Structure determination of Ba_5AlF_{13} by coupling electron, synchrotron and neutron powder diffraction, solid-state NMR and ab initio calculations†

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Electronic Supplementary Information.

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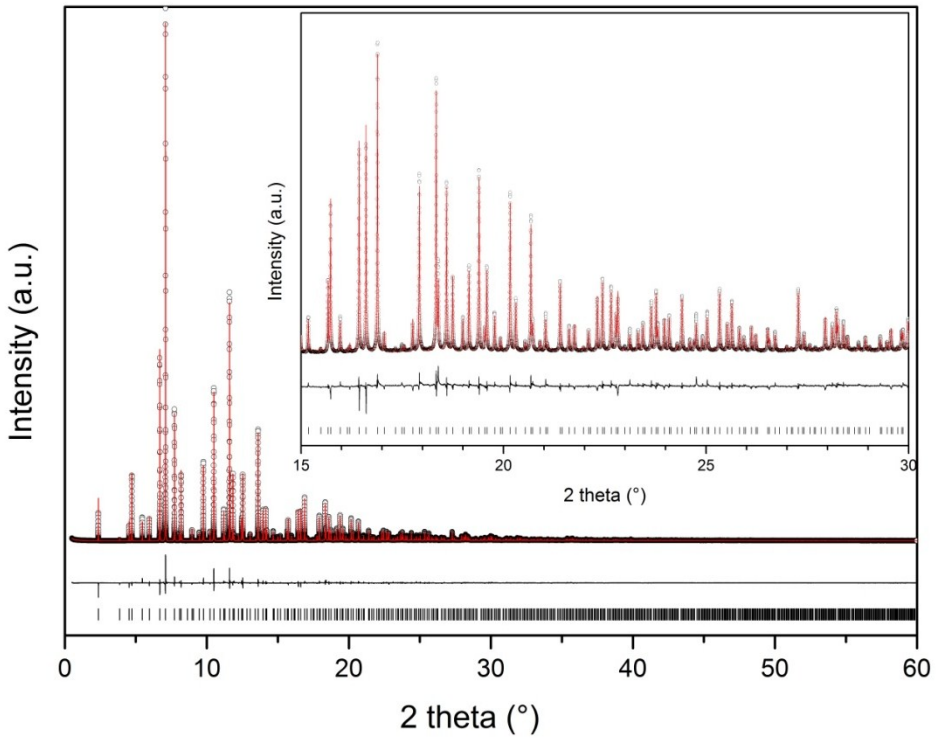

Fig. S1. Experimental (dots) and calculated (red line) room-temperature SPD patterns of Ba_5AlF_{13}. The Bragg positions (vertical ticks) and the difference between the experimental and calculated data are shown. The fit statistics are: R_p = 6.07%, R_{wp} = 8.93%, R_{Bragg} = 4.79%.

Table S1. Atomic coordinates of Ba_5AlF_{13} according to the experimental SPD and NPD data (SPD, NPD) after geometry optimization (SPD_GO), in the ordered model.

	Atom	Site	Occupancy	Symmetry	x	y	z
SPD	Al1	16d	1	-3m	0.5	0.5	0.5
SPD_GO					0.5	0.5	0.5
NPD					0.5	0.5	0.5
SPD	Ba1	32e	1	3m	0.2898(2)	0.2898(2)	0.2898(2)
SPD_GO					0.2899	0.2899	0.2899
NPD					0.2898(2)	0.2898(2)	0.2898(2)
SPD	Ba2	48f	1	2.mm	0.0718(3)	1/8	1/8
SPD_GO					0.06618	1/8	1/8
NPD					0.0717(3)	1/8	1/8
SPD	F1	96g	1	mm	0.4789(2)	0.4789(2)	0.1417(2)
SPD_GO					0.4786	0.4786	0.1411
NPD					0.4786(2)	0.4786(2)	0.1409(2)
SPD	F2	96g	1	mm	0.3192(1)	0.3192(1)	0.5357(2)
SPD_GO					0.3195	0.3195	0.5358
NPD					0.3198(1)	0.3198(1)	0.5353(2)
SPD	F3	8a	1	-43m	1/8	1/8	1/8
SPD_GO					1/8	1/8	1/8
NPD					1/8	1/8	1/8
SPD	F4	8b	1	-43m	3/8	3/8	3/8
SPD_GO					3/8	3/8	3/8
NPD					3/8	3/8	3/8

Table S2. Al-F distances (Å) in Ba_5AlF_{13} according to the experimental SPD and NPD data (SPD, NPD) after geometry optimization (SPD_GO) in the ordered model.

SPD	1.812	NPD	1.823
SPD_GO	1.818		

Table S3. Ba-F distances (Å) in Ba_5AlF_{13} according to the experimental SPD and NPD data (SPD, NPD) after geometry optimization (SPD_GO) in the ordered model.

