



**HAL**  
open science

## Room temperature study of the optical switching of a spin crossover compound inside its thermal hysteresis loop

G. Gallé, D. Deldicque, Jérôme Degert, Thibaut Forestier, Jean-François Létard, Eric Freysz

► **To cite this version:**

G. Gallé, D. Deldicque, Jérôme Degert, Thibaut Forestier, Jean-François Létard, et al.. Room temperature study of the optical switching of a spin crossover compound inside its thermal hysteresis loop. Applied Physics Letters, 2010, 96 (4), pp.041907. 10.1063/1.3294312 . hal-00466328

**HAL Id: hal-00466328**

**<https://hal.science/hal-00466328>**

Submitted on 8 Mar 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Room temperature study of the optical switching of a spin crossover compound inside its thermal hysteresis loop

G. Gallé,<sup>1</sup> D. Deldicque,<sup>1</sup> J. Degert,<sup>1</sup> Th. Forestier,<sup>2</sup> J.-F. Létard,<sup>2</sup> and E. Freysz<sup>1,a)</sup>

<sup>1</sup>CPMOH, Université Bordeaux, UMR CNRS 5798, 351 Cours de la Libération, 33405 Talence, Cedex, France

<sup>2</sup>ICMCB, Université Bordeaux, UPR CNRS 9048, 87 Avenue du Docteur Albert Schweitzer, 33608 Pessac, Cedex, France

(Received 20 October 2009; accepted 26 December 2009; published online 27 January 2010)

We have studied the low-spin to high spin state phase transition induced by a single or a sequence of nanosecond laser pulses within the thermal hysteresis loop of the  $[\text{Fe}(\text{NH}_2\text{-trz})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  spin crossover compound. We demonstrate that the final state that is photoinduced can be finely controlled by changing the central wavelength and the energy of the laser pulses. A simple model accounts for the observed phenomena and paves the way for the practical applications to optical data storage at room temperature of spin state transition compounds. © 2010 American Institute of Physics. [doi:10.1063/1.3294312]

The bistable nature of spin crossover (SCO) molecular materials coupled to their very high sensitivity to light stimuli is of particular interest for the development of data recording media.<sup>1-4</sup> At very low temperature, typically below 70 K, Light-induced excited spin state trapping (LIESST) and reverse LIESST effects make it possible to record and to erase optical information in these compounds.<sup>5,6</sup> To extend the use of these materials, many work are currently performed to identify the key factors that could stabilize, around room temperature, the metastable states that are photoinduced.<sup>7,8</sup> Parallel to that, some years ago, we have proposed to take advantage of the meta-stability of the high spin (HS) and low spin (LS) states in the thermal hysteresis loop<sup>9</sup> that occur in many different SCO compounds around room temperature.<sup>1,2,4</sup> Indeed, within the hysteresis loop, the laser-induced phase transition makes possible to switch back and forth the system between its two metastable states. Such an optically induced phase transition has been first recorded at low temperature.<sup>10</sup> More recently some examples of compounds working at room temperature have been reported.<sup>11</sup> All of them were excited using single laser pulses delivered by frequency doubled Q-switched Nd:YAG laser.<sup>12</sup> Practical applications require first to synthesize spin state compounds with a larger hysteresis loop around room temperature and second to master the final state of the system that is photoinduced upon laser excitation. Practically this will be possible if one understands and controls the physical mechanisms responsible for the laser induced phase transition in such compounds. Very recently, with this goal in mind, different groups have developed pump-probe time resolved optical experiments.<sup>12,13</sup> These experiments, performed using a single laser pulse, were realized either outside the hysteresis loop of an SCO system<sup>12</sup> or with a compound that does not have a hysteresis loop.<sup>13</sup> They indicate that the absorption of the laser pulse by the compound induces a large local heating of the sample. However, the impact of laser-induced heating within the hysteresis loop has never been truly investigated and reported for such compounds. Such a study is of particular interest, since it has been shown that a sample that is

