



HAL
open science

Nature and mechanism of the photoinduced spin transition in $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$.

Kouhei Ichiyanagi, Johan Hebert, Loic Toupet, Hervé Cailleau, Philippe Guionneau, Jean-François Létard, Eric Collet

► **To cite this version:**

Kouhei Ichiyanagi, Johan Hebert, Loic Toupet, Hervé Cailleau, Philippe Guionneau, et al.. Nature and mechanism of the photoinduced spin transition in $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$.. Physical Review B: Condensed Matter and Materials Physics (1998-2015), 2006, 73 (6), p. 060408 (4 p.). 10.1103/PhysRevB.73.060408 . hal-00020192

HAL Id: hal-00020192

<https://hal.science/hal-00020192>

Submitted on 19 Feb 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.

Nature and mechanism of the photoinduced spin transition in $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ K. Ichiyanagi,^{1,2} J. Hebert,¹ L. Toupet,¹ H. Cailleau,^{1,3} P. Guionneau,⁴ J.-F. Létard,⁴ and E. Collet^{1,3,*}¹Groupe Matière Condensée et Matériaux, UMR 6626 CNRS, Université de Rennes 1, 35042 Rennes Cedex, France²Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan³Non-equilibrium Dynamics Project, ERATO, Japan Science and Technology Agency, c/o KEK, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan⁴Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS 9048, Université Bordeaux I, 33608 Pessac, France

(Received 14 October 2005; published 21 February 2006)

We report the investigation of a prototype cooperative photoinduced spin transition in $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ by x-ray diffraction. The structural rearrangement accompanying the change of an electronic state between the low spin and the photoinduced out-of-equilibrium high spin phases is similar to the one occurring around the phase transition at thermal equilibrium. The cooperative behavior of the light-induced optical hysteresis and light-induced thermal hysteresis phenomena investigated here show a strong similarity with thermal hysteresis around first-order phase transitions, since they are driven by a domain nucleation process.

DOI: 10.1103/PhysRevB.73.060408

PACS number(s): 78.20.Ls, 61.10.-i, 64.70.-p, 64.90.+b

Photoinduced phase transitions represent a fascinating way to manipulate at the macroscopic scale the physical properties of a material by light.¹ These out-of-equilibrium phenomena go beyond what has been done up to now under external fields of a different nature such as pressure, temperature, electric field, or magnetic field. In some materials it is possible to take advantage of the interactions between the constituent molecules of a solid to generate cooperative photoinduced phase transformations. The molecular multistability between degenerate or quasidegenerate states involves changes in the molecular identity, such as spin or charge, and light excitation makes it possible to switch between different molecular states. However, contrary to conventional photochemical processes,² in highly cooperative solids the excited molecular sites are no longer independent of each other and the photoswitching gives rise to photoinduced cooperative phenomena, such as nucleation processes and hysteresis. This opens new possibilities to store digital information, as long as the photoinduced macroscopic state can be stabilized. Therefore, it is of crucial interest to understand the mechanisms driving such photoswitching at the macroscopic scale in order to design future materials. Up to now these cooperative effects have been investigated mainly by optical and magnetic measurements. As illustrated in this paper, x-ray-diffraction investigation makes it possible to get key information, both at the molecular and macroscopic scales, on the nature and mechanisms surrounding photoinduced transition.

The photoinduced spin transition investigated here represents a prototype of molecular bistability and cooperative transformation in solids.³ It represents an attractive effect, since it is possible to trigger the spin state of the complex by light irradiation,³ also associated with changes to the other physical properties of the material such as optical reflectivity. In this class of material, the switching from a diamagnetic low spin state [(LS), $S=0$] to a paramagnetic high spin state [(HS), $S=2$] can occur under the effect of external stimuli such as pressure and temperature, but also under continuous or pulsed light irradiation, namely the light-induced excited spin-state trapping (LIESST) effect.³ It is only recently that

such photoinduced effects have begun to be investigated by x-ray diffraction. In addition to the determination of the structural changes in the photoinduced state, as performed in some of these materials,⁴⁻⁷ it is important to distinguish between a phase nucleation process and a homogeneous one. This is key information also for modeling such photoinduced phenomena, which are multiscale processes from the isolated excited molecule to the macroscopic switching. Up to now, theoretical models mainly discussed homogeneous processes within a mean-field approach.

