β-Po Phase of Sulfur at 162 GPa: X-Ray Diffraction Study to 212 GPa

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Using diamond anvil cell techniques and powerful synchrotron sources, we carried out an energy dispersive x-ray diffraction study on sulfur to 212 GPa and detected a transition to a new phase at 162 ± 5 GPa. This new phase has been indexed as the β-Po structure based on agreement with the d spacings and the measured diffraction peaks. This is consistent with the published results on high pressure phases of Se and Te. The Raman spectra of the fully recovered sulfur indicate permanent changes in the molecular structure. This paper represents the first experimental results in which a structural determination has been made for the low-atomic-number materials above 100 GPa.

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Two very recent high pressure studies of sulfur by Luo and Ruoff [1] using energy-dispersive x-ray diffraction (EDXD) techniques and Akahama, Kobayashi, and Kawamura [2] using the angle-dispersive x-ray diffraction method with an imaging plate detector have found an amorphous phase [1] and a base-centered orthorhombic (bco) phase [2] at about 25 and 83 ± 2 GPa, respectively. The phase transition observed by Akahama, Kobayashi, and Kawamura at 83 GPa is near to the previously reported pressure-induced metallization of sulfur at 95 GPa detected by the optical methods [3], although with a 12 GPa difference in the transition pressure, which could be due to the sensitivity of the experimental methods used and experimentalist's judgment in determining phase transition as well as some other factors, such as pressure calibration method. Thus, sulfur joins the other two VIA elements, selenium and tellurium, in exhibiting the bco structure under high pressure [4,5]. Experimentalists have found two other higher pressure phases, β-Po and body-centered cubic (bcc), for Se [4,6] and Te [7,8]. It is of considerable interest and an experimental challenge to search for a systematic phase transition sequence in sulfur. The β-Po phase was estimated (by analogy with Se) to occur in sulfur at about 180 GPa [2], and the bcc phase at multimegabars. Also, sulfur is a relatively low atomic number material for which the atomic scattering factor for x rays is small. Both of these make a megabar (1 Mbar = 100 GPa) x-ray diffraction study on sulfur difficult.

In this paper we present the x-ray diffraction results of sulfur to 212 GPa with emphasis on the phase transition above 100 GPa.

Sulfur powders of orthorhombic structure with a purity of 99.9995% were placed in a 50 μm diam sample chamber of a spring-steel gasket (1% C). Diamond anvils with 50 μm flats and 7.5° bevel angle reaching a culet diameter of 350 μm were used in the experiments. The gold acted as an internal pressure marker, and the pressures were determined by comparing the x-ray measured cell volume of the fcc Au based on its first three or four diffraction peaks to the isothermal equation of state of gold by Jamieson, Fritz, and Manghnani [9] deduced from shock-wave data. The experiments were performed at the Cornell High Energy Synchrotron Source (CHESS) using EDXD techniques. The diffraction angle was set at $2\theta = 17.01°$. Details of the experimental apparatus and techniques have been described in Refs. [10,11]. In addition, two experimental improvements have been made in the present experiments. One is on the collimation of the x-ray beam by use of a tungsten x-ray aperture of 20×20 μm size [12]. This helped us to avoid the presence of gasket diffraction peaks in the sample diffraction patterns and to reduce the pressure gradient effects [13]. The other improvement is on the Compton scattering slit [14]. By moving the slit closer to the sample at a distance of 50 mm and closing the slit down to 100 μm, we greatly decreased the background, which was mostly due to the Compton scattering from diamond anvils. This is crucial for this experiment above 100 GPa. The experiments were terminated without obtaining decompressing data because the scheduled time at CHESS ended. The Raman spectroscopic measurements on the totally recovered sulfur were taken on a triple monochromator (Spex model 1877C) equipped with a cooled optical multichannel detector. The 488 nm line of an A^+ laser was used to excite the Raman signals.

In agreement with Akahama, Kobayashi, and Kawamura [2], the recrystallization process from the amorphous phase of sulfur was observed starting at 37 GPa with a single intense peak at $E = 21.0$ keV. The second intense peak appeared at 42 GPa with $E = 23.3$ keV. Strong preferred orientations in the sample were present as a result of the recrystallization process. This process seemed completed at 75 GPa. A diffraction pattern at 78 GPa is shown in Fig. 1(a). The structure is unknown at this pressure.