photoexcited within its thermal hysteresis loop is set in a state where molecules coexist in their HS and LS states.<sup>9</sup> Accordingly and considering that the laser-induced thermal heating is partly responsible for the recorded phenomena, one can ask, for instance, whether another laser pulse may further change the HS/LS molecular ratio of the sample. Similarly, by tuning the wavelength of the laser pulse toward the absorption bands of the low-spin or the high spin species, one may also expect to directly impact the final HS/LS molecular ratio.<sup>14</sup> Finally, it is interesting to notice that, within the hysteresis loop, one has a permanent signature of the HS state that is reached during the thermal evolution of the photoexcited LS sample within its temperature-HS fraction ( $T, \gamma_{\text{HS}}$ ) phase diagram. With that respect, such an experiment, will directly confirm the scheme we recently proposed to describe the evolution of a photoexcited LS SCO compound in its ( $T, \gamma_{\text{HS}}$ ) phase diagram.<sup>15</sup>

Hereafter, we report on the optical study of the SCO complex  $[\text{Fe}(\text{NH}_2\text{-trz})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  coordination polymer ( $\text{NH}_2\text{-trz}=4\text{-amino-1,2,4-triazole}$ ) known to display a well-defined thermal hysteresis loop centered at room temperature.<sup>16,17</sup> We demonstrate that one can measure very simply the impact of the energy, the central wavelength and the number of nanosecond laser pulses on this SCO compound. Our data clearly indicate that these parameters make it possible to finely control the equilibrium photoinduced state of the system within its thermal hysteresis loop. A simple model accounts for the observed phenomena. It underlines that such compounds are good candidates for optical data recording at room temperature.

The sample studied is constituted of micro crystallites a few microns in diameter. It is sandwiched between two optical windows that are placed into a thermally regulated oven. The color of the powder, which is pink when the sample is in the LS state, becomes almost white when the sample is heated and brought in the HS state (Fig. 1). Indeed in the LS state this material displays a broad absorption band at around  $\lambda=520$  nm, which is characteristic of the d-d transition of  $\text{Fe}^{2+}$  ( ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ ), while in the HS state a d-d-transition is recorded at lower energy in the near infrared region (i.e.,  $\lambda=830$  nm). To characterize the phase transition

<sup>a)</sup>Electronic mail: e.freysz@cpmoh.u-bordeaux.fr.

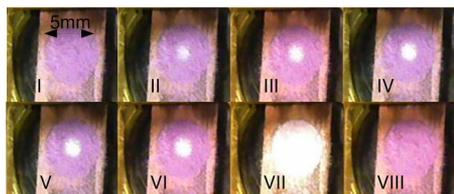


FIG. 1. (Color online) I-VII: color of the sample in its LS state (I), HS state (VII), when the sample initially in its LS state within the hysteresis loop is excited at 355 nm by either a single (II), two (III), three (IV), four (V) and five (VI) nanosecond laser pulses. Fig. 1(VIII) shows the sample brought back in the LS state after photoexcitation.

between the HS and the LS state, a halogen lamp is used to record the spectrum reflected by the sample versus its temperature. For that purpose, the specular light reflected by the compound is focused by a lens and sent through an optical fiber that is connected to a compact spectrometer. This latter records the reflected spectrum between 400 and 900 nm. The Q-switched Nd:YAG laser used to excite the sample is a Minilite II provided by Continuum. It delivers  $\sim 6$  ns laser pulses that have a maximum energy of  $\sim 60$  mJ,  $\sim 30$  mJ, and  $\sim 10$  mJ at respectively  $\lambda = 1064$  nm,  $\lambda = 532$  nm, and  $\lambda = 355$  nm. The pulses were slightly focused on the sample using a lens. Figure 1 I-VIII shows the evolution of the sample impacted by a sequence of pulses centered at  $\lambda = 355$  nm. The laser fluence on the sample is  $E_p \sim 52$  mJ cm $^{-2}$ . The same experiment has also been performed exciting the sample using laser pulses centered at  $\lambda = 532$  nm with the same laser fluence. For both laser wavelengths (i.e.,  $\lambda = 355$  and 532 nm), we noticed that the spot of the sample excited by the laser pulse becomes whiter and remains in this state as long as the temperature of the sample is kept within the thermal hysteresis loop. Moreover, the whole sample recovers its original pink color when it is cooled down to 320 K (i.e., in the LS state) [see Fig. 1(VIII)]. One can therefore discard any laser induced irreversible change of the sample. This also indicates that within the hysteresis loop, micro-crystallites impacted by the laser pulses are partly brought in the HS state. The state of the compound that is photoinduced is more clearly revealed by recording the spectrum reflected by the sample after each laser shot. The associated normalized reflectivity changes are presented in Fig. 2(a). The reflectivity normalization proceeds as follow. The signals recorded by the spectrometer for the sample in the HS, LS states and after each laser shot, labeled S(HS), S(LS), and S, respectively, were stored. The normalized reflectivity presented in Fig. 2(a) is obtained by computing  $[S - S(LS)] / [S(HS) - S(LS)] \times 100$ . It is equal to 100% (respectively 0%) if the sample is in the HS (respectively, LS) state. The more important noise recorded in Fig. 2(a) at the edge of the spectrum is due to the smaller spectral density of the flash light in the UV spectral range and to the smaller sensitivity of the spectrometer at these wavelengths.

