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First study of the photo-induced metastable (paramagnetic) high-spin state in a $[Fe(ptz)_6](BF_4)_2$ single crystal by polarised neutron diffraction

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Abstract

Some spin-crossover solids can show photo-convertibility at low temperatures, which generally makes this class of compounds interesting for studies towards application as optical switches and memories in numerical displays. The mechanism of the optical switching is the light-induced excited spin state trapping (LIESST) and the reverse-LIESST, as reported before [Inorg. Chem. 24 (1985) 2174; J. Phys. Chem. 94 (1991) 2741]. These processes can be combined with the relaxation in order to cycle the excited state, which involves temperature scanning of the title system [Polyhedron 20 (2001) 1599]. In this paper, we report the spin density map in the $[Fe(ptz)_6](BF_4)_2$ single crystal in its undercooled $R3i$ space group in the photo-induced metastable high-spin state, which is paramagnetic, at $T = 2$ K. The experiment was carried out on the 5C1 polarised neutron diffractometer at LLB newly equipped with an optical fiber for the light-coupled measurements. The photo-excitation reaches a steady state within an hour and a half. The lifetime of the photo-induced high-spin state at 40 K exceeds 10 h, as in accordance with previous spectroscopic, magnetic and Mössbauer measurements. The first results obtained on $[Fe(ptz)_6](BF_4)_2$ can serve as a base to future investigations of other photo-convertible materials.

Keywords: $[Fe(ptz)_6](BF_4)_4$; Polarised neutron diffraction; Light-induced excited spin state trapping; Spin density

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1. Introduction

The development of new materials showing molecular magnetism is tightly bound to their photo-physical properties in view of their utilisation as optical devices or memories [1]. Much fundamental research is still needed, concerning the materials involved, their physical properties during the switching process and their resistibility to the change. The optical switching seems to be the ideal way to follow, since it has been shown that it can be a property of a single molecule [2]. The process of interaction of the light with one class of molecular magnets, the spin-crossover materials [3], was discovered on $[Fe(ptz)_6](BF_4)_2$ single crystal some 20 years ago [4], 2 years after this compound was synthesised [5]. The mechanism of the reverse-LIESST process was interpreted as the intersystem crossing dynamics also in other Fe(II) coordination compounds [6]. The combination of LIESST and reverse-LIESST can optically cycle the system from one spin-state (and therefore also magnetic state) to another. In Fig. 1, we show the scheme of

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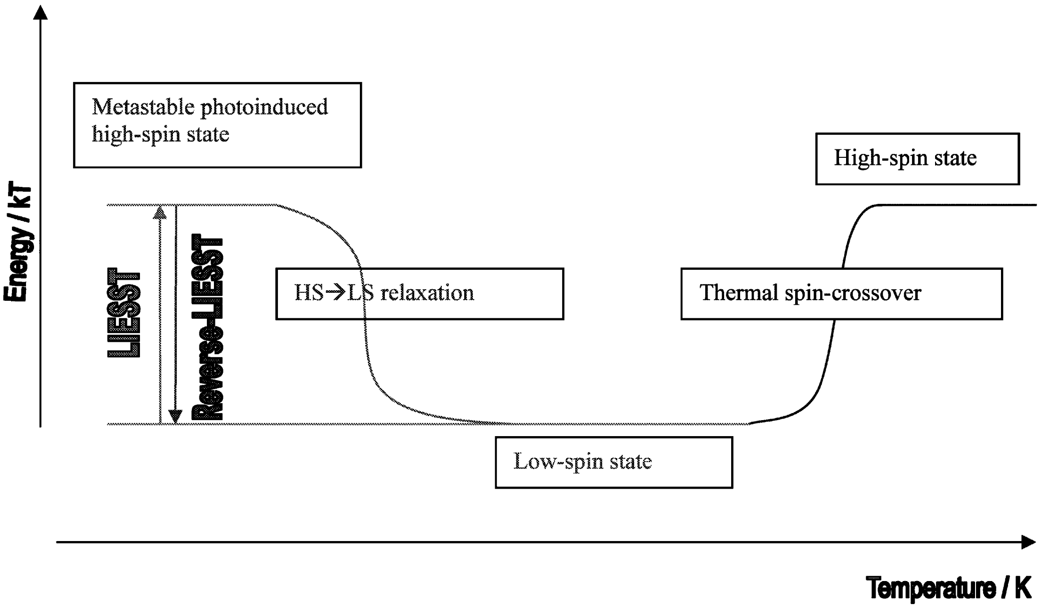

Fig. 1. Summary of processes involved in discussion and temperature regions of their appearance: LIESST, reverse-LIESST, high-spin → low-spin relaxation, thermal spin-crossover (schematic representation).

temperature region concerning the LIESST and reverse-LIESST, that is generally lower compared to the relaxation and the thermal spin-crossover.

