Supporting information

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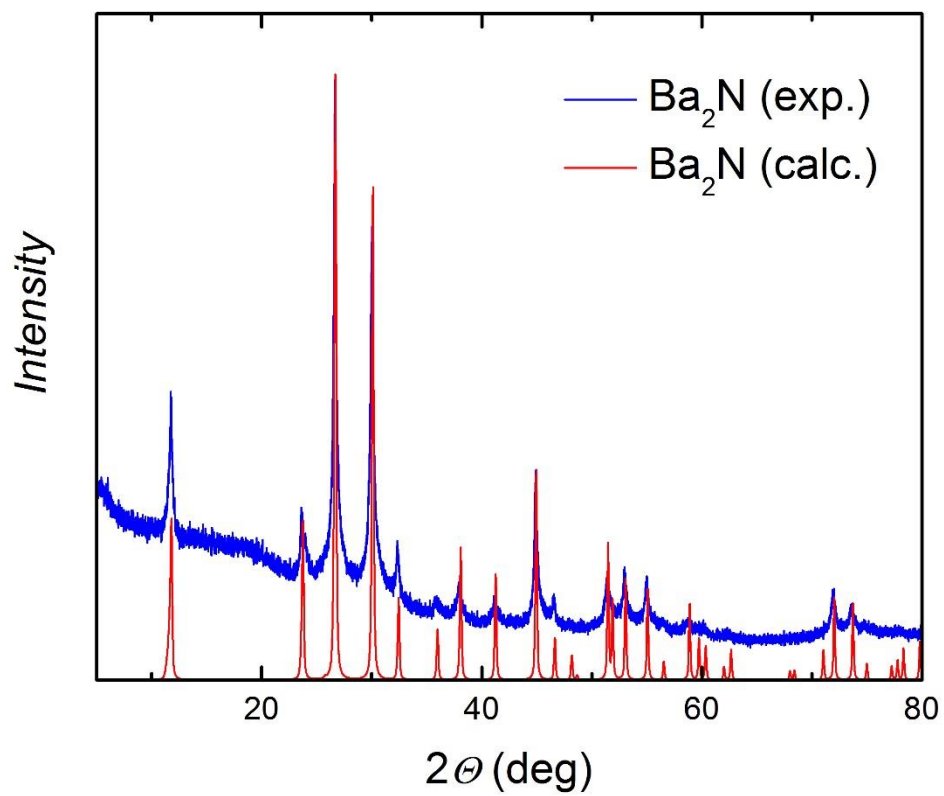
- **Powder pattern of Ba₂N**

Figure S1. Powder pattern of Ba₂N starting material

- **Chemical analysis**

Table S1. Results of chemical analysis for $Ba_4[Mn_3N_6]$

Element	mass % (found)	mass % (calculated from the formula)
Ba	69.2(8)	68.82
Mn	20.3(2)	20.65
N	10.49(8)	10.53
C	<0.3, below detection limit	0
H	<0.1, below detection limit	0
O	<0.25, below detection limit	0
Ta	<0.25, below detection limit	0

- **Selected bond lengths/angles**

Table S2. Selected interatomic distances and angles for $Ba_4[Mn_3N_6]$

Atoms	Distance (Å)	Atoms	Angle (°)
Ba1–N1	2.663(7)	N2–Mn1–N2	107.5(3)
–N2	2.720(7)	N2–Mn1–N3	88.5(3) × 2
–N2	3.171(7)	N2–Mn1–N3	120.1(3) × 2
–N2	3.443(7)	N3–Mn1–N3	132.6(3)
–N3	2.730(7)	Mn2–Mn1–Mn2	149.93(5)
–N3	2.766(7)	N1–Mn2–N1	96.8(3)
Ba2–N1	2.817(7)	N1–Mn2–N2	114.8(3)
–N1	2.916(7)	N1–Mn2–N3	119.0(3)
–N1	3.068(7)	N1–Mn2–N2	112.3(3)
–N2	2.874(7)	N1–Mn2–N3	110.3(3)
–N2	2.993(7)	N2–Mn2–N3	103.8(3)
–N3	2.968(7)	Mn1–Mn2–Mn2	173.03(8)
–N3	3.005(7)		
Mn1–N2	2.090(7) × 2		
–N3	1.980(7) × 2		
–Mn2	2.520(2) × 2		
Mn2–N1	1.870(7)		
–N1	1.914(7)		
–N2	1.788(7)		
–N3	1.821(7)		
–Mn1	2.520(2)		
–Mn2	2.513(2)		

