

Making the Most of Neutron-Diffraction Data

Lithium Diffusion Pathways in Ramsdellite-Like $\text{Li}_2\text{Ti}_3\text{O}_7$



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Aims and Scope

Although experimental scientists strive for the best possible data, they must often deal with **mistakes, systematic errors, unforeseen behavior, and model limitations**. Having several methods for evaluation^[1] at hand helps to avoid unsound interpretation and frustration when quality expectations are not met.

Herein, we give an example of this by presenting our multimethod study of **lithium diffusion in ramsdellite-like $\text{Li}_2\text{Ti}_3\text{O}_7$** , a fast and strongly anisotropic conductor with a range of proposed applications from energy storage to lithium processing.^[2]

Probability Densities and Migration Barriers

Derivation of the **probability-density function (PDF)** and the **one-particle potential (OPP)** are the top tier of probing ion diffusion *via* neutron diffraction. The former models the probability of finding an ion at a specific position (*i.e.*, the **diffusion pathway**), the latter gives the associated effective potential energy (*i.e.*, the **activation barrier** for migration). Unfortunately, their determination requires unambiguous high-quality data, which is often hard to obtain.

In ramsdellite-like $\text{Li}_2\text{Ti}_3\text{O}_7$, we found a case of **severe lithium disorder** that we were unable to treat with the **discrete models** needed for PDF/OPP analysis. Only one position could be resolved accordingly, hinting at diffusion in spacious channels along *b*.

