Formation of transition metal hydrides at high pressures

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Abstract

Silane (SiH\textsubscript{4}) is found to (partially) decompose at pressures above 50 GPa at room temperature into pure Si and H\textsubscript{2}. The released hydrogen reacts with surrounding metals in the diamond anvil cell to form metal hydrides. A formation of rhenium hydride is observed after the decomposition of silane. From the data of a previous experimental report (Eremets et al., Science \textbf{319}, 1506 (2008)), the claimed high-pressure metallic and superconducting phase of silane is identified as platinum hydride, that forms after the decomposition of silane. These observations show the importance of taking into account possible chemical reactions that are often neglected in high-pressure experiments.

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1. Introduction

Pressure causes extraordinary changes in materials, reducing interatomic distances and modifying their properties. This often provides a path for synthesis of novel materials. Substantial progress has been made in the high pressure synthesis of hydrides, carbides, borides, and nitrides in recent
years [1, 2, 3, 4, 5], mainly due to the development of high-pressure high-
temperature experimental techniques. New materials can often be obtained
following a decomposition of the starting materials, as for example in the
high pressure synthesis of transition metal hydrides that do not form at nor-
mal conditions. In this case, hydrogen-containing compounds such as AlH₃,
LiAlH₄ etc that decompose on thermal compression releasing hydrogen are
routinely used as internal hydrogen sources [1, 6]. Decomposition and chem-
ical reactions at high pressure can be harnessed to develop new materials for
technological applications [7]. These phenomena can be used to advantage
in many different respects, as for example was demonstrated for pure hy-
drogen [8] that was obtained using decomposition and chemical reactions of
other materials to study fundamental physical properties of its dense state.
On the other hand, the systematic studies of binary phase dia-
grams showed that in these simple systems the phase equilibrium changes under pressure
allowing for decomposition of existing phases and synthesis of new phases
[9]. The negligence of this and the possible high pressure chemical reactions
in a studied sample can lead to erroneous interpretation of results.

The hydrogen-dominated group IVa alloys (CH₄, SiH₄, GeH₄ etc.) have
been a subject of much scientific interest as candidates for high temperature
superconductors in their dense metallic states. As proposed by theoretical
studies [10, 11], due to the chemical pre-compression of hydrogen these mate-
rials may require pressures far less than expected for pure hydrogen to enter
metallic states. Recent experiments reported metallization of SiH₄ (silane)
above 50 GPa [13, 12] with a formation of a hexagonal close-packed (hcp)
structure of space group P6₃ (Ref. [12]). Above 100 GPa, this metallic phase
was claimed to transform to a transparent insulating phase [12] with a vol-
ume increase of ∼25% upon transition, co-existing with the metallic phase up
to at least 192 GPa. The observed transparent insulating phase of silane [12]
was identical to the I₄₁/a phase earlier predicted by ab-initio calculations
to be stable between 50 and 250 GPa, above which a metallic phase with
space group C2/c was predicted to become stable [14]. Here we note that
the positive volume change on pressure increase and the co-existence of two
thermodynamically stable phases with different volumes at constant tem-
perature and composition stoichiometry contradicts Le Chatelier’s principle
[15]. Indeed, the recent ab initio calculations on the experimentally reported
metallic P6₃ phase of silane showed that this structure is mechanically highly
unstable and is unlikely to form at these pressure conditions [16, 17, 18], sug-
gesting that the P6₃ phase might be of a different chemical composition [18].
The analysis of these arguments suggests that a chemical reaction needs to be taken into account to explain the presence of the metallic hcp phase in silane.

Here we report a (partial) decomposition of silane at high pressures and room temperature into pure Si and hydrogen, where released hydrogen reacts with the surrounding metals in the diamond anvil cell chamber forming metal hydrides. We find a formation of Re hydride after decomposition of silane and reaction of hydrogen with the Re gasket, and identify the recently reported metallic phase of silane [12] as PtH [19].

2. Experimental

Electronic grade 99.998+% silane (SiH$_4$) from Sigma Aldrich was used for cryogenic loading of diamond anvil cells in a dry argon purged glove box by pre-cooling the cells in a liquid nitrogen bath. The loading procedure was similar to previous experimental studies of SiH$_4$ (Ref. [20]). Diamond anvil cells with 250$\mu$m and 100$\mu$m culets were used, with rhenium gaskets. Pressure was estimated from the first-order Raman spectra of the diamond anvil [21] for some experiments, while other loadings contained a ruby chip for measuring the pressure from the shift of the $R_1$ ruby fluorescence line using the ruby scale from [22]. Powder x-ray diffraction data were mostly collected at the beamline ID09 at the European Synchrotron Radiation Facility (ESRF), Grenoble, while the spectrum at 108 GPa, the maximum pressure reached in this study, was collected at the beamline ID27 of ESRF. A focused monochromatic beam was used, with wavelengths 0.4130 Å and 0.3738 Å, and the data were recorded on a MAR image plate. Diffraction data were integrated azimuthally using FIT2D [23]. Five independent loadings of silane were used to study the sample in the pressure range from 10 to 108 GPa with three experiments performed at room temperature and two experiments made at low temperature of 100 K using the on-line cryostat of the beamline ID09.

