How can ab initio simulations help the PV industry ?

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EDF R&D

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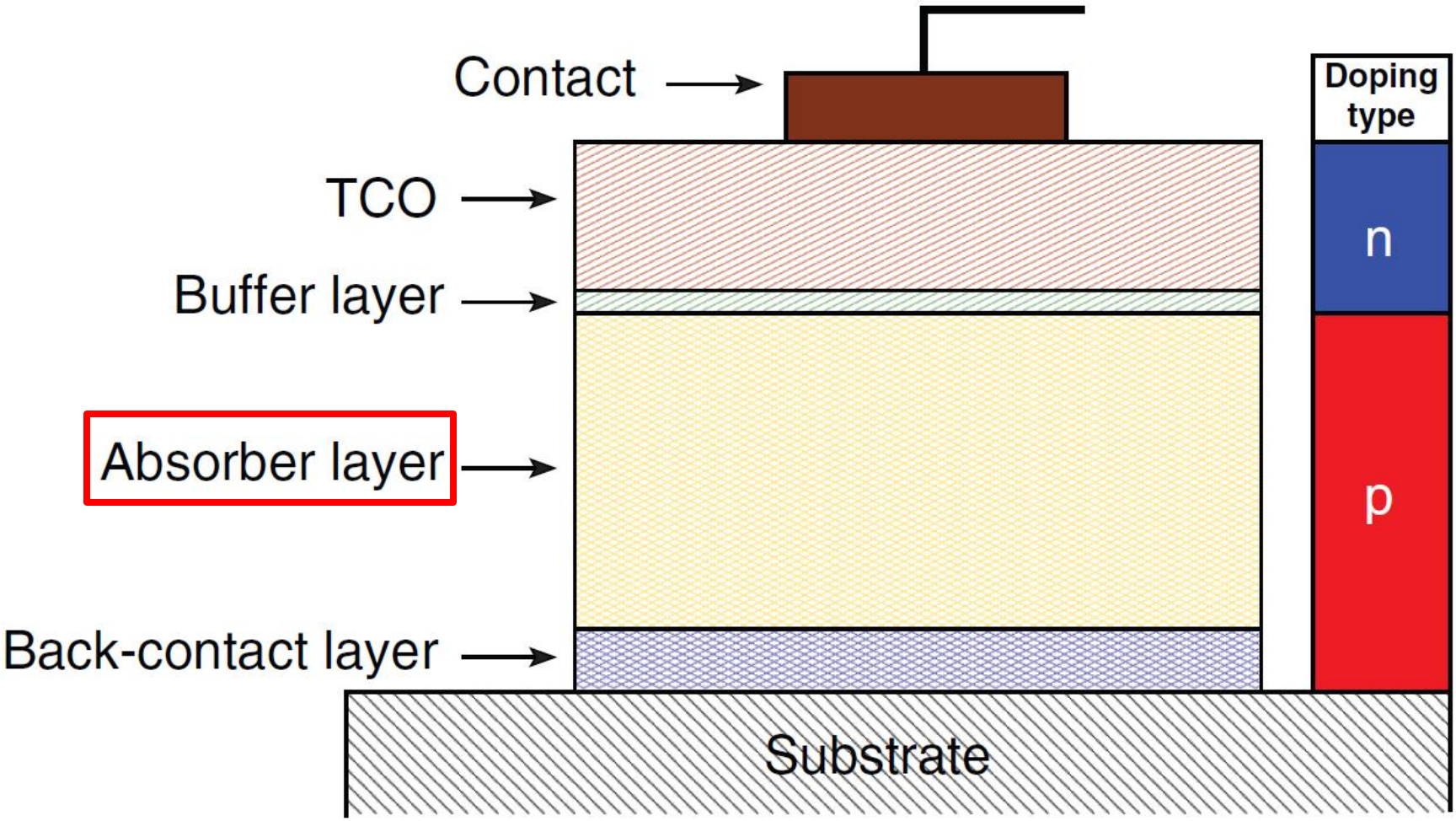
Plan

- Thin film solar cells
- Pros and cons of discovery of new materials, an industrial view
- Project Cu-N: new materials
- Project SnS: a rediscovered material
- Project CZTS: a promising material ?
- Conclusion and perspectives

1 THIN FILM SOLAR CELLS

Design of the solar cells



Absorbing layer materials

What is the most critical property for an absorber material ?

Absorbing layer materials

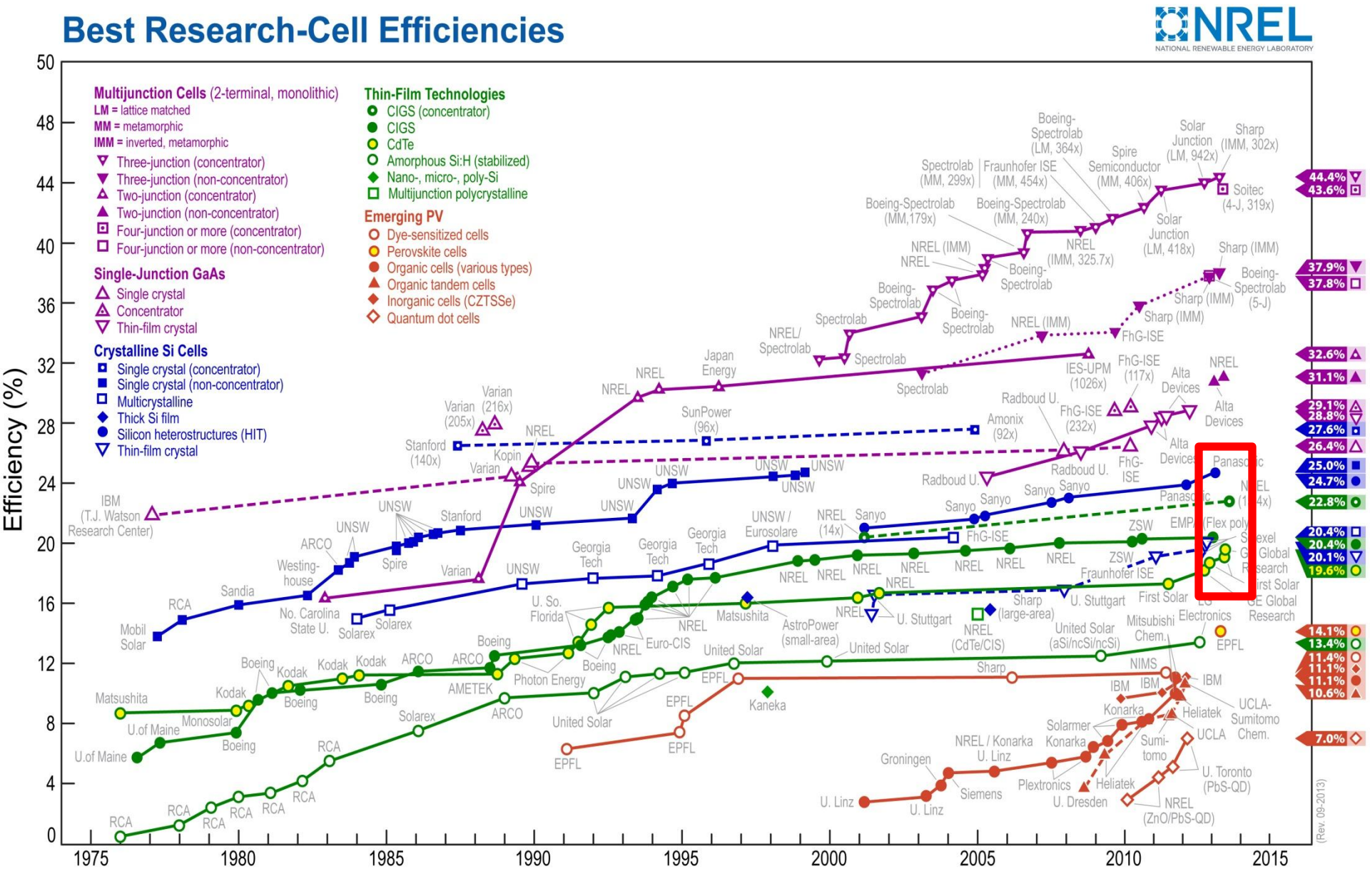
What is the most critical property for an absorber material ?

Counterexample: silicon

The most important quantity for the absorber is carrier lifetime (in Si millisecond)

Other important quantities: ***moderate p-type doping, low minority carrier effective mass, stability under operating conditions, good light absorbing capability*****.**

Absorbing layer materials



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PROS AND CONS OF DISCOVERY OF NEW MATERIALS

Pros: commonly publicized motivations

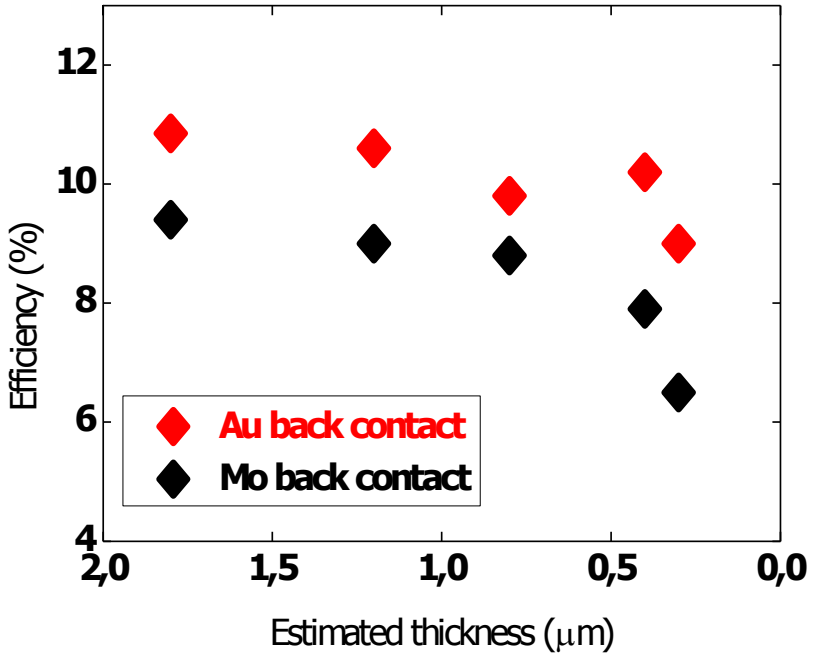
- **Socio-economical interest in finding *new materials* with *desired properties*:**
  - Indium/Tellurium is rare/expensive preventing the large deployment of CIGS and CdTe-based solar modules.
  - Good for the economy !!!!! Lower price for PV modules
  - ***Consequences***: new PV thin film absorbers such as SnS, CZTS, Fe_2S
- **New properties and potentially new physics → new materials:**
  - Recent discovery of topological states at the surface of HgTe and Bi_2Se_3
  - ***Consequences***: lots of **theoretically predicted** new topological insulators , few of them actually **realized experimentally**.

Kesong Yang et al., Nature materials, **11**,614, (2012)

Lot of research initiatives to develop the search for new materials but is it really necessary ?

Cons: not so publicized critics

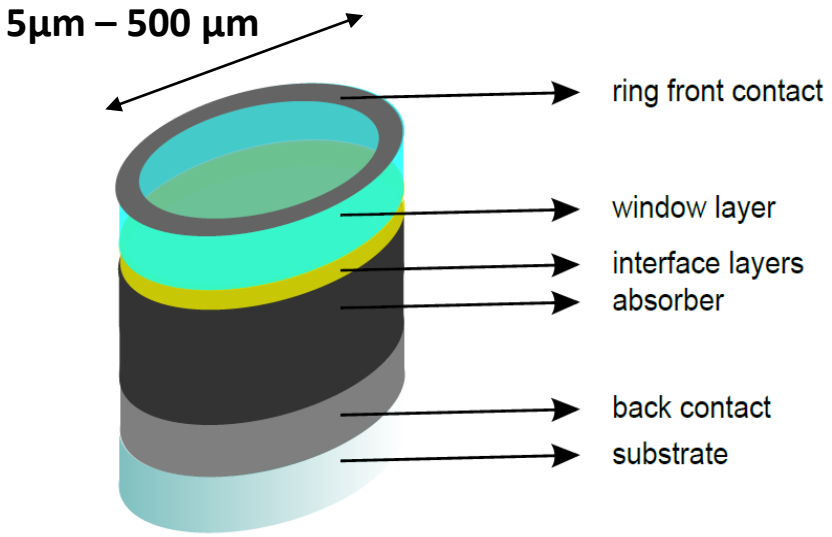
- **New design could overcome shortage of elements**
  - **Ultra thin CIGS solar cell** → improved light management , new back contact → new materials !!!



Z. Jehl Li Kao et al., Progress in Photovoltaics, 20, 582, 2012

Cons: not so publicized critics

- **New design could overcome shortage of elements**
  - **Micro solar cell under concentration → 0D system**



No concentration+regular thin film: 16% !!!

