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A Mössbauer and x-ray diffraction investigation of Li-Ti ferrites

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Abstract. $\text{Li}_{0.5+0.5x}\text{Ti}_x\text{Fe}_{2.5-1.5x}\text{O}_4$, $x \leq 0.7$, has been investigated using x-ray powder diffraction ($17-70^\circ 2\theta$) and Mössbauer spectroscopy (300 and 77 K). All compositions show single cubic spinel structure with a constant lattice parameter of 0.833 nm. The room temperature Mössbauer spectra gave magnetic sextets which broadened with increasing x ; in addition, a small paramagnetic component started to develop for higher Ti substitution. The 77 K measurements are less broadened, but the intensity of the central doublet has not changed. The Zeeman patterns were fitted with two models: two six-line Lorentzian subspectra assigned to the tetrahedral and octahedral sites and a distribution of magnetic hyperfine fields. The hyperfine fields at both temperatures for the A and B sites decrease as x increases, but at a faster rate for the former site when $x > 0.3$. Similar distribution profiles have been deduced using the latter model. An asymmetric distribution is observed for $x \leq 0.4$, with the hyperfine fields derived from the Lorentzian fit falling inside the distribution. As x increases a peak at lower hyperfine fields develops and becomes more prominent as x increases. The influence of Li and Ti substitution on the hyperfine field is discussed.

1. Introduction

There have been many investigations of mixed ferrites containing Li and/or Ti, using Mössbauer and other magnetic techniques to study their magnetic properties. Temperature- and external-magnetic field-dependent Mössbauer measurements show spectra that are similar to those for ferrites with diamagnetic substitution. At certain temperatures, and for magnetic dilution within certain ranges, the Mössbauer spectrum consists of an asymmetric broadened sextet component and a central quadrupole doublet. The contribution of the latter component is commonly found to increase with increasing temperature, with decreasing concentration of magnetic ions and with decreasing external magnetic fields. These observations were commonly explained as the occurrence of superparamagnetic clusters of non-uniform size having blocking temperatures that depend on the cluster size. Mössbauer and other supporting techniques, such as magnetization and susceptibility, measurements have given very useful data for the interpretation of the magnetic structure and canting effects of these systems [1].

Mössbauer data on the Li-Zn, Mg-Ti and Li-Ti ferrites have shown evidence for spin canting. In Li-Zn ferrites a relatively large amount of reversed spin has been suggested [2]. Cluster formation has been proposed for the interpretation of the temperature-dependent Mössbauer spectra of Mg-Ti ferrites with an increased probability of formation as the

number of magnetic A–O–B linkages decreases [3]. Brand and co-workers [4] have made similar studies with increased diamagnetic substitution and have reported two successive magnetic transitions: a paramagnetic-to-ferrimagnetic transition and a ferrimagnetic-to-spin-glass transition, with a strong spin canting observed starting at the latter transition [4].

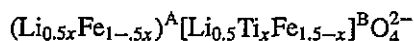
The Li–Ti spinels were also investigated and spectra for compositions with a higher Ti content ($x > 0.7$) show relaxed patterns with a central doublet that has been attributed to superparamagnetic clusters [5]. Dormann and co-workers [6] performed detailed investigations on disordered Li–Ti ferrites with high Ti substitution. For $x = 1.25$, they observed two magnetic transitions similar to those reported by Brand and co-workers for Mg–Ti ferrites [6]. Their data were interpreted as spin canting at both A and B sites combined with a transverse-component relaxation between preferential directions between the two transition temperatures. In the light of these new interpretations we have reinvestigated the system for low Ti content.

2. Experimental

The polycrystalline samples of the mixed ferrite $\text{Li}_{0.5+0.5x}\text{Ti}_x\text{Fe}_{2.5-1.5x}\text{O}_2$, $x \leq 0.7$, were prepared by the standard ceramic techniques using high-purity analytic reagents LiCO_3 , Fe_2O_3 and TiO_2 . Powder x-ray diffraction (XRD) patterns were recorded for the finest powder samples on a Philips diffractometer (model PW 1024/00) and a $\text{Co K}\alpha$ source. Mössbauer measurements were performed on powder samples in a continuous liquid nitrogen flow cryostat using a $^{57}\text{CoRh}$ source with a spectrometer in the transmission mode interfaced to a PC-based multichannel analyser; metal iron was used for the calibration. Data analyses were performed using least-square fitting programs.

