The role of native defects and their diffusivity in CdTe

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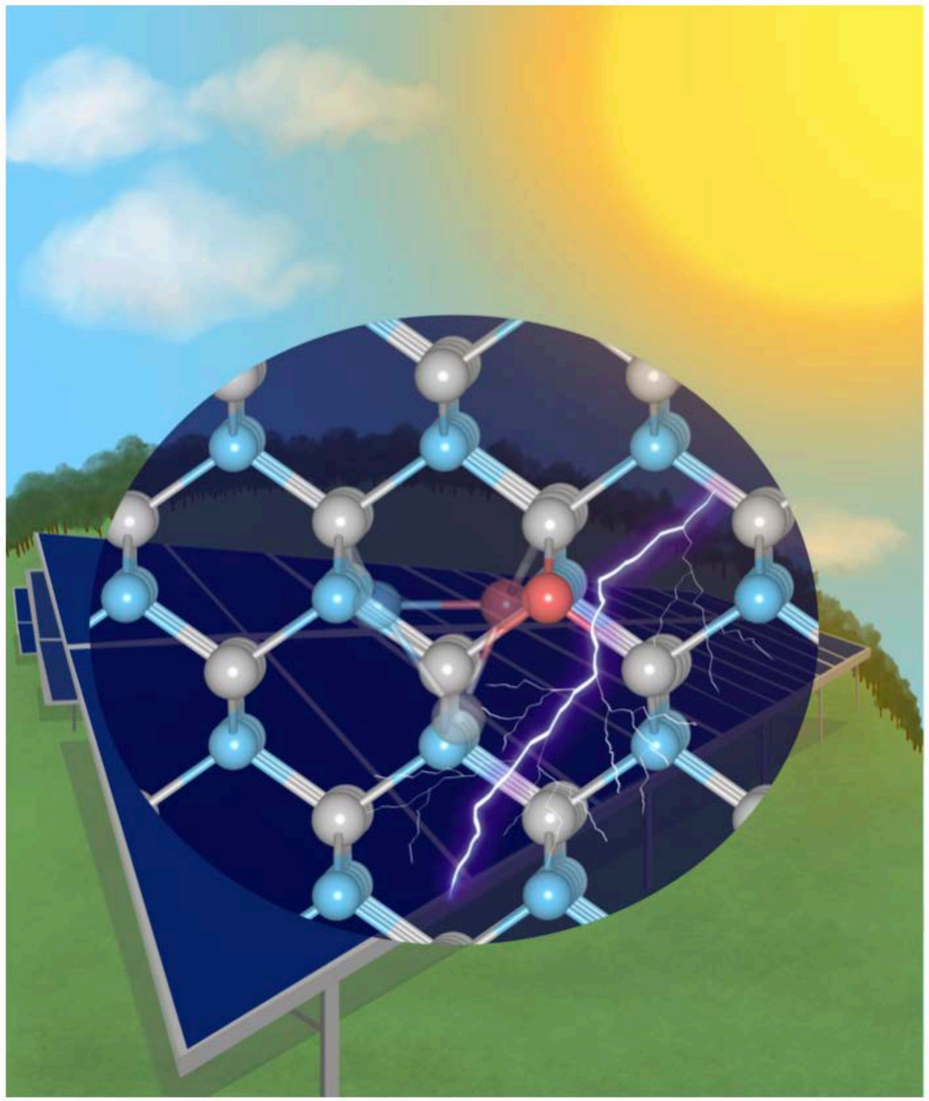

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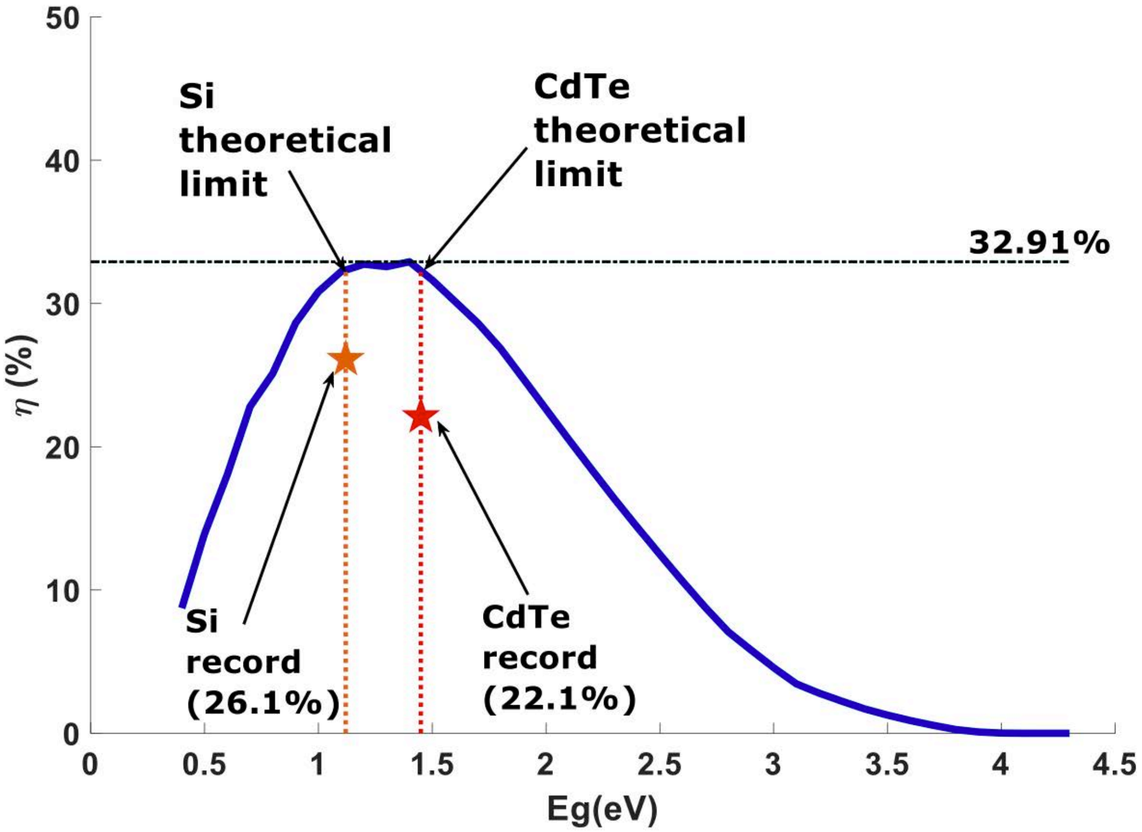
CdTe solar cells

- **Most competitive PV thin-film technology**
  - low production cost
  - simple manufacturing
  - record efficiency is 19 % for modules (First Solar)

Barbato *et. al.* J. Phys. D Appl. Phys. **54**, 333002 (2021)
First Solar Series 7, https://www.firstsolar.com/en/Modules/Series-7

- **Current record in lab > 22%**
  - low Voc (<< E_g)
  - short carrier lifetime
  - low hole concentration (~10^{14} cm^{-3})
  - defects in ***bulk*** and at interface/surface

