CH1622
Investigations into the Structural Phase Transition in Spin Transition Compound $[Fe(bpp)_2(NCS)_2].2H_2O$

A. Bhattacharjee[1], J. Kusz[2], M. Zubko[2], H.A. Goodwin[3], P. Gütlich[1]

[1]Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität, Mainz, Germany,
[2]Institute of Physics, University of Silesia, Katowice, Poland
[3]School of Chemistry, University of New South Wales, Sydney, Australia

Beamline: ID31
Date of experiment: 28.11.2003 – 1.12.2003

We have studied the high spin and low spin structural phases of the two-step spin transition compound $[Fe(bpp)_2](NCS)_2.2H_2O$ (bpp: 2,6-bis(pyrazol-3-yl)pyridine) of different sample history with X-ray synchrotron powder diffraction at different temperatures. The synchrotron data were collected for λ = 0.32696Å on the high-resolution powder diffractometer at the beamline ID31 at different temperatures for samples with different history. For these measurements the powder sample was enclosed in a quartz capillary of diameter 0.5mm. The measurements were performed within 0.5° $\leq 2\theta \leq$ 30° range with steps of 0.002°.

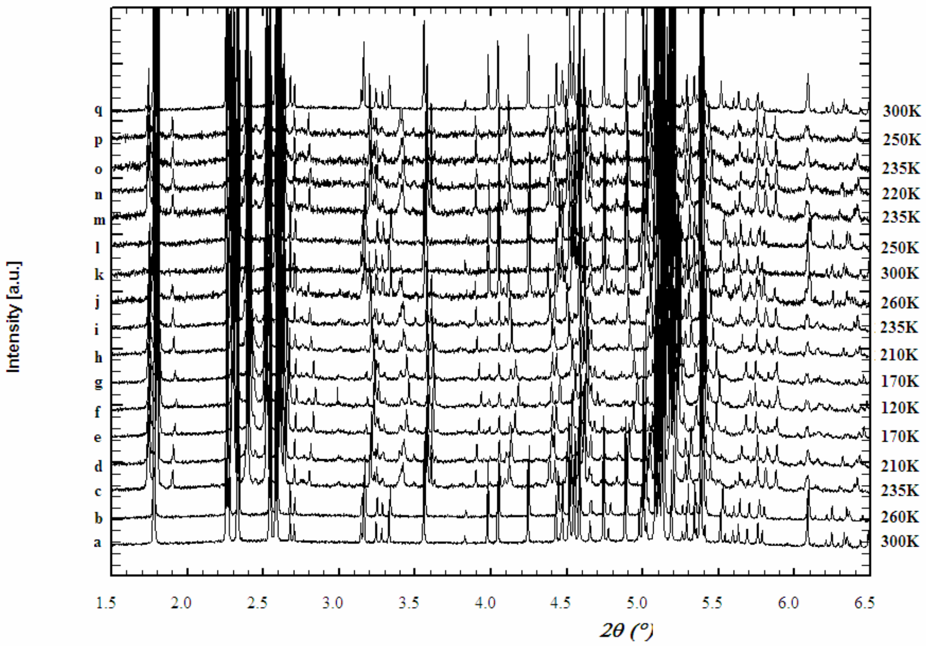

Figure 1: Synchrotron diffraction patterns of the *as grown* and the thermally cycled samples of $[Fe(bpp)_2](NCS)_2.2H_2O$ at different temperatures within the cooling-heating cycle. From bottom to top: *as grown* : (a) 300, (b) 260, (c) 235, (d) 210, (e) 170, (f) 120, (g) 170, (h) 210, (i) 235, (j) 260 and (k) 300 K; thermally cycled: (l) 250, (m) 235, (n) 220, (o) 235, (p) 250 and (q) 300 K.

The synchrotron powder diffraction patterns were obtained on the *as grown* as well as the once *thermally cycled* samples at different pre-selected temperatures along the spin transition curves obtained earlier for these samples and are shown in Figure 1. The first cycle of measurements was

carried out on the *as grown* sample sequentially at 300, 260, 235, 210, 170, 120K, 170, 210, 235, 260 and 300K. A second sequential measurement was carried out on the once *thermally cycled* sample at 250, 235, 220, 235, 250 and 300K. Two satellites clearly visible in the 235 K pattern of the *as grown* sample as well as the additional peak indicate the existence of a super-structure, i.e., a new phase has occurred at this temperature. Thus, below 235 K the crystals have a different structure (say, low temperature (LT) structure) which prevails till the lowest working temperature. With subsequent heating of the *as grown* sample the LT phase remains till 260 K as indicated by the marked presence of the satellites (Figure 2).

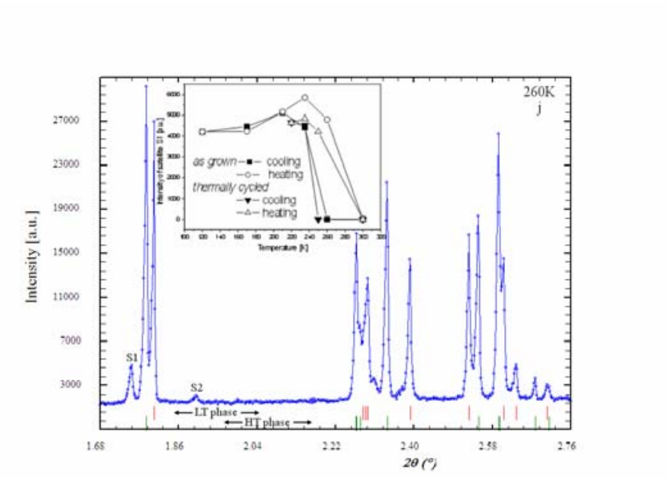

Figure 2: Extended view of the synchrotron diffraction pattern of the *as grown* $[Fe(bpp)_2](NCS)_2.2H_2O$ sample at 260 K where the HT and LT phases coexist. Inset shows the temperature variation of the satellite (S1) intensity of the *as grown* and the *thermally cycled* samples.

The *as grown* sample undergoes structural change at different temperatures while cooling and heating and this observation is consistent with the occurrence of the large thermal hysteresis (235-270 K) in the first step of the two-step spin transition as revealed from the earlier magnetic studies on this sample. During the first step of the spin transition the cell volume and all lattice parameters decrease drastically indicating a simultaneous structural phase transition. In contrast, during the second step of the spin transition the volume and lattice parameter changes are very small. The small changes that are observed are quite normal and give no indication of the thermal hysteresis which is revealed for this step by the measurements of the magnetism for this sample.

It is very interesting to note in Figure 2 that while heating the *as grown* sample both the HT and LT phases coexist at 260 K as is indicated by the two characteristic peaks and the satellites. However, at 300 K the *as grown* sample regains its HT phase while being heated from 260 K. Consideration of the scan patterns obtained for the once *thermally cycled* sample, clearly shows that that system remains in the HT phase till 250 K while being cooled, and below this the LT phase originates at 235 K indicated by the emergence of the satellites as well as the characteristic peak. Below 235 K there is no further change of phase. This behavior is the same as is observed while cooling the *as grown* sample in this temperature range [1].

From the present results it is clear that the low temperature structure of $[Fe(bpp)_2](NCS)_2.2H_2O$ is complicated. Further study of this low temperature structure will be necessary in understanding the complete spin transition behaviour of this compound. In this regard it is essential to carry out further synchrotron structural study of this compound with better resolution (e.g., $\lambda = 0.7$ Å).

Reference

[1] A. Bhattacharjee, J. Kusz, M. Zubko, H.A. Goodwin, P. Gütlich, Journal of Molecular Structure, 890(2008)178-183