Compensation centers in group-V doped CdTe

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

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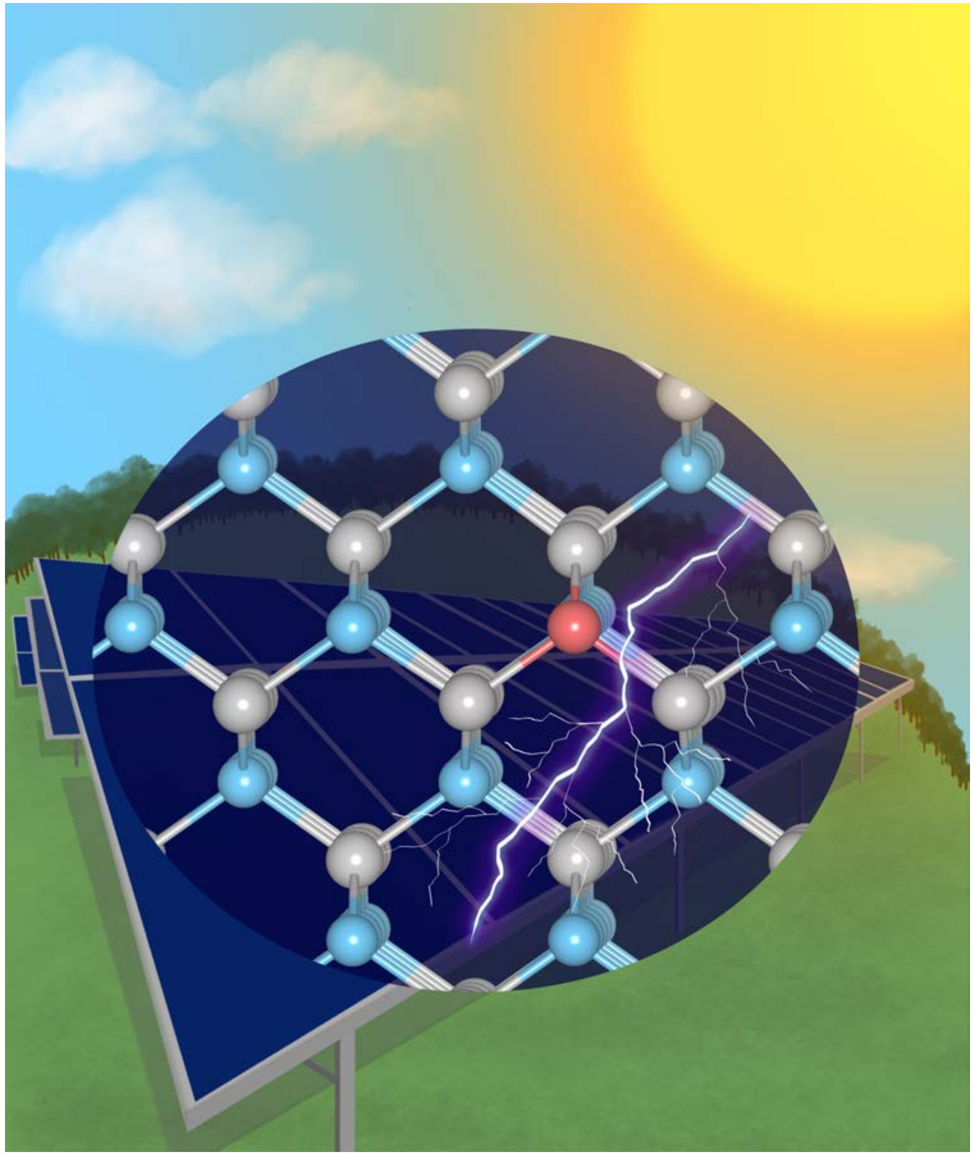
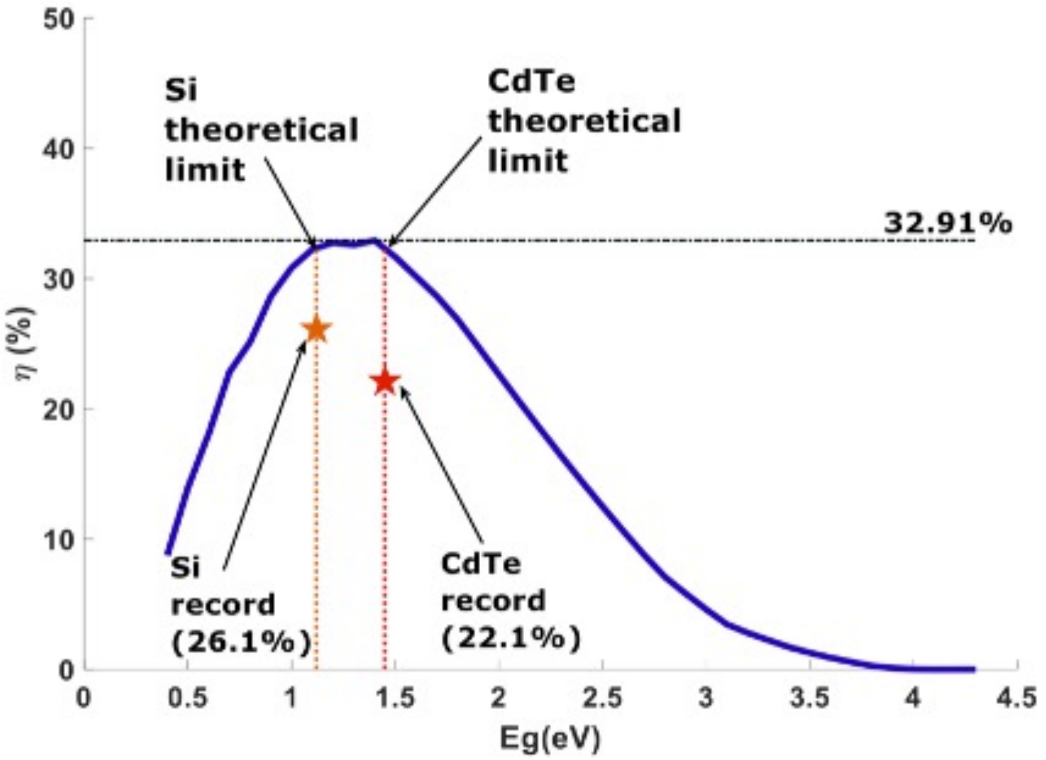


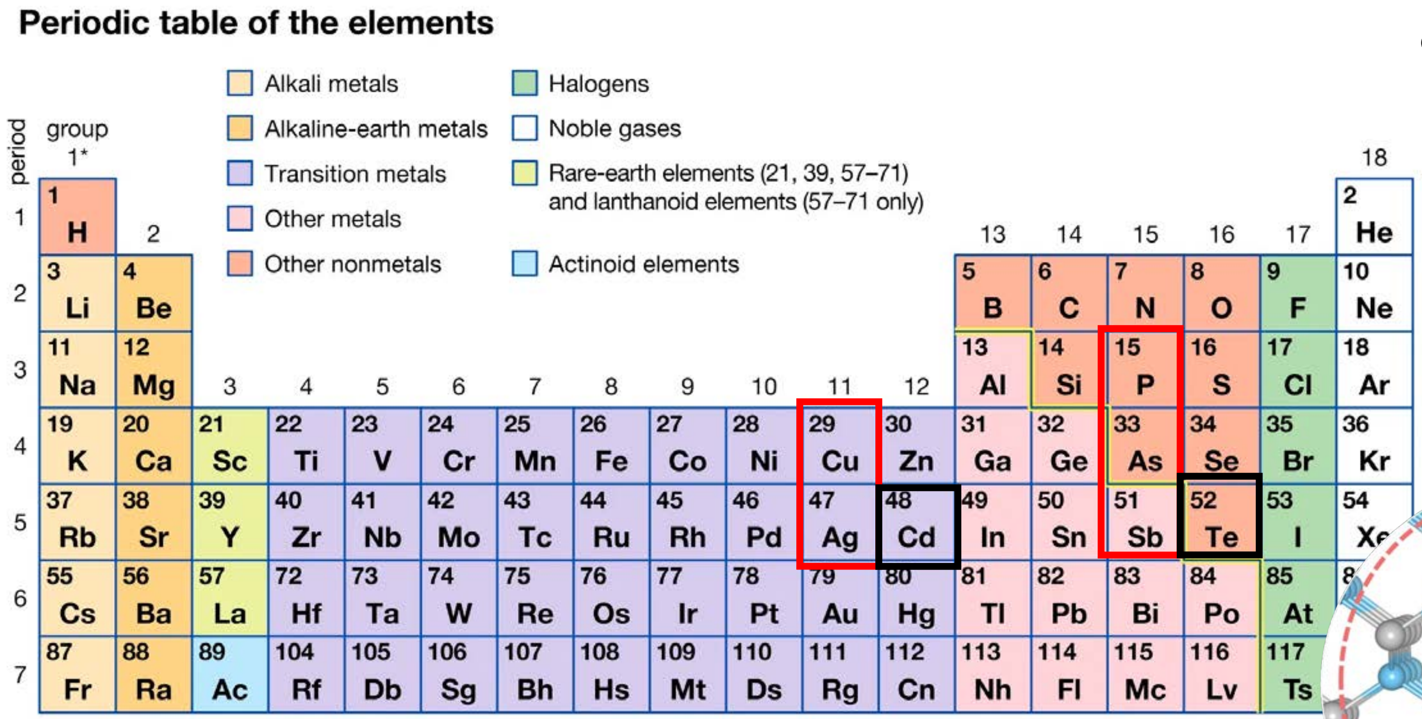
CdTe for thin-film solar cells

- Most competitive PV thin-film technology in the market
  - low production cost
  - simple manufacturing
- Current solar cell record > 22%
  - theoretical limit of 32%
  - low Voc (<< E_g)
  - low hole concentration (~10^{14} cm^{-3})
- efficiency up to 25 % can be achieved if hole concentration > 10^{16} cm^{-3} is achieved
  - hole from doping



