

The 3rd Innovation Camp for Computational Materials Science
Tendo, Yamagata, Japan
2019/10/09

High-throughput computations on oxygen vacancies and their machine learning

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JST, PRESTO

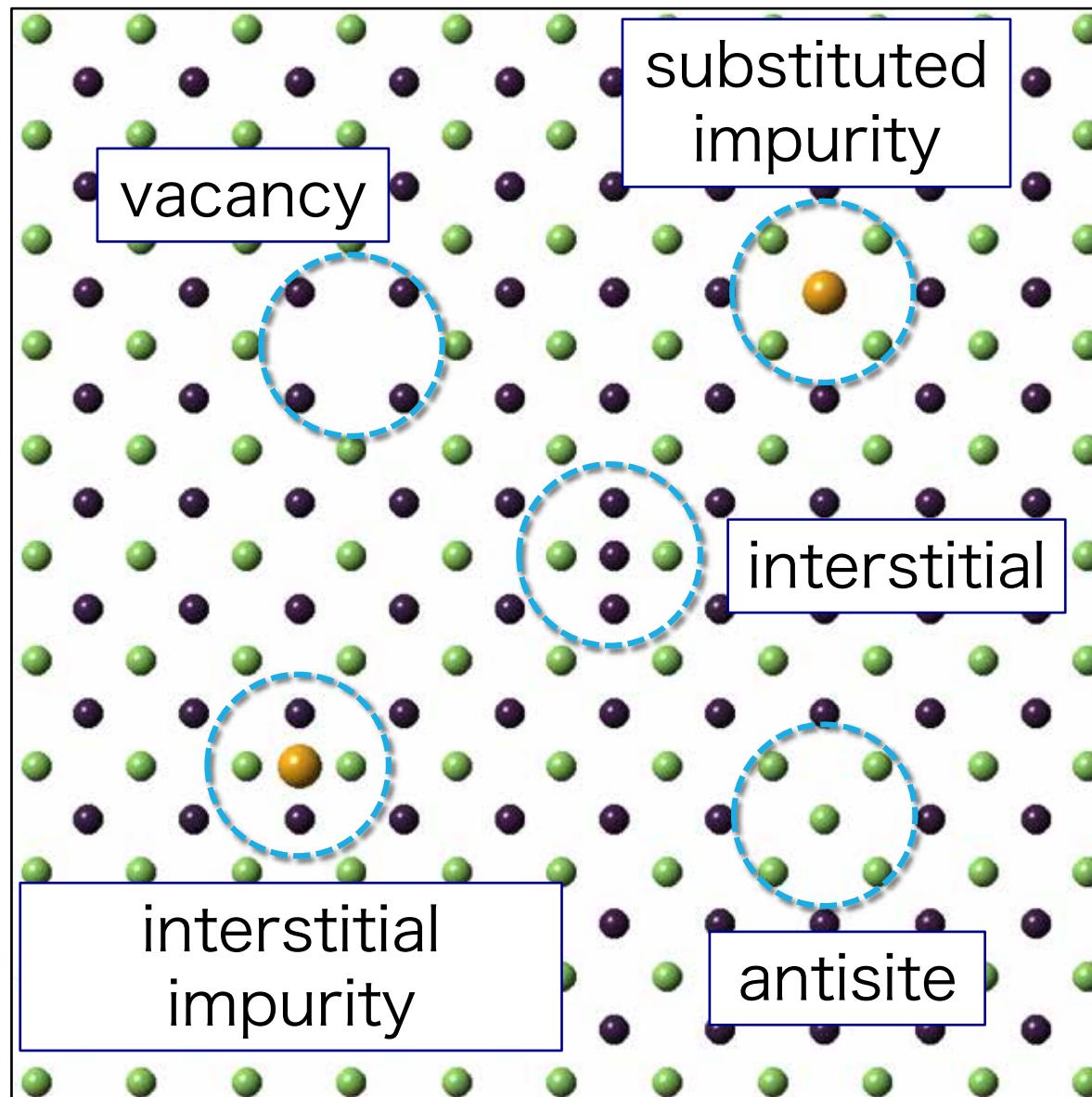


Research carriers

- 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 **MCES, Tokyo Institute of Technology**
Prof. Fumiyasu Oba
- Sep. 2015 - Nov. 2016: Research Lecturer at the same place
- Dec. 2016 - Nov. 2018: Research Associate Professor at the same place
- Nov. 2016 - : **JST PRESTO**
- Dec. 2018 - May 2019: Research Associate Professor at Kyoto University
- Jun. 2019 - : Associate Professor
at **Laboratory for Materials and Structures, Tokyo Institute of Technology**



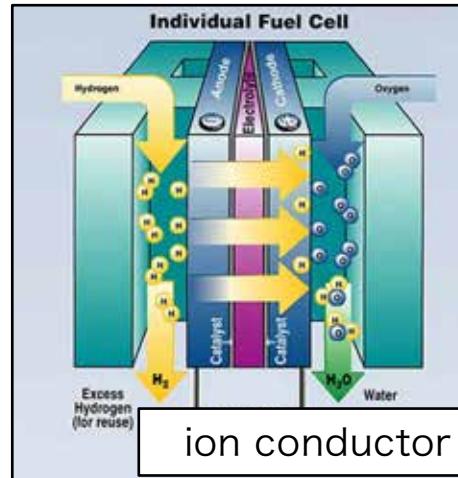
Point defects in semiconductors and insulators



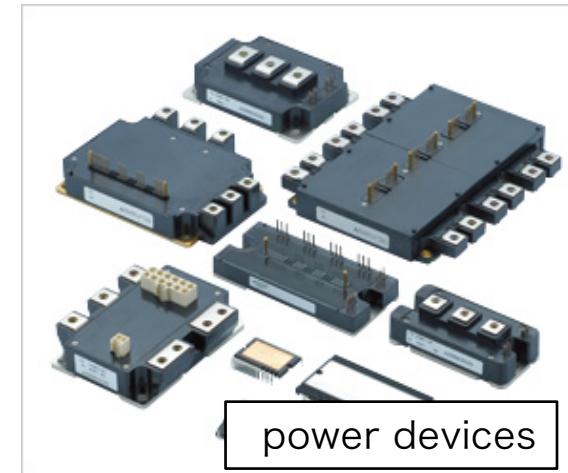
Applications related to point defects



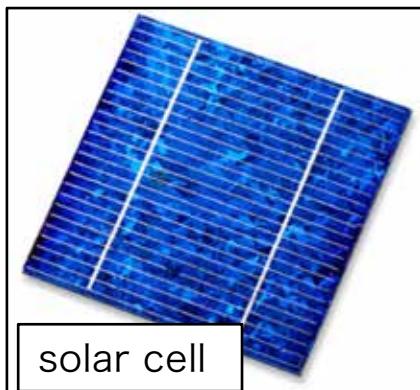
<http://www.greenprophet.com>



<http://www.hygen.com>

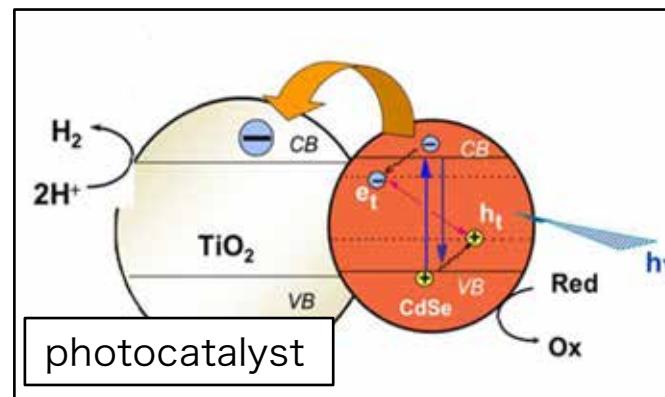


<http://melcopowerdevice.co.jp/>

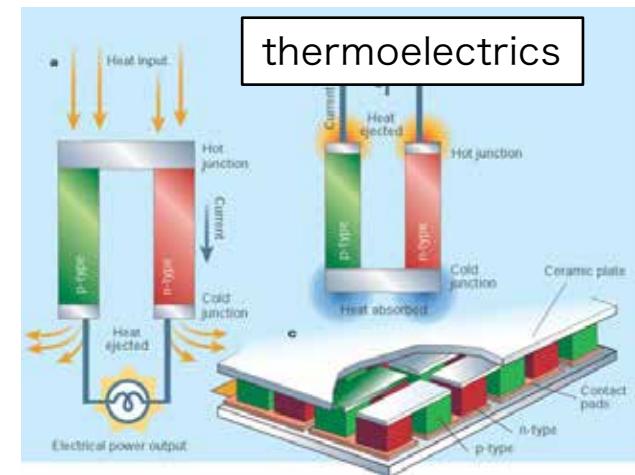


solar cell

<http://www.itmedia.co.jp>



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

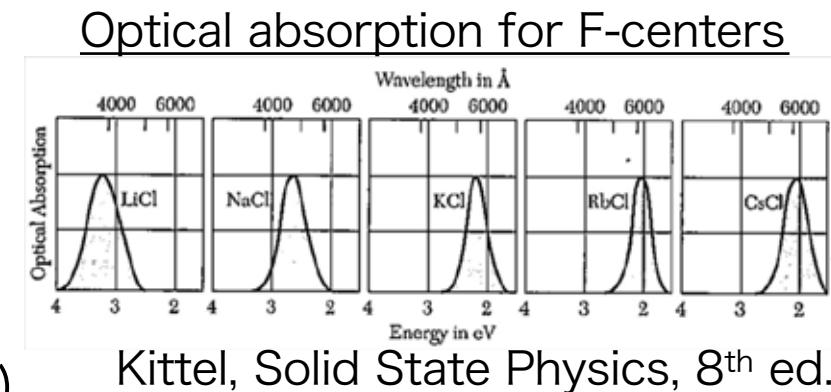


<http://www.nature.com/nature/journal/v413/n6856/images/413577aa.2.jpg>

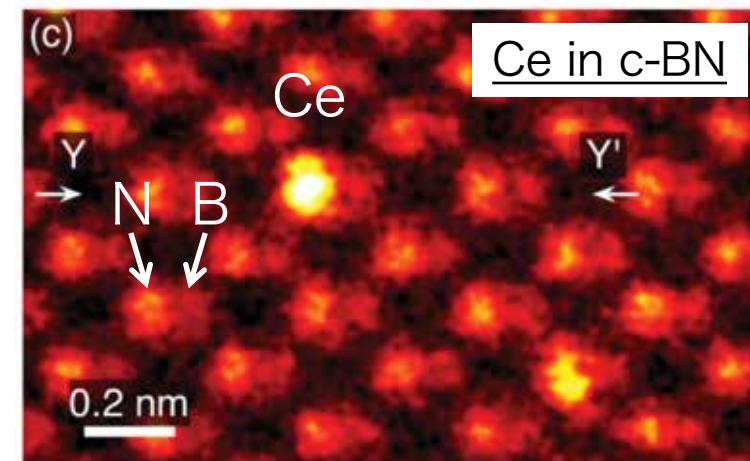
Experimental techniques

- ◆ chemical composition (ICP)
- ◆ optical spectra (XPS, XAS)
- ◆ ion diffusion (impedance analysis)
- ◆ carrier type and concentration
(Hall measurement)
- ◆ direct image (TEM/STEM)
- ◆ magnetic state (EPR)

None of them are perfect!!



Kittel, Solid State Physics, 8th ed.



Ishikawa et al., PRL, 2013

Combination of experiments **and first-principles calculations**

Defect formation energy

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

①

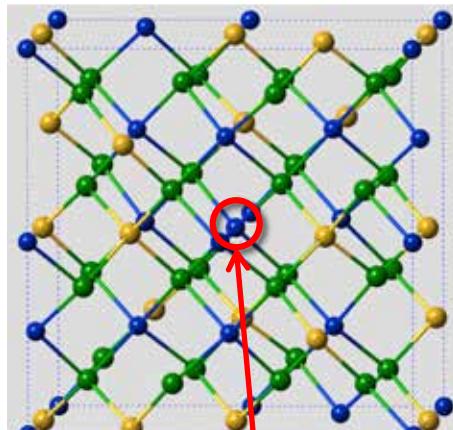
②

③

④

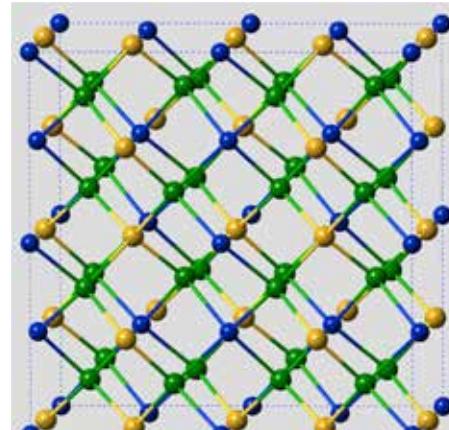
ex: $\text{Sn}_{\text{Zn}}^{+2}$ antisite in ZnSnP_2

