MS24 Inorganic and metal-organic magnetic structures

Chairs: Georg Eickerling, Dominik Schaniel

MS24-P1 Structure determination of coordination polymers of [Co(II)(Htrz)Cl_2] by powder x-ray diffraction and x-ray absorption spectroscopy

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IIn 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-triazloe to chelate with transition metals. The spin crossover compound, [Fe(II)$(Htrz)_2$(trz)] (BF_4), (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_2] (**1**) and its related compounds based on the combination with EXAFS and XRD data. The results indicate that complex **1** is crystalized 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 Co-N1 = 2.15(2) Å. The electronic structures and magnetism are also discussed in this report.

Keywords: EXAFS, XRD, coordination polymer

MS24-P2 Interplay of structural complexity and magnetism in $Pr_2NiO_{4+\delta}$ 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 $Pr_2NiO_{4+\delta}$. 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[1]. Regarding this, $Pr_2NiO_{4+\delta}$ is a promising candidate due to its superior low-temperature oxygen conductivity over currently employed materials. Associated with oxygen intercalation in Pr_2NiO_4 is the emergence of structural complexity in the form of a long-range ordered oxygen superstructure, and partial oxidation of Ni^{2+} ions to Ni^{3+}. This motivates a deeper understanding of the influence of superstructure and transition metal valence states on the electronic properties of the non-stoichiometric compounds. $Pr_2NiO_{4+\delta}$ 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: $Pr_2NiO_{4.12}$, $Pr_2NiO_{4.25}$ and $Pr_{1.5}Sr_{0.5}NiO_4$, which is isoelectronic to $Pr_2NiO_{4.25}$ 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).

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