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Crystal structure of high-pressure phase-IV solid hydrogen sulfide

S. Endo and A. Honda
Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560, Japan

K. Koto
Faculty of Integrated Arts and Sciences, Tokushima University, Tokushima 770, Japan

O. Shimomura* and T. Kikegawa
National Laboratory for High Energy Physics, Tsukuba 770, Japan

N. Hamaya
Department of Physics, Ochanomizu University, Bunkyoku, Tokyo 112, Japan

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The crystal structure of high-pressure phase-IV solid hydrogen sulfide was studied by *in situ* angle-dispersive x-ray diffractometry using synchrotron radiation and an imaging plate. Analysis for the diffraction pattern obtained at 11.4 GPa shows that phase IV is monoclinic (space group Pc) as to the positions of sulfur atoms, which is structurally distorted from the cubic phases I and I′ stable at low pressures. The volume reduction of the phase I′–to–IV transition is 2.3%. The variation of the neighboring S-S distance in phase IV is different from phases I and I′, resulting in the disappearance of the orientationally disordered hydrogen bond. [S0163-1829(98)05209-6]

I. INTRODUCTION

Hydrogen sulfide (H_2S) exists as a typical hydrogen-bonded molecular solid at temperatures lower than 187.6 K under ambient pressure; three different crystalline phases named I, II, and III appear as temperature decreases.[1] In 1987 Anderson, Demoor, and Hanson[2] discovered another solid phase in the pressure range 3.3–8.0 GPa at 25 K by Raman scattering studies. Using a similar method, Shimizu, Nakamichi, and Sasaki[1] found a pressure-induced phase above 11 GPa at room temperature and named it phase IV. They assumed that phase IV may be the same phase as previously found by Anderson and co-workers.[2]

By high-pressure x-ray-diffraction experiments at room temperature, we have observed two successive pressure-induced phase transitions from phase I.[3] The first transition occurs at about 8 GPa, involving a symmetry change from F to P in the cubic lattice and the high-pressure phase was named as phase I′, in which sulfur atoms form a primitive cubic lattice. The second one takes place at 11 GPa, and we concluded that this transition is the same as that previously observed at 11 GPa by Raman scattering method;[1] the high-pressure phase above 11 GPa is, therefore, phase IV. Recently we have determined the pressure-temperature diagram for these five phases by Raman spectroscopy at high pressures up to 20 GPa and at low temperatures down to 30 K,[4] and have confirmed that the high-pressure low-temperature phase found by Anderson and co-workers is the same as phase IV.

Very recently we have found phase IV transforms again to another high-pressure phase at about 27 GPa at room temperature by an x-ray-diffraction experiment and we have called it phase V.[5] This is probably the highest pressure phase of solid H_2S detected so far.

In this paper we report the result of the structure analysis of phase IV stable above 11 GPa using the powder-diffraction patterns obtained with synchrotron radiation.

II. EXPERIMENT

High pressure was generated by a diamond anvil cell. Gaseous H_2S was condensed in a hole of a metal gasket between two diamond anvils cooled by liquid nitrogen. The details have been described in a previous paper.[1] Whereas the x-ray-diffraction experiment by which phase IV was confirmed,[3] was carried out with a rotating-anode-type x-ray generator and a position-sensitive proportional counter, the present one has been made by an angle-dispersive diffractometry using synchrotron radiation and an imaging plate.[6] The radiation from a bending magnet beam line of the storage ring operating at 2.5 GeV and 360 mA was monochromatized to $\lambda = 0.6888$ Å at the Photon Factory, National Laboratory for High Energy Physics. A collimated beam was 75 μm in diameter and the distance between the sample and the imaging plate was 164.489 mm. Pressure was determined from the ruby fluorescence technique.

