

Fig. 1. One asymmetrical unit of β_1 -K₂UF₆. One-fourth unit cell is outlined.

Table 3. Observed and calculated structure factors for β_1 -K₂UF₆, F_o, F_c and $\alpha \times 10$

L	FOB	S F	CAL,	ALPHA	ų	F085	FCAL	ALPHA	Ļ	F085	FCAL	ALPHA	Ļ	F085	FCAL	ALPHA	L	FOBS	FCAL	ALPHA	Ľ	F885	FCRL 207	ALPHA 220	L	F085_F		LINA
1234 0123	249172		241 580 192 292 1 385 400 296 267	179 70 199 117 113 106 137 142	1234 01234	1005 235 235 235 180 556 293 293 293 293 293 293 293 293 295 293 295 293 295 295 295 295 295 295 295 295 295 295		95 169 131 203 148 98 163 138	012 01	845 25 25 25 25 25 25 25 25 25 25 25 25 25	241 213 249 254 215 254 215 303 180	159 167 157 151 172 123 206	LN4 01234 0	188 227 270 439 210 286 169 283	162 220 278 408 237 271 166 1 3	134 303 275 257 181	0 1 2 0 1 0 1	+085 368 155 298 197 260 406 198	138 138 289 289 253 253 253 253 253 253 253 253 253 253	47 160 72 212 138 240 271	L# 012 012m	201 252 252 2015 202 178	207 2 3 1 223 318 198 2 199 276 179 210	126 151 150 168 168 163 183	0123 02 0	354 354 226 292 174 178 162 151	04L 0 327 2279 173 L 179 162 L 179 162 L	67 240 87 249 176 190 218
4	19 31	6 0 3	188 2 L 277	183 155	0	303 281	285 276	142 145	1012	528 293 343	451 201 349	186 80	1 2 3	329 224 240	322 229 236	96 190 133	23	287 159	315 169	227 261	2	209	2 229	210	0	241	4 L 242	107

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The crystal structure of γ -Na₂ZrF₆.* By GEORGE BRUNTON, Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.

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The crystal structure of γ -Na₂ZrF₆ 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 Na₂ZrF₆ has four polymorphs (Barton, Grimes, Insley, Moore & Thoma, 1958) which can be distinguished from one another by their optical and X-ray properties. γ -Na₂ZrF₆ is biaxial positive; $2V=75^{\circ}$, $N_x=1.408$ and $N_z=1.412$. The equilibrium $\beta-\gamma$ transition is at

505C and the γ - δ transition is at 460C. The crystal structure of γ -Na₂ZrF₆ is a new structure type.

Experimental

Single crystals of γ -Na₂ZrF₆ were obtained from a rapidly cooled ingot of the composition NaF-ZrF₄-UF₄ (55-40-5 mole%). The crystals were ground in a small air race, and

* Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation. Table 1. The lattice and atomic parameters of γ -Na₂ZrF₆

	$a_0 = 5$	-5562 (7), $b_0 = 5$	\cdot 4069 (6), $c_0 =$	16·073 (2) Å;	$\beta = 95.886$ (6)	5)°. $\rho_c = 3.472$	28 g.cm ⁻³ , Z	= 4.	
	$x \times 10^3$	$y \times 10^{3}$	$z \times 10^{3}$	$\beta_{11}^* \times 10^3$	$\beta_{22} imes 10^3$	$\beta_{33} imes 10^4$	$\beta_{12} \times 10^3$	$\beta_{13} imes 10^4$	$\beta_{23} imes 10^4$
Zr	176.1 (2)	448.0 (3)	98.90 (5)	21.0 (6)	18 (2)	20.0 (7)	0.8 (3)	4 (2)	1.0 (7)
Na(1)	326.7 (8)	499 (2)	407.7 (3)	26 (3)	25 (3)	27 (3)	-2(2)	11 (6)	-4(5)
Na(2)	246.7 (9)	962 (2)	247.7 (4)	26 (2)	33 (4)	34 (3)	4 (2)	24 (6)	15 (6)
F(1)	20 (2)	709 (2)	335.8 (5)	31 (3)	15 (4)	33 (3)	2 (3)	-4(7)	2 (8)
F(2)	55 (2)	176 (2)	350.3 (5)	27 (3)	35 (4)	33 (3)	-7(3)	14 (6)	10 (9)
F(3)	346 (2)	224 (2)	24.2(5)	31 (3)	22 (4)	39 (3)	1 (3)	5 (7)	1 (9)
F(4)	598 (2)	229 (2)	364.8 (4)	30 (3)	28 (4)	27 (3)	3 (2)	11 (6)	7 (7)
F(5)	430 (2)	286 (2)	183·5 (4)	29 (3)	37 (5)	30 (3)	-1(3)	-11(7)	31 (9)
F(6)	871 (2)	328 (2)	11.6(4)	23 (2)	17 (4)	32 (3)	-4(2)	-9(6)	9 (8)

