Pressure-Induced Phases of Sulfur

Abstract. *At least three phases of sulfur may be induced at pressures between 16 and 65 kilobars. A fibrous form obtained at pressures of 27 kilobars and higher appears to be closely related to the form obtained when plastic sulfur is chilled and stretched. Crystals of the fibrous form are orthorhombic with* $a = 13.8$, $b = 32.4$, *and* $c = 9.25$ *Å. Thus far the results are in accord with deductions made by Prins and co-workers that the sulfur atoms are arranged in helices with ten atoms and three turns per 13.8-Å period, and that these helices are essentially close-packed. The unit cell contains 16 ten-atom chain lengths. The probable space groups to which the crystal may belong are* $Ccmm$, $Cc2m$, *or* $Ccm2_1$. *These imply that the structure must contain both right- and left-handed helices and that at least half the helices have some disorder about their axes. The other two phases appear to have structures related to that of the fibrous form, but analyses of them has not progressed as far. One of these phases appears to be* ω*-sulfur.*

Three pressure-induced phases of sulfur have been obtained reproducibly, retained metastably at zero pressure for long periods of time, and have not been affected by long exposure to MoKα or CuKα x-irradiation. Two of these phases may have been obtained earlier by other means. Difficulties in obtaining good single crystals have thus far allowed us to determine lattice constant and space group data for only one of these phases. Partial information of this type has been obtained for another.

Specimens of 99.999+ percent sulfur (ASARCO grade A-58) were packed into tantalum or stainless steel containers and subjected to pressures to 65 kbar and temperatures to 1000°C in furnaces and piston cylinder devices similar to those described by others (*1*). To map phase boundaries, experiments were carried out with 1.25-cm (½-inch) diameter furnaces; 2.5-cm diameter furnaces were used in attempts to grow single crystals.

Table 1. Summary of experiments and produced phases. P, plastic.

Pressure (kbar)	Temp. annealed (°C)	Phases obtained
10	125	P + α
15	150	P + α
16	100	P + α
16	195	P + α + I
17.5	240	P + I
20	280	I
23.5	290	I
25	200	P†
25	250	P + III
27	150	P†
27	330	I + II
27	380	P‡
29	260	P + III
34	200	P†
34	275	P + II + III
34	350*	II
35	430	P‡
35	455	P‡
40	225	P†
40	260	P†
40	300	II
65	300	II

* After 3 hours at 350°C, the specimen was cooled to 130°C in 13 hours and then quenched. All others as in text. † Temperature too low to induce nucleation. ‡ Temperature probably above melting point.

In all cases the pressure-induced phases were obtained by first melting the sulfur at a given pressure, then reducing the temperature to points below melting and holding at these temperatures for 3 hours. If the annealing temperature was too low (Table 1), the specimen did not crystallize; on cooling and releasing pressure, the specimen was plastic. If the specimen was quenched from the melt and pressure was released, it was plastic also. In no case was a new form obtained if the specimen was not melted. The new forms may all be retained metastably for periods, thus far, in the range of several months and at least two of these (phases I and II) are not affected by exposure to MoKα and CuKα irradiation in excess of 200 hours.

Table 1 gives the results of our experiments with respect to the regions of existence of the high-pressure phases. In all cases a correction of 10 percent was made on the pressure for friction; pressures are probably good to ± 1 kbar. No correction was made for temperature, but most of these are probably good to 5°C (*2*). Chromel-alumel thermocouples were used.

At first, I made use of the melting diagram of Deaton and Blum (*3*), but after some experiments that gave the plastic form at temperatures at which this apparently should not have occurred, I was informed by Deaton and Ward (*4*) that they had redetermined part of this diagram with new results which were closer to those of Susse, Épain, and Vodar (*5*), and which made my results appear to be more plausible.

The highest pressure phase (II) is fibrous; phase I has a foliated texture: thin films of the material may be cleaved from crystals. No sizable crystals of phase III have as yet been obtained. The well-known orthorhombic phase α appears to be stable to about 16 kbar. Phase I exists in the pressure region of 16 to 27 kbar, phase II in the range $\geqq 27$ kbar, and phase III in the range ~ 25 to 34 kbar but at somewhat lower temperatures than phase I. All the pressure-induced phases were actually obtained in the temperature range 200° to 350°C.