All these measurements were performed at different temperatures. The results are summarized in the Fig. 2(b). On this figure, we have reported the normalized reflectivity changes recorded at  $\lambda = 550$  nm. On Figs. 2(a) and 2(b), one can notice that after the fifth laser pulse, the HS fraction remains almost unchanged. Let-us also stress that the final state depends largely on the initial temperature of the sample. Moreover, one should also notice that for pulses centered at  $\lambda = 355$  nm under our experimental conditions and whatever

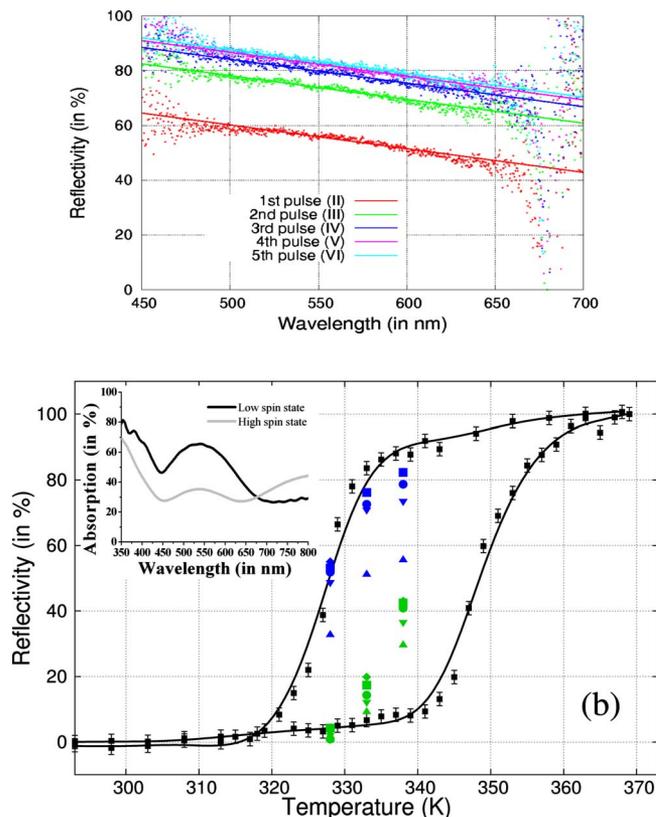


FIG. 2. (Color online) (a) Normalized spectral changes of the sample reflectivity recorded after successive laser shots. The reflectivity changes have been normalized as explained in the text. (b) (■) Thermal hysteresis loop deduced from the evolution of the sample reflectivity at 550 nm vs the temperature. The sample, set at a temperature of 328, 333, and 338 K, respectively, is excited by one ( $\Delta$ ), two ( $\nabla$ ), three ( $\circ$ ), four ( $\square$ ), and five ( $\diamond$ ) nanosecond pulses centered at  $\lambda = 355$  nm (in grey) and  $\lambda = 532$  nm (in black). The laser fluence on the sample is  $\sim 52$  mJ cm $^{-2}$  in both cases. The inset presents the absorption of the compound in the HS and LS states vs the wavelength.

the temperature, we were able to achieve an almost complete conversion from the LS to the HS state. This behavior is directly related to the higher absorption of the compound in this spectral range [See inset of Fig. 2(b)]. As expected a higher absorption of the compound induces a higher heating of the sample, resulting in an increase of the HS molecular fraction and therefore in an increase of the reflectivity of the sample. In conclusion, our results confirm that within the thermal hysteresis loop, the use of optical stimuli allows to store optical information in these compounds. We have also performed similar measurements at lower laser fluence. The most important results are first that within the hysteresis loop there is a critical laser fluence below which the sample remains unchanged and second that this critical fluence strongly depends on the central wavelength of the laser pulses.

