Magnetic properties, magnetic structure, and possible magnetoelectric effect in orthorhombic corundumlike Li 2 Ni 2 W 2 O 9

Simon Redor, Maxim Avdeev, David Hrabovsky, Jean-Marie Tarascon, Gwenaëlle Rousse

Magnetic properties, magnetic structure, and possible magnetoelectric effect of orthorhombic corundum-like $Li_2Ni_2W_2O_9$

Authors: Simon Redor[1,2], Maxim Avdeev[3,4], David Hrabovsky[2,5], Jean-Marie Tarascon[1] and Gwenaëlle Rousse[1,2,*]

Institution adress: Chimie du Solide et de l'Energie, UMR 8260, Collège de France, 75231, Cedex 05 Paris, France.

Affiliations:

1 – Chimie du Solide et de l'Energie, UMR 8260, Collège de France, 75231, Cedex 05 Paris, France.

2 – Sorbonne Université, 4 Place Jussieu, F-75005, Paris, France

3 – Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales 2234, Australia

4 – School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia

5 – Plateforme Mesures Physiques à Basses Températures (MPBT), Sorbonne Université, 75005 Paris, France

Supplementary information

The results from the Rietveld refinements performed on laboratory XRD and neutron powder diffraction data for $Li_2Ni_2W_2O_9$ samples are summarized in Tables S1 and S2, respectively. The laboratory XRD data (Table S1) was not suited for the refinement of the B_{iso} parameters, or the positions of Li^+ or O^{2-} cations; only the lattice parameters, and the Ni^{2+} and W^{6+} were refined.

Element	Wyckoff site	*x/a*	*y/b*	*z/c*	B_{iso} (Å^2)	Occupancy
Li	8*d*	0.342	0.517	0.4939	1.80	1
Ni	8*d*	0.6624(5)	0.497(4)	0.8153(18)	0.34	1
W	8*d*	0.5237(12)	-0.004(12)	0.64356(5)	-0.01	1
O1	4*c*	1/2	0.281	3/4	0.23	1
O2	8*d*	0.5081	0.6793	0.9085	0.23	1
O3	8*d*	0.6494	0.8519	0.7469	0.23	1
O4	8*d*	0.8423	0.6635	0.8953	0.23	1
O5	8*d*	0.3389	0.1542	0.9255	0.23	1

Element	Wyckoff site	*x/a*	*y/b*	*z/c*	B_{iso} (Å^2)	Occupancy
Li	8*d*	0.342(2)	0.517(4)	0.4939(7)	1.80(14)	1
Ni	8*d*	0.6633(2)	0.5009(6)	0.81316(9)	0.34(17)	1
W	8*d*	0.5240(3)	0.002(12)	0.6641(15)	-0.01(4)	1
O1	4*c*	1/2	0.281(11)	3/4	0.23(14)	1
O2	8*d*	0.5081(4)	0.6793(7)	0.9085(2)	0.23(14)	1
O3	8*d*	0.6494(4)	0.8519(7)	0.7469(2)	0.23(14)	1
O4	8*d*	0.8423(5)	0.6635(6)	0.8953(2)	0.23(14)	1
O5	8*d*	0.3389(5)	0.1542(6)	0.9255(18)	0.23(14)	1

Table S1 – Results of the Rietveld refinement for the room temperature XRD of the $Li_2Ni_2W_2O_9$ sample used for the bulk magnetic measurements. Nuclear space group: *Pbcn*. Lattice parameters: *a* = 8.69663(7) Å, *b* = 5.06468(4) Å, *c* = 14.3514(11) Å, V = 632.117(8) Å^3, Z = 4. Relaibility parameters: χ^2 = 2.11, R_{Bragg} = 6.60 %. Phase composition: *Pbcn* $Li_2Ni_2W_2O_9$: 100.0 wt% / No other phase detected with XRD.

Table S2 – Results of the Rietveld refinement for the room temperature neutron powder diffraction of the $Li_2Ni_2W_2O_9$ sample used for the magnetic structure study. Nuclear space group: *Pbcn*. Lattice parameters: *a* = 8.69523(8) Å, *b* = 5.06407(5) Å, *c* = 14.3451(18) Å, V = 631.66(12) Å^3, Z = 4. Relaibility parameters: χ^2 = 2.65, R_{Bragg} = 3.32 %. Phase composition: *Pbcn* $Li_2Ni_2W_2O_9$: 100.0(5) wt% / *P*2/*c* $NiWO_4$: 0.02(1) wt%.

