Face-sharing octahedra in $Cs_3Al_2F_9$ and Cs_2AlF_5

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The structure of Cs_2AlF_5 obtained by thermal dehydration of $Cs_2AlF_5•H_2O$ is determined *ab initio* from powder diffraction data, space group $Pmn2_1$, $a = 6.36216$ (17) Å, $b = 12.7523$ (4) Å, $c = 11.4102$ (3) Å, and $Z = 6$. Contrarily to most A_2MF_5 compounds presenting MF_5 *cis* or *trans*-chains of corner-sharing MF_6 octahedra, Cs_2AlF_5 is characterized by the rare occurrence of the face-sharing anion $Al_2F_9^{3-}$ combined with an isolated AlF_6^{3-} octahedron, the sum leading to $Al_3F_{15}^{6-}$. The structure of $Cs_3Al_2F_9$ [space group $P6_3/mmc$, $a = 6.2535$ (2) Å, $c = 14.7193$ (6) Å, $Z = 2$] is confirmed to be isostructural with $Cs_3Fe_2F_9$, built up from the same $M_2F_9^{3-}$ dimers (M = Fe, Al). Both crystal structures are optimized by energy minimization density funtional theory (DFT) in the solid state using a hybrid PBE0 functional, and their relations with the hexagonal perovskites and elpasolites are discussed. © *2015 International Centre for Diffraction Data*. [doi:10.1017/S0885715614001444]

Key words: cesium aluminium fluoride, powder diffraction, crystal structure, *ab initio*, DFT

I. INTRODUCTION

In the AlF_3–CsF system, only one phase has been characterized by a single-crystal structure determination, that of hexagonal ($P\bar{6}2m$, $Z = 3$) α-$CsAlF_4$ (Lösch and Hebecker, 1979), isostructural to $CsCrF_4$ (Babel and Knoke, 1978). The structure is built up from condensed infinite triple chains of corner-sharing AlF_6 octahedra leading to the $(Al_3F_{12})_n^{3n-}$ formula. Two other $CsAlF_4$ phases (named β and γ) were characterized later (Bentrup *et al.*, 1992) by a structure determination by powder diffractometry (SDPD), being products of the dehydration of $Cs[AlF_4(H_2O)_2]$ under different conditions. The γ-$CsAlF_4$ phase (orthorhombic, $Pnma$, $Z = 12$), built up from condensed chains of corner-sharing AlF_6 octahedra, is formed at 150°C from the above hydrate at atmospheric pressure and under inert atmosphere. The β-$CsAlF_4$ phase (tetragonal, $I\bar{4}c2$, $Z = 20$), isostructural with β-$RbAlF_4$ (Fourquet *et al.*, 1980), built up from the disconnected tetragonal-tunsten-bronze-like layers, is formed at 200°C at atmospheric pressure and under inert atmosphere from an amorphous $CsAlF_4$ form obtained also from the hydrate, but at 150°C under vacuum. The following irreversible transitions were established at atmospheric pressure: $\beta \rightarrow \gamma$ at 344°C under anhydrous and inert atmosphere, whereas $\beta \rightarrow \alpha$ at 350°C with traces of water. It was thus believed that the γ-form was the stable one, obtained in strictly anhydrous conditions of synthesis, the β-form being metastable and the α-form favoured by a synthesis in presence of water traces. A reversible reaction γ-$CsAlF_4 \leftrightarrow Cs_3Al_2F_9 + AlF_3$ was observed at 442°C, and this $Cs_3Al_2F_9$ was claimed to be isostructural with $Cs_3Fe_2F_9$ (Dance *et al.*, 1986), so that it should contain the face-sharing fluoroaluminate anion $Al_2F_9^{3-}$. However, neither *ab initio* structure solution nor a structure refinement was presented.

During a more recent study of the phase diagram of the AlF_3–CsF system (Chen *et al.*, 1997), the existence of β-, γ-$CsAlF_4$, and $Cs_3Al_2F_9$ were not confirmed. If β-$CsAlF_4$ may not appear in that diagram, as explained above, the two others should (Figure 1). In that study, the method of synthesis is questionable since the samples were not prepared in the solid state by direct mixing of the adequate proportions of AlF_3 and CsF, but "*25 samples* (were prepared) *by reacting mixtures of anhydrous AlF_3 with solutions of CsF in HF*". These samples were furthered heated until dry at 200°C, and then annealed for 48 h at higher temperatures (between 400 and 600°C depending on the composition). The problem here is that reactions may take place in solution at the beginning (i.e. formation of definite compounds in the solution, even at ambient or warm temperatures), so that the final compositions will be eventually different from the initial ones. A strong argument in this sense is the fact that the proposed "$CsF–2AlF_3$" compound ($CsAl_2F_7$) is found to have a hexagonal cell ($a = 9.455$ Å, $c = 3.703$ Å) identical to that of α-$CsAlF_4$. Indexation of the powder patterns was proposed, but structure solutions were not presented for any of the claimed four compounds Cs_3AlF_6, $CsAlF_4$ (α- and β-forms), Cs_2AlF_7, and $CsAl_3F_{10}$. The form α-$CsAlF_4$ was proposed to have a reversible transition to a β-form at 422°C, this later form (indexed in orthorhombic symmetry from only 12 reflexion positions) being obviously different from the β-$CsAlF_4$ listed in the paper of Bentrup *et al.* (1992); so let us call it β'.

Existence of Cs_2AlF_5, another compound of the Cs–Al–F family with yet unknown crystal structure, was for the first time mentioned by Bentrup (1991), who claimed to have prepared it by dehydration of $Cs_2[AlF_5(H_2O)]$ at 171°C. Symmetry of the cell was proposed to be orthorhombic, space group not determined, and it was concluded that "*merely*

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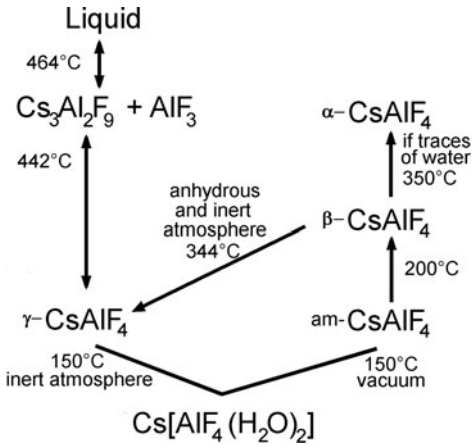


Figure 1. Origin of $Cs_3Al_2F_9$, β-, and γ-$CsAlF_4$. If β-$CsAlF_4$ may not appear in the solid-state AlF_3–CsF system, the two others should.

the chain type of Cs_2AlF_5 has not been determined up to now." If assuming isostructurality with orthorhombic Rb_2FeF_5 (Dance *et al.*, 1980), the structure would be built of corner-sharing $(AlF_6)^{3-}$ octahedra.

