Magnetic properties of the mixed spinel $Co_{1+x}Si_xFe_{2-2x}O_4$

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Abstract. The structural and magnetic properties of the mixed spinel $Co_{1+x}Si_xFe_{2-2x}O_4$ system for $0.1 \leq x \leq 0.6$ have been studied by means of X-ray diffraction, magnetization, and Mössbauer spectroscopy measurements. X-ray intensity calculations indicate that Si^{4+} ions occupy only tetrahedral (A) sites replacing Fe^{3+} ions, and the added Co^{2+} ions substitute for (B) site Fe^{3+} ions. The Mössbauer spectra at 300 K have been fitted with two sextets in the ferrimagnetic state corresponding to Fe^{3+} at the A and B sites, for $x \leq 0.3$. The Mössbauer intensity data shows that Si possesses a preference for the A site of the spinel. The variation of the saturation magnetic moment per formula unit measured at 300 K with the Si content, is explained on the basis of Neel's collinear spin ordering model for $x \leq 0.3$ which is supported by Mössbauer, and X-ray data. The Curie temperature decreases nearly linearly with increase of the Si content, for $x = 0.1$–0.6.

Keywords. Magnetic properties; mixed spinel; $Co_{1+x}Si_xFe_{2-2x}O_4$.

1. Introduction

Ferrites having high resistivity and low eddy current losses, have been found to be the most versatile to be used for technological application. The cobalt ferrite $CoFe_2O_4$, possesses an inverse spinel structure and the observed degree of inversion depends upon the heat treatment (Sawatzky *et al* 1968). The addition of tetravalent ions like Ti^{4+} and Ge^{4+} in $CoFe_2O_4$ influences electrical and magnetic properties of the system. We have studied magnetic properties of the $Co_{1+x}Ge_xFe_{2-2x}O_4$ (Joshi *et al* 1991) and $Co_{1+x}Ti_xFe_{2-2x}O_4$ (Joshi and Kulkarni 1986; Joshi *et al* 1993) systems, which reveal that while the Ge^{4+} ion has a strong preference for the tetrahedral (A) site, the Ti^{4+} ion has an octahedral (B) site preference. Since, Si and Ge ions are both tetravalent as well as are well known for their semiconducting behaviour, an attempt has been made to understand the effect of Si^{4+} substitution in $CoFe_2O_4$ on the cation distribution. We have investigated the $Co_{1+x}Si_xFe_{2-2x}O_4$ system, to determine the effect of Fe : Si : Co ratio on the structural and magnetic properties of the system, using X-ray diffraction, magnetization, and Mössbauer effect measurements.

2. Experimental

Six samples of Si and Co co-substituted $Co_{1+x}Si_xFe_{2-2x}O_4$ system were prepared by the usual double-sintering

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ceramic method for $x \leq 0.6$ in steps of 0.1, using the analytical reagent grade oxides, Fe_2O_3 (Thomas Baker), CoO (J. T. Baker) and SiO_2 (E. Merck). The oxides were mixed in the required proportions and were presintered at 990°C for 24 h. In the final sintering process, the material was held at 1050°C for 24 h and subsequently cooled down slowly to room temperature (2°C min⁻¹). The X-ray diffraction (XRD) patterns for all the ferrite samples were obtained using FeKα radiation on a Philips X-ray diffractometer. Magnetization measurements of each sample at 300 K were carried out using high field hysteresis loop technique (Radhakrishnamurthy *et al* 1971). The Mössbauer spectra were obtained at 300 K in transmission geometry with a source of 5 mCi ⁵⁷Co(Rh), and a constant acceleration transducer.

3. Results and discussion

All the compositions of the system $Co_{1+x}Si_xFe_{2-2x}O_4$ could be indexed as single-phase cubic structure. No reflections other than those belonging to spinel structure were observed in the XRD patterns (figure 1). The values of lattice constant 'a' determined from XRD data with an accuracy of ± 0.002 Å for $x = 0.0$–0.6 are shown in figure 2. The 'a' parameter gradually increases on increasing x, displaying a maximum at $x \approx 0.2$, and then decreases with further increase in x from 0.3 to 0.6 (figure 2). The decrease in 'a' when x is increased from 0.3 to 0.6, is due to the replacement of larger ionic size radius of Fe (0.64 Å) by the smaller Si(0.42 Å).