With further increasing pressure, a phase transition to the bco structure was observed starting at 84 GPa [see Fig. 1(b)] that has been reported by Akahama, Kobayashi, and Kawamura [2]. However, our data showed that this phase transition was not completed until about 100 GPa because of the persistence of a peak from the

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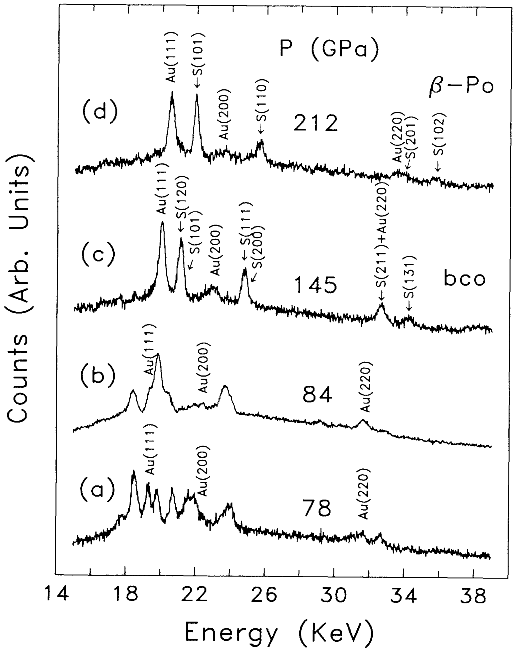

FIG. 1. Energy-dispersive x-ray diffraction spectra as taken at the CHESS for sulfur at four selected pressures. The diffraction angle (2θ) for all spectra was 17.01°. Symbols S and Au stand for sulfur and gold, respectively. (a) An unknown phase at 78 GPa, (b) mostly transformed phase (bco) at 84 GPa, (c) bco phase at 145 GPa, and (d) β-Po phase at 212 GPa.

previous phase at about 18.5 keV. A selected diffraction spectrum of the bco phase at 145 GPa is shown in Fig. 1(c). The lattice parameters of the bco structure at 145 GPa are $a=3.3093$ Å, $b=4.9698$ Å, $c=2.1446$ Å, $Z=4$, and $V_{\mathrm{atom}}=8.82$ Å^3/atom. For comparison, at ambient pressure the atomic volume of orthorhombic sulfur is $V_{\mathrm{atom}}=25.64$ Å^3/atom. The volume reduction at 145 GPa is 0.34.

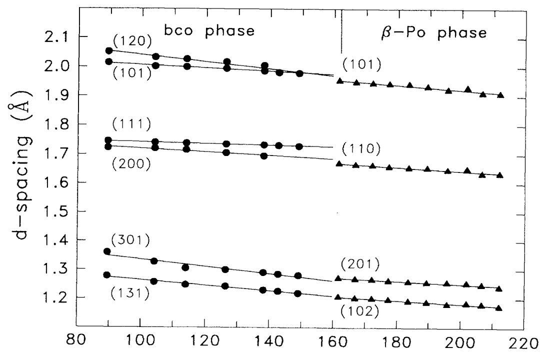

FIG. 2. Observed d spacings of diffraction peaks of sulfur above 85 GPa as a function of pressure. The data points are fitted by straight lines. A discontinuity of the data points was observed at 162 ± 5 GPa.

TABLE I. Observed and calculated d spacings for β-Po sulfur at 206.5 GPa. Referring to a hexagonal cell, $a=3.277$ Å, $c=2.584$ Å, $c/a=0.789$, and $V_{\mathrm{cell}}=24.03$ Å^3 with $Z=3$. This corresponds to a primitive rhombohedral cell with one atom and $a=2.079$ Å, $\alpha=104.03°$.

hkl	d_{obs} (Å)	d_{calc} (Å)
101	1.911	1.911
110	1.635	1.638
201	1.244	1.244
102	1.178	1.176