This study provides a resolution of aluminium coordination ambiguity in the structures of $Cs_3Al_2F_9$ and Cs_2AlF_5. As these compounds do not form single crystal of reasonable size for X-ray diffraction, their structures were solved from laboratory powder diffraction data, refined by Rietveld (1969) method and finished by energy minimization in the solid state (see, e.g., Le Bail and Smrčok, 2011; Oszajca *et al.*, 2013; Smrčok *et al.*, 2013).

II. EXPERIMENTAL

A. Synthesis of Cs_2AlF_5

A sample of Cs_2AlF_5 was prepared according to the Bentrup (1991) process. It was maintained at 280°C for several days in order to improve its originally poor crystallinity and then used for data collection. Cs_2AlF_5 decomposes into a mixture of $CsAl_3F_{10}$ as defined by Chen *et al.* (1997) and an unknown at 300°C, for which a rhombohedral cell was proposed (see the supplementary material).

B. Synthesis of $Cs_3Al_2F_9$

According to the reversible reaction γ-$CsAlF_4 \leftrightarrow Cs_3Al_2F_9 + AlF_3$ (at 442°C) (Bentrup *et al.*, 1992), a sample was quenched at 460°C (a platinum tube quickly dropped in cold water). The presence of AlF_3 is hence unavoidable and it was also not possible to completely exclude the presence of γ-$CsAlF_4$ back reaction product.

III. RESULTS

A. Crystal structure determination and Rietveld refinement of Cs_2AlF_5 and $Cs_3Al_2F_9$

Indexing of the powder pattern of Cs_2AlF_5 was realized using the *McMaille* software (Le Bail, 2004) leading to a primitive orthorhombic cell. The figures of merit (FoMs) were $M_{20} = 35.7$ (de Wolff, 1968), $F_{20} = 54.6$ (0.0099, 37) (Smith and Snyder, 1979), and $McM_{20} = 132.5$ (Le Bail, 2008). The space-group determination was ambiguous, obscured by peak overlapping for three reasons: (i) the fortuitous fact that $b \sim 2a$; (ii) the pseudo-hexagonal cell consequence of $c \sim a\sqrt{3}$ (Table I); and (iii) the broadened peak shapes because of the still poor crystallinity, in spite of the long heating at 280°C. The structure solution was carried out in direct space using the *ESPOIR* software (Le Bail, 2001), moving in the cell the appropriate number of Cs, Al, and F atoms by a Monte Carlo process. Calculations were performed in a quite long series (>20) of centric or acentric space groups selected because they were all leading to similarly satisfying Le Bail fits (Le Bail, 2005). A partial starting model was finally recognized (octahedra making sense) in the $Pmn2_1$ space group and the structure could be completed by alternating Rietveld refinements using the *FULLPROF* software (Rodriguez-Carvajal, 1993) and Fourier difference synthesis calculated using *SHELX* (Sheldrick, 2008). The main impurity (traces of the higher temperature rhombohedral phase cited above) was treated by the Le Bail method. A series of weak peaks appeared to correspond well to the $Cs_3Al_2F_9$ powder pattern, so that this contribution was modelled with the fixed atomic coordinates (Figure 2). No missing symmetry was found using the *PLATON* software (Spek, 2009) and acentricity of the structure was confirmed.

For $Cs_3Al_2F_9$, the Rietveld refinement was readily managed by starting from the $Cs_3Fe_2F_9$ atomic coordinates

TABLE I. Experimental and Rietveld refinement details for Cs_2AlF_5 and $Cs_3Al_2F_9$.

Diffractometer	Siemens D500	
Geometry	Bragg–Brentano	
Goniometer	Vertical	
Radiation type	Cu $K\alpha$	
Wavelengths (Å)	1.54056, 1.54433	
Monochromator	Graphite	
Temperature (°C)	22	
Chemical formula	Cs_2AlF_5	$Cs_3Al_2F_9$
Pattern refinement range (°2θ)	5–138.5	10–130
Step size (°2θ)	0.02	0.04
Space group	$Pmn2_1$	$P6_3/mmc$
Z	6	2
Cell parameter (Å, °)		
a	6.36216 (17)	6.2535 (2)
b	12.7523 (4)	
c	11.4102 (3)	14.7193 (6)
Volume (Å^3)	925.74 (5)	498.50(3)
No. of contributing reflections	996	199
No. of refined parameters (total)	93	61
No. of atomic coordinates parameters	41	5
No. of restraints	25	None
No. of thermal parameters	3	6
No. of background parameters (interpolated from a set of points)	37	32
Profile shape	Pseudo-Voigt	
η	1.34 (4)	0.70 (4)
U	0.22 (1)	0.056 (5)
V	−0.15 (1)	−0.057 (6)
W	0.052 (2)	0.033 (2)
Conventional Rietveld reliability factors	(Rietveld, 1969)	
R_P (%)	10.4	16.3
R_{WP} (%)	11.7	19.3
R_{exp} (%)	4.56	6.11
R_B (%)	3.95	6.10
R_F (%)	2.30	5.59

