Table S1: Anisotropic displacement parameters in 10^4 pm^2 of $InAlF_6(NH_3)_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In	0.0066(1)	0.0064(1)	0.0062(1)	0	0.00122(6)	0
Al	0.0040(3)	0.0030(4)	0.0034(3)	0	0.0004(3)	0
F(1)	0.0102(4)	0.0098(4)	0.0104(4)	–0.0026(4)	0.0015(3)	–0.0007(3)
F(2)	0.0100(6)	0.0093(6)	0.0104(6)	0	0.0001(5)	0
N(1)	0.0080(8)	0.0102(8)	0.0103(8)	0	0.0015(6)	0

Table S2. Anisotropic displacement parameters in 10^4 pm^2 of $[In(NH_3)_6][AlF_6]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In	0.0184(2)	0.0184(2)	0.0184(2)	–0.00004(6)	–0.00004(6)	–0.00004(6)
Al	0.0147(3)	0.0147(3)	0.0147(3)	0.0003(2)	0.0003(2)	–0.0003(2)
F	0.0329(7)	0.0278(6)	0.0296(7)	–0.0033(5)	0.0009(5)	0.0087(5)
N	0.0232(9)	0.036(1)	0.023(1)	0.0020(7)	0.0012(7)	–0.0029(7)

Table S3. Fractional atomic coordinates and isotropic displacement parameters in 10^4 pm^2 of $[In_2F(NH_3)_{10}]_2[SiF_6]_5 \cdot 2\ NH_3$.

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
In(1)	4*c*	0.48037(4)	¼	0.38183(5)	0.0147(2)
In(2)	4*c*	0.29487(4)	¼	0.63848(5)	0.0149(2)
In(3)	8*d*	0.38072(3)	0.05146(2)	0.01898(4)	0.0167(2)
Si(1)	8*d*	0.0694(2)	0.11121(8)	0.8058(2)	0.0240(4)
Si(2)	4*c*	0.3768(2)	¼	0.0161(2)	0.0174(5)
Si(3)	8*d*	0.2181(2)	0.11339(7)	0.3267(2)	0.0177(4)
N(1)	4*c*	0.3476(6)	¼	0.2964(7)	0.018(2)
H(1A)	8*d*	0.320(5)	0.275(3)	0.298(6)	0.022
H(1B)	4*c*	0.343(8)	¼	0.237(9)	0.022
N(2)	4*c*	0.1000(6)	¼	0.0101(7)	0.023(2)
H(2A)	8*d*	0.095(5)	0.277(3)	–0.039(6)	0.027
H(2B)	4*c*	0.146(9)	¼	0.038(9)	0.027
N(3)	4*c*	0.0698(6)	¼	0.2576(7)	0.023(2)
H(3A)	4*c*	0.029(8)	¼	0.321(9)	0.028
H(3B)	8*d*	0.108(5)	0.278(3)	0.267(6)	0.028
N(4)	8*d*	0.4813(4)	0.3389(2)	0.3958(5)	0.020(2)
H(4A)	8*d*	0.520(6)	0.351(3)	0.359(6)	0.023
H(4B)	8*d*	0.489(6)	0.353(3)	0.451(6)	0.023
H(4C)	8*d*	0.426(6)	0.357(3)	0.381(6)	0.023
N(5)	4*c*	0.1701(6)	¼	0.5356(7)	0.022(2)

