

—Supporting information—

Evaluating optimal U for $3d$ transition-metal oxides within the SCAN+ U framework

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S1 Projector augmented-wave potentials

Table S1: Elements and their corresponding projector augmented-wave (PAW¹) potentials used in our calculations. We used the “potPAW.52” set, which is designed for the Perdew-Burke-Ernzerhof functional² and contains information on the kinetic energy of the core electrons. The quoted text in the PAW potential column indicates the specific potential file that is available with the Vienna ab initio simulation package.^{3,4} For example, “Cr_pv” indicates “POTCAR.Cr_pv.gz”. For each PAW potential, we also indicate the number of valence electrons treated self-consistently. In the case of copper, we used the “Cu_pv” potential listed below in all our calculations except in **Figure S2** (see below), where we used both “Cu_pv” and “Cu” potentials.

Element	PAW potential	Number of valence electrons
Oxygen	“O”	6
Scandium	“Sc_sv”	11
Titanium	“Ti_pv”	10
Vanadium	“V_pv”	11
Chromium	“Cr_pv”	12
Cobalt	“Co_pv”	15

Nickel	“Ni_pv”	16
Copper	“Cu_pv”	17
Zinc	“Zn”	12
Lithium	“Li”	1

S2 Additional crystal structures

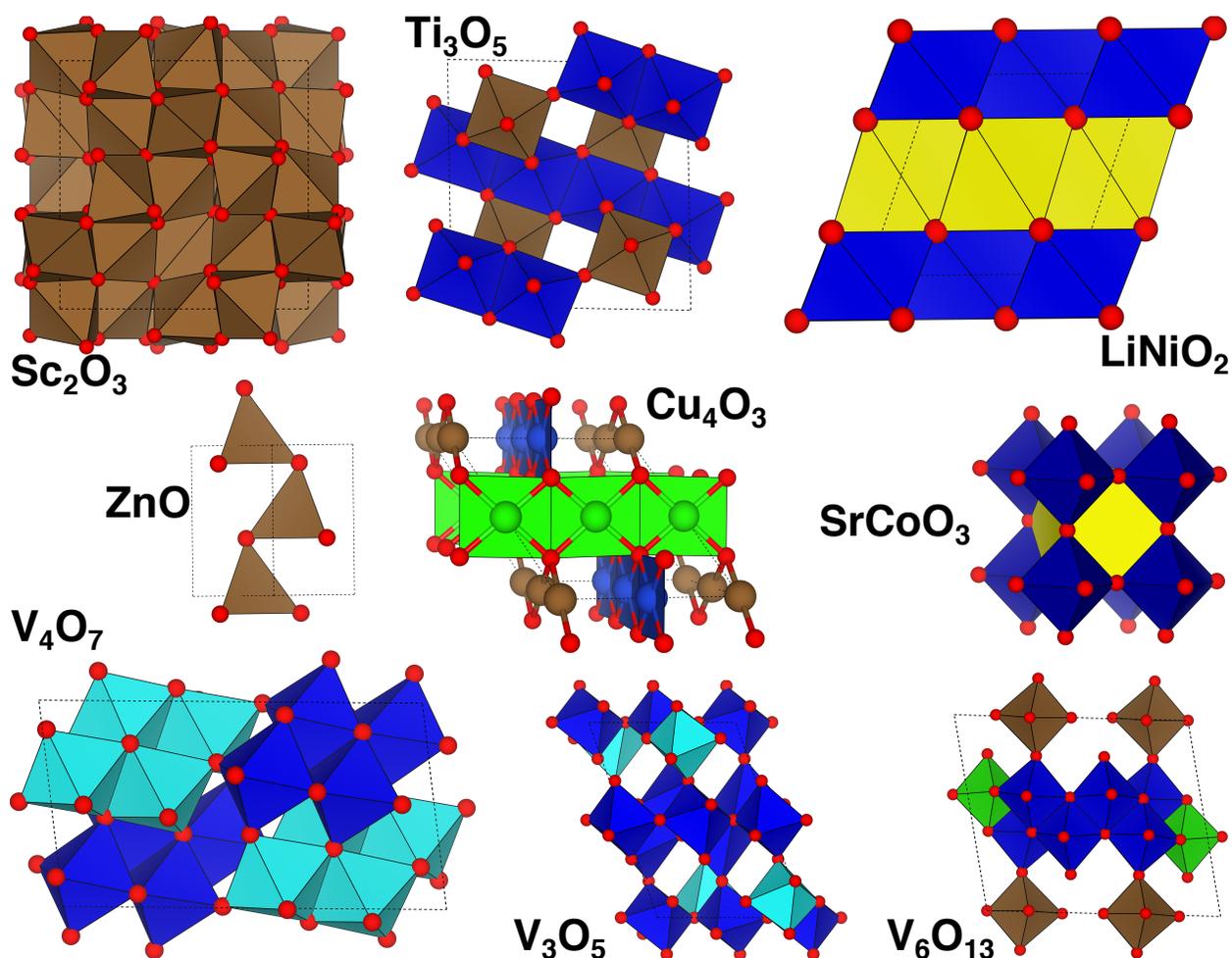


Figure S1: Initial crystal structures considered in evaluating the transferability of optimal U values determined for the various transition-metal systems. Dark blue and green polyhedra indicate atoms of identical oxidation states but with opposite magnetic spin. Brown polyhedra indicate metal atoms without any magnetic moment. In V_4O_7 (space group: $P2_1/c$) and V_3O_5 ($A\bar{1}$) the dark and light blue polyhedra respectively signify V atoms with lower and higher oxidation states. In the case of Ti_3O_5 ($C2/m$), Cu_4O_3 ($I4_1/amd$), and V_6O_{13} ($C2/m$), the brown polyhedra represent Ti^{4+} , Cu^+ , and V^{5+} , while the yellow polyhedra in $LiNiO_2$ ($C2/m$) and $SrCoO_3$ ($Pm\bar{3}m$) show Li and Sr, respectively. The initial structure of NiO_2 ($C2/m$, see **Figure S7**) is obtained by removing the Li atoms of the $LiNiO_2$ ($C2/m$) structure shown here. The space groups of Sc_2O_3 and ZnO are $Ia\bar{3}$ and $P6_3mc$, respectively.

