CMD32
Osaka University, 1. Mar. 2018

First-principles calculations toward developing novel semiconductors

Yu Kumagai

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PRESTO, JST, Japan

Career

Apr. 2007 – Mar. 2010 : Master course and Ph. D student at the Department of Material science and engineering, Kyoto university (adviser: Prof. Isao Tanaka)

Apr. 2010 – Mar. 2011 : Posdoc at the same place

Apr. 2011 – Nov. 2012 : JSPS fellow at the Department of Materials, ETH Zurich Prof. Nicola A. Spaldin

Dec. 2012 - Aug. 2015: Research Assistant Professor at Tokyo Tech, MCES Prof. Fumiyasu Oba

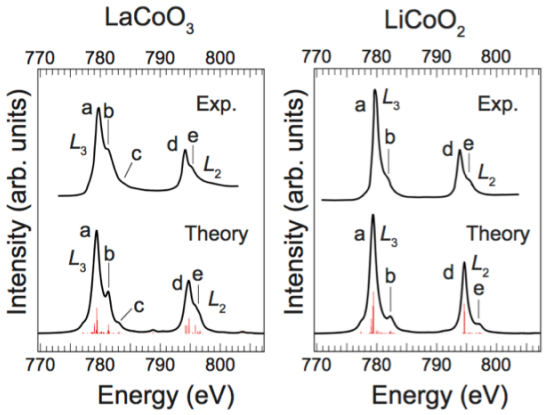
Sep. 2015 - Nov. 2016: Research Lecturer at the same place

Dec. 2016 - : Research Associate Professor at the same place

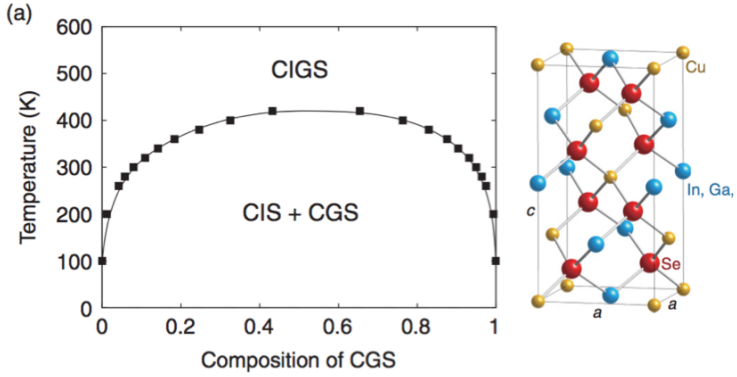
Nov. 2016 - : JST PRESTO

Brief view of my old works

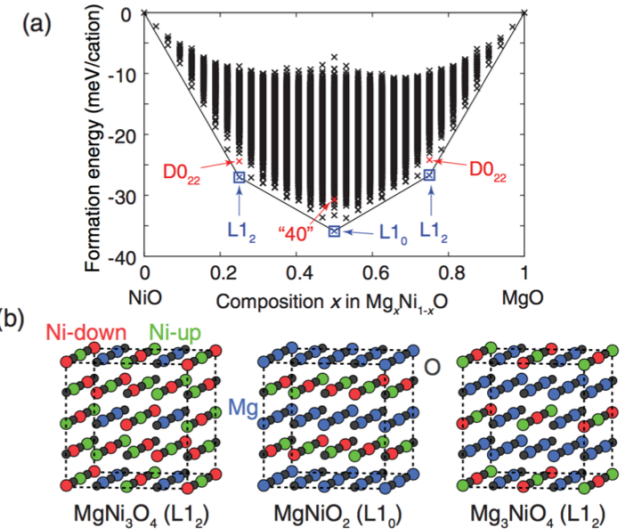
- Student days：transition metal compounds.



YK *et al.*, PRB (2008)
YK *et al.*, JPCM (2009) etc.

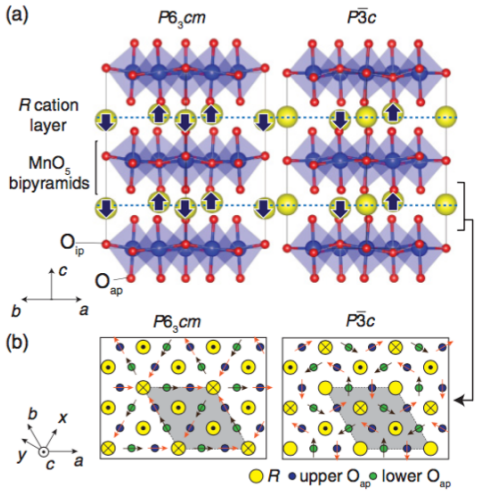


YK *et al.*, PRB (2012) etc.

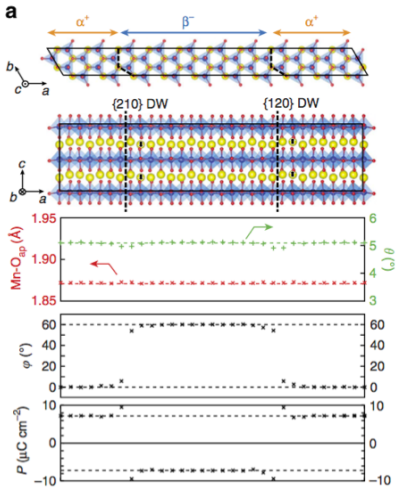


YK *et al.*, PRB (2009)
YK *et al.*, PRB (2012) etc.

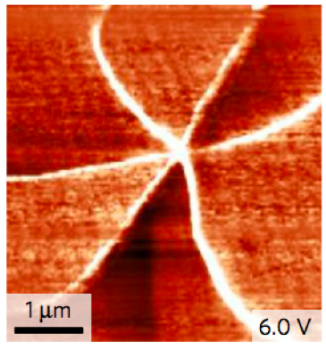
- Pos-doc era：hexagonal manganese oxides

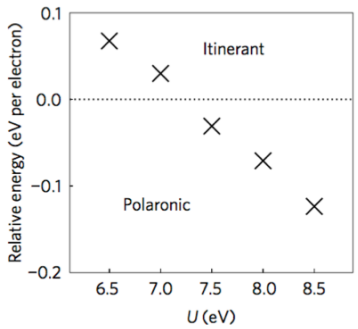


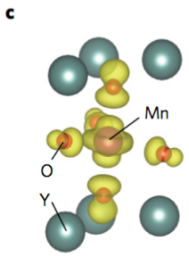
YK *et al.*, PRB (2012)



YK and Spaldin, Nat. Comm. (2013)







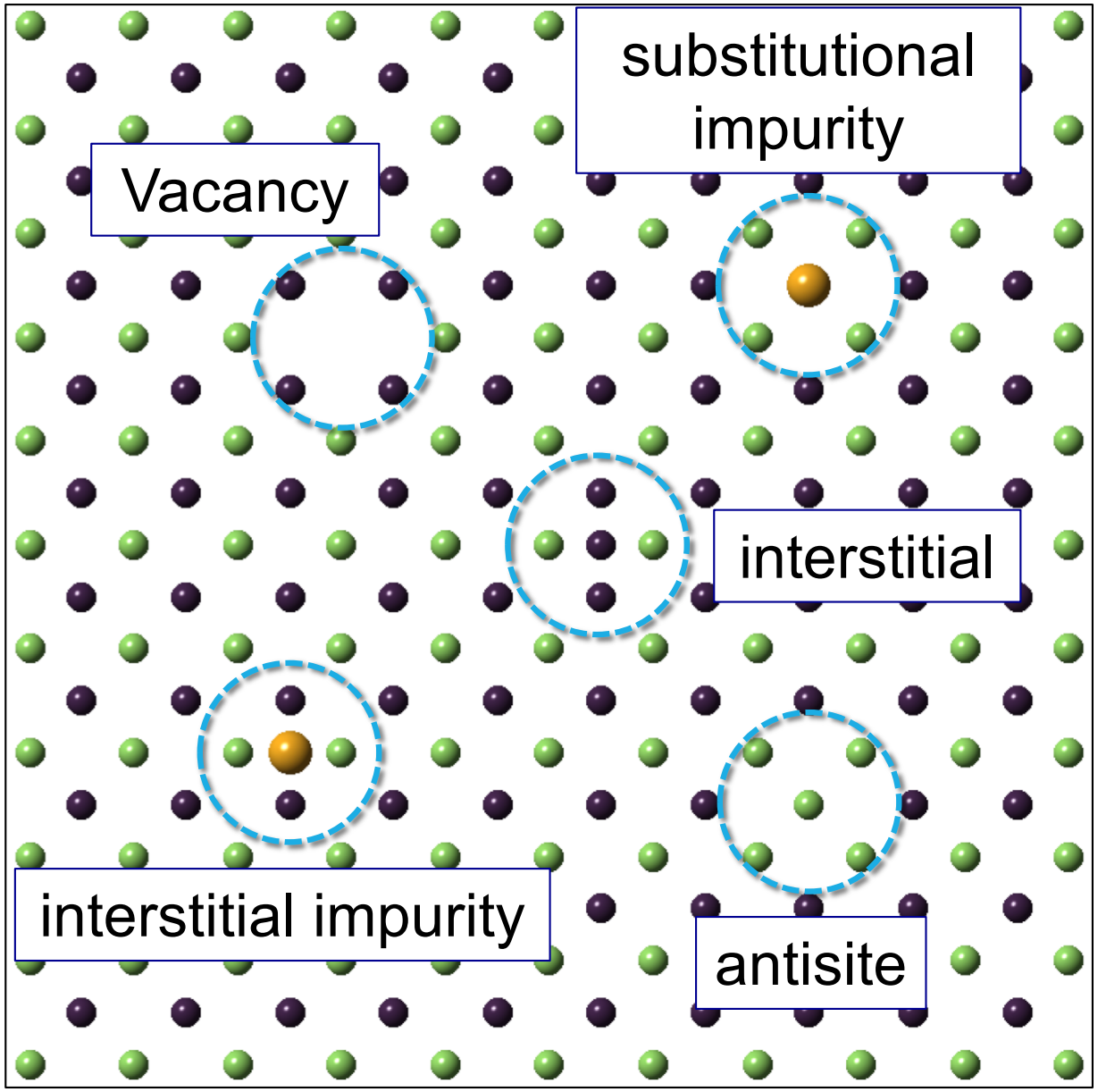
Mundy, Schaab, YK (co-first authors), *et al.*, Nat. Mat. (2017)

Contents

- First-Principles Calculations on Point Defects in semiconductors and insulators
- Computational Materials Database toward Discovering Novel Semiconductors

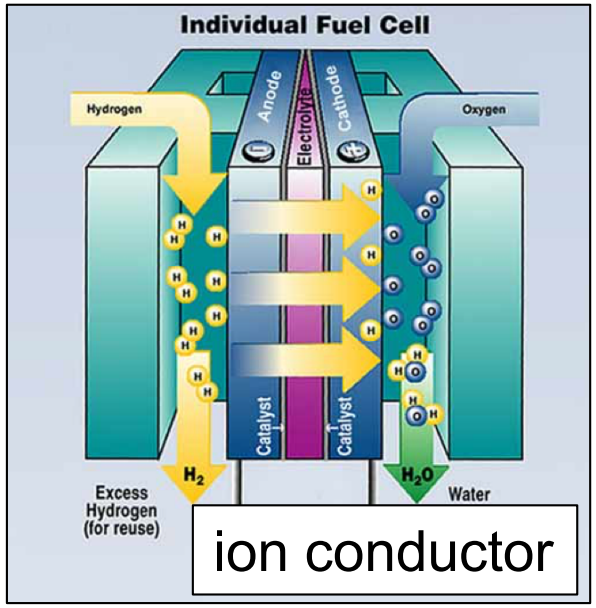
First-Principles Calculations on Point Defects in semiconductors and insulators

Point defects in semiconductors and insulators

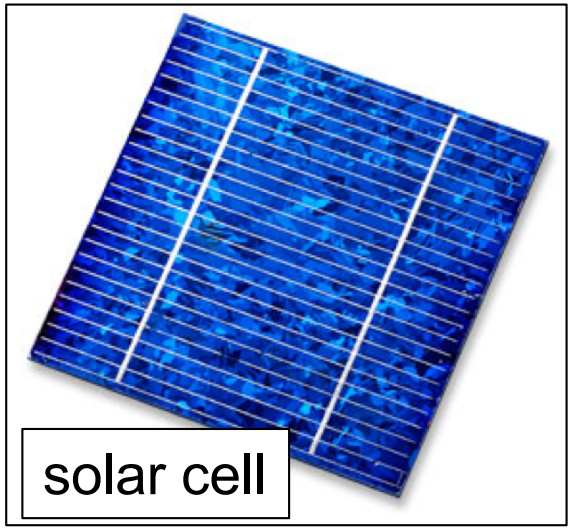


Related applications

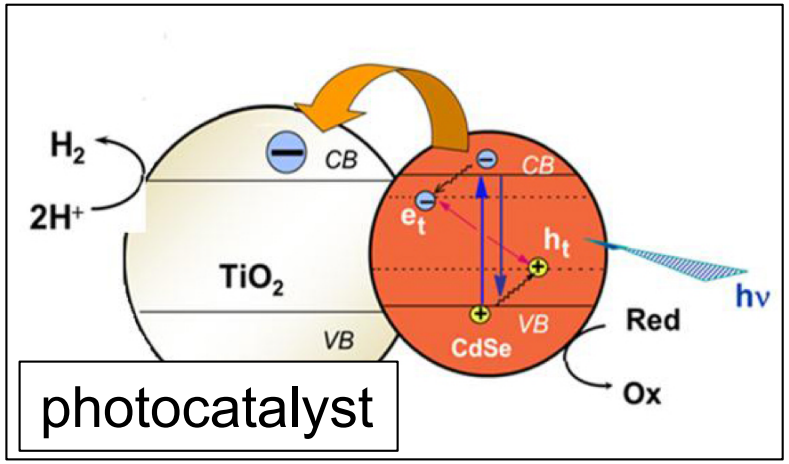
http://www.greenprophet.com



http://www.hygen.com



http://www.itmedia.co.jp

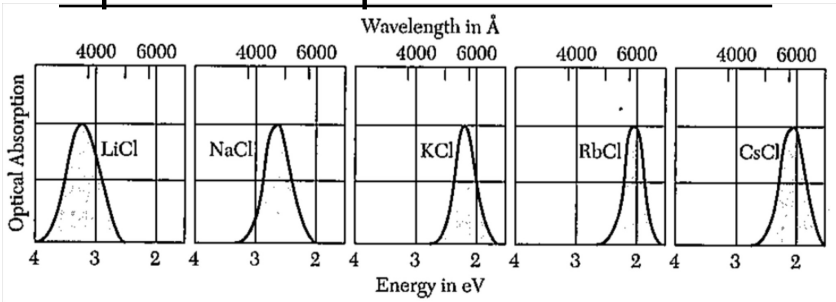


http://www3.nd.edu/~kamatlab

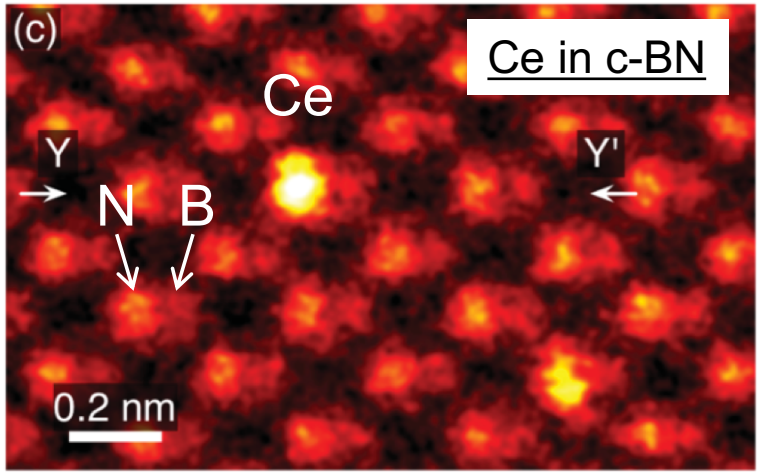
Experimental techniques

- Chemical composition (ICP)
- Optical spectra (XPS, XAS)
- Ion diffusion (impedance analysis)
- Carrier type and concentration (Hall measurement)
- Direct image (TEM/STEM)
- Magnetic state (EPR)

Optical absorption for F-centers



Kittel, Solid State Physics, 8th ed.



Ishikawa *et al.*, PRL, 2013

None of them are not perfect!!

Combination of experiments and first-principles calculations

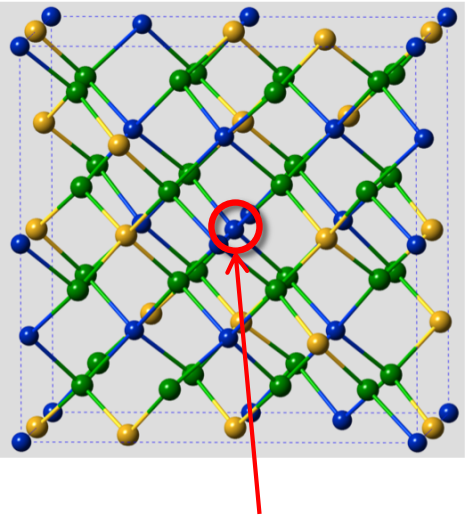
Defect formation energy

Zhang and Northup (1991)

$$E_f[D^q] = \Big\{ \underbrace{E[D^q] + E_{\mathrm{corr}}[D^q]}_{①} \Big\} - \underbrace{E_P}_{②} - \underbrace{\sum n_i \mu_i}_{③} + \underbrace{q\Big\{ \epsilon_{\mathrm{VBM}} + \Delta\epsilon_F \Big\}}_{④}$$

