

LOW-T OXYGEN DIFFUSION PATHWAYS EXPLORED BY SINGLE CRYSTAL NEUTRON DIFFRACTION METHODS IN NON-STOICHIOMETRIC OXIDES

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Non-stoichiometric transition metal oxides are an important class of compounds academic and applied interest. They can undergo important variations of their oxygen stoichiometry, enabling to tune physical and chemical properties. In this context, oxygen diffusion was demonstrated to exist at ambient temperature for a few transition metal oxides with brownmillerite/perovskite/Ruddlesden-Popper-type frameworks, showing reversible chemical or electrochemical oxygen intercalation at already ambient conditions [1-2]. Recently, spontaneous oxygen mobility at room temperature has been evidenced for $\text{Pr}_2\text{NiO}_{4+\delta}$, coupled to the formation of unprecedented long-range oxygen ordering up to the lower mesoscale [3]. Thereby small changes in the oxygen stoichiometry and/or temperature induce an easy switching between different 3D modulated structures of well-defined lock-in phases, all showing translational periodicities for oxygen ordering beyond 100 Å.

In order to better explore related diffusion mechanisms, we studied related structural changes by in situ powder and single crystal neutron diffraction experiments at different oxygen partial pressures and temperatures. Scattering density analysis to directly explore oxygen diffusion pathways were undertaken using the Maximum Entropy Method [4-5]. Further on we report on T-dependent neutron single crystal studies using 2D area detectors, allowing to directly explore subtle changes in the modulation vectors. Our findings suggest a rather correlated, cooperative character of the migration of the interstitial oxygen atoms, in a sufficiently flexible oxide matrix and linked dynamics, compatible with a phonon-assisted diffusion mechanism [6].

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