



TOFA

20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
20 - 24 September 2026
BLED - SLOVENIA

Ab initio thermodynamic modeling of solid solutions made simple

Pedro Nunes Ferreira

Institute of Theoretical and Computational Physics

Graz University of Technology



TOFA

20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
20 - 24 September 2026
BLED - SLOVENIA

Ab initio thermodynamic modeling of solid solutions made simple

Pedro Nunes Ferreira
Institute of Theoretical and Computational Physics
Graz University of Technology





20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
20 - 24 September 2026
BLED - SLOVENIA

Ab initio thermodynamic modeling of solid solutions made simple

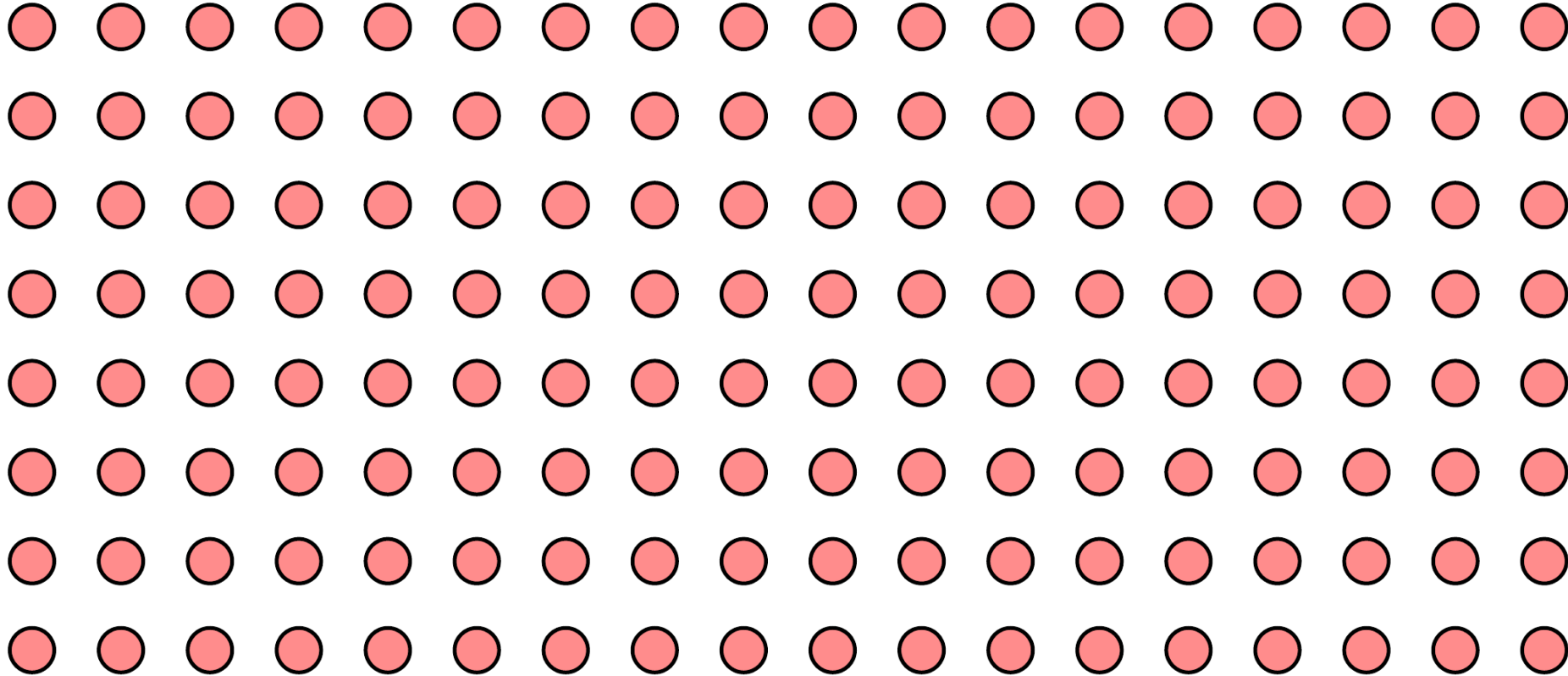
Pedro Nunes Ferreira
Institute of Theoretical and Computational Physics
Graz University of Technology



You
physicists don't
hear us!

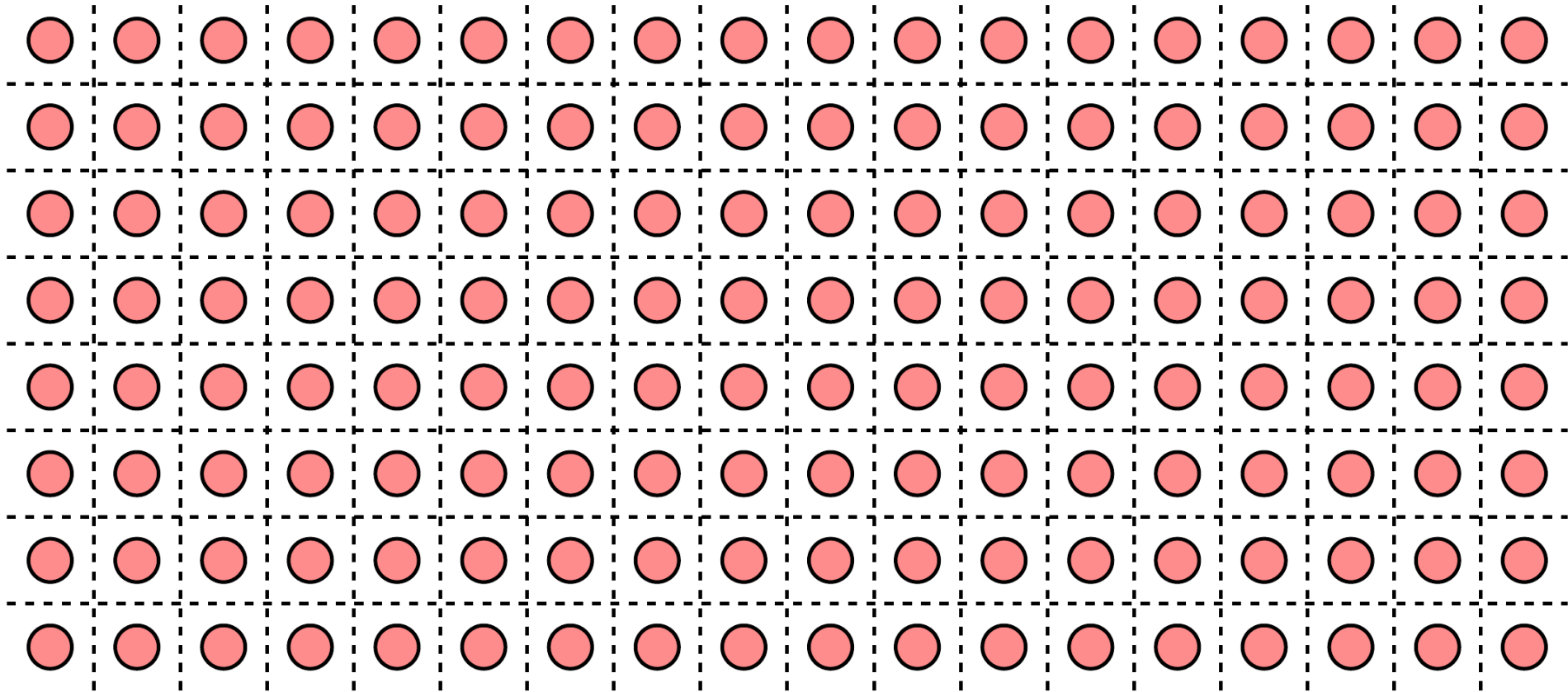
Ab initio modeling of alloys

Ab initio modeling of alloys



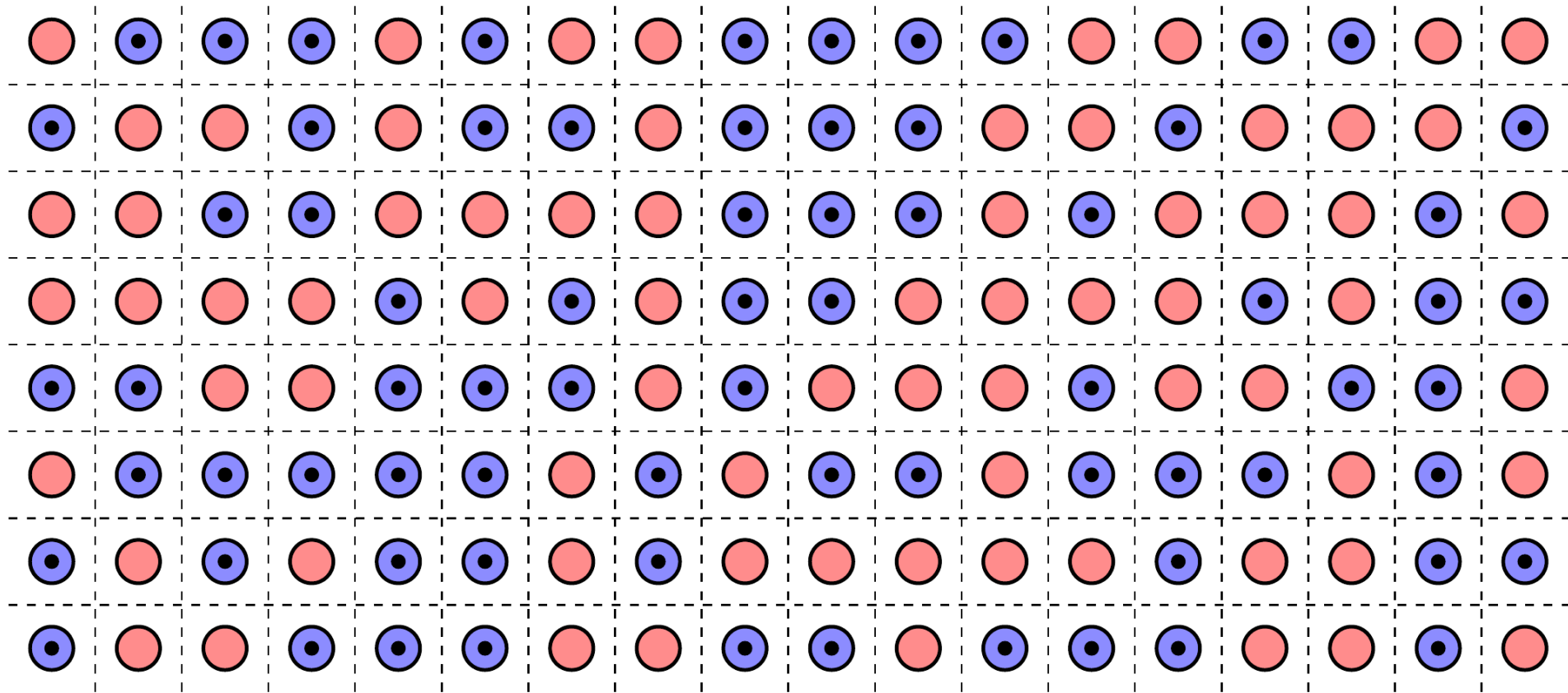
 Red (plain)

Ab initio modeling of alloys



● Red (plain)

Ab initio modeling of alloys

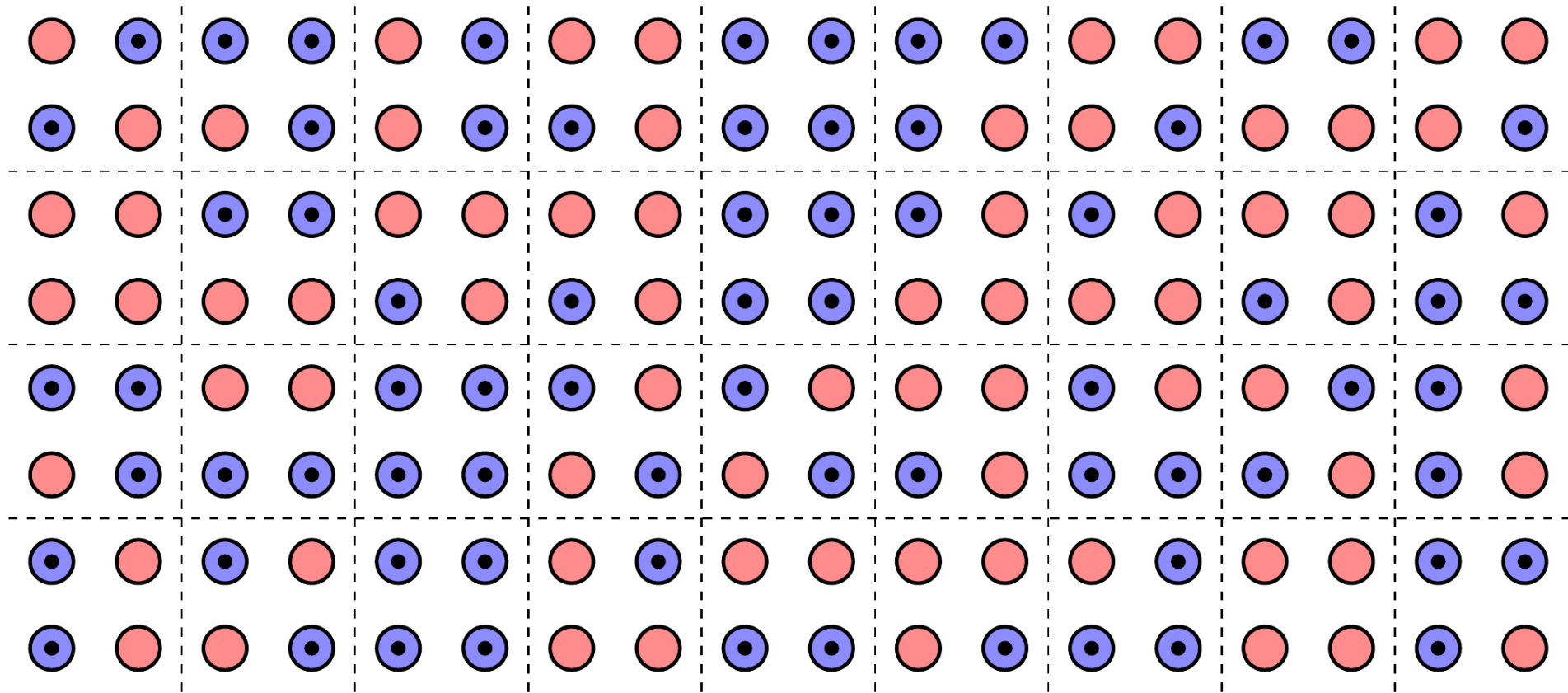


Red (plain)



Blue (dotted)

Ab initio modeling of alloys

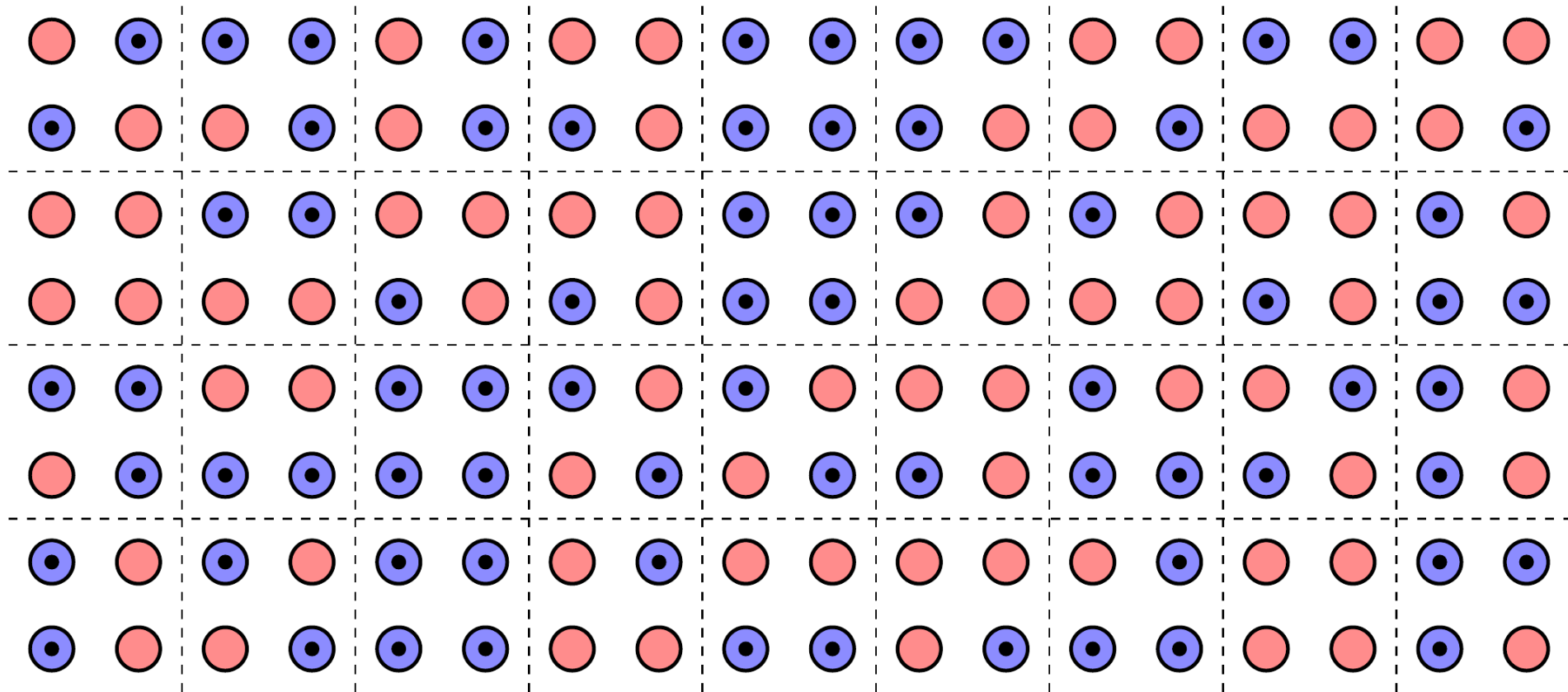


Red (plain)



Blue (dotted)

Extended generalized quasichemical approximation (EGQCA)

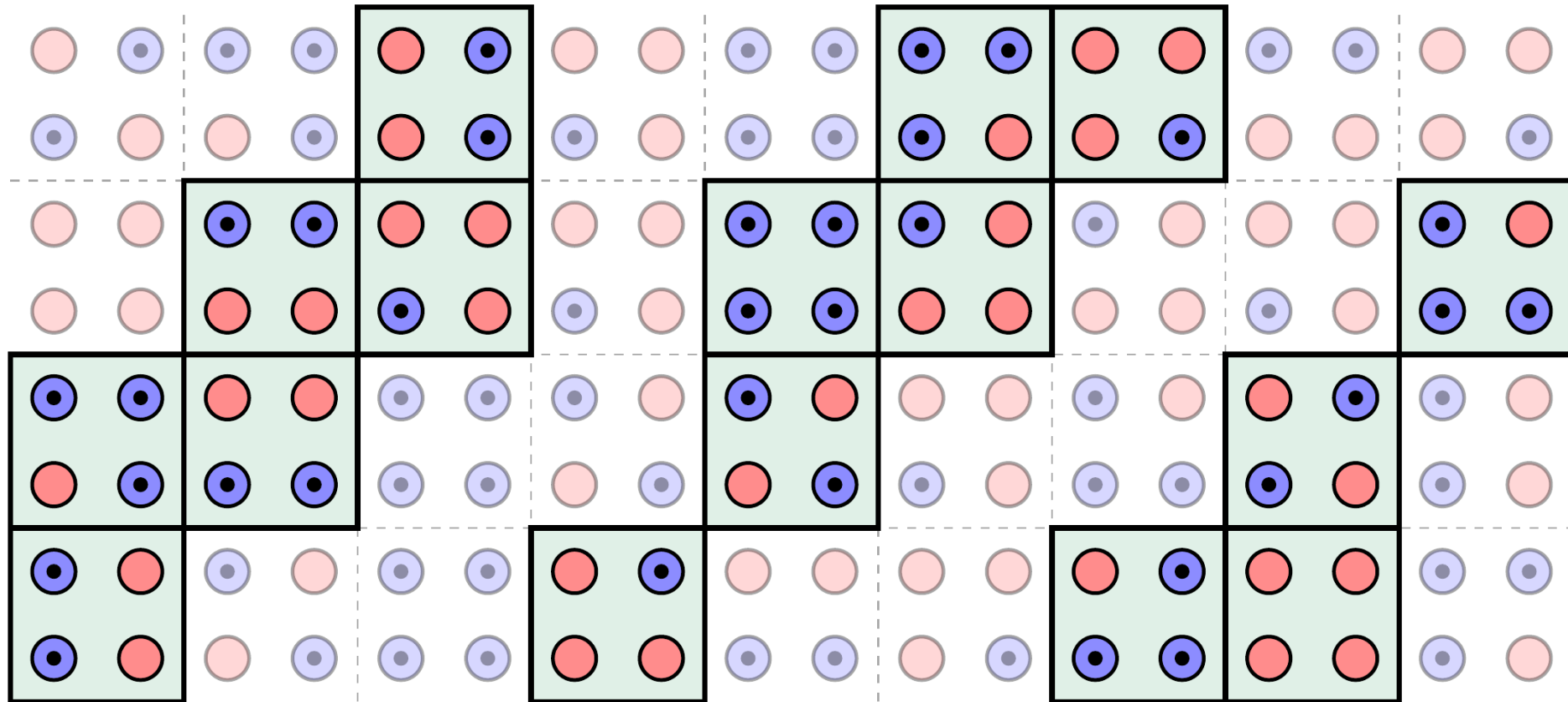


Red (plain)



Blue (dotted)

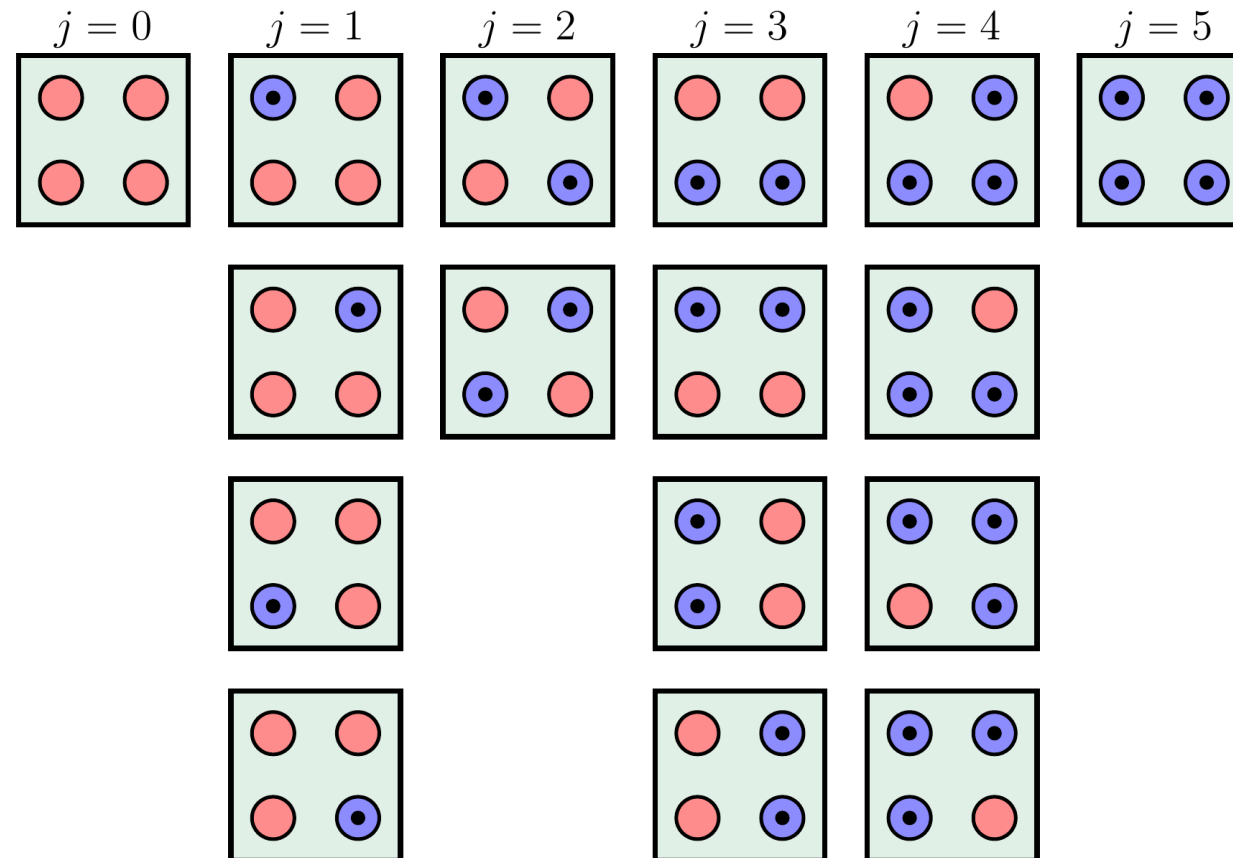
How does EGQCA model disorder?



