

Pressure-Induced Hydrogen Bonding: Structure of D₂S Phase I'

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The full structure of the high-pressure cubic phase I' of hydrogen sulfide has been solved using neutron diffraction data. The molecules are partially rotationally disordered about the $\langle 111 \rangle$ axes, as in phase II at ambient pressure but with markedly greater nonuniformity of the toroidal D distribution. The changes in structure at the II \rightarrow I' transition signal the onset of significant pressure-induced hydrogen bonding.

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There has been considerable recent interest [1–10] in the behavior of hydrogen sulfide at high pressure. At the molecular level it is an analog of water, but its properties and behavior are significantly different. While water is strongly hydrogen bonded, the ambient pressure structures of hydrogen sulfide do not appear to be influenced by H bonding at all [11]. Hydrogen sulfide is thus a good simple molecular system for exploring intermolecular interactions in the very weakly H-bonded regime. Spectroscopic data indicate that pressure increases the strength of the H bonds in hydrogen sulfide. Recent modeling studies [10] have concluded that the structure of phase IV—found above ~ 11 GPa at room temperature—shows evidence that the onset of significant H bonding is the driving force behind the transition to this phase.

The structural behavior of hydrogen sulfide is dominated by increasing orientational ordering on both cooling and compression. The first solid phase on cooling at ambient pressure—phase I (Fig. 1)—has a face-centered cubic (fcc) structure and a disordered molecular arrangement in which the maxima in D density [12] are directed with equal probability towards all twelve nearest-neighbor molecules [11]. Further cooling results in the formation of the primitive-cubic phase II whose partial molecular ordering will be described below. At the lowest temperatures phase III forms, with a fully ordered molecular arrangement [11]. The high-pressure phase diagram has been explored by piston-displacement studies up to 2 GPa [13] and also extensively explored by Raman studies to ~ 15 GPa [5]. High-pressure structural information has been obtained at room temperature from x-ray studies [3,8,9]. The transition sequence found on compression is similar to that found on cooling. Phase I forms above 0.47 GPa at room temperature [3,5]. Further compression results in a primitive cubic phase I' at 9.1 GPa which then transforms to phase IV at 11 GPa [3]. The structure of phase IV is the subject of some disagreement. X-ray studies have proposed orthorhombic [8] and monoclinic [9] structures, while the recent *ab initio* modeling studies proposed a tetragonal structure [10].

The nature of the two primitive cubic phases II and I' is also uncertain. X-ray [14] and neutron [11] powder diffraction studies at ambient pressure suggest that the sulfur atoms in phase II occupy fcc sites. Neutron studies show that the D sites lie on planes containing the sulfur atoms and normal to $\langle 111 \rangle$ directions. (The structure shown for phase II in Fig. 1(f) of Rousseau *et al.* [10] is incorrect and is that of phase I.) Each sulfur atom is then surrounded by a torus of deuterium density whose axes are $\langle 111 \rangle$ directions. This arrangement strongly suggests that the molecules in phase II rotate about $\langle 111 \rangle$ directions and is very unusual—the only other known structure with such a toroidal arrangement is that of phase Ib of HBr [15]. Phase I' has a Raman spectrum indistinguishable from that of phase II [5], but differs from phase II through the presence of weak non-fcc peaks in x-ray patterns [3]. These led Endo *et al.* [3] to suggest that the S atoms were slightly displaced from the fcc positions on the $4a$ site within space

