

X-ray single-crystal diffraction study of the light-induced short-lived metastable HS state of the [Fe(pyrazine)Pt(CN)₄] polymeric network structure.

Since good quality single crystals could not be obtained for this experiment, powder diffraction was used. The following are extracts from an article to be submitted in October 2014.

Synchrotron powder X-Ray diffraction reveals that a quantitative photo-induced LS-to-HS conversion, based on the Light-Induced Excited Spin State Trapping effect can be achieved at 10 K on a microcrystalline powder. Time-resolved measurements evidences that the HS-to-LS relaxation proceeds by a two steps mechanism: a random HS to LS conversion at the beginning of the relaxation is followed by a nucleation-growth process, which proceeds until a quantitative HS to LS transformation is reached.

In a first experiment, long exposure diffraction patterns were collected at 10 K in the dark and under continuous irradiation ($\sim 2 \text{ mW/mm}^2$) at 532 nm (figure 1a). Upon continuous irradiation, an increase of the unit cell volume, V_c , is observed, while the tetragonal space group P4/mmm is maintained. The increase in V_c of 49 \AA^3 is consistent with a close to quantitative photo-induced LS to HS conversion. The obtained variation of the Fe-Ligand bond length upon photo-excitation is $\sim 0.19 \text{ \AA}$, which is in good agreement with **complete photo-induced LS to HS conversion**.

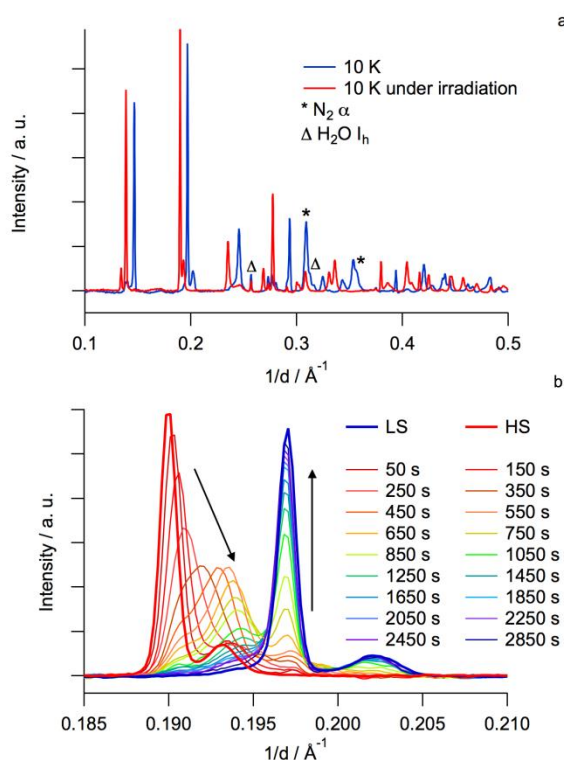


Figure 1. (a) Powder XRD pattern of [Fe(pz)Pt(CN)₄] \cdot 2.6H₂O at 10 K in the dark and under continuous irradiation at 532 nm, (b) Time evolution of the (110) and the (011) diffraction peaks during the photo-induced HS \rightarrow LS relaxation.

Subsequently XRD patterns in the dark after irradiation at 10 K were collected over intervals of 100 s each. As a representative example, the time evolution of the (110) and (011) peak profiles is presented in Figure 1b.

