Advances in Structural Analysis of Fluoroaluminates Using DFT Calculations of ^{27}Al Electric Field Gradients

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Compounds	S. G.	a	b	c	α	β	γ	method
α-AlF_3[1]	$R\bar{3}c$	5.0314	5.0314	5.0314	58.68	58.68	58.677	XRPD
α-Na_3AlF_6[2]	$P2_1/n$	5.4139	5.6012	7.7769	90	90.18	90	SCXRD
$Na_5Al_3F_{14}$[3]	P4/mnc	7.0138	7.0138	10.402	90	90	90	SCXRD
α-$CaAlF_5$[4]	C2/c	8.712	6.317	7.349	90	115.04	90	SCXRD
β-$CaAlF_5$[5]	$P2_1/c$	5.3361	9.8298	7.3271	90	109.91	90	XRPD
Ca_2AlF_7[6]	Pnma	7.685	6.998	9.549	90	90	90	SCXRD
α-$BaAlF_5$[7]	$P2_12_12_1$	13.71	5.60	4.93	90	90	90	SCXRD
β-$BaAlF_5$[8]	$P2_1/n$	5.1517	19.5666	7.5567	90	92.43	90	NPD
γ-$BaAlF_5$[8]	$P2_1$	5.2584	9.7298	7.3701	90	90.88	90	NPD
$Ba_3Al_2F_{12}$[9]	Pnnm	10.203	9.885	9.522	90	90	90	SCXRD
Ba_3AlF_9-Ib[10]	Pnma	10.063	5.567	14.88	90	90	90	SCXRD
β-Ba_3AlF_9[11]	Pnc2	7.5318	14.8674	14.5732	90	90	90	XRPD
α-$BaCaAlF_7$[12]	P2/n	5.3664	5.3846	18.8262	90	92.32	90	SCXRD
α-$NaCaAlF_6$[13]	$P2_1/c$	8.7423	5.1927	20.3514	90	91.5	90	XRPD
β-$NaCaAlF_6$[14]	P321	8.9295	8.9295	5.0642	90	120	90	XRPD
$Na_2Ca_3Al_2F_{14}$[15]	$I2_13$	10.257	10.257	10.257	90	90	90	SCXRD

Table S2. Initial fractional atomic coordinates[1] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for α-AlF_3.

Atom	Site	x	y	z	x'	y'	z'	d
Al	6b	0	0	0	0	0	0	0
F	18e	0.6775	1/4	0.8225	0.6646	1/4	0.8354	0.064

Table S3. Al-F bond length (Å), F-Al-F and Al-F-Al bond angles[a] (°) as deduced from powder X-ray structure refinement and WIEN2k optimization (in italic) for α-AlF_3.

Bond lengths			Bond angles		
Al-F	1.797	*1.811*	F-Al-F	90.02	*90.45*
			F-Al-F	89.98	*89.55*
			Al-F-Al	157.1	*153.1*

[a] F-Al-F bond angles between two opposite bonds are equal to 180° since the site symmetry of Al is $\bar{3}$.

Table S4. Initial fractional atomic coordinates[2] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for α-Na_3AlF_6.

Atom	Site	x	y	z	x'	y'	z'	d
Al	2a	0	0	0	0	0	0	0.000
Na(1)	2b	0	0	1/2	0	0	1/2	0.000
Na(2)	4e	-0.0121	0.4492	0.2526	-0.0124	0.4483	0.2529	0.006
F(1)	4e	0.1016	0.0442	0.2188	0.1034	0.0456	0.2208	0.020
F(2)	4e	0.2278	0.3267	0.5450	0.2252	0.3259	0.5463	0.018
F(3)	4e	0.1622	0.2687	0.9383	0.1646	0.2716	0.9369	0.023

Table S5. Al-F bond lengths (Å), F-Al-F and Al-F-Na(1) bond angles[a] (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for α-Na_3AlF_6.

Bond lengths			Bond angles		
Al-F(2)	1.800	*1.816*	F(2)-Al-F(1)	89.4	*89.3*
Al-F(1)	1.804	*1.822*	F(2)-Al-F(1)	90.6	*90.7*
Al-F(3)	1.808	*1.831*	F(2)-Al-F(3)	90.1	*90.4*
Bond angles			F(2)-Al-F(3)	89.9	*89.6*
Al-F(1)-Na(1)	145.1	*144.5*	F(1)-Al-F(3)	89.4	*89.3*
Al-F(2)-Na(1)	149.7	*149.1*	F(1)-Al-F(3)	90.6	*90.7*
Al-F(2)-Na(1)	143.4	*143.0*			

[a] F-Al-F bond angles between two opposite bonds are equal to 180° since the site symmetry of Al is $\bar{1}$.

Table S6. Initial fractional atomic coordinates[3] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for $Na_5Al_3F_{14}$.

Atom	Site	x	y	z	x'	y'	z'	d
Na(1)	2b	0	0	1/2	0	0	1/2	0.000
Na(2)	8g	0.2768	0.7768	1/4	0.2766	0.7766	1/4	0.002
Al(1)	2a	0	0	0	0	0	0	0.000
Al(2)	4c	0	1/2	0	0	1/2	0	0.000
F(1)	4e	0	0	0.1711	0	0	0.1730	0.020
F(2)	8h	0.0642	0.2477	0	0.0700	0.2477	0	0.041
F(3)	16i	0.1794	0.5364	0.1198	0.1810	0.5374	0.1208	0.017

Table S7. Al-F bond lengths (Å) and F-Al(2)-F bond angles[a] (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for $Na_5Al_3F_{14}$.

Bond lengths			Bond angles		
Al(1)-F(1)	1.780	*1.800*	F(3)-Al(2)-F(2)	88.0	*87.2*
Al(1)-F(2)	1.795	*1.806*	F(3)-Al(2)-F(3)	91.7	*91.8*
Al(2)-F(3)	1.789	*1.805*	F(3)-Al(2)-F(2)	92.0	*92.8*
Al(2)-F(2)	1.826	*1.836*	F(3)-Al(2)-F(3)	88.3	*88.2*

[a] The site symmetry of Al(1) is 4/m. Consequently, F-Al(1)-F bond angles are equal to 90° and 180° between two adjacent bonds and between two opposite bonds respectively. F-Al(2)-F bond angles between two opposite bonds are equal to 180° since the site symmetry of Al(2) is 2/m.

