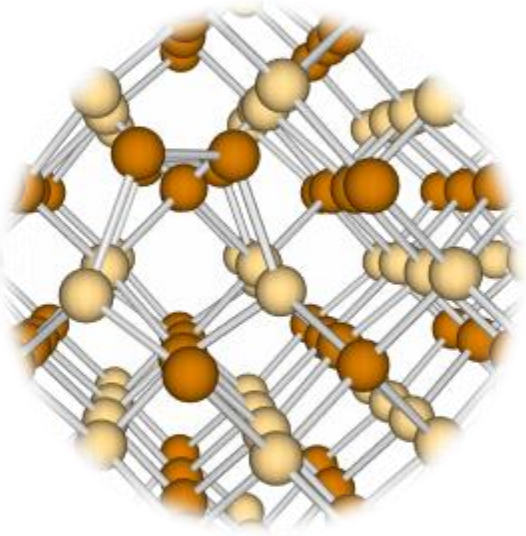
IMPERIAL

Modelling Point Defects at Device Operating Conditions

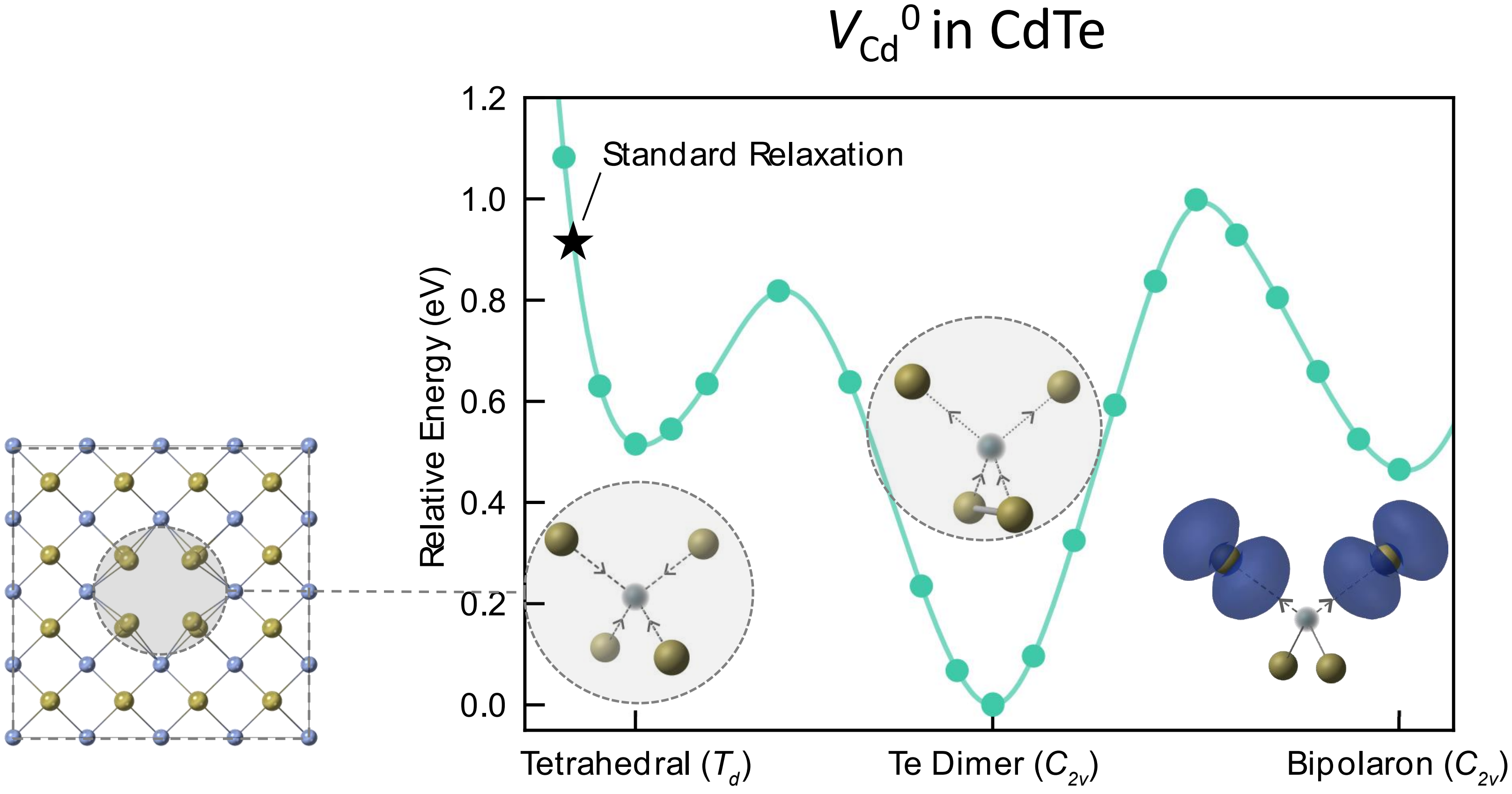
I. Mosquera-Lois & A. Walsh

WG2 meeting in Birmingham

25/03/2025



Point defects have complex landscapes



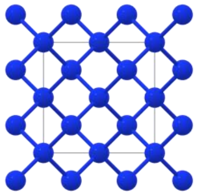
I. Mosquera-Lois & S. R. Kavanagh, *Matter,* 2021
I. Mosquera-Lois†, S. R. Kavanagh†, A. Walsh & D. O. Scanlon, *npj Comput. Mater.,* 2023

Defect symmetry-breaking is widespread

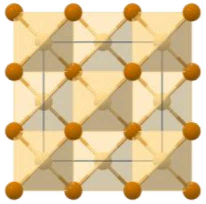
ShakeNBreak

Complex energy surfaces observed in ***every* material** we studied

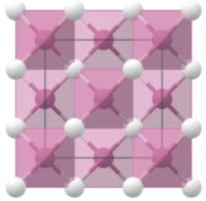
Si



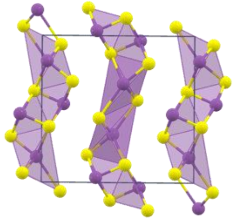
CdTe



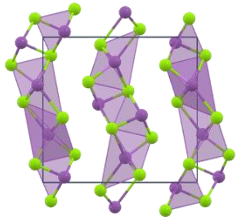
GaAs



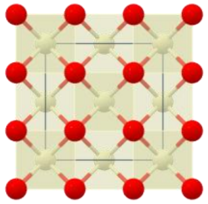
Sb_2S_3



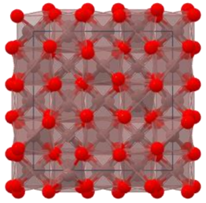
Sb_2Se_3



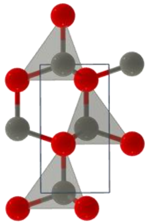
CeO_2



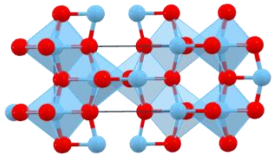
In_2O_3

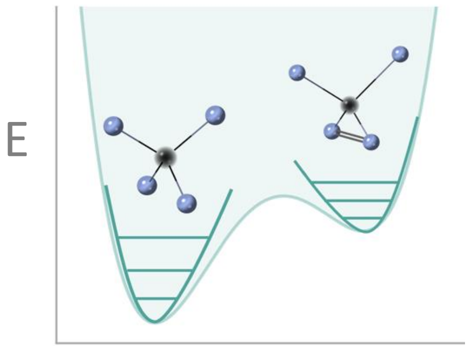


ZnO



TiO_2





I. Mosquera-Lois[†], S. R. Kavanagh[†], A. Walsh & D. O. Scanlon, *J. Open Source Softw.*, 2022
I. Mosquera-Lois[†], S. R. Kavanagh[†], A. Walsh & D. O. Scanlon, *npj Comput. Mater.*, 2023
I. Mosquera-Lois, S. R. Kavanagh, A. M. Ganose & A. Walsh, *npj Comput. Mater.*, 2024

How does this affect predicted concentrations?

Thermodynamic description of defect formation at $T_{synthesis}$

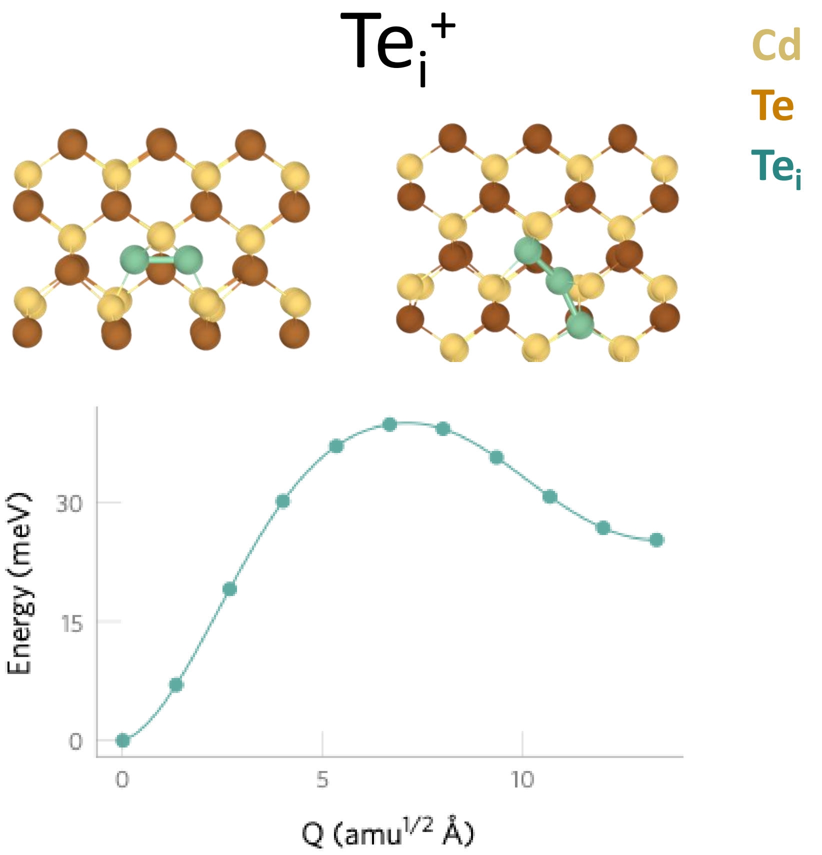
Cd_xTe_x + Te → Cd_xTe_{x+1}

$$c_{eq} = \exp\left(\frac{-g_f(T)}{k_B T}\right)$$

$$g_f(T) \approx u_f(T) - \cancel{T \cdot s_f(T)}$$
$$\approx u_f(0\ \mathrm{K})$$

Standard approach neglects $s_f(T)$

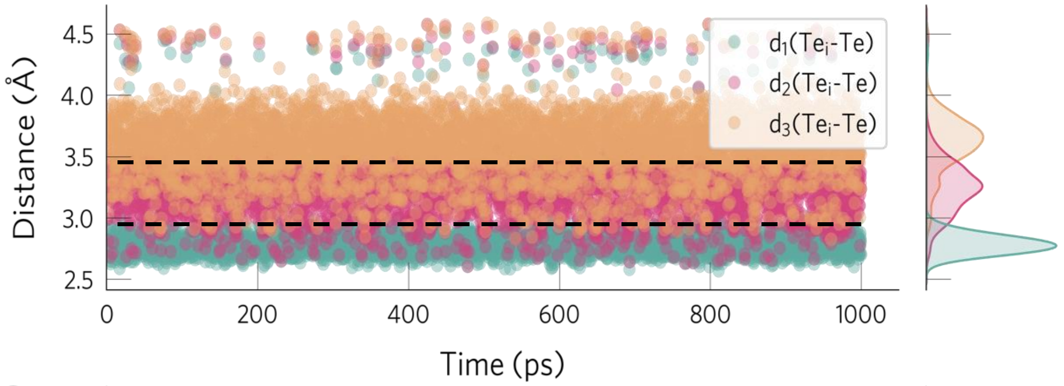
→ How does $s_f(T)$ affect predicted c_{eq}?

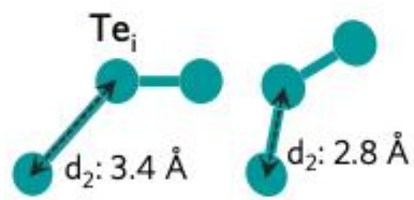


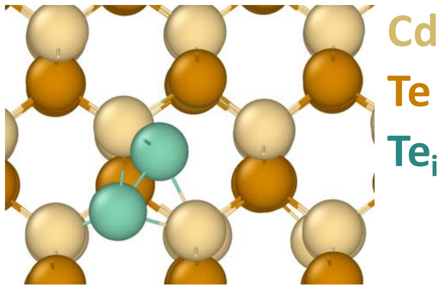
S. R. Kavanagh, D. O. Scanlon, A. Walsh & Freysoldt, *Faraday Diss.* 2022
I. Mosquera-Lois, J. Klarbring & A. Walsh, *arXiv.* 2024

What happens at $T_{\text{operation}}$? (1 ns, 300 K)