- **DTA-TG curves**

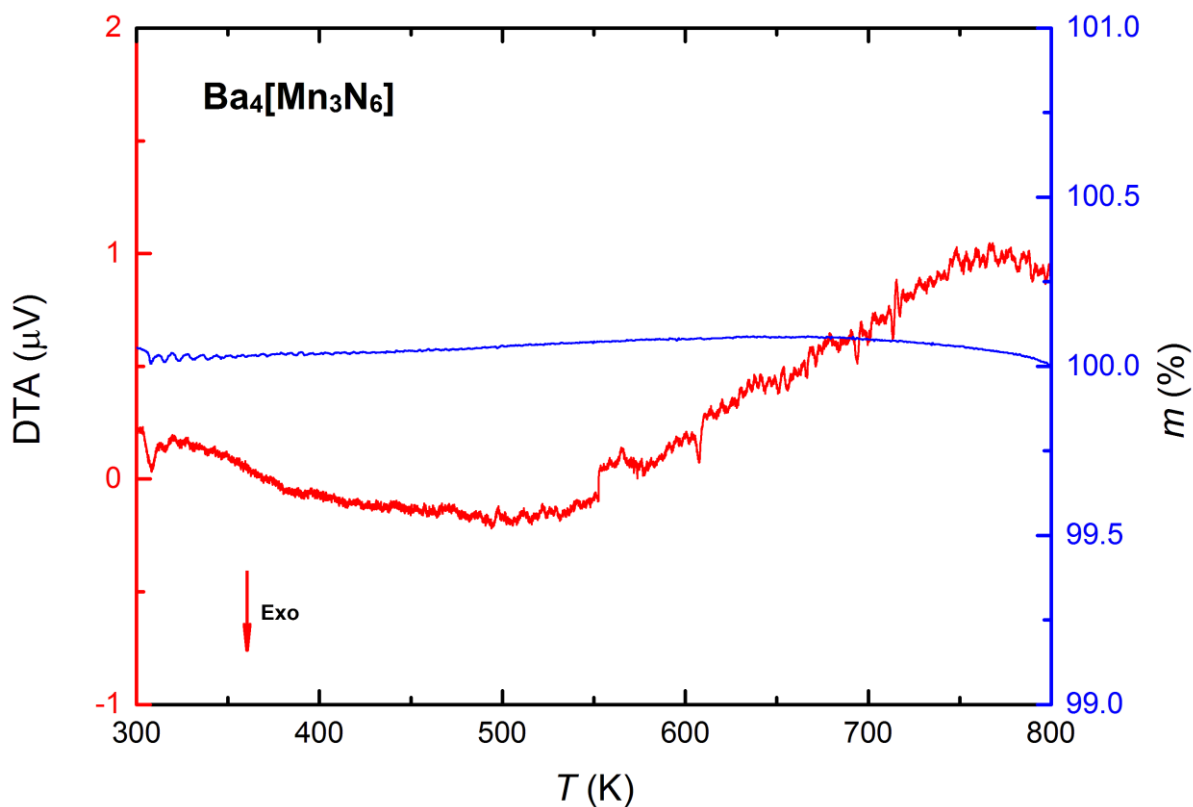**Figure S2**. DTA-TG curves for a $Ba_4[Mn_3N_6]$ sample ($m = 41.79$ mg). Heating under flowing Ar (100 ml/min) with a rate of 5 K/min. A slight mass gain in the range $T = 300–575$ K is probably due to sample oxidation by traces of oxygen.

