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RAPID COMMUNICATIONS

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High-pressure phase of solid hydrogen sulfide

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Hydrogen-bonded molecular solid H_2S has been studied up to 42 GPa to search for a high-pressure phase by x-ray diffraction at room temperature. New diffraction peaks appeared above 27 GPa, which indicates a transition from phase IV to another phase, phase V. A color change from a thin yellow to black was observed at this transition, which indicates a large decrease of the energy gap at the IV-V phase transition. Phase V may be metallic in the region of 27–42 GPa. [S0163-1829(96)50126-8]

I. INTRODUCTION

Solid hydrogen sulfide (H_2S) is a typical hydrogen-bonded molecular material. Hitherto, three crystalline phases (I, II, and III) were observed below the melting point at ambient pressure,[1,2] and two phases (I′ and IV) at high pressure.[3–5]

As to the low-temperature phases, phase I which is stable between 187.6 and 126.2 K and II between 126.2 and 103.5 K have cubic lattices with four molecules in the unit cells, in which each H_2S molecule has twelve (phase I) or six (phase II) equally probable equilibrium orientations and the random flips among them occur by breaking and remaking of temporary hydrogen bonds, i.e., they exist in plastic crystals. 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,[6,7] whereas phase II has the space group $Pa\bar{3}$ and the orientations of S-H bonds are symmetric about only one C_3 axis.[6,7] The lowest-temperature phase III below 103.5 K is orientationally ordered[1] and has a tetragonal $(P4_2)^1$ or orthorhombic $(Pbcm)^7$ lattice.

On the other hand, a high-pressure phase different from each of phases I, II, and III was found in the pressure range of 3.3–8.0 GPa at 25 K by Anderson, Demoore, and Hanson[3] using Raman spectroscopy. Later, Shimizu, Nakamichi, and Sasaki[4] found a phase with a similar Raman spectrum above 11 GPa at room temperature. They assumed it to be the same phase as that by Anderson *et al.*,[3] and named it ‘‘phase IV.’’ Endo *et al.*[5] confirmed this phase IV above 11 GPa at room temperature by an *in situ* x-ray-diffraction experiment. In addition, they observed another high-pressure phase I′ which exists in the intermediate-pressure region of phases I and IV, that is, between 8 and 11 GPa at room temperature. Phase I′ has a primitive cubic cell as to the position of sulfur atoms. Recently, Shimizu *et al.*[8] determined the pressure-temperature diagram for the above five phases by Raman spectroscopy and proved the identity for the phase observed by Anderson *et al.*[3] and phase IV by Shimizu *et al.*[4] In order to search for a further high-pressure phase, we have made an *in situ* x-ray-diffraction experiment using a diamond anvil cell (DAC) at room temperature.

II. EXPERIMENT

Gaseous H_2S was condensed to the solid state in a gasket hole of a DAC cooled by liquid N_2 below the freezing point

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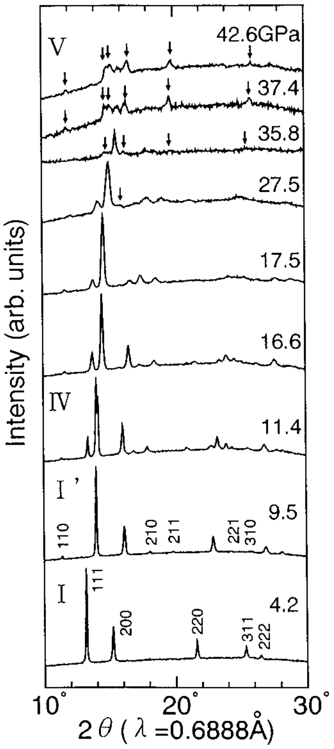

FIG. 1. Some x-ray-diffraction patterns obtained with synchrotron radiation for solid H_2S under high pressure at room temperature. The successive phase transitions, I-I′-IV, can be seen with increasing pressure up to 11.4 GPa. The peaks indexed as 110, . . . ,310 in the pattern at 9.5 GPa are forbidden for the fcc structure of phase I, and all peaks in that pattern belong to the simple cubic structure of phase I′. All peaks at 11.4 GPa also below to phase IV. A peak of another phase, phase V, marked by an arrow begins to appear at 27.5 GPa, and the other peaks of it gradually appear and grow with increasing pressure up to 42 GPa.

of H_2S.[4] Two high-pressure x-ray systems based on angle-dispersive diffractometry were used: the combination of a position sensitive detector and a rotating-anode type x-ray generator (Mo $K\alpha$ radiation) at Osaka University and that of an imaging plate and a monochromized synchrotron radiation ($\lambda = 0.6888$ Å) at National Laboratory for High Energy Physics.

III. RESULTS AND DISCUSSION

Some x-ray-diffraction patterns obtained with synchrotron radiation in the compression process at room temperature are shown in Fig. 1. A collimator 80 μm in diameter was used for the gasket hole of 150 μm in diameter. The *d* spacings of all diffraction lines in all the patterns are plotted as a function of pressure in Fig. 2. In the pattern at 9.5 GPa in Fig. 1, five diffraction peaks indexed as cubic 110, 210, 211, 221, and 310 appear. They are forbidden for fcc structure formed by the sulfur atoms in phase I, but belong to the simple cubic lattice previously proposed for phase I′ on the basis of only one diffraction line, 210.[5]

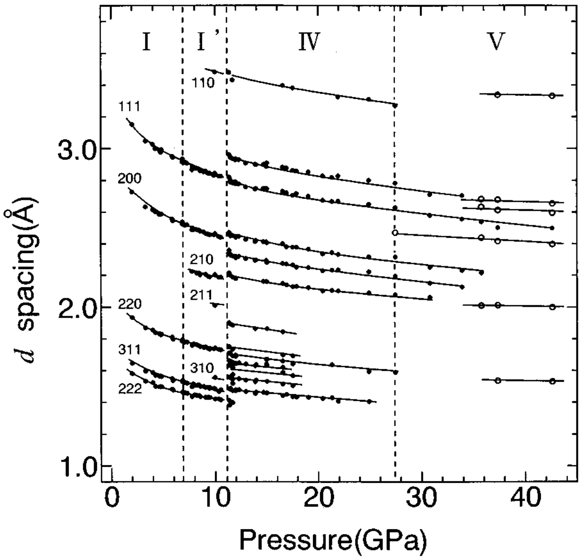

FIG. 2. The *d* spacings of the diffraction lines in all the patterns of H_2S obtained in the compression process at room temperature. The vertical dotted lines indicate the boundaries between the four phases. Some *d* spacings of the metastably existing phase IV are plotted in the region of phase V.

The relative intensities of the diffraction lines of phase IV above 11 GPa change as pressure increases, which is probably due to the preferred orientation of the crystal grains of H_2S because no liquid pressure medium was used. At 27 GPa the diffraction peaks of phase IV begin to diminish and, instead, a new line marked by an arrow appears. Six new lines are observed at 37 GPa. We have found a high pressure phase of solid H_2S and named it ‘‘phase V.’’

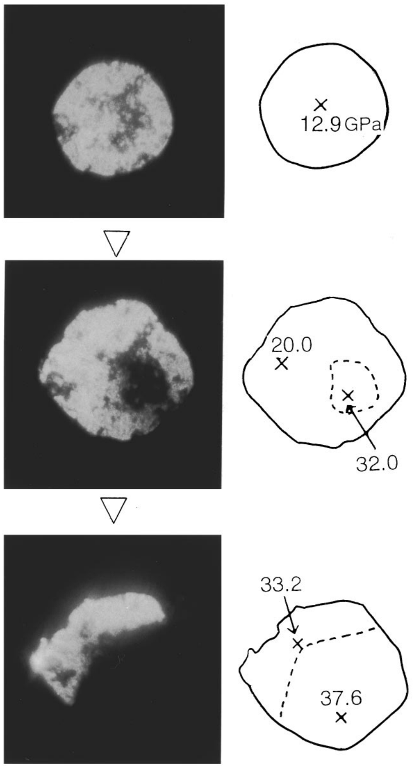

FIG. 3. The photomicrographs of H_2S and the pressure distributions in the hole of a metal gasket of a diamond cell in the compression process at room temperature. A thin yellow color of phase IV at 12–20 GPa turns to black in the region above 30 GPa. The black area corresponds to another phase, phase V.

A microscopic observation was also made for the sample in the DAC. The photographs of the sample in a gasket hole are shown in Fig. 3, where the pressure distributions obtained by a ruby fluorescent method are sketched. Phase IV at 12-20 GPa assumes a thin yellow color, but it gradually changes to black as the pressure increases above 30 GPa. In the bottom photograph of Fig. 3, half of the area of the sample is black and is indistinguishable from a metal gasket. By comparing the x-ray-diffraction data in Figs. 1 and 2 with the color changes of the sample in Fig. 3, we can conclude that phase V assumes a black color. A brown color of the intermediate region is of the mixture of phases IV and V.

In the decompression process, the reverse change of the color from black to a thin yellow was observed, and the diffraction peaks of phase V disappeared and those of phase IV reappeared. The transition between phases IV and V was confirmed to be reversible.

As seen in Fig. 1, the x-ray pattern of phase V is substantially different from those of phases I, I′, and IV, which is in strong contrast with the relative similarity between those three phases. These results suggest a significant change in the structure of H_2S crystals. The color of the sample also changes remarkably at the transition from phase IV to V. It indicates the large decrease of the energy gap at the IV-V transition. Phase V may be metallic in the pressure range 27.5–42 GPa.

The detailed structure and properties of phase V must be investigated by various methods including an electric resistance measurement to determine if phase V is metallic. If so, to our knowledge, it will be the first pressure-induced metallization of a hydrogen-bonded material.

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[1] E. Sandor and S. O. Ogunade, Nature **224**, 905 (1969).

[2] A. Anderson, O. S. Binbrek, and H. C. Tang, J. Raman Spectrosc. **6,** 213 (1977).

[3] A. Anderson, S. Demoor, and R. C. Hanson, Chem. Phys. Lett. **140**, 471 (1987).

[4] H. Shimizu, Y. Nakamichi, and S. Sasaki, J. Chem. Phys. **95**, 2036 (1991).

[5] S. Endo, N. Ichimiya, K. Koto, S. Sasaki, and H. Shimizu, Phys. Rev. B **50**, 5865 (1994).

[6] M. J. Collins, C. I. Ratcliffe, and J. A. Ripmeester, J. Phys. Chem. **93**, 7495 (1989).

[7] J. K. Cockkroft and A. N. Fitch, Z. Kristallogr. **193**, 1 (1990).

[8] H. Shimizu, H. Yamaguchi, S. Sasaki, A. Honda, S. Endo, and M. Kobayashi, Phys. Rev. B **51**, 9391 (1995).