# Vacancy Ordering in Mullite: A Superspace Model

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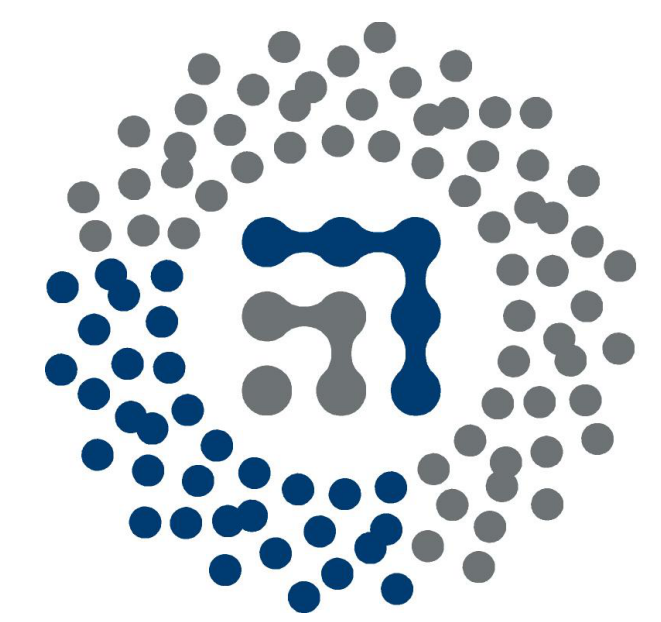
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1. Abstract
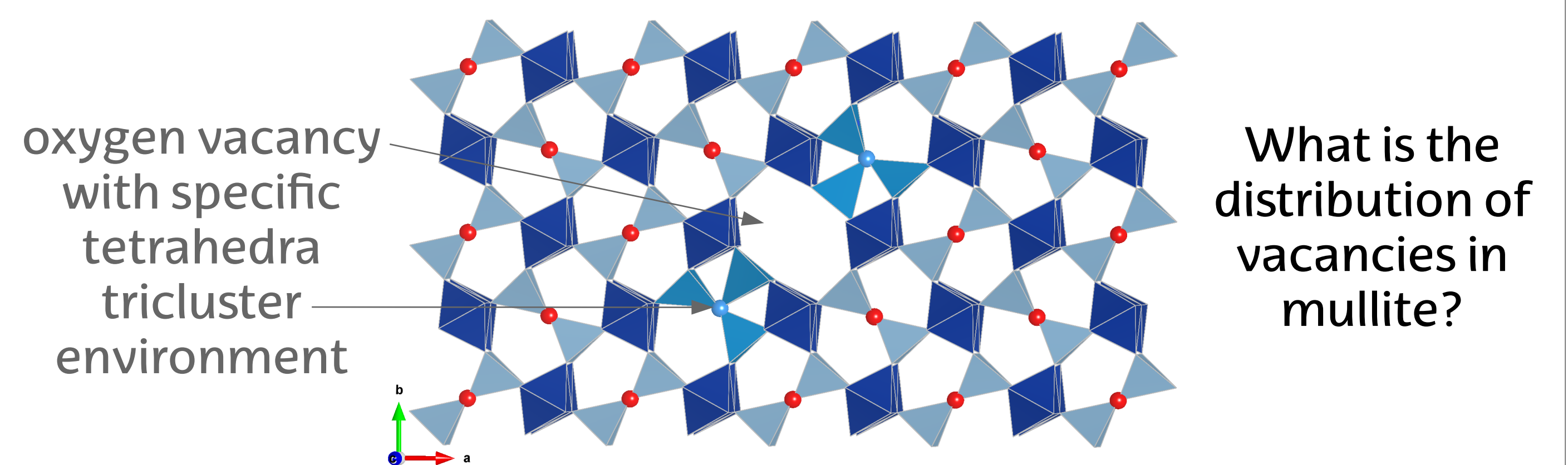
Mullite ($Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}[vacancy]_x$) is a well known material with numerous applications in traditional to high-tech ceramics. From a fundamental point of view its crystal structure is not completely understood, especially concerning the ordering of oxygen vacancies, which was commonly investigated either as short-range ordered (SRO) [1, 2] or long-range ordered (LRO) [3, 4, 5] property.

Indications for SRO	Indications for LRO
Complex diffuse scattering in reciprocal sections ⊥ $c*$ [1, 2]	Satellite reflections up to 7th order visible (ED) [4]
Satellite reflections usually not detected in powder XRD [3]	Modulation wave vector q depends on composition [4, 6]

We here present a model that simultaneously accounts for SRO and LRO, where the modulated LRO phase is refined in superspace.