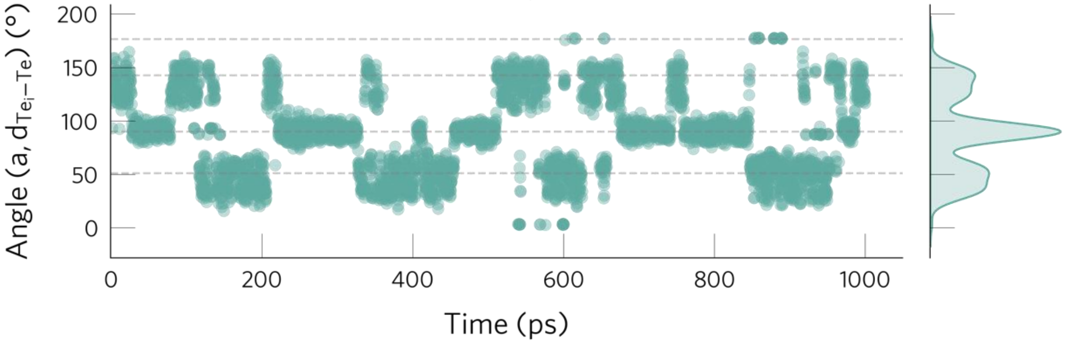
Configuration change

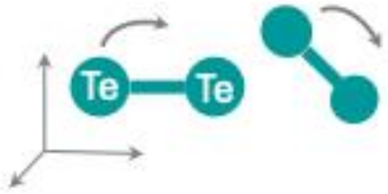


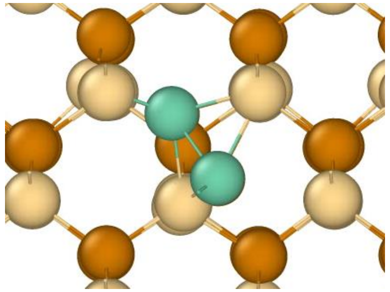




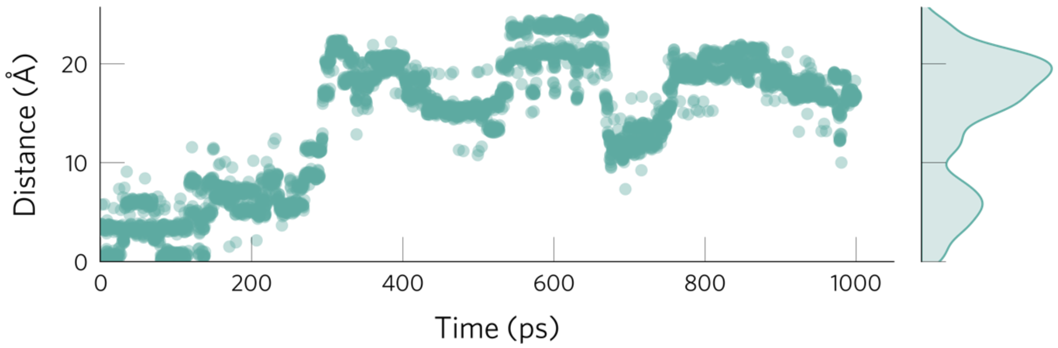
Rotation

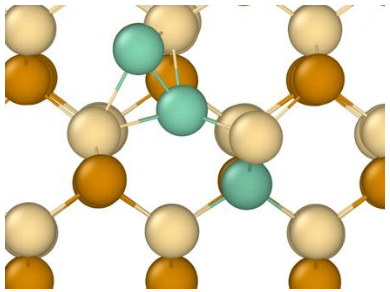






Migration

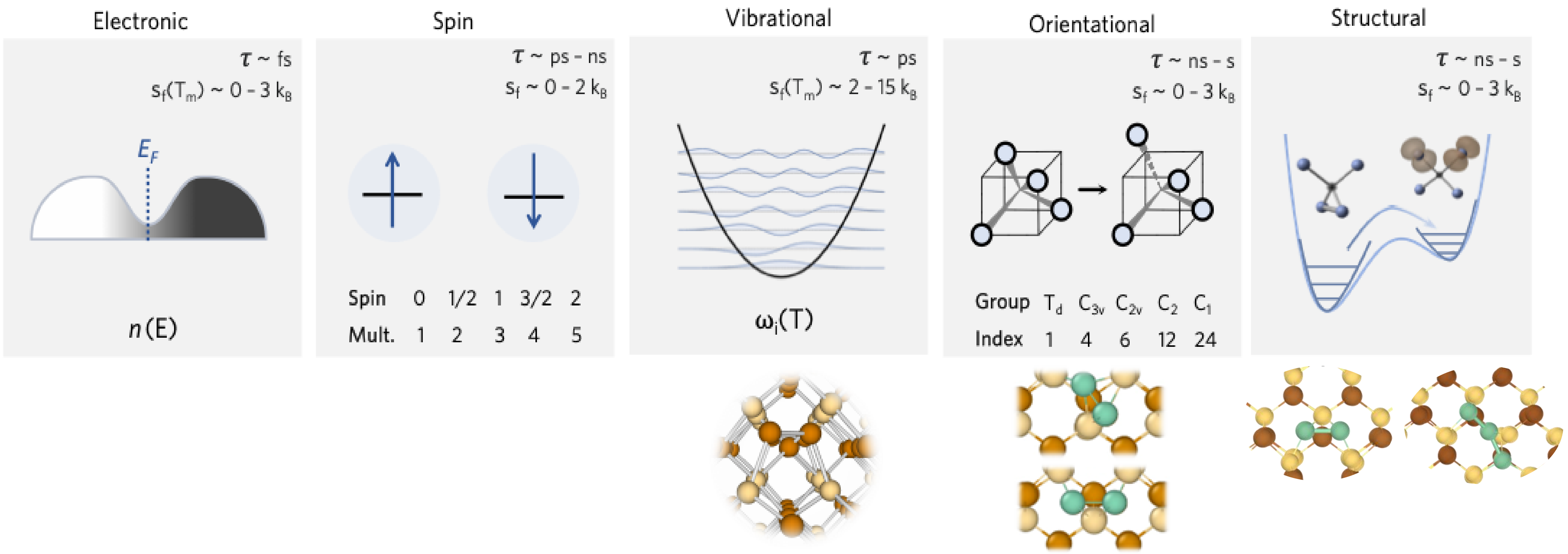




I. Mosquera-Lois, J. Klarbring & A. Walsh. *arXiv,* 2024

How do we calculate $s_f(T)$?

Degrees of freedom that change upon defect formation

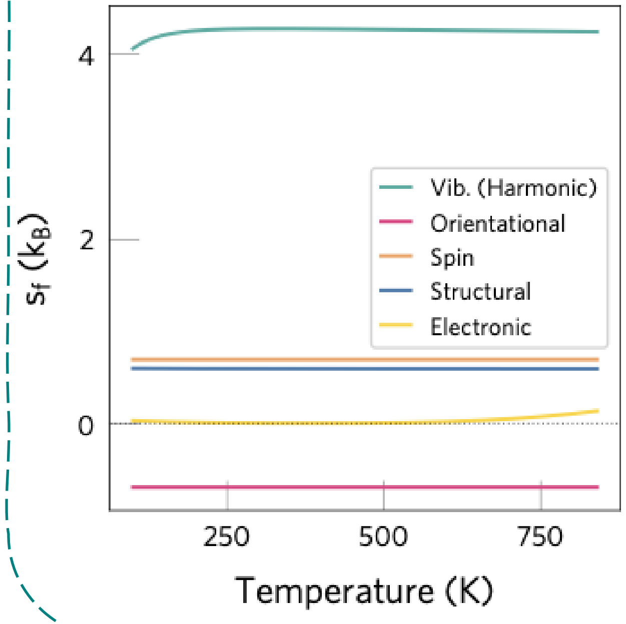


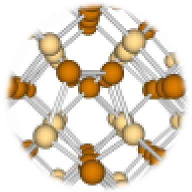
$$s_f \approx s_f^{elec} + s_f^{spin} + s_f^{vib} + s_f^{orient} + s_f^{structural}$$

I. Mosquera-Lois, J. Klarbring & A. Walsh. *arXiv,* 2024

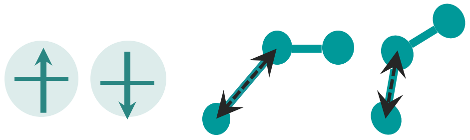
How much do thermal effects impact [c]?

$$s_f \approx s_f^{elec} + s_f^{spin} + s_f^{orient} + s_f^{struc} + s_f^{vib}$$



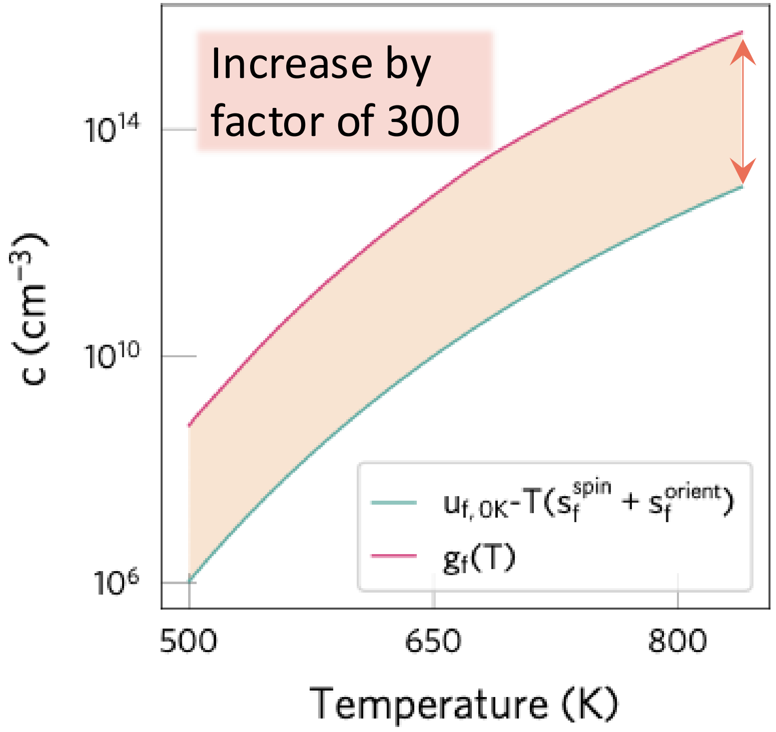


Vibrational contribution dominates



$$g_f(T) \approx u_f(T) - T\cdot s_f(T)$$

$$c_{eq} \propto \exp\left(\frac{-g_f}{k_B T}\right)$$



Increase by factor of 300

I. Mosquera-Lois, J. Klarbring & A. Walsh. *arXiv,* 2024

When will thermal effects be important?

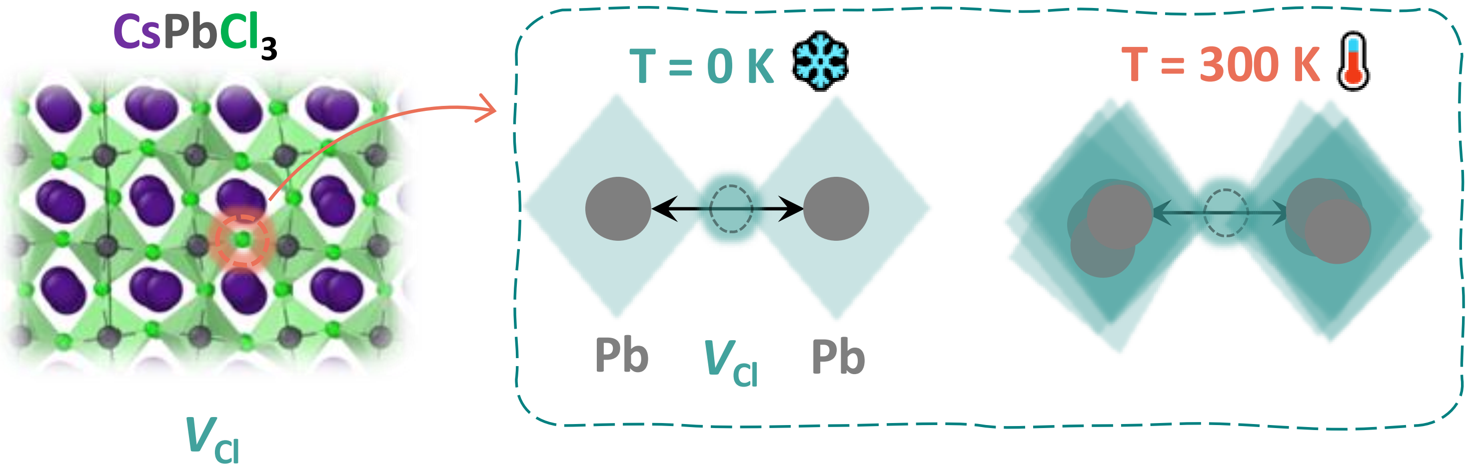
Calculating s_f (T) is 💸 – When to bother?

- Defect-wise
  - Structural reconstruction: $s^{\mathrm{vibrational}}$
  - Low-symmetry: $s^{\mathrm{orientational}}$
  - Low-energy metastable configurations: $s^{\mathrm{structural}}$
- Materials
  - Soft/dynamic/disordered lattices
  - High $T_{\mathrm{synthesis/processing}}$ 🌡️

I. Mosquera-Lois, J. Klarbring & A. Walsh. *arXiv,* 2024

How do thermal effects affect **electronic behaviour**?

- Thermal effects are important for **accurate concentrations**
- What about **electronic behaviour**?



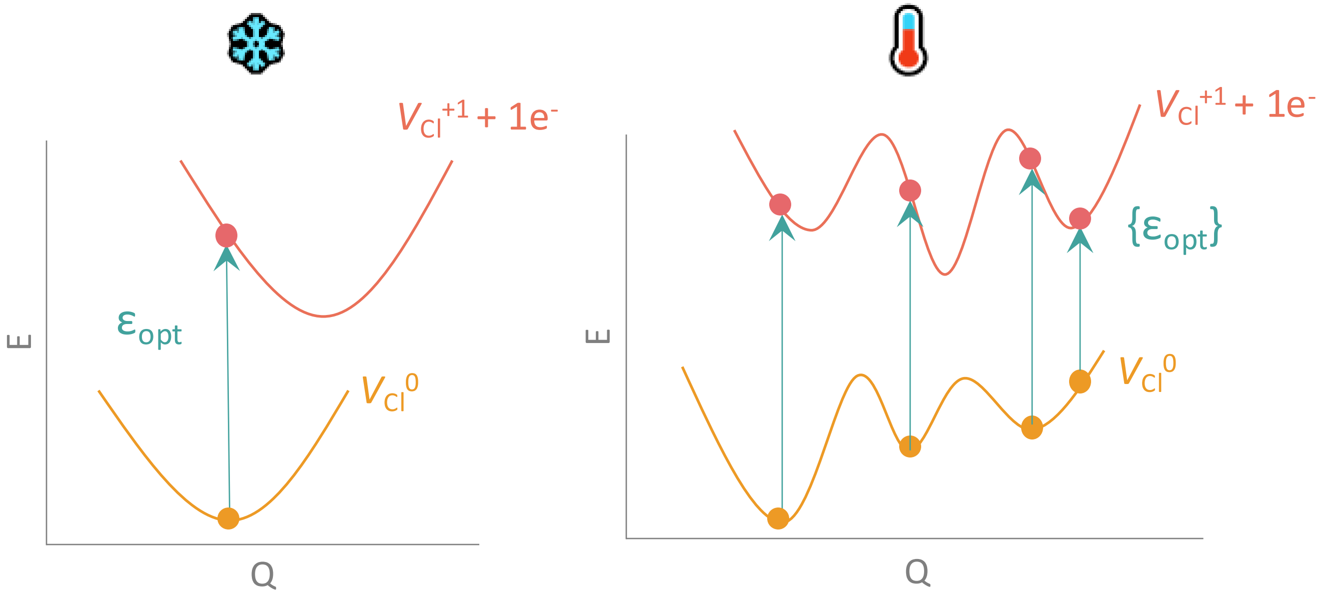
At $T_{operation}$ defect is **dynamic**

I. Mosquera-Lois & A. Walsh. *In preparation*, 2025

From 0 K to $T_{operation}$: $\varepsilon_{opt}(0/+1)$

Optical behaviour: Optical defect level

- Fast electronic transition between two charge states without atomic relaxation
- Exciting an e^- from V_{Cl} to CBM: $V_{Cl}^0 + h\upsilon \rightarrow V_{Cl}^{+1} + 1e^-$ (CBM)

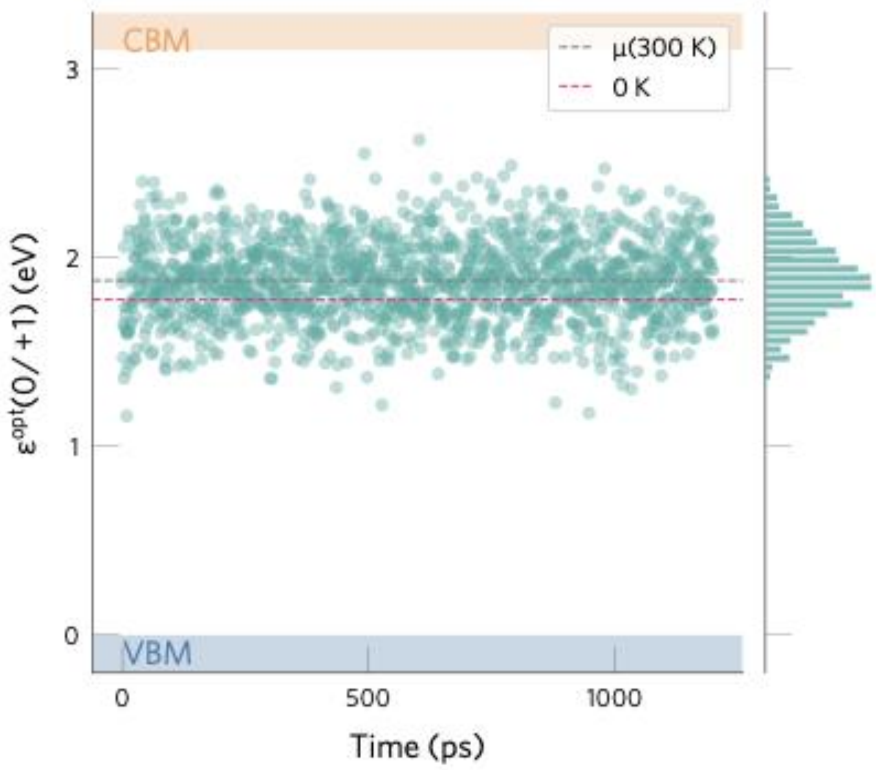


I. Mosquera-Lois & A. Walsh. *In preparation,* 2025

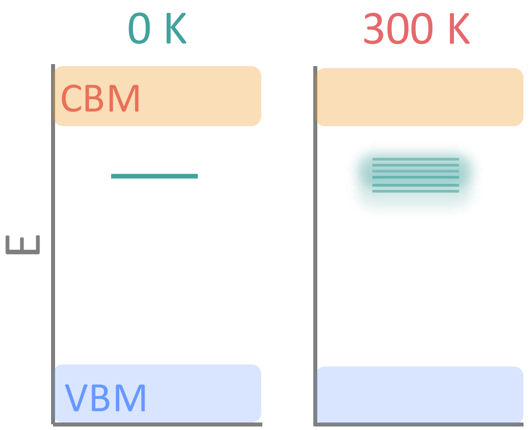
From 0 K to $T_{operation}$: $\varepsilon_{opt}(0/+1)$

- MD at 300 K for V_{Cl}^0 → Sample configurations → Calculate $\{\varepsilon_{opt}\}$

Distribution of $\varepsilon_{opt}(0/+1)$ at 300 K



- ε_{opt} increases by **0.1 eV** at 300 K → ε_{opt} (0K) ✅
- **2σ = 0.4 eV** → Significant variation of observed ε_{opt}



When will 🌡️ be non-negligible?