①
Defect model

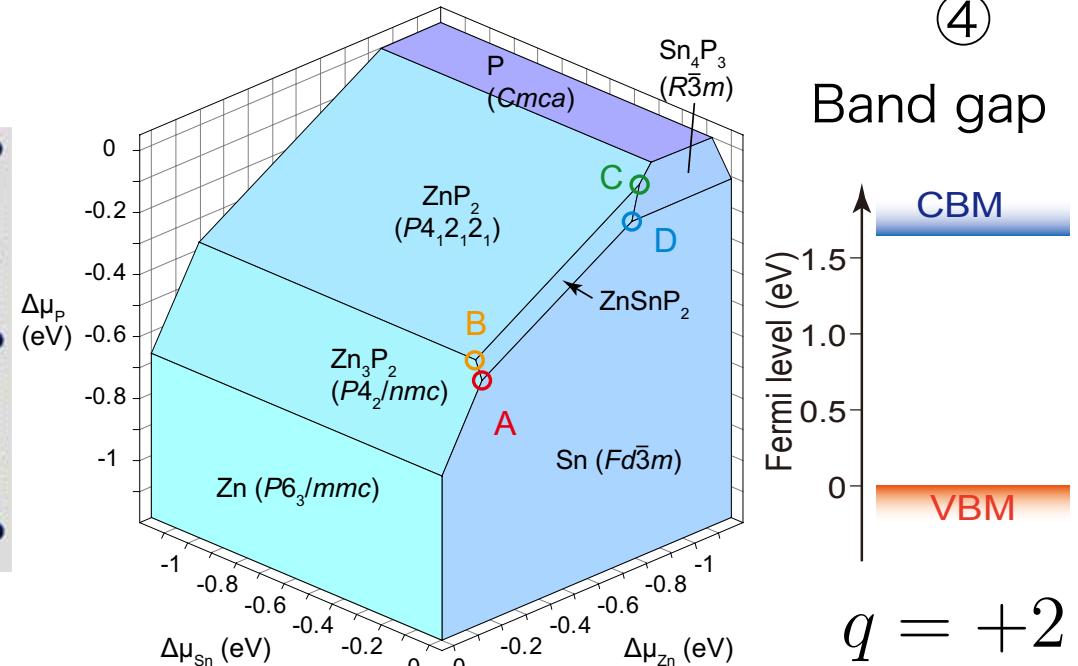


$\text{Sn}_{\text{Zn}}^{+2}$ antisite

②
Perfect system



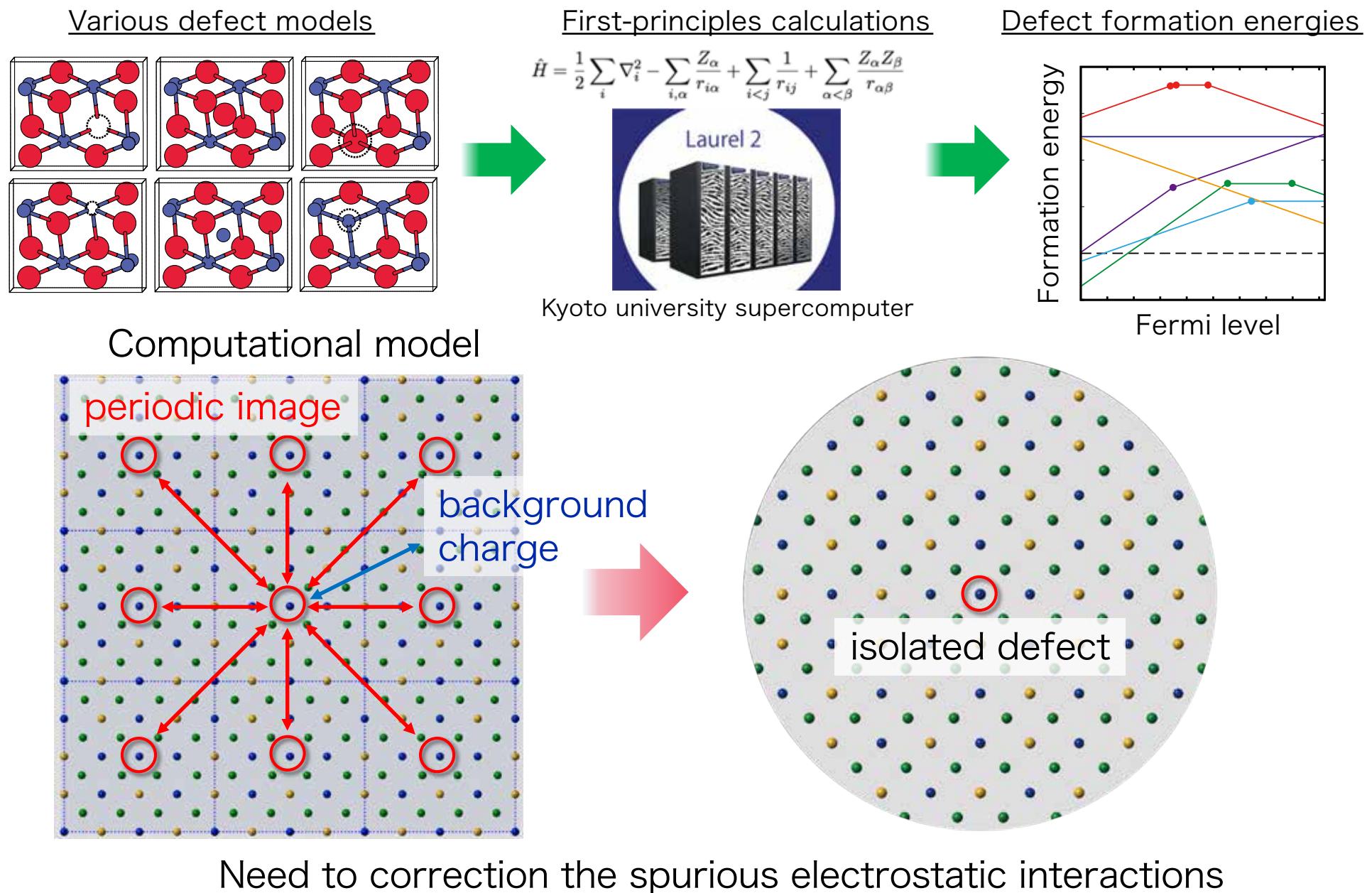
③
Chemical potential diagram



$q = +2$

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

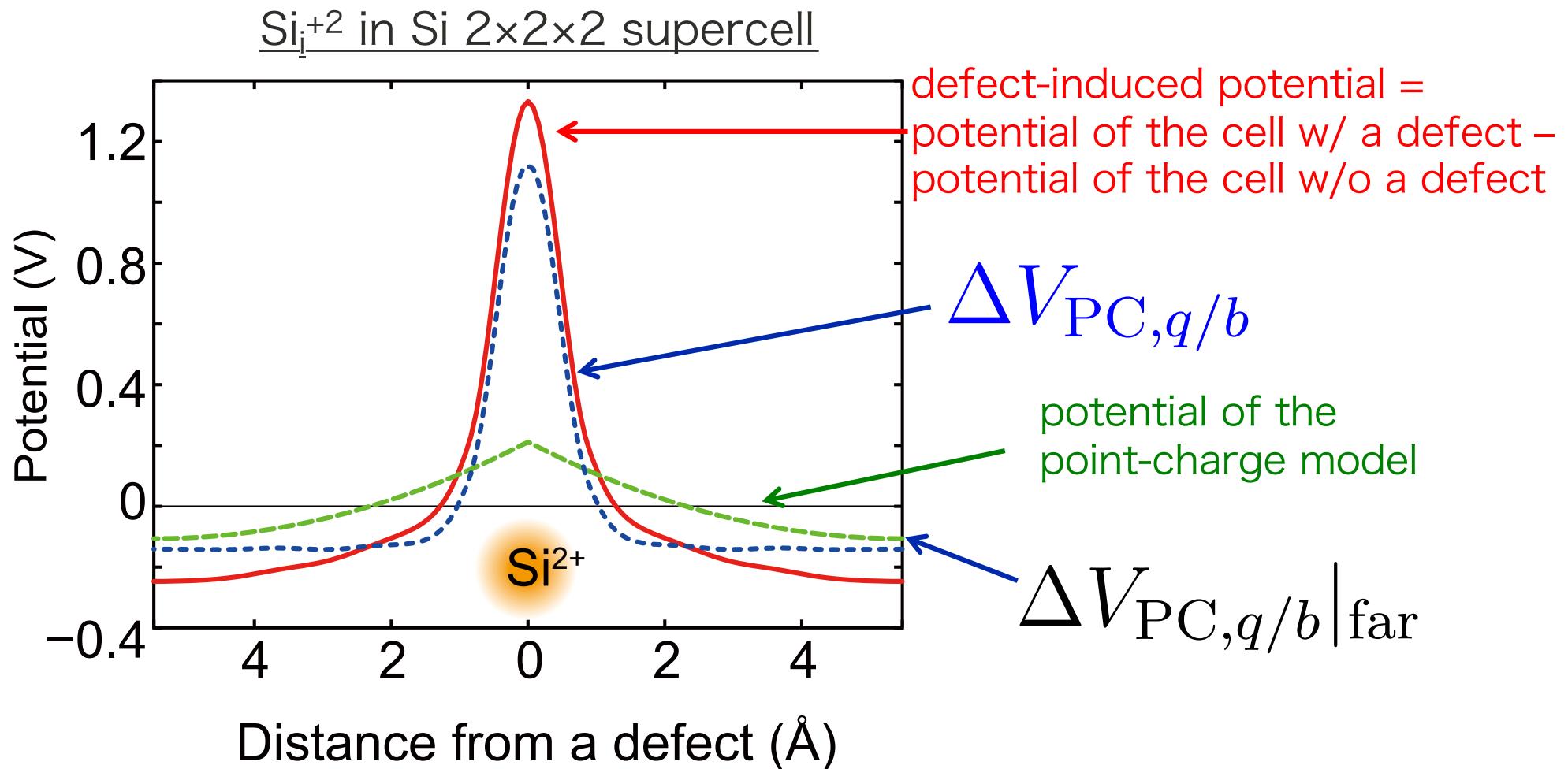
Point-defect calculations



Freysoldt-Neugebauer-Van de Walle (FNV) scheme

Freysoldt, Neugebauer, and Van de Walle,
Phys. Rev. Lett., 2009

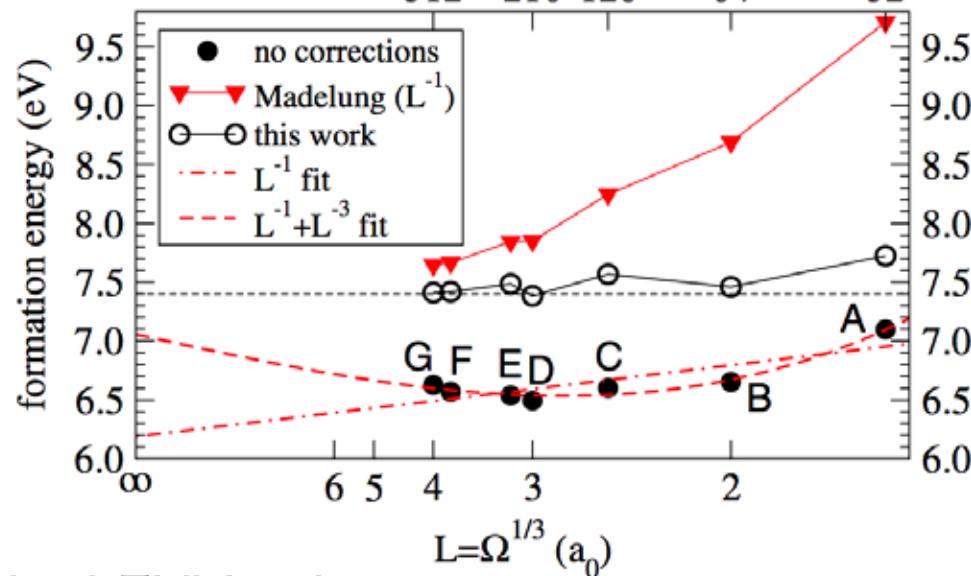
$$E_{\text{FNV}} = E_{\text{PC}} - q \Delta V_{\text{PC},q/b} \Big|_{\text{far}}$$



An example of FNV scheme

ex. $V_{C^{+2}}$ in diamond

N_{atoms} Freysoldt, Neugebauer, and Van de Walle,
Phys. Rev. Lett., 2009



Limitation of original FNV scheme

- systems without atomic relaxation (Komsa et al., 2012)

→ atomic-site potential

- isotropic systems

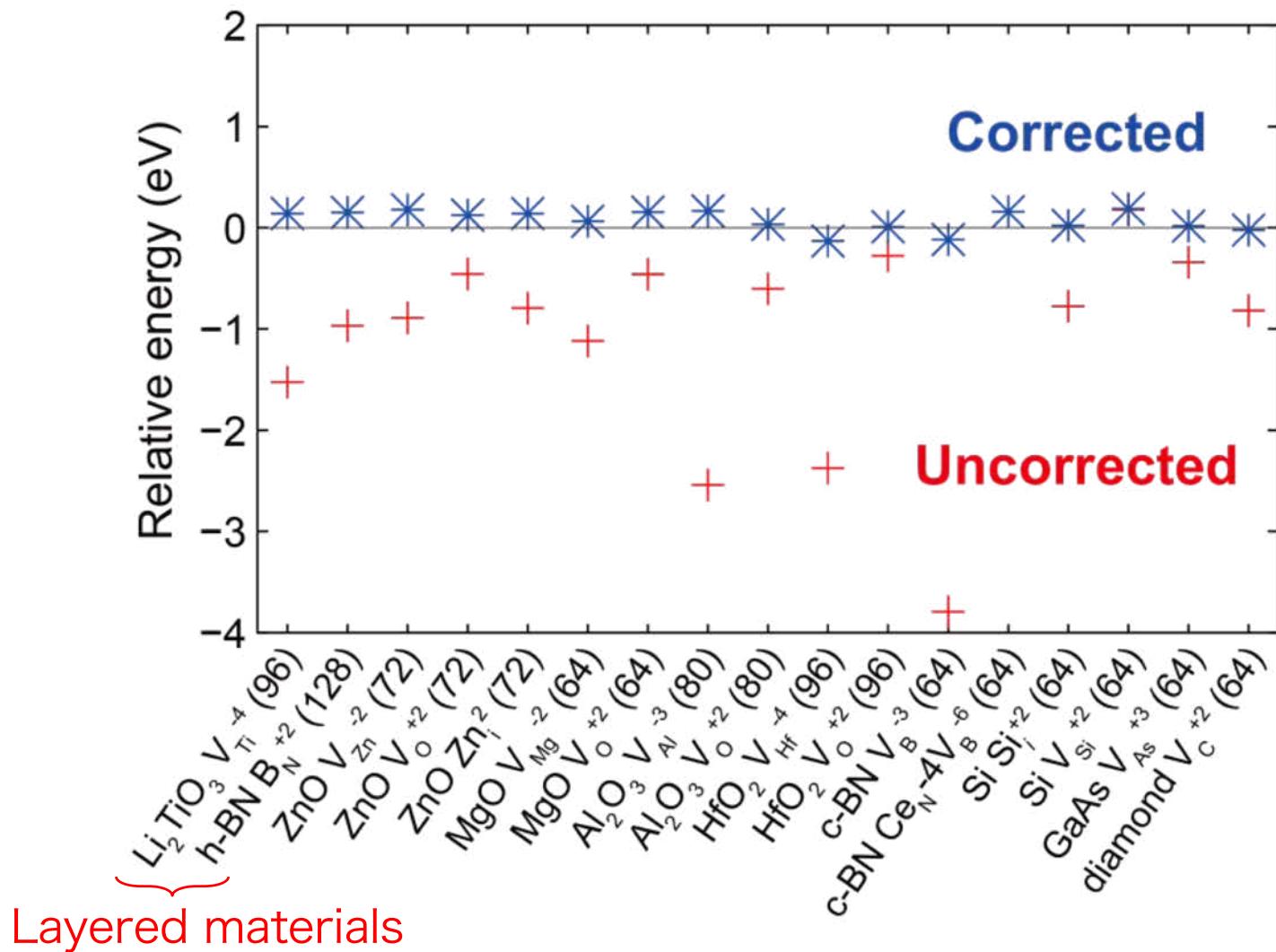
→ anisotropic formalism

$$V_{PC,q}^{\text{aniso}}(\mathbf{r} \neq \mathbf{0}) = \sum_{\mathbf{R}_i} \frac{q}{\sqrt{|\epsilon|}} \frac{\text{erfc}(\gamma \sqrt{\mathbf{R}_i \cdot \bar{\epsilon}^{-1} \cdot \mathbf{R}_i})}{\sqrt{\mathbf{R}_i \cdot \bar{\epsilon}^{-1} \cdot \mathbf{R}_i}} - \frac{\pi q}{V_c \gamma^2} + \sum_{\mathbf{G}_i}^{i \neq 0} \frac{4\pi q}{V_c} \frac{\exp(-\mathbf{G}_i \cdot \bar{\epsilon} \cdot \mathbf{G}_i / 4\gamma^2)}{\mathbf{G}_i \cdot \bar{\epsilon} \cdot \mathbf{G}_i} \cdot \exp(i\mathbf{G}_i \cdot \mathbf{r}). \quad (14)$$

YK and Oba., Phys. Rev. B Editors' suggestion (2014)

Extend the FNV scheme to be applicable to diverse materials

Extended FNV correction method

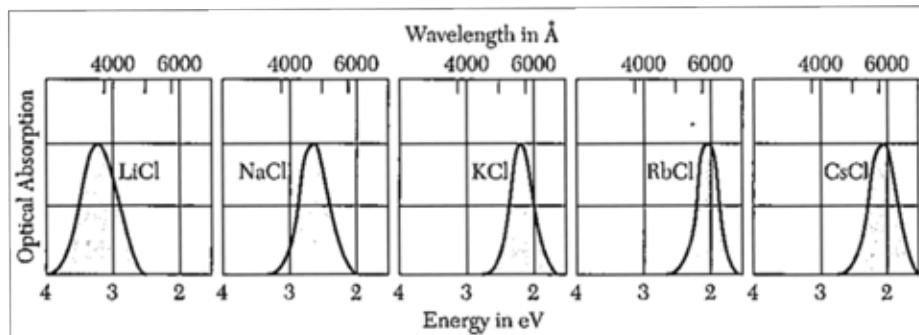


YK and Oba., Phys. Rev. B Editors' suggestion (2014)

→ Also implemented by Materials Project group (Broberg, *et al.*, 2018)

Defect-mediated optical transitions

Optical absorption relevant to F-centers



Kittel, Solid State Physics, 8th ed.

Blue-light emission by oxygen vacancies in SrTiO₃



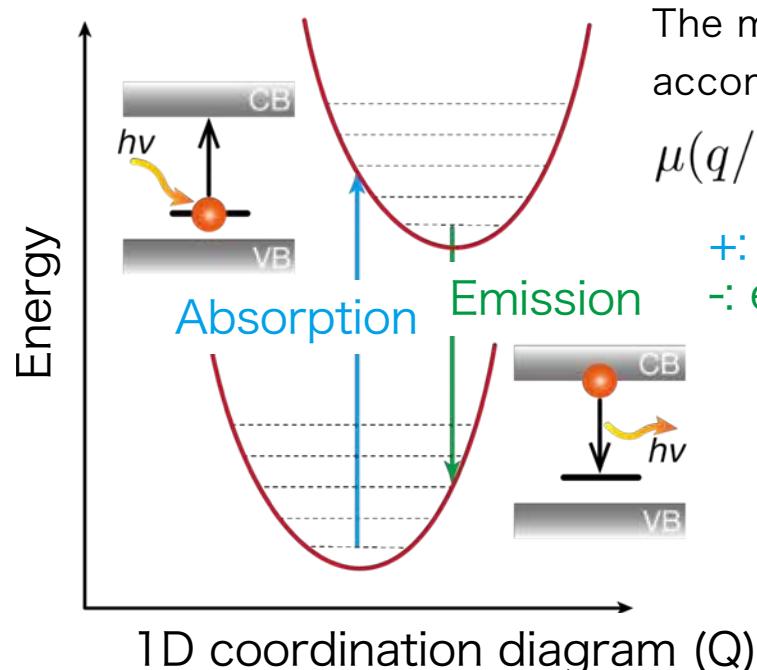
D. Kan *et al.*, Nat. Mater. 4, 816 (2005).

Frank-Condon principles

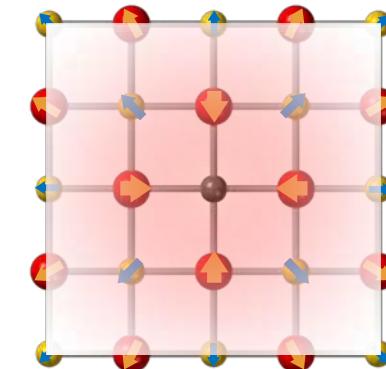
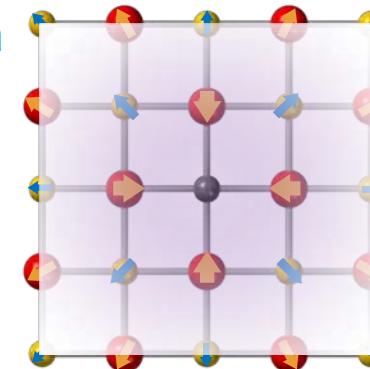
The most likely optical absorptions and emissions do not accompany with the atomic relaxation

$$\mu(q/q \pm 1; Q(q)) = [E(q \pm 1; Q(q)) - E(q; Q(q))] \pm \varepsilon_{\text{CBM}}$$

