

Direct synthesis of pure H₃S from S and H elements: No evidence of the cubic superconducting phase up to 160 GPa

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(Received 6 September 2016; revised manuscript received 1 December 2016; published 23 January 2017)

The H₃S compound was reproducibly synthesized by laser heating hydrogen-embedded solid sulfur samples at various pressures above 75 GPa in a diamond anvil cell. X-ray diffraction studies were conducted up to 160 GPa and the crystal structure has been identified with space group *Cccm*. The stability of this sole orthorhombic H₃S phase up to 160 GPa contradicts *ab initio* calculations that predict the stability of a sequence of two metallic superconductive structures above 110 GPa, with *R3m* and *Im $\bar{3}m$* symmetries. This work also has strong implications for the current understanding of the 200 K superconductivity phenomenon in H₂S since it seems to rule out the hypothesis of the decomposition of H₂S into sulfur and superconducting H₃S.

DOI: [10.1103/PhysRevB.95.020104](https://doi.org/10.1103/PhysRevB.95.020104)

The recent experimental discovery of a 200 K superconductivity phenomenon in hydrogen sulfide under compression at 150 GPa [1] has aroused great interest. This discovery came after two predictions from *ab initio* calculations: one on hydrogen sulfide (H₂S) with a T_C of around 80 K [2] and another one for sulfur trihydride (H₃S) with a T_C of around 200 K [3], both in the same pressure range. Since H₂S was calculated to be superconductive with a much lower T_C than the one measured experimentally, the interpretation of the 200 K superconductivity phenomenon has been inspired by the calculations on H₃S. This interpretation posits that H₃S is responsible for the superconductivity observed, through the decomposition of H₂S into H₃S+S. More precisely, the experimental evolution of the T_C with pressure is explained by the stability in H₃S of the *R3m* phase above 110 GPa and of the *Im $\bar{3}m$* phase above 150 GPa [1]. Numerous theoretical studies have then elaborated on this interpretation with the implication that the calculations were reliable enough to predict novel hydrides and to accurately estimate their T_C , hence paving the way for the design of hydrogen-rich compounds with near ambient temperature superconductivity. However, experimental validation is still needed to make sure that the stable structures of H₃S are indeed first *R3m* above 110 GPa and then *Im $\bar{3}m$* above 150 GPa. Recently, three experimental structural studies have aimed at characterizing H₂S under pressure [4–6]. They all three seem to support that metallic superconductive H₃S could be found among several other by-products of the decomposition of H₂S under pressure. However, the poor crystalline quality of the samples after the dissociation (even after temperature annealing) as well as the complexity of these multiphase patterns prevent an unambiguous refinement of the structures observed.

In this context, the present Rapid Communication aims at accurately determining the most thermodynamically stable structures of pure H₃S as a function of pressure at room temperature owing to the direct synthesis of pure H₃S by laser heating sulfur in hydrogen at various pressures. This is critical to have a confirmation of the calculated phase diagram of H₃S and to make sure that metallic H₃S is indeed stable in the

pressure range in which superconductivity occurs in the H₂S system. The structural changes of H₃S have been measured from 75 up to 160 GPa. Previous structural studies of H₃S had been performed up to 30 GPa on (H₂S)₂H₂ (hereafter always referred to as H₃S even in its nonmetallic state, out of commodity) by Strobel *et al.* from a mixture of H₂S and H₂ [7]. Two structures with *I4/mcm* and *I222* space groups had then been proposed to account for the diffraction pattern observed. Later, Duan *et al.* calculated the structural evolution of H₃S. A more stable *P1* structure was found to match the diffraction patterns as well and it is expected to then transform into a *Cccm* structure above 40 GPa. Above 110 GPa, a structural transformation into a trigonal metallic phase with space group *R3m* was predicted to be concurrent with the dissociation of the H₂ molecules, and the creation of H₃S entities. H₃S is then expected to become a high critical temperature superconductor with $T_C = 200$ K through a displacive phase transition into a bcc phase with space group *Im $\bar{3}m$* [3]. Duan *et al.*'s theoretical work has been supported by the calculations performed by Li *et al.* which have found the same pressure for the metallization and the superconducting transition but proposed a *C2/c* structure instead of the *Cccm* one. In both calculations, the *R3m*-to-*Im $\bar{3}m$* transition was predicted to occur at around 180 GPa. A recent theoretical work has shown that taking into account the H zero point motion significantly lowers the transition pressures [8], with the transition from *R3m* to *Im $\bar{3}m$* occurring at around 103 GPa. It should be noted that the well-known deficiency of *ab initio* calculations, performed in the density functional framework associated with generalized gradient approximation, could lead to an underestimation of the metallization pressure, and hence of the transition pressure from the *Cccm* structure to the *R3m* one. While there is a theoretical consensus on the structural transformations of H₃S under pressure, the transition pressures to these various phases are still uncertain.