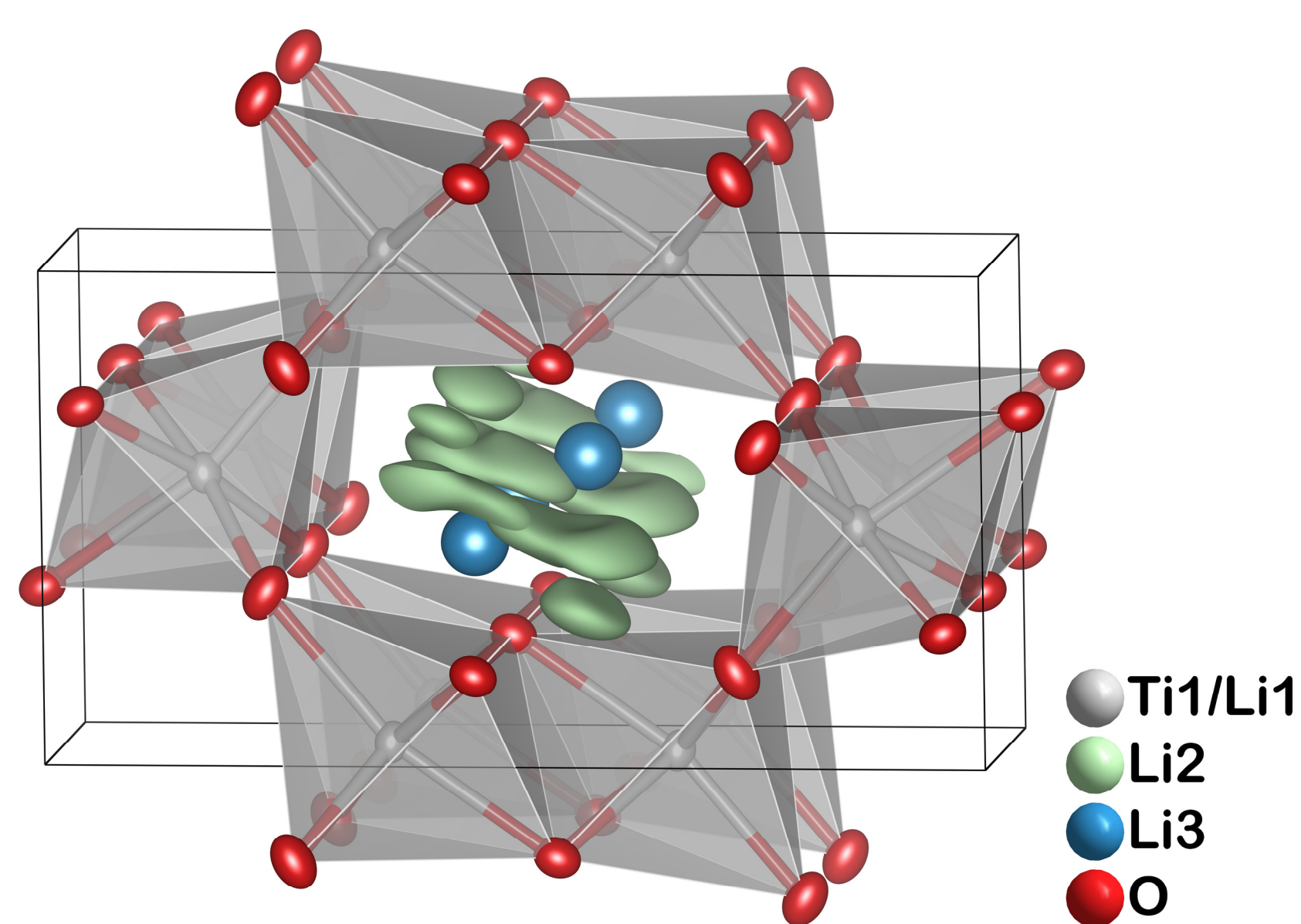


Figure 1. Crystal-structure detail of $\text{Li}_2\text{Ti}_3\text{O}_7$ at 24 °C. View approximately along *b*, Li2 as PDF isosurface of 0.1 \AA^{-3} , other ions as spheres and ellipsoids of 50% probability, unit cell in black.

Maps of Scattering-Length Density (SLD)

The **SLD** is the neutron analogue of the electron density probed in X-ray diffractometry. However, classical “Fourier maps” (acquired from observed intensities and modelled phases) are prone to **artifacts and structured noise**. The reconstruction of SLD using **maximum-entropy methods (MEM)** overcomes this by yielding densities with the least additional information (*i.e.*, the highest entropy) in the range of measurement error.

For $\text{Li}_2\text{Ti}_3\text{O}_7$, the MEM reconstruction shows a **smearing of negative SLD in the channels** along *b*, caused by disorder/migration of lithium-7. This hints at many energetically similar ion positions and the structure being a **metastable “snapshot”** of the highly dynamic situation during synthesis at more than 950 °C.

