Supplementary Information

for

Successive Short- and Long-Range Magnetic Ordering in Rosiaite-type $CoGeTeO_6$ Prepared by Ion-Exchange Reaction

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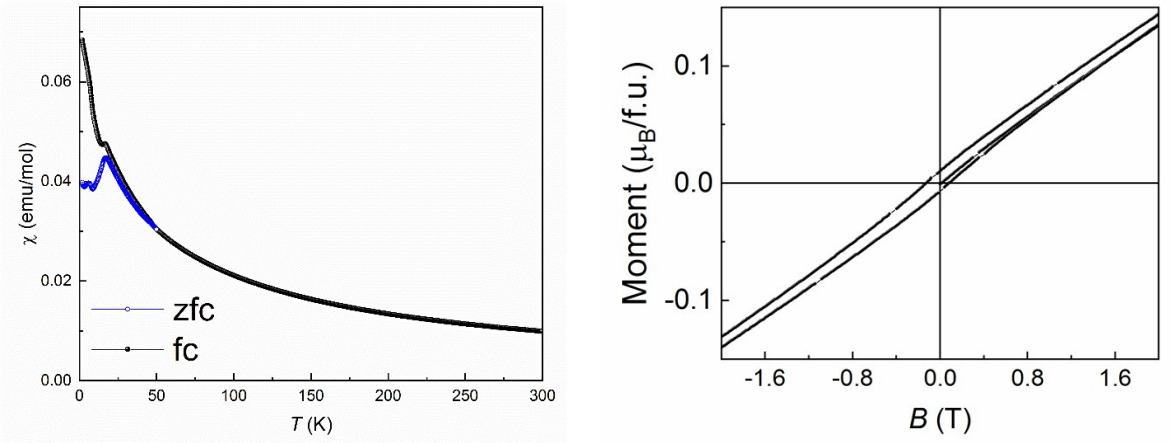


Fig. S1. (left panel) The temperature dependences of the magnetic susceptibility in $CoGeTeO_6$ recorded in ZFC (blue open circle) and FC (black sphere) at B = 0.1 T (right panel). Zoom of the magnetization loop in $CoGeTeO_6$ at 2 K.

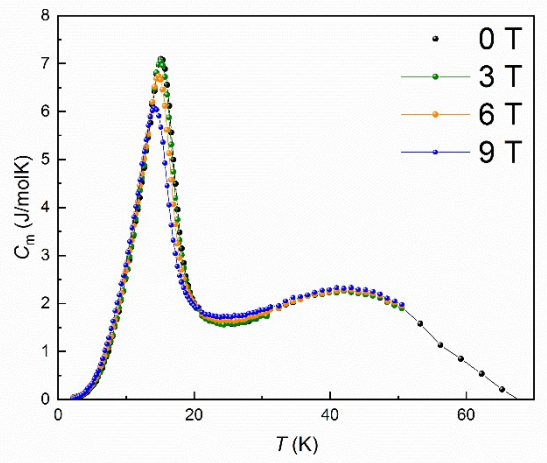
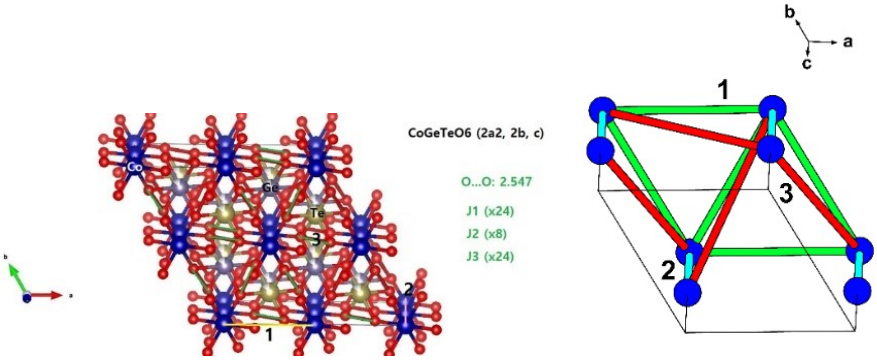


Fig. S2. Magnetic specific heat in $CoGeTeO_6$ measured at various magnetic fields.

