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Single Laser Shot Spin State Switching of $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ Inside Thermal Hysteresis studied by x-ray diffraction

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Abstract: We study by x-ray diffraction and optical microscopy the photoswitching, initiated by a single ns laser pulse, of the spin-crossover $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ material inside its thermal hysteresis. The single-crystal study shows that a complete conversion from low spin to high spin states can be reached with a single laser shot. Partial conversions obtained with weaker laser energy gives rise to HS domains. Our results indicate that the non-linear response to light excitation is mainly driven by the temperature jump of the crystal following laser excitation.

Keywords: Hysteresis; Microscopy; Phase transition; Photoswitching; Spin cross-over; x-ray diffraction.

1. INTRODUCTION

The transformation of materials by light is an important emerging topic in materials science. In addition to photochemistry where the transformation is limited to a molecular level, photoinduced phase transitions are associated with the macroscopic transformation of materials and cooperative response to light excitation [1]. It is then possible to generate by light different physical properties, control metallic or ferroelectric states, induce SHG [2-4]. This light-driven bistability also competes with thermal bistability and a complex transformation pathway from molecular to material scales involves different degrees of freedom.

Fe^{II} spin crossover (SCO) compounds [5] are prototypical bistable magnetic systems, undergoing a spin-state transition from a diamagnetic low spin state (LS, $S=0$) at low temperature to a paramagnetic high spin state (HS, $S=2$) of higher entropy at high temperature. This change of spin state is associated with changes of diverse physical properties (magnetic, optical, electrical...). It is also possible to trigger the change of spin state by light excitation [5]: this is the so-called Light-Induced Excited Spin State Trapping (LIESST) effect, easily observed at low temperature (typically below 100 K) where the photoinduced HS state is long-lived. At higher temperature, the use of time-resolved technique is required for observing transient LIESST and reverse LIESST with a ms or shorter life-time [6]. There are many SCO systems in the literature undergoing a first-order phase transition between LS and HS states and describing a thermal hysteresis. Some reports have demonstrated that the photoexcitation of the LS state inside the thermal hysteresis can generate the HS phase [7,8,9].

The single shot photoswitching inside the thermal hysteresis of the $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ (pz=pyrazine) compound studied here was evidenced by Bousseksou *et al* by Raman, optical spectroscopy and magnetic measurements [9-12]. In crystals, the photoinduced out-of-equilibrium dynamics initiated by a laser pulse involves several steps [13-18]. First the LS to HS photoswitching occurs [6,19-20]: the photoexcited molecules are trapped within less than 200 femtoseconds in the HS potential by the ultrafast activation and damping of the molecular breathing phonon, through a coherent structural reorganization [21-23]. The consecutive volume expansion drives additional conversion to the HS state during the so-called elastic step on nanosecond time scale [16,17]. The crystal heating due to the absorption of the laser pulse finally induces a transient temperature jump, resulting in a thermal population of the HS state on μs time scale [14,15].

SCO hysteresis at thermal equilibrium, or under light excitation at low temperature, is associated with a phase separation mechanism: the growing of HS domains inside a LS lattice. It is well characterized by x-ray diffraction: since LS and HS phases have quite different lattice parameters [24-28], their Bragg peaks split on LS and HS reciprocal lattices. Regarding the photoswitching process inside the thermal hysteresis, the question of the formation of domains induced by light also appears, especially because of the non-linear response to light excitation. In addition, the change of electronic distribution between LS and HS states is associated with important changes of colour and optical microscopy is a powerful tool for characterizing spin-state conversion, and a direct imaging of HS domains growing was recently reported [29-33].

Here we present a single crystal study, performed by x-ray diffraction and microscope imaging, of the spin-state switching of $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ inside its thermal hysteresis initiated by a single ns laser pulse.

