ESRF	**Experiment title:** Electron density distribution of the photo-induced state of $Fe(phen)_2(NCS)_2$	**Experiment number**: **01-02-665**
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Names and affiliations of applicants (* indicates experimentalists):

Sébastien PILLET*, Claude LECOMTE, Vincent LEGRAND*, Mohamed SOUHASSOU, Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, UMR CNRS 7036, Faculté des Sciences, BP 239, 54506 Vandoeuvre lès Nancy, France.

Hans-Peter WEBER*, EPFL Laboratoire de Cristallographie, Ecole Polytechnique de Lausanne, EPFL-SB-IPMC-LCR, CH-1015 Lausanne, Switzerland.

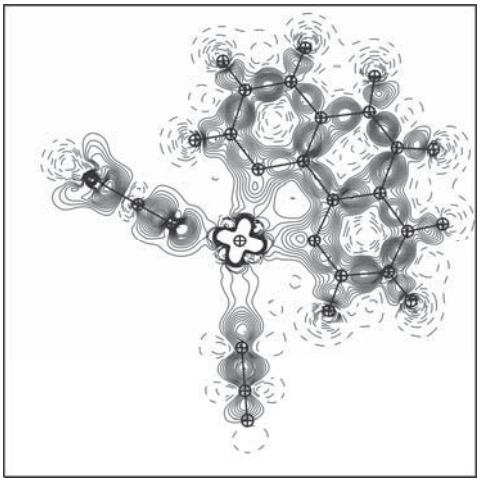
Report :

We aimed at determining for the first time the electron density distribution of the ground and light-induced metastable state of the spin transition compound $Fe(phen)_2(NCS)_2$. The single crystal samples have been synthesized according to two different procedures: by slow solvent diffusion (D) and by extraction (E). The extraction method leads to a complete thermal spin transition whereas the diffusion one exhibits an incomplete thermal spin transition (~ 14 % trapped HS species at low temperatures). We therefore aimed also at characterizing the structural differences between these two samples while the thermal phase transition occurs. Two kinds of experiment have been successfully performed on BM1A :

- a photo-crystallographic high-resolution diffraction measurement at very low temperature on the ground and light-induced metastable state of a D sample for the electron density (ED) analysis
- temperature dependent diffraction measurements from 100 K to 200 K on D and E samples

Electron density distribution of the ground and light-induced states of $Fe(phen)_2(NCS)_2$

We have measured high resolution diffraction data at λ = 0.71 Å using the KUMA 6 circles diffractometer of BM1A in the 4 circles mode and the Onyx CCD. Cryogenic temperatures (T ~ 17 K) have been reached and almost well stabilized with the helijet system to prevent the probed metastable state of $Fe(phen)_2(NCS)_2$ from relaxing to the ground state. This metastable state has been generated using an aligned He-Ne laser (λ = 632 nm, P = 1 mW) under continuous excitation. Data have been collected to 1.0 $Å^{-1}$ in several detector positions and reduced with the inhouse softwares for rejecting shadowed reflections (~20000 measured reflections, merged in ~6500 unique reflections, R_{int} = 0.04). The ED distribution has been refined based on a multipolar model (MOLLY program). The high resolution of the data enabled us to clearly deconvolute thermal smearing effects from the deformation ED, the Hirshfeld rigid bond test being fullfield for all interatomic bonds (this was not the case for our preliminary laboratory measurements due to the lack of high resolution data). The modelled static deformation density is of high quality, as shown on figure 1. The Fe^{II} 3d atomic orbital populations have been derived and are consistent with a high spin electron configuration $(t_{2g})^4(e_g)^2$, these populations indicates also significant σ-donation from the ligands HOMO's. This shows that despite the small size of the samples, which did not permit us to get a reliable data collection using laboratory equipment, the high flux available at the SNBL was absolutely necessary for our project.



