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# Rubidium Manganese Hexacyanoferrate Solid Solutions: Towards Hidden Phases

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**Abstract.** The search for hidden phase using photo-induced phase transition is an important challenge in multistable materials. In this work we report the study of Prussian blue analogs  $\text{Rb}_x\text{Mn}[\text{Fe}(\text{CN})_6]_{(x+2)/3} \cdot z\text{H}_2\text{O}$  solid solutions. For composition of  $\text{Rb}^+$  above 65 %, a thermal hysteresis loop is observed as a reflect of the electron-transfer phase transition from  $\text{Mn}^{\text{II}}$  ( $S=5/2$ )-NC- $\text{Fe}^{\text{III}}$  ( $S=1/2$ ) at high temperature (HT phase) to  $\text{Mn}^{\text{III}}$  ( $S=2$ )-NC- $\text{Fe}^{\text{II}}$  ( $S=0$ ) at low temperature (LT phase). At low temperature the HT phase can be thermally quenched up to the  $T(\text{TIESST})$  temperature (TIESST = Thermally-Induced Excited Spin-State Trapping) above which it relaxes back to the LT phase. Upon the decrease of  $\text{Rb}^+$  amount, the thermal hysteresis and the  $T(\text{TIESST})$  are getting closer and overlap for values of  $x$  below 65 %. For the latter compounds, the phase transition is inhibited and the hysteresis loop is hidden. By this simple consideration we explain the observation of Light-Induced Phase Collapse already reported giving also some trends to obtain new hidden phases.

**Keywords:** Photomagnetism, hidden phase, Prussian Blue Analogs, phase transition.

## 1. INTRODUCTION

Photo-induced phase transition (PIPT) in molecular materials could be observed in spin-crossover (SCO) or intramolecular electron transfer (ET) systems. In most cases the PIPT phenomenon is reported in materials that also undergo a thermal phase transition. In molecular magnetic materials based on spin-crossover or electron transfer, three ways of switching the magnetic properties by light irradiation were mainly reported. One way named *LD-LISC* (Ligand-Driven Light-Induced Spin Change)[1] consists in using the reversible photo-isomerization of the ligand so as to affect the ligand-field strength and then the iron(II) spin state. The phenomenon is operative at room temperature but can suffer from the large structural reorganization induced by the ligand change in solid state. A second possibility of inducing a photo-conversion of spin state was based on pulsed irradiation within the thermal hysteresis range of cooperative materials.[2] This phenomenon, based on photo-thermal effect due to an energetic pulse irradiation, opened the way of room temperature information storage by light. However industrial application requires large hysteresis loop which are not yet available. The third possibility is the Light-Induced Excited Spin State Trapping (LIESST)[3] that is operant at low temperature. This phenomenon reported for spin-crossover compound has been widely studied to understand and control the chemical parameters that stabilize the photo-induced metastable state.[4-6] For example, the

temperature range of observation of the photo-induced metastable state has been estimated through a  $T(\text{LIESST})$  measurements. The  $T(\text{LIESST})$  value characterizes the temperature at which the thermal decay of the photo-excited metastable state occurs when the system (initially saturated in the metastable state) is heated in a monotonous way at a constant temperature scan rate, usually 0.3 K/min. Based on this approach, a large number of SCO materials have been compared and an inverse  $T(\text{LIESST})$  relationship to the thermal spin-transition temperature ( $T_{1/2}$ ) has been evidenced.[6] in agreement with the Hauser's inverse energy gap law.[4] A detailed analysis of this relationship allowed the identification of crucial chemical parameters for increasing the  $T(\text{LIESST})$  values, from 60 K in the late 90's to 130 K for pure iron(II) SCO materials,[7] and even 150 K in Prussian Blue analogues[8]. The highest value found up to now for a molecular cluster with electron transfer is about 180 K.[9]

In such studies to increase the  $T(\text{LIESST})$  value toward high temperature a particular case was recently investigated concerning the meeting of the spin-crossover with the  $T(\text{LIESST})$  curve, as function of the cooperativity.[10-11] This overlap is particularly interesting for cooperative materials where a change of regime occurs when  $T(\text{LIESST})$  enters within the hysteresis loop. This can lead to the disappearance of the spin crossover to end up with materials in their high temperature phase. These studies shed some light on the possibility to observe hidden phases in such systems.

