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Ionic valences and spin structure of \( \text{Co}_{0.6}\text{Fe}_{0.9}\text{Mn}_{1.5}\text{O}_{4} \) investigated by NMR and XAS

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Abstract. The oxidation and spin states of the three cations in \( \text{Co}_{0.6}\text{Fe}_{0.9}\text{Mn}_{1.5}\text{O}_{4} \), showing a nano-checkerboard structure, were investigated using nuclear magnetic resonance (NMR) and x-ray absorption spectroscopy (XAS) techniques. Comparison of the Co, Fe and Mn 2p XAS spectra with reference spectra suggests the presence of Co\(^{2+} \), Co\(^{3+} \), Fe\(^{3+} \), Mn\(^{2+} \) and Mn\(^{3+} \). Four distinctive NMR peaks were observed in the wide spectral range of 50–610 MHz. The external field dependence of the peaks and comparison of the peaks with those in other spinels also confirm the existence of the cation oxidation states suggested by XAS. Analysis of these results, combined with the magnitude of saturated magnetization, indicates an average chemical formula of \((\text{Mn}^{2+}\text{Co}^{2+}_{1-x})_{x}[\text{Co}^{3+}_{x-0.4}\text{Mn}^{3+}_{1.5-x}\text{Fe}^{3+}_{0.91}\text{O}_{4}]\) with \( x \sim 0.9 \). Thus, \( \text{Co}_{0.6}\text{Fe}_{0.9}\text{Mn}_{1.5}\text{O}_{4} \) appears to be a ferrimagnet with the majority spins from Fe\(^{3+} \), Co\(^{2+} \) and Mn\(^{3+} \) and the minority spins from Co\(^{3+} \) and Mn\(^{2+} \).

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1. Introduction

Nanotechnology aims to create and use structures and devices on the nanometer scale. Well-ordered nanostructures might introduce new possibilities to industries facing serious difficulties in continuing miniaturization, particularly in microelectronics and magnetic data storage. One of the interesting classes of nanostructured materials with extraordinary functional properties is the self-assembled inorganics. Recently, reports that the spinels ZnMnGaO$_4$, MgMn$_{1.5}$Fe$_{0.5}$O$_4$ and Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ show a nano-checkerboard pattern have attracted much interest. These materials have a single structure when quenched but have a checkerboard pattern composed of two different structures with different chemical phases when properly annealed. One of the structures is cubic and the other is tetragonal or orthorhombic.

This structural and chemical phase separation is explained by the Jahn–Teller (JT) distortion frequently found in spinels. In the spinels, whose chemical formula is expressed as AB$_2$O$_4$, transition metal ions occupy either the tetrahedral (A) site or the octahedral (B) site. The highest energy level occupied by the 3d$^4$ electrons of an Mn$^{3+}$ ion in the B site is the e$_g$ state. A distortion along the z-axis, usually elongation, removes the degeneracy of the e$_g$ state and lowers the energy of this JT ion. In a material with the nano-checkerboard pattern, two rods consisting of the pattern have different amounts of the JT ions. A rod with fewer JT ions will have cubic structure and a rod with more JT ions will have tetragonal or orthorhombic structure because of the distortion.

ZnMnGaO$_4$ is a paramagnet at room temperature with a well-defined nano-pattern [1]. By contrast, MgMn$_{1.5}$Fe$_{0.5}$O$_4$ is ferromagnetic at room temperature where the rod with cubic structure has magnetization but the rods are not well distinguished [2]. Among the spinels showing the checkerboard pattern, Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ has the most promising properties. That is, the nano-structure of this material is well defined and both of the rods have magnetization [3]. A material showing a nano-pattern composed of two different magnets has high potential as a magnetic medium. The structure and the saturated magnetization of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ change with the annealing time in the preparation process. While water-quenched samples have an unstable cubic structure, samples annealed for several tens of minutes have an unstable tetragonal structure. Samples annealed for several tens of hours have both the cubic and tetragonal structures simultaneously. The saturated magnetization decreases with an increase in annealing time.

