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# Refinement of the crystal structure of $\beta_1$-$K_2UF_6$†

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Zachariasen's structure is confirmed from single-crystal data.

Zachariasen (1948*a*, *b*) determined the crystal structure of $\beta_1$-$K_2UF_6$ from powder data. He described $\beta_1$-$K_2ThF_6$, $\beta_1$-$KLaF_4$ and $\beta_1$-$KCeF_4$ as having this new type of structure. Sears (1967) has since shown that the structure of $\beta_1$-$KLaF_4$ is different from that of $\beta_1$-$K_2UF_6$. The continuing interest in complex fluorides related to molten salt breeder reactors prompted the redetermination of the $\beta_1$-$K_2UF_6$ structure and refinement of the lattice and atomic parameters.

Zachariasen (1948*a*, *b*) gave the lattice parameters of $\beta_1$-$K_2UF_6$ as $a_0 = 6{\cdot}53 \pm 0{\cdot}01$, $c_0 = 3{\cdot}77 \pm 0{\cdot}01$ Å, $Z = 1$ and space group $P\bar{6}2m$. The refined parameters are $a_0 = 6{\cdot}5528 \pm (0{\cdot}0002)$ and $c_0 = 3{\cdot}749 \pm (0{\cdot}0001)$ Å (Cu $K\alpha_1 = 1{\cdot}5405$ Å, Cu $K\alpha_2 = 1{\cdot}54434$ Å), the calculated density is 5·1235 g.cm$^{-3}$, 23 °C. The $\beta_1$-$K_2UF_6$ structure is found to be essentially as described by Zachariasen. While there are differences in the old and new interatomic distances, those distances reported by Zachariasen are within $3\sigma$ of those reported in Table 2.

## Experimental

Single crystals of $\beta_1$-$K_2UF_6$ were selected from an ingot of the composition 75·0 mole % KF and 25 mole % $UF_4$. Some of the single crystals were ground in an air race, and an ellipsoid with diameters 108 by 90 by 126 microns was selected for diffraction. The diffraction intensities were measured with a computer operated Picker four-circle goniostat and a scintillation-counter detector using unfiltered Cu $K\alpha$ radiation. Sixty-eight independent reflections out to $2\theta = 145°$ were measured by the $2\theta$ scan technique. The linear absorption for Cu $K\alpha$ radiation in $\beta_1$-$K_2UF_6$ is 1317·6 cm$^{-1}$ and an absorption correction was calculated for each reflection.

## Refinement and results

The structure of $\beta_1$-$K_2UF_6$ was refined by iterative least-squares using a modification of the Busing, Martin & Levy (1962) computer program. Starting values for the atomic parameters were those given by Zachariasen (1948*b*) and the final refined parameters are given in Table 1. Scattering factors for $K^+$, $U^{4+}$ and $F^-$ were taken from Cromer & Waber (1965) and the values of $\Delta f' = -5$ and $\Delta f'' = 15$ electrons were used for the anomalous dispersion of Cu $K\alpha$ radiation by uranium (Dauben & Templeton, 1955). Trial structural models were also run with $\Delta f'' = -15$ electrons but the $R$ value from the model with $\Delta f'' = 15$ electrons is significantly the better of the two. The quantity minimized was $\Sigma w|s|F_o^2| - |F_c^2||^2$ with weights, $w$, equal to the reciprocals of the variances which were estimated from the empirical equation: $\sigma^2(F_o^2) = s[T + B + 0{\cdot}01\,(T-B)^2]/A(\mathrm{Lp})^2$, in which $s$ = scale factor, $T$ = total, $B$ = background counts, $A$ = the absorption correction, and Lp = Lorentz-polarization correction (Busing & Levy, 1957). Anisotropic temperature factors were calculated for $K^+$ and $U^{4+}$. The interatomic distances are listed in Table 2 and the observed and calculated structures factors in Table 3. The discrepancy indices are $R_1 \equiv \Sigma\,||F_o^2| - |F_c^2||/\Sigma\,|F_o^2| = 0{\cdot}1320$, $R_2 \equiv \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o| = 0{\cdot}0605$ for all reflections and the standard deviation of an observation of unit weight, $[\Sigma\, w(F_o - F_c)^2/(n_o - n_v)]^{1/2}$ is 1·653 where $n_o$ is the number of reflections and $n_v$ the number of variables.

