Electronic Supplementary Information for:

Experimental and Computational Study of the Magnetic Properties of $ZrMn_{2-x}Co_xGe_4O_{12}$

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Calculation of exchange constants and Curie-Weiss temperature

The spin exchange magnetic interactions can be simply described by the general Heisenberg spin Hamiltonian representing a series of pair-wise spin exchange interactions:

$$E_{total} = E_{Non-magnetic} + H_{magnetic}$$

$$H_{magnetic} = -\sum_{j<k} J_i \vec{S}_j \cdot \vec{S}_k = -|\vec{S}|^2 \sum_{j<k} J_i \hat{S}_j \cdot \hat{S}_k ,$$

where J_i are the spin exchange constants, $\hat{S}_j, \hat{S}_k$ are the unit length vectors representing the spin up or down state of the magnetic atom and $|\vec{S}|^2$ represents the total spin magnitude of the pair of magnetic atoms. $|\vec{S}|^2$ is a constant for systems with all atoms of the same total magnetic moment and in this case can be moved outside of the summation.

If a series of different magnetic configurations are selected and other contributions to total energy are kept constant (for example, by fixing the ionic positions of the atoms), these equations can be represented in matrix form and re-arranged to express the spin exchange constants as a function of the total energies. The constant energy due to non-magnetic factors can be absorbed into the spin interaction matrix 'M' as an extra column of constants. An extra magnetic configuration must be selected to distinguish the structural energy from the magnetic energy. Care must be taken so that the selected magnetic configurations do not lead to linear dependencies, which can be tested by making sure that the determinant of the spin interaction matrix 'M' is not zero. For our 1x1x2 and 2x1x2 skew supercells and the selected magnetic configurations in Figure 14, the spin interaction matrices 'M' are shown in Table S2.

$$M_{jk} = \sum_{j<k} \hat{S}_j \cdot \hat{S}_k$$

$$\vec{E} = -|\vec{S}|^2 M \vec{J},$$

$$\vec{J} = -\frac{1}{|\vec{S}|^2} M^{-1} \vec{E}$$

$$\det(M) \neq 0$$

Once the energies of these magnetic configurations have been calculated, the spin exchange constants can then be calculated as well as the mean field approximation to Curie-Weiss temperature:

$$\theta \approx \frac{S(S+1)}{3k_B} \sum_b z_b J_b = \frac{S(S+1)}{3k_B} \vec{z} \cdot \vec{J}^T$$

$$z_b = count\ of\ bonds\ of\ type\ (b)\ per\ atom$$

Table S1 – Calculated magnetic energies, exchange constants (J_{1-6}) and calculated Curie-Weiss temperature for a range of U-values and supercell sizes. J_{3+4} value averaged from J_3 and J_4 values for 2x1x2 skew supercell and the 2x1x2 skew super cell refers to the larger unit cell whose vectors are defined by ($a_c = 2a$, $b_c = b$, $c_c = a + 2c$). Experimental Curie-Weiss temperatures provided for reference from Table 2.

	$ZrMn_2Ge_4O_{12}$						$ZrCo_2Ge_4O_{12}$					
U-J (eV)	**3**	**4**	**5**		**6**		**3**	**4**		**5**		**6**
Supercell size	1x1x2	1x1x2	1x1x2	2x1x2 skew	1x1x2		1x1x2	1x1x2	2x1x2 skew	1x1x2	2x1x2 skew	1x1x2
K/FU (per Mn atom)												
C-type	0	0	0	0	0		0	0	0	0	0	0
A-type	8.0272	6.259	4.964	4.993	3.988		7.743	5.264	5.282	3.657	3.670	2.572
Diagonal				9.031					10.196		7.614	
Stripey	16.448	12.724	9.910	9.943	7.722		18.698	14.173	14.204	10.754	10.779	8.121
G-type	26.749	20.615	15.958	15.989	12.351		30.761	23.887	23.932	18.445	18.482	14.107
Ferromagnetic	40.451	31.395	24.611	24.654	19.408		37.205	28.122	28.178	21.278	21.324	16.027
J1 (K)	-0.227	-0.181	-0.148	-0.147	-0.123		0.144	0.114	0.115	0.091	0.0920	0.072
J2 (K)	-0.435	-0.341	-0.272	-0.273	-0.221		-0.788	-0.528	-0.529	-0.361	-0.362	-0.250
J3 (K)				-0.188					-0.423		-0.313	
J4 (K)				-0.525					-2.179		-1.694	
J3+4 (K)	-0.592	-0.458	-0.356	-0.356	-0.278		-1.673	-1.298	-1.301	-1.002	-1.004	-0.766
J5+6 (K)	-0.0376	-0.0285	-0.0221	-0.0219	-0.0179		-0.062	-0.045	-0.0448	-0.033	-0.0329	-0.024
Calculated Curie-Weiss temperature (K)	-20.640	-16.038	-12.603	-12.617	-9.982		-20.616	-15.561	-15.591	-11.758	-11.781	-8.844
Experimental Curie-Weiss temperature (K)			-11.38(2)					-15.93(2)				

Table S2 – Spin interaction matrices: Count of bonds per magnetic atom, a. 1x1x2 supercell and b. 2x1x2 skew supercell. Note that diagonal magnetic configuration breaks the degeneracy of the J_3 and J_4 pathways for the 2x1x2 skew supercell. Count of spin exchange pathways per atom per pathway type used in calculating Curie-Weiss temperature also shown.

a.

Magnetic configuration	Total energy constant	J1	J2	J3+4	J5+6
C-type	1	1	-2	-4	2
A-type	1	-1	2	-4	2
Stripey	1	-1	0	0	-2
G-type	1	-1	-2	4	2
Ferromagnetic	1	1	2	4	2
Spin exchange interaction pathways per magnetic atom	N/A	2	4	8	4

b.

Magnetic configuration	Total energy constant	J1	J2	J3	J4	J5+6
C-type	1	1	-2	-2	-2	2
A-type	1	-1	2	-2	-2	2
Diagonal	1	0	0	1	-1	0
Stripey	1	-1	0	0	0	-2
G-type	1	-1	-2	2	2	2
Ferromagnetic	1	1	2	2	2	2
Spin exchange interaction pathways per magnetic atom	N/A	2	4	4	4	4