Comparing the site preference energies of the constitu-

ent ions (Goodenough and Loeb 1953) and from the earlier studies (Pettit and Forester 1971), the cation distribution of $CoFe_2O_4$ has been accepted as:

$$(Co_{0.10}Fe_{0.90})^A [Co_{0.90}Fe_{1.10}]^B O_4. \tag{1}$$
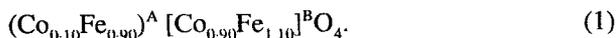
In order to determine the cation distribution, XRD intensities were calculated using the formula suggested by Buerger (1960),

$$I_{hkl} = | F_{hkl} |^2 PL_p, \tag{2}$$

where notations have their usual meanings. In the present $Co_{1+x}Si_xFe_{2-2x}O_4$ series of ferrites, variation of Si concentration, x, results in the replacement of $2xFe^{3+}$ ions by xSi^{4+} and xCo^{2+} ions. In accordance with the site preference energies, the Si^{4+} ions occupy the A site and Co^{2+} ions occupy the B site, whereas the Fe^{3+} ion shows no definite site preference (Goodenough and Loeb 1953). Accepting the cation distribution of $CoFe_2O_4$ (1), the cation distribution for the $Co_{1+x}Si_xFe_{2-2x}O_4$ can be written as:

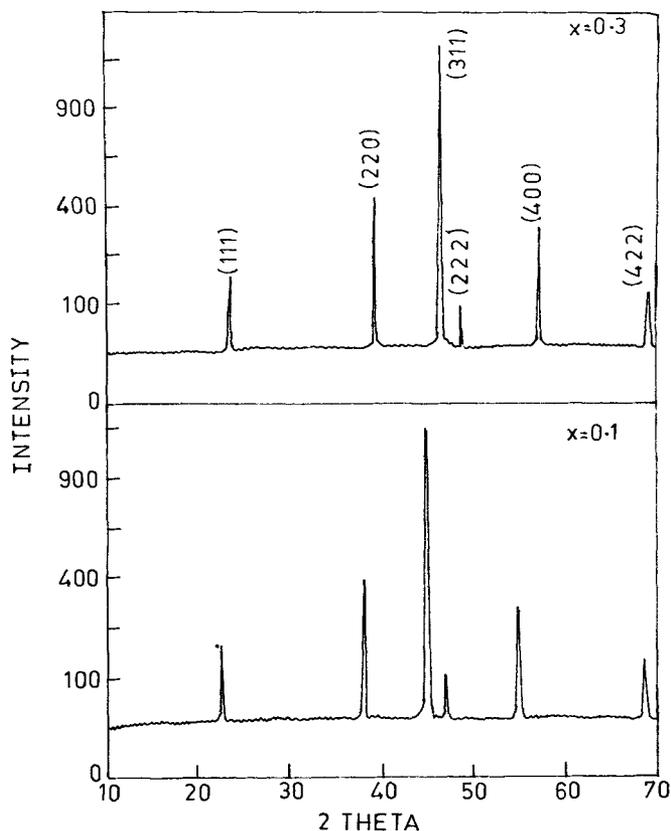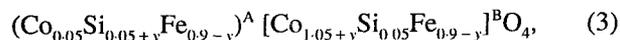$$(Co_{0.05}Si_{0.05+y}Fe_{0.9-y})^A [Co_{1.05+y}Si_{0.05}Fe_{0.9-y}]^B O_4, \tag{3}$$

where $x = 0.1–0.6$, $x = 0.1+y$ and $y = 0.1–0.5$. The distribution of divalent, trivalent and tetravalent cations amongst octahedral and tetrahedral sites in the $Co_{1+x}Si_xFe_{2-2x}O_4$ was determined from the ratio of X-ray diffraction lines (figure 3), I_{220}/I_{400} and I_{400}/I_{422}. The results of X-ray intensity calculations for various possible models have been tried for samples $x = 0.1–0.6$ and those which agree with the experimental intensity ratios are shown in figure 3. It is evident from figure 3 that tetravalent Si ions occupy tetrahedral (A) site replacing A-site iron and the added Co^{2+} ions substitute for octahedral (B) site iron without any change with x in the initial degree of inversion i.e. (1). Though the calculated I_{220}/I_{400} and I_{400}/I_{422} ratios agree reasonably well with the experimental values up to $x = 0.3$, they clearly differ from the observed values for $0.3 < x < 0.6$, indicating change in spin ordering.

