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Structural Studies into the Spin Crossover Behaviour of $Fe(abpt)_2(NCS)_2$ Polymorphs B and D

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Supplementary information

Table S1 Crystal data and structure refinement for Polymorph B

Identification code	**300(2) K**	**100(2) K**	**ambient**	**9 kbar**	**11.5 kbar**	**13.5 kbar**	**16 kbar**	**23.4 kbar**
Empirical formula	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$
Formula weight	648.53	648.53	648.53	648.53	648.53	648.53	648.53	648.53
Temperature/K	300(2)	100(2)	296.15	296.15	296.15	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-1	P-1	P-1
a/Å	11.5730(6)	11.47261(8)	11.5739(6)	11.3795(5)	11.3439(6)	9.2535(13)	9.1367(16)	8.985(4)
b/Å	9.6589(5)	9.58685(8)	9.6588(8)	9.4118(7)	9.3494(9)	11.3483(8)	11.3660(11)	11.328(3)
c/Å	12.8541(7)	12.72647(10)	12.8455(9)	12.4288(7)	12.3371(9)	12.2374(15)	12.1110(19)	12.013(5)
α/°	90	90	90	90	90	101.283(7)	101.644(9)	101.89(2)
β/°	101.2740(10)	100.5225(7)	101.244(4)	100.972(3)	100.984(4)	90.790(8)	91.715(10)	92.74(3)
γ/°	90	90	90	90	90	90.653(9)	90.844(11)	91.31(3)
Volume/Å^3	1409.14(13)	1376.197(18)	1408.44(17)	1306.81(14)	1284.49(17)	1260.0(3)	1231.0(3)	1194.4(8)
Z	2	2	2	2	2	2	2	2
ρ_{calc}g/cm^3	1.528	1.565	1.529	1.648	1.677	1.709	1.750	1.803
μ/mm^{-1}	0.730	0.747	0.384	0.414	0.421	0.429	0.439	0.453
F(000)	664.0	664.0	664.0	664.0	664.0	664.0	664.0	664.0
Crystal size/mm^3	0.56 ×0.42 × 0.34	0.56 ×0.42 × 0.34	0.24 × 0.20 × 0.1	0.24 × 0.20 × 0.1	0.24 × 0.20 × 0.1	0.24 × 0.20 × 0.1	0.24 × 0.20 × 0.1	0.24 × 0.20 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)
2θ range for data collection/°	4.334 to 52.744	5.286 to 52.726	3.422 to 47.228	3.512 to 47.21	4.278 to 47.346	2.888 to 45.82	2.888 to 47.076	2.9 to 47.216
Index ranges	$-14 \le h \le 14$, $-11 \le k \le 12$, $-16 \le l \le 11$	$-14 \le h \le 14$, $-11 \le k \le 11$, $-15 \le l \le 15$	$-16 \le h \le 16$, $-11 \le k \le 10$, $-16 \le l \le 13$	$-16 \le h \le 16$, $-9 \le k \le 10$, $-13 \le l \le 16$	$-15 \le h \le 16$, $-10 \le k \le 10$, $-16 \le l \le 14$	$-10 \le h \le 9$, $-15 \le k \le 15$, $-12 \le l \le 15$	$-9 \le h \le 10$, $-15 \le k \le 15$, $-15 \le l \le 13$	$-9 \le h \le 9$, $-15 \le k \le 15$, $-12 \le l \le 12$
Reflections collected	8218	44396	20877	19633	17152	17608	14154	6813
Independent reflections	2875 [R_{int} = 0.0205, R_{sigma} = 0.0222]	2806 [R_{int} = 0.0342, R_{sigma} = 0.0113]	2101 [R_{int} = 0.0557, R_{sigma} = 0.0446]	1928 [R_{int} = 0.0540, R_{sigma} = 0.0423]	1924 [R_{int} = 0.0512, R_{sigma} = 0.0404]	1985 [R_{int} = 0.0564, R_{sigma} = 0.0445]	1805 [R_{int} = 0.0607, R_{sigma} = 0.0551]	1305 [R_{int} = 0.0679, R_{sigma} = 0.0866]
Data/restraints/parameters	2875/0/202	2806/0/202	2101/0/202	1928/0/202	1924/0/202	1985/346/375	1805/346/369	1305/346/363
Goodness-of-fit on F^2	1.029	1.073	1.081	1.054	1.079	1.060	1.006	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0283, wR_2 = 0.0717	R_1 = 0.0221, wR_2 = 0.0552	R_1 = 0.0387, wR_2 = 0.0924	R_1 = 0.0369, wR_2 = 0.0946	R_1 = 0.0362, wR_2 = 0.0800	R_1 = 0.0399, wR_2 = 0.0994	R_1 = 0.0364, wR_2 = 0.0817	R_1 = 0.0514, wR_2 = 0.1196
Final R indexes [all data]	R_1 = 0.0352, wR_2 = 0.0754	R_1 = 0.0229, wR_2 = 0.0556	R_1 = 0.0800, wR_2 = 0.1159	R_1 = 0.0632, wR_2 = 0.1107	R_1 = 0.0615, wR_2 = 0.0884	R_1 = 0.0699, wR_2 = 0.1127	R_1 = 0.0756, wR_2 = 0.0947	R_1 = 0.0980, wR_2 = 0.1373
Largest diff. peak/hole / e Å^{-3}	0.19/-0.20	0.26/-0.25	0.25/-0.25	0.30/-0.28	0.22/-0.24	0.20/-0.21	0.22/-0.19	0.23/-0.27

