

Supplementary Data

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Structure-property correlation in $\text{Pb}_5\text{Al}_3\text{F}_{19}$ and the transitions between its five successive phases

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Abstract

$\text{Pb}_5\text{Al}_3\text{F}_{19}$ undergoes four phase transitions. Cooling from prototypic paraelectric phase I to paraelectric phase II results in a transition at 670(5) K without thermal hysteresis. The transition at 360(5) K on cooling from phase II to ferroelastic phase III is also without thermal hysteresis, that from phase III to antiferroelectric phase IV at 305(5) K has a hysteresis of 10(5) K and that from phase IV to ferroelectric phase V at 125(5) K a hysteresis of 135(5) K. The structures of phases II, IV and V were reported previously; that of phase III, determined jointly from a consideration of the neighboring phase structures and by group theoretical/normal mode analysis, is refined in this study by Rietveld analysis of combined X-ray and neutron diffraction powder profiles. In addition, the structure of phase I is predicted based on the atomic arrangement in phases II–V. Maximum total atomic displacement magnitudes at a phase transition in $\text{Pb}_5\text{Al}_3\text{F}_{19}$ are $\sim 0.6 \text{ \AA}$ by a Pb, $\sim 0.3 \text{ \AA}$ by an Al and $\sim 1.5 \text{ \AA}$ by a F atom. The upper limit for acceptable atomic displacements at a structurally-predicted new phase transition, commonly taken as 1.0 \AA , may hence require revision. The structural arrangement observed throughout the entire phase sequence is correlated both with the primary physical properties of each phase and the characteristics of each phase transition.

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Table 13S. Atomic displacements (\AA) between corresponding atoms in paraelastic phase II at 370 K* and prototypic phase I of $\text{Pb}_5\text{Al}_3\text{F}_{19}$ and the thermal/static (u_{eq}) displacements in \AA .

Figure captions

Figure 1S. (upper). View of phase V structure at 160 K along the c axis.
(lower). View along the a axis.

Figure 2S. (upper). View of phase IV structure at 295 K along the c axis, oriented as in
Figs. 1S and 4S.
(lower). View along the a axis. .

Figure 3S(a). Normal probability plot of the phase III atomic coordinates based on the
two sets of values in Table 9S.
(b). Normal probability plot of the Bravie *et al.* (2000) and Rietveld analysis
phase III atomic coordinates.

Figure 4S. (upper). View of phase II structure at 370 K along the c axis.
(lower). View along the a axis

Table 1S.

Atomic coordinates of ferroelectric Pb₅Al₃F₁₉ in phase V at 160 K*

	<i>x</i>	<i>y</i>	<i>z</i>
Pb1	0.42602(4)	0.27489(4)	0.0351*
Pb2	0	0.50000	0.1350(3)
Al1	0.1628(4)	0.3372	-0.021(1)
Al2	0	0	0.188(2)
F1	0.1140(10)	0.2478(9)	-0.174(2)
F2	0.1970(10)	0.4294(8)	0.142(2)
F3	0.0761(6)	0.4239	-0.097(3)
F4	0.2479(7)	0.2521	0.069(3)
F5	0	0	0.438(2)
F6	-0.0540(10)	0.1175(6)	0.673(2)
F7	0.3835(8)	0.1165	0.021(4)

* Origin; values of *z* have been replaced by *z* + 0.0.0351 here and in Table 2,
 see §3.0 and Table 4S. Parameters without uncertainties are derived (*e.g.*,
 $y = \frac{1}{2} - x$) or are at special positions (Sarraute *et al.*, 1996).

Table 2S.

Atomic coordinates of antiferroelectric $\text{Pb}_5\text{Al}_3\text{F}_{19}$ in phase IV at 295 K[†]

	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>
Pb1	8(g)	0.1734(1)	0.0867(1)	0.0091(5)
Pb2	8(g)	0.1102(1)	0.1741(1)	0.5037(4)
Pb3	8(g)	0.1700(1)	0.8889(1)	0.0007(5)
Pb4	8(g)	0.9118(1)	0.1722(1)	0.4958(5)
Pb5	8(g)	0.9932(2)	0.9858(2)	0.2352(9)
Al1	2(c)	1/4	1/4	0.2389(68)
Al2	2(c)	1/4	1/4	0.7580(110)
Al3	4(f)	1/4	3/4	0.2437(50)
Al4	8(g)	0.0072(9)	0.1663(9)	0.0054(32)
Al5	8(g)	0.8345(10)	0.0097(9)	0.4921(29)
F1	2(c)	1/4	1/4	0 [‡]
F2	2(c)	1/4	1/4	1/2 [‡]
F3	8(g)	0.2150(15)	0.1686(17)	0.2322(63)
F4	8(g)	0.2809(15)	0.3322(16)	0.7553(69)
F5	2(a)	1/4	3/4	0
F6	8(g)	0.8334(16)	0.2171(16)	0.2232(60)
F7	8(g)	0.1669(16)	0.7821(17)	0.2329(67)
F8	2(b)	3/4	1/4	1/2
F9	8(g)	0.0695(18)	0.1718(18)	0.8438(60)
F10	8(g)	0.9509(17)	0.1383(18)	0.8415(55)
F11	8(g)	0.9445(18)	0.1475(19)	0.1578(52)
F12	8(g)	0.0664(17)	0.1931(18)	0.1682(57)
F13	8(g)	0.9883(16)	0.2519(16)	0.9837(76)
F14	8(g)	0.0307(19)	0.0820(18)	0.0434(51)
F15	8(g)	0.9230(17)	0.0331(17)	0.5062(71)
F16	8(g)	0.8569(17)	0.9462(17)	0.3154(54)
F17	8(g)	0.8428(17)	0.9424(17)	0.6774(55)
F18	8(g)	0.8170(17)	0.0732(18)	0.6731(64)
F19	8(g)	0.8316(17)	0.0740(16)	0.3176(59)
F20	8(g)	0.7487(17)	0.9896(18)	0.4546(71)
F21	8(g)	0.8980(18)	0.0227(20)	-0.0096(63)
F22	8(g)	0.0190(19)	0.1064(17)	0.5122(70)

[†] As given by Andriamampianina *et al.* (1994) in space group $P4/n$. Average refined value of B_{iso} for all Al or all F atoms.