The samples were prepared following a similar protocol to the one followed for the synthesis of iron and beryllium hydrides [9,10]. As shown in Fig. 1, solid sulfur samples of about 20 μm were loaded in a diamond anvil cell, embedded in hydrogen in excess as a pressure medium. Rhenium gaskets were used, with a gold coating of about 700 Å in order to prevent the loss of hydrogen by diffusion. Pressure was

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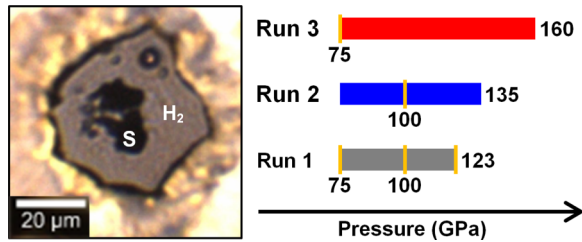


FIG. 1. Left: Picture of the experimental chamber (run 1) taken at 65 GPa. In the middle, one can see the metastable sulfur, surrounded by solid H_2 . A ruby, two gold micromarbles, and *c*-BN grains are also present. A rhenium gasket with a gold coating of about 700 Å prevents the diffusion of H_2 outside the experimental chamber. Right: Representation of the different runs in this experiment. The orange bars indicate the pressure of the laser annealing processes.

measured using the equation of state of a small piece of gold loaded close to the sulfur sample [11]. The sulfur sample was thermally insulated from the diamond culets by *c*-BN grains. A chemical reaction was initiated between the two compounds using a YAG-laser heating system. Hydrogen being in excess, the highest stable stoichiometry is expected to form. The pressure was increased up to around 70 GPa before turning on the heating. At lower pressures, the sulfur could melt and H_2S could also form (which would lead to several dissociation products when increasing the pressure). The chemical reaction between sulfur and hydrogen was quick and signaled by a flash of light during the increase of the laser power. The laser power was then slowly increased again to observe thermoemission coming from the sample. The temperature reached during such a process is at least 1300 K, which corresponds to the weakest thermoemission one can roughly observe through the camera setup. There is a subtle balance to find between the power and the time of the heating process in order to obtain the best powder of H_3S without sulfur; indeed, an excessively long heating process would lead to a very marked preferred orientation. Three samples were studied with different pressure ranges and annealing pressures, as shown in Fig. 1. In the first run, the laser heating process was repeated at several pressures, in order to make sure that the most thermodynamically stable structure was obtained. X-ray diffraction (XRD) data were collected at the ID27 beamline of the ESRF with a wavelength of 0.3738 Å. The XRD data were then analyzed using DIOPTAS [12] and the FULLPROF software suite [13].

As illustrated in Fig. 2(a), the XRD signal recorded on the image plate clearly evidenced the formation of a new phase after laser heating the $S+H_2$ mixture. An integrated diffraction pattern of the pure new phase at 100 GPa is shown in Fig. 2(b). The Rietveld refinement gives an orthorhombic unit cell with the *Cccm* symmetry and 16 atoms in Wyckoff positions $8l$ (0.756,0.0701,0.5) and $8l$ (0.423,0.746,0). Because of the low atomic scattering power of the H atom, it was impossible to determine the position of the H atoms. Nevertheless, this *Cccm* structure for the S atoms matches the one predicted by Duan *et al.* [3] quite well. The *C2/c* symmetry proposed in the other theoretical works [5,8] fails to correctly reproduce our data. The quality of the diffraction pattern of run 3 at high pressure was unfortunately deteriorated by the small size of the sample and the presence of the Re gasket and the Au pressure