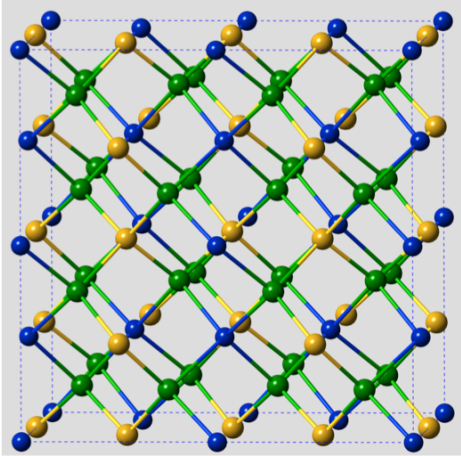
ex: Sn_{Zn}^{+2} antisite in $ZnSnP_2$

① Defect model

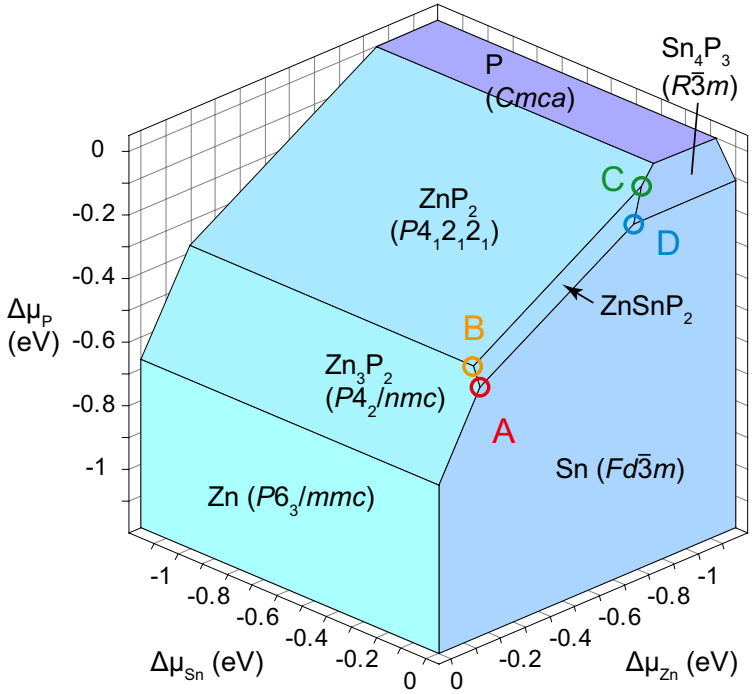


Sn_{Zn}^{+2} antisite

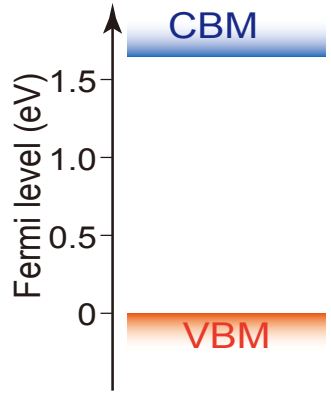
② Perfect system



③ Chemical potential diagram



④ Band gap

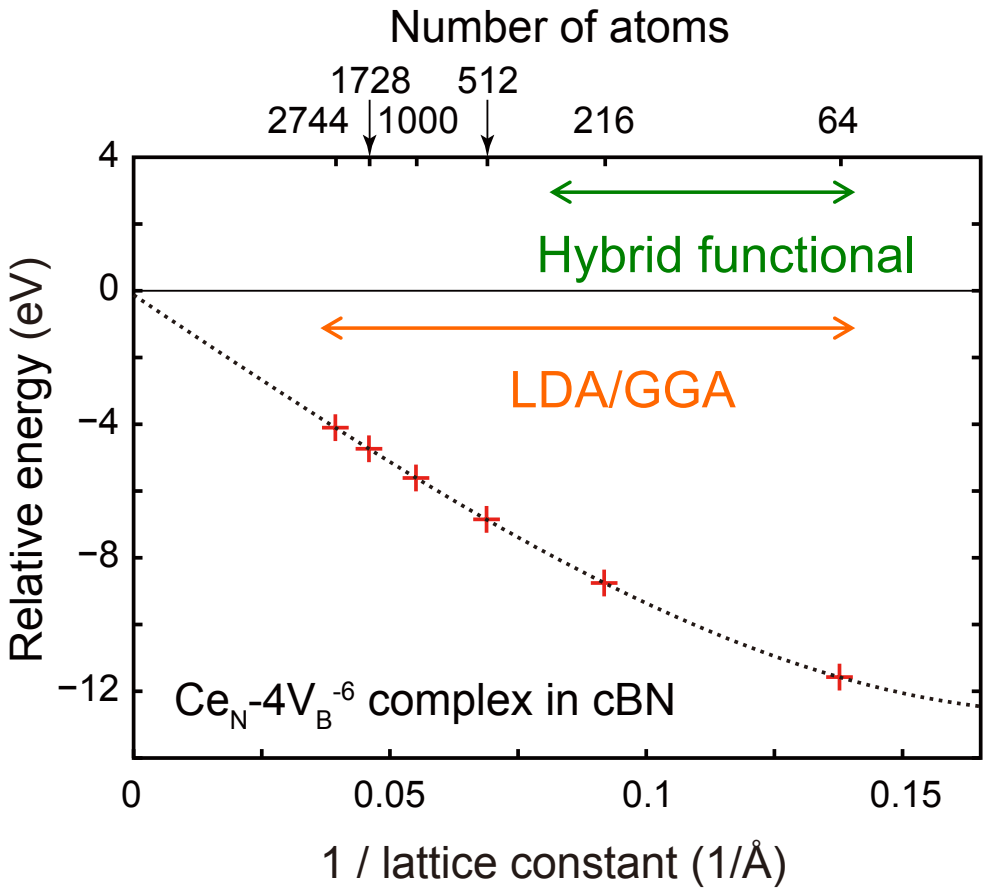


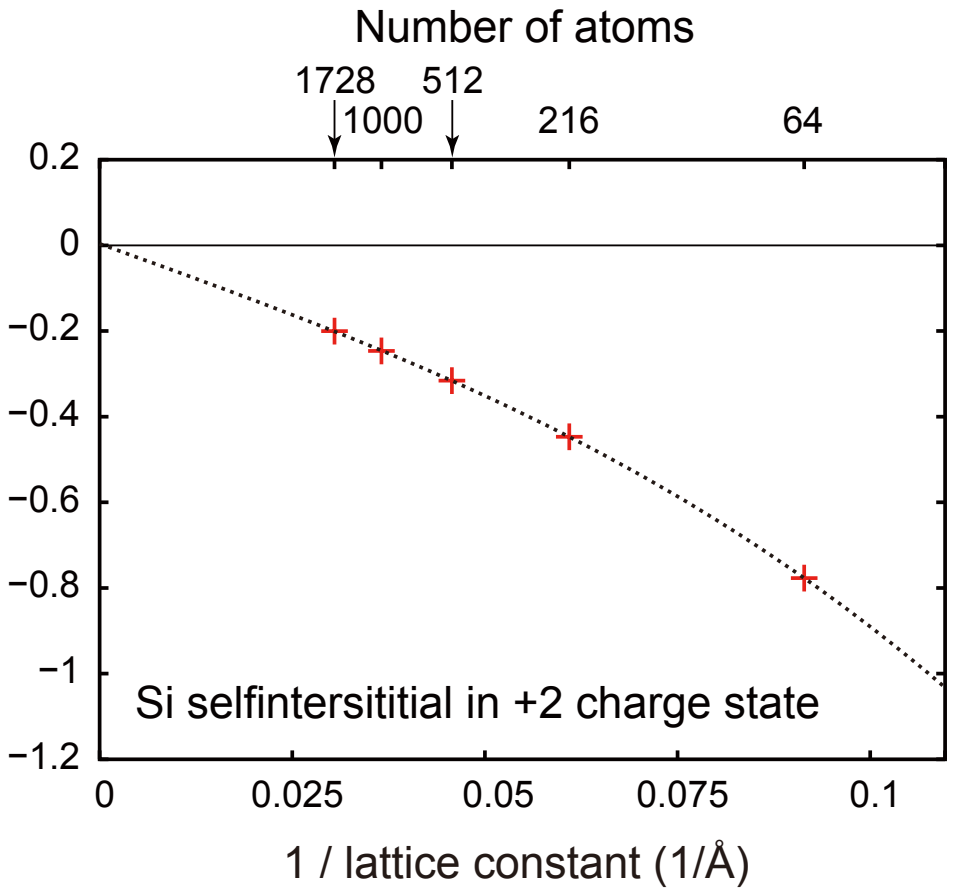
$$q = +2$$

$$n_{\mathrm{Zn}} = -1; n_{\mathrm{Sn}} = +1$$

Defect formation energy

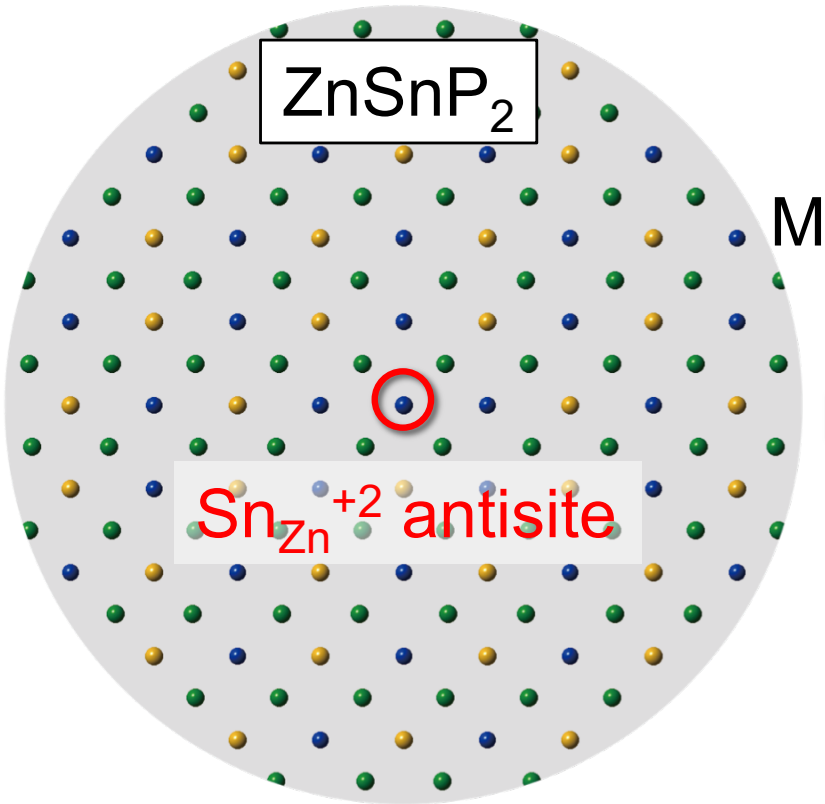
$$E_f[D^q] = \left\{ E[D^q] + \boxed{E_{\mathrm{corr}}[D^q]} \right\} - E_P - \sum n_i \mu_i + q\left\{ \epsilon_{\mathrm{VBM}} + \Delta\epsilon_F \right\}$$



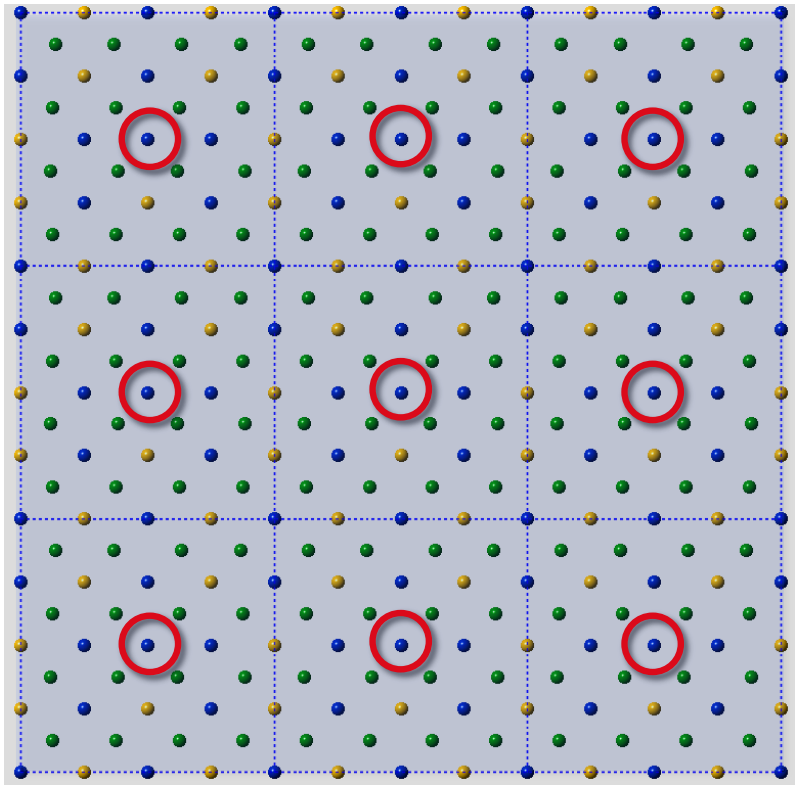


VASP code (Kresse and Hafner, 1993); PBE-GGA (Perdew, Burke and Ernzerhof, 1996)

Origin of the cell size dependence



Modeling using a supercell



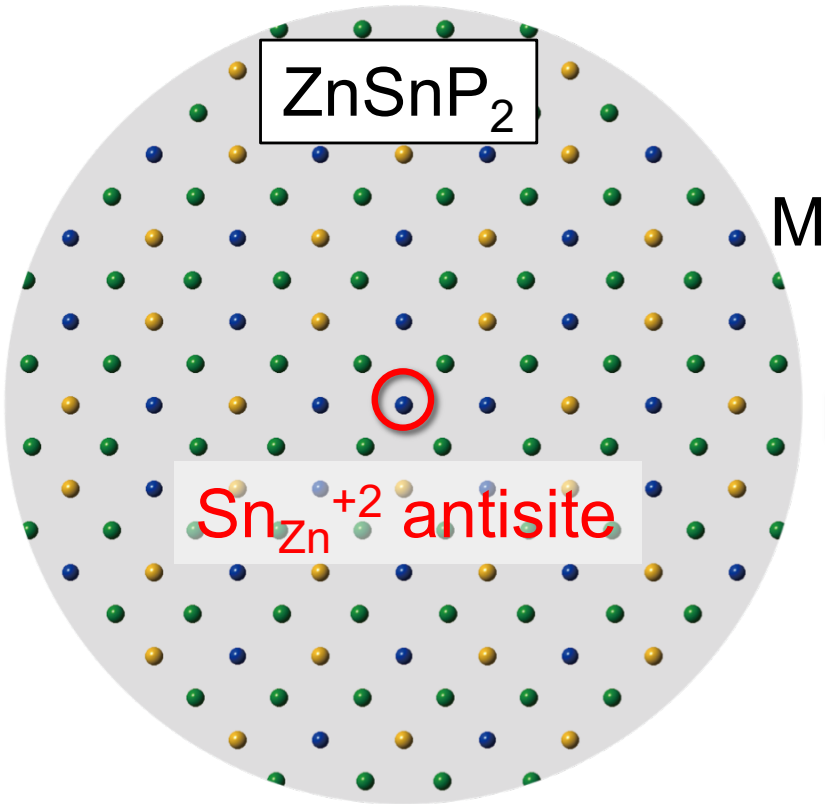
-2|e|/cell

An isolated charged defect

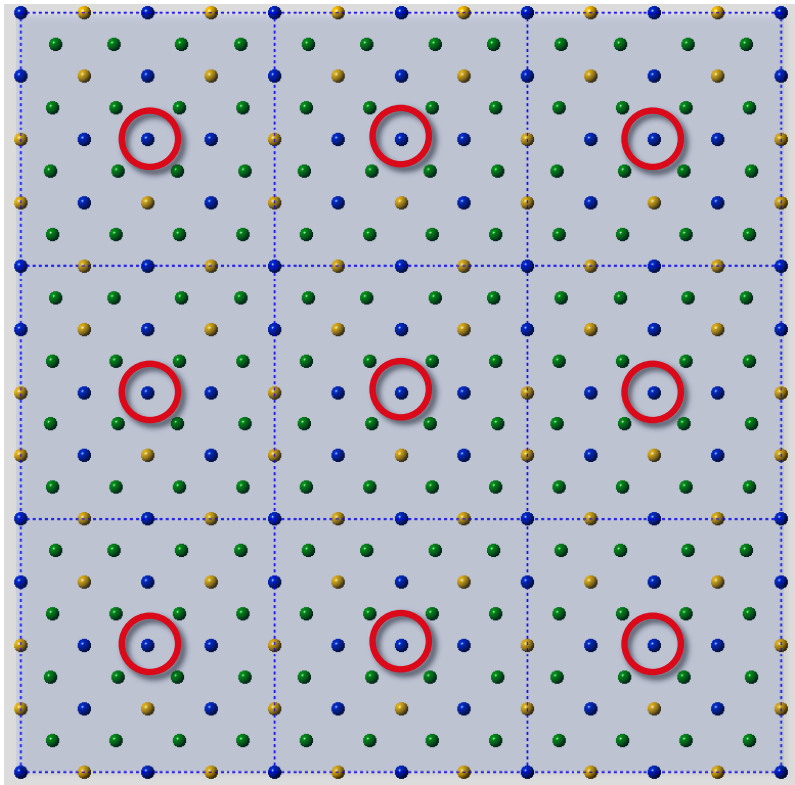
Spurious electrostatic interactions

1. Periodic defect-defect interactions
2. Defect-background charge interactions

Origin of the cell size dependence



Modeling using a supercell



-2|e|/cell

An isolated charged defect

$$E_{\mathrm{cor}} = E_{\mathrm{isolated}} - E_{\mathrm{periodic}} = \frac{1}{2}\int_{\Omega} V_{\mathrm{cor}}(\boldsymbol{r})\rho_d(\boldsymbol{r})d\boldsymbol{r}$$

$$V_{\mathrm{cor}} = V_{\mathrm{isolated},q} - V_{\mathrm{periodic},q}$$

Finite cell-size corrections

$$E_{\mathrm{cor}} = E_{\mathrm{isolated}} - E_{\mathrm{periodic}} = \frac{1}{2}\int_{\Omega} V_{\mathrm{cor}}(\boldsymbol{r})\rho_d(\boldsymbol{r})d\boldsymbol{r}$$

$$V_{\mathrm{cor}}(\boldsymbol{r}) = -V^{\mathrm{iso}}_{\mathrm{PC,q}} - \frac{2\pi q}{3\varepsilon L^3}r^2 + \frac{4\pi}{3\varepsilon L^3}\boldsymbol{p}\cdot\boldsymbol{r} - \frac{2\pi Q}{3\varepsilon L^3} + O(r^4)$$

Point-charge correction
(Leslie and Gillan, 1985)

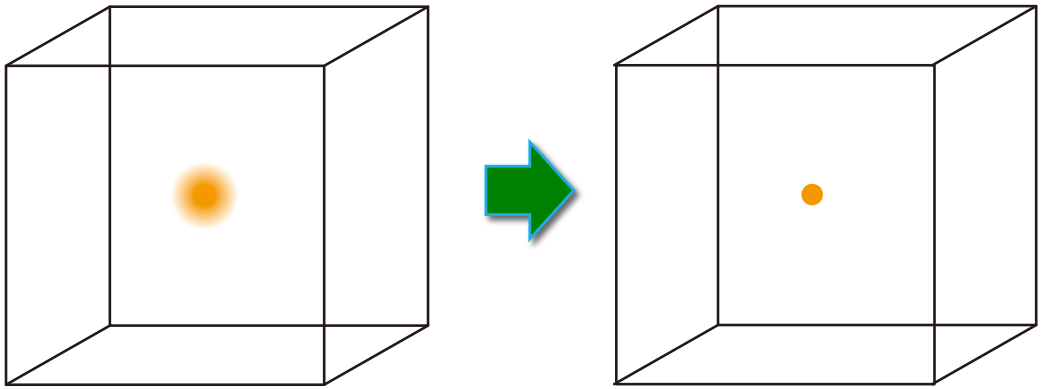
$$E_{\mathrm{PC}} = \frac{\alpha q^2}{2\varepsilon L}$$

q : charge

α : Madelung constant

ϵ : Dielectric constant

L : Side of the cell



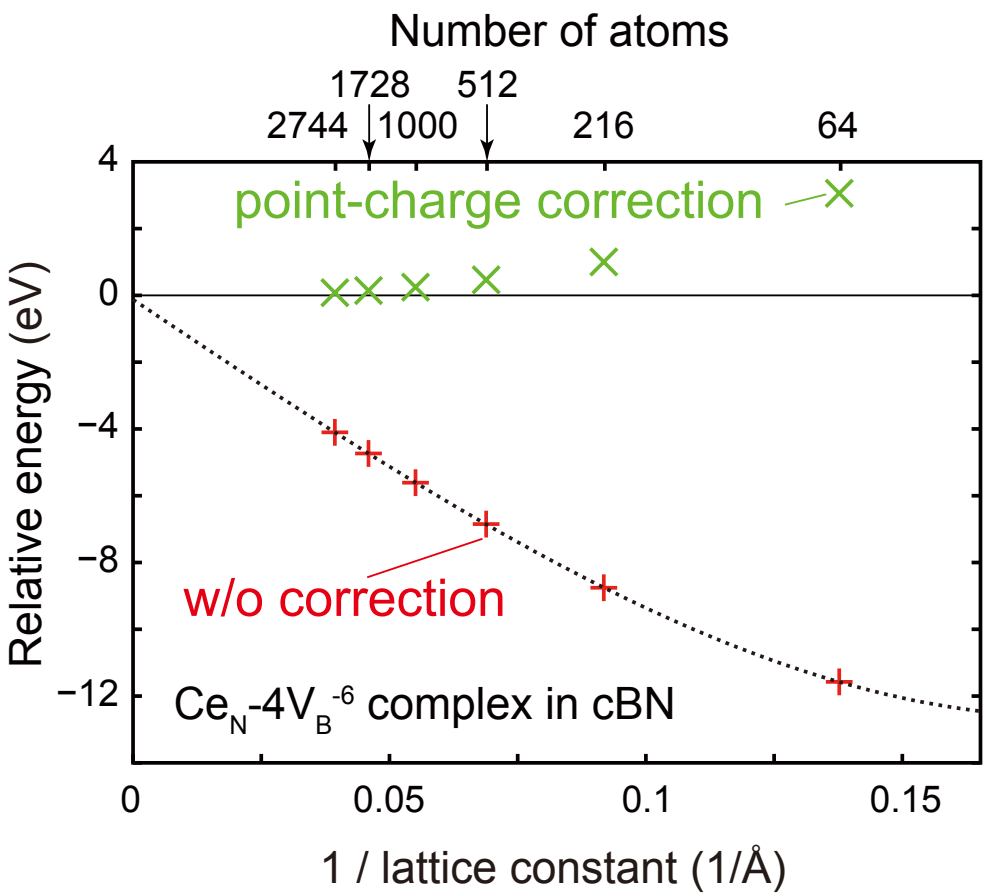
Finite defect

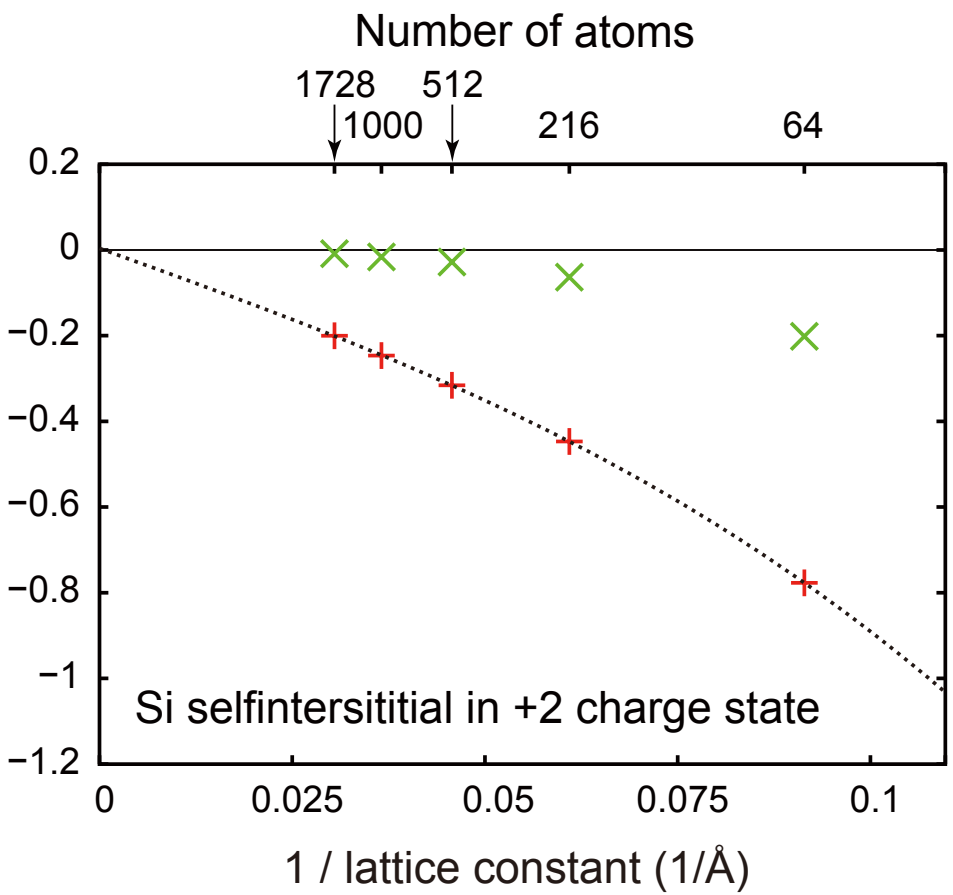
Point charge

Point-charge corrections

Point-charge correction
(Leslie and Gillan, 1985)

$$E_{\mathrm{PC}} = \frac{\alpha q^2}{2\varepsilon L}$$





Finite cell-size corrections

$$E_{\mathrm{cor}} = E_{\mathrm{isolated}} - E_{\mathrm{periodic}} = \frac{1}{2}\int_{\Omega} V_{\mathrm{cor}}(\boldsymbol{r})\rho_d(\boldsymbol{r})d\boldsymbol{r}$$

$$V_{\mathrm{cor}}(\boldsymbol{r}) = -V^{\mathrm{iso}}_{\mathrm{PC,q}} - \frac{2\pi q}{3\varepsilon L^3}r^2 + \frac{4\pi}{3\varepsilon L^3}\boldsymbol{p}\cdot\boldsymbol{r} - \frac{2\pi Q}{3\varepsilon L^3} + O(r^4)$$