* Coefficients in the temperature factor: exp $\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$.

The number in parentheses is the standard error in terms of the last significant figure.

an ellipsoid $0.156 \times 0.156 \times 0.208$ mm was mounted on a computer operated Picker four-circle goniostat. The intensities of 489 independent reflections were measured with a scintillation-counter detector using unfiltered Cu K\alpha radiation ($K\alpha_1 = 1.54050$ and $K\alpha_2 = 1.54434$) out to $145^{\circ}2\theta$ by the 2θ scan technique. The linear absorption for Cu K\alpha radiation by γ -Na₂ZrF₆ is 225.53 cm⁻¹ and an absorption correction was calculated for each reflection.

Refinement and results

The observed conditions for diffraction: hkl – no conditions, h0l - l = 2n and 0k0 - k = 2n are consistent for the space group $P2_1/c$ (14). The lattice parameters were refined from 17 Cu K α_1 reflections in the 2θ range $92-110^\circ$, Table 1.

The structure was refined by iterative least-squares using a modification of the Busing, Martin & Levy (1962) computer program. The starting parameters were determined from a three-dimensional Patterson function, and the results are listed in Table 1. An extinction correction was made on F_c by the method suggested by Zachariasen (1967). The scattering factors for the ions were taken from Cromer & Waber (1965) and the values of $\Delta f' = -0.6$ and $\Delta f'' = 2.5$ electrons were used for the anomalous dispersion of Cu K α radiation by zirconium (Dauben & Templeton, 1955).

The quantity minimized by the least-squares program was $\Sigma w ||sF_0| - |F_c||^2$ with weights, w, equal to the reciprocals of the variances which were estimated from the emprirical equation:

$\sigma^2(F_a^2) = [T + B + \{0.15(T - B)\}^2]/[A(Lp)^2]$

where T =total counts, B = background counts, A = absorp-

tion correction and Lp = Lorentz-polarization (Brown & Levy, 1964); $\sigma(F_o) = \sigma(F_o^2)/2F_o$. Anisotropic temperature factors were calculated for all atoms (Table 1) and a stereoscopic pair of drawings of the structure of γ -Na₂ZrF₆ is shown in Fig.1.

The discrepancy factor $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0536$ for 489 independent reflections. The standard deviation of an observation of unit weight, $[\Sigma w(F_o - F_c)^2/(n_o - n_v)]^{1/2}$ where n_o is the number of reflections and n_v the number of variables, is 1.307. The interatomic distances are listed in Table 2, and the observed and calculated structure factors are listed in Table 3.