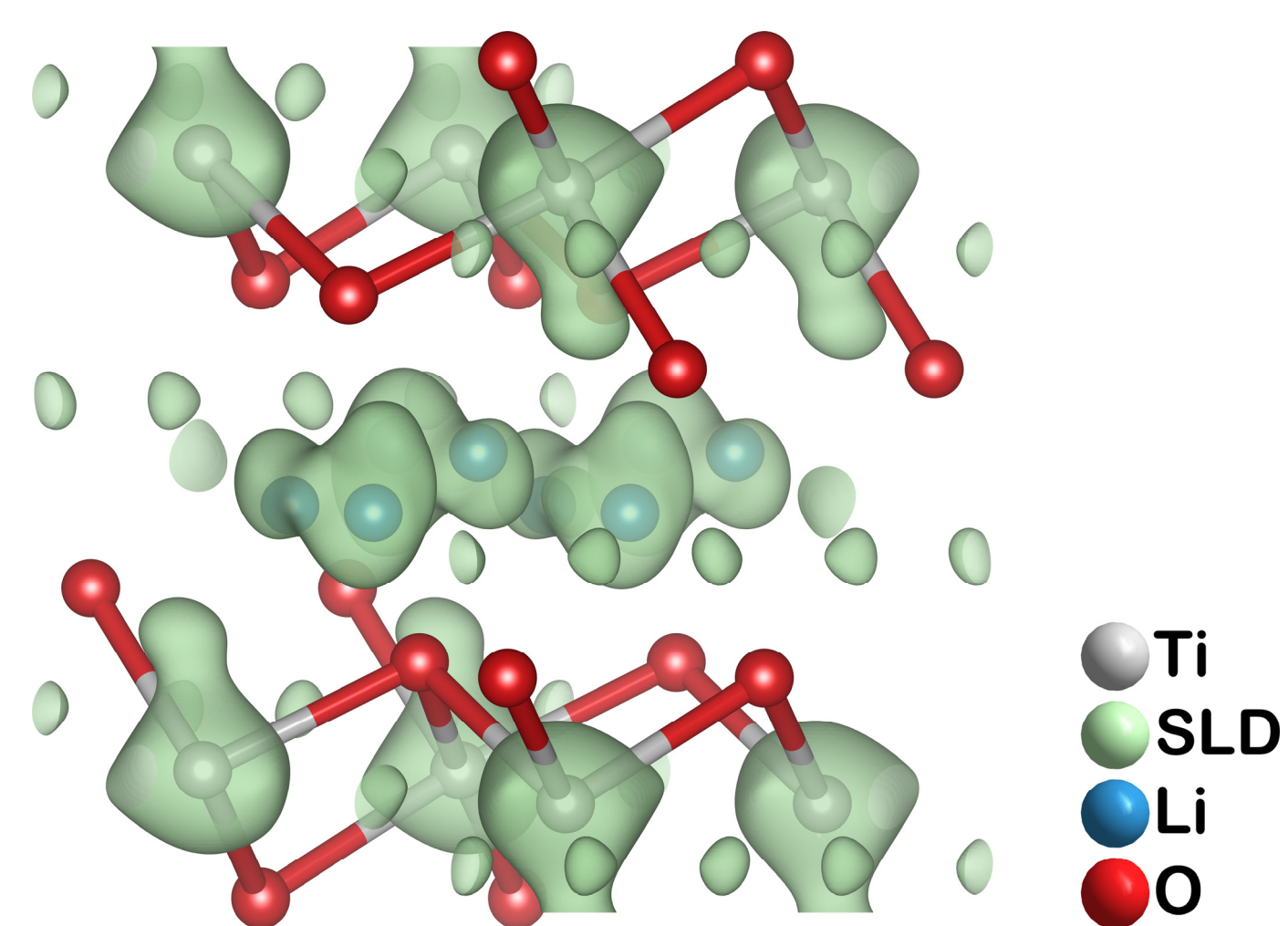


Figure 2. Crystal-structure detail of $\text{Li}_2\text{Ti}_3\text{O}_7$ at 422 °C with SLD isosurface for $\rho_b = -0.08 \text{ fm \AA}^{-3}$. View approximately along $[3 \ 10 \ 0]$, ions with arbitrary radii.

References and Acknowledgements

- [1] D. Wiedemann, M. M. Islam, T. Bredow, M. Lerch, *Z. Phys. Chem.* **2017**, in preparation.
- [2] D. Wiedemann, S. Nakhal, A. Franz, M. Lerch, *Solid State Ionics* **2016**, 293, 37–43.



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Voronoi–Dirichlet Partitioning (VDP)

The **VDP** is a kind of **topological analysis** that requires a division of the crystal into static (framework) and mobile (interstitial) species. The method assigns each point in space to the nearest atomic center; only the **crystal structure of the framework** is needed. Inference of **prior knowledge** about the mobile species’ steric and electrostatic requirements yields **more and less preferred diffusion paths**.

For $\text{Li}_2\text{Ti}_3\text{O}_7$, this method was especially appealing, as it does not rely on the position of the lithium ions. **Two possible pathways** were revealed: a preferred one through the channels along *b* and a less preferred one through framework cation vacancies.

