Orbital-Lattice-Spin Interactions in Functional Materials

Cesare Franchini

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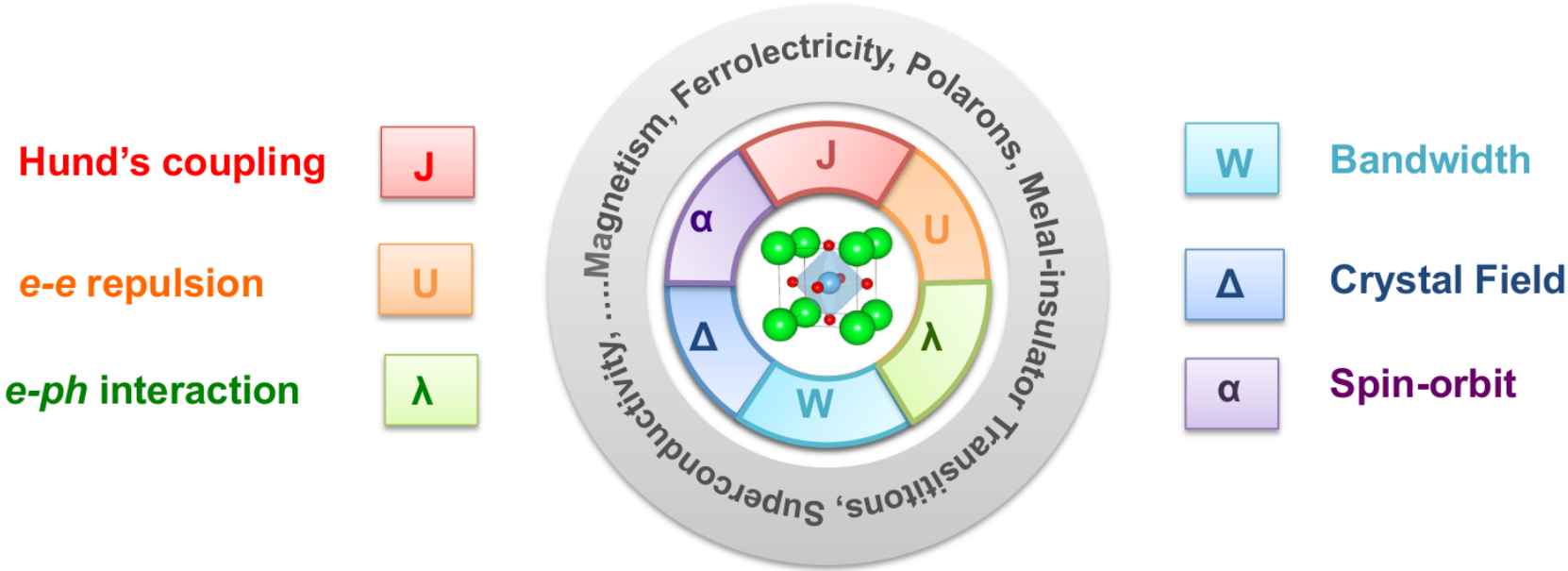

universität wien

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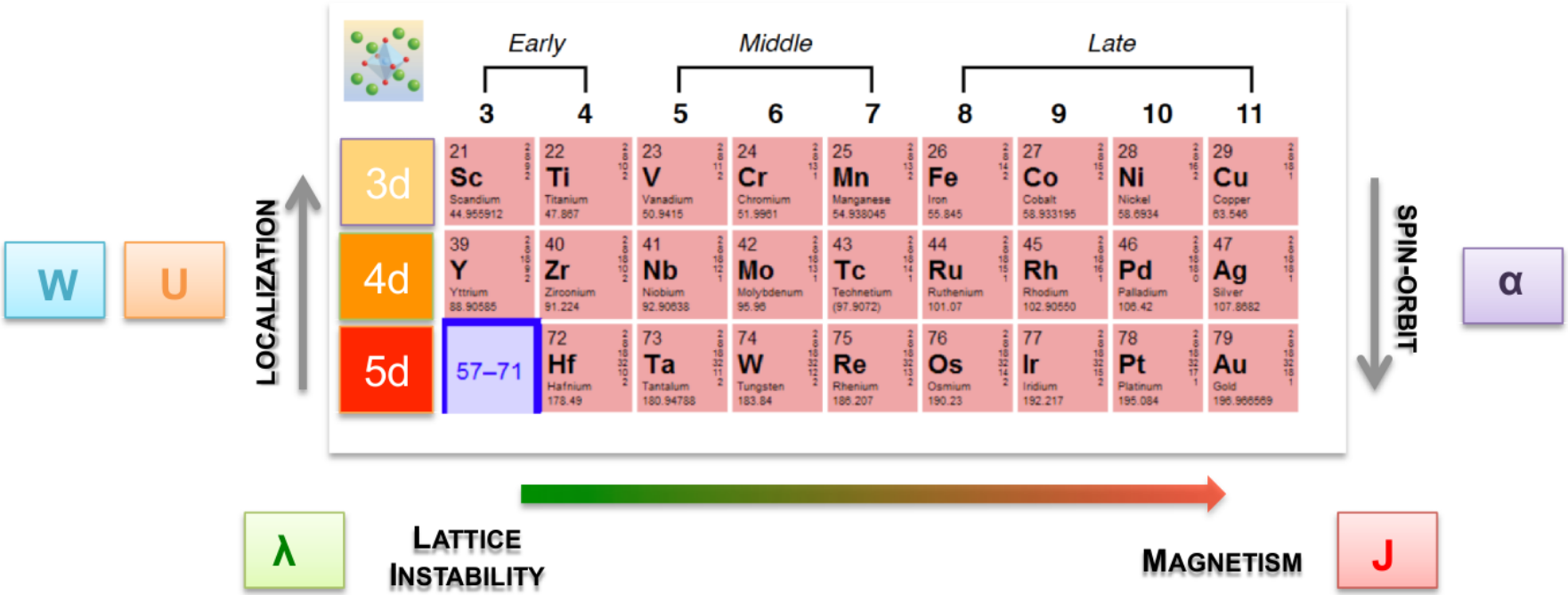
Vienna Computational Materials Laboratory ViCoM

FWF

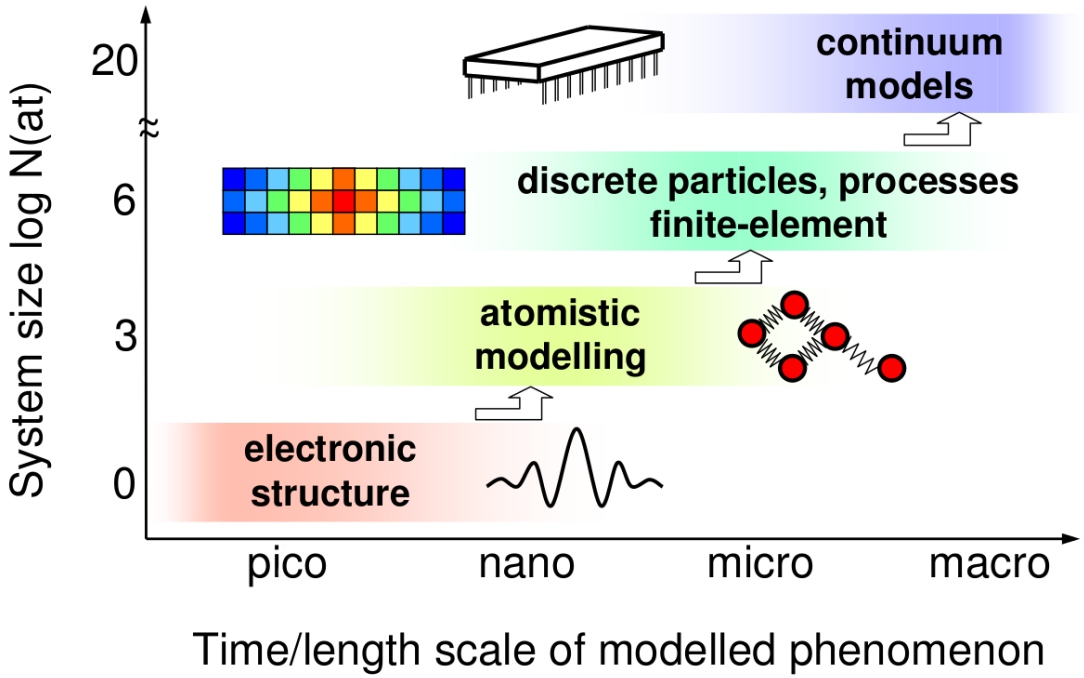
What

- Understanding of materials properties and functions
- Optimization of materials properties
- Design of Materials with desirable functionalities



Tuning the strength of the competing interactions through the choice of the TM ion

How



Electronic structure ⇒ Computational Quantum Mechanics

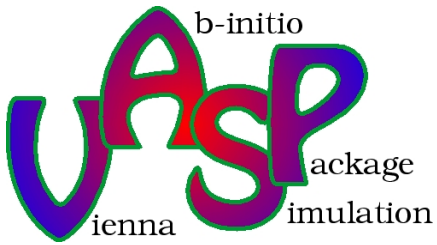
Numerical solution of the many-body Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\begin{aligned}\hat{H} = & -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{n=1}^{M}\frac{\hbar^2}{2M_n}\nabla_n^2 + \frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{i,j=1;i\neq j}^{N}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & -\frac{1}{4\pi\epsilon_0}\sum_{n}^{M}\sum_{i}^{N}\frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{n,m=1;n\neq m}^{M}\frac{Z_n Z_m e^2}{|\mathbf{R}_n - \mathbf{R}_m|}\end{aligned}$$

Computationally prohibitive. Approximations needed:

1. Density Functional Theory
2. Hartree-Fock Theory
3. Many-Body Perturbation Theory
   - GW approximation: quasi particle energies
   - Bethe-Salpeter equation: electron-hole interaction



Outline

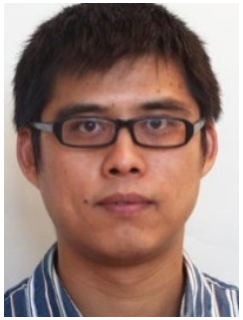
1. *electron-lattice*: TiO_2 and $SrTiO_3$ (polaron)
   $\Rightarrow$ Oxide electronics, Photocatalysis, photoelectrochemical applications

2. *spin-orbit & electron-hole*: Halide perovskites (Optical spectra and excitons)
   $\Rightarrow$ Solar cells

3. *spin-orbital-lattice*: Sr_2IrO_4 (non-collinear magnetism)
   $\Rightarrow$ Magnetic storage media & spintronics

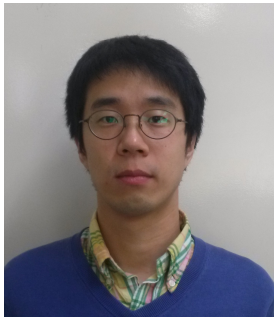
Collaborators

University of Vienna [DFT+U, Hybrids, cRPA, GW, BSE & MD]


Xianfeng Hao


Menno Bokdam


Peitao Liu


Bongjae Kim


Georg Kresse

UCSB [Hybrids] TU Budapest [Magnetism] TU Vienna [STM, STS, ARPES]


A. Janotti


CG Van de Walle


S. Khmelevskyi

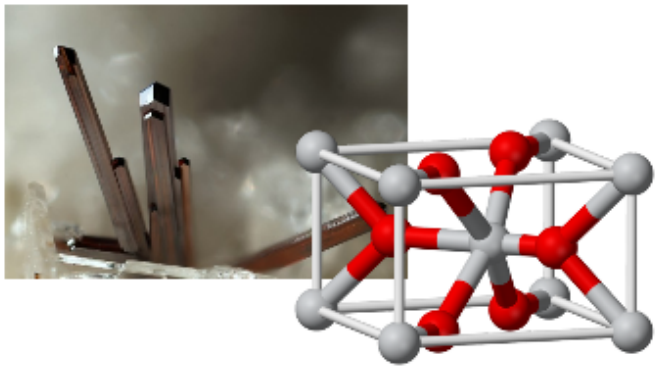

M. Setvin, M. Schmid & U. Diebold

Polarons in TiO_2

electron-lattice

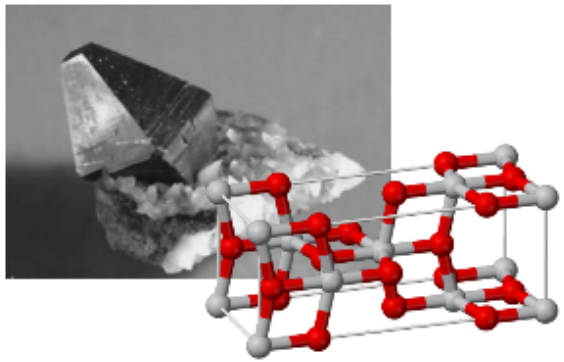
TiO_2 Rutile and Anatase

Rutile
(stable)



- Density:4240 kg/m^3
- Gap: 3.0 eV
- e mobility: 1 cm^2/(Vs)
- Nb-doped: black, bad conductor

Anatase
(metastable)



- Density:3830 kg/m^3
- Gap: 3.2 eV
- e mobility: 10 cm^2/(Vs)
- Nb-doped: transparent, metallic

Anatase exhibits a higher photocatalytic activity

U. Diebold, Surf. Sci. Rep. 48, 53 (2003).

M. A. Henderson, Surf. Sci. Rep. 66, 185 (2011).

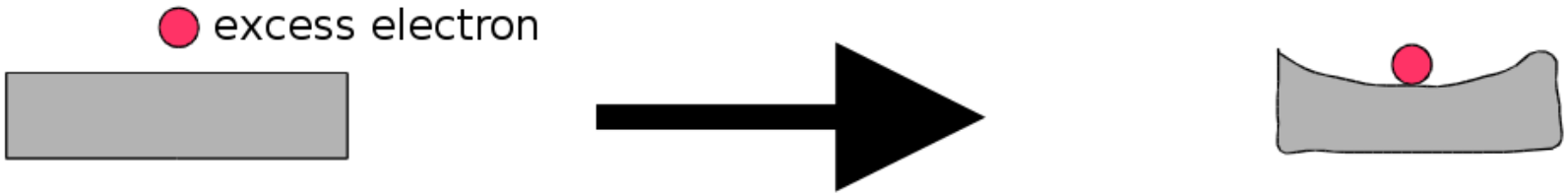
Polaron

Polaron: quasiparticle formed by the coupling between a conduction electron (or hole) and the lattice field in a polar semiconductor (or an ionic crystal).