- Defects
  - Metastability
- Soft crystals
  - Thermal motion (Oh tilting)
  - Thermal expansion
  - Disorder

I. Mosquera-Lois & A. Walsh. *In preparation*, 2025

Conclusions

- Point defects often have **complex configurational landscapes**

- Entropic effects can be important to predict **accurate c_{defect}**
  - Vibrational term dominates
  - High $T_{synthesis}$

- Thermal effects can affect predicted **electronic behaviour**
  - Soft crystals
  - Complex defects (metastability, structural reconstructions)

I. Mosquera-Lois & A. Walsh. *In preparation,* 2025

Acknowledgements

Aron Walsh

Johan Klarbring

Seán R. Kavanagh

David O. Scanlon

"la Caixa"

IMPERIAL

MATERIALS AND MOLECULAR MODELLING HUB

archer2

ShakeNBreak

doped

Thank you!

Calculating g_f (T) is challenging

→ Approximations

1. Neglect s_f

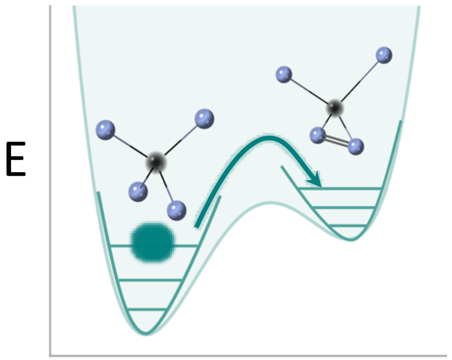
$$g_f(T) \approx u_f(T) - \cancel{T\cdot s_f(T)}$$

- Calculating s_f is
- $u_f >> Ts_f$

2. Static picture

Defect is ***frozen*** in ground state (0 K) configuration

Properties sensitive to defect structure



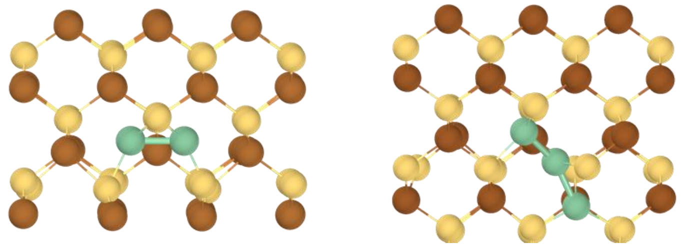
1. S. R. Kavanagh, A. Walsh & D. O. Scanlon, *ACS Energy Lett.* 2021
2. S. R. Kavanagh, D. O. Scanlon, A. Walsh & Freysoldt, Faraday Diss. 2022

1. How much will thermal effects impact predicted concentrations & metastable configurations?
2. How to accurately describe **defect entropies**?

➡ MLFF to reduce the computational cost

Test systems: CdTe

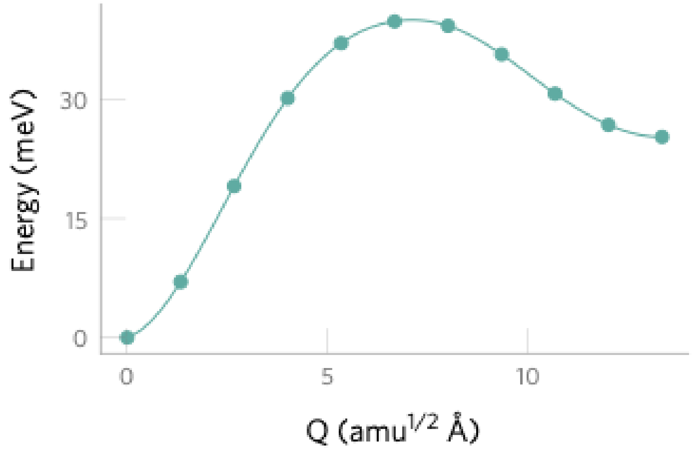
Te_i^+



Cd

Te

Te_i



Defect formation

$Cd_xTe_x + Te \rightarrow Cd_xTe_{x+1}$

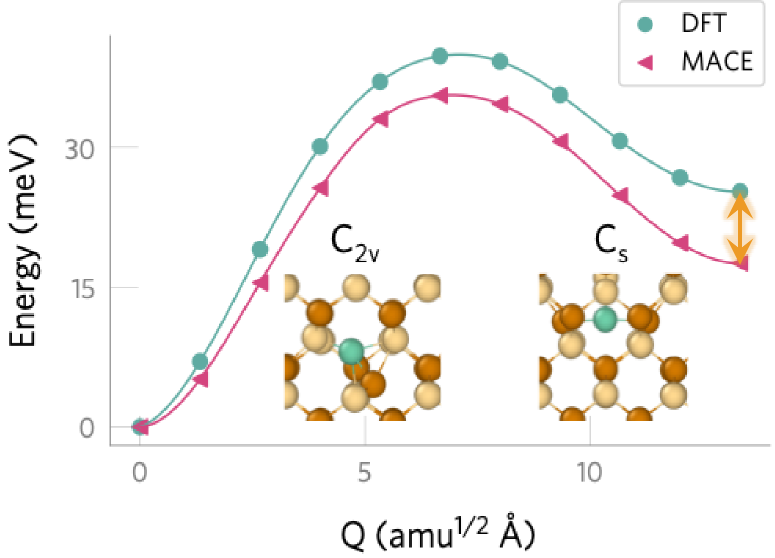
CdTe
Te_i^+
Te

Conditions

T_{anneal}= 840 K, P=1 atm
$T_{operation}$= 300 K

MACE force field 0-900 K

Test MAE(Energy) < 1 meV/atom

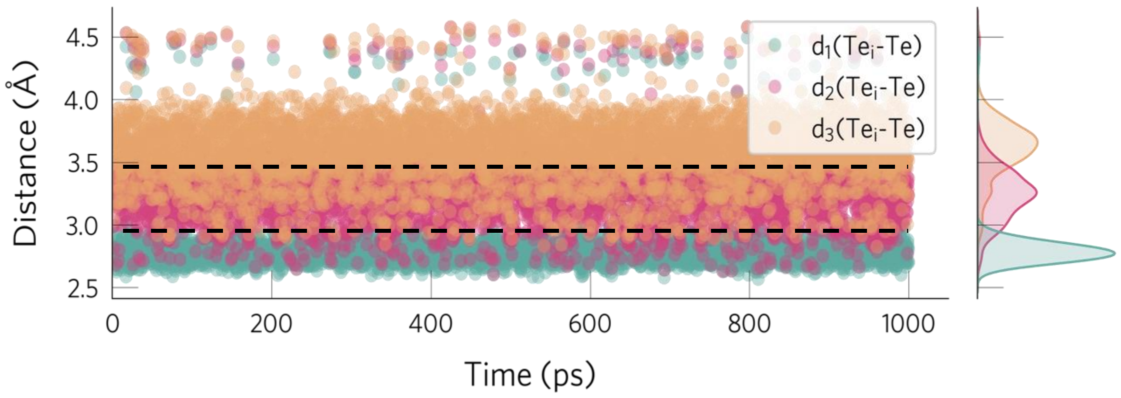


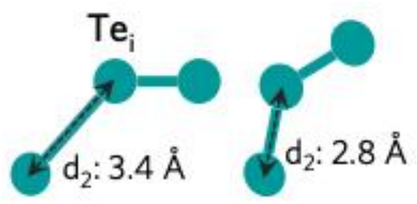
0.1 meV/atom

S. R. Kavanagh, D. O. Scanlon, A. Walsh & Freysoldt, *Faraday Diss.* 2022
S. Hamadna and J.G. Amar, *J. Condens. Matter Phys.* 2024

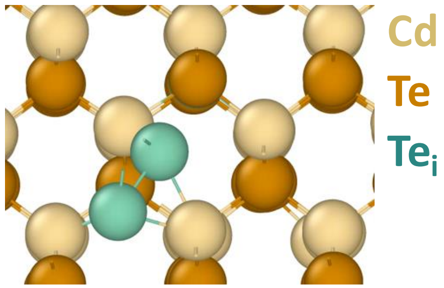
Defect behaviour at operating temperature (1 ns, 300 K)

Configuration change





50% 50%



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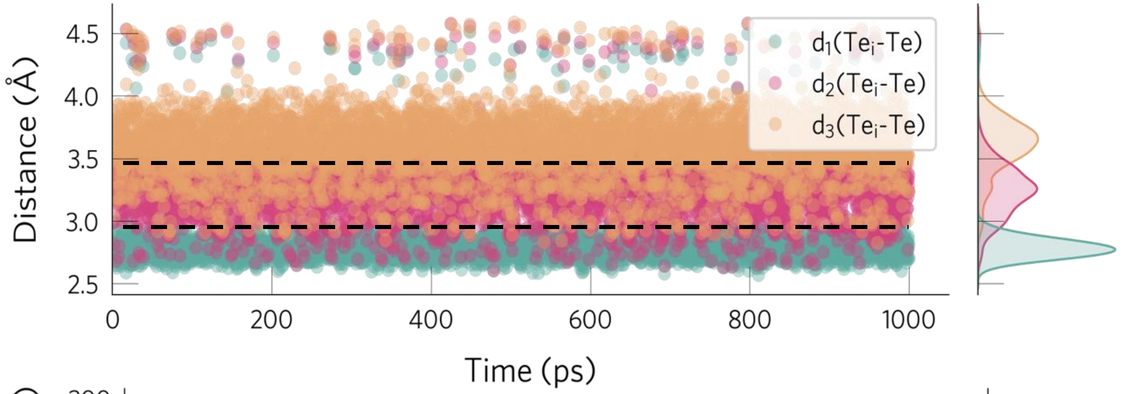
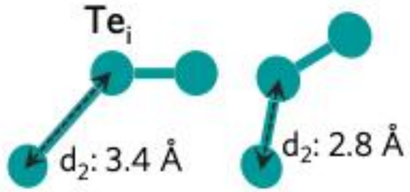
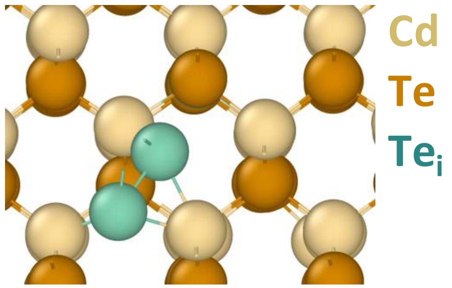
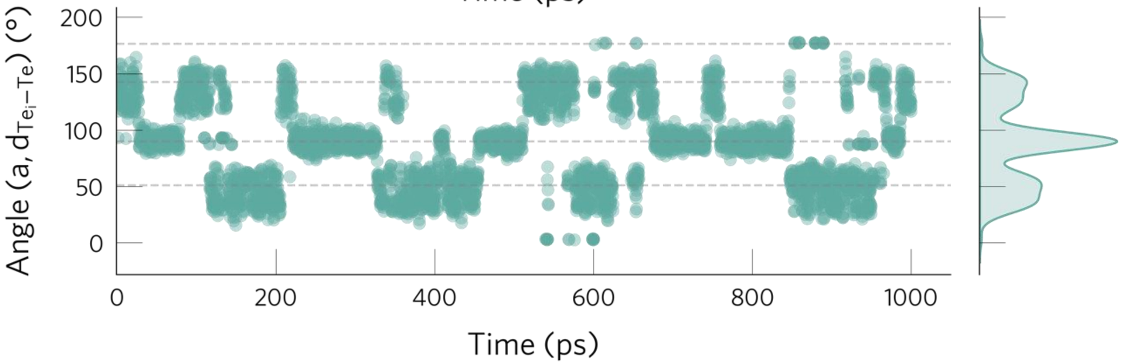
Configuration change

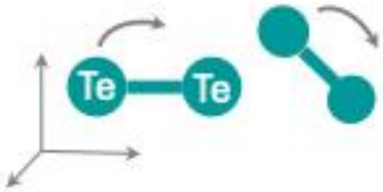


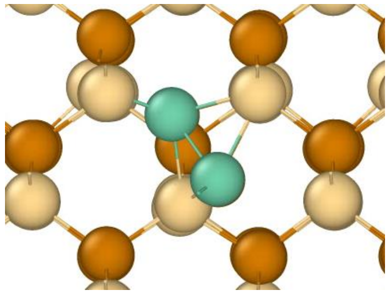




Rotation

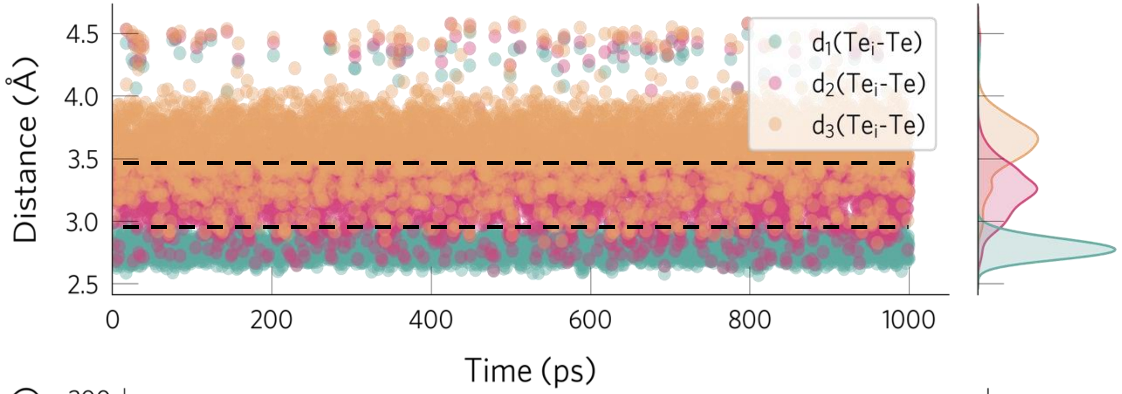


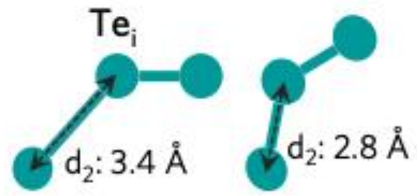


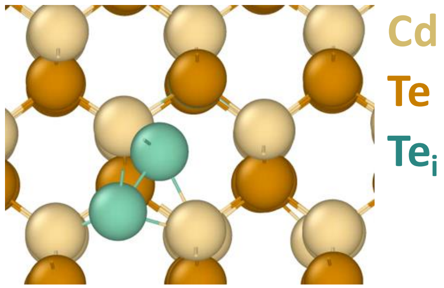


Defect behaviour at operating temperature (1 ns, 300 K)