[‡] Unvaried coordinate in least squares refinement by Andriamampianina *et al.*, (1994).

Table 3S.

Atomic coordinates of antiferroelectric $\text{Pb}_5\text{Al}_3\text{F}_{19}$ in phase IV at 295 K,^{*} in the setting of Table I, also the corresponding atomic identification in phase V

phase IV	phase V	<i>x</i>	<i>y</i>	<i>z</i>
Pb1	1	0.2601(1)	0.4133(1) [*]	0.5091(5)
Pb2	1	0.2843(1)	-0.4361(1)	0.0037(4)
Pb3	1	0.0589(1)	0.2189(1)	0.5007(5)
Pb4	1	0.0840(1)	-0.2396(1)	0.9958(5)
Pb5	2	-0.0210(2)	-0.5074(2)	0.7352(9)
Al1	2	$\frac{1}{2}$	$\frac{1}{2}$	0.7389(68)
Al2	2	$\frac{1}{2}$	$\frac{1}{2}$	0.2580(110)
Al3	2	0	0	0.7437(50)
Al4	1	0.1735(9)	-0.3409(9)	0.5054(32)
Al5	1	0.8442(10)	-0.3248(9)	0.9921(29)
F1	5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$ [‡]
F2	5	$\frac{1}{2}$	$\frac{1}{2}$	0 [‡]
F3	6	0.3836(15)	0.4536(17)	0.7322(63)
F4	6	0.6131(15)	0.5513(16)	0.2553(69)
F5	5	0	0	$\frac{1}{2}$
F6	6	0.0505(16)	-0.1163(16)	0.7232(60)
F7	6	-0.0510(16)	0.1152(17)	0.7329(67)
F8	5	0	0	0
F9	1	0.2413(18)	-0.3977(18)	0.3438(60)
F10	1	0.0892(17)	-0.3126(18)	0.3415(55)
F11	2	0.0920(18)	-0.2970(19)	0.6578(52)
F12	2	0.2595(17)	-0.3733(18)	0.6682(57)
F13	4	0.2402(16)	-0.2364(16)	0.4837(76)
F14	3	0.1127(18)	-0.4487(19)	0.5434(51)
F15	3	-0.0439(17)	-0.3899(17)	0.0062(71)
F16	1	0.8031(17)	-0.4107(17)	0.8154(54)
F17	2	0.7852(17)	-0.4004(17)	0.1774(55)
F18	2	0.8902(17)	-0.2438(18)	0.1731(64)
F19	1	0.9056(17)	-0.2576(16)	0.8176(59)
F20	4	0.7383(17)	-0.2591(18)	0.9546(71)
F21	7	0.9207(18)	-0.3753(20)	0.4904(63)
F22	7	0.1254(19)	-0.4126(17)	0.0122(70)

^{*} Andriamampianina, Gravereau, Ravez & Abrahams (1994).

[‡] Coordinate unvaried in least squares refinement, see Table 2S.

Table 4S.

Atomic displacements (\AA) between corresponding atoms in antiferroelectric phase IV at 295 K^{*} and ferroelectric phase V of $\text{Pb}_5\text{Al}_3\text{F}_{19}$ at 160 K[†]

phase IV	phase V	Δx	Δy	Δz	$\Delta(xyz)$
Pb1	Pb1	0.208	0.180	0.189	0.334
Pb2	Pb1	0.134	0.143	0.228	0.301
Pb3	Pb1	0.214	0.089	0.250	0.341
Pb4	Pb1	0.141	0.204	0.286	0.379
Pb5	Pb2	0.297	0.105	0.474	0.569
Al1	Al2	0	0	0.115	0.115
Al2	Al2	0	0	0.254	0.254
Al3	Al2	0	0	0.150	0.150
Al4	Al1	0.151	0.052	0.063	0.172
Al5	Al1	0.099	0.175	0.160	0.257
F1	F5	0	0	0.196	0.196
F2	F5	0	0	0.196	0.196
F3	F6	0.883	1.006	0.175	1.350
F4	F6	0.038	0.062	0.343	0.351
F5	F5	0	0	0.196	0.196
F6	F6	0.050	0.017	0.110	0.122
F7	F6	0.042	0.033	0.180	0.188
F8	F5	0	0	0.196	0.196
F9	F1	0.154	0.166	0.126	0.259
F10	F1	0.917	0.351	0.143	0.992
F11	F2	0.085	0.303	0.140	0.344
F12	F2	0.884	0.794	0.065	1.190
F13	F4	0.222	0.109	0.876	0.910
F14	F3	0.518	0.351	0.762	0.986
F15	F3	0.481	0.456	0.492	0.825
F16	F1	0.782	0.349	0.332	0.918
F17	F2	0.252	0.410	0.002	0.481
F18	F2	0.838	0.555	0.029	1.006
F19	F1	0.139	0.277	0.316	0.443
F20	F4	0.195	0.099	1.088	1.110
F21	F7	0.526	0.116	0.478	0.719
F22	F7	0.126	0.412	0.319	0.536

* Andriamampianina, Gravereau, Ravez & Abrahams (1994).

† Sarraute, Ravez, von der Mühl, Bravic, Feigelson & Abrahams (1996), with origin shifted 0.0351, see §3.

Table 5S.

Atomic displacements (\AA) between corresponding atoms in antiferroelectric phase IV at 295 K and the triclinic ferroelastic phase III at 320 K

