

# FORMATION OF TRANSITION METAL HYDRIDES AT HIGH PRESSURES

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## Introduction

There is a considerable interest in producing metallic, and possibly superconducting, states of hydrogen at multimegabar pressures; the pressures that are thought to be needed for metallization (400 GPa) are however currently not achievable with static compression techniques. It has been recently suggested that hydrogen-rich compounds such as CH<sub>4</sub>, SiH<sub>4</sub>, and GeH<sub>4</sub> with hydrogen being “chemically pre-compressed” will require pressures far less than expected for pure hydrogen at equivalent densities to enter metallic states [1,2]. As is the case for pure hydrogen, these compounds are considered to be good candidates for high temperature superconductors in their dense metallic forms. Silane (SiH<sub>4</sub>) was predicted to metallise above 91 GPa [2] while subsequent theoretical papers gave a much higher metallization pressure of 220-250 GPa [3,4].

An experimental study claimed a discovery of metallization and superconductivity of silane at pressures above 50 GPa and reported a hexagonal close-packed (hcp) structure, space group P6<sub>3</sub>, for the metallic phase of silane [5]. On further compression above 110 GPa this phase is found to partially transform to a molecular insulating phase *I*<sub>4</sub><sub>1</sub>/*a* with a positive volume change of ~25% which co-existed with the metallic hcp phase up to 190 GPa [5]. Subsequent *ab initio* calculations [4,6] showed that the hcp structure proposed for the metallic SiH<sub>4</sub> is “mechanically highly unstable” suggesting a possible partial dissociation and a phase of a different composition. These discrepancies between various theoretical studies as well as experimental work prompted us to further investigate the crystal structure of silane at high pressures. Using x-ray diffraction techniques we found that silane decomposes and released hydrogen reacts with the surrounding metals to form hydrides.

## Results and discussion

Our Raman and x-ray diffraction data on silane up to 50-60 GPa show a SnBr<sub>4</sub>-type structure consisted of tetrahedral molecules in agreement with previous experiment [7]. Above 90 GPa, we observed a molecular *I*<sub>4</sub><sub>1</sub>/*a* phase, again in agreement with previous work [3,5]. However, in

the pressure range between 50-60 and 90 GPa, our data could not be explained by the previous reports. We obtained a diffraction pattern that contained an hcp phase from rhenium metal (used as a gasket material in our diamond anvil cell set-up) with an atomic volume 13.02(1) Å<sup>3</sup> at 65 GPa and another hcp phase that looked like Re but had a larger atomic volume of 13.84(1) Å<sup>3</sup>. The “expanded Re” phase can be explained as a formation of Re hydride if one takes into account the fact that hydrogen is known to increase the volume of a metal by approx. 2 Å<sup>3</sup> per hydrogen atom. The volume difference between pure and “expanded” Re phases of 0.8 Å<sup>3</sup> gives a composition ReH<sub>0.4</sub>. This corresponds within error bars to the known composition ReH<sub>0.38</sub> of the saturated Re hydride obtained above 8.6 GPa that has an hcp structure with a *c/a* ratio of 1.58 [8] very close to *c/a*=1.57 of the hcp phase of “expanded” Re obtained in our data.

This hcp phase has a different axial ratio from that reported for the metallic phase of silane (1.68) in [5], beside there was no Re in their experimental set-up. We note that the x-ray diffraction pattern of the metallic hcp phase of silane [5] is identical to the hcp phase of platinum hydride [9] (Fig. 1). Axial ratio of the hcp silane [5] is very close to that of PtH (*c/a*=1.70) [9] and the atomic volume data of [5] lie very close to that of PtH [9] (Fig. 2). These characteristics identify the proposed hcp phase of silane uniquely as PtH. Platinum hydride of 50/50 composition can be synthesized under pressure above 27 GPa stable to at least 42 GPa [9]. Taken into account that the experimental set-up of [5] included platinum wires for measuring conductivity, it is very plausible that at around 50 GPa due to decomposition and/or chemical reaction the silane sample released hydrogen to form PtH. One should note that some hydrogen-containing compounds such as AlH<sub>3</sub>, LiAlH<sub>4</sub> etc, known to decompose on thermal compression releasing hydrogen, are routinely used as hydrogen donors for high-pressure synthesis of transition metal hydrides that do not form at normal conditions [10, 11].

