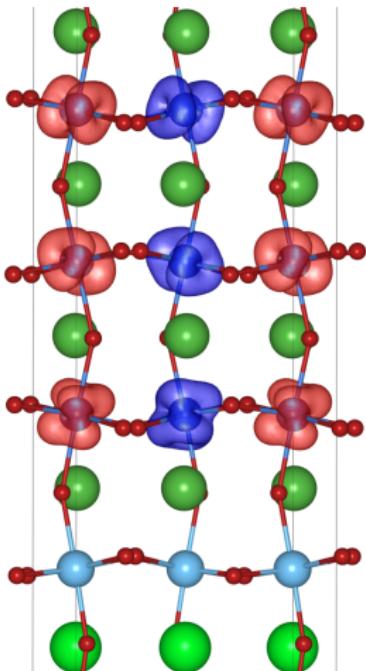


Oxide Heterostructures for Solar Cells

Elias Assmann

Institute of Solid State Physics, Vienna University of Technology

WIEN2013@PSU, Aug 14



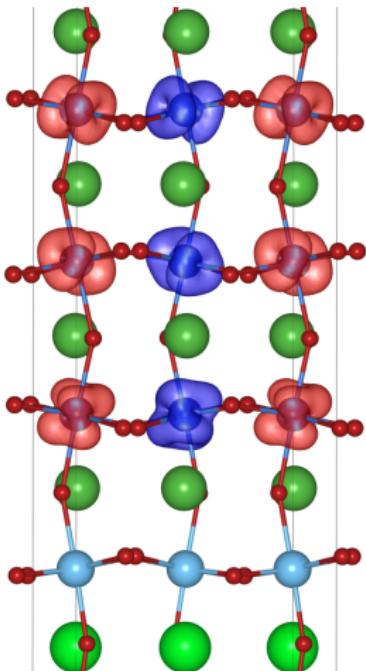
- ▶ $\text{LaVO}_3|\text{SrTiO}_3$ proposed as photovoltaic absorber.
Phys. Rev. Lett. **110**, 078701 (2013)
 - 1 large intrinsic electric field
 - 2 conducting interface(s)
 - 3 direct gap of 1.1 eV
 - 4 flexible multijunction design
- ▶ Outlook: dynamical mean-field theory for correlated heterostructures

Oxide Heterostructures for Solar Cells

Elias Assmann

Institute of Solid State Physics, Vienna University of Technology

WIEN2013@PSU, Aug 14



- ▶ $\text{LaVO}_3|\text{SrTiO}_3$ proposed as photovoltaic absorber.
Phys. Rev. Lett. **110**, 078701 (2013)
 - 1 large intrinsic electric field
 - 2 conducting interface(s)
 - 3 direct gap of 1.1 eV
 - 4 flexible multijunction design
- ▶ Outlook: dynamical mean-field theory for correlated heterostructures

Prototype Heterostructure: LaAlO₃|SrTiO₃

- ▶ cubic perovskites [room temp]
- ▶ wide-gap band insulators
- ⇒ two types of interfaces [(001) direction]:

p-type

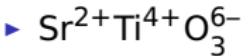
- ▶ (AlO₂)⁻|SrO
- ▶ insulating

n-type

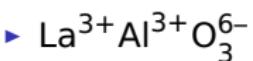
- ▶ (LaO)⁺|TiO₂
- ▶ conducting: insulator + insulator = metal
- ▶ interesting features, e.g., two-dimensional electron gas, superconducting

Polarized Layers in $\text{LaAlO}_3\text{SrTiO}_3$

Formal valences:



► neutral SrO, TiO_2 layers



► alternatingly charged $(\text{LaO})^+, (\text{AlO}_2)^-$ layers

1-	$\text{Al}^{3+}\text{O}_2^{4-}$
1+	$\text{La}^{3+}\text{O}^{2-}$
1-	$\text{Al}^{3+}\text{O}_2^{4-}$
1+	$\text{La}^{3+}\text{O}^{2-}$
0	$\text{Ti}^{4+}\text{O}_2^{4-}$
0	$\text{Sr}^{2+}\text{O}^{2-}$
0	$\text{Ti}^{4+}\text{O}_2^{4-}$
0	$\text{Sr}^{2+}\text{O}^{2-}$

adapted from N. Nakagawa et al., Nature Mat. 5, 204 (2006)

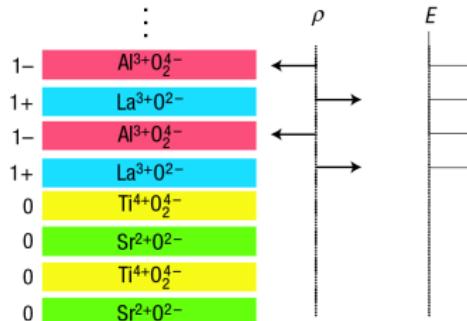
- ⇒ Plate capacitor model: large internal electric field ($\sim \frac{1}{\epsilon} 47 \text{ V}/\text{unit cell}$), potential gradient
- ⇒ “polarization catastrophe”

Polarized Layers in $\text{LaAlO}_3\text{SrTiO}_3$

Formal valences:

