

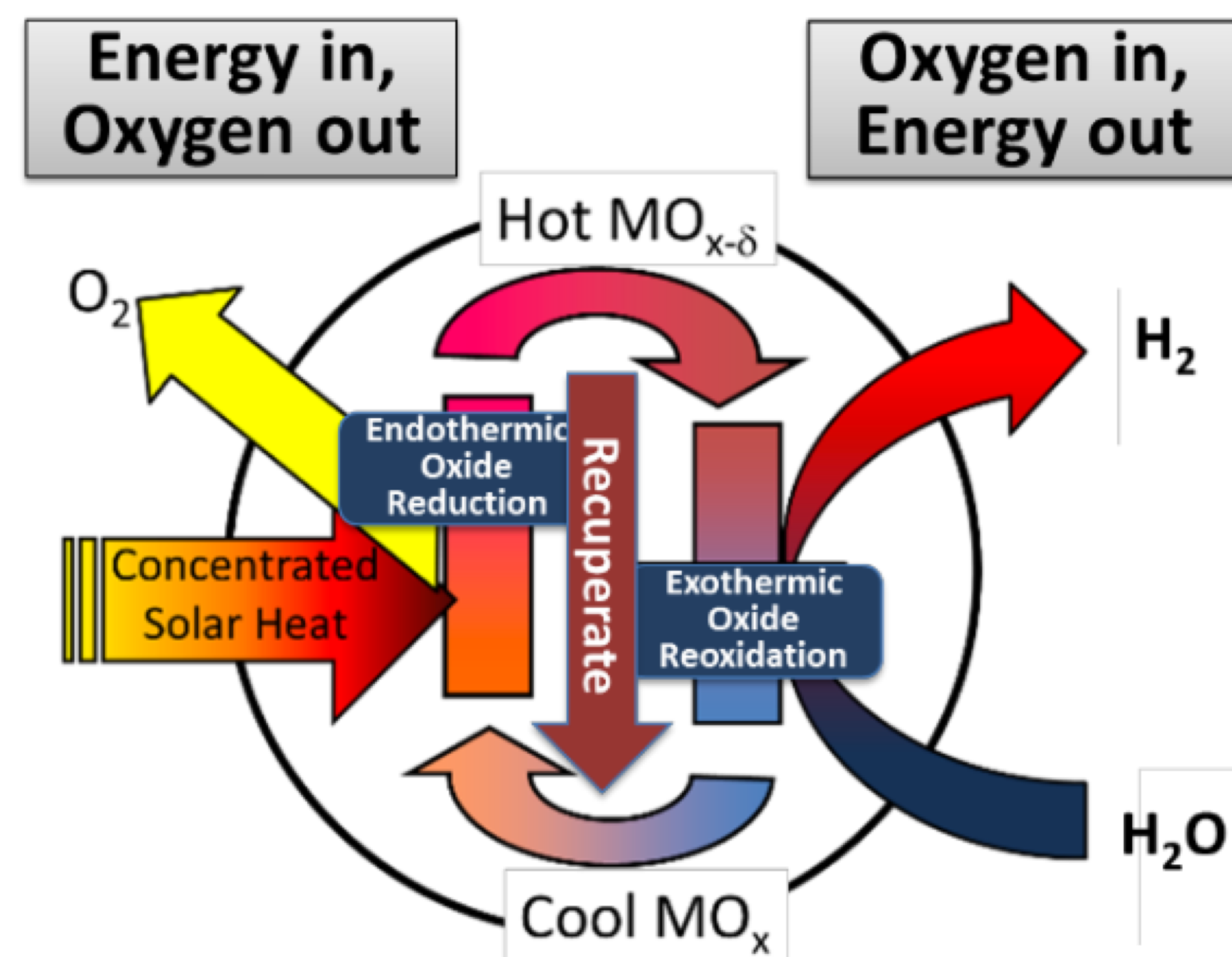
Need for a SCAN+U framework to describe the energetics of transition metal oxides

