Oral presentation

Experimental charge density and phase transition of a new hybrid perovskite: a combination of experimental approaches for a complete description

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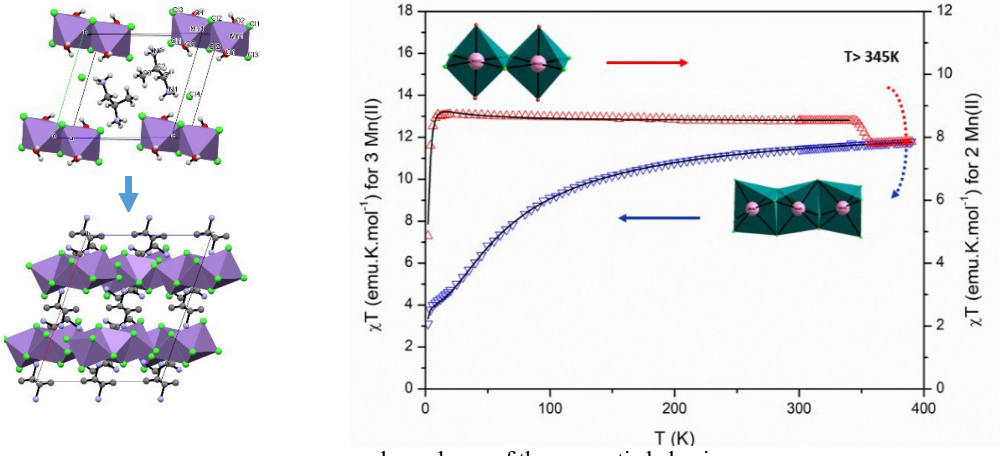
The crystal structure of bis(1,2diamine propane) di-μ-chloro-bis[diaquadichloromanganate(II)] dichloride (1) is built as layers of centrosymmetric binuclear units made of two (MnIICl4(H2O)2)- octahedra sharing one edge along the a direction and distributed in the a,c basal plane (P-1 triclinic space group, figure 1, left). These doubly negative charged layers are separated along the b axis by positive di-amine propane layers. Non-coordinated chloride anions ensure the electroneutrality and stabilize the structure through hydrogen bonds with coordinated water molecules and to the ammonium groups of organic layers.
We modeled the experimental charge density based on a high-resolution single crystal X diffraction experiment in order to calculate the electrostatic properties of this material to understand how the electrostatic interactions contribute to the stability of the structure.

Figure 1. Left: 3D view of the structure at 100K before (along **a** axis) and after (along **b** axis) high temperature heating. Right: Temperature dependence of the magnetic behavior.



Differential scanning calorimetry (DSC) shows two endothermic peaks attributed to a two-step transition (main peaks at T= 366 K and T= 375 K) ascribed to the release of the coordinated water molecules. Meanwhile, SQUID magnetometry reveals new magnetic properties after the transitions. Below 346 K the temperature dependence of χT is almost constant down to 10K (Figure 1). After heating up to 390 K χT rapidly decreases with temperature. As the dehydrated crystals were extremely small, a combination of X-rays and electron diffraction experiments was necessary to solve the structure: 12 data sets merged (0.80Å resolution) for 3064 unique reflexions (observed R factor: 27.9%). Surprisingly, the dinuclear Mn(II) cations rearrange into a trinuclear Mn(II) one (figure 1, right) in a new monoclinic unit cell. This dehydrated structure allowed a thorough fit of the magnetic behavior. Last, this structural and magnetic transition is reversible on a long time scale (months) leading to the starting hydrated phase as confirmed both by magnetic and X-rays diffraction experiments.
We will detail the results of the experimental charge density modelling on the hydrated phase and focus on the multi experimental approach used to validate the surprising dehydrated structure.

[1] Synthesis, crystal structure and phase transitions of novel hybrid perovskite: bis(1,2-diaminopropane) di-μ-chloro-bis[diaquadichloro-manganate(II)] dichloride, S. K. Abdel-Aal, M. Souhassou, P. Durand, C. Lecomte, A. S. Abdel-Rahman and N. Claiser, Acta Cryst. (2023). B79, 314-319