Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for:

Structural transition in $KMnCrF_6$ – a chemically ordered magnetic ferroelectric.

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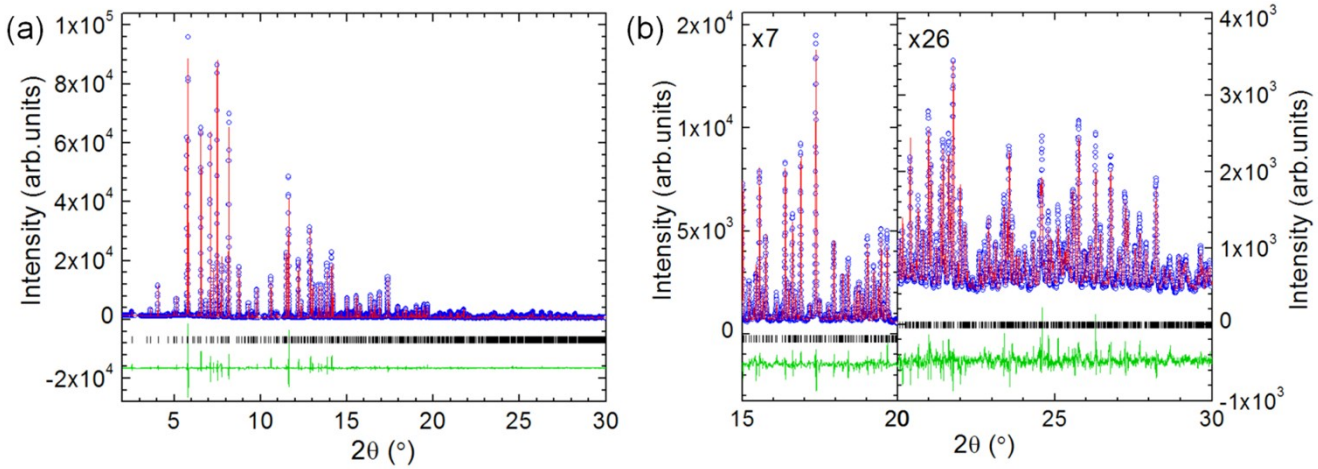

Fig. S1 (a) Final observed (open blue circles), calculated (red line) and difference (green line) synchrotron X-ray powder diffraction profile of $KMnCrF_6$ (space group $P4_2/mbc$), collected on ID31 (ESRF), $\lambda = 0.39992$ Å, $T = 5$ K. The lower solid green line shows the difference profiles and the tick marks show the reflection positions. (b) Magnification of the high 2θ region.

