

Structural and magnetic properties of high-energy ball-milled nanoparticles CoFe_2O_4 via neutron diffraction study

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Abstract. In this study, we investigated the structural and magnetic properties of high-energy ball-milled CoFe_2O_4 nanoparticles using neutron powder diffraction. Rietveld refinement confirmed the structural stability of the single-phase cubic spinel ($Fd\bar{3}m$) during milling for 120 min. However, the lattice parameters, including the lattice constant, bond lengths, and bond angles, change with milling time. In particular, milling leads to B–O–B bond angles widening and A–O–B bond angles narrowing, enhancing the antiferromagnetic superexchange interaction J_{AB} . The refinement also reveals significant changes in the magnetic moments at the tetrahedral and octahedral sites. The variation in the average magnetic moments closely follows the evolution of the inversion degree, indicating that the reduction in magnetic moments is associated with the decrease in inversion degree during milling. These findings contribute to a deeper understanding of structure-property relationships in nanosized CoFe_2O_4 and provide meaningful guidance for tuning its magnetic performance through mechanical processing.

Keywords: spinel ferrite, neutron diffraction, milling, antiferromagnetism, nanoparticles

1 Introduction

Among spinel-structured materials, cobalt ferrite oxide (CoFe_2O_4 – CFO) has been extensively studied for its numerous potential technological applications, including outstanding hard-magnet properties, ultra-dense information storage, catalysts, sensors, ferromagnetic fluids, cancer therapy, drug delivery, and biomedical imaging [1–4]. Furthermore, this material is of great interest from a fundamental science perspective because of magnetic attraction phenomena arising from interactions between geometrically frustrated

lattice arrangements and complex cation distributions at crystallographic sites [5, 6]. In general, numerous factors influence the physical properties of spinel-type ferrites, including synthesis methods, chemical composition, crystallinity, nanoparticle shape, and cation distribution. Understanding the role of these factors is crucial for designing advanced magnetic materials and novel electronic devices.

In the spinel structure, there are two distinct cation sites: the A-site is coordinated with oxygen in a tetrahedral unit, and the B-site is coordinated with oxygen in an octahedron. The cations at the

A-site are arranged in a diamond sublattice, while those at the B-site form a pyrochlore lattice of corner-sharing tetrahedra. Cobalt ferrite oxide typically adopts a partially inverted spinel structure represented by the general formula $(\text{Co}_\delta\text{Fe}_{1-\delta})[\text{Co}_{1-\delta}\text{Fe}_{1+\delta}]\text{O}_4$, where parentheses and square brackets denote the A and B sites, respectively, and $\lambda = 1 - \delta$ is the degree of inversion [7]. In the CFO structure, the lattice sites are primarily occupied by Fe^{3+} ions.

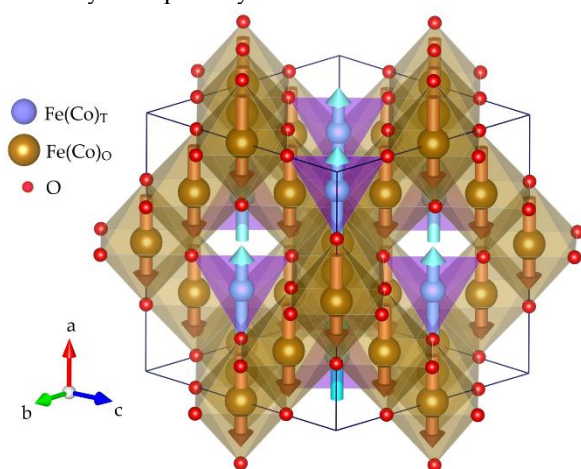


Fig. 1. Ferrimagnetic order of Fe(Co) spins in tetrahedral (blue) and octahedral (orange) sites

Structural changes significantly affect the magnetic exchange interactions within the A (J_{AA}) and B (J_{BB}) sublattices, as well as between the inter-sublattices (J_{AB}) [8]. The intra-sublattice interactions have weak antiferromagnetic (AFM) intensity and are overridden by the stronger inter-sublattice J_{AB} interactions, resulting in a ferrimagnetic (FIM) alignment between the A and B magnetic sublattices (Fig. 1) [8]. The net magnetisation of CFO is determined by the difference between magnetisations at the A and B sites. Additionally, CFO compounds exhibit magnetocrystalline anisotropy, primarily because of the presence of Co^{2+} ions at the B-site [8]. Therefore, redistributing cations between the A and B sites alters the balance of magnetic interactions and magnetisation, leading to changes

in the spin arrangement and overall magnetic properties.

