Electronic Supplementary Information

Simultaneous manipulation of iron(II) spin crossover and LIESST behaviour by pressure, temperature and light

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Figure S5. Comparison of the Fe-N bond contraction in **FeNb** under high pressure at 100 K reported in this work (pink points) with the Fe^{II}_{HS} molar fraction calculated from the magnetic data at low temperature around 100 K reported in Figure S5 of the ref. 37.

Table S6. Selected bond lengths and angles for **FeNb** in nine consecutive diffraction experiment (steps in Figure 4) at three different pressures before and after light irradiation, with the crystallographic data collected at 5 K.

High pressure scXRD experimental setup description

The experiments were performed at the high-pressure beamline ID15B of the European Synchrotron Radiation Facility (ESRF). The high intensity of the X-ray synchrotron beam allows rapid data collection with relatively high completeness compared to commercial diffractometers equipped with Merrill-Bassett diamond anvil cells (DACs).

A single crystal of **FeNb** (approx. 0.10 x 0.10 x 0.03 mm) was loaded into a membrane-type DAC filled with helium gas as a pressure transmitting medium. The pressure of the membrane was controlled using GE Druck Pace5000 pressure controller and was determined by an in-situ ruby fluorescence measurement before and after each X-ray diffraction experiment. The ruby photoexcitation was performed inside the DAC at the measurement conditions in between the diffraction experiments using 488 nm laser diode. A liquid helium cooled cryostat suitable for X-ray diffraction was used to perform low temperature measurements down to 5 K.

All X-ray diffraction experiments described in this paper were carried out on a high quality single crystal of **FeNb**. Due to the technical limitations in controlling the pressure during the decompression of the DAC, it was necessary to combine as many experiments as possible in a single run. In addition, it was necessary to make all pressure changes at a temperature of at least 70 K due to the membrane-type diamond-anvil cell characteristics. Further small pressure changes inside the cell during the experiments were caused by changing the temperature. First, the diamond-anvil cell containing **FeNb** crystal was filled with helium gas to reach a pressure of 0.58 GPa at 200 K. The cell was then gradually cooled and X-ray diffraction experiments were carried out during cooling. At the same time, the pressure was gradually reduced.

Details of the successive single-crystal X-ray diffraction measurements and refinements and the CCDC numbers assigned to the exact crystal structures are given in Tables S1-S4. Data reduction, scaling and absorption corrections (spherical harmonics) were performed using Agilent CrysAlisPro software. Structures were determined using OLEX2 (ShelXT).[1-3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated by a mixture of independent and constrained refinement. All structural models for the single **FeNb** crystal under different conditions are deposited in the CSD database. The dource data are available using the ESRF DOI portal at https://data.esrf.fr/doi/.[4]

High-pressure experiments at 100 K

Table S1. Crystal structure solution and refinement parameters for **FeNb** under high pressure (HP) at 100 K.

***p* (GPa)**	**0.08(1)**	**0.37(1)**	**0.38(1)**	**0.51(1)**
CCDC	**2326694**	**2326495**	**2326697**	**2326507**
Radiation	Synchrotron radiation, λ = 0.41008 Å			
Temperature	100 K			
Formula	$C_{32}H_{40}Fe_2N_{24}NbO_4$			
Formula weight g/mol	1029.49			
Space group	$I4_1/a$			
Unit cell / Å	a = 21.6050(4)	a = 21.4750(3)	a = 21.4558(4)	a = 21.4180(3)
	c = 9.5533(18)	c = 9.4576(7)	c = 9.4642(13)	c = 9.4229(8)
Volume / Å^3	4459.3(9)	4361.6(3)	4356.9(6)	4322.6(4)
Z	4			
Density / g cm^{-3}	1.533	1.568	1.569	1.582
F(000)	2100			
Abs. coeff. / mm^{-1}	0.532	0.544	0.544	0.548
Independent reflections	1481	2053	1840	2028
Parameters	152	147	152	152
Restraints	3	3	3	3
R_1 [$F_o > 4\sigma(F_o)$] / %	4.01	3.8	4.35	3.46
wR_2 [all] / %	9.60	9.56	11.23	9.17
I/s / %	13.7	14.9	12.5	16.2
GOF on F^2 [all refl.]	0.999	1.081	1.030	1.065
Max/min resid. density / e·Å^3	0.38, -0.35	0.45, -0.38	0.49, -0.26	0.30, -0.24
Collected reflections	2238	4490	4054	4459
R_{int} / %	4.37	5.18	5.17	5.07
Completeness / %	48.6	65.9	59.2	66.0

