MATERIALS SCIENCE & ENGINEERING

UNIVERSITY OF DELAWARE

Effects of spin-orbit coupling and very large supercells on the description of acceptor states in CdTe

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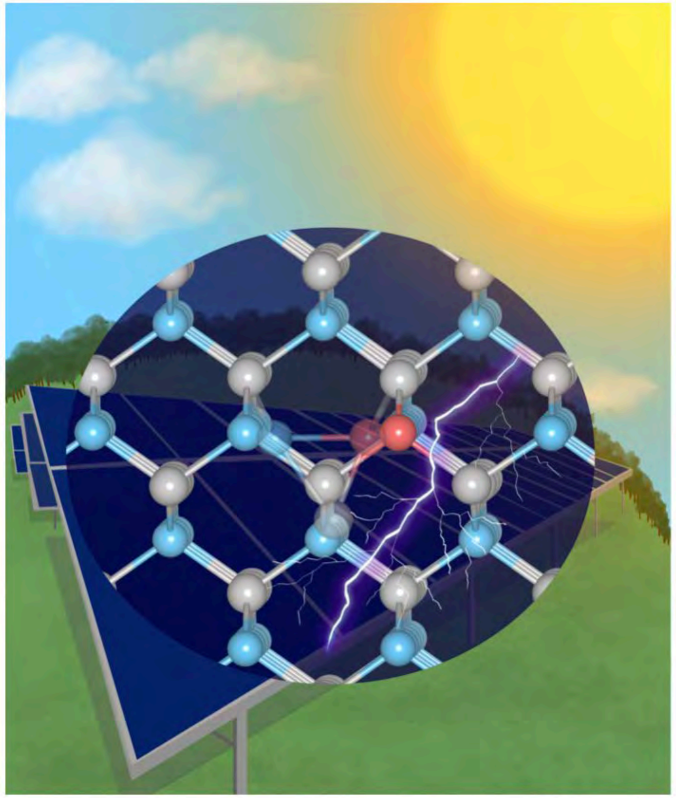

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The 32nd ICDS

International Conference on Defects in Semiconductors

Atlantic Sands Hotel
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September 10-15, 2023

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Topics: Theory and experiments on
Wide-band-gap oxides and nitrides
Quantum defects, qubits, single-photon emitters
Conventional IV-IV, III-V, and II-VI semiconductors
Complex oxide and halide perovskites
Electronics, optoelectronics, photovoltaic, thermoelectric, magnetic, ferroelectric, and spintronic materials, radiation detectors
2D materials
…

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Abstract submission will be open soon

Chairs
Anderson Janotti (U. Delaware)
John Lyons (NRL)

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Ohio State University

Aayush Nahar, Mike Miller, Aaron Arehart

National Renewable Energy Laboratory

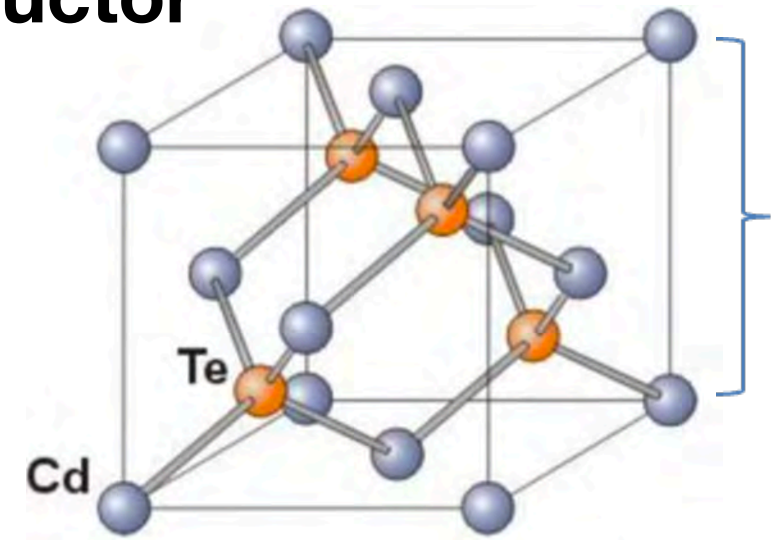
Harvey Guthrey

CdTe semiconductor

member of the II-VI family

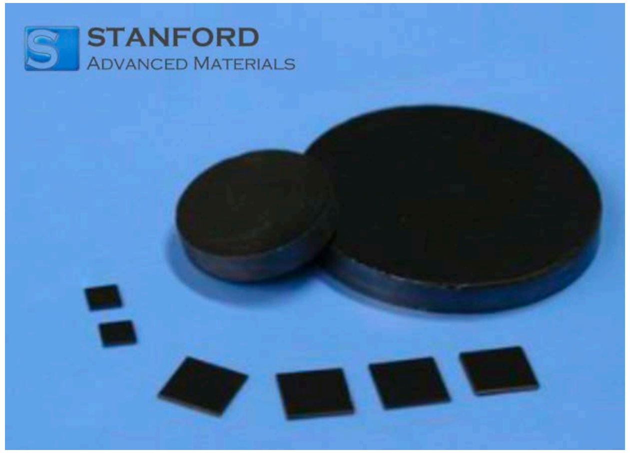
zinc blende crystal structure

direct band gap = 1.5 eV

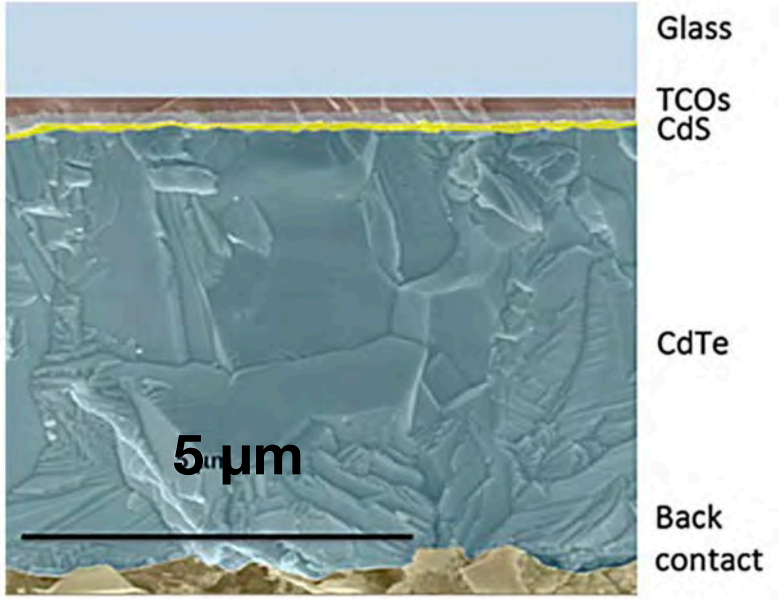


6.481 Å

single crystals



thin films **vapor transport deposition**



Matt Reese (NREL)

Applications:

thin film solar cells

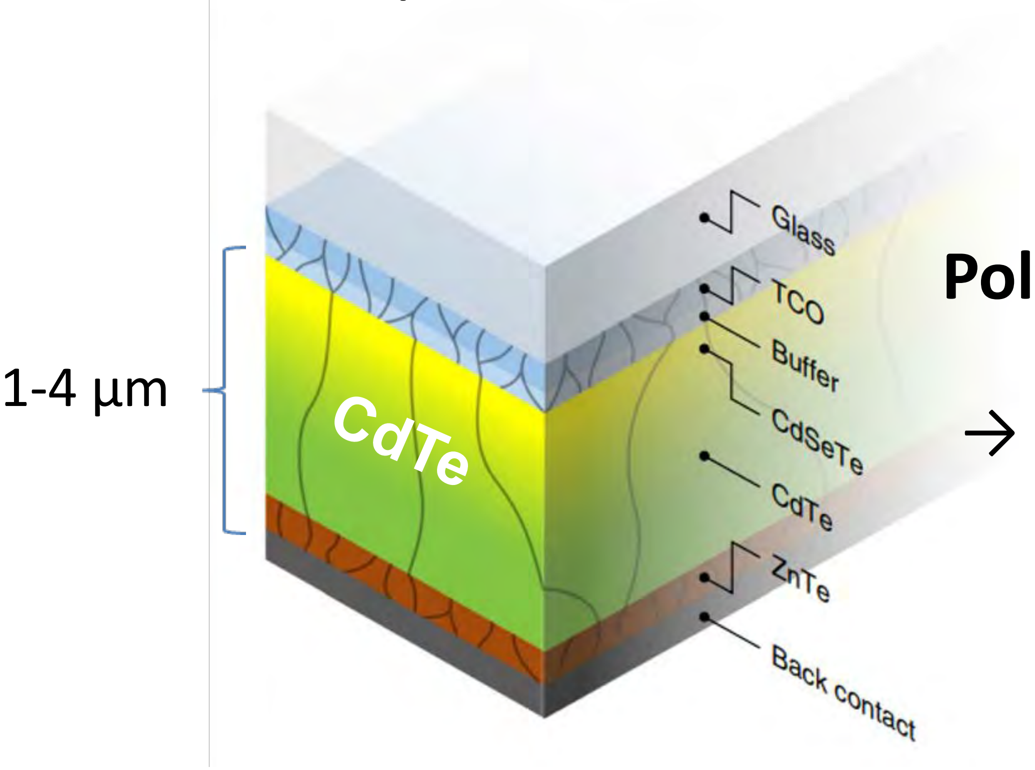
infrared optical windows/lenses

electro-optic modulators

scintillators

CdTe in solar cells

thin-film photovoltaic technology



Metzger *et al.* Nat. Energy **4,** 837 (2019)

Polycrystalline

→ grain boundaries

Commercially available

19.3%
HIGH BIN EFFICIENCY

30YR
LINEAR PERFORMANCE WARRANTY

Series 7

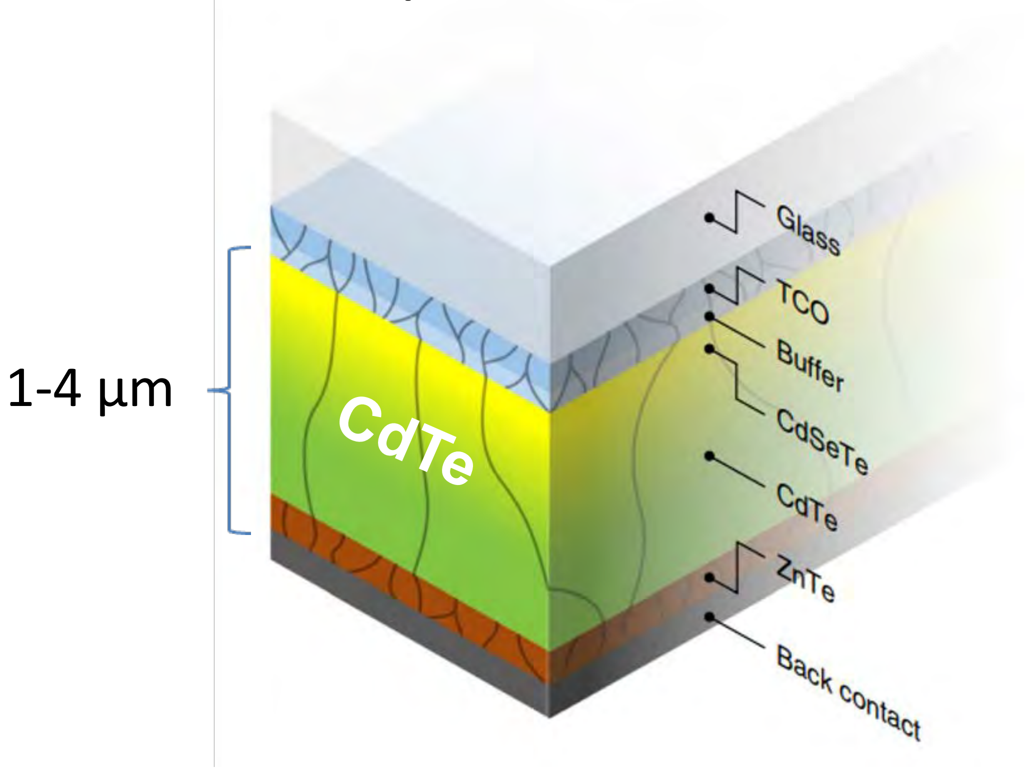
vapor transport deposition
→ low production cost

Made using same process to fabricate modules

record efficiency in the lab cells: 22.3%

CdTe in solar cells

thin-film photovoltaic technology



Metzger *et al.* Nat. Energy **4,** 837 (2019)

Typical minority-carrier device

Current limitations:

- low open-circuit voltage V_{oc} (~0.8-0.9 eV) << E_g (1.5 eV)
- undoped, low hole concentrations ~10^{14} cm^{-3}
- layers doped with As show very low doping efficiency

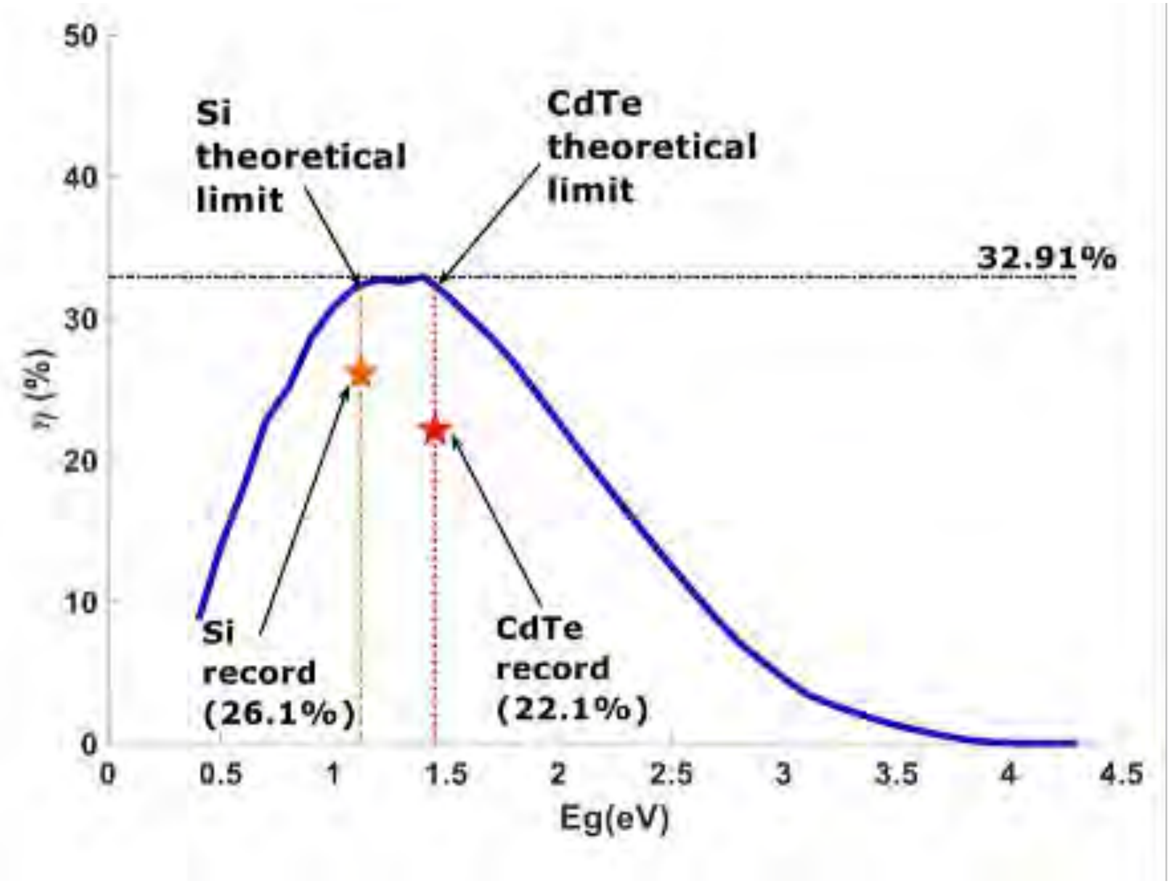
  → [As] ~10^{18} cm^{-3} , [holes] ~10^{16} cm^{-3}
  where do the dopants go?

