

Pressure-induced structural phase transition in sulfur at 83 GPa

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The pressure-induced phase sequence of sulfur up to 90 GPa has been studied by an angle-dispersive x-ray-diffraction method. The orthorhombic sulfur (S-I) with S_8 cyclic molecules transforms to a high-pressure crystal phase (S-II) between 6 and 55 GPa. The second structural phase transition takes place at 83 ± 2 GPa. The highest-pressure phase (S-III) can be explained as a base-centered orthorhombic lattice. This lattice is isomorphous to that in the metallic high-pressure phase of selenium. Metallization for sulfur reported by Luo *et al.* is ascribed to the second transition.

Orthorhombic sulfur (S-I), a group VIb elemental material, is the most stable form of many modifications of sulfur under ambient conditions. The crystal consists of S_8 cyclic molecules with a van der Waals-like force and is an insulator with an energy gap of 2.89 eV. Efforts to pursue the pressure-induced metallization have been made by many investigators.¹⁻⁶ The recent high-pressure optical study on S by Luo *et al.*⁷ has shown a sudden increase of reflectivity between 88 and 95 GPa. They attributed this behavior to pressure-induced metallization. They also reported a discontinuous change in the absorption edge at 23 GPa. A high-pressure phase transition in sulfur has been reported from the results of x-ray⁸ and Raman^{8,9} studies in a pressure region from 15 to 30 GPa. But the structure of this high-pressure phase has not been determined.

On the other hand, sister elements Se and Te, under normal conditions, also form molecular crystals with a similar bond nature of S. The most stable form for both elements is the semiconducting hexagonal phase with a spiral chain structure. Recently, systematic studies on the crystal structure of Se under high pressure to 150 GPa have been conducted and five stages of structural phase transitions shown in Table I are revealed.¹⁰ The pressure-induced phase transitions of Se exhibit a similar sequence to those of Te.¹¹⁻¹³ The sequence corresponds to a change to a higher symmetry structure with an in-

crease in the coordination number, accompanied by the collapse of covalent and van der Waals bonds. Actually, both elements take place in a semiconductor to metal transition corresponding to the transition to a monoclinic phase with a layered structure.¹⁴ Such systematics in the high-pressure behavior of Se and Te is expected to be applicable to S.

In this paper, we show a high-pressure x-ray-diffraction experiment of S up to 90 GPa and report a pressure-induced phase transition to a base-centered orthorhombic structure at 83 ± 2 GPa.

The starting sample S was the orthorhombic form (S-I) with 99.9999% purity. A diamond-anvil cell was used for pressure generation. The powdered sample was placed into a 75- μm -diameter hole of a metal gasket (Udimet 700 of a Ni-based alloy) with a Au thin film of 2- μm thickness and a ruby chip, and was pressurized by diamond anvils with a central flat diameter of 150 μm , a bevel angle of 10° , and a culet diameter of 400 μm . Pressure was determined by the equation of state of Au.¹⁵ The ruby fluorescence method was also used as an additional pressure indicator. No pressure transmitting medium was used. The pressure gradient in the sample was estimated to be about ± 2 GPa at 89.4 GPa from the width of a half-maximum of the Au(111) diffraction line. High-pressure x-ray-diffraction experiments at room temperature were carried out by an angle-dispersive method by using an imaging plate detector. Powder x-ray patterns were obtained with a Mo $K\alpha$ from a rotating anode-type generator. A triple pinhole collimator with diameters of 300, 70, and 90 μm was inserted in the beam path between a graphite monochromator and a diamond-anvil cell. The obtained image data were read with a pixel size of 125 (μm)² and analyzed by using the MAC Science DIP system.¹⁶

Observed diffraction patterns to 90 GPa suggested two structural phase transitions. d values of diffraction lines in profiles are shown in Fig. 1 as a function of pressure. Profiles at 6.6 and 17.5 GPa were assigned to the orthorhombic phase (S-I). However, the intensity of diffraction lines, with increasing pressure, decreased and at 26.5 GPa no line could be recognized in the profile except for pressure markers or a metal gasket. The next pattern at

TABLE I. A sequence of pressure-induced structural phase transitions and transition pressures P_{tr} for Se and Te, respectively.

