ESRF	**Experiment title:** Pressure induced spin crossover photomagnet: crystal structure determination below the magnetic ordering temperature of 10 K under high pressure and with light irradiation	**Experiment number**: CH-6296
Beamline: ID15B	**Date of experiment**: from: 08.04.2022 to: 11.04.2022	**Date of report**:
Shifts: 9	**Local contact(s)**: HANFLAND Michael	*Received at ESRF:*

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Report:

During the experiment CH-6296 we managed to determine the crystal structure of a multifunctional molecular material $\{[Fe^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H2O\}_n$ (FeNb) [1,2] at various temperature and pressure conditions with light irradiation in order to gain insight and understand the pressure-induced/ light-induced spin crossover (SCO) phenomenon in this compound and its relation to the magnetic and photomagnetic properties of FeNb described in ref. [1].

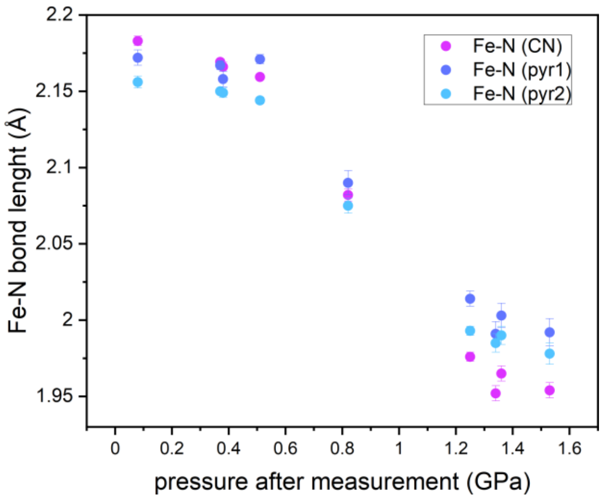

Fig. 1. Fe-N bond length changes in the FeNb compound under various pressures at 100 K.

First, the single-crystal X-ray diffraction data were collected under various pressures (from 0.00 to 1.50 GPa) at 100 K. This led to meaningfull crystal structures with highly accurate unit cell parameters and atomic positions. Increasing pressure led to a significant reduction of the unit cell and the shortening of the Fe-N bonds from ca. 2.15 Å typical for octahedral Fe^{II} in the high spin state to 2.00 Å characteristic for the low spin state of Fe^{II} centers (Figure 1). This led to the following interpretation: up to 0.60 GPa all Fe^{II} centers are in the high spin state and at 0.80 GPa the pressure-induced changes start to affect the Fe-N bonds leading to partial SCO. Above 1.2 GPa all Fe^{II} centers reach the low spin state with the bond lengths reaching 1.97 Å. These new high quality results at 100 K supplement the previous research done at room temperature using a commercial diffractometer.[1] Compared to the 100 K experiment performed at the ID15B beamline, which shows SCO transition at ca. $p_{1/2}$ = 0.80 GPa, the 296 K data clearly show that much higher pressure is needed with the $p_{1/2}$ value of 1.80 GPa in order to induce the SCO.

As stated in the proposal, the main goal of the experiment was to demonstrate the possibility of the simultanous *in-situ* tuning of the thermodynamic conditions in order to observe the light induced excited spin state trapping (LIESST) effect using single-crystal X-ray diffraction technique. The experiment was successful in this regard, we have demonstrated that at a pressure of 0.87 GPa and at 5 K the irradiation of the FeNb crystal with blue laser (488 nm, 150 mW) results in the spin excitation from the low spin state to the high spin state of the Fe^{II}. This conclusion is based on the analysis of the Fe-N bond lengths changes in the 5 experimental steps described below and depicted in Figure 2: first the scXRD data were collected before blue light irradiation at 0.87 GPa and 5 K (step 1 in Figure 2) with the average Fe-N bond length of 2.038(5) Å. After that the crystal was irradiated under the same thermodynamic conditions for 30 minutes using blue laser (480 nm, 150 W; step 2 in Figure 2) and the experiment was repeated leading to the observation of Fe-N bond length increase to the average value of 2.088(3) Å. Further irradiation for 20 min (step 3 in Figure 2) did not lead to additional changes – the Fe-N bond similar with 2.086(4) Å. Such bond length changes are associated with the LIESST effect, which was observed for the first time under pressure using scXRD technique.

After the irradiation, the temperature was increased to 60 K and then back to 5 K while keeping the presssure at 0.87 GPa. The scXRD data were collected again (step 4 in Figure 2) which revelaed the shortening of the Fe-N bond lengths to 2.046(5) Å as compared with steps 2 and 3. This shortening is due to the thermal relaxation of the metastable high spin state of Fe^{II} back to the low spin state. The data collection was performed again after 6 h confirming shorter Fe-N bonds with average value of 2.049(5) Å - fully consistent with the relaxation of the photo-excited high spin state back to the low spin state under pressure.