Polaron physics is central in:

- Transport properties (hopping vs. free-electron like)
- Optical properties (transparent vs. opaque)
- Chemistry (transfer of electrons)
- Photocatalysis (trapping of electrons/holes)
- Superconductivity (bi-polarons)

Polaron vs. free carrier



A. Janotti, C. Franchini, J. B. Varley, G. Kresse, C. G. Van de Walle, Phys. Status Solidi RRL, 1 (2013).
Fröhlich, H. *Electrons in lattice fields*, Adv. Phys. 3, 325 (1954).
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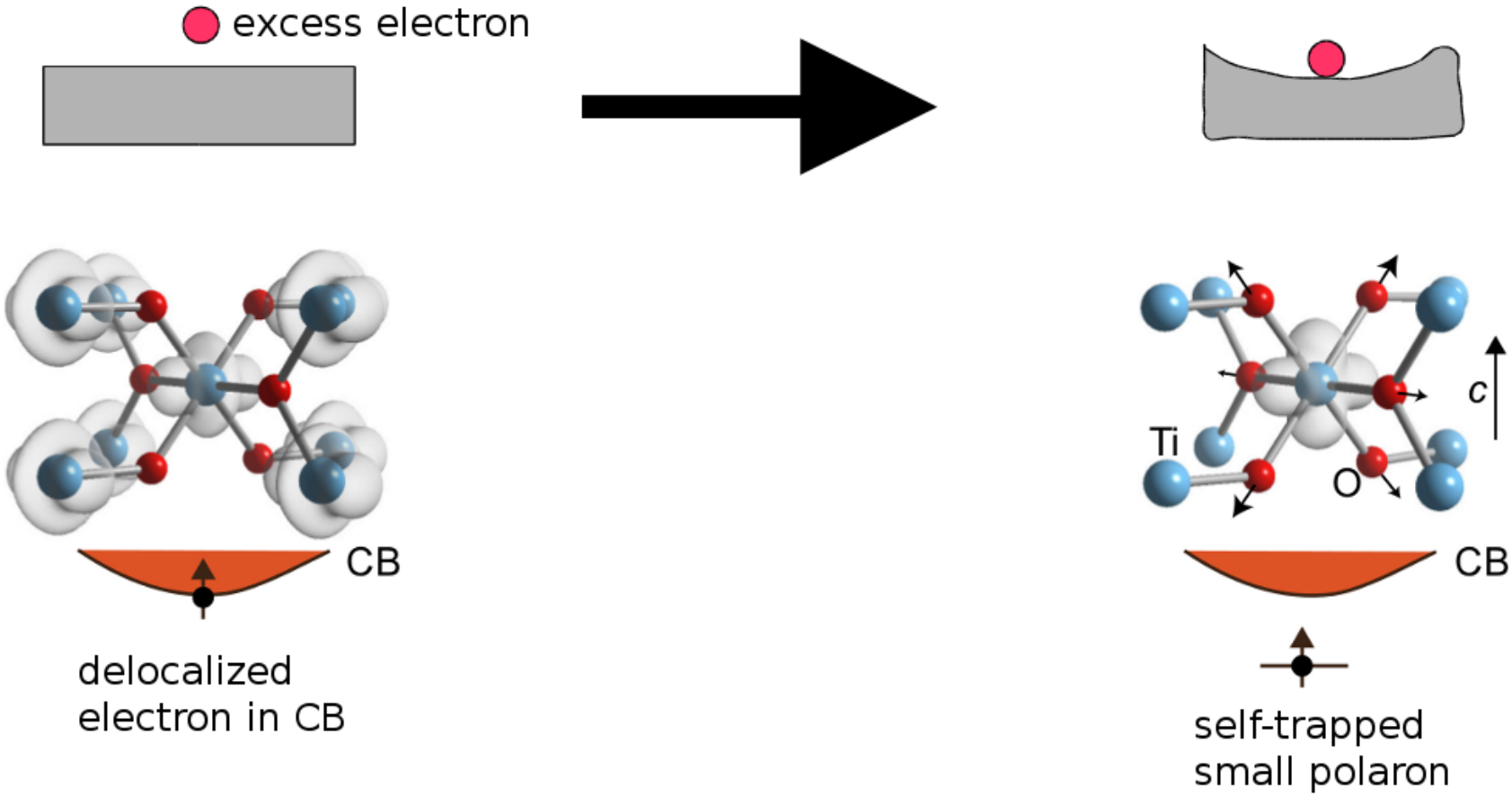
Polaron vs. free carrier



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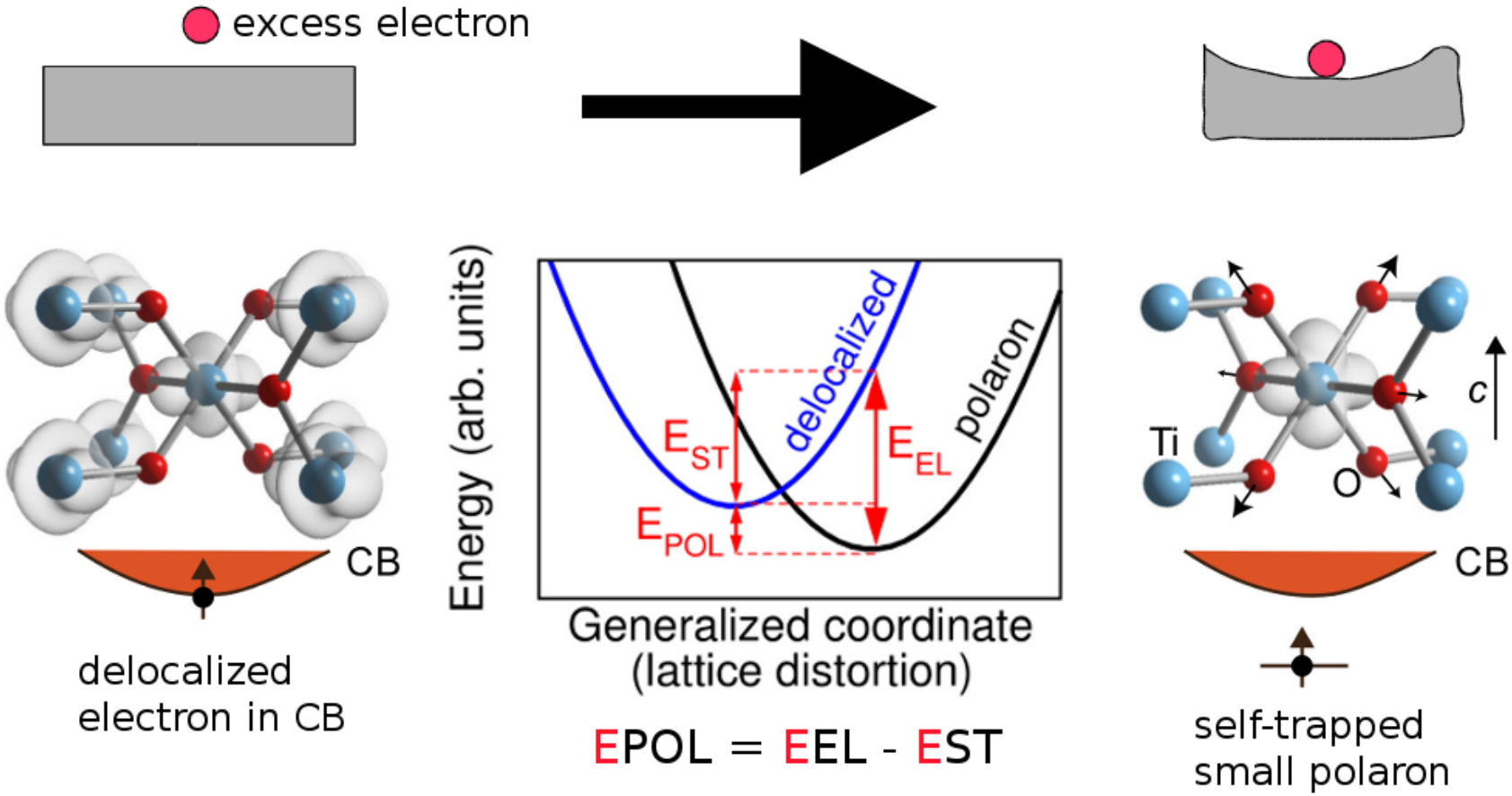

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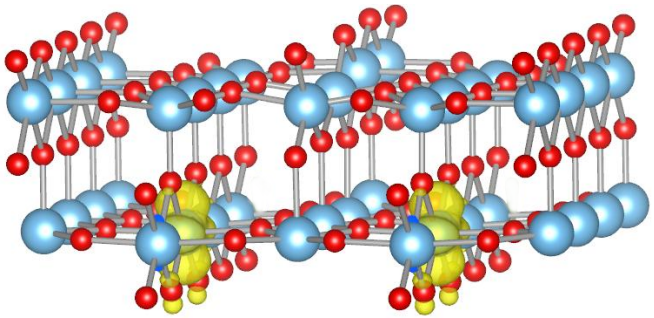
Austin, I.G. & Mott, N.F. *Polarons in crystalline and non-crystalline materials*, Adv. Phys. 50, 812 (2001).

Small & Large polarons

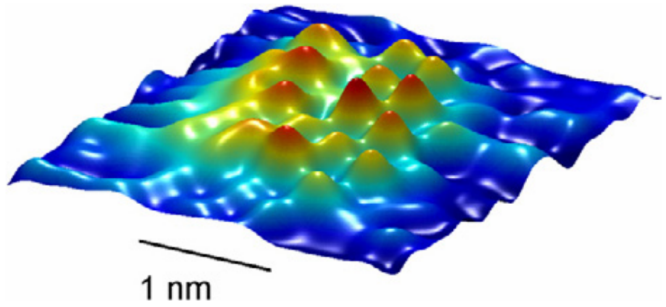
The spatial extent of wavefunction/structural-distortions determines the polaron *type*

Small "Holstein" polaron



- Short-range $el - ph$ interaction
- Local distortions ($\sim$ lattice constant)
- Localized mid-gap states ($\sim$ 1 eV)
- Thermally activated hopping mobility

Large "Fröhlich" polaron



- Long-range $el - ph$ interaction
- Several lattice sites
- Shallow donor ($\sim$ 10-50 meV)
- Free-carrier (high) mobility

J.T. Devreese, Encyclopedia of Applied Physics Vol. 14, 383 (1996).

Ronnow H M, Renner Ch, Aeppli G, Kimura T and Tokura Y, Nature 440 1025 (2006).

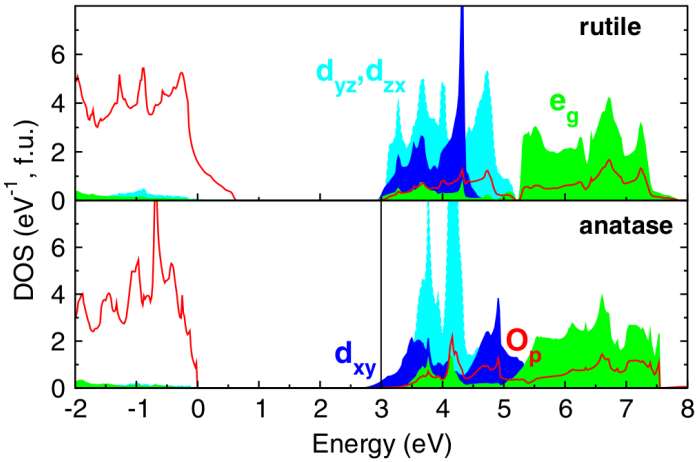
Excess electron in a perfect (defect-free) crystal

Rutile → the excess electron forms a small polaron.

Anatase → the excess electron exhibits a free-carrier delocalized character:

$$E_{POL} = E_{EL} - E_{ST}$$

⇒ E_{ST} the same in Anatase and Rutile
⇒ Smaller energy gain E_{EL} in Anatase (CDM wider and lower in energy)



M. Setvin, C. Franchini, *et al.* PRL 113, 086402 (2014).

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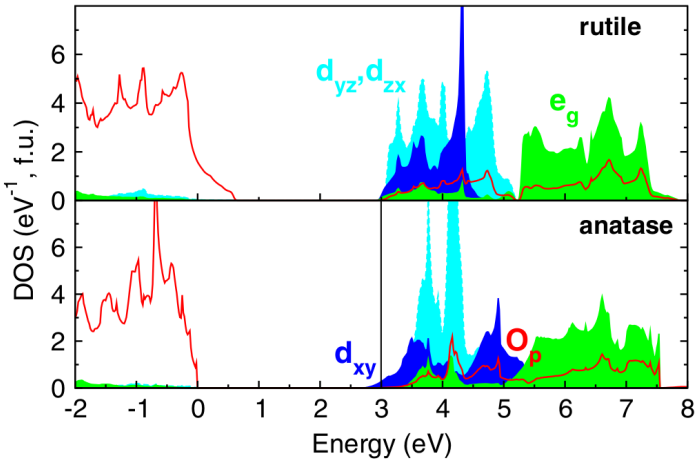

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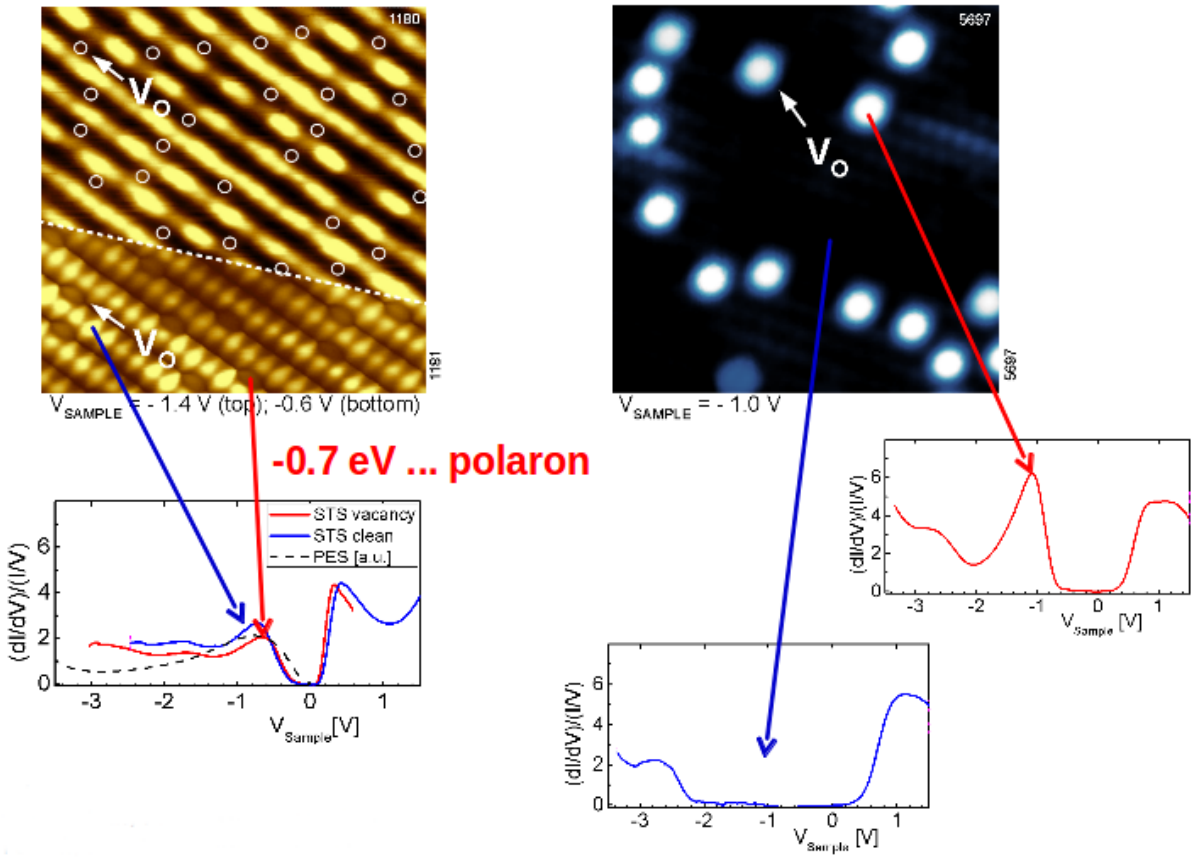
Oxygen vacancies (V_O): STM-DFT

Rutile (110) Anatase (101)



Rutile (110): Signature of small polarons, but NOT only next to V_O

Anatase (101): small polarons near V_O

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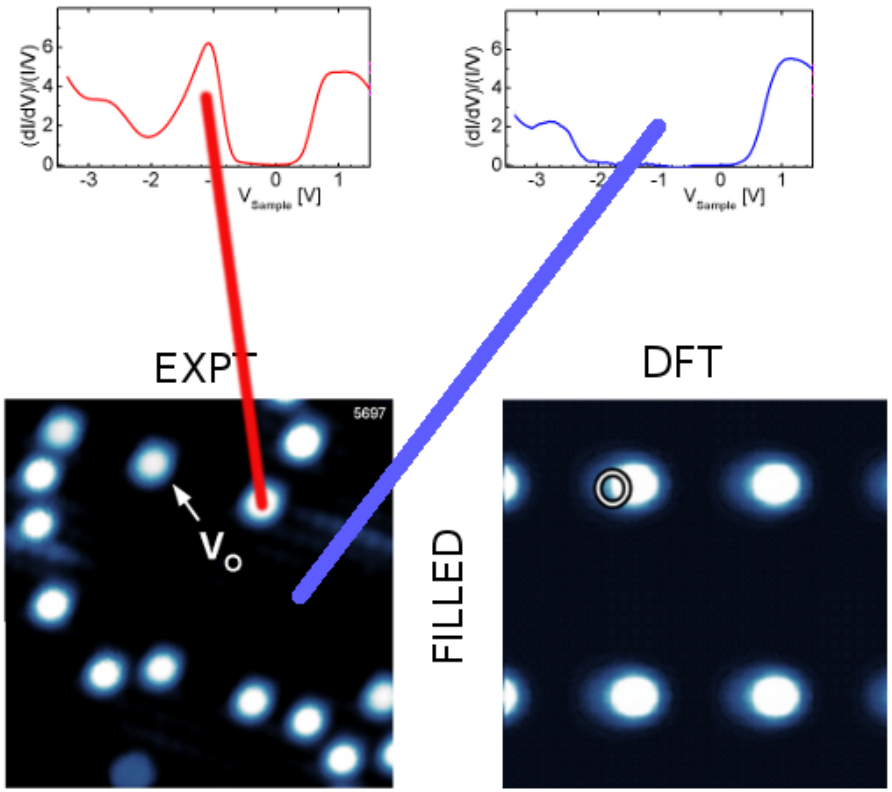
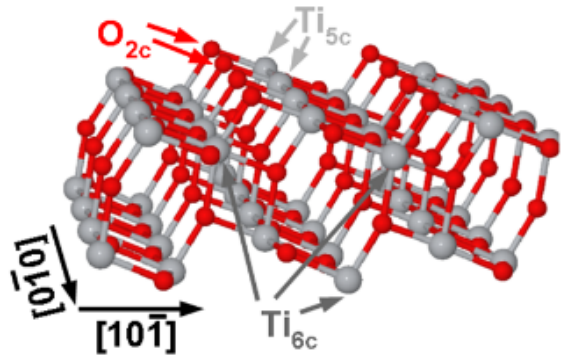
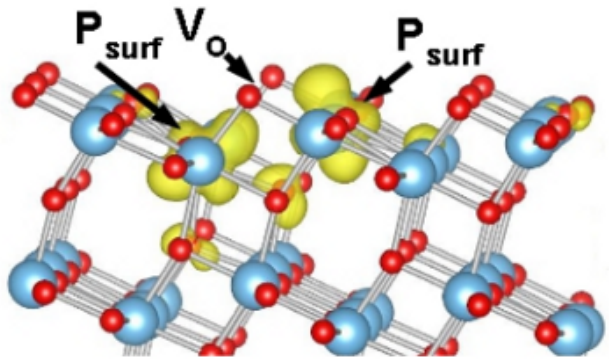
Anatase (101)







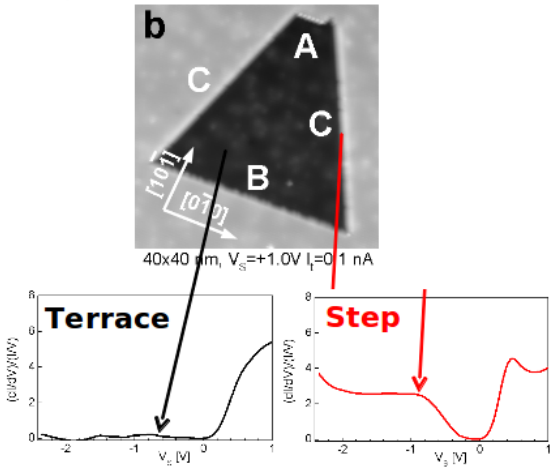
M. Setvin, C. Franchini, *et al.* PRL 113, 086402 (2014).

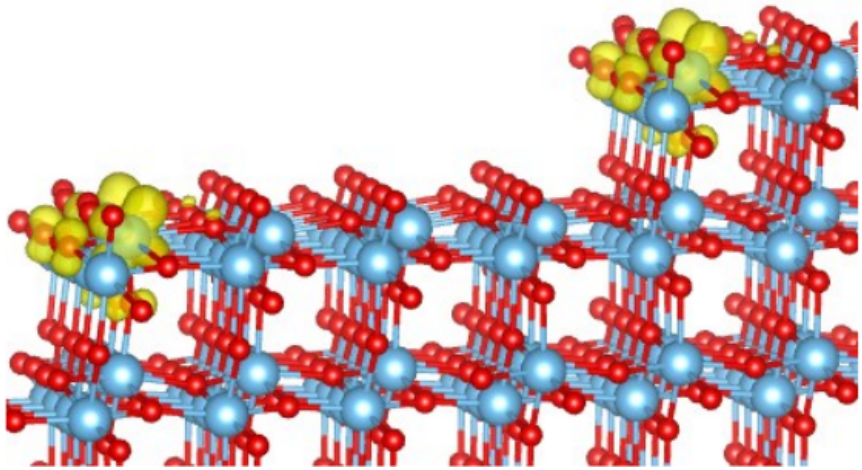
Anatase

No polaron in anatase except at defects

⇒ No small polarons in a perfect crystal

⇒ Small polarons near structural defects (smaller E_{ST}): V_O & Steps





⇒ Structural defects: Nb-doping ?

M. Setvin, X. Hao, B. Daniel, J. Pavelec, Z. Novotny, G. S. Parkinson, M. Schmid, G. Kresse, C. Franchini, and U. Diebold, Angew. Chem. Int. Ed. 53, 4714 (2014).

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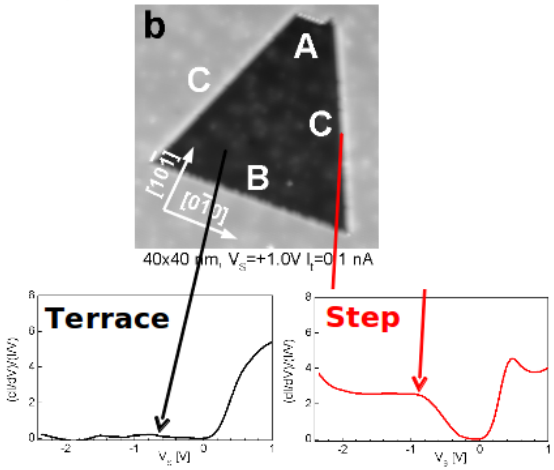

