

## Electronic Supplementary Information

### **Two-dimensional ferromagnetic semiconductors of monolayer $\text{BiXO}_3$ ( $\text{X} = \text{Ru}, \text{Os}$ ) with direct band gaps, large magnetic anisotropy and high Curie temperatures**

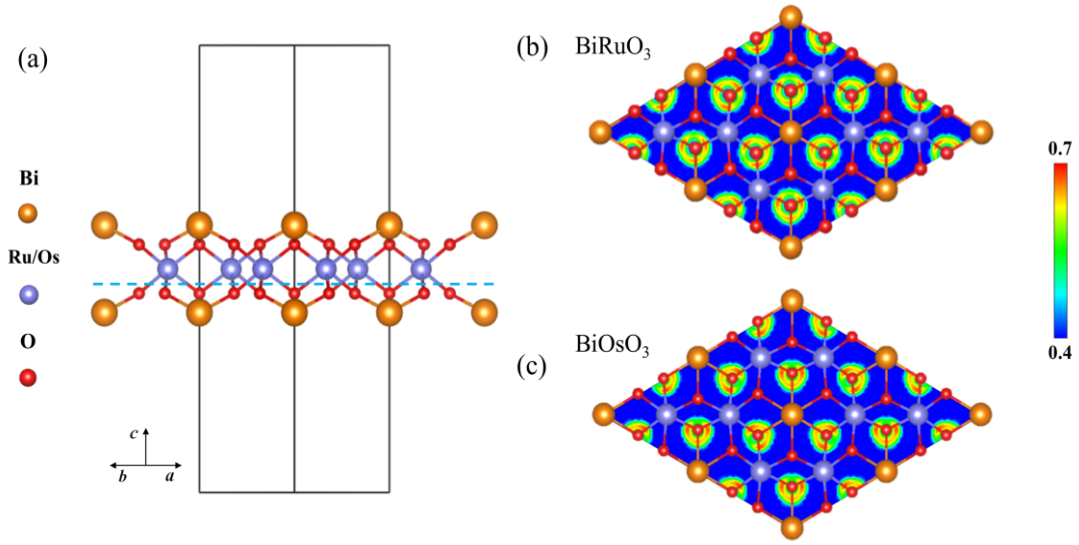
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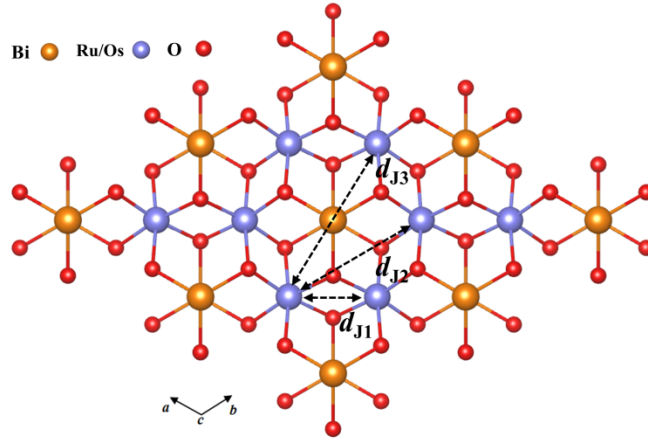
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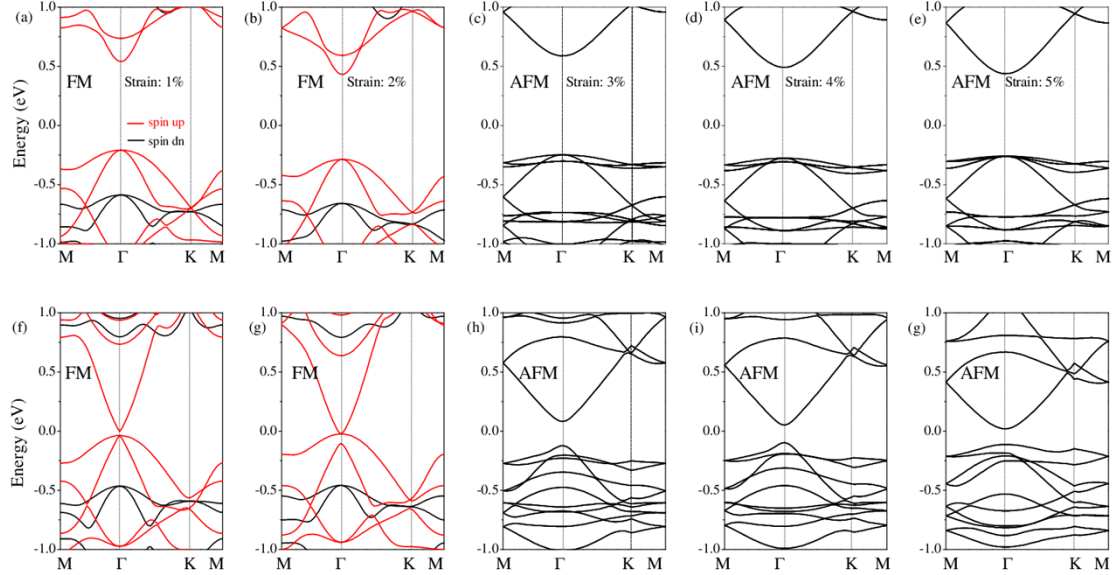
**Figure S1.** Electron localization function (ELF) of BiRuO<sub>3</sub> and BiOsO<sub>3</sub> monolayers. (a) The side view of the crystal structure. (b-c) The ELF of BiRuO<sub>3</sub> and BiOsO<sub>3</sub> on (001) plane. The position of the cut plane for ELF is indicated by the blue dashed line in (a).



