Structural Study of Solid Hydrogen Sulfide under High Pressure

H. Fujihisa, K. Aoki, H. Yamawaki, and M. Sakashita
National Institute of Materials and Chemical Research
1-1 Higashi, Tsukuba 305, Japan

An x-ray powder diffraction experiment on solid H_2S was performed with a diamond anvil cell and an image plate to determine the unknown structures of phases I' and IV up to 25 GPa at room temperature. The structures of phases I' and IV were found to be cubic $T^4 - P2_13$ and tetragonal $D_{4h}^{20} - I4_1/acd$, respectively. In phase I', the H_2S molecule had 6-fold asymmetric coordination which brought a displacement from face-center. In phase IV, the molecules were found to form spiral chains along the c axis with partial loss of molecularity. The chains were linked by hydrogen bonds.
[hydrogen sulfide, hydrogen bond, phase transition, structure, pressure]

1. Introduction

Hydrogen sulfide H_2S forms a molecular solid in which the molecules are bound by hydrogen bonds as H_2O molecules in ice. The P-T phase diagram of H_2S is very different from that of H_2O ice in spite of the similarities in their molecular structures and hydrogen bonds. Many high pressure studies have been done intensively in the last five years.

Five crystalline phases are known under pressure at room temperature as follows: (1) Phase I between 0.47 to 8 GPa has an fcc ($O_h^5 - Fm\bar{3}m$) structure with orientationally disordered hydrogen bonds. (2) Phase I', which has been found by an x-ray experiment between 8 and 11 GPa at room temperature, has a primitive cubic lattice ($T^4 - P2_13$) [1], but its atomic parameter has not been determined yet. (3) Phase IV is shown to exist above 11 GPa [2], which has thin yellow color. It is stable over an extended temperature region from 30 to 300 K under high pressure [3]. Its structure is still unknown. (4) Phase V has been found by an x-ray experiment above 27.5 GPa [4] at room temperature. The color of phase V is black. An infrared (IR) absorption measurement [5] has shown presence of hydrogen bond system in phase V to 45 GPa. (5) Our recent IR experiment up to 100 GPa has revealed a transition to phase VI with dissociation of H_2S molecules above 46 GPa [6]. We have also found that H_2S becomes metallic around 96 GPa.

The optical properties have been intensively studied for solid H_2S under pressure, however, the structures have remained very uncertain. Therefore we started an x-ray powder diffraction experiment on H_2S with a diamond anvil cell (DAC) and Rietveld analysis. In the present study, we focused on phases I' and IV, and discussed their structural features.

2. Experimental

We prepared H_2S powder specimen as follows: Gaseous H_2S was introduced in a stainless steel bowl cooled to 77 K and was solidified in the bowl. Then it was ground into fine powders and was subsequently mounted on a gasketed diamond anvil cooled down to 77 K. The DAC was immediately closed and pressurized to a few GPa. This specimen loading procedure

was carried out in a gaseous nitrogen atmosphere. We tightened screw the DAC's piston up little by little to keep the pressure sufficiently far from a melting curve on the P-T phase diagram. The finely ground powder could be neither melt nor recrystallized in this process, and was able to be retrieved at room temperature. The gasket hole size was 180 μm in diameter and 120 μm in thickness.

Angle dispersive powder patterns were taken with a rotating-anode x-ray generator (Mo-K α), a pyrolytic graphite monochromator, a pin-hole collimator (80 $\mu\text{m}\phi$), and an image plate detector. The average exposure time for each pattern was 24 hours. All x-ray measurements were carried out at room temperature. A scanned image had a resolution of 50x50 μm^2 per one pixel and contained 2300x2300 pixels. Smooth Debye-Scherrer rings without spots were obtained as insets of Fig. 1.

Fig. 1. Rietveld analyses of H_2S for phase I' at 9.5 GPa (top) and for phase IV at 14.0 GPa (bottom). Insets are parts of raw diffraction image before integration.

3. Analysis

Two-dimensional diffraction images were integrated along the ring direction with an adequate 2θ step. The pattern of phase I' at 9.5 GPa was explained well only with cubic space group $T^4 - P2_13$ as described in Ref. 1. The lattice and atomic parameters of sulfur were determined to be $a_f = 4.931$ and S 4a : ($x=0.240\pm0.005$, x , x), respectively, as the top of Fig. 1. The sulfur position in phase I' has a small displacement along $\langle 111 \rangle$ direction when compared with an exact face-centered position as in phase I. The bottom of Fig. 1 represents a pattern of phase IV obtained at 14.0 GPa. All peaks were well indexed by tetragonal cell $a_{IV} = 6.850$ and $c_{IV} = 9.203$. Its space group was determined to be $D_{4h}^{20} - I4_1/acd$. The unit cell contains sixteen H_2S molecules and corresponds to that obtained by multiplying the cubic cell of phases I and I' by $\sqrt{2} \times \sqrt{2} \times 2$. Its atomic parameter at 14.0 GPa was determined to be S 16e : ($1/4$, $y=0.044\pm0.005$, $1/8$) in cell choice 1.

Figure 2 represents the pressure dependence of twelve neighboring interatomic distances of sulfur. A nearest S-S distance in phase I ($3.544 \text{ \AA}$: 12-fold at 8 GPa) split into two components (3.419 and $3.558 \text{ \AA}$: 6-fold for each) in phase I' at 9.5 GPa. They split again in phase IV, (3.048 , 3.367 , 3.425 , 3.477 and $3.659 \text{ \AA}$: 2-, 4-, 2-, 2-, and 2-fold for each) at 14.0 GPa, suggesting complex arrangement of H_2S molecules.

