Supplementary Information for 'Momentum-dependent band spin splitting in semiconducting MnO_2: A density functional calculation'

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We have performed DFT+U calculations of the α-, β-, δ-, and λ-MnO_2 crystals in order to confirm the total energy difference between FM and AFM configurations. The structures of the α-, β-, δ-, and λ-MnO_2 crystals with other AFM configurations are shown in Figs. S1–S4, respectively. Like the figures of the MnO_2 structures in the main text of our paper, magenta-, green-, and red-coloured balls denote up-spin Mn, down-spin Mn, and O atoms, respectively. We compared total energies of the MnO_2 crystals (see Table S1). From these results, other AFM systems are energetically less stable than the most stable one.

Table S1: Total energies of the MnO_2 crystals with both FM and AFM configurations per MnO_2 unit in the case of $U_{\rm eff}$ = 4.00 eV. The unit of the energy is eV. The lowest total energies are set to be 0.000 eV.

Spin configuration	α-MnO_2	β-MnO_2	δ-MnO_2	λ-MnO_2
FM	0.006	0.006	0.000	0.000
AFM	0.000	0.000	0.000	0.017
AFM2	0.014	0.026	0.062	0.037
AFM3	0.003		0.062	
AFM4	0.007		0.062	
AFM5	0.018		0.062	

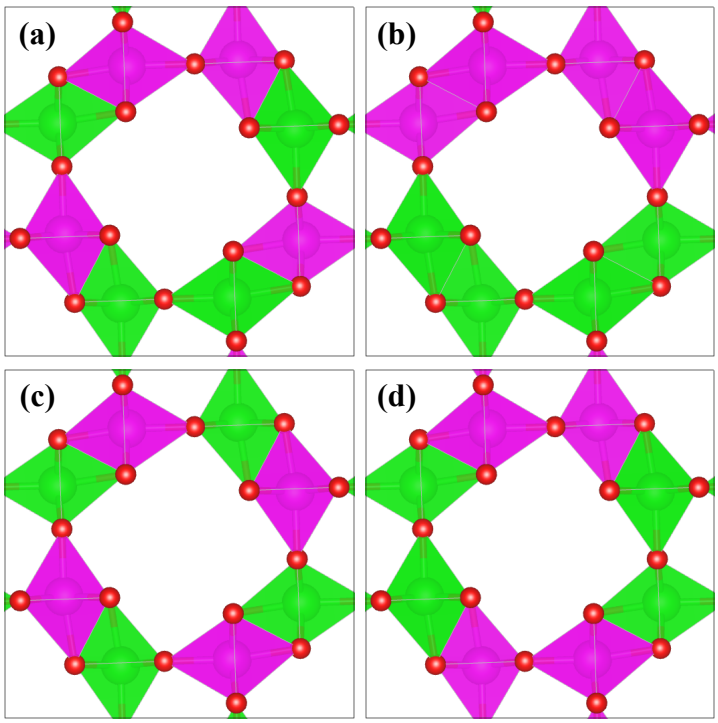

Fig. S1: Structures of α-MnO_2 with AFM configurations (a) AFM2, (b) AFM3, (c) AFM4, and (d) AFM5. These systems except AFM2 are obtained with the tetragonal supercells. All systems have FM coupling along c axis.

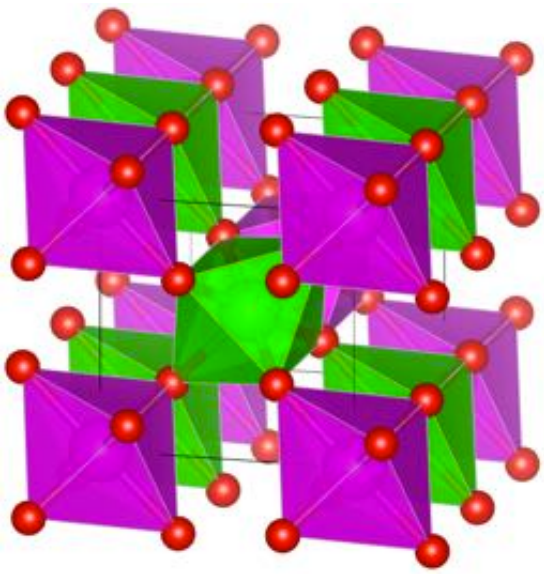

Fig. S2: Structure of β-MnO_2 with AFM configuration labeled AFM2. The system has the tetragonal supercell.