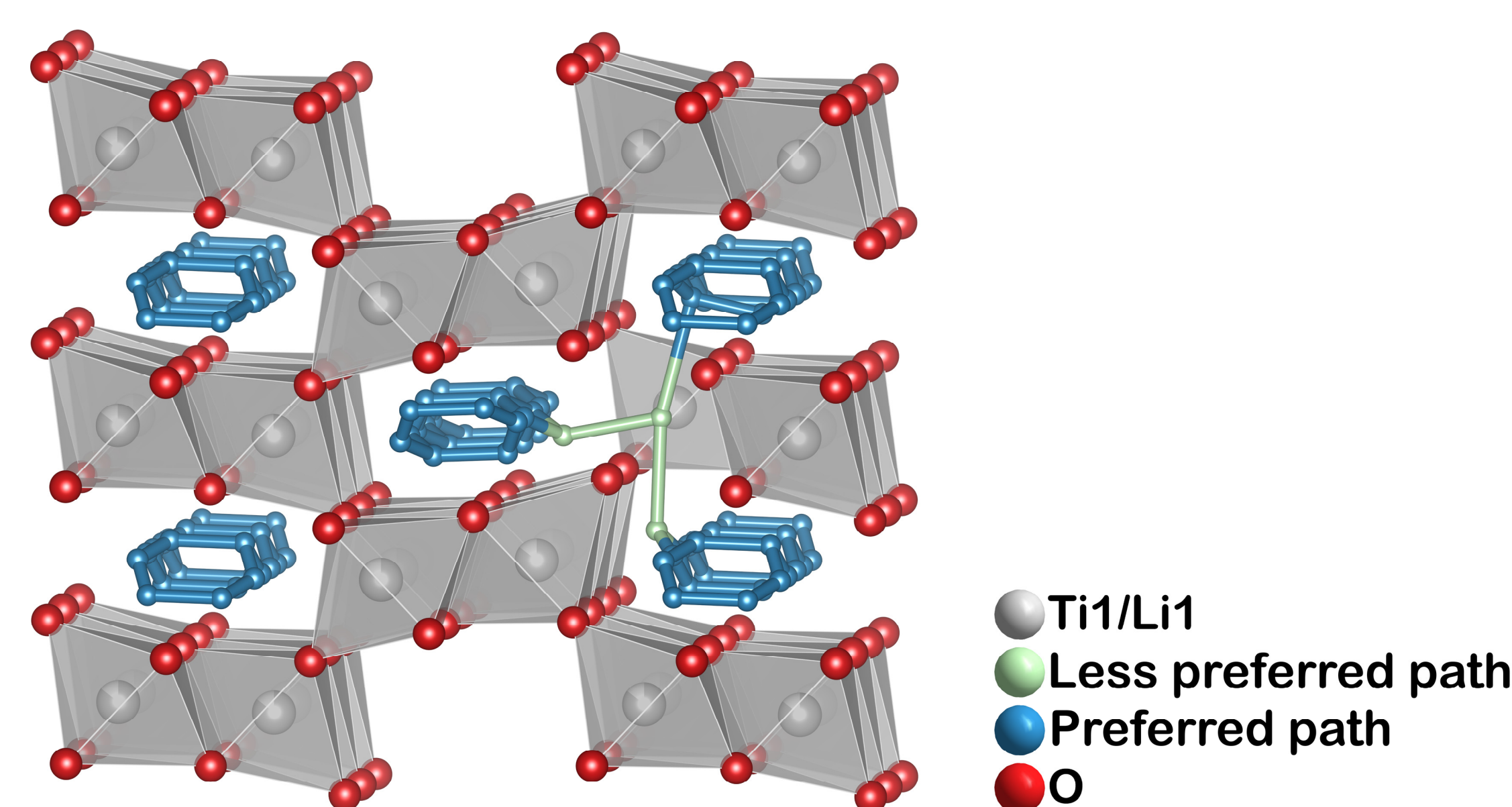


Figure 3. Void structure of the $\text{Ti}_3\text{O}_7^{2-}$ framework at 422 °C as found by VDP. Intact channels on the left, framework vacancy on the right; ions, void centers, and channels with arbitrary radii.

Procrystal-Void Analysis (PVA)

Another topological method, the PVA, relies on the same information as the VDP, but uses different prior knowledge. It approximates all framework atoms as **spheres of diffuse electron density**, constructing the so-called “procrystal”. Its **voids** (defined by an upper density limit ρ_{pro}) are the **places to preferably host and conduct** mobile species. This method appeals because of its **ease of use and availability**, even if empirical data for steric and electrostatic demands are inaccessible. It is, however, more **prone to misinterpretation** and does not rationalize preference for one pathway over another.

For ramsdellite-like $\text{Li}_2\text{Ti}_3\text{O}_7$, PVA has **corroborated the abovementioned pathways** and their relative likeliness.