S3 Effect of including outer-core states of Cu

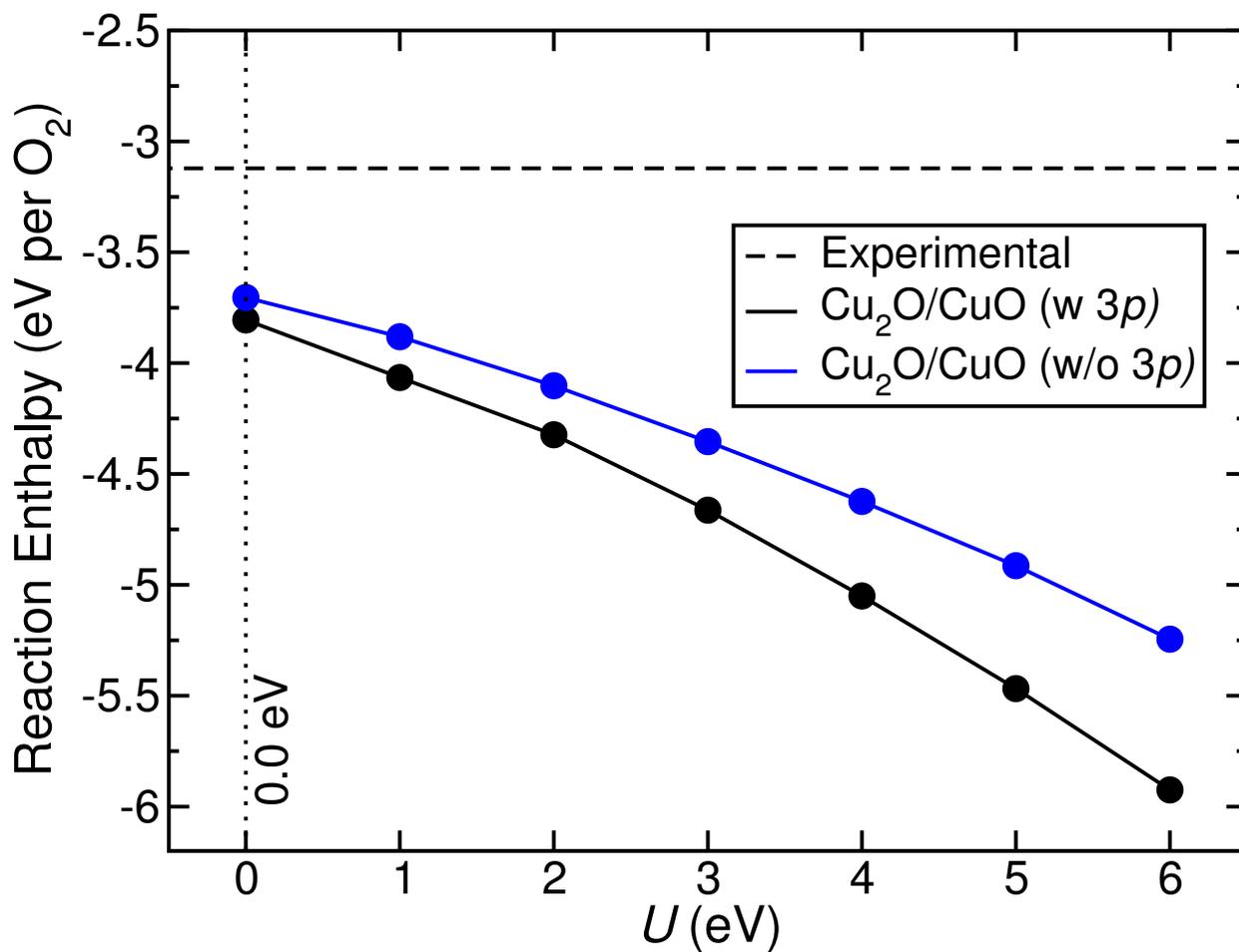


Figure S2: Variation of the $2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO}$ reaction enthalpy with increasing magnitude of U within the SCAN+ U framework. Blue circles and the blue solid line indicate calculations without considering the 3p outer-core states of Cu self-consistently, while black circles and the black solid line correspond to the 3p electrons being treated self-consistently. Dashed black line is the experimental reaction enthalpy and the dotted black line indicates the optimal U (= 0.0 eV).

