

Electronic Supplementary Information for Jahn-Teller distortion induced two-dimensional ferroelasticity in Mn_2CuO_6 monolayer with antiferromagnetic ordering[†]

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Table S1 The summary of SCAN+rVV10 calculations predicted relative potential energies ΔE (in meV/f.u.) and the corresponding crystal symmetries of the 10 different magnetic spin textures we considered for Mn_2CuO_6 monolayer, where nAFM, zAFM, sAFM and FiM1-6 represent Neel-AFM, Zigzag-AFM, Stripy-AFM and 6 ferrimagnetic spin textures, respectively. The schematic diagrams of spin-polarized crystal structures are shown in Fig.S1. Obviously, the configuration with sAFM spin texture is most thermodynamically stable with the $C2/m$ crystal symmetry. In addition, according to our simulation, the parental PE phase with the hexagonal crystal structure adopts the FiM1 spin texture.

Mag	FM	nAFM	zAFM	sAFM	FiM1	FiM2	FiM3	FiM4	FiM5	FiM6
Space group	$P\bar{3}1m$	$P2/c$	$C2$	$C2/m$	$P\bar{3}1m$	$C2$	$P2/m$	$P2/m$	$P2$	$P\bar{3}1m$
ΔE	232.2	96.8	167.2	0	94.2	96.2	165.1	141.1	166.1	130.6

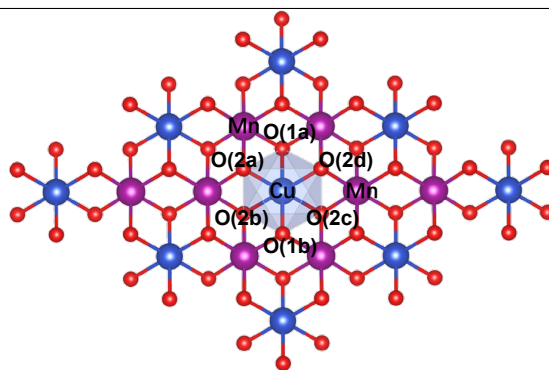
Table S2 Our SCAN+rVV10 calculations predicted crystallographic cell information for FE and PE phases of Mn_2CuO_6 monolayers.

Structure (space group, point group)		FE- Mn_2CuO_6 ($C2/m$, C_{2h})		
Primitive cell dimensions		$a = b = 4.945 \text{ \AA}$, $c = 22.967 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120.5^\circ$		
2D crystallographic cell parameters		$a = 8.587 \text{ \AA}$, $b = 4.907 \text{ \AA}$, $\gamma = 90^\circ$		
Atoms	Wyckoff positions	x	y	z
Mn(1)	4 h	0.00000	0.33060	0.50000
Cu(1)	2 c	0.00000	0.00000	0.50000
O(1)	8 j	0.82737	0.17182	0.45797
O(2)	4 i	0.32847	0.00000	0.45972
Full general positions: (1) x, y, z ; (2) $-x, y, -z$; (3) $x, -y, z$; (4) $x+1/2, y+1/2, z$; (5) $-x, -y, -z$; (6) $-x+1/2, y+1/2, -z$; (7) $-x+1/2, -y+1/2, -z$; (8) $x+1/2, -y+1/2, z$				

Structure (space group, point group)		PE- Mn_2CuO_6 ($P\bar{3}1m$, D_{3d})		
Primitive cell dimensions		$a = b = 4.936 \text{ \AA}$, $c = 22.967 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$		
2D crystallographic cell parameters		$a = b = 4.936 \text{ \AA}$, $\gamma = 120^\circ$		
Atoms	Wyckoff positions	x	y	z
Mn(1)	2 d	0.33333	0.66667	0.50000
Cu(1)	1 b	0.00000	0.00000	0.50000
O(1)	6 k	0.33738	0.00000	0.45859
Full general positions: (1) x, y, z ; (2) $-y, x-y, -z$; (3) $-x+y, -x, z$; (4) $x, x-y, -z$; (5) $-x+y, y, -z$; (6) $-y, -x, -z$; (7) $-x, -y, -z$; (8) $y, -x+y, -z$; (9) $x-y, x, -z$; (10) $-x, -x+y, z$; (11) $x-y, -y, z$; (12) y, x, z				

Table S3 Our SCAN+rVV10 calculations predicted crystallographic data, including cation-anion bond lengths and angles for FE and PE phases of Mn_2CuO_6 monolayers, where the cations within octahedral framework have six coordination numbers.

