ESRF	**Experiment title:** Structural investigation of the influence of high pressure on unusual spin transition and photo-switching in multifunctional coordination framework	**Experiment number**: CH-7499
Beamline: ID15B	**Date of experiment**: from: 28.08.2025 to: 01.09.2025	**Date of report**: 23.10.2025
Shifts: 12	**Local contact(s)**: Dr. Gaston Garbarino	*Received at ESRF:*

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Report:

The aim of the experiment CH-7499 was to study the origin of unusual spin crossover (SCO) behavior of $\{[Fe^{II}(4CN\text{-}py)_4]_2[W^{IV}(CN)_8]\}_n$ (4CN-py = 4-cyanopyridine; **Fe_2W**) coordination polymer under high pressure using single crystal X-ray diffraction (scXRD). The preliminary magnetic measurements performed in our laboratory have shown that the nature of SCO in **Fe_2W** can be modulated with the application of high pressure. However, the observed response is not typical for SCO compounds under pressure (**Figure 1**). At relatively low values of ca. 0.1 GPa and temperatures below 60 K, the number of Fe^{II} centers in the high spin (HS) state initially increases and only then starts to decrease again. The initial increase of the HS fraction is counterintuitive as the HS state structure is characterized by a larger unit cell volume than that of the low spin (LS) state structure.

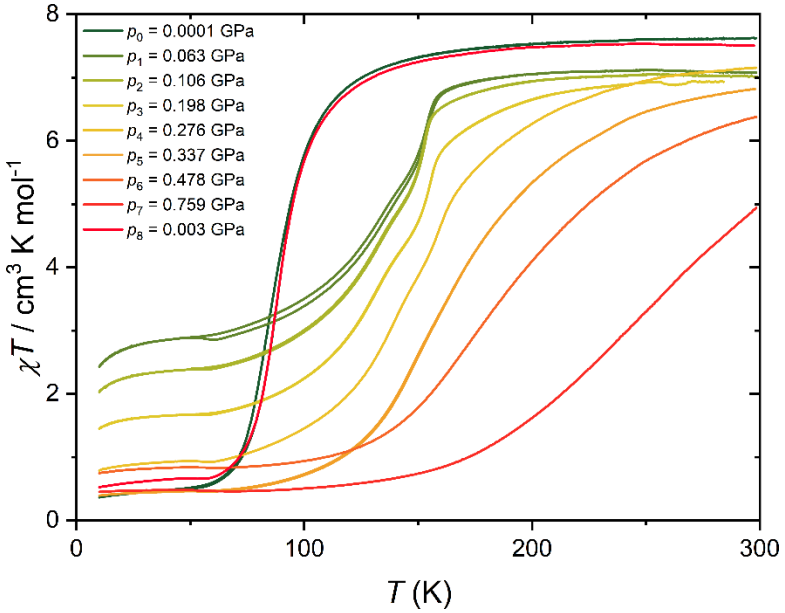

Fig 1. $\chi T(T)$ dependence recorded for **Fe_2W** at different values of applied hydrostatic pressure (measurements performed at Jagiellonian University).

In the first experiment (denoted as **Fe_2W_1**), all the measurements were performed on the single crystals that were activated at 40 °C in vacuum ($p \approx 10^{-2}$ mbar) before the start of the beamtime. Three crystals were loaded into diamond anvil cell (DAC) with a few microcrystals of ruby (acting as a pressure gauge) inside the argon-filled glovebox of the Central Chemistry Lab at the ESRF. Under argon armosphere, all crystals were identified as the known crystalline phase *I*-42*d* of $\{[Fe^{II}(4CN\text{-}py)_4]_2[W^{IV}(CN)_8]\}_n$, discovered previously by us (**Fe_2W_CCDC2240345**).[1] The best crystal was selected for further measurements (**Fe_2W_1_Ar_293K**, **Table 1**). Upon succesful identification of the desired anhydrous phase of the compound, the argon atmosphere in the DAC was exhanged for high-pressure helium medium. The application of high-pressure (p = 0.22 GPa) resulted only in anisotropic compression of the unit cell (**Fe_2W_1_He_293K**; $\Delta a/a$ = -0.5%, $\Delta c/c$ = -1.0%).

Table 1. Comparison of crystal data and refinement parameters for the first crystal (**Fe_2W_1**).