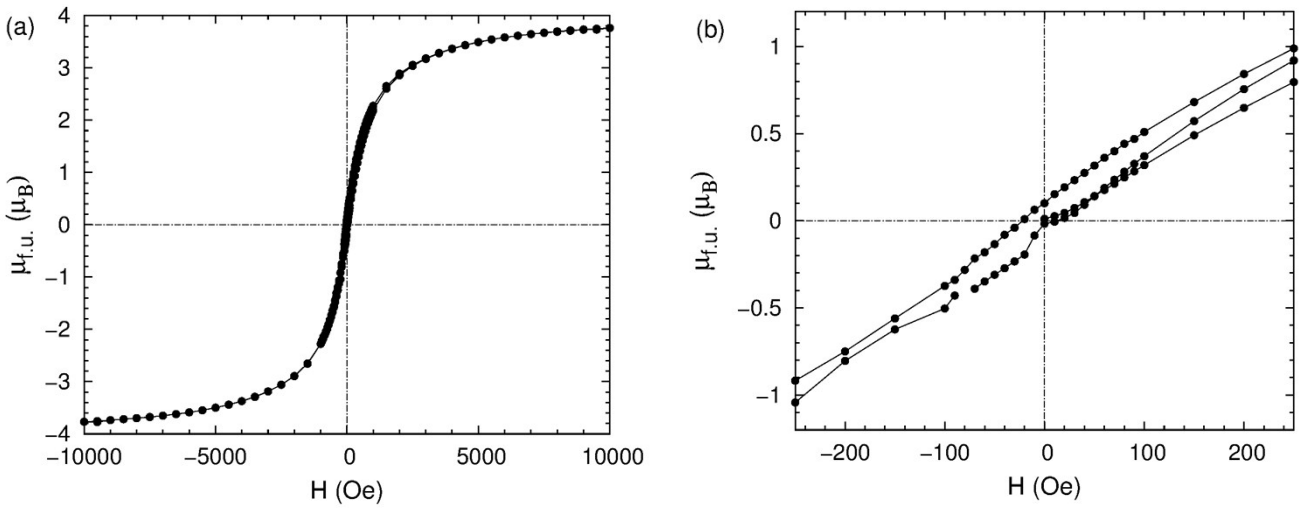

Fig. S2 (a) The magnetic hysteresis loop measured at $T = 5$ K with $H_{max} = 10000$ Oe with an almost saturated moment of 3.76 μ_B per formula unit of $KMnCrF_6$. (b) The magnification of the low field regime shows the small coercive field of ~50 Oe.

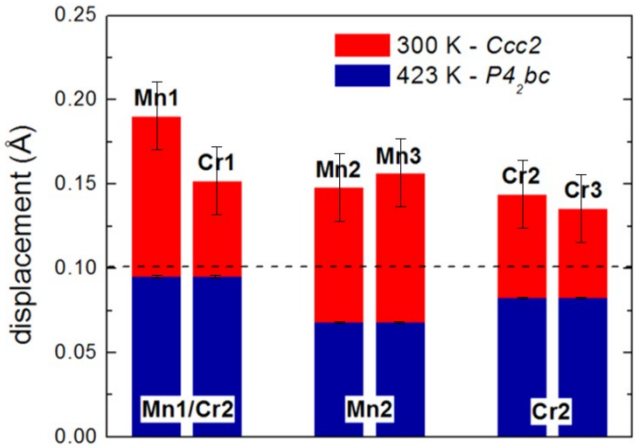

Fig. S3 The displacements of Mn and Cr from the basal plane of the coordination octahedra, which is defined by the mean plane of coordinating fluorine. Whilst the displacement along the polar *c*-axis is small in the tetragonal phase, it exceed 0.1 Å at and below 300 K.

Table S1 Rietveld refinement results at 423 K in space group $P4_2bc$.[a]

space group: $P4_2bc$		No. 106			T = 423 K	
a = 12.68202(1) Å		c = 7.97617(1) Å			V = 1282.837(2) Å^3	
		x	y	z	B_{iso}/ Å^2	Occ.
Mn1	4*b*	0	0.5	0.012(1)	0.70(3)	0.5
Cr1	4*b*	0	0.5	0.012(1)	0.70(3)	0.5
Mn2	8*c*	0.0738(3)	0.7873(2)	0.5085(5)	0.57(5)	1
Cr2	8*c*	0.4250(3)	0.2886(2)	0.0103(5)	0.85(6)	1
K1	8*c*	0.8359(2)	0.6801(2)	0.759(1)	2.81(4)	1
K2	4*a*	0	0	0.751(2)	1.17(7)	0.584(2)
F1	8*c*	0.5675(6)	0.3492(5)	-0.012(1)	2.44(3)	1
F2	8*c*	0.9277(6)	0.8633(5)	0.498(1)	2.44(3)	1
F3	8*c*	0.7837(5)	0.2753(5)	0.001(2)	2.44(3)	1
F4	8*c*	0.4966(4)	0.1542(7)	-0.010(1)	2.44(3)	1
F5	8*c*	0.9822(4)	0.6547(7)	0.501(1)	2.44(3)	1
F6	4*b*	0	0.5	0.745(2)	2.44(3)	1
F7	8*c*	0.2089(4)	0.0746(5)	0.750(2)	2.44(3)	1
F8	8*c*	0.2914(4)	0.5782(5)	0.261(2)	2.44(3)	1

[a] wR_p = 7.88 %; R_p = 6.00 %.

