Anomalous Excitons in Titanium Dioxide

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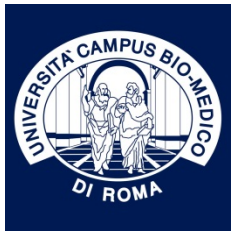


Workshop on Spectroscopy and Dynamics of Photoinduced Electronic Excitations
Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, 8-12 May 2017

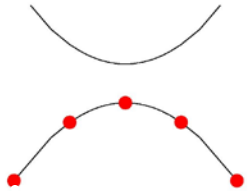
Outline

- introduction on TiO_2
- new data: experiments, theory, the role of doping and temperature on
  - electronic gap
  - optical response
- the nature of excitons in anatase
- further peculiar behaviour of excitons in TiO_2

3-steps theoretical/computational ab initio method for optics: MBPT

DFT-GGA

Ground State properties (Total energy):

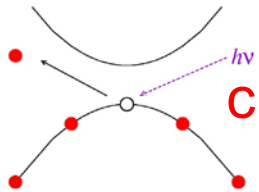


ground state

$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H + V_{xc})\phi_j^{KS}(\vec{r}) = \varepsilon_j^{KS}\phi_j^{KS}(\vec{r})$$

GW

1 particle excitations (photoemission)

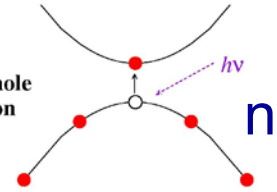


charged excitations

$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H)\Psi_j^{QP}(\vec{r}) + \int \Sigma(\vec{r},\vec{r'},\varepsilon_j^{QP})\Psi_j^{QP}(\vec{r'})d\vec{r'} = \varepsilon_j^{QP}\Psi_j^{QP}(\vec{r})$$

BSE

2 particle excitations (absorption)



neutral excitations

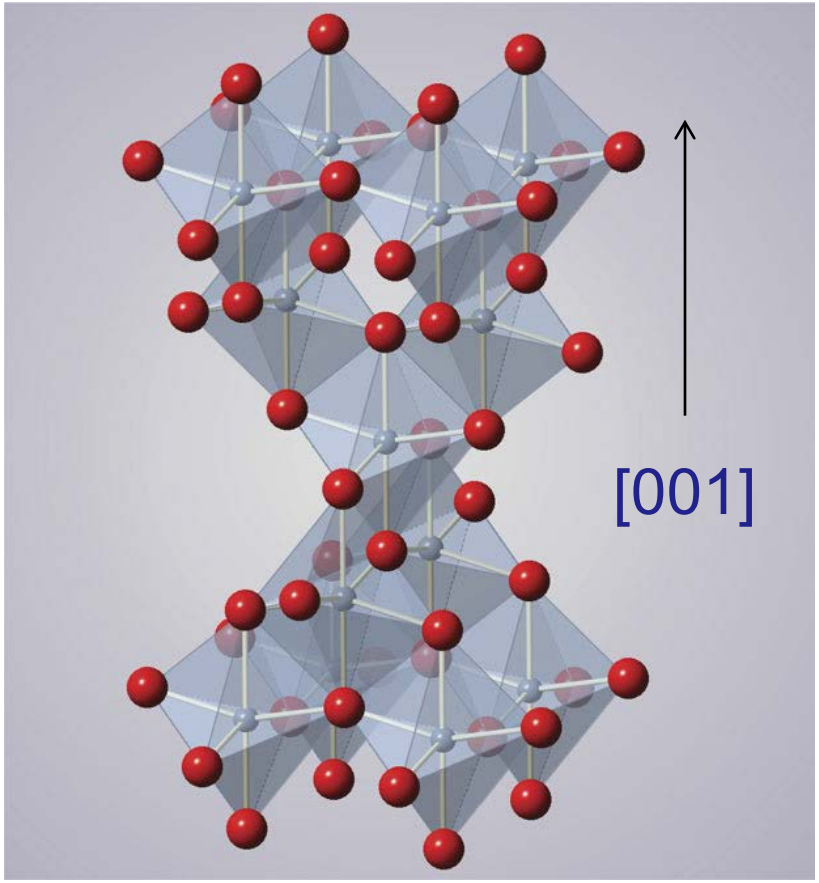
G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. 74 (2002) 601, and references therein

CODES

Quantum Espresso (DFT)

BerkeleyGW, *Yambo* (GW+BSE)

Anatase Crystal Structure



blue atoms: titanium
red atoms: oxygen
TiO_6 polyhedra highlighted

tetragonal, anisotropic unit cell
network of corner-sharing or edge sharing TiO_6 octahedra

Ti-3d O-2p orbital interactions run mainly in TiO_2 bilayers, perpendicular to [001]
minor contribution along [001]

ANATASE TiO_2

- material easily fabricated and widely available, useful for energy conversion and transport
- we started working at it in 2008-2009, with GW+BSE
  - GW direct gap at Γ, 4.29 eV (exp. unknown at the time)
  - GW indirect gap at XΓ, 3.83 eV
  - first optical transition at 3.90 eV

Phys. Rev. B 82, 045207 (2010)

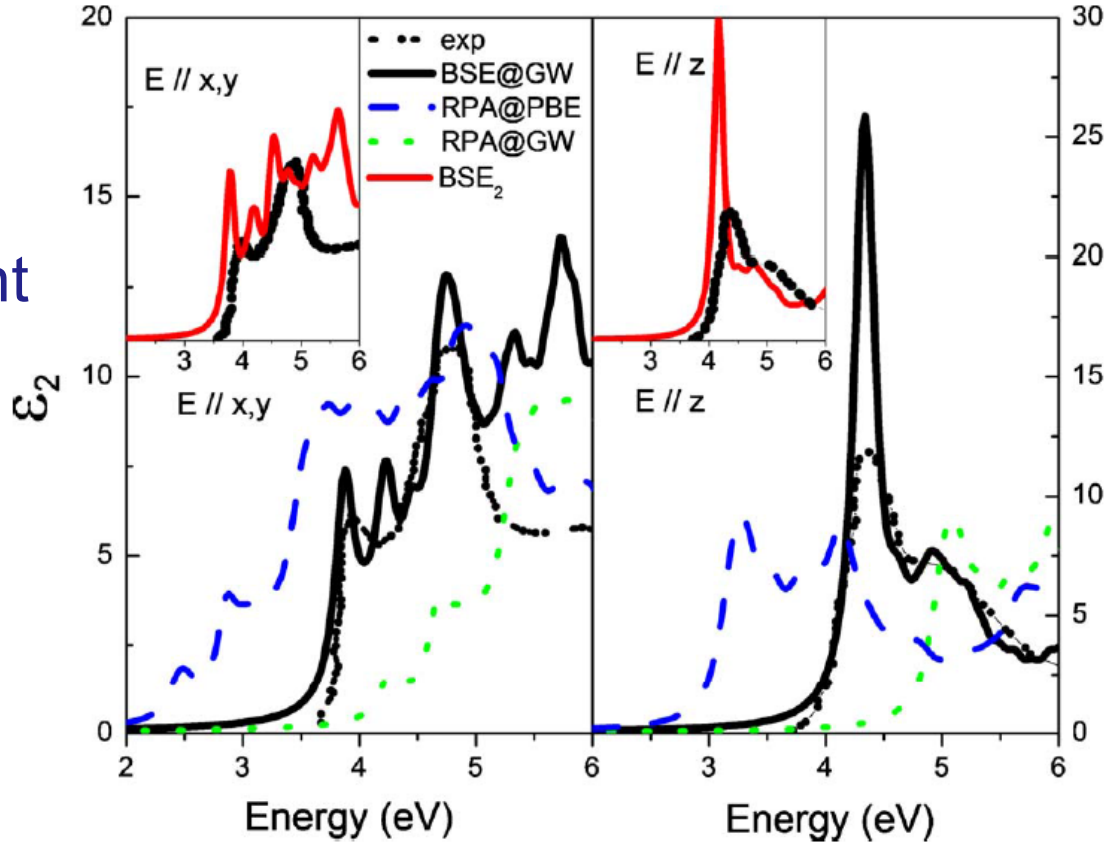
ANATASE TiO_2

- the optical direct gap is at 3.9 eV (not at 3.2 eV)