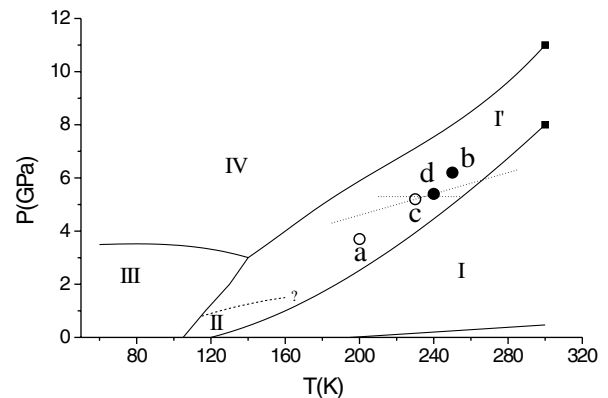


FIG. 1. The phase diagram of hydrogen sulfide. The solid lines are after Shimizu *et al.* [5]. The dashed line is the density discontinuity reported by Stewart [13] but not found in Ref. [5]. The solid squares show transition points reported by Shimizu *et al.* [1] and Endo *et al.* [3]. The circles correspond to the four spectra shown in the upper inset of Fig. 2 for phase I' (solid circles) and phase II (open circles). The dotted lines are the estimated maximum and minimum slopes for the II/I' transition line and their point of intersection marks the estimated transition.

group $P2_13$, which has since been confirmed by Rietveld profile refinement [8].

The structural similarity of phases II and I' raises the important question as to their precise relationship. Their space groups $Pa\bar{3}$ (phase II) and $P2_13$ (phase I') differ only in that $Pa\bar{3}$ has a center of inversion symmetry. In view of the indistinguishability of their Raman spectra, Shimizu *et al.* [5] suggested that the two phases are the same and that the displacement of the S atoms from fcc sites—the only difference between phase II and phase I' observed to date—is simply unmeasurably small at ambient pressure and increases progressively with pressure. Fujihisa *et al.* [8] proposed a quite different structure with three H sites in the plane normal to $\langle 111 \rangle$ and a further three H sites located out of this plane, such that their S-H bonds are directed along $\langle 110 \rangle$, $\langle 101 \rangle$, and $\langle 011 \rangle$ directions. But this model conflicts with the observation that phases II and I' have indistinguishable Raman spectra [5].

We now report neutron diffraction studies of phases II and I' which reveal a clear structural transition between them, at ~ 5 GPa, and suggest that the transition is driven by the onset of significant H bonding. We thus find that pressure induces H bonding in H_2S , as proposed by Rousseau *et al.* [10], but at a much lower pressure and in a different phase.

Neutron diffraction studies were carried out using the Paris-Edinburgh opposed-anvil large-volume cell [16,17]. The sample was loaded using the procedure for gaseous samples described by Klotz *et al.* [18]. Neutron diffraction data were collected using time-of-flight techniques on the high-pressure station (HiPr) on the PEARL beam line of the U.K. pulsed-neutron source, ISIS, at the Rutherford Appleton Laboratory, and analyzed using the GSAS program [19].

The upper plot of Fig. 2 shows the neutron diffraction pattern collected at 200 K, which gives a lattice parameter of 5.2188(11) Å. Based on the room temperature equation of state [8] corrected for the volume change at the $I \rightarrow II$ transition [11] and an estimated volume thermal expansion of $2 \times 10^{-4} \text{ K}^{-1}$, this lattice parameter corresponds to a pressure of 3.7(2) GPa. All sample reflections are consistent with the unit cell and $Pa\bar{3}$ space group found for phase II at ambient pressure [11], and no evidence was found for the presence of $0kl$ (k odd) reflections which would indicate a lowering of symmetry to $P2_13$. The load on the cell was increased, and the lower plot of Fig. 2 shows the pattern collected at 6.2 GPa and 250 K (lattice parameter = 5.6060(11) Å). The pattern can again be indexed with a primitive cubic unit cell, but is characterized by the appearance of a strong 031 reflection (marked by an arrow) which indicates a change in symmetry to $P2_13$. The region of the 031 reflection is shown enlarged in the lower inset, and is shown again in profile (b) in the upper inset, where the same region of the phase II profile is shown in (a).