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2. MATERIALS AND METHOD

Single crystals of $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\} \cdot n\text{H}_2\text{O}$ ($n \approx 2$) were synthesized by slow diffusion in a H-shaped vessel (total volume 10 mL). One arm of the vessel contained an aqueous solution (1 mL) of $[\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2] \cdot 6\text{H}_2\text{O}$ (39.2 mg, 0.1 mmol) and pz (8mg, 0.1 mmol), while the other arm contained a water solution (1 mL) of $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (43.13 mg, 0.1 mmol). The vessel was carefully filled with a 1:1 mixture of water-methanol. The H-shaped vessel was sealed and left in a quiet place for 1 month. During this time small cube-shaped yellow-orange single crystals of the title compound were formed. The crystals were dehydrated in vacuum. Structural investigations by x-ray diffraction at thermal equilibrium and after ns laser excitation were performed on single crystals. Partial crystallographic data were collected both at thermal equilibrium or after laser excitation for monitoring changes of lattice parameters. Complete data collections were also performed for characterizing the changes of the crystal structure at thermal equilibrium from the LS phase at 250 K to the HS phase at 310 K. Additional data collections were performed at 293 K for characterizing the changes of the crystal structure from the LS phase to the photoinduced HS phase inside the thermal hysteresis after ns laser irradiation at 532 nm. Data were collected on a four-circle Oxford Diffraction Xcalibur 3 diffractometer (MoK_α radiation) with a 2D Sapphire 3 CCD detector, on samples with typical sizes around $50 \times 50 \times 50 \mu\text{m}^3$. The single crystals were mounted in an Oxford Cryosystems nitrogen-flow cryostat. The unit cell parameters and the data reduction were obtained with CrysAlis software from Agilent. The structures were solved with SIR-97 and refined with SHELXL. Photographs of the single crystal obtained with the diffractometer microscope were also used for monitoring the change of spin state associated with a change of colour.

3. RESULTS AND DISCUSSIONS:

3.1. LS-HS hysteresis at thermal equilibrium

The LS to HS phase transition at thermal equilibrium was investigated by combined x-ray diffraction and microscope imaging. Fig. 1 shows the thermal dependence of the crystal lattice parameters measured in cooling and warming modes, indicating a first-order phase transition with a thermal hysteresis. The observed phase transition temperatures in cooling ($T_{1/2\downarrow} \approx 279$ K) and warming ($T_{1/2\uparrow} \approx 298$ K) are in good agreement with the ones observed by magnetic susceptibility measurements [9-12]. This change of spin state is confirmed by the change of colour (Fig. 1). The observed change of lattice parameters is also directly related to the change of spin state. Fig. 2 shows the P4/mmm crystal structures in the LS (250 K) and HS (310 K) phases. The pz ligands are bridging Fe layers along the 4-fold axis. Since the HS state is less bonding, the equatorial and axial Fe-N bond lengths increase in average from $\langle \text{Fe-N} \rangle_{\text{LS}} = 1.96$ (11) Å to $\langle \text{Fe-N} \rangle_{\text{HS}} = 2.21$ (5) Å. The ≈ 0.25 (8) Å elongation along the c axis of the bond lengths between the Fe and the two N of the pz ligand explains the expansion of the lattice parameters c from $c_{\text{LS}} \approx 6.756$ (4) Å to $c_{\text{HS}} \approx 7.223$ (7) Å.

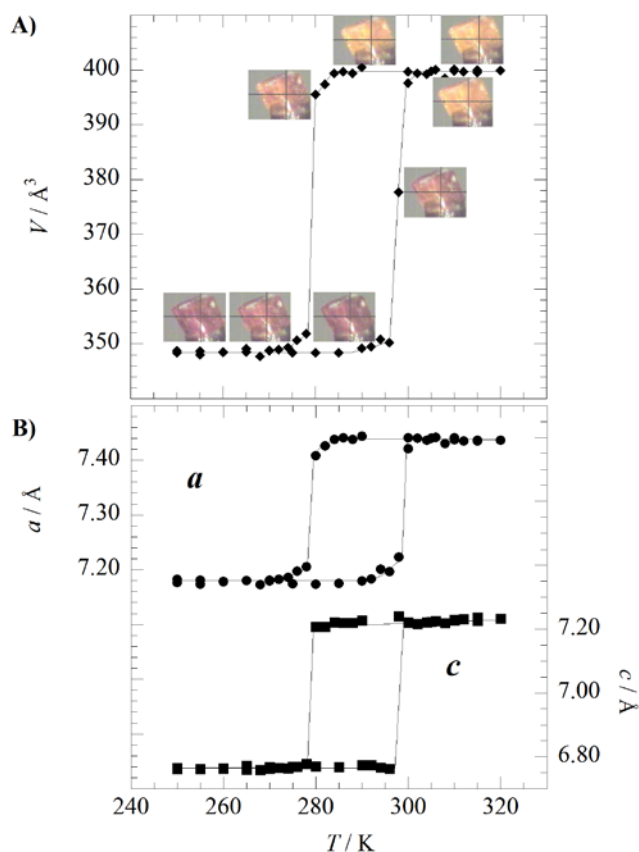


Fig. (1). Thermal variation of the lattice parameter a and c and volume V of $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\}$, accompanied by the change of crystal colour from pink (LS) to yellow (HS).

