

**Experiment title:**

Reverse-LIESST experiments on a truly light-induced bistable system

**Experiment****number:**

01-02 971

**Beamline:****Date of experiment:**

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**Date of report:****Shifts:****Local contact(s):**Phil Pattison*Received at ESRF:***Names and affiliations of applicants** (\* indicates experimentalists):**Besnard Celine \*****Chakraborty Pradip \*****Guénée Laure \*****Hauser Andreas \****University of Geneva**Switzerland***Report:****The results of this experiment have been published in****P. Chakraborty, R. Bronisz, C. Besnard, L. Guénée, P. Pattison, A. Hauser, J. Am. Chem. Soc., ASAP  
DOI:10.1021/ja211897t.**

During this experiment, we used the modified version of a Cryovac KONTI - cryostat (Figure 1). The crystal is mounted inside a capillary which is opened on both sides and contacted to the copper plates of the cryostat. To improve the thermal contacts, the crystal was embedded in Apiezon N grease and a copper rod was put inside the capillary with one end inside the grease, close to the crystal, and the other contacted to the copper

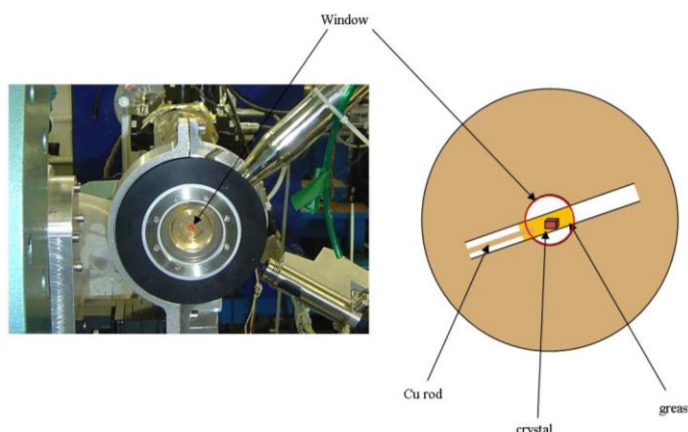


Figure 1 : the cryostat

plate of the cryostat. Although the cryostat was nominally cooled to 9 K, due to the low efficiency of the heat conduction between the crystal and the cryostat plate and the low heat conductivity of the crystal itself, the estimated temperature at the crystal was about 70K, based on comparison with the spectroscopic measurements. The structure

before irradiation corresponds to the reported high-spin structure. After irradiation (15 minutes at 830 nm) the  $c$  - axis is doubled, with diffuse scattering appearing along the  $c^*$  axis (Figure 2). Moreover, splitting of the reflections is observed (Figure 3). The unit- cell seems undergoes a phase transition to a triclinic crystal system. As the crystal goes back to the HS state, either by heating to above 120 K or by irradiating at 472 nm, the splitting of the diffraction peaks completely disappears. We believe therefore that this splitting is associated to a twinning of the crystal due to a lowering of the symmetry from  $P\bar{3}$  to  $P\bar{1}$ . Due to the shadowing of the cryostat, only a small fraction of the reciprocal space could be covered during the diffraction experiment. An average structure could nevertheless be refined in the small unit- cell using the  $P\bar{3}$  symmetry. This refinement gives an average distance of  $1.99(2)$  Å compatible with a full conversion to the LS state.

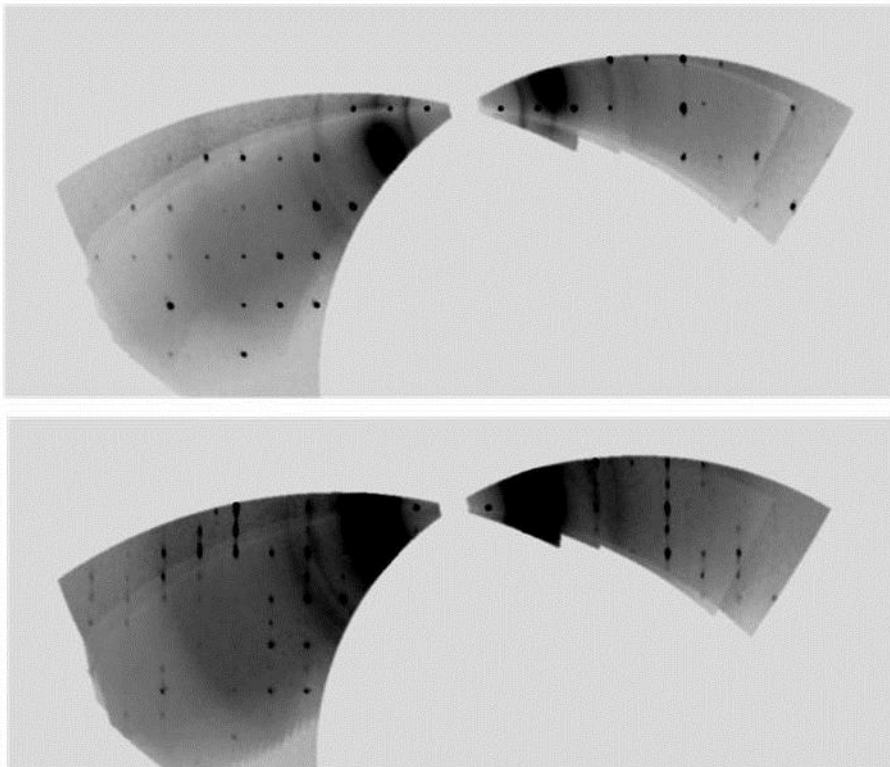


Figure 2 : Reconstruction of the  $h0l$  layer

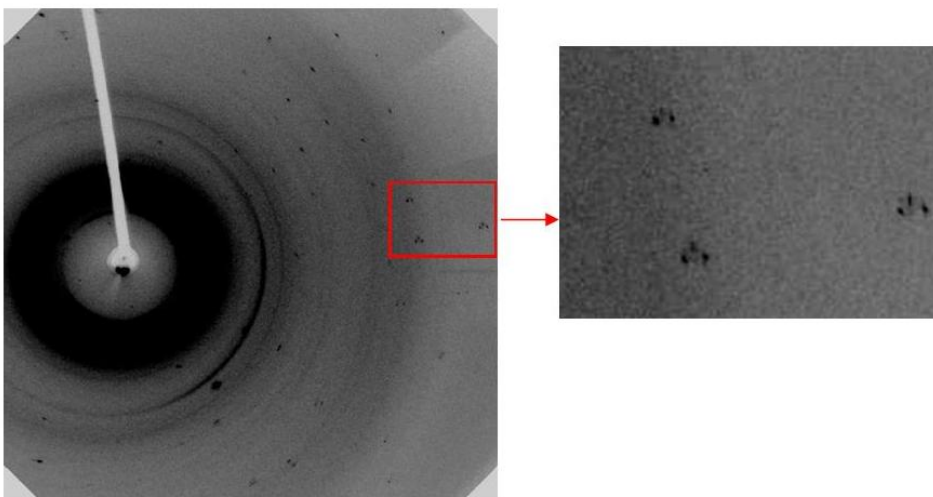


Figure 3: splitting of the diffraction peaks after irradiation