Our previous study considered the quasi-static nature of the light-induced thermal hysteresis (LITH) on the title compound [7], by magnetic and optical spectroscopy measurements. The term LITH was introduced by Letard et al. [8] for a partially induced photo-excitation on a newly synthesised spin-crossover compound and a thermal cycling to the relaxation region under permanent irradiation. In parallel, a thorough study of physical properties of LITH phenomenon was performed on another spin-crossover powdered sample, by Varret and coworkers [9] and explained in terms of master equation considering the photo-excitation and the relaxation process. On the other hand, the structure investigations of excited states are of crucial importance. It is important to know the structure of the compound under investigation, if possible during the process of photo-excitation or relaxation. To our knowledge, no structure of any photoexcited state has been published so far.

This paper deals with the structural type of investigations which aims to determine a precise description of the electronic structure of the photo-excited state, in terms of the spin distribution in the molecule and describes the first experiment of determining a preliminary spin density map on the well-known $[Fe(ptz)_6](BF_4)_2$ spin-crossover system. Knowing the importance of the precise structural determination in order to understand the physical or chemical properties of any compound, such experimental study seems to be promising for a much wider family of photo-convertible molecular magnets [10].

2. Experimental

2.1. Sample

A single crystal of $[Fe(ptz)_6](BF_4)_2$, first synthesised by Franke et al. [5], of dimensions $6 \times 4 \times 0.2$ mm^3 was placed in a sample holder constructed for polarised neutron diffraction (PND) under light [10]. The morphology of the crystal is a hexagonal plate with the large face perpendicular to the crystallographic c direction. In Fig. 2, the complex $[Fe(ptz)_6]^{2+}$ is presented, based on the structural parameters for $R3i$ phase from the Ref. [11].

The crystal was quenched in order to undercool the crystallographic phase transition and thus preserved in the high-temperature rhombohedric phase, of the space group $R3i$. In that way we can avoid breaking of the crystal which can follow the structural phase transformation.

The possible unwanted Fe(II) → Fe(III) oxidation was avoided by mounting the crystal in the He(g) inert atmosphere prior to cooling it, which also enabled good thermal conductivity at low temperature.

2.2. PND of the photoexcited state of the crystal

PND was performed on a single crystal in the 2-axis polarised neutron diffractometer, 5C1, situated in the Laboratory Léon Brillouin, in Saclay, France. A mono-

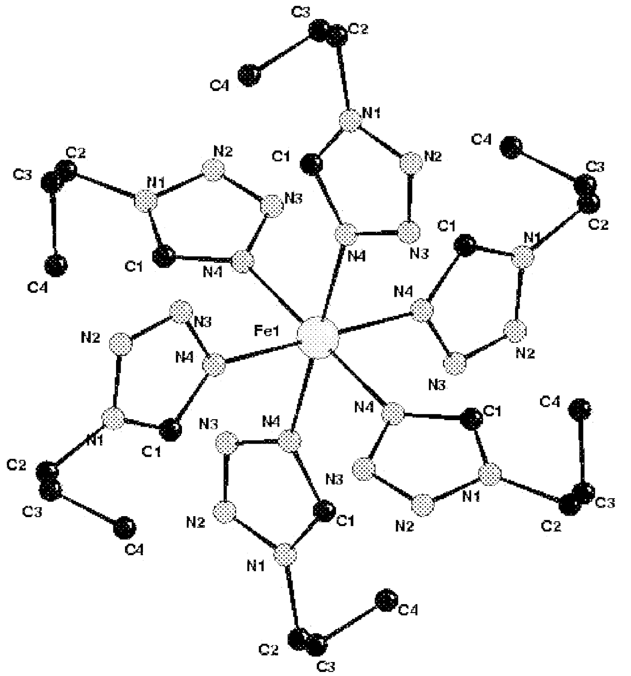

Fig. 2. Structural representation of $[Fe(ptz)_6]^{2+}$ [12].

chromatic polarised neutron beam, with a beam polarisation equal to 0.920(4) and a wavelength 0.84 Å, is obtained by using the (1 1 1) Bragg reflection of a Cu_2MnAl single crystal, the so-called Heusler monochromator [12]. A flipping device permits to invert alternatively the direction of the neutron polarisation. The information concerning the polarised neutron data are given in Table 1.