Table S1. (continued)

***p* (GPa)**	**0.83(1)**	**1.25(1)**	**1.36(1)**	**1.53(1)**
CCDC	**2327450**	**2326556**	**2327431**	**2327700**
Radiation	Synchrotron radiation, λ = 0.41008 Å			
Temperature	100 K			
Formula	$C_{32}H_{40}Fe_2N_{24}NbO_4$			
Formula weight g/mol	1029.49			
Space group	$I4_1/a$			
Unit cell / Å	a = 21.1151(5)	a = 20.7576(7)	a = 20.7181(6)	a = 20.6618(4)
	c = 9.3661(17)	c = 9.3174(17)	c = 9.3075(13)	c = 9.2789(9)
Volume / Å^3	4175.9(8)	4014.7(8)	3995.1(6)	3961.3(4)
Z	4			
Density / g cm^{-3}	1.638	1.703	1.712	1.726
F(000)	2100			
Abs. coeff. / mm^{-1}	0.568	0.590	0.593	0.598
Independent reflections	1737	1788	1889	1743
Parameters	151	152	151	152
Restraints	4	3	10	93
R_1 [$F_o > 4\sigma(F_o)$] / %	5.43	4.54	7.42	9.59
wR_2 [all] / %	14.73	10.83	21.62	32.70
I/s / %	13.9	11.9	5.7	3.2
GOF on F^2 [all refl.]	1.058	0.949	1.025	1.049
Max/min resid. density / e·Å^3	0.34, -0.28	0.46, -0.32	1.07, -0.45	1.39, -0.74
Collected reflections	3895	3719	3742	3321
R_{int} / %	5.13	5.53	7.99	10.89
Completeness / %	58.9	64.2	67.2	61.0

Table S2. The Fe-N bond lengths under HP at 100 K.

Pressure (GPa)	Fe-N_{CN} (Å) (Fe1-N2)	Fe-N_{pyr1} (Å) (Fe1-N3)	Fe-N_{pyr2} (Å) (Fe1-N5)
0.08	2.183(3)	2.172(5)	2.156(4)
0.37	2.169(2)	2.167(3)	2.150(2)
0.38	2.166(3)	2.158(5)	2.149(3)
0.51	2.159(2)	2.171(3)	2.144(2)
0.83	2.082(4)	2.090(8)	2.075(5)
1.25	1.976(3)	2.014(5)	1.993(3)
1.36	1.965(5)	2.003(8)	1.990(6)
1.53	1.954(5)	1.992(9)	1.978(7)

Irradiation experiment at 0.28(2) GPa, 5K

Table S3. Crystal structure solution and refinement parameters for **FeNb** in an irradiation experiment at 5 K and 0.28(2) GPa (steps 1-3).