The x-ray powder data (CuKα radiation) for phases I and II are given in Tables 2 and 3, respectively. All the phases are related; phase III has essentially the pattern of phase II, but with the following lines missing or much reduced in intensity, *d*-spacings: 3.53, 2.66, and 2.32 Å. Lines with spacing smaller than 2.32 Å are broader than those of phase I. The missing lines are definitely not a result of preferred orientation.

The crystals of phases I and II obtained with larger furnaces and longer annealing times were always twinned.

Table 2. Pressure-induced phase I sulfur and ω-sulfur. Abbreviations: w, weak; m, medium; s, strong; v, very; *I*, intensity; rel., relative.

Phase I		ω-Sulfur	
d (Å)	$I_{\rm rel.}$	*d* (Å)	$I_{\rm rel.}$
4.47	s	4.50	m-s
4.05	vs	4.02	s
3.53	vvs	3.56	s
3.04	vvs	3.07	s
2.66	m-s	2.71	vw
2.32	m	2.30	vw
2.24	w		
2.09	m-s	2.10	w
2.07	m		
2.02	m		
1.93	w-m		
1.88	w		
1.82	m		
1.78	m		
1.75	m		
1.72	vw		
1.69	w-m		
1.65	vw		
1.61	w-m		
1.57	w-m		
1.55	w		
1.53	m		
1.50	vw		
1.47	vw		
1.41	w		
1.33	m		

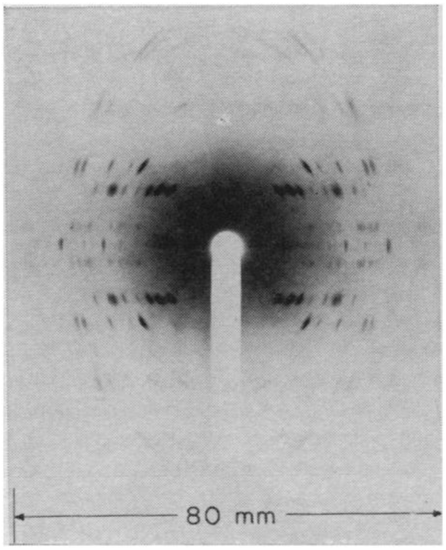

Fig. 1. Rotation photograph about fiber axis (a) of phase II (CuKα radiation, 57.3-mm diameter camera).

It has been possible, however, to determine the unit cell and probable space groups of phase II. The crystals are pseudohexagonal, but the diffraction symmetry appears to be *mmm*. The lattice constants are $a = 13.8$, $b = 32.4$, $c = 9.25$ Å (probably not better than to ± 0.5 percent). The powder pattern of phase II has been indexed on this basis (Table 3). For conciseness, the indices of those reflections not observed on the Weissenberg photographs (~ 24-hour exposures) have been omitted. The pseudohexagonal c-axis is in the a-direction which is the axis of the fibers.

The "single crystal" Weissenberg and Buerger precession camera patterns of phase II also indicate C-centering, that is, all reflections with $h + k \neq 2n$ are absent. Further, reflections $0kl$ are present only when k and l are both even. Thus the probable space groups are $C\,c\,m\,m$, $C\,c\,m\,2_1$, or $C\,c\,2\,m$.

A fibrous form of sulfur was discovered over 30 years ago by Trillat and Forestier (*6*), studied further by Meyer and Go (*7*), and elucidated by Prins, Schenk, and Wachters (*8*). The last authors found that the fibrous sulfur obtained by extending plastic sulfur consists of two crystalline constituents, only one of which is actually fibrous and which they designated Ψ-sulfur. The rotation photograph of these fibers shown by Prins *et al.* bears a close resemblance to the rotation photograph (Fig. 1) taken about the a-axis of a crystal of phase II. In our case, the coherent reflections are obtained to much larger Bragg angles than indicated by Prins *et al.* (*8*, fig. *d*).