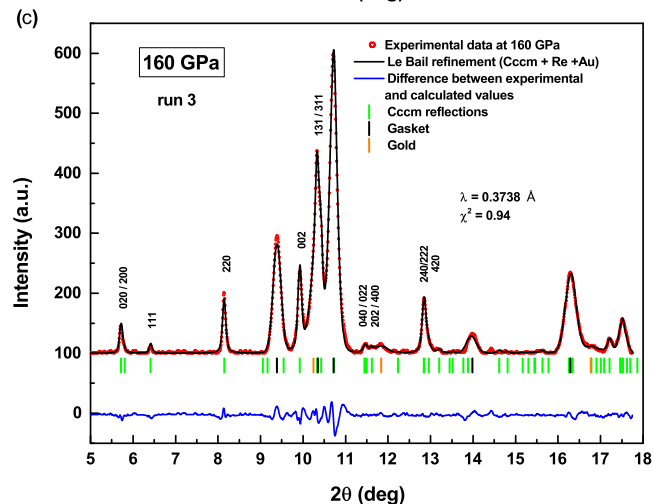
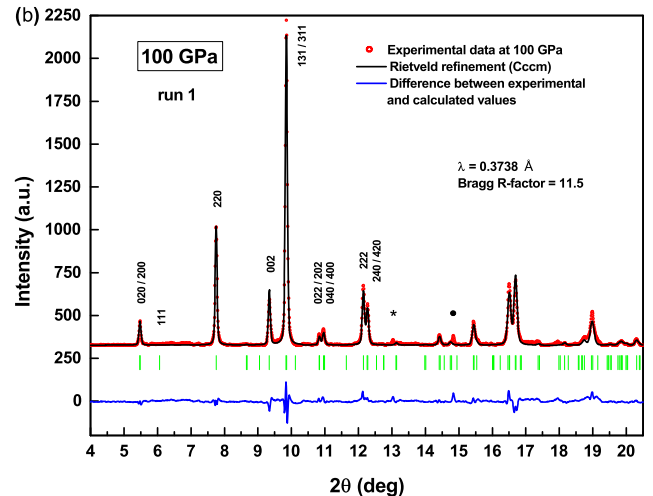
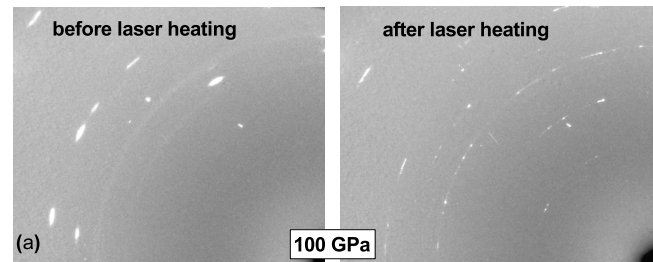


FIG. 2. (a) Comparison of image plates before and after laser heating at 100 GPa (run 2). (b) Rietveld refinement at 100 GPa. The star indicates the hydrogen peak and the dot indicates an impurity line which does not come from the sample. H_3S is described as a *Cccm* unit cell ($a = 7.81$ Å, $b = 7.83$ Å, $c = 4.59$ Å) with S atoms in positions $8l$ (0.756,0.0701,0.5) and $8l$ (0.423,0.746,0) (run 1). (c) Le Bail refinement at 160 GPa of the *Cccm* structure ($a = 7.38$ Å, $b = 7.50$ Å, $c = 4.32$ Å) combined with gold and hydrided rhenium (run 3).

gauge next to it. A Rietveld refinement was not possible, but a three-phase Le Bail refinement gives satisfactory results with the *Cccm* symmetry for H_3S , as shown in Fig. 2(c). It is interesting to note that the sulfur is still in phase III at 100 GPa before heating, whereas according to previous studies it was expected to be in its metallic phase IV above 80 GPa [14,15]. This could be attributed to higher nonhydrostaticity in the