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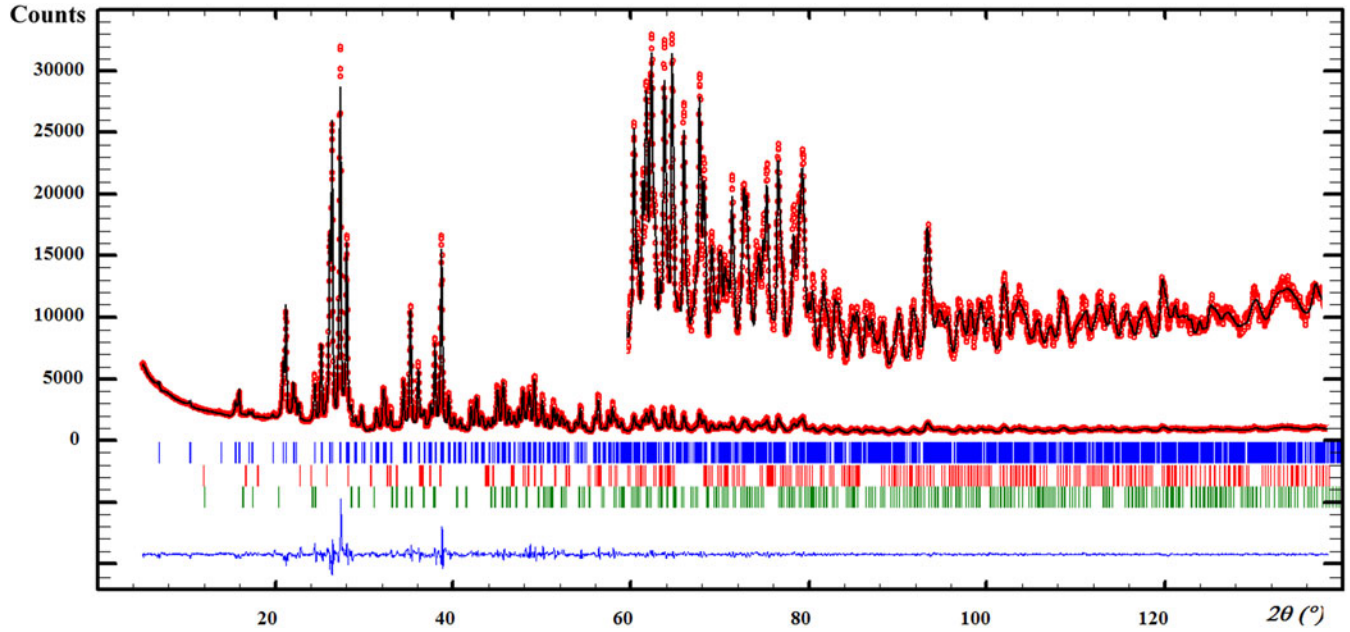


Figure 2. (Color online) Refined diffraction pattern from the laboratory data (Cu$K\alpha$) for Cs_2AlF_5 at 22°C. Red dots represent the observed data, and the black line represents the calculated ones. Bragg ticks are the peak positions (three sets from up to down: 97% Cs_2AlF_5, rhombohedral high-temperature form – Le Bail fit, thus not taken into account for the percentages estimations – and $Cs_3Al_2F_9 < 3\%$) and the blue curve shows the difference between the observed and calculated patterns.

(Dance *et al.*, 1986) and by adding the AlF_3 and γ-$CaAlF_4$ impurities with their atomic coordinates fixed. The contribution of a very small quantity of the cubic Cs_3AlF_6 (Chen *et al.*, 1997) was finally concluded and added through a Le Bail fit (Figure 3).

Atom numbering in AlF_6 octahedra is shown in Figure 4, for both structures. Rietveld refinement details and selected geometric parameters are shown in Tables I and II, respectively, and the X-ray diffraction data are in Tables III and IV. For the atomic coordinates and more geometric parameters, see the supplementary material including the CIF files.

B. Solid-state DFT structure optimization

As the accuracy of the resulting atomic coordinates is in both structures influenced by the presence of the heavy

