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# Structural investigation of the photoinduced spin transition in the [Fe(PM-BiA)<sub>2</sub>(NCS)<sub>2</sub>] compound

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**Abstract.** We investigated the thermo- and photo-induced phase transitions between low spin (LS) and high spin (HS) states of the molecular crystal of [Fe(PM-BiA)<sub>2</sub>(NCS)<sub>2</sub>] in the orthorhombic form, by using X-ray diffraction. The structure of the photoinduced HS state, generated from the LS state at low temperature, is compared to the structures of the HS and LS phases at thermal equilibrium and to the thermally trapped HS state. The preliminary results presented here show that the structural reorganization is similar in the different HS states.

## Introduction

The switching effects driven by light irradiation is of special interest in physics around molecular materials where electronic and structural degrees of freedom are so strongly coupled that photoinduced phase transition can be generated [1,2]. Spin transition materials represent a very nice example of highly cooperative phenomenon around photo excitation [3,4]. Accordingly, a photo-switching in solids can be driven with laser excitation, and the resulting change of the physical properties of the material may be applied in optical devices for digital information storage for instance.

The [Fe (PM-BiA)<sub>2</sub>(NCS)<sub>2</sub>] compound investigated here exhibits a phase transition between a diamagnetic low spin state (LS, S=0) and a paramagnetic high spin state (HS, S=2) [5]. X-ray diffraction investigations evidenced two phases with orthorhombic (phase I) and monoclinic (phase II) structures [5,6]. The phase I shows an extremely abrupt spin transition with a thermal hysteresis around 170 K (Figure 1) [6]. The phase II shows a gradual spin conversion centered at 205 K [5]. It was demonstrated that in this family of compound it is possible to photo-switch from the LS state (stable at low temperature) to a metastable HS state, by using

the appropriate light irradiation conditions, of continuous or pulsed nature [5,7]. This photo-induced effect is referred as LIESST effect (light-induced excited spin state trapping) and was discovered in 1994 [3,4]. The LIESST effect in the compound  $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$  has been studied by magnetic techniques [5,6]. The present paper deals with the investigation by X-ray diffraction of the photoinduced spin transition in the orthorhombic phase I, and the comparison with the structural changes driven by the thermal effects.

The irradiation with a continuous laser excitation at 830 nm ( $5\text{mW}/\text{cm}^2$ ) of the LS state at low temperature (10 K) makes it possible to switch from the LS state to the photoinduced HS state. It was also evidenced that the HS state stable at high temperature can be trapped at low temperature by a flash cooling [8]. The lifetime of the metastable photoinduced or trapped HS state in this compound can reach several days at low temperature [6], and is decreasing as the temperature is increased. The T (LIESST) temperature, where the relaxation to the LS state becomes very fast without laser excitation was estimated to be 78 K for  $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$  [6]. This photoinduced HS state can also be kept while increasing the temperature under laser excitation up to about 80 K. The competition between the thermal relaxation process which depends non-linearly on the fraction of HS molecule and the transformation of HS molecules generated by laser excitation, gives rise to another interesting phenomenon known as LITH (Light-Induced Thermal Hysteresis). As shown in Figure 1, the fraction of HS molecules depends on the thermal history of the material under laser excitation [5].

## Experiment

The photoinduced phase transition was investigated by using a four-circle diffractometer Xcalibur3 with a 2D sapphire 3 CCD (Oxford-Diffraction) using the  $\text{Mo K}\alpha$  radiation. The system was coupled to a continuous laser to generate the photo-induced phase (808 nm,  $50\text{mW}/\text{cm}^2$ ), as shown in Figure 2. The typical sample size of the crystals of  $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$  compound used for the X-ray diffraction experiments was  $50 \times 50 \times 100\ \mu\text{m}^3$ . The single crystal were mounted with a Oxford Diffraction Helijet Helium flow cryostat, allowing to reach 20 K on the crystal, or in an Oxford nitrogen flow cryostat allowing a better control of the temperature above 78 K. The HS and LS structures of  $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$  correspond to the same crystallographic space group (*Pccn*, with  $Z = 4$ ). The molecular structures were solved and refined with the *Sir97* program and *SHELXL97* program [9] at 300 K (HS), 150 K (LS), as well as for the thermally trapped and photoinduced HS states at 20 K, in order to compare both to the already known structures of LS and HS states [6,8,10]. Up to now, such structural investigations of the photoinduced spin transition were performed in a limited number of materials [11-14].