S4 Electronic structure of titanium oxides

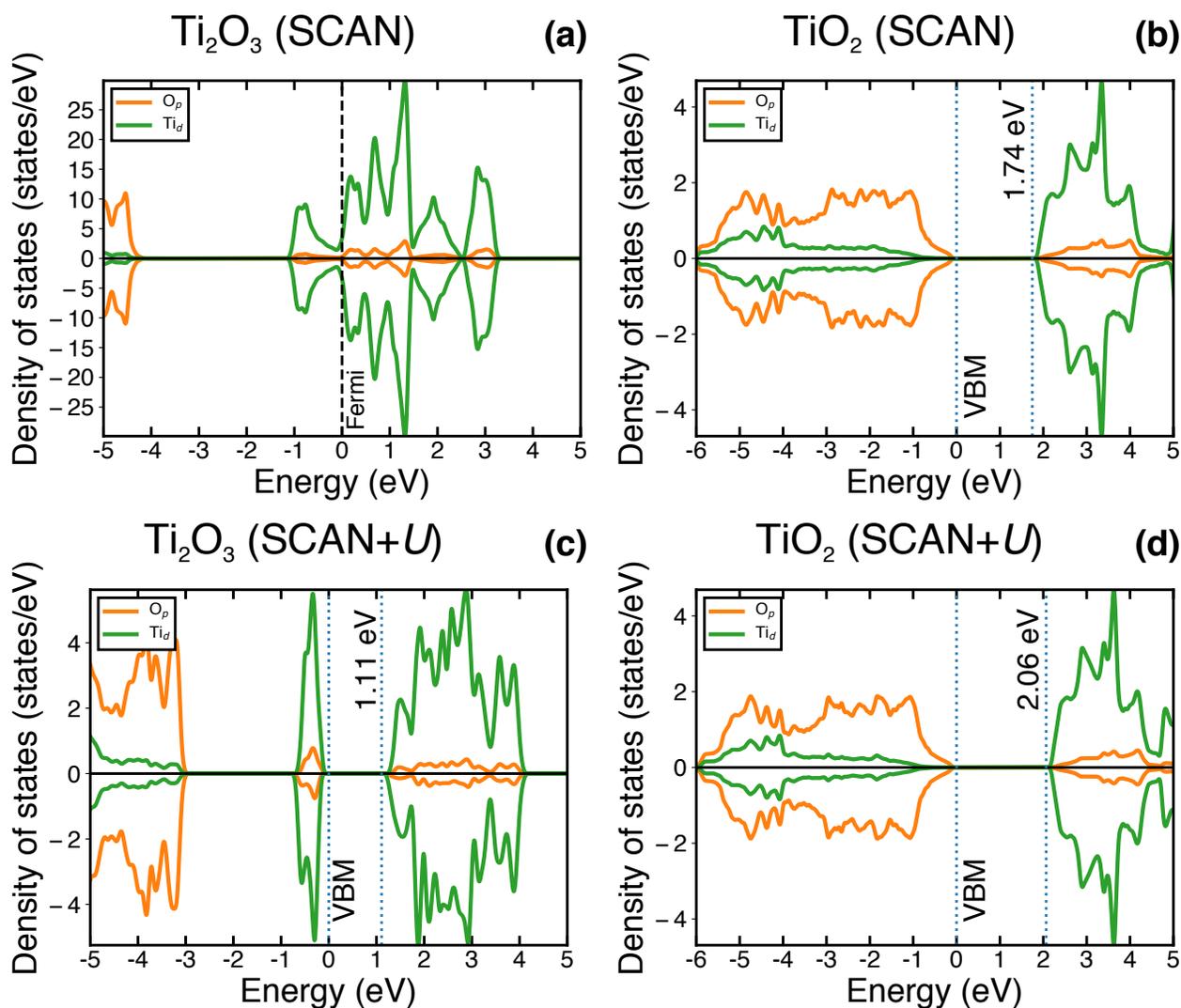


Figure S3: Densities of states (DOS) for the ground-state antiferromagnetic configuration of Ti_2O_3 (panels a and c) and non-magnetic rutile- TiO_2 (panels b and d) calculated using DFT-SCAN (panels a and b) and SCAN+ U_{Ti} ($U_{\text{Ti}} = 2.5$ eV, panels c and d). Orange and green lines correspond to O $2p$ and Ti $3d$ states. Dashed black lines are Fermi levels in metallic system(s) while dotted blue lines are valence and conduction band edges for non-metallic system(s). The zero on the energy scale is set to either the Fermi level (metallic systems) or the valence band maximum (VBM, non-metallic systems). For structure(s) with a band gap, the value of the gap is indicated by the text annotation at the conduction band edge. States/eV below zero are minority spin and states/eV above zero are majority spin.

S5 Electronic structure of vanadium oxides

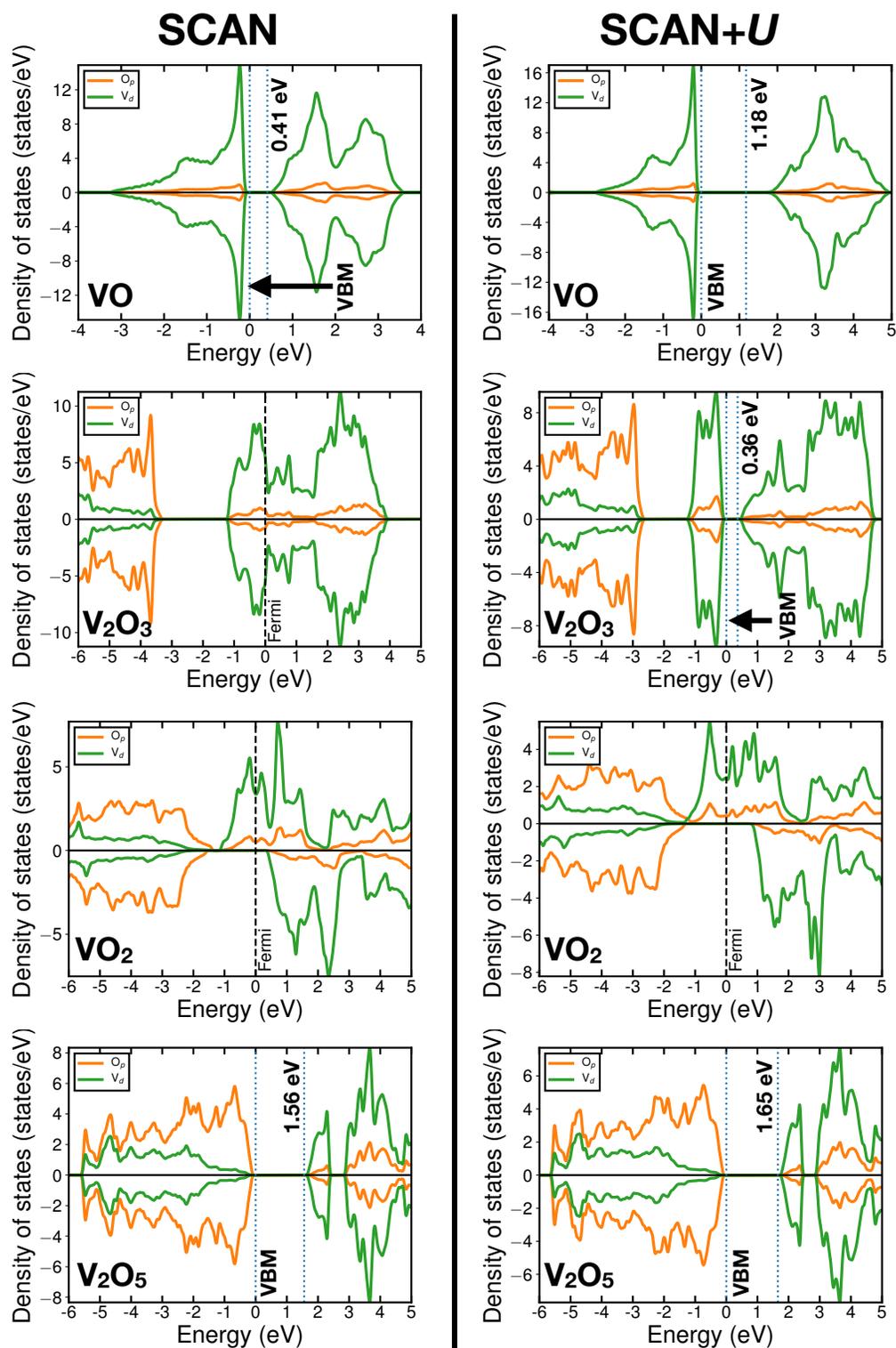


Figure S4: DOS for the ground-state magnetic configurations of VO (top row), V_2O_3 (second row), VO_2 (third row), and V_2O_5 (bottom row) as calculated by DFT-SCAN (left column) and SCAN+ U_V for $U_V = 1.0$ eV (right column). Notations used within each panel are identical to **Figure S3**.