Red (plain)

Blue (dotted)

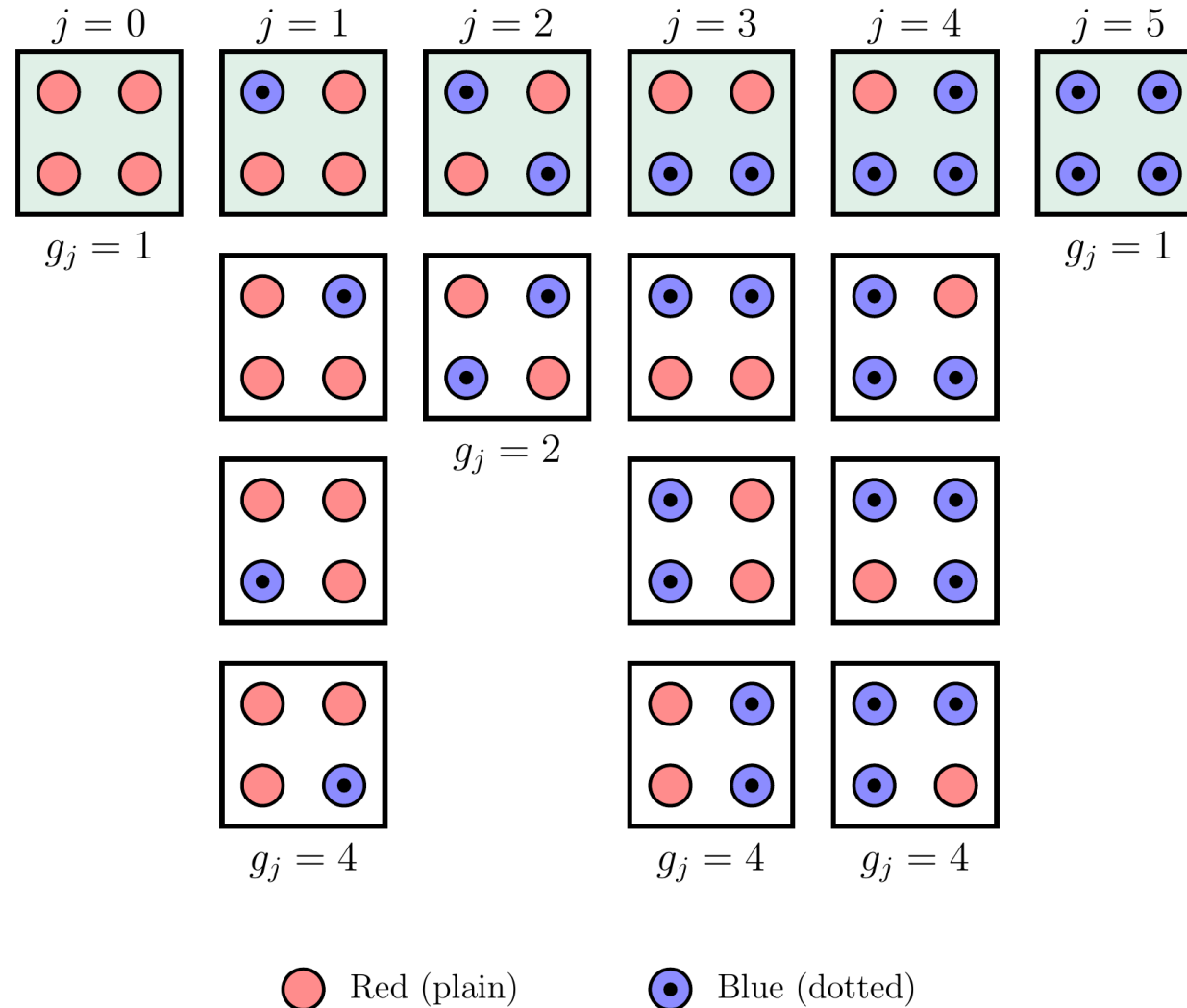
How does EGQCA model disorder?



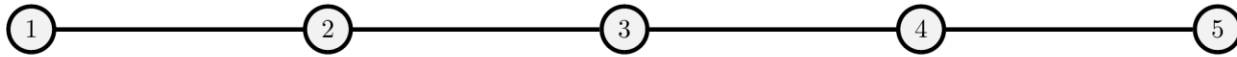
Red (plain)

Blue (dotted)

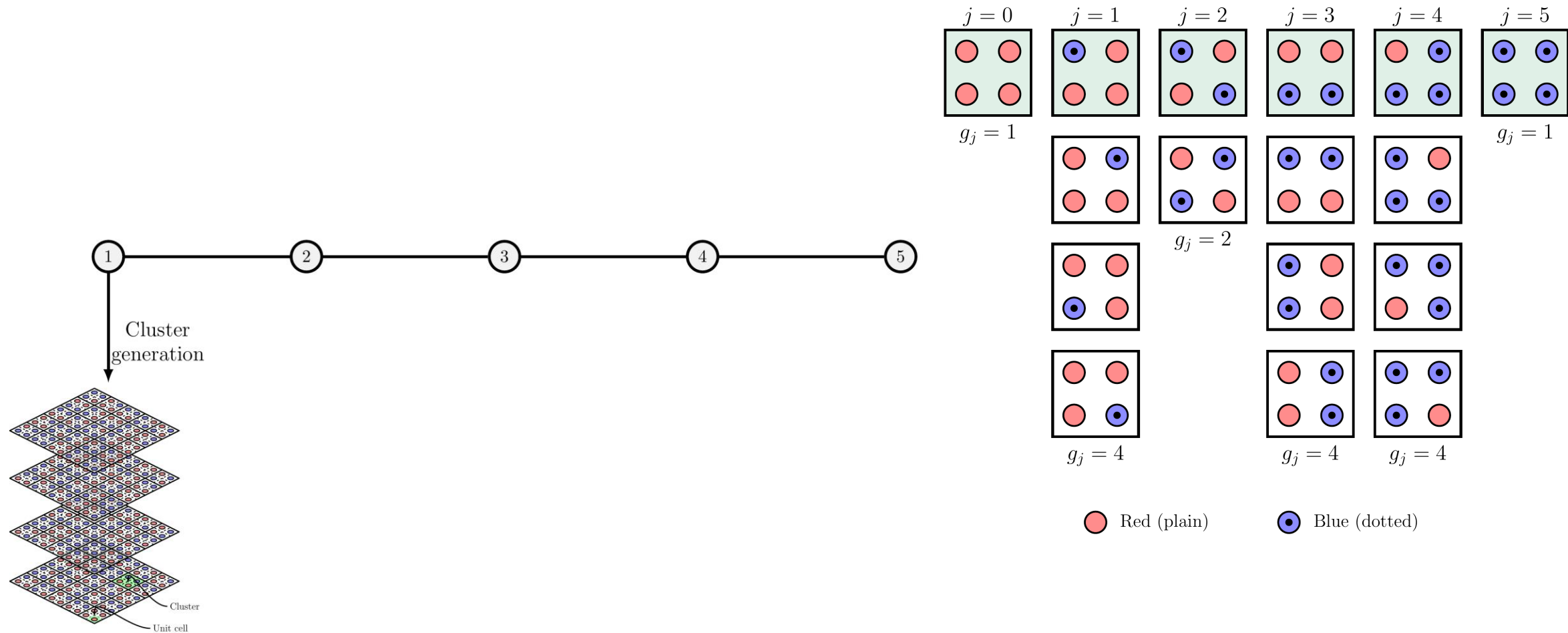
How does EGQCA model disorder?



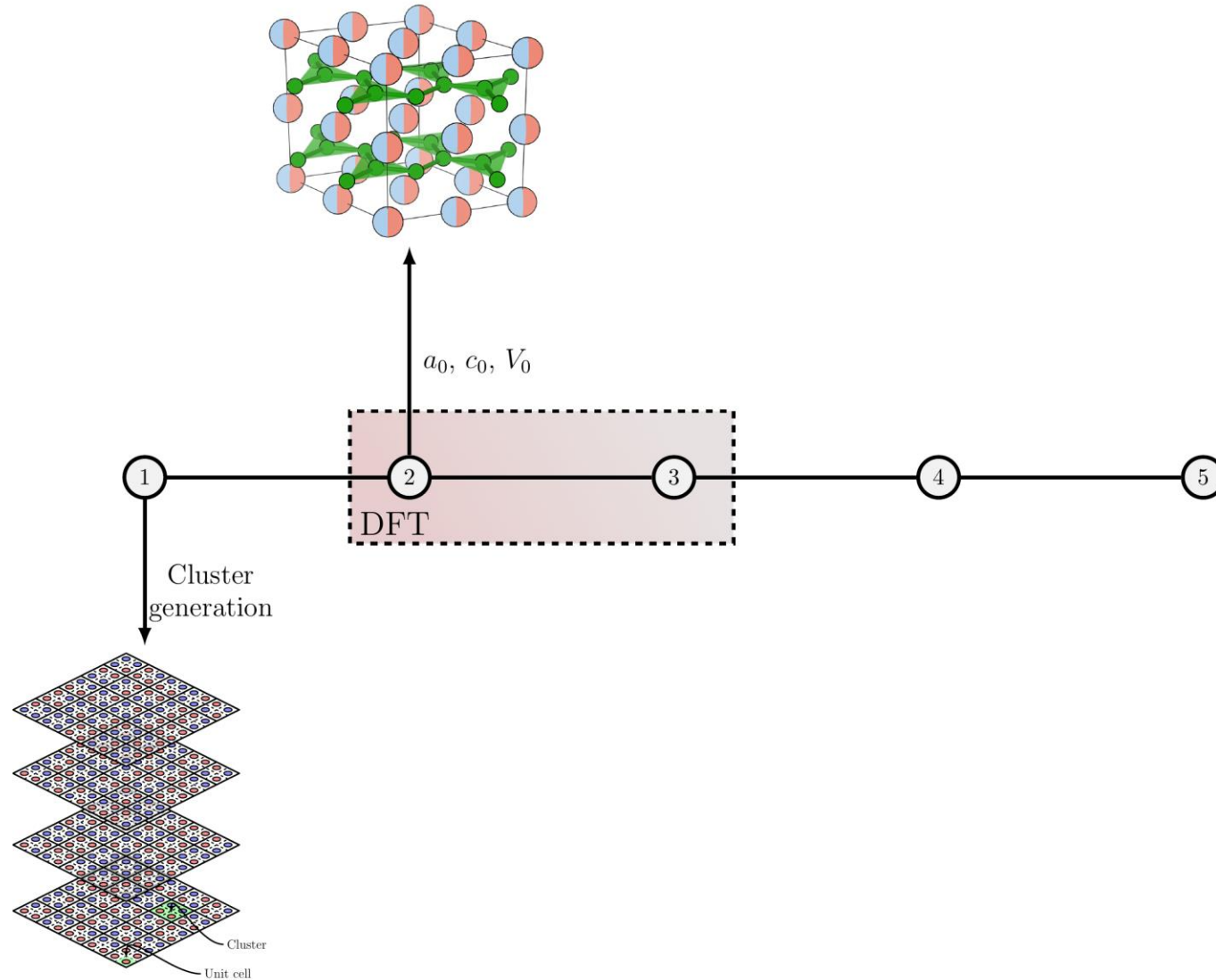
EGQCA in 5 steps



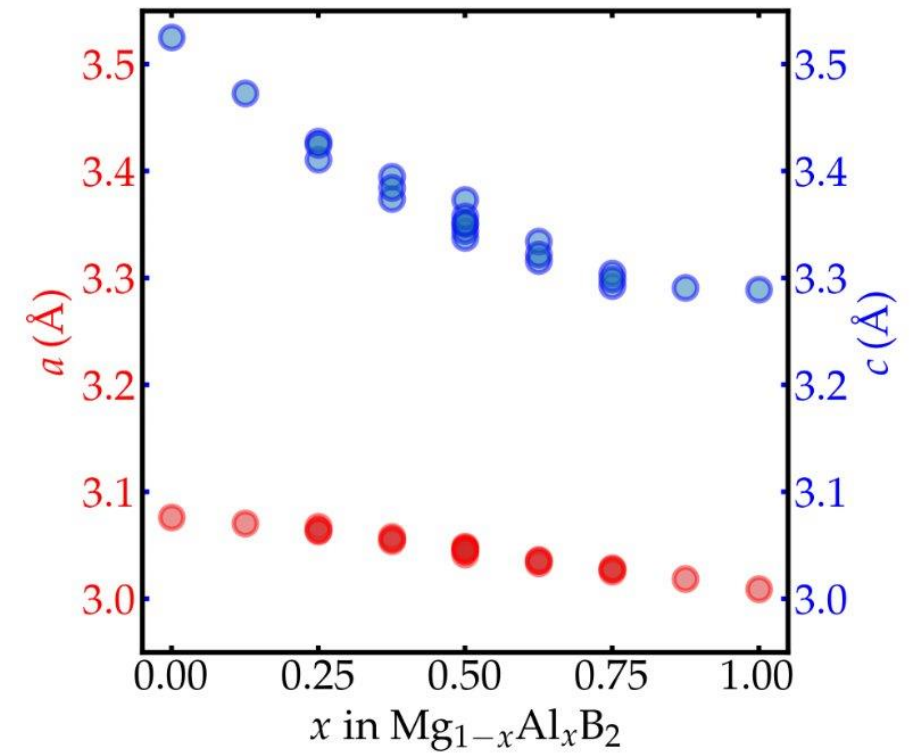
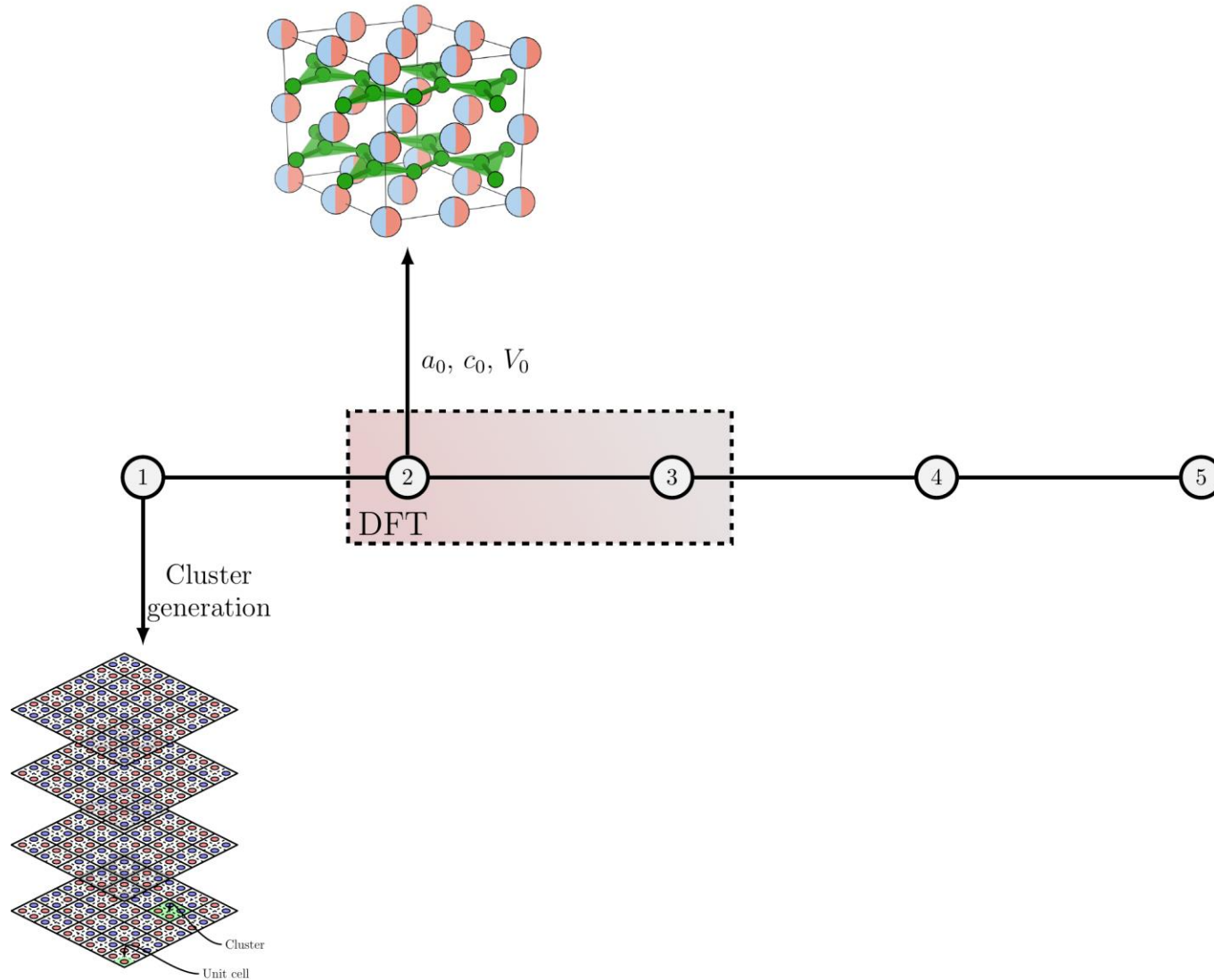
EGQCA in 5 steps: cluster generation



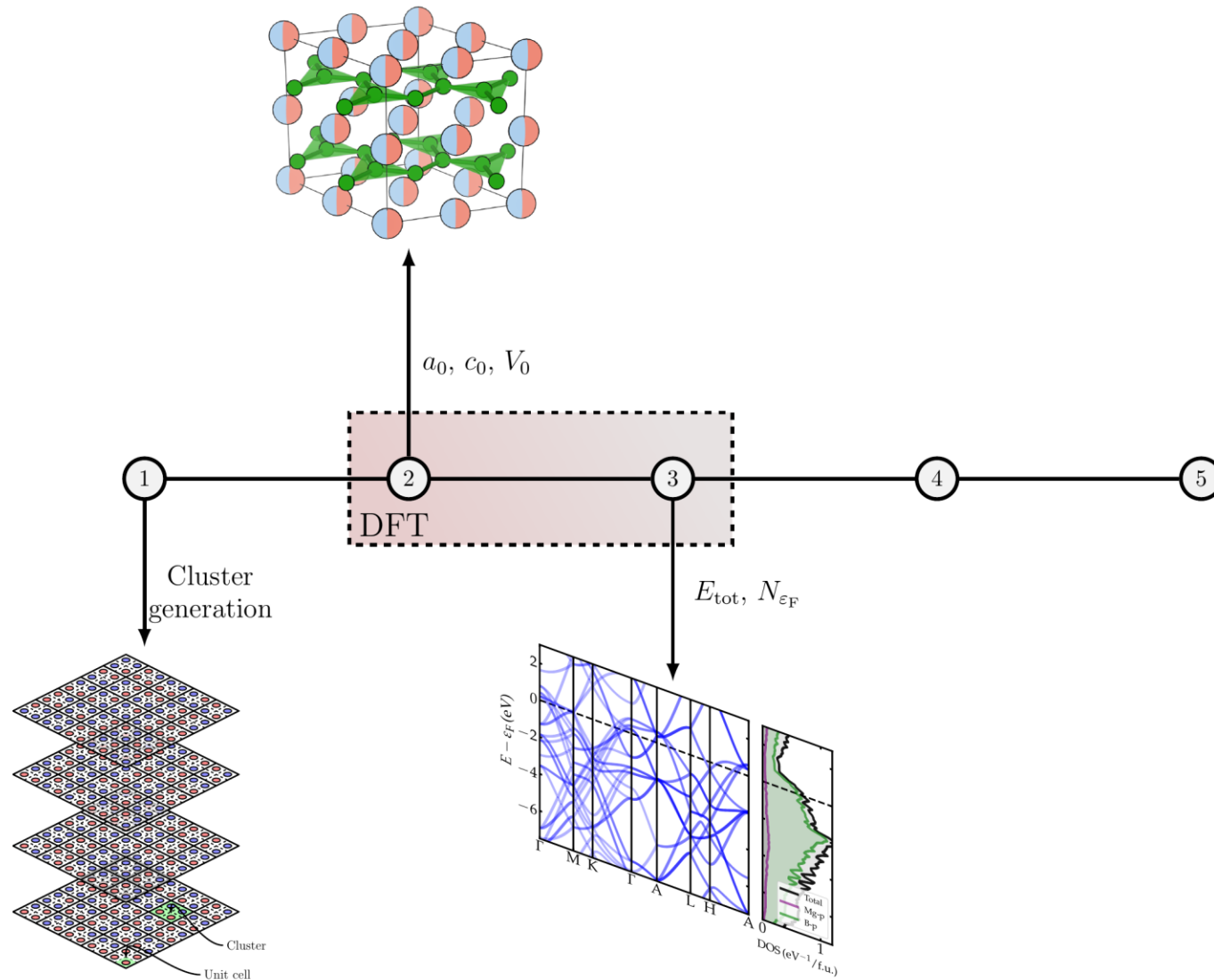
EGQCA in 5 steps: structural optimization