+: absorption
-: emission



w/ only electronic screening
and displacement **at $Q(q)$**



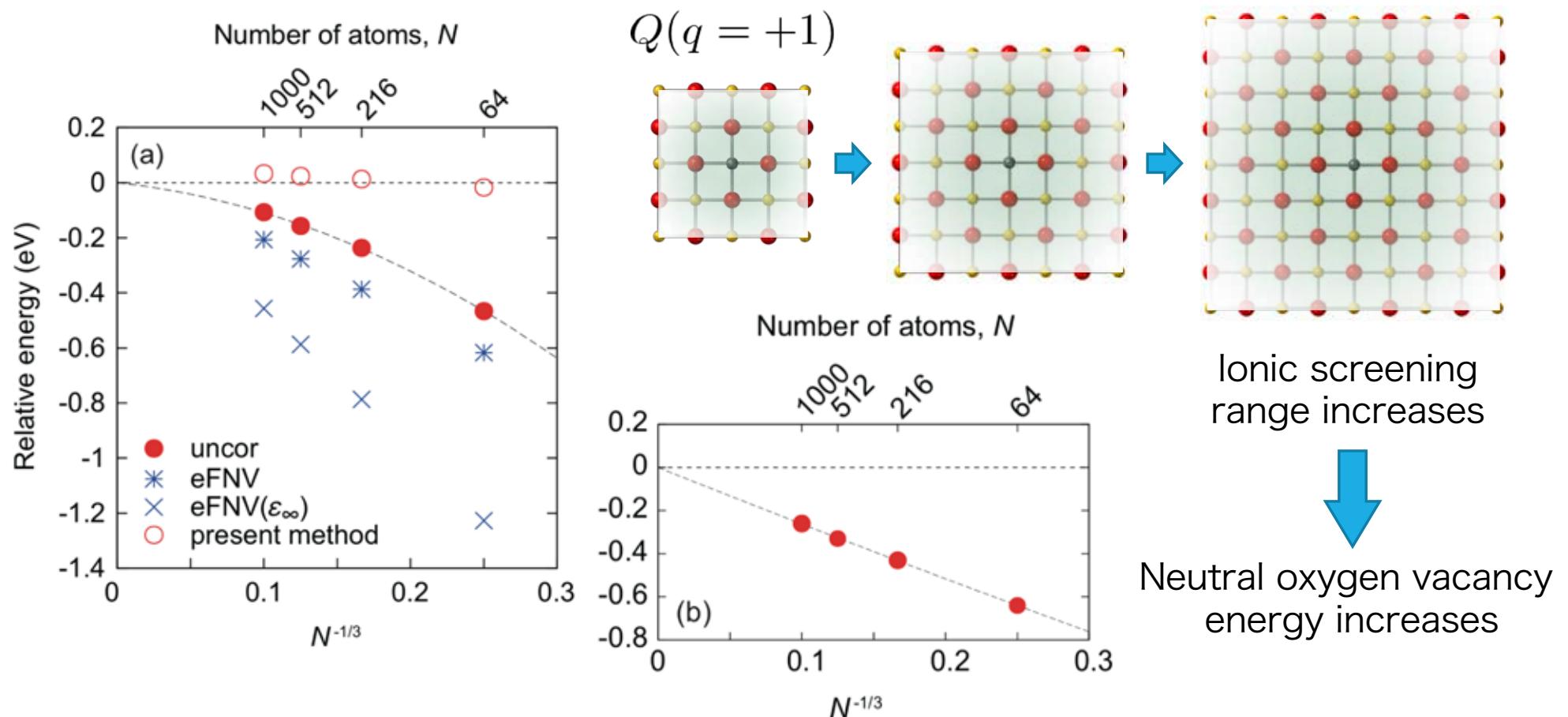
w/ both electronic
and ionic screening

Calculations of vertical transition levels

VTLs from 1+ to 0 charge states of the oxygen vacancy in MgO.

$$\mu(+1/0; Q(q = +1)) = \{E(q = 0; Q(q = +1)) - E(q = +1; Q(q = +1))\} - \varepsilon_{\text{CBM}}$$

no correction?? conventional correction



Calculations of vertical transition levels

Divide the correction energy difference into electronic and ionic parts.

$$\Delta E_{\text{cor}} = E_{\text{cor}}(q \pm 1; Q(q)) - E_{\text{cor}}(q; Q(q)) \\ = \{E_{\text{cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{el}}(q; Q(q))\} + \{E_{\text{cor}}^{\text{ion}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{ion}}(q; Q(q))\}$$

Depend on charge state but not on Q



conventional screening
with electronic dielectric constant

Depend on Q but not on charge state

Janak's theorem



$$E(q \pm 1; Q(q)) - E(q; Q(q)) = \mp \int_0^1 \varepsilon(f; Q(q)) df$$



$$\mp \varepsilon_{\text{cor}}^{\text{ion}}(Q(q))$$

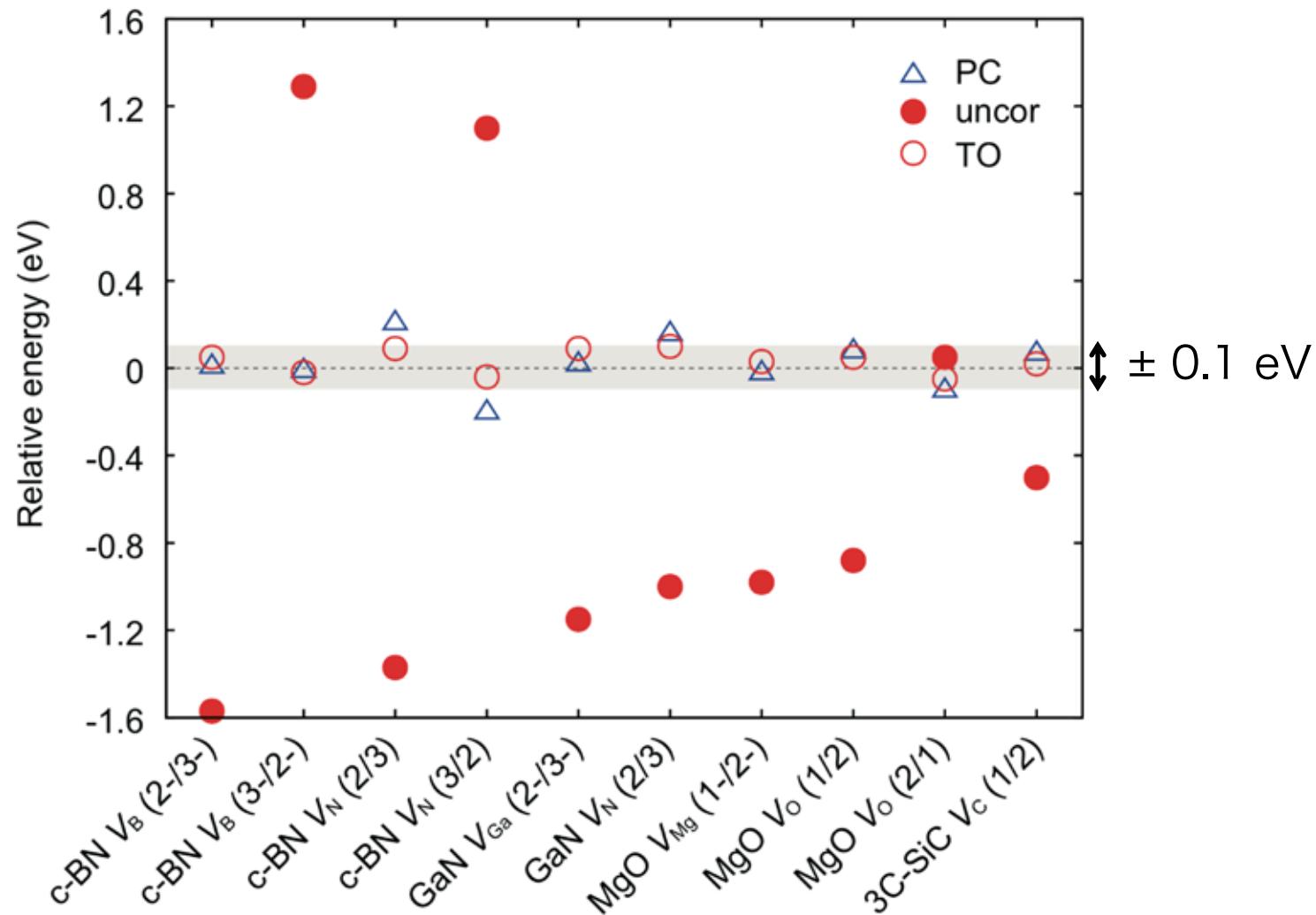
$$\Delta E_{\text{cor}} = \{E_{\text{cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{el}}(q; Q(q))\} \mp \varepsilon_{\text{cor}}^{\text{ion}}(Q(q))$$

Apply FNV correction

$$\Delta E_{\text{cor}} = \{E_{\text{PC cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{PC cor}}^{\text{el}}(q; Q(q))\} \mp \varepsilon_{\text{PC cor}}^{\text{ion}}(Q(q)) \mp \Delta V_{\text{PC}, q/b} |_{\text{far}}$$

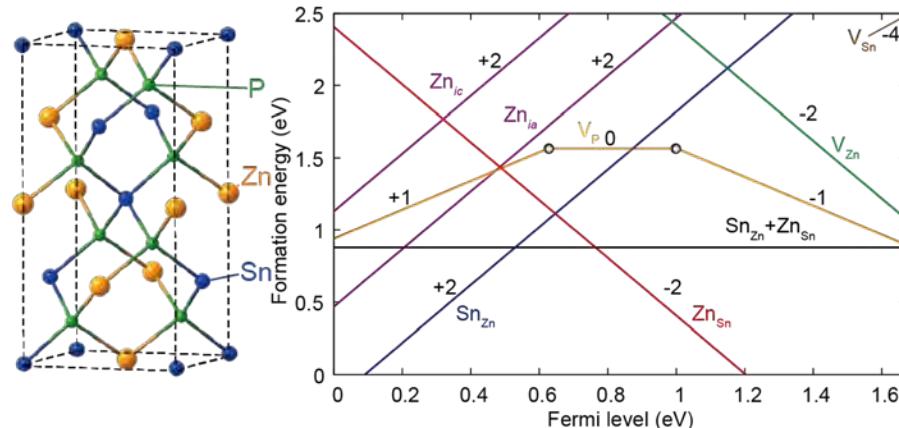
Calculations of vertical transition levels

$$\Delta E_{\text{cor}} = \{E_{\text{PC cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{PC cor}}^{\text{el}}(q; Q(q))\} \mp \varepsilon_{\text{PC cor}}^{\text{ion}}(Q(q)) \mp \Delta V_{\text{PC}, q/b}|_{\text{far}}$$



Applications

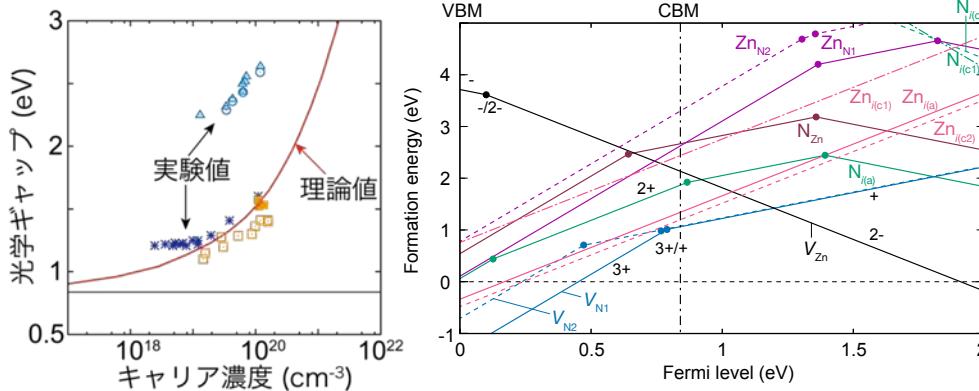
Native defects in $ZnSnP_2$



Antisite-type native defects are dominant.

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

Native defects in Zn_3N_2

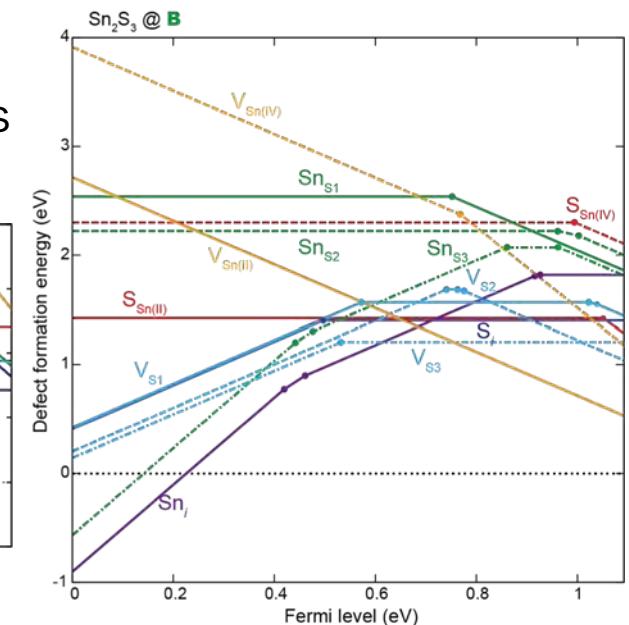
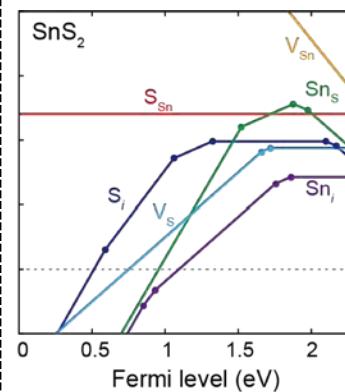


Explain origin of wide range of band gaps

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

Wang, Ohsawa, YK, et al., Appl. Phys. Lett. (2019).

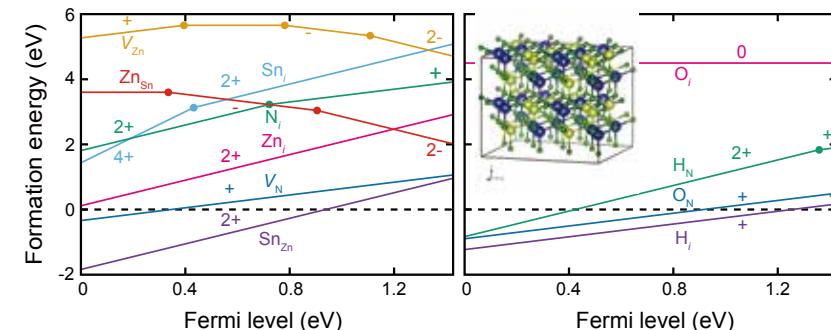
Native defects in SnS_x



Elucidation of point defects introducing n-type conductivity in SnS_2 and Sn_2S_3 .

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

Native defects in $ZnSnN_2$

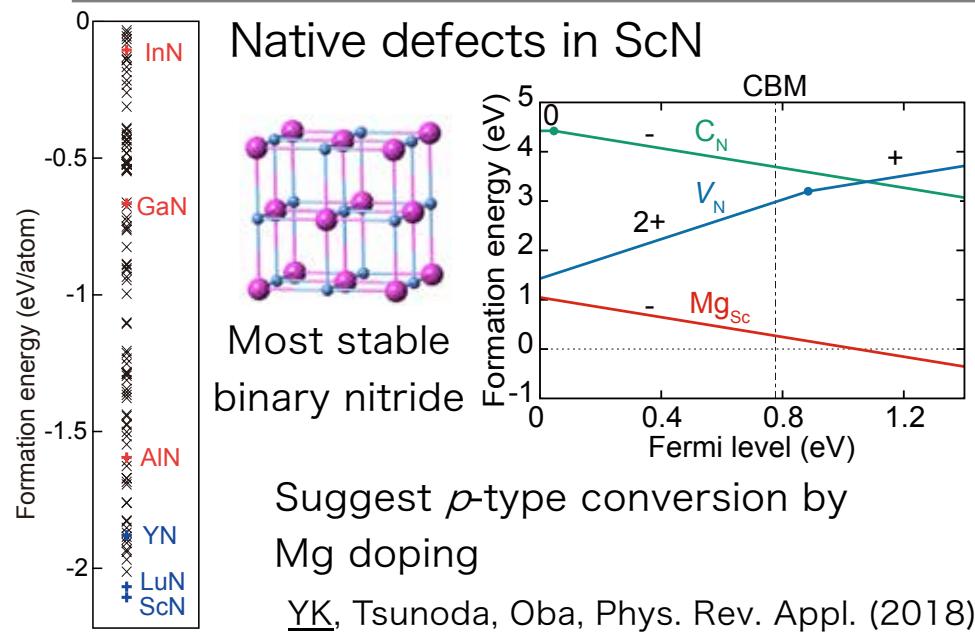


No low energy defects with deep levels.

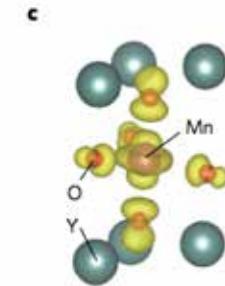
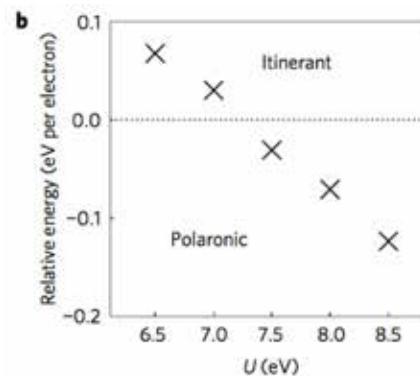
Dominant donors are unintentional oxygen on nitrogen sites and hydrogen interstitials.