Table 1
Summary of the spin density refinement of the neutron diffraction data

Chemical formula	$[Fe(ptz)_6](BF_4)_2$
Mr	902.3
Space group	$R3i$
Cell parameters	
a (Å)	10.890(1)
b (Å)	10.890(1)
c (Å)	32.330(1)
α (°)	90
β (°)	90
δ (°)	120
Polarised neutron data collection	
Monochromator	Heusler
Neutron wavelength, λ (Å)	0.84
Beam polarisation	0.90(4)
Flipping efficiency	1
Magnetic field (T)	5
Temperature (K)	2
Number of reflections	40
Spin density refinement	
Number of unique reflections used	7
Number of parameters	2
R_w agreement factor	0.108

The crystal was set in the cryomagnet installed on the 5C1 diffractometer, with its c-direction vertical. It has been observed that the crystal in its high-temperature phase was twinned and that one individual has a c-axis in the direction opposed to the second individual. The presence of a second individual is reflected by reflections $(h\ k\ -l)_2$ separated by 60° in rotation around the vertical axis from the $(h\ k\ l)_1$ reflections of the first individual, except for special types of reflections like (1 1 ±3), (3 0 ±3) for which the contributions coming from the two crystals are superimposed.

In order to attain the magnetic saturation and to work at maximised signal values, the sample was cooled down to the temperature of 2 K, and exposed to a vertical magnetic field of 5 T. The orientation of the field was parallel to the c-axis of the crystal that remain in its rhombohedric phase by quenching.

The crystal was exposed to continuous Nd-YAG laser irradiation arriving to the crystal holder through an optical fiber. The detailed description of this new experimental setup will be given separately [10].

The wavelength chosen was in the green region ($\lambda = 532$ nm), where the LIESST effect is very efficient, and the starting light power was on the order of 30 mW cm^{-2}. The crystal was completely irradiated as calculated from the spin-flipping ratio (Eq. (1)). The flipping ratio was measured every half an hour for over 10 h on two separate reflections at low angles (small value of $\sin\theta/\lambda$). Two reflections chosen to follow the photo-excitation process among those most intense obtained had the ratio signal to noise around 5:1.

$$R(\vec{k}) = \frac{I\uparrow}{I\downarrow} = \frac{1 + 2q^2P_0\gamma + q^2\gamma^2}{1 - 2q^2P_0\gamma + q^2\gamma^2} \qquad (1)$$

where γ is the ratio between the nuclear and magnetic structure factors F_N and F_M, q^2 is $(\sin\alpha)^2$, α the angle between the scattering vector and the direction of the applied field, and P_0 the polarisation rate of the neutron beam.

The time of measurement at two separate reflections was half an hour each, and the time to orient the detector between the two measurements about 1 min maximum. Therefore, the interval between two points $R(t)$, where R is the flipping ratio and t the time, for one reflection is on the order of an hour.

3. Results and discussion

3.1. Following the photo-excitation process and the LS → HS conversion by LIESST

Two reflections that were not influenced by twinning phenomenon were chosen to follow the flipping ratio (Eq. (1)). Fig. 3 shows that photo-excitation starts

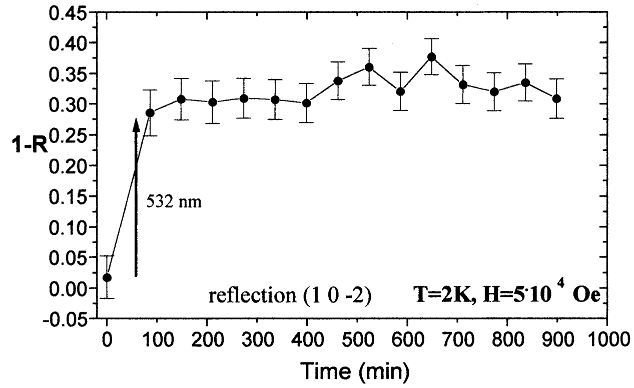

Fig. 3. Photo-excitation process ($\lambda = 532$ nm, $T = 2$ K, $H = 5$ T) of $[Fe(ptz)_6](BF_4)_2$.

within half an hour after the light is switched on and is completed in less than one hour and half, the interval needed to complete the measurement at two separate reflections. At given temperature, the photo-saturation by the green laser light implies a complete conversion from the low-spin state to the photo-excited metastable high-spin state [2,4,7].

