# Modelling Materials and Processes for Solar Cells

## Point Defects, Hetero-Junctions & Solid-Solutions

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Centre for Sustainable Chemical Technologies
EPSRC Engineering and Physical Sciences Research Council
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# Talk Outline

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1. Introduction to Solar Energy Conversion
2. Point Defects in Materials
3. Valence Band Alignment
4. Semiconductor Alloys
5. Outlook for Material Design

# Atomistic Materials Modelling

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**Classical, Quantum & Multi-Scale Computational Chemistry Techniques**

## Materials Characterisation:

- Bulk physical and chemical properties.

## Chemical Reactions:

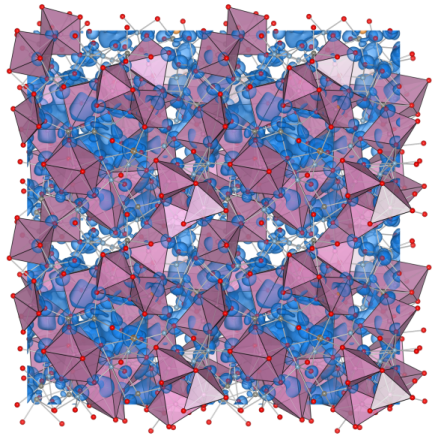
- Catalysis; lattice defects; redox chemistry.

## Materials Engineering:

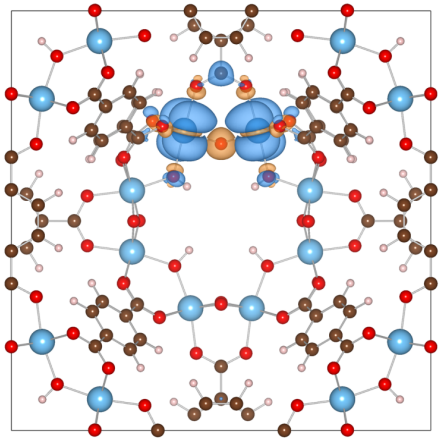
- Beneficial dopants or alloys.

## Substrate & Device Effects:

- Interfacial & strain phenomena.



**Amorphisation:**
Conduction states in $(In,Ga,Zn)O_4$



**MOFs:**
Redox Activity

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# European Solar Energy

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15 TW

Global Consumption

86,000 TW

Solar

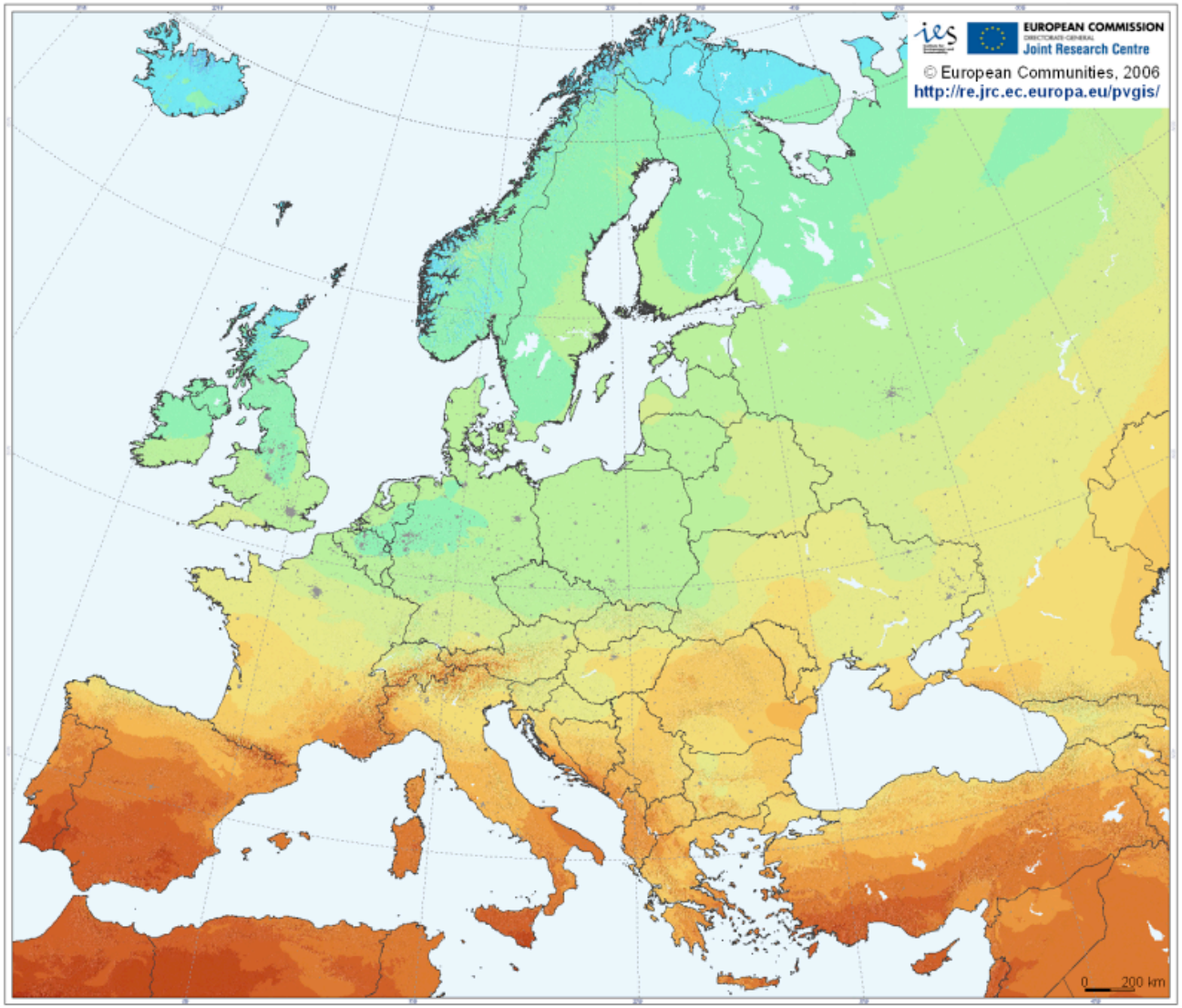
870 TW

Wind

32 TW

Geothermal

## Photovoltaic Solar Electricity Potential in European Countries



# Bath versus Berlin

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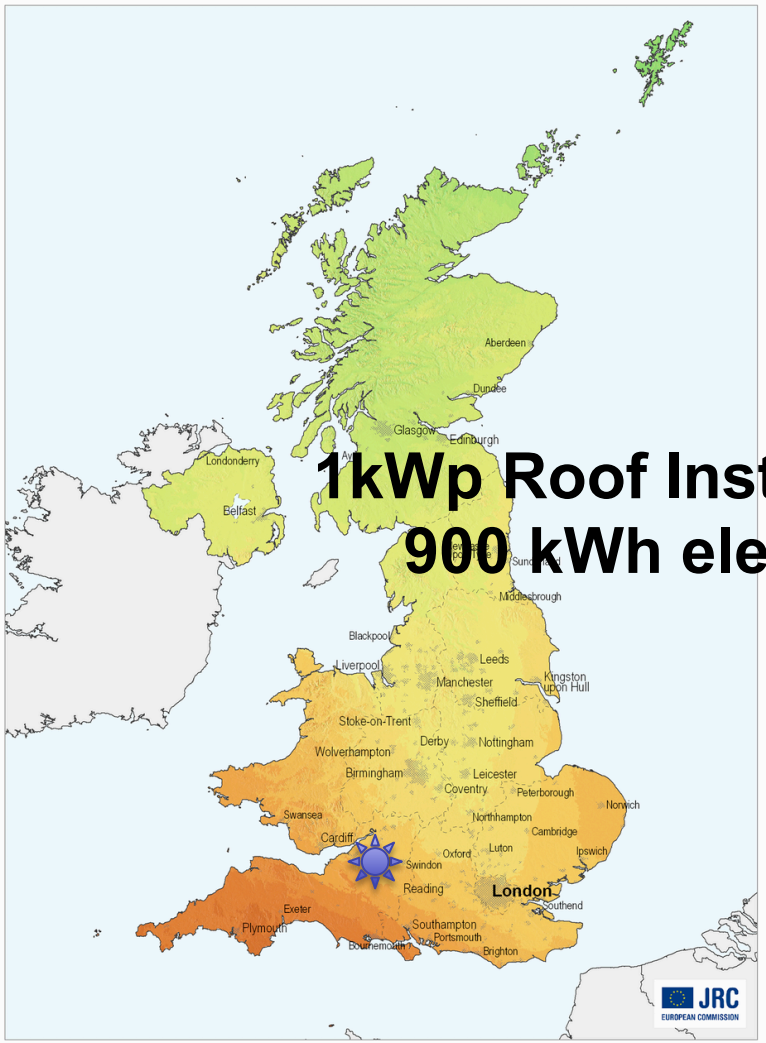
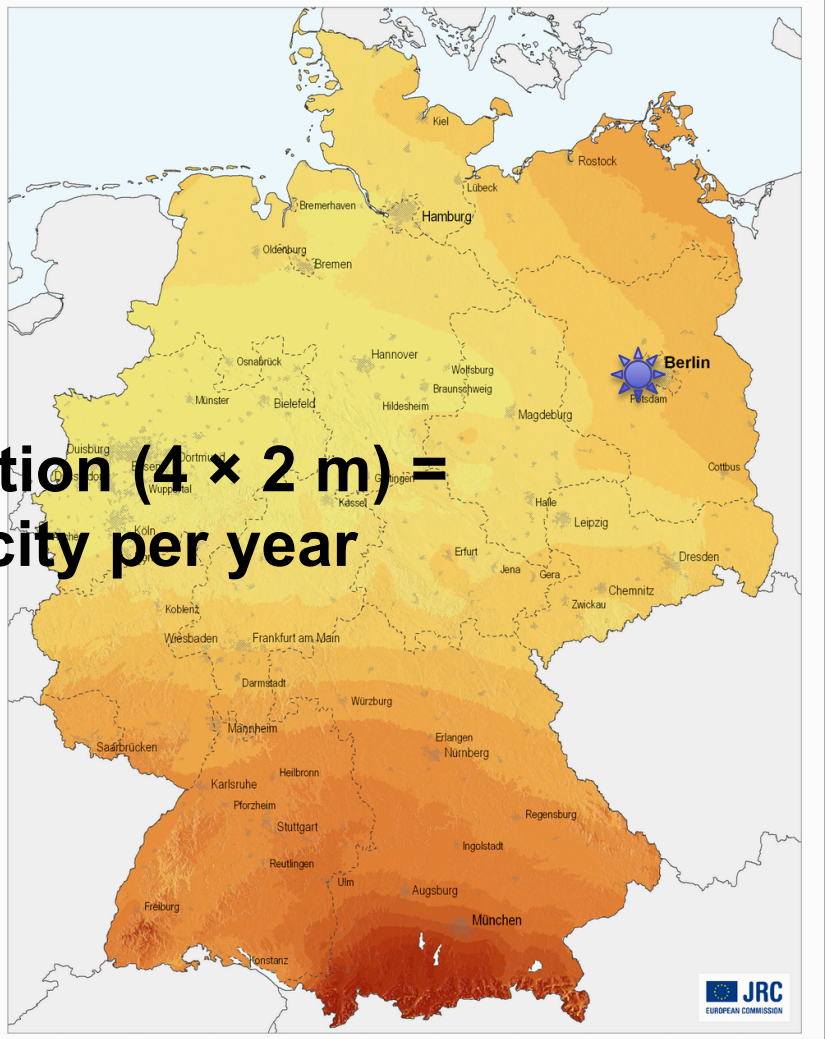
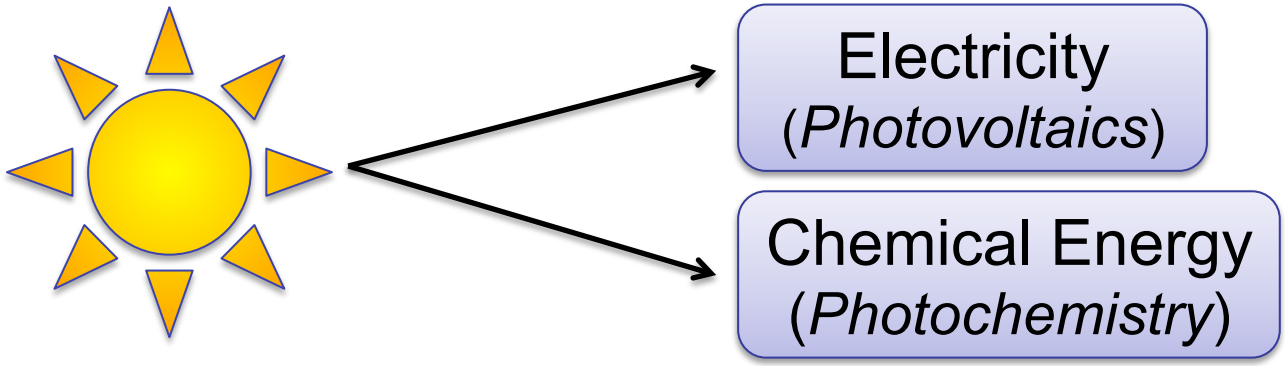
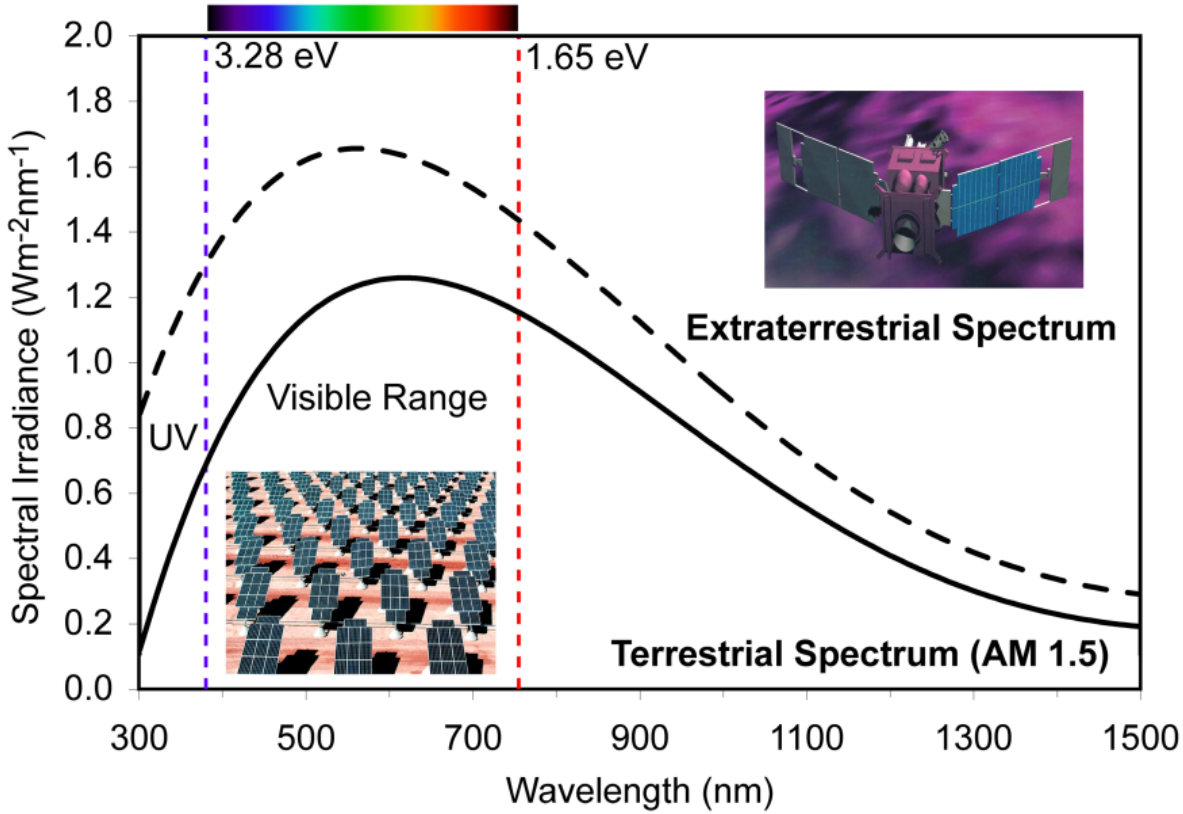



