ESRF	**Experiment title:** Structural studies of photo-induced phase transitions	**Experiment number**: CH-1725
Beamlines: ID31	**Date of experiment**: from: 31/3/04 to 6/4/04	**Date of report**: 1/9/04
Shifts: 18/18	**Local contact(s)**: A N Fitch	*Received at ESRF:*

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Report:

Abstract of publication resulting from this proposal:

Large lattice responses in a mixed valence Prussian blue analogue due to electronic and spin transitions induced by X-ray light, ***Angew. Chem.*** 2004**,** ***in press*****.**

Mixed valence metal cyanides with general formula $A_xM^{II}_y[M'^{III}(CN)_6]\cdot nH_2O$ (where A is an alkali cation, and M and M' are divalent and trivalent transition metal cations, respectively) have attracted considerable interest because of their unusual electronic and magnetic properties. In addition to molecular-based ferromagnetic properties with Curie temperatures higher than room temperature, the availability of degenerate or quasi-degenerate electronic states has made them ideal systems to explore switching phenomena at the molecular level. For example, in some of these materials visible light irradiation at low temperatures can drive optically-controlled phase transitions to long-lived metastable states where the optical and/or magnetic properties change dramatically, thereby raising the potential of applications in memory devices and magneto-optical switching. Metal-to-metal electron transfer was also induced by X-ray irradiation at very low temperatures in the Prussian blue analogue, $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3}\cdot 13H_2O$ with the resulting phase transformation followed by energy-dispersive synchrotron X-ray diffraction. Here, we show that X-ray light can also induce interconversion between the ground and excited states in another such compound,

$Rb_{0.7}Mn^{II}_{1.15}[Fe^{III}(CN)_6]\cdot 2H_2O$, over a broad temperature range between room temperature and 10 K. Depending on the experimental conditions, a variety of internal charge transfer processes and spin transitions are triggered resulting in either continuous or abrupt phase transformations that are accompanied by large lattice relaxations and can be accurately followed by high-resolution angle-dispersive synchrotron X-ray diffraction.

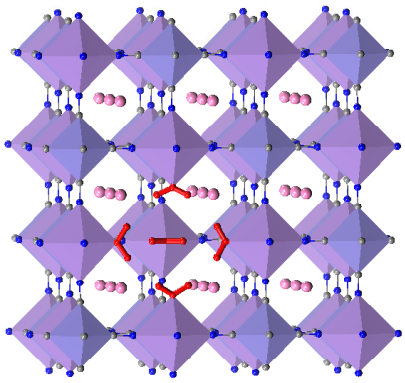

Fig. 1 Building block of the cubic framework structure of $Rb_{0.7}Mn^{II}_{1.15}[Fe^{III}(CN)_6]\cdot 2H_2O$.

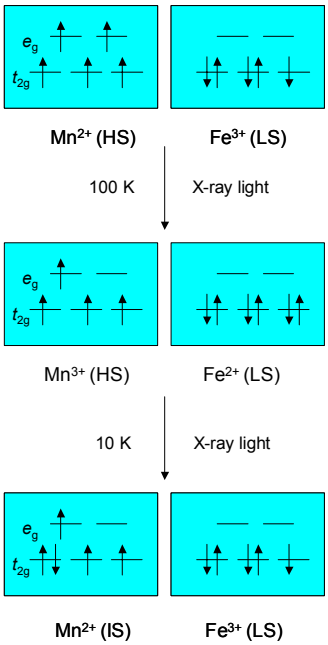

Fig. 3 Electronic and spin configurations of the Mn and Fe ions following the X-ray-induced first-order phase transitions.

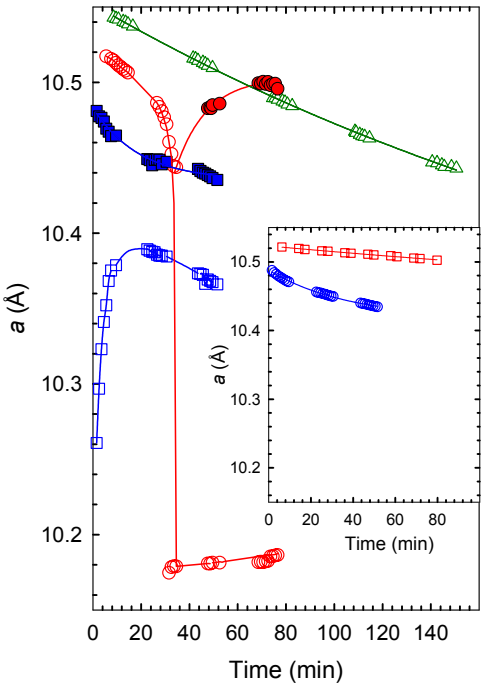

Fig. 2 Evolution with increasing X-ray (E = 14.587 keV) illumination time of the cubic lattice constant at different temperatures: 295 K (green triangles), 100 K (red circles), 10 K (blue squares). Open (full) symbols represent the lattice constants of the majority (minority) phases at 100 and 10 K. The inset in (a) shows the time dependence of the lattice constants at 10 K (E = 14.575 keV) after cooling in the dark (blue circles) and at 100 K for an incident photon energy of 28.854 keV (red squares).