The orthorhombic form of the $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ compound (Fig. 1) investigated here undergoes a first-order phase transition at around 170 K between the high-temperature HS phase and the low-temperature LS one,^{8,9} as shown by magnetic susceptibility measurements (Fig. 1). Above 78 K, transient photoinduced states were evidenced

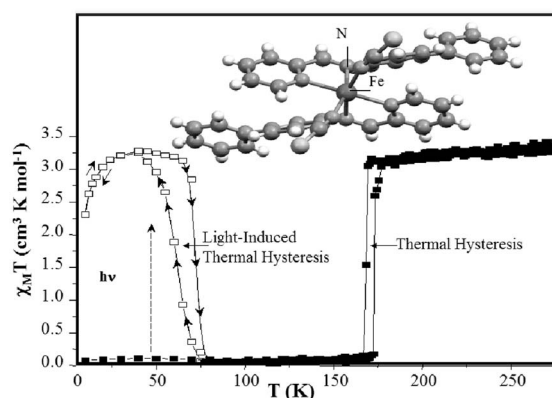


FIG. 1. Temperature dependence of the magnetic susceptibility times the temperature $\chi_M T$ on cooling and heating modes for the $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ compound represented here. The first-order transition occurs around 170 K with a thermal hysteresis of 5 K. Under continuous laser irradiation (5 mW/cm^2 at 830 nm) the HS state can be photoinduced (arrow) and a quasistatic light-induced thermal hysteresis (LITH) appears between the cooling and warming modes.

by the nanosecond laser-induced transition.¹⁰ Below 78 K, the HS state can be generated under continuous laser excitation⁸ (at 830 nm and 5 mW/cm²) as shown in Fig. 1. For this fluence, when the photostationary state is reached, the transformation of the crystal is complete below 35 K and partial above. Once the complete HS state is photoinduced at 10 K and the temperature is increased under the same laser excitation condition, the critical temperature where the relaxation to the ground state becomes very fast is shifted to a higher temperature compared to the one without laser excitation [defined as T(LIESST) (Ref. 11)]. A light induced thermal hysteresis⁸(LITH) is thus generated and the fraction of HS molecules then depends on the thermal history. Such an effect is associated with the competition between two opposite kinetic processes¹²: photo-excitation and thermal relaxation. The first process depends linearly on the fraction of LS molecules in a first approximation, whereas for the second cooperative interactions between the molecules of the crystal exist: They do not behave in an independent site-to-site way since a self-acceleration is observed.

This photoinduced phase transition was investigated by x-ray diffraction. Data collections were performed as a function of temperature in order to compare both the already known structures of the LS and HS states^{8,13,14} (high temperature and thermally trapped at 20 K) with the photoinduced one at 20 K and 78 K. The single crystals were mounted either in an Oxford Diffraction Helijet helium flow cryostat, allowing us to reach 20 K on the crystal or in an Oxford Cryosystems nitrogen flow cryostat, which allowed a better control of the temperature down to 78 K. Diffraction data were collected under different experimental conditions.¹⁵ The structures of the HS state trapped at 20 K by a flash cooling was also determined. The photoinduced HS state was generated from the LS state by a continuous laser excitation (a few minutes with 800 mW/cm² at 808 nm) at 20 K, where complete transformation is easily reached. The laser was then switched off in order to perform the data collection, since the lifetime of the HS state at 20 K is of the order of several days.⁸ The structure of the photostationary HS state at 78 K was obtained by trapping the HS phase by flash cooling and keeping the crystal in the HS state by a continuous laser irradiation (800 mW/cm² at 808 nm). Notice that this effect is not due to a laser heating effect since at 85 K under the same laser excitation, the system relaxes to the LS state. The main results of the structural analysis are given in Fig. 2, with the lattice parameters *a*, *b*, and *c*, the average $\langle\text{Fe-N}\rangle$ bond length, and the distortion parameter Σ , which represents the sum of the deviation from 90° of the 12 N-Fe-N octahedral angles.¹³ It is well known that such a structural rearrangement around the Fe atom (Fig. 1) signals the change between the HS and the LS states. All the different phases have the same symmetry, corresponding to the space group *Pccn*. The structural results (Fig. 2) for the HS, LS, and thermally trapped HS states are in good agreement with the ones obtained previously.¹³ It is clear from all these data that the photoinduced and thermally trapped HS states are very similar and look like the high-temperature HS phase when no phase transition occurs. If we can easily understand this point for the thermally trapped state, it is not obvious *a priori* for the photoinduced HS

