ESRF	**Experiment title:** Structural analysis of the incommensurate metastable phase of $\{Fe(abpt)_2[N(CN)_2]_2\}$	**Experiment number**: HS 2980
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Names and affiliations of applicants (* indicates experimentalists):

Sébastien PILLET*, Claude LECOMTE, Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, UMR CNRS 7036, Nancy Université, 54506 Vandoeuvre lès Nancy, France.

I-Jui HSU*, Yu WANG, Chemistry Dpt, Taiwan National University, Sec 4 Roosevelt Road, Taipei, Taiwan.

Michal DUSEK*, Institute of Physics, Cukrovarnicka 10, 16253 Praha, Czech Republic.

Report:

We have analysed, by x-ray diffraction using laboratory equipment, the structural properties of the spin crossover complexe $\{Fe(abpt)_2[N(CN)_2]_2\}$ which exhibits a two step spin transition. Its crystal structure consists of two independent molecules in the asymmetric unit (Fe1 and Fe2). The magnetic properties indicate a complete thermal transition in two steps centered at 87 K where 50 % of the high spin (HS) to low spin (LS) conversion occurs. The first step corresponds to the spin transition of only one molecule of the asymetric unit, while the second step corresponds to the spin transition of the second molecule. At very low temperature, light irradiation induces a complete conversion to a metastable HS-HS phase (both Fe1 and Fe2 in HS state), which can also be obtained by flash cooling from room temperature (thermal trapping). Preliminary diffraction measurements using laboratory equipment have shown that the diffraction pattern of the metastable phase exhibits satellite reflections related to an incommensurate ordering of the structure. Only first order satellites were observable and of poor quality in the preliminary laboratory measurement.

We aimed at collecting high quality single crystal diffraction data on the thermally quenched metastable state on the SNBL. The metastable state was generated by rapid thermal trapping from room to very low temperature using the Helijet system and kept at 15 K to prevent from thermal relaxation to the ground state. In order to get a high signal to noise ratio for the satellite and main reflections, we specifically used the MAR 345 Image Plate detector. We collected a complete data set up to $0.7 Å^{-1}$ resolution. Owing to a problem in temperature stability and calibration of the Helijet system, part of the data set had to rejected. However, a descent data set has been obtained which allowed a complete structural refinement of the modulated structure. Compared to the laboratory measurements, the SNBL data is of much higher accuracy, especially for the satellite reflections: (lab data: R_{int} (m=0) = 0.044, R_{int} (m=±1) = 0.287) and (SNBL data: R_{int} (m=0) = 0.017, R_{int} (m=±1) = 0.045). In addition, it is to be noted that second order satellites have even been measured on the SNBL (see figure 1).

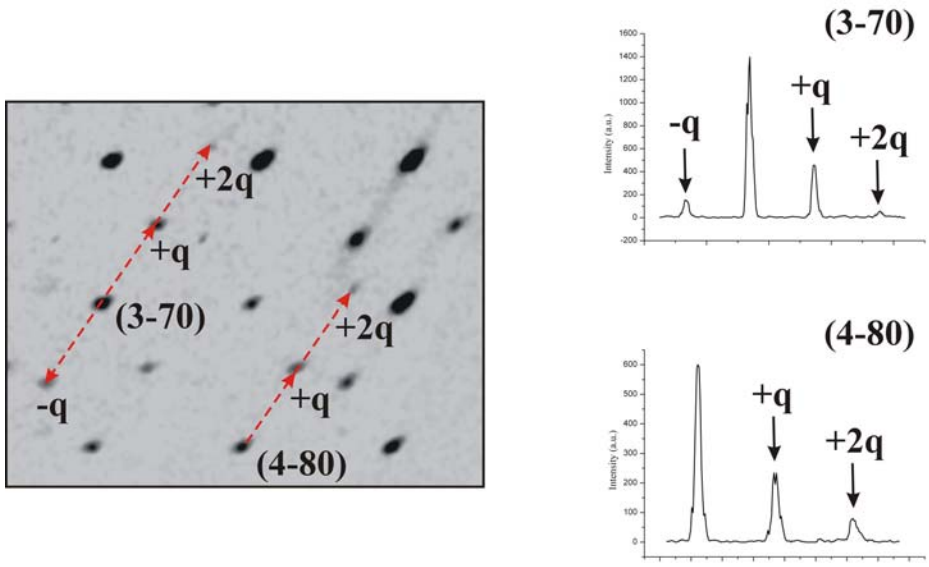

Figure 1. Part of reciprocal space enlightening the presence of second order satellites (ESRF data set).

The modulated crystal structure has been solved directly in the superspace group P-1(αβγ) and refined using JANA2000. Rigid molecular groups have been defined for each of the two molecules of the asymetric unit. These rigid groups exhbit displacive harmonic modulations and one dicyanamide ligand presents in addition a crenel occupational modulation. The complete structural model includes 73 modulation parameters. An example of a section of the superspace Fourier synthesis is given in figure 2, showing the displacive modulation of Fe2. Correlatively, the structural parameters such as Fe-N bond lengths present a high modulation as illustrated in figure 2.

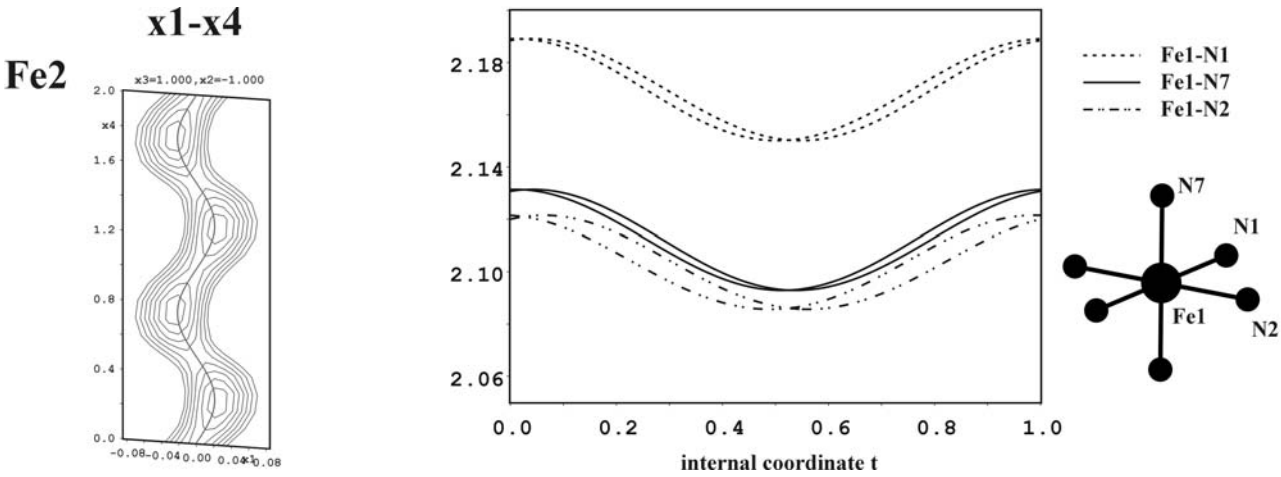

Figure 2. x1-x4 section of the superspace Fourier synthesis and modulation of the Fe1-N bond lengths

The refined crystal structure of the metastable state of $\{Fe(abpt)_2[N(CN)_2]_2\}$ has allowed us to propose a mechanism for the incommensurate ordering, based on a competition of local interactions. A paper corresponding to these results is under preparation and will be submited shortely for publication.