

## Supplementary Materials of First-principles predictions of room-temperature ferromagnetism in orthorhombic $\text{MnX}_2$ ( $\text{X}=\text{O}, \text{S}$ ) monolayers

Xuli Cheng,<sup>1</sup> Shaowen Xu,<sup>1,§</sup> Tao Hu,<sup>2</sup> Shunbo Hu,<sup>1,\*</sup> Heng Gao,<sup>1</sup> David J. Singh,<sup>3</sup> and Wei Ren<sup>1,4,†</sup>

□□□□□□□□

<sup>1</sup>Department of Physics, Materials Genome Institute, Shanghai Key Laboratory of High Temperature Superconductors, International Centre of Quantum and Molecular Structures, Shanghai University, Shanghai 200444, China

<sup>2</sup>State Key Laboratory of Advanced Special Steels, School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

<sup>3</sup>Department of Physics and Astronomy, University of Missouri, Columbia MO 65211 USA

<sup>4</sup>Zhejiang Laboratory, Hangzhou 311100, China

§[xswprincess@shu.edu.cn](mailto:xswprincess@shu.edu.cn); \*[shunbohu@shu.edu.cn](mailto:shunbohu@shu.edu.cn); †[renwei@shu.edu.cn](mailto:renwei@shu.edu.cn)

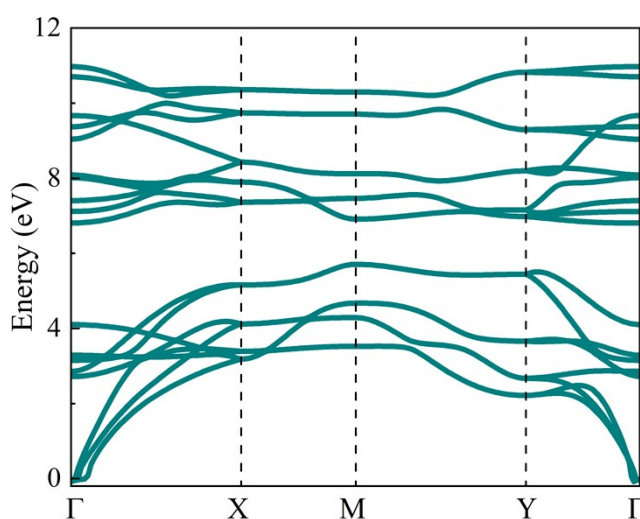


Figure S1. The phonon spectra of  $\text{MnS}_2$  monolayer.

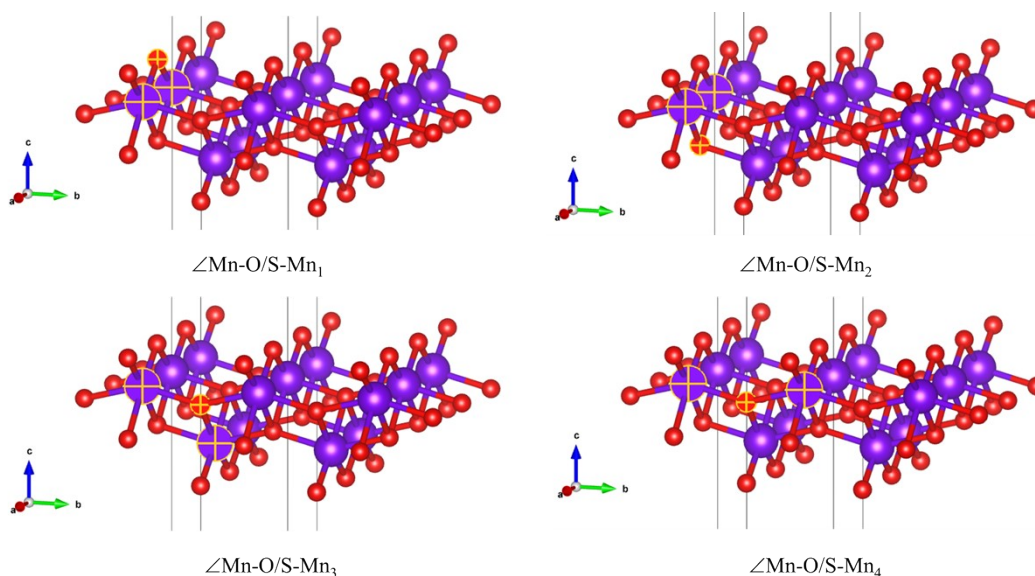


Figure S2. The definition of angles for  $\text{MnO}_2$  and  $\text{MnS}_2$  monolayers are indicated by the selected atoms.

