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SUPPLEMENTARY MATERIALS

Nuclear and Magnetic Structures and Magnetic Properties of $Co_3(OH)_2(SO_4)_2(H_2O)_2$. Comparison to the Mn and Ni Analogues

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Table S1. Final Atomic Parameters for $Co_3(OH)_2(SO_4)_2(H_2O)_2$ from X-ray Data

	x/a	y/b	z/c	U_{eq}*	U_{11}*	U_{22}*	U_{33}*	U_{12}*	U_{13}*	U_{23}*
Co1	0.05291(5)	0.02821(3)	0.12832(2)	76(1)	79(2)	79(2)	72(2)	1(1)	3(1)	5(1)
Co2	0.29376(6)	0.74100(5)	0.25	67(1)	74(3)	64(2)	63(2)	-1(2)	0	0
S1	0.79328(12)	0.25	0	65(2)	75(4)	63(4)	58(4)	0	0	-1(3)
S2	0.30640(12)	0.41891(8)	0.25	71(2)	64(4)	66(4)	82(4)	4(3)	0	0
O1	0.5757(4)	0.0430(2)	0.25	110(5)	81(12)	58(11)	192(13)	14(9)	0	0
O2	0.0853(3)	0.1258(2)	-0.0033(1)	95(3)	107(8)	80(7)	98(8)	22(7)	-3(7)	1(6)
O3	0.3267(3)	0.7456(2)	0.0916(1)	104(4)	113(9)	123(8)	76(8)	2(7)	-22(7)	-3(7)
O4	0.4204(3)	0.2949(3)	0.25	103(5)	78(12)	77(11)	153(12)	23(9)	0	0
O5	0.1869(3)	0.4173(2)	0.1559(1)	129(4)	130(9)	141(9)	117(9)	46(7)	34(7)	38(7)
OH1	0.8006(4)	0.4407(3)	0.25	81(5)	69(12)	83(11)	92(11)	17(10)	0	0
OH2	0.0270(4)	0.6609(3)	0.25	91(5)	72(12)	76(12)	126(12)	0(10)	0	0
OW	0.2908(3)	0.1151(2)	0.0666(2)	176(4)	143(11)	238(11)	148(10)	92(8)	-18(8)	-13(9)
H1	0.717(8)	0.480(6)	0.25	262(156)						
H2	0.022(9)	0.227(6)	0.25	417(219)						
HW1	0.379(7)	0.139(5)	0.094(4)	529(147)						
HW2	0.298(7)	0.386(5)	0.509(4)	615(169)						

* $U_{ij} = U_{ij}10^4$, $U_{eq} = (U_{11} + U_{22} + U_{33})/3$

Table S2. Atomic Coordinates and Isotropic Thermal Parameters at 300 K from Neutron Powder Data for the Deuterated Compound (upper part). Position of the Co Magnetic atoms and Orientation of Their Magnetic Moments from 1.4 K Data Refinement (lower part).