Table S8. Initial fractional atomic coordinates[4] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for α-$CaAlF_5$.

Atom	Site	x	y	z	x'	y'	z'	d
Ca	4e	0	0.54240	1/4	0	0.54285	1/4	0.003
Al	4a	0	0	0	0	0	0	0
F(1)	4e	0	0.9422	1/4	0	0.9416	1/4	0.004
F(2)	8f	0.0114	0.7169	0.9737	0.0114	0.7151	0.9736	0.011
F(3)	8f	0.7789	0.9822	0.8870	0.7769	0.9821	0.8858	0.016

Table S9. Al-F bond lengths (Å) and F-Al-F bond angles[a] (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for α-$CaAlF_5$.

Bond lengths			Bond angles		
Al-F(3)	1.749	*1.765*	F(3)-Al-F(2)	90.9	*90.9*
Al-F(2)	1.806	*1.817*	F(3)-Al-F(2)	89.1	*89.1*
Al-F(1)	1.873	*1.874*	F(3)-Al-F(1)	90.2	*90.2*
			F(3)-Al-F(1)	89.8	*89.8*
			F(2)-Al-F(1)	86.3	*86.1*
			F(2)-Al-F(1)	93.7	*93.9*

[a] F-Al-F bond angles between two opposite bonds are equal to 180° since the site symmetry of Al is $\bar{1}$.

Table S10. Initial fractional atomic coordinates[6] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for Ca_2AlF_7.

Atom	Site	x	y	z	x'	y'	z'	d
Ca(1)	4c	0.1137	1/4	0.7410	0.1144	1/4	0.7411	0.005
Ca(2)	4c	0.8032	1/4	0.1053	0.8037	1/4	0.1052	0.004
Al	4c	0.3103	1/4	0.0565	0.3101	1/4	0.0567	0.002
F(1)	4c	0.3726	1/4	0.6295	0.3725	1/4	0.6292	0.003
F(2)	4c	0.0296	1/4	0.5083	0.0324	1/4	0.5091	0.023
F(3)	4c	0.0965	1/4	0.1265	0.0941	1/4	0.1270	0.019
F(4)	8d	0.2503	0.0748	0.9254	0.2496	0.0730	0.9244	0.017
F(5)	8d	0.3693	0.0719	0.1848	0.3696	0.0705	0.1859	0.015

Table S11. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for Ca_2AlF_7.

Bond lengths			Bond angles		
Al-F(3)	1.774	*1.790*	F(3)-Al-F(5)	88.7	*88.8*
Al-F(2)	1.795	*1.820*	F(3)-Al-F(4)	91.4	*91.3*
Al-F(5)	1.805	*1.819*	F(2)-Al-F(5)	89.9	*89.9*
Al-F(4)	1.812	*1.830*	F(2)-Al-F(4)	90.0	*90.0*
Bond angles			F(5)-Al-F(5)	87.3	*87.3*
F(5)-Al-F(4)	178.9	*178.9*	F(5)-Al-F(4)	93.8	*93.7*
F(3)-Al-F(2)	178.0	*178.2*	F(4)-Al-F(4)	85.2	*85.2*

Table S12. Initial fractional atomic coordinates[7] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for α-$BaAlF_5$.

Atom	Site	x	y	z	x'	y'	z'	d
Ba	4a	-0.09380	0.0888	0.0199	-0.0936	0.0890	0.0204	0.004
Al	4a	-0.1650	0.5971	0.4367	-0.1646	0.5972	0.4370	0.006
F(1)	4a	-0.2773	0.1482	0.8147	-0.2728	0.1443	0.8136	0.066
F(2)	4a	-0.4195	0.2154	0.1170	-0.4198	0.2140	0.1180	0.010
F(3)	4a	-0.1055	0.3354	0.5497	-0.1043	0.3312	0.5511	0.030
F(4)	4a	-0.0796	0.5991	0.1570	-0.0790	0.5995	0.1550	0.013
F(5)	4a	-0.2490	0.4122	0.2251	-0.2486	0.4095	0.2255	0.016

Table S13. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for α-$BaAlF_5$.

Bond lengths			Bond angles		
Al-F(1)	1.738	*1.789*	F(1)-Al-F(2)	89.1	*90.1*
Al-F(3)	1.767	*1.794*	F(1)-Al-F(4)	91.5	*92.5*
Al-F(2)	1.798	*1.804*	F(1)-Al-F(5)	89.9	*88.3*
Al-F(4)	1.809	*1.819*	F(1)-Al-F(5)	88.9	*88.3*
Al-F(5)	1.848	*1.854*	F(3)-Al-F(2)	91.8	*92.1*
Al-F(5)	1.867	*1.876*	F(3)-Al-F(4)	86.9	*87.0*
Bond angles			F(3)-Al-F(5)	91.6	*92.2*
F(2)-Al-F(5)	175.6	*175.9*	F(3)-Al-F(5)	90.1	*89.5*
F(4)-Al-F(5)	178.6	*179.2*	F(2)-Al-F(4)	87.5	*87.7*
F(1)-Al-F(3)	178.1	*177.8*	F(2)-Al-F(5)	92.7	*92.5*
			F(4)-Al-F(5)	88.7	*88.6*
			F(5)-Al-F(5)	91.2	*91.2*

Table S14. Initial fractional atomic coordinates[8] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for β-$BaAlF_5$.

Atom	Site	x	y	z	x'	y'	z'	d
Ba(1)	4e	0.2820	0.0389	0.7400	0.2870	0.0396	0.7403	0.029
Ba(2)	4e	0.2560	0.2700	0.4743	0.2580	0.2698	0.4790	0.037
Al(1)	4e	0.2460	0.8680	0.5280	0.2487	0.8684	0.5279	0.016
Al(2)	4e	0.7676	0.8925	0.8495	0.7683	0.8922	0.8515	0.016
F(1)	4e	0.9456	0.4002	0.8494	0.9481	0.4009	0.8506	0.021
F(2)	4e	0.7470	0.4830	0.6195	0.7498	0.4828	0.6144	0.042
F(3)	4e	0.2134	0.1983	0.1826	0.2122	0.1986	0.1841	0.014
F(4)	4e	0.5056	0.1142	0.0141	0.5070	0.1173	0.0139	0.061
F(5)	4e	0.4438	0.4037	0.7870	0.4413	0.4044	0.7846	0.026
F(6)	4e	0.2670	0.4543	0.0587	0.2683	0.4548	0.0601	0.016
F(7)	4e	0.0584	0.3489	0.1469	0.0567	0.3395	0.1482	0.184
F(8)	4e	0.5226	0.3841	0.4567	0.5242	0.3830	0.4528	0.038
F(9)	4e	0.5420	0.3446	0.0892	0.5450	0.3453	0.0874	0.025
F(10)	4e	0.2749	0.7882	0.6440	0.2766	0.7881	0.6437	0.009

Table S15. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from neutron powder data refinement and WIEN2k optimization (in italic) for β-$BaAlF_5$.