Tsunoda, YK, et al., Phys. Rev. Appl. (2018)

Applications



Polarons in h -RMnO₃

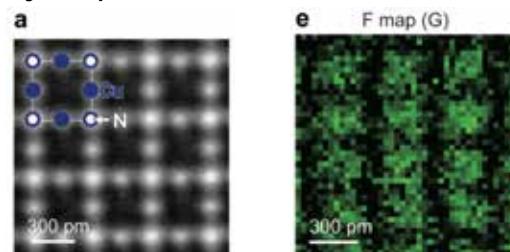


Indicate existence of electron polarons at the head-to-head domain walls

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

Collaborations

- Suggest F as p-type dopants in Cu₃N and confirmed by experiments

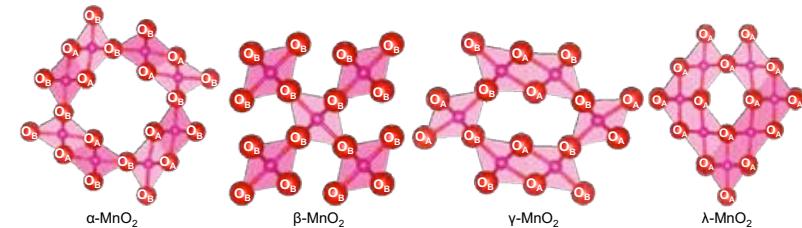


Matsuzaki, Harada, YK, *et al.*, Adv. Mater. (2018)

- Native defects in CaZn₂N₂

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

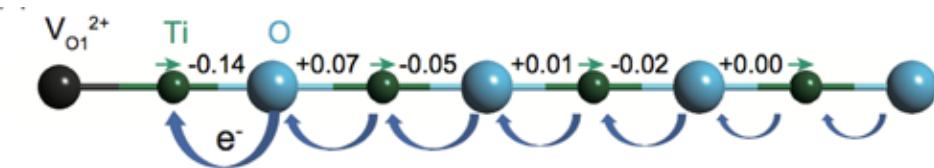
- Heterogeneously Catalyzed Aerobic Oxidation of Sulfides with a BaRuO₃ Nanoperovskite
Kamata, Sugahara, Kato, Muratsugu, YK, Oba, and Hara, ACS Appl. Mater. Interfaces (2018)
- Effect of MnO₂ Crystal Structure on Aerobic Oxidation of 5-HMF to 2,5-FDCA



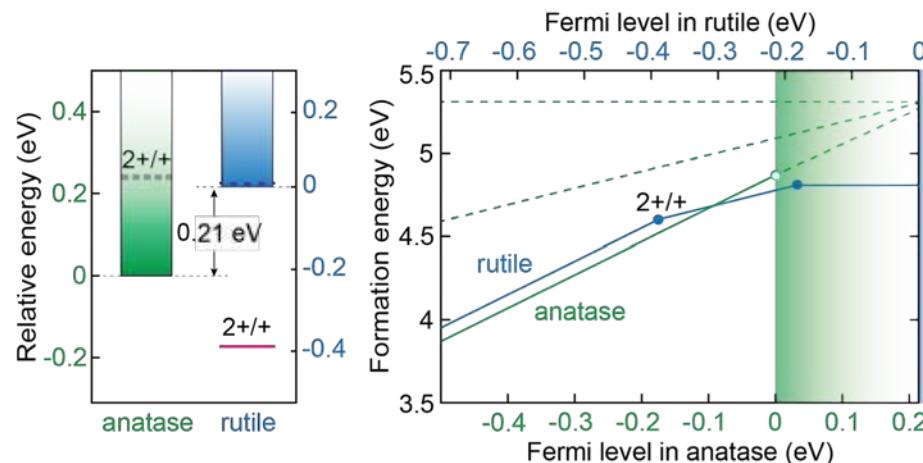
Hayashi, Yamaguchi, Kamata, Tsunoda, YK, Oba, and Hara, J. Am. Chem. Soc. (2019).

Latest applications

One-dimensionally extended oxygen vacancy states in perovskite oxides



Long-range charge transfer emerges along $-B-O-B-$ direction in perovskite oxides with anomalous Born effective charges

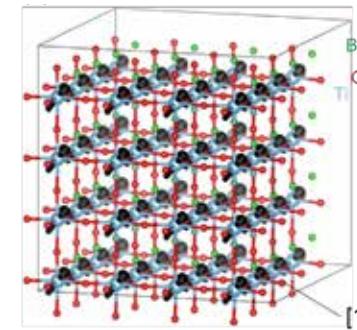


This explains why oxygen vacancies are shallow in anatase while deep in rutile.

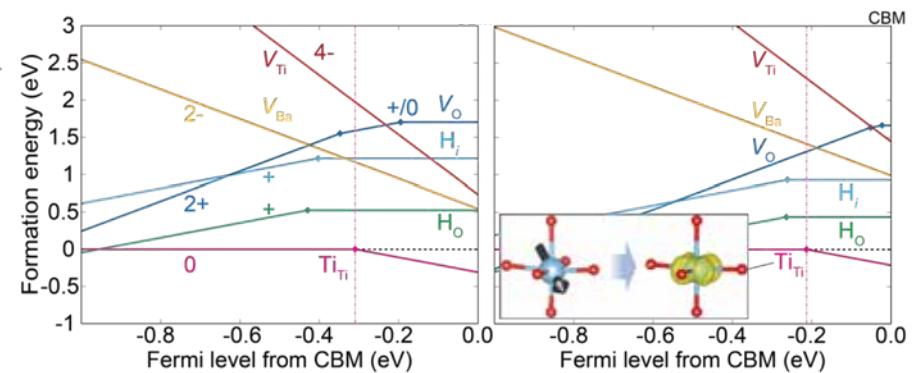
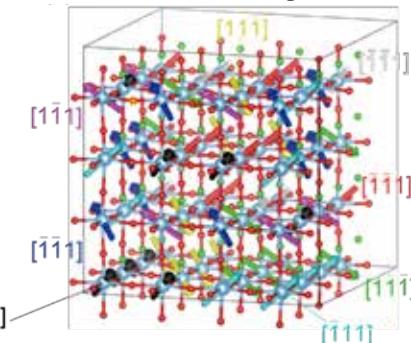
Tsunoda, YK (co-first), et al., Phys. Rev. B(R) (2019)

Native point defects in BaTiO_3

Rhombohedral model



Ti-off centering cubic model



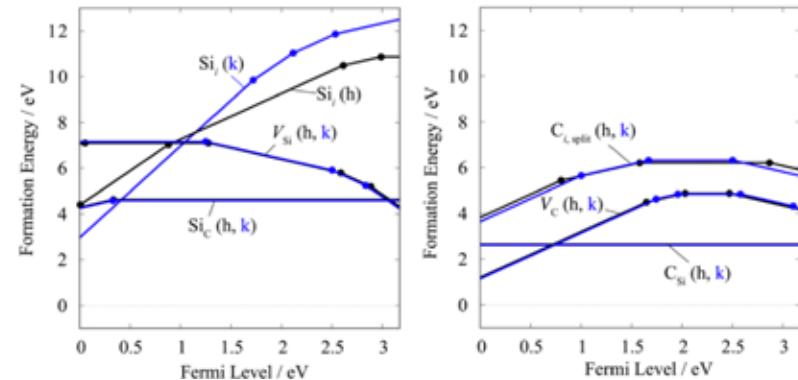
Carrier electrons tend to be trapped at the Ti-site when the Ti shows off-centering

- explains polaron conductivity at low T
- indicates coexistence of polarons/carrier electrons at room T

Tsunoda, YK, et al., Phys Rev. Mater, accepted (2019)

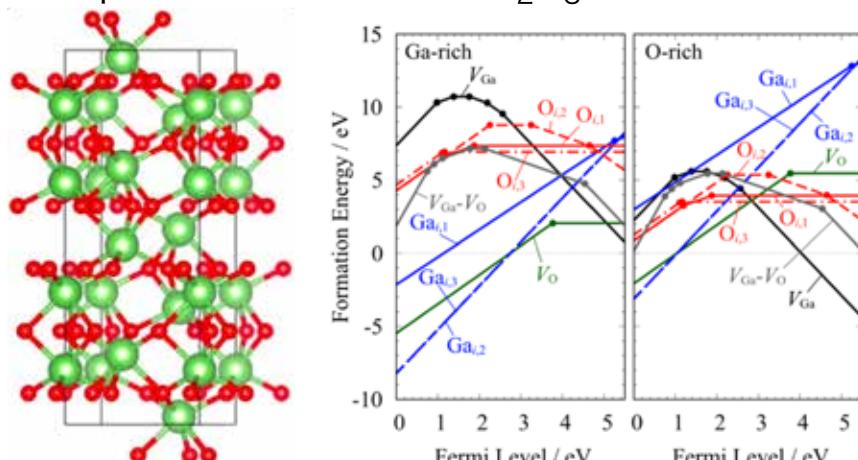
Latest applications

Native point defects and carbon clusters
in 4H-SiC



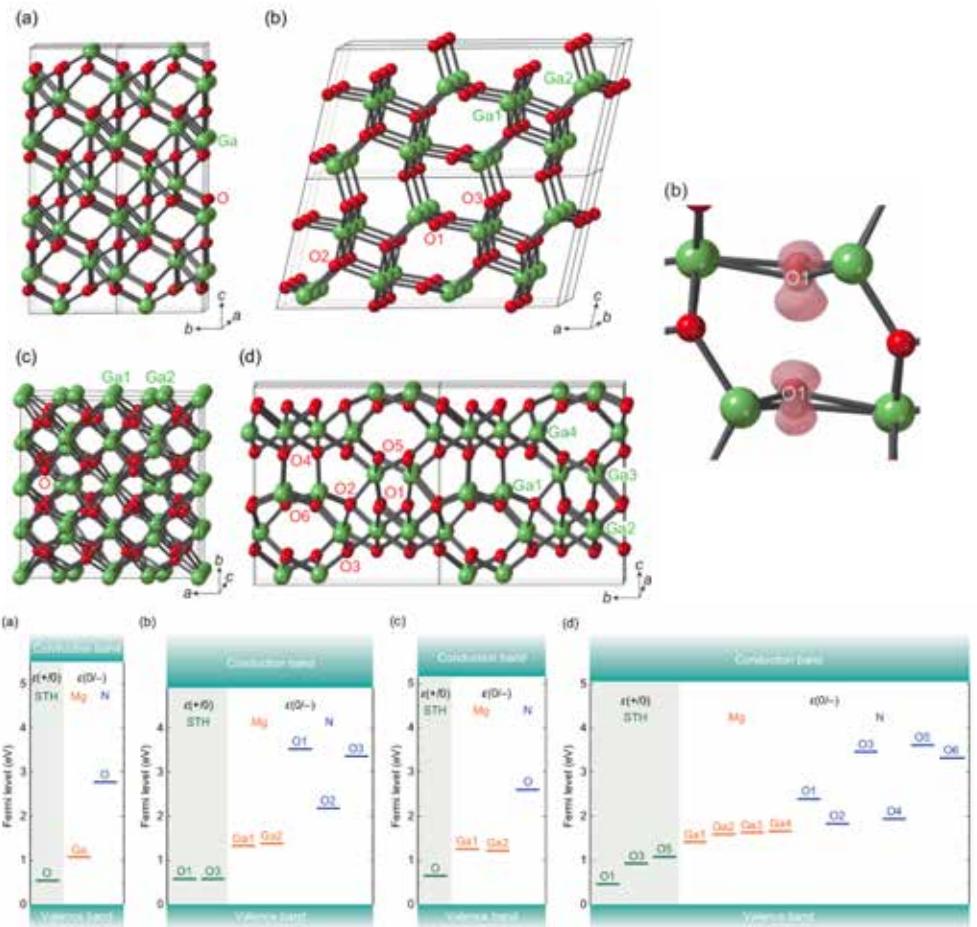
Kobayashi, Harada, YK, Oba, Matsushita,
J. Appl. Phys. (2019)

Energetics and electronic structure of
native point defects in α -Ga₂O₃



Kobayashi, Gake, YK, Oba, Matsushita,
Appl. Phys. Express (2019)

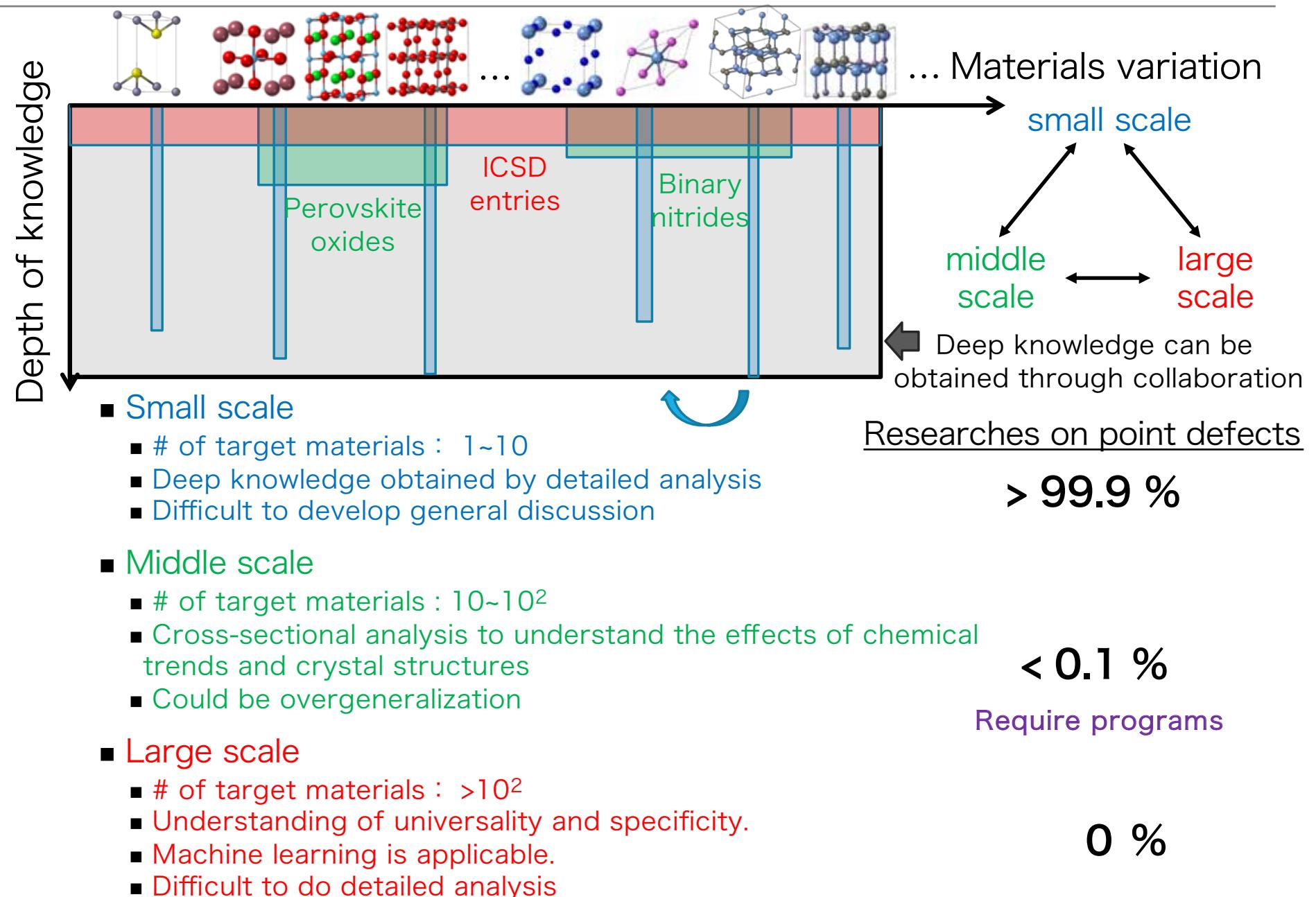
Self-trapped holes and acceptor impurities
in Ga₂O₃ polymorphs



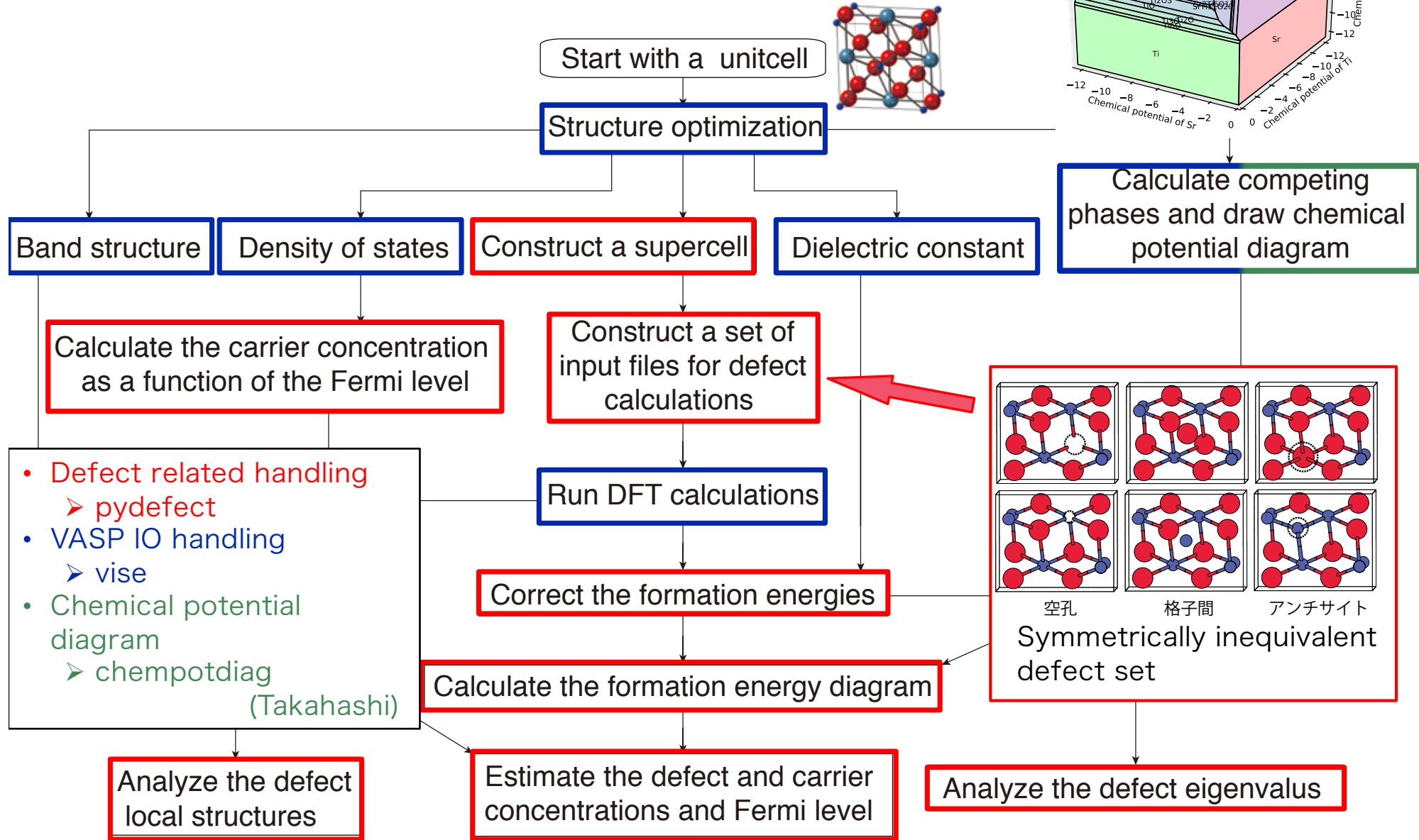
In all of the polymorphs, holes localize with high self-trapping energies.