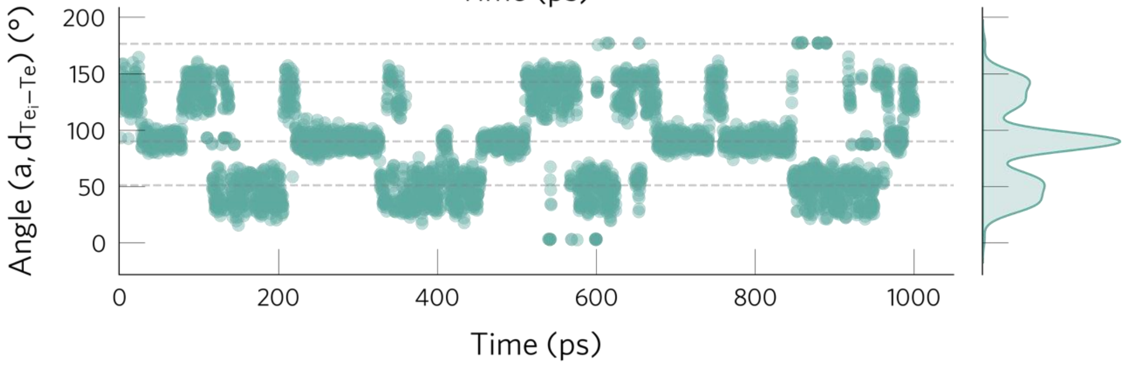
Configuration change

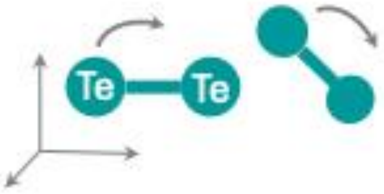


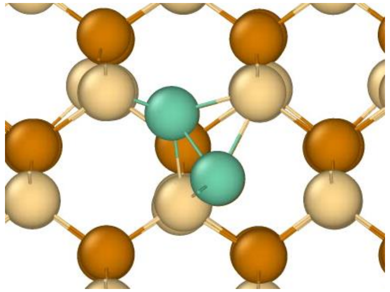




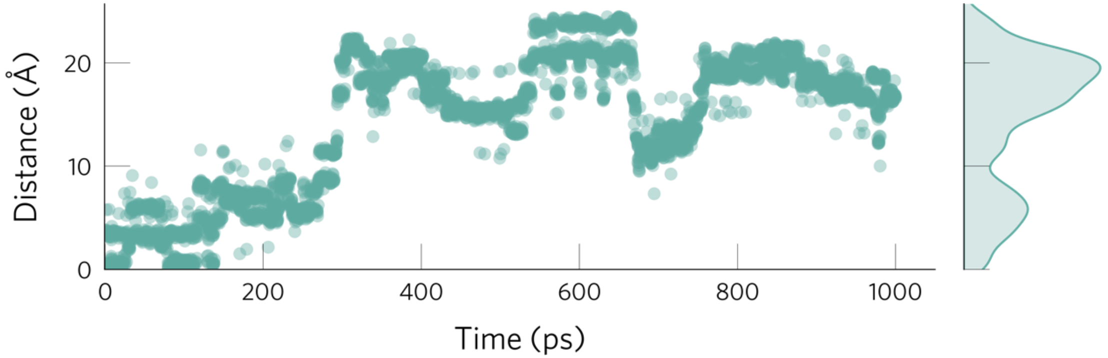
Rotation

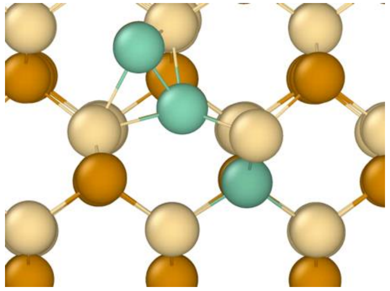






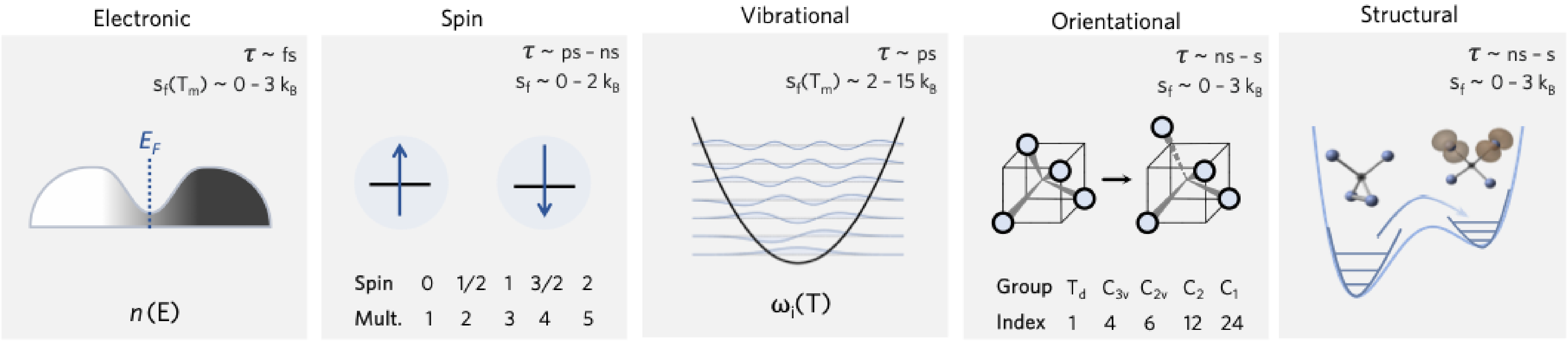
Migration

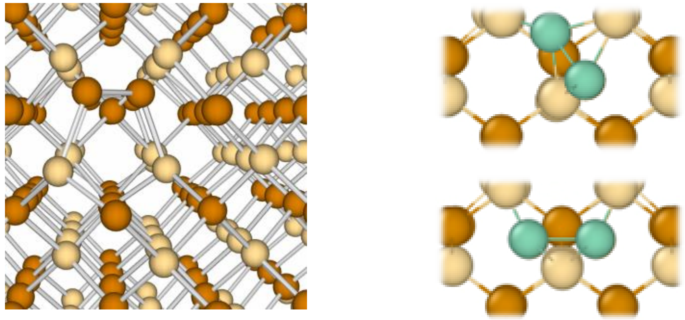




Modelling thermal effects

What factors contribute to s_f?





$$s_f \approx s_f^{elec} + s_f^{spin} + s_f^{vib} + s_f^{orient} + s_f^{structural}$$

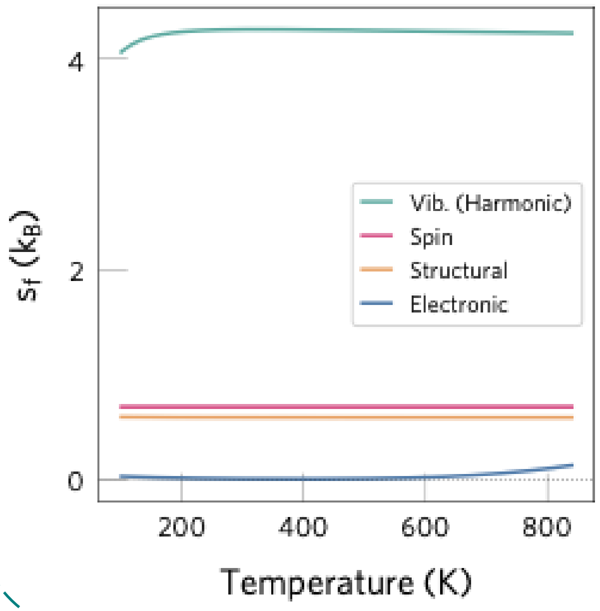
I. Mosquera-Lois, S. R. Kavanagh, J. Klarbring, K. Tolborg & A. Walsh, *Chem. Soc. Rev.*,. 2023

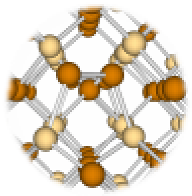
Defect formation entropy

a) Decoupling **all** degrees of freedom

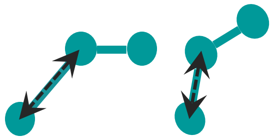
- Harmonic approximation

$$S_f \approx S_f^{\mathrm{elec}} + S_f^{\mathrm{spin}} + S_f^{\mathrm{struc}} + S_f^{\mathrm{vib}}$$





↑ ↓ 1 unpaired electron



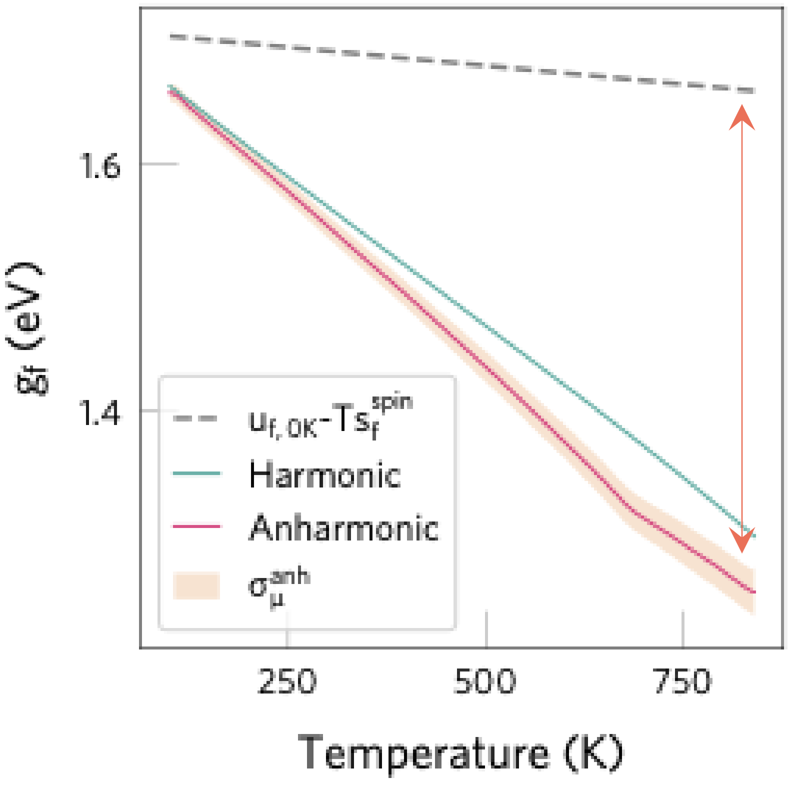
b) Decoupling electronic from ionic

- Ionic motions coupled at high T
- Thermodynamic integration

$$S_f \approx S_f^{\mathrm{elec}} + S_f^{\mathrm{spin}} + S_f^{\mathrm{ionic}}$$

Effect on predicted Te_i^+ concentration

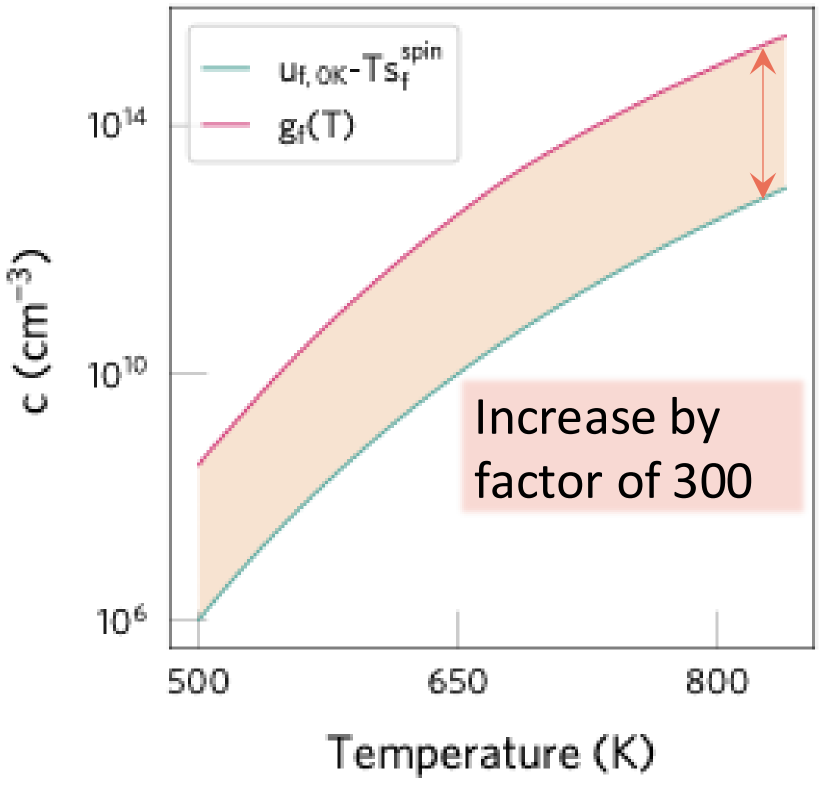
$g_f(T) \approx u_f(T) - T \cdot s_f(T)$



Thermal effects are important

Decoupling approach ✅

$c_{eq} \propto \exp\left(\frac{-g_f}{k_B T}\right)$

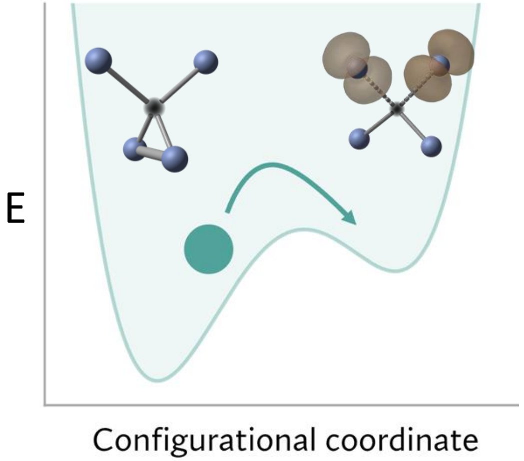


Increase by factor of 300

Conclusions

🌡️ effects are important

- **Defects** with accessible metastable configurations
  ➡ different behaviour than ground state configuration
  - High $T_{operation}$

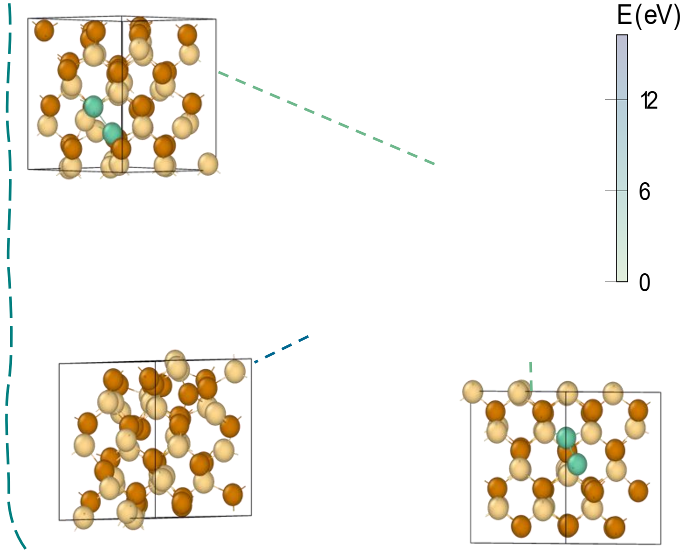


- **Concentrations**
  - Harmonic approximation ✅
    - Dynamic defect
  - Applications with high $T_{synthesis}$ (e.g. T>1000 K)
    - Thermochemical water splitting, exhaust automotive catalysts, solid-state fuel cells

- MLFFs to go beyond '0 K static' picture
  - Longer length and timescales

How accurate are MLFFs for defects?