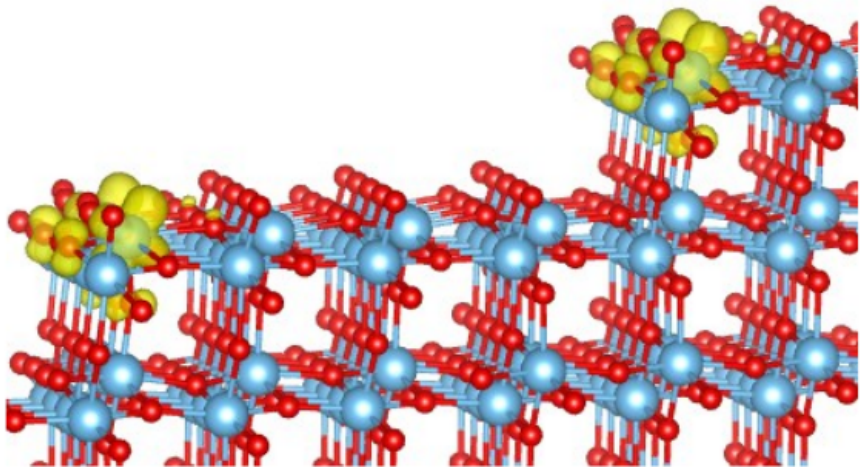

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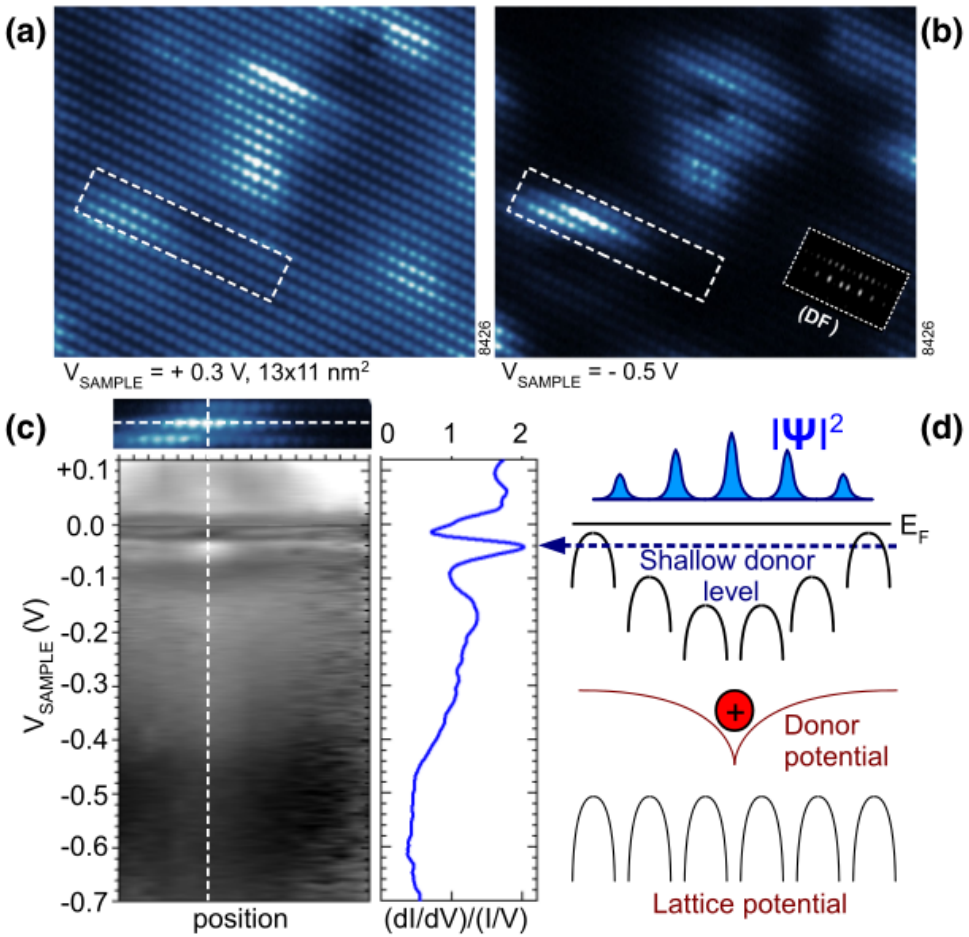
Nb-doped Anatase (101) doped with 1% Nb



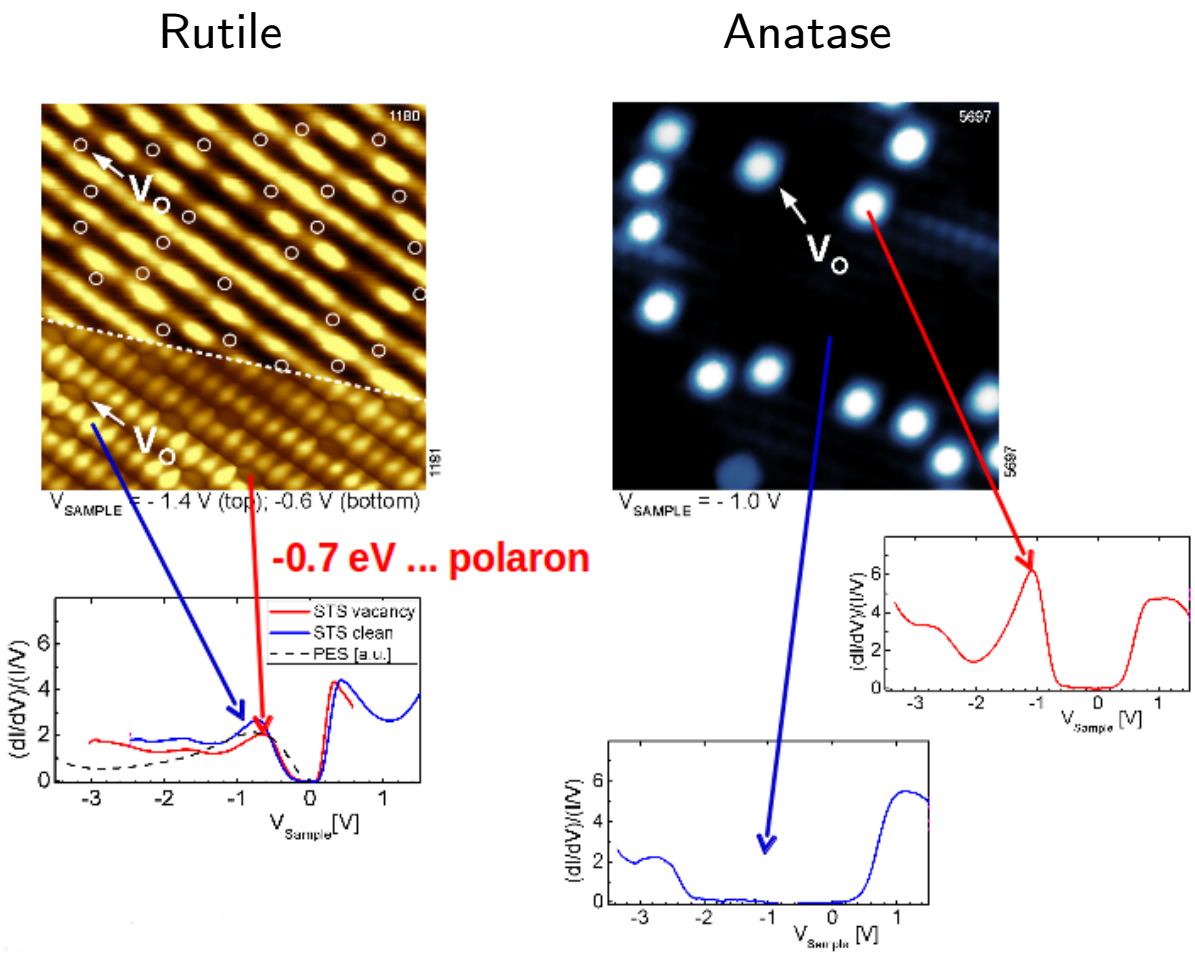
- STM: 2D modulated charge density
- STS: Shallow donor at $\approx$ 50 meV.

MODEL:
The electron wave function is spread over several unit cells around the donor, and is modulated by the periodic potential of the crystal lattice.

$\Rightarrow$ Fingerprint of a large polaron

M. Setvin, C. Franchini, *et al.* PRL 113, 086402 (2014).

Rutile (110)



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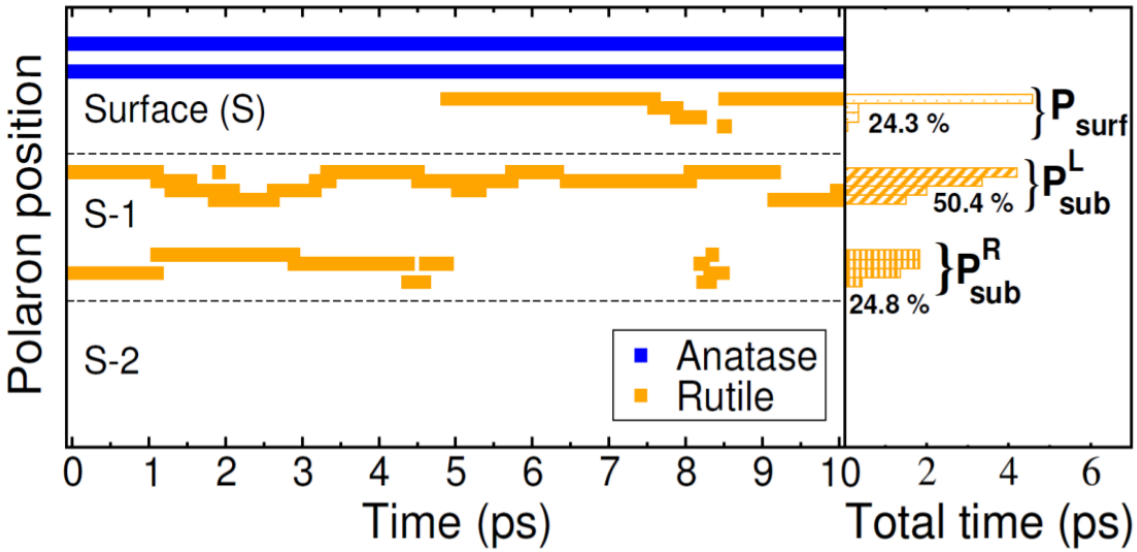
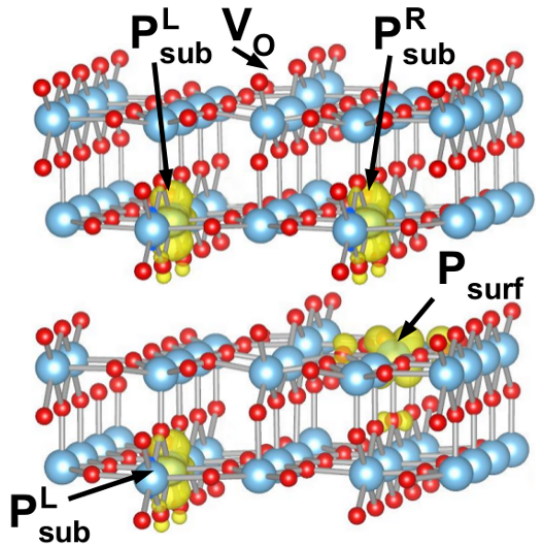
Rutile (110)

DFT+U + Molecular Dynamics (700 K for 10 ps)





Rutile (110): Many energetically equivalent small polarons solutions: polaron hopping

Anatase (101): immobile polarons @ V_O

M. Setvin, C. Franchini, *et al.* PRL 113, 086402 (2014).

P. M. Kowalski, *et al.* PRL. 105, 146405 (2010).

TiO_2: Summary

Anatase

1. No small polarons in a perfect crystal
2. Small immobile polarons near structural defects: V_O & Steps
3. Large polarons in Nb-doped samples

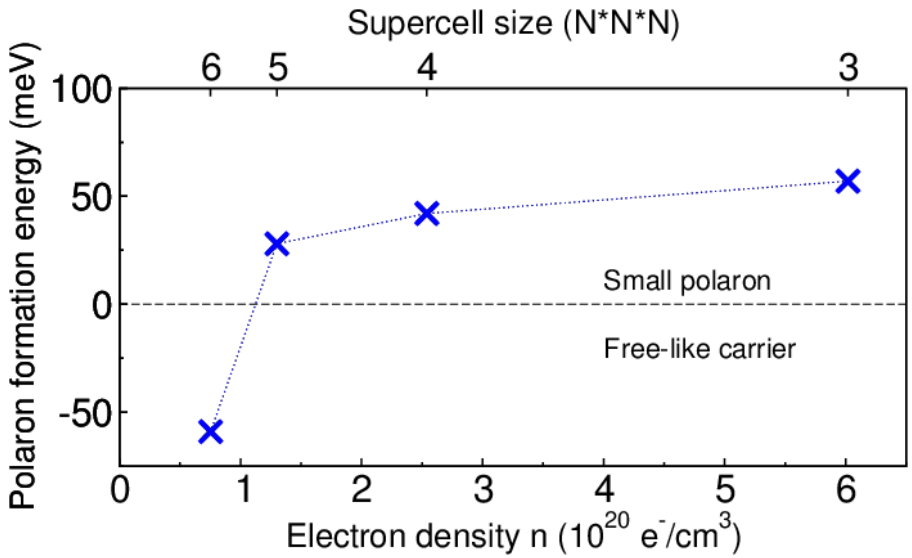
Rutile

1. Small polarons in a perfect crystal
2. Small polarons not necessarily near structural defects
3. Small polarons in Nb-doped samples
4. Small polaron can be thermally activated (mobile)

Polarons and 2DEG in $SrTiO_3$

electron-lattice

Nd-doped $SrTiO_3$: Large or small polarons? (controversial experimental data)

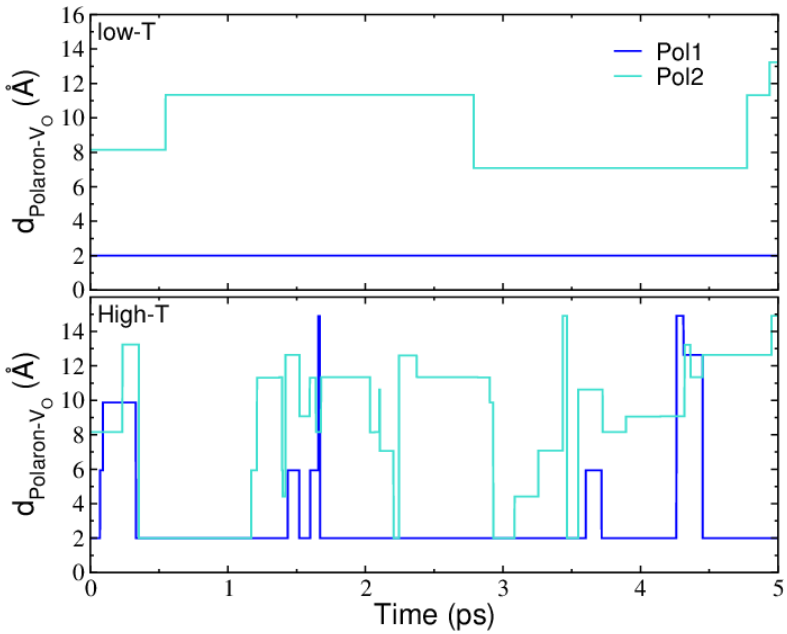


Carrier-density (n) dependent transition between a polaronic semiconducting behavior and a conductive regime:

- $n \gtrsim 1 \times 10^{20}$ cm^{-3}: small polarons
- $n \lesssim 1 \times 10^{20}$ cm^{-3}: large polaron (extension: 10-20 Å)

X. Hao, Z. Wang, M. Schmid, U. Diebold, C. Franchini, PRB 91, 085204 (2014).

V_O in $SrTiO_3$: T-driven MIT



- Low-T: excess electrons are confined in polaron sites (semiconducting regime)
- High-T: polarons become mobile when thermally activated: hopping mobility.

