

## Pressure-Induced Phases of Sulfur

S. Geller

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**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  $Ccm$ ,  $Cc2m$ , 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  $\omega$ -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  $MoK_{\alpha}$  or  $CuK_{\alpha}$  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

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

Pressure (kbar)	Temp. annealed (°C)	Phases obtained
10	125	P + $\alpha$
15	150	P + $\alpha$
16	100	P + $\alpha$
16	195	P + $\alpha$ + 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.

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 ( $\frac{1}{2}$ -inch) diameter furnaces; 2.5-cm diameter furnaces were used in attempts to grow single crystals.

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  $MoK_{\alpha}$  and  $CuK_{\alpha}$  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  $\pm 1$  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  $\alpha$  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  $\geq 27$  kbar, and phase III in the range  $\sim 25$  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 ( $CuK_{\alpha}$  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  $\omega$ -sulfur. Abbreviations: w, weak; m, medium; s, strong; v, very; I, intensity; rel., relative.

Phase I		$\omega$ -Sulfur	
$d$ (Å)	$I_{rel.}$	$d$ (Å)	$I_{rel.}$
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		