Electronic structure of sulfur under high pressure

Atsushi Nishikawa
Chiba-Keizai College, 4-3-30 Todoroki-cho, Inage-ku, Chiba 263-0021, Japan
E-mail: nisikawa@chiba-kc.ac.jp

Abstract. We have calculated the bandstructures and the total energies of the high-pressure phases of sulfur by means of the full potential linearized APW (FP-LAPW) method to investigate the structural stability. The tetragonal sulfur-II phase with spiral chain structure is a semiconductor with narrow energy gap, whereas the monoclinic sulfur-III with incommensurate modulation is metallic and the modulation yields a large dip near the Fermi-level of the density of states and contributes to the lowering of the bandstructure energy.

1. Introduction
Sulfur, selenium, and tellurium of the group-VIb elements undergo pressure-induced successive structural phase transitions and also show insulator-metal transition under pressure. Numerous high-pressure forms are reported for these elements, and they have the similar structure sequence under high pressure, and it is found very recently that they have the same incommensurately modulated monoclinic structure under pressure.

Sulfur forms a stable orthorhombic structure, sulfur-I (S-I), consisting of $\text{S}_8$ ring molecules at ambient conditions[1], and this orthorhombic form undergoes a gradual transition to an amorphous form above 20 GPa on compressing at room temperature[2]. Recrystallization is occurred on further compression around 35 GPa, and the sulfur-II (S-II) is a body-centered tetragonal structure with unique spiral chains of $4_1$ and $4_3$ screw, and is made up of 16 atoms in the unit cell[3].

A further phase transition to sulfur-III (S-III) is observed at 83-86 GPa, and though S-III was reported to have a base-centered orthorhombic structure[4],[5], S-III is very recently found to be isostructural with Te-III and Se-IV, and has a body-centered monoclinic structure with incommensurate modulation[6],[7]. Hejney et al. also found a previously unreported phase between S-II and S-III on pressure decrease, and this phase is the same triclinic structure as Te-II and Se-III[6]. On further pressure increase S-III transforms to the rhombohedral $\beta$-Po structure at 162 GPa, and this phase is stable to at least 212 GPa[4],[5]. The electrical property of S-II is a semiconductor, and that of S-III is a metal[8].

The purpose of this report is to investigate the electronic structure and the structural stability of S-II and S-III, and this is the first calculation on the complex structure of S-II from first principles.

2. Calculation
We have investigated the band structures and the total energies of high pressure phases of sulfur by means of the full-potential linearized augmented plane wave (FP-LAPW) method.
implemented in WIEN2k code [9] within the local spin density approximation (LSDA) [10]. The plane-wave cut-off energy is set for 14 Ry, and we have used 99 – 385 k-sampling points in the irreducible Brillouin zone for the self-consistent cycle and the total energy is converged within 0.1 mRy.

We have first of all calculated the electronic structure of the body-centered tetragonal structure of S-II. The lattice constants and the positions of atoms are taken from the experiments[3].

We then calculated the electronic structure of the unmodulated monoclinic structure of S-III[6],[7]. The observed incommensurate monoclinic structure of S-III is characterized by the incommensurate wave vector \( \vec{q} = (0, q, 0) \), \( q = 0.28 \sim 0.30 \). Thus we adopt the \( 1 \times 3 \times 1 \) supercells for a model of the modulated structure of S-III, the \( b \) axis of which is tripled in length of the original monoclinic cell with some displacements of atoms in the \( ac \) plane to investigate the effect of the modulation on the band structure.

3. Results and Discussion

We have shown the electronic band structure and the density of states of the body-centered tetragonal structure of S-II in Fig. 1. The space group is \( D^{2h}_{2h} \) (\( I4_1/acd \)), and the lattice constants are set to \( a = 7.841 \) Å and \( c = 3.100 \) Å. Sulfur atoms are in the 16f positions of \((x, x, 1/4)\) with \( x = 0.136 \) in the unit cell [3]. The calculated bands have a narrow indirect gap \( E_g \sim 0.025 \) Ry (0.34 eV). The lower eight bands are mainly originating from 3s-orbitals of S, and above bands are mainly originating from 3p-orbitals and they also contain 3d-orbitals slightly. This valence bands have splitted into two parts and the Fermi-level is just located in the energy gap, and thus sulfur-II phase is a semiconductor.