H(5A)	4*c*	0.106(8)	¼	0.562(9)	0.027
H(5B)	8*d*	0.163(6)	0.275(3)	0.495(6)	0.027
N(6)	4*c*	0.4296(6)	¼	0.7259(7)	0.022(2)
H(6A)	4*c*	0.430(8)	¼	0.783(10)	0.026
H(6B)	8*d*	0.457(6)	0.276(3)	0.726(6)	0.026
N(7)	4*c*	0.2045(5)	¼	0.7770(6)	0.020(2)
H(7A)	4*c*	0.242(8)	¼	0.846(9)	0.024
H(7B)	8*d*	0.166(5)	0.276(3)	0.782(6)	0.024
N(8)	8*d*	0.2956(4)	0.1613(2)	0.6266(5)	0.022(2)
H(8A)	8*d*	0.244(6)	0.145(3)	0.659(6)	0.027
H(8B)	8*d*	0.342(6)	0.144(3)	0.656(6)	0.027
H(8C)	8*d*	0.292(6)	0.146(3)	0.573(7)	0.027
N(9)	8*d*	0.4811(4)	0.1143(2)	0.9716(5)	0.024(2)
H(9A)	8*d*	0.498(6)	0.115(4)	0.924(7)	0.029
H(9B)	8*d*	0.469(6)	0.150(3)	1.000(6)	0.029
H(9C)	8*d*	0.526(6)	0.107(3)	1.004(6)	0.029
N(10)	8*d*	0.2067(5)	0.0174(2)	0.5662(5)	0.028(2)
H(10A)	8*d*	0.262(7)	0.007(3)	0.580(7)	0.034
H(10B)	8*d*	0.176(6)	0.038(3)	0.613(7)	0.034
H(10C)	8*d*	0.207(6)	0.051(3)	0.510(7)	0.034
N(11)	8*d*	0.2617(4)	0.1081(2)	0.0425(5)	0.022(2)
H(11A)	8*d*	0.213(6)	0.103(3)	–0.010(6)	0.026
H(11B)	8*d*	0.274(6)	0.141(3)	0.033(6)	0.026
H(11C)	8*d*	0.241(6)	0.100(3)	0.088(7)	0.026
N(12)	8*d*	0.3415(4)	0.0397(2)	0.8565(5)	0.022(2)
H(12A)	8*d*	0.394(5)	0.049(3)	0.807(6)	0.026
H(12B)	8*d*	0.297(6)	0.056(3)	0.843(6)	0.026
H(12C)	8*d*	0.338(6)	0.011(3)	0.835(6)	0.026
N(13)	8*d*	0.4348(4)	0.0587(2)	0.1778(5)	0.023(2)
H(13A)	8*d*	0.433(6)	0.033(3)	0.213(6)	0.027
H(13B)	8*d*	0.401(6)	0.081(3)	0.220(6)	0.027
H(13C)	8*d*	0.495(6)	0.067(3)	0.173(6)	0.027
N(14)	8*d*	0.4090(5)	–0.0180(3)	0.5949(7)	0.050(2)
F(1)	4*c*	0.3872(3)	0.2500	0.5105(4)	0.021(2)
F(2)	4*b*	0	0	½	0.021(2)
F(3)	8*d*	0.050(1)	0.0761(3)	0.9044(6)	0.146(5)
F(4)	8*d*	0.4571(3)	0.1130(3)	0.7306(5)	0.069(2)
F(5)	8*d*	0.1839(5)	0.1139(4)	0.8362(6)	0.107(3)
F(6)	8*d*	0.0855(6)	0.0596(2)	0.7296(6)	0.096(3)
F(7)	8*d*	0.0933(5)	0.1517(3)	0.7085(5)	0.076(2)
F(8)	8*d*	0.0528(4)	0.1657(2)	0.8761(5)	0.060(2)
F(9)	8*d*	0.4247(5)	0.2037(2)	0.0910(4)	0.056(2)
F(10)	4*c*	0.2812(5)	¼	0.0903(6)	0.108(5)

F(11)	8*d*	0.3267(5)	0.2042(2)	0.9423(4)	0.059(2)
F(12)	4*c*	0.4705(5)	¼	0.9419(6)	0.087(4)
F(13)	8*d*	0.2422(3)	0.0559(2)	0.2703(4)	0.032(1)
F(14)	8*d*	0.2945(3)	0.0999(2)	0.4207(4)	0.040(2)
F(15)	8*d*	0.1410(3)	0.1293(2)	0.2347(4)	0.038(2)
F(16)	8*d*	0.1302(3)	0.0843(2)	0.3933(3)	0.0272(9)
F(17)	8*d*	0.1949(4)	0.1720(2)	0.3818(4)	0.043(2)
F(18)	8*d*	0.3076(3)	0.1413(2)	0.2597(3)	0.0239(8)