M. Green *et at.*, Solar Cell Efficiency Tables, Progress in Photovoltaics: Research and Applications **29**, 3 (2021)



Doping and defects in CdTe

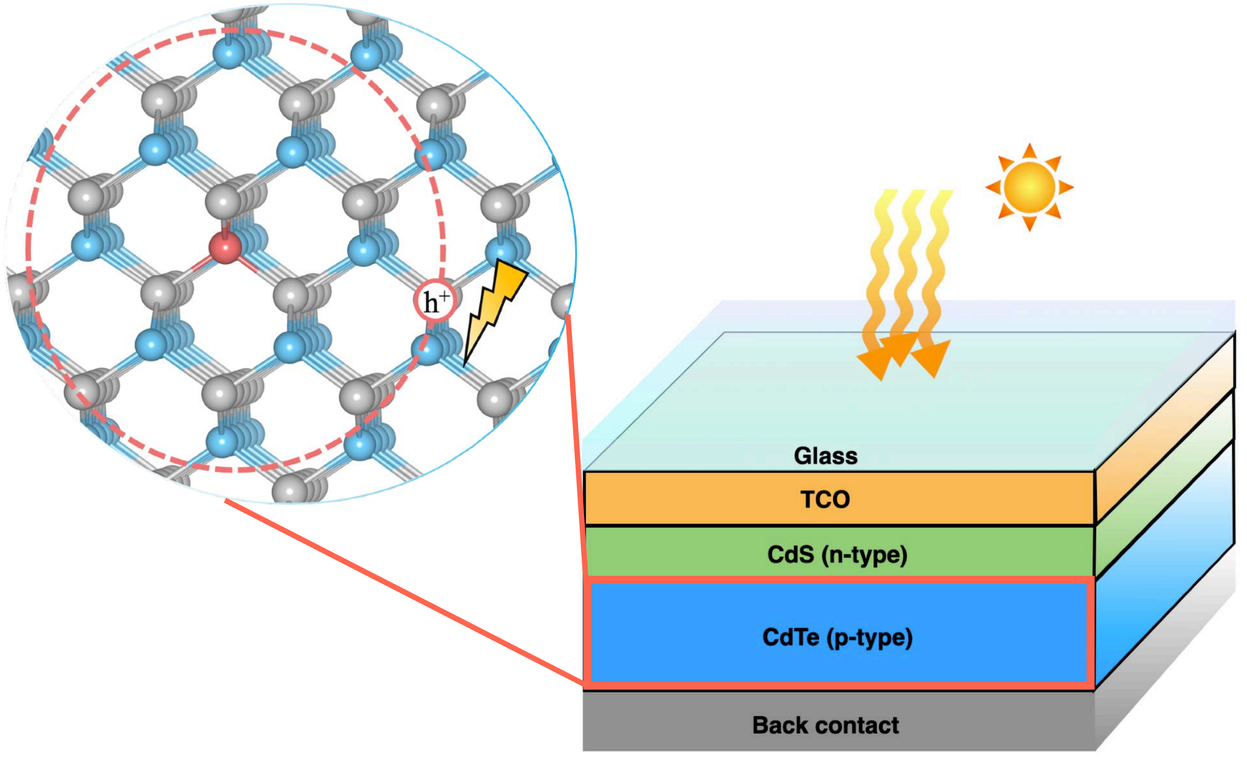
- Group-V impurities (As, P and Sb) are shallow acceptors in CdTe

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

- Observed doping efficiencies are quite low; source of hole compensation is unknown

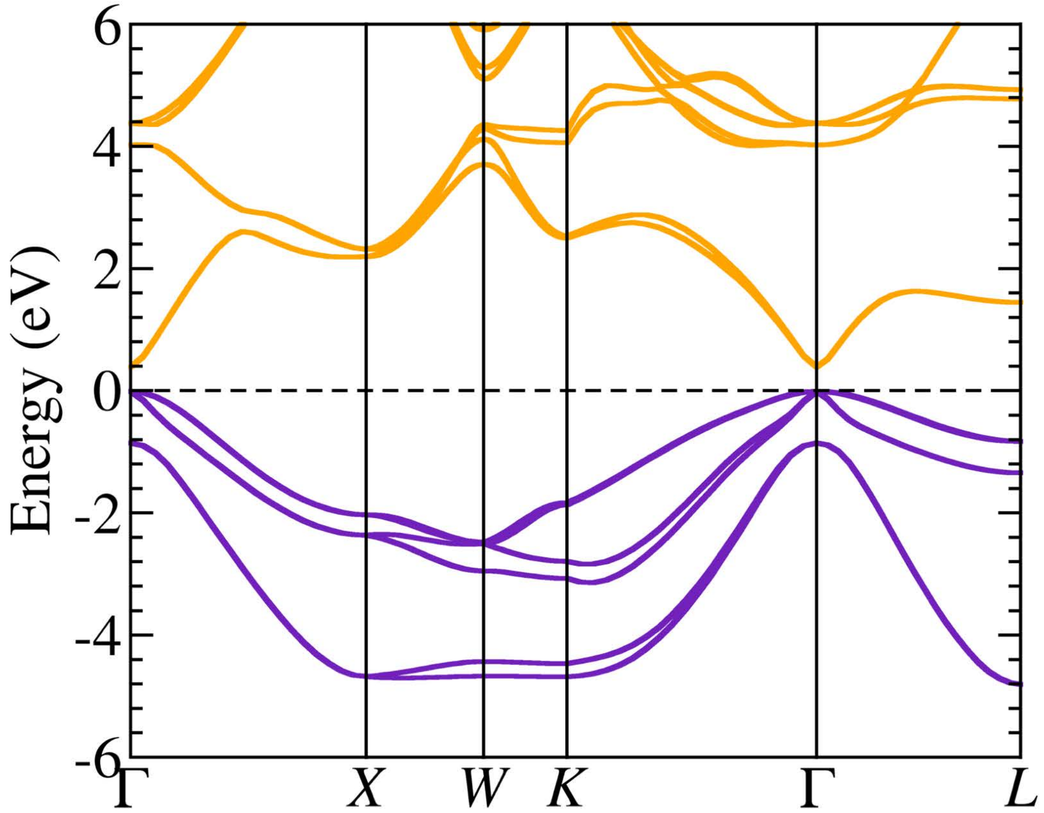
Which defects act as hole killers?
Formation energies and stability

S.-H. Wei and S. B. Zhang, Phys Rev B **66**, 155211 (2002)
M.-H. Du *et al.*, J Appl Phys **104**, 93521 (2008)
J.-H. Yang *et al.*, Semicond Sci Technol **31**, 083002 (2016)
J. Pan *et al.*, Phys Rev B **98**, 054108 (2018)
S. R. Kavanagh *et al.*, ACS Energy Lett **6**, 1392 (2021)