Point-charge correction (Leslie and Gillan, 1985)

Makov-Payne correction (1995)

$$E_{\mathrm{PC}} = \frac{\alpha q^2}{2\varepsilon L}$$

$$E_{\mathrm{MP}} = E_{\mathrm{PC}} - \frac{2\pi q Q}{3\varepsilon L^3} + \cancel{\frac{2\pi \boldsymbol{p}^2}{3\varepsilon L^3}} + O(L^{-5})$$

q : charge

α : Madelung constant

ϵ : Dielectric constant

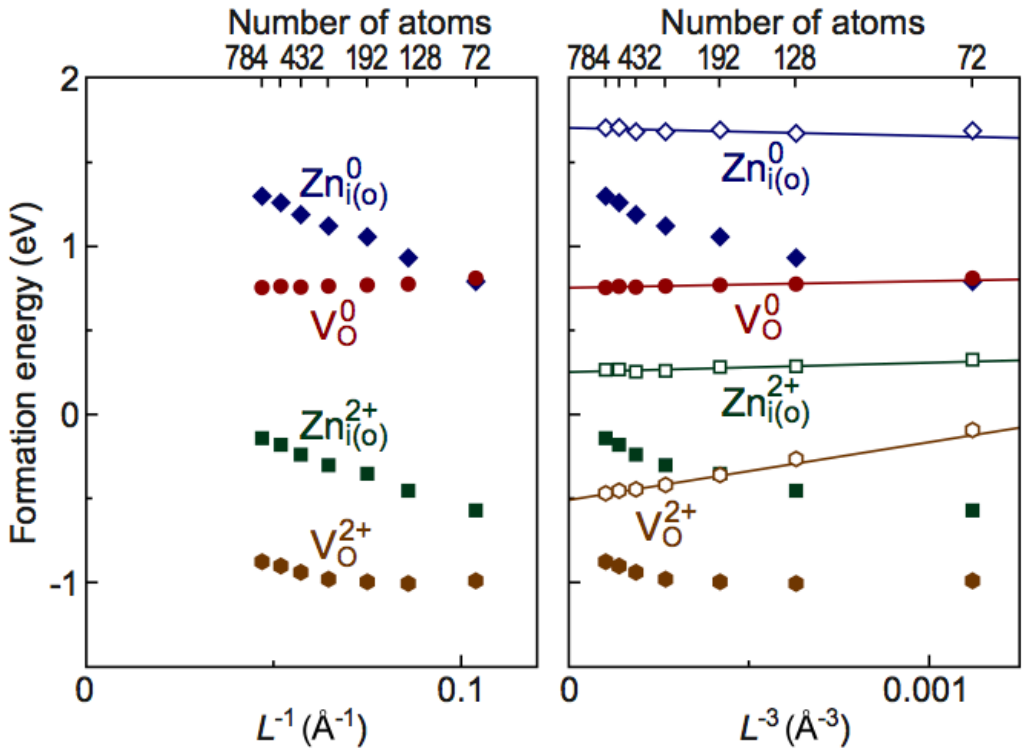
L : Side of the cell

$Q = \int r^2 \underline{\rho_d}(\boldsymbol{r})d\boldsymbol{r}$: second radial moment

defect charge distribution ← ill-defined ☹

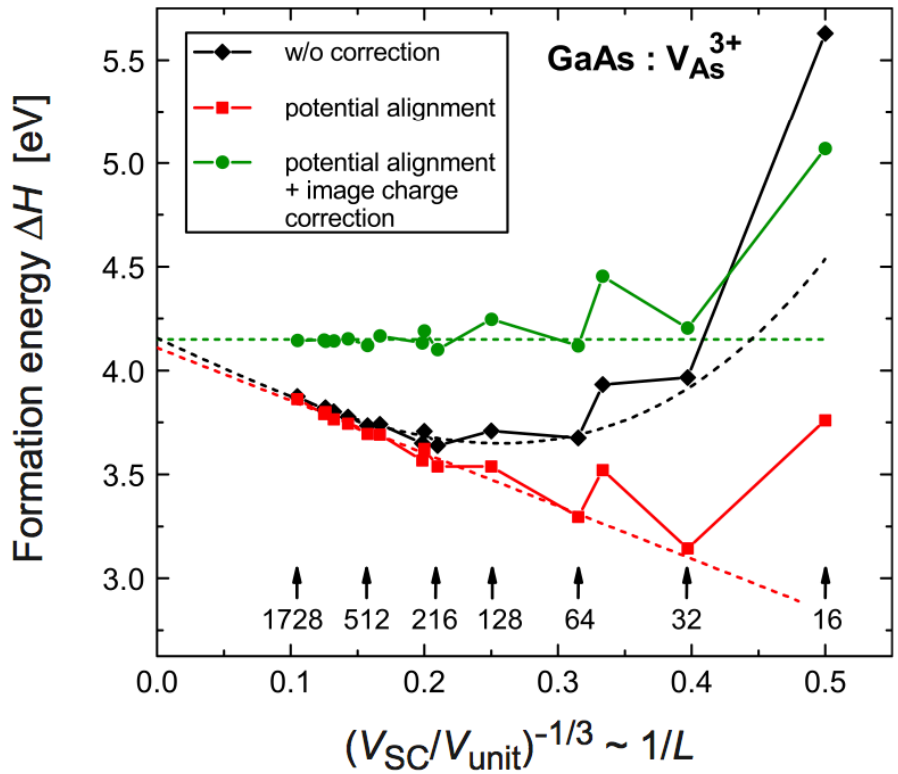
Third-order corrections

ZnO



Oba et al., 2008

GaAs

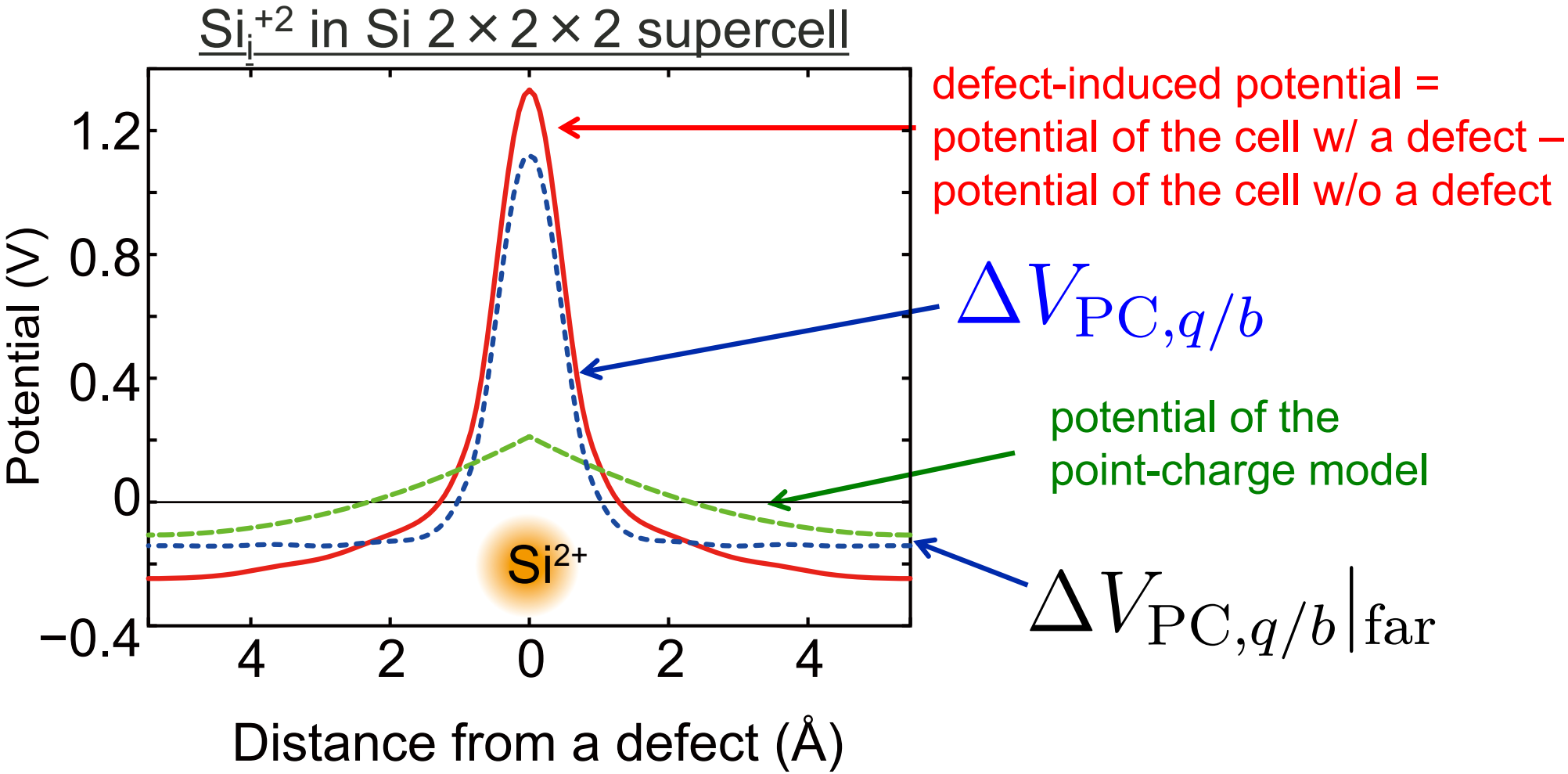


Lany and Zunger, 2008

Freysoldt-Neugebauer-Van de Walle (FNV) scheme

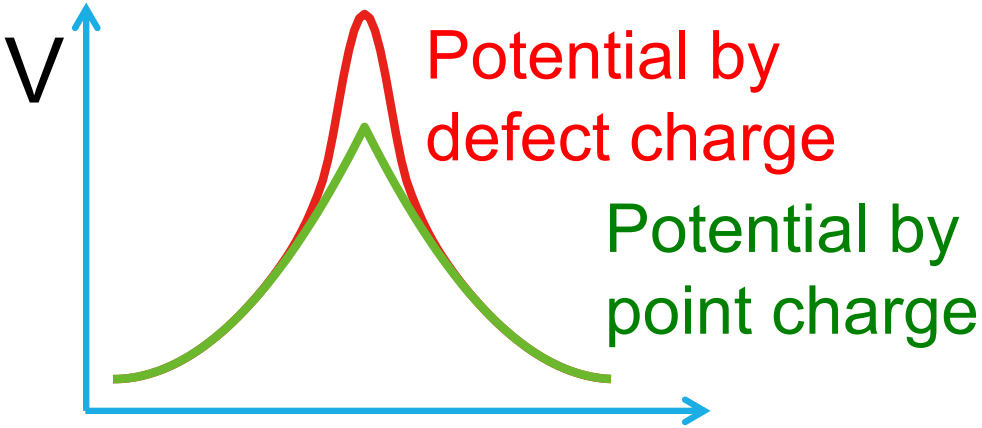
$$E_{\mathrm{FNV}} = E_{\mathrm{PC}} - q\Delta V_{\mathrm{PC},q/b}\big|_{\mathrm{far}}$$

Freysoldt et al., PRL, 2009

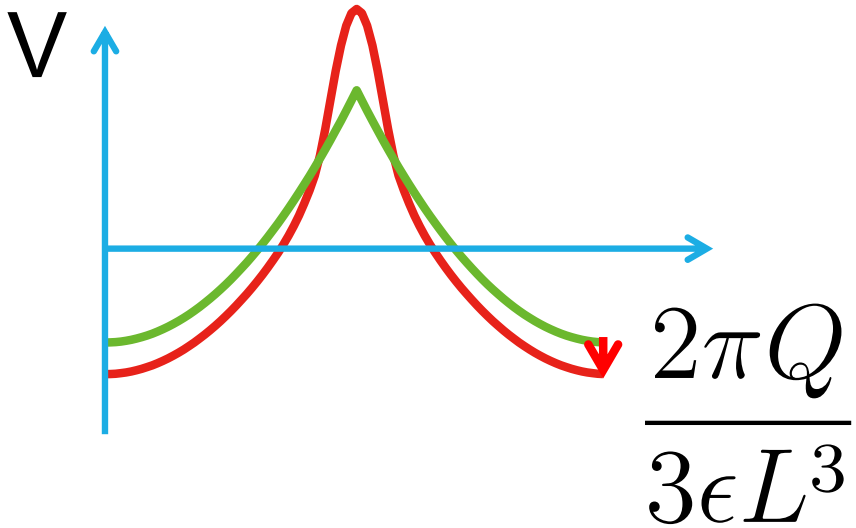


Relation between MP and FNV

Open boundary condition



Periodic boundary condition



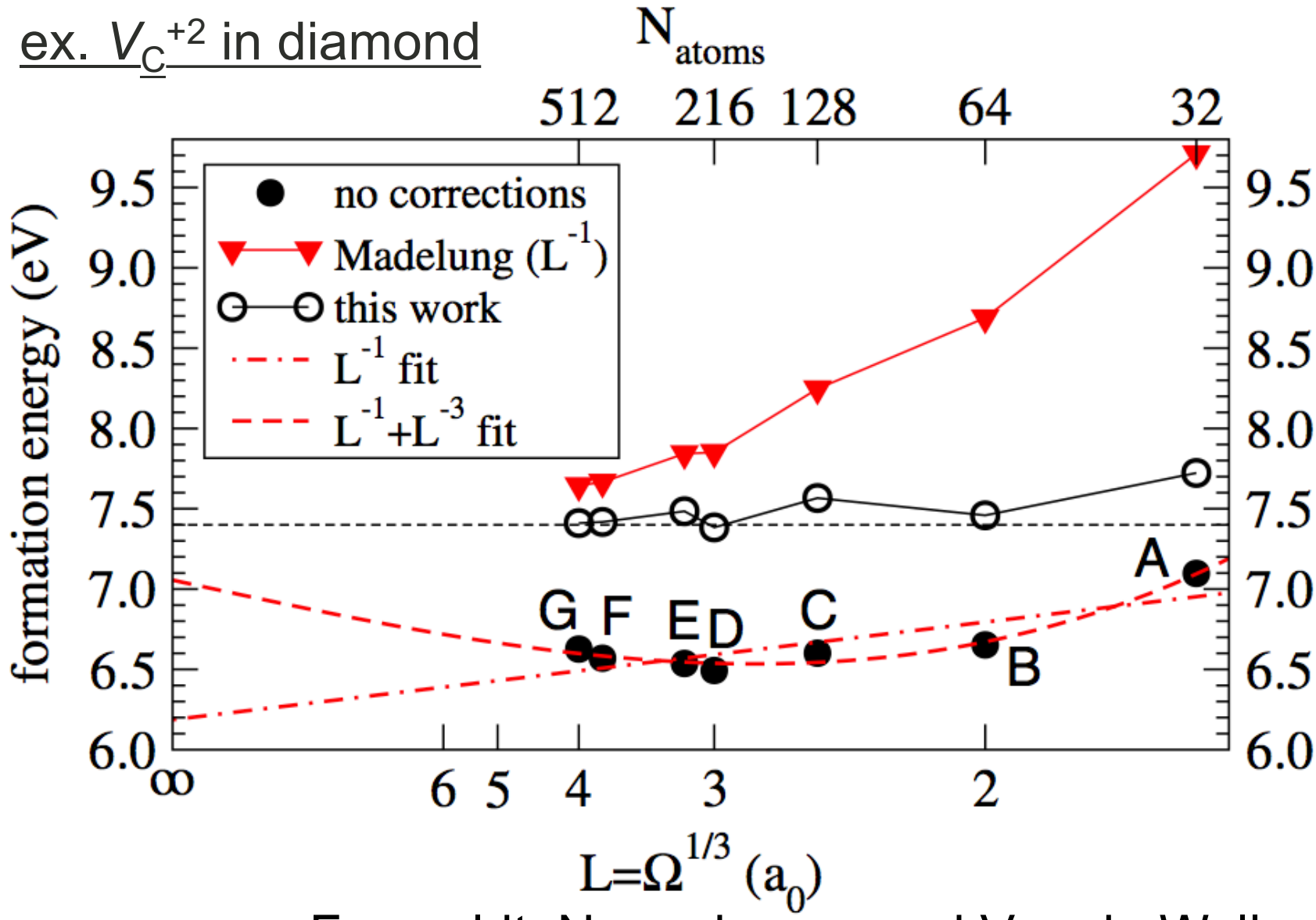
$$E_{\mathrm{FNV}} = E_{\mathrm{PC}} - \underline{q\Delta V_{\mathrm{PC},q/b}\big|_{\mathrm{far}}}$$

$$E_{\mathrm{MP}} = E_{\mathrm{pc}} + E_{\mathrm{MP3}} = \frac{q^2\alpha}{2\epsilon L} - \frac{2\pi q Q}{3\epsilon L^3}$$

