A(\mathrm{Fe}^{3+}) \\ H_{B_1}(\mathrm{Cu}^{2+}) \\ H_{B_1}(\mathrm{Fe}^{3+}) \\ H_{B_2}(\mathrm{Cu}^{2+}) \\ H_{B_2}(\mathrm{Fe}^{3+}) \end{bmatrix} = \begin{bmatrix} \lambda_{AA} & \alpha & \beta & \alpha & \beta \\ \alpha & \gamma' & \epsilon' & \gamma & \epsilon \\ \beta & \epsilon' & \delta' & \epsilon & \delta \\ \alpha & \gamma & \epsilon & \gamma' & \epsilon' \\ \beta & \epsilon & \delta & \epsilon' & \delta' \end{bmatrix} \begin{bmatrix} (1-x)\mathbf{m}_A(\mathrm{Fe}^{3+}) \\ \frac{1}{2}(1-x)\mathbf{m}_{B_1}(\mathrm{Cu}^{2+}) \\ \frac{1}{2}(1+x)\mathbf{m}_{B_1}(\mathrm{Fe}^{3+}) \\ \frac{1}{2}(1-x)\mathbf{m}_{B_2}(\mathrm{Cu}^{2+}) \\ \frac{1}{2}(1+x)\mathbf{m}_{B_2}(\mathrm{Fe}^{3+}) \end{bmatrix}, \qquad (2)$$

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

$$\begin{aligned} |\mathbf{m}_A(\mathrm{Fe}^{3+})| &= |\mathbf{m}_{B_1}(\mathrm{Fe}^{3+})| = |\mathbf{m}_{B_2}(\mathrm{Fe}^{3+})| \\ &= \frac{(N_A d)}{M}(5\mu_B), \\ |\mathbf{m}_{B_1}(\mathrm{Cu}^{2+})| &= |\mathbf{m}_{B_2}(\mathrm{Cu}^{2+})| = \frac{(N_A d)}{M}(1\mu_B), \\ \mathbf{m}_{B_1}\cdot\mathbf{m}_A &= -|\mathbf{m}_{B_1}|\,|\mathbf{m}_A|\cos\alpha_{YK}, \\ \mathbf{m}_{B_2}\cdot\mathbf{m}_A &= -|\mathbf{m}_{B_2}|\,|\mathbf{m}_A|\cos\alpha_{YK} \end{aligned}$$

and

$$\mathbf{m}_{B_1}\cdot\mathbf{m}_{B_2} = |\mathbf{m}_{B_1}|\,|\mathbf{m}_{B_2}|\cos 2\alpha_{YK}. \qquad (3)$$

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

$$\begin{aligned} &\lambda_{AA}: \mathrm{A}(\mathrm{Fe}^{3+}) \rightarrow \mathrm{A}(\mathrm{Fe}^{3+}); \\ &\alpha: \mathrm{A}(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_i(\mathrm{Cu}^{2+}); \\ &\beta: \mathrm{A}(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_i(\mathrm{Fe}^{3+}); \\ &\gamma: \mathrm{B}_1(\mathrm{Cu}^{2+}) \rightarrow \mathrm{B}_2(\mathrm{Cu}^{2+}); \\ &\gamma': \mathrm{B}_i(\mathrm{Cu}^{2+}) \rightarrow \mathrm{B}_i(\mathrm{Cu}^{2+}); \\ &\delta: \mathrm{B}_1(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_2(\mathrm{Fe}^{3+}); \\ &\delta': \mathrm{B}_i(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_i(\mathrm{Fe}^{3+}); \\ &\epsilon: \mathrm{B}_1(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_2(\mathrm{Cu}^{2+}); \end{aligned}$$

and

$$\epsilon': \mathrm{B}_i(\mathrm{Fe}^{3+}) \rightarrow \mathrm{B}_i(\mathrm{Cu}^{2+}),$$

where $i = 1, 2$.

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

$$\begin{aligned} E(\mathrm{YK}) = {} & [|\mathbf{m}_A(\mathrm{Fe}^{3+})|\,|\mathbf{m}_{B_1}(\mathrm{Cu}^{2+})|\,(1-x)^2\alpha \\ & + |\mathbf{m}_A(\mathrm{Fe}^{3+})|\,|\mathbf{m}_{B_1}(\mathrm{Fe}^{3+}) \\ & \times (1-x^2)\beta]\cos\alpha_{YK} \\ & -\tfrac{1}{4}[|\mathbf{m}_{B_1}(\mathrm{Cu}^{2+})|\,|\mathbf{m}_{B_2}(\mathrm{Cu}^{2+})|(1-x)^2\gamma \\ & + |\mathbf{m}_{B_1}(\mathrm{Fe}^{3+})|\,|\mathbf{m}_{B_2}(\mathrm{Fe}^{3+})|(1+x)^2\delta \\ & + 2\,|\mathbf{m}_{B_1}(\mathrm{Fe}^{3+})|\,|\mathbf{m}_{B_2}(\mathrm{Cu}^{2+})| \\ & \times (1-x^2)\epsilon]\cos 2\alpha_{YK}. \end{aligned} \qquad (4)$$