phase IV	phase III	Δx	Δy	Δz	$\Delta(xyz)$
Pb1	Pb1	0.030	0.019	0.039	0.053
Pb2	Pb3	0.038	0.038	0.027	0.122
Pb3	Pb4	0.048	0.110	0.001	0.120
Pb4	Pb2	0.031	0.024	0.022	0.045
Pb5	Pb5	0.258	0.214	0.157	0.339
Al1	Al3	0	0	0.080	0.080
Al2	Al3	0	0	0.058	0.058
Al3	Al3	0	0	0.045	0.045
Al4	Al2	0.055	0.144	0.185	0.241
Al5	Al1	0.088	0.189	0.044	0.213
F1,F5	F14	0	0	0	0
F2,F8	F13	0	0	0	0
F3	F15	0.060	0.100	0.280	0.303
F4	F16	0.926	0.718	0.250	1.198
F6	F18	0.053	0.162	0.222	0.280
F7	F17	0.270	0.047	0.441	0.519
F9	F2	0.221	0.094	0.211	0.320
F10	F6	0.471	0.051	0.357	0.593
F11	F7	0.262	0.053	0.312	0.411
F12	F8	0.576	0.411	0.107	0.716
F13	F12	0.381	0.429	0.197	0.606
F14	F9	0.351	0.571	0.457	0.811
F15	F10	0.921	1.079	0.196	1.432
F16	F4	0.730	0.347	0.084	0.813
F17	F1	0.219	0.003	0.004	0.219
F18	F5	0.720	0.474	0.246	0.896
F19	F3	0.491	0.453	0.133	0.682
F20	F11	0.229	0.188	0.710	0.769
F21	F20	0.593	0.594	0.069	0.842
F22	F19	0.149	0.087	0.088	0.194

Table 6S.

Atomic coordinates and isotropic displacement parameters (\AA^2) for $\text{Pb}_5\text{Al}_3\text{F}_{19}$ in the phase initially assumed as monoclinic $\text{III}m$ at 320 K

Symmetry related atomic coordinates are given without uncertainties.

Phase IV	Phase $\text{III}m$	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}
Pb1, 3	Pb1 ^a	0.228(9)	-0.074(4)	$\frac{1}{2}$	2.74(9)
Pb2, 4	Pb1	0.4262(2)	0.2724(2)	0	"
Pb5	Pb2	0	$\frac{1}{2}$	$\frac{1}{4}$	2.4 (2)
Al4,5	Al1	0.17720(71)	0.32280	0	0.7(2)
Al1,2,3	Al2	0	0	$\frac{1}{4}$	"
F11,16	F1	0.29(3)	0.093(3)	0.325(2)	3.05(3)
F17,18,	F1 ^b	0.0932(7)	0.287(1)	0.175(1)	3.05(3)
F9,10	F2	0.29(3)	0.093(3)	-0.325(1)	"
F12,19	F2 ^c	-0.093(4)	0.29(1)	-0.325 (1)	"
F14,15	F3	0.1041(8)	0.3959	0	"
F13,20	F4	0.2431(4)	0.2569	0	"
F1,2,5,8	F5	0	0	$\frac{1}{2}$	"
F3,4	F6 ^d	-0.0892(5)	0.0892	$\frac{3}{4}$	"
F6,7	F6	0.09(2)	-0.09(6)	$\frac{3}{4}$	"
F21,22	F7	0.3800(8)	0.1200	0	"

^a Coordinates of the symmetry-independent Pb1-2 atom are related to those of Pb1-1 as $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}+z$ is to xyz ; ^b those of the symmetry-independent atoms F1-2 to F1-1 as $y, x, \frac{1}{2}-z$ is to xyz and ^c F2-2 to F2-1 as \bar{y}, x, z is to xyz ; and ^d those of symmetry-independent F6-2 to F6-1 as \bar{y}, x, z is to xyz .

Table 7S.

Atomic displacements (\AA) between corresponding atoms in antiferroelectric $\text{Pb}_5\text{Al}_3\text{F}_{19}$ phase IV at 295 K* and ferroelastic phase $\text{III}m$ at 320 K

phase IV	phase $\text{III}m$	Δx	Δy	Δz	$\Delta(xyz)$
Pb1	1	0.175	0.144	0.066	0.236
Pb2	1	0.141	0.184	0.027	0.233
Pb3	1	0.215	0.130	0.050	0.256
Pb4	1	0.145	0.171	0.030	0.226
Pb5	2	0.299	0.105	0.107	0.334
Al1	2	0	0	0.080	0.080
Al2	2	0	0	0.058	0.058
Al3	2	0	0	0.045	0.045
Al4	1	0.053	0.258	0.039	0.266
Al5	1	0.304	0.028	0.057	0.311
F1	5	0	0	0	0
F2	5	0	0	0	0
F3	6	0.387	0.609	0.128	0.733
F4	6	0.340	0.540	0.038	0.639
F5	5	0	0	0	0
F6	6	0.562	0.374	0.193	0.702
F7	6	0.555	0.359	0.123	0.672
F8	5	0	0	0	0
F9	2	0.445	0.132	0.136	0.484
F10	2	0.054	0.322	0.119	0.348
F11	1	0.014	0.100	0.124	0.160
F12	2	0.704	0.480	0.049	0.853
F13	4	0.238	0.095	0.118	0.282
F14	3	0.122	0.751	0.313	0.823
F15	3	0.857	0.085	0.045	0.862
F16	1	0.186	0.053	0.069	0.205
F17	1	0.026	0.091	0.017	0.096
F18	1	0.236	0.615	0.014	0.659
F19	2	0.461	0.020	0.053	0.464
F20	4	0.780	0.228	0.327	0.876
F21	7	0.152	0.067	0.069	0.180
F22	7	0.077	0.464	0.088	0.479

* Andriamampianina, Gravereau, Ravez & Abrahams (1994)

Table 8S.

Symmetry-adapted atomic displacements from $\text{Pb}_5\text{Al}_3\text{F}_{19}$ phase I to ferroelastic phase III based on normal mode analysis

Orbit	Atom	B_{1g}	B_{2g}	E_g^{11}
4(a)	Al2			0.27(4)
4(b)	Pb2		-0.031(6)	-0.364(7)
8(h)	Al1	-0.15(3)	0.30(2)	
8(h)	F3	0.37(2)	(+)0.28(4)	-0.14(3)
8(h)	F4			0.21(3)
8(h)	F7	-0.36(2)	-0.21(4)	
16(i)	F6	0.70(2) -0.36(2)	-0.38(2)	-0.09(2) -0.08(2) 0.13(2)
16(k)	Pb1	0.063(4)	0.132(4)	-0.019(6)
32(m)	F1	-0.055(14)	-0.109(13)	-0.209(18) 0.399(18) 0.205(18)

Table 9S.