2. Objective

→ Investigate vacancy ordering in mullite applying modern tools of aperiodic crystallography (superspace formalism)

oxygen vacancy with specific tetrahedra tricluster environment
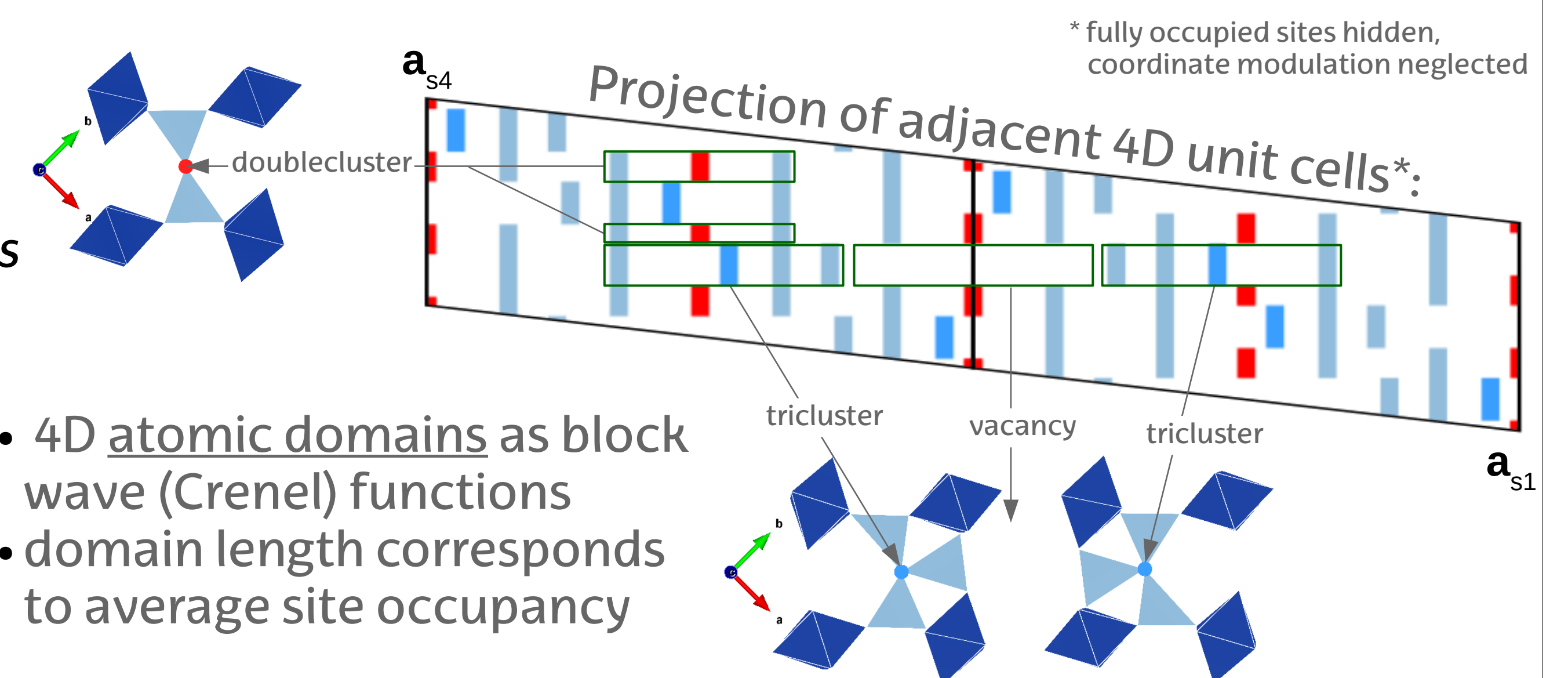
What is the distribution of vacancies in mullite?

3. Methodology

- Sample: one small grain of commercial sample (Sigma-Aldrich)
- Single crystal X-ray diffraction, 2 measurements (Mo Kα, Cu Kα)
- STOE Stadivari, microfocus sources, Dectris Pilatus 100K detector
- Refinement in (3+1)d superspace using Jana2006 [7]

4. Structure model refinement

- Disordered phase ≙ basic structure with statistical distribution of vacancies
  → refinement based on main reflections   → space group $Pbam$
- Ordered phase ≙ modulated structure with superspace group $Pbam(α0\frac{1}{2})0ss$
  → only ordered fraction of the sample generates satellite reflections
  → **different scale factors** for satellite and main reflections required

$Al_{4.822}Si_{1.178}O_{9.589(4)}$ ≙ 2.05 $Al_2O_3 \cdot SiO_2$	a = 7.5805(7) Å
68 (Cu) and 33 (Mo) observed, independent satellite reflections	b = 7.6843(7) Å
wR (observed, satellites): 8.69 (Cu), 13.66 (Mo)	c = 2.8881(3) Å
wR (all, main+satellites): 7.22 (Cu+Mo combined)	q = [0.2988(13), 0, $\frac{1}{2}$]