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Introduction

Solar Thermochemical (STC) Technology – sustainable fuel production



Generating reusable fuel or fuel precursors from solar energy is important for developing carbon-neutral energy technologies

Theoretically, STC can achieve high solar-to-fuel efficiencies [Ind. Eng. Chem. Res. 51, 11828 (2012)]

- Thermochemical: > 30%
- Photoelectrolysis: < 15%
- Photochemistry: < 5%
- Higher efficiencies by utilizing entire solar spectrum

Thermal reduction (TR)

- Oxide substrate heated to high temperatures to induce oxygen deficiency

Steam/CO₂ Gas Splitting (GS)

- Oxygen-deficient oxide cooled to a lower temperature, in a metastable manner, and spontaneously splits steam/CO₂

Efficiency and fuel yield of STC depends on oxide precursor

- CeO₂ is current state-of-the-art
- Better candidates are needed

Figure: Two-step thermochemical cycle splitting steam to generate reusable H₂ and/or CO. Generation of a CO+H₂ mixture is a fuel precursor that can be used to generate sustainable re-usable fuels. Figure courtesy: Dr. Ellen Stechel, Arizona State University.

Identify oxide candidates to improve STC efficiency and yield

So far, three material classes have been explored for STC applications, all possessing redox-active metallic species

AO₂-Fluorite: CeO₂/Zr-doped CeO₂; Ce⁴⁺/Ce³⁺ ABO₃-Perovskite: (La,Sr)MnO₃; Mn⁴⁺/Mn³⁺/Mn²⁺ AB₂O₄-Spinel: Fe(Fe,Al)₂O₄; Fe³⁺/Fe²⁺

Any theory-based evaluation, e.g. density functional theory (DFT)-based calculations, of potential STC candidates requires a rigorous and accurate description of reduction and oxidation energetics of transition-metal oxides (TMOs) and rare-earth oxides (REOs)

The strongly constrained and appropriately normed (SCAN) functional was recently developed [Phys. Rev. Lett. 115, 036402 (2015)] to describe electronic exchange-correlation (XC) within the DFT framework and impressively satisfies 17 known constraints for any XC functional

Does SCAN accurately describe the redox energetics, electronic properties, and ground-state polymorphism in TMOs and REOs, especially in the above material classes relevant for STC?