Using the values of saturation magnetization from M–H curve at 300 K, the magnetic moment per formula unit, n_B, in Bohr magneton has been calculated and is shown in figure 4. It is evident from figure 4 that n_B increases with x up to $x \le 0.3$ and thereafter it decreases. The Curie temperatures (T_c) obtained from Loria method are shown in figure 5. The decrease in T_c with increasing Si content displays the reduction in ferrimagnetic ordering and the weakening of magnetic coupling.

Typical Mössbauer spectra recorded at 300 K for samples with $x = 0.1$, 0.2, and 0.4 are displayed in figure 6.
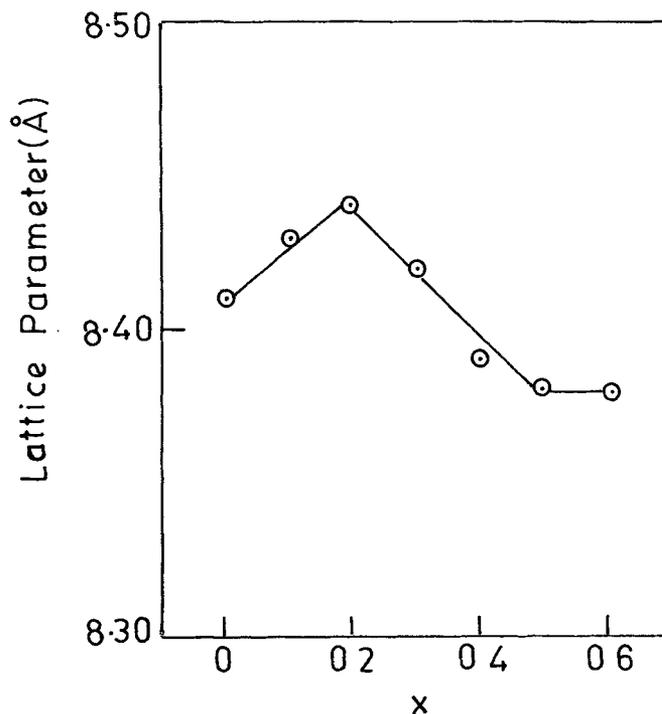

Figure 1. Typical X-ray diffractograms of the $Co_{1+x}Si_xFe_{2-2x}O_4$ for $x = 0.1$ and 0.3.

Figure 2. Variation of lattice parameters a (Å) with Si concentration (x).

For $x \le 0.3$, the spectra exhibit a superposition of two Zeeman sextets, one due to the Fe^{3+} ions at the tetrahedral (A) site and the other due to the Fe^{3+} ions at the octahedral (B) site, and the spectrum for $x = 0.4$ shows
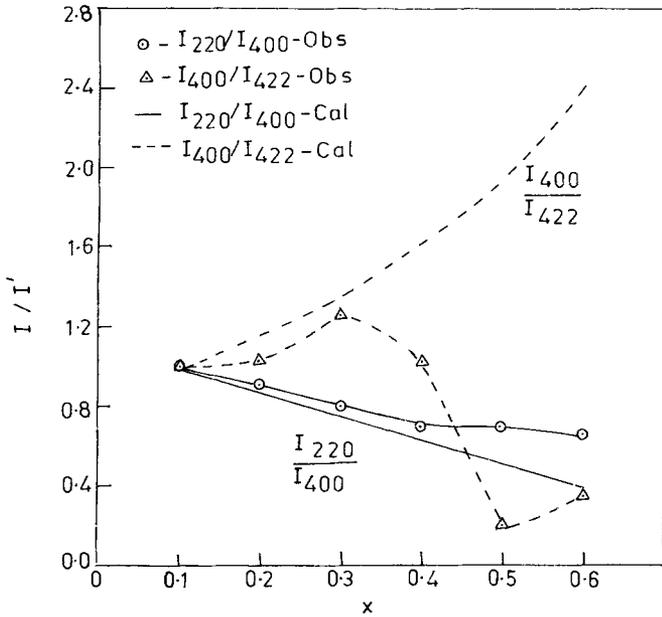
nearly relaxation behaviour. The solid lines through the data points in figure 6 are the results of computer fits of spectra obtained, assuming equal line widths for the A and B sites. The parameters derived from least squares fits are listed in table 1.

