In-depth investigations of size and occupancies in cobalt ferrite nanoparticles by joint Rietveld refinements of X-ray and neutron powder diffraction data

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Powder X-ray diffraction (PXRD) and neutron powder diffraction (NPD) have been used to investigate the crystal structure of CoFe$_2$O$_4$ nanoparticles prepared via different hydrothermal synthesis routes, with particular attention given to accurately determining the spinel inversion degrees. The study is divided into four parts. In the first part, the investigations focus on the influence of using different diffraction pattern combinations (NPD, Cu-source PXRD and Co-source PXRD) for the structural modelling. It is found that combining PXRD data from a Co source with NPD data offers a robust structural model. The second part of the study evaluates the reproducibility of the employed multipattern Rietveld refinement procedure using different data sets collected on the same sample, as well as on equivalently prepared samples. The refinement procedure gives reproducible results and reveals that the synthesis method is likewise reproducible since only minor differences are noted between the samples. The third part focuses on the structural consequences of (i) the employed heating rate (achieved using three different hydrothermal reactor types) and (ii) changing the cobalt salt in the precursors [aqueous salt solutions of Co(CH$_3$COOH)$_2$, Co(NO$_3$)$_2$ and CoCl$_2$] in the synthesis. It is found that increasing the heating rate causes a change in the crystal structure (unit cell and crystallite sizes) while the Co/Fe occupancy and magnetic parameters remain similar in all cases. Also, changing the type of cobalt salt does not alter the final crystal/magnetic structure of the CoFe$_2$O$_4$ nanoparticles. The last part of this study is a consideration of the chemicals and parameters used in the synthesis of the different samples. All the presented samples exhibit a similar crystal and magnetic structure, with only minor deviations. It is also evident that the refinement method used played a key role in the description of the sample.

1. Introduction

Permanent magnets (PMs) have a large number of both domestic and industrial applications (Lewis & Jiménez-Villacorta, 2013; Coey, 2002; Cullity & Graham, 2009; Furlani, 2001; Jiles, 2015; López-Ortega, Estrader et al., 2015). They constitute key components in e.g. electric motors/generators (Lewis & Jiménez-Villacorta, 2013; Coey, 2002; Cullity & Graham, 2009; Jiles, 2015), magnetic recording/storage media (Cullity & Graham, 2009; Furlani, 2001; Jiles, 2015) and microphones/loudspeakers (Lewis & Jiménez-Villacorta, 2013; Coey, 2002; Cullity & Graham, 2009; Jiles, 2015; Mathew & Juang, 2007; López-Ortega, Estrader et al., 2015), are used in medical magnetic resonance imaging (Lewis & Jiménez-Villacorta, 2013; Coey, 2002; Cullity & Graham, 2009; Jiles, 2015; Pankhurst et al., 2003), and even have a number of both
established and potential biomedical applications (Pankhurst et al., 2003; Valenzuela, 2012; Ramanujan, 2009). The utilization of PMs has expanded drastically over the years, making the PM materials industry a multi-billion-dollar global market (Valenzuela, 2012; Granados-Miralles et al., 2018; Quesada et al., 2016; Coey, 2010a). The most powerful PMs are made from materials that contain rare-earth elements (REE), e.g. NdFe12B and SmCo5, but due to political and environmental concerns related to REE mining, there is now an increasing drive and demand for developing REE-free alternatives (Lewis & Jiménez-Villacorta, 2013; López-Ortega, Estrader et al., 2017; Song & Zhang, 2004), crystal engineering particle size control (Andersen & Christensen, 2015; Stingaciu et al., 2015; Gandha et al., 2016; Gutfleisch et al., 2015; Granados-Miralles et al., 2016; Abalakin, 2006; Leite et al., 2016; Leite et al., 2017; Kahnes et al., 2019). In the literature, the structural characterization of CoFe2O4 is predominantly carried out by conventional Cu-source laboratory powder X-ray diffraction (PXRD) as this technique is readily available, plus it has higher intensity compared with other anode materials and, for most materials, provides

in-depth investigations of CoFe2O4 nanoparticles

Figure 1

Spinel structure of CoFe2O4. Brown–blue atoms represent the proportion of Fe and Co in the structure, with Fe as brown atoms and Co as blue ones. Red atoms show the position of O. Td sites are shown by the green tetrahedra and Oh sites by white octahedra. This figure was made using the VESTA software (Momma & Izumi, 2011).
Table 1
Comparison between the resonant scattering terms of \(^{8}\text{O}, ^{26}\text{Fe}\) and \(^{27}\text{Co}\) for Cu \(K\alpha_{1,2}\) and Co \(K\alpha_{1,2}\) radiation sources, as well as their neutron scattering lengths, \(b_r\).

|          | Cu \(K\alpha_{1,2}\) \((\lambda = 1.79 \text{ Å})\) | Cu \(K\alpha_{1,2}\) \((\lambda = 1.54 \text{ Å})\) | Neutron scattering length \(b_r\) \((10^{-12} \text{ m})\) |
|----------|-----------------------------------------------|-----------------------------------------------|-------------------------------------------------|
| \(^{8}\text{O}\) \((Q = 0)\) | \(f_{\text{iso}O}(Q = 0) = 10\)                      | \(f_{\text{iso}O}(Q = 0) = 5.803\) \((4)\)                          |                                                  |
|          | \(f' = +0.0630\)                                  | \(f' = +0.0492\)                                 |                                                  |
|          | \(f'' = +0.0440\)                                 | \(f'' = +0.0322\)                                |                                                  |
| \(^{26}\text{Fe}\) \((Q = 0)\) | \(f_{\text{iso}Fe}(Q = 0) = 23\)                   | \(f_{\text{iso}Fe}(Q = 0) = 9.45\) \((2)\)                      |                                                  |
|          | \(f' = -3.5307\)                                  | \(f' = -1.1336\)                                 |                                                  |
|          | \(f'' = +0.4901\)                                 | \(f'' = +3.1974\)                                |                                                  |
| \(^{27}\text{Co}\) \((Q = 0)\) | \(f_{\text{iso}Co}(Q = 0) = 25\)                  | \(f_{\text{iso}Co}(Q = 0) = 2.49\) \((2)\)                      |                                                  |
|          | \(f' = -2.0230\)                                  | \(f' = -2.3653\)                                 |                                                  |
|          | \(f'' = -0.5731\)                                 | \(f'' = +3.6143\)                                |                                                  |
| Fe/Co contrast \((Q = 0)\) | \(\frac{f_{\text{Co}}(0, \lambda) - f_{\text{Fe}}(0, \lambda)}{f_{\text{Fe}}(0, \lambda)} = 16.8\%\) | \(3.5\%\)                                             | \(\frac{b_{\text{Co}} - b_{\text{Fe}}}{b_{\text{Fe}}} = 74\%\) |

The Fe/Co contrast at \(Q = 0\) was calculated for resonant scattering terms and for the neutron scattering length, ignoring the imaginary term. The atomic form factor is given by \(f(Q, \lambda) = f_{\text{el}}(Q) + f'(\lambda) + if''(\lambda)\), where \(f_{\text{el}}\) is the Thomson scattering, which is proportional to the number of electrons \((Z)\) around the atom, while \(f'\) and \(f''\) are the energy-dependent resonant scattering terms (Creagh, 2004). Here, \(Q\) represents the scattering vector magnitude and \(\lambda\) the wavelength of the incident X-rays. At \(Q = 0\) the atomic form factor equals \(Z\), plus the resonance terms.

