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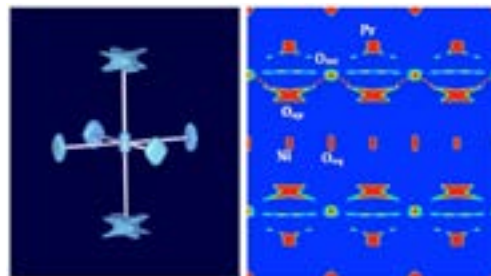
PHONON ASSISTED OXYGEN DIFFUSION VS. OXYGEN AND ELECTRONIC ORDERING MECHANISMS IN NON-STOICHIOMETRIC CORRELATED OXIDES

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Transition Metal Oxides with strongly correlated electrons have been studied intensively due their interesting physical properties. This includes colossal magnetoresistance (CMR) where huge variations in resistance are achieved just by small changes in the applied magnetic field, or high temperature superconductivity (HTC) to name two of them [3-6]. These materials are characterized by the existence of several competing states such as charge, spin and orbital ordering, interacting in a synergetic way and leading to fairly complex phase diagrams. Thereby the physical properties can be tuned in a wide range via hole doping, e.g. by cation substitution as is the case for RE₂-xSr_xMO₄. An alternative way of hole doping presents oxygen intercalation, generally proceeding at ambient temperature via a topotactic oxygen uptake along shallow potential diffusion pathways. Contrary to the cation substitution, requiring high reaction temperatures, oxygen intercalation reactions allow the controlled synthesis of strongly correlated oxides far away from thermodynamic equilibrium, essentially resulting in kinetically stabilized and thus metastable phases. Low temperature reactivity of solids may thus be used as a concept, to investigate the limits of available structural and electronic complexity in transition metal oxides. The reaction pathway to insert oxygen at low temperatures in solid oxides becomes a decisive parameter to tune correlations, leading to extremely complex phase relations as physical and structural properties are not only depending on the overall stoichiometry, but decisively on the sample history. Taking these oxides as oxygen 'sponges' operating at low reaction temperatures down to ambient, structural and electronic correlation lengths could then be influenced by the reaction conditions and kinetics. We here discuss here the challenges, low temperature solid state reactivity implies for the synthesis of new complex oxides but equally the current understanding of the relying oxygen diffusion

mechanisms, having a huge fundamental and technological interest.



Pr₂NiO_{4.25}: Representations of the NiO₆ isosurfaces (left) for indicate the anharmonic double potential of the apical oxygen atoms present at 673 K, obtained from single crystal neutron diffraction and Maximum Entropy Analysis. The large anisotropic displacements of the apical oxygen atoms along [110] directly point towards the interstitial oxygen sites, forming a shallow oxygen diffusion pathway which is dynamically activated

Recent Publications

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Biography

Werner Paulus is exploring low temperature oxygen diffusion mechanisms in transition metal oxides. Oxygen doping, via topotactic reaction mechanisms while proceeding at ambient temperature is a powerful tool to access structural and electronic complexity in a controlled way. It also allows to better explore the underlying diffusion mechanisms on an atomic scale, having huge importance in solid state ionics, e.g. for the optimisation of battery materials, fuel cell membranes/electrolytes or sensors. Research activities cover synthesis methods from powder to large single crystals and to explore oxygen intercalation reactions in especially dedicated electrochemical cells on single crystals and polycrystalline electrodes by neutron and X-ray diffraction (synchrotron & laboratory), spectroscopy (XAFS, Raman, INS, IXS, NMR) combined with ¹⁸O/¹⁶O oxygen isotope exchange reactions and sophisticated data analysis (Maximum Entropy, twinning).

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