

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: High pressure X-ray diffraction study of an unprecedented sequence of first-order phase transitions	Experiment number: HS-4196
Beamline: ID27	Date of experiment: from: 17/11/10 to: 21/11/10	Date of report: 10/03/11
Shifts: 12	Local contact(s): Gaston Garbarino	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Helena J. Shepherd*, Sylvestre Bonnet*, Philippe Guionneau, Salma Bedoui*, William Nicolazzi*, Gábor Molnár*		

Report:

The relative energy of the molecular orbitals (and hence the spin state of the complex) may be manipulated by the application of external pressure. High pressure studies of spin crossover (SCO) complexes using any experimental techniques are still relatively scarce; investigations which employ a variety of methods to probe both the structure and properties of these materials under pressure remain largely absent in the literature, but are **vital to understanding the mechanism of SCO**.ⁱ The application of an external pressure allows the fine-tuning of energy gaps ($P\Delta V$) as well as the separation (in many cases) of structural and spin-state changes.ⁱⁱ For example, in the $[\text{Fe}(\text{2-pic})_3] \text{Cl}_2 \cdot \text{EtOH}$ complex the temperature-induced spin transition does not show a step at 1.35 kbar applied pressure.ⁱⁱⁱ While thermally induced stepped spin transitions have been observed at elevated pressures, such a transition has never been observed in the isothermal regime purely as a function of pressure. A stepped transition with crystallographic symmetry breaking has not been observed in either regime; it is expected that increasing pressure will result in more gradual SCO behaviour and thus possibly preclude such symmetry-breaking phase transitions.^{iv} However, it is certainly possible that the lack of such an observation is merely a result of the paucity of high pressure structural studies in this field.^v Indeed, the majority of high pressure investigations involving SCO systems have used spectroscopic techniques or magnetic studies to characterise the effect of applied pressure on the spin transition.^{vi} Very few studies to date have used diffraction techniques to explore the relationship between structure and properties of spin crossover materials under pressure, but such investigations are essential to establishing the driving forces behind the pressure-induced spin transition, as well as to investigating more complex phenomena such as stepped transitions.

We performed a high pressure single crystal X-ray diffraction study of $[\text{Fe}(\text{bapbpy})(\text{NCS})_2]$ at ESRF ID27, which was complimented by high pressure magnetic and Raman spectroscopic investigations in our laboratory in Toulouse, allowing the mechanism of the unusual 2-step spin transition and associated symmetry breaking phase transition to be probed in detail. This mononuclear complex is known to undergo a two-step thermal spin transition involving an ordered high spin – low spin – high spin [HS-LS-LS] intermediate phase. Both steps involved in the spin transition are first order, show hysteresis associated with nucleation and domain growth phenomena and are accompanied by a crystallographic phase transition. In the intermediate phase one third of the iron sites are in the HS state and the remaining sites are LS. Combined variable pressure and temperature diffraction experiments were performed on beamline ID27 at the ESRF (X-

ray wavelength = 0.3738 Å), using a MAR 345 image-plate detector and a beam focused to a diameter of approx. 3 μm. The sample was enclosed in a gas membrane driven DAC (culet diameter 600 μm) using a steel gasket; helium gas was used as the pressure transmitting medium. Pressure determination was performed using the ruby fluorescence technique. The cell was held in and a helium cryostat for cooling the sample or a heating collar for measurements above room temperature. On increasing the pressure a tripling of the c-axis was observed and associated with the appearance of an intermediate phase (IP), demonstrated by the appearance of supercell reflections at $(h,k,l\pm\frac{1}{3})$ relative to the lattice at ambient pressure (see Figure 1). For further increase of the pressure the diffraction pattern is complicated by the presence of multiple peaks which cannot be assigned to one lattice and was thus attributed to twinning (LS phase). Data collected at several values of pressure and temperature were used for phase identification and construction of a phase diagram, as shown in Figure 2. Rather than the disappearance of the intermediate phase with pressure, as in the case of $[\text{Fe}(\text{2-pic})_3] \cdot \text{Cl}_2 \cdot \text{EtOH}$, it is clear that in **1** the IP may be observed across a large range of temperature and pressure. The pressure dependent crystallographic experiments presented here are indispensable to correctly interpret the spin transition curves obtained from magnetic and Raman measurements. They confirm clearly the unexpected stability of the intermediate phase under pressure. Theoretical simulations have been undertaken to account for these observations using Ising-like models.