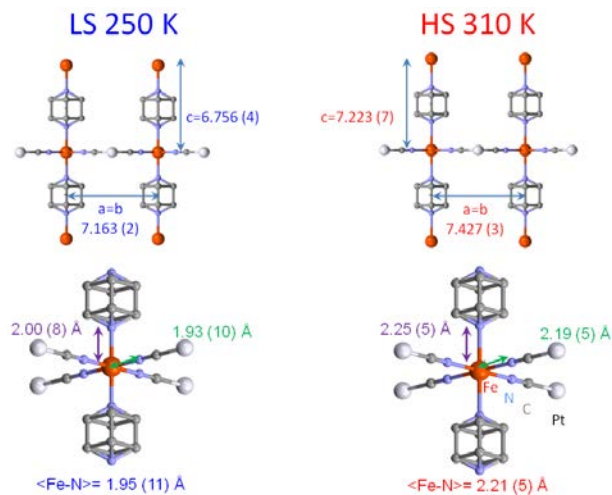


Fig. (2). Structure of $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ at 250 K (LS) and 310 K (HS) with lattice parameters and Fe-N bond lengths.

The thermal expansion in this temperature range is negligible with respect to the expansion resulting from the change of spin-state. Therefore, the values of the lattice parameters are direct fingerprints of the spin state and allows a direct characterization of the spin state of the system.

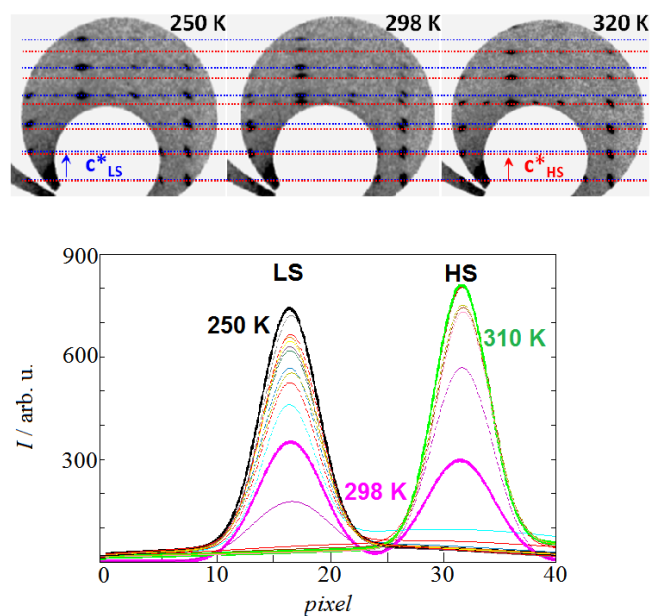


Fig. (3). (top) Diffracted intensity in the reciprocal (a^* , c^*) plane collected in the warming mode at 250 K, 298 K and 320 K. The Bragg peaks are located on the HS (c_{HS}^*) or LS (c_{LS}^*) reciprocal lattices. (bottom) Temperature dependence of the intensity diffracted on the LS and HS Bragg peaks.

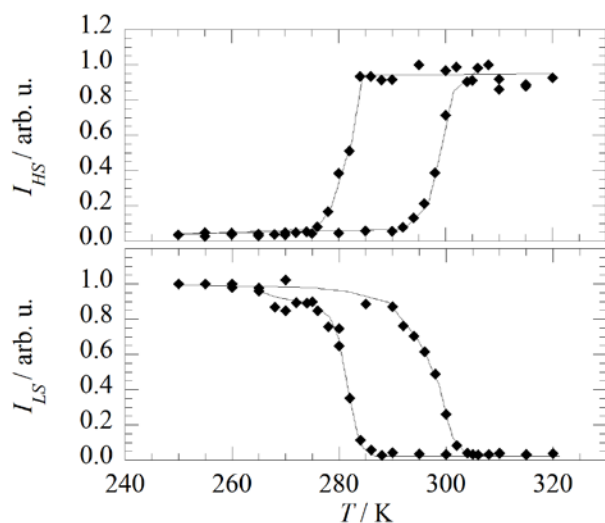


Fig. (4). Temperature dependence of the relative intensity of the HS (top) and LS (bottom) Bragg peaks with temperature.

