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Band Energy Dependence of Defect Formation in the Topological Semimetal Cd_3As_2

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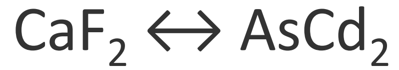
Cd_3As_2 structure

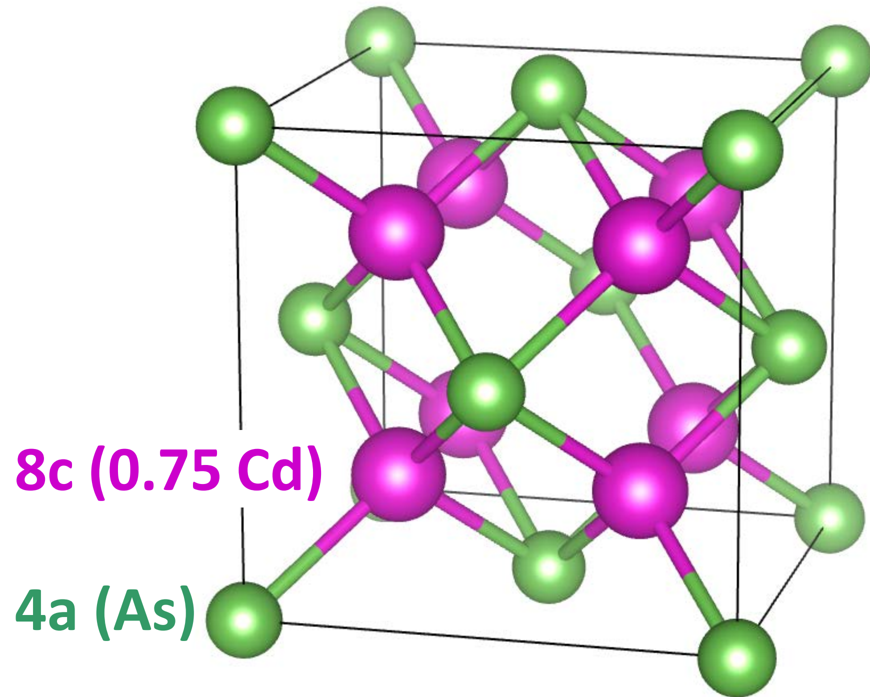
Fluorite structure (sg 225)

$CaF_2 \leftrightarrow AsCd_2$

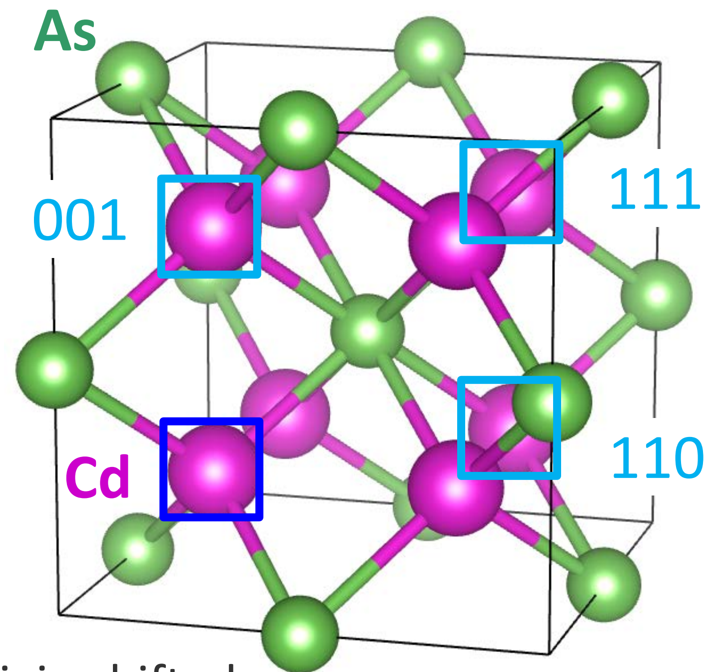


Conventional cell: 12 atom (sc)

Primitive cell: 3 atom (fcc)