We prepared some of the fibrous sulfur by extending plastic sulfur. The powder photograph of the Ψ-skeleton obtained after washing with CS_2 appeared to be very close to, but not precisely the same as, the photograph of phase II. A rotation photograph of the ϕ-sulfur (*8*) about the fiber axis showed the presence of the Ψ-phase. The superposition of the Ψ-phase photograph on the photograph of phase II was very close.

Thus the main deductions made by Prins *et al.* on the structure of Ψ-sulfur also apply to phase II, namely that there exist helical chains of sulfur atoms along the a-axis of 13.8 Å, this period including 10 sulfur atoms in 3 turns. Further, Prins *et al.* have deduced that, as in hexagonal Se, the helices are close-packed with side length (for S) equal to 4.7 Å. Our c-axis is 2×4.63 Å, and $b = 8 \times 4.05 \cong 8 \times 4.63 \times \frac{1}{2}\sqrt{3}$ Å. This implies that the unit cell of phase II contains 160 atoms and the x-ray density at atmospheric pressure is 2.06 g/cm^3 (slightly lower than that, 2.09 g/cm^3, of α-sulfur). The density of phase II was determined by obtaining a mixture of 1-bromo-2-iodobenzene and 1-chloro-3-iodobenzene in which pieces of phase II sulfur remained suspended. This mixture had a density of exactly 2.06 g/cm^3, further demonstrating the validity of the Prins *et al.* proposal. As indicated by Prins *et al.*, the pitch of the S helix is less than that of the Se helix, while the reverse is true of the helix radii. Because of the orthorhombic symmetry of phase II, we refer here only to an "average" pitch and radius.

In further experiments on the Ψ-phase, Prins and Tuinstra (*9*) have speculated on the possibility, which I think is reasonable, that the crystal may contain alternating left- and right-hand S helices. But our phase II does not appear to be monoclinic. Because the crystals are not yet very good, the rotation-photograph interlayer spacings are difficult to measure accurately. However, the data collected on Weissenberg and Buerger precession camera photographs indicate that the fiber axis most likely is 13.8 Å long (*9*).

The phase II twin-axis is the fiber axis (our a-axis) and the twinning repeats at very nearly 120° (Figs. 2 and 3). According to our axial lengths, the 001 plane makes an angle of almost 120° with the $02\bar{1}$ plane, the angle between the $02\bar{1}$ and 021 planes is about 119°, and the angle between the 010 and 021 plane is very nearly 120°. The 100 pinacoidal reflections of phase II are related to the 001 pinacoidal reflections of hexagonal Se. The transformation of indices from the hexagonal to the orthorhombic (related to the pseudoorthohexagonal) cell is: $8h_h + 4k_h = K_o$, $2k_h = L_o$. Thus the hexagonal $h00$ transform into the orthorhombic $0K0$, $K = 8n$ accounting for the presence only of $0K0$, for $K = 8n$. The hexagonal 010 transforms into the orthorhombic 042, 020, into 084, and so on, and these are the only orders of orthorhombic 021 present. The $\{080\}_o$ and $\{042\}_o$ reflections are by far the most intense among the $0KL$ reflections. Among the moderately intense reflections not orders of 010 or 021, the orthorhombic 0,20,2 derives from the hexagonal 210, the 0,16,4 from the 120. In brief, the $0KL$ reflections are present only when $L = 2n$ and $K = 4m$. Thus the hexagonal indices from which these derive are $h = \frac{1}{2}(m - n)$ and $k = n$. Of course, as is to be expected, there are some reflections present for which $m - n$ is odd.

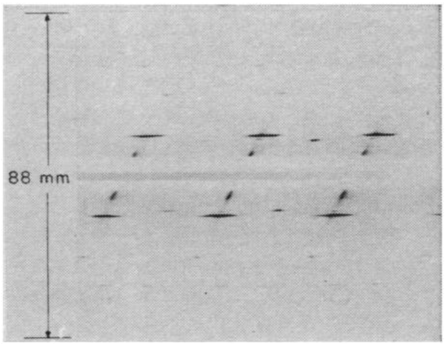

Fig. 2. Zeroth-layer Weissenberg photograph (CuKα radiation, 57.3-mm diameter camera) about the a-axis of phase II. Note the pseudohexagonal character and that one of the twins is much larger than the others.