In Figures S1 to S8, the simulated patterns for the 8 Shubnikov space groups derived from the *Pbcn* nuclear space group are shown. For each magnetic space group, different peaks are observed depending on the number and the direction of the magnetic components taken into account in the calculations. For every simulated pattern M_n was set to 1 μ_B (n = x or y or z).

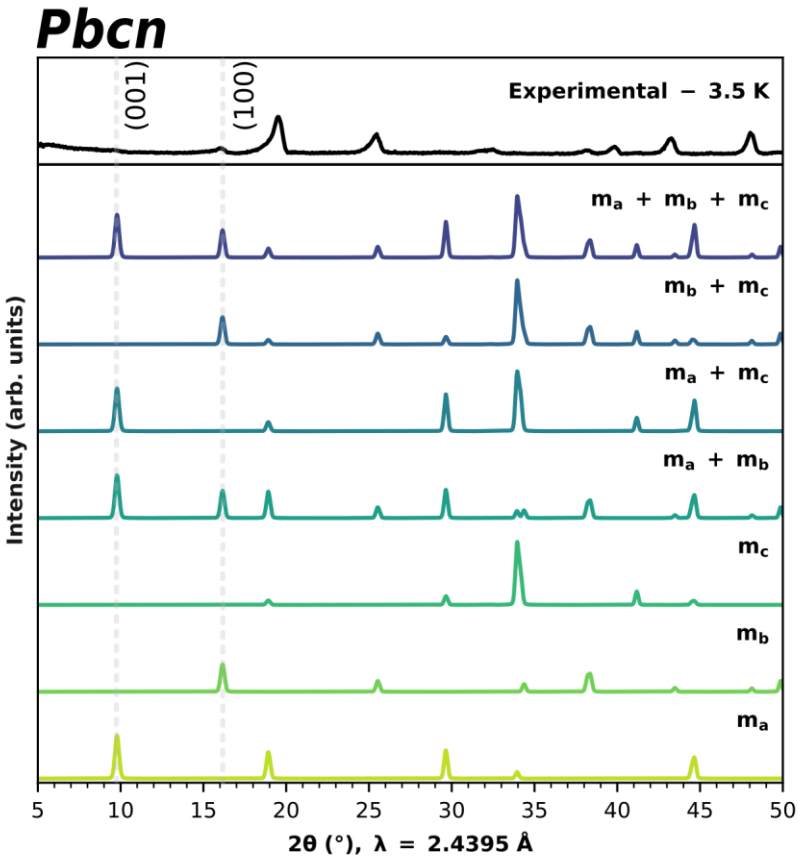

Figure S1 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pbcn* Shubnikov space group (colored, bottom). Note that the (001) and (100) peaks appear if the magnetic moment results from two components along **a** and **b**.