The diffraction spectra above 160 GPa were indexed as the β-Po structure, similar to that proposed for selenium in the pressure range of 60–140 GPa by Akahama, Kobayashi, and Kawamura [4]. The β-Po structure has a primitive rhombohedral cell containing one atom. Four to five peaks were observed and could be assigned to this phase. We referred the cell to the hexagonal cell that has 3 times the volume of the rhombohedral cell and contains three atoms. The diffraction patterns are analogous to those of the β-Po phase of Se presented in Ref. [4]. A typical diffraction pattern of the β-Po phase of sulfur at 212 GPa, the highest pressure attempted, is shown in Fig. 1(d). Figure 2 presents a plot of observed d values of diffraction lines above 85 GPa as a function of pressure. A discontinuity can be seen at around 162 GPa in Fig. 2. The bco to β-Po transition took place very gradually and subtly as the peaks at 21.1 and 24.7 keV of 145 GPa became a singlet. This beginning of the phase transition is set at 162 ± 5 GPa based on the following observations: (1) disappearance of the (101) and (200) peaks of the bco phase; (2) discontinuity in the relationship between d values and pressure (Fig. 2); and (3) volume per atom.

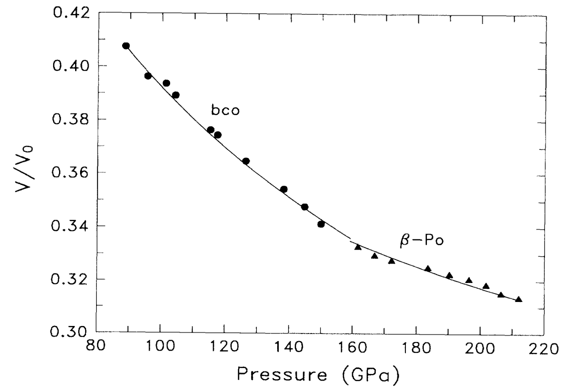

FIG. 3. Plot of the reduced atomic volume V/V_0 versus pressure for sulfur. Fits of the data points to first-order Birch equations are shown by the solid curves. Circles are for the bco phase, and triangles are for the β-Po phase. The atomic volume V_0 used here is 25.64 Å^3. The fitting parameters are listed in Table II.

TABLE II. Parameters obtained by a fit of the first-order Birch equation to the reduced atomic volume vs pressure data points of sulfur.

Phase	Pressure range (GPa)	B_0 (GPa)	B_0'	$(V/V_0)_{P=0}$
Orthorhombic	0–4.9	14.5	7	1
Monoclinic	5.3–24	17.3	5	0.76
Amorphous	25–37	⋯	⋯	⋯
Unknown	37–84	⋯	⋯	⋯
Base-centered orthorhombic	100–162	21.9	4	0.93
β-Po	162–212	30.6	6	0.67

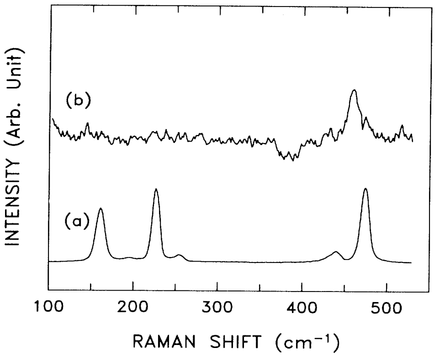

FIG. 4. Raman spectra of sulfur at ambient conditions. (a) Sample has not been compressed. (b) Sample has been compressed to 212 GPa and then decompressed to 0 GPa. Note that the above two spectra were taken under the same conditions except a higher laser power (3 times higher) was used for the recovered sample (b).

At 162 GPa, both bco and β-Po indices give the same atomic volume of 8.5 Å^3/atom.

Table I presents the indexing of the β-Po phase of sulfur at 207 GPa. At 207 GPa, the six coordinated S atom has its six nearest neighbors at a distance of 2.079 Å and two second nearest neighbors at 2.584 Å, and the volume reduction has reached a value of 0.31 compared to 0.39 at the beginning of the metallic phase at 95 GPa. The relation of the reduced atomic volume V/V_0 versus pressure above 85 GPa is plotted in Fig. 3 along with first order Birch [15] fits to the data points. The parameters fitted to the Birch equation are summarized in Table II together with our previous results for the low pressure phases [1]. The volume discontinuity at the bco to β-Po transition, if any, is negligible, indicating the transition is of a second order. The β-Po phase remains stable to at least 212 GPa.