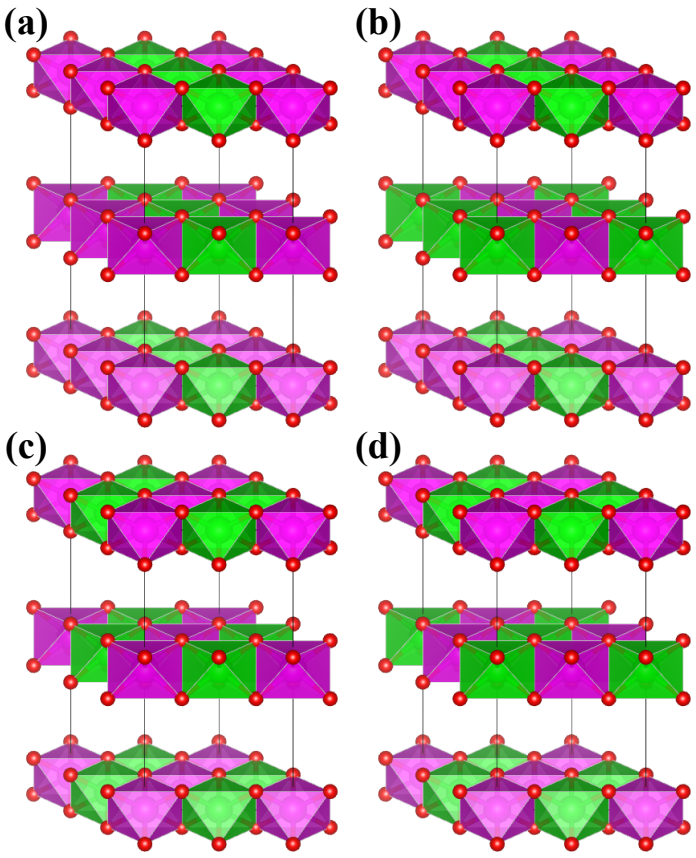

Fig. S3: Structures of δ-MnO_2 with AFM configurations (a) AFM2, (b) AFM3, (c) AFM4, and (d) AFM5. All systems are obtained with the hexagonal supercells.

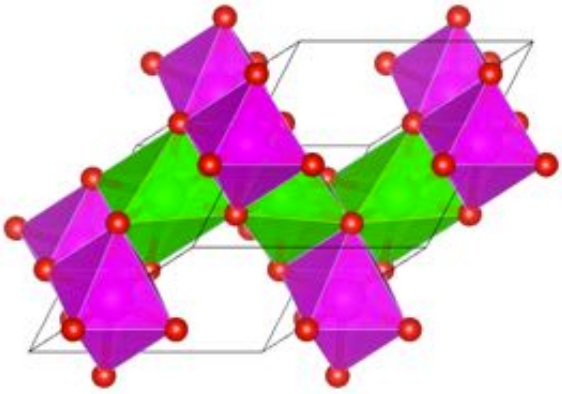

Fig. S4: Structure of λ-MnO_2 with AFM configuration labeled AFM2. The system has the original FCC lattice.

In order to reveal the origin of the magnetic energy difference between the different spin configurations, we have estimated the penalty energies, E_{P}^{ρ} and E_{R}^{ρ}, of the MnO_2 crystals with a point sharing being FM coupling and a ridge sharing being AFM coupling. Here, we define the point-sharing (ridge-sharing) penalty energy E_{P}^{ρ} (E_{R}^{ρ}) as the total energy enhancement in the FM (AFM) magnetic coupling from the more stable AFM (FM) magnetic coupling between adjacent point-sharing (ridge-sharing) octahedra in the ρ-MnO_2 (ρ = α, β, δ, and λ). Then, the total penalty energy $\Delta E_{\mathrm{penal}}^{\rho,\sigma_1,\sigma_2}$, which is defined as the difference between the total energy $E_{\mathrm{tot}}^{\rho,\sigma_1}$ of the less stable σ_1 spin configuration and the total energy $E_{\mathrm{tot}}^{\rho,\sigma_2}$ of the most stable σ_2 spin configuration of the ρ-MnO_2, can be expressed as