From previous works on Prussian blue derivative, it has been shown that such materials seem to follow the same

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trends than the SCO compounds.[12] For example, the RbMnFe hexacyano based materials exhibit an electron-transfer phase transition from Mn<sup>II</sup> ( $S=5/2$ )-NC-Fe<sup>III</sup> ( $S=1/2$ ) at high temperature (HT phase) to Mn<sup>III</sup> ( $S=2$ )-NC-Fe<sup>II</sup> ( $S=0$ ) at low temperature (LT phase).[13] This transition is accompanied by a structural change from cubic to tetragonal structure due to the Jahn-teller distortion on Mn<sup>III</sup> in the LT phase. This LT phase exhibits ferromagnetic order while the HT phase is antiferromagnetic. By changing the composition, the number of interstitial Rb<sup>+</sup> cation affects the number of Fe(CN)<sub>6</sub><sup>3-</sup> vacancies and therefore tune the ligand field around the Mn ion. In the Rb<sub>0.88</sub>Mn[Fe(CN)<sub>6</sub>]<sub>0.96</sub>·0.5 H<sub>2</sub>O compound, the ferromagnetic LT phase can be switched to the antiferromagnetic HT phase by a green light irradiation at low temperature.[14] This process was shown to be reversible using a blue light irradiation. In addition, within the hysteresis loop, the LT to HT phase transition can be also photo-induced using a pulsed shot of green light.[15] Finally, on Rb<sub>0.43</sub>Mn[Fe(CN)<sub>6</sub>]<sub>0.81</sub>·3H<sub>2</sub>O derivative, the presence of hidden magnetic phase was evidenced.[16]

Therefore, this family of Rb<sub>x</sub>Mn[Fe(CN)<sub>6</sub>]<sub>(x+2)/3</sub>·zH<sub>2</sub>O materials has interesting properties we wanted to rationalize by a study of the evolution of the thermo- and photo-induced phase transition as function of the composition. We present in this paper the behavior of 8 compounds with x varying from 1 to 0.43.

## 2. MATERIALS AND METHOD

The samples were prepared by reacting an aqueous solution (0.1 mol dm<sup>-3</sup>) of MnCl<sub>2</sub> with a mixed aqueous solution of RbCl (0.05 – 1.2 mol dm<sup>-3</sup>) and K<sub>3</sub>[Fe(CN)<sub>6</sub>] (0.1 mol dm<sup>-3</sup>) to yield precipitates.[11] The formulas of the compounds were confirmed by inductively coupled plasma mass spectrometry and a standard microanalytical method. The composition was controlled by the concentration of the RbCl aqueous solution and the resulting compositions are listed in table 1.

**Table 1. Composition of compounds 1-8 with the corresponding phase transition temperatures.**

composition	n°	T <sub>1/2</sub> (↑) [K]	T <sub>1/2</sub> (↓) [K]	ΔT [K]	T(TIESST) [K]
RbMn[Fe(CN) <sub>6</sub> ] <sup>a</sup>	1	300	225	75	
Rb <sub>0.94</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.98</sub> ·0.2H <sub>2</sub> O	2	298	234	64	120
Rb <sub>0.88</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.96</sub> ·0.6H <sub>2</sub> O	3	292	220	72	122
Rb <sub>0.82</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.94</sub> ·1.1H <sub>2</sub> O	4	278	208	70	125
Rb <sub>0.76</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.92</sub> ·1.2H <sub>2</sub> O	5	280	204	76	127
Rb <sub>0.73</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.91</sub> ·1.5H <sub>2</sub> O	6	261	174	87	150
Rb <sub>0.61</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.87</sub> ·2.2H <sub>2</sub> O	7	-	-	-	-
Rb <sub>0.43</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.81</sub> ·3H <sub>2</sub> O <sup>b</sup>	8	-	-	-	-

<sup>a</sup> from [14], <sup>b</sup> from [16]

