MATERIALS SCIENCE & ENGINEERING

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Group-V acceptor ionization energies and compensation centers in CdTe revisited

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In-situ antimony doped polycrystalline CdTe films for simplified cell processing and maximized energy

US DOE - Solar Energy Technologies Office: Award # DE-EE0009344

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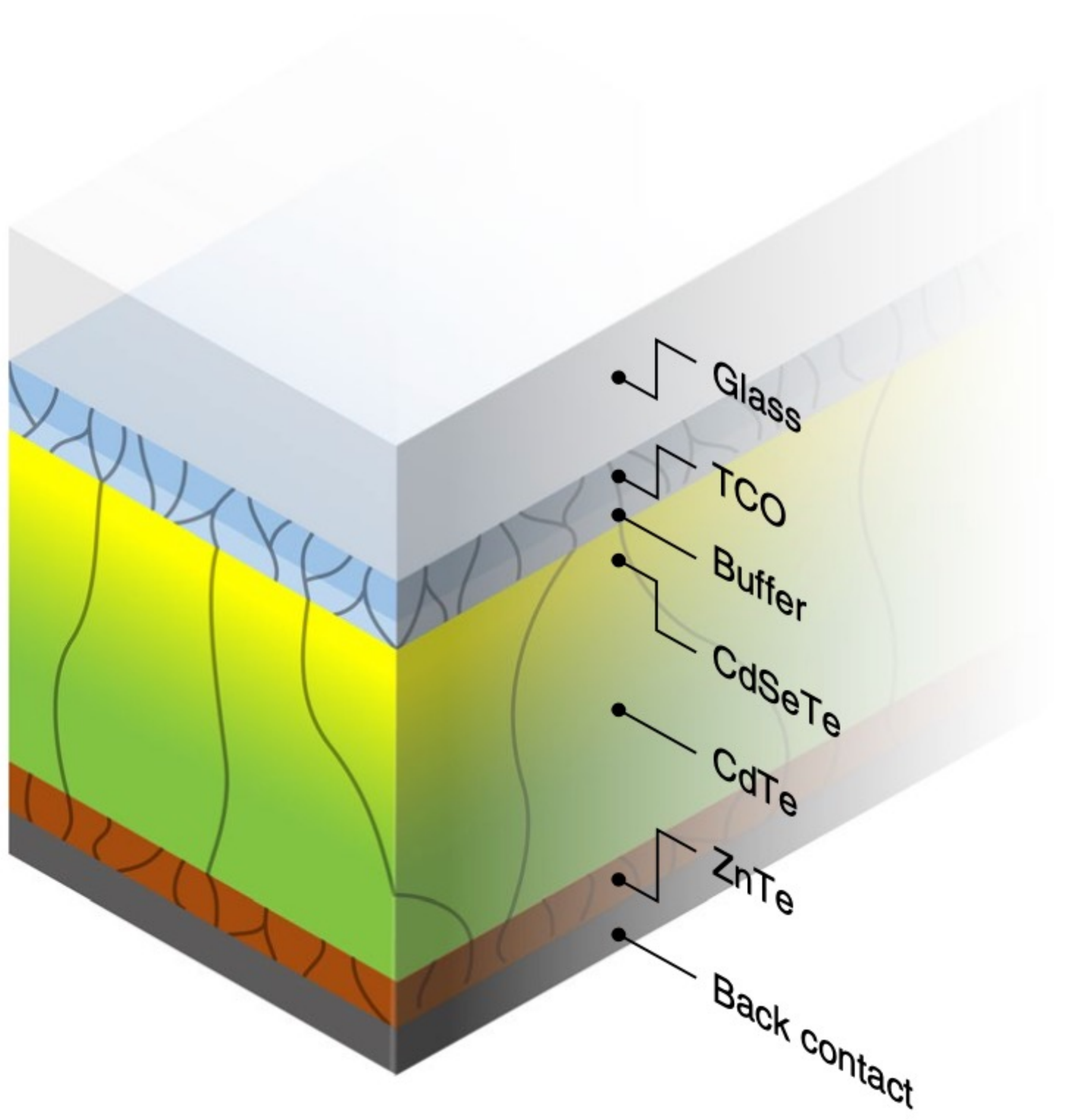
Polycrystalline CdTe-based thin-film solar cells

Record power conversion efficiency (PCE) > 22%, First Solar (2016-2017)

> 18% for modules

- **limited by low V_{OC} < 0.9 V**
- **low carrier concentration (~2x10^{14} cm^{-3})**
- **poor bulk and surface passivation**



Device modeling indicates that efficiency can be increased from 22% to 25% by increasing hole density to > 2x10^{16} cm^{-3}, provided that long carrier lifetimes and low interface recombination velocities can be attained

Single-crystal CdTe with hole density p > 10^{16} cm^{-3} demonstrated,
⇒ maintaining ~20-nanosecond carrier lifetimes can increase the V_{OC} to > 1

W. K. Metzer *et al.*, Nature Energy **4**, 837 (2019)

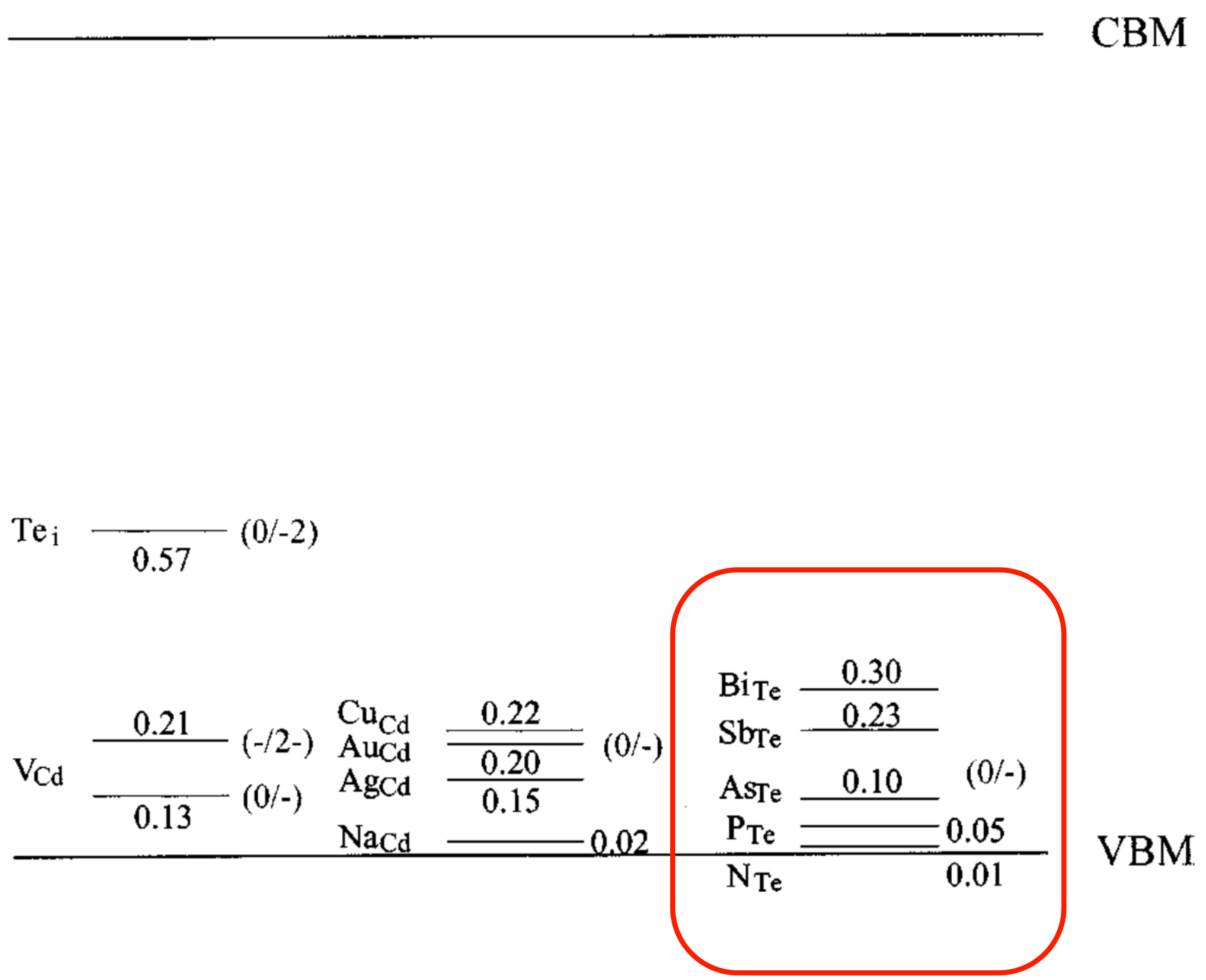
20.8% efficiency without antireflection coatings demonstrated for polycrystalline film, with hole density of 10^{16}-10^{17} cm^{-3} without compromising the lifetime
⇒ resolving interfacial and potential fluctuation issues may enable further improvement

Green *et al.*, Solar cell efficiency tables (version 56), *Prog. Photovolt. Res. Appl.* **28**, 629 (2020)

A. Romeo and E. Artegiani, Energies **14**, 1684 (2021)

M. Gloeckler, FSLR, presented at 44th IEEE PVSC, Washington (2017)

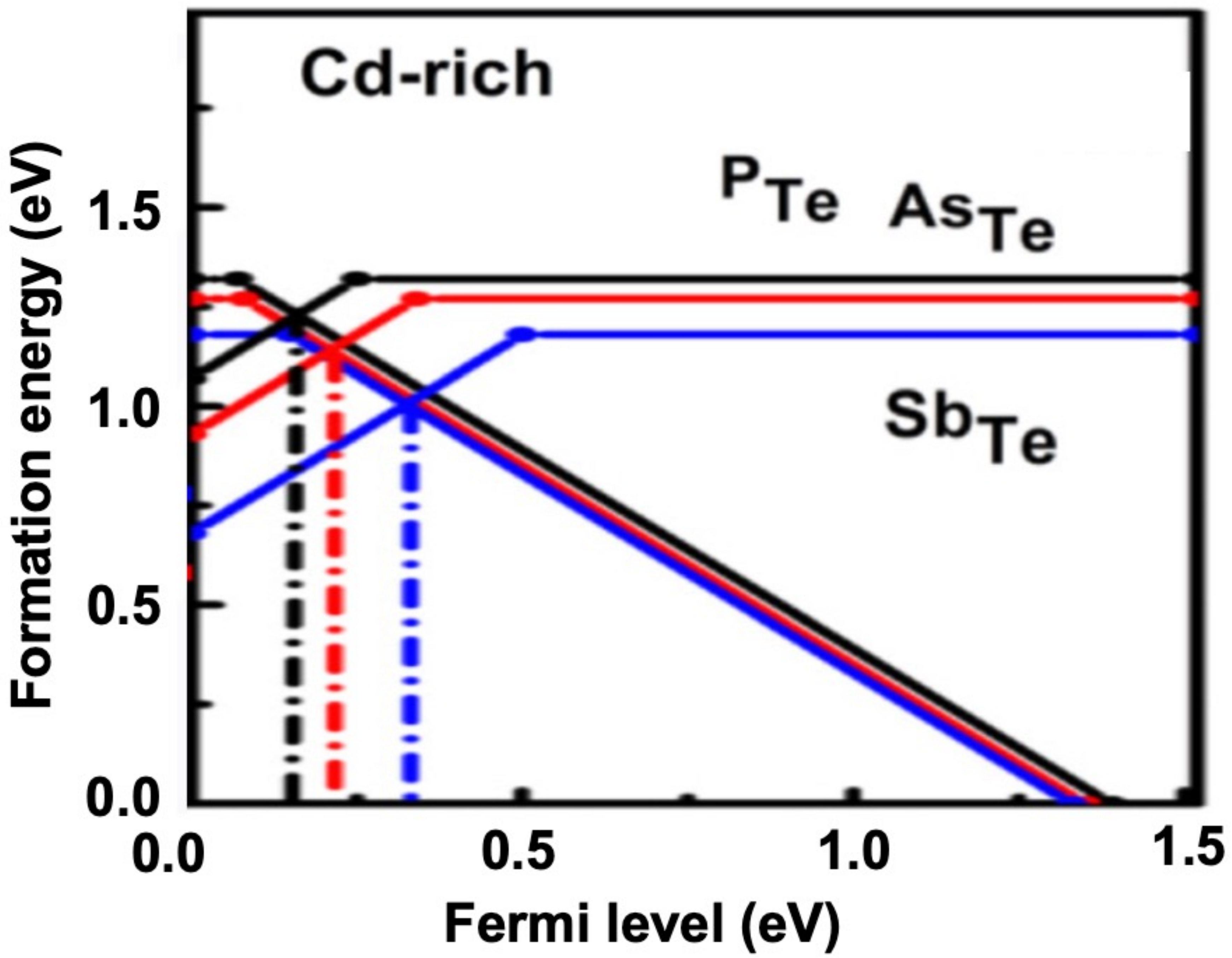
Are Sb, As, and P shallow acceptors in CdTe? How shallow? Do they suffer from self compensation (i.e., by AX formation)?