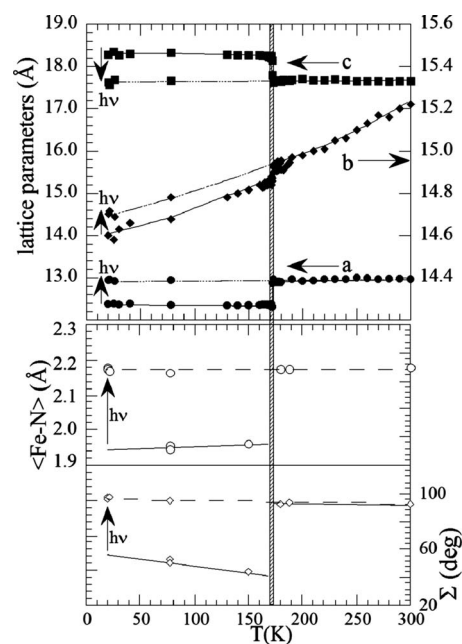


FIG. 2. Temperature dependence of the lattice parameters *a*, *b*, and *c* (top) and of the molecular deformation characterized by the average $\langle\text{Fe-N}\rangle$ bond length and the distortion parameter Σ . The thermal phase transition is associated with a drastic change of these parameters around the thermal hysteresis (shaded area). At 20 K the HS phase was trapped by flash cooling and also photoinduced from the LS phase as shown by the arrow. The thermally trapped HS state at 78 K can be stabilized under continuous laser excitation.

phase generated in a different way than the thermally induced one. The fascinating possibility to photoinduce a new phase has been discussed in a $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{EtOH}$ complex,¹⁶ but x-ray investigation indicated that the photoinduced phase was of the same nature as the HS one, stable at high temperature.⁷ However this is an important point to determine, since it was recently reported that in the $[\text{Fe}(\text{bt})(\text{NCS}_2)_2](\text{bpm})$ system the choice of the excitation wavelength makes it possible to reach different states.¹⁷

In order to understand the mechanism driving the macroscopic switching, it is of fundamental interest to investigate the photoinduced transformation and the thermal equilibrium recovery process. When the transformation is partial, as in the LITH loop, one may ask whether it is due to a random distribution of the transformed molecules with possibly short-range clustering or to a phase separation process involving the coexistence of macroscopic domains with different long-range order. In order to investigate the LITH, we have used an excitation condition similar to that of Fig. 1 at 65 K. Figure 3(a) shows the (a^*, b^*) plane, reconstructed with CrysAlis software¹⁵ from the x-ray-diffraction data. It is clearly observed that the Bragg peak split in two inside the LITH cycle, defining two coexisting sublattices. One of them defines the HS lattice parameters, the other defines the LS lattice parameters. This is the direct signature of the photo-generation of macroscopic HS domains, known to be growing as the photoinduced transformation occurs.^{18,7} Therefore the LITH cycle is associated with a phase separation process similar to that generally observed in a thermal hysteresis.¹⁹