Table S4. Anisotropic displacement parameters U_{ij} in 10^4 pm^2 of $[In_2F(NH_3)_{10}]_2[SiF_6]_5 \cdot 2\ NH_3$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In(1)	0.0091(3)	0.0163(3)	0.0188(3)	0	0.0004(2)	0
In(2)	0.0103(3)	0.0153(3)	0.0190(3)	0	0.0010(2)	0
In(3)	0.0143(2)	0.0134(2)	0.0224(2)	0.0007(2)	0.0020(2)	0.0019(2)
Si(1)	0.027(1)	0.0206(9)	0.025(1)	–0.0038(7)	–0.0011(8)	0.0083(8)
Si(2)	0.014(1)	0.017(2)	0.022(2)	0	–0.0018(9)	0
Si(3)	0.0140(8)	0.0173(8)	0.0216(9)	–0.0003(7)	0.0008(6)	–0.0002(7)
N(1)	0.015(4)	0.019(4)	0.020(4)	0	–0.001(3)	0
N(2)	0.017(4)	0.031(5)	0.019(4)	0	0.000(3)	0
N(3)	0.016(4)	0.025(4)	0.028(5)	0	–0.003(3)	0
N(4)	0.014(3)	0.018(3)	0.027(3)	–0.001(2)	0.003(2)	0.000(2)
N(5)	0.022(4)	0.026(4)	0.019(4)	0	–0.007(3)	0
N(6)	0.021(4)	0.028(4)	0.015(4)	0	–0.004(3)	0
N(7)	0.012(4)	0.023(4)	0.026(4)	0	0.003(3)	0
N(8)	0.016(3)	0.015(3)	0.035(3)	0.000(2)	0.002(3)	0.002(2)
N(9)	0.020(3)	0.019(3)	0.033(4)	0.002(3)	0.000(3)	–0.001(2)
N(10)	0.030(3)	0.018(3)	0.036(4)	–0.001(3)	–0.007(3)	–0.005(3)
N(11)	0.022(3)	0.019(3)	0.025(3)	0.001(2)	0.007(2)	0.003(2)
N(12)	0.020(3)	0.018(3)	0.027(3)	–0.001(2)	0.001(2)	0.000(2)
N(13)	0.016(3)	0.024(3)	0.028(3)	0.003(2)	0.001(2)	0.004(2)
N(14)	0.038(4)	0.052(5)	0.061(5)	0.003(4)	–0.006(4)	–0.006(4)
F(1)	0.012(2)	0.026(3)	0.024(3)	0	0.002(2)	0
F(2)	0.016(2)	0.018(3)	0.028(3)	0.001(2)	–0.004(2)	0.005(2)
F(3)	0.31(2)	0.085(6)	0.044(4)	0.030(4)	–0.021(6)	–0.091(8)
F(4)	0.022(2)	0.112(5)	0.075(4)	0.056(4)	0.000(3)	–0.006(3)
F(5)	0.060(4)	0.172(8)	0.088(5)	–0.062(5)	–0.048(4)	0.076(5)
F(6)	0.154(7)	0.059(4)	0.074(5)	–0.037(4)	–0.031(5)	0.054(5)
F(7)	0.075(4)	0.106(5)	0.045(4)	0.016(4)	–0.010(3)	–0.055(4)
F(8)	0.071(4)	0.038(3)	0.070(4)	–0.029(3)	–0.025(3)	0.012(3)
F(9)	0.105(5)	0.026(2)	0.038(3)	–0.008(2)	–0.036(3)	0.020(3)
F(10)	0.018(4)	0.29(2)	0.019(4)	0	–0.004(3)	0

F(11)	0.110(5)	0.025(2)	0.041(3)	0.010(2)	–0.045(3)	–0.029(3)
F(12)	0.014(3)	0.22(2)	0.026(4)	0	0.003(3)	0
F(13)	0.029(2)	0.016(2)	0.050(3)	–0.006(2)	0.015(2)	–0.003(2)
F(14)	0.025(2)	0.062(3)	0.033(3)	0.016(2)	–0.010(2)	–0.011(2)
F(15)	0.024(2)	0.051(3)	0.040(3)	0.017(2)	–0.003(2)	0.009(2)
F(16)	0.016(2)	0.033(2)	0.033(2)	0.003(2)	0.007(2)	–0.002(2)
F(17)	0.052(3)	0.025(2)	0.051(3)	–0.010(2)	0.026(2)	–0.001(2)
F(18)	0.020(2)	0.018(2)	0.034(2)	0.000(2)	0.004(2)	–0.005(2)

Table S5. Selected interatomic distances in pm and angles in degree of the hydrogen bonds in $[In_2F(NH_3)_{10}]_2[SiF_6]_5 \cdot 2\ NH_3$.