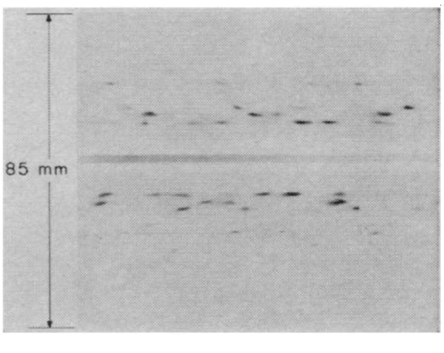

Fig. 3. Third-layer Weissenberg photograph (CuKα radiation) about the a-axis of phase II. The twinning is more evident because of larger deviation from hexagonality.

Examination of the possible space groups deriving from the systematically absent diffraction data (see above) leads to the conclusion that a structure consisting of S helices and the given unit cell could not belong to space group *C c m m*. In space group *C c* 2 *m*, all the S helices must be disordered about their axes, while in space group *C c m* 2_1, half the helices must be so disordered. Both these space groups, however, require the presence of both right- and left-handed helices. If the condition requiring a glide plane is relaxed, the additional possible space groups still do not permit packing of the S helices in a completely ordered manner. Partial disorder of S_8 puckered rings has been found in β-monoclinic sulfur. The evidence, therefore, appears to support the main ideas of the proposal made by Prins and coworkers regarding the nature of fibrous sulfur. Needless to say, the complete structure analysis is required for confirmation.

Table 3. Powder data for pressure-induced fibrous sulfur (phase II). CuKα radiation. Abbreviations: w, weak; m, medium; s, strong; v, very.

hkl	*d* (Å)		$I_{\mathrm{rel.}}$
	Calc.	Obs.	
002	4.63	4.59	vw*
310	4.55		
080	4.05	4.03	vvs*
042	4.02		
370	3.26		
191	3.26	3.24	m-s
312	3.25		
352	2.91	2.92	m
390	2.84	2.84	m
372	2.67	2.67	w-m*
392	2.42	2.41	vvw*
423	2.27	2.28	m*
3,11,2	2.19	2.18	vw*
463	2.12	2.11	vw
660	2.12		
0,16,0	2.03		
334	2.03	2.02	w*
084	2.01		
3,13,2	1.98	1.99	w-m
6,10,0	1.88		
4,14,1	1.88	1.88	vw†
4,10,3	1.87		
3,15,2	1.80		
394	1.79	1.79	w*
205	1.79		
175	1.70		
791	1.70	1.70	w*
3,11,4	1.69		
733	1.64		
2,16,3	1.64		
6,14,0	1.63		
195	1.63	1.63	w*
4,14,3	1.63		
624	1.62		
425	1.62		
7,11,1	1.61	1.61	w-m*
753	1.61		
1,17,3	1.61		
4,18,1	1.57		
773	1.56		
2,10,5	1.56		
664	1.56	1.56	w-m*
465	1.56		
1,11,5	1.56		
2,20,1	1.55		
10,0,1	1.36		
6,18,2	1.36		
3,23,0	1.35		
0,24,0	1.35		
992	1.35	1.35	w†
715	1.35		
10,4,1	1.35		
9,11,1	1.35		
2,16,5	1.34		
735	1.34		
0,12,6	1.34	1.34	w-m*
6,14,4	1.33		

* Broad. † Very broad.

The twinning of crystals and pseudosymmetry of phase I has thus far prevented a clear determination of its unit cell. It appears to be pseudotetragonal but may be monoclinic. The axis perpendicular (or almost so) to the principal cleavage plane is exactly equal in length to the *b*-axis of the fibrous form, that is, 32.4 Å. In fact, in both cases, reflections are present only when the order is equal to 8*n*. The other two (possibly pseudo) axes of phase I are very nearly equal with length $\approx$ 6.55 Å, that is, $\approx 4.6\sqrt{2}$ Å. It is probable that the eight-membered rings characteristic of the α-orthorhombic (*10*) and β-monoclinic (*11*) forms or the six-membered rings characteristic of the rhombohedral (*12*) form are not present in this modification. Inasmuch as it is highly unlikely that the S atoms have other than 2-coordination, it is probable that, because this form is film-like as contrasted with the fibrous nature of phase II, the sulfur-helix axes in the former, as in the latter, lie in planes perpendicular to the 32.4 Å axis, but are skew to each other from plane to plane.