Bond lengths			Bond angles		
Al(1)-F(7)	1.736	*1.791*	F(7)-Al(1)-F(9)	93.7	*92.7*
Al(1)-F(9)	1.756	*1.772*	F(7)-Al(1)-F(10)	98.4	*92.9*
Al(1)-F(10)	1.794	*1.801*	F(7)-Al(1)-F(6)	86.5	*92.4*
Al(1)-F(6)	1.811	*1.817*	F(7)-Al(1)-F(1)	86.7	*89.4*
Al(1)-F(5)	1.875	*1.892*	F(9)-Al(1)-F(10)	94.0	*93.7*
Al(1)-F(1)	1.912	*1.888*	F(9)-Al(1)-F(6)	92.5	*91.7*
Al(2)-F(4)	1.784	*1.790*	F(9)-Al(1)-F(5)	91.0	*90.3*
Al(2)-F(2)	1.788	*1.794*	F(10)-Al(1)-F(5)	89.7	*89.7*
Al(2)-F(8)	1.790	*1.797*	F(10)-Al(1)-F(1)	90.0	*90.6*
Al(2)-F(3)	1.796	*1.800*	F(6)-Al(1)-F(5)	84.8	*84.8*
Al(2)-F(1)	1.830	*1.860*	F(6)-Al(1)-F(1)	83.4	*83.7*
Al(2)-F(5)	1.858	*1.866*	F(5)-Al(1)-F(1)	88.0	*87.4*
Bond angles			F(4)-Al(2)-F(2)	87.6	*88.5*
F(9)-Al(1)-F(1)	175.8	*175.1*	F(4)-Al(2)-F(8)	89.1	*88.9*
F(10)-Al(1)-F(6)	171.6	*172.2*	F(4)-Al(2)-F(3)	93.1	*91.9*
F(7)-Al(1)-F(5)	170.3	*175.9*	F(4)-Al(2)-F(1)	91.1	*90.8*
F(8)-Al(2)-F(1)	179.4	*179.4*	F(2)-Al(2)-F(8)	90.6	*90.8*
F(2)-Al(2)-F(3)	179.2	*179.6*	F(2)-Al(2)-F(1)	89.9	*89.7*
F(4)-Al(2)-F(5)	177.1	*178.2*	F(2)-Al(2)-F(5)	89.7	*90.0*
			F(8)-Al(2)-F(3)	89.2	*89.4*
			F(8)-Al(2)-F(5)	89.7	*90.2*
			F(3)-Al(2)-F(1)	90.3	*90.2*
			F(3)-Al(2)-F(5)	89.6	*89.6*
			F(1)-Al(2)-F(5)	90.0	*90.1*

Table S16. Initial fractional atomic coordinates[8] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for γ-$BaAlF_5$.

Atom	Site	x	y	z	x'	y'	z'	d
Ba(1)	2a	0.0105	0.0000	0.8864	0.0106	0.0002	0.8878	0.011
Ba(2)	2a	0.4871	0.3472	0.6389	0.4874	0.3471	0.6398	0.007
Al(1)	2a	0.0101	0.6266	0.5701	0.0116	0.6300	0.5745	0.047
Al(2)	2a	0.5145	0.7334	0.8680	0.5190	0.7351	0.8709	0.036
F(1)	2a	0.2518	0.0464	0.5324	0.2523	0.0464	0.5344	0.015
F(2)	2a	0.2519	0.2536	0.9442	0.2532	0.2527	0.9461	0.018
F(3)	2a	0.7654	0.0361	0.5553	0.7654	0.0349	0.5581	0.024
F(4)	2a	0.2677	0.7345	0.0329	0.2669	0.7350	0.0330	0.006
F(5)	2a	0.0387	0.5110	0.7553	0.0385	0.5113	0.7569	0.012
F(6)	2a	0.5064	0.9165	0.8419	0.5052	0.9164	0.8417	0.007
F(7)	2a	0.9916	0.2619	0.6009	0.9919	0.2595	0.5995	0.026
F(8)	2a	0.4485	0.0569	0.1350	0.4481	0.0546	0.1361	0.024
F(9)	2a	0.2832	0.7286	0.6782	0.2844	0.7295	0.6774	0.012
F(10)	2a	0.7924	0.7449	0.7038	0.7918	0.7444	0.7029	0.009

Table S17. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from neutron powder data refinement and WIEN2k optimization (in italic) for for γ-$BaAlF_5$.

