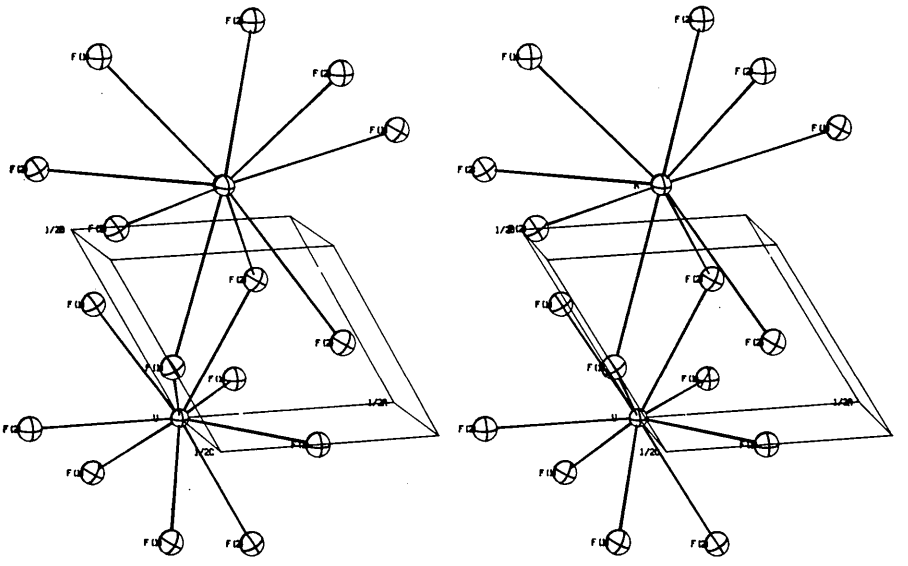

Fig. 1. One asymmetrical unit of β_1-K_2UF_6. One-fourth unit cell is outlined.

Table 3. *Observed and calculated structure factors for* β_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 γ-Na_2ZrF_6.*

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The crystal structure of γ-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. γ-Na_2ZrF_6 is biaxial positive; $2V = 75°$, $N_x = 1{\cdot}408$ and $N_z = 1{\cdot}412$. The equilibrium β–γ transition is at 505C and the γ–δ transition is at 460C. The crystal structure of γ-Na_2ZrF_6 is a new structure type.

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Experimental

Single crystals of γ-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

Table 1. *The lattice and atomic parameters of* γ-Na_2ZrF_6

$a_o = 5{\cdot}5562$ (7), $b_o = 5{\cdot}4069$ (6), $c_o = 16{\cdot}073$ (2) Å; $\beta = 95{\cdot}886$ (6)°. $\varrho_c = 3{\cdot}4728$ g.cm^{-3}, $Z = 4$.

	$x \times 10^3$	$y \times 10^3$	$z \times 10^3$	β_{11}* $\times 10^3$	$\beta_{22} \times 10^3$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^3$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
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: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.
The number in parentheses is the standard error in terms of the last significant figure.

an ellipsoid $0{\cdot}156 \times 0{\cdot}156 \times 0{\cdot}208$ 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 ($K\alpha_1 = 1{\cdot}54050$ and $K\alpha_2 = 1{\cdot}54434$) out to $145°2\theta$ by the 2θ scan technique. The linear absorption for Cu $K\alpha$ radiation by γ-Na_2ZrF_6 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 $K\alpha_1$ reflections in the 2θ range 92–110°, 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 $\Delta f' = -0{\cdot}6$ and $\Delta f'' = 2{\cdot}5$ electrons were used for the anomalous dispersion of Cu $K\alpha$ radiation by zirconium (Dauben & Templeton, 1955).

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

$$\sigma^2(F_o^2) = [T + B + \{0{\cdot}15(T-B)\}^2]/[A(\mathrm{Lp})^2]$$

where T = total counts, B = background counts, A = absorption 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-Na_2ZrF_6 is shown in Fig. 1.