## EXPERIMENTAL:

Magnetic susceptibilities were measured in the 5-300 K temperature range, under an applied magnetic field of 1T, using a MPMS5 SQUID magnetometer (Quantum Device). The samples were precisely weighted and corrections were applied to account for the compound and sample holder diamagnetic contributions. The thermally-induced excited spin-state trapping was obtained by fast cooling of the sample from room temperature to 10 K within the SQUID cavity. Strictly speaking this is not a thermal quenching from room temperature to 10 K within a second but rather a fast cooling that deserves few minutes to cool the sample down and get a stable temperature. After thermal stabilization, the temperature was increased at a rate of 0.3 K/min and the magnetisation measured every 1 K to determine the T(TIESST) value given by the minimum of the  $d\chi_M T / dT$  vs T curve for the relaxation.[5,6]

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis

Rubidium manganese hexacyanoferrates Rb<sub>x</sub>Mn[Fe(CN)<sub>6</sub>]<sub>(x+2)/3</sub>·zH<sub>2</sub>O were prepared by reacting an aqueous solution of MnCl<sub>2</sub> with a mixed aqueous solution of RbCl in appropriate proportion and K<sub>3</sub>[Fe(CN)<sub>6</sub>] to yield a light brown precipitates that were filtered and dried.

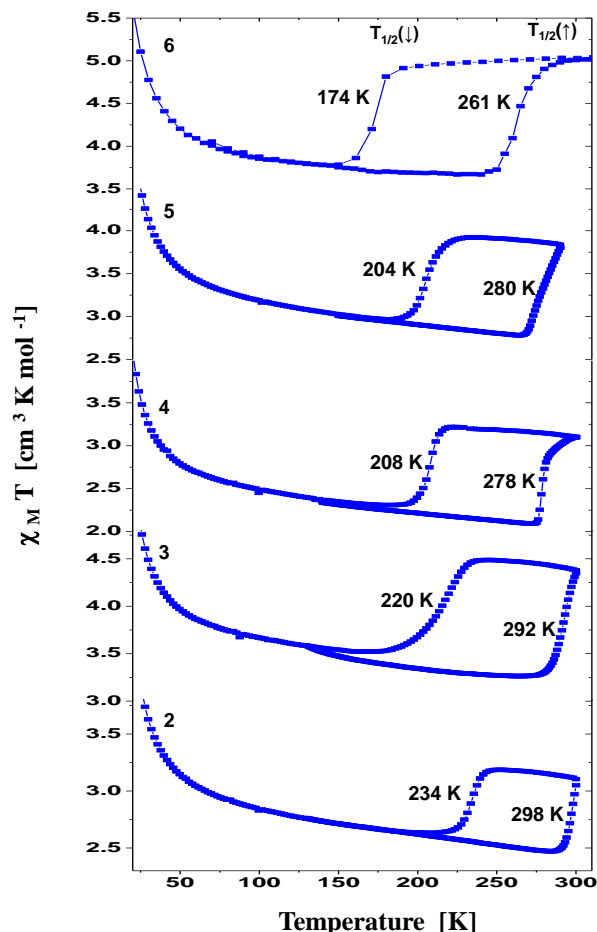


Figure 1. Thermal dependence of the magnetic susceptibility  $\chi_M$  times the temperature of compounds 2-6.

### 3.2. Temperature-induced phase transition

Figure 1 presents the product of the molar magnetic susceptibility ( $\chi_M$ ) and the temperature ( $T$ ) versus the temperature ( $T$ ) behaviors of compounds **2-6**. At high temperature, the compounds are in the HT phase made of  $\text{Mn}^{\text{II}}$  ( $S=5/2$ ) and  $\text{Fe}^{\text{III}}$  ( $S=1/2$ ). Decreasing the temperature induces a phase transition towards LT phase constituted of  $\text{Mn}^{\text{III}}$  ( $S=2$ ) and  $\text{Fe}^{\text{II}}$  ( $S=0$ ) due to the electron transfer. After this phase transition the  $\chi_M T$  product increases due to the presence of ferromagnetic ordering in the materials.[13-16] On warming, the HT phase is recovered at a higher temperature than the HT to LT transition, giving rise to a large hysteresis loop.

From **2** to **6**, figure 1 also shows that the hysteresis loops is slightly shifted to low temperature while its width is increasing from 75 K in the pure  $\text{RbMn}[\text{Fe}(\text{CN})_6]$  compound to 87 K in **6**. Table 1 reports the transitions temperature as well as the hysteresis width. The shift in temperature agrees with the decrease number of interstitial  $\text{Rb}^+$  cation which increases the number of  $\text{Fe}(\text{CN})_6^{3-}$  vacancies and therefore weakens the ligand field around the Mn ion. This tunes the energy difference between the LT and HT phases.