	Fe_2W_1_Ar_293K	**Fe_2W_1_He_293K**	**Fe_2W_1_He_200K**	**Fe_2W_CCDC2240345**
Crystal system	Tetragonal			
Space group	*I*-42d			
***T* (K)**	293		200	
***p* (GPa)**	0.0001	0.22	0.34	0.0001
***a*=*b* (Å)**	19.2529(4)	19.1523(10)	19.0960(4)	19.1966(4)
***c* (Å)**	15.9051(18)	15.739(3)	15.6994(14)	15.8129(5)
***V* (Å^3)**	5895.6(7)	5773.2(11)	5724.9(6)	5827.2(3)
Radiation type	synchrotron, λ = 0.40979 Å	synchrotron, λ = 0.40979 Å	synchrotron, λ = 0.40979 Å	Mo Kα λ = 0.71073 Å
R_{int}	0.035	0.066	0.039	0.050
R_1 [$F^2>2\sigma(F^2)$]	0.051	0.049	0.041	0.039
S	1.01	0.99	1.03	1.14
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.39/-0.68	1.20/-1.15	1.69/-1.27	1.49/-2.49

In the magnetic measurements under pressure, the peculiar spin crossover behavior was observed only for p < 0.34 GPa at temperatures T < 170 K. For this reason, we continued gradual cooling of the crystal at 2 K·min^{-1} rate, with diffraction measurements being performed at the selected temperatures, while keeping the pressure in the DAC as low as possible without its rupture. The measurement conditions are demonstrated in **Table 2**. The variation of the average Fe-N_{py} bond length was used to estimate the fraction of high-spin iron(II) (γ_{HS}) in the **Fe_2W** structure, assuming $d_{Fe\text{-}Npy}$ = 2.239 Å for pure high-spin (HS) state (same as in the **Fe_2W_1_He_293K**), and $d_{Fe\text{-}Npy}$ = 2.007 Å for pure low-spin (LS) state (as in the **Fe_2W_1_He_60K_relaxed**). Surprisingly, no evidence of peculiar phase transition similar to that shown in **Fig. 1** was observed down to 60 K, with diffraction data collected at ID15B in the pressure range of 0.12-0.34 GPa showing only the shift of spin crossover temperature (T_{SCO}) from 93(1) K to 120(5) K (**Fig. 2**).

Table 2. Temperature-pressure conditions during measurements of the **Fe_2W_1**.

***T* (K)**	***p* (GPa)**
297	0.22
200	0.34
170	0.34
140	0.31
120	0.27
100	0.23
80	0.17
60	0.13
40	0.12
20	0.11
60 (relaxed)	0.23

