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Supporting Information

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Supplementary Information

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1. The effect of magnetic moments in Mn_3Sn to NRR

In heterogeneous catalysis, the interaction between the catalyst and the reactive species cannot be too strong or too weak. The Sabatier principle expresses the general relationship between binding strength and catalytic turnover, stating that catalysis is most effective when the interaction between a catalyst and reactants is of intermediate strength. To reveal the effect of Weyl antiferromagnet Mn_3Sn to NRR, we focus on the magnetic moments of Mn atoms. Comparative calculations are performed for NRR on the (001) surface of antiferromagnetic (AFM) Mn_3Sn (set LNONCOLLINEAR = T in VASP) and nonmagnetic (NM) Mn_3Sn (i.e., spin-unpolarized, set LNONCOLLINEAR = F and ISPIN = 1 in VASP).

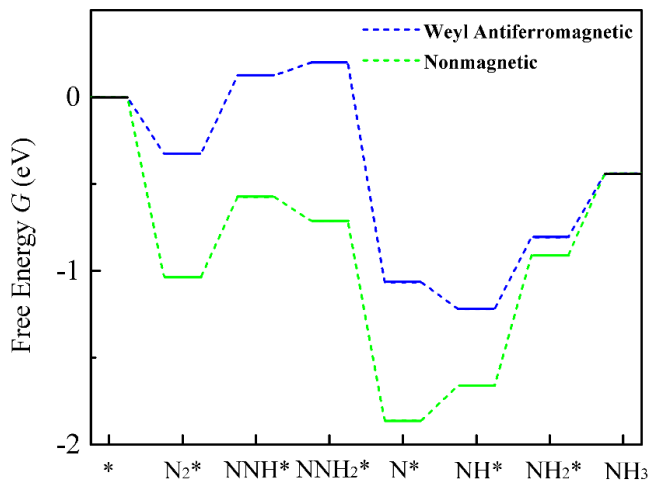

Fig. S1 The free energy diagram of NRR on Weyl AFM and NM Mn_3Sn. The surface is (001).

Fig. S1 shows the free energies of reaction intermediates for the two cases. The

free energy evolution of NRR on NM Mn_3Sn is low and deep. According to the Sabatier principle, NRR on NM Mn_3Sn is not effective. By contrast, the free energy evolution of NRR on AFM Mn_3Sn is moderate. Therefore, NRR on NM Mn_3Sn is effective. This is mainly presented in: (a) The adsorption of N_2 on NM Mn_3Sn is too strong, making the free energy profile too deep at the beginning; (b) The free energy ΔG(NH*) on NM Mn_3Sn is much lower than that of AFM Mn_3Sn, which lead to a large energy increase from NH* to NH_2* (on NM Mn_3Sn $\Delta G(NH_2^*) - \Delta G(NH^*) = 0.75$ eV, on AFM Mn_3Sn $\Delta G(NH_2^*) - \Delta G(NH^*) = 0.41$ eV).

