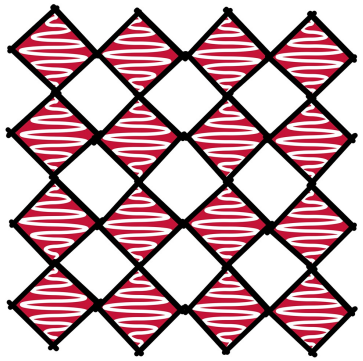
# Designing new materials using quantum chemistry and high-performance computing



**Dr Lucy Whalley**

Northumbria University, Newcastle upon Tyne, United Kingdom

Northumbria University NEWCASTLE

ReNU Renewable Energy Northeast Universities

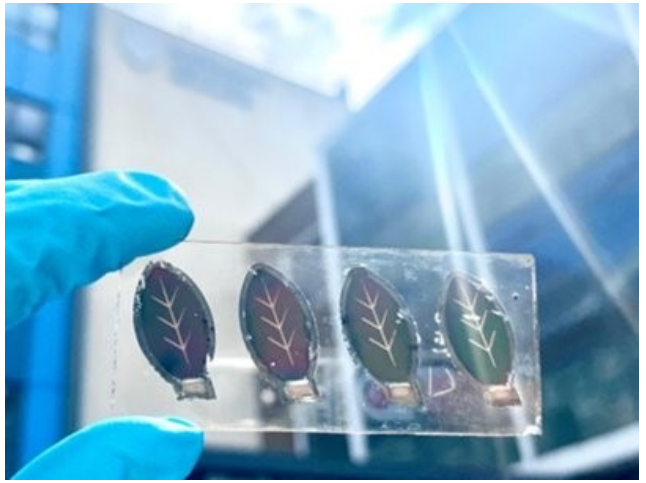
EPSRC Centre for Doctoral Training in Renewable Energy Northeast Universities

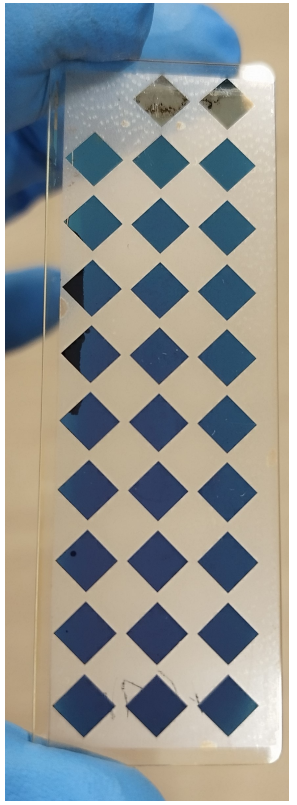
HEC MCC UK

Software Sustainability Institute

# Hello!! 👋

Northumbria University
NEWCASTLE





ReNU Renewable Energy Northeast Universities

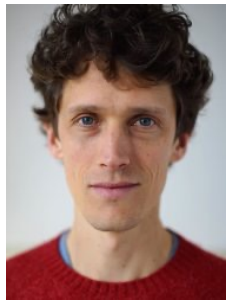
EPSRC Centre for Doctoral Training in Renewable Energy Northeast Universities

# Research Themes

**Computational materials science**:

solid state physics +
quantum chemistry +
high-performance-computing +

Prof. Aron Walsh, Imperial



Dr Jarvist Frost, Imperial

**Energy materials**:

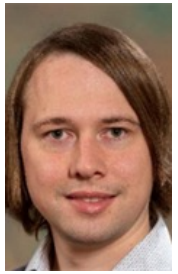
Photovoltaics: halide and chalcogenide perovskites
Battery applications

Prakriti Kayastha, Northumbria

Dr Giulia Longo, Northumbria

**Software sustainability** (*better software, better research*):

documentation +
testing +
maintenance +



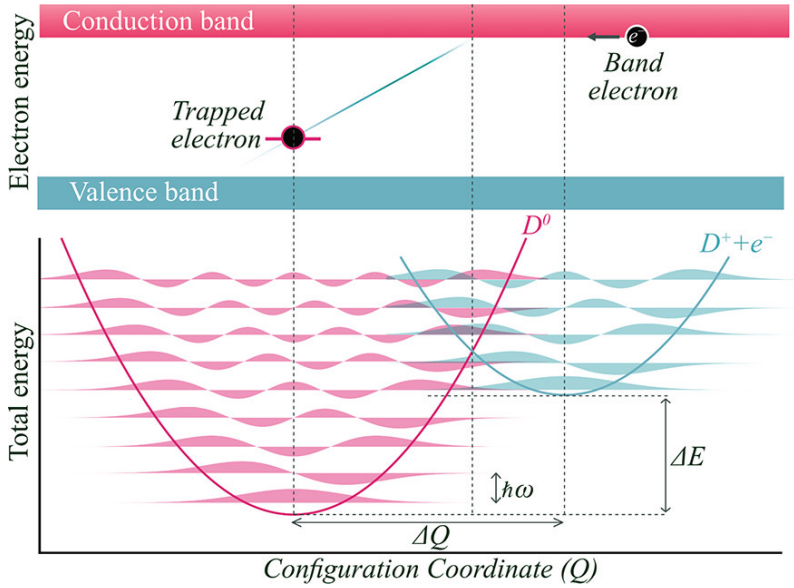
Dr. Adam Jackson, STFC

Software Sustainability Institute

# Outline

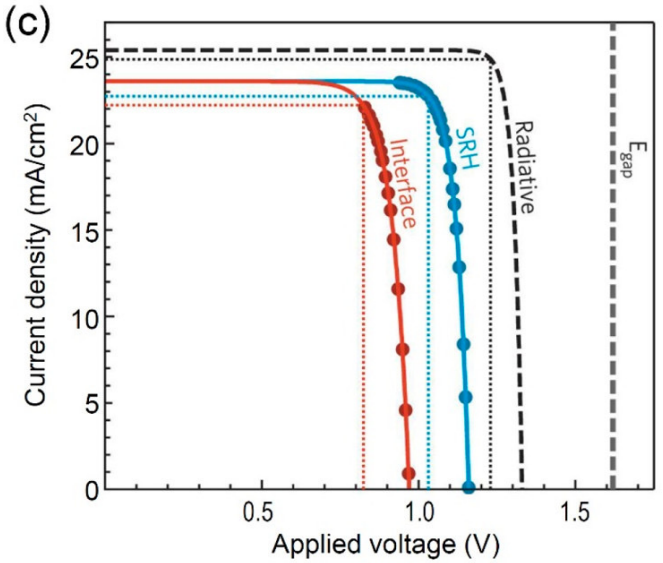
1) Introduction: Materials modelling
2) Background: Lead halide perovskites
   - Lattice anharmonicity
   - Defect physics
3) Results: Steric engineering of point defects in lead halide perovskites

# Modelling microscopic behaviour



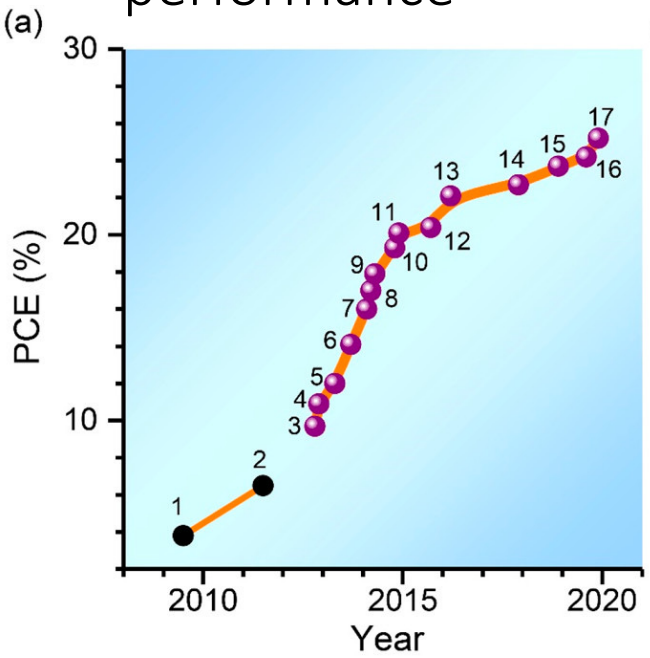

e.g. rate of electron capture

## Predicting experimental observables




e.g. Shockley-Reed-Hall model for open circuit voltage

## Optimising device performance




e.g. solar cell efficiency

# Materials Modelling: The Dream

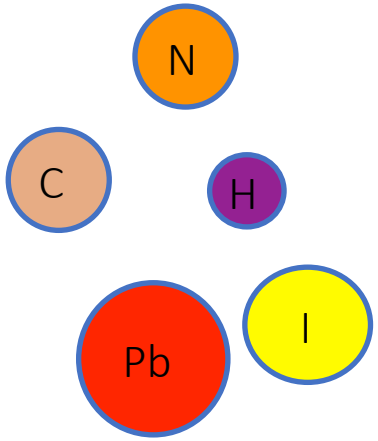
The Schrödinger Equation (1926)

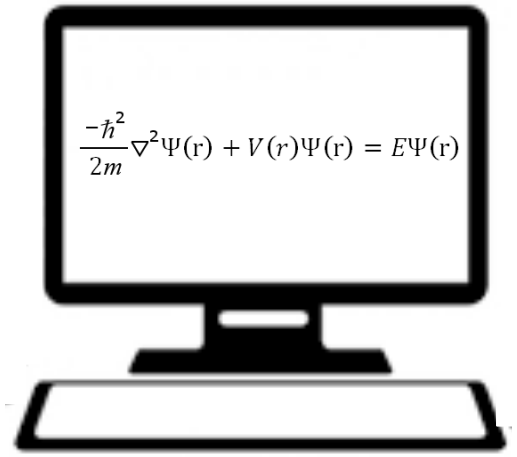
$$i\hbar\frac{\partial\psi}{\partial t}\psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r},t)\psi(\mathbf{r},t)$$

"The underlying physical laws necessary for a large part of physics and the whole of chemistry are thus completely known…."

Paul Dirac (1929)

# Materials Modelling: The Dream




Band gap

Bulk modulus

Electrical conductivity

Curie temperature

Thermal expansion

**Input Composition** → **Solve Schrödinger Equation** → **Output properties**

# Materials Modelling: The Harsh Reality

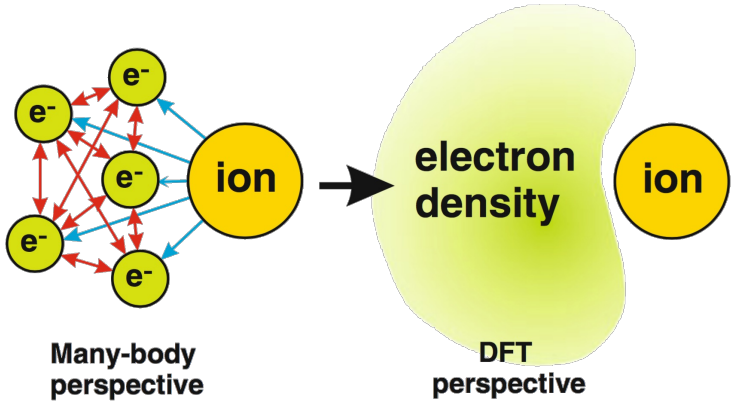
The Schrödinger equation cannot be solved exactly for systems of interest (3N dimensional equation)

"…the difficulty is only that the exact applications of these laws lead to equations much too complicated to be soluble."

10's picoseconds
1000's atoms

archer2

Quantum Chemistry to the rescue!
Density Functional Theory




From F. Bechstedt - *Many-body approach to electronic excitations* (2015)

# Materials Model tions

*Approximate model:* static lattice

*Real behaviour:* lattice distortions due to temperature

*Approximate model:* perfect defect-free lattice

*Real behaviour:* defect formation at finite temperature


eat flow, thermal
se transitions….

evice performance
mobility, carrier

# Materials Modelling: So what can we do?

"Theoretical materials science and technology has several levels, and also several roles. It provides a framework in which to organize empirical results. It can be used to scope a new field. It can be used to separate out the components of some complex system, where experiment alone still confuses. And one can imagine cases—especially for the shortest or the longest timescales—where theory can outreach experiment."

Marshall Stoneham
*Defects in semiconductors and oxides: where are the gaps in first principles theory?*

# Complex system: Lead halide perovskites

## ‘Revolutionary’ solar power cell innovations break key energy thr

**Next generation cells surpass limits of today’s cells and will accelerate rollout of cheaper, more efficient solar power**

INDEPENDENT PREMIUM

IN FOCUS

## Hundreds of years after it was discovered, one material is about to change the world

Rapid breakthroughs in recent months mean 2023 could be the year that perovskite’s potential is finally realised, bringing cheaper and more efficient ways of harvesting the Sun’s energy, writes **Anthony Cuthbertson**

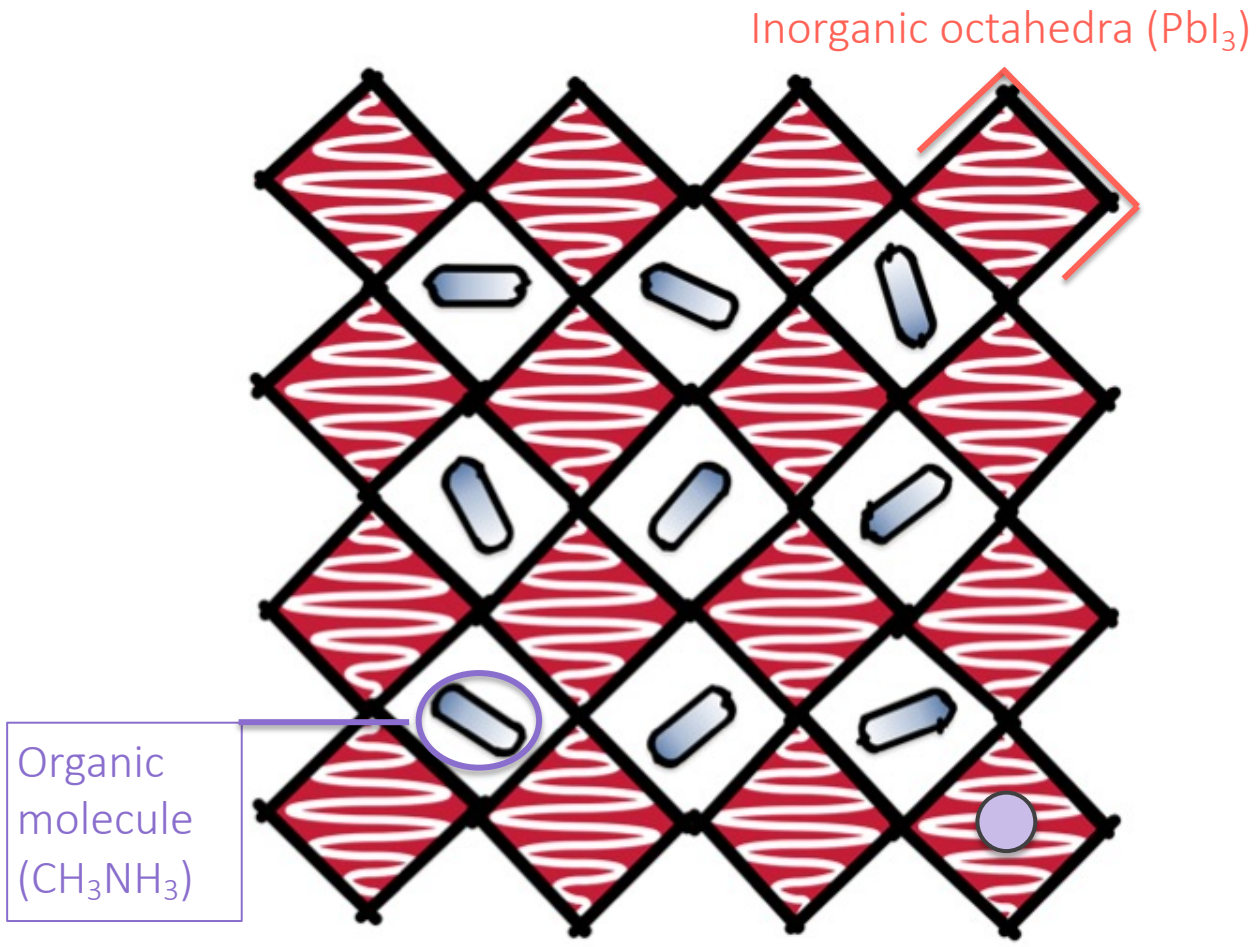
Wednesday 02 August 2023 17:26 • 4 Comments

The record-breaking solar cell converted 28.6% of the sun’s energy into electricity, as independently certified by Fraunhofer ISE. The cell was made by depositing a thin film of the material perovskite onto a conventional silicon solar cell. The combined ‘perovskite-on-silicon’ tandem solar cell achieves a conversion efficiency that is substantially higher than that of mainstream silicon-only solar cells, which average 22–24%.

# Lead halide perovskites, $APbX_3$

## A challenge for experimental characterisation and computational modelling

- Sensitive to light and oxygen
- Large anharmonic tilting
- High defect densities
- Self-healing
- Mobile ions
- Halide segregation
- Spin-orbit effects




Methylammonium lead iodide = "MAPI"

See for example: *J. Chem. Phys.* 146, 220901 (2017)

# Lead halide perovskites, $APbX_3$

## Large anharmonic tilting

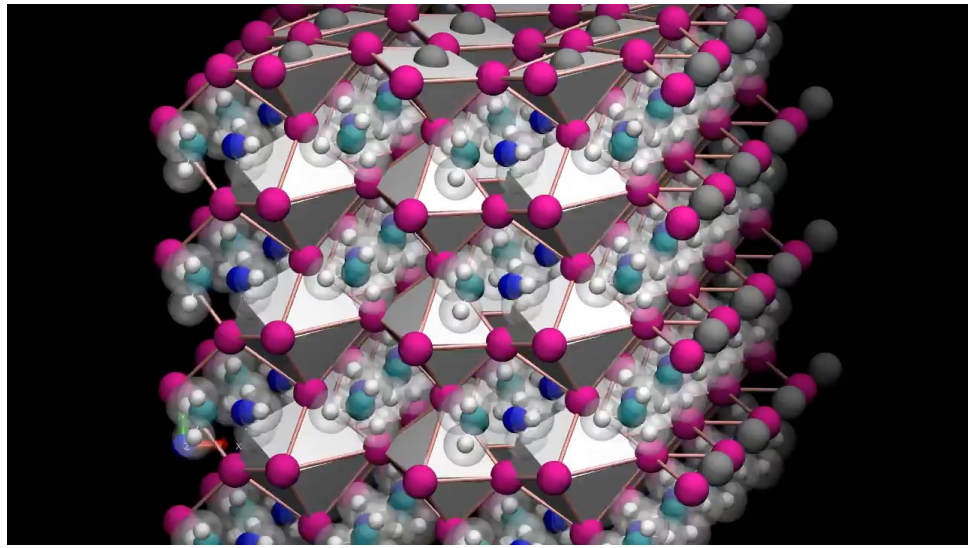
→ Band gap broadening (30meV at RT) Phys. Rev. B **94**, 220301 (2017)

→ Ultra-low thermal conductivity (0.05 $Wm^{-1}K^{-1}$) Phys. Rev. B **94**, 220301 (2017)

→ Slow cooling of hot polarons (100's ps) *ACS Energy Lett.* 2, 12, 2647–2652 (2017)

→ Coupled strongly to defect levels ($S_{HR}$ = 350) *J. Am. Chem. Soc.* 143, 24, 9123−9128 (2021)

A dynamically disordered, anharmonic pseudo-cubic phase above 330K



Video from Dr Jarvist Frost, Imperial College London
Youtube channel: JarvistMooreFrost

THE JOURNAL OF PHYSICAL CHEMISTRY C
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pubs.acs.org/JPCC

Article

# Steric Engineering of Point Defects in Lead Halide Perovskites

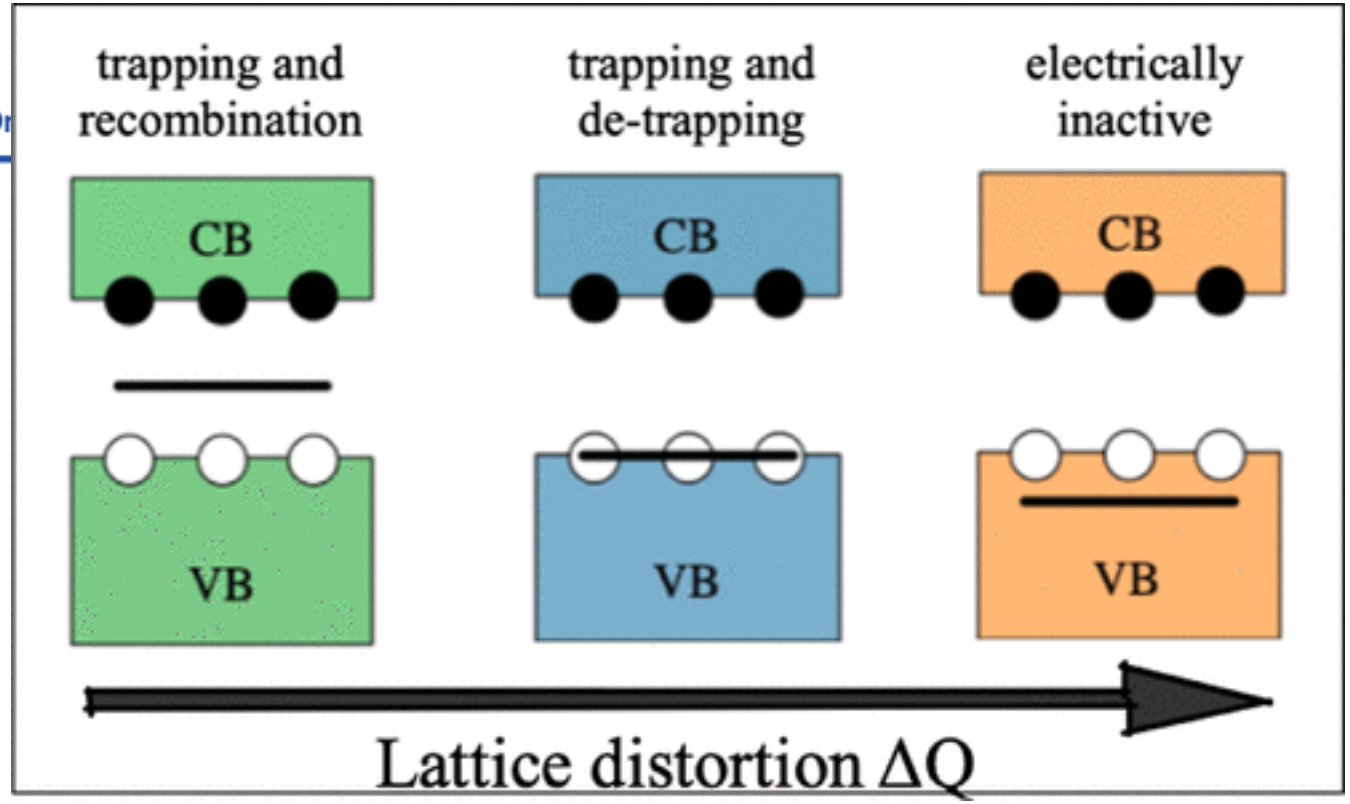
*Published as part of The Journal of Physical Chemistry C virtual special issue "The Physical Chemistry of Perovskites".*

Lucy D. Whalley*

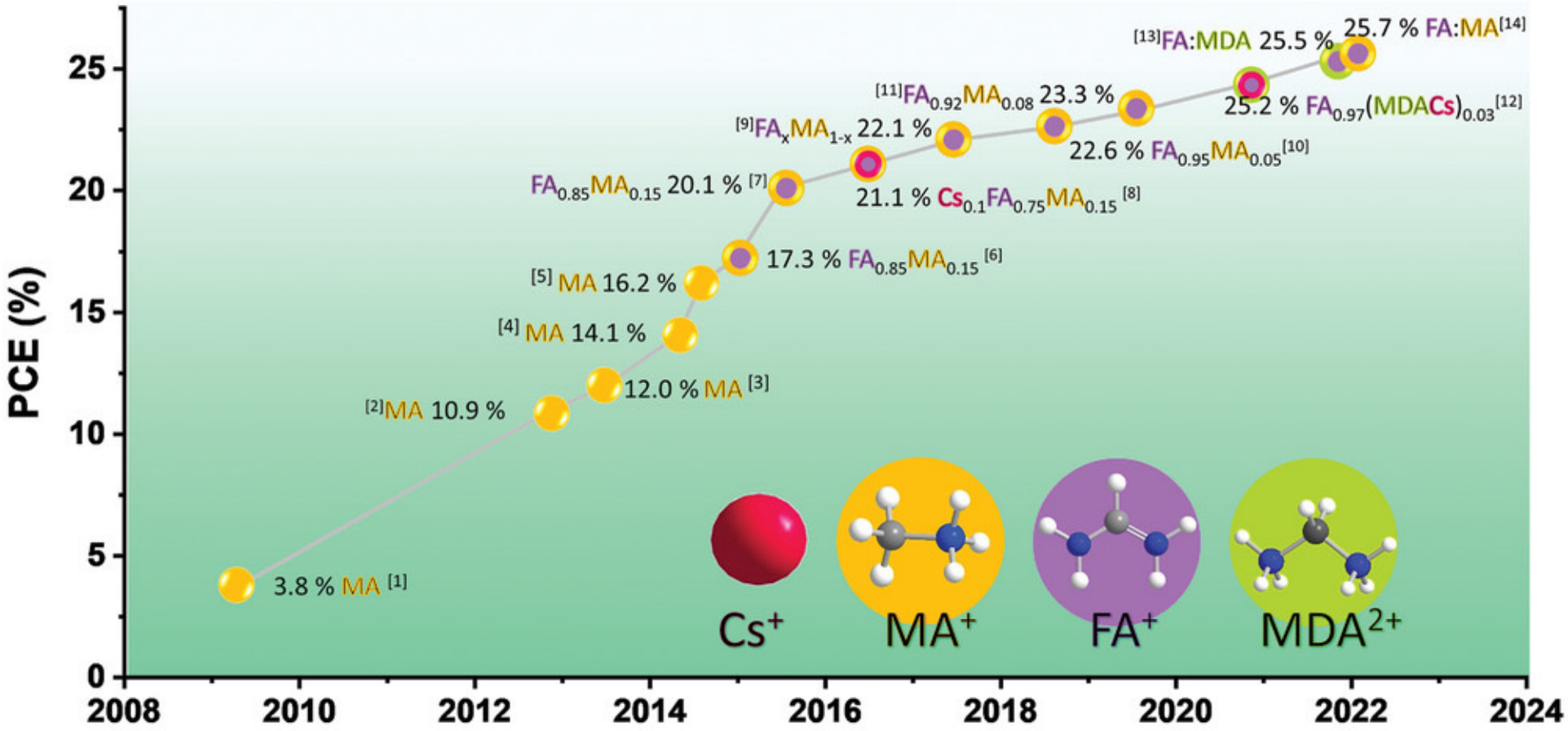
Cite This: *J. Phys. Chem. C* 2023, 127, 15738–15746

Read On

How can we *exploit* lattice anharmonicity in hybrid perovskites?