Energy mapping analysis

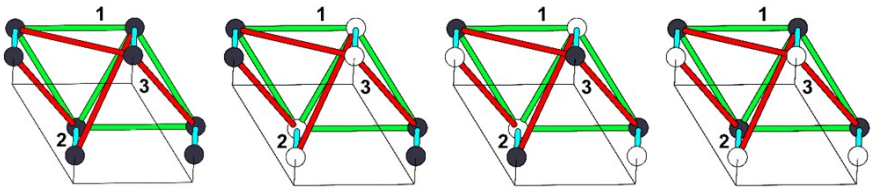
The arrangements of the spin exchange paths $J_1 - J_3$ are presented in **Fig. S3**. To determine the values of these exchanges by using the energy-mapping analysis [32-34], we employ the four ordered spin states shown in **Fig. S4**. The energies of these states in terms of the spin exchanges $J_1 - J_3$ using the spin Hamiltonian of **Eq. 2** are summarized in **Table S1**. We then determine the relative energies of these states (**Table S2**) by DFT calculations using the frozen core projector augmented plane wave (PAW) [35, 36] encoded in the Vienna ab Initio Simulation Packages (VASP) [37] and the PBE potential [38] for the exchange-correlation functional. The electron correlation associated with the 3*d* states of Co was taken into consideration by DFT+*U* calculations with an effective on-site repulsion $U_{eff} = U - J = 3$ and 4 eV [39] All our DFT+*U* calculations used the plane wave cutoff energy of 450 eV, a set of (3x3x5) *k*-points, and the threshold of 10^{-6} eV for self-consistent-field energy convergence. Finally, the numerical values of $J_1 - J_3$ (in K) are obtained by mapping the relative energies of the seven ordered spin states onto the corresponding energies determined by DFT+*U* calculations (**Table S2**). The results of these energy-mapping analyses are summarized in **Table 2.**

(a) Figures



(a) (b)

Fig. S3. (a) Perspective view of the $CoGeTeO_6$ structure and (b) spin exchange paths, J_1 to J_3. The numbers 1, 2, and 3 indicate the J_1, J_2 and J_3 paths, respectively.



(a) FM (b) AF1 (c) AF2 (d) AF3

Fig. S4. Ordered spin arrangements where the white circles represent the down spin sites of Co^{2+} ions.

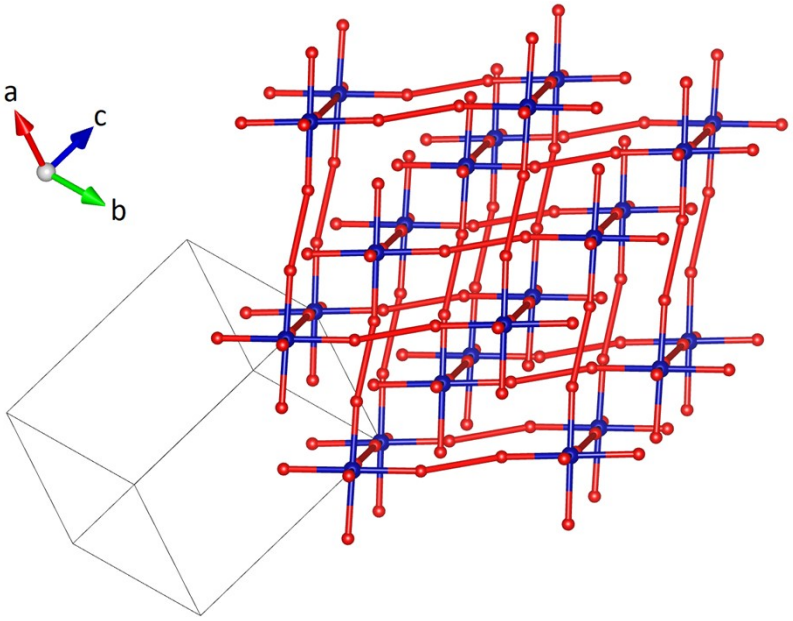


Fig. S5. Three interpenetrating rhombic boxes made up of eight CoO_6 octahedra joined by the spin exchange paths J_3.

(b) Tables

Table S1. Values of n_i in the energy expressions, $E_{spin} = -\sum_{i=1}^{3} n_i J_i S^2$, for the ordered spin states FM and AF_i (i = 1 – 3) of $CoGeTeO_6$

	J_1	J_2	J_3
E_{FM}	-24	-8	-24
E_{AF1}	8	-8	8
E_{AF2}	8	8	-8
E_{AF3}	-24	8	24

Table S2. Relative energies (in meV/FU) of the FM and AF_i (i = 1 – 3) of $CoGeTeO_6$ obtained from DFT+U calculations

	U = 3 eV	U = 4 eV
FM	11.54	8.78
AF1	3.66	2.76
AF2	6.78	5.09
AF3	0	0

(c) Energy mapping

$J_3 = (1/64)(4/N^2)[(E_{AF3} - E_{FM}) - (E_{AF2} - E_{AF1})]$

$$J_2 = (1/16)[(4/N^2)(E_{AF2} - E_{AF1}) + 16J_3]$$
$$J_1 = (1/32)[(4/N^2)(E_{AF2} - E_{AF3}) + 32J_3]$$