

## Rapid Communications

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### Pressure-temperature phase diagram of solid hydrogen sulfide determined by Raman spectroscopy

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With Raman spectroscopy, the pressure-temperature ( $P$ - $T$ ) phase diagram for solid hydrogen sulfide has been determined at high pressures up to about 20 GPa and at low temperatures down to 30 K. The triple point between the II, III, and IV phases of solid  $\text{H}_2\text{S}$  exists at about 3.1 GPa and 153 K. Phase IV is stable in the wide  $P$ - $T$  region, and the phase diagram of solid  $\text{H}_2\text{S}$  is simple in comparison with that of  $\text{H}_2\text{O}$  ice, which has many high-pressure phases.

#### I. INTRODUCTION

Hydrogen sulfide ( $\text{H}_2\text{S}$ ) is a typical molecular solid showing hydrogen bonding and molecular orientation.<sup>1</sup> At ambient pressure  $\text{H}_2\text{S}$  shows three solid phases with decreasing temperature:<sup>1,2</sup> The high-temperature phase I is orientationally disordered with isotropic motions<sup>3,4</sup> and has a space group of cubic  $Fm\bar{3}m$ .<sup>4</sup> The middle phase II is orientationally disordered with anisotropic motions<sup>3,4</sup> and has cubic  $Pa\bar{3}$ .<sup>4</sup> The lowest-temperature phase III is orientationally ordered and has orthorhombic  $Pbcm$  (Ref. 4) or tetragonal  $P4_2$ ,<sup>1</sup> forming a quasi-two-dimensional hydrogen-bonded network. Miller and Leroi<sup>5</sup> characterized these phases by Raman spectra of intramolecular stretching vibrations around the frequency of  $2500\text{ cm}^{-1}$ ; phase I: a broad structureless band indicating orientational disorder, phase II: additional weak shoulder at higher-frequency side of the main broad band of phase I, and phase III: the sharp multiplets indicative of an ordered structure.

Stewart<sup>6</sup> determined the pressure-temperature ( $P$ - $T$ ) phase diagram at low pressures for the above phase from the volume change by a piston cylinder apparatus. In 1987, Anderson *et al.*<sup>7</sup> found a pressure-induced new phase above 3.3 GPa at 25 K by Raman scattering study. At this phase transition point, they observed clear changes in Raman spectra of intramolecular stretching and intermolecular lattice vibrations.

In 1991, we found a pressure-induced phase transition at about 11 GPa and room temperature by Raman measurements; a broadband changes dramatically into two narrow bands associated with symmetric  $\nu_1$  and antisymmetric  $\nu_3$  stretching vibrations.<sup>8,9</sup> This new phase named IV persists to at least 23 GPa at 300 K. Moreover, we suggested that this phase IV seems to be the same as that previously found by

Anderson *et al.*<sup>7</sup> above 3.3 GPa at 25 K. Recently, we made *in situ* x-ray-diffraction measurements under pressures up to 20 GPa at 300 K, and found the transition from phase I to I' at about 8 GPa.<sup>10</sup> This transition was identified to the phase change from the face-centered cubic (fcc) structure to the primitive cubic (space group  $P2_13$ ) as to the sulfur atoms. Furthermore, we observed an obvious change from the cubic to the lower symmetry structure at about 11 GPa, which is consistent with our previous high-pressure Raman study.<sup>8,9</sup>

It is well known that  $\text{H}_2\text{O}$  ices exist in many different phases at various pressures and temperatures,<sup>11-14</sup> which is due partly to the structural versatility in the tetrahedral hydrogen-bonding possibilities of  $\text{H}_2\text{O}$  molecules and partly to the possibilities of proton ordering.<sup>12,15</sup> However, the  $P$ - $T$  phase diagram of simple molecular  $\text{H}_2\text{S}$  is still little known, despite its many similarities to  $\text{H}_2\text{O}$ . The purpose of this paper is to determine the  $P$ - $T$  phase diagram of condensed  $\text{H}_2\text{S}$  by Raman scattering measurements at high pressures and low temperatures.