Step no. in Figure 4	**1**	**2**	**3**
p (GPa)	0.28(2)	0.28(2)	0.28(2)
T (K)	5	5	5
Details	before irradiation	After 65 min of blue light irradiation	After 105 min of blue light irradiation
CCDC	**2326497**	**2326501**	**2326517**
Radiation	Synchrotron radiation, λ = 0.41008 Å		
Formula	$C_{32}H_{40}Fe_2N_{24}NbO_4$		
Formula weight g/mol	1029.49		
Space group	$I4_1/a$		
Unit cell / Å	a = 21.4595(4)	a = 21.4722(3)	a = 21.4699(3)
	c = 9.4491(10)	c = 9.4522(8)	c = 9.4581(7)
Volume / Å^3	4351.4(5)	4358.0(4)	4359.8(3)
Z	4		
Density / g cm^{-3}	1.571	1.569	1.568
F(000)	2100		
Abs. coeff. / mm^{-1}	0.545	0.544	0.544
Independent reflections	2028	2039	2033
Parameters	152	152	152
Restraints	3	3	3
R_1 [$F_o > 4\sigma(F_o)$] / %	3.70	3.51	4.08
wR_2 [all] / %	10.01	9.30	10.78
I/s / %	15.0	16.2	15.2
GOF on F^2 [all refl.]	1.060	1.048	1.058
Max/min resid. density / e·Å^3	0.41, -0.33	0.36, -0.33	0.53, -0.43
Collected reflections	4496	4513	4499
R_{int} / %	5.01	4.62	4.82
Completeness / %	65.6	66.0	65.9

Irradiation experiment at 0.82(1) GPa, 5K

Table S4. Crystal structure solution and refinement parameters for **FeNb** in an irradiation experiment at 5 K and 0.82(1) GPa (steps 4-5).

Step no. in Figure 4	**4**	**5**
p (GPa)	0.82(1)	0.82(1)
T (K)	5	5
Details	before irradiation	After 50 min of blue light irradiation
CCDC	**2327702**	**2326557**
Radiation	Synchrotron radiation, λ = 0.41008 Å	
Formula	$C_{32}H_{40}Fe_2N_{24}NbO_4$	
Formula weight g/mol	1029.49	
Space group	$I4_1/a$	
Unit cell / Å	a = 21.091(1)	a = 21.1680(7)
	c = 9.379(2)	c = 9.3545(17)
Volume / Å^3	4171.8(11)	4191.6(8)
Z	4	
Density / g cm^{-3}	1.639	1.631
F(000)	2100	
Abs. coeff. / mm^{-1}	0.568	0.566
Independent reflections	1782	1832
Parameters	152	152
Restraints	75	3
R_1 [$F_o > 4\sigma(F_o)$] / %	6.55	6.12
wR_2 [all] / %	20.52	16.57
I/s / %	7.8	8.2
GOF on F^2 [all refl.]	1.011	1.103
Max/min resid. density / e·Å^3	0.50, -0.37	0.66, -0.41
Collected reflections	3566	3895
R_{int} / %	6.99	6.5
Completeness / %	60.0	62.6

Irradiation experiment at 0.87(1) GPa, 5K

Table S5. Crystal structure solution and refinement parameters for **FeNb** in an irradiation experiment at 5 K and 0.87(1) GPa (steps 6-9).

Step no. in Figure 4	**6**	**7**	**8**	**9**
p (GPa)	0.87(1)	0.87(1)	0.87(1)	0.87(1)
T (K)	5	5	5	5
Details	before irradiation	after 30 min of blue light irradiation	after 50 min of blue light irradiation	after thermal relaxation at 60 K
CCDC	**2326519**	**2326523**	**2326553**	**2327391**
Radiation	Synchrotron radiation, λ = 0.41008 Å			
Formula	$C_{32}H_{40}Fe_2N_{24}NbO_4$			
Formula weight g/mol	1029.49			
Space group	$I4_1/a$			
Unit cell / Å	a = 20.9186(13)	a = 21.0746(7)	a = 21.0773(6)	a = 20.9206(17)
	c = 9.372(3)	c = 9.3334(15)	c = 9.3291(13)	c = 9.371(3)
Volume / Å^3	4101.0(13)	4145.3(7)	4144.5(6)	4101.3(15)
Z	4			
Density / g cm^{-3}	1.667	1.650	1.650	1.667
F(000)	2100			
Abs. coeff. / mm^{-1}	0.578	0.572	0.572	0.578
Independent reflections	1796	1857	1862	1864
Parameters	152	152	152	147
Restraints	3	3	3	3
R_1 [$F_o > 4\sigma(F_o)$] / %	4.91	4.17	4.45	6.40
wR_2 [all] / %	11.31	9.84	10.30	20.54
I/s / %	10.5	14.7	13.7	5.9
GOF on F^2 [all refl.]	0.939	0.961	0.970	0.943
Max/min resid. density / e·Å^3	0.61, -0.43	0.47, -0.33	0.66, -0.45	0.49, -0.74
Collected reflections	3764	4011	4037	3847
R_{int} / %	5.92	4.93	4.88	7.48
Completeness / %	64.1	64.9	64.8	63.2