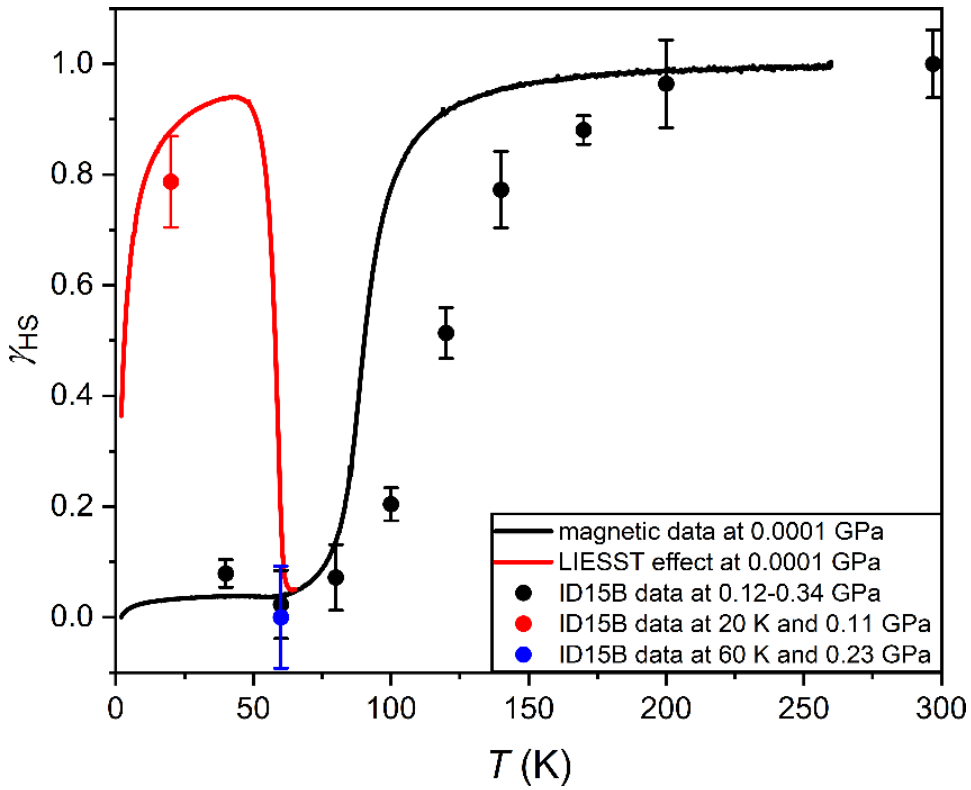

Fig. 2 $\gamma_{HS}(T)$ dependence recorded for **Fe₂W** at different values of applied hydrostatic pressure by magnetic measurements at Jagiellonian University (solid lines) and $\gamma_{HS}(T)$ dependence estimated from diffraction data for **Fe₂W_1** obtained at ID15B (dots).

Despite the lack of apparent phase transition for the **Fe₂W_1** crystal in the 60-293 K range with only gradual HS to LS conversion on cooling, below 60 K the trend is inversed. The Fe-N_{py} bond length of 2.012(14) Å at 60 K increases slightly to 2.025(6) Å at 40 K and more significantly to 2.189(19) Å at 20 K. This effect is attributed to the LIESST (light-induced excited spin state trapping) effect, which in the diffraction measurements could have been trigerred by: 1) white light used to visualize the crystals on the camera during crystal centering; 2) blue light scattered from 473 nm laser utilized for the measurement of ruby fluorescence (pressure indicator in the DAC) or 3) hard X-ray irradiation itself (so-called HAXIESST effect – hard X-ray induced excited spin state trapping). The observation of the LIESST effect is further confirmed by the sample going back to the LS state upon heating to 60 K that coincides with the relaxation temperature of the photoinduced state observed in the magnetic measurements.

Having noticed that **Fe₂W_1** sample did not show the same peculiar spin crossover behavior as that observed in the magnetic measurements, we have decided to repeat the experiment on other crystals. As lack of the expected behavior raised questions about the sample condition, the DAC loaded with new crystals of **Fe₂W** (**Fe₂W_2**) was subjected to overnight heating at 70 °C inside the argon-filled glovebox, in order to ensure the anhydrous state of the sample. Again, the initial diffraction measurements under argon (**Table 3**; **Fe₂W_2_Ar_293K**) confirmed the presence of the known *I*-42*d* phase of $\{[Fe^{II}(4CN\text{-}py)_4]_2[W^{IV}(CN)_8]\}_n$. However, following the cell loading with helium, the measurement recorded under the pressure of 0.50 GPa led us to a completely new structure in the *Pnna* space group (**Fig. 3; Fe₂W_2_He_293K**). The phase transition from the tetragonal to the orthorombic crystal system is associated with an anisotropic expansion of *a* and *b* unit cell parameters coinciding with a significant decrease of the *c* parameter. The expansion of *a* and *b* is associated with the Fe-N-C angle increase from 163(1)° in **Fe₂W_2_Ar_293K** to 169(1)° in **Fe₂W_2_He_293K**. The related reorganization of the Fe^{II} coordination environment could be the reason for the change in the magnetogyric ratio of Fe^{II} and the observed drop in the room-temperature value of χT under pressure, as depicted in **Fig. 1**.

Table 3. Comparison of crystal data and refinement parameters for the second crystal (**Fe_2W_2**).