Atomic coordinates for $\text{Pb}_5\text{Al}_3\text{F}_{19}$ phase III, upper as refined by Rietveld analysis and lower as derived from Table 2

	x_{RA}	y_{RA}	z_{RA}
Pb1	0.2614(3)	0.4154(3)	0.5037(6)
	0.272(11)	0.427(12)	$\frac{1}{2}$
Pb2	0.4138(3)	-0.2621(3)	0.4928(5)
	0.427(12)	-0.272(11)	$\frac{1}{2}$
Pb3	0.2237(3)	-0.0612(3)	0.4999(7)
	0.228(11)	-0.073(12)	$\frac{1}{2}$
Pb4	0.0623(3)	0.2112(2)	0.5006(6)
	0.073(12)	0.228(11)	$\frac{1}{2}$
Pb5	0.0029(6)	0.4776(2)	0.2574(13)
	0	$\frac{1}{2}$	$\frac{1}{4}$
Al1	0.1620(14)	0.3115(15)	-0.014(3)
	0.163(8)	0.332(8)	0
Al2	0.6696(18)	0.1692(17)	0.031(3)
	0.668(8)	0.163(8)	0
Al3	0	0	$\frac{1}{4}$
	0	0	$\frac{3}{4}$
F1	0.3006(11)	0.0998(14)	0.678(2)
	0.278(28)	0.099(14)	0.665(13)
F2	0.5957(14)	-0.2568(15)	0.373(3)
	0.599(10)	-0.228(11)	0.329(12)
F3	0.2769(11)	0.6262(11)	0.336(2)
	0.272(11)	0.599(10)	0.329(12)
F4	-0.2482(11)	0.3863(12)	0.327(2)
	-0.228(11)	0.401(10)	0.329(12)
F5	0.5765(11)	0.2056(13)	0.139(2)
	0.599(14)	0.222(29)	0.165(13)
F6	0.4144(14)	0.2205(13)	0.292(3)
	0.401(10)	0.228(11)	0.329(12)
F7	0.1846(12)	0.4117(14)	0.201(2)
	0.222(28)	0.401(14)	0.65(13)

F8	-0.0978(12)	0.2810(11)	0.683(2)
	0.099(10)	0.272(11)	0.671(12)
F9	0.0880(12)	0.4086(12)	-0.020(3)
	0.103(18)	0.444(14)	0
F10	0.6197(12)	0.0454(10)	-0.021(2)
	0.603(18)	0.056(14)	0
F11	0.2544(15)	0.2541(15)	0.053(2)
	0.259(8)	0.258(4)	0
F12	0.7368(10)	0.2703(9)	0.011(2)
	0.742(4)	0.259(8)	0
F13	0	0	$\frac{1}{2}$
	0	0	$\frac{1}{2}$
F14	0	0	0
	0	0	0
F15	0.1206(14)	0.0394(14)	0.271(3)
	0.104(28)	0.062(27)	$\frac{1}{4}$
F16	-0.1174(13)	-0.0627(15)	0.290(3)
	-0.062(27)	-0.104(28)	$\frac{1}{4}$
F17	-0.0320(14)	0.1119(15)	0.794(3)
	-0.062(27)	0.104(28)	$\frac{3}{4}$
F18	0.0542(14)	-0.1049(16)	0.754(3)
	0.062(27)	-0.104(28)	$\frac{3}{4}$
F19	0.1359(14)	0.5813(13)	0
	0.113(18)	0.601(23)	0
F20	0.5830(1)	-0.1210(13)	0
	0.601(23)	-0.113(18)	0

Table 10S

Atomic coordinates in phase III reported by Bravic *et al.* (2000) for the composition $\text{Pb}_5\text{Al}_{2.96}\text{Cr}_{0.04}\text{F}_{19}$ at room temperature as transformed to space group $I\bar{1}$, and total differences $\Delta(xyz)$ from the coordinates derived by Rietveld analysis, see §6.4.2[†]

Table 9S

name for

Atom	Bravic- $x_{300\text{ K}}$	Bravic- $y_{300\text{ K}}$	Bravic- $z_{300\text{ K}}$	Bravic name for	Atom	$\Delta(\xi_B - \xi_{RA})$	\AA^{\ddagger}	$\sigma(\Delta) \text{\AA}^{\dagger\dagger}$	$\Delta/\sigma(\Delta)$
Pb1	0.2606(3)	0.4148(3)	0.5063(3)	Pb12	0.0236	0.0097	2.43		
Pb2	0.4151(2)	-0.2605(2)	0.5068(3)	Pb11	0.1055	0.0084	12.56		
Pb3	0.2164(2)	-0.0615(2)	0.4989(3)	Pb22	0.1045	0.0089	11.74		
Pb4	0.0611(1)	0.2181(1)	0.5003(2)	Pb21	0.0999	0.0074	13.5		
Pb5	0.0236(4)	0.5069(4)	0.2517(5)	Pb3	0.513	0.0151	33.97		
Al1	0.1581(10)	0.3265(10)	0.0009(14)	Al11	0.245	0.043	5.69		
Al2	0.6736(10)	0.1579(10)	0.0054(14)	Al12	0.252	0.0484	5.21		
Al3	0.0025(10)	-0.0011(10)	0.2466(14)	Al2	0.046	0.0226	2.04		
F1	0.295(3)	0.094(3)	0.671(4)	F42	0.135	0.0754	1.79		
F2	0.610(3)	-0.252(3)	0.323(4)	F51	0.420	0.0758	5.54		
F3	0.243(3)	0.598(3)	0.339(3)	F53	0.6392	0.0709	9.02		
F4	-0.258(3)	0.381(3)	0.314(4)	F54	0.1843	0.0734	2.51		
F5	0.596(1)	0.210(1)	0.167(2)	F43	0.3489	0.038	9.18		
F6	0.403(3)	0.248(3)	0.334(3)	F52	0.5165	0.0726	7.11		
F7	0.193(3)	0.411(3)	0.180(3)	F41	0.1917	0.0717	2.67		
F8	-0.089(3)	0.308(3)	0.668(3)	F44	0.4201	0.0708	5.93		
F9	0.048(3)	0.392(3)	-0.008(4)	F71	0.6127	0.0738	8.30		
F10	0.609(3)	0.048(3)	0.040(4)	F72	0.4691	0.0728	6.44		
F11	0.264(3)	0.260(3)	0.013(4)	F61	0.3296	0.0755	4.37		
F12	0.742(3)	0.265(3)	-0.026(3)	F62	0.2867	0.0698	4.11		
F13	0	0	0.5	F2	0	0	0		
F14	0	0	0	F1	0	0	0		
F15	0.115(2)	0.051(2)	0.253(3)	F31	0.2179	0.0464	4.69		
F16	-0.113(2)	-0.052(2)	0.258(3)	F32	0.2945	0.0464	6.35		
F17	-0.051(2)	0.117(2)	0.746(3)	F34	0.4433	0.0585	7.58		
F18	0.050(2)	-0.112(2)	0.747(3)	F33	0.1268	0.0593	2.14		
F19	0.126(1)	0.587(1)	0.002(2)	F82	0.1636	0.0366	4.47		
F20	0.586(2)	-0.124(2)	0.003(3)	F81	0.0643	0.0532	1.21		

