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Structures of H_2S: Phases I′ and IV under high pressure

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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, by the Rietveld method. Both structures were derived from an fcc structure of phase I by slight atomic displacements of sulfur. Likely positions of hydrogen were examined by using the sulfur positions. In phase I′, the H_2S molecule had sixfold asymmetric coordination which brought the displacement from phase I. In phase IV, the molecules were found to form spiral chains along the c axis with partial loss of molecularity. The chains would be linked by hydrogen bonds. [S0163-1829(98)06106-2]

INTRODUCTION

Hydrogen sulfide forms a molecular solid in which the molecules are bound by hydrogen bonds, similar to H_2O molecules in ice. The pressure-temperature 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. This led to an interest in understanding what kind of interactions make the difference. From this reason, many high-pressure studies have been done intensively in the last five years.

Five crystalline phases are known under pressure at room temperature. (1) Phase I between 0.47 to 8 GPa has an fcc (O_h^5-$Fm\overline{3}m$) structure with orientationally disordered hydrogen bonds.[1] (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-$P2_13$),[2] but its atomic parameter has not been determined yet. A P-T phase-diagram investigation by Raman spectroscopy[3] has suggested that phase I′ is the same as low-temperature phase II (T_h^6-$Pa\overline{3}$)[4,5] existing from 104 to 126 K at ambient pressure. (3) Phase IV has been found by a Raman experiment[6] at 25 K above 3.3 GPa. At room temperature, phase IV is shown to exist above 11 GPa,[2,7] which has a thin yellow color. Phase IV is stable over an extended temperature region from 30 to 300 K under high pressure.[3] There are no known structures of phase IV. (4) Phase V has been found by an x-ray experiment above 27.5 GPa (Ref. 8) at room temperature. The color of phase V is black against visible light. An infrared (IR) absorption measurement[9] has shown the presence of a 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.[10] The molecular dissociation process in H_2S is different from that in H_2O ice recently observed above 60 GPa by an IR absorption experiment[11] in which hydrogen atoms move to the midpoints between O atoms. We have also found that H_2S becomes metallic around 96 GPa.[10]

The optical properties have been intensively studied for solid H_2S under pressure, however, the structures of the high-pressure phases have remained very uncertain, probably because of the difficulty of getting high-quality diffraction data applicable to a structural analysis. Structural data are fundamental bases for understanding vibrational properties, electronic states in high-pressure phases, and transformation mechanisms. They also allow a detailed comparison of the molecular arrangement of H_2S with those of other hydrogen bonded materials such as H_2O, NH_3, and hydrogen halides. 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 appearing on compression at room temperature, and discussed the transformation mechanism based on the determined structures.

EXPERIMENTAL

Powder-diffraction images of samples solidified from liquids and gases commonly show strong texture effects by their coarse grains. The large grain may be crushed into smaller grains by pressure and temperature cycling, however, they do not have random orientation but still have the preferred orientation of the original grain, eventually giving nonideal Debye-Scherrer rings. To avoid this problem, we prepared the H_2S powder specimen as follows. First, gaseous H_2S was introduced in a stainless steel bowl cooled to 77 K and solidified. Then it was ground into fine powders and was subsequently mounted on a gasketted diamond anvil (DA) 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. During the warming process to room temperature, we loaded pressure little by little to keep the pressure sufficiently far from a melting curve on the P-T phase diagram. The finely ground powder could neither be melted nor recrystallized in this pro-