### 3.3. Thermal quenching

The life-time of the metastable state in Prussian Blue Analogs was investigated in several compounds[17]. In such systems, the ferromagnetic LT phase can be switched to the antiferromagnetic HT phase by a green light irradiation at low temperature. This process has been shown to be reversible using a blue light irradiation. Moreover, within the hysteresis loop, the LT to HT phase transition can be also photo-induced using a pulsed shot of green light. [14] In such systems, the antiferromagnetic HT phase reached by light irradiation is a metastable state that relaxes back to the LT phase above a temperature equivalent to the  $T(\text{LIESST})$  temperature recorded in spin-crossover compounds.[3,4] This metastable state can also be reached by thermal quenching of the material at low temperature. Figure 2 reports the thermal quenching of the HT phase. For all compounds, the  $\chi_M T$  value of the quenched phase is lower than the  $\chi_M T$  value of the LT phase due to the antiferromagnetic exchange. Upon warming at a given scan rate of 0.3 K/min, the  $\chi_M T$  increases to reach a maximum above 100 K. This is typical of the antiferromagnetic exchange that is overcome by the temperature like in binuclear compounds[18]. Above this temperature the quenched HT phase relaxes back to the LT phase. Since the LT ferromagnetic phase as a lower magnetic response,  $\chi_M T$  decreases. An estimation of the relaxation temperature is given by the minimum of derivative of the curve as for spin-crossover compounds.[3,4] This  $T(\text{TIESST})$  temperature (TIESST = Thermally-Induced Excited Spin-State Trapping) slightly increases from **1** to **6** (table 1).

Few relaxation kinetics of the metastable state were recorded. The sigmoidal character of the relaxation curves due to cooperativity was observed. To understand the origin of the increase of the hysteresis width from **1** to **6** a detailed analysis of the relaxations is needed. This study goes beyond the main message of this article.

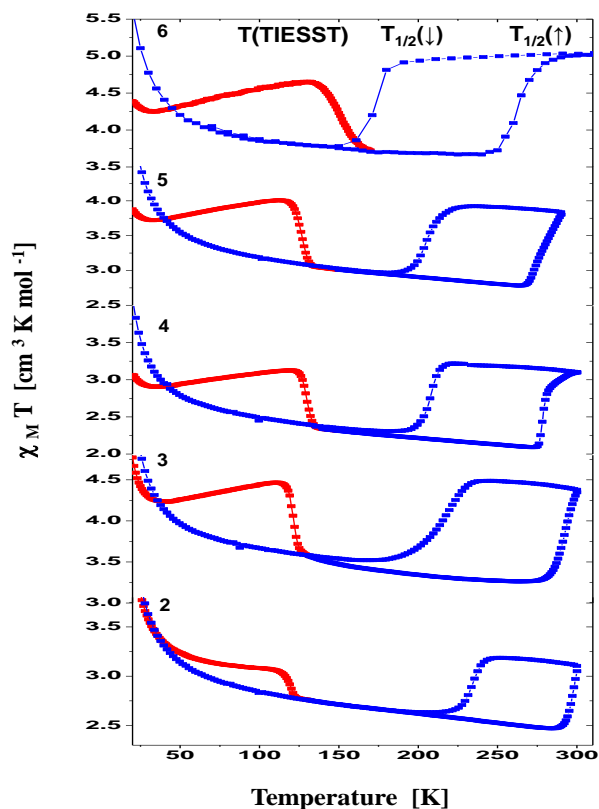


Figure 2. Thermal dependence of the magnetic susceptibility  $\chi_M$  times the temperature of compounds **2-6** before thermal quenching (blue) and after thermal quenching (red).