The cation distribution within spinel ferrite structures can be investigated by a multitude of local spectroscopy techniques, such as Mössbauer spectroscopy (Smith et al., 1978; Murray & Linnett, 1976a,b), X-ray absorption spectroscopy with extended X-ray absorption fine structure (Yang et al., 2005; Calvin et al., 2002), X-ray absorption near-edge structure analysis (Nakashima et al., 2007) or Raman spectroscopy (Chandramohan et al., 2011). The site occupation fractions of \(^{26}\text{Fe}\) and \(^{27}\text{Co}\) can also be extracted by structural modeling of NPD data because of the large scattering length \((b_r)\) difference between the two elements (see Table 1) (Sears, 1992). In addition, neutron diffraction data contain information about the magnetic structure of the sample. Notably, a more accurate and robust description of the atomic structure can be obtained by conducting a joint structural modelling of multiple diffraction patterns from different radiation sources.

The present study is based on a compilation of data from three of our earlier studies on CoFe\(_2\)O\(_4\) nanoparticles (Granados-Miralles et al., 2018; Ahlburg et al., 2020; Stingaciu et al., 2017), as well as previously unpublished data. The X-ray and neutron diffraction patterns stem from different CoFe\(_2\)O\(_4\) samples and have been collected using both Co and Cu in-house X-ray diffractometers, as well as various NPD instruments. Here, the data have been re-analysed, yielding a detailed study of the CoFe\(_2\)O\(_4\) nanoparticle structures and the effect of different modelling parameters on the structural analysis. The study is divided into the following four parts:

Part 1, reliable extraction of Fe/Co occupancies in CoFe\(_2\)O\(_4\). This work is based on a study by Granados-Miralles et al. (2018). Two major points are investigated in this refinement study. (a) Pattern weighting influence: investigation of the effect of using an equal weighting (Ew) for each pattern in the joint refinement compared with a weighting based on information available, i.e. the number of peaks available for each individual pattern (Iw), and with an arbitrary weighting scheme (Aw). (b) Combining different patterns: comparison of the influence of using out the joint structural modelling of different combinations of available data from three diffraction sources, i.e. Cu \(K\alpha_{1,2}\) and Co \(K\alpha_{1,2}\) PXRD data and NPD data from the DMC instrument at SINQ (Switzerland). Both the crystal and magnetic structures are analysed and compared, with emphasis on determining which combination gives the most reliable and accurate description.

Part 2, reproducibility of synthesis and refinements. This part investigates the reproducibility of the synthesis using data from samples prepared under identical conditions from a study by Ahlburg et al. (2020). Diffraction data have been measured multiple times on each individual sample as well as equivalently prepared samples using identical conditions at
the DMC instrument. This allows us to investigate the reproducibility of both the synthesis method and the data acquisition and refinement procedure.

Part 3, effect of different synthesis approaches. Here, the effect of different hydrothermal synthesis approaches on the structural and magnetic properties of CoFe₂O₄ is investigated. This part is divided into two subsections. (a) Different hydrothermal reactors: an extensive study prepared CoFe₂O₄ using different hydrothermal reactors (autoclave, spiral reactor and continuous flow reactor) conducted by Stingaciu et al. (2017). From this study four samples were investigated using NPD. (b) Different Co salts: comparison of the structural consequences of employing different Co salt precursors [Co acetate, CoCl₂ and Co(NO₃)₂] in the synthesis of CoFe₂O₄.

Part 4, effect of synthesis conditions. This part compares and discusses four samples presented in the paper that have been synthesized using the autoclave reactor. The chemicals and synthesis parameters used are considered in the comparison of their crystal and magnetic structures to deduce possible trends.

2. Experimental

2.1. Sample preparation

The CoFe₂O₄ samples used for these investigations were all prepared using variations of the same hydrothermal method. An overview of all samples is given in Table 2 and the sample preparation is described in the following paragraphs.

For part 1, the CoFe₂O₄ powder was prepared following the method described by Granados-Miralles et al. (2018). Aqueous solutions of 2.0 M Co(NO₃)₂·6H₂O and 2.0 M Fe(NO₃)₃·9H₂O were mixed in the ratio 1:2, and precipitates were formed by adding 16 M NaOH in a ratio of 2:1 with respect to OH⁻:NO₃⁻. All reagents used were technical grade with purity >98% from Sigma–Aldrich. The obtained precursor was diluted with deionized water to a metal concentration of 0.45 M. The formed precipitate was stirred for 30 min and 80 ml were transferred to a 170 ml Teflon-lined steel autoclave. The autoclave was placed in a preheated convection oven at 240°C, held for 2 h and subsequently cooled in air. Finally, the sample was washed with deionized water several times to remove the counter-ions and neutralize the supernatant, and then dried in a vacuum oven for 4 h at 70°C. The same cleaning method was also applied in the following unless stated otherwise.

For part 2, the CoFe₂O₄ powders were prepared using the method described by Ahlburg et al. (2020). Two autoclave syntheses similar to the method described in part 1 were used with the exception of the usage of higher reagent concentrations of 3.0 M Co(NO₃)₂·6H₂O and 2.3 M Fe(NO₃)₃·9H₂O, but still with a 1:2 Co:Fe ratio and an OH⁻:NO₃⁻ molar ratio of 1.25:1 when adding NaOH. The same heating process was used as for part (1), but the samples were dried in a vacuum oven for 24 h at 50°C.

For part 3, three different hydrothermal reactors (autoclave, spiral reactor and flow reactor) with different heating rates were used. In addition, three different Co salts were used to prepare the precursors for the autoclave synthesis. The details are as follows:

(a) Different hydrothermal reactors. In this part, the precursor consisted of 2.0 M Co(NO₃)₂·6H₂O, 2.0 M Fe(NO₃)₃·9H₂O and 16.0 M NaOH with the molar ratios of Co:Fe and OH⁻:NO₃⁻ being 1:2 and 2:1, respectively. The synthesis was carried out using the following reactors and specific conditions:

- Autoclave (AC): the synthesis was carried out in a conventional Teflon-lined steel AC (170 ml filled with 80 ml precursor) over a period of 1 h at 240°C. The corresponding sample name is AC240.
- Spiral reactor (SR): the synthesis was carried out in a custom-built Swagelok steel tube spiral reactor (Granados-Miralles et al., 2016). The precursor solution was diluted to a metal concentration of 0.45 M, before being loaded into the 1/16 inch (1.59 mm) steel tube spiral. The reactor was pressurized to 210 bar (1 bar = 100 kPa) using a high-performance liquid chromatography pump. The precursor was subsequently submerged in a hot oil bath at 240°C for 20 min (Granados-Miralles et al., 2016). The corresponding sample name is SR240.

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**Table 2**

Overview of the presented samples and references to papers where some of the results have previously been presented.

* indicates this work, x data published in the cited references.

| Sample | Temperature (°C) | Time (h) | Heating rate (°C s⁻¹) | VSM | PXRD | NPD | Occupancy reported | Refined |
|--------|-----------------|----------|----------------------|-----|------|-----|---------------------|---------|
| DMC CoFe₂O₄ (Granados-Miralles et al., 2018) | 240 | 2 | 0.15 | x | x | x | Yes | * |
| DMC A1-3* | 240 | 2 | 0.15 | x | x | x | No | * |
| B1-2* | 240 | 2 | 0.15 | x | x | x | No | * |
| Cl-1 (Ahlburg et al., 2020) | 240 | 2 | 0.15 | x | x | x | Yes | * |
| PUS FR220 (Stingaciu et al., 2017) | 220 | 3 × 10⁻³ | 500 | x | x | * | * | * |
| FR320 (Stingaciu et al., 2017) | 320 | 3 × 10⁻³ | 500 | x | x | * | * | * |
| SR240 (Stingaciu et al., 2017) | 240 | 1/3 | 25 | x | x | * | * | * |
| AC240 (Stingaciu et al., 2017) | 240 | 1 | 0.15 | x | x | x | Yes | * |
| HRPT Co(Ac)₂* | 200 | 1 | 0.15 | * | * | * | * | * |
| Co(NO₃)₂* | 200 | 1 | 0.15 | * | * | * | * | * |
| CoCl₂* | 200 | 1 | 0.15 | * | * | * | * | * |
Flow reactor (FR): the synthesis was carried out using a single-stage continuous solvothermal flow reactor (Hellstern et al., 2015; Søndergaard et al., 2011). The precursor solution was diluted to a concentration of 0.05 M to avoid clogging the tubing of the FR before being transferred to a 200 ml injector. The system was pressurized to 250 bar and the precursor and preheated solvent (water) were pumped continuously at flow rates of 5 and 15 ml min\(^{-1}\), respectively (Stingaciu et al., 2017). Two samples were prepared, at 220°C (sample name: FR220) and at 320°C (sample name: FR320).