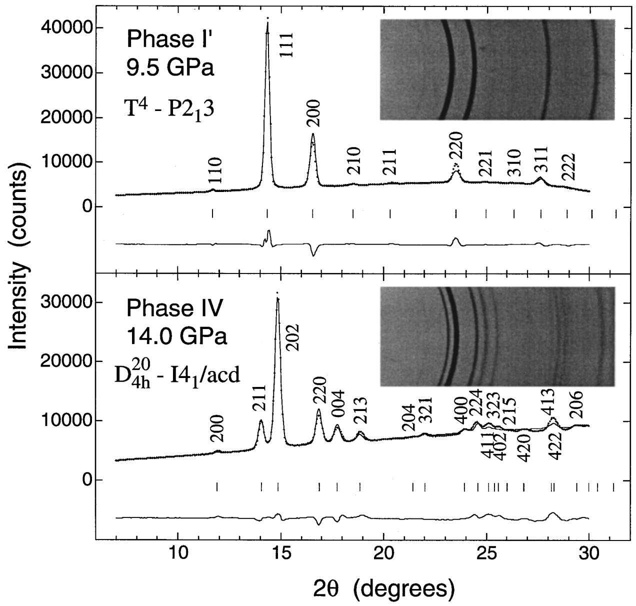

FIG. 1. Rietveld analyses of H_2S for phase I′ at 9.5 GPa with space group $P2_13$ (top) and for phase IV at 14.0 GPa with $I4_1/acd$ (bottom). Each inset shows part of raw diffraction image before integration.

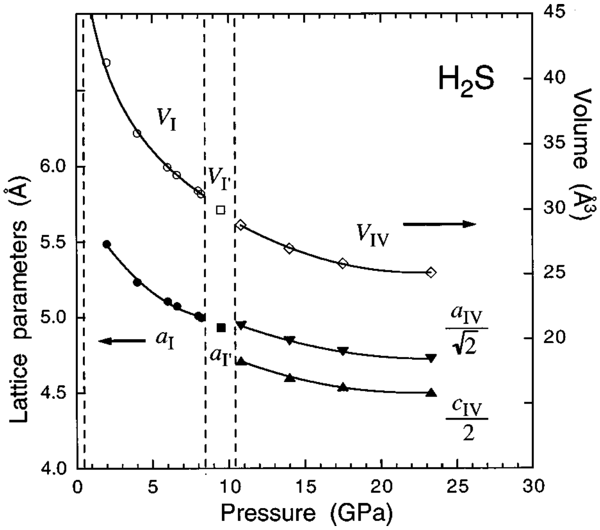

FIG. 2. Pressure dependence of lattice parameters (closed symbols) and the volume per one molecule (open symbols) of H_2S. Three dashed vertical lines show phase boundaries which separate the four phases of liquid I, I′, and IV.

cess, and was able to be retrieved at room temperature.

DA's with 500 μm culet, 3.0 mm in diameter, and 1.5 mm in height were used. The gasket hole size was 180 μm in diameter and 120 μm in thickness to get enough powder volume to give smooth Debye-Scherrer rings. Pressures were determined by the ruby fluorescence method.[12] Angle dispersive powder patterns were taken with a rotating-anode x-ray generator (Mo$K\alpha$ operated with 50 kV and 200 mA) with a pyrolytic graphite (002) monochromator and an image plate (IP) detector ($125\times125\ \mathrm{mm}^2$). A pin-hole collimator of 80 μm ϕ was used. The average exposure time for each pattern was 24 h. All x-ray measurements were carried out at room temperature. A blue IP, commercially available from Fujifilm Co. Ltd., and an R-axis drum scanner from Rigaku Co. Ltd. were employed to obtain two-dimensional powder-diffraction images. The image had a resolution of $50\times50\ \mu\mathrm{m}^2$ per one pixel and contained 2300×2300 pixels. Smooth Debye-Scherrer rings without spots were obtained and are displayed in the insets of Fig. 1.

ANALYSIS

Two-dimensional diffraction images were integrated along the ring direction with an adequate 2θ step. The obtained conventional diffraction patterns provided good powder averages. The pattern of phase I′ at 9.5 GPa was explained well with cubic space group $P2_13$ as described in Ref. 1. The lattice and atomic parameters of sulfur were determined to be $a_{\mathrm{I}'}=4.931$ and S $4a{:}(x=0.240\pm0.005,\ x,\ x)$, respectively, using the computer program RIETAN[13] as displayed at the top of Fig. 1. Phase I′ should be discriminated from low-temperature cubic phase II ($Pa3$),[4,5] since we clearly observed 110 reflection prohibited for $Pa3$. The sulfur position in phase I′ has a small displacement along the ⟨111⟩ direction when compared with the exact face-centered positions in phases I and II. The bottom of Fig. 1 represents a pattern of phase IV obtained at 14.0 GPa. All peaks were well indexed by tetragonal cell $a_{\mathrm{IV}}=6.850$ and $c_{\mathrm{IV}}=9.203$. Its space group was refined 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, II, and I′ by $\sqrt{2}\times\sqrt{2}\times2$. Its atomic parameter at 14.0 GPa was determined to be S $16e{:}(\frac{1}{4},\ y=0.044\pm0.005,\ \frac{1}{8})$ in cell choice 1.