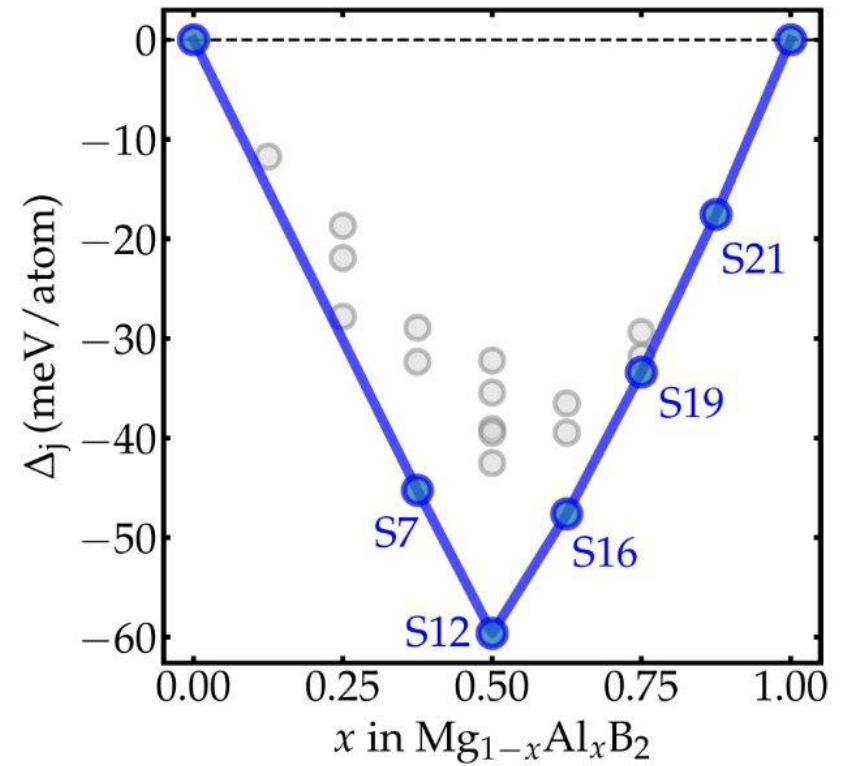
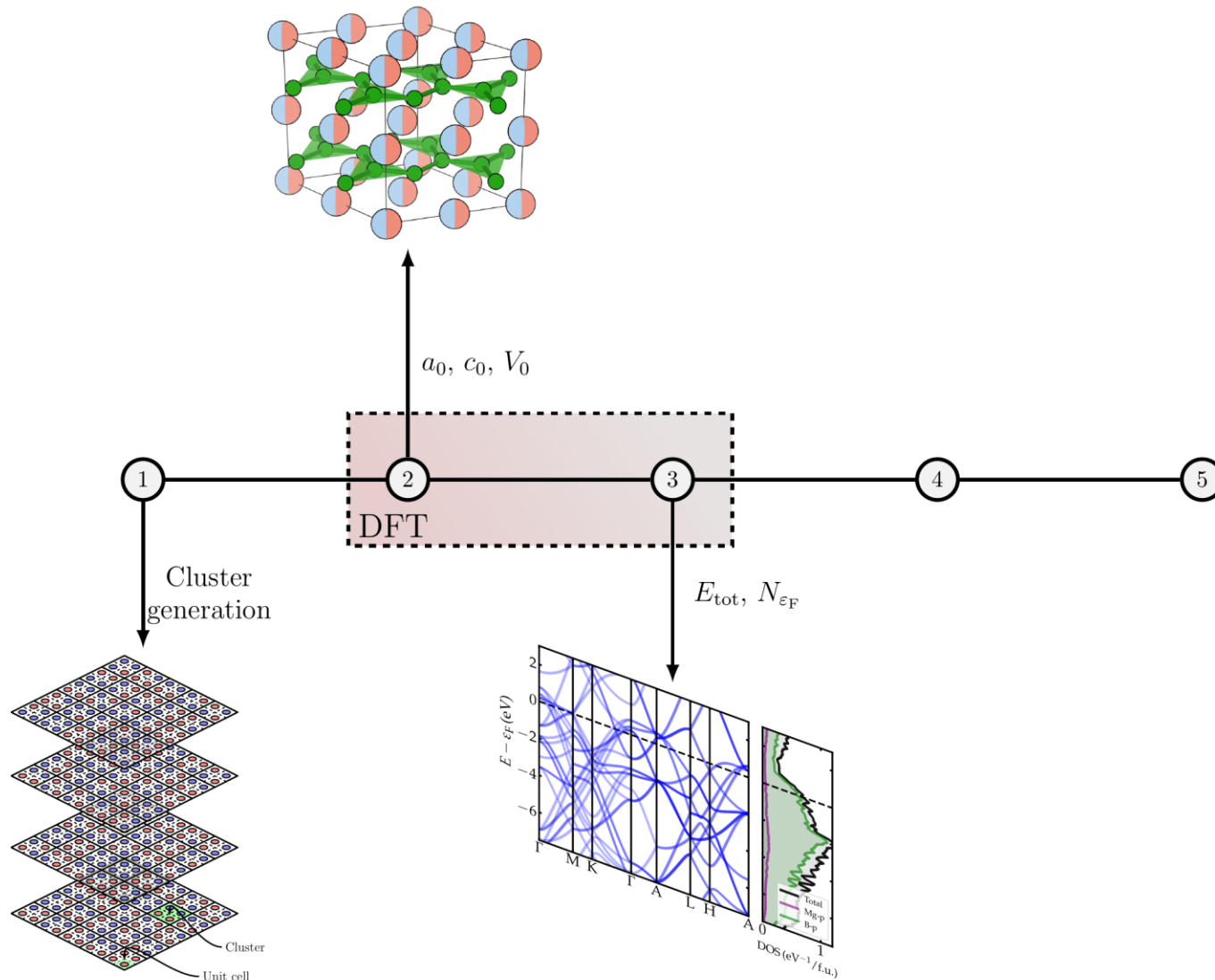
EGQCA in 5 steps: structural optimization



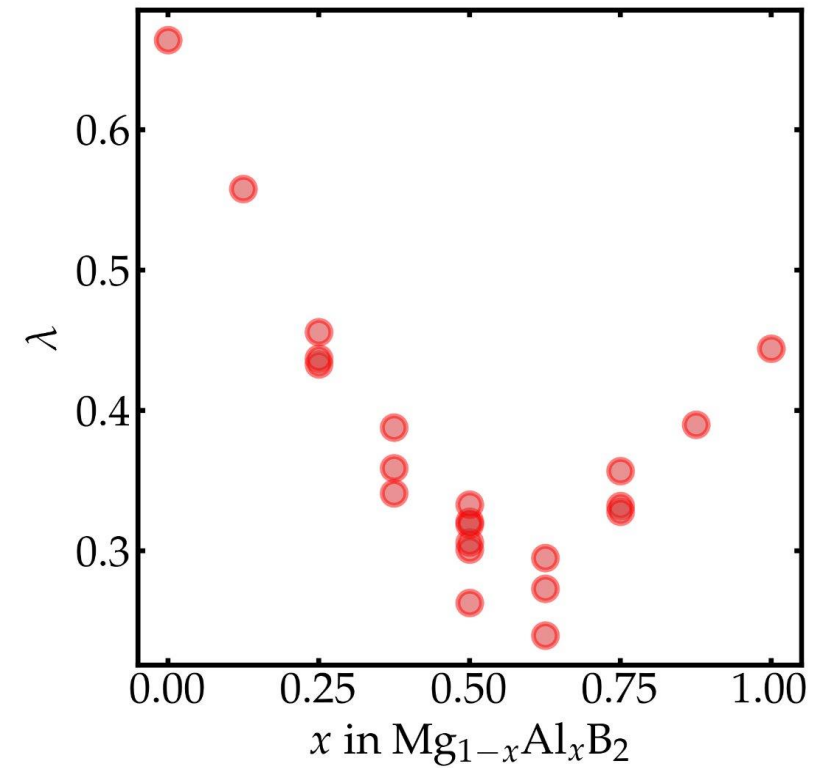
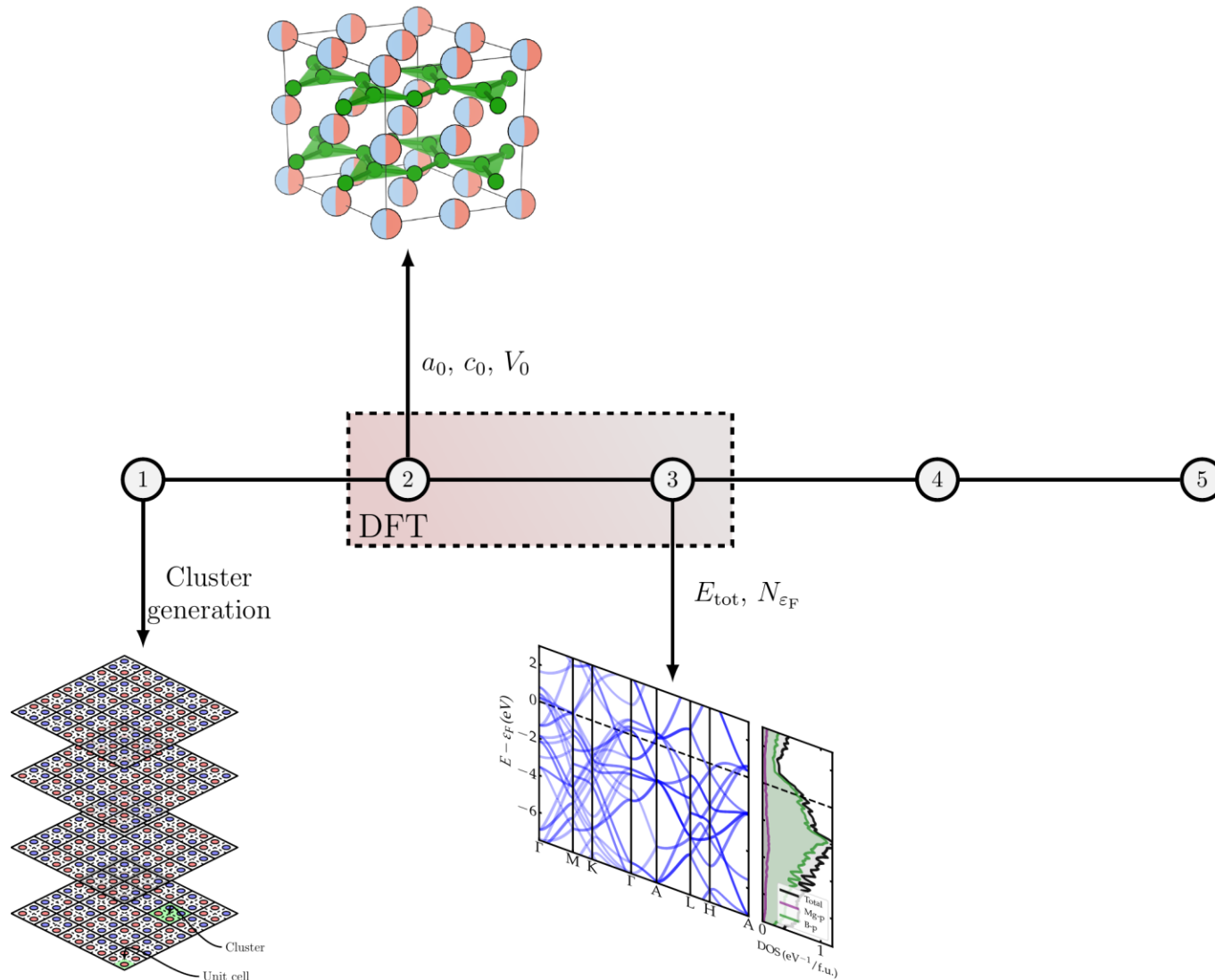
EGQCA in 5 steps: total energy and properties



EGQCA in 5 steps: total energy and properties

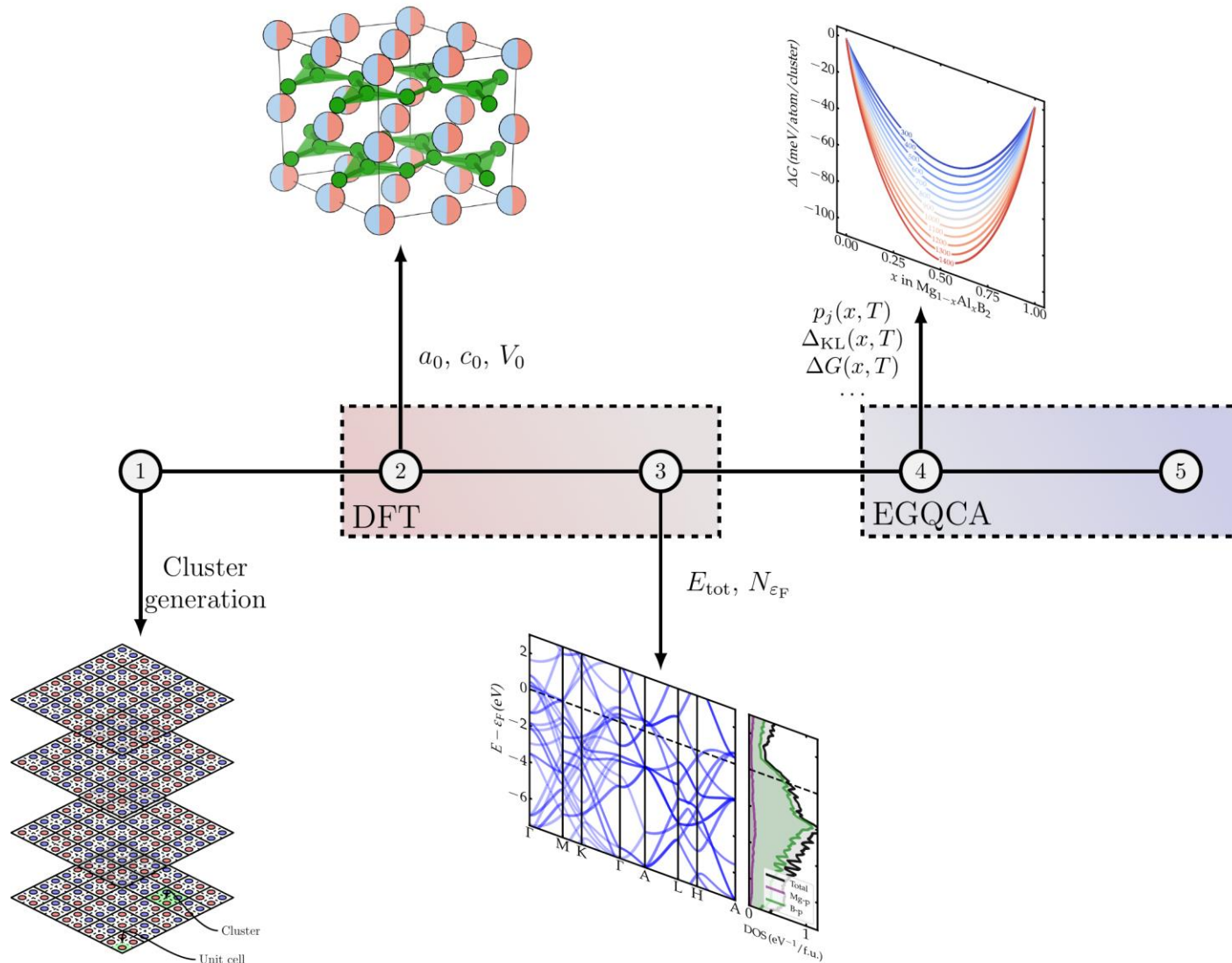


EGQCA in 5 steps: total energy and properties

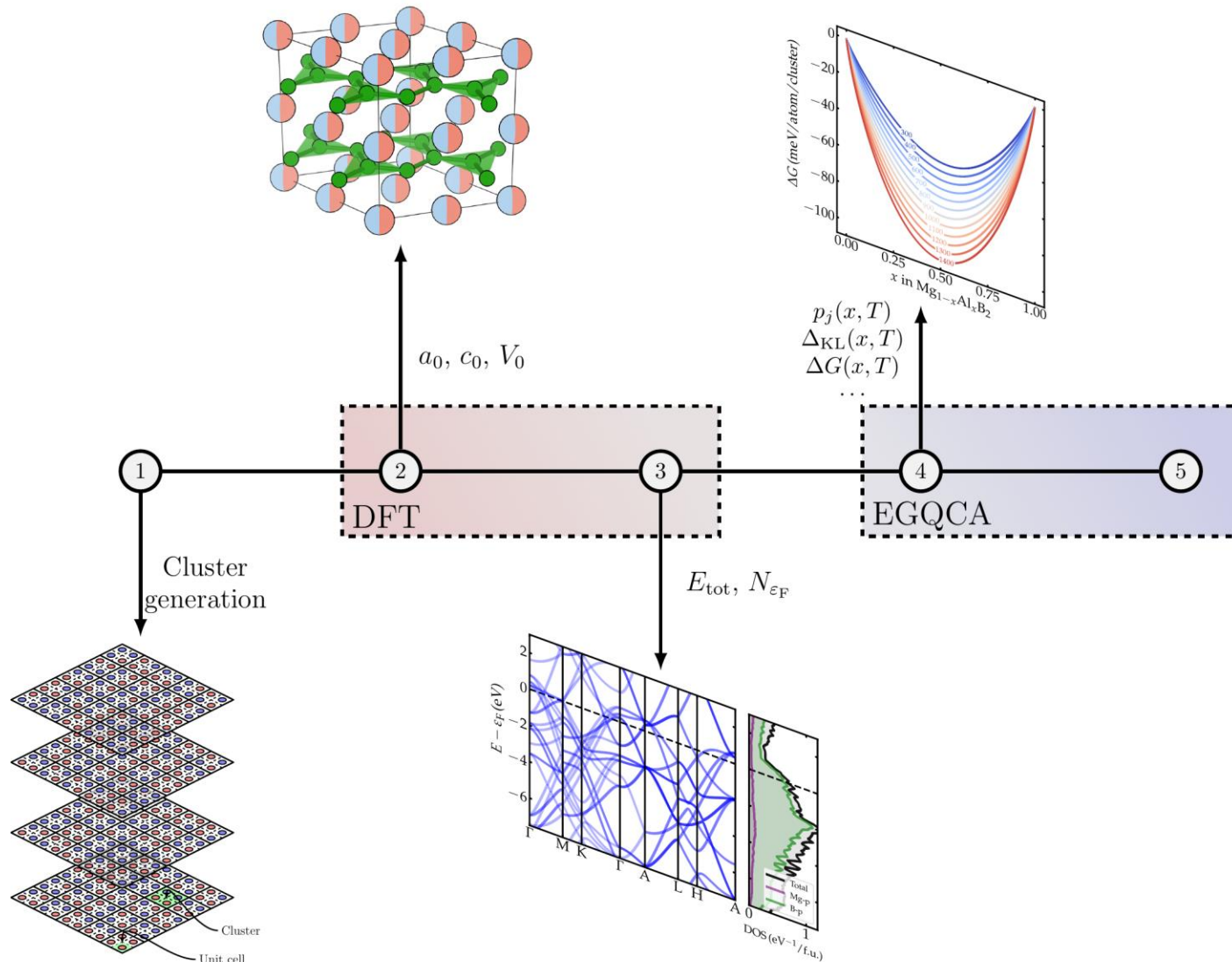


EGQCA in 5 steps: free energy minimization

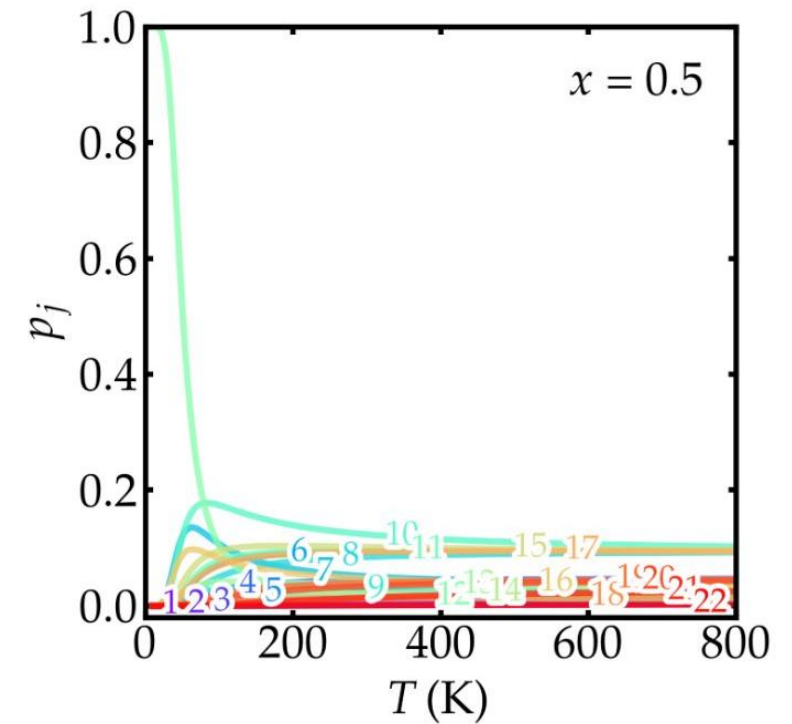
$$\min \Delta G(x, T) \mapsto p_j(x, T)$$