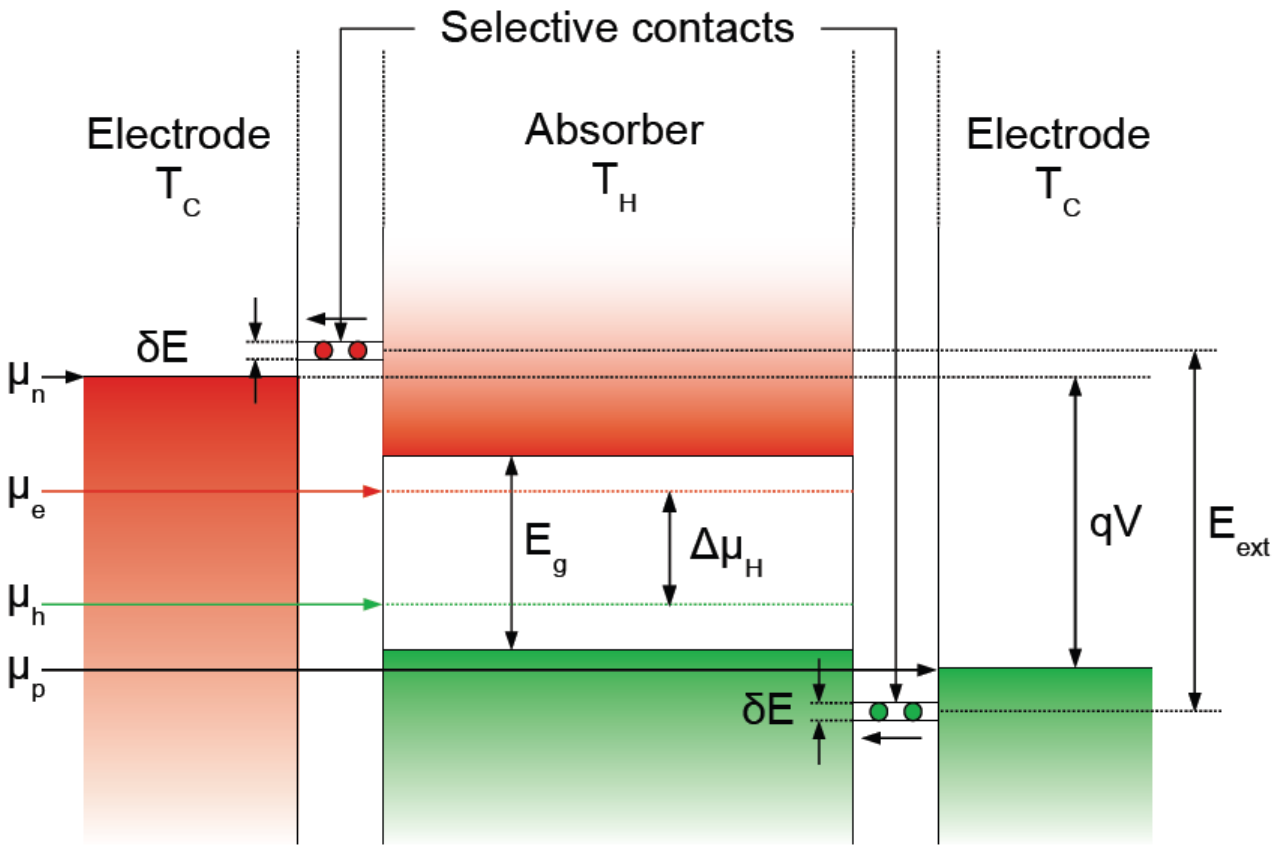
475 x concentration+micro cell: 21.3 % !!!

M. Paire *et al.*, Journal of Renewable Sustainable Energy, 5, 011202 (2013)

M. Paire *et al.*, Energy and Environmental Science, 4, 12, 4972 (2012)

Device design vs desired properties

New design: Hot Carrier Solar cells

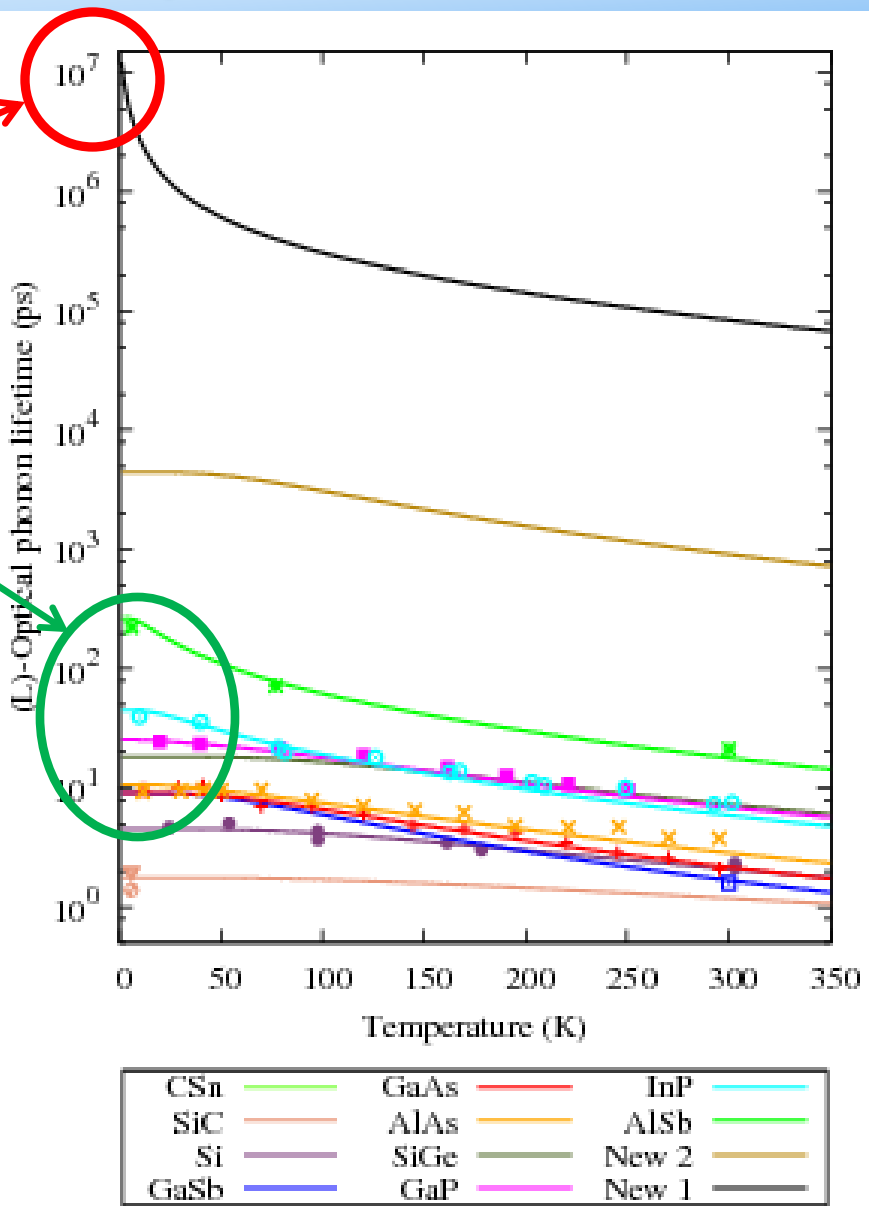


Desired properties for the absorber: long lifetime of LO phonons

Ross 1982, Wurfel 1998

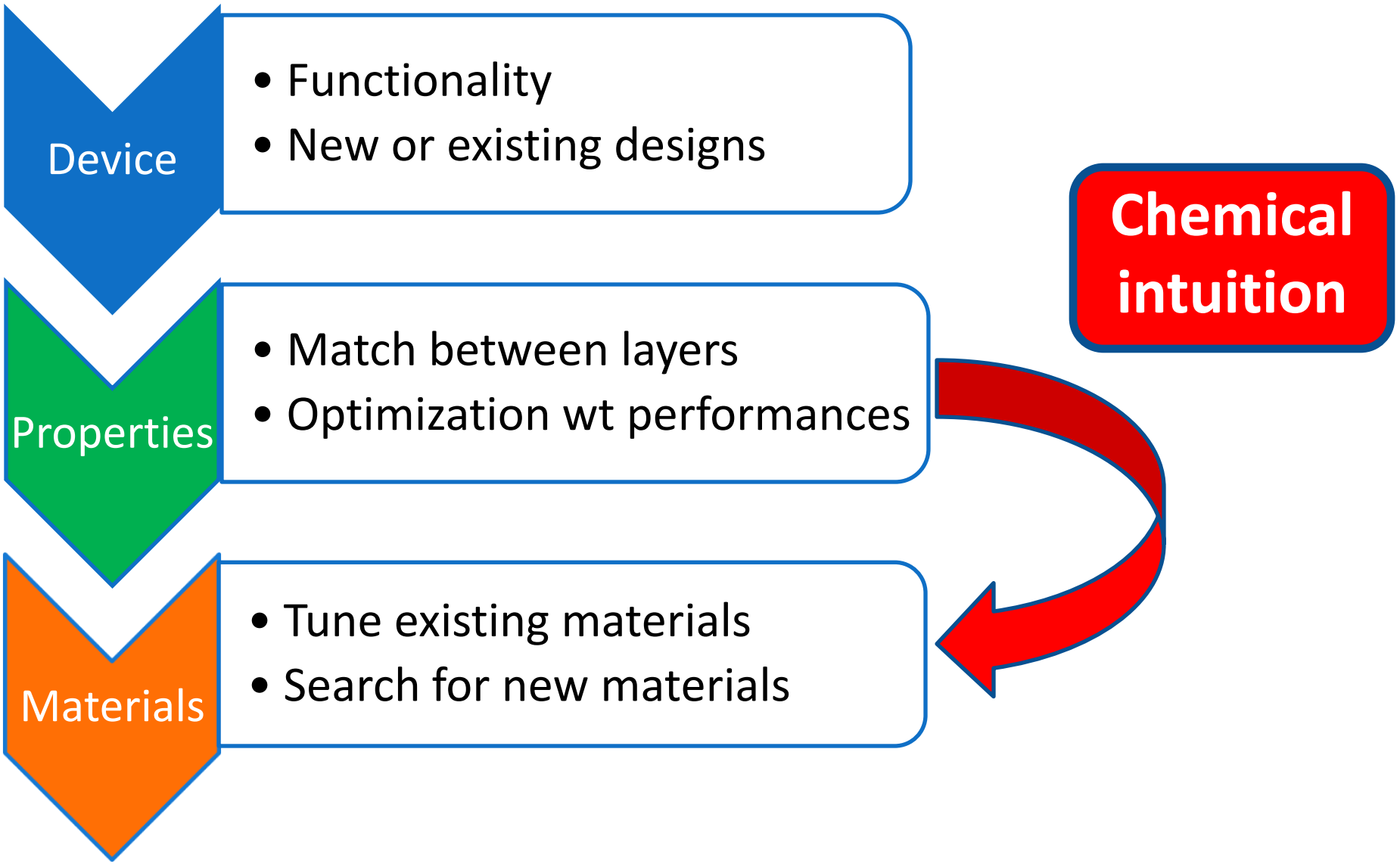
Search for the optimal absorber in HCSC

6 orders of magnitude higher than III-V



Courtesy of Hugo Levard, EDF R&D

Current flow chart: top-down



What about bottom up ?

New ideas !!!

Device

- New functionalities !!!
- New designs !!!

Properties

- New properties !!!
- New understanding !!!

Materials

- Tune existing materials
- Search for new materials

Fe-based superconductors: Magnetism plays an active role in HTS

3

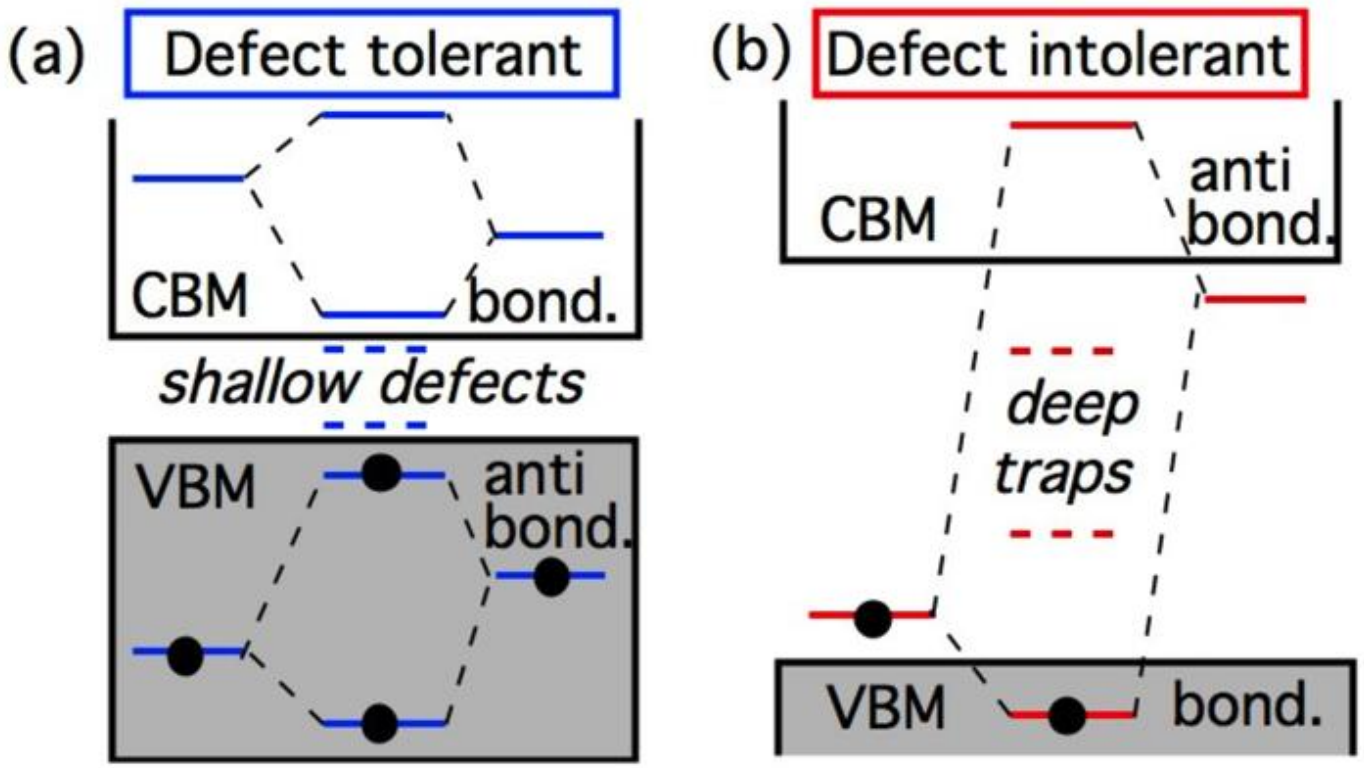
CU-N PROJECT

Design and Physical intuitions

- **Design chosen: thin film solar cells**
  - p-type doping: 10^{16}-10^{17} cm-3 with no recombination centers.
  - High optical absorption in the visible range.
  - Good collection properties *i.e.* effective mass
- **Physical intuition**
  - Defect immunity and p-doping of CIGS stems from structure of the valence.

