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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 $\frac{\bar{1}}{2}\frac{1}{2}0|001|100$ 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.

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

Tuinstra	Present Work		
Q_o	Q_o	Q_c	<u>h</u> <u>k</u> <u>l</u>
473	478	467	002
613	613	610	080
		620	042
1842	1847	1839	0,12,2
		1870	004
2050	2046	2022	044
2431	2422	2439	0,16,0
2470	2475	2480	084
2868	2894	2906	0,16,2
3244	3234	3242	0,12,4
4265	4271	4208	006
		4278	0,20,2
4316	4345	4309	0,16,4
		4360	046
4845	4843	4817	086
5449	5455	5487	0,24,0
5618	5619	5579	0,12,6
		5680	0,20,4
*	6631	6646	0,16,6
962	967	941	191
1146	1133	1113	113
1300	1318	1322	1,11,1
1361	1380	1342	153
1933	1934	1876	193
2250	2251	2257	1,11,3
2978	2948	2922	1,17,1
3113	3086	3060	135
3255	3233	3212	155
		3248	1,15,3
3470	3454	3441	175
3560	3548	3608	1,19,1
3790	3750	3746	195
3860	3875	3857	1,17,3
5130	5135	5118	1,15,5
5900	5858	5789	117
		5865	137
6200	6096	6123	1,25,1
		6144	1,23,3
	6321	6246	177
*	7005	6932	1,11,7
		7058	1,25,3

Tuinstra	Present Work		
Q_o	Q_o	Q_c	<u>h</u> <u>k</u> <u>l</u>
*	2625	2634	2,12,3
*	3253	3284	245
*	3713	3701	2,16,3
		3742	285
*	4092	4137	2,20,1
*	4451	4501	2,12,5
*	5582	5570	2,16,5
*	5839	5814	2,24,1
*	6099	6089	247
*	6610	6547	287
946	950	939	370
		950	312
*	1032	1026	332
1165	1160	1178	352
1222	1224	1244	390
1414	1414	1407	372
1691	1706	1712	392
2104	2107	2093	3,11,2
	2377	2352	314
	2431	2428	334
2500	2532	2550	3,13,2
	2578	2581	354
		2616	3,15,0
3110	3099	3083	3,15,2
		3114	394
*	3171	3226	3,17,0
3517	3489	3495	3,11,4
*	5547	5512	3,23,0
*	6295	6290	3,13,6
*	7916	7885	3,27,2
		7962	318
*	8263	8296	3,25,4
*	8856	8881	3,21,6
*	9270	9287	3,27,4
1318	1316	1300	461
1942	1936	1910	4,10,1
		1930	423
2250	2253	2235	463
2866	2856	2824	4,14,1
		2844	4,10,3

Tuinstra	Present Work		
Q_o	Q_o	Q_c	<u>h</u> <u>k</u> <u>l</u>
3792	3774	3759	4,14,3
	3826	3800	425
4093	4036	4043	4,18,1
	4110	4105	465
4751	4719	4715	4,10,5
*	5639	5629	4,14,5
*	6472	6503	4,22,3
*	6957	6910	467
2250	2230	2233	660
2379	2372	2396	622
2707	2706	2701	662
2800	2823	2843	6,10,0
3284	3300	3311	6,10,2
3797	3807	3798	624
4172	4089	4103	664
	4202	4225	6,14,2
*	4762	4712	6,10,4
*	4923	4977	6,18,0
*	5484	5444	6,18,2
*	5640	5628	6,14,4
*	6171	6136	626
*	6521	6501	6,22,0
*	6952	6968	6,22,2
*	7070	7050	6,10,6
2732	**	2699	711
2808	**	2776	731
2950	**	2928	751
3470	**	3461	791
3712	**	3710	733
3867	**	3843	7,11,1
		3863	753
4136	**	4092	773
4337	**	4397	793
5414	**	5406	10,2,1
5550	**	5520	10,4,1
6017	**	5978	10,8,1

* 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.

References

GELLER, S. (1966). *Science*, **152**, 644.

LIND, M. D. & GELLER, S. (1969). *J. Chem. Phys*. In the press.

PRINS, J. A., SCHENK, J. & WACHTERS, L. H. J. (1957). *Physica*, **23**, 746.

PRINS, J. A. & TUINSTRA, F. (1963). *Physica*, **29**, 328, 884.

TUINSTRA, F. (1966). *Acta Cryst*. **20**, 341.

TUINSTRA, F. (1967). *Physica*, **34**, 113.

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