

Formation process of superconducting phase of sulfur hydride with $T_c \sim 203$ K

At the end of 2014, a joint theoretical and experimental investigation broke the record for the superconducting critical temperature T_c by more than 30 K, reaching 203 K for hydrogen sulfide under a high pressure of above 100 GPa, which was the first increase in 20 years [1]. This material has two superconducting phases. One phase, called the “low- T_c phase”, is obtained by compressing over 100 GPa at a low temperature of around 200 K, and exhibits $T_c \sim 150$ K at 200 GPa. The second phase, called the “high- T_c phase”, exhibiting $T_c \sim 203$ K, appears upon annealing the low- T_c phase at room temperature. The material shows “conventional” superconductivity, which can be explained by Bardeen-Cooper-Schrieffer (BCS) theory, because of its strong isotope effect in the superconductivity of H_2S and D_2S . On the basis of this theory, Ashcroft proposed that metallic hydrogen and hydrogen-rich compounds will become high- T_c superconductors because hydrogen is the lightest element and thus has the highest phonon frequency ω_{ph} for a given value of T_c among the elements in the periodic table [2]. For metallization, an extremely high pressure will be required (a pressure above 400 GPa was predicted for pure hydrogen in recent theoretical work). However, hydrogen-rich compounds are expected to require a lower pressure. On the basis of this proposal, some hydride superconductors have been searched theoretically, but only silane (SiH_4) with $T_c \sim 17$ K has been observed experimentally so far.

H_2S has been theoretically predicted to have a relatively high T_c of ~ 80 K above 100 GPa compared with other hydrides [3]. This value is consistent with the experimentally observed superconductivity in the low T_c phase. However, T_c of ~ 200 K does not follow from this prediction. Around the same time as Ref. 1, a theoretical work proposed that high-pressure-synthesized H_3S will show superconductivity in its hexagonal and cubic structures under pressure [4]. In particular, the cubic structure was predicted to yield a high T_c of ~ 200 K by contribution from metallic hydrogen realized in this phase. Other stoichiometries of H_xS_y were further studied theoretically by different groups in numerous works. Most of the results supported the hypothesis that the high T_c is related not to H_2S but to H_3S in the cubic structure; H_2S is unstable at high pressures and should decompose to sulfur and higher hydrides, probably to H_3S ($3H_2S \rightarrow 2H_3S+S$). Thus, it was suggested that molecular H_2S decomposes to sulfur hydride with a higher content of hydrogen upon compression and annealing.

In order to elucidate the mechanism of the superconductivity and search for synthesize materials

having a higher T_c towards achieving a room-temperature superconductor, the crystal structure of the superconducting phase and its phase diagram of sulfur hydride must be revealed. To investigate the formation process of the superconducting phases, we performed *in situ* X-ray diffraction (XRD), at the high-pressure beamline BL10XU, SPring-8 (Fig. 1) using a diamond anvil cell (DAC). At this beamline, simultaneous XRD, electrical resistance and Raman spectroscopy measurements can be performed at low temperatures in the upstream experimental hut. For the generation of an extremely high pressure of over 100 GPa, a small sample chamber with a diameter of less than 50 μm is needed. For such a small chamber, a focused X-ray beam with a diameter of about 2 μm can be used in the downstream hut. The DAC was used for the generation of high pressures. Hydrogen sulfide loaded in a small hole in a rhenium gasket was set on a pressure cell with electrodes (vapor-deposited gold or platinum on a diamond surface) for electrical resistance measurement. Pressurization, XRD, resistivity and Raman scattering measurements with the DAC can be performed at the same time in a Gifford-McMahon type refrigerator in the beamline. The first-order Raman spectra of the diamond anvil was measured using the on-line Raman spectroscopy system in the beamline for pressure determination.

H_2S is a gas under ambient conditions and is liquefied by cooling to around 200 K. After loading liquid H_2S into the sample chamber of the DAC, we pressurized H_2S to over 100 GPa in the cryostat while maintaining a low temperature of ~ 200 K, and then the cell temperature was increased to room temperature. From the *in situ* XRD measurements, we observed that the intensity of the diffraction peaks from the sample suddenly decreases upon cooling to 200 K and the peaks disappeared at pressures of around 20 GPa at 200 K. This also occurred

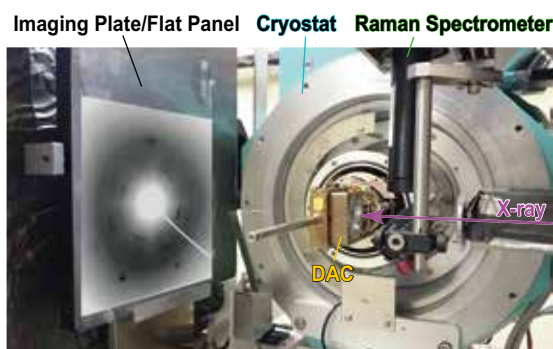


Fig. 1. Measurement system in the upstream-side chamber of BL10XU. X-ray diffraction, electrical resistance and Raman scattering measurements at low temperatures were performed at the same time.