EGQCA in 5 steps: free energy minimization

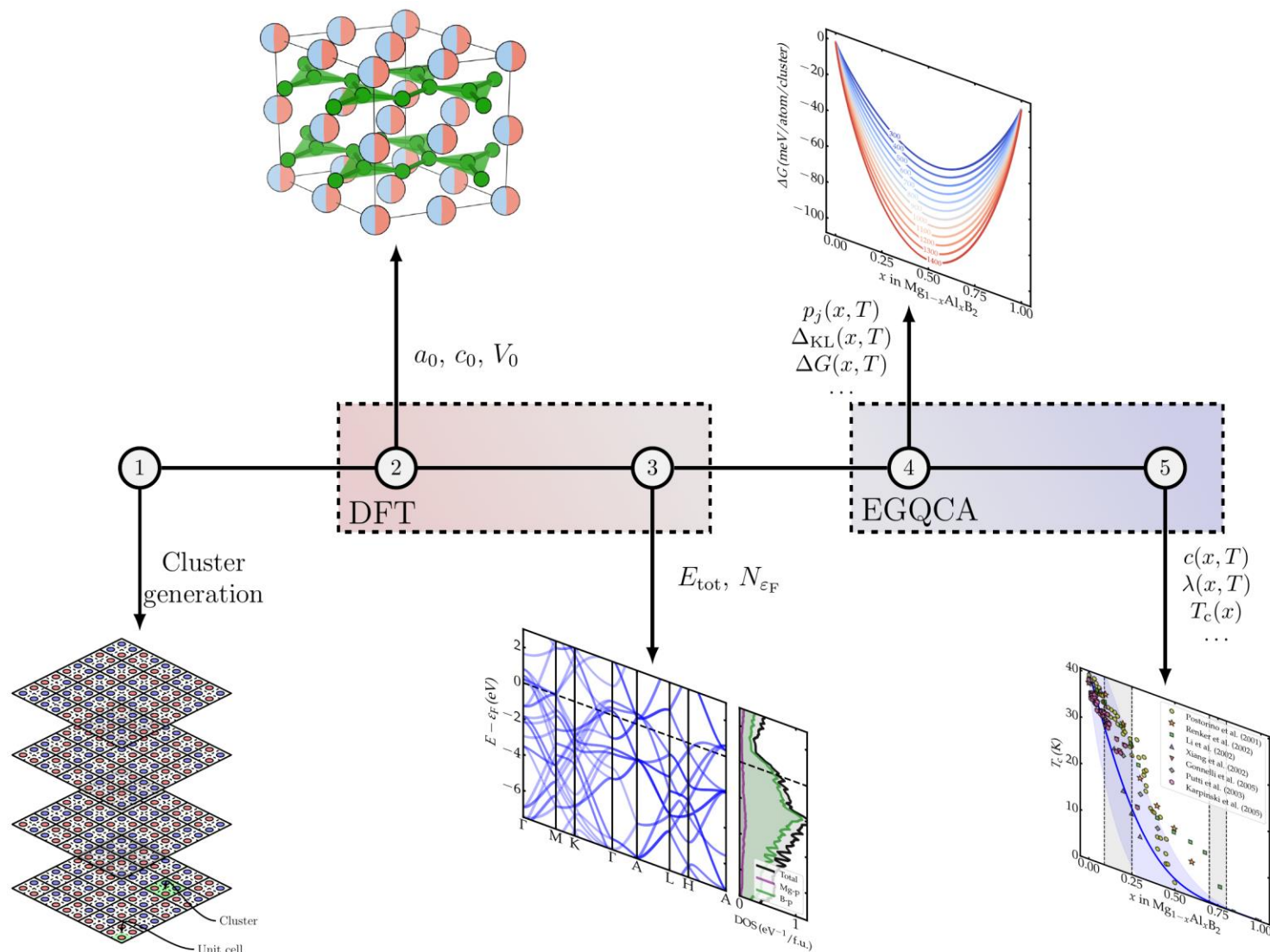


$$\min \Delta G(x, T) \mapsto p_j(x, T)$$

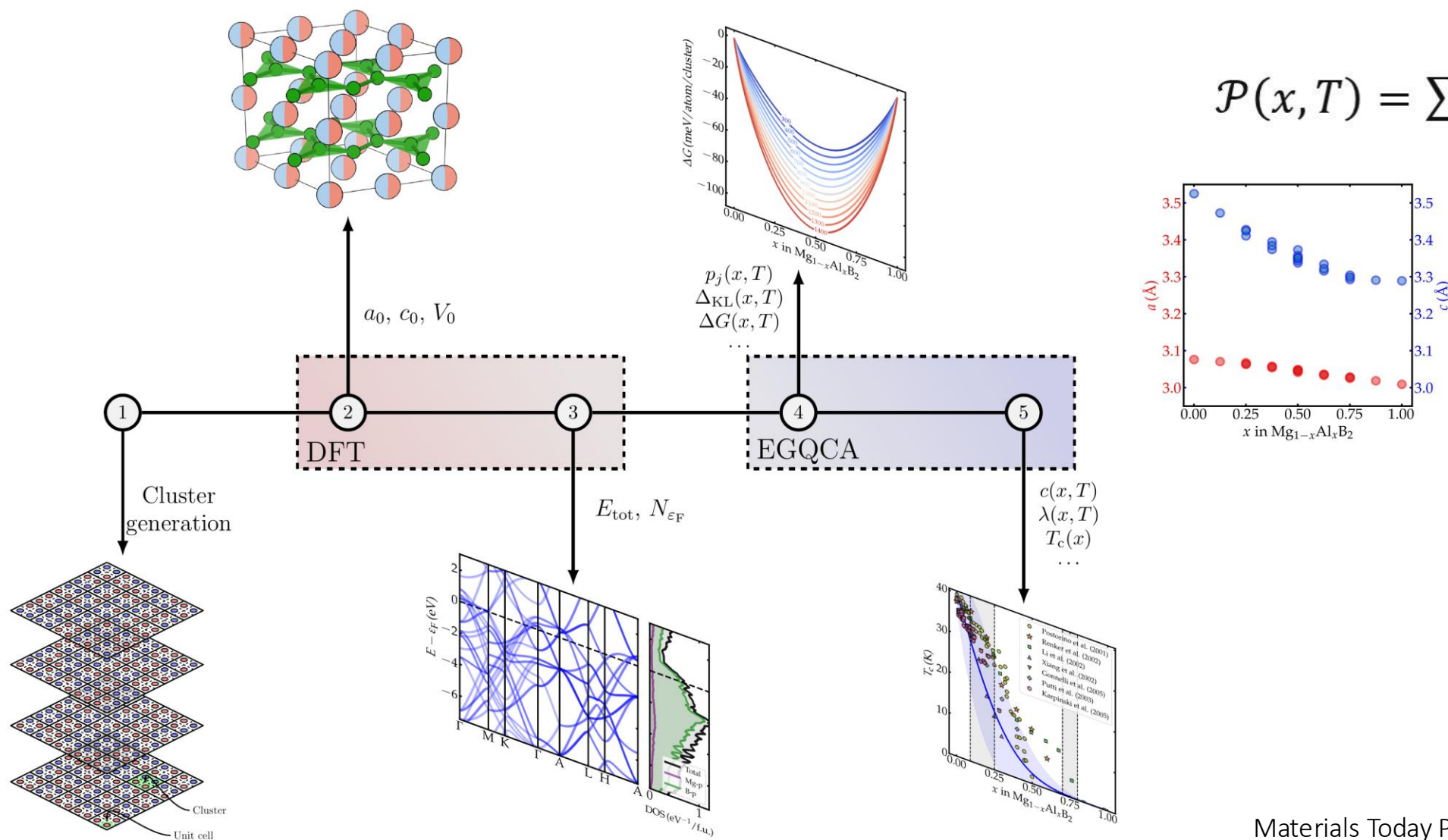


EGQCA in 5 steps: averaging properties

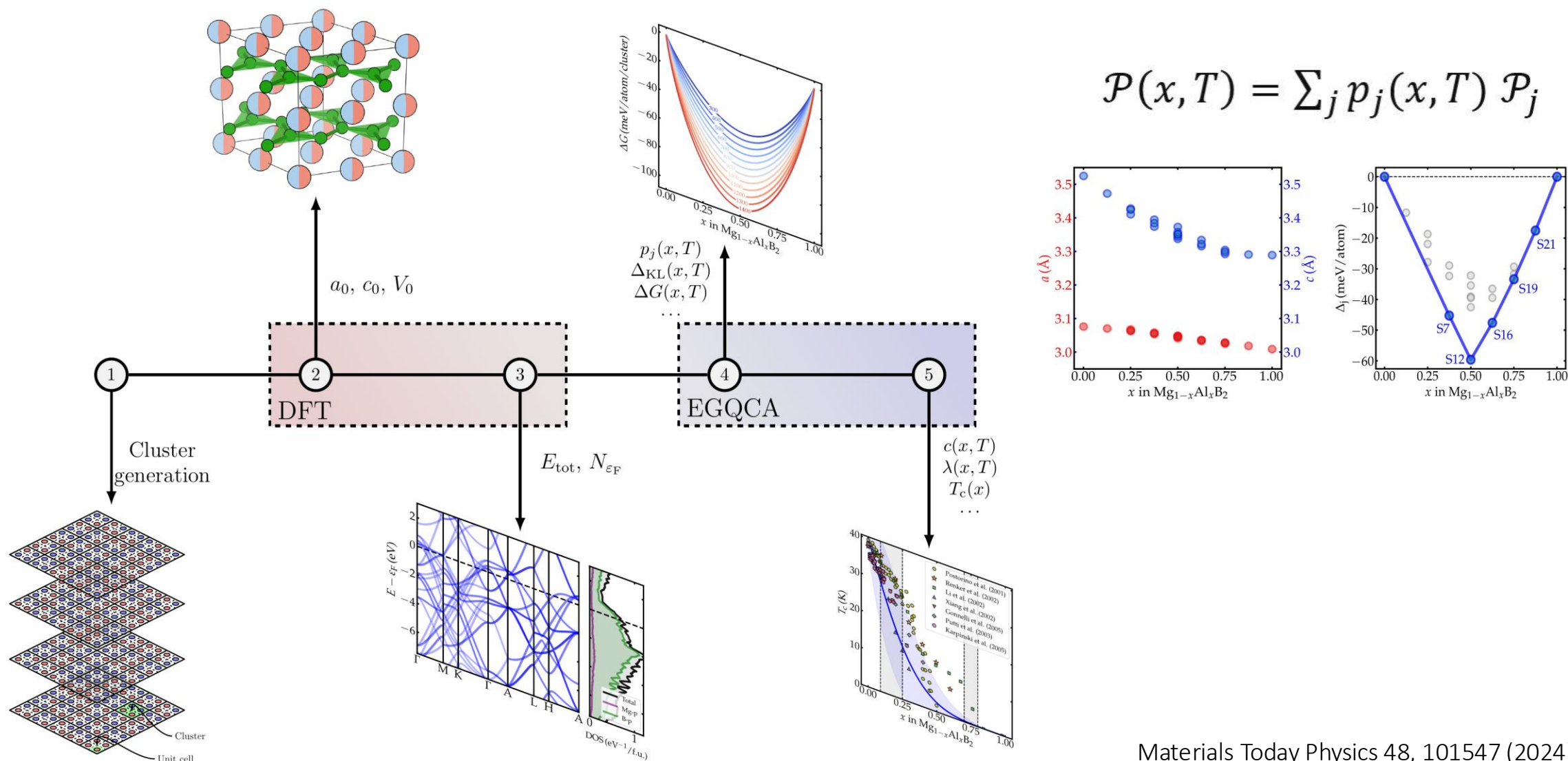
$$\mathcal{P}(x, T) = \sum_j p_j(x, T) \mathcal{P}_j$$



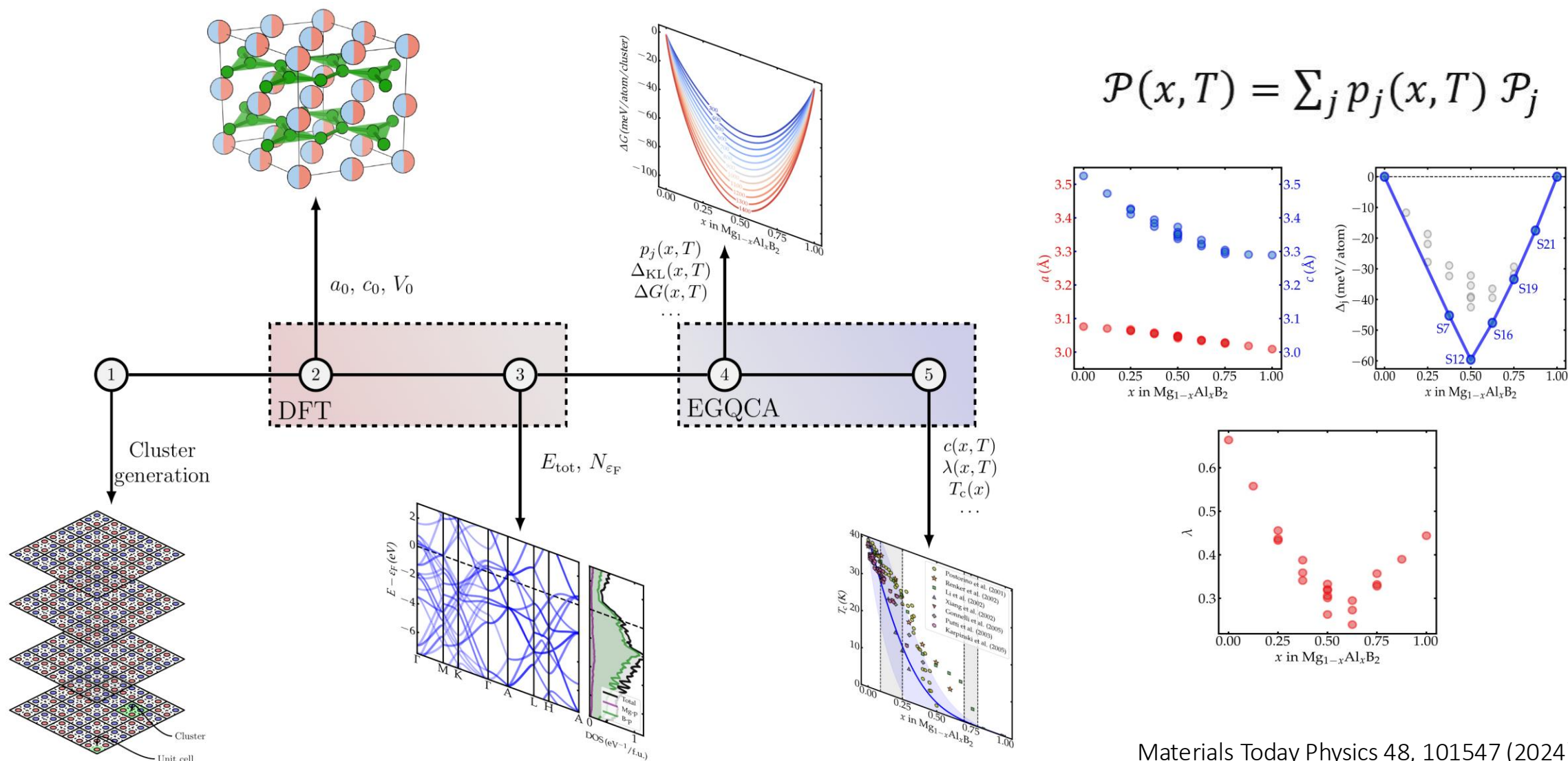
EGQCA in 5 steps: averaging properties



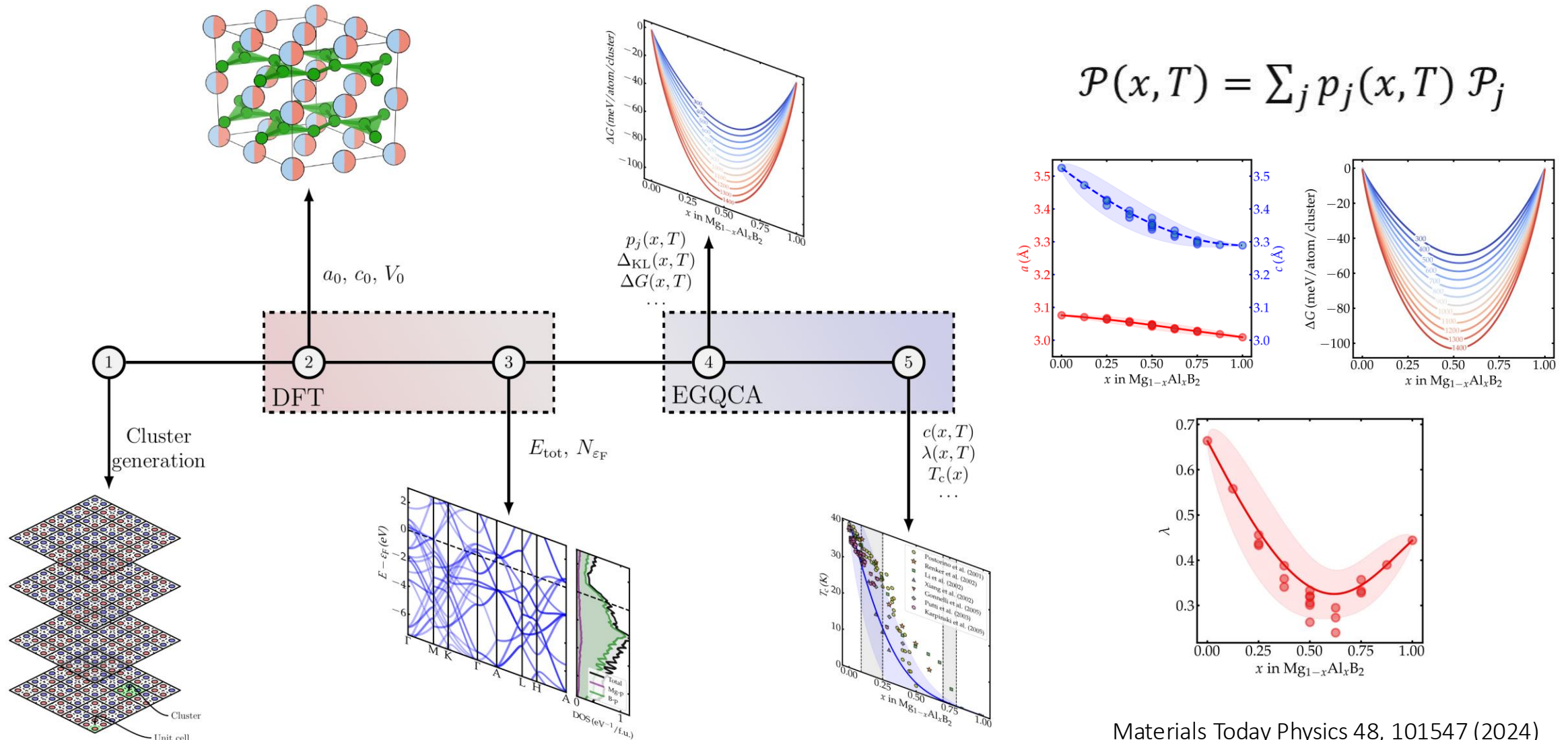
EGQCA in 5 steps: averaging properties



EGQCA in 5 steps: averaging properties

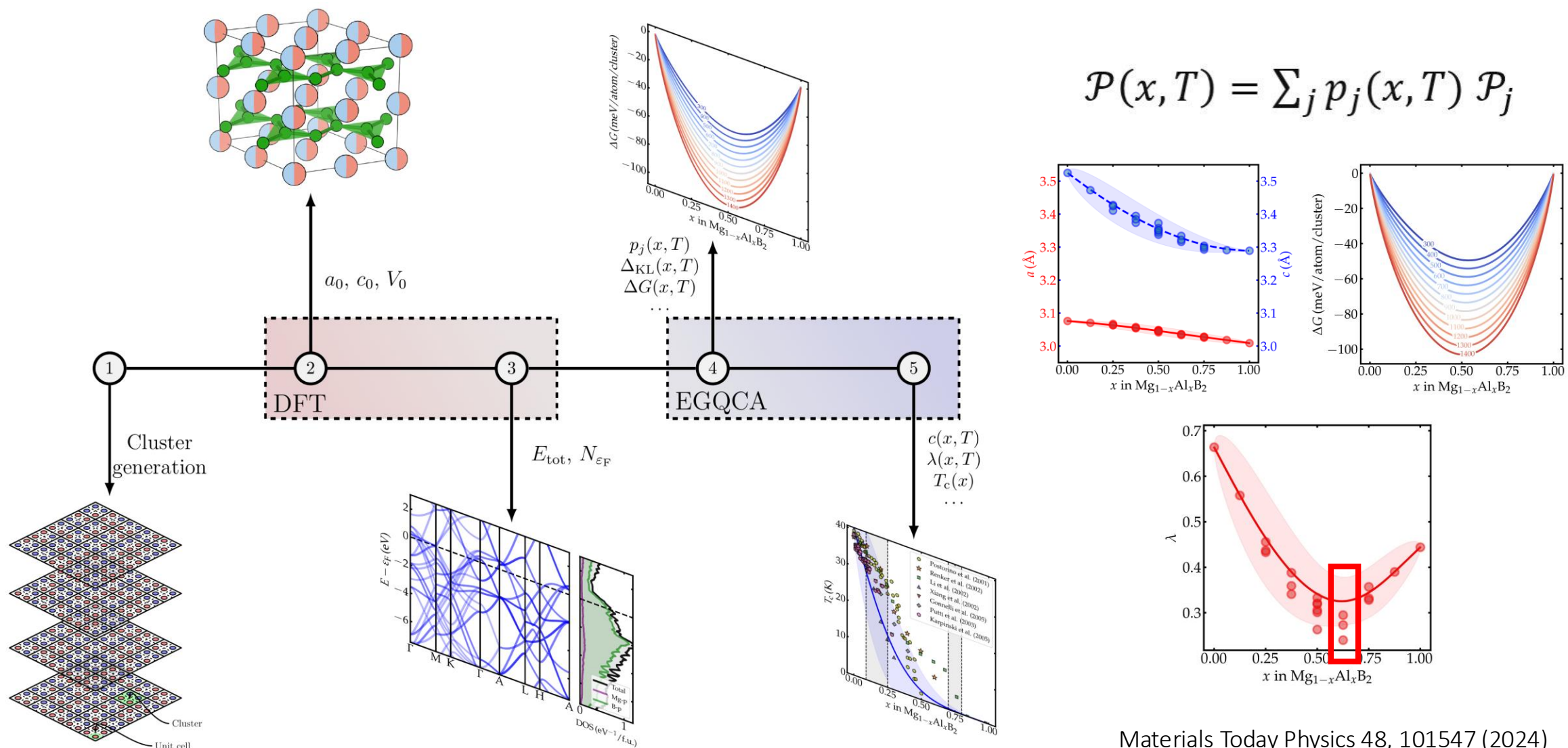


EGQCA in 5 steps: averaging properties



$$\mathcal{P}(x, T) = \sum_j p_j(x, T) \mathcal{P}_j$$

EGQCA in 5 steps: averaging properties

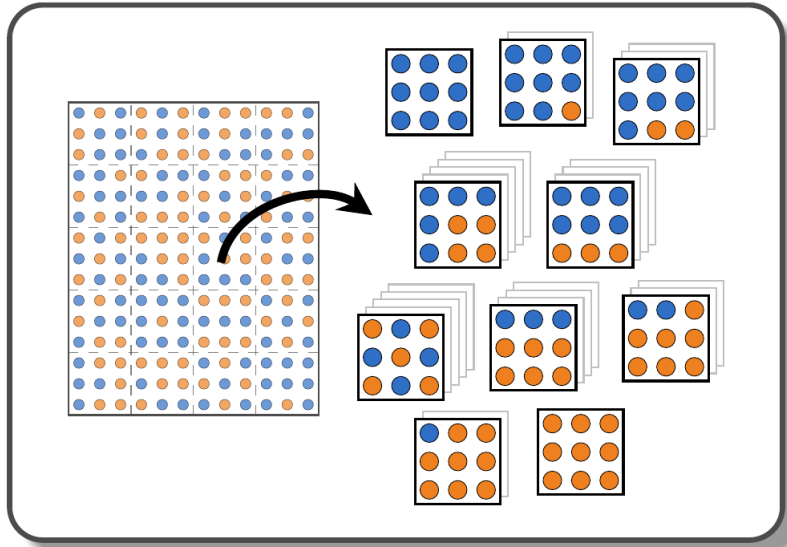


EGQCA code

EGQCA code

1. Cluster Generation

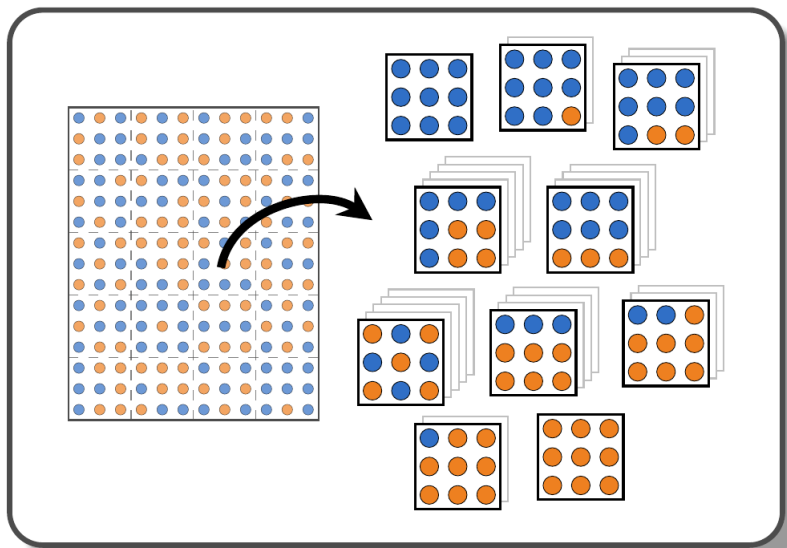
Required



EGQCA code

1. Cluster Generation

Required



Optional

Generate DFT input files

FHI-aims

QE

VASP



Cluster 1

...