Defect training set



Validation on unseen test set

Energy MAE: 0.6 meV/atom

Validating the MLFF

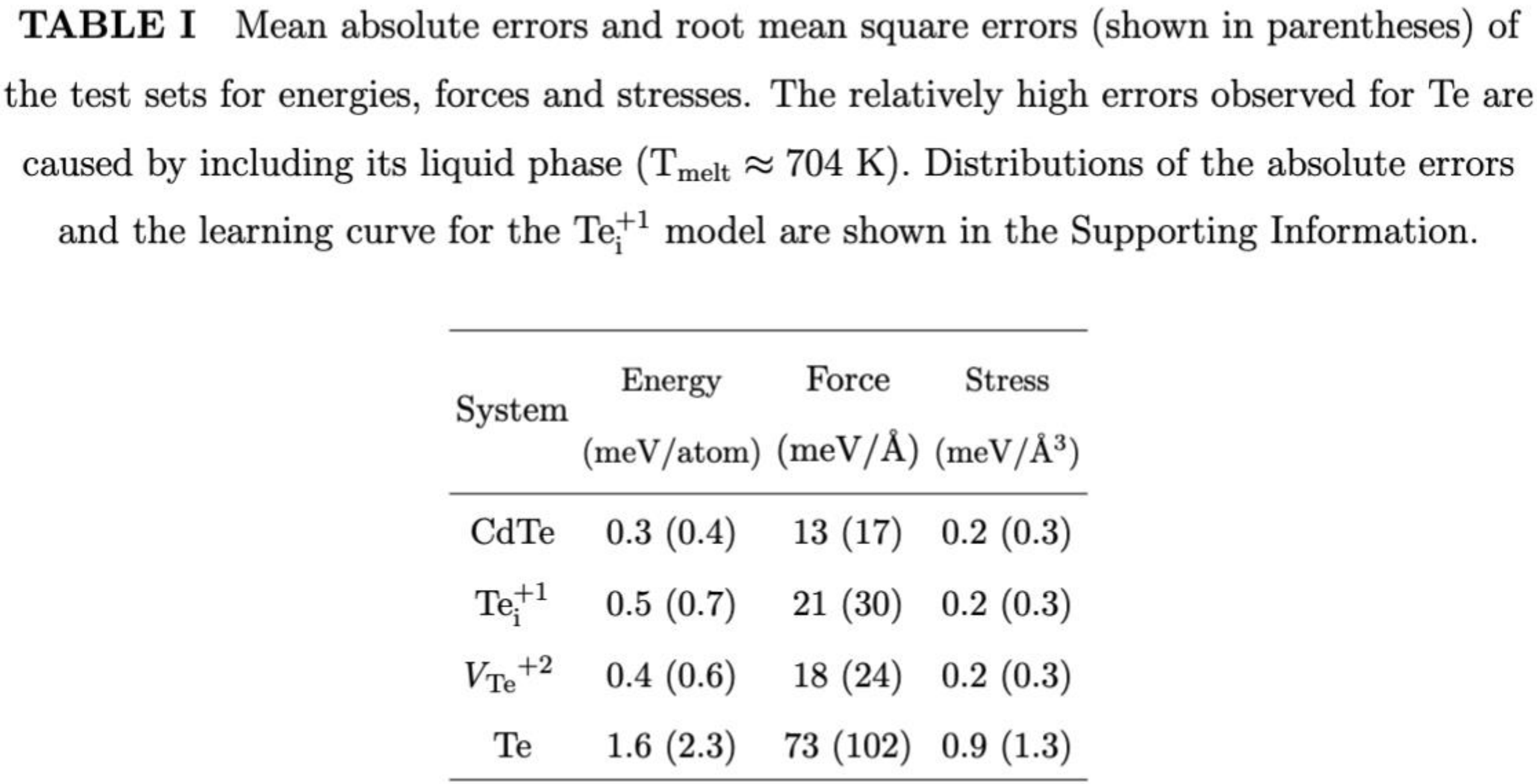
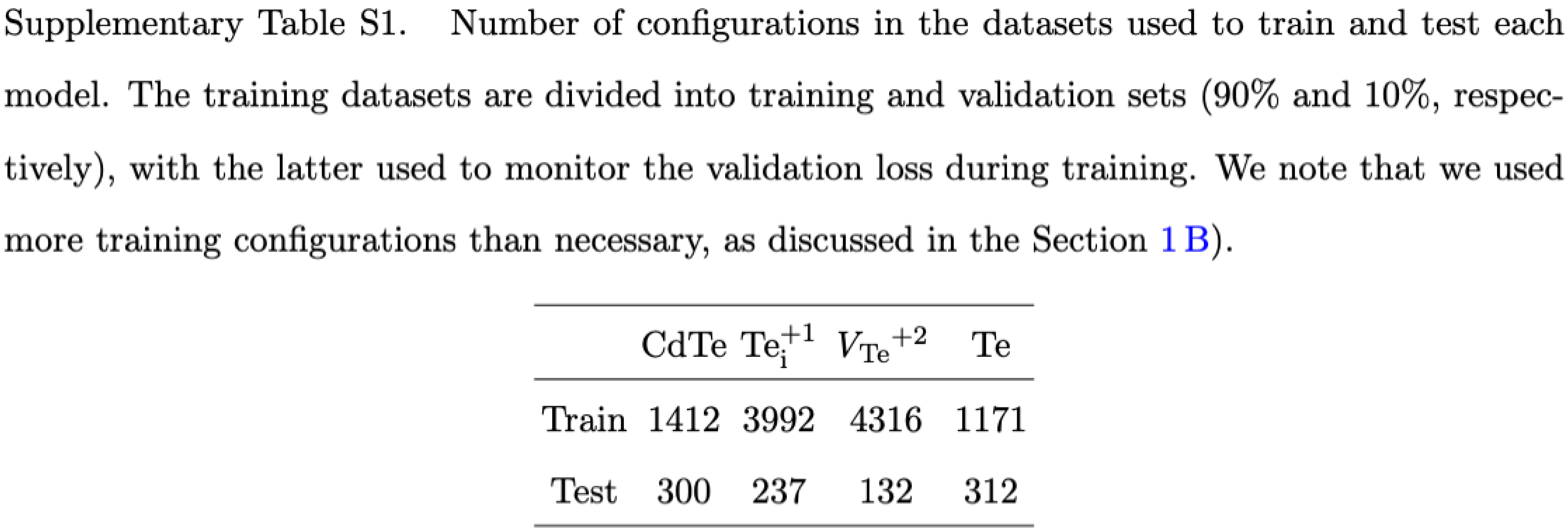


TABLE I Mean absolute errors and root mean square errors (shown in parentheses) of the test sets for energies, forces and stresses. The relatively high errors observed for Te are caused by including its liquid phase ($T_{\mathrm{melt}} \approx 704$ K). Distributions of the absolute errors and the learning curve for the $\mathrm{Te}_{\mathrm{i}}^{+1}$ model are shown in the Supporting Information.

System	Energy (meV/atom)	Force (meV/Å)	Stress (meV/Å^3)
CdTe	0.3 (0.4)	13 (17)	0.2 (0.3)
$\mathrm{Te}_{\mathrm{i}}^{+1}$	0.5 (0.7)	21 (30)	0.2 (0.3)
$V_{\mathrm{Te}}{}^{+2}$	0.4 (0.6)	18 (24)	0.2 (0.3)
Te	1.6 (2.3)	73 (102)	0.9 (1.3)

Validating the MLFF

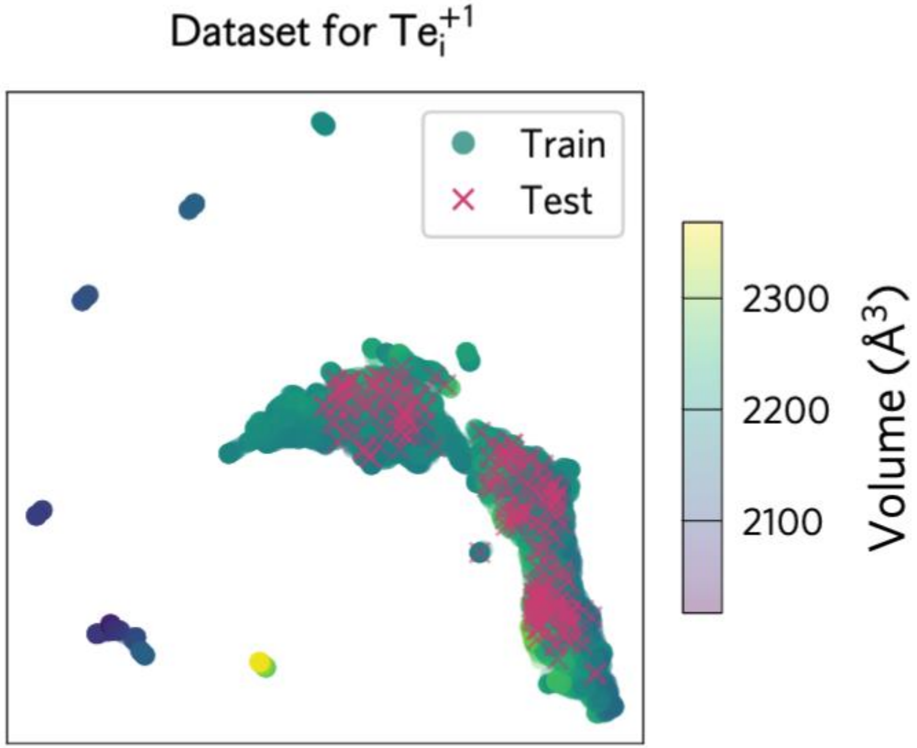


Supplementary Table S1. Number of configurations in the datasets used to train and test each model. The training datasets are divided into training and validation sets (90% and 10%, respectively), with the latter used to monitor the validation loss during training. We note that we used more training configurations than necessary, as discussed in the Section 1 B).

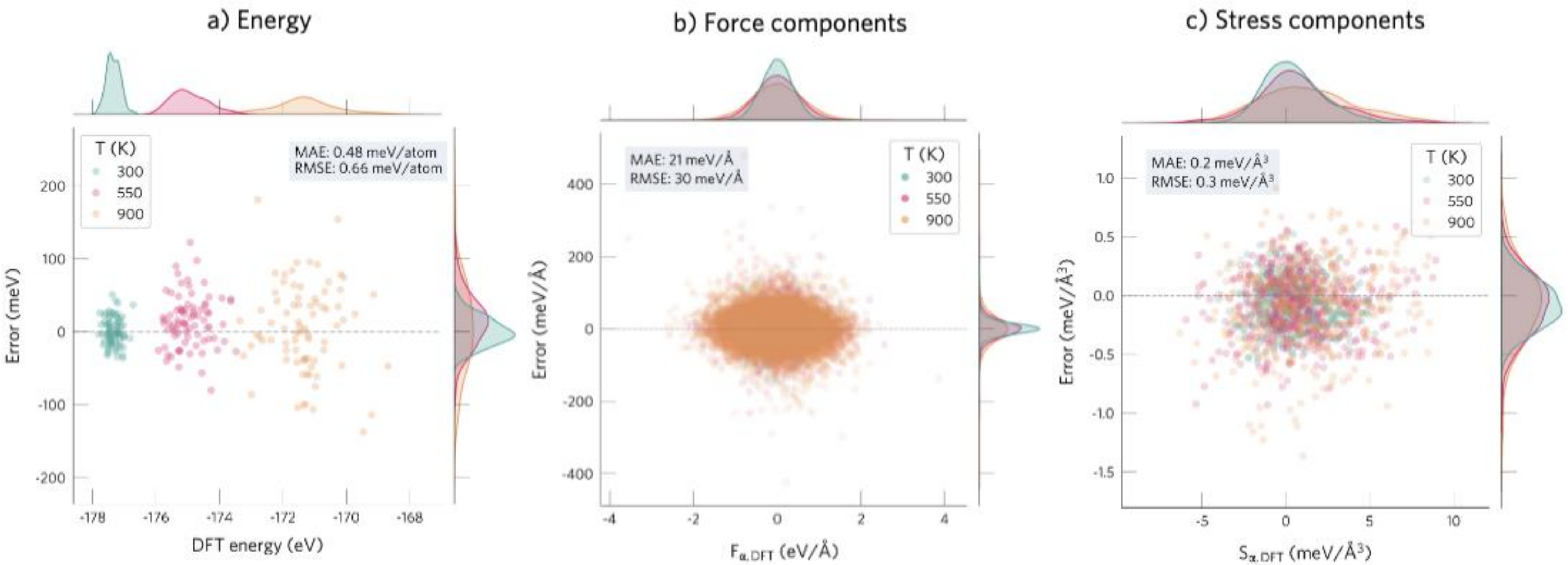
	CdTe	$\mathrm{Te}_\mathrm{i}^{+1}$	$V_{\mathrm{Te}}{}^{+2}$	Te
Train	1412	3992	4316	1171
Test	300	237	132	312

Validating the MLFF

- NPT simulations with the trained models at 3 T (300, 550 and 900 K)
  - 5 independent 24 ps runs at each T
- Sampled **100-300 equally-spaced configurations**
- DFT calculations → MAE and RMSE of each model.

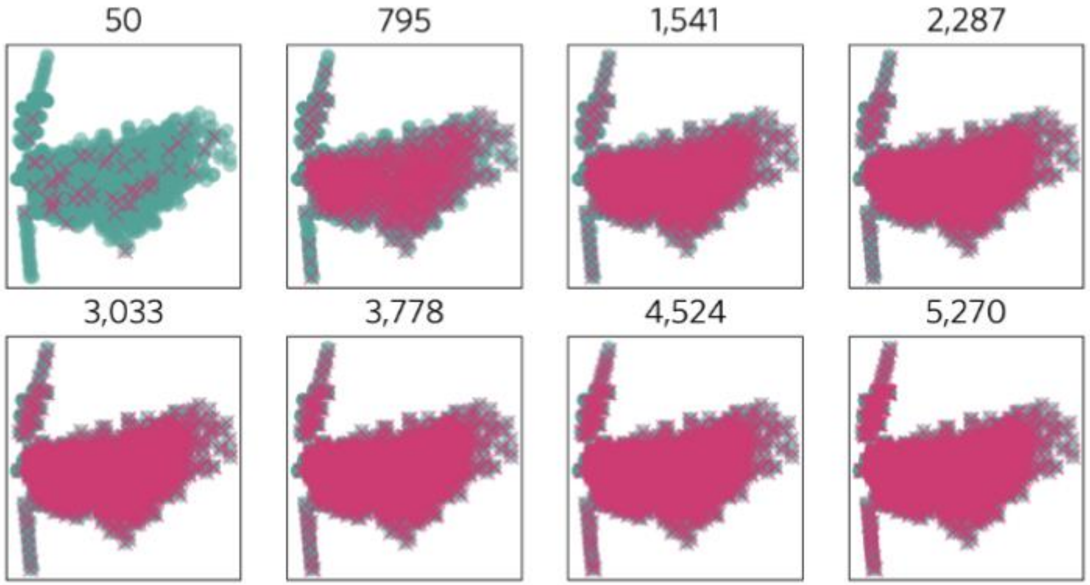


Validating the MLFF

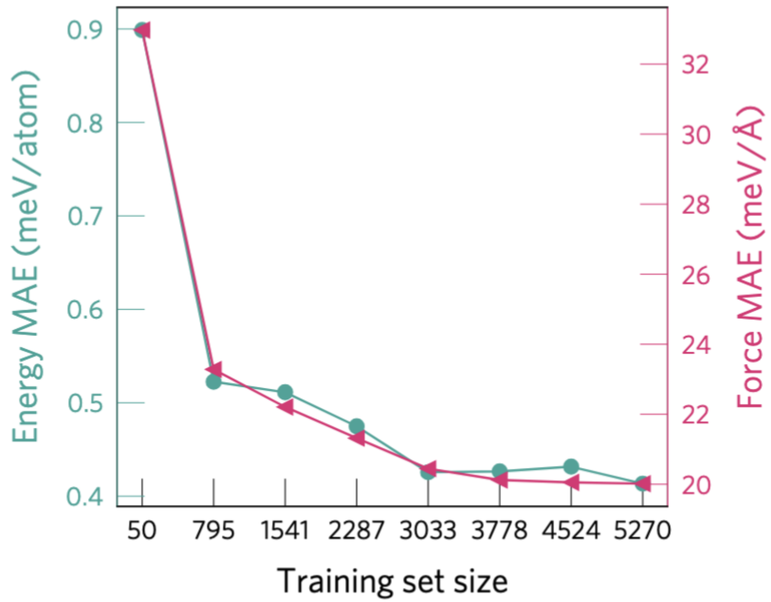


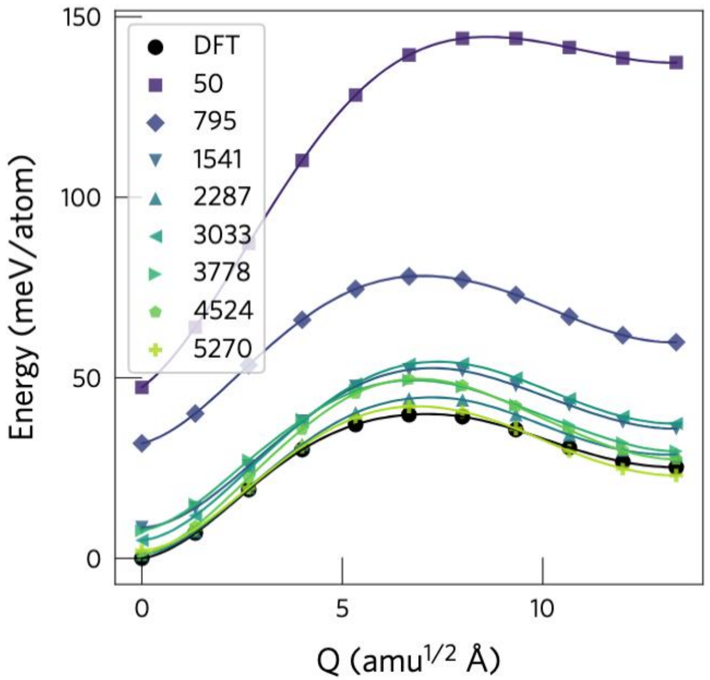
Supplementary Figure S2. Distribution of mean absolute and root mean squared errors (MAE, RMSE) for the test set of Te_i^{+1}. The distribution of the test and training configurations are illustrated in Fig. S5.

Learning curve for Te$_i$



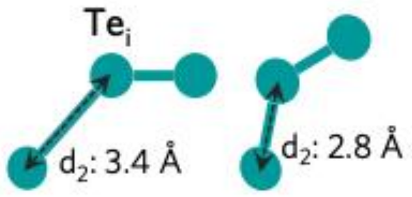
Supplementary Figure S7. Training sets of increasing size generated by sampling increasing number of configurations from the full dataset of 6016 Te$_i^{+1}$ structures. Green circles illustrate the full dataset of configurations, while the selected structures are shown in pink crosses. Sampling was performed with the `DIRECT` algorithm[2]. Each structure was encoded with its MACE descriptor (averaged over sites) and the dimensions were reduced using Principal Component Analsysis, as implemented in the `maml` package[3].