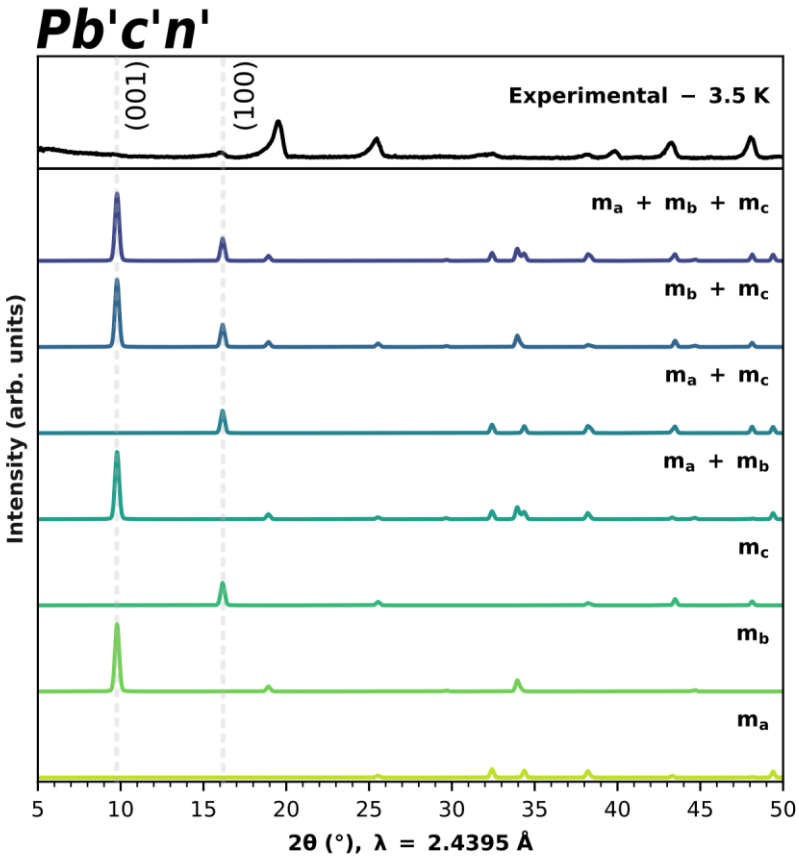

Figure S2 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pb'c'n'* Shubnikov space group (colored, bottom). Note that the (001) and (100) peaks appear if the magnetic moment results from two components along **b** and **c**.

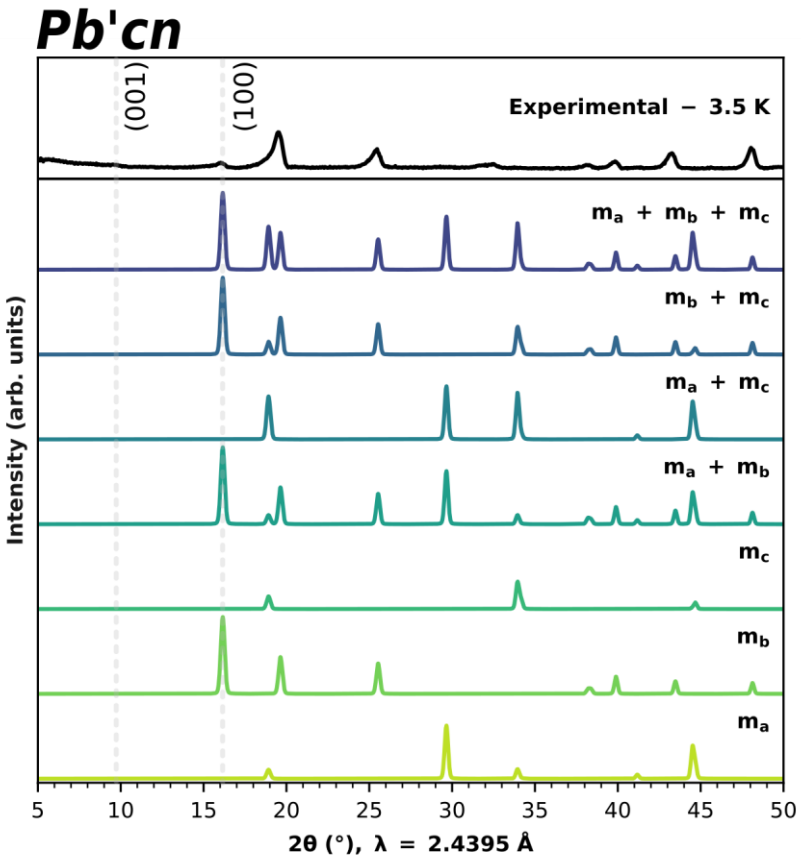

Figure S3 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pb'cn* Shubnikov space group (colored, bottom). Note that the (001) peak does not appear in any of the simulated patterns.