- short minority carrier lifetimes
- polycrystalline films

  → carrier recombination in the bulk
  and at grain boundaries

CdTe solar cells - room for improvement

Current efficiencies are well below the theoretical limit of 33%



Barbato et. al. J. Phys. D. Appl. Phys. **54**, 333002 (2021)

Device modeling indicate that efficiency of 25% can be achieved if:

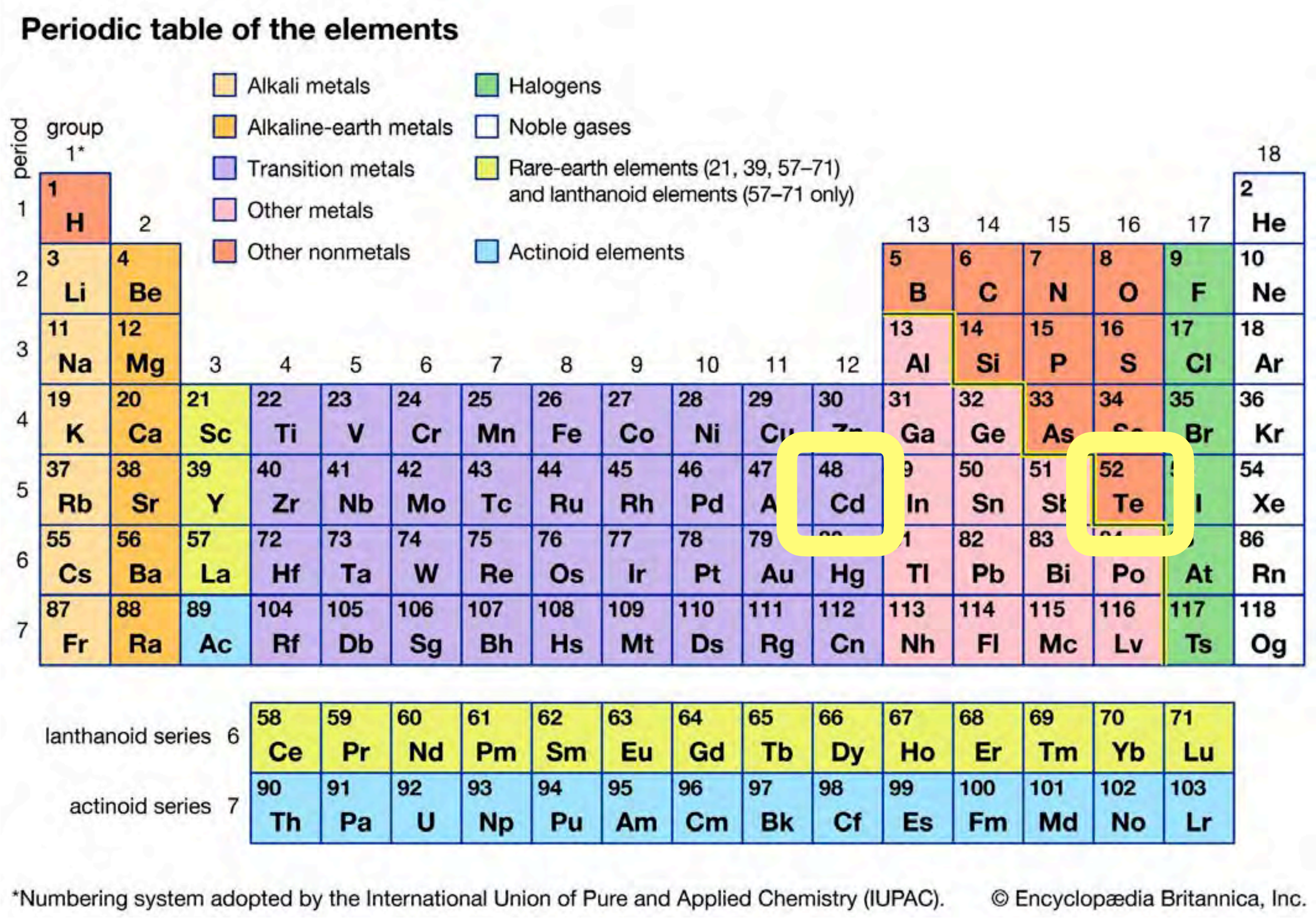
hole concentration > 10^{16} cm^{-3}
while keeping everything else the same

carrier lifetime ≥100 ns,
interface recombination velocity ≤1000 cm/s

Burst *et al.*, Nature Energy **1**, 16015 (2016).

Kanevce, *et al.*, J. Appl. Phys. **121**, 214506 (2017).

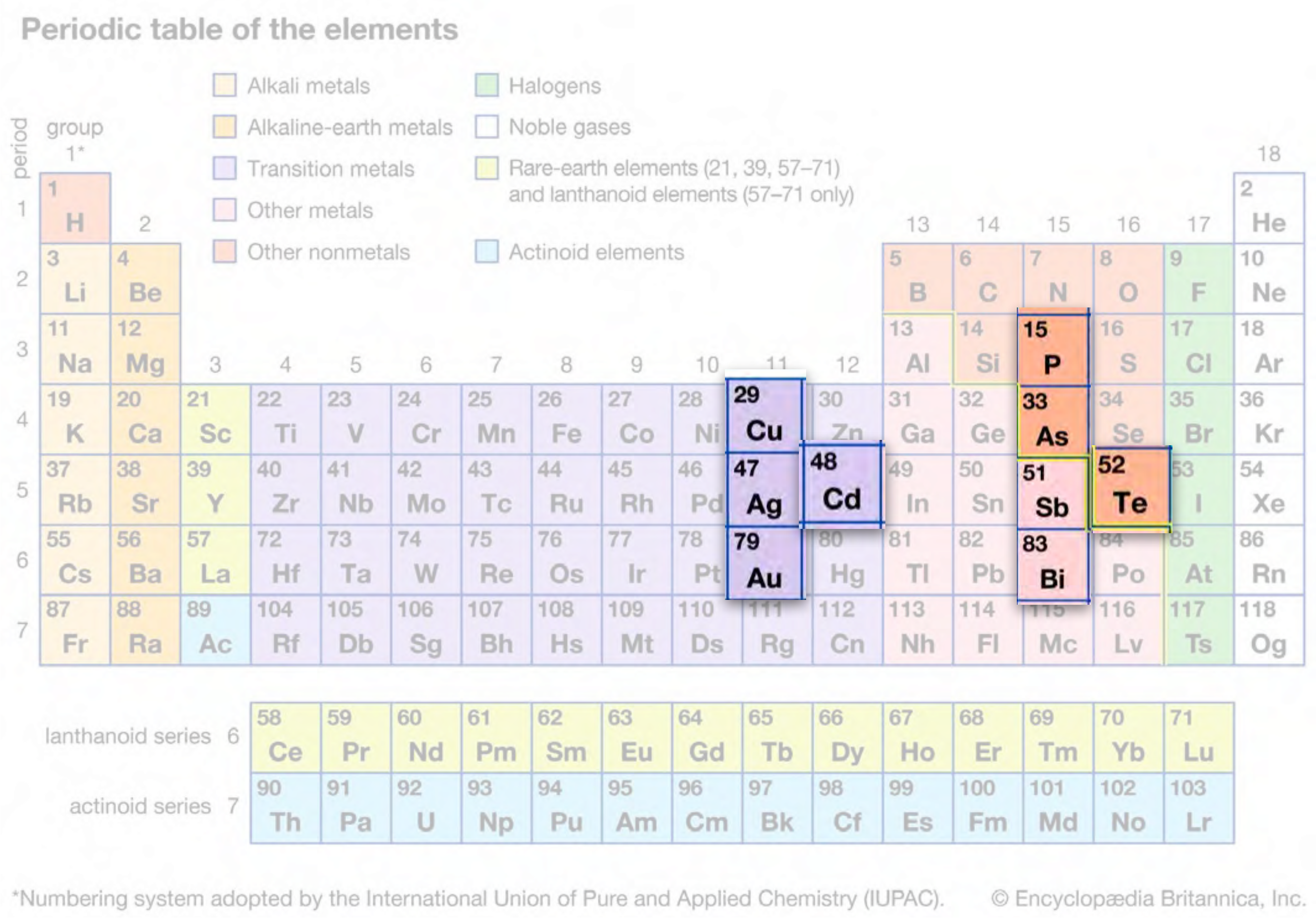
Back to the basics of doping CdTe



For p-type doping:

Look to the left of Cd or Te

Back to the basic aspects of doping CdTe



For p-type doping:

Look to the left of Cd or Te

Try and minimize chemical and size mismatches

Cu, Ag on the Cd site

P, As, or Sb on the Te site

Typical experimental data on doping p-type of CdTe

Cu-doped CdTe absorber layers < 10^{15} cm^{-3}

+ stability issues → Cu interstitials are highly mobile

Corwine *et al.*, *Sol. Energy Mater. Sol. Cells* 82, 481 (2004)

Grecu, *et al.*, *J. Appl. Phys.* 88, 2490 (2000)

Burst *et al.*, *APL Mater.* 4, 116102 (2016)

As, P, Sb doping: 10^{15} - 10^{16} holes/cm^{-3}

very low doping efficiency, [free carrier] << [dopant]

highly compensated

+ short carrier lifetimes

McCandless et al.," *IEEE J. Photovolt.* 9, 912 (2019)

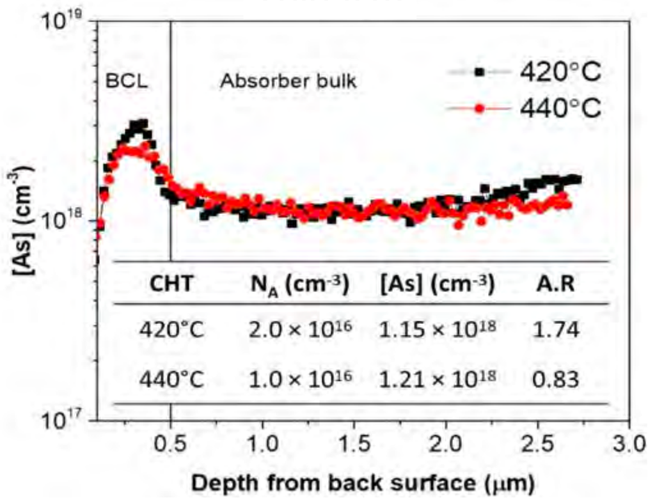
Metzger et al., *Nature Energy*, 4 837 (2019)

Kartopuetal., *Sol. Energy Mater. Sol. Cells* 194, 259 (2019)

Source of compensation unknown!

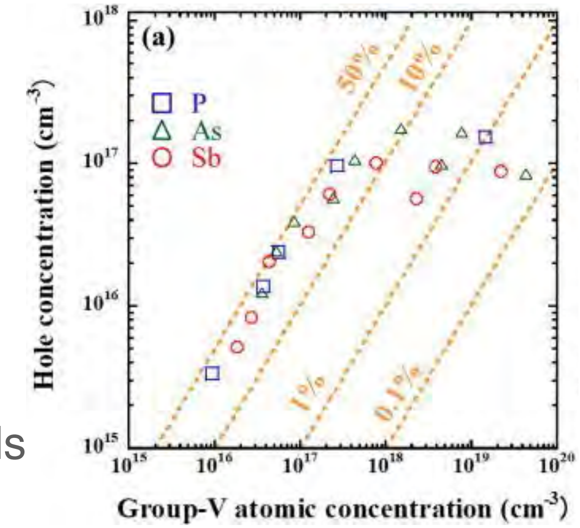
Dopants in the grain boundaries?

Thin film



Oklobia *et. al.* IEEE J. Photovolt. **12**, 1296 (2022)

Single crystals



Nagaoka *et. al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Sb, As and P doping in CdTe single crystals

Temperature dependent Hall data

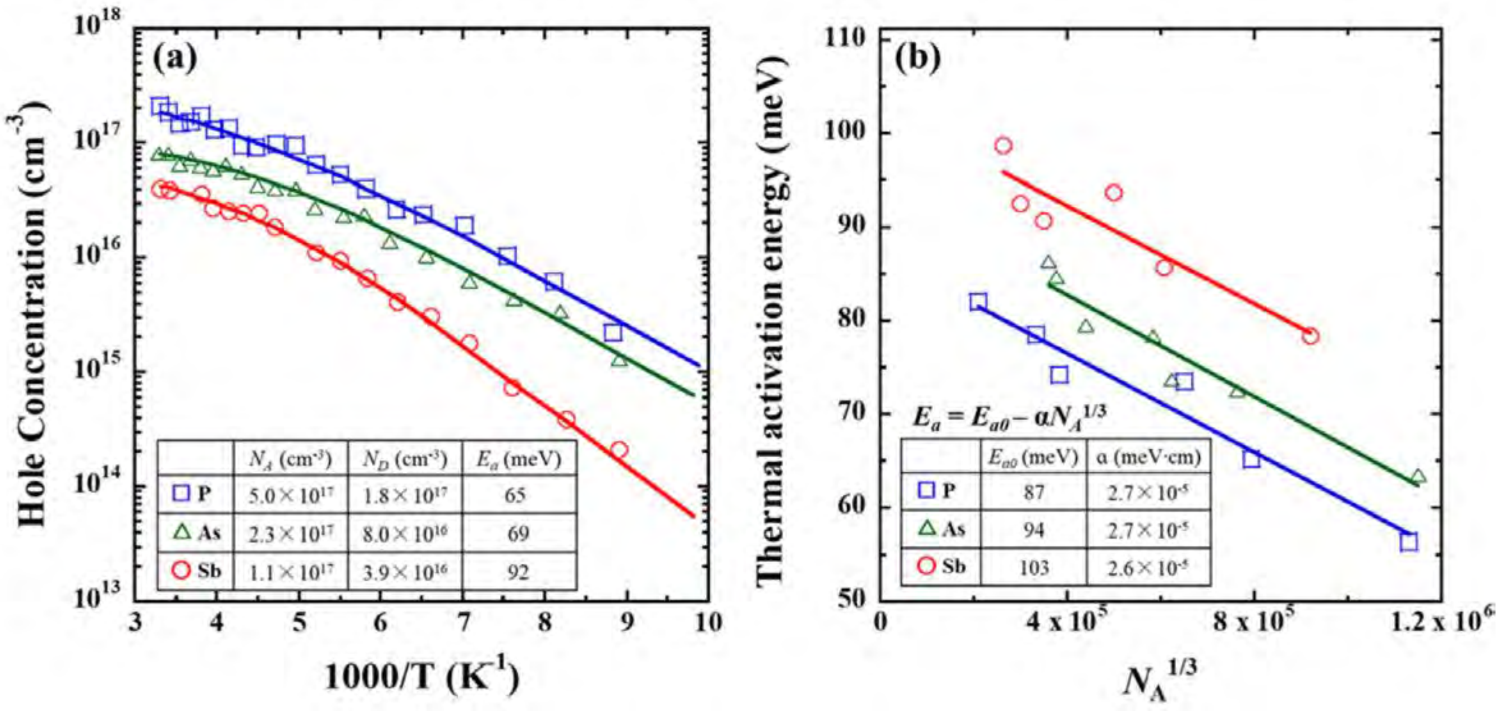
Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Partially compensated acceptors

$$p = -A + \sqrt{A^2 + \frac{N_V}{2}(N_A - N_D)\exp\left(-\frac{E_a}{k_B T}\right)}$$

$$A = \frac{1}{2}\left[N_D + \frac{N_V}{2}\exp\left(-\frac{E_a}{k_B T}\right)\right]$$

Blakemore, Semiconductor statistics (Courier Corp.,2002)



Data fit to obtain E_a, N_A,....