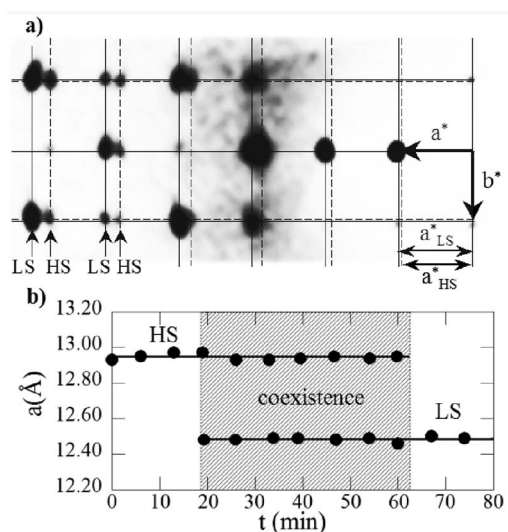


FIG. 3. (a) Reconstruction of the $(hk2)$ plane in the LITH loop at 65 K. The split Bragg peaks (LS and HS spots marked by the arrows) define two lattices corresponding to the reciprocal lattices of the HS phase (dashed lines a_{HS}^*) and LS phase (solid lines a_{LS}^*). This shows the coexistence of macroscopic domains of HS and LS phases. (b) Time dependence of the lattice parameter a during the relaxation from the photoinduced HS to stable LS state, under laser irradiation (400 mW/cm^2 at 808 nm). As in (a) there is a time interval during which the Bragg peaks of the HS and LS phases associated with different lattice parameters (Fig. 2) coexist as schematically indicated by the shaded area.

Note that short-range clustering would be associated with diffuse scattering and not with the coexistence of Bragg peaks. Such a phase separation process is very different from photochemical systems in which local molecular excitations are generated.² The same coexistence of phases is observed in Fig. 3(b) during the opposite process of the transformation from the HS state to the LS one at 78 K under a continuous laser excitation with a fluence of 400 mW/cm^2 (808 nm), not large enough to compensate the thermal relaxation to the LS state. The coexistence of the HS and LS phases is also associated with the coexisting Bragg peaks corresponding to the lattice parameters of the HS and LS phases. When the transformation (the top of the LITH loop) or the relaxation (the bottom of the LITH loop) is complete, only a set of single Bragg peaks is observed. The domain size would influence the width of the Bragg peaks, but the experimental resolution during this experiment does not make it possible to investigate it precisely. We can only conclude that the size of the domains is above the 100 nm range.

These results are of fundamental interest since models describing these photoinduced transformation and relaxation processes are usually based on the mean-field approach, considering homogeneous processes. The macroscopic switching of the materials takes place over different scales, from the electronic excited state, the local molecular relaxation to the macroscopic nucleation. Now it is of considerable importance to take into account the possibility of the nucleation of domains in theoretical models, as it is essential to describe a system around the thermal hysteresis. Such an approach was performed recently by Monte Carlo simulations of the coop-

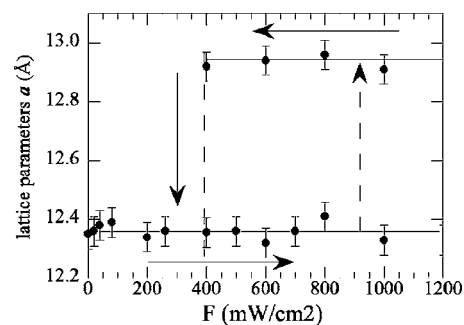


FIG. 4. Evolution of the lattice parameter a with the laser fluence around $T(\text{LIESST})=78 \text{ K}$, describing the light-induced optical hysteresis. When the crystals are thermally trapped in the HS state at 78 K ($a \approx 12.95 \text{ \AA}$) by flash cooling under laser irradiation, the relaxation to the LS phase ($a \approx 12.35 \text{ \AA}$) occurs within a few minutes if the laser fluence is below 400 mW/cm^2 . Above this value, there is a large fluence range where a crystal in the HS state can be maintained HS, but where a crystal in the LS state cannot switch to the HS state. It is a direct signature of the nonlinear effect associated with the cooperative phenomena.