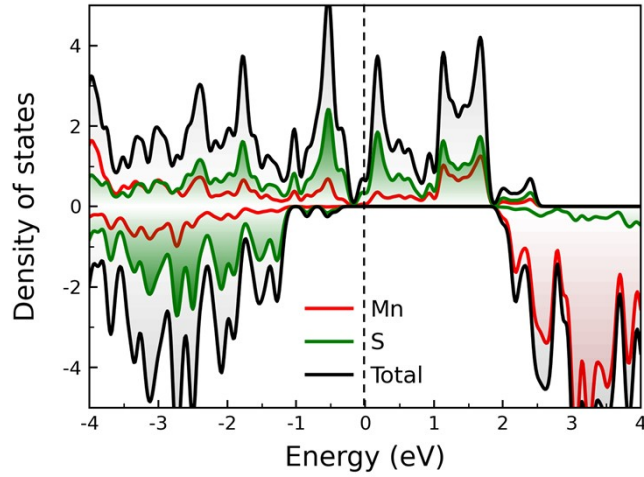


Figure S3. The element resolved partial density of states for MnS<sub>2</sub> monolayer.

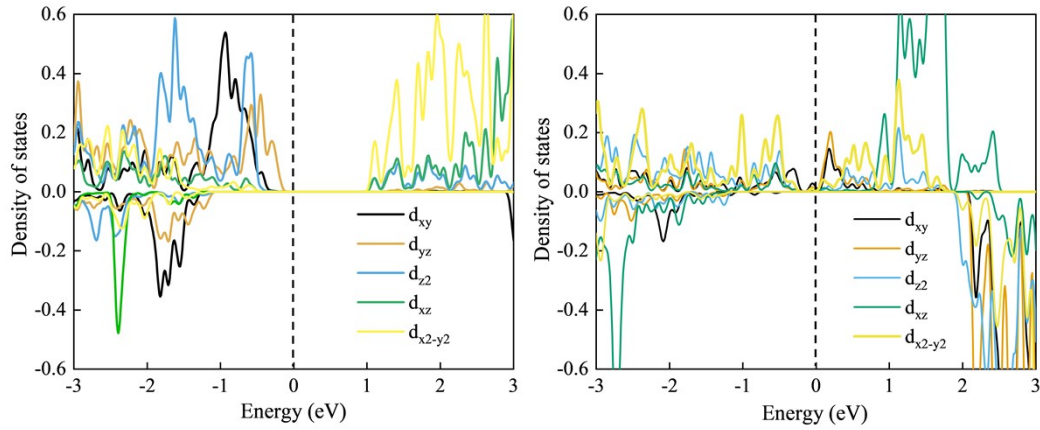


Figure S4. Resolved density of states for the *d* orbitals of Mn elements in (a) MnO<sub>2</sub> monolayer and (b) MnS<sub>2</sub> monolayer.