$$\Delta E_{\mathrm{penal}}^{\rho,\sigma_1,\sigma_2} = nE_{\mathrm{P}}^{\rho} + mE_{\mathrm{R}}^{\rho} = E_{\mathrm{tot}}^{\rho,\sigma_1} - E_{\mathrm{tot}}^{\rho,\sigma_2}, \tag{S1}$$

where n and m are the numbers of penalty pairs of the FM-coupling point sharings and the AFM-coupling ridge sharings, respectively. The numbers n and m are listed in Table S2. In the case of α-MnO_2, the following equations are established:

$$\Delta E_{\mathrm{penal}}^{\alpha,\mathrm{FM,AFM}} = 2E_{\mathrm{P}}^{\alpha} = E_{\mathrm{tot}}^{\alpha,\mathrm{FM}} - E_{\mathrm{tot}}^{\alpha,\mathrm{AFM}} = 0.006, \tag{S2a}$$

$$\Delta E_{\mathrm{penal}}^{\alpha,\mathrm{AFM2,AFM}} = E_{\mathrm{P}}^{\alpha} + 2E_{\mathrm{R}}^{\alpha} = E_{\mathrm{tot}}^{\alpha,\mathrm{AFM2}} - E_{\mathrm{tot}}^{\alpha,\mathrm{AFM}} = 0.014, \tag{S2b}$$

$$\Delta E_{\mathrm{penal}}^{\alpha,\mathrm{AFM3,AFM}} = E_{\mathrm{P}}^{\alpha} = E_{\mathrm{tot}}^{\alpha,\mathrm{AFM3}} - E_{\mathrm{tot}}^{\alpha,\mathrm{AFM}} = 0.003, \tag{S2c}$$

$$\Delta E_{\mathrm{penal}}^{\alpha,\mathrm{AFM4,AFM}} = 2E_{\mathrm{R}}^{\alpha} = E_{\mathrm{tot}}^{\alpha,\mathrm{AFM4}} - E_{\mathrm{tot}}^{\alpha,\mathrm{AFM}} = 0.007, \tag{S2d}$$

$$\Delta E_{\mathrm{penal}}^{\alpha,\mathrm{AFM5,AFM}} = 2E_{\mathrm{P}}^{\alpha} + 2E_{\mathrm{R}}^{\alpha} = E_{\mathrm{tot}}^{\alpha,\mathrm{AFM5}} - E_{\mathrm{tot}}^{\alpha,\mathrm{AFM}} = 0.018. \tag{S2e}$$

From Eqs. (S2a) and (S2c), we obtain E_{P}^{α} = 0.003 eV. And, from Eq. (S2d), E_{R}^{α} = 0.0035 $\approx$ 0.004 eV. In addition, from Eqs. (S2b) and (S2e), we obtain E_{P}^{α} = 0.004 eV and E_{R}^{α} = 0.005 eV. Therefore, we estimate E_{P}^{α} = 0.003–0.004 eV and E_{R}^{α} = 0.004–0.005 eV. In the case of β-MnO_2, the following equations are established:

$$\Delta E_{\mathrm{penal}}^{\beta,\mathrm{FM,AFM}} = 2E_{\mathrm{P}}^{\beta} = E_{\mathrm{tot}}^{\beta,\mathrm{FM}} - E_{\mathrm{tot}}^{\beta,\mathrm{AFM}} = 0.006, \tag{S3a}$$

$$\Delta E_{\mathrm{penal}}^{\beta,\mathrm{AFM2,AFM}} = E_{\mathrm{P}}^{\beta} + E_{\mathrm{R}}^{\beta} = E_{\mathrm{tot}}^{\beta,\mathrm{AFM2}} - E_{\mathrm{tot}}^{\beta,\mathrm{AFM}} = 0.026. \tag{S3b}$$

From the two equations, we estimate E_{P}^{β} = 0.003 eV and E_{R}^{β} = 0.023 eV. In the case of δ-MnO_2,

Table S2: Numbers of n and m for each MnO_2 crystal per MnO_2 unit.

