Supplement

In our XRD investigation, a set of reflections is determined by the Bragg equation:

 $2d \times sin\Theta = n \times \lambda$, where n = 1, 2, 3, ..., is the order of the reflections (1)

Their intensity is determined as

$I(hkl) = K \times Lp \times T \times A \times G \times m \times F(hkl)^2$ (2)

Where, K is a scaling constant related to the intensity of X-ray beam. Lp is the Lorentz and polarization factor. T is the overall temperature factor of the structure. A is the absorption correction for flat specimen that can be observed and detected. G is the preferred orientation correction. m is the reflection multiplicity. F is the so-called structure factor (or atomic factor) derived from the packing (i.e. Fourier transform) of all atoms in a unit cell.

Table 1. Indexing of $CoFe_2O_4$ with cubic spinel structure (Fd3m-277: a=b=c=8.234Å). 2Theta(o): Observed angular; 2Theta(c): Correction angular; d (Å): d-spacing; (hkl): All possible reflections of a given unit cell. I(hkl) is normalized to the strongest reflection in the list and reported as relative percentage I%. (-----: Parameters are not selected for analysis and evaluation).

2Theta(o)	(hkl)	2Theta(c)	DeltaO	d(c)	d(o)	Del-d	١%
18.471	(111)	18.445	-0.026	4.8061	4.7994	0.0067	11.3
30.396	(220)	30.345	-0.052	2.9431	2.9382	0.0049	29.1
35.765	(311)	35.745	-0.020	2.5099	2.5085	0.0014	100.0
37.422	(222)	37.392	-0.031	2.4030	2.4011	0.0019	10.8
43.481	(400)	43.447	-0.034	2.0811	2.0796	0.0015	24.6
	(331)	47.574		1.9097			
53.831	(422)	53.913	0.083	1.6992	1.7016	-0.0024	9.70
57.491	(511)	57.477	-0.014	1.6020	1.6017	0.0004	34.0
62.056				1.4944			7.1
63.134	(440)	63.127	-0.007	1.4716	1.4714	0.0001	43.0
	(531)	66.382		1.4071			
	(442)	67.449		1.3874			
71.642	(620)	71.638	-0.004	1.3162	1.3161	0.0001	8.2
74.679	(533)	74.714	0.0350	1.2695	1.2700	-0.0005	11.6
75.730	(622)	75.729	-0.001	1.2550	1.2549	0.0000	7.1
	(444)	79.746		1.2015			
	(551)	82.724		1.1656			
75.730					1.2549		7.1
83.416				1.1577			7.9

87.647	(642)	87.649	0.002	1.1124	1.1124	0.0000	7.5
87.944				1.1094			8.8
90.547	(731)	90.593	0.046	1.0837	1.0842	-0.0004	12.5

Rietveld Refinement to XRD patterns

The X-ray diffraction patterns of metal and oxide particle products were recorded by a X-ray diffractometer (Rigaku D/max 2550V) at 40kV/200 mA and using Cu Kα radiation (1.54056 Å). Here, the general theoretical foundation for the investigation of crystals by X-rays is Bragg's law. It describes the diffraction of waves by the crystal lattice

$$n\lambda = 2d_{(hkl)}\sin\theta \tag{1.1}$$

where λ – wavelength, d - spacing of reflecting planes, θ - angle of incidence and reflection, n - order of diffraction. For crystal structure with lattice parameter, monochromatic radiation of diffractometer, and order of reflection, we can calculate the interplanar spacing and the diffraction angle for the set of planes. To calculate crystallite size of α -Fe₂O₃ and CoFe₂O₄ particles, we have additionally used Debye-Sherrer's equation as estimation [1,2]

$$D = 0.89\lambda / (\beta \cos \theta) \tag{1.2}$$

Here, structural parameters are crystallite size (D), wavelength of X-ray radiation (λ), Full width at half maximum with the most intense peak in XRD patterns (β), Bragg angle (θ), respectively.