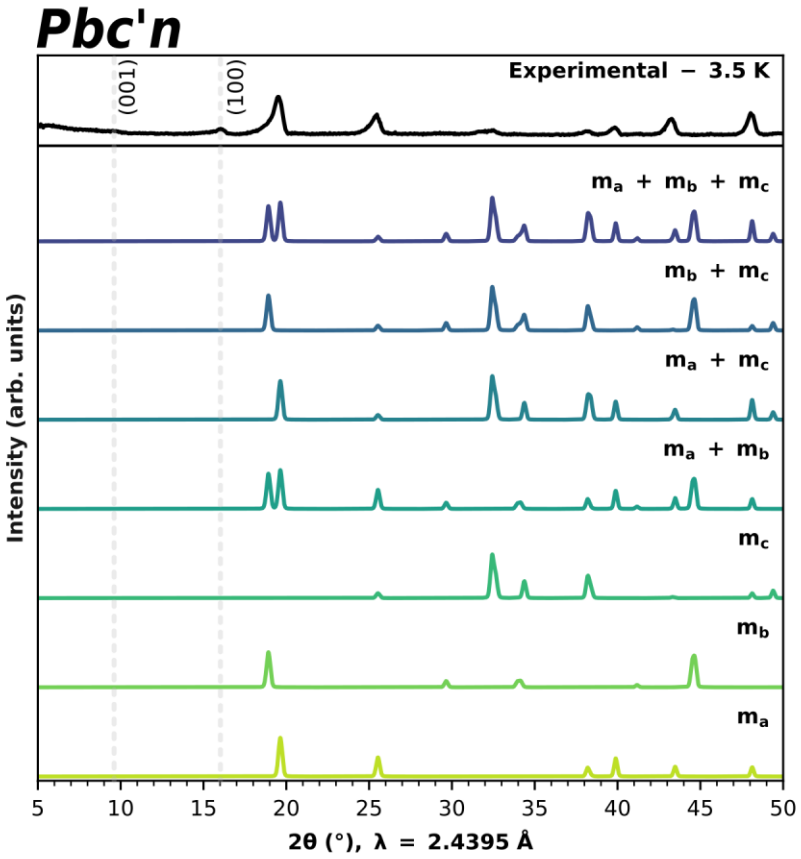

Figure S4 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pbc'n* Shubnikov space group (colored, bottom). Note that neither the (001) peak, nor the (100) peak appear in any of the simulated patterns.

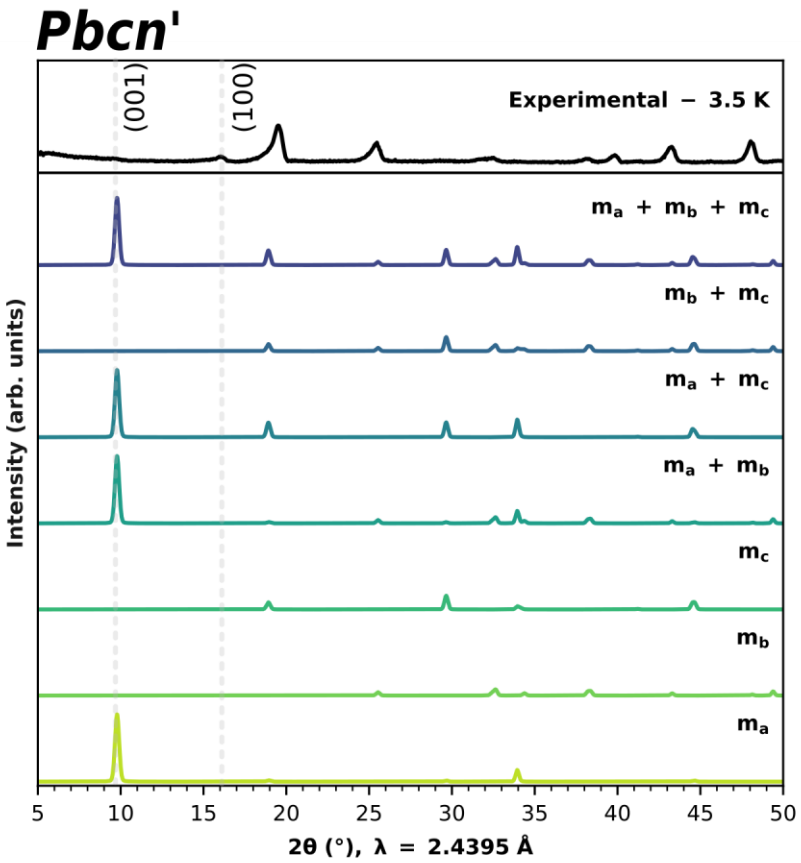

Figure S5 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pbcn'* Shubnikov space group (colored, bottom). Note that the (100) peak does not appear in any of the simulated patterns.