Design and Physical intuitions

- **Physical intuition**
  - **Defect immunity** and **p-doping** of CIGS stems from **structure of the valence**.

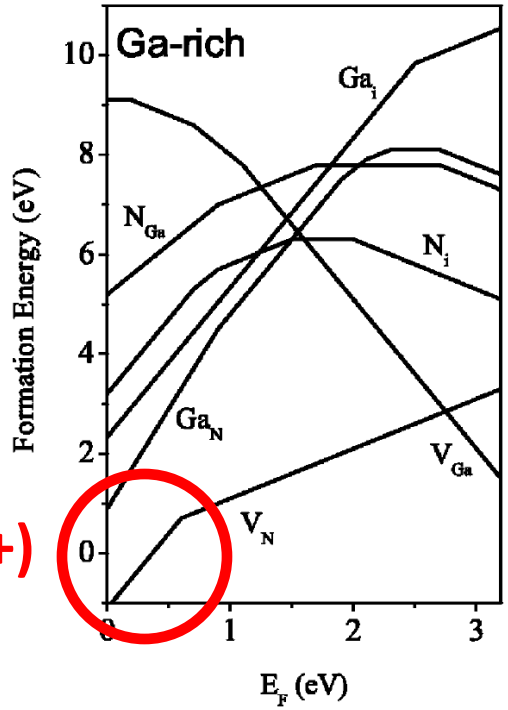


Raebiger et al., PRB, 76 , 045209, (2007)

Zakutayev et al., submitted (2013)

Tuning the Cu-X bonding

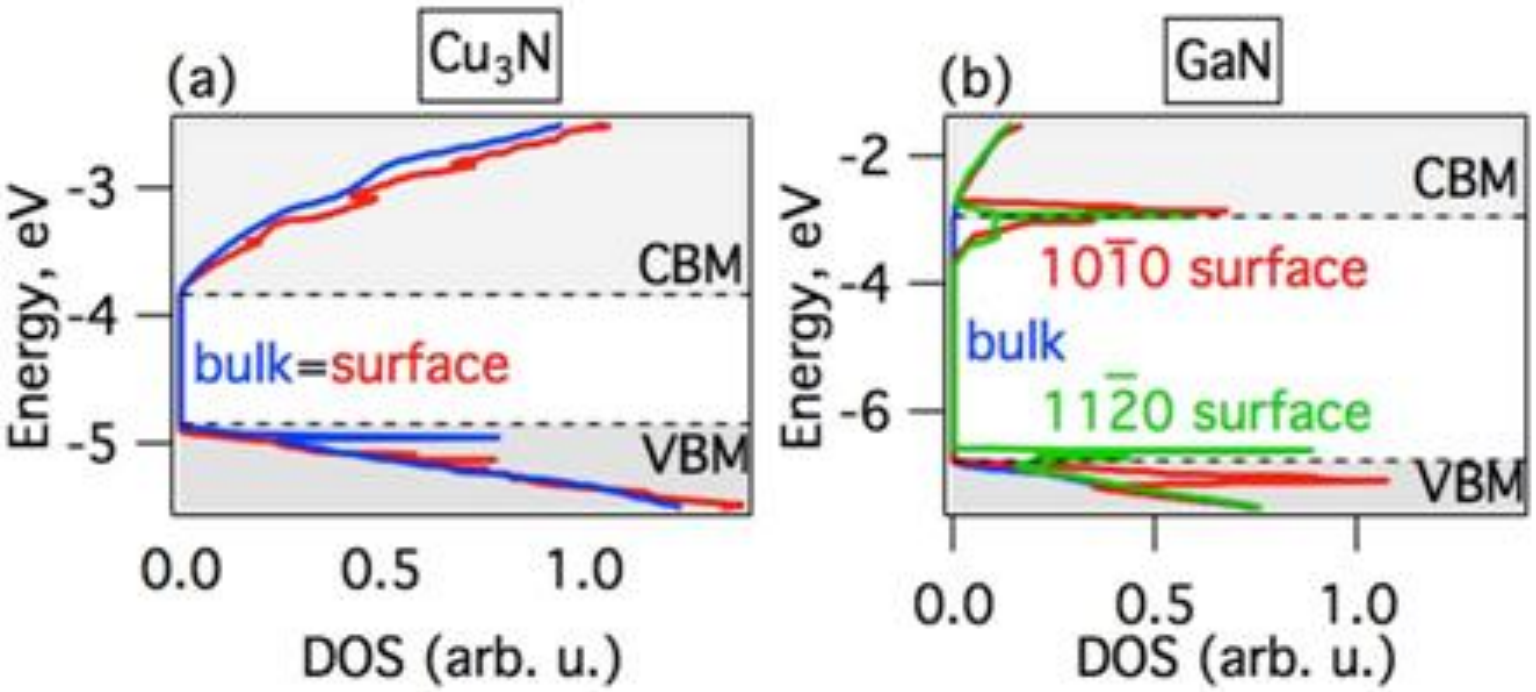
- **How to tune Cu-X valence width ?**
  - Match the energy of **p-orbital of X** to the the energy of **d-orbital of Cu**
  - Best match: ***Cu-N***
- **Nitrides and PV ?**
  - Serious game player in high efficiency multijunction solar cell
  - With respect to CIGS **thin film designs** ??



- **Binary Cu-N → Cu_3N $\Delta H_f > 0$ unstable**
- **Low formation energy of V_N → n-type**
- **Incorporation of O as O_N → n-type**
- **Weird crystal structures → ???**
- **GaN 3.4 eV to InN 0.7 eV → tunable gap**

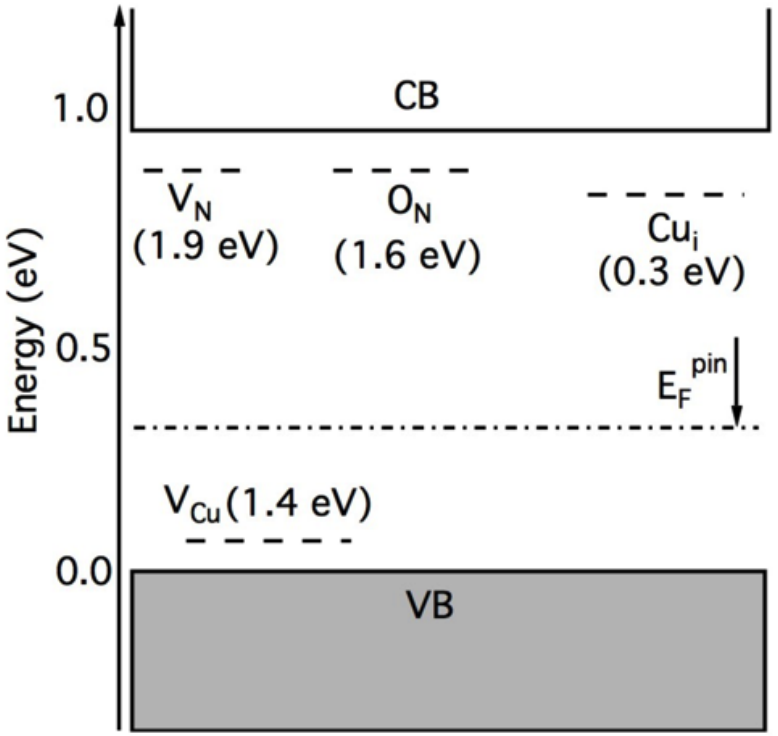
C G Van de Walle et al., JAP, 95, 3851 (2004)

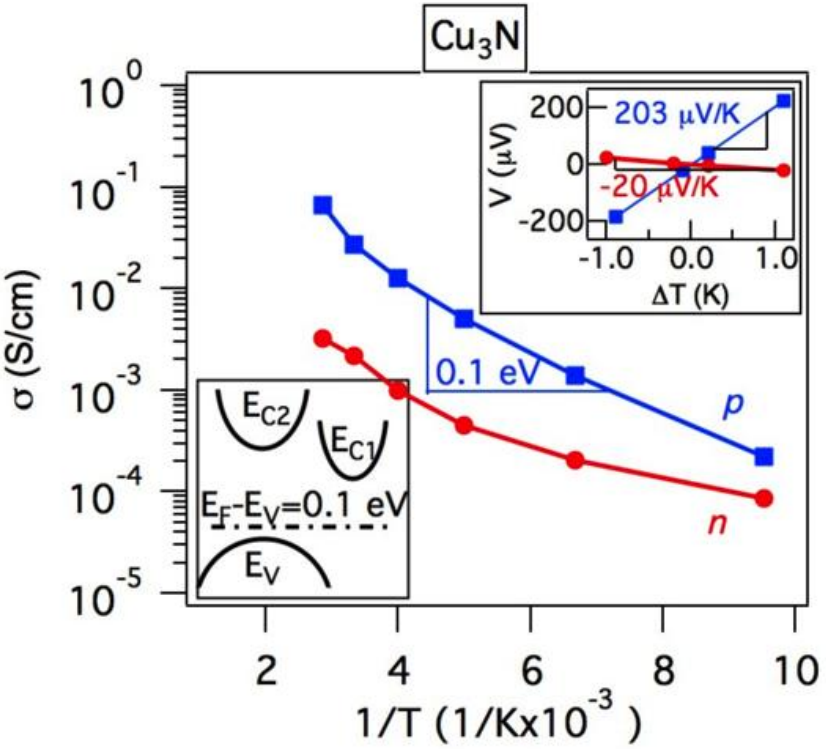
Sanity check: design principle at work



- Cu_3N surface show no surface states.
- GaN surface shows couple of surface states.

Formation energy of defects in Cu_3N





- **No deep level in the gap**
- **p-type doping is achievable despite V_N and O_N**
- **Transition levels confirmed in conductivity measurements.**

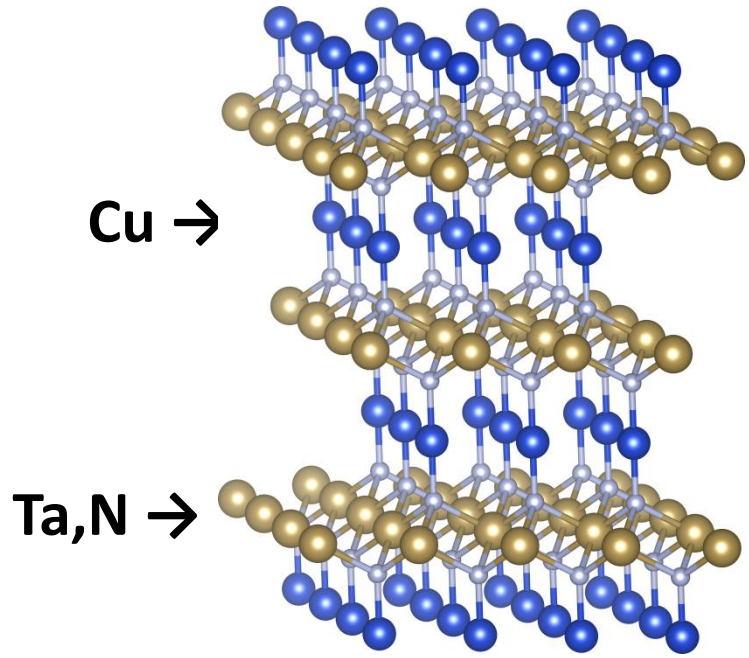
Zakutayev et al., to be published

First case: $CuTaN_2$

Crystal structure: delafossite

- **$CuAlO_2$: p-type TCO**
  (Kawazoe *et al.*, Nature, 389,939 (1997))
- **quasi-2D → large excitonic effect**

(Laskowski *et al.*, PRB, 79, 165209 (2009))