Atom	x/a	y/b	z/c	Occupancy	B (Å^2)
Co1	0.046(2)	0.024(1)	0.1287(7)	8.0	0.7(2)
Co2	0.293(2)	0.734(2)	0.25	4.0	0.8(2)
S1	0.795(2)	0.25	0.0	4.0	0.9(2)
S2	0.289(3)	0.424(2)	0.25	4.0	0.8(3)
O1	0.581(1)	0.0385(9)	0.25	4.0	0.8(1)
O2	0.9148(7)	0.1265(6)	-0.0037(4)	8.0	0.91(8)
O3	0.6724(8)	0.2541(6)	0.9086(3)	8.0	0.64(8)
O4	0.422(1)	0.2979(8)	0.25	4.0	0.9(1)
O5	0.8119(9)	0.5803(6)	0.6567(3)	8.0	1.5(1)
OH1	0.801(1)	0.4442(7)	0.25	4.0	0.7(1)
OH2	0.973(1)	0.1611(8)	0.25	4.0	0.9(1)
OW	0.290(1)	0.3850(6)	0.5664(4)	8.0	1.9(1)
D1	0.678(1)	0.4821(9)	0.25	4.0	2.2(1)
H2	0.064(2)	0.235(1)	0.25	0.91(4)	1.2(1)
D2	0.064(2)	0.235(1)	0.25	3.09(4)	1.2(1)
HW1	0.397(1)	0.3531(8)	0.5993(6)	0.64(8)	4.3(2)
DW1	0.397(1)	0.3531(8)	0.5993(6)	7.36(8)	4.3(2)
HW2	0.305(1)	0.3819(8)	0.0060(6)	0.71(7)	3.4(1)
HW2	0.305(1)	0.3819(8)	0.0060(6)	7.29(7)	3.4(1)
Atom	x/a	y/b	z/c	Mz (μ_B)	
Co11	0.050(2)	0.033(1)	0.124(2)	2.95(5)	
Co12	$1-x_1$	$1-y_1$	$1-z_1$	-2.95(5)	
Co13	$1-x_1$	$1-y_1$	$_+z_1$	-2.95(5)	
Co14	x_1	y_1	$_-z_1$	2.95(5)	
Co15	x_1	$_-y_1$	$1-z_1$	-2.95(5)	
Co16	$1-x_1$	$_+y_1$	z_1	2.95(5)	
Co17	$1-x_1$	$_+y_1$	$_-z_1$	2.95(5)	
Co18	x_1	$_-y_1$	$_+z_1$	-2.95(5)	
Co21	0.299(2)	0.736(2)	1/4	-3.31(6)	
Co22	$1-x_2$	$1-y_2$	3/4	3.31(6)	
Co23	$1-x_2$	$_+y_2$	1/4	-3.31(6)	
Co24	x_2	$_-y_2$	3/4	3.31(6)	

D/(D+H) ratio = 0.91

Table S3. Values of the Magnetic Moments for LRO and SRO Phases and the Coherence Length for SRO

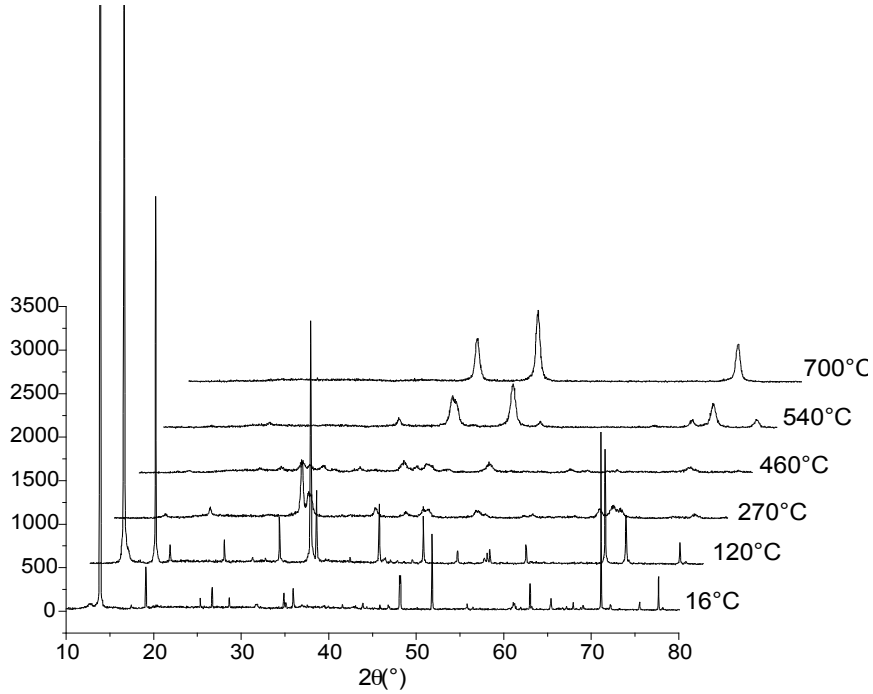
	LRO		SRO		
	M_z(Co1) (μB)	M_z(Co2) (μB)	M_z(Co1) (μB)	M_z(Co2) (μB)	Coherence length (Å)
1.43	2.95(5)	3.31(6)			
4.09	2.97(5)	3.28(6)			
7.08	2.98(4)	3.39(6)			
10.13	3.02(5)	3.38(6)			
15.22	2.98(5)	3.40(6)			
25.37	2.82(5)	3.41(6)			
30.44	2.59(5)	3.30(6)			
34.50	1.86(6)	2.93(8)	0.9(3)	1.4(4)	58(32)
37.50	1.26(7)	2.34(9)	1.5(3)	2.7(4)	23(5)
40.53			2.2(3)	3.4(3)	17(2)
43.60			2.4(3)	3.4(3)	13(2)
50.66			2.4(4)	3.3(4)	11(2)
60.72			1.8(4)	3.1(4)	17(3)
70.66			1.8(4)	3.1(4)	17(3)