	D–H	A	H···A	D···A	∢(DHA)
N(1)–H(1a)	73(7)	F(18)	219(7)	284.5(4)	149(8)
N(1)–H(1a)	73(7)	F(17)	248(8)	312.6(8)	148(8)
N(1)–H(1b)	79(12)	F(9)	254(11)	315.0(10)	136(8)
N(1)–H(1b)	79(12)	F(9)	254(11)	315.0(10)	136(8)
N(1)–H(1b)	79(12)	F(10)	213(12)	288.0(11)	161(11)
N(2)–H(2a)	94(8)	F(8)	193(8)	285.0(8)	165(7)
N(2)–H(2b)	74(12)	F(10)	203(12)	276.3(11)	170(13)
N(3)–H(3a)	102(12)	F(9)	221(10)	309.0(9)	144(4)
N(3)–H(3a)	102(12)	F(9)	221(10)	309.0(9)	144(4)
N(3)–H(3b)	90(7)	F(15)	243(7)	322.6(5)	148(7)
N(3)–H(3b)	90(7)	F(17)	232(8)	311.1(8)	146(7)
N(4)–H(4a)	79(8)	F(15)	216(9)	294.5(7)	170(8)
N(4)–H(4b)	82(9)	F(8)	251(8)	318.2(9)	141(7)
N(4)–H(4c)	92(8)	F(18)	231(8)	307.6(7)	140(6)
N(4)–H(4c)	92(8)	F(14)	221(8)	306.6(7)	154(7)
N(5)–H(5a)	97(12)	F(12)	207(8)	282.5(11)	157(10)
N(5)–H(5b)	82(8)	F(17)	198(8)	285.4(8)	160(8)
N(6)–H(6a)	76(13)	F(12)	218(13)	291.4(11)	165(12)
N(6)–H(6b)	76(7)	F(8)	241(8)	306.1(9)	143(8)
N(7)–H(7a)	106(11)	F(11)	209(10)	301.3(9)	144(3)
N(7)–H(7a)	106(11)	F(11)	209(10)	301.3(9)	144(3)
N(7)–H(7b)	86(7)	F(8)	250(7)	328.9(9)	154(7)
N(7)–H(7b)	86(7)	F(7)	231(7)	307.2(8)	149(7)
N(8)–H(8a)	93(9)	F(7)	223(9)	305.5(9)	147(7)
N(8)–H(8b)	87(9)	F(4)	206(9)	292.4(8)	173(8)
N(8)–H(8c)	81(9)	F(14)	232(9)	313.4(8)	175(8)
N(9)–H(9a)	68(9)	F(7)	239(9)	300.9(9)	153(10)
N(9)–H(9a)	68(9)	F(4)	262(9)	320.5(10)	146(9)
N(9)–H(9b)	100(9)	F(9)	190(9)	286.8(8)	160(7)
N(9)–H(9b)	100(9)	F(11)	254(8)	316.7(9)	121(6)

N(9)–H(9c)	78(9)	F(16)	209(9)	285.9(8)	171(9)
N(10)–H(10a)	84(9)	N(14)	217(9)	300.8(10)	173(8)
N(10)–H(10b)	91(9)	F(6)	207(9)	295.3(10)	161(8)
N(10)–H(10c)	112(9)	F(16)	207(9)	304.0(8)	143(6)
N(10)–H(10c)	112(9)	F(14)	212(9)	309.5(8)	144(7)
N(11)–H(11a)	99(8)	F(5)	209(8)	294.4(9)	144(6)
N(11)–H(11b)	86(8)	F(11)	213(9)	291.4(8)	152(7)
N(11)–H(11c)	70(8)	F(15)	251(9)	310.4(8)	144(9)
N(12)–H(12a)	102(8)	F(4)	210(8)	297.4(8)	143(6)
N(12)–H(12b)	78(8)	F(5)	215(9)	291.6(9)	166(8)
N(12)–H(12c)	79(8)	F(16)	256(9)	319.7(8)	139(7)
N(12)–H(12c)	79(8)	F(13)	220(9)	292.0(7)	152(8)
N(13)–H(13a)	80(8)	F(6)	237(8)	308.0(9)	150(8)
N(13)–H(13b)	92(8)	F(18)	208(8)	295.6(7)	157(7)
N(13)–H(13b)	92(8)	F(13)	242(8)	297.5(7)	119(6)
N(13)–H(13c)	87(8)	F(16)	215(9)	297.7(7)	160(8)