S6 Electronic structure of chromium oxides

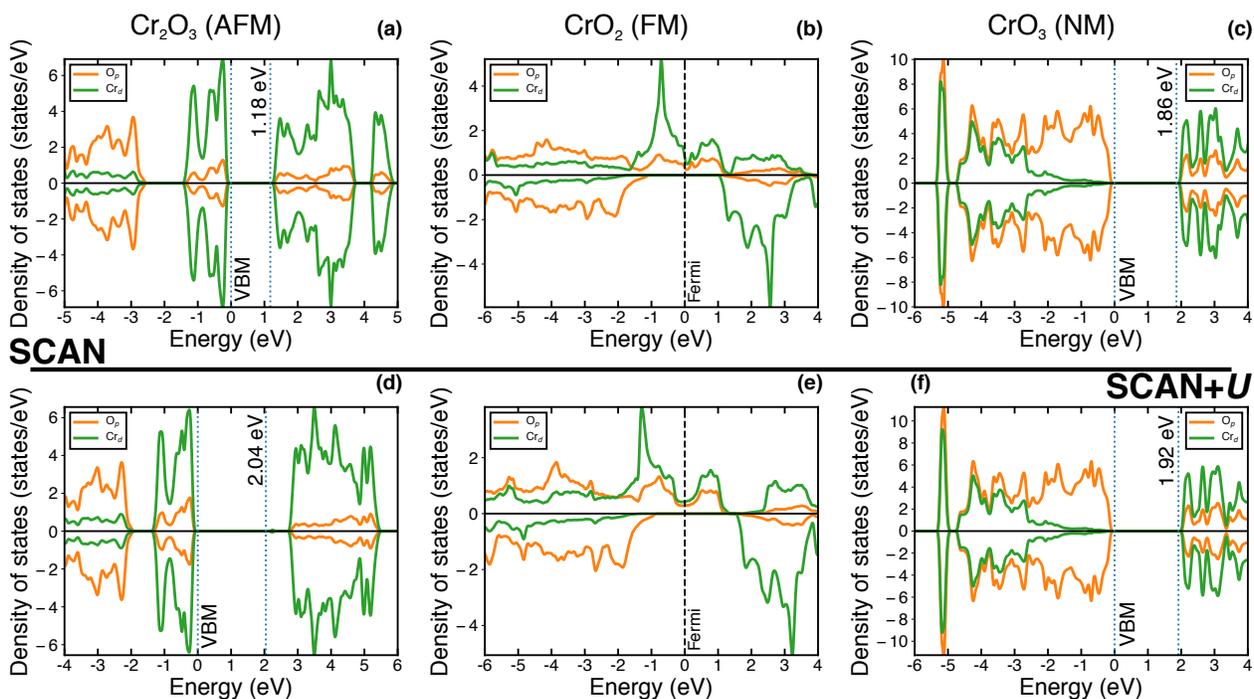


Figure S5: DOS for the ground-state magnetic configurations of Cr_2O_3 (panels a, d), CrO_2 (b, e), and CrO_3 (c, f) as calculated by DFT-SCAN (panels a – c) and SCAN+ U for $U=0.5$ eV (panels d – f). Notations used within each panel are identical to **Figure S3**.

Figure S5 shows the DOS plotted for ground-state magnetic configurations of Cr_2O_3 , CrO_2 , and CrO_3 for DFT-SCAN and SCAN+ U ($U=0.5$ eV). DFT-SCAN and SCAN+ U predict qualitatively similar behavior for all Cr oxides considered, highlighting that a U correction is not required for accurately modeling Cr oxides with SCAN. For example, DFT-SCAN and SCAN+ U both rightly yield half-metallic behavior in rutile- CrO_2 (**Figure S5b** and **e**), signified by the metallic and insulating behaviors of the majority (DOS above zero) and minority (DOS below zero) spin channels, respectively, in agreement with experiments.⁵ Importantly, CrO_2 is the only thermodynamically stable MO_2 oxide ($M=3d$ metal) which remains (half) metallic under sub-298 K conditions.⁵ Additionally, DFT-SCAN and SCAN+ U both predict similarly insulating behavior for CrO_3 (band gaps of 1.86 and 1.92 eV, panels c and f in **Figure S5**), in qualitative agreement with experiments (band gap ~ 3.80 eV⁶). Also, the charge-transfer behavior of CrO_3 , highlighted by O $2p$ states (orange lines) at the VBM and Cr $3d$ states (green lines) at the CBM is captured equally well by DFT-SCAN and SCAN+ U . Significantly, DFT-SCAN and SCAN+ U 's predicted band gaps in Cr_2O_3

differ by ~ 0.86 eV (**Figure S5a and d**), although both frameworks produce insulating behavior, in qualitative agreement with experiments (band gap ~ 3.2 eV⁷). The deviation in DFT-SCAN versus SCAN+ U band gaps can be attributed to the presence of the highest number of unpaired d electrons on each Cr ion in Cr_2O_3 (three) among the Cr oxides considered and hence this oxide is impacted most by the addition of U .