(b) Different cobalt salts. The syntheses using different cobalt sources required slight modifications compared with the previous synthesis, due to the reduced aqueous solubilities of the used cobalt salts. The salts used were cobalt(II) chloride (CoCl\(_2\)), cobalt(II) nitrate [Co(NO\(_3\))\(_2\)] and cobalt(II) acetate [Co(CH\(_3\)COO)\(_2\)]. Here, 20 ml of Fe(NO\(_3\))\(_3\) (2.0 M) were mixed with 20 ml of either CoCl\(_2\), Co(NO\(_3\))\(_2\) or Co(CH\(_3\)COOH)\(_2\) (1.0 M) to obtain a Co:Fe molar ratio of 1:2.

After thorough mixing, 30 ml of NaOH (12 M) was added, giving an \(\text{OH}^-/\text{Cl}^-/\text{NO}_3^-/\text{CH}_3\text{COOH}\) ratio of 2.25:1. The precursor was sealed in a 170 ml Teflon-lined steel autoclave and placed in a convection oven at 200°C for 1 h. In the following, cobalt(II) acetate will be abbreviated as Co(AC)\(_2\).

2.2. Structural characterization

Several different X-ray and neutron powder diffraction instruments were used for the structural characterization. An overview of the employed instruments is given in Table 3 and they are described below.

Room-temperature PXRD patterns were collected on two in-house Rigaku SmartLab powder X-ray diffractometers (Rigaku, Japan), one equipped with a Cu source (Cu K\(_{\alpha 1,2}\); \(\lambda_1 = 1.54059\ \text{Å}; \lambda_2 = 1.54441\ \text{Å}\)) and the other equipped with a Co source (Co K\(_{\alpha 1,2}\); \(\lambda_1 = 1.78892\ \text{Å}; \lambda_2 = 1.79278\ \text{Å}\)), both in Bragg–Brentano geometry. The powder diffraction patterns were collected using a Dtex/Ultra detector in fluorescence suppression mode and a diffracted beam monochromator was placed in front of the detector on the Cu-source instrument. The data collection is summarized in Table 3.

The NPD patterns were measured at room temperature at two different neutron sources: at the Swiss spallation neutron source (SINQ) (Blau et al., 2009; Allenspach, 2000), Paul Scherrer Institute (PSI), in Switzerland, and at the Institute for Energy Technology (IFE), Kjeller, Norway, using different instrumentation. At SINQ two diffractometers were used: DMC, the cold neutron powder diffractometer (https://www.psi.ch/en/sinq/dmc), and HRPT, the high-resolution powder diffractometer for thermal neutrons (https://www.psi.ch/en/sinq/hrpt) (Fischer et al., 2000). At IFE the PUS diffractometer was used (Hauback et al., 2000).

The instrumental contributions to the peak broadening of the collected patterns were determined from data collected on standard reference materials at equivalent instrumental configurations. An LaB\(_6\) NIST 660B standard was used for the in-house PXRD experiments (Black et al., 2011), while an Na\(_2\)Ca\(_2\)Al\(_4\)F\(_{14}\) standard was used for the NPD data at DMC and HRPT (Courbion & Ferey, 1988), and a CeO\(_2\) standard was used at PUS.

2.3. Vibrating sample magnetometry

The magnetic properties of the samples were characterized using a Physical Property Measurement System (PPMS), from Quantum Design, equipped with a vibrating sample magnetometer (VSM). The measurements were performed on cold-pressed cylindrical pellets with a diameter of 3 mm, gently compacted using a hand-held press. The field-dependent magnetization curves (expressed in A m\(^{-2}\) kg\(^{-1}\)) of the pellets were measured by scanning the externally applied field, \(H_{\text{app}}\), between ±3 T at 27°C. The saturation magnetization \(M_{\text{sat}}\) was obtained by applying the law of approach to saturation to the data (Zhang et al., 2010).

2.4. Structural refinement

The structural analyses were carried out using the FullProf Suite software (Rodriguez-Carvajal, 1993). The crystalline CoFe\(_2\)O\(_4\) phase was in all cases described in the space group \(Fd\bar{3}m\) with the Laue class \(m\bar{3}m\). As described by Andersen et al. (2019), the magnetic structure was implemented as an
additional magnetic phase with the lowest-symmetry space group of the corresponding centring, i.e. $F\bar{2}$. The special positions of $Fe^{3+}$ and $Co^{3+}$ cations were specified, and the first 24 symmetry operations of the $Fd\bar{3}m$ space group were provided to generate all atomic magnetic moments. Additional scattering factors (resonant terms) were added for each of the X-ray sources (see Table 1) to distinguish Fe and Co.

The peak profile parameters were described using the Thompson–Cox–Hastings (TCH) pseudo-Voigt function (Thompson et al., 1987), while the crystallites were assumed to be strain free. The crystallite size was extracted from the Lorentzian isotropic size parameter, $Y$, which was constrained between data sets through appropriate consideration of the wavelength. This constraining process is explained in detail in the supporting information.

The scale factors for X-ray data sets were refined individually, in contrast to the scale factors for nuclear and magnetic phase for the neutron data, which were kept identical as they belong to the same data set. The backgrounds were described by Chebyshev polynomials, with a maximum of six refinable coefficients ($Bck_0, 1, 2, 3, 4$ and $5$). The wavelength for the neutron data was refined, allowing a single common unit-cell parameter to be refined for all the diffraction patterns, along with the zero point. The fractional coordinates of oxygen $(x, x, x)$ were also refined. The site occupation fraction (Occ) was refined with a constraint, as were the atomic displacement parameters (ADPs) and the atomic magnetic dipolar moment $(R_i)$. The refinement of these three parameters is described below.

For low-$Q$-coverage neutron data ($Q_{\text{max}} < 4 \, \text{Å}$, i.e. DMC), the ADPs were refined as one common isotropic displacement parameter $(B_{\text{iso}})$ for all atoms. We set the Td and Oh sites to be fully occupied while refining the relative Co and Fe occupancies with the total Co and Fe content constrained to the nominal Co:Fe ratio of 1:2. This means that $\text{CoFe}_2\text{O}_4$ was refined as $(\text{Co}^{2+}_{x=1 - x}, \text{Fe}^{3+}_x)\text{Fe}^{3+}_{x=1 - x}(\text{Fe}^{3+}_{x=1 - x}, \text{Co}^{2+}_x)\text{O}_4\text{O}_4$, with $x$ being the inversion degree, where $x = 0$ is normal spinel and $x = 1$ is fully inverse.

