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

L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL
0 0 L			17	3	3	19	35	-32	-8	2	2	15	27	-24	-5	14	-14	-8	7	-6	-7	41	-37	-14	3	-2
2	38	35	0 4 L			1 2 L			-7	4	4	16	16	15	-4	17	18	-7	25	-24	-6	30	-29	-13	35	34
4	115	-112	0	70	68	-13	24	-22	-6	9	-8	17	25	-31	-3	17	18	-6	22	24	-5	15	-13	5	31	31
6	41	-39	1	70	68	-12	18	19	-5	29	-31	18	10	-7	-2	6	6	-5	5	5	-4	29	-27	6	12	-12
8	68	69	2	2	1	-11	4	4	-4	2	0	2 2 L			-1	58	62	-4	43	44	-3	40	43	7	51	52
10	70	72	3	67	65	-10	25	24	-3	22	-24	-12	13	13	0	18	-16	-3	30	31	-2	3	-1	8	11	12
12	68	68	4	26	-25	-9	33	32	-2	8	8	-11	12	12	1	18	20	-2	30	-31	-1	45	50	9	7	-6
14	58	-54	5	6	-4	-8	43	-42	-1	23	26	-10	14	-14	2	15	-15	-1	31	33	0	12	12	10	13	14
16	47	-44	6	23	-20	-7	5	5	0	16	-15	-9	16	17	3	27	-25	0	66	-67	1	13	-15	11	25	-26
0 1 L			7	65	-61	-6	62	-59	1	95	97	-8	49	-52	4	16	-15	1	46	-49	2	6	-6	5 2 L		
1	99	-92	8	9	9	-5	89	-92	2	20	-19	-7	44	-42	5	57	-57	2	10	7	3	45	-48	7	6	-5
2	48	-44	1 0 L			-4	10	9	3	22	22	-6	7	6	14	3	-2	3	60	-63	4	3	2	8	10	-10
3	36	33	-18	16	-12	-3	70	-77	4	6	-4	-5	66	-65	3 0 L			4	39	40	5	3	-1	9	21	-21
4	21	-18	0	50	56	-2	41	43	5	66	-64	-4	85	90	-18	1	0	5	8	8	6	0	-3	10	15	17
5	77	73	2	102	-86	-1	40	41	6	5	-4	-3	5	-5	-16	25	25	6	16	15	7	33	36	5 3 L		
6	55	-52	4	89	-80	0	34	32	7	30	-26	-2	149	144	0	32	-41	7	28	27	9	29	31	8	22	23
7	4	4	6	35	31	1	26	23	2 0 L			-1	81	81	2	18	-19	8	24	-22	10	26	27	6 0 L		
8	10	8	8	85	81	2	26	-24	-18	36	-35	0	124	-118	4	43	47	9	2	-1	11	12	-10	-10	49	44
9	60	-56	10	5	5	3	13	-12	0	48	-57	1	9	-8	6	49	53	13	29	-29	12	21	21	-8	13	-11
10	15	16	12	25	-23	4	45	-43	2	76	-76	2	98	-92	8	26	-24	14	21	19	13	26	-26	-6	36	-31
11	49	-47	14	31	-28	5	34	-32	4	91	-91	3	65	-59	10	62	-59	15	3	-2	14	7	-7	-4	16	-14
12	62	-60	16	3	-1	6	10	8	6	172	173	4	11	12	12	12	-10	3 3 L			4 2 L			-2	39	36
13	17	17	18	45	39	7	60	-59	8	85	82	5	54	-50	14	45	44	-8	26	24	-8	77	71	0	37	33
14	29	-26	1 1 L			8	57	56	10	25	-24	6	69	66	16	16	16	-7	24	-23	-7	22	21	2	15	15
15	36	37	-19	10	10	9	17	17	12	66	-61	7	22	19	3 1 L			-6	22	21	-6	29	28	4	44	-42
16	13	13	-14	30	27	10	29	29	14	5	4	8	19	18	-18	8	11	-5	71	-72	-5	26	25	6	21	-20
17	13	13	-13	48	-49	11	50	50	16	48	45	9	22	19	-12	16	-16	-4	43	-42	-4	21	-19	6 1 L		
19	28	-24	-12	5	-2	12	40	-36	18	43	38	10	23	-20	-11	84	80	-3	20	-6	-3	19	20	-11	25	-22