**1kWp Roof Installation (4 × 2 m) =**
**900 kWh electricity per year**

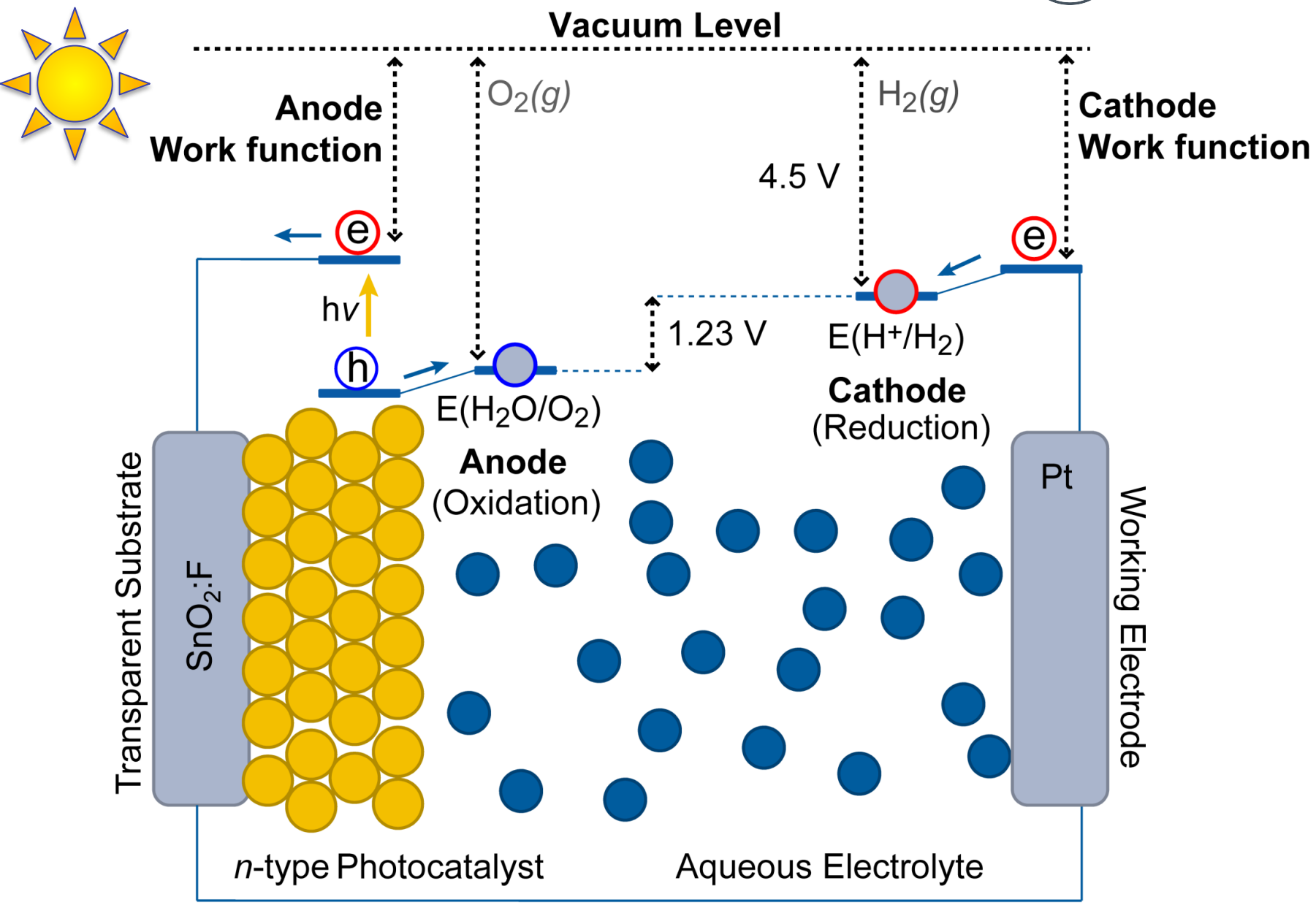


# Solar Energy Conversion



# Photoelectrochemical $H_2$



# Solar Cell Conversion Efficiency

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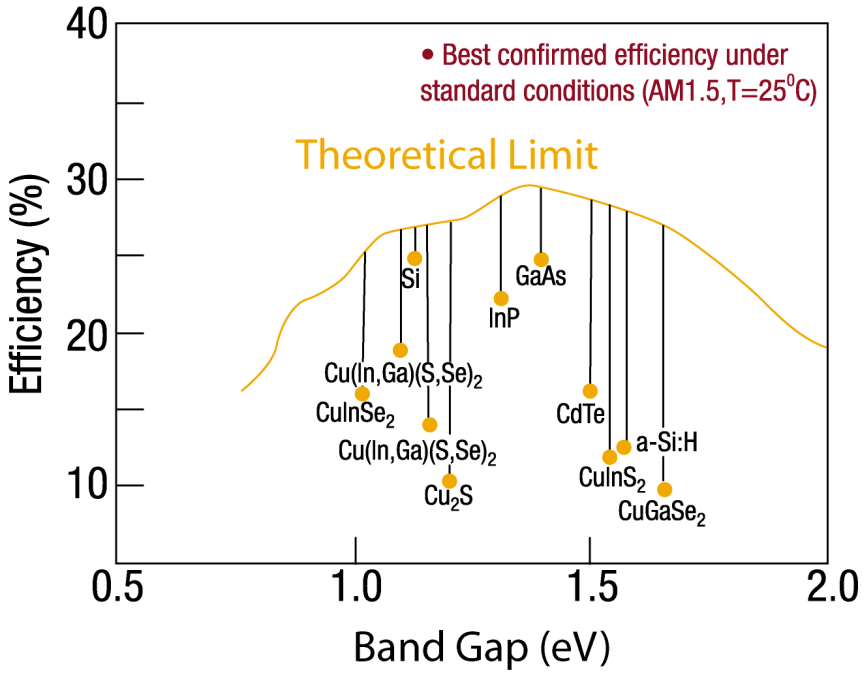
Thermodynamic Limits:

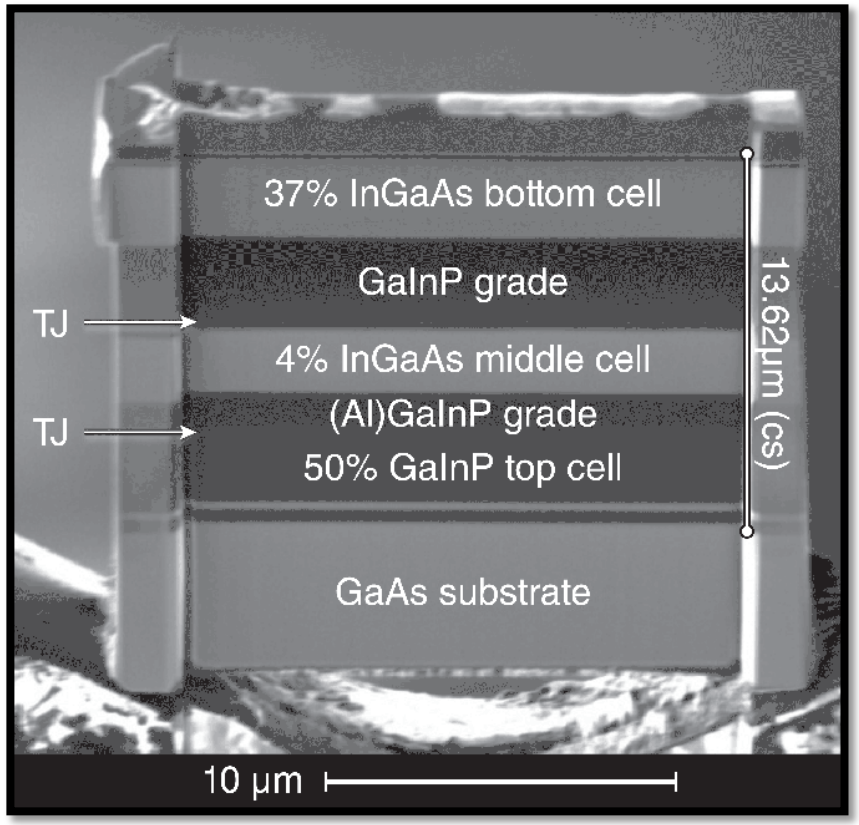
## Single Junction < 30 %




**Record 25.0 %**

Single Crystal Si

## Multi-junction < 66 %




**Record 41.6 %**

Metamorphic 3-junction

# High Efficiency + Low Cost

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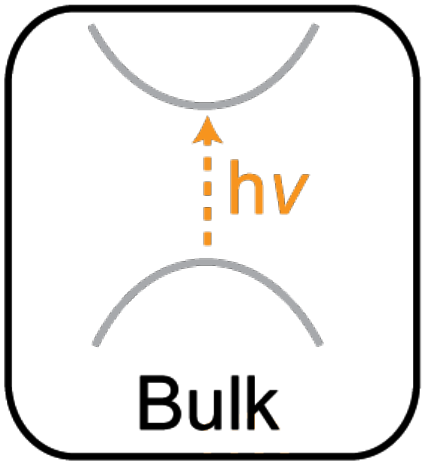
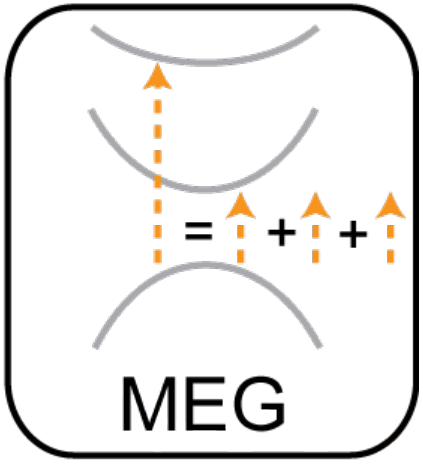
## Convert sub band-gap photons

Intermediate band (**IB**) states (*e.g.* dopants).