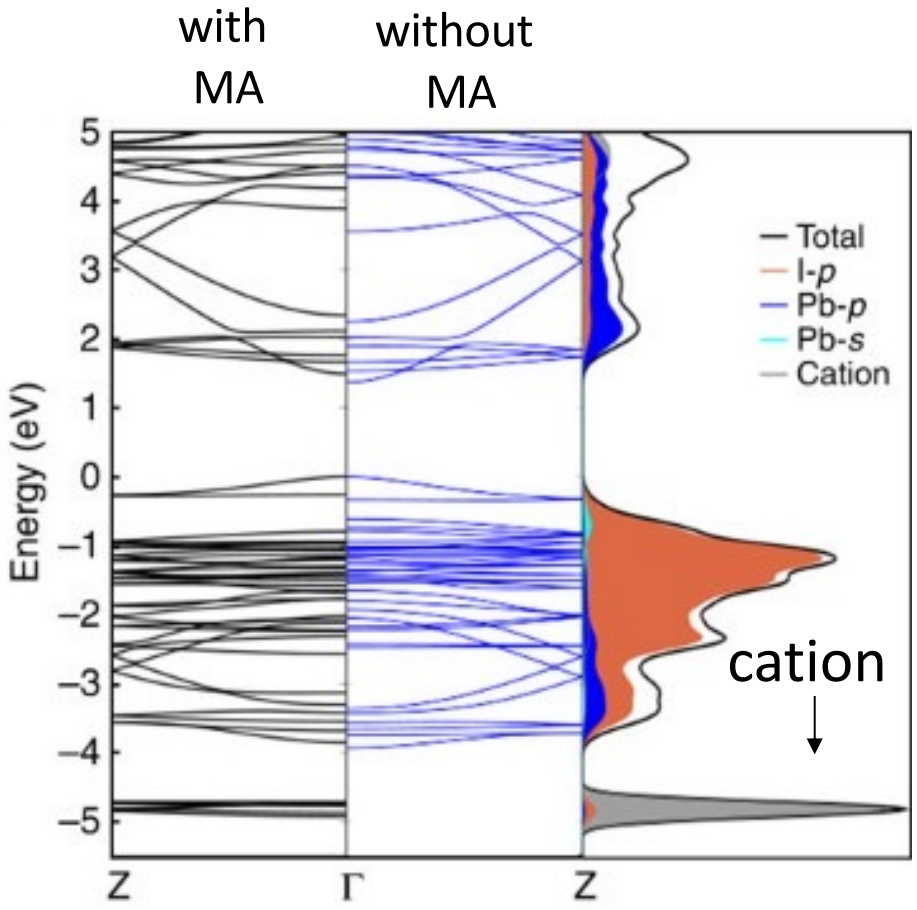
# The most stable and efficient $ABX_3$ perovskite solar cells employ mixed A-site cations




Byranvand *et al., Adv. Optical Mater.* 2022, 10, 2200423

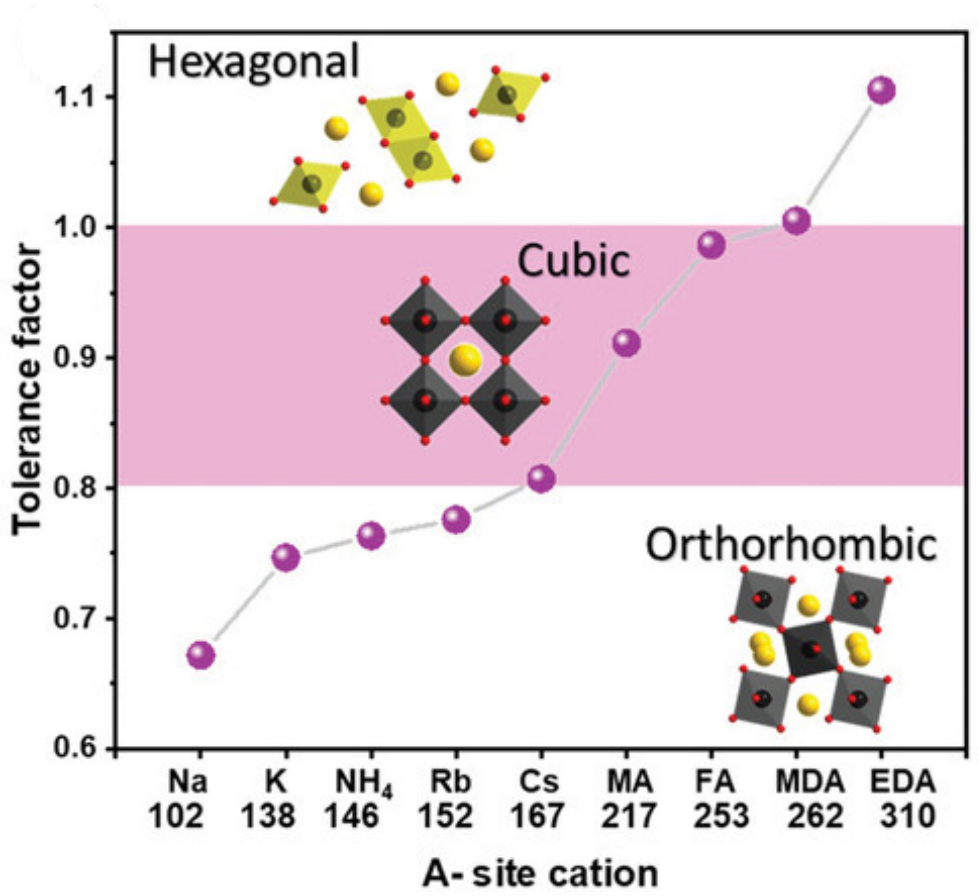
# The A-site cation in $ABX_3$ *indirectly* affects the electronic structure at band edge

Fixed perovskite structure ($PbI_3$)




Filip et al., *Nat. Commun.* 2014, **5**, 5757

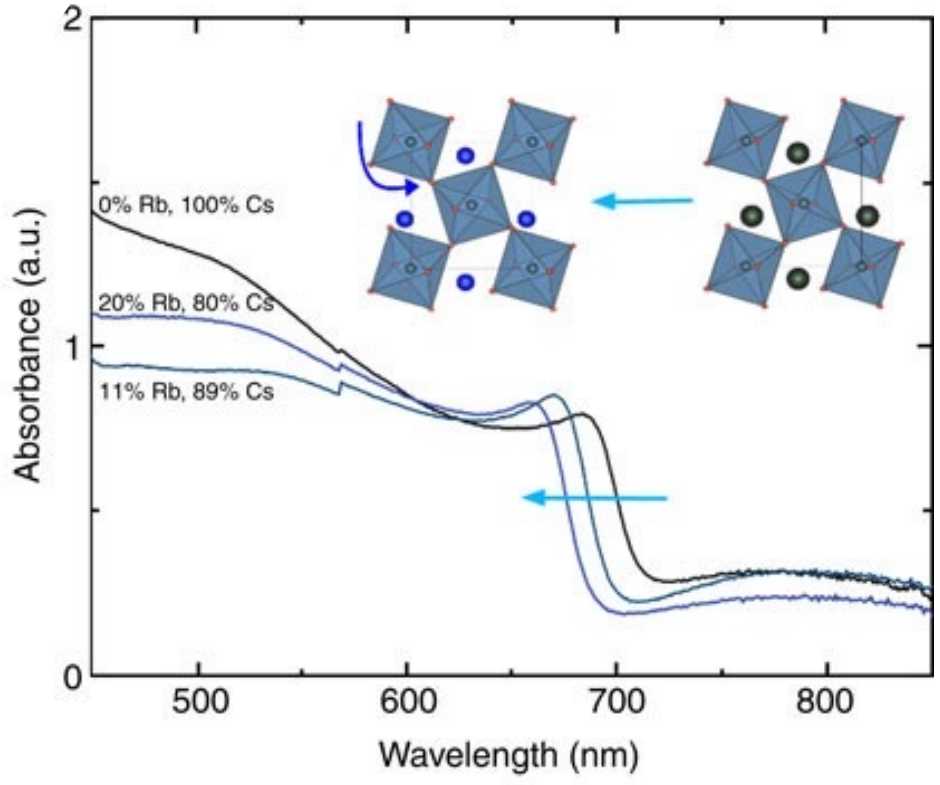
$$T = \frac{R_A + R_X}{\sqrt{2}\,(R_B + R_X)}$$




Byranvand *et al., Adv. Optical Mater.* 2022, **10**, 2200423

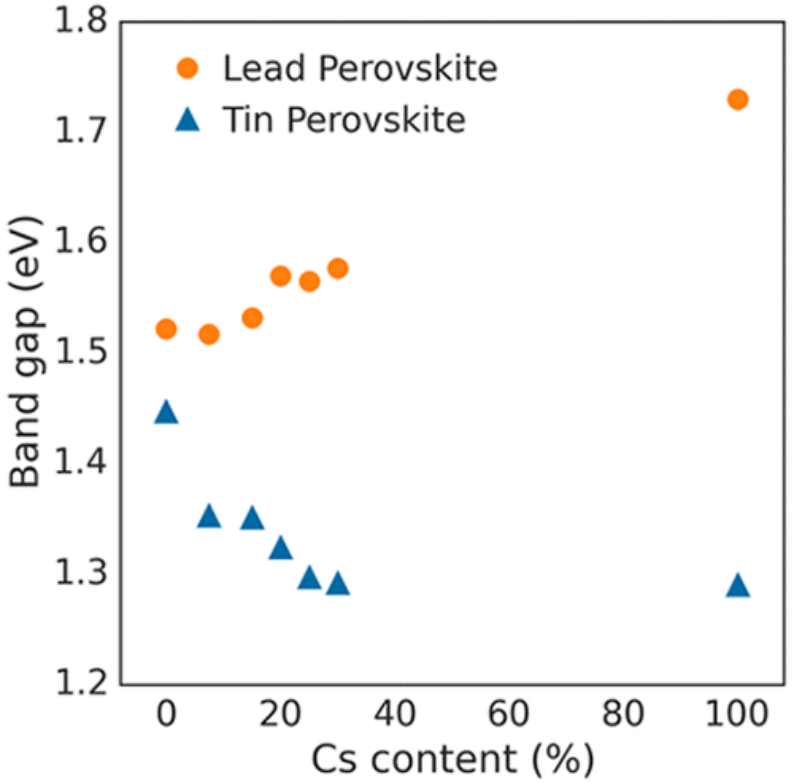
# Steric engineering: tuning the electronic band gap via A-site cation size

Band gap shift with Rb:Cs ratio




Filip et al., *Nat. Commun.* 2014, **5**, 5757

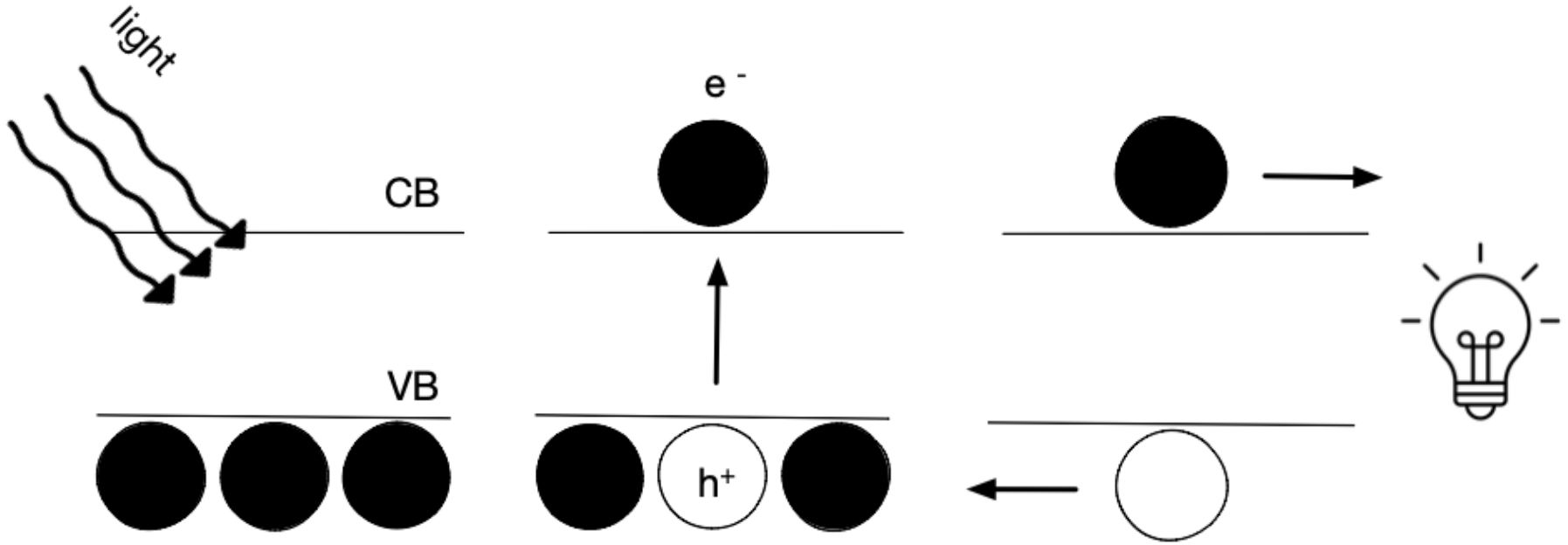
$FA_{1-x}Cs_xMI_3$




Prasanna et al., *J. Am. Chem. Soc.* 2017, 139, 32

Can we use steric engineering to determine defect activity?

In a perfect crystal….



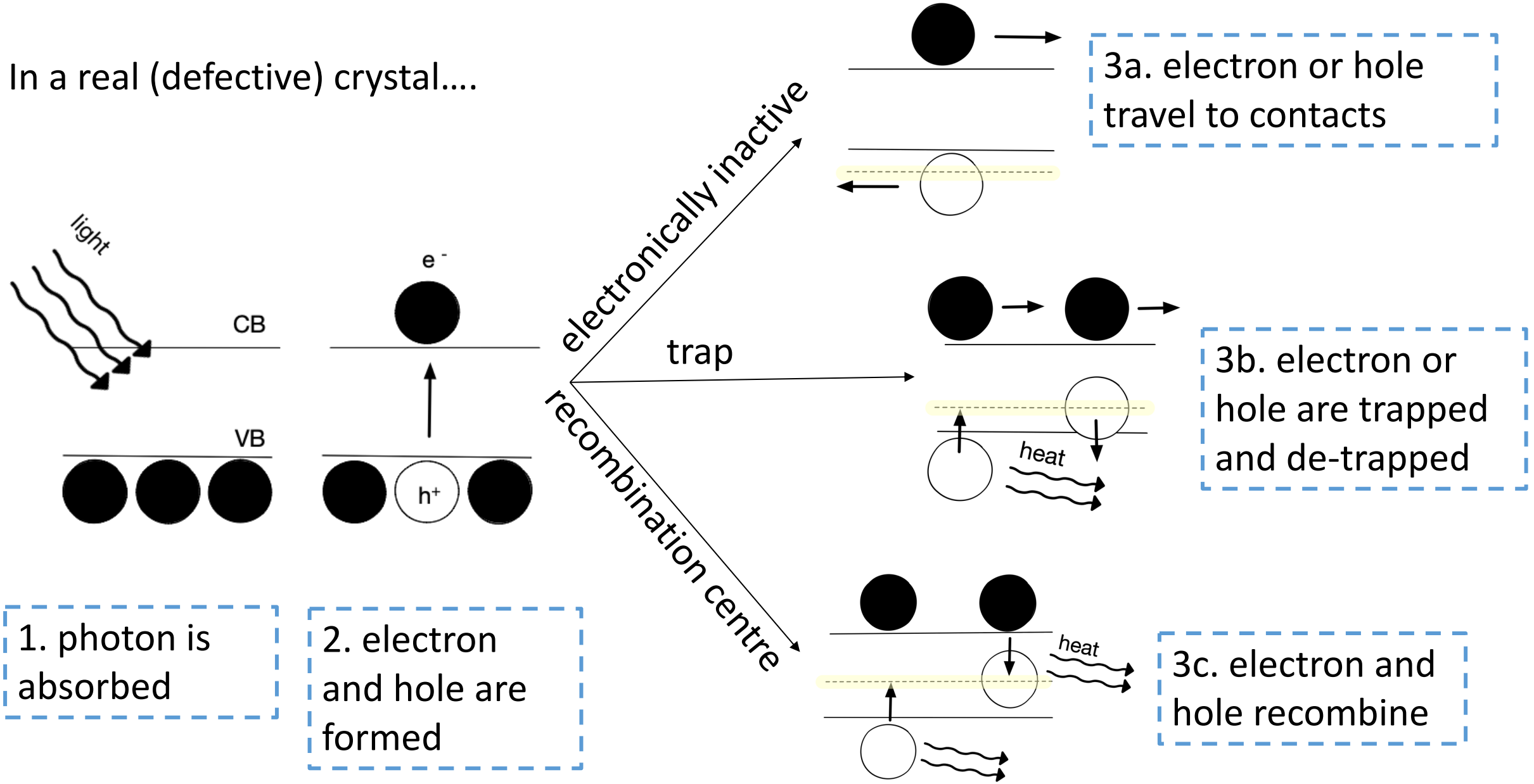

1. photon is absorbed

2. electron and hole are formed

3. electron and hole travel to contacts

# Non-radiative processes reduce photovoltaic performance

In a real (defective) crystal….




1. photon is absorbed

2. electron and hole are formed

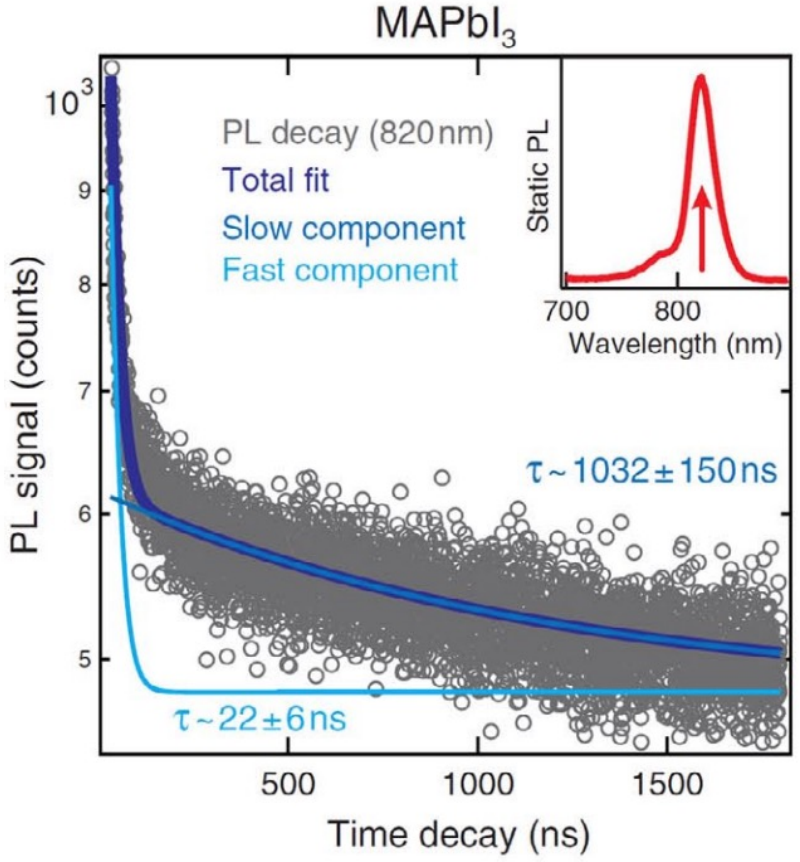
3a. electron or hole travel to contacts

3b. electron or hole are trapped and de-trapped

3c. electron and hole recombine

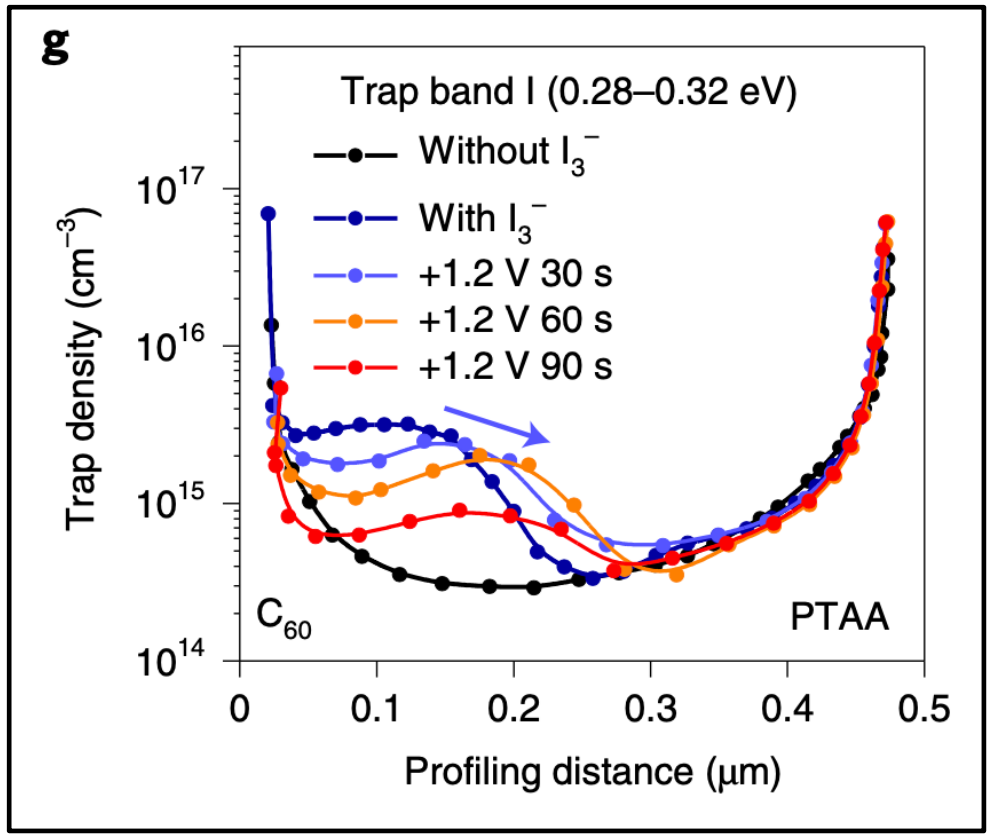
# Experimental measurements of defect activity in $ABX_3$ (X=halide)

Single crystals have a very low density of trap states (<$10^{12}$ $cm^{-3}$)




Shi et al., *Science.* 2015, 347, 6221, 519-522
Siekmann et al., *ACS Energy Lett.* 2021, 6, 3244−3251

Trap states are associated with the iodine interstitial at grain boundaries

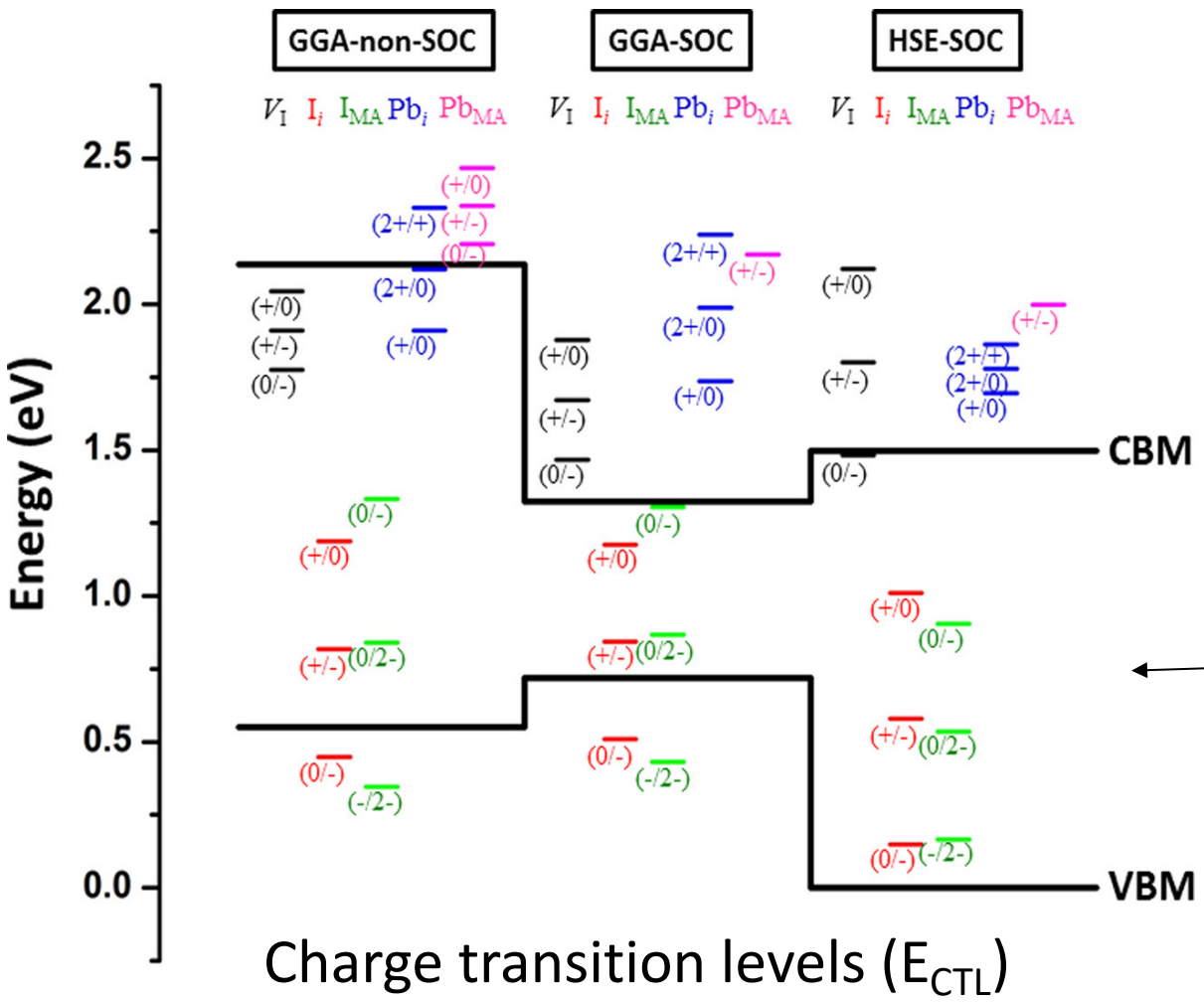



Thermal admittance spectroscopy + capacitance-voltage

Ni et al., *Nat Energy* **7**, 65–73 (2022).