Since this peculiar structural transition is generated by transport of the JT ions, information on the oxidation states and locations of the ions in the lattice (A or B sites) is essential for understanding the phenomenon. Interpretation of the variation of the saturated magnetization requires knowledge of the magnetic moment of each ion. In this work, the oxidation states of
three transition metal ions in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ found by x-ray absorption spectroscopy (XAS) are reported. The oxidation states were also estimated from the nuclear magnetic resonance (NMR) spectrum obtained in zero external field, and the result was compared with that obtained in the XAS measurement. The directions of the magnetic moments of the cobalt and manganese ions were determined by measuring the NMR spectral shift in the external field, and suggested the chemical formula of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$, based on the analysis of all the experimental data.

2. Experiment

A polycrystalline Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ sample was made by the solid-state reaction method. A mixed powder of Co$_3$O$_4$, MnO$_2$ and Fe$_2$O$_3$Fe$_2$O$_3$ was quenched immediately after having been sintered at 900–1150 °C. Commercially available CoFe$_2$O$_4$ powder with 99% purity (Kojundo Chemical Lab; Lot. No. 212451) was also used in the NMR experiment for comparison. Soft XAS experiments were performed at the 8A1 undulator beamline of the Pohang Accelerator Laboratory (PAL). The base pressure of the chamber was $\sim 5 \times 10^{-10}$ Torr. The sample was cleaned in situ by repeated scraping with a diamond file. XAS data were collected in the total electron yield mode. All the XAS data were obtained at room temperature and the total resolution for the XAS was $\sim 100$ meV at $h\nu \sim 600$ eV. NMR spectra were obtained by measuring spin echo intensity using a purpose-built spectrometer in the wide spectral range of 50–610 MHz at liquid helium temperature. The echo height was measured as a function of frequency after partial excitation by a pulse with a width of 1 $\mu$s because the spectrum was several tens of MHz wide.

3. Results and discussion

NMR is a useful tool for measuring the local magnetic field. The resonance frequency of the NMR spectrum is given by

$$f = \frac{\gamma_n}{2\pi} |\vec{H}_{\text{ext}} - A\vec{\mu}|,$$

where $\gamma_n$ is the nuclear gyromagnetic ratio that varies with nuclear species. $\vec{H}_{\text{ext}}$ represents the external field, and $A$ and $\vec{\mu}$ represent the hyperfine constant and magnetic moment, respectively. In zero external fields, the resonance frequency is proportional to the magnetic moment of the ion to which the nucleus belongs. Since the magnetic moment $\vec{\mu}$ is closely related to the ionic oxidation state, the NMR spectrum of magnets provides information on the ionic oxidation state of a selected nucleus. An NMR experiment in an external field can determine the direction of magnetic moments. Although our sample is polycrystalline, the hyperfine field is either parallel or antiparallel to the external field because the external field strength used in the experiment is much higher than the anisotropy field of the sample. Equation 1 predicts that the resonance frequency decreases with an increase in the external field if the direction of the magnetic moment is parallel to that of the external field, because the hyperfine constants of manganese and cobalt with respect to their spins are positive, and increases if antiparallel.

Figure 1(a) is a plot of the NMR spectrum for the water-quenched Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ obtained in zero external field at 8 K. Since the spectral range is quite broad, the relative peak heights cannot be rigorously compared. In the entire spectral range of 50–610 MHz, four
Figure 1. NMR spectra of Co$_{0.6}$Fe$_{0.3}$Mn$_{1.5}$O$_4$ obtained in zero magnetic field at 8 K (a) and in external magnetic field at 4 K (b). In (b), peaks 1, 2 and 3 were obtained at 4 T, whereas peak 4 was obtained at 1 T. NMR spectrum of CoFe$_2$O$_4$ obtained in zero magnetic field at 4 K (c).

distinctive peaks were observed, as shown in the figure. The peaks are designated as peaks 1, 2, 3 and 4, from the left. To match the magnetic ions with the peaks, the NMR spectrum was measured at 4 T and compared with the one obtained in zero field (figure 1(b)). The peaks 1, 2 and 3 shifted about 40 MHz from the original position at 4 T and peak 4 disappeared out of the experimental spectral range. Since the gyromagnetic ratios of Fe, Co and Mn nuclei are 1.38, 10.07 and 10.57 MHz T$^{-1}$, respectively, the spectral shifts expected at 4 T are 5.52, 40.28 and 42.28 MHz, respectively. Therefore, peaks 1, 2 and 3 are not spectra issuing from Fe ions but from Co or Mn ions. The spectral shift of peak 4 was measured again at 1 T because it was believed to shift outside of the available spectral range at 4 T. In figure 1(b), the shifted spectra of peaks 1, 2 and 3 were obtained at 4 T and that of peak 4 at 1 T. The spectral shift of peak 4 at 1 T should be about 8 MHz; therefore, peak 4 is not the spectrum coming from Fe ions but from Mn or Co ions. All four experimentally observed peaks came from Co or Mn ions. Considering the gyromagnetic ratio and usual hyperfine field of Fe nuclei in spinels, the Fe NMR spectrum is expected to overlap the broad peak 1, but its shifted
The entire spectrum was compared with that of other spinel magnets to determine whether a Co or Mn ion produces each peak. The NMR frequency is proportional to the hyperfine constant and the magnetic moment of the ion that the nucleus belongs to in the zero external field, according to equation (1). Since the hyperfine constant of a magnetic ion does not vary much in materials of the same structure, the NMR frequency of an ion in the spinel magnets is roughly proportional to the magnetic moment. The oxidation states of manganese ions in the A and B sites of MnFe$_2$O$_4$ are 2+ and 3+, respectively. The NMR frequency of the Mn$^{2+}$ ion was observed to be in the range of 540–600 MHz, and that of the Mn$^{3+}$ ion was observed to be in the range of 300–490 MHz [4, 5]. In figure 1(a), peak 4 was observed in the range of 550–610 MHz, which is similar to the spectral range of Mn$^{2+}$ in MnFe$_2$O$_4$, and peak 3 was observed in the range of 390–500 MHz, which is similar to the spectral range of the Mn$^{3+}$ ion in MnFe$_2$O$_4$. Therefore, peaks 3 and 4 are believed to come from the Mn$^{3+}$ and Mn$^{2+}$ ions, respectively, and peaks 1 and 2 from the Co ions. Mn$^{4+}$ ions, which may generate the NMR spectrum at a frequency lower than that of Mn$^{3+}$ and Mn$^{2+}$, were not considered because they were not observed in the XAS result.

The Co ion in the B site of CoFe$_2$O$_4$, which also has the spinel structure, has an oxidation state of 2+. The spectrum of Co NMR for CoFe$_2$O$_4$ has been observed in the wide frequency range of 250–600 MHz [6]. The same NMR experiment was repeated here in order to determine a more accurate spectrum. The spectrum observed in this experiment (figure 1(c)) was also in the wide range of 200–600 MHz, but shows a distinctive peak at 220 MHz. Another spinel of Co$_3$O$_4$ has Co$^{2+}$ ions in the A site and Co$^{3+}$ ions in the B site. It was claimed that the NMR spectrum of the Co$^{2+}$ ion was observed in the range of 50–58 MHz and that of the Co$^{3+}$ ion was observed only in the external magnetic field because the Co$^{3+}$ ion is in the low-spin state (t$_{2g}$)$^6$ (S = 0) [7]. Since peaks 1 and 2 are observed in a frequency range similar to that of previous Co NMR experiments, they are believed to come from the Co ions. However, Co ions of the same oxidation state can have different spin states and their spectra are found in several different frequency ranges. Therefore, it is difficult to determine the oxidation state of the Co ions generating peaks 1 and 2 by NMR experiments alone. As far as the Co ions are concerned, the result of the NMR experiment reveals only that there are two Co ions of different magnetic moments, and their oxidation states can be determined by the XAS experiment.