III. RESULTS AND DISCUSSION

Some of the x-ray-diffraction patterns obtained under pressure at room temperature are shown in Fig. 1, and the d spacings of diffraction lines in all the diffraction patterns obtained in the present study are plotted in Fig. 2. The patterns at 4.2 and 7.8 GPa are of phase I with space group $Fm\bar{3}m$, which is orientationally disordered face-centered cubic (fcc), i.e., a plastic crystal.[7] The disordered S-H bond orientations are isotropic or pseudoisotropic, i.e., symmetric about all four C_3 axes of the cube. At 9.5 GPa, in contrast to

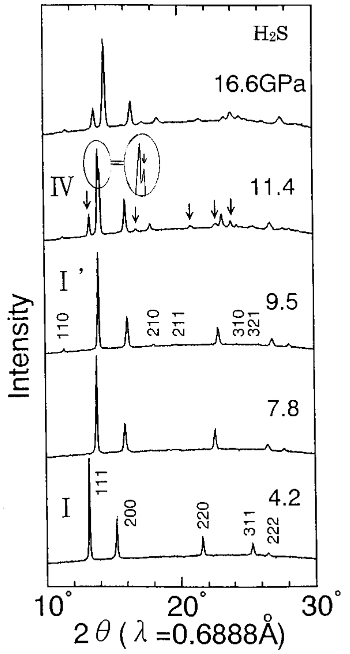

FIG. 1. X-ray diffraction patterns of phases I, I′, and IV of solid H_2S obtained using synchrotron radiation at various pressures and room temperature. The inset shows the strongest peak at 11.4 GPa is split into, at least, two peaks.

the single additional line in our previous experiment with a rotating-anode type x-ray generator,[3] we now have five diffraction peaks indicating positively the presence of a new phase. All diffraction lines in the pattern at 9.5 GPa can be indexed on the basis of a cubic cell. The fact that 110, 210, 211, 310, and 321 assigned for the new peaks are all forbidden for fcc provides an unambiguous confirmation that the fcc unit cell (phase I) changes into a primitive cubic cell (phase I′) as previously suggested.[3] In phase I′ sulfur atoms form a primitive cubic lattice with respect to sulfur atoms as described before.[3]

In the pattern at 11.4 GPa all diffraction lines of phase I′

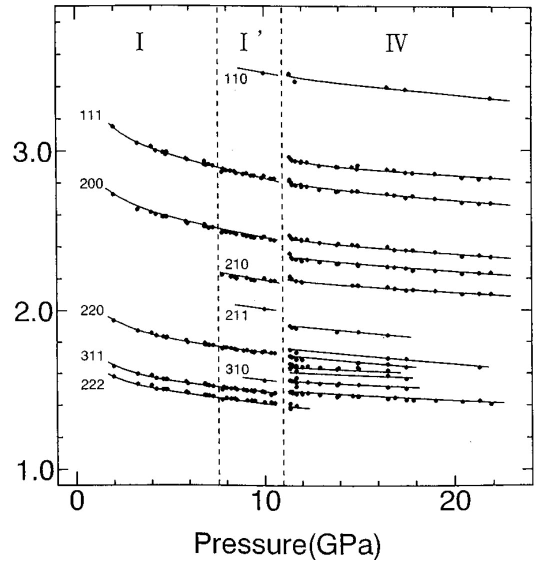

FIG. 2. The *d* spacings of the diffraction lines of phases I, I′, and IV plotted as a function of pressure.

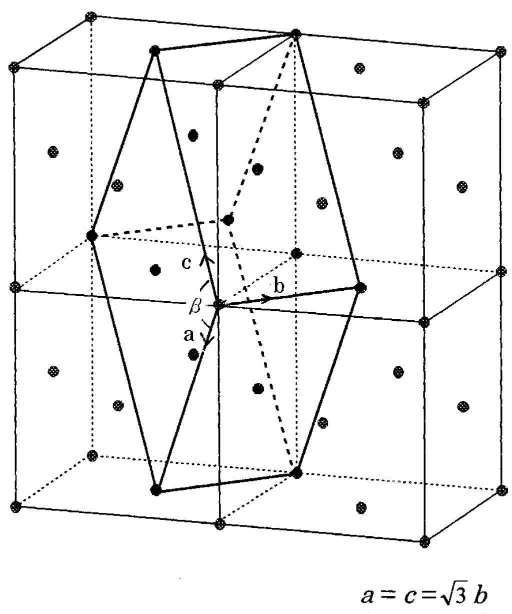

FIG. 3. A monoclinic lattice converted from the face-centered lattices.