The Mössbauer data for the system under investigation ($Co_{1+x}Si_xFe_{2-2x}O_4$) has shown that while Si^{4+} enters A site only, Co^{2+} enters B site. We have used intensities calculated from the tetrahedral (I_A) and octahedral (I_B) magnetic sextets measured at 300 K and the data obtained from other reported measurements on $CoFe_2O_4$. Cobalt ferrite has been reported to be partially inverse. For example, using intensities of the Fe^{3+} magnetic sites in $Co_{1.2}Si_{0.2}Fe_{1.6}O_4$ measured at 300 K, we find that while 0.79 Fe^{3+} enters the A site, 0.81 Fe^{3+} enters the B site. This suggests that a maximum of 0.11 Si^{4+} + 0.10 Co^{2+} enters the A site, and 0.09 Si^{4+}+1.10 Co^{2+} occupies the B site, provided the initial cation distribution of $CoFe_2O_4$ (1) is retained throughout. But it is observed that the
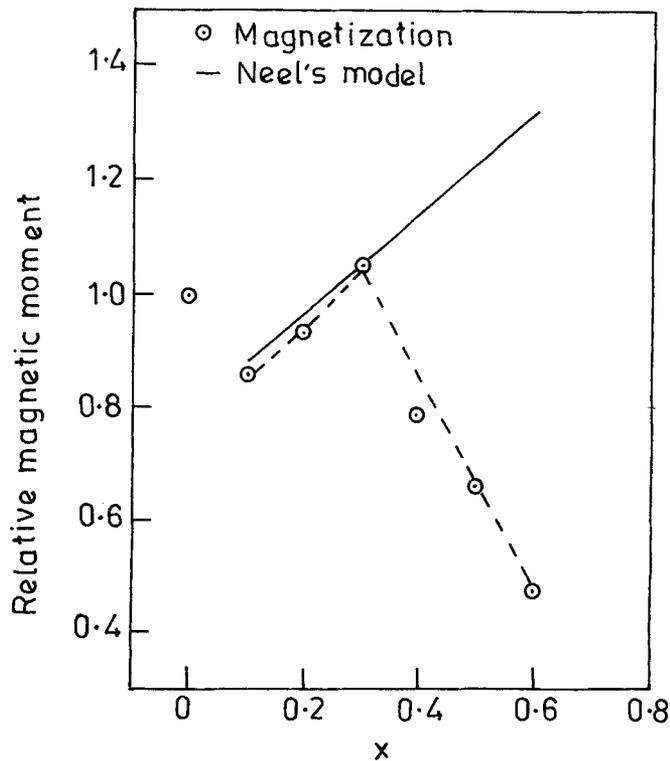

Figure 3. X-ray intensity ratio (I/I') vs Si and Co concentrations (x).

Figure 4. Variation of relative magnetic moment with concentration x.