Synthesis: ion exchange reaction

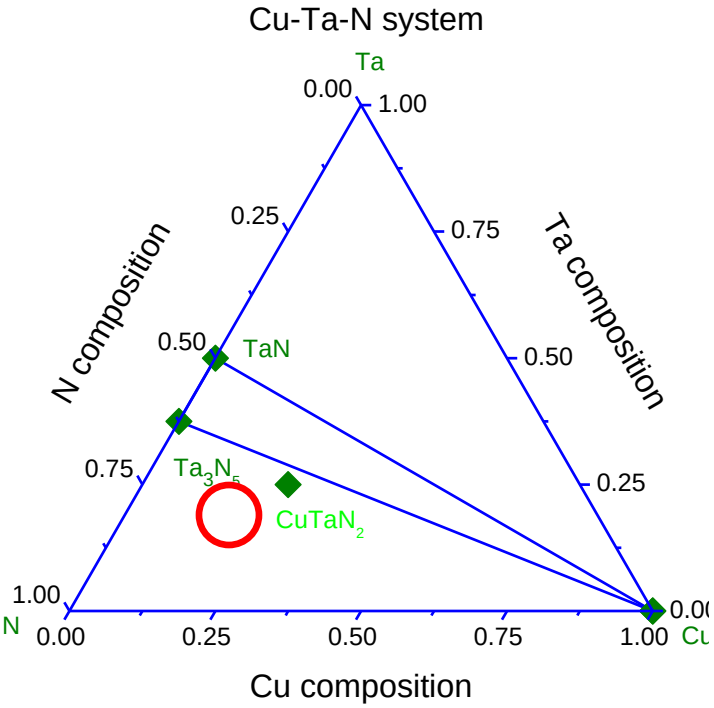
- **$CuCl + NaTaN_2 \rightarrow NaCl + CuTaN_2$**
  (Zachwieja, U.; Jacobs, H. *Eur J Sol State Inor* 1991, *28*, 1055)
- **$CuI + NaTaN_2 \rightarrow NaI + CuTaN_2$**
  (this work)

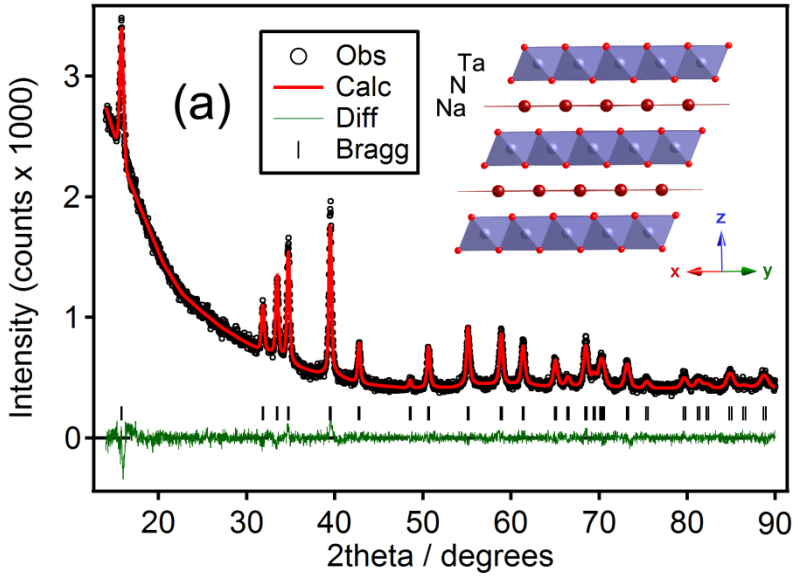
Yang M. et al., accepted in Energy and Environmental Science, 2013

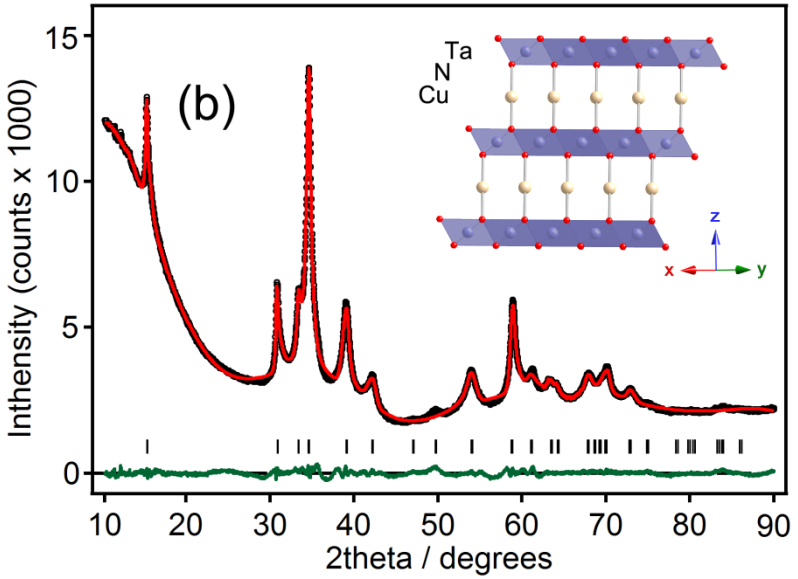
First case: $CuTaN_2$

Results of synthesis

- **Different delafossite structure confirmed by theory.**
- **$CuTaN_2$ not thermodynamically stable wr to N_2, Cu and Ta_3N_5**
- **Crystals with grains 50 to 300 nm**

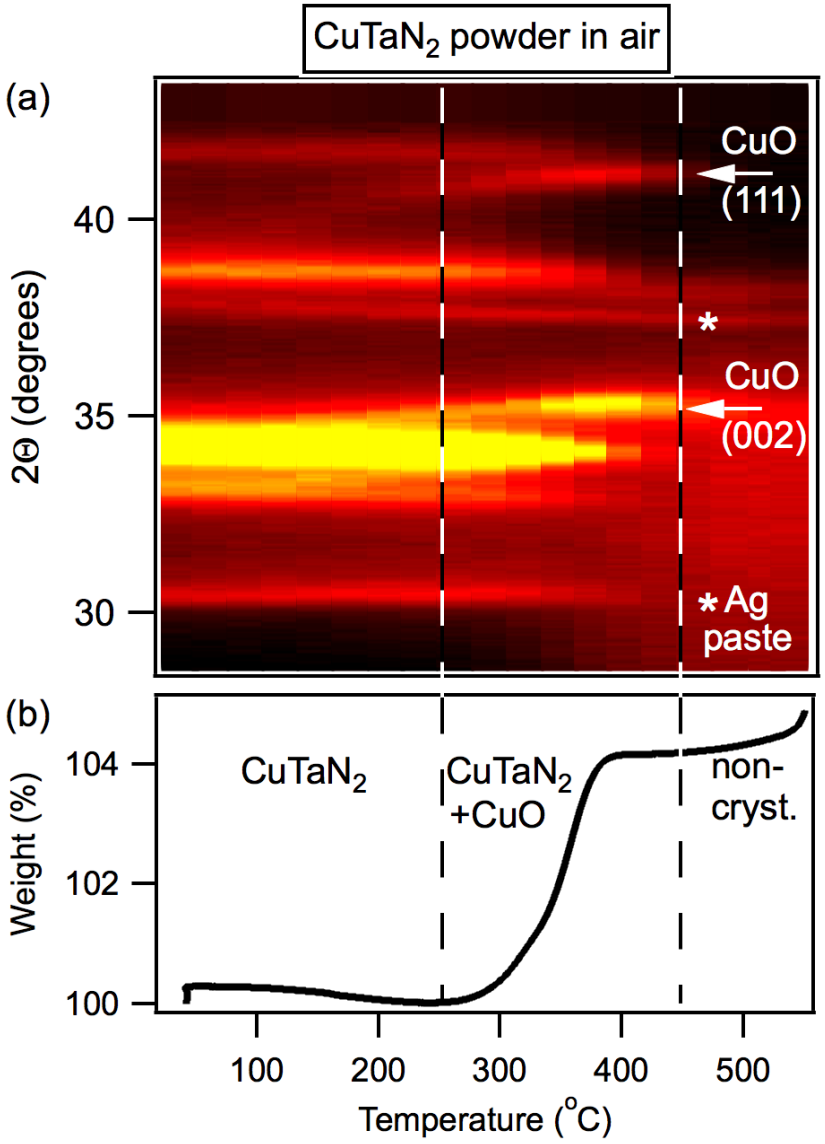






Is $CuTaN_2$ PV-interesting ?

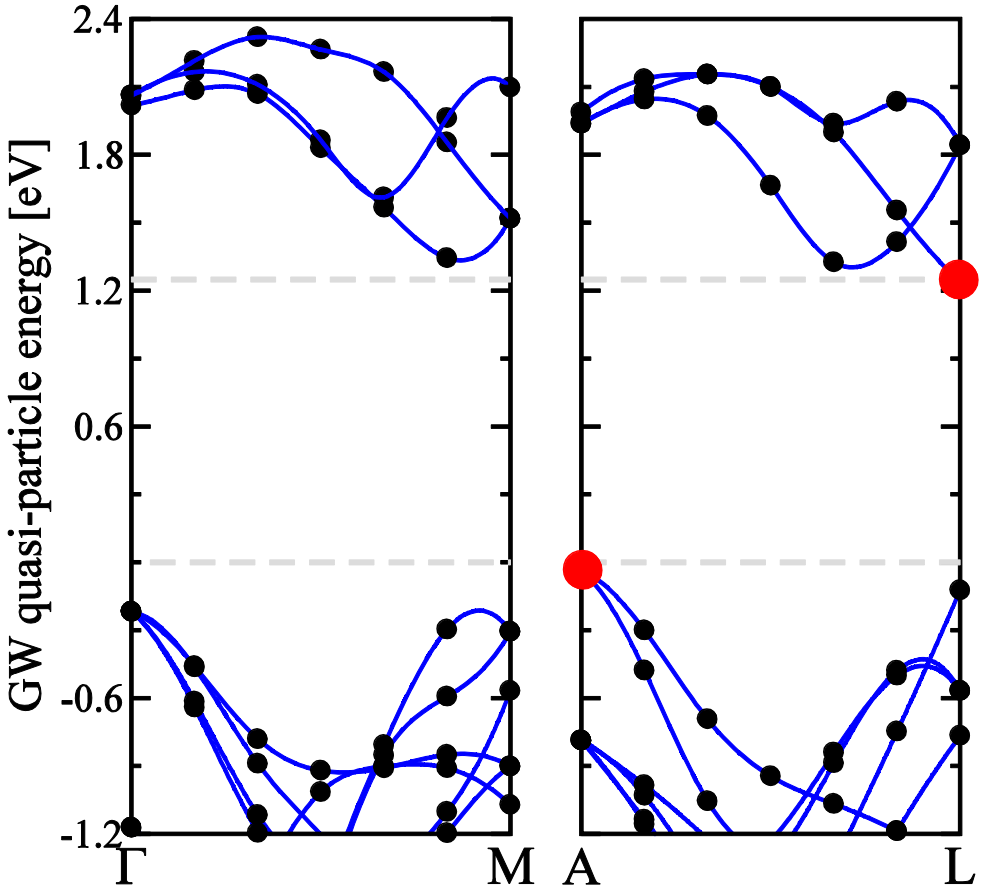
- **Kinetic stability of CuTaN2: T-dependent XRD and TGA**



Is $CuTaN_2$ PV-interesting ?

- **Band structure and absorption properties**

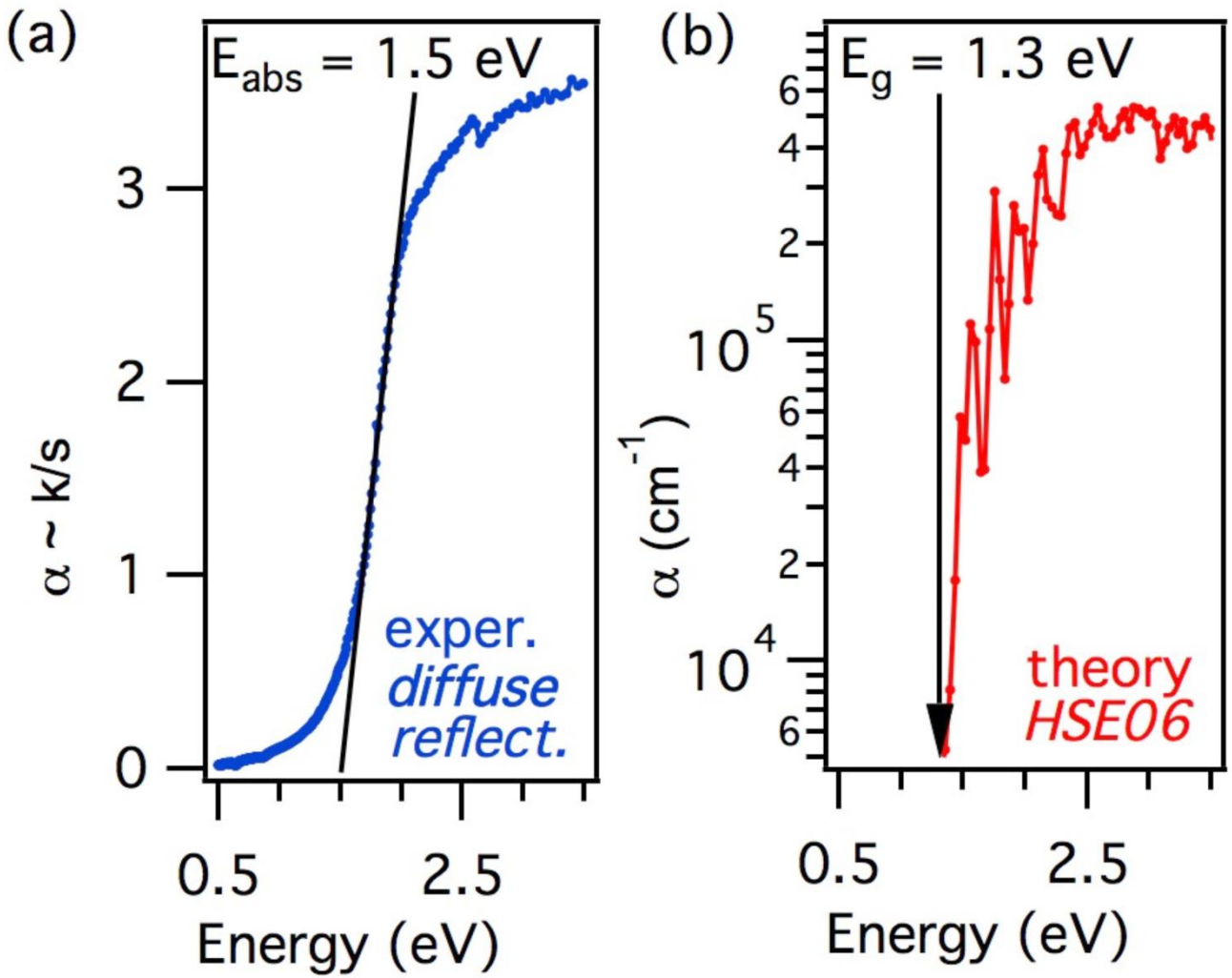
E_g is indirect at 1.3 eV with a direct transition at 1.5 eV



Is $CuTaN_2$ PV-interesting ?