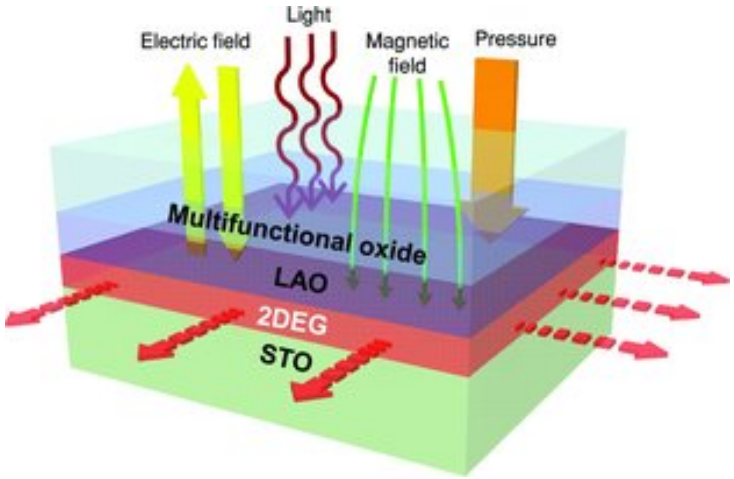
X. Hao, Z. Wang, M. Schmid, U. Diebold, C. Franchini, PRB 91, 085204 (2014).

Z.Q. Liu et al., Phys. Rev. Lett. 107, 146802 (2011).

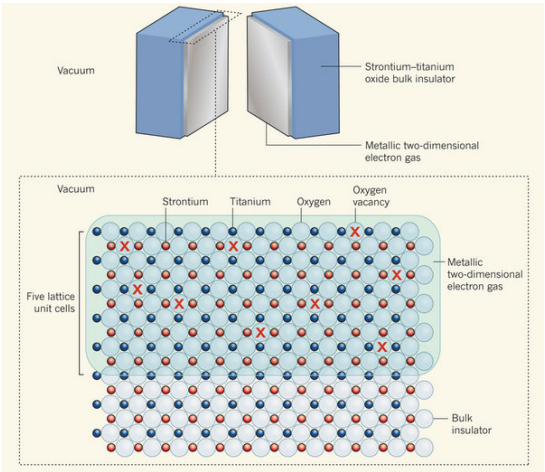
Two dimensional electron gas (2DEG) in $SrTiO_3$

Oxide-based 2DEG: The conducting face of an insulator, an opportunity for electronics

- 2DEG @ $LaAlO_3/SrTiO_3$ interface: [A. Ohtomo & H. Y. Hwang, Nature 427, 423 (2004)]



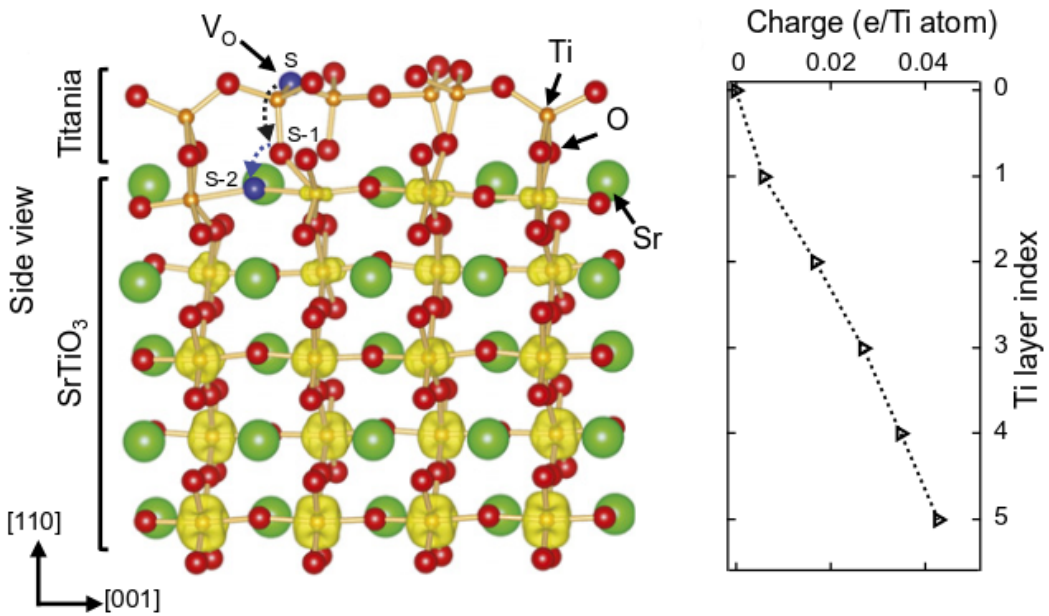
- 2DEG @ $SrTiO_3(100)$: [A. F. Santander-Syro *et al.*, Nature 469, 189 (2011)]



Two dimensional electron gas (2DEG) in $SrTiO_3$

2DEG@$SrTiO_3$(110): [Z. Wang, $\cdots$, C. Franchini, K. Held, and U. Diebold, PNAS 111, 3933 (2014)]

- Polar surface reconstruction: tetrahedrally coordinated titania overlayer
- Oxygen vacancies (V_O) spontaneously migrate beneath the titania overlayer
- V_O electrons $\rightarrow$ 2DEG (2 nm thickness) beneath the titania overlayer



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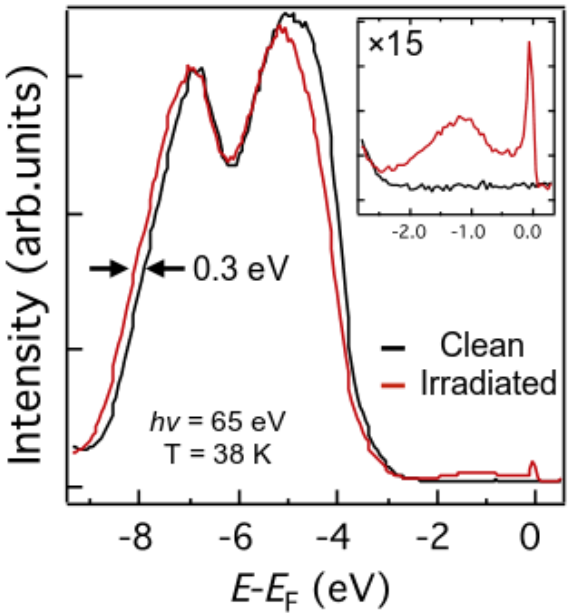
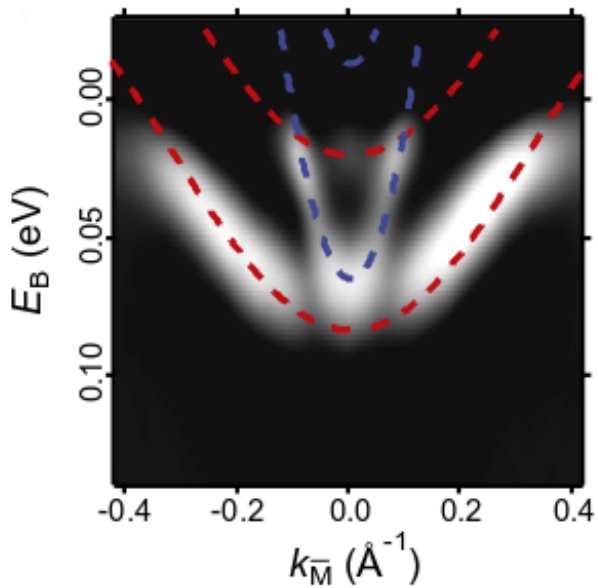
- V_O electrons $\rightarrow$ 2DEG (2 nm thickness) beneath the titania overlayer





$SrTiO_3$: Summary

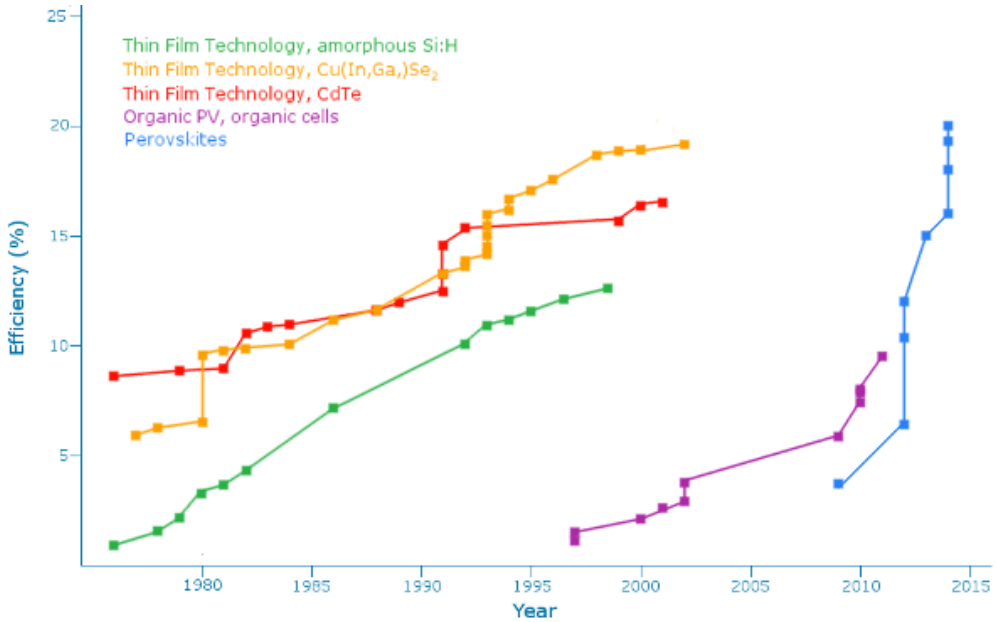
1. Coexistence of small and large polarons in Nb-doped $SrTiO_3$
2. T-driven V_O-induced MIT in $SrTiO_3$
3. V_O-induced 2DEG@$SrTiO_3$(110)

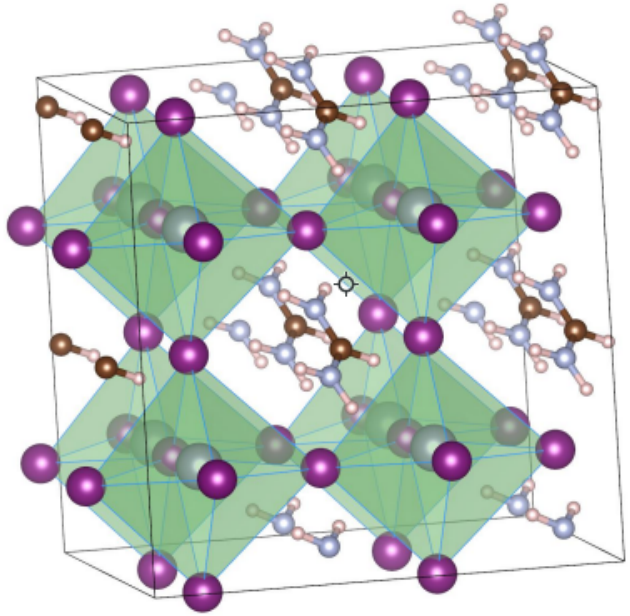
Optical absorption spectra and excitons of organometal halide perovskites

electron-hole & spin-orbit

Perovskite (AMX_3) Solar Cells

A=organic molecule (MA=methylammonium; FA=formamidinium)
M=Pb, Sn
X=halide (Cl, Br, I)