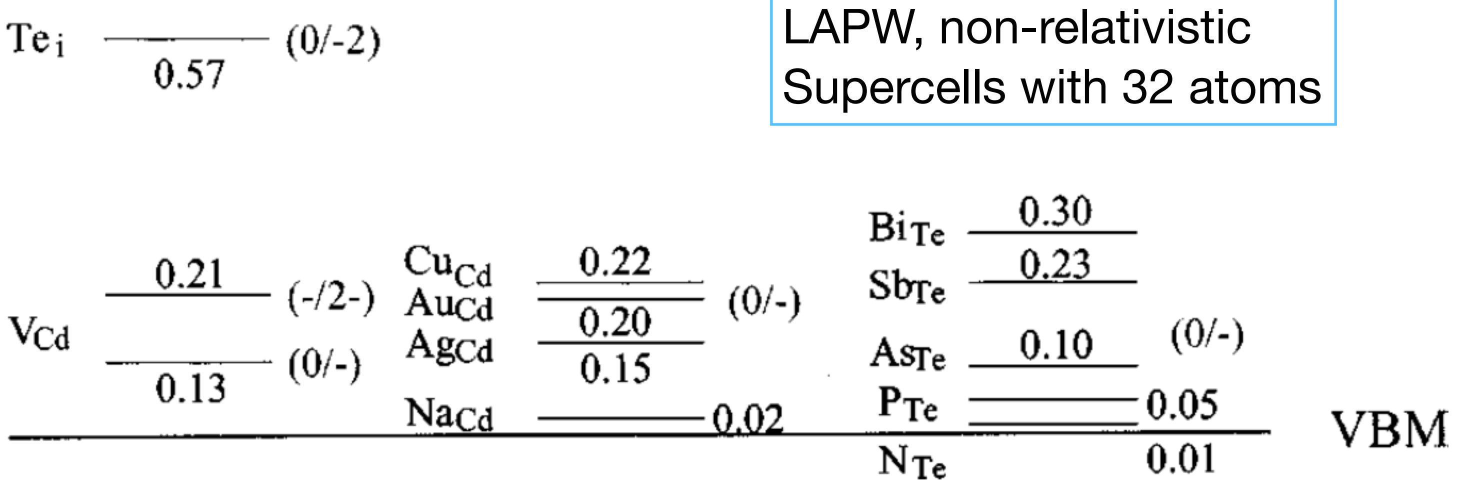
	N_A (cm^{-3})	N_D (cm^{-3})	E_a (meV)
□ P	5.0×10^{17}	1.8×10^{17}	65
△ As	2.3×10^{17}	8.0×10^{16}	69
○ Sb	1.1×10^{17}	3.9×10^{16}	92

$$E_a = E_{a0} - \alpha N_A^{1/3}$$

	E_{a0} (meV)	α (meV·cm)
□ P	87	2.7×10^{-5}
△ As	94	2.7×10^{-5}
○ Sb	103	2.6×10^{-5}

dilute limit

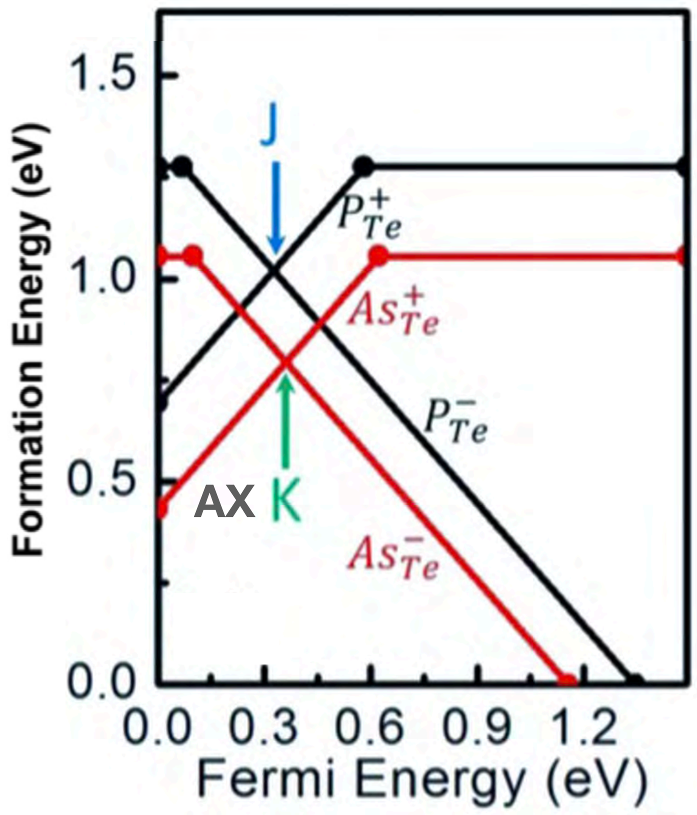
What do we know about acceptor impurities in CdTe from theory



DFT-LDA
LAPW, non-relativistic
Supercells with 32 atoms

Wei and Zhang, Phys. Rev. B **66**, 155211 (2002)

HSE06 hybrid functional
Supercell 64 atoms
no spin-orbit



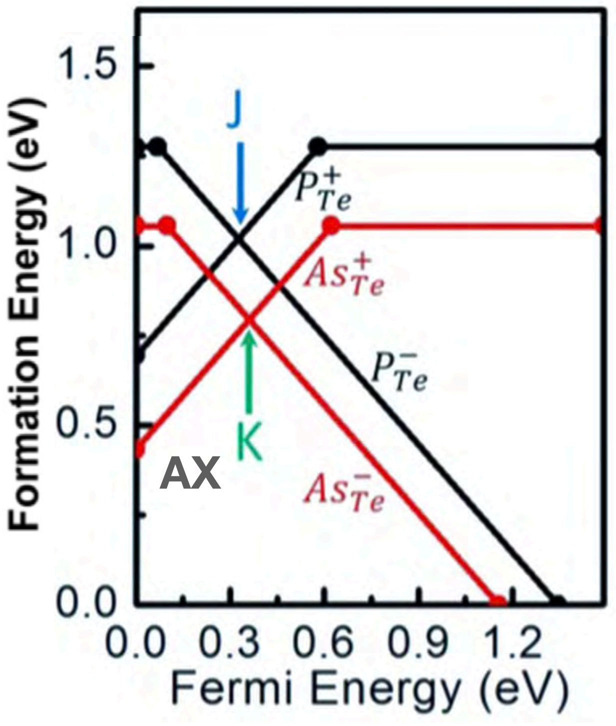
P and As are shallow acceptors
Self-compensation by AX centers
Fermi level pinned in the gap
negligible hole concentration

Yang *et. al.*, Semicond. Sci. Technol. **31**, 083002 (2016)

These predictions indicate that it Would be impossible to make CdTe p-type with As or P

What do we know about acceptor impurities in CdTe from theory

HSE06 hybrid functional
Supercell 64 atoms
no spin-orbit

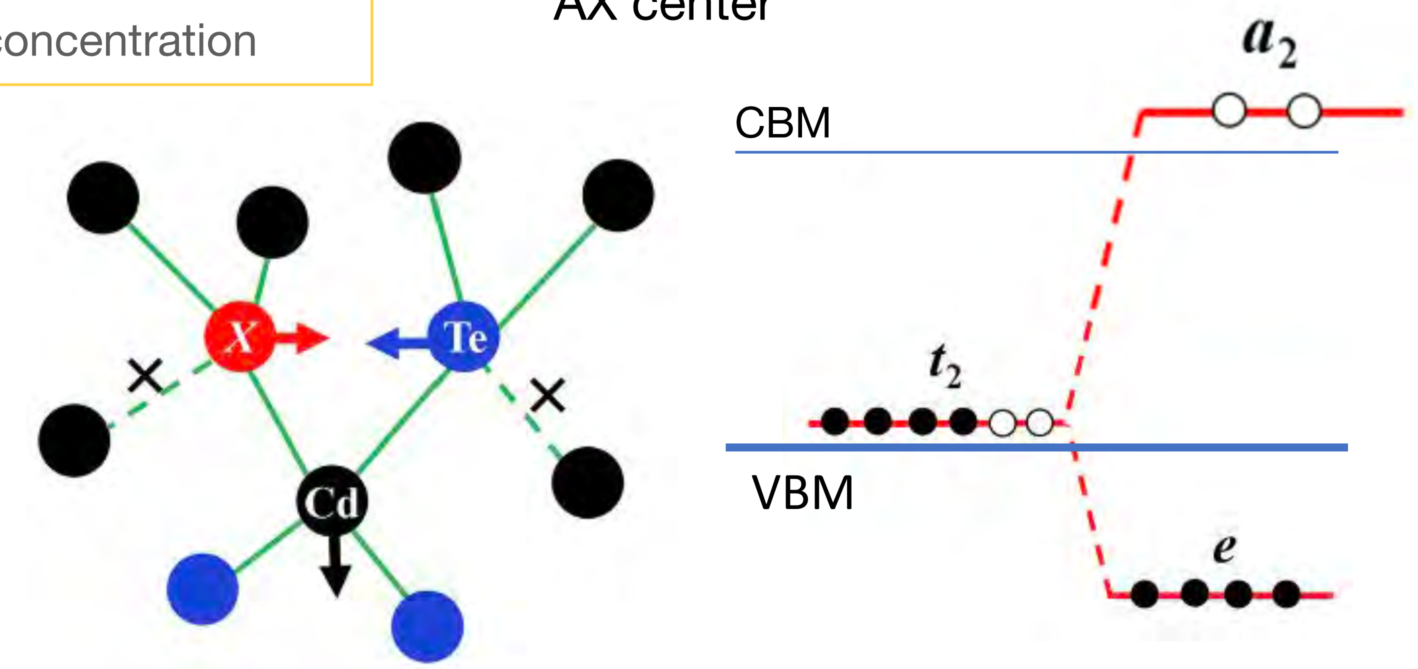


Yang *et. al.*, Semicond. Sci. Technol. **31**, 083002 (2016)

P and As are shallow acceptors
Self-compensation by AX centers
Fermi level pinned in the gap
negligible hole concentration

Chadi, Phys. Rev. B **59**, 15181 (1999)

AX center

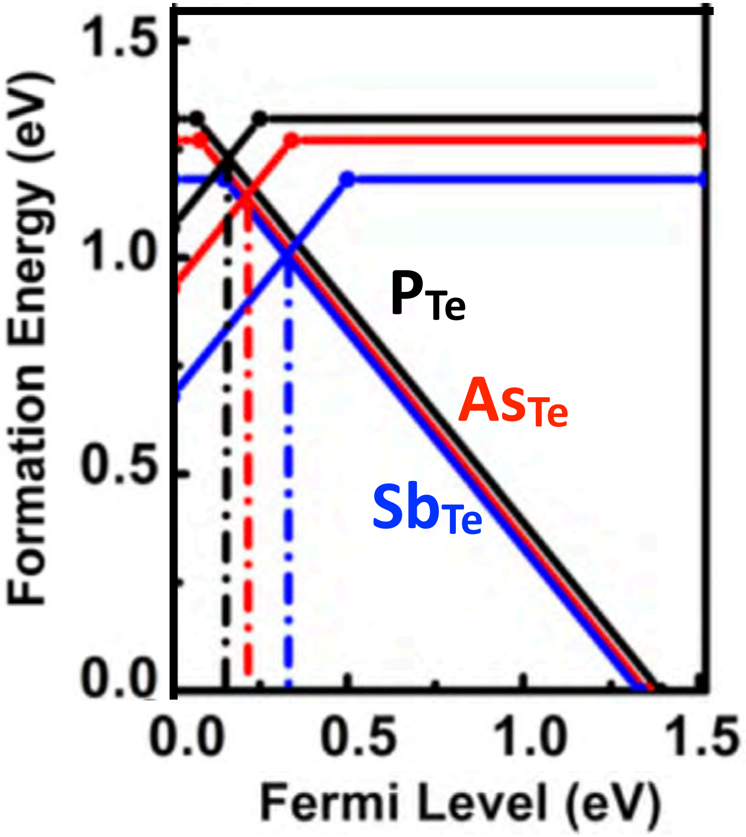


Large local lattice relaxation

Breaking two bonds and forming a X_{Te}-Te bond

What do we know about acceptor impurities in CdTe from theory

HSE06 hybrid functional
Supercell 216 atoms
no spin-orbit



(0/-) transition levels

P	**70 meV**
As	**80 meV**
Sb	**150 meV**

Fermi level pinned at the (+/-) level
→ negligible hole concentration
→ full self-compensation by AX centers

Had to use arguments based nonequilibrium
or kinetics to explain observed hole concentrations

Dou *et. al.*, Phys. Rev. Appl. **15**, 054045 (2021)

Te is a heavy atom → large splitting at the top of the valence band expected due to spin-orbit coupling

What are the effect of SOC?

band structure → push up the valence-band maximum (VBM)

defect levels

defect formation energies

Acceptor ionization energies and dependence on the supercell size

Stability of the AX centers

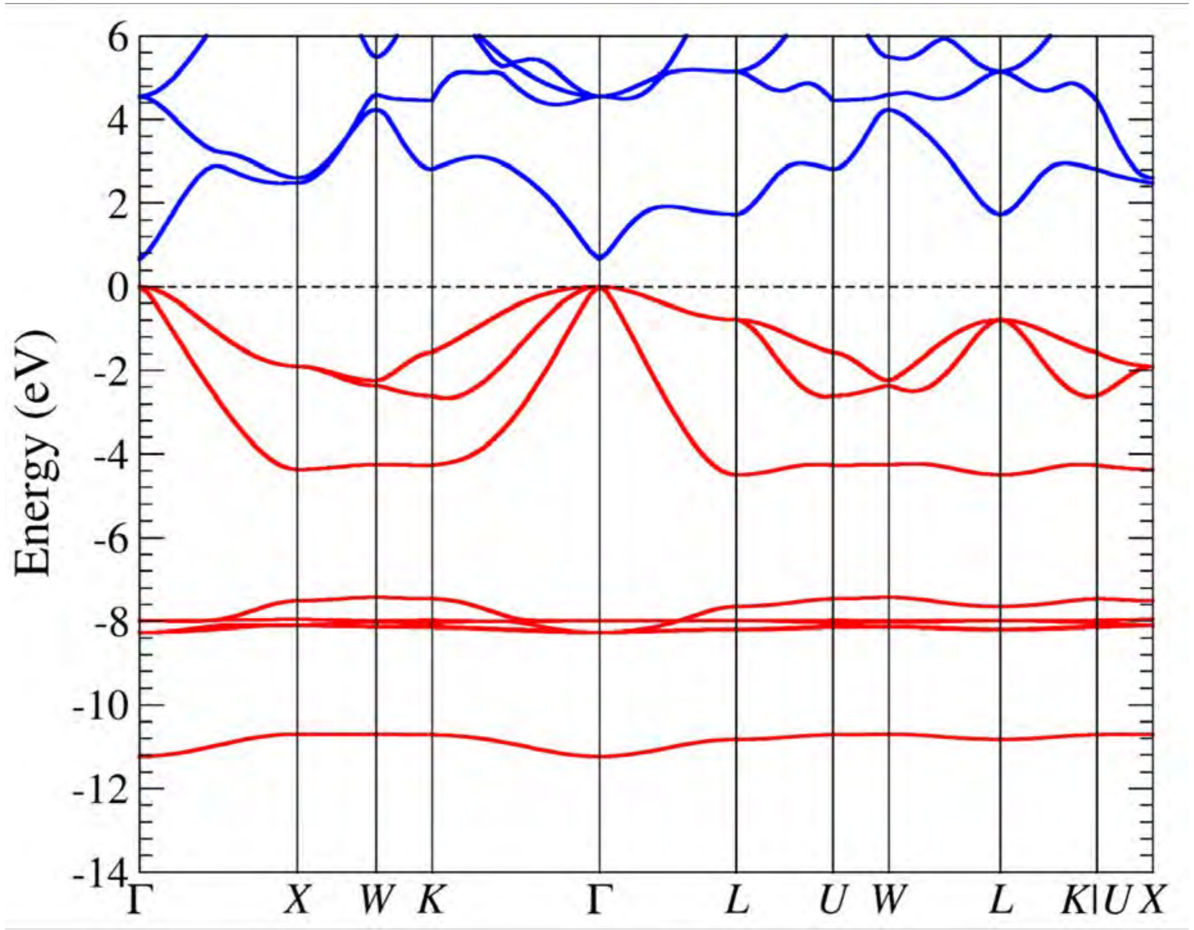
CdTe basic properties, different functionals

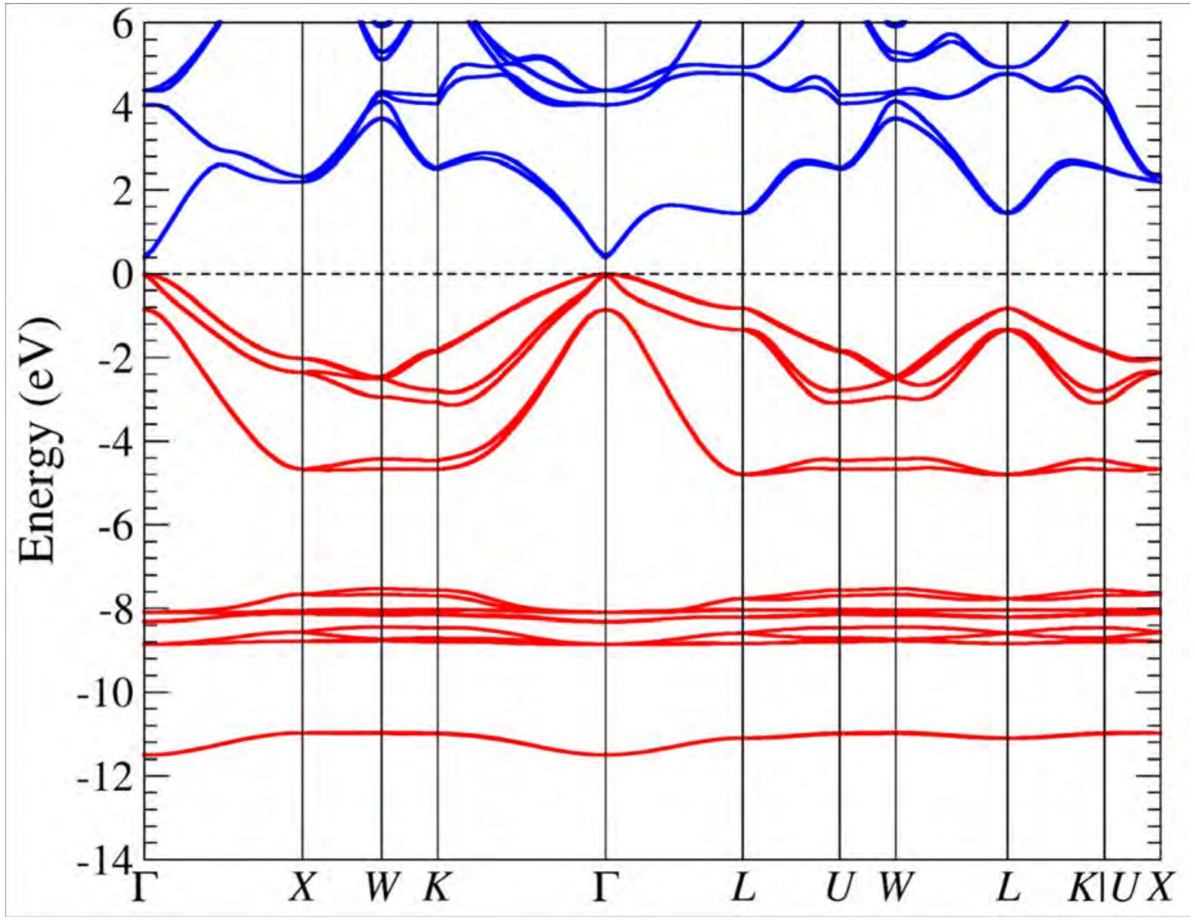
	PBEsol		HSE06		HSE(0.33)		Exp.
	no SOC	with SOC	no SOC	with SOC	no SOC	with SOC	
a (Å)	6.471		6.569		6.545		6.481
E_g (eV)	0.667	0.397	1.500	1.197	1.814	1.502	1.513 (T=300K)
ΔH_f (eV)	0.759		1.147		1.307		-0.96 -1.17

Sirdeshmukh *et al.*, Cryst. Res. Technol. **28**, 15 (1993)
Fonthal *et al.,* J. Phys. Chem. Solids **61**, 579 (2000)
Dean, Lange's Handbook of Chemistry (McGraw–Hill, New York, 1999)
Yamaguchi *et al.,* Materials transactions, JIM **41**, 790 (2000)

CdTe electronic structure, with and without SOC

DFT-GGA (PBEsol) with SOC



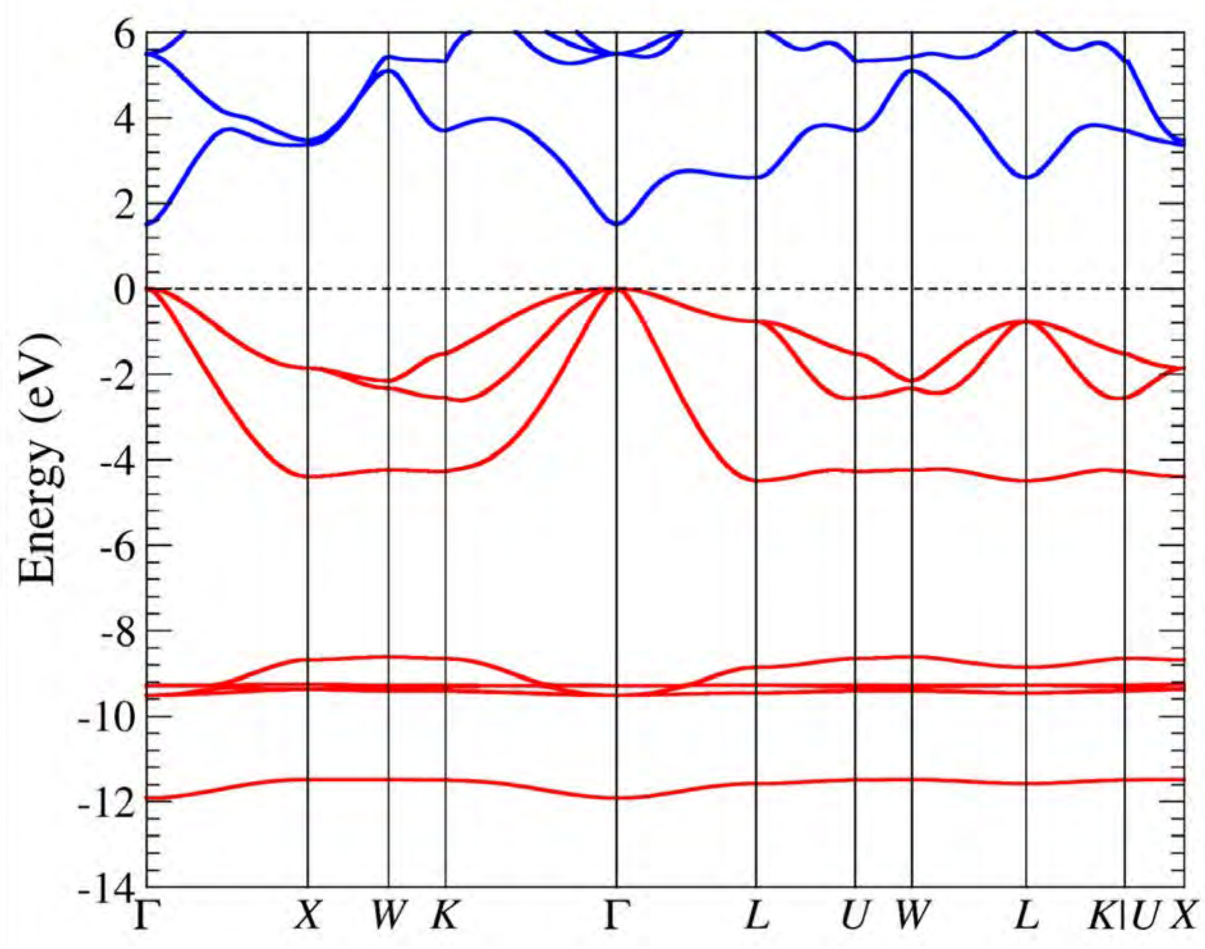


Band gap = 0.667 eV

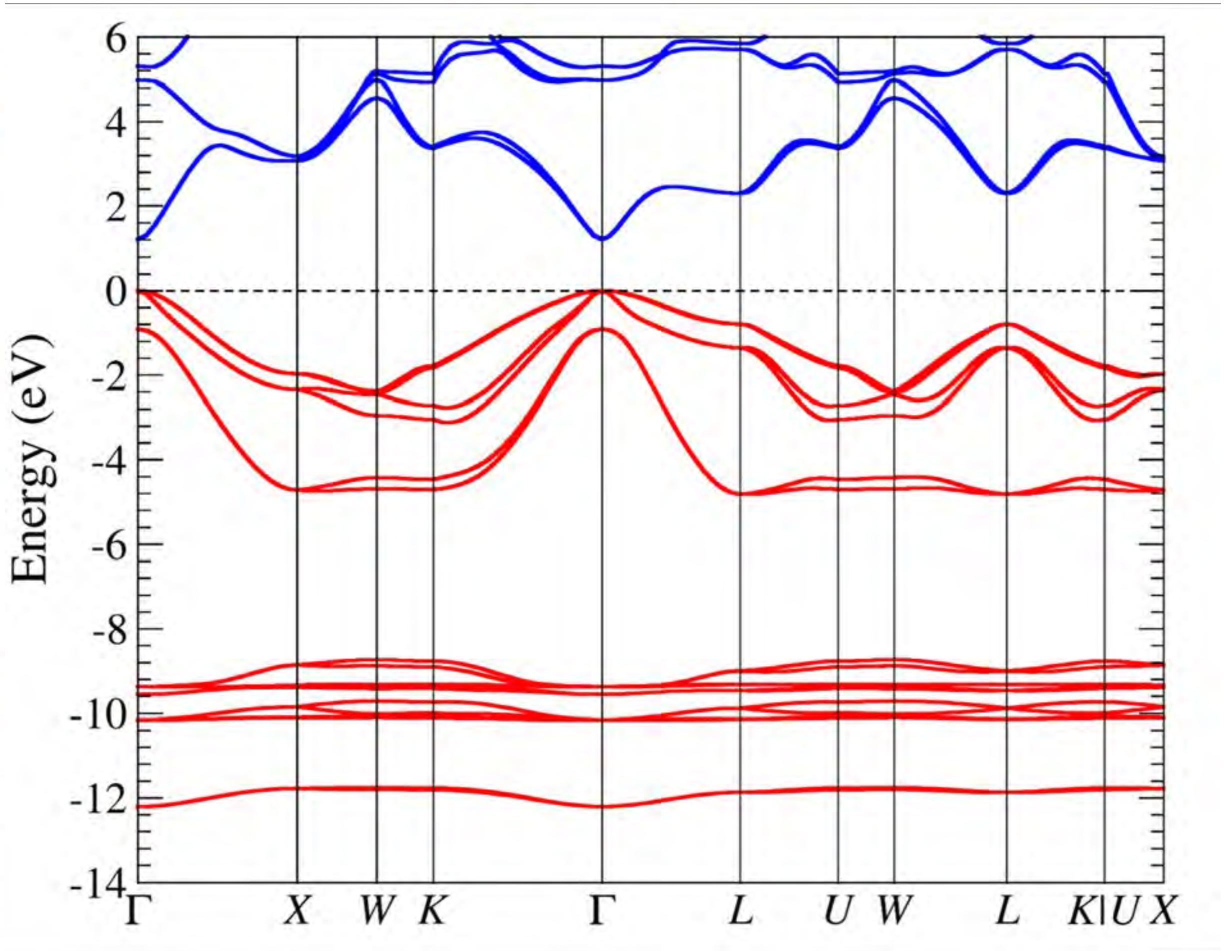
Band gap = 0.397 eV

CdTe electronic structure, with and without SOC

HSE06 with SOC



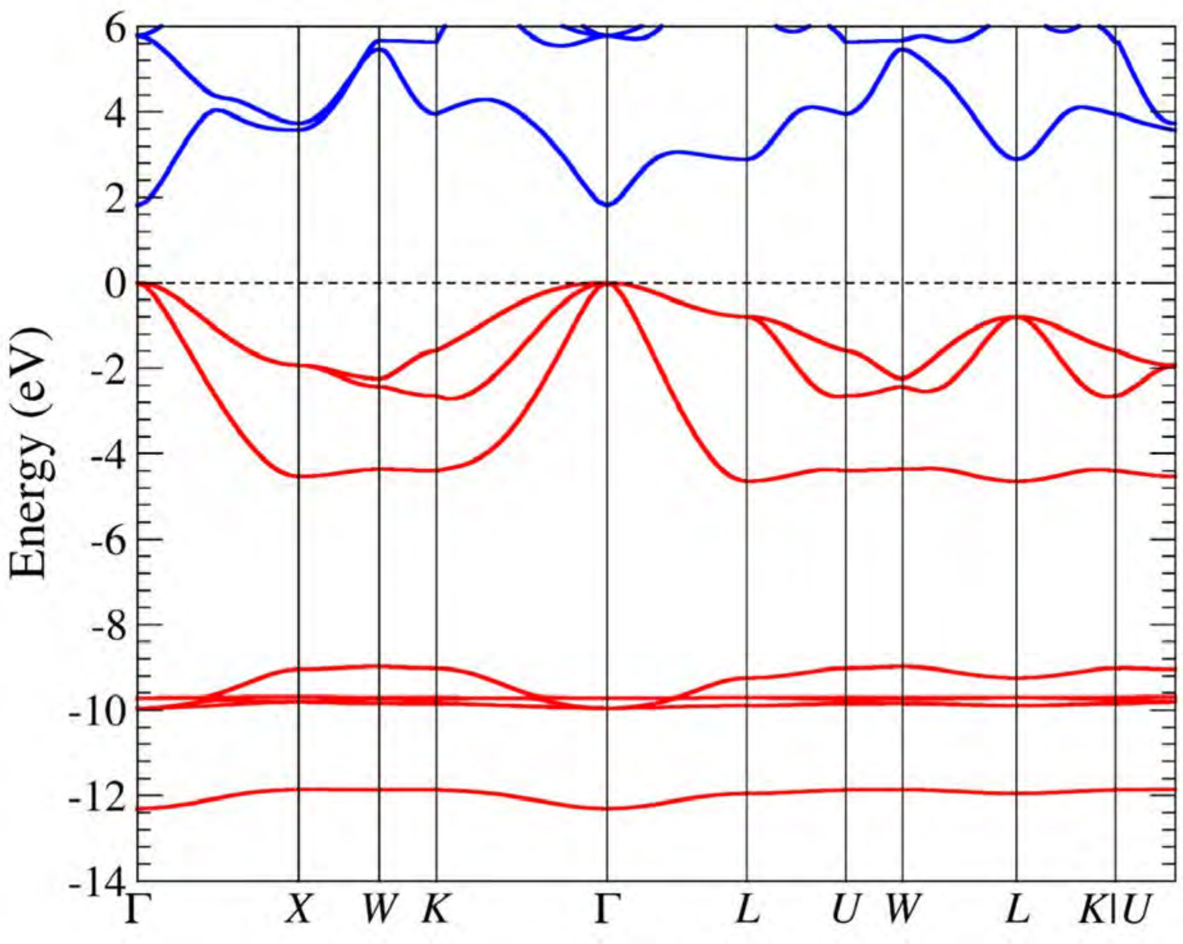
Band gap = 1.500 eV

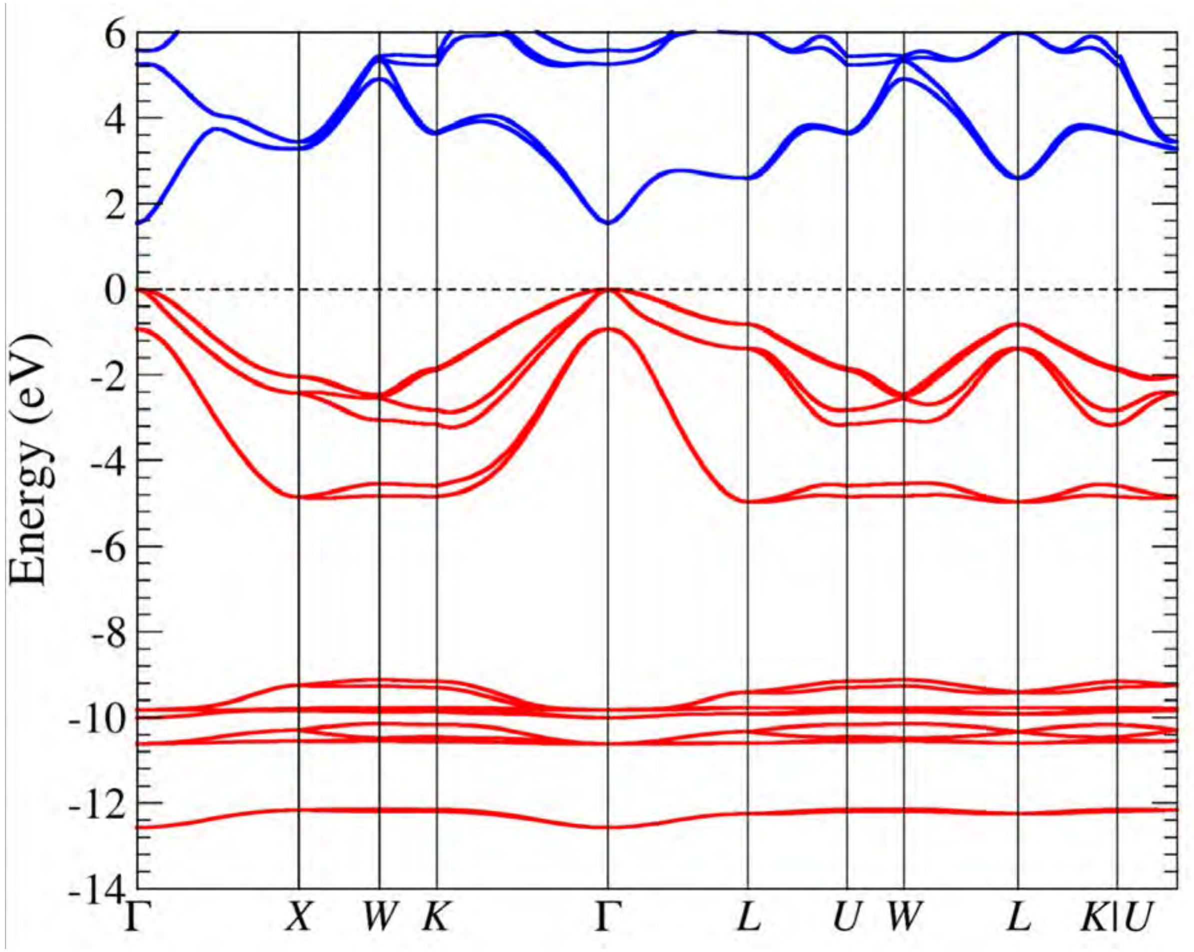


Band gap = 1.197 eV

CdTe electronic structure, with and without SOC

HSE 33% mixing with SOC



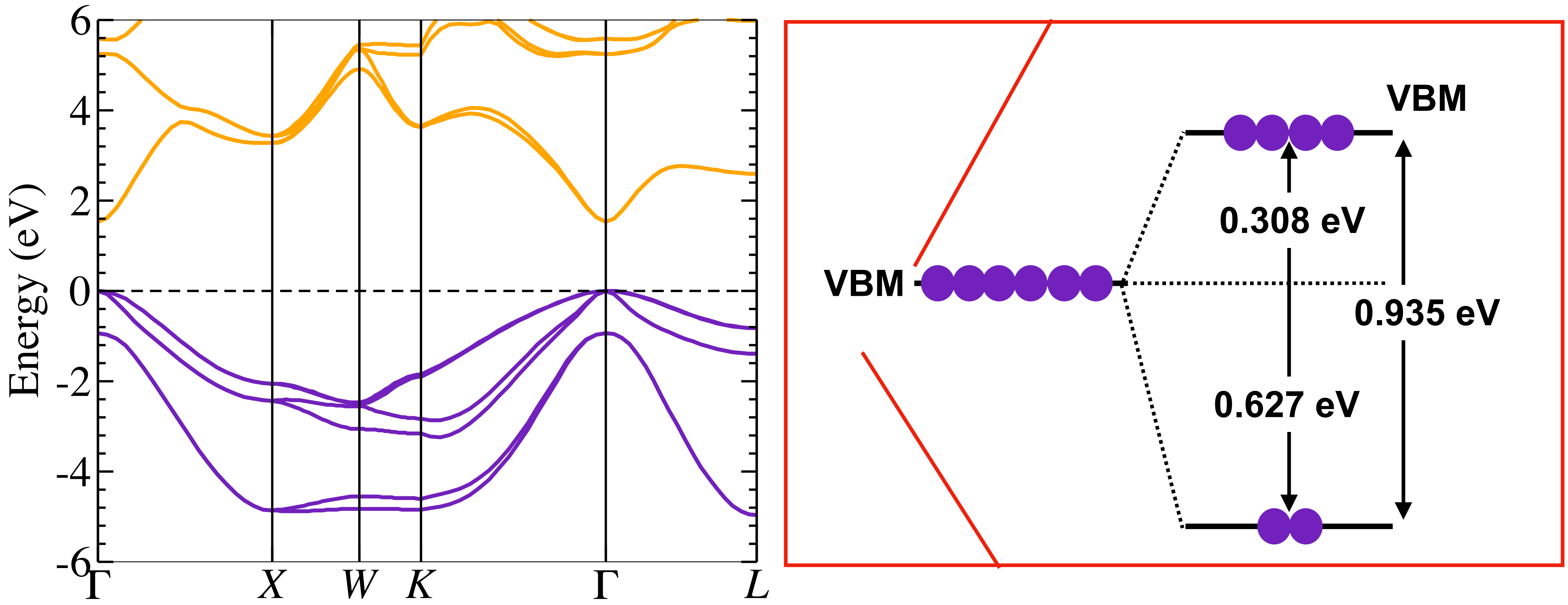


Band gap = 1.814 eV

Band gap = 1.502 eV

CdTe electronic structure HSE $\alpha = 0.33$

spin-orbit splitting



see also Pan *et al.*, Phys. Rev. B **98** 054108 (2018)

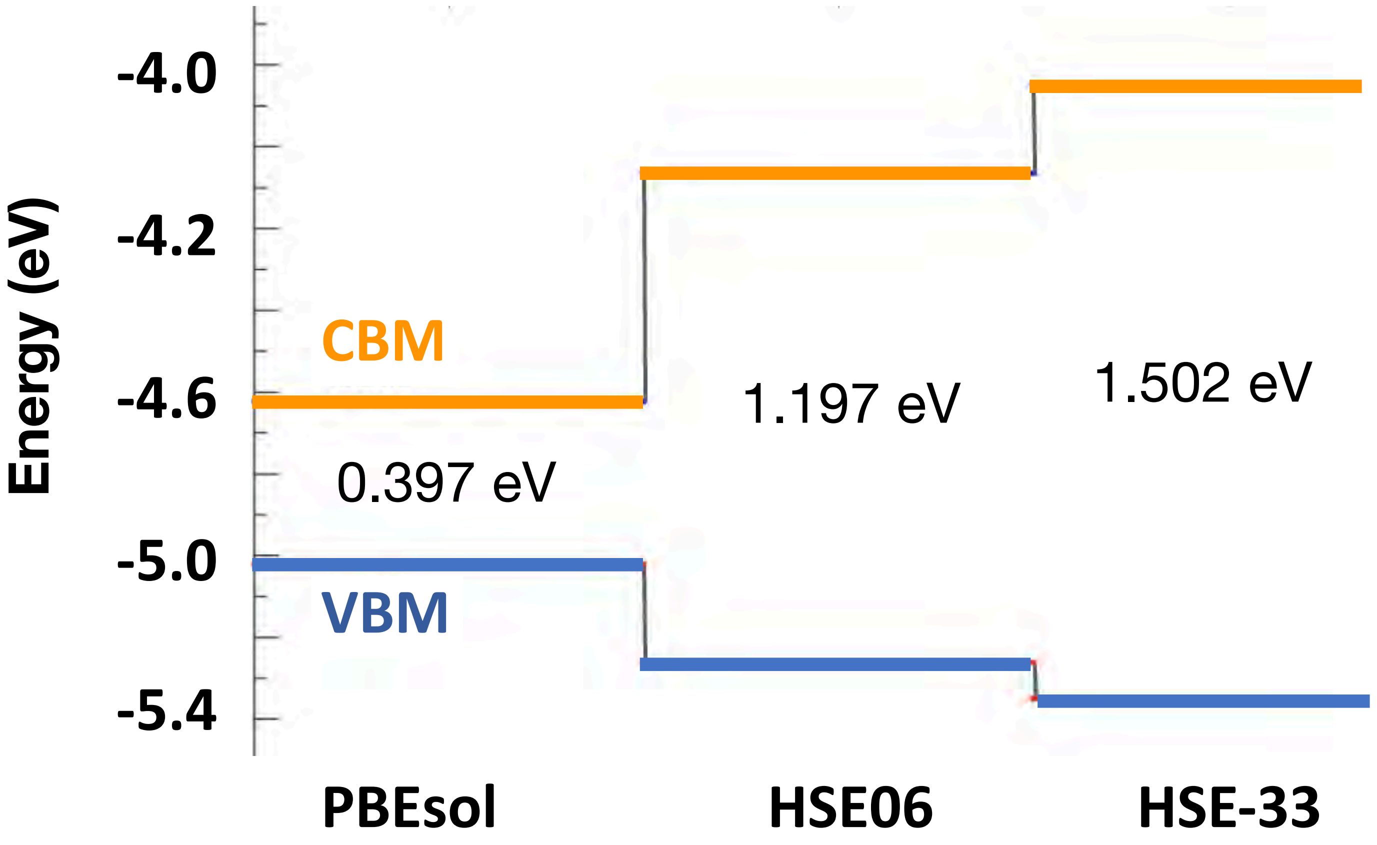
CdTe effective masses HSE $\alpha = 0.33$

	PBEsol		HSE06		HSE(0.33)		Exp.
Effective mass	no SOC	with SOC	no SOC	with SOC	no SOC	with SOC	
[100] G-X	m_{hh}= 0.504 m_{lh}= 0.064 m_e= 0.063	m_{hh}= 0.440 m_{lh}= 0.060 m_{sp}= 0.246 m_e= 0.053	m_{hh}= 0.533 m_{lh}= 0.103 m_e= 0.100	m_{hh}= 0.474 m_{lh}= 0.113 m_{sp}= 0.307 m_e= 0.094	m_{hh}= 0.522 m_{lh}= 0.113 m_e= 0.110	m_{hh}= 0.471 m_{lh}= 0.129 m_{sp}= 0.321 m_e= 0.106	m_{hh}= 0.72 m_{lh}= 0.1 m_e= 0.094
[110] G-K	m_{hh}=2.586,0.502 m_{lh}=0.060 m_e=0.065	m_{hh}= 0.797 m_{lh}= 0.060 m_{sp}= 0.243 m_e= 0.055	m_{hh}= 2.581,0.530 m_{lh}= 0.090 m_e= 0.102	m_{hh}= 0.865 m_{lh}= 0.105 m_{sp}= 0.303 m_e= 0.096	m_{hh}=2.612,0.520 m_{lh}=0.097 m_e=0.111	m_{hh}=0.860 m_{lh}=0.117 m_{sp}=0.317 m_e=0.108	m_{hh}= 0.81 m_{lh}= 0.12 m_e= 0.096
[111] G-L	m_{hh}= 1.083 m_{lh}= 0.056 m_e= 0.062	m_{hh}= 1.112 m_{lh}= 0.055 m_{sp}= 0.244 m_e= 0.051	m_{hh}= 1.132 m_{lh}= 0.085 m_e= 0.100	m_{hh}= 1.024 m_{lh}= 0.101 m_{sp}= 0.304 m_e= 0.094	m_{hh}= 1.127 m_{lh}= 0.092 m_e= 0.110	m_{hh}= 1.191 m_{lh}= 0.111 m_{sp}= 0.320 m_e= 0.106	m_e= 0.095
ionization potential (eV)	-5.022		-5.261		-5.350		-5.6, -5.8

HSE-33% improves the description of effective masses and ionization potential

CdTe ionization potential

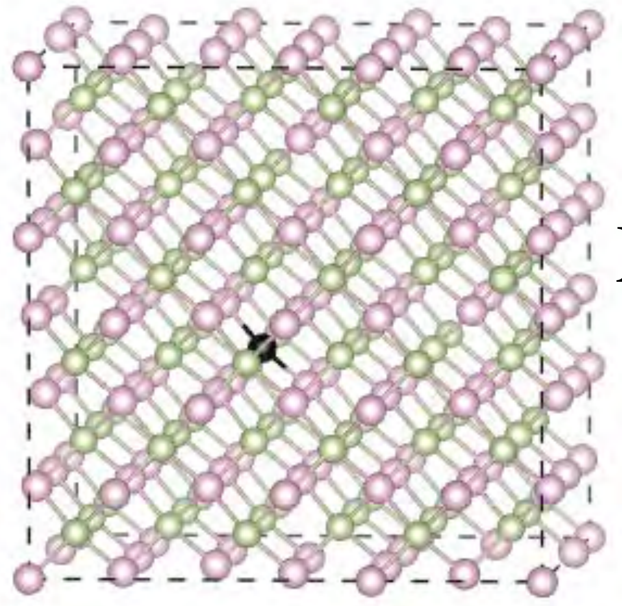
different functionals



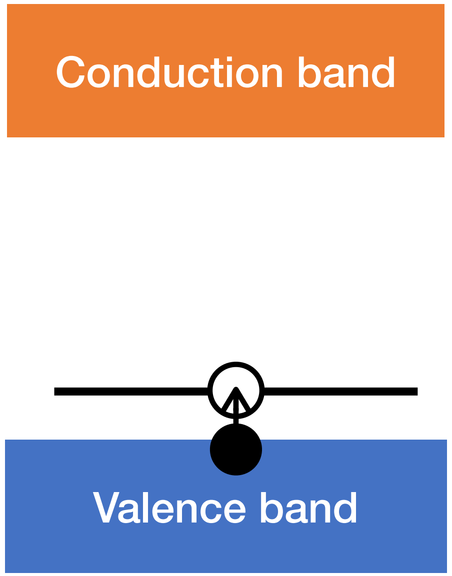
affects both valence and conduction band, almost equally

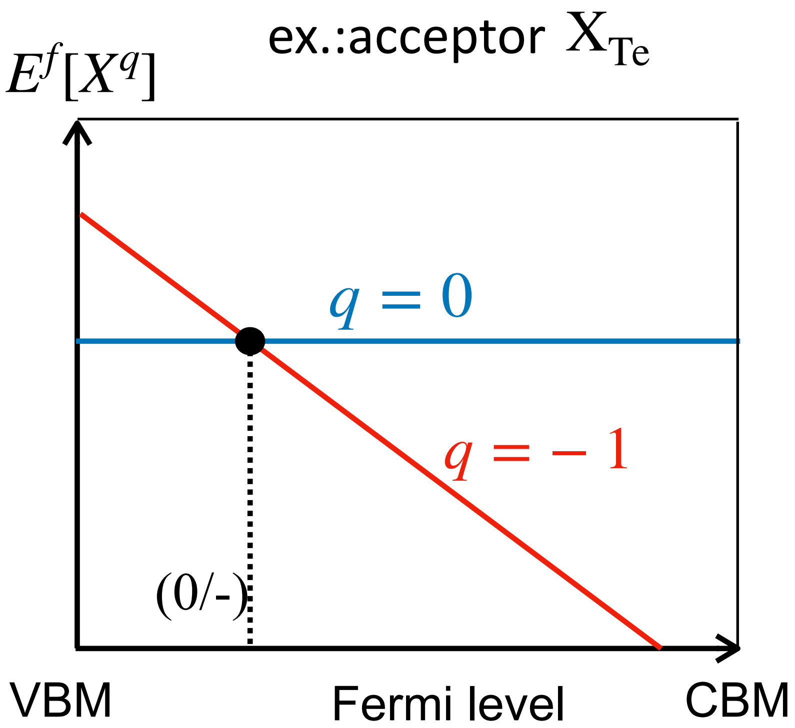
Dopant/defect formation energy and transition level

supercell
with dopant



X_{Te}



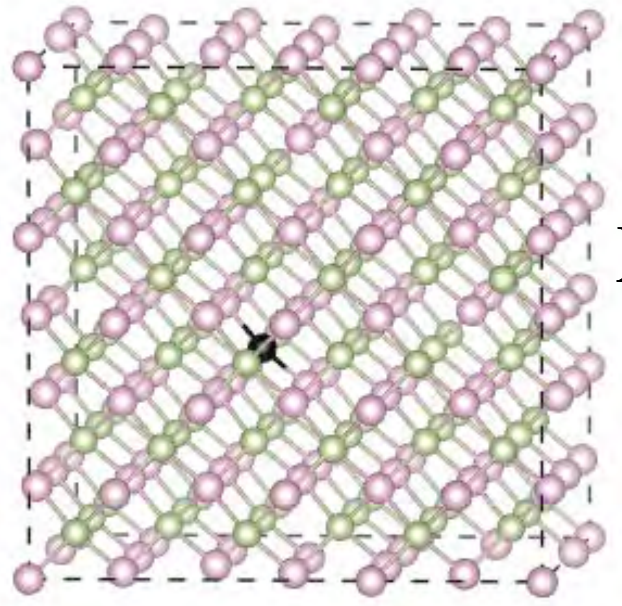


$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[bulk] + \sum_i n_i \mu_i + q(\varepsilon_f + E_{VBM}) + \Delta^q$$

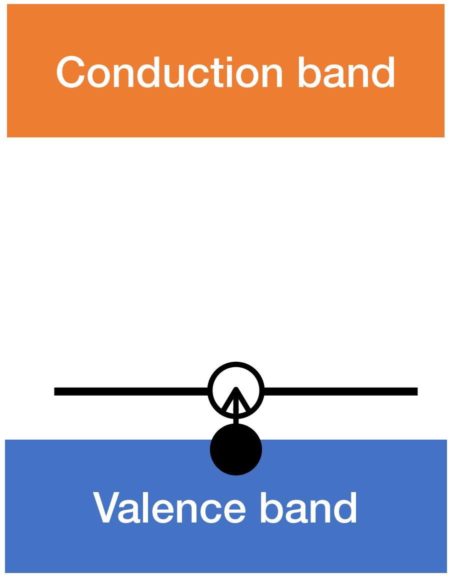
Freysoldt *et. at.*, Rev. Mod. Phys. **86**, 253 (2014)

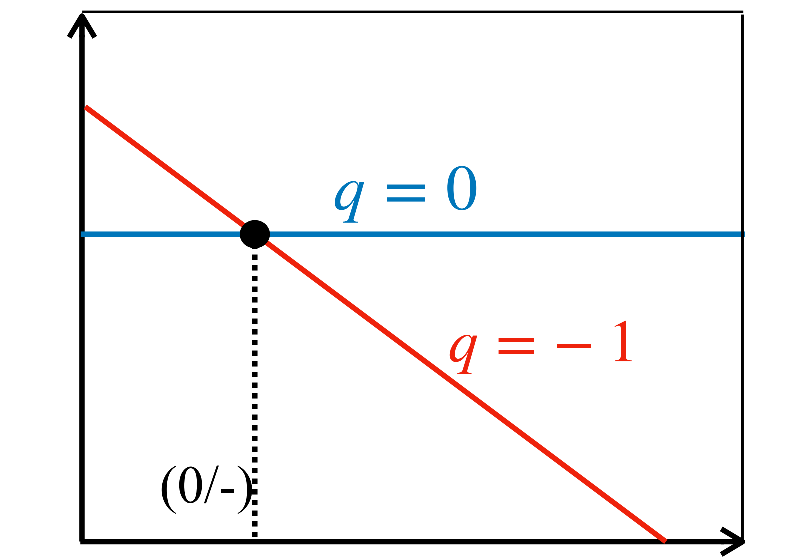
Dopant/defect formation energy and transition level

supercell
with dopant



$\mathrm{X_{Te}}$





$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[bulk] + \sum_i n_i \mu_i + q(\varepsilon_f + E_{VBM}) + \Delta^q$$