S.-H. Wei and S. B. Zhang,
phys. stat. sol. (b) **229**, 305 (2002);
Phys. Rev. B **66**, 155211 (2002)

DFT-LDA, supercell of 32 atoms, no spin-orbit coupling (SOC)

- **Very large ionization energy for Sb**



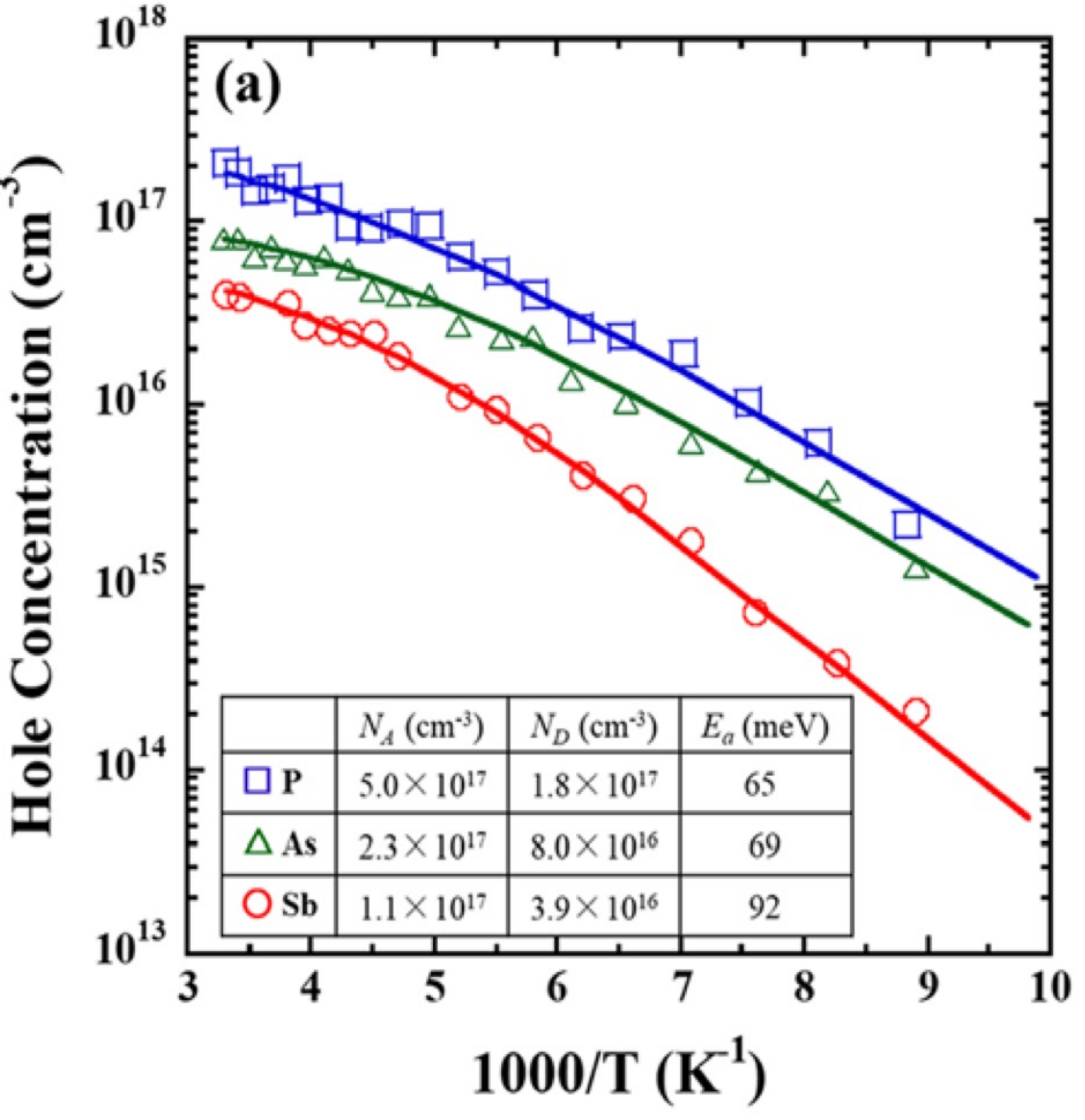
B. Dou, Q. Sun, and S.-H. Wei,
Phys. Rev. Appl. **15**, 054045 (2021)

DFT- hybrid functional, supercell of 216 atoms, no SOC

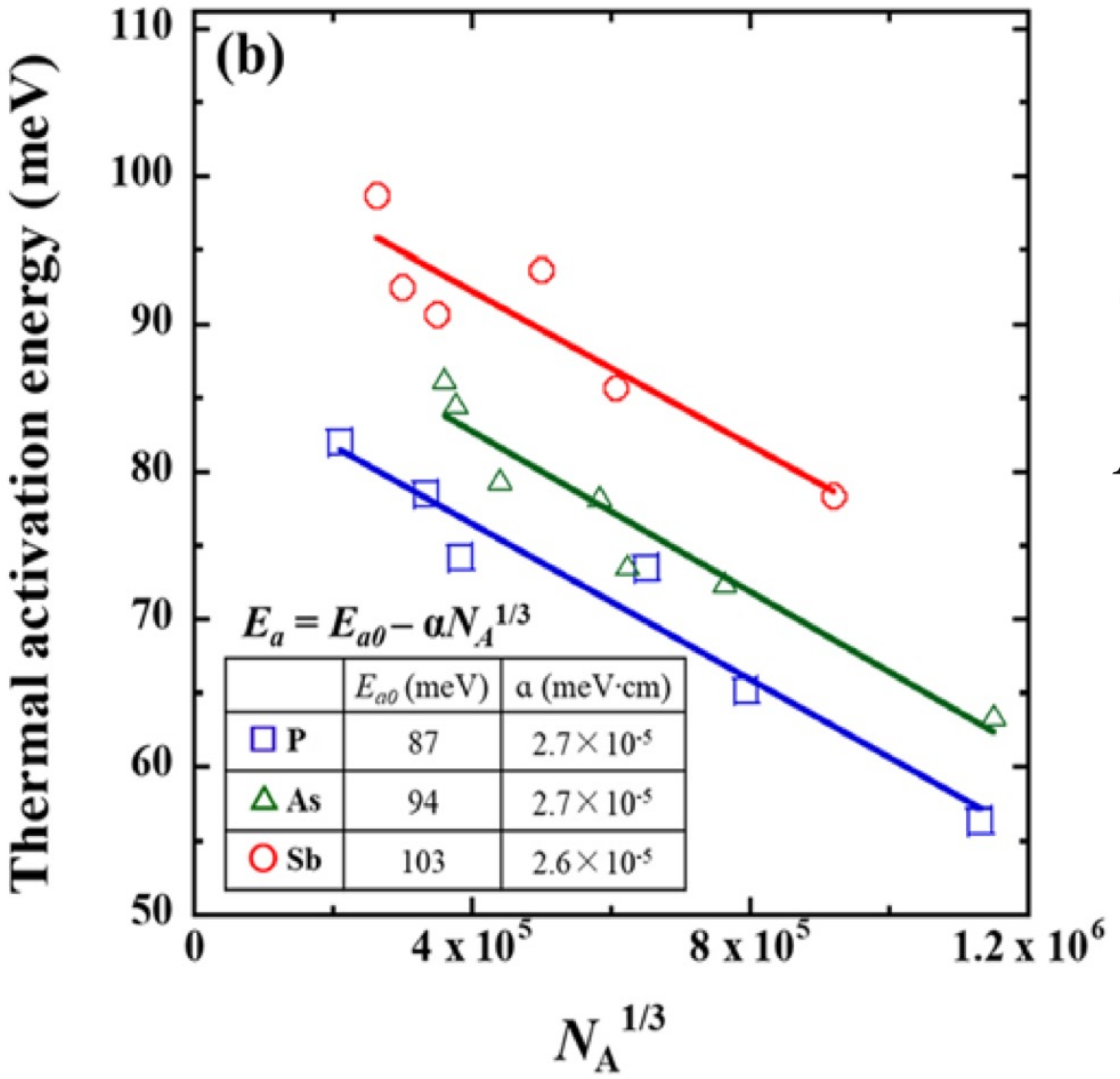
- **Still large ionization energy for Sb (150 meV)**
- **P, As, and Sb will form AX, killing hole conductivity**

Sb, As and P doping of CdTe single crystals

Recent experiments indicate that Sb, As and P are shallow acceptors with ionization energies of ~100 meV



Temperature dependence of hole concentration for group V-doped samples



Thermal activation energy vs acceptor concentration

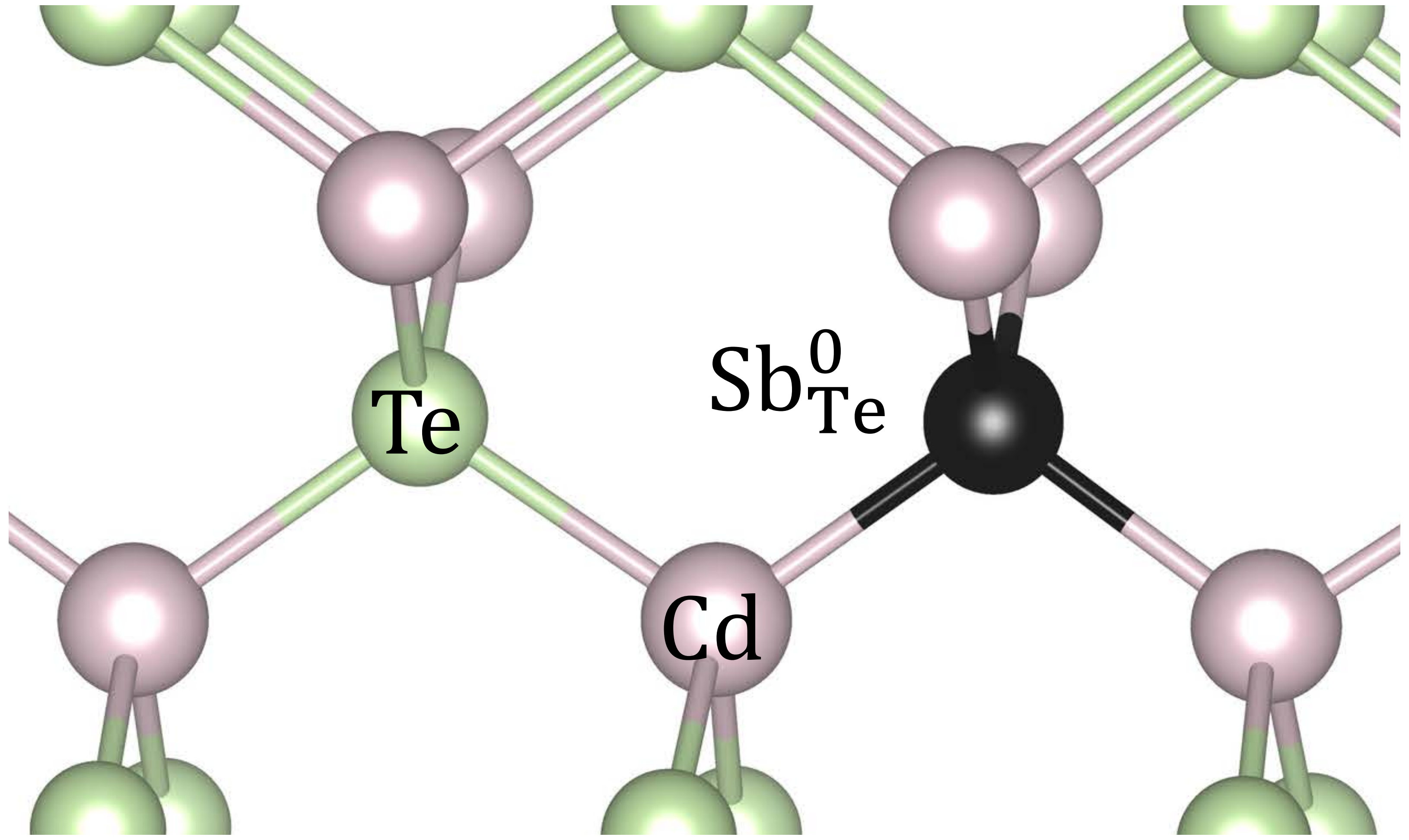
$$p = -A + \sqrt{A^2 + \frac{N_V}{2}(N_A - N_D)\exp\left(-\frac{E_a}{k_B T}\right)},$$

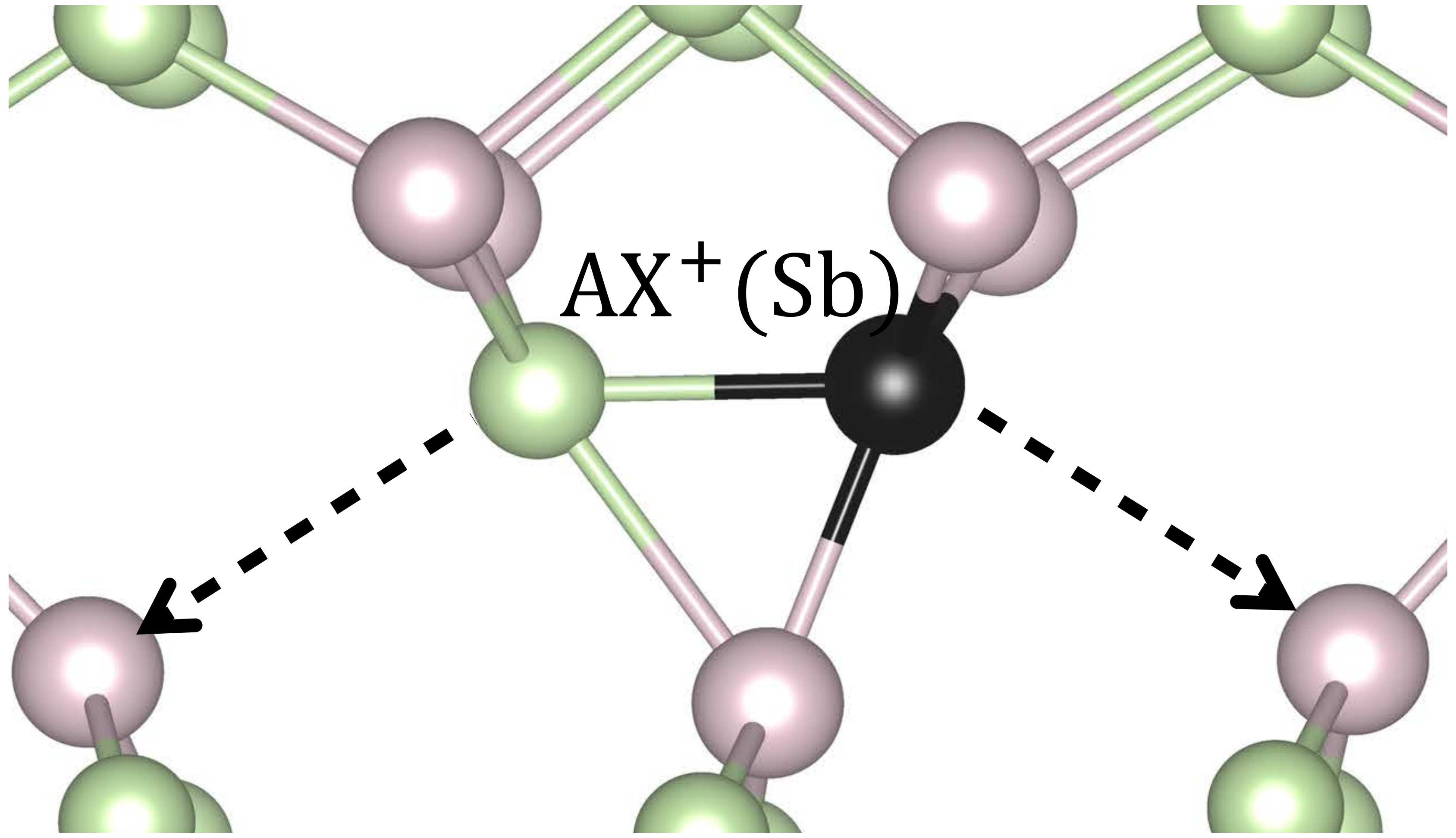
$$A = \frac{1}{2}\left[N_D + \frac{N_V}{2}\exp\left(-\frac{E_a}{k_B T}\right)\right],$$