Table S4. Evolution of the Maxima (°C) of the Endothermal Effects Associated to the Weight Losses

Thermal effect	$Mn_3(OH)_2(SO_4)_2(H_2O)_2$	$Co_3(OH)_2(SO_4)_2(H_2O)_2$	$Ni_3(OH)_2(SO_4)_2(H_2O)_2$
H_2O loss	300	349	465
OH loss	400	507	589
SO_3 loss	770	843	820
Oxide reduction	900 $Mn_2O_3 \rightarrow Mn_3O_4$	922 $Co_3O_4 \rightarrow CoO$	

Table S5. Observed (cm^{-1}) Infrared Bands in the $M_3(OH)_2(SO_4)_2(H_2O)_2$ Family and Their Related Deuterated Analogues

Attribution	$Mn_3(OH)_2(SO_4)_2(H_2O)_2$		$Co_3(OH)_2(SO_4)_2(H_2O)_2$		$Ni_3(OH)_2(SO_4)_2(H_2O)_2$	
	H	D	H	D	H	D
O-H(D) stretching		2645	3572 (sh)		3570 (sh)	
	3547	2624	3545	2640	3541	2636
	3465	2544	3479		3477	
	3395	2515	3433	2542	3442	2549
H-O-H bending	1623		1620		1619	
	1602		1596		1600	
ρ_r $H(D)_2O$	835	682	852	710	881	737
	797		813		852	
ν_3 SO_4	1177	1177	1186	1184	1202	1207
	1148	1149	1160	1158	1159	1141
	1103	1102	1108	1108	1109	1097
ν_1 SO_4	1044	1044	1027	1026	1035	1027
	993	993	993	992	995	988
ν_4 SO_4	635	634	642	642	648	650
			625	627	627	623
	603	603	597	599	600	601



S1. X-ray powder patterns recorded at various temperatures (Co $K_{\alpha 1}$, λ = 1.7890 Å).