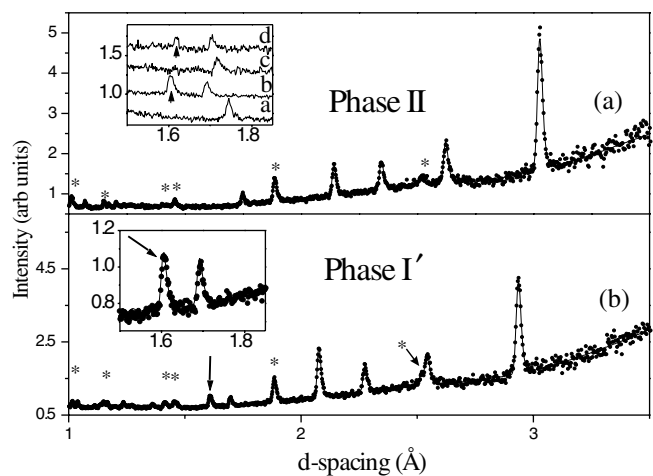


FIG. 2. Rietveld profile refinements of neutron data collected from (a) D_2S phase II at 3.7 GPa and 200 K and (b) D_2S phase I' at 6.2 GPa and 250 K. The observed data are shown as dots and the calculated profile as a solid line. The asterisks mark peaks due to scattering from the tungsten carbide anvils. The lower inset shows in detail the region of the arrowed 031 reflection in (b); the upper inset shows this region again in profiles (a) and (b) and also in profiles (c) at 5.2 GPa and (d) at 5.4 GPa.

The sample was then decompressed to 5.2 GPa and cooled to 230 K, where the 031 reflection disappeared [(c) in Fig. 2 inset] as the sample transformed back to phase II. Recompression in smaller steps led to the reappearance of the 031 reflection at 5.4 GPa and 240 K [(d) in the inset]. The fact that the 031 reflection is absent up to ~ 5 GPa, and then appears over a small pressure range, shows that II and I' are distinct phases separated by a clear, quite abrupt transition contrary to the suggestion of Shimizu *et al.* [5]. We estimate the transition pressure to be 5.3 GPa at 235 K. This is a much higher pressure than the density discontinuity shown as the dashed line in Fig. 1. (No discontinuity along this line has been reproduced in any subsequent study, including the work of Shimizu *et al.* [5] which explored this region of the phase diagram in detail.) As will be shown below, phase I' is more ordered than phase II, and so dT_c/dp must be positive. The detection of phase I' also at 5.4 GPa and 230 K, between points *c* and *d* in Fig. 1, indicate that dT_c/dp must be greater than 50 K/GPa. The dotted lines in Fig. 1 then represent the range of possible values for dT_c/dp .

To solve the full structure of I' , the sulfur atom was fixed at the coordinates determined at 9.1 GPa and 300 K [8]. An initial deuterium arrangement with approximate spherical disorder was modeled by distributing two D atoms equally over three rings of twelve sites with S-D bonds at angles of 90° and $\pm 45^\circ$ to $\langle 111 \rangle$, plus two polar sites on $\langle 111 \rangle$ axes. The S-D distance was fixed to the ambient-pressure value of 1.3 Å [11]. When the occupancies of these “equatorial,” $\pm 45^\circ$, and polar groups of D sites were refined, all of the density refined into the equatorial ring within error. This shows that phase I' , like phase II, has a

toroidal deuterium arrangement. The model proposed by Fujihisa *et al.* [8] gave a much poorer fit, and when the positions of the D atoms were varied it proved impossible to obtain a stable refinement. For these reasons, the Fujihisa *et al.* model is rejected.

The isotropy of the deuterium distribution around the toroid was explored for both phases II and I'. Refinements of the data shown in Fig. 2 were carried out using models with three, six, and twelve D sites equally spaced in an equatorial ring around $\langle 111 \rangle$. The optimal arrangement was found for each model from the goodness-of-fit as the site positions were stepped in 10° intervals around $\langle 111 \rangle$. Only the three-site model was able to fit the strong 031 reflection observed in phase I', which is thus characterized by a threefold nonuniformity of the deuterium distribution around the torus, in addition to the displacement of the sulfur atoms from fcc sites identified from x-ray data [8].