[†] The atomic designation is that of Bravic *et al.* (2000). The x_B, y_B, z_B coordinates are for one of the corresponding equivalent positions $x, y, z; x \ y \ z; \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z; \text{ or } \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$. The designation in Table 5 of the present investigation is also given.

[‡] Δ is the distance between the ξ -atom at locations ξ_B and ξ_{RA} , with corresponding coordinates $(x_B, y_B, z_B)_{300\text{ K}}$ from Bravic *et al.* 's (2000) refinement, $(x_{RA}, y_{RA}, z_{RA})_{320\text{ K}}$ from the Rietveld analysis.

^{††} $\sigma(\Delta)$ is the uncertainty in Δ , taking the total variance in a quantity as the sum of all contributing variances, in \AA .

Table 11S

Atomic coordinates and isotropic displacement parameters (\AA^2) for paraelastic $\text{Pb}_5\text{Al}_3\text{F}_{19}$ phase II at 370 K*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Pb1	0.08474(7)	-0.23970(6)	0	0.018(1)
Pb2	-0.06116(6)	-0.21768(5)	$\frac{1}{2}$	0.013(2)
Pb3	0	$\frac{1}{2}$	$\frac{1}{4}$	0.072(2)
Al1	0.1581(4)	0.3255(4)	0	0.012(4)
Al2	0	0	0.2460(1)	0.012(4)
F1	0	0	0	0.038(5)
F2	0	0	$\frac{1}{2}$	0.038(5)
F3	0.3854(9)	0.4500(8)	0.2460(2)	0.038(5)
F4	0.2001(9)	0.4076(9)	0.1730(2)	0.038(5)
F5	0.3921(9)	0.2494(9)	0.6700(2)	0.038(5)
F6	0.2630(10)	0.2610(10)	0	0.038(5)
F7	0.4530(10)	0.1120(10)	$\frac{1}{2}$	0.038(5)
F8	0.4170(10)	0.1250(10)	0	0.038(5)

* Atomic coordinates of Sarraute *et al.* (1995), with numbering related as in Table 2. The symmetry equivalent coordinate in Table 2 for F5 of phase II is 0.2506, 0.1079, 0.3300 corresponding to F1 in phase V.

Table 12S.

Atomic displacements (\AA) between corresponding atoms in ferroelastic phase III of $\text{Pb}_5\text{Al}_3\text{F}_{19}$ at 320 K (Table 5) and paraelastic phase II at 370 K (Table 10S)

Phase III	Phase II	Δx	Δy	Δz	$\Delta(xyz)$
Pb1 [†]	Pb1	0.001	0.016	0.027	0.031
Pb2	Pb1	0.021	0.026	0.052	0.062
Pb3	Pb2	0.000	0.093	0.001	0.085
Pb4	Pb2	0.016	0.130	0.004	0.131
Pb5	Pb3	0.041	0.319	0.053	0.326
Al1	Al1	0.055	0.199	0.100	0.229
Al2	Al1	0.158	0.075	0.224	0.283
Al3	Al2	0.	0.	0.029	0.029
F14	F1	0.	0.	0.	0.
F13	F2	0.	0.	0	0.
F15	F3	1.004	1.071	0.180	1.479
F16	F3	0.945	0.739	0.317	1.241
F17	F3	0.256	0.038	0.346	0.432
F18	F3	0.060	0.138	0.058	0.161
F1	F4	0.010	0.105	0.036	0.111
F5	F4	0.078	0.226	0.245	0.342
F7	F4	0.221	0.058	0.202	0.305
F8	F4	0.269	0.077	0.072	0.289
F2	F5	0.105	0.174	0.088	0.221
F3	F5	0.391	0.261	0.043	0.472
F4	F5	0.017	0.083	0.022	0.088
F6	F5	0.411	0.317	0.274	0.587
F11	F6	0.243	0.219	0.382	0.503
F12	F6	0.373	0.446	0.079	0.587
F9	F7	0.341	0.632	0.144	0.732
F10	F7	0.947	1.035	0.151	1.411
F19*	F8*	0.753	0.622	0.	0.977
F20*	F8*	0.541	0.598	0	0.806

[†] Atom designations as used in phases II and III.

* Isolated F⁻ ion.

Table 13S.

Atomic displacements (\AA) between corresponding atoms in paraelectric phase II at 370 K* and prototypic phase I of $\text{Pb}_5\text{Al}_3\text{F}_{19}$ and the thermal/static (u_{eq}) displacements in \AA .

phase II	phase I	Δx	Δy	Δz	$\Delta(xyz)$	u_{eq}
Pb1	Pb1	0.161	0.166	0	0.23	0.13
Pb2	Pb1	0.174	0.146	0	0.23	0.11
Pb3	Pb2	0	0	0	0	0.27
Al1	Al1	0.135	0.098	0	0.17	0.11
Al2	Al2	0	0	0.029	0.03	0.11
F4	F1	0.360	0.088	0.024	0.37	0.19
F7	F3	0.494	0.429	0	0.65	0.19
F6	F4	0.172	0.169	0	0.24	0.19
F1,2	F5	0	0	0	0	0.19
F3	F6	0.464	0.453	0.029	0.65	0.19
F8 [†]	F7	0.335	0.261	0	0.42	0.19

* See Table 8 for predicted values of atomic coordinates in phase I.

† Isolated atom.