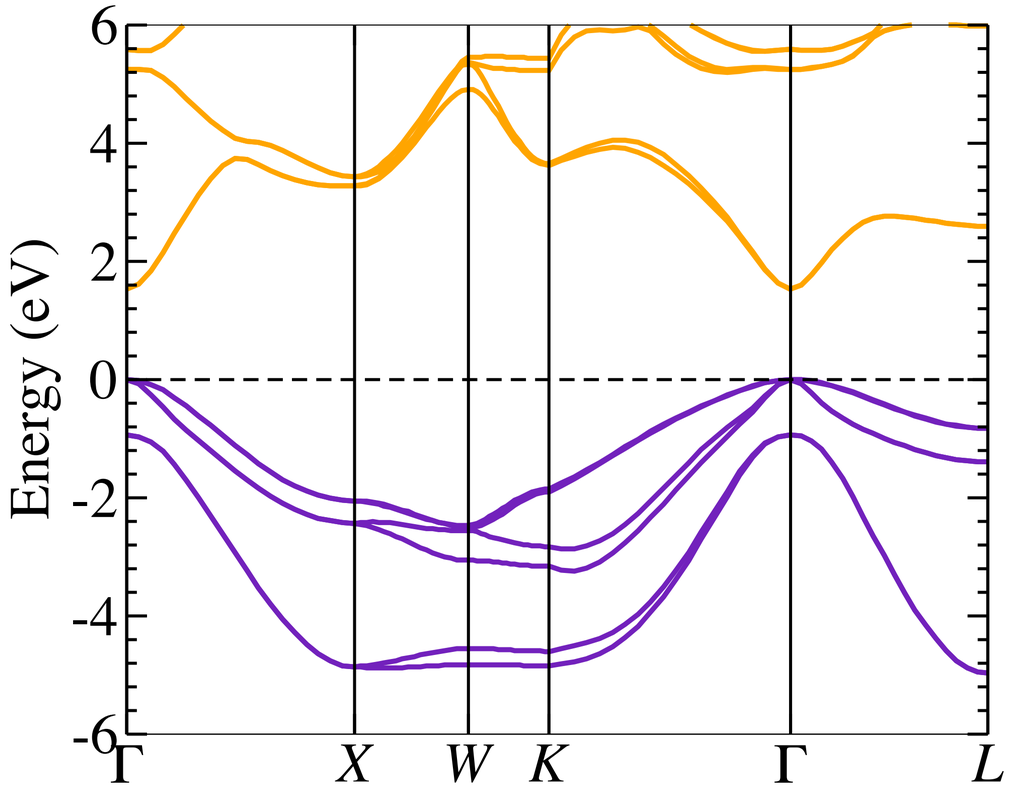
Electronic structure of CdTe

DFT-GGA + SOC



Band gap drastically underestimated

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

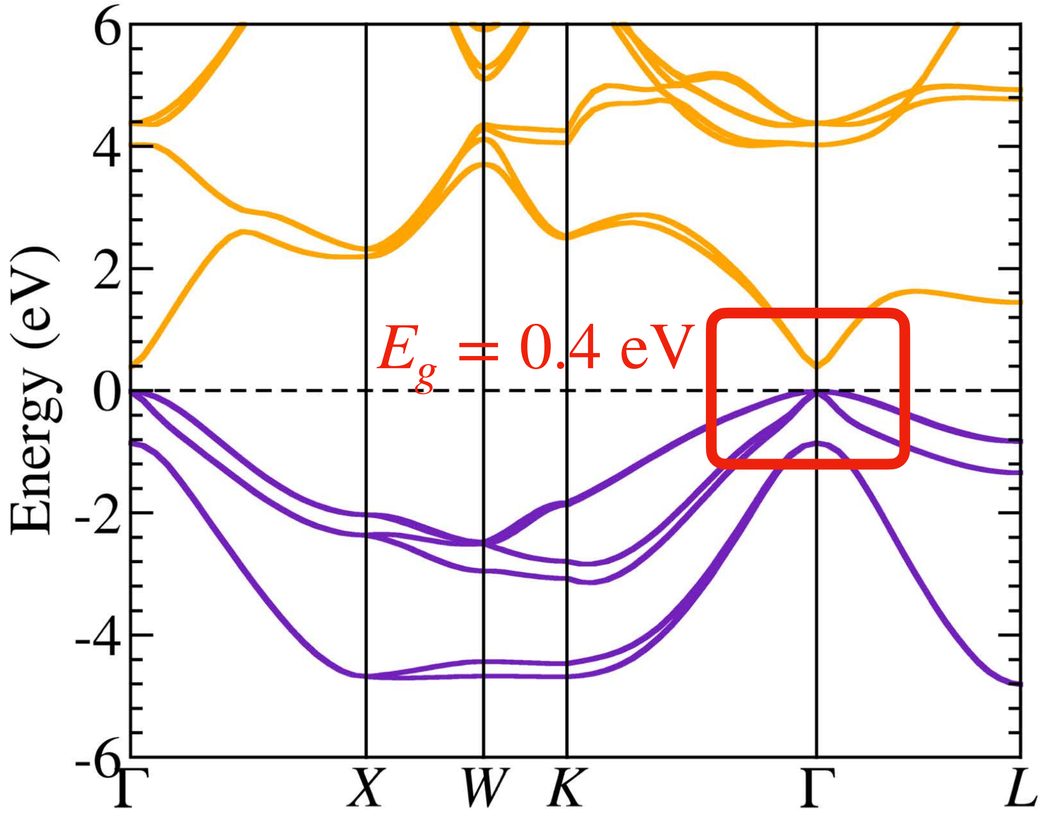


Correct band gap, effective masses, and ionization potential

I. Chatratin, B. Dou, S.H. Wei and A. Janotti, J. Phys. Chem. Lett. **14**, 273 (2023)

