Supplementary Information for:

Competing magnetic interactions and the role of unpaired 4f electrons in oxygen-deficient perovskites $Ba_3RFe_2O_{7.5}$ (R = Y, Dy)

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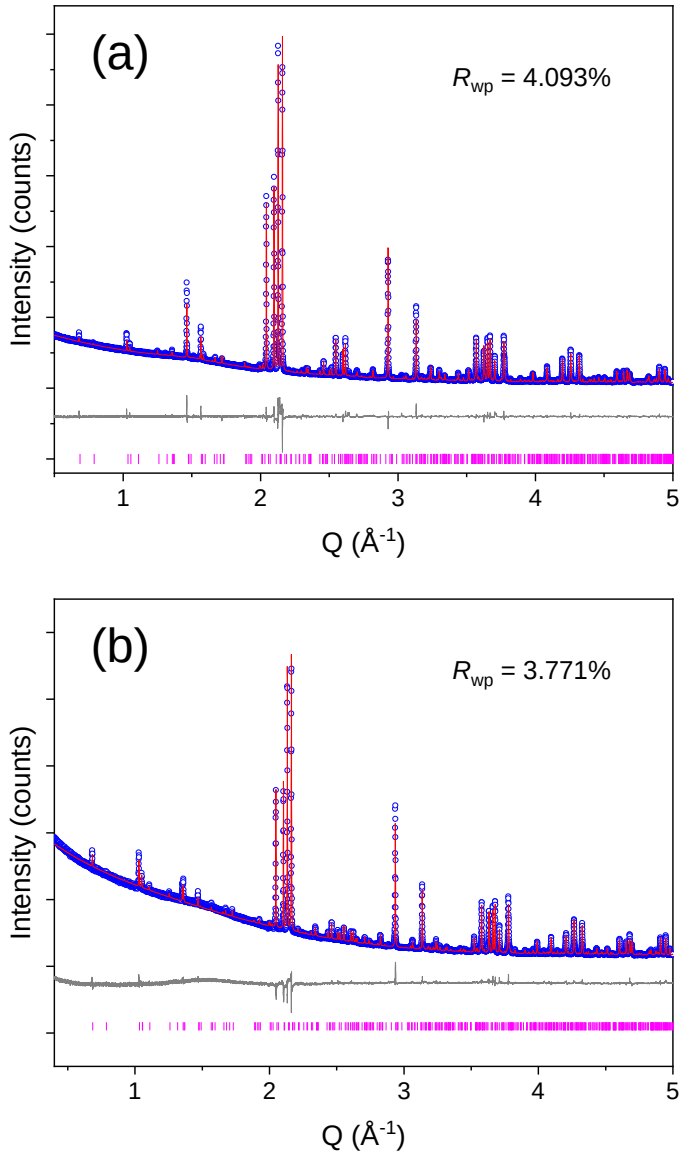

Figure S1 Rietveld fits of the *P*2/*c* structure of (a) $Ba_3YFe_2O_{7.5}$ and (b) $Ba_3DyFe_2O_{7.5}$ to room-temperature S-XRPD data.