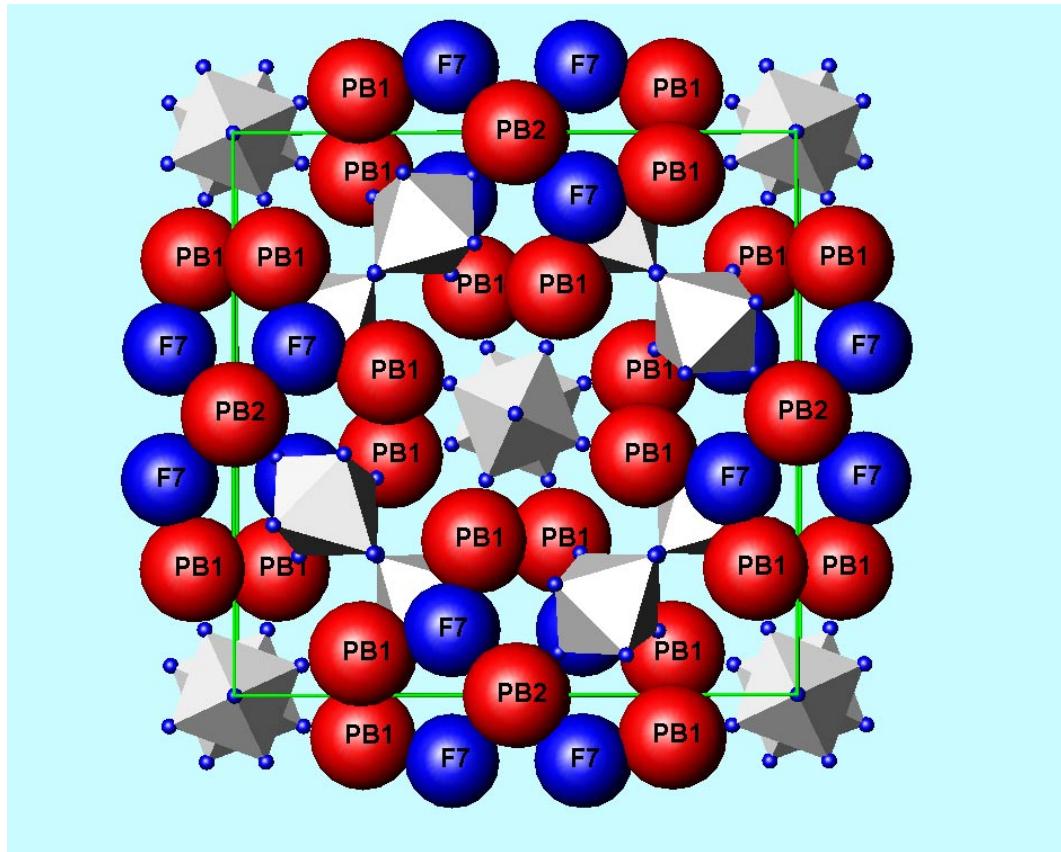


Fig. 1S (upper)

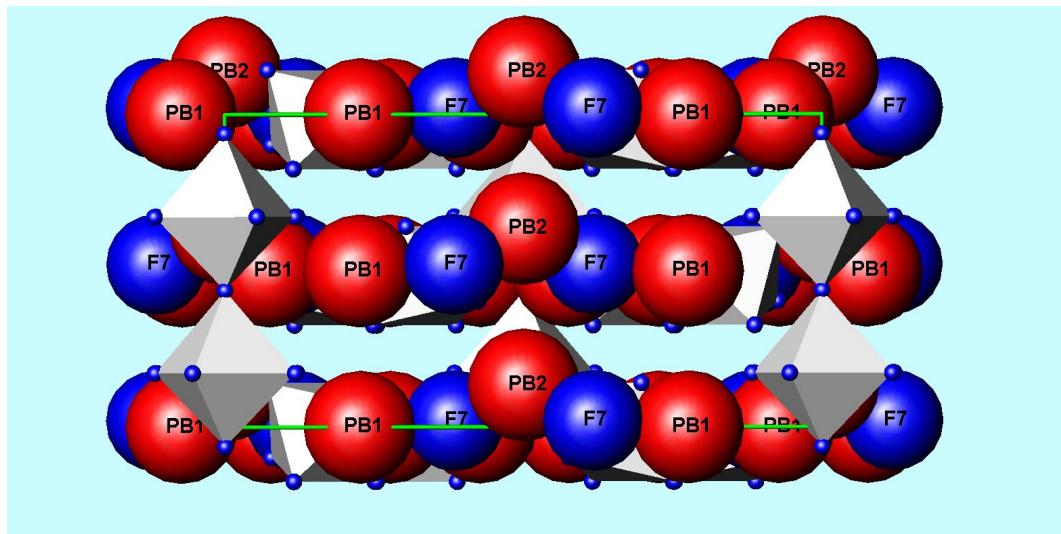


Fig. 1S (lower)