Atomic structure for Mn_2CuO_6 monolayer



FE- Mn_2CuO_6				PE- Mn_2CuO_6			
Bond lengths		Bond angles		Bond lengths		Bond angles	
Cu-O(1)	1.858 Å	O(1a)-Cu-O(2a)	82.5°	Cu-O(1)	1.912 Å	O(1a)-Cu-O(2a)	82.5°
Cu-O(2)	1.959 Å	O(2a)-Cu-O(2b)	82.1°	Cu-O(2)	1.912 Å	O(2a)-Cu-O(2b)	82.5°
Mn-O(1)	1.918 Å	O(2a)-Cu-O(2d)	97.9°	Mn-O(1)	1.891 Å	O(2a)-Cu-O(2d)	97.5°
Mn-O(2a)	1.874 Å	O(1a)-Cu-O(2b)	97.4°	Mn-O(2)	1.891 Å	O(1a)-Cu-O(2b)	97.5°
Mn-O(2d)	1.873 Å	O(1a)-Mn-O(2a)	83.1°			O(1a)-Mn-O(2a)	83.9°
		O(2a)-Mn-O(2b)	86.6°			O(2a)-Mn-O(2b)	83.9°

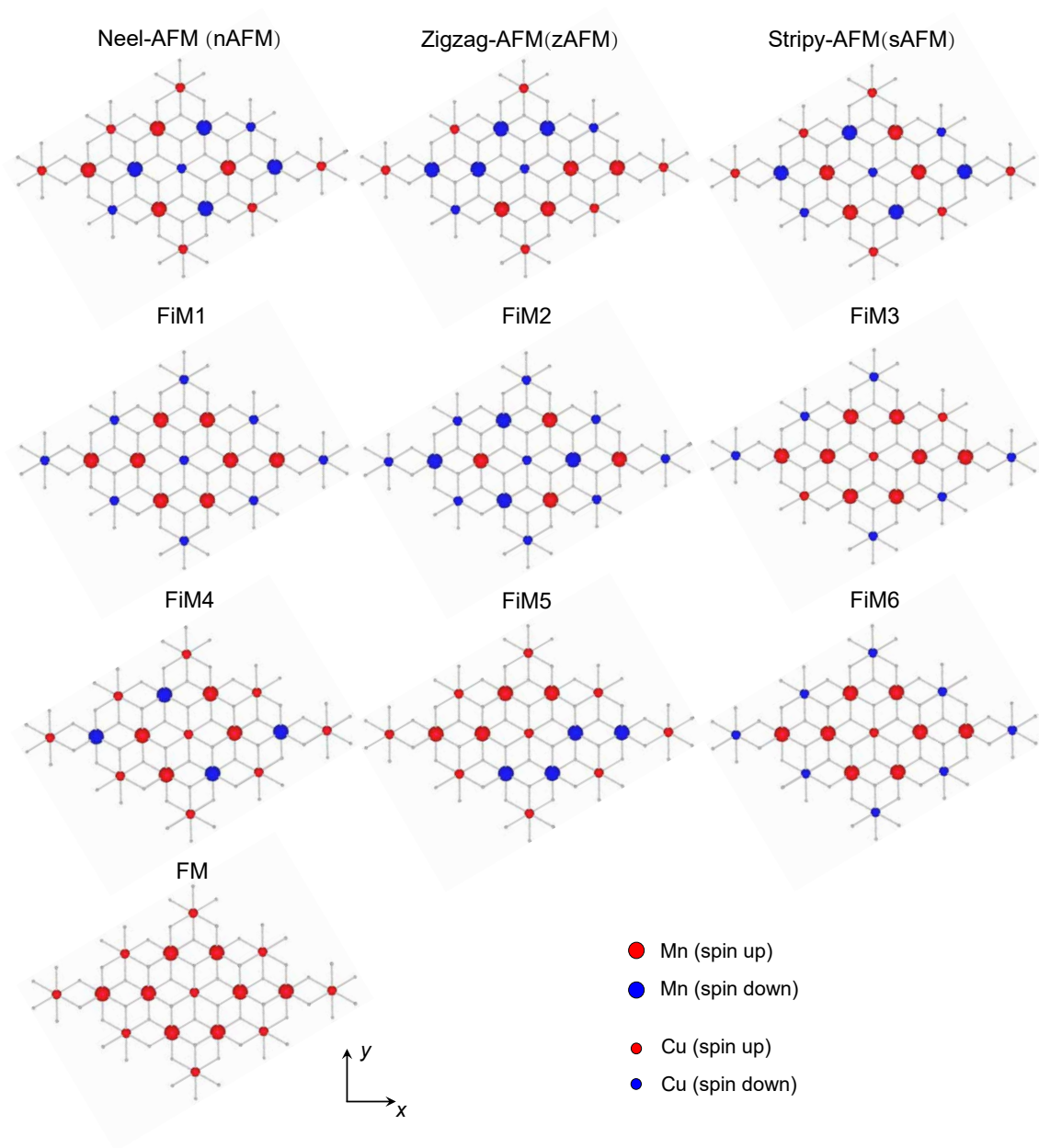


Figure S1 The schematic diagrams of spin-polarized crystal structures for Mn_2CuO_6 monolayer with the 10 different magnetic spin