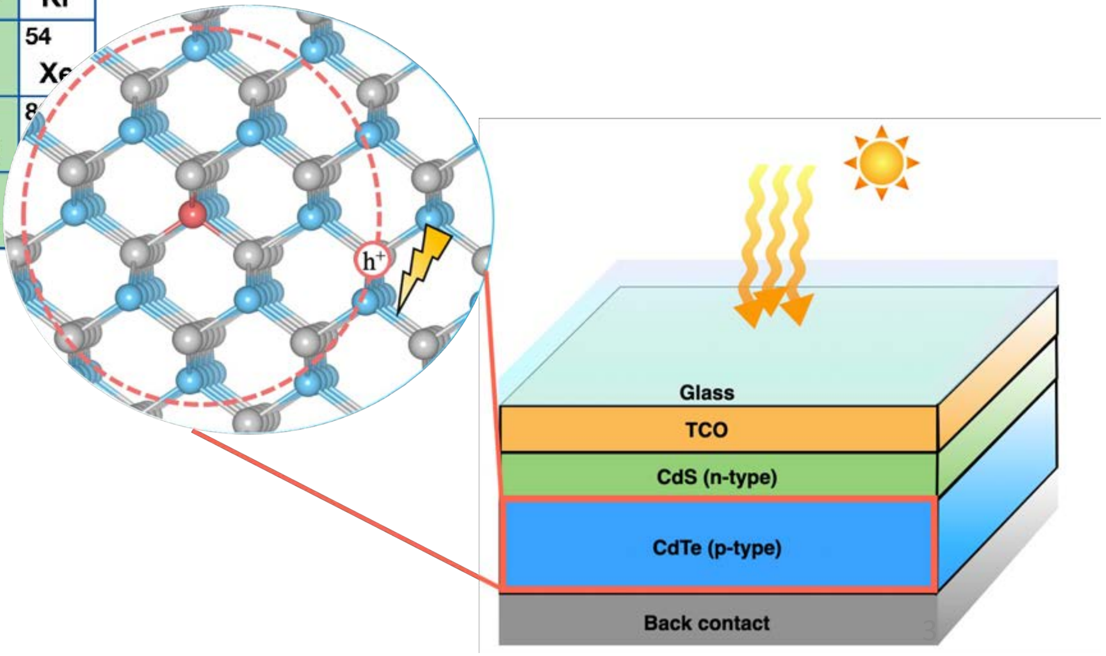
Barbato *et. al.* J. Phys. D. Appl. Phys. **54**, 333002 (2021)

Group-V doping to increase the hole density in CdTe



- Group-V impurities (As, P and Sb) are shallow acceptors in CdTe

McCandless *et al.*, Sci. Rep. **8**, 14519 (2018)
Metzger *et al.*, Nat. Energy **4**, 837 (2019)
Nagaoka et al., Appl. Phys. Lett. **116**, 132102 (2020)
Chatratin *et al.*, J. Phys. Chem. Lett. **14**, 273 (2023)



- For p-type doping, look to the left of Cd/Te

- Cu doping leads to a short carrier lifetime and instability

Group-V leads to low doping efficiency

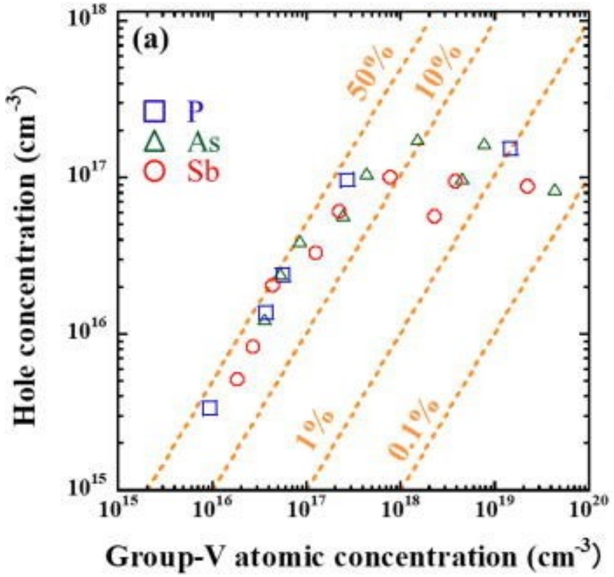
⇒ source of hole compensation is unknown

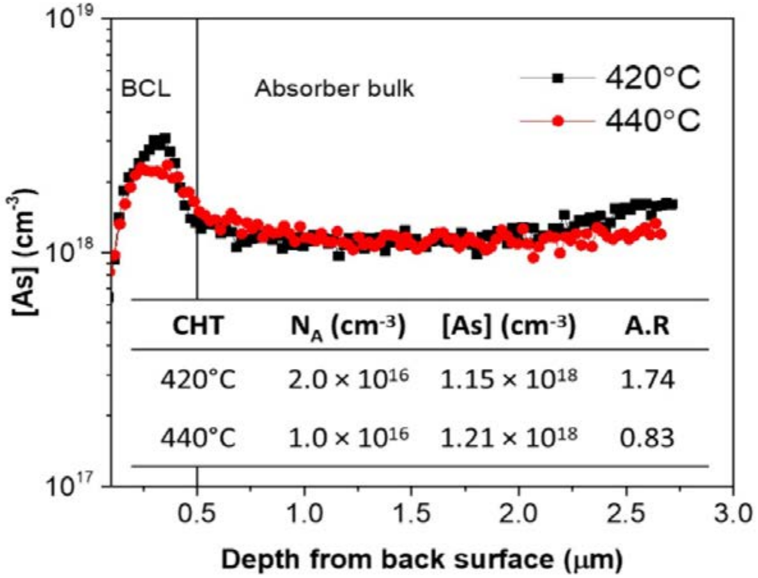
- Low doping efficiency in single crystal at high doping concentration

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

- > 10 % doping efficiency in As-doped CdTe film

  Oklobia *et al.* IEEE J. Photovolt. **12**, 1296-1302 (2022)



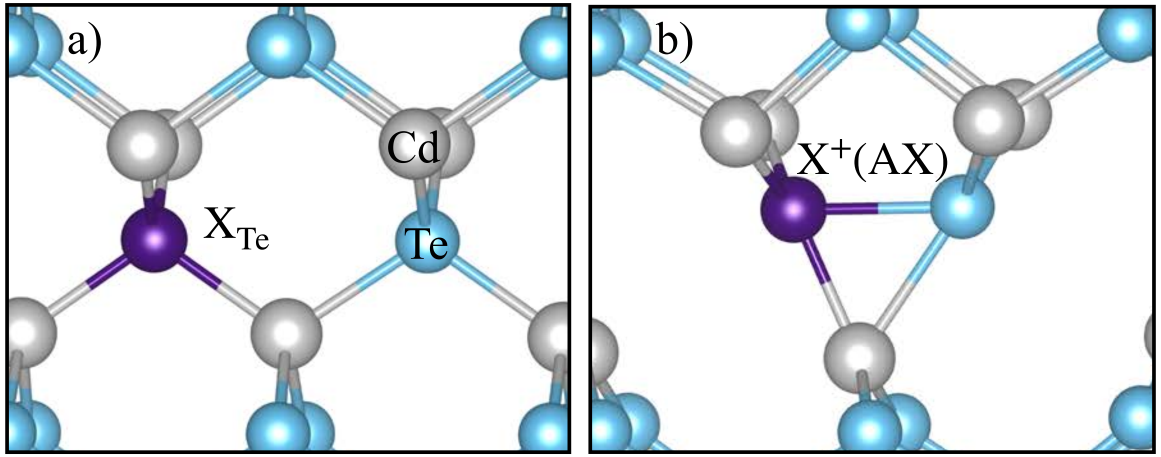


CHT	N_A (cm^{-3})	[As] (cm^{-3})	A.R
420°C	2.0×10^{16}	1.15×10^{18}	1.74
440°C	1.0×10^{16}	1.21×10^{18}	0.83

AX center as main compensation centers according to previous DFT calculations

Wei and Zhang, Phys. Rev. B **66**, 155211 (2002)
Yang *et al.*,Semicond. Sci. Technol. **31**, 083002 (2016)
Dou *et al.*, Phys. Rev. Appl. **15**, 054045 (2021)