In Fig. 4, one observes that the lifetime of the photo-excited state on the temperature exceeds 10 h at the temperature of 40 K. This result is in agreement with previous spectroscopic, magnetic and Mössbauer measurements [3,7].

3.2. Interpreting the preliminary spin-density map in $[Fe(ptz)_6](BF_4)_2$

PND was applied to determine the experimental magnetic structure factors F_M of the photo-induced high-spin state in $[Fe(ptz)_6](BF_4)_2$. These factors are the Fourier components of the spin density $\rho(r)$ [13]. The magnetic structure factors were deduced from the experimental flipping ratios with the help of the low-temperature structure factors (see Table 2).

$$\vec{F}_{\mathrm{M}}(\vec{K}) = \vec{s}\int_{\text{lattice}} \rho(r)\, e^{iKr}\, \mathrm{d}r \tag{2}$$

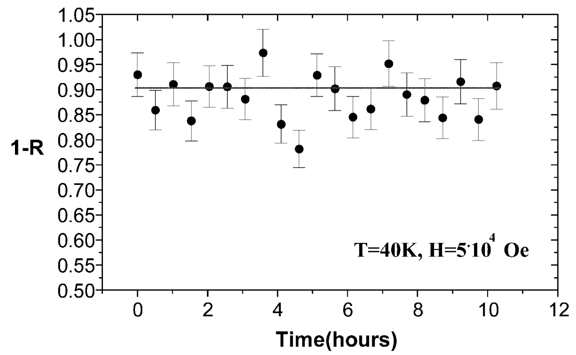

Fig. 4. Lifetime of the photo-excited state at 40 K. The red line is a guide for the eyes.

Table 2
Summary of the flipping ratios and magnetic structure factors obtained for seven unique reflections

h k l	*R*	d*R*	F_M	dF_M
2 0 −7	0.78	0.04	7.94	1.73
2 0 −4	0.69	0.02	7.17	0.62
1 0 −2	0.66	0.02	9.03	0.53
1 0 1	0.24	0.08	16.90	3.91
2 0 2	1.24	0.03	8.78	0.54
2 0 5	1.14	0.04	8.70	1.14
2 0 8	0.93	0.04	5.07	1.84

A data set of flipping ratios, *R*, of only the seven strongest unique reflections could be recorded because of the weakness of the diffracted intensities. The limited data set obtained was not sufficiently large to allow a complete free-parameter data refinement. The induced spin density in the unit cell was reconstructed from the F_M data set, using a multipole model refinement given by Eq. (3) [14]:

$$\rho(r) = \sum_i P^i_{00} N_i r^4\, \mathrm{e}^{-\zeta_i r_i} \tag{3}$$

where ζ_i is a Slater exponent deduced from wavefunction calculations reported in the literature [15], P^i_{00} the monopole population centered on the atom i, and N_i is a normalisation coefficient. The radial expansion and the first monopole were refined only for the Fe atom. No significant density was observed in the iterative refinement procedure on the atoms omitted from the final model. The projection of the spin density map along the crystallographic c-axis of the cell is presented in Fig. 5. As expected, the magnetisation is well localised on the iron atoms, and density is not found elsewhere.

The induced moment per iron is given by the monopole population. A moment of $3.2(1)\mu_B$ on the iron sites was obtained by the refinement. At 2 K, under 5 T, the magnetisation of the Fe^{2+} ion in the high-spin state is expected to have reached the magnetic saturation. The theoretical value of the Fe^{2+} moment at saturation, in the case of a completely photo-excited compound, and thus in the 100% high-spin paramagnetic state, is $4\mu_B$ ($S = 2$). The interpretation of the flipping ratios, for seven unique reflections, shows that around 80% of irons were in the high-spin state, which corresponds to the photo-converted part of the crystal. The other part, low-spin, is diamagnetic and it does not contribute to the signal.