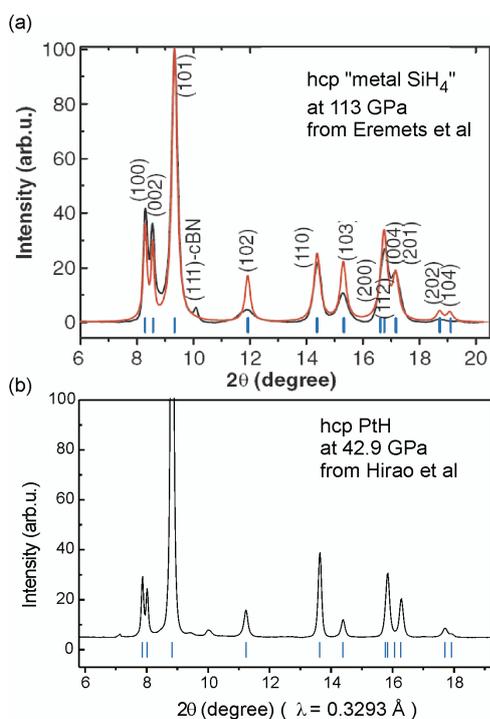


Fig. 1. Powder diffraction spectra of (a) "hcp phase of metallic silane" from Eremets et al [5] and (b) hcp phase of PtH synthesized at high pressure by Hirao et al [9].

The question remains what happens with the silane itself above 50 GPa. At pressures of 50-60 GPa, all crystalline diffraction and Raman peaks disappear and an amorphous halo was measured in the x-ray spectrum (inset in Fig. 2). We interpret this as a pressure-induced amorphization of silane. The amorphous x-ray diffraction signal from the silane sample is very weak, which apparently was missed in the experiment of [5], and instead a stronger diffraction signal from crystalline PtH was measured. On further compression (>90 GPa) we observed a slow re-crystallization of the amorphous silane into 2 phases ( $I-42d$  and  $I4_1/a$ ) in agreement with theoretical predictions of [3].

## Conclusions

At high pressure, silane decomposes releasing hydrogen that reacts with surrounding metals forming hydrides. The fact that silane undergoes a pressure induced amorphization at around 50-60 GPa, remains amorphous up to 90 GPa where it re-crystallizes into an insulating molecular phase suggests that the metallization and superconductivity of silane are yet to be discovered most probably at pressures above 220-250 GPa.

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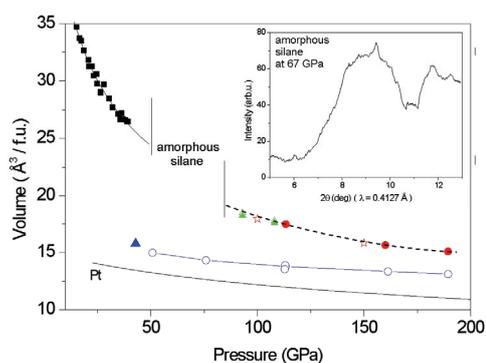


Fig. 2. Equation of state for silane shown in comparison with PtH and Pt. Upper line: filled squares are from [7], filled circles show  $I4_1/a$  phase from [5], stars show the predicted points from [3]; the open and filled triangles show data from this work on  $I-42d$  and  $I4_1/a$  phases. Middle line: the triangle is for the hcp phase of PtH from [9]; the open circles are for the "hcp silane" from [5]. The lower solid line shows equations of state for pure Pt. The inset shows diffraction spectrum of amorphous  $\text{SiH}_4$  at 67 GPa from this work.

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