Gake, YK, Oba., Phys Rev. Mater (2019)

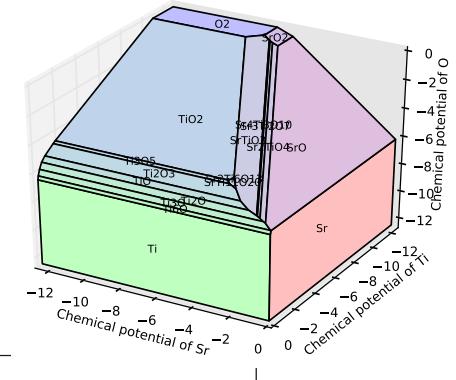
Scale of target materials



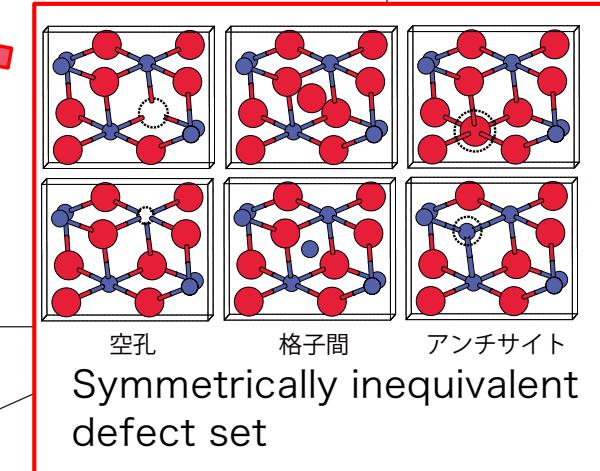
Calculation flow of the point defects



Chemical potential diagram of Sr, Ti, and O



Calculate competing phases and draw chemical potential diagram

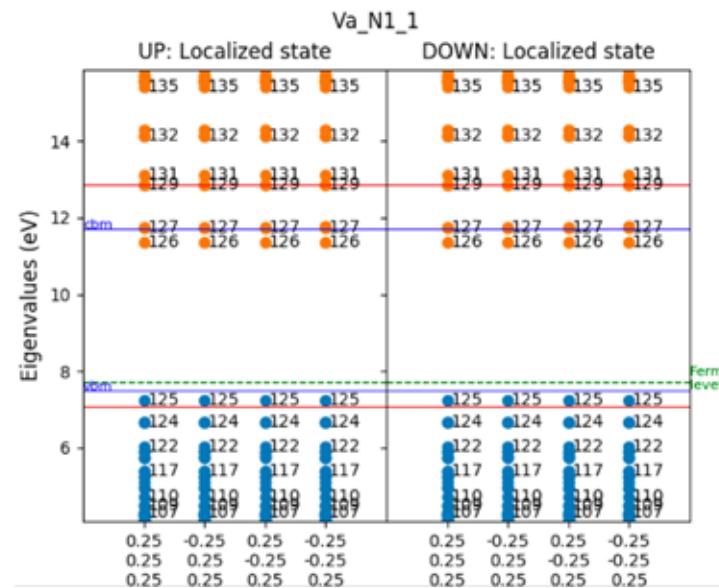
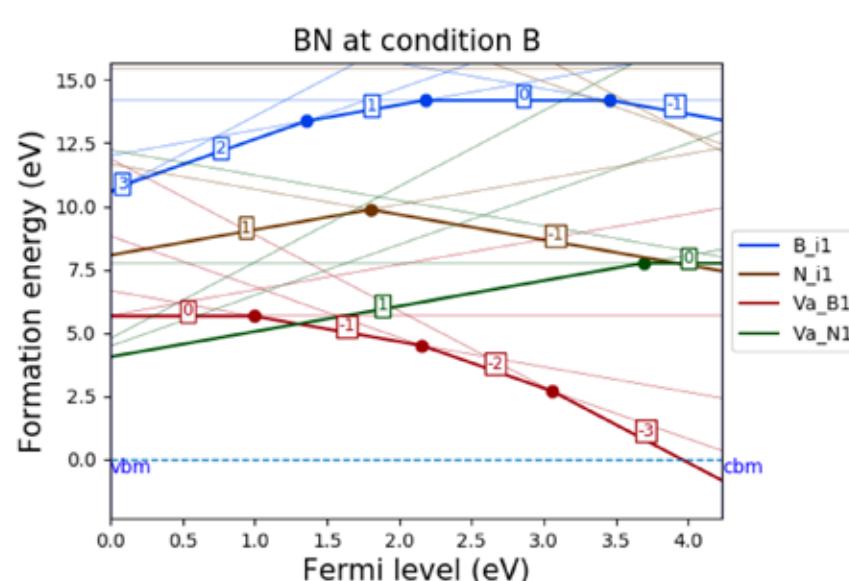


Pydefect package

defect input files

- Use various excellent external packages
 - pymatgen (Ong, et al., 2013)
 - spglib (Togo and Tanaka, <https://atztogo.github.io/spglib/>)
- Support functions for point-defect calculations
 - Generate a proper supercell and a set of point defects
 - Flexible modification of defaults
 - Recommend interstitial sites (pymatgen)
 - Handle complex defects
 - Analyze vasp calculation results
 - Plot and print various defect-related data

```
Space group: Fm-3m
Transformation matrix: -2 2 2 2 -2 2 2 2 -2
Cell multiplicity: 32
Irreducible element: Mg1
Wyckoff letter: a
Site symmetry: m-3m
Coordination: 0: 2.12 2.12 2.12 2.12 2.12 2.12
Equivalent atoms: 0..31
Fractional coordinates: 0.500000 0.000000 0.000000
Electronegativity: 1.31
Oxidation state: 2
Irreducible element: O1
Wyckoff letter: b
Site symmetry: m-3m
Coordination: Mg: 2.12 2.12 2.12 2.12 2.12 2.12
Equivalent atoms: 32..63
Fractional coordinates: 0.750000 0.250000 0.250000
Electronegativity: 3.44
Oxidation state: -2
Interstitials: all
Complex defects:
Antisite defects:
Substituted defects:
Maximum Displacement: 0.2
Exceptionally included:
Exceptionally excluded:
Cutoff region of neighboring atoms: 2.97
Symprec: 0.01
Angle tolerance: 5
```



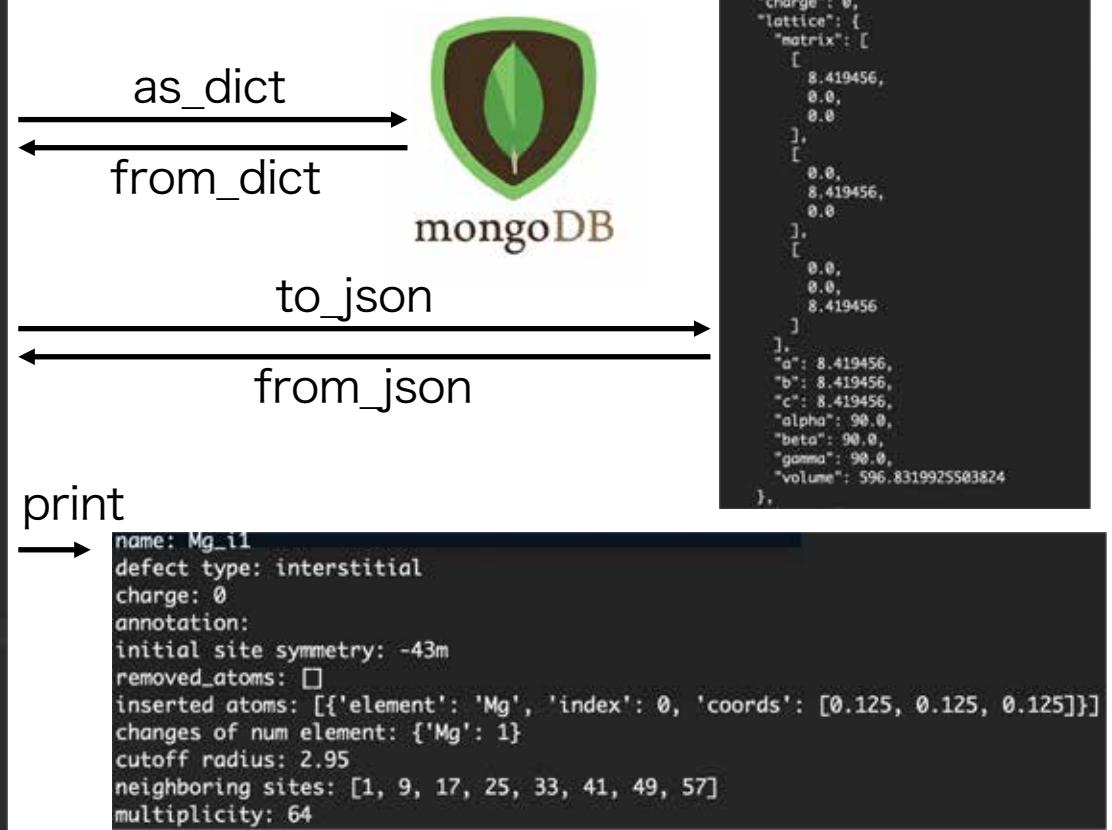
Pydefect package

- Still beta version composed of 11,819 lines with python3.6 (2019.10.6)
- Write all the unittests and check the code coverage.
- Write all the documents and annotations.
- Implement APIs that are easily incorporated to the other codes.
- Most of the class used for analysis has `as_dict`/`from_dict`,
`from_json`/`to_json` methods and `_repr__`.

```
class DefectEntry(MSONable):
    """ Holds information related to initial setting of a single defect. """

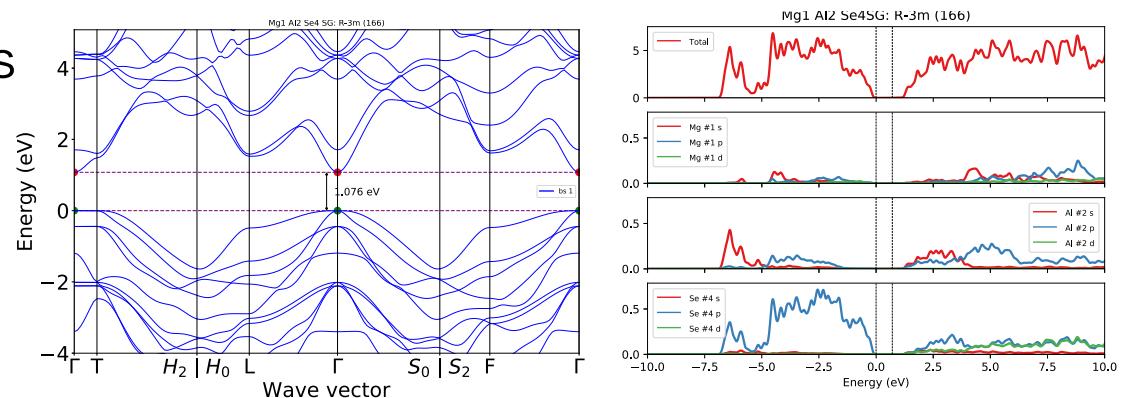
    def __init__(self,
                 name: str,
                 defect_type: DefectType,
                 initial_structure: Structure,
                 perturbed_initial_structure: Structure,
                 removed_atoms: list,
                 inserted_atoms: list,
                 changes_of_num_elements: dict,
                 charge: int,
                 initial_site_symmetry: str,
                 cutoff: float,
                 neighboring_sites: list,
                 annotation: Optional[str] = None,
                 multiplicity: Optional[int] = None):
        ...

    Args:
        name (str):
            Name of a defect without charge.
        defect_type (DefectType):
            Defect type defined in DefectType enumeration.
        initial_structure (Structure):
            Structure with a defect before the structure optimization.
        perturbed_initial_structure (Structure):
            Initial structure with perturbation of neighboring atoms.
        removed_atoms (list):
            List of dict with the following values.
            + "element" (str):
            + "index" (int): Removed index in the original supercell.
            + "coords" (list):
```

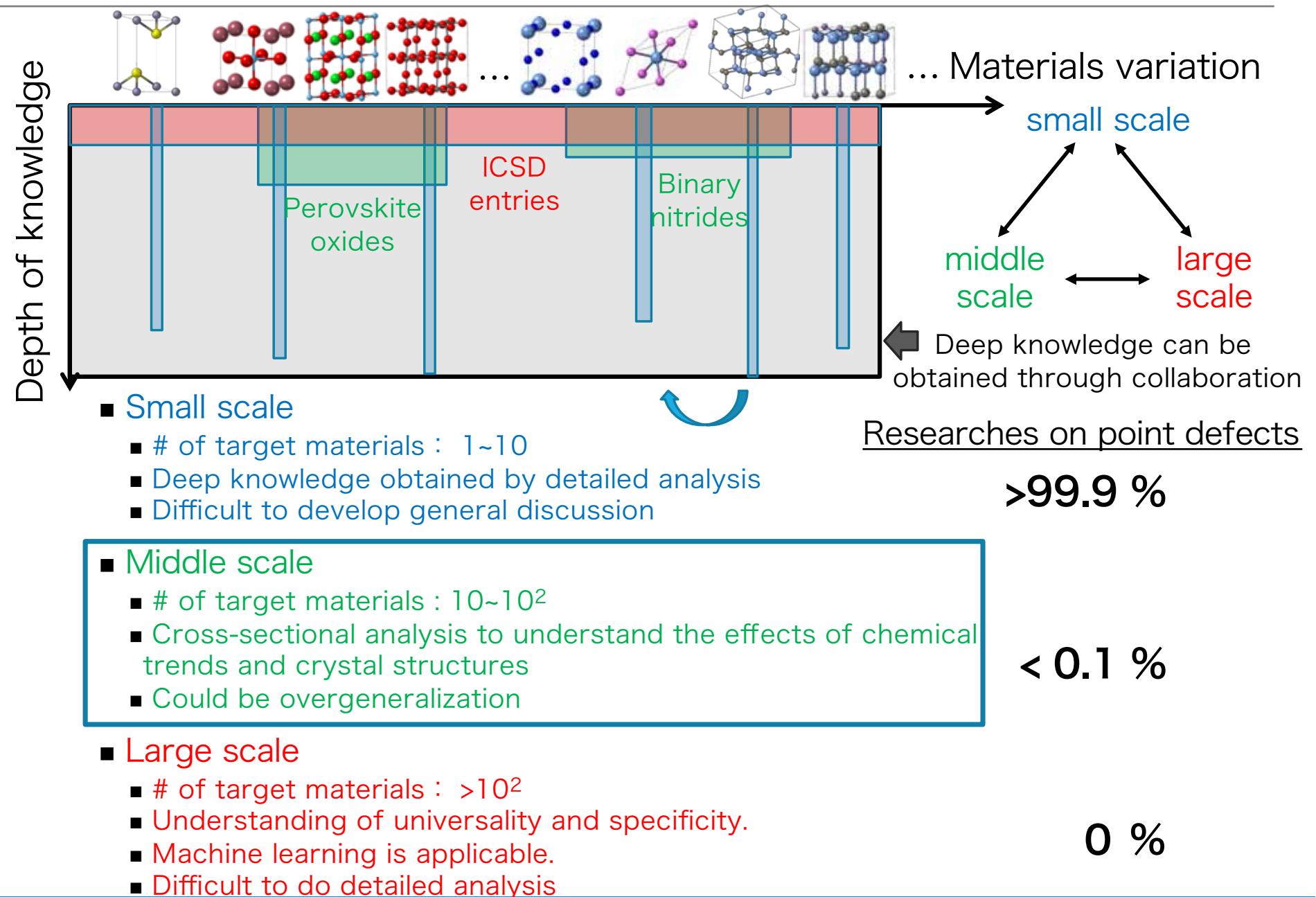


Vise

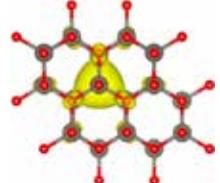
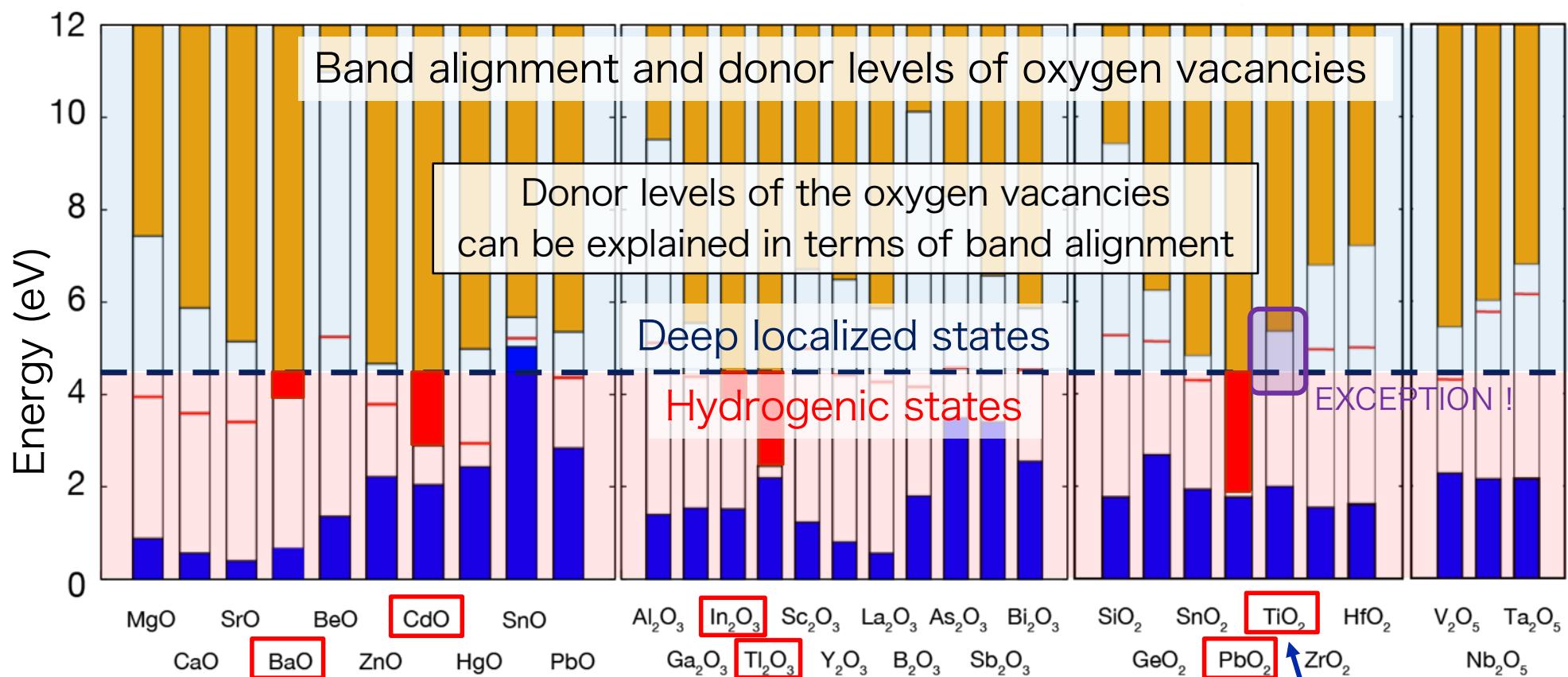
- Vasp Integrated Simulation Environment
- Still beta version composed 6,496 lines with python3.6 (2019.10.6)
- Use following excellent external packages
 - pymatgen (Ong, et al., 2013)
 - custodian (Ong, et al., 2013)
 - seekpath (Pizzi, <https://www.materialscloud.org/work/tools/seekpath>)
 - spglib (Togo and Tanaka, <https://atztogo.github.io/spglib/>)
- Support functions
 - Generate vasp input files
 - Handling vasp calculations
 - analyze vasp outputs
- Coding rules are basically the same as pydefect