# Theory predicts halide ions are active and mobile

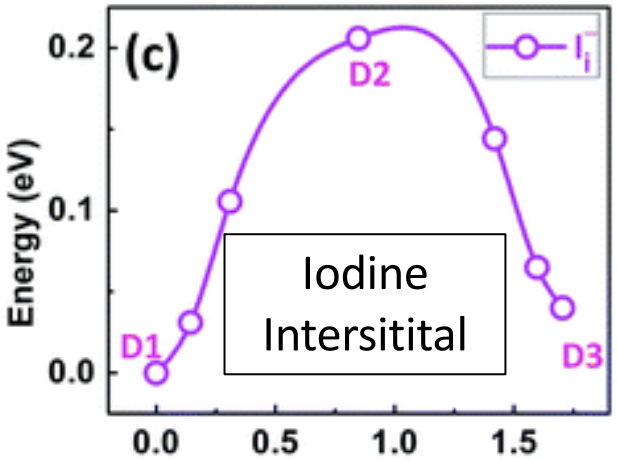
Increasing level of theory




Charge transition levels ($E_{CTL}$)

Du, *J. Phys. Chem. Lett.* 2015, 6, 8, 1461–1466

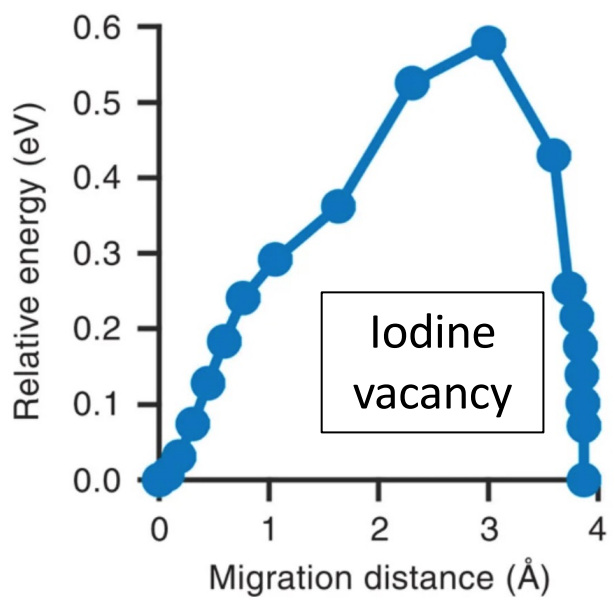
Yang et al., *J. Mater. Chem. A*, 2016, 4, 13105-13112



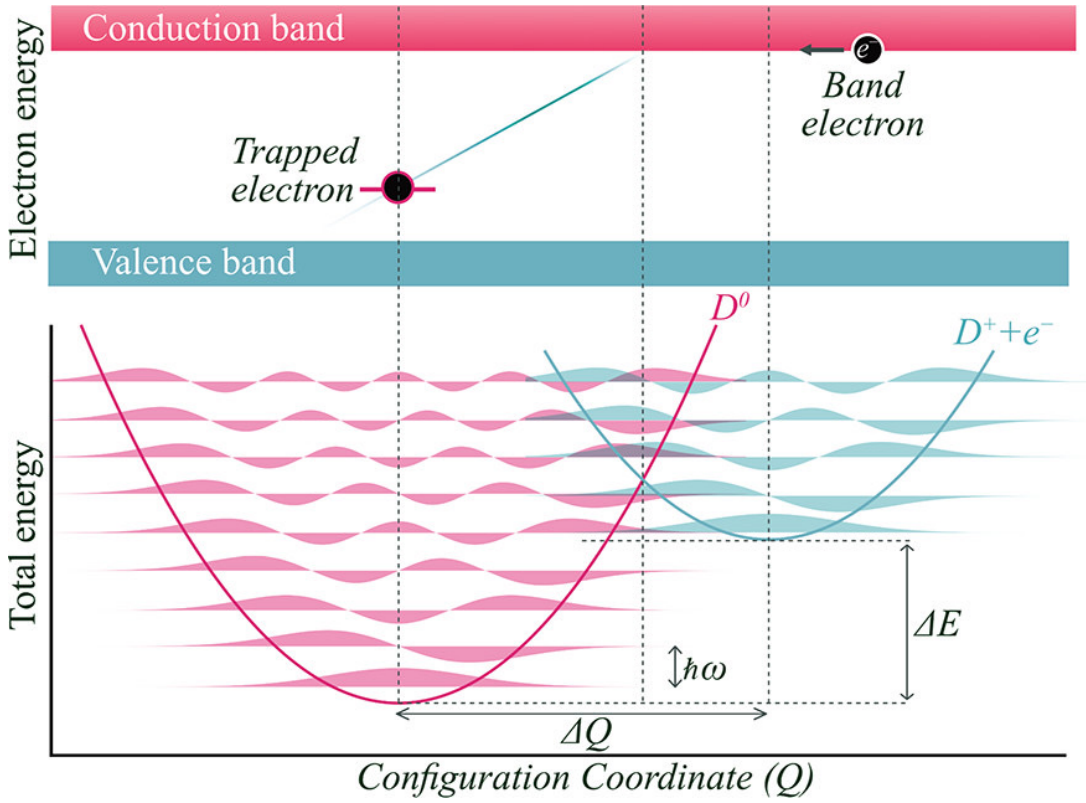

Single cation $CH_3NH_3PbI_3$

Ionic migration activation energies

Eames et al., *Nat. Commun.*, 2015, 6, 7497



# A configuration coordinate diagram is used to describe the change in energy and geometry after carrier capture




capture rate = C x trap density x carrier density

**Semi-classical picture**

Three key quantities which determine capture rate:

$\Delta Q$, $\Delta E$ (=$E_{CTL}$), $\hbar\omega$

More generally, PES curvature

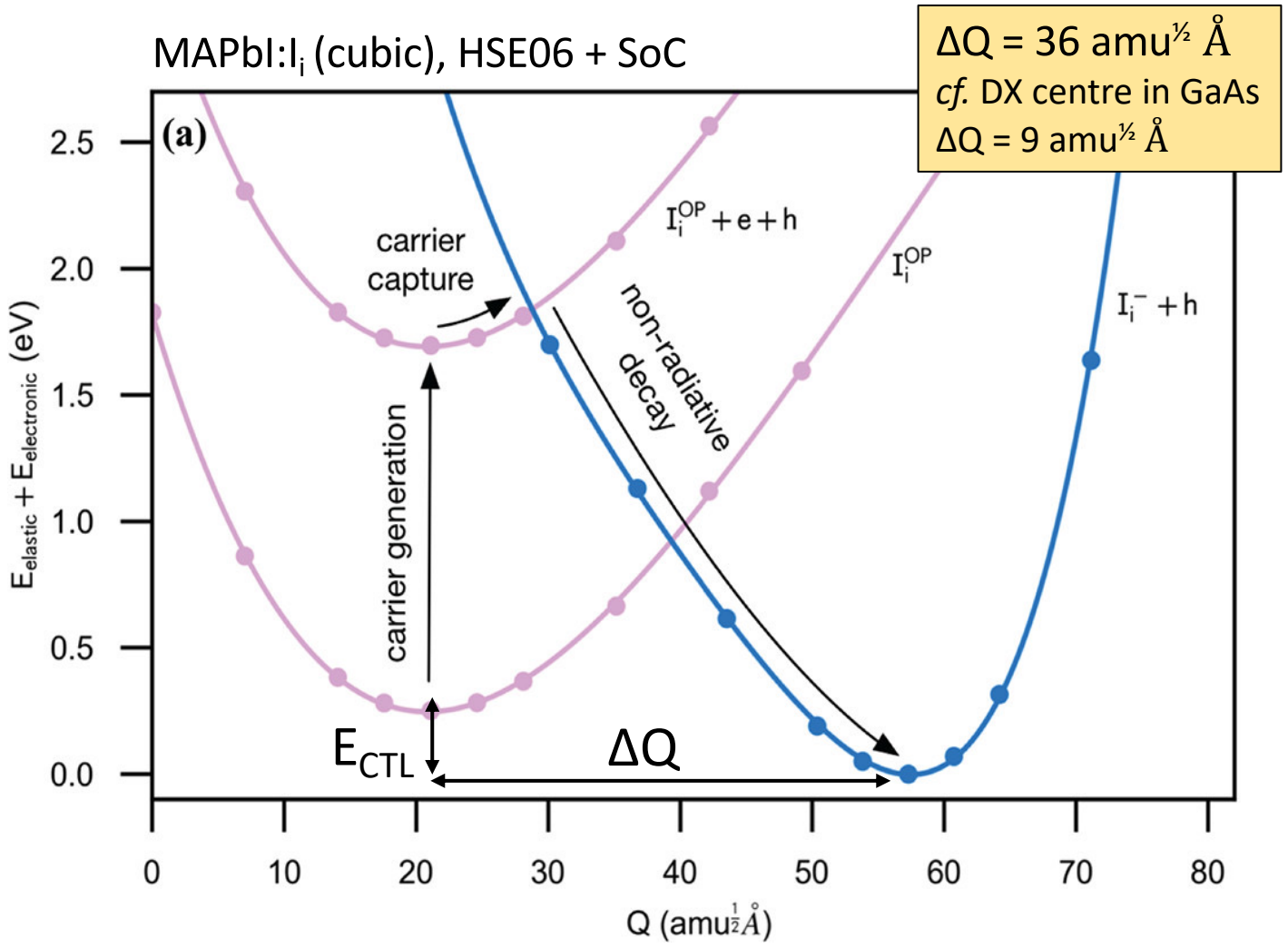
Fermi's golden rule is used to give a quantum mechanical prediction of carrier capture coefficient *C*

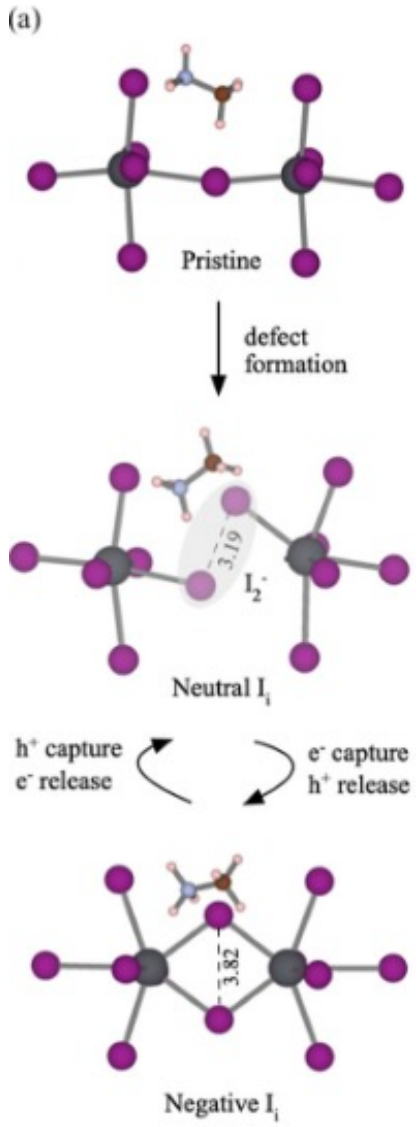
$$C = V\frac{2\pi}{\hbar}gW_{\mathrm{if}}^2\sum_m \Theta_m \sum_n |\langle\chi_{im}|\Delta Q|\chi_{fn}\rangle|^2$$

$$\times\, \delta(\Delta E + m\hbar\omega_{\mathrm{i}} - n\hbar\omega_{\mathrm{f}})$$

Alkauskas et al., Phys. Rev. B **90**, 075202 (2014)

# An easily distorted (‘soft’) perovskite lattice leads to large lattice relaxation after carrier capture

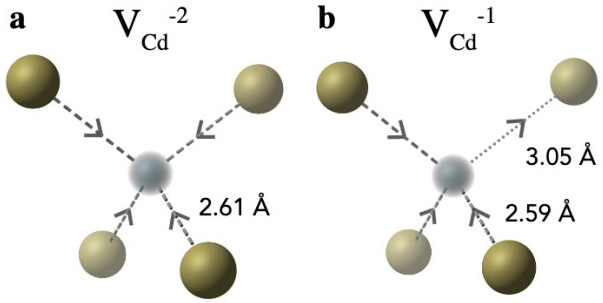


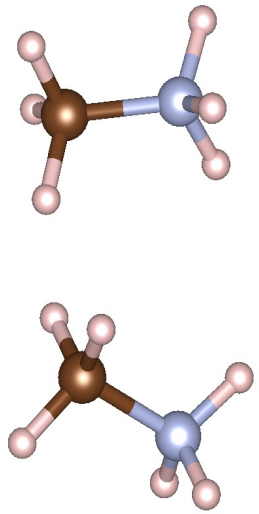

Whalley et al., *J. Am. Chem. Soc.* 2021, 143, 9123−9128

# How best to describe distortions in a hybrid material?

**Inorganic materials**
Lattice relaxation corresponds to translational motion




**Hybrid materials**
Lattice relaxation corresponds to rotational motion of molecule



Molecular rotations after carrier capture

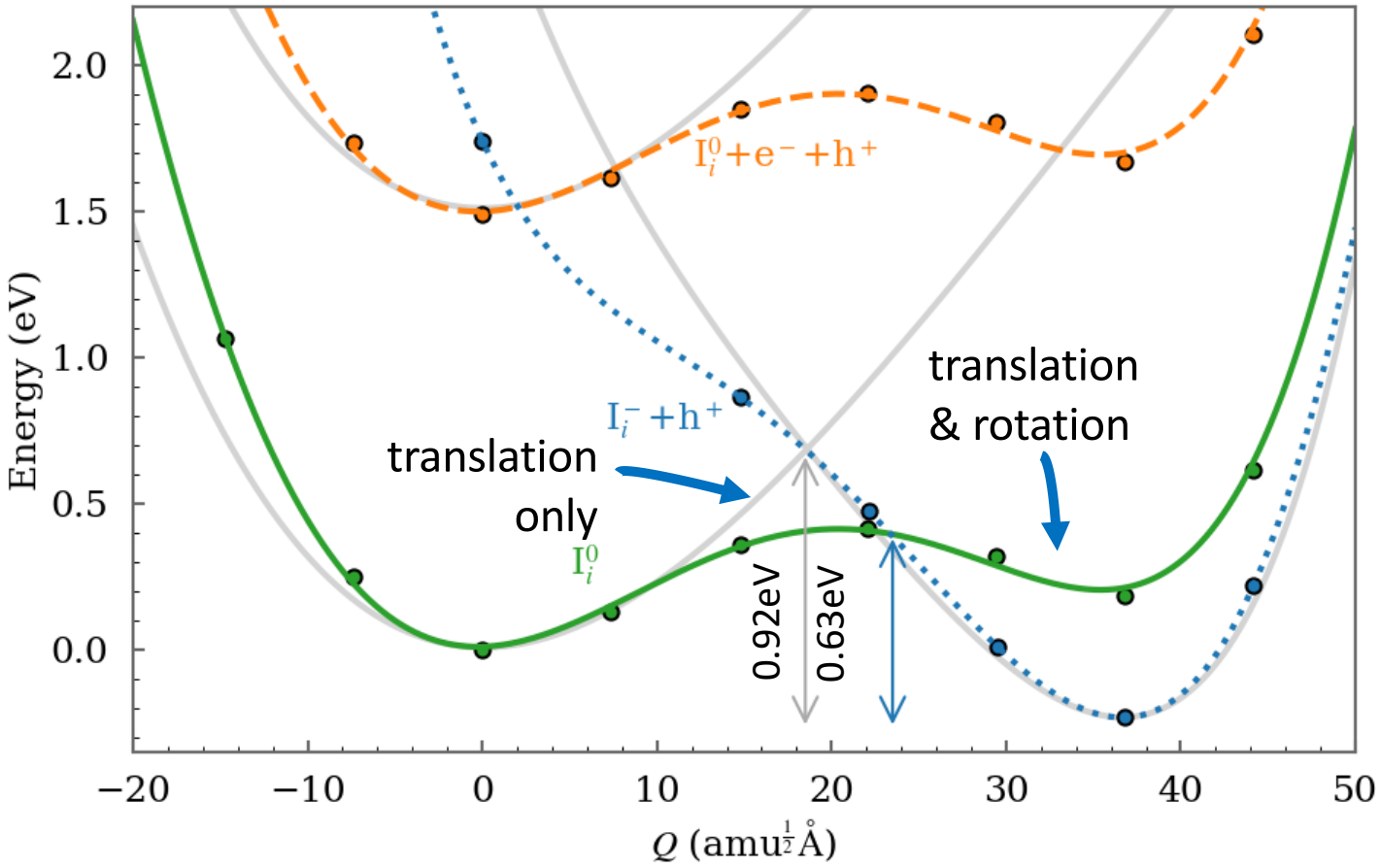
**Solution:** Kabsch interpolation to describe translational and rotational motion

$$L(C) = \frac{1}{2}\sum_{i=1}^{n} w_i \left\| \mathbf{a}_i - C\mathbf{b}_i \right\|^2,$$

**a** and **b** are the vector components. Minimise *L(C)* to solve for rotation matrix *C*.

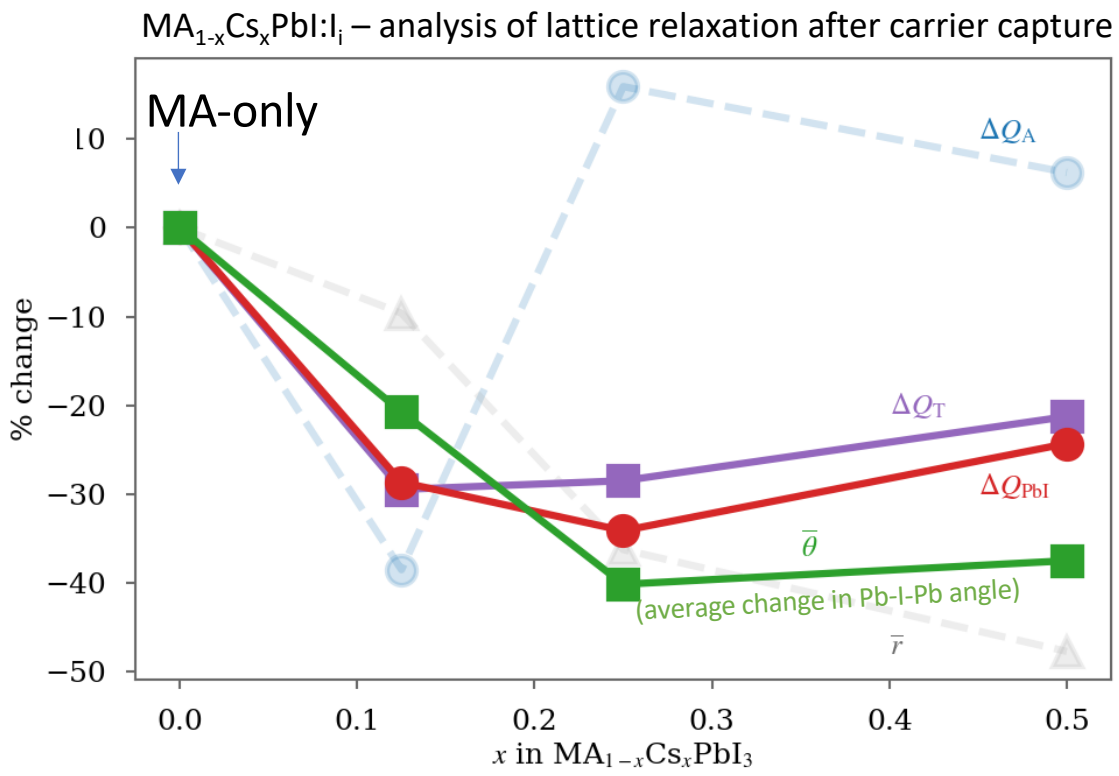
**NU-CEM/Kabsch_interpolation**

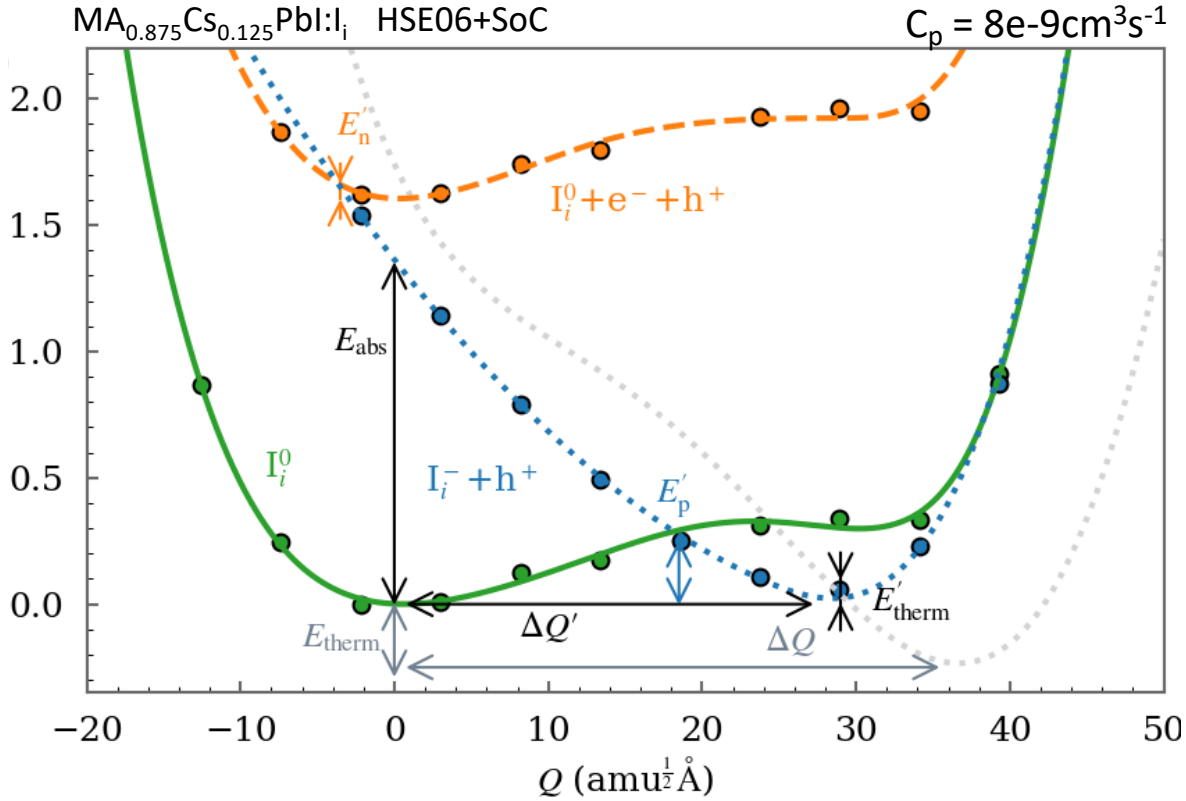
# How best to describe distortions in a hybrid material?




Energy is dissipated through rotations of the MA cation, resulting in significant reductions in the hole capture/release barrier height.