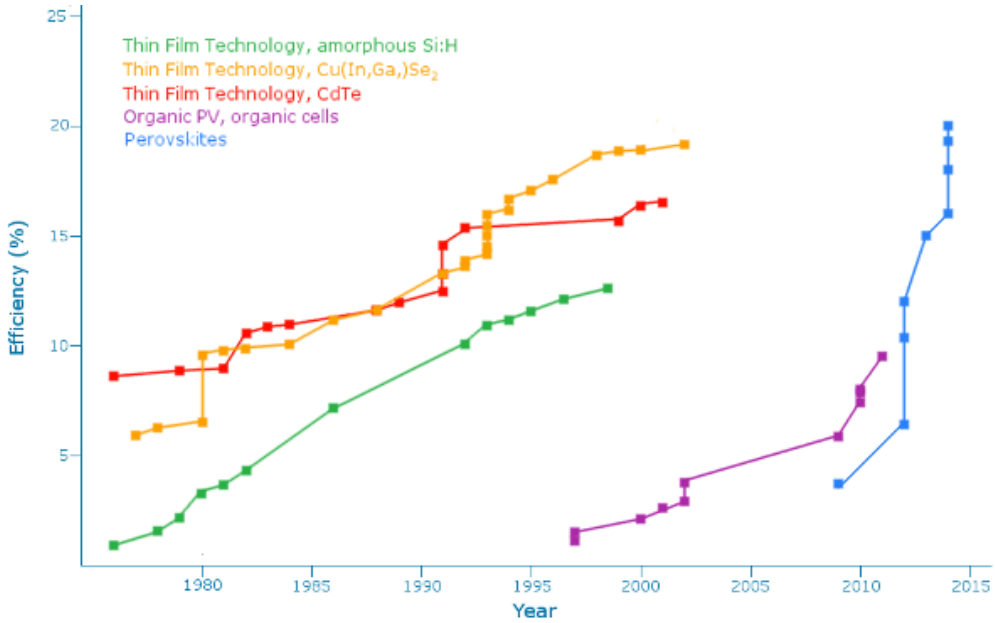


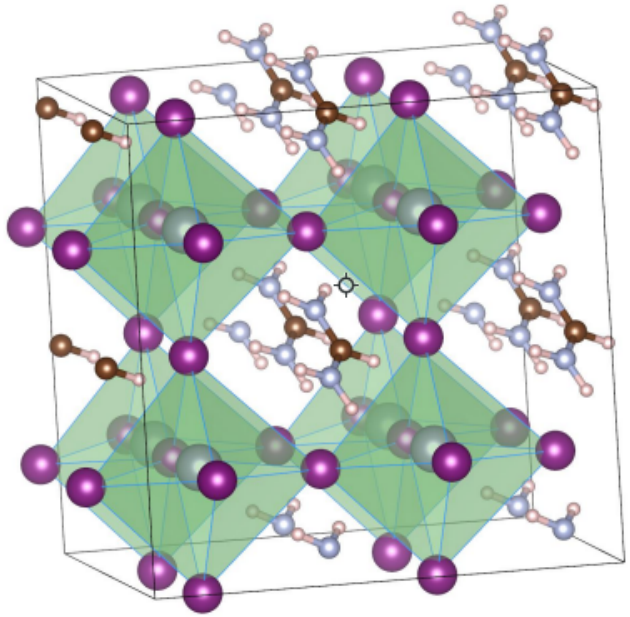


- Cheap
- High efficiencies (20.1 %)

Perovskite (AMX_3) Solar Cells

A=organic molecule (MA=$(CH_3NH_3)^+$; FA=$NH_2CHNH_2)^+$)
M=Pb, Sn
X=halide (Cl, Br, I)





Advantages

- Cheap
- High efficiencies (20.1 %)

Disadvantages

- Poor environmental stability ($\sim$ 1000 hours)
- Toxic (Pb)

Electronic structure + Optical properties

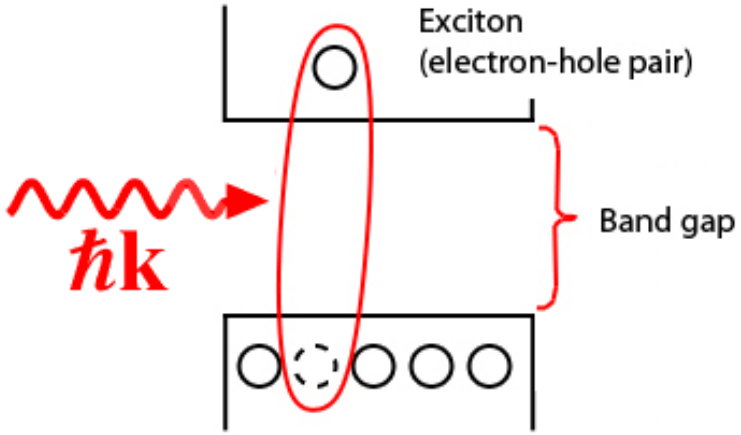
- DFT electronic structure studied before first perovskite solar cell reported
  [I. Borriello, G. Cantele, and D. Ninno PRB 77, 235214 (2001)]

- *Ab initio* description very challenging:
  1. small band gap (1.6 eV): beyond DFT methods needed
  2. heavy elements: relativistic calculations including spin-orbit coupling needed
  3. optical properties: electron-hole interaction (exciton)
  4. organic molecules: van der Waals corrections

Umari, P.; Mosconi, E.; Angelis, F. D. Scientific Reports 4, 4467 (2014).
Brivio, F.; Butler, K. T.; Walsh, A.; van Schilfgaarde, M. PRB 89, 155204 (2014)
Filip, M. R.; Giustino, F. PRB 90, 245145 (2014)
A. Stroppa, D. Di Sante, P. Barone, M. Bokdam, G. Kresse, C. Franchini, M.-H. Whangbo, S. Picozzi
Nat. Comm., 5, 5900 (2014)

Exciton

A quasiparticle excitation consisting of a Coulomb-bound electron-hole pair.



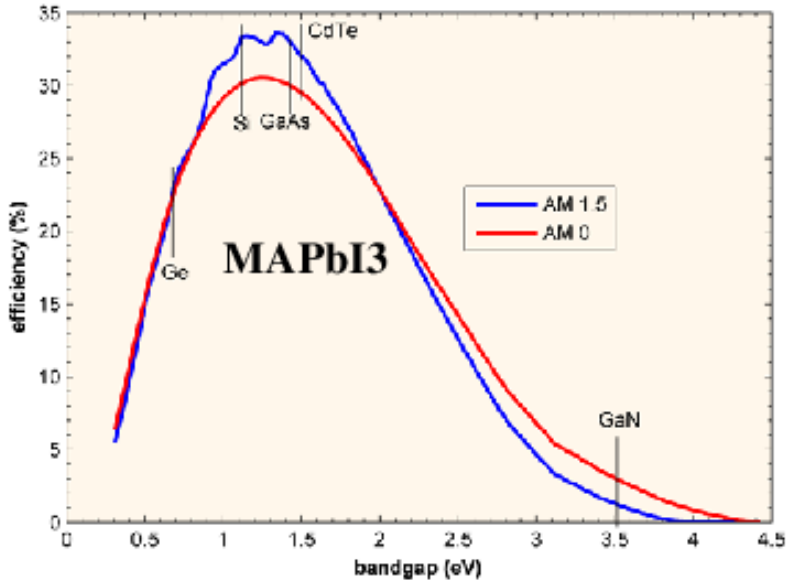
1. Low dielectric constant $\rightarrow$ strong e-h Coulomb interaction $\rightarrow$ small exciton

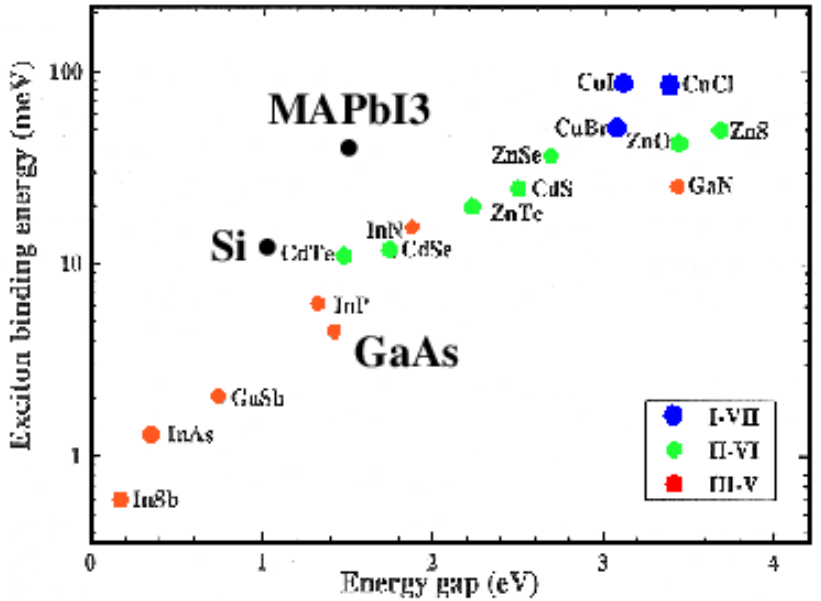
   Binding energy: $\mathrm{E_{xb}} \approx$ 0.1-1 eV strongly bound Frenkel exciton

2. High dielectric constant $\rightarrow$ reduced e-h Coulomb interaction $\rightarrow$ large exciton

   Binding energy: $\mathrm{E_{xb}} \approx$ 0.01 eV weakly bound Wannier-Mott exciton

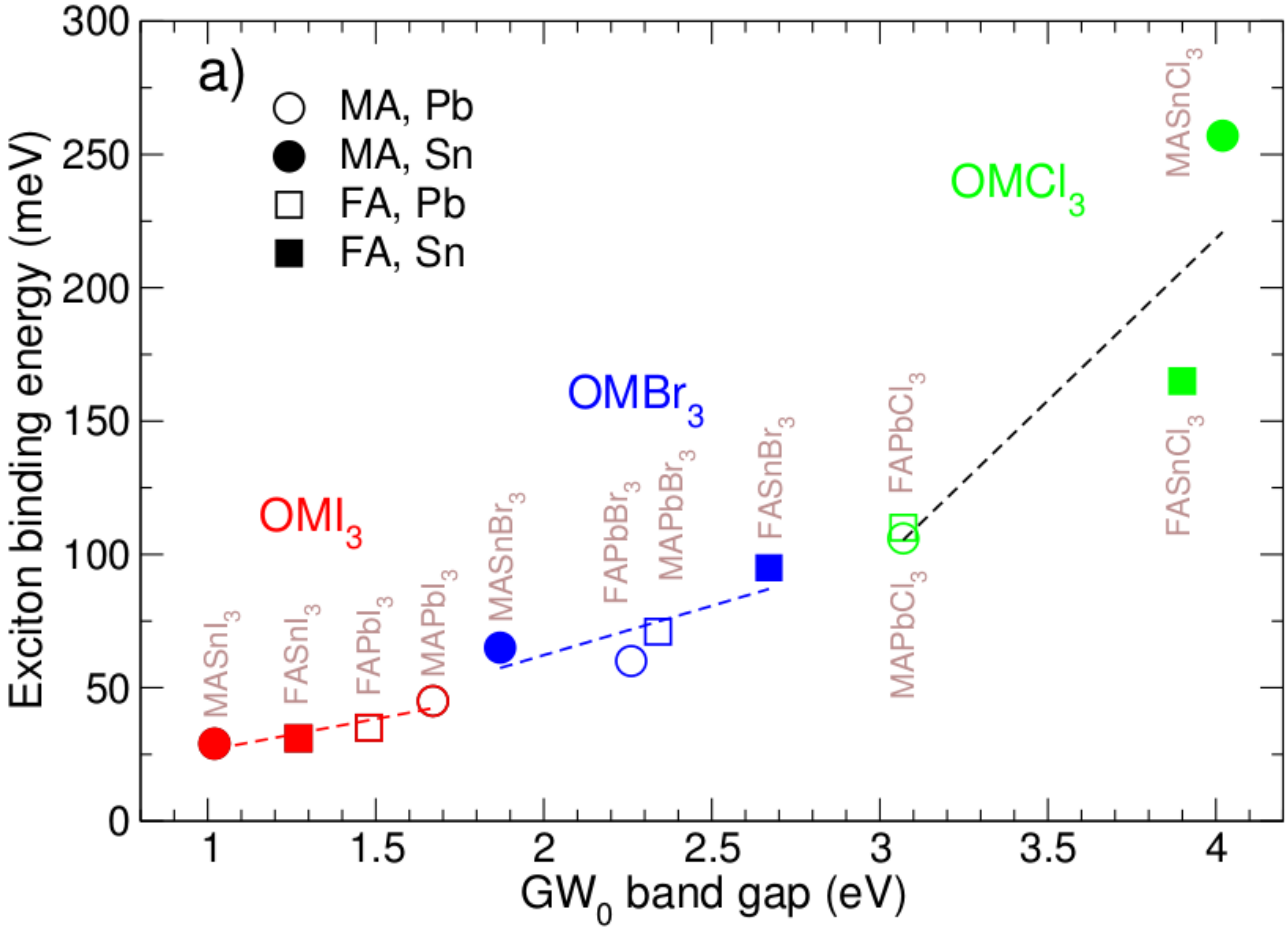
In photovoltaic cells, excitons are broken up into free electrons and holes





Organometal halide perovskite with gap=1-2 eV and $E_{xb} < 100$ meV wanted

Fully-relativistic GW + BSE (e-h)