- ▶ $\text{Sr}^{2+}\text{Ti}^{4+}\text{O}_3^{6-}$
 - ▶ neutral SrO, TiO_2 layers

- ▶ $\text{La}^{3+}\text{Al}^{3+}\text{O}_3^{6-}$
 - ▶ alternatingly charged $(\text{LaO})^+, (\text{AlO}_2)^-$ layers



adapted from N. Nakagawa et al., Nature Mat. 5, 204 (2006)

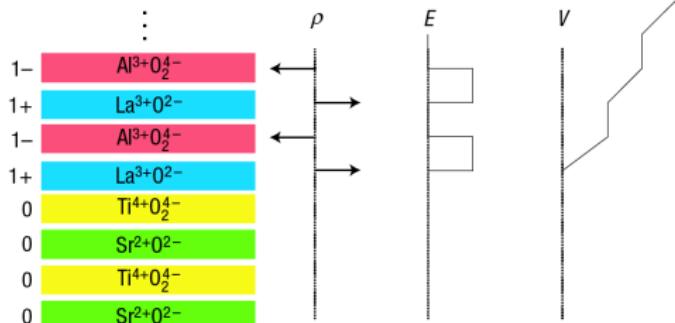
- ~~ Plate capacitor model: large internal electric field ($\sim \frac{1}{\epsilon} 47 \text{ V}/\text{unit cell}$), potential gradient
- ⇒ “polarization catastrophe”

Polarized Layers in $\text{LaAlO}_3\text{SrTiO}_3$

Formal valences:

- ▶ $\text{Sr}^{2+}\text{Ti}^{4+}\text{O}_3^{6-}$
 - ▶ neutral SrO, TiO_2 layers

- ▶ $\text{La}^{3+}\text{Al}^{3+}\text{O}_3^{6-}$
 - ▶ alternatingly charged $(\text{LaO})^+, (\text{AlO}_2)^-$ layers



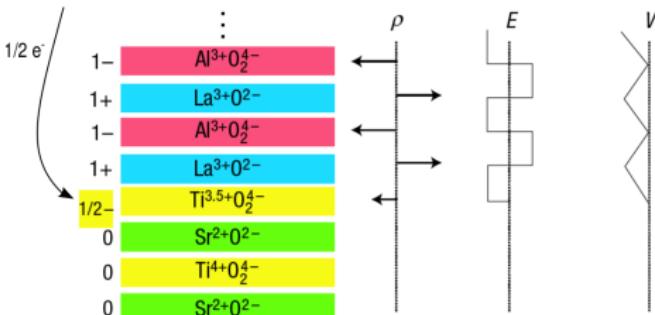
adapted from N. Nakagawa et al., Nature Mat. 5, 204 (2006)

- ~~ Plate capacitor model: large internal electric field ($\sim \frac{1}{\epsilon} 47 \text{ V}/\text{unit cell}$), potential gradient
- ⇒ “polarization catastrophe”

Avoiding the polarization catastrophe

- ▶ Electronic reconstruction
 - ⇒ electron doped n-interface, hole doped p-interface
 - ▶ experimental support: critical thickness
 - ▶ problem: why is the p-interface insulating?

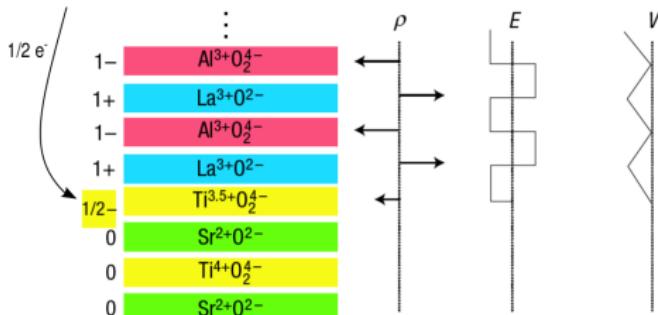
- ▶ Oxygen vacancies
 - ▶ O^{2-} vacancy contributes 2 holes
- ▶ Ionic reconstruction
 - ▶ structural relaxation in DFT



adapted from N. Nakagawa et al., Nature Mat. 5, 204 (2006)

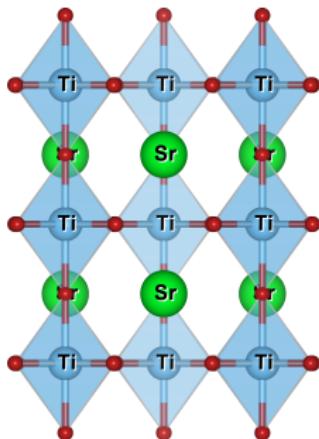
Avoiding the polarization catastrophe

- ▶ Electronic reconstruction
 - ⇒ electron doped n-interface, hole doped p-interface
 - ▶ experimental support: critical thickness
 - ▶ problem: why is the p-interface insulating?
- ▶ Oxygen vacancies
 - ▶ O^{2-} vacancy contributes 2 holes
- ▶ Ionic reconstruction
 - ▶ structural relaxation in DFT



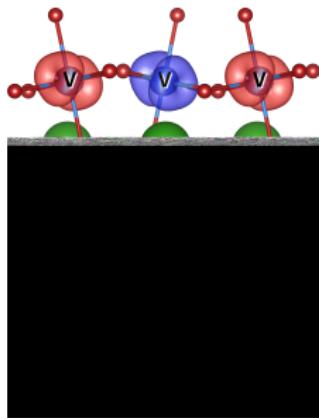
adapted from N. Nakagawa et al., Nature Mat. 5, 204 (2006)