# Carrier capture at the iodine interstitial in $MA_{1-x}Cs_xPbI_3$

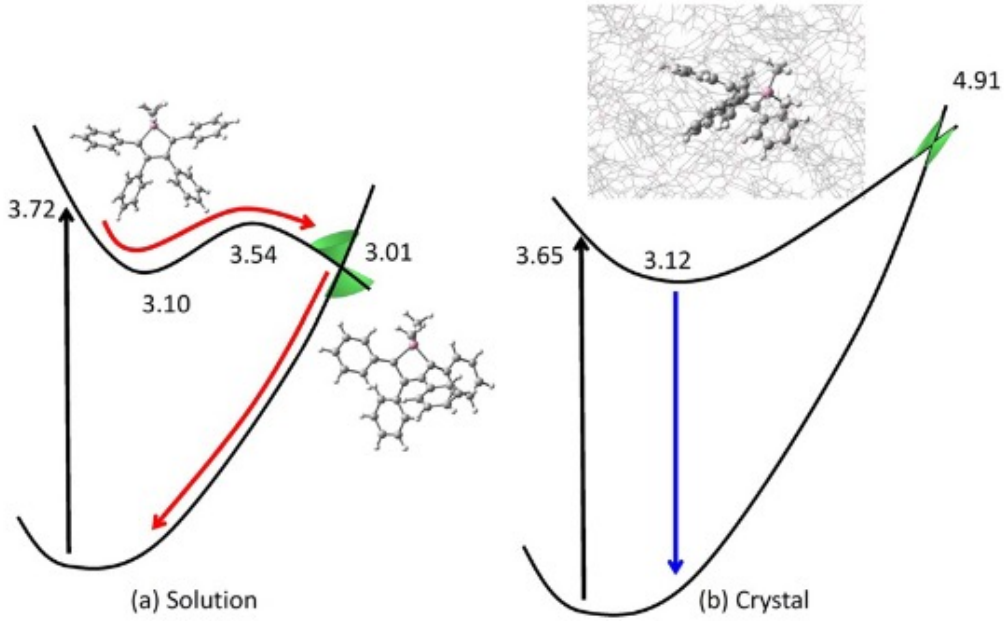



A-site cation mixing in $MA_{1-x}Cs_xPbI_3$ impedes $PbI_6$ octahedral tilting after carrier capture, **leading to a reduction in ΔQ.**

# Why the reduction in ΔQ? Lessons from organic photochemistry

Aggregation induced emission



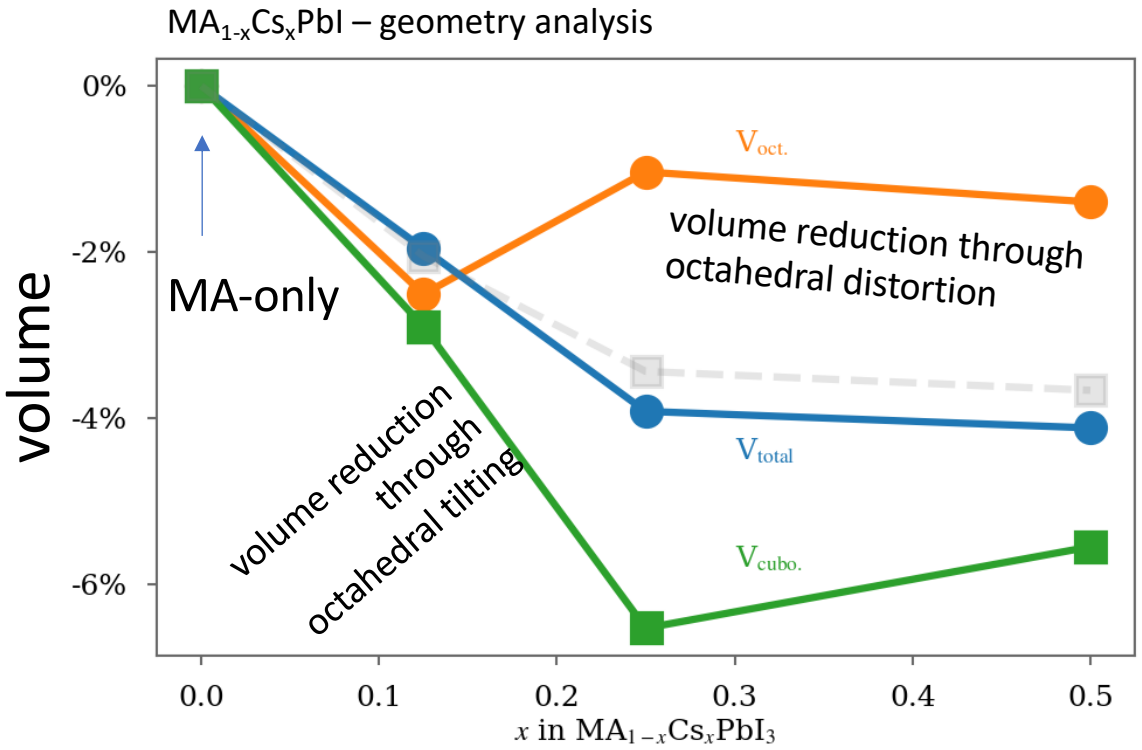

"Restricted Access to Conical Intersection" (RACI) model

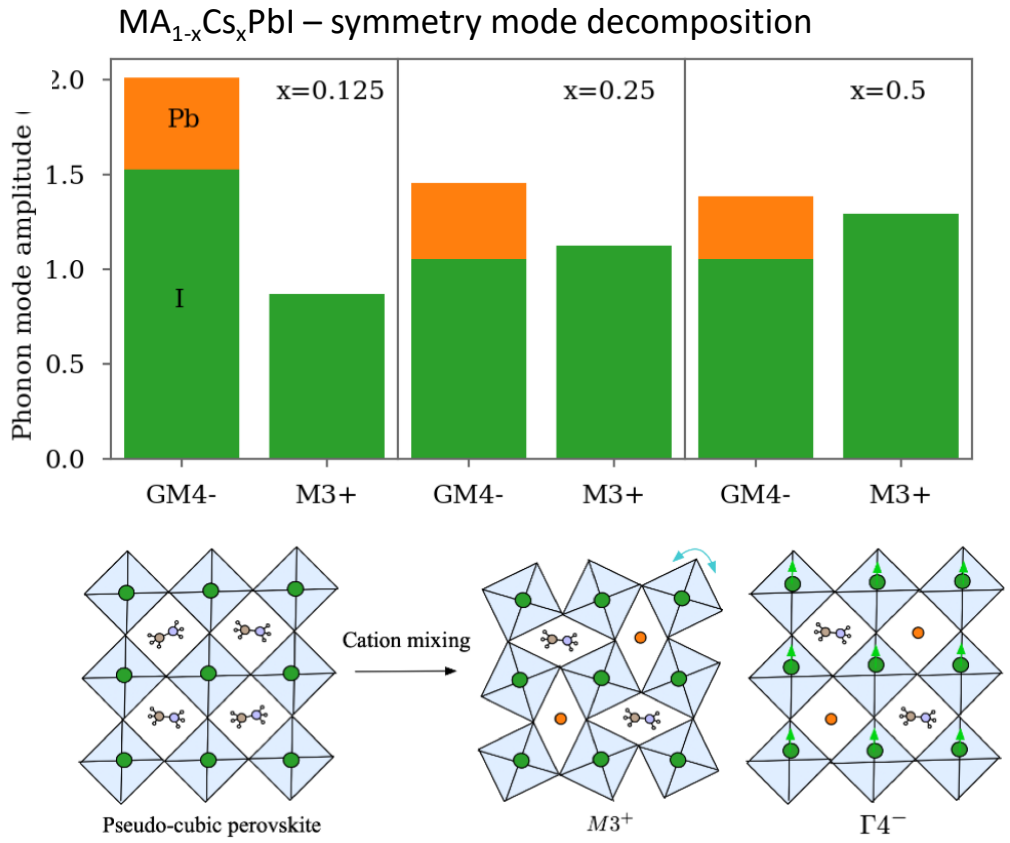
dimethyl tetraphenylsilole (DMTPS)

Peng et al., *J. Mater. Chem. C*, 2016, 4, 2802-2810

**Steric hindrance is used to engineer charge transport pathways in organic materials**

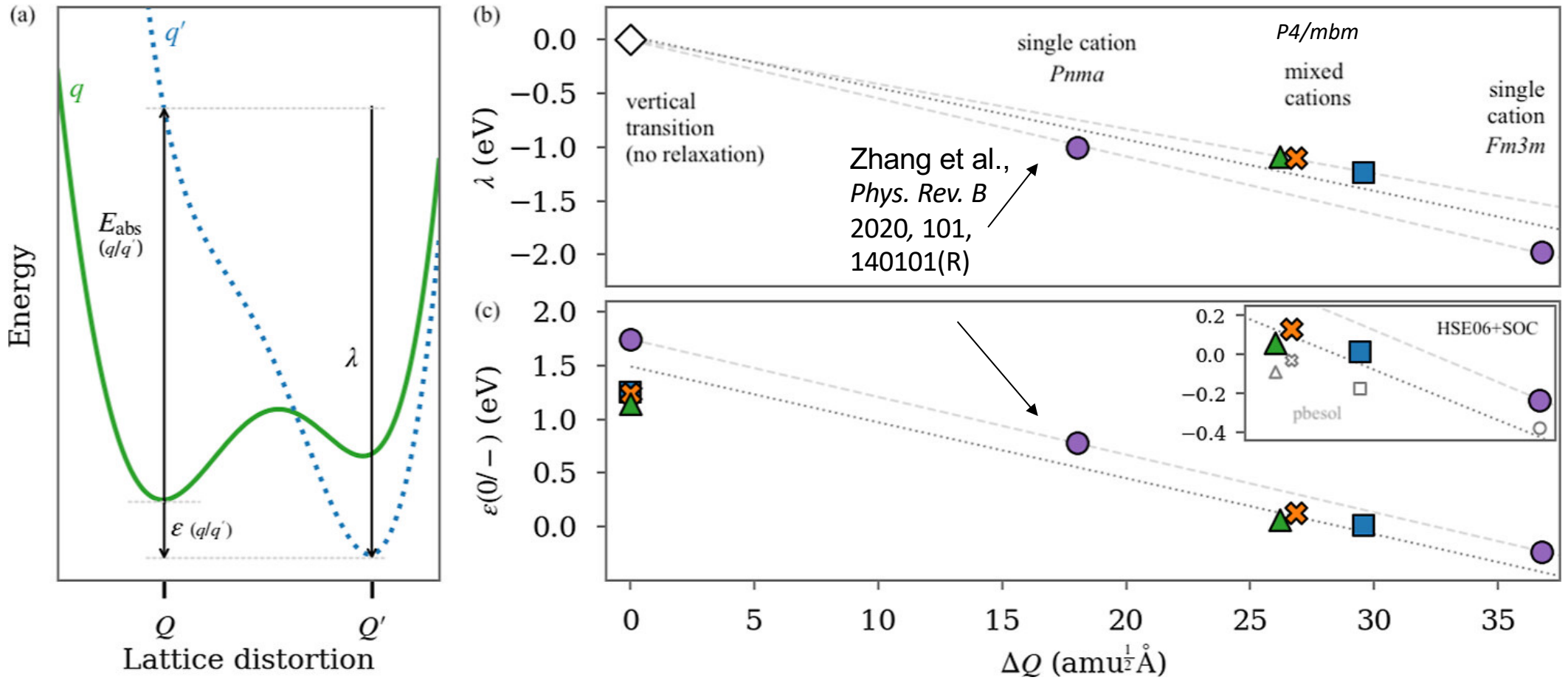
# A-cation mixing produces a symmetry-lowering lattice distortion to a tetragonal phase.



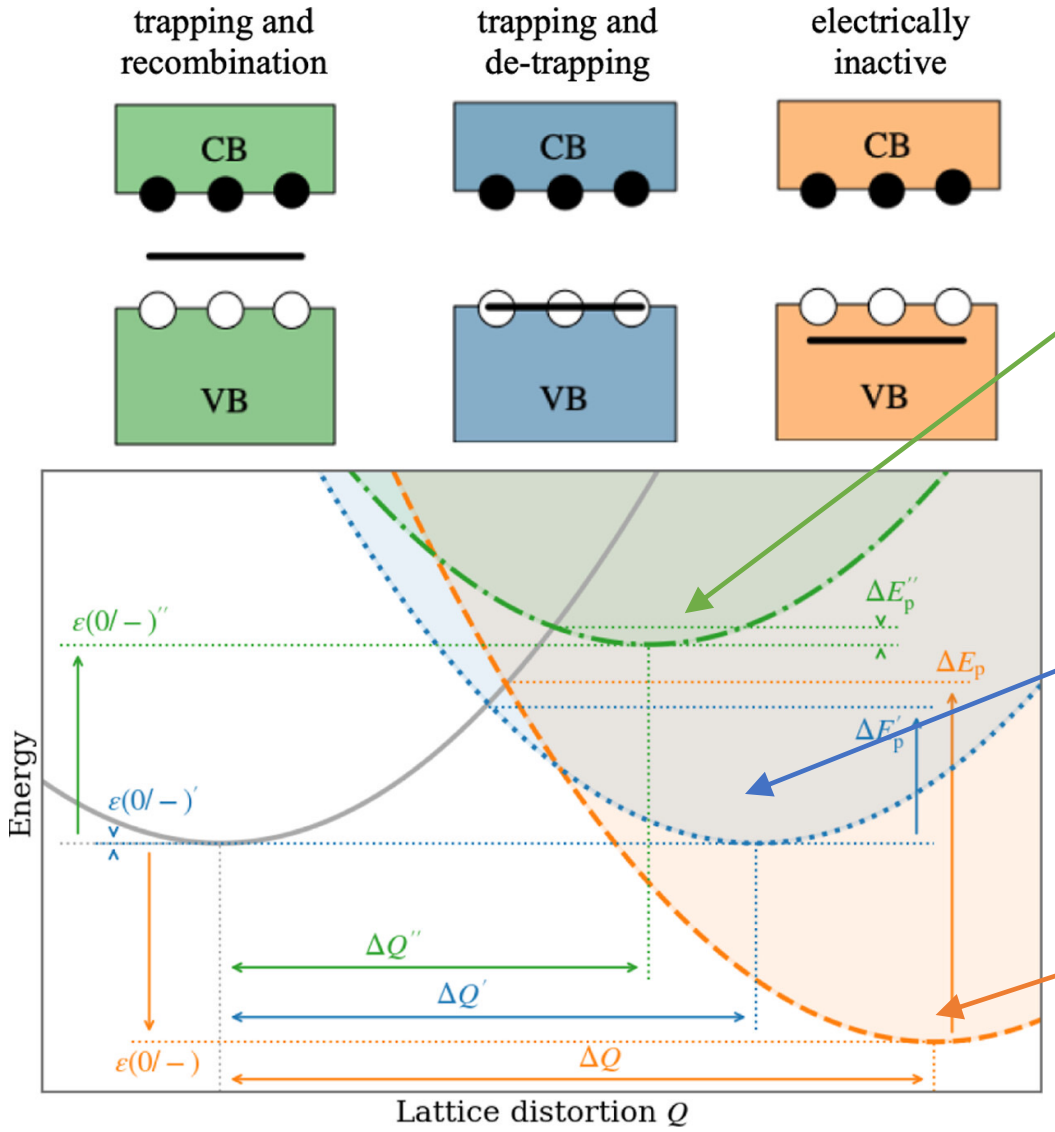

The reduced steric size of Cs (1.81 Å) compared to MA (2.70 Å) leads to a volume reduction **mediated through condensation of the M3+ octahedral tilting mode.**

# The iodine interstitial in $MA_{1-x}Cs_xPbI_3$ can display a wide range of defect activity




Defect activity is highly sensitive to ΔQ

# The iodine interstitial in $MA_{1-x}Cs_xPbI_3$ can display a wide range of defect activity



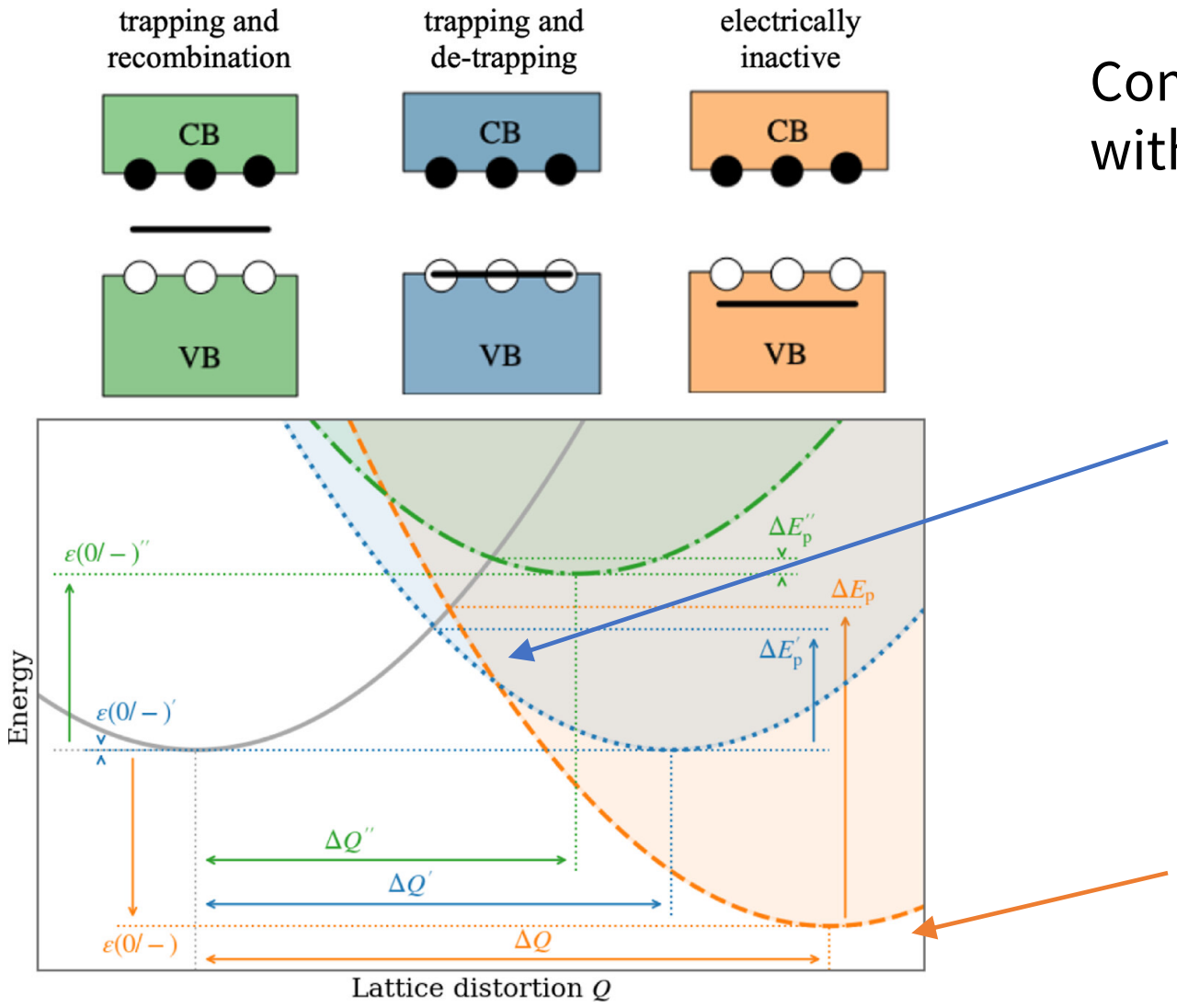

Single cation
Low-T orthorhombic phase
$C_p = 10^{-8}cm^3s^{-1}$, $C_{tot} = 10^{-8}cm^3s^{-1}$

Zhang et al., *Phys. Rev. B* 2020, 101, 140101(R)

Mixed cation
Tetragonal phase
$C_p \approx 10^{-8}cm^3s^{-1}$, $C_{tot} = 10^{-10}cm^3s^{-1}$

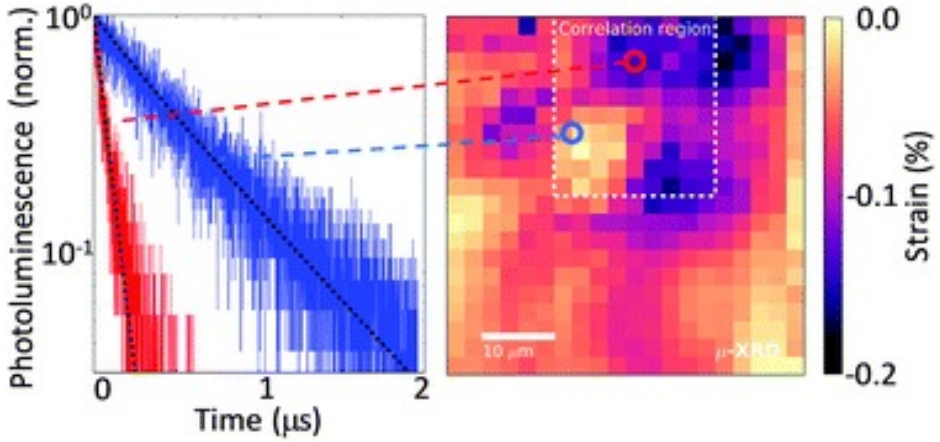
Single cation
Cubic phase
$C_p \approx C_{tot} \approx 10^{-17}cm^3s^{-1}$

# The iodine interstitial in $MA_{1-x}Cs_xPbI_3$ can display a wide range of defect activity




Compressively strained regions are associated with increased non-radiative decay

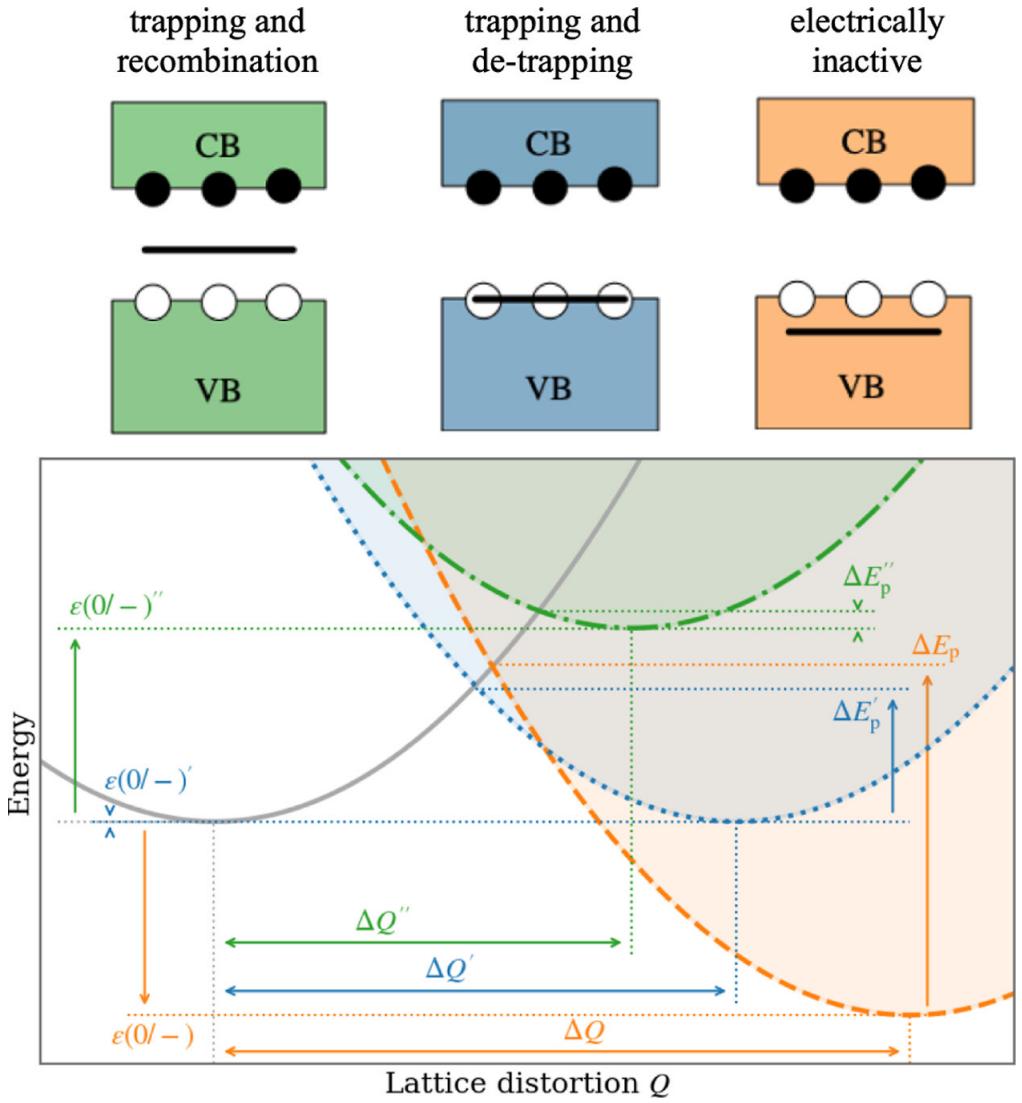
Jones et al., *Energy Environ. Sci.*, 2019,12, 596-606




Single crystals have a very low density of trap states ($<10^{12}$ $cm^{-3}$)

Shi et al., *Science.* 2015, 347, 6221, 519-522

# The iodine interstitial in $MA_{1-x}Cs_xPbI_3$ can display a wide range of defect activity




Defect activity is highly sensitive to ΔQ, ΔQ is sensitive to crystal phase

The same defect can display a wide range of defect activity – from electrically inactive to recombination centre

Similar behaviour reported with molecular dynamics


Nan et al., *Adv. Energy Mater.* 2018, 8, 1702754
Cohen et al. *J. Phys. Chem. Lett.* 2019, 10, 16, 4490−4498
Wang el al., . *Phys. Chem. Lett.* 2022, 13, 25, 5946−5952

# Thank you

- For accurate predictions of defect activity, translations & **rotations** of molecules need to be considered
- Defect activity is sensitive to the available lattice relaxation pathways
- Cation mixing (Cs/MA) → phase transition → reduced ΔQ → increased trapping
- The iodine interstitial in $MA_{1-x}Cs_xPbI_3$ can display a wide range of defect activity: electrically inactive, trapping & de-trapping, recombination site.

**Can we use ΔQ to engineer for particular defect properties ?**

✅ Control through composition, temperature, particle size, dimension…

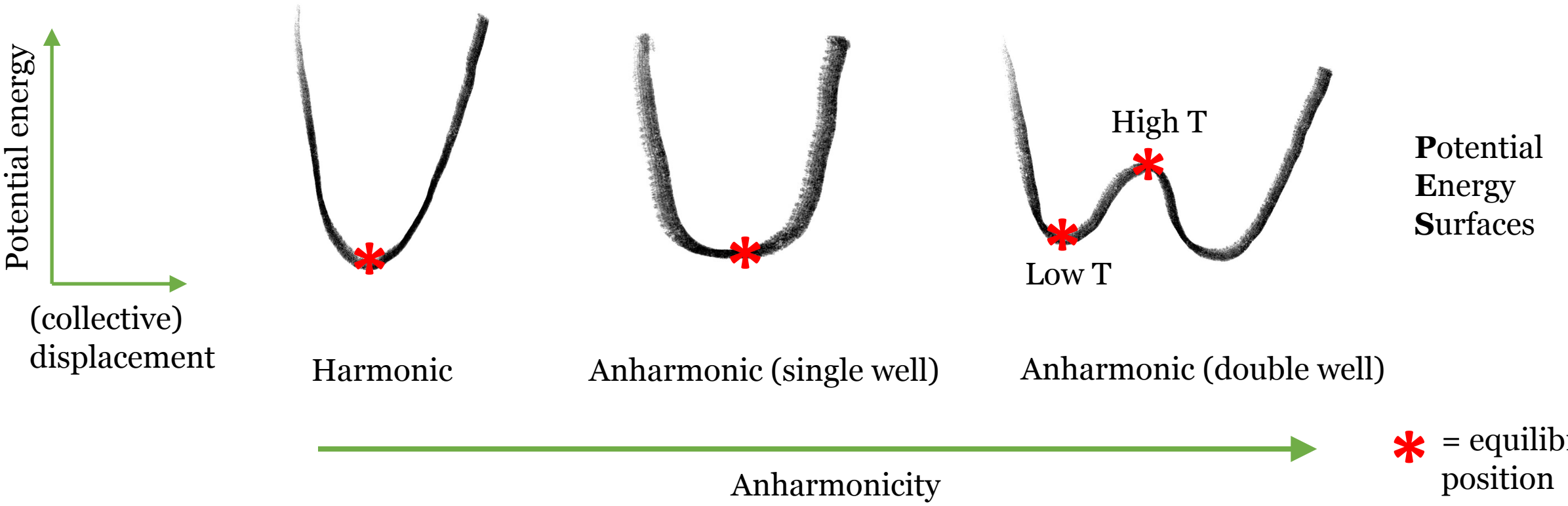
❌ Side effects: defect concentration, phase transformations, ion transport, polaron formation

*Thank-you to software developers:*
CarrierCapture, ICET (SQS), ISOTROPY, ASE, PIEFACE, Nonrad (EP coupling) , sxdefectalign

**Dr Lucy Whalley** Northumbria University ✉ l.whalley@northumbria.ac.uk lucydot.github.io

# Potential Energy Surface (PES)

**To predict atom motion we need to model the potential within which the atoms move**



# A platter of methods to choose from

## Attempted classification of *ab-initio* methods for phonons

how the potential energy surface is sampled

This lecture

Lattice dynamics – perturbative approaches

$$H = H_0 + \Phi_i^\alpha u_i^\alpha + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta$$

method of computing the force constant tensor

Finite Displacement

$$\Phi_{ij}^{\alpha\beta} = \frac{\partial^2 H}{\partial u_i^\alpha \partial u_j^\beta} = -\frac{\partial F_i^\alpha}{\partial u_j^\beta} \approx -\frac{\partial F_i^\alpha(\mathbf{R}) - F_i^\alpha(0)}{|\mathbf{R}|}$$

Density Functional Perturbation Theory

$$H(\lambda) = H^{(0)} + V_{\text{ext}}(\lambda)$$

Ab-initio Molecular Dynamics

$$M_I \ddot{R}_I = -\nabla_I [\varepsilon_0(\mathbf{R}) + V_{\text{NN}}(\mathbf{R})]$$

method for extracting vibrational properties

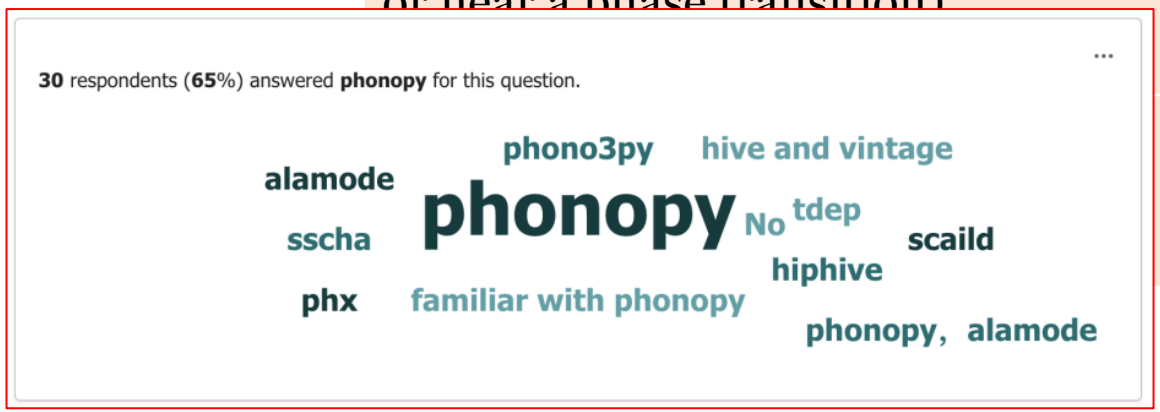
Velocity autocorrelation function

??