3. Results and discussion

At all compositions the Li–Ti ferrites samples could be indexed in terms of a single-phase cubic spinel structure. The x-ray diffraction patterns for the samples in the $17\text{--}60^\circ 2\theta$ range are presented in figure 1. The main reflection planes (220), (311), (400), (511) and (440) appear in all patterns. While the reflections of the (111) plane do not show up for the samples with $x = 0.1$ and 0.2 , other low-angle resolved peaks, such as those for the (210) and (211) planes, appear for samples with low Ti content ($x \leq 0.3$). The d spacings were calculated and lattice parameters extracted from the reflection planes. These parameters were fitted using the extrapolation function $F(\theta) = \frac{1}{2}(\cos^2 \theta / \sin^2 \theta - \cos^2 \theta / \theta)$ and precise lattice parameters (a_{exp}) have been taken as those extrapolated to $\theta = 90^\circ$ ($F(\theta) = 0$). The measured lattice parameter is nearly constant for all samples ($a_{\text{exp}} = 0.833$ nm) in agreement with those reported by Blasse [7] (0.834 nm for $x = 0.33$ and 0.835 nm for $x = 0.67$). This is not unexpected on replacement of cations of about equal radii ($r_{\text{Fe}^{3+}} = 0.64$ nm, $r_{\text{Li}^+} = 0.68$ nm, $r_{\text{Ti}^{4+}} = 0.68$ nm), and thus the cationic substitution has not affected the total size of the lattice in the whole concentration range. The cationic distribution for the polycrystalline ferrite is taken as [8]



where Ti is localized in the octahedral (B) sites and Li for more than 0.5 atoms move into tetrahedral (A) sites.

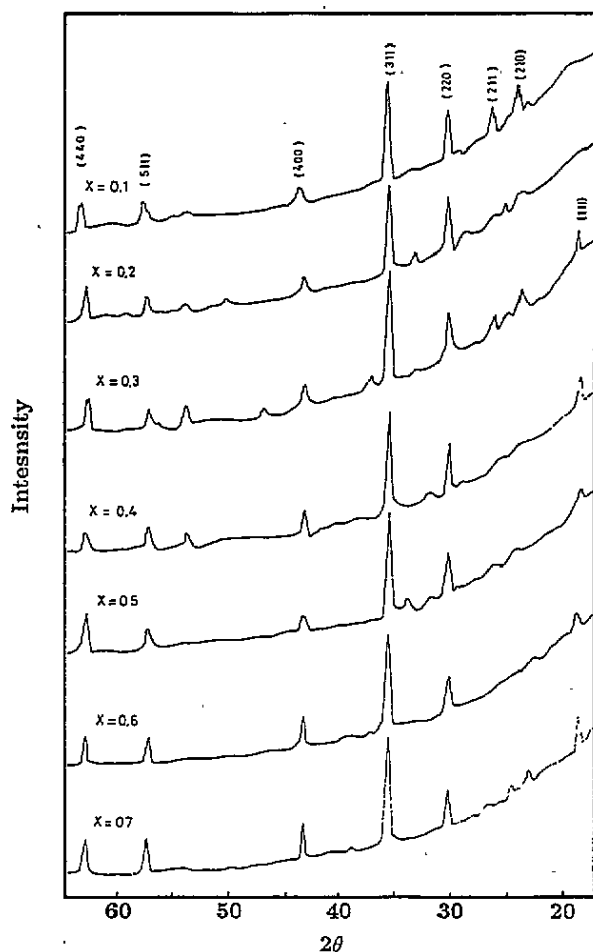


Figure 1. X-ray diffraction patterns of $\text{Li}_{0.5+0.5x}\text{Ti}_x\text{Fe}_{2.5-1.5x}\text{O}_4$.