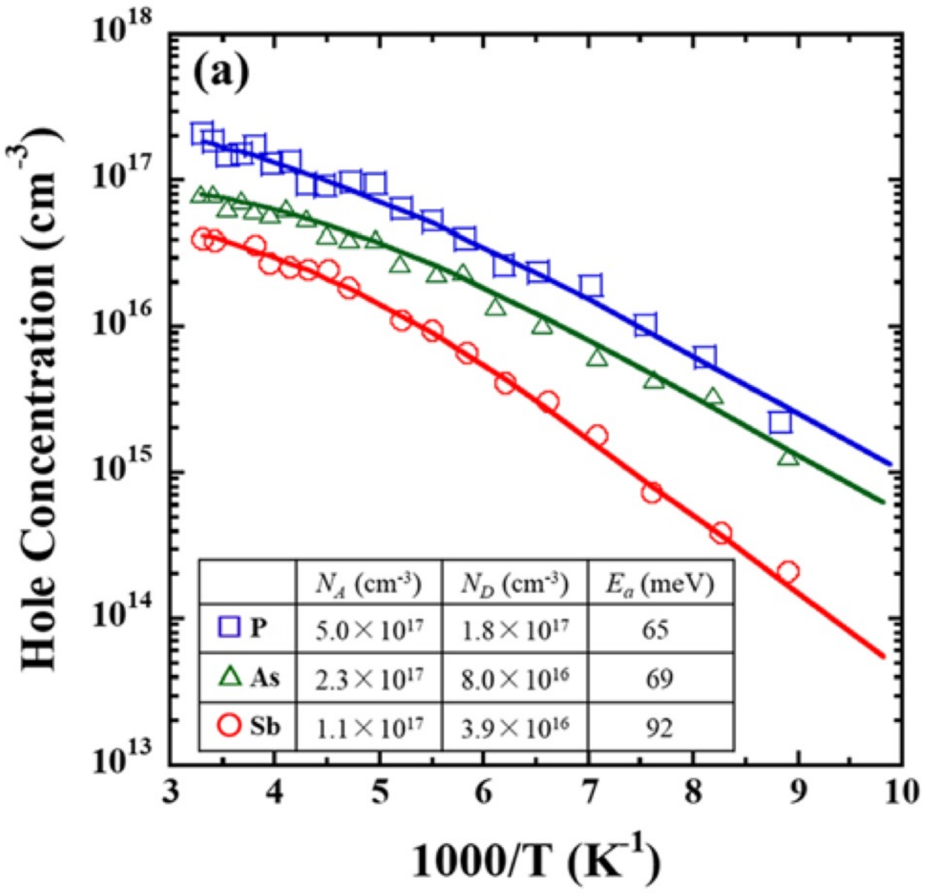
$$\mathrm{Sb}_{\mathrm{Te}}^{0} \rightarrow \mathrm{AX}^{+}(\mathrm{Sb}) + \mathrm{e}^{-}(\mathrm{CB})$$



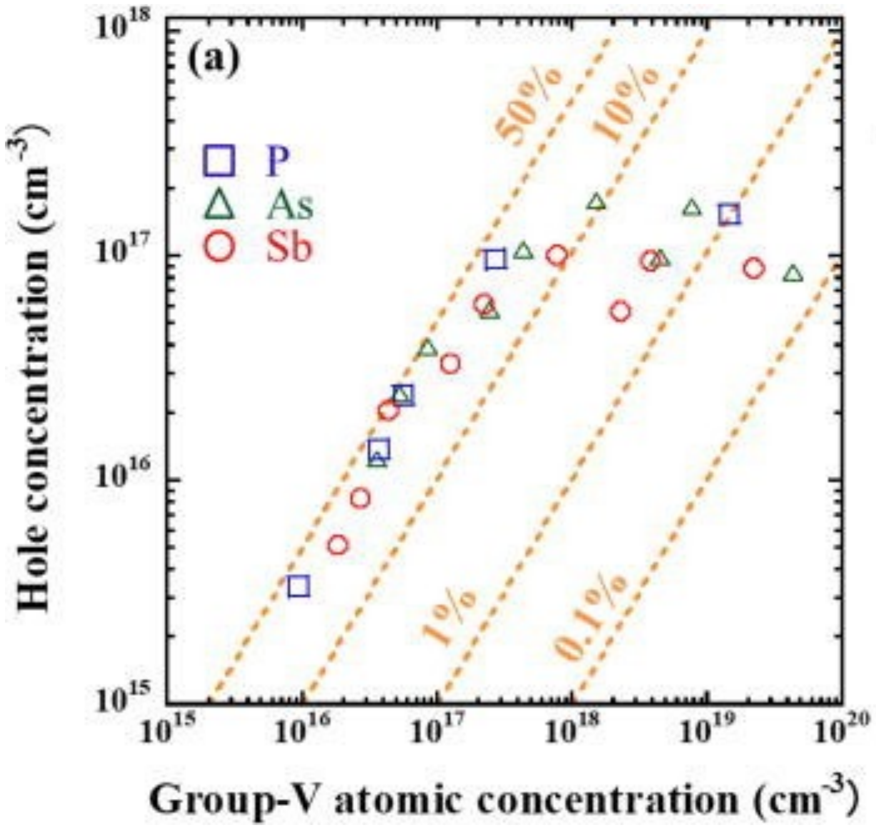
- AX centers were predicted to limit hole concentration to 10^{14} cm^{-3} in CdTe

Recent experiments indicate **high** hole concentrations from P, As, and Sb in single crystal CdTe

temperature-dependent Hall measurements



achieved hole concentration > 10^{16} cm^{-3}

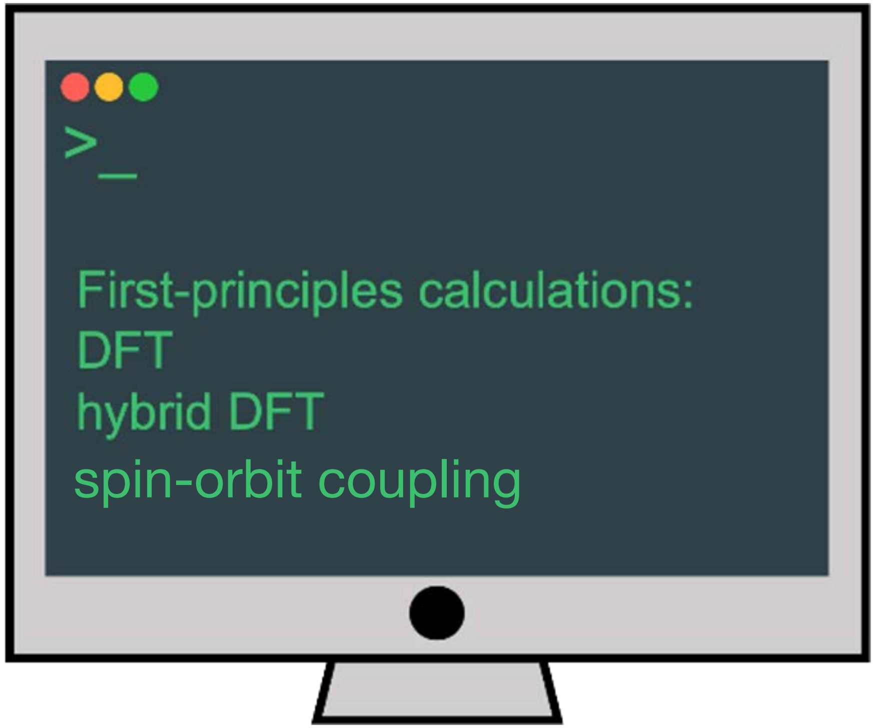


Nagaoka *et. al.*, Appl. Phys. Lett. **116**, 132102 (2020)

- ***No experimental evidence of AX centers***

Goal: Revisit AX centers and native defects

Using hybrid functional including effects of spin-orbit coupling

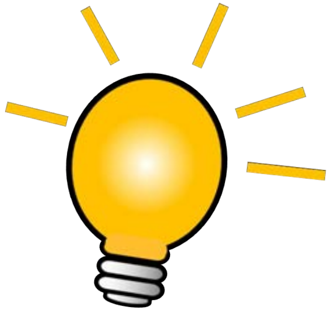


Group-V (Sb, As, P) doping

Extrapolation to the dilute limit (very large supercells)

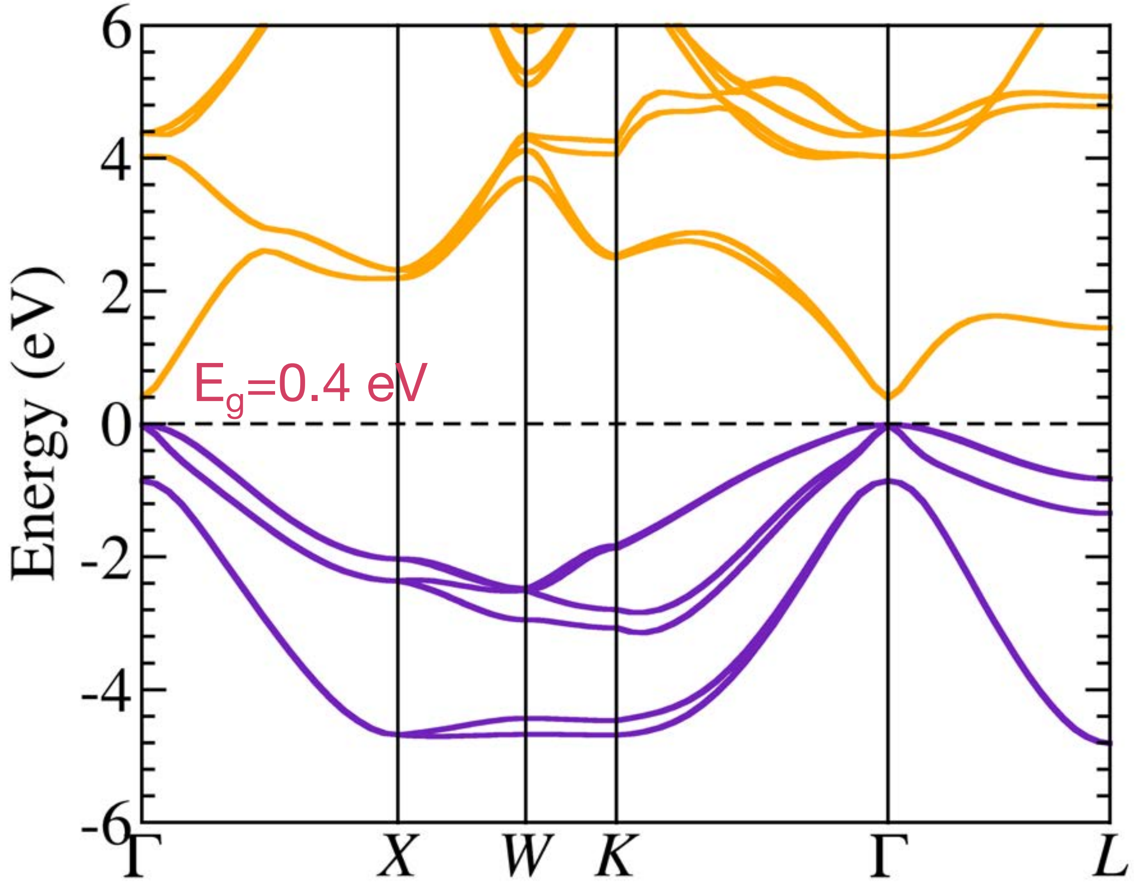
Search for possible compensation centers

