

Oral presentation

Ultrafast photoinduced phase transition dynamics in the RbMnFe Prussian Blue Analogue studied by streaming crystallography

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Modern ultrafast laser technologies have opened new perspectives in controlling bistable photo-active materials, where light can be used to switch between different phases and thus different properties down to ultrashort timescales [1]. In this context, *Prussian Blue Analogues* (PBAs) represent attractive photo-active materials as they exhibit wide *bistability* regimes. The electronic charge transfer involved in the phase transition of PBAs induces large structural changes leading to symmetry breaking, that can be triggered by light absorption.

Thanks to the application of a novel method for picosecond time-resolved crystallography, hereafter called *streaming crystallography*, we studied the dynamics of photo-induced phase transition occurring within the thermal hysteresis of the *Co-doped RbMnFe(CN)₆ PBA* following laser excitation with 650nm photons at 115 mJ.cm⁻² [2-4]. The thermal hysteresis of the studied *Co-doped RbMnFe(CN)₆ PBA*, probed by magnetic susceptibility measurements together with laser excitation at 293 K, is shown in Fig. 1 (*left side*). It displays a *wide bistability regime* (245 K to 335 K) between the low-temperature (LT, tetragonal) and high-temperature (HT, cubic) phases. Fig. 1 (*right side*) depicts the shift of Bragg peaks towards lower Q values, showing that its photo-induced also occurs with tetragonal-to-cubic symmetry change within less than 500 ps. The lattice parameters of the photo-induced state at 500 ps, obtained from Rietveld refinement, are of a cubic phase with $a = 10.507(4)$ Å and correspond to the ones of thermally stabilized HT phase. Coupling between the photo-induced charge transfer and the large volume strain resulting from the structural rearrangements, including both symmetry-breaking bond changes (Jahn-Teller distortion) and non-symmetry-breaking bond elongation (due to charge transfer), stabilizes here the photo-induced HT phase [2-4].

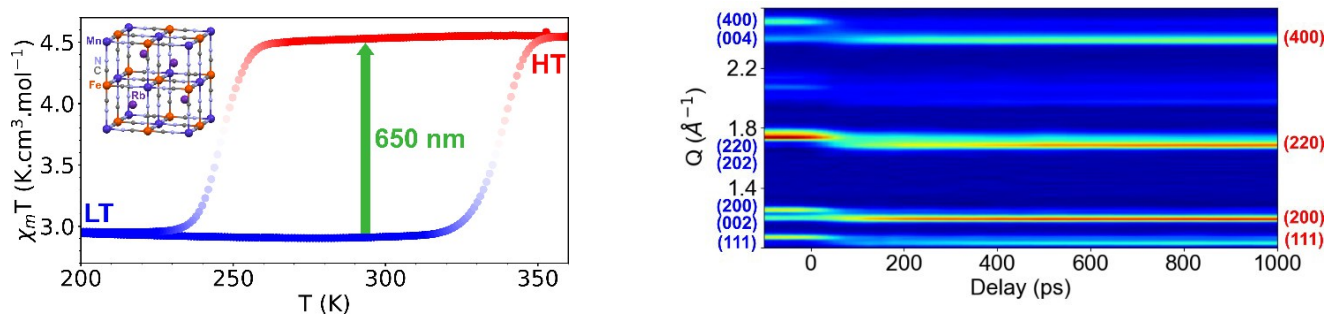


Figure 1. On the left side, magnetic susceptibility measurements of the *Co-doped RbMnFe PBA*, displaying the $\chi_m T$ product as a function of temperature, together with laser excitation at 293 K. On the right side, evolution of the time-resolved X-ray diffraction pattern of the *Co-doped RbMnFe PBA*, with (hkl) indices for the initial, tetragonal and final, cubic phases following laser excitation with 650nm photons at 115 mJ.cm⁻².

These results open a broad field for dynamical studies in bistable materials using ultrafast streaming crystallography, questioning the role of the different degrees of freedom and their couplings.

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