Electronic Supplementary Information for:

Ferri- and ferro- magnetism in CaMn*M*ReO_6 double double perovskites of late transition metals *M* = Co, Ni

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Supplementary Figures:

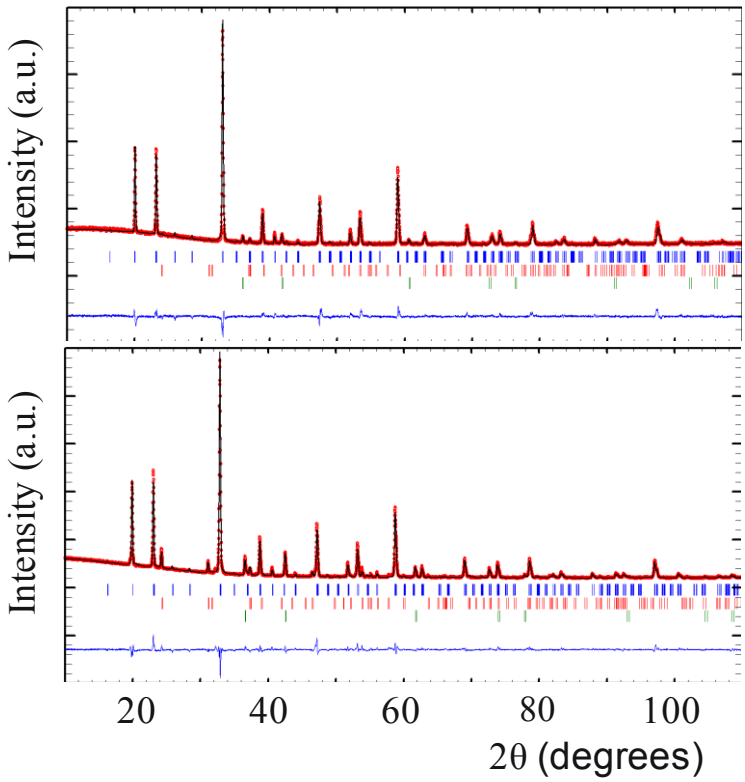

Figure S1. Rietveld fits of XPD patterns collected at room temperature for $CaMnCoReO_6$ (top) and $CaMnNiReO_6$ (bottom). Bragg markers from top to bottom are the DDPv phase, ReO_2 and M_2MnO_3 secondary phases.

