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Refinement of the Room-Temperature Structure of α-$CaAlF_5$

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Abstract. α-Calcium aluminium pentafluoride, M_r = 162·05, monoclinic, $C2/c$, a = 8·712 (3), b = 6·317 (2), c = 7·349 (3) Å, β = 115·04 (3)°, V = 366·4 (4) Å^3, Z = 4, D_x = 2·94 Mg m^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 1·90 mm^{-1}, $F(000)$ = 312, room temperature, R = 0·020 for 1201 unique reflections. The sample was prepared by the chloride flux method. α-$CaAlF_5$ is isotypic with $CaCrF_5$ and is characterized by linked chains of AlF_6 octahedra along the c axis between which Ca ions are inserted in pentagonal bipyramidal sites.

Experimental. Chloride flux was grown from a mixture of composition $NaF + CaF_2 + AlF_3 + 3{\cdot}3ZnCl_2 + CaCl_2$ in a platinum crucible, under an argon atmosphere, by heating to 998 K then cooling at 1 K h^{-1} to 973 K with air quenching. Needle-shaped crystals (0·02 × 0·002 × 0·0009 mm). Data collected on a Siemens AED2 four-circle diffractometer. ω–2θ step-scan mode in N steps of $\Delta\omega°$, $37 \le N \le 49$, $0{\cdot}025 \le \Delta\omega \le 0{\cdot}027°$; time per step 1–4 s. Profile fitting data analysis (Clegg, 1981); isotropic linewidth $\Gamma = (0{\cdot}89 - 0{\cdot}06\tan\theta)°$. Aperture D = 3·5 mm.

Lattice constants based on 26 reflections measured in double step-scan mode at $\pm(2\theta \approx 30°)$; absorption correction by the Gauss method, A_{max} = 0·96, A_{min} = 0·89. Intensity measurements to $2\theta \le 85°$ of one and a half independent sets of reflections within the range $-16 \le h \le 16$, $0 \le k \le 12$, $0 \le l \le 13$. Standard reflections ($\bar{3}13$, $\bar{3}31$, $33\bar{1}$) showed intensity variation of 1·0%. 1945 reflections measured, 1201 independent reflections used for refinements [$|F| > 6\sigma(|F|)$], R_{int} = 0·015.

Structure solved from atomic parameters of $CaCrF_5$ in space group $C2/c$ (Kun Wu & Brown, 1973). F magnitudes used in least-squares refinements, 36 parameters refined, maximum $|\Delta/\sigma| = 0{\cdot}002$, secondary-extinction factor $x = 1{\cdot}3 \times 10^{-6}$ [$F^* = F(1 - x10^{-4}F^2/\sin\theta)$], atomic scattering factors for Ca, Al and F from *International Tables for X-ray Crystallography* (1974, Vol. IV), calculations performed with the *SHELX*76 program (Sheldrick, 1976), all atoms refined anisotropically [R = 0·020, wR = 0·018, $w = 1/\sigma^2(F)$]. Maximum and minimum heights in final difference F map +0·6 and −0·75 e Å^{-3}. The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1 and some characteristic interatomic distances and selected angles are given in Table 2.*

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for* α-$CaAlF_5$ (*e.s.d.'s in parentheses*)

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

		x	y	z	B_{eq}
Ca^{2+}	4(*e*)	0	0·5424 (0)	¼	0·51 (1)
Al^{3+}	4(*a*)	0	0	0	0·42 (1)
F(1)	4(*e*)	0	0·9422 (1)	¼	0·87 (3)
F(2)	8(*f*)	0·0114 (1)	0·7169 (1)	0·9737 (1)	0·84 (2)
F(3)	8(*f*)	0·7789 (1)	0·9822 (1)	0·8870 (1)	1·26 (3)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* α-$CaAlF_5$ (*e.s.d.'s in parentheses*)

Al^{3+} octahedron			
2 × Al—F(1)	1·873 (1)	F(1)—F(2)	2·516 (1)
2 × Al—F(2)	1·806 (1)	F(1)—F(3)	2·558 (1)
2 × Al—F(3)	1·749 (1)	F(2)—F(3)	2·495 (1)
$\langle d_{Al-F}\rangle$ = 1·809		$d_{Shannon}$ = 1·820	
F(1)—Al—F(2)	86·3 (0)	F(2)—Al—F(3)	89·1 (0)
F(1)—Al—F(3)	89·8 (0)	Al—F(1)—Al	157·5 (0)
Ca^{2+} pentagonal bipyramid			
Ca—F(1)	2·525 (1)	2 × Ca—F(2)	2·293 (1)
2 × Ca—F(2)	2·349 (1)	2 × Ca—F(3)	2·207 (1)
$\langle d_{Ca-F}\rangle$ = 2·318		$d_{Shannon}$ = 2·345	

