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WHY OXIDES?

WIDE DIVERSITY OF PROPERTIES

- Metals: CrO2, Fe3O4 T>120K
- Insulators: Cr2O3, SrTiO3,CoO
- Semiconductors: Cu2O
- Semiconductor metal: VO2, V2O3, Ti4O7
- Superconductors: La(Sr)2CuO4, LiTiO4, YBCO
- Piezo and Ferroelectric: BaTiO3
- Catalysts: Fe,Co,Ni Oxides
- Ferro and Ferri magnets: CrO2, gammaFe2O3
- Antiferromagnets: alfa Fe2O3, MnO,NiO ---
- Ionic conductors (batteries) LixNi1-xO
- Oxide fuel cells use manganites and cobaltates



- Introduction electron structure of atoms and ions, oxidation states
- Structure bulk and surfaces, thermodynamics
- Electronic structure, functional
- Case studies
 - 1. CH₄/PdO
 - 2. Thin oxide layers
 - 3. Fe_2O_3/TiO_2

PERIODIC TABLE TO PROPERTIES: STEREOTYPICAL THEORIST'S VIEW

PeriodicTable



Ignore details: write Quantum Field Theory

$$rac{\kappa}{2}\epsilon^{\mu
u\lambda}\mathbf{A}_{\mu}\partial_{
u}\mathbf{A}_{\lambda}+...$$



official name designated by the IUPAC • 1 kJ/mol ≈ 96.485 eV. · all elements are implied to have an

axidation state of zero.





Maximal oxidation states for 2nd & 3rd row transition metals in Groups 3 thru 8 *increase* from +3 for Y and La to +8 for Ru and Os. Going farther to right, maximum oxidation state *decreases*, reaching +2 for elements of Group 12

GENERAL FEATURES OF TRANSITION METALS

The electronic structures of the d block elements shown are:



3*d* subshell fill based on aufbau principle & Hund's rule You will notice that the pattern of filling isn't entirely tidy! It is broken at both chromium and copper.

FORMING TRANSITION METAL IONS

When metals do oxidize, they lose electrons, and so form positive ions. Some transition metals only make one type of ion, for example, silver only forms Ag⁺ ions and zinc only forms Zn²⁺ ions.

However, most transition metals can form more than one type of ion, as they can lose different numbers of electrons.

The rule is quite simple. Take the 4s electrons off first, and then as many 3d electrons as necessary to produce the correct positive charge One of the key features of transition metal chemistry is the wide range of oxidation states (oxidation numbers) that the metals can show.

Iron: has two common oxidation states (+2 and +3) in, for example, Fe^{2+} and Fe^{3+} . It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO_4^{2-} .

Manganese: has a very wide range of oxidation states in its compounds. For example: +2 in Mn^{2+} , +3 in Mn_2O_3 , +4 in MnO_2 , +6 in MnO_4^{2-} , +7 in MnO_4^{-1}

DESCRIPTIVE CHEMISTRY OF TRANSITION METALS:

| Scandium | [Ar]4s ² 3d ¹ | +3 | |
|-----------|---|----------------|--|
| Titanium | $[Ar]4s^23d^2$ | +4 | Strong, light, corrosion-resistant, steel alloys, white pigments, ore is rutile |
| Vanadium | $[Ar]4s^23d^3$ | +2, +3, +4, +5 | Catalysts, steel alloys |
| Chromium | [Ar]4s ¹ 3d ⁵ | +2, +3, +6 | Colorful, $Cr_2O_7^{2-}OA$, stainless steel, chrome plating |
| Manganese | [Ar]4s ² 3d ⁵ | +2, +4, +7 | MnO_4^-OA , MnO_2 catalyst, Mn steels |
| Iron | [Ar]4s ² 3d ⁶ | +2, +3 | Ores are hematite, magnetite, and pyrite (fool's gold), steel, hemoglobin, blast furnace, magnetic |
| Cobalt | $[Ar]4s^23d^7$ | +2, +3 | Blue cobalt glass, , AlNiCo, magnetic |
| Nickel | $[Ar]4s^23d^8$ | +2 | Coins, AlNiCo, Monel, magnetic |
| Copper | [Ar]4s ¹ 3d ¹⁰ | +1, +2 | Coins, brass, bronze, Statue of Liberty, patina, electric wires, ores are chalcocite, chalcopyrite and malachite, unreactive w/ HCl and H ₂ SO ₄ but very reactive w/HNO ₃ |
| Zinc | $[Ar]4s^23d^{10}$ | +2 | Coins, brass, biochemistry, RA |
| | | | |
| Gold | [Xe]6s ¹ 4f ¹⁴ 5d ¹⁰ | +1, +3 | Coins, jewelry, soft as pure metal, alloys are harder, CN ⁻ used to extract Au from ores |
| Silver | [Kr]5s ¹ 4d ¹⁰ | +1 | Coins, jewelry, most electrically conductive of all metals |
| Mercury | $[Xe]6s^{2}4f^{14}5d^{10}$ | +1, +2 | Quicksilver, poisonous, "mad as a hatter", Minimata |