Effective force constants

# Perturbative approaches vs AIMD

| Perturbative Taylor expansion | Ab initio molecular dynamics |
|---|---|
| (Most often) less computationally intensive | Computationally intensive: phase space sampling & frequency resolution |
| Treating anharmonic effects as a perturbation– validity? | Anharmonicity at all orders |
| Limited to smaller amplitude displacements (not suitable at high-T or near a phase transition) | Suitable for large amplitude displacements |
| | Equilibrium position can change with temperature |

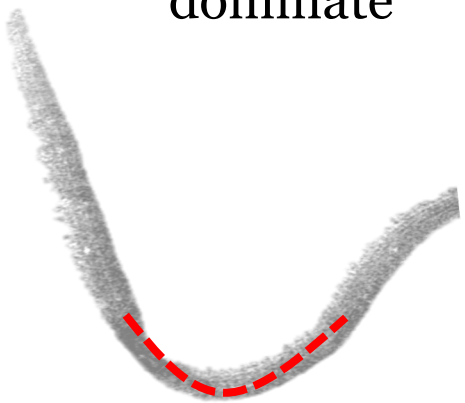


# (An)harmonicity

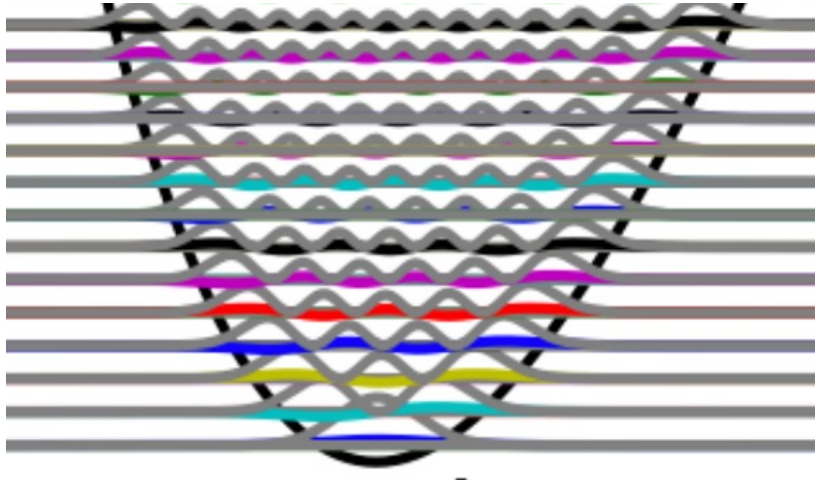
See e.g. Whalley et al (2016) Phys. Rev. B **94**, 220301(R)

## Model validity depends on the shape of the PES *and* the mode occupation $\bar{n}_i(T)$ from Bose-Einstein statistics

Low temperature,
low energy eigenstates
dominate

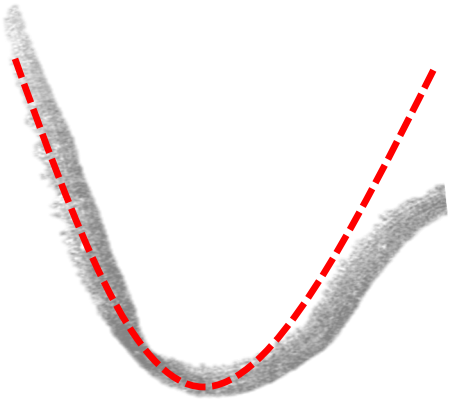


Harmonic approximation valid



PES as potential in 1D Schrodinger equation
→ solve to give vibrational eigenstates

High temperature,
higher energy eigenstates
contribute



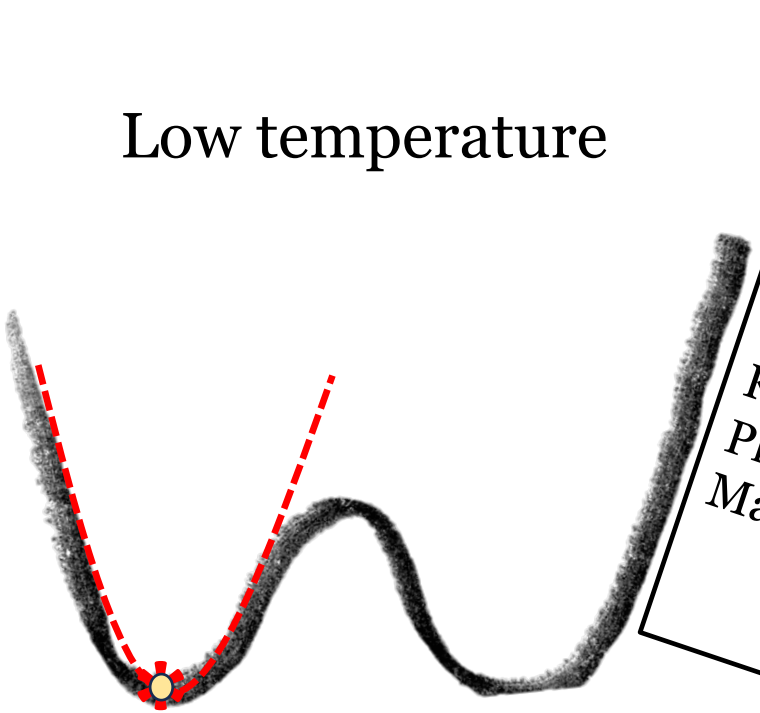
Harmonic approximation invalid

# (An)harmonicity

See e.g. Whalley et al (2016) Phys. Rev. B **94**, 220301(R)

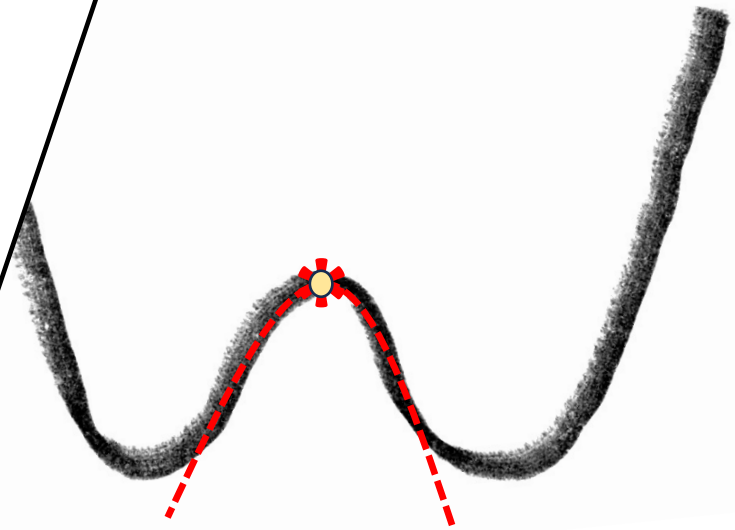
**Model validity depends on the shape of the PES *and* the mode occupation $\bar{n}_i(T)$ from Bose-Einstein statistics**

Low temperature



Restorative force proportional to distance
Harmonic approximation valid


High temperature



**N**on-restorative force proportional to distance
Harmonic approximation invalid

# Harmonic approximation

$$H \approx H_0 + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta$$

Taylor expansion of energy to second order

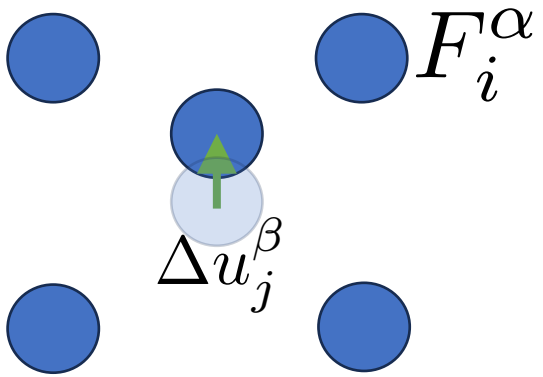
$$u = r - r_0$$

$$\Phi_{ij}^{\alpha\beta} = \frac{\partial^2 H}{\partial u_i^\alpha \partial u_j^\beta} = -\frac{\partial F_i^\alpha}{\partial u_j^\beta} \approx \frac{F_i^\alpha}{\Delta u_j^\beta}$$

$i, j$ Atom labels

$\alpha, \beta$ Cartesian directions

$l$ Unit cells



# Harmonic approximation

$$H \approx H_0 + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta}$$

Taylor expansion of energy to second order

$i, j$ Atom labels

$\alpha, \beta$ Cartesian directions

$l$ Unit cells

$$D(\mathbf{q})_{ij}^{\alpha\beta} = \frac{1}{\sqrt{m_i m_j}} \sum_l \Phi_{i0jl}^{\alpha\beta} \exp\{i\mathbf{q} \cdot [\mathbf{r}_{jl} - \mathbf{r}_{j0}]\}$$

Dynamical matrix from fourier transform of Φ

$$D(\mathbf{q})W(\mathbf{q}) = \omega^2(\mathbf{q})W(\mathbf{q})$$

Diagonalise to get squared phonon frequencies $\omega^2$ and eigenvectors W

$$H(Q) \approx H_0 + \frac{1}{2}\omega^2 Q^2$$

Harmonic energy is expressed as a function of displacement amplitude Q

# (An)harmonicity

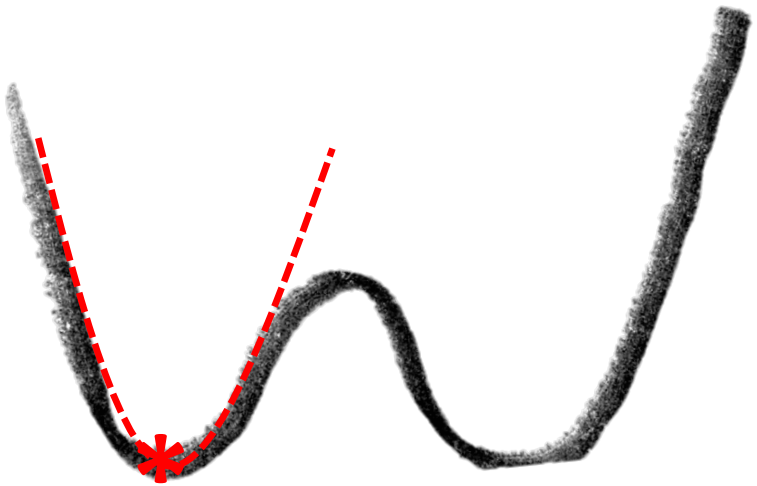
Pallikara *et al* 2022 *Electron. Struct.* **4** 033002

$$H(Q) \approx H_0 + \frac{1}{2}\omega^2 Q^2$$

Harmonic energy is expressed as a function of displacement amplitude Q

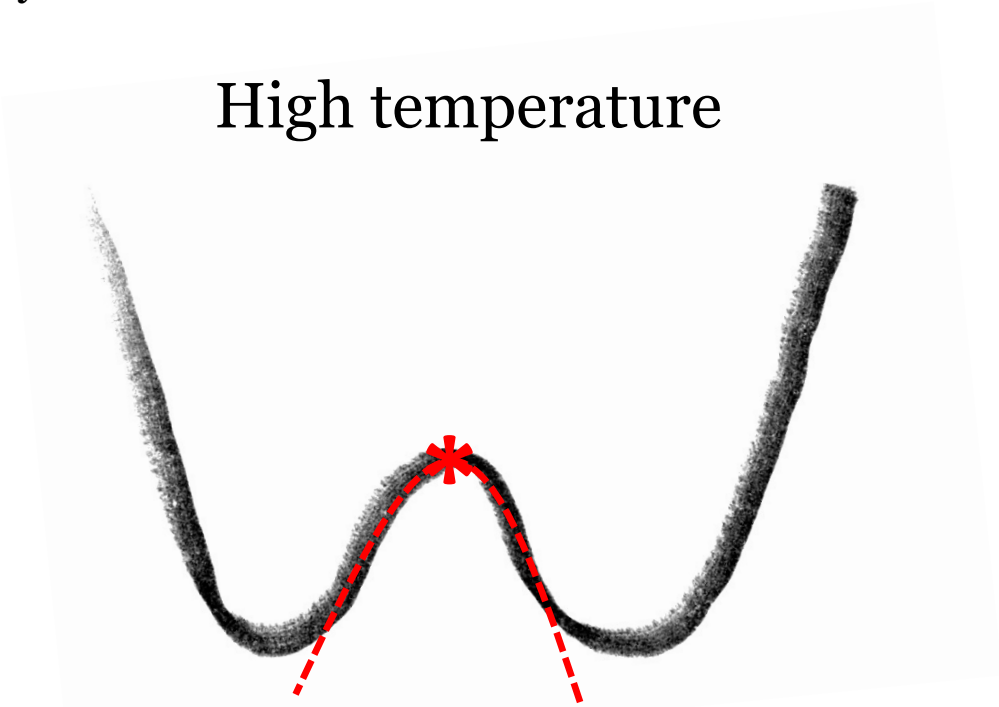
Phonon mode frequency

Low temperature



Restorative force – **real positive phonon frequency**
Harmonic approximation valid

High temperature



Non-restorative force – **imaginary phonon frequency**
Harmonic approximation invalid

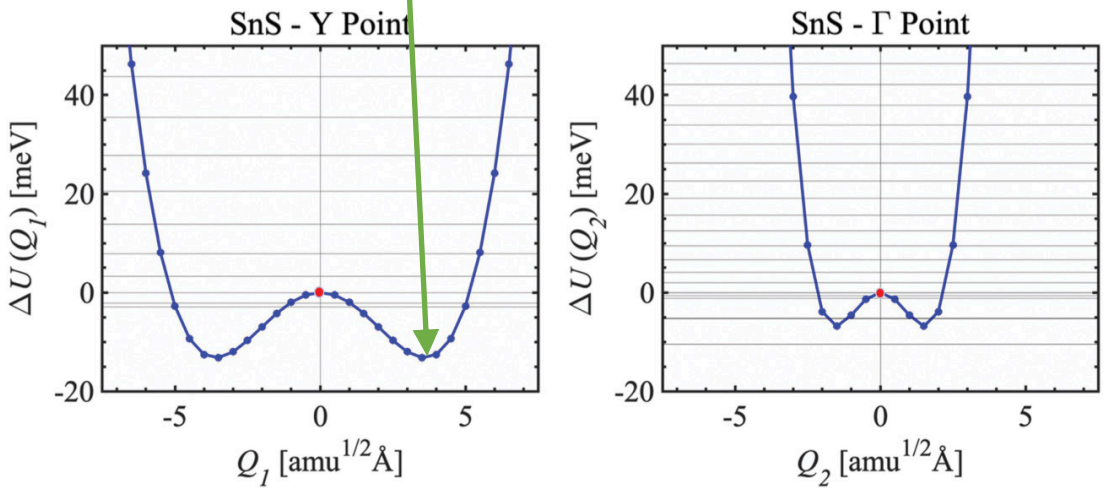
# Dynamical instabilities

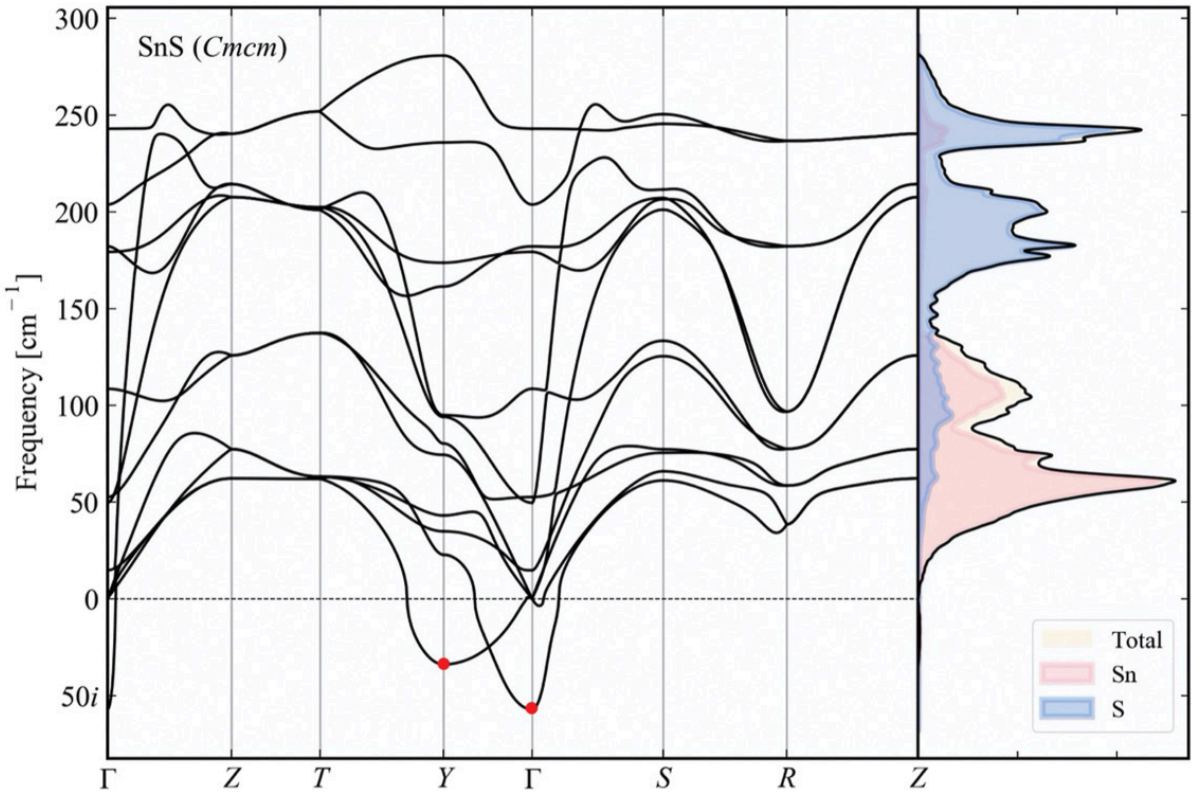
Pallikara *et al* 2022 *Electron. Struct.* **4** 033002

$$H(Q) \approx H_0 + \frac{1}{2}\omega^2 Q^2$$

Low-T Pnma phase geometry

Frequency




`Mode-mapping': distort the crystal structure along a particular phonon eigenvector(s) to map out the Potential Energy Surface

# Higher order Taylor expansion

**Taylor expansion of the potential energy surface**

**Crystal Potential**
Static model

**Harmonic Phonons**
Non-interacting phonons
"Infinite lifetimes"

$$H = H_0 + \Phi_i^{\alpha} u_i^{\alpha} + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \frac{1}{6}\Phi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_j^{\beta} u_k^{\gamma} + \dots$$

**Ionic Forces**
= 0 at equilibrium

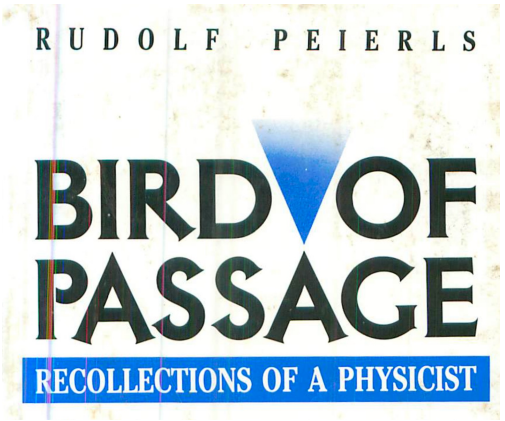
**Anharmonicity**
Phonon scattering
Required for e.g. thermal conductivity

# Higher order Taylor expansion

"But it was also known that [....] the so-called anharmonic terms, were important. These terms cause a coupling between the otherwise independent waves of different length and direction. They are responsible for the absorption of sound waves, which, in the linear approximation, could travel indefinite distances without damping, and for the heat conductivity."

-- Rudolf Peierls, Bird of Passage (or see "Recollections of early solid state physics")

$$H = H_0 + \Phi_i^\alpha u_i^\alpha + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{6}\Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \dots$$

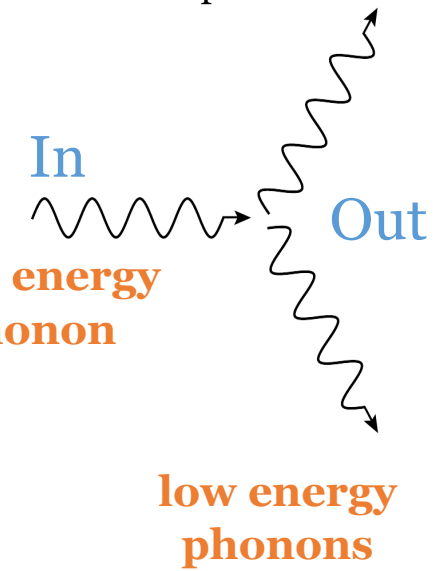



**Anharmonicity**

Phonon scattering

Required for e.g. thermal conductivity

Example 3-phonon process



# Force constants are the key ingredient

**Crystal Potential**

Static model

**Harmonic Phonons**

Non-interacting phonons

"Infinite lifetimes"

**Force constant tensors describe the PES**

$$H = H_0 + \Phi_i^{\alpha} u_i^{\alpha} + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \frac{1}{6}\Phi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_j^{\beta} u_k^{\gamma} + \dots$$

$2^{nd}$ order

$3^{rd}$ order

**Ionic Forces**

= 0 at equilibrium

**Anharmonicity**

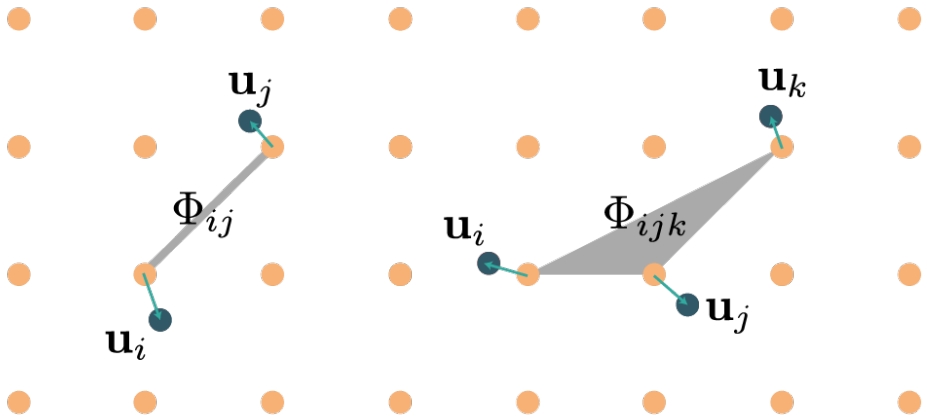
Phonon scattering

Required for e.g.

thermal conductivity

# Calculating force-constants

From TDEP Code documentation




- Force constants are the essential ingredient for phonon calculations
- Calculating force constants is often the most computationally intensive part of a lattice dynamics calculation
- Computational cost is determined by:
  - Rank of tensor ($2^{nd}$/$3^{rd}$/$4^{th}$ order)
  - Number of atoms in system (supercell expansion)
  - Crystal symmetry

# Calculating force constants

| Real space finite displacement (AKA Direct, Supercell) | Density Functional Perturbation Theory |
|---|---|
| Intuitive approach to understand | Less intuitive theoretical approach |
| Flexible: can be combined with a variety of functionals, and levels of theory | Requires implementation for a particular level of theory |
| Can be split into many smaller jobs: can “game” the computer queues | Consists of one larger job which requires significant memory |
| Can only calculate perturbations at the gamma point: supercells commensurate with $q$ are required | Perturbation of of any wave vector $q$ possible (note: not available in VASP) |
| Scales poorly with system size | Improved scaling with system size; for larger jobs can be computationally cheaper |

# Stop! Do you need to do the calculation?

Phonon databases

- phonondb
- Materials Project
- NOMAD

Not Secure | phonondb.mtl.kyoto-u.ac.jp/ph20180417/d000/mp-252.html

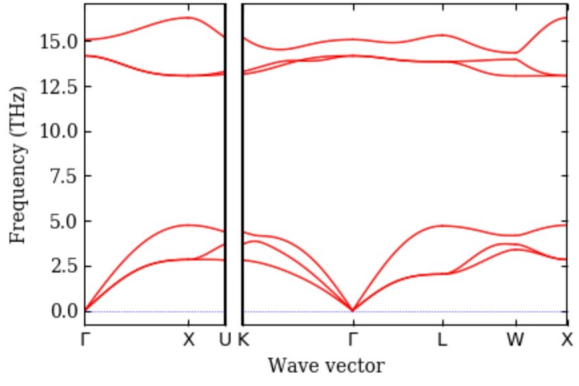
phonondb@kyoto-u

Search

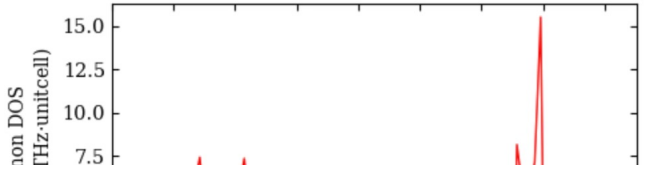
## Materials id 252 / BeTe / F-43m (216)