Scale of target materials



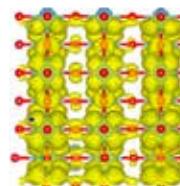
Oxygen vacancies in 86 binary oxides



Deep
localized
states

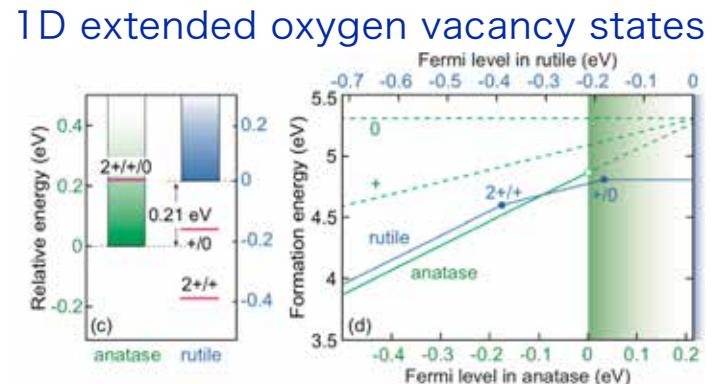


Conduction bands
Valence bands

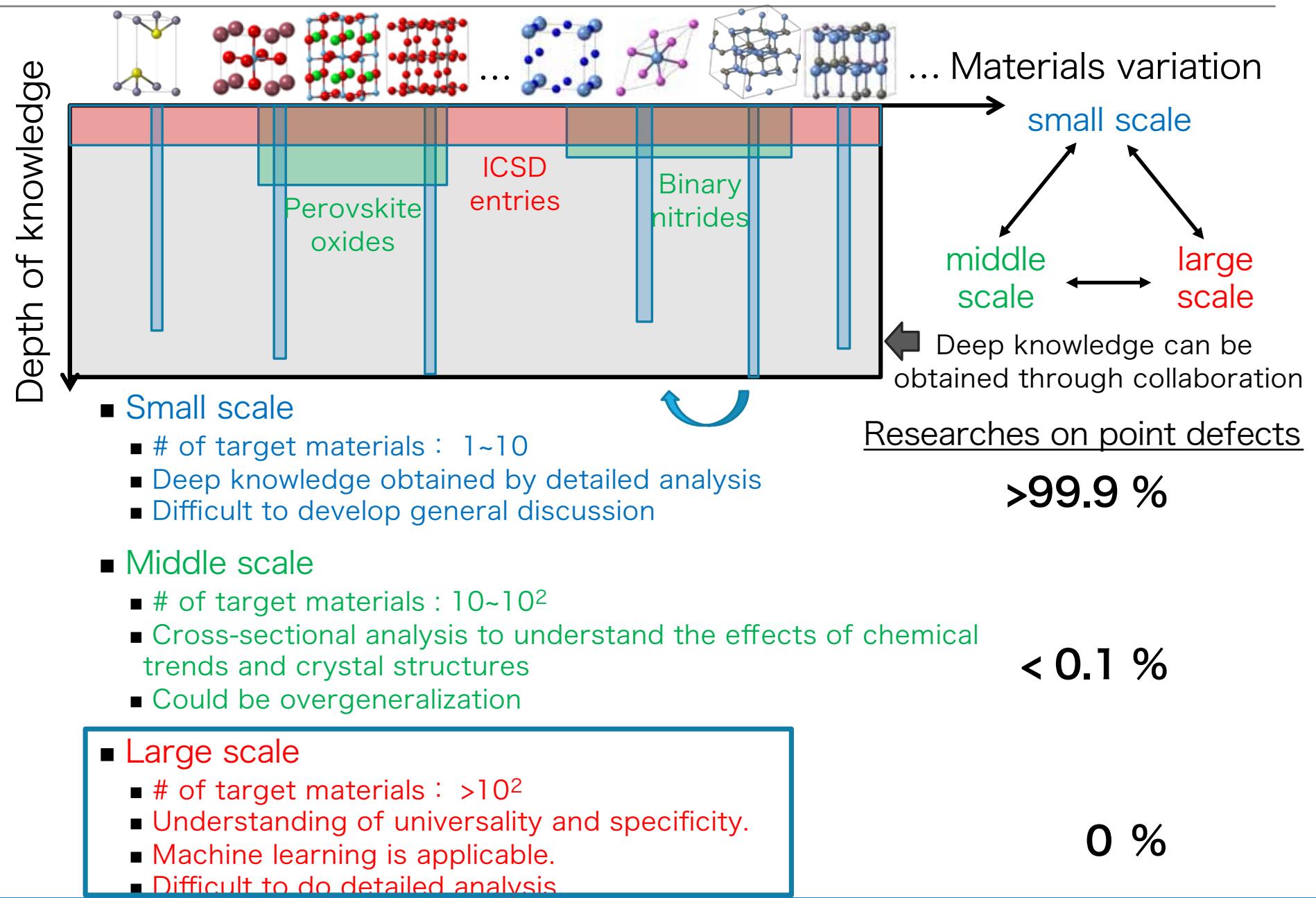


Hydrogenic
states

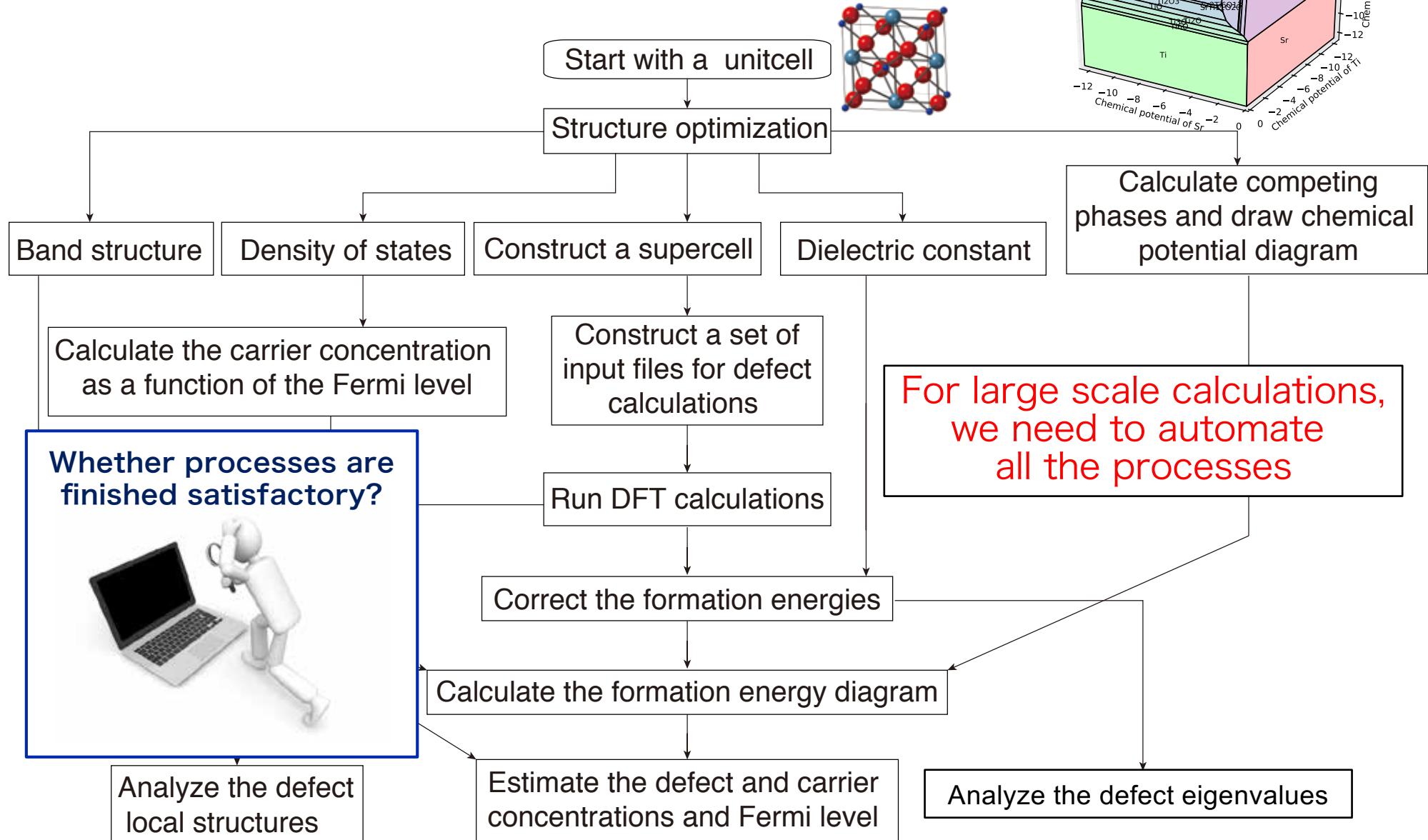
Tsunoda,
YK, et al.,
PRB(R)



Scale of target materials



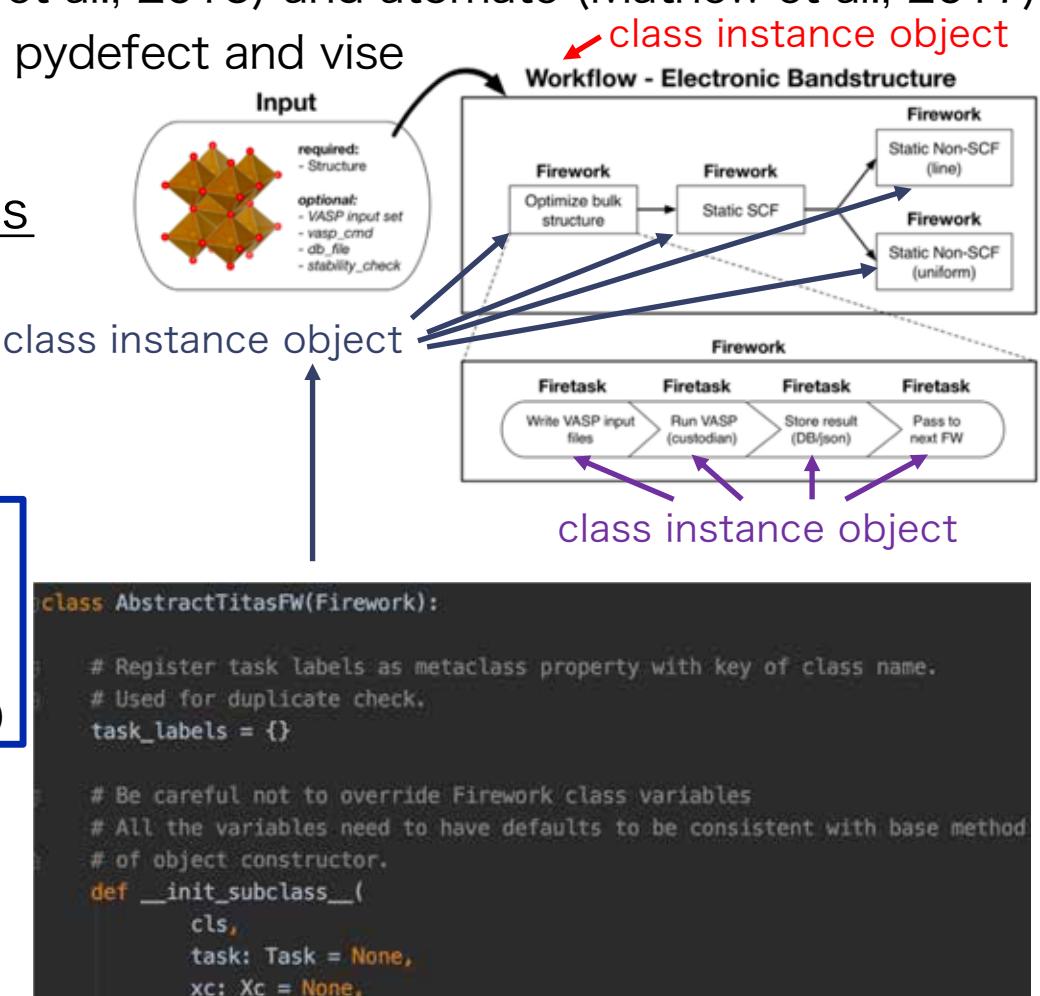
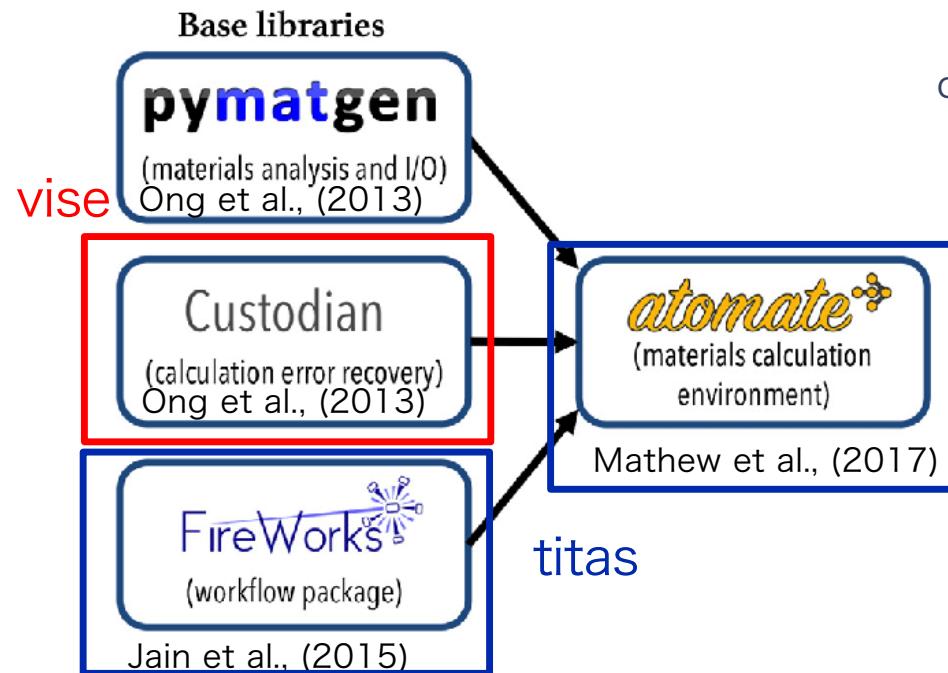
Calculation flow of the point defects



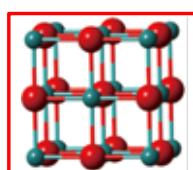
Titas package

- Tokyo Institute of Technology Automatic Simulation package
- Main authors are Akira Takahashi and Yu Kumagai.
- Still beta version composed 4,371 lines with python3.6 (2019.10.6)
- In-house extension to FireWorks (Jain, et al., 2015) and atomate (Mathew et al., 2017)
- Coding rules are basically the same as pydefect and vise