Methodology

Density functional theory-based calculations

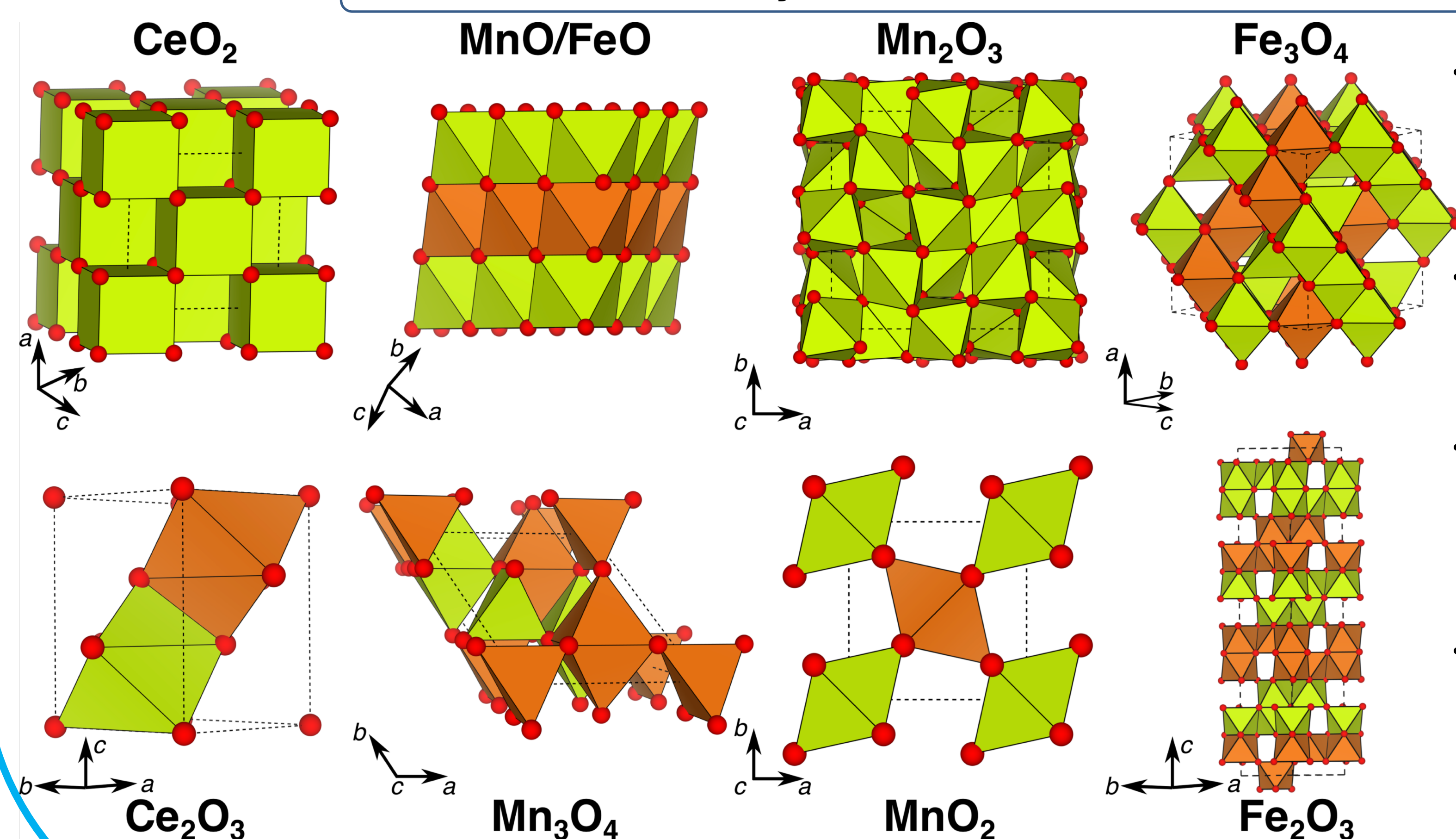
- DFT as implemented in the Vienna ab-initio simulation package and using the all-electron, frozen-core projector augmented wave potentials; planewave-basis kinetic energy cutoff: 520 eV; Γ -centered k -point spacing of $\sim 0.03 \text{ \AA}^{-1}$
- SCAN+U calculations done using the rotationally invariant framework, with the U applied only on transition-metal or rare-earth redox centers
- Band-gaps evaluated using total density of states (DOS) calculations

For a given oxidation reaction, $MO_x + \frac{z-x}{2} O_2 \rightarrow MO_z$, we can define experimental and theoretical oxidation enthalpies

$$\Delta H_o^e = \frac{H_{MO_z}^0 - H_{MO_x}^0}{\frac{z-x}{2}} \quad \Delta H_o^c = \frac{E_{MO_z}^{SCAN+U} - E_{MO_x}^{SCAN+U} - \frac{z-x}{2} E_{O_2}^{SCAN}}{\frac{z-x}{2}} \quad H: \text{experimental enthalpy at 298 K, 1 atm} \quad E: \text{calculated internal energy at 0 K}$$

Optimal U minimizes the absolute error between experimental and theoretical enthalpies

Crystal Structures



The structures displayed here are the ground-state configurations within the SCAN+U framework, at the optimal U value

Electronic spin of each metal atom is initialized to its highest spin state in all calculations