The phase I or one very closely related to it is the "white sulfur" designated ω by Das (*13*) who prepared it by hydrolysis of S_2Cl_2. The spacings and relative intensities of the seven lines of Das' powder pattern agree well with those of the strongest lines of the powder pattern of phase I (Table 1).

We know least about phase III; it is even possible that it is not an equilibrium phase because experiments in larger furnaces involving longer annealing periods do not seem to produce it even under the same conditions of temperature and pressure as given in Table 1. But because it is so closely related to phase I, it is possible that it cocrystallizes with it, and perhaps this is one of the reasons that we have not yet been able to clarify phase I. We intend to continue the studies of these phases also.

Recently, a new high-pressure form of sulfur was reported by Bååk (*14*). While my experiments were not carried out by this technique, in several cases pressure and temperature in the appropriate region of Bååk's proposed phase diagram were reduced very rapidly. My experiments did not yield this form. I cannot argue that this is not a high-pressure form of sulfur simply because it was not reproduced. However, it must be pointed out that Bååk has not indexed his x-ray powder pattern properly; it is unlikely that the pattern is one of a cubic material or that a cubic modification of sulfur would exist except perhaps at ultra-high pressures. If indeed the S helices give greater packing efficiency at the moderately high pressures than any of the ring forms, it is difficult to see how such helices could be arranged in a cubic crystal so as to maximize density.

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References and Notes

1. G. C. Kennedy and P. N. LaMori, in *Progress in Very High Pressure Research*, F. P. Bundy, W. R. Hibbard, Jr., H. M. Strong, Eds. (Wiley, New York, 1961), pp. 304–13; G. C. Kennedy and R. C. Newton, in *Solids Under Pressure*, W. Paul and R. M. Warshauer, Eds. (McGraw-Hill, New York, 1963); F. R. Boyd and J. L. England, *J. Geophys. Res.* **65**, 741 (1960).
2. R. E. Hanneman and H. M. Strong, *J. Appl. Phys.* **36**, 523 (1965).
3. B. C. Deaton and F. A. Blum, Jr., *Phys. Rev.* **137**, A1131 (1965).
4. B. C. Deaton and K. B. Ward, in preparation.
5. C. Susse, R. Épain, B. Vodar, *Compt. Rend.* **258**, 4513 (1964).
6. J. J. Trillat and H. Forestier, *Bull. Soc. Chem. France* **51**, 248 (1932).
7. K. H. Meyer and Y. Go, *Helv. Chim. Acta* **17**, 1081 (1934).
8. J. A. Prins, J. Schenk, L. H. J. Wachters, *Physica* **23**, 746 (1957). See also J. A. Prins, J. Schenk, P. A. M. Hospel, *ibid.* **22**, 770 (1956); A. Liquori and A. Ripamonti, *Ricerca Sci.* **29**, 2186 (1959); L. Pauling, *Proc. Natl. Acad. Sci. U.S.* **35**, 495 (1949); M. L. Huggins, *J. Chem. Phys.* **13**, 37 (1945).
9. J. A. Prins and F. Tuinstra, *Physica* **29**, 328 (1963).
10. B. E. Warren and J. T. Burwell, *J. Chem. Phys.* **3**, 6 (1935). See also S. C. Abrahams, *Acta Cryst.* **8**, 661 (1955).
11. D. E. Sands, *J. Amer. Chem. Soc.* **87**, 1395 (1965).
12. J. Donohue, A. Caron, E. Goldish, *ibid.* **83**, 3748 (1961).
13. S. R. Das, *Indian J. Phys.* **12**, 163 (1938).
14. T. Bååk, *Science* **148**, 1220 (1965).
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