Komsa, Rantala, and Pasquarello, 2012

An example of FNV scheme

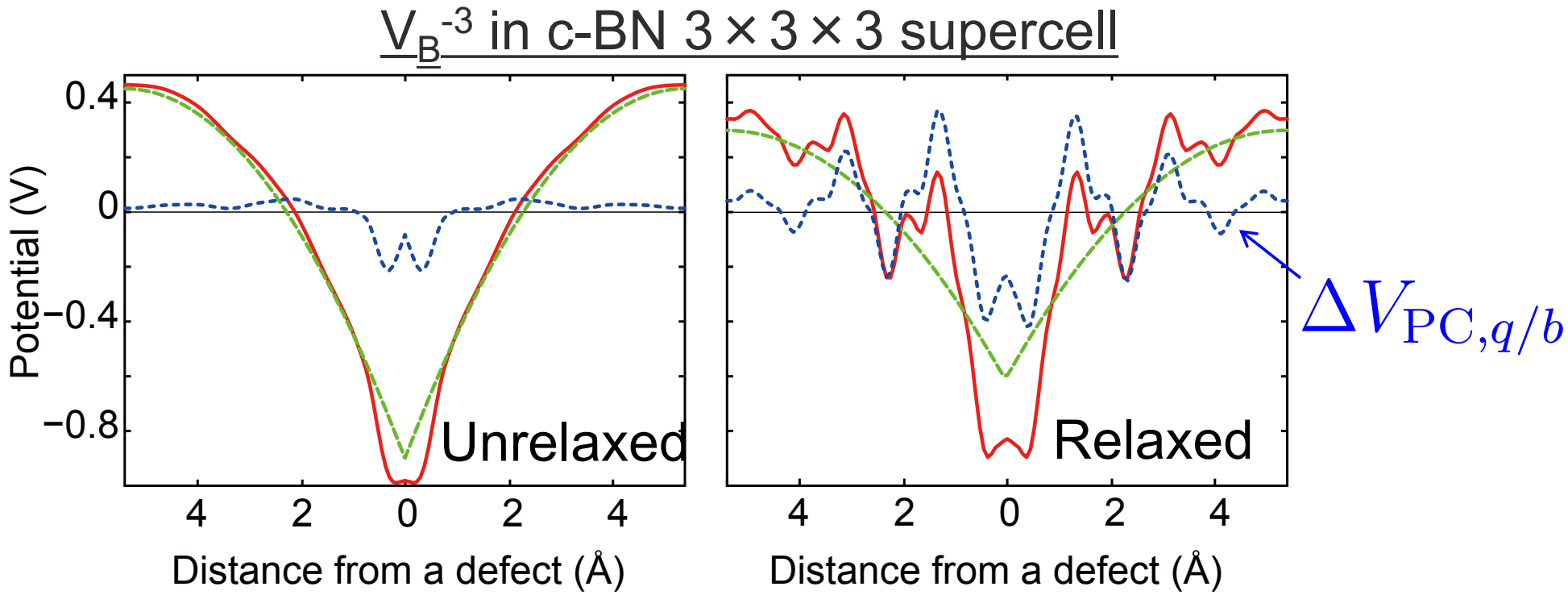
ex. V_C^{+2} in diamond



Freysoldt, Neugebauer, and Van de Walle, 2009

Limitation of original FNV scheme

1. Systems without atomic relaxation (Komsa *et al*., 2012)



2. Isotropic systems

$$V_{q/0}(\mathbf{r}) \rightarrow V_q^{\mathrm{lr}}(\mathbf{r}) = \frac{1}{\varepsilon}\int d^3\mathbf{r}' \frac{q_d(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.$$

Extend the FNV scheme to be applicable to diverse materials

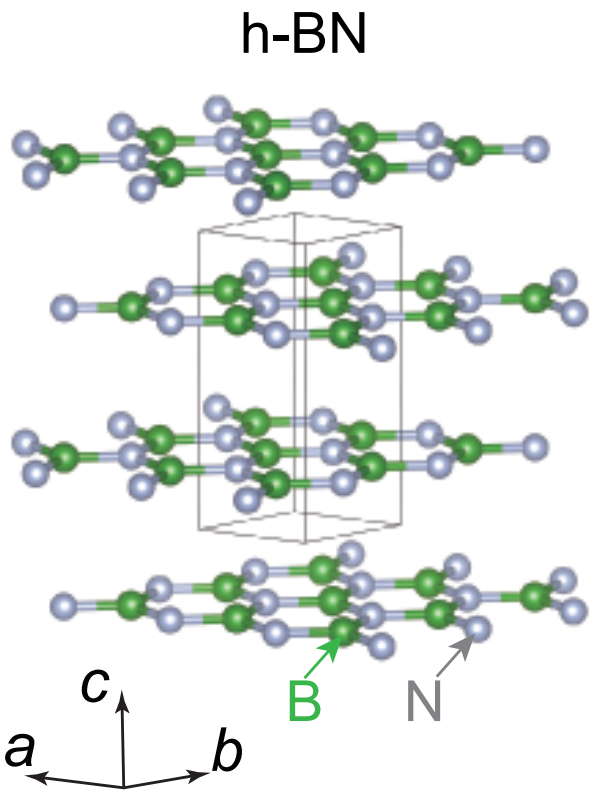
Point-charge potential in the anisotropic medium

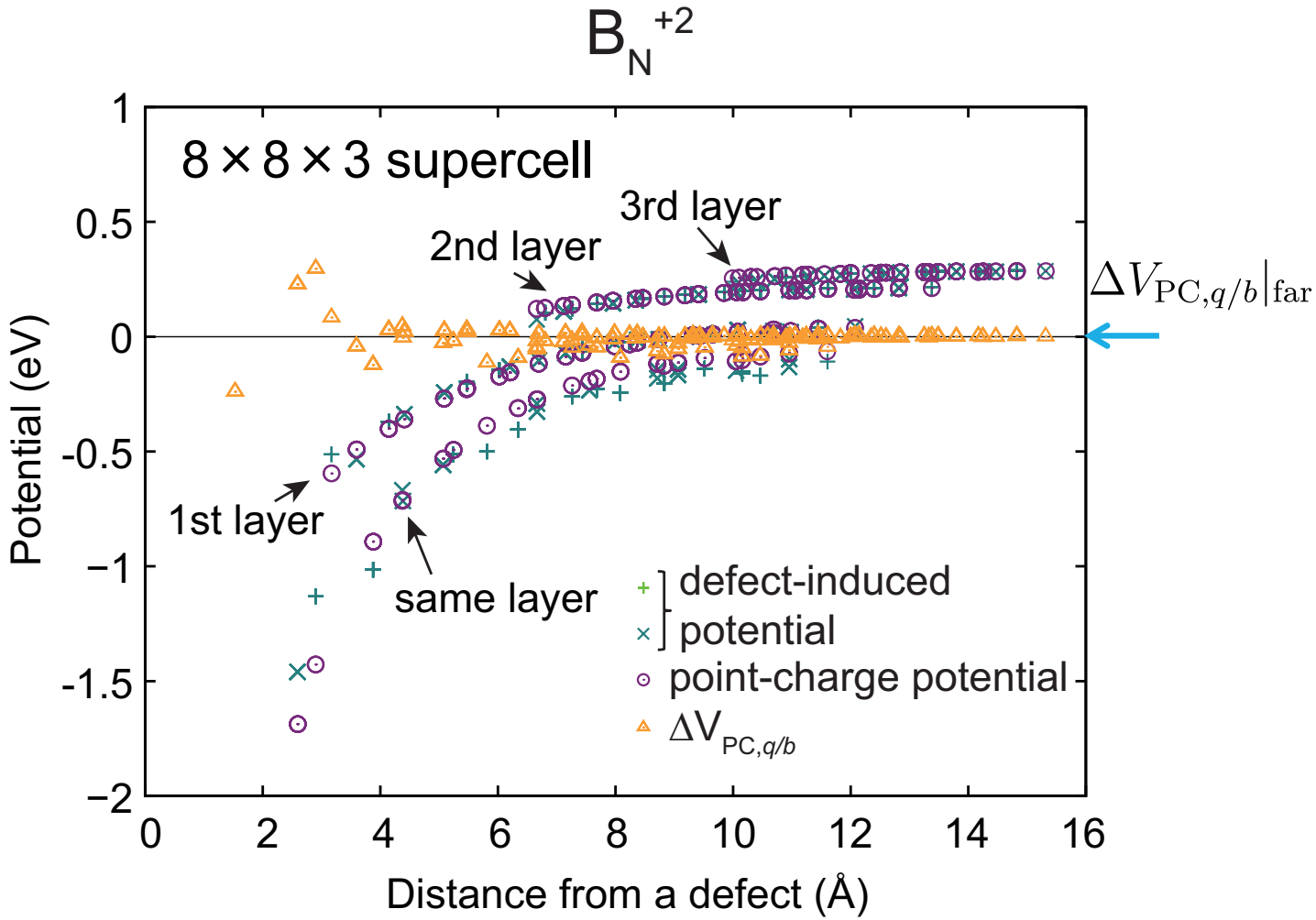
$$V_{\mathrm{PC},q}^{\mathrm{aniso}}(\boldsymbol{r} \neq \boldsymbol{0}) = \sum_{\boldsymbol{R}_i} \frac{q}{\sqrt{|\overline{\epsilon}|}} \frac{\mathrm{erfc}(\gamma \sqrt{\boldsymbol{R}_i \cdot \overline{\epsilon}^{-1} \cdot \boldsymbol{R}_i})}{\sqrt{\boldsymbol{R}_i \cdot \overline{\epsilon}^{-1} \cdot \boldsymbol{R}_i}} - \frac{\pi q}{V_c \gamma^2}$$

$$+ \sum_{\boldsymbol{G}_i}^{i \neq 0} \frac{4\pi q}{V_c} \frac{\exp(-\boldsymbol{G}_i \cdot \overline{\epsilon} \cdot \boldsymbol{G}_i / 4\gamma^2)}{\boldsymbol{G}_i \cdot \overline{\epsilon} \cdot \boldsymbol{G}_i} \cdot \exp(i\boldsymbol{G}_i \cdot \boldsymbol{r}). \quad (14)$$

Kumagai and Oba, Phys. Rev. B, 2014

Example 1: antisite defect in h-BN

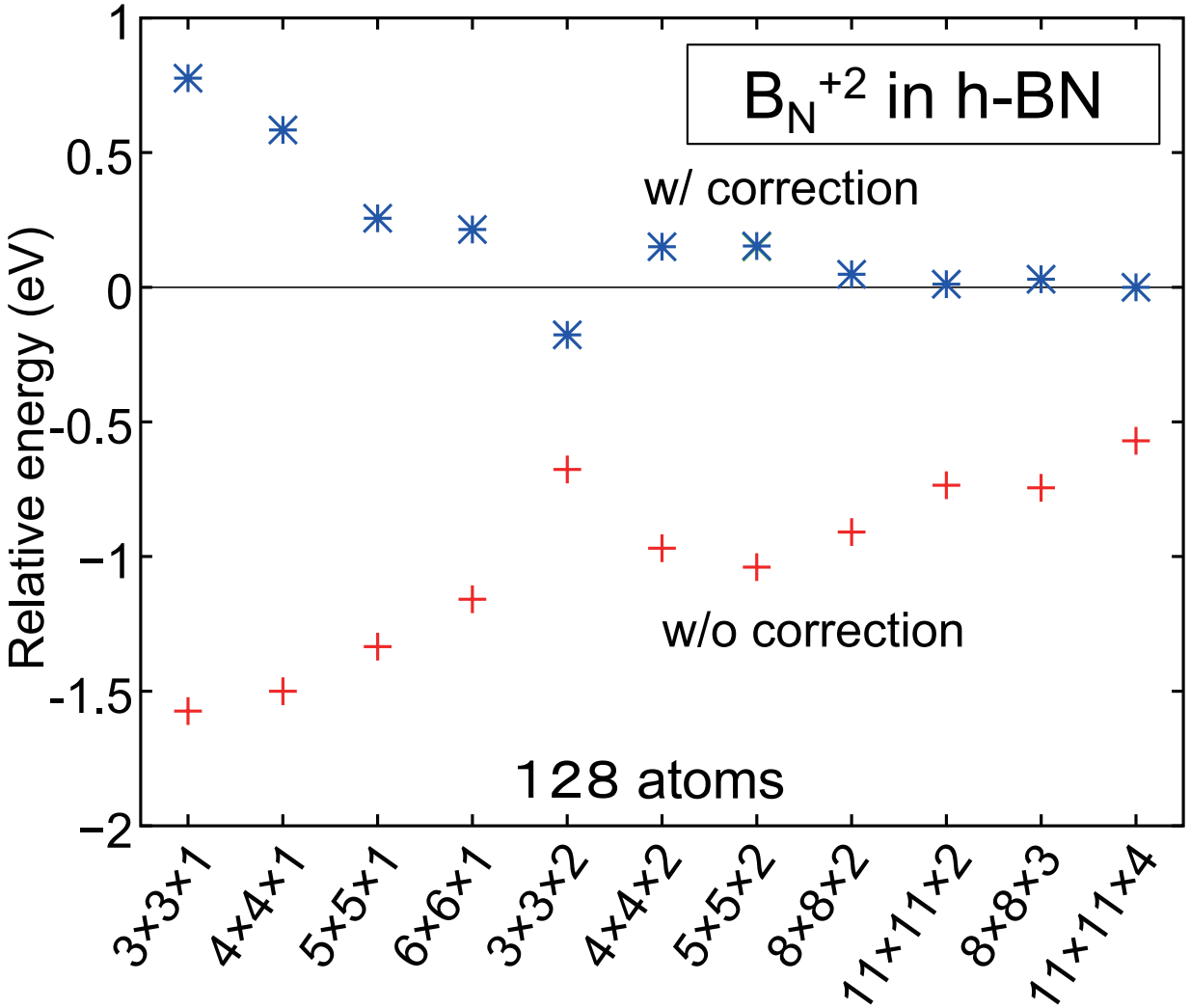




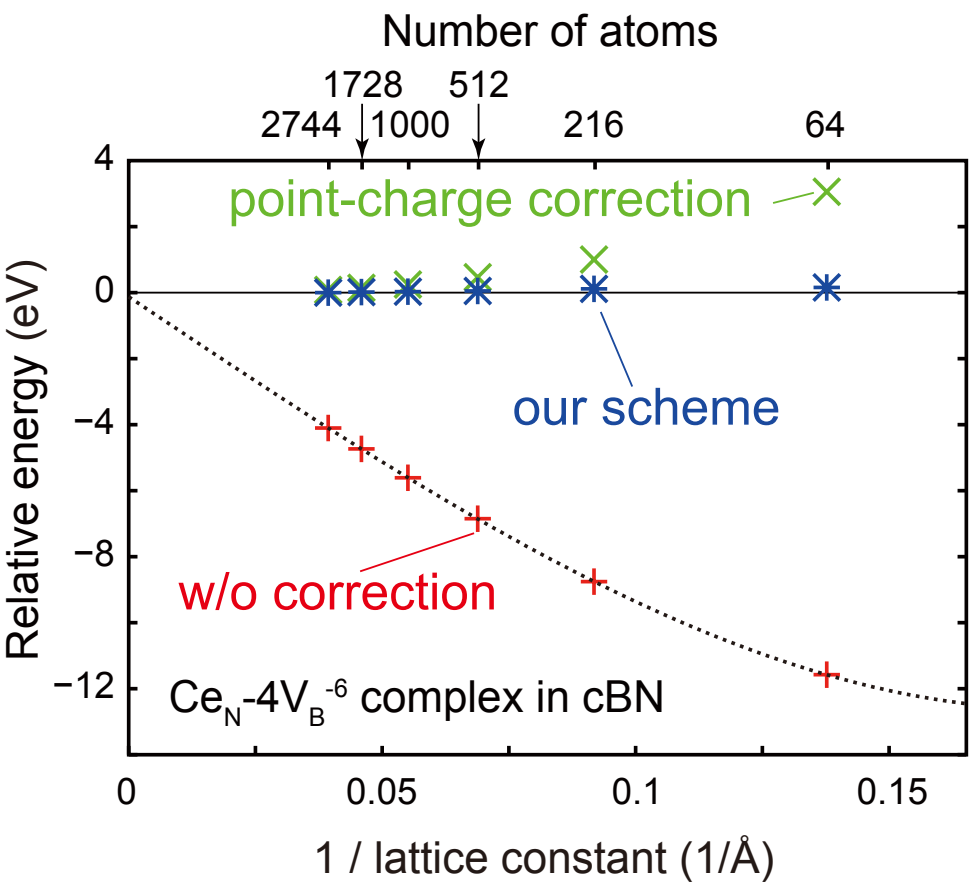
$$\bar{\epsilon} = \begin{pmatrix} 6.39 & 0 & 0 \\ 0 & 6.39 & 0 \\ 0 & 0 & 3.12 \end{pmatrix}$$

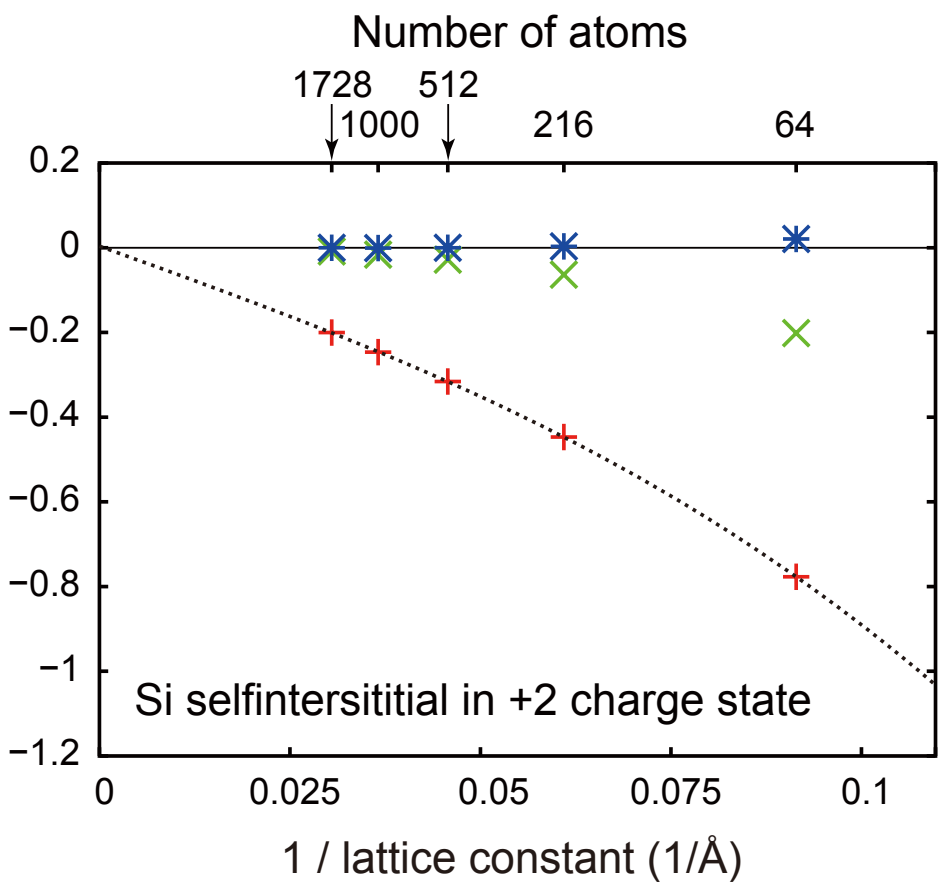
Example 1: antisite defect in *h*-BN

$$E_{\mathrm{FNV}} = E_{\mathrm{PC}} - q\Delta V_{\mathrm{PC},q/b}\big|_{\mathrm{far}}$$