On the other hand, the properties of CFO are also affected by the synthesis route and particle sizes [9–12]. Various methods have been used to synthesise CFO nanoparticles, such as combustion, co-precipitation, precipitation [13], sol-gel [14], and hydrothermal synthesis [15]. Mechanical and chemical effects also have a role, especially high-energy ball milling [16, 17]. These effects are obtained by 1.5-hour mechanical milling of the initial CFO powder prepared via the hydrothermal method [16]. Their results showed an enhancement in the coercivity and saturation magnetisation after milling [16]. Similarly, Manh et al. used co-precipitation and ball milling and observed a rapid decrease in crystallite size and a sharp increase in coercive force during the first 40 minutes of milling [17]. Beyond that point, both the average crystallite size (D) and the coercive force gradually declined [17]. In the latest study, Kmječ et al. investigated the structural, electronic, and magnetic properties of CoFe_2O_4 nanoparticles processed with high-energy ball milling and revealed that D ranged from 334 nm for the initial bulk material to 11.7 nm after 120 minutes of grinding [18]. Their observations show that high-energy milling leads to the migration of Co^{2+} ions from the B-site to the A-site, and vice versa for Fe^{3+} ions [18]. The concentration of Co^{2+} ions at the A-site increases linearly with the value of $1/D$. Unlike previous studies on CFO, it was found that spin canting of Fe^{3+} ions occurs at both A and B sites inside the core, rather than being restricted to the nanoparticle surface. The spin canting angles φ_A and φ_B increase as particle size decreases. Although the cation redistribution and spin canting are predicted to increase saturation magnetisation, this effect is overshadowed by the reduction caused by surface spin disorder. In other words, surface effects play a dominant role in

influencing the magnetic properties of milled CFO nanoparticles [18].

Neutron diffraction is a powerful experimental technique for the simultaneous investigation of crystal structures and magnetic ordering in crystal materials. Neutron scattering characteristics enable the precise localisation of atomic positions within the unit cell and grant neutrons a significantly greater penetration depth compared with X-rays [19]. Furthermore, since neutrons have an intrinsic magnetic moment, neutron diffraction patterns allow the establishment of the magnetic structure of the materials [19]. Therefore, we used the solid-state reaction method to synthesise the initial CFO material and subsequently investigated the effects of high-energy ball milling on its crystal and magnetic structures by using neutron diffraction.

2 Experimental

2.1 Synthesis nanoparticle CoFe_2O_4

High-purity Co_2O_3 (99.5%) and Fe_2O_3 (99.995%) chemicals from Sigma-Aldrich were used as precursors for the preparation of CFO materials. In addition, a methanol solution was used in the milling of the precursors and for cleaning the experimental equipment.

Bulk CFO samples were synthesised with the conventional solid-state reaction method from precursors at 1250 °C for 12 hours with a heating rate of 300 °C/hour in air, as described in a previous work [18]. After the initial synthesis, the bulk material was partitioned into several portions to undergo high-energy ball milling for various milling times (t_m) ranging from 1 to 120 minutes. The milling process was conducted by using a SPEX SamplePrep 8000-series mixer/mill equipped with stainless steel vials and grinding balls.

Notably, utilising the solid-state reaction method for the precursor material ensured superior particle size uniformity and crystalline

quality that are often difficult to obtain when using wet-chemical techniques such as the co-precipitation method.

