

*Modulated and high Z' phases in Λ -Cobalt(III) sepulchrate trinitrate*Somnath Dey¹, Andreas Schönleber², Sander van Smaalen², Finn Krebs Larsen³¹Crystal Lab, Department Of Chemical Science, IISER Kolkata, Mohanpur, India, ²Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany, ³Department of Chemistry, Aarhus University, Aarhus, Denmark
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Λ -Cobalt (III) sepulchrate trinitrate, a metal organic salt with chemical formula $C_{12}H_{18}N_8Co_3 \cdot 3(NO_3)^-$, crystallizes at room temperature (phase I) in symmetry P6322 [1]. The Co(sep) cation and two of the three nitrate anions are all centered on threefold rotation axes and are linked to each other via N-H \cdots O hydrogen bonds. The third nitrate anion close to the origin exhibits sixfold orientational disorder [1].

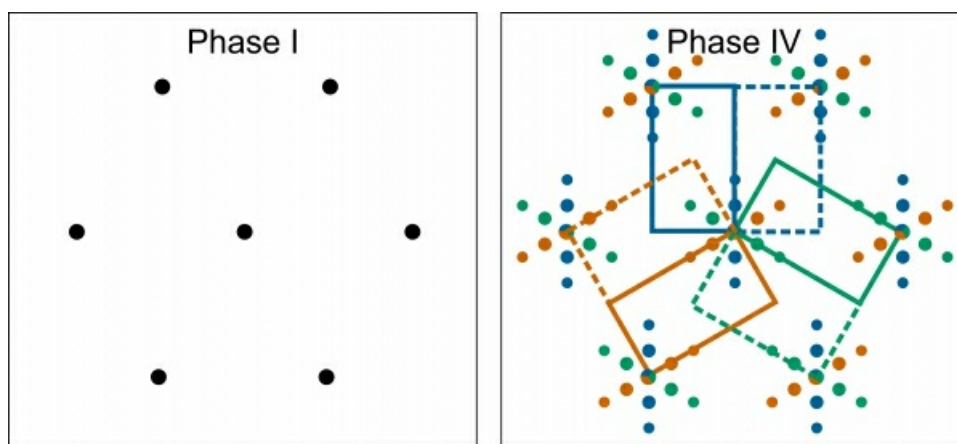
Two phase transitions reported have been observed at $T_{c1} = 133$ K and at $T_{c2} = 107$ K, respectively, by means of light microscopy and spectroscopic measurements [2]. As found by temperature dependent single crystal neutron diffraction satellite reflections are present in the diffraction pattern below T_{c1} , varying their positions continuously as function of temperature. Also a third phase transition was observed at $T_{c3} = 98$ K.

We have performed single crystal X-ray diffraction at beamlines F1 and D3 of Hasylab (DESY, Hamburg, Germany) at temperatures of $T_1 = 115$ K, $T_2 = 100$ K and $T_3 = 95$ K to investigate the crystal structures of the three low temperature phases II, III and IV. Phase III at T_2 possesses an incommensurately modulated structure while phase IV at T_3 is commensurately modulated and alternatively can be described as a twelvefold superstructure ($Z' = 12$) of the structure in phase I [3]. Crystal symmetries in both phases III and IV are found to be monoclinic and six twin domains of pseudo merohedral nature have been found. The crystal structures in both phase III and IV are found to be completely ordered due to increased packing density of the cations around the third nitrate anion. The origin of modulation in phases III and IV is argued to lie in the avoidance of repulsive C-H \cdots O interactions unfavourable for crystal packing rather than attractive N-H \cdots O hydrogen bonds between the Co(sep) cages and the nitrate anions [3].

[1] Schönleber, A. et al. (2010). Acta Cryst. C66, 107–109.

[2] Dubicki, L. et al. (1984) J. Phys. Chem. 88, 4254–4258.

[3] Dey, S. et al. (2016). Acta Cryst. B72, 372–380.



Keywords: [High Z'](#), [twinning](#), [hydrogen interactions](#)