Table S2 The atomic positions as determined from Rietveld refinements in space groups $P4_2bc$ and $P4_2/mbc$ at T = 423 K. The displacement $d(z)$ is calculated by comparing the atomic positions of group ($P4_2bc$) and subgroup ($P4_2/mbc$).

	Wyckoff site					
	$P4_2bc$	$P4_2/mbc$	$z(P4_2bc)$	$z(P4_2/mbc)$	$d(z)$	$d(z)\cdot c$/ Å
Mn1	4*b*	4*c*	0.0119	0	0.0119	0.095
Cr1	4*b*	4*c*	0.0119	0	0.0119	0.095
Mn2	8*c*	8*h*	0.5085	0.5	0.0085	0.068
Cr2	8*c*	8*h*	0.0103	0	0.0103	0.082
K1	8*c*	8*g*	0.759	0.75	0.009	0.072
K2	4*a*	4*b*	0.751	0.75	0.001	0.008
F1	8*c*	8*h*	-0.012	0	-0.012	-0.096
F2	8*c*	8*h*	0.498	0.5	-0.002	-0.016
F3	8*c*	8*h*	0.001	0	0.001	0.008
F4	8*c*	8*h*	-0.010	0	-0.010	-0.080
F5	8*c*	8*h*	0.501	0.5	0.001	0.008
F6	4*b*	4*d*	0.745	0.75	-0.005	-0.040
F7	8*c*	16*i*	0.750	0.7409	0.0091	0.073
F8	8*c*		0.261	0.2409	0.0201	0.160

Table S3 The atomic positions as determined from Rietveld refinements in space groups *Ccc*2 and *Cccm* at $T = 300$ K. The displacement $d(z)$ is calculated by comparing the atomic positions of group (*Ccc*2) and subgroup (*Cccm*).

	Wyckoff site					
	*Ccc*2	*Cccm*	z(*Ccc*2)	z(*Cccm*)	$d(z)$	$d(z)\cdot c$/ Å
Mn1	4*b*	4*c*	0.520	0.5	0.020	0.159
Cr1	4*a*	4*d*	0.024	0	0.024	0.191
Mn2	8*d*	8*l*	0.519	0.5	0.019	0.151
Mn3	8*d*	8*l*	0.020	0	0.020	0.159
Cr2	8*d*	8*l*	0.019	0	0.019	0.151
Cr3	8*d*	8*l*	0.518	0.5	0.018	0.143
K1	8*d*	8*h*	0.268	0.25	0.018	0.143
K2	8*d*	8*g*	0.769	0.75	0.019	0.151
K3	4*c*	8*k*	0.765	0.750	0.015	0.119
K4	4*c*		0.266	0.250	0.016	0.127
F1	8*d*	8*l*	0.014	0	0.014	0.111
F2	8*d*	8*l*	0.502	0.5	0.002	0.016
F3	8*d*	8*l*	0.985	0	-0.015	-0.119
F4	8*d*	8*l*	0.497	0.5	-0.003	-0.024
F5	8*d*	8*l*	0.003	0	0.003	0.024
F6	8*d*	8*l*	0.505	0.5	0.005	0.040
F7	8*d*	8*l*	0.007	0	0.007	0.056
F8	8*d*	8*l*	0.487	0.5	-0.013	-0.103
F9	8*d*	8*l*	0.996	1	-0.004	-0.032
F10	8*d*	8*l*	0.512	0.5	0.012	0.095
F11	8*d*	16*m*	0.256	0.240	0.006	0.127
F12	8*d*		0.756	0.760	-0.005	-0.040
F13	8*d*	16*m*	0.767	0.741	0.026	0.206
F14	8*d*		0.268	0.259	0.009	0.071
F15	4*a*	4*a*	0.256	0.25	0.006	0.048
F16	4*a*	4*b*	0.745	0.75	-0.005	-0.040

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