Element Phase	Se		Te	
	Structure	P_{tr} (GPa)	Structure	P_{tr} (GPa)
I	hexagonal		hexagonal	
II	intermediate	14	monoclinic	4
III	monoclinic	23	orthorhombic	6
IV	orthorhombic	28	β -Po type	11
V	β -Po type	60	bcc	27
VI	bcc	140		

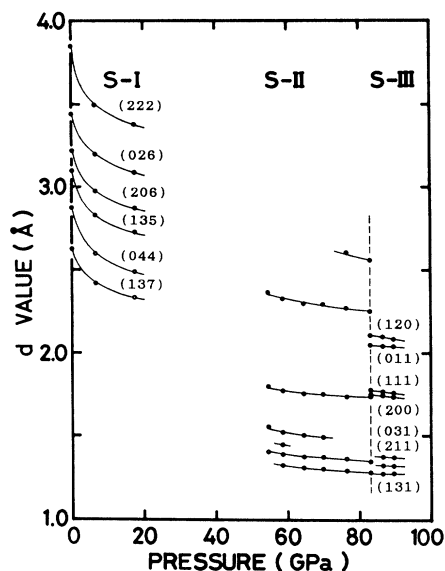


FIG. 1. d values of diffraction lines of sulfur are shown as a function of pressure. These results indicate two structural phase transitions at a pressure between 17.5 and 55 GPa, and at 83 GPa, respectively.

54.5 GPa indicated very spotty Bragg reflections like a single crystal. Three strong lines were observed in d spacing. These results suggest that the structural transition from S-I to a new high-pressure phase (S-II) at room temperature is accompanied by recrystallization and re-orientation. Further, at 82.8 ± 1.9 GPa, S-II transformed to a higher pressure phase (S-III), which gave uniform and smooth Debye rings. This paper concentrates on the structural transition from S-II to S-III. Full reports will be published elsewhere.

Figure 2 shows the x-ray-diffraction profiles at various pressures around the transition. Symbols S, Au, R, and G show lines from the sample S, the Au pressure marker, a ruby chip, and a metal gasket, respectively. The bottom profile at 76.3 ± 1.3 GPa comes from S-II. We can see two strong lines around $2\theta = 18$ and 23.5 , and two weak lines around $2\theta = 30$ and 32 . With increasing pressure, those lines become weak in intensity and new diffraction lines appear at 82.8 ± 1.9 GPa. At 89.4 ± 2 GPa, lines from S-II completely vanish and seven new lines for S-III are observed. These lines can be explained as an orthorhombic system. The system is satisfied with an extinction rule of a base-centered space lattice A^* . The lattice constants of the base-centered orthorhombic (bco) lattice at 89.4 ± 2 GPa are $a = 3.4696(36)$ Å, $b = 5.2422(68)$ Å, $c = 2.2202(34)$ Å, and $V = 40.38(15)$ Å³. These structural and diffraction data are summarized in Table II. These facts show an onset of the bco phase (S-III) at 82.8 ± 1.9 GPa. When the pressure was lowered, the transition was found to be reversible with a hysteresis of about 6 GPa. Coexistence of the two phases seen at 82.8 ± 1.9 and 86.4 ± 1.9 GPa is due to the nature of the first-order transition as well as the pressure distribution present in the sample.

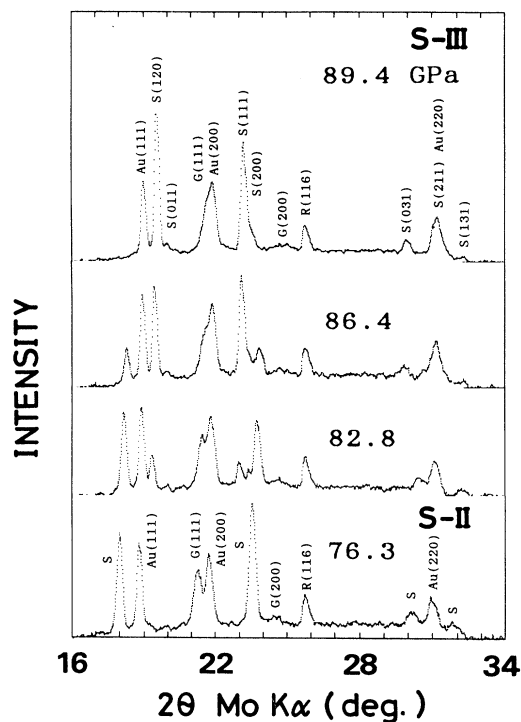


FIG. 2. Diffraction profiles around the transition from S-II to S-III (orthorhombic). Symbols S, Au, R, and G show lines from the sulfur sample, the Au pressure marker, a ruby chip, and a metal gasket, respectively. Exposure time of most runs was 20 h and the pattern at 89.4 GPa was obtained by adding up three runs.