Table S2 Crystal data and structure refinement for Polymorph D variable temperature.

Identification code	**300(2) K**	**275(2) K**	**250(2) K**	**225(2) K**	**200(2) K**	**175(2) K**	**150(2) K**	**125(2) K**
Empirical formula	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$
Formula weight	648.53	648.53	648.53	648.53	648.53	648.53	648.53	648.53
Temperature/K	300(2)	275(2)	250(2)	225(2)	200(2)	175(2)	150(2)	125(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	10.8097(3)	10.8017(4)	10.7949(3)	10.7881(3)	10.7828(3)	10.7833(3)	10.7982(4)	10.8057(3)
b/Å	15.9326(4)	15.9218(5)	15.9119(5)	15.9005(5)	15.8845(5)	15.8575(5)	15.8008(5)	15.7552(5)
c/Å	17.4617(5)	17.4303(6)	17.3979(5)	17.3637(5)	17.3213(5)	17.2623(5)	17.1570(6)	17.0726(5)
α/°	90	90	90	90	90	90	90	90
β/°	106.8470(10)	106.8250(10)	106.8040(10)	106.8010(10)	106.8280(10)	106.9690(10)	107.3830(10)	107.6380(10)
γ/°	90	90	90	90	90	90	90	90
Volume/Å^3	2878.30(14)	2869.38(17)	2860.78(15)	2851.36(15)	2839.74(15)	2823.27(14)	2793.64(17)	2769.90(14)
Z	4	4	4	4	4	4	4	4
ρ_{calc}g/cm^3	1.497	1.501	1.506	1.511	1.517	1.526	1.542	1.555
μ/mm^{-1}	0.714	0.717	0.719	0.721	0.724	0.728	0.736	0.742
F(000)	1328.0	1328.0	1328.0	1328.0	1328.0	1328.0	1328.0	1328.0
Crystal size/mm^3	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.532 to 52.744	3.536 to 52.744	3.54 to 52.744	3.544 to 52.74	3.55 to 52.738	3.562 to 52.734	3.582 to 52.74	3.598 to 52.742
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -17 ≤ l ≤ 21	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -17 ≤ l ≤ 21	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 17	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -17 ≤ l ≤ 21	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -17 ≤ l ≤ 21
Reflections collected	23130	28078	17086	17075	17015	16896	27288	16506
Independent reflections	5880 [R_{int} = 0.0340, R_{sigma} = 0.0298]	5863 [R_{int} = 0.0340, R_{sigma} = 0.0255]	5831 [R_{int} = 0.0296, R_{sigma} = 0.0320]	5818 [R_{int} = 0.0291, R_{sigma} = 0.0311]	5804 [R_{int} = 0.0306, R_{sigma} = 0.0333]	5775 [R_{int} = 0.0299, R_{sigma} = 0.0326]	5709 [R_{int} = 0.0323, R_{sigma} = 0.0241]	5660 [R_{int} = 0.0303, R_{sigma} = 0.0332]
Data/restraints/parameters	5880/1/407	5863/0/403	5831/1/407	5818/1/407	5804/7/407	5775/1/407	5709/7/407	5660/1/407
Goodness-of-fit on F^2	1.018	1.025	1.021	1.013	1.028	1.020	1.024	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0792	R_1 = 0.0356, wR_2 = 0.0837	R_1 = 0.0331, wR_2 = 0.0754	R_1 = 0.0328, wR_2 = 0.0756	R_1 = 0.0334, wR_2 = 0.0760	R_1 = 0.0315, wR_2 = 0.0732	R_1 = 0.0285, wR_2 = 0.0683	R_1 = 0.0312, wR_2 = 0.0701
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.0864	R_1 = 0.0481, wR_2 = 0.0899	R_1 = 0.0483, wR_2 = 0.0821	R_1 = 0.0453, wR_2 = 0.0812	R_1 = 0.0460, wR_2 = 0.0819	R_1 = 0.0434, wR_2 = 0.0787	R_1 = 0.0363, wR_2 = 0.0720	R_1 = 0.0410, wR_2 = 0.0738
Largest diff. peak/hole / e Å^{-3}	0.20/-0.28	0.70/-0.70	0.22/-0.30	0.23/-0.30	0.21/-0.36	0.30/-0.33	0.26/-0.36	0.31/-0.41