METAL OXIDES AND COLOUR

As most metals can form different ions, this means they can form multiple compounds.





Copper can form Cu^+ , which can make the red compound copper (I) oxide – Cu_2O .

Copper can also form Cu²⁺, which can make the black compound copper (II) oxide – CuO.

METAL OXIDES AND COLOUR

Most transition metals form coloured compounds. For example:

Iron (II) oxide (FeO₂) is black.

Iron (III) oxide (Fe₂O₃) is red/brown

 when hydrated this is rust.

 Copper (II) sulfate crystals (CuSO₄.H₂O) is blue – these can be turned white by heating the crystals to remove the water.









Structure bulk and surfaces

DENSITY FUNCTIONAL THEORY

The KS decomposition is important as it separates contributions that are (in principle) possible to compute from those that are complicated.



The E_{xc} is on an absolute scale a minor contribution to the total energy. It is crucial that the kinetic energy is evaluated to a high accuracy (this is not done in Thomas-Fermi theory).

DENSITY FUNCTIONAL THEORY

The KS decomposition is important as it separates cr are (in principle) possible to compute from those *' tions that



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Graphs of connectivity in crystals: Atoms are nodes and edges (the lines that connect nodes) indicate short (near-neighbor) distances.

 CO_2 : The molecular structure is O=C=O. The graph is: Each C connected to 2 O, each O connected to a 1 C



OsO₄: The structure comprises isolated tetrahedra (molecular). The graph is below: Each Os connected to 4 O and each O to 1 Os



Monovalent ions: A_2O





Linear coordination is unusual. Found usually in Cu⁺ and Ag⁺.

Na₂O (anti-fluorite)





4-coordination for Na⁺ and 8coordination for O^{2–} are unusual.

Divalent ions: AO

ZnO (wurtzite), sp³





PbO (litharge), lone pairs









Ubiquitous for AO oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, ...

Tetravalent ions: AO₂

TiO₂ (rutile)





 $\rm TiO_2$ also crystallizes as anatase and brookite.

SiO₂ takes on this structure, and can be quenched to it, (stishovite) under pressure.

CeO₂ (fluorite)





Also the structure of ThO_2 , and of ZrO_2 and HfO_2 at elevated temperatures.

Ordered variants abound.

α -Al₂O₃ (corundum)





Also the structure of Cr_2O_3 and Fe_2O_3 .

 Ga_2O_3 does funny things.

 In_2O_3 is different (bixbyite).

Perovskite

BaZrO₃



LaMnO₃Pnma (Jahn-Teller distorted)



Note that the space group *Pnma* (#62) can be written in a variety of ways.

+4/6

Zr

This is the most common perovskite space group.



+2/12

Hexagonal ABO₃ structures



Ferroelectric YMnO₃ ("YAlO₃")



LiNbO₃ (ferroelectric R3c)



Unusual 5-fold coordination (trigonal bibyramid) of MnO₅

Spinel AB₂O₄



Ubiquitous structure when ions have similar sizes, around 0.6 Å. A is tetrahedrally coordinated, and B octahedral (actually with a slight trigonal distortion).

In general, lower oxidation states and smaller bandwidths than in perovskites.



Many oxides have similar lattice constants allowing for a good match at the interfaces



What would happen if we could mix materials with different properties?