PRL **78**, 5014 (1997)

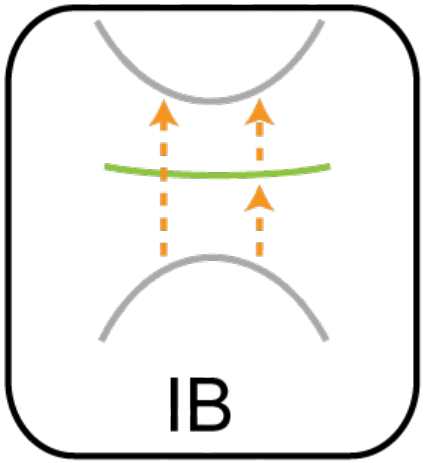


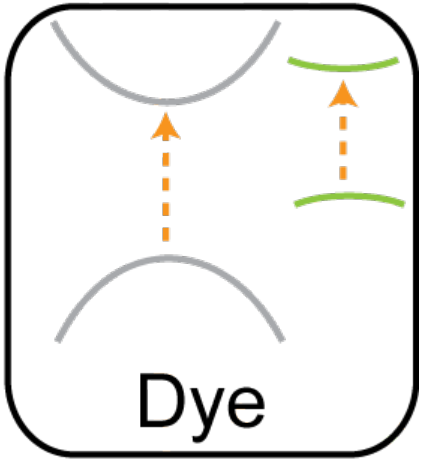




## Efficient use of "hot" electrons

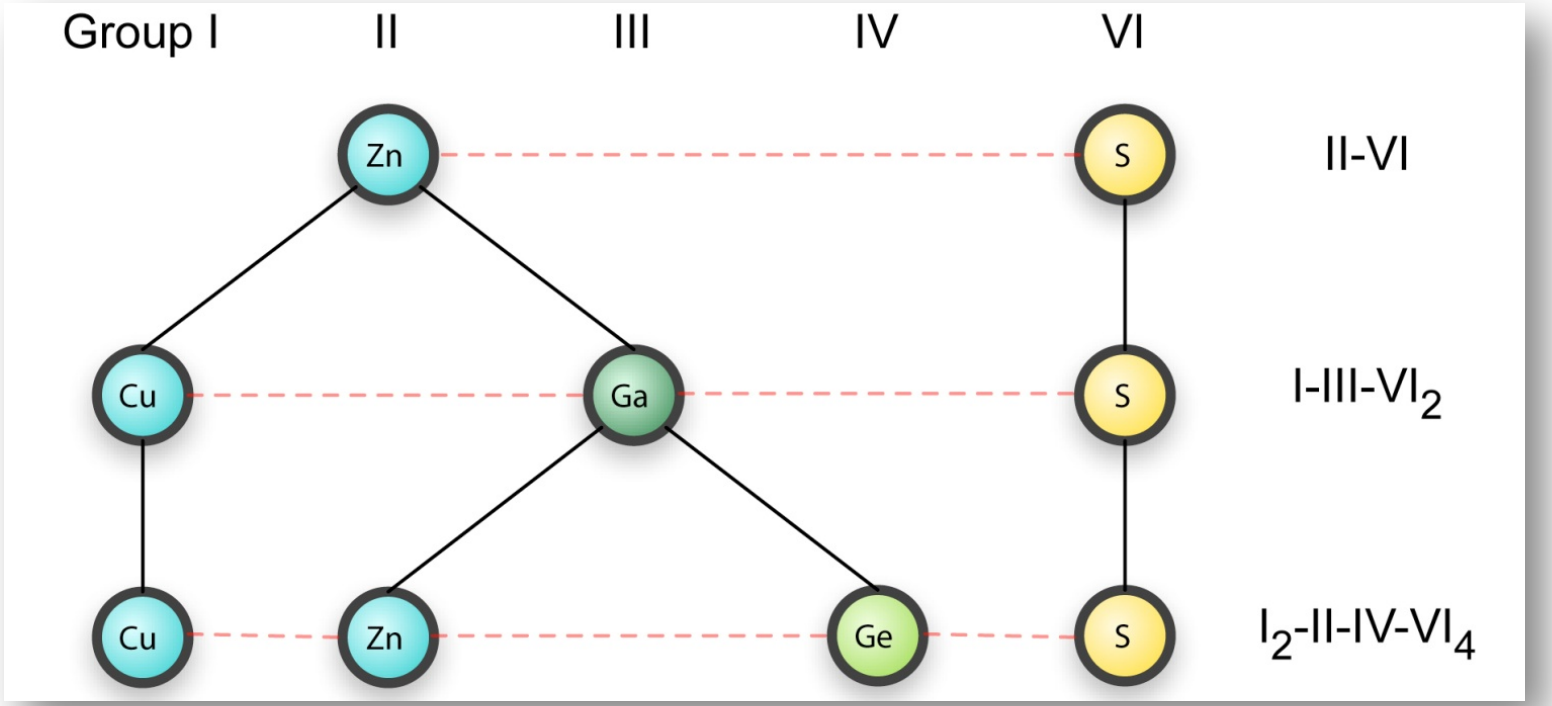
Multiple exciton generation (**MEG**) for a single short wavelength photon.

Nano Lett. **5**, 865 (2005)



# Complex Material Design




## Multernary Semiconductor Screening

- Build database of plausible materials (stoichiometric).
- Assess structural, electronic and thermodynamic properties.
- Screen / tailor for specific applications.

# Quaternary Semiconductors

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## Predicted (and Confirmed) Solar Cell Materials

- $Cu_2ZnSnS_4$, $Cu_2ZnSnSe_4$ and $Cu_2ZnGeS_4$

*Applied Physics Letters* ***94*** *041903 (2009)*

## Predicted Spintronic Materials

- $ZnSiAl_2As_4$, $CdGeAl_2As_4$ and $CuAlCd_2Se_4$

*Applied Physics Letters* ***95*** *052102 (2010)*

## Predicted Topological Insulators

- $Cu_2HgPbSe_4$, $Cu_2CdPbSe_4$ and $Ag_2HgPbSe_4$

*Physical Review B* ***83*** *245202 (2011)*

# Band Gaps and Offsets

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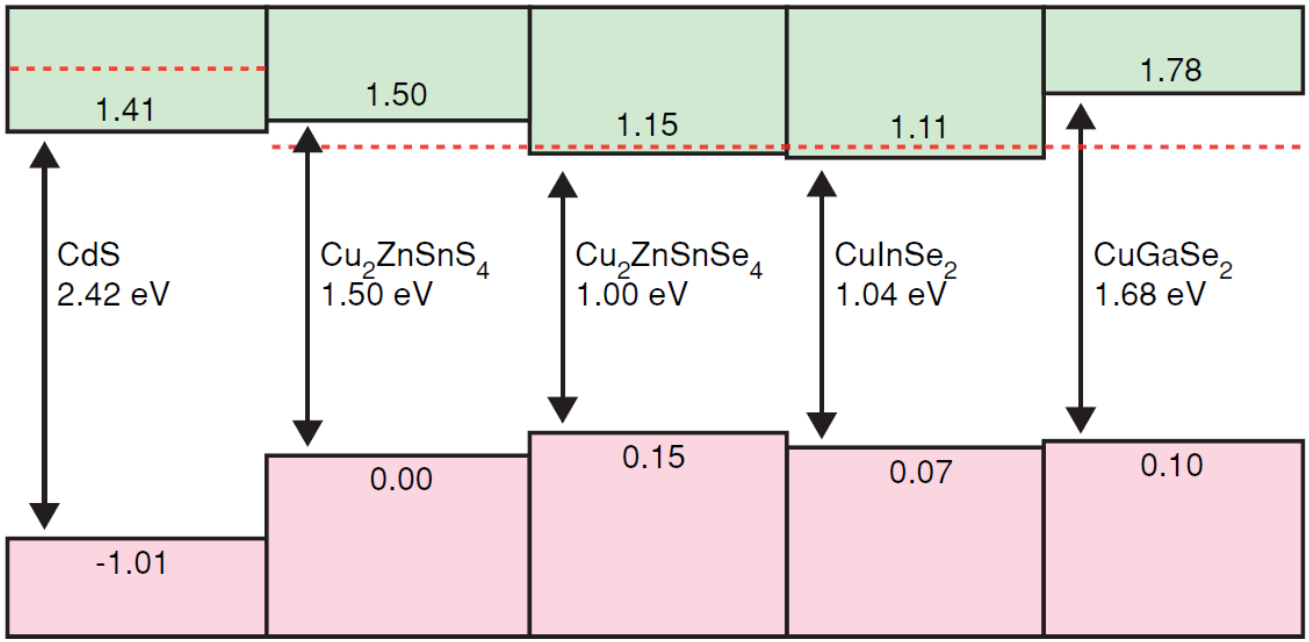
| Material | Structure | $E_g$ (eV) |
|---|---|---|
| $Cu_2ZnSnS_4$ | Kesterite | 1.5 |
| $Cu_2ZnSnSe_4$ | Kesterite | 1.0 |

**Hybrid Density Functional:** HSE06 (Confirmed by *GW* )




Applied Physics Letters **94,** 041903 (2009)

# $Cu_2ZnSnS_4$ Defect Reactions

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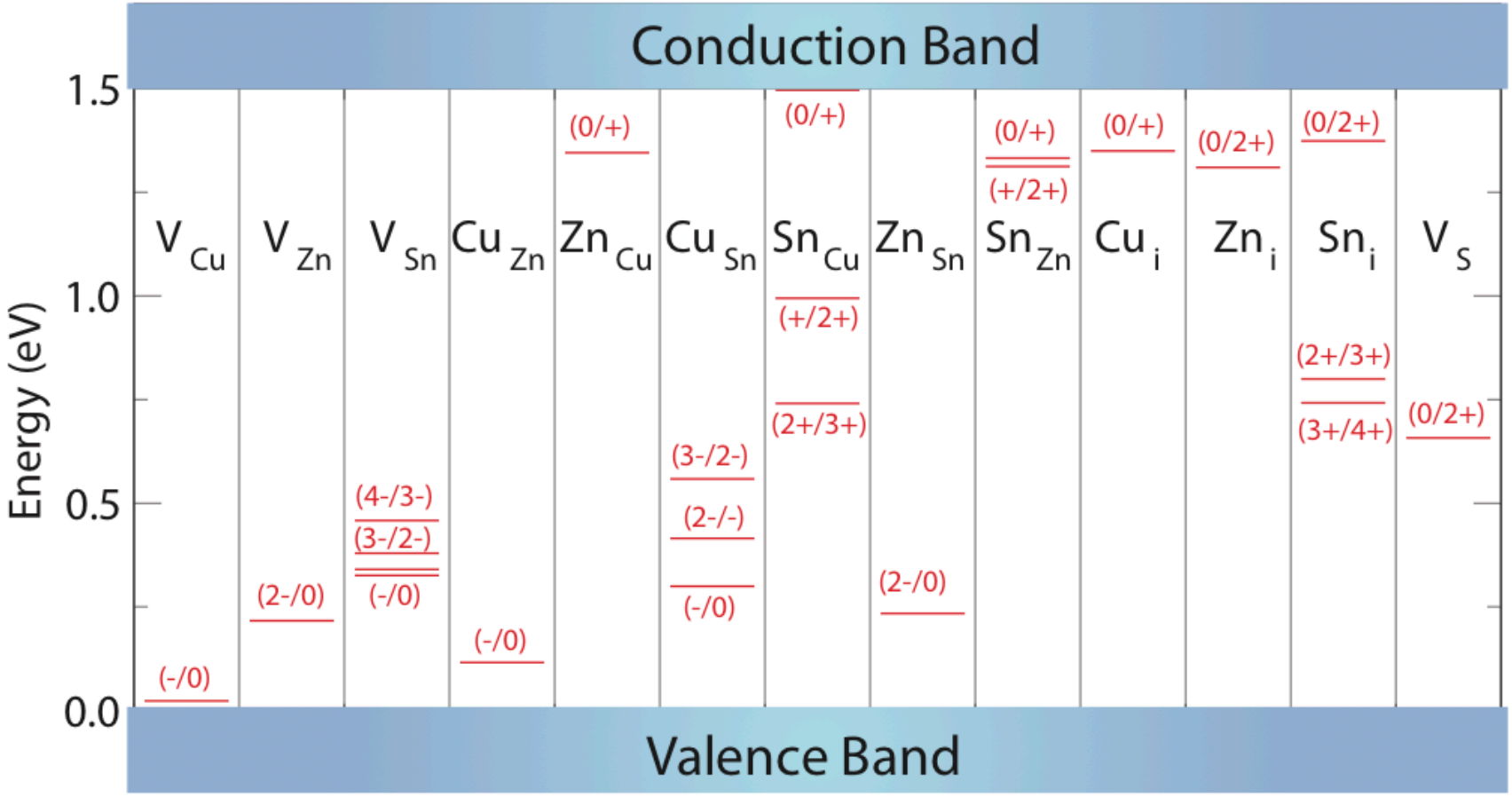


Cu poor / Zn rich growth conditions are optimal for robust *p*-type conductivity.