Table 2. Interatomic distances y-Na₂ZrF₆

Zr - F(4)	2·012 (7) Å	Na(1) - F(3)	2·218 (9) Å
ZrF(3)	2·019 (8)	Na(1) - F(1)	2.249 (9)
Zr - F(2)	2.024(7)	Na(1) - F(4)	2·264 (9)
Zr - F(5)	2.035(7)	Na(1) - F(3)	2.35 (1)
Zr - F(1)	2.058(8)	Na(1) - F(2)	2.41(1)
Zr - F(6)	2.138(7)	Na(1) - F(6)	2.53 (2)
Zr - F(6)	2.167 (6)	Na(1) - F(5)	2.62(2)
Na(2) - F(5)	2.211(8)	Na(2) - F(1)	2.429 (9)
Na(2) - F(1)	2.302 (8)	Na(2) - F(4)	2.447 (9)
Na(2) - F(5)	2.33(1)	Na(2) - F(2)	2.66 (1)
Na(2) - F(2)	2.369 (9)	Na(2)-F(4)	2.922 (8)
F(1)F(5)	2.515 (9)	F(1)-F(6)	2.54 (1)
F(1) - F(2)	2.54(2)	F(1) - F(2)	2.89 (2)
F(1) - F(2)	2.98 (2)	F(2) - F(5)	2·595 (9)
2[F(2)-F(6)]	2·90 (1)	F(3) - F(5)	2·569 (9)
F(3) - F(6)	2.685 (9)	F(3) - F(6)	2·74 (2)
F(3) - F(6)	3.000 (9)	F(4) - F(5)	2.52 (2)
F(4) - F(6)	2.665 (9)	F(4) - F(5)	2.968 (8)



Fig.1. The crystal structure of γ -Na₂ZrF₆. The four nearest neighbor Na(1) and Na(2) polyhedra are shown around one Zr polyhedron. One fourth unit-cell outlined.