Potential for novel behavior

P. Yu, et al. Materialstoday, 7-8, 320 (2012) D. G. Schlom *et al.*, Annu. Rev. Mater. Res. 37, 589 (2007)

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Some surprises at the interfaces between two oxides

The interface between two good insulators (LaAIO₃ and SrTiO₃) is metallic and even, under certain conditions, superconducting



N. Reyren et al., Science 317, 1196 (2007) A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004)

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Structure bulk and surfaces

CUBIC STRUCTURES E.G. MGO



RUTILE STRUCTURES E.G. RUO₂



Cutting plane and corresponding surface termination of RuO_2 (110) surface

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SURFACE TERMINATIONS ACCORDING TO TASKER



(a) Type 1 ($Q = 0, \mu = 0$)



(b) Type 2 ($Q \neq 0, \mu = 0$)



(c) Type 3 ($Q \neq 0$, $\mu \neq 0$)

P.W. Tasker, J. Phys. C: Solid State Phys. 12 4977 (1979)

TYPES OF RECONSTRUCTION



K₃C₆₀: R. Hesper *et al*., Phys. Rev. B 62, 16046 (2000). NiO(111): D. Cappus *et al*., Surf. Sci. 337, 268 (1995). Kresse et al. Phys. Rev. B 68 (2003) 245409 M.A. Hossain *et al.*, Nat. Phys. 4, 527 (2008) Lauritsen et al. ACS Nano 5 (2011) 5987

OCTAPOLAR RECONSTRUCTION OF MGO (111) SLAB



A. Wander, I. J. Bush, and N. M. Harrison Phys. Rev. B 68, 233405 C. Franchini, V. Bayer, R. Podloucky, G. Parteder, S. Surnev, and F. P. Netzer Phys. Rev. B 73, 155402

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LSDA BAND STRUCTURE OF CAO (111) SLAB TERMINATED WITH CA AND O



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AB INITIO ATOMISTIC THERMODYNAMICS

Motivation:

- extend length scale
- consider finite temperature effects

Approach:

- separate system into sub-systems (exploit idea of reservoirs!)
- calculate properties of sub-systems separately (cheaper...)
- connect by implying equilibrium between sub-systems

Drawback:

- no temporal information
 - ("system properties after infinite time")
- equilibrium assumption

Ab initio atomistic thermodynamics and statistical mechanics of surface properties and functions K. Reuter, C. Stampfl and M. Scheffler, Handbook of Materials Modeling Vol. 1, (Ed.) S. Yip, Springer (Berlin, 2005).



AB INITIO ATOMISTIC THERMODYNAMICS

$$\gamma_{\text{surf.}} = 1/A \left[G_{\text{surf.}}(N_{\text{O}}, N_{\text{M}}) - N_{\text{O}} \mu_{\text{O}} - N_{\text{M}} \mu_{\text{M}} \right]$$



Forget about *F*^{vib} and *F*^{conf} for the moment:

 $\gamma(T,p) \approx (E_{\text{surf.}}^{(\text{slab})} - N_{\text{M}} E_{\text{M}}^{\text{bulk}})/A - N_{\text{O}} \mu_{\text{O}}(T,p)/A$

OXIDE FORMATION ON PD(100)



 $p_{O_2}(atm)$ 600 K 10⁻²⁰ 10¹⁰ 10 $10^{-50}\,10^{-40}\,10^{-30}\,10^{-20}\,10^{-10}$ 300 K 1 -100 γ - γ_{clean} (meV/Ų) clean Pd(100) 0 P(2 × 2) 100 adlay surf metal bulk oxide 200-1.5 -1.0 -0.5 -2.0 $\Delta \mu_{0}$ (eV)

OXIDE FORMATION ON PD(100)



Rogal et al, PRB 75 (2007) 205433

Anders Hellman, Department of Physics, Chalmers

SURFACE STRUCTURE OF RUO₂ IN OXYGEN EXCESS



K. Reuter and M. Scheffler, PRB, 65, 035406 (2001)

SURFACE STRUCTURE OF Fe_2O_3 in oxygen excess



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Insulators have very low conductivity, but when measured, the conductivity is found to increase with an increase in temperature. In general, there is a huge band gap between both the valence band and the conduction band. Semi-conductors are materials with an conductivity that increases with increasing temperature. Semi-conductors characteristically have a band gap between the valence and conduction bands that is smaller than that found in the insulators. Metals are conducting, and the conductivity decreases as the temperature increases. Usually the valence band is not completely filled. Other properties of metals are that they have a luster and are very malleable. A diagram of the band structure can be seen below