Theoretical lattice constants (a_{th}) may be estimated from the ionic radii of the A sites (r_{A}), B sites (r_{B}) and the radius of oxygen ion (r_{O}) [9], using

$$a_{\text{th}} = (8/3\sqrt{3}) [(r_{\text{A}} + r_{\text{O}}) + \sqrt{3}(r_{\text{B}} + r_{\text{O}})].$$

The cationic distribution defined above has been employed to calculate the ionic radius of each site (r_{A} and r_{B}) for the different compositions using

$$r_{\text{A}} = 0.5[xr_{\text{Li}^{1+}} + (1 - 0.5x)r_{\text{Fe}^{3+}}]$$

$$r_{\text{B}} = 0.5[0.5r_{\text{Li}^{1+}} + xr_{\text{Ti}^{4+}} + (1.5 - x)r_{\text{Fe}^{3+}}].$$

The experimental values for the lattice parameters were approximately constant at 0.833 nm. The theoretical lattice parameters calculated using the above cationic distribution were 0.828 nm for $x = 0.1$ to 0.833 nm for $x = 0.7$. A model that assigns more than 0.5Li^{1+} onto the octahedral sites would give theoretical lattice constants that are much smaller than the measured ones. These results support the cationic distribution proposed above.

The Mössbauer spectrum measured at room temperature for each sample shows broadened Zeeman patterns with a small paramagnetic doublet superimposed on the

Table 1. Intensities of the Mössbauer components for Fe^{3+} on A and B sites from the fit of the room temperature measurements and calculated distribution of Li, Ti and Fe on the two sites.

x	I_A (%)	I_B (%)	Fe_A	Li_A	Fe_B	Li_B	Ti_B
0.1	40.1(17)	59.9(19)	0.94(4)	0.05	1.41(4)	0.5	0.1
0.2	41.3(06)	58.7(07)	0.91(1)	0.10	1.29(2)	0.5	0.2
0.3	39.3(10)	60.7(08)	0.81(2)	0.15	1.24(2)	0.5	0.3
0.4	43.9(08)	56.1(14)	0.83(2)	0.20	1.07(3)	0.5	0.4
0.5	44.2(12) ^a	55.8(07)	0.77(2)	0.25	0.98(1)	0.5	0.5
0.6	44.5(13)	55.5(07) ^b	0.71(2)	0.30	0.89(1)	0.5	0.6
0.7	44.1(09)	55.9(11) ^c	0.64(1)	0.35	0.81(2)	0.5	0.7

^a On accounting for a paramagnetic component 3.0% comes from this site.

^b On accounting for a paramagnetic component 3.4% comes from this site.

^c The paramagnetic contribution is 3.4% added to this site.

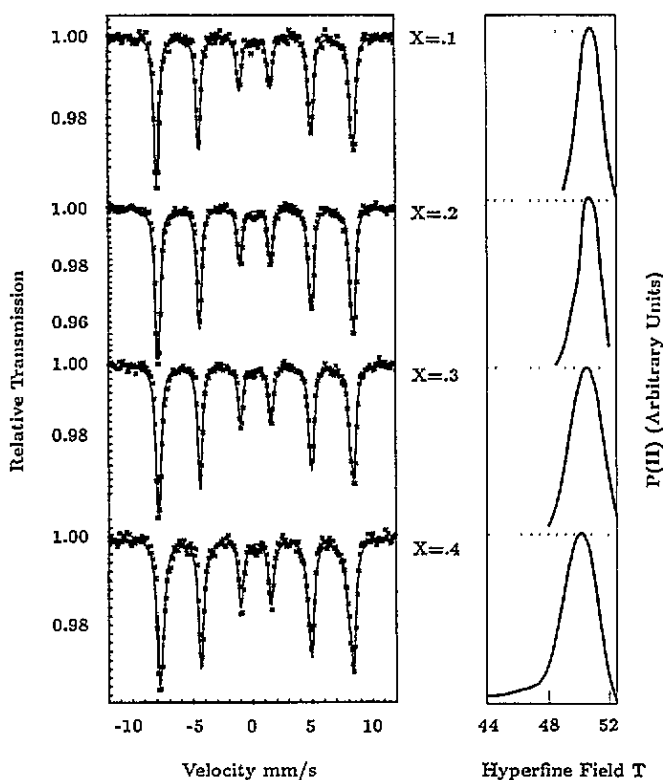


Figure 2. Room temperature Mössbauer spectra and distribution $P(H)$ for $x \leq 0.4$.

magnetic sextets, which slightly increases for higher values of x . The magnetic sextets become more broadened as x increases. The spectra were fitted with two sextets or with two sextets and a singlet Lorentzian, as the spectrum requires. Figure 2 shows room temperature spectra for $x \leq 0.4$ fitted with Lorentzian lines, and table 1 presents the intensities of the Mössbauer components of Fe^{3+} and calculated site distribution of Li, Ti and Fe at the tetrahedral and octahedral sites. The data strongly supports the cationic distribution suggested above. On the other hand, the occupation of all Li ions onto the