2.2 Neutron diffraction

Neutron powder diffraction (NPD) experiments were performed on a DN-6 diffractometer in an IBR-2 high-flux pulse reactor (JINR, Russia) [20]. Data were measured in the temperature range of 10–300 K, with a data collection time of two hours for each temperature point. The measurements were performed at a fixed scattering angle of 90°, and the spectral resolution was $\Delta d/d = 0.02$. The NPD data were refined with the Rietveld method by using the FullProf software suite [21].

3 Results and discussion

3.1 Crystal structure of CoFe_2O_4 nanoparticles

The NPD measurements were performed to investigate the crystal structure and magnetic ordering of the CFO materials milled for different times, t_m . As shown in Fig. 2, all studied materials display identical NPD patterns, with the exception of a gradual peak broadening when increasing the milling time, originating from the combined effects of crystallite size reduction and increased lattice microstrains introduced during milling [18]. The refinement results confirm that the cubic spinel structure with space group $Fd\bar{3}m$ remains stable over the entire milling range, which is in good agreement with recent data [6, 22, 23].

Furthermore, the Rietveld refinement, performed assuming a single-phase cubic model, yielded high-quality fits to the experimental data with good agreement values for the R -factors [24]. This confirms that all prepared CFO nanoparticles are single-phase. Based on the refinement results, the dependencies of structural parameters, including the lattice parameters, the oxygen atomic position, and the bond lengths and angles, were

obtained and presented in Table 1 and in Figs. 3–5. The calculated crystallite size D decreased with increasing milling times, according to X-ray diffraction data [18].

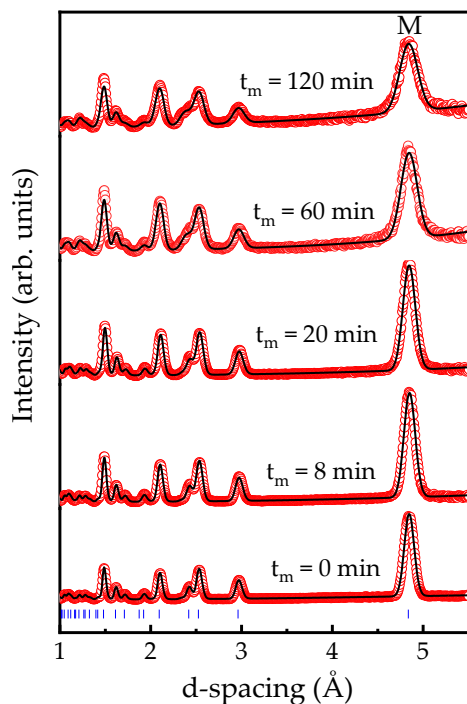


Fig. 2. NPD patterns (red open circle symbols) and fitted curves (solid lines) obtained by using Rietveld method for high-energy ball-milled CFO samples. The positions of Bragg peaks of $Fd\bar{3}m$ cubic spinel-type phase are indicated by vertical ticks. The symbol “M” denotes the (111) diffraction peak with the strongest magnetic contribution

Fig. 3 shows the variation of the lattice parameter a of the cubic phase of milled CFO samples as a function of the inverse crystallite size $1/D$. The lattice constant initially increases almost linearly with reduced crystallite size D and then reaches a saturation. The increase in the lattice constant is associated with the reduction of ionic valence, the increase in oxygen vacancies, and/or changes in the inversion degree [18].

Therefore, the observed increase in the lattice parameters is attributed to cation redistribution during the milling process. For nanosized particles, surface effects tend to contract the lattice, which eventually leads to the saturation

of the lattice constant, as shown in Fig. 3. The D^{-1} dependence of parameter a is consistent with the findings from our previous XRD data [18]. Besides, the D^{-1} dependence of bond lengths and angles among Fe^{3+} , Co^{2+} , and O^{2-} ions of the milled CFO samples is shown in Figs. 4 and 5. Notably, the bond length $\text{Fe}(\text{Co})\text{-O}$ at the B-site ($\text{Fe}(\text{Co})_{\text{O}}\text{-O}$ or B-O bond) is larger than that at the A-site ($\text{Fe}(\text{Co})_{\text{T}}\text{-O}$ or A-O bond). As $1/D$ increases, the B-O bond lengths decrease while the A-O bond lengths increase. In addition, the widening of the B-O-B bond angles and the narrowing of the A-O-B bond angles (Fig. 5) lead to a reinforcement in the inter-sublattices superexchange interaction J_{AB} between Fe^{3+} ions, thereby enhancing the magnetic properties of the materials.