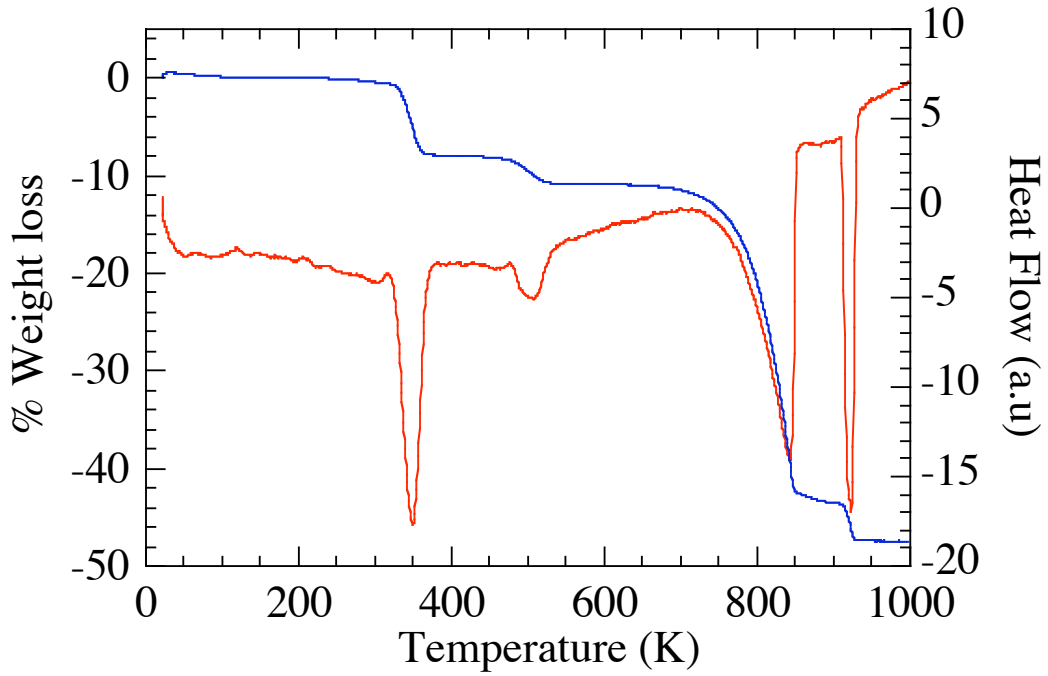


Figure S2. DT-TGA traces of $Co_3(OH)_2(SO_4)_2(H_2O)_2$ recorded under air at a 5°C/min heating rate.

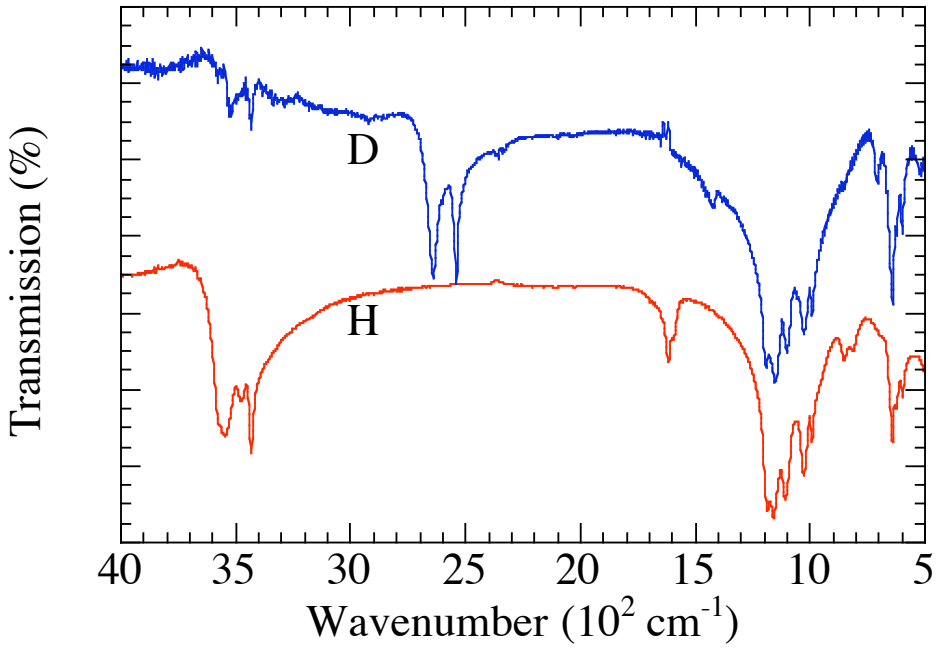


Figure S3. Infrared transmission spectra of $Co_3(OH)_2(SO_4)_2(H_2O)_2$ and $Co_3(OD)_2(SO_4)_2(D_2O)_2$.