The discrepancy factor $R = \Sigma\,||F_o| - |F_c||\,/\,\Sigma\,|F_o| = 0{\cdot}0536$ 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* γ-Na_2ZrF_6

Zr——F(4)	2·012 (7) Å	Na(1)–F(3)	2·218 (9) Å
Zr——F(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)

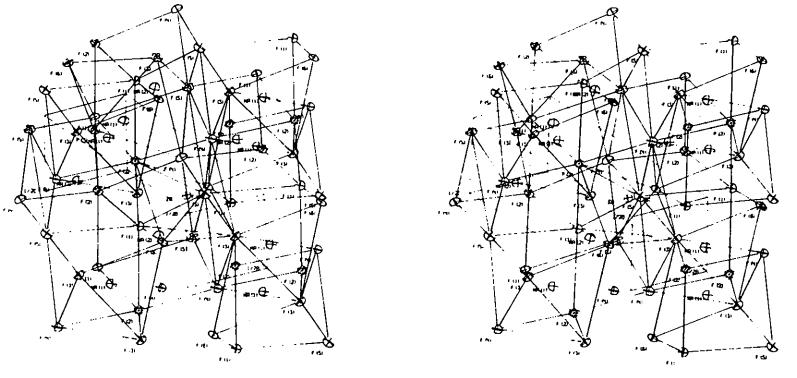
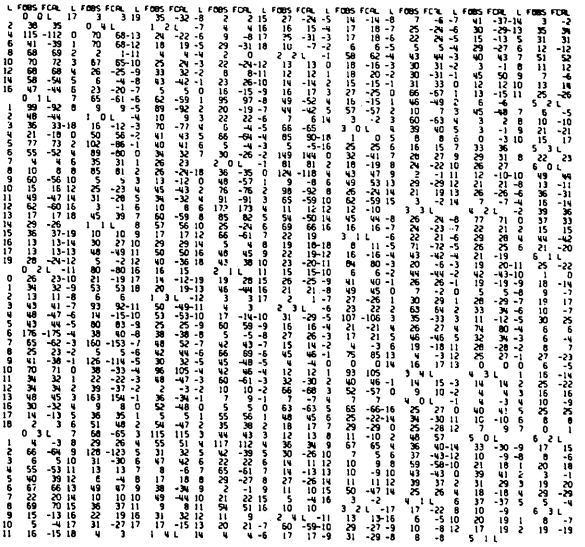


Fig. 1. The crystal structure of γ-Na_2ZrF_6. The four nearest neighbor Na(1) and Na(2) polyhedra are shown around one Zr polyhedron. One fourth unit-cell outlined.

Table 3. *Observed and calculated structure factors for γ-Na_2ZrF_6*



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 Na_3ZrF_7. 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 F^- polyhedra similar to Na(1) and Na(2) with centers at approximately $x=0{\cdot}25$, $y=0{\cdot}04$, $z=0{\cdot}75$ and $x=0{\cdot}33$, $y=0{\cdot}50$, $z=0{\cdot}90$. 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 e.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-Na_2ZrF_6 below 460°C.

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Indexing of the ψ-sulfur fiber pattern.

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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 $a=13{\cdot}8$, $b=32{\cdot}4$ and $c=9{\cdot}25$ 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 single-crystal-type diffraction data from the pressure-induced phase indicated that the crystals are *C*-centered orthorhombic with lattice constants $a=13{\cdot}8$, $b=32{\cdot}4$ and $c=9{\cdot}25$ Å. The structure determination (Lind & Geller, 1969) has led to the conclusion that the crystal symmetry is more likely *P*2 and that the apparent orthorhombic symmetry results from a fine-grained twinning. The true monoclinic cell then has the lattice constants $a=17{\cdot}6$, $b=9{\cdot}25$, $c=13{\cdot}8$ Å, $\beta=113°$. The orthorhombic indices listed for the powder pattern (Geller, 1966) may be transformed to the monoclinic indices by application of the two matrices $\bar{\frac{1}{2}}\frac{1}{2}0|001|100$ and $\frac{1}{2}\frac{1}{2}0|001|\bar{1}00$ 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_o ($Q=10^4/d^2$), measured on his fiber photographs of the stretched, CS_2-extracted, annealed fibrous sulfur. In the second column, we give our values of Q_o, measured on a rotation photograph (2 hr exposure, 57·3 mm dia. camera, Cu $K\alpha$ 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, CS_2-extracted, 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_o 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-

* 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.