(where an Urbach tail, related to the indirect gap, is present)

reasonable agreement with experiments

note the anisotropy



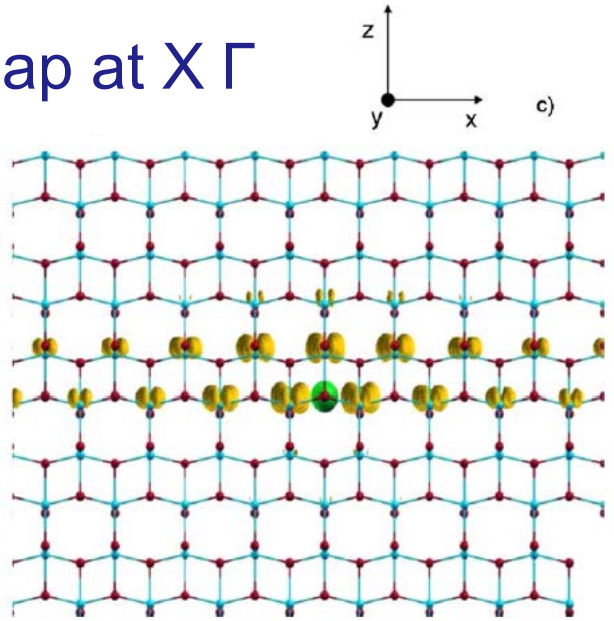
these were the facts….. BUT

PRB 82, 045207 (2010)

ANATASE TiO_2

BUT ..

- first optical transition is ABOVE direct gap at Γ
- first optical transition is BELOW indirect gap at X Γ
- first optical transition has an associated wavefunction of peculiar shape



PRB 82, 045207 (2010)

so, there were the 'OPEN QUESTIONS':

- is the first optical transition **bound**? why?
- is there a certain degree of **localization**? why?

Why it is difficult

- difficulty of measuring the exciton binding energy (E_B) for an indirect gap material

- perfect, infinite crystal in calculations

- experimental anatase crystals show defects

- nanoparticles (mostly used in applications) are
- in solvent
- disordered
- doped and defected

How to reconcile everything?

New Experimental andTheoretical Data

collaboration with EPFL experimental group

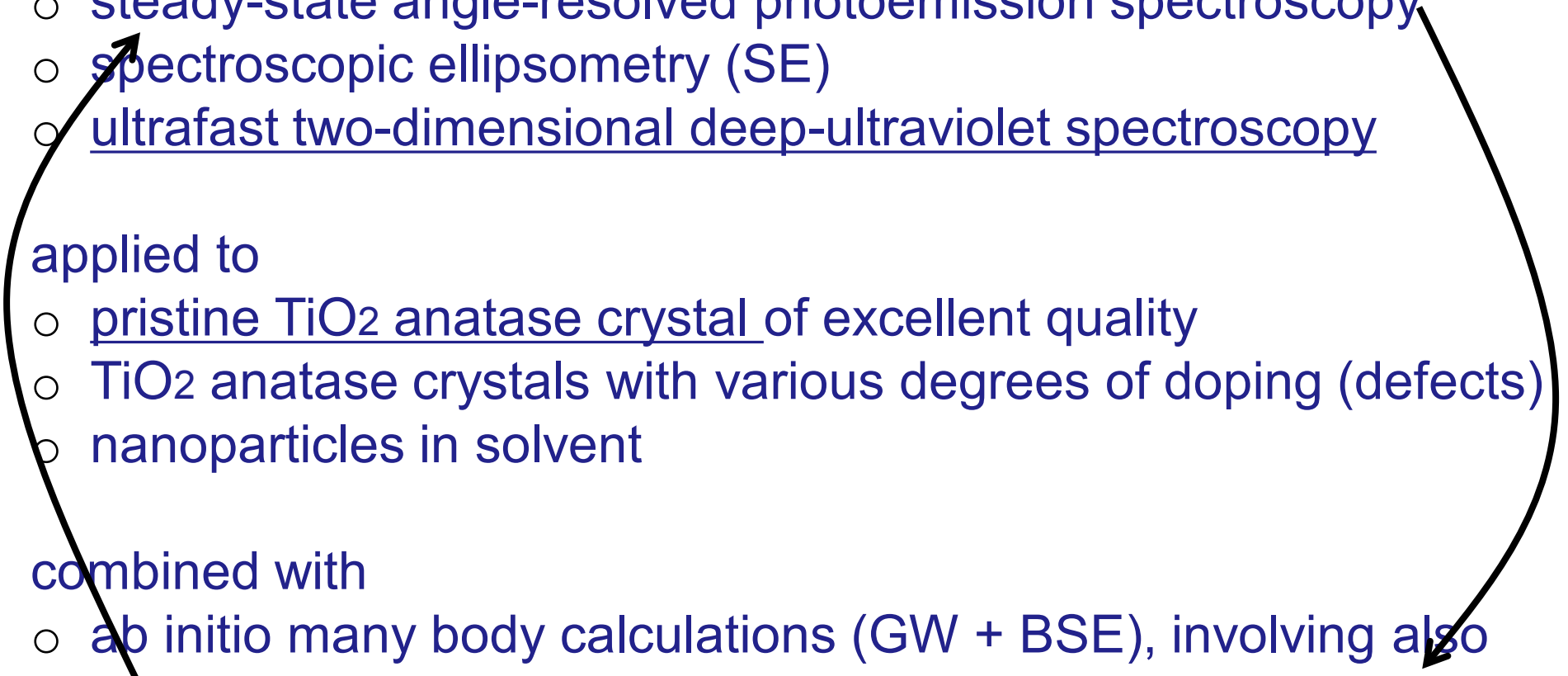
- steady-state angle-resolved photoemission spectroscopy
- spectroscopic ellipsometry (SE)
- ultrafast two-dimensional deep-ultraviolet spectroscopy

applied to

- pristine TiO_2 anatase crystal of excellent quality
- TiO_2 anatase crystals with various degrees of doping (defects)
- nanoparticles in solvent

combined with

- ab initio many body calculations (GW + BSE), involving also DOPING and TEMPERATURE effects