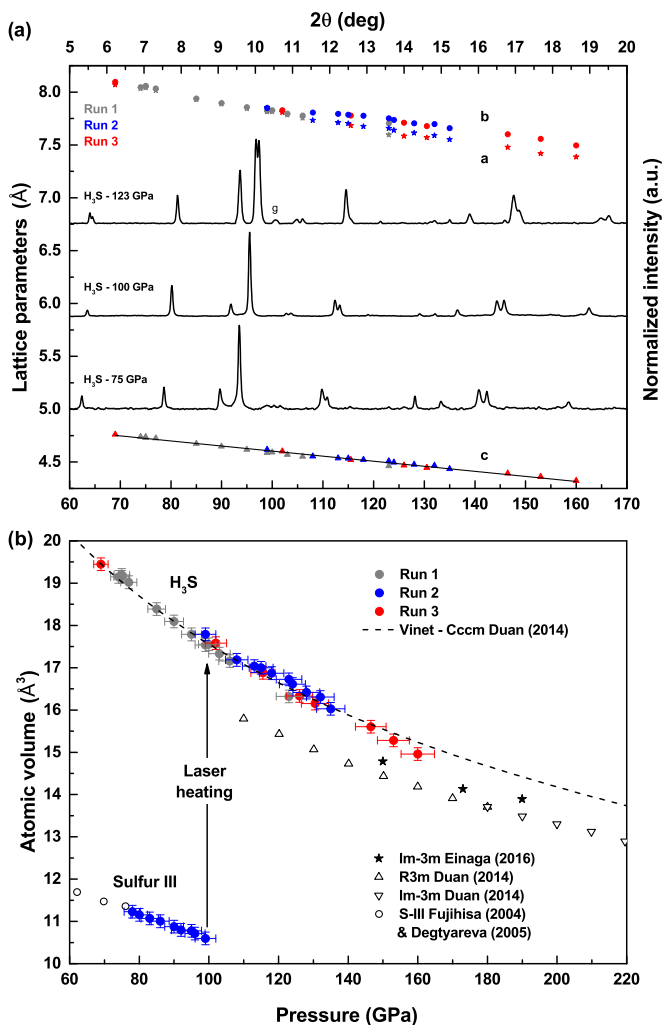


FIG. 3. (a) Top and bottom: Evolution of the lattice parameters of the *Cccm* structure as a function of pressure. Middle: Evolution of the normalized x-ray pattern as a function of pressure. (b) Atomic volume as a function of pressure. Experimental data for H₃S with the *Cccm* symmetry are represented together with literature data [3,4,14,15]. The uncertainty in pressure is $\pm 3\%$ and in volume $\pm 0.15 \text{ \AA}^3/\text{S}$.

previous experiments, since they used no pressure transmitting medium or neon, as opposed to hydrogen.

The evolution of the lattice parameters under pressure and the equation of state of the *Cccm* phase are reported in Fig. 3. At about 100 GPa, the lattice parameters *a* and *b* start to diverge, as can be seen in Fig. 3(a). This deviation in the lattice parameters induces a noticeable change in the diffraction peak of the (311/131) reflections, which starts to split. The peak separation is well described by the *Cccm* structure, which comforts us in this structure in the 100–160 GPa pressure range. This change in the lattice parameters' behavior could be interpreted as a phase transition, from a tetragonal structure with $a = b$ to an orthorhombic structure. The tetragonal *I4/mcm* structure, proposed by Strobel *et al.* at low pressure, fits our data with a quality index as good as for the *Cccm* structure. However, we chose to model our data with the orthorhombic *Cccm* structure below 100 GPa too. Indeed, based on Duan *et al.*'s work [3], the *Cccm* structure is

more stable than the *I4/mcm* one, even with a very slight orthorhombic distortion as in our experiment. Moreover, the main difference between these two structures is the orientation of the H₂S and H₂ molecules in the structure, which is not visible with our XRD data, and the positions of the S atoms are very close from one structure to another. Note that when extrapolating the cell parameters at 55 GPa ($a \approx b \approx 8.32 \text{ \AA}$ and $c \approx 4.80 \text{ \AA}$), and simulating a diffraction pattern with $\lambda = 0.31 \text{ \AA}$, there is a strong agreement with Goncharov *et al.*'s XRD data [6], which were interpreted with the *Cccm* structure as well for H₃S.

