



PHOTOINDUCED MOLECULAR SWITCHING STUDIED BY POLARISED NEUTRON DIFFRACTION

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The design of molecules that could be utilised for information storage is one of the main challenge in molecular material science and optical switching is one of the most intense areas of interest in memory molecules.

Spin crossover solids represent a promising example of photo-switchable materials, studied for future applications 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 a 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 a LS and a HS spin states characterized by spins of $S=0$ (diamagnetic) and $S=2$ (paramagnetic). Photo-excitation at low temperature, with a suitable light wavelength, can provide a switching of the system to a photoinduced 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 $\text{LS} \rightarrow \text{HS}$ process are located around ~ 500 (Metal Ligand Charge Transfer), 550 (d-d) respectively. The reverse process ($\text{HS} \rightarrow \text{LS}$) occurs by irradiation at ~ 750 nm, with a lower efficiency, due to branching ratio 4:1 for the direct and reverse processes, respectively.

Polarised neutron diffraction is a powerful tool to study the magnetisation densities in crystals and has never been applied so far to the study of photo-induced magnetic states. Figure 1 shows the new experimental setup designed to carry out “in situ” photo-excitation experiments, we have developed for this purpose. The photo-switching process of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ compound was observed by polarised neutron diffraction measurements (PND) as shown on Figure 2. The moment of $4.05(7) \mu_B$

on the iron site (with $\chi^2 = 5.11$) obtained by refinement is very close to the theoretical value of the Fe^{2+} moment at saturation ($S=2$). This evidences a complete photo-transformation of the crystal.

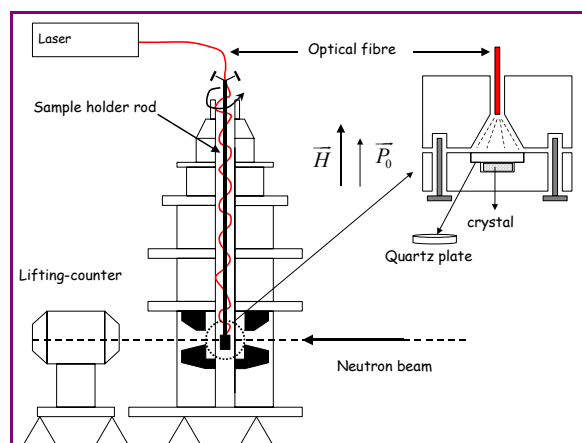


Figure 1 Schematic experimental setup of the polarized neutron diffractometer. In the inset, the sample holder allowing light irradiation is sketched. P_0 corresponds to the neutron polarisation direction.

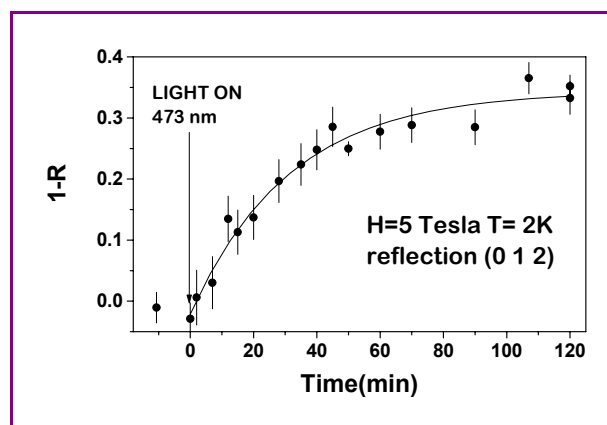


Figure 2 Kinetics of the photo-excitation of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 473 nm, 2 K, 5 T. Flipping ratio of (1 0 2) reflection with the magnetic field parallel to the [001] direction as a function of time. The first point is measured before illumination and corresponds to a reference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



In Figure 3, the temperature dependence of the magnetisation in the photo-excited state of the crystal, measured under different fields, is displayed. Experimental curves were well fitted with a model that takes into account the magnetic anisotropy due to crystal field and spin-orbit coupling on the 5D state of high spin Fe^{2+} in trigonal symmetry. For each field and on warming the sample up to 70 K, the relaxation of the excited electronic state is also observed at ~ 55 -60 K.