Bulk SrTiO₃ and LaVO₃



SrTiO₃

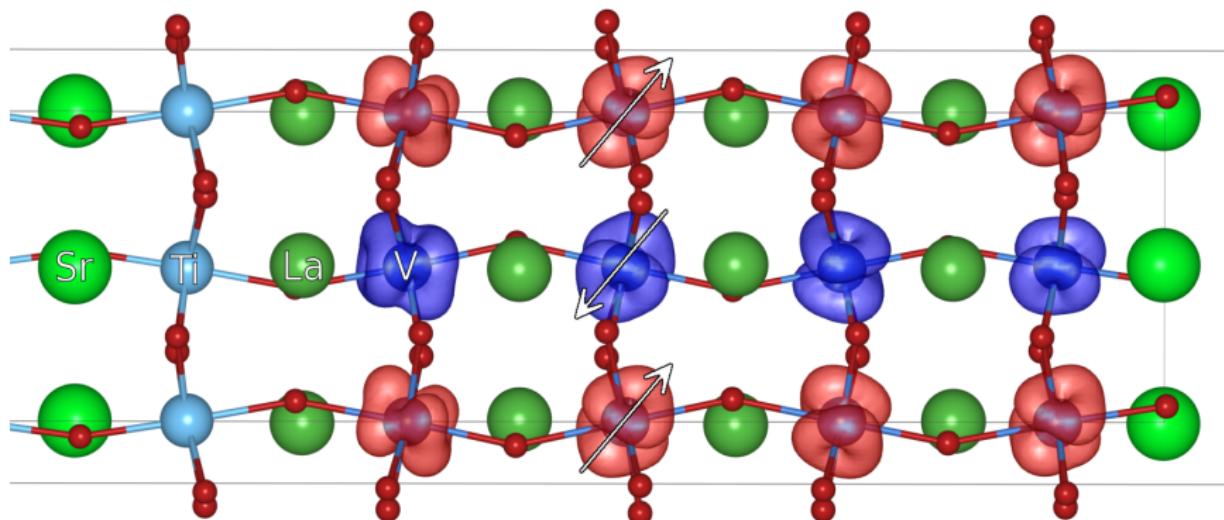
- ▶ (almost) cubic Perovskite
- ▶ TiO₆ octahedra
- ▶ d^0 band insulator



LaVO₃

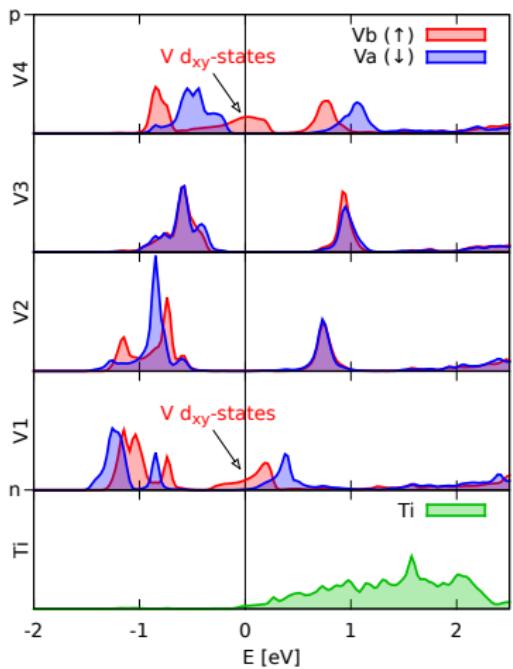
- ▶ distorted Perovskite (VO₆ octahedra)
- ▶ d^2 Mott insulator
- ▶ band gap: 1.1 eV
- ▶ AF-C spin, AF-G orbital order

Computational method: GGA + $U_V = 3 \text{ eV}$, $U_{\text{Ti}} = 9.8 \text{ eV}$



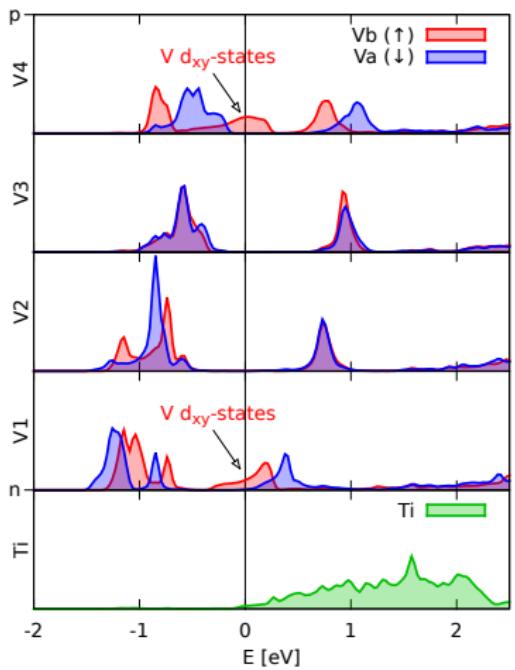
- ▶ spin order: AF-C
- ▶ orbital order: AF-G ($d_{xz} | d_{yz}$)
- ▶ *multi-layer vs. thin-film*

density-functional theory (GGA+U):

