Non-stoichiometric oxides can undergo important variations in the oxygen stoichiometry, enabling to tune physical and chemical properties. Combining neutron diffraction, inelastic neutron scattering and \textit{ab initio} lattice dynamics calculations, we have recently evidenced the importance of lattice dynamics, i.e. soft phonon modes, triggering low temperature oxygen mobility in Brownmillerite type (Ca/Sr)Fe/CoO$_{2.5}$ and Ruddlesden Popper type oxides, e.g. (Pr/Nd)$_2$NiO$_{4+d}$ [1-4]. This new concept has technological relevance for the optimization of oxygen membranes and electrolytes in SOFCs.

We report here on single-crystal synchrotron diffraction experiments on non-stoichiometric Pr$_2$NiO$_{4+d}$ uncovering unprecedented oxygen ordering up to the sub meso-scale. Complex oxygen ordering is established during a topotactic solid-state reaction already proceeding at ambient temperature, following small oxygen release. The resulting 3D-incommensurate modulated structure is described in terms of modulation vectors and related twin domain structures. Melting of the oxygen ordering around 365°C strongly amplifies the oxygen mobility, evidenced by $^{18}$O/$^{16}$O oxygen isotope exchange, and associated with phonon softening manifested in a pronounced increase of thermal diffuse scattering. Our results thus strengthen the idea of a phonon assisted oxygen diffusion mechanism, which can be more generally applied to understand cooperative diffusion mechanisms.