- **Band structure and absorption properties**

High optical absorption at 1.5 eV !!!!

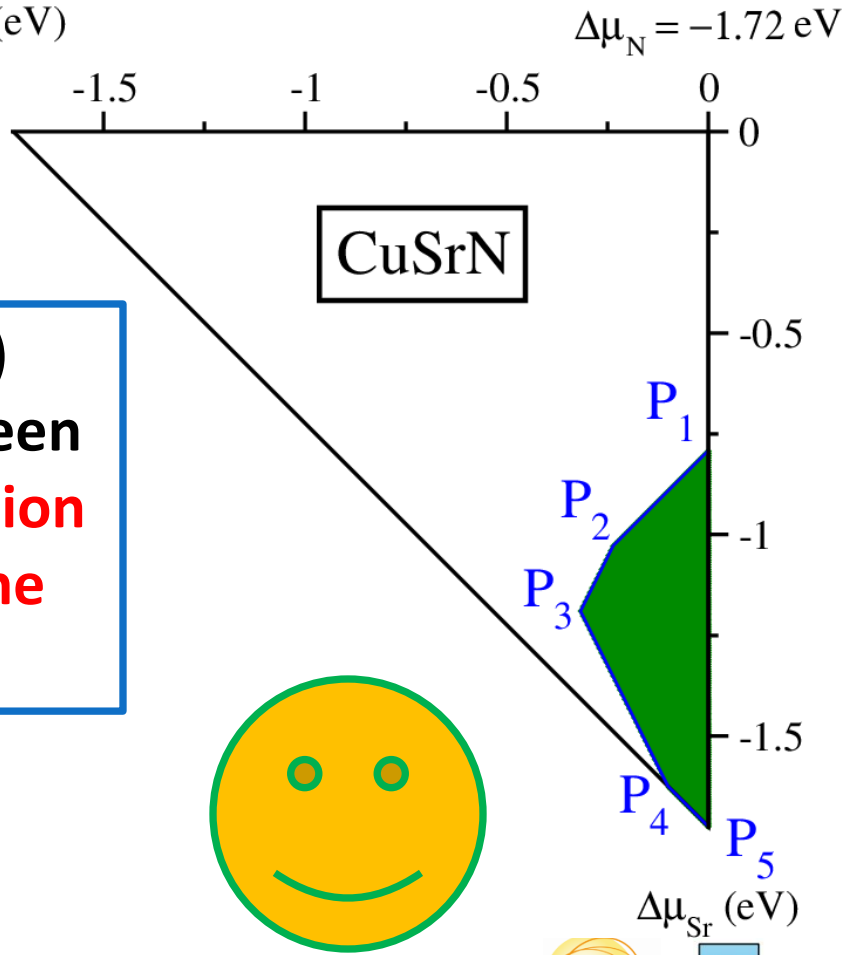


Second case: CuSrN

- **Thermodynamically stable *i.e.* $\Delta H_f < 0$ and wr to binary and ternary compounds.**

CuSrN stable under (N,Cu)-rich and Sr-poor growth conditions

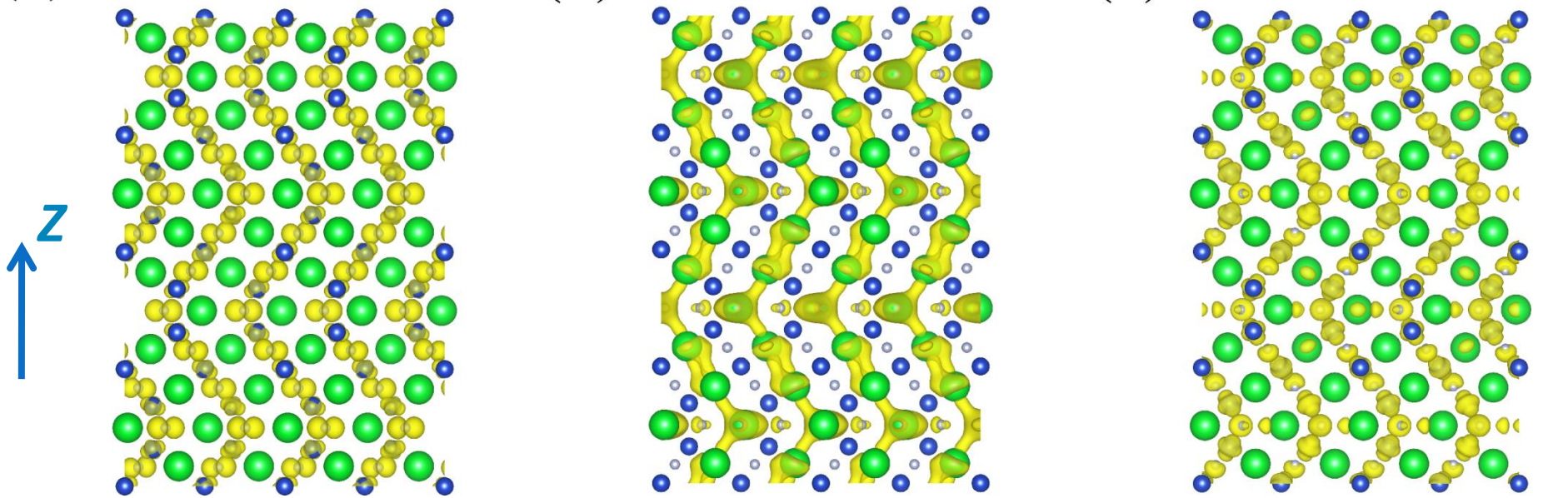
CuSrN only ternary stable (so far) because has to find a balance between attractivity of N with the second cation X and the formation enthalpy of the binary X_kN_l.



Is CuSrN PV-friendly ?

- **A unique crystal structure → extraordinary conduction properties !!**

(a) (b) (c)

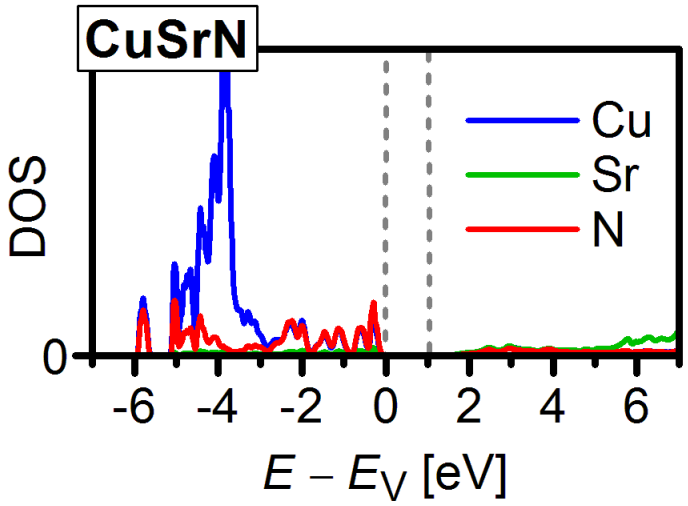


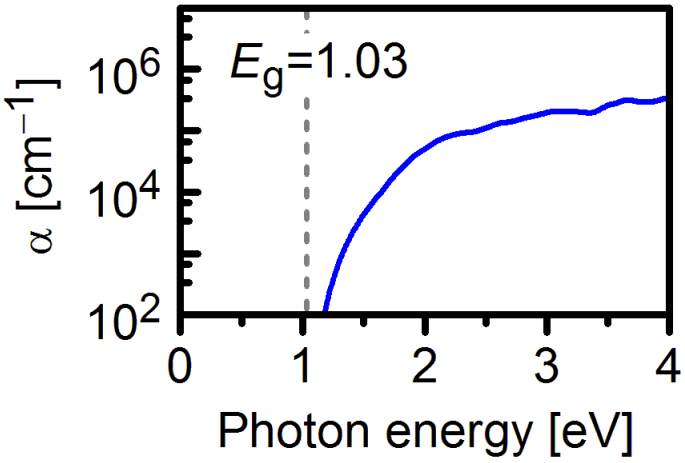
Valence band max	Conduction band min	Conduction band II
$m^x_{eff} = 1.3\ m_0$	$m^z_{eff} = 0.05\ m_0$	$m^z_{eff} = 0.15\ m_0$

if p-type …

Is CuSrN PV-friendly ?

- **Electronic properties: direct band gap (E_g=1.03 eV) with an optical transition at 1.3 eV !!!**

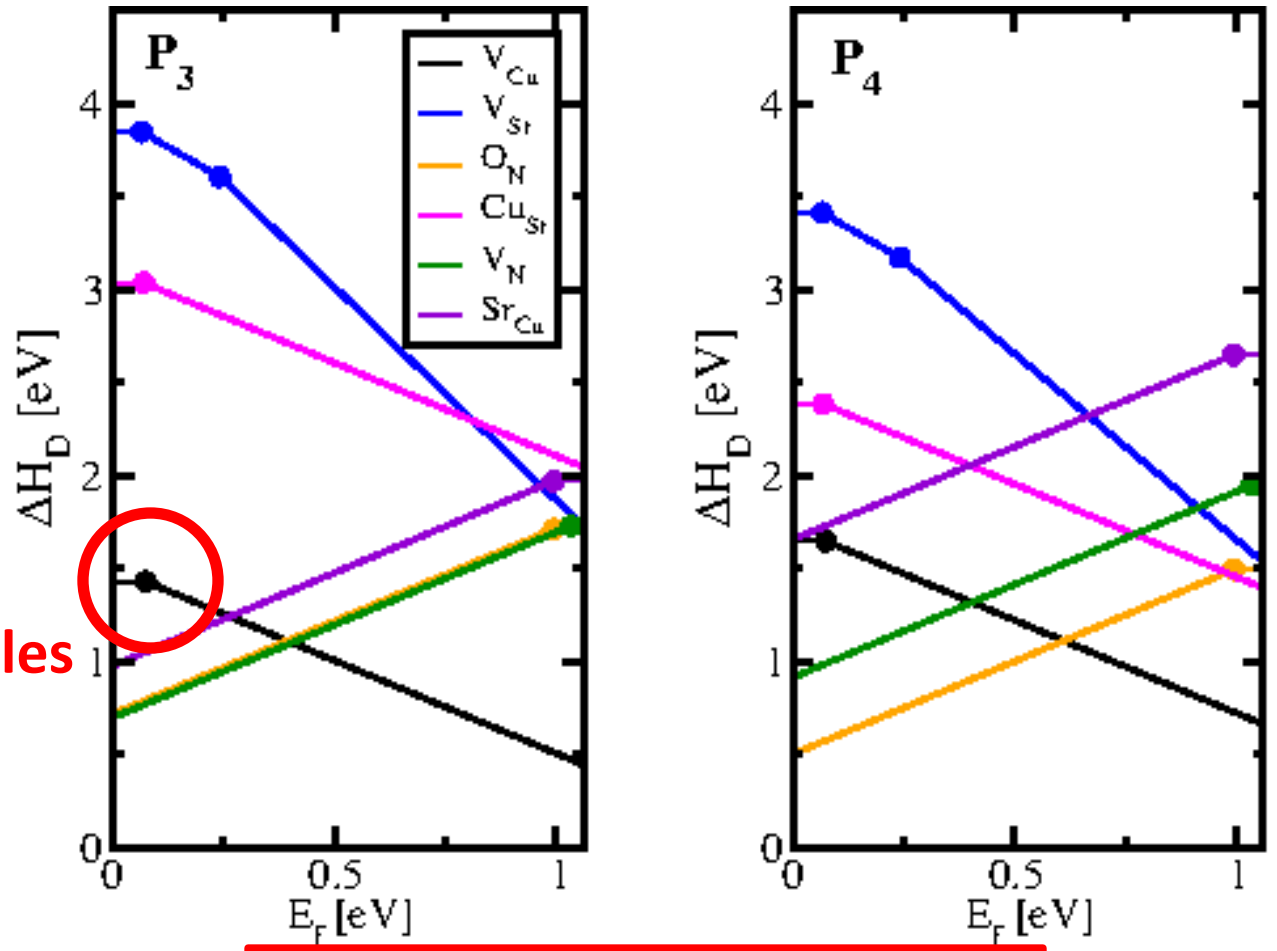




Excitonic effect ? On-going work

Is CuSrN PV-friendly ?