textures. The different size of circles are used to distinguish between the two cations (larger for Mn and smaller for Cu), the spinors with spin up and spin down are marked in red and blue, respectively.

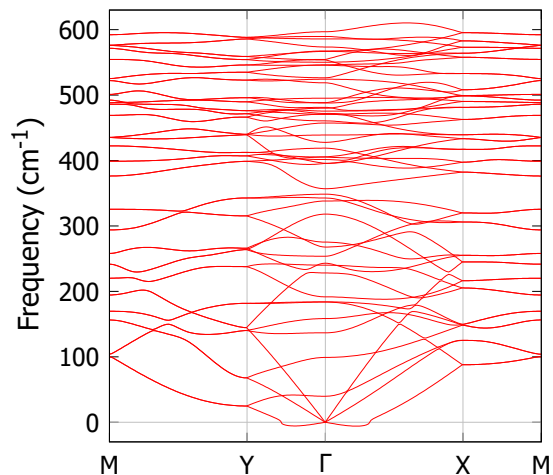


Figure S2 The simulated phonon spectra of FE Mn_2CuO_6 monolayer using PHONOPY code¹.

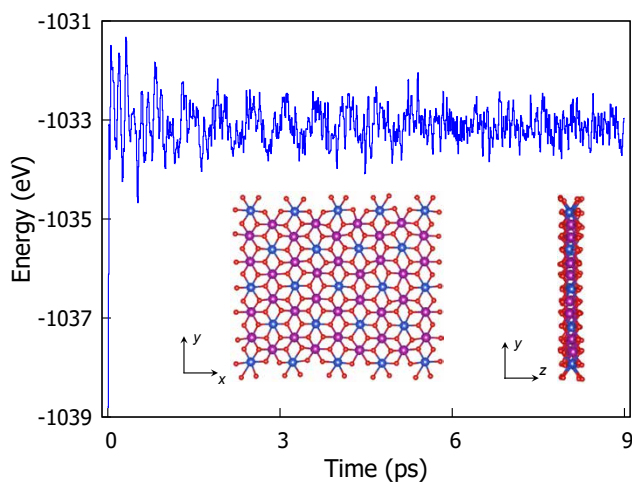


Figure S3 Full time evolution of the total energy for FE Mn_2CuO_6 monolayer composed of the primitive cell corresponds to the 4×2 supercell of the orthorhombic configuration, during *ab initio* MD simulations performed at 300 K up to 9 ps. The inset is a snapshot of Mn_2CuO_6 monolayer structure at the end of MD simulations.