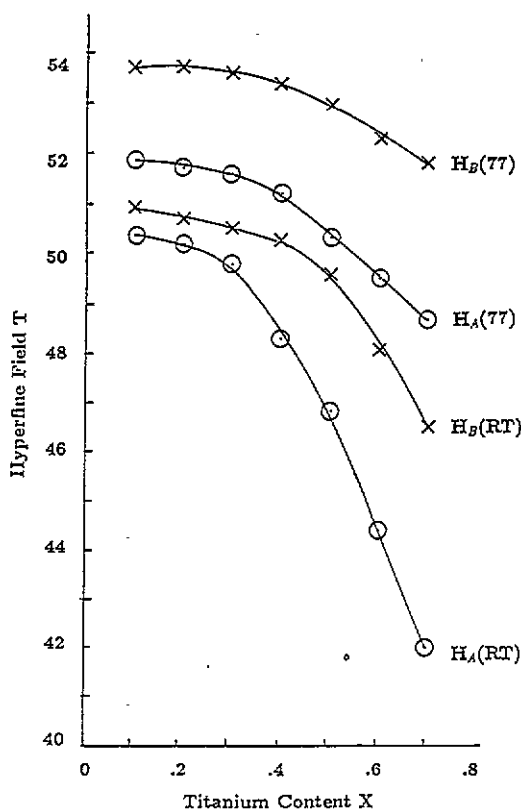


Figure 3. The dependence of the hyperfine fields at the A and B sites on Ti content derived from the room temperature and 77 K measurements.

octahedral sites would have shown a higher relative intensity of the Fe_A component. An estimate of the average hyperfine field at the A (H_A) and B (H_B) sites has been derived and plotted in figure 3. The linewidth of the outer absorption lines of each site gives an estimate of the distribution of the hyperfine fields at that site, and has been measured as $\Gamma = 0.38 \text{ mm s}^{-1}$ (1.2 T) for $x = 0.1$ which increases to $\Gamma = 0.70 \text{ mm s}^{-1}$ (2.2 T) for $x = 0.7$. The 77 K measurements for all samples show similar patterns to the room temperature ones, but with less-broadened sextets coexisting with a central doublet at higher values of x . The spectra were fitted in a similar manner and the values of the hyperfine fields plotted along with the room temperature values. Both the hyperfine field and isomer shift for ferric ions at the octahedral sites are larger than the corresponding ones at the tetrahedral sites, as expected in spinel oxides. This has been explained by van Loef as due to the more covalent character of the Fe^{3+} bonds to the oxygen neighbours at the tetrahedral sites as compared to the octahedral ones [10]. The hyperfine fields at the tetrahedral and octahedral sites decrease with diamagnetic substitution (Li^{1+} and Ti^{4+}). Both the room temperature and 77 K measurements show the same trend of H_A and H_B , namely the same rate of decrease for $x \leq 0.3$, but as the substitution increases, a faster rate of decrease has been observed at the A sites. We substitute simultaneously Ti^{4+} on the octahedral sites and Li^{1+} on the tetrahedral sites for Fe^{3+} in steps of $0.1Ti^{4+}$ and $0.05Li^{1+}$. It appears that in this concentration range (for $x > 0.3$) a weaker superexchange interaction has been monitored at the A sites, which may reflect the influence of substitution of more Ti on the B sites compared to Li on the A sites. The trend of the hyperfine field dependence with Ti substitution (in steps of 0.1) shown in figure 3, is qualitatively similar to that