The magnetic structure was constrained on the basis of the number of unpaired electrons in $Fe^{3+}$ $(3d^5)$ and $Co^{2+}$ $(3d^7)$. Thus, the magnetic moments of $Co^{2+}$ and $Fe^{3+}$ were refined in a 3:5 ratio, without taking the Co orbital contribution into account, i.e. assuming the orbit moment is quenched. The moment was refined along the (100) direction using the $R_x$ parameter, where $R_y$(Oh) was chosen to be positive and $R_x$(Td) negative. The effect of including the Co orbital contribution to the magnetic moment was investigated and is reported in the supporting information. It is not straightforward to determine which model is better suited to describe the magnetic structure of $\text{CoFe}_2\text{O}_4$. According to the VSM measurement, a better match between the experimental data and the refined NPD values was found when the orbit moment for Co was quenched.

For the uncertainties, the standard deviation provided by the FullProf Suite software was used except for the crystallite size. Here, the uncertainty was chosen to be equal to the unit-cell length, i.e. 0.8 nm, instead of the very low (0.001–0.01 nm) mathematical uncertainties provided by FullProf. Given that the unit cell constitutes the smallest crystal unit, we consider using the cell parameter as the uncertainty for the average crystallite size to be more appropriate from a physical perspective. The uncertainty of the calculated net intrinsic magnetization $(M_{\text{neutron}})$ is based on the standard deviation of each element constituting the calculation.

3. Results and discussion
3.1. Part 1, reliable extraction of Fe/Co occupancies in $\text{CoFe}_2\text{O}_4$

(a) Pattern weighting influence. When jointly refining multiple diffraction patterns, the weighting between data sets must be carefully considered as this may significantly influence the outcome of the refinement. As noted by both Deutsch et al. (2012) and Coppens et al. (1981), the weighting scheme constitutes one of the main issues in joint refinement strategies. Yet, this remains a topic of much debate, with the literature providing no definitive answer, and thus the weighting schemes are generally somewhat subjectively chosen. Two weighting schemes seem to be prevalent: (i) a weighting that minimizes the sum of the goodness of fit $(R$ factors and $\chi^2$) of each pattern (Deutsch et al., 2012; Coppens et al., 1981; Duckworth et al., 1969; Kibalin et al., 2017) and (ii) a weighting scheme that minimizes the sum of the goodness of fit normalized per data number for each pattern, by using log functions (Deutsch et al., 2012; Kibalin et al., 2017; Gillet & Becker, 2004). The scheme adopted by the FullProf Suite software corresponds to (i), by considering the residual function defined as $\chi^2 = \sum_{\alpha} w_i [y_i - y_{\alpha}(\alpha)]^2$, where $[y_i - y_{\alpha}(\alpha)]^2$ represents the difference between the experimental and the calculated patterns, while the statistical weight $w_i$ is defined as the inverse of the squared variance of the observed pattern, $\sigma_i$. In our refinement, the minimized function of the whole refinement can be defined as $\chi^2_{\text{tot}} = \sum_{\alpha} w_P \chi^2_{\alpha}$ with $w_P$ and $\chi^2_{\alpha}$ the weight and chi-squared of the individual pattern $P$, respectively. Therefore step size, uncertainties and intensities are to be considered if a proper weighting of different data is to be carried out.

Here, we have considered three weighting schemes and made a simple comparative study of the influence of the pattern weighting on the refinement of atomic and microstructural parameters of cobalt ferrite. In conclusion, we found that the three tested weighting models gave very similar results and/or are within the uncertainty of each other, indicating that the weighting scheme does not hugely affect the refinements of the present data. Therefore, in the following, we have used the standard FullProf weighting model using equivalent weight of all patterns. The study of the three weighting schemes can be found in the supporting information.

(b) Combining different patterns. Joint refinements of different combinations of the PXRD (Co and/or Cu) and NPD data are evaluated, with special emphasis on investigating the reliability/consistency of the Co/Fe occupation fractions.
obtained from the refinements. Refinements of seven different combinations of the three patterns were tested using equal weighting: (i) DMC/Co/Cu, (ii) DMC/Co, (iii) DMC/Cu, (iv) Co/Cu, (v) DMC, (vi) Co and (vii) Cu. Table 4 gives an overview of the extracted refinement parameters. Each individual pattern is described in the supporting information. The refined powder diffraction patterns from combination (i) (DMC/Co/Cu) can be seen in Fig. 2, while the six remaining combinations of patterns are reported in Fig. S2 (see the supporting information).

The in-depth investigation of the different combinations reveals the models that best describe the crystal and magnetic structure, as well as the Co/Fe occupation fraction. The different models are discussed in the following.

Using only the data set (vii) (Cu) is not a good choice for refining the Co/Fe site occupation fractions as unphysical values are obtained. This is not surprising because the Cu data have almost no scattering contrast between Co and Fe. The neutron data with limited Q range alone [model (v)] are also not a good choice, as the refinement yields an unrealistic description of the ADPs due to the limited number of Bragg peaks (Andersen, Bøjesen et al., 2018). It is perhaps more surprising that the data set (vi) (Co) actually performs very well compared with the combined X-ray and neutron models.

If information on Fe/Cu occupation is sought, using data set (vi) (Co) alone saves time with regard to data collection. The refinement of data set (vi) (Co) is close to identical to combinations (i) (DMC/Cu/Co) and (ii) (DMC/Co). This contradicts the common notion that in-house PXRD data alone cannot be used to extract reasonable occupation fractions for neighbouring elements. When using Co radiation, it is the resonant scattering terms \((f', f'')\) of Fe and Co that enhance the contrast between the elements.

Also the joint refinement of Cu and DMC [data set (iii)] provides a good structural description, making this a feasible data set combination for future diffraction experiments.

Table 4
List of refined parameters for the seven different combinations of data sets.

| combination | (i) DMC/Co/Cu | (ii) DMC/Co | (iii) DMC/Cu | (iv) Co/Cu | (v) DMC | (vi) Co | (vii) Cu |
|-------------|---------------|------------|------------|-----------|-------|-------|-------|
| Unit cell (Å) | 8.3892 (1) | 8.3890 (1) | 8.3891 (3) | 8.3890 (1) | 8.3889 (1) | 8.3890 (1) | 8.3891 (1) |
| Crystallite size (nm) | 13.2 (8) | 13.1 (8) | 13.3 (8) | 12.4 (8) | 13.3 (8) | 13.8 (8) |
| \(B_{\text{iso}} (Å^2)\) | 1.07 (1) | 1.22 (1) | 0.89 (4) | 1.22 (1) | 0.13 (8) | 1.20 (1) | 1.05 (2) |
| \(\text{Occ}(\text{Co}^{2+})_{\text{Oh}} \%)\) | 38 (1) | 38 (1) | 35 (1) | 40 (1) | 36 (1) | 40 (1) | 74 (13) |
| \(\text{Occ}(\text{Fe}^{3+})_{\text{Oh}} \%)\) | 62 (1) | 62 (1) | 65 (1) | 60 (1) | 60 (1) | 60 (1) | 26 (4) |
| \(\chi\) | 0.76 (2) | 0.76 (2) | 0.71 (1) | 0.80 (2) | 0.72 (1) | 0.79 (2) | 1.47 (35) |
| \(R_{\text{wp}}\) | 4.7/4.8/1.0 | 5.0/5.0 | 3.3/1.0 | 5.0/1.0 | 2.5 | 5.1 | 0.9 |
| \(R_{\text{Bragg}}\) | 2.5/2.8/5.1 | 2.5/2.5 | 1.1/7.2 | 2.4/8.7 | 0.5 | 2.4 | 6.9 |
| \(\text{mag} \%)\) | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 |
| \#reflections | 6/18/18 | 6/18 | 6/18 | 18/18 | 6 | 18 | 18 |

Figure 2
Combined Rietveld refinement of CoFe_{2}O_{4} diffraction patterns obtained using neutrons (DMC), Co and Cu as radiation sources. The data are shown as red circles, the refined model as a black line and the residual as a blue line. Weighted profile, \(R_{\text{wp}}\), and Bragg, \(R_{\text{Bragg}}\). \(R\) factors are indicated for each diffraction pattern. For visualization purposes, a specified frequency of data points has been selected: frequencies of 3, 20 and 10 points have been drawn for DMC, Co Ka and Cu Ka patterns, respectively.
The magnetic moment dipole was refined anti-parallel on the Td and Oh sites. Net intrinsic magnetization ($M_{\text{net}}$) was calculated on the basis of the $R_x$ values obtained from the refinement. The multiple measurements are referred as A1, A2, A3, B1, B2, and C1, C2, C3. The ‘Average’ column is based on the multiple measurements for samples A, B and C. The uncertainties of the average column are based on the standard deviation. The neutron diffraction data are part of an in situ study published by Ahlburg et al. (2020), but all refinements were redone for this work. All measurements made using model (ii) (DMC/Co).