3. Results and discussion

Firstly we note that the x-ray diffraction pattern of the "metallic hcp phase of silane" reported in Ref. [12] is identical to the hcp phase of platinum hydride [13] (Fig. 1 a,b). Platinum and hydrogen do not form compounds at normal conditions, however PtH with a hcp structure can be synthesized
under pressure at above 27 GPa as recently reported by Hirao et al. [19], stable to at least 42 GPa. The "metallic hcp phase of silane" has the same crystallographic characteristics as that of PtH. The axial ratio of the hcp silane is c/a=1.681 [12], very close to that of PtH (c/a=1.702) [19] and the atomic volume data of Ref. [12] lie very close to that of PtH [19] (Fig. 2). The peculiarly small compressibility of the proposed metallic hcp silane [12] (Fig. 2) can be understood as the hcp phase of PtH that has similar compressibility to platinum [19] (bulk modulus 274 GPa [24]). These characteristics identify the proposed hcp phase of silane uniquely as PtH [25]. Since the experimental set-up of Eremets et al. [12] included platinum wires and foil for measuring conductivity, it is very probable that at around 50 GPa due to decomposition and chemical reaction the silane sample released hydrogen to form PtH.

The composition of the Pt hydride synthesised by Hirao et al. is proposed to be 50/50 [19]. Indeed, the atomic volume of Pt at 42.9 GPa is 13.42 Å³ (Ref. [24]) compared to the atomic volume of Pt-H by Hirao et al. of 15.77 Å³ (Ref. [19]). This gives a difference in atomic volume of metal and its hydride of about 2.35 Å³. It is known that during the formation of a hydride, the volume of a transition metal increases by 2.1 ± 0.2 Å³ for one hydrogen atom occupying interstitial octahedral sites in the structure of transition metals [26] (the values up to 2.8 Å³ can be found in literature [27]). This yields an estimate of the composition of platinum hydride as PtH. The volume data for the "metallic hcp phase of silane" [12] for the highest pressure give approximately 2.1 Å³ for the difference between the volumes of platinum and platinum hydride yielding an estimated composition close to PtH. At lower pressures, a smaller difference (<2.0 Å³) is observed between Pt and platinum hydride (Fig. 2), which indicates that an unsaturated PtHₓ with x < 1 is probably formed and that the hydrogen content of PtHₓ might be increasing with pressure.

The question remains about superconductivity, as the "metallic hcp phase of silane" is reported to be superconducting with a strong pressure dependence of Tc, that reaches a maximum of 17 K (see Fig. 2 in Ref. [12]). The superconducting state is characterized by exactly zero electrical resistance (if measured by a 4-probe technique) and the exclusion of the interior magnetic field (the Meissner effect). However, in the paper by Eremets et al. [12] there is a residual resistance of 8 Ω in the silane sample evident from Fig. 2b of Ref. [12], while the Meissner effect has not been measured. We argue that the superconductivity of the "metallic hcp phase of silane" has not been shown convincingly. Moreover, no plausible explanation has been given in
Ref. [12] for the pressure dependence of \( T_c \) which is quite unusual for such a simple hcp structure with low compressibility. Here however, we offer our explanation of the experimental observations. Although the superconductivity of PtH has not been measured in a separate experiment and it is not known if it is superconducting, it is plausible that the reported superconductivity [12] could originate from the PtH formed in the diamond anvil cell. The quasi-four electrode scheme used in the experiment of Ref. [12] “involves contribution of resistance of small piece of platinum foil”, and this Pt foil after forming PtH would show a drop in resistivity observed in Ref. [12] if PtH were superconducting. Also, the formation of PtH means a 15% volume expansion of Pt (estimated for the pressure of 113 GPa), and this would lead to a formation of a uniform PtH phase between the Pt electrodes taking into account a small separation between electrodes due to a very small size of the sample chamber in the experimental set-up of Eremets et al (see Fig 2a of Ref. [12]). The peculiar pressure dependence of the \( T_c \) (the rise and the subsequent drop) can be connected with the change of the hydrogen content in the hydride under pressure (see discussion above). Pt-group metal hydrides (for example Pd-H) are known to superconