Exploiting superspace to enable DFT calculations of modulated structures with disordered sites using the example of mullite

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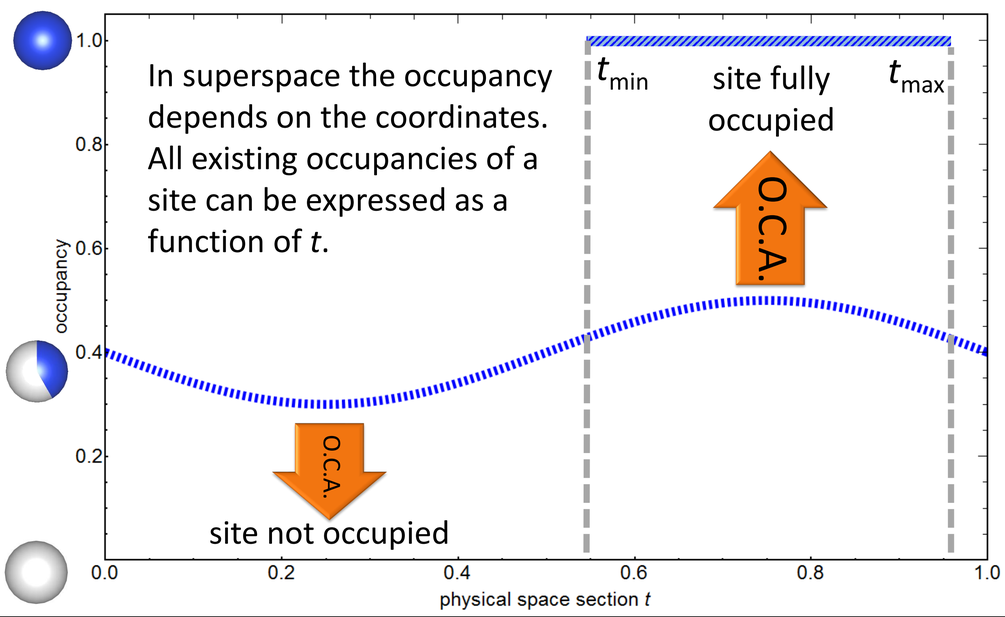
DFT of incommensurate, disordered structures seems impossible

Density functional theory calculations (DFT) allow to investigate crystal structures and their properties including the electronic structure or elastic properties, but are limited to small structures (few hundred atoms) with fully occupied sites. Modulated structures with harmonic occupational modulations at first sight are not suitable for DFT. Here we describe an approach exploiting superspace [1] using the example for mullite [2].

Approach to obtain an ordered commensurate approximation (O.C.A.)



Disordered model

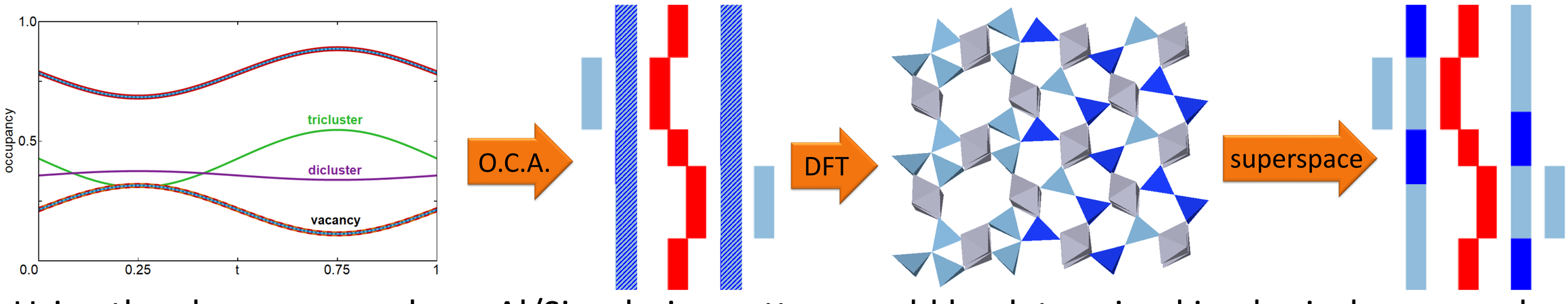
- Harmonic occupational modulation
- Incommensurate modulation

O.C.A.

Ordered approximation

- Block wave function
- Commensurate approximation

Example: Al/Si ordering in disordered, modulated mullite not known



Using the above approach, an Al/Si ordering pattern could be determined in physical space and in superspace. The ordering pattern of several different compositions results to be the same.

Comparison with experimental Al/Si ordering

Al/Si ordering of a superspace model of mullite could not be refined directly, but could be derived from the modulation of the volumes of the tetrahedra [3]. These results are in good agreement with the Al/Si ordering determined with the above approach.

cluster type		Si-Si	Si-Al	Al-Si	Al-Al-Al*	Al*-Al-Al	Si-Al-Al	Al-Al-Si
***t* of highest probability (refined model)**		0.75	0.13	0.37	0.60	0.90	0.63	0.87
block wave function	t_{left}	0.7	0	0.35	0.5	0.85	0.65	0.8
(DFT model)	t_{right}	0.8	0.15	0.5	0.65	1	0.7	0.85

References

[1] Pinheiro & Abakumov, (2015), IUCrJ 2, 137

[2] Schneider *et al*. (2008), J Eur Cer Soc 28, 329

[3] Klar *et al*. (2018), IUCrJ, *accepted*

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