Thumb rules for the k-mesh

The product, k*a, between the number of k-points, k, in any direction, and the length of the basis vector in this direction, a, should be

k*a ~ 30 Å, for metals k*a ~ 20 Å, for semiconductors k*a ~ 15 Å, for insulators

$$E[\rho] = \sum_{i}^{occ} \epsilon_{i} - \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} v_{\mathsf{XC}}(\mathbf{r})n(\mathbf{r}) + E_{xc}[n(\mathbf{r})]$$

Decomposition of DOS into contributions from different atomic functions φ_i :



CRYSTAL FIELD THEORY

Bonding model explaining many important properties of transition-metal complexes:

Central assumption are metal-ligand connections with electrostatic interactions between a central metal ion and a set of negatively charged ligands (or ligand dipoles) arranged around metal ion.

Octahedral hole

The octahedral hole is surrounded by six atoms.





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CRYSTAL FIELD THEORY

The $d_x^2 - y^2$ and d_z^2 orbitals (e_g orbitals) point directly at the six (-) charges, which increase their energy compared with a spherical distribution of negative charge. The d_{xy} , d_{xz} , & d_{yz} (t_2g orbitals) are all oriented at a 45° angle to the coordinate axes and point between the 6 (-) charges, which decreases their energy compared with a spherical distribution of charge.



CRYSTAL FIELD THEORY

Additional e⁻'s placed in **lowest orbital** available while keeping their spins *parallel*



Metal ions with d⁴, d^5 , d^6 , or $d^7 e^-$ configurations can be either high spin or low spin, depending on magnitude of Δ_0

BAND GAP VARIATION

| Compound | Eg (eV) | γ* |
|--------------------------------|---------|------|
| P.O. | 10.5 | 2 15 |
| BeU | 10.5 | 5.15 |
| B_2O_3 | 8.45 | 3.45 |
| MgO | 7.8 | 2.86 |
| Al ₂ O ₃ | 6.96 | 3.18 |
| Si ₂ O ₂ | 9.24 | 3.38 |
| CaO | 6.26 | 2.26 |
| TiO ₂ | 3.6 | 3.12 |
| Cr ₂ O ₃ | 2.58 | 3.22 |
| MnO | 4 | 3.13 |
| FeO | 3.2 | 3.33 |
| CoO | 3.2 | 3.37 |
| NiO | 2.86 | 3.38 |
| Cu ₂ O | 2.04 | 3.38 |
| ZnO | 3.3 | 3.25 |
| Ga ₂ O ₃ | 5.4 | 3.3 |
| GeO ₂ | 5.35 | 3.44 |
| Se ₂ O ₃ | 5 | 3.64 |
| SrO | 6.5 | 2.11 |

| MoO ₃ | 2.74 | 3.51 |
|--------------------------------|------|------|
| CdO | 2.5 | 3.24 |
| In ₂ O ₃ | 3.55 | 3.31 |
| SnO ₂ | 3.57 | 3.41 |
| BaO | 5.2 | 1.9 |
| La_2O_3 | 5.5 | 2.5 |
| CeO ₂ | 3.78 | 2.54 |
| Pr ₂ O ₃ | 3.8 | 2.56 |
| Nd_2O_3 | 4.6 | 2.58 |
| Sm ₂ O ₃ | 5 | 2.64 |
| Eu ₂ O ₃ | 4.3 | 2.69 |
| Gd_2O_3 | 5.4 | 2.69 |
| Tb ₂ O ₃ | 3.8 | 2.69 |
| Dy ₂ O ₃ | 4.9 | 2.72 |
| Ho ₂ O ₃ | 5.3 | 2.74 |
| Er ₂ O ₃ | 5.3 | 2.76 |
| Tm ₂ O ₃ | 5.4 | 2.77 |
| Yb ₂ O ₃ | 4.9 | 2.5 |
| Lu_2O_3 | 5.5 | 2.8 |
| HgO | 2.58 | 3.43 |
| Tl ₂ O ₃ | 2.25 | 3.19 |
| PbO | 2.75 | 3.57 |
| Bi ₂ O ₃ | 2.85 | 3.44 |