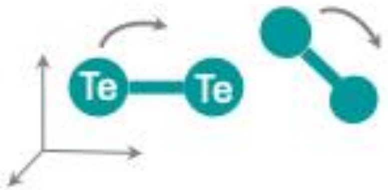


Defect dynamics at 300 K (1 ns, 1000 atoms)

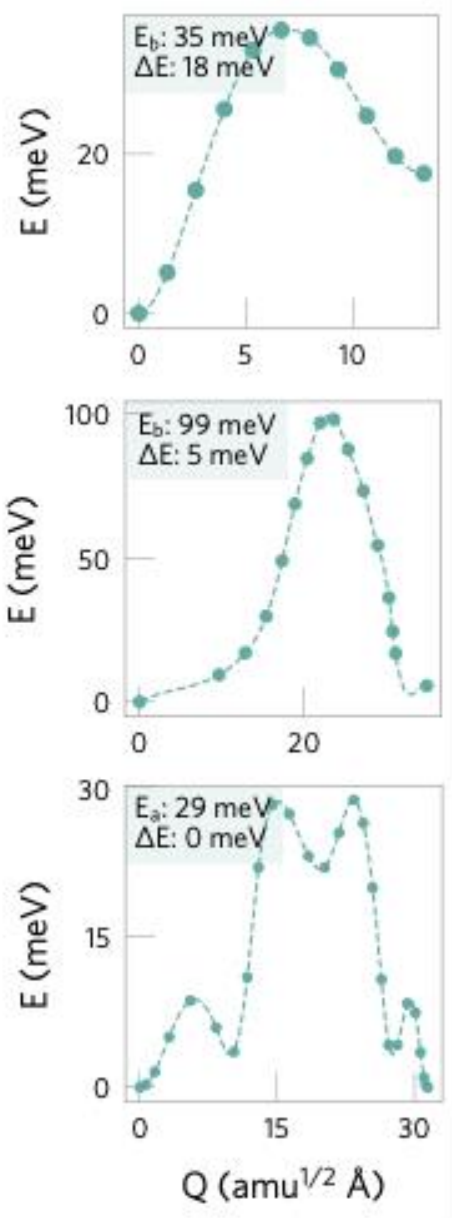
Configuration change



Rotation



Migration

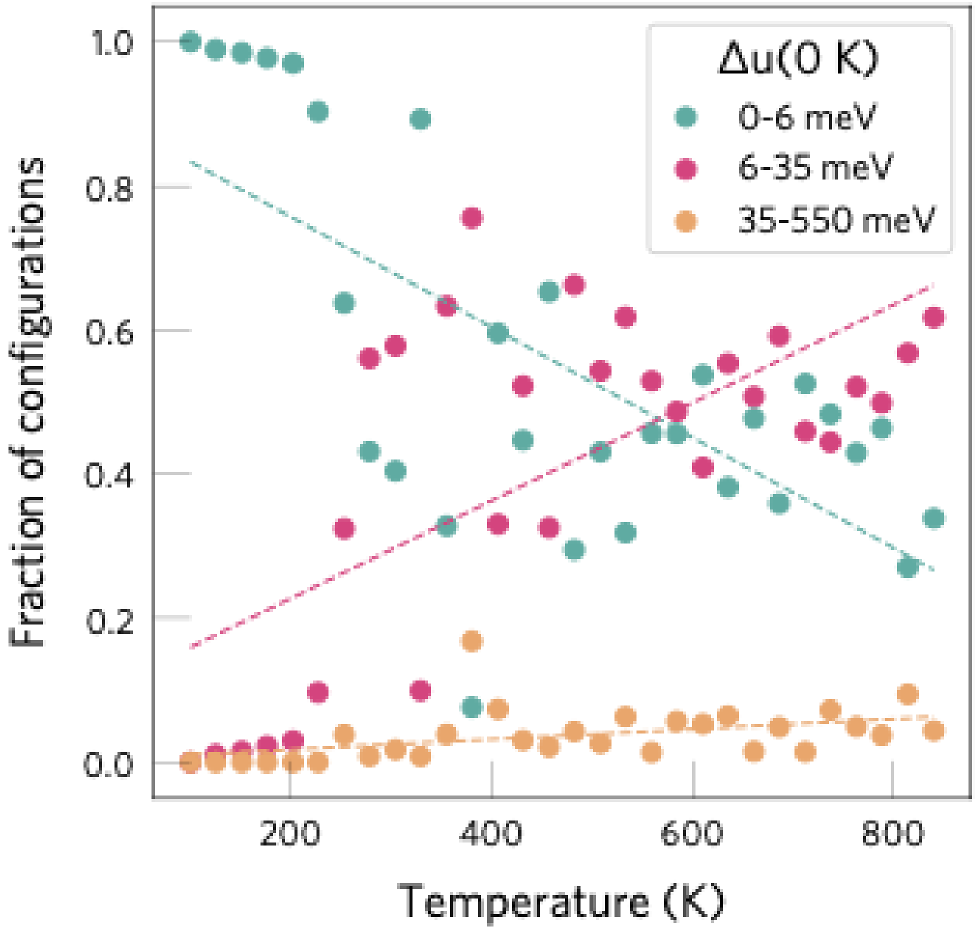


Barriers are low compared to thermal energy: ~30-100 meV vs 25 meV @300K

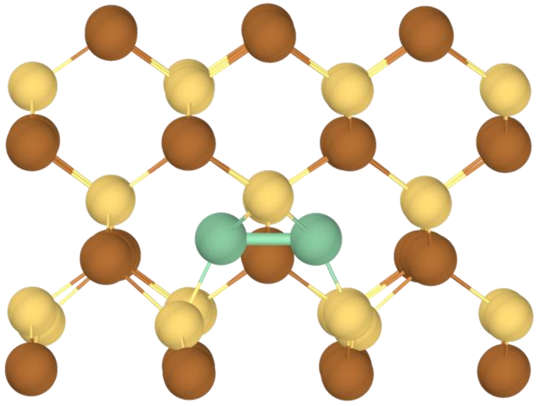
- $K_{conf} = 10^{10}\ s^{-1}$
- $K_{rot} = 10^{8}\ s^{-1}$
- $K_{hopping} = 10^{10}\ s^{-1}$

Configurational entropy

2) Quenching to 0K ('Inherent structures' method)

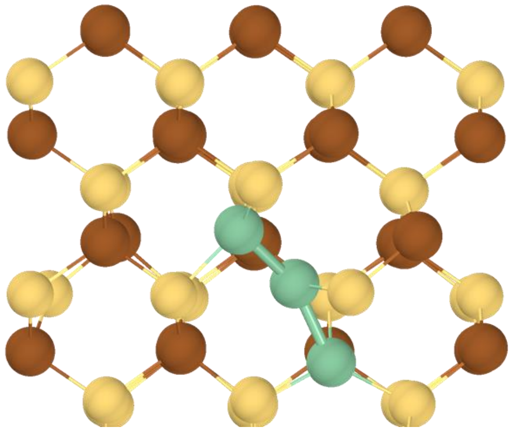


C_{2v}



Δu=0 meV

C_s



Δu=18 meV

Spin & orientational entropies

$$\left.\begin{aligned}\Omega^{\text{spin}} &= \frac{Z_d^{\text{spin}}}{Z_b^{\text{spin}}} = 2S+1 \\ \Omega^{\text{orient}} &= \frac{Z_d^{\text{orient}}}{Z_b^{\text{orient}}} = \frac{N_b}{N_d}\end{aligned}\right\} \quad s_f = k_B \ln(\Omega)$$

$$[\boldsymbol{c_{eq}}] = \frac{N_{sites}}{V}\,\Omega^{orient}\exp\left(\frac{-\boldsymbol{u_f} + \boldsymbol{Ts_f^{vib}} + \boldsymbol{Ts_f^{spin}} + \boldsymbol{Ts_f^{struc}}}{k_B T}\right)$$

Configurational entropy I

a) From defect structure searching at 0 K

Probability of configuration *i*

$$s_f^{config} = -k_B \sum_i p_i \ln(p_i)$$

$$p_i = \frac{e^{-\frac{G_i}{k_B T}}}{\sum_j e^{-\frac{G_j}{k_B T}}} = \frac{\Omega_i^{elec}\Omega_i^{spin}\Omega_i^{orient}\Omega_i^{vib} e^{-\frac{U_i}{k_B T}}}{\sum_j \Omega_j^{elec}\Omega_j^{spin}\Omega_j^{orient}\Omega_j^{vib} e^{-\frac{U_j}{k_B T}}}$$

Configurational entropy II

b) Inherent structures formalism

1. MD NPT runs at a series of temperatures (30 T from 100 K to 900 K)
2. Quench to 0 K by gradient descent optimization
3. Calculate $\langle U_{IS}^{V} \rangle$ at each T
4. Integrate

$$s_f^{config} = s_f^{config}(T_i) + \int_{T_i}^{T_f} \frac{1}{T} \frac{\partial \langle e_{IS}^{V}(T) \rangle}{\partial T} dT$$

Luo et al, *Phys Rev Mat*, **6**, 064603 (2022)

Thermodynamic integration

a) CdTe, Te_i

Einstein crystal (100 K) → Real crystal (100 K) → Real crystal (840 K)

b) Te → Melting

- Einstein crystal (100 K) → Real crystal (100 K) → Real crystal (840 K)
- Ideal gas (840 K) → Liquid (840 K) → Liquid (500 K)

→ ($T_{melting}$ = 704 K compared to exp. value of 722 K)

Thermodynamic integration

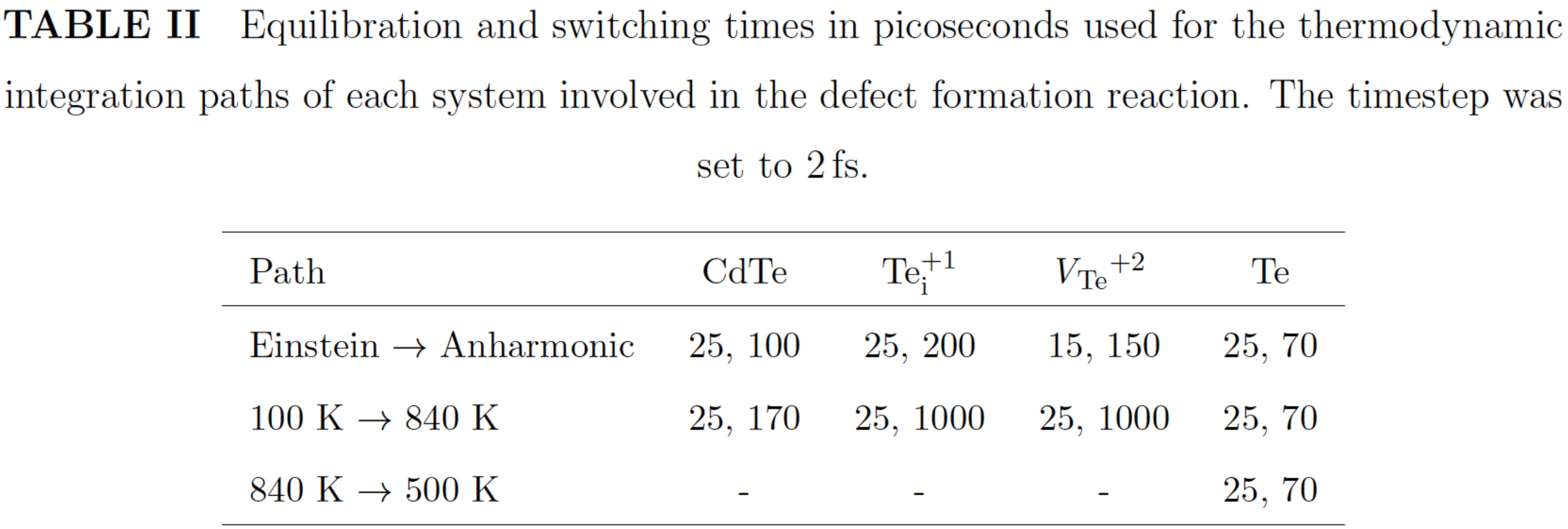


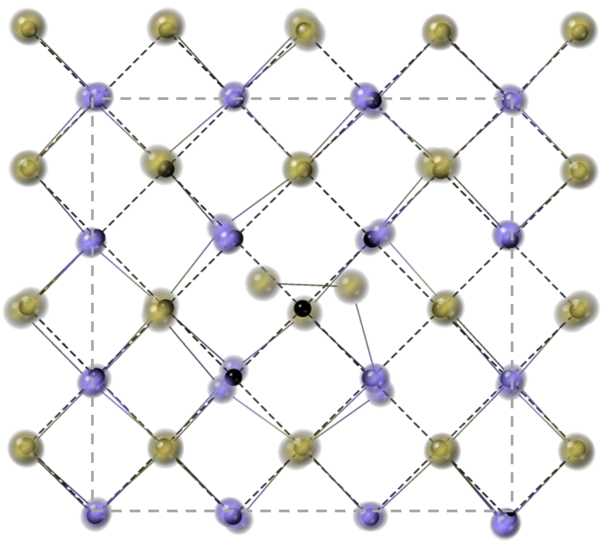
TABLE II Equilibration and switching times in picoseconds used for the thermodynamic integration paths of each system involved in the defect formation reaction. The timestep was set to 2 fs.

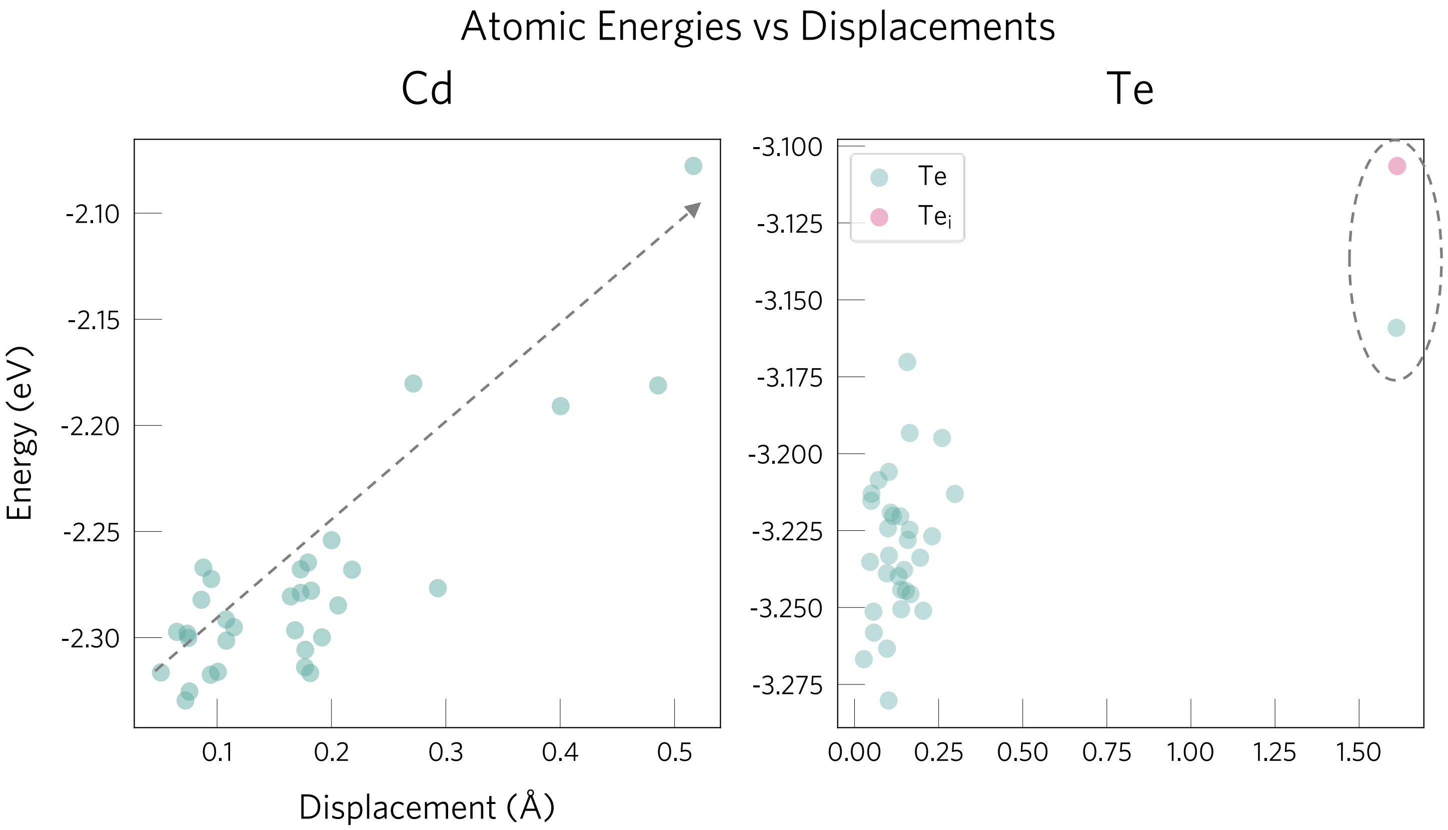
Path	CdTe	$\mathrm{Te}_\mathrm{i}^{+1}$	${V_{\mathrm{Te}}}^{+2}$	Te
Einstein → Anharmonic	25, 100	25, 200	15, 150	25, 70
100 K → 840 K	25, 170	25, 1000	25, 1000	25, 70
840 K → 500 K	-	-	-	25, 70

Machine learning forcefields: How interpretable?