4. Discussion

We examine the atomic positions of hydrogen in phases I' and IV based on the positions of sulfur. A structural model of phase I' is displayed in Fig. 3. Sulfur atoms are put on the site of S 4a: ($x=0.240$, x , x) which was experimentally determined by

Rietveld analysis. We assumed that hydrogen atoms are located on the lines between the first nearest S-S distance ($3.419 \text{ \AA}$: 6-fold) and at S-H distance of $1.3 \text{ \AA}$. Then the positions of hydrogen atoms are given with sites of H1 12b : ($x=0.430$, $y=0.248$, $z=0.058$) and H2 12b : (0.050 , 0.248 , 0.058) as drawn with dark and light grays in Fig. 3, respectively. Molecules should be flipping (not ordered) to occupy these sites with an equal probability of one third to keep the first nearest S-S distance 6-fold. Such disordering in phase I' was suggested by a Raman experiment [3].

When we compare this six coordination of phase I' with the twelve coordination of low temperature phase II ($T_h^6 - Pa\bar{3}$) [7], a close relation between them can be found. The molecular symmetry in phase I' is $C_{3v} - 3m$ as shown in Fig. 3 (b). Two hydrogen atoms should be paired like 1-1', 2-2', and 3-3' as labeled, since this pairing makes a reasonable molecular bond angle of 92.3 degrees which is very close to that of a free molecule. The molecular symmetry in phase II is $D_{3d} - \bar{3}m$ as shown in Fig. 3 (c). In this case, two hydrogen atoms should be paired like 1-1', , , 6-6' to make a bond angle approximately 90 degrees. The atomic configuration in phase I' is obtained simply by losing an inversion center from that in phase II. This could occur when the molecular rotations are partially frozen by compression. This asymmetry is responsible for the displacement of the sulfur atom along the $\langle 111 \rangle$ direction from the face-centered position in phase I'.

The structure of phase IV has the characteristic feature of spiral chains along the c axis as shown with solid lines in Fig. 4. An intrachain S-S bond, which has never been seen in lower pressure phases, would cause thin yellow color of phase IV to

Fig. 2. Pressure dependence of neighboring S-S distances of H_2S . The numbers inside mean how many equivalent distance degenerated.

Fig. 3 (a) Structural model for phase I' of H_2S . The molecular configurations are drawn in (b) phase I' and (c) phase II. They have 6- and 12-fold coordinations, respectively.

be appeared. The hydrogen atom forms a hydrogen bond with a sulfur atom on an adjacent spiral chain as shown with dashed lines in Fig. 4. We made this model by the following considerations: The first nearest S-S distance is $3.050 \text{ \AA}$ (2-fold) in phase IV at 14.0 GPa as shown with Fig. 2. If one hydrogen atom is located on each S-S line to form a hydrogen bond, only half (16) of hydrogen atoms can exist in the unit cell. However, when we put no hydrogen atom on the first nearest S-S line but on the second nearest S-S line ($3.367 \text{ \AA}$: 4-fold) to form a hydrogen bond, all 32 hydrogen atoms in the unit cell can occupy a 32g site of this space group. Hydrogen atoms should be located at $32g$: ($x=0.412, y=0.179, z=0.288$) in cell choice 1 to fix the molecular shape of an S-H bond length $1.3 \text{ \AA}$ and a molecular bond angle 92 degrees.

The structure and bonding nature could well explain the pressure dependence of the interatomic distances of sulfur. As shown with Fig. 2, the first nearest S-S distance shortened by

pressure effectively than the others in spite of its shorter distance. It means that the first nearest S-S bond consists of weak binding force such as van der Waals interaction (van der Waals radius of sulfur= 1.85). The second nearest S-S bond consists of a hydrogen bond including hydrogen atom between sulfur atoms. Raman study [2] has shown that the symmetric S-H stretching frequency ν_1 drops constantly with pressure ($\frac{d\nu_1}{dP} = -10.1 \text{ cm}^{-1} / \text{GPa}$) up to 23 GPa . This can be explained by our model where hydrogen bonded S-S distances in phases I and I' can connect smoothly with the second nearest S-S distance in phase IV rather than the first nearest one as shown in Fig. 2.

The spiral chain structure has never been seen in any phases of H_2O even after molecular dissociation. A variety of polymorphs in H_2S must be derived from a coexistence of hydrogen and covalent bonds. As described our previous IR study [6], optical properties of phase VI and elemental sulfur behave similarly above 46 GPa . This has been interpreted that three-dimensional S-S covalent bonds are associated, then hydrogen atoms move to interstitial positions in phase VI. Accordingly, successive transitions from IV, V, to VI would be characterized by losing hydrogen bonds and molecularity, and an increasing covalency of the S-S bonds.

The x-ray powder diffraction gave useful information to understand the bonding state of solid H_2S . Theoretical calculations would help to understand why such spiral structure is formed, and how a hydrogen bond influences phase transitions. Further study should be done for higher pressure phases V and VI successively appearing along the isothermal compression at room temperature toward molecular dissociation and metallization.

Fig. 4 Structural model for phase IV of H_2S viewed from (a) $\langle 421 \rangle$ and (b) $\langle 100 \rangle$ directions. Two spiral chains of four are drawn in (b).

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