The refinements of data set combinations (iv) (Co/Cu) and (vi) (Co) yield very similar structural descriptions, indicating that, in this case, the inclusion of the Cu pattern does not significantly degrade the accuracy of the results.

In conclusion, four of the examined data combinations can be used to obtain a reliable refinement of Fe/Co occupancies in CoFe$_2$O$_4$: (i) (DMC/Co/Cu), (ii) (DMC/Co), (iii) (DMC/Co/Cu) and (vi) (Co). A neutron diffraction pattern with a larger $Q$ range would also be able to produce reliable refinements of Fe/Co occupancies and the magnetic moment. Despite the limited $Q$ range of the DMC instrument, it was shown that only six peaks in NPD data are sufficient to extract reliable magnetic moments. Combining NPD with PXRD data gives a more robust refinement of the occupation factors as it removes correlations between ADPs and magnetic moments inherent to a single data set. Moreover, the refined formula unit magnetic moment $m_{\text{f.u.}}$ value is close to that of the bulk CoFe$_2$O$_4$, and good agreement was seen between the calculated net intrinsic magnetization and the saturation magnetization obtained by VSM measurement. Even if combinations (ii) (DMC/Co) and (iii) (DMC/Co/Cu) are comparable, we recommend using the model involving the Co source (ii) as it also carries information about the Fe/Co occupancies. Combination (i) (DMC/Co/Cu) constituted our benchmark as it has the largest quantity of data; however, the joint refinement of combination (ii) (DMC/Co) gives close to identical values to combination (i) (DMC/Co/Cu), and therefore combination (ii) is favoured as it involves collecting and treating fewer data to obtain the same result. The PXRD data in this case provide better peak resolution and $Q$ coverage, which is essential for describing the microstructure (lattice parameter, crystallite size and thermal vibrations). While it is preferable to have multiple patterns, the study reveals that it is possible to achieve a reasonable refinement of the Fe/Co occupancies using data from a Co X-ray source alone [model (vi)].

### Table 5

List of refined parameters for samples A, B and C.

| Sample | A1 | A2 | A3 | B1 | B2 | C1 | C2 | C3 | Average |
|--------|----|----|----|----|----|----|----|----|---------|
| $\text{Unit cell (Å)}$ | $8.3912(1)$ | $8.3912(1)$ | $8.3912(1)$ | $8.3927(1)$ | $8.3927(1)$ | $8.3919(1)$ | $8.3919(1)$ | $8.3919(1)$ | $8.3919(6)$ |
| $\text{Crystallite size (nm)}$ | $13.2(8)$ | $13.1(8)$ | $13.2(8)$ | $12.6(8)$ | $12.6(8)$ | $13.1(8)$ | $13.1(8)$ | $13.2(8)$ | $13.0(3)$ |
| $\text{Unit cell (Å)}$ | $8.3912(1)$ | $8.3912(1)$ | $8.3912(1)$ | $8.3927(1)$ | $8.3927(1)$ | $8.3919(1)$ | $8.3919(1)$ | $8.3919(1)$ | $8.3919(6)$ |
| $\text{Occ(Co)}_{\text{Oh}}$ (%) | $41(1)$ | $41(1)$ | $41(1)$ | $40(1)$ | $40(1)$ | $40(1)$ | $40(1)$ | $40(1)$ | $40(1)$ |
| $\text{Occ(Co)}_{\text{Td}}$ (%) | $18(1)$ | $19(1)$ | $18(1)$ | $21(1)$ | $20(1)$ | $19(1)$ | $19(1)$ | $19(1)$ | $19(1)$ |
| $\text{Occ(Fe)}_{\text{Oh}}$ (%) | $59(1)$ | $59(1)$ | $59(1)$ | $60(1)$ | $60(1)$ | $60(1)$ | $60(1)$ | $60(1)$ | $60(1)$ |
| $\text{Occ(Fe)}_{\text{Td}}$ (%) | $82(2)$ | $81(2)$ | $82(2)$ | $79(2)$ | $80(2)$ | $81(2)$ | $81(2)$ | $81(2)$ | $81(1)$ |
| $\text{R}_x$ (%) | $7.2/2.3$ | $6.7/2.4$ | $7.1/2.3$ | $5.7/2.4$ | $4.5/2.4$ | $4.2/2.4$ | $4.2/2.4$ | $4.2/2.4$ | $4.2/2.4$ |
| $\text{M}_{\text{net}}$ (A m$^{-1}$ kg$^{-1}$) | $72.9(1)$ | $72.9(1)$ | $72.9(1)$ | $73.8(4)$ | $73.8(4)$ | $73.8(4)$ | $73.8(4)$ | $73.8(4)$ | $75(4)$ |
| $\text{R}_x$ (%) | $14.8/5.3$ | $12.3/5.3$ | $15.1/5.3$ | $12.6/6$ | $16.9/6/6$ | $20.2/6.1$ | $20.1/6.1$ | $21.4/6.1$ | $21.4/6.1$ |
| $\chi$ | $1.83$ | $2.43$ | $1.73$ | $1.92/2$ | $1.4/2.3$ | $1.1/2.4$ | $1.2/2.4$ | $2.5/4.2$ | $2.5/4.2$ |
| $\text{R}_{\text{ave}}$ (%) | $7.2/2.3$ | $6.7/2.4$ | $7.1/2.3$ | $5.7/2.4$ | $4.5/2.4$ | $4.2/2.4$ | $4.2/2.4$ | $4.2/2.4$ | $5.5/2$ |
| $\text{R}_{\text{ave}}$ (%) | $4.7/2$ | $4.2/2$ | $3.6/2$ | $3.1/2$ | $4.2/2$ | $3.3/2$ | $5.0/2$ | $6.3/2$ | $5.5/2$ |
| $\text{f.reflections}$ | $6/16$ | $6/16$ | $6/16$ | $6/16$ | $6/16$ | $6/16$ | $6/16$ | $6/16$ | $6/16$ |

3.2. Part 2, reproducibility study

This second part of the study investigates the reproducibility of the autoclave synthesis method on the basis of data from three CoFe$_2$O$_4$ nanoparticle samples (A, B and C), reported by Ahlburg et al. (2020), synthesized under identical conditions. The reproducibility of the PXRD and NPD measurements, as well as the Rietveld refinements, was investigated. The NPD data were measured three times for the samples A and C, while sample B was measured twice at the DMC instrument. All these multiple measurements were acquired under identical conditions. Table 5 shows the refined structural values obtained for samples A, B, and C, while their diffraction patterns can be found in the supporting information (Figs. S3–S5).

The unit cell, apparent crystallite size (ACS) and oxygen position are all identical within the uncertainties of each repetition and between all samples. Only minute variations were noticed in the unit cell and thermal vibration parameters between the different samples; this can be attributed to a reduced probed sample volume for the $Q$ range exceeding 5 Å$^{-1}$ due to penetration of the sample as revealed by an Al(222) reflection originating from the sample holder (see the supporting information). This could also explain the larger $B_{\text{ov}}$ found here compared with values reported in the literature (~0.65 to ~1.05 Å$^2$) (Ferreira et al., 2003; Waseda et al., 1995; Tanaka et al., 2016), and the one found for model (ii) [1.22 (1) Å$^2$, DMC/Co] in part 1(b) (see Table 4).