	α-MnO_2		β-MnO_2		δ-MnO_2		λ-MnO_2	
Spin configuration	n	m	n	m	n	m	n	m
FM	2	0	2	0		0		0
AFM	0	0	0	0		0		3/4
AFM2	1	2	1	1		2		2
AFM3	1	0				2		
AFM4	0	2				2		
AFM5	2	2				2		

the following equations are established:

$$\Delta E_{\mathrm{penal}}^{\delta,\mathrm{AFM,FM}} = 0 = E_{\mathrm{tot}}^{\delta,\mathrm{AFM}} - E_{\mathrm{tot}}^{\delta,\mathrm{FM}} = 0.000, \tag{S4a}$$

$$\Delta E_{\mathrm{penal}}^{\delta,\mathrm{AFM2,FM}} = 2E_{\mathrm{R}}^{\delta} = E_{\mathrm{tot}}^{\delta,\mathrm{AFM2}} - E_{\mathrm{tot}}^{\delta,\mathrm{FM}} = 0.062, \tag{S4b}$$

$$\Delta E_{\mathrm{penal}}^{\delta,\mathrm{AFM3,FM}} = 2E_{\mathrm{R}}^{\delta} = E_{\mathrm{tot}}^{\delta,\mathrm{AFM3}} - E_{\mathrm{tot}}^{\delta,\mathrm{FM}} = 0.062, \tag{S4c}$$

$$\Delta E_{\mathrm{penal}}^{\delta,\mathrm{AFM4,FM}} = 2E_{\mathrm{R}}^{\delta} = E_{\mathrm{tot}}^{\delta,\mathrm{AFM4}} - E_{\mathrm{tot}}^{\delta,\mathrm{FM}} = 0.062, \tag{S4d}$$

$$\Delta E_{\mathrm{penal}}^{\delta,\mathrm{AFM5,FM}} = 2E_{\mathrm{R}}^{\delta} = E_{\mathrm{tot}}^{\delta,\mathrm{AFM5}} - E_{\mathrm{tot}}^{\delta,\mathrm{FM}} = 0.062. \tag{S4e}$$

Eqs. (S4b–S4e) are equivalent to each other because the energy difference and the numbers n and m are the same. Therefore, we estimate $E_{\mathrm{R}}^{\delta} = 0.031$ eV. In the case of λ-MnO_2, the following equations are established as follows:

$$\Delta E_{\mathrm{penal}}^{\lambda,\mathrm{AFM,FM}} = \frac{3}{4}E_{\mathrm{R}}^{\lambda} = E_{\mathrm{tot}}^{\lambda,\mathrm{AFM}} - E_{\mathrm{tot}}^{\lambda,\mathrm{FM}} = 0.017, \tag{S5a}$$

$$\Delta E_{\mathrm{penal}}^{\lambda,\mathrm{AFM2,FM}} = 2E_{\mathrm{R}}^{\lambda} = E_{\mathrm{tot}}^{\lambda,\mathrm{AFM2}} - E_{\mathrm{tot}}^{\lambda,\mathrm{FM}} = 0.037. \tag{S5b}$$

From the two equations, we estimate $E_{\mathrm{R}}^{\lambda} = 0.013$–$0.019$ eV. Summarized results of E_{P}^{ρ} and E_{R}^{ρ} are shown in Table S3.

Table S3: Penalty energies for each MnO_2 crystal in the case of U_{eff} = 4.00 eV. The unit of the energy is eV.

Phase	E_{P}^{ρ}	E_{R}^{ρ}
α-MnO_2	0.003–0.004	0.004–0.005
β-MnO_2	0.003	0.023
δ-MnO_2		0.031
λ-MnO_2		0.013–0.019

In addition, we have confirmed spin-split and spin-degenerate band dispersions of the MnO_2 crystals. Figs. S5–S7 show the band structures of AFM α-MnO_2 with U_{eff} = 0.00, 3.00, and 5.00 eV, respectively. They can be compared with Fig. 3(c) (in the case of U_{eff} = 4.00 eV) in the main text of our paper. In their band structures, all band dispersions along the $\mathbf{\Gamma - Z \,|\, Z_1 - M}$ lines are spin degenerate, whereas, the other band dispersions are spin split. We found that the description of the spin splitting and degeneracy of the MnO_2 crystals does not depend on the strength of the Hubbard U correction.