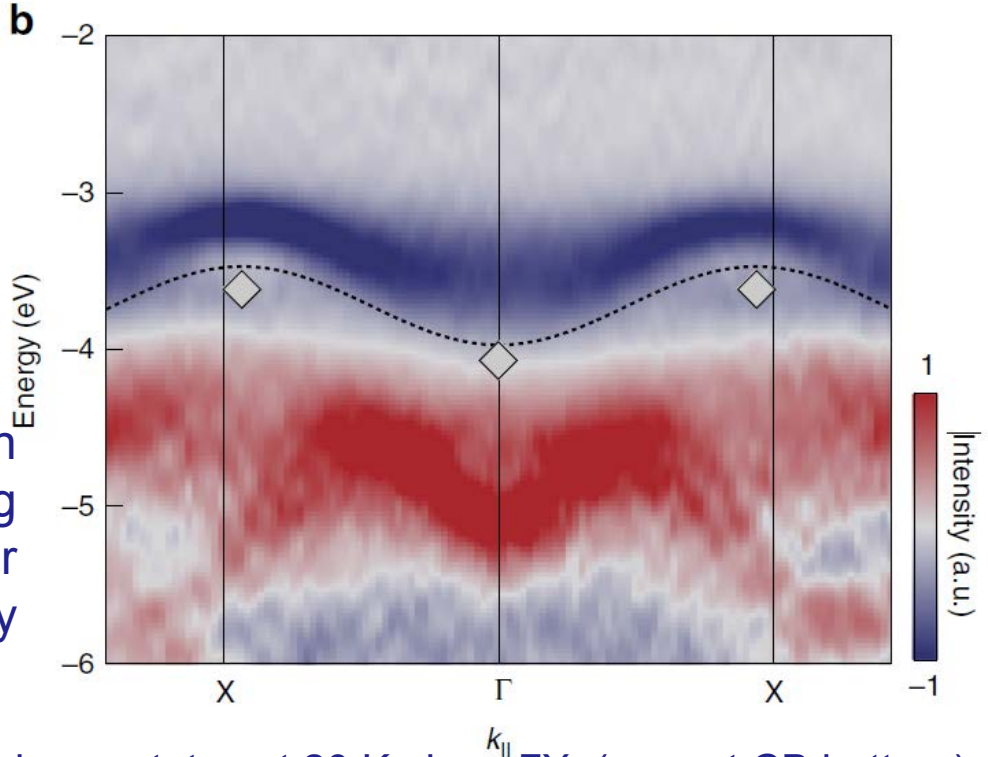


Electronic Band Gap

- to reveal a direct exciton, an accurate determination of the **direct electronic bandgap** is needed
- ARPES measurements on anatase TiO_2 single crystal (doped in a controlled manner)

X −3.47 eV
Γ −3.97 eV

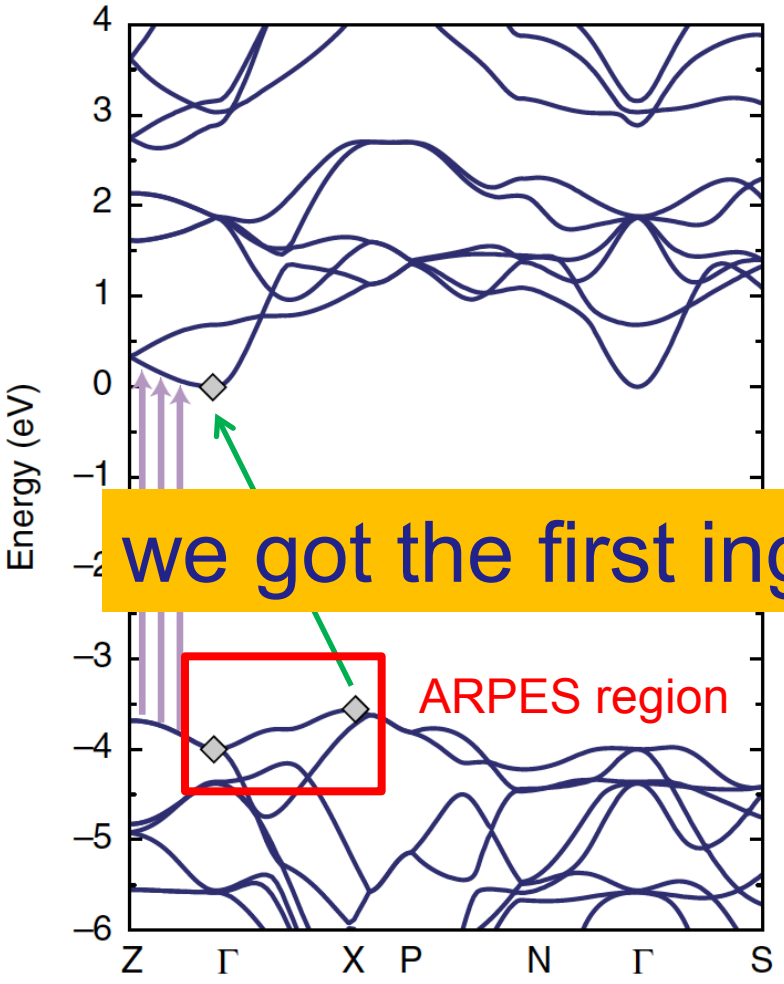
no measurable bandgap renormalization (BGR) at the Γ point upon doping (increased electron concentration over three orders of magnitude, confirmed by many-body perturbation theory results)



valence states at 20 K along ΓX (zero at CB bottom)

Nat Commun **8**, 13 (2017)

Electronic Band Gap



GW electronic structure
almost **flat bands along ΓZ**
direction of the 3D Brillouin zone

X −3.61 eV
Γ −4.07 eV

we got the first ingredient for a bound exciton

sources of differences:
- ~~doping~~ (slight blueshift)
- temperature (E_u, A_{2u} modes)

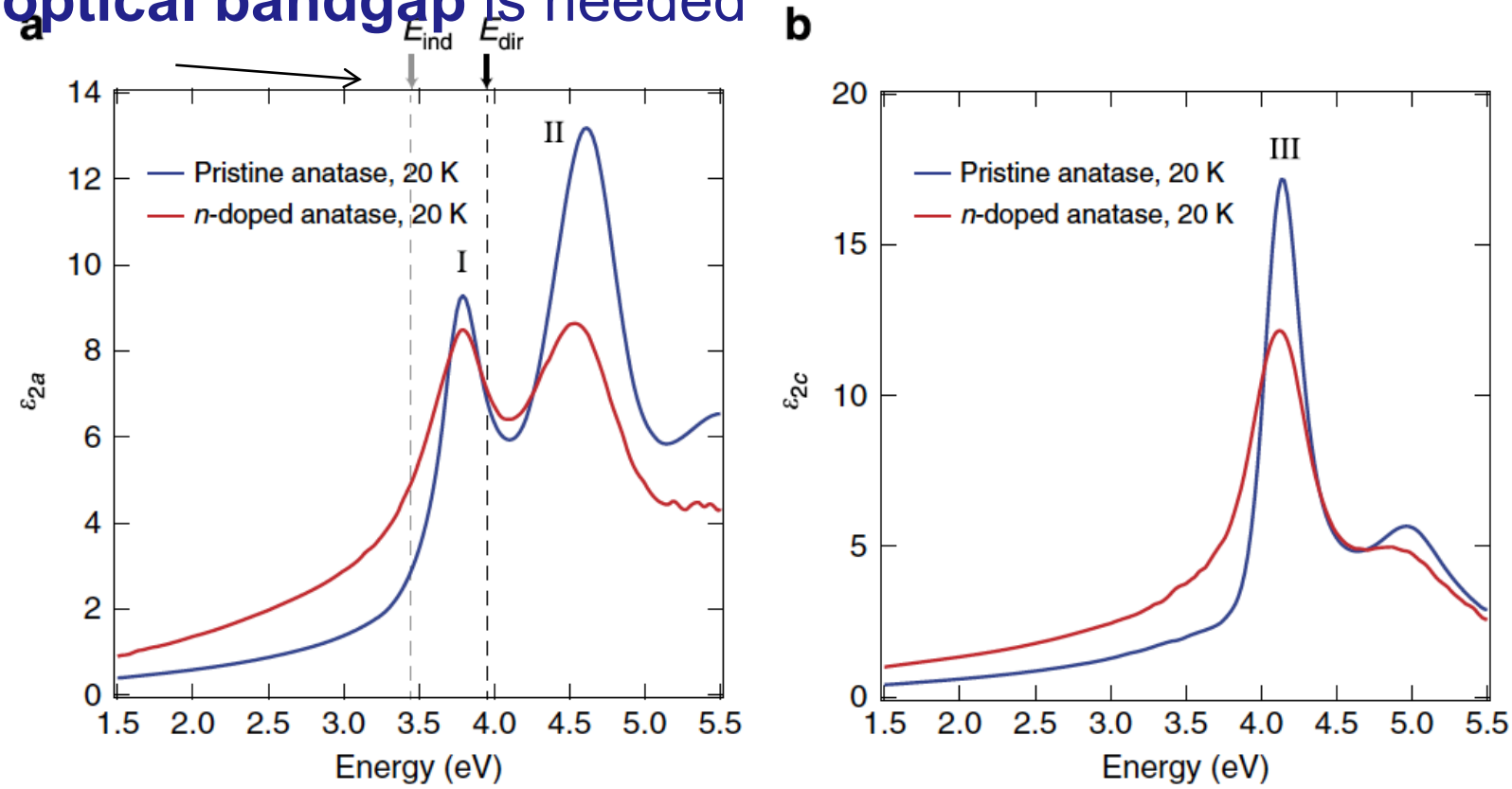
at low T, GW calculations for main modes give negligible blueshift