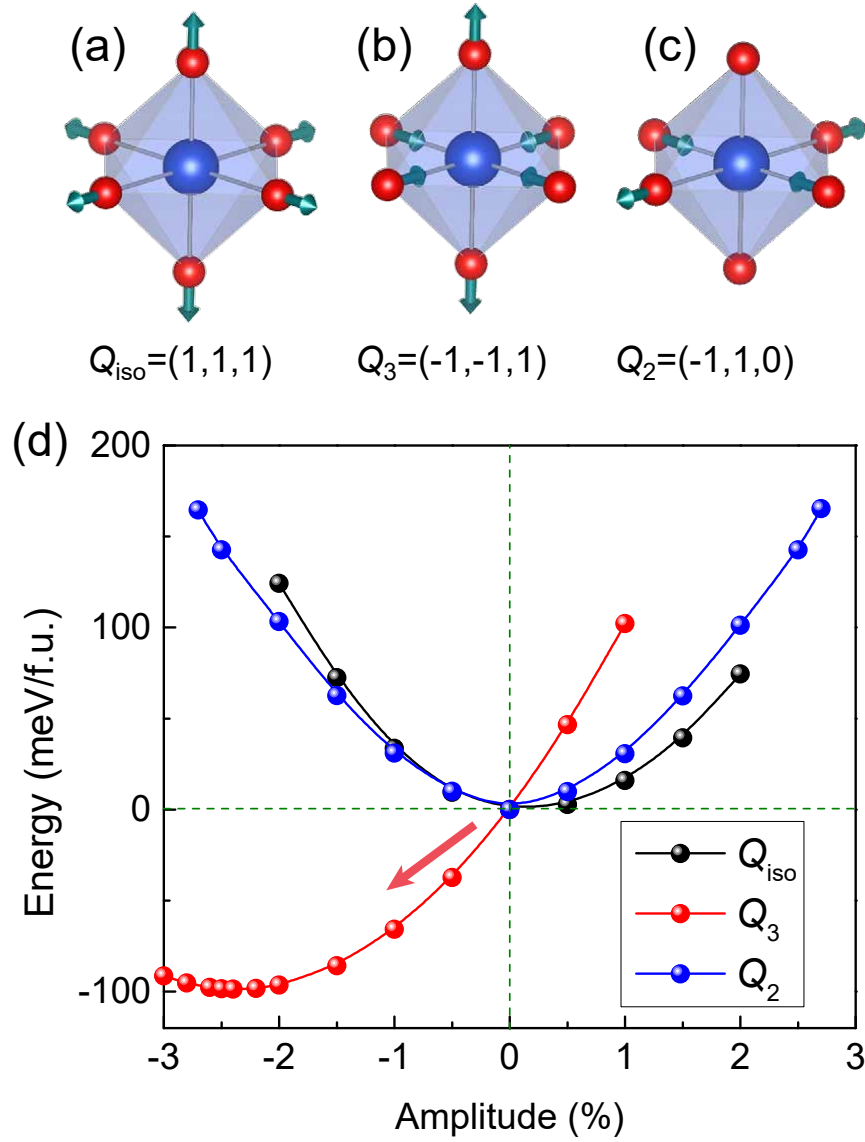


Figure S4 Vibrational modes and the adiabatic potential energy profile for FE Mn_2CuO_6 monolayer. Definition of vibrational modes: (a) isotropic mode $Q_{iso}=(1, 1, 1)$, (b) $Q_3=(-1, -1, 1)$, (c) $Q_2=(-1, 1, 0)$. (d) The adiabatic potential energy profile of the three specific vibrational modes as a function of amplitudes is obtained based on our *ab initio* simulations, where the calculated Mn_2CuO_6 model with the fixed sAFM-O1 magnetic texture is adopted. The energy (in meV/f.u.) shown in (d) is with respect to the energy of the isotropic structure (high-symmetry state). Under the static Jahn-Teller effect, Mn_2CuO_6 monolayer can fall to the minimum of the adiabatic potential energy profile through the spontaneous structural distortion, driving the system to a stable low-symmetry state.