The band structure of FM δ-MnO_2 is calculated with lattice constants a and c being experimental values (See Fig. S8). Compared with the band structure of FM δ-MnO_2 shown in Fig. 7(c), it is evident that the characteristic of the spin-dependent band dispersions remains unchanged qualitatively regardless of the lattice constants.

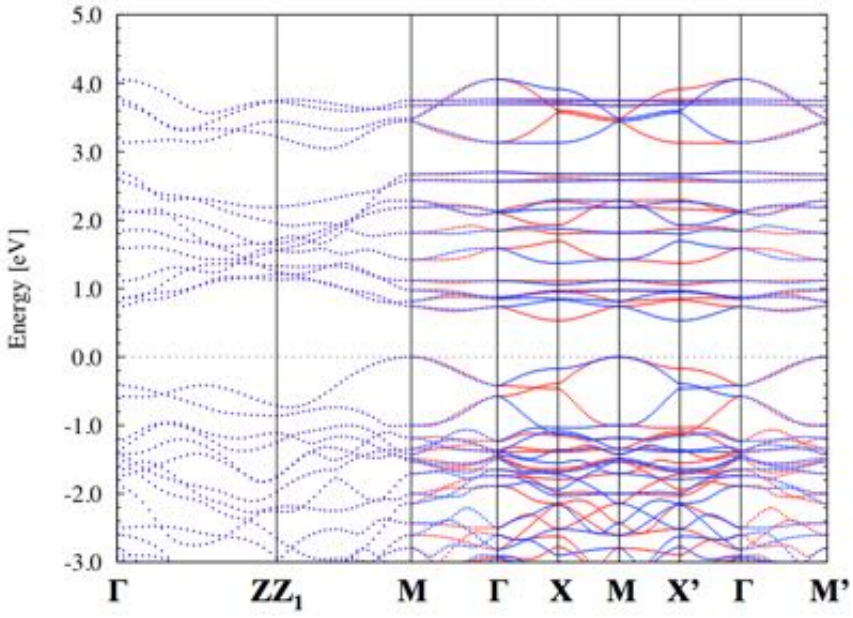

Fig. S5: Band structure of AFM α-MnO_2 along the **Γ – Z | Z$_1$ – M – Γ – X – M–X'–Γ–M'** lines (U_{eff} = 0.00 eV)

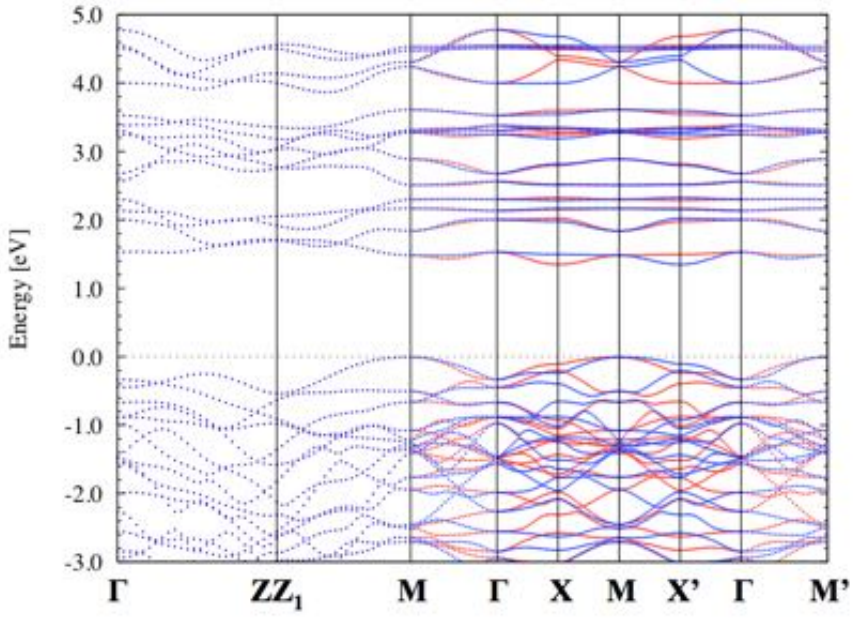

Fig. S6: Band structure of AFM α-MnO_2 along the **Γ – Z | Z$_1$ – M – Γ – X – M–X'–Γ–M'** lines (U_{eff} = 3.00 eV)