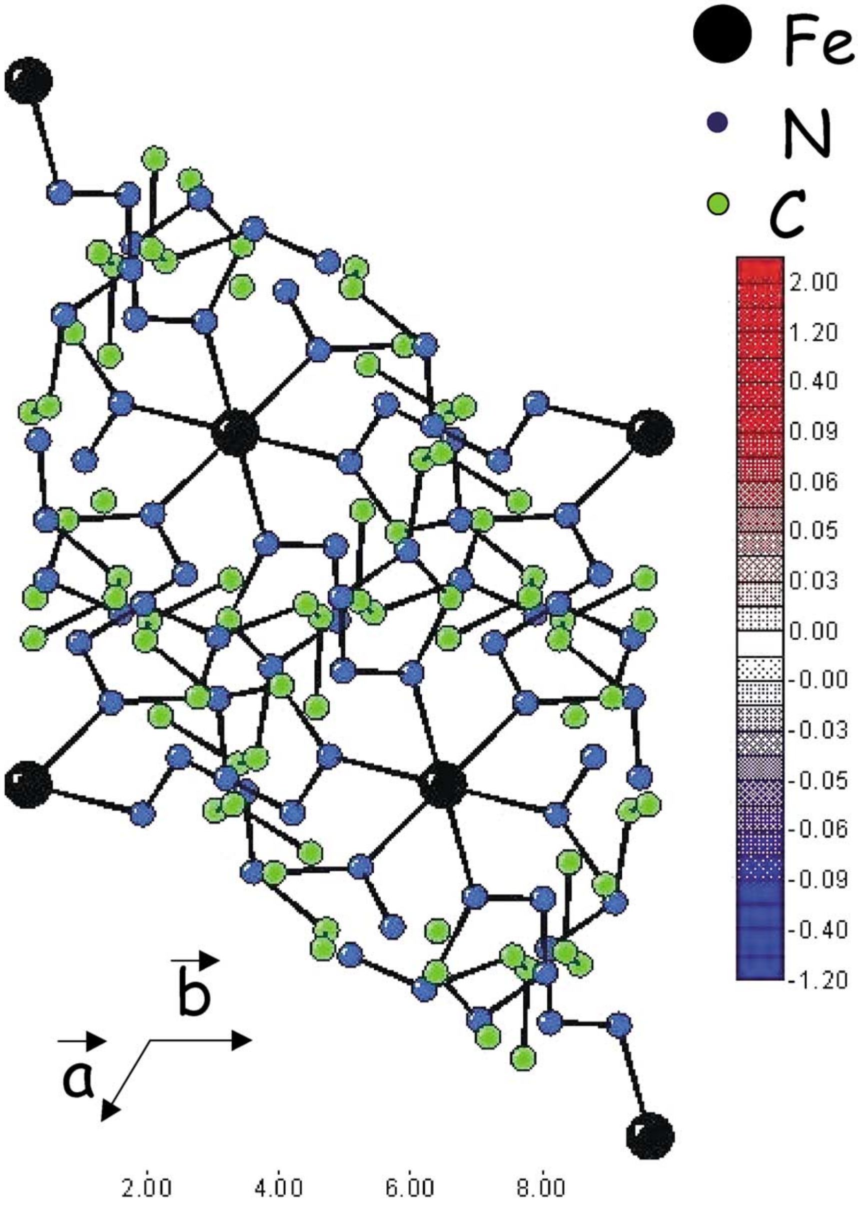

Fig. 5. Spin density map of the photo-induced state of $[Fe(ptz)_6](BF_4)_2$ at 2 K under 5 T projected along the crystallographic c-axis. The scale is given in Bohr magneton and the axis in angströms. The rhombohedric lattice is superposed to a spin density map, and the red regions represent the highest spin density around the iron.

4. Conclusion

The PND technique, using an optical fiber, enabled measurements of the spin density map on a photo-excited state of the spin-crossover single crystal $[Fe(ptz)_6](BF_4)_2$. The photo-excitation curve was deduced by following the flipping ratio of two known reflections. This validated new experimental setup is actually under optimisation for all geometries of the crystal [10]. Baring in mind that the spin density map is one of the descriptions of the magnetic state that contains the largest number of information, the possibility to examine magnetic nature of photo-induced states in various compounds should be useful for future studies of photo-switchable magnetic materials.

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