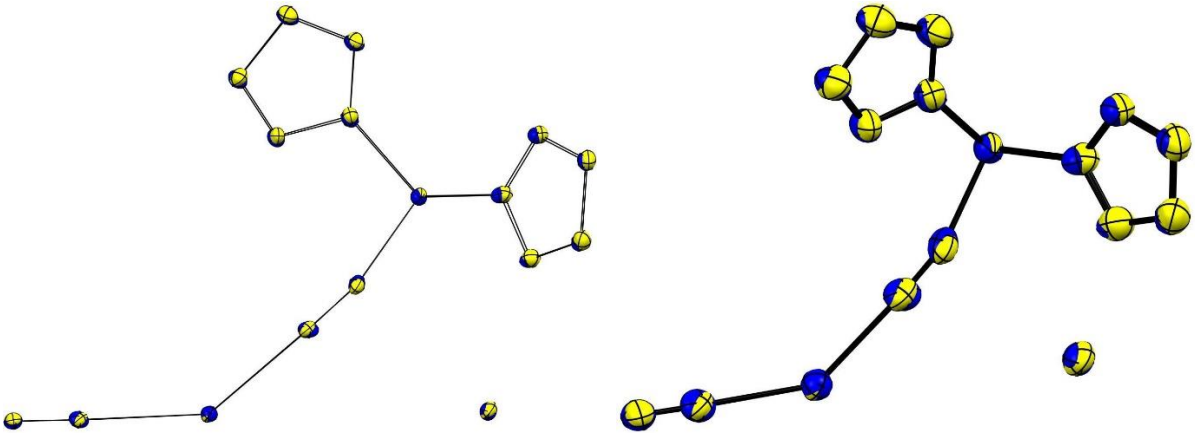

Figure S1. Asymmetric unit of the crystal structure before irradiation (blue; step 6) and after irradiation (yellow; step 7). 10% or 50% probability level for ellipsoids.