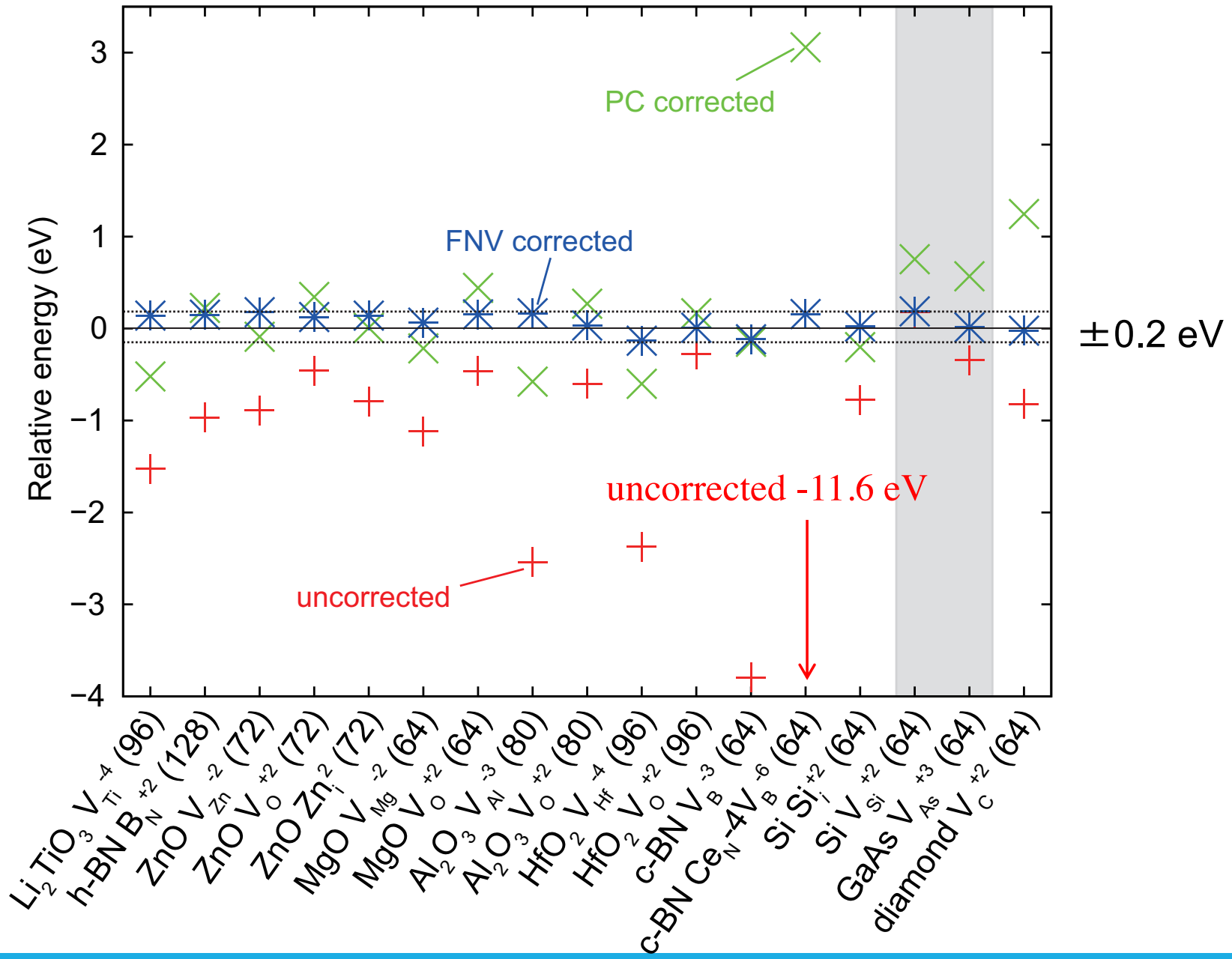


Example 2: Ce in *c*-BN and silicon interstitial





Application to defects in diverse materials

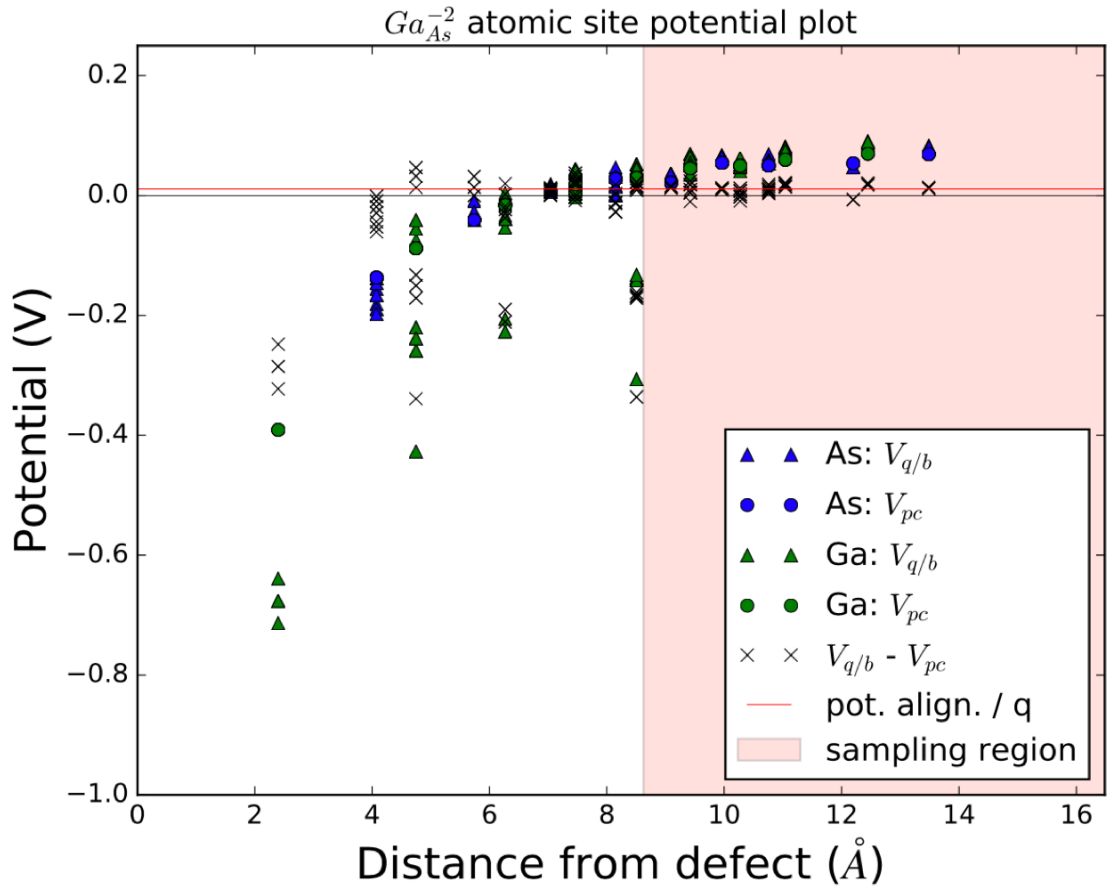


Implementation by other groups

- Some groups have implemented our scheme

PyCDT: A Python toolkit for modeling point defects in semiconductors and insulators

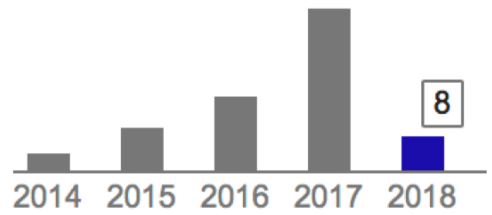
Danny Broberg, Bharat Medasani, Nils Zimmermann, Andrew Canning, Maciej Haranczyk, Mark Asta, Geoffroy Hautier



Materials Project G

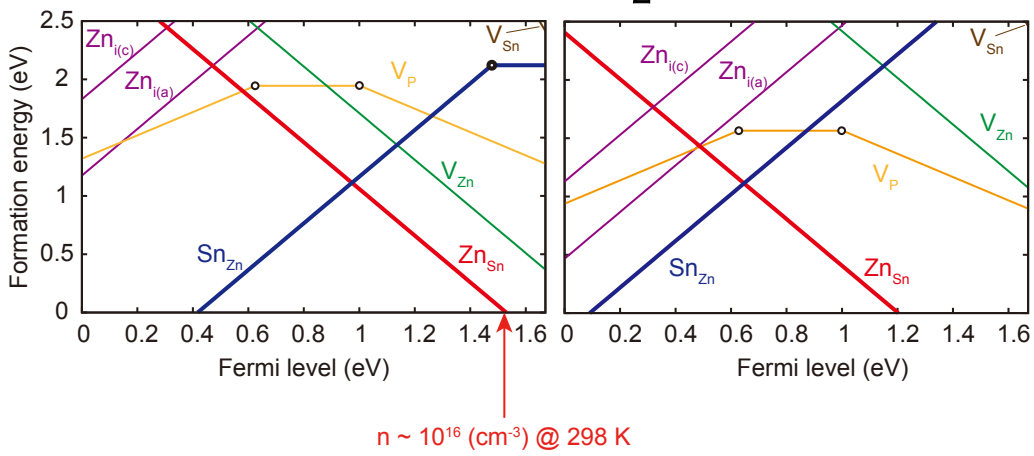
19. Feb. 2018

citation 79



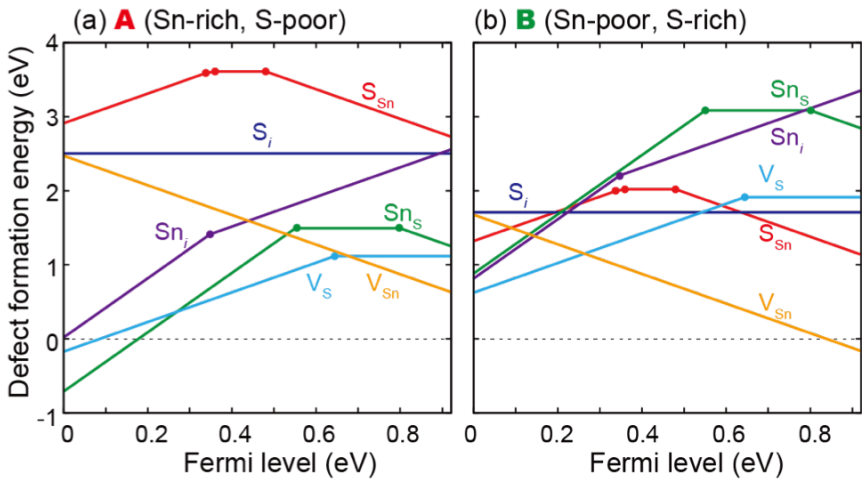
Various applications

$ZnSnP_2$

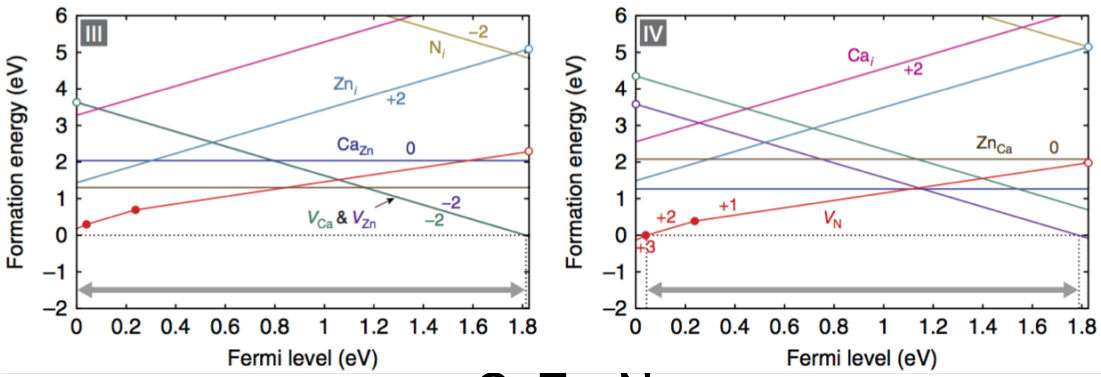


YK *et al.*, Phys. Rev. B (2014)

SnS_x

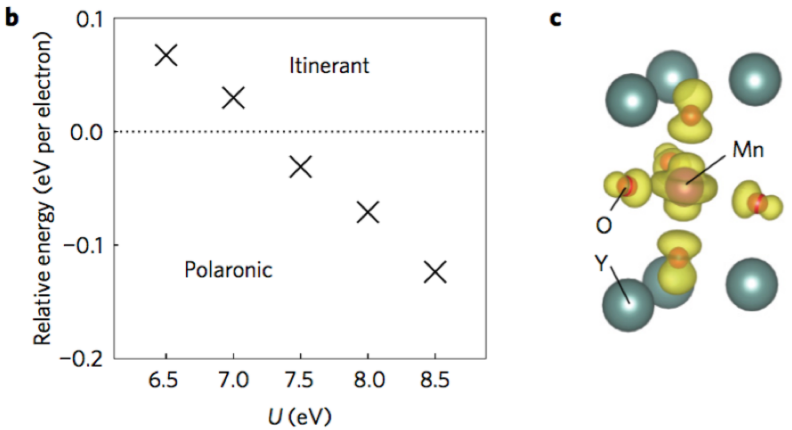


YK *et al.*, Phys. Rev. Appl. (2016)



$CaZn_2N_2$

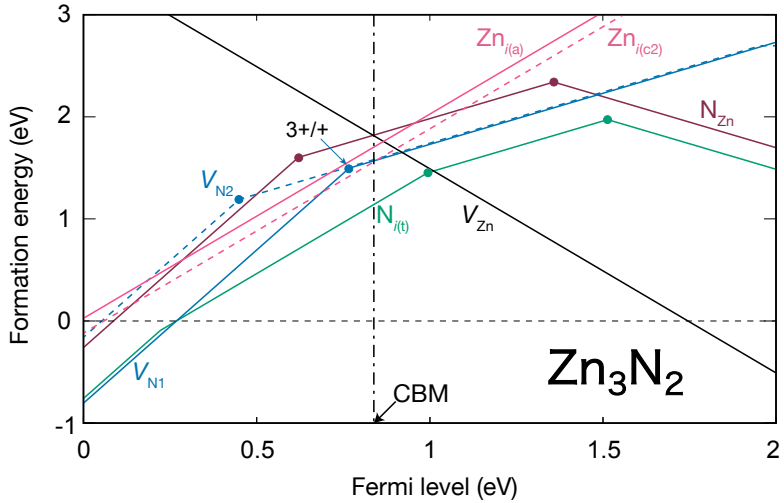
Hinuma, Hatakeyama, YK, *et al.*, Nat. Comm. (2016)



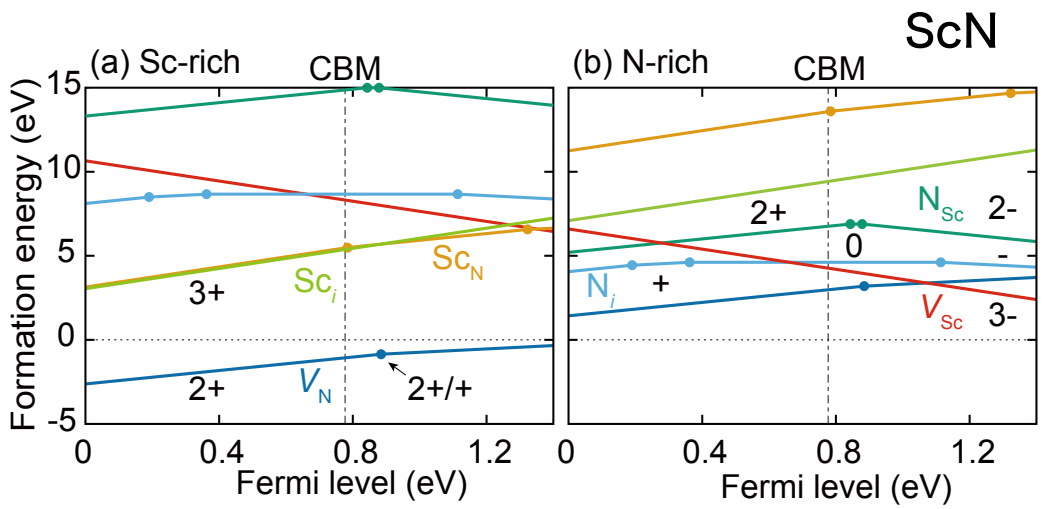
Polarons in $RMnO_3$

Mundy, Schaab, YK (co-first author), *et al.*, Nat. Mat. (2017)

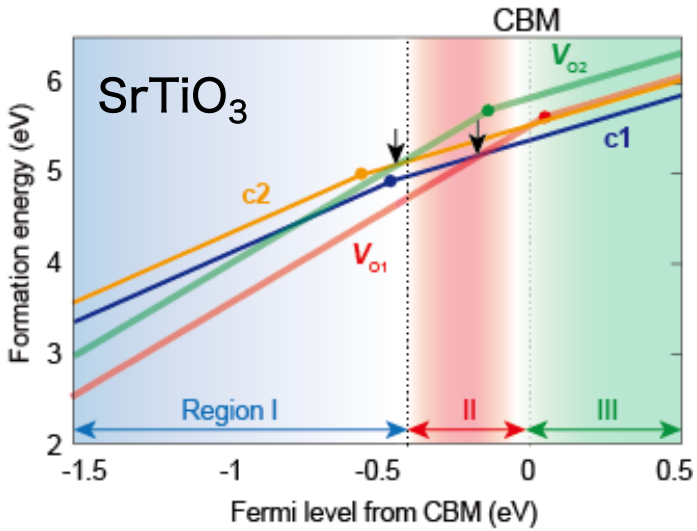
Various applications



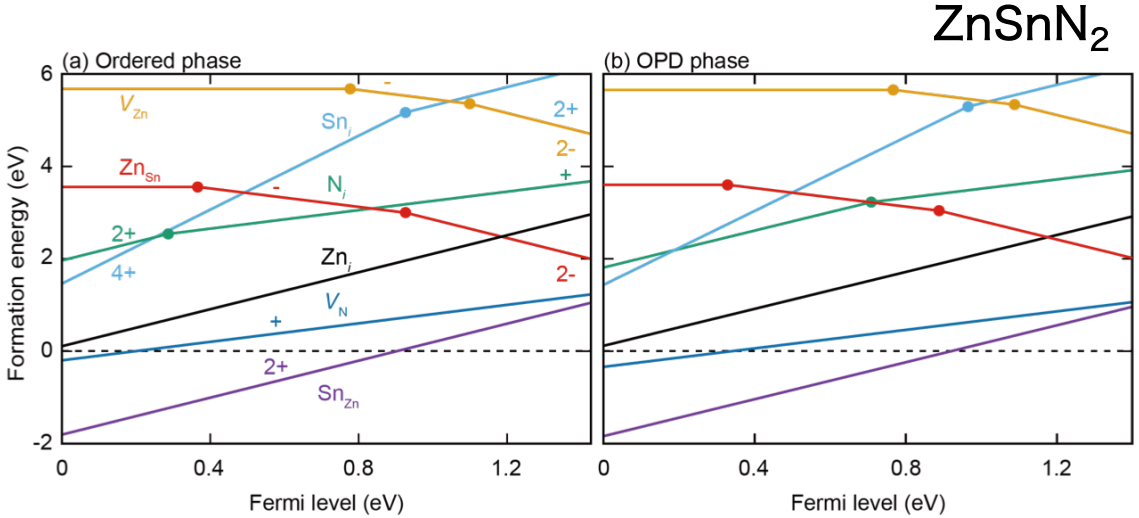
YK *et al.*, Phys. Rev. Appl., Editors' suggestion (2017)



YK, Tsunoda, and Oba, Phys. Rev. Appl, in-press.



YK and Oba, in preparation



Tsunoda, YK *et al*, in preparation

Summary

Finite-size corrections on defect formation energies

- Defect formation energies contain huge errors w/o corrections
- Propose how to extend the FNV correction scheme
  - use atomic-site potential in conjunction with a dielectric tensor
  - application to defects in diverse materials
  - remaining errors are less than 0.2 eV
- Some applications

PHYSICAL REVIEW B **89**, 195205 (2014)

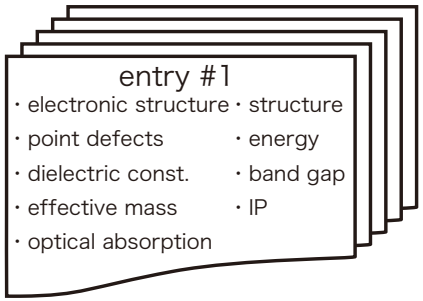
Electrostatics-based finite-size corrections for first-principles point defect calculations

Yu Kumagai[1,*] and Fumiyasu Oba[1,2]
[1]*Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
[2]*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*
(Received 9 February 2014; revised manuscript received 22 April 2014; published 23 May 2014)

Computational Materials Database toward Discovering Novel Semiconductors

Why computational materials database?

① Screening of materials at an early stage

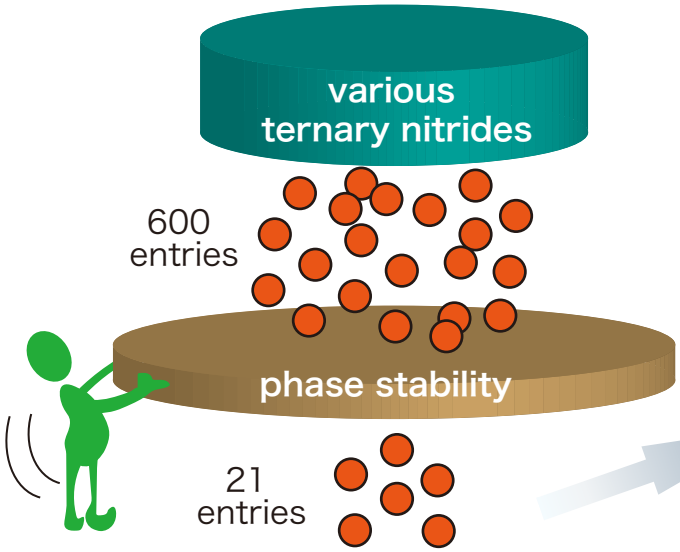


Continue?

change?

abort?

② Rediscovery of reported materials



Promising semiconductors

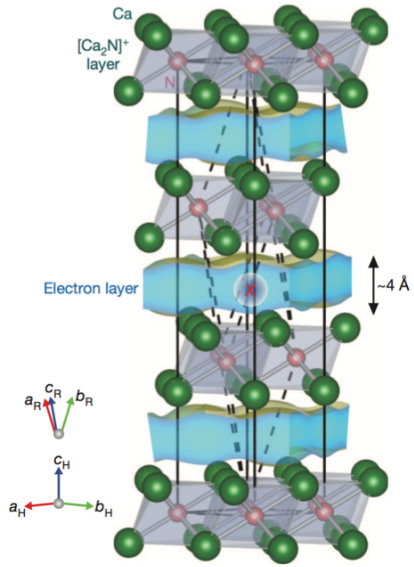
Hinuma, Hatakeyama, YK *et al.*, Nat. Comm. (2016)

- 11 new compounds
  We synthesized
  a new semiconductor $CaZn_2N_2$
- 2 theoretically reported
- 8 experimentally reported

Out of 4 had not been
considered as semiconductors

Extract full potential
of reported materials

Ca_2N:2-D electride

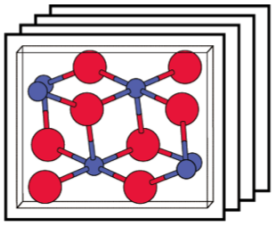


Lee *et al.*, Nature (2013)

Why computational materials database?