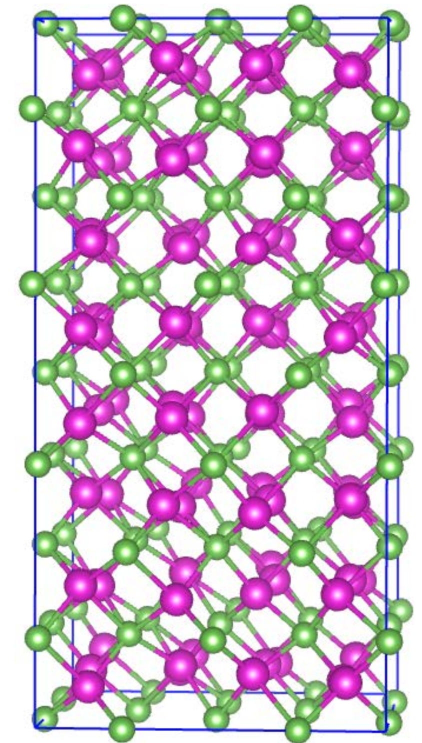


2 empty sites per sc cell
for Cd_3As_2 stoichiometry



origin shifted
by (0.5, 0.5, 0.5)

ground state
sg 142, centrosymmetric
no spin splitting
80 atom primitive cell



Ali *et al*, Inorg Chem 53, 4062 (2014)