THE EXCHANGE-CORRELATION LADDER



Mardirossian, Head-Gordon, PCCP 16, 9904 (2014)

SIMULATIONS OF OXIDES



Heyd et al. J. Chem. Phys. 123, 174101 2005

Castelli, at al. Energy Environ. Sci., 2012, 5, 5814

NIO BULK





Ni²⁺: $3d^8$

- Rock salt structure
- AFM insulator (Exp. Gap ~4eV)



FE_2O_3 BULK



Figure 2: Density of states of bulk α -Fe₂O₃ calculated using (a) PBE, (b) PBE + U, (c) rPBE + U, (d) PBEsol + U, (e) HSE06, (f) PBE0 and (g) HSE (12 %). Color code: gray total DOS, red Fe 3d T_g, blue Fe 3d e_{2g}, green O 2p

B. Wang, et al. J. Phys.: Condens. Matter 30 (2018) 275002

FE₂**O**₃ SURFACE



Figure 14: Density of states of R-Fe-Fe-3O terminated surface calculated using PBE, PBE + U and hybrid functional: (a) PBE, (b) PBE + U, and (c) HSE(12%).

B. Wang, et al. J. Phys.: Condens. Matter 30 (2018) 275002



When simulating oxides: Structure is everything Right level of theory

WHAT CAN WE USE THIS FOR?

A PERSPECTIVE ON ACTIVE SITES: FROM NEAR-SIGHTEDNESS TO FAR-SIGHTEDNESS





Short range

Long range

WHAT IS ACTIVE PHASE OF PD DURING METHANE OXIDATION?



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OXIDATION OF PALLADIUM SURFACES



Adsorbed atoms $\theta = 0.25 \text{ ML}$

Surface oxide



Bulk oxide PdO



METHANE OXIDATION OVER PD(100) - EXPERIMENTS



Temperature ramp

A. Hellman, *et al.*, J. Phys. Chem. Lett. 3 (2012) 678 N.M. Martin, *et al.*, ACS Catalysis 4 (2014) 3330

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METHANE OXIDATION OVER PD(100) - EXPERIMENTS



N.M. Martin, et al., ACS Catalysis 4 (2014) 3330

METHANE DISSOCIATION OVER 1 ML PDO(101)



METHANE DISSOCIATION OVER 2 ML PDO(101)

TS



-0.14 eV

Intitial

0.66 eV

-0.43 eV

Final

A. Hellman, *et al.*, J. Phys. Chem. Lett. 3 (2012) 678 N.M. Martin, *et al.*, ACS Catalysis 4 (2014) 3330

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METHANE DISSOCIATION OVER PDO(101) LAYERS



A. Hellman, *et al.*, J. Phys. Chem. Lett. 3 (2012) 678 N.M. Martin, *et al.*, ACS Catalysis 4 (2014) 3330

METHANE ACTIVATION ON FREE-STANDING PDO(101)



METHANE ACTIVATION ON FREE-STANDING PDO(101)







METHANE ACTIVATION ON FREE-STANDING PDO(101)



METHANE DISSOCIATION OVER PD-AGO(101) LAYERS



A. Trinchero, et al., Phys. Status Solidi RRL 8, 605 (2014)

A PERSPECTIVE ON ACTIVE SITES: FROM NEAR-SIGHTEDNESS TO FAR-SIGHTEDNESS





Short range

Long range

DISPROPORTIONATION REACTION: $2NO_2 \leftrightarrow NO^+ + NO_3^-$



H. Grönbeck, J. Phys. Chem. B (2006)

EXPERIMENTAL EVIDENCE FOR NO₂ STABILIZATION

J. Phys. Chem. C 2009, 113, 7355–7363

7355

NO₂ Adsorption on Ag(100) Supported MgO(100) Thin Films: Controlling the Adsorption State with Film Thickness