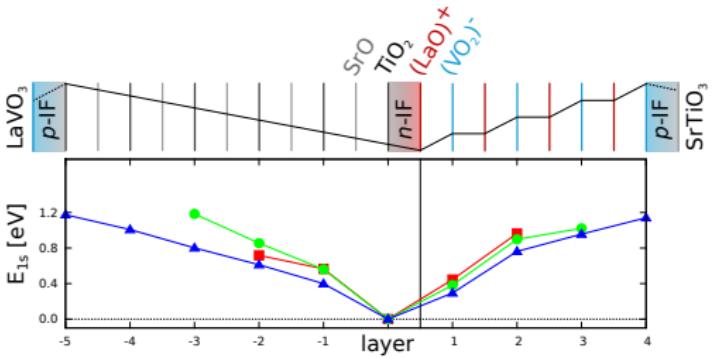


- ▶ layer-resolved density of states:
band shift = potential gradient
- ▶ $\sim 0.3 \text{ eV/u.c.} = 0.08 \text{ eV/\AA}$
- ▶ core-level energy $E_{1s}(z)$

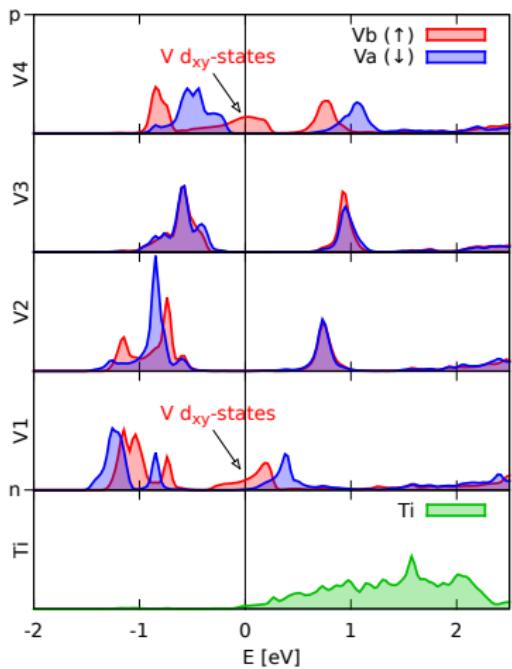
density-functional theory (GGA+U):



- ▶ layer-resolved density of states: band shift = potential gradient
- ▶ $\sim 0.3 \text{ eV/u.c.} = 0.08 \text{ eV/\AA}$
- ▶ core-level energy $E_{1s}(z)$

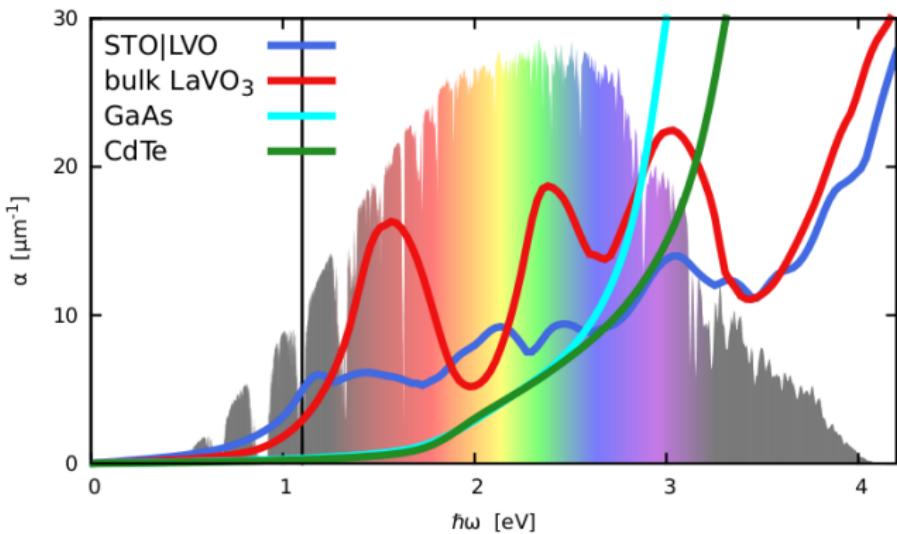


density-functional theory (GGA+U):



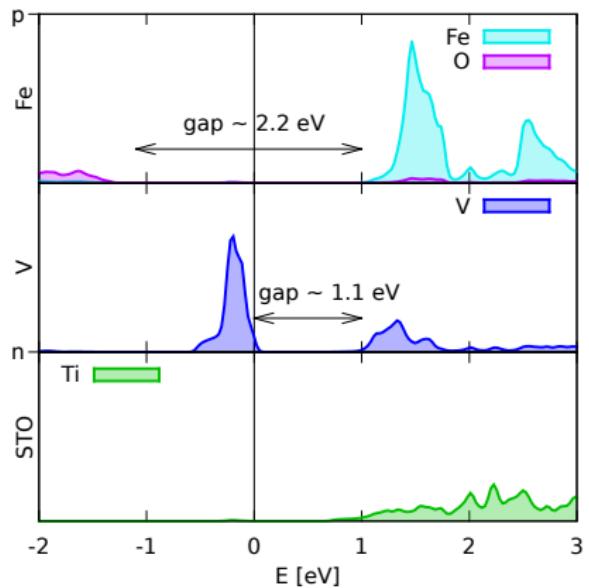
- ▶ layer-resolved density of states:
band shift = potential gradient
- ▶ $\sim 0.3 \text{ eV/u.c.} = 0.08 \text{ eV/\AA}$
- ▶ core-level energy $E_{1s}(z)$
- ▶ DFT: n- and p-interface conducting
- ▶ both interfaces occur by
periodic boundary conditions