Bond lengths			Bond angles		
Al(1)-F(1)	1.745	*1.788*	F(1)-Al(1)-F(3)	94.6	*91.7*
Al(1)-F(3)	1.748	*1.795*	F(1)-Al(1)-F(5)	96.1	*95.5*
Al(1)-F(5)	1.773	*1.776*	F(1)-Al(1)-F(7)	91.6	*90.0*
Al(1)-F(7)	1.822	*1.798*	F(1)-Al(1)-F(10)	91.0	*90.9*
Al(1)-F(10)	1.908	*1.872*	F(3)-Al(1)-F(5)	92.1	*91.8*
Al(1)-F(9)	1.910	*1.880*	F(3)-Al(1)-F(7)	89.7	*88.4*
Al(2)-F(8)	1.728	*1.766*	F(3)-Al(1)-F(9)	88.4	*89.1*
Al(2)-F(4)	1.791	*1.798*	F(5)-Al(1)-F(10)	91.7	*92.7*
Al(2)-F(6)	1.792	*1.778*	F(5)-Al(1)-F(9)	87.4	*88.7*
Al(2)-F(9)	1.840	*1.872*	F(7)-Al(1)-F(10)	85.7	*86.8*
Al(2)-F(2)	1.847	*1.798*	F(7)-Al(1)-F(9)	84.8	*85.8*
Al(2)-F(10)	1.915	*1.911*	F(10)-Al(1)-F(9)	85.7	*87.9*
Bond angles			F(8)-Al(2)-F(4)	95.6	*95.3*
F(5)-Al(1)-F(7)	171.9	*174.5*	F(8)-Al(2)-F(9)	92.2	*90.7*
F(3)-Al(1)-F(10)	172.8	*174.6*	F(8)-Al(2)-F(2)	92.4	*93.0*
F(1)-Al(1)-F(9)	175.2	*175.7*	F(8)-Al(2)-F(10)	87.9	*87.3*
F(9)-Al(2)-F(2)	175.3	*176.1*	F(4)-Al(2)-F(6)	92.9	*93.0*
F(4)-Al(2)-F(10)	175.0	*177.1*	F(4)-Al(2)-F(9)	92.2	*91.3*
F(8)-Al(2)-F(6)	171.4	*170.7*	F(4)-Al(2)-F(2)	88.4	*89.5*
			F(6)-Al(2)-F(9)	85.9	*84.9*
			F(6)-Al(2)-F(2)	89.4	*91.3*
			F(6)-Al(2)-F(10)	83.8	*84.5*
			F(9)-Al(2)-F(10)	91.3	*90.0*
			F(2)-Al(2)-F(10)	87.8	*89.0*

Table S18. Initial fractional atomic coordinates[9] (x, y, z), WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for $Ba_3Al_2F_{12}$.

Atom	Site	x	y	z	x'	y'	z'	d
Ba(1)	4f	0	1/2	0.24839	0	1/2	0.24778	0.006
Ba(2)	4g	0.22891	0.21000	0	0.23060	0.21115	0	0.021
Ba(3)	4g	0.64465	0.35061	0	0.64389	0.35101	0	0.009
Al	8h	0.39852	0.35746	0.31415	0.39770	0.35675	0.31355	0.012
F(1)	4e	0	0	0.1348	0	0	0.1344	0.004
F(2)	4g	0.0927	0.8003	0	0.0941	0.7983	0	0.024
F(3)	4g	0.4751	0.1442	0	0.4761	0.1444	0	0.010
F(4)	4g	0.1416	0.4654	0	0.1426	0.4655	0	0.010
F(5)	8h	0.3121	0.2032	0.2786	0.3106	0.2016	0.2773	0.025
F(6)	8h	0.0508	0.2323	0.2150	0.0516	0.2337	0.2162	0.020
F(7)	8h	0.3965	0.4075	0.1363	0.3963	0.4078	0.1342	0.020
F(8)	8h	0.2530	0.4472	0.3515	0.2501	0.4490	0.3519	0.035

Table S19. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for $Ba_3Al_2F_{12}$.

Bond lengths			Bond angles		
Al-F(7)	1.764	*1.781*	F(7)-Al-F(8)	92.4	*92.5*
Al-F(8)	1.766	*1.798*	F(7)-Al-F(5)	92.9	*93.0*
Al-F(5)	1.794	*1.806*	F(7)-Al-F(6)	90.0	*89.8*
Al-F(6)	1.811	*1.829*	F(7)-Al-F(1)	92.6	*92.6*
Al-F(1)	1.815	*1.828*	F(8)-Al-F(5)	93.0	*93.3*
Al-F(2)	1.860	*1.869*	F(8)-Al-F(1)	92.0	*91.7*
Bond angles			F(8)-Al-F(2)	90.1	*90.1*
F(5)-Al-F(1)	172.3	*172.3*	F(5)-Al-F(6)	88.6	*88.7*
F(8)-Al-F(6)	177.0	*176.8*	F(5)-Al-F(2)	86.8	*86.6*
F(7)-Al-F(2)	177.5	*177.4*	F(6)-Al-F(1)	86.1	*86.0*
			F(6)-Al-F(2)	87.5	*87.5*
			F(1)-Al-F(2)	87.3	*87.5*

Table S20. Initial fractional atomic coordinates[10] (x, y, z). WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for Ba_3AlF_9-Ib.

Atom	Site	x	y	z	x'	y'	z'	d
Ba(1)	4c	0.4463	1/4	0.3995	0.4467	1/4	0.3994	0.004
Ba(2)	4c	0.3306	1/4	0.9577	0.3298	1/4	0.9579	0.009
Ba(3)	4c	0.2343	1/4	0.6801	0.2344	1/4	0.6803	0.003
Al	4c	0.0236	1/4	0.3320	0.0236	1/4	0.3318	0.003
F(1)	4c	0.3660	1/4	0.2257	0.3643	1/4	0.2263	0.019
F(2)	4c	0.1728	1/4	0.4001	0.1743	1/4	0.4006	0.017
F(3)	4c	0.1403	1/4	0.8490	0.1408	1/4	0.8487	0.007
F(4)	8d	0.1489	-0.0029	0.0440	0.1489	-0.0029	0.0440	0.000
F(5)	8d	0.4563	0.0187	0.0934	0.4551	0.0168	0.0927	0.019
F(6)	8d	0.0837	0.0204	0.2601	0.0849	0.0178	0.2590	0.025

Table S21. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for Ba_3AlF_9-Ib.

Bond lengths			Bond angles		
Al-F(6)	1.773	*1.796*	F(6)-Al-F(6)	92.2	*92.1*
Al-F(1)	1.803	*1.822*	F(6)-Al-F(1)	90.7	*90.9*
Al-F(2)	1.811	*1.828*	F(6)-Al-F(2)	93.1	*93.0*
Al-F(5)	1.830	*1.850*	F(6)-Al-F(5)	89.1	*89.4*
Bond angles			F(1)-Al-F(5)	87.9	*87.7*
F(1)-Al-F(2)	174.4	*174.4*	F(2)-Al-F(5)	88.1	*88.3*
F(6)-Al-F(5)	178.1	*178.0*	F(5)-Al-F(5)	89.4	*89.1*

Table S22. Initial fractional atomic coordinates[12] (x, y, z). WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for α-$BaCaAlF_7$.

