Hyperfine Interactions (2020) 241:7
https://doi.org/10.1007/s10751-019-1680-x

Effect of etching on spin canting in hydrothermally synthesized Co-Ni ferrite particles

Sonia Sharmin[1] · Eiji Kita[1] · Mikio Kishimoto[1] · Hideto Yanagihara[1]

Abstract
Spinel cobalt-nickel ferrite nanoparticles, having a particle size of around 40 nm, were produced by undergoing a succession of synthesis routes comprised of chemical co-precipitation, hydrothermal treatment (HT), and etching in hydrochloric acid (ET) of concentration 2.0 mol/L. The room temperature high-field Mössbauer spectra were analyzed in detail and significant spin canting associated with Fe^{3+} ions at both A- and B-sites were observed for both the HT and ET samples in the presence of external magnetic field of 5 T. The effect of etching on various Mössbauer parameters such as the hyperfine field distribution, isomer shift, quadrupole splitting and the linewidth was noted. The A site and B site canting angles of the HT sample were respectively 17° and 22°, while canting angle of approximately 13° was observed for both A and B sites in the ET sample.

Keywords Spin canting · Etching · Spinel ferrite · Defects

1 Introduction

Recent progress in nanotechnology has initiated renewed interest in polycrystalline ferrites which are relatively inexpensive and have extensive applications in electronics and telecommunication industries because of their intriguing structural and magnetic properties [1]. The magnetic properties of nanoparticles can differ in many respects from those of their corresponding bulk materials [2]. They mainly depend on the magnetic interactions between cations with magnetic moments situated on tetrahedral (A-site) and octahedral (B-site) sites [3]. To

---

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME2019), 1-6 September 2019, Dalian, China*
Edited by Tao Zhang, Junhu Wang and Xiaodong Wang

✉ Sonia Sharmin
sonia.sharmin.gb@u.tsukuba.ac.jp

[1] Department of Applied Physics, University of Tsukuba, Tsukuba 305-8577, Japan

probe the magnetic properties of these materials, Mössbauer spectroscopy has been proven as one of the most sensitive techniques in terms of energy (and hence frequency) resolution.

Spin canting is one of the most important aspects in understanding magnetism in ferrites [2–5]. Spin structures in nanoparticles of ferrimagnetic materials may deviate locally in a nontrivial way from ideal collinear spin structures. For instance, magnetic frustration due to the reduced numbers of magnetic neighbors at the particle surface or around defects in the interior can lead to spin canting and hence a reduced magnetization. For many applications of magnetic nanoparticles, a large saturation magnetization is desirable, and it is therefore important to control and minimize spin canting. In very small magnetic particles, the magnetization direction is not fixed but fluctuates at finite temperatures and the magnetization may spontaneously be reversed (superparamagnetic relaxation) above the blocking temperature. Near the surface, the low local symmetry can result in a large contribution to the local magnetic anisotropy, which can influence the spin orientations. Both in nanoparticles and in bulk materials, defects in the interior, such as diamagnetic substitution or cation vacancies, can also lead to noncollinearity. Moreover, exchange interaction between surface atoms of neighboring particles can have a profound influence on the magnetic properties because this can affect both the superparamagnetic relaxation and the spin structure [2]. Spin canting has been observed in a variety of spinels and it is still not clear whether spin canting in nanometer-sized particles occurs only at the surface but also in the inner core of these particles. Somewhat different experimental results point to their dependence on sample preparation [6]. A possible way of measuring the amount of canted spins is Mössbauer spectroscopy with a large applied external field, in which the bulk ions' spins, but not the surface ions' spins align.

In this paper we report results of a study on nanoparticles of cobalt-nickel ferrite. Cobalt-nickel ferrite crystallizes to the spinel structure, which is a cubic lattice of closed-packed oxygen ions, in which the tetrahedral (A) and octahedral (B) sites are occupied by Co^{2+}, Ni^{2+} or Fe^{3+} cations. It exhibits ferrimagnetism. The X-ray diffraction patterns confirm the formation of single phase cubic spinel structure with space group Fd-3 m for all the samples [7]. From magnetization studies, the saturation magnetization (M_s) of the HT particles was found to be 52 Am^2/kg and for ET particles it was 60.7 Am^2/kg at room temperature. This is close to the reported value of 55 Am^2/kg for the bulk $NiFe_2O_4$ sample, although much less than the M_s of $CoFe_2O_4$ (80.5 Am^2/kg) [8]. Another interesting characteristic was the presence of significant amount of coercivity. The coercive field (H_c) was 359 kA/m and 445 kA/m for HT and ET samples respectively. H_c is inversely related to M_s through Brown's relation [3]. According to this relation as H_c increases, M_s. decreases which holds for the materials with cubic magneto-crystalline anisotropy. Our experimental results however were not in accordance with the aforesaid relation.