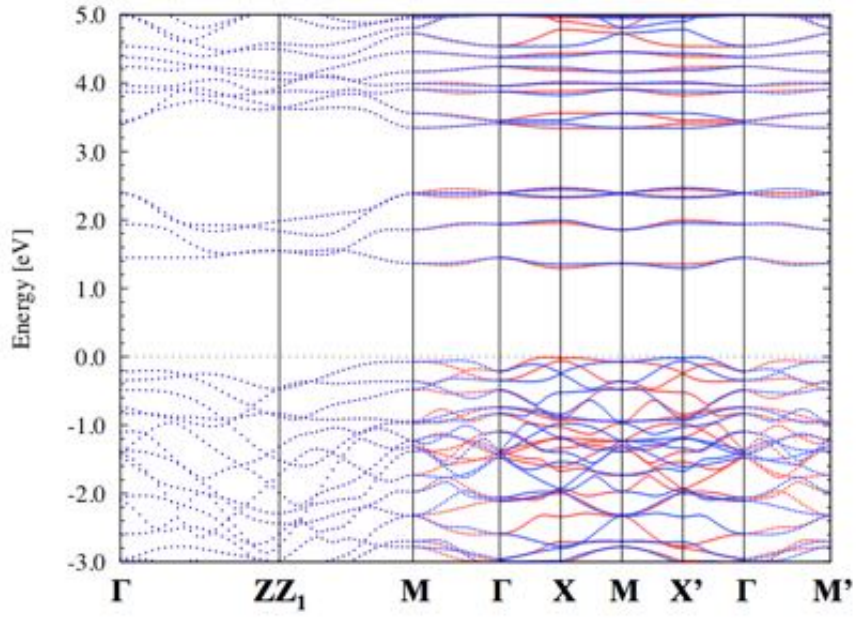

Fig. S7: Band structure of AFM α-MnO_2 along the **Γ – Z | Z$_1$ – M – Γ – X – M–X'–Γ–M'** lines (U_{eff} = 5.00 eV)

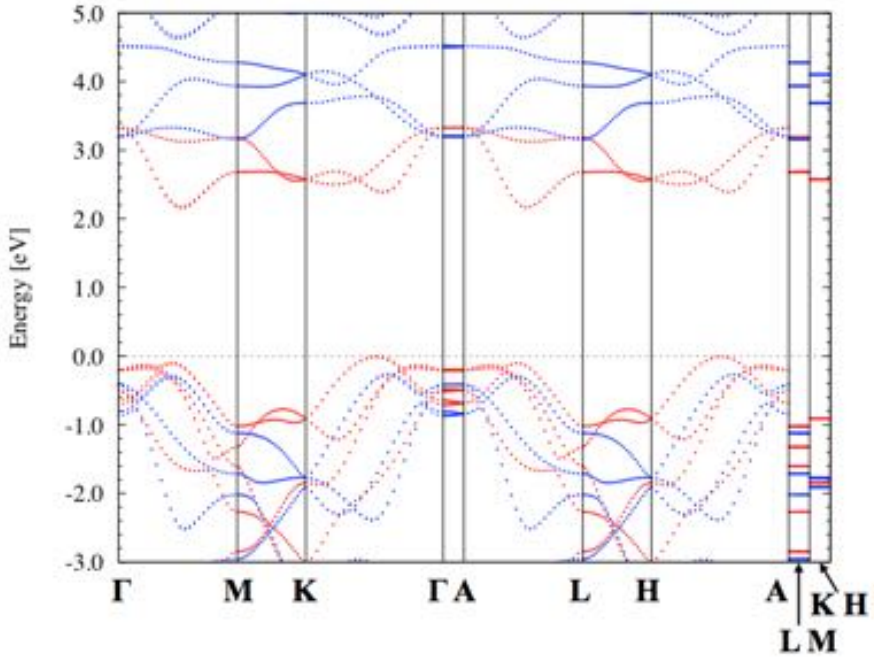

Fig. S8: Band structure of FM δ-MnO_2 along the **Γ – M – K – Γ – A – L – H – A | L – M | K – H** lines (U_{eff} = 4.00 eV, the lattice parameters are fixed to the experimental values from Ref. 51 in our paper)