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Structural and spectroscopic characterisation of the spin crossover in $[Fe(abpt)_2(NCS)_2]$ polymorph A

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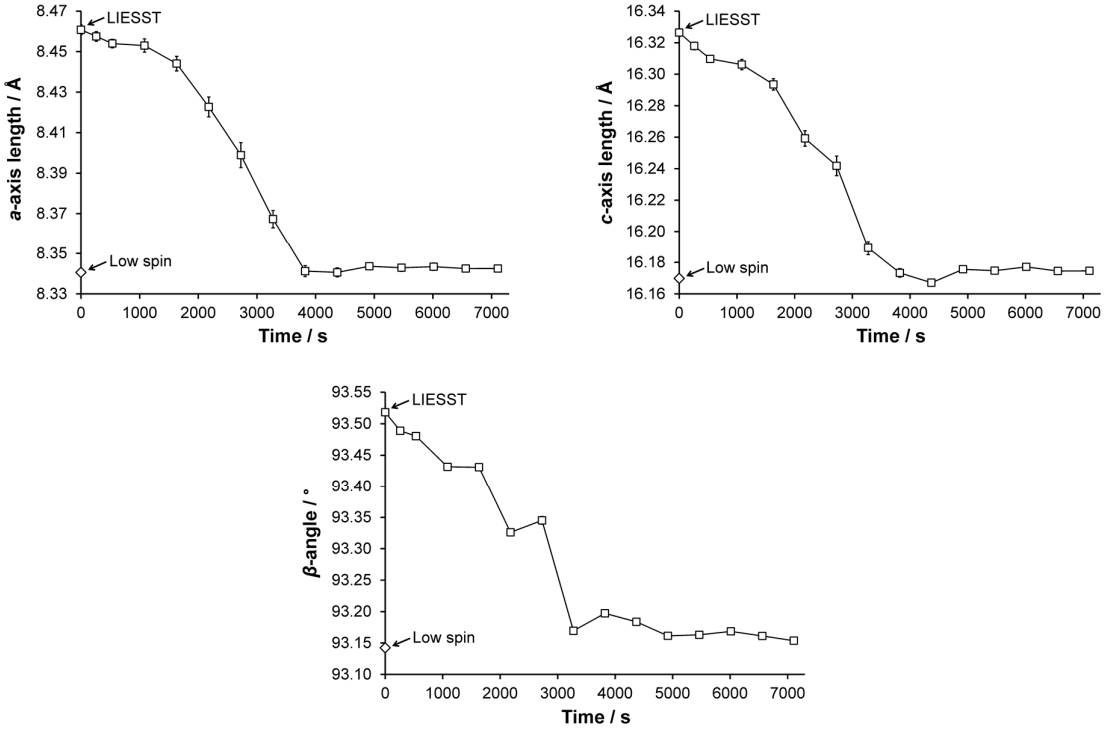

Figure S1 - Illustration of the change in the *a*-axis, *b*-axis and *β*-angle as a function of time at 30 K as a result of the relaxation of the LIESST HS* state. Note: Each data point is plotted at the time mid-point of its two consecutive omega runs, therefore an error between +/-(535 to 538) s is associated with all data points except the 1st data point after turning the laser off (at 262 s) where the error is +/-262 s.

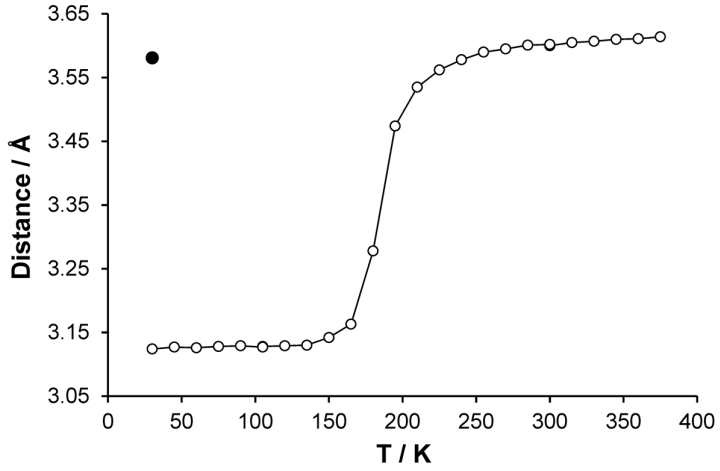

Figure S2 - Change in D···A distance for the C2-H2···N4#1 (#1 = -*x*+1, -*y*+1, -*z*+1) hydrogen bond in **A**: (o) as a function of temperature, (●) LIESST HS* structure.