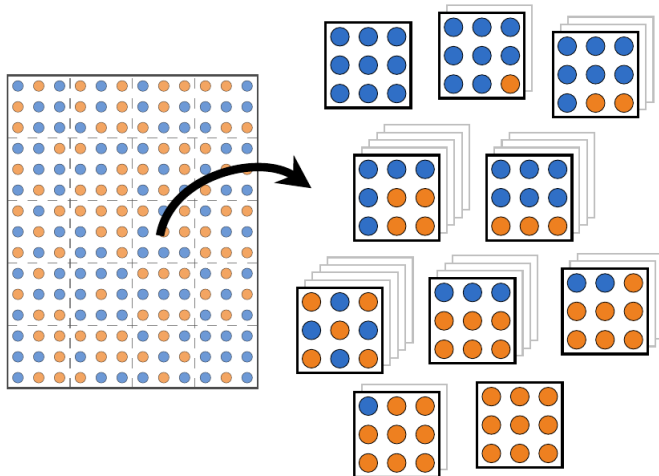


Cluster J

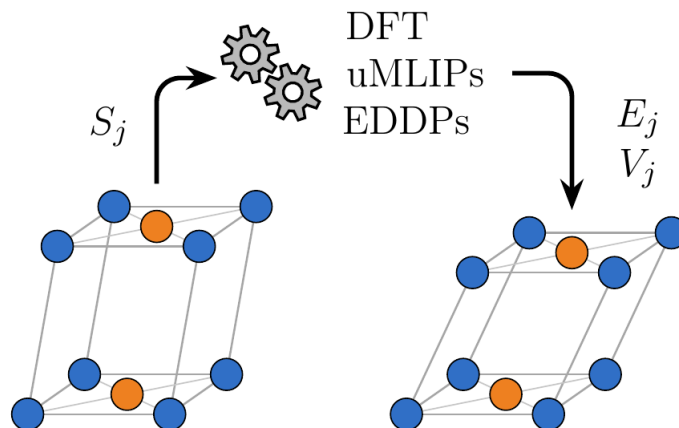
EGQCA code

1. Cluster Generation

Required



2. Relaxation



Optional

Generate DFT input files

FHI-aims
QE
VASP



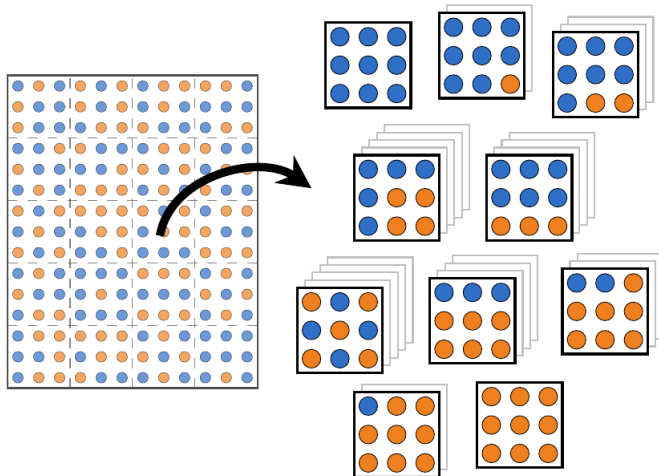
...



EGQCA code

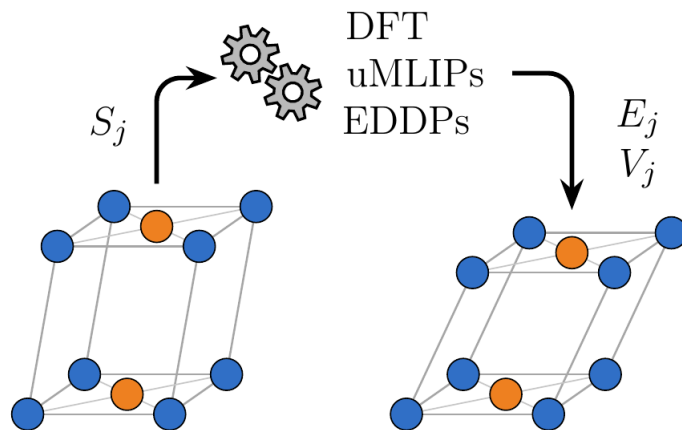
1. Cluster Generation

Required



2. Relaxation

Optional



Generate DFT input files

FHI-aims
QE
VASP



Cluster 1

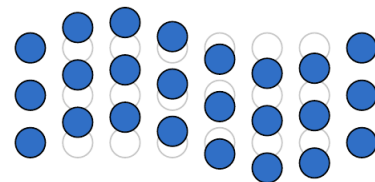
...



Cluster J

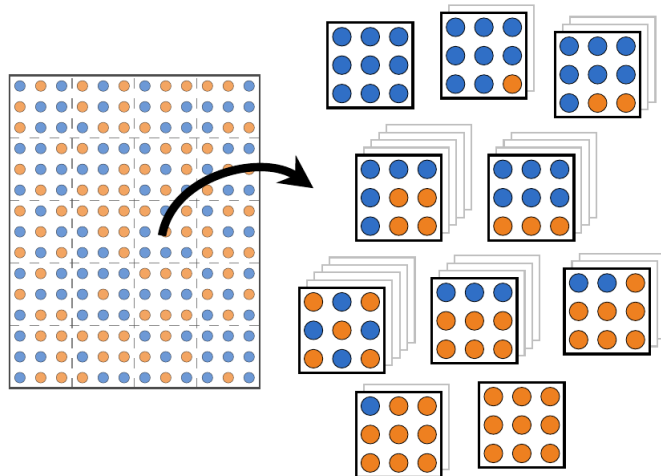
Phonon calculations

$D(\omega)$
 $\alpha^2 F(\omega)$
 $\lambda(\omega)$



EGQCA code

1. Cluster Generation



Generate DFT input files

FHI-aims
QE
VASP



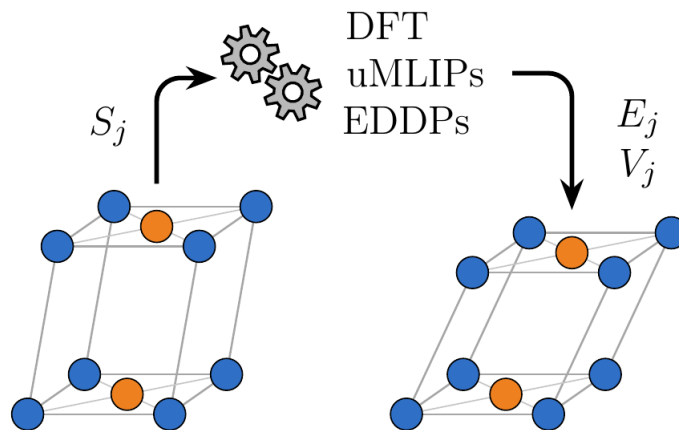
Cluster 1

...



Cluster J

2. Relaxation

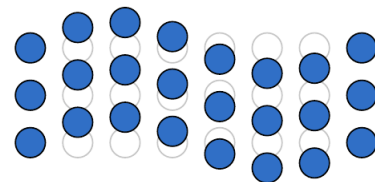


Phonon calculations

$$D(\omega)$$

$$\alpha^2 F(\omega)$$

$$\lambda(\omega)$$



3. EGQCA

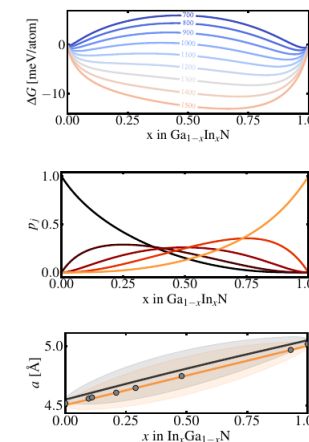
$$\Delta G(x, T, P)$$



$$p_j(x, T, P)$$

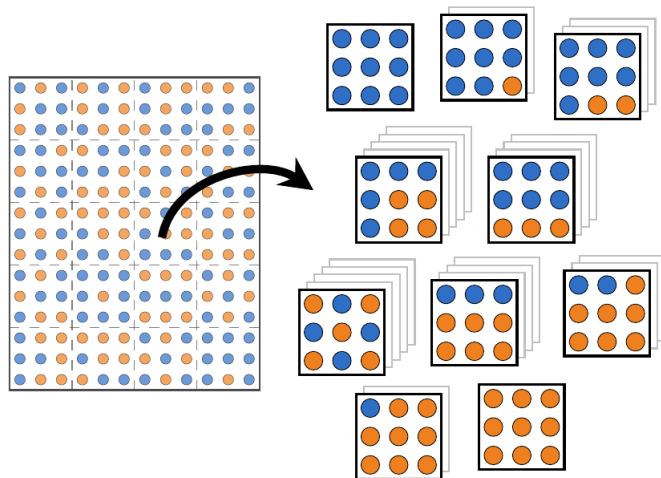


$$a(x, T)$$



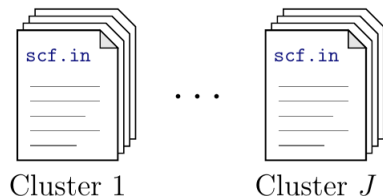
EGQCA code

1. Cluster Generation

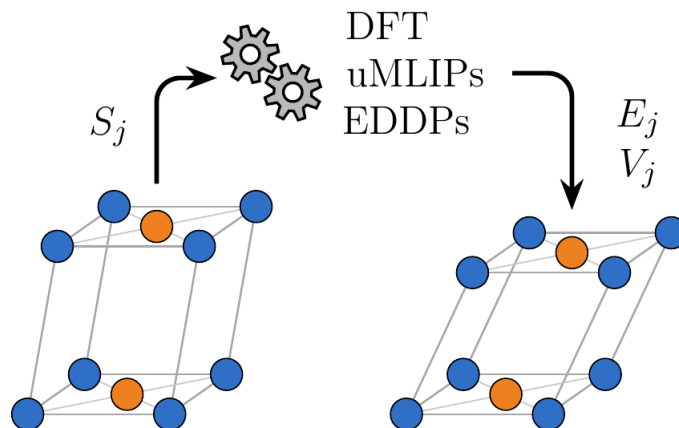


Generate DFT input files

FHI-aims
QE
VASP



2. Relaxation

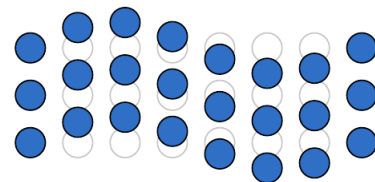


Phonon calculations

$$D(\omega)$$

$$\alpha^2 F(\omega)$$

$$\lambda(\omega)$$

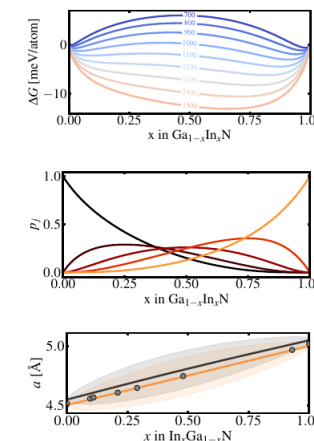


3. EGQCA

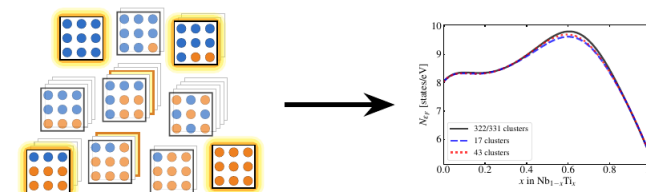
$$\Delta G(x, T, P)$$

$$p_j(x, T, P)$$

$$a(x, T)$$



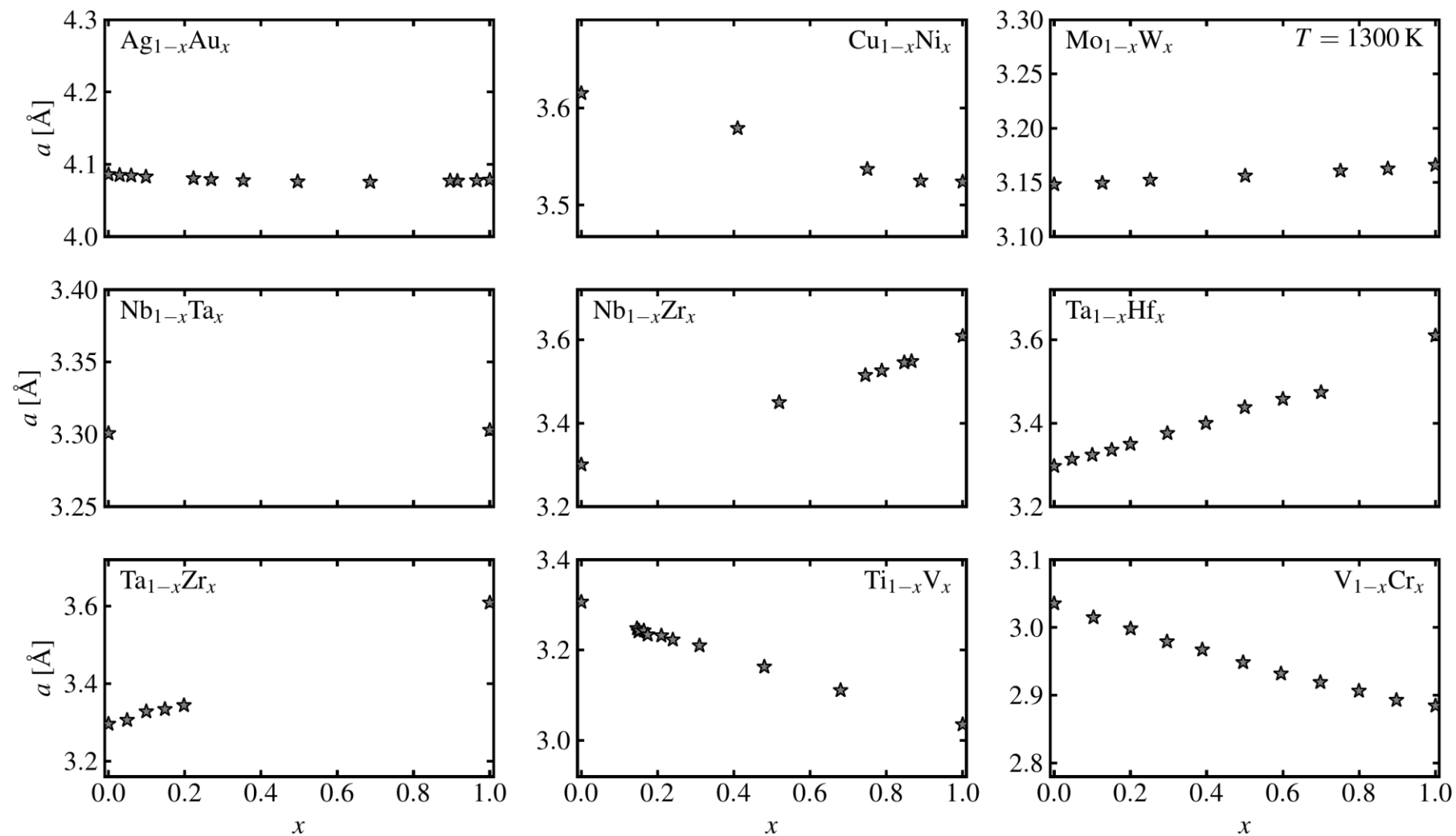
Most important clusters



Required

Optional

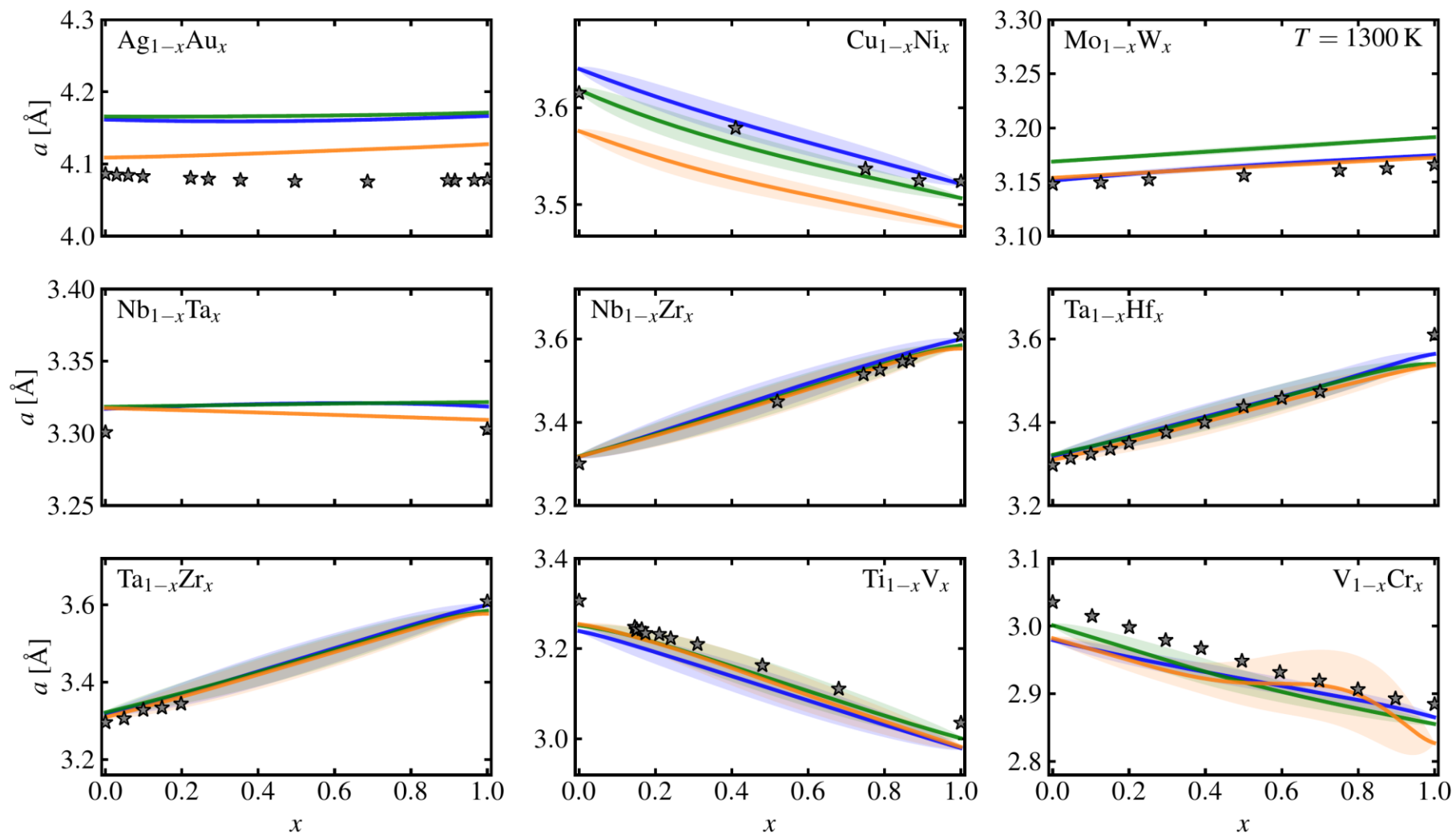
EGQCA code: HT automated modeling



★ experiment

Unpublished. Work in progress!