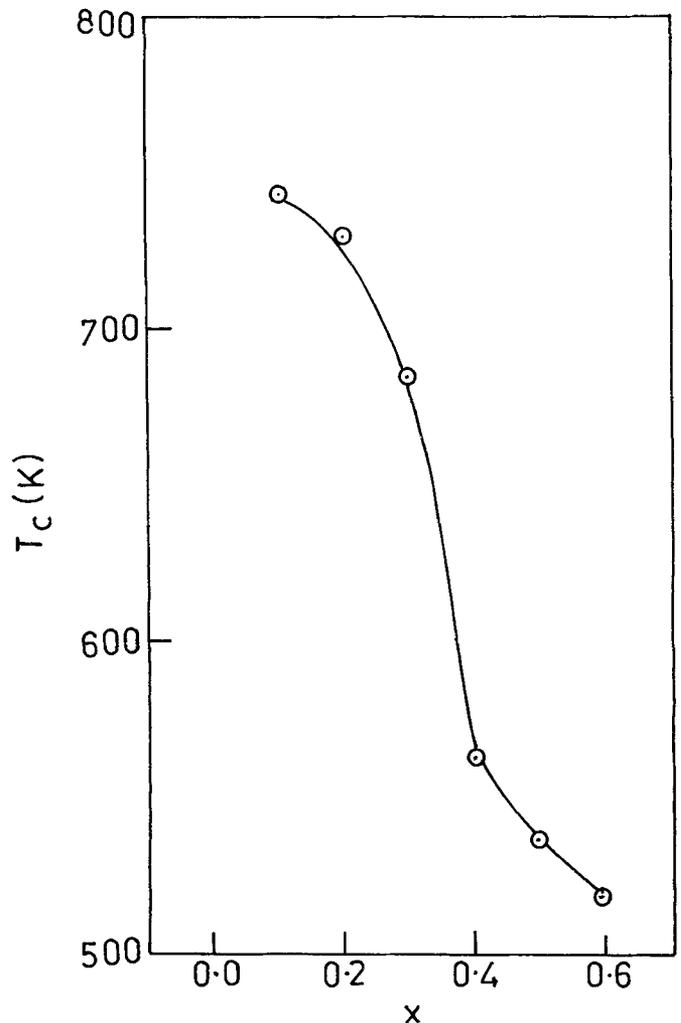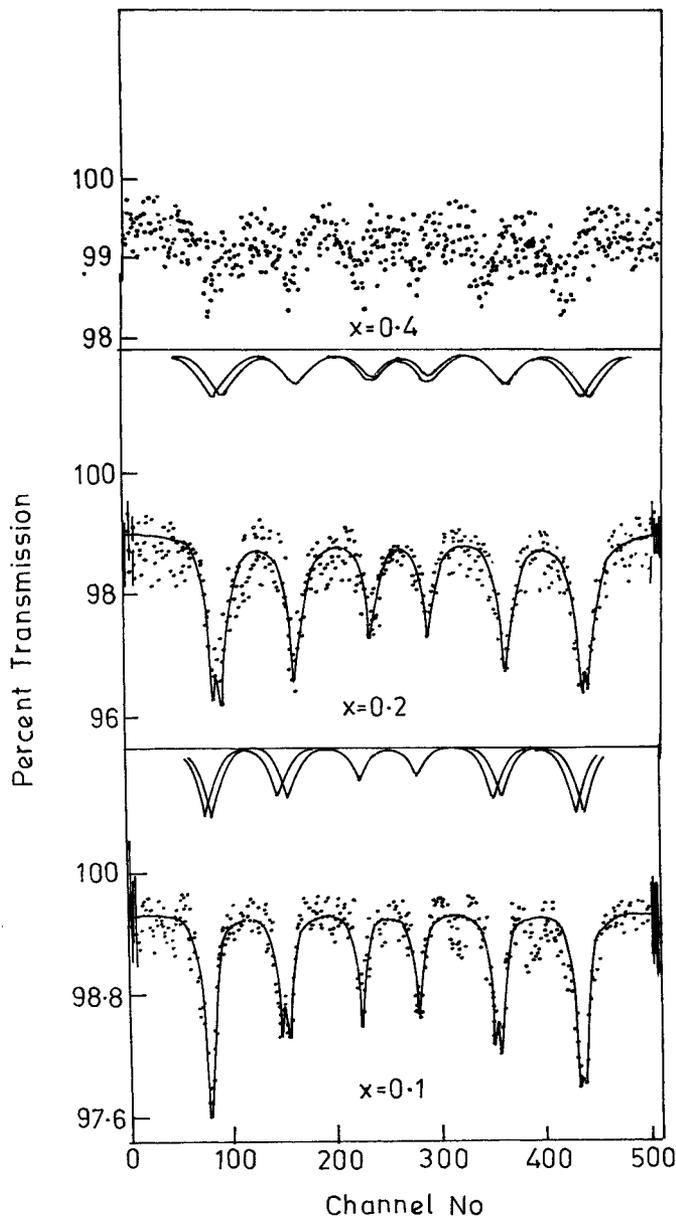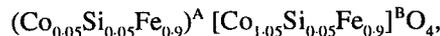**Figure 5.** Variation of Curie temperature with concentration x.