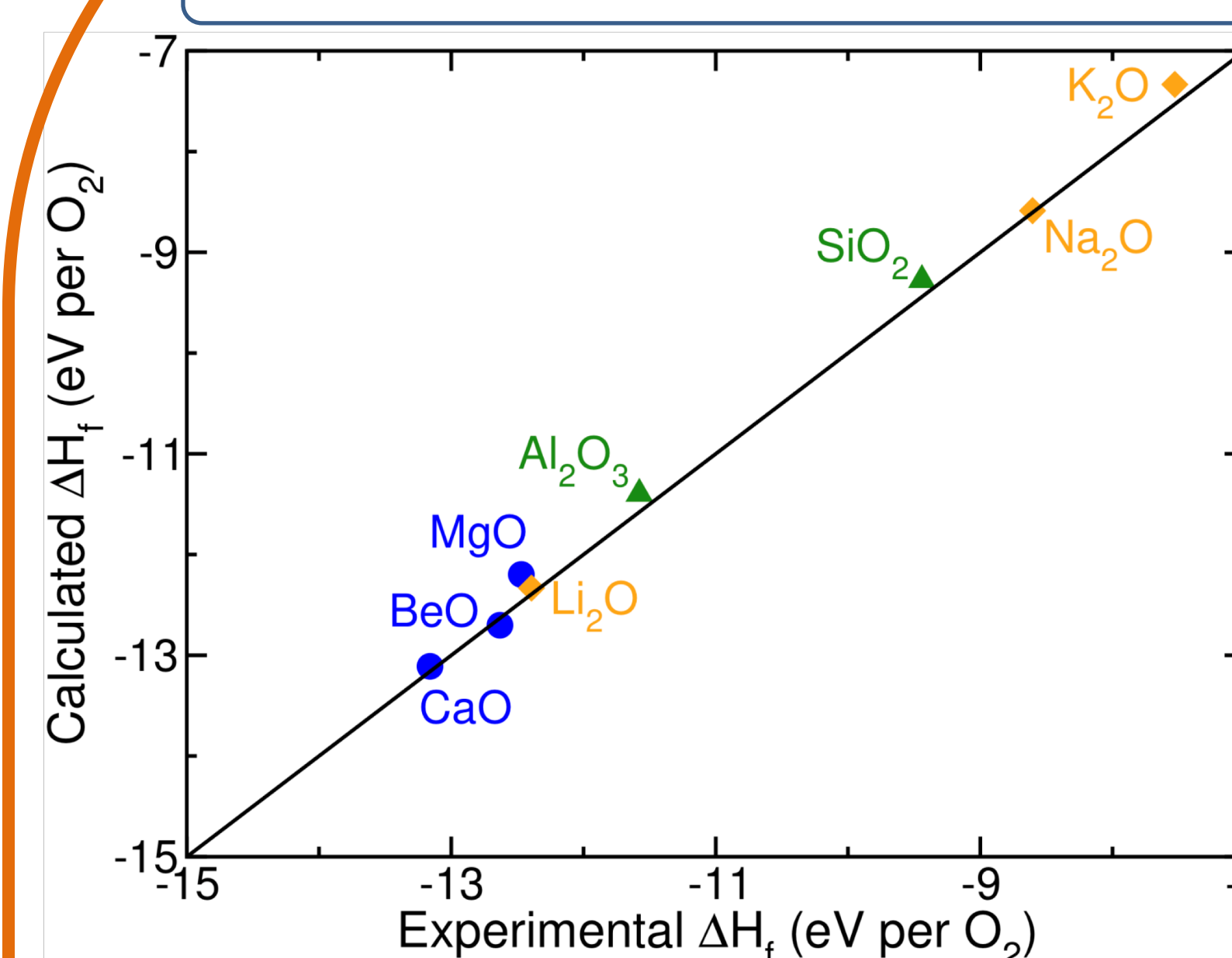
For main-group oxide and element calculations: corresponding ground-state structures of oxides and elements are used

O₂ molecule and O-atom: 15Å × 16Å × 17Å asymmetric cell used to obtain triplet spin ground states

Figure: Crystal structures of all TMOs and REOs considered. Yellow and orange polyhedra indicate metal atoms adopting up and down magnetic moments. All crystal structures obtained from the Inorganic Crystal Structure Database (ICSD).