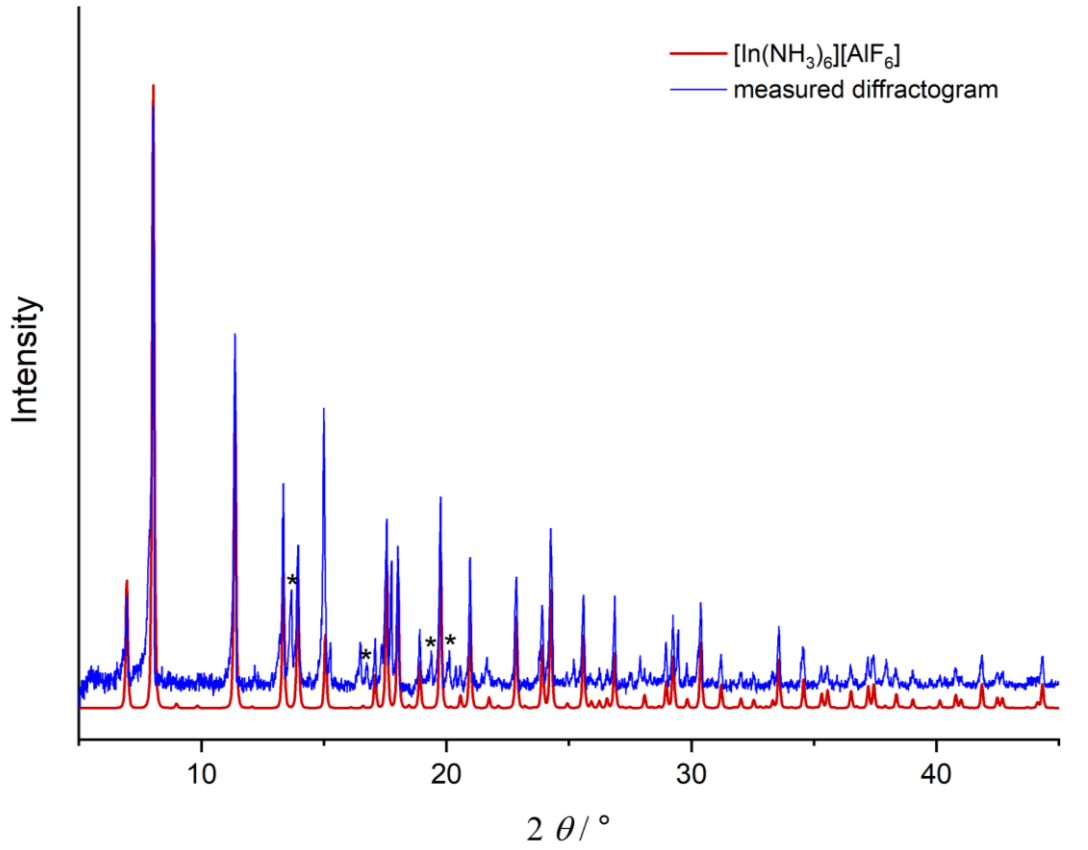

Figure S1. Powder X-ray diffraction pattern of $[In(NH_3)_6][AlF_6]$. Blue: measured diffractogram, red: simulated powder pattern according to results from structure determination. KF [1] and In [2] were identified as side phases. Unassigned reflections are marked with an asterisk.