Electronic structure of CdTe

DFT-GGA + SOC



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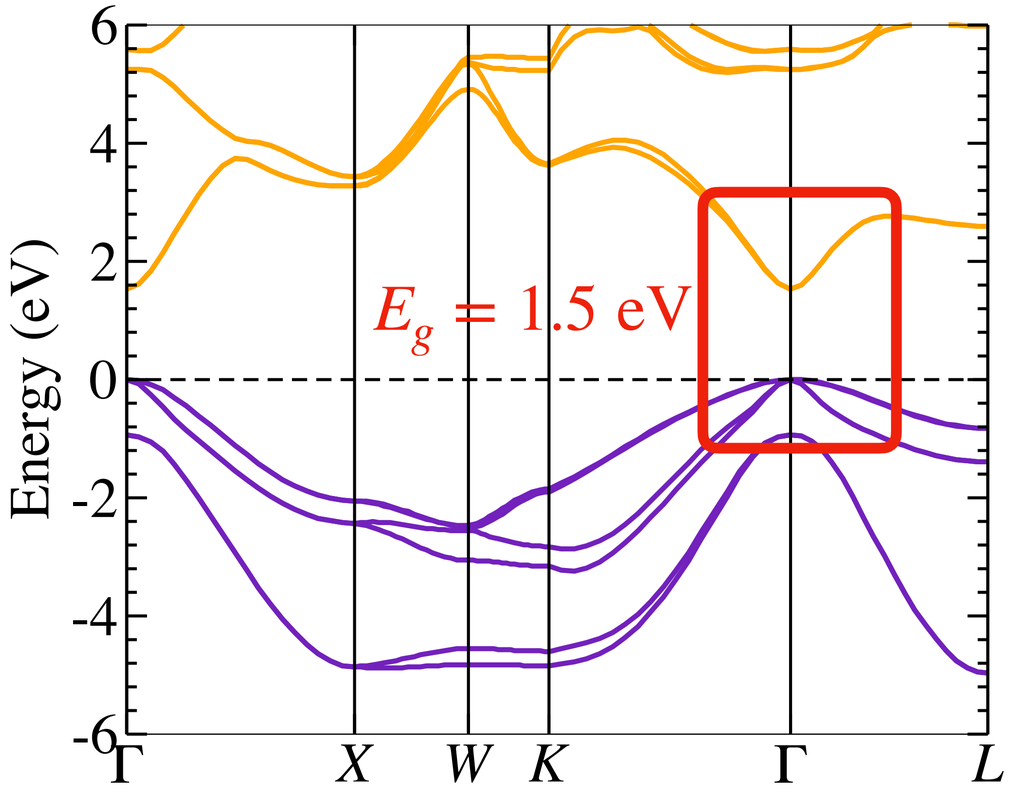
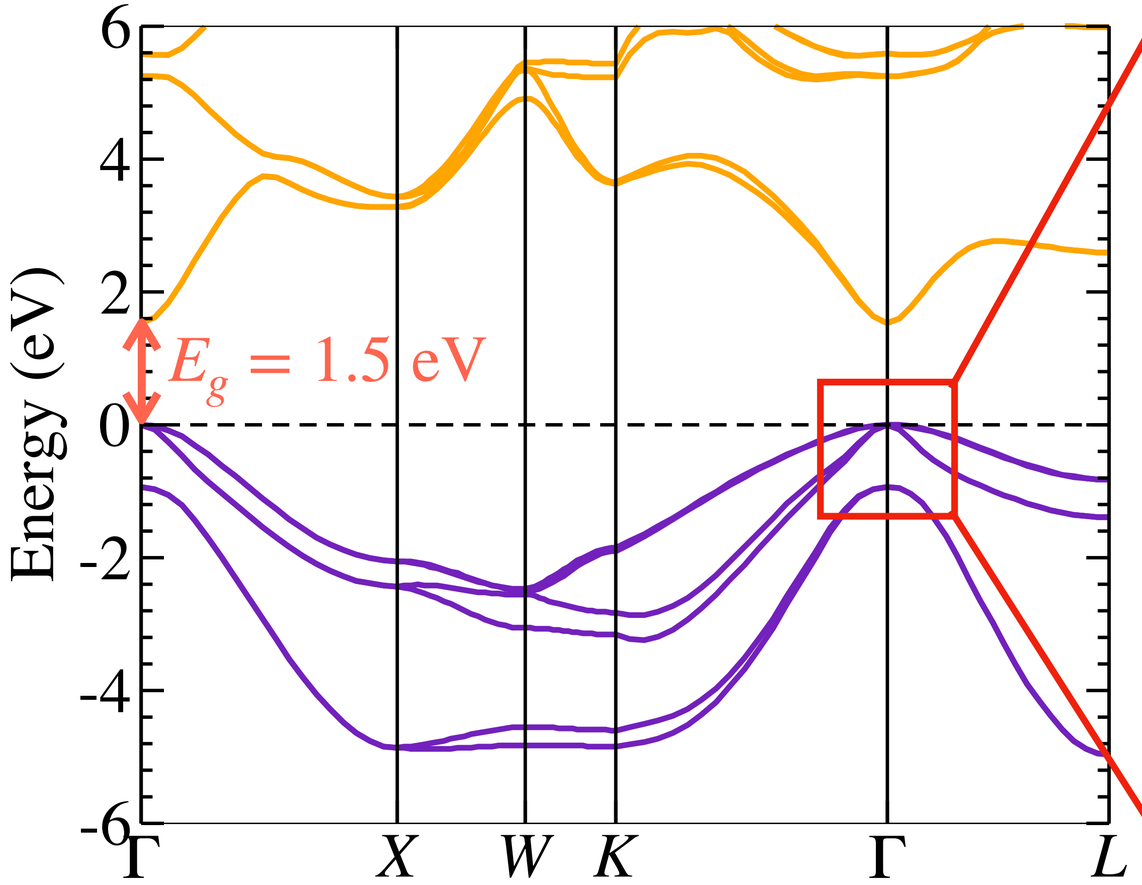


Correct band gap, effective masses, and ionization potential

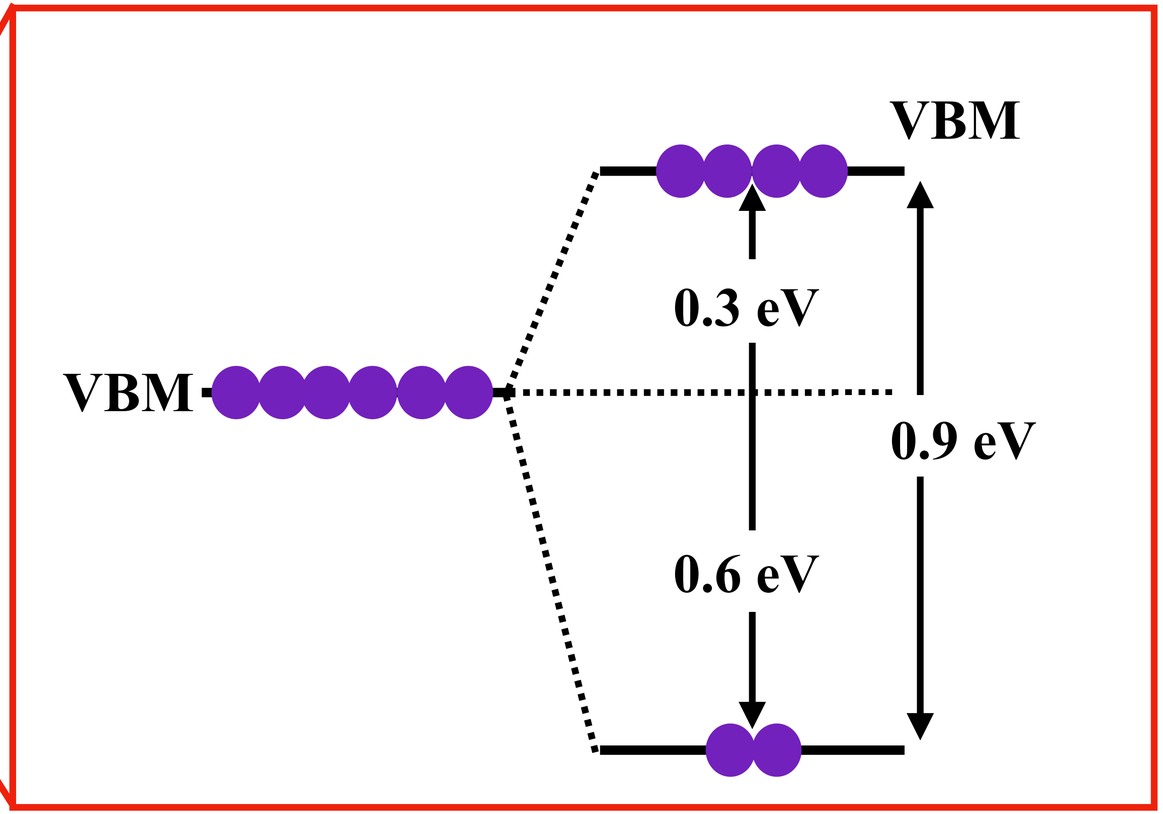
I. Chatratin, B. Dou, S.H. Wei and A. Janotti, J. Phys. Chem. Lett. **14**, 273 (2023)