The effect of different thermal vibration values was tested on sample C, by fixing $B_{\text{ov}}$ to 1.57 Å$^2$ (the value from sample A). The refinements are shown in the supporting information (Table S5) and named C$_{\text{BovFIX}}$. Only $R_x$ is affected by

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changing $B_{ov}$ and the obtained values are well within the uncertainties. The changes in $B_{ov}$ do not even affect the $R$ factors.

The parameters that differ between samples and repetitions are the site occupancy and the magnetic parameters. They are discussed individually below.

Site occupancy. The obtained inversion degree, $x$, is comparable for all data sets and the values range between 0.79 (3) and 0.82 (3). In other words, $x$ is identical between the multiple measurements, but is higher than other reported inversion degrees for CoFe$_2$O$_4$ nanoparticles ($x = 0.69$–0.79) (Sawatzky et al., 1968; Ferreira et al., 2003; Chandramohan et al., 2011; Tanaka et al., 2016). The values reported here are comparable to those reported by Granados-Miralles et al. (2018) and by Ahlburg et al. (2020), which are based on the same data, but with slight differences in the applied refinement model.

The cation distribution within a spinel ferrite compound is reported to be synthesis dependent (Andersen et al., 2019; Sawatzky et al., 1968; Ferreira et al., 2003; Chandramohan et al., 2011; Moumen et al., 1996). Here it is demonstrated that the autoclave synthesis is robust and the repeated data collection gives identical cation distributions.

Atomic ($R_x$) and formula unit magnetic moment ($m_u$). The extracted atomic magnetic dipole moments ($R_x$) reveal small differences between the different multiple measurements of the same sample, and across the batches. Sample A has identical $R_x$ within uncertainties while the variations of the atomic magnetic moment are larger in the case of samples B and C. For sample C3 an additional Bragg peak in the NPD pattern is observed at $\sim$3.1 Å$^{-1}$ – this peak is attributed to Ni(111) from a thermocouple used for monitoring the sample temperature. The Ni peak affects the residual between the experimental and calculated patterns (see Fig. S5), possibly affecting the refinement of the background, which in turn could reduce $R_x$ compared with C1 and C2.

Considering the magnetic moment per formula unit ($m_u$), it is found that all samples have similar values [2.9 (2)–3.4 (2) $\mu_B$] within 2$\sigma$ uncertainties, and that the multiple measurements yield the same refined value.

Net intrinsic magnetization ($M_{\text{neutron}}$) and saturation magnetization ($M_{\text{sat}}$). For sample A, the calculated $M_{\text{neutron}}$ values are close to identical between the three measurements, and all values are within the same uncertainty range. Comparison with macroscopic experimental values ($M_{\text{sat}}$) reveals good agreement between macroscopic and microscopic magnetization.

Sample C exhibits the highest net magnetization [77 (5)–81 (5) A m$^{-2}$ kg$^{-1}$] as extracted from the occupancies and magnetic moment. The obtained values are higher than the saturation magnetization [73.9 (1) A m$^{-2}$ kg$^{-1}$] measured by VSM. Nonetheless, the relatively large uncertainties on the extracted magnetization show that the obtained $M_{\text{neutron}}$ is within 2$\sigma$ of $M_{\text{sat}}$.

Comparing $M_{\text{sat}}$ for the three samples shows that they have close to identical saturation magnetization [72.9 (1)–73.9 (1) A m$^{-2}$ kg$^{-1}$], meaning that the AC synthesis yields reproducible results. Sample C exhibits an $M_{\text{neutron}}$ higher than the saturation magnetization from $M_{\text{VSM}}$. This deviation cannot arise from impurities in the sample, because an impurity would result in a reduced $M_{\text{VSM}}$ saturation magnetization. There is no apparent reason for the higher $M_{\text{neutron}}$ value in sample C. The other samples have $M_{\text{neutron}}$ and $M_{\text{VSM}}$ corresponding very well.

Average. To determine the reproducibility of the autoclave synthesis, an ‘Average’ column was added in Table 4. The ‘Average’ compares the statistical average of the refined values of all samples. As a statistical average is employed, the uncertainty of each parameter was based on the standard deviation method. Generally, the statistical average corroborates the individual parameters of each sample.

In summary, the comparison of the refinements of multiple data sets from the same sample shows hardly any variations, which clearly indicates that both the data collection of the DMC instrument and the Rietveld refinements yield strongly reproducible results. Additionally, by comparing the refined parameters between samples A, B and C we can conclude that the synthesis method is likewise reproducible, since the refined crystal/magnetic structures are almost identical with only minor deviations. The PXRD and NPD patterns do not show traces of impurities or eventual amorphous phase, and by comparing the theoretical magnetization ($M_{\text{neutron}}$) and the measured saturation magnetization ($M_{\text{VSM}}$), we can argue that all samples are highly crystalline.

3.3. Part 3, effect of different synthesis approaches

For high-$Q$-coverage neutron data ($Q_{\text{max}} > 4$ Å), some additional degrees of freedom may be included in the refinement since more data are available. In order to investigate this statement, a study was performed to compare the effect of the ADP being described by one parameter ($B_{ov}$) or by two distinct isotropic displacement parameters ($B_{iso}$) for the metal ions and oxygen. This study is detailed in the supporting information (Tables S6 and S7) and was performed on part 3(a) data. In short, it was observed that the $B_{iso}(\text{Fe/Co})$ values were larger than the $B_{ov}$ and caused a discrepancy between the Fe occupancy and $R_x$ between the $B_{ov}$ and $B_{iso}$ models. The $R_x$ in the $B_{iso}$ model is slightly higher than that in the $B_{ov}$, but within the uncertainties. The $B_{ov}$ model is reported in the following, as the $M_{\text{neutron}}$ values correspond better to the experimental $M_{\text{VSM}}$ data and the model is more similar to the model used in the previous parts of the paper. The $B_{iso}$ model, on the other hand, results in samples closer to the ideal stoichiometry of the CoFe$_2$O$_4$ spinel. The larger-$Q$-range data allowed the occupancy of the Td and Oh sites to be refined individually. This leads to the nominal formula (Co$^{2+}$)$_{1-x}$Fe$^{3+}$)$_{x}$Fe$^{3+}$)$_{y}$OH$_2$O$_4$, with $x$ and $y$ representing the inversion degrees for the Td and Oh sites, respectively. The formula unit charge balance was ignored for the obtained overall structure, when refining $x$ and $y$ freely.

(a) Effect of different hydrothermal reactors. This study is based on the work of Stingaciu et al. (2017), and the purpose is to investigate the crystal and magnetic structures of four
cobalt ferrite spinel samples prepared using different hydrothermal reactors: AC, SR and FR. The main difference between these three reactors is the time it takes for the reactor to reach the desired reaction temperature (heating rate) and how long the sample is held at the elevated temperature. The slowest heating takes place in the AC (~0.15°C s⁻¹), followed by the SR (25°C s⁻¹), while in the FR the heating is almost instantaneous (~500°C s⁻¹). Four samples were investigated by PXRD and NPD using a Cu Kα₁,₂ source Rigaku diffractometer and the neutron diffractometer PUS: two samples were made using the FR at 220°C (FR220) and 320°C (FR320), one from the SR at 240°C (SR240), and one from the AC at 240°C (AC240). The collected powder diffraction patterns of these samples are shown in Fig. 3. The presence of an impurity (main peaks at 1.7, 2.3 and 3.4 Å⁻¹) can be observed in Fig. 3(a), and it is identified as hematite, α-Fe₂O₃ (space group R₃c, No. 167). The formation of α-Fe₂O₃ cannot be avoided when using a precursor with pH below 12 (Cote et al., 2003; Zhao et al., 2007). However, regarding the quantity of OH⁻ ions introduced by the sodium hydroxide solution, the pH is estimated as being equal to 15.2. Therefore the presence of hematite is unexpected, and the hematite content within sample FR220 is estimated to be <1 wt%.