#### II. EXPERIMENT

The system for the loading of  $\text{H}_2\text{S}$  gas into a diamond anvil cell (DAC) is the same as in previous reports on  $\text{H}_2\text{S}$ .<sup>8,16</sup> The coexistence pressure of liquid and solid  $\text{H}_2\text{S}$  in DAC was about 0.47 GPa at room temperature. Pressure was measured by the ruby-scale method;<sup>17,18</sup> at low temperature we used the following equation:  $P(\text{GPa}) = 0.1325[R_1(0.1\text{ MPa}, T) - R_1(P, T)]$ , where  $R_1(0.1\text{ MPa}, T)$  is the wave number ( $\text{cm}^{-1}$ ) of  $R_1$  ruby fluorescence at 0.1 MPa and  $T(\text{K})$ ,<sup>19</sup> and  $R_1(P, T)$  is the  $R_1$  line at  $P(\text{GPa})$  and  $T(\text{K})$ . The 488.0 and 514.5 nm lines of an argon-ion laser were used for Raman scattering excitation at power levels from 100 to 250 mW input. Scattered light was collected in a back-scattering

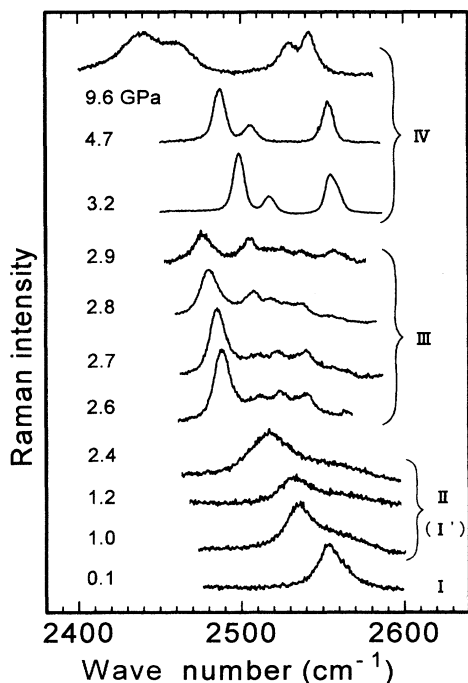


FIG. 1. Raman spectra of the stretching vibrational modes in solid H<sub>2</sub>S under various pressures at 150 K. With increasing pressure, phases I, II (or I'), III, and IV appear sequentially.

geometry. The Raman spectra were recorded by a Jobin Yvon triple monochromator (T-64000) having a diode array detector with an image intensifier. For the low-temperature experiments in a cryostat, we used a temperature controller of Iwatani Plantech Co. (Shiga), by which the temperature fluctuations during the present experiments were within  $\pm 0.5$  K.

### III. RESULTS AND DISCUSSION

The Raman spectra of symmetric  $\nu_1$  and antisymmetric  $\nu_3$  stretching modes and lattice vibrational modes were measured for the pressure-induced crystalline H<sub>2</sub>S in DAC up to about 20 GPa at low temperatures down to 30 K. Figure 1 shows the typical spectra in the stretching vibrational region under various pressures at 150 K. At 0.1 GPa we can see a symmetric-shape Raman band of the  $\nu_1$  stretching mode, which indicates the existence of phase I. At pressures from about 1.0 to 2.5 GPa, the weak shoulder appears at the higher-frequency side of the broad  $\nu_1$  stretching band. This antisymmetric band shape shows the feature of phase II (Refs. 5 and 8) or phase I'.<sup>10</sup> Next, the phase transition to phase III is clearly observed on the multiplet bands<sup>2,5</sup> at about 2.6 GPa. Furthermore, the typical phase-IV bands associated with two  $\nu_1$  and one or two  $\nu_3$  (higher-frequency side) vibrational modes appear at pressures above 3.2 GPa. These data points for phases I, II (or I'), III, and IV are plotted in the  $P$ - $T$  phase diagram as shown in Fig. 2. For intermolecular vibrations, we observed Raman spectra indicating the above phase relation: no lattice vibrational band in phases I and II (or I'), two or three bands in phase III, and