Including spin-orbit coupling (SOC)



Electronic band structure of CdTe

DFT-GGA + SOC

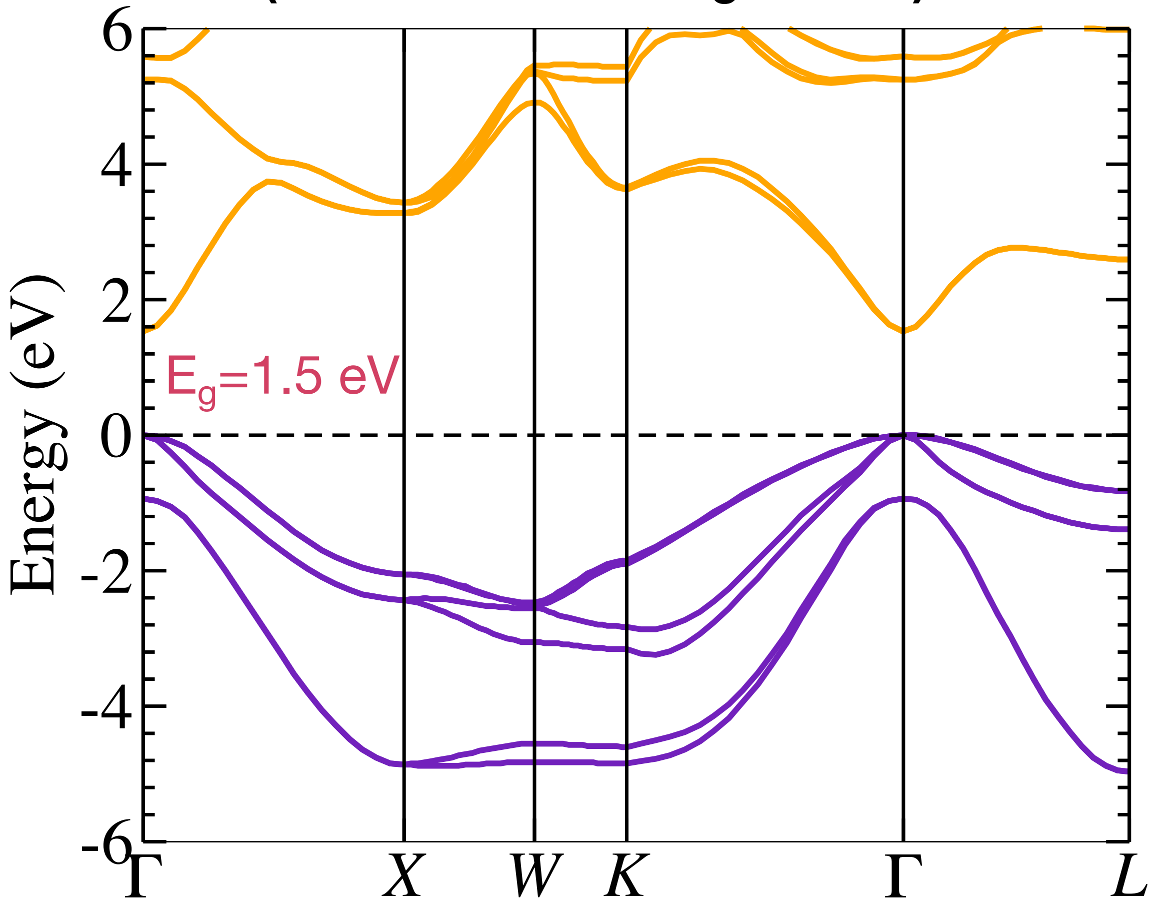


Band gap drastically underestimated

E_g (exp.) = 1.5 eV

Fonthal *et al*, *J. Phys. Chem. Solids*, ***61***, 579 (2000)

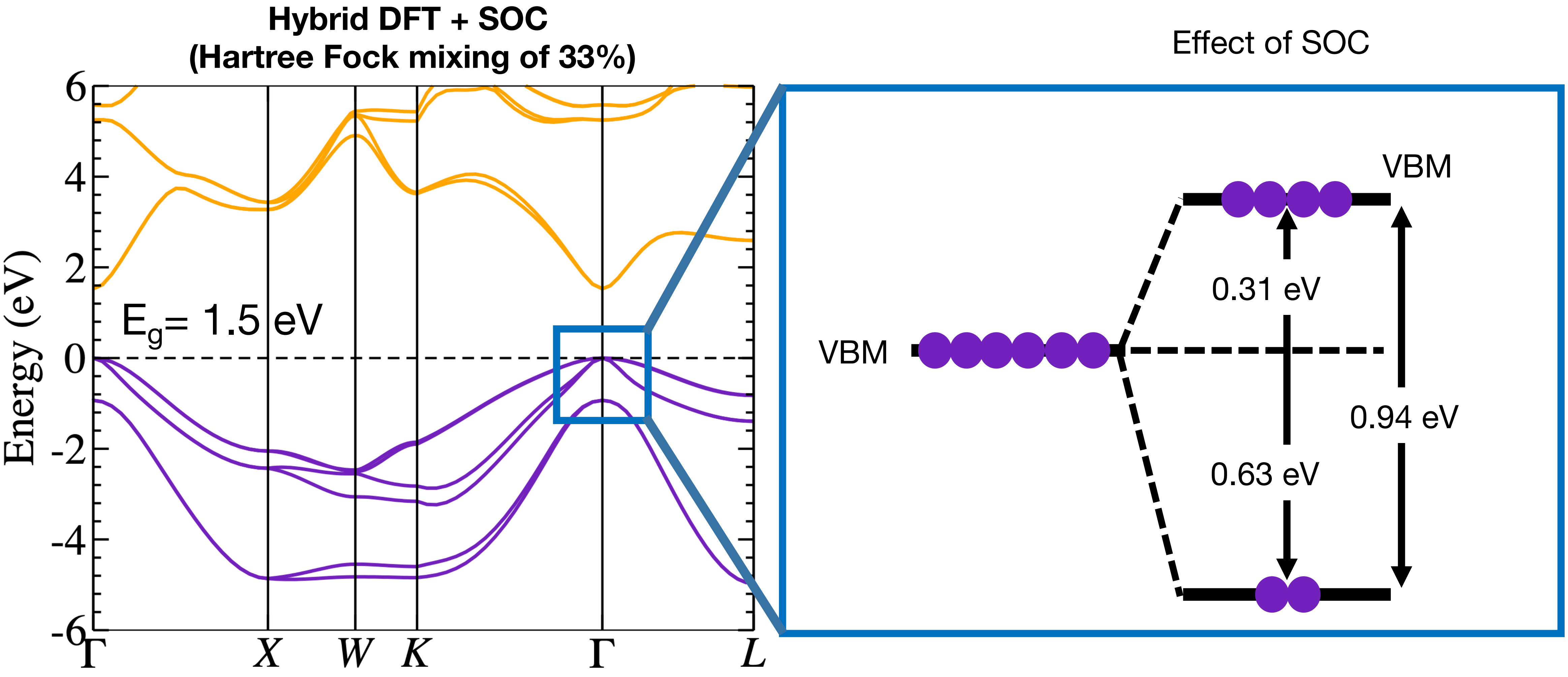
Hybrid DFT + SOC
(Hartree Fock mixing of 33%)



Correct band gap, effective masses, and ionization potential

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

Effects of SOC on the electronic properties of CdTe

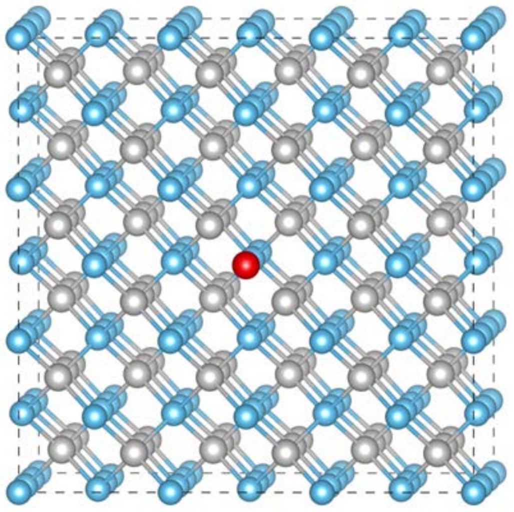


Fonthal *et al*, *J. Phys. Chem. Solids*, ***61***, 579 (2000)