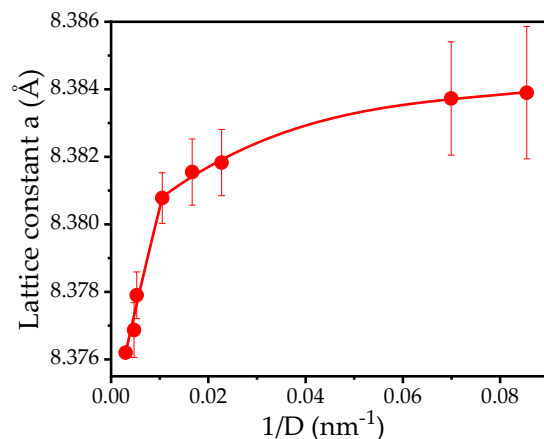


Fig. 3. Variation of lattice constants of milled CFO samples as function of inverse crystalline size

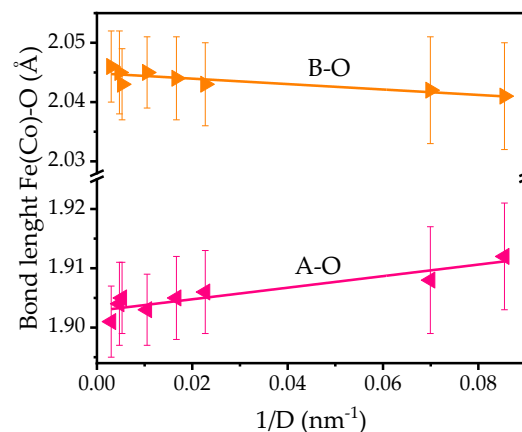


Fig. 4. $1/D$ dependence of $\text{Fe}(\text{Co})\text{-O}$ bond lengths in the milled CFO samples

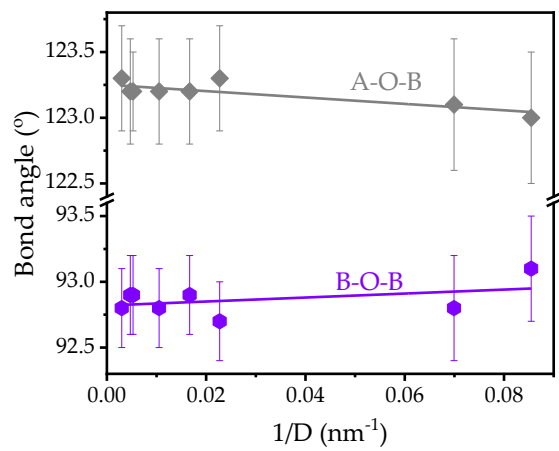


Fig. 5. D-1 dependence of Fe(Co)-O-Fe(Co) bond angles in milled CFO samples

3.2 Magnetic ordering in CoFe₂O₄ nanoparticles

In addition to the structural peaks, the NPD patterns exhibit a significant magnetic contribution to the intense (111) reflection at $d_{hkl} \approx 4.85 \text{ \AA}$, as well as weaker magnetic contributions to the (220) peak at $d_{hkl} \approx 2.96 \text{ \AA}$, peak (222) at $d_{hkl} \approx 2.42 \text{ \AA}$, and peak (400) at $d_{hkl} \approx 2.09 \text{ \AA}$ [23–25]. The average magnetic moments of Fe and Co ions at the A and B sites (m_A and m_B , respectively) were obtained through the refinement of the NPD data, and the results are summarised in Table 1 and Fig. 6. m_B decreases

almost linearly with increasing $1/D$, whereas m_A first decreases and then slightly increases when $1/D$ increases.