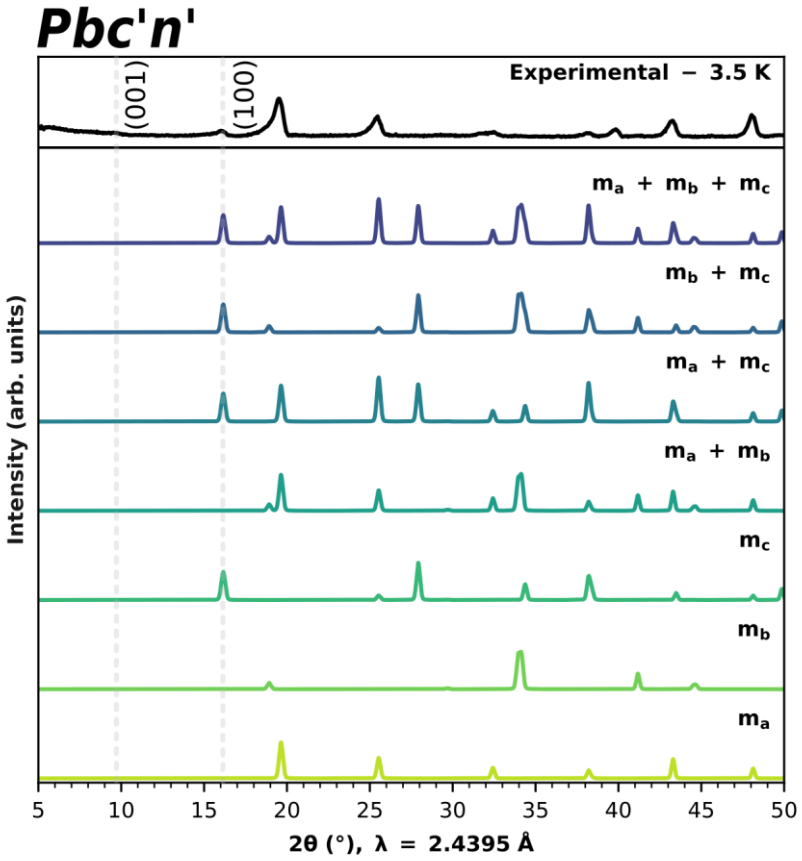

Figure S6 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pbc'n'* Shubnikov space group (colored, bottom). Note that the (001) peak does not appear in any of the simulated patterns.