Results

Oxides in DFT-SCAN

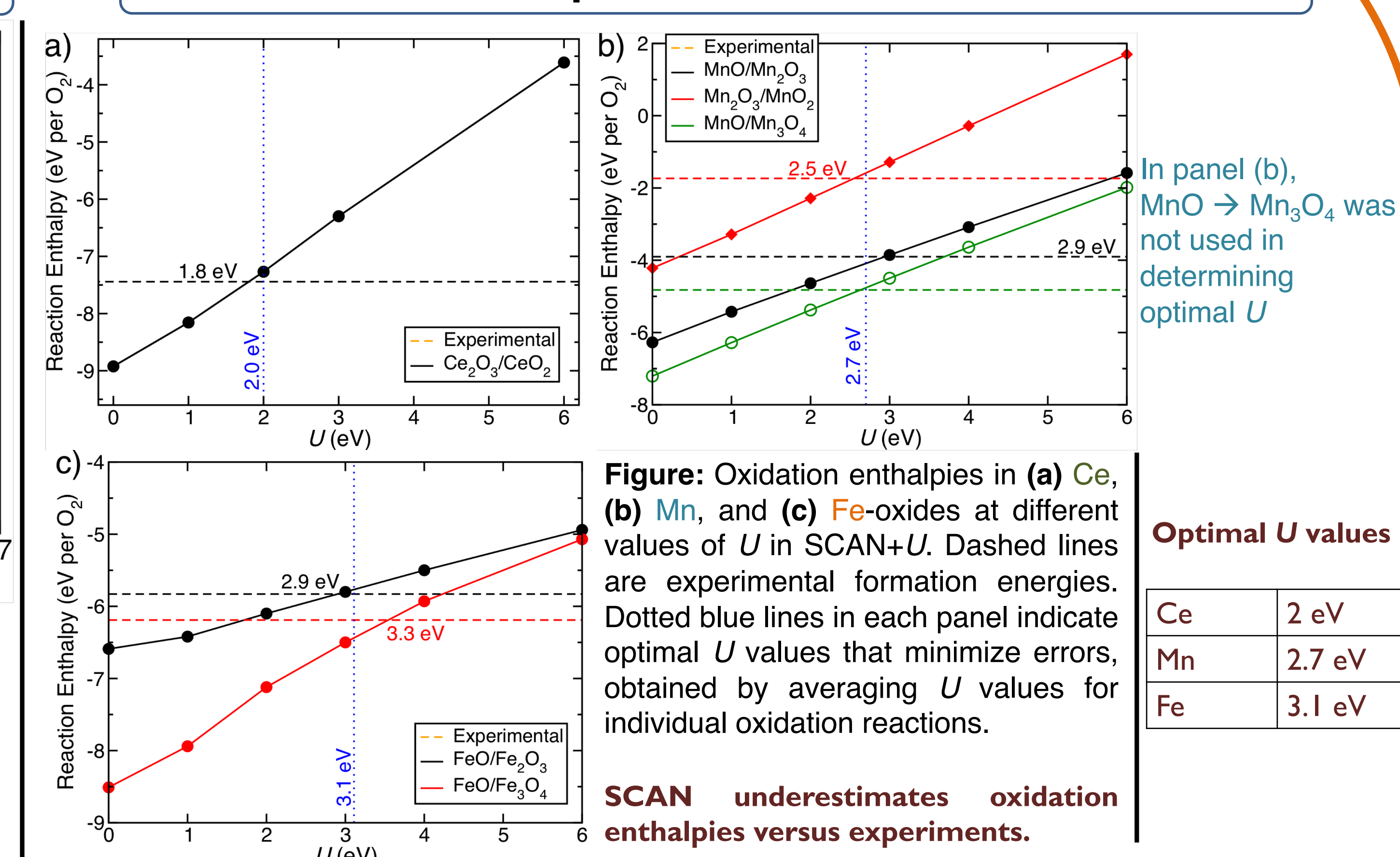


Good agreement between DFT-SCAN formation energies of main group (s and p) oxides versus experimental data