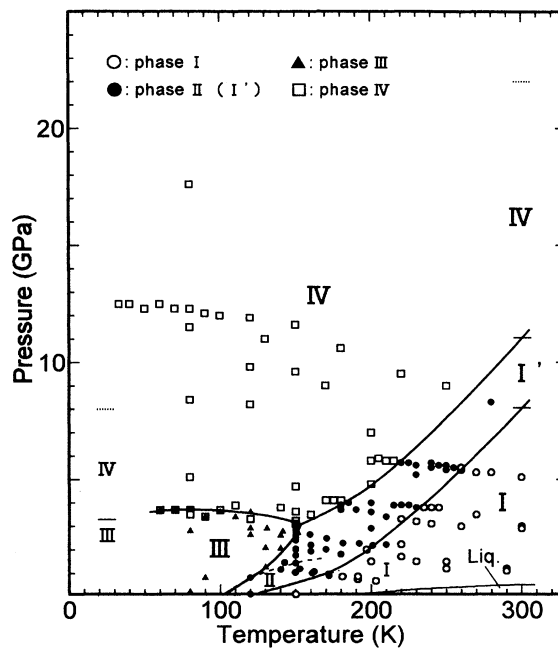


FIG. 2. Pressure-temperature phase diagram of H<sub>2</sub>S. The phase boundaries by solid lines are drawn from our present and previous (Refs. 8 and 10) studies. The data points of phase I (open circles), II (or I') (solid circles), III (solid triangles), and IV (open squares) were determined by the present Raman measurements. The triple point between II, III, and IV phases exists at about 3.1 GPa and 153 K. Phase boundaries at 300 K and 25 K are from Refs. 8 and 10, and Ref. 7, respectively. Broken lines at low pressures are from Ref. 6.

several sharp bands in phase IV, which are the same characteristics as in the previous studies.<sup>5,7,8</sup> In each phase at 150 K (Fig. 1), we can confirm the red shift in frequency for all  $\nu_1$  stretching bands with increasing pressure:  $d\nu_1/dP = -14.2$  cm<sup>-1</sup>/GPa in phase II (or I'),  $-36$  cm<sup>-1</sup>/GPa in phase III, and  $-10.0$  cm<sup>-1</sup>/GPa in phase IV. These features imply the existence of the hydrogen bonds in all phases.

Next, the temperature dependence of stretching vibrational spectra around 5.5 to 5.9 GPa is shown in Fig. 3. With decreasing temperature, the pressure in DAC increases a little as indicated on the spectrum, which is probably due to the contraction of the gasket hole. The symmetric band shape characterizing phase I changes to the antisymmetric profile of phase I' (or II) with decreasing temperature, and the spectrum shows a rapid change into the typical phase-IV bands below 215 K. These data points are plotted in the  $P$ - $T$  phase diagram in Fig. 2.

The phase boundaries in Fig. 2 are drawn from the present data points of Raman measurements and our previous Raman<sup>8</sup> and x-ray<sup>10</sup> studies at 300 K. These results support the previous indication<sup>8</sup> that phase IV at pressures above 11 GPa at 300 K seems to be the same phase as found above 3.3 GPa at 25 K. The triple point between phases II (or I'), III, and IV exists at about 3.1 GPa and 153 K. Phase IV has

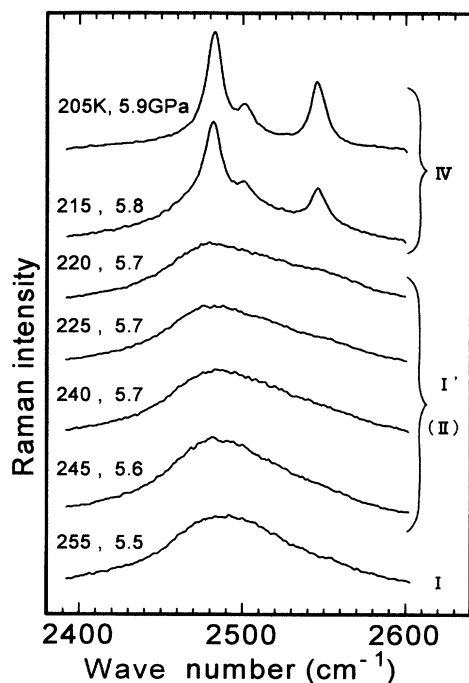


FIG. 3. Temperature dependence of Raman spectra of the stretching vibrational modes in solid  $\text{H}_2\text{S}$  around 5.5–5.9 GPa. With decreasing temperature, phases I, I' (or II), and IV appear subsequently.