③ Dataset for machine learning

Massive and homogeneous dataset



strcutre database (ICSD)

DFT calc. → E_f, E_g, $\boldsymbol{P}$, $\boldsymbol{m}^*$, IP dataset

→ $\boldsymbol{x} = (x_1, x_2, x_3, \ldots)$ feature quantity

→ **machine learning** → modeling

$E_f(\boldsymbol{x})$, $E_g(\boldsymbol{x})$, $\boldsymbol{P}(\boldsymbol{x})$, $\boldsymbol{m}^*(\boldsymbol{x})$, IP($\boldsymbol{x}$)

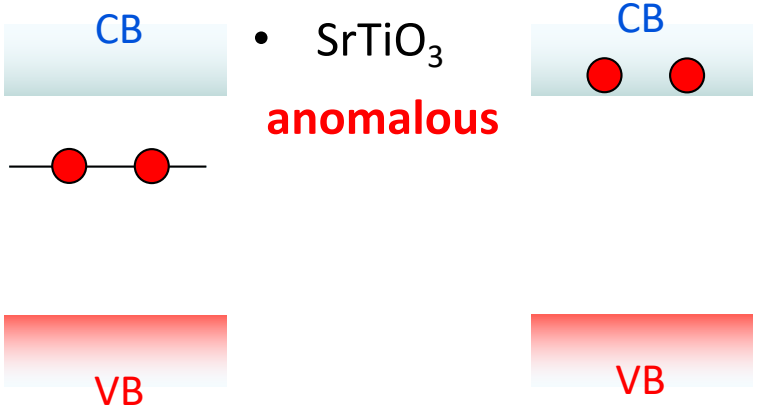
④ Construction of theories

Ex：Oxygen vacancy

Deep level

- ZnO
- SnO_2
- In_2O_3
- CdO
- HfO_2
- ……

universal



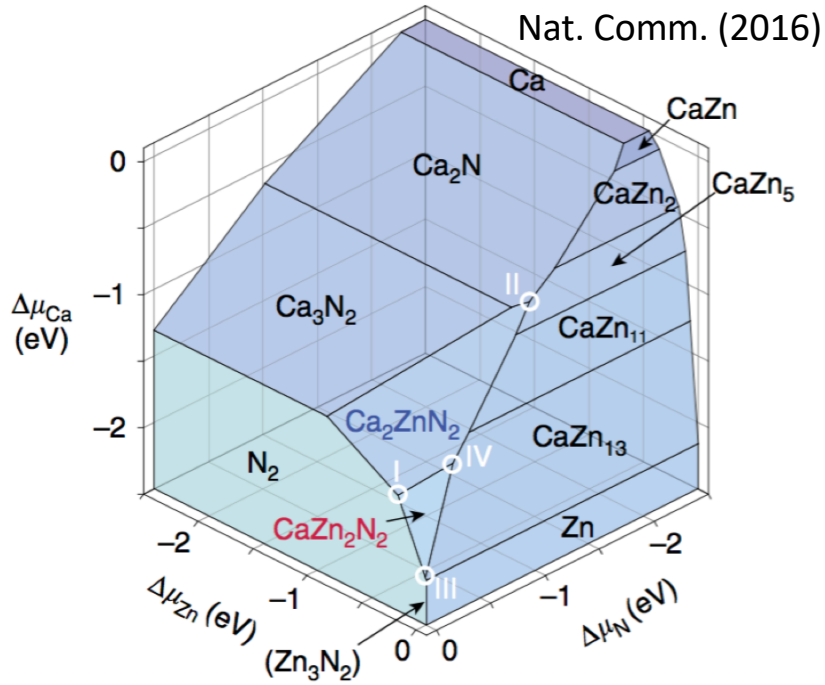
Shallow level

- $SrTiO_3$

anomalous

⑤ Energies for discovering new materials

Nat. Comm. (2016)

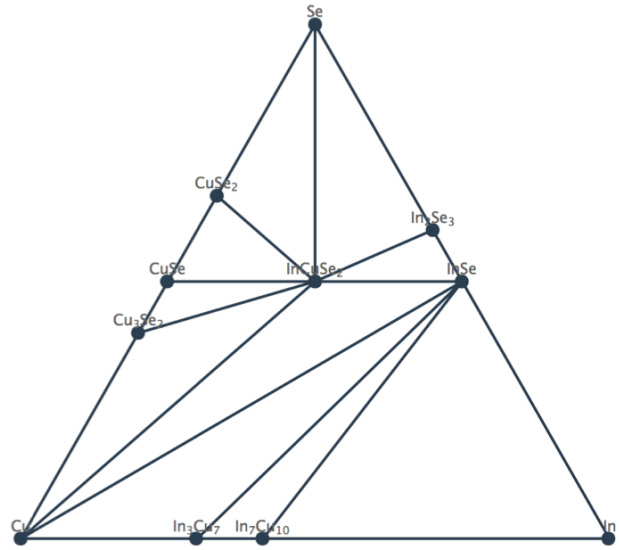


Freely available databases

MATERIALS PROJECT

69,623	54,058
INORGANIC COMPOUNDS	BANDSTRUCTURES

The Materials Project: A materials genome approach to accelerating materials innovation, Jain, Ceder *et al.*, APL Mat. 1, 011002 (2013).

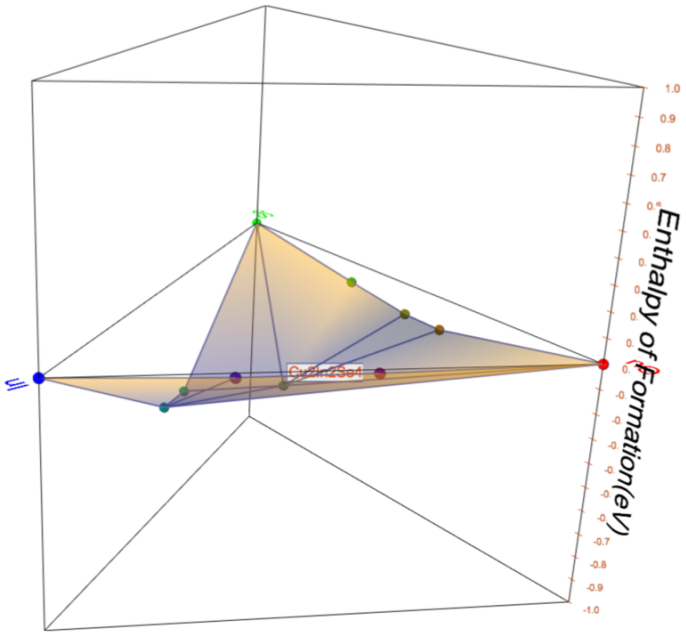


AFLOW

Automatic - FLOW for Materials Discovery

Aflow is a globally available database of **1,668,252** material compounc

AFLOW: An automatic framework for high-throughput materials discovery,
Curtarolo *et al.*, Comp. Mat. Sci., 58, 218 (2012).

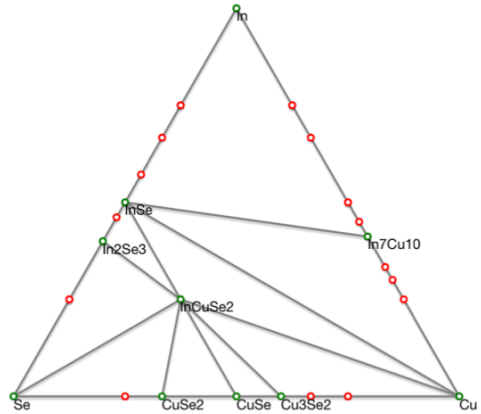


Freely available databases

OQMD: The database now contains **471857** entries.

The Open Quantum Materials Database

Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD), Saal, Wolverton, *et al.*, JOM 65, 1501 (2013).



NOMAD

Computational data repository

High Performance Computing Center Materials Database

CMDB from NREL group

<u>Problems of existing databases for researching semiconductors</u>

① Lack of physical properties (e.g., ionization potential, point-defect properties)

② Lack of accuracy of some properties (e.g., crystal structures, band gaps)

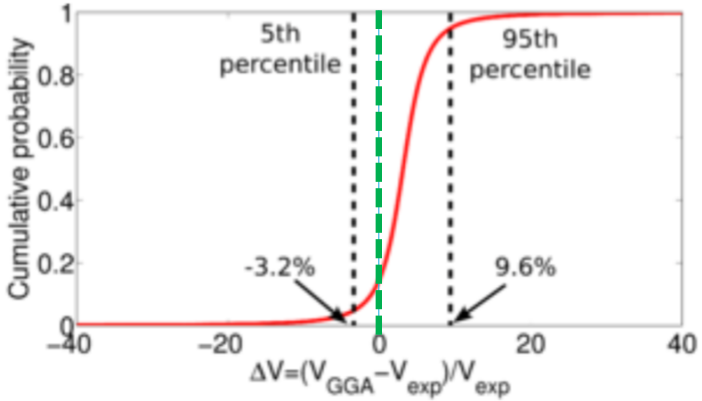
→ We need a new computational materials database toward investigating/discovering novel semiconductors

Crystal structures in available databases

ex. 1) Materials Project

Cumulative distribution of the volume

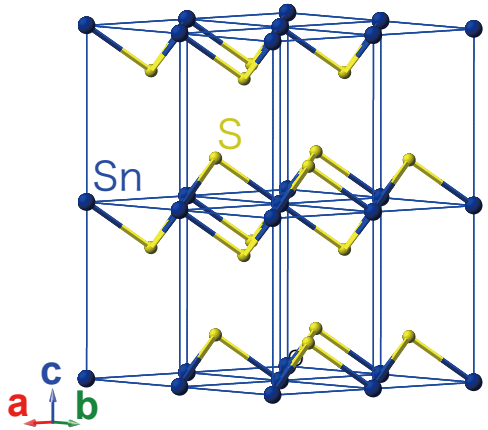
Sun *et al.*,
Sci. Adv. (2016)



Mean error: 3.2 %
(# of structures : 29,902)
by PBE functional

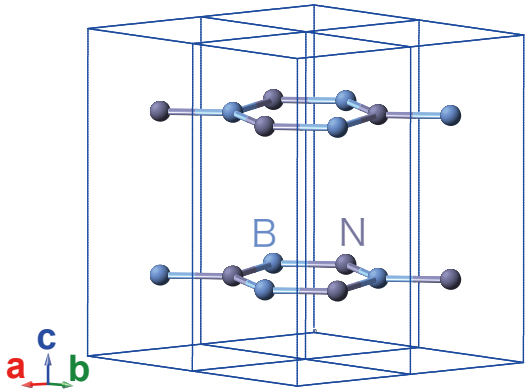
ex. 2) Layered materials: c-axis in SnS_2

exp.	Materials Project	aflow	OQMD	NoMad	NREL MatDB
5.90 Å	6.98	6.67	6.23	NA	6.3



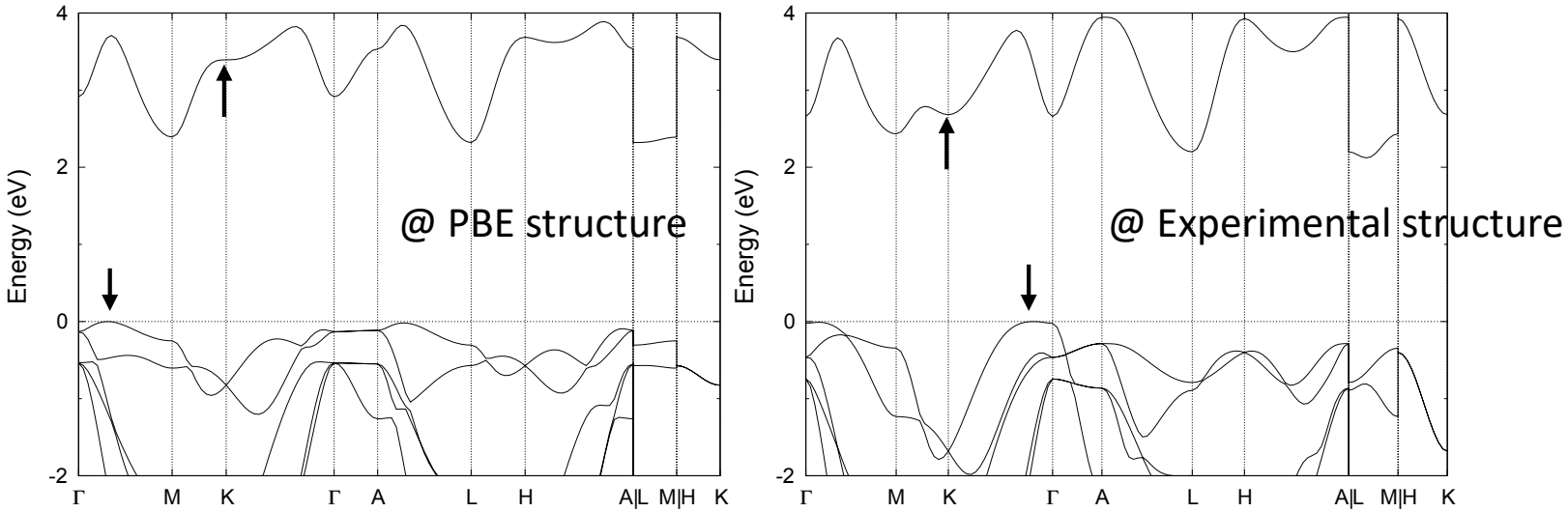
ex. 3)) Layered materials: c-axis in *h*-BN

exp.	Materials Project	aflow	OQMD	NoMad	NREL MatDB
6.661 Å	7.71	7.88	6.43 (LDA)	NA	7.6

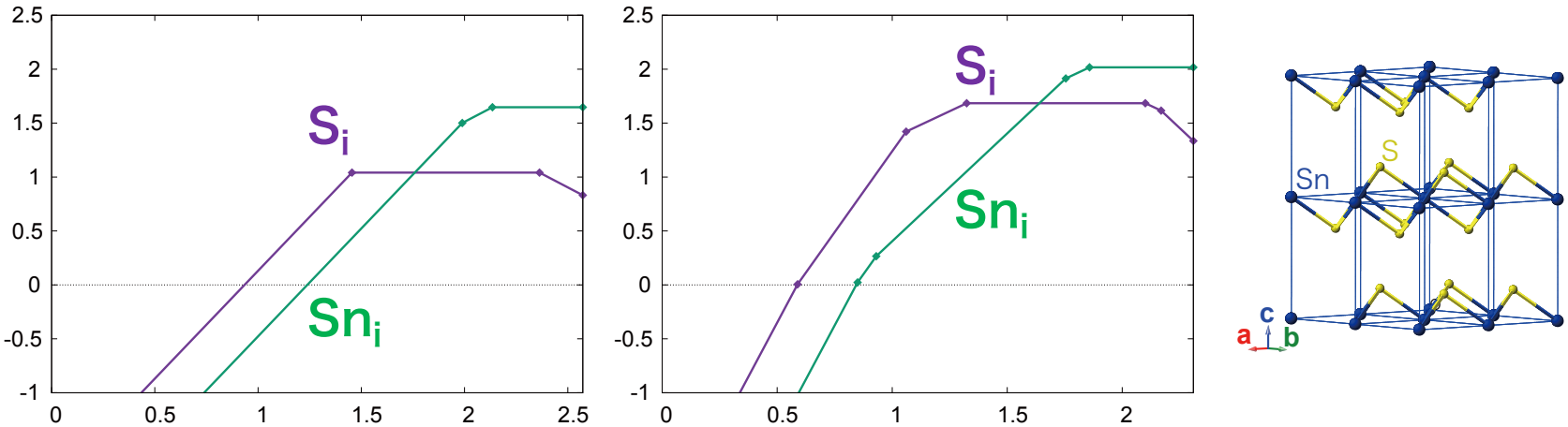


Importance of reproducibility of structures

ex. 1) Electronic structure of SnS_2

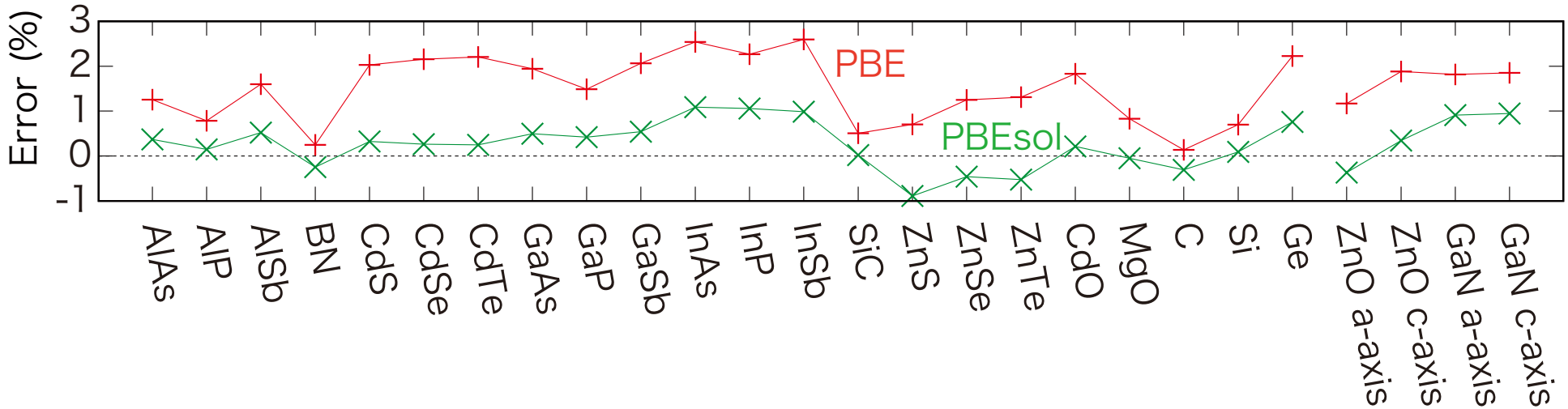


ex. 2) Formation energy of interstitials in SnS_2



Structures are of crucially importance for semiconductor researches

PBEsol+*U*



Errors of interlayer distances in layered oxides

	PBE+U	PBEsol+U
ME	5.9%	0.4%
RMSE	5.5%	3.0%

Hinuma, Hayashi, YK, Tanaka, Oba., submitted.