S7 Electronic structure of Co_3O_4 and CoO_2

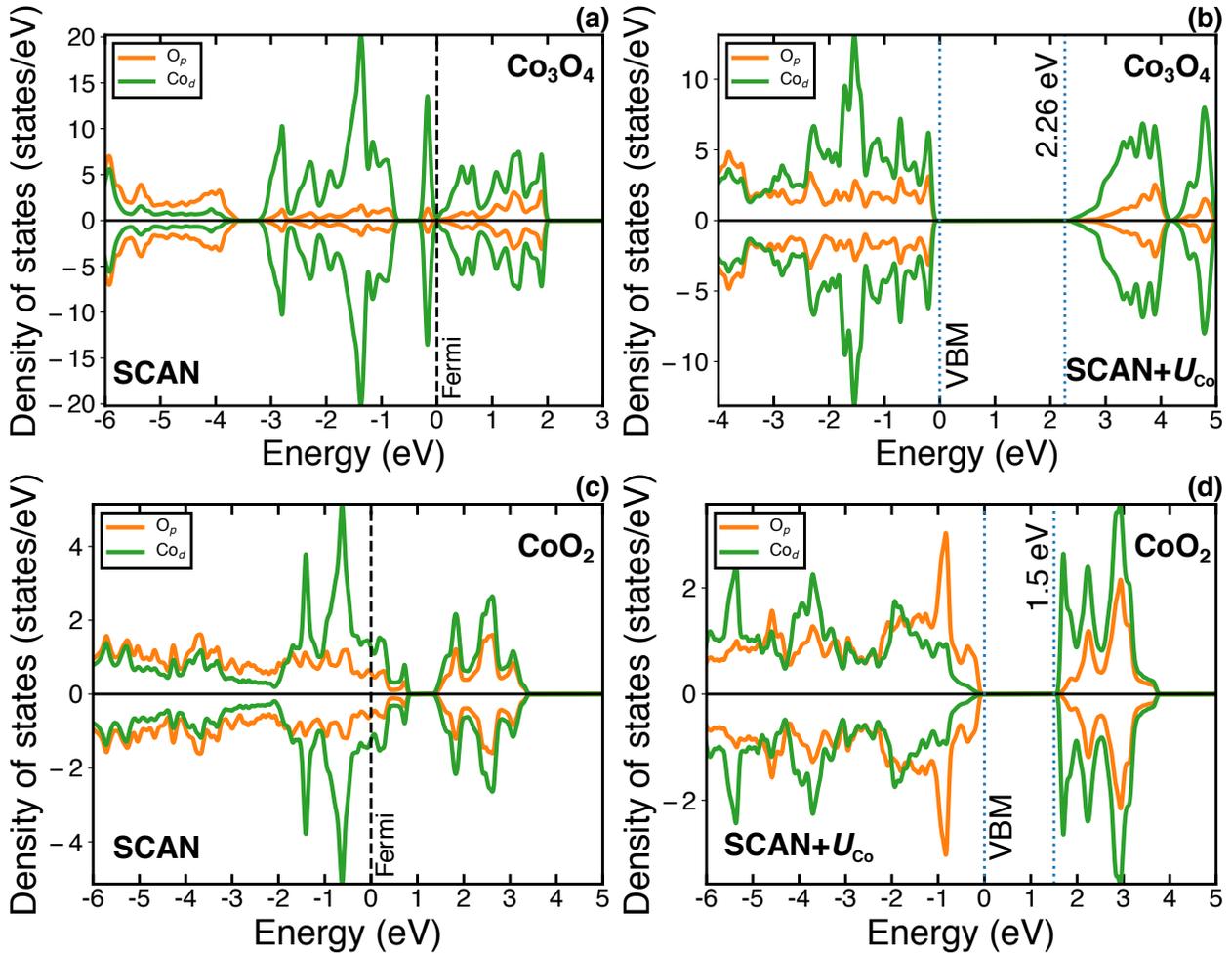


Figure S6: DOS for the ground-state magnetic configuration of spinel- Co_3O_4 (panels a and b) and antiferromagnetic O1- CoO_2 (panels c and d) as calculated by DFT-SCAN (panels a and c) and SCAN+ U_{Co} for $U_{\text{Co}} = 3.0$ eV (panels b and d). Notations used within each panel are identical to **Figure S3**.

S8 Electronic structure of nickel oxides

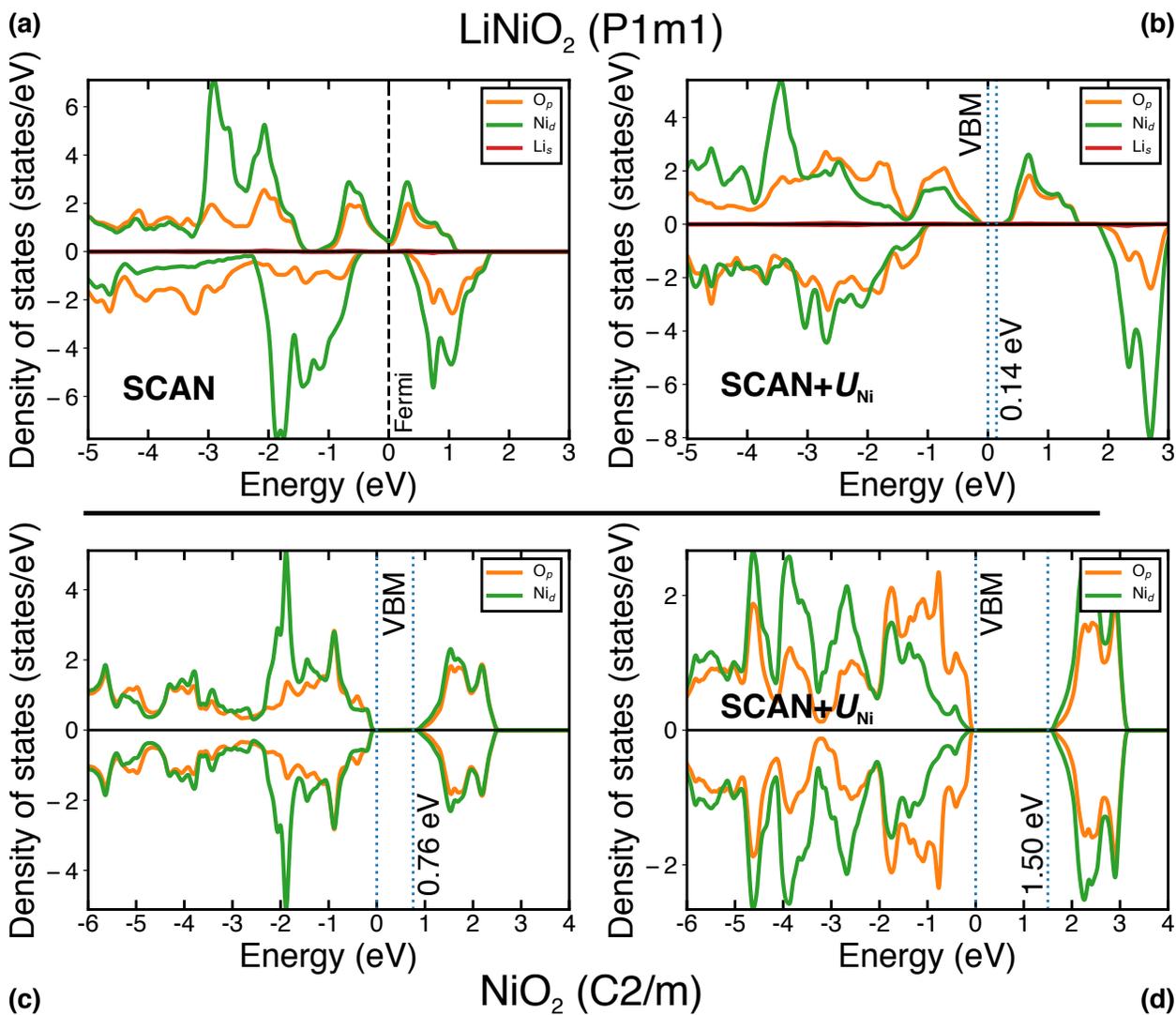


Figure S7: DOS for the ferromagnetic LiNiO_2 (panels a and b) and NiO_2 (panels c and d), as calculated by DFT-SCAN (left column) and SCAN+ U_{Ni} for $U_{\text{Ni}} = 2.5$ eV (right column). The LiNiO_2 polymorph considered here was used to obtain the U_{Ni} value (Figure 2e in the main text) and is different from the one considered in Figure S11. The initial structure of NiO_2 was obtained by removing the Li atoms from the LiNiO_2 structure shown in Figure S1. Notations used within each panel are identical to Figure S3.