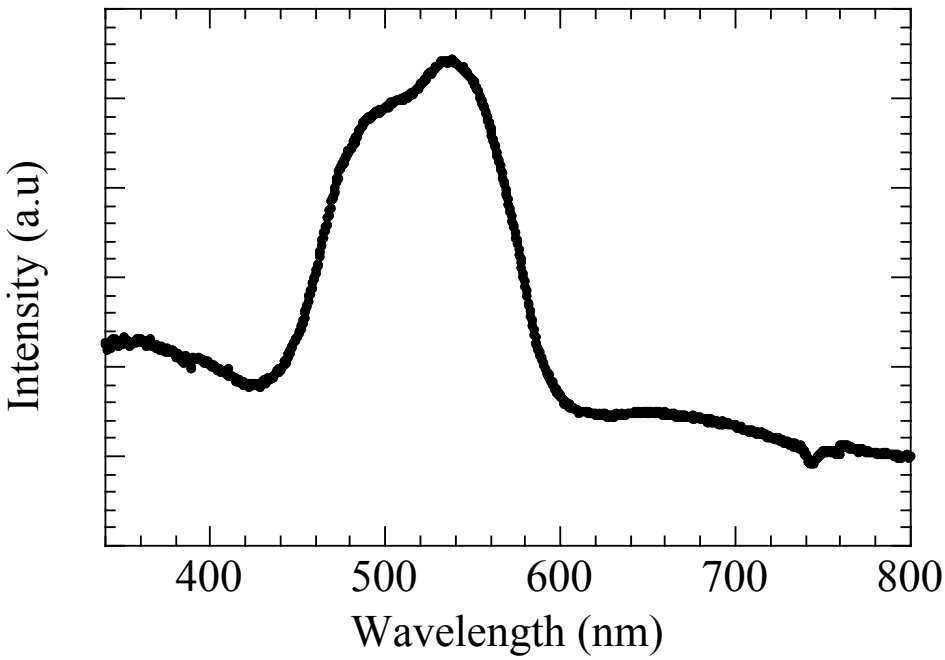
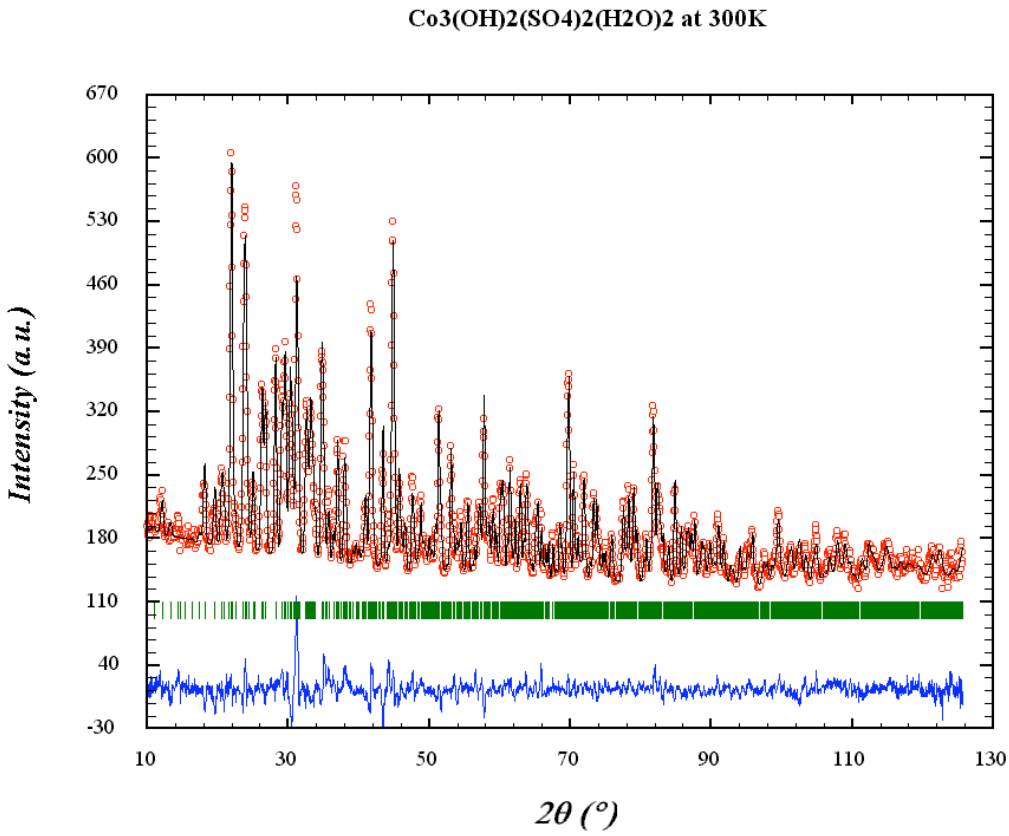


Figure S4. UV-Visible absorption spectrum of $Co_3(OH)_2(SO_4)_2(H_2O)_2$.



