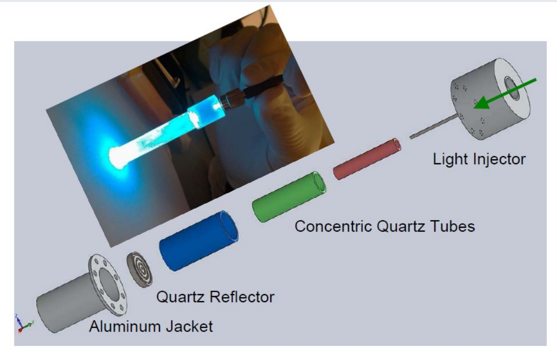
Probing photoinduced spin states in spin-crossover molecules with neutron scattering

K. Ridier, F. Damay, G. Chaboussant (LLB), G. A. Craig, M. Murrie (University of Glasgow), T. Fennell (Paul Scherrer Institut).

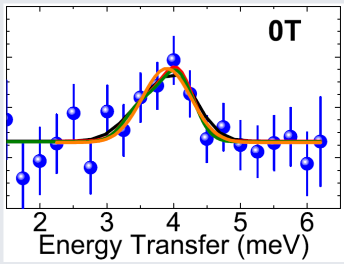
We report a neutron-scattering investigation of the spin-crossover compound [Fe(ptz)6](BF4)2,which undergoes an abrupt thermal spin transition from high spin (HS), S = 2, to low spin (LS), S = 0, around 135 K. The HS magnetic state can be restored at low temperature under blue/green light irradiation. We have developed a specially designed optical setup for neutron scattering to address the magnetic properties of the light-induced HS state (see Figure 1).



Sample Holder used for INS experiments. The sample holder consists of two concentric 1-mm-thick quartz unpolished cylinders fixed on one end to a quartz injector equipped with a plano-convex lens and at the other end to a quartz reflector. Light, inserted from an optical fiber, is transported across the cylinder and is scattered laterally to irradiate as much of the sample as possible. A fine-powder sample (m=400 mg) is placed in the void between the cylinders. The irradiated surface area is about 3000 mm2, and we estimate that the areal light power may be as high as 0.13 mW/mm2 at a nominal source power of P = 400 mW. A similar setup is used in the diffraction experiment. In no instance did the sample suffer from light damage.

By using neutron diffraction, we demonstrate that significant HS/LS ratios (of up to 60%) can be obtained with this experimental setup on a sample volume considered large (400 mg), while a complete recovery of the LS state is achieved using near-infrared light. With inelastic neutron scattering (INS) we have observed magnetic transitions arising from the photo-induced metastable HS S = 2 state split by crystal-field and spin-orbit coupling (see Figure 2). We interpret the INS data assuming a spin-only model with a zero-field splitting of the S = 2 ground state. The obtained parameters are D ≈ −1.28 ± 0.03 meV and |E| ≈ 0.08 ± 0.03 meV. The present results show that in situ magnetic inelastic neutron-scattering investigations on a broad range of photomagnetic materials are now possible.

One-dimensional cuts along energy transfer with an integrated Q range of 0.6–3.0 Å−1 and energy binning of 0.25 meV. Solid lines are best fits to the INS peaks (using Gaussian line shapes). The existence of such INS peak is a proof that a sizeable amount of Fe(II) ions have been phototransformed to a High-Spin state.



The most important result is the INS study of the photoinduced HS state of a spin-crossover system. From INS magnetic transitions, we have interpreted our data in terms of a spin-only Hamiltonian model to describe the metastable S = 2 ground state and the presence of a zero-field splitting. We demonstrate that it is possible to perform inelastic neutron-scattering studies of photoinduced metastable states of photoswitchable materials. This result opens promising prospects for in situ magnetic inelastic neutron-scattering investigations of a broad range of photomagnetic materials.

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