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Photoinduced molecular switching studied by polarized neutron diffraction

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The photo-induced magnetization density of the photoswitchable $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ (ptz = 1-propyltetrazole) spin crossover compound is reported. The photoswitching process is observed by using a experimental setup allowing both light illumination and polarized neutron diffraction measurements (PND). We studied the photoexcitation kinetics, and the photoinduced magnetic properties of the $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ compound by PND, which evidenced a complete photoprocess. The temperature dependence of the photoinduced magnetization obtained by PND is well described by an Ising model taking into account the magnetic anisotropy and the spin-orbit coupling. The thermal relaxation towards the stable electronic state was observed in the 55–60-K temperature interval. The magnetization density around the Fe position is well described by the Fe^{2+} magnetic form factor.

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There is currently a worldwide drive to develop devices where the spin of the electron is used to store or process information, either in addition to or instead of the charge. Although many device designs have been put forward, finding materials with which to implement them remains a significant experimental challenge. The field of molecular magnetism has received a boost in recent years courtesy of the development of new compounds possessing physical properties which may be of relevance to applications related to information storage and optical commutation. Indeed, the magnetic, optical, and electronic nature of these systems can be easily controlled and tuned by light, pressure, or magnetic field.[1]

Optical switching is one of the most intense areas of interest in memory molecules. Spin crossover solids represent a promising example of photoswitchable materials, studied for future applications such as optical memories or numerical displays.[1] They contain an octahedrally coordinated transition metal ion with the $3d^n$ electronic configuration and can cross over between a low spin (LS) and high spin (HS) state. The flip between the two states usually occurs with a temperature change, under pressure or under light illumination. Spin crossover compounds containing the Fe^{2+} ion have LS and HS spin states characterized by spins of $S=0$ (diamagnetic) and $S=2$ (paramagnetic). Photoexcitation at low temperature, with light of a suitable wavelength, can induce a switching of the system to a metastable state having an extremely long lifetime at low temperatures. Therefore the effect is called light induced excited spin state trapping (LIESST).[2] The photo-process involves, either a metal to ligand charge transfer, or d-d transitions. For typical Fe^{2+} compounds, absorption bands for the LS→HS process are located around ~ 500 nm (metal ligand charge transfer), 550 nm (d-d) respectively. The reverse process (HS→LS) occurs by irradiation at ~ 750 nm, with a lower efficency, due to a branching ratio of 4:1 for the direct and reverse processes, respectively.

Polarized neutron diffraction is a powerful tool to study the magnetization densities in crystals, due to the fact that it provides direct information about the three-dimensional distribution of the magnetization throughout the unit cell. PND experiments yield the Fourier transform of the magnetic moment density within the crystal. Although PND is a widely used technique for mapping unpaired electron densities, to our knowledge it has never been applied to the study of photoinduced magnetic states. For this purpose we have developed an experimental setup designed to carry out *in situ* photoexcitation experiments. The present paper reports on the study of the photo-induced magnetic state of the $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ (ptz = 1-propyltetrazole) spin crossover compound by PND.

The $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2]$ spin crossover compound is one of the most extensively studied photo-switchable molecular based magnets.[2] Single crystals of $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ in the form of hexagonal plates were obtained by slow evaporation from a saturated nitromethane solution.[3] According to Ref. 2, $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ crystallizes in the trigonal $R\bar{3}$ space group; $a=b=10.720(1)$ Å, $c=31.640(1)$ Å, $\alpha=90°$, $\beta=90°$, and $\delta=120°$ at 2 K. Upon slow cooling, $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ exhibits a thermal spin transition (low temperature = low spin, high temperature = high spin) followed by a crystallographic phase transition with $T_c^{\downarrow}=128$ K and $T_c^{\uparrow}=135$ K at ambient pressure. The space group is $R\bar{3}$ above $T_c^{\uparrow}$ and $P1$ below $T_c^{\downarrow}$. The thermal spin transition in both cases is quite abrupt due to the cooperative effects of elastic origin present in such a neat spin-crossover crystal (see Ref. 4 for details). Upon fast cooling, the crystallographic phase transition can be suppressed,[4] so that the crystal remains in the $R\bar{3}$ space group even below $T_c^{\downarrow}$. Therefore, before photo-excitation experiments, the crystal was quenched in liquid nitrogen in order to suppress the crystallographic phase transition and to keep the high-temperature rhomboedric phase. To avoid a possible $\mathrm{Fe}^{2+}\rightarrow\mathrm{Fe}^{3+}$ oxidation, the sample was encapsulated in a contaner having a quartz disc to allow light illumination.

