ESRF	**Experiment title:** A new type of spin transition curve in Fe(II) tris(2-picolylamine) chloride allyl solvate	**Experiment number**: CH-1631
Beamline: BM01A	**Date of experiment**: from: 01st July 2004 at 08h00 to: 06th July 2004 at 08h00	**Date of report**: 19/01/2005
Shifts: 15	**Local contact(s)**: Philip Pattison	*Received at ESRF:*

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Report: The allyl alcohol solvate of $[Fe^{II}(2\text{- picolylamine})_3]Cl_2$ exhibits a temperature dependent spin crossover with an intermediate plateau in the spin transition curve at an unusual concentration of about 30% high-spin (HS) molecules (Fig. 1) [1]. This is well below the plateau with a 50% concentration observed in the case of the isomorphous ethanol solvate [2]. For the allyl alcohol solvate two crystal morphologies have been observed, one pinacoid and a parallepiped. Since the spin transition curves are derived from SQUID data collected on a milligram amount of sample, it is not clear whether the appearance of a plateau in the transition curve at 30% HS concentration is due to the superimposition of two spin transition curves associated with the different morphologies or is inherent to the allyl alcohol solvate compound. In order to address this question we have proposed to collect diffraction data on a single crystal as a function of temperature.

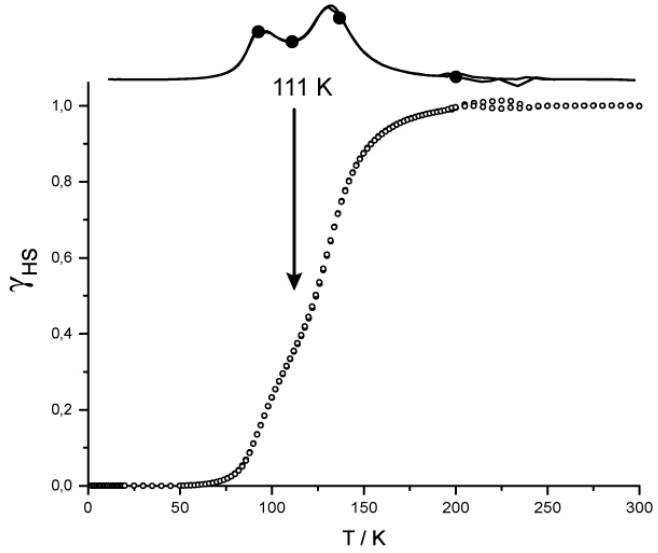

Fig. 1. The fraction of high-spin molecules as a function of temperature derived from magnetization experiment (SQUID) for the allyl alcohol solvate (open circles). The arrow at 111 K indicates the temperature at which the data were collected in the plateau region appearing at 30% rather than at the usual 50% HS concentration. The upper curve is the first derivative of the spin transition curve and shows the existence of two transitions bracketing the plateau. The solid black circles show the temperature points for which diffraction data have been collected.

Four data sets were collected on a crystal with pinacoid habitus using a MAR image plate detector and a nitrogen cooling device at T = 200, 132, 111 and 94 K. The nitrogen device was then replaced by a helium cooler (Helijet). Severe icing problems forced us to switch to a back-up project (p-dichlorobenzene, p-DCB). The cell dimensions obtained for the allyl alcohol solvate are given in Table 1. The systematic absences are consistent with $B2_1/c$ space group symmetry at 200 and 132 K. At 111 K, i.e. in the range of the plateau, a superstructure was observed (Fig. 2). The additional reflections violate the original *B*-centering and correspond to $P2_1/c$ space group symmetry with doubled unit cell volume. At 94 K the original unit cell with $B2_1/c$ space group symmetry is recovered, thus indicating a reentrant sequence of phase transformations. This observation shows that, as in the cases of the ethanol [2] and 2-propanol solvates [3], a plateau in the transition curve reflects the appearance of a new ordered structure. The plateau region is likely to be a result of the coupling of the spin transition to two successive structural phase transformations. Further investigation of the superstructure, the two phase transitions and the disorder at 50% HS concentration requires the unique combination of high flux, high level of monochromatization and extreme low temperature environment offered only by synchrotron radiation.

Table 1. Unit cell parameters of the allyl solvate for the four investigated temperatures.

T / K	a / Å	b / Å	c / Å	β / °	Vol / Å^3	SPGR
94	11.4675(9)	21.7753(9)	19.3972(16)	94.433(7)	4829.13	$B2_1/c$
111	11.4763(7)	21.8295(7)	19.4324(12)	94.311(5)	4854.46	$P2_1/c$
132	11.4970(13)	21.9305(12)	19.5073(24)	93.923(10)	4906.93	$B2_1/c$
200	11.5318(13)	22.1135(12)	19.6548(23)	93.527(9)	5002.65	$B2_1/c$

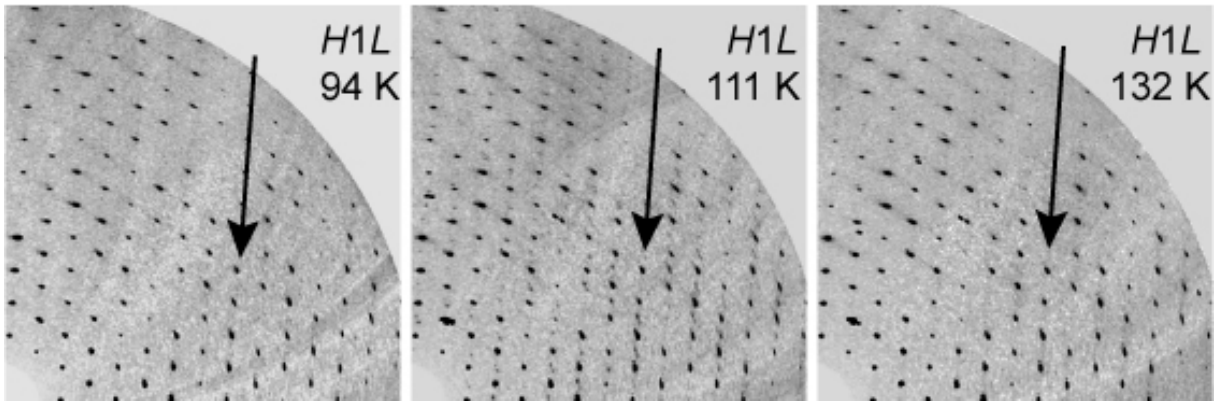

Fig. 2. Reciprocal layers reconstructed from the diffraction intensity. Note the weak superstructure reflections appearing at 111 K, indicating a doubling of the unit cell axis as shown by the arrow.

References:

[1] M. Hostettler, K. W. Törnroos, D. Chernyshov, B. Vangdal & H.-B. Bürgi, *Angew. Chem. Int. Ed.* 43: 4589-4594 (2004).

[2] D. Chernyshov, M. Hostettler, K. W. Törnroos & H.-B. Bürgi, *Angew. Chem. Int. Ed.* 42: 3825-3830 (2003).

[3] H.-B. Bürgi, D. Chernyshov, M. Hostettler, K. W. Törnroos & B. Vangdal, *in preparation.*