Let us discuss the different mechanisms responsible for the recorded phenomenon. At first, the metastability of the photoinduced HS state indicates that the sample experiences a first order phase transition. Figure 3 describes the path followed by the compound after each pulse excitation within its ( $T$ ,  $\gamma_{HS}$ ) phase diagram. For a similar compound, we have previously shown that the laser pulse is absorbed within a thin layer of the particles (1–400 nm).<sup>15</sup> This absorption heats the particles which temperature rises up very quickly

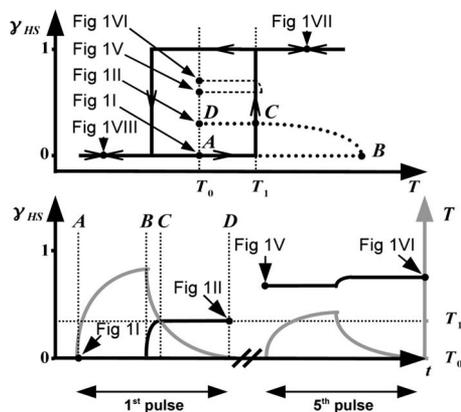


FIG. 3. Top: Path followed by the sample in the Temperature—high spin state Fraction phase diagram, after excitation by the first and the fifth laser pulse. Bottom: Evolution of the temperature (gray line) and the HS fraction (black line) of the sample after the first (dotted line) and the fifth (dashed line) laser shot.

above the thermal hysteresis loop.<sup>15</sup> Consequently, the sample is thermally quenched toward the point B of the phase diagram (step A→B in Fig. 3). This latter process lasts about 100 ns. Then, two phenomena take place. First, since at the point B of the phase diagram, the molecules in LS state are thermodynamically unstable, the HS molecular fraction increases within the particles. Second, as time goes on, the sample cools down. Consequently, the path of the sample within its phase diagram takes into account both phenomena (step B→C in Fig. 3). We have shown that this process lasts about 10  $\mu$ s.<sup>15</sup> Then as the sample further cools down, its temperature reaches the ascending branch of the hysteresis loop. At this point of the phase diagram, no more molecules are converted from the LS to the HS state and the system reaches a status where the molecules are either in the LS or the HS state. Both states then coexist within the sample. Finally, as the temperature of the particles further decreases, the powder relaxes toward its equilibrium temperature (step C→D in Fig. 3). This latter process lasts about 100  $\mu$ s.<sup>15</sup> Now, it is important to notice that, as the HS molecular fraction increases, the overall absorption of the sample decreases at the wavelengths used to photoexcite the sample (Fig. 2). Hence, the subsequent laser pulses exciting the sample is less absorbed and the particles are less heated. As a result, the growth of the HS-domains lasts lesser time and the increase of the HS-fraction is lesser. As a consequence, after a sequence of few laser pulses, the sample reaches a state that is, in its phase diagram, located either on or within the thermal hysteresis loop [see Fig. 2(b)]. In this latter case, one can further improve the LS to HS conversion efficiency by increasing the pulse laser energy. The process that we described accounts well for the existence of critical laser fluence. Indeed, the growth of the HS fraction takes place only if the temperature of the sample is brought above its thermal hysteresis loop. This quenching temperature mainly depends on the initial temperature of the sample, its absorption coefficient at the used laser wavelength and the laser fluence. Finally our model also accounts for the evolu-

tion of the reflectivity change versus the wavelength. As we already mentioned, only a thin layer of the particles absorbs the laser light. After the laser excitation, the heat deposited at the surface of the particles diffuses toward their centers. In consequence, the surface of the particles is brought at a higher temperature and the growth of HS domain last longer at the surface compare to the bulk. Now since the smaller wavelengths have a lower penetration depth in such compounds,<sup>18</sup> they are probing a volume of the particle where the HS fraction is the larger. Therefore in agreement with Fig. 2(a), one expects to have a higher reflectivity change at the lower wavelengths.

