Supplemental Material

Two-dimensional multiferroic metal with voltage-tunable magnetization and metallicity

Xu Duan,[1,2,*] Jiawei Huang,[3,2,*] Bin Xu,[4] and Shi Liu[2,5,6,†]

[1]*Fudan University, Shanghai 200433, China*

[2]*School of Science, Westlake University, Hangzhou, Zhejiang 310024, China*

[3]*Zhejiang University, Hangzhou, Zhejiang 310058, China*

[4]*Jiangsu Key Laboratory of Thin Films, School of Physical Science and Technology, Soochow University, Suzhou 215006, China*

[5]*Institute of Natural Sciences, Westlake Institute for Advanced Study, Hangzhou, Zhejiang 310024, China*

[6]*Key Laboratory for Quantum Materials of Zhejiang Province, Hangzhou Zhejiang 310024, China*

[*] These two authors contributed equally

[†] liushi@westlake.edu.cn

I. DEFECT FORMATION ENERGY

The formation energy (ΔE) of As_{Se} is defined as following:

$$\Delta E = E_{\text{tot}}[\text{As@In}_2\text{Se}_3] - E_{\text{tot}}[\text{In}_2\text{Se}_3] - \mu[\text{As}] + \mu[\text{Se}]$$

where E_{tot} and μ are the DFT total energy and chemical potential. $E_{\text{tot}}[\text{As@In}_2\text{Se}_3]$ is the total energy of a 45-atom $3 \times 3 \times 1$ supercell with one As replacing one Se atom, $E_{\text{tot}}[\text{In}_2\text{Se}_3]$ is the total energy of the same supercell without As dopant. The chemical potentials of As and Se are taken as the total energies per atom of bulk As and bulk Se. The formation energy of As_{Se} is 1.85 eV, comparable with the formation energies of typical dopants in bulk semiconductors and 2D materials (listed in Table S1)

TABLE S1. Formation energy (ΔE in eV) of typical dopants in 2D/bulk materials.

Defect	ΔE (eV)	Defect	ΔE (eV)
N_{Te} (CdTe)[a]	2.62	P_{Te} (CdTe)[a]	1.83
As_{Te} (CdTe)[a]	1.68	Sb_{Te} (CdTe)[a]	1.72
Bi_{Te} (CdTe)[a]	1.96	Ga_{Cd} (CdTe)[a]	1.23
B_C (Graphene)[b]	1.19	C_B (h-BN)[c]	1.66
C_N (h-BN)[c]	4.28	Mn_{Mo} (MoS_2)[c]	1.91
Co_{Mo} (MoS_2)[d]	4.63	Be_{Ga} (GaN) [e]	1.68
Zn_{Ga} (GaN)[e]	4.63	Mg_{Ga} (GaN)[e]	3.39

a. Phys. Rev. B 66, 15521 (2002); *b. J. Chem. Phys.* 148, 241716 (2018); *c. Phys. Rev. X* 4, 031044 (2014); *d. Sci. Rep.* 6, 24153 (2016); *e. Int. J. Energy Res.* 44, 6058 (2020);

II. THE STONER CRITERION

The Stoner parameter I related to the exchange interaction can be estimated from the exchange splitting and magnetic moment, and $N(E_F)$ is the non-spin-polarized DOS at the corresponding Fermi level [RSC Adv. 6, 54027 (2016)]. In the case of hole doping at a concentration of $p = 14.6 \times 10^{13}$ cm^{-2} as shown in Fig. 1d of the manuscript, the computed Stoner parameter I and $N(E_F)$ are 0.53 and 4.27 (see Fig. S1), respectively, clearly satisfying the Stoner criterion $IN(E_F) > 1$. This confirms that the itinerant ferromagnetism occurred at this doping concentration is indeed due to the Stoner-type instability. In the presence of SOC, the Stoner parameter I and $N(E_F)$ are 0.47 and 5.439, respectively, for monolayer α-In_2Se_3 at $p = 10.5 \times 10^{13}$ cm^{-2} under a biaxial strain of 2%. This again satisfies the Stoner criterion.

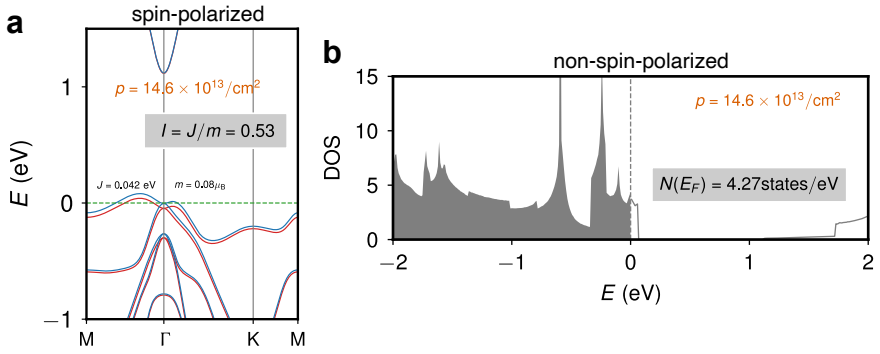

FIG. S1. (**a**) Spin-polarized band structure and (**b**) non-spin-polarized density of states at $p = 14.6 \times 10^{13}/\text{cm}^2$.