Applied Physics Letters **96,** 021902 (2010)

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# Point Defect Formation

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- Materials are imperfect: defects create unique properties.
- Point defects are present in equilibrium due to configurational entropy: $n_d = N \exp(-\Delta G/k_B T)$

## Charge Neutrality Condition

$$[e^-]+[A^-]=[h^+]+[D^+]$$

## Charge Carrier Generation

Non-stoichiometry: $O_O \rightarrow V_O^{++} + 2e^- + \frac{1}{2}O_2$

Extrinsic doping: $D_O \rightarrow D_O^+ + e^-$

## Ionic Defect Compensation

Electrons: $e^- + \frac{1}{2}O_2 \rightarrow O_i^-$

Holes: $h^+ \rightarrow V_O^+ + \frac{1}{2}O_2$

# Point Defect Properties

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| Calculable | Observable |
| --- | --- |
| Total Energy | • Heats of formation and reaction: relative stabilities and concentrations.<br>• Diffusion barriers. |
| Defect Ionization Energy (Vertical) | Optical absorption, photoluminscence, photoconductivity. |
| Defect Ionization Energy (Adiabatic) | Deep-level transient spectroscopy; thermally stimulated conductivity. |
| Defect Vibrational Modes | • IR / Raman spectra.<br>• Diffusion rates; free energy. |

# Defect Calculation (Finite System)

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## Defect Reaction in Metal Oxides (Neutral Case)

**Oxygen Loss:** $O_O \rightarrow V_O + \frac{1}{2}O_2$

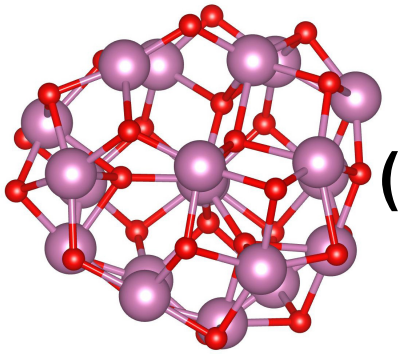
**Reaction Energy:** E[$\frac{1}{2}O_2$] + E[Defect] - E[Perfect]

## PBE0 Functional (FHI-AIMS)

E[$\frac{1}{2}O_2$] = *-2049.217 eV (Spin Triplet)*

E[Defect] = -3302202.055 *eV*

E[Perfect] = -3304251.751 *eV*



**$(In_2O_3)_{10}$**

**ΔH** = 0.479 eV

Walsh and Woodley, PCCP **12**, 8446 (2010)

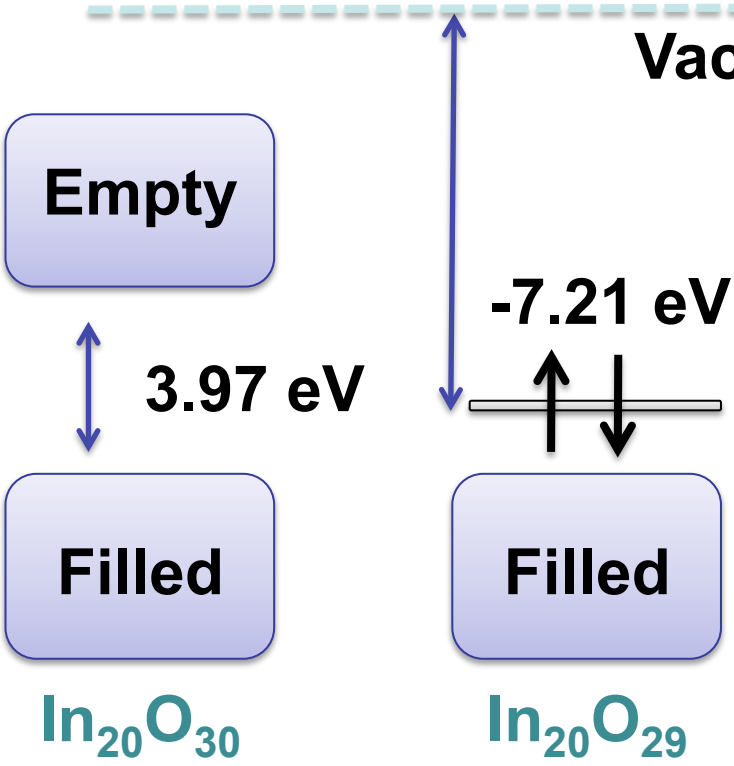
# Defect Ionisation (Finite System)

## Defect Reaction ($In_2O_3$)

Oxygen Loss: $O_O \rightarrow V_O + ½O_2$

1st Ionisation: $V_O \rightarrow V_O^+ + e^-$

2nd Ionisation: $V_O^+ \rightarrow V_O^{++} + e^-$




1. Koopman's: 7.21 eV
2. ΔSCF: 8.56 eV
3. $G_0W_0$: 8.25 eV

# Defect Calculation (Infinite System)

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## Point Defect Reaction

**Oxygen Loss:** $O_O \rightarrow V_O + ½O_2$

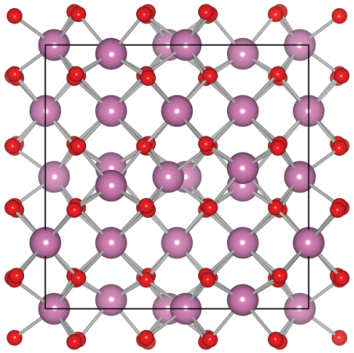
**Reaction Energy:** E[½$O_2$] + E[Defect] - E[Perfect]

## PBE Functional (FHI-AIMS)

E[½$O_2$] = *-2046.716 eV (Spin Triplet)*

E[Defect] = -21143773.388 *eV*

E[Perfect] = -21145821.960 *eV*



**$(In_2O_3)_\infty$**

**ΔH** = 1.856 eV

(640 atom supercell)

# Defect Ionisation (Infinite System)

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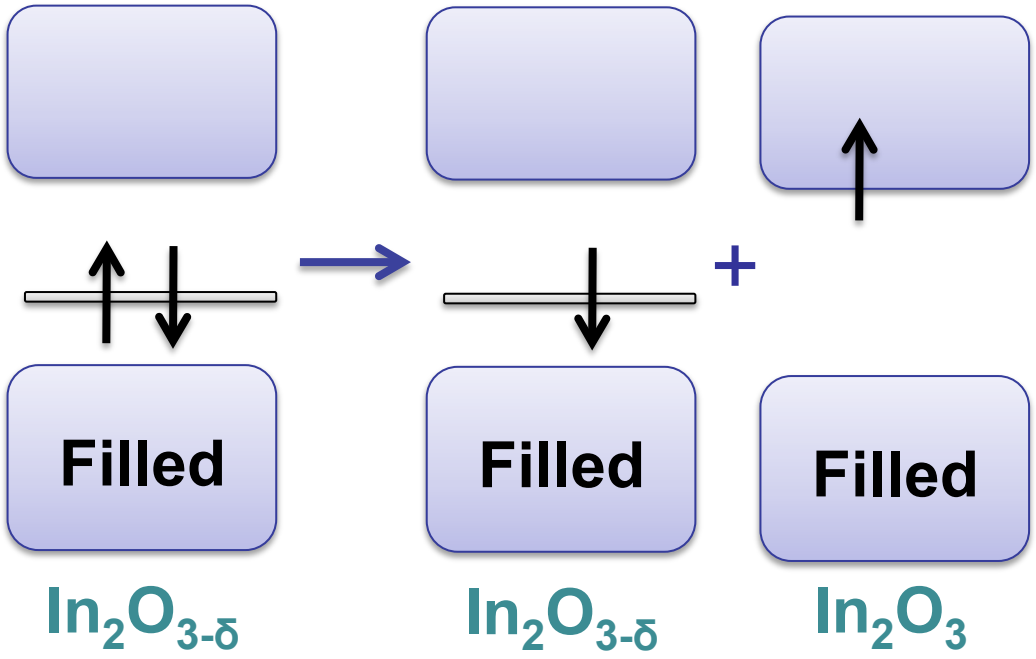
## Defect Reaction ($In_2O_3$)

Oxygen Loss: $O_O \rightarrow V_O + ½O_2$

1st Ionisation: $V_O \rightarrow V_O^+ + e^-$

2nd Ionisation: $V_O^+ \rightarrow V_O^{++} + e^-$

**No vacuum level: ensure that all energies are relative!**



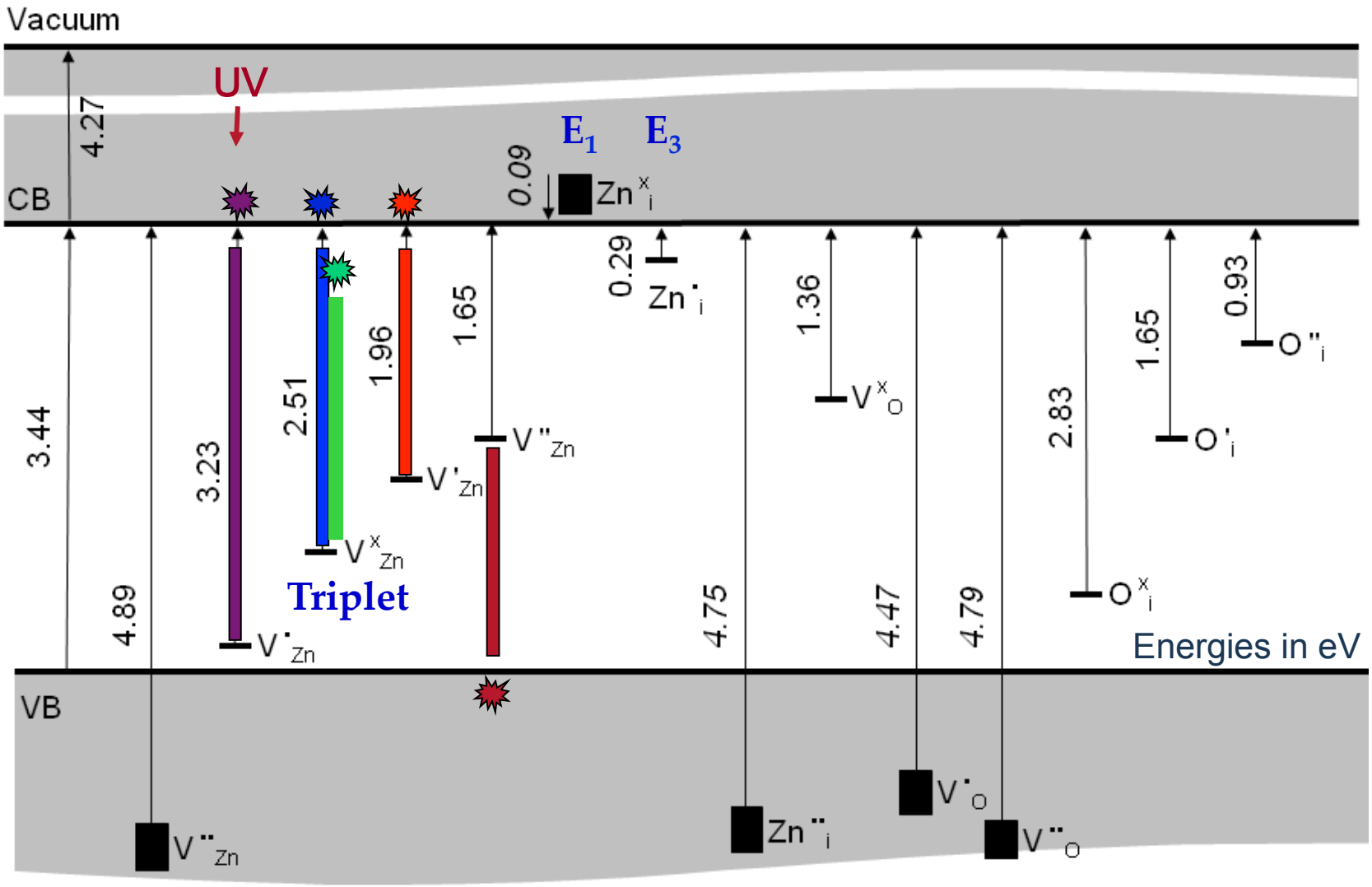

Charged periodic systems: finite-size effects. See:

Leslie & Gillan (1985)

Makov & Payne (1995)

Freysoldt *et al* (2009)

# ZnO Defect Spectroscopy




Sokol et al, Faraday Discussions **137**, 267 (2007)

# Electron Chemical Potential

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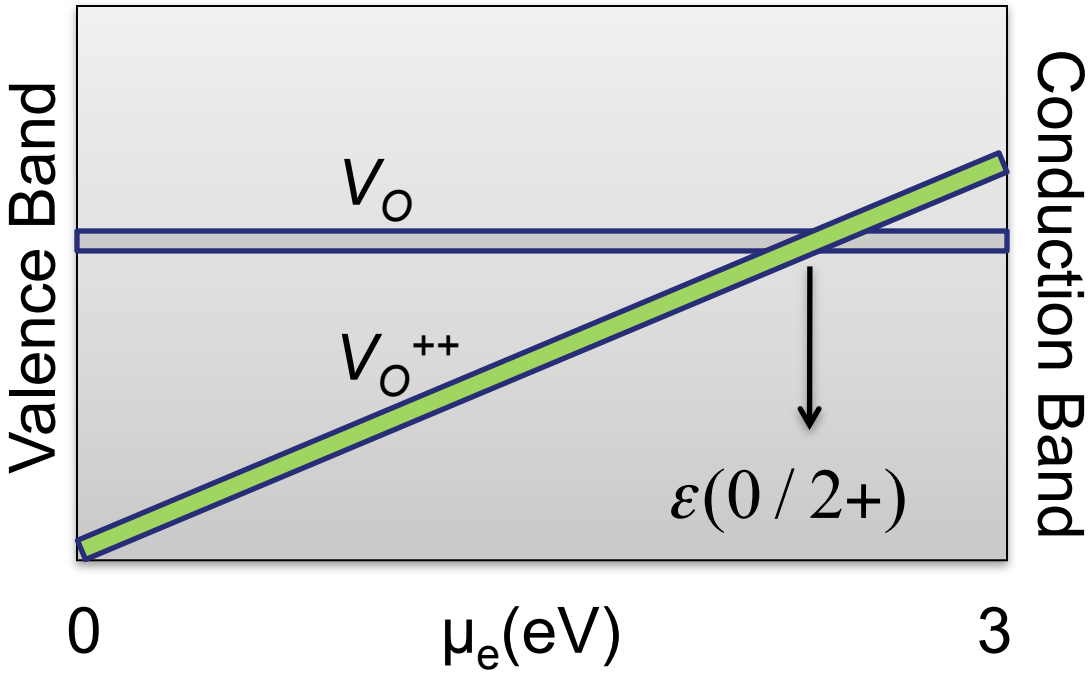
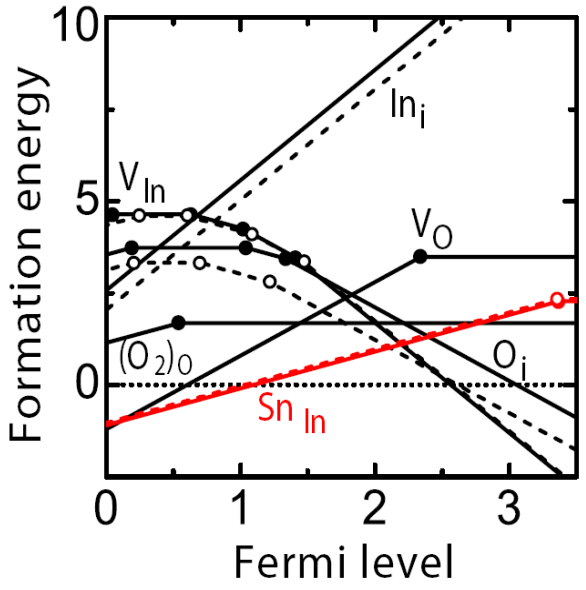
## Charge States

$V_O$ ; $[V_O^+ + e^-]$; $[V_O^{++} + 2e^-]$

*For semiconductor $\mu_e$ is not fixed.*




*Spaghetti defects?*




**$In_2O_3$:** Lany and Zunger, Phys. Rev. Lett. **98**, 045501 (2007).

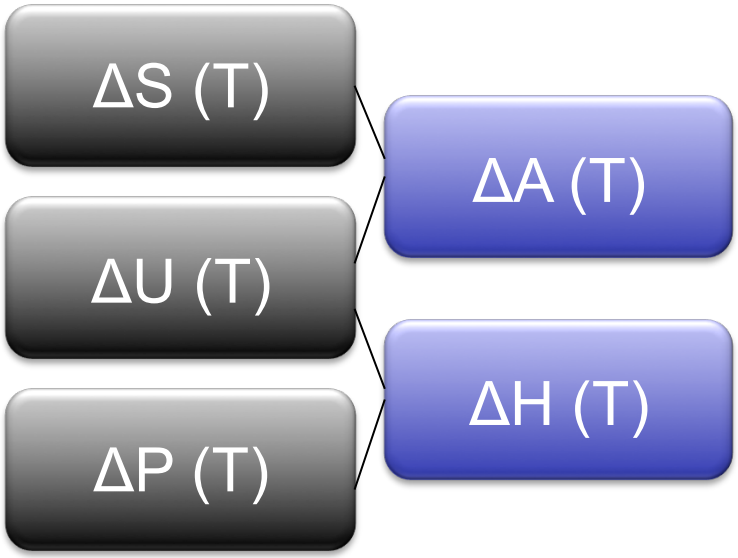
*Can perform self-consistent solution for $n_e$, $n_h$ and $n_d$*

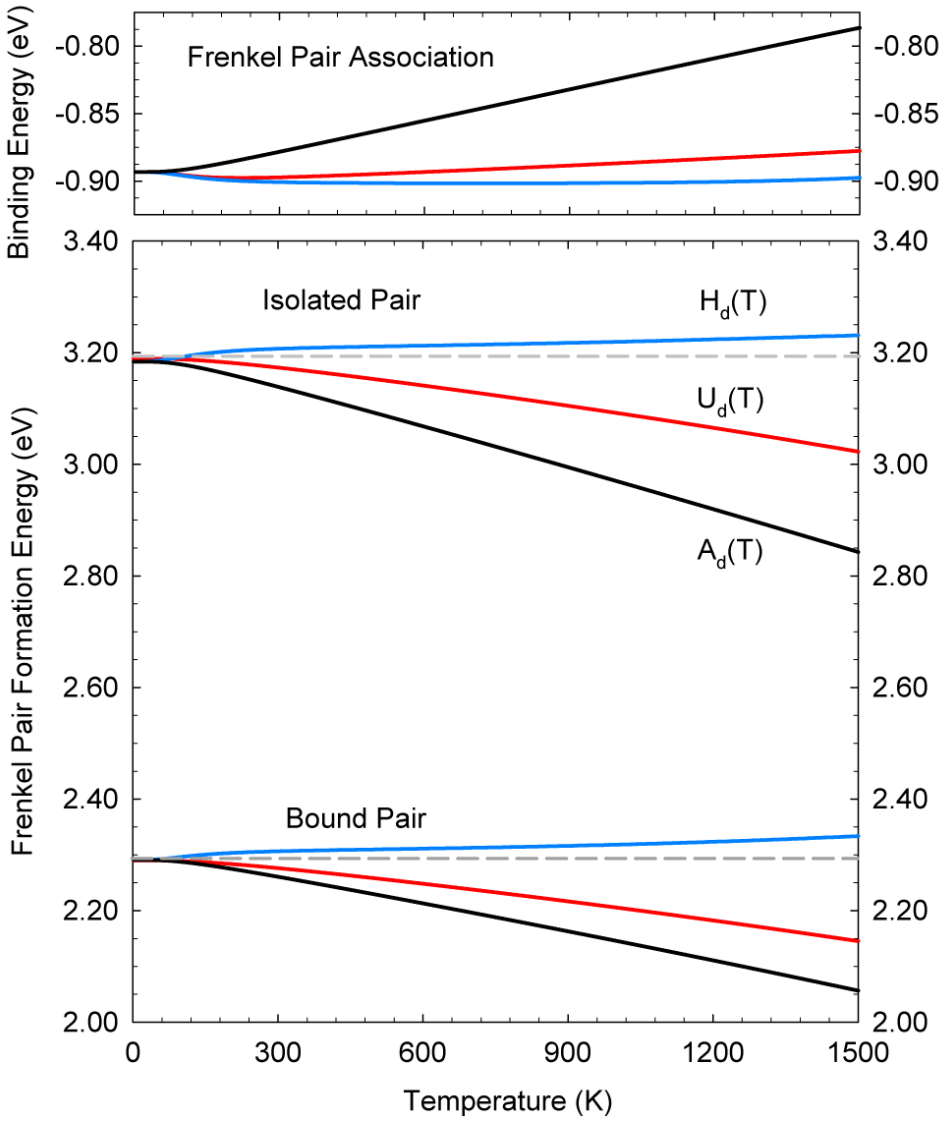
Baraff, Kane and Schlüter, Phys. Rev. B **21**, 5662 (1980)

# Defect Free Energies

## Temperature Dependence

$$n_d = N \exp(-\Delta G / k_B T)$$




Physical Review B **83,** 224105 (2011)

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# “Natural” Valence Band Offsets

