Electronic supplementary information

Out-of-equilibrium lattice response to photo-induced charge-transfer in a MnFe Prussian blue Analogue

G. Azzolina,^a R. Bertoni,^a C. Mariette,^a M. Cammarata,^a E. Trzop,^a C. Ecolivet,^a M. Sander,^b M. Levantino,^b H. Tokoro,^{*,c} K. Imoto,^d M. Yoshikiyo,^d S. Ohkoshi,^{*,d} E. Collet,^{*,a}

^a Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France.

^b European Synchrotron Radiation Facility, F-38000 Grenoble, France

^c Division of Materials Science, Faculty of Pure and Applied Sciences, Univ Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan.

^d Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

* E-mail: tokoro@ims.tsukuba.ac.jp, ohkoshi@chem.s.u-tokyo.ac.jp, eric.collet@univ-rennes1.fr

Content

Samples preparation	S1	&	S2
••••••••••••••••••••••••••••••••••••••		-	

X-ray diffraction set-up	
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Time-resoved X-ray data analysis S4 - S8

Electronic band structure calculation S10

Samples preparation

We used microcrystals of Rb_{0.94}Mn[Fe(CN)₆]_{0.98}•2.5H₂O synthesized by mixing a polyethylene glycol monolaurate (PEGM) matrix containing MnCl₂ (aq) and RbCl (aq) with another PEGM matrix containing K₃[Fe(CN)₆] (aq) and RbCl (aq). The obtained precipitate was centrifuged, washed in methanol and dried in air as described in ref¹. The chemical formula was confirmed using elemental analysis and infrared spectroscopy and SEM analysis revealed that the crystals are plate-shaped and with good crystallinity as shown in Fig. S1. The sample we used is a dispersion of microcrystals in ethanol. Fig. S2 shows the χ_M . T vs T (χ_M being the molar magnetic susceptibility and T the temperature).¹ The χ_M . T value (≈ 4.75 cm³.K.mol⁻¹ at 300 K) of the HT phase Fe^{III}(S=1/2)Mn^{III}(S=5/2) decreases around T_{1/2} $\downarrow \approx 185$ K on cooling, as the LT phase Fe^{III}(S=0)Mn^{III}(S=2) forms. Conversely, on warming the sample from the LT phase, the χ_M . T value increases around T_{1/2} $\downarrow \approx 285$ K.



Fig. S1 Rb_{0.94}Mn[Fe(CN)₆]_{0.98}•2.5H₂O sample in solution (a) and deposited on glass substrate changing color between the HT and LT phases (b). Sem image of the sample (c).



Fig. S2 – Thermal transition probed through the χ_M . T product (χ_M = molar magnetic susceptibility and T = temperature).

X-ray diffraction

The X-ray diffraction experiment was performed at the ID09 beamline of the ESRF synchrotron. The beam was focused using a toroidal mirror and the beam size at the focal point was $150 \times 150 \mu m^2$. The footprint on the sample, due to the grazing angle experimental geometry was roughly $0.150 \times 3 mm^2$. We performed the measurements by keeping the sample surface close to grazing angle with respect to the X-rays incident direction (14.8 keV). The samples were fixed to a goniometer head mounted on a Huber 1-Circle Goniometer (model 410a) with the rotation axis perpendicular both to the X-rays and laser directions. Temperature control during the experiment was achieved using an Oxford Cryosystems Cryostream 800 liquid nitrogen cooler positioned along the rotation axis of the goniometer. The thermal scans shown in Fig. 1 and Fig. 2 were performed using a cooling/heating rate of 6 K/min.



Fig. S3 - Schematic representation of the experimental setup used for the time-resolved measurements at ID09.

