

X-ray-diffraction study of solid hydrogen sulfide under high pressure

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Solid H_2S was studied by x-ray diffraction under pressure up to 20 GPa at room temperature. An $F \rightarrow P$ symmetry change in the cubic lattice was observed at 8 GPa. At 11 GPa where a previous Raman study indicated a pressure-induced transition, an obvious crystal structure change from the cubic symmetry to a lower symmetry was observed.

I. INTRODUCTION

Hydrogen sulfide (H_2S) is known to have three solid phases (I, II, and III) with hydrogen bonding at low temperatures under ambient pressure. Phase I, which is stable between 187.6 and 126.2 K, and phase II between 126.2 and 103.5 K have cubic lattices with four molecules in their unit cells.¹ Phase I has the space group $Fm\bar{3}m$ and the orientations of S—H bonds are disordered and symmetric about all four C_3 axes of the cube. Phase II has the space group $Pa\bar{3}$ and the orientations of S—H bonds are symmetric about only one C_3 axis.² The lowest-temperature phase III below 103.5 K is tetragonal¹ or orthorhombic.³ Shimizu, Nakamichi, and Sasaki⁴ recently measured the Raman spectra of solid H_2S up to 23 GPa at 300 K using a diamond anvil cell and observed the various features indicating a pressure-induced phase transition near 11 GPa. They identified the solid phase from 0.47 to about 11 GPa as phase I. They also proposed the existence of the high pressure phase IV above 11 GPa to at least 23 GPa and considered it to be the same phase as that previously found by the Raman study above 3.3 GPa at 25 K by Anderson, Demoor, and Hanson.⁵ We have made an *in situ* x-ray-diffraction experiment under high pressure to confirm the existence of the new phase IV from the viewpoint of crystallography.

II. EXPERIMENTAL

A diamond anvil cell (DAC) was used for pressure generation. The culet size of the diamond anvils was 0.7 mm and that of the gasket hole 0.3 mm. Gaseous H_2S sample used in the present study was the same as that used in the Raman study,⁴ and the method to load it as a solid in the gasket hole is described therein. Pressure was determined from the wavelength of the R_1 fluorescence of ruby pieces placed in the gasket hole. No pressure medium was used, since the hydrostatic or nearly hydrostatic condition was guaranteed without it.⁴ X-ray powder patterns were obtained by an angle dispersive diffractometry

using a position-sensitive proportional counter and $\text{Mo } K\alpha$ radiation from a rotating-anode-type x-ray generator (Rigaku RU-200).

The pressure at which liquid and solid H_2S coexist at room temperature was found to be about 0.47 GPa in the two previous studies.^{4,6} The x-ray-diffraction pattern of phase I obtained at 4.8 GPa compressed from 0.47 GPa in the present study is shown in Fig. 1(a). The calculated intensities for the reflections based on the face-centered-cubic structure of sulfur atoms are shown in Fig. 1(b) for comparison. The most intense diffraction line (111) cannot be observed in the experimental pattern, although other relatively weak three lines (200, 220, and 311) can be observed. This disagreement is considered to be due to a small number of crystals, which are too few to give an ideal Debye-Scherrer pattern. We obtained polycrystals on the basis of our previous observation that a single

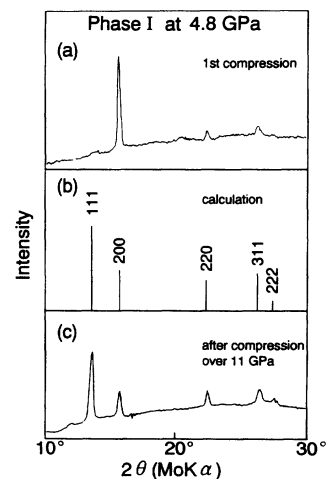


FIG. 1. (a) the x-ray-diffraction pattern of phase I at 4.8 GPa in a diamond-anvil cell for the initial compression from the melt, (b) the calculated pattern, and (c) pattern after once compressed over 11 GPa (the transition pressure to phase IV).

crystal became polycrystalline when the pressure exceeded the transition pressure of 11 GPa. The diffraction pattern of the sample at 4.8 GPa decompressed from above 11 GPa is shown in Fig. 1(c). The good agreement can be seen between Figs. 1(b) and 1(c). The polycrystalline form of phase I thus prepared in DAC was used for x-ray-diffraction experiments under high pressure in the present study.