The structure (Fig. 1) is built from chains of AlF_6 octahedra sharing opposite corners and running in the [001] direction. The AlF_6 octahedra are distorted and the longest Al—F distances involve the shared F(1) atoms, the mean Al—F distance being very close to the sum of the ionic radii (Shannon, 1976) and to the Al—F distances observed in compounds with the *trans*-octahedra connection (Hemon & Courbion, 1990). Within these chains the Al—F(1)—

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53838 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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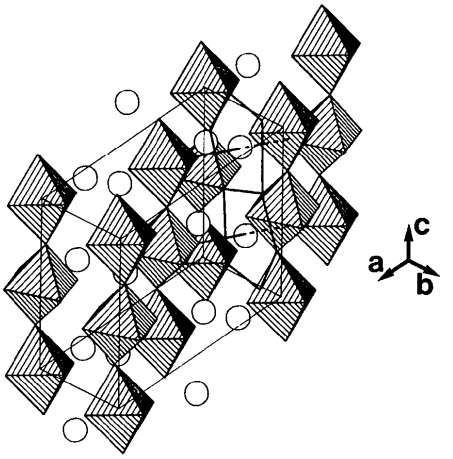

Fig. 1. Perspective view of chains of *trans*-linked AlF_6 octahedra and of CaF_7 polyhedra in α-$CaAlF_5$. Ca ions are represented as open circles.

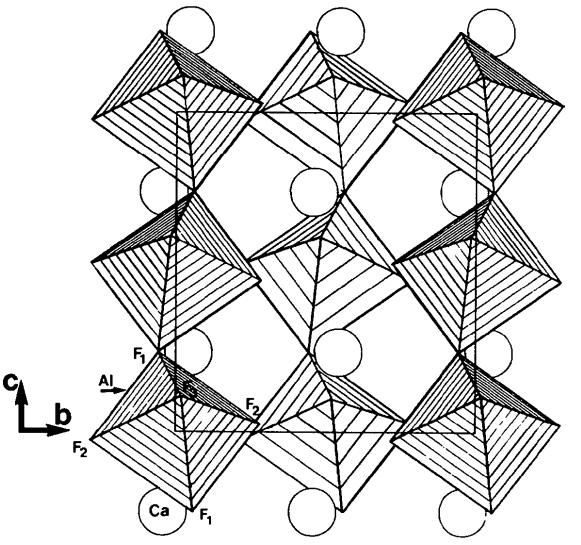

Fig. 2. (100) projection of α-$CaAlF_5$.

Al angle is bent to 157·5° (Fig. 2). Ca atoms exhibit a pentagonal bipyramidal coordination which is formed by edge-sharing chains of CaF_7 polyhedra running along [001] (Fig. 1).

As claimed many years ago, α-$CaAlF_5$ is isotypic with $CaCrF_5$. Our refinement confirms the results of Kun Wun & Brown (1973) [refinement of $CaCrF_5$ in $C2/c$ from the data given by Dumora, Von der Mühll & Ravez (1971) (non-centrosymmetric space group Cc) but with better agreement for the reliability factor.

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Structure of *catena*-Poly{bis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato-κ^2O,O']copper-μ-(4,4′-bipyridine)-$\kappa N:\kappa N'$}–*N*,*N*-dimethylformamide (1/2)

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Abstract. $[Cu(C_8H_4F_3O_2S)_2(C_{10}H_8N_2)].2C_3H_7NO$, $M_r = 808·25$, triclinic, $P\bar{1}$, $a = 9·637$ (2), $b = 9·820$ (2), $c = 11·505$ (2) Å, $\alpha = 73·40$ (1), $\beta = 65·41$ (1), $\gamma = 69·29$ (1)°, $V = 913·76$ (3) Å^3, $Z = 1$, $D_x = 1·469$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 7·82$ cm^{-1}, $F(000) = 413$, $T = 293$ K, $R = 0·064$, wR

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