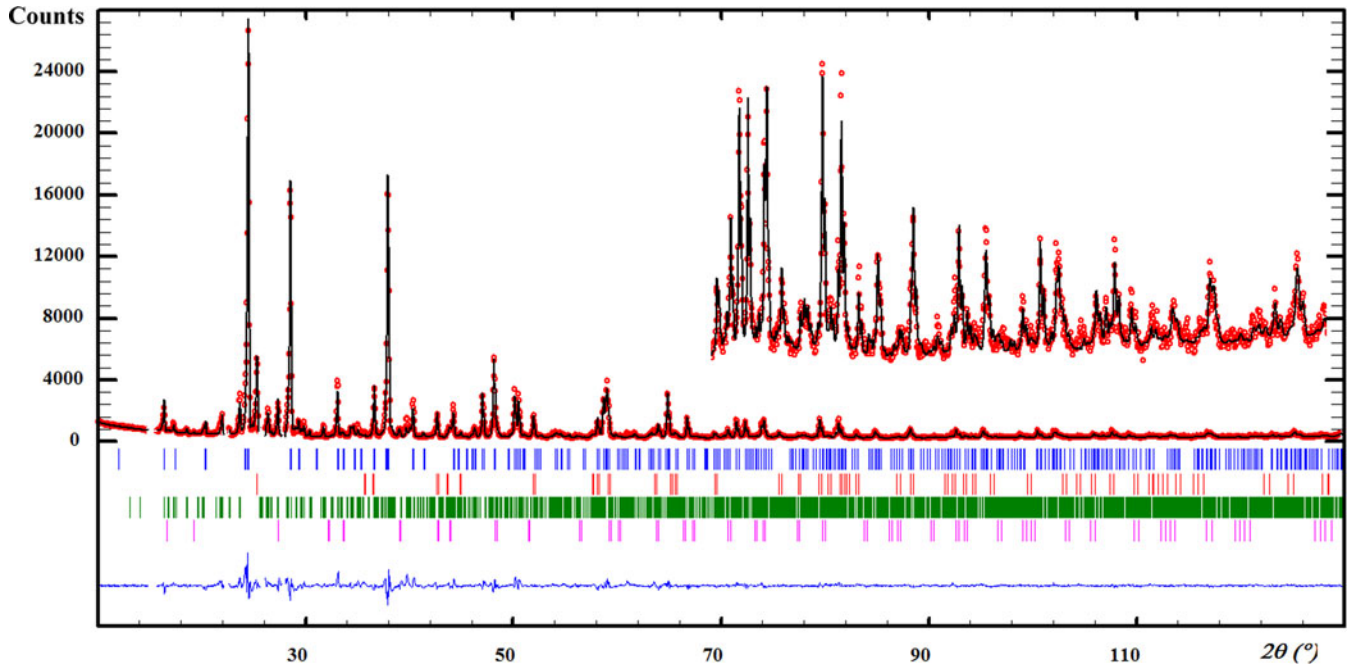


Figure 3. (Color online) Refined diffraction pattern from laboratory data (Cu$K\alpha$) for $Cs_3Al_2F_9$ at 22°C. Red dots represent the observed data, the black line represents the calculated ones. Bragg ticks are the peak positions (four sets from up to down: 61% $Cs_3Al_2F_9$, 25% rhombohedral AlF_3, 14% γ-$CsAlF_4$, and cubic Cs_3AlF_6 – Le Bail fit, thus not taken into account for the percentages estimations) and the blue curve shows the difference between the observed and calculated patterns.

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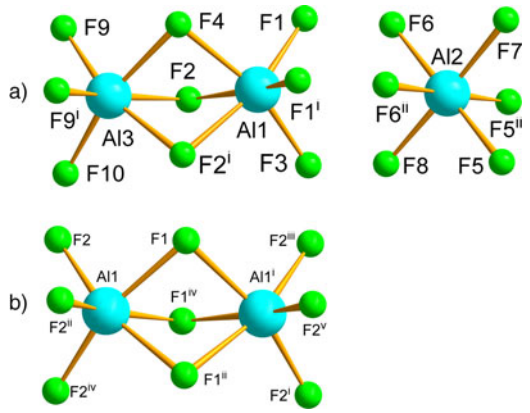


Figure 4. (Color online) Atom numbering in Al–F polyhedra. (a) Cs_2AlF_5, (b) $Cs_3Al_2F_9$. Symmetry codes for Cs_3AlF_9: (*i*) $-y, -x, -z+1/2$; (*ii*) $-y, x-y, z$; (*iii*) $x, x-y, -z+1/2$; (*iv*) $-x+y, -x, z$; (*v*) $-x+y, y, -z+1/2$; Cs_2AlF_5: (*i*) $1-x, y, z$; (*ii*) $-x, y, z$.

Cs atom and by poor ratios of the number of refined parameters to the number of structure factors, the structures were further optimized by energy minimization in the solid state, whose accuracy is comparable with that of single-crystal refinements. All the solid-state calculations were performed using the *VASP* code (Kresse and Hafner 1993; Kresse and Furthmüller 1996a, b). To optimize the structures, a hybrid PBE0 functional (Perdew *et al.*, 1996) was used. Plane waves formed a basis set and the calculations were performed using the projector-augmented wave method (Blöchl, 1994; Kresse and Joubert, 1999) and atomic pseudo-potentials (Kresse and Hafner, 1994). The energy cutoff controlling the accuracy of structure optimization calculations was in both cases set to 700 eV and the Brillouin zones were sampled in four *k*-points. The positions of all 48 (Cs_2AlF_5) and 28 ($Cs_3Al_2F_9$) atoms in the computational *P*1 cells were fully relaxed (i.e. without having imposed any restriction) while keeping the lattice parameters of the respective cells fixed at the values obtained from the diffraction data. Geometrical analysis of the optimized structures done by means of the *PLATON* program (Spek, 2009) showed that the originally proposed space groups were correct.

Prior to optimization of the structures of the title compounds the accuracy of the DFT method was assessed by comparing an accurately experimentally determined crystal structure with that obtained by the solid-state theoretical approach. For this purpose a compound with similar chemical and structural compositions, α-$CsAlF_4$ (Lösch and Hebecker 1979) was chosen. Its crystal structure solved from single-crystal data consists of triangle chains of interlinked AlF_6 octahedra alternating with isolated Cs cations.

IV. DISCUSSION

A. Assessing accuracy

From comparison of the experimentally determined and the theoretically calculated geometry of the moieties in α-$CsAlF_4$ it is seen (Table CAL, supplementary material) that the optimized solid-state calculation provides excellent agreement for the Al–F2 and Al–F3 bond distances and slightly overestimate the Al–F1 bond length, but all these differences are smaller than 2σ. Similarly, Cs–F bond and F···F contact distances are very close to the experimental values.

B. Crystal structures of Cs_2AlF_5 and $Cs_3Al_2F_9$

The DFT-optimized geometry of face-sharing fluoroaluminate anion $Al_2F_9^{3-}$ anion is in both structures in very good agreement with the experimentally determined geometry

TABLE II. Selected interatomic and contact distances (Å) for Cs_2AlF_5 and $Cs_3Al_2F_9$.

	Cs_2AlF_5				
Al1–F1 × 2	1.720 (13)	Al2–F5 × 2	1.784 (15)	Al3–F2 × 2	1.903 (11)
	1.741		*1.82*		*1.92*
Al1–F2 × 2	1.885 (11)	Al2–F6 × 2	1.811 (15)	Al3–F9 × 2	1.722 (13)
	1.925		*1.823*		*1.745*
Al1–F3	1.744 (14)	Al2–F7	1.791 (18)	Al3–F4	1.887 (12)
	1.745		*1.829*		*1.925*
Al1–F4	1.911 (12)	Al2–F8	1.785 (17)	Al3–F10	1.736 (14)
	1.919		*1.809*		*1.749*
Al1···Al3	2.57 (1)	Cs1···F (12×)	<3.06, 3.49>	Cs2···F (7×) (8×)	<2.83, 3.45>
	2.709		*<3., 3.33 >*		*<2.88, 3.4 >*
		Cs3···F (10×)	<2.97, 3.32>	Cs4···F (8×) (7×)	<2.85, 3.46>
			<2.97, 3.28 >		*< 2.79, 3.19>*
		Cs5···F (9×)	<2.85, 3.41>	Cs6···F (12×)	<2.79, 3.38>
			< 3.06, 3.43>		*< 2.87, 3.42>*
				F···F	<2.33, 2.7>
					< 2.36, 2.67>
	$Cs_3Al_2F_9$				
Al–F1 × 3	1.962 (18)	Cs1···F (12×)	<3.14, 3.17>	F···F	<2.64, 2.71>
	1.927		*<3.03, 3.16 >*		*< 2.36, 2.65>*
Al–F2 × 3	1.79 0 (19)	Cs2···F (12×)	<3.16, 3.34>		
	1.744		*<3.19, 3.54 >*		
Al1···Al1^{i}	2.49 (4)				
	2.727				

DFT-optimized values are in italics. Note that only the Cs···F contact distances <3.5 Å are considered.
(*i*) $-y, -x, -z+1/2$.