reported by Kishan and co-workers [5] for $0 \leq x \leq 0.8$ (in steps of 0.2). However, the magnitude of their reported hyperfine fields are consistently smaller. For $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ we extract, from their figure, $H_A(300) = 47.9 \text{ T}$, $H_B(300) = 48.7 \text{ T}$, $H_A(77) = 49.1 \text{ T}$ and $H_B(77) = 50.7 \text{ T}$. These values are smaller than those reported by Des Barros and co-workers [11] ($H_A(300) = 50.5 \text{ T}$, $H_B(300) = 51.0 \text{ T}$); Dormann and co-workers [12] ($50.0 \leq H_A(300) \leq 50.7 \text{ T}$, $50.7 \leq H_B(300) \leq 51.6 \text{ T}$, $51.1 \leq H_A(77) \leq 52.2 \text{ T}$ and $52.4 \leq H_B \leq 53.4 \text{ T}$). On extrapolating to $x = 0$ from figure 3 of the present studies, we get $H_A(300) = 50.5 \text{ T}$, $H_B(300) = 51.0 \text{ T}$, $H_A(77) = 51.9 \text{ T}$ and $H_B(77) = 53.7 \text{ T}$, in excellent agreement with those reported by the latter authors. A similar trend has been reported for Cd-substituted copper ferrites, where diamagnetic Cd^{2+} occupies the A sites resulting in a more pronounced decrease of the hyperfine field at the B sites [13]. The isomer shifts at both sites show no significant variation with Ti^{4+} , indicating that the s electron density is not influenced by the substitution. Weighted-average isomer shifts at 77 K have been calculated, giving $\delta_A = 0.29(0.02) \text{ mm s}^{-1}$ and $\delta_B = 0.40(0.02) \text{ mm s}^{-1}$, in good agreement with the $(\delta_B - \delta_A) = 0.14 \text{ mm s}^{-1}$ reported by Vandenberghe and De Grave [1].

The occurrence of a paramagnetic component superimposed on broadened magnetic sextets in ferrites with diamagnetic substitution indicates various competing short-range order effects with the long-range order. Superparamagnetism has been cited as the cause for the phenomenon in many systems such as Li-Z ferrites [14] and in $\text{Mg}_{1+x}\text{Fe}_{2(1-x)}\text{Ti}_x\text{O}_4$, $x \geq 0.4$ [3]. It has been suggested that in these systems magnetically ordered clusters are separated from each other by the non-magnetic ions. In the system $\text{Li}_{0.5+0.5x}\text{Ti}_x\text{Cr}_{0.3}\text{Fe}_{2.2-1.5x}\text{O}_4$, $0.0 \leq x \leq 1.0$, the relative intensity of the central doublet was observed to increase as diamagnetic substitution increases and as the temperature decreases from 300 to 77 K [15]. Entropic clusters have been suggested as the cause for the origin of the doublet. In the present studies a minor paramagnetic component of Fe ions appears and increases slightly in intensity as Ti increases. This central component, although reduced in some samples, does not disappear completely in the 77 K spectra. The x-ray patterns do not suggest any other iron-bearing impurities in the samples. Moreover, similar paramagnetic contributions appeared in the room temperature spectra that were presented by Kishan and co-workers [5], where a significant component of the central doublet was observed for the $x = 0.2$ sample, which slightly reduces in the $x = 0.4$ down to a minor component for $x = 0.6$. In addition, their 77 K data have shown that the intensity of the central doublet has not changed significantly from the room temperature one in all samples. Dormann and co-workers [16] have investigated a Li-Ti ferrite system with high Ti substitution ($0.735 \leq x \leq 1.25$). They observed relaxed patterns and a paramagnetic doublet for high Ti content, and explained their data by two relaxation mechanisms: a spin-spin relaxation and a relaxation between the possible directions of the canted spins related to a semi-spin-glass order. At higher Ti content ($x > 0.9$) the central doublet persists at 77 K, decreasing in intensity as the temperature decreases and completely disappearing at 4.2 K. The presence of the doublet has been explained as due to some cluster-type magnetic ordering. Although a conclusive explanation could not be given for the minor paramagnetic component that has been detected in the present studies, the development of clusters with the introduction of Ti in $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ is likely to be the cause. The growth of a central doublet superimposed on the magnetic pattern in ferrites with diamagnetic substitution has been observed in many systems reflecting increased probability of cluster formation with decreasing number of magnetic A-O-B linkages [1]. It should be noted that when discrete subspectra were used to fit the patterns of the present study, including the central component, it was observed that the Fe ions of this component showed no preference for either A or B sites (table 1).