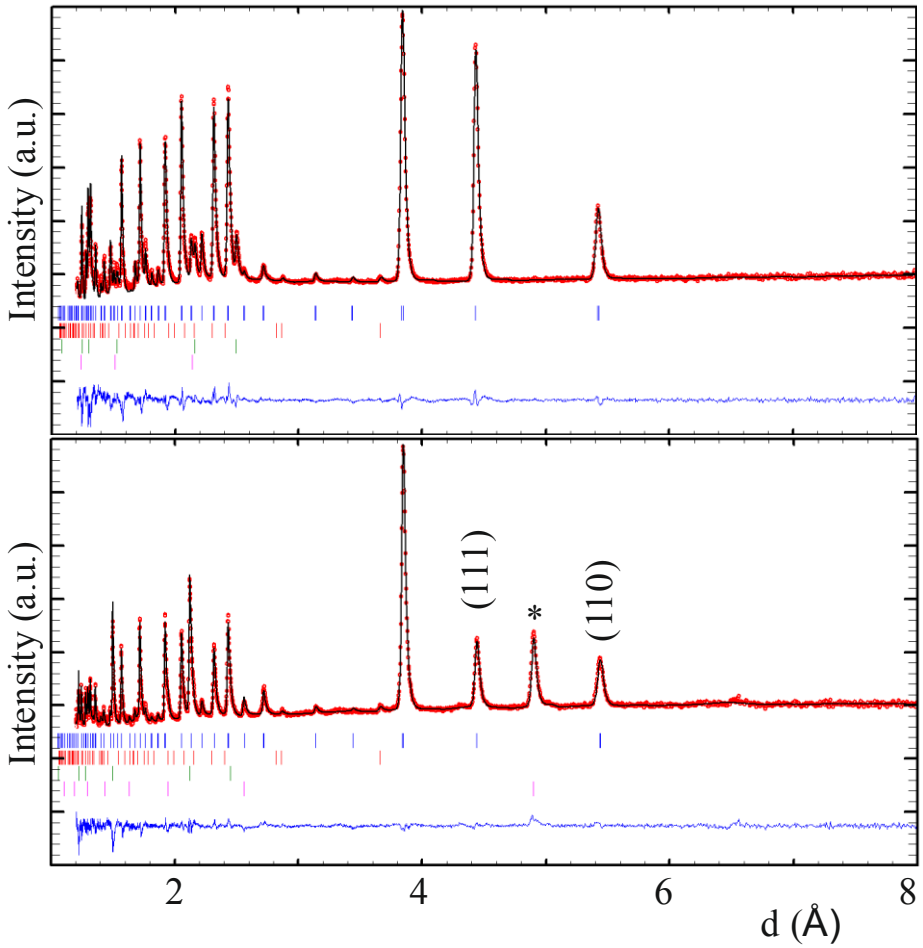

Figure S2. Rietveld fits of NPD patterns collected at room temperature for $CaMnCoReO_6$ (top) and $CaMnNiReO_6$ (bottom). The (110) and (111) peaks revealing the A and B cation site orders respectively are labelled. The asterisk shows the main magnetic peak of the $Ni_{0.67}Mn_{0.33}O$ secondary phase. Bragg markers from top to bottom are the nuclear structure of the DDPv phase, ReO_2 and M_2MnO_3 secondary phases. The top panel includes an additional row for V from the sample holder and the refinement of the magnetic phase of M_2MnO_3 is also included in the bottom row for the M = Ni sample.

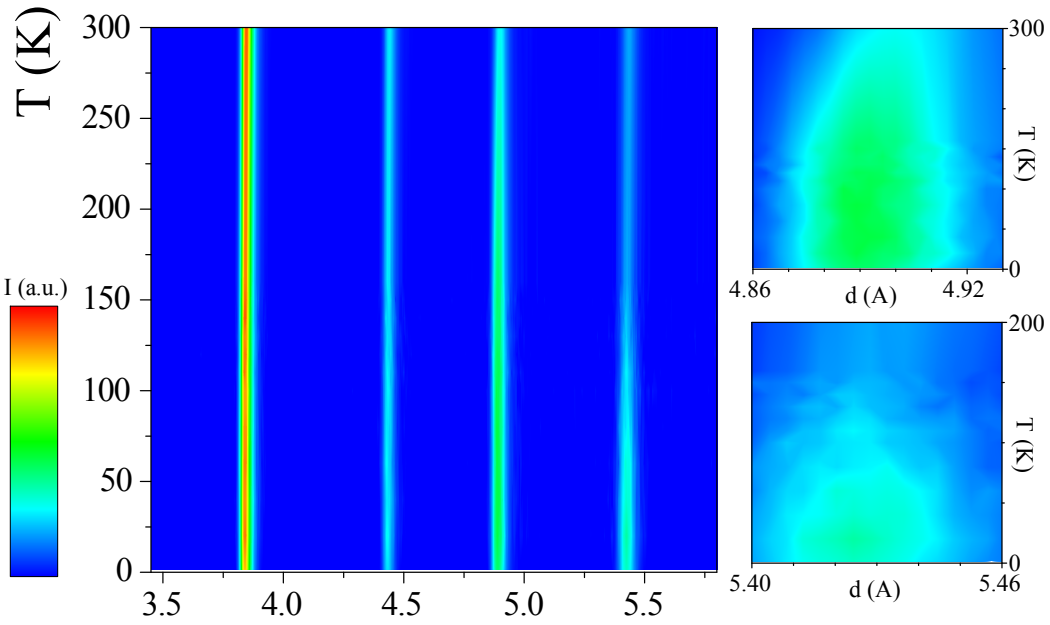

Figure S3. Thermal evolution of the NPD patterns collected at WISH for $CaMnNiReO_6$ focussed on the 3.5 Å < d < 6 Å region. The peaks at 4.88 Å and 5.43 Å are enlarged on the right panels to show their different thermal dependence. Data were collected at 300, 180, 160, 150, 140, 130, 120, 110, 100, 80, 60, 40, 20 and 1.5 K. The intermediate temperatures are interpolated.