- **High-temperature magnetic susceptibility**

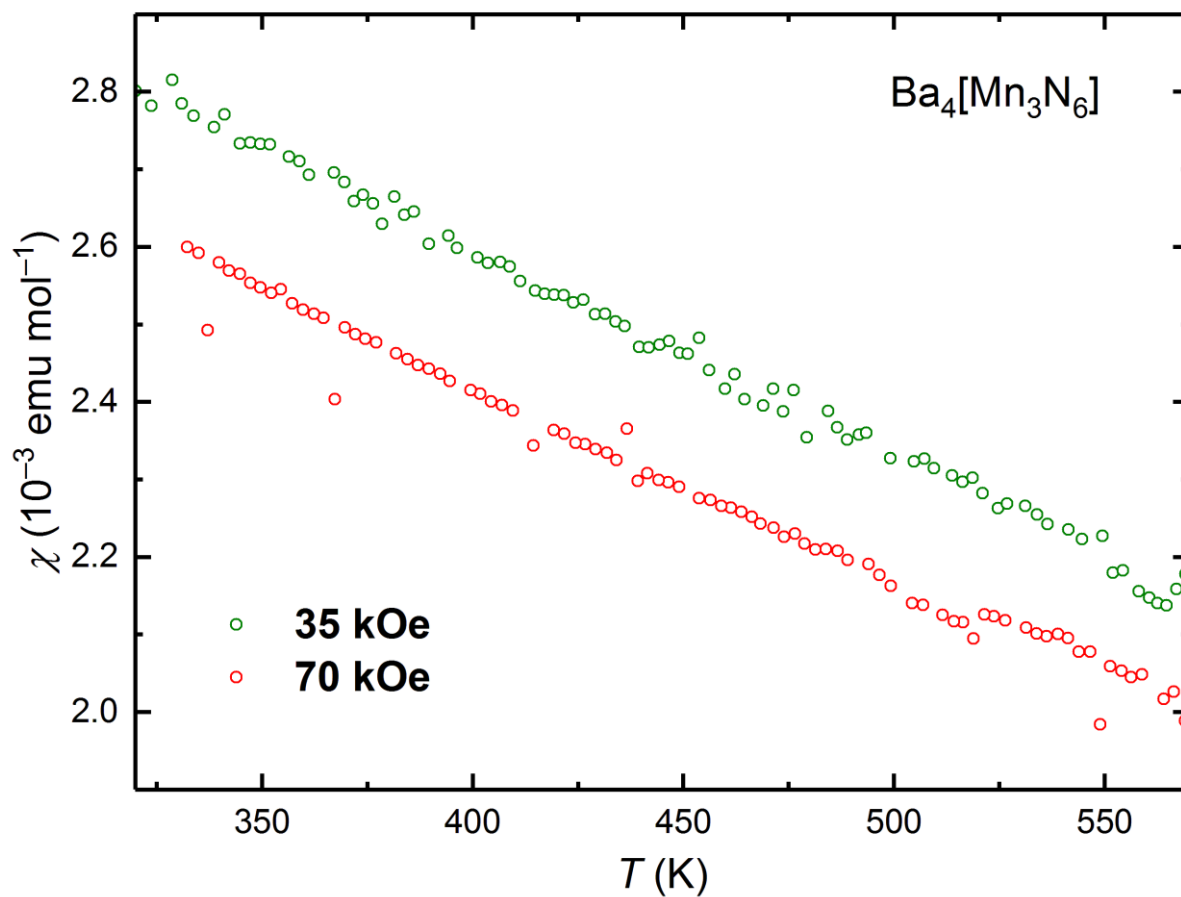**Figure S3**. Temperature dependence of magnetic susceptibility for Ba$_4$[Mn$_3$N$_6$] between 320 and 575 K.