The direction of the magnetic moments can be determined by the spectral shift of the NMR peaks in the external field. In the external field, peak 4 (Mn$^{2+}$) shifted to the high-frequency side and peak 3 (Mn$^{3+}$) to the low side. The NMR spectrum shifts to the low (high)-frequency side when the direction of the magnetic moment is (anti-)parallel with the external field. Therefore, the magnetic moment of the Mn$^{2+}$ ion is antiparallel with the external field and that of the Mn$^{3+}$ ion is parallel. In the same way, the magnetic moment of peak 1 is antiparallel with the external field, while that of peak 2 is parallel.

Figure 2(a) compares the measured Mn 2p XAS spectrum of water-quenched Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ with those of reference manganese oxides, such as divalent MnO (Mn$^{2+}$: 3d$^5$) [8], divalent MnS [9], trivalent Mn$_2$O$_3$ (Mn$^{3+}$: 3d$^4$) [10] and tetravalent MnO$_2$ (Mn$^{4+}$: 3d$^3$) [8, 10]. This comparison shows that the lineshape of the Mn 2p XAS spectrum of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ is in-between those of MnO/MnS (Mn$^{2+}$) and Mn$_2$O$_3$ (Mn$^{3+}$), suggesting that Mn ions are in the Mn$^{2+}$–Mn$^{3+}$ mixed-valent states in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$.
Figure 2. (a) Comparison of the Mn 2p XAS spectrum of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ (CFMO) with those of reference manganese oxides. Similarly for (b) the Co 2p XAS spectrum and (c) the Fe 2p XAS spectrum of CFMO, respectively.

Figure 2(b) compares the measured Co 2p XAS spectrum of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ with those of reference cobalt oxides, such as trivalent LiCoO$_2$ (Co$^{3+}$: 3d$^6$) [11], divalent CoO (Co$^{2+}$: 3d$^7$) [12] and that of Co metal [13]. The lineshape of the Co 2p XAS spectrum of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ is similar to that of trivalent LiCoO$_2$, suggesting that Co ions in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ are mainly trivalent (3+). Some minor differences between LiCoO$_2$ and Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ seem to reflect the different local environments between them. In addition, a larger shoulder is observed in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ on the low-energy side (∼774 eV, marked with an arrow) than in LiCoO$_2$. This feature suggests that there is a small mixture of a divalent Co$^{2+}$ component in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$. Thus, Co ions in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ are probably in the Co$^{3+}$–Co$^{2+}$ mixed-valent states.

Figure 2(c) compares the measured Fe 2p XAS spectrum of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ (dots) with those of reference iron oxides, such as trivalent α-Fe$_2$O$_3$ (Fe$^{3+}$: 3d$^5$) (green line) [12, 14], trivalent γ-Fe$_2$O$_3$ (Fe$^{3+}$: 3d$^5$) (black line) [14], divalent FeO (Fe$^{2+}$: 3d$^6$) [12] and Fe metal [15]. The lineshape of the Fe 2p XAS spectrum of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ is qualitatively similar to those of α-Fe$_2$O$_3$ (Fe$^{3+}$) and γ-Fe$_2$O$_3$ (Fe$^{3+}$), but quite different from that of FeO (Fe$^{2+}$), indicating that the oxidation states of Fe ions in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ are mainly trivalent (3+). In particular, the peak positions and the lineshape of the Fe L$_2$ (2p$_{1/2}$) peak of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ are very similar to those of α-Fe$_2$O$_3$ (Fe$^{3+}$) and γ-Fe$_2$O$_3$ (Fe$^{3+}$), but different from those of FeO, which also supports the above conclusion.