To increase knowledge of local magnetic behavior, zero-field and in-field Mössbauer measurements at room temperature were carried out in the present work on nanoscale particles prepared by undergoing a succession of synthesis routes comprised of chemical co-precipitation, hydrothermal treatment (HT), and etching in hydrochloric acid (ET) of concentration 2.0 mol/L.

2 Experimental details

Co-Ni ferrite nanoparticles were prepared employing three synthesis routes in succession: co-precipitation, hydrothermal treatment and etching in HCl. In a typical synthesis method, 0.02 mol of $FeCl_3.H_2O$, 0.005 mol of $CoCl_2$, and 0.003 mol of $NiCl_2$ (Wako Pure Chemical Industries, Ltd., 99.0% purity) were dissolved in 20 mL of distilled water, to obtain a 2.5 times molar ratio of Fe^{3+} against (Co^{2+} + Ni^{2+}). The solution containing Fe^{3+}, Co^{2+} and Ni^{2+} was added to an aqueous solution of 0.228 mol of NaOH to prepare co-precipitant while stirring with a magnetic stirrer at room temperature. The suspension containing the co-precipitant composed of Fe^{3+}, Co^{2+} and Ni^{2+} ions was then treated hydrothermally using an autoclave at 180 °C for 2 h to grow the Co-Ni spinel ferrite particles. After the hydrothermal treatment, the suspension containing the Co-Ni spinel ferrite particles was washed with pure water until a neutral pH was reached. The particles in this state contained not only particles grown by the hydrothermal treatment but also very fine particles. Thereafter, the hydrothermally treated particles were etched in 40 mL of HCl solution diluted with water at concentration of 2.0 mol/L for 2 h to remove the fine particles by dissolution.

The XRD patterns corresponded to a single phase of cubic spinel cobalt-nickel ferrite while the particle size obtained from transmission electron microscopy (TEM) yielded a mean value of 40 nm for both HT and ET samples [7].

The ^{57}Fe Mössbauer spectra of the studied materials were measured at room temperature employing a constant acceleration spectrometer equipped with a ^{57}Co(Rh) source. For Mössbauer measurements at 5 T and room temperature, the sample was clamped to the finger of a liquid helium flow cryostat and placed in the bore of a superconducting magnet (Spectromag (SM4000)) such that the field direction coincided with the γ-ray beam. Spectra were taken in constant acceleration mode, and analyzed using least mean square fits. Isomer shifts are quoted relative to α-Fe. Mössbauer spectra were analyzed with the MossWinn software, using Lorentzian doublets and sextets.

3 Results and discussion

To clarify the effect of etching on the samples, zero-field and high-field Mössbauer spectra at 300 K were measured (Fig. 1) for the HT and ET samples.

Spectra were best fitted with two magnetic sextets. In Fig. 1, the dots represent the experimental data and solid lines through the data points are the least square fitted lines. Because part of the hyperfine magnetic field (HMF) is supertransferred from neighboring magnetic cations, Fe^{3+} cations with proximity to the particle surface are expected to have reduced HMF values [9]. The resulting HMF values for the HT sample were 43 and 49 T, and for the ET sample they were 50 and 48 T. It was not possible to assign these fields to either sublattice with any degree of certainty.

To separate the signals from the two sublattices and to probe the magnetic state, Mössbauer measurements were made at room temperature in a 5 T external field directed along the γ-ray. The two distinct sextets from the A sites and B sites can be seen in Fig. 2. A total field of 53 T for the A-site and a total field of 45 T for the B-site was found for both HT and ET samples. The presence of the second and fifth peaks ($\Delta m = 0$) provides unambiguous evidence for the existence of localized spin canting. The relative intensity of these peaks indicates that the spin canting is greater in the B sites in the HT sample and it is more intense in the HT sample than in the ET sample. There was an increase in magnetic hyperfine field upon application of the external magnetic field for one of the sextets, which indicates that the iron spins are oriented antiparallel to the applied field; this was assigned to iron in tetrahedral A sites. The other sextet revealed nearly unchanged hyperfine splitting upon application of field (Table 1). This is also a

