

Microsymposium

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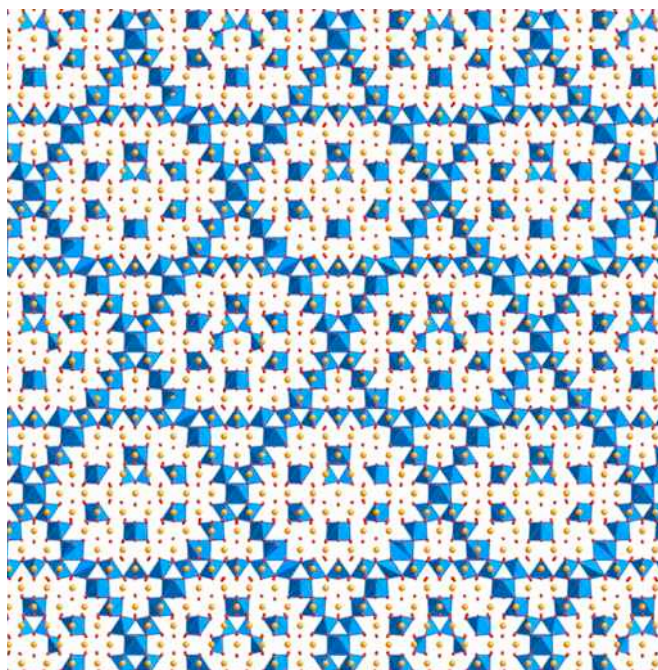
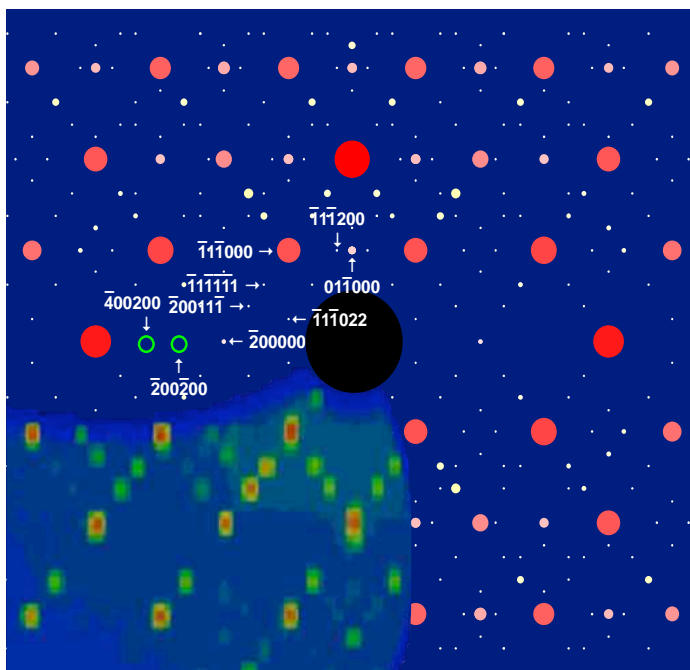
Modulated order in ionic conductors: a fine line between helping and hindering

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Solid-state ionic conduction relies on essentially conflicting structural properties: long-range crystalline order, to provide structural stability (as fuel cell membranes, battery cathodes etc.); and short-range disorder, to provide smooth conduction pathways without deep local energy minima that could trap the conducting species. Materials that combine these features are generally metastable, and prone to ordering into complex modulated structures that can only be described in (3+n) dimensions using the superspace formalism. Such ordering would normally be expected to seriously compromise conduction properties. However, low-temperature modulated structures can be effective and stable precursors to high-temperature ionic conductors - and, in some cases, can coexist with regions of local disorder that actually enhance conduction. The relationship between modulated order and ionic conduction is relatively little studied, but some of our recent work points to its potential importance. This presentation will focus on two examples: the (3+3)-dimensional commensurately modulated proton conductor $\text{Ba}_4\text{Nb}_2\text{O}_9.1/3\text{H}_2\text{O}$; [1,2] and the (3+3)-dimensional incommensurately modulated oxide ion conductor "Type II" $\text{Bi}_2\text{O}_3.x\text{Nb}_2\text{O}_5$ (for which a single-crystal neutron diffraction pattern and the refined structure are shown below). [3] The aim is to show how modulated structures can be designed and manipulated to optimise technological performance by striking a balance between stabilising the overall framework while destabilising the conduction pathways.

[1] C.D. Ling, M. Avdeev, R. Kutteh, V.V. Kharton, A.A. Yaremchenko, S. Fialkova, N. Sharma, R.B. Macquart, M. Hoelzel, M. Gutmann, *Chemistry of Materials*, 2009, 21, 3853-3864, [2] M.T. Dunstan, F. Blanc, M. Avdeev, G.J. McIntyre, C.P. Grey, C.D. Ling, *Chemistry of Materials*, 2013, 25, 3154-3161, [3] C.D. Ling, S. Schmid, P.E.R. Blanchard, V. Petricek, G.J. McIntyre, N. Sharma, A. Maljuk, A.A. Yaremchenko, V.V. Kharton, M. Gutmann, R.L. Withers, *Journal of the American Chemical Society*, 2013, 135, 6477-6484



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