- Date page updated: 2018-4-17
- Space group type: F-43m (216) / F -4 2 3
- Number of formula units (Z): 4
- Phonon raw data: **mp-252-20180417.tar.lzma**
- Link to Materials Project: https://www.materialsproject.org/materials/mp-252/

### Phonon band structure




### Phonon DOS

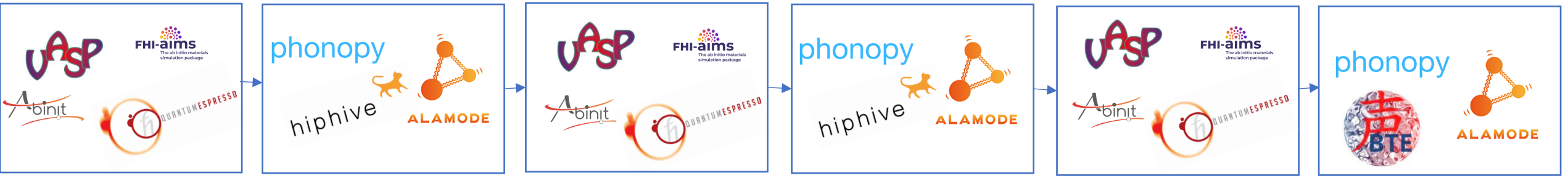


# Finite displacement workflow (harmonic)

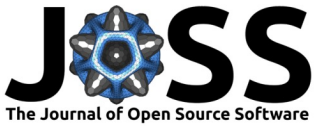
TASKS

| Relax unit cell | → | Build supercell and generate displacements | → | Calculate forces | → | Extract forces, build and diagonalise dynamical matrix | → | (optional) calculate born effective charges & dielectric tensor | → | Post-process e.g. dispersion, heat capacity |
|---|---|---|---|---|---|---|---|---|---|---|

CODES

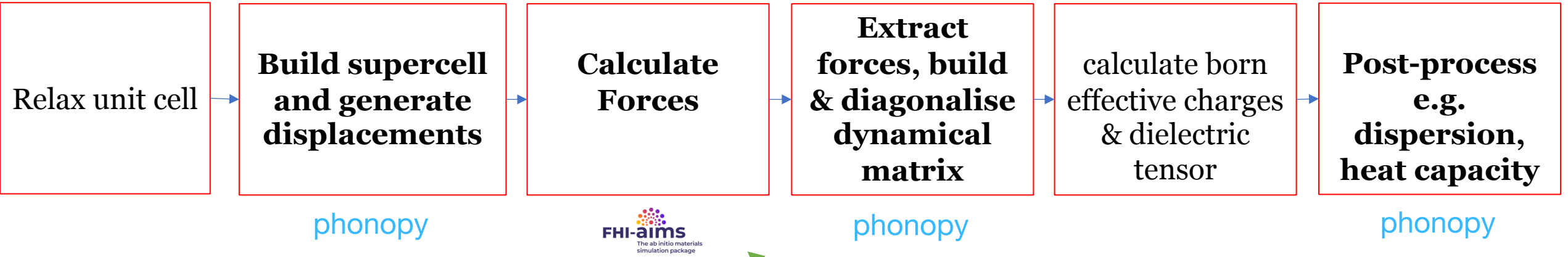


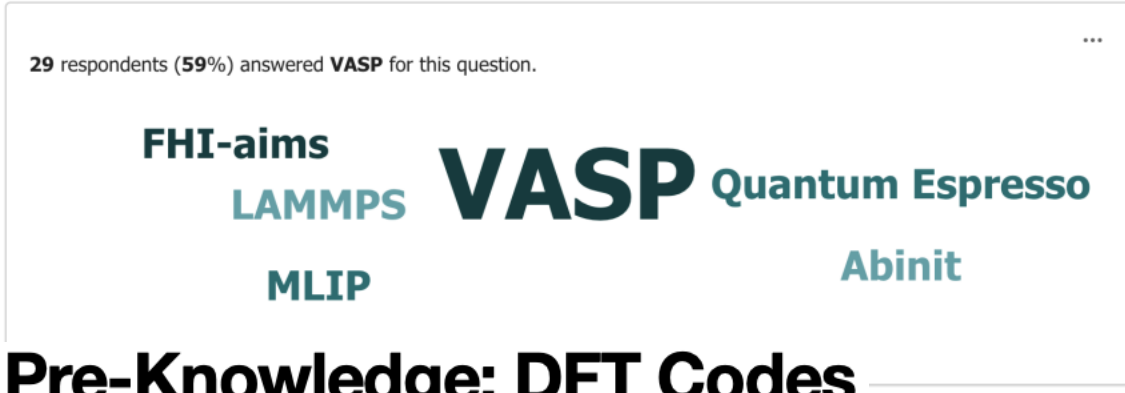

+ codes that can stitch it all together, e.g. fhivibes


Knoop et al., (2020) Journal of Open Source Software, 5(56), 2671

# Live example




Files available here:
http://github.com/nu-CEM/phonons_tutorial/

# Choosing a suitable supercell

**The sum over the unit cells in the dynamical matrix requires supercells that adequately capture all pairwise interactions**

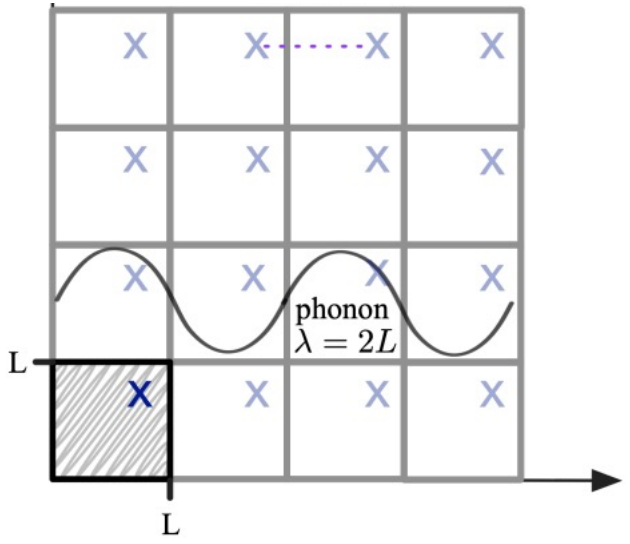
$$D(\mathbf{q})_{ij}^{\alpha\beta} = \frac{1}{\sqrt{m_i m_j}} \sum_l \Phi_{i0jl}^{\alpha\beta} \exp\{i\mathbf{q} \cdot [\mathbf{r}_{jl} - \mathbf{r}_{j0}]\}$$

- For this reason you may want a cell that is fairly cubic
- For this reason you need to do convergence testing

```
from ase.build import bulk
from ase.build import find_optimal_cell_shape, get_deviation_from_optimal_cell_shape
import numpy as np
conf = bulk('Au')
P1 = find_optimal_cell_shape(conf.cell, 32, 'sc')
```

Atomic Simulation Environment

Atom-atom interaction



# Choosing a suitable supercell

**The finite displacement method requires a supercell to capture off-Γ phonons**

If you want to access a off-Γ wave vector *q*, you need to map that wave vector *q* to the Γ-point by using a commensurate supercell

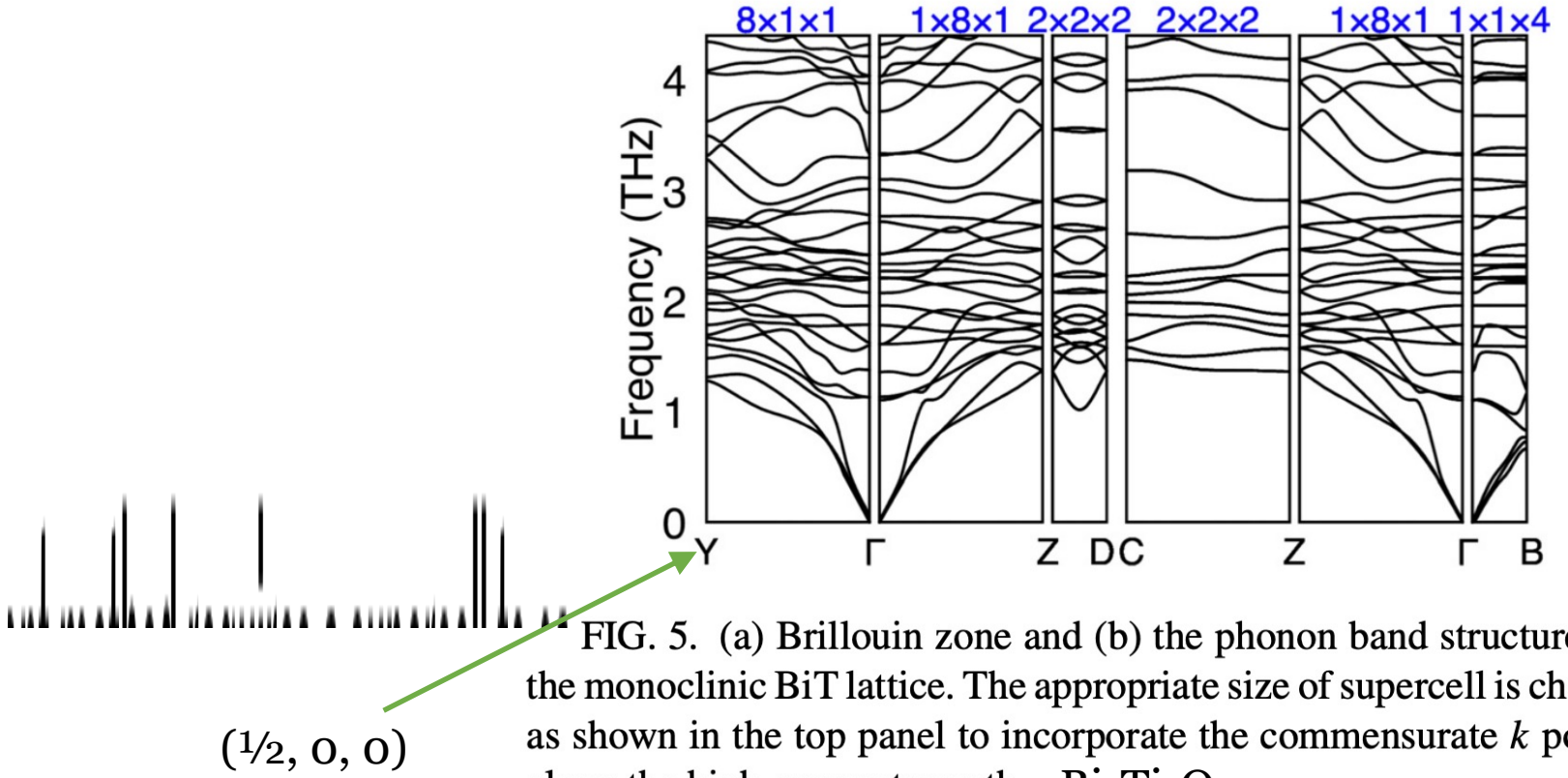
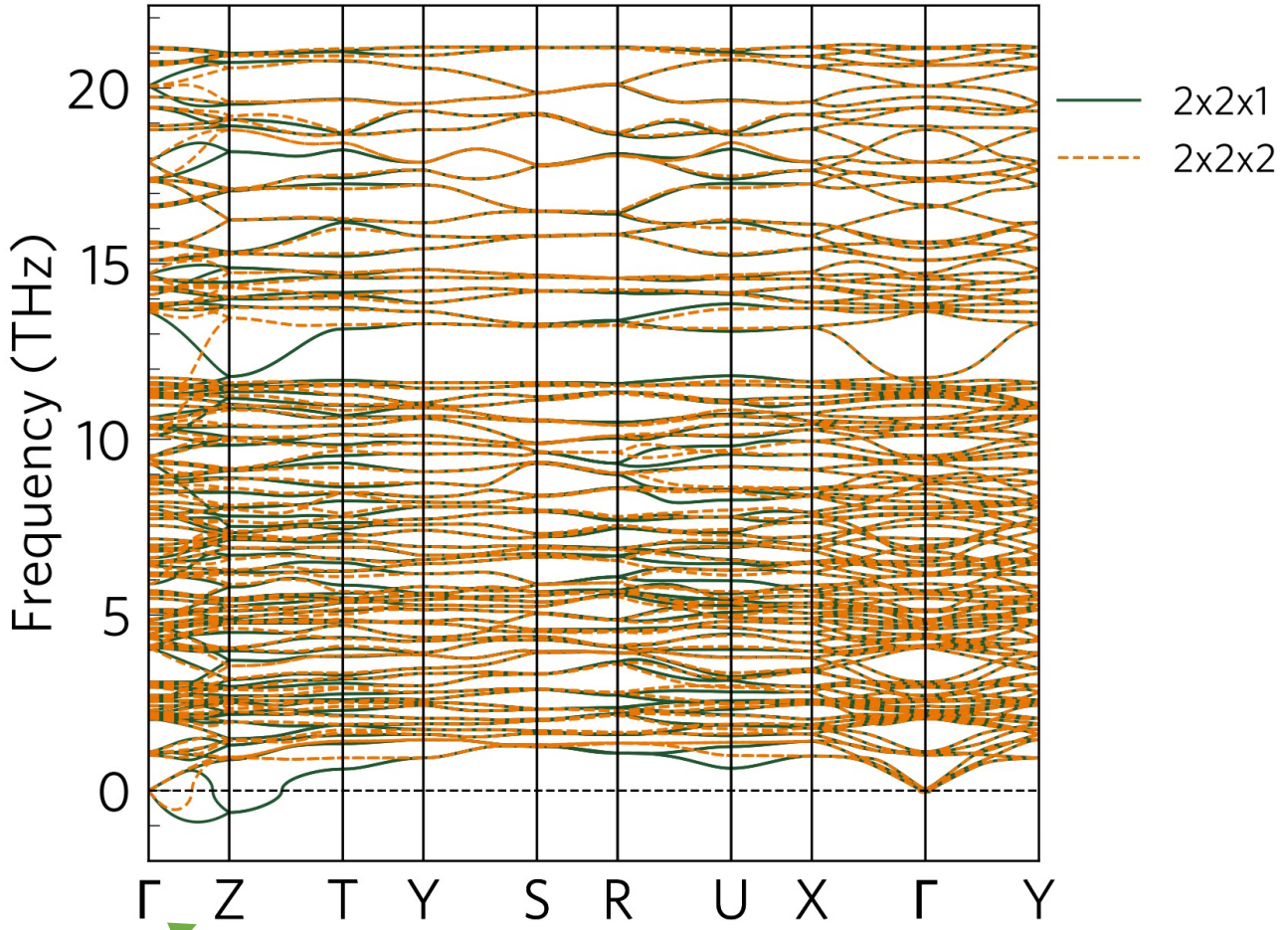



FIG. 5. (a) Brillouin zone and (b) the phonon band structure for the monoclinic BiT lattice. The appropriate size of supercell is chosen as shown in the top panel to incorporate the commensurate *k* points along the high-symmetry path. $Bi_4Ti_3O_{12}$

Maurya et al Physical Review B 96, 134114 (2017)

# Choosing a suitable supercell

**Imaginary modes can be formed from interpolation at q-points incommensurate with the supercell**




(0, 0, ½)

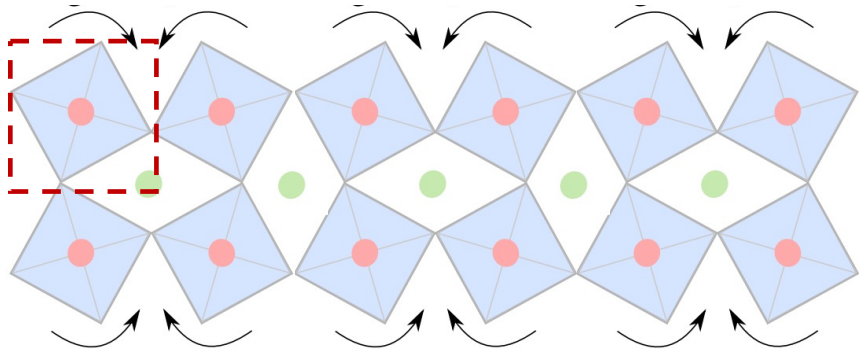
$Bi_2Sn_2O_7$

Rahim et al, *Chem. Sci.*, 2020,11, 7904-7909

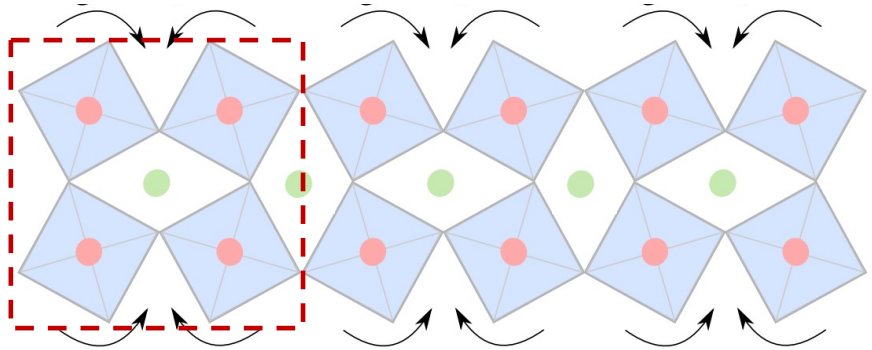
# Choosing a suitable supercell

**Some supercell expansions can suppress distortions and lead to incorrect results (bigger isn't always better)**

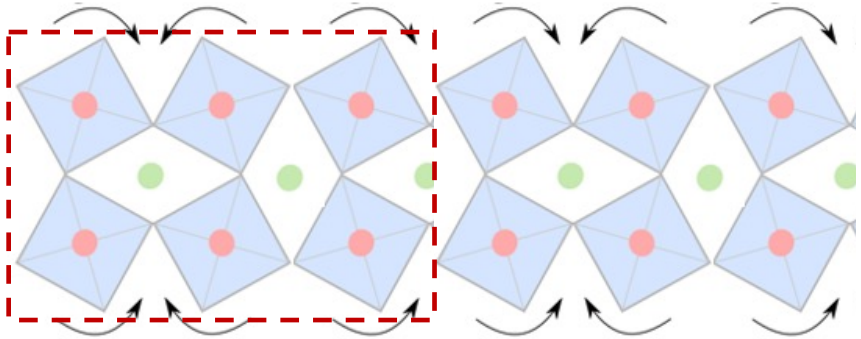
$CsPbI_3$ tilting distortion to tetragonal phase



2x2



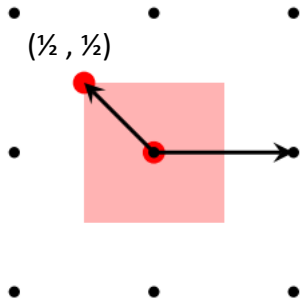
3x2



# Choosing a suitable supercell

**Most studies use diagonal supercells, but non-diagonal supercells can be used to reduce computational cost**

$$\begin{pmatrix} \mathbf{a}_{s_1} \\ \mathbf{a}_{s_2} \\ \mathbf{a}_{s_3} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} \mathbf{a}_{p_1} \\ \mathbf{a}_{p_2} \\ \mathbf{a}_{p_3} \end{pmatrix}$$




Diagonal elements. Supercell is $S_{11}$x $S_{22}$x $S_{33}$ primitive cells.
e.g. "2x3x1 supercell" is 6 primitive cells

$$S = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$$ diagonal supercell
4 primitive cells

$$S = \begin{pmatrix} 1 & 1 \\ 0 & 2 \end{pmatrix}$$ non-diagonal supercell
2 primitive cells

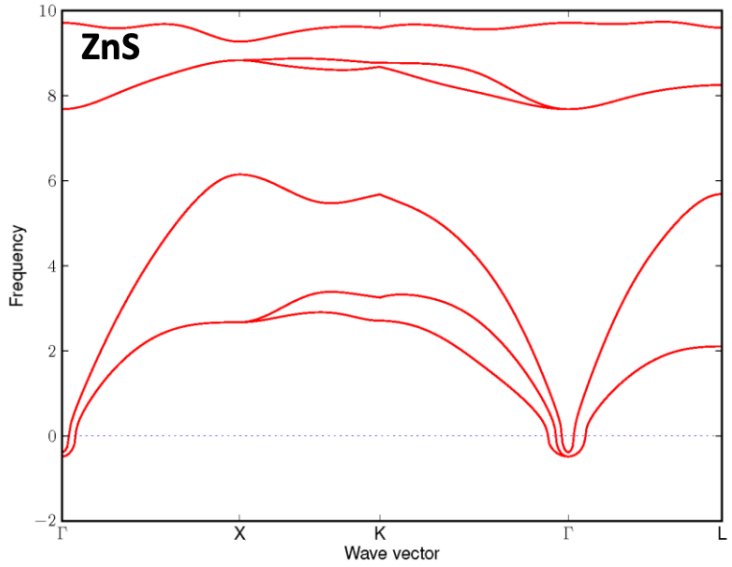
Lloyd-Williams and Monserrat, Phys. Rev. B **92**, 184301

# Acoustic Sum Rule

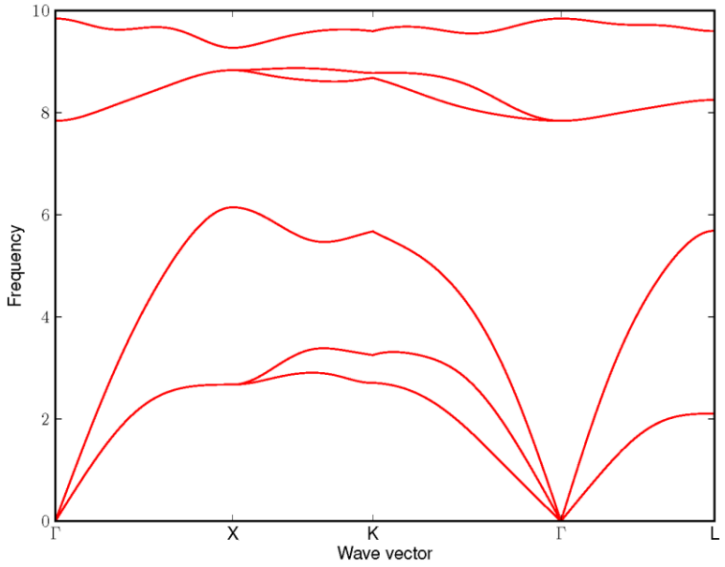
**Numerical approaches can lead to broken translational symmetry and small imaginary frequencies around the gamma point.**

To fix this either increase size of the FFT grid (plane wave basis) or integration grid (atom-centred basis), or apply a post-hoc correction

FC_SYMMETRY = .FALSE.




FC_SYMMETRY = .TRUE.

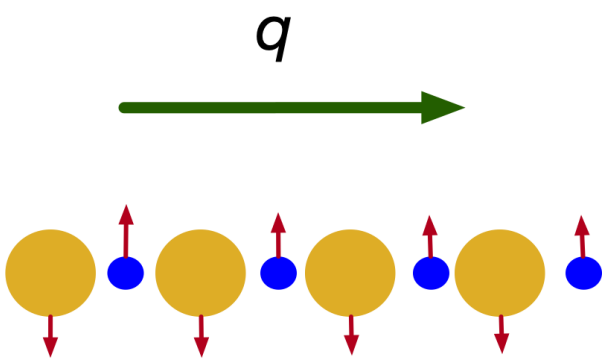



"Phonons & Phonopy: Pro Tips" from J.M. Skelton (available on SlideShare)

# Non-Analytical Corrections

**LO/TO splitting results from the macroscopic electric field associated with a separation of ions (Coloumb interaction)**

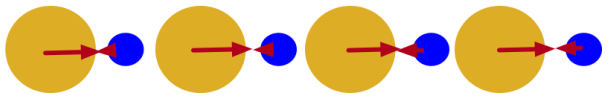
Transverse Optic




For TO mode:

- $E \perp q \Rightarrow E.q = 0$

Longitudinal Optic



For LO mode:

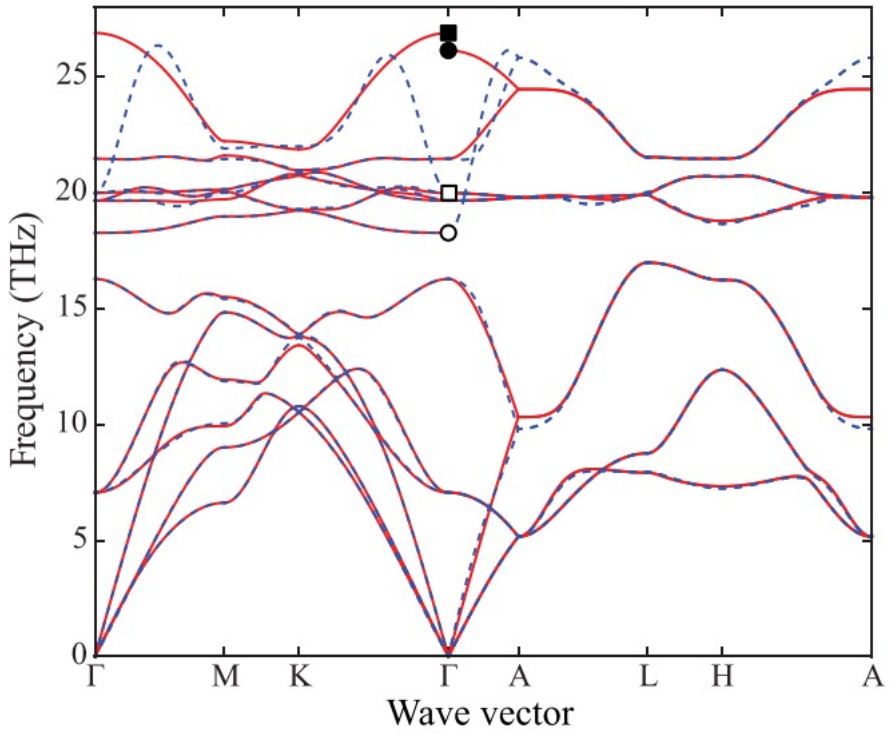
- E.q is non-zero
- E-field adds restoring force.
- Frequency is upshifted.