EGQCA code: HT automated modeling



— MACE-MPA-0-medium

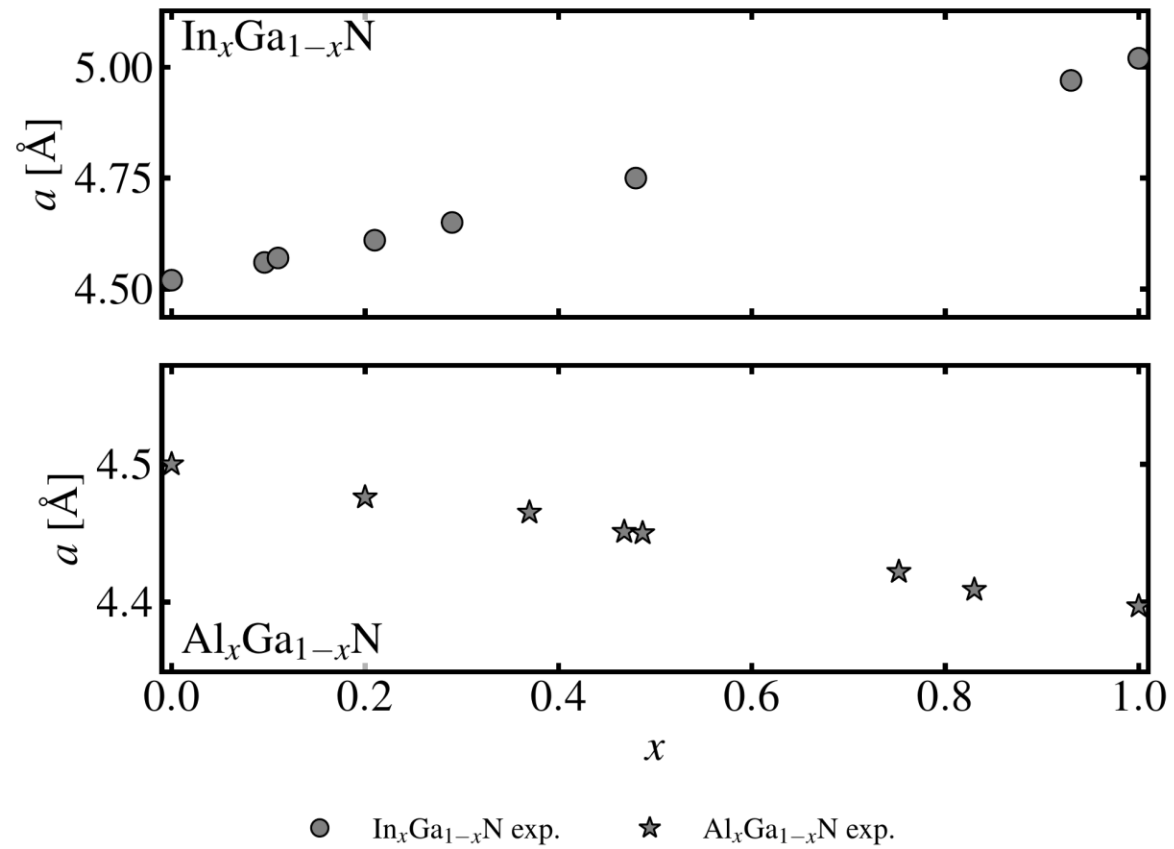
— MatterSim-5M

— PET-OMATPES-L

★ experiment

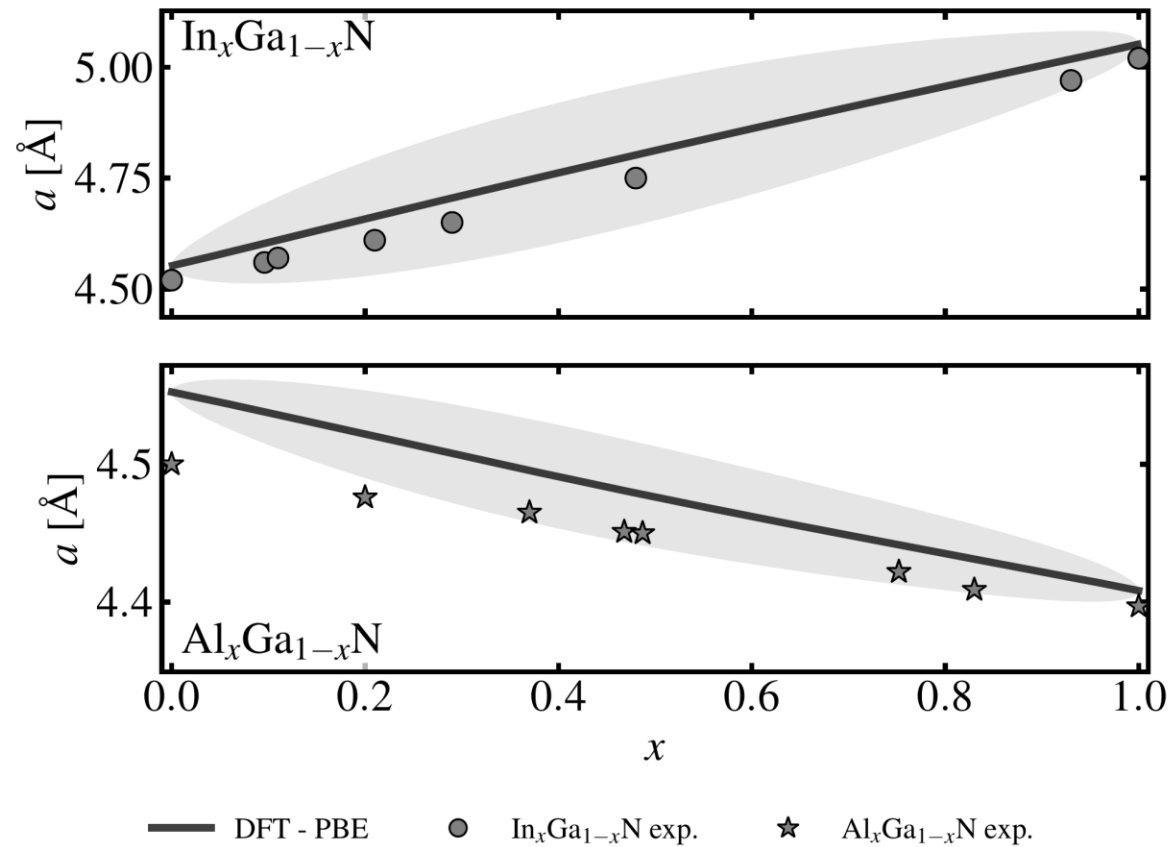
Unpublished. Work in progress!

EGQCA code



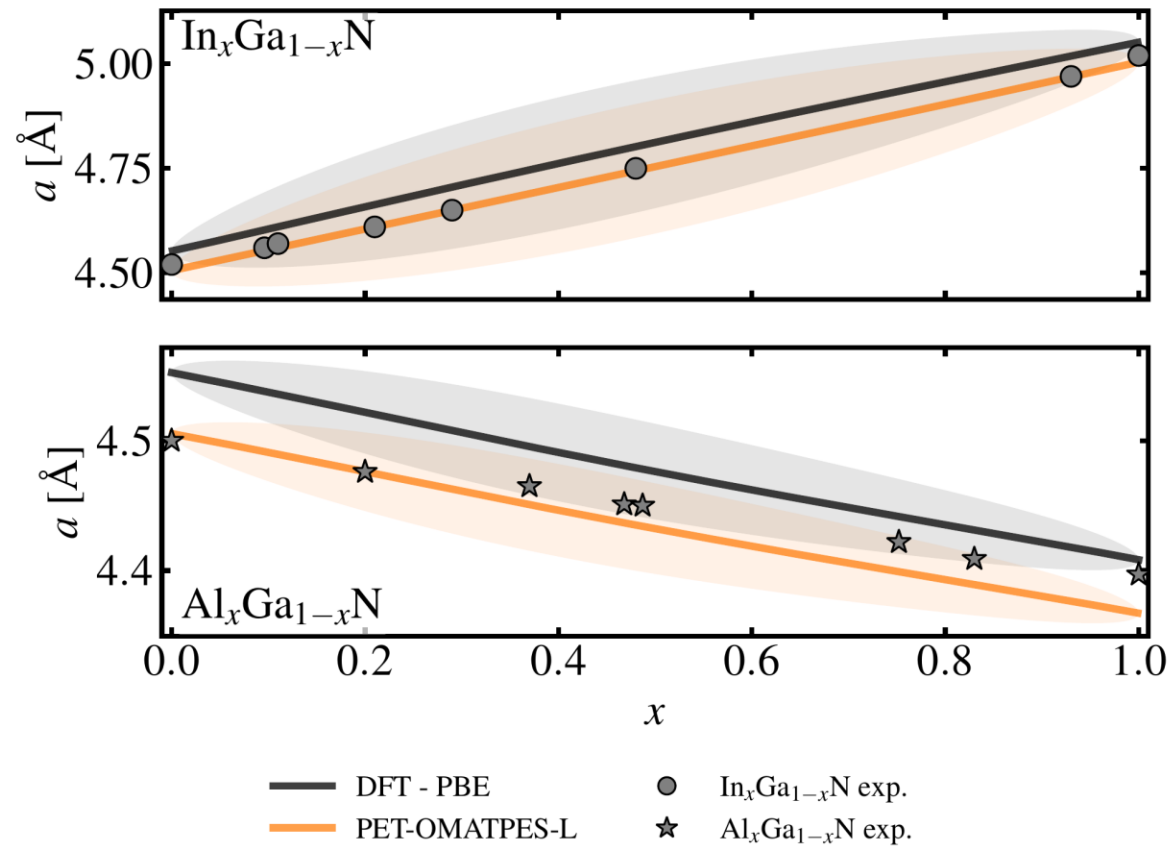
Unpublished. Work in progress!

EGQCA code



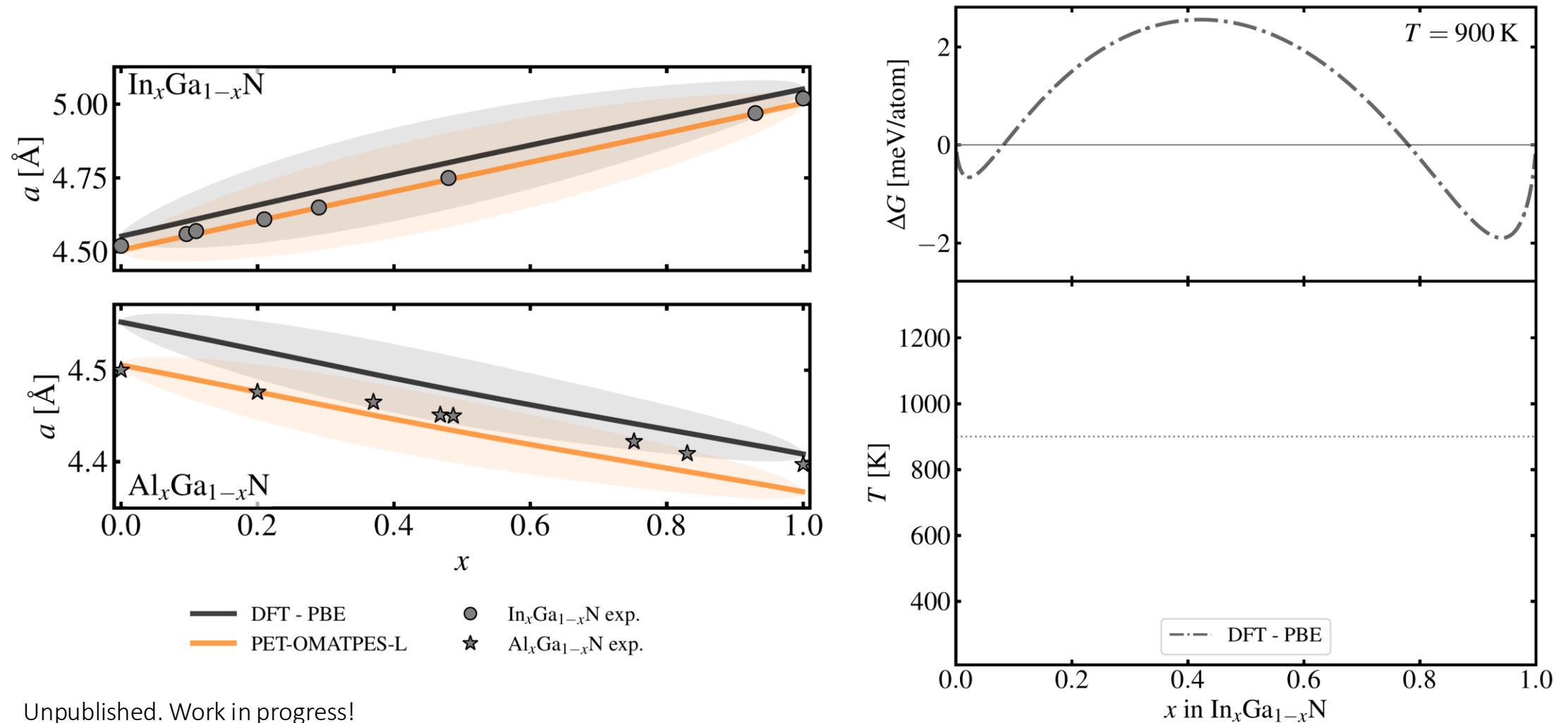
Unpublished. Work in progress!

EGQCA code



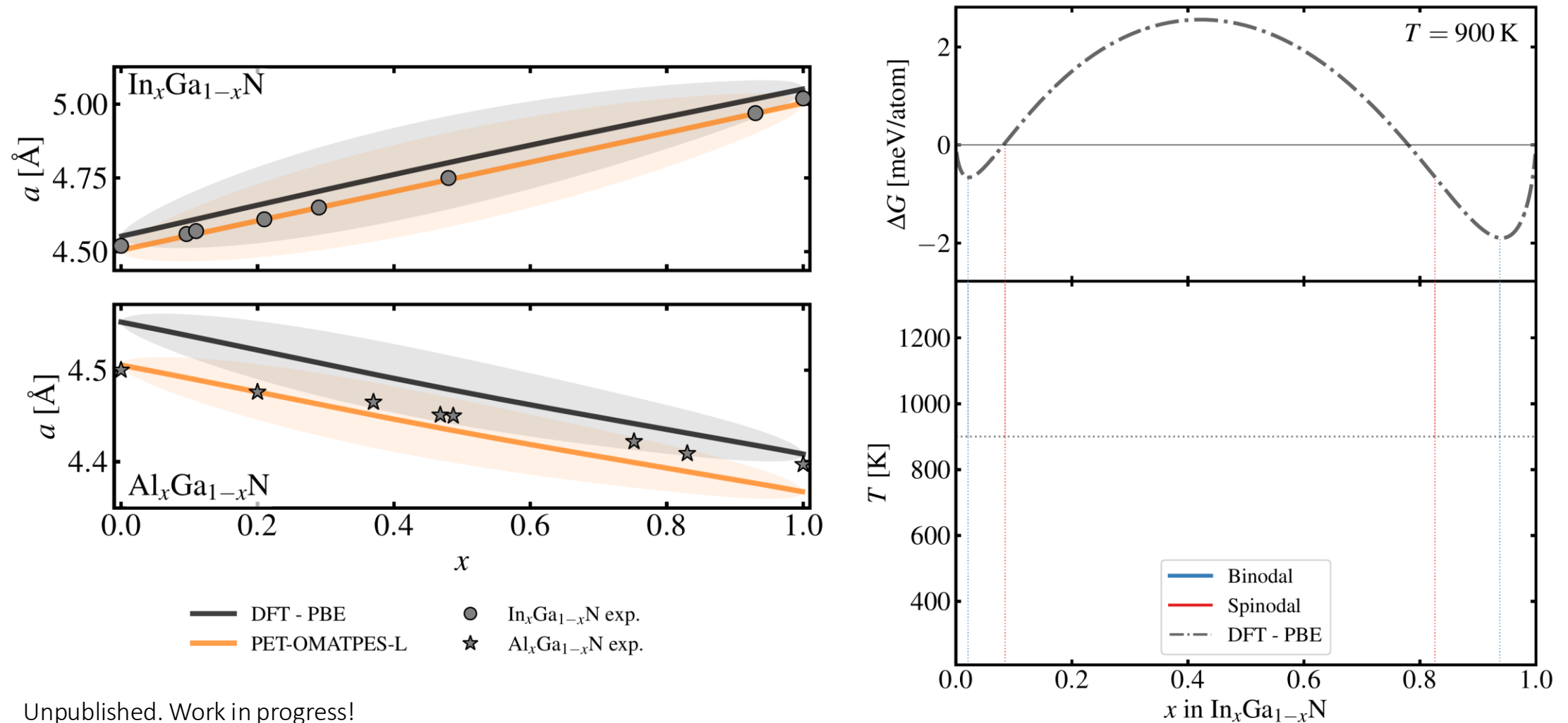
Unpublished. Work in progress!

EGQCA code: automated thermo assessment



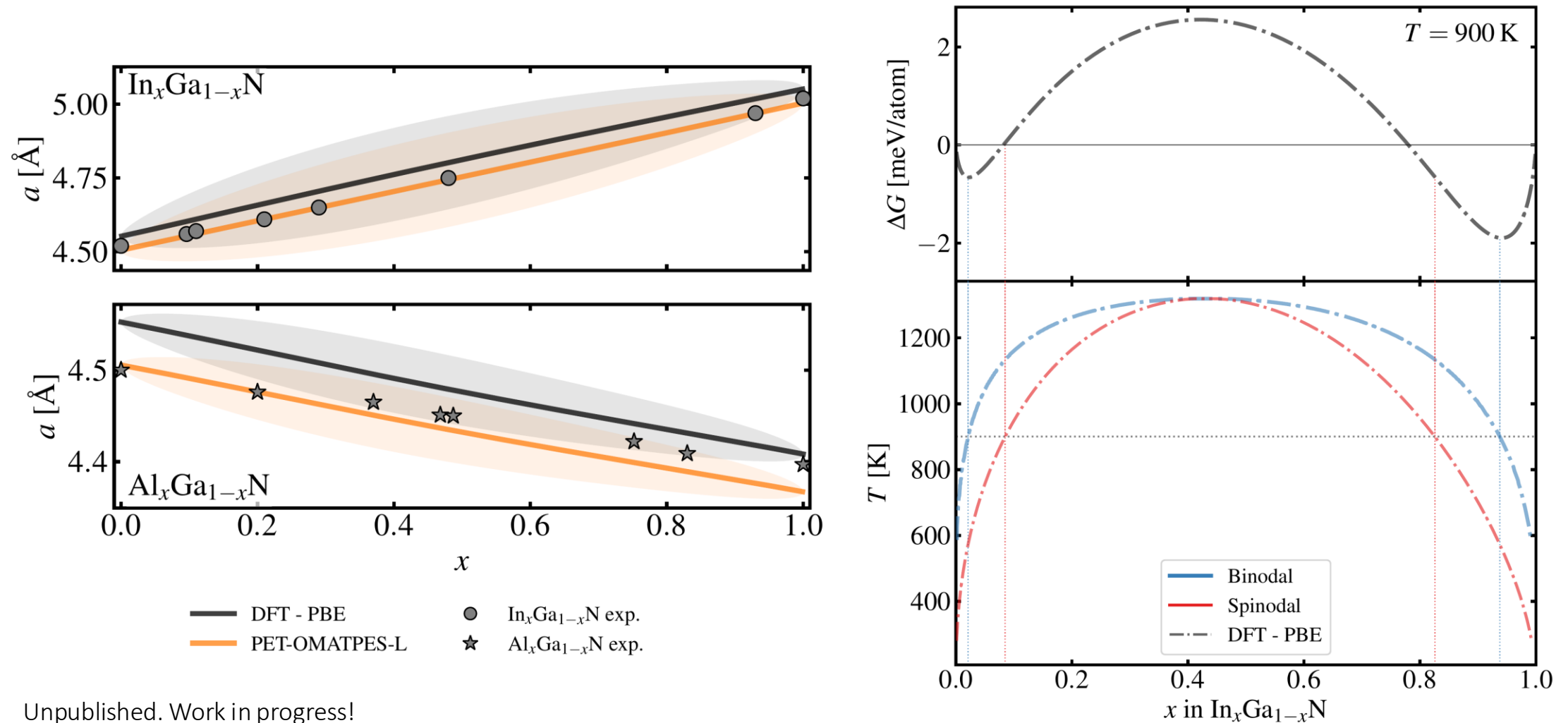
Unpublished. Work in progress!

EGQCA code: automated thermo assessment



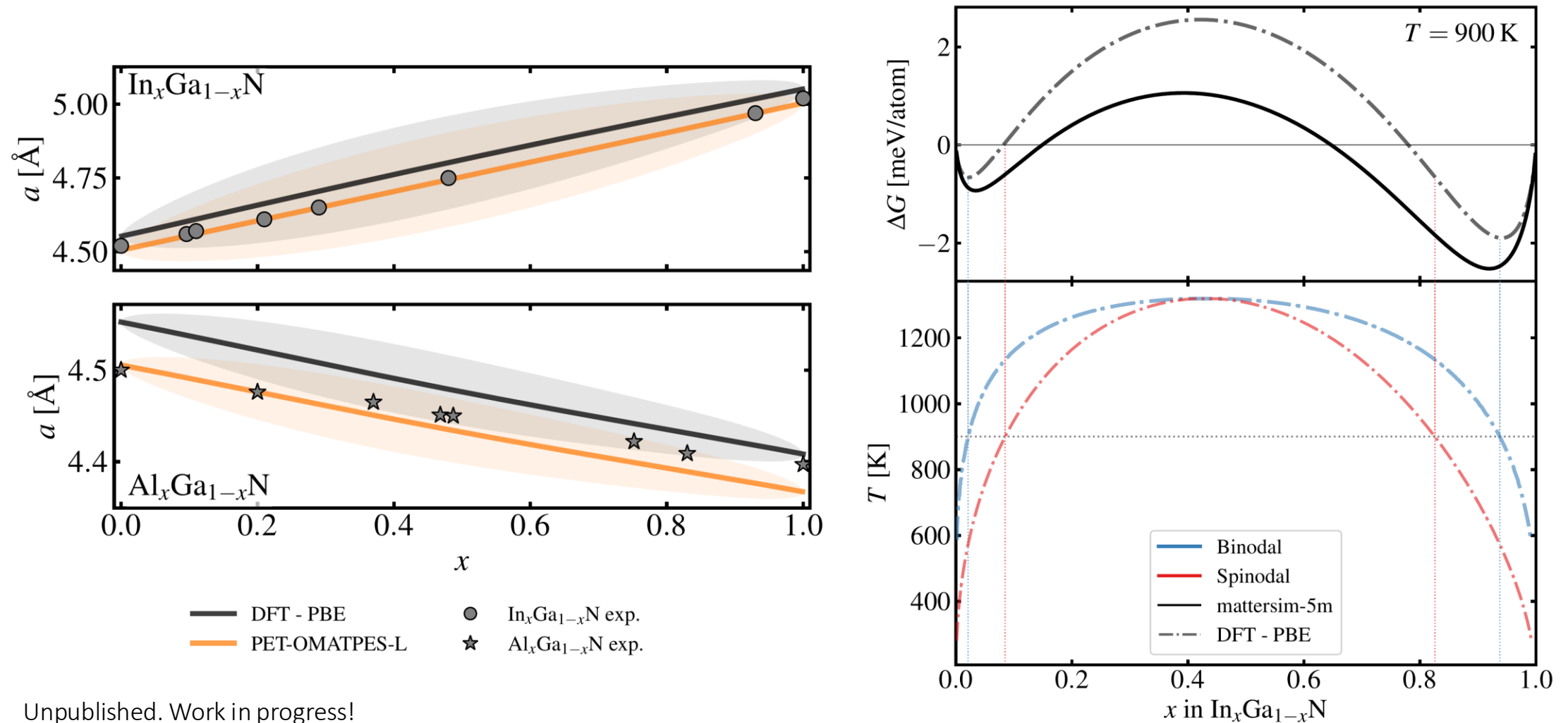
Unpublished. Work in progress!