Atom	Site	x	y	z	x'	y'	z'	d
Ba	4g	0.24906	0.24041	-0.06776	0.24892	0.24086	-0.06755	0.005
Al	4g	0.20069	0.22470	0.38092	0.20058	0.22471	0.38079	0.002
Ca(1)	2e	3/4	0.20769	3/4	3/4	0.20779	3/4	0.001
Ca(2)	2f	1/4	0.68150	3/4	1/4	0.67911	3/4	0.013
F(1)	4g	0.5997	0.5949	0.56404	0.5973	0.5927	0.56359	0.019
F(2)	4g	0.5649	0.8622	0.68045	0.5629	0.8630	0.68119	0.018
F(3)	4g	0.0901	0.4812	0.32626	0.0885	0.4835	0.32571	0.018
F(4)	4g	0.4141	0.3614	0.69206	0.4145	0.3617	0.69200	0.003
F(5)	4g	0.0530	0.7185	0.56042	0.0554	0.7174	0.55992	0.017
F(6)	4g	0.0154	-0.0288	0.67494	0.0171	-0.0278	0.67530	0.012
F(7)	4g	0.2750	-0.0454	0.43446	0.2766	-0.0480	0.43508	0.020

Table S23. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for α-$BaCaAlF_7$.

Bond lengths			Bond angles		
Al-F(1)	1.753	*1.774*	F(1)-Al-F(2)	95.6	*95.5*
Al-F(2)	1.804	*1.821*	F(1)-Al-F(7)	90.0	*89.9*
Al-F(7)	1.805	*1.826*	F(1)-Al-F(3)	95.3	*95.3*
Al-F(3)	1.808	*1.824*	F(1)-Al-F(5)	90.1	*90.1*
Al-F(5)	1.813	*1.831*	F(2)-Al-F(7)	90.3	*90.3*
Al-F(6)	1.861	*1.872*	F(2)-Al-F(3)	93.2	*93.2*
Bond angles			F(2)-Al-F(6)	85.7	*85.8*
F(7)-Al-F(3)	173.4	*173.5*	F(7)-Al-F(5)	87.1	*87.2*
F(2)-Al-F(5)	173.7	*173.8*	F(7)-Al-F(6)	88.7	*88.9*
F(1)-Al-F(6)	178.2	*178.2*	F(3)-Al-F(5)	88.9	*88.8*
			F(3)-Al-F(6)	85.9	*85.9*
			F(5)-Al-F(6)	88.5	*88.5*

Table S24. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from powder X-ray structure refinement and WIEN2k optimization (in italic) for α-$NaCaAlF_6$.

Bond lengths			Bond angles		
Al(1)-F(10)	1.709	*1.812*	F(10)-Al(1)-F(2)	87.5	*88.5*
Al(1)-F(2)	1.715	*1.859*	F(10)-Al(1)-F(4)	88.5	*92.6*
Al(1)-F(4)	1.781	*1.854*	F(10)-Al(1)-F(6)	90.2	*86.0*
Al(1)-F(6)	1.801	*1.855*	F(10)-Al(1)-F(9)	89.2	*89.7*
Al(1)-F(9)	1.840	*1.773*	F(2)-Al(1)-F(4)	90.9	*84.7*
Al(1)-F(11)	1.882	*1.805*	F(2)-Al(1)-F(6)	79.5	*83.8*
Al(2)-F(1)	1.710	*1.823*	F(2)-Al(1)-F(11)	94.8	*93.2*
Al(2)-F(12)	1.713	*1.779*	F(4)-Al(1)-F(9)	91.6	*93.5*
Al(2)-F(3)	1.765	*1.829*	F(4)-Al(1)-F(11)	94.0	*93.2*
Al(2)-F(7)	1.818	*1.831*	F(6)-Al(1)-F(9)	97.9	*98.0*
Al(2)-F(8)	1.828	*1.829*	F(6)-Al(1)-F(11)	87.6	*88.6*
Al(2)-F(5)	1.903	*1.829*	F(9)-Al(1)-F(11)	88.3	*88.6*
Bond angles			F(1)-Al(2)-F(12)	102.5	*95.0*
F(4)-Al(1)-F(6)	170.4	*168.4*	F(1)-Al(2)-F(3)	94.1	*91.0*
F(2)-Al(1)-F(9)	175.8	*177.5*	F(1)-Al(2)-F(7)	87.4	*92.5*
F(10)-Al(1)-F(11)	176.5	*174.1*	F(1)-Al(2)-F(8)	87.9	*86.0*
F(3)-Al(2)-F(7)	178.5	*176.3*	F(12)-Al(2)-F(3)	94.9	*90.6*
F(12)-Al(2)-F(8)	166.9	*178.5*	F(12)-Al(2)-F(7)	84.7	*87.8*
F(1)-Al(2)-F(5)	166.8	*172.2*	F(12)-Al(2)-F(5)	90.2	*92.7*
			F(3)-Al(2)-F(8)	92.2	*90.5*
			F(3)-Al(2)-F(5)	88.2	*88.0*
			F(7)-Al(2)-F(8)	87.8	*91.0*
			F(7)-Al(2)-F(5)	90.4	*88.7*
			F(8)-Al(2)-F(5)	79.0	*86.3*

Table S25. Initial fractional atomic coordinates[14] (x, y, z). WIEN2k optimized fractional atomic coordinates (x', y', z') and corresponding atomic displacements d (Å) for β-$NaCaAlF_6$.

Atom	Site	x	y	z	x'	y'	z'	d
Ca 1	3e	0.3720	0	0	0.3711	0	0	0.008
Na 1	3f	0.7145	0	1/2	0.7138	0	1/2	0.006
Al 1	1a	0	0	0	0	0	0	0.000
Al 2	2d	0.3333	0.6667	**0.4990**[a]	0.3333	0.6667	**0.4997**[a]	**0.004**[a]
F 1	6g	0.9136	0.1041	0.7960	0.9143	0.1091	0.7988	0.044
F 2	6g	0.5541	0.4101	0.7030	0.5524	0.4110	0.7096	0.039
F 3	6g	0.2517	0.7771	0.7030	0.2512	0.7767	0.7083	0.027

[a] This table was reported in SI of ref.[16] but the three values in boldface were inaccurate.

Table S26. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from powder X-ray structure refinement and WIEN2k optimization (in italic) for β-$NaCaAlF_6$.