# Non-Analytical Corrections

**LO/TO splitting results from the macroscopic electric field associated with a separation of ions (Coloumb interaction)**

Post-hoc correction using Born effective charge and high-frequency (optical, ion-clamped) dielectric tensors

$$D_{\alpha\beta}(jj', \mathbf{q} \to \mathbf{0}) = D_{\alpha\beta}(jj', \mathbf{q} = \mathbf{0}) + \frac{1}{\sqrt{m_j m_{j'}}} \frac{4\pi}{\Omega_0} \frac{\left[\sum_\gamma q_\gamma Z^*_{j,\gamma\alpha}\right]\left[\sum_{\gamma'} q_{\gamma'} Z^*_{j',\gamma'\beta}\right]}{\sum_{\alpha\beta} q_\alpha \epsilon^\infty_{\alpha\beta} q_\beta}.$$




Togo *et al* J. Phys. Condens. Matter 35 (2023) 353001

# Calculation Tips and Tricks

"Phonons are fussy little buggers" - Dr Adam Jackson, STFC UK

- **A very well relaxed structure is a pre-requisite**
  - tighten force convergence criteria for structure relaxation (e.g. to $< 0.01$ eV Å$^{-1}$)
- **Accurate forces are essential**
  - converge forces with respect to the basis set, k-point sampling density and SCF criteria
  - plane-wave basis: increase cut-off energy by at least 25% above default, up to 2× may be required.
  - numerical atom-centered basis: the default cut-offs tightened by an order of magnitude.
- **Avoid interpolation artefacts (imaginary frequencies or flat bands)**
  - use supercell (finite displacement) or q-point grid (DFPT) commensurate with wavevector
- **Make use of the short (or free queue)**
  - Finite difference consists of several small jobs – possible to be done "for free"

See Pallikara *et al* 2022 *Electron. Struct.* **4** 033002

# Quasi Harmonic Approximation

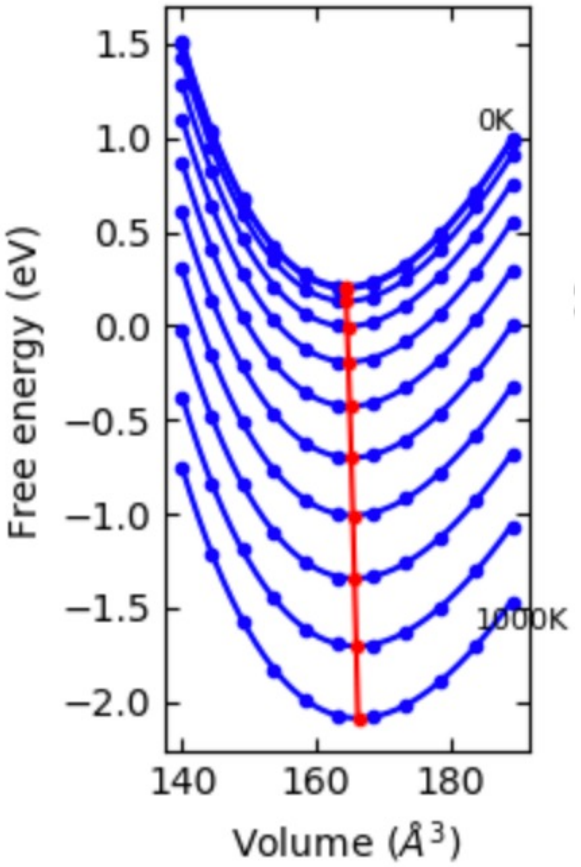
## Quasi-harmonic approximation can be used to model the effects of thermal lattice expansion

- In the harmonic approximation, the lattice parameters are temperature independent, so cannot predict (the effects of) thermal expansion
- At finite temperature, the system will minimise its free energy rather than its lattice internal energy

$$\min\left[E_i^{\mathrm{DFT}} + E_i^{\mathrm{ZP}} + \int_0^T C_p \mathrm{d}T + PV - TS_{\mathrm{vib}}(T)\right]$$

- The fit provides **equilibrium volume V(T)** and the **bulk modulus B(T)**. From this a number of other properties can be derived:

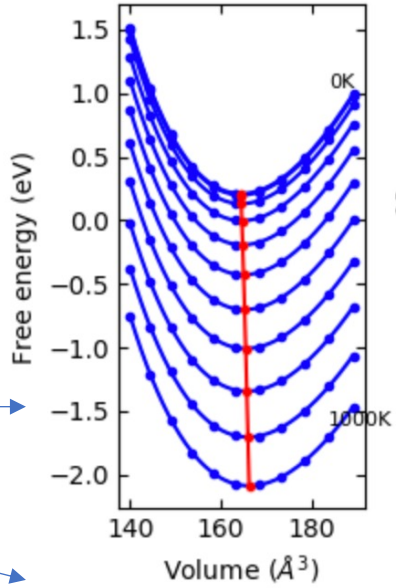
| | |
|---|---|
| Gruneisen | $V\beta B_T/C_V$ |
| Entropy | $-\left(\frac{\partial G}{\partial T}\right)_p$ |
| Heat capacity | $-T\frac{\partial^2 G}{\partial T^2}$ |



# Quasi Harmonic Approximation

**Quasi-harmonic approximation can be used to model the effects of thermal lattice expansion**

Relax unit cell → Expand and contract structures → *For each structure* calculate $E_i^{\mathrm{DFT}}$ → *For each structure* calculate thermal properties with harmonic phonons → Run phonopy-qha for post-processing

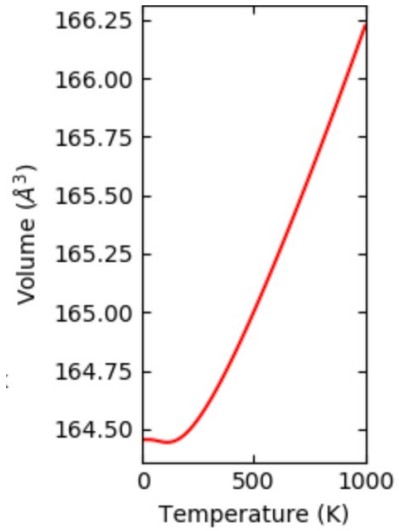



```
#   cell volume   energy of cell other than phonon
     140.030000            -42.132246
     144.500000            -42.600974
     149.060000            -42.949142
     153.720000            -43.188162
     158.470000            -43.326751
     163.320000            -43.375124
     168.270000            -43.339884
     173.320000            -43.230619
     178.470000            -43.054343
     183.720000            -42.817825
     189.070000            -42.527932
```

e-v.dat

thermal_properties.yaml

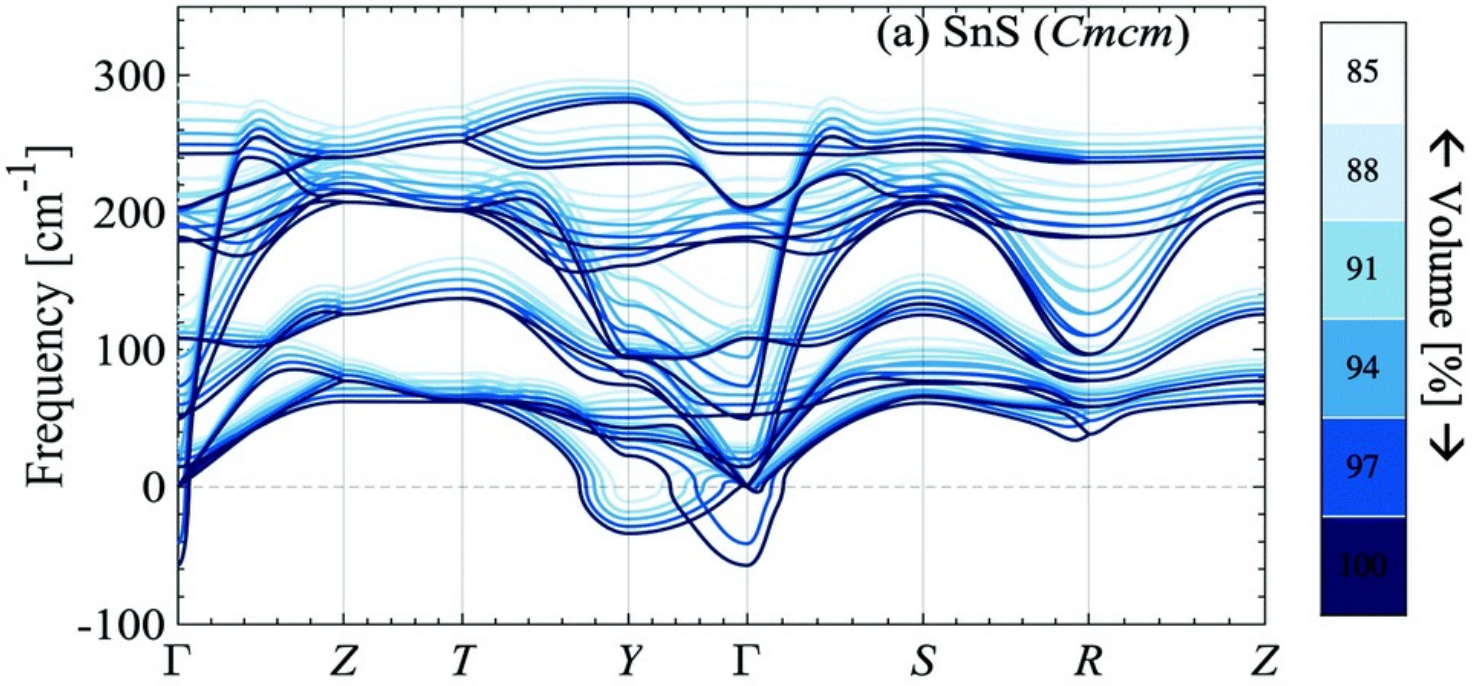
```
Cp-temperature.dat
Cp-temperature_polyfit.dat
Cv-volume.dat
bulk_modulus-temperature.dat
dsdv-temperature.dat
entropy-volume.dat
gibbs-temperature.dat
gruneisen-temperature.dat
helmholtz-volume.dat
thermal_expansion.dat
volume-temperature.dat
```

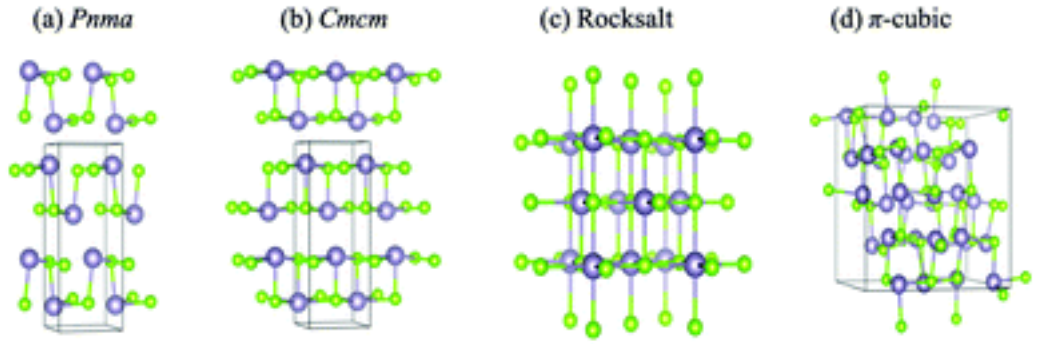


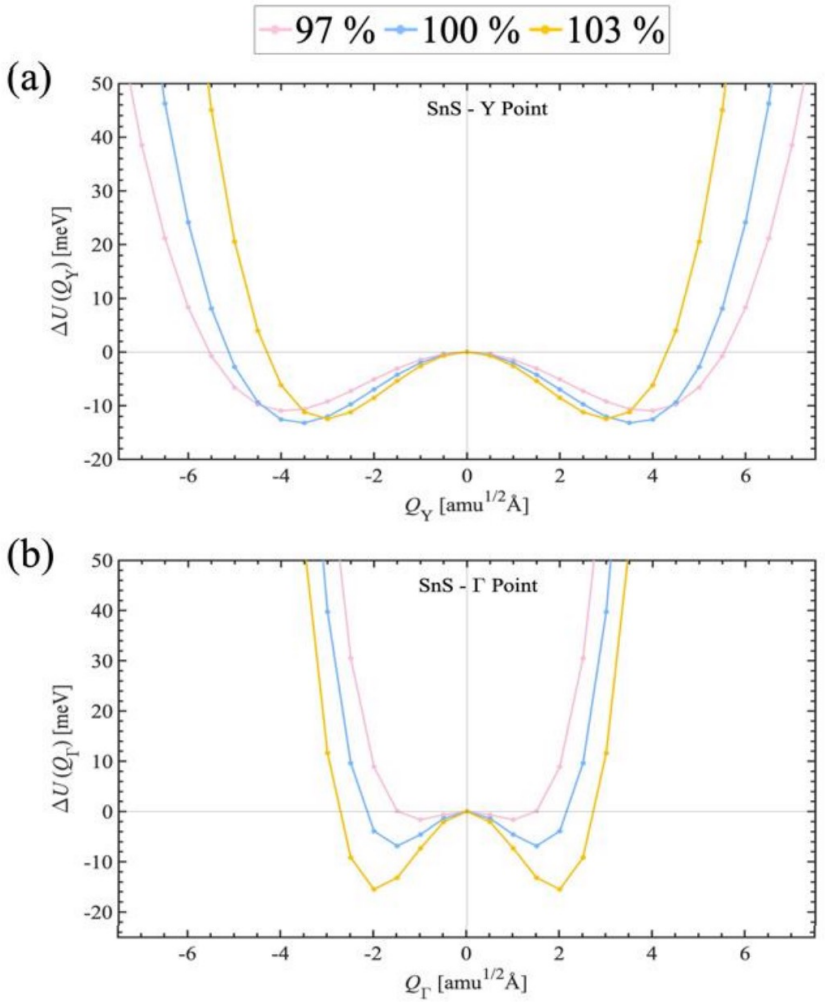

fv Also see fhi-vibes

# Quasi Harmonic Approximation

Pallikara et al., Phys. Chem. Chem. Phys., 2021,23, 19219-19236



# 3rd order phonons

Togo et al., Phys. Rev. B **91**, 094306

## 3-phonon interactions give a finite phonon lifetime which can be used to calculate thermal conductivity

Single mode relaxation time approximation to the Boltzmann transport equation

$$\kappa = \frac{1}{NV_0} \sum_{\lambda} C_{\lambda} \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} \tau_{\lambda}^{\mathrm{SMRT}}$$

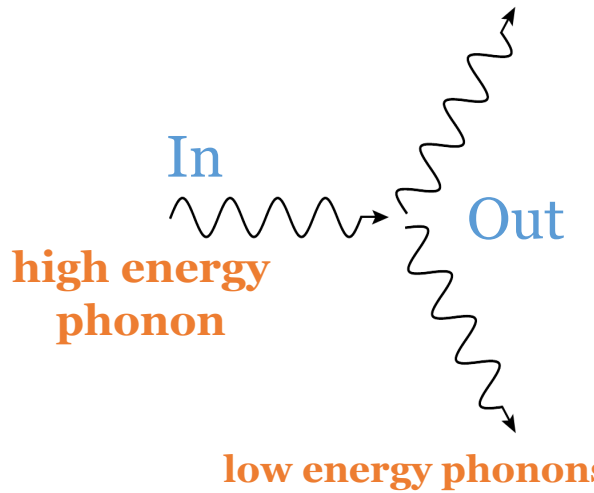
Num. of $q$ in sum

unit cell volume

Heat capacity

Group velocity

Example 3-phonon process




*Note:* This approach ignores higher order terms (e.g. 4-phonon interactions), volume expansion, and scattering from other sources (e.g. impurities or crystal boundaries).

# 3rd order phonons

Togo et al., Phys. Rev. B **91**, 094306

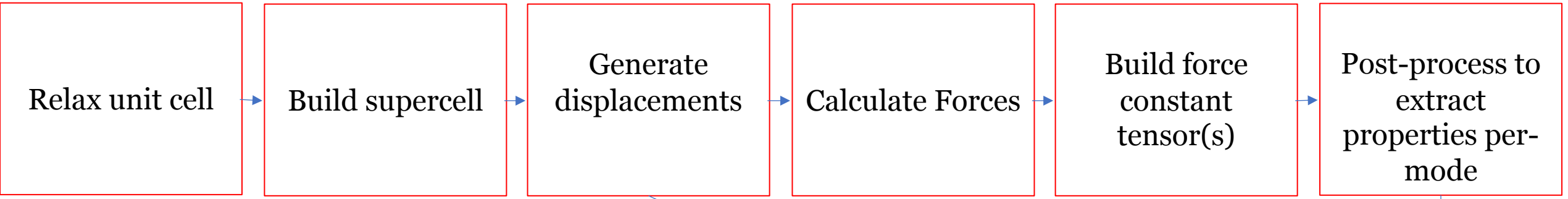
## 3-phonon interactions give a finite phonon lifetime which can be used to calculate thermal conductivity

Now calculating:

$$\Phi_{\alpha\beta\gamma}(i,j,k) = \frac{\partial^3 E}{\partial r_{i,\alpha}\partial r_{j,\beta}\partial r_{k,\gamma}} \approx \frac{-F_{i,\alpha}}{\Delta r_{j,\beta}\Delta r_{k,\gamma}}$$

Similar to the harmonic calc BUT

- Many more displacements
- New parameter "cutpair"
- Computationally demanding post-processing



# Thermal transport

Togo et al., Phys. Rev. B **91**, 094306

## Harmonic phonons also give key insights into thermal transport properties

2nd order calculation

3rd order calculation

$$\kappa = \frac{1}{NV_0} \sum_{\lambda} C_\lambda \mathbf{v}_\lambda \otimes \mathbf{v}_\lambda \tau_\lambda^{\mathrm{SMRT}}$$

$$\tau_\lambda \propto \frac{1}{\Gamma_\lambda}$$

coupling between states

$$\Gamma_\lambda(\omega) = \frac{18\pi}{\hbar^2} \sum_{\lambda'\lambda''} \left|\Phi_{-\lambda\lambda'\lambda''}\right|^2 \{(n_{\lambda'} + n_{\lambda''} + 1)\delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}) + (n_{\lambda'} - n_{\lambda''})\left[\delta(\omega + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''})\right]\},$$

conservation of energy and momentum; are there available states to scatter into?

# Approximation for defect systems

Moxon et al, J. Mater. Chem. A, 2022, 10, 1861

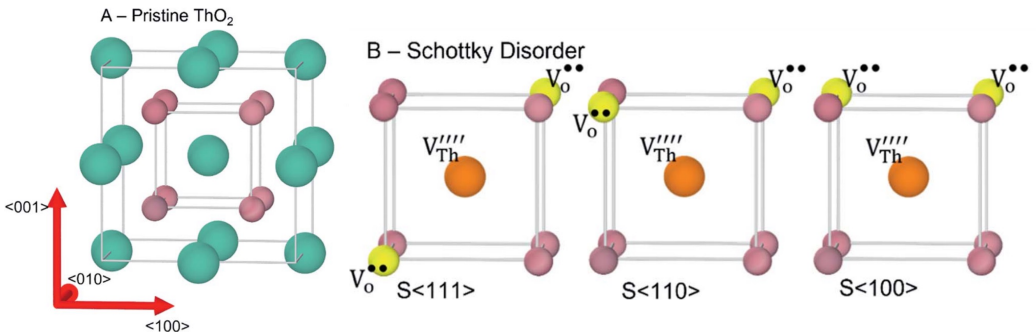
Calculate harmonic phonons for defect systems

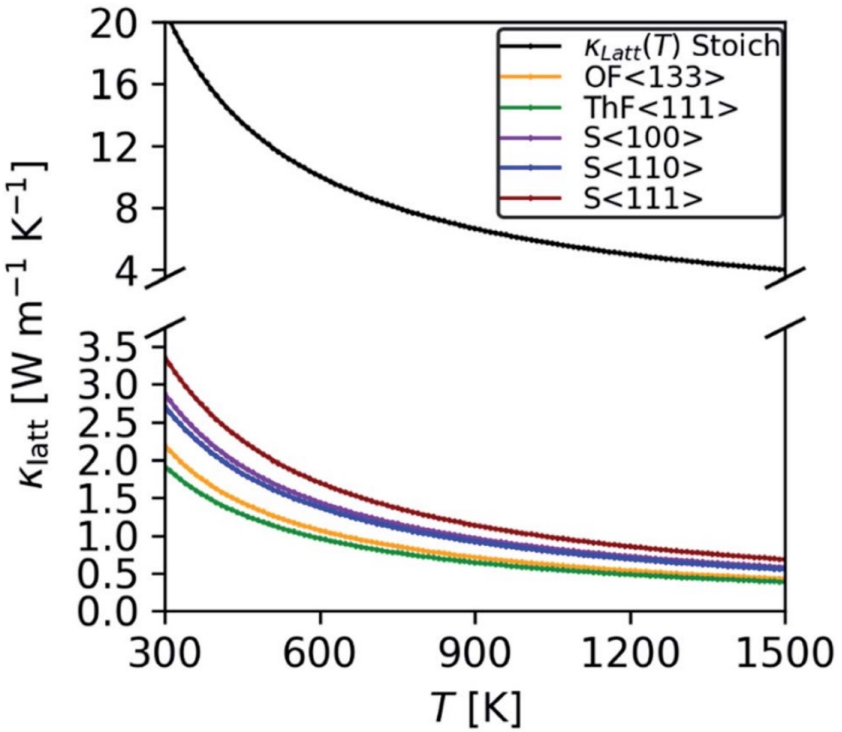
$$\kappa = \frac{1}{NV_0} \sum_{\lambda} C_\lambda \mathbf{v}_\lambda \otimes \mathbf{v}_\lambda \tau_\lambda^{\mathrm{SMRT}}$$

$$\tau_\lambda \propto \frac{1}{\Gamma_\lambda}$$

Calculate interaction strengths for perfect bulk only

$$\Gamma_\lambda(\omega) = \frac{18\pi}{\hbar^2} \sum_{\lambda'\lambda''} \left|\Phi_{-\lambda\lambda'\lambda''}\right|^2 \{(n_{\lambda'} + n_{\lambda''} + 1)\delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}) \ldots$$

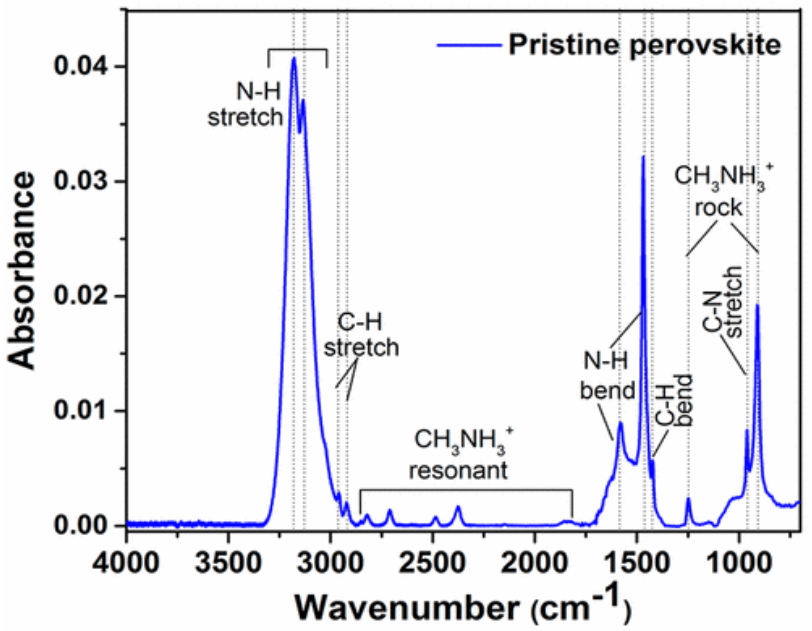


# Physics from Phonons

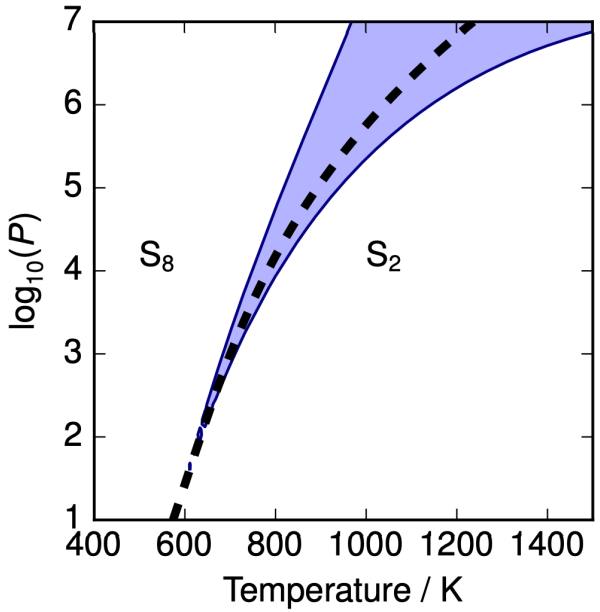
## Various physical observables can be gotten from phonon modes and frequencies

Vibrational spectra



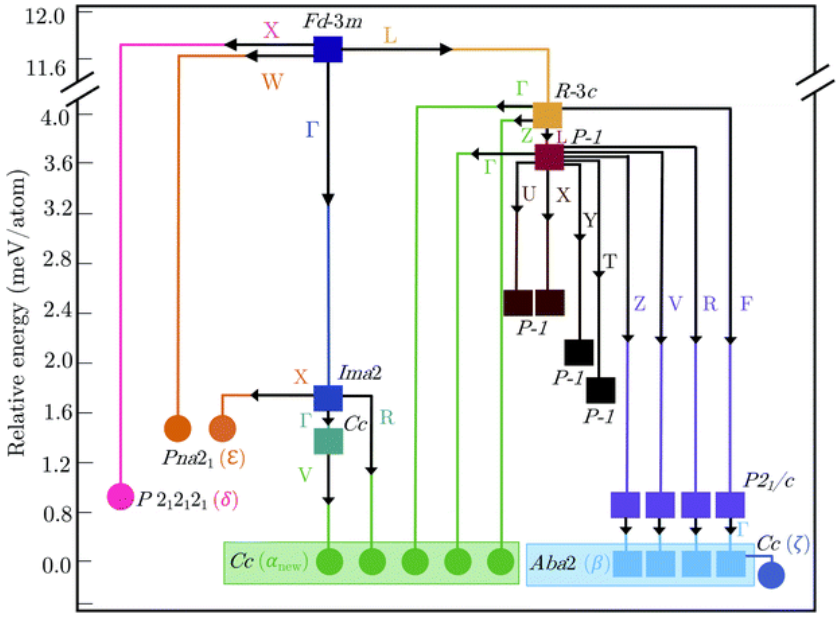

Ruan et al J. Phys. Chem. C 2020, 124, 4, 2265−2272

Free Energies




Jackson et al, Chem. Sci., 2016,7, 1082-1092

Crystal structure prediction




Rahim et al. Chem. Sci., 2020,11, 7904-7909

# Physics from Phonons

Dr Giulia Longo

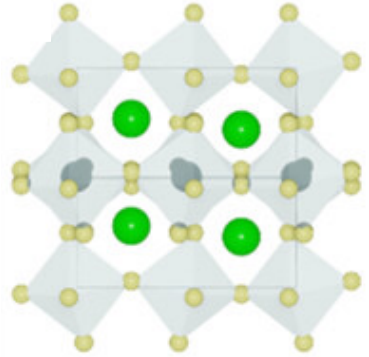
## Case Study: High temperature equilibrium of 3D and Ruddlesden-Popper ($Ba_{n+1}Zr_nS_{3n+1}$) chalcogenide perovskites