Strain analysis

Values of the individual strains were obtained by first fitting a function of the form

$$a_o = a_1 + a_2\Theta_s \coth\left(\frac{\Theta_s}{T}\right) \quad \text{(S1)}$$

to lattice parameters in a temperature range well above the HS to LS transition. Extrapolation to low temperatures of the fit gives the reference parameters, a_o, b_o, $(c\sin\beta)_o$ and $(\cos\beta^*)_o$. The saturation temperature, Θ_s, gives the correct form for approaching T = 0 K with zero slope. Linear strains are then given by (after Carpenter *et al*., *Eur. J. Mineral.,* 1998, **10**, 621-691)

$$e_1 = \frac{a - a_o}{a_o} \quad \text{(S2)}$$

$$e_2 = \frac{b - b_o}{b_o} \quad \text{(S3)}$$

$$e_3 = \frac{c\sin\beta - (c\sin\beta)_o}{(c\sin\beta)_o} \quad \text{(S4)}$$

and the non-zero shear strain is

$$e_5 \approx \frac{\cos\beta^* - (\cos\beta^*)_o}{(\cos\beta^*)_o}. \quad \text{(S5)}$$

A value of Θ_s = 90 K was found to give a good representation of the four baselines shown in Figure S3(a)-(d) and ties in well with the single data point for the HS* state at 30 K. The same procedure can be followed for the volume strain, V_s, (Fig. S3(e)) which is given by

$$V_s = \frac{V - V_o}{V_o}. \quad \text{(S6)}$$

The resulting values of all the strains are shown as a function of temperature in Figure S3(f).