Unintentional *n*-doping in Cd_3As_2

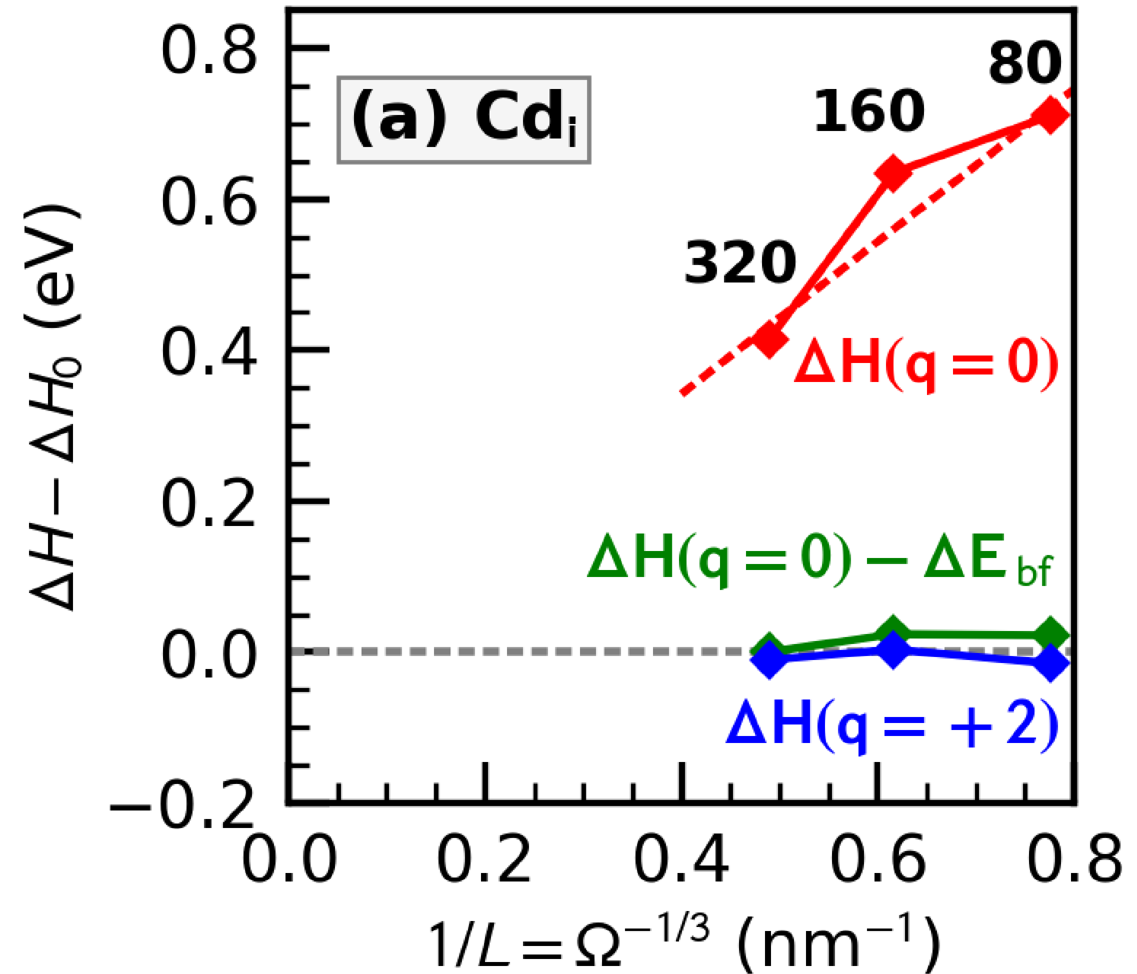
First principles defect calculations

- Cd interstitial on empty site
- Cell size dependence
  80 to 320 atoms
- DFT-PBE functional (vasp)
- DFT-SCAN + spin-orbit
- QSGW electronic structure (questaal)

Defect formation energy

- Charged states in semiconductors
- In metals usually only neutral (q=0)

$$\Delta H_{\mathrm{D},q}(E_{\mathrm{F}},\{\mu\}) = [E_{\mathrm{D},q} - E_{\mathrm{h}}] + \sum_{\alpha} n_{\alpha}\mu_{\alpha} + qE_{\mathrm{F}}$$