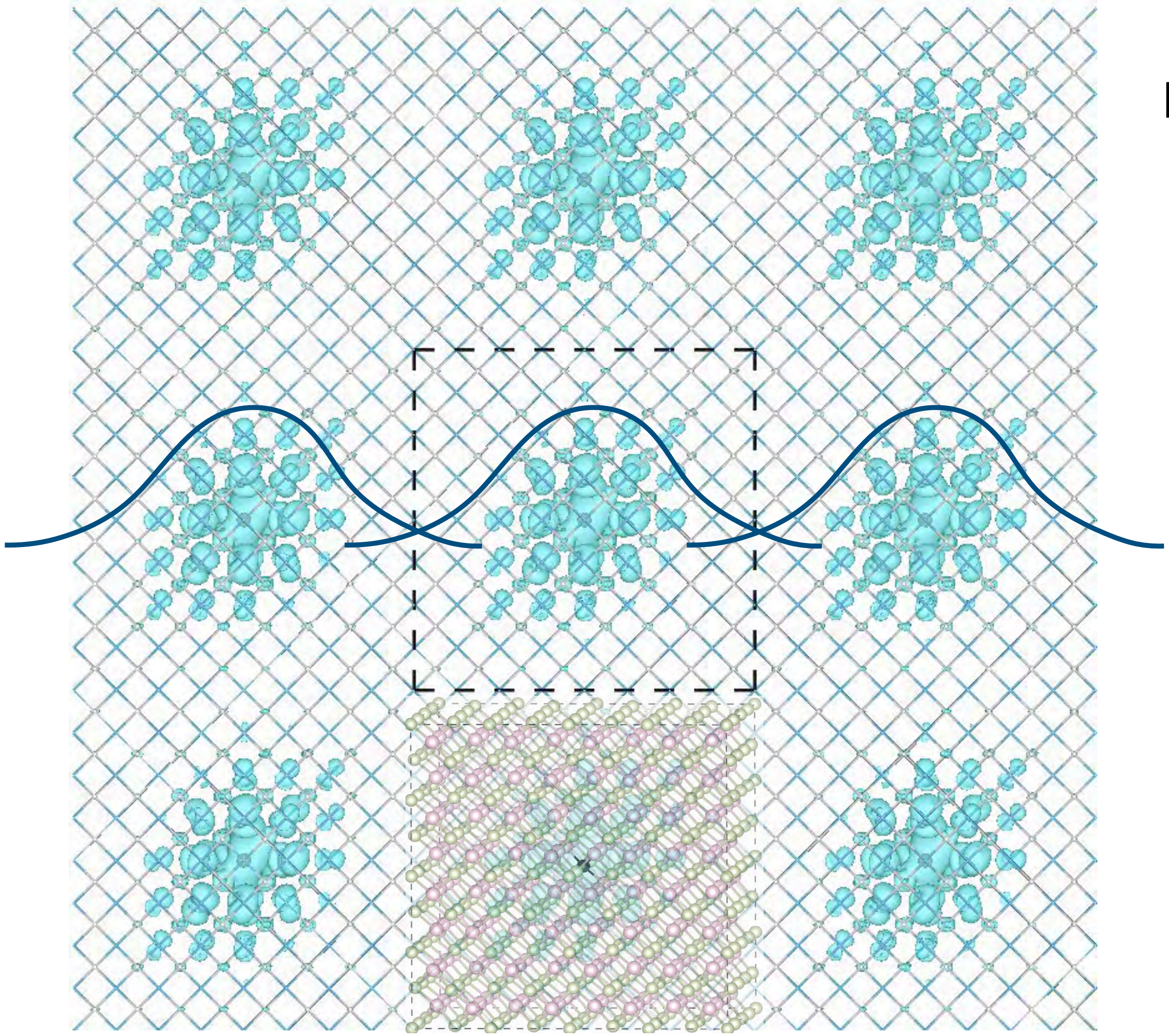
Typical supercell sizes are not large enough to describe an isolated shallow center

Swift *et al.*, Npj Comput. Mater. **6**, 181 (2020)

King and Wang, Phys. Rev. Appl. 18, 064001 (2022)

Freysoldt *et. at.*, Rev. Mod. Phys. **86**, 253 (2014)

Interactions between defects in neighboring cells

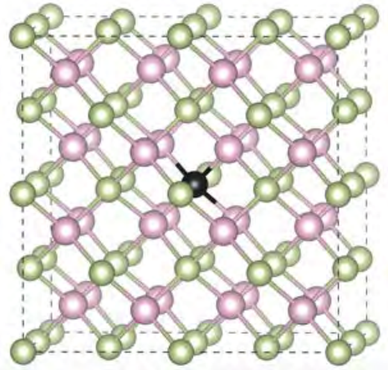


For typical supercell sizes of few 100 atoms

Errors in transition levels (~0.1 eV)
are of the order of the transition-level values
for shallow centers

Extrapolating to the dilute limit

576 electrons

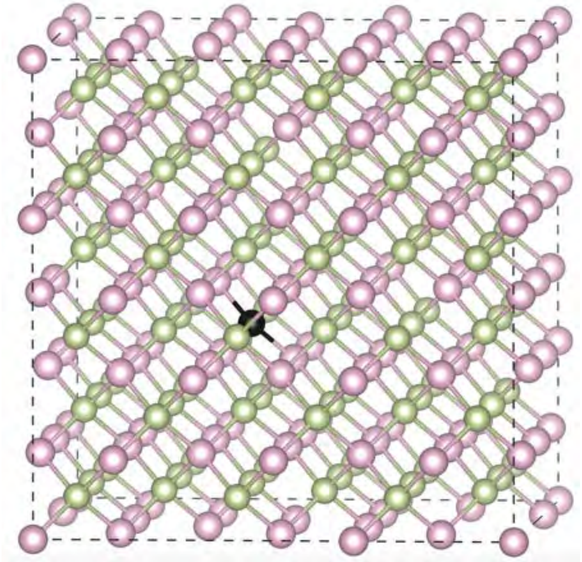


64 atoms

2x2x2
x 8-atom cubic
unit cell

→

1,944 electrons

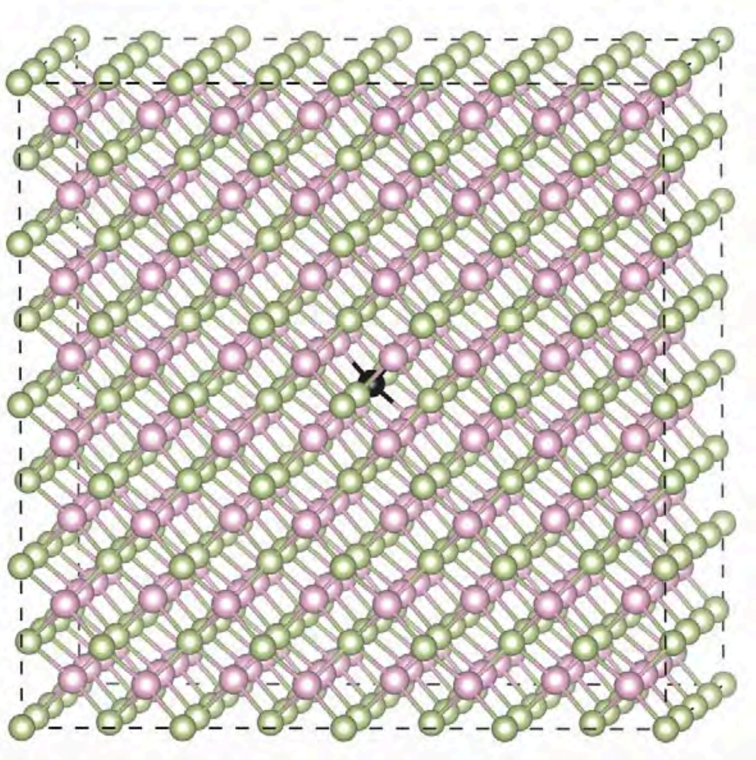


216 atoms

3x3x3

→

4,608 electrons



512 atoms

4x4x4

9,000 electrons

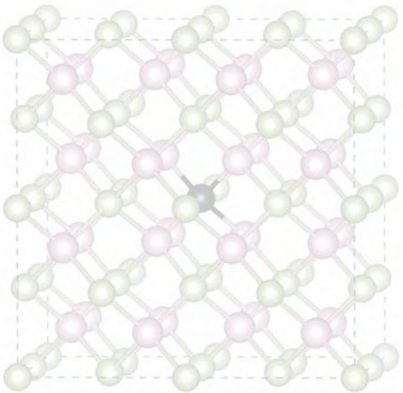
→ ...

5x5x5

dilute

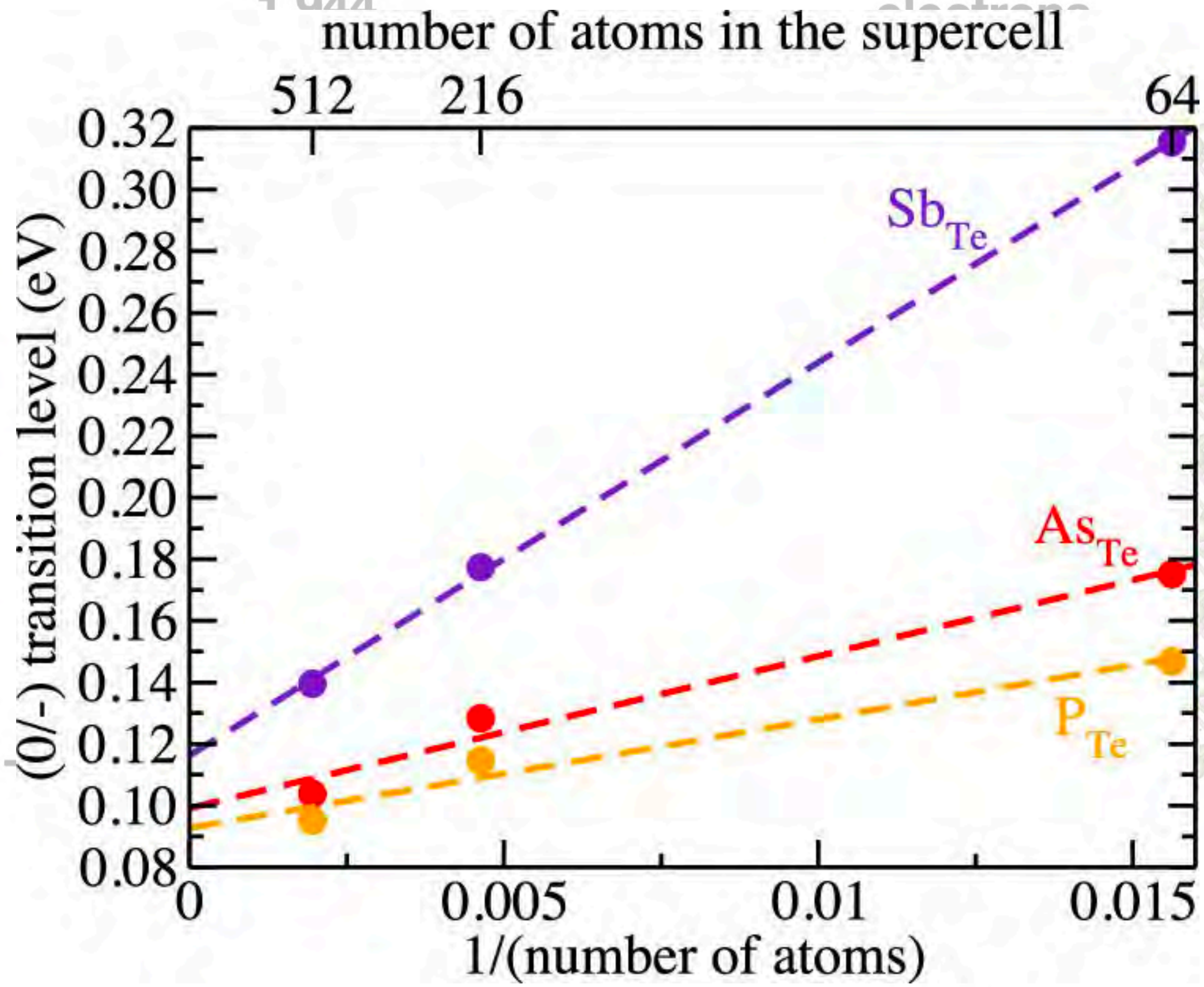
Extrapolating to the dilute limit

576
electrons

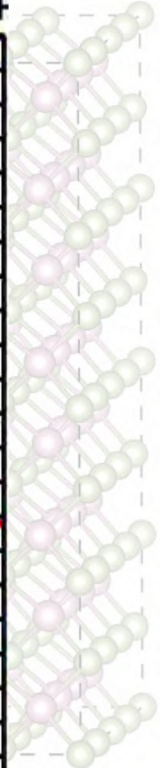


64 atoms

2x2x2
repetition of the
8-atom cubic
unit cell



4,608



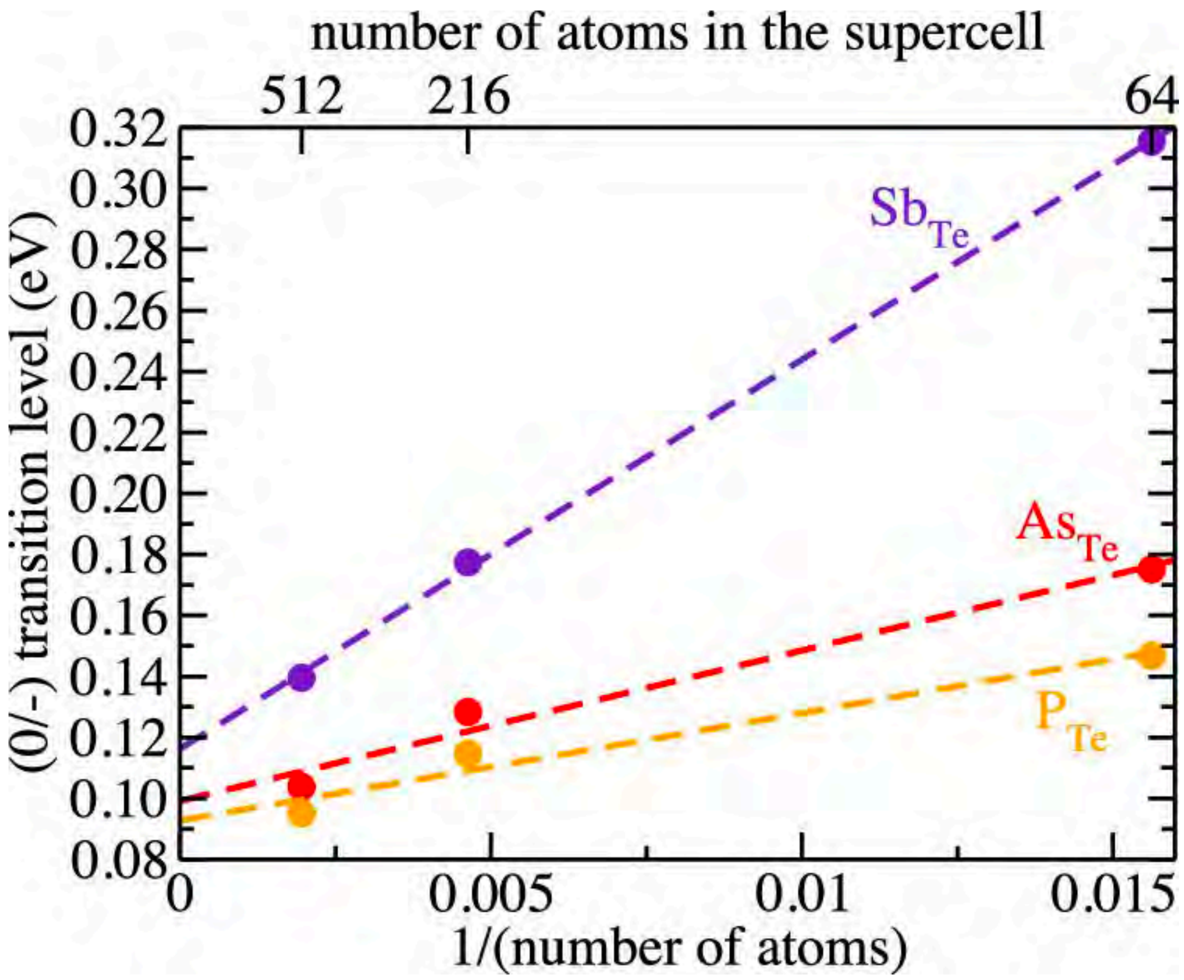
9,000
electrons

→ ▪▪▪

dilute

5x5x5

Extrapolating to the dilute limit



At dilute limit:

P(0/-) = 93 meV

As(0/-) = 99 meV

Sb(0/-) = 116 meV

Exp.

