ESRF	**Experiment title:** Direct synthesis of pure H3S from S and H elements at 150 GPa: does the Im-3m superconductive phase exist?	**Experiment number**: HC-3679
Beamline: ID27	**Date of experiment**: from: 13/06/2018 to: 17/06/2018	**Date of report**: 17/02/2019
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Report:

In 2015, a record superconducting temperature of 200 K was observed in compressed H_2S at 150 GPa [1]. Three structural studies [2-4] later confirmed the proposition that H_2S was decomposing at high pressure into H_3S+S, and that the Im-3m structure of H_3S was the superconductive phase. However, by direct synthesis of pure H_3S from S and H elements we observed only the insulating Cccm structure up to 160 GPa, hence challenging this interpretation of superconductivity due to H_3S [5]. Recently though, another study showed the synthesis of the Im-3m H_3S structure from the S and H elements at 150 GPa [6].
Nonetheless, apart from our study, these x-ray measurements were all of insufficient quality to perform a Rietveld or even a Le Bail refinement since the samples were poorly crystallized and of mixed composition.
So, the experimental picture on the stable structure of H_3S at 150 GPa remains not entirely clear. The main uncertainty of our study arises from the fact that H_3S was synthesized at 120 GPa under laser heating and then compressed to 160 GPa. Therefore, we cannot rule out a possible metastability of the Cccm phase.
The aim of this proposal was to perform direct synthesis of pure H_3S from H and S in a laser heating Diamond Anvil Cell at 150 GPa and above. It is crucial to demonstrate unambiguously what is the thermodynamically stable phase of H_3S at 150 GPa because that is directly related to the key question about the mechanism of this record high T_C in compressed H_2S.The sulfur sample was annealed using a YAG laser at 160 GPa directly, the pressure was then decreased down to 135 GPa, and finally increased again up to 150 GPa. Various laser-heating processes were performed to fully investigate the stability and metastability domains of the Cccm and Im-3m phases of H_3S. The pressure was measured using either a gold volumic gauge or ruby luminescence gauge. The volume was measured using angular-dispersive x-ray diffraction.

As one can see on Fig. 1a, laser-heating at 160 GPa made the sulfur sample react with hydrogen and transform into Im-3m H3S. A picture of the sample is provided on Fig. 1b, and one can clearly see that hydrogen is still present in the experimental cavity. The sample appears to be reflective, indicating a possible metallic state, coherent with the Im-3m phase synthesis. The *bcc* phase remained stable down to 135 GPa, at which the *Cccm* phase was synthesized using laser-heating. Upon compression, laser-heating at 150 GPa turned the sample back to the *bcc* phase of H_3S, which remained metastable down to 101 GPa upon decompression. The equation of state of *Im-3m* H_3S is plotted on Fig. 2, together with data from ref. 2, 3 and 4.

This experiment allowed us to link our previous study based on sulfur with ones based on H_2S, as we successfully synthesized the *bcc* superconducting phase of H_3S. However, some questions are yet to be answered, as we measured the transition pressure between the Cccm and Im-3m phases to be about 140 GPa, thus way above the superconductivity measurements shown in ref 1. A possible explanation for this discrepancy is a lowering of the equilibrium pressures due to impurities, or more likely a mixed phase such as the Magnéli H_2S/H_3S progressively turning into pure H_3S as pressure is increased in H_2S, and responsible for the low T_C superconductivity phenomenum observed below 140 GPa in ref 1.