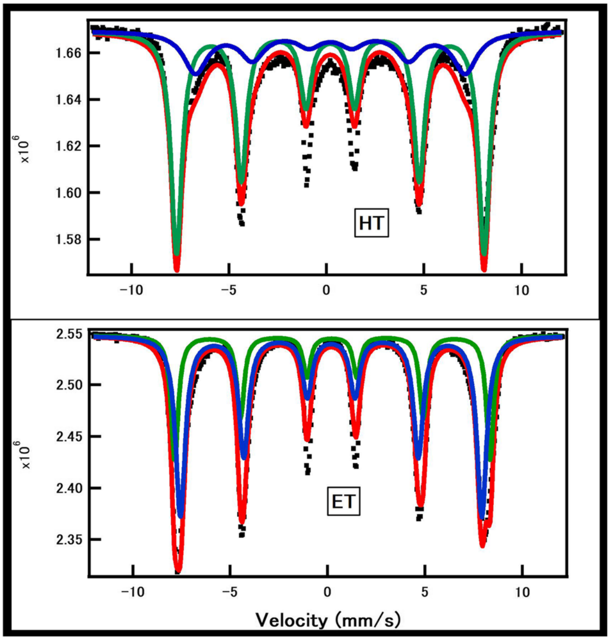

Fig. 1 Mössbauer spectra at room temperature of HT and ET samples. The black dots indicate experimental data while the green and blue lines are the calculated sub spectra and the solid red line is their sum

clear indication for strong spin canting [5]. This second sub-spectra is considered to be associated with iron occupying the octahedral B-sites.

It is well known that the ratio of areas under lines 2 and 5 with respect to those under lines 3 and 4 is given by $A_{2,5}/A_{3,4} = 4\sin^2\theta/(1+\cos^2\theta)$, where $p = A_{2,5}/A_{3,4}$ and θ is the angle between the directions of the γ-ray and applied field [5]. For the HT sample, the intensity of lines 2 and 5 of the A-site component gave a p value of 0.18, whereas the relative areas of lines 2 and 5 for the B-site component gave a value of $p = 0.30$, corresponding to an average canting angle of

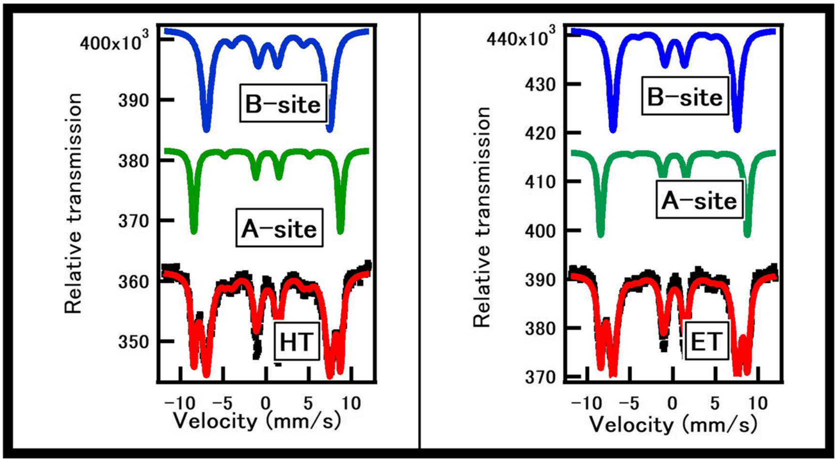

Fig. 2 Mössbauer spectra at room temperature at 5 T for the (**a**) HT and (**b**) ET samples. The black dots indicate experimental data while the green and blue lines are the calculated sub spectra and the solid red line is their sum

Table 1 Canting angle (θ), area under curve (a), relative area ratios a(A)/a(B), line width (LW), isomer shift (IS), quadrupole splitting (QS), effective hyperfine field (H_{eff}), average hyperfine field (H) obtained by fitting the high field Mössbauer spectra at room temperature

Sample	Subspectrum	θ	Area	a_A/a_B	LW	IS	QS	H_{eff} (T)	H (T)
HT	A	17	30.1	0.4	1.20	0.16	−0.025	53.3	48.3
	B	22	69.9		0.65	0.24	0.039	44.8	49.8
ET	A	13	36.8	0.6	0.71	0.19	−0.047	53.3	48.3
	B	13	63.2		1.02	0.27	0.042	45.1	50.1

17° and 22° for respectively the A and B-site spins. For the ET sample, the A and B-site components both gave *p* values of 0.1, corresponding to an average canting angle of approximately 13° for the A and B-site spins. These results show that there is essentially the same canting in A-sites as in B-sites (Table 1). The canting can affect all A and B-site ions or be restricted to a fraction of the spins with large canting angles, but the data can explain at least qualitatively the increased value of the saturation magnetization with etching as a result of the decrease of the canting component. The significant amount of canting present in both samples is reasonably expected in a highly magneto anisotropic cobalt-nickel ferrite system.