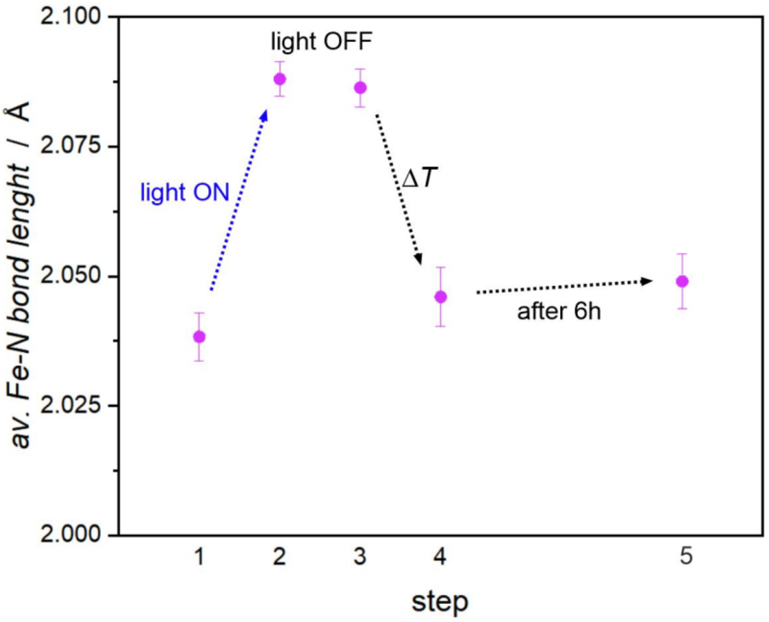

Fig. 2. F*e-N bond length changes extracted from the scXRD data collected at 0.87 GPa and 5 K. Steps: step 1 - before irradiation, step 2 - after 1st irradiation for 30 min. using 480 nm light, step 3 - after 2nd irradiation for 20 min., step 4 – after relaxation at 60 K and cooling back to 5 K while maintaining the pressure constant at 0.87 GPa, step 5 – re-measured after 6 hours at 0.87 GPa and 5 K.*

Structural packing diagram in Figure 3 presents the crystal structures of FeNb obtained before (step 1) and after irradiation (step 2) to emphasize the 'swelling' of FeNb induced by the blue light irradiation under 0.87 GPa and at 5 K.

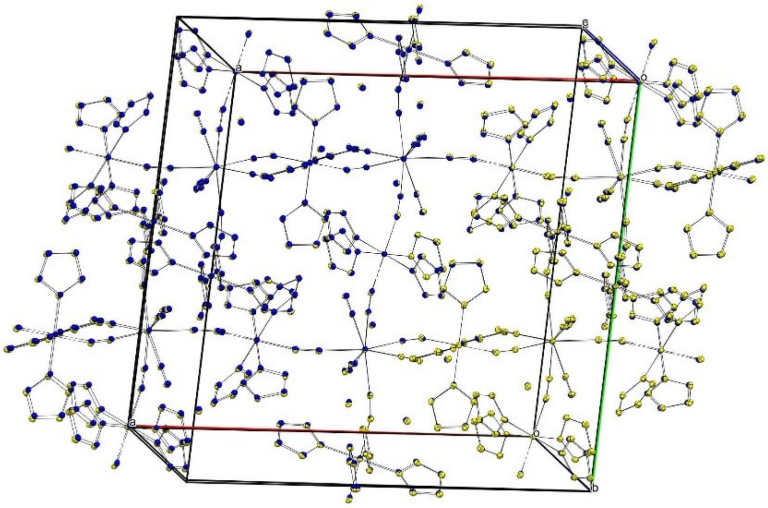

Fig. 3. Overlaid crystal structures obtained before irradiation (blue) and after irradiation (yellow) demonstrating the swelling of the unit cell in response to light. T = 5 K, p = 0.87 GPa.

To summarize, the experiment executed at the ESRF demonstrates the simultaneous control of the photoswitching properties of a molecular magnet using pressure, temperature and light irradiation. It forms a basis for better understanding of the complex magnetic behavior of the studied compound FeNb at high pressure, low temperature and in response to light. Previous scXRD study has shown the impact of the pressure only at room temperature,[1] because of the limitations of the commercial diffractometers and low temperature devices. The results obtained within the CH-6296 experiment, confirm what was observed by low-temperature magnetic/photomagnetic studies under variable pressure[1]. The experiment conducted at the ESRF shows directly the structural changes occuring in FeNb under high pressure and low temperature with simultanous light irradiation. It also shows how the structural changes induced by the mechanical stimulus can be reversed by photons. This is the first example of the simultanous control of the spin state by three different stimuli which will be published soon in a peer-reviewed general chemistry journal.

References:

[1] D. Pinkowicz, M. Rams, M. Misek, K. Kamenev, H. Tomkowiak, A. Katrusiak, B. Sieklucka, *J. Am. Chem. Soc.* **137**, 8795-8802 (2015).