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TABLE III. X-ray diffraction data for Cs_2AlF_5 at 22°C (Cu$K\alpha1$).

$2\theta_{obs}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{cal}$	d_{cal}	I_{cal}	$\Delta 2\theta$
6.893	12.8128	0.7	0	1	0	6.926	12.7523	2.4	−0.033
10.410	8.4910	0.5	0	1	1	10.395	8.5033	2.0	0.015
13.870	6.3796	0.3	0	2	0	13.877	6.3762	0.2	−0.007
15.557	5.6912	3.5	0	0	2	15.519	5.7051	2.7	0.038
			1	1	0	15.552	5.6930	2.0	0.005
15.926	5.5604	6.2	0	2	1	15.909	5.5661	1.8	0.017
			1	0	1	15.936	5.5567	7.3	−0.010
17.030	5.2023	1.4	0	1	2	17.012	5.2077	1.8	0.018
17.410	5.0896	1.5	1	1	1	17.394	5.0941	1.8	0.016
20.905	4.2458	15.0	0	2	2	20.876	4.2516	13.7	0.029
21.199	4.1876	28.6	1	2	1	21.191	4.1892	34.9	0.008
22.043	4.0291	9.9	1	1	2	22.039	4.0298	10.3	0.004
22.302	3.9830	5.9	0	3	1	22.300	3.9833	6.3	0.002
24.427	3.6410	13.0	0	1	3	24.402	3.6447	5.3	0.025
25.172	3.5349	20.9	1	2	2	25.172	3.5350	18.9	0.000
			1	3	0	25.175	3.5345	4.5	−0.003
26.138	3.4064	50.6	0	3	2	26.121	3.4087	45.3	0.017
26.379	3.3758	79.2	1	3	1	26.376	3.3762	89.5	0.003
27.296	3.2645	100.0	0	2	3	27.280	3.2664	4.5	0.016
			1	0	3	27.296	3.2645	95.5	0.000
28.032	3.1804	50.2	2	0	0	28.026	3.1811	50.1	0.006
29.059	3.0703	2.7	0	4	1	29.058	3.0705	2.6	0.001
29.705	3.0050	5.8	1	3	2	29.709	3.0046	6.9	−0.004
31.380	2.8484	5.4	0	0	4	31.332	2.8526	1.1	0.048
			1	4	0	31.358	2.8502	4.2	0.022
			2	2	0	31.401	2.8465	0.4	−0.021
31.549	2.8334	3.0	0	3	3	31.538	2.8433	3.0	0.011
32.163	2.7807	10.9	0	1	4	32.127	2.7838	5.0	0.036
			0	4	2	32.136	2.7830	2.0	0.027
			2	0	2	32.191	2.7784	4.3	−0.028
32.331	2.7667	8.2	1	4	1	32.348	2.7653	5.1	−0.017
			2	2	1	32.389	2.7619	2.5	−0.058
32.971	2.7144	6.0	2	1	2	32.968	2.7147	4.9	0.003
34.417	2.6036	13.1	0	2	4	34.414	2.6030	14.0	0.003
35.198	2.5476	32.4	0	5	0	35.157	2.5505	9.0	0.041
			1	1	4	35.159	2.5503	2.2	0.039
			1	4	2	35.168	2.5497	2.5	0.030
			2	2	2	35.206	2.5471	21.0	−0.008
			2	3	0	35.209	2.5469	1.8	−0.011
36.075	2.4877	17.70	0	5	1	36.054	2.4890	9.6	0.021
			2	3	1	36.104	2.4857	6.7	−0.029
36.764	2.4426	4.9	0	4	3	36.754	2.4433	4.4	0.010
37.269	2.4107	2.9	1	2	4	37.282	2.4098	1.1	−0.013
37.503	2.3962	6.9	2	1	3	37.495	2.3966	6.3	0.008
37.935	2.3699	24.1	0	3	4	37.955	2.3687	19.9	−0.020
38.694	2.3251	51.0	2	3	2	38.684	2.3257	50.9	0.010
39.511	2.2789	9.8	2	2	3	39.510	2.2789	9.2	0.001
40.106	2.2464	4.0	0	1	5	40.107	2.2464	3.7	0.001
40.823	2.2086	2.7	2	4	1	40.811	2.2092	3.0	0.012
41.275	2.1855	0.7	1	5	2	41.254	2.1866	1.3	0.011
42.012	2.1488	7.4	0	2	5	42.017	2.1486	6.6	−0.005
42.660	2.1177	8.7	0	5	3	42.647	2.1183	1.9	0.013
			1	1	5	42.649	2.1182	2.5	0.011
			2	2	3	42.690	2.1162	4.3	−0.030
43.172	2.0937	4.5	2	1	4	43.147	2.0949	3.0	0.025
43.349	2.0856	3.3	3	0	1	43.362	2.0850	2.0	−0.013
43.964	2.0579	2.8	3	1	1	43.967	2.0577	2.1	−0.003
44.474	2.0354	2.9	1	2	5	44.469	2.0356	3.5	0.005
44.965	2.0143	11.8	1	4	4	44.920	2.0162	3.2	0.045
			1	6	0	44.929	2.0159	1.7	0.036
			2	2	4	44.951	2.0149	4.8	0.014
			0	3	5	45.052	2.0106	2.6	−0.087
			1	5	3	45.071	2.0098	3.4	−0.106
45.529	1.9907	9.9	0	6	2	45.505	1.9917	5.7	0.024
			2	5	0	45.549	1.9899	1.8	−0.020
45.687	1.9842	12.8	1	6	1	45.663	1.9851	8.8	0.024