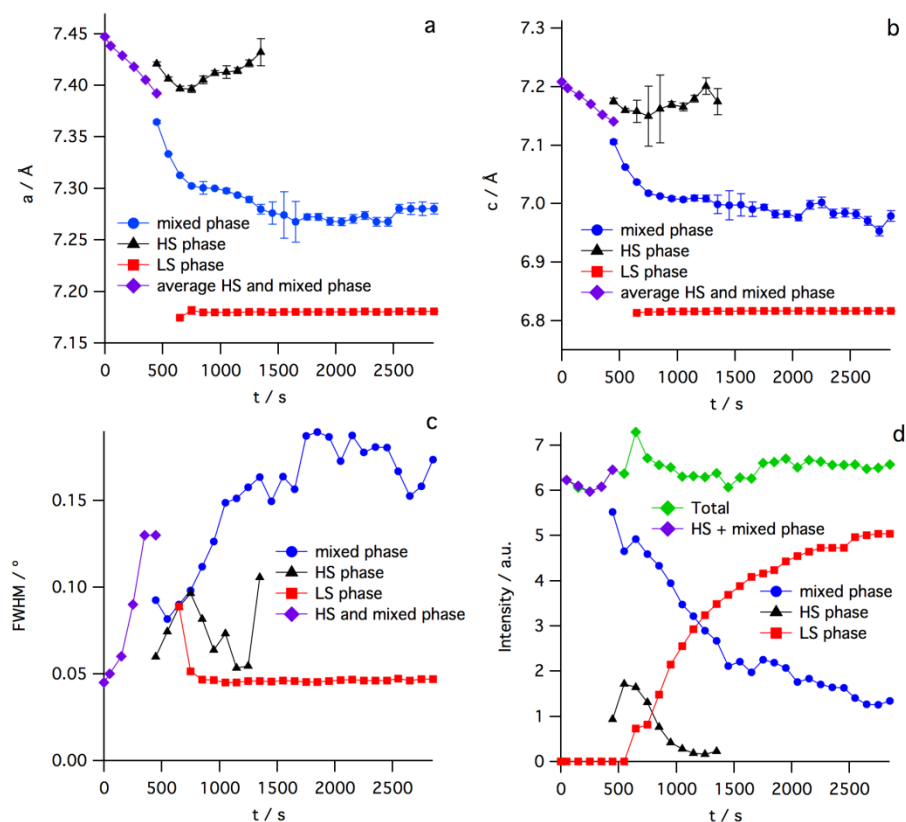


Figure 2 Evolution of (a) the cell parameter a , (b) the cell parameter c , (c) the FWHM of the (110) diffraction peak and (d) the intensity of the (110) diffraction peak as a function of time at 10 K for the three phases during the HS→LS relaxation after irradiation at 532 nm. Below 500 s, the HS like phase and the majority mixed phase cannot be distinguished, in this time interval average values of a and c , the total FWHM of the two phases and the sum of their intensities is given. In addition the total intensity as sum of all three phases is given in (d).

After 100 s, the diffraction pattern is still almost identical to the one of the pure HS state obtained under continuous irradiation. The diffraction peaks then become broader and shift towards higher angles, indicating a decrease of the unit-cell volume, consistent with the HS→LS relaxation and the **formation of a mixed HS/LS phase**. After an incubation time of around 500 s, new diffraction peaks situated at higher angles start to appear. This new set of peaks can be identified as belonging to the pure LS phase at 10 K. The intensity of the LS peaks then grows with time, while the intensity of the other set of peaks decreases. After 3000 s, the only remaining peaks are those corresponding to the pure LS phase.

Closer inspection of Figure 1 shows that the initial (110) peak not only shifts towards higher angles and broadens, but it also splits into two distinct components at around 400 s. One of the split components remains almost at the original position but with rapidly decreasing intensity, while the other one decreases much slower and dominates the observed shift. The XRD patterns during the relaxation were therefore analysed by considering three phases: namely the slowly varying mixed phase, the phase resembling the HS phase as minority phase, and the pure LS phase. Accordingly, Figure 4 shows the result of a Pawley refinement on the low angle part of the XRD patterns by taking the cell dimensions a and c , the full width at half maximum (FWHM) and the intensity for each phase as free parameters. Of course

before 500 s, the first two phases cannot be distinguished. For the majority mixed phase two distinct time domains can be distinguished, indicating *two types of HS→LS relaxation mechanisms*:

- (i) Between 0 and 700 s the unit-cell parameters of this phase continuously decrease, indicating a continuous decrease of the HS fraction. Vegard's law can be used to quantitatively evaluate the evolution of the HS fraction in the **mixed phase**, which decreases from $\gamma_{\text{HS}} = 1$ at $t = 0$ to $\gamma_{\text{HS}} \approx 0.5$ at $t = 700$ s. Moreover, the FWHM of the diffraction peaks associated with this phase gradually increase. The gradual shift of the diffraction peaks is consistent with a close to random HS to LS conversions. The progressive increase of the FWHM of the diffraction peaks indicates a distribution of relaxation rate constants. Such a distribution may be due to the presence of inhomogeneities as for instance the size distribution of the microparticles, a temperature gradient, and a distribution in water content. Below 700 s, the intensity of the diffraction peaks of this phase in all probability does not vary much, although this is of course difficult to affirm due to the presence of the HS like minority phase.
- (ii) (ii) After 700 s the unit-cell parameters of the majority mixed phase reach a plateau corresponding to $\gamma_{\text{HS}} \approx 0.4$ at $t > 1000$ s. At the same time the intensity of the diffraction peaks of this phase now decreases and continues to decrease also in the region of the plateau in the unit cell parameters. Simultaneously, the new phase gradually appears with unit-cell parameters consistent with a pure LS phase. The appearance of a new phase with an incubation period and as pure LS phase indicates a **nucleation and growth type relaxation mechanism**.

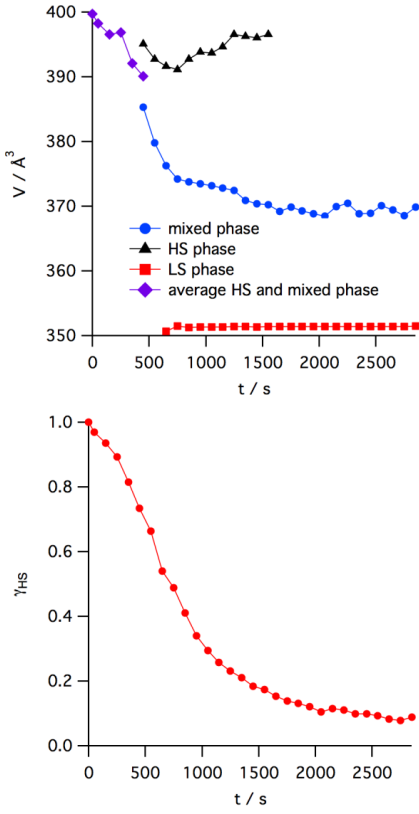


Figure 3. Evolution of the unit cell volumes (top) and the photo-induced HS fraction as a function of time at 10 K extracted from the evolution of the unit-cell volumes (bottom).

The sum of the (110) diffraction peak intensities of the three different phases considered is almost time independent. Therefore, we can assume that the population of each of the three phases is proportional to the (110) diffraction peak intensity. The sample averaged time evolution of the total HS fraction can then be calculated with equation 1.

$$\gamma_{HS}(t) = \sum_{i=1}^3 \frac{I_i(t)}{I_{tot}} \gamma_{HS}^i(t) \quad (1)$$

where $\gamma_{HS}(t)$ is the total HS fraction at time t , $I_i(t)$ is the (110) peak intensity of phase i at time t , I_{tot} is the total (110) peak intensity and $\gamma_{HS}^i(t)$ is the HS fraction of phase i at time t . The HS fraction in each phase $\gamma_{HS}^i(t)$, in turn, can be calculated with Vegard's law according to equation 2.

$$\gamma_{HS}^i(t) = \frac{V_i(t) - V_{LS}}{V_{HS} - V_{LS}} \quad (2)$$

where $V_i(t)$ is the unit-cell volume of the phase i at the time t , V_{HS} is the unit-cell volume of the HS state at 10 K (obtained under continuous irradiation) and V_{LS} is the unit-cell volume of the LS state at 10 K. The time evolution of the unit cell volumes and the corresponding sample averaged total HS fraction are shown in Figure 3. The obtained HS→LS relaxation curve is sigmoidal, with around half of the HS centres relaxed back to the LS state within 700 s. This value is in good agreement with the 10 K lifetime obtained by optical measurements on the compound dispersed in a KBr pellet (Figure S7, $\tau \sim 900$ s). The relaxation curve is sigmoidal, indicating cooperative effects in the solid state.