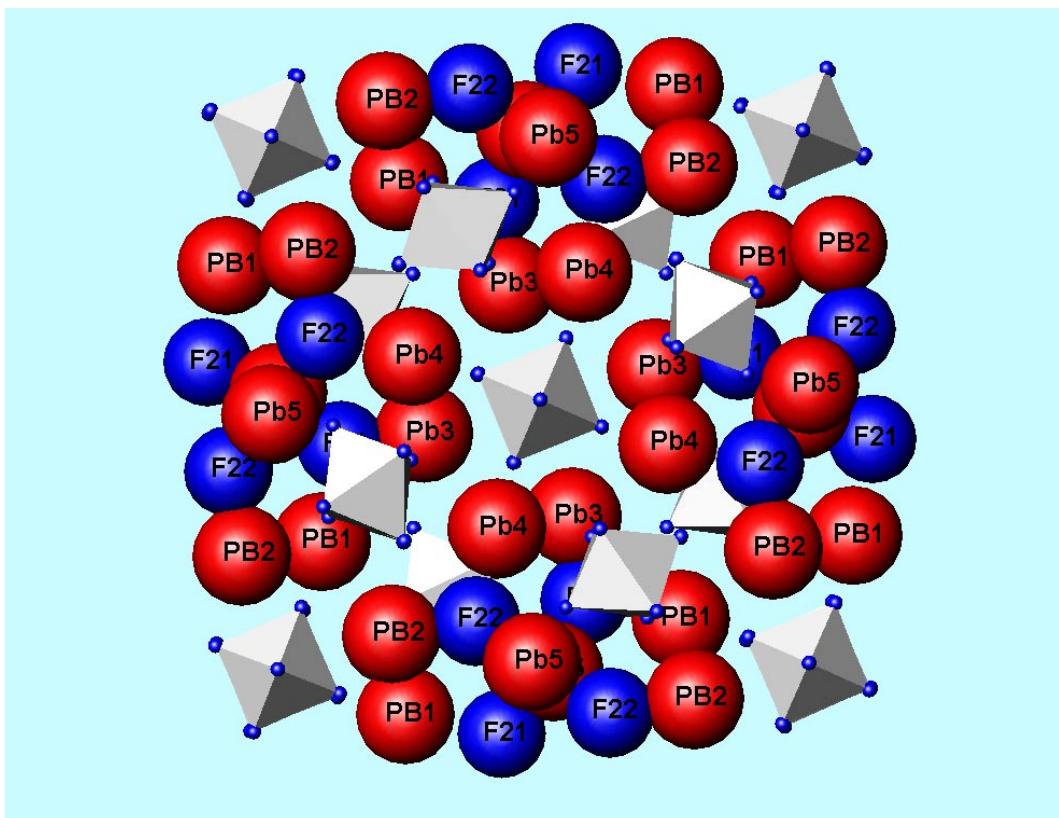


Fig. 2S (upper)

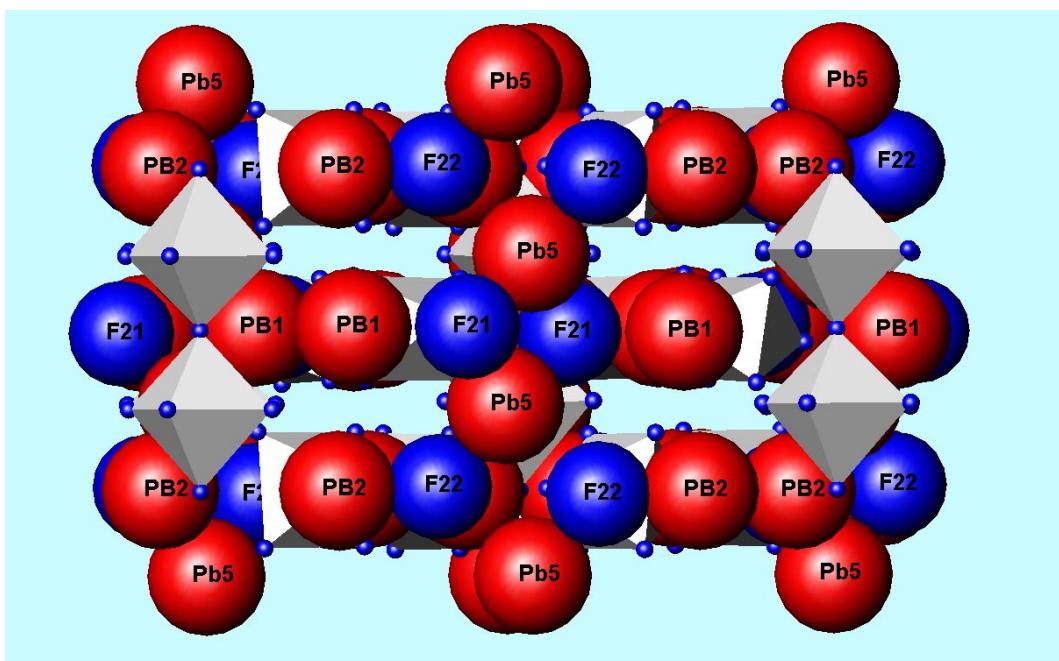


Fig. 2S (lower)

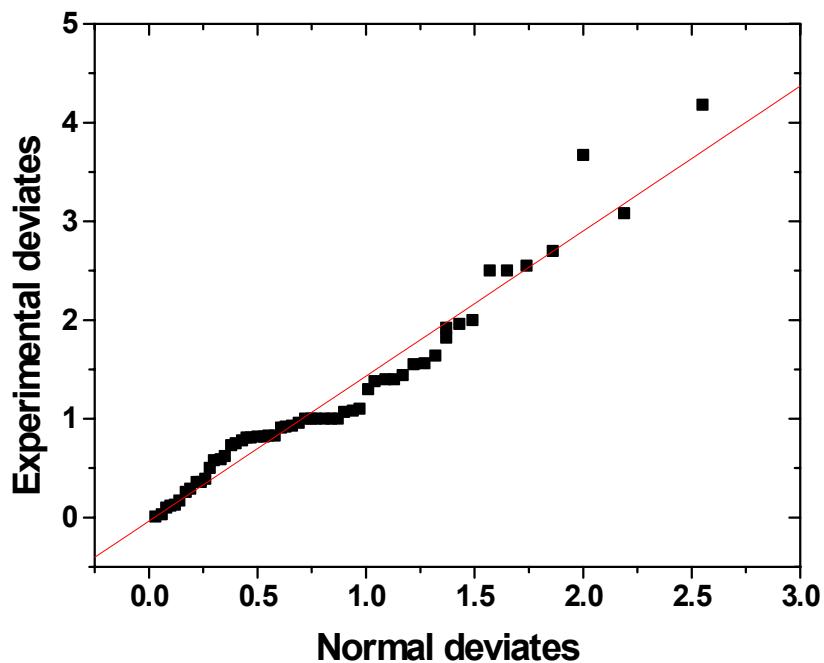


Figure 3S(a)