3: Strong absorption across solar spectrum



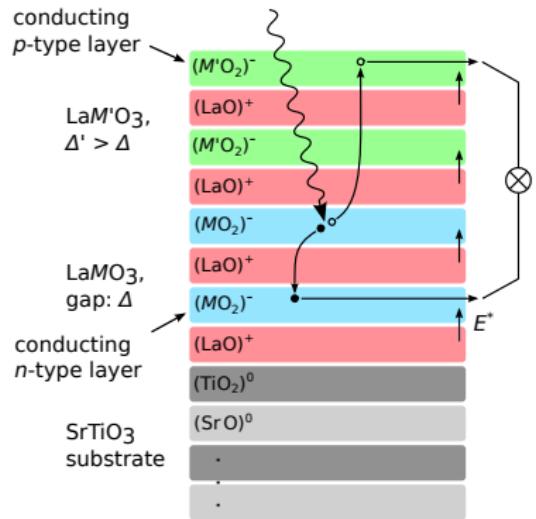
- ▶ band gap 1.1 eV is in the optimal range for efficiency
 - ▶ Shockley-Queisser limit
- ▶ optical absorption of LaVO₃ compares favorably to e.g. GaAs, CdTe

4: Flexible gap grading



- ▶ heterostructures grown by pulsed laser deposition (PLD)
- ⇒ layer-by-layer band gap grading
- ▶ e.g., for a tandem cell, combine LaVO_3 and LaFeO_3 (gap: 2.2 eV)
- ▶ gradient, conducting interfaces persist

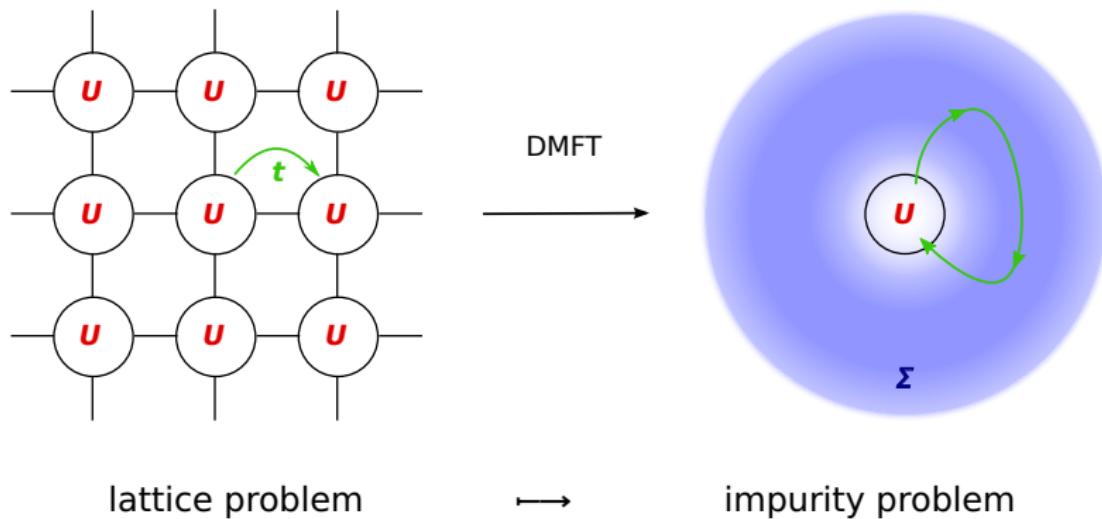
Summary: Solar Cells



- 1 large intrinsic electric field
- 2 conducting interface(s)
- 3 LaVO₃: direct gap 1.1 eV
- 4 combine oxides for multijunction cell
 - ▶ experimental realization in progress
(R. Claessen & J. Pflaum, Würzburg)

- ▶ EA, P. Blaha, R. Laskowski, K. Held, S. Okamoto, and G. Sangiovanni, PRL 110, 078701 (2013)
- ▶ synopsis in APS Physics
- ▶ popular-level coverage in various media

Dynamical mean field theory (DMFT) in 1 slide



- ▶ 1 interacting site in a “bath” of non-interacting electrons
- ▶ non-local correlations neglected: $\Sigma(k, \omega) \mapsto \Sigma_{\text{imp}}(\omega)$
- ▶ self-consistency: $G_{\text{imp}} = G_{\text{loc}}$

[Georges *et al.*, RMP (1996); Kotliar & Vollhardt, Phys. Today (2004)]

- ▶ N_{neq} nonequivalent correlated atoms

N_d d -Bands per atom

$N := N_{\text{at}} \cdot N_d$ dimensional space

- ▶ Local Green function (big $N \times N$ matrix)

$$G(\omega) = \sum_k \frac{1}{(\omega + \mu) - H^{\text{DFT}}(k) - \Sigma(\omega)}$$