Effect of spin-orbit coupling

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



Effect of SOC

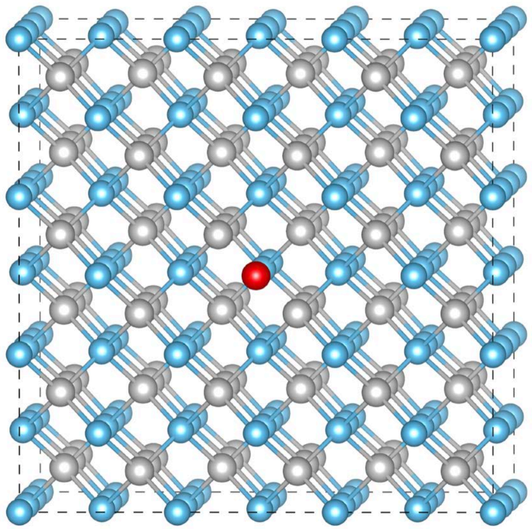


I. Chatratin, B. Dou, S.H. Wei and A. Janotti, J. Phys. Chem. Lett. **14**, 273 (2023)

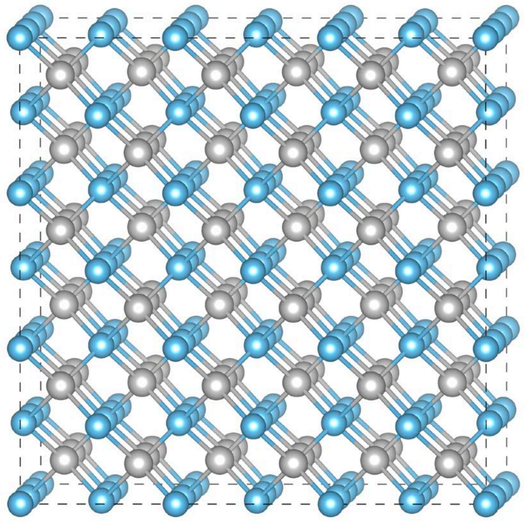
J. Pan *et al.,* Phy. Rev. B ***98***, 054108 (2018)

Formation energies of defects

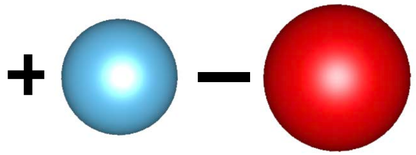
$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[bulk] + \sum_i n_i\mu_i + q(\varepsilon_f + E_{VBM}) + \Delta^q$$