The magnetic properties of CFO materials strongly depend on the distribution of cations Co and Fe at A and B sites, which was estimated from the Mössbauer spectroscopy in our previous study [18]. The variation of the average magnetic moments with $1/D$ closely follows the trend of the inversion degree ($1 - \delta$) reported in our previous work [18], suggesting that the reduction in magnetic moments is associated with the decrease in the inversion degree during the milling process.

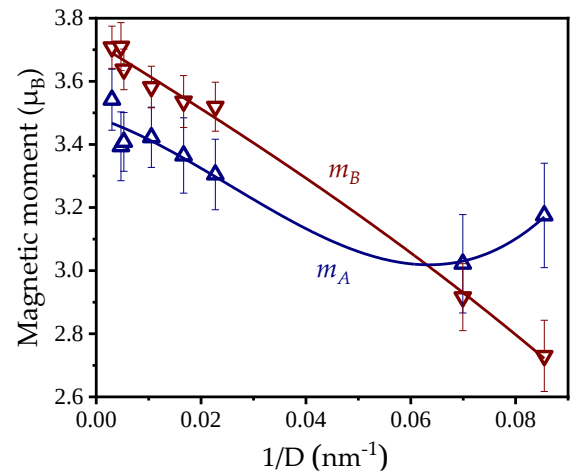


Fig. 6. Average magnetic moments of Fe and Co ions at A and B-sites as a function of D^{-1}

Table 1. Refined structural parameters of CFO samples. Space group $Fd\bar{3}m$ with the atomic positions A site 8a (1/8, 1/8, 1/8), B site 16d (1/2, 1/2, 1/2) and O 32e (x_o, x_o, x_o). The R-factor [26] of the Rietveld analysis are presented

t_m (min)	0	4	8	20	60	120
D (nm)	334(9)	190(5)	95(2)	44(1)	14.3(4)	11.7(3)
a (Å)	8.3762(2)	8.3779(6)	8.3808(7)	8.3818(1)	8.3837(2)	8.3839(2)
V (Å ³)	587.68(17)	588.038(8)	588.645(9)	588.867(12)	589.266(20)	589.302(23)
x_o	0.2560(71)	0.2563(67)	0.2561(68)	0.2559(82)	0.2561(97)	0.2567(97)
A-O (Å)	1.901(6)	1.905(6)	1.903(6)	1.906(7)	1.908(9)	1.912(9)
B-O (Å)	2.046(6)	2.043(6)	2.044(6)	2.043(7)	2.042(9)	2.041(9)
A-O-B (°)	123.3(4)	123.2(3)	123.2(4)	123.2(4)	123.1(5)	123(5)
B-O-B (°)	92.8(3)	92.9(3)	92.8(3)	92.7(3)	92.8(4)	93.1(4)
m_A (μB)	3.541(6)	3.408(3)	3.422(5)	3.304(11)	3.021(15)	3.175(16)
m_B (μB)	3.708(6)	3.638(6)	3.481(5)	3.519(7)	2.916(10)	2.729(11)

R_t (%)	3.96	3.75	4.55	4.22	5.51	5.9
R_p (%)	2.93	3.41	3.76	6.02	4.74	4.45
R_{wp} (%)	3.83	4.52	4.94	7.77	5.95	5.6

4 Conclusion

In summary, neutron powder diffraction data provided detailed insights into the structural and magnetic evolution of high-energy ball-milled CoFe_2O_4 nanoparticles. The cubic spinel structure $Fd\bar{3}m$ remains stable throughout milling up to 120 min, although notable variations in the lattice constant, bond lengths, and bond angles were observed. Milling-induced modifications of the B–O–B and A–O–B bond angles suggest an enhancement of the antiferromagnetic superexchange interaction J_{AB} . Significant changes in the magnetic moments at both tetrahedral and octahedral sites were also identified. The correlation between the evolution of magnetic moments and the inversion degree indicates that the reduction in magnetic moments is primarily governed by the decrease in inversion degree during milling.

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