III. SWITCHING BARRIER FROM NEB CALCULATIONS

We computed the minimum energy pathways for the 180° out-of-plane polarization reversal process in both monolayer α-In_2Se_3 and asymmetrically As-doped α-In_2Se_3 using the nudged elastic band (NEB) method. Compared to the activation barrier of 0.78 eV for an undoped monolayer, the forward barrier for the As-doped monolayer 0.57 eV and the reverse barrier is 1.2 eV, indicating that the switching process remains feasible despite a high doping concentration. The link to the files is `https://github.com/sliutheorygroup/structure/tree/main/L28_Defect_induced_2D_magnetism`

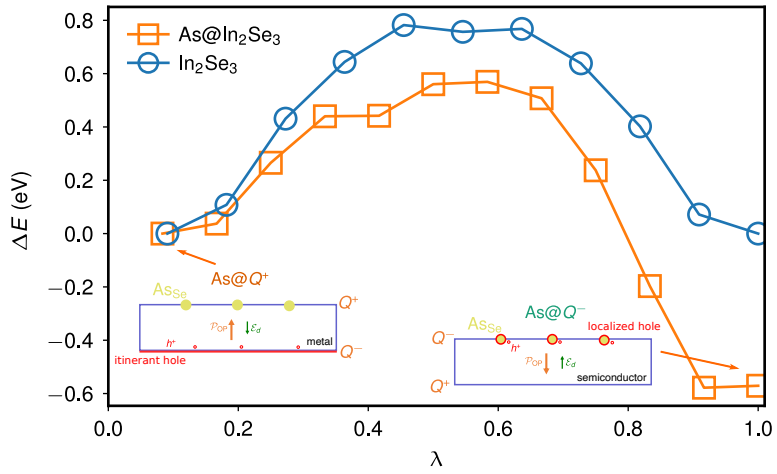

FIG. S2. 180° out-of-plane polarization reversal pathways for monolayer α-In_2Se_3 and asymmetrically As-doped α-In_2Se_3 obtained with NEB using a 2×2 supercell.

IV. METALLIC LOCAL MINIMUM

Figure 2 in the main text reports the electronic structure of asymmetrically doped monolayer obtained by replacing one surface Se atom with one As atom in a 2×2 hexagonal supercell, corresponding to a nominal carrier concentration of $p = 17.2 \times 10^{13}/\mathrm{cm}^2$ (assuming one As atom introduces one hole carrier). This is actually a rather high doping concentration. When the monolayer has a downward polarization $\mathcal{P}_{\mathrm{OP}}$, denoted as the As@$Q^-$ configuration, there is a metallic state as well with an energy slightly higher than the semiconducting state by 16 meV per a 2×2 supercell (Fig. S3a, left). We also carefully compared the structures of semiconducting and metallic states, identifying a subtle difference in the local structure around the As dopant (Fig. S3b). We found that the bond length of As-In in the semiconducting state (2.66 Å) is smaller than that in the metallic state (2.74 Å), whereas the size of the In_3 triangle around the As dopant in the semiconducting state is larger (In-In bond length of 4.25 Å) than that in the metallic state (In-In bond length of 4.04 Å). Moreover, we estimated the change in energy along the interpolated pathway connecting the two states and identified a small barrier. Because the semiconducting state has lower energy, we focus on this gapped state in the manuscript.

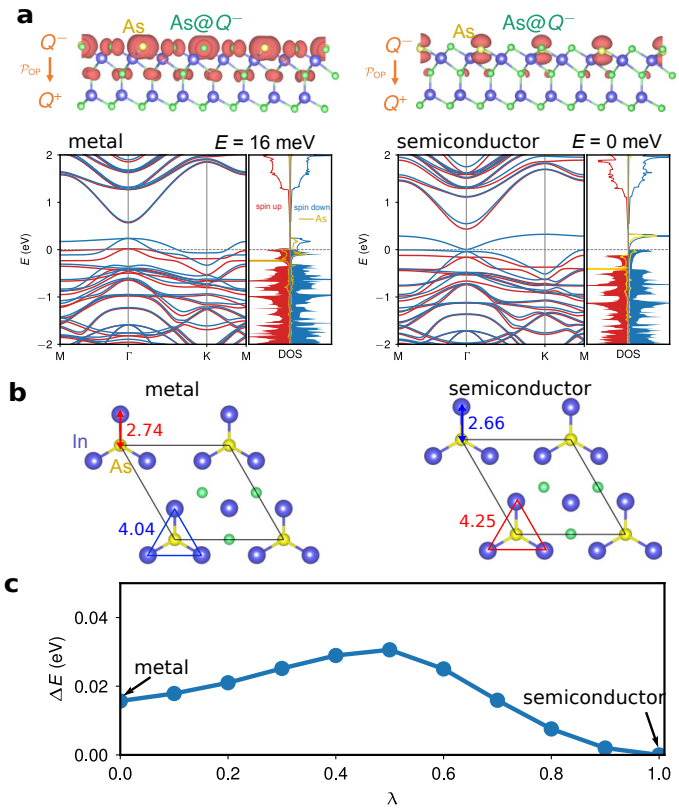

FIG. S3. (**a**) Metallic (left) and gapped states (right) for the As@Q^- configuration. The gapped semiconducting state is lower in energy by 16 meV per a 2×2 supercell. (**b**) Local atomic structure around As dopant. (**c**) Interpolated pathway connecting the metallic state and the gapped semiconducting state.