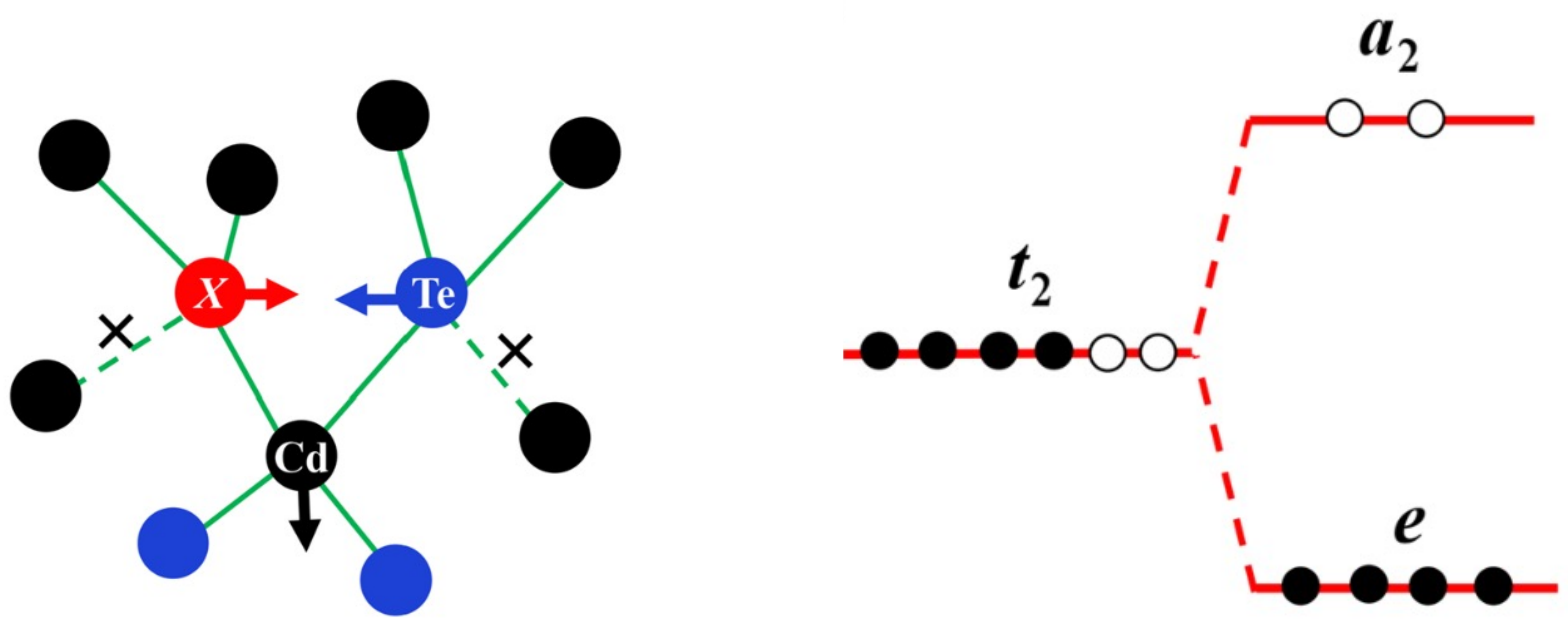
A. Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Substitutional acceptor vs. AX donor

$$\mathrm{Sb_{Te}^{0}} \rightarrow \mathrm{AX^{+}(Sb)} + \mathrm{e^{-}@\ cb}$$





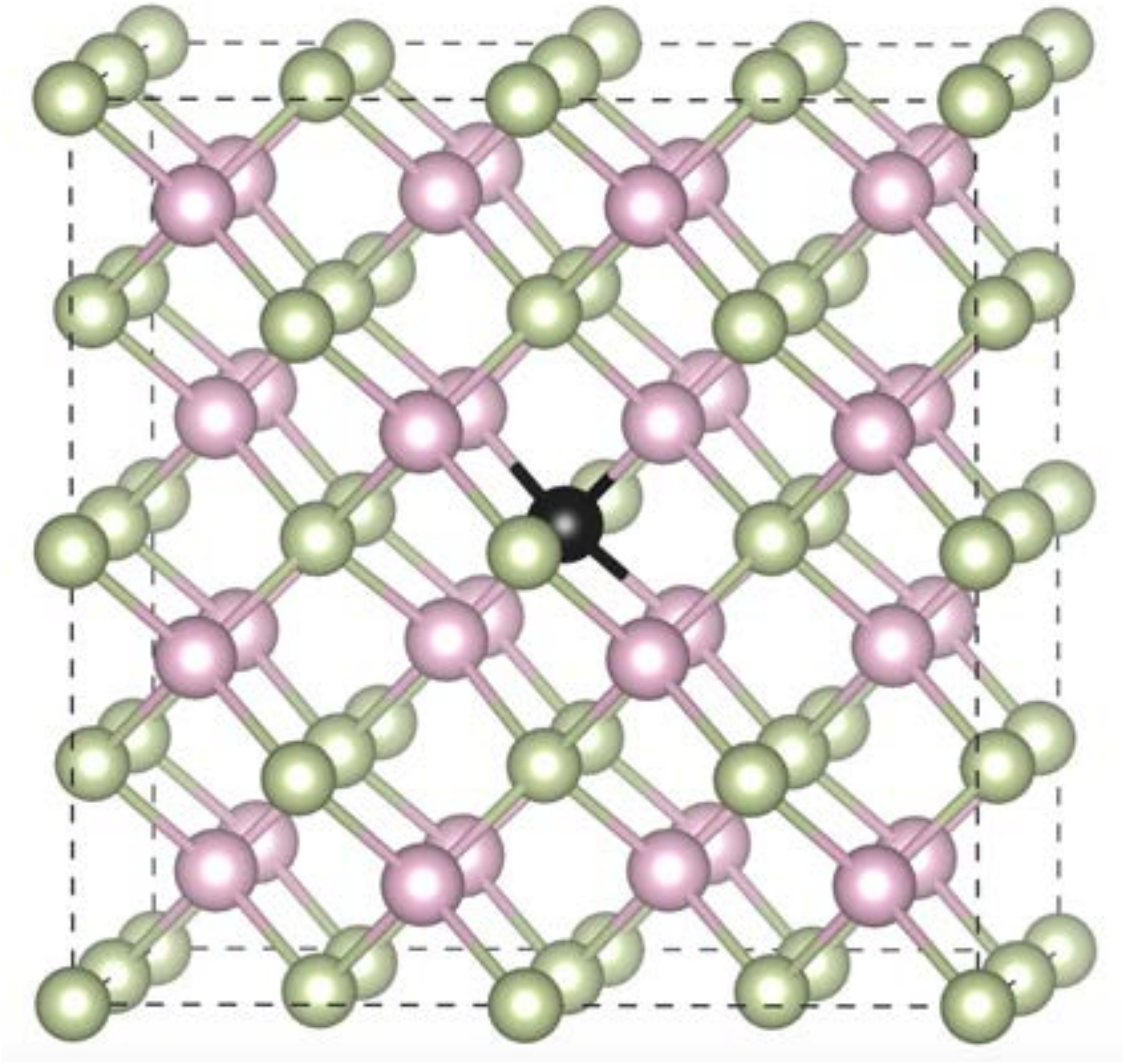


S.-H. Wei and S. B. Zhang, Phys. Rev. B **66**, 155211 (2002)
J.-H. Yang et al., Semicond. Sci. Technol. **31**, 083002 (2016)
B. Dou et al., Phys. Rev. Appl. **15**, 054045 (2021)
C. H. Park and D. J. Chadi, Phys. Rev. Lett. **75**, 1134 (1995)

The acceptor is displaced along the [110] direction, forming a bond with a second nearest neighbor Te becoming a donor

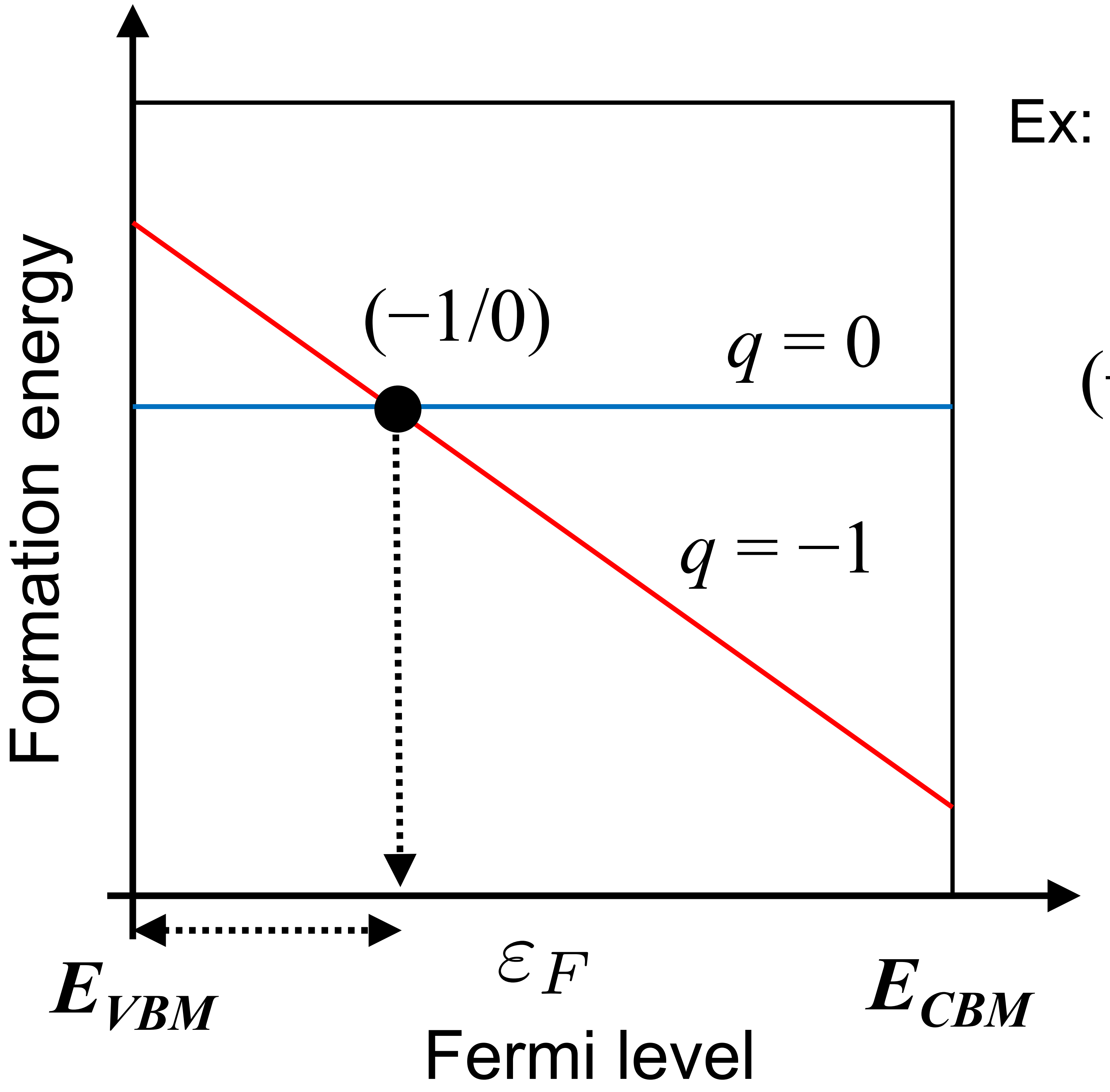
How to calculate defect formation energies

64-atoms, zinc blende



Supercell with a defect
periodically repeated in 3D
All atoms in the supercell are allowed to relax
(minimizing forces and total energy)

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



Ex: acceptor defect

$(-1/0)$: acceptor transition level
or ionization energy

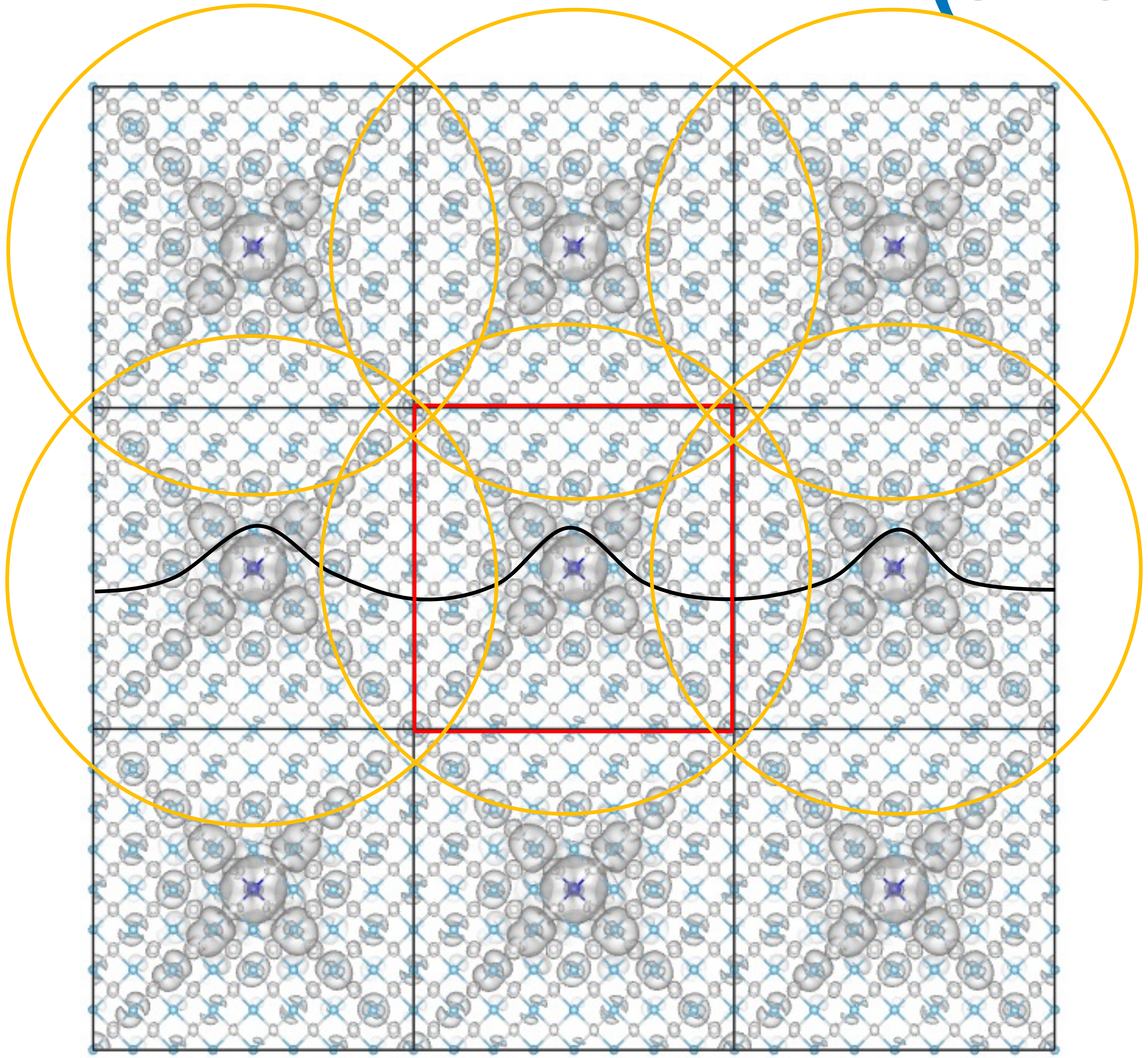
For shallow acceptors,
$(-1/0) \sim$ few k_BT at RT

