High-pressure phases of sulfur: crystal structure prediction and topological analysis

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Abstract

High-pressure behaviour of sulfur above 100 GPa is studied with density functional theory (DFT) and evolutionary structure prediction algorithms. Based on DFT calculations energetical relations between experimentally fixed S-III, S-V and β-Po are determined. S-V is found to be the lower pressure phase transforming to S-III at 90 Gpa. The second order character of transformation from S-III to β-Po is theoretically approved and calculations yield a value of around 300 Gpa for the transition pressure at 0 K. β-Po structure is not stable in trigonal symmetry below this pressure and spontaneously transforms in monoclinic structure identical to S-III. The calculations yield values of 333 Gpa and 460 Gpa for the transitions from β-Po to simple cubic and from simple cubic to body centered cubic structures respectively. Crystal structure prediction method let to reveal a new phase, named S-V(II), which is energetically more favourable than S-III above 100 GPa.

Introduction

High pressure investigation of sulfur as well as other group VI elements attracts considerable interest of physicists and crystallographers due to metallization of the initially covalent S-S bonds [1-3], transition from insulator through semiconductor to superconductor [4-6], occurrence of several monoclinic and triclinic phases [7, 8], pressure dependent incommensurate modulations [7, 8] and amorphization [2, 3, 9, 10]. Being the leader among elements by amount of different polymorphs under ambient conditions [11] it is probably preserves among leaders in high pressure region, although the number of polymorphs is drastically decreases.

The well-known orthorhombic structure of α-S, comprising of S_8 rings, [12] is stable up to 20-30 Gpa and became gradually amorphous on further compression [2, 3, 10]. Recrystallization starts around 37 Gpa [3] and fully completes only at 75 Gpa [3]. Sulfur recrystallize in structure with tetragonal helic (4_1 and 4_3) chains of sulfur atoms [13, 14], named S-II. Unfortunately, different authors use different numerical notations of high-pressure phases of sulfur. For example, the same phase denoted as S-III by Hejny and co-authors [7] and as S-IV by Degtyareva and co-authors [8]. In this work we will follow the notation of Hejny and co-authors [7]. Further compression of S-II leads to crystallizations of S-III at 83-86 GPa. Based on assumption on orthorhombic symmetry and type of centering of the unit cell this phase was named *bco* (body-centered orthorhombic). Zakharov and co-authors [4] were first who indicate on probable mistake in symmetry determination of S-III, showed that in the orthorhombic model the energy of this phase is higher than the energy β-Po in all pressure range. Then Nishikawa and coauthors [15] based on symmetry and density of state considerations make assumption about monoclinic character of S-III. This assumption was experimentally confirmed by Hejny and co-authors [7] and Degtyareva and co-authors [14]. In addition the incommensurately modulated character of S-III was revealed in these experiments. As the assumption about orthorhombic character of S-III turns out to be wrong, *bco* designation was changed to *bcm* (body-centered monoclinic). Our results on crystal structure prediction confirms a monoclinic character of this phase. The additional triclinic phase S-V, appearing on decompression of S-III around 90 GPa and traced down to 62 Gpa, was fixed by Hejny and co-authors [7]. Structural relations of S-V phase with S-III was not still analysed. We present this analysis complemented by ab-initio calculations in the present work. On further compression S-III transforms to β-Po at 153-162 Gpa [3, 8]. β-Po was experimentally traced up to 212 Gpa [8] and further high-pressure region is investigated only theoretically. According to theoretical results β-Po structure first transforms to simple cubic (*sc*) structure and then to body-centered cubic (*bcc*) structure at 280 Gpa and 540 Gpa respectively [5, 6].

Details of calculations

Crystal structure prediction performed on the basis of evolutionary algorithms implemented in USPEX (Universal Structure Predictor: Evolutionary Xtallography) package [16-20]. Local optimization performed in the frame of DFT theory with VASP code [21, 22], using the plane wave basis set and projector augmented wave method [23]. Exchange-correlation effects were taken into account in the generalized gradient approximation (GGA) by the Perdew–Burke–Ernzerhof (PBE) functional [24]. For the crystal structure searches, we used a plane-wave basis set cutoff of 350 eV and performed the BZ integrations using uniform Gamma-centred k-

point meshes with a k-point grid of spacing $2\pi \times 0.035\,\text{Å}^{-1}$. Iterative relaxation of atomic positions was stopped when all forces were smaller than $0.001\,\text{eV}\,\text{Å}^{-1}$. Calculations were carried out for 100, 200, 300, 400 and 500 GPa with 8 atoms per unit cell. Temperature in all calculations was 0 K. Phonon dispersion curves were calculated in PHONOPY package [25]. Topological analysis was performed with TOPOSPro package [26-28].

Results and discussion

Structures descriptions and ab-initio calculations of S-III, S-V and β-Po structures

In S-III, S-V and β-Po structures each sulfur atom has six strong and eight weak contacts with neighbouring atoms. The structure representation corresponding to the first set of bonds is the stacking of ideal, in the case of β-Po, or deformed, in the cases of S-III and S-V rhombohedrons. Structure representation corresponding to the second set of bonds is the stacking of deformed body-centered cubes. The second structure representation is useful for crystallographic description of the transitions from this family of structures to *bcc* structure, as in such representation this transitions corresponds to transformation of deformed *bcc* structure to ideal one. The first representation is useful for description of transitions between closely related S-III, S-V and β-Po structures.

To transform rhombohedral β-Po structure into S-III, it should be stretched along one of the two-fold axes or mirror planes. As the result of such deformation the symmetry decreases from trigonal to monoclinic and the lengths of the edges adopt two different values: 2.208 Å and 2.225 Å (Fig.1a). The difference between length of edges of such pseudorhombohedron does not exceed 1% of the smallest value. As well as S-III, S-V can be represented as deformed β-Po structure, but the deformation is more complex in this case and reduce trigonal symmetry to triclinic. The difference between pseudorhombohedron edges of S-V is much higher than that for S-III and achieves 18% (Fig.1b).