	Fe_2W_2_Ar_293K	**Fe_2W_2_He_293K**	**Fe_2W_2_He_200K**	**Fe_2W_CCDC2240345**
Crystal system	Tetragonal	Orthorombic		Tetragonal
Space group	*I*-42d	*Pnna*		*I*-42d
***T* (K)**	293		200	
***p* (GPa)**	0.0001	0.50	0.71	0.0001
***a* (Å)**	19.2626(6)	20.1017(7)	19.9262(7)	19.1966(4)
***b* (Å)**	19.2626(6)	19.4614(10)	19.3575(13)	19.1966(4)
***c* (Å)**	15.9174(17)	13.783(2)	13.648(2)	15.8129(5)
***V* (Å^3)**	5906.1(7)	5392.2(10)	5264.2(9)	5827.2(3)
Radiation type	synchrotron, λ = 0.40979 Å	synchrotron, λ = 0.40979 Å	synchrotron, λ = 0.40979 Å	Mo Kα λ = 0.71073 Å
R_{int}	0.053	0.064	0.043	0.050
R_1 [$F^2>2\sigma(F^2)$]	0.056	0.043	0.042	0.039
S	1.05	1.02	1.02	1.14
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	2.78/-0.65	0.65/-0.45	0.83/-0.60	1.49/-2.49