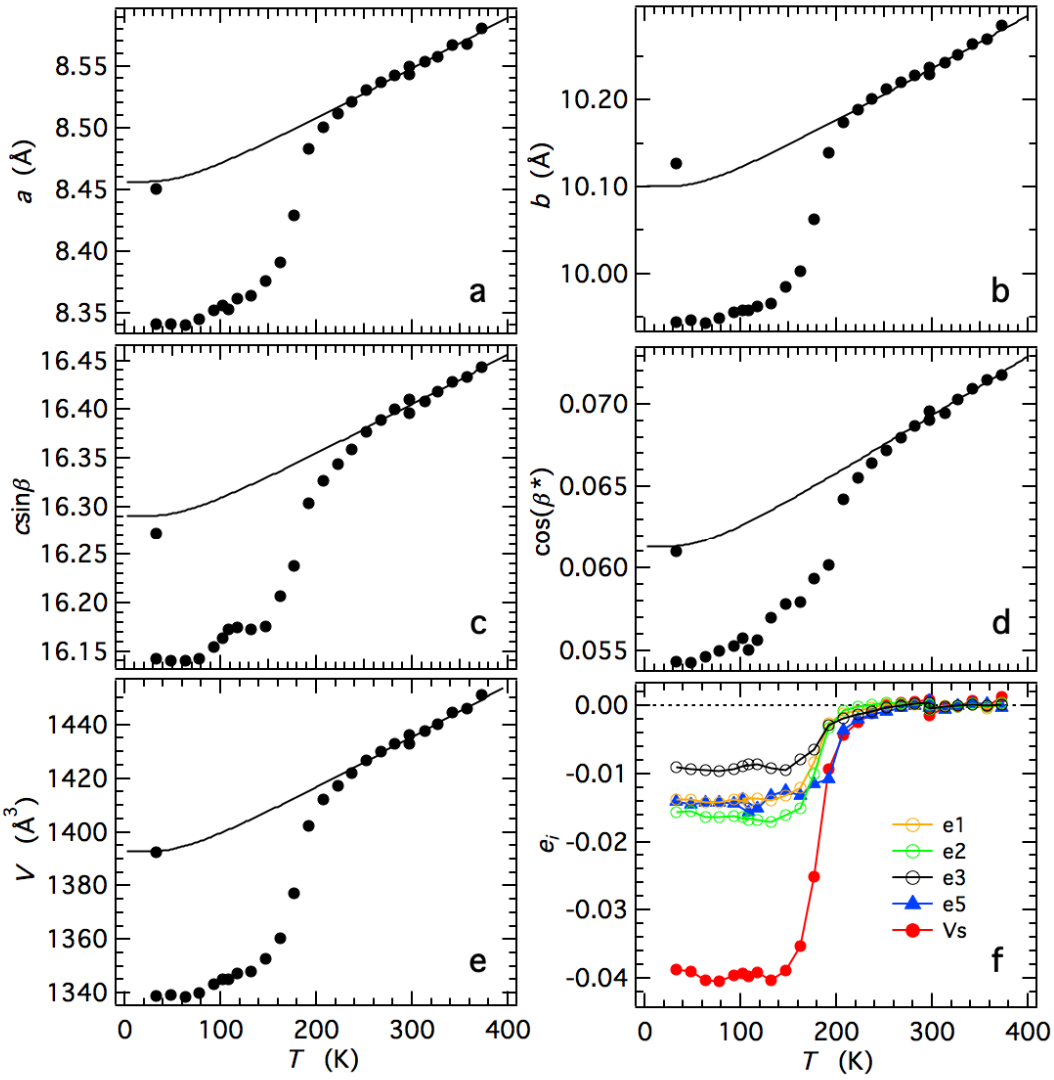

Figure S3 - Strain analysis from lattice parameter data. The solid curves in (a) – (e) are baseline (a_o, b_o, c_o, etc) fits to the highest temperature data using Equation S1, with the value of Θ_s = 90 K giving a good fit and passing through the 30 K data point for the high spin state induced by laser irradiation. (f) Strains determined using Equations S2-6.