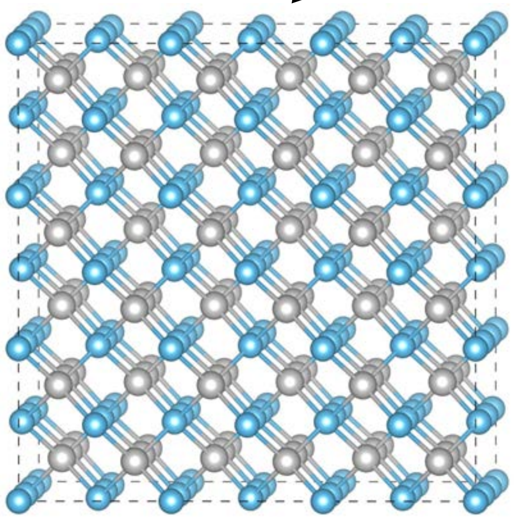
Pan *et al*, *Phy. Rev. B*, ***98***, 054108 (2018)

Defect formation energies

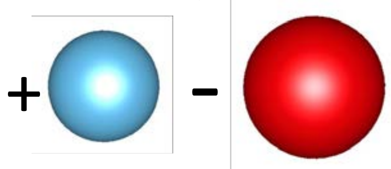
$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[bulk] + \sum_i n_i \mu_i + q(\varepsilon_f + E_{VBM})$$



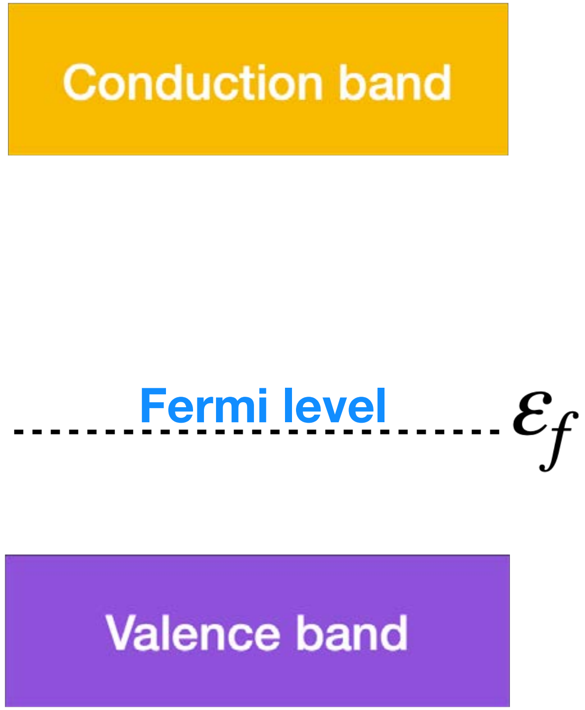
supercell with
a defect in charge q



perfect supercell



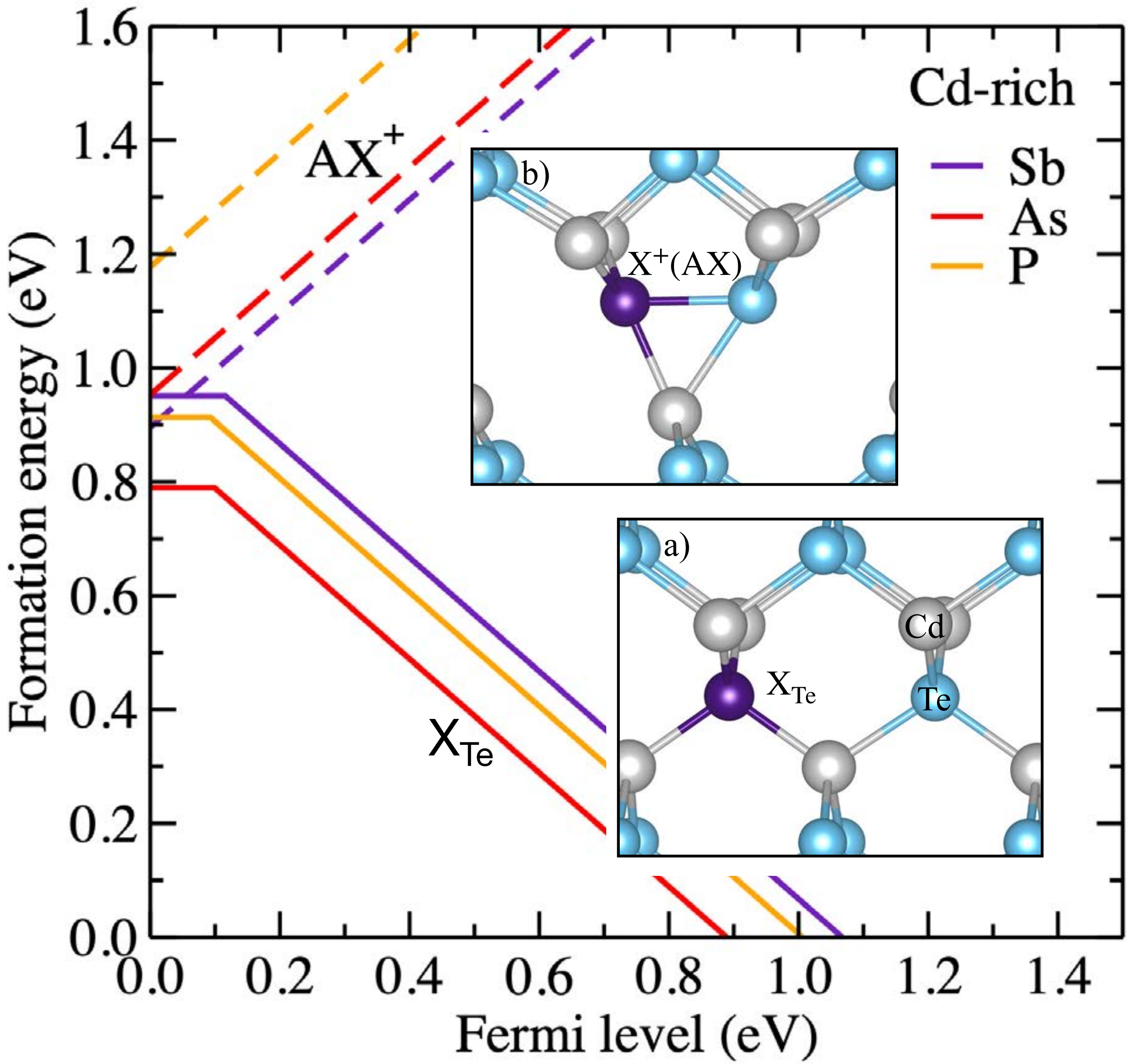
Chemical potential



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

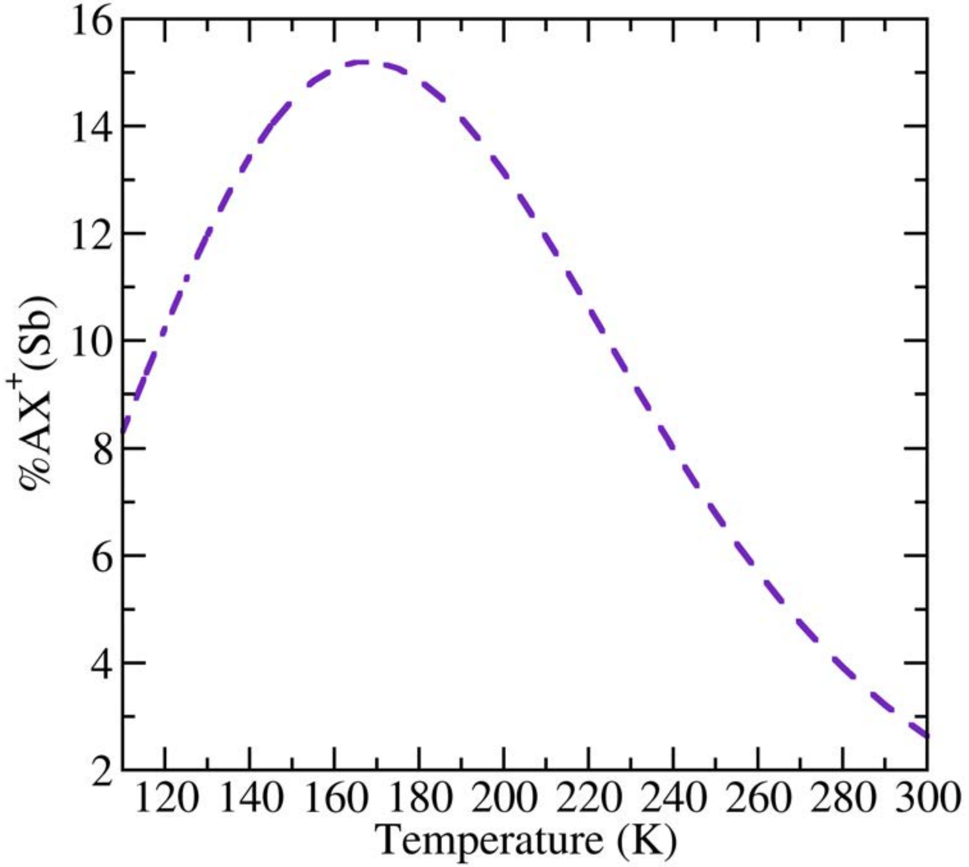
Group-V impurities in CdTe

AX centers are unstable!