We have also looked into the details of the hyperfine field distribution of the room

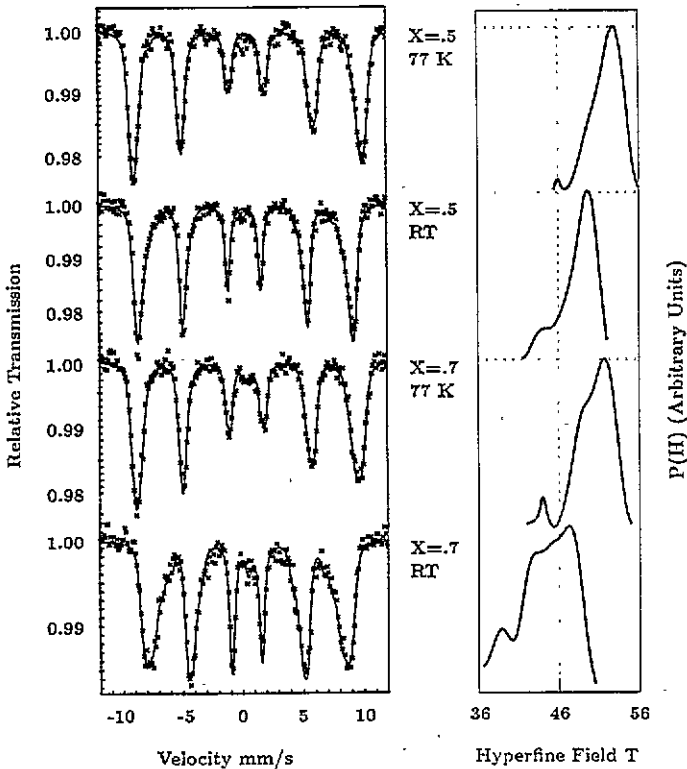


Figure 4. Mössbauer spectra and calculated distribution $P(H)$ at room temperature and 77 K for $x = 0.5$ and 0.7 .

temperature and 77 K spectra by fitting the spectra with a hyperfine field distribution and one doublet as necessary, using the NORMOS fitting program described by Brand and co-workers [17]. Similar distribution profiles have been deduced for the two measurements of each sample, with the peak of the distribution shifting towards high hyperfine fields in the 77 K spectra. The right-hand side of figure 2 presents the distribution for the $x \leq 0.4$ spectra. We also show in figure 4 representative spectra for $x \geq 0.5$ and their theoretical curve using a fit with a distribution of hyperfine fields, and the calculated distributions are plotted alongside. The high field is dominated by the distribution of the magnetic field at the B sites with a steeper slope for low Ti substitution. The low field slope extends over a broad distribution as x increases. The average hyperfine fields at the A and B sites for $x \geq 0.5$ derived from the Lorentzian fit fall inside the distribution. A peak at hyperfine fields lower than H_A and H_B , which becomes more prominent in strength and lower in field value, develops as the Ti concentration increases. From the room temperature data we find 7% of iron atoms distributed in the lower magnetic field region around a peak value of 43.5 T. The population of this magnetic component has increased to 17% around a peak of 39 T at $x = 0.7$. Well resolved but less intense profiles have been observed for the same from the 77 K data. Less than 2% remains in this magnetic component around a peak field of 46 T for the $x = 0.5$ sample, while about 5% is found in the $x = 0.7$ sample around a peak field of 43.5 T. The occurrence of this magnetic component could be related to the onset of clusters triggered by the presence of non-magnetic ions in the Li-Ti system ($x \geq 0.5$). Preferred configurations start to take shape at, and above, these concentrations

and have manifested themselves in the occurrence of the component which may be related to development of the various magnetic phases reported for higher Ti concentrations.

4. Conclusion

We have analysed the Mössbauer spectra of $\text{Li}_{0.5+0.5x}\text{Ti}_x\text{Fe}_{2.5-1.5x}\text{O}_4$ with two models: two sextets and a singlet and a distribution of hyperfine fields. The x-ray diffraction and Mössbauer data support the cationic distribution having 0.5Li and Ti occupying the B sites and excess Li on the A sites. The hyperfine fields at the tetrahedral and octahedral sites decrease with diamagnetic substitution, but with a faster rate at the former for $x \geq 0.4$. The small paramagnetic component that develops with Ti substitution indicates cluster formation. The distribution function resulted from the fit of the Zeeman patterns using the second model show the development of a low magnetic field component for $x > 0.5$. The intensity of the latter increases with Ti substitution and decreases with temperature. The development of this magnetic component starting from $x = 0.5$ indicates cluster formation that may be related to other magnetic phases that have been reported for highly diluted systems.

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