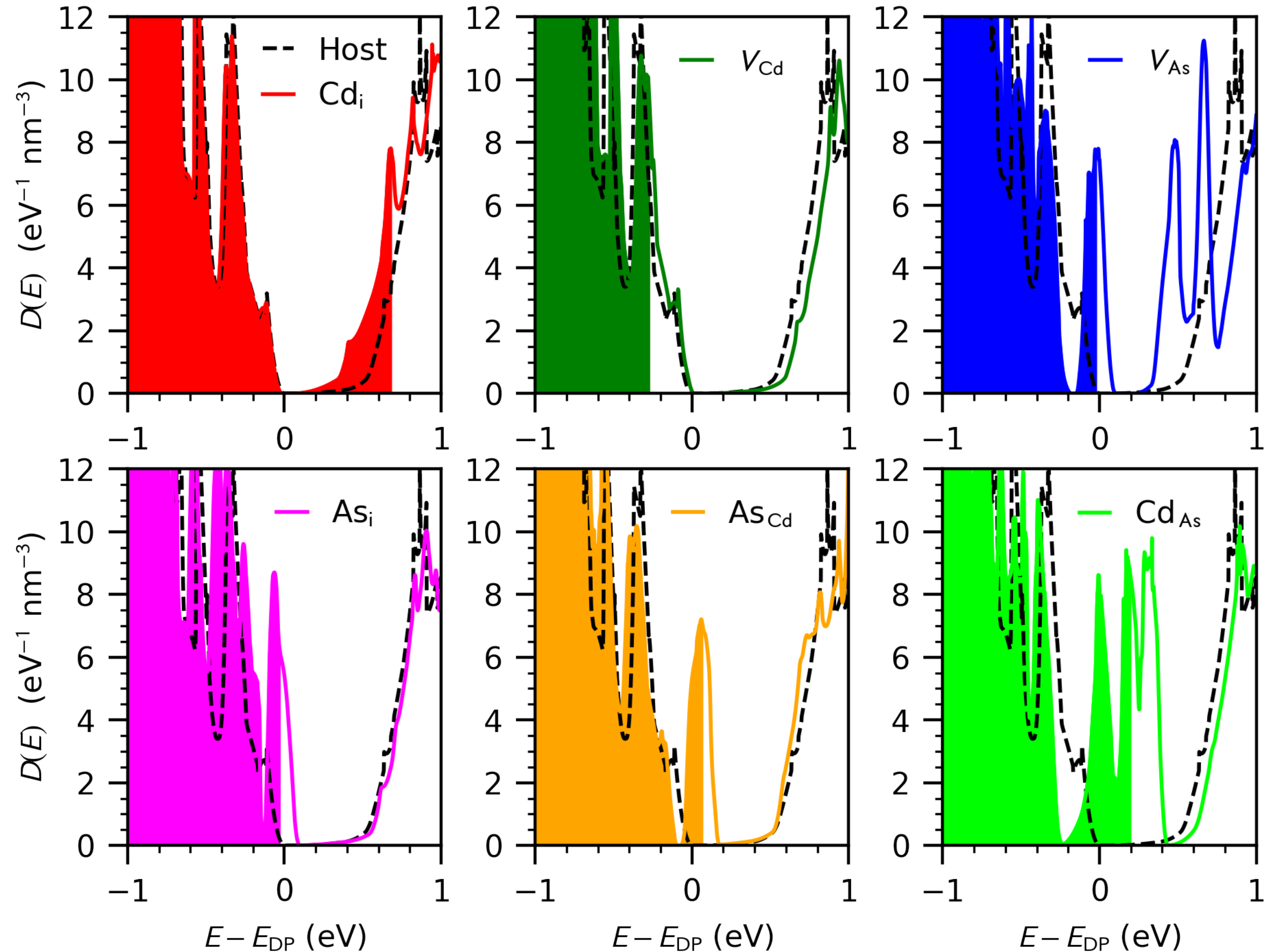


Brooks *et al*, under review

DOS

Defect behavior

- Defect state vs band continuum
- Cd_i donors
- V_{Cd} acceptor
- V_{As} amphoteric

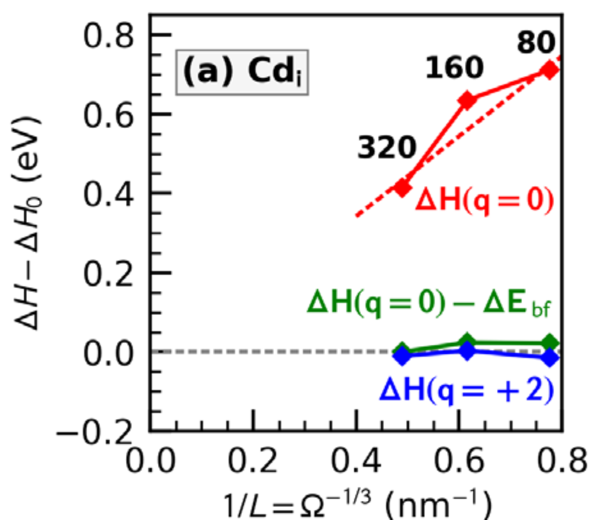


Origin of cell size dependence of ΔH_D

$$\Delta E_{\mathrm{bf}} = \sum_{\substack{n,\mathbf{k} \\ \varepsilon_{n,\mathbf{k}} > E_{\mathrm{DP}}}} w_{\mathbf{k}} f_{n,\mathbf{k}} (\varepsilon_{n,\mathbf{k}} - E_{\mathrm{DP}})$$

Band filling energies

- Dopant donates electrons
- Concentration dependence
- BF energy recovers charged defect ΔH_D
- Cd_i^0 better described as Cd_i^{2+} + 2e