O₂ bond dissociation energy by DFT-SCAN ~ 5.15 eV is in excellent agreement with experiments (5.12-5.23 eV)

SCAN describes O₂ molecule accurately – no errors in oxide formation energies

Optimal U values



In panel (b), MnO \rightarrow Mn₂O₄ was not used in determining optimal U

Optimal U values

Ce	2 eV
Mn	2.7 eV
Fe	3.1 eV

SCAN underestimates oxidation enthalpies versus experiments.

Polymorph selection in Ce₂O₃

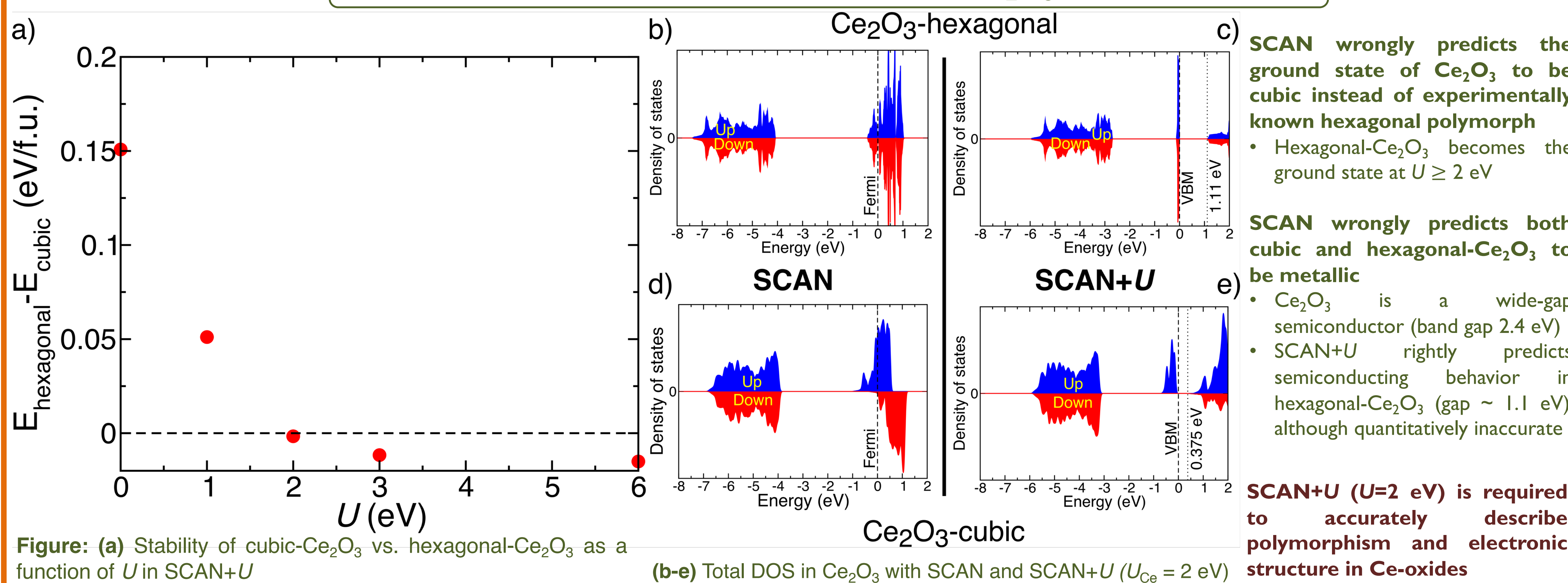


Figure: (a) Stability of cubic-Ce₂O₃ vs. hexagonal-Ce₂O₃ as a function of U in SCAN+U