supercell with
a defect in charge q



216-atom perfect
supercell



Chemical potential
Cd-rich → Cd-poor

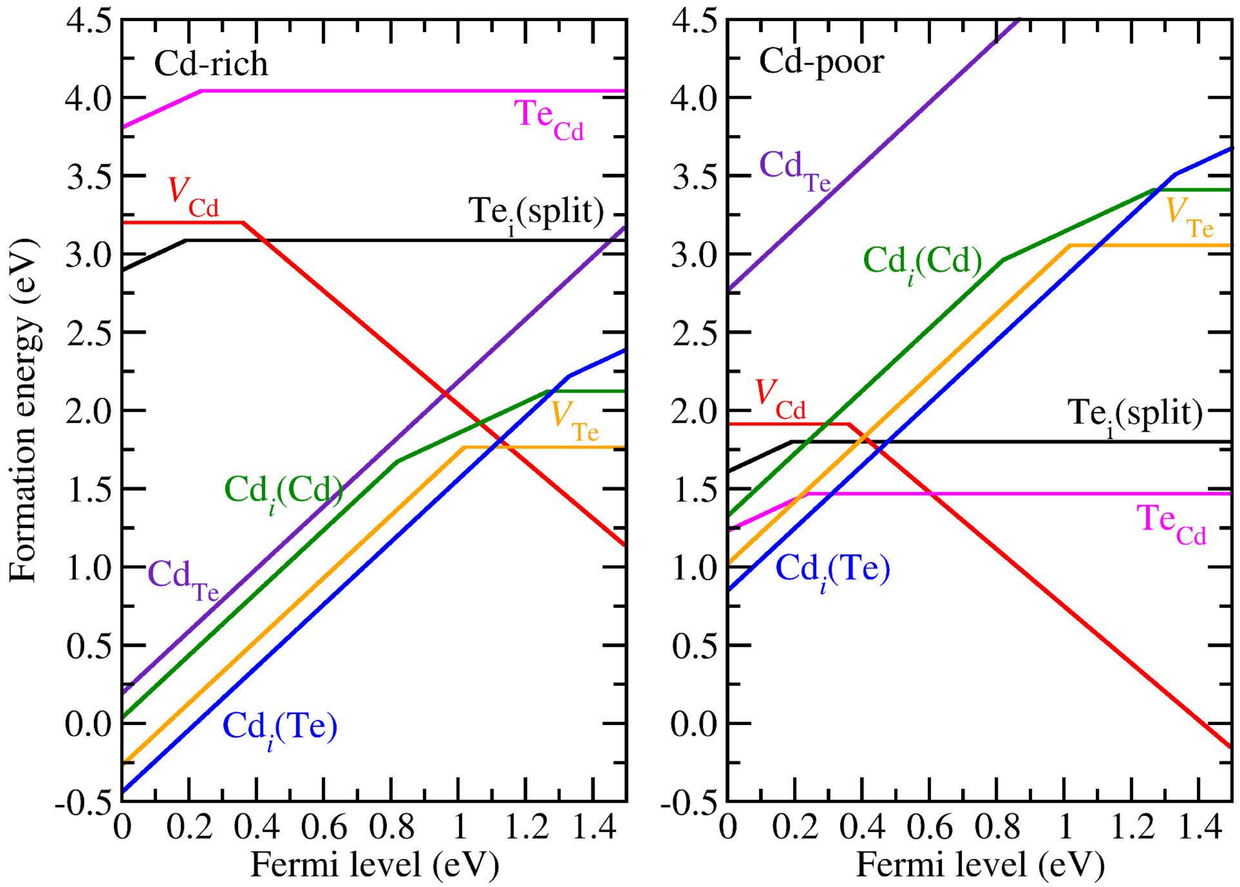
Conduction band

ε_f Fermi level

Valence band

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

Formation energies of native defects in CdTe

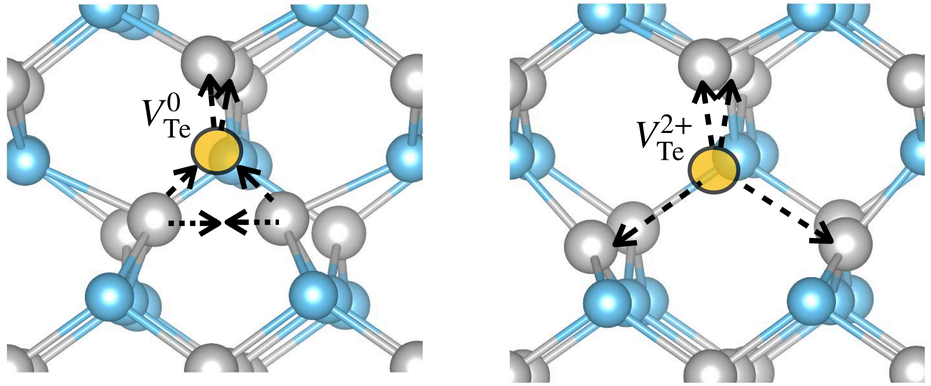


Similar to previous calculations, but not quite

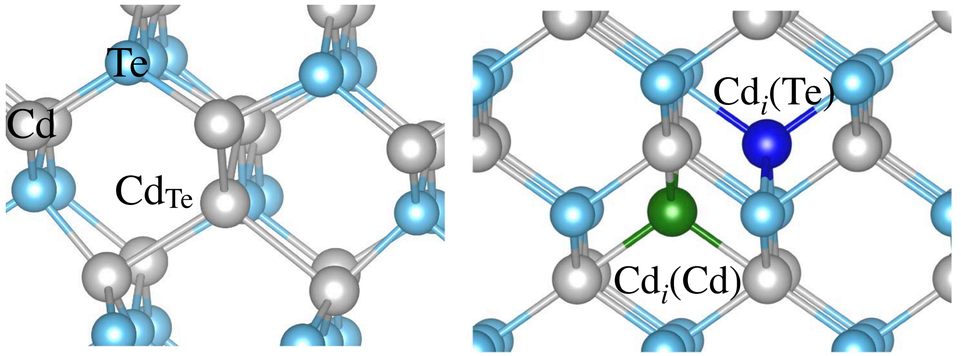
J.-H. Yang *et al.*,Semicond Sci Technol **31**, 083002 (2016)
J. Pan *et al.*, Phys Rev B **98**, 054108 (2018)
S. R. Kavanagh *et al.*, ACS Energy Lett **6**, 1392 (2021)

Cd-rich conditions

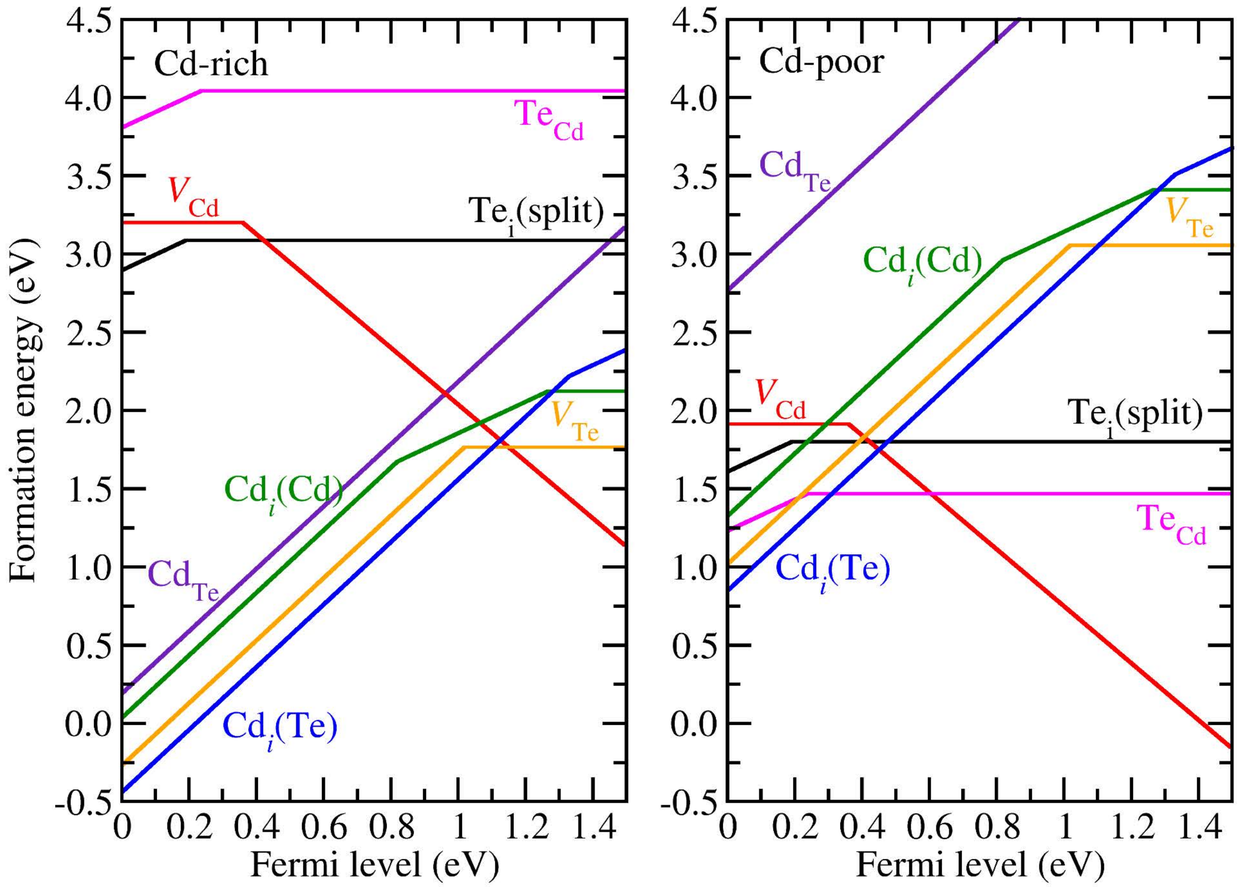
- Lowest energy defects are donors
  ⇒ Cd$_i$ V_{Te} Cd$_{Te}$
- V_{Te} is deep donor with (2+/0) at 1.0 eV



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

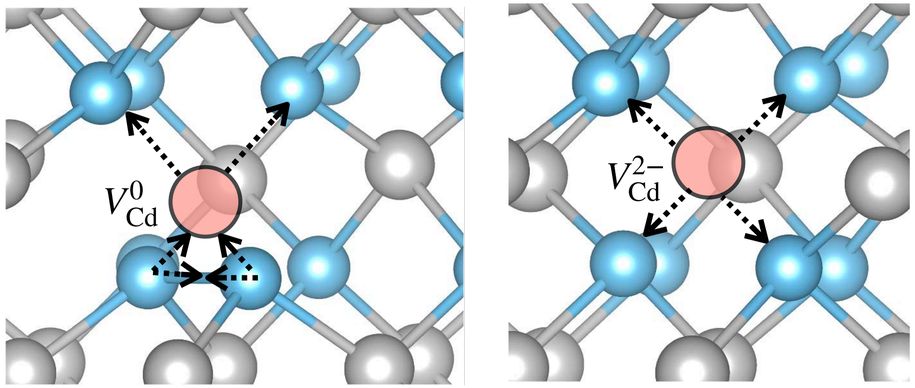


Formation energies of native defects in CdTe



Cd-poor conditions

- Cd_i, V_{Te} and Te_{cd} are the lowest energy defects in p-type CdTe
- V_{Cd} is the dominant acceptor in *n*-type CdTe
- V_{Cd} is deep acceptor with (0/2-) at 0.36 eV
  ⇒ cannot lead to *p*-type conductivity



