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Order and Disorder in the Mn-based Prussian Blue Analogue: Synchrotron Diffraction and Magnetic Susceptibility Study

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The metal-substituted analogues of Prussian Blue have attracted renewed interest due to their unique combination of magnetic and optical properties. Current research in this field is aimed at designing transparent and optically tunable magnetic materials. A fundamental problem for such design is the presence of intrinsic structural disorder - $M(CN)_6$ vacancies filled by $(H_2O)_6$ clusters - which strongly affects magnetic and optical properties. We characterize the $Mn^{2+}[Mn^{3+}(CN)_6]_{2/3}\bullet(6H_2O)_{1/3}$ analogue with synchrotron diffraction, neutron magnetic scattering and magnetization measurements. Synchrotron diffraction from a single crystal revealed a pronounced diffuse signal linked to a correlated distribution of $[Mn^{3+}(CN)_6]$ vacancies filled by $(H_2O)_6$ water clusters. A complex frequency dependence of the real and imaginary parts of the magnetic susceptibility near T_c, somewhat similar to that of a cluster-glass, indicates a correlated disorder of magnetic centres.

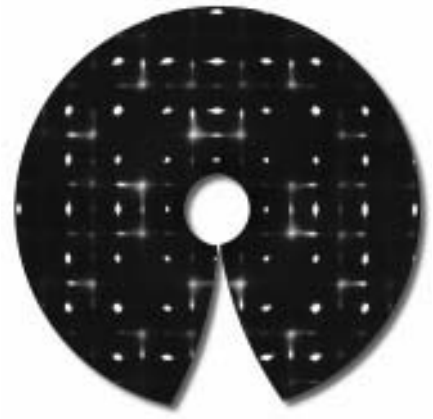

Fig. 1 Structural Disorder in $Mn^{2+}[Mn^{3+}(CN)_6]_{2/3}((6H_2O)_{1/3}$ as seen from diffuse scattering.

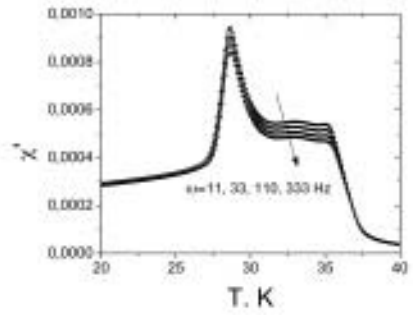

Fig. 2 Frequency dependence of the real part of the ac-susceptibility.

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Advanced automated charge density refinement & interaction energy analyses

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The ultra high resolution crystallographic refinement program MoPro [1, 2] applications extends from small compound crystals to protein/ligand complexes. The software employs a multipolar representation of atoms enabling to model the deformation of the atomic electron distribution due to chemical bonding and interactions. The number of biological macromolecular structures determined at high resolution increases regularly. The feasibility of multipolar refinement of protein structures has been proved [3, 4], assuming subatomic resolution and sufficiently low thermal motion.
The latest functionalities in the program, which concern notably restraints, constraints, refinement strategies and automation will be described.
Electrostatic properties are of major importance in biological and molecular recognition processes. The method employed in the VMoPro software to calculate experimental accurate electrostatic interaction energy uses focused numerical grid integration at high Taylor order. The electron density parameters are obtained either from a crystallographic refinement for small compounds or from a database transfer [5] in the case of macromolecules. Some energy computations will be exemplified.

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