

## MS24 Inorganic and metal-organic magnetic structures

### MS24-P2 Interplay of structural complexity and magnetism in Pr<sub>2</sub>NiO<sub>4+δ</sub> single crystals.

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The discovery of high- $T_c$  superconductivity in substituted lanthanum cuprate, belonging to the Ruddlesden-Popper phase, fuelled a general interest in the structural and electronic properties of rare-earth transition metal oxides. In this regard, there have been few reports on electronic properties of Pr<sub>2</sub>NiO<sub>4+δ</sub>. On the other hand, Ruddlesden-Popper-type structures reversibly intercalate oxygen ions, and may thus find application in high-performance solid-oxide fuel cells. It was reported that low-temperature oxygen mobility in such compounds is triggered by low-energy phonons<sup>[1]</sup>. Regarding this, Pr<sub>2</sub>NiO<sub>4+δ</sub> is a promising candidate due to its superior low-temperature oxygen conductivity over currently employed materials. Associated with oxygen intercalation in Pr<sub>2</sub>NiO<sub>4</sub> is the emergence of structural complexity in the form of a long-range ordered oxygen superstructure, and partial oxidation of Ni<sup>2+</sup> ions to Ni<sup>3+</sup>. This motivates a deeper understanding of the influence of superstructure and transition metal valence states on the electronic properties of the non-stoichiometric compounds. Pr<sub>2</sub>NiO<sub>4+δ</sub> presents a system where there could be multiple and complex ordering mechanism at play - including charge-, orbital- and spin-ordering - which presents a complex albeit fundamentally interesting physical system to study. Work towards this direction is expected to give insight into emergence of novel electronic properties *via* hole-doping in Ruddlesden-Popper phases.

We present here results of macroscopic magnetic measurements and single crystal neutron diffraction measurements on DMC and TriCS (SINQ) on three variants of the parent compound: Pr<sub>2</sub>NiO<sub>4.12</sub>, Pr<sub>2</sub>NiO<sub>4.25</sub> and Pr<sub>2</sub>Sr<sub>0.5</sub>NiO<sub>4</sub>, which is isoelectronic to Pr<sub>2</sub>NiO<sub>4.25</sub> but devoid of oxygen superstructure. Through a careful comparison of the experimental results, it is seen that while the general exchange interaction in the compounds is anti-ferromagnetic, the oxygen superstructure and transition metal valence states each play their own distinct role to bring about a complex magnetic order in these compounds (Figure 1).

[1] W. Paulus, H. Schober, S. Eibl, M. Johnson, T. Berthier, O. Hernandez, M. Ceretti, M. Plazanet, K. Conder and C. Lamberti, *J. Am. Chem. Soc.* 2008, 130, 16080-16085.

[2] S. Mishra, *M.Sc. Thesis*, Université de Montpellier, France and Paul Scherrer Institut, Switzerland, 2015, LNS-Report No. 255.

Chairs: Georg Eickerling, Dominik Schaniel

### MS24-P1 Structure determination of coordination polymers of [Co(II)(Htrz)Cl<sub>2</sub>] by powder x-ray diffraction and x-ray absorption spectroscopy

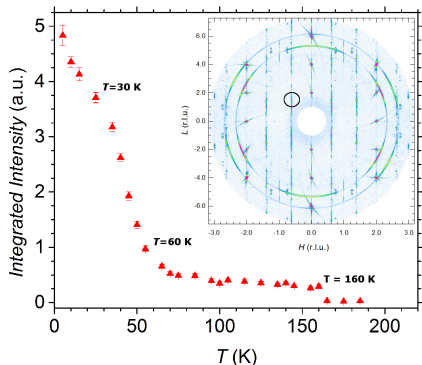
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In developing advanced functional materials, the design and building of metal coordination polymers by forming polynuclear complexes is one way to synthesize potentially applicable materials in separation, catalysis, gas storage, molecular recognition, and magnetism. To achieve this purpose, one of strategies is using polydentate ligands such as 4,4'-bipyridine, pyrazine, and 1,2,4-triazole to chelate with transition metals. The spin crossover compound, [Fe(II)(Htrz)<sub>2</sub>(trz)](BF<sub>4</sub>), (Htrz = 1,2,4-4H-triazol and trz = 1,2,4- triazolato), was one of the examples synthesized based on such concepts to increase the cooperative effect. However, such kinds of coordination polymers are often not easy to get good quality of single crystal for x-ray single crystal structure determination. Thus, *ab initio* structure determination from powder x-ray diffraction (XRD) data becomes one of important methods. Moreover, extended x-ray absorption fine structure (EXAFS) is an element specific technique to explore the local structure of metal site, which may assist to build a better model for further structure determination in XRD data. Here, we present the structure determination of coordination polymers of [Co(II)(Htrz)Cl<sub>2</sub>] (1) and its related compounds based on the combination with EXAFS and XRD data. The results indicate that complex 1 is crystallized in orthorhombic system with Ima2 space group, and the cell constants are  $a = 7.0882(2)$  Å,  $b = 11.7408(4)$  Å, and  $c = 6.7152(6)$  Å, with  $\text{Co-N1} = 2.15(2)$  Å. The electronic structures and magnetism are also discussed in this report.

**Keywords:** EXAFS, XRD, coordination polymer



**Figure 1.** Temperature-dependent scan along  $(-0.62, k, 1.46)$  on  $\text{Pr}_2\text{NiO}_{7-x}$  single crystal, showing a three-step transition. The scanned magnetic peak is marked in the (HOL) reciprocal map, where a combined 2D and 3D magnetic order is seen<sup>[2]</sup>.

**Keywords:** Ruddlesden-Popper, Neutron Scattering, Magnetism, Oxygen Superstructure, Fuel Cell, Oxygen Transport

## MS24-P3 Electron density analysis in Quantum Magnets

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We have investigated the correlation between the accurate electron density distribution and the magnetic properties of two metal-organic polymeric quantum magnets, the  $\{[\text{Cu}(\text{pyz})_2\text{Cl}]\text{BF}_4\}_n$  and the  $\{[\text{Cu}(\text{pyz})_2\text{Br}]\text{BF}_4\}_n$  (pyz = pyrazine), using high resolution single crystal X-ray diffraction and density functional theory (DFT) calculations in the crystalline state as well as in the gas phase on selected fragments of the framework. Topological Analysis based on Quantum Theory of Atoms in Molecules (QTAIM) has been applied to characterize the possible magnetic exchange coupling constants. Electron density analysis confirmed the orientation of the magnetic orbital. The magnetic properties have been examined and correlated with the topological and integrated properties of the electronic distribution. This has enabled the detailed rationalization of the experimental antiferromagnetic exchange coupling constants in terms of the interchain Cu-Cu interactions. Molecular orbital and spin density analysis have been used to identify the atomic and group sources of magnetism. In particular, halogens and pyrazine act as typical non-innocent ligands, with large part of the spin density developed on their atoms. In both cases, the experimentally observed antiferromagnetic coupling can be explained by the copper-copper super-exchange coupling mediated by the pyrazine ligands. Moreover, our results suggest a non-negligible coupling through the halogens although the electron density shows a much weaker interaction than the one observed along pyrazine. From this study, it is clear that systematic electron density analysis on transition metal compounds could lead to a better understanding of the super exchange mechanism with a topological description of the involved interactions.

**Keywords:** MOF quantum-magnets electron-density