Dependence on atom chemical potential

$$\mu_{\text{Cd}} + \mu_{\text{Te}} = \Delta H_f(\text{CdTe})$$

Cd-rich or Te-rich just shift up/down
the two curves together

Problems with describing shallow acceptors or donors with (small) finite supercell sizes



Sb_{Te}^{-} related state at the top of VBM

supercell of 216 atoms, periodically repeated

Overlap of “hydrogenic” wavefunctions
leads to artificially increased ionization energies

1) DFT within LDA/GGA severely underestimate band gaps

⇒ large errors in formation energies and transition levels (>> 0.2 eV)

2) Need to correct band structure (both band gap and ionization potential)

⇒ Hybrid functionals, have to include spin-orbit coupling

Still, errors in transition levels are typically ~0.1 eV

In the case of shallow donors/acceptor,
the overlap of the hydrogenic wavefunction between the impurity and its images using typical supercell sizes lead to overestimation of ionization energies

“central-cell” effects

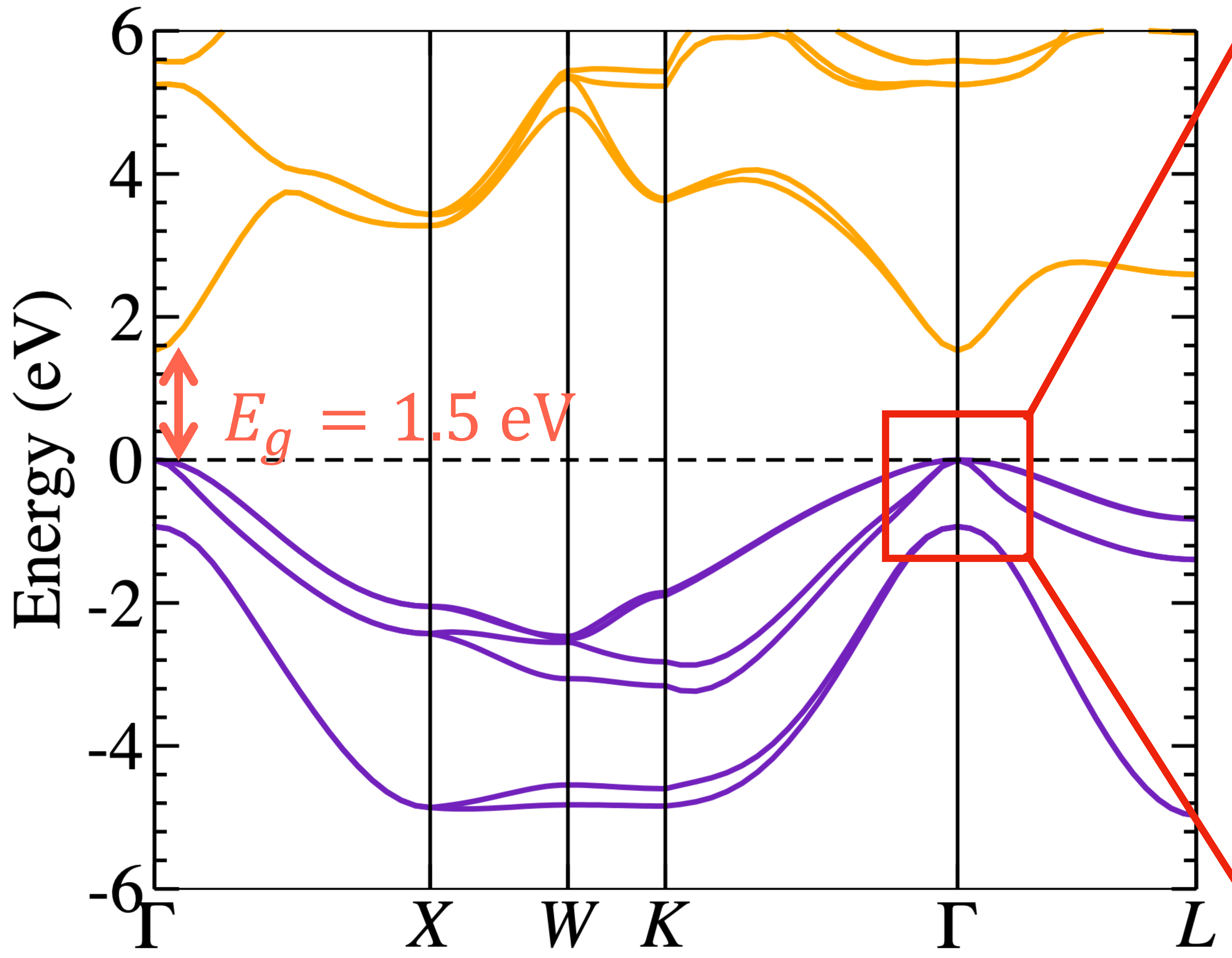
M.W. Swift *et al.,* Npj Comput. Mater. **6**, 181(2020)

L.-W. Wang, J. Appl. Phys. **105**, 123712 (2009)

Solution ⇒ calculate transition levels as function of supercell size and extrapolate to the dilute limit

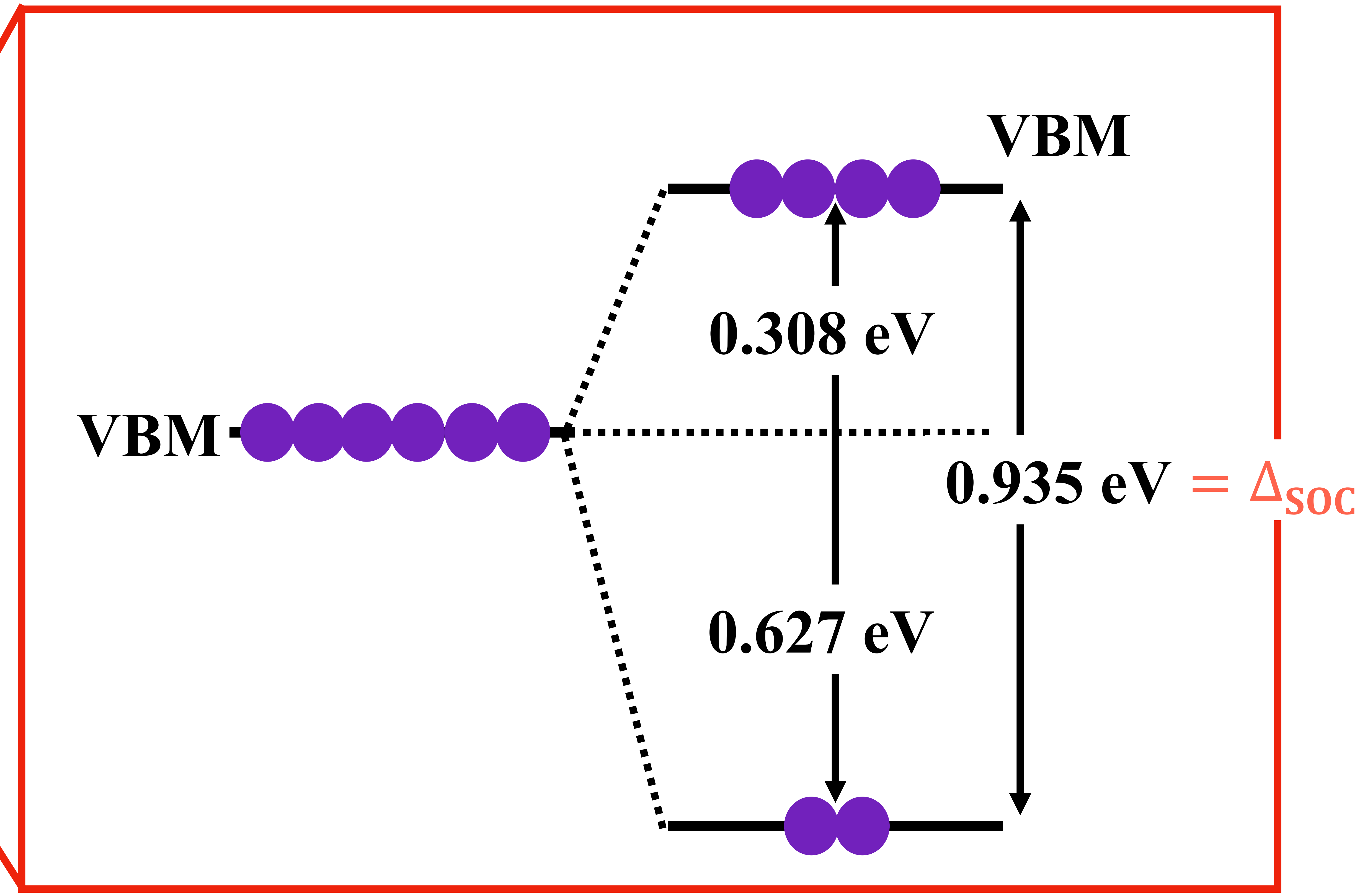
Band structure of CdTe, effects of spin-orbit coupling

HSE α =0.33 with SOC



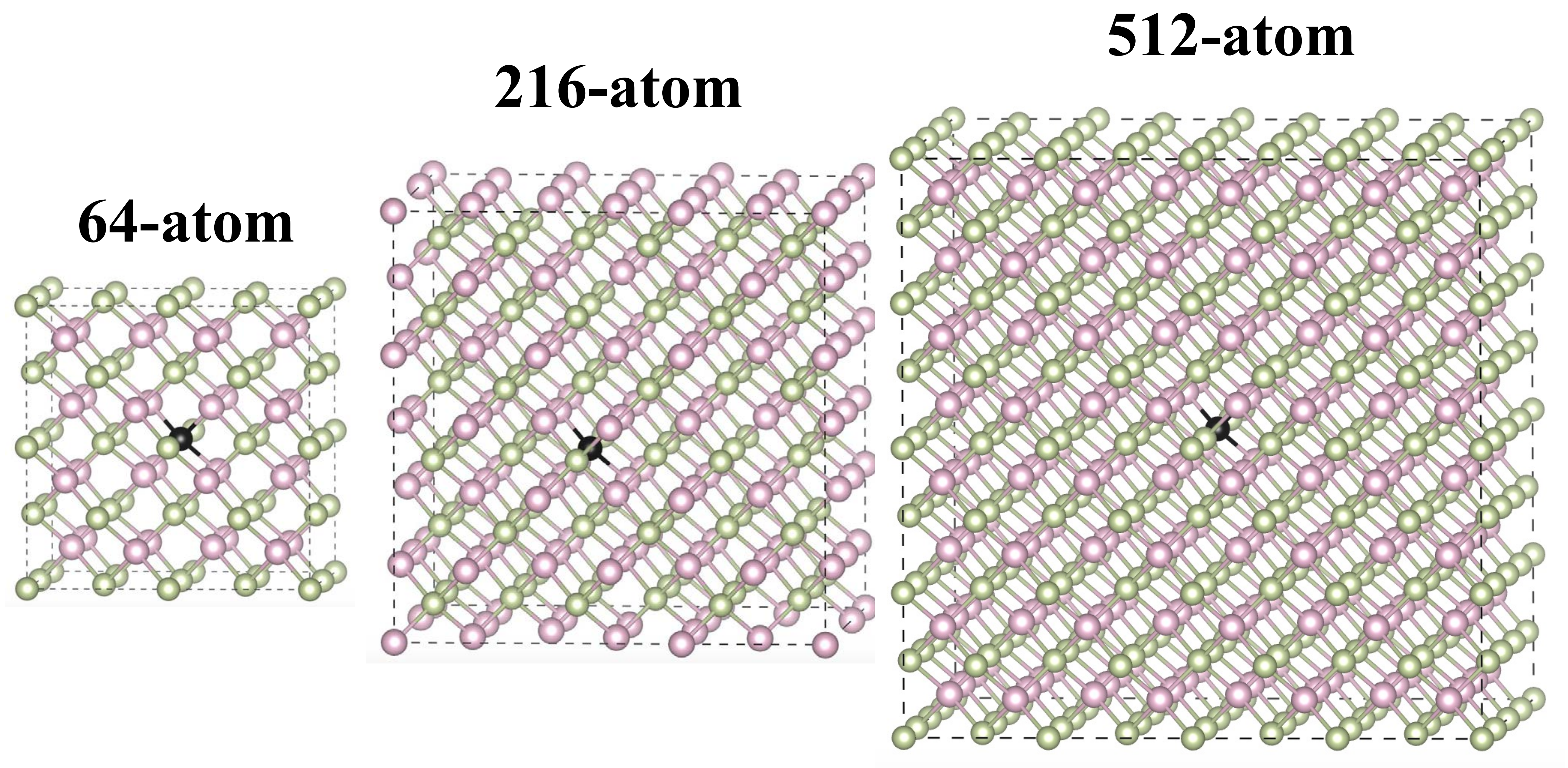
Ionization potential in much better agreement with exp. data compared to DFT-LDA/GGA