The Cu source was used because the Co source had not yet been installed in the laboratory. The sloping background can be explained by the fluorescence signal decaying at a high angle (Q > 5 Å⁻¹) and is clearly visible in all of the PXRD patterns in Fig. 3. From the results in part 1(b) and the refinements of model (iii) (DMC/Cu), it was expected that replacing DMC data with data from PUS, which has twice the Q range (Table 2), would yield a robust description. Table 6 shows the refined parameters for the four samples; the refined parameters are discussed below.

Unit-cell parameter. The largest unit cell is obtained for samples AC240 (slowest heating rate), followed by SR240 (medium heating rate), while the two FR samples (fastest heating rate) exhibit smaller unit cells. In the literature (Cedeño-Mattei & Perales-Pérez, 2009; Andersen & Christensen, 2015; Cote et al., 2003), the unit-cell lengths for CoFe₂O₄ have previously been reported to be between 8.31 and 8.43 Å, and all the values found here are within this range.

On the basis of the in situ studies by Andersen & Christensen (2015) on the formation of CoFe₂O₄, the largest unit-cell parameters were expected for the smallest crystallites. However, the opposite trend is seen here, suggesting the unit-cell dimension is not only related to the crystallite size but also very dependent on the stoichiometry and specific site occupation of Co/Fe and potential vacancies.

Apparent crystallite size. Stingaciu et al. (2017) reported that heating rates, pressure and temperature play an important role in the formation of hematite and the apparent crystallite size. The results in this study show a similar trend, with the FR samples exhibiting smaller apparent crystallite sizes compared to the AC and SR samples.

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Apparent crystallite size. Stingaciu et al. (2017) reported that heating rates, pressure and temperature play an important role in the formation of hematite and the apparent crystallite size. The results in this study show a similar trend, with the FR samples exhibiting smaller apparent crystallite sizes compared to the AC and SR samples.
Table 6
Refinement comparison of four samples synthesized by either FR, SR or AC.

|            | FR220 | FR320 | SR240 | AC240 |
|------------|-------|-------|-------|-------|
| Unit cell (Å) | 8.353 (4) | 8.378 (2) | 8.386 (2) | 8.392 (1) |
| Crystallite size (nm) | 5.2 (8) | 10.9 (8) | 10.7 (8) | 15.1 (8) |
| Crystallite size (nm) | 8.2 (1) | 10.6 (1) | 11.6 (1) | 15.3 (1) |

The temperature used during the synthesis is included in the name of the sample. The refinement model employed a combination of PXRD data (Cu Kα) and NPD data from PUS. Due to the high Q range of the NPD data, the Td and Oh site occupancies could be refined independently. The distribution of both Fe³⁺ and Co²⁺ within Td and Oh sites is detailed as x and y, respectively. m_{t.a.} and M_{neutrom} were calculated on the basis of the refined site occupancy and R_s. The X-ray and magnetic data were previously published by Stingaciu et al. (2017), but the neutron data and all refinements have not been previously published.

Increasing ACS. Indeed, it is found in the literature that increasing the particle diameter enhances the saturation magnetization (Stingaciu et al., 2017; Andersen et al., 2019; López-Ortega, Lottini et al., 2015; Maaz et al., 2007). Despite variations in R_s, FR320, SR240 and AC240 have the same m_{t.a.} (3.0 μB f.u.⁻¹), while for FR220 it is lower (2.7 μB f.u.⁻¹). The differences are explained by variations in the occupancy of the different sites and the Co/Fe ratio. Comparing FR220 and FR320, it is revealed that increasing the temperature enhances the magnetic properties.

Regarding the saturation magnetization obtained from VSM measurements, a large discrepancy is seen in the FR220 and FR320 samples: M_{sat}(FR320) is almost twice as large as M_{VSM}(FR220). Concerning the FR220 sample, the reason why M_{sat} is significantly smaller than the others (38.68 A m² kg⁻¹) is probably the small ACS, which increases the surface area to volume ratio, thus increasing the relative amount of surface structural reordering. It could also be due to cation vacancies and defects in the octahedral sites, reducing the magnetic moment (Huang et al., 2017). With the present structural model, vacancies on the octahedral site would be modelled as an increased Co²⁺ occupancy on the octahedral site. Another explanation for the low saturation magnetization of FR220 is that the sample is partly superparamagnetic, since the ACS is small enough to allow such magnetic behaviour (Alzoubi et al., 2020; Mooney et al., 2004; Ahn et al., 2003; Moumen & Pileni, 1996; Sangeneni et al., 2018). An impurity phase of α-Fe₂O₃ was also identified in FR220, although the content was <1 wt%. Hematite is an antiferromagnet/weak ferromagnet at ambient temperature (Tadic et al., 2014; Aharoni et al., 1962). However, the possibility cannot be excluded that other non-crystalline phases are contributing to the mass of the sample. Such impurities can explain the low M_{sat} observed for FR320. It is also noted that the remaining samples have higher M_{neutrom} than M_{sat} only for AC240. The ACS for AC240 are close, with a deviation of just 2 A m² kg⁻¹, compared with 6 and 8 A m² kg⁻¹ for FR320 and SR240, respectively.

In parts 1(b) and 2 it was found that the AC synthesis produced highly crystalline materials, as corroborated by the values of M_{neutrom} and M_{sat}. The most likely explanations for the discrepancies for the other samples are the presence of non-crystalline impurities adding to the mass of the sample. Additionally, for FR220 the model may not correctly describe the system, because the interstitial sites are forced to be fully occupied and vacancies could occur on the octahedral site.
Table 7
List of refined parameters for CoFe$_2$O$_4$ samples prepared with different Co-containing salts.

| Parameter               | Co(Ac)$_2$      | Co(NO$_3$)$_2$    | CoCl$_2$     |
|-------------------------|-----------------|------------------|--------------|
| Unit cell (Å)           | 8.4031 (2)      | 8.4058 (2)       | 8.4060 (2)   |
| Crystalite size (nm)    | 10.2 (8)        | 10.6 (8)         | 10.7 (8)     |
| $x$ (O)                 | 0.2430 (1)      | 0.2430 (1)       | 0.2430 (1)   |
| $B_0$ (Å$^3$)           | 0.65 (1)        | 0.74 (1)         | 0.69 (1)     |
| Occ(Co$^{3+}$)$_{Oh}$ (%)| 39 (1)         | 40 (1)           | 39 (1)       |
| Occ(Co$^{3+}$)$_{Td}$ (%)| 61 (1)        | 60 (1)           | 61 (1)       |
| Occ(Fe$^{3+}$)$_{Oh}$ (%)| 39 (1)        | 40 (1)           | 40 (1)       |
| Occ(Fe$^{3+}$)$_{Td}$ (%)| 61 (1)        | 60 (1)           | 60 (1)       |
| $M_{\text{neutron}}$   | (Co$_{0.39}$Fe$_{0.61}$)$_{Oh}$ | (Co$_{0.40}$Fe$_{0.60}$)$_{Oh}$ | (Co$_{0.39}$Fe$_{0.61}$)$_{Oh}$ |
| $M_{\text{neutron}}$   | [Co$_{0.78}$Fe$_{1.22}$]$_{Oh}$ | [Co$_{0.80}$Fe$_{1.20}$]$_{Oh}$ | [Co$_{0.80}$Fe$_{1.20}$]$_{Oh}$ |
| $M_{\text{neutron}}$   | 77 (2)          | 75 (2)           | 76 (2)       |
| $M_{\text{sat}}$ (A m$^2$ kg$^{-1}$) | 66.81          | 69.32            | 66.67        |
| $R_{\text{exp}}$ (%)  | 8.06/9.8        | 9.19/5           | 8.90/3       |
| $R_{\text{mag}}$ (%)   | 2.91/3          | 3.1/1.4          | 3.0/1.3      |
| $R_{\text{mag}}$ (%)   | 2.94/3          | 3.5/2.4          | 3.4/3.3      |
| $R_{\text{mag}}$ (%)   | 4.9/-           | 5.6/-            | 5.5/-        |
| $M_{\text{sat}}$ (%)   | 31/21           | 31/21            | 31/21        |