EGQCA code: automated thermo assessment



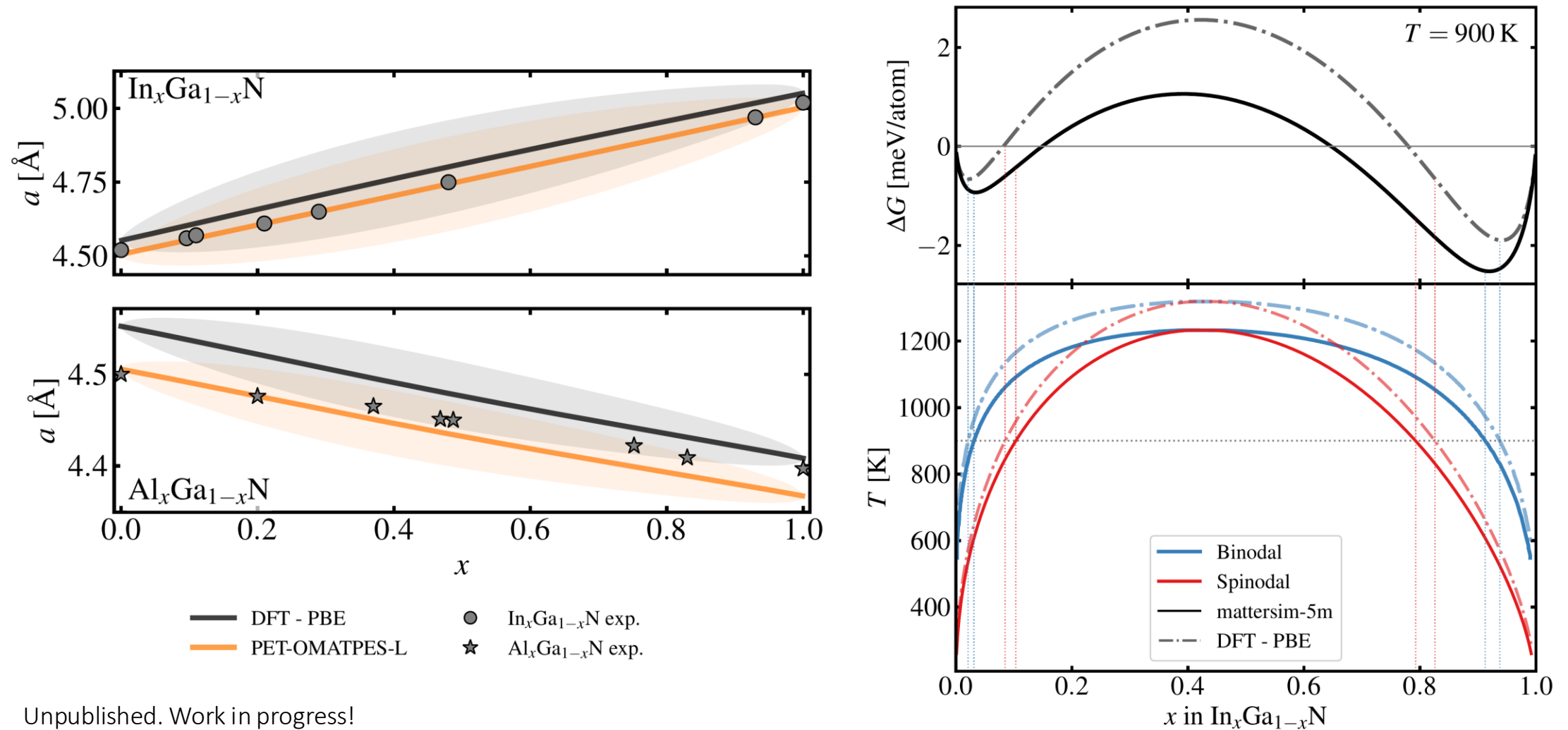
Unpublished. Work in progress!

EGQCA code: automated thermo assessment



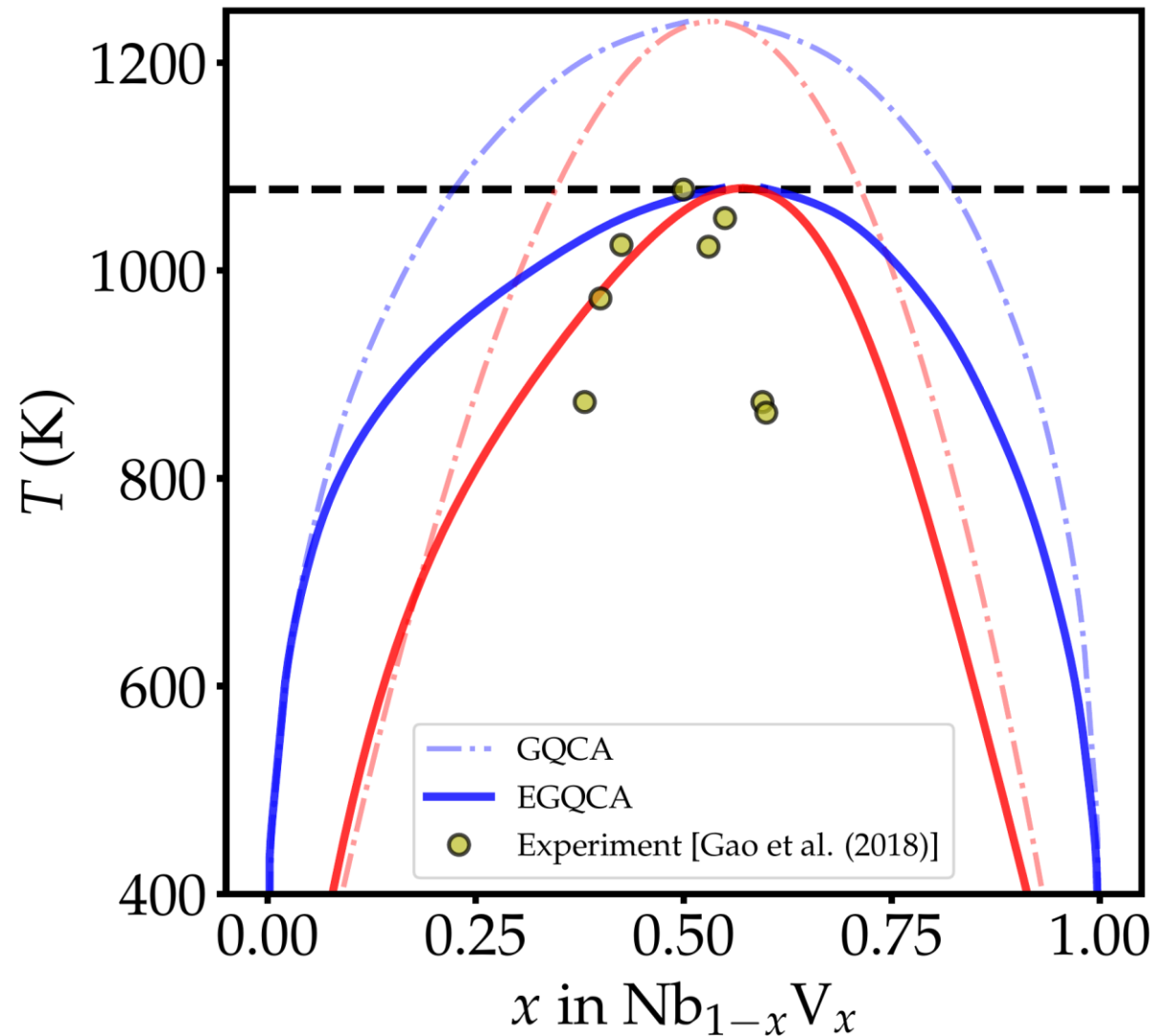
Unpublished. Work in progress!

EGQCA code: automated thermo assessment

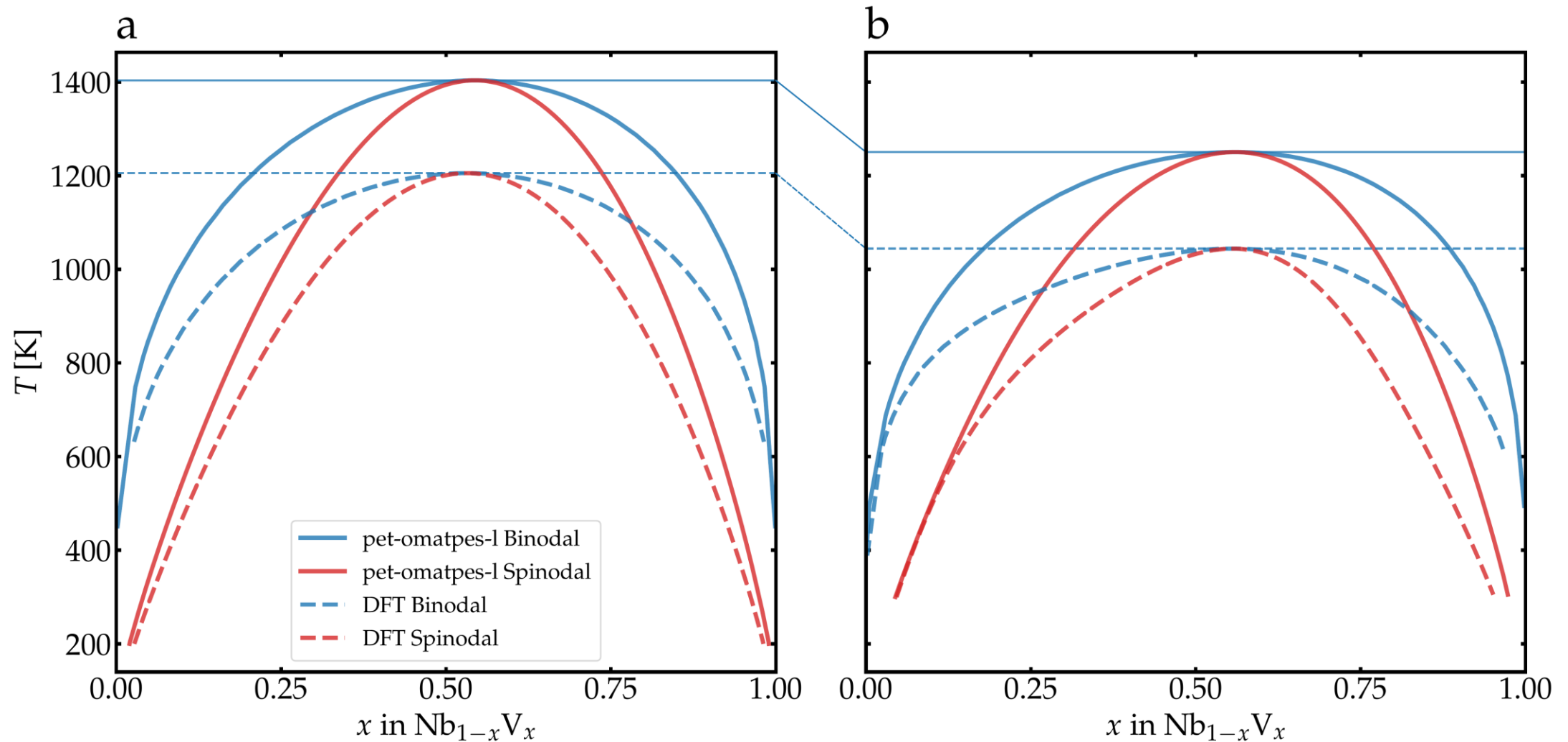


Unpublished. Work in progress!

EGQCA code: including vibrational effects



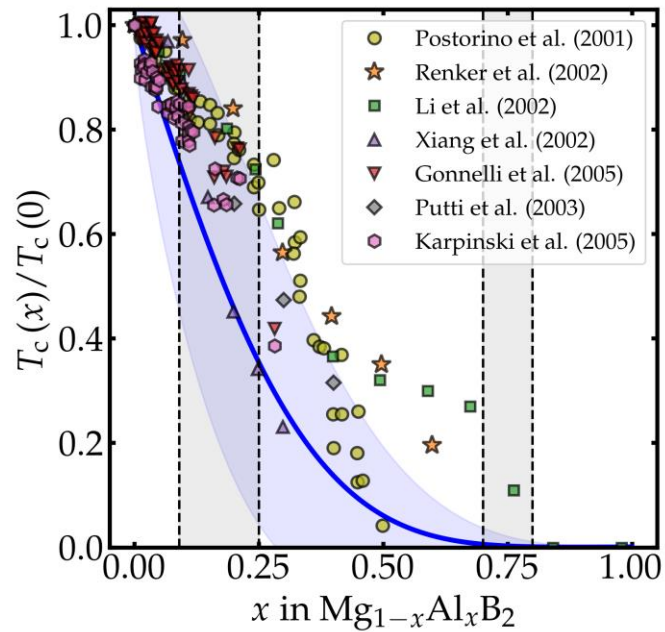
EGQCA code: including vibrational effects



Unpublished. Work in progress!

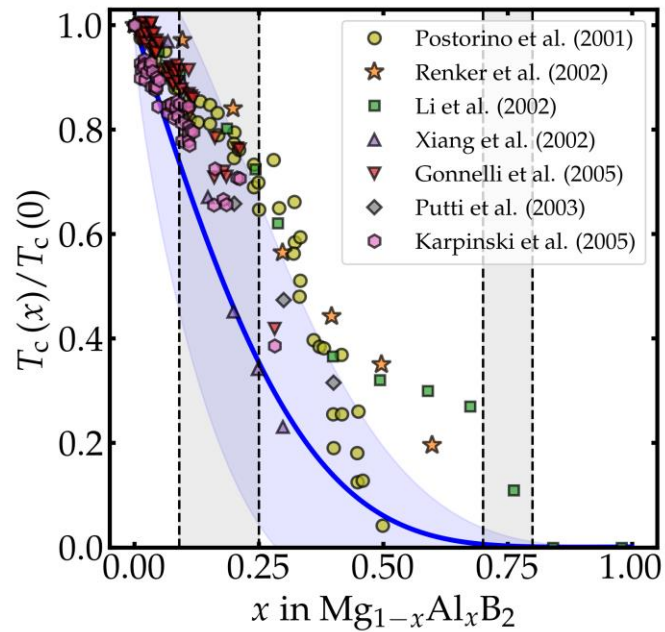
EGQCA code: beyond thermodynamics

EGQCA code: beyond thermodynamics

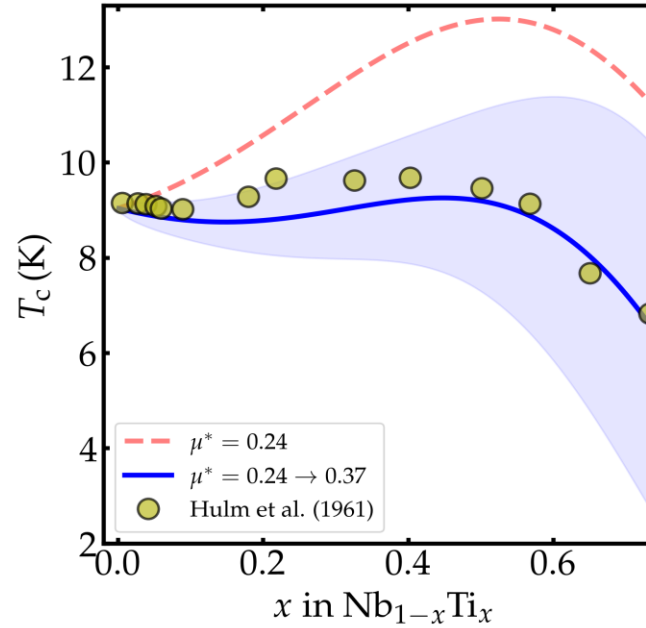


Al-doped MgB_2

EGQCA code: beyond thermodynamics

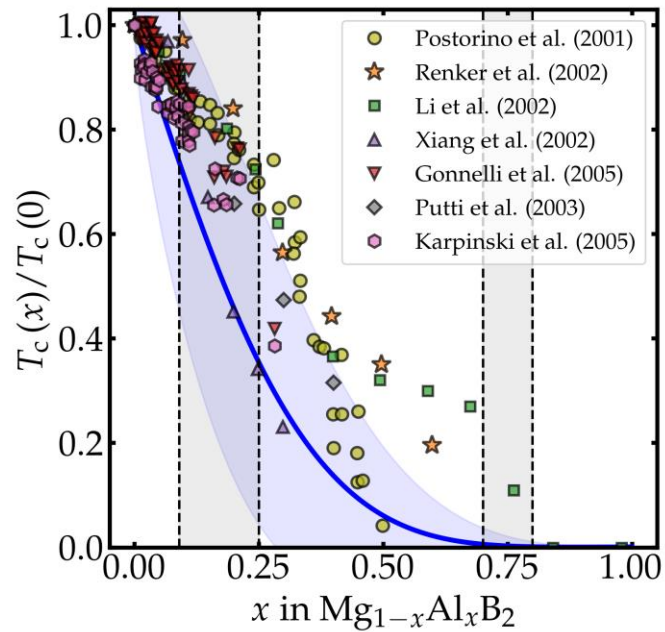


Al-doped MgB_2

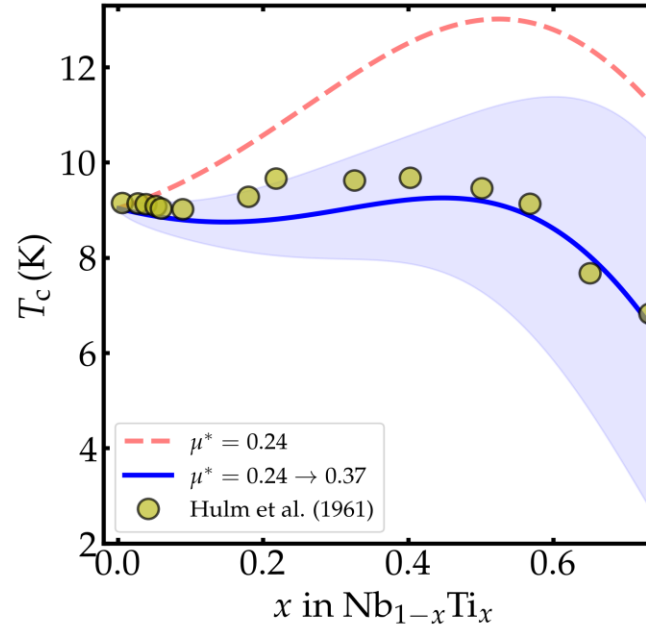


Nb-Ti

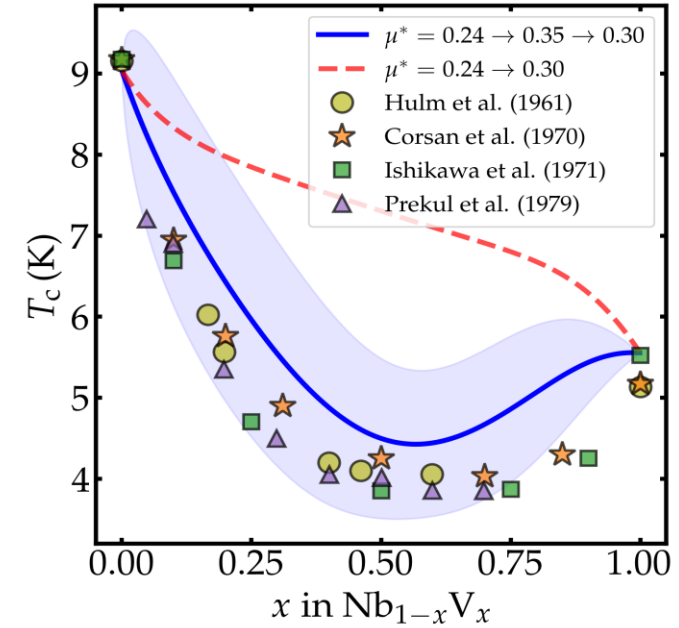
EGQCA code: beyond thermodynamics



Al-doped MgB_2



Nb-Ti



Nb-V

Take-home messages

- EGQCA is more than a thermodynamic model.

Take-home messages

- EGQCA is more than a thermodynamic model.



Take-home messages

- EGQCA is more than a thermodynamic model.



CVM is better!

Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.

Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.



Tim Strobel, Carnegie

Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.



Tim Strobel, Carnegie

Which
composition is
better?

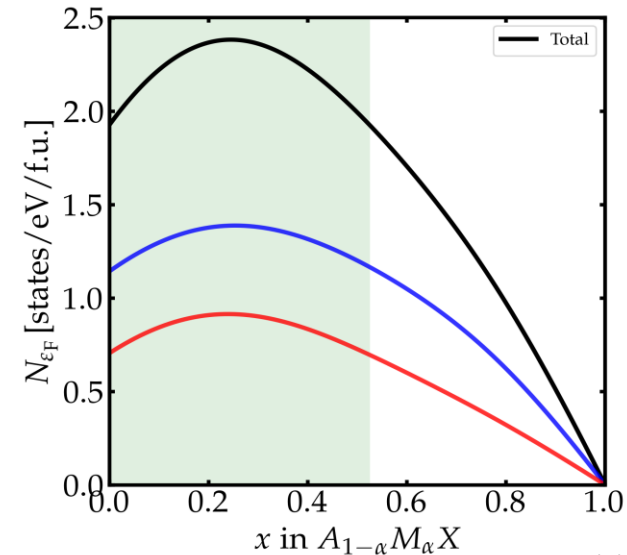
Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.



Tim Strobel, Carnegie

Which composition is better?



Unpublished. Intellectual property

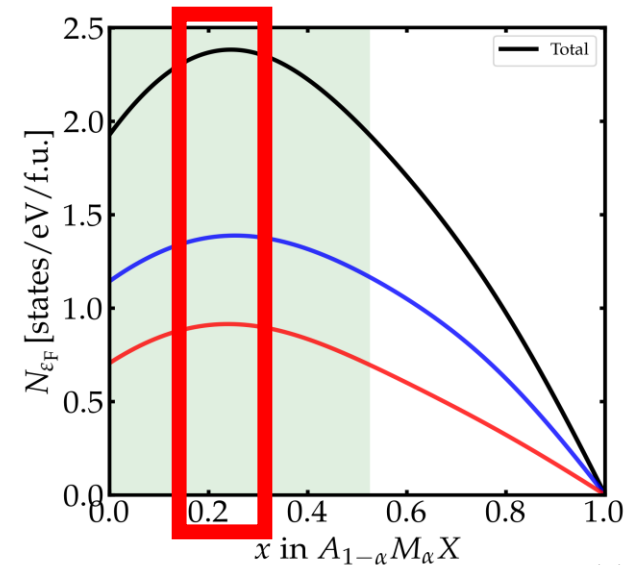
Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.



Tim Strobel, Carnegie

Which composition is better?



Unpublished. Intellectual property

Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.

Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.



Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.



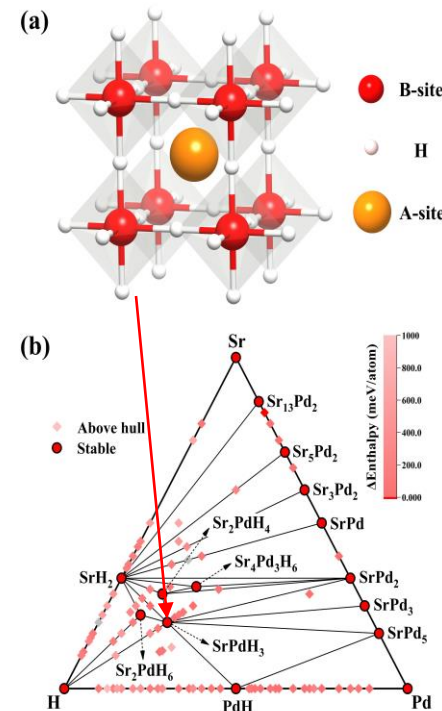
You still need to know the phases from experiments!

Take-home messages

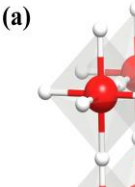
- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.



You still need to know the phases from experiments!