Γ −3.92 eV (based on ZPR for rutile, PRB 93, 100301 (2013))

Nat Commun **8**, 13 (2017)

SE Optical Absorption

- to reveal a direct exciton, an accurate determination of the **optical bandgap** is needed



strong optical anisotropy for light polarised in the (001) plane and perpendicular to it

high quality sample, ε direct measure, low T

→ HIGH QUALITY SPECTRA

SE Optical Absorption

pristine crystal, at 20 K

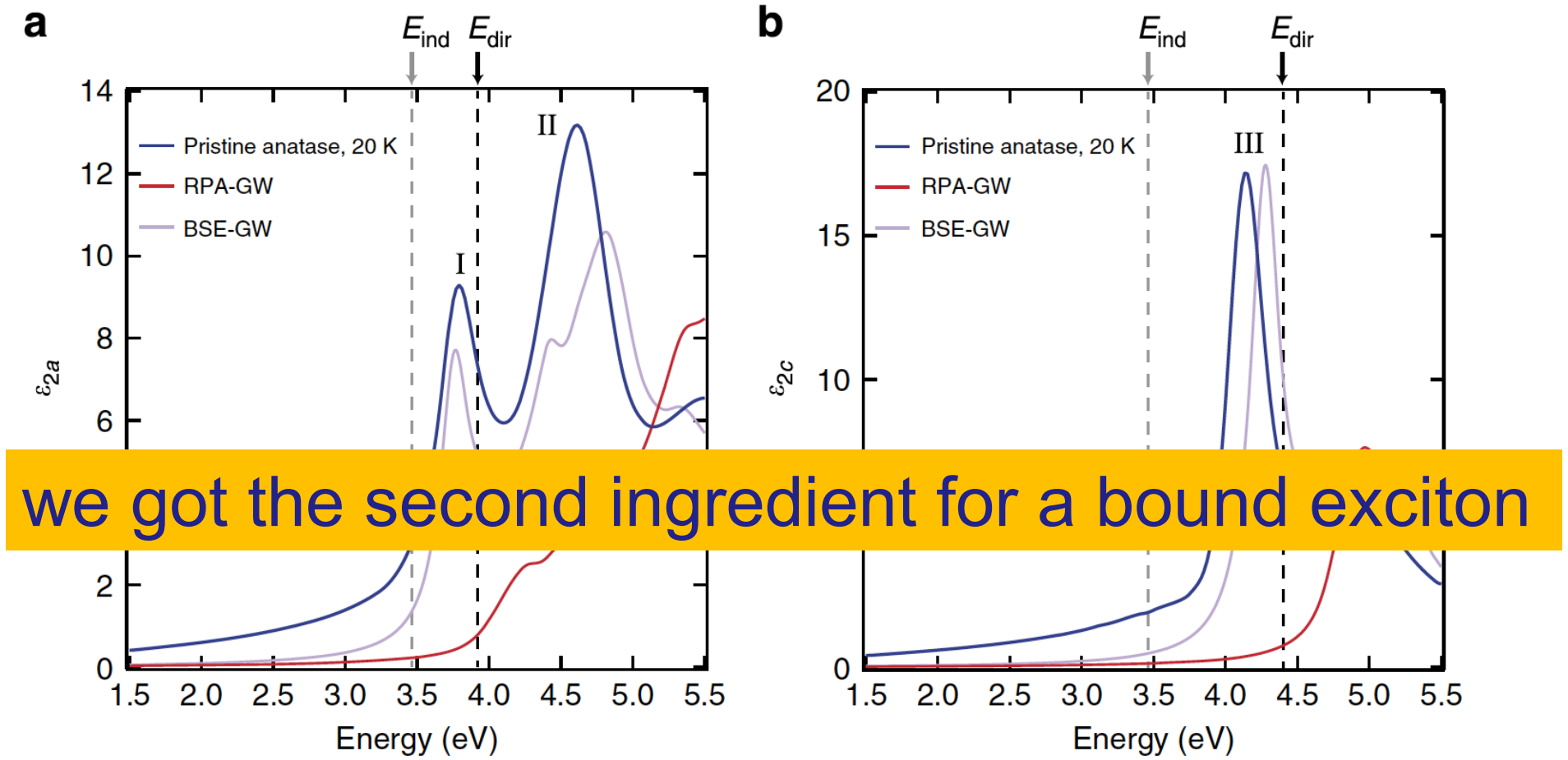
direct absorption for E ⊥ [001]
- sharp peak at **3.79 eV (I)**
- long Urbach tail at lower energies
- broader charge excitation at 4.61 eV (II) (up to 5.00 eV)

direct absorption for E || [001]
- peak at 4.13 eV (III) (with a shoulder at 5.00 eV)

all these excitations are still clear-cut in the **n-doped sample**

→ doping does not affect the peak (I) position (verified by GW-BSE calculations)

Ab Initio Optical Absorption



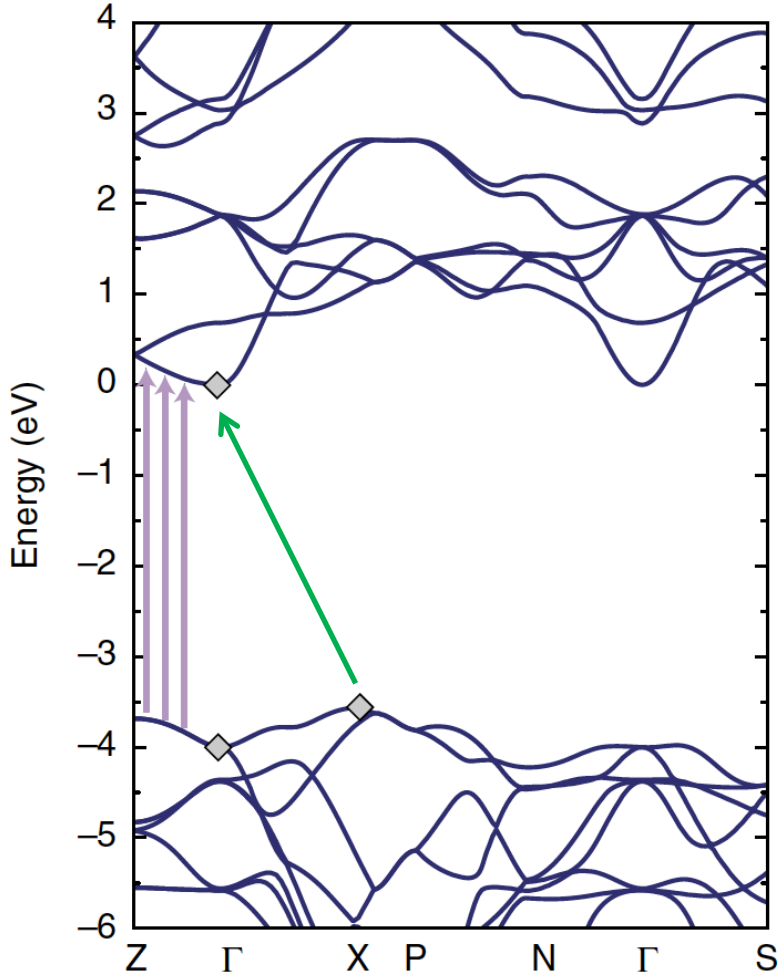
we got the second ingredient for a bound exciton