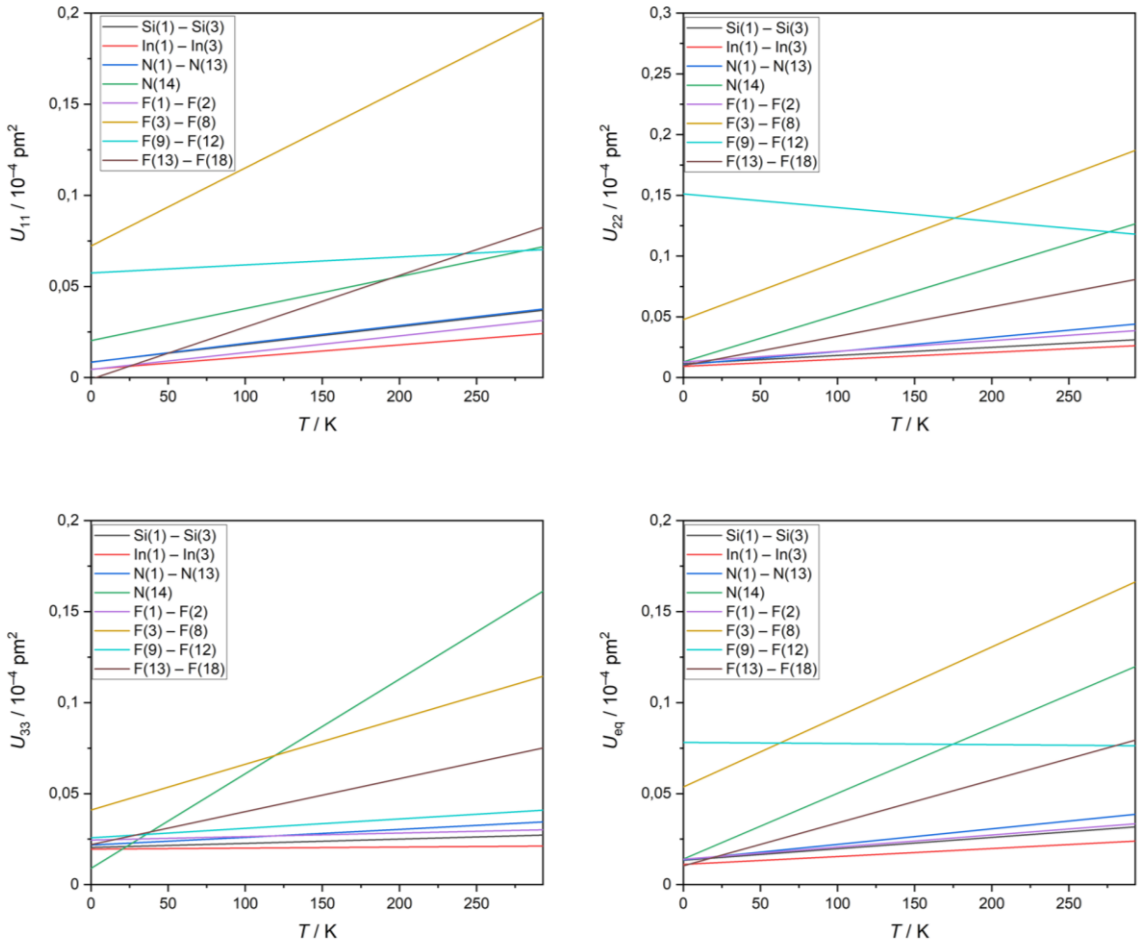

Figure S2. Extrapolation of U_{11}, U_{22}, U_{33} and U_{eq} to 0 K, according to refinements of single crystal X-ray diffraction data obtained at 293 and 100 K, for specific atom groups of $[In_2F(NH_3)_{10}]_2[SiF_6]_5 \cdot 2\ NH_3$.

Table S6**.** Extrapolation of U_{11}, U_{22}, U_{33} and U_{eq} to 0 K (in 10^{-4} pm^2), according to refinements of single crystal X-ray diffraction data obtained at 293 and 100 K, for specific atom groups of $[In_2F(NH_3)_{10}]_2[SiF_6]_5 \cdot 2\ NH_3$.

Atom group	U_{eq}	U_{11}	U_{22}	U_{33}
In(1–3)	0.0120	0.0118	0.0159	0.0204
Si(1–3)	0.0143	0.0182	0.0192	0.0231
N(1–13)	0.0146	0.0179	0.0240	0.0264
N(14)	0.0149	0.0137	0.0229	0.0269
F(1–2)	0.0149	0.0137	0.0229	0.0269
F(3–8)	0.0543	0.1149	0.0962	0.0663
F(9–12)	0.0794	0.0618	0.1416	0.0316
F(13–18)	0.0112	0.0283	0.0349	0.0398

References

1. Borch, E.; Oftedal, I.; Pabst, A. Neubestimmung der Gitterkonstanten von KF, CsCl und BaF_2. *Z. Phys. Chem., Abt. B* **1929**, *3*, 209–214.
2. Wołcyrz, M.; Kubiak, R.; Maciejewski, S. X-ray investigation of thermal expansion and atomic thermal vibrations of tin, indium, and their alloys. *Phys. Status Solidi B* **1981**, *107*, 245–253, doi:10.1002/pssb.2221070125.