The canting phenomena was also investigated by considering the cation distribution of these particles. For spinels having ferrimagnetic order, the areal fraction of the A sextet (f_A) and the B sextet (f_B) represents the fraction of Fe^{3+} cations on A sites and B sites, respectively. The calculated f_A and f_B values correspond to 30% of Fe^{3+} cations occupying the A sites and 70% Fe^{3+} cations occupying the B sites in the HT sample. For the ET sample, 37% of Fe^{3+} cations occupy the A sites and 63% Fe^{3+} cations occupy the B sites. In the present work the ratio of recoilless fraction at A-(f_A) and B-(f_B) sites, f_B/f_A, is assumed to be 0.94 at room temperature at 5 T [10]. For determining the cation distribution from in-field Mössbauer spectra the area ratio of tetrahedral to octahedral spectra i.e. $(a_A)/(a_B)$ is calculated, which is then directly related to the ratio of the number of iron ions present at A- and B-sites respectively [11]. The degree of inversion, γ, defined as the fraction of tetrahedral sites occupied by Fe^{3+} cations, is 0.55 and 0.72 respectively for the HT and ET samples.

Taking into consideration the relative strength of preference of B-site occupation of Ni^{2+} cations, and on the premise that all of the Fe^{3+}, Co^{2+}, and Ni^{2+} metal ions, with the molar ratio 20:5:3, were used to form the spinel ferrite, the cation distributions for the HT sample and ET sample were assumed to be respectively $(Fe_{0.55}Co_{0.45})_A[Co_{0.04}Ni_{0.3}Fe_{1.6\ 0.06}]_BO_4$ and $(Fe_{0.72}Co_{0.28})_A[Co_{0.22}Ni_{0.3}Fe_{1.4\ 0.08}]_BO_4$. Here, indicates vacancy. Vacancies are usually observed on B sites, as commonly known [9]. For the ET system, the intensity of the outermost A-site peak increases, while the B-site peak remains the same for both samples. Coupled with the degree of inversion value, we can assume that less Co^{2+} ions are occupying the A-site than in the HT sample. However, although the Ni^{2+} ions have a strong preference for the B-site, it cannot be said conclusively that they do not occupy the A-site at all. Indeed, the increase in intensity of the outermost A-site in the ET sample with regard to the HT sample may indicate that there is a transfer of both Ni^{2+} ions as well as Co^{2+} ions from A to B-site with the advent of etching [3].

Consequently, this cation distribution yields a magnetic moment of 4.6 μ_B for the HT sample and a value of 3.8 μ_B in a state of collinear ferrimagnetic order. The experimental value from magnetization measurements yields a value of 2.13 μ_B for the HT sample, and a value of 2.48 μ_B for the ET sample. The experimental value is expected to be lower if there is local canting involved, especially at the majority B sites. Our results thus confirm separately the existence of spin canting as well as its decrease with etching.

The line width changes only slightly between HT and ET samples, reflecting the changes in tetrahedral and octahedral environments of Fe^{3+} ions present at A- and B-sites. The B-site line width is found to be larger than for the A-site. Spin canting by itself has no influence on the value of magnetic hyperfine field (HMF). The HMF in an applied magnetic field of 5 T is around 53 T for ^{57}Fe ions occupying A-sites having moments antiparallel to applied field. The HMF values near to 45 T correspond to ^{57}Fe ions in octahedral sites; HMF corresponding to B-site iron ions are in good agreement with values found earlier [12].

The molecular weight of the ferrite sample was calculated and the magnetic moments (n_B) of the HT and ET sample were obtained using the saturation magnetization values derived from magnetization data. To see the extent of canting in the considered ferrites we further calculated the average B-site canting angles (θ) based on the values of these magnetic moments: $n_B = M_B \cos\theta - M_A$, where the respective octahedral (B-) and tetrahedral (A-) sub-lattice magnetizations M_B and M_A are deduced from the cation distribution. For the HT and ET samples, the θ values were respectively 45° and 33°. Certainly, the average canting angles of the B-site spin moments, determined using magnetization data and the canting angles of B-site Fe^{3+} spin moments calculated through the Mössbauer resonance (Table 1) are fairly different. This difference in the values of canting angles can be attributed to the different measurement techniques used, the magnetization study being a macroscopic and Mössbauer spectroscopy a microscopic technique.