The closed symbols in Fig. 2 represent the pressure dependence of lattice parameters. The tetragonal a_{IV} and c_{IV} of phase IV were plotted with values divided over $\sqrt{2}$ and 2, respectively, to be compared with the original cubic cell. The phase transition from I′ to IV was found to be first order type judging from jumps in the lattice parameters. The pressure dependence of the volume per one molecule is plotted with open symbols in Fig. 2. No significant volume changes were observed with the successive phase transitions from I, I′, to IV.

Figure 3 represents the pressure dependence of twelve neighboring interatomic distances of sulfur. A nearest S-S distance in phase I (3.544 Å: twelvefold at 8 GPa) split into two components (3.419 and 3.558 Å: sixfold 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 Å: two, four, two, two, and twofold for each) at 14.0 GPa, suggesting complex and low symmetry arrangement of H_2S molecules.

DISCUSSION

We examine the atomic positions of hydrogen in phases I′ and IV. The information on hydrogen positions is lacking in the x-ray-diffraction analysis, but is crucial for understanding the role of hydrogen bonding in their molecular arrangements. A structural model of phase I′ is displayed in Fig. 4(a). Sulfur atoms are put on the $4a$ site which was experi-

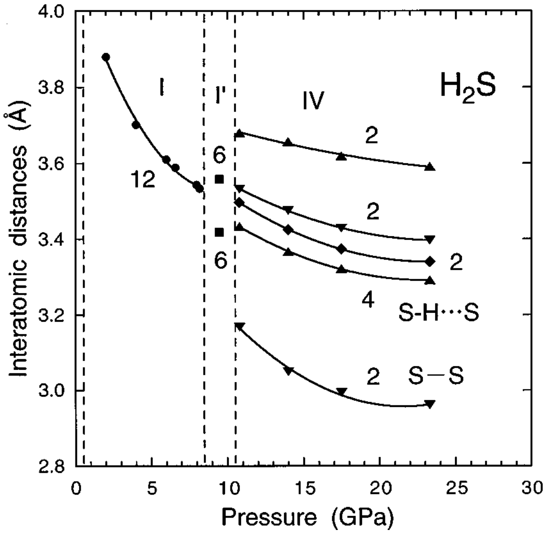

FIG. 3. Pressure dependence of neighboring S-S distances of H_2S. The numbers inside mean how many equivalent distances degenerated. The first and second nearest distances in phase IV consist of S-S covalent bonds and hydrogen bonds, respectively.

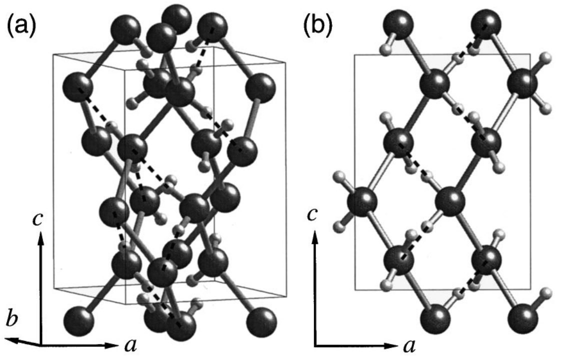

FIG. 5. (a) Structural model for phase IV of H_2S viewed from the ⟨421⟩ direction. (b) Projection of the *ac* plane. Two spiral chains of four in the unit cell are drawn. Dashed lines represent hydrogen bonds.