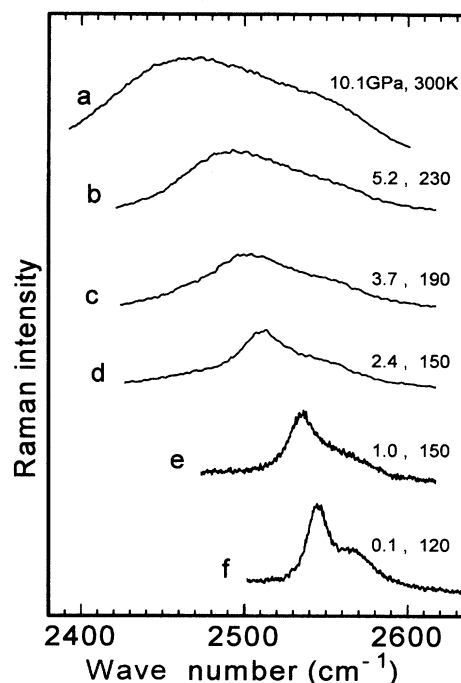


FIG. 4. Typical Raman spectra of the stretching vibrational modes in phase II or I' of solid  $\text{H}_2\text{S}$  under various pressures and temperatures; (a) 10.1 GPa, 300 K, (b) 5.2 GPa, 230 K, (c) 3.7 GPa, 190 K, (d) 2.4 GPa, 150 K, (e) 1.0 GPa, 150 K, (f) 0.1 GPa, 120 K.

the wide stability region. The conclusive phase diagram of  $\text{H}_2\text{S}$  is simple in comparison with that of the  $\text{H}_2\text{O}$  ice having extremely rich phases. Their difference may be due to the following characteristics: the motional flexibility of  $\text{H}_2\text{S}$  molecules (rotations) and the structural versatility of  $\text{H}_2\text{O}$  molecules (bondings), which might be basically influenced by their molecular bonding angles of  $92.2^\circ$  and  $104.5^\circ$  formed by two S-H and two O-H bonds, respectively.

Finally, we investigate the relation of phase I' and phase II from our Raman spectra. For this purpose, the  $\nu_1$  stretching Raman spectra in the regions of phase I' or II (Fig. 2) are picked up and shown in Fig. 4. The broadband and the weak shoulder at the higher-frequency side (antisymmetric profile) characterizing the disordered phase II (Ref. 5) are clearly seen on all spectra. Therefore, the present Raman studies strongly indicate that phase I' is the same as phase II. However, at present, the structural result of phase II from the neutron-diffraction measurements at 0.1 MPa and low temperatures<sup>4</sup> does not coincide with the result of phase I' from the x-ray-diffraction measurements at high pressures at 300 K.<sup>10</sup> Crockcroft and Fitch<sup>4</sup> state that deuterium atoms

are disordered in phase II, but sulfur atoms are still forming at fcc lattice. Endo *et al.*<sup>10</sup> reported that the sulfur atoms slightly shift from the site of the fcc cell, resulting in the primitive cubic lattice in phase I'. We suspect, at present, the magnitude of this slight shift at high pressures at 300 K in phase I' may become nearly zero at low pressures and low temperatures in phase II. More neutron- and x-ray-diffraction studies are needed at high pressures and at low temperatures, respectively, in order to clarify the above investigation by our Raman study.

In conclusion, the pressure-temperature phase diagram for the typical molecular solid  $\text{H}_2\text{S}$  was determined at pressures up to about 20 GPa and at temperatures from 300 to 30 K by the high-pressure Raman measurements using a diamond anvil cell. The phase boundaries among I, II (or I'), III, and IV were clearly determined by the stretching vibrational spectra characterizing each phase of solid  $\text{H}_2\text{S}$ . The triple point between II, III, and IV phases exists at about  $P=3.1$  GPa and  $T=153$  K. Phase IV shows the wide stability region, and the conclusive phase diagram of  $\text{H}_2\text{S}$  is simple in comparison with that of  $\text{H}_2\text{O}$  ice, which has many high-pressure phases.

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