Kayastha et al, Solar RRL (2023) 7: 2201078

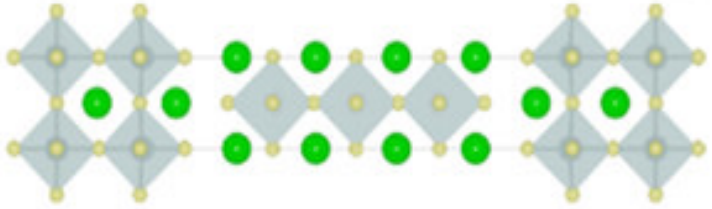
Primary challenge for chalcogenide perovskites: phase control

"The synthesis is pretty damn hard"
- Jonathan Scragg, MRS Fall 2022

$BaZrS_3$ (target)



$Ba_4Zr_3S_{10}$ (RP phase)



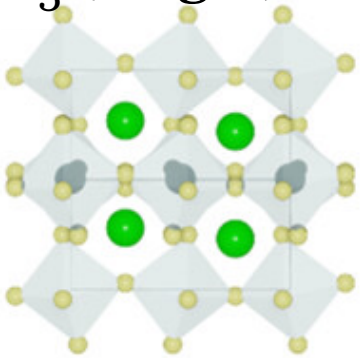
Harmonic phonon spectra →

1) Vibrational spectra
2) Free Energies

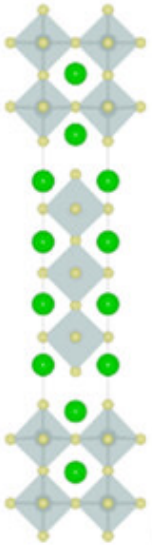
# Raman spectra of chalcogenide perovskite

Kayastha et al, Solar RRL (2023) 7: 2201078

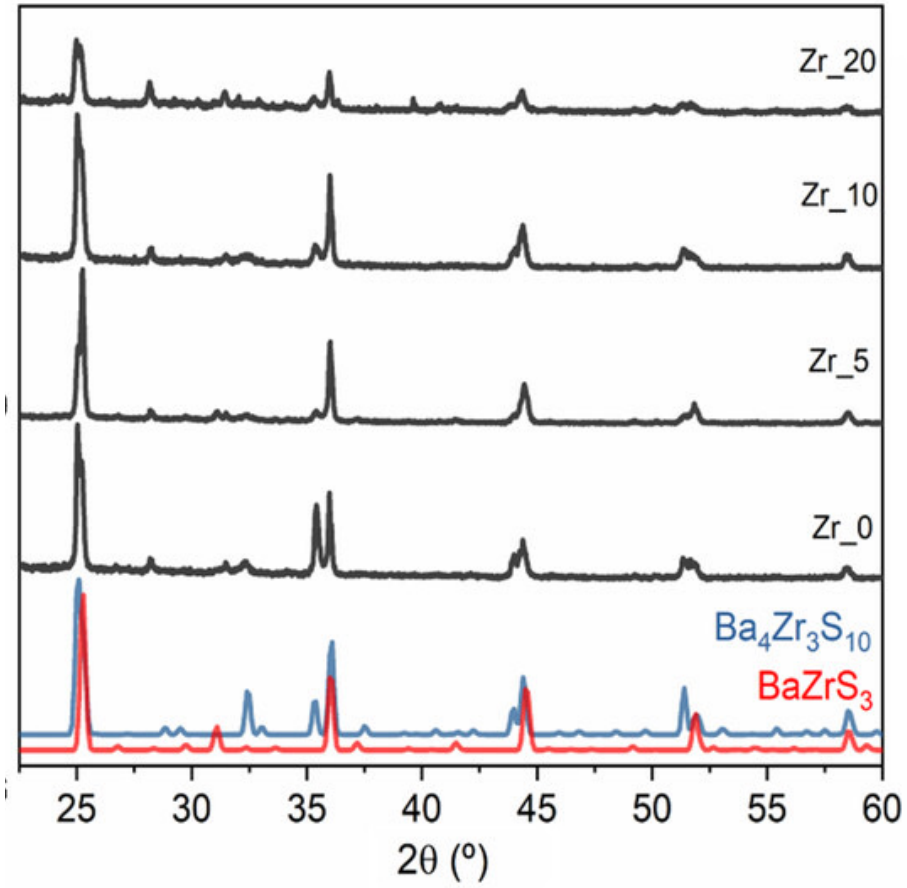
$BaZrS_3$ (target)

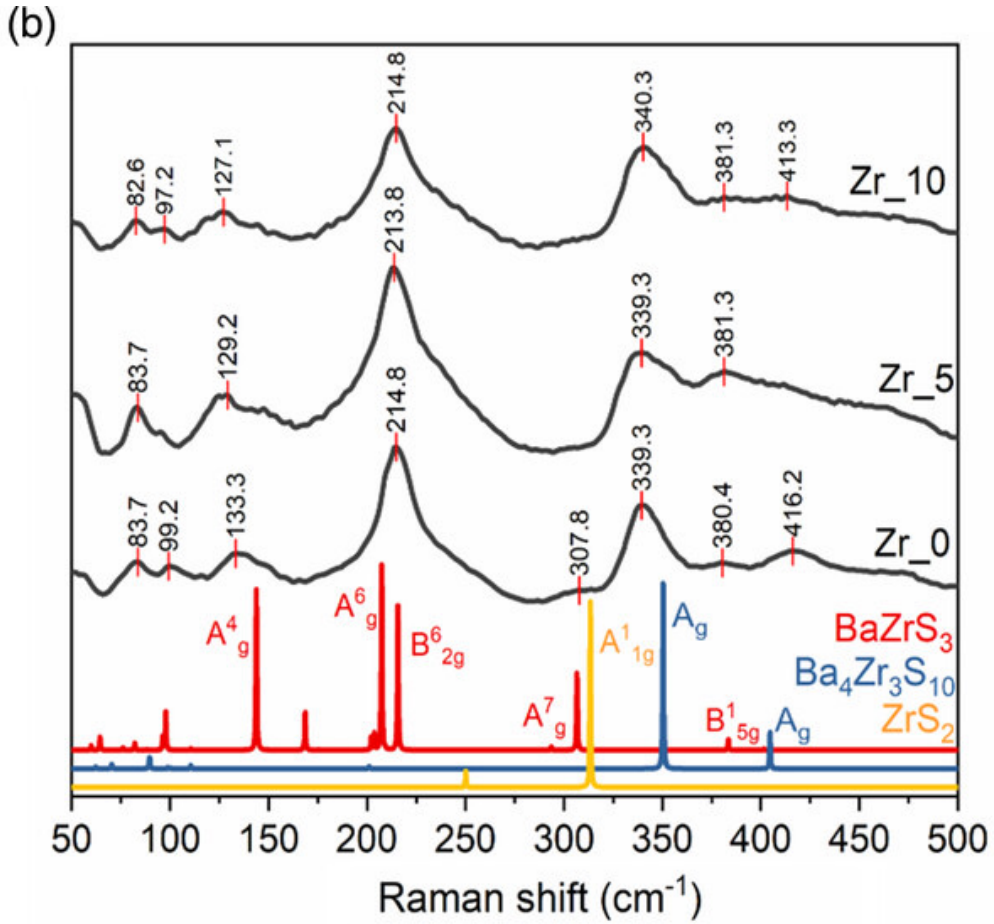


$Ba_4Zr_3S_{10}$

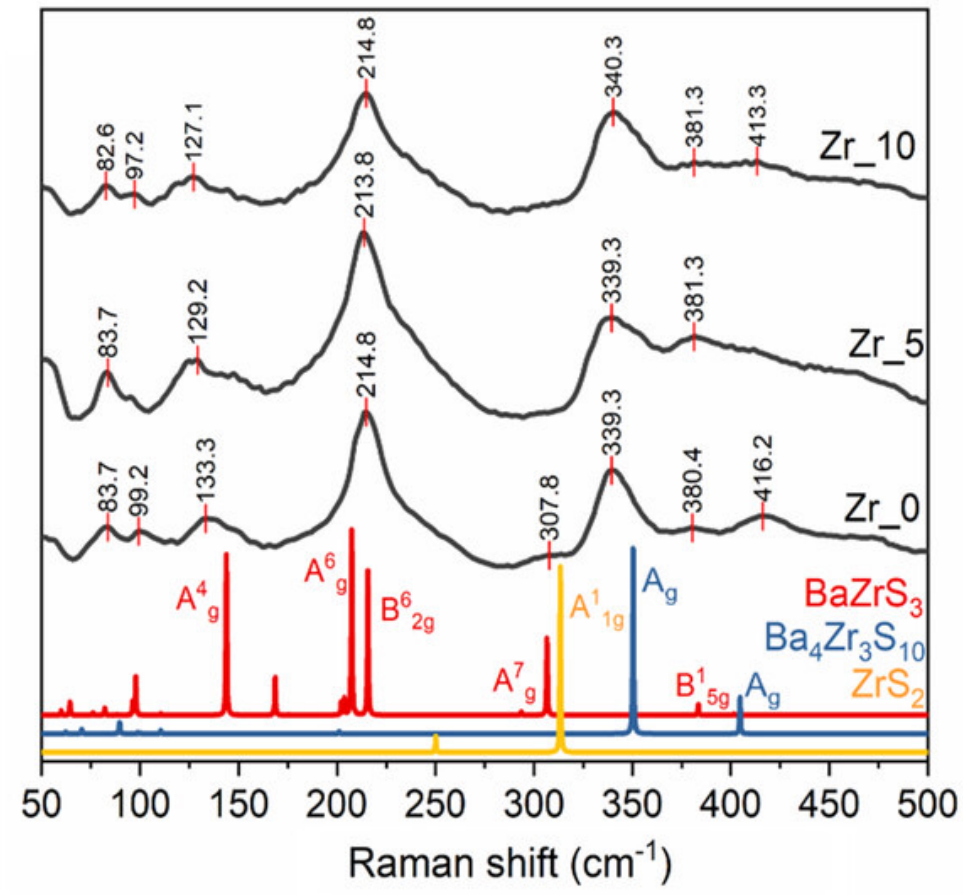


There is a characteristic peak in the Raman spectra for layered RP phases



# Calculating Raman spectra




Prakriti Kayastha
Poster presentation

phonopy + VASP / FHI-aims
The ab initio materials simulation package

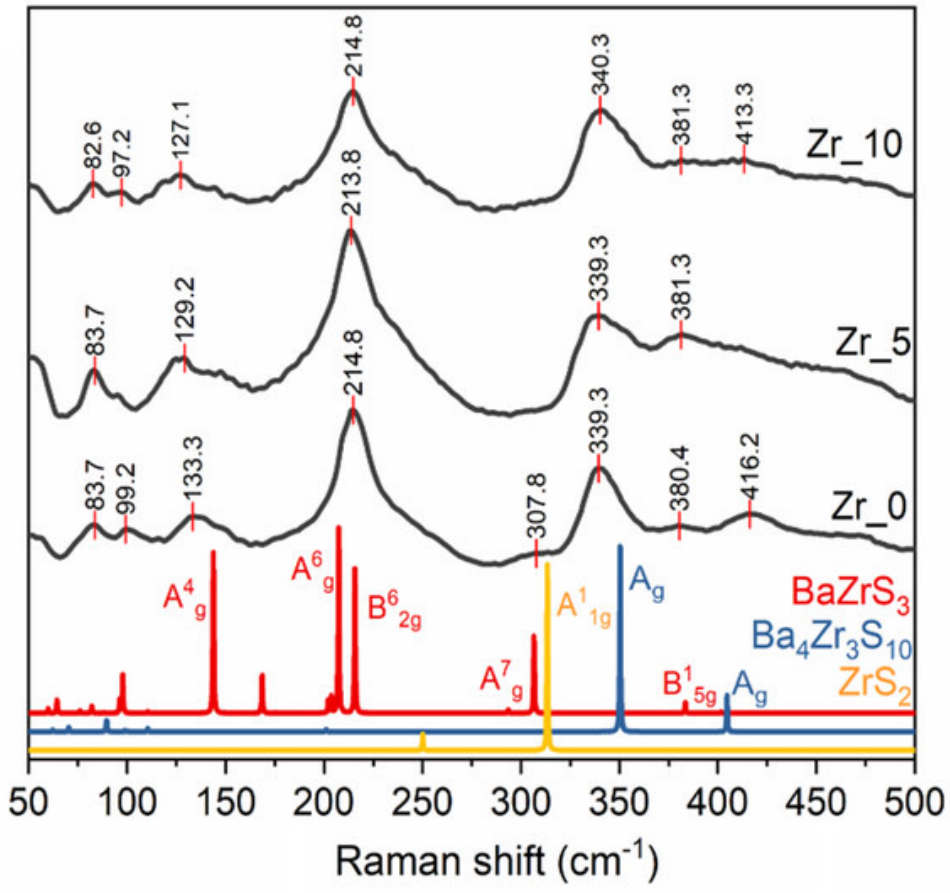
**Phonopy-Spectroscopy**
**github.com/skelton-group/Phonopy-Spectroscopy**

**The Skelton Research Group**
First-principles materials modelling and structural dynamics

- Calculate infrared (IR) intensities
- Calculate Raman-activity tensors
- Output simulated spectra
- Include first-principles mode linewidths

# Calculating Raman spectra

Kayastha et al, Solar RRL (2023) 7: 2201078




## Phonopy-Spectroscopy

**github.com/skelton-group/Phonopy-Spectroscopy**

$$I_{\text{Raman}}(s) \propto \frac{\partial \boldsymbol{\alpha}}{\partial Q(s)} \equiv \frac{\partial \boldsymbol{\varepsilon}^{\infty}}{\partial Q(s)} \approx \frac{\Delta \boldsymbol{\varepsilon}^{\infty}}{\Delta Q(s)}$$

Polarisability tensor

High-frequency dielectric constant

Mode eigenvector

1) Identify Raman active modes
2) Generate displaced structures along each mode
3) Calculate dielectric constants for each structure

Prakriti Kayastha
Poster presentation

----> database of Raman spectra for all competing phases in Ba-Zr-S system

# Thermodynamic Free Energies

See Jackson and Walsh *Phys. Rev. B* 2013 88, 165201

Available online: NU-CEM/ThermoPot

$$\Delta G = \sum_i \Delta n_i \mu_i .$$

$$\mu_i(T,P) = E_i^{\mathrm{DFT}} + E_i^{\mathrm{ZP}} + \int_0^T C_p \mathrm{d}T + PV - TS_{\mathrm{vib}}(T)$$

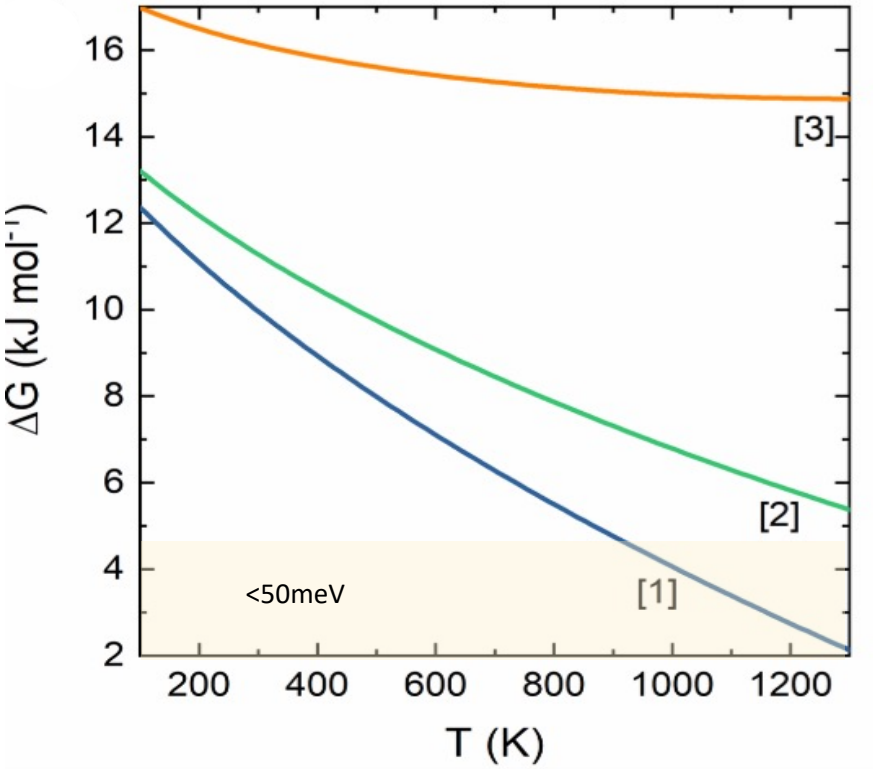
phonon calcs

Three degradation processes to RP phases:

$$\mathbf{BaZrS_3} \rightarrow \tfrac{1}{4}\,\mathbf{Ba_4Zr_3S_{10}} + \tfrac{1}{4}\,\mathbf{ZrS_2} \quad [1]$$

$$\mathbf{BaZrS_3} \rightarrow \tfrac{1}{3}\,\mathbf{Ba_3Zr_2S_7} + \tfrac{1}{3}\,\mathbf{ZrS_2} \quad [2]$$

$$\mathbf{BaZrS_3} \rightarrow \tfrac{1}{2}\,\mathbf{Ba_2ZrS_4} + \tfrac{1}{2}\,\mathbf{ZrS_2} \quad [3]$$




$Ba_3Zr_2S_7$ and $Ba_4Zr_3S_{10}$ are energetically accessible during synthesis at high T

# First-principles Lattice Dynamics

Presentation and example files available here:
http://github.com/nu-CEM/phonons_tutorial/

Dr Giulia Longo
Northumbria
Experimental characterization
BaZrS3

Prakriti Kayastha
Ab-initio calcs
BaZrS3
Poster presentation

Dr Jonathan Skelton
Uni. Manchester
Phonopy-spectroscopy

Dr Adam Jackson
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Ab-initio Thermodyna-mics

**Dr Lucy Whalley**

Northumbria University, Newcastle upon Tyne, United Kingdom

Northumbria University NEWCASTLE

ReNU Renewable Energy Northeast Universities

EPSRC Centre for Doctoral Training in Renewable Energy Northeast Universities

HEC MCC UK

# Help! I have imaginary modes

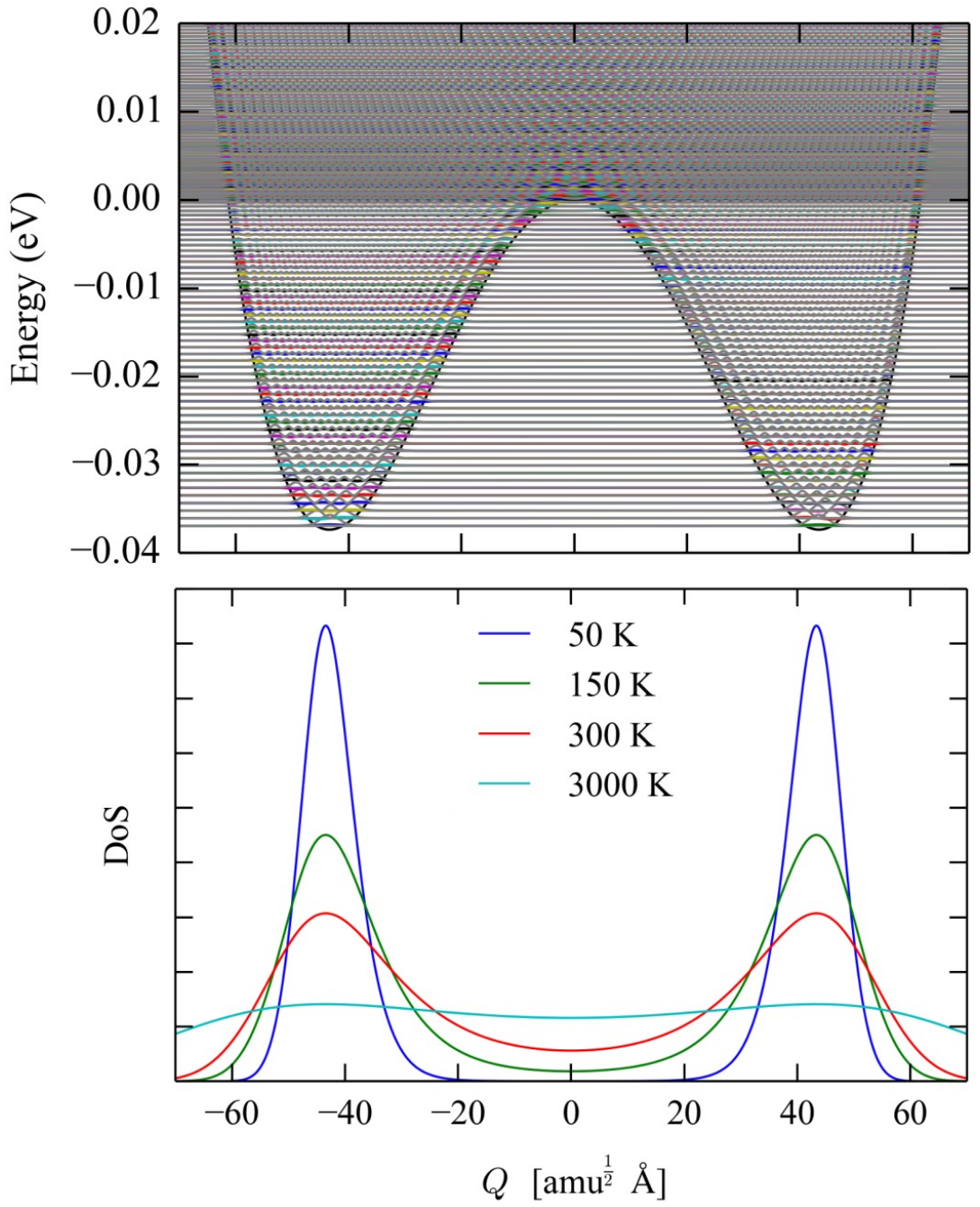
| | Origin of imaginary mode | Solution |
|---|---|---|
| Implementation | Inadequately relaxed structure<br>Inadequately converged technical parameters | Tighten force convergence criteria (e.g. to  eV $Å^{-1}$)<br>Converge forces with respect to the basis set, **k**-point sampling density and SCF convergence criteria |
| | Broken translational symmetry | Increase the size of the density grids and/or enforce the acoustic sum rule as a post-hoc correction |
| | Interpolation artefacts | For finite-difference calculations, select supercells commensurate with the wavevector where the imaginary mode is found (consider using non-diagonal supercells if needed). For DFPT calculations, ensure the **q**-point grid includes the wavevector |
| Physical model | Strongly correlated electrons | Use a suitable exchange–correlation functional for DFT calculations (e.g. DFT + *U* or a hybrid functional), or a suitable alternative theory (e.g. dynamical mean field theory) to calculate forces |
| | Spin-phonon coupling | Include the effects of spin and spin–orbit coupling in calculations |
| Dynamical instability | Dynamic instability (Γ wavevector) | Use phonon mode-mapping to locate lower-energy structure along imaginary mode |
| | Dynamic instability (off-Γ wavevector, typically a zone-boundary point) | Ensure point is commensurate with supercell (finite-differences) or included in the **q**-point sampling grid DFPT, then use mode-mapping as for Γ-point imaginary modes |
| | Dynamic instability in a defective structure | Use mode mapping or break crystal symmetry to allow for localised distortions during geometry optimisation |

From Ioanna Pallikara *et al* 2022 *Electron. Struct.* **4** 033002

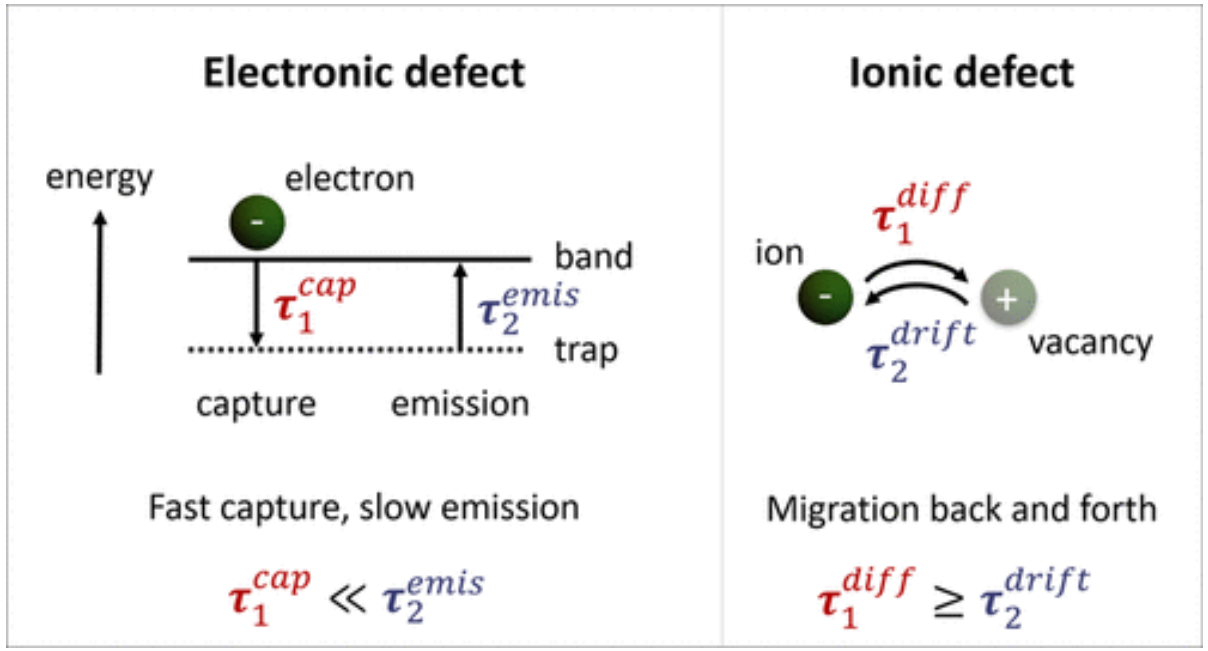
# Final Note: Reproducible science

Jupyter Notebooks as SI
Adam Jackson Repo
Publishing Data
Zenodo DOIs

# Ab-initio p rials



# i. Defect properties are difficult to measure




Futscher and Deibel, *ACS Energy Lett.* 2022, 7, 1, 140−144

The ionic response can dominate over the electronic response

*Caution when interpreting e.g. DLTS*