TABLE III Saturation magnetization per formula unit in Bohr magnetons at 300 K. The values of the exchange constants in K used in calculating α_{YK} are as follows: $J_\alpha = -5.25; J_\beta = -14.8; J_\delta = -10; J_\gamma = -389; J_\epsilon = -4.53$

x	n_B (300 K)	α_{YK} (experiment)	α_{YK} (calculated)
0.0	1.04	0°	0°
0.2	2.10	10° 6′	10° 36′
0.4	2.13	36° 12′	34° 18′
0.5	2.00	46° 12′	42° 48′
0.6	0.98	63° 6′	55° 30′
0.8	0.14	80° 24′	75° 2′

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

$$E(\text{YK}) = [5(1-x)^2\alpha + 25(1-x^2)\beta] \cos\alpha_{YK} - \tfrac{1}{4}[(1-x)^2\gamma + 25(1-x)^2 + 10(1-x^2)\epsilon] \cos 2\alpha_{YK}. \quad (5)$$

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

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

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

$$\alpha = \frac{2Z_{AB}J_\alpha(Fe^{3+}\text{–}Cu^{2+})}{N_{B_i}g_A g_{B_i}\mu_B^2}, \quad (7)$$

where J_α is the interaction between A(Fe^{3+}) and B_i(Cu^{2+}). Z_{AB_i} is the B_i nearest neighbours to A. N_{B_i} is the number of ions per unit volume. μ_B is the Bohr magneton and g denotes the Landé'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, but they are not necessarily equal. This is so since $ZnFe_2O_4$ (for which only δ and δ' exist) is magnetically ordered at low temperatures and $\delta = \delta'$ is not permissible.

The molecular field constants can be obtained from the observed variation of the saturation magnetization with zinc concentration. The exchange constants so obtained should be consistent with the existing data on similar ferrimagnetic systems. Srivastava *et al.* [13] have found $J\alpha = -21$ K and $J\beta = -28$ K for the $Zn_xFe_{3-x}O_4$ system. in the case of $Zn_xFe_{3-x}O_4$, J_α is the interaction between A (Fe^{3+}) and B_i(Fe^{2+}), while in the present case it corresponds to the interaction between A(Fe^{3+}) and B_i(Cu^{2+}). Assuming J_α is approximately equal to the product of the moments of the ions, one gets J_α (Fe^{3+} $-Fe^{2+}$) = -20 K and J_α (Fe^{3+} $-Cu^{2+}$) = -5 K. The value $J_\alpha = -20$ K compares reasonably with the $J_\alpha = -21$ K value of Srivastava *et al.* [13] for $Zn_xFe_{3-x}O_4$. So $J_\alpha = -5.25$ K and $J_\beta = -14.8$ K values are accepted for $Zn_xCu_{1-x}Fe_2O_4$. In accordance with Srivastava *et al.* [13] the value of J_δ is taken as $J_\delta = -10$ K and $J_{\delta'} = -11$ K. Finally, the values of γ and ϵ are estimated from the best fit for the variation of saturation magnetization with zinc concentration using the relation

$$n_B = (6+x)\cos\alpha_{YK} - 5(1-x), \quad (8)$$

where n_B has been expressed in units of Bohr magnetons. It is found that $J_\delta = -389$ K and $J_\epsilon = -4.53$ 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.

The values of the exchange constants used in calculating Yafet–Kittel angles, α_{YK}, from [6] are listed in Table III along with α_{YK} values. The experimental values of α_{YK} have been obtained from the observed variation of n_B with x using [8] These values have also been given in Table III. There is a satisfactory agreement between the experimental and theoretical values of α_{YK}. Thus the observed variation of the saturation magnetization has been explained on the basis of the existence of Yafet–Kittel angles on the B-site spins.

Acknowledgments

One of the authors (VUP) is thankful to the Council of Scientific and Industrial Research, New Delhi, for providing financial support in the form of a fellowship.

References

1. J. L. SNOCK, "New Developments in Ferrimagnetic Materials" (Elsevier, New York 1949).

2. E. W. GORTER, *Philips Res. Report* **9** (1954)295.
3. J. B. GOODENOUGH, "Magnetism and Chemical Bond" (Interscience, London 1962).
4. G. BLASSE, *Philips Res. Reports.* Suppl. No. 3 (1964).
5. V. U. PATIL and R. G. KULKARNI, *Solid State Commun.* **31** (1979) 551.
6. N. S. SATYA MURTHY, M. G. NATERA, S. I. Youseff, R. J. BEGUN and G. M. SRIVASTAVA, *Phys. Rev.* **181** (1969) 969.
7. S. SOMLENSKIJ, *Dok. Akad. Nauk. SSSR* 78 (1951) 921.
8. V. U. PATIL and R. G. KULKARNI, *Solid State Commun.* **24** (1977) 113.
9. J. SMIT and H. P. J. WIJN, "Ferrites" (John Wiley, New York, (1959).
10. L. K. LEUNG, B. J. EVANS and A. H. MORRISH, *Phys. Rev.* **B8** (1973) 29.
11. G. M. SRIVASTAVA, S. N. SHRINGI and R. G. SRIVASTAVA, *ibid.* **B14** (1976) 2014.
12. J. M. DANIELS and A. ROSENWAIG, *Can. J. Phys.* **48** (1970) 381.
13. C. M. SRIVASTAVA, S. N. SHRINGI, R. G. SRIVASTAVA and N. G. NANDIKAR, *Phys. Rev.* **B14** (1976) 2032.

Received 6 April
and accepted 14 August 1981