Atoms near Te_i should have higher **displacement** from ideal bulk position

Higher displacement → Higher atomic energy?

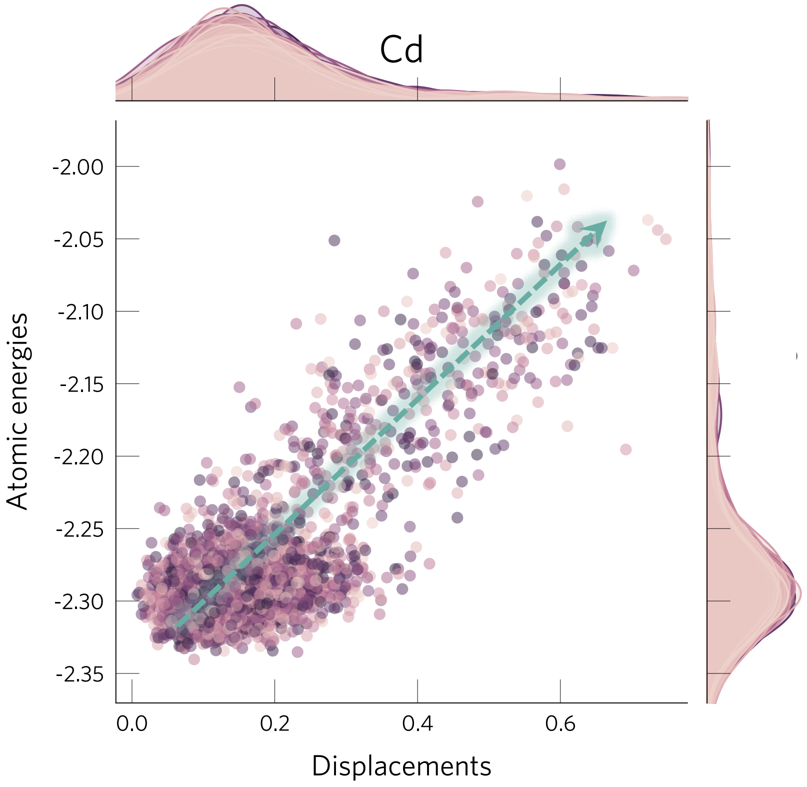


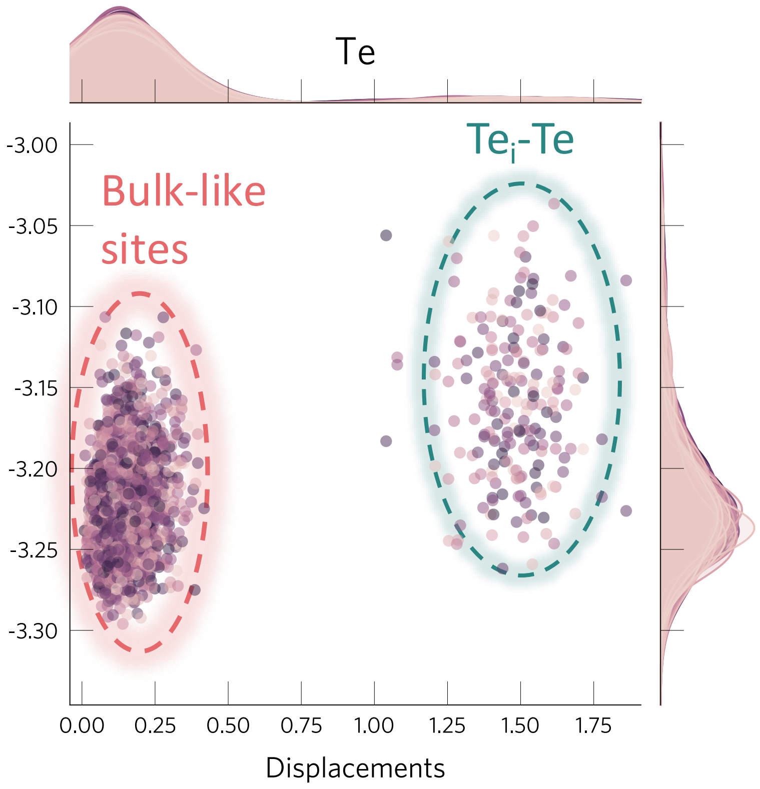


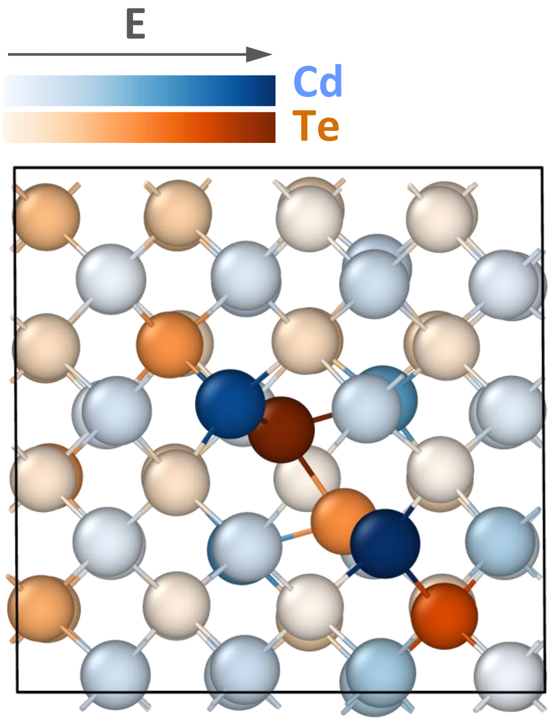
Machine learning forcefields: How interpretable?

Atoms near Te$_i$ should have higher **displacement** from ideal bulk position

Higher displacement → Higher atomic energy? ✅



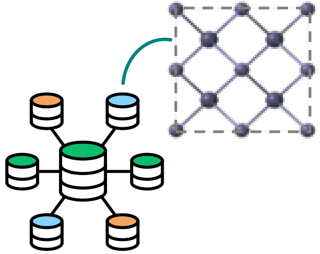




Reduce cost with machine learning force fields

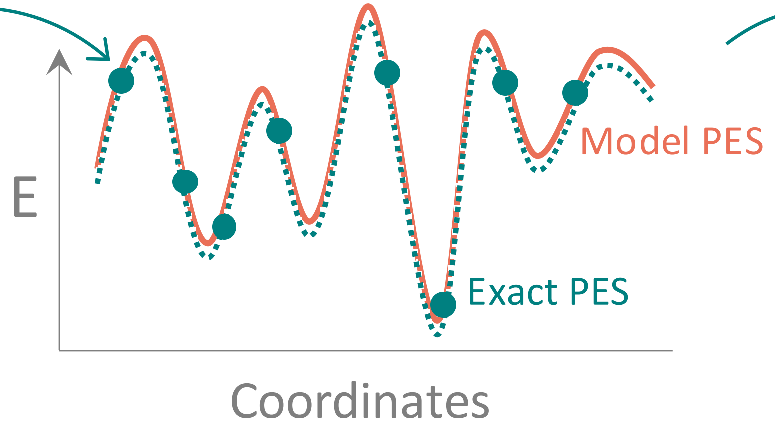
Model to describe time evolution of the defect at different temperatures

1. Build reference database

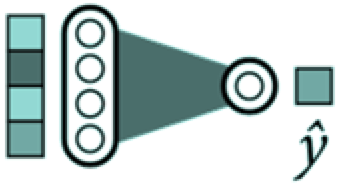


$\hat{H}\Psi = E\Psi$

2. Learning of potential energy surface



3. Fast model with near quantum accuracy

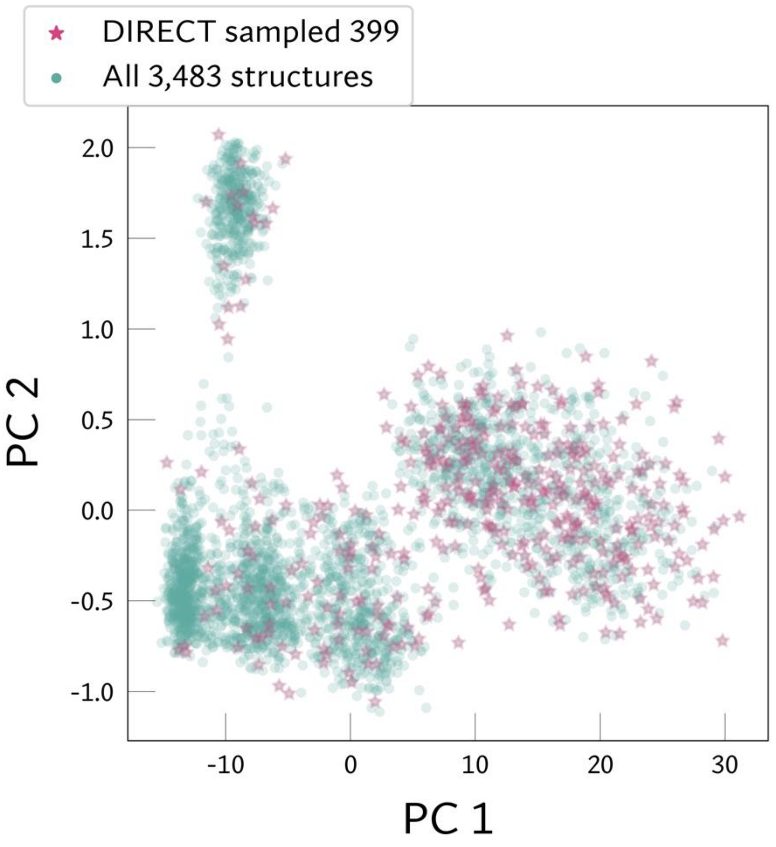


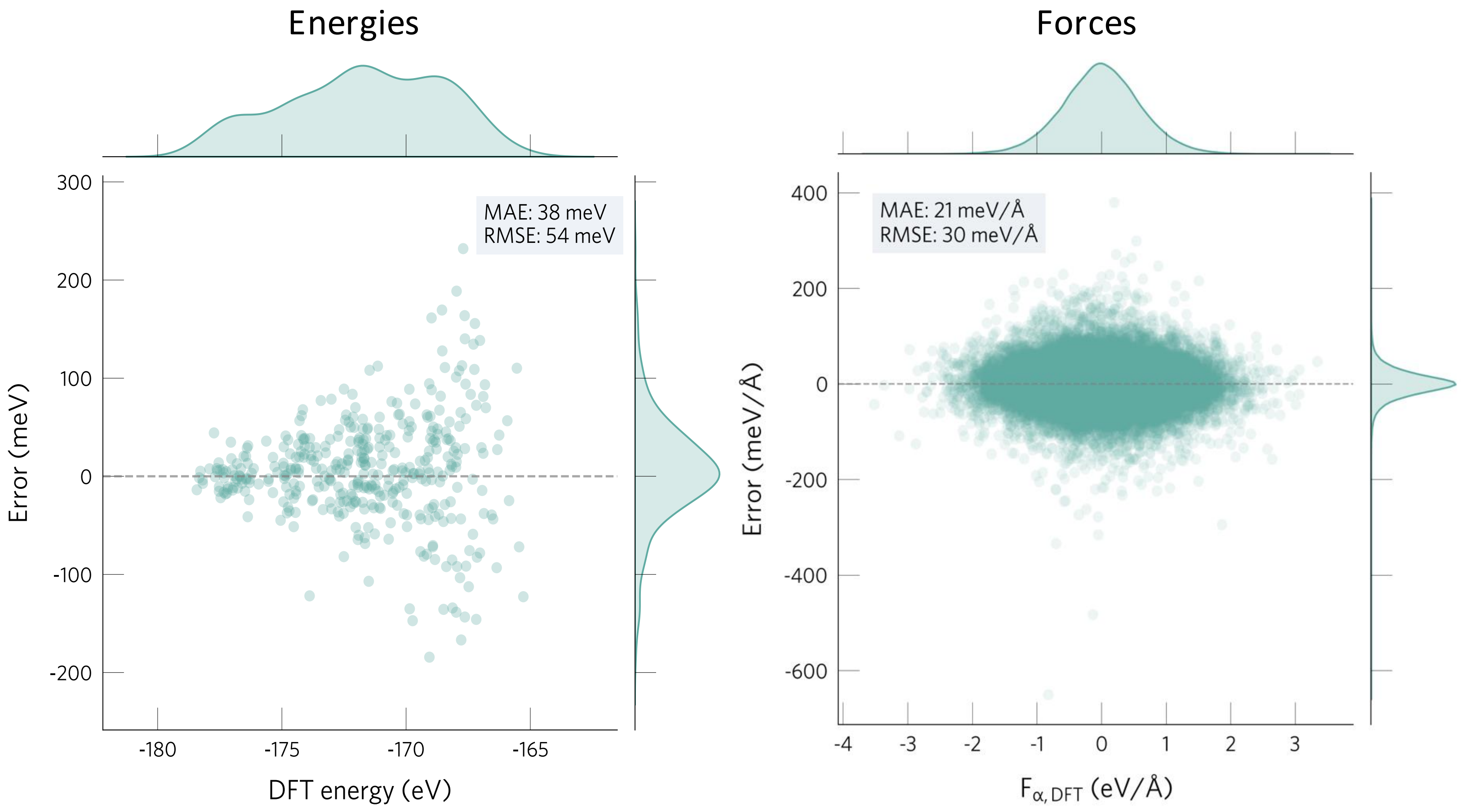
Defect dynamics at finite T
Long time- & length-scales

Figure adapted from V. Deringer, M. A. Caro & G. Csányi, *Adv. Mater.*, 2019

Validating MLFF

- MD NPT runs (24 ps) at 6 temperatures (200, 300, 400, 600, 839, 1091 K)
  - 1091 K is 30% above $T_{synthesis}$ (higher errors) – still reliable ✅
- Select diverse set of 300 configurations using DIRECT sampling method





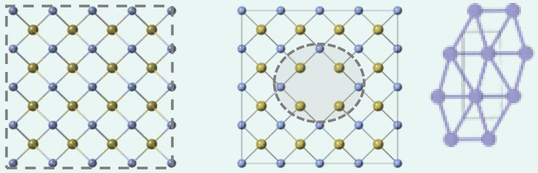
Key property: defect **concentrations**

→ Free energy of defect formation (g_f) at synthesis temperature

$$c_{eq} = \exp\left(\frac{-g_f(T)}{k_B T}\right)$$

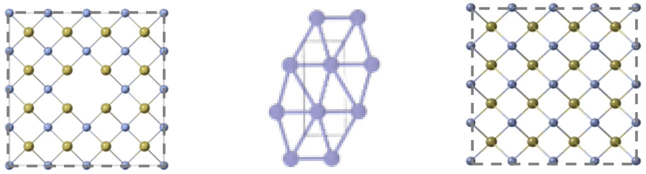
V_{Cd}:

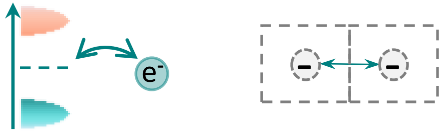
$Cd_xTe_x \rightarrow Cd_{x-1}Te_x + Cd$



$$g_f = G_{products} - G_{reactants} + \text{correction}$$

$$g_f = G_{defect} + g_{phase} - G_{bulk} + \underbrace{q(E_{VBM} + E_F) + E_{corr}}_{\text{Charged defects}}$$





Calculating g_f (T) is challenging

➡ Approximations

1. Neglect s_f

$$g_f(T) \approx u_f(T) - \cancel{T\cdot s_f(T)}$$

- Calculating s_f is 🩹
- $u_f \gg Ts_f$

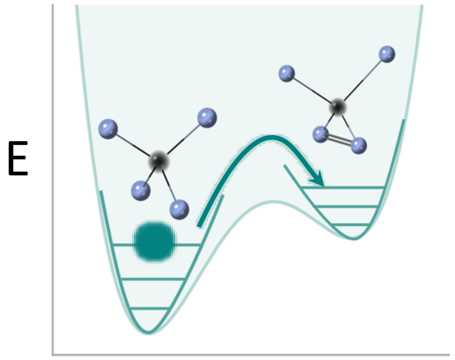
How accurate are these approximations?