Table 2. *Interatomic distances for* $\beta_1$-$K_2UF_6$

| | | | |
|---|---|---|---|
| 3[U–F(2)] | 2·22 (6) Å | 3[K–F(1)] | 2·62 (5) Å |
| 6[U–F(1)] | 2·38 (4) | 6[K–F(2)] | 2·87 (3) |
| 2[F(1)–F(2)] | 2·70 (4) | 2[F(1)–F(1)] | 2·53 (11) |

Fig. 1 is a stereoscopic pair of drawings showing one asymmetric unit of $K_2UF_6$. The structure consists of chains of $9F^-$ coordinated $U^{4+}$ polyhedra parallel to $c_0$. The polyhedra are trigonal prisms with a pyramid on each of the prism faces. In $\beta_1$-$K_2UF_6$ the basal faces of the trigonal prisms are shared by the polyhedra along the chains. The $U^{4+}$ chains are crosslinked by the $K^+$–$F^-$ bonding where each $K^+$ is at the center of $9F^-$ and the $K^+F^-$ polyhedra share edges with the $U^{4+}$–$F^-$ polyhedra.

Zachariasen (1948*b*) reports that all $9F^-$ around each of the $K^+$ and $U^{4+}$ ions are equidistant; U–9F, 2·36 Å and K–9F, 2·73 Å. The interatomic distances listed in Table 2 show that the $K^+$ ion is coordinated by $6F^-$ at 2·87(3) and $3F^-$ at 2·62(5) Å. The $U^{4+}$ ion is coordinated by $6F^-$ at 2·38(4) and $3F^-$ at 2·22(6) Å. However, all of Zachariasen's distances are within $3\sigma$ of those listed in Table 2.

† Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Table 1. *Atomic and thermal parameters for* $\beta_1$-$K_2UF_6$

Standard errors in parentheses, corresponding to last significant digit, are as given by the variance–covariance matrix.

| | $x$ | $y$ | $z$ | $\beta_{11} \times 10^3$* | $\beta_{22}$ | $\beta_{33} \times 10^3$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| U | 0 | 0 | 0 | 4 (1) | † | 15 (3) | † | 0 | 0 |
| K | $\frac{1}{3}$ | $\frac{2}{3}$ | $\frac{1}{2}$ | 6 (3) | † | 33 (9) | † | 0 | 0 |
| F(1) | 0·223 (9) | 0 | $\frac{1}{2}$ | 16 (3) | ‡ | | | | |
| F(2) | 0·662 (9) | 0 | 0 | 15 (3) | ‡ | | | | |

* Coefficients in the temperature factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
† $2\beta_{12} = \beta_{22} = \beta_{11}$.
‡ Temperature factors for F(1) and F(2) were constrained to be isotropic.

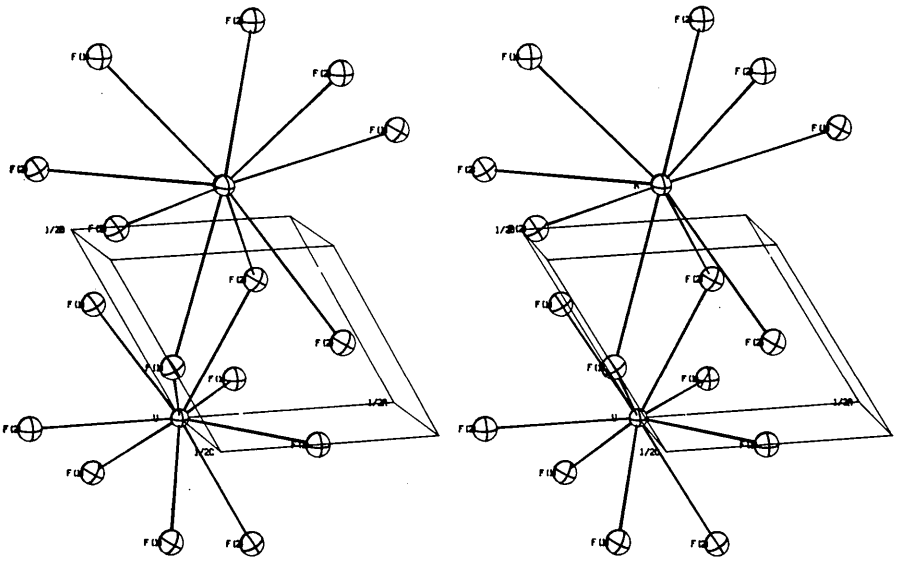

Fig. 1. One asymmetrical unit of $\beta_1$-$K_2UF_6$. One-fourth unit cell is outlined.