S9 Crystal structures of anatase and brookite TiO₂

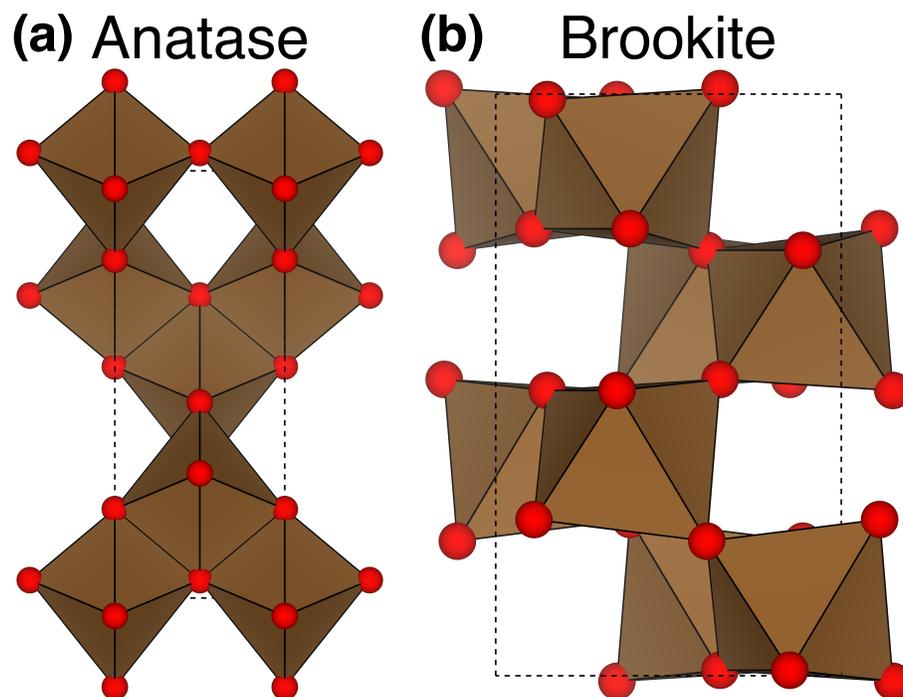


Figure S8: Unit cells of anatase (space group: $I4_1/amd$) and brookite ($Pbca$) TiO₂. Red spheres represent oxygen, brown polyhedra titanium.

S10 Antiferromagnetic configurations in zinc blende CoO

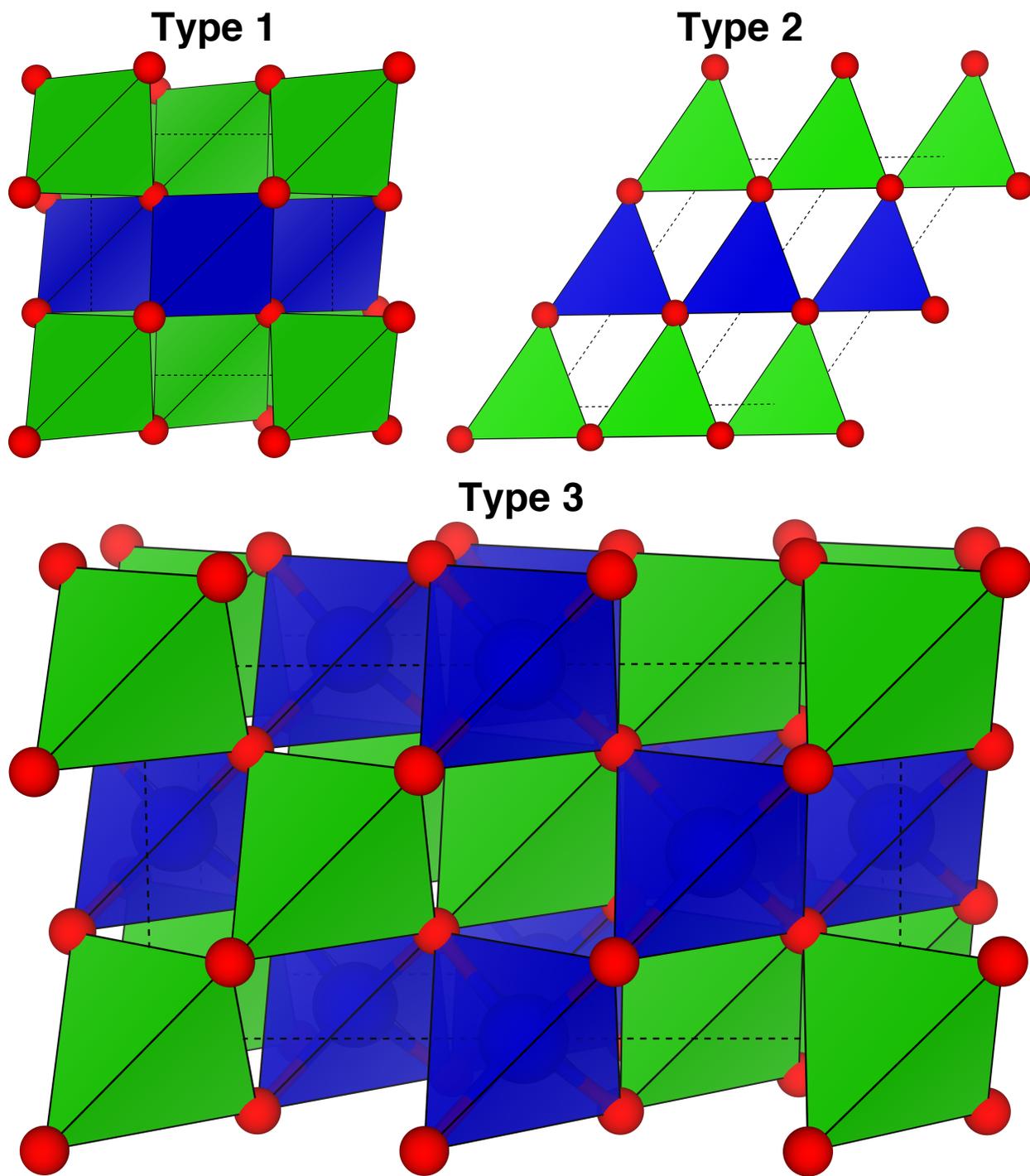


Figure S9: Three common types of antiferromagnetic configurations possible in zinc blende (space group: $F\bar{4}3m$) CoO. Red spheres indicate oxygen. Green and blue polyhedra represent Co atoms with opposite magnetic moments.

S11 Transferability checks in cobalt oxides: SrCoO₃ and CoO₂

Table S2: Lattice parameters and magnetic moments (on Co atom) in the primitive cell of cubic SrCoO₃. We attempted three different initializations of the magnetic moment, namely 5 (signifying high-spin Co⁴⁺), 3 (intermediate-spin), and 1 (low-spin). Both DFT-SCAN and SCAN+ U_{Co} always converged to the intermediate-spin state for the Co atom during structure relaxation.