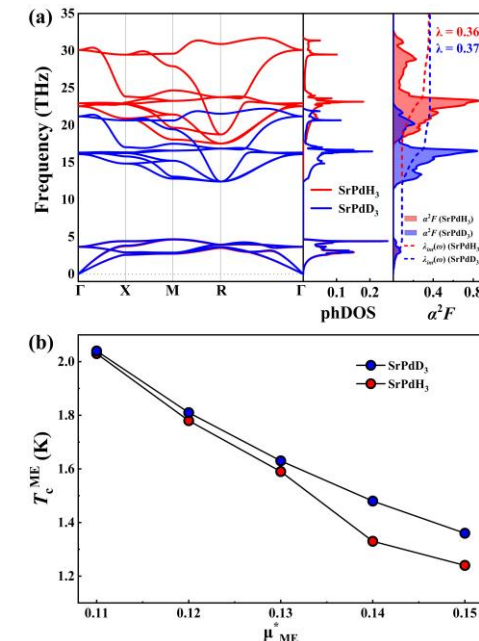
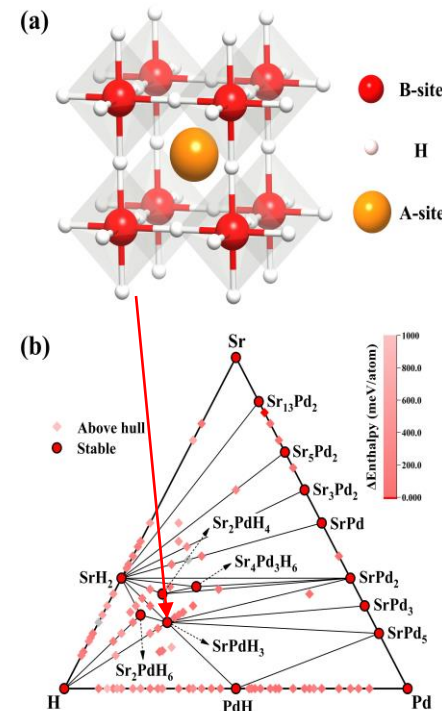


Take-home messages

- EGQCA is more than a thermodynamic model.
 - Bridges thermodynamic modeling and physical properties.
 - Truly ab initio.
- 



You still need to know the phases from experiments!

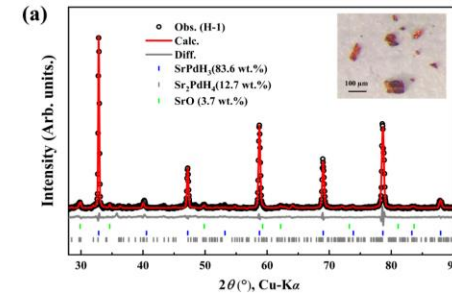
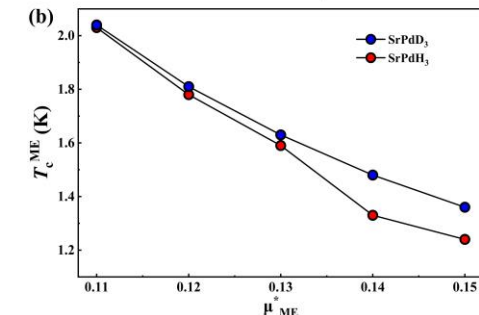
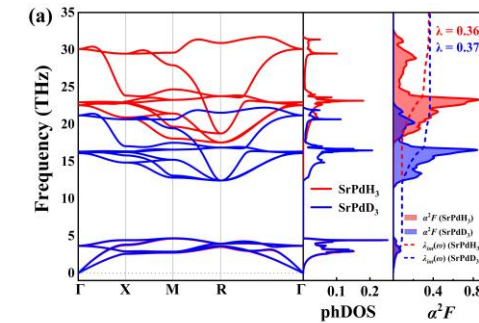
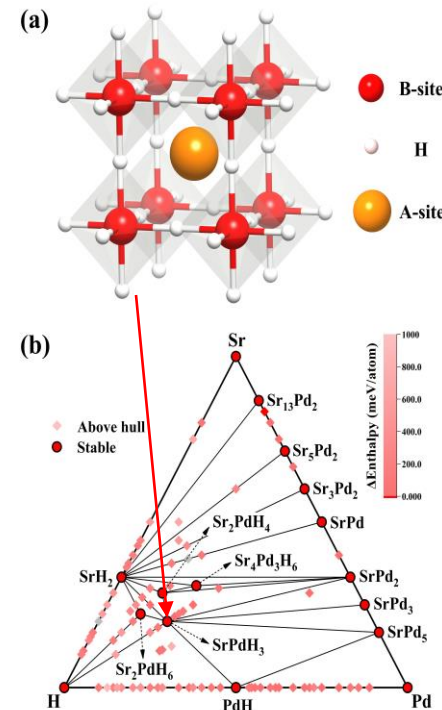


Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.



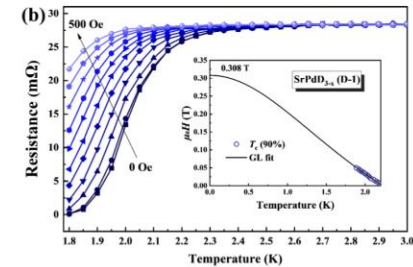
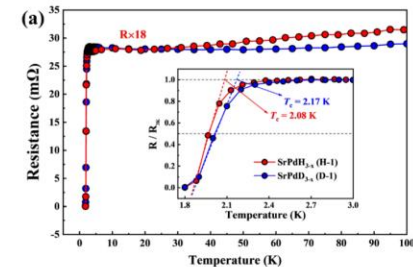
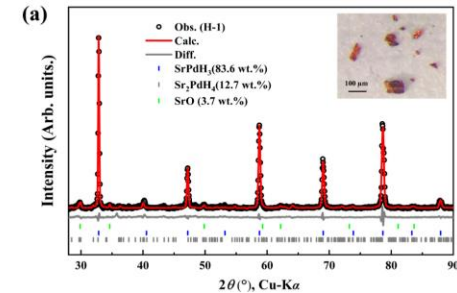
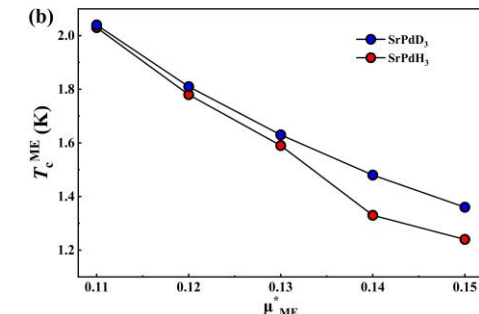
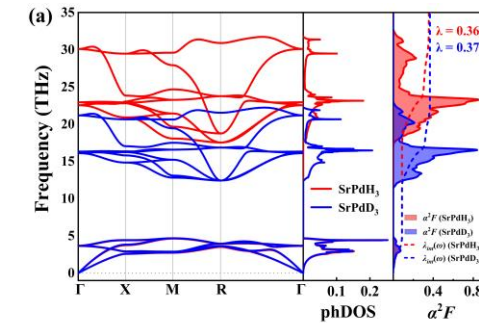
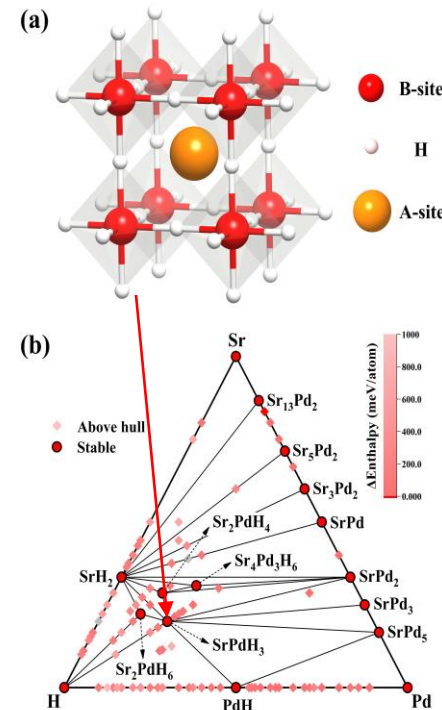
You still need to know the phases from experiments!



Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.

You still need to know the phases from experiments!

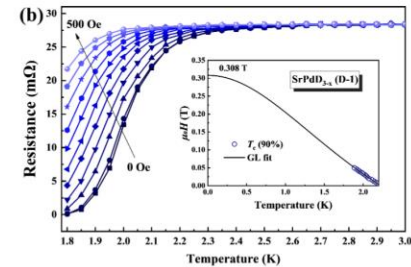
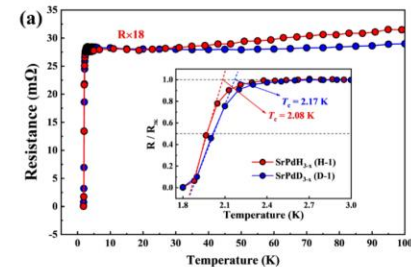
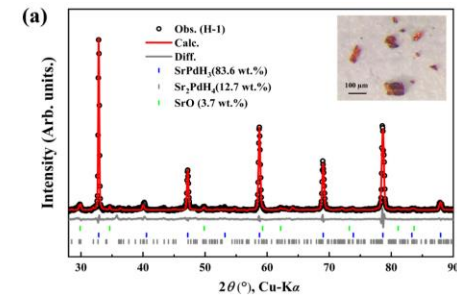
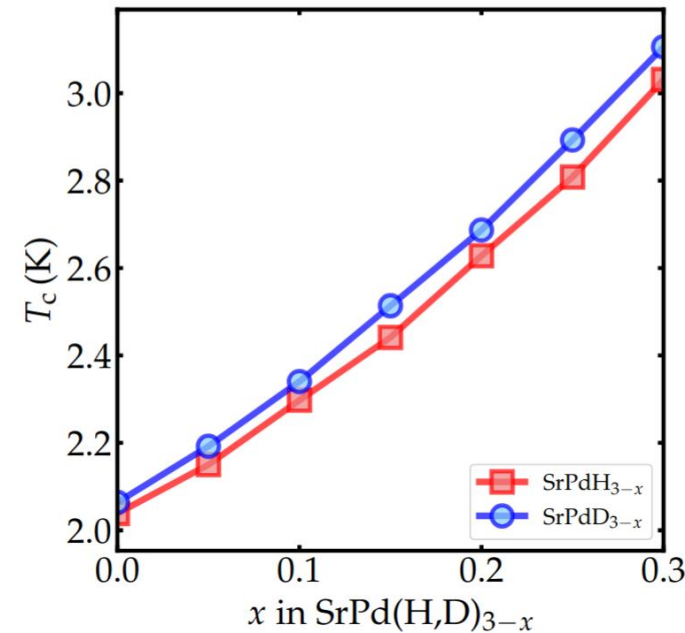


Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.



You still need to know the phases from experiments!

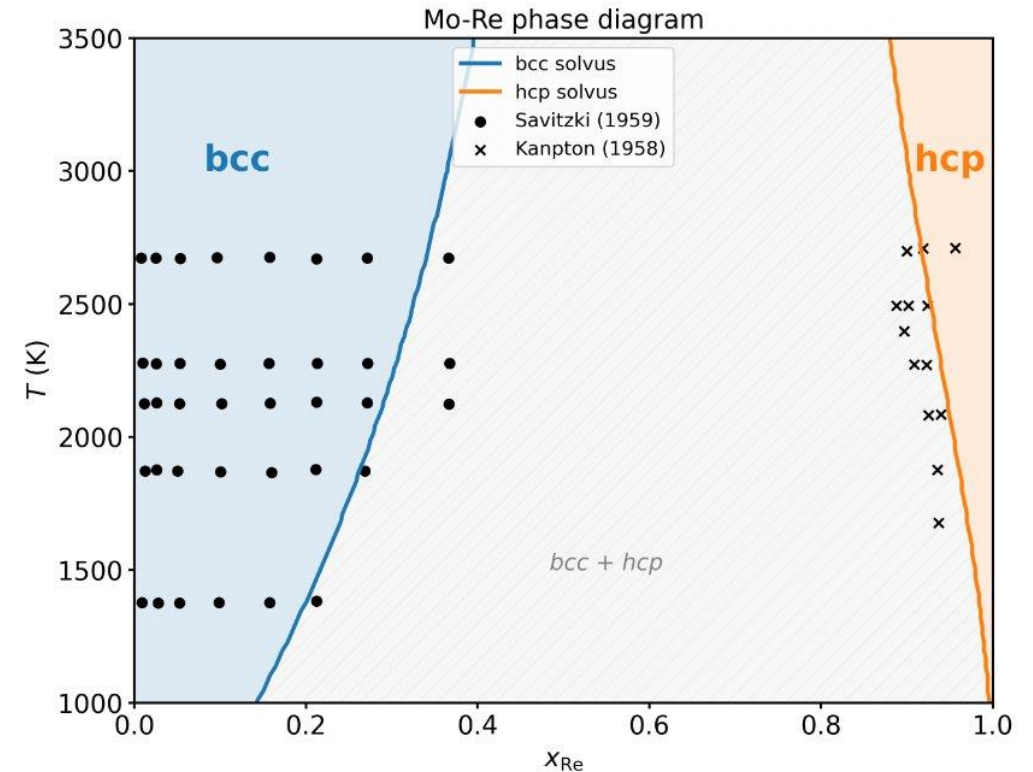


Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.
- Phase diagram calculations?

Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.
- Phase diagram calculations?



Take-home messages

- EGQCA is more than a thermodynamic model.
- Bridges thermodynamic modeling and physical properties.
- Truly ab initio.
- Phase diagram calculations?
- It's designed to make your life easier!

Thank you!

- **Dominik Spath (TU Graz)**
- **Luka Wibmer (TU Graz)**
- Eva Kogler (TU Graz)
- Christoph Heil (TU Graz)
- Markus Aichhorn (TU Graz)
- Simone Di Cataldo (University of Rome)
- Luiz T. F. Eleno (University of São Paulo)
- Kieran Bozier (University of Cambridge)
- Chris Pickard (University of Cambridge)



Check out our work here:

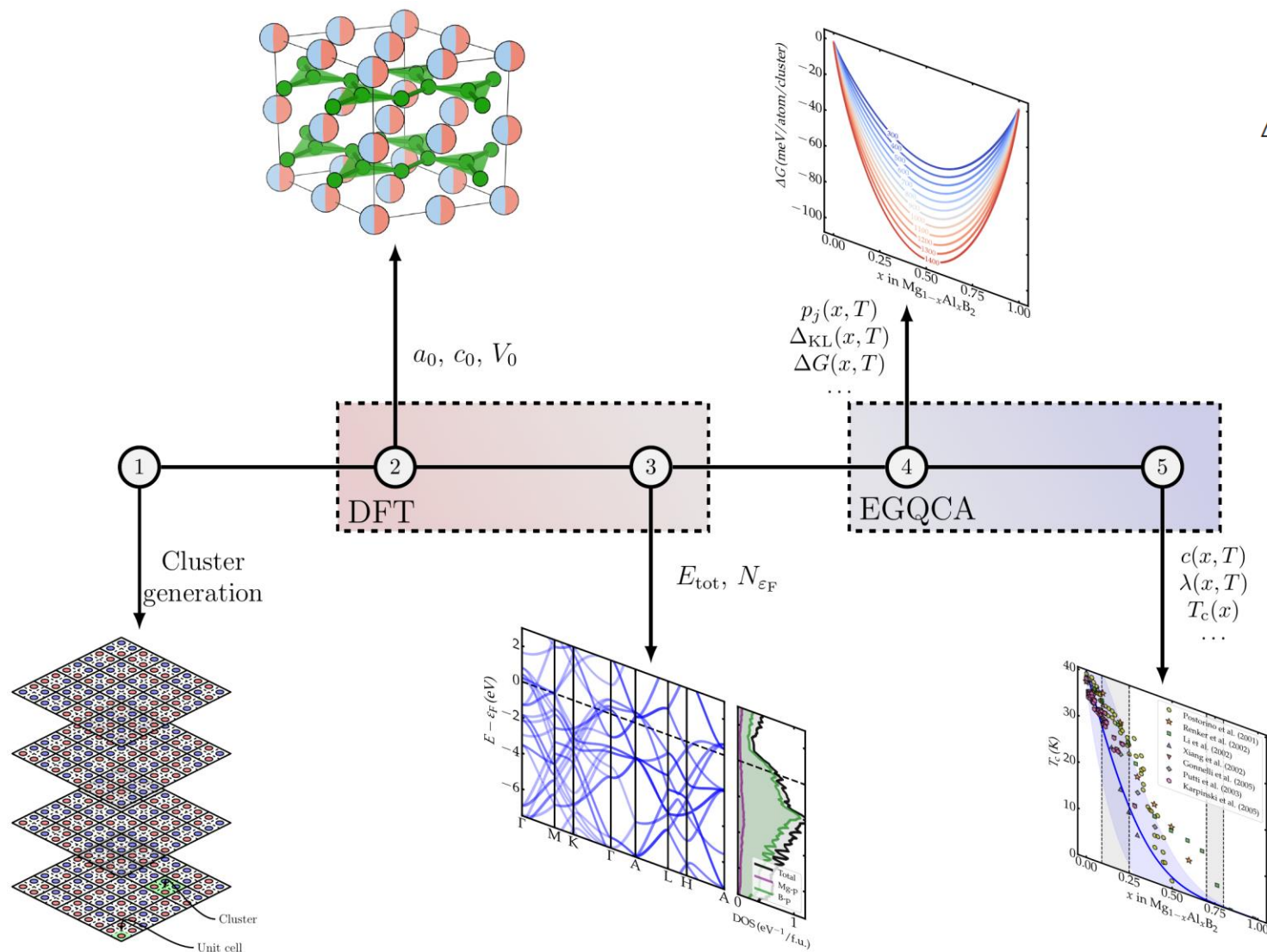


New cool stuff coming soon!

FWF Austrian Science Fund **INTELLECTUAL VENTURES®**

nunesferreira@tugraz.at

GQCA free energy



$$\Delta G = \Delta H - T \Delta S$$

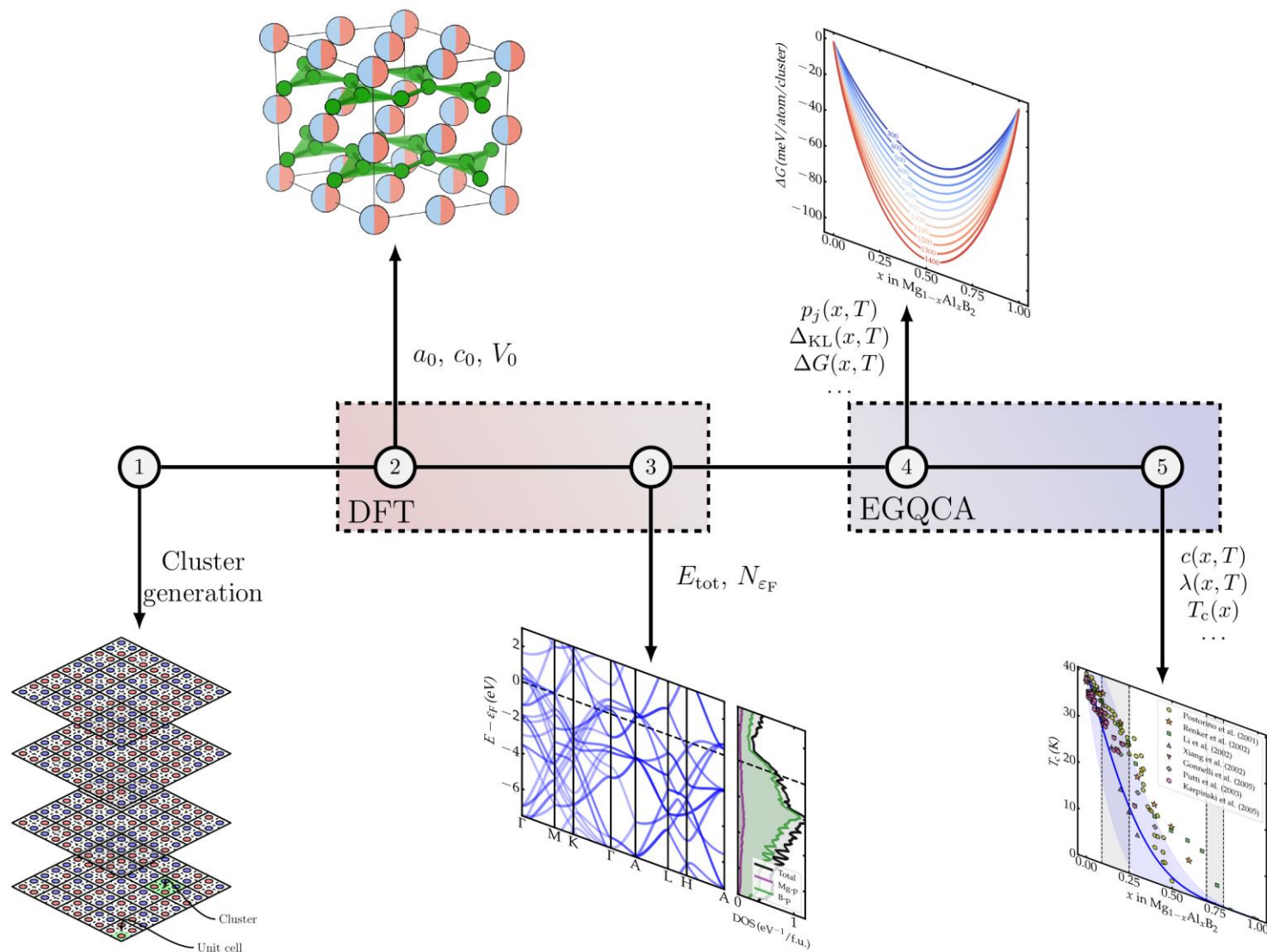
$$\Delta H(x, T, P) = M \sum_{j=1}^J p_j \Delta_j, \quad \Delta S(x, T, P) = k_B \ln W,$$

$$\Delta G(x, T, P) = M \sum_{j=1}^J p_j \Delta_j + N k_B T [x \ln x + (1-x) \ln(1-x)] + M k_B T \sum_{j=1}^J p_j \ln \left(\frac{p_j}{p_j^0} \right).$$

$$p_j = \frac{g_j \eta^{n_j} e^{-(\varepsilon_j + \Delta_j)/k_B T}}{\sum_{j=1}^J g_j \eta^{n_j} e^{-(\varepsilon_j + \Delta_j)/k_B T}}$$

$$\sum_{j=1}^J (n x - n_j) g_j e^{-(\varepsilon_j + \Delta_j)/k_B T} \eta^{n_j} = 0.$$

EGQCA free energy



$$\Delta G(x, T, P) = \Delta H(x, T, P) - T\Delta S(x, T, P) + \Delta A(x, T).$$

$$\Delta A(x, T) = M \sum_{j=1}^J p_j \varepsilon_j(T)$$

$$\varepsilon_j(T) = A_j(T) - \frac{n - n_j}{n} A_A(T) - \frac{n_j}{n} A_B(T)$$

$$A_j(T) = k_B T \int_0^\infty D_j(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2 k_B T} \right) \right] d\omega.$$