The diffracted intensity was collected using a Rayonix MX170-HS CCD detector with an active area of 170 x 170 mm² and a pixel size of 89 μ m. We chose a distance of ~23 cm from the sample as a trade-off between *q*-resolution and portion of *q*-space explored. A typical diffraction image is shown in Fig. S3. In order to increase the statistics, each image was collected using the integration of numerous X-ray shots. In order to extract the diffraction patterns each image was treated using the python library PyFAI², an open-source software package designed to perform azimuthal integration on area-detector images for X-ray scattering experiments. The diffraction data were refined using the software TOPAS-Academic version 6³. For monitoring the thermally-induced phase transition, we collected x-ray diffraction during a continuous thermal ramp, averaging the data collected within 10 K intervals. The almost zero thermal expansion showed by the MnFe system, revealed by high resolution diffraction studies ¹ could not be probed by our experimental set-up due to the relatively poor *q*-resolution. The refinement process had to take into account the presence of crystals of a known and passive Rb₂Mn[Fe(CN)₆]•3.5H₂O impurity. The temperature dependent of the lattice parameters of the Rb_{0.94}Mn[Fe(CN)₆]_{0.98}•2.5H₂O sample shown in Fig. 2 exhibits a phase transition around 280 K on warming, in good agreement with the magnetic susceptibility (Fig. S2).

In order to study the out-of-equilibrium dynamics, we used a regenerative amplifier coupled to an OPA in order to generate ~1 ps pulses centered around λ =520 nm (Fig. S3). This wavelength has been shown to efficiently promote the intervalence charge transfer from Mn^{III}Fe^{III} to Mn^{II}Fe^{III} (LT to HT) using both continuous⁴ and pulsed⁵ irradiation. The penetration depth in RbMnFe can be calculated starting from the values of the real and imaginary parts of the dielectric constant reported in ref ⁶ and the penetration depth at 520 nm is around 320 nm, which is similar to the 300 nm average size of the microcrystals composing the sample. This ensures a rather homogeneous excitation at the individual microcrystal scale. We used a quasi-grazing incidence geometry with the sample surface tilted around 4° with respect to the X-ray direction and a laser incidence perpendicular to the direction of the film Fig. S3. This allows for increasing the diffracted signal from the thin film of microcrystals by maximizing the excited area of the sample. This geometry is used to compensate the relatively low X-ray flux, due to the chopper system, for time resolved measurements. In order to maximize the signal, the sample plate was oriented at an angle $\phi \approx 4^\circ$ between the sample surface and the beam (Fig. S3). The optical pump – X-ray probe experiment was performed with ~70 ps time resolution, at a repetition rate of 1 kHz. The time resolution of the experiment was limited by the X-ray pulse duration. The time delay between

the pump and the probe was controlled electronically. Each diffraction pattern was collected by integrating the diffracted intensity of up to 3000 X-ray shots at a given time delay. The negative delay signal (-10 ns) was used as reference and was collected several times during each scan to check the complete relaxation of the sample. For the time-resolved measurements, we used excitation fluences up to 42 μ Jmm⁻². Higher fluences may have resulted in photo-induced residual effects indicating an incomplete relaxation of the sample that would make the data interpretation inconclusive. We collected data at several temperatures (110 K, 130 K and 160 K) outside the bistability region to allow for complete relaxation of the sample.

Fig. S4 shows an example of a time-resolved (top) X-ray diffraction pattern I(q). The bottom pannel shows the differences between the intensity measured at a give time delay and the reference signal prior to excitation measured at -10 ns. Due to the limitation given by the grazing incidence experimental geometry, the presence of the impurity in the sample and the small intensity of the photoinduced signal, it was not possible to perform a Rietveld refinement on the data. We used a Pawley refinement to retrieve the value of the lattice parameters as function of the time delay, using the software TOPAS-Academic version 6.³ The data at negative delays were refined using the tetragonal LT phase and the cubic impurity.



Fig. S4 - Diffraction patterns measured 10 ns before laser excitation (top) and difference signal for different time delays (bottom)

The data presented in Figure 3 were obtained by allowing volume expansion of the passive $Rb_2Mn[Fe(CN)_6] \cdot 3.5H_2O$ impurity, which exhibits a weak thermal expansion. Fig. S5 compares the results of the Pawley analysis by allowing lattice expansion of the impurity (a_{imp}) or not. In both cases we observe for the photoactive $Rb_{0.94}Mn[Fe(CN)_6]_{0.98} \cdot 2.5H_2O$ crystals the same qualitative response with an initial opposite shift of the lattice parameters a and c, decreasing the symmetry breaking order parameter η and a global volume expansion, characteristic of the out-of-equilibrium decoupling in time of the volume strain and the ferroelastic distortion.