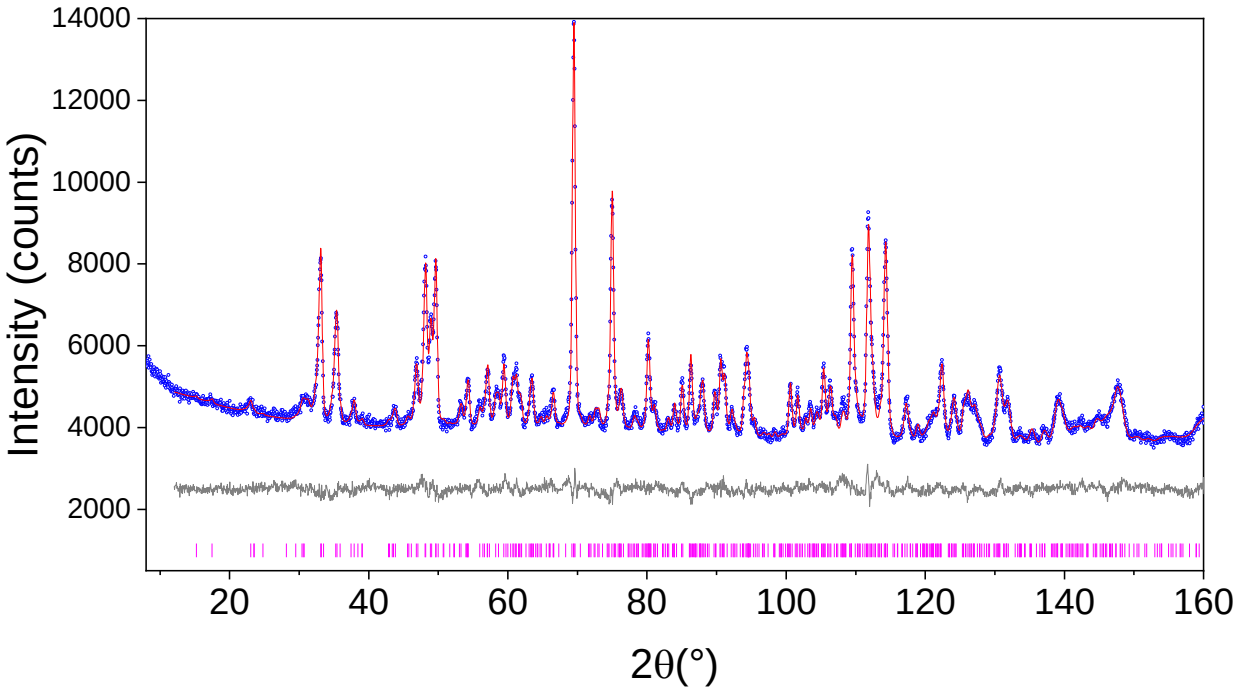

Figure S2 Rietveld fit of the nuclear structural model of $Ba_3YFe_2O_{7.5}$ to 15 K CW-NPD data (λ = 2.4395 Å), with R_{wp} = 5.213%.

Table S1: Nuclear *P*2/*c* structural model of $Ba_3YFe_2O_{7.5}$ refined from TOF-NPD at 15 K *a* = 8.0252(2) Å, *b* = 5.9818(2) Å, c = 18.4381(5) Å, β = 91.13(2), unit cell volume 884.96(4) $Å^3$

Atom	**Wyckoff Site**	**x**	**y**	**z**	**Occ.**	**B_{iso} (A^2)**
Ba1	2e	0.00	0.296(3)	0.25	1	0.86(33)
Ba2	2f	0.25	0.312(3)	0.25	1	2.62(41)
Ba3	4g	0.01921(1)	0.75	0.0905(4)	1	0.19(1)
Ba4	4g	0.5001(2)	0.248(2)	0.5771(4)	1	0.16(2)
Y1	4g	0.2448(8)	0.255(1)	0.4089(3)	1	0.7(1)
Fe1	4g	0.24527(5)	0.2507(1)	0.06052(2)	1	0.6(1)
Fe2	4g	0.2334(6)	0.7729(1)	0.2635(2)	1	0.65(1)
O1	2e	0	0.785(2)	0.25	1	0.8(2)
O2	4g	0.04081(8)	0.765(2)	0.61007(3)	1	0.2(2)
O3	4g	0.4702(8)	0.245(2)	0.0909(3)	1	0.2(2)
O4	4g	0.2714(6)	0.058(1)	0.3061(4)	1	0.2(2)
O5	4g	0.241(2)	0.546(3)	0.339(2)	1	0.8(2)
O6	4g	0.244(1)	0.478(1)	0.5028(4)	1	0.2(2)
O7	4g	0.0047(3)	1.01(2)	-0.0034(3)	1	1.6(2)
O8	4g	0.3060(2)	0.3390(6)	0.6817(2)	1	0.9(2)