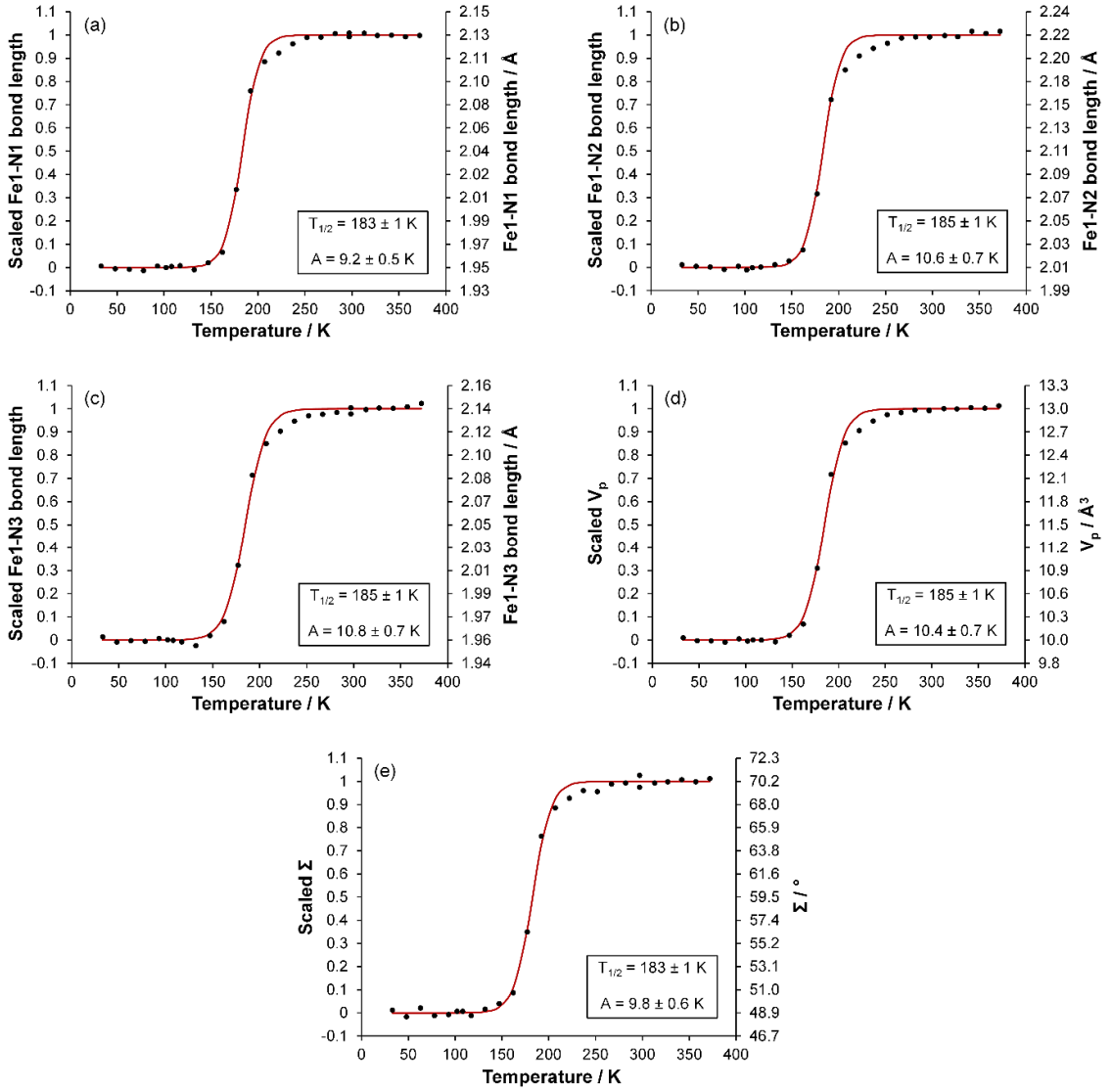

Figure S4 - Change in crystallographic parameters (rescaled to values between 0 and 1) as a function of temperature: (a)-(c) Fe-N bond lengths, (d) the volume of the Fe octahedron (V_p) and (e) the distortion parameter (Σ, the sum of the absolute value of the deviation of all 12 *cis* N-Fe-N angles from 90°). The red curve illustrates the fit of a sigmoidal function based on Equation 4 and the fit parameters, $T_{1/2}$ and A, are shown on each individual plot. Note: The sigmoid is not a perfect fit to the data, there is a slight deviation just above $T_{1/2}$ and this will influence the fit parameters.

Table S1 - Crystal data and refinement results for $[Fe(abpt)_2(NCS)_2]$ polymorph **A** at 120 K, 150 K, 165 K, 180 K and 210 K.

	120(2) K (LS)	**150(2) K**	**165(2) K**	**180(2) K**	**210(2) K**
Empirical formula	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$
Formula weight	648.53	648.53	648.53	648.53	648.53
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.3636(8)	8.3770(9)	8.3913(4)	8.4290(4)	8.5008(3)
b (Å)	9.9597(10)	9.9820(11)	10.0025(5)	10.0626(5)	10.1744(4)
c (Å)	16.198(2)	16.198(2)	16.2339(8)	16.2671(8)	16.3606(6)
β (°)	93.114(2)	93.306(2)	93.321(1)	93.402(1)	93.684(1)
V (Å^3)	1347.3(2)	1352.2(3)	1360.29(12)	1377.31(12)	1412.11(9)
Z	2	2	2	2	2
Temperature (K)	120(2)	150(2)	165(2)	180(2)	210(2)
D_c (Mg m^{-3})	1.599	1.593	1.583	1.564	1.525
μ (mm^{-1})	0.763	0.760	0.756	0.746	0.728
F(000)	664	664	664	664	664
Crystal size (mm^3)	0.36 x 0.30 x 0.26	0.36 x 0.30 x 0.26	0.36 x 0.30 x 0.26	0.36 x 0.30 x 0.26	0.36 x 0.30 x 0.26
θ range for data collection (°)	2.40 - 28.28	2.40 - 28.29	2.39 - 28.27	2.38 - 28.28	2.36 - 28.30
Ranges of h, k, l	$-10 \le h \le 11$, $-13 \le k \le 9$, $-21 \le l \le 15$	$-11 \le h \le 11$, $-13 \le k \le 12$, $-21 \le l \le 21$	$-10 \le h \le 11$, $-13 \le k \le 9$, $-21 \le l \le 15$	$-11 \le h \le 10$, $-13 \le k \le 9$, $-16 \le l \le 21$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-21 \le l \le 21$
Refl. collected	9018	14820	9138	9303	15676
R_{int}	0.0312	0.0336	0.0288	0.0309	0.0340
Data/parameters	3333/202	3357/202	3374/202	3428/202	3521/202
Absorption coef. min/max	0.756/1.000	0.825/1.000	0.732/1.000	0.844/1.000	0.870/1.000
GooF (F^2)	1.040	1.043	1.022	1.034	1.044
Final R_1 [$I > 2\sigma(I)$]	0.0328	0.0293	0.0311	0.0335	0.0320
wR_2 [$I > 2\sigma(I)$]	0.0762	0.0700	0.0697	0.0760	0.0767
Largest diff. peak/hole (e Å^{-3})	0.36/-0.41	0.34/-0.33	0.33/-0.33	0.32/-0.27	0.37/-0.37