(b-e) Total DOS in Ce₂O₃ with SCAN and SCAN+U ($U_{Ce} = 2$ eV)

SCAN wrongly predicts the ground state of Ce₂O₃ to be cubic instead of experimentally known hexagonal polymorph

- Hexagonal-Ce₂O₃ becomes the ground state at $U \geq 2$ eV

SCAN wrongly predicts both cubic and hexagonal-Ce₂O₃ to be metallic

- Ce₂O₃ is a wide-gap semiconductor (band gap 2.4 eV)
- SCAN+U rightly predicts semiconducting behavior in hexagonal-Ce₂O₃ (gap ~ 1.1 eV), although quantitatively inaccurate

SCAN+U ($U=2$ eV) is required to accurately describe polymorphism and electronic structure in Ce-oxides

Magnetic configurations in Mn₂O₃

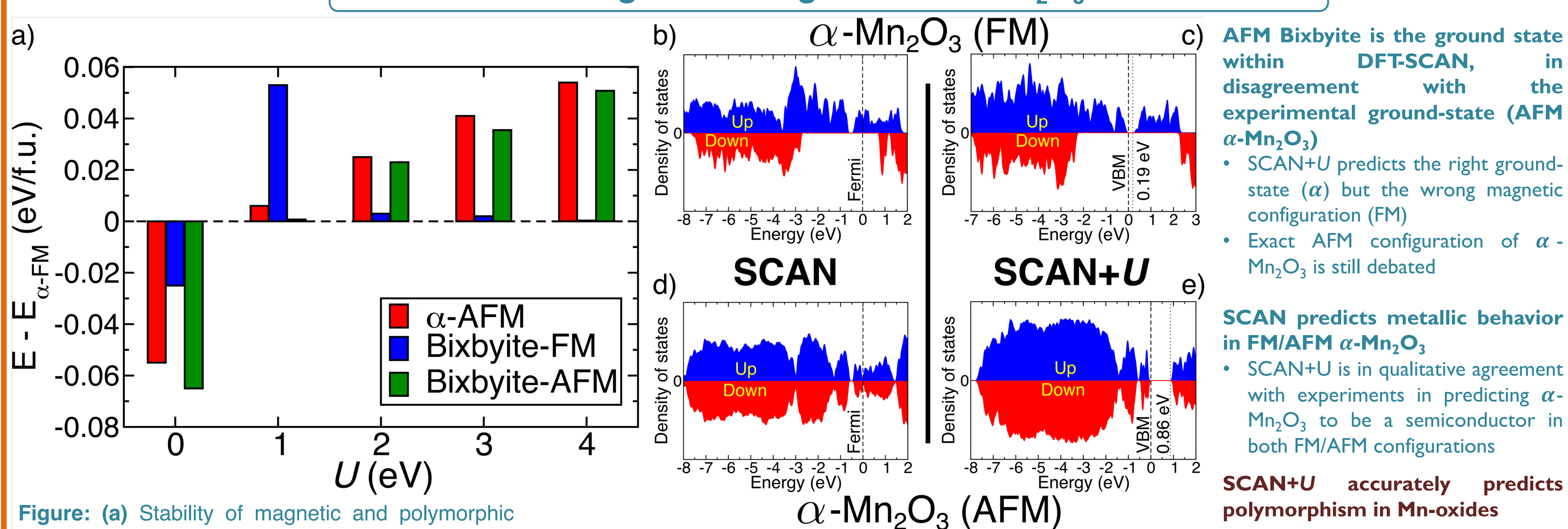


Figure: (a-b) Total DOS in ferrimagnetic spinel-Fe₃O₄, calculated using SCAN and SCAN+U ($U_{Fe} = 3.1$ eV)