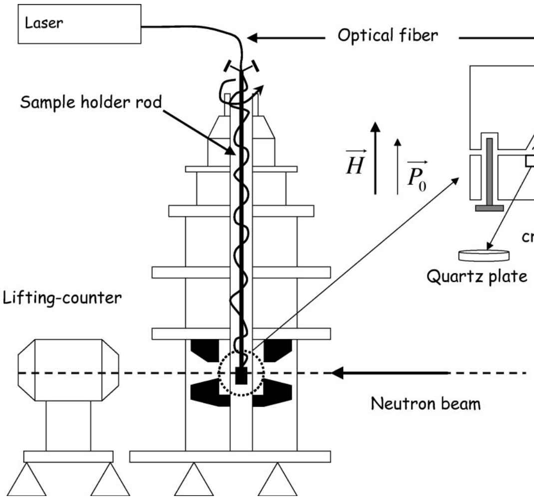

FIG. 1. Schematic experimental setup of the polarized neutron diffractometer. In the inset, the sample holder allowing light irradiation is sketched. P_0 corresponds to the neutron polarization direction.

Polarized neutron measurements were performed on the two-axis lifting-counter diffractometer 5C1 at the ORPHEE reactor, LLB CEA/Saclay, using a wavelength $\lambda = 0.845$ Å (Heusler alloy monochromator, polarization of the incident neutron beam $P_0 = 0.91$). Higher-order contamination was suppressed to less than 0.01% by means of erbium filters. By using a polarized beam, one measures the flipping ratio R of Bragg reflections (hkl), which is the ratio of scattered intensities for "up" (parallel to the applied field, $I\uparrow$) and "down" (antiparallel $I\downarrow$) polarizations of the incident beam. If the crystal is centrosymmetric, the nuclear and magnetic structure factors $F_N(\mathbf{Q})$ and $F_M(\mathbf{Q})$ are real quantities, and the flipping ratios are related to the magnetic structure factors $F_M(\mathbf{Q})$, by the following expressions:

$$R(h,k,l) = \frac{I\uparrow}{I\downarrow} = \frac{F_N^2 + F_{M\perp}^2 + 2F_N F_{M\perp z}}{F_N^2 + F_{M\perp}^2 - 2F_N F_{M\perp z}},$$

$$F_{M\perp} = F_M \sin\alpha, \quad F_{M\perp z} = F_M \sin^2\alpha,$$

where α is the angle between the scattering vector (hkl) and **z**. The F_M's s may be directly deduced from the experimental flipping ratios if the crystal structure of the compound is known.[6]

The sample rod of the 5C1 diffractometer has been modified to carry out photoexcitation experiments. The principle of the experimental setup is shown in Fig. 1. The sample, placed inside of a superconducting cryomagnet, was exposed to laser light. For this purpose, an access port to run optical fibre from top to bottom of the sample rod was created.

Prior to PND measurements, superconducting quantum interference device (SQUID) magnetization measurements have been carried out on a small crystal of about 0.15 mm^3 to determine the easy magnetic axis. The magnetization as a function of magnetic field at 2 K and the magnetization as a function of temperature in 5 T have been measured. From these experiments the **c**-axis was found to be the easy magnetization axis.

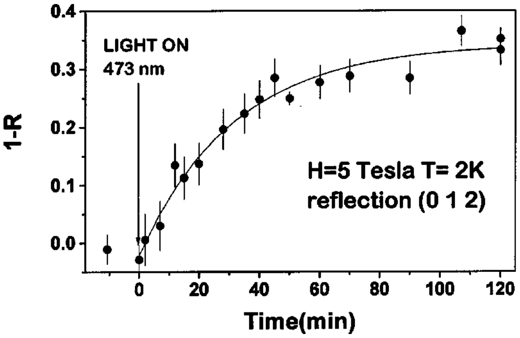

FIG. 2. Kinetics of the photoexcitation of $[\text{Fe(ptz)}_6](\text{BF}_4)_2$. at 473 nm, 2 K, and 5 T. Flipping ratio of (1 0 2) reflection with the magnetic field parallel to the [001] direction as a function of time. The first point is measured before illumination and corresponds to a reference point. Solid line is a guide to the eye.