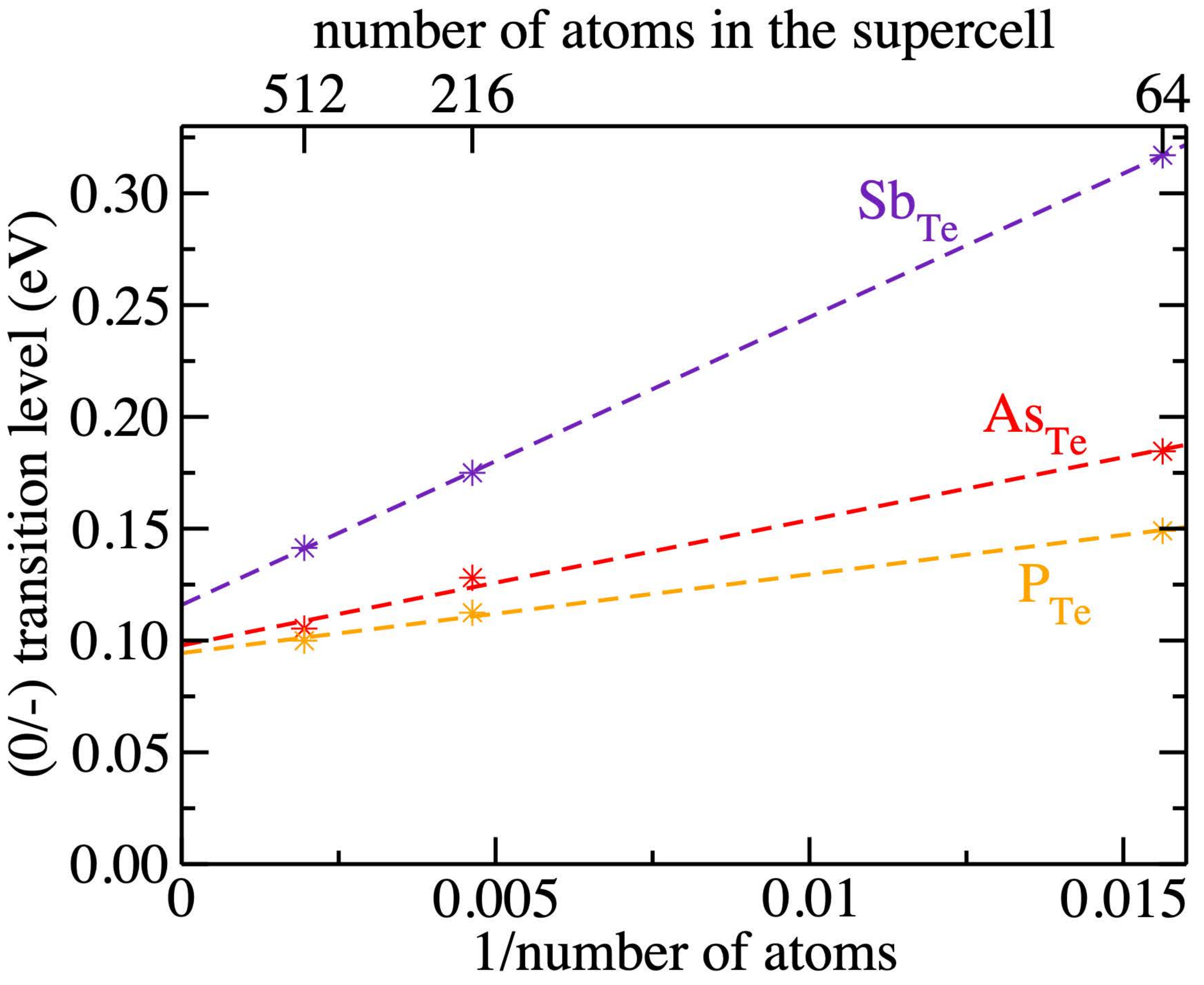
Effect of SOC



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

Extrapolation of the acceptor level to the dilute limit





- At dilute limit, Sb(0/-)=116 meV, As(0/-)= 99 meV and P(0/-)=93 meV
  (close to hydrogenic model ~100 meV)
- From experiment, Sb(0/-)=0.103 eV, As(0/-)=0.094eV and P(0/-)=0.087 eV

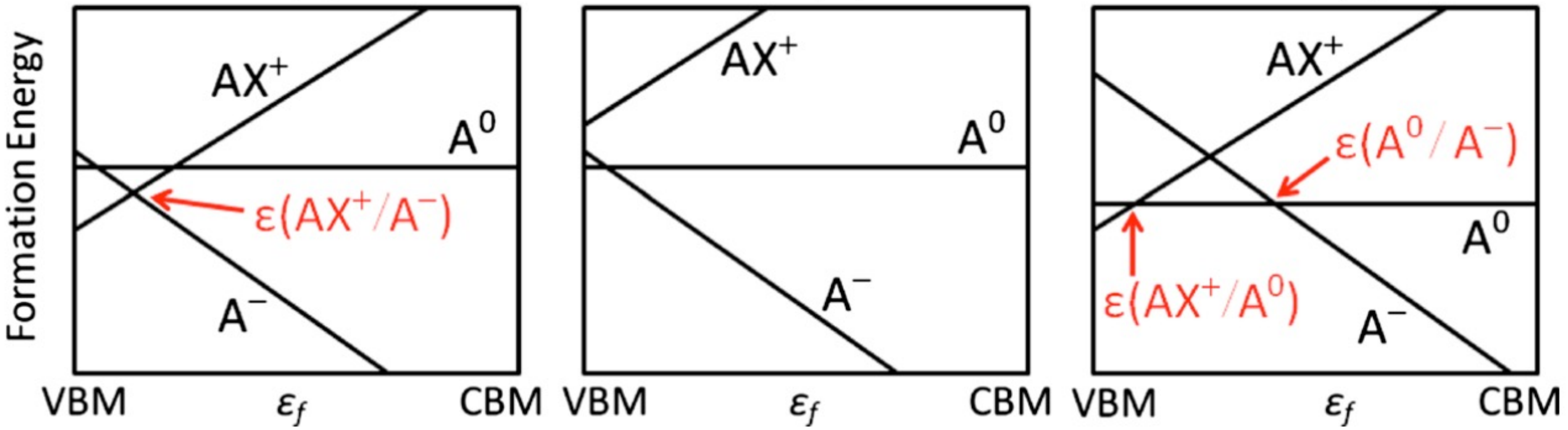
A. Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Formation of AX centers: Three possible scenarios

AX is stable,
kills hole conductivity

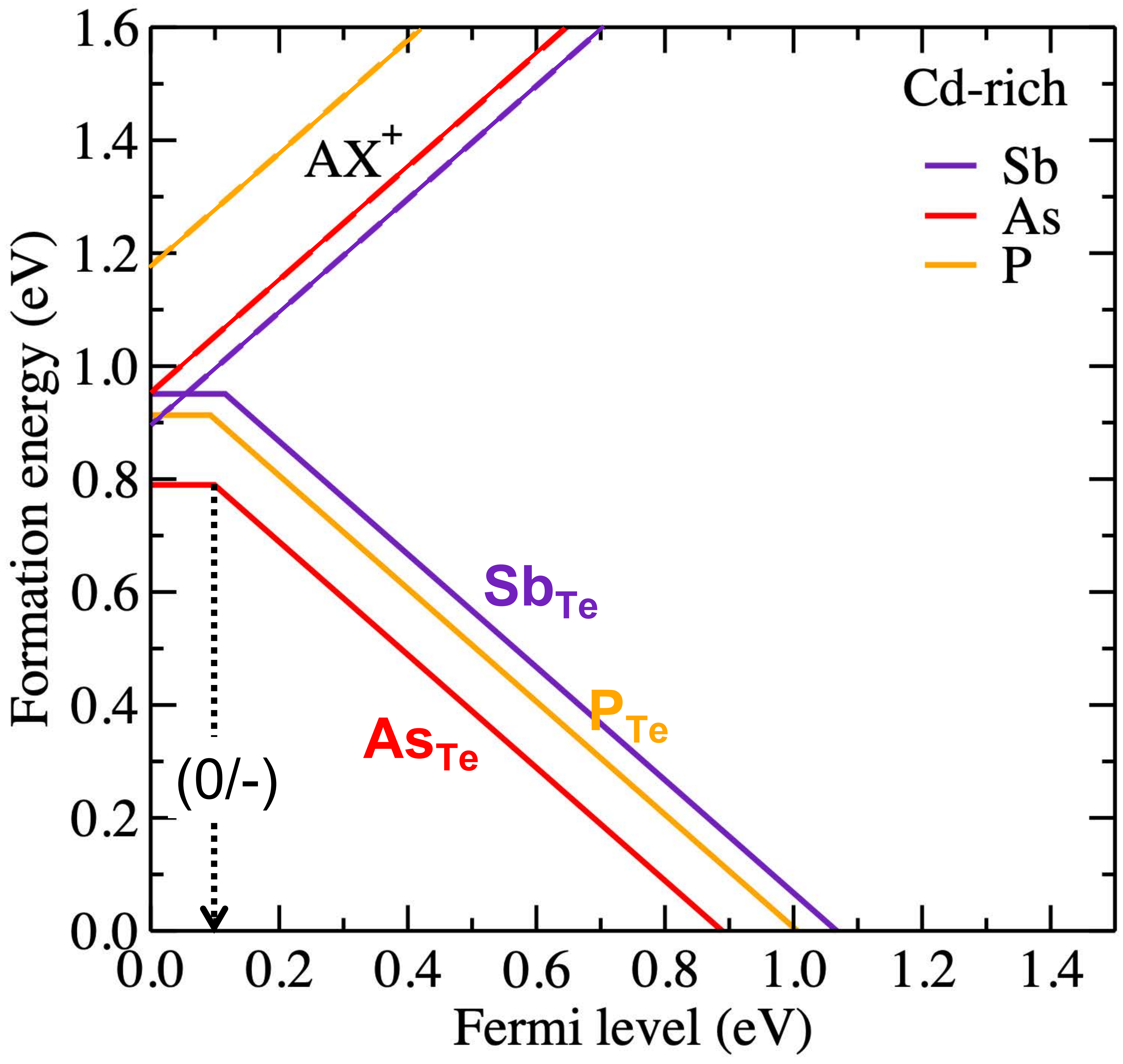
AX is unstable,
hole conductivity limited by (A^0/A^-)

AX is stable,
hole conductivity may be limited by (A^0/A^-) and AX



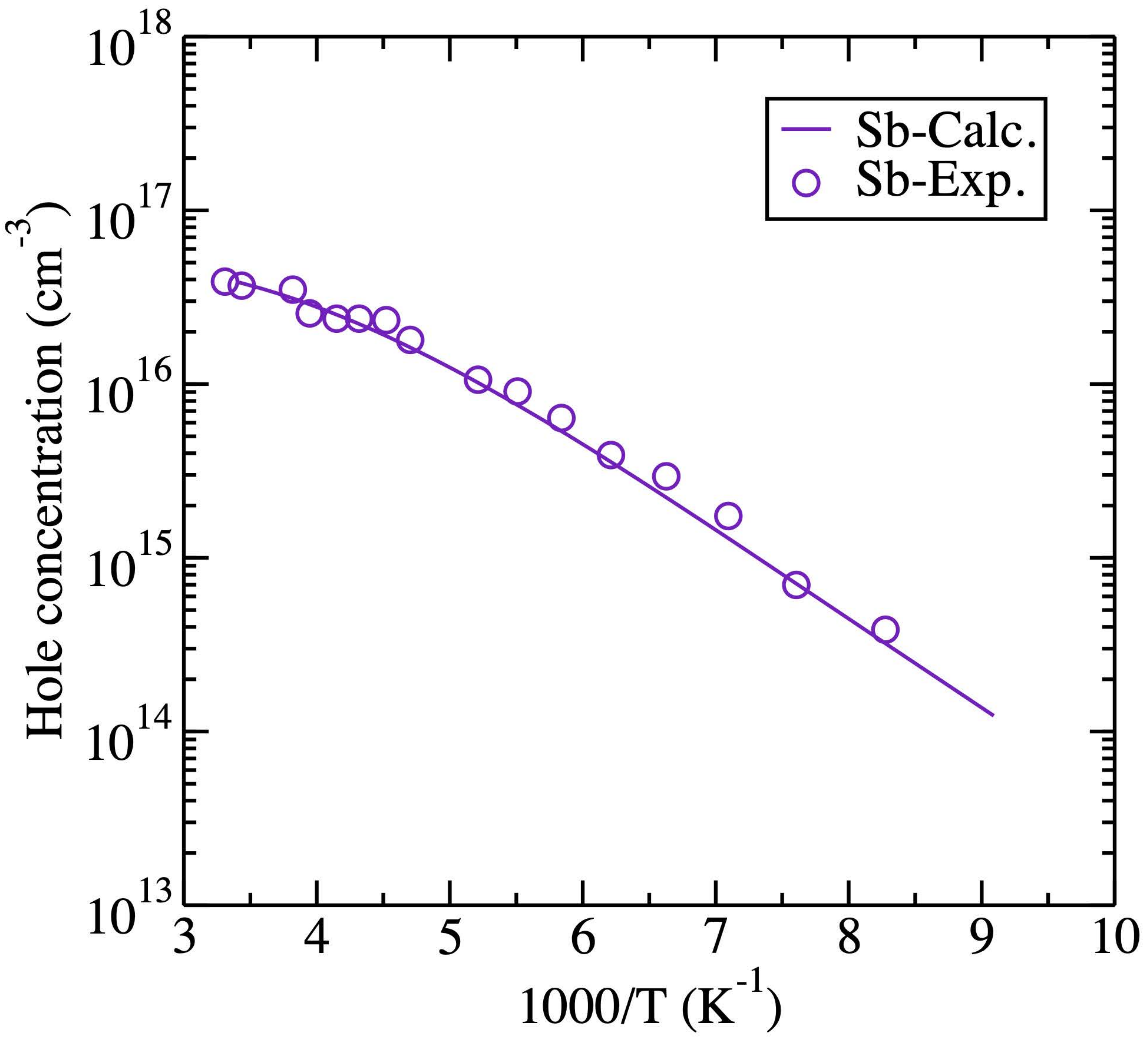
K. Biswas and M.-H. Du, Appl. Phys. Lett. **98**, 181913 (2011)

Group-V acceptors and their corresponding AX centers



- AX is unstable in the case of As and P
  i.e., does not play any role in the doping efficiency
  ⇒ problems with As doping must be caused by something else (or some other center)
- In the case of Sb, AX will have a limited effect since the Fermi level typically does not reach (+/0) level near the VBM

Temperature-dependent hole concentration for Sb doping of CdTe



Use:

- Calculated E_a= 116 meV
- Calculated (+/-) level (AX+/Sb_{Te}-)

Solve partially compensated semiconductor equation to obtain N_a that best fits experimental data

