

Supporting Information

Effects of crystallite sizes on the structure and magnetism of ferrihydrite

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SI-1. XRD fitting

The main purpose for the XRD fitting was to obtain the crystallite size of the ferrihydrite samples using the TOPAS software. The operation procedures were simply introduced as follows. Firstly, the raw data were loaded in the software, and the basic parameters were set in the “Parameters Window”, including emission profile, background function, instrument settings, and correction items. Then, an hkl-phase (for lattice parameter refinements) was added and the structural parameters from the Michel model (space group: P63mc, crystal cell parameters $a = 5.928$, $c = 9.125$, and $v = 277.7$) were entered as the initial values. Finally, the fitting was achieved by iteration to get the smallest R_{wp} . The fitted results are shown in Figure S1. The good fit between the fitting curves and experimental data, assures that the obtained crystallite sizes are correct. However, the obtained crystal cell parameters are less realistic because there was no strict restriction for the atomic positions by this method. Better results for the crystal cell parameters have been obtained with the PDF fitting (see the manuscript).

Table SI-1. The cell parameters obtained by Rietveld fitting for the ferrihydrites.

Samples	a (Å)	c (Å)	Crystallite size (nm)	Cell volume v (Å ³)	R_{wp} (%)
2LFh_1	5.776	9.256	1.6	267.4	2.18
5LFh_2	5.652	9.180	2.6	254.0	1.68
5LFh_3	5.667	9.321	3.4	259.3	1.75
6LFh_4	5.901	9.480	4.4	285.9	2.49
Michel model	5.928	9.125		277.7	

SI-2. Mössbauer results at 20 K

The spectra are depicted in Fig. 4 c of the manuscript. The parameters obtained by fitting the results with a doublet and sextet or with two sextets are summarized in Table SI-2.

Table SI-2. Hyperfine parameters at 20 K of the four ferrihydrite samples fitted with one doublet and one sextet for 2LFh_1 and 5LFh_2 and with two sextets for 5LFh_3 and 6LFh_4.

Samples	Sites	C_s (mm s ⁻¹)	Q_s (mm s ⁻¹)	Hyperfine field (T)	Site population (%)
2LFh_1	Doublet 1	0.435	0.860		21.4
	Sextet 1	0.428	-0.023	39.2	78.6
5LFh_2	Doublet 1	0.412	0.786		46.8
	Sextet 1	0.413	-0.063	45.4	53.2
5LFh_3	Sextet 1	0.585	0.032	42.8	52.6
	Sextet 2	0.063	-0.307	42.0	47.4
6LFh_4	Sextet 1	0.480	-0.040	45.8	45.1
	Sextet 2	0.491	-0.053	39.5	54.9