- Ionization energies (0/-) ~100 meV

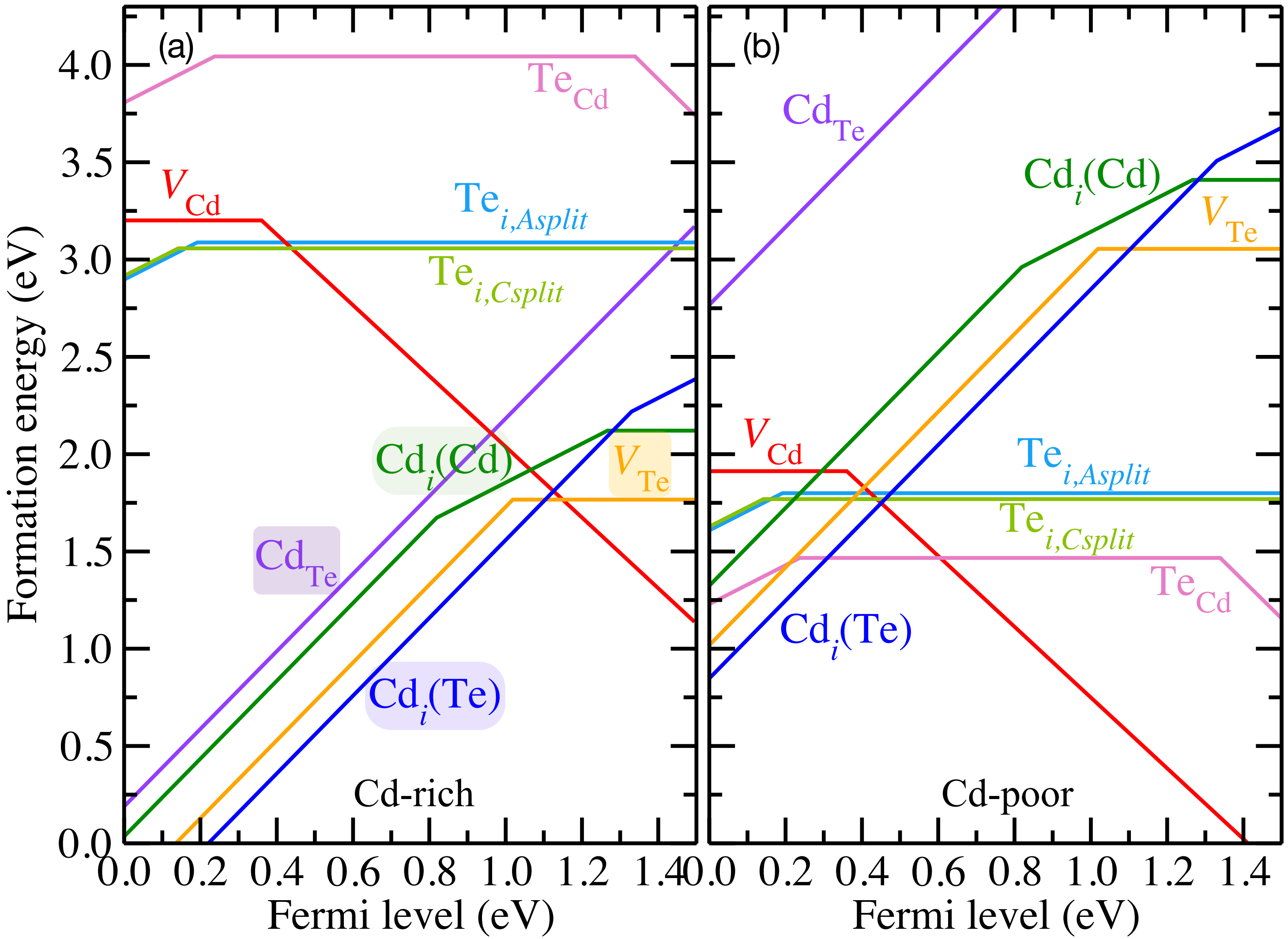
Only 15% of total [Sb] form AX center



Where does the compensation come from?