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

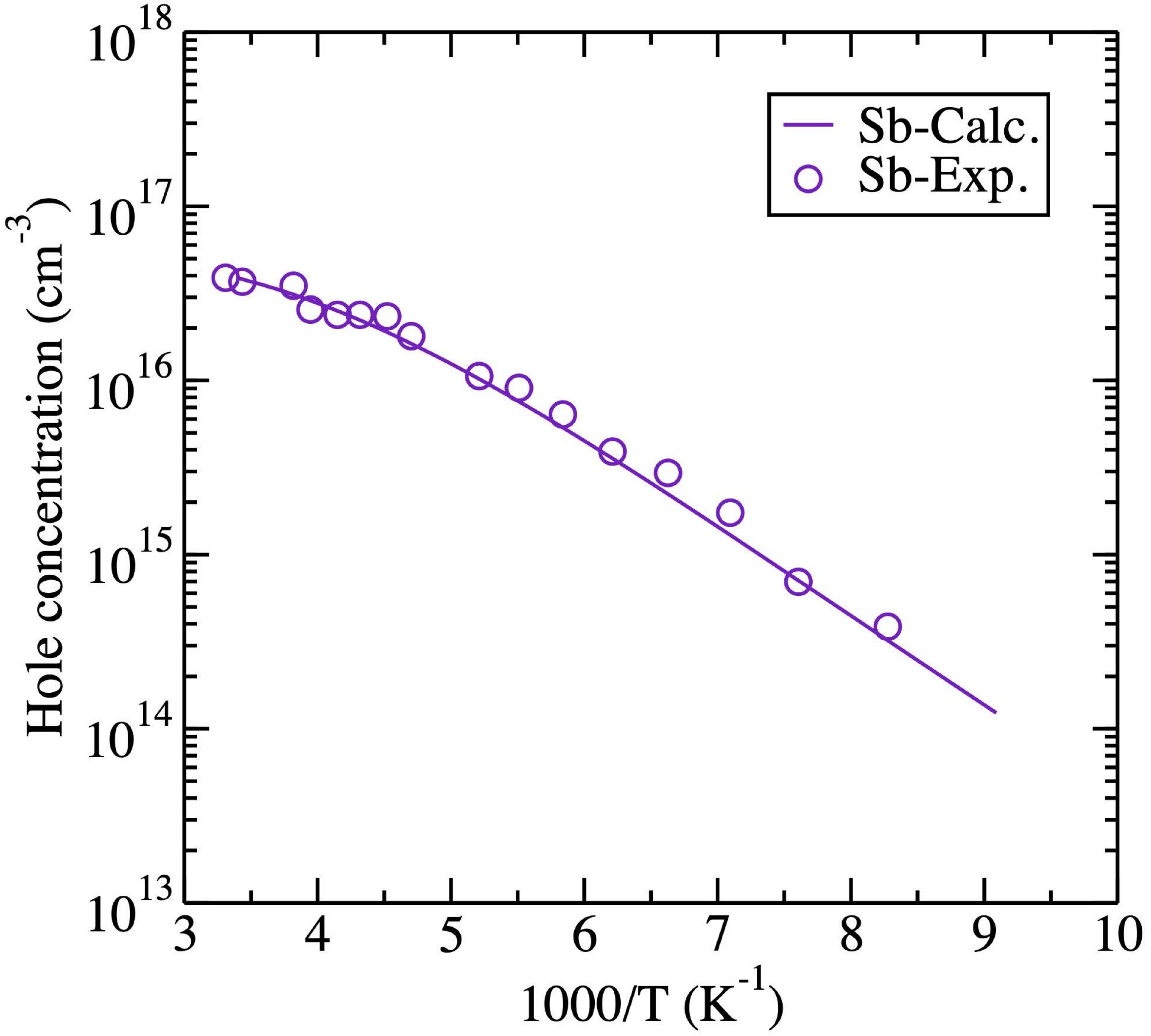
J. S. Blakemore, Semiconductor Statistics (Pergamon, New York, 2013)

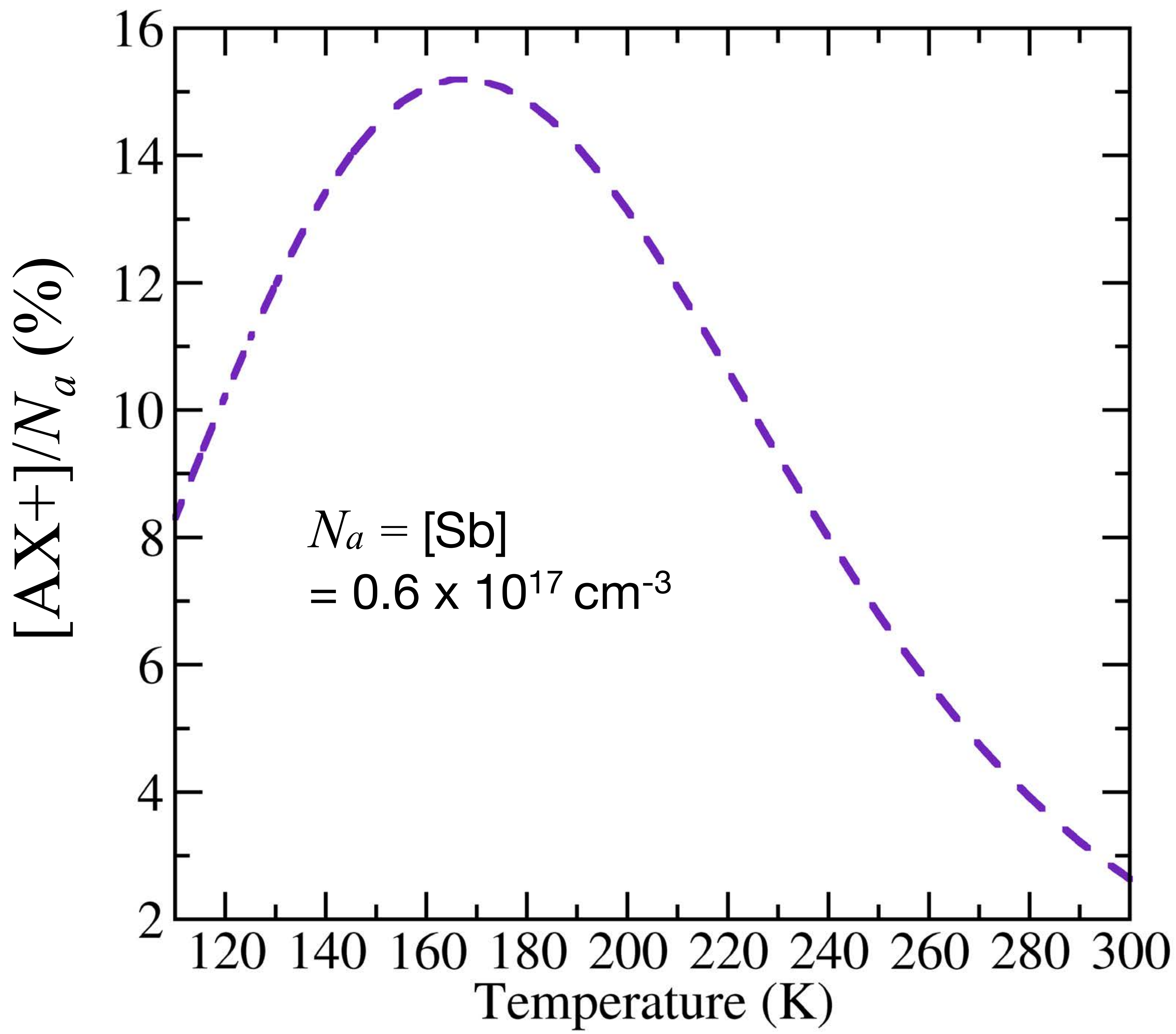
Best fit: N_a = [Sb] = 0.6 x 10^{17} cm^{-3}

Compared to 1.1x10^{17} cm^{-3} from exp.

Exp. data from
A. Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Temperature-dependent hole concentration for Sb doping of CdTe

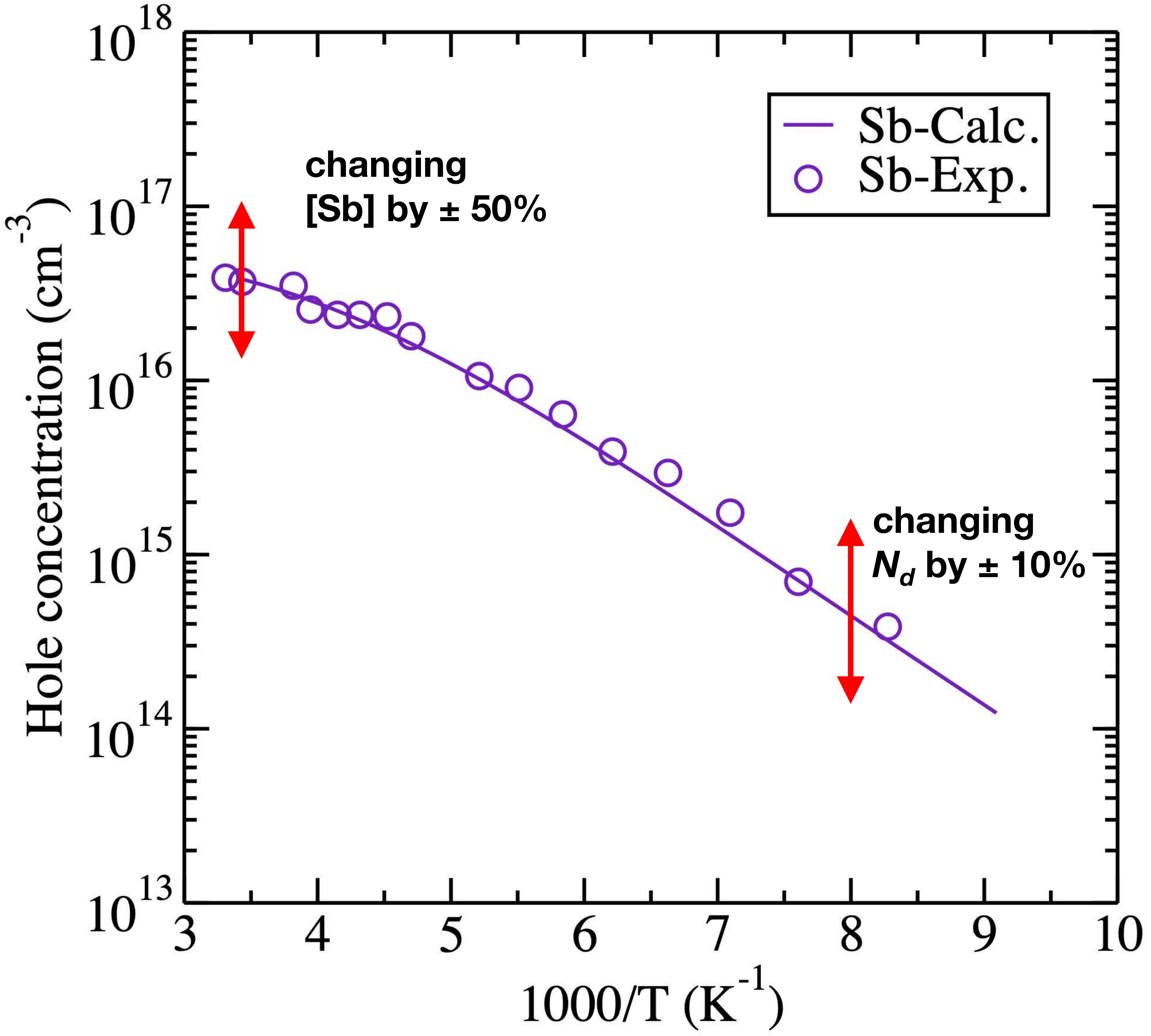


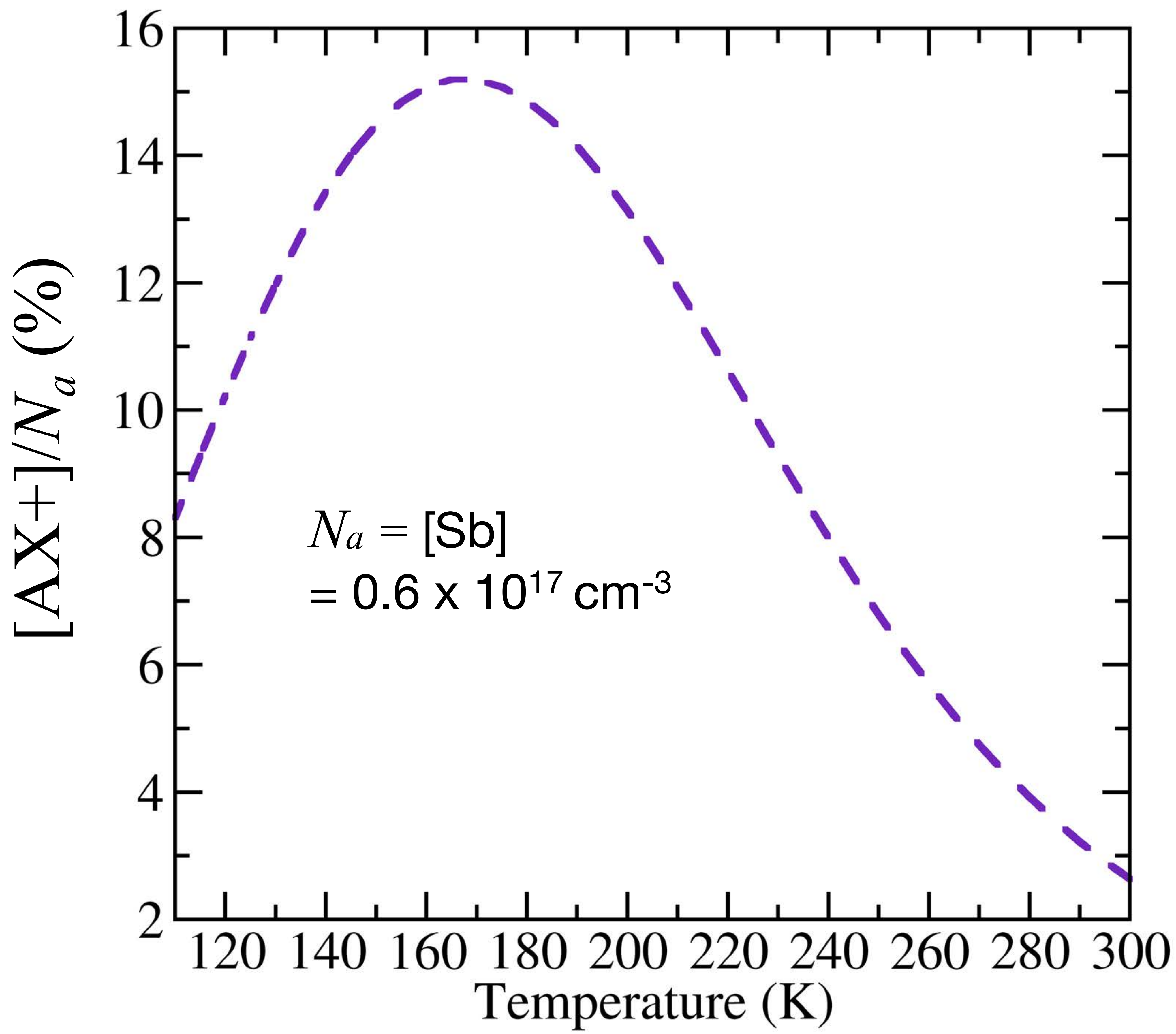


- [AX] < 16% of total Sb concentration
- Becomes less important at room temp.