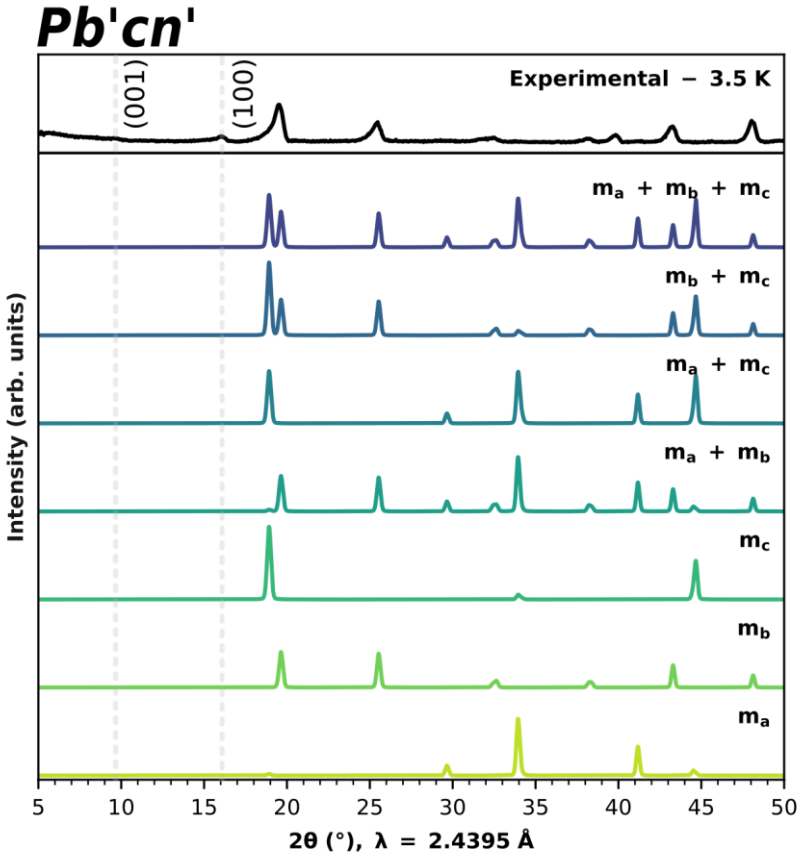

Figure S7 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pb'cn'* Shubnikov space group (colored, bottom). Note that neither the (001) peak, nor the (100) peak appear in any of the simulated patterns.

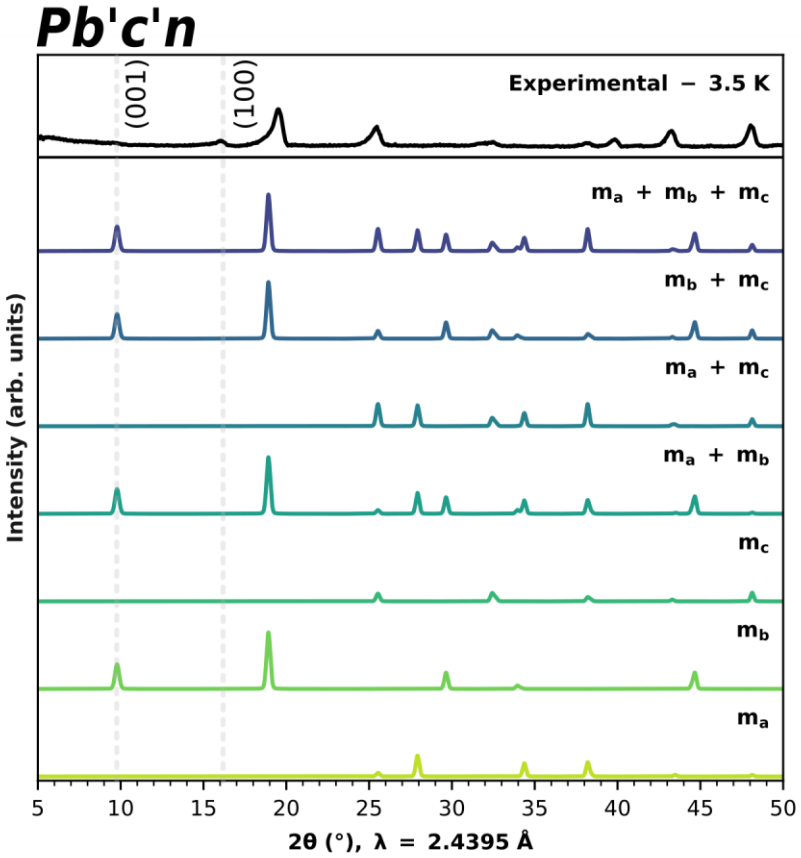

Figure S8 – Experimental neutron powder diffraction data at T = 3.5 K for $Li_2Ni_2W_2O_9$ (black, top), and simulated patterns for k = (0, 0, 0) in the *Pb'c'n* Shubnikov space group (colored, bottom). Note that the (100) peak does not appear in any of the simulated patterns.