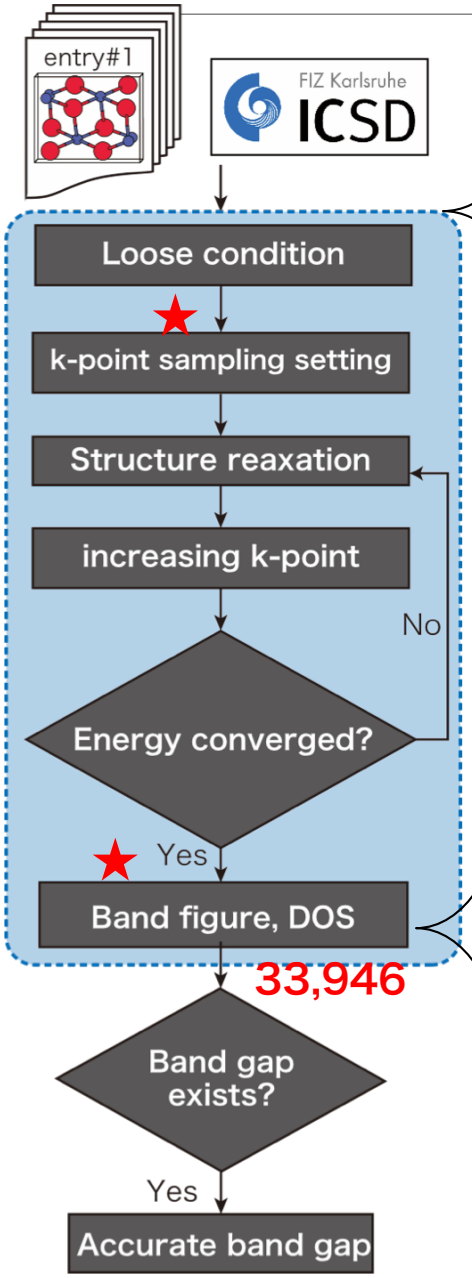
c-axis in SnS_2

exp.	Materials Project	aflow	my DB
5.90 Å	6.98	6.67	5.91

c-axis in *h*-BN

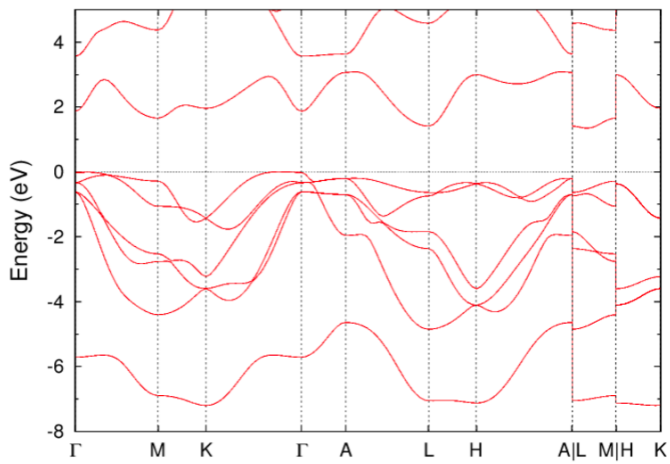
exp.	Materials Project	aflow	my DB
6.661 Å	7.71	7.88	6.69

Flowchart

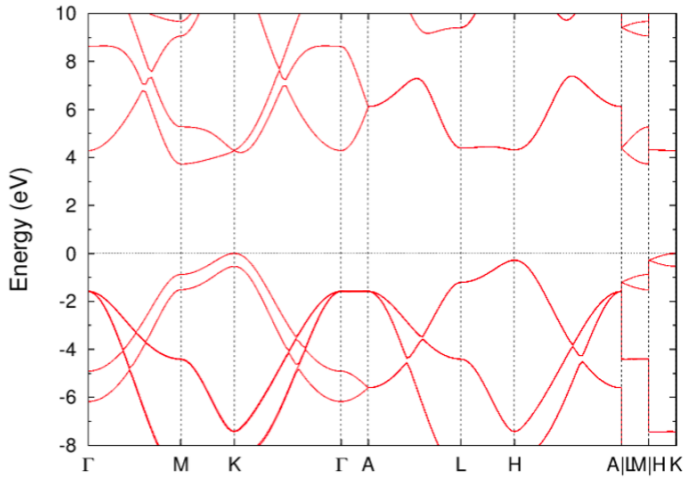


1. Remove entries with partial occupancies
2. Search for symmetries and transform the unit cell based on crystallography★
3. Remove redundant structures ★
4. Remove entries with lanthanide and/or actinide elements
5. Remove entries containing more than 100 atoms
   →# of remaining entries: 46,969
6. Classify entries by space groups ★

SnS_2



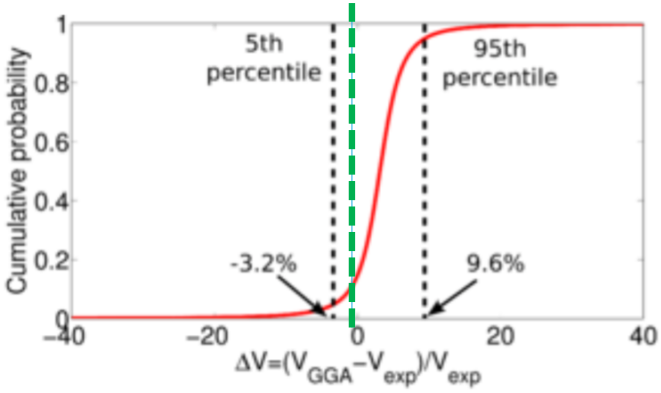
h-BN



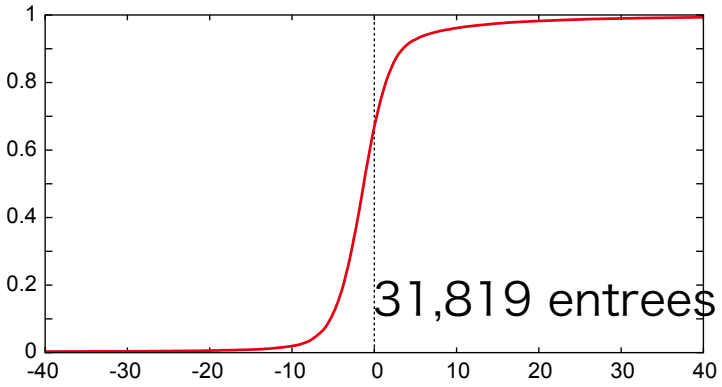
Automation of band paths: Hinuma, Pizzi, YK, Oba, Tanaka, Comput. Mater. Sci. (2017).

Analysis of the structures

Cumulative distribution of the volume



PBE-sol



ME=-0.82% compared to experiments including high-temperature phases

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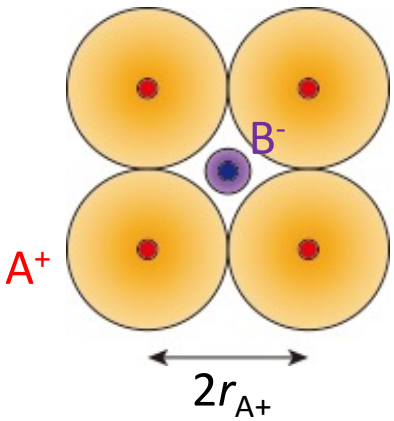
Acta Cryst. (1976). A**32**, 751

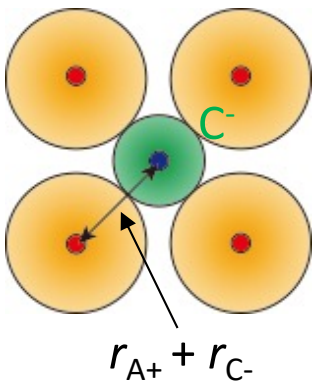
Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides

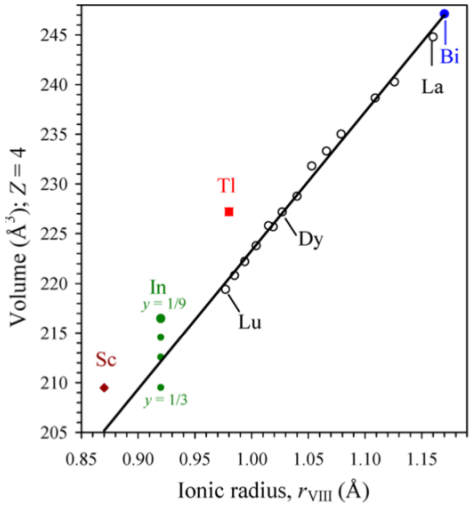
BY R. D. SHANNON

AB crystal



AC crystal

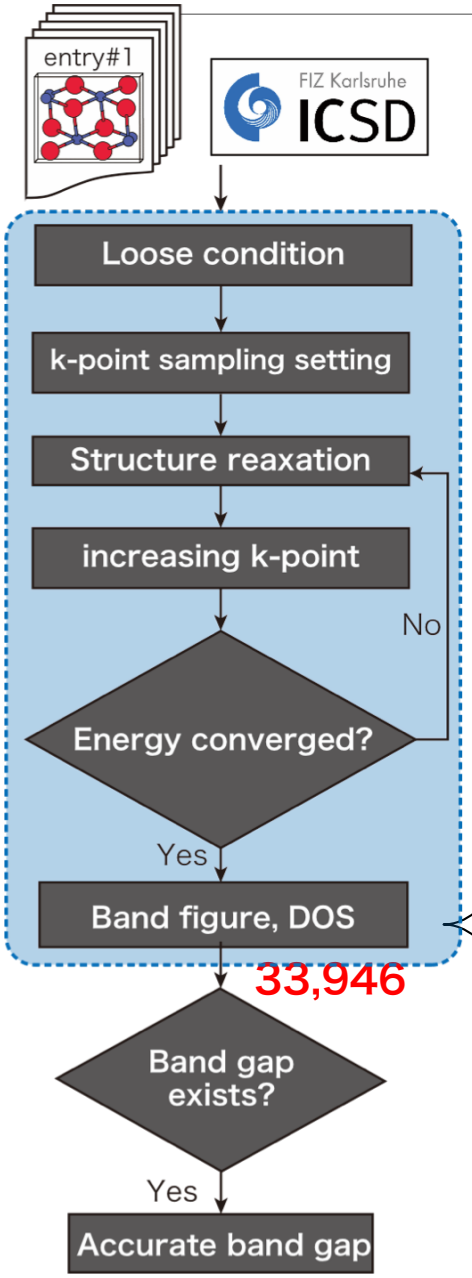


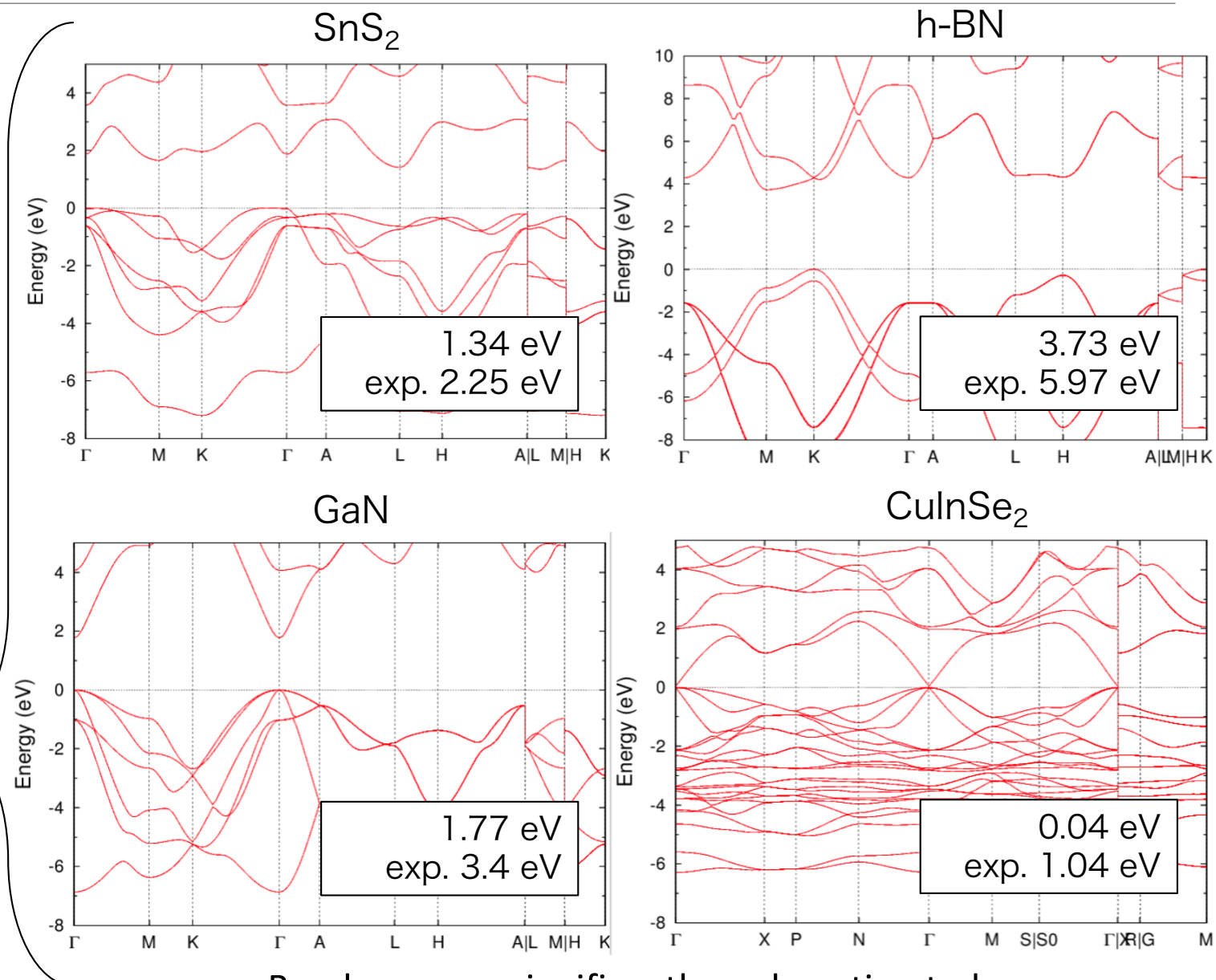


including inaccurate data

Yi, YK, *et al.*, Inorg. Chem. (2014).

Flowchart

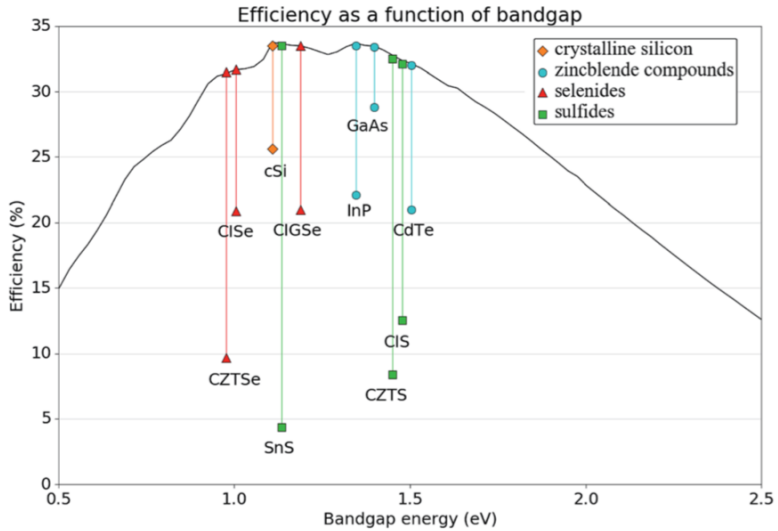




Band gaps are significantly underestimated.

Applications related to band gaps

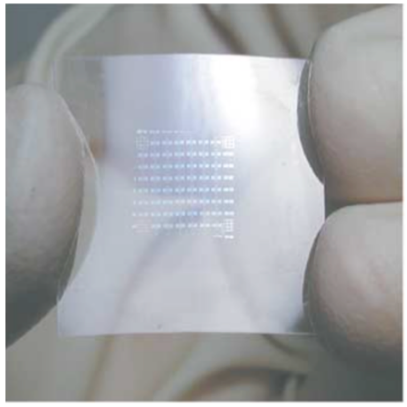
Solar cell



Lee, YK, Walsh, Oba, J. Mat. Chem. A (2017).

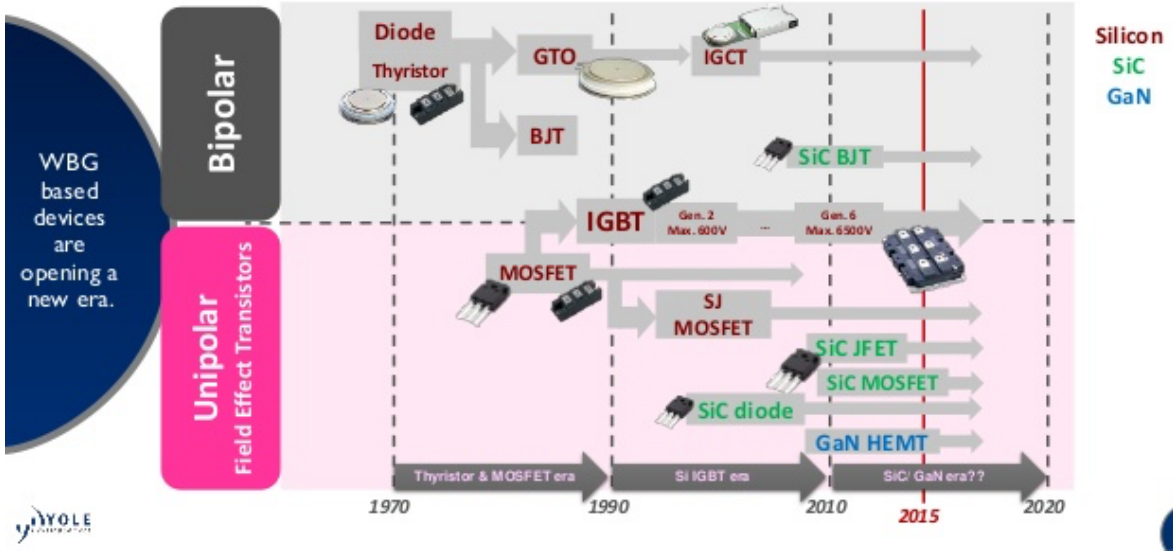
LED

Transparent conductors

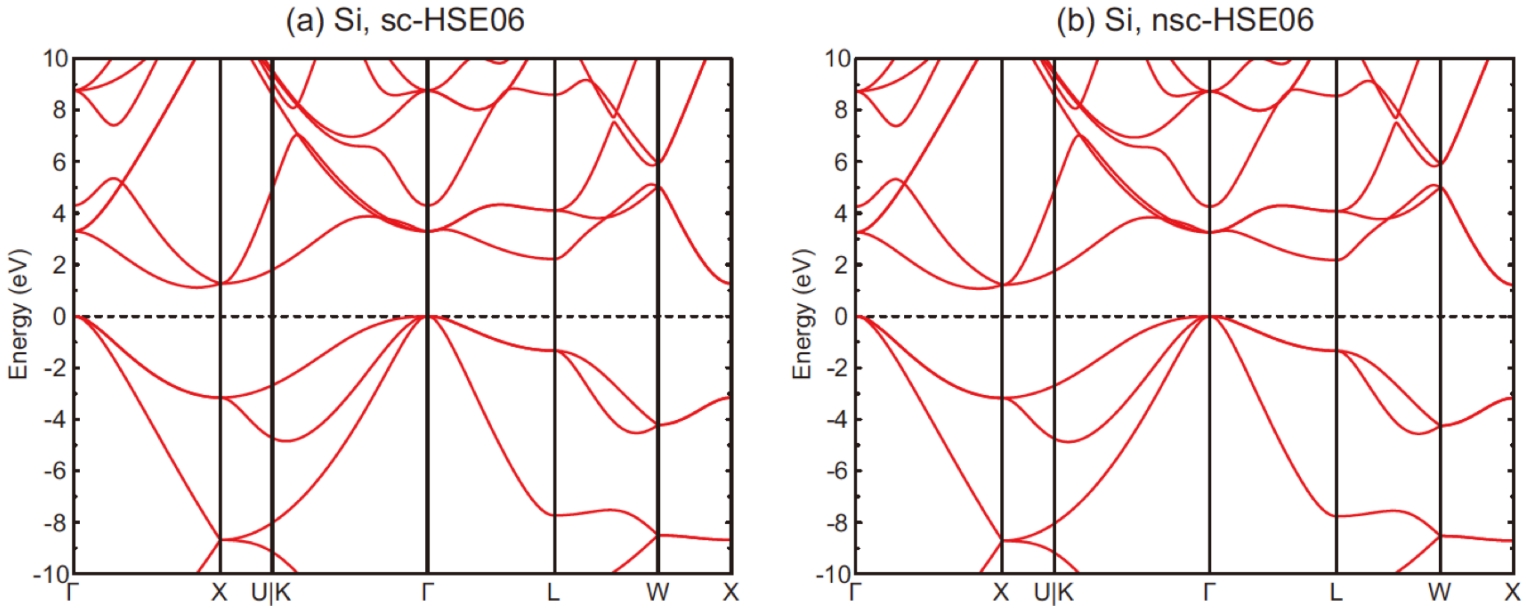


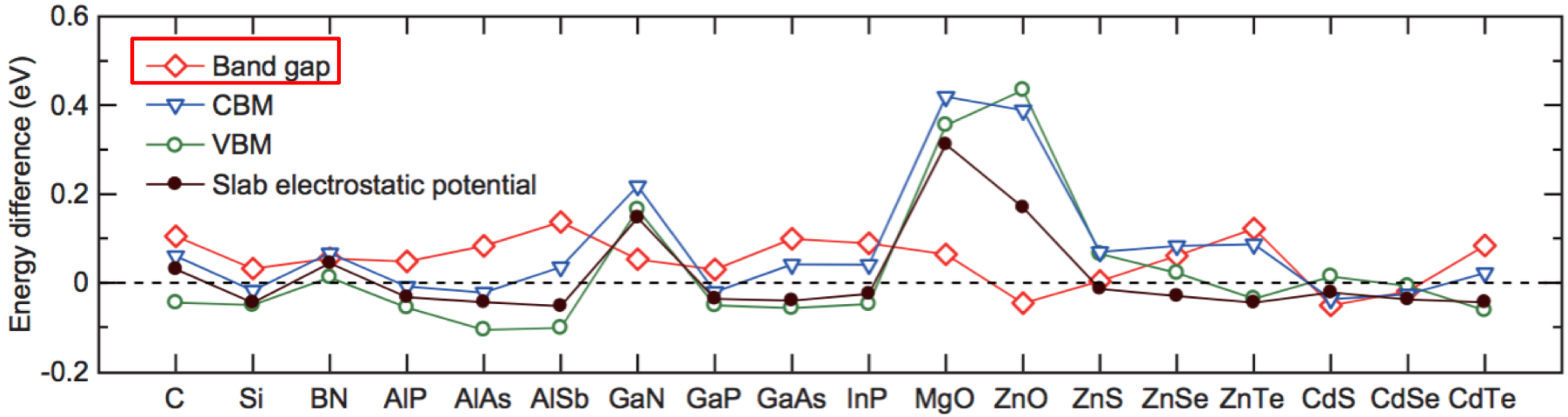
Nomura, *et al.*, Nature (2004).