For phase II, the twelvefold model gave the best fit. And a lack of any change in the goodness-of-fit with site positions around $\langle 111 \rangle$ suggests that the D distribution in phase II is close to uniform. This conflicts with Cockcroft and Fitch's report of a sixfold nonuniformity at ambient pressure [11]. However, their sixfold distribution cannot be reconciled with the 92.2° D-S-D angle [11] and the $\bar{3}$ point symmetry of the S site which, together, imply at least twelvefold nonuniformity.

Final refinements of the I' structure were carried out with the D-S-D angle fixed to 92.2° while the D-S bond length and the molecular orientation were refined. Anisotropic thermal motion was refined for the D atoms, constrained so that two of the principal axes of the thermal-motion ellipsoids were parallel to the S-D bond and parallel to $\langle 111 \rangle$. This constraint is the simplest description of a liberating molecule, and gave a significant improvement in fit over models with isotropic thermal motion. These refinements produced the fit shown in Fig. 2 and the molecular orientation shown in Fig. 3 [20]. The plane of the molecule is slightly canted at $\sim 10^\circ$ to a plane normal to $\langle 111 \rangle$ through the sulfur site, so that one D site lies in this plane and the other is displaced slightly out of it. The threefold symmetry around $\langle 111 \rangle$ and the molecular geometry imply a deuterium distribution with two sites $\sim 28^\circ$ apart every 120° around $\langle 111 \rangle$, as shown in Fig. 3(a). Strong librational motion is observed with an rms amplitude of $0.36(6) \text{ \AA}$ which is equivalent to an angular amplitude of $\sim 18^\circ$. The refined apparent S-D bond length of $1.158(11) \text{ \AA}$ is significantly shorter than at ambient pressure ($1.25\text{--}1.35 \text{ \AA}$ [11]) but, because of the large libration, this apparent shortening of S-D is consistent with a true S-D unchanged by pressure. The displacement of the S site from the fcc position was $0.05(10) \text{ \AA}$ —zero within error, and much smaller than the value of $\sim 0.1 \text{ \AA}$ determined at room temperature from x-ray data [8]. Low-temperature x-ray studies will be required to show whether this is really the result of the difference in P-T conditions between the x-ray and

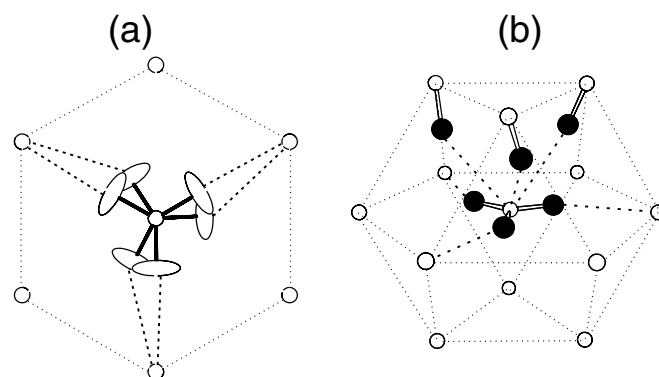


FIG. 3. Structure of D_2S phase I'. (a) The six nearest neighbors of a sulfur atom lying in the plane normal to $\langle 111 \rangle$, and the refined positions and thermal-motion ellipsoids of the deuterium sites around the central sulfur atom, as described in the text. (b) The full nearest-neighbor coordination, with each pair of independent D sites represented as a single (isotropic) site for clarity. The dotted lines mark the S site planes. In both diagrams the dashed lines denote proposed H-bond contacts.

neutron work or simply the effect of sample texture and the low sensitivity of the neutron data to the scattering from sulfur. (S has a neutron scattering cross-section smaller than that of D by a factor of ~ 4 .)