Fig. S5 - Relative temporal evolution of the lattice parameters a, c, V and η, with respect to values prior to photoexcitation at 130 K, for pump fluences of 24 µJ.mm⁻² (blue) and 42 µJ.mm⁻² (orange). The analysis performed by allowing (left) a thermal expansion of the passive crystals of the Rb₂Mn[Fe(CN)₆]•3.5H₂O impurity or by fixing the lattice parameter (right) provide similar qualitative features for the time dependence of V and V and η, which are the key parameters related to the phase transition.

The fits of the time dependent volume $\frac{V(t)}{V_{LT}}$ in Fig. 3c and 3e were performed using a convolution of the Instrumental Response Function (IRF) with a step function H(t): $\frac{V(t)}{V_{LT}} = IRF_X(t)\otimes[A,H(t)]$ A is the amplitude of the step and the IRF:

$$IRF_X(t) = \frac{1}{\sqrt{2\pi}\sigma_X} \exp(-\frac{t^2}{2\sigma_X^2})$$

is characterized by the Gaussian RMS width $\sigma_x = 30 \ ps$ corresponding to an overall time resolution of ~70 ps. For the fits of the temporal dependence s(t) of the others lattice parameters, we add an exponential component;

$$s(t) = IRF_X(t) \otimes \left[A - B \exp\left(\frac{-t}{\tau_1}\right)\right] \cdot H(t)$$

with τ_1 =300 ps providing a satisfactory guide for the eye. Typical fits are shown in Fig. S6. Fig. S7 shows the almost linear response with excitation density.

Fig. S8 shows the evolution of the diffraction signal 75ps and 600 ps after excitation. Fig. S9 shows the decay of the photoinduced $Mn^{\parallel}Fe^{\parallel}$ CT state monitored by optical density in *ref*⁷ and the volume relaxation probed here by X-ray diffraction.



Fig. S6 – Fit of the temporal dependence of $\frac{a(t)}{a_{LT}} a(t)$ (left) and $\frac{V(t)}{V_{LT}}$ (right). The volume variation $\Delta V^{h\nu}$ as function of the pump fluence is described with a linear fit and , and scaled to γ (red right axis).



Fig. S7 – Evolution of the shift of lattice parameters **a** and **c** at 75 ps (left) and photoinduced volume expansion $\Delta V^{h\nu}$ as function of the pump fluence (right). The volume change is scaled to γ (green right axis).

Fig. S8 Evolution of the time-resolved differential X-ray diffraction signal, with respect to negative delay, measured 75 ps and 600 ps after photoexcitation. The contribution of the lattice contraction along **c** is stronger at 75 ps than at 600 ps, where it is mainly the lattice expansion along **a** that contributes to the signal change.



Fig. S9 Optical density change (Δ OD) probed at 650 nm for the RbMnFe compound after femtosecond laser excitation at 530 nm, monitoring the decay of the photoinduced Mn^{III}Fe^{II} state (left, reprinted from ref ⁷). The volume relaxes on a similar timescale as probed by time-resolved X-ray diffraction.

Electronic structure calculations

1.5

1.0

0.0

0

5

AOD (10-2) 0.5

Electronic structure calculations were conducted by first-principles calculations using the Vienna ab initio simulation package (VASP) program. The wave functions based on the plane waves and the potentials of the core orbitals were represented by the projector augmented wave of Blöchl. The exchange-correlation functional was approximated with generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE). The U–J value was set to 4.0 eV for Fe and Mn. The basis set was regulated by the cutoff energy of 500 eV. The Brillouin zone was integrated with k-mesh of 4×4×4. Fig S10 shows the density of states in the LT phase for α and β spins, with a focus on the Mn dx²-y² – N character of the lowest unoccupied crystalline orbital (LUCO) populated after CT.



Fig. S10 (a) Schematic repartition of α spins in the Mn orbitals in the LT and HT phases. (b) and (c) show the band structure calculation in the LT phase and the density of states. The electronic density of the LUCO reveals the clear Mn dx²-y² – N character of this anti-bonding orbital populated after CT.

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