# First-principles study of electronic structure and photocatalytic properties of $MnNiO_3$ as an alkaline oxygen-evolution photocatalyst

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**Supplementary Matserials**

## Structure relaxation

The primitive cell of rhombohedral $MnNiO_3$ (black dashed line) used in our DFT-HSE calculations is shown in Fig. 1. The Mn and Ni atoms are both surrounded by a distorted oxygen octahedron, with nearest neighbour distances ranging from 1.932 to 1.957 Å for Mn and from 2.029 to 2.141 Å for Ni. The structure of the ilmenite $ABO_x$ is similar to that of $Cr_2O_3$, where both A and B sites are occupied by Cr atoms.[1] In ilmenite structures, A and B atoms form an AB-BA-AB-BA arrangement with oxygen atom layers stacked along the rhombohedron body diagonal. The positions of the A, B, and O atoms in the rhombohedral cell of the ilmenite structure can be described with the following Wyckoff positions [2]: metal A: ±u, u, u; metal B: ±v, v, v; oxygens: ±(xyz, zxy, yzx) with the restriction of the oxygen positions as $x + y = 2z$.[3]

**Table S1** Equilibrium lattice parameters for various magnetic phases of $MnNiO_3$ obtained with DFT-PBE+U and DFT-HSE calculations. The experimental data from Ref.2 is also listed for comparison.

| Functional | Magnetic configuration | a = b = c (Å) | α = β = γ (degree) | Volume (Å$^3$) |
|---|---|---|---|---|
| PBE+U | Ferrimagnetic (ground state) | 5.419 | 54.763 | 98.783 |
| | Ferromagnetic | 5.431 | 54.861 | 99.743 |
| | Antiferromagnetic (+-++) | 5.432 | 54.654 | 99.200 |
| | Antiferromagnetic (+++-) | 5.423 | 54.854 | 99.250 |
| | Antiferromagnetic (+-+-) | 5.431 | 54.691 | 99.237 |
| | Antiferromagnetic (+--+) | 5.433 | 54.603 | 99.114 |
| HSE | Ferrimagnetic (ground state) | 5.334 | 54.622 | 93.871 |
| | Ferromagnetic | 5.351 | 54.677 | 94.905 |
| | Antiferromagnetic (+-++) | 5.341 | 54.578 | 94.128 |
| | Antiferromagnetic (+++-) | 5.344 | 54.623 | 94.363 |
| | Antiferromagnetic (+-+-) | 5.337 | 54.658 | 94.128 |
| | Antiferromagnetic (+--+) | 5.353 | 54.448 | 94.416 |
| Experimental[2] | Ferrimagnetic (ground state) | 5.343 | 54.650 | 94.411 |

**Table S2** Equilibrium lattice parameters and atomic coordinates of MnNiO3 in the ferrimagnetic ground state obtained from HSE calculations. The experimental data from Ref.[2] is also listed for comparison.

| | Experimental[2] | HSE (ferrimagnetic) |
|---|---|---|
| a = b = c (Å) | 5.3529 | 5.3341 |
| $\alpha = \beta = \gamma$ (Degree) | 54.4480 | 54.6224 |
| Volume (Å$^3$) | 94.4163 | 93.8712 |
| u | 0.352 | 0.343 |
| v | 0.148 | 0.146 |
| x | 0.560 | 0.550 |
| y | -0.060 | -0.059 |
| z | 0.250 | 0.272 |

## Magnetic properties of $MnNiO_3$

In order to find the DFT magnetic ground state of $MnNiO_3$, we calculate several possible magnetic configurations corresponding to ferromagnetic, ferromagnetic, and antiferromagnetic states with both PBE+U and HSE functionals. The initial magnetic moments are set on Mn and Ni atoms along the rhombohedron body diagonal (Mn1, Ni1, Ni2, Mn2) as shown in Fig. 1. To simulate a ferromagnetic state, the initial magnetic moments are all positive (++++) from the top Mn1 to the bottom Mn2 atom. It is experimentally confirmed in Ref.[2, 4-8] that the ground state of $MnNiO_3$ is ferrimagnetic with magnetic moments of alternating sign and differing magnitude on the A and B atoms, respectively. We set the initial magnetic moments as -++-, which means the magnetic moments on Mn atoms are negative while those on Ni atoms are positive. We also consider four different antiferromagnetic configurations in the unit cell with the magnetic moments from Mn1 atom to Mn2 atom along the rhombohedron body diagonal set as: +-++, +++-, +-+-, +--+.

The obtained final magnetic moments after structural and electronic relaxations for ferrimagnetic, ferromagnetic, and four antiferromagnetic states are shown in Table S3. We calculate that the ferrimagnetic state is the ground state using both PBE+U and HSE approaches, consistent with previous experimental observations[2, 4-8]. As shown in Table S3, the energy per magnetic atom of the ferromagnetic state is 26 meV higher than that of the ferrimagnetic state with PBE+U, and 70 meV higher with the HSE functional. For antiferromagnetic states, the energy difference is between 13 to 34 meV for PBE+U, and 38 to 58 meV for HSE, respectively. Overall, the strength of the magnetic interactions is predicted to be greater with HSE method than PBE+U. Although HSE and PBE+U differ significantly in the absolute value of the band gap, the trend remains the same: the band gap for the ferromagnetic state is lowest compared with other magnetic states, and the antiferromagnetic phase with a +-+- configuration exhibits the largest band gap.

**Table S3** Calculated total energy differences, the magnetic moments of each Mn and Ni ion for various magnetic phases of $MnNiO_3$, and the band gaps obtained with DFT-PBE+U and DFT-HSE. All total energies are reported relative to the ferrimagnetic state.

| Functional | Magnetic configuration | Final magnetic moments for Mn and Ni atoms ($\mu_B$) | | | | Energy difference per magnetic atom (meV) | Band gap (eV) |
|---|---|---|---|---|---|---|---|
| | | Mn1 | Mn2 | Ni1 | Ni2 | | |
| PBE+U | Ferrimagnetic (ground state) | -3.1 | -3.1 | +1.8 | +1.8 | 0 | 1.75 |
| | Ferromagnetic | +3.3 | +3.3 | +1.8 | +1.8 | 26 | 1.40 |
| | Antiferromagnetic (+-++) | +3.2 | -3.1 | +1.8 | +1.7 | 25 | 1.78 |
| | Antiferromagnetic (+++-) | +3.2 | +3.2 | +1.8 | -1.8 | 13 | 1.56 |
| | Antiferromagnetic (+-+-) | +3.1 | -3.1 | +1.8 | -1.8 | 34 | 1.98 |
| | Antiferromagnetic (+--+) | +3.2 | -3.2 | -1.7 | +1.7 | 21 | 1.82 |
| HSE | Ferrimagnetic (ground state) | -2.9 | -2.9 | +1.7 | +1.7 | 0 | 2.98 |
| | Ferromagnetic | +3.1 | +3.1 | +1.7 | +1.7 | 70 | 2.87 |
| | Antiferromagnetic (+-++) | +3.1 | -2.9 | +3.0 | +3.0 | 50 | 3.07 |
| | Antiferromagnetic (+++-) | +3.0 | +3.0 | +1.7 | -1.7 | 37 | 2.94 |
| | Antiferromagnetic (+-+-) | +2.9 | -2.9 | +1.7 | -1.7 | 57 | 3.21 |
| | Antiferromagnetic (+--+) | +3.0 | -3.0 | -1.7 | +1.7 | 37 | 3.14 |


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