David E. Starr, $^{\perp,\dagger}$ Christoph Weis, $^{\bigtriangledown,\ddagger}$ Susumu Yamamoto, $^{\#}$ Anders Nilsson, $^{\parallel}$ and Hendrik Bluhm*, †


O₂ ADSORPTION



A. Hellman, et al., JACS communication 131, 16636 (2009)

O₂ ADSORPTION



A. Hellman, et al., JACS communication 131, 16636 (2009)

LOW TEMPERATURE CO OXIDATION



A. Hellman, et al., JACS communication 131, 16636 (2009)

CONTRIBUTIONS TO THE STABILIZATION



Frondelius et al., Phys. Rev. B. 78, (2008) 085426

Anders Hellman, Department of Physics, Chalmers

CABRERA-MOTT MODEL OF METAL OXIDATION



N. Cabrera and N. F. Mott, Rept. Progr. Phys. 12 (1948-49) 163

Anders Hellman, Department of Physics, Chalmers

O₂ Adsorption Energy as a function of the number of Oxide Layers



J. Baran, et al., Phys. Rev. Lett. 114, (2014) 146103

Tuning the Limiting Thickness of Al₂O₃ on Al(111) with O₂ Pressure



J. Baran, et al., Phys. Rev. Lett. 114, (2014) 146103

Tuning the Limiting Thickness of Al₂O₃ on Al(111) with O₂ Pressure



N. Cai, et al., Phys. Rev. Lett. 107, 035502 (2011)

A PERSPECTIVE ON ACTIVE SITES: FROM NEAR-SIGHTEDNESS TO FAR-SIGHTEDNESS





Short range

Long range

PHOTOELECTROCHEMISTRY ON HEMATITE: A FIRST-PRINCIPLES VIEW

HEMATITE AS PHOTOANODE



Hematite: crystalline Fe₂O₃ (rust)



- Absorbs visible light (Eg ~2 eV)
- Inexpensive and abundant
- Stable in aqueous solutions with pH > 3
- X Position of conduction band is too low for HER
- X Indirect bandgap \rightarrow low $\eta_{absorption}$
- X low conductivity
- X short hole diffusion length (4-5 nm) \rightarrow low $\eta_{transport}$

MICROSCOPIC PROCESSES



- Photon absorption $\rightarrow \eta_{e-/h+}$
- Charge transport $\rightarrow \eta_{tr}$
- Charge transfer $\to \eta_{ct}$

A Hellman, B Wang, Inorganics 5 (2017), 37 B. Iandolo, et al., J. Mat. Chem. A, 3 (2015) 16896

MICROSCOPIC PROCESSES





A Hellman, B Wang, Inorganics 5 (2017), 37 B. landolo, et al., J. Mat. Chem. A, 3 (2015) 16896

TAILORING CHARGE RECOMBINATION IN PHOTOELECTRODES USING OXIDE NANOSTRUCTURES



B. landolo, B. Wickman, E. Svensson, D. Paulsson, A. Hellman, Nano Lett. 16, (2016) 2381

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FLAT HEMATITE



B. Wickman, et al., Scientific Report 7, (2017) 40500

FARADAIC EFFICIENCY & STABILITY



B. landolo, B.Wickman, B. Seger, I. Chorkendorff, I. Zoric, A. Hellman, PCCP, 16 (2014) 1271

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B. landolo, T. J. Antosiewicz, A. Hellman, I. Zoric, Phys. Chem. Chem. Phys., 15 (2013) 4947



B. landolo, T. J. Antosiewicz, A. Hellman, I. Zoric, Phys. Chem. Chem. Phys., 15 (2013) 4947

INHOMOGENEOUS BAND BENDING



R.T. Tung, Appl. Phys. Rev. 1, 011304 (2014)