The volume per S atom of the *Cccm* phase is plotted in Fig. 3(b), with different colors for the three runs. A good reproducibility is observed, implying that the same compound is synthesized each time, in particular, with the same H stoichiometry. The volume expansion of the S lattice upon the formation of the hydride from pure sulfur is $+7 \text{ \AA}^3$ per S atom. Assuming that H₃S is formed, the volume expansion per H atom is thus about $+2.3 \text{ \AA}^3$, which is close to the value determined from the volume expansion in the formation of *3d* metal monohydrides [16] and recently of Fe polyhydrides [9]. Remarkably, the measured volume of H₃S is in strong agreement with the calculated volume of *Cccm* H₃S [3]. That is a strong indication of the formation of a trihydride H₃S, since the electronic *ab initio* calculations using Perdew-Burke-Ernzerhof generalized gradient approximation (PBE GGA) functionals are known to correctly reproduce the compression curve of hydrides [9,10,17]. To sum up, the pure *Cccm* H₃S phase was reproducibly formed above 75 GPa and remained stable up to 160 GPa, even after heating the sample until visible thermoemission in order to overcome potential kinetic barriers. No evidence of a transition of H₃S into the predicted *R3m* above 110 GPa or into *Im3m* above 150 GPa phases was detected. Thus, this *Cccm* structure is the thermodynamically stable phase of H₃S up to at least 160 GPa. As seen in Fig. 3(b), the expected volume of the metallic phases of H₃S, *R3m* or *Im3m*, is around 10% smaller than the *Cccm* one, which is quite significant and could indicate that some H atoms are still in the molecular form even at 160 GPa in the *Cccm* phase. The sample configuration with the sulfur embedded in hydrogen favors the synthesis of the stable hydride with the highest stoichiometry on the convex hull. Thus, the H₃S stoichiometry observed is also in agreement with calculations which predict that sulfur trihydride is stable above 5 GPa and that it remains the sulfur trihydride with the highest H:S ratio at least up to 300 GPa [5]. But the stability of the *Cccm* structure contradicts the predicted sequence of phase transition *Cccm* \rightarrow *R3m* \rightarrow *Im3m*. In the calculations, the transition from *Cccm* to *R3m* is concurrent with the closure of the electronic gap in the *Cccm* phase. Given the well-known deficiency of density functional theory (DFT), the band gap is likely to be underestimated and so the transition to the metallic state should be shifted to higher pressures, hence also the transition to the *R3m* phase.

In Fig. 4, we compare the integrated XRD pattern of H₃S measured here at 150 GPa to the ones obtained in three other structural experimental studies directly compressing hydrogen sulfide, yet following different paths for compressing and annealing the sample [4–6]. In these experiments, H₂S is loaded at around 180 K, and the pressure is increased. When

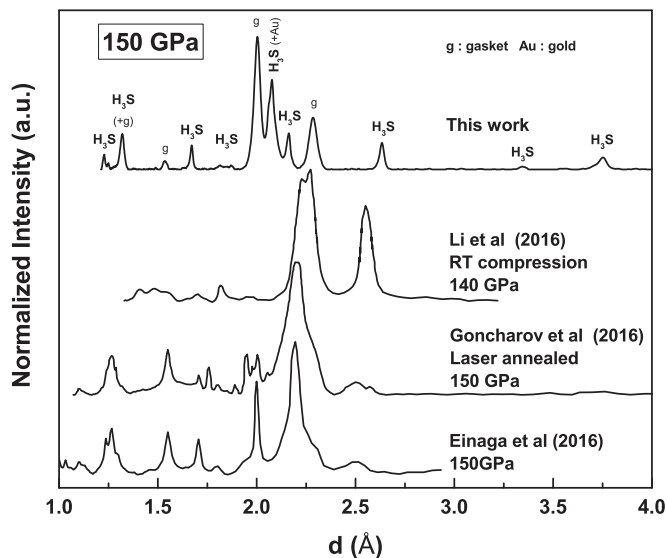


FIG. 4. Comparison of the XRD pattern obtained at 150 GPa in this experiment with those obtained in other works by directly compressing H_2S (from Refs. [4–6]).