Exp. data from
A. Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Temperature-dependent hole concentration for Sb doping of CdTe

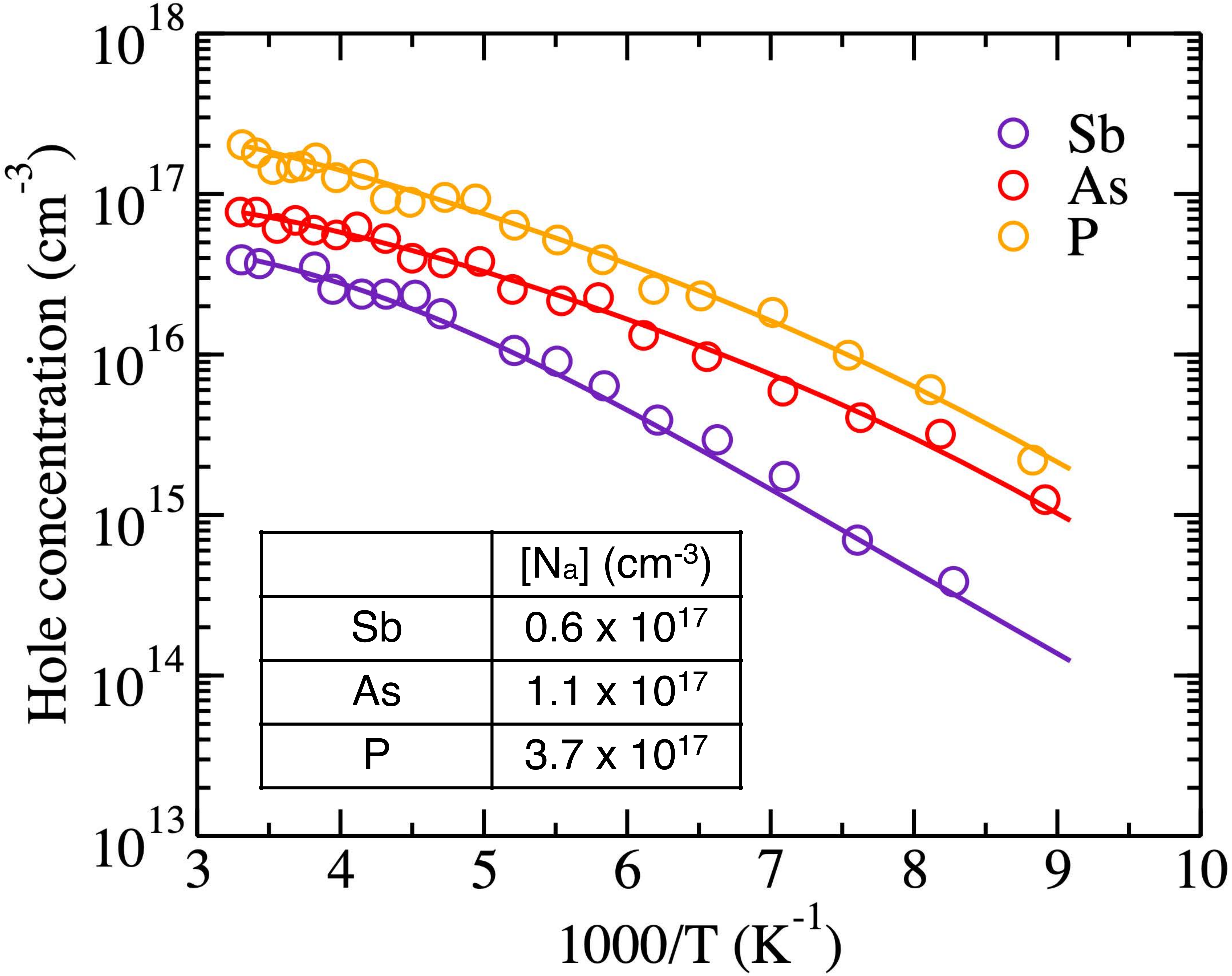




- [AX] < 16% of total Sb concentration
- Becomes less important at room temp.

Exp. data from
A. Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Temp.-dependent hole concentration for Sb/As/P doping of CdTe



	$[N_a]$ (cm^{-3})
Sb	0.6×10^{17}
As	1.1×10^{17}
P	3.7×10^{17}

Sb → E_a = 116 meV

As → E_a = 99 meV
Compensation = 6%

P → E_a = 93 meV
Compensation = 6%

Have to assume ~6% compensation (not AX) in the case of As and P doping

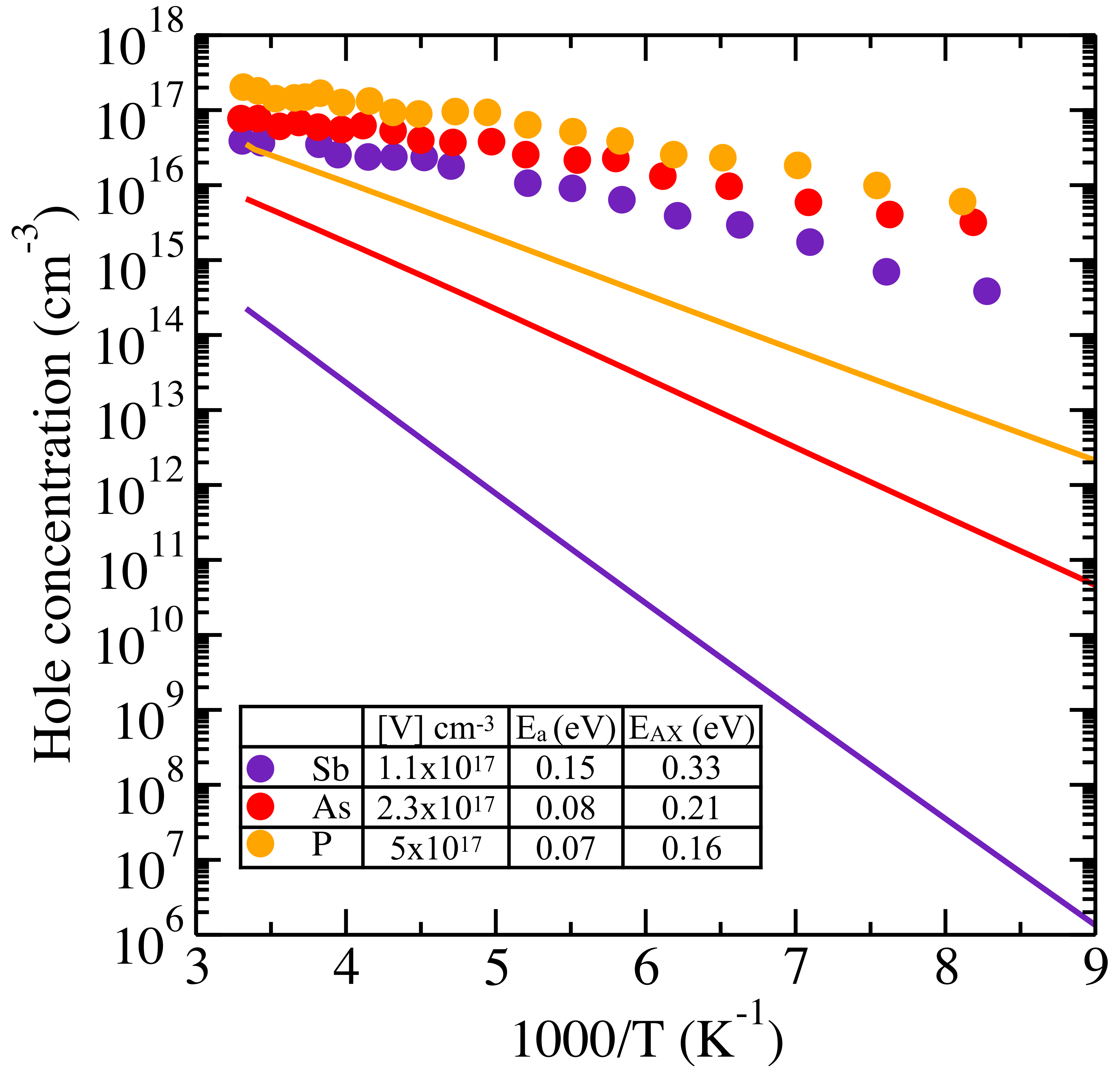
Similar compensation mechanisms for As and P? Point defects?

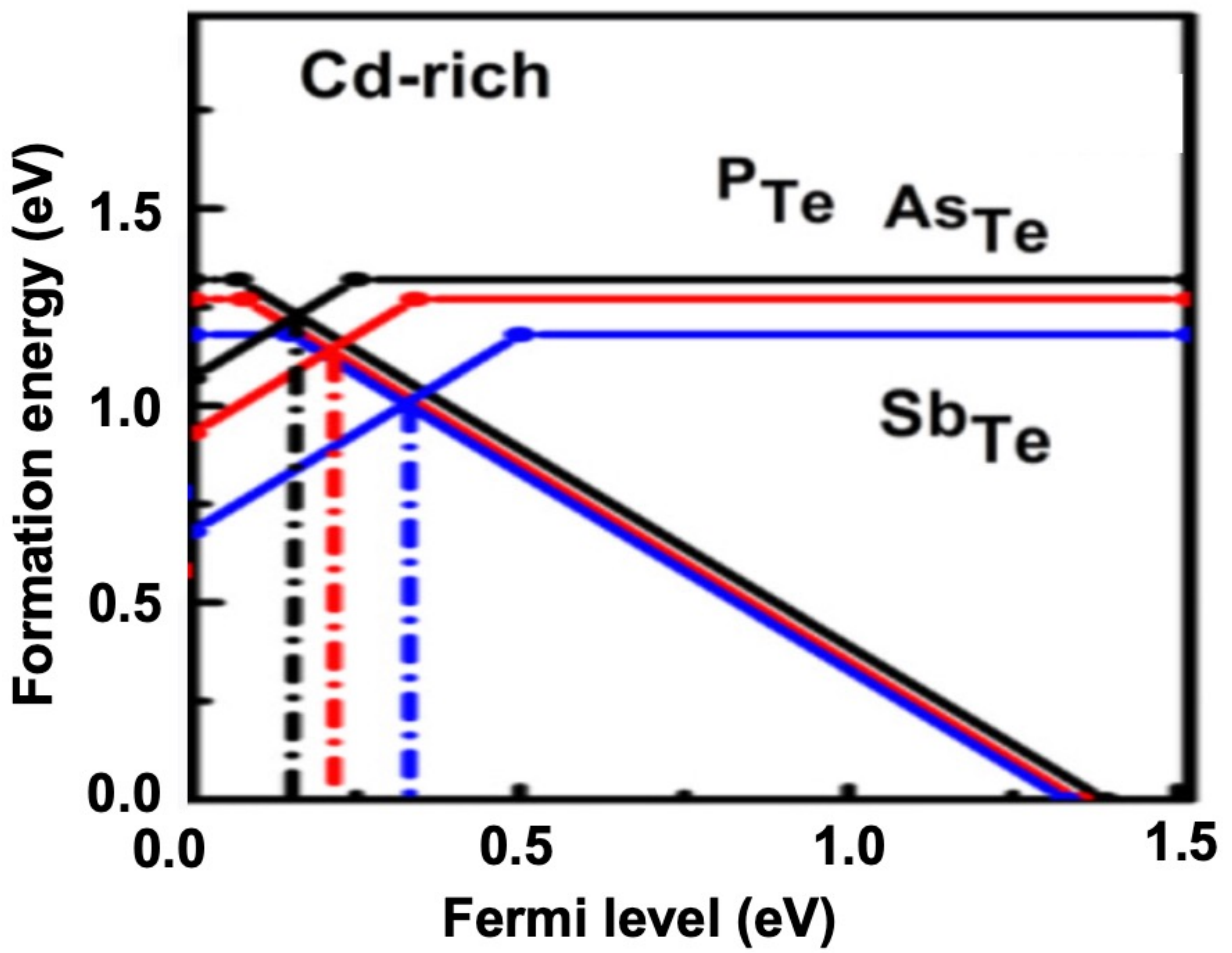
[*h*] from Sb doping drops faster at low temperatures due to higher ionization energy

Exp. data from
A. Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Temp.-dependent hole concentration for Sb/As/P doping of CdTe

