Supplementary Information

Half-metallicity and spin-valley coupling in 5*d* transition metal substituted monolayer $MnPSe_3$

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Table SI Total energies (meV/unitcell) relative to the Néel-AFM configuration among Néel-AFM, zigzag-AFM, stripy-AFM and FM configurations for 2×2×1 5*d* TM-substituted $MnPSe_3$ supercells

	FM (meV)	Néel (meV)	Zigzag (meV)	Stripy (meV)	GS
Hf	33.18	0	-179.73	-109.32	FM
Ta	-64.64	0	73.15	71.28	Zigzag
W	-161.05	0	-37.25	3.72	Stripy
Re	-103.18	0	-44.23	-51.58	Néel
Os	-115.57	0	-44.6	-57.41	Néel
Ir	-90.17	0	-53.41	-22.13	Néel
Pt	-216.65	0	-35.82	-139.43	Néel
Au	-89.17	0	6.09	-0.07	Zigzag
Hg	-110.66	0	-38.1	-52.85	Néel

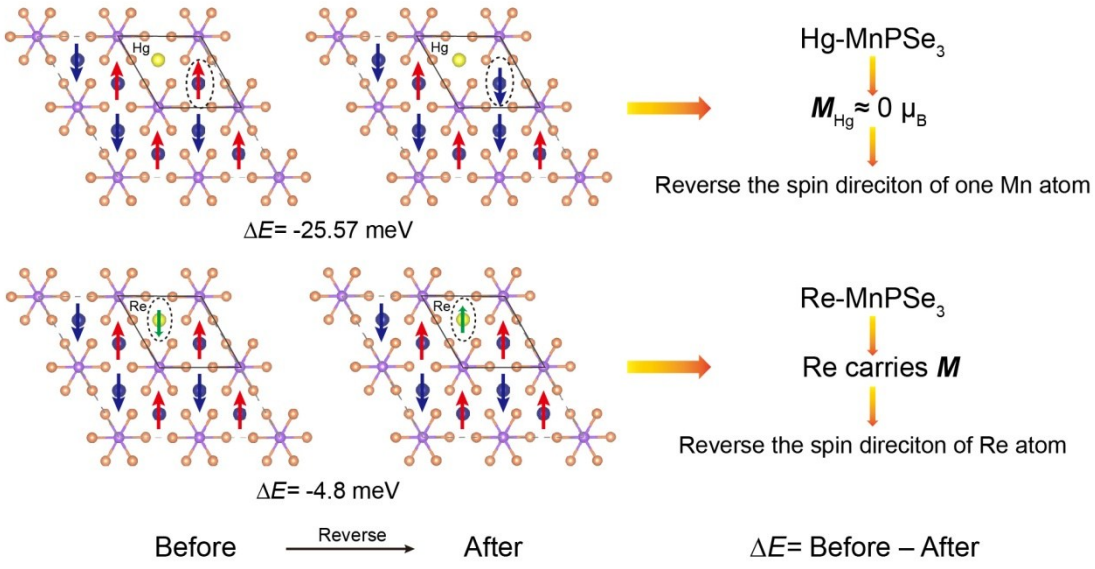
Table SI lists the total energies relative to the Néel-AFM configuration among FM, Néel-AFM zigzag-AFM and stripy-AFM configurations for 2×2×1 5*d* TM-substituted $MnPSe_3$ supercells. After comparing the total energies of four possible spin configurations we initially set, it is found that Ta- and Au-substituted $MnPSe_3$ tend to form zigzag-AFM configurations. The stripy-AFM order is energetically favorable for W-substituted systems. The magnetic structure with the lowest energy for Hf-$MnPSe_3$, however, is that Hf has the antiparallel spins with Mn atoms. The remaining five substituted systems (i.e., Re-, Os-, Ir-, Pt- and Hg-$MnPSe_3$) are stable in Néel-AFM order, retaining the intrinsic spin configuration of monolayer $MnPSe_3$.