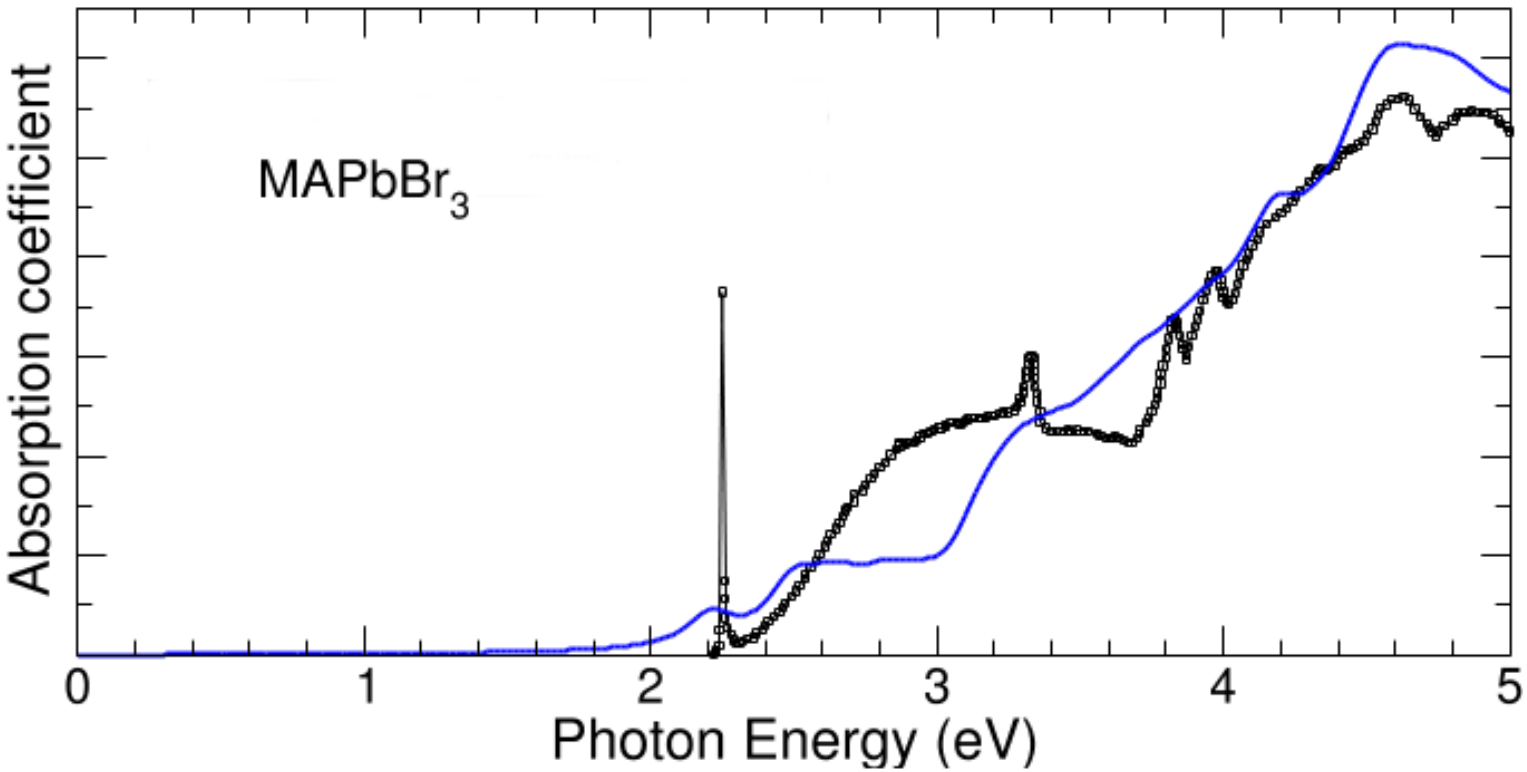
M. Bokdam, T. Sander, A. Stroppa, D.D. Sarma, S. Picozzi, C. Franchini, G. Kresse, under review.

Fully-relativistic GW + BSE (e-h)

	$\Delta_{\rm opt}$ (eV)	$\Delta_{\rm opt}^{\rm EXP}$ (eV)	$\rm E_{xb}$ (meV)	$E_{\rm xb}^{\rm EXP}$ (meV)
$MASnI_3$	1.00	*1.21*,[3] *1.63*[7]	29	-
$FASnI_3$	1.23	*1.41*[3]	31	-
$FAPbI_3$	1.45	*1.43*,[8] *1.45*,[3] *1.48*[5]	35	-
$MAPbI_3$	1.63	*1.65*,[7] 1.63[9,10] *1.57*,[5] *1.52*[3]	45	38,[9] 50[10]
$MASnBr_3$	1.80	*2.25*[7]	65	-
$FAPbBr_3$	2.20	*2.23*[5]	60	-
$MAPbBr_3$	2.27	2.26,[10] *2.33*,[7] *2.35*[6]	71	76[10]
$FASnBr_3$	2.58	-	95	-
$FAPbCl_3$	2.96	-	110	-
$MAPbCl_3$	2.97	*3.11*,[6] *3.13*[7]	106	-
$FASnCl_3$	3.74	-	165	-
$MASnCl_3$	3.77	-	257	-

M. Bokdam, T. Sander, A. Stroppa, D.D. Sarma, S. Picozzi, C. Franchini, G. Kresse, under review.

Fully-relativistic GW + BSE (e-h)

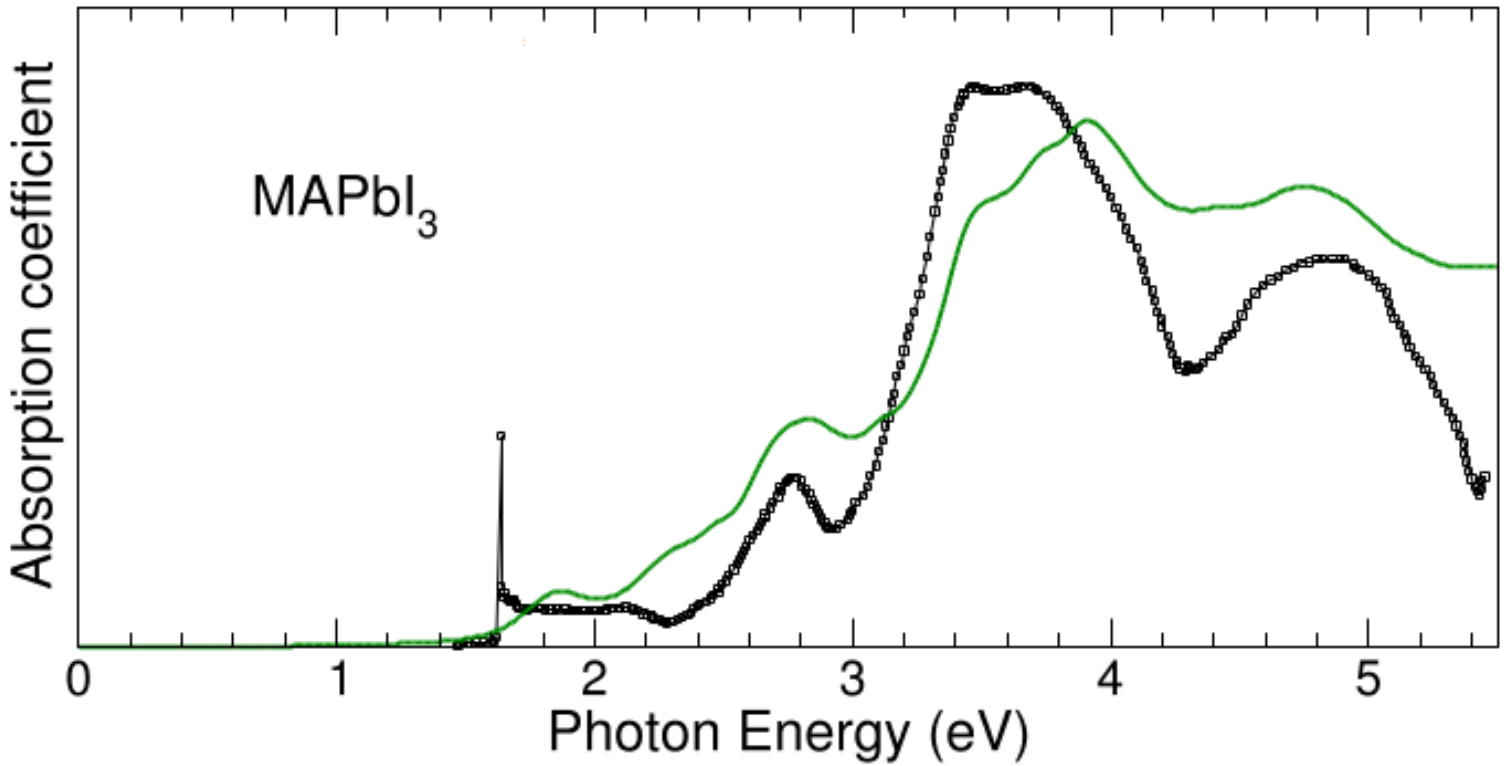


Experiment: M. Tanaka, et al., Sol. State Comm. 127, 619 (2003).

Experiment: M. Hirasawa, T. Ishihara, T. Goto, J. Phys. Soc. Jpn. 63, 3870 (1994).

Th.: M. Bokdam, T. Sander, A. Stroppa, D.D. Sarma, S. Picozzi, C. Franchini, G. Kresse, under review.

Fully-relativistic GW + BSE (e-h)



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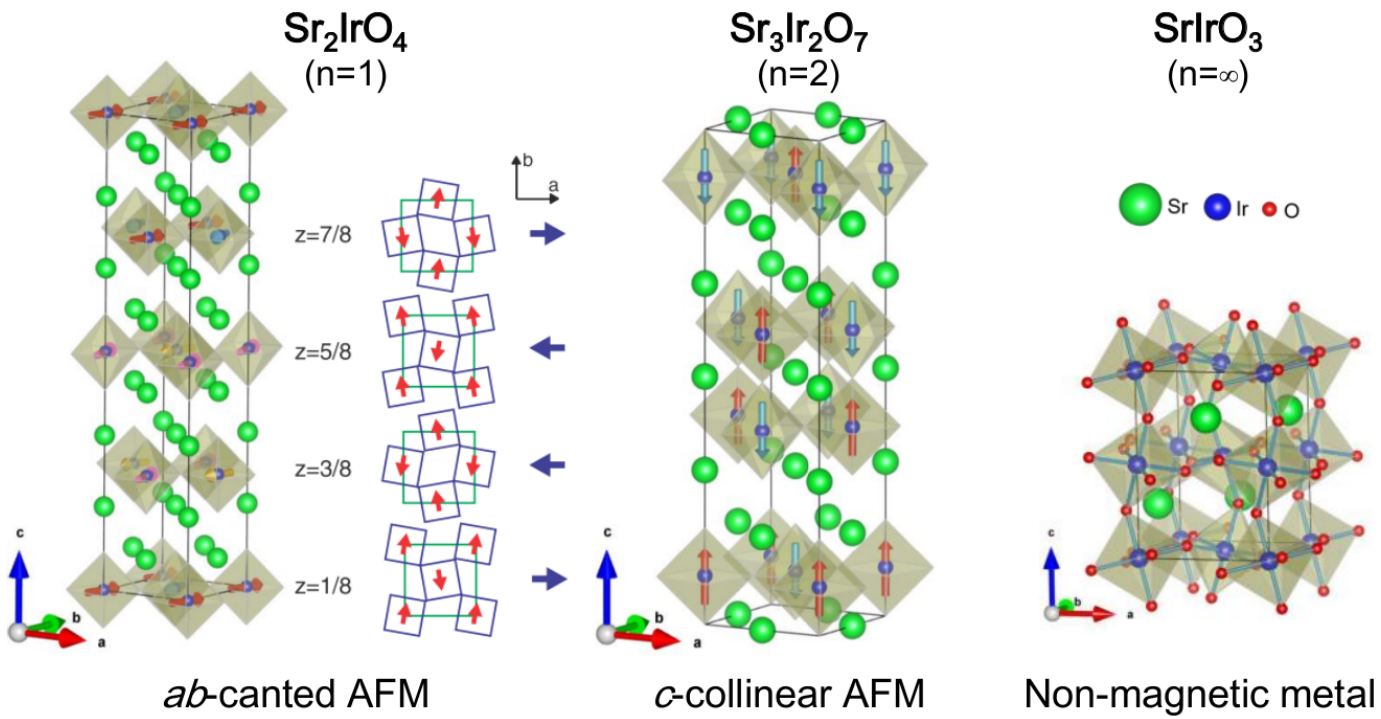
Th.: M. Bokdam, T. Sander, A. Stroppa, D.D. Sarma, S. Picozzi, C. Franchini, G. Kresse, under review.