The bco lattice of S-III exhibits a similarity with those of Se-IV (Ref. 10) and Te-III.¹² As compared with the lattice constants of S-III at 89.4 ± 2 GPa and Se-IV at 34.9 GPa [$a = 4.0054(16)$ Å, $b = 6.0572(58)$ Å, $c = 2.5881(13)$ Å], the ratio of each lattice constant, a_{Se}/a_S , b_{Se}/b_S , and c_{Se}/c_S , gives a unique value of

TABLE II. Powder-diffraction data for the high-pressure phase (S-III) of sulfur at 89.4 ± 2.0 GPa.

Lattice constants			Space group	
Orthorhombic			A^*	
			(Base centered)	
$a = 3.4696(36)$ Å				
$b = 5.2422(68)$ Å				
$c = 2.2202(34)$ Å				
$V = 40.38(15)$ Å ³				
$Z = 4$				
No.	d (obs)	hkl	d (cal)	Δd
1	2.0874	120	2.0915	-0.0041
2	2.0436	011	2.0444	-0.0008
3	1.7648	111	1.7614	0.0034
4	1.7379	200	1.7348	0.0031
5	1.3725	031	1.3732	-0.0007
6	1.3211	211	1.3228	-0.0017
7	1.2779	131	1.2768	-0.0011

1.161±0.005. This value corresponds to the ratio 1.15 of the bond lengths of Se and S under normal conditions (the bond lengths, Se-Se and S-S are 2.37 and 2.06 Å, respectively). Intensity ratios of diffraction lines of S-III also resemble those of Se-IV.¹⁰ Therefore, these facts suggest that the crystal structure of S-III is isomorphous to Se-IV. The proposed structure consists of a puckered layer.¹⁰ Each layer slides alternately by one-half along the *c* axis and stacks in the *b*-axis direction. The number of atoms in the unit cell *Z* is 4. Each atom has four neighbors in the layer. The atomic volume of S-III at 82.8±1.9 GPa is calculated to be 10.34(12) Å³. This value is 0.40 of that in S at normal pressure, 25.64 Å³, and is smaller than 13.2 Å³ in Se at 83 GPa.¹⁰

From visual observation under the metallurgical microscope, we see that the appearance of the sample has become even shinier than the metallic gasket after the S-II to S-III transition. The behavior has also been observed by Luo *et al.*⁷ They have reported that the change in the appearance of the sample corresponds to the sudden increase in reflectivity. The bco phases of Se and Te are metals with the superconducting transition temperature (*T_c*) (Ref. 14) of about 5 and 4 K, respectively. Therefore, S-III should also be metallic and a recent

report of the pressure-induced metallization by Luo *et al.*⁷ is attributed to the structural phase transition to S-III. Though the critical pressure of the structural transition to bco phase is slightly lower than that of metallization, considering the pressure gradient in the sample and their pressure determination method by the pressure-shifted ruby R-line luminescence from only one ruby chip, the difference is easily explained. According to a self-consistent pseudopotential calculation¹⁷ for the high-pressure monoclinic Te phase (Te-II), a configuration that the bond formed by each atom and its four nearest neighbors lie along nearly mutually perpendicular axes, leads to a metallic electronic state. Namely, the states forming collinear bonds along the *c* axis comprise four one-dimensional-like *p* bands, which cross the Fermi level along the direction from Γ to *Z* in the Brillouin zone. The proposed structure of S-III is satisfied with such an atomic configuration.

With the present assignment of the bco structures to S-III, a similarity to Se or Te was clarified. From the analogy to the result of Se,¹⁰ the critical pressure of the structural transition from the bco to the β -Po-type phase is estimated to be about 180 GPa. Research of the β -Po-type phase in S is in progress.

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