- ***Without external dopants, CdTe cannot be p-type***
- ***Increasing hole concentration must rely on Group-V (As, P, and Sb) doping***

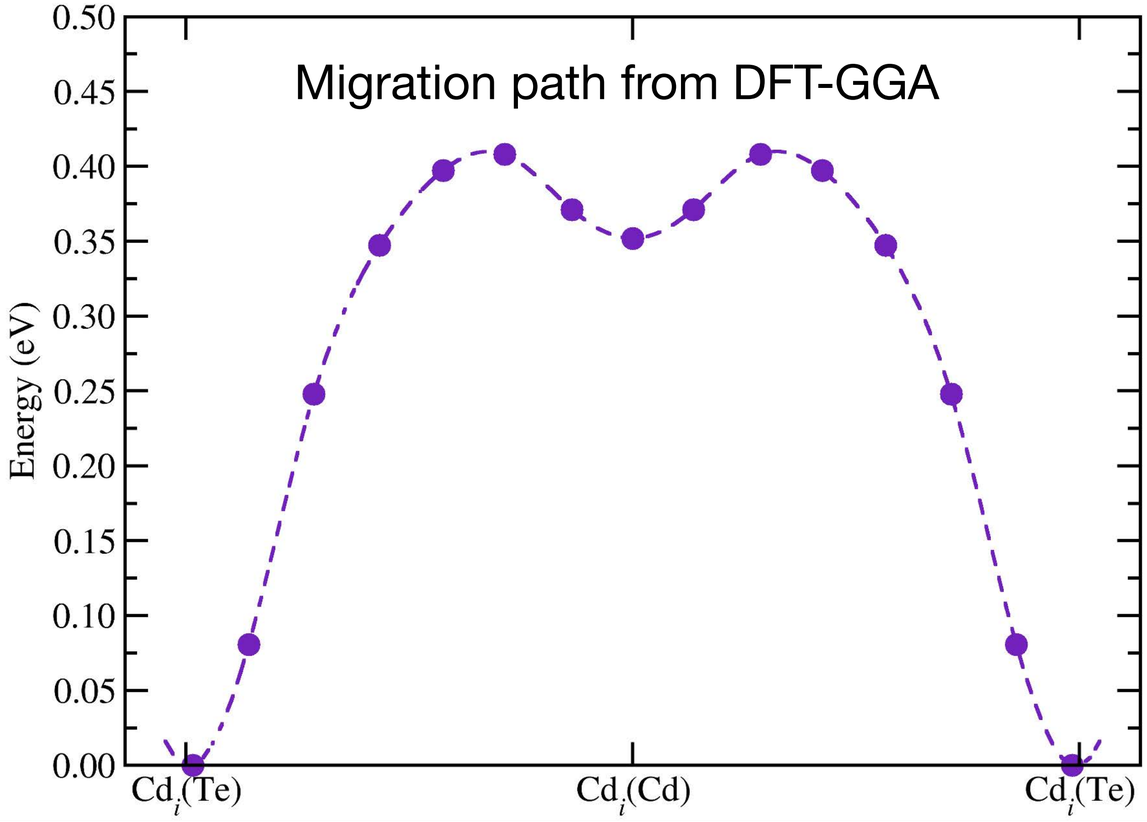
Cd interstitial stability

$\Gamma = \Gamma_o e^{-E_b/k_B T}$, assuming Γ_o=5 THz

- Cd_i has a very low migration barrier

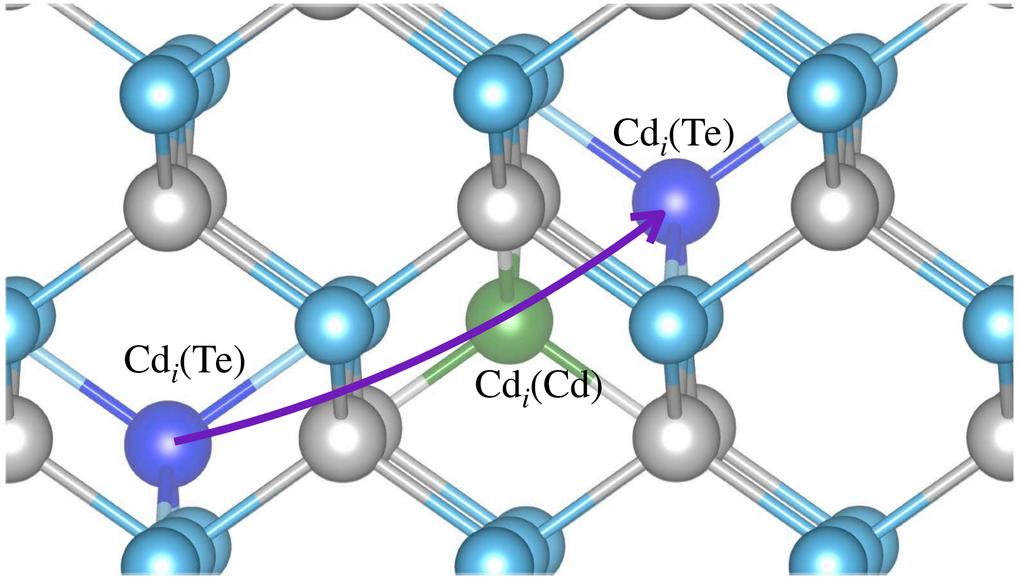
  ⇒ unstable

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

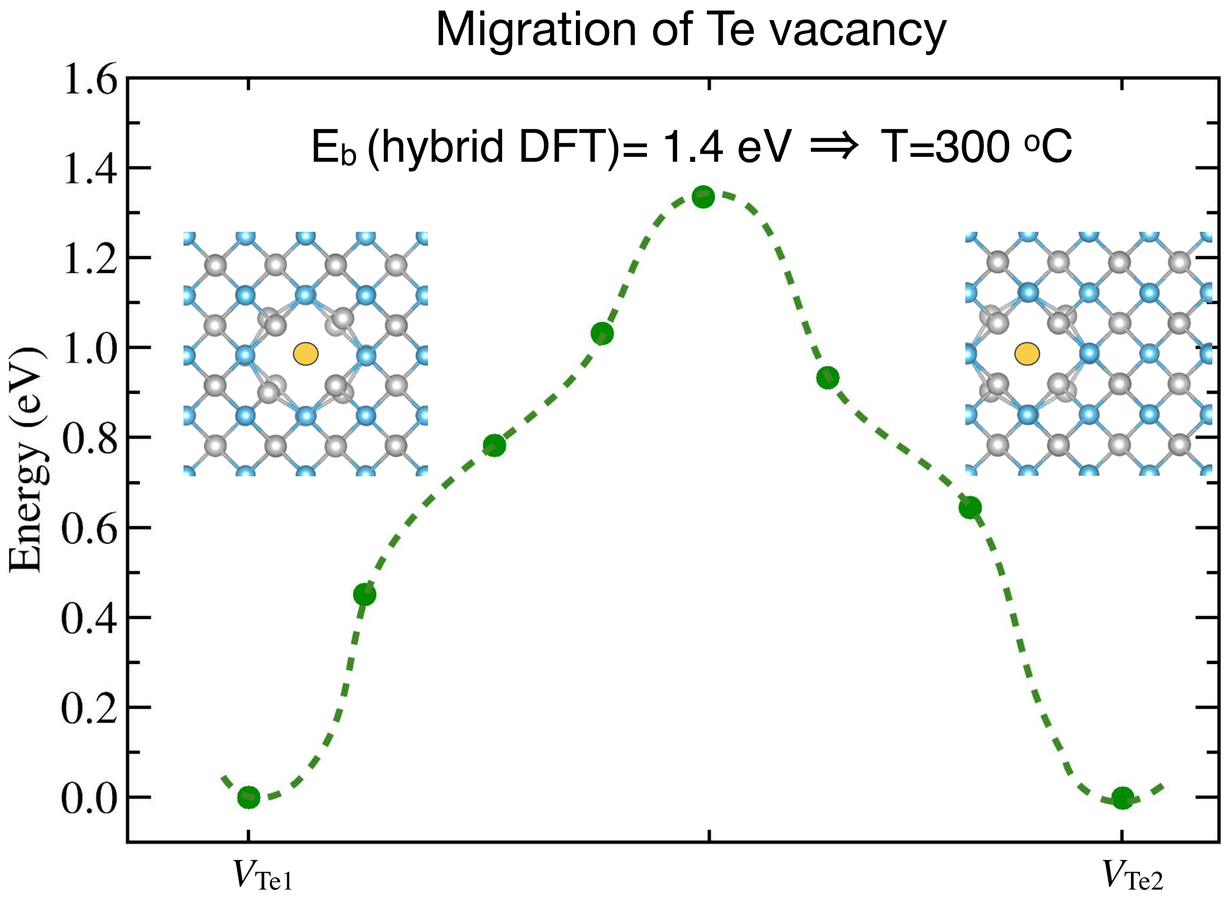


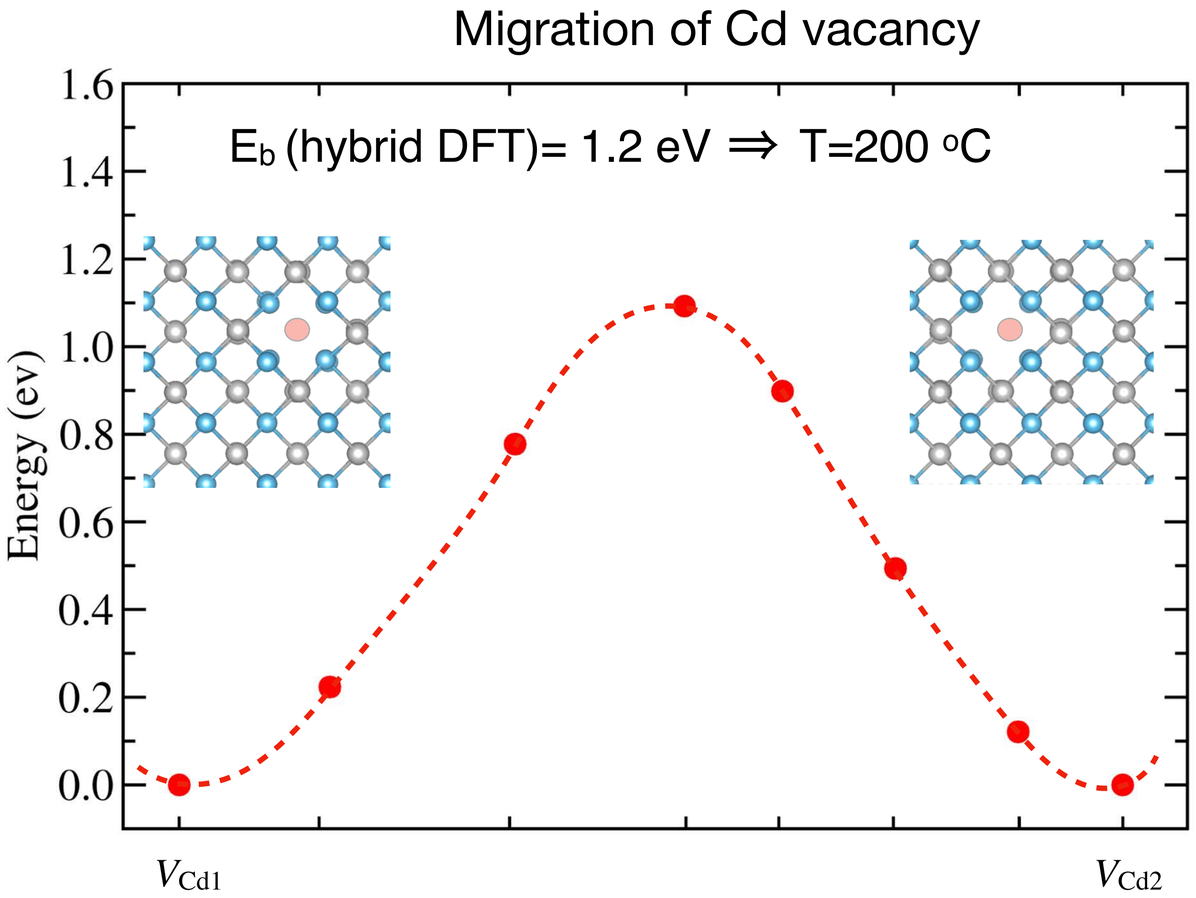
E_b(hybrid DFT) = 0.5 eV

⇒ mobile at well below RT



Te and Cd vacancies





- The vacancies are stable at the room temperature
- V_{Te} limits hole concentration, acting as a stable compensation center
- V_{Cd} is more mobile than V_{Te}
- V_{Te} may survive post-treatment of p-type CdTe layer ($CdCl_2$ treatment and annealing at 400-500°C)

J. D. Major *et al.*, Nature **511**, 334 (2014)

Summary

- To explain the electronic properties of CdTe, the inclusion of SOC and the additional Hartree Fock mixing of 33% is required
- For p-type CdTe growth under Cd-rich conditions, Te vacancy is a limiting defect, decreasing hole concentration
- Cd_i is not stable at room temperature and is not a compensation center in *p*-type CdTe
- Cd vacancies is a deep acceptor; cannot lead to *p*-type conductivity

Thank you

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