Materials project automation packages



Example of automation system



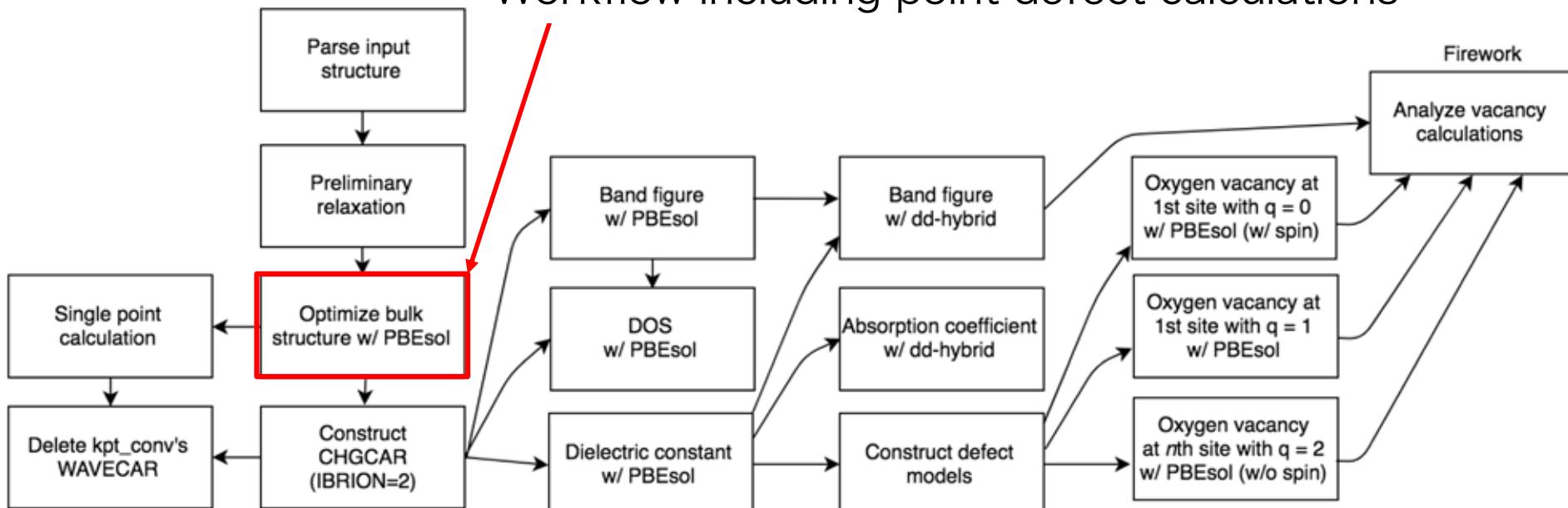
- Check the convergence of k-point set

```

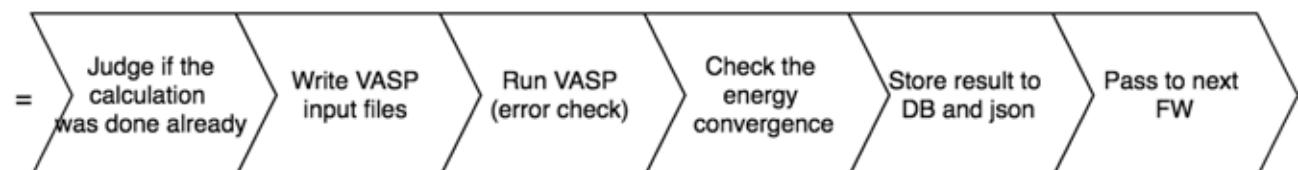
4 x 4 x 2 total-kpt= 32 spg= 182 a= 5.1131 b= 5.1131 c= 8.6294 alpha= 90.000 beta= 90.000 gamma= 120.000 energy= -7.9115 eV/atom
6 x 6 x 4 total-kpt= 144 spg= 182 a= 5.1131 b= 5.1131 c= 8.6294 alpha= 90.000 beta= 90.000 gamma= 120.000 energy= -7.9115 eV/atom
8 x 8 x 4 total-kpt= 256 spg= 182 a= 5.1131 b= 5.1131 c= 8.6294 alpha= 90.000 beta= 90.000 gamma= 120.000 energy= -7.9115 eV/atom
Converged k-points (Criterion: 0.003 eV/atom): 4 x 4 x 2
  
```



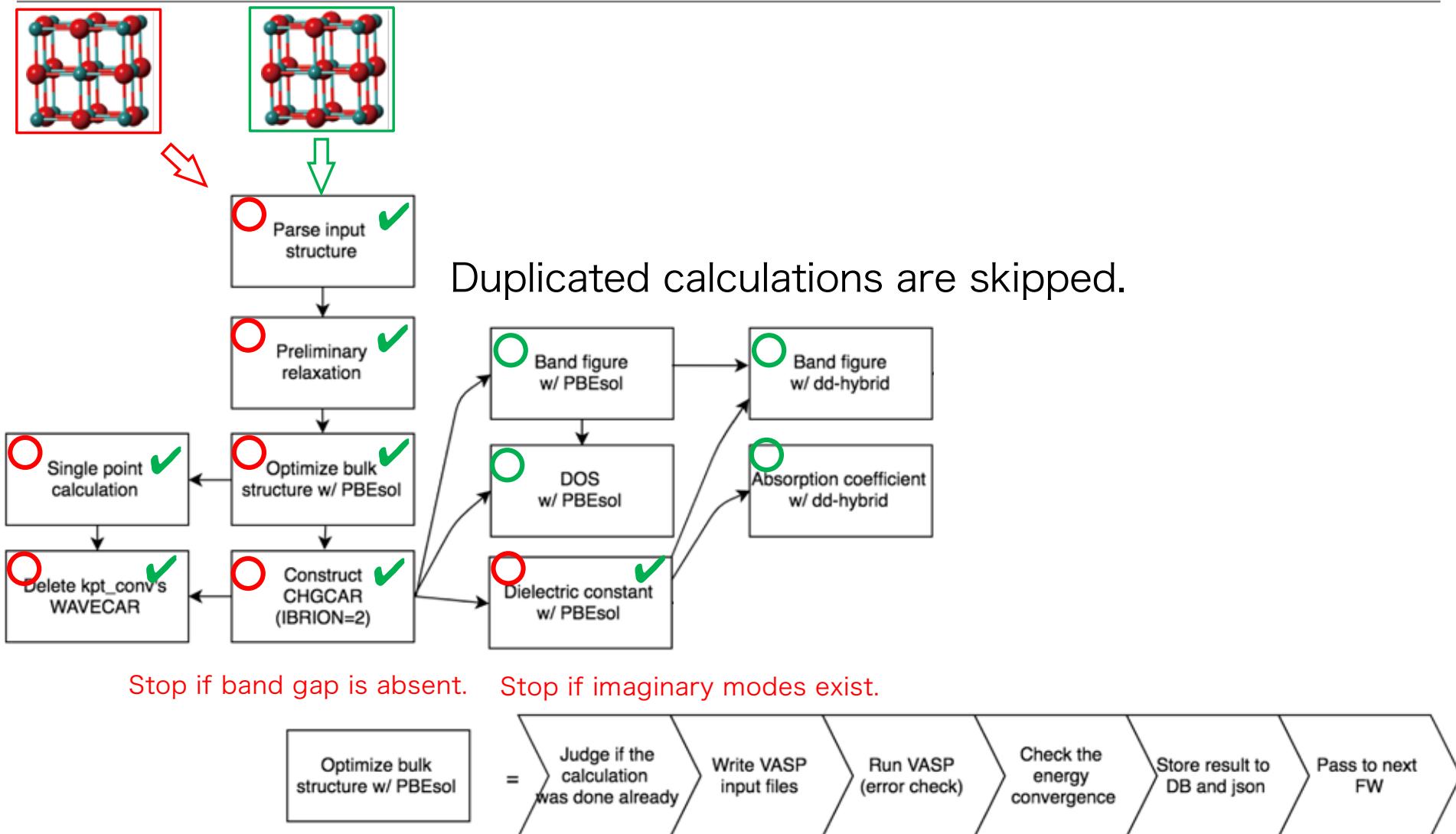
Workflow including point defect calculations



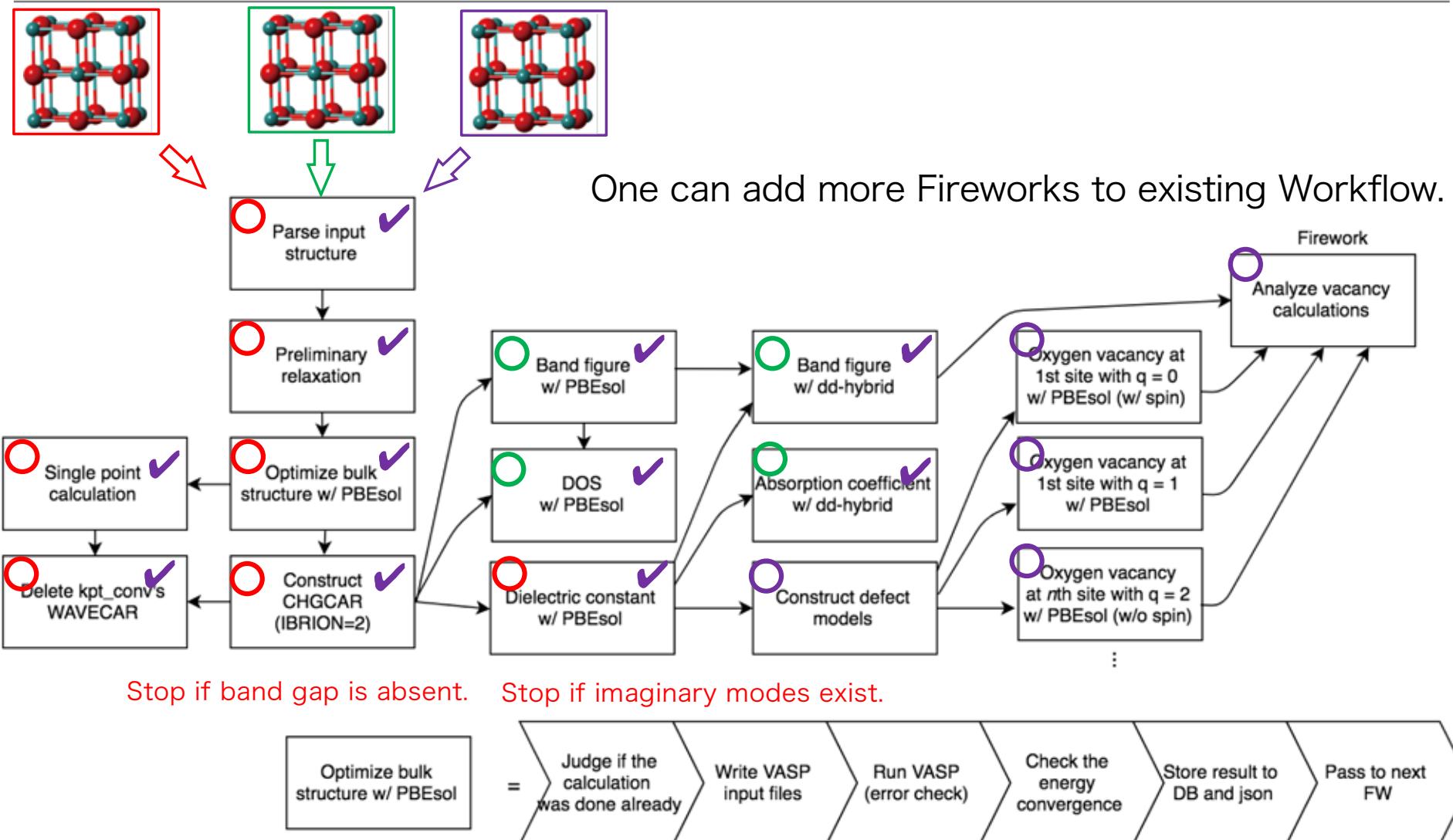
Optimize bulk structure w/ PBEsol



Automation system: simple workflow management



Automation system: simple workflow management



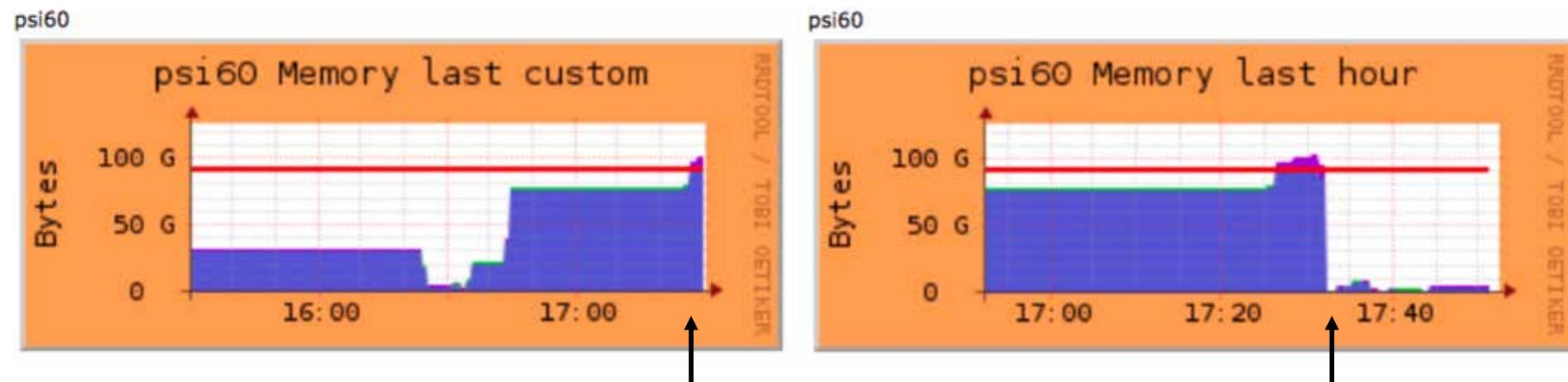
Easy to extend the Workflow.

Automation system: easy error handling

Ex1 : When atomic positions do not relax → tighten SCF convergence or add FFT grid

Ex2 : When wavefunctions do not converge
→ Reduce the mixing parameter of wavefunctions during SCF.

Ex3 : When memory is swapped, and the calculation is jammed

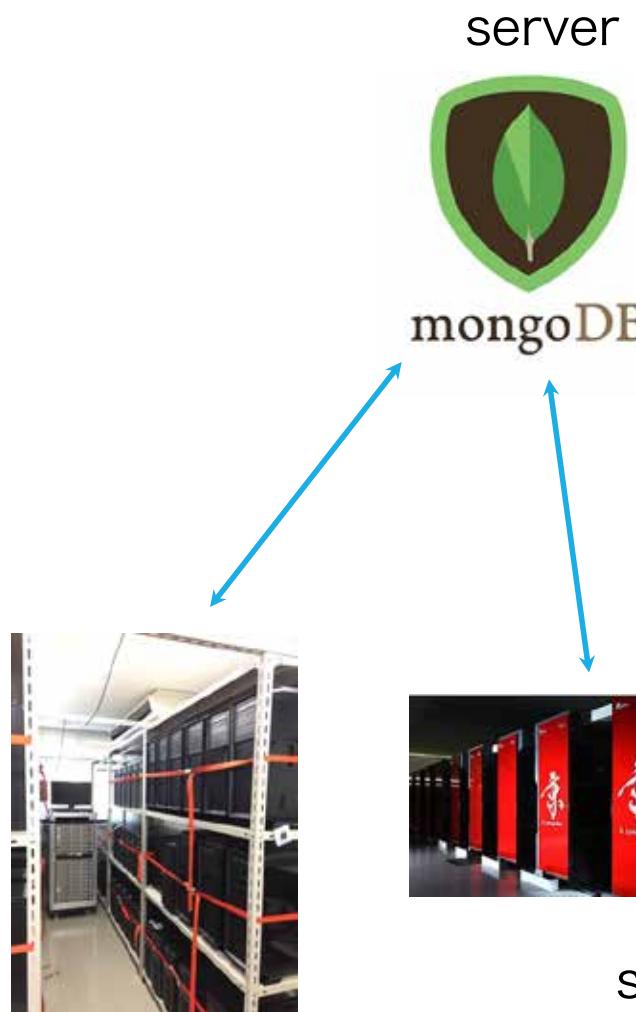


When memory usage is increased more than 95%, the calculation is killed within 5 min.

→ Run the same calculations with fat nodes

Automatic error handling reduces the human cost drastically.

Automation system: easy data management



NoSQL system: flexible data structure

```
_id: ObjectId("5c025ec635b878225cdb68db")
created_at: 2018-12-01 10:13:26.894
> _tasksbuilder: Object
> spacegroup: Object
> structure: Object
material_id: "m-1"
sg_symbol: "P2_1/m"
sg_number: 11
> mp_ids: Array
> icsd_ids: Array
formula_anonymous: "ABC3"
formula_pretty: "MgSb03"
formula_reduced_abc: "Mg1 03 Sb1"
> elements: Array
nelements: 3
chemsys: "Mg-O-Sb"
> bandstructure: Object
bandgap: 1.009399999999994
> thermo: Object
energy_per_atom: -5.8692697695
> calc_settings: Object
> descriptors: Object
> dielectric: Object
> bandgap_estimation: Object
```

easy query system

local clusters

Application to dielectric constants

Materials Project (Jain et al., 2013)

Oxide structures

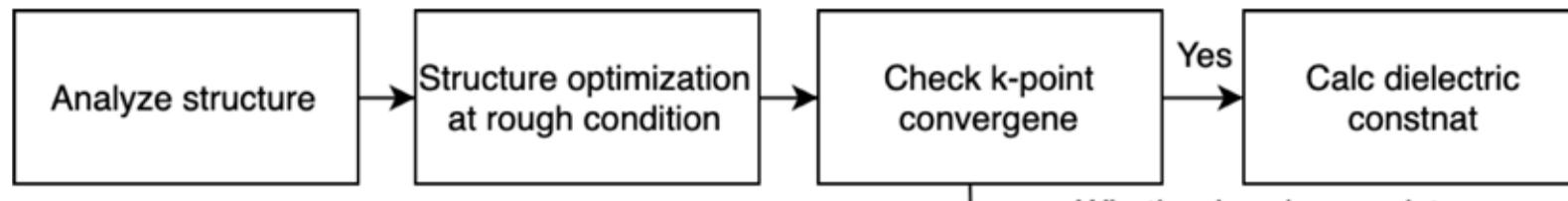
- Non-magnetic
- only oxygen as anions
- not P1 space group
- less than 40 atoms in the unitcell

✓ Dielectric constants of 4,572 oxides are calculated within 8 days

✓ Nearly zero human costs

Assuming 1min for handling 1 material,
76 hours are reduced!