Figure 1. Deformed rhombohedrons outlined by the strong bonds of structures (a) S-III, (b) S-V, (c) S-V(II). Numbers under bonds corresponds to bond lengths in Å. Structural data are taken from [29] for S-III and from our calculations for S-V(II).

To clarify the influence of deformation on energy of β-Po structures, we perform *ab-initio* density functional theory calculations on S-III [7], S-V [7] and β-Po [8] structures in the pressure range 0-500 GPa. The effect of modulations was not concerned and calculations of S-III structure were

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performed with average model. The analysis of phases is limited to the lower boundary on pressure around 30-40 Gpa. Below this pressure structures became unstable and their energy starts to increase rapidly. This can be clearly seen from dependence of cell parameters of S-III on pressure which is presented in *Supplementary*. This probably corresponds to amorphization, which was experimentally fixed nearly at the same pressure. The transition from S-III to S-V was reproduced at 90 Gpa, but the energy difference between S-III and S-V is very small, around several thousandths of eV. This small difference explain the joint occurrence of S-V and S-III in high-pressure experiments. As was shown by Nishikawa [1] the energy of modulated S-III structure is lower than that of unmodulated S-III, hence the transformation from S-V to modulated S-III should be slightly lower than presented value, 90 GPa. Taking into account this correction the calculated value of pressure for transition from S-V to S-III is in good agreement with experimental value, 83-86 Gpa.

Optimization of β-Po structure shows that in trigonal symmetry it can exist only above 300 Gpa, below this pressure the symmetry of the optimized structure is monoclinic with space group *C*2/*m* (Fig.2). This monoclinic structure is identical to S-III. For comparison, at 100 Gpa the space group and unit cell parameters of monoclinic β-Po is *C*2/*m*, a=2.769Å, b=3.445Å, c=2.261Å, β=112.483° and of S-III is *C*2/*m*, a=2.804Å, b=3.455Å, c=2.208Å, β=113.24°. The deviation from trigonal symetry increases with decreasing pressure. For example, at 290 Gpa the difference between edges of rhombohedron is 0.005%, at 100 Gpa this value reaches 2.3 % [1]. Thus according to our calculations transition from S-III to β-Po is a continuous second-order transition, completing around 300 GPa. The second order character of this transition is confirmed by experimental results [8]. However, the experimental value of pressure for this transition is almost two time lower than that determined in calculations. This difference can be attributed to the influence of temperature, the effect of which was not considered in our calculations. As structural difference between S-III and β-Po is very small and slight deformation can transform one structure into another, the small contribution of entropic member into Gibbs energy can be crucial and change phase relations determined at 0 K, made more symmetrical β-Po phase more favourable. As the result the transition pressure can be sufficiently decreased.

Figure 2. The dependence of *a*- and *c*–axis of β-Po on pressure in rhombohedral setting; *b*-axis is equal to *c*-axis.

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[1] This value is different from value of 1% mentioned above because this value is based on theoretical results and 1% - on experimental results

Crystal structure prediction

Among three structures experimentally fixed around 100 Gpa, S-III, S-V and β-Po, two lasts were found in our crystal structure prediction calculations at 100 GPa. In addition, one new structure, designated as S-V(II), was found at this pressure. The choice of the name is explained by the fact, that this structure is characterized by the same triclinic symmetry as S-V and can be presented as deformed β-Po structure. The deformation is higher than that of S-III but less than that of S-V, thus structurally S-V(II) occupies the intermediate place between S-III and S-V (Fig.1). For example at 100 Gpa, the difference between edges of rhombohedron formed by S-S bonds is 18% for S-V, 8.6% for S-V(II), and 2.3% for S-III (Fig.1). The new phase is more favourable than both S-V and S-III above 100 Gpa (Fig.3). The maximum difference in energy between S-V(II) and S-III, S-V is reached around 200 Gpa and it is equal to 0.007 eV/atom for difference between S-V(II) and S-III, and 0.01 eV/atom for difference between S-V(II) and S-V (Fig.3). The calculation of phonon dispersion curves, presented in the *Supplementary*, shows the dynamical stability of the new phase. Despite the fact, that predicted S-V(II) phase was not found in high-pressure experiments, there is a possibility of its missing in experiments due to its similarity to S-III and S-V structures and complex character of diffraction pattern of incommensurately modulated S-III. *But irrespectively of possibility of experimental synthesis of S-V(II), the fact of its theoretical existence shows that two known type of deformation of β-Po structure, S-III and S-V, are not unique and exist at least one other type of deformation which is even more favourable energetically than known S-III and S-V.*

Figure 3. Energetical relations of predicted and experimental phases (a) below and (b) above 300 Gpa .

The calculations at 200, 300, 400 and 500 Gpa reveal known β-Po, *sc* and *bcc* as the most energetically favourable. Any new phases was not found in this calculations. *The absence of the new phases in calculations at 200-500 Gpa shows that phase diagram inferred from the analogy with other group VI elements is quite complete and future synthesis of the new phases with less than 8 atoms in the unit cell in this pressure range seems unlikely.* According to our calculations, that transition pressure from β-Po to *sc* is 333 Gpa, from sc to bcc – 460 Gpa (fig.3). While transition from β-Po to open *sc* structure at such high pressure [6] is unusual it has a strict analogy with other group VI element, polonium, which under heating to 348 K transforms from sc to β-

Po structure [30-32]. Thus unique for element under ambient conditions *sc* structure has one more unique occurrence under high-pressure.

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