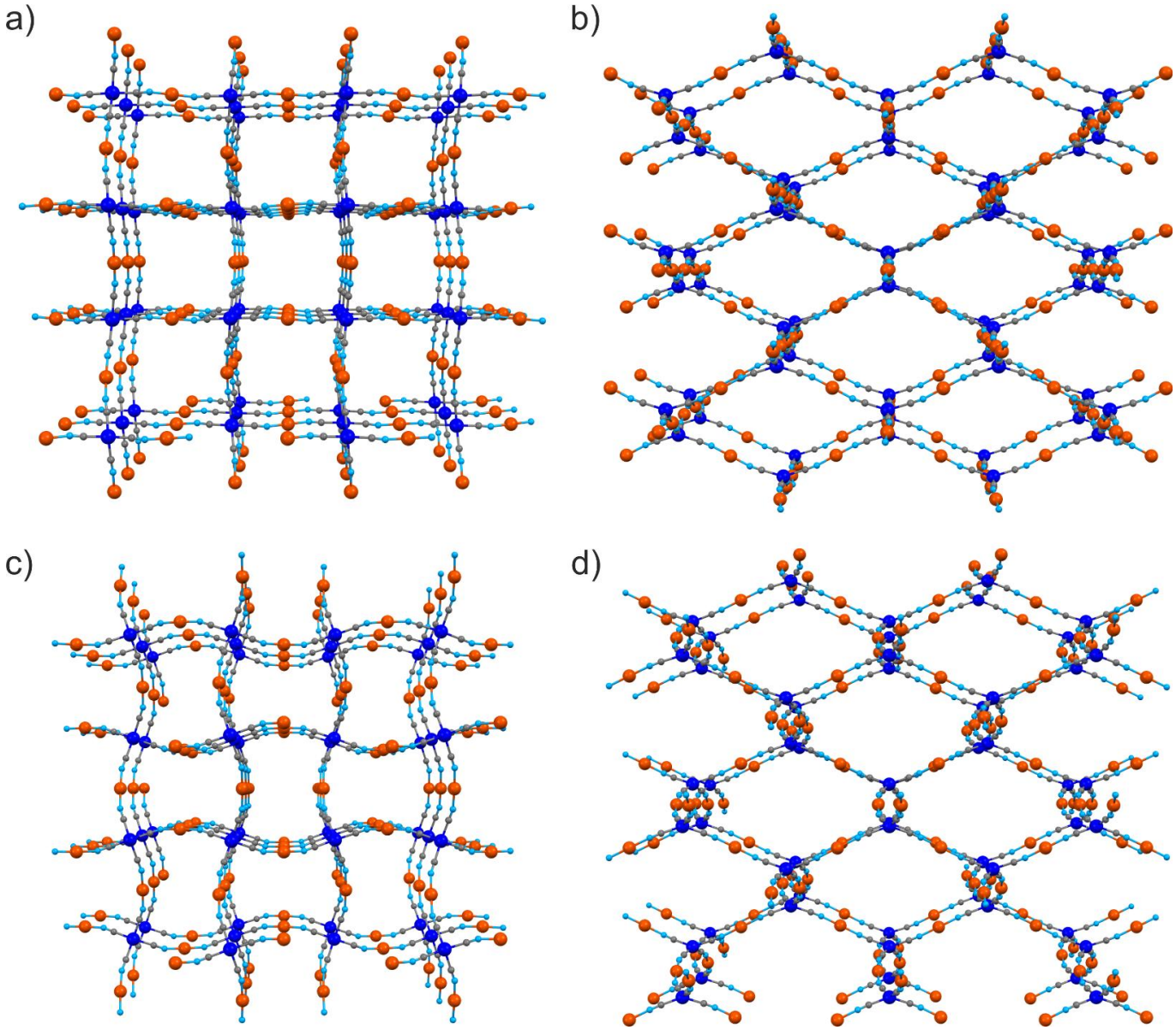

Fig. 3 Comparison of crystal structures for **Fe_2W_2_Ar_293K** and **Fe_2W_2_He_293K** along the *c* crystallographic axis (a and c, respectively), and along the *a* crystallographic axis (b and d, respectively).

Upon establishing the existence of the pressure-induced phase transition in **Fe$_2$W_2**, we continued high-pressure measurements upon cooling the sample, in order to correlate them with the magnetic behavior observed in high-pressure magnetic measurements. Again, the high-spin iron(II) fraction (γ_{HS}) was estimated based on the variation of Fe-N_{py} bond distances. It is important to note that in magnetic measurements pressure value is determined by the temperature of superconducting transition in tin indicator, which is observed below 10 K. At the same time, the pressure medium used in magnetic measurements shows variation of pressure of ca. 0.2 GPa as it expands on heating to room temperature. For this reason, magnetic measurements used for the comparison of γ_{HS} with the diffraction measurements are described for a given pressure range and not a single pressure value. The temperature dependence of the high-spin iron(II) fraction for the *Pnna* phase under 0.67-0.71 GPa and 0.50-0.53 GPa range is in agreement with the pressure-induced behaviour observed in the magnetic measurements (**Fig. 4** and **Fig. 5**). However, due to the inherent behaviour of the DAC cell, pressure values below 0.3 GPa could be achieved only at 60 K and below. The high-spin fraction observed at the lowest temperature points (5 and 40 K) is much higher than detected in the magnetic measurements, which points out towards LIESST behavior of the sample (**Fig. 6**). On the other hand, the measurement performed at 60 K and 0.30 GPa shows only small high-spin fraction. While this agrees with the magnetic measurements, the uncertainty of the spin-state determination in the diffraction measurements yields this result for a single temperature-pressure point unconvincing.

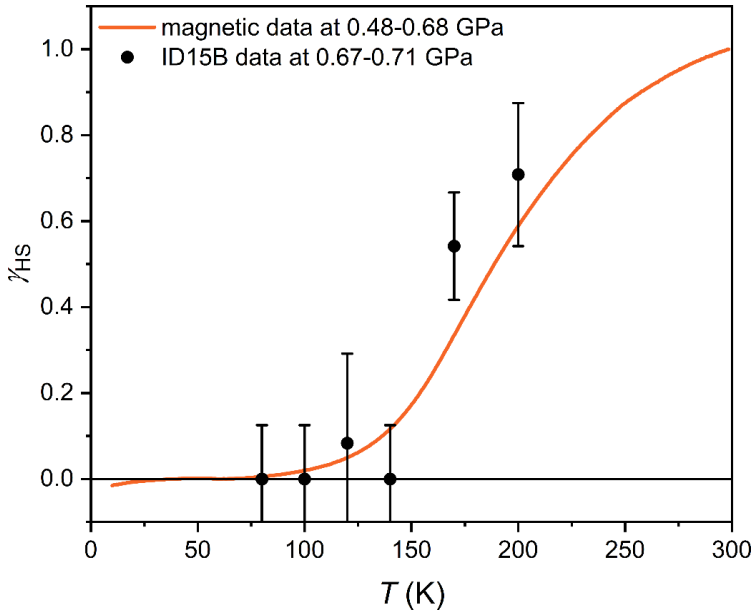

Fig. 4. $\gamma_{HS}(T)$ dependence recorded for **Fe$_2$W** at 0.48-0.68 GPa by magnetic measurements (solid lines) and $\gamma_{HS}(T)$ estimated from the diffraction data obtained for **Fe$_2$W_2** at 0.67-0.71 GPa (black dots).