Table 3. Observed and calculated structure factors for γ -Na₂ZrF₆

2	F085.FCAL L 0 0 L 17 36 35	F0095 FCAL L 3 3 19 0 4 L	F085 FC9L L / 35 -32 -8 1 2 L -7	2 2 15	F085 FCAL L 27 -24 -5 16 15 -4	F085 FCAL L 14 -14 -8	F085 FC1L L	F0855 FCRL L F0855 FCRL VI - 37-14, 3 - 2 20 - 37-13 8
4 6 8	115 -112 0 41 -39 1 68 69 2	70 68-13 70 68-12 2 1-11	24 -22 -6 18 19 -5 4 4 -4	29 -8 17	35 - 31 - 3 10 - 7 - 2	17 18 -6 6 6 -5 58 62 -0	22 33 -5	15 -13 5 31 31
10 12	70 72 3 68 68 4 58 -54 5	67 65-10 26 -25 -9 6 -4 -8	20 21-3	22 -24-12 8 8-11 21 36-10	1 51 51	18 -16 -3	30 31 -2	3 -1 8 11 12 45 50 9 7 -6
16	47 -44 6 0 1 L 7 99 -92 8	23 -20 -7	5 5 0 62 - 59 1	16 -15 -9 95 97 -8	16 17 3 49 -52 4	27 - 26 0	66 -67 1 46 -49 2	13 -15 11 25 -26 6 -6 5 2 L
ŝ	48 -44 36 33-18	16 -12 -3	10 9 3 70 -77 4	22 22 -6	7 6 14	3 .2 3	60 -63 4 39 40 5	45 -48 7 6 -5 3 2 8 10 -10 3 -1 9 21 -21
56	77 73 2 55 -52 W	102 -86 -1	40 41 6 34 32 7	5 -4 -3	5 +5-16 149 144 0	25 25 6	8 8 0 16 15 7 26 27 9	0 -310 15 17 33 36 5 3 L 29 31 8 22 23
9	10 8 8	35 31 1 85 61 2 5 5 3	26 23 26 -24-18 13 -12 0	20L-1 36-350 48-571	61 81 2 124 -118 4 9 -8 6	18 -19 8 43 47 9 49 53 13	24 -22 10 2 -1 11 29 -29 12	26 27 6 0 1 12 -10-10 49 44 21 21 -8 13 11
11	15 16 12 49 -47 14 62 -60 16	25 -23 4 31 -28 5 3 -1 6	45 -43 2 34 -32 4 10 8 6	76 -76 2 91 -91 3 172 173 4	98 -92 8 65 -59 10 11 12 12	26 -24 14 62 -59 15 12 -10	21 19 13	26 - 26 - 6 36 - 31 7 - 4 16 - 14
14	29 -26 36 37-19	45 39 7 1 1 6 10 10 9	50 -59 8 57 56 10 17 17 12	85 82 5	54 -50 14 69 66 16 22 19	45 44 -8 16 16 -7 3 1 L -6	26 24 -8	77 71 0 37 33 22 21 2 15 15 29 29 1 2 15 15
16 17 19	13 13-14 13 13-13 28 -24-12	30 27 10 48 -49 11 5 -2 12	29 29 14 50 50 16 40 -36 18	5 4 8 46 45 9 43 38 10	19 10-18 22 19-12 23 -20-11	8 11 -5 16 -16 -4	71 -72 -5	26 25 6 21 -20
0	26 23-10 26 23-10 32 -9	80 -80 16 21 -19 17 53 53 18	16 15 14 -12-19 20 19-13	2 1 1 11	15 15-10 26 -25 -9 21 21 -8	6 6-2 NI 40-1	44 -44 -2 26 26 -1	42 -43-10 1 0 19 -19 -9 18 -14
3	13 11 -8 43 41 -7 48 -47 -6	6 6 93 92-11 14 -15-10	1 3 L -12 50 -49-11 51 -53-10	3 3 17	2 1 7 2 3 L 6	27 -26 1	30 29 1	26 - 29 - 7 19 17 33 34 - 6 10 - 7
567	43 44 -5 176 -175 -4 65 -62 -3	80 83 -9 38 40 -8	25 25 9 38 -38 -8	50 59 -9 5 -5 -8	16 16 4	21 -21 4	26 27 4	11 - 12 - 5 30 25 74 80 - 4 6 6 32 34 - 3 6 - 4
8 9	25 23 -2	5 5-6	¥2 ¥4 -6 30 32 -5	56 69 -6 45 -48 -5	45 46 -1	75 85 13	19 -18 11 4 -3 12 16 17 13	26 -26 -2 8 7 25 27 -1 27 -23 0 0 0 6 -5
12	N 32 1	22 - 22 - 3	10	60 -61 -3 10 10 -2	32 -30 2	40 46 -1 52 -57 0	14 15 -3 9 10 -2	4 3 L 1 16 -14 14 14 2 25 -22 4 4 3 16 16
16	30 -32 4	9 8 0 36 35 1	S2 -48 0	5 50 55 56 1	63 -63 5 48 45 6	65 -66-16 25 -22-14	10L-1 25270 34-3011	4 -3 4 10 -9 40 41 5 25 25 10 -10 6 8 8
1	0 3 L 7	68 -65 3 29 26 4	115 115 3 55 51 4	44 43 3 117 112 4	18 17 7 12 13 8 36 34 9	29 -29 0 11 -10 2 67 65 4	25 -28 12 48 57 36 40-14	7 9 7 0 1 5 0 L 6 2 L 33 - 30 - 9 17 15
14.07	6 5 10 55 -53 11	31 -30 6 13 13 7	31 32 5 47 42 6 8 -6 7	42 -39 5 22 22 6 65 -61 7	30 -26 10 14 11 12 14 -13 13	7 5 6 10 9 8 10 -9 10	37 -43-12 59 -58-10 43 -43 0	10 -9 -8 0 -6 21 18 1 20 18 39 41 2 3 -1
67	40 39 12 67 66 13 79 12	49 47 9	38 - 34 9 49 - 44 10	29 -27 8 2 -1 9 21 22 15	27 -26 14 11 10 15 5 -4 16	11 11 12 50 -47 14 3 -2	39 37 2	31 29 3 19 20 18 -18 4 29 -29
9 10	15 -13 16 5 -4 17	26 37 11 22 19 16 31 -27 17	9 8 11 31 32 12 17 -15 13	54 51 16 11 9 20 21 -7	10 10 2 4 L -11 60 -59-10	3 2 L -17 13 13 16 29 -27 -9	17 -22 B 6 -5 10 10 -8 12	10 -9 6 3L 20 19 1 8 -7 17 19 3 19 -19
11	16 -15 18	ч 3	1 4 L 14	4 4-6	17 17 -9	31 -29 -8	8 -8	5 11 13 13 13