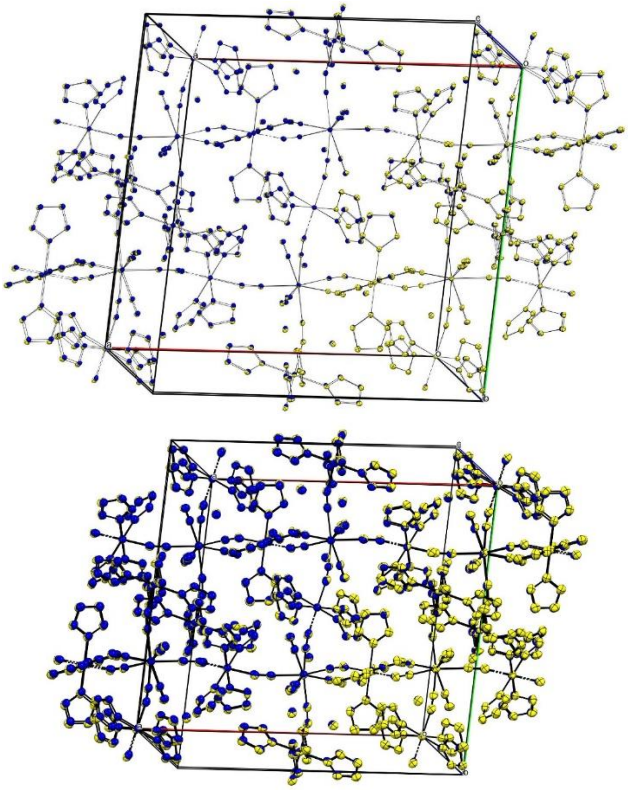

Figure S2. Packing of the crystal structure before irradiation (blue; step 6) and after irradiation (yellow; step 7). 10% or 50% probability level for ellipsoids.

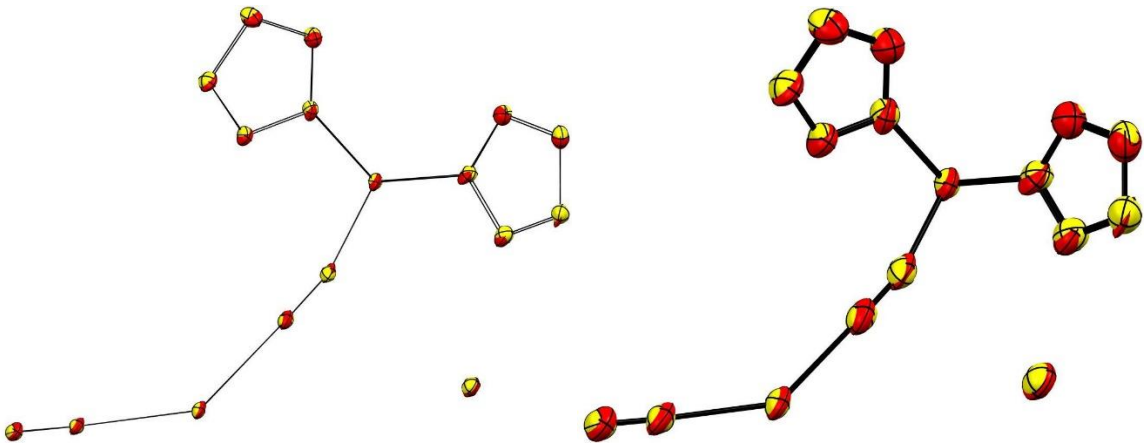

Figure S3. Asymmetric unit of the crystal structure after irradiation (yellow; step 7) and after thermal relaxation (red; step 9). 10% or 50% probability level for ellipsoids.

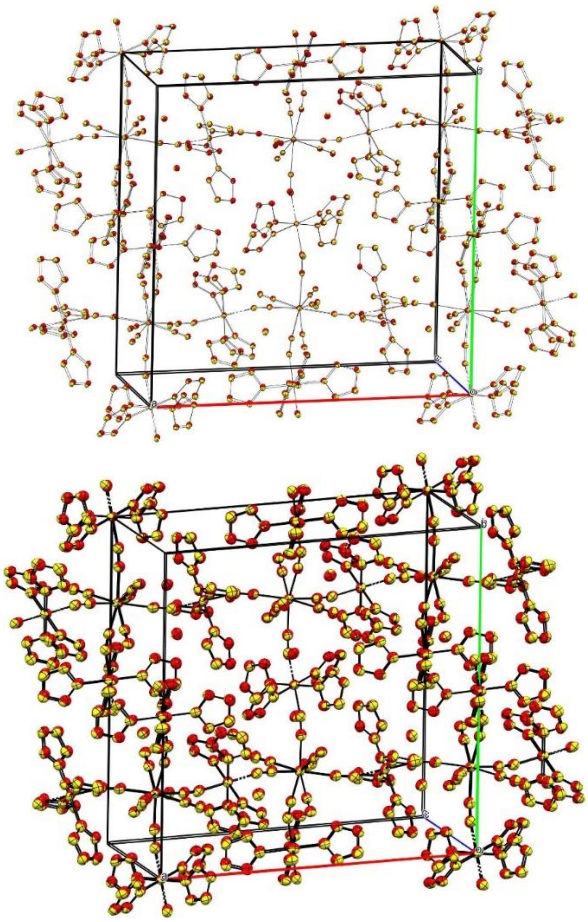

Figure S4. Packing of the crystal structure after irradiation (yellow; step 7) and after thermal relaxation (red; step 9). 10% or 50% probability level for ellipsoids.