The PND experiment was performed on a single crystal of about 15 mm^3. The crystal was first quenched in liquid nitrogen to keep the high symmetry and then cooled down to 2 K and set in the cryomagnet installed on the 5C1 diffractometer. The magnetic field was applied parallel to the **c** axis. The crystal was exposed to a laser illumination of 3 mW/cm^2. The light direction was perpendicular to the crystal surface. The optical wavelength ($\lambda = 473$ nm) was slightly shifted from the maximum absorption wavelength for Fe^{2+} (550 nm), but the LIESST (Ref. 2) effect (the low spin to high spin phototransformation) is still very efficient for this wavelength.

The time dependence of the photoexcitation process of the crystal was followed directly by PND in a constant magnetic field of 5 T. For this purpose, the flipping ratio of the (0 1 2) reflection was measured as a function of time. To avoid the heating of the sample by the laser light, we carried out a chopped light experiment.[5] The time evolution of $(1\text{-}R)$ of the crystal under illumination by the laser at 2 K is shown in Fig. 2. Under illumination, the decrease of flipping ratio (R) and thus the increase of the magnetization of the $[\text{Fe(ptz)}_6](\text{BF}_4)_2$ crystal is clearly seen. After ~1 h 30 min of illumination, the saturation was reached and the light turned off. The kinetics of the photoswitching is in good agreement with previous results obtained by Mössbauer spectroscopy and magnetization measurements.[2,6]

The magnetization curves of the photoinduced state as a function of field, at 2 K, obtained by PND and SQUID experiments, are presented in Fig. 3. As seen from Fig. 3, the magnetic saturation is obtained for a field of about 1 T. The magnetic data derived from the flipping ratios agree quite well to those obtained in a SQUID magnetometer under the same conditions. The experimental data can be fitted by a simple Ising model, described by a $S = 1/2$ fictitious spin and a magnetic splitting $\Delta = g_{//}\mu_B B_z$. In this model, the magnetic anisotropy due to crystal field and spin-orbit coupling[7,8,11] on the ${}^5D$ state of high spin Fe^{2+} in trigonal symmetry is taken into account. As the magnetization along an easy magnetic axis is measured this situation results in a highly anisotropic ground doublet. The magnetization is given by

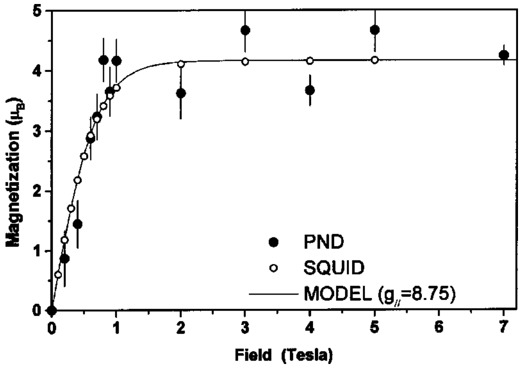

FIG. 3. Magnetization as a function of field of $[\mathrm{Fe(ptz)}_6]$ $\times(\mathrm{BF}_4)_2$ at 2 K after photoexcitation, recorded in the dark. PND (●) and SQUID (○) data on the same crystal. Solid line is computed using the Ising model (see the text). SQUID data have been normalized with the theoretical value of the high spin Fe^{2+} moment at saturation.

$$\mathrm{M}(T,H)=A\tanh\left(\frac{g_{//}\mu_B H}{2k_B T}\right).$$

The fit of the experimental data reported in Fig. 3 using this model yields the parameter value $g_{//}=8.75$. This value is slightly larger than the spin-only value $(g_{//}=8)$ expected for the pure high-spin state $S=2$, suggesting the existence of a sizeable orbital contribution due to the spin-orbit coupling.

The temperature dependence of the magnetization in the photo-excited state of the $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$ crystal was measured by PND and SQUID at 2 K and 5 T and a good agreement between the two techniques was found (Fig. 4). Below 50 K, the model fits well the PND and SQUID data with $g_{//}=8.75$. Above this temperature, the effect of the relaxation towards the electronic ground state dominates and thus the model is no longer valid. The relaxation of the photoexcited state towards the stable state, due to thermal activation of the HS→LS relaxation process,[9] is observed at $\sim$55–60 K, merely resulting in a rather sharp (irreversible) drop of the magnetization at the temperature sweeping rate $\sim 0.1\ \mathrm{K\,min}^{-1}$. The shift between PND and SQUID relaxation temperatures is due to kinetics effect. Indeed, the sweeping rate was faster during the SQUID experiment $(\sim 0.5\ \mathrm{K\,min}^{-1})$ and increased artificially the relaxation temperature. These results are also in good agreement with those obtained by reflectivity measurements.[8]