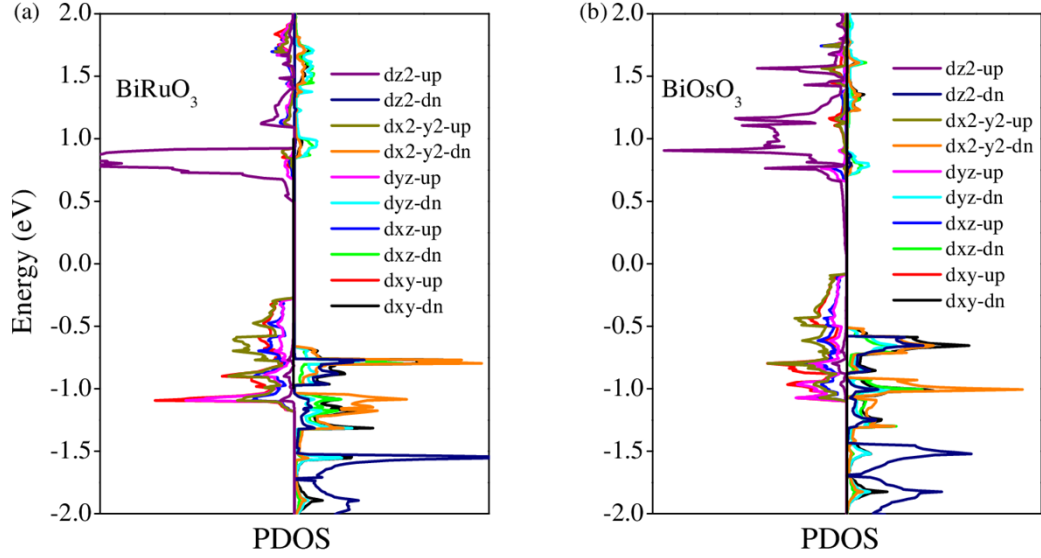
**Figure S2.** Schematically illustration of the X...X (X = Ru, Os) distances for the exchange interactions  $J_1$  ( $d_{J1}$ ),  $J_2$  ( $d_{J2}$ ), and  $J_3$  ( $d_{J3}$ ) in 2D BiXO<sub>3</sub>.