The HS and LS structures (see Fig. 2) are similar to the ones already reported for the hydrated and dehydrated compounds [34,35], which display exactly the same SCO behaviour. We could not find water molecules in the pores. Because of the dehydration, the crystal parameters found here and the unit cell volumes, $V_{HS}=398.29(4) \text{ \AA}^3$ and $V_{LS}=346.64(2) \text{ \AA}^3$, are smaller than the ones reported for the hydrated compound [34,35], for which $V_{HS}=403.6(4) \text{ \AA}^3$ and $V_{LS}=350.01(5) \text{ \AA}^3$. However, the expansion of volume ($\approx 53 \text{ \AA}^3$), c lattice parameter (0.474 \AA) and $\langle Fe-N \rangle$ are similar in both compounds and characterize the change of spin state. Fig. 3 shows the intensity diffracted in the reciprocal space by the crystal for different temperatures, measured in the

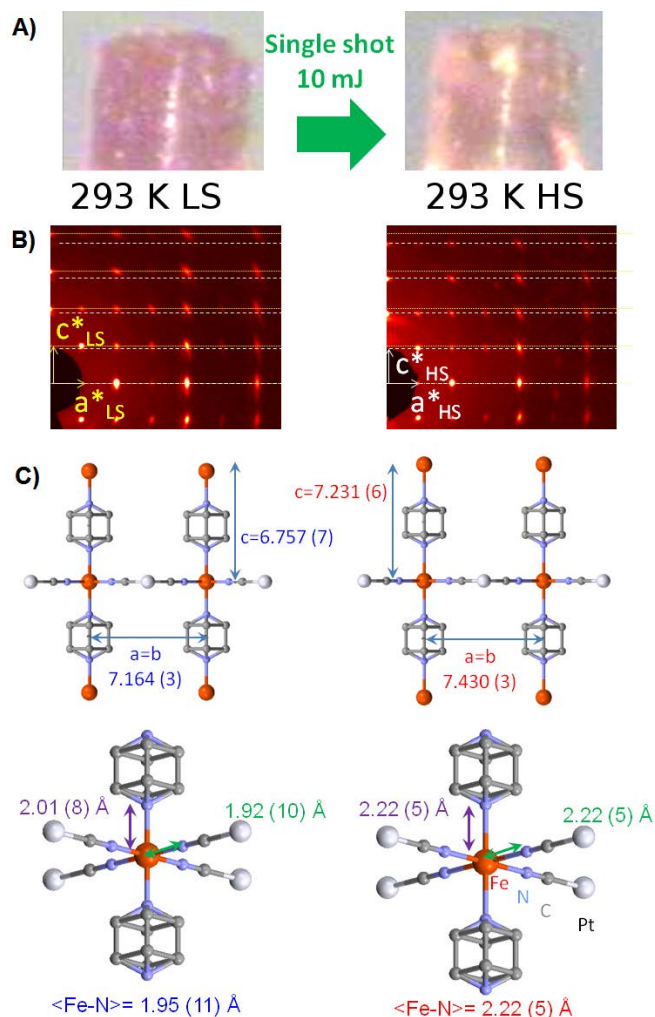


Fig. (5). Colour change of $\{Fe^{II}(pz)[Pt(CN)_4]\}$ crystal (A), diffracted intensity in the reciprocal space with Bragg peaks on the LS (a_{LS}^*, c_{LS}^*) or HS (a_{HS}^*, c_{HS}^*) lattices (B) and structure (C) of the photoinduced HS phase (right) resulting from excitation by the 10 mJ laser pulse (532 nm) of the LS phase (293 K left).