- **Ambipolar doping achievable ranging from *moderate p-type***



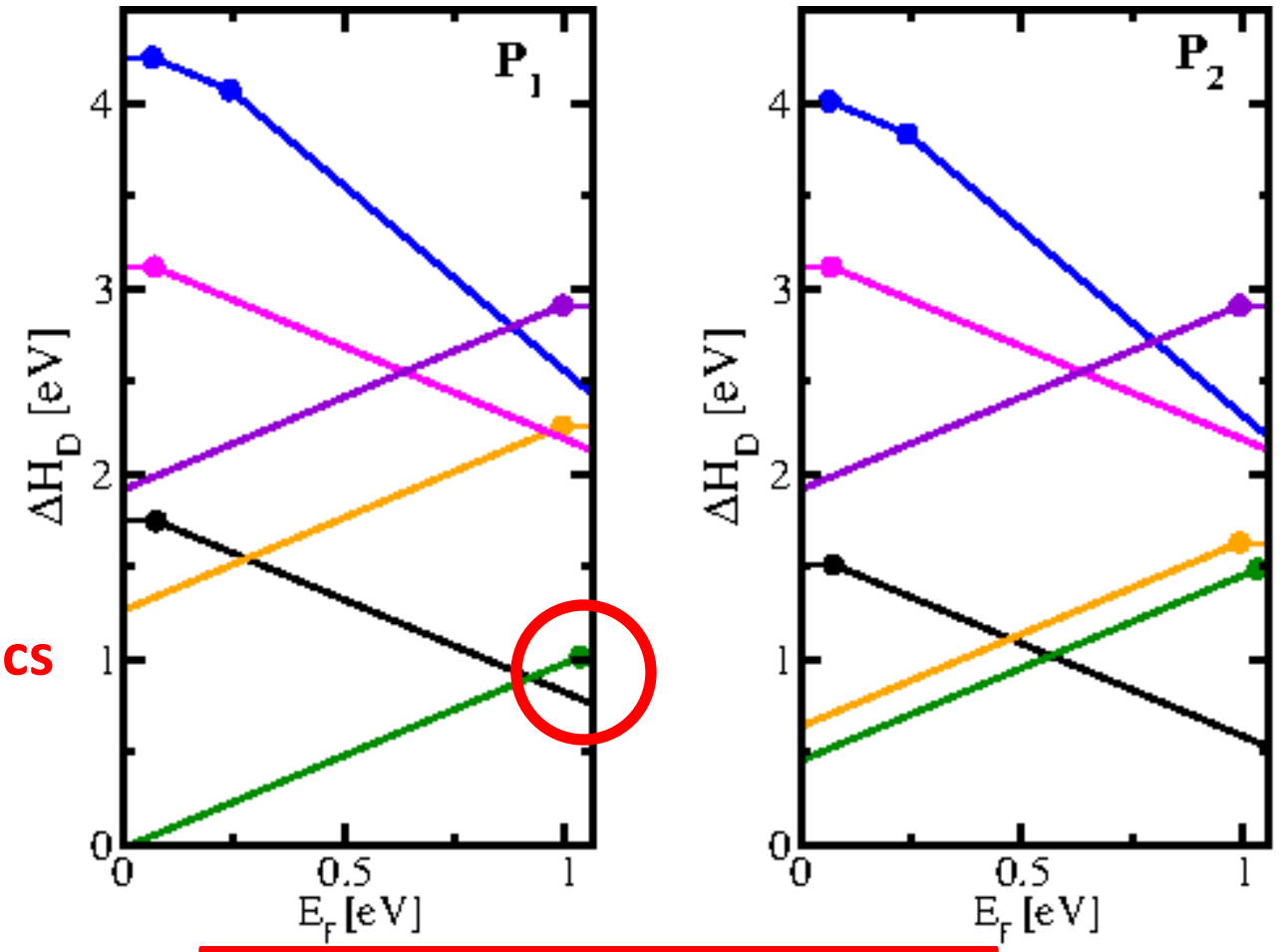
Origin of holes

V_{Cu}

N_A = 3-6 x10^{16} cm^{-3}

Is CuSrN PV-friendly ?

- to ***highly doped n-type: HOMOJUNCTION !!!***



Origin of elecs

V_N

$N_D = 6 \times 10^{19}$ cm^{-3}

4 PROJECT SNS

SnS: an « old » PV material

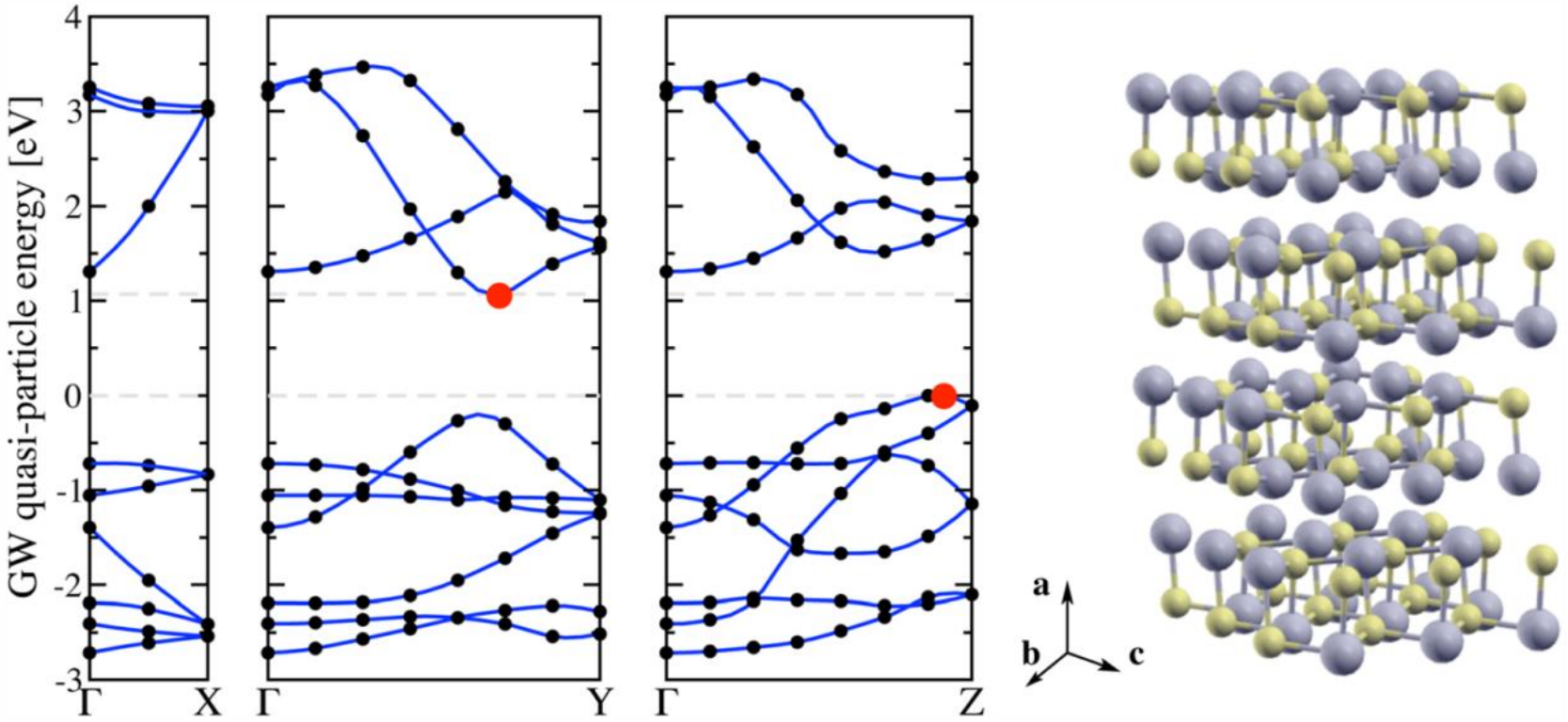
- **What makes SnS attractive?**
  - ✓ Earth abundant inexpensive elements
  - ✓ Band gap near optimal (often quoted as 1.3 eV direct gap)
  - ✓ Synthesis methods:
    Solution-based, physical vapor, chemical vapor
  - ✓ "Buffer layer" issue:
    - ✓ Homojunction: ambipolar dopability (G. Yue *et al.,* J. Mater. Chem. **22**, 16437, 2012)
    - ✓ Tunable window layer (Sinsermsuksakul *et al.,* APL, **102**, 053901, 2013)

APPLIED PHYSICS LETTERS **100**, 032104 (2012)

Band-structure, optical properties, and defect physics of the photovoltaic semiconductor SnS

Julien Vidal,[1] Stephan Lany,[1,a)] Mayeul d'Avezac,[1] Alex Zunger,[1,b)] Andriy Zakutayev,[2,c)] Jason Francis,[2] and Janet Tate[2]
[1]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*
[2]*Department of Physics, Oregon State University, Corvallis, Oregon 97331, USA*

Band structure of SnS



- **Band gap of 1.07 eV is indirect**
- **Effective masses:**

  Minority carriers (electrons): $m^*_{\perp} = 0.5\ m_e$, $m^*_{||} = 0.2\ m_e$

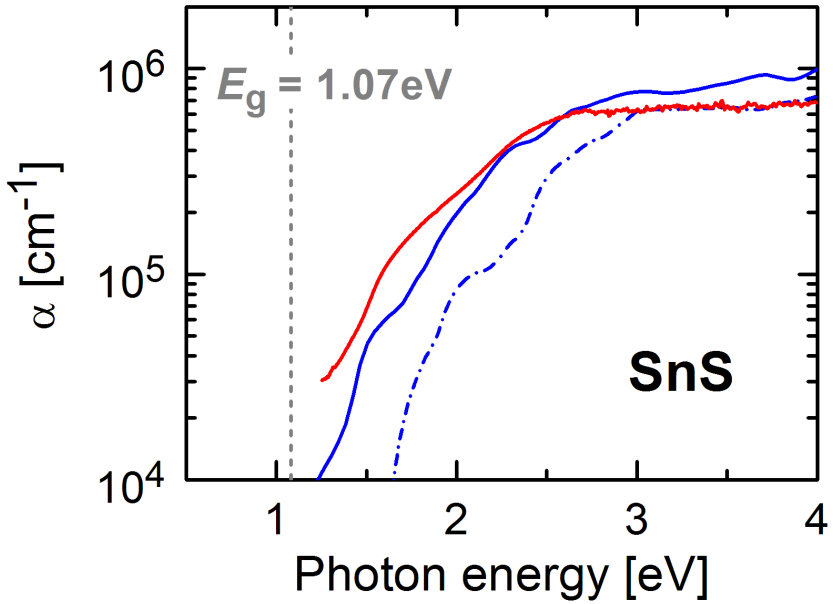
  Majority carriers (holes): $m^*_{\perp} = 1.5\ m_e$, $m^*_{||} = 0.3\ m_e$

- **ALD-grown SnS oriented either ⊥ or || to substrate (P. Sinsermsuksakul *et al.*, Adv. En. Mat., 1, 1116 (2011)) → Different collection length when buffer tuned ?**

Optical absorption: theory and experiments

Band gap (E_g) vs absorption threshold (E_{abs})

- E_g determines max. V_{OC} (V_{OC} - E_g = 0.3 eV (GaAs) to 0.6 eV (CdTe))
- E_{abs} determines photon collection (J_{SC})



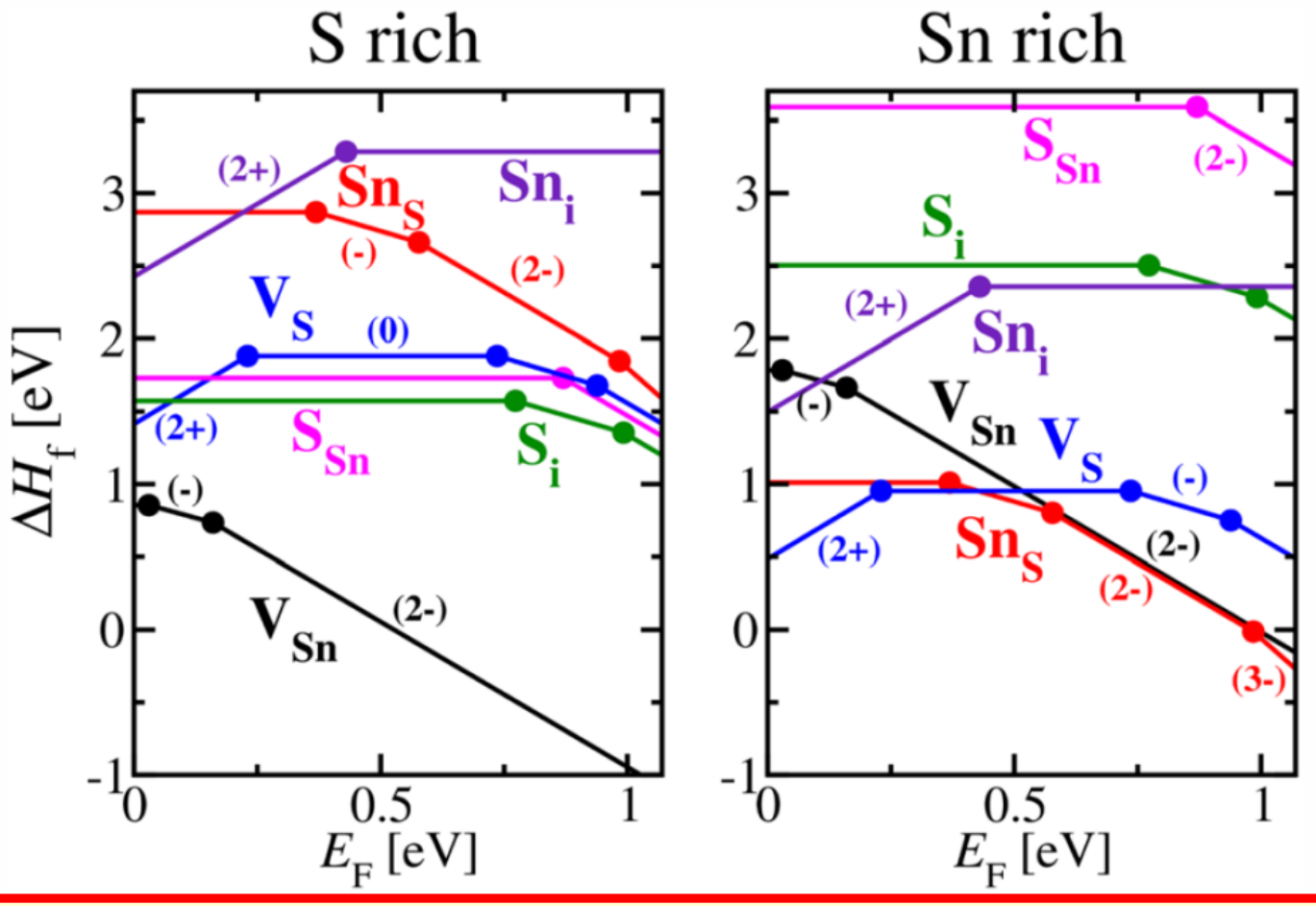
Measured and calculated optical absorption spectra