TABLE I. X-ray diffraction data of phase IV of solid H_2Sat 11.4 GPa and room temperature.

I_{obs}[a]	d_{obs} (Å)	d_{calc}[b] (Å)	*hkl*	I_{obs}[a]	d_{obs} (Å)	d_{calc}[b] (Å)	*hkl*
		5.650	100			1.663	021
vw	3.482	3.482	010			1.657	310
m	2.965	2.964	110			1.647	013
		2.958	011	vw	1.634	1.633	$\bar{1}21$
		2.861	$\bar{1}02$			1.617	$\bar{3}12$
vs	2.822	2.825	200			1.612	$\bar{2}13$
		2.803	002			1.566	212
s	2.799	2.802	$\bar{1}11$	vw	1.559	1.559	121
m	2.472	2.471	111			1.490	$\bar{2}21$
vw	2.359	2.359	$\bar{2}02$			1.489	311
		2.265	102	w	1.487	1.487	$\bar{1}22$
w	2.217	2.218	$\bar{2}11$			1.483	113
		2.211	$\bar{1}12$			1.482	220
		2.194	210			1.479	022
		2.184	012			1.463	$\bar{1}04$
		1.953	$\bar{2}12$			1.439	$\bar{4}02$
vw	1.905	1.903	211			1.433	$\bar{3}13$
		1.898	112			1.431	$\bar{2}04$
		1.883	300	vw	1.413	1.412	400
		1.826	$\bar{3}02$			1.402	004
vw	1.753	1.753	202			1.401	$\bar{2}22$
		1.741	020			1.389	302
m	1.712	1.711	$\bar{3}11$	vw	1.382	1.382	221
		1.701	$\bar{1}13$			1.380	122
w	1.664	1.664	120			1.357	$\bar{4}11$

[a] Relative intensity where vs, s, m, w, and vw represent very strong, strong, medium, weak, and very weak, respectively.

[b] Calculated on the basis of a monoclinic unit cell with $a = 5.900$ Å, $b = 3.482$ Å, $c = 5.856$ Å, $\beta = 106.76°$, and $V = 115.20$ Å^3.