![Figure 1. Band structure and density of states of the body-centered tetragonal S-II. The lattice parameters are taken from the experiments; \( a = 7.841 \) Å and \( c = 3.100 \) Å. The broken lines in the band gap denote the Fermi-level.](image)

The valence electron density plotted in the (100) plane of S-II is shown in Fig. 2. The numbers give the values of the density along lines of constant density in units of electrons per cubic angstrom. The first nearest neighbor S-S distance (1.95 Å) is depicted with sticks and the second nearest neighbor distance (2.64 Å) is drawn with dashed lines.

![Figure 2. Electron density in the (100) plane of S-II. The numbers give the values of the density along lines of constant density in units of electrons per cubic angstrom. The first nearest neighbor S-S distance (1.95 Å) is depicted with sticks and the second nearest neighbor distance (2.64 Å) is drawn with dashed lines.](image)
the ring molecule of $S_8$ in S-I is 2.05 Å, and the first nearest neighbor distance is almost same between S-I and S-II.

We have next shown the electronic band structure and the density of states of the body-centered monoclinic sulfur in Fig. 3. The lattice constants are set to $a = 2.802$ Å, $b = 3.455$ Å, $c = 2.208$ Å, and $\alpha = 90^\circ, \beta = 113.15^\circ, \gamma = 90^\circ$ with two atoms in the unit cell. The lower two bands are mainly originating from 3s-orbitals of S and the above bands are mainly originating from 3p-orbitals. The latter bands have some peaks in the density of states and the Fermi-level is located in the middle of the broad peak. Though there are two first nearest neighbor atoms in the distance of 1.95 Å, and four second nearest neighbor atoms in the distance of 2.64 Å in different chains in S-II, in monoclinic S-III without modulation two atoms are in the distance of 2.208 Å and four atoms are in the distance of 2.225 Å. Therefore the coordination number is nearly six.

![Fig 3. Band structure and density of states of the monoclinic S-III. The lattice parameters are taken from the experiments. The horizontal lines at about 1.2 Ry denote the Fermi-level.](image)

![Fig 4. Band structure and density of states of the modulated structure of S-III. The modulation period along b axis is three times as long as the b lattice parameter of the monoclinic S-III.](image)

We have then calculated the electronic structure and the total energy of the modulated structure, the lattice constants of which are set to $a = 2.802$ Å, $b = 10.365$ Å, $c = 2.208$ Å, and $\alpha = 90^\circ, \beta = 113.15^\circ, \gamma = 90^\circ$ with six atoms in the unit cell, and the band structure and the density of states are shown in Fig. 4.

Since the $b$ axis is tripled in length, the bands on the $k_y$ axis are folded, and the modulation also affects the distances to the nearest-neighbor atoms. While the distance to the two nearest neighbor atoms at 2.208 Å corresponds to the lattice constant of c-axis and is therefore unaffected by the modulation, the four atoms at 2.225 Å assume different distances in the modulated structure in the range 2.089 Å to 2.425 Å. Thus the band gap yields on the $k_y$ axis ($\Gamma - Y$) near the Fermi-level. This yields a large dip in the density of states at 1.25 Ry just above the Fermi level. The Fermi-level is just located in the dip, and it suggests that the band structure energy of the modulated structure should be lower than that of the original monoclinic structure. The calculated total energy of the modulated structure is slightly lower than that of the monoclinic S-III.

In summary, S-II is a semiconductor with strong covalent bonds in the intrachain atoms, and S-III is metallic and the modulation contributes to the lowering of the band structure energy and yields the structural stability.
Acknowledgments
Part of the calculation in this research were performed using supercomputing resources at Information Synergy Center, Tohoku University.

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