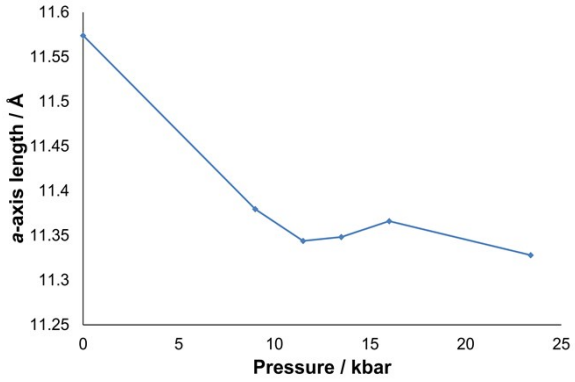
Table S2 Crystal data and structure refinement for Polymorph D variable temperature continued

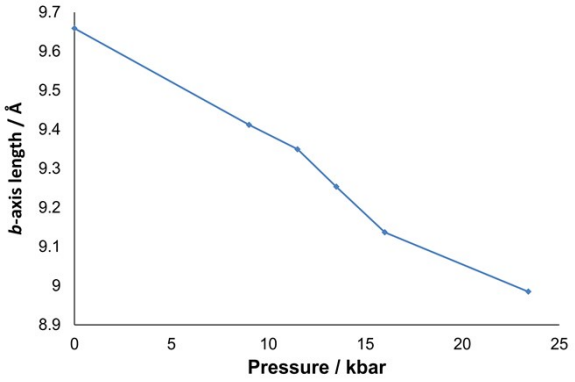
Identification code	**100(2) K**	**75(2) K**	**50(2) K**	**30(2) K**	**30(2) K LIESST**
Empirical formula	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}FeN_{14}S_2$
Formula weight	648.53	648.53	648.53	648.53	648.53
Temperature/K	100(2)	75(2)	50(2)	30(2)	30(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	10.8090(3)	10.8076(3)	10.8072(4)	10.8082(4)	10.7016(4)
b/Å	15.7339(5)	15.7173(5)	15.7062(6)	15.6979(5)	15.9017(6)
c/Å	17.0294(5)	17.0045(5)	16.9907(7)	16.9850(6)	17.1557(6)
α/°	90	90	90	90	90
β/°	107.6660(10)	107.6570(10)	107.6310(10)	107.6180(10)	106.0400(10)
γ/°	90	90	90	90	90
Volume/Å^3	2759.57(14)	2752.41(14)	2748.53(19)	2746.61(17)	2805.79(18)
Z	4	4	4	4	4
ρ_{calc}g/cm^3	1.561	1.565	1.567	1.568	1.535
μ/mm^{-1}	0.745	0.747	0.748	0.749	0.733
F(000)	1328.0	1328.0	1328.0	1328.0	1328.0
Crystal size/mm^3	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16	0.4 × 0.24 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.606 to 52.744	3.61 to 52.742	3.612 to 52.744	3.614 to 52.734	3.558 to 52.742
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-10 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 18	-11 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-12 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	31337	16384	18564	31139	22558
Independent reflections	5646 [R_{int} = 0.0334, R_{sigma} = 0.0223]	5631 [R_{int} = 0.0289, R_{sigma} = 0.0321]	5622 [R_{int} = 0.0332, R_{sigma} = 0.0336]	5621 [R_{int} = 0.0363, R_{sigma} = 0.0245]	5744 [R_{int} = 0.0357, R_{sigma} = 0.0312]
Data/restraints/parameters	5646/1/407	5631/0/403	5622/0/403	5621/0/403	5744/0/403
Goodness-of-fit on F^2	1.024	1.027	1.042	1.039	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0266, wR_2 = 0.0636	R_1 = 0.0296, wR_2 = 0.0693	R_1 = 0.0302, wR_2 = 0.0695	R_1 = 0.0279, wR_2 = 0.0646	R_1 = 0.0293, wR_2 = 0.0682
Final R indexes [all data]	R_1 = 0.0326, wR_2 = 0.0664	R_1 = 0.0377, wR_2 = 0.0729	R_1 = 0.0393, wR_2 = 0.0730	R_1 = 0.0336, wR_2 = 0.0673	R_1 = 0.0379, wR_2 = 0.0719
Largest diff. peak/hole / e Å^{-3}	0.33/-0.39	0.34/-0.38	0.32/-0.39	0.34/-0.45	0.36/-0.38

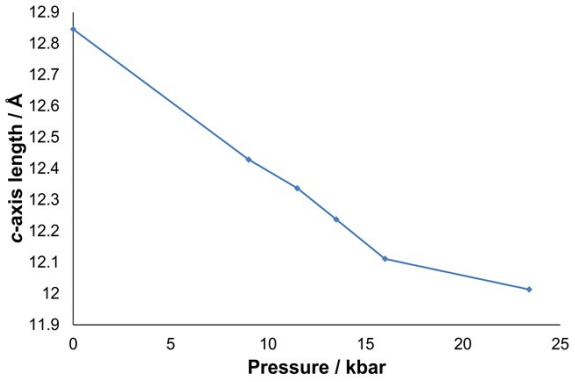
Table S3 Crystal data and structure refinement for Polymorph D variable pressure.

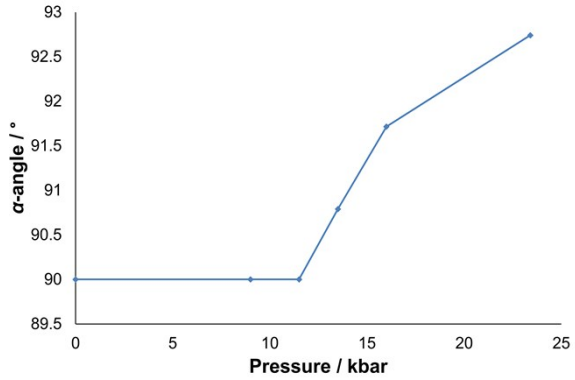
Identification code	**Ambient start**	**1.8(2) kbar**	**7.5(2) kbar**	**9.6(2) kbar**	**12.0(2) kbar**	**15.0(2) kbar**	**Ambient end**
Empirical formula	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}FeN_{14}S_2$	$C_{26}H_{20}N_{14}S_2Fe$	$C_{26}H_{20}N_{14}S_2Fe$
Formula weight	648.53	648.53	648.53	648.53	648.53	648.53	648.53
Temperature/K	296.15	296.15	296.15	296.15	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	10.7819(15)	10.760(2)	10.7361(7)	10.6923(8)	10.6433(7)	10.4607(17)	10.777(2)
b/Å	15.870(4)	15.808(6)	15.4827(17)	15.3683(18)	15.3285(16)	15.203(4)	15.859(5)
c/Å	17.415(3)	17.253(4)	16.6888(11)	16.4865(12)	16.4392(11)	16.348(3)	17.450(5)
α/°	90	90	90	90	90	90	90
β/°	106.875(10)	106.721(12)	107.567(4)	107.682(4)	107.475(4)	105.886(11)	106.734(12)
γ/°	90	90	90	90	90	90	90
Volume/Å^3	2851.7(9)	2810.5(14)	2644.7(4)	2581.1(4)	2558.2(4)	2500.7(9)	2856.2(13)
Z	4	4	4	4	4	4	4
ρ_{calc}g/cm^3	1.511	1.533	1.629	1.669	1.684	1.723	1.508
μ/mm^{-1}	0.377	0.382	0.409	0.416	0.420	0.430	0.376
F(000)	1328.0	1328.0	1328.0	1328.0	1328.0	1328.0	1328.0
Crystal size/mm^3	0.18 × 0.14 × 0.12	0.18 × 0.14 × 0.12	0.18 × 0.14 × 0.12	0.18 × 0.14 × 0.12	0.18 × 0.14 × 0.12	0.18 × 0.14 × 0.12	0.18 × 0.14 × 0.12
Radiation	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)	AgKα (λ = 0.56086)
2θ range for data collection/°	2.796 to 39.206	3.118 to 39.072	2.896 to 39.048	2.926 to 39.064	2.932 to 39.018	2.94 to 39.182	2.794 to 38.994
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -19 ≤ l ≤ 19	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -19 ≤ l ≤ 18	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 19	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 19	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -18 ≤ l ≤ 17	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16	-12 ≤ h ≤ 12, -16 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	15847	23079	23039	22491	22284	13610	24875
Independent reflections	2524 [R_{int} = 0.0858, R_{sigma} = 0.0948]	2717 [R_{int} = 0.0567, R_{sigma} = 0.0436]	2697 [R_{int} = 0.0562, R_{sigma} = 0.0426]	2669 [R_{int} = 0.0599, R_{sigma} = 0.0403]	2601 [R_{int} = 0.0545, R_{sigma} = 0.0352]	2354 [R_{int} = 0.0727, R_{sigma} = 0.0687]	2832 [R_{int} = 0.0610, R_{sigma} = 0.0428]
Data/restraints/parameters	2524/346/403	2717/351/407	2697/346/403	2669/346/403	2601/346/393	2354/346/393	2832/350/407
Goodness-of-fit on F^2	1.047	1.059	1.100	1.084	1.112	1.085	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0821, wR_2 = 0.1916	R_1 = 0.0396, wR_2 = 0.0925	R_1 = 0.0467, wR_2 = 0.1124	R_1 = 0.0498, wR_2 = 0.1220	R_1 = 0.0466, wR_2 = 0.1111	R_1 = 0.0735, wR_2 = 0.1762	R_1 = 0.0455, wR_2 = 0.1204
Final R indexes [all data]	R_1 = 0.1318, wR_2 = 0.2231	R_1 = 0.0604, wR_2 = 0.1028	R_1 = 0.0649, wR_2 = 0.1234	R_1 = 0.0705, wR_2 = 0.1343	R_1 = 0.0642, wR_2 = 0.1213	R_1 = 0.1088, wR_2 = 0.1986	R_1 = 0.0700, wR_2 = 0.1354
Largest diff. peak/hole / e Å^{-3}	0.48/-0.42	0.26/-0.24	0.28/-0.27	0.31/-0.34	0.30/-0.27	0.46/-0.52	0.23/-0.28