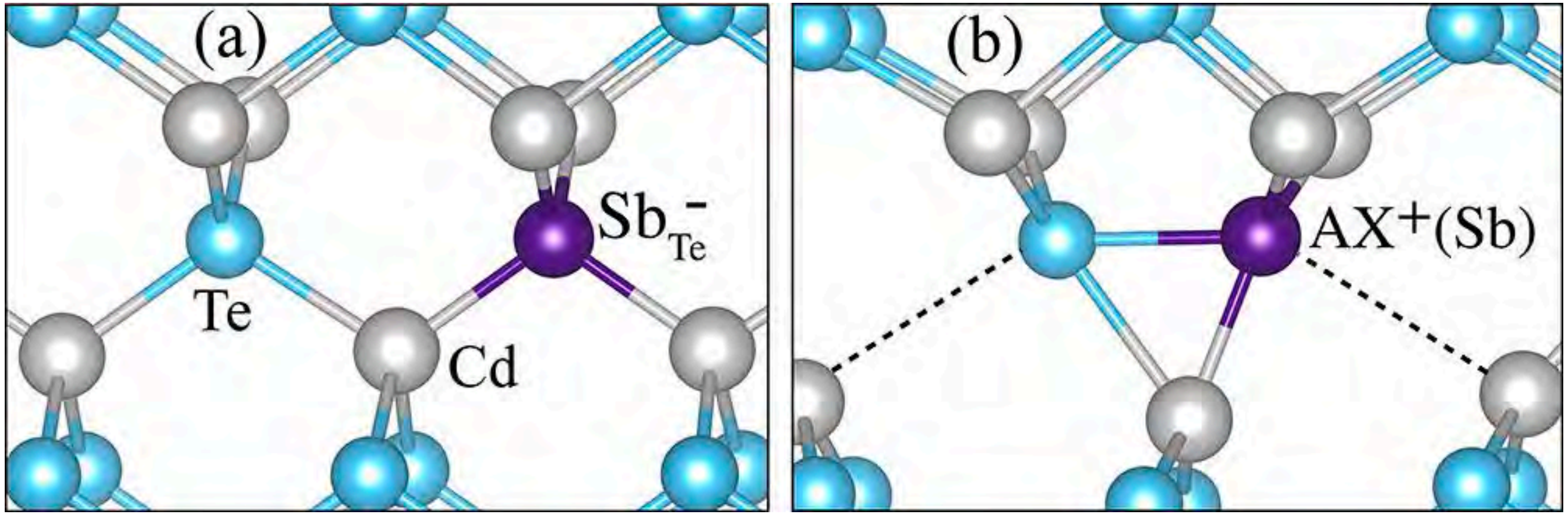
P(0/-) = 87 meV

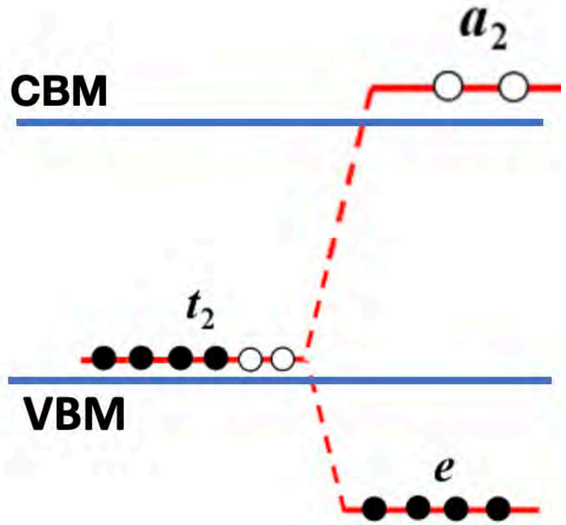
As(0/-) = 94 meV

Sb(0/-) = 103 meV

Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

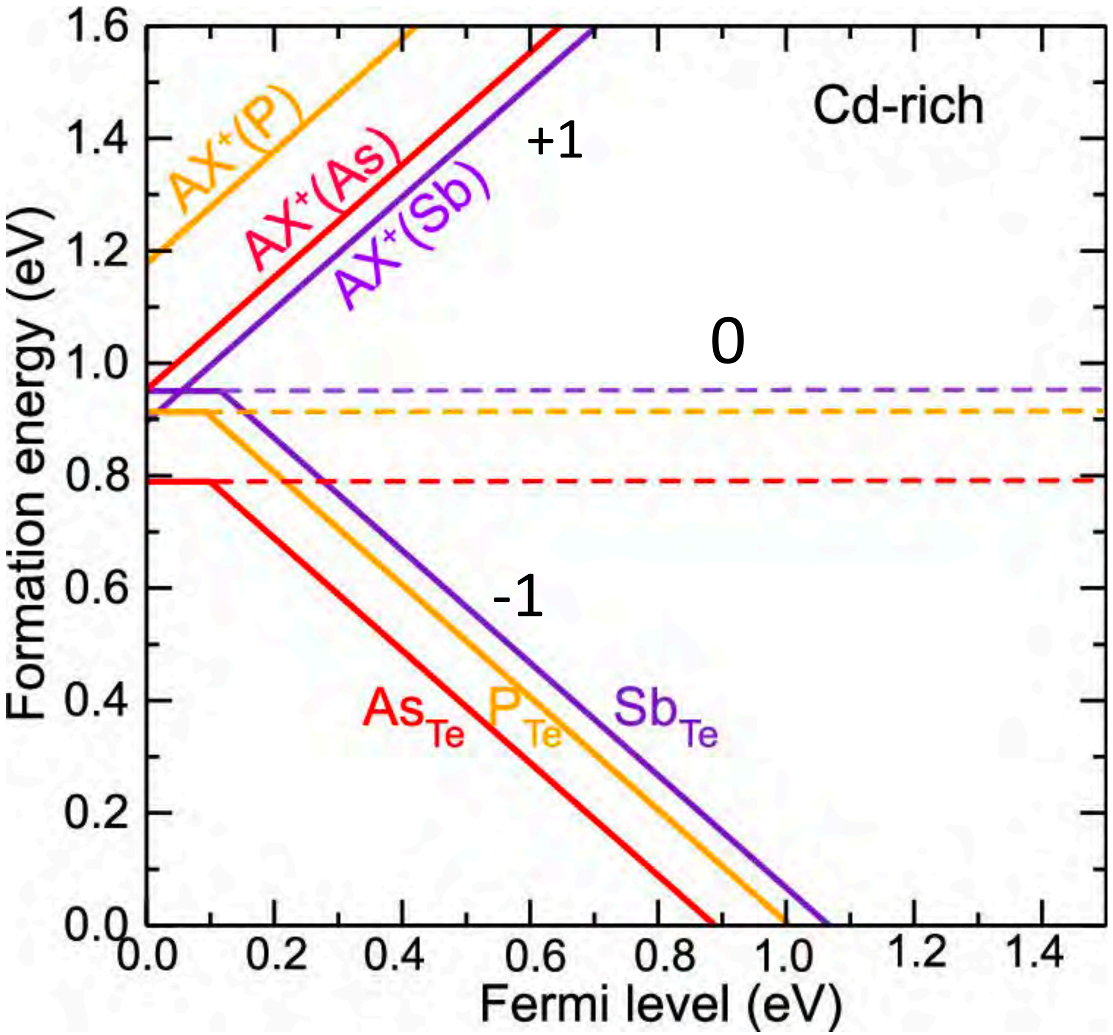
Substitutional acceptors vs. AX centers





electronic energy gain
vs.
lattice strain loss

Substitutional acceptors vs. AX centers



- AX centers are not stable
- P, As, and Te are shallow donors

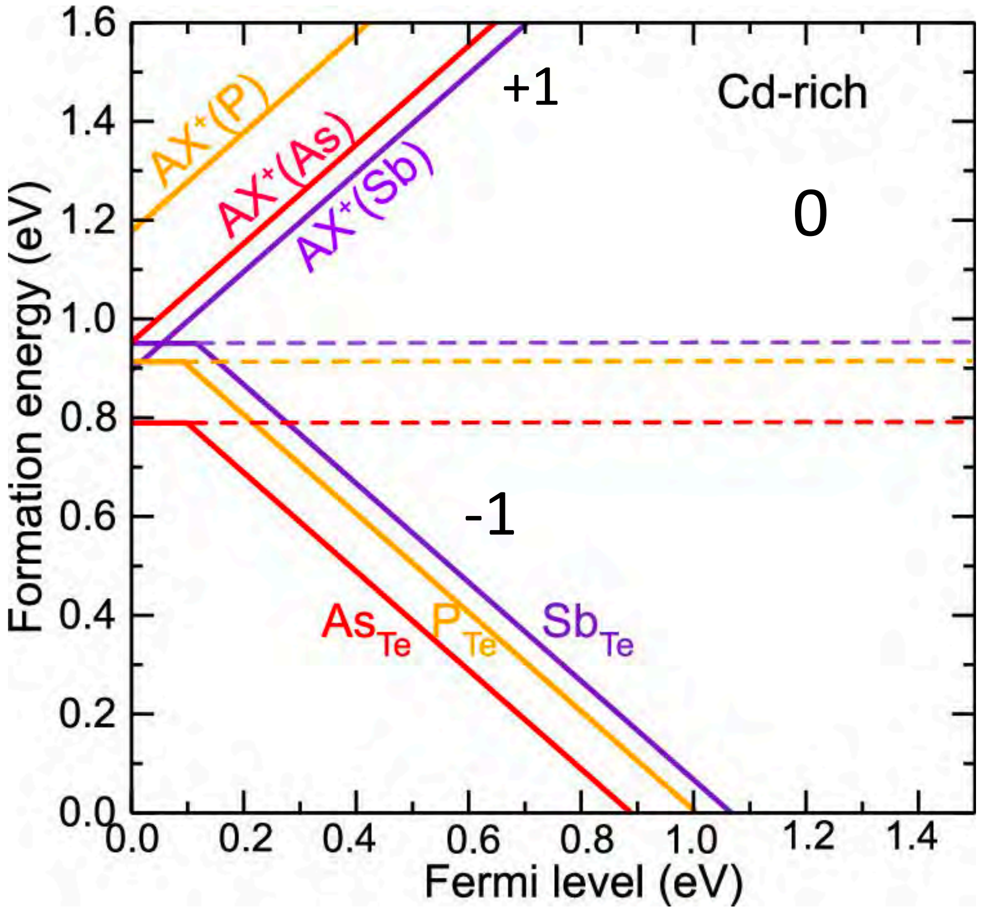
- (0/-) ionization energies close to expected from hydrogen model

$$13.6 \text{ eV } m^*/\varepsilon^2 \approx 100 \text{ meV}$$

Chatratin *et al.*, J. Phys. Chem. Lett. **14**, 273 (2023)

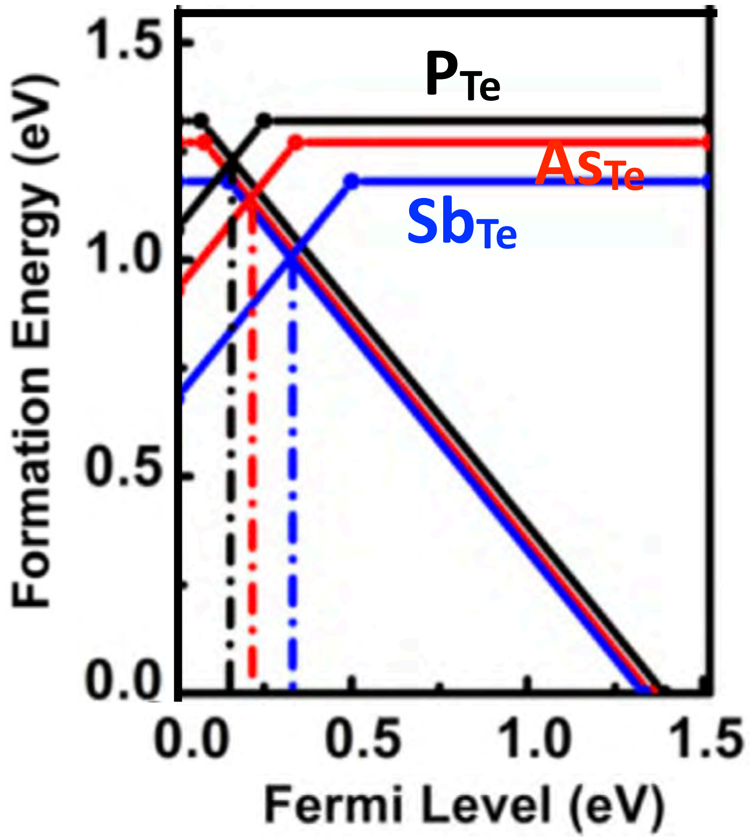
Substitutional acceptors vs. AX centers

HSE-33 hybrid functional
with spin-orbit
Extrapolated to the dilute limit



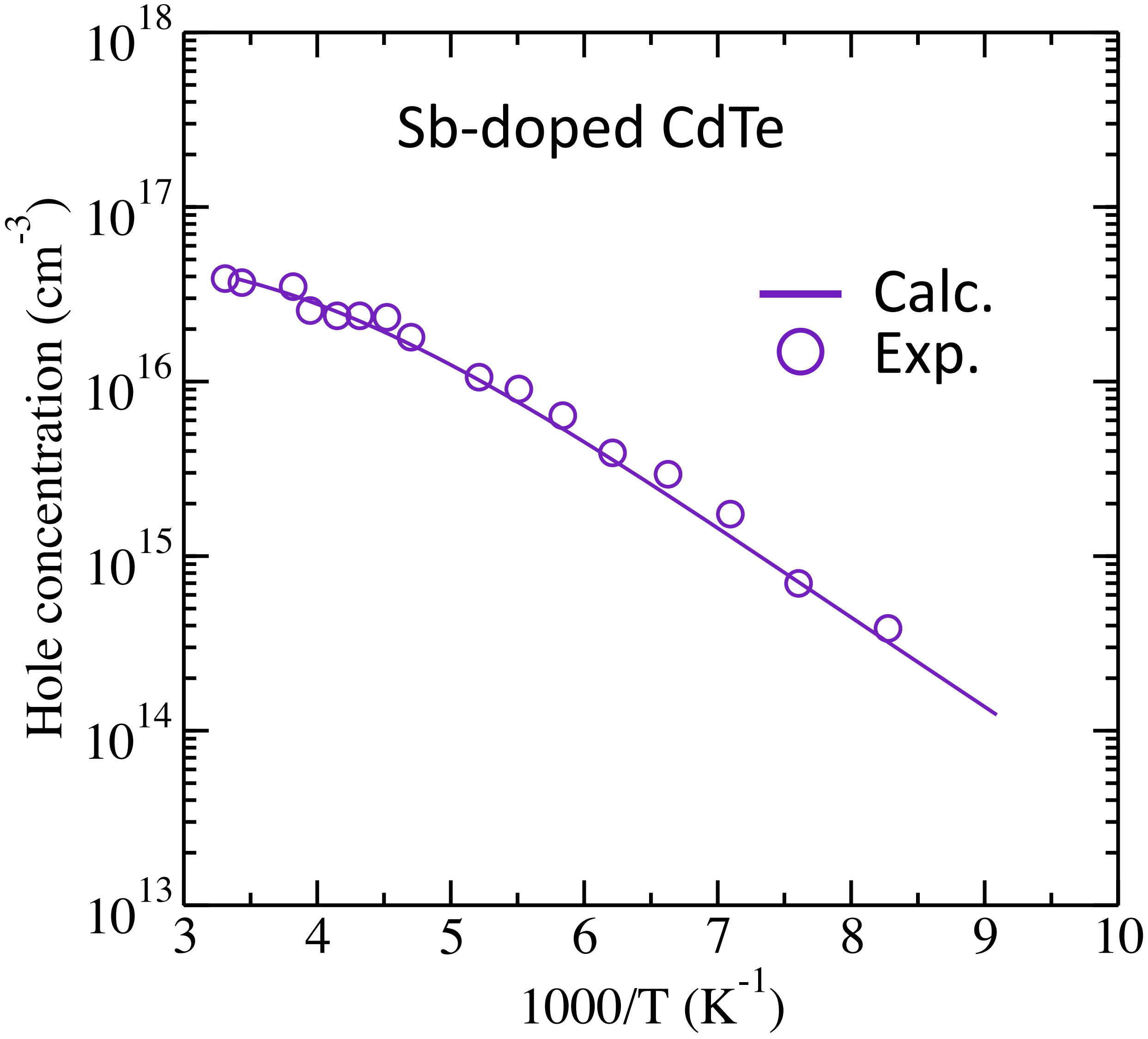
Chatratin et al., J. Phys. Chem. Lett. **14**, 273 (2023)

HSE06 hybrid functional
no spin-orbit
Supercell 216 atoms



Dou *et. al.*, Phys. Rev. Appl. **15**, 054045 (2021)