- **According to previous theoretical prediction where AX centers are stable**

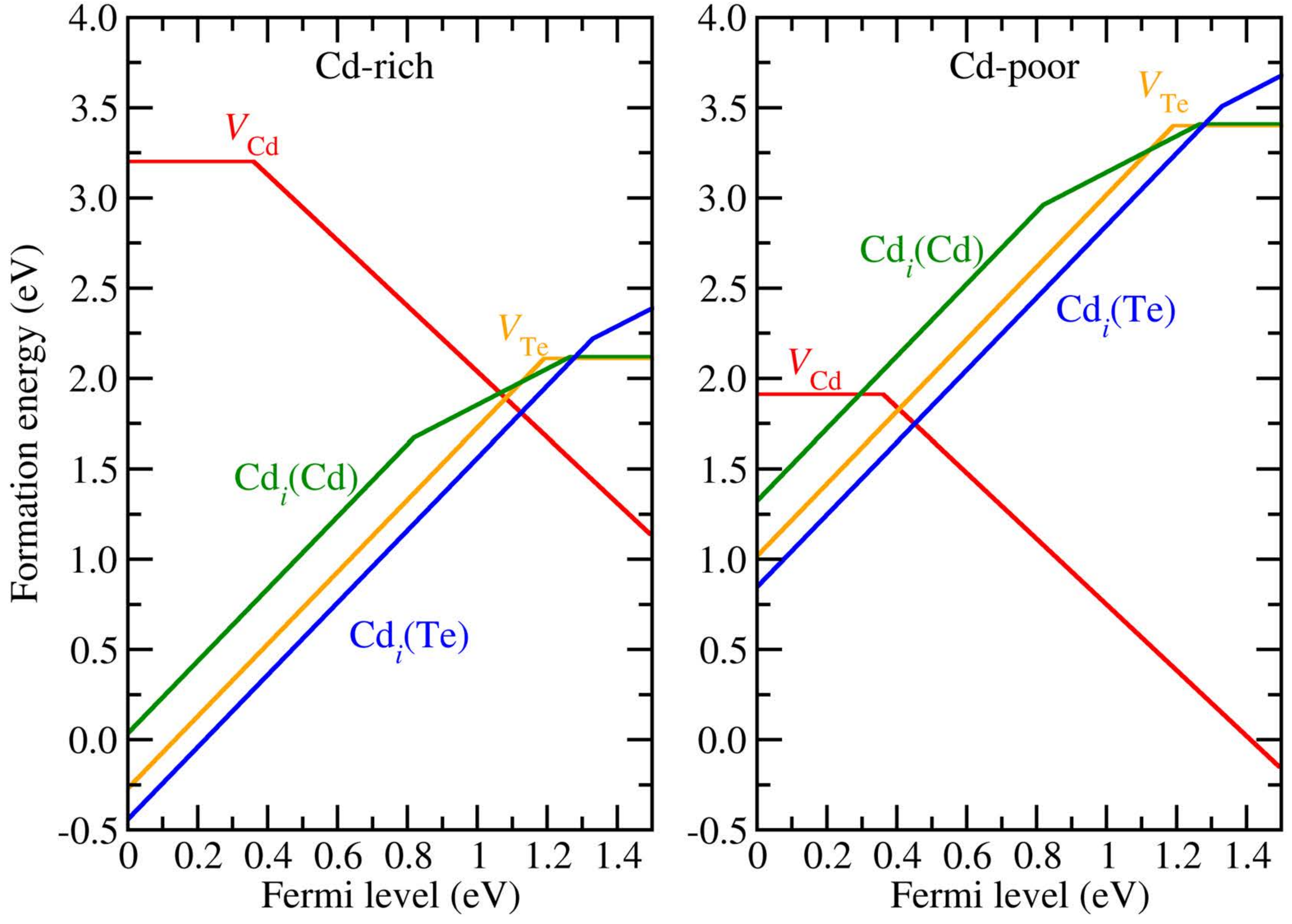




B. Dou, Q. Sun, and S.-H. Wei,
Phys. Rev. Appl. **15**, 054045 (2021)

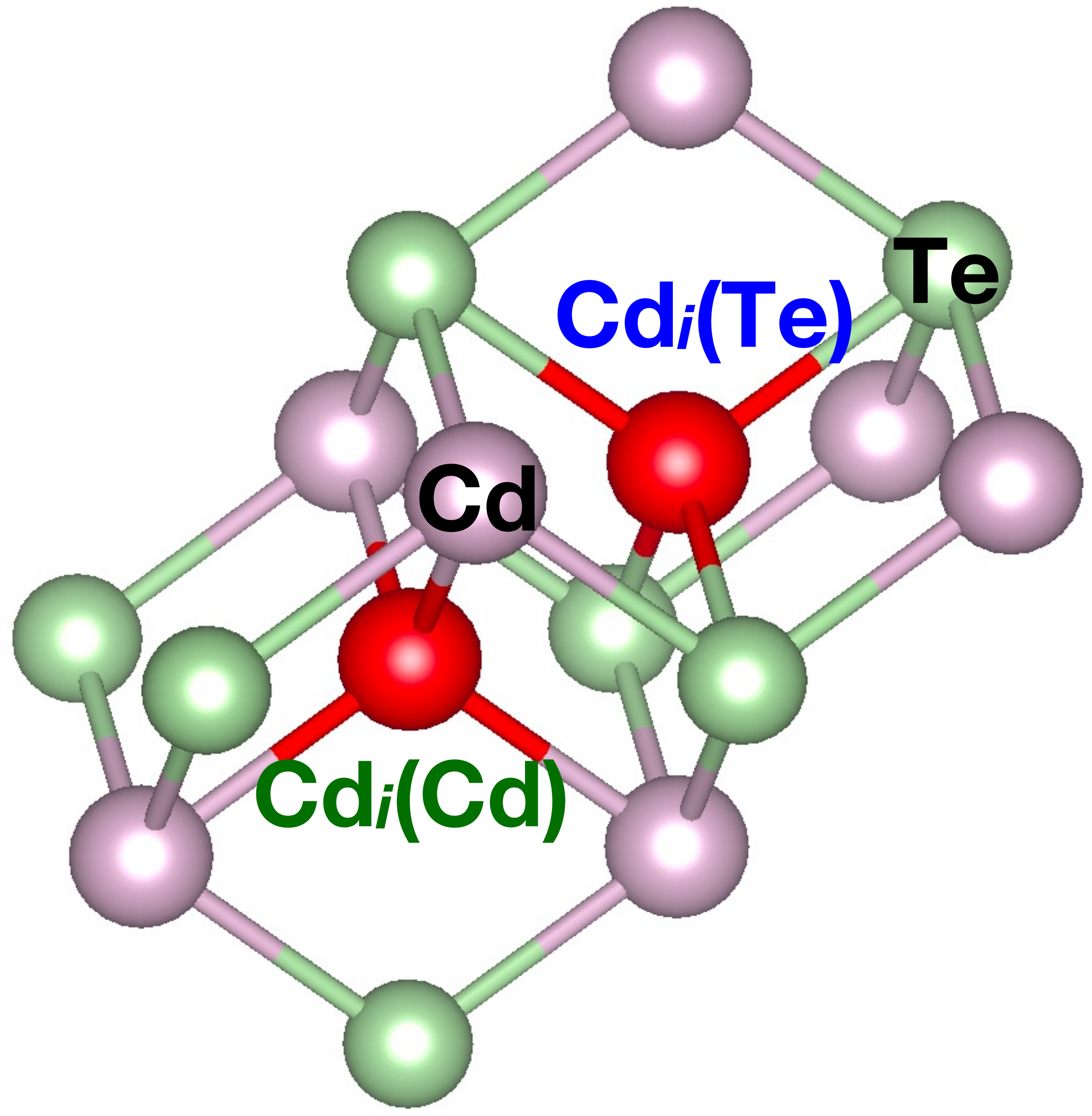
Exp. data from
A. Nagaoka *et al.*, Appl. Phys. Lett. **116**, 132102 (2020)

Possible intrinsic defects that act as compensation centers in p-type CdTe



Similar to J. Pan, W. K. Metzger, and S. Lany, Phys. Rev. B **98**, 054108 (2018)

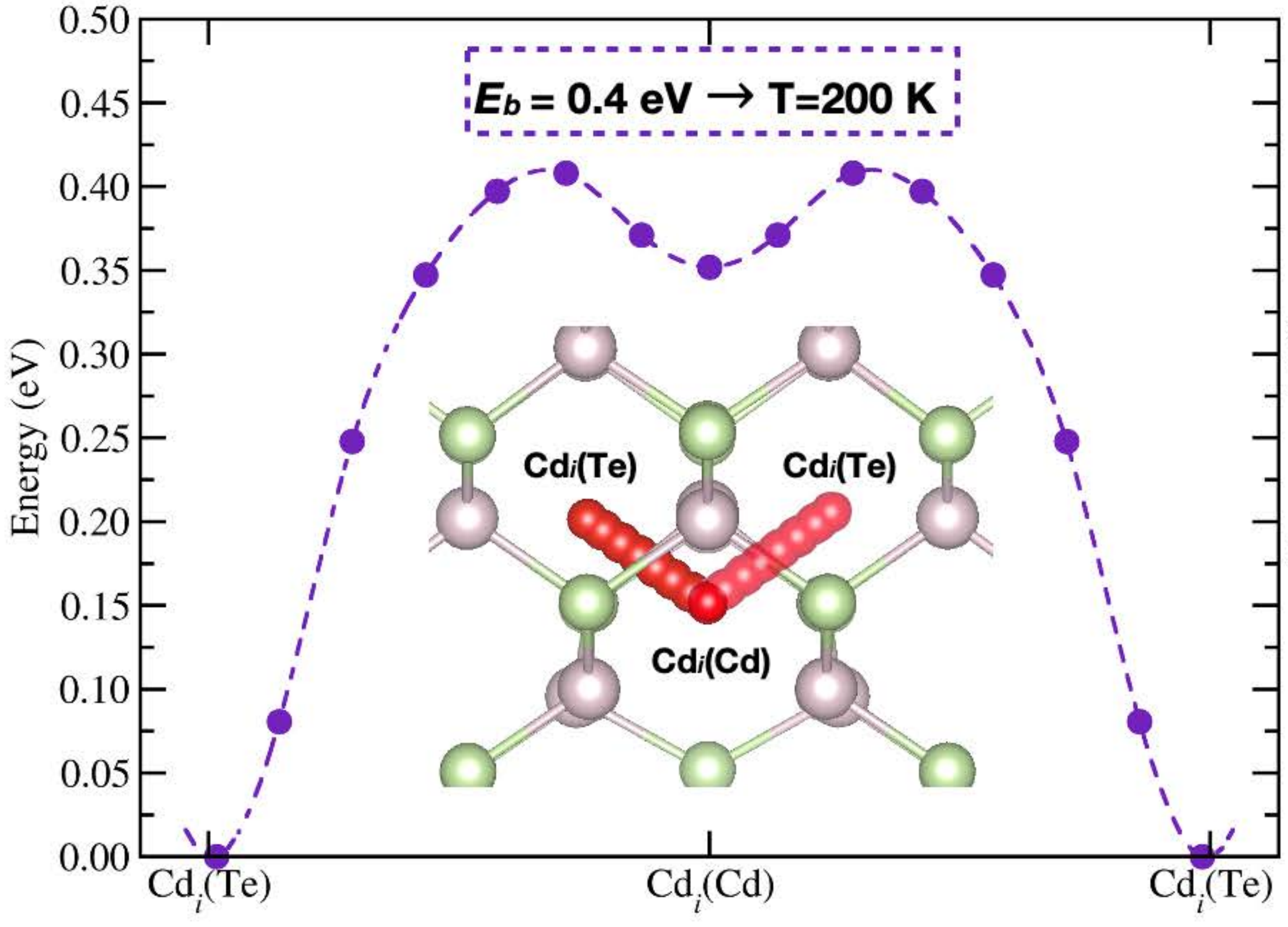
- Cd_i and V_{Te} and are the lowest energy defects in *p*-type and in Cd-rich (Te-poor) limiting conditions

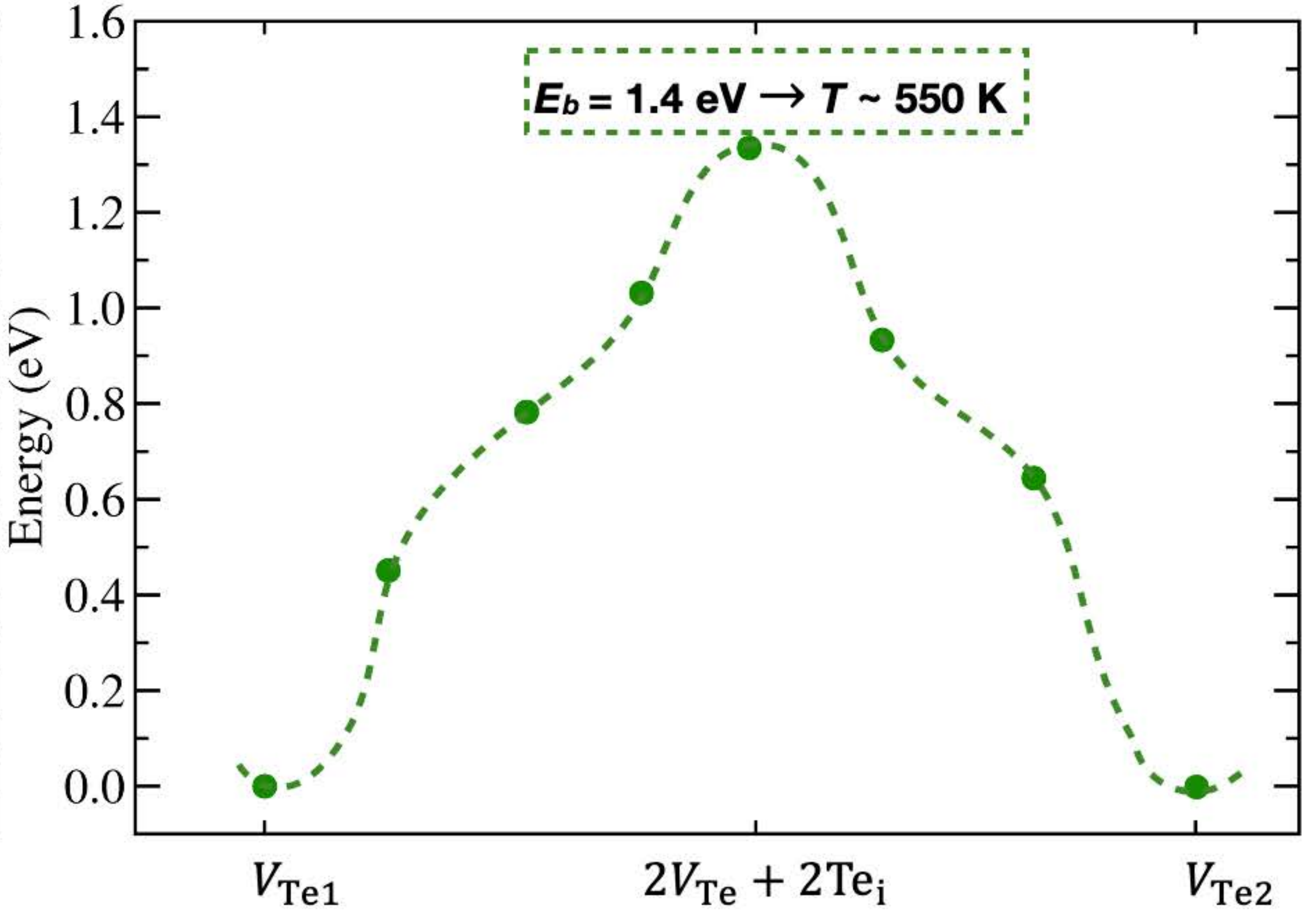


Calculated migration barriers of Cd_i and V_{Te}

- Cd_i is unstable, with very low migration barrier, will move even at room temp.

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





Cd interstitial will be highly mobile at room temperature, making it unstable; will either move out or combine with other defects

Te vacancy more likely to be a compensating donor, stable up to 550 K

Summary

- SOC is crucial to describe the band structure of CdTe and the properties of group-*V* acceptors in CdTe; explains the difference between present work and previous calc.
- P, As, and Sb are shallow acceptors in CdTe, with the ionization energies ~100 meV, in agreement with recent Hall measurements in bulk crystals
- AX center is not the dominant compensation center in *p*-type CdTe; unstable in the case of As and P, barely stable in the case of Sb doping
- Intrinsic defects, such as V_{Te}, are potentially important compensation centers
- Cd_i is unstable with low migration barrier

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