Table S2 - Hydrogen bonds for $[Fe(abpt)_2(NCS)_2]$ polymorph **A**. Symmetry transformations used to generate equivalent atoms: #1 = *x*+1/2, -*y*+3/2, *z*+1/2; #2 = -*x*+1, -*y*+1, -*z*+1.

D-H···A		**270(2) K**	**210(2) K**	**180(2) K**	**165(2) K**	**150(2) K**	**120(2) K**
N6-H6B···N7	d(D-H) (Å)	0.93(2)	0.89(2)	0.87(2)	0.89(2)	0.88(2)	0.91(2)
	d(H···A) (Å)	2.12(2)	2.13(2)	2.17(2)	2.13(2)	2.16(2)	2.13(2)
	d(D···A) (Å)	2.847(3)	2.851(2)	2.851(2)	2.850(2)	2.850(2)	2.851(2)
	<(DHA) (°)	135(2)	137.4(19)	135(2)	138.4(19)	135.3(18)	136.1(19)
N6-H6A···S1#1	d(D-H) (Å)	0.89(2)	0.93(2)	0.93(2)	0.93(2)	0.92(2)	0.93(2)
	d(H···A) (Å)	2.69(2)	2.65(2)	2.60(2)	2.59(2)	2.61(2)	2.61(2)
	d(D···A) (Å)	3.450(2)	3.4314(19)	3.403(2)	3.3958(18)	3.3890(17)	3.3862(18)
	<(DHA) (°)	143.1(19)	142.1(17)	144.2(18)	144.5(17)	142.4(17)	142.1(18)
C2-H2···N4#2	d(D-H) (Å)	0.93	0.94	0.95	0.95	0.95	0.95
	d(H···A) (Å)	2.82	2.75	2.49	2.38	2.36	2.35
	d(D···A) (Å)	3.596(3)	3.536(3)	3.279(3)	3.163(2)	3.142(2)	3.128(2)
	<(DHA) (°)	142.2	141.6	140.6	140	139.6	139.3

D-H···A		**30(2) K**	**30(2) K LIESST**	**296 K, ambient**	**296 K, 1.4(2) kbar**	**296 K, 5.1(2) kbar**
N6-H6B···N7	d(D-H) (Å)	0.88(2)	0.90(2)	0.86(2)	0.87(2)	0.86(2)
	d(H···A) (Å)	2.16(2)	2.11(2)	2.12(6)	2.29(7)	2.22(5)
	d(D···A) (Å)	2.853(2)	2.852(2)	2.841(10)	2.839(8)	2.847(7)
	<(DHA) (°)	134.5(19)	139.4(17)	141(9)	122(6)	130(5)
N6-H6A···S1#1	d(D-H) (Å)	0.89(2)	0.93(2)	0.87(2)	0.867(19)	0.882(19)
	d(H···A) (Å)	2.61(2)	2.63(2)	2.80(7)	2.75(5)	2.70(5)
	d(D···A) (Å)	3.3814(18)	3.4170(15)	3.482(9)	3.437(7)	3.382(6)
	<(DHA) (°)	145.0(19)	143.0(15)	137(8)	138(6)	136(5)
C2-H2···N4#2	d(D-H) (Å)	0.95	0.95	0.93	0.93	0.93
	d(H···A) (Å)	2.34	2.79	2.81	2.77	2.44
	d(D···A) (Å)	3.124(2)	3.580(2)	3.579(13)	3.551(11)	3.215(11)
	<(DHA) (°)	139.6	141.8	141	142.7	140.4