0 2 L			-11	80	-80	16	16	15	2 1 L			11	15	15	-10	6	6	-2	44	-44	-2	42	-43	-10	1	0
0	26	23	-10	21	-19	17	14	-12	-19	19	28	15	26	-25	-9	41	40	-1	26	26	-1	19	-19	-9	18	-14
1	34	32	-9	53	53	18	20	19	-13	46	-44	16	21	21	-8	49	45	0	7	-2	0	5	5	-8	9	-7
2	13	11	-8	6	6	1 3 L			-12	3	3	17	2	1	-7	27	-26	1	30	29	1	28	-29	-7	19	17
3	43	41	-7	93	92	-11	50	-49	-11	4	3	2 3 L			-6	23	22	2	63	64	2	33	34	-6	10	-7
4	48	-47	-6	14	-15	-10	53	-53	-10	17	-14	-10	31	-29	-5	107	-106	3	35	-33	3	11	-12	-5	30	25
5	43	44	-5	80	83	-9	25	25	-9	60	59	-9	16	16	-4	21	-21	4	26	27	4	74	80	-4	6	6
6	176	-175	-4	38	40	-8	38	-38	-8	5	-5	-8	27	26	-3	17	21	5	46	-46	5	32	34	-3	6	-4
7	65	-62	-3	160	-153	-7	48	52	-7	42	43	-7	15	14	-2	4	-3	6	19	-18	11	28	-28	-2	8	7
8	25	23	-2	5	5	-6	42	44	-6	66	69	-6	45	46	-1	75	85	13	4	-3	12	25	27	-1	27	-23
9	41	-38	-1	126	-114	-5	30	32	-5	45	-48	-5	4	-4	0	0	0	14	16	17	13	0	0	0	6	-5
10	70	71	0	38	-33	-4	96	105	-4	42	46	-4	12	12	1	93	105	3 4 L			4 3 L			1	16	-14
11	34	32	1	22	-22	-3	48	-47	-3	60	-61	-3	32	-30	2	40	46	-1	14	15	-3	14	14	2	25	-22
12	34	34	2	39	-37	-2	2	-3	-2	10	10	-2	66	-68	3	52	-57	0	9	10	-2	4	4	3	16	16
13	48	45	3	163	154	-1	36	-34	-1	7	9	-1	7	-7	4	7	7	4 0 L			-1	4	-3	4	10	-9
16	30	-32	4	9	8	0	52	-48	0	5	5	0	63	-63	5	65	-66	-16	25	27	0	40	41	5	25	25
17	14	-13	5	38	35	1	5	5	1	55	56	1	48	45	6	25	-22	-14	34	-30	11	10	-10	6	8	8
18	2	3	6	51	48	2	54	-47	2	35	38	2	18	17	7	29	-29	0	25	-28	12	7	9	7	0	1
0 3 L			7	68	-65	3	115	115	3	44	43	3	12	13	8	11	-10	2	48	57	5 0 L			6 2 L		
1	4	-3	8	29	26	4	55	51	4	117	112	4	36	34	9	67	65	4	36	40	-14	33	-30	-9	17	15
2	66	-64	9	128	-123	5	31	32	5	42	-39	5	30	-26	10	7	5	6	37	-43	-12	10	-9	-8	8	-6
3	6	5	10	31	-30	6	47	42	6	22	22	6	14	11	12	10	9	8	59	-58	-10	21	18	1	20	18
4	55	-53	11	13	13	7	8	-6	7	65	-61	7	14	-13	13	10	-9	10	43	-43	0	39	41	2	3	-1
5	40	39	12	6	-4	8	17	18	8	29	-27	8	27	-26	14	11	11	12	39	37	2	31	29	3	19	20
6	67	66	13	49	47	9	38	-34	9	2	-1	9	11	10	15	50	-47	14	25	26	4	18	-18	4	29	-29
7	22	20	14	10	10	10	49	-44	10	21	22	15	5	-4	16	3	-2	4 1 L			6	37	-37	5	5	-4
8	69	70	15	38	37	11	9	8	11	54	51	16	10	10	3 2 L			-17	17	-22	8	10	-9	6 3 L		
9	15	-13	16	22	19	12	31	32	12	11	9	2 4 L			-11	13	13	-16	6	-5	10	20	19	1	8	-7
10	5	-4	17	31	-27	13	17	-15	13	20	21	-7	60	-59	-10	29	-27	-9	10	-8	12	17	19	2	19	-19
11	16	-15	18	4	3	1 4 L			14	4	4	-6	17	17	-9	31	-29	-8	8	-8	5 1 L					