Table S4 Supercell matrices of PE and FE (including variant O1, O2 and O3) phases for Mn_2CuO_6 monolayer. The supercell matrices have the form $\mathbf{Q} = (\vec{q}_1, \vec{q}_2)$, where the column vectors \vec{q}_1 and \vec{q}_2 are the two vectors along the diagonal directions of the 2×2 supercells based on the 2D planes of the parental PE phase (see main text for details). The unit of length is Å.

\mathbf{Q}_{PE}	FE variants		
	\mathbf{Q}_{O1}	\mathbf{Q}_{O2}	\mathbf{Q}_{O3}
$\begin{pmatrix} 17.0967 & 0 \\ 0 & 9.8708 \end{pmatrix}$	$\begin{pmatrix} 17.1758 & 0 \\ 0 & 9.8148 \end{pmatrix}$	$\begin{pmatrix} 17.0437 & -0.0880 \\ 0 & 9.8904 \end{pmatrix}$	$\begin{pmatrix} 17.0436 & 0.0880 \\ 0 & 9.8904 \end{pmatrix}$

Table S5 The calculated magnetic anisotropy energy (MAE) per cation of the considering directions, against the [001] direction (in $\mu\text{eV}/\text{cation}$) in FE Mn_2CuO_6 monolayer.

Directions	[001]	[100]	[010]	[110]	[210]	[111]	[011]	[101]	[012]
MAE	0	242.2	183.2	212.7	201.1	110.0	91.4	120.9	74.4

The Heisenberg spin Hamiltonians in FE Mn₂CuO₆ monolayer

To quantitatively estimate the magnetic properties of FE Mn₂CuO₆ monolayer, we construct Heisenberg spin Hamiltonians based on the equation (7) of the main text. In Mn₂CuO₆ monolayer, we should consider the two different magnetic cations (Mn and Cu). The energy eigenvalue E of the Hamiltonians can be thus approximatively expressed as:

$$E = - (J_{1a} \sum_{J_{1a}} \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} + J_{1c} \sum_{J_{1c}} \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Cu}} + J_{1d} \sum_{J_{1d}} \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Cu}} + J_{1b} \sum_{J_{1b}} \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} + J_{2a} \sum_{J_{2a}} \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} + J_{2c} \sum_{J_{2c}} \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + J_{2b} \sum_{J_{2b}} \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} + J_{2d} \sum_{J_{2d}} \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}}). \quad (\text{S1})$$

We can simulate nearest-neighbor and next-nearest-neighbor exchange interaction parameters with the whole magnetic spin textures shown in Fig. S1 described by:

$$\left\{ \begin{array}{l} E_{\text{nAFM}} = (8J_{1a} + 4J_{1b} - 8J_{2a} - 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (4J_{2c} - 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{zAFM}} = - (8J_{1a} - 4J_{1b} + 8J_{2a} - 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (4J_{2c} - 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{sAFM}} = (8J_{1a} - 4J_{1b} - 8J_{2a} + 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (8J_{1c} - 16J_{1d}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Cu}} \\ \quad - (4J_{2c} - 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{FiM1}} = - (8J_{1a} + 4J_{1b} + 8J_{2a} + 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} + (8J_{1c} + 16J_{1d}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Cu}} \\ \quad - (4J_{2c} + 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{FiM2}} = (8J_{1a} + 4J_{1b} - 8J_{2a} - 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (4J_{2c} + 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{FiM3}} = - (8J_{1a} + 4J_{1b} + 8J_{2a} + 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (4J_{2c} - 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{FiM4}} = (8J_{1a} - 4J_{1b} - 8J_{2a} + 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (4J_{2c} + 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{FiM5}} = - (8J_{1a} - 4J_{1b} + 8J_{2a} - 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (4J_{2c} + 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{FiM6}} = - (8J_{1a} + 4J_{1b} + 8J_{2a} + 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} + (4J_{1c} + 8J_{1d}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Cu}} + E_0, \\ E_{\text{FM}} = - (8J_{1a} + 4J_{1b} + 8J_{2a} + 16J_{2b}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Mn}} - (8J_{1c} + 16J_{1d}) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Cu}} \\ \quad - (4J_{2c} + 8J_{2d}) \vec{S}_{\text{Cu}} \cdot \vec{S}_{\text{Cu}} + E_0. \end{array} \right. \quad (\text{S2})$$