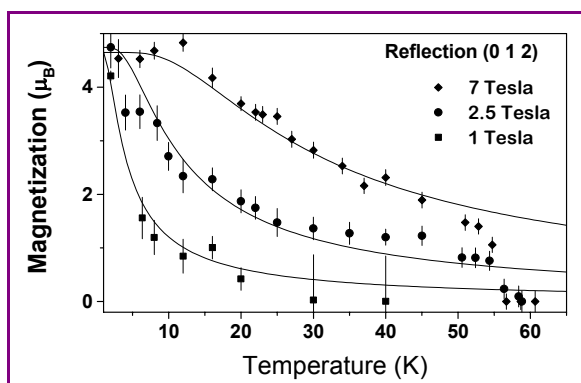


Figure 3 Magnetic data for the thermal relaxation decay, in the dark, of the photo-excited state, created by illumination at $\lambda = 473$ nm, $P = 3$ mW/cm 2 , $t = 1$ h 30, recorded for different values of the magnetic field : 1, 2.5, 7 T. The temperature sweeping rate is ~ 0.1 K/min. Solid line is computed using the static Ising model

A data set of flipping ratios, of 67 strongest unique reflections has been recorded for the photoexcited electronic state at 2K and 5 Tesla. The magnetic structure factors of all measured reflections were obtained using the F_N derived from X-ray diffraction structural parameters. The distribution of magnetisation density in the unit cell was reconstructed from the $F_M(Q)$ data, using a multipole model refinement. 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. The photo-induced magnetisation density is presented in Figure 4 and Fe^{2+} magnetic form factor have been obtained

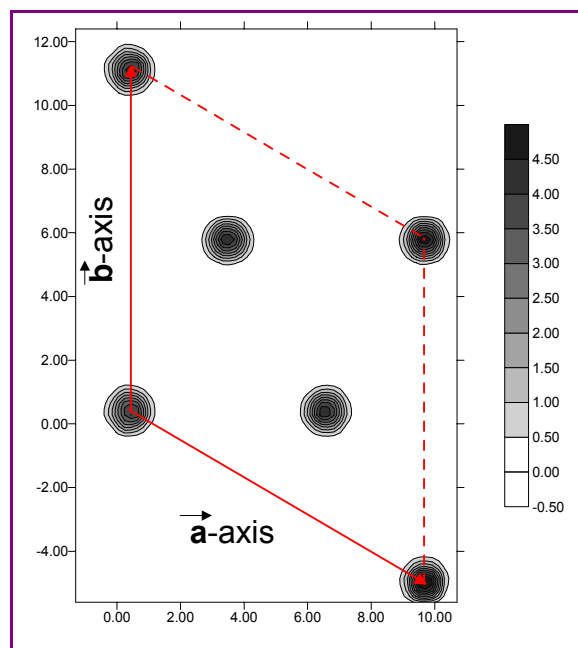


Figure 4. Reconstructed magnetisation density map of the photo-induced state of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 2K, 5T, projected along the c-axis.

The large possibilities of PND in providing information on the magnetic coupling scheme, the spin density distribution and spin delocalisation effects could be useful for other photo-magnetic crystals. PND investigations of photoinduced state could reveal to be very informative in a variety of systems, including cyanometalate-based magnets,[3] spin crossover complexes [4], diluted magnetic semiconductors[5], doped manganites[6], and spinel ferrite films where photoinduced magnetic effects have been evidenced.

References

- [1] Kahn O., La Recherche **262** (1994) 160.
- [2] Decurtins S., Gütllich P., Hasselbach M. K., Spiering H., and Hauser A., Inorg. Chem. **24** (1985) 2174.
- [3] Sato O., Iyoda T., Fujishima A., and Hashimoto K., Science **272** (1996) 704.
- [4] Ogawa Y., Koshihara S., Koshino K., Ogawa T., Urano C., and Takagi H., Phys. Rev. Lett. **84** (2000) 3181.
- [5] Koshihara S., Oiwa A., Hirasawa M., Katsumoto S., Iye Y., Urano C., Takagi H., and Munekata H., Phys. Rev. Lett. **78**(1997) 4617.
- [6] Matsuda K., Machida A., Moritomo Y., and Nakamura A., Phys. Rev. B **58** (1998) 4023.