The Zr^{4+} ion and the Na(1)⁺ ion are surrounded by an irregular array of 7F⁻ ions. The resulting Zr-F polyhedron has nine triangular faces and the Na(1)-F polyhedron has

three triangular faces and two trapezium faces. Zachariasen (1948) found similar Zr-7F polyhedra in the structure of Na₃ZrF₇. The Zr-F polyhedron shares edges with three Na(1)-F polyhedra and a corner with one other. The Na(2)+ ion is coordinated by 8F- at the corners of an six faced trapezohedron. The Zr-F polyhedron shares edges with four of the Na(2)-F trapezohedra. There are two other Fpolyhedra similar to Na(1) and Na(2) with centers at approximately x=0.25, y=0.04, z=0.75 and x=0.33, y=0.50, z=0.90. These polyhedra are vacant and too small to contain Na or Zr cations. The final difference electron density map has no peaks greater than $1.60 \text{ e.}\text{Å}^{-3}$ and scattering matter put on the vacant sites does not give a model which converges with a least-squares refinement. The vacancies perhaps explain why this polymorph is metastable with respect to Δ -Na₂ZrF₆ below 460°C.

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Indexing of the ψ -sulfur fiber pattern. By S. GELLER AND M. D. LIND, Science Center, North American Rockwell Corporation, Thousand Oaks, California, U.S.A.

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The fiber pattern of ψ -sulfur reported by Tuinstra and the rotation photograph of the pressure-induced fibrous modification of sulfur (II) about the fiber axis (a) are essentially the same and have been indexed completely on the pseudo-orthorhombic C-face-centered cell with $a=13\cdot8$, $b=32\cdot4$ and $c=9\cdot25$ Å.

We have recently completed a study of the structure of the pressure-induced fibrous form of sulfur (Lind & Geller, 1969). There is strong evidence that this form of sulfur is the same as the ψ -sulfur reported by Prins, Schenk & Wachters (1957; see also Prins & Tuinstra, 1963). Especially important is the exact match of the rotation photograph about the fiber (a) axis of a crystal of the pressure-induced phase and that of a fiber pattern of the ψ -sulfur.* Inasmuch as the literature (Tuinstra, 1966, 1967) contains questionable conclusions regarding the indexing of this pattern, it seemed worthwhile to give the results which follow.

It has already been reported (Geller, 1966) that the singlecrystal-type diffraction data from the pressure-induced phase indicated that the crystals are C-centered orthorhombic with lattice constants $a=13\cdot8$, $b=32\cdot4$ and c= $9\cdot25$ Å. The structure determination (Lind & Geller, 1969) has led to the conclusion that the crystal symmetry is more likely P2 and that the apparent orthorhombic symmetry results from a fine-grained twinning. The true monoclinic cell then has the lattice constants $a=17\cdot6$, $b=9\cdot25$, c= 13.8 Å, $\beta = 113^{\circ}$. The orthorhombic indices listed for the powder pattern (Geller, 1966) may be transformed to the monoclinic indices by application of the two matrices $\frac{1}{2}20|001|100$ and $\frac{1}{2}20|001|100$ to each reflection.

We show the indexing of the rotation photograph in Table 1. Listed in the first column are Tuinstra's (1966) observed values, Q_0 ($Q = 10^4/d^2$), measured on his fiber photographs of the stretched, CS₂-extracted, annealed fibrous sulfur. In the second column, we give our values of Q_0 , measured on a rotation photograph (2 hr exposure, 57.3 mm dia. camera, Cu Ka radiation, Ni filtered) taken of the same crystal used to obtain the data in the paper by Lind & Geller (1969). (The photograph to which Tuinstra (1967) refers is exactly the same except perhaps for exposure time.) We do not list the qualitative intensities; as we said earlier, the photographs of stretched, CS2extracted, annealed fibrous sulfur and pressure-induced fibrous sulfur superimpose exactly and quantitative F_{hkl} are given in the Lind & Geller (1969) paper. We see that the two sets of Q_0 agree quite well although ours are considerably better resolved. Our Q_c and indices based on the pseudo-orthorhombic lattice constants are given in the third and fourth columns, respectively. It is seen that the agreement in Q's is excellent, so that even though it is possible that the fiber axis is very long, as Tuinstra (1966) sug-

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^{*} The best ψ -sulfur photograph we have seen has been made by J. Donohue and S. H. Goodman. This is the one that superposes exactly on our (pseudo-orthorhombic) *a*-axis rotation photograph.