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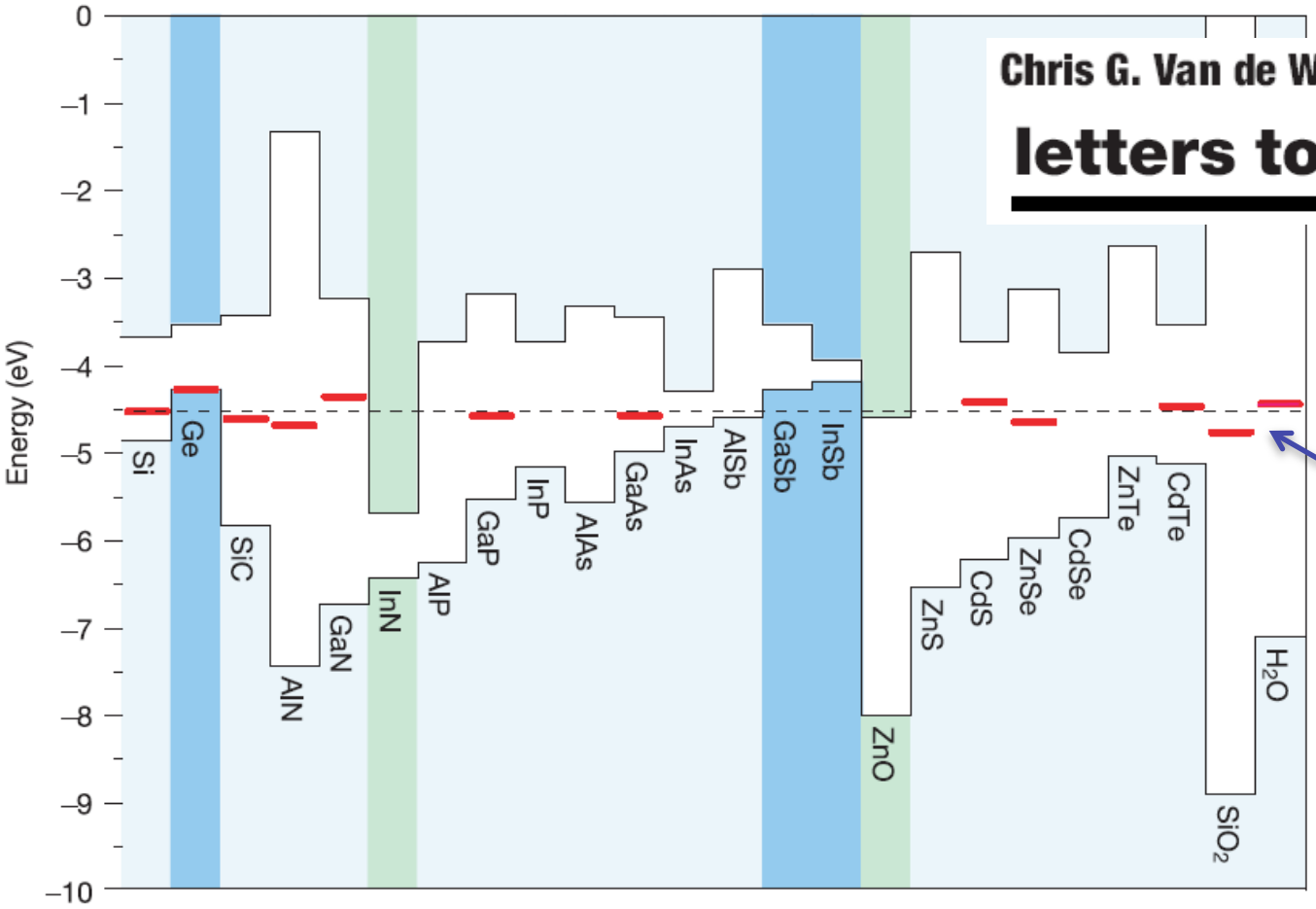
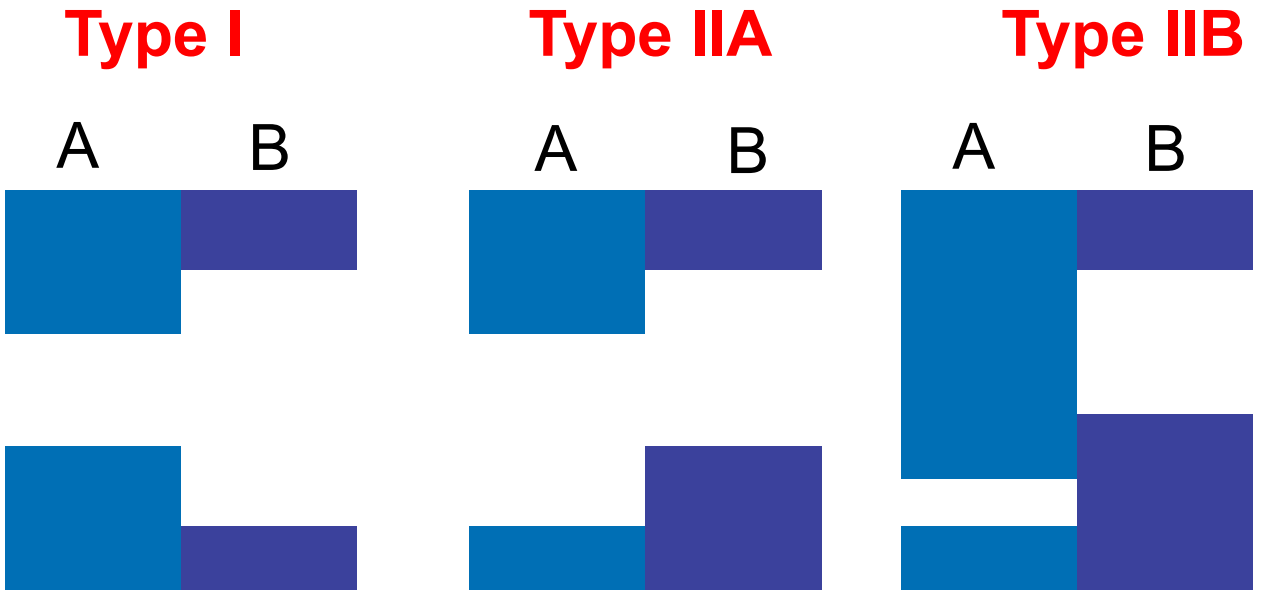



- Essential for device engineering and modelling.
- Provides understanding of many processes (e.g. redox levels, material doping limits).

# Band Offset Classification




*e.g.* **(GaAs|GaAlAs)** **(AlAs|GaAs)** **(InAs|GaSb)**

- Type I: Electrons and holes confined in one layer (A).
- Type IIA: ‘Spatially Indirect’. Electron and hole separation.
- Type IIB: Effective ‘zero gap’. Electron transfer from B to A.

# Experimental Offsets

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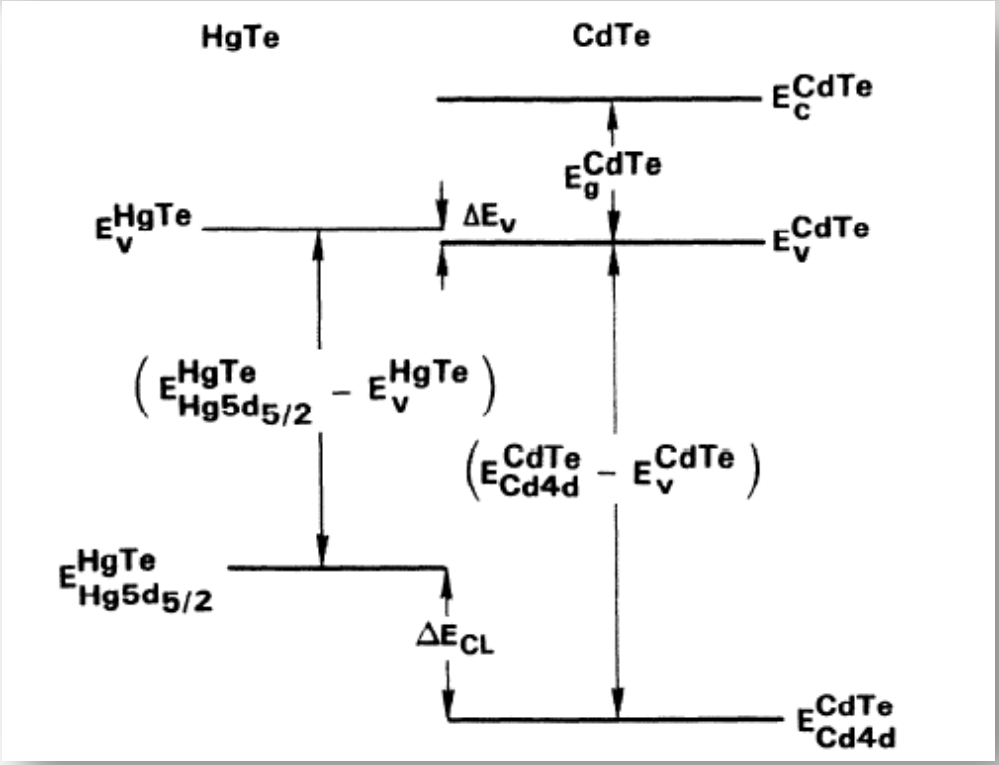
VOLUME 56, NUMBER 15 PHYSICAL REVIEW LETTERS 14 APRIL 1986

## CdTe-HgTe $(\bar{1}\bar{1}\bar{1})$ Heterojunction Valence-Band Discontinuity: A Common-Anion-Rule Contradiction

Steven P. Kowalczyk,[a] J. T. Cheung,[b] E. A. Kraut,[a] and R. W. Grant[a]

*Microelectronics Research and Development Center, Rockwell International Corporation, Thousand Oaks, California 91360*

(Received 7 January 1986)



# Theory: Choice of Reference Level

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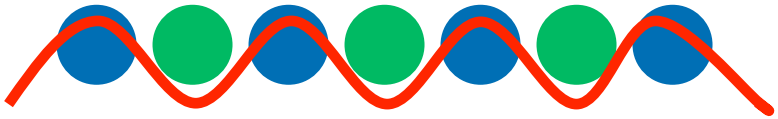
**Different studies adopt different reference levels, even within the same code (here VASP). This applies to both band offsets and charged defect cell alignment.**

**Q. Is this choice important?**

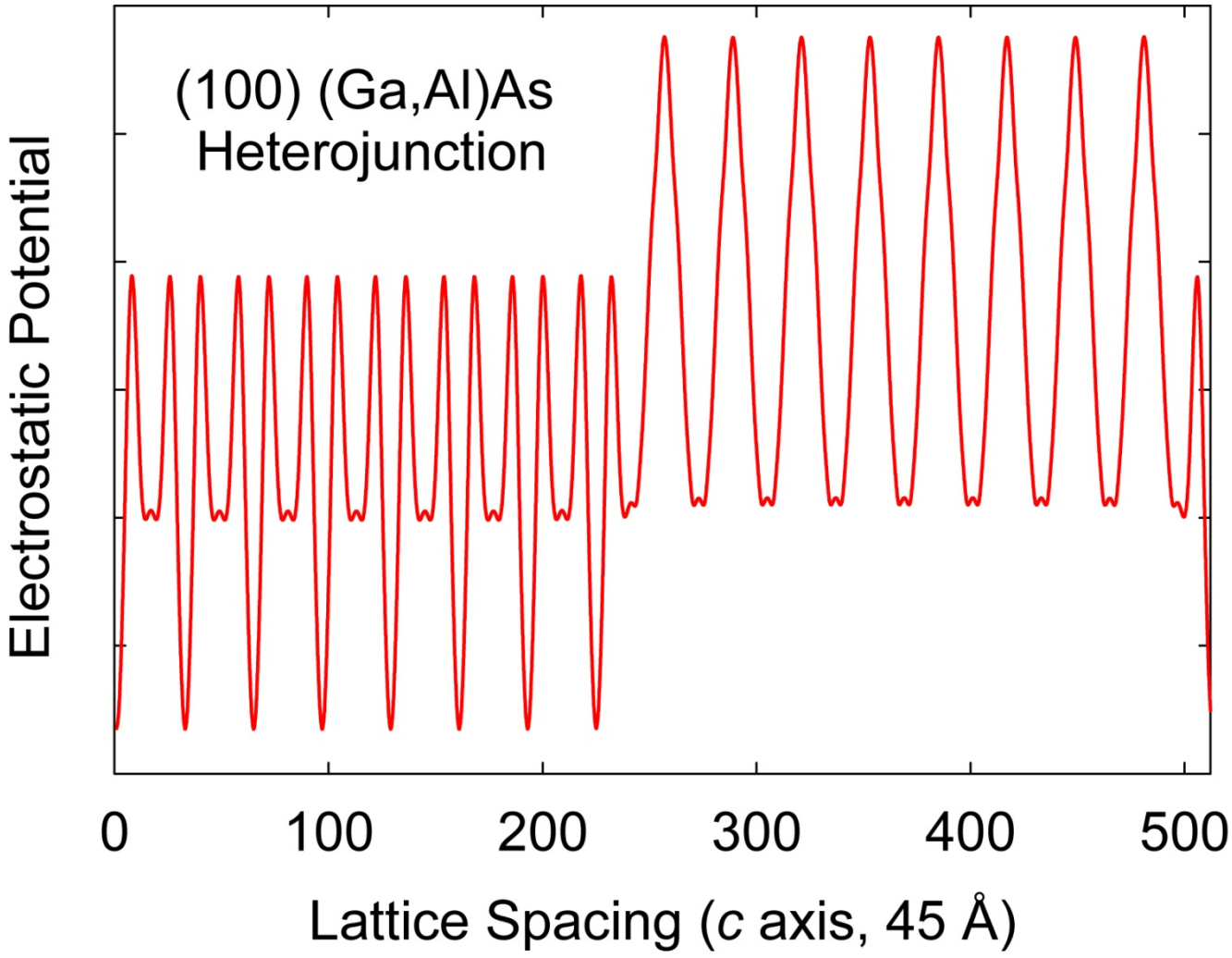
• Deep (atomic-like) core level, e.g. O 1*s*.
*Walsh & Wei, Phys. Rev. B 76, 195208 (2007).*

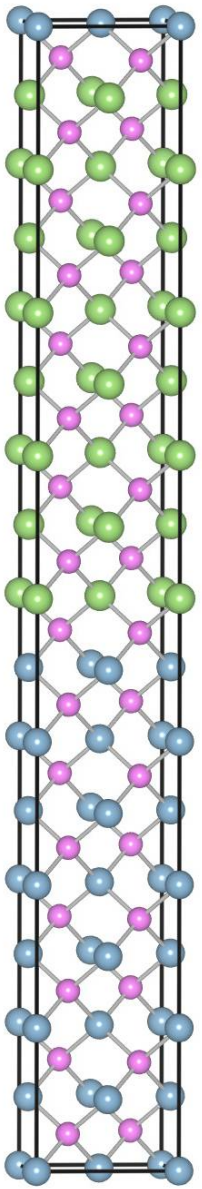
• Local electrostatic potential (integrated in fixed radius).
*Lany & Zunger, Phys. Rev. B 78, 235104 (2008).*



• Averaged electrostatic potential.
*Janotti & Van de Walle, Phys. Rev. B 75, 121201 (2007).*