mentally determined by Rietveld analysis. We assumed that hydrogen atoms are located on the lines between the first nearest S-S distance (3.419 Å: sixfold) and at a S-H distance of 1.3 Å. 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, 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 sixfold. 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 phase I (O_h-m3m), a close relation between them can be found. The molecular symmetry in phase I′ is C_{3v}-$3m$ as shown in Fig. 4(b), with the threefold axis along the ⟨111⟩ direction. Two hydrogen atoms should be paired as 1-1′, 2-2′, and 3-3′, since this pairing makes a reasonable H-S-H bond angle of 92.3° which is very close to that of a free molecule. The molecular motion in phase I′ can be obtained when the motion in phase I, $m\bar{3}m$ as shown in Fig. 4(c), is partially frozen by compression. The asymmetric motion in phase I′ is responsible for the displacement of the sulfur atom along the ⟨111⟩ direction from the face-centered position. It is notable that deuterated ammonia ND_3, which has the same $3m$ point symmetry, forms an ordered phase below 203 K of the same space group of $P2_13$ with N $4a{:}(x=0.2107,\ x,\ x)$ and D $12b{:}(x=0.3689,\ y=0.2671,\ z=0.1159)$.[14]

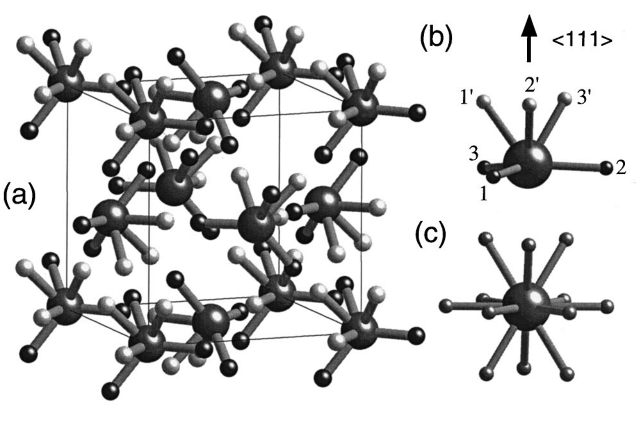

FIG. 4. (a) Structural model for phase I′ of H_2S viewed from the ⟨112⟩ direction. The unit cell frame was drawn with an offset of $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. The molecular configuration with a sixfold hydrogen coordination is shown in (b). For comparison, the twelvefold coordination of phase I is also shown in (c).

The structure of phase IV has the characteristic feature of spiral sulfur chains along the *c* axis, as displayed in Fig. 5(a). An intrachain S-S bond, which to the best of our knowledge has never been seen in lower pressure phases, is the cause of the thin yellow color of phase IV. The hydrogen atom forms a hydrogen bond with the sulfur atom on an adjacent spiral chain as shown by the dashed lines in Figs. 5(a) and 5(b). We made this model keeping the following consideration in mind. The first nearest S-S distance is 3.050 Å (twofold) in phase IV at 14.0 GPa. If one hydrogen atom is located on each S-S line to form a hydrogen bond, only 16 hydrogen atoms can exist in the unit cell. However, when we put no hydrogen atom on the first nearest S-S line but one on the second nearest S-S line (3.367 Å: fourfold) to form a hydrogen bond, all 32 hydrogen atoms can exist in the unit cell. Hydrogen atoms should be located at $32g{:}(x=0.412,\ y=0.179,\ z=0.288)$ to fix the molecular shape of the S-H bond length (1.3 Å) and the H-S-H bond angle (92°).

The nature of this structure and bonding could well explain the pressure dependence of the lattice parameters and the interatomic distances of sulfur. The shortening of $c_{\mathrm{IV}}/2$ at the transition pressure in Fig. 2 is attributed to a formation of the spiral chains along the *c* axis. As shown in Fig. 3, the first nearest S-S distance is shorter than the doubled van der Waals radius of 3.7 Å and shortened by pressure effectively. This means that the covalency of the spiral chain increases with pressure. A Raman study[7] has shown that the symmetric S-H stretching frequency ν_1 drops constantly with pressure $(d\nu_1/dP=-10.1\ \mathrm{cm}^{-1}/\mathrm{GPa})$ 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.

We could only obtain atomic positions of sulfur by x-ray-powder diffraction, however, it would be useful information to understand the bonding state of solid H_2S deeply. A spiral chain structure to the best of our knowledge 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. The successive transitions from IV, V, to VI are characterized by a loss of hydrogen bonds and molecularity, and an increasing covalency of the S-S bonds. Further structural study should be done for higher-pressure phases toward molecular dissociation and metallization.

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