excellent agreement with exp SE

univocal assignment of peaks → exc (I) is the FIRST direct transition

→ exc (I) is used as optical gap

what about the indirect gap?

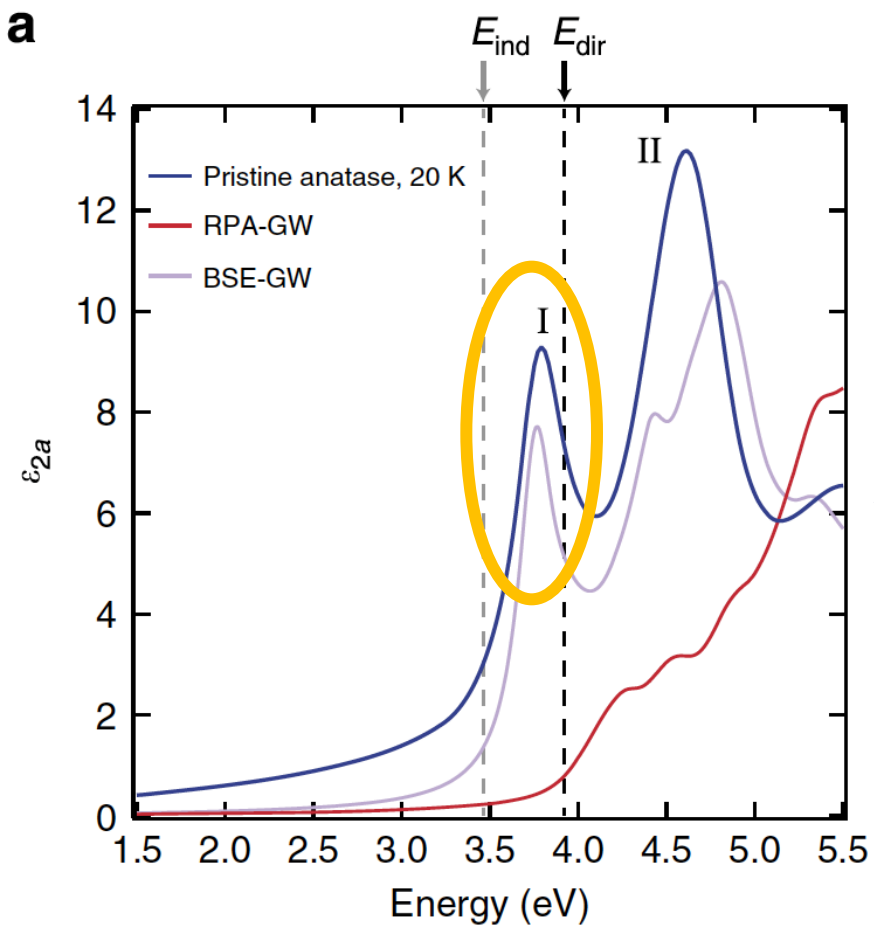


exc (I) comes from ΓZ region
VB and CB are almost parallel

indirect gap is at XΓ

supercell calculations exclude contributions to exc (I) from indirect transitions (no resonant)

PES + SE + (GW-BSE) =



bound exciton in anatase
E_B surprisingly large!

E_B exp. (20 K) = 180 meV
E_B th. (frozen atoms) = 160 meV

again, more questions than answers….

is exciton (I) stable at RT?
why it is so strongly bound?

is the exciton (I) delocalized, or not, in the crystal? why?

is the exciton (I) present, and how, in real samples (e.g. NPs)?
what to do with this 'bound' exciton?

is exciton (I) stable at RT?

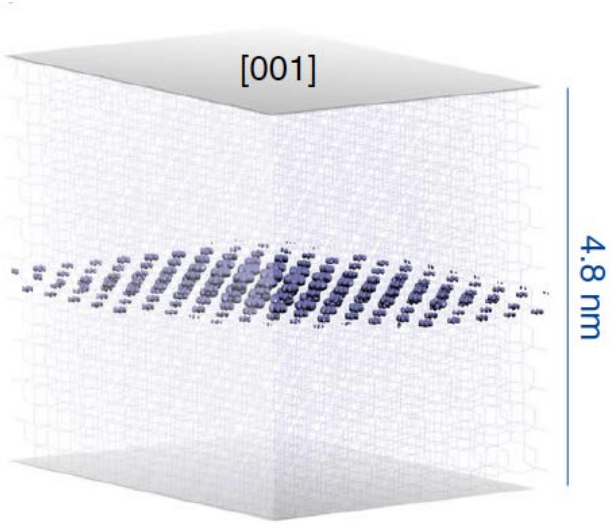
el-ph coupling effects on electronic and optical gap:
an overall blueshift is observed (experimental - computational)
→ at RT the exciton(I) is still bound

why it is so strongly bound?

- ε (anisotropic, depending on both energy and momentum) and **electronic structure** (parallel bands along ΓZ) give the overall behaviour of excitons binding
- intermediate binding energy: Wannier-Mott / Frenkel exciton

$SrTiO_3$: E_B 220 meV (Phys B 407, 2632 (2012), PRB 87, 235102 (2013))

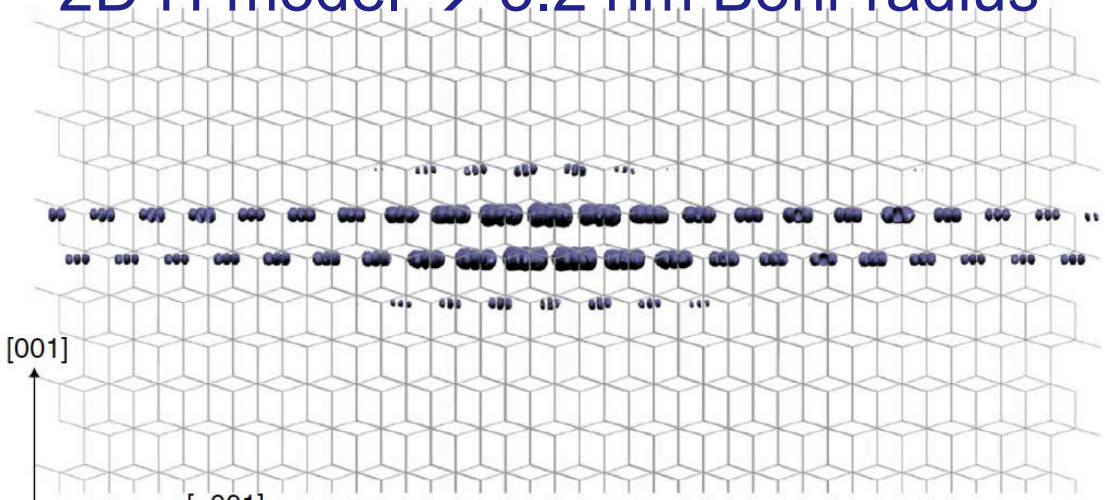
Localized Exciton (I)