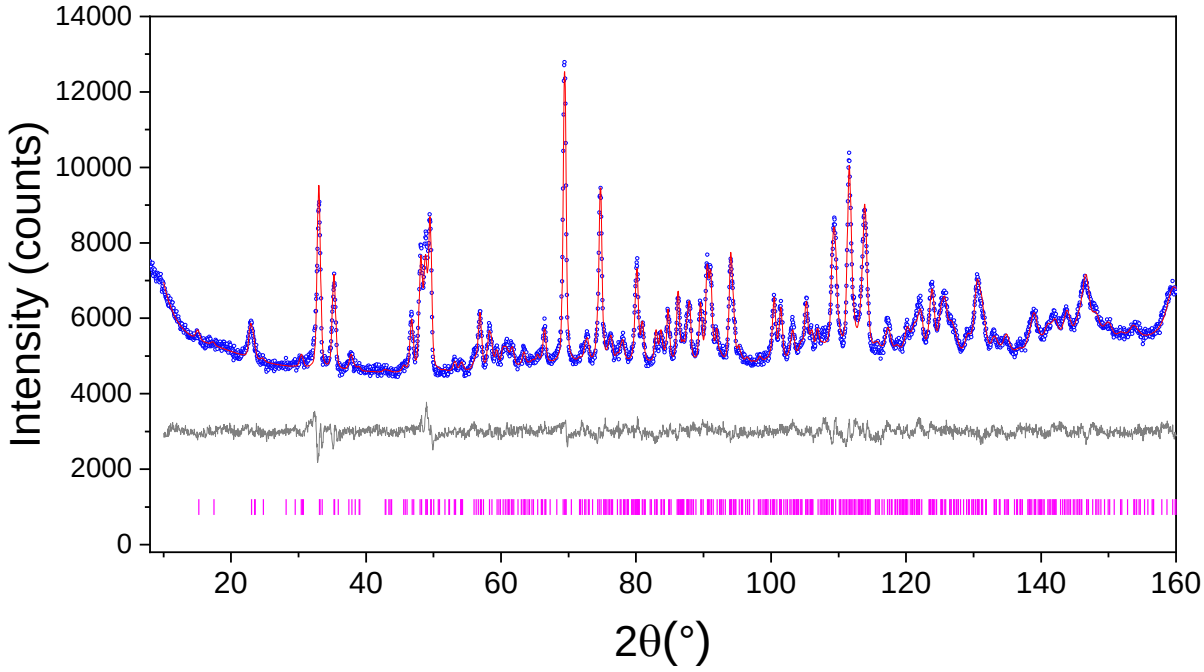

Figure S3 Rietveld fit of the nuclear structural model of $Ba_3DyFe_2O_{7.5}$ to 20 K NPD data (λ = 2.4395 Å), with R_{wp} = 2.224%.

Table S2: Crystal structure model for *P*2/*c* model of $Ba_3DyFe_2O_{7.5}$ refined from CW-NPD at 20 K *a* = 8.0340(3) Å, *b* = 5.97140(2) Å, c = 18.4168(4) Å, β = 91.1(2), unit cell volume 883.36(4) $Å^3$

Atom	**Wyckoff Site**	**x**	**y**	**z**	**Occ.**	**B_{iso} (A^2)**
Ba1	2e	0	0.28(3)	0.25	1	0.5(1)
Ba2	2f	0.5	0.32(3)	0.25	1	0.8397
Ba3	4g	0.029(2)	0.75	0.090(3)	1	0.5228
Ba4	4g	0.500(2)	0.2358(5)	0.5804(2)	1	0.7477
Dy1	4g	0.2448(8)	0.255(1)	0.4089(3)	1	0.1(1)
Fe1	4g	0.2432(4)	0.2484(4)	0.0617(4)	1	0.76(1)
Fe2	4g	0.2312(2)	0.7657(5)	0.2647(4)	1	0.90(2)
O1	2e	0	0.765(3)	0.25	1	0.8(2)
O2	4g	0.0472(3)	0.76(2)	0.6102(3)	1	0.5(2)
O3	4g	0.47(1)	0.255(5)	0.093(4)	1	0.5(2)
O4	4g	0.2657(5)	0.0723(2)	0.304(3)	1	0.4(2)
O5	4g	0.249(2)	0.548(2)	0.334(2)	1	0.8(2)
O6	4g	0.233(2)	0.4880(6)	0.4972(3)	1	0.5(3)
O7	4g	0.2315(4)	0.9943(4)	-0.0024(2)	1	0.5(2)
O8	4g	0.3098(3)	0.3343(2)	0.6801(5)	1	0.5(2)