# Choice of Heterojunction Interface



**Ensure no dipole across hetero-structure!**

# Theory: Choice of Reference Level

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**An example: (AlAs|GaAs); isovalent, isostructural, lattice matched.**

**Isolated**

| | AlAs: Reference – VBM (eV) | GaAs: Reference – VBM (eV) | Bulk Difference | Superlattice (Δ Reference) | Total Difference |
|---|---|---|---|---|---|
|  | 11714.407 | 11715.316 | 0.909 | -0.426 | 0.48 |
|  | 53.543 | 54.339 | 0.796 | -0.304 | 0.49 |
|  | 4.183 | 4.604 | 0.421 | 0.106 | 0.53 |

# Quantitative Calculations

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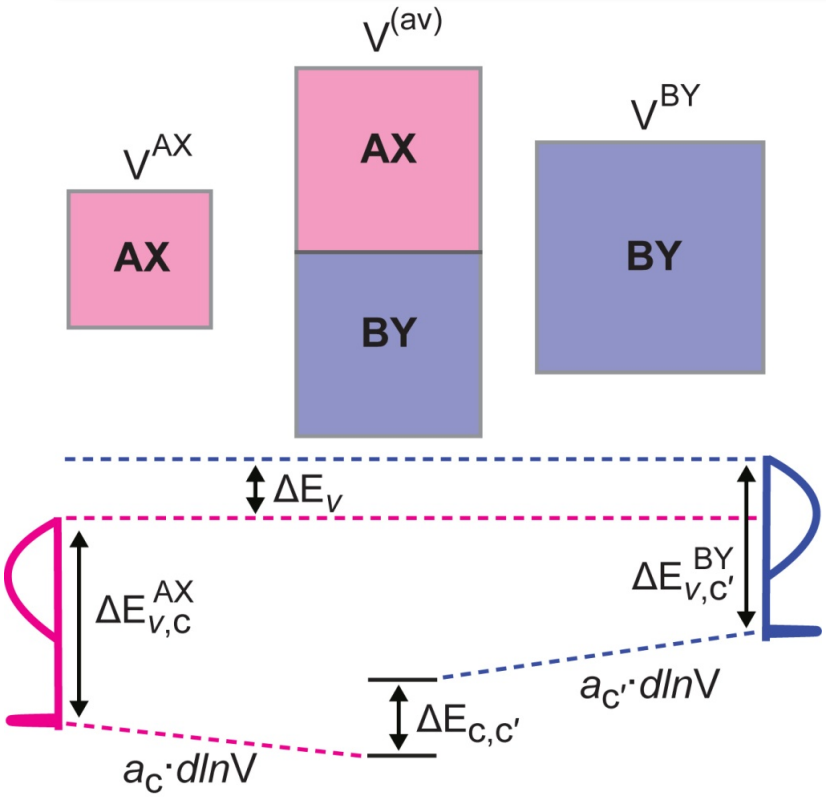
APPLIED PHYSICS LETTERS **94**, 212109 (2009)

**Revised *ab initio* natural band offsets of all group IV, II-VI, and III-V semiconductors**

Yong-Hua Li,[1] Aron Walsh,[2,a)] Shiyou Chen,[1] Wan-Jian Yin,[1] Ji-Hui Yang,[1] Jingbo Li,[3] Juarez L. F. Da Silva,[2] X. G. Gong,[1] and Su-Huai Wei[2,b)]
[1]*Department of Physics, Fudan University, Shanghai 200433, People's Republic of China*
[2]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*
[3]*Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, People's Republic of China*




Core level correction
(lattice harmonic expansion)

$$a_c = \frac{d\varepsilon_c}{d\ln V}$$

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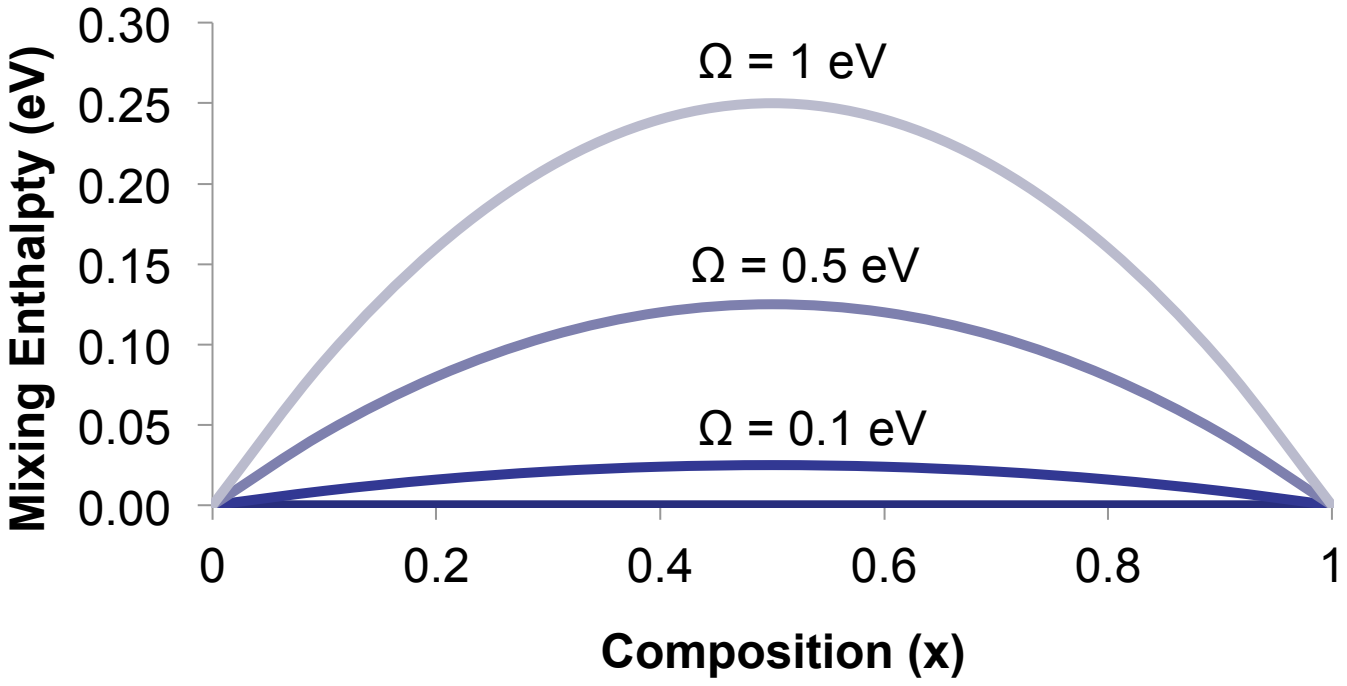
# Binary Solid-Solution ($A_{1-x}B_x$)

**Reaction:** (1-x)A + (x)B → $A_{1-x}B_x$

**Mixing Enthalpy:** $E[A_{1-x}B_x] - E[A] - E[B]$

**"Ideal Solution"** $\Delta H_{mix} = 0$

**"Regular Solution"** $\Delta H_{mix} = \Omega x(1-x)$




$T_C$ = 5800 K

$T_C$ = 2900 K

$T_C$ = 580 K

$T_c = \Omega/2R$

# Homogeneous Alloys

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**No translational symmetry for random alloy.**

**Number of configurations ($A_{0.5}B_{0.5}$):** $\dfrac{N!}{\left(\frac{N!}{2}\right)\left(\frac{N!}{2}\right)}$

**16 atoms: 12,870**

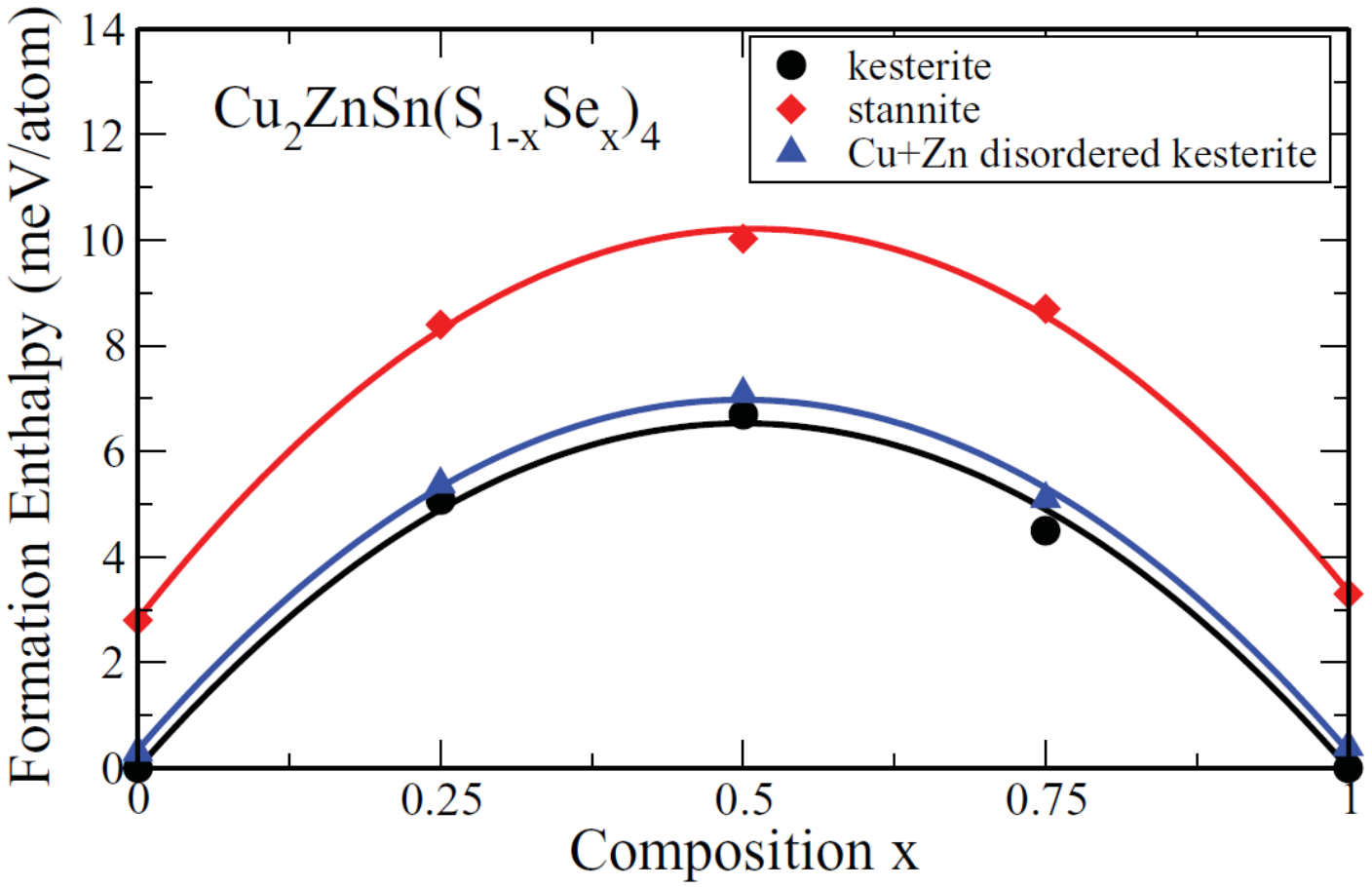
**32 atoms: $6 \times 10^{8}$**

**64 atoms: $1.8 \times 10^{18}$**

**Need to approximate!**

- Site Occupational Disorder (**SOD**) – sample all symmetry inequivalent configuration: http://www.ucl.ac.uk/~uccargr/sod.htm
- Special Quasirandom Structures (**SQS**) – single representative structures: http://www.its.caltech.edu/~avdw/atat/