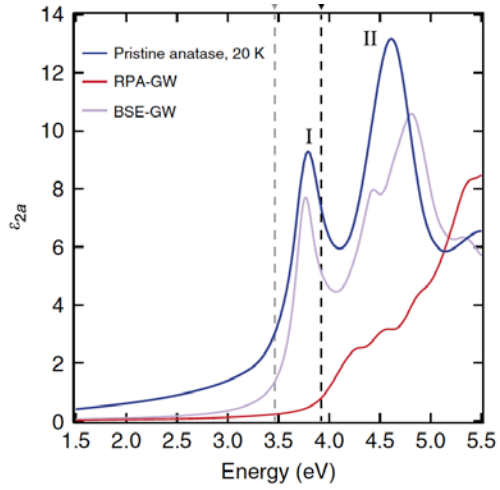


2D exciton in a 3D crystal:
similar to 2D materials!
(MoS2 ML, PRL 111, 216805 (2013))
not observed in rutile TiO_2 and $SrTiO_3$

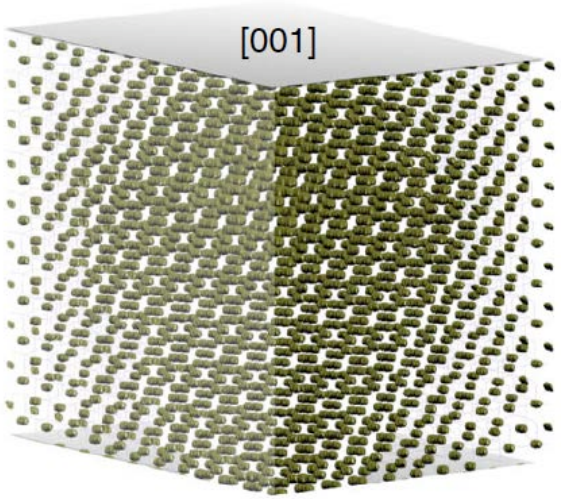
due to crystal & wavefunction symmetries (octahedra packing → along ΓZ, VB and CB are almost flat)