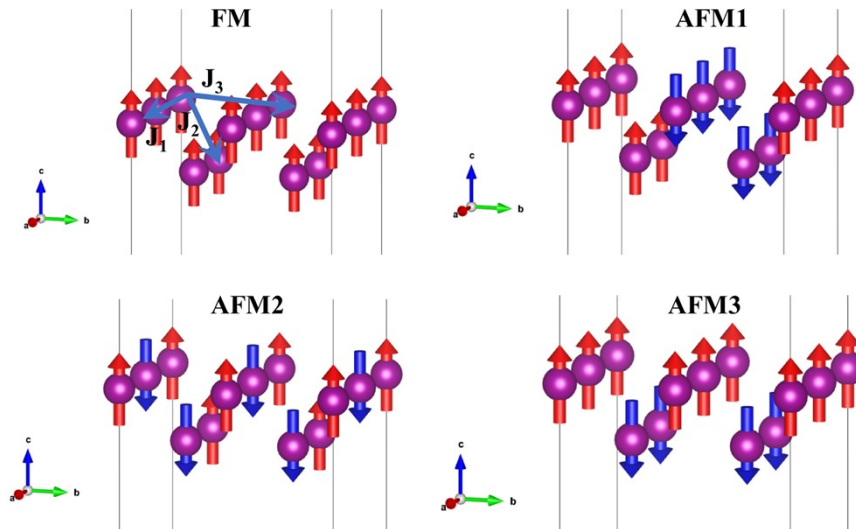


Figure S5. The schematic illustrations of FM, AFM1, AFM2 and AFM3 configurations. For clarity, only Mn atoms are shown in purple.

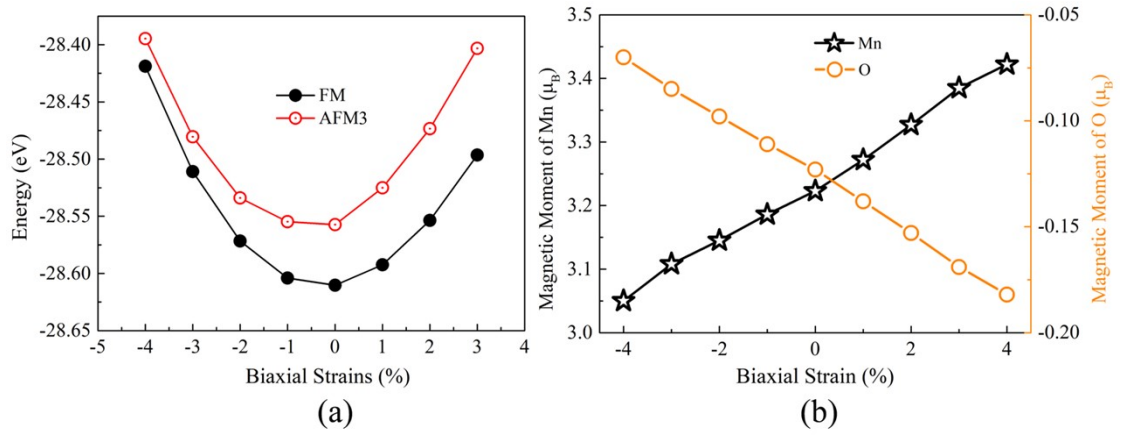


Figure S6. (a) The energy and (b) magnetic moment of  $\text{MnO}_2$  monolayer of AFM3 and FM configurations under different biaxial strains.

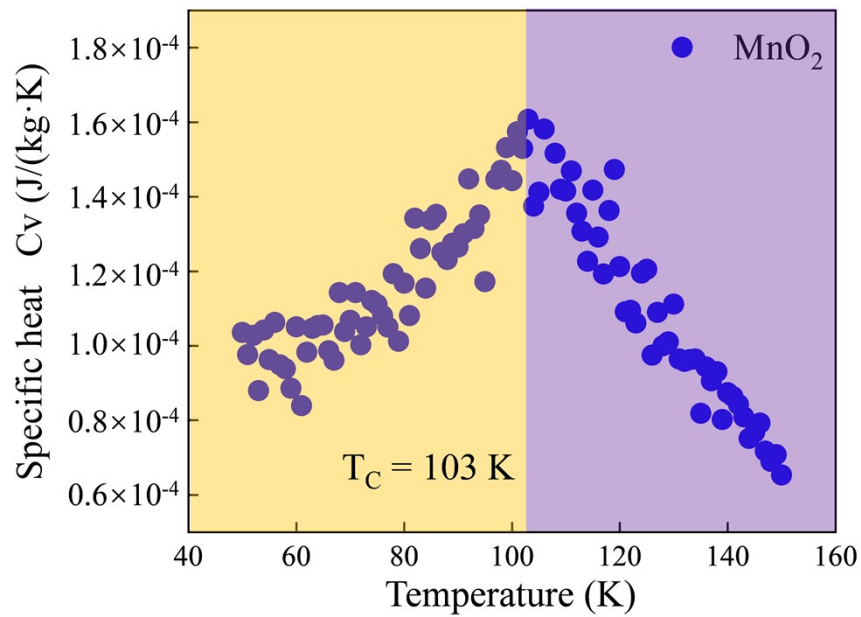


Figure S7. The simulated specific heat as a function of temperature by using the Heisenberg model for rhombohedral  $\text{MnO}_2$  monolayer.