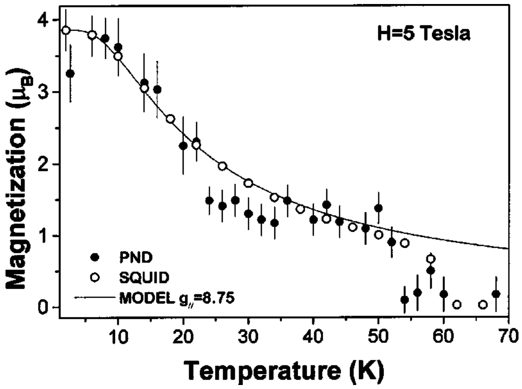

FIG. 4. Magnetization as a function of temperature at 5 T, of the photo-excited state of $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$, created by illumination at $\lambda=473$ nm, $P=3\ \mathrm{mW/cm}^{-2}$ t=1 h 30, H=5 Tesla. Temperature sweeping rate is $\sim$0.1 K/min. PND (●) and SQUID (○) data on the same crystal. The solid line is computed using the static Ising model (see the text).

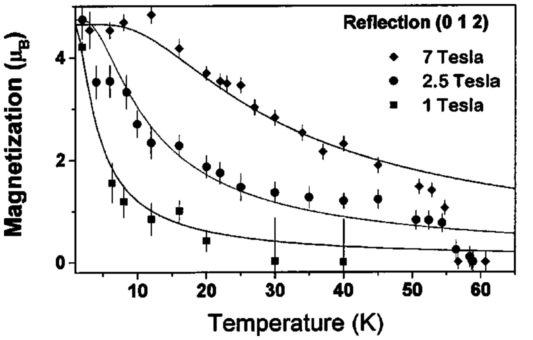

FIG. 5. Magnetic data for the thermal relaxation decay, in the dark, of the photoexcited state of $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$, created by illumination at $\lambda=473$ nm, $P=3\ \mathrm{mW/cm}^{-2}$, and $t=1$ h 30, recorded for different values of the magnetic field: 1, 2.5, 7 T. The temperature sweeping rate is $\sim$0.1 K/min. Solid line is computed using the static Ising model (see the text).

Figure 5 sums up the results obtained on the photoinduced state after renewed photo-excitation for magnetic fields of 1, 2.5, and 7 T. For all the fields, the relaxation of the excited electronic state is observed at $\sim$55–60 K. The plateau below 20 K, due to the spin-orbit coupling, is enlarged in a magnetic field of 7 Tesla compared to 5 T (Fig 4). The typical paramagnetic $(1/T)$ behavior is clearly seen for weaker magnetic fields (1 and 2.5 T). The field-temperature dependence of the magnetization is well described by the above model using the same $g_{//}=8.75$.

A data set of flipping ratios, of 67 strongest unique reflections has been recorded for the photoexcited electronic state at 2 K and 5 T. The magnetic structure factors of all measured reflections were obtained using the F_N derived from x-ray diffraction structural parameters. The measured magnetic structure factors normalized by iron are shown in Fig. 6 together with the theoretical (spin only) magnetic form factor of a free Fe^{2+} ion. As seen from Fig. 6, the majority of measured magnetic amplitudes lie reasonably close to the theoretical curve. There are however, some reflections, especially those at low **Q**, for which the disagreement between

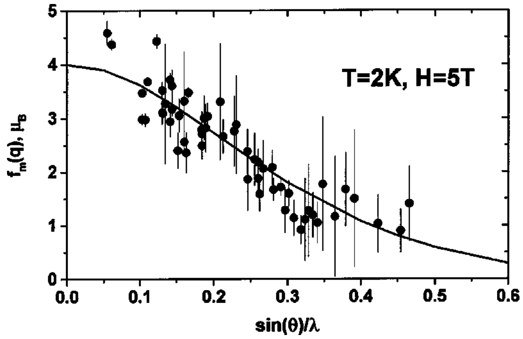

FIG. 6. Photoinduced state of $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$ at 2 K, 5 T: the magnetic amplitude per iron atom as a function of sin θ/λ, compared to the theoretical form factor of high-spin Fe^{2+} (solid line).

experimental and theoretical values is noticeable. This can be due to errors introduced when using the x-ray structure to determine F_N, particularly with respect to hydrogen atom positions.