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 $1{\cdot}60$ 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. 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 $a=13{\cdot}8$, $b=32{\cdot}4$ 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 $P2$ 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 $\bar{\tfrac{1}{2}}\tfrac{1}{2}0|001|100$ and $\tfrac{1}{2}\tfrac{1}{2}0|001|\bar{1}00$ 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.

Table 1. *Indexing of rotation photograph of ψ-sulphur*

Tuinstra	Present Work			Tuinstra	Present Work			Tuinstra	Present Work		
Q_o	Q_o	Q_c	h k l	Q_o	Q_o	Q_c	h k l	Q_o	Q_o	Q_c	h k l
473	478	467	002	*	2625	2634	2,12,3	3792	3774	3759	4,14,3
613	613	610	080	*	3253	3284	245		3826	3800	425
		620	042	*	3713	3701	2,16,3	4093	4036	4043	4,18,1
1842	1847	1839	0,12,2			3742	285		4110	4105	465
		1870	004	*	4092	4137	2,20,1	4751	4719	4715	4,10,5
2050	2046	2022	044	*	4451	4501	2,12,5	*	5639	5629	4,14,5
2431	2422	2439	0,16,0	*	5582	5570	2,16,5	*	6472	6503	4,22,3
2470	2475	2480	084	*	5839	5814	2,24,1	*	6957	6910	467
2868	2894	2906	0,16,2	*	6099	6089	247				
3244	3234	3242	0,12,4	*	6610	6547	287	2250	2230	2233	660
4265	4271	4208	006					2379	2372	2396	622
		4278	0,20,2	946	950	939	370	2707	2706	2701	662
4316	4345	4309	0,16,4			950	312	2800	2823	2843	6,10,0
		4360	046	*	1032	1026	332	3284	3300	3311	6,10,2
4845	4843	4817	086	1165	1160	1178	352	3797	3807	3798	624
5449	5455	5487	0,24,0	1222	1224	1244	390	4172	4089	4103	664
5618	5619	5579	0,12,6	1414	1414	1407	372		4202	4225	6,14,2
		5680	0,20,4	1691	1706	1712	392	*	4762	4712	6,10,4
*	6631	6646	0,16,6	2104	2107	2093	3,11,2	*	4923	4977	6,18,0
					2377	2352	314	*	5484	5444	6,18,2
962	967	941	191		2431	2428	334	*	5640	5628	6,14,4
1146	1133	1113	113	2500	2532	2550	3,13,2	*	6171	6136	626
1300	1318	1322	1,11,1		2578	2581	354	*	6521	6501	6,22,0
1361	1380	1342	153			2616	3,15,0	*	6952	6968	6,22,2
1933	1934	1876	193	3110	3099	3083	3,15,2	*	7070	7050	6,10,6
2250	2251	2257	1,11,3			3114	394				
2978	2948	2922	1,17,1	*	3171	3226	3,17,0	2732	**	2699	711
3113	3086	3060	135	3517	3489	3495	3,11,4	2808	**	2776	731
3255	3233	3212	155	*	5547	5512	3,23,0	2950	**	2928	751
		3248	1,15,3	*	6295	6290	3,13,6	3470	**	3461	791
3470	3454	3441	175	*	7916	7885	3,27,2	3712	**	3710	733
3560	3548	3608	1,19,1			7962	318	3867	**	3843	7,11,1
3790	3750	3746	195	*	8263	8296	3,25,4			3863	753
3860	3875	3857	1,17,3	*	8856	8881	3,21,6	4136	**	4092	773
5130	5135	5118	1,15,5	*	9270	9287	3,27,4	4337	**	4397	793
5900	5858	5789	117								
		5865	137	1318	1316	1300	461	5414	**	5406	10,2,1
6200	6096	6123	1,25,1	1942	1936	1910	4,10,1	5550	**	5520	10,4,1
		6144	1,23,3			1930	423	6017	**	5978	10,8,1
	6321	6246	177	2250	2253	2235	463				
*	7005	6932	1,11,7	2866	2856	2824	4,14,1				
		7058	1,25,3			2844	4,10,3				