# CZT(S,Se) Alloy Thermodynamics



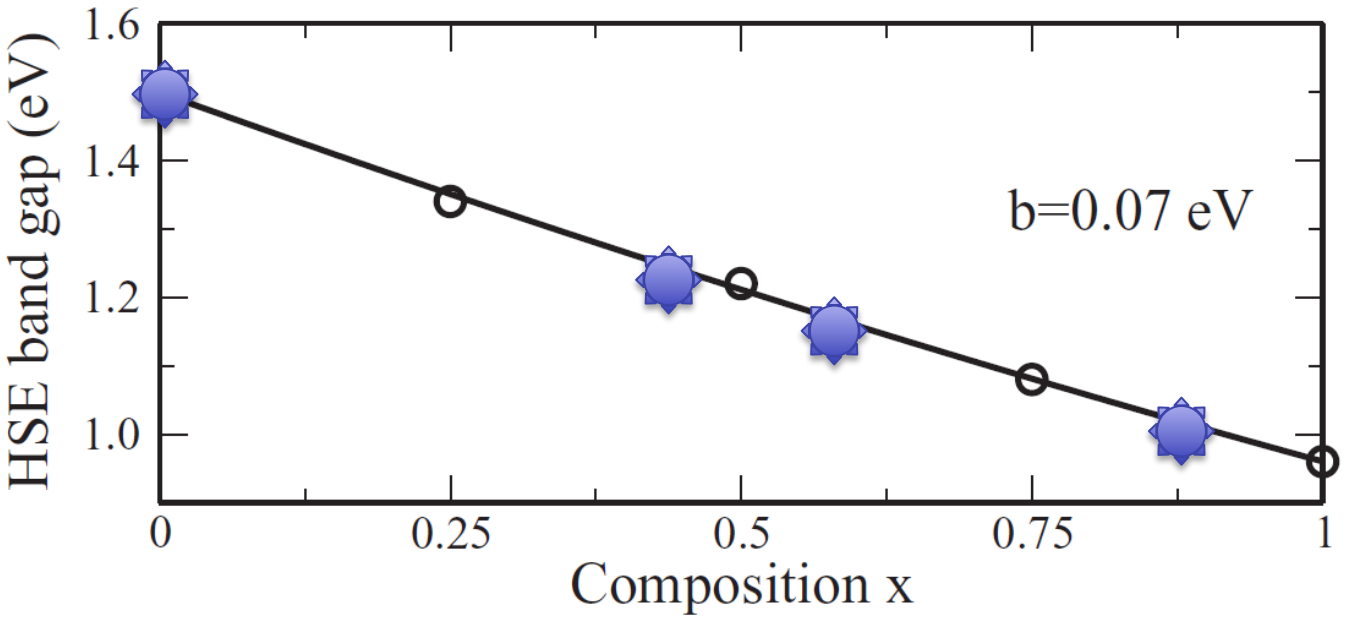

Regular solution model: Ω = 52 meV/mixed atom (302 K)

CIGS: Ω = 176 meV/mixed atom (1021 K)

Physical Review B **83**, 125201 (2011)

# CZT(S,Se) Alloy Thermodynamics

IBM Experiments: Applied Physics Letters **98**, 253502 (2011)




Well behaved alloy: small quadratic bowing parameter.

Physical Review B **83**, 125201 (2011)

# Talk Outline

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1. Introduction to Solar Energy Conversion
2. Point Defects in Materials
3. Valence Band Alignment
4. Semiconductor Alloys
5. Outlook for Material Design

# New Directions: Hot Carriers

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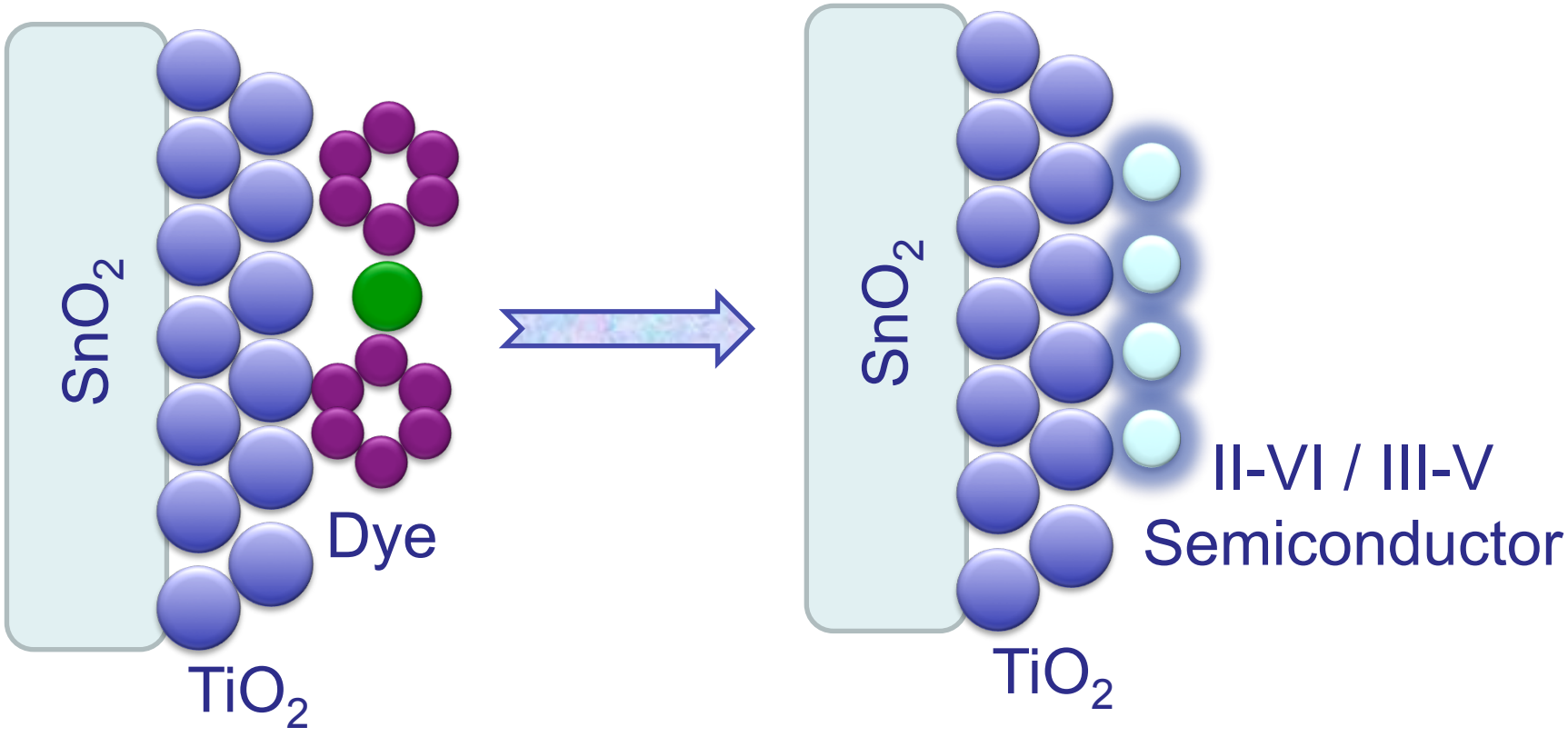
## Semiconductor Nanocrystals for Solar Cells

**1991 (11.1%): Grätzel Cell** **2011 ("66% limit")**




Funded by EPSRC – Chinese Academy of Sciences (2011 - 2014)

# New Directions: Hybrid Materials

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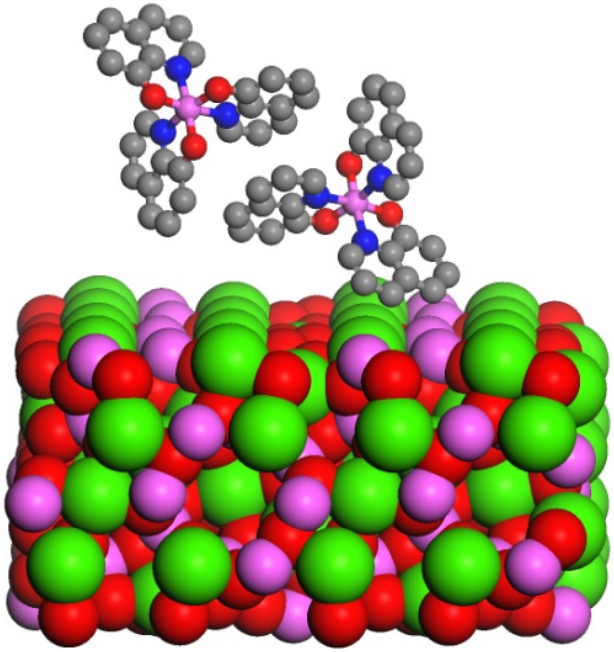
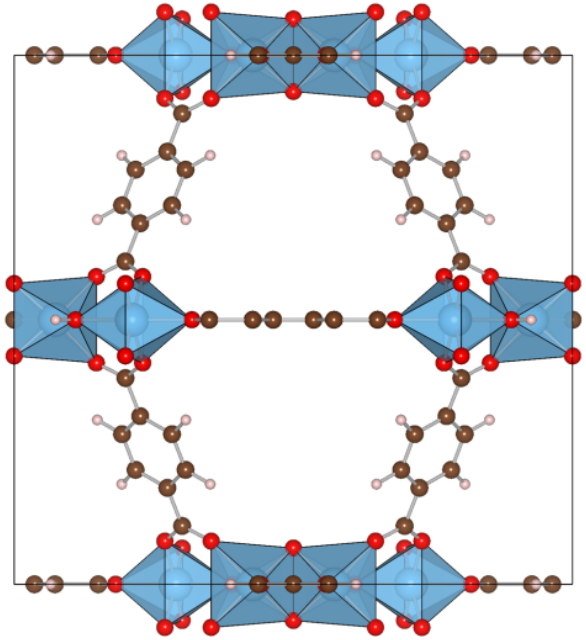
## Functional Organic-Inorganic Systems



**Interfaces**



**Networks**

Funded by ERC Starting Grant (2011 - 2016)

# QM/MM in ChemShell

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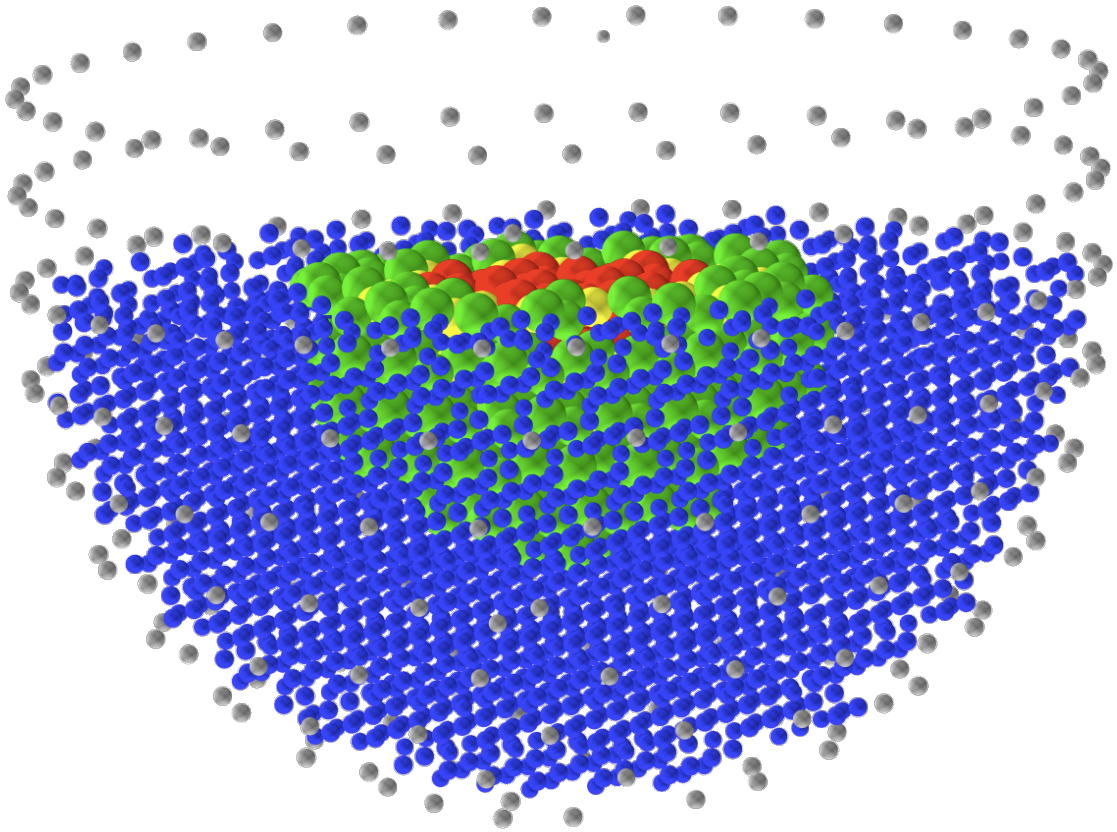
## FHI-AIMS ChemShell Module Under Development

**Elastic & Electrostatic Embedding**

| |
|---|
| QM active site |
| Interface |
| MM active |
| MM frozen |
| Point charges |



# Summary and Advice


Electronic structure methods can be used to provide new insights and directions to a wide range of systems and process with real applications.

## Key rules for sensible thermodynamic quantities:

- Convergence (Electronic, Ionic, Basis Set, *k*-points).
- Conservation of mass.
- Conservation of charge.
- Care with finite size effects (supercells).

## Not mentioned (but equally important):

- Band gaps (errors and corrections).
- Electron localisation (self-interaction).

Slides: http://people.bath.ac.uk/aw558/presentations/2011/