S5. Observed (circles) and calculated (line) profiles of the powder neutron pattern of $Co_3(OD)_2(SO_4)_2(D_2O)_2$ obtained on the 3T2 diffractometer at 300 K with position of the Bragg reflections (short vertical lines) and difference between observed and calculated profiles (λ = 1.2522Å).

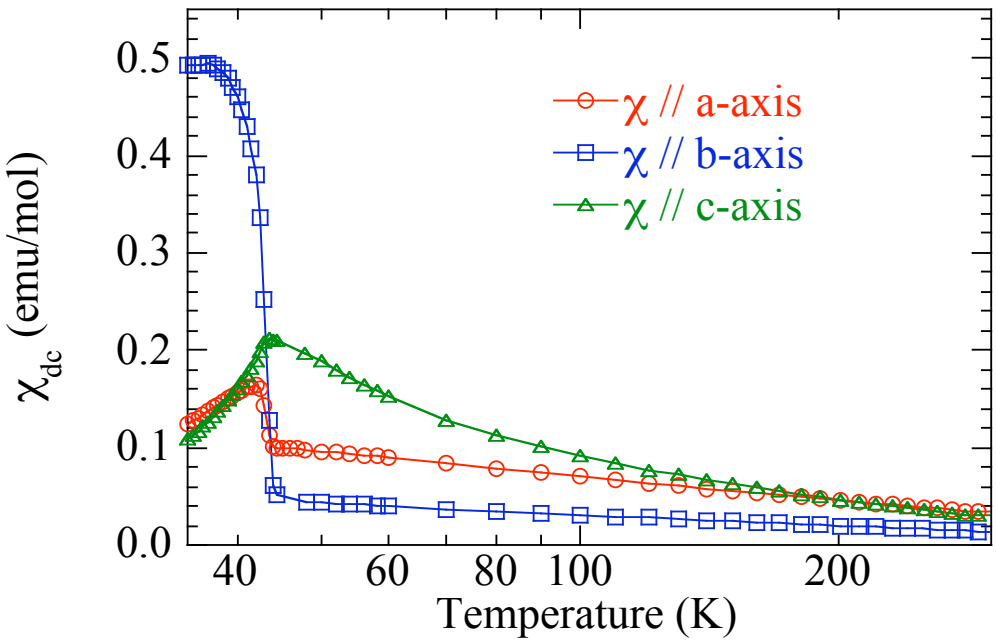


Figure S6. Temperature dependence of the susceptibility of single crystal_1 of $Co_3(OH)_2(SO_4)_2(H_2O)_2$ along its three orthogonal axes of the orthorhombic cell.