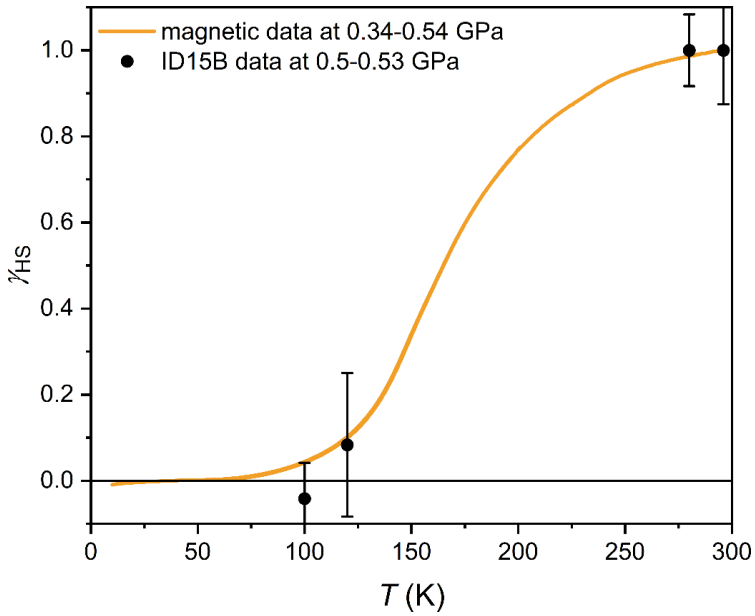

Fig. 5. $\gamma_{HS}(T)$ dependence recorded for **Fe$_2$W** at 0.34-0.54 GPa by magnetic measurements (solid lines) and $\gamma_{HS}(T)$ estimated from the diffraction data obtained for **Fe$_2$W_2** at 0.50-0.53 GPa (black dots).

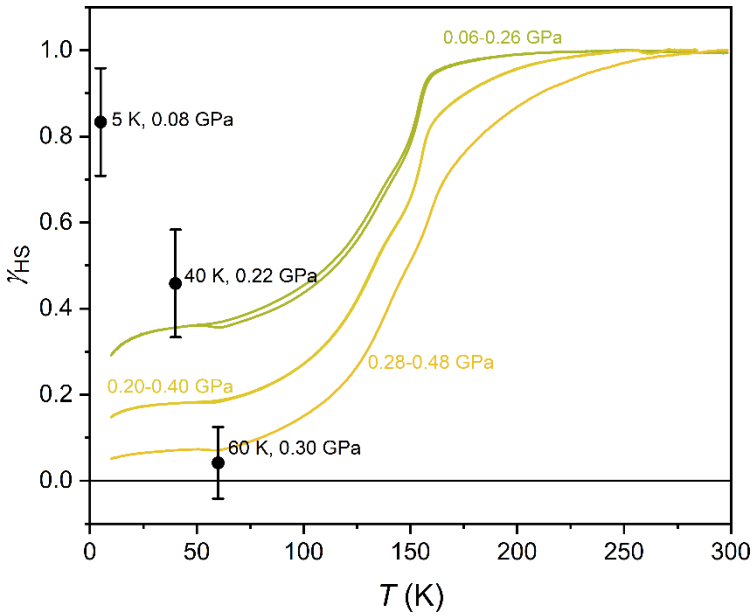

Fig. 6. $\gamma_{HS}(T)$ dependence recorded for **Fe$_2$W** at different values of applied hydrostatic pressure by magnetic measurements (solid lines) and $\gamma_{HS}(T)$ estimated from the diffraction data obtained for **Fe$_2$W_2** (black dots).

In conclusion, **experiment CH-7499 revealed the formation of a new pressure-induced *Pnna* phase of the {[Fe^{II}(4CN-py)$_4$]$_2$[W^{IV}(CN)$_8$]}$_n$ coordination polymer**. However, observation of this phase only in one of two attempts raises questions whether the effect is serendipitous in nature (appearing only for some fraction of crystals exposed to the pressure), or is it dependent on the crystal activation method, which requires further studies. Moreover, the future low-temperature experiments for the **Fe$_2$W** sample at lowest temperatures (< 60 K) will require careful elimination of the light sources, including scattered radiation from 473 nm laser utilized for pressure measurements, in order to avoid simultaneous photoexcitation of the LIESST effect.

[1] M. Magott, K. Płonka, B. Sieklucka, K. Dziedzic-Kocurek, W. Kosaka, H. Miyasaka, D. Pinkowicz *Chem. Sci.*, **2023**, *14*, 9651.