In summary, the crystal and magnetic structures of CoFe$_2$O$_4$ nanoparticles prepared from three different precursors [containing Co(OAc)$_2$, CoCl$_2$ and Co(NO$_3$)$_2$] have been compared. The three samples exhibit similar ACS, oxygen positions and site occupancies. Only the unit-cell parameter, thermal vibrations and magnetic moments reveal slight differences. The three samples are also magnetically similar and their net intrinsic magnetization is almost identical, as is their macroscopic magnetization ($M_{\text{sat}}$), further evidence that the investigated precursor anions are not influencing the final product in the autoclave synthesis. The observed difference between $M_{\text{neutron}}$ and $M_{\text{mag}}$ may be due to the presence of amorphous phases or size and/or size distribution effects with regards to macroscopic magnetic properties.

3.4. Part 4, effect of synthesis conditions

This part of the paper features the four CoFe$_2$O$_4$ samples synthesized by the autoclave reactor, which were prepared from Co(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O in a ratio of 1:2. The four samples were characterized using three different NPD instruments and two different in-house X-ray diffractometers.

Table 8 gives a summary of the obtained structural parameters. The first two columns are extracted from part 1 and show model (ii) (DMC/Co) and model (iii) (DMC/Cu), while the third column is the average column from Table 5. The results are in general remarkably similar, with minor deviations related to crystallite size and unit cell, which can be attributed to the differences in synthesis conditions. The refined occupancies on the octahedral sites are nearly identical, while larger deviations are found for the tetrahedral site.
especially for the average of samples A, B and C (third column), as well as the sample synthesized at 200°C (last column). Some of the differences may also be attributed to the Co:Fe ratio being fixed in the refinement of the DMC data, which does not allow deviations from the nominal composition or introduction of vacancies. The thermal vibration also deviates, and since this parameter correlates strongly with the occupancies it may also help explain the discrepancy. Regarding the atomic magnetic dipole moment, the average of samples A, B and C from part 2 is the sample that exhibits the highest values, and the samples from parts 1(a) and 2 are identical. This may be expanded to other elements, e.g. Fe/Mn and Fe/Ni, allowing in-house determination of site occupancies in spinel structures and other transition metal oxides with mixed occupancies, e.g. battery materials. Here neutron diffraction data improved the robustness of the model, even if only six Bragg peaks were included.

Part 2 was focused on the reproducibility of the synthesis, data collection and refinements of the low-Q-range neutron data. Comparing multiple measurements on the same sample clearly showed that the low-Q-range neutron data collection and Rietveld refinements are highly reproducible. The comparison of three samples with identical synthesis procedure showed that the synthesis method was reproducible, with only minute deviations.

Part 3(a) compared three samples prepared using different hydrothermal reactors, with different heating rates, namely, a continuous flow reactor (FR), spiral reactor (SR) and autoclave (AC). The size is the parameter most affected, while the distribution of Co/Fe between the octahedral and tetrahedral sites in the structure is less influenced by the heating rate and holding time.

### Table 8

| Sample | Model (ii) DMC/Co | Model (iii) DMC/Cu | Average of A, B and C | AC240 | Co(NO₃)₂₂⁻
|--------|-------------------|--------------------|----------------------|-------|----------------
| Temperature/time (°C/h) | 240/2 | 240/2 | 240/2 | 240/1 | 200/1 |
| Fe:Co:NaOH (M) | 2.16 | 2.16 | 2.16 | 2.16 | 2.16 |
| pH:NaOH | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 |
| Unit cell (Å) | 8.3890 (1) | 8.3891 (3) | 8.3919 (6) | 8.3925 (1) | 8.4058 (2) |
| Crystal size (nm) | 13.3 (8) | 13.1 (8) | 13.0 (3) | 15.1 (8) | 10.6 (8) |
| Crystallinity (%) | 35 (1) | 35 (1) | 35 (1) | 35 (1) | 35 (1) |
| Occ(Co²⁺)Oh (%) | 38 (1) | 35 (1) | 35 (1) | 35 (1) | 35 (1) |
| Occ(Co²⁺)Td (%) | 24 (1) | 29 (1) | 29 (1) | 29 (1) | 29 (1) |
| Occ(Fe³⁺)Oh (%) | 62 (1) | 65 (1) | 65 (1) | 65 (1) | 65 (1) |
| Occ(Fe³⁺)Td (%) | 7 (1) | 7 (1) | 7 (1) | 7 (1) | 7 (1) |
| Mᵣ (A m² kg⁻¹) | 73 (3) | 77 (2) | 75 (4) | 70 (2) | 75 (2) |
| Mₑ (A m² kg⁻¹) | 73.5 (2) | 73.5 (2) | 73.5 (6) | 68.58 (2) | 69.32 |

All samples summarized here were synthesized using an autoclave reactor.
Part 3(b) was dedicated to the investigation of the influence of using different cobalt salts in the precursors: CoCl₂, Co(NO₃)₂, and Co(CH₃COOH). The three CoFe₂O₄ nanoparticle samples prepared from the different precursors have practically identical crystal and magnetic structures, demonstrating that the cobalt salt anions used have no influence on the final product.

Finally, part 4 described considerations regarding differently prepared samples of CoFe₂O₄ nanoparticles using an autoclave. Despite differences in the macroscopic magnetic properties, all samples exhibited similar crystal and magnetic structure.

The presented study revealed that the hydrothermal synthesis of CoFe₂O₄ is highly reproducible. The net crystallographic magnetizations calculated from refined occupancies and the atomic dipolar magnetic moment are generally in good agreement with macroscopic magnetic measurements, except for the smaller crystallite where superparamagnetic behaviour or disorder and amorphous phases may play a role. Reliably establishing this link between crystal/magnetic structure and observed magnetic properties is key to investigating the structure–property relationship in spinel ferrites as well as other magnetic compounds.

5. Related literature

The following references are cited in the supporting literature:

Langford & Wilson (1978), Rodriguez-Carvajal (2003), Shanmugavani et al. (2015).

Acknowledgements

We gratefully acknowledge neutron beamtime at PSI and IFE and support by the beamline staff Emmanuel Canévet and Denis Sheptyakov at PSI and Magnus Sorby at IFE. Affiliation with the ESS lighthouses SMART and Q-MAT as well as the Center for Integrated Materials Research (iMAT) at Aarhus University is gratefully acknowledged.

Funding information

MC and HLA are grateful for support from the Carlsberg Foundation (grant Nos. CF16-0084, CF18-0519 and CF19-0143). CG-M acknowledges financial support from MICINN through the ‘Juan de la Cierva’ Program (FJJC2018-035532-I). JVA acknowledges financial support from Nordforsk (project No. 106874). We thank the Danish Agency for Science, Technology and Innovation for funding the instrument center DanScatt (7129-00003B).

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