Continued

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TABLE III. Continued

$2\theta_{obs}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{cal}$	d_{cal}	I_{cal}	$\Delta 2\theta$
			3	2	1	45.746	1.9817	3.9	−0.059
46.279	1.9601	5.9	2	5	1	46.276	1.9603	5.2	0.003
46.856	1.9374	4.4	2	4	3	46.847	1.9377	3.6	0.009
47.381	1.9171	5.9	1	3	5	47.379	1.9172	6.1	0.002
47.840	1.8998	11.0	0	0	6	47.788	1.9017	3.1	0.052
			0	5	4	47.799	1.9013	0.9	0.041
			2	3	4	47.838	1.8998	5.3	0.002
			3	2	2	47.894	1.8977	2.2	−0.054
48.429	1.8780	7.8	2	5	2	48.406	1.8789	3.5	0.023
48.609	1.8715	11.5	3	3	1	48.596	1.8719	10.0	0.013
49.147	1.8522	14.5	3	0	3	49.147	1.8522	13.1	0.000
49.653	1.8346	3.5	2	1	5	49.641	1.8350	2.5	0.012

in $[C_{18}Mim]_3[Al_2F_9](CH_2Cl_2)_{1.754}$ ($C_{18}MIm^+$ = 1-methyl-3-octadecylimidazolium cation) and also with molecular MP2/aug-cc-pVTZ calculations (Xu *et al.*, 2013). As the ionic radii of Al^{3+} and Fe^{3+} are close, the optimized bond angles in the anion are in both structures also close to those in $Fe_2F_9^{3-}$ in $Cs_3Fe_2F_9$ (Dance *et al.*, 1986). Calculated geometry of the isolated AlF_6 octahedron in the structure of Cs_2AlF_5 is well-comparable with that of analogous octahedron in the structure of a hybrid fluoride solved from the X-ray single-crystal data (Adil *et al.*, 2004). The Al–Al separations in

TABLE IV. X-ray diffraction data for $Cs_3Al_2F_9$ at 22°C (Cu$K\alpha$1).

$2\theta_{obs}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{cal}$	d_{cal}	I_{cal}	$\Delta 2\theta$
11.985	7.3783	0.2	0	0	2	12.015	7.3596	0.2	−0.030
16.362	5.4130	6.0	1	0	0	16.354	5.4157	6.3	0.008
20.356	4.3591	2.3	1	0	2	20.342	4.3620	3.2	0.014
24.461	3.6361	100.0	1	0	3	24.461	3.6361	100.0	0.000
28.511	3.1281	65.2	1	1	0	28.523	3.1267	60.1	−0.012
29.323	3.0433	3.8	1	0	4	29.319	3.0437	3.6	0.004
33.044	2.7086	14.9	2	0	0	33.053	2.7078	11.4	−0.009
36.613	2.4523	14.0	0	0	6	36.599	2.4532	13.5	0.014
37.921	2.3707	70.1	2	0	3	37.920	2.3707	68.8	0.001
40.313	2.2354	10.3	1	0	6	40.327	2.2346	7.9	−0.014
44.201	2.0474	9.4	2	1	0	44.210	2.0469	6.5	−0.009
46.274	1.9603	3.0	1	0	7	46.278	1.9602	1.7	−0.004
47.058	1.9295	12.3	1	1	6	47.043	1.9301	12.0	0.015
48.139	1.8887	23.7	2	1	3	48.126	1.8891	21.0	0.013
50.131	1.8182	14.3	2	0	6	50.135	1.8181	11.4	−0.004
50.518	1.8052	13.7	3	0	0	50.516	1.8052	9.6	0.002
54.069	1.6947	1.6	3	0	3	54.086	1.6942	0.9	−0.017
54.527	1.6815	1.4	2	1	5	54.560	1.6806	1.0	−0.033
55.289	1.6601	0.8	2	0	7	55.265	1.6608	0.5	0.024
58.699	1.5716	11.5	2	1	6	58.694	1.5717	10.9	0.005
59.011	1.5640	16.5	1	0	9	58.943	1.5656	5.0	0.068
			2	2	0	59.037	1.5634	10.3	−0.026
61.698	1.5022	1.4	3	1	0	61.704	1.5020	1.0	−0.006
63.321	1.4675	1.7	2	1	7	63.359	1.4667	1.2	−0.038
63.952	1.4546	3.6	3	0	6	63.980	1.4540	3.6	−0.028
64.839	1.4368	13.8	3	1	3	64.866	1.4362	13.1	−0.027
66.741	1.4004	6.0	2	0	9	66.764	1.3999	6.1	−0.023
69.347	1.3540	1.3	4	0	0	69.351	1.3539	0.7	−0.004
70.652	1.3321	2.7	1	1	10	70.676	1.3317	1.3	−0.024
71.485	1.3186	5.5	2	2	6	71.500	1.3184	5.0	−0.015
72.320	1.3055	4.9	4	0	3	72.341	1.3051	4.9	−0.021
73.452	1.2881	0.7	3	0	8	73.422	1.2886	0.6	0.030
73.920	1.2811	4.3	3	1	6	73.928	1.2810	3.3	−0.008
74.145	1.2778	3.8	2	1	9	74.149	1.2778	3.6	−0.004
79.480	1.2049	6.3	3	2	3	79.515	1.2044	5.9	−0.035
81.032	1.1857	2.4	4	0	6	81.056	1.1854	1.8	−0.024
81.322	1.1822	5.5	4	1	0	81.353	1.1818	4.7	−0.031
84.864	1.1416	2.0	1	1	12	84.841	1.1419	2.0	0.023
88.046	1.1084	1.5	3	2	6	88.046	1.1084	1.0	0.000
			1	0	13	88.057	1.1083	0.5	−0.011
88.234	1.1065	2.6	3	1	9	88.259	1.1063	3.1	−0.025