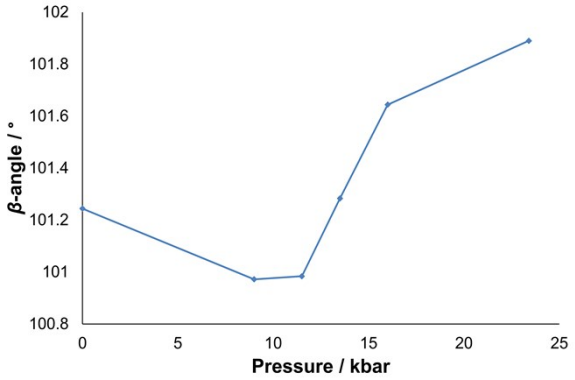
Figure S1 – Polymorph B effect of pressure on the unit cell parameters. Note that to allow direct comparison with the original monoclinic cell *a* and *b* and alpha and beta on the conventional triclinic cell have been switched for these plots.

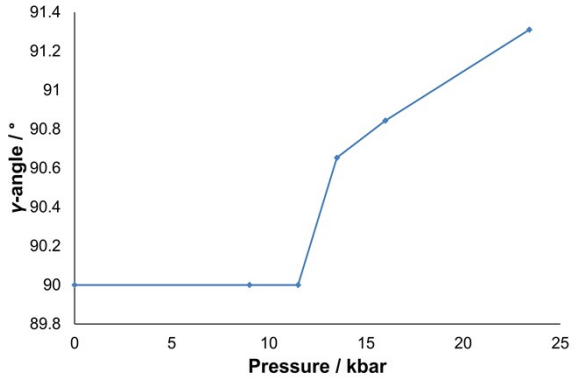












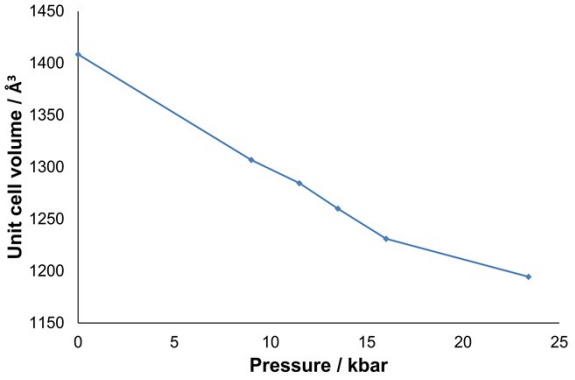


Figure S2 – Polymorph D effect of temperature on unit cell parameters. Point shown in red dashed circle is the LIESST structure.