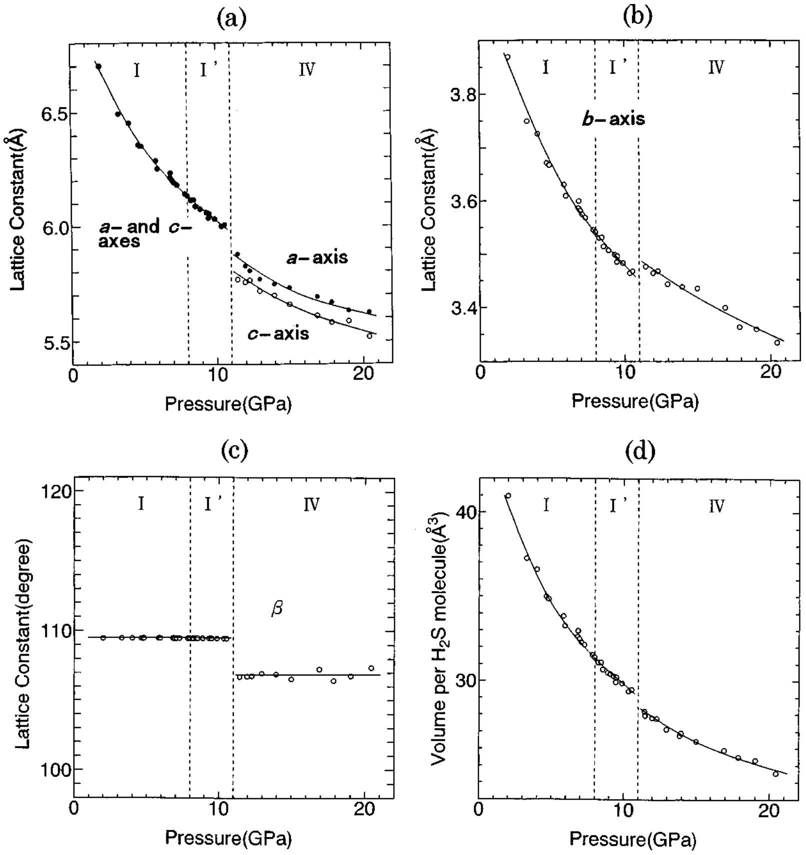

FIG. 4. The lattice parameters of a monoclinic cell and the volume per formula unit in phase IV plotted as a function of pressure. Those values in phases I and I′ are also plotted for the monoclinic cells converted from the cubic ones.

seem to remain, but their intensities did not diminish when pressure was increased. It was discussed previously too[3] that they are not of the residual phase I′, but all lines including several new ones (indicated by arrows) belong to the higher pressure phase IV. This fact suggests that phase IV has a structure slightly distorted from phase I′, probably due to more highly ordered arrangement of hydrogen and sulfur atoms. We have attempted to determine the crystal structure of phase IV.

Several candidates of the crystal structure were nominated for the arrangements of sulfur atoms in phase IV by a computer fitting using the program POWDMULT (Ref. 8) of the obtained diffraction pattern, and then their validities were examined by taking into account the characteristics required for the real structure. As a result a monoclinic cell was selected.

Phase I′, from which phase IV was obtained with the application of pressure, has a primitive cubic cell (the space group $P2_13$) with regard to sulfur atoms as mentioned above.[3] Since the shift of their positions from fcc is very small, the arrangements of sulfur atoms in phase I′ can be assumed as in fcc in the following discussion. One of the nominated lattices by a computer fitting is monoclinic cell delineated in the fcc lattice as shown in Fig. 3. One can distort this cell so that the x-ray-diffraction pattern observed for phase IV are well explained. The calculated *d* spacings of the monoclinic cell thus determined for phase IV at 11.4 GPa are listed together with the observed ones in Table I. The lattice parameters for the monoclinic cell converted directly without distortion from the cubic cell of phase I′ at 11.0 GPa are given as $a = 6.002$ Å, $b = 3.465$ Å, $c = 6.002$ Å, $\beta = 109.47°$, and the cell volume $V = 117.6$ Å^3, which are comparable with those of phase IV in Table I; the distortion from the cubic (phase I′) to the monoclinic (phase IV) cell is relatively small.

Anderson and co-workers[2] tentatively assigned the structure of their high-pressure and low-temperature phase to the orthorhombic or monoclinic system. In a previous study,[3] we also examined a few candidates with a lower symmetry than cubic, such as monoclinic or rhombohedral for phase IV, but the proposed structure model would not satisfy the patterns obtained with an in-house x-ray generator. The present success is ascribed to the high quality of new patterns, which has been achieved by the combination of synchrotron radiation and an imaging plate. For instance, we can see that the strongest diffraction line at 11.4 GPa in Fig. 1 is not a single peak, but split into, at least, two peaks, which are essential, as shown in Table I.