- ▶ Weiss field (small $N_d \times N_d$ -matrix for each atom i)

$$g_i^{-1}(\omega) = \left[G(\omega)|_{\text{loc}}^{\text{atom } i} \right]^{-1} + \Sigma_i(\omega)$$

- ▶ impurity solver: self-energy matrix with N_{neq} independent entries

CT-QMC code `w2dynamics`, Parragh *et al.* PRB (2012)

- ▶ N_{neq} nonequivalent correlated atoms

N_d d -Bands per atom

$N := N_{\text{at}} \cdot N_d$ dimensional space

- ▶ Local Green function (big $N \times N$ matrix)

$$G(\omega) = \sum_k \frac{1}{(\omega + \mu) - H^{\text{DFT}}(k) - \Sigma(\omega)}$$

- ▶ Weiss field (small $N_d \times N_d$ -matrix for each atom i)

$$g_i^{-1}(\omega) = \left[G(\omega)|_{\text{loc}}^{\text{atom } i} \right]^{-1} + \Sigma_i(\omega)$$

- ▶ impurity solver: self-energy matrix with N_{neq} independent entries

CT-QMC code `w2dynamics`, Parragh *et al.* PRB (2012)

- ▶ N_{neq} nonequivalent correlated atoms

N_d d -Bands per atom

$N := N_{\text{at}} \cdot N_d$ dimensional space

- ▶ Local Green function (big $N \times N$ matrix)

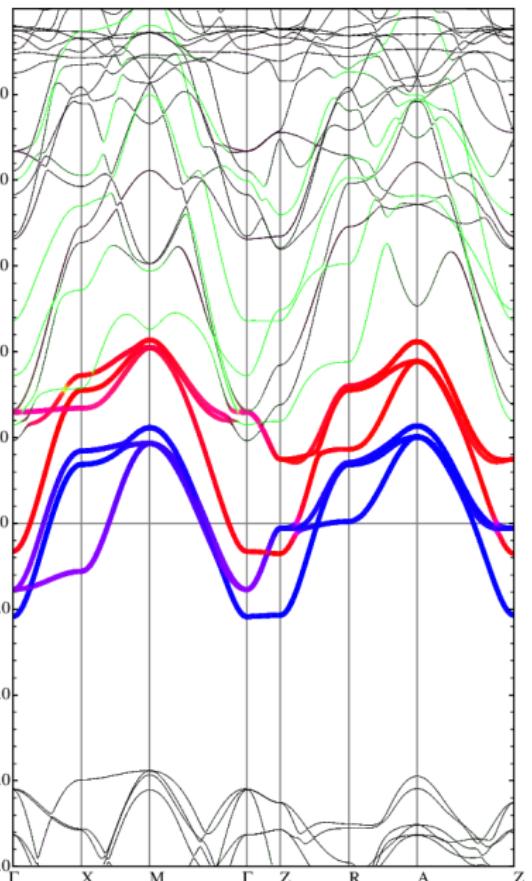
$$G(\omega) = \sum_k \frac{1}{(\omega + \mu) - H^{\text{DFT}}(k) - \Sigma(\omega)}$$

- ▶ Weiss field (small $N_d \times N_d$ -matrix for each atom i)

$$g_i^{-1}(\omega) = \left[G(\omega)|_{\text{loc}}^{\text{atom } i} \right]^{-1} + \Sigma_i(\omega)$$

- ▶ impurity solver: self-energy matrix with N_{neq} independent entries

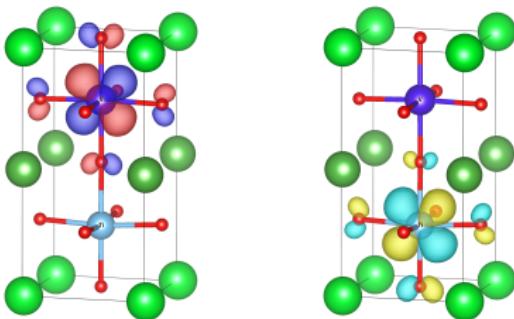
CT-QMC code `w2dynamics`, Parragh *et al.* PRB (2012)



Maximally-Localized Wannier Functions

$$w_{mR} = \frac{v}{(2\pi)^3} \int_{BZ} dk e^{-ik \cdot R} \sum_n U_{nm}(k) \psi_{nk}$$

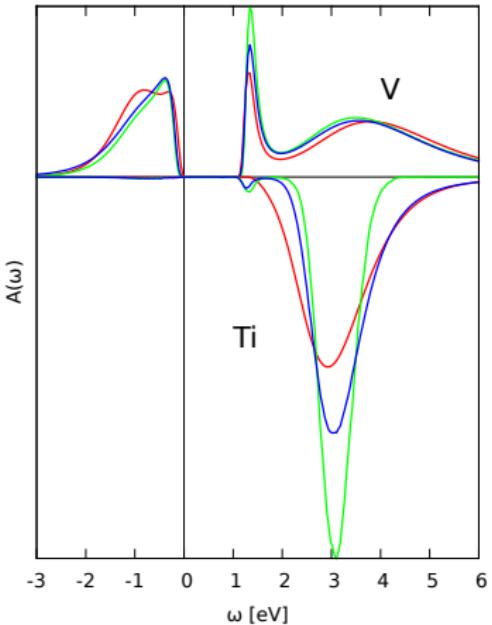
unitary $U(k)$ minimize spread $\langle \Delta r^2 \rangle$.