warming mode. At 250 K the Bragg peaks are located at the nodes of the LS reciprocal lattice and at 320 K the Bragg peaks are located at the nodes of the HS reciprocal lattice. At 298 K, Bragg peaks split and diffraction is observed on the nodes of both the LS and on the HS reciprocal lattices. This is the direct evidence of the coexistence of LS and HS domains also evidenced in other materials [24-28]. The growing of HS domains can be monitored by measuring the intensity of the LS and HS Bragg peaks. Fig. 3 shows the intensity transfer from LS to HS peaks as temperature increases, with a similar intensity around 298 K for LS and HS peaks. Fig. 4 shows the evolution of the normalized intensity of the LS and HS peaks measured in warming and cooling modes. On the descending branch, it is clear that the LS and HS phases coexist in the 275-284 K range, whereas in the ascending branch LS and HS phases coexist in the 294-302 K range. Below 275 K the system is purely LS, above 302 K it is purely HS and in the 284-294 K range it is LS or HS depending on the thermal history of the sample. The spin state is therefore easily characterized by the colour or the lattice parameters of the crystal.

3.2. Single shot photoswitching at 293 K

We performed a single laser shot switching from LS to HS states by exciting a completely LS single crystal with a ns laser pulse (532 nm). x-ray probe all the crystal volume in the transmission diffraction mode, whereas the laser penetration depth (around few 10s μm) and spot size (300 μm \varnothing) allow a quite homogeneous sample excitation. The crystal structure was measured first at 293 K and corresponded to a completely LS phase, as characterized by the structural parameters shown in Fig. 5 (lattice parameters, Fe-N bond lengths), which are similar to the ones of the LS phase observed at 250 K (Fig. 2). The diffracted intensity located only on the nodes of the LS reciprocal lattice shows that the system is purely LS. This LS crystal was then photoexcited by a single ns laser pulse of 10 mJ (with a fluence ≈ 2.0 mJ/mm²). The crystal structure obtained after laser excitation is shown in Fig. 5 and the structural parameters indicate that the crystal is in the HS phase, with a structure similar to the one obtained at thermal equilibrium at 310 K in the pure HS phase. The complete conversion from LS to HS phases is characterized by the fact that the x-ray diffraction peaks are located only on the nodes of the HS reciprocal lattice (a_{HS}^* and c_{HS}^*) after photo-excitation. The colour change of the crystal is also similar to the one observed during the complete thermal conversion. The changes of colour and volume of the crystal during the switching from LS to HS phases driven by the ns laser can be directly observed in the supplemental material video.

3.3. Effect of laser energy and temperature

Previous reports indicated a threshold laser excitation energy for generating the spin state switching inside the thermal hysteresis [9-12]. We used different laser energies for trying to generate the HS phase from the completely LS phase at 293 K. Fig. 6 shows that a 1 mJ laser pulse is too weak for switching the system towards the HS state: the sample colour remains the one of the LS phase and the diffraction pattern is only made of LS Bragg peaks. A 5 mJ laser pulse completely switches the crystal to the HS state, as characterized by the change of colour and by the only presence of HS Bragg peaks after a single shot excitation. An intermediate 2.5 mJ laser pulse partially convert the system to the HS phase, as characterized by the partial colour change of the crystal (circle in Fig. 6) and by the coexistence

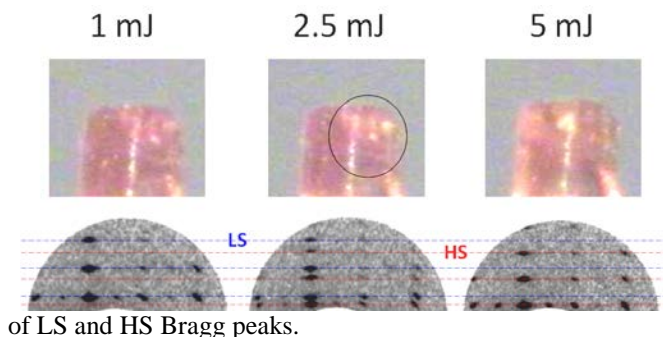


Fig. (6). Change of crystal colour (top), and diffracted intensity on LS and HS reciprocal lattices (bottom) after photoexcitation of the pure LS phase by a single ns laser pulse of 1 mJ, 2.5 mJ and 5 mJ.

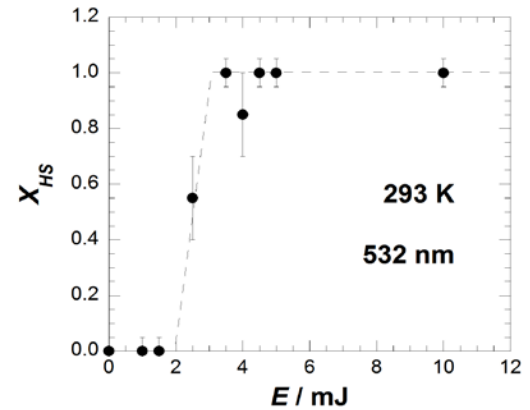


Fig. (7). HS fraction reached after photoexcitation of the pure LS crystal at 293 K for different laser energy.