In conclusion, we have presented experimental results and a scenario that demonstrate and describe the mechanism for optical switching of SCO-compounds within their thermal hysteresis loop. We have shown how, within the hysteresis loop of such compounds, a sequence of nanosecond laser pulses can improve the LS to HS conversion efficiency. These results indicate that these SCO compounds offer many interesting prospects for optical data recording.

The authors acknowledge support through ANR (ANR-09-BLAN-0212-03) via the project ULTIMATE, Région Aquitaine via the project COMMODORE and GIS Matériaux via the project COMET. G.G. thanks CNRS and Région Aquitaine for financial support.

<sup>1</sup>*Spin Crossover in Transition Metal Compounds I-III*, Topics in Current Chemistry, edited by P. Gülich and H. A. Goodwin (Springer, New York, 2004), Vol. 233–235.

<sup>2</sup>O. Kahn and C. Jay Martinez, *Science* **279**, 44 (1998).

<sup>3</sup>P. Gülich, Y. Garcia, and T. Woiike, *Coord. Chem. Rev.* **219**, 839 (2001).

<sup>4</sup>J.-F. Létard, P. Guionneau, and L. Goux-Capes *Topics in Current Chemistry*, Eds. P. Gülich and H.A. Goodwin (Springer, New York, 2004), Vol. 235, p. 221.

<sup>5</sup>S. Decurtins, P. Gülich, C. P. Köher, H. Spiering, and A. Hauser, *Chem. Phys. Lett.* **105**, 1 (1984).

<sup>6</sup>A. Hauser, *Chem. Phys. Lett.* **124**, 543 (1986).

<sup>7</sup>J.-F. Létard, P. Guionneau, O. Nguyen, J. S. Costa, S. Marcen, G. Chastanet, M. Marchivie, and L. Goux-Capes, *Chemistry* **11**, 4582 (2005).

<sup>8</sup>J.-F. Létard, *J. Mater. Chem.* **16**, 2550 (2006).

<sup>9</sup>E. Freysz, S. Montant, S. Létard, and J.-F. Létard, *Chem. Phys. Lett.* **394**, 318 (2004).

<sup>10</sup>A. Hauser, R. Hinek, H. Spiering, and P. Gülich, *Chemistry* **2**, 1435 (2006).

<sup>11</sup>S. Bonhommeau, G. Molnár, A. Galet, A. Zwick, J.-A. Real, J. J. McGarvey, and A. Bousseksou, *Angew. Chem., Int. Ed.* **44**, 4096 (2005).

<sup>12</sup>O. Fouché, J. Degert, G. Jonusauskas, C. Baldé, C. Desplanche, J.-F. Létard, and E. Freysz, *Chem. Phys. Lett.* **469**, 274 (2009).

<sup>13</sup>M. Lorenc, J. Hebert, N. Moisan, E. Trzop, M. Servol, M. Buron-Le Cointe, H. Cailleau, M.-L. Boillot, E. Pontecorvo, W. Wulff, S. Koshihara, and E. Collet, *Phys. Rev. Lett.* **103**, 028301 (2009).

<sup>14</sup>A. Hauser, *J. Chem. Phys.* **94**, 2741 (1991).

<sup>15</sup>O. Fouché, J. Degert, G. Jonusauskas, N. Daro, J.-F. Létard, and E. Freysz, *Phys. Chem. Chem. Phys.* (unpublished).

<sup>16</sup>L. G. Lavrenova, V. N. Ikorskii, V. A. Varnek, I. M. Oglezneva, and S. V. Larionov, *Koord. Khim.* **12**, 207 (1986).

<sup>17</sup>In agreement with thermogravimetric experiments, the elemental analysis performed on the powder is consistent with the presence of one molecule of water. Anal. Calculated [Fe(NH<sub>2</sub>-trz)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·1H<sub>2</sub>O: C, 16.01; H, 3.14; N, 43.57; Fe, 12.41; Found: C, 16.13; H, 2.94; N, 43.80; Fe, 12.07.

<sup>18</sup>E. D. Loutete-Danguy, F. Varret, E. Codjovi, P. R. Dahoo, H. Tokoro, S. Ohkoshi, C. Eypert, J.-F. Létard, J. M. Coanga, and K. Boukheddaden, *Phys. Rev. B* **75**, 184425 (2007).