The changes of the lattice parameters of the monoclinic phase IV thus determined are plotted as a function of pressure in Figs. 4(a)–4(c), in which those converted from the cubic phases I and I′ are also plotted. At the transition from phase I′ to phase IV, the lattice parameters *a* and *c* decrease by the amount of 1.5 and 3.0 %, respectively, but that of *b* increases by 1.1%. The value of β decreases by 2.3% at the transition, but it is almost constant up to 21 GPa. The volume per formula unit is plotted as a function of pressure in Fig. 4(c), showing that a reduction of 2.3% is observed at the

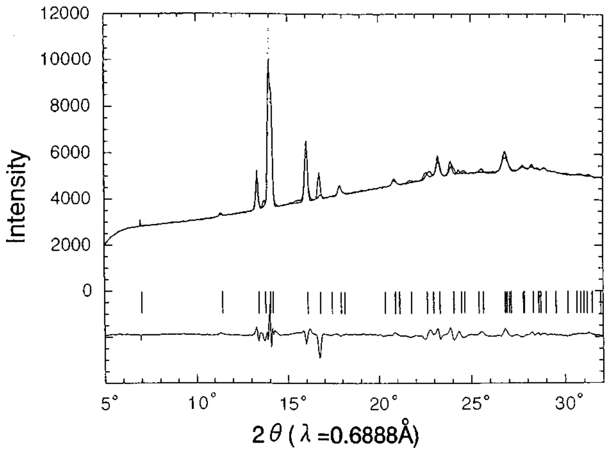

FIG. 5. Rietveld refinement performed for the diffraction pattern of phase IV at 11.4 GPa.

transition from phase I′ to phase IV, and that a finite decrease is not observed at the transition from phase I to phase I′ as reported previously.[3]

There are thirteen space groups belonging to the monoclinic system. Since some of the planer indices of the observed diffraction lines in Table I do not satisfy the possible reflection conditions for the base-centered lattice (C), phase IV must belong to a primitive monoclinic lattice (P). Furthermore, from the extinction rule, we found that Pc (No. 7) and $P2/c$ (No. 13) remained as the candidates. In order to narrow down our selection between the two, we have performed the intensity calculation of each diffraction line for various small shifts of the sulfur atoms and compared the result with the observed intensity, leading to an apparent conclusion that Pc is the most appropriate space group of phase IV.

In order to further refine the positions of sulfur atoms in the Pc-monoclinic cell, we have carried out Rietveld refinement using the program RIETAN.[9] Figure 5 shows the result for the diffraction pattern at 11.4 GPa and the positions of sulfur atoms have been determined as given in Table II. The R factor for the refinement, R_{wp} is 2.46% and the goodness-of-fit parameter is 1.6. The positions of sulfur atoms in phase IV represented by solid circles are also drawn in Fig. 6, in which their original positions in phase I′ represented by open circles are drawn for comparison, assuming that the monoclinic cell converted from the cubic one of phase I′ has the same dimensions as those of phase IV. The shifts of sulfur atoms from open circles to closed circles are clearly verified. The shifts are not large as predicted beforehand, but they induce the lattice deformation at the I′→IV phase transition. The distances from sulfur atoms, S(1) and S(2), respectively, to their surrounding sulfur atoms in phase IV are listed in Table III.

TABLE II. The lattice parameters and the positions of sulfur atoms determined by Rietveld refinement ($R_{\mathrm{wp}}=2.46\%$) for x-ray pattern at 11.4 GPa in Fig. 5.

	Pc	$xyz;\ x,\ y,\ \frac{1}{2}+z$	
Atom	x	y	z
S(1)	0.270±0.010	0.842±0.007	0.246±0.011
S(2)	0.750±0.010	0.308±0.008	0.291±0.011