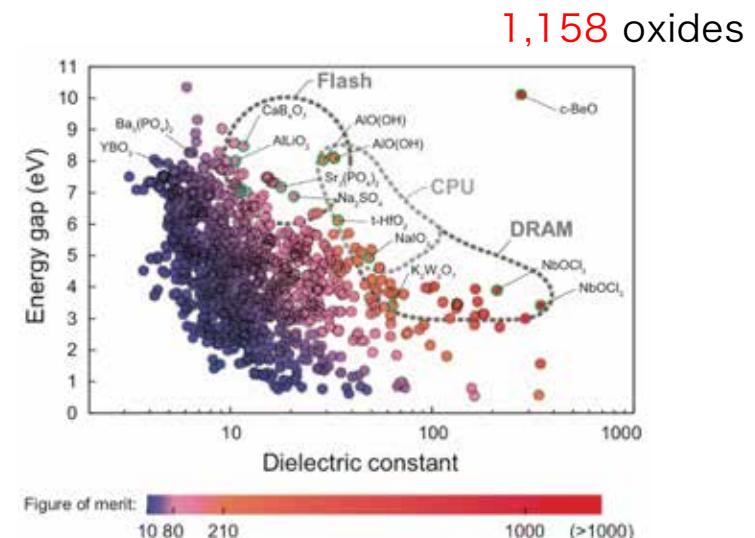
✓ Human errors are also almost zero



Data Descriptor: High-throughput screening of inorganic compounds for the discovery of novel dielectric and optical materials

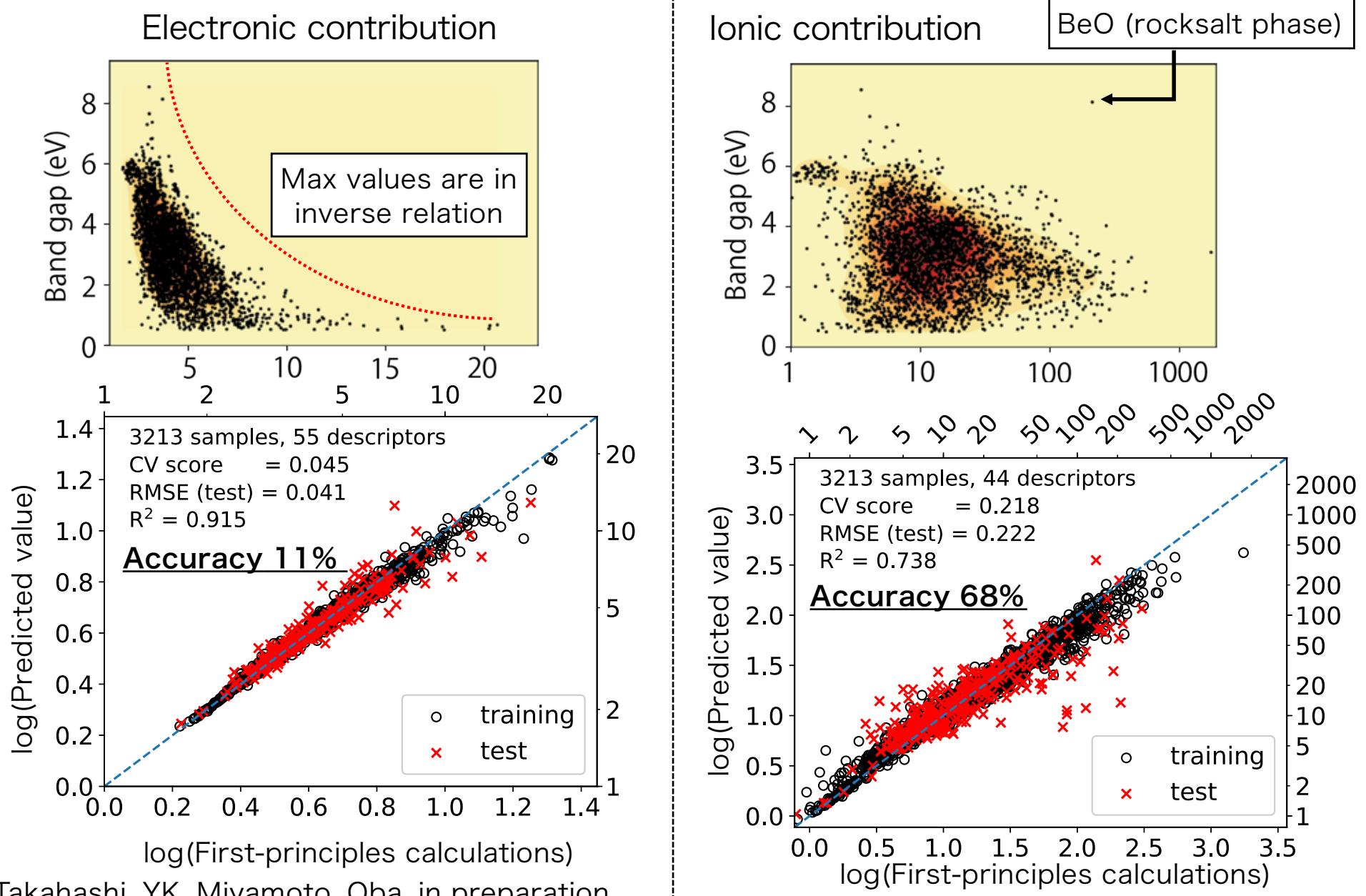
Petousis et al., Sci. Data 4, 160134 (2017)

the largest dielectric tensors database to date,
containing 1,056 compounds

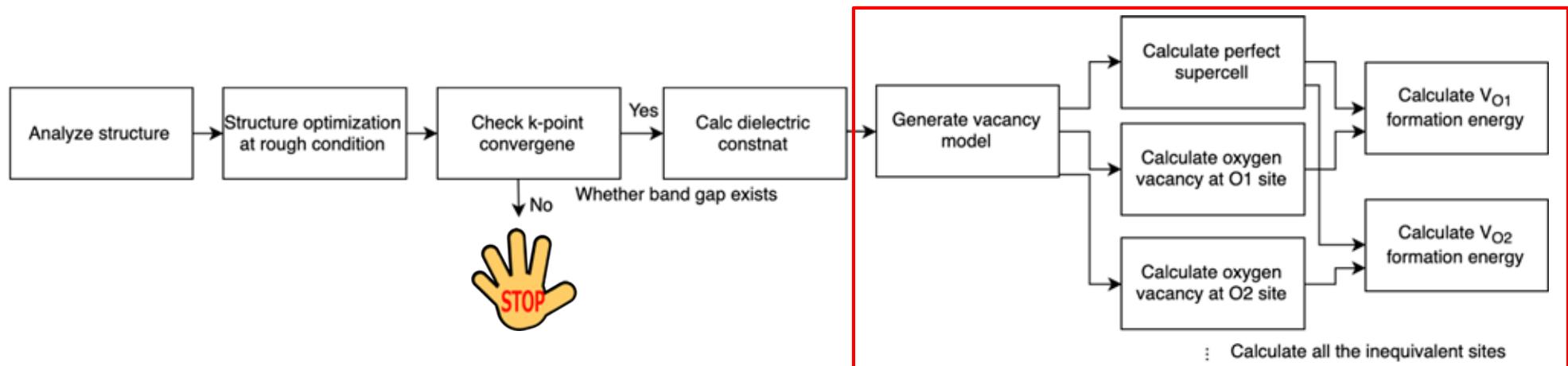


Yim et al., NPG Asia Mat. 7, e190 (2015)

Distribution and machine learning of dielectric constants

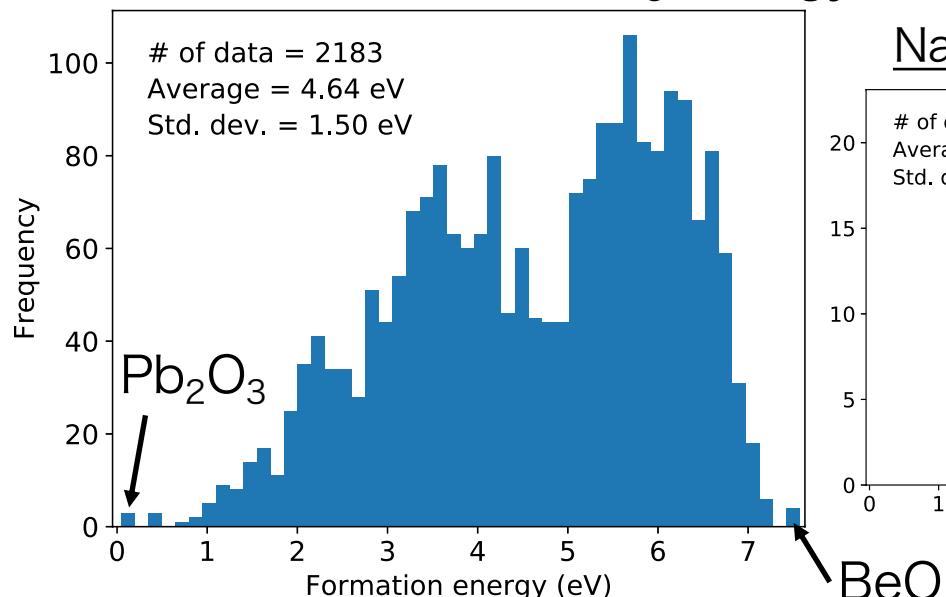


High-throughput oxygen vacancy calculations

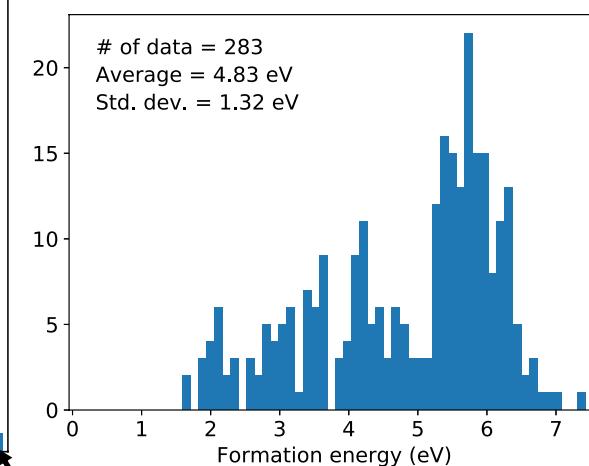


Add Fireworks to the Workflow

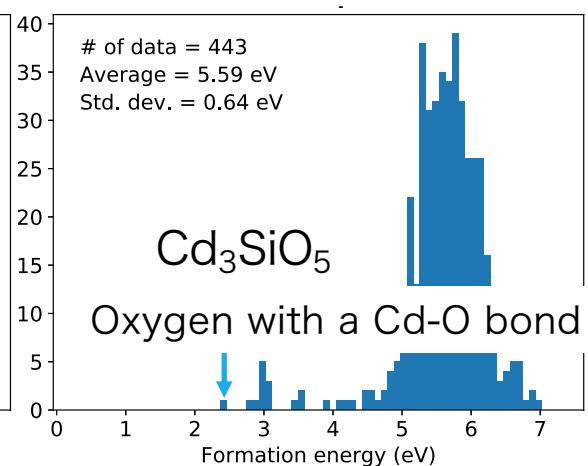
Distribution of neutral V_O energy



Na containing results

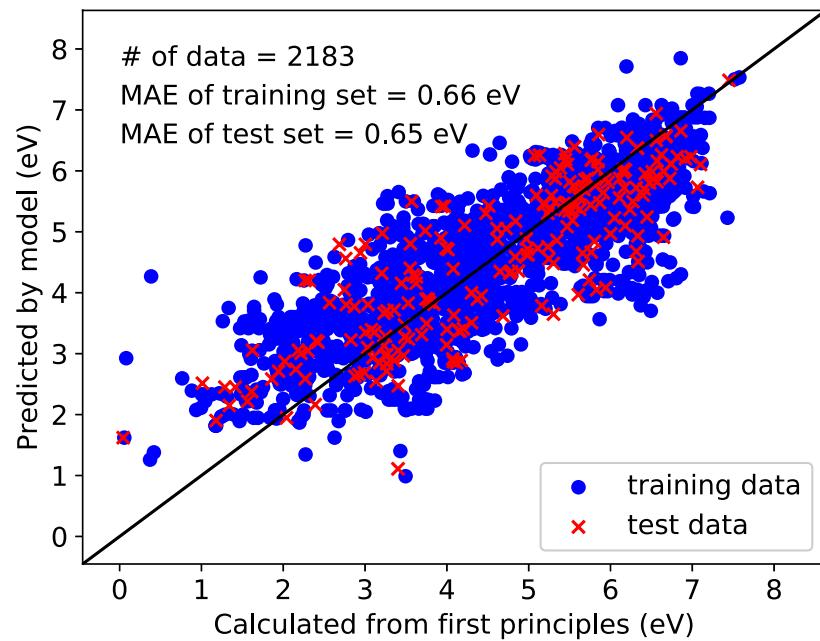


Si containing

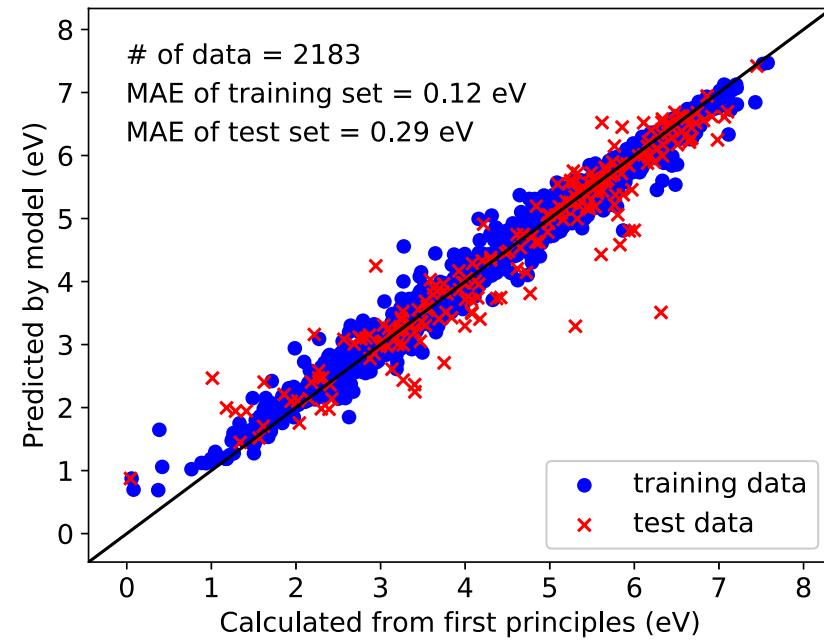


Machine learning of oxygen vacancy formation energies

Reproduce Deml's procedure

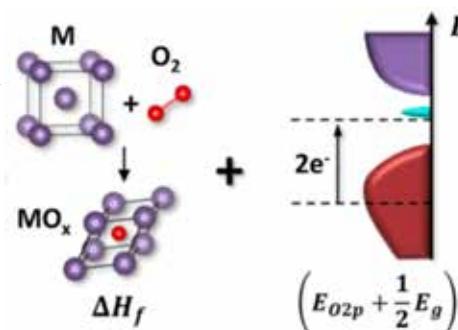


ML with Random forest



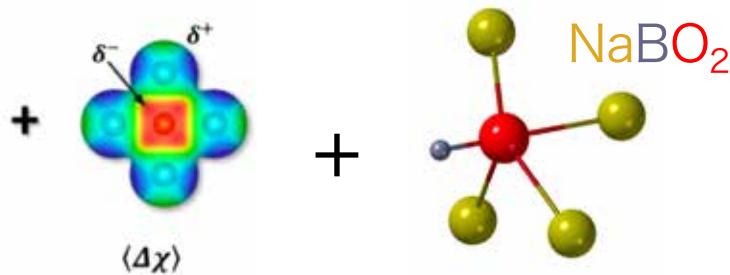
Descriptors

- oxide formation energy
- band gap
- center of O-2p band
- electronegativity



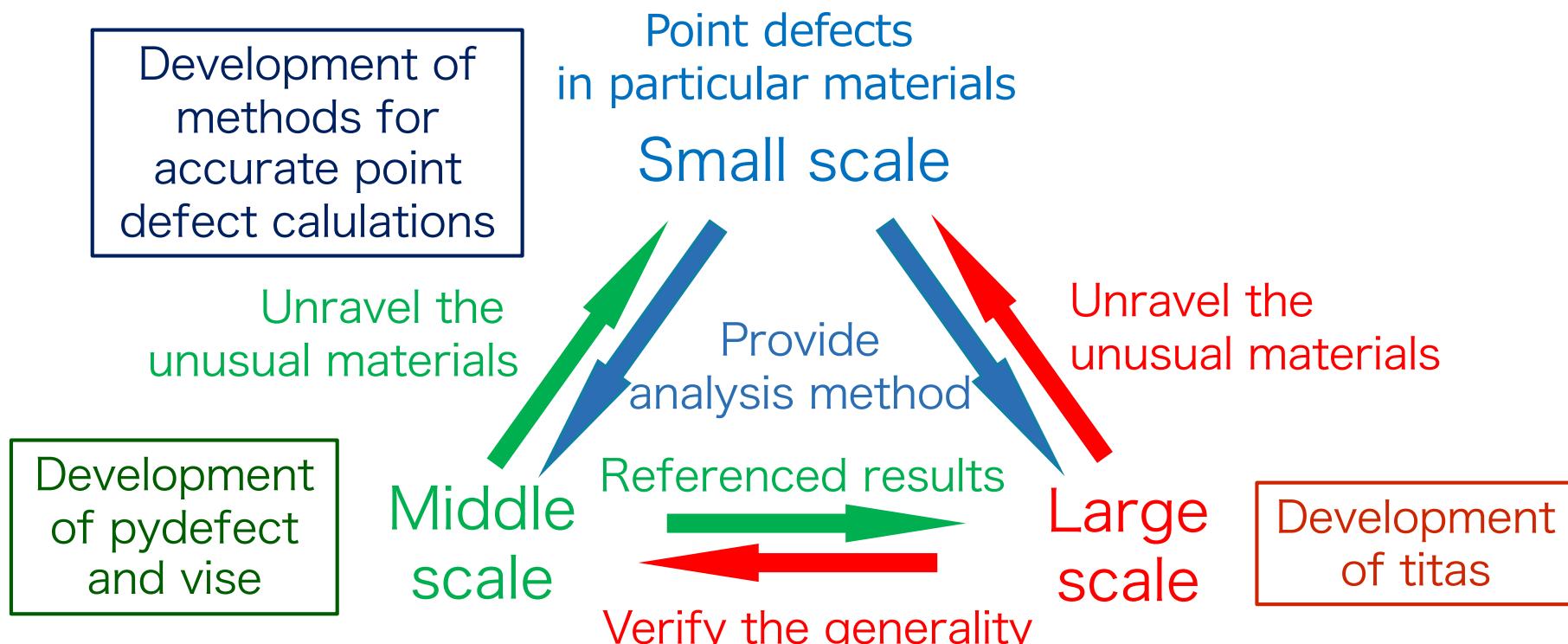
Deml et al., 2015

YK, Takahashi, Oba, in preparation



Coordination numbers to each element

Summary



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Oba/Kumagai group is seeking two posdocs and one research assistant professor.