1. Native defects
2. Other complexes (not AX center)

Native defects in CdTe



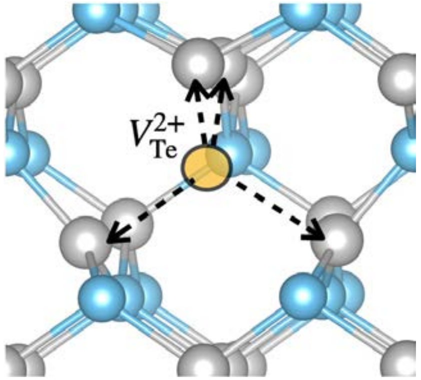
Cd-rich conditions

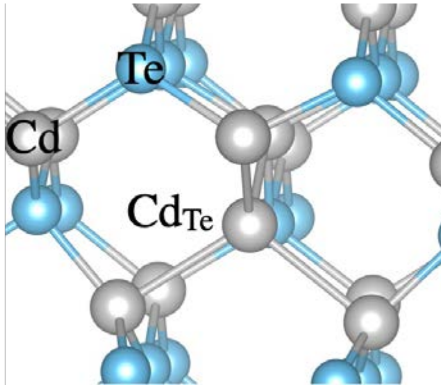
- Lowest energy defects are donors

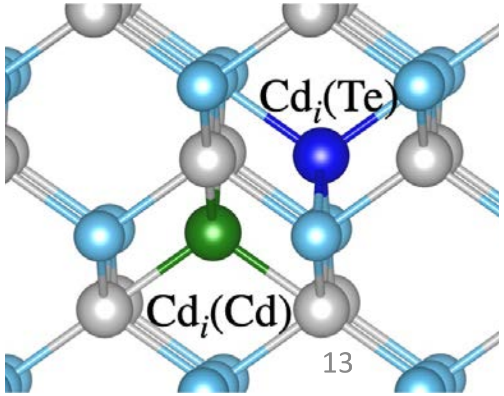
⇒ Cd$_i$ V_{Te} Cd$_{Te}$

- V_{Te} is deep donor with (2+/0) at 1.0 eV

- Cd$_i$ and Cd$_{Te}$ are shallow donors



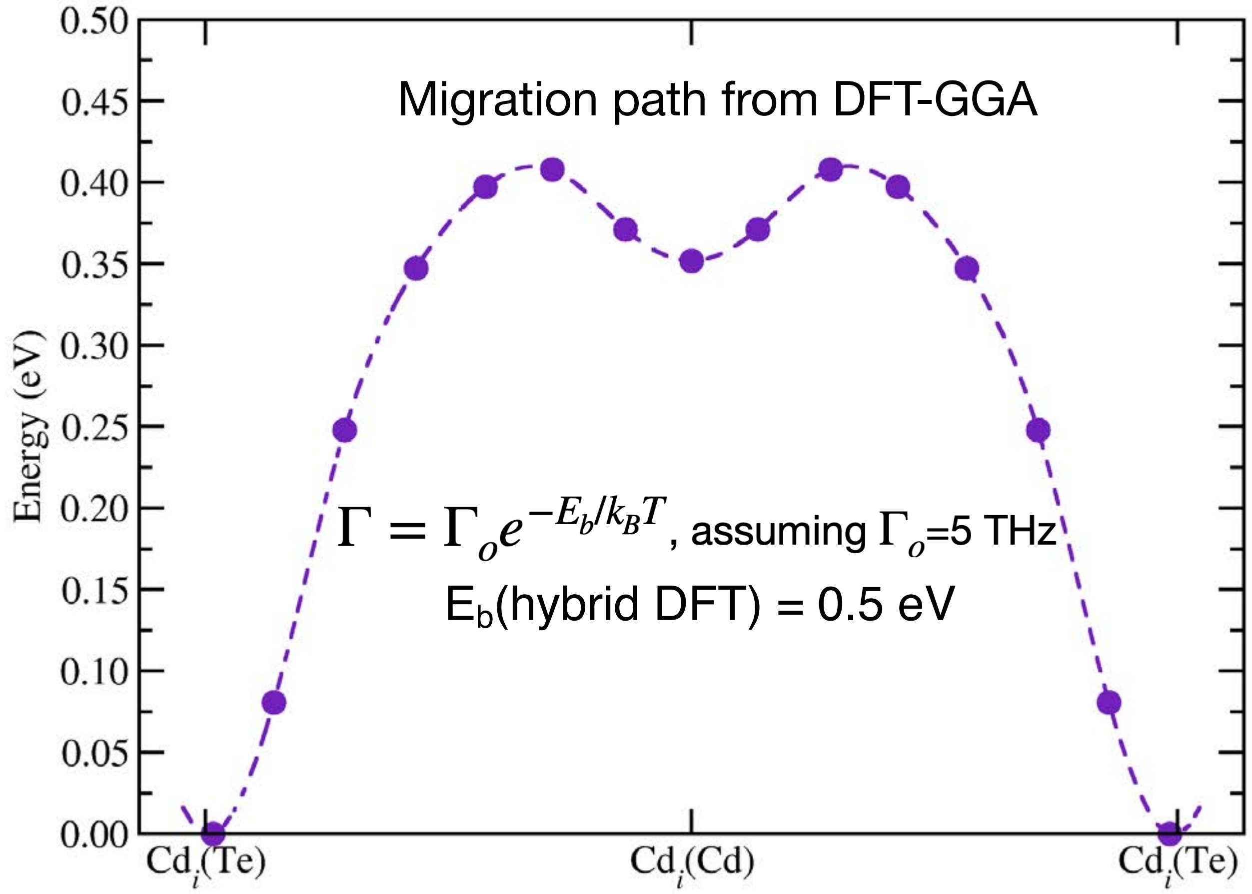


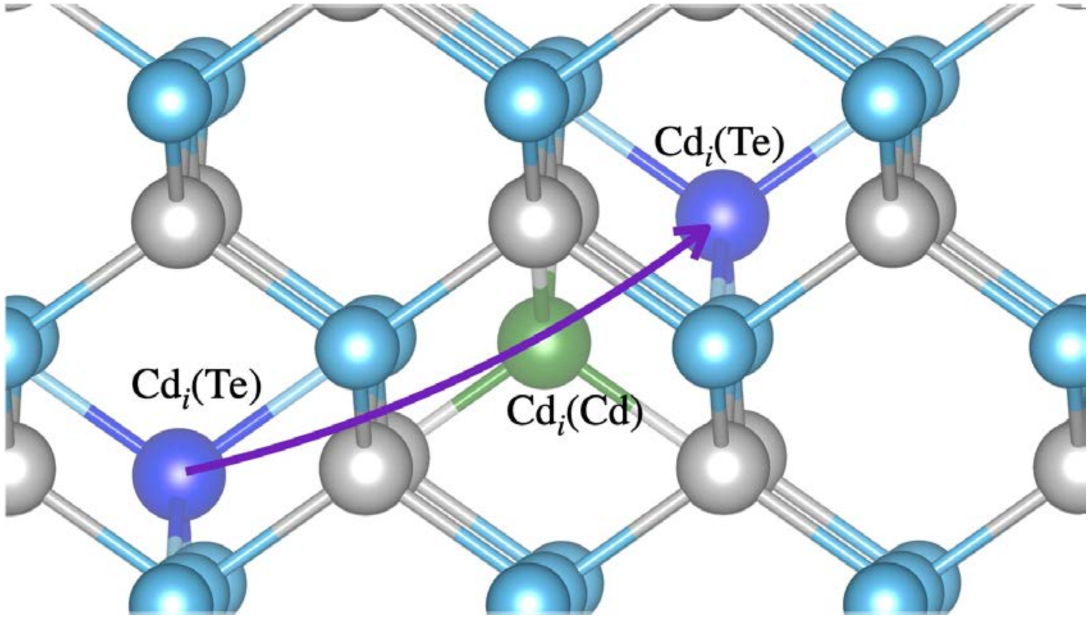


Cd interstitial is unstable!

- Cd_i has a very low migration barrier ⇒ mobile at well below RT

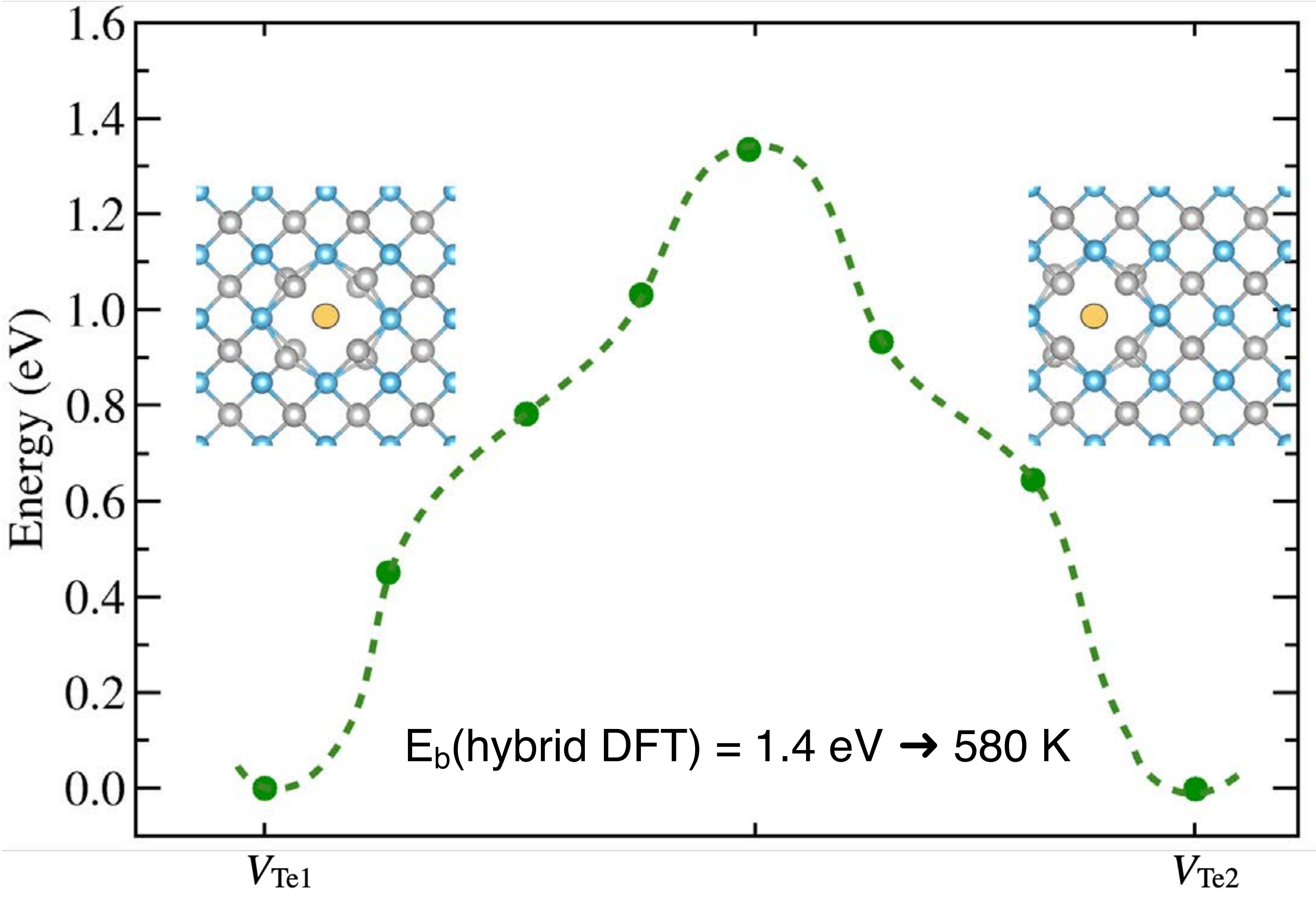
  ⇒ not likely a compensation center, will move out or form complexes