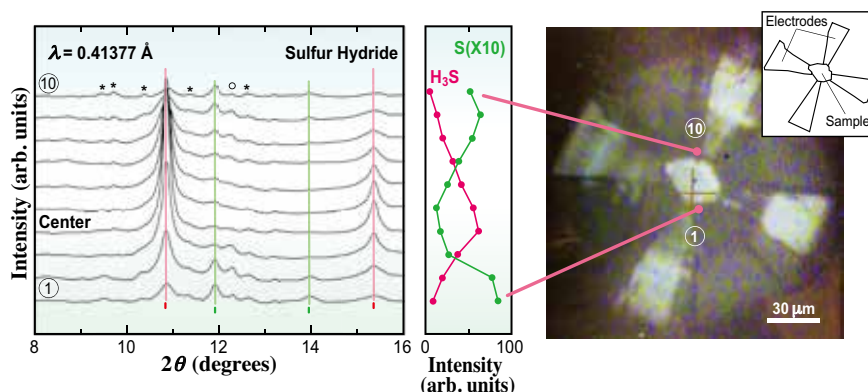


Fig. 2. XRD profiles of the sulfur hydride and pure sulfur along the line indicated in the image (150 GPa). The scanning was performed using an X-ray beam with a diameter of 2 μm from No. 1 to No. 10 shown in the photograph of the sample chamber. The red and green lines in the plots on the left indicate the reflections from cubic H₃S and β-Po sulfur, respectively. Open circles indicate the reflection possibly from the high-pressure phase IV of elemental sulfur. The reflections indicated by the asterisks (*) do not belong to the sample. The center graph indicates the position dependence of the intensity of the main peaks of H₃S and β-Po sulfur.

during compression to 150 GPa at 200 K and during heating to 256 K at around 150 GPa. A diffraction peak corresponding to the body-centered cubic (bcc) structure appeared from 260 K and its intensity was enhanced with increasing temperature up to room temperature. By using the X-ray scanning method with a focused synchrotron X-ray beam, the peaks of the obtained XRD profile of the high T_c phase were separated into the theoretically predicted cubic H₃S and the β-Po sulfur phase, which is the high-pressure phase of pure sulfur (Fig. 2). Raman scattering measurements elucidated that there were no hydrogen molecules in the sample chamber. Therefore, it is considered that H₂S lost its long-range periodic order as a result of low-temperature compression and dissociated into H₃S and elemental sulfur. It was also confirmed that the cubic H₃S is the high T_c phase from the electrical resistance measurements. However, the XRD measurements were only able to determine the positions of sulfur atoms because of the relatively weak scattering of X-rays by hydrogen atoms. As shown in Fig. 3, the theoretically predicted structures of the high T_c phase have the same bcc symmetry of the positions of sulfur atoms in both structures and the only difference is in the positions of the hydrogen atoms. However, electrical resistance measurements might allow us to distinguish these phases from the change in the pressure dependence of T_c around 150 GPa as shown by the dashed line in Fig. 3 [5].

In this article, the recent progress in the crystal structural investigation of the sulfur hydride system has been reported. The discovery of this high- T_c superconductor has accelerated technical advances and both experimental and theoretical research on superconductivity at pressure of over 100 GPa. It is expected that the novel experimental process (compression at low temperatures) for obtaining the high- T_c phase of sulfur hydride clarified in recent experiments will enable the high-pressure synthesis and further investigation of not only other hydrides but also new materials.

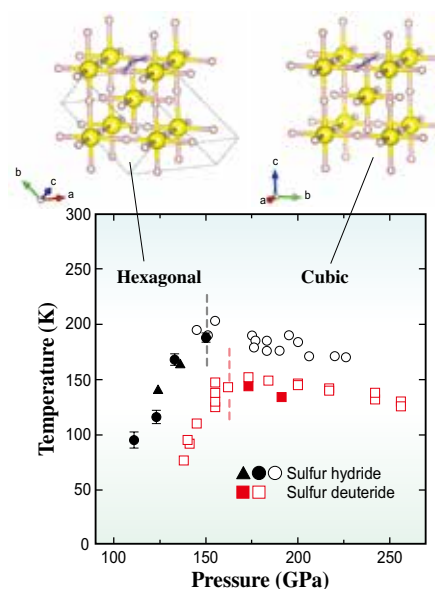


Fig. 3. Pressure dependence of T_c for high- T_c phases. Open circles and squares are from Ref. 1, and closed circles and squares are from Ref. 5. The dashed line indicates the phase boundary between the hexagonal and cubic structures shown at the top of this figure.

Mari Einaga
 KYOKUGEN, Osaka University
 Email: einaga@hpr.stec.es.osaka-u.ac.jp

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