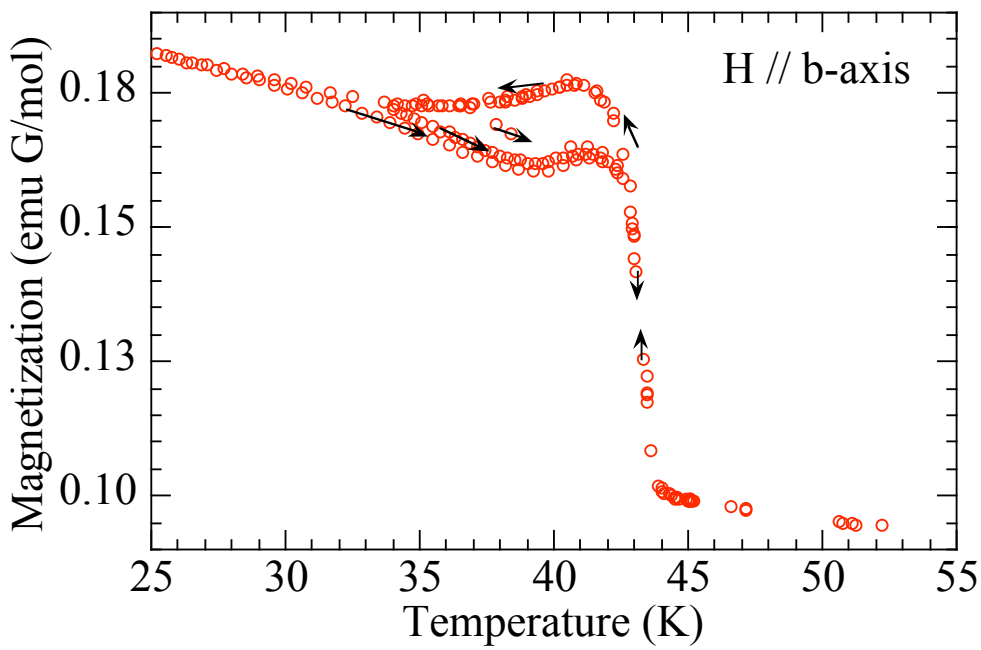
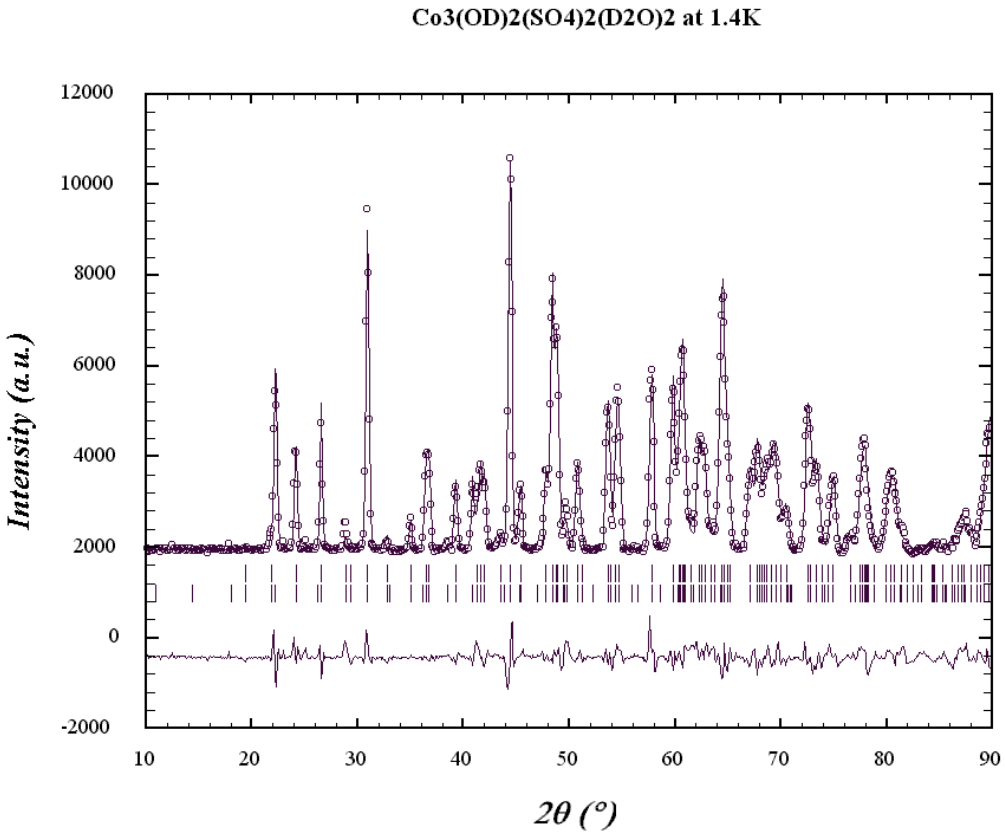


Figure S7. Hysteresis in the temperature dependence of the magnetization of single crystal_1 of $Co_3(OH)_2(SO_4)_2(H_2O)_2$ along the *b*-axis.



S8. Observed (circles) and calculated (line) profiles of the powder neutron pattern of $Co_3(OD)_2(SO_4)_2(D_2O)_2$ obtained on the G4.1 diffractometer at 1.4 K with position of the Bragg reflections (short vertical lines, nuclear $Co_3(OD)_2(SO_4)_2(D_2O)_2$, magnetic $Co_3(OD)_2(SO_4)_2(D_2O)_2$) and difference between observed and calculated profiles (λ = 2.4266Å).