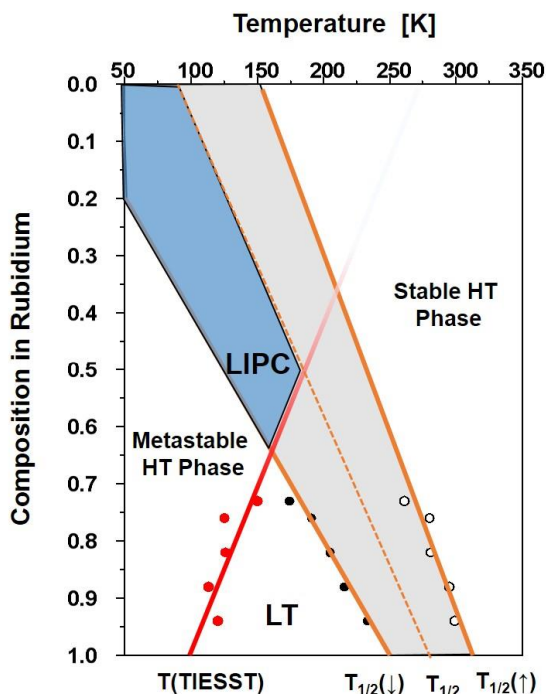


Figure 3. "Phase diagram" of switching temperatures  $T_{1/2}(\downarrow)$ ,  $T_{1/2}(\uparrow)$  and  $T(\text{TIESST})$  as function of the composition parameter  $x$ . The straight lines are eye-guide to show the meeting between  $T(\text{TIESST})$  and the thermal hysteresis. The blue area is related to the Light-Induced Phase Collapse as discussed in the text.

### 3.4. “Phase diagram”

Fig 3 reports the reverse plot of the switching temperatures  $T_{1/2}(\downarrow)$ ,  $T_{1/2}(\uparrow)$  and  $T(TIESST)$  as function of the composition parameter  $x$ . Since the  $T(TIESST)$  is influenced by the dynamic of the measurement due to the metastable state involved in its observation, the same temperature scan rate was used for all the  $T(TIESST)$  curves. The values reported are those collected in table 1. While the thermal hysteresis is shifted toward low temperature, the  $T(TIESST)$  increases to get closer to the thermal hysteresis upon  $x$  decreasing. If one considers a linear evolution for  $T(TIESST)$ ,  $T_{1/2}(\downarrow)$  and  $T_{1/2}(\uparrow)$  the  $T(TIESST)$  and  $T_{1/2}(\downarrow)$  are crossing each other below 70 % of rubidium. This implies that materials with  $Rb^I$  compositions  $x$  smaller than 0.7 should not exhibit any phase transition and should stay in the HT phase in the whole temperature range. Figure 4 clearly shows that compounds **7** and **8** with  $x = 0.61$  and  $0.43$  do not present any spin state switching, in agreement with the “phase diagram”.

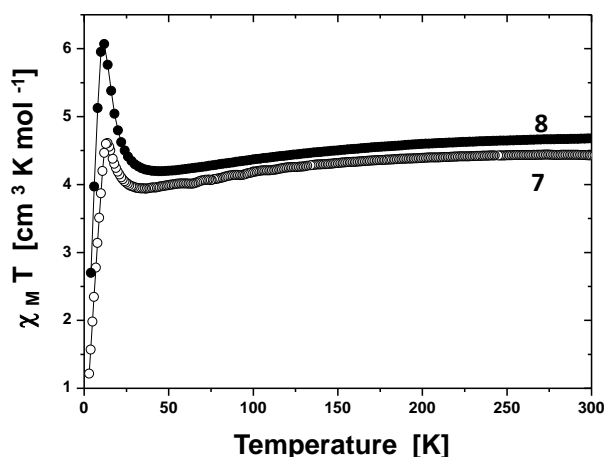


Figure 4. Thermal dependence of the magnetic susceptibility  $\chi_M$  times the temperature of compounds **7** (o) and **8** (●).

From such simple “phase diagram” view the presence or absence of phase transition on these materials could be understood. When the thermal hysteresis is shifted toward low temperature (grey area) it reaches a region where the lifetime of the metastable HT state is long enough to be observable. There is an overlap between the thermal hysteresis and the metastable state quenched at low temperature. Below the  $T(TIESST)$  and  $T_{1/2}(\downarrow)$  crossing point, the hysteresis is hidden by the long lived metastable state. One can hardly know what occurs in this region.