The Rietveld method is commonly used to determine and refine crystal structures from powder diffraction data. We have two spaces, the direct or crystal space (experimental), and the reciprocal space (theory), which is connected by Fourier transformation. The experiment itself is a Fourier-transformation.

$$\phi = \sum_{i} w_i (y_i(obs) - y_i(calc))^2 = Minimum$$
(1.3)

 y_i is the measured intensities at each step. The summation index i is running over all points in the diffraction pattern. In the weights w_i of above equation are given to each observation. They are taken from the experimental error margins σ_i , which are assumed to be proportional to the square root of the count rate $y_i(obs)$ following Poisson counting statistics

$$w_i = 1/\sigma_i^2 \tag{1.4}$$

The profile shape functions can be used in profile fitting programs, such as Gaussian, Lorentzian, Pseudu-Voigt, and Person VII. They are the functions of diffraction involved in angle, peak intensity, shape parameter, and others. The parameters are $2\Theta_0$ =peak position, I₀=peak intensity, ω =FWHM/2, and m=shape parameter in the following functions [3e] and Made MDI data

Gaussian:
$$G = I_0 \exp\left(-\ln 2\left(\frac{2\theta - 2\theta_0}{\omega}\right)^2\right)$$
(1.5)

Lorentzian:
$$L = I_0 \left(1 + \left(\frac{2\theta - 2\theta_0}{\omega} \right)^2 \right)^{-n} \quad \text{with } n = 1; 1.5; 2 \quad (1.6)$$

Pseudo – Voigt :
$$V = \eta L + (1 - \eta)G \qquad (0 \le \eta \le 1) \qquad (1.7)$$

PeasonVII:
$$P = I_0 \left(1 + \left(\frac{2\theta - 2\theta_0}{ma^2} \right)^2 \right)^{-m}$$
(1.8)

In MDI Jade 6 software, Rietveld method is used for analysis of powder diffraction data of XRD data from experimental. The procedures for crystal structure determination from powder data are applied. In criteria of fit, at the end of a refinement it is necessary to check whether the results are meaningful, and whether they meet certain standard criteria. This holds both for single peaks and for full pattern refinements. The overall best criteria for the fit are without doubt difference plots between observed and calculated data.

1. Criteria for single resolved reflections:

(a) $y_i(obs) - y_i(calc)$ difference plot. (b) maximum deviation at any point in the difference plot. (c) goodness of fit, R-index for one (or several) isolated individual reflection. (d) variance range, observed vs. calculated.

2. Criteria for the whole pattern in a Rietveld analysis:

(a) $y_i(obs) - y_i(calc)$ difference plot. (b) maximum deviation at any point in the difference plot. (c) index R_{wp} for the profile fit. (d) index R_B (B for Bragg) for the agreement of

integrated peak values. It must be kept in mind that the values I(obs) are calculated on the calculated ones, and are not directly comparable to single crystal R-indices. There are structural parameters and their standard deviations (if possible in comparison to similar single crystal results). The powder diffraction data are not directly comparable to single crystal data, but the R-indices used are close to the single crystal structure R-value. Only R_p and R_{wp} shown are of real value. We can define R-indices used in Rietveld analyses as follows

$$R_{F} = \frac{\sum \left| \left(I_{K} (obs) \right)^{1/2} - \left(I_{K} (calc) \right)^{1/2} \right|}{\sum \left(\left(I_{K} (obs) \right) \right)^{1/2}}$$
(1.9),

$$R_{B} = \frac{\sum \left| \left(I_{K} \left(obs \right) \right) - \left(I_{K} \left(calc \right) \right) \right|}{\sum \left(\left(I_{K} \left(obs \right) \right) \right)^{1/2}} (= R_{l}) (1.10)$$

$$R_{p} = \frac{\sum |(y_{i} (obs)) - (1/c)y_{i} (calc)|}{\sum y_{i} (obs)} \quad (1.11),$$

$$R_{wp} = \frac{\sum \left| \left(\sum w_i \left(y_i (obs) \right) \right) - \left((1/c) y_i (calc) \right)^2 \right|^{1/2}}{\sum w_i \left(y_i (obs) \right)^2}$$
(1.12)

Of the several R-indices which are used to check on the quality of the fit and refinement R_{wp} is statistically the most meaningful indicator of the overall fit since the numerator is the residual that is minimized in the least squares procedure. Any R-index presented is meaningful only if the background has been subtracted.

References:

- (1) G. Will, Powder Diffraction, The Rietveld Method and the Two Stage Method to Determine and Refine Crystal Structures from Powder Diffraction Data, Springer-Verlag Berlin Heidelberg (2006).
- (2) MDI Jade 6.5, Materials science, Inc.