* Not reported by Tuinstra.
** Not measured in present work.

gests, or even that there is not crystallographic order in that direction in the usual sense, there is little doubt that it is very nearly a multiple of 13·8 Å. Further, there is no point in entering into a discussion of the elements of crystallography regarding the long pseudo-orthorhombic *b* axis (Tuinstra, 1967). The crystal diffraction data, some of which were shown in Geller (1966), and indeed the results shown in Table 1, should suffice.

Tuinstra (1966) says that 'only in the direction of the b^* axis (our c^*) is an ordinary indexing possible', a conclusion which is negated by the results shown in Table 1. His approach is an arbitrary one; certainly with respect to order in the directions perpendicular to the helix axes, he has decided arbitrarily on the disorder. Tuinstra (1966) claims that the periods along the fiber axis are not indicative of order along this direction, that, for example, the ratio of the heights of the layers '3' and '1' is 2·85. The evidence he gives is not convincing: First, note the good agreement of our Q_c's with the Q_o's. Second, measurements made parallel to the rotation axis of rotation photographs cannot be considered to give very reliable spacings. Third, and most important, measurements on our photograph from equator to layer line, and the identity period calculated from them are:

Layer number	Distance (mm)	Identity period (Å)
1	3·25	13·69
2	6·58	13·78
3	10·20	13·79
4	14·47	13·67
5	not observed	
6	25·75	13·84

The average value is 13·75 Å, but it is not better than 13·8 Å.

We emphasize, nevertheless, that we accept the possibility of either a very long axis or lack of order in the fiber axis direction. The nature of the reflections themselves indicates this; some appear sharper than others, and we are not sure that those that are supposed to be in the same layer are all precisely aligned. (However, the crystals are not like those with which most crystallographers usually deal.)

It is difficult to see how Tuinstra did 'index' (his quotes) his data. On page 344 of his paper (1966), he indicates a rectangular prismatic cell, then discusses a β angle of 170°, then that β is undetermined, then speaks of taking as origin for the *h* index in each reciprocal lattice layer, the 'point nearest to the origin in reciprocal space'. When we look at his Table 2, we find positive and negative *h* indices; when his $h=3$ for example, he does seem to take a β angle of 170° between his *a* and *c* axes of 8·11 and 13·8 Å length, respectively. This means that the third layer belongs to a cell with $a=8{\cdot}11$, $b=9{\cdot}20$, $c=13{\cdot}8$ Å, $\beta=170°$. Other layers are indexed differently; thus, we must wonder how the intensities were calculated.

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