wannier90: Mostofi *et al.*, CPC (2008)

Wien2Wannier: Kuneš *et al.*, CPC (2010)

woptic: Wissgott *et al.*, PRB (2012)



- ▶ DMFT for inequivalent atoms
 - ▶ independent $\Sigma_i(\omega)$ coupled in $G(\omega)$
- ⇒ paramagnetic insulator
- ▶ construct minimal model (MLWF)
 - ▶ [Wien2Wannier](#), [wannier90](#)
- ▶ optical properties
(d-d transitions dominate!)
 - ▶ [woptic](#)
- ▶ structural optimization with DMFT
 - ▶ charge self consistency

Big Thanks to ...



Peter Blaha
TU Vienna



Karsten Held
TU Vienna



Robert Laskowski
TU Vienna



Satoshi Okamoto
Oak Ridge National Lab



Giorgio Sangiovanni
Uni Würzburg

Experiment (Würzburg):

- ▶ Ralph Claessen
- ▶ Jens Pflaum

Big Thanks to ...



Peter Blaha
TU Vienna



Karsten Held
TU Vienna



Robert Laskowski
TU Vienna



Satoshi Okamoto
Oak Ridge National Lab



Giorgio Sangiovanni
Uni Würzburg

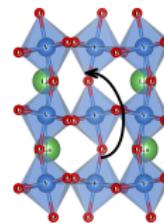
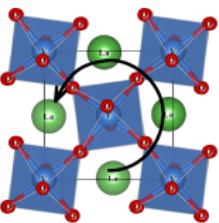
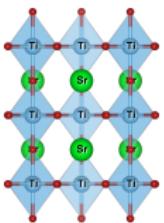
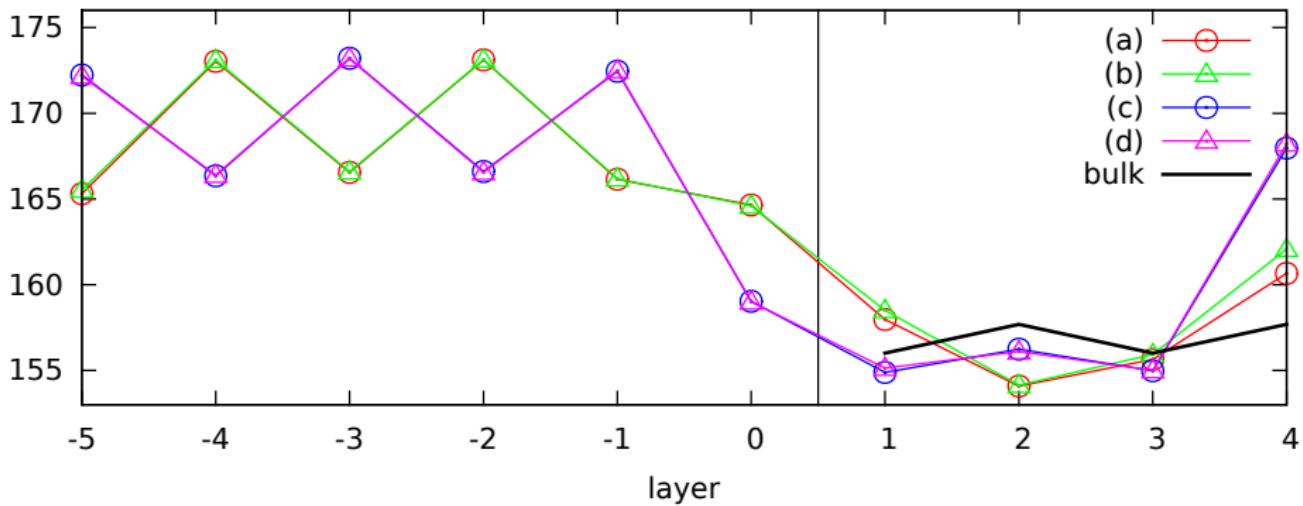
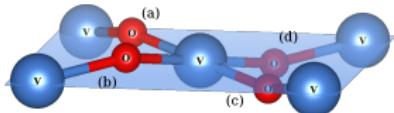
Experiment (Würzburg):