With the observation of the β-Po phase in sulfur, the similarity in the transition sequence for the metallic phases of the Group VIB elements, S, Se, and Te, is confirmed, except for the eightfold coordinated bcc phase which has not been reached for sulfur. Based on the crystallographic analyses at the β-Po to bcc transition in Se [4] and Te [8], the ratio of the c/a in the β-Po phase needs to reach a critical value of 0.72. Our data show that the c/a ratio slowly decreases with increasing pressure at a rate of -1.23×10^{-4}/GPa, which indicates that the bcc phase will take place in the neighborhood of 700 GPa. For comparison, the corresponding rate for the β-Po Se is about -7.8×10^{-4}/GPa. This estimated pressure for sulfur to transform to the bcc phase sets an upper bound of the transition pressure if the volume change is continuous. From the view of atomic packing, the initial molecular crystal of sulfur has become a quasifourfold coordinated layered structure in the metallic bco phase, and then a sixfold coordinated monatomic β-Po structure. Table III summarizes the structural transition sequence in the metallic S, Se, and Te.

TABLE III. Comparison of transition pressures for S, Se, and Te in the metallic phases. All pressures are in gigapascal (GPa).

Element	bco	β-Po	bcc	Ref.
S	84	162	700^{a}	[2] and this work
Se	28	60	140	[4,6]
Te	6	11	27	[5,7,8]

^{a}The transition pressure for sulfur to the bcc phase is estimated as an upper bound from an extrapolation of the experimental c/a rate of this work.

The Raman spectrum of the totally recovered sulfur is shown in Fig. 4(b) along with a normal Raman pattern [Fig. 4(a)] of sulfur for comparison. Figure 4(b) shows no Raman modes in the region below 400 cm^{-1} and only two weak peaks above 400 cm^{-1} at 459.2 and 475.1 cm^{-1}, respectively, indicating permanent changes in the molecular structure. Apparently, the eight-atom ring type sulfur molecule no longer exists after the megabar compression and decompression. These two peaks are in the frequency range of the S-S stretching mode. It was also observed that the recovered sample was transparent.

In summary, similarity in the phase transition sequence between sulfur and the other two Group VIB elements, Se and Te, in the metallic phases has been confirmed up to the β-Po phase which occurs in sulfur at 162 ± 5 GPa. The initial eight-atom ring type molecular solid of sulfur is a monatomic metal with six nearest neighbors above 162 GPa.

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[1] H. Luo and A. L. Ruoff, Phys. Rev. B **48**, 569 (1993).
[2] Y. Akahama, M. Kobayashi, and H. Kawamura, Phys.

Rev. B **48**, 6862 (1993).

[3] H. Luo, S. Desgreniers, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. Lett. **67**, 2998 (1991).

[4] Y. Akahama, M. Kobayashi, and H. Kawamura, Phys. Rev. B **47**, 20 (1993).

[5] K. Aoki, O. Shimomura, and S. Minomura, J. Phys. Soc. Jpn. **48**, 803 (1980).

[6] G. Parthasarathy and W. B. Holzapfel, Phys. Rev. B **38**, 10 105 (1988).

[7] J. C. Jamieson and D. B. McWhan, J. Chem. Phys. **43**, 1149 (1965).

[8] G. Parthasarathy and W. B. Holzapfel, Phys. Rev. B **37**, 8499 (1988).

[9] J. C. Jamieson, J. Fritz, and M. H. Manghnani, Adv. Earth Planet. Sci. **12**, 27 (1980).

[10] M. Baublitz, Jr., V. Arnold, and A. L. Ruoff, Rev. Sci. Instrum. **52**, 1616 (1981).

[11] K. E. Brister, Y. K. Vohra, and A. L. Ruoff, Rev. Sci. Instrum. **57**, 2560 (1986).

[12] A. L. Ruoff, H. Luo, C. Vanderborgh, H. Xia, and V. Arnold (to be published).

[13] A. L. Ruoff, H. Xia, and Q. Xia, Rev. Sci. Instrum. **63**, 4342 (1992).

[14] R. G. Greene, H. Luo, and A. L. Ruoff (to be published).

[15] F. Birch, J. Geophys. Res. **83**, 1257 (1978).