III. RESULTS AND DISCUSSION

The x-ray-diffraction patterns obtained on increasing pressure from 4.8 to 20 GPa and then on decreasing pressure down to 4.8 GPa are shown in Figs. 2(a) and 2(b), respectively. The d values calculated from the 2θ values of the diffraction lines in these patterns are plotted in Fig. 3 together with those in the successive reincreasing pressure process up to 15 GPa.

A. Phase I stable up to 8 GPa

Five diffraction lines in all the patterns at pressures up to 8 GPa can be indexed as 111, 200, 220, 311, and 222 based on the fcc phase I. A line at the low-angle side of the line 111 in these patterns is that of 111 for Mo $K\beta$ radiation. Phase I is confirmed stable in the pressure range from 0.47 to about 8 GPa at room temperature.

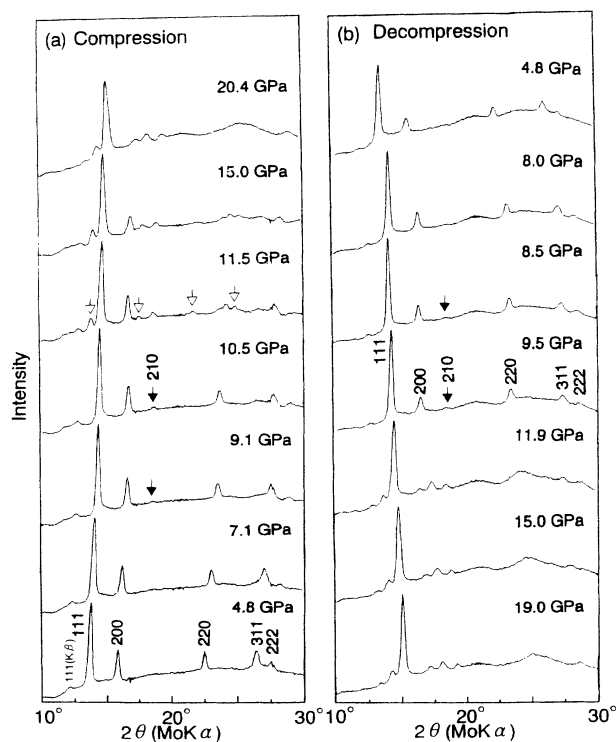


FIG. 2. X-ray-diffraction patterns in the compression and decompression processes. Note the line 210 for the cubic phase I', indicated by the solid arrows and the new lines appearing for phase IV, indicated by the open arrows.

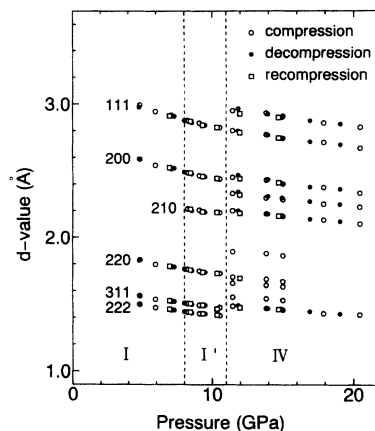


FIG. 3. Pressure dependence of the d values for all the diffraction lines in the compression, decompression and successive recompression processes. The d values for the newly appeared lines of phase IV are also plotted.

B. The primitive cubic phase I' between 8 and 11 GPa

In the pattern at 10.5 GPa in Fig. 2(a), a new weak line appeared at around 18.5° in 2θ . The other five lines are indexed the same as those of phase I. The new line is indexed as 210 based on the cubic lattice constant calculated from the other five lines. However, the reflection 210 is forbidden by extinction rule for the fcc structure. This indicates phase I (fcc) transformed to a primitive cubic phase at about 8 GPa. This phase is named phase I' in the present study. The change of the lattice constant at the I-I' transition is zero or negligibly small as shown later.

As the atomic scattering factor of hydrogen atom for x rays is very small compared with that of sulfur atom, most contribution to the intensity of the line 210 is considered due to sulfur atoms. This means that sulfur atoms form a primitive cubic lattice. A possible structure of phase I' is that where sulfur atoms are situated in the following sites of the space group $P2_13$.

4a (Wyckoff letter):

$$x, x, x; \bar{x}, x + \frac{1}{2}; \bar{x}, x + \frac{1}{2}; \bar{x}, x + \frac{1}{2}; x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{x},$$

where x is very small, resulting in the nearly face-centered arrangement of sulfur atoms.

According to a neutron diffraction study of phase II,³ deuterium atoms are disordered but sulfur atoms still form a fcc lattice and are sited on the special position $4a:0,0,0$ of the space group $Pa\bar{3}$. If this is true, phase I' is not identical with phase II.