Source	Lattice constants (Å)			Lattice vector angles (°)			M (μB)	
	a	b	c	α	β	γ	Initial	Relaxed
Expt.	3.86			90.0			2.5	
DFT-SCAN	3.79			90.0			5	2.05
							3	
							1	
SCAN+ U_{Co}	3.82			90.0			5	2.91
							3	
							1	

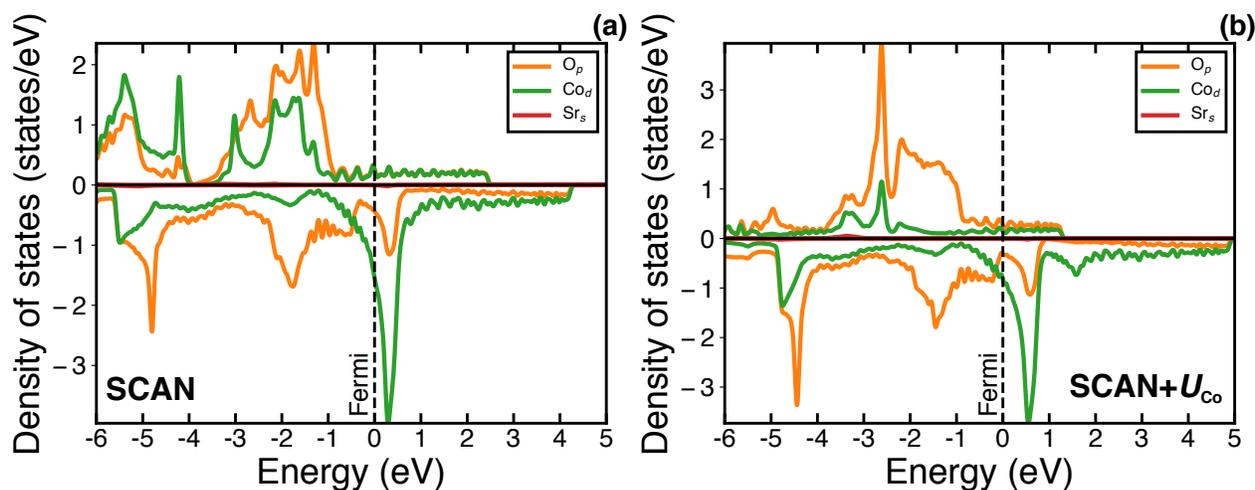


Figure S8: DOS for ferromagnetic, cubic-SrCoO₃ as calculated by DFT-SCAN (panel a) and SCAN+ U_{Co} for $U_{\text{Co}} = 3.0$ eV (panel b). Notations used within each panel are identical to **Figure S3**.

Table S3: Lattice parameters in ferromagnetic and antiferromagnetic O1-CoO₂ and ferromagnetic O3-CoO₂, as calculated using DFT-SCAN and SCAN+ U_{Co} ($U_{Co} = 3.0$ eV). Alternate Co layers along the c -axis were aligned with opposite spins to model the antiferromagnetic O1-CoO₂ structure, resulting in the use of a $1 \times 1 \times 2$ supercell compared to using just the unit cell for the ferromagnetic configuration. No experimental lattice parameters are available for the O3-CoO₂ structure as it is identical to O3-LiCoO₂ with all the Li atoms removed.

Compound	Source	Lattice constants (Å)			Lattice vector angles (°)		
		a	b	c	α	β	γ
O1-CoO ₂ (Ferromagnetic)	Expt.	2.82		4.24	90.0	120.0	
	DFT-SCAN	2.78		4.35			
	SCAN+ U_{Co}	2.80		4.49			
O1-CoO ₂ (Antiferromagnetic)	Expt.	2.82		8.48	90.0	120.0	
	DFT-SCAN	2.78		8.71			
	SCAN+ U_{Co}	2.80		8.76			
O3-CoO ₂ (Ferromagnetic)	Expt.	N/A					
	DFT-SCAN	2.78		13.34	90.0	120.0	
	SCAN+ U_{Co}	2.80		13.50			

S12 Transferability checks in nickel oxides: LiNiO₂ and NiCr₂O₄

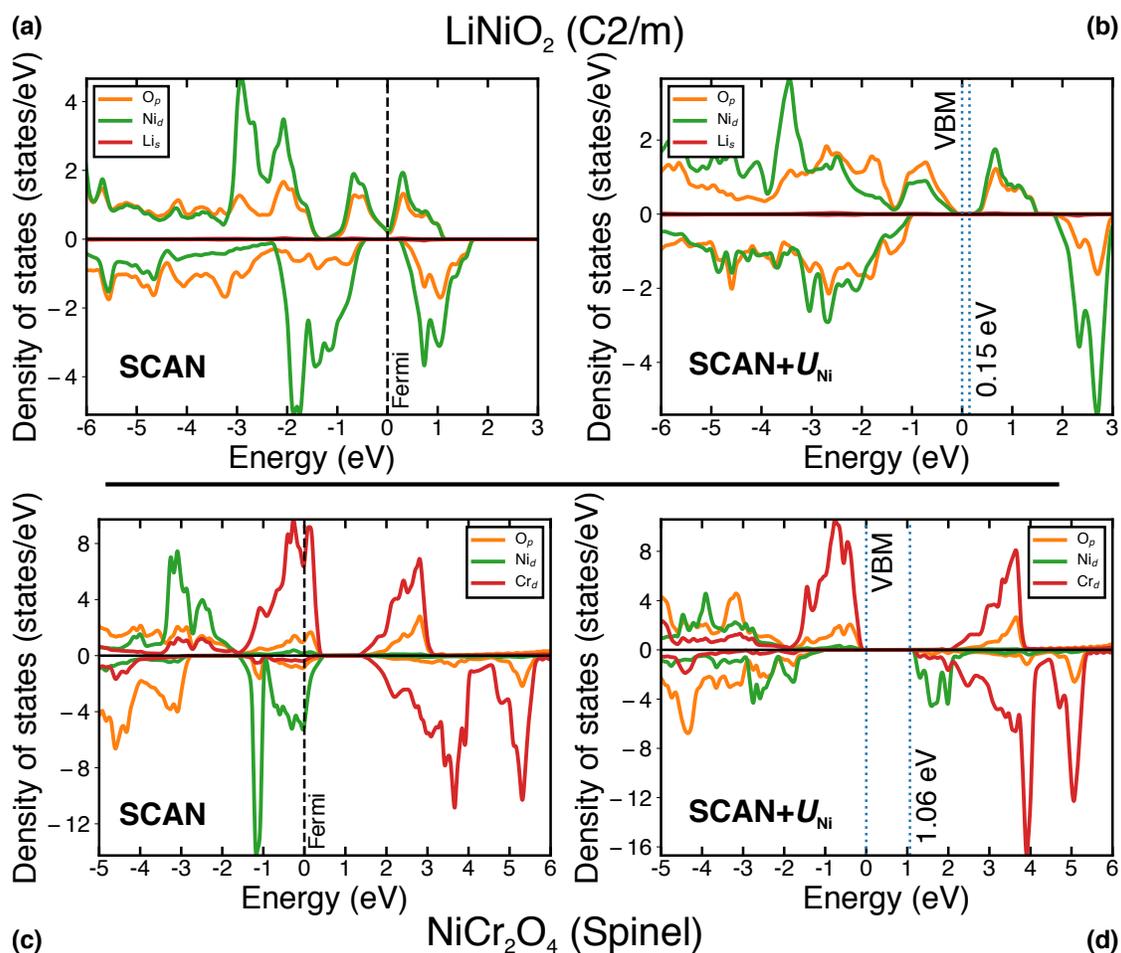


Figure S9: DOS for (a, b) LiNiO₂ (space group: *C2/m*) and (c, d) spinel-NiCr₂O₄ as predicted by DFT-SCAN and SCAN+ U_{Ni} , where $U_{\text{Ni}} = 2.5$ eV. Orange and green lines correspond to O 2*p* and Ni 3*d* states, while the red lines indicate Li 2*s* states in panels (a, b) and Cr 3*d* states in panels (c, d). Notations used in the figure are similar to **Figure S3**.