The ratio of the intensities of LS and HS Bragg peaks gives a rough estimate of a 55% ($\pm 15\%$) conversion to the HS phase for 2.5 mJ. Fig. 7 shows the energy dependence of the conversion rate from pure LS to HS states at 293 K. A marked non-linear response appears with a threshold: we can't detect any conversion to the HS state below 2 mJ. This non-linear response may have several origins. Indeed, it was evidenced in other SCO materials that the energy deposited by a laser pulse drives a complex out-of-equilibrium dynamics. The cooperative transformation of SCO materials may be mediated by elastic coupling during the volume expansion occurring on ns timescale [17]. In addition, the laser pulse warms up the crystal and induces a transient temperature jump on the μs -ms time-scale [13-18]. It takes few 10 ms to reach the initial temperature imposed by the cold nitrogen stream. Time-resolved studies on other isolated SCO single crystals underlined that the thermal effect was dominant [15-19]. Therefore, the observed non linear response may be associated with a laser heating effect inducing the thermal population of the HS state.

In the present study on the consequence of the excitation by a ns laser pulse inside the thermal hysteresis of $\{\text{Fe}^{\text{II}}(\text{pz})[\text{Pt}(\text{CN})_4]\}$, we observe that a single ≈ 3.5 mJ laser pulse corresponds to the threshold value necessary to reach a completely HS phase from the initial LS phase at 293 K. If we assume that this effect results mainly from laser heating, the comparison with Fig. 4 makes it possible to estimate that a single 3.5 mJ laser pulse produces a ≈ 7 K temperature jump, bringing the crystal to 300 K where it is fully HS. We then estimate, by assuming that the temperature jump is proportional to the laser energy, that a 10 mJ pulse, which also induces the full conversion, induces a ≈ 20 K temperature jump. In Fig. 8 we draw a very likely scenario of the spin-state change induced by a laser pulse. A 10 mJ laser excites the crystal in the pure LS phase at 293 K (point A on the ascending branch of the hysteresis). It warms up the crystal transiently up to ≈ 313 K, where the full HS state is reached (point B) within less than 1 ms [13-18]. This is too fast for our standard camera and we could only observe the crystal, with a colour characteristic of the HS state, 20 ms after laser excitation (point C). 60 ms after laser excitation (point D) the crystal reaches again 293 K, but it is now on the descending branch of the hysteresis where it is completely HS and remains stable in this state.