1. $[O_i^{2-}]$ in CeO_2 underpredicted by 10^9

2. Metastable configurations key to predict **photovoltaic efficiency** of CdTe[1,2]

2. Static picture

Defect is ***frozen*** in ground state (0 K) configuration



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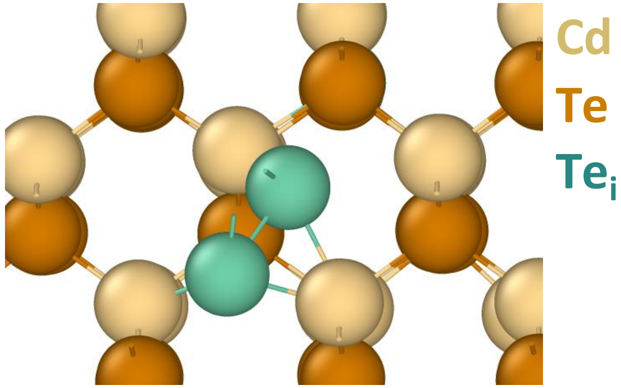
1. S. R. Kavanagh, A. Walsh & D. O. Scanlon, *ACS Energy Lett.* 2021
2. S. R. Kavanagh, D. O. Scanlon, A. Walsh & Freysoldt, Faraday Diss. 2022

Objective

- Assess **importance** of thermal effects on predicted **concentrations** 🌡
- Establish reliable **approach** to model them 📊

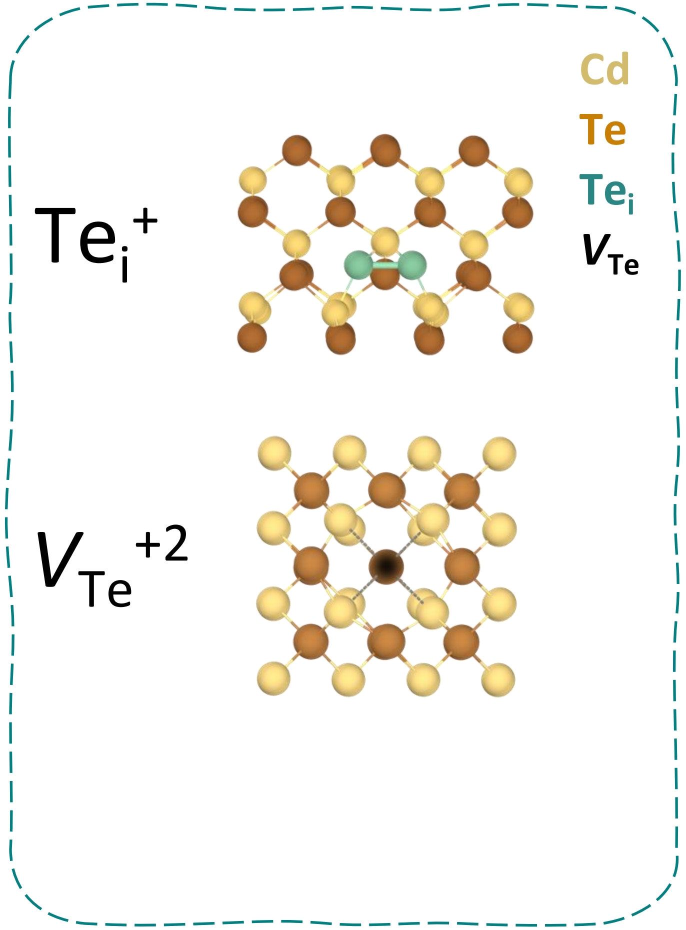
Test system: Te_i^+ in CdTe



- Predicted to be highly dynamic
- Metastable configurations key for carrier capture in solar cells

S. R. Kavanagh, D. O. Scanlon, A. Walsh & Freysoldt, *Faraday Diss.* 2022
S. Hamadna and J.G. Amar, *J. Condens. Matter Phys.* 2024

Test systems: CdTe



Defect formation

$Cd_xTe_x + Te \rightarrow Cd_xTe_{x+1}$

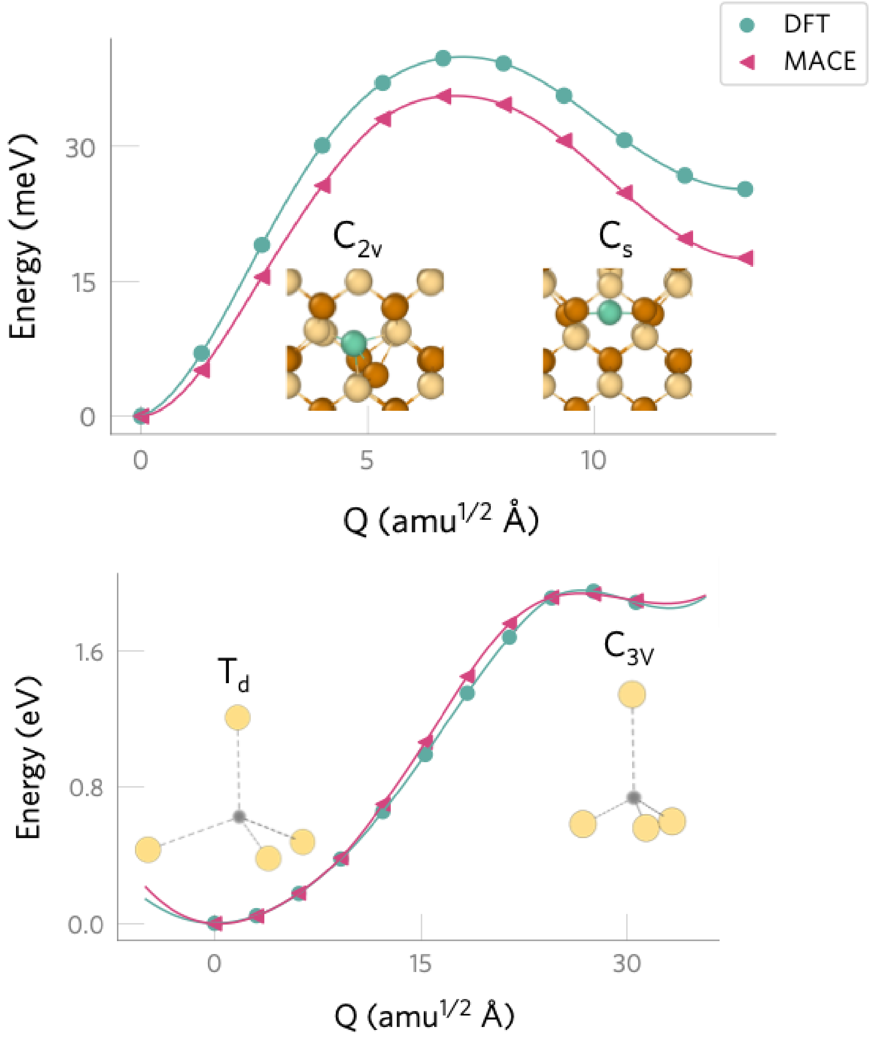
$Cd_xTe_x \rightarrow Cd_xTe_{x-1} + Te$

CdTe
Te_i^+
V_{Te}^{+2}
Te

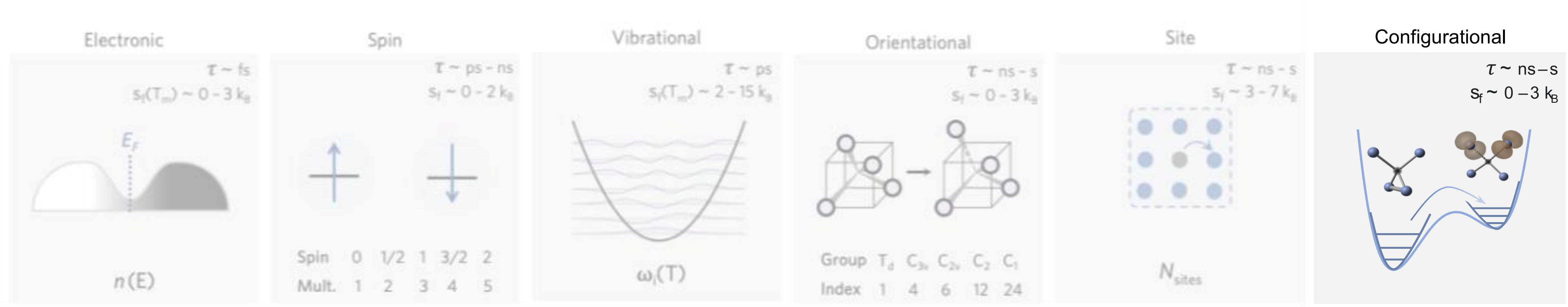
Conditions

T_{anneal}= 840 K, P=1 atm
$T_{operation}$= 300 K

MACE force field 0-900 K
Test MAE(Energy) < 1 meV/atom



Modelling thermal effects

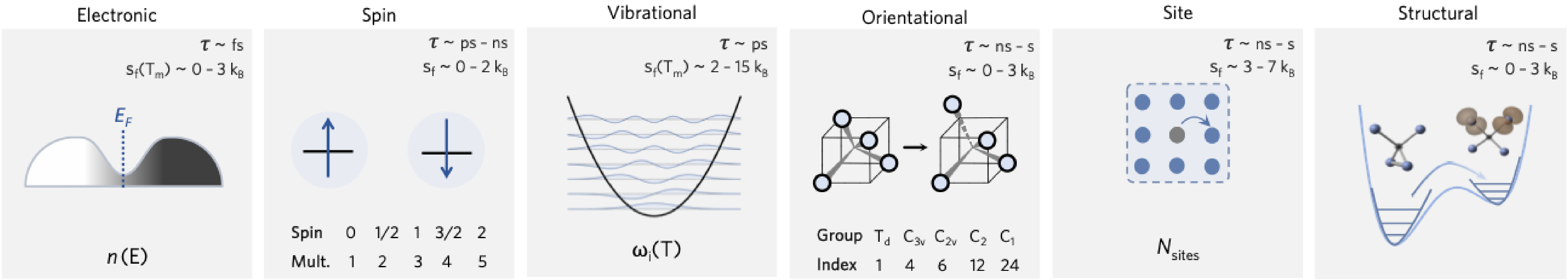


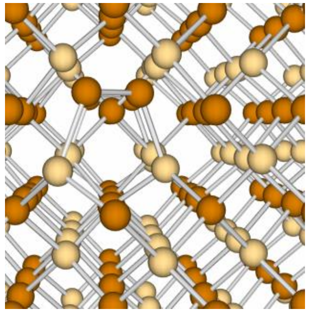
$$c = \sum_{i=0}^{n} c_i = \sum_{i=0}^{n} \exp\left(\frac{-g_{f,i}}{k_B T}\right) \approx \sum_{i=0}^{n} \exp\left(\frac{s_{f,i}}{k_B}\right) \exp\left(\frac{-u_{f,i}}{k_B T}\right)$$

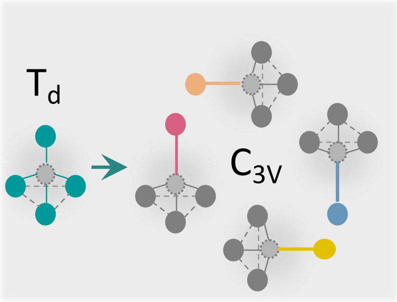
S. R. Kavanagh, D. O. Scanlon, A. Walsh & Freysoldt, *Faraday Diss.* 2022
I. Mosquera-Lois, S. R. Kavanagh, J. Klarbring, K. Tolborg & A. Walsh, *Chem. Soc. Rev.*,. 2023

Modelling thermal effects

What factors contribute to s_f?







$$s_f \approx s_f^{elec} + s_f^{spin} + s_f^{vib} + s_f^{orient} + s_f^{site} + s_f^{structural}$$

I. Mosquera-Lois, S. R. Kavanagh, J. Klarbring, K. Tolborg & A. Walsh, *Chem. Soc. Rev.*,. 2023

Calculating defect entropy

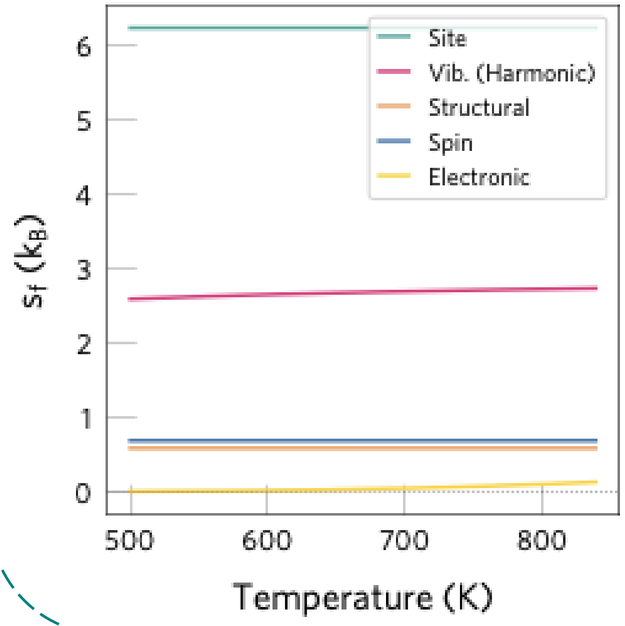
Two approaches

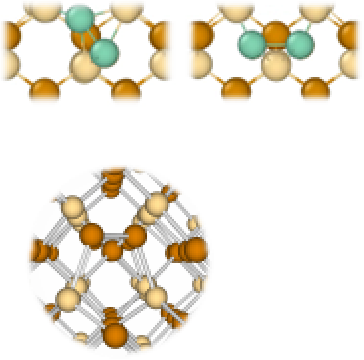
a) Decoupling all degrees of freedom
- Different timescales
- Harmonic approximation

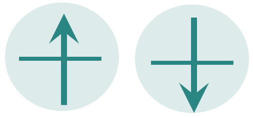
b) Decoupling **electronic from ionic**
- Ionic: Thermodynamic integration

a) Decoupling all degrees of freedom

$$S_f \approx S_f^{elec} + S_f^{spin} + S_f^{struc} + S_f^{vib} + S_f^{site}$$







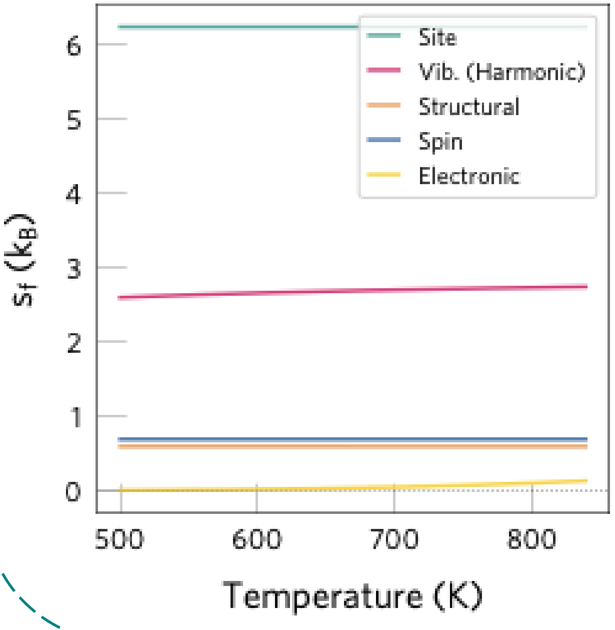
1 unpaired electron

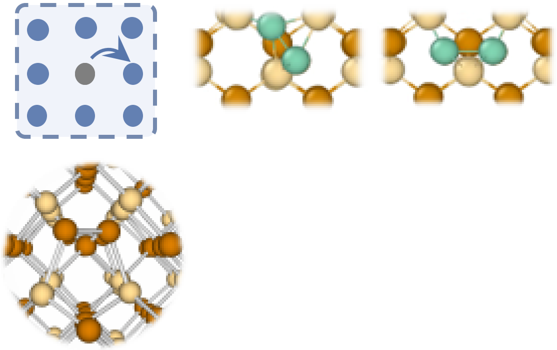
Defect formation entropy

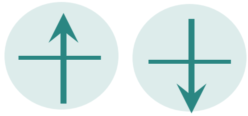
a) Decoupling all degrees of freedom

- Different timescales
- Harmonic approximation

$$S_f \approx S_f^{elec} + S_f^{spin} + S_f^{struc} + S_f^{vib} + S_f^{site}$$







1 unpaired electron

b) Decoupling electronic from ionic

- Ionic motions strongly coupled at high T
- Thermodynamic integration

$$S_f \approx S_f^{elec} + S_f^{spin} + S_f^{ionic}$$