Ba1

SPD	2.565	NPD	2.565
	2.631		2.612
	2.827		2.815
SPD_GO	2.564		
	2.627		
	2.825		

Ba2

SPD	2.703	NPD	2.706
	2.824		2.821
	2.833		2.830
SPD_GO	2.677		
	2.861		
	2.914		

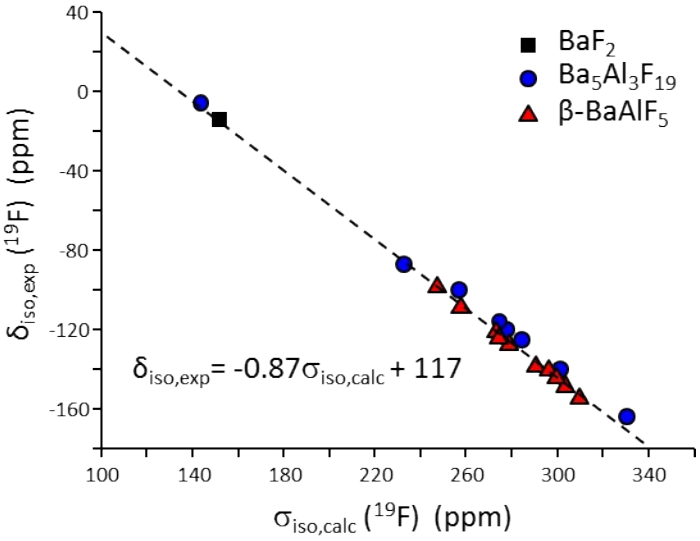

Fig. S2 Correlation between the ^{19}F GIPAW calculated isotropic shieldings and experimental isotropic chemical shift values for BaF_2 (black squares), $Ba_5Al_3F_{19}$. (blue circles) and β-$BaAlF_5$ (red triangles). The dashed line is the linear regression: $\delta_{iso,exp}/CFCl_3 = -0.87\ \sigma_{iso,cal} + 117$ ($R^2 = 0.993$).

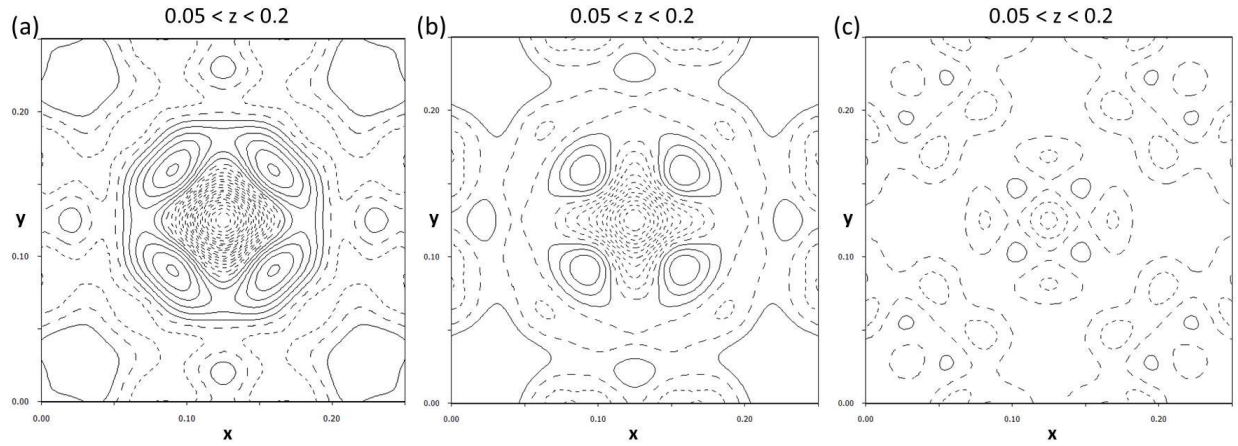

Fig. S3 Residual density on difference Fourier maps obtained for different approximation models of the thermal parameter of F3: (a) harmonic anisotropic, (b) anharmonic third order and (c) anharmonic fourth order.

Table S4 Comparison of the final reliability factors and number of independent thermal parameters for the different refinement models.

	Number of independent thermal parameters	GOF (%)	R_p (%)	wR_p (%)
Harmonic anisotropic 32e site	2	1.63	2.59	3.30
Anharmonic 3rd order 32e site	6	1.54	2.45	3.11
Anharmonic 4th order 32e site	7	1.37	2.20	2.78

Table S5 Gram-Charlier expansion parameters (third and fourth order anharmonic tensors (x10^2)) for Ba_5AlF_{13}.

Atom	*C111*	*C112*	*C113*	*C122*	*C123*	*C133*	*C222*	*C223*	*C233*	*C333*
F3	-3.4921	-5.4514	-5.4514	-5.4514	-6.1281	-5.4514	-3.4921	-5.4514	-5.4514	-3.4921

Equations due to the site symmetry *32e* for F3: C111=C222=C333 ; C112=C113=C122=C133=C223.

Atom	*D1111*	*D1112*	*D1113*	*D1122*	*D1123*	*D1133*	*D1222*	*D1223*	*D1233*	*D1333*
F3	4.4035	-9.634	-9.634	-4.2394	-1.5601	-4.2394	-9.634	-1.5601	-1.5601	-9.634

D2222	*D2223*	*D2233*	*D2333*	*D3333*
4.4035	-9.634	-4.2394	-9.634	4.4035

Equations due to the site symmetry *32e* for F3: D1111=D2222=D3333 ;
D1112=D1113=D1222=D1333=D2223=D2333 ; D1122=D1133=D2233 ; D1123=D1223=D1233

Table S6 Atomic coordinates of Ba_5AlF_{13} resulting from anharmonic 4th order Rietveld refinement of the NPD data.

Atom	Site	Occupancy	Symmetry	x	y	z
Al1	16*d*	1	-3m	0.5	0.5	0.5
Ba1	32*e*	1	3m	0.2902(2)	0.2902(2)	0.2902(2)
Ba2	48*f*	1	2.mm	0.0723(2)	1/8	1/8
F1	96*g*	1	mm	0.4768(1)	0.4768(1)	0.1438(2)
F2	96*g*	1	mm	0.3194(1)	0.3194(1)	0.5353(2)
F3	32*e*	0.25	3m	0.099(4)	0.099(4)	0.099(4)
F4	8*b*	1	-43m	3/8	3/8	3/8