erative photoinduced LS to HS transformation,^{20,21} showing that the volume striction effect can drive the macroscopic phase separation. However, if the cooperativity is not strong enough, a gradual and homogeneous change of the concentration of HS molecules can be expected as for the thermal spin crossover from the HS to LS phases, above the critical point.

The light-induced optical hysteresis²² (LIOH) observed in the present material in Fig. 4 in the vicinity of the $T(\text{LIESST})$ is very good evidence of the cooperative nature of the macroscopic switching, since the transformation rate does not behave in a linear way with the excitation density. When the crystal is trapped in the HS state at 78 K, it can be kept for several days in the HS state under continuous laser irradiation with fluence above 400 mW/cm^2 at 808 nm, whereas it relaxes to the LS state within a few minutes below this value. A crystal in the LS state remains LS up to large excitation densities (it can switch to the HS state for high excitation densities but the reproducibility is not so good since the laser beam was not homogeneous). The appearance of a large fluence range where the system remains LS if already LS or HS if already HS is known to be associated with strong cooperative effects.²² In the LS phase the instantaneously photoinduced HS molecules in low concentration rapidly relax since they are weakly coupled, whereas in the HS phase the laser compensates for the slow relaxation. Below 400 mW/cm^2 the laser cannot compensate for this relaxation to the LS phase, and the phase separation occurs as illustrated in Fig. 3(b). Therefore, the LIOH phenomenon is demonstrated here to be controlled by the domain nucleation process.

To conclude, we have investigated the photoinduced spin transition in the $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ compound. The photoinduced HS state is very similar to the thermally induced ones. We have shown that the quasistatic LITH and LIOH loops are similar to thermal hysteresis in the sense that they are driven by nucleation-of-domains phenomena. This shows that the physics associated with the out-of-equilibrium

phenomena driving the photoinduced phase transition has some important similarities with thermal instabilities associated with the first-order phase transitions. In this way for photoswitching driven by a single-laser pulse inside the thermal hysteresis observed in this compound,¹⁰ or in another one around room temperature,²³ domains should again play a key role. An important challenge for future experiments is to detect the formation of precursor clusters and the growing of small domains. The use of improved experimental condi-

tions, such as the ones provided around the synchrotron source, will make it possible to directly observe the dynamics of the photoinduced and the thermal equilibrium recovery processes.

This work was partly supported by the Région Bretagne and Ministère de la Recherche, and was performed within the European FLASH network (MRTN-CT-2003-503641) and NOE MAGMANet.

*Author to whom correspondence should be addressed. E-mail address: Eric.collet@univ-rennes1.fr

¹*Photoinduced Phase Transitions*, edited by K. Nasu (World Scientific, Singapore, 2005).

²P. Coppens, I. I. Vorontsov, T. Graber, M. Gembicky, and A. Y. Kovalevsky, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **61**, 162 (2005).

³See for general review *Spin Crossover in Transition Metal Compounds*, edited by P. Gütllich and H. A. Goodwin (Springer, New York, 2004).

⁴J. Kusz, H. Spiering, and P. Gütllich, *J. Appl. Crystallogr.* **33**, 201 (2000).

⁵J. Kusz, H. Spiering, and P. Gütllich, *J. Appl. Crystallogr.* **34**, 229 (2001).

⁶M. Marchivie, P. Guionneau, J. A. K. Howard, G. Chastanet, J. F. Létard, A. E. Goeta, and D. Chasseau, *J. Am. Chem. Soc.* **124**, 194 (2002).