Calculated hole concentration for Sb-doped CdTe



Use calc. E_a= 116 meV

Fit: [Sb] = [N_a] = 0.58 x 10^{17} cm^{-3}

$$\frac{p(p+N_d)}{N_a - N_d - p} = \frac{N_V}{\beta} e^{-E_a/k_B T}$$

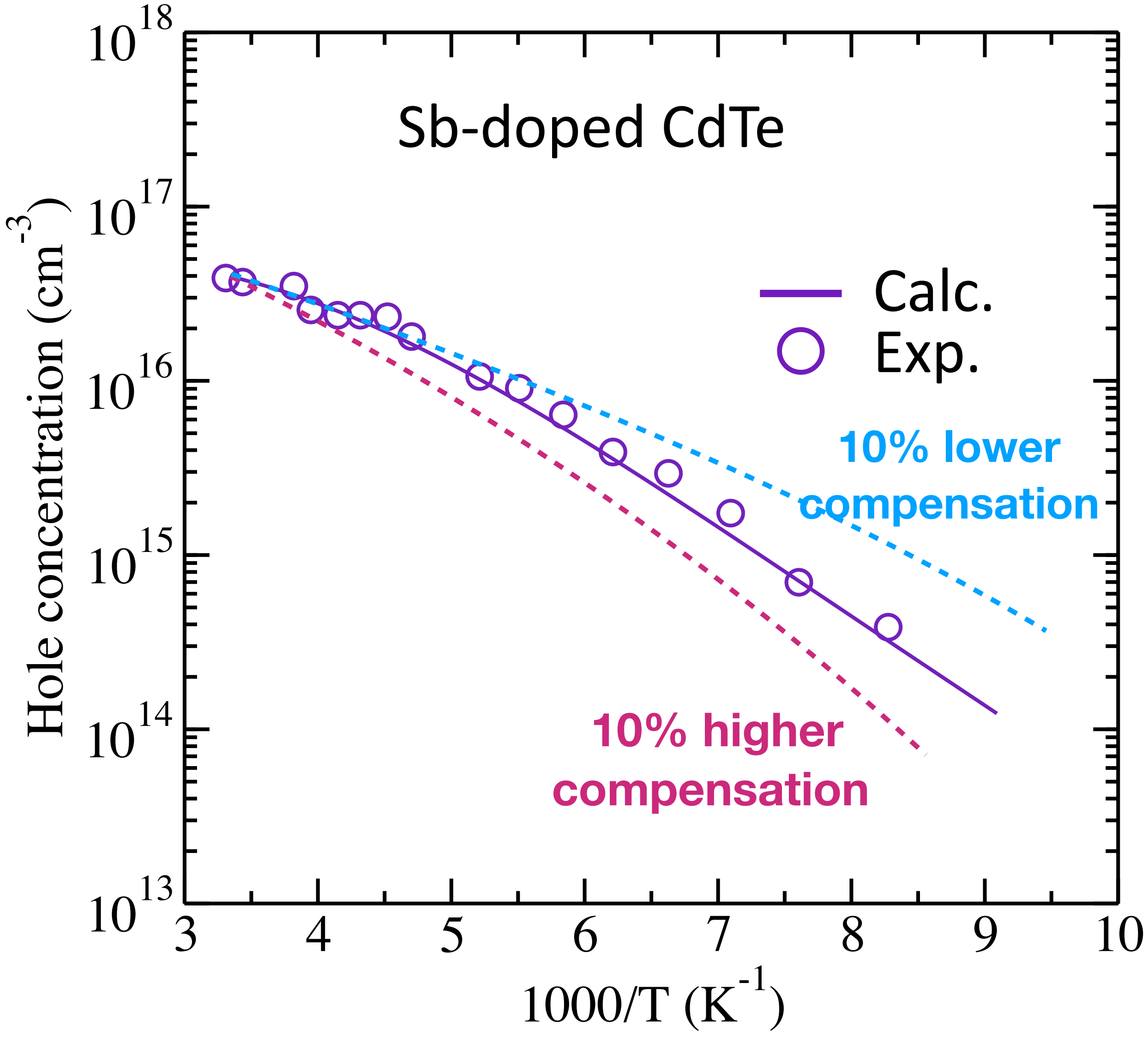
Blakemore, Semiconductor statistics (Courier Corp., 2002)

N_d are AX centers ~3% of [Sb]

Exp. data:

Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Calculated hole concentration for Sb-doped CdTe

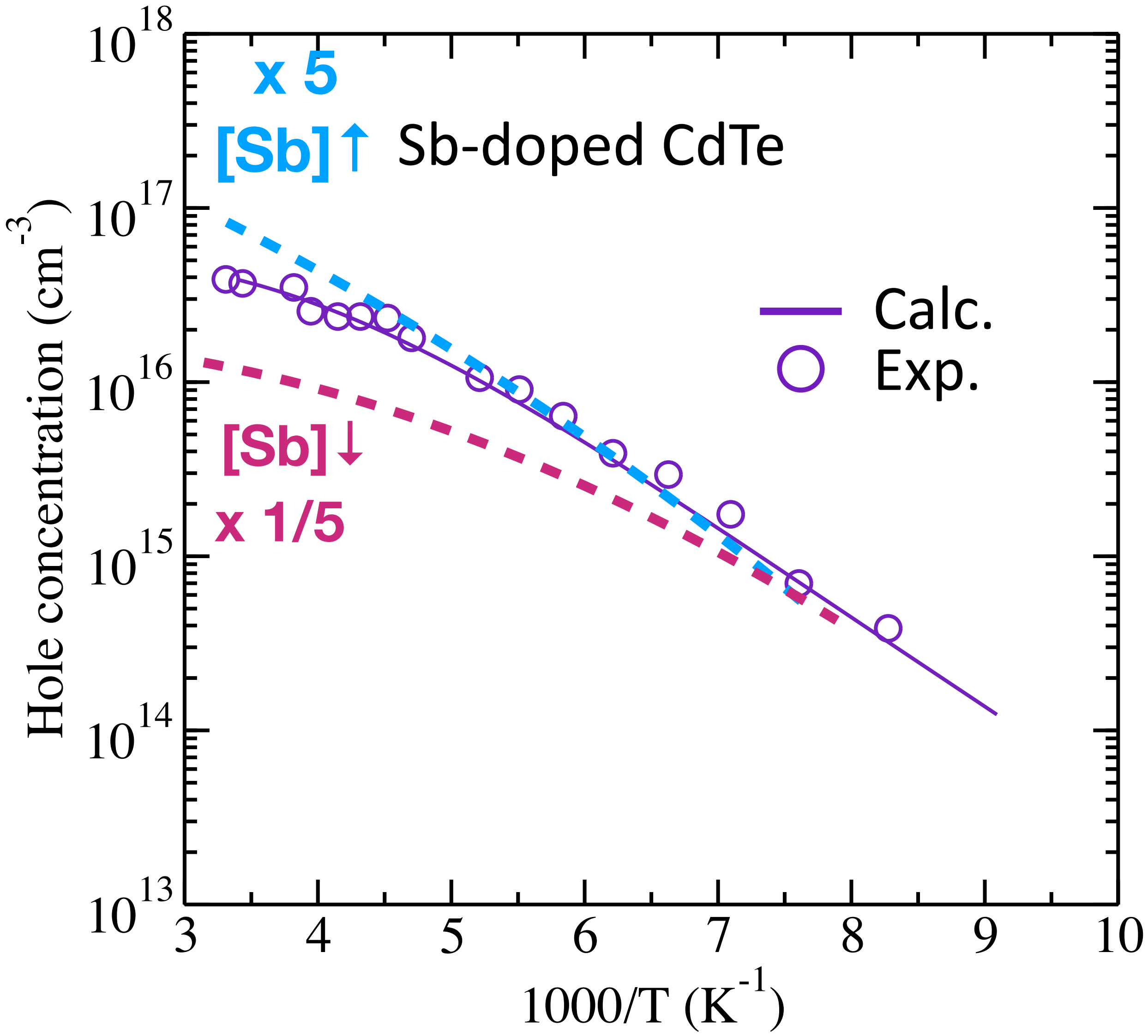


Changing the level of compensation (assuming unknown donor) makes the agreement with experiments worse at low temperatures

Exp. data:

Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Calculated hole concentration for Sb-doped CdTe

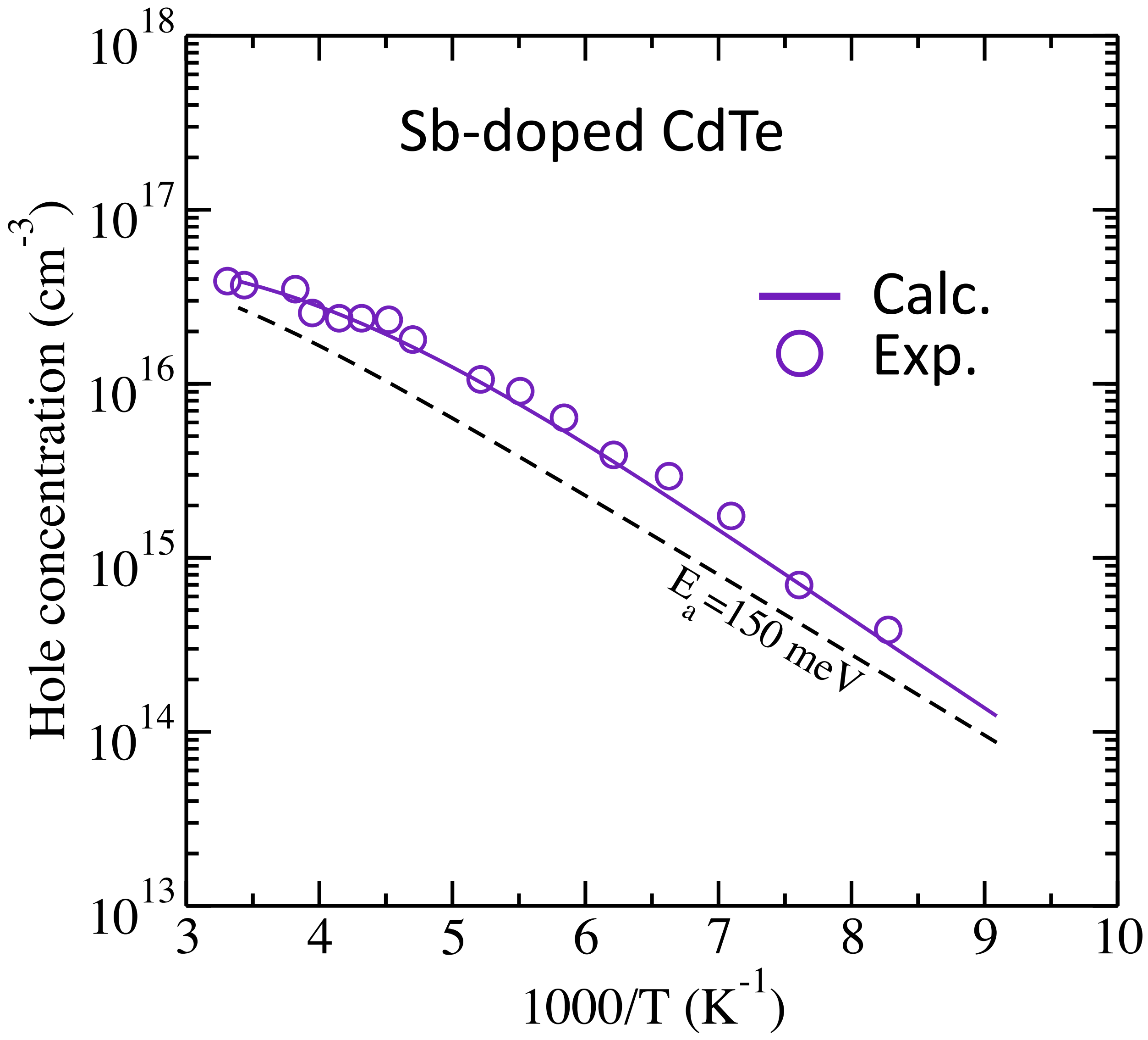


Changing the total Sb concentration by a factor of 5 makes the agreement worse at room temperature

Exp. data:

Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Calculated hole concentration for Sb-doped CdTe



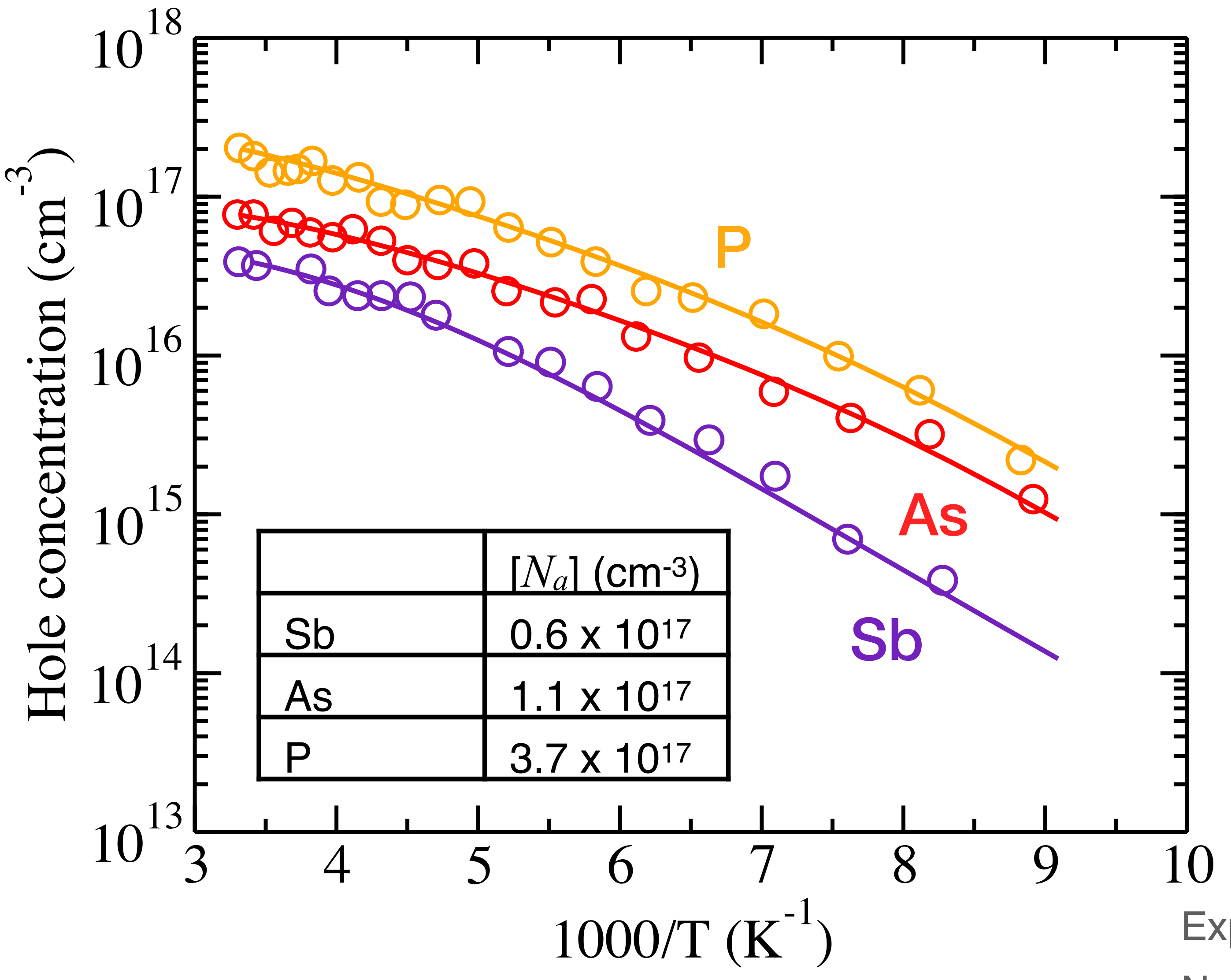
Changing E_a from 116 meV to 150 meV leads to overall lower hole concentration

→ cannot explain experimental data over the whole temperature range

Exp. data:

Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Calculated hole concentration for P, As, and Sb-doped CdTe



Using calc. E_a

P(0/-) = 93 meV

As(0/-) = 99 meV

Sb(0/-) = 116 meV

For P and As, using [N_d] = 6% [N_a] gives best fit

Source of the compensating donor in the case of P and As still unknown

Exp. data:

Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Summary

- Need to include spin-orbit coupling and use very large supercell to describe shallow acceptor centers in CdTe
- P, Sb, As in CdTe are shallow acceptors with ionization energies ~100 meV, around that of the hydrogen model
- AX center do not play a role as self-compensation center, expect perhaps in the case of Sb under high doping levels
- Best fit to the exp. data of P and As-doped single crystals indicate presence of compensating donors with 6% of the dopant concentration
- Doping efficiency in single crystals decreases at higher doping (>1E17 cm^{-3}), the cause of which is still unknown
- Low doping efficiency in thin films likely to have contribution from grain boundaries that serve as source or sink of compensating defects.

Chatratin *et al.*, J. Phys. Chem. Lett. **14**, 273 (2023)