Normally, the next-nearest-neighbor interaction  $J_2$  should be larger than that of the second-next-nearest-neighbor interaction  $J_3$ . But some exceptions show  $J_2$  can be smaller than  $J_3$ . One typical example is the Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub> monolayer, whose  $J_2$  is 0.08 meV, while its  $J_3$  displays a larger absolute value of 0.16 meV<sup>1</sup>. Importantly, our predicted BiRuO<sub>3</sub> monolayer shares the same structure with that of Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>. In fact, the exchange interaction is sensitive to the atom distances<sup>2</sup>. In our predicted systems, we believe the non-local magnetic exchange interactions, i.e. the superexchange interaction can be an important factor to affect the energy of magnetic exchange

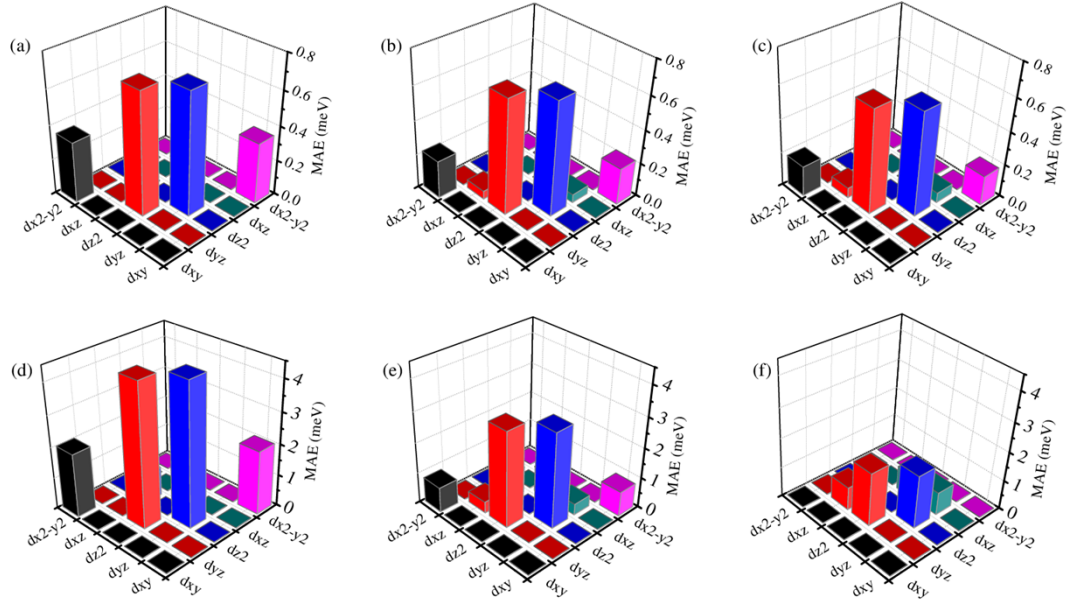
interactions between ions at different distances (see Figure S2). We notice that for BiOsO<sub>3</sub>, the Os···Os distance for J<sub>2</sub> is  $d_{J_2}^{Os} = 5.39 \text{ \AA}$  and that for J<sub>3</sub> is  $d_{J_3}^{Os} = 6.23 \text{ \AA}$  (Table S1). For BiRuO<sub>3</sub>, the Ru···Ru distance for J<sub>2</sub> is  $d_{J_2}^{Ru} = 5.29 \text{ \AA}$  and that for J<sub>3</sub> is  $d_{J_3}^{Ru} = 6.11 \text{ \AA}$ . The difference  $D_{J_2}$  of J<sub>2</sub> between the two systems is  $d_{J_2}^{Os} - d_{J_2}^{Ru} = 0.10 \text{ \AA}$ . Similarly, we can get the difference for J<sub>3</sub> is  $D_{J_3} = 0.12 \text{ \AA}$ . As  $D_{J_3}$  is larger than  $D_{J_2}$ , it means the J<sub>3</sub> interaction in BiRuO<sub>3</sub> monolayer could be significantly enhanced due to the relatively short Ru···Ru distance (compared with Os···Os distance). This can be one reason why the J<sub>3</sub> is greater than J<sub>2</sub> in BiRuO<sub>3</sub>.



**Figure S3.** The band structures of monolayers (a-e) BiRuO<sub>3</sub> and (f-g) BiOsO<sub>3</sub> under tensile strain at PBE+U level. The Fermi level has been shifted to zero.



**Figure S4.** The calculated  $d$  orbital projected partial density of states (PDOS) near the Fermi level of Ru and Os atoms for monolayer (a) BiRuO<sub>3</sub> and (b) BiOsO<sub>3</sub>. The Fermi level has been shifted to zero in each panel.