the target pressure is reached, the sample is warmed up to room temperature and the XRD experiment is performed. Note that Goncharov *et al.* use laser heating (with temperature up to 1000 K) to better crystallize their sample at room temperature, thus approaching the experimental conditions presented in our work. The XRD patterns found in these three experiments have been said to be the results of the contributions of different compounds, mainly H_3S , H_4S_3 , and S with different phase fractions. The broadness of the diffraction peaks seems to indicate that the decomposed H_2S is poorly crystallized. Thus, it is difficult to be entirely sure of the different phases with their relative fractions which are refined from the XRD patterns. Goncharov *et al.* have identified the Ccm structure of H_3S in the 55–110 pressure range only [6]. However, at 150 GPa, it is clear that most of the peaks corresponding to the Ccm phase of H_3S are absent. On the other hand, in Einaga’s [4] and Goncharov’s [6] experiments, the major diffraction peaks were attributed to the bcc sulfur sublattice of the $R3m$ and $Im\bar{3}m$ structures of H_3S . If it is present in dissociated hydrogen sulfide, H_3S would thus be in a metastable state.

Metastability seems an obvious hypothesis to account for the discrepancy between the structures of H_3S obtained either

through decomposition of hydrogen sulfide under pressure or by the synthesis of pure H_3S from the direct reaction of sulfur with hydrogen at high pressure. However, in Goncharov’s experiment, laser heating of the H_3S $R3m$ (or $Im\bar{3}m$) phase only showed a narrowing of the diffraction peaks. It seems that with such an annealing process, a metastable phase should have evolved to the thermodynamically stable phase, now known as Ccm in this pressure range (as shown here). The other hypothesis is that the diffraction peaks selected in these multiphase patterns do not characterize the H_3S $R3m$ (or $Im\bar{3}m$) phase but belong to the diffraction pattern of a compound with another stoichiometry. Indeed, two recent calculations give credit to this hypothesis. First, a DFT calculation showed that the perovskite structure $(\text{HS}^-)(\text{H}_3\text{S}^+)$ is thermodynamically more stable than the H_3S $Im\bar{3}m$ phase in the 100 GPa pressure range [18]. Interestingly, the structural signature of this phase would be the same as the one of the H_3S $R3m$ (or $Im\bar{3}m$), with diffraction peak intensity built from a bcc S sublattice only. Second, the calculated small formation enthalpy for the H_2S - H_3S boundary suggests a possibility of alloying the phases of these two compositions by an intergrowth of slablike regions of both phases on a microscopic scale [19]. Furthermore, the simulated XRD patterns of these “Magnéli” phases could provide an explanation for the experimentally observed x-ray patterns in compressed hydrogen sulfide. The pressure dependence of T_C and its saturation at 200 K are explained by the increasing fraction of H_3S . In this hypothesis, the present work would thus imply that the $Im\bar{3}m$ high T_C superconductive phase is stabilized by the topology of the “Magnéli” phase.

In summary, we report the successful direct synthesis of pristine H_3S above 75 GPa from S and H elements. The structure of the synthesized H_3S has been investigated up to 160 GPa, and an orthorhombic phase with Ccm space group has been found to be stable. No phase transition to the metallic bcc phase of H_3S has been observed in this pressure range, unlike what had been predicted in DFT calculations. Moreover, this result is at odds with the previous structural analysis of the compressed H_2S system, and more work is still needed to discover the microscopic nature of this intriguing 200 K superconductivity phenomenon.

The authors acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation on beamline ID27. More particularly, we would like to thank M. Mezouar, G. Garbarino, and V. Svitlyk for their precious help with the XRD experiments.

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