— **Experiment**
–·– **GW (independent particle)**
— **GW (+ excitonic effects)**

Theory includes direct-allowed transitions, but no phonon-assisted or disorder-induced indirect or forbidden transitions

- **Effective absorption threshold: E_{abs} ~1.5 eV lies ~0.4 eV above E_g**
- **Small V_{oc} obtained in practice 0.3 eV despite new buffer (except for SnS NW)**

Defect formation energy



- **Sn-vacancies (V_{Sn}) are native *p*-type dopant**
- **Deep defects (V_S, Sn_S) acting as recombination centers form under S-rich conditions**

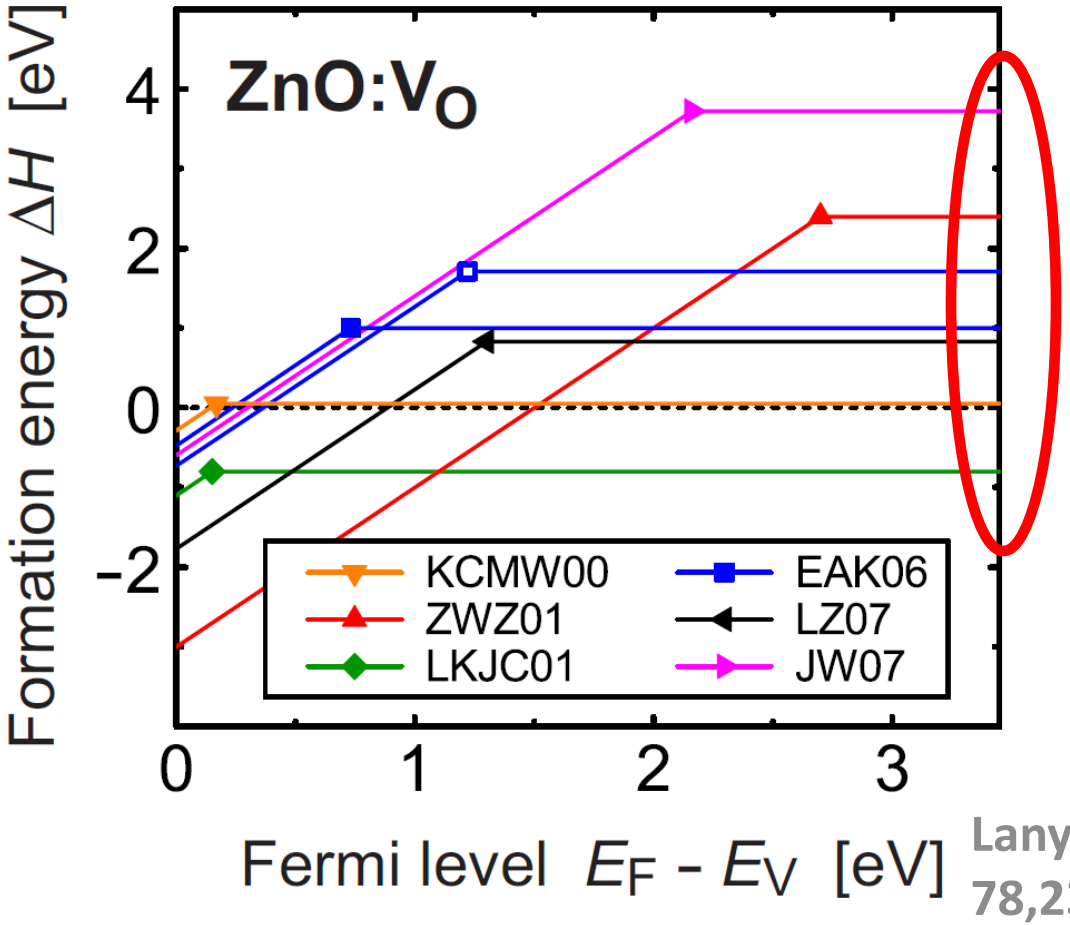
From defect formation energy to carrier concentration

Defect formation energy	$\Delta H = \Delta H_{D,q}(\mu, E_F)$
Defect concentration	$c_D \approx N_{site} \times \exp(-\Delta H/kT)$
Electron/hole density	$c_e = \int f_{FD}(E-E_F)\, g(E)\, dE$
Charge neutrality	$-c_e + c_h + \Sigma\,[q \cdot c(D^q)] = 0$
Self-consistent solution	$\Delta H(E_F)$ $\quad$ $c_D(\Delta H)$ $\quad$ E_F
pO_2 dependence of μ_O (ideal gas)	$\Delta\mu_O(T,P_0) = \frac{1}{2}[H_0+\Delta H(T)] - \frac{1}{2}T\cdot[S_0+\Delta S(T)]$ $\Delta\mu_O(T,P) = \Delta\mu_O(T,P_0) + \frac{1}{2}kT\ln(P/P_0)$

High conc.	Account for competition of defects and host atoms for N_{site} Association/dissociation of *defect-clusters* (law of mass action)
Direct	Given $\Delta H(\mu)$, find concentrations c_D
Inverse	Given a target concentration, find ΔH (i.e., find μ)

Are defect formation energy good enough ?

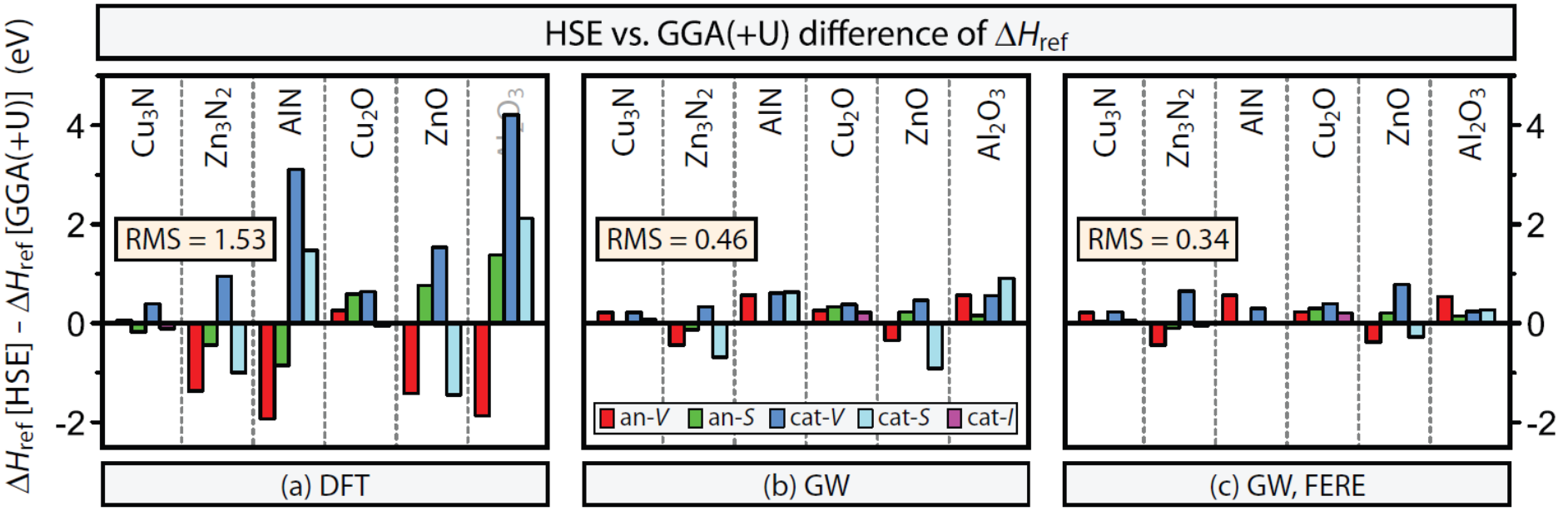
Difference in transition levels is linked to the gap underestimation by DFT. Therefore, **people use hybrid functional for total energy because it gives the right band gap.**



Lany et al., PRB, 78,235104, 2008

Transition levels were the main concern but absolute formation energies display large variations too !!!

Unification of hybrid and DFT formation energy

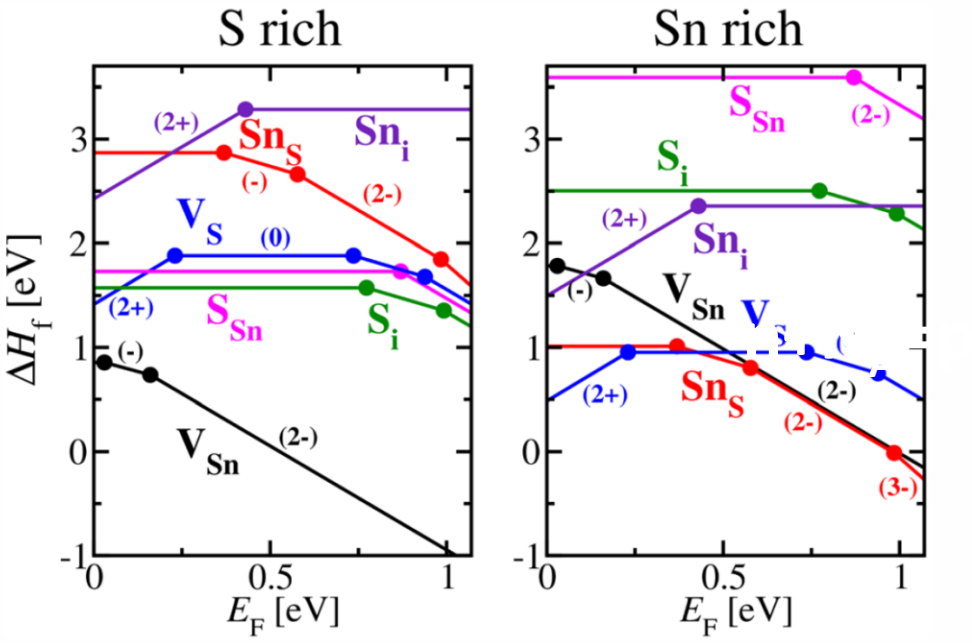


- **Compounds heat of formation should be corrected by a fitting mechanism FERE**
- **For shallow defects, GW corrections must be added**
- **Sanity check: GW corrections must give the right ionization energy.**
- **Conclusion: HSE06 and DFT can be made equivalent**

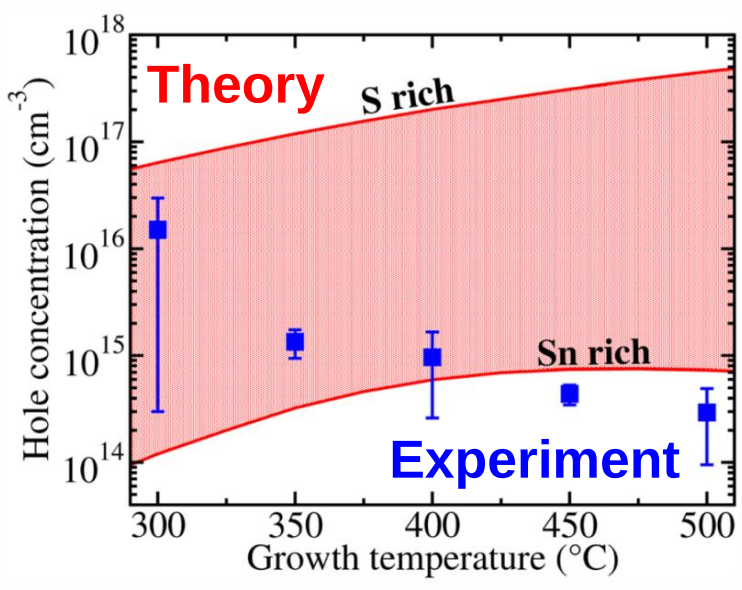
H. Peng, et al., PRB, 88, 115201 (2013)

Carrier concentration and PV assessment

DFT supercell calculations for defects in SnS



Thermodynamic modeling of doping and Hall-measurements



- p = 10^{14}-10^{17} cm^{-3} due to V_{Sn}
- Sulfur-rich growth is desired to avoid deep centers (V_S, Sn_S): Reduced V_{oc}
- Trade-off with growth temperature

5

PROJECT CZTS

Cu_2ZnSnS_4 (CZTS)

- Based on the compound $CuInS_2$, replace 2 In by 1 Sn and 1 Zn.
- Historically, CZTS was thought to be the same as CIGS.