$E_{F,\ defect}$

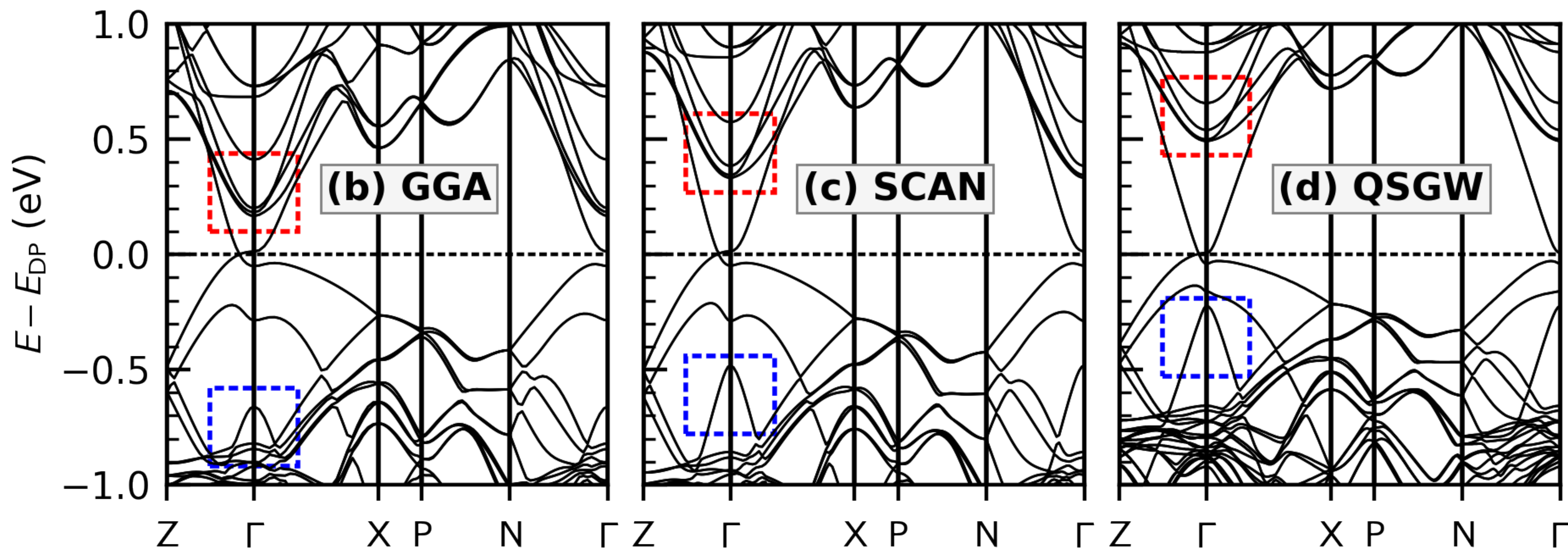
ΔE_F

$E_{F,\ host}$

Z Γ X

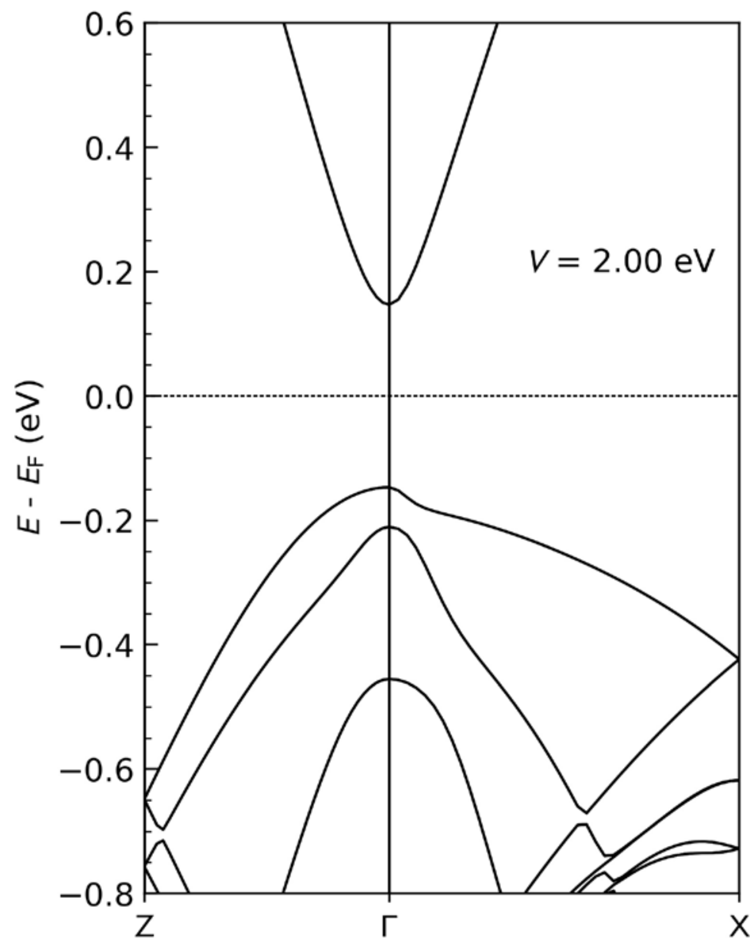
Z Γ X

Electronic structure: Level of theory



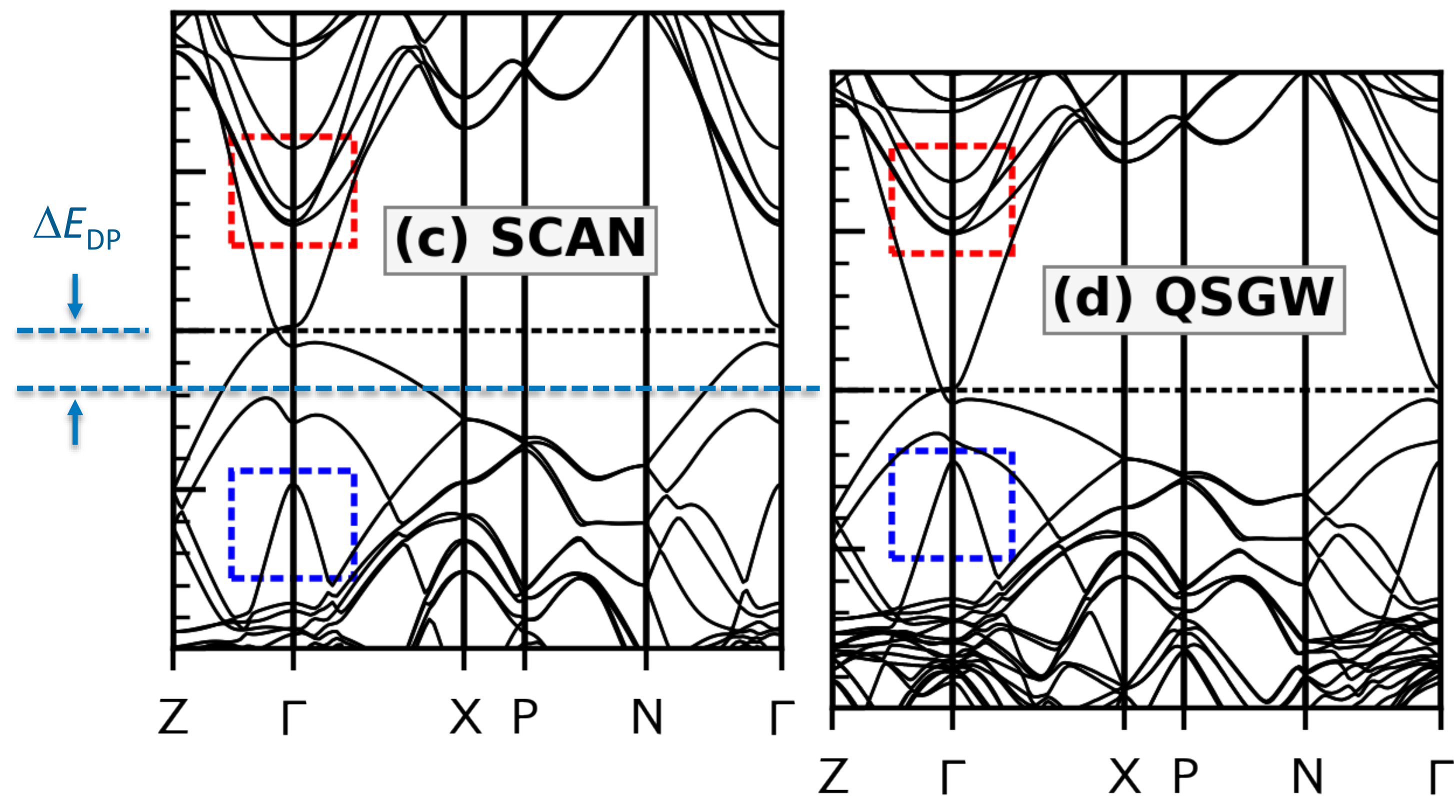
- SCAN lies halfway between standard DFT (GGA) and QSGW
- Upward shift of *s*-like Cd and As states, analogous to semiconductors
- Offset ΔE_{DP} –0.19 eV on absolute energy scale