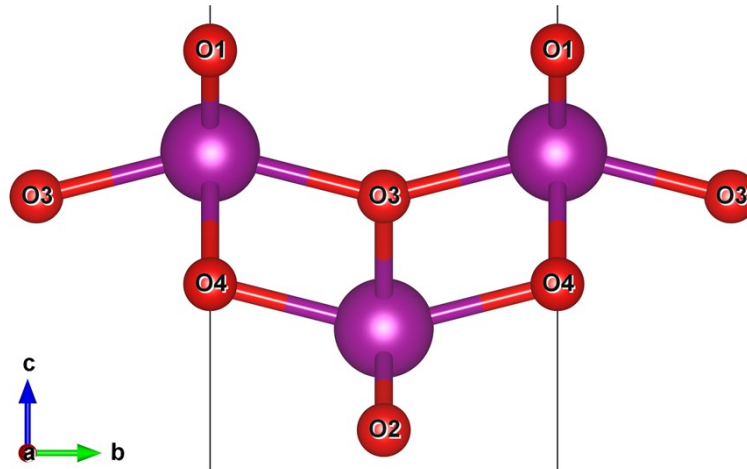


Figure S8. The positions of  $\text{O}_{1,2,3,4}$  in the  $\text{MnX}_2$  monolayer.

Table S1. The formation energy ( $E_f$ , meV/atom) and exfoliation energy ( $E_{exf}$ , meV/atom) of MnO<sub>2</sub> monolayer with  $Pmmn$  ( $o$ -phase) and  $P\bar{3}m1$  ( $r$ -phase) space group. The  $E_{exf}$  of graphene and SrTiO<sub>3</sub> monolayer are listed for comparison.

System	MnO <sub>2</sub> ( $Pmmn$ )	MnO <sub>2</sub> ( $P\bar{3}m1$ )	1L $o$ - MnO <sub>2</sub>	1L $r$ - MnO <sub>2</sub>	Graphene	1L SrTiO <sub>3</sub>
$E_f$	-1.64	-1.80	-1.58	-1.73	/	/
$E_{exf}$	/	/	53	56	10~20	119

Table S2. The elastic constant (N/m<sup>2</sup>) and the energy difference between FM and AFM  $E_{AFM_i-FM}$  (eV) of MnO<sub>2</sub> monolayer.

$C_{11}$	$C_{12}$	$C_{22}$	$C_{66}$	$E_{AFM1-FM}$	$E_{AFM2-FM}$	$E_{AFM3-FM}$
296	4	125	11	0.542	0.491	0.242

Table S3. The magneto-crystalline anisotropy energy ( $\mu$ eV/Mn) of MnO<sub>2</sub> monolayer along (001), (010) and (100) directions under different biaxial strains.

Strain	$E_{001}$	$E_{010}$	$E_{100}$
-4%	0	208.3	76.3
-3%	0	222.0	76.3
-2%	0	234.5	75.2
-1%	0	244.8	72.1
0	0	252.0	67.0
1%	0	256.1	60.1
2%	0	256.9	51.8
3%	0	254.2	42.7
4%	0	248.6	33.4

Table S4. The magneto-crystalline anisotropy energy ( $\mu$ eV/Mn) of MnS<sub>2</sub> monolayer along (001), (010) and (100) directions under different biaxial strains.

Strain	$E_{010}$	$E_{100}$	$E_{001}$
-4%	0	133.6	187.7
-3%	0	135.6	196.4
-2%	0	138.1	198.7
-1%	0	142.1	197.2
0	0	148.3	195.0
1%	0	158.2	192.6
2%	0	171.9	188.3
3%	0	188.5	180.1
4%	0	205.9	167.2

Table S5. The charge transfer value (e) of MnO<sub>2</sub> and MnS<sub>2</sub> monolayers.