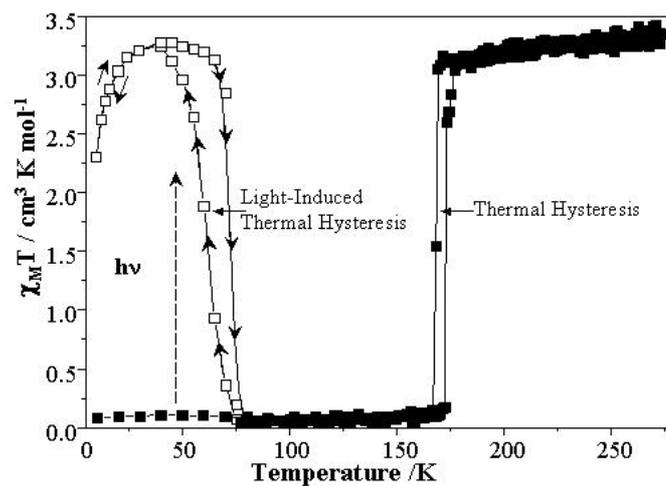
## Results and discussion

An important signature associated with the change of spin state is the variation of the lattice parameters, as shown in Table 1a. The thermal contraction of the lattice parameter *b* is quite important, but the huge jumps of *a* and *c* sign the thermal phase transition between the HS and LS phases around 170 K. It is associated

with the pronounced first order aspect of the phase transition. When a sample in the HS phase at room temperature is directly put in a helium flow (20 K), the HS state is trapped by the flash cooling as the molecular structural relaxation is frozen. This thermally trapped HS structure is very similar to the HS state stable at high temperature [10]. The photoinduced HS state was also easily generated at 20 K from the LS state by using a continuous laser excitation (a few minutes with 800 mW/cm<sup>2</sup> at 808 nm). The lattice parameters and the unit-cell volume of the photoinduced HS state and the trapped HS state are almost similar to the HS one (Table 1a). It is well known that the Fe-N<sub>6</sub> octahedral conformation is strongly coupled to the spin states. Therefore the main structural modifications during the spin conversion occur around the Fe atom [4], and are characterized by the change of the parameters <Fe-N> (the average bond length) and  $\Sigma$  (sum of the deviation from 90° of the N-Fe-N angles). The molecular structure analysis as a function of temperature is shown in Table.1b and Figure 3. The results we obtained on the thermally trapped HS state at low temperature are in good agreement with previous X-ray diffraction measurements [10,13]. The photoinduced HS state is here again very similar to the other HS states. We also present here the inter-molecular hydrogen contacts between the H and S atoms involving the NCS branch. The molecular structures and inter-molecular interactions of the photoinduced HS, thermally trapped HS and thermal HS states are here again almost similar, as shown on Figure 3 with the S...H-C contact (Table. 1(b)). This inter-molecular hydrogen contact is well depending on the changes of the lattice parameters. It was also reported that this molecular hydrogen bond influences the stability feature of the photoinduced state [10]. All the results presented here indicate a high similarity between the structural changes associated with the thermal phase transition and the ones associated with the photoinduced transition.

To conclude, we have investigated the phase transition in the [Fe(PM-BiA)<sub>2</sub>(NCS)<sub>2</sub>] compound by using X-ray diffraction on a four- circle X-ray diffractometer. We concluded that the photoinduced and thermally trapped HS states are consistent with the HS state stable at high temperature. The results presented here also stress the coupling between the intra-molecular reorganization and the inter-molecular contacts, known to be playing a key role to stabilize the photoinduced or thermally trapped states.