Electronic structure: Band inversion and absolute energy scale



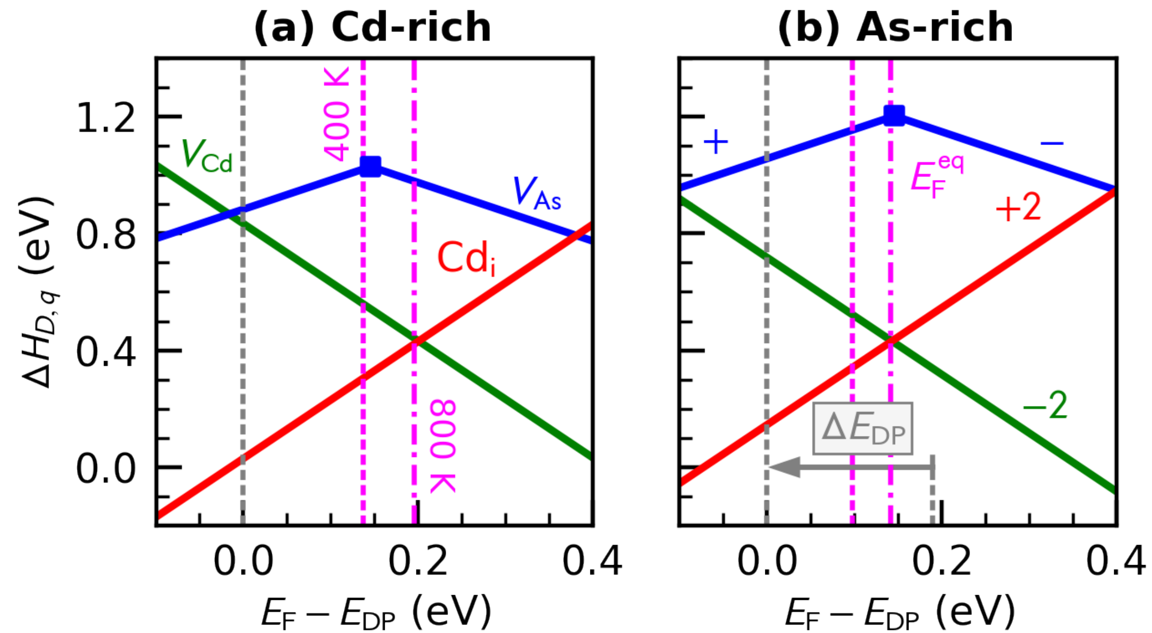
Cd-*s* and As-*s* onsite potential

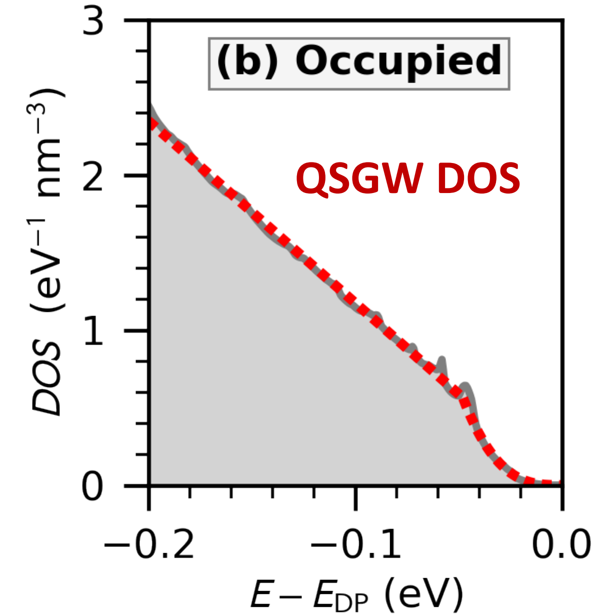
$$\hat{V} = \sum_{i,j} \left| p_i \right\rangle \left\langle \phi_i^{AE} \right| V_s \left| \phi_j^{AE} \right\rangle \left\langle p_j \right|$$

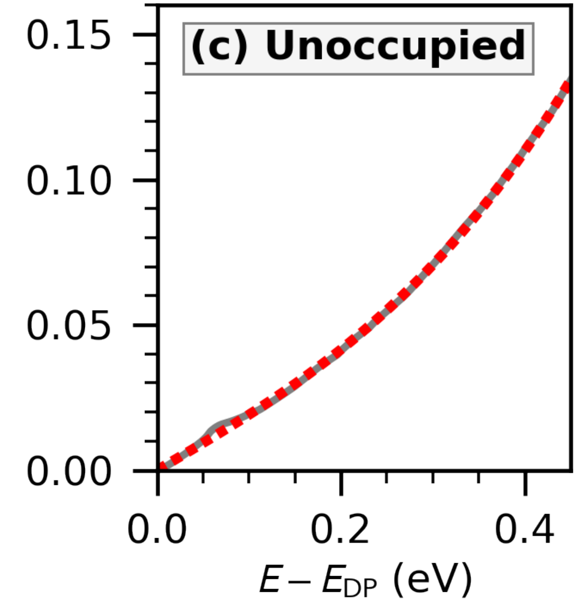


Offset ΔE_{DP} –0.19 eV on absolute energy scale

Defect equilibria







- Cd_i and V_{Cd} are dominant defect, difference determines doping
- Defect equilibrium with charge balance (defects and carriers)