Figure 6. Typical Mössbauer spectra of $Co_{1+x}Si_xFe_{2-2x}O_4$ taken at 300 K for $x = 0.1$, 0.2 and 0.4.

cation distribution of $Co_{1.1}Si_{0.1}Fe_{1.8}O_4$ can be best fitted by Mössbauer, magnetization and X-ray intensity data as:

$$(Co_{0.05}Si_{0.05}Fe_{0.9})^A \, [Co_{1.05}Si_{0.05}Fe_{0.9}]^B O_4,$$

and this cation distribution is maintained throughout the series for $x = 0.1-0.6$ as shown in (3). Accordingly, the cation distribution of $Co_{1.2}Si_{0.2}Fe_{1.6}O_4$ is modified to

$$(Co_{0.05}Si_{0.16}Fe_{0.79})^A \, [Co_{1.15}Si_{0.04}Fe_{0.81}]^B O_4,$$

which agrees very well with (3).

Both hyperfine fields (H_A and H_B) decrease with increasing x (table 1) thereby demonstrating a reduction in ferrimagnetic behaviour and magnetic coupling, J_{AB}, which is in agreement with the Curie temperature behaviour (figure 5). Isomer shifts, $IS(A)$ and $IS(B)$, show an increase in increasing Si content thereby indicating that s-electron distribution of Fe^{3+} ions is greatly influenced by Si distribution. No significant change in quadrupole splitting (QS) for both A- and B-sites has been observed.

According to Neel's (1950) two-sublattice model of ferrimagnetism, the magnetic moment per formula unit in μ_B, n_B^N, is expressed as:

$$n_B^N(x) = M_B(x) - M_A(x), \tag{4}$$

where M_B and M_A are the B and A sublattice magnetic moments in μ_B. $n_B^N (\mu_B)$ values for $x = 0.1-0.6$ were calculated using (3), and also the ionic magnetic moments of Fe^{3+} ($5\,\mu B$), $Co^{2+}(3\,\mu B)$ and Si^{4+} ($0\,\mu B$). As the experimental $n_B(x)$ values are obtained at 300 K, they can not be compared with $n_B^N (\mu_B)$ values which are valid at $0°K$. Therefore, the relative magnetic moments $n_B(x)/n_B(0)$ at 300 K are shown in figure 4. The calculated $n_B^N (x)/n_B^N(0)$ values for $x = 0.0-0.3$ are in good agreement with the experimentally recorded $n_B (x)/n_B(0)$ values, confirming the collinear spin ordering. But for $x = 0.4-0.6$, they clearly differ from the observed values (figure 4) and thereby indicate that significant canting exists on B

Table 1. Mössbauer parameters obtained at 300 K for $Co_{1+x}Si_xFe_{2-2x}O_4$. The isomer shift is with respect to iron metal.

Sample x	Site	Hyperfine field H_f (kOe)	Isomer shifts (mm/s)	Quadrupole splitting (mm/s)	Area ratio (Fe(B)/Fe(A))
0.1	B	500 ± 2	0.14 ± 0.07	0.17 ± 0.08	1.0
	A	483 ± 2	0.14 ± 0.07	0.09 ± 0.08	
0.2	B	493 ± 2	0.23 ± 0.07	0.02 ± 0.02	1.0
	A	472 ± 2	0.24 ± 0.10	0.03 ± 0.02	
0.4		Relaxation spectrum			

site and the magnetic structure is noncollinear. Thus the change of spin ordering from collinear to noncollinear displays a strong influence on the variation of saturation magnetic moment per molecule as observed by magnetization (figure 4) with chemical composition. A noteworthy observation is similar anomalous behaviour in X-ray intensity data (figure 3), lattice parameter (figure 2) and Mössbauer data (figure 6) for $x > 0.3$ which has been observed due to the change of spin ordering from collinear to noncollinear.

The experimentally integrated intensity ratios of the A and B sites ^{57}Fe spectra, and those calculated on the basis of the cation distribution given in (3), are in good agreement with each other for $x \leq 0.3$. This confirms the cation distribution formula (3) as it agrees with X-ray intensity, Mössbauer and magnetization data satisfactorily.

4. Conclusion

X-ray and Mössbauer intensity data analyses have estimated the cation distribution of the system $Co_{1+x}Si_xFe_{2-2x}O_4$, showing that the Si^{4+} ions substitute for A site iron and the added Co^{2+} for the B site iron, without any change with x in the initial degree of inversion. Magnetization measurements exhibit Neel's collinear magnetic structure for $x = 0.0-0.3$, which is further supported by the Mössbauer, X-ray, and T_c data.

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