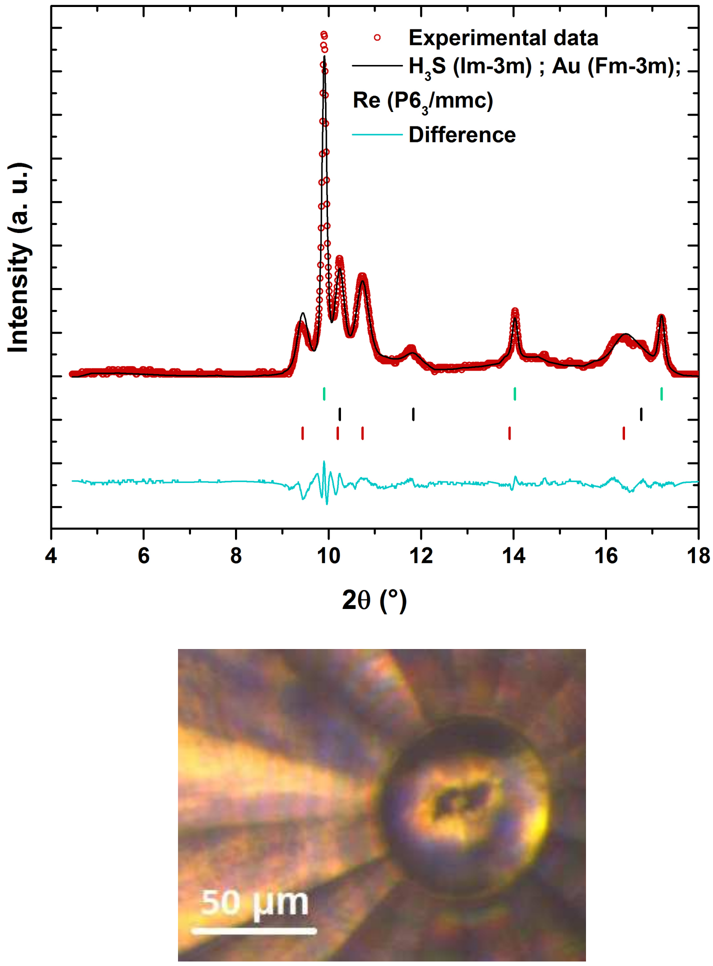

Figure 1: (a) Diffraction pattern obtained at 160 GPa after laser-heating, with a Le Bail fit of the Im-3m symmetry.
(b) Picture of the sample at 160 GPa.

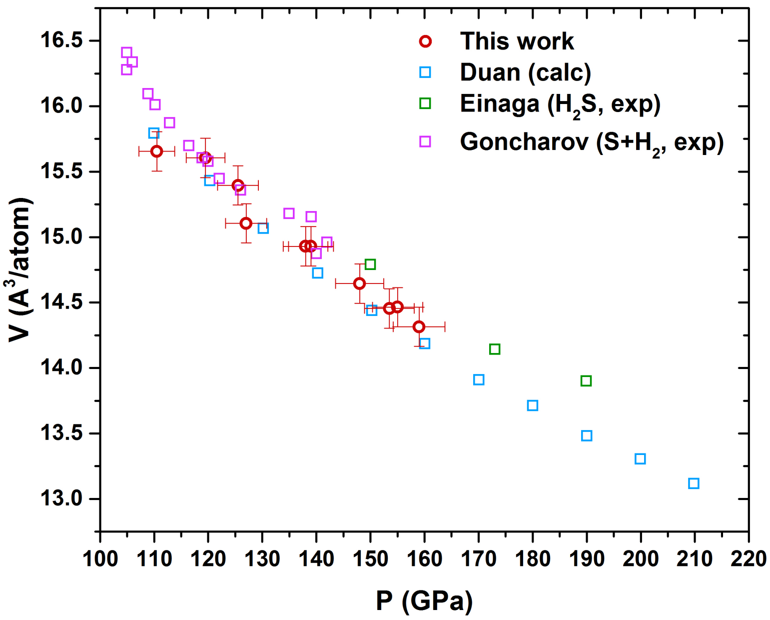

Figure 2: Evolution of the volume as a function of pressure for Im-3m H_3S, compared with data from ref 2, 3 and 4.

References:

[1] A. P. Drozdov, Nature 525, 73 (2015)
[2] M. Einaga, Nature Physics 12, 835 (2016)
[3] Y. Li, Phys. Rev. B 93, 020103 (R) (2016)
[4] A. F. Goncharov, Phys. Rev. B 93, 174105 (2016)
[5] B. Guigue, Phys. Rev. B 95, 020104(R) (2017)
[6] A. F. Goncharov, Phys. Rev. B 140101(R) (2017)