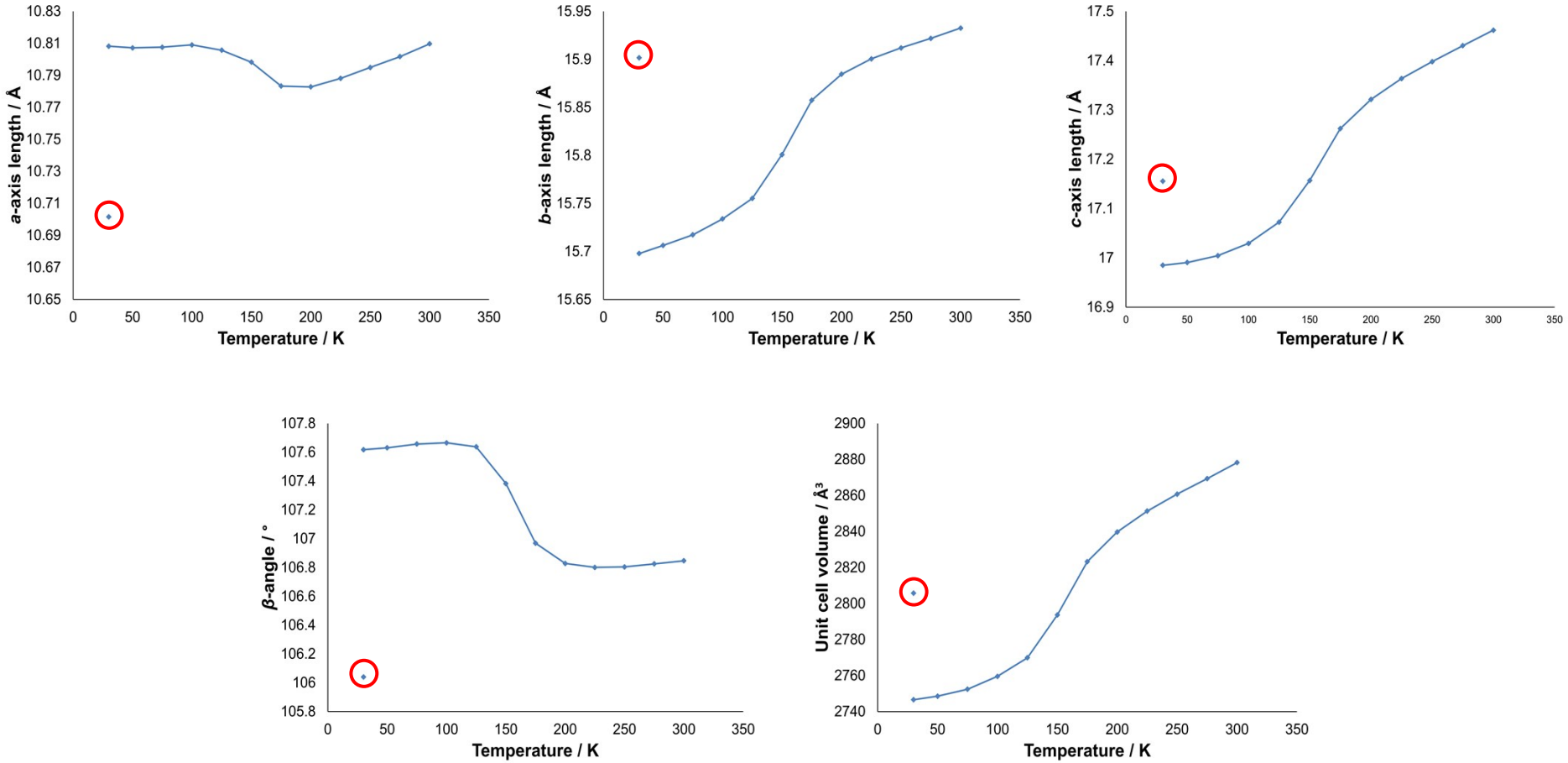


Figure S3 – Polymorph D effect of pressure on unit cell parameters