Anisotropic Magnetic Couplings in Sr_2IrO_4

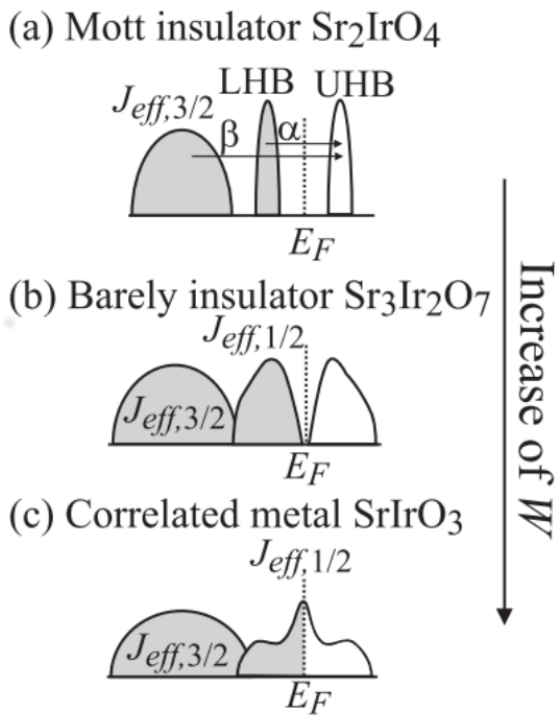
spin-orbital-lattice

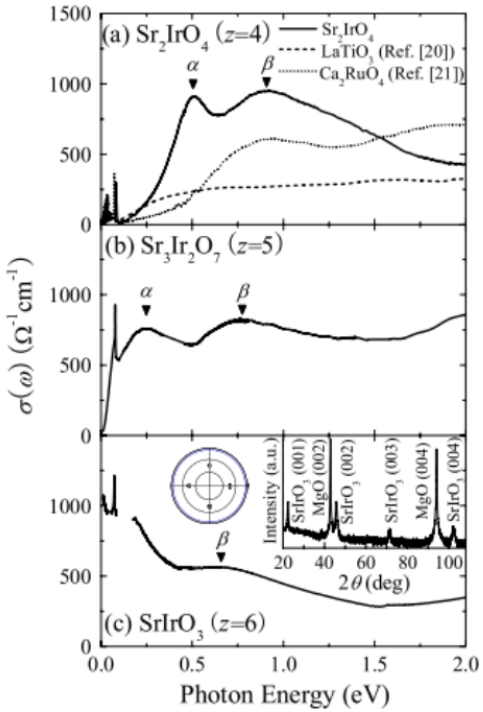
Structural and magnetic characteristics

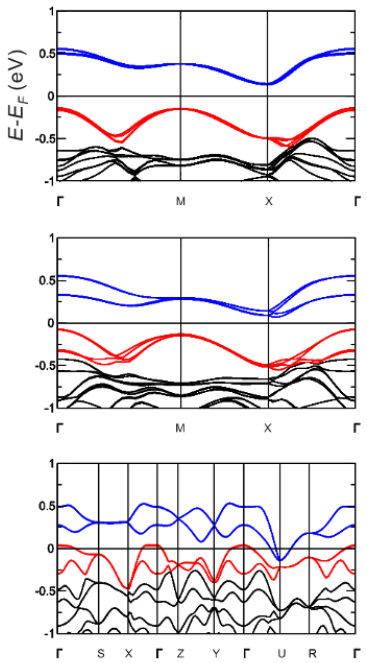


B. J. Kim *et al.*, Science 323, 1329 (2009) S. Fujiyama *et al.*, Phys. Rev. B 86, 174414 (2012)

Dimensionality-controlled insulator-metal transition

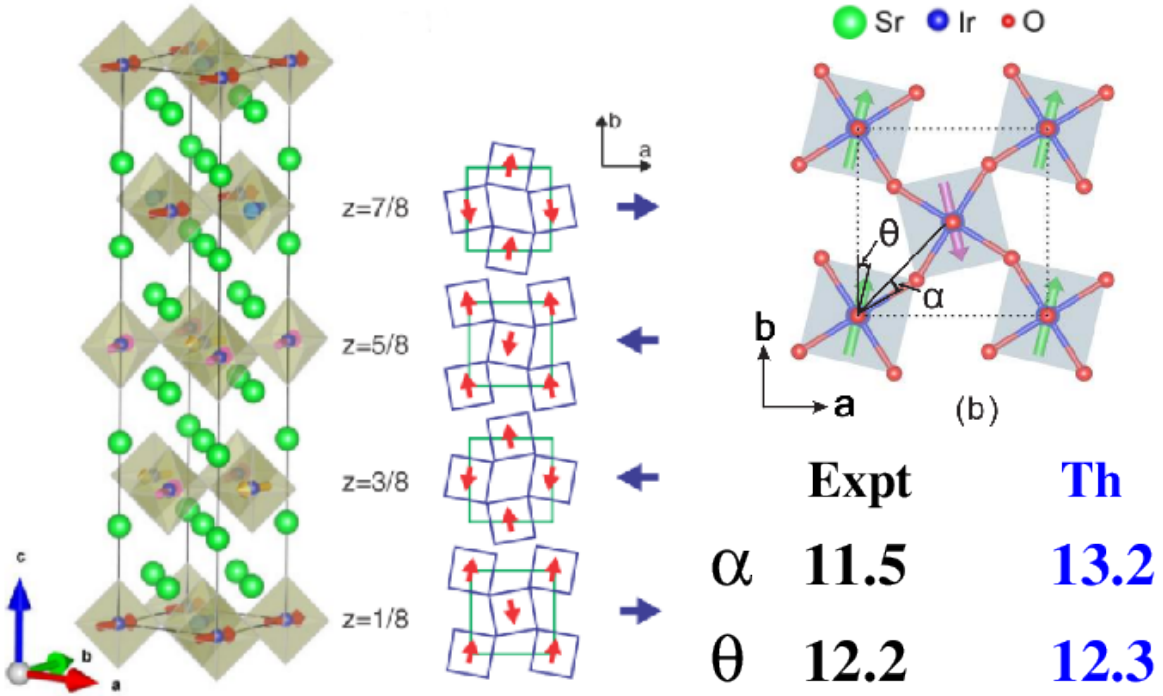






Moon S. J. *et al.*, PRL. 101, 226402 (2008).

Anisotropic magnetism in Sr_2Ir_4: Canted AFM ordering



	Expt	Th
α	11.5	13.2
θ	12.2	12.3
m	0.06–0.01	0.08

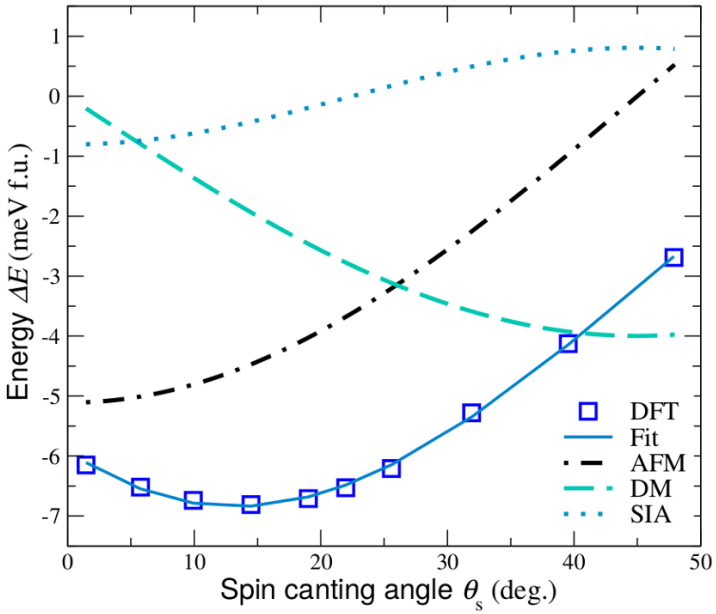
Feng Ye, Songxue Chi, Bryan C. Chakoumakos, Jaime A. Fernandez-Baca, Tongfei Qi, and G. Cao, PRB 87, 140406(R) (2013).

P Liu, S Khmelevskyi, B Kim, M Marsman, D Li, X Chen, DD Sarma, G Kresse, C Franchini, arXiv:1503.06753.

Anisotropic magnetism in Sr_2Ir_4: spin-dependent Hamiltonian

$$\Delta E = -\sum_{i<j} \mathbf{J}_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + \sum_i \varepsilon^i_{an}(\mathbf{S}_i) + \sum_{i<j} \mathbf{D}_{ij} \cdot [\mathbf{S}_i \times \mathbf{S}_j]$$

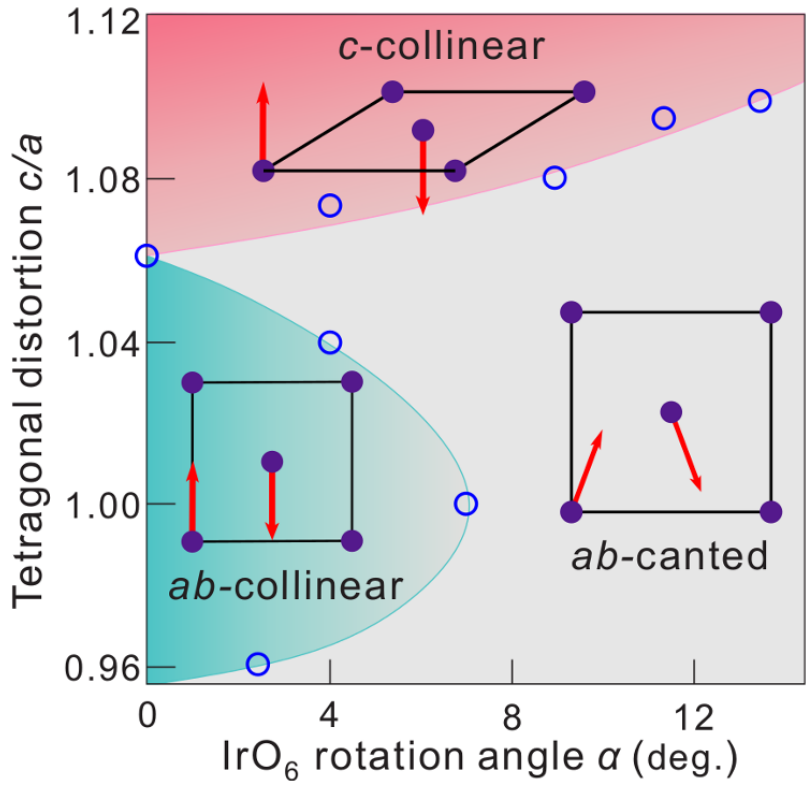
$$\Delta E = 16JS^2 \cos(2\theta_s) + 8K \cos(4\theta_s) + 16D_z S^2 \sin(2\theta_s) \quad [\text{meV}]$$



- $-\sum_{i<j} \mathbf{J}_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$
  isotropic AFM exchange, JS^2=-0.32
  → prefers collinear alignment of spins
- $\sum_i \varepsilon^i_{an}(\mathbf{S}_i)$
  single-ion (magnetocrystalline) anisotropy, K=-0.10
  → preferential orientation of the spins (easy axes)
- $\sum_{i<j} \mathbf{D}_{ij} \cdot [\mathbf{S}_i \times \mathbf{S}_j]$
  Dzyaloshinskii-Moriya interaction, D_zS^2=-0.25
  → prefers orthogonal coupling of the spins

P Liu *et al.*, arXiv:1503.06753.

Anisotropic magnetism in Sr_2Ir_4: Magnetic phase diagram

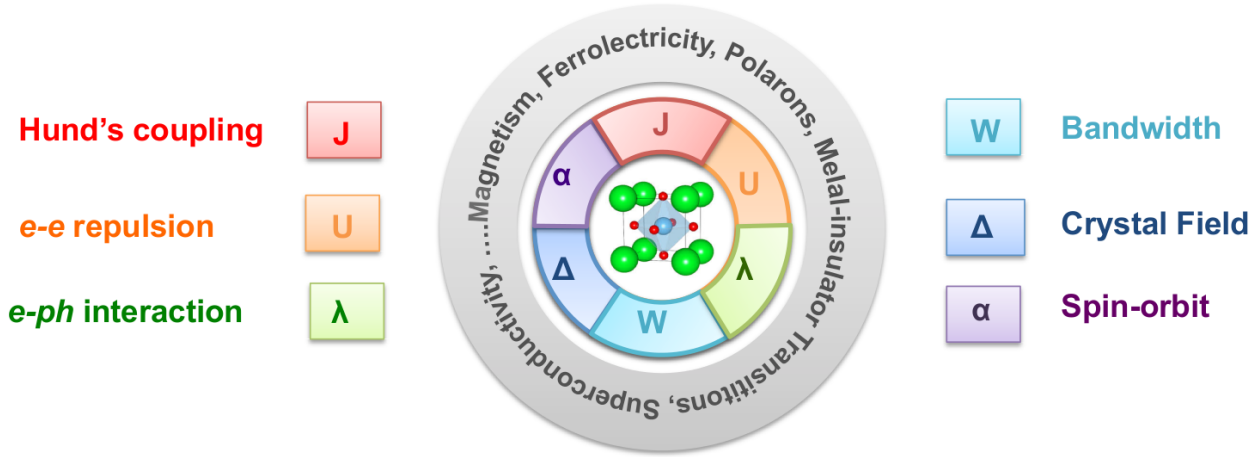


Two types of structure-induced canted to collinear magnetic transitions:

1. Spin-flop transition with increasing tetragonal distortion
2. Quenching of the basal weak FM moment below a critical α

P Liu *et al.*, arXiv:1503.06753.

Summary



1. electron-phonon: Polarons vs. free-carrier (2DEG) in TiO_2 and $SrTiO_3$
2. spin-orbit & electron-hole: Excitons in perovskite solar cells
3. spin-orbital-lattice: Non collinear magnetism in Sr_2IrO_4

Thank you for your attention