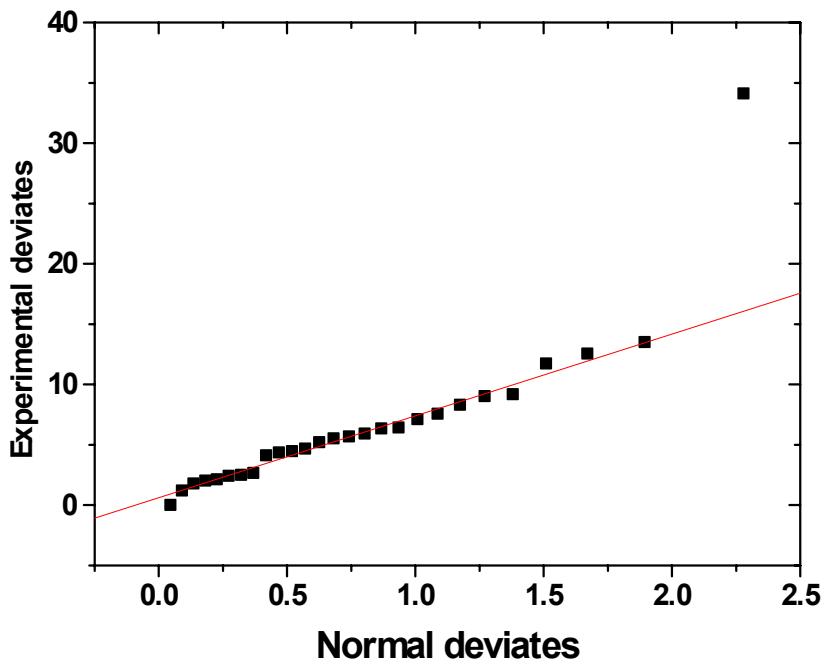


Figure 3S(b)

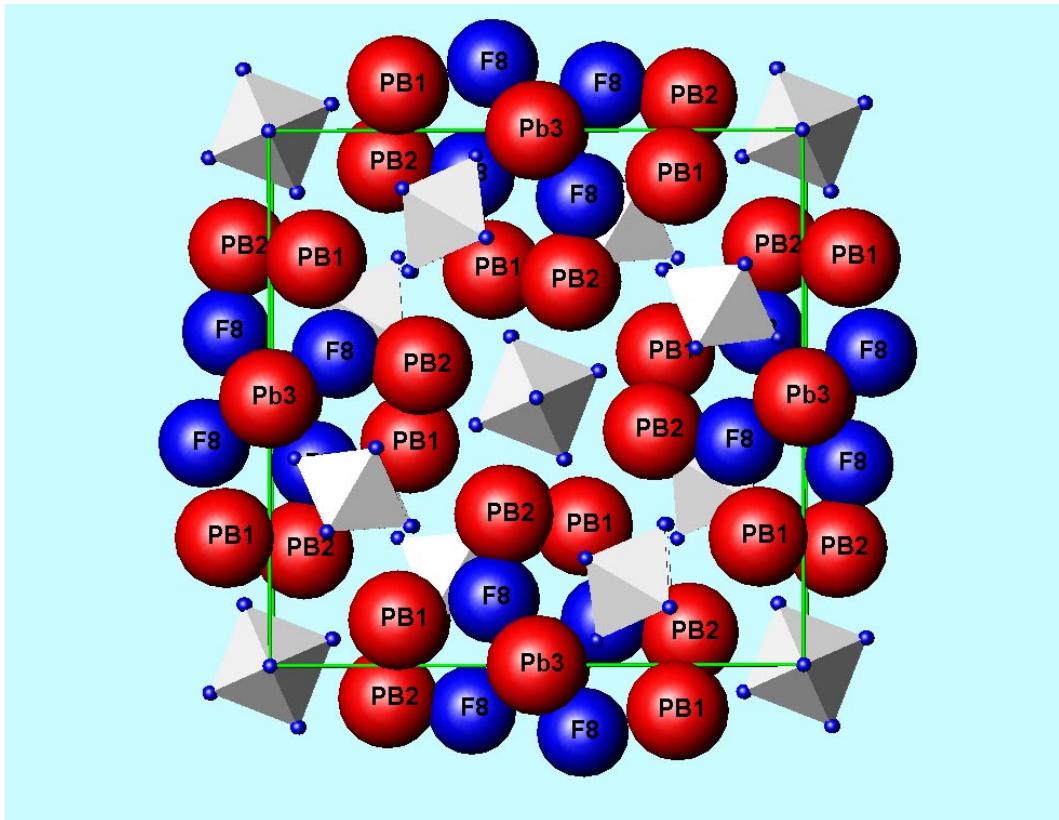


Fig. 4S (upper)

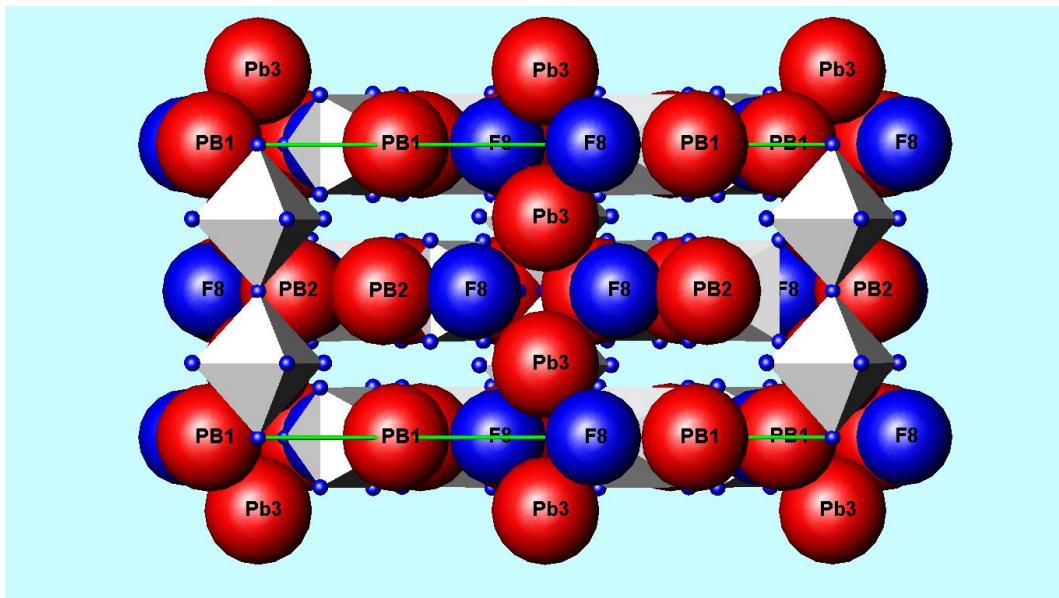


Fig. 4S (lower)