⁷N. Huby, L. Guérin, E. Collet, L. Toupet, J. C. Ameline, H. Cailleur, T. Roisnel, T. Tayagaki, and K. Tanaka, *Phys. Rev. B* **69**, 020101(R) (2004).

⁸J. F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, and O. Kahn, *Inorg. Chem.* **37**, 4432 (1998).

⁹J. F. Létard, G. Chastanet, O. Nguyen, S. Marcen, M. Marchivie, P. Guionneau, D. Chasseau, and P. Gütllich, *Monatsch. Chem.* **134**, 165 (2003).

¹⁰E. Freysz, S. Montant, S. Létard, and J.-F. Létard, *Chem. Phys. Lett.* **394**, 318 (2004).

¹¹J.-F. Létard, L. Capes, G. Chastanet, N. Moliner, S. Létard, J. A. Real, and O. Kahn, *Chem. Phys. Lett.* **313**, 115 (1999).

¹²F. Varret, K. Boukheddaden, E. Codjovi, C. Enachescu, and J. Linares, in *Spin Crossover in Transition Metal Compounds II*, edited by P. Gütllich and H. A. Goodwin (Springer, New York, 2004), Vol. 234, Chap. 8, p. 199.

¹³M. Marchivie, P. Guionneau, J. F. Létard, and D. Chasseau, *Acta Crystallogr., Sect. B: Struct. Sci.* **59**, 479 (2003).

¹⁴M. Marchivie, P. Guionneau, J. F. Létard, D. Chasseau, and J. A. K. Howard, *J. Phys. Chem. Solids* **65**, 17 (2004).

¹⁵X-ray data were collected on samples with typical sizes of $0.05 \times 0.05 \times 0.10 \text{ mm}^3$ at 300, 188, and 180 K for the HS states, 150 and 78 K for the LS states, 20 K for the trapped HS state, 20 and 78 K for the photoinduced and photostationary HS states, respectively, on a four-circle Oxford Diffraction Xcalibur 3 diffractometer (Mo $K\alpha$ radiation) with a two-dimensional Sapphire 3 charge-coupled device detector. The cell parameters and the data reduction were obtained with CrysAlis from Oxford Diffraction and the structure were refined with SHELXL97: Sheldrick, G.M. (1997). SHELX97 Program for the Refinement of Crystal Structures, Univ. of Göttingen, Germany. Typical results of the structure refinement gave the final R factor as $0.03 < R < 0.05$. The detailed structural analysis will be published elsewhere.

¹⁶T. Tayagaki and K. Tanaka, *Phys. Rev. Lett.* **86**, 2886 (2001).

¹⁷N. O. Moussa, G. Molnar, S. Bonhommeau, A. Zwick, S. Mouri, K. Tanaka, J. A. Real, and A. Bousseksou, *Phys. Rev. Lett.* **94**, 107205 (2005).

¹⁸Y. Ogawa, S. Koshihara, K. Koshino, T. Ogawa, C. Urano, and H. Takagi, *Phys. Rev. Lett.* **84**, 3181 (2000).

¹⁹S. Pillet, J. Hubsch, and C. Lecomte, *Eur. Phys. J. B* **38**, 541 (2004).

²⁰O. Sakai and T. Ogawa, in *Photoinduced Phase Transitions*, edited by K. Nasu (World Scientific, Singapore, 2005), Chap. 3, and references therein.

²¹M. Nishino, S. Miyashita, and K. Boukheddaden, *J. Chem. Phys.* **118**, 4594 (2003).

²²A. Desaix, A. Desaix, O. Roubeau, J. Jeffic, J. G. Haasnoot, K. Boukheddaden, E. Codjovi, J. Linares, M. Nogues, and F. Varret, *Eur. Phys. J. B* **6**, 183 (1998).

²³S. Bonhommeau, G. Molnar, A. Galet, A. Zwick, J. A. Real, J. J. Mc Garvey, and A. Bousseksou, *Angew. Chem., Int. Ed.* **44**, 4069 (2005).