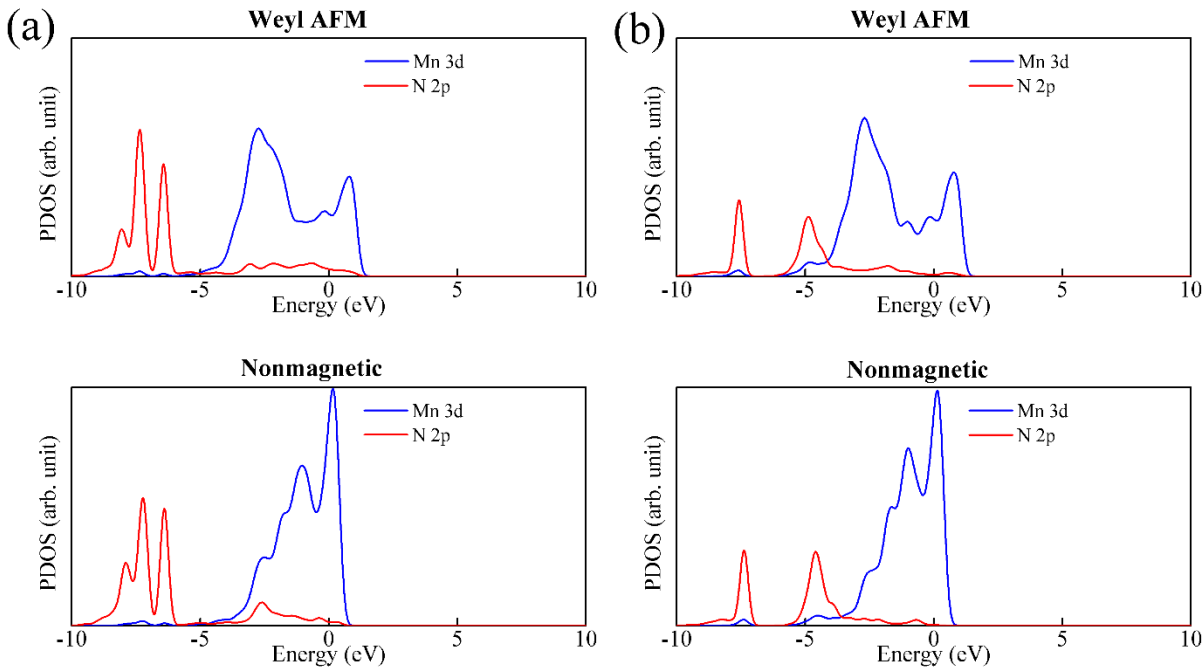

Fig. S2 The PDOS of **(a)** N_2* and **(b)** NH* on Weyl AFM and NM Mn_3Sn. The surface is (001). The Fermi energy is set to zero.

To understand the reason, we plot the projected density of states (PDOS) for N_2* and NH* on AFM and NM Mn_3Sn (**Fig. S2**). We also calculate the atomic magnetic moments of N_2* and NH*. The results are almost zero. In the Mn 3d band, we can see the coupling with N 2p orbitals. By comparison, the coupling in NM Mn_3Sn is stronger (correspond to larger PDOS of N 2p orbitals) than that in AFM Mn_3Sn. The spin states of electrons in AFM Mn_3Sn orient to different directions. This leads to less coupling with spin-unpolarized N atoms.

To further determine the spin states, the atomic magnetic moments of Mn atoms in bare (001) surface of AFM Mn_3Sn, the (001) surface with N_2* and the (001) surface with NNH* are plotted in **Fig. S3**. The vectors exhibit the magnitudes and directions of atomic magnetic moments. We can see that they do not have obvious distinction. The Mn magnetic moments remain unchanged under the adsorbate. This can also be seen by comparing the PDOS of Mn in **Fig. S2**. With the adsorbate, the Mn magnetic moments are not weakened or quenched. The moderate interaction between the AFM substrate and spin-unpolarized adsorbate is then kept.

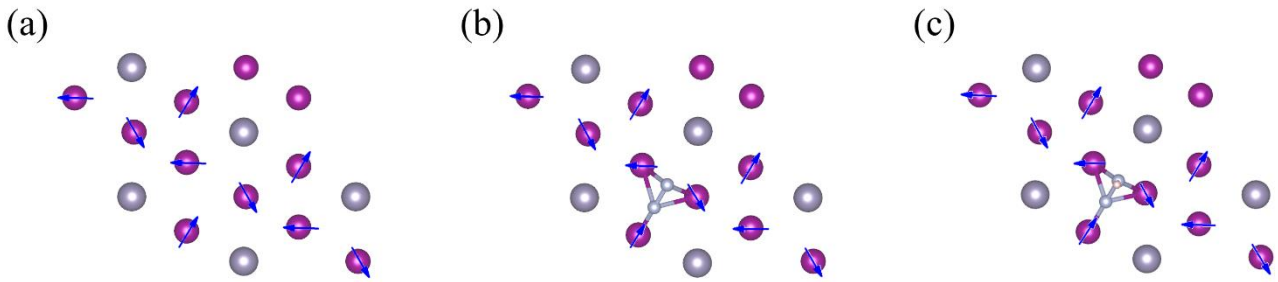

Fig. S3 The magnetic moments of Mn atoms on the (001) surface of AFM Mn_3Sn: **(a)** bare surface; **(b)** with N_2*; **(c)** with NNH*.