Bond lengths			Bond angles		
Al(1)-F(1)	1.801	*1.822*	F(1)-Al(1)-F(1)	90.4	*91.8*
Al(2)-F(2)	1.793	*1.831*	F(1)-Al(1)-F(1)	86.2	*83.7*
Al(2)-F(3)	1.814	*1.827*	F(1)-Al(1)-F(1)	93.3	*93.1*
Bond angles			F(2)-Al(2)-F(2)	90.7	*89.9*
F(1)-Al(1)-F(1)	175.0	*173.4*	F(2)-Al(2)-F(3)	88.5	*89.3*
F(2)-Al(2)-F(3)	178.9	*178.8*	F(2)-Al(2)-F(3)	90.0	*91.0*
			F(3)-Al(2)-F(3)	90.8	*89.9*

Table S27. Al-F bond lengths (Å) and F-Al-F bond angles (°) as deduced from single crystal X-Ray structure refinement and WIEN2k optimization (in italic) for $Na_2Ca_3Al_2F_{14}$.

Bond lengths			Bond angles		
Al-F(2)	1.783	*1.799*	F(2)-Al-F(2)	91.5	*91.6*
Al-F(1)	1.824	*1.842*	F(2)-Al-F(1)	86.8	*86.7*
Bond angles			F(2)-Al-F(1)	92.3	*92.2*
F(2)-Al-F(1)	175.9	*175.8*	F(1)-Al-F(1)	89.6	*89.5*

Table S28. Compounds, Al sites, total contributions and contributions from the lattice, valence electrons and p-p electrons to the ^{27}Al EFG tensor elements, V_{zz}, V_{xx} and V_{yy} (10^{21} V/m^2).

Compound	Site	Contribution	V_{zz}	V_{xx}	V_{yy}
α-AlF_3	Al(1)	Total	-0.0701	0.0350	0.0350
		Lattice	-0.0053	0.0027	0.0027
		Valence	-0.0647	0.0323	0.0323
		p-p	-0.0637	0.0318	0.0318
α-Na_3AlF_6	Al(1)	Total	-0.141	0.131	0.0099
		Lattice	0.015	-0.015	0.0004
		Valence	-0.156	0.146	0.0095
		p-p	-0.149	0.139	0.0096
$Na_5Al_3F_{14}$	Al(1)	Total	-1.52	0.759	0.759
		Lattice	-0.10	0.052	0.052
		Valence	-1.41	0.707	0.707
		p-p	-1.40	0.699	0.699
	Al(2)	Total	2.02	-1.21	-0.810
		Lattice	0.10	-0.06	-0.039
		Valence	1.93	-1.16	-0.770
		p-p	1.89	-1.13	-0.759
α-$CaAlF_5$	Al(1)	Total	2.73	-2.63	-0.0968
		Lattice	0.05	-0.06	0.0033
		Valence	2.67	-2.57	-0.1001
		p-p	2.61	-2.51	-0.0982
β-$CaAlF_5$	Al(1)	Total	2.60	-1.41	-1.19
		Lattice	0.06	-0.03	-0.03
		Valence	2.55	-1.39	-1.16
		p-p	2.48	-1.35	-1.13

Table S28. Continued

Compound	Site	Contribution	V_{zz}	V_{xx}	V_{yy}
Ca_2AlF_7	Al(1)	Total	0.590	-0.577	-0.0125
		Lattice	-0.019	-0.013	0.0324
		Valence	0.609	-0.564	-0.0449
		p-p	0.586	-0.549	-0.0364
α-$BaAlF_5$	Al(1)	Total	-1.61	0.903	0.707
		Lattice	-0.03	0.009	0.016
		Valence	-1.58	0.894	0.690
		p-p	-1.55	0.871	0.675
β-$BaAlF_5$	Al(1)	Total	-0.929	0.682	0.247
		Lattice	-0.029	0.003	0.027
		Valence	-0.899	0.679	0.220
		p-p	-0.882	0.663	0.219
	Al(2)	Total	-1.24	0.649	0.588
		Lattice	-0.03	0.024	0.006
		Valence	-1.21	0.625	0.582
		p-p	-1.18	0.614	0.566
γ-$BaAlF_5$	Al(1)	Total	-1.55	0.894	0.654
		Lattice	-0.03	0.015	0.014
		Valence	-1.52	0.879	0.640
		p-p	-1.48	0.859	0.624
	Al(2)	Total	-2.13	1.24	0.884
		Lattice	-0.03	0.01	0.019
		Valence	-2.10	1.24	0.865
		p-p	-2.05	1.20	0.845

Table S28. Continued

Compound	Site	Contribution	V_{zz}	V_{xx}	V_{yy}
$Ba_3Al_2F_{12}$	Al(1)	Total	-0.938	0.623	0.315
		Lattice	-0.057	0.038	0.019
		Valence	-0.881	0.585	0.296
		p-p	-0.868	0.577	0.291
Ba_3AlF_9-Ib	Al(1)	Total	0.106	-0.0798	-0.0262
		Lattice	0.017	-0.0053	-0.0142
		Valence	0.089	-0.0745	-0.0120
		p-p	0.084	-0.0753	-0.0087
β-Ba_3AlF_9	Al(1)	Total	-0.377	0.299	0.077
		Lattice	-0.007	0.036	-0.029
		Valence	-0.370	0.263	0.106
		p-p	-0.361	0.262	0.099
	Al(2)	Total	-0.416	0.382	0.0338
		Lattice	-0.022	0.035	-0.0133
		Valence	-0.394	0.347	0.0471
		p-p	-0.385	0.342	0.0435
	Al(3)	Total	0.937	-0.502	-0.435
		Lattice	-0.009	0.000	0.008
		Valence	0.946	-0.502	-0.443
		p-p	0.920	-0.490	-0.430
α-$BaCaAlF_7$	Al(1)	Total	-0.360	0.328	0.0321
		Lattice	0.016	-0.006	-0.0097
		Valence	-0.376	0.334	0.0418
		p-p	-0.360	0.321	0.0388