Power devices



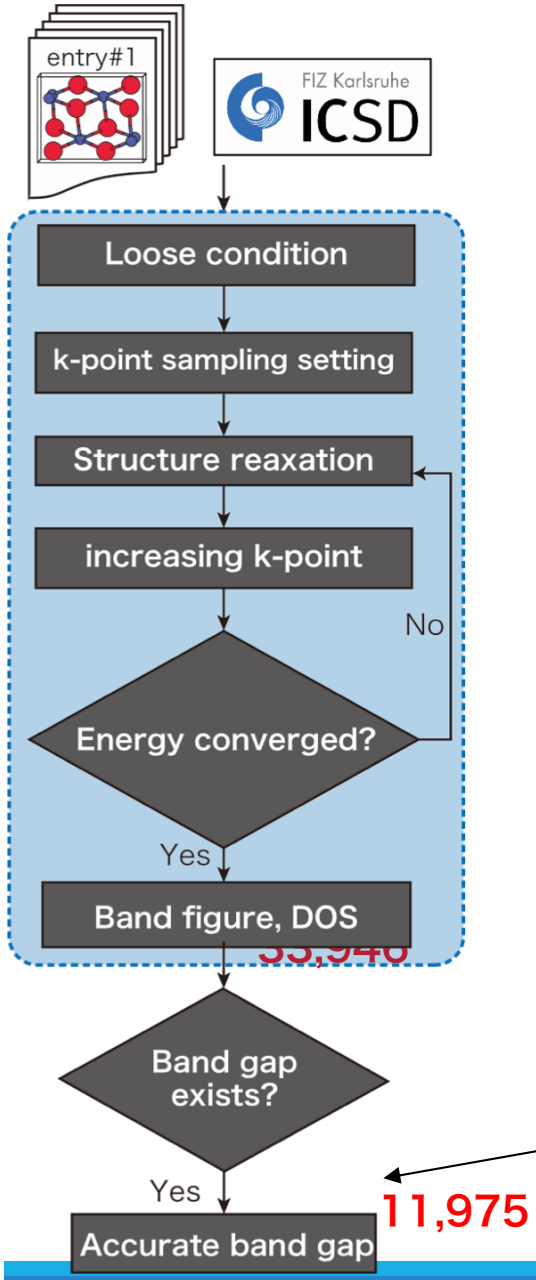
non-selfconsistent (nsc) HSE06

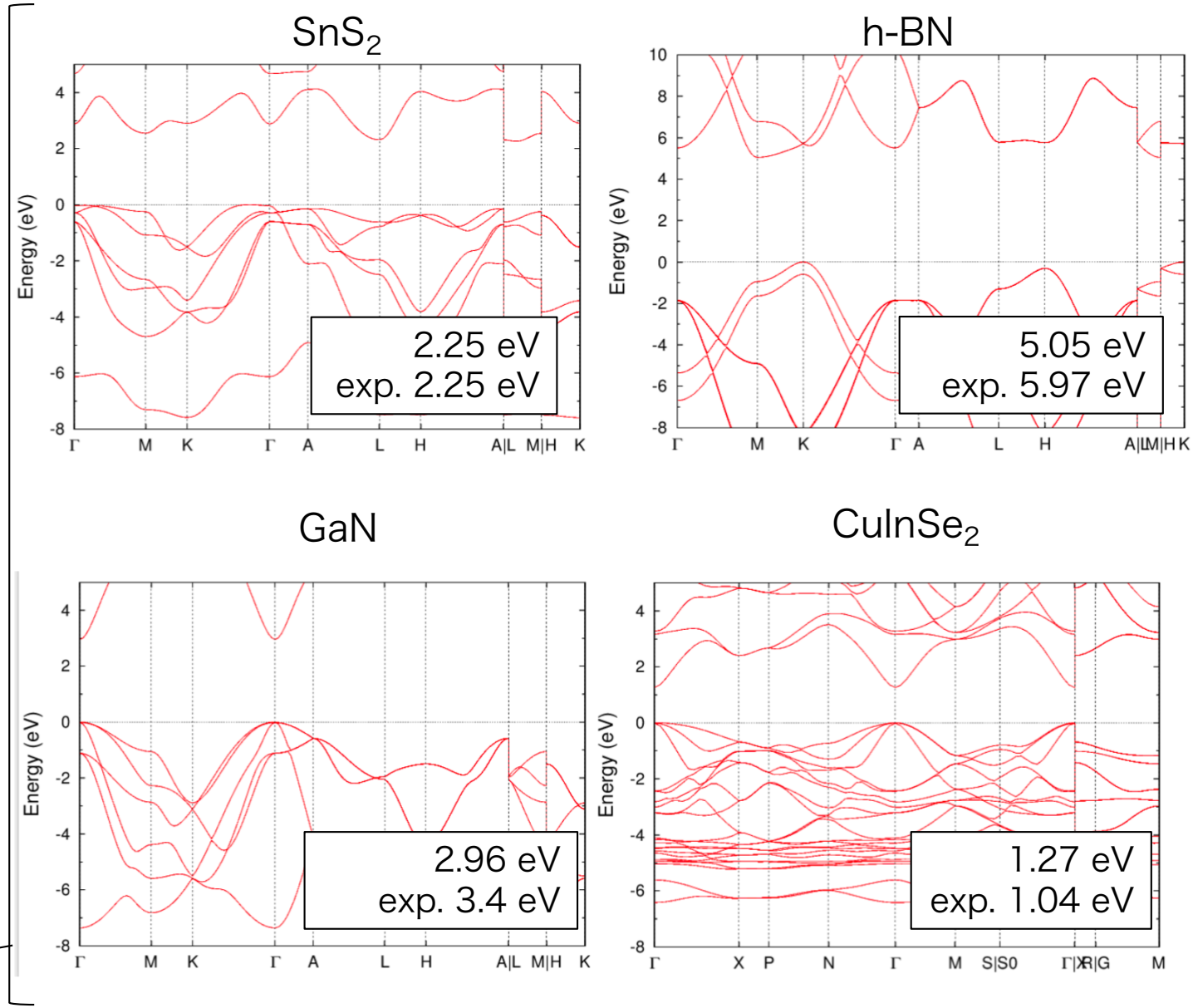




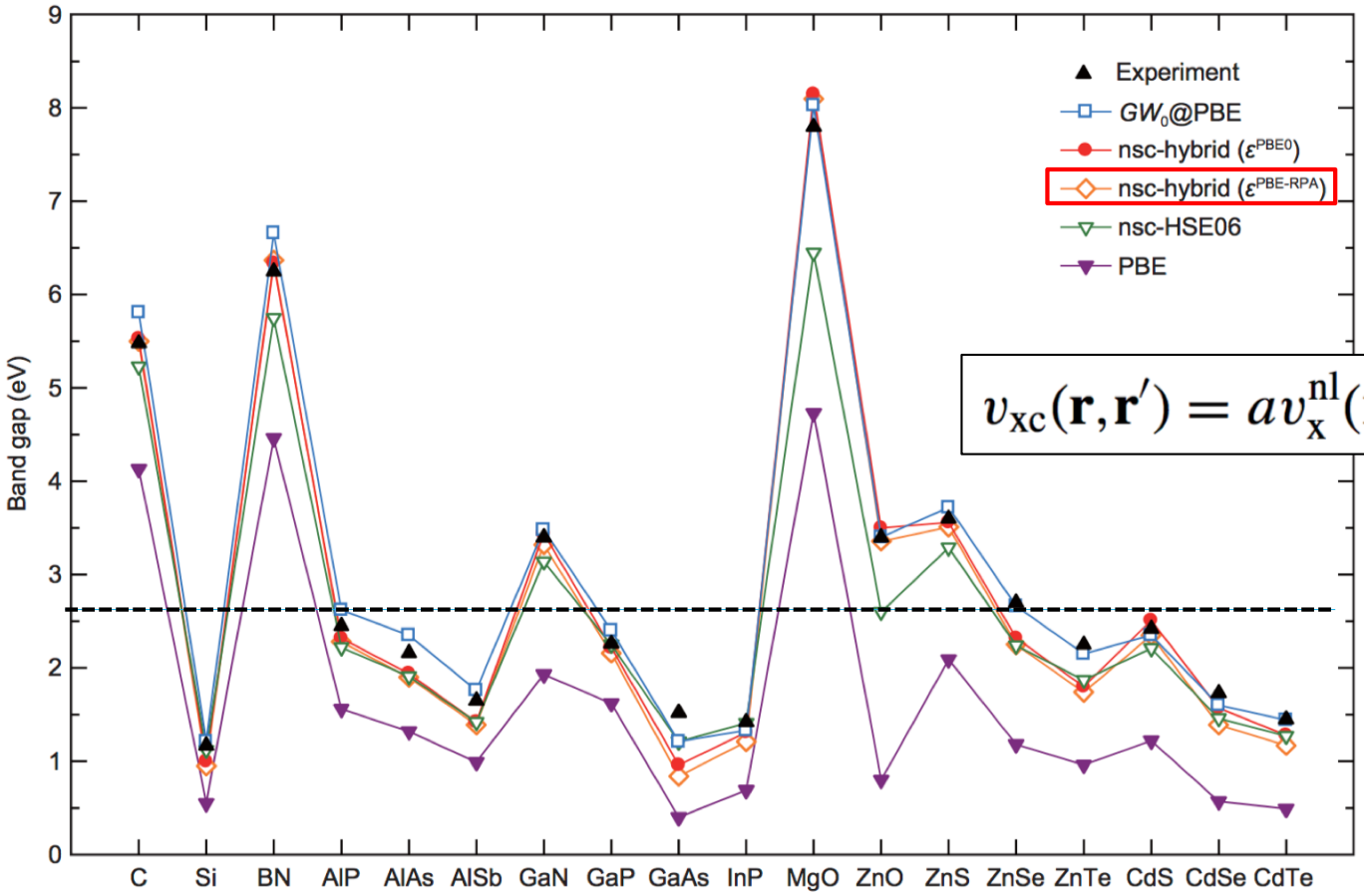
Hinuma, YK, Tanaka, and Oba, Phys. Rev. B (2017)

nsc HSE06


entry#1
FIZ Karlsruhe
ICSD
Loose condition
k-point sampling setting
Structure reaxation
increasing k-point
No
Energy converged?
Yes
Band figure, DOS
33,946
Band gap exists?
Yes
Accurate band gap
11,975


SnS2
2.25 eV
exp. 2.25 eV
h-BN
5.05 eV
exp. 5.97 eV
GaN
2.96 eV
exp. 3.4 eV
CuInSe2
1.27 eV
exp. 1.04 eV
Energy (eV)
Γ M K Γ A L H A|L M|H K
Γ X P N Γ M S|S0 Γ|X R|G M

Band gaps for wide gap materials



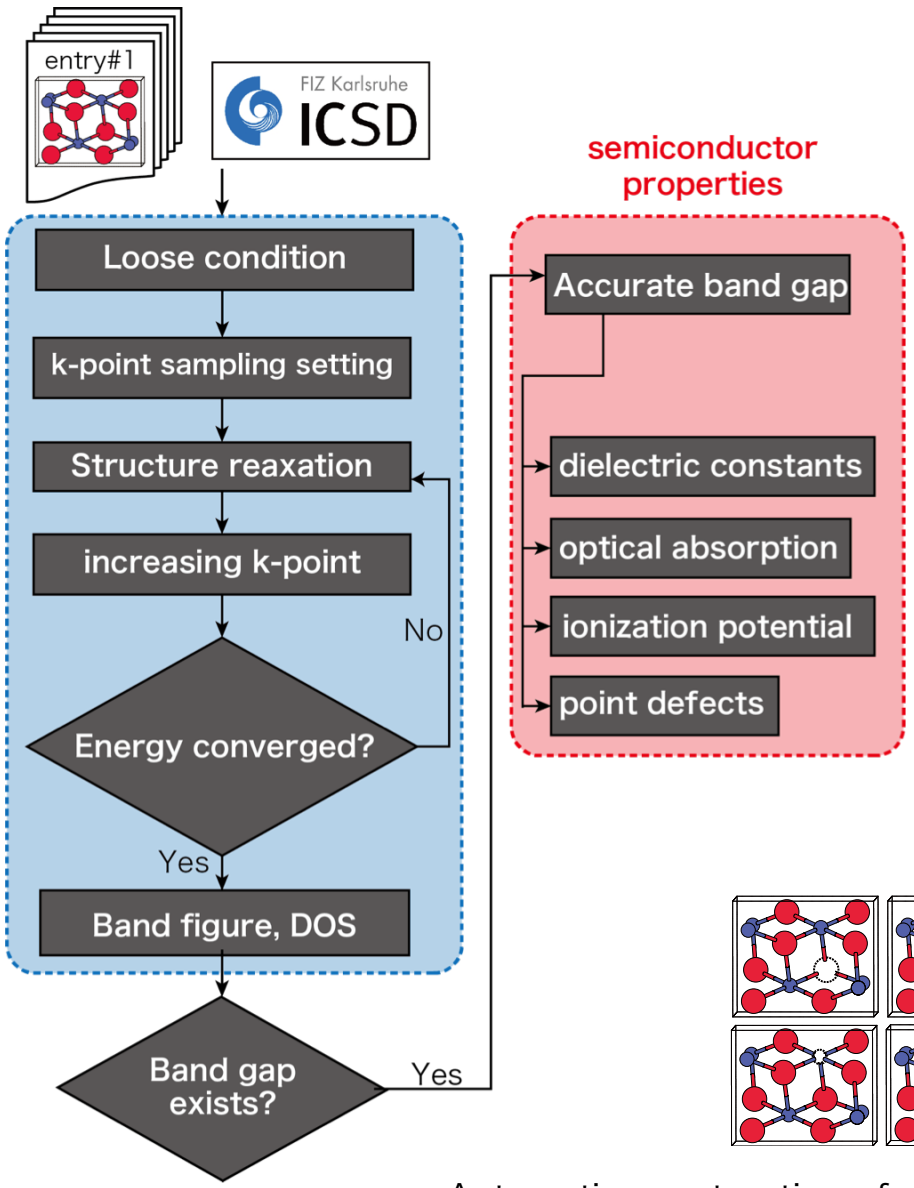
$$v_{xc}(\mathbf{r},\mathbf{r}') = a v_x^{nl}(\mathbf{r},\mathbf{r}') + (1-a) v_x^{l}(\mathbf{r}) + v_c(\mathbf{r})$$

$$a = \varepsilon_\infty^{-1}$$

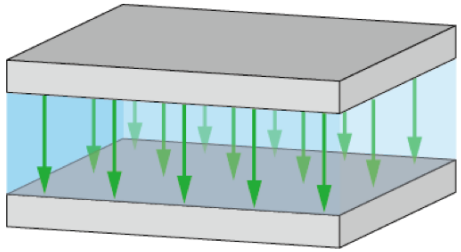
Hinuma, YK, Tanaka, and Oba, Phys. Rev. B (2017)

	PBE	nsc-HSE06	nsc-hybrid($\varepsilon_\infty^{PBE-RPA}$)	nsc-hybrid($\varepsilon_\infty^{PBE0}$)	GW_0@PBE	Experiment
			⋮			
CdS	1.22	2.21	2.35	2.51	2.35	2.42
CdSe	0.57	1.46	1.39	1.57	1.60	1.73
CdTe	0.49	1.27	1.17	1.28	1.44	1.45
MAE	1.30	0.34	0.23	0.19	0.14	

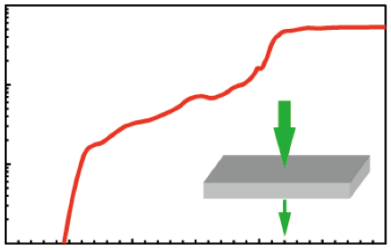
Further properties…



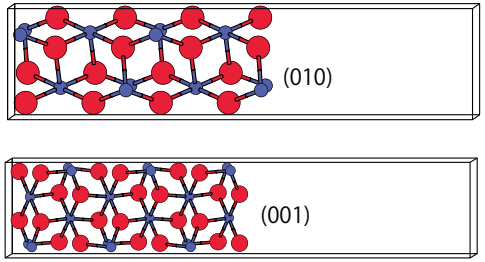
- Dielectric constant



- Optical absorption

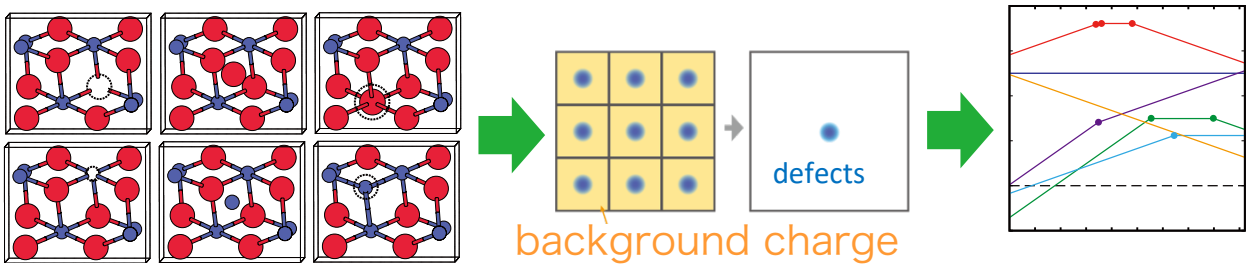


- Ionization potential



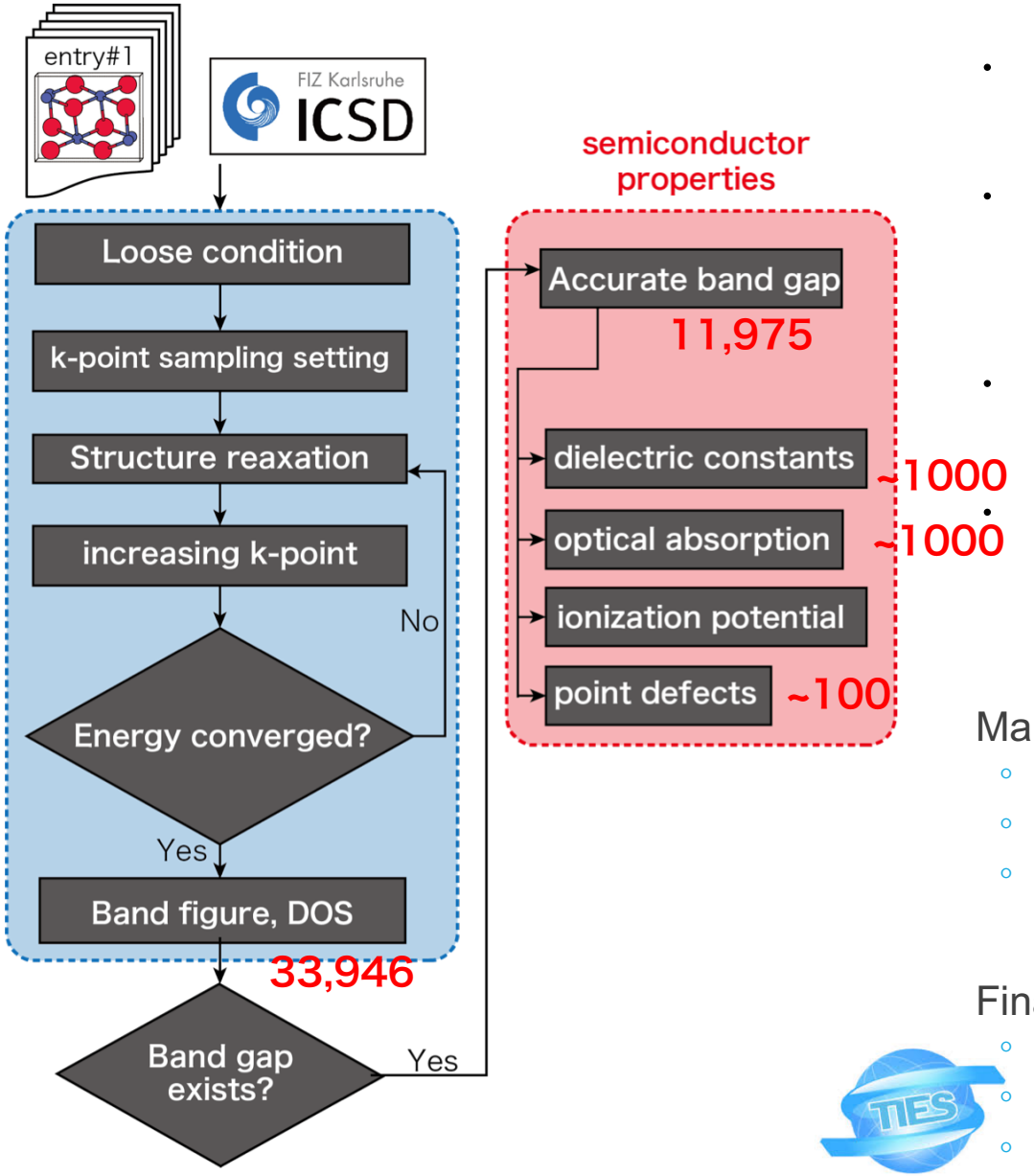
Automatic construction of surface models
Hinuma, YK, Oba, Tanaka, Comput. Mater. Sci. (2016).

- Point defects



Automatic construction of point defect calculations, YK, Takahashi, and Oba, in preparation

Summary



- Construction of computational materials database
- PBEsol+U functional works well for reproducing the experimental structures
- non-selfconsistent HSE06 works well for predicting the band gaps
- Further semiconductor properties will be calculated in the future

Main collaborators
- Prof. Fumiyasu Oba
- Prof. Yoyo Hinuma
- Prof. Akira Takahashi

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- PRESTO