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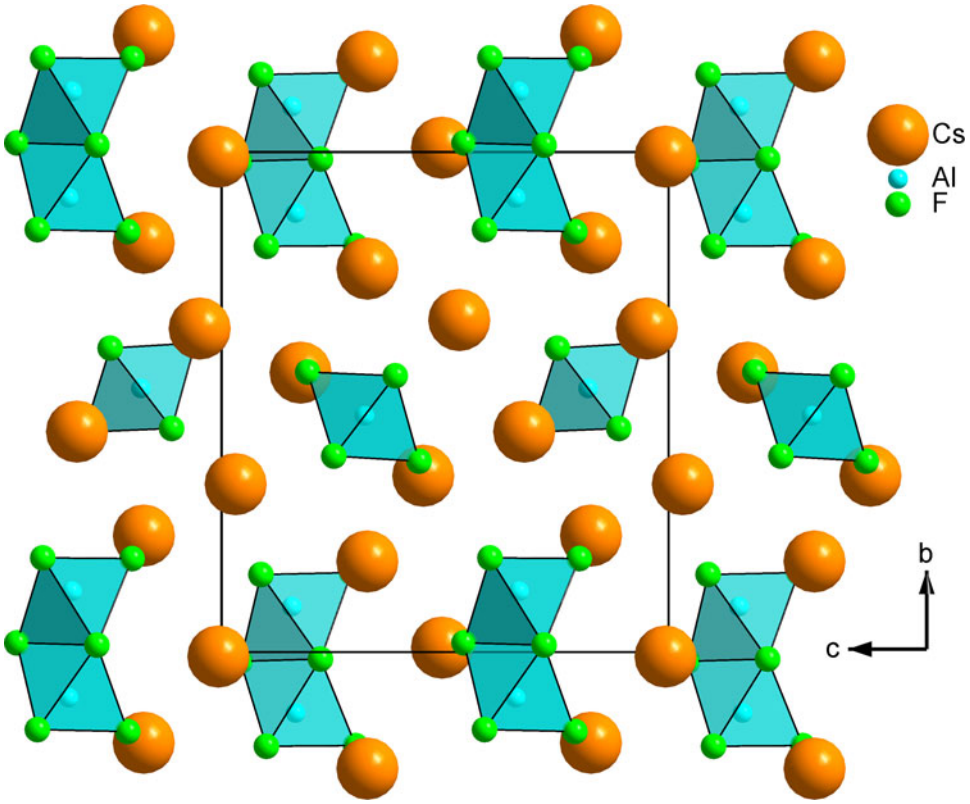


Figure 5. (Color online) Projection along the short *a*-axis of the structure of Cs_2AlF_5 showing the isolated AlF_6 octahedra and the face-sharing octahedra dimers $Al_2F_9^{3-}$.

Cs_2AlF_5 (2.709 Å) and $Cs_3Al_2F_9$ (2.727 Å) are in line with the Al–Al distance [2.687 (2) Å] in the structure by Xu *et al.* (2013).

Most A_2MF_5 crystal structures (A = K, Rb, NH_4; M = Fe, Cr, V, Ga) are characterized structurally by the presence of MF_5 octahedral chains, either *cis*- or *trans*-linked. There are four forms for K_2FeF_5 (Le Bail, 2013), two for $(NH_4)_2FeF_5$ (Fourquet *et al.*, 1989) showing a total of six different known ways of organizing such octahedral chains. It was thus a surprise to disclose the presence of the $Al_2F_9^{3-}$ anion in Cs_2AlF_5 (Figure 5), this anion presence being confirmed in $Cs_3Al_2F_9$, increasing to three the number of established crystal structures containing it. Indeed, face sharing is not rare for $M \neq$ Al since it occurs in all hexagonal perovskites AMF_3 and elpasolites A_2BMF_6 (Massa and Babel, 1988). This is especially frequent with A = Cs, and for instance, $CsNiF_3$ is representative of the so-called 2L stacking type, 6L is observed for $CsMnF_3$, 9L for the high-pressure form of $CsNiF_3$ (etc.). Their hexagonal cell parameters have a in common ($5.8 < a < 6.4$ Å), c being the variable depending on the stacking sequence. $Cs_3Fe_2F_9$ was described (Dance *et al.*, 1986) as a member of the series, being a cation-deficient variant of the $CsNiF_3$ structure characterized by infinite chains of NiF_6 face-sharing octahedra (Figure 6). The Cs_2AlF_5 structure projection onto the (*ac*)-plane allows us to conclude that it belongs to the same family as these hexagonal series when the relation $c \sim a\sqrt{3}$ with a = 6.36216 (17) Å, c = 11.4102 (3) Å (~11.02) evidence the pseudo-hexagonal distribution of the Cs atoms and AlF_6 octahedra, making obvious the similarity with the $Cs_3Al_2F_9$ structure (Figure 7). Consequently, the Cs_2AlF_5 structure is orthorhombic pseudo-*B*-centred.

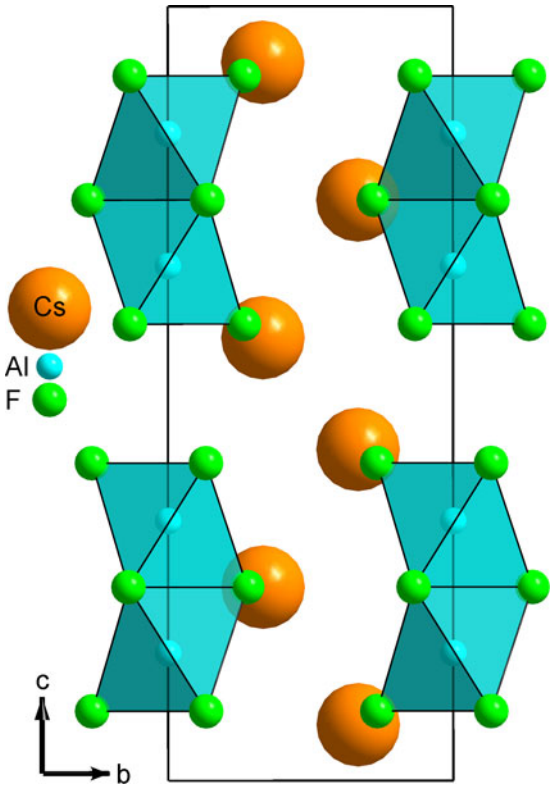


Figure 6. (Color online) Projection of the $Cs_3Al_2F_9$ structure along the *a*-axis, being a cation-deficient variant (1/3 lacking) of the $CsNiF_3$ structure in which infinite chains of face-sharing octahedra extend along the *c*-axis.