Table 3. *Observed and calculated structure factors for* $\beta_1$-$K_2UF_6$, $F_o$, $F_c$ *and* $\alpha \times 10$

| L | FOBS | FCAL | ALPHA | L | FOBS | FCAL | ALPHA | L | FOBS | FCAL | ALPHA | L | FOBS | FCAL | ALPHA | L | FOBS | FCAL | ALPHA | L | FOBS | FCAL | ALPHA | L | FOBS | FCAL | ALPHA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 L | | 1 | 456 | 443 | 95 | 2 | 246 | 241 | 159 | 3 | 188 | 162 | 39 | | | 1 4 L | | 4 | 201 | 207 | 220 | | | 3 3 L | | |
| 1 | 247 | 241 | 178 | 2 | 235 | 239 | 169 | 3 | 215 | 213 | 167 | 4 | 227 | 220 | 134 | 0 | 368 | 343 | 47 | 4 | 2 | 3 L | | 0 | 364 | 327 | 67 |
| 2 | 469 | 480 | 70 | 3 | 295 | 295 | 131 | | | 0 5 L | | | | 1 2 L | | 1 | 155 | 138 | 160 | 0 | 252 | 223 | 126 | 1 | 226 | 227 | 240 |
| 3 | 170 | 192 | 199 | 4 | 180 | 168 | 203 | 0 | 258 | 249 | 157 | 0 | 270 | 278 | 303 | 2 | 298 | 289 | 72 | 1 | 324 | 318 | 151 | 2 | 292 | 279 | 87 |
| 4 | 295 | 292 | 117 | | | 0 3 L | | 1 | 262 | 254 | 151 | 1 | 439 | 408 | 28 | | | 1 5 L | | 2 | 202 | 198 | 150 | 3 | 174 | 173 | 249 |
| | | 1 L | | 0 | 556 | 521 | 80 | 2 | 225 | 215 | 172 | 2 | 210 | 237 | 275 | 0 | 197 | 210 | 212 | | | 2 4 L | | | | 3 4 L | |
| 0 | 410 | 385 | 113 | 1 | 293 | 278 | 148 | | | 0 6 L | | 3 | 286 | 271 | 88 | 1 | 260 | 253 | 138 | 0 | 204 | 199 | 168 | 0 | 178 | 179 | 176 |
| 1 | 369 | 400 | 106 | 2 | 412 | 400 | 98 | 0 | 292 | 303 | 123 | 4 | 169 | 166 | 257 | | | 2 2 L | | 1 | 275 | 276 | 168 | 2 | 162 | 162 | 190 |
| 2 | 263 | 296 | 137 | 3 | 212 | 202 | 183 | 1 | 184 | 180 | 206 | | | 1 3 L | | 0 | 406 | 382 | 240 | 2 | 178 | 179 | 183 | | | 3 5 L | |
| 3 | 259 | 267 | 142 | 4 | 266 | 239 | 138 | | | 1 1 L | | 0 | 283 | 267 | 181 | 1 | 198 | 209 | 271 | 3 | 214 | 210 | 183 | 0 | 154 | 173 | 218 |
| 4 | 196 | 188 | 183 | | | 0 4 L | | 0 | 528 | 451 | 48 | 1 | 329 | 322 | 98 | 2 | 287 | 315 | 227 | | | 2 5 L | | | | 4 4 L | |
| | | 0 2 L | | 0 | 303 | 295 | 142 | 1 | 293 | 201 | 186 | 2 | 224 | 229 | 150 | 3 | 159 | 169 | 261 | 2 | 209 | 229 | 210 | 0 | 241 | 242 | 107 |
| 0 | 313 | 277 | 155 | 1 | 281 | 276 | 145 | -2 | 343 | 349 | 80 | 3 | 240 | 236 | 133 | | | | | | | | | | | | |

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# The crystal structure of $\gamma$-$Na_2ZrF_6$.*

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The crystal structure of $\gamma$-$Na_2ZrF_6$ is a new structure type with space group $P2_1/c$. The Zr ions are coordinated by $7F^-$ ions at distances of 2·012 to 2·167 Å. The structure is metastable below 460 °C.

The complex fluoride $Na_2ZrF_6$ has four polymorphs (Barton, Grimes, Insley, Moore & Thoma, 1958) which can be distinguished from one another by their optical and X-ray properties. $\gamma$-$Na_2ZrF_6$ is biaxial positive; $2V = 75°$, $N_x = 1{\cdot}408$ and $N_z = 1{\cdot}412$. The equilibrium $\beta$–$\gamma$ transition is at 505C and the $\gamma$–$\delta$ transition is at 460C. The crystal structure of $\gamma$-$Na_2ZrF_6$ is a new structure type.

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## Experimental

Single crystals of $\gamma$-$Na_2ZrF_6$ were obtained from a rapidly cooled ingot of the composition NaF–$ZrF_4$–$UF_4$ (55–40–5 mole%). The crystals were ground in a small air race, and