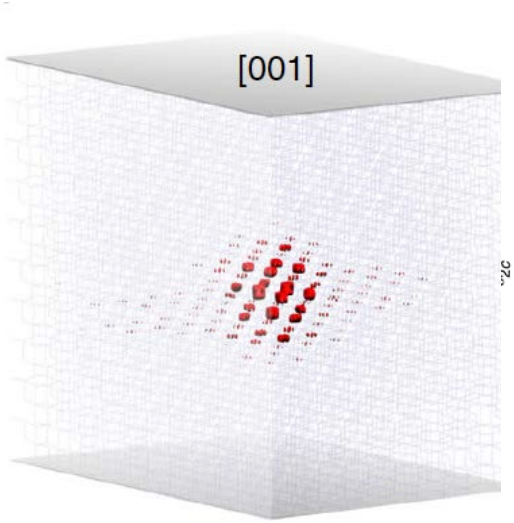
2D H-model → 3.2 nm Bohr radius

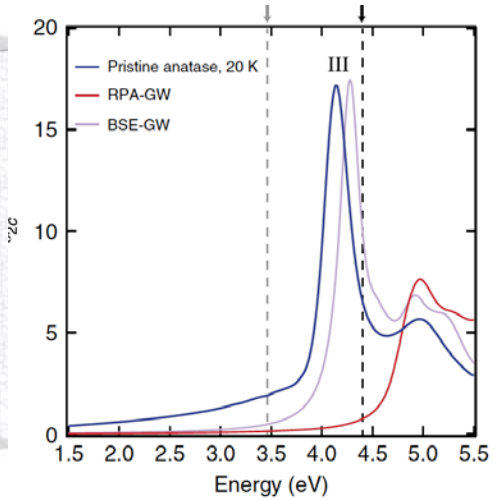




Resonant and Mixed Excitons



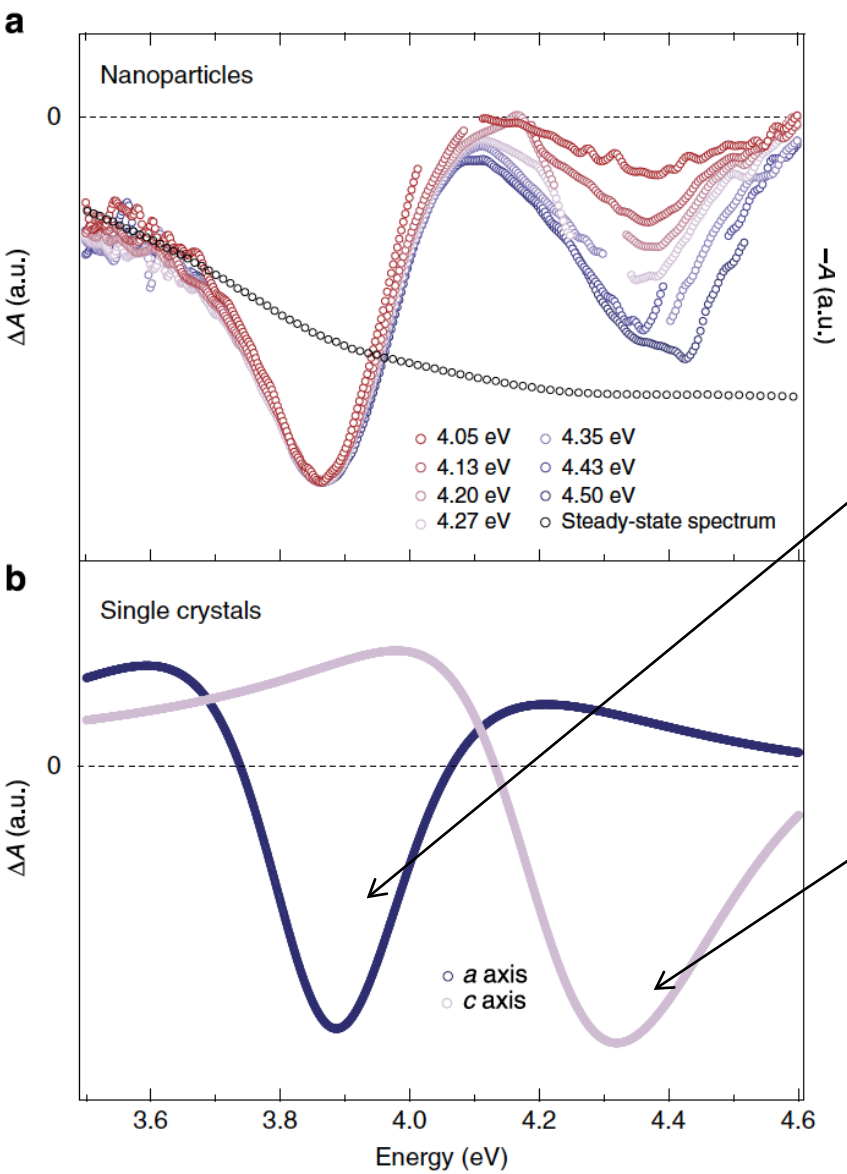


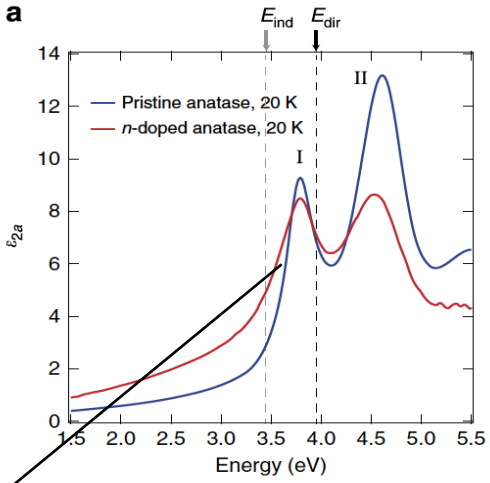


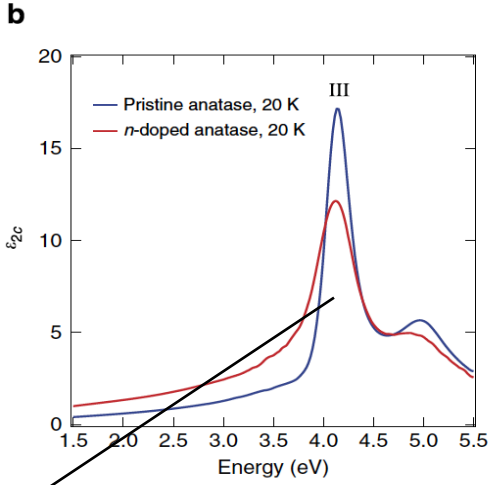
exciton (II):
resonant
onset at the GW
continuum rise

exciton (III):
resonant & localized
3D H-model (localized part)
→ 0.27 nm Bohr radius
E_B=150 meV