To test the transferability of the optimal $U_{\text{Ni}} = 2.5$ eV, we applied the correction to monoclinic LiNiO₂ with the *C2/m* space group (**Figure S1**) and to spinel-NiCr₂O₄. Note that the LiNiO₂ structure considered here is different from the P1*m*1 structure of **Figure 1** of the main text because an accurate band gap (at the $G_0W_0@GGA+U$ level⁸) was calculated only for the *C2/m* polymorph whereas band gap measurements do not exist yet for LiNiO₂. In the case of NiCr₂O₄ (structure similar to Co₃O₄ in **Figure 1**), where the Ni²⁺ and Cr³⁺ ions occupy respectively the tetrahedral and octahedral sites, band gap measurements are available for the FM structure that is stable under ambient conditions.⁹ Thus, **Figure S11** plots the DOS predicted by DFT-SCAN (panels a and c) and SCAN+ U_{Ni} (panels b and d) for LiNiO₂ (panels a and b) and NiCr₂O₄

(panels c and d). In the case of LiNiO_2 , DFT-SCAN incorrectly predicts half-metallic behavior, while SCAN+ U_{Ni} predicts a band gap of ~ 0.15 eV, qualitatively consistent with the $G_0W_0@GGA+U$ prediction (band gap ~ 0.96 eV⁸). Similarly, for NiCr_2O_4 , SCAN+ U_{Ni} is in better agreement with experiments (measured band gap ~ 1.7 eV¹⁰) with its predicted ~ 1.06 eV band gap compared to DFT-SCAN's metallic prediction. DOS calculations via DFT-SCAN and SCAN+ U_{Ni} in binary, metastable NiO_2 (space group: C2/m), also show similar trends of a larger gap with the latter (**Figure S7**). Thus, our transferability checks with LiNiO_2 and NiCr_2O_4 confirm that the U_{Ni} correction (in SCAN+ U) is necessary to describe accurately the electronic structure of Ni oxides.

S13 Transferability check in copper oxides: Cu_4O_3

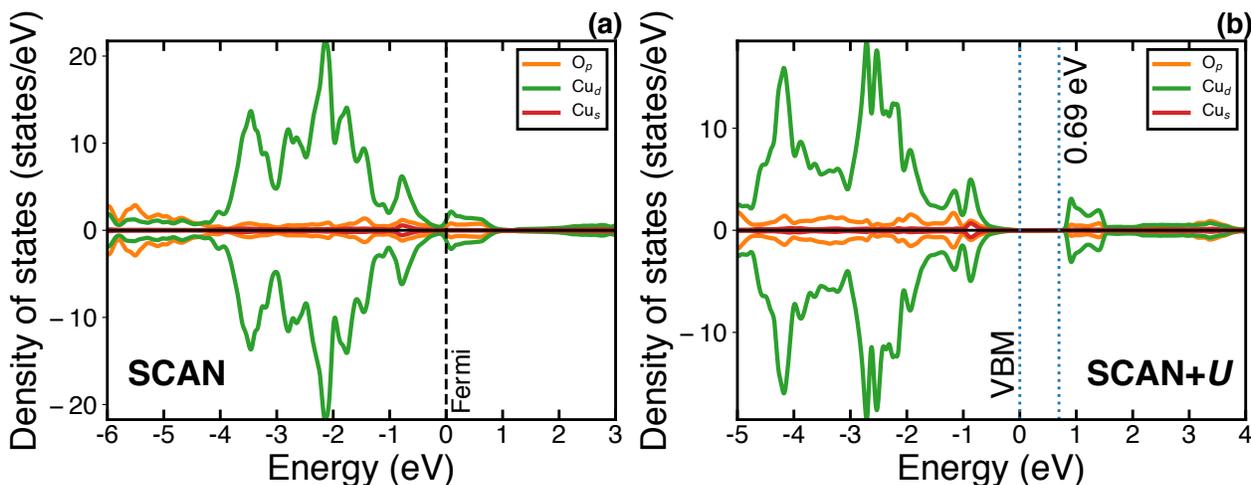


Figure S10: DOS for Cu_4O_3 calculated by (a) DFT-SCAN and (b) SCAN+ U , where $U = 2$ eV. Orange, green, and red lines correspond to O $2p$, Cu $3d$, and Cu $4s$ states. Notations within each panel are similar to **Figure S3**.

Finally, we tested the effect of including a U correction on Cu_4O_3 for copper oxides. Note that we used $U = 2$ eV here, since there is no need for a U correction based on the oxidation enthalpy of $\text{Cu}_2\text{O} \rightarrow \text{CuO}$ (**Figure 2f** of the main text). Cu_4O_3 exhibits mixed oxidation states of +1/+2 and adopts an AFM, tetragonal configuration in its ground state,¹¹ and is known to be a semiconductor with a band gap of ~ 1.34 eV.¹² Due to the large size of the AFM unit cell of Cu_4O_3 ($2 \times 2 \times 2$ supercell of the primitive cell¹¹), we only considered the AFM configurations possible within the primitive cell (14 atoms) to reduce computational cost, similar to Ref.¹³. **Figure S12** plots the DOS for Cu_4O_3 in its most stable AFM configuration (structure

shown in **Figure S1**), as predicted by DFT-SCAN (panel a) and SCAN+ U (panel b). Similar to trends observed in CuO (**Figure 7** of the main text), DFT-SCAN incorrectly predicts metallic behavior in Cu₄O₃ whereas SCAN+ U predicts a 0.69 eV band gap. Thus, although adding a U correction worsens predictions of redox thermodynamics in Cu oxides, including the U will be essential to model the electronic behavior (and related properties).

S14 Calculated formation energies of Sc₂O₃ and ZnO

Table S4: Formation energy of Sc₂O₃ and ZnO (eV/O₂), as calculated by DFT-SCAN.

Compound (space group)	Reaction	Formation energy (eV/O ₂)	
		Expt.	DFT-SCAN
Sc ₂ O ₃ (Ia $\bar{3}$)	$\frac{4}{3} \text{Sc} + \text{O}_2 \rightarrow \frac{2}{3} \text{Sc}_2\text{O}_3$	-13.18	-13.09
ZnO (P6 ₃ mc)	$2 \text{Zn} + \text{O}_2 \rightarrow 2 \text{ZnO}$	-7.22	-6.63

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