Table S28. Continued

Compound	Site	Contribution	V_{zz}	V_{xx}	V_{yy}
α-$NaCaAlF_6$	Al(1)	Total	0.981	-0.610	-0.371
		Lattice	-0.005	0.010	-0.005
		Valence	0.986	-0.619	-0.366
		p-p	0.954	-0.597	-0.357
	Al(2)	Total	-0.761	0.424	0.337
		Lattice	0.003	-0.006	0.003
		Valence	-0.764	0.430	0.334
		p-p	-0.742	0.416	0.326
β-$NaCaAlF_6$	Al(1)	Total	0.375	-0.188	-0.188
		Lattice	-0.013	0.006	0.006
		Valence	0.388	-0.194	-0.194
		p-p	0.372	-0.186	-0.186
	Al(2)	Total	-0.102	0.0510	0.0510
		Lattice	-0.022	0.0111	0.0111
		Valence	-0.080	0.0399	0.0399
		p-p	-0.081	0.0405	0.0405
$Na_2Ca_3Al_2F_{14}$	Al(1)	Total	0.132	-0.0658	-0.0658
		Lattice	0.012	-0.0061	-0.0061
		Valence	0.120	-0.0597	-0.0597
		p-p	0.117	-0.0583	-0.0583

Table S29. Components of the directions of the calculated ^{27}Al EFG tensor elements, after WIEN2k optimization (except α-AlF_3 and α-Na_3AlF_6), expressed in the crystallographic axis for the studied compounds.

Compound	Site	Axis	V_{XX}	V_{YY}	V_{ZZ}
α-AlF_3	Al(1)	a	0.1171	-0.2028	0.0803
		b	0.1171	0.2028	0.0803
		c	-0.2342	0	0.0803
α-Na_3AlF_6	Al(1)	a	0.0431	0.1432	0.1084
		b	0.1300	0.0465	-0.1131
		c	-0.0827	0.0743	-0.0646
$Na_5Al_3F_{14}$	Al(1)	a	0.1426	0	0
		b	0	0.1426	0
		c	0	0	0.0961
	Al(2)	a	0.1410	0	-0.0208
		b	0.0208	0	0.1410
		c	0	0.0961	0
α-$CaAlF_5$	Al(1)	a	0.1260	0.0128	-0.0007
		b	0.0159	-0.1571	-0.0105
		c	0.0649	-0.0025	0.1354
β-$CaAlF_5$	Al(1)	a	0.0644	0.1886	-0.0021
		b	-0.0957	0.0328	0.0109
		c	0.0303	0.0434	0.1352
Ca_2AlF_7	Al(1)	a	0.0525	0.1191	0
		b	0.1307	-0.0577	0
		c	0	0	0.1047
α-$BaAlF_5$	Al(1)	a	0.0298	-0.0544	0.0384
		b	0.0935	-0.0502	-0.1436
		c	0.1517	0.1225	0.0560

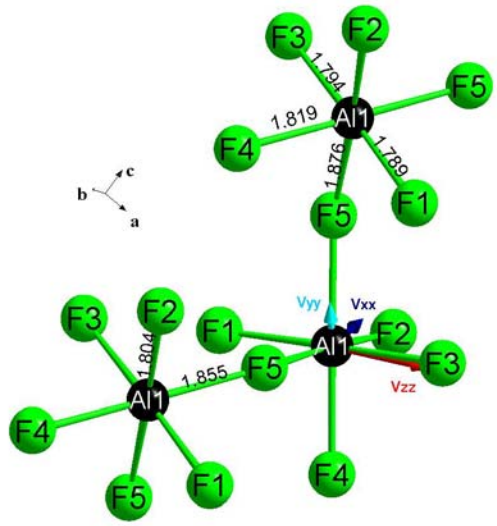
Table S29. Continued

Compound	Site	Axis	V_{XX}	V_{YY}	V_{ZZ}
β-$BaAlF_5$	Al(1)	a	-0.0257	0.1917	-0.0187
		b	0.0204	0.0072	0.0463
		c	0.1193	0.0163	-0.0551
	Al(2)	a	-0.0355	0.1895	0.0243
		b	0.0073	0.0078	-0.0500
		c	-0.1297	-0.0158	-0.0215
γ-$BaAlF_5$	Al(1)	a	-0.0279	0.1872	0.0185
		b	-0.0795	0.0054	0.0649
		c	0.0839	-0.0208	0.1046
	Al(2)	a	-0.1438	0.1234	-0.0169
		b	-0.0054	0.0078	0.1023
		c	0.0870	0.1041	-0.0033
$Ba_3Al_2F_{12}$	Al(1)	a	0.0461	-0.0289	0.0815
		b	0.0417	-0.0769	-0.0508
		c	0.0819	0.0608	-0.0248
Ba_3AlF_9-Ib	Al(1)	a	-0.0572	0	0.0812
		b	0.1468	0	0.1034
		c	0	0.0672	0
β-Ba_3AlF_9	Al(1)	a	0.0815	0.0786	-0.0694
		b	-0.0377	-0.0094	-0.0549
		c	0.0382	-0.0545	-0.0169
	Al(2)	a	0	0.0986	0.0889
		b	0	-0.0450	0.0500
		c	0.0686	0	0
	Al(3)	a	0.1273	0	0.0377
		b	-0.0191	0	0.0645
		c	0	0.0686	0

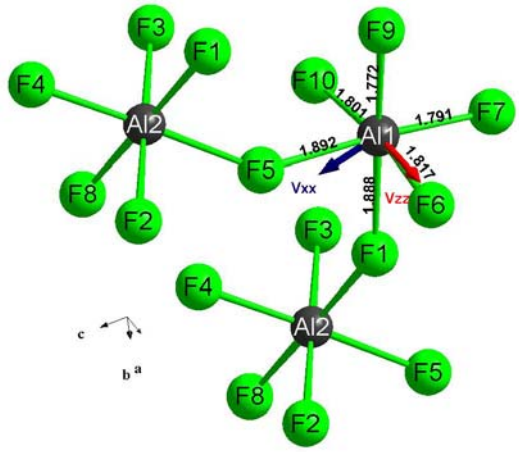
Table S29. Continued

Compound	Site	Axis	V_{XX}	V_{YY}	V_{ZZ}
		a	-0.1151	0.1335	0.0608
α-$BaCaAlF_7$	Al(1)	b	-0.1263	-0.1289	0.0439
		c	0.0197	-0.0025	0.0493
		a	0.0568	0.0590	-0.0799
	Al(1)	b	0.1671	-0.0509	0.0812
		c	-0.0010	0.0407	0.0275
α-$NaCaAlF_6$		a	0.0233	0.0494	0.1005
	Al(2)	b	0.1824	0.0269	-0.0555
		c	0.0124	-0.0432	0.0198
		a	0.1293	0	0
	Al(1)	b	0.0647	0.1120	0
		c	0	0	0.1975
β-$NaCaAlF_6$		a	0.1293	0	0
	Al(2)	b	0.0647	0.1120	0
		c	0	0	0.1975
		a	0.0689	0.0398	0.0563
$Na_2Ca_3Al_2F_{14}$	Al(1)	b	-0.0689	0.0398	0.0563
		c	0	-0.0796	0.0563

a)



b)