In order to verify the rationality of spin configurations obtained in the 2×2×1 supercells. Re- and Hg-$MnPSe_3$ are selected as benchmarks to check the real GS. In the test I, owing to the non-magnetism of impurity Hg, we reverse the spin direction of one Mn atom for Hg-$MnPSe_3$ 2×2×1 supercell. By comparing the energy difference before and after reversal, the spin arrangement

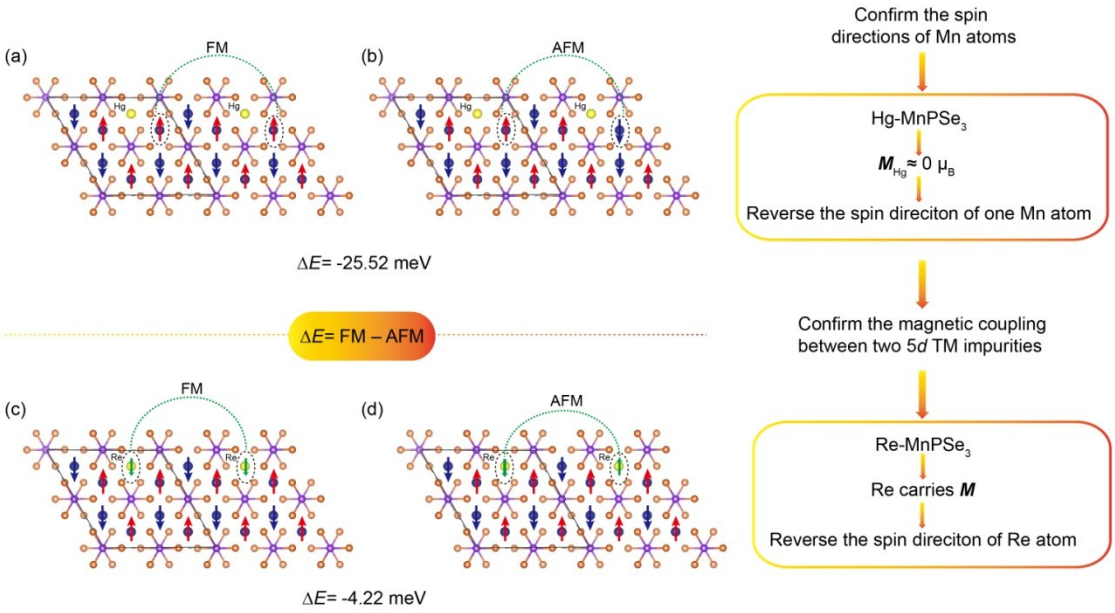
before reversal is energetically favorable, and thus the spin direction of Mn atom in the supercell is ensured. Then, for Re-substituted system, the impurity carries magnetic moment. The spin direction of Re is reversed for comparison. It can be found that the pristine structure is still more stable than the reversed. All the investigations performed here show the validity of magnetic arrangement in our 2×2×1 models.

Next, the same strategy is performed on 4×2×1 Hg- and Re-$MnPSe_3$ supercells. For Hg-$MnPSe_3$, we reverse the spin direction of one Mn atom nearest to Hg atom, and the total energies of FM and AFM coupling between two considered Mn atoms are calculated, respectively. The result shows FM coupling between two Mn atoms is more stable than the AFM coupling, with an energy difference of -25.52 meV. Meanwhile, we also perform the same calculations on another Mn atom nearest to Hg atom, where the result is the same including the energy difference. When the substitution is Re atom, the FM and AFM coupling between two Re atoms are also considered as shown in the Test II. It is noted that FM coupling has the lower energy than AFM coupling, and thus the magnetic interactions between two impurities are confirmed to be FM.

Test I For 2×2×1 Hg- and Re-substituted $MnPSe_3$ supercells



Test II For Hg- and Re-substituted 4×2×1 supercells



Through a series of tests, we demonstrate the FM coupling between unpaired Mn atoms in systems where the impurities are non-magnetic, while in systems where the impurities are magnetic, FM coupling between impurities is also confirmed. All the results obtained above indicate that a larger supercell will not offset the magnetism of unpaired Mn atom or the impurity. For the balance between the computational consumption and the effectiveness of illustration, no further tests on 4×4×1 supercell are performed.