Fe ions in both α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ are formally trivalent (Fe$^{3+}$), and the differences in the lineshapes between the two are due to the different site occupations between them [15, 16]: Fe ions in α-Fe$_2$O$_3$ occupy the A sites only, whereas Fe ions in γ-Fe$_2$O$_3$ occupy both the A and
B sites. Note that the relative intensity of the first peak ($\sim 707$ eV) with respect to the main peak ($\sim 709$ eV) in the L$_3$ (2p$_{3/2}$) edge of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ is larger than that of $\gamma$-Fe$_2$O$_3$ ($\text{Fe}^{3+}$) even though the broad line shape of the first peak in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ is similar to that of $\gamma$-Fe$_2$O$_3$. Considering the sharpness of this first peak in $\alpha$-Fe$_2$O$_3$, the integrated intensity of the first peak in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ would be comparable with that of $\alpha$-Fe$_2$O$_3$, but is certainly larger than that of $\gamma$-Fe$_2$O$_3$. Since such differences in the Fe 2p$_{3/2}$ peak between $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ arise from the different local environments of Fe ions [16], i.e. the octahedral versus tetrahedral sites, this finding suggests that most of the Fe$^{3+}$ ions in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ occupy the octahedral sites. Therefore, figure 2(c) shows that Fe ions are mainly trivalent ($\text{Fe}^{3+}$) and that most of the Fe$^{3+}$ ions occupy the B sites.

The distribution of the cations in the A and B sites can be estimated by analyzing the experimental results with the numbers and oxidation states of the cations and the number of the A and B sites in a chemical unit of a spinel. The results of the NMR and XAS experiments suggest that the chemical formula of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ is expressed by Mn$^{2+}$Mn$^{3+}_{1-x}$Co$^{2+}$Co$^{3+}_{x}$Fe$^{3+}$O$_4$ within experimental error. Considering the fact that the total oxidation of the cations is 8, $x + y = 1$, the chemical formula can therefore be rewritten as Mn$^{2+}_{1-x}$Mn$^{3+}_{1-x}$Co$^{2+}_{1-x}$Co$^{3+}_{x-0.4}$Fe$^{3+}_{0.9}$O$_4$. The XAS result indicates that the majority oxidation state of the Co ions is 3+, which leads to the condition that the ionic distribution parameter $x$ is less than but close to 1 ($x \lesssim 1$). Since the ratio of the numbers of the A and B sites in a spinel is 1 : 2, it is impossible that all 1.5 Mn ions occupy the A site. The XAS result predicting that most of the 0.9 Fe$^{3+}$ ions are located in the B site per chemical unit makes it also impossible that all 1.5 Mn ions occupy the B site. Therefore, it is believed that the Mn ions of different oxidation states occupy different sites. Since the Mn$^{3+}$ ions evoke JT distortion in the B site when this material makes the nano-checkerboard pattern, the case that the Mn$^{3+}$ ions are in the B site and the Mn$^{2+}$ are in the A site was considered. The opposite case is inconsistent with the experimental results in the most plausible model as described later.

The Co$^{2+}$ and Co$^{3+}$ ions can be located in either the A or B sites. If the Co$^{3+}$ ions are in the A site, $x$ is either 0.4 or 0.7 depending on whether Co$^{2+}$ ions are in the A site or B site, neither of which is consistent with the condition $x \lesssim 1$. Permitting a small Fe ion population in the A site or minor Fe ions other than Fe$^{3+}$, this is still far from being consistent with the experimental results, because $x \lesssim 0.7$ means Co$^{2+}$ is the major Co ion. If both of the Co ions are in the B site, $x = 1$, which is also contradictory to the condition of $x$ although it is theoretically possible if a small population of Fe ions are permitted in the A site. Contrary to these cases, any value of $x$ is allowed when the Co$^{2+}$ and Co$^{3+}$ ions are in the A and B sites, respectively.