* fully occupied sites hidden, coordinate modulation neglected

Projection of adjacent 4D unit cells*:

doublecluster   tricluster   vacancy   tricluster

- 4D atomic domains as block wave (Crenel) functions
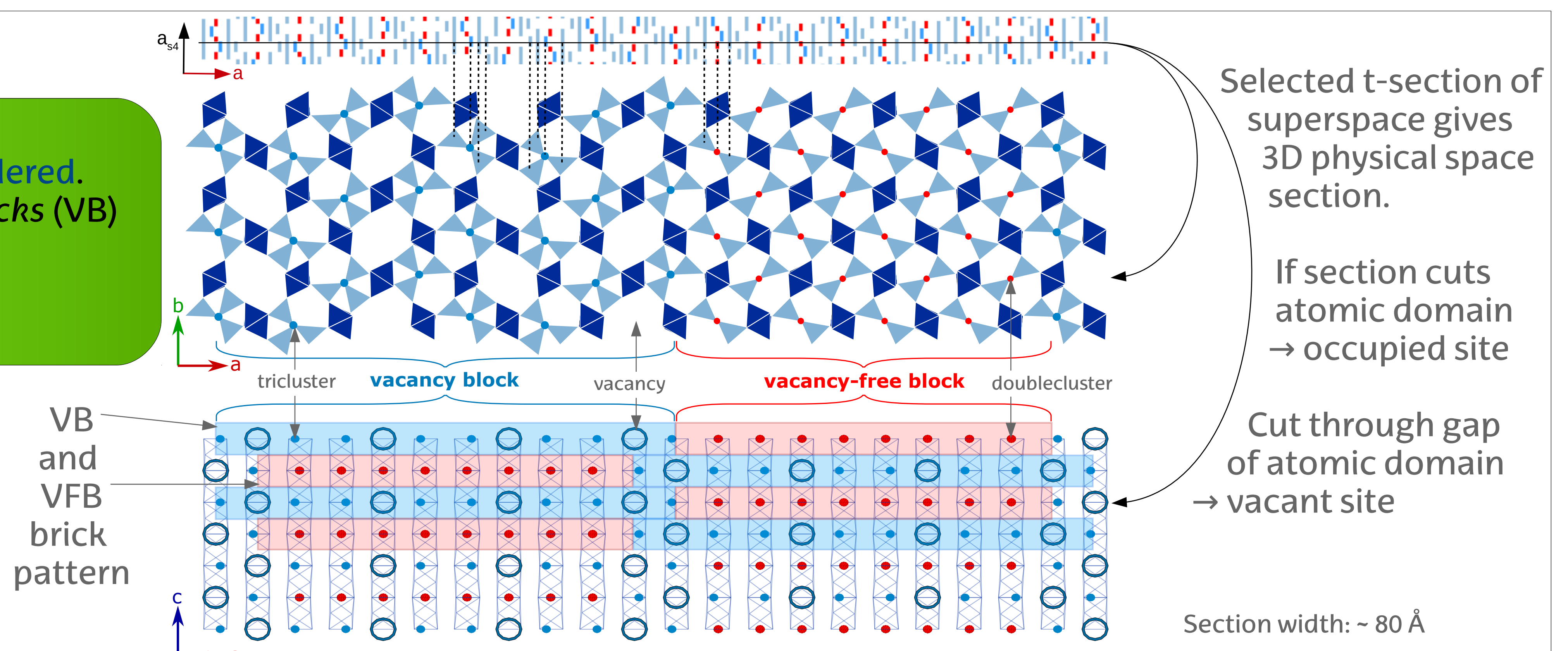- domain length corresponds to average site occupancy

5. Results

Ordered Mullite:
- Vacancies are completely long-range ordered.
- Vacancies group together in *vacancy blocks* (VB)
- *Vacancy-free blocks* (VFB) separate VB
- Length of VB and VFB varies slightly
  → depends on composition and q

Volume fraction of **ordered phase**:
9±1 %
(calculated from scale factors)

Al/Si ordering is not included in the model.

tricluster   **vacancy block**   vacancy   **vacancy-free block**   doublecluster

VB and VFB brick pattern

Selected t-section of superspace gives 3D physical space section.

If section cuts atomic domain → occupied site

Cut through gap of atomic domain → vacant site

Section width: ~ 80 Å

6. Conclusion & Outlook

- Mullite crystals are built out of ordered and disordered domains.
- Disordered domains (~90 vol%) dominate, though the ratio is probably variable. (Diffuse scattering → more disordered domains, high order satellite reflections → more highly ordered domains)
- In ordered domains vacancies are long-range ordered and group together in *vacancy blocks* of variable length.
- Similar block models were suggested before for different compositions, but a refinement was not carried out [3, 4, 5].
- Superspace formalism is appropriate approach to describe vacancy ordering in modulated crystal structures.

The model will be tested with other samples from different synthesis routes and of different compositions.

7. References

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