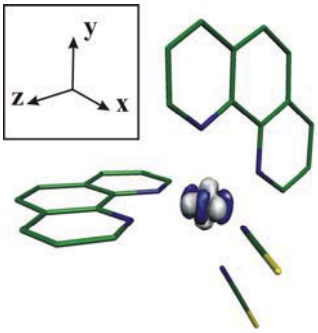
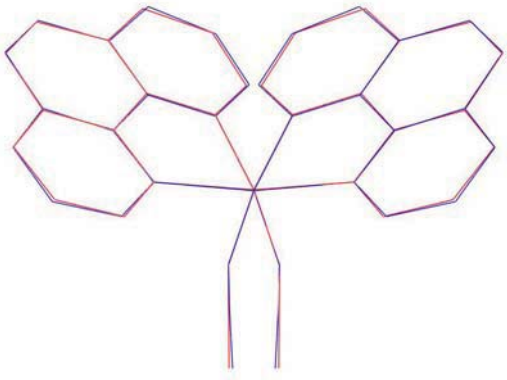


Figure 1. Deformation density of the light-induced high spin metastable state of Fe $(Phen)_2$ $(NCS)_2$ and Fe deformation density with respect to the local coordinate system.

Structural characterization of the thermal spin transition

We have measured diffraction data on the D and E samples at three different temperatures on passing through the thermal spin transition : at T = 112 K, T = 165 K and T = 200 K. The corresponding crystal structures have been determined by direct methods and refined by least squares using Shelx. The comparison of the crystal structures indicates some small differences (figure 2) as one might expect since the thermal spin transitions of E is complete whereas D exhibits a residual 14% HS state below the thermal transition (T < 185 K). However, a systematic lengthening of the Fe-N bond lengths is not observed in the D case. This observation can be rationalized if one consider a random distribution of the residual HS species, which do not contribute to the Bragg diffracted intensity, but instead give diffusion around. The derived anisotropic displacement parameters of the D sample are higher than the E one, which can be correlated to static disorder in this former case.



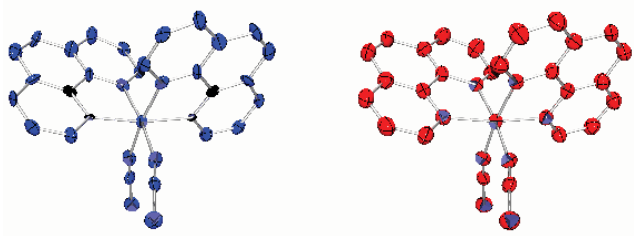


Figure 2. Comparison of the molecular structure of the D and E samples at T = 165 K, just before the thermal spin transition (D in red, E in blue).

In a separate experiment, we have measured diffraction data increasing the temperature from 112 K to 200 K. The measurement consists of a single frame of an ω rotation of 30 ° with a crystal oriented along its *a* axis. We have observed for the D and E samples an evolution of the crystal lattice caracteristic of spin-like domains formation during the thermal spin transition (figure 3). We have already observed such an effect for the thermal spin transition of $Fe(btr)_2(NCS)_2.H_2O$. This suggest that the phase transition in Fe $(Phen)_2$ $(NCS)_2$ does not follow a random process but occurs through nucleation and growing of spin like domains whatever the sample preparation method D or E.

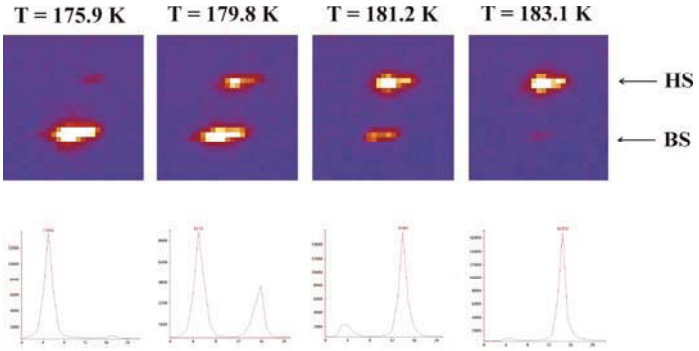


Figure 3. Thermal evolution of the intensity of the (-6 0 -2) reflection for an E sample on increasing the temperature through the thermal spin transition.