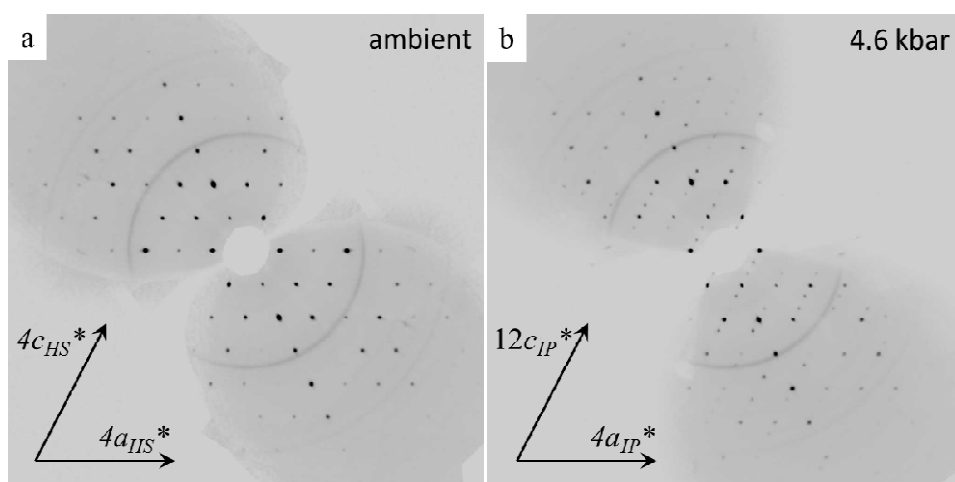


Figure 1. The reciprocal lattice in the $(h0l)$ plane for **1** at (a) ambient pressure (inside the DAC) and (b) 4.6 kbar, reconstructed from the collected diffraction images.

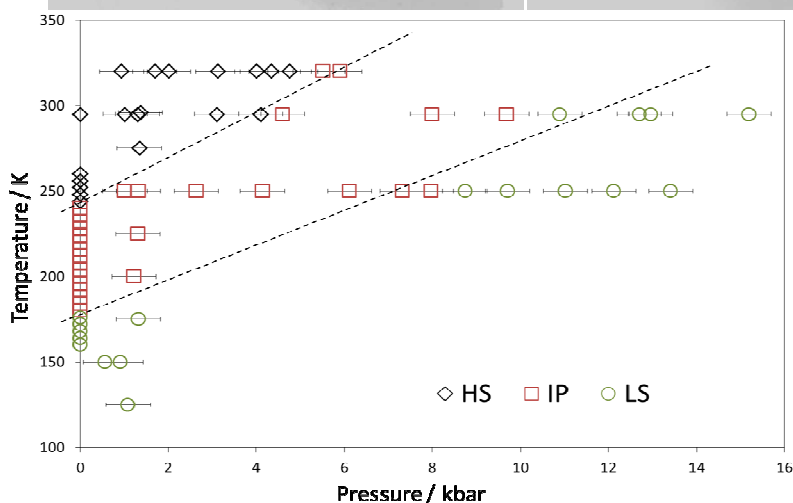


Figure 2. Pressure-Temperature phase diagram of **1** derived from diffraction data. Ambient pressure phases are as determined in REF^{vii}. Dashed lines are drawn as a guide for the eye

ⁱ Top. Curr. Chem. 235 (2004) 23

ⁱⁱ V. Ksenofontov A. B. Gaspar, and P. Gütllich, Top. Curr. Chem. 235, 23 (2004).

ⁱⁱⁱ C. P. Köhler, R. Jakobi, E. Meissner, L. Wiehl, H. Spiering and P. Gütllich, J. Phys. Chem. Solids 51, 239 (1990).

^{iv} P. Gütllich, A. Hauser, and H. Spiering, Angew. Chem. Int. Ed. Engl. 33, 2024 (1994).

^v P. Guionneau M. Marchivie G. Bravic J.-F. Létard, and D. Chasseau, Top. Curr. Chem. 234, 97 (2004).

^{vi} P. Gütllich, A. B. Gaspar, Y. Garcia, and V. Ksenofontov, C. R. Chimie 10, 21 (2007).

^{vii} S. Bonnet, M. A. Siegler, J. Sánchez Costa, G. Molnár, A. Bousseksou, A. L. Spek, P. Gamez and J. Reedijk, Chem. Commun. 5619 (2008)