$a=5.882\pm0.004$ Å

$b=3.459\pm0.002$ Å

$c=5.880\pm0.005$ Å

$\beta=106.67\pm0.03°$

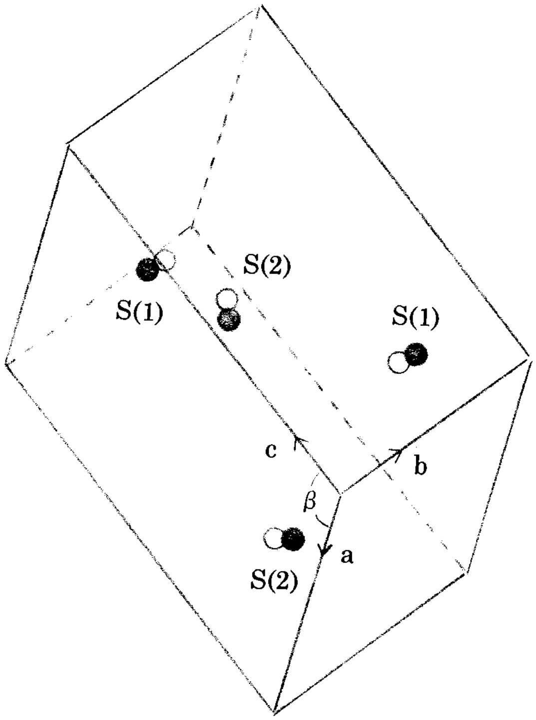

FIG. 6. The position of sulfur atoms in phase IV (●) corresponding to Table II and their approximate positions in phase I′ (○). The shift, ○→●, is realized at the phase I′→IV transition.

In the orientationally disordered phase I, the random flips between equilibrium orientations occur by breaking and remaking of temporary hydrogen bonds. Shimizu and co-workers[1] suggested on the basis of their Raman spectroscopic measurement that these orientational flippings are more and more hindered by the decrease in the intermolecular distance with increasing pressures and the molecules tend

TABLE III. The distances of neighboring sulfur atoms from S(1) and S(2) atoms in phase IV. The estimated errors are ±0.01 Å for all the distances.

Around S(1)		Around S(2)	
Distance (Å)	Total number	Distance (Å)	Total number
3.14	2[S(1),S(1)]	3.20	1[S(1)]
3.20	1[S(2)]	3.23	2[S(2),S(2)]
3.32	1[S(2)]	3.32	1[S(1)]
3.46	1[S(1)]	3.46	1[S(2)]
3.48	1[S(2)]	3.48	1[S(1)]
3.53	1[S(2)]	3.53	1[S(1)]
3.64	1[S(2)]	3.63	2[S(2),S(2)]
3.65	1[S(2)]	3.64	1[S(1)]
3.77	2[S(1),S(1)]	3.65	1[S(1)]
4.45	1[S(2)]	4.45	1[S(1)]

to stay a longer time in one of the probable equilibrium orientations. At the transition pressure of 11 GPa, they observed a sudden decrease of the half width of the O-H stretching vibration mode ν_1 and concluded that hydrogen atoms are fixed and the reorientational molecular motions stop and change to vibrational motions around the equilibrium orientation; the orientationally disordered phase, therefore, disappears.

We can understand the above description on the present x-ray study as follows: in phase I sulfur atoms lying at the face-center positions in a fcc lattice are surrounded disorderly by the equivalent twelve nearest neighboring sulfur atoms via hydrogen bonds. In phase I′ of the cubic lattice with *P* symmetry, sulfur atoms are a little apart from the face center, and the interatomic distances corresponding to the nearest neighbors in fcc are almost equal (∼3.5 Å at 11.0 GPa),[3] and then the situation for the orientational disorder does not change so largely. However, the distances between the neighboring sulfur atoms in phase IV cover a wide range between 3.13 and 4.44 Å at 11.4 GPa as shown in Table III. Hydrogen atoms are probably fixed between the sulfur atoms with the short interatomic distance and as a result the S-H bond in phase IV would become orientationally ordered. A neutron-diffraction study would be valuable for the determination of the positions for hydrogen atoms.

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*Present address: SPring-8, Kamigoricho, Ako, Hyogo 678-12, Japan.

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