2. The free energy of the key intermediates of NRR on the (001) face of M_3Sn

Liu et al. reported the reaction free energy of each proton-coupled electron transfer step is linearly correlated to the adsorption energy of N*, and these scaling relations indicate that the formation of NNH* and NH_2* are the potential-determining steps[1]. The one-end NRR path is as the following.

$$N_2\ (g) + H^+ + e \rightarrow NNH^*$$

$$NNH^* + H^+ + e \rightarrow NNH_2^*$$

$$NNH_2^* + H^+ + e \rightarrow N^* + NH_3\ (aq)$$

$$N^* + H^+ + e \rightarrow NH^*$$

$$NH^* + H^+ + e \rightarrow NH_2^*$$

$$NH_2^* + H^+ + e \rightarrow NH_3\ (aq)$$

If the free energy G(NNH*) < 0, then the first reaction $N_2 + H^+ + e \rightarrow NNH^*$ is

thermodynamically feasible. If $G(NH_2^* + NH_3) > G(2NH_3)$, the last reaction $NH_2^* + H^+ + e \rightarrow NH_3$ is thermodynamically feasible. If $G(NNH^*) > G(NH_2^* + NH_3)$, the free energy shows a downhill trend from the first intermediate NNH* to the last intermediate NH_2*. **Table S1** lists the free energies of the key intermediates of NRR on the (001) face of M_3Sn. A simplified free energy diagram is plotted in **Fig S4**.

Table S1 The free energies of the key intermediates of NRR on M_3Sn.

Free energy (eV)	Co_3Sn	Cr_3Sn	Mn_3Sn	Mo_3Sn	Ni_3Sn	Fe_3Sn
G(NNH*)	1.02	0.02	0.13	0.34	1.09	0.87
$G(NH_2^*+NH_3)$	-0.39	-1.10	-0.81	-1.13	-0.37	-0.58

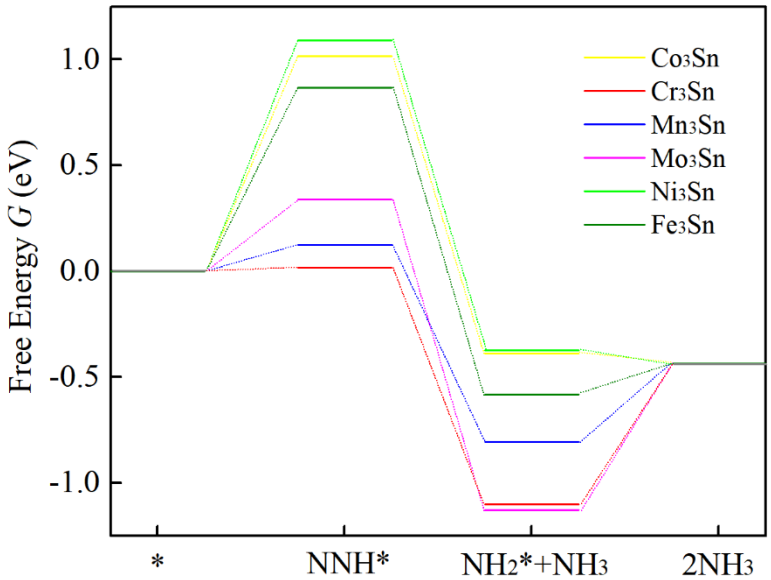

Fig. S4 A simplified free energy diagram of NRR on the (001) face of M_3Sn.

References

[1] X. Liu, Y. Jiao, Y. Zheng, M. Jaroniec, S.-Z. Qiao, **Building Up a Picture of the Electrocatalytic Nitrogen Reduction Activity of Transition Metal Single-Atom Catalysts**. *J. Am. Chem. Soc.* **141**, 9664 (2019).