However, a hysteresis can be divided in two parts, from either side of the equilibrium temperature  $T_{1/2}$  which is roughly equal to  $(T_{1/2}(\downarrow) + T_{1/2}(\uparrow))/2$ . From the thermodynamical point of view, the HT phase is stable down to  $T_{1/2}$  which corresponds to a minimum of the free energy, and the LT phase is metastable. Below this temperature the situation is reversed and the HT phase becomes metastable. This metastability disappears when the hysteresis is completed. The light-induced metastability observed at low

temperature has essentially a molecular origin. As already mentioned, the photo-induced LT to HT phase transition can be achieved within the hysteresis, but also at low temperature by green light irradiation. At low temperature, this process is reversible and the HT to LT phase transition can be induced by irradiation at 410 nm. One should expect that for the compounds with  $x < 0.7$  the HT phase could be switched into the LT phase by blue light irradiation below a temperature corresponding to the expected  $T_{1/2}$ .

This experiment has been done on compound **8**[16] and is reported on figure 5. This figure shows that between 75 and 175 K, the HT to LT light-induced phase transition can be observed. This has been called the Light-Induced Phase Collapse (LIPC) effect.[16] Astonishingly, this effect was not observed at lower temperature. This range of temperature corresponds in the phase diagram to the region where the thermodynamic metastable state from the hysteresis overlap the molecular metastable state from the low temperature quenched state (Figure 3).

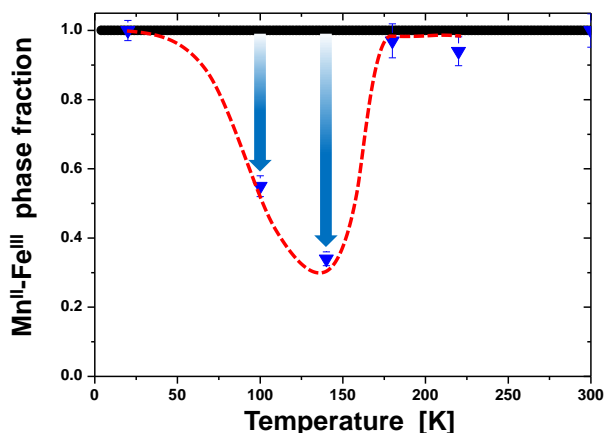


Figure 5. Irradiation at 410 nm at different temperatures of compound **8** showing the limited region of observation of LIPC (adapted from ref 16).

It follows from this observation that on this series of compounds hidden phase should be present and observed for composition with  $x$  lower than 0.7, in temperature ranges that will depend on the compound. In figure 3 this region of LIPC is represented by the blue area.

Other experiments should complete this view, particularly to understand why this region is limited by the pseudo-  $T_{1/2}(\downarrow)$  value and the effect not accessible down to low temperature. Moreover, this could also imply that in the compounds for which hysteresis are observed, irradiation in the HT phase by a blue light could induce the population of the LT phase. This could lead to the reversible photo-switching around room temperature of the magnetic properties of such materials.



## CONCLUSION

The study of the magnetic properties before and after thermal quenching of a series of Rubidium manganese hexacyanoferrates  $\text{Rb}_x\text{Mn}[\text{Fe}(\text{CN})_6]_{(x+2)/3} \cdot z\text{H}_2\text{O}$  as function of the composition allowed to observe the meeting between the thermal hysteresis loop and the  $T(\text{LIESST})$  curve arising from the thermal trapping. This meeting induces the metastable HT state from the hysteresis to overlap the metastable state region of the thermal quenching. This overlap induces particular properties. First of all, the phase transition becomes inhibited and only the HT phase can be observed in the whole temperature range. Secondly, in a specific temperature region the LT phase is hidden and can be accessible by blue light irradiation inducing a disinhibition of the phase transition that has been called Light-Induced Phase Collapse. This particular phenomenon is observable in a given temperature range that correspond to the hidden hysteresis loop and more precisely to the part of the pseudo hysteresis loop where the HT phase is metastable (below  $T_{1/2}$ ). Outside this hidden hysteresis loop, nothing was observed indicating that this is only in the thermodynamic region that this phenomenon is observed.

Regarding this study and other overlaps induced in spin-crossover compounds [11, 19] the HS materials that do not exhibit any phase change should be reexamined with our work in mind since some inhibition could be present and hidden phase probably accessible. This is particularly interesting if the hidden hysteresis is located at room temperature which could give rise to a bi-directional switching of properties by light.

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