The increase in the spin-canting component seems to go along with a decrease of the relative area of both sublattice components, site A and site B [4]. One may speculate that the larger surface to volume ratio in the HT sample leads to a larger number of surface ions, and thus a larger relative area of the spin-canting component in the Mössbauer spectrum.

4 Summary

The in-field Mössbauer spectroscopy reveals the noncollinear spin arrangement in these materials. From an analysis of the Mössbauer spectra, it can be concluded that the present system exhibits a partial inverse spinel structure. The area of the spin-canting component is higher in the HT sample than in the ET sample. Magnetic frustration due to the reduced numbers of magnetic neighbors at the particle surface may be responsible for the spin canting. However, since the particle sizes are approximately the same and the canting does not disappear completely with the removal of the fine particles observed by transmission electron microscopy existing in the HT sample, this strongly suggests that the canting is not only a surface effect but also occurs around defects in the interior of the particles. This was also investigated by considering the cation distribution of these particles, which also strongly suggests the presence of defects or voids in these spinel structures.

Acknowledgments The authors would like to acknowledge the University of Tsukuba Tandem Accelerator Complex (UTTAC) at the University of Tsukuba for providing the facilities for Mössbauer spectroscopy. This work was supported by the Japan Science and Technology Agency (JST) under Collaborative Research Based on Industrial Demand “High Performance Magnets: Towards Innovative Development of Next Generation magnets” (#JPMJSK1415).

References

1. Sugimoto, M.: The past, present, and future of ferrites. J. Am. Ceram. Soc. **82**(2), 269 (1999)
2. Mørup, S., Brok, E., Frandsen, C.: Spin structures in magnetic nanoparticles. J. Nanomater. **2013**, 720629 (2013)
3. Pandit, R., Sharma, K.K., Kaur, P., Reddy, V.R., Kumar, R., Shah, J.: Spin canting observation and cation distribution in $CoFe_2-$ xIn_xO_4 (0.0??? x??? 1.0) ferrites through low temperature–high field Mössbauer spectral study. J. Alloys Compd. **596**, 39 (2014)
4. Marx, J., Huang, H., Salih, K.S.M., Thiel, W.R., Schünemann, V.: Hyperfine Interactions. Spin canting in ferrite nanoparticles. **237**(1), 41 (2016)
5. Pandey, B., Litterst, F.J., Baggio-Saitovitch, E.M.: Preferential spin canting in nanosize zinc ferrite. J. Magn. Magn. Mater. **385**, 412 (2015)
6. Dormann, J.L., Nogues, M.: Magnetic structures in substituted ferrites. J. Phys. Condens. Matter. Magnetic structures in substituted ferrites. **2**(5), 1223 (1990)
7. Sharmin, S., Kita, E., Kishimoto, M., Latiff, H., Yanagihara, H.: Effect of Synthesis Method on Particle Size and Magnetic and Structural Properties of Co–Ni Ferrites. IEEE Trans. Magn. **54**(11), 1 (2018)
8. Khan, M., Karim, S., Mashiatullah, A., Liu, J., Hou, M.D., Sun, Y.M., Duan, J., Yao, H., Mo, D., Chen, F.Y.: Structural analysis of nickel doped cobalt ferrite nanoparticles prepared by coprecipitation route. Physica B: Condens. Matter. **404**, 3947–3951 (2009)
9. Hamdeh, H.H., Hikal, W.M., Taher, S.M., Ho, J.C., Thuy, N.P., Quy, O.K., Hanh, N.: Mössbauer evalutation of cobalt ferrite nanoparticles synthesized by forceed hydrolysis. Journal of Applied Physics. **97**(6), 064310 (2005)
10. Salazar-Tamayo, H., García, K.E., Barrero, C.A.: New method to calculate Mössbauer recoilless f-factors in $NiFe_2O_4$. Magnetic, morphological and structural properties. J. Magn. Magn. Mater. **471**, 242 (2019)
11. Sawatzky, G.A., Van Der Woude, F., Morrish, A.H.: Cation Distributions in Octahedral and Tetrahedral Sites of the Ferrimagnetic Spinel $CoFe_2O_4$. J. Appl. Phys. **39**(2), 1204 (1968)
12. Chinnasamy, C.N., Narayanasamy, A., Ponpandian, N., Chattopadhyay, K., Guerault, H., Greneche, J.M.: Magnetic properties of nanostructured ferrimagnetic zinc ferrite. J. Phys. Condens. Matter. **12**(35), 7795 (2000)