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PHOTOCURRENT DENSITY VS. POTENTIAL MEASUREMENTS



i_{TiO2} ≈ 4 x i_{ref} i_{Cu2O} ≈ i_{ref} / 3

B. landolo, B. Wickman, E. Svensson, D. Paulsson, A. Hellman, Nano Lett. 16, (2016) 2381

Hypothesis



Hypothesis





Hypothesis



PHOTOCURRENT DENSITY VS. POTENTIAL MEASUREMENTS



B. landolo, B. Wickman, E. Svensson, D. Paulsson, A. Hellman, Nano Lett. 16, (2016) 2381

Anders Hellman, Department of Physics, Chalmers

COMPUTATIONAL DETAILS

- VASP(PAW method, energy cut-off 600 eV, k-point mesh of 3x3x1)
- □ DFT(PBE) + U calculations with a U J = 4.3 eV on Fe and U – J = 4.2 eV on Ti.
- ❑ Ab initio molecular dynamics was performed on the strained TiO₂ slab





BAND ALIGNMENT IN OXIDES

The valance band offset (VBO) is calculated via:

$$VBO = \Delta E_v + \Delta V$$

 ΔE_v is the difference between the two ¹ band edges and ΔV is the the lineup owing to the interface



L. Colombo et al., *Phys. Rev. B*, 44 (1991) 5572 X. Luo et al., *Phys. Rev. B*, 84 (2011) 195309 H. Seo et al., *Phys. Rev. B*, 86 (2012) 075301

BAND ALIGNMENT IN OXIDES

The valance band offset (VBO) is calculated via:

 $VBO = \Delta E_v + \Delta V$

 ΔE_v is the difference between the two band edges and ΔV is the the lineup owing to the interface



THE INDUCED DIPOLE AT THE INTERFACE

Charge density difference at the interface:

$$\Delta \rho = \rho(Fe_2O_3/TiO_2) - \rho(Fe_2O_3) - \rho(TiO_2)$$

The dipole density is calculated by:

$$\mu = \int \Delta \rho z \mathrm{d} z$$



CHANGE IN BAND ALIGNMENT OWING TO DOPING



Both the position and electronegativity of dopants determine the potential differences at the interface.

IDENTIFY THE CHARGE TRANSFER AND THE TRAPPED ELECTRONS



Ti, Si, and Sn doping work as n-type doping at the interface; the additional electron is transferred and trapped at amorphous TiO_2 side, forming Ti^{3+} species.

IDENTIFY THE CHARGE TRANSFER AND THE TRAPPED ELECTRONS



the hole is localized and trapped at its neighboring O atoms.

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THE INDUCED DIPOLE AT THE DOPED INTERFACE



SUMMERY PART I

- ❑ We have studied the built-in E-field at Fe₂O₃/TiO₂ interface using first-principle methods.
- Our results show that the defects created at the interface can strongly alter the interface dipole field both strength and direction, depending on the dopants and their doping positions.
- Our results can be employed for designing new nanostructured semiconducting heterojunction to enhancing the photoelectrochemical properties.

PHOTOCURRENT DENSITY VS. POTENTIAL MEASUREMENTS



B. landolo, B. Wickman, E. Svensson, D. Paulsson, A. Hellman, Nano Lett. 16, (2016) 2381

FROM THE LITERATURE WE KNOW THAT H-TREATMENT IS BENEFICIAL



G. Wang, et al., Nano Letters 11 (2011) 3026

H IN ANATASE TIO₂


BAND ALIGNMENT IN OXIDES



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H IN ANATASE TIO₂



H IN ANATASE TIO₂



H IN ANATASE TIO₂



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DOS OF H-TREATED AMORPHOUS-TIO₂



PHOTOCURRENT DENSITY VS. POTENTIAL MEASUREMENTS



CONCLUSIONS

- □ We have studied the Fe_2O_3/TiO_2 interface with firstprinciples methods and experiment. In particular, we focus on the built-in E-field at Fe_2O_3/TiO_2 interface.
- Our results show that defects at the interface strongly alter interface dipole field strength and direction, depending on the dopants and their doping positions.
- Our results show that H-treatment modify the TiO₂ phase, e.g. band-position and localized states.
- Our results can be employed for designing new nanostructured semiconducting heterojunction to enhancing the photoelectrochemical properties.

SUMMARY

- □ When simulating oxides: Structure is everything
- □ Right level of theory
- What are the relevant questions
- Oxides can be near-sighted and long-sighted (and of course anything in between.
- Photoelectrochemistry is truly an interdisciplinary field; a natural nexus between chemistry and physics.