Figure 3(b) shows the full nearest-neighbor environment of a D_2S molecule in phase I'. For clarity, the maxima of the threefold nonuniformity of the deuterium arrangement are shown as single (isotropic) sites. The maxima associated with the central molecule are directed approximately towards three of the six nearest-neighbor sulfur atoms in the basal plane normal to $\langle 111 \rangle$ [as shown in detail in Fig. 3(a)]. The sulfur atom of the central molecule has maxima directed towards it from molecules in only one of the two adjacent planes parallel to the basal plane. Thus, six of the twelve nearest-neighbor S...S contacts for a given molecule are H bonded. This arrangement with S-D bonds directed along S...S contacts suggests that hydrogen bonding is the driving force behind the transition from phase II to I'.

At ambient pressure the hydrogen bonding in hydrogen sulfide appears to be absent or very weak. The H(D)...S distances ($\sim 2.8 \text{ \AA}$) are close to the sum of the van der Waals radii for hydrogen and sulfur, and Cockcroft and Fitch [11] concluded that the dominant interactions between molecules in phase III were dipole-dipole interactions. Raman studies [5] show that the S-H stretch vibration softens with increasing pressure, and Brillouin scattering measurements of sound velocities [4] show a reduction in translation/rotation coupling. Both of these effects are considered indicative of strengthening of the hydrogen bonding with pressure [4,5]. As mentioned, Rousseau *et al.* concluded from their modeling studies that phase IV was hydrogen bonded and they speculated that hydrogen bonding was the driving force behind the transition to phase IV [10]. We conclude that hydrogen sulfide does have a transition driven by the onset of

significant H-bonding but that this occurs at a much lower pressure than suggested [10] and involves phase I' instead of phase IV.

Fujihisa *et al.* [8] noted the similarity between the heavy-atom structures of phase I' of H_2S and phase I of ammonia [21]. Our studies reveal that the H-bond arrangement in H_2S-I' —with three donated H bonds all in the plane normal to $\langle 111 \rangle$ and three accepted H bonds from one adjacent plane—is also very similar to that found in ammonia-I [21].

It is interesting that an arrangement in which H bonds donated from the central molecule are confined to a single plane of six nearest-neighbor molecules is also found in the time and space averaged $P4_2/nmc$ structure proposed by Rousseau *et al.* for phase IV [10]. Although the unit cell of this structure is inconsistent with the measured x-ray diffraction [22], the simulated scattering [Figs. 2(a) and 3(b) of Rousseau *et al.*] is consistent with the measured scattering [22,23]. The true structure is likely to be a (possibly more orientationally ordered) supercell of the $P4_2/nmc$ structure but with the same basic features. These probable similarities in structural arrangement between phase IV and phase I' suggest that phase I' is the first step in the progressive H-bonded orientational ordering of the D_2S molecules with pressure.

We have seen that there is a definite, relatively abrupt transition between phases II and I' and that the structural differences are consistent with the onset of structurally significant H bonding at the $II \rightarrow I'$ transition. Hydrogen sulfide is the only example yet known of a simple molecular ice [H_2O , H_2S , CH_4 , NH_3 , HX ($X = F, Cl, Br, I$)] where the application of pressure has this effect. We thus have a molecular analog of water in which the H-bond strength can be tuned from absent or very weak to structurally significant. That this involves a change as simple as suppressing free rotation about a single axis invites other experimental investigations and further computational studies. It is interesting that hydrogen sulfide's tendency to undergo progressive orientational ordering with increasing P or decreasing T is preserved at pressures where the H bonding becomes structurally significant. If phase IV is also dynamically disordered—as Rousseau *et al.* find—then H_2S will provide a good model system to explore the way increasing H-bond strength quenches orientational disorder. Clearly neutron studies of phase IV at variable temperature are needed to explore this, and to resolve the current controversy as to the nature of the structure of phase IV.

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