The distribution of the magnetization density in the unit cell was reconstructed from the $F_M(\mathbf{Q})$ data, using a multipole model refinement given by equation $\rho(\mathrm{r})=\Sigma_{\mathrm{i}}\mathrm{P}_{00}{}^{\mathrm{i}}\mathrm{N}_{\mathrm{i}}\mathrm{r}^4\mathrm{e}-\zeta_{\mathrm{i}}\mathrm{r}_{\mathrm{i}}$,[10] where ζ_{i} is a Slater exponent deduced from the wave function calculations reported in literature,[11] $\mathrm{P}_{00}{}^{\mathrm{i}}$ is the population of the monopole centered on the atom i, and N_{i} is a normalization coefficient. The radial expansion and the first monopole population were refined for the Fe and N atoms. No significant density was observed in the refinement procedure on the nitrogen atoms $[0.03(5)\mu_{\mathrm{B}}]$. The projection of the magnetization density map on the crystallographic **c** axis of the cell is presented in Fig. 7. As already mentioned, the value of F_N were not accurate enough to go beyond the monopoles refinement. Further neutron diffraction measurements are scheduled to define the hydrogen positions and improve the F_N values. A moment of $4.05(7)\mu_{\mathrm{B}}$ on the iron site (with $\chi^2=5.11$) obtained in the refinement is very close to the theoretical value of the Fe^{2+} moment at saturation $(S=2)$. This provides direct evidence of a complete phototransformation of the crystal.

To summarize, the photoexcitation process of a $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$ crystal was unambiguously evidenced by PND. Thermal relaxation towards the stable electronic state was observed in the 55–60-K temperature interval. The field-temperature dependence of the magnetization was well described by an Ising model taking into account the magnetic anisotropy due to crystal field and the spin-orbit coupling on the ^5D state of high spin Fe^{2+} in trigonal symmetry. The magnetization density around the Fe position was well described by the Fe^{2+} magnetic form factor. Moreover, the magnetization density map does not show any significant spin delocalization at the sites of N (less than $0.08\mu_{\mathrm{B}}$).

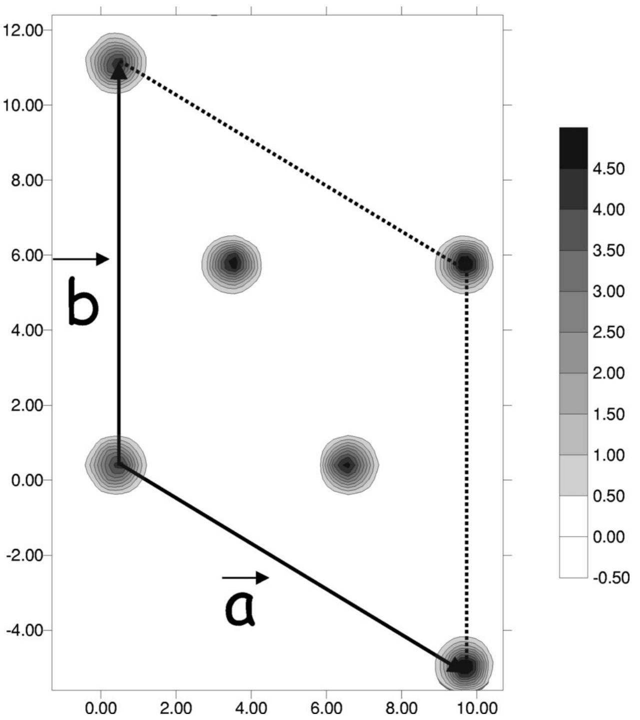

FIG. 7. Reconstructed magnetization density map of the photo induced state of $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$ at 2 K, and 5 T, projected along the *c* axis.

More generally, polarized neutron diffraction provides the spatial distribution[12,13] of the magnetization density. This information cannot be obtained by the most sensitive macroscopic technique (SQUID) which has been used up to now in the LIESST studies. The investigation of the photoinduced magnetic state at the microscopic level by PND should allow to look further into knowledge of the photoinduced magnetic states.

We believe that the PND have a great potential in studies of a variety of systems, like cyanometalate-based magnets,[14,15] spin crossover complexes,[16] diluted magnetic semiconductors,[17] doped manganites,[18] and spinel ferrite films,[19] where photoinduced magnetic effects have been evidenced.

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