- **Magnetic models used for LSDA calculations**

∘ **spin up**   • **spin down**

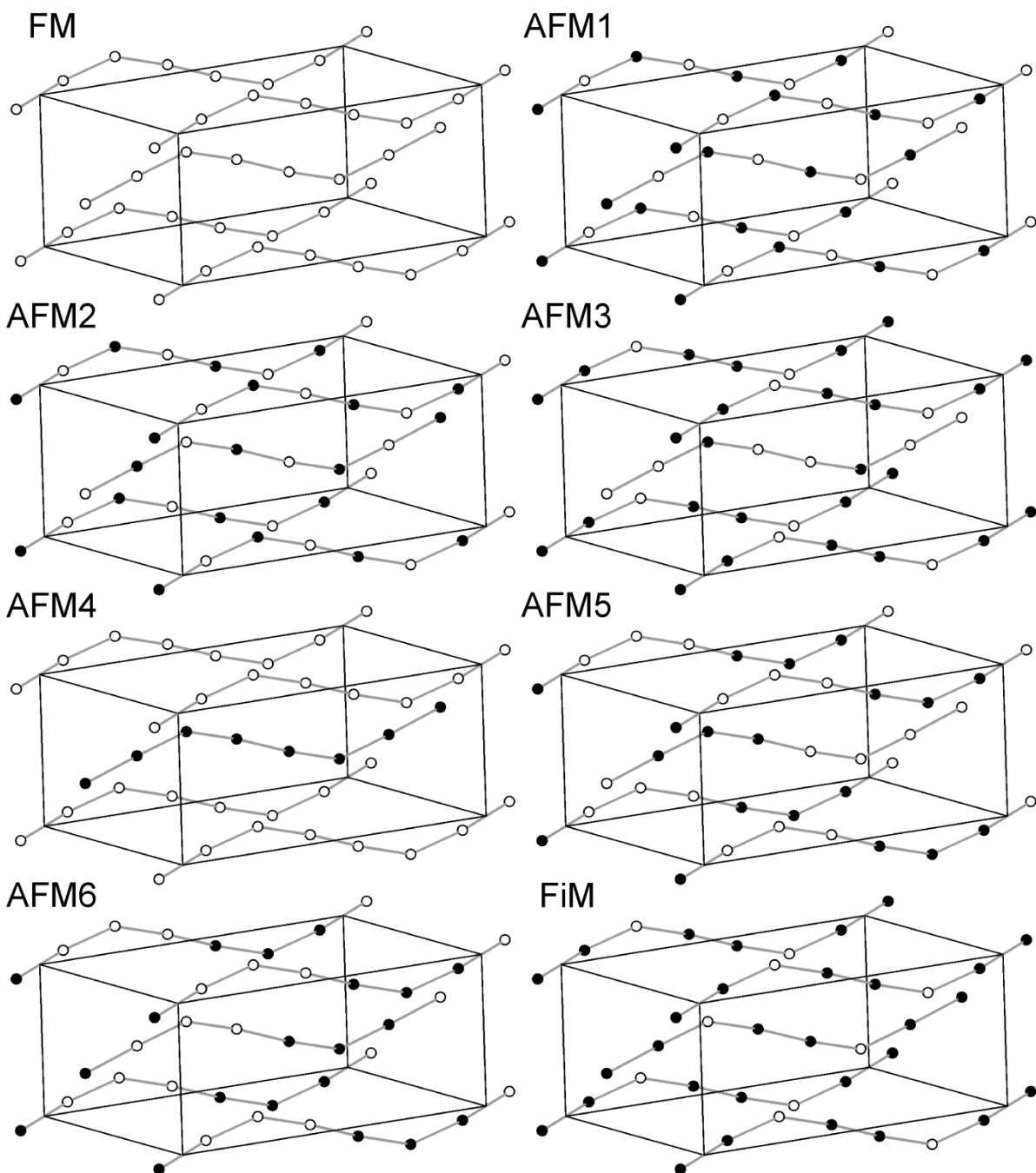**Figure S4**. Model magnetic arrangements used for the total energy calculations (FM −

ferromagnetic, AFM − antiferromagnetic, FiM − ferrimagnetic).