Excitons in NanoParticles





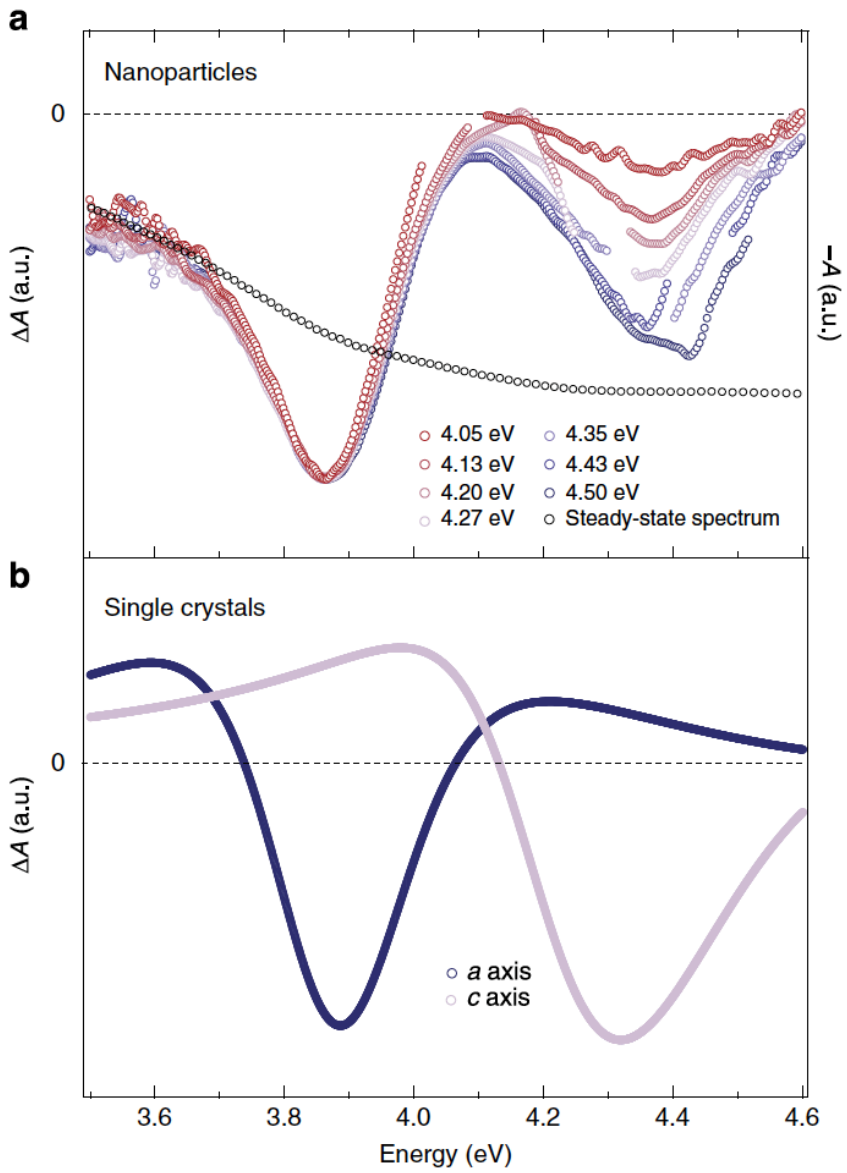


colloidal NPs (25 nm radius) doped single crystal

ultrafast two-dimensional deep-ultraviolet spectroscopy

only localized excitons appear

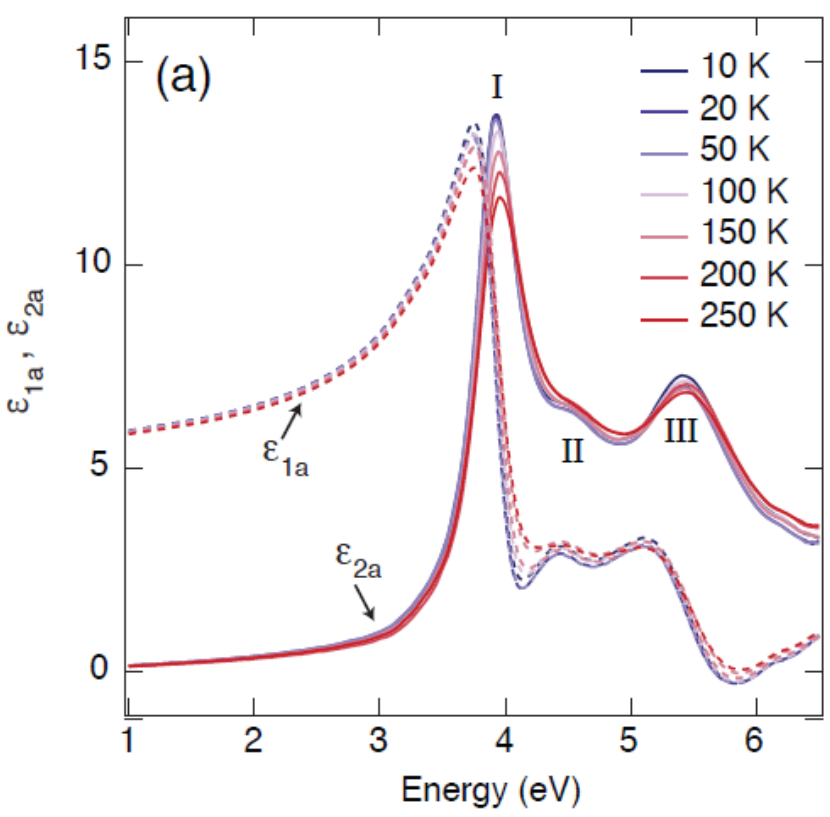
Excitons in NanoParticles

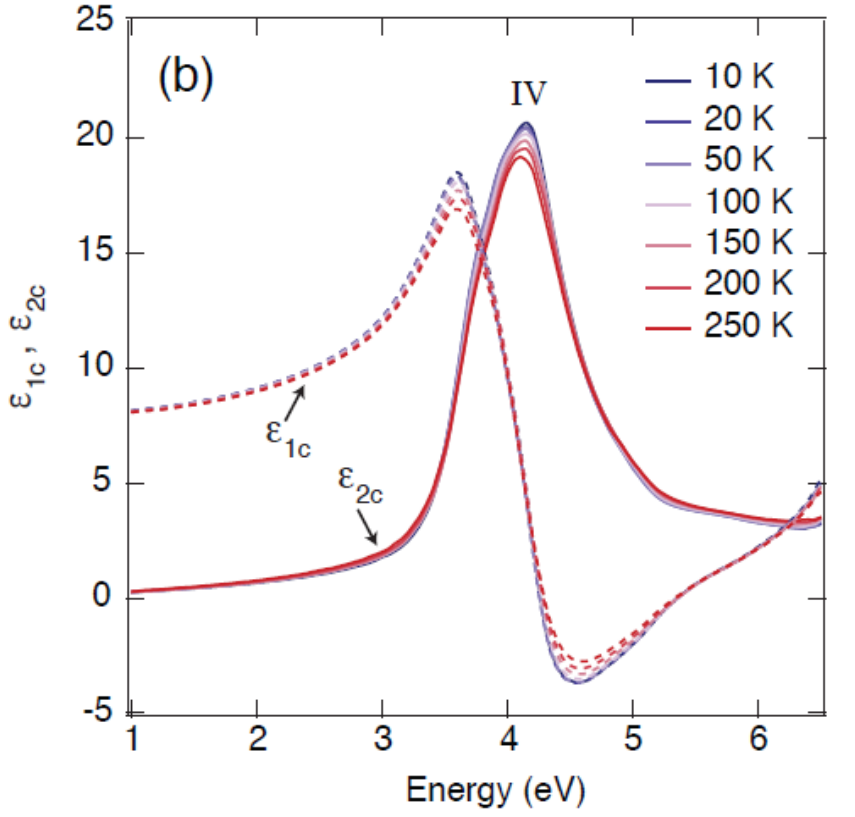


same elementary localized and bound excitations are observed in pure crystals and in defect-rich samples (doped single crystals and nanoparticles)

Excitons in Rutile

anomalous blueshift in rutile optical spectra with temperature
el-ph coupling at work

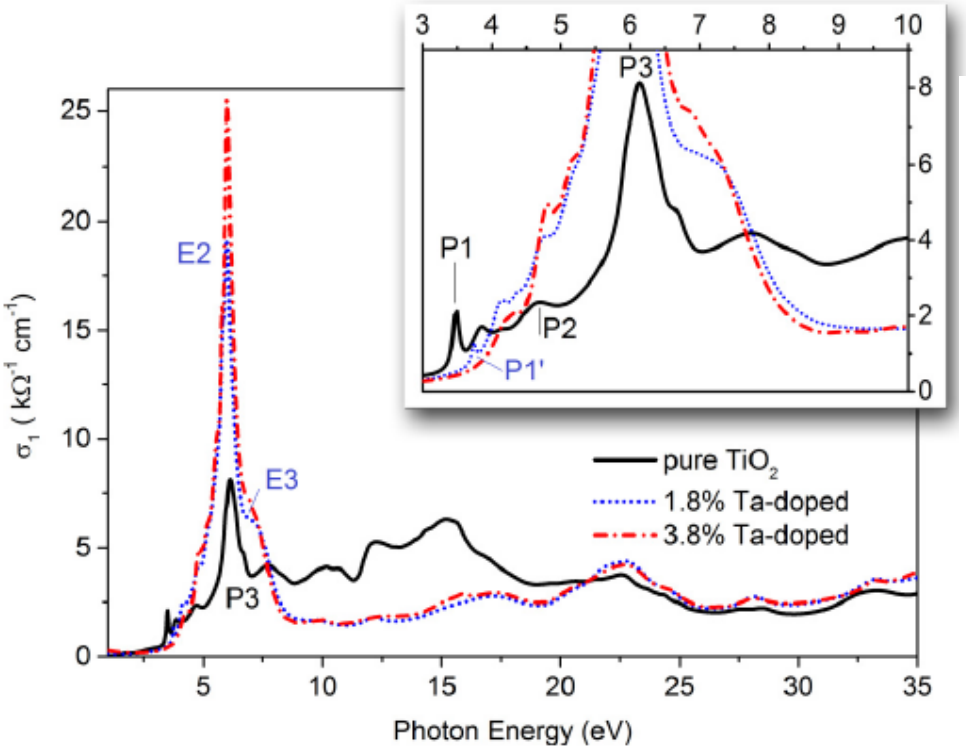


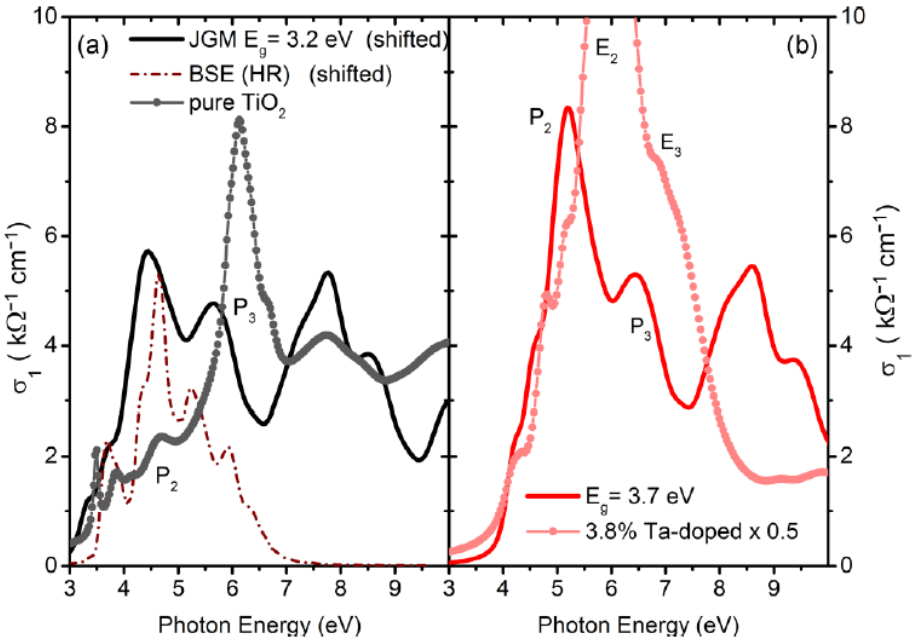


arXiv:1704.00176

Strong Correlation in Doped Anatase

anomalous resonant excitonic absorption induced by Ta doping





Ta-f electrons induce a transition, with a band gap opening, similar to strongly correlated materials (cuprates)

PRB 93, 205118 (2016)

Conclusions

- TiO_2 is not a 'simple' materials: it hides peculiar properties

- advanced experimental and theoretical techniques provide a unified and coherent description of a **bound localized 2D** exciton in anatase single **crystals**, pure and defected, and in more applicative samples as **colloidal NPs**
- a **3D localized** exciton is also observed at higher energies and different polarization
- anomalos T-effects in both rutile and anatase excitons
- anomalous doping-effects in anatase

→ doping, defects, el-ph may alter the optical response

- how to tune and optimize excitons behaviour via doping, strain, .

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