BUT

- Phase diagram is much more complex due to binary and ternary compounds.
- ZnS is very stable and always present in thin films.
- SnS tends to evaporate and forms detrimental voids.
- Efficiency of devices has been limited to 11% under wet process while the best CIGS-based devices are made in vacuum.

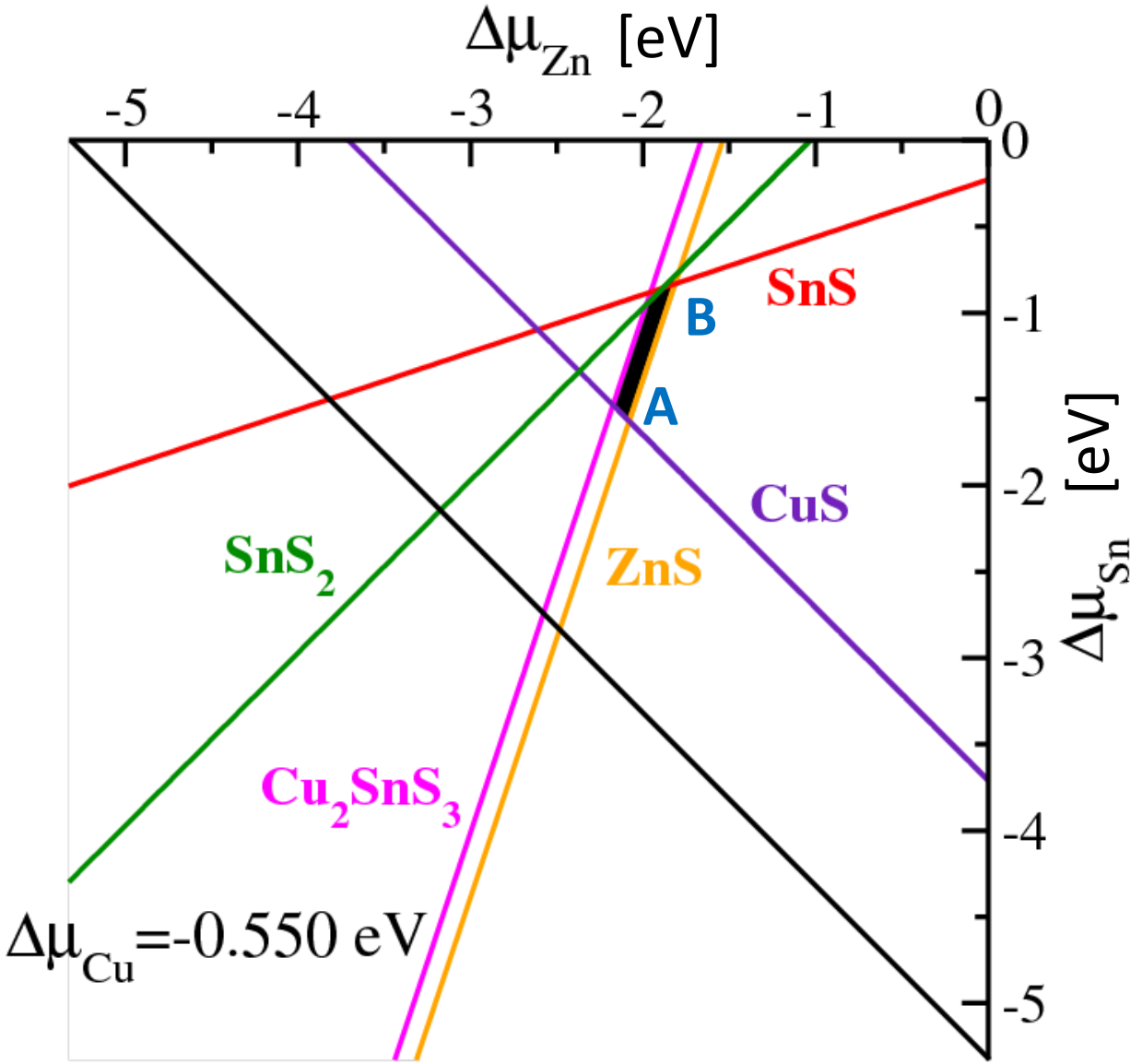
How to compute a phase diagram ?

- **Competing binary and ternary compounds**
  - ✓ ***Cu-Sn-S***: Cu_2SnS_3, Cu_4SnS_4, Cu_4SnS_6, $Cu_4Sn_7S_{16}$
  - ✓ ***Cu-S***: Cu_2S, Cu_9S_5, Cu_7S_4, CuS, CuS_2
  - ✓ **Sn-S**: SnS, SnS_2, Sn_2S_3
  - ✓ ***ZnS***
- **Ab initio-calculated phase diagram**
  - ✓ Define the deviation of the chemical potential w.r.t. standard ref.
  - ✓ Preventing formation of competing phases with condition
  - ✓ Allowing formation of CZTS

$$a\Delta\mu_A + b\,\Delta\mu_B + c\Delta\mu_X < \Delta H_f(A_aB_bX_c)$$

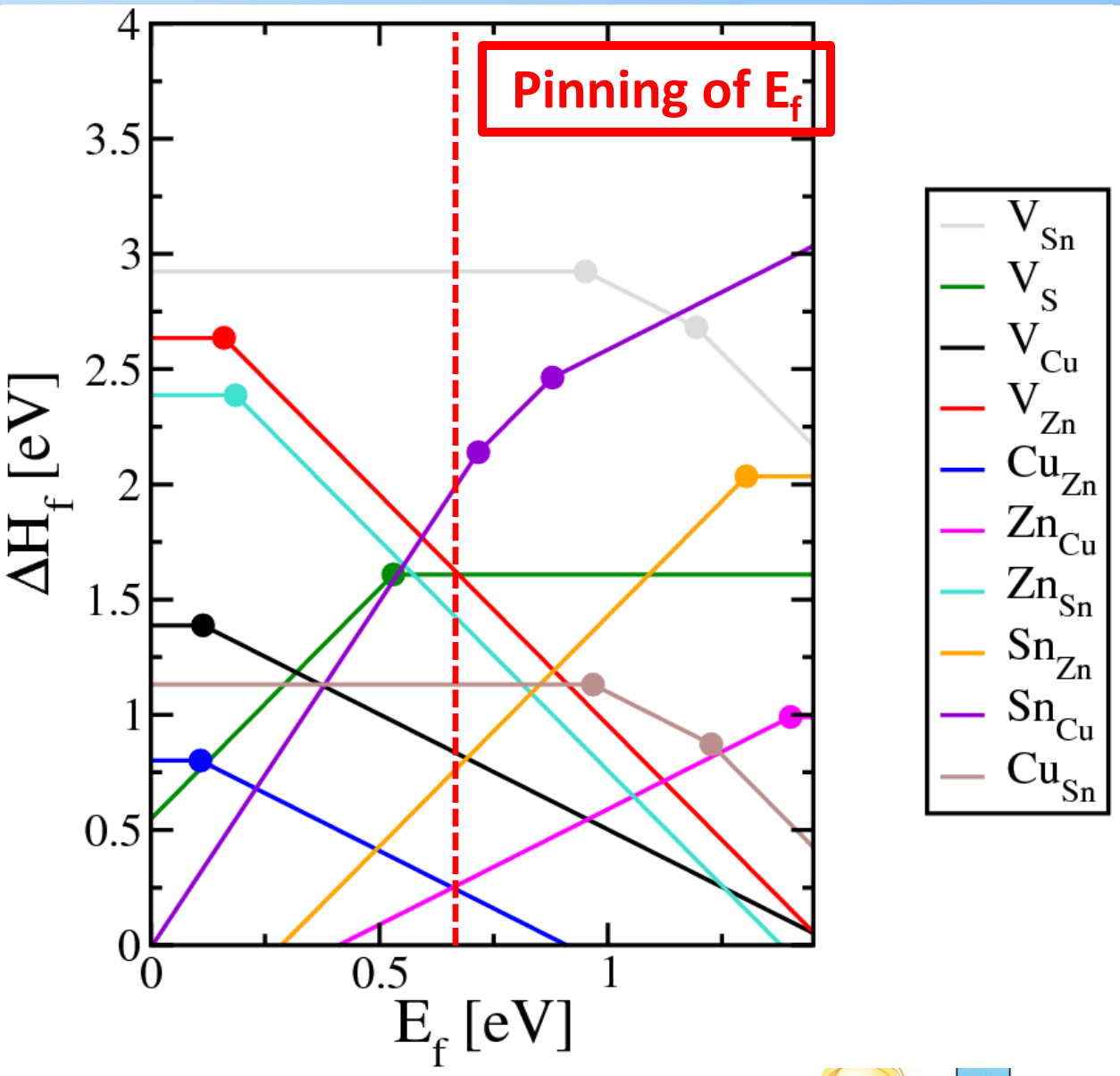
$$2\Delta\mu_{Cu} + \Delta\mu_{Zn} + \Delta\mu_{Sn} + 4\Delta\mu_S = \Delta H_f(CZTS)$$

Phase diagram of CZTS

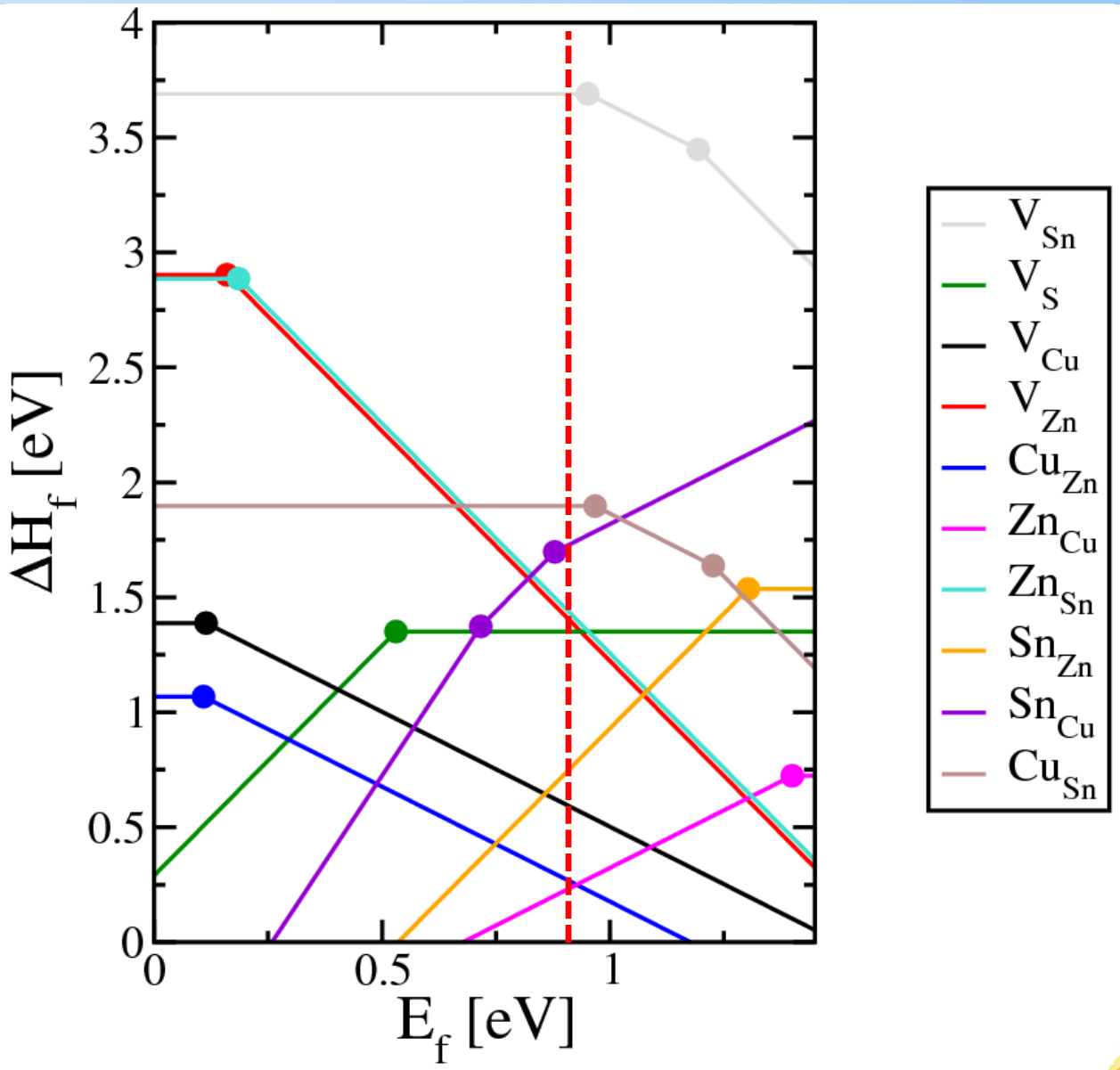


Defect formation energy at A

- Copper vacancy is not the main defect as in CIGS.
- Cu_{Zn} and Zn_{Cu} have similar formation energy.
- CZTS is highly compensated materials, with intrinsic conductivity limiting efficiency.



Defect formation energy at B



3 CONCLUSIONS AND PERSPECTIVES

Conclusions and perspectives

- **Search for new materials allow to understand better existing champion materials.**
- **Technological applications and material properties are narrowly linked.**
- **PV is not about light absorption, famous counterexample being Si.**
- **Apparent harmless change of a material can have deep consequences like CZTS.**
- **Explore the unexplored without any industrial or economical constraints because it can shine light on the existing phenomenon**