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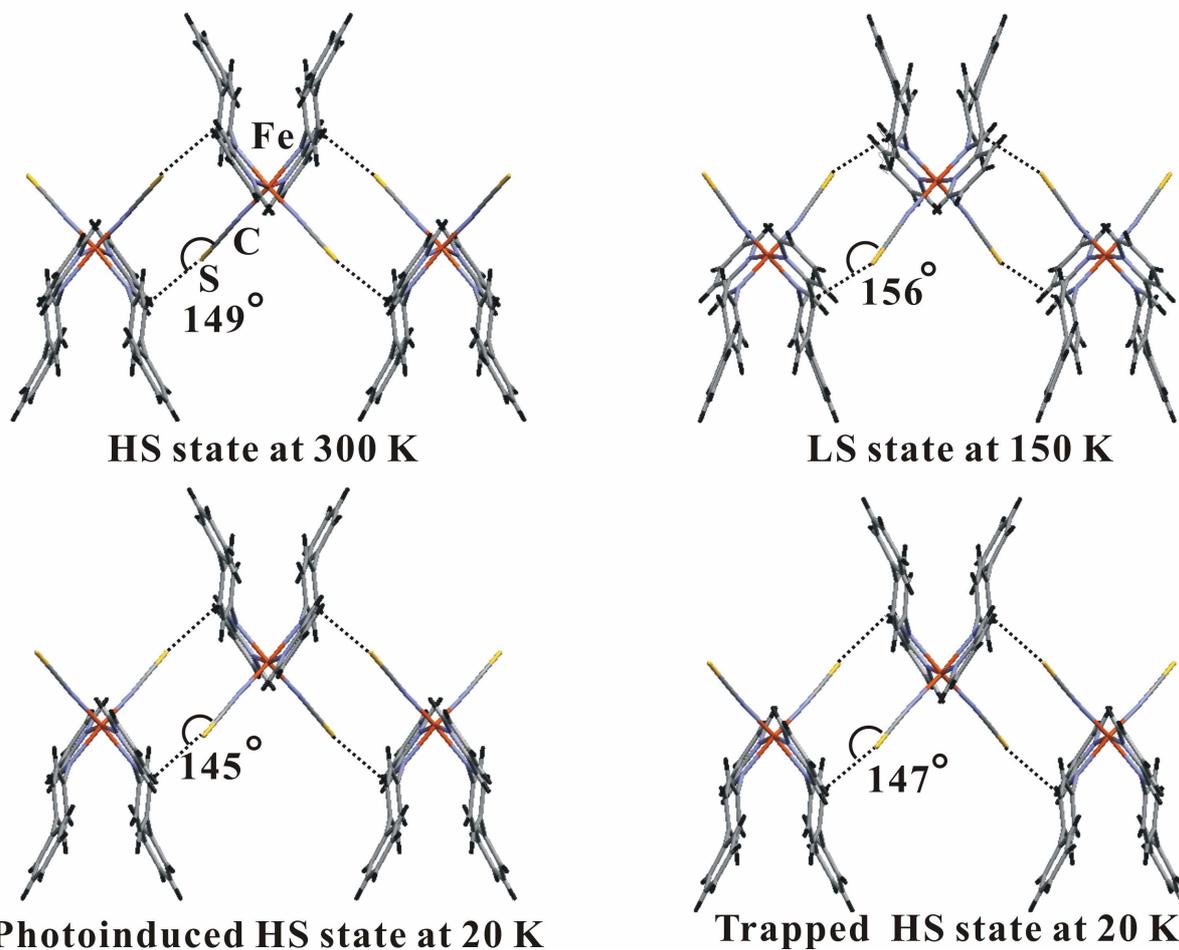
**Figure. 1**

Temperature dependence of the magnetic susceptibility measurements in the cooling and warming mode. The arrow line represents the switching from LS state to photoinduced HS state under laser irradiation (830 nm,  $5\text{mW}/\text{cm}^2$ )



**Figure. 2**

The four-circle X-ray diffractometer Xcalibur3 with He or N<sub>2</sub> flow cryostat and laser systems.



**Figure. 3**

View of the molecular structures and intermolecular contacts of LS state at 150 K, photoinduced HS state at 20 K, thermal HS state at 300 K and thermally trapped HS state along the *b* axis.

**Table. 1**(a) The lattice parameters of the  $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$  compound

spin state	experimental condition	a (Å)	b (Å)	c (Å)
HS	300 K	12.962(1)	15.222(1)	17.644(1)
LS	150 K	12.394(1)	14.827(1)	18.983(1)
HS	20 K (photoinduced)	12.928(1)	14.656(1)	17.593(1)
HS	20 K (trapped)	12.943(1)	14.700(1)	17.622(1)

(b) X-ray diffraction Fe-N<sub>6</sub> octahedron geometry versus spin state

spin state	experimental condition	<Fe-N> (Å)	$\Sigma$ (°)	S···HC angle (°)
HS	300 K	2.178(4)	91.9(2)	149 (1)
LS	150 K	1.961(4)	44.2(2)	156 (1)
HS	20 K (photoinduced)	2.178(5)	92.0(2)	147 (1)
HS	20 K (trapped)	2.171(5)	97.5(2)	145 (1)

<Fe-N> is the average bond length of Fe-N<sub>6</sub> octahedron.  $\Sigma$  is defined as the sum of the absolute values of the deviation from 90° of the 12 cis angles in the coordinate sphere [10].

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