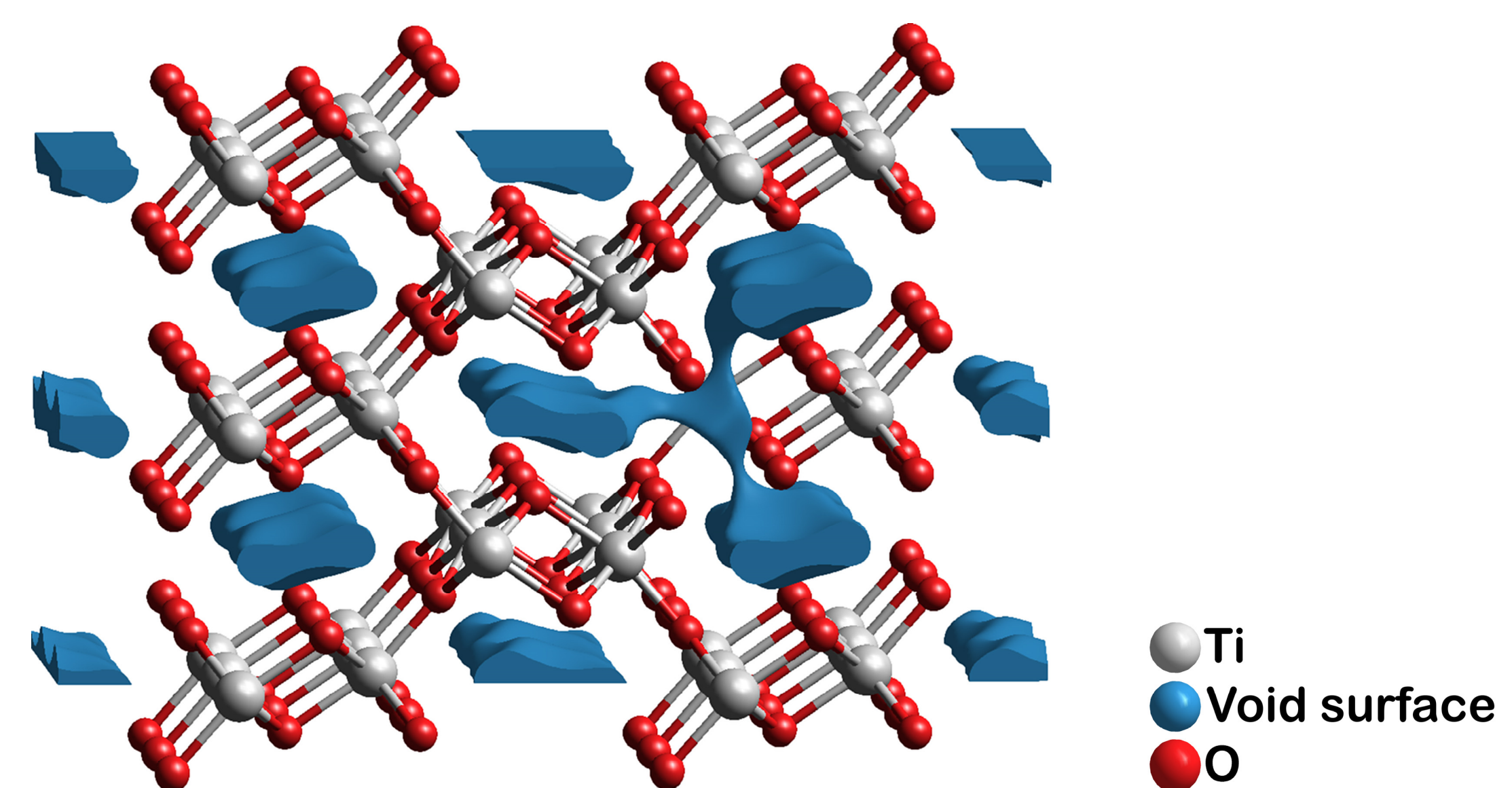


Figure 4. Procrystal-void surface of the $\text{Ti}_3\text{O}_7^{2-}$ framework at 422 °C for $\rho_{\text{pro}} = 0.006 \text{ a.u.}$ Intact channels on the left, framework vacancy on the right; ions with arbitrary radii.

Conclusion

When dealing with neutron diffraction, **ion diffusion pathways** in solids can be explored, *e.g.*, *via* analyses of the PDF and OPP, of MEM-reconstructed SLD maps, or of the framework topology. Different requirements for **data and model quality** reflect the amount of extractable information, be it (semi-)quantitative or qualitative. Lower-demand approaches may be used as **heuristic, supporting, or even standalone methods**—if data quality prohibits more sophisticated evaluation.

In our experience, measured data sometimes **fail to reach the expected quality**, but hardly ever have to be completely discarded. However, it is imperative **not to overstrain** them or to treat them sloppily and to **resist bold claims** to maintain scientific standards.