- ▶ Ralph Claessen
- ▶ Jens Pflaum

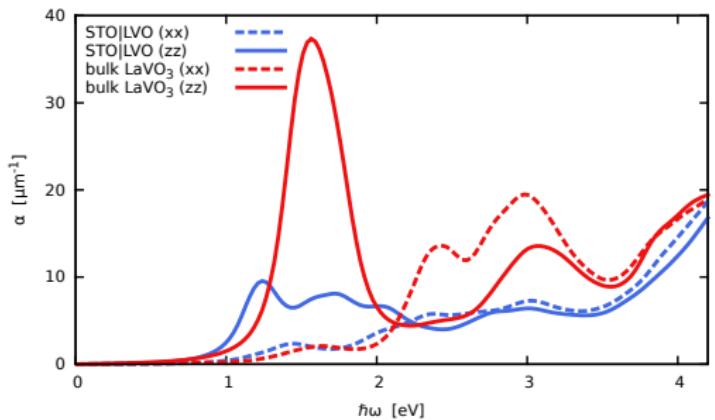
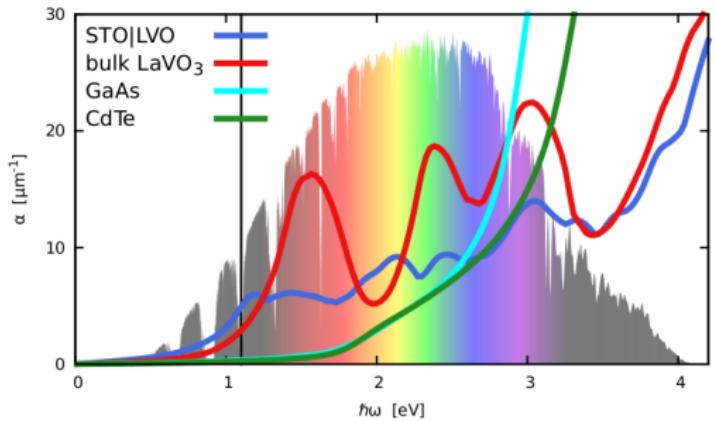
Thank you for listening

$M\text{-O}\text{-}M$ bond angle ($M = \text{V}, \text{Ti}$)

Lattice distortion in the heterostructure:



LaVO₃ absorption: Details



► Absorption: $I(x) \sim e^{-\alpha x}$

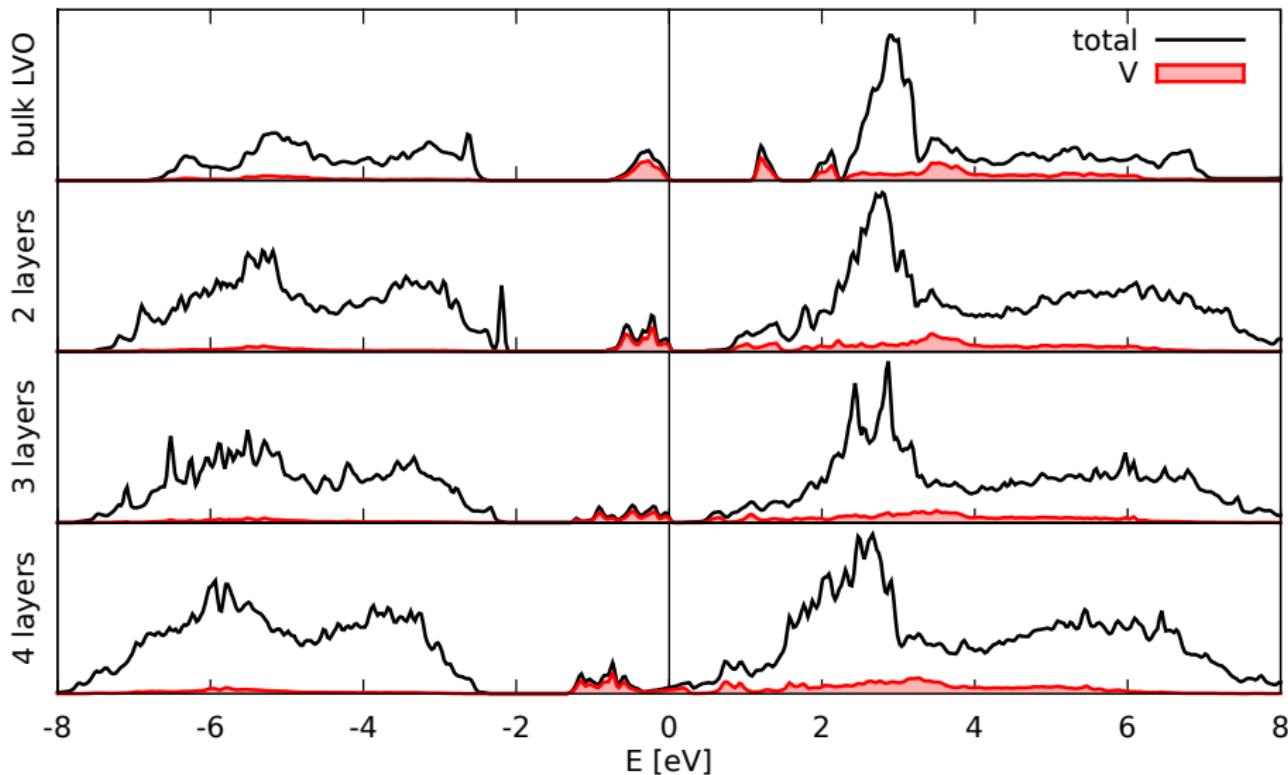
► Lattice distortion:
 $\alpha(\omega) \rightsquigarrow \alpha_{ij}(\omega)$

☞ for comparison, plot

$$\bar{\alpha} = \frac{1}{3} \sum_{ij} \alpha_{ij}$$

[◀ back](#)

Heterostructure DOS for different sizes



Critical thickness: 4 layers LaVO₃