System	MnO <sub>2</sub>	MnS <sub>2</sub>
Mn	-1.84	-1.21
O <sub>1,2</sub>	0.80	0.70
O <sub>3,4</sub>	1.04	0.52

### Appendix. Monte Carlo simulation details:

To get the magnetic ground state and the magnetic exchange constants, we constructed four 2×2×1 supercells, each containing 4 magnetic atoms (Figure S4). The energy difference  $E_{AFM_i-FM}$  ( $i=1, 2$  and  $3$ ) values are displayed in Table S1. Exchange coupling parameters  $J_1$ ,  $J_2$  and  $J_3$  are obtained by solving the linear equations of the energy differences between the FM and three AFM configurations as follows.

$$\frac{E_{FM}}{8} = -E_0 - (4J_1 + 2J_2 + 2J_3)|S|^2 - A|S|^2$$

$$\frac{E_{AFM1}}{8} = -E_0 - (2J_2 - 2J_3)|S|^2 - A|S|^2$$

$$\frac{E_{AFM2}}{8} = -E_0 - (2J_2 + 2J_3)|S|^2 - A|S|^2$$

$$\frac{E_{AFM3}}{8} = -E_0 - (4J_1 - 2J_2 + 2J_3)|S|^2 - A|S|^2$$

The exchange coupling parameters can be calculated as follows:

$$J_1 = \frac{E_{AFM2} - E_{FM}}{32|S|^2}$$

$$J_2 = \frac{E_{AFM3} - E_{FM}}{32|S|^2}$$

$$J_3 = \frac{E_{AFM1} - E_{AFM2}}{32|S|^2}$$

The uniaxial anisotropy energy parameter  $A$  obtained by using the magnetic anisotropy energies is:

$$A = \frac{E_{max}(axis) - E_{easy}(axis)}{|S|^2}$$

For MnO<sub>2</sub> monolayer:

$$J_1 = \frac{E_{AFM2} - E_{FM}}{32|S|^2} = 0.007 \text{ eV}$$

$$J_2 = \frac{E_{AFM3} - E_{FM}}{32|S|^2} = 0.0034 \text{ eV}$$

$$J_3 = \frac{E_{AFM1} - E_{AFM2}}{32|S|^2} = 0.00071 \text{ eV}$$

$$A = \frac{E_{max}(axis) - E_{easy}(axis)}{|S|^2} = 90 \text{ } \mu\text{eV/Mn}$$

For MnS<sub>2</sub> monolayer:

$$J_1 = \frac{E_{AFM2} - E_{FM}}{32|S|^2} = 0.016 \text{ eV}$$

$$J_2 = \frac{E_{AFM3} - E_{FM}}{32|S|^2} = 0.012 \text{ eV}$$

$$J_3 = \frac{E_{AFM1} - E_{AFM2}}{32|S|^2} = 0.011 \text{ eV}$$

$$A = \frac{E_{max}(axis) - E_{easy}(axis)}{|S|^2} = 86 \text{ } \mu\text{eV/Mn}$$

## Computational Methods

The hybrid functional HSE06 combines a portion of nonlocal Fock exchange with the generalized gradient approximation (GGA) exchange-correlation functional. The HSE06 calculations were performed using a plane-wave basis set with a cutoff energy of 600 eV. The Brillouin zone was sampled using 8×6×1 k-point mesh. Convergence criteria for the electronic self-consistency loop and total energy calculations were set to 10<sup>-6</sup> eV.