**Figure S5.** The  $d$  orbital-resolved MAE of Ru and Os atoms for (a-c) BiRuO<sub>3</sub> and (d-f) BiOsO<sub>3</sub> monolayers under strains of (a)/(d) -3%, (b)/(e) 0%, and (c)/(f) +2%.

### The origin of large MAE

According to the second-order perturbation theory proposed by Wang *et al.*<sup>3</sup>, the MAE consists of two items, where the contributions of the same spin channel with upward orientation (uu) and downward orientation (dd) can be expressed as

$$\text{MAE} = E_z - E_x = \xi^2 \sum_{o, u} \frac{|\langle o | L_z | u \rangle|^2 - |\langle o | L_x | u \rangle|^2}{E_o - E_u}$$

(1)

where  $\xi$  is the SOC constant, o (u) stand for the occupied (unoccupied) states, and the energy of occupied (unoccupied) states is represented by  $E_o$  ( $E_u$ ).  $L_z$  and  $L_x$  are the angular momentum operators. Likewise, the contributions of the coupling between opposite spin channel (ud) can be expressed as

$$\text{MAE} = \frac{E_z - E_x}{\xi^2} = \sum_{o,u} \frac{|\langle o | L_x | u \rangle|^2 - |\langle o | L_z | u \rangle|^2}{E_o - E_u} \quad (2)$$

Based on the equations above, the MAE is determined by matrix elements of the spin-orbital interaction between occupied and unoccupied states. The projected DOS of d orbitals of Ru/Os atoms in Fig. S4 shows that the the occupied and unoccupied spin-up d states of Ru/Os atoms are near the Fermi level. The d orbital-resolved MAE of Ru and Os atoms for strain-free and strained BiXO<sub>3</sub> monolayers are presented in Fig. S5. For the strain-free structures (Fig. S5b and e), the large MAE in BiXO<sub>3</sub> are mainly contributed by the matrix element differences between  $d_{xy}$  and  $d_{x^2-y^2}$  as well as  $d_{yz}$  and  $d_{z^2}$  orbitals, and both contributions are positive. Under compressive strain, the contributions to the MAE from the matrix element differences  $d_{xy}$  and  $d_{x^2-y^2}$  as well as  $d_{yz}$  and  $d_{z^2}$  orbitals are significantly increased. Consequently, the values of MAE for both structures increase as well. Under tensile strain, we can see the matrix element differences  $d_{xy}$  and  $d_{x^2-y^2}$  as well as  $d_{yz}$  and  $d_{z^2}$  decrease, leading to the reduced values of MAE under tensile strain. Therefore, the evolution of the spin-orbital matrix element differences between d orbitals of Ru and Os atoms is responsible for the change of MAE in monolayers BiRuO<sub>3</sub> and BiOsO<sub>3</sub> under strain effect.

**Table S1.** The X···X (X = Ru, Os) distances for J<sub>2</sub> and J<sub>3</sub> in the BiXO<sub>3</sub> monolayer, as well as the difference between atom distance  $D_{J_x} (D_{J_x} = d_{J_x}^{Os} - d_{J_x}^{Ru})$ .

Exchange interaction	Os···Os (Å)	Ru···Ru (Å)	$D_{J_x}$ (Å)
J <sub>2</sub>	$d_{J_2}^{Os} = 5.39$	$d_{J_2}^{Ru} = 5.29$	$D_{J_2} = 0.10$

$$J_3 \quad d_{J_3}^{Os} = 6.23 \quad d_{J_3}^{Ru} = 6.11 \quad D_{J_3} = 0.12$$

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1. C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia and X. Zhang, *Nature*, 2017, **546**, 265-269.
2. C. Autieri, G. Cuono, C. Noce, M. Rybak, K. M. Kotur, C. E. Agrapidis, K. Wohlfeld and M. Birowska, *J. Phys. Chem. C* 2022, **126**, 6791-6802.
3. D.-s. Wang, R. Wu and A. J. Freeman, *Phys. Rev. B*, 1993, **47**, 14932-14947.