(b-e) Total DOS calculations, using SCAN and SCAN+U in FM and AFM α -Mn₂O₃. SCAN+U calculation corresponds to $U_{Mn} = 2.7$ eV

AFM Bixbyite is the ground state within DFT-SCAN, in disagreement with the experimental ground-state (AFM α -Mn₂O₃)

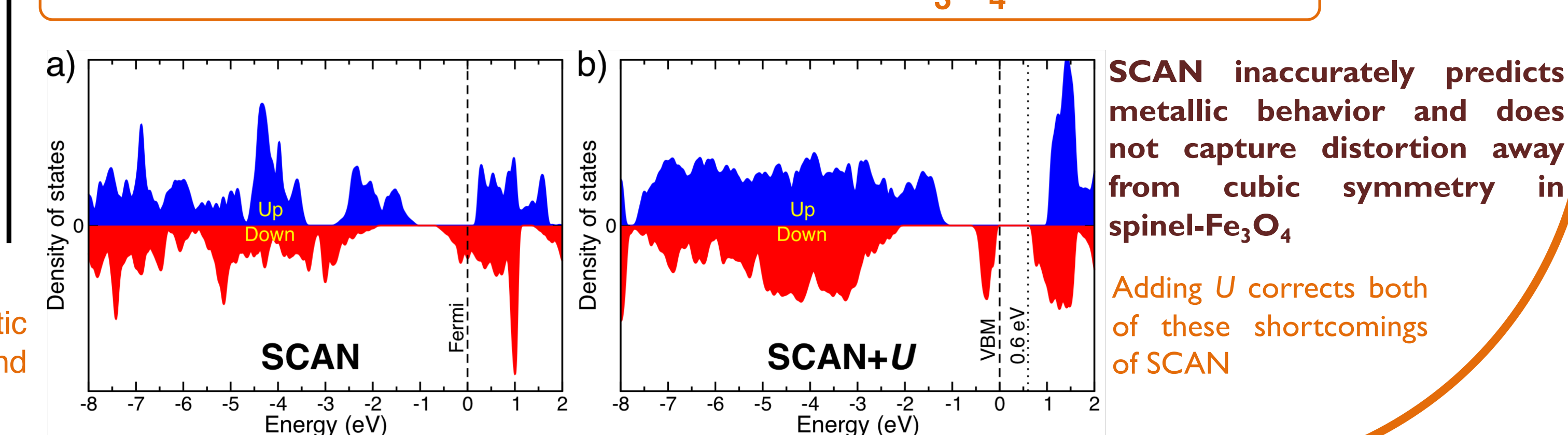
- SCAN+U predicts the right ground-state (α) but the wrong magnetic configuration (FM)
- Exact AFM configuration of α -Mn₂O₃ is still debated

SCAN predicts metallic behavior in FM/AFM α -Mn₂O₃

- SCAN+U is in qualitative agreement with experiments in predicting α -Mn₂O₃ to be a semiconductor in both FM/AFM configurations

SCAN+U accurately predicts polymorphism in Mn-oxides

Electronic Structure in Fe₃O₄



SCAN inaccurately predicts metallic behavior and does not capture distortion away from cubic symmetry in spinel-Fe₃O₄

Adding U corrects both of these shortcomings of SCAN

Conclusions

- STC requires oxide substrates that yield higher efficiencies and a theoretical tool accurately describing redox energetics can aid in identification of promising candidates
- The SCAN XC functional within DFT, while accurately describing the formation enthalpies of main group oxides and the oxygen dissociation energy, displays shortcomings in identifying the ground-state polymorph and/or the electronic structure in TMOs and REOs – systems of interest in STC
- Adding a +U to SCAN corrects several imprecise predictions of SCAN, and the resulting SCAN+U framework can be used to screen for candidates for STC applications

References

G. Sai Gautam and E. A. Carter, *Phys. Rev. Mater.* 2, 095401 (2018)

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