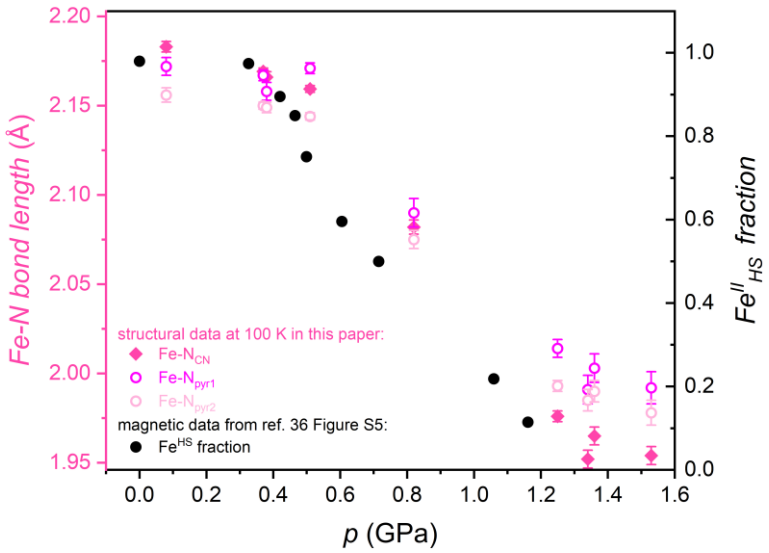

Figure S5. Comparison of the Fe-N bond contraction in **FeNb** under high pressure at 100 K reported in this work (pink points) with the Fe^{II}_{HS} molar fraction calculated from the magnetic data at low temperature around 100 K reported in Figure S5 of the ref. 37.

Table S6. Selected bond lengths and angles for **FeNb** in nine consecutive diffraction experiment (steps in Figure 4) at three different pressures before and after light irradiation, with the crystallographic data collected at 5 K.

Step	*p* (GPa)	*T* (K)	Details	Fe-N_{CN} (Å) Fe1-N2	Fe-N_{pyr} (Å) Fe1-N3	Fe-N_{pyr} (Å) Fe1-N5	Fe-N (Å) average
1	0.28(2)	5	Before irradiation	2.163(2)	2.166(3)	2.149(2)	2.16(1)
2			After 1st irradiation for 65 min	2.165(2)	2.171(4)	2.153(2)	2.16(1)
3			After 2nd irradiation for 40 min	2.162(2)	2.172(4)	2.152(3)	2.16(1)
4	0.82(1)	5	Before irradiation	2.072(5)	2.106(8)	2.087(6)	2.09(2)
5			After irradiation for 50 min	2.089(4)	2.124(7)	2.101(5)	2.11(2)
6	0.87(1)	5	Before irradiation	2.023(4)	2.054(6)	2.038(4)	2.04(1)
7			After 1st irradiation for 30 min	2.076(3)	2.106(4)	2.082(3)	2.09(1)
8			After 2nd irradiation for 20 min	2.079(5)	2.099(5)	2.081(3)	2.09(1)
9			After thermal relaxation at 60 K	2.028(5)	2.066(7)	2.041(5)	2.04(2)

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2. G. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.
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4. D. Pinkowicz, G. Handzlik, K. Dziubek and M. Magott, dataset, 2025, DOI: doi.org/10.15151/ESRF-ES-708312219.