The discussion up to this point is the best information we can obtain from our experiment. Further analysis is sensitive to the Fe ion distribution as shown above and requires an exact population of them, which can never be obtained experimentally. If we can assume that all the Fe ions are trivalent and located in the B site for brevity, however, we obtain a more detailed chemical formula considering our result together with magnetization data. This assumption eliminates the case that both of the Co ions are in the B site and leaves us with only the case that the Co$^{2+}$ and Co$^{3+}$ ions are in the A and B sites, respectively, that is, (Mn$^{2+}_{1-x}$Co$^{2+}_{x-0.4}$Mn$^{3+}_{1-x}$Fe$^{3+}_{0.9}$)$_3$B$_2$O$_4$. A degree of freedom in the ionic distribution makes this last case look the most plausible model.

The saturated magnetization of the sample is 3 $\mu_B$ per chemical unit [3]. The magnitude of the magnetic moment of each ion can be guessed from its oxidation state and from the direction of the NMR spectral shift in the external field. The magnetic moment of the Mn$^{2+}$ ion
is expressed as $-5 \mu_B$ and that of the Mn$^{3+}$ ion as $+4 \mu_B$, where the $+$ (−) sign represents the case that the magnetic moment is (anti-)parallel with the external field. The magnetic moment of the Co$^{2+}$ in the A site is $-3 \mu_B$ and that of the Co$^{3+}$ in the B site is $+4 \mu_B$ if it is in the high-spin state. The magnitude of the magnetic moment of the Fe$^{3+}$ ions is $5 \mu_B$, but its direction could not be determined in the experiments. In this case, $x = 1.45$ when the sign of the magnetic moment of the Fe ion is positive and $-3.05$ when negative, neither of which satisfies the condition of $x$. The Co$^{3+}$ ions in the B site have zero magnetic moment in its low-spin state where all the low energy levels (t$_{2g}$) are occupied by six electrons. $+3 \mu_B$ for the magnetic moment of the Co$^{2+}$ ion in the A site and $0 \mu_B$ for that of the low-spin Co$^{3+}$ ion in the B site were therefore considered. Then, $x = 0.875$ when the sign of the magnetic moment of the Fe is positive and 0.125 when negative. Only the former case satisfies the condition of $x$ and, therefore, the chemical formula of Co$_{0.5}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ is finally estimated to be (Mn$_{0.875}$Co$_{0.125}$)$_A$[Co$_{0.475}$Mn$_{0.525}$Fe$_{0.9}$]$_B$. It is worth noting that this is just one of the most plausible conclusions we can get from the experiment and there is no way to exclude other possibilities when the analysis is based on the assumption of Fe ion distribution. Moreover, the possibilities that the magnetic moments of the ions have non-integer values due to the effect of orbital moments and spin canting can lead to a different conclusion. If the locations of the Mn$^{2+}$ and Mn$^{3+}$ ions are exchanged, the magnetization estimated from the ratio of the number of the A and B sites and the XAS results is very different from the experimental value of $3 \mu_B$.

4. Conclusion

NMR and XAS were used to determine the oxidation states and the magnetic moments of the three cations in Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$. The results of the XAS experiment shows that there are Fe$^{3+}$ (B site), Co$^{2+}$, Co$^{3+}$, Mn$^{2+}$ and Mn$^{3+}$ ions present. The results of the NMR experiment indicate that the magnetic moments of the Fe$^{3+}$, Co$^{2+}$ and Mn$^{3+}$ ions are the majority spins and that those of the Co$^{3+}$ and Mn$^{2+}$ ions are the minority spins. From the fact that the total number of cations in a unit is 3 and their total oxidation is 8, the chemical formula of Co$_{0.6}$Fe$_{0.9}$Mn$_{1.5}$O$_4$ can be expressed as Mn$_{2x}$Mn$_{3−x}$Co$_{1−x}$Fe$_{0.9}$O$_4$. The ratio of the number of the A and B sites in a unit formula gave the distribution of the cations. Finally, comparison with the saturation magnetization gave the more detailed chemical formula of (Mn$_{2x}$Co$_{1−x}$)$_A$[Co$_{3−x}$Mn$_{1.5}$Fe$_{0.9}$]$_B$ with $x \sim 0.9$.

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References