In the previous Raman study the symmetric stretching mode ν_1 in phase I shows a dramatic broadening with increasing pressure. Shimizu, Nakamichi, and Sasaki⁴ con-

sidered this phenomenon to be due to an increasing coupling between the intramolecular S-H vibration and the lattice linked by hydrogen bonds. In addition, the orientational correlation between neighboring molecules in the plastic phase produced by the decreasing intermolecular distance at higher pressure may result in the broadening in the ν_1 mode. In their study the increase of the halfwidth of ν_1 mode with pressure is saturated at around 8 GPa and an asymmetric broad profile has a distinct shoulder at its higher-frequency side at about 8 GPa. The appearance of these features is considered to be related to the crystallographic transition from fcc (phase I) to a primitive cubic lattice (phase I'). The Raman spectra of the primitive cubic phase II at low temperatures and ambient pressure were also characterized by the shoulder at higher-frequency side of ν_1 main band,⁷ which may suggest still a possibility that phase I' is the same as phase II. The situation will be clarified with a Raman study planned under high pressure and low temperature.

C. Phase IV above 11 GPa

An x-ray-diffraction pattern at 11.5 GPa shows the new diffraction lines indicated by the open arrows in Fig. 2(a). In the Raman study,⁴ many new features were observed at 11 GPa, such as the appearances of the asymmetric stretching band ν_3 and five low-frequency vibrational modes. They concluded that the pressure-induced phase transition from phase I with the orientationally disordered structure of hydrogen atoms to a new phase IV took place at 11 GPa, and phase IV is the same as the low-temperature-high-pressure phase discovered by Anderson, Demoor, and Hanson.⁵ The present x-ray study has revealed that this transition is accompanied by a structure change and that phase I does not directly transform to phase IV, but must go by way of phase I'. As shown in Fig. 2(b), the reverse transition takes place at around 11 GPa, too, although the line, 210, of phase I' is not so clear on decreasing pressure.

In Figs. 2(a) and 2(b), all the diffraction lines of phase I', including the 210, seem to exist still in the stability field of phase IV. The lattice constant was calculated using each 2θ value of the line on the assumption of the primitive cubic lattice. The obtained values are plotted in Fig. 4, in which the lattice constants of phase I and I' at lower pressures are also plotted. The values of phase I' coincide with one another in the pressure region between 8 and 11 GPa, but those above 11 GPa scatter remark-

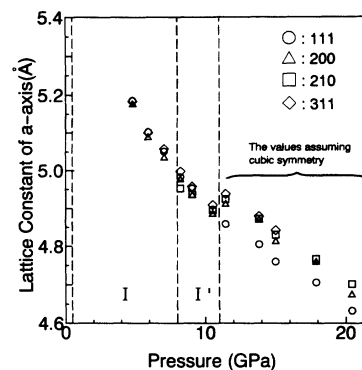


FIG. 4. Pressure dependence of the lattice constants of phase I of fcc and phase I' with the primitive cubic lattice. The values above 11 GPa are of phase IV on the assumption of cubic symmetry. Disagreement of the values indicates that phase IV has lower symmetry than cubic.

ably. That is, they cannot be indexed based on cubic symmetry, indicating a different symmetry from phase I'. It is considered that phase I' transformed to phase IV and all the lines including those newly appeared above 11 GPa are from phase IV. That is, only phase IV is stable above 11 GPa and phase IV has a slightly distorted structure from cubic symmetry. The transition from phase I' to phase IV takes place drastically at definite pressure.

From the above result, it is indicated that phase IV has a slightly distorted structure from phase I', probably due to more highly ordered arrangement of hydrogen and sulfur atoms. A few candidates with lower symmetry than cubic such as tetragonal and rhombohedral have been examined, but the structure model satisfying the obtained patterns has not been obtained yet.

IV. CONCLUSION

Solid H₂S was studied by *in situ* powder x-ray diffraction under high pressure at room temperature, and the following results were obtained: (i) phase I transforms to phase I' at about 8 GPa. This is the $F \rightarrow P$ symmetry transition in a cubic lattice, and (ii) phase I' transforms to phase IV at about 11 GPa. This transition pressure agrees with the one previously obtained by the Raman spectroscopy, (iii) these two transitions are drastic and indicate no pressure hysteresis, and (iv) phase IV has a lower symmetry than cubic and a slightly distorted structure from phase I'.

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