## Monte Carlo simulations code

### mc.m

```
%%  
%%      _ _ _ _ _  
%%      | v | _ _ / _ _ | v | _ _ / _ _ |  
%%      ||M|/ _ `|| ||M|/ _ \||  
%%      || || (| | _ _ | | | (| | _ _ |  
%%      | | | \ _ , \ _ _ | | | \ _ / \ _ _ |  
%%      V6.0_2020/11/11  
%% +------(y-▽)y-----+  
%% |  
%% |          Guo-Dong Zhao, Wei Ren          |  
%% |          ICQMS of Shanghai University      |  
%% |  
%% |          Contact: renwei@shu.edu.cn        |  
%% +-----+  
  
%% 1. Initial Configuration by hand  
%global model Lat J1 J2 J3 A Sp L estep mstep Ts para kb  
Name = 'MnO2_H' ; % Report Folder Name  
model = 3 ; % 1: ising; 2: XY; 3: heisenberg; 4: heisenberg+anisotropy_exchange  
Lat = 'c' ; % Lattice, 'h' for hex, 't' for tri, 'c' for cub  
J1 = 7.00e-3 ; % Fir-Nearest Strength of interaction (eV)  
J2 = 3.40e-3 ; % Sec-Nearest Strength of interaction (eV)  
J3 = 7.00e-4 ; % Thi-Nearest Strength of interaction (eV)  
A = 0.90e-4 ; % Single ion anisotropy (eV), only for heisenberg  
Sp = 3/2 ; % Sum of Spin  
L = 40 ; % Size of the grid  
epass = 4e4 ; % eqs=esteps for equilibrium  
mpass = 4e4 ; % mcs=msteps for statistic  
Ts = 500:-20:0 ; % [80:-2:2] ; % linspace(100,0,10) ; % Always in a descending order!  
para = 6 ; % Parallel workers (cores), depending on your CPU, spare one for urself.(revise  
code)  
kb = 8.617333262145e-5 ; % Boltzmann constant in eV/kelvin %1.380649e-23 in Joules/kelvin  
% (3*S^2*J1/Kb) / (4*I^2/1) = Tc / 2.269 , this is good for estimating Tc. '3' is for hexagonal  
% i.e. (3*((2/2)^2)*1.966e-3)*2.269/(4*8.617333262145e-5)  
estep = epass*L^2 ; % eqs=esteps for equilibrium  
mstep = mpass*L^2 ; % mcs=msteps for statistic  
%need add a time estimation functional  
  
%% 2. Declare the physical quantities  
Ms = [] ; % Averaged magnetisation per site per MC step  
Cs = [] ; % Specific heat, but careful that it's calculated in S not M  
Mx = [] ; % Magnetic Susceptibility, but careful that it's calculated in S not M
```

```

Es = [] ; % Energy per site

%% 3. Equilibrium and Monte Carlo Loops
%par = parpool('local',para); % Accelerate with parpool & parfor, 3 cores
%if you want to make it parallel, change the corresponding .m file, e.g. ising.m.

if model == 1
[Ms, Cs, Mx, Es, time1] = ising(model,Lat,J1,J2,J3,D,Sp,L,estep,mstep,Ts,para,kb);
elseif model == 2
[Ms, Cs, Mx, Es, time1] = xy(model,Lat,J1,J2,J3,D,Sp,L,estep,mstep,Ts,para,kb);
elseif model == 3
[Ms, Cs, Mx, Es, time1] = heisenberg(model,Lat,J1,J2,J3,D,Sp,L,estep,mstep,Ts,para,kb);
elseif model == 4
[Ms, Cs, Mx, Es, time1] = plusl(model,Lat,J1,J2,J3,D,A,Sp,L,estep,mstep,Ts,para,kb);
end

%delete(par) ; %delete(gcf); % Shutdown the parpool
%Ts=rot90(rot90(Ts));

%% 4. Show
%where is the Tc and how much time (Sec) taken
[a,b] = max(Cs) ;
c = sprintf('Transition T (K): %.2f \nTime used (min): %.0f',Ts(b),time1/60);
disp(c)

%% 5. Figure Generation
%Name=num2str(Name);
mkdir(Name);
plotmc(Ts, Ms, Cs, Mx, Es, Sp);
%print(fig,'result','-dtiff');
set(gcf,'PaperPositionMode','auto')
print(['./',Name,'/',Name,'.tif'],'-dtiff','-r0')

f=[Ts', Ms', Cs', Es', Mx'];
%save results.dat f -ascii
fid = fopen(['./',Name,'/',Name,'.dat'],'w');
fprintf(fid,'%12s %12s %12s %12s %12s \n','T','M','Cv','E','Xm');
fprintf(fid,'%12.8e %12.8e %12.8e %12.8e %12.8e \n',f);
fclose(fid);

save(['./',Name,'/',Name,'.mat'])
%clear

```