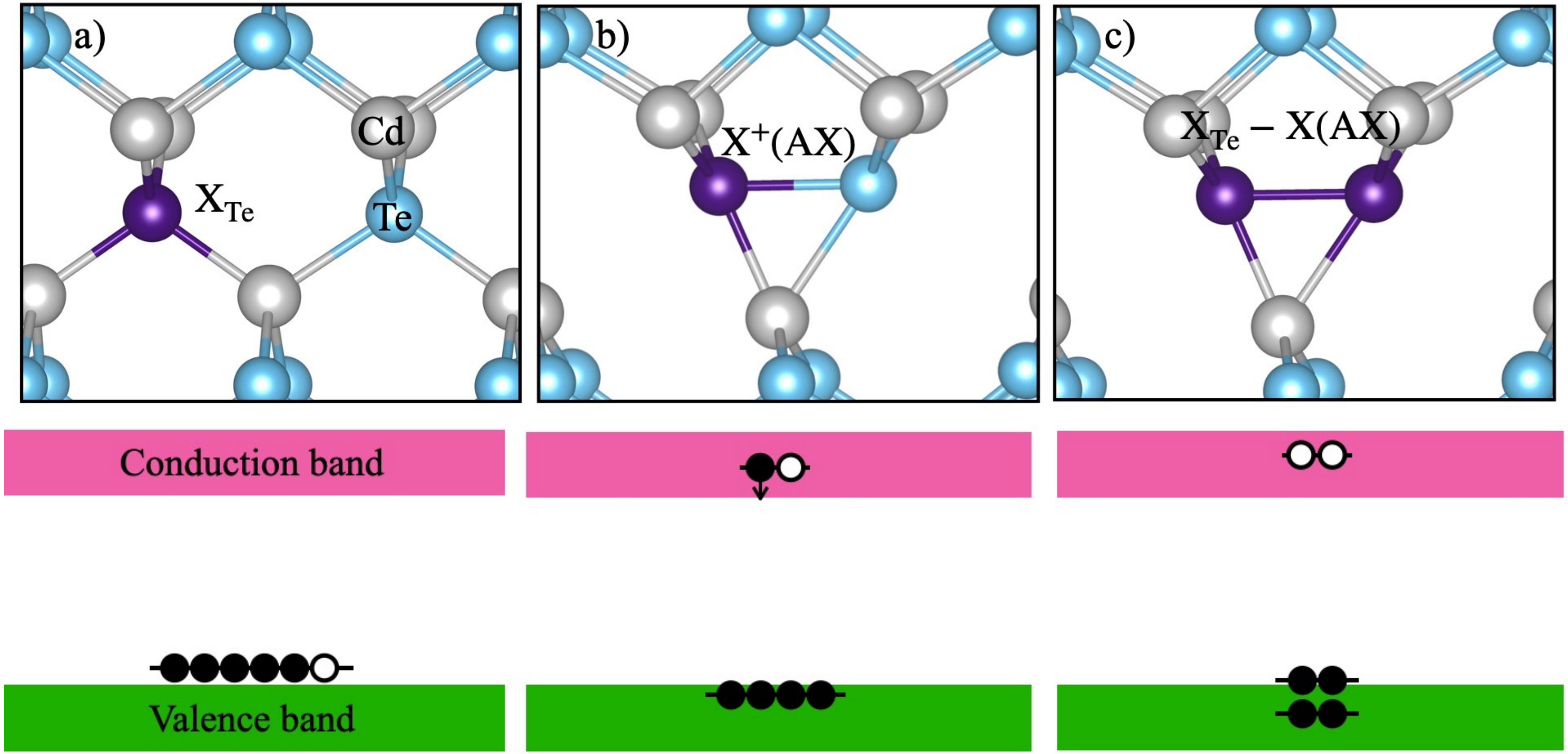
Te vacancy in CdTe

Migration path barrier



- V_{Te} becomes mobile @ 580 K
- Might need high-T annealing ($CdCl_2$ treatment)
- Compensation center in p-type CdTe
- V_{Te} can be removed by annealing post treatment of p-type CdTe layer

Formation group-V pair as possible source of compensation

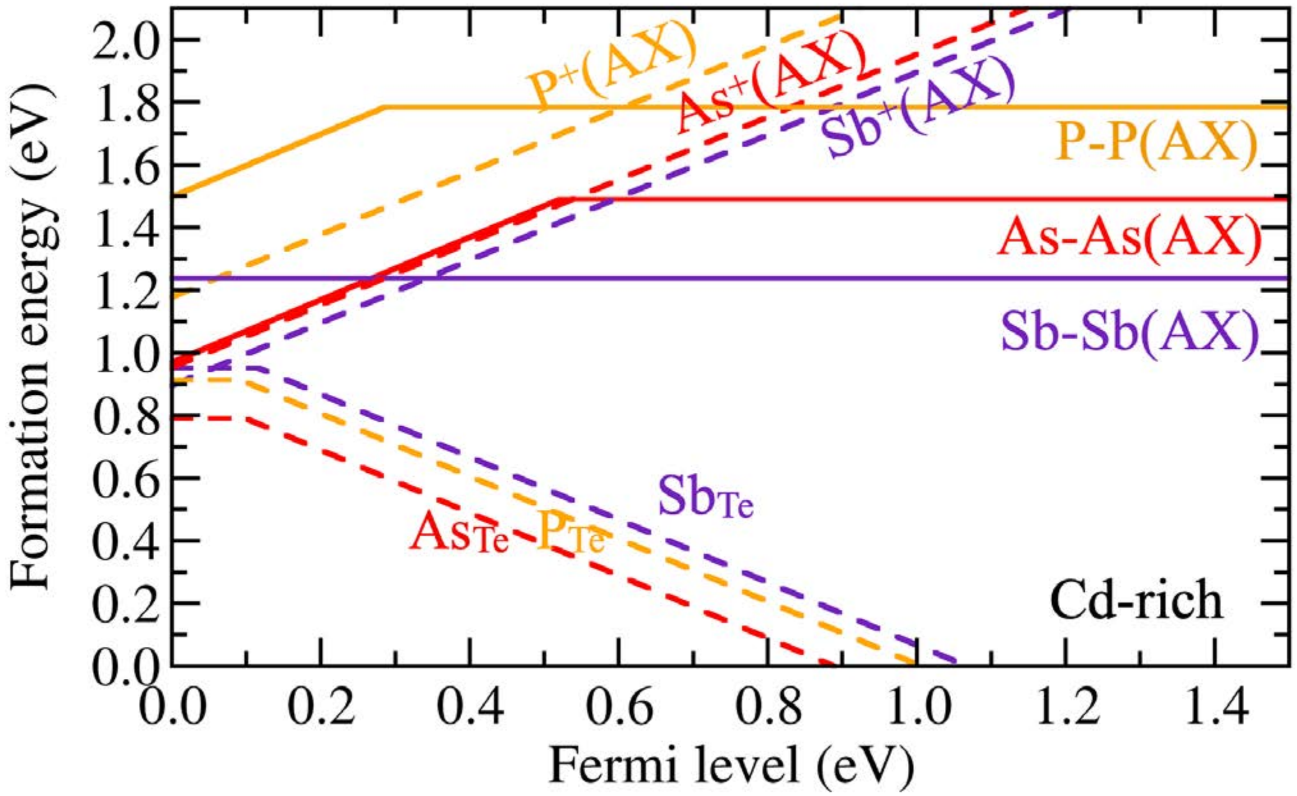


Shallow acceptor

AX center is not stable

X-X(AX) pair is electrically inactive or reduce holes

The X-X(AX) pair behave as compensation/passivation



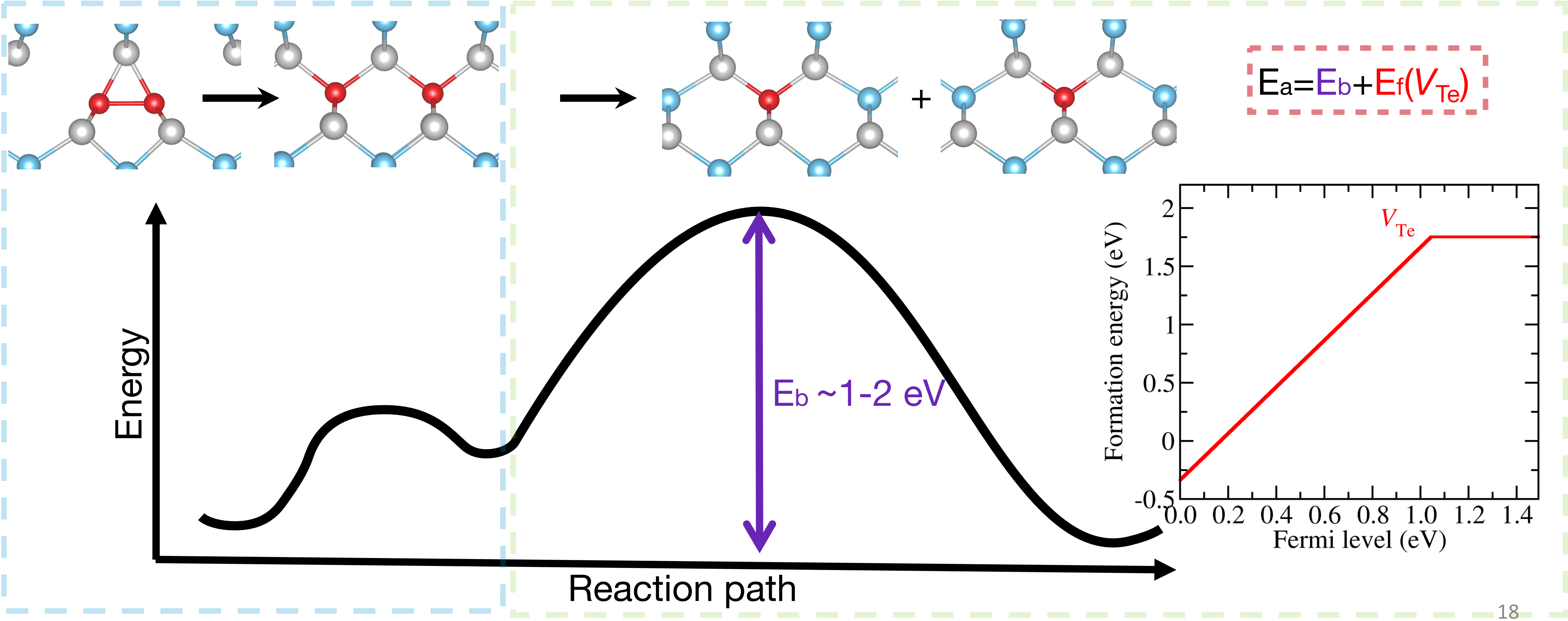
- For As and P, the X-X(AX) pair is a donor, reducing hole density in p-type CdTe
- Sb-Sb(AX) pair is electrically inactive, passivating Sb_{Te} acceptor

- They have high formation energies at *equilibrium condition* ⇒ unlikely to occur ?

- Dimer form of dopant could stabilize the X-X(AX) pair

Separation of X-X(AX) pairs involve high activation energies

- Once X-X (AX) pair is formed, barrier to dissociation is high
- Activation energy contains the barrier to separate X -X(AX) into X_{Te}-X_{Te} and to take the X_{Te} further apart
- Need a Te vacancy to move X_{Te} apart -> high activation energy



Summary

- AX center is unstable! Not a compensation center in group-V doped CdTe
- Native defects (V_{Te}) are likely the most important compensation centers
- Dopants as stable as pairs, if pairs are formed during growth

    -> lead to self-compensation
- Once formed, X-X pairs required high activation energy to dissociation into two separated acceptors
- More studies of the self-compensation mechanism of group-V doping are needed

Thank you

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