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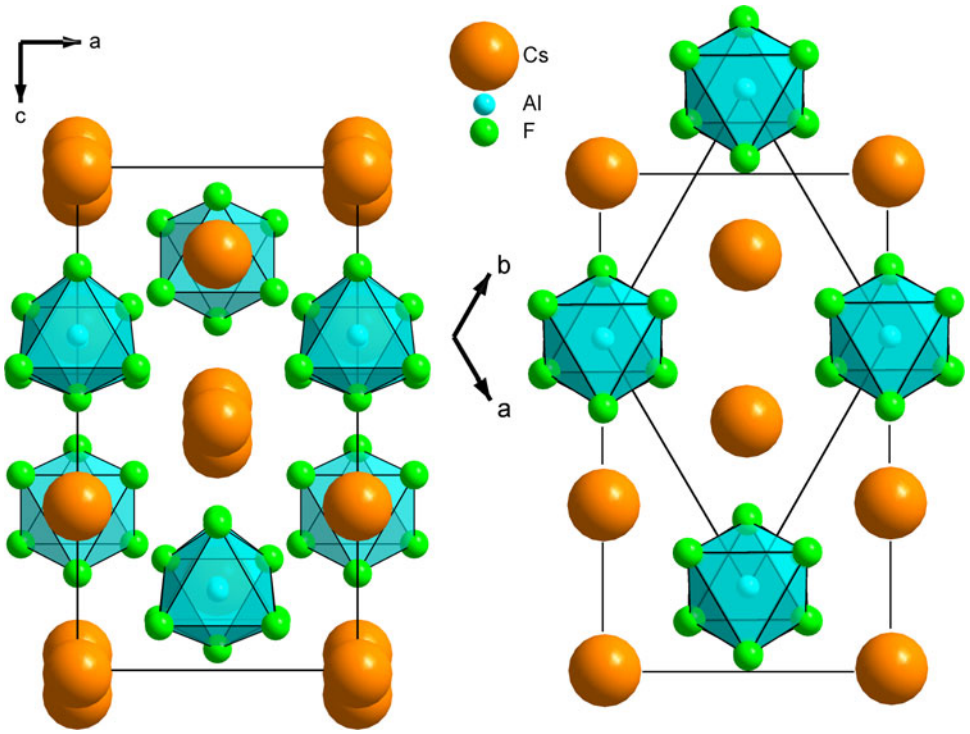


Figure 7. (Color online) Projection of the $Cs_3Al_2F_9$ structure along the hexagonal *c*-axis (right) compared with that of Cs_2AlF_5 along the *b*-axis (left), evidencing strong similarities. The face-sharing octahedra dimers and the Cs atoms are distributed in the same way in both the structures, and the isolated octahedra in Cs_2AlF_5 replace one of the Cs atoms at 1/3, 2/3, *z*-position in $Cs_3Al_2F_9$.

In $Cs_3Al_2F_9$, both Cs atom-sites are 12-coordinated in anti-cuboctahedra. In Cs_2AlF_5, Cs1, and Cs6 adopt the same coordination and polyhedron, distorted, but the other Cs atoms are differently coordinated: the $Cs2F_8$ polyhedron is a bicapped trigonal prism; the $Cs3F_{10}$ polyhedron is a half-cuboctahedron with a 10th fluorine atom caping the other side of the hexagonal face; the $Cs4F_8$ polyhedron is a pentagonal pyramid with two fluorine atoms caping the other side of the pentagonal face; $Cs5F_9$ is a half-cuboctahedron, which would become a complete cuboctahedron if Cs–F distances were considered up to 3.8 Å (Figure 8).

V. CONCLUSION

Five crystal structures have been now established in the AlF_3–CsF system, α-, β-, γ-$CsAlF_4$, Cs_2AlF_5, and $Cs_3Al_2F_9$ so far, although their existence during the synthesis in the solid state, in totally anhydrous conditions, is not established. Four of them were determined from the powder diffraction data, of which three were solved *ab initio* and one was refined isostructurally with its Fe analog. No MF_5 chain is observed in Cs_2AlF_5, which makes it an exception among the A_2MF_5 structure types. The Cs_3AlF_6, $CsAl_3F_{10}$, and the β'-$CsAlF_4$ (Chen *et al.*, 1997) crystal structures are still to be determined, as well as that of the thermal decomposition product of Cs_2AlF_5.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at http://www.journals.cambridge.org/PDJ

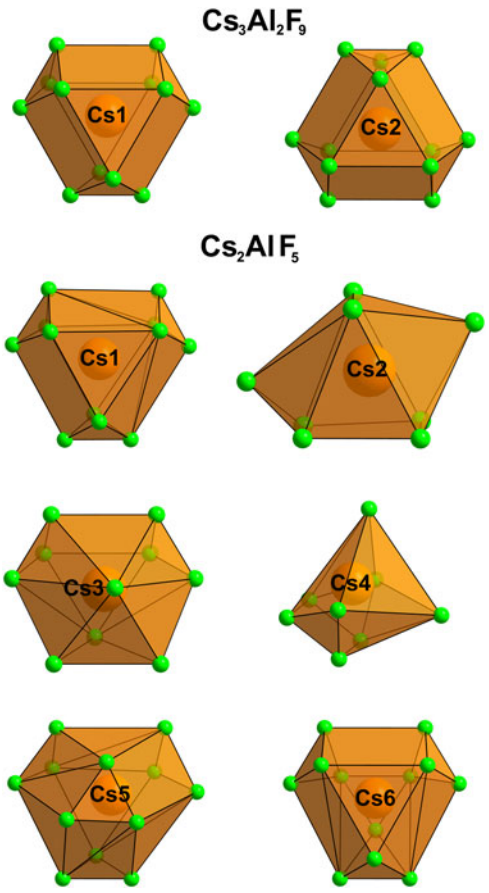


Figure 8. (Color online) Cesium atom coordination polyhedra in $Cs_3Al_2F_9$ and Cs_2AlF_5.

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