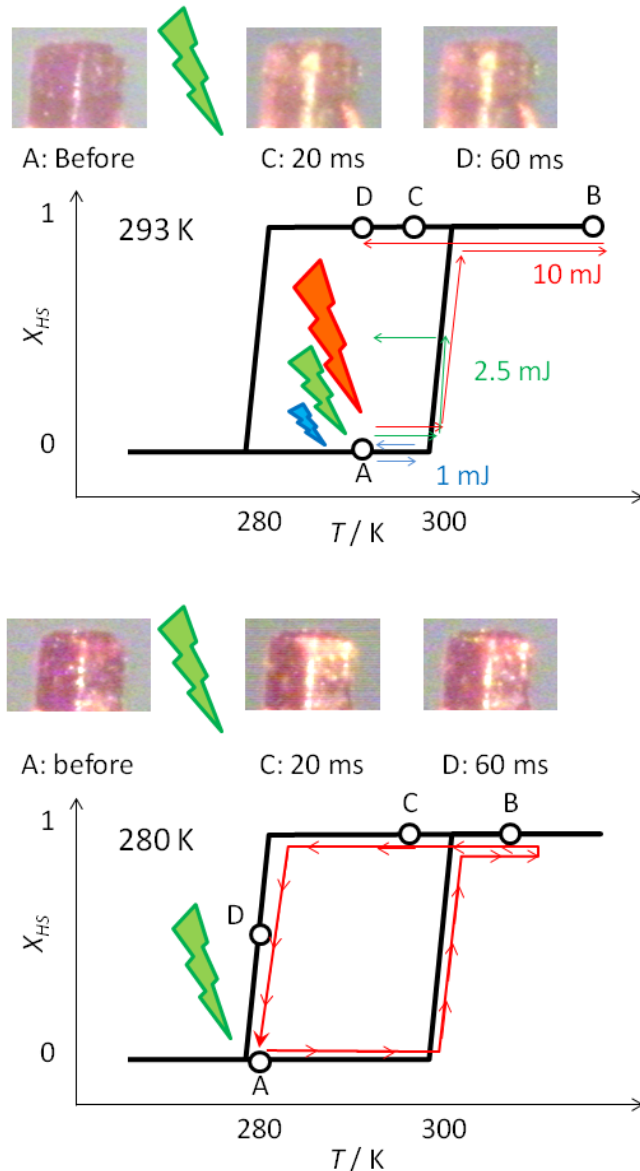


Fig. (8). Change of colour after ns laser excitation at 293 K and 280 K and schematic switching process due to laser heating.

The crystal remains in this HS state later as characterized by x-ray diffraction (Fig. 5). Such a ≈ 20 K temperature jump is consistent with other estimates obtained by time-resolved techniques on other SCO materials [13-18]. In addition, a transient temperature jump due to heating by a ns laser was also reported outside the thermal hysteresis in a similar material by time-resolved electron diffraction studies [36].

Again, by assuming a temperature jump proportional to light excitation energy, we can estimate that a 2.5 mJ laser pulse induces a ≈ 5 K temperature jump. This will bring transiently the system to a temperature close to $T_{1/2\uparrow} \approx 298$ K. The crystal is then on the ascending branch of the hysteresis but the conversion to the HS state is only partial. HS domains form and remain when the crystal cools down to 293 K inside the hysteresis (Fig. 8). In the same way, a 1 mJ laser pulse induces only a 2 K temperature jump, which only

brings the crystal to ≈ 295 K, where it remains fully LS. Consequently it cannot populate thermally HS domains.

In order to confirm this ≈ 20 K temperature jump with a 10 mJ excitation, we performed other experiments from the pure LS state for different initial temperatures inside the hysteresis down to 284 K. The HS phase was always completely reached and remained stable. At 280 K (Fig. 8), the excitation by a the 10 mJ laser pulse (from the pure LS phase, point A) warms the crystal above ≈ 300 K (point B) where the system reaches a mainly HS state, as characterized by the crystal colour (point C). After 60 ms (point D), the crystal reaches again 280 K and the colour indicates a mixing of HS and LS phases, as expected on the descending branch of the hysteresis. This slow process corresponds well to the typical timescale for the recovery to thermal equilibrium of the crystal with the cryostat.

CONCLUSION

We have investigated the spin-state switching induced by a single ns laser excitation inside the thermal hysteresis of $[\text{Fe}^{\text{II}}(\text{pz})\text{Pt}(\text{CN})_4]$. Combined x-ray diffraction and optical microscopy demonstrate the possibility to generate a complete switching from LS to HS state when the energy of a single laser pulse is high enough. Around the threshold energy value, the conversion is partial and HS domains form. Below the threshold value the system remains in the LS state. In the framework of previous time-resolved studies, the spin-state switching and the non-linear response to laser energy inside the hysteresis are very likely due to a transient temperature jump (of the order of 20 K) moving the system on the thermal hysteresis. The temperature jump induced by laser heating plays an important role in the switching process, as observed in other isolated SCO single crystals [19]. However, some cooperative elastic effects mediated by lattice expansion [16] can also play their role in the process and recent calorimetric studies suggest that the photoinduced phenomena cannot be explained by considering solely thermal effect [37]. Future time-resolved x-ray measurements may help to understand better the relative weight of elastic and thermal effects because the intrinsic timescales of volume expansion (ns) and thermal HS population (μs) are significantly different [13-17].

CONFLICT OF INTEREST

The authors declare no competing financial interests.

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LPL and JAR synthesized the crystals. EC, LH and LT performed the x-ray diffraction and microscopy studies and

analyzed the data. The manuscript was written by EC and JAR. All the authors have given approval to the final version of the manuscript.

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SUPPLEMENTARY MATERIAL

The supplementary material contains a video showing the change of colour and volume of the crystal during the switching from LS to HS phases driven by the ns laser.

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