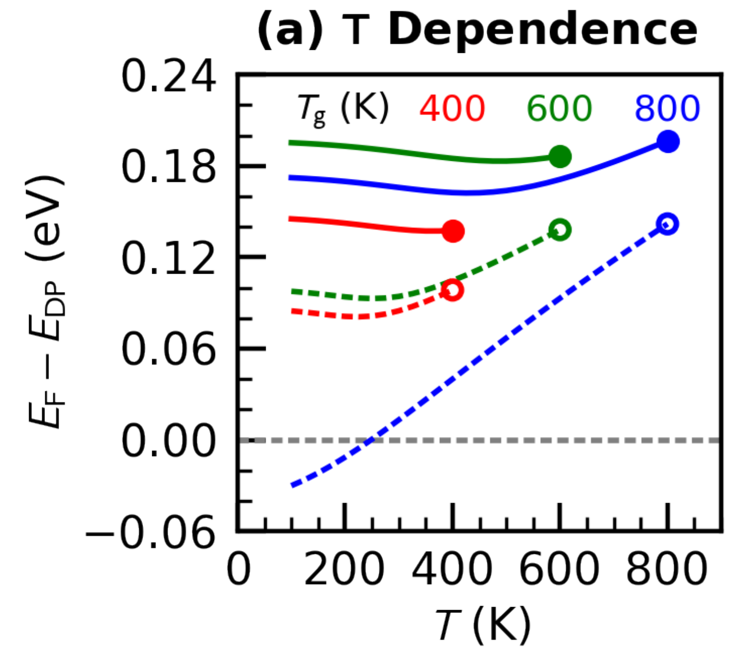
$$c_{\mathrm{D},q}(E_{\mathrm{F}}, \{\mu\}, T) = N_{\mathrm{D}} e^{-\Delta H_{\mathrm{D},q}(E_{\mathrm{F}}, \{\mu\})/k_{\mathrm{B}}T}$$

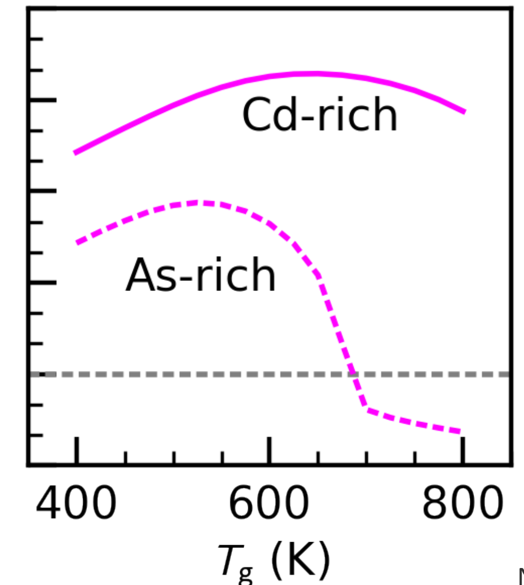
$$n_{\mathrm{e}} = \int_{E_{\mathrm{DP}}}^{\infty} \frac{g_{\mathrm{QSGW}}(E)}{e^{(E-E_F)/k_{\mathrm{B}}T} + 1} dE$$

Doping type inversion

Cd/As rich	T_g (K)	c_D (cm^{-3}) Cd$_i$	V_{Cd}	V_{As}	c_{nd} (cm^{-3})
Cd	400	1.0×10^{18}	8.2×10^{14}	1.3×10^{9}	2.0×10^{18}
	600	3.0×10^{18}	1.2×10^{18}	3.0×10^{13}	3.7×10^{18}
	800	1.6×10^{19}	1.5×10^{19}	4.6×10^{15}	2.9×10^{18}
As	400	3.5×10^{17}	2.4×10^{15}	2.2×10^{7}	6.9×10^{17}
	600	2.1×10^{18}	1.7×10^{18}	1.0×10^{12}	9.1×10^{17}
	800	1.5×10^{19}	1.6×10^{19}	3.6×10^{14}	-2.7×10^{18}

- Non-monotonic temperature dependence of E_F
- Doping inversion from *n*- to *p*-type (As-rich high T_g)





Brooks *et al*, (2023, under review)

Thank you

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