Where the J_{ij} ($i=1$ or 2 , and $j=a, b, c$ or d) represent nearest-neighbor and next-nearest-neighbor exchange interaction parameters between the magnetic cations. E_0 is set as the zero potential energy in our DFT calculations. \vec{S}_{Mn} and \vec{S}_{Cu} denote the unit vectors of the local spin moment at Mn and Cu sites, where these spin moments collinear with each other, and therefore we can select their modulus lengths as parameters. Based on the Equation (S2), we can obtain exchange interaction parameters, listed in Table. S4.

Table S6 The calculated Nearest-neighbor and next-nearest-neighbor exchange interaction parameters (in meV) of the cation (Mn and Cu) for FE Mn_2CuO_6 monolayer.

J_{1a}	J_{1b}	J_{1c}	J_{1d}	J_{2a}	J_{2b}	J_{2c}	J_{2d}
-11.55	-10.81	37.01	-52.45	-3.98	2.94	0.76	0.43

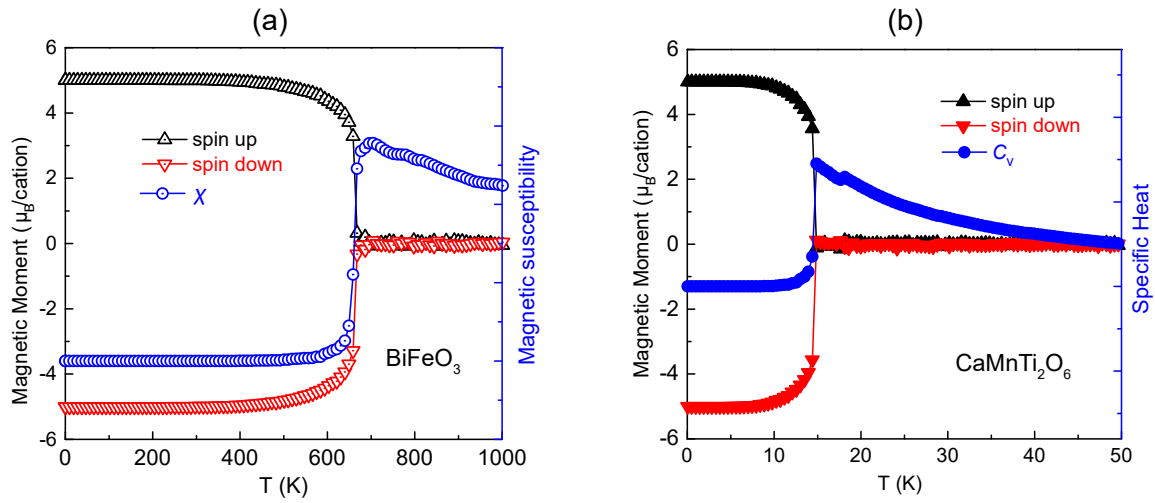


Figure S5 The MC simulations temperature-dependent magnetic phase transitions for perovskite oxides (a) BiFeO_3 and (b) $\text{CaMnTi}_2\text{O}_6$, including magnetic moments μ_B (per cation), magnetic susceptibility χ and specific heat C_v . According to our MC simulations, the T_N of BiFeO_3 and $\text{CaMnTi}_2\text{O}_6$ are around 675 K and 14.8 K, respectively.

References

- [1] A. Togo, F. Oba and I. Tanaka, *Phys. Rev. B*, 2008, **78**, 134106.