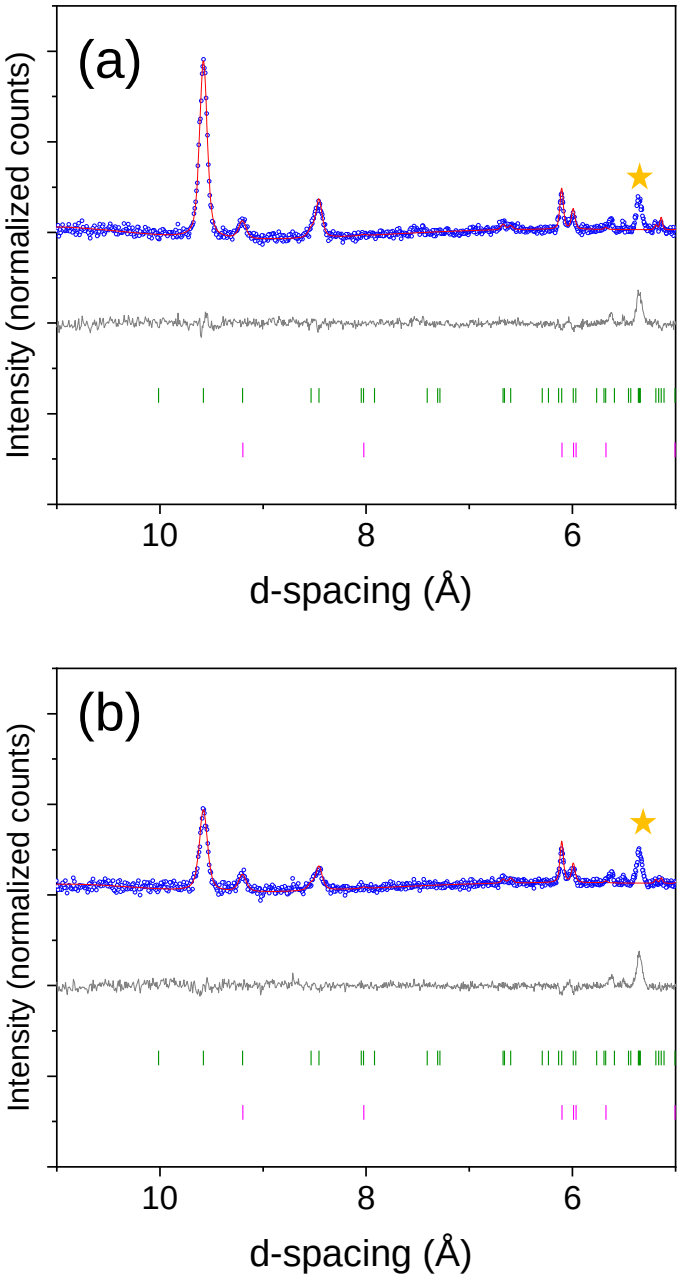

Figure S4 Rietveld fit of a combined nuclear and magnetic mC1^{+} model of $Ba_3DyFe_2O_{7.5}$ to (a) 2 K and (b) 12 K TOF-NPD data with R_{wp} = 2.120 % and 1.964% respectively. Asterisks mark peaks due to an unidentified magnetic impurity. Note the reduction in intensity of the magnetic Bragg peaks for the 12 K data, demonstrating the drop in refined Dy^{3+} magnetic moment. Vertical green *hkl* markers are magnetic reflections and pink markers are nuclear reflections.