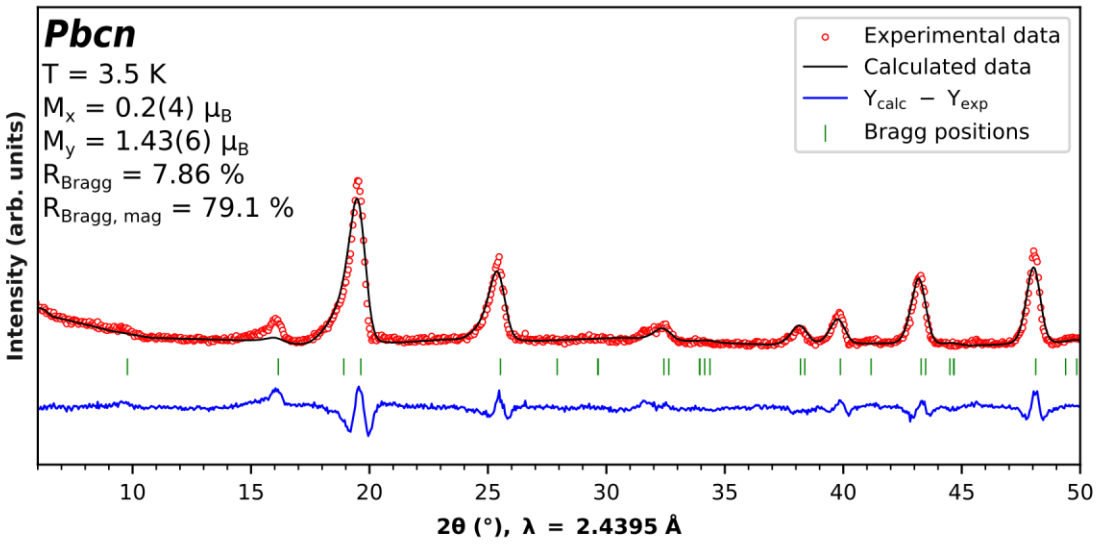

Figure S9 – Rietveld refinement of the neutron diffraction pattern of $Li_2Ni_2W_2O_9$ powder at T = 3.5 K, using the *Pbcn* Shubnikov space groups for the calculations.

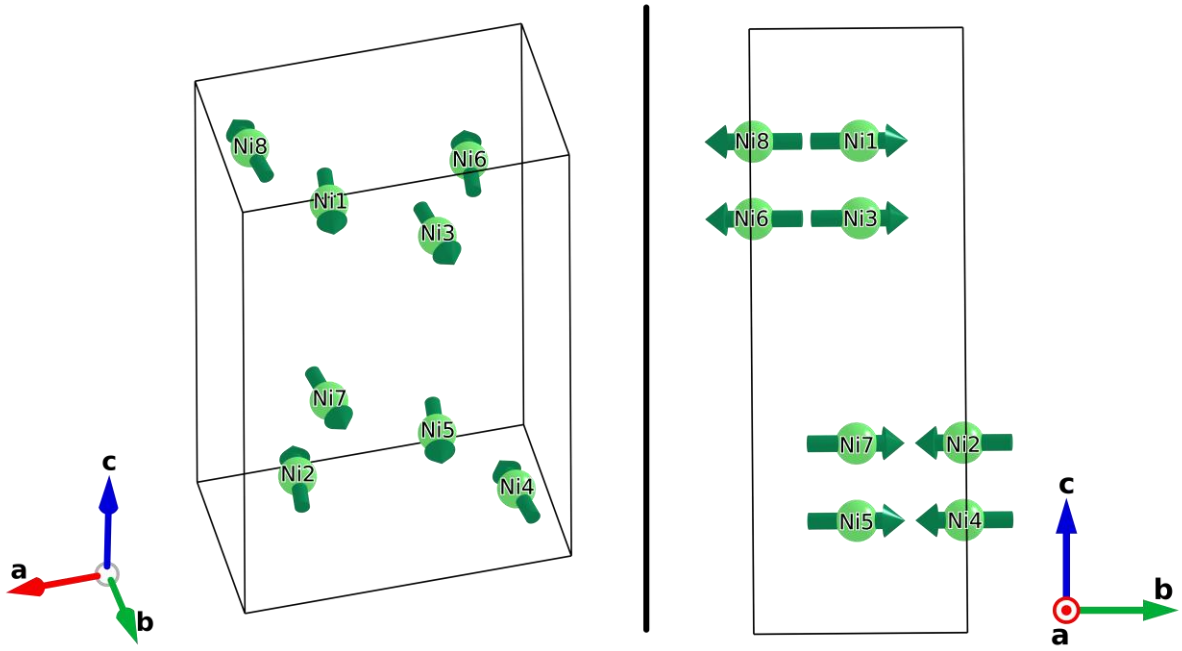

Figure S10 – Magnetic structure that would be displayed by $Li_2Ni_2W_2O_9$ at $T < T_N$ if its Shubnikov space group was *Pbcn*. For the sake of clarity, only the nickel atoms are shown. The green arrows represent the magnetic moments.