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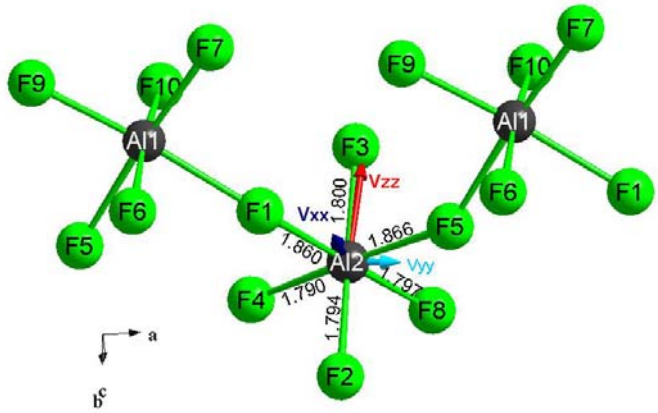

Figure S1. Orientation of the calculated ^{27}Al EFG tensor elements for (a) α-$BaAlF_5$, (b) Al1 and (c) Al2 in β-$BaAlF_5$. Al-F distances and atom labels are indicated. For each, the vector lengths are proportional to the magnitudes of the contributions (see Table S28).

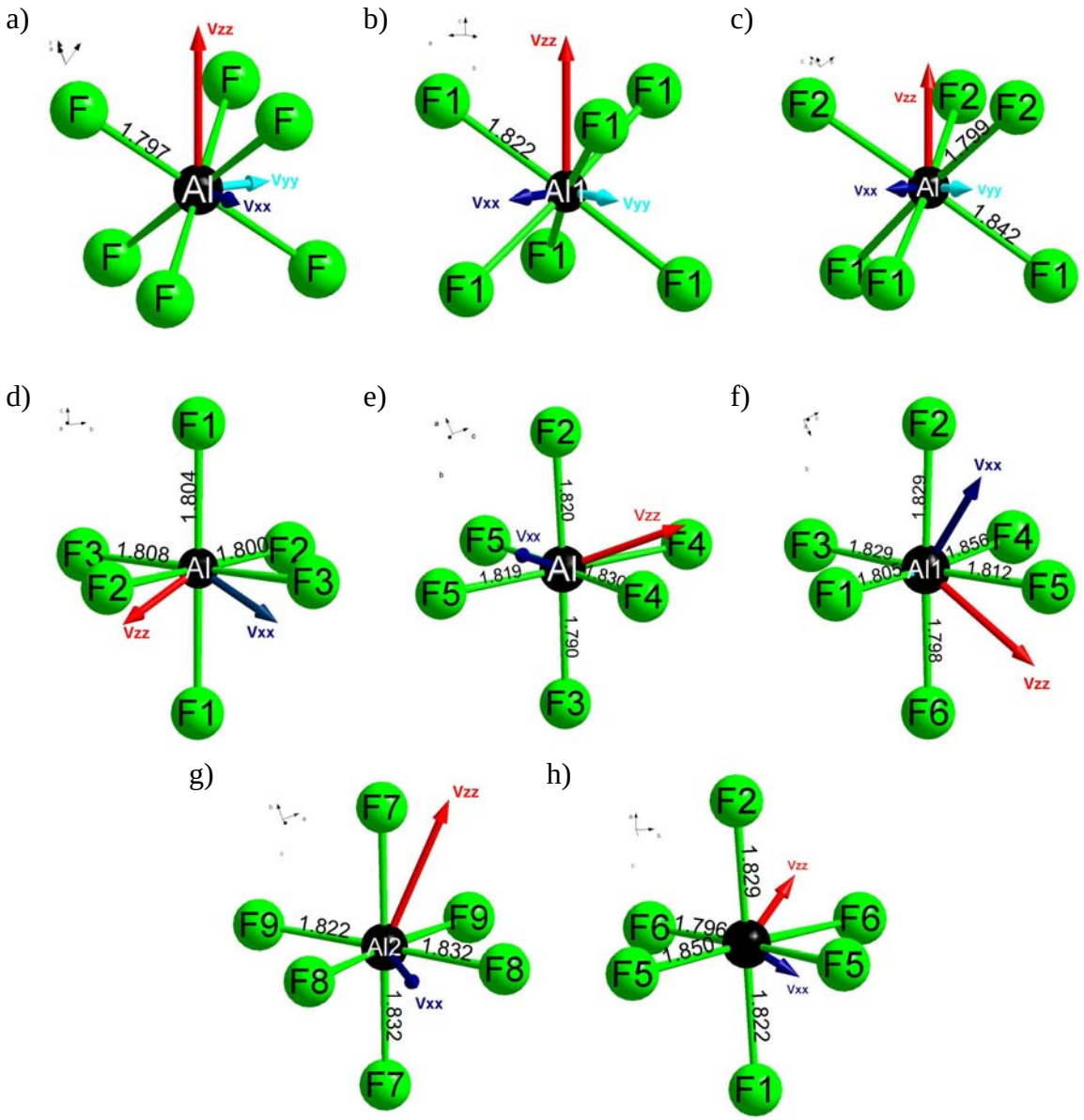

Figure S2. Orientation of the calculated ^{27}Al EFG tensor elements for (a) α-AlF_3, (b) Al1 in β-$NaCaAlF_6$, (c) $Na_2Ca_3Al_2F_{14}$, (d) α-Na_3AlF_6, (e) Ca_2AlF_7, (f) Al1 and (g) Al2 in β-Ba_3AlF_9 and (h) Ba_3AlF_9-Ib. Al-F distances and atom labels are indicated. For each, the vector lengths are proportional to the magnitudes of the contributions (see Table S28).

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