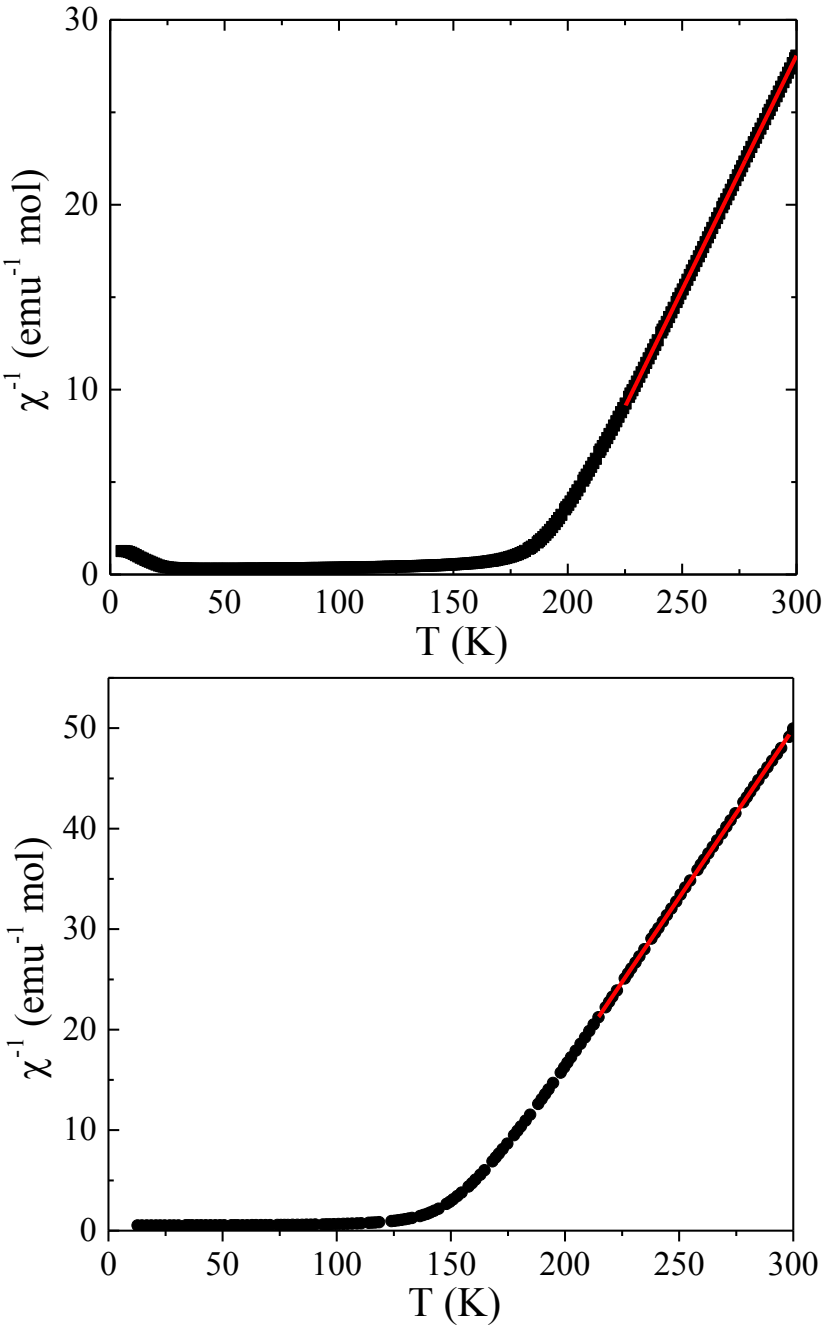

Figure S4. Reciprocal susceptibilities of $CaMnCoReO_6$ (top) and $CaMnNiReO_6$ (bottom). The red line shows the fit to the Curie-Weiss law.

Supplementary Tables:

Table S1. Bond lengths ($d_{M\text{-}O}$), average M-O distances (d_{AV}), angles and octahedral distortions (Δ) of CaMn*M*ReO_6 compounds with *M* = Co and Ni. Δ calculated from $1/n*\Sigma[(d-d_{Av})/d_{Av}]^2$

M	$d_{A'\text{-}O}$ (Å)	$d_{A''\text{-}O}$ (Å)	$d_{M\text{-}O}$ (Å)	$d_{Re\text{-}O}$ (Å)	<*M*-O-A'>°	<*M*-O-A''>°
Co	4 x 2.065(4)	4 x 2.10(1)	2 x 2.08(1) 2 x 2.12(1) 2 x 2.09(1) d_{Av} = 2.10(1) Δ = 6.8E-5	2 x 1.89(1) 2 x 1.93(1) 2 x 1.94(1) d_{Av} = 1.92(1) Δ = 9.8E-5	104.9(5)	104.5(5)
Ni	4 x 2.09(1)	4 x 2.13(2)	2 x 2.09(2) 2 x 2.10(3) 2 x 2.08(3) d_{Av} = 2.09(1) Δ = 1.5E-5	2 x 1.87(2) 4 x 1.95(3) d_{Av} = 1.92(1) Δ = 3.9E-4	105.2(9)	104.6(9)

Table S2. Magnetic modes in the Γ_1^+ irreducible representation (defined from the Isotropy Suite) for $CaMnMReO_6$ magnetic structures, for ***k*** = (0 0 0) propagation vector in space group $P4_2/n$. A_S and A_T correspond to A" and A' sites in Table 1. Magnetic modes A_g3 were used for B site spins.

B-sites mag. modes:	A_g1		A_g2		A_g3	A-sites mag. modes:	A
Atom	m_x	m_y	m_x	m_y	m_z	Atom	m_z
M1, Re1[a]	n/a	-	-	n/a	+	A_T1, A_T2[e]	+
M2, Re2[b]	n/a	+	+	n/a	+		
M3, Re3[c]	+	n/a	n/a	-	+	A_S1, A_S2[f]	+
M4, Re4[d]	-	n/a	n/a	+	+		

B-Sites: [a]M1=(0, 0.5, 0), Re1=(0, 0.5, 0.5); [b]M2=(0.5, 0, 0), Re2=(0.5, 0, 0.5); [c]M3=(0.5, 0.5, 0.5), Re3=(0.5, 0.5, 0); [d]M4=(0, 0, 0.5), Re4=(0, 0, 0).

A-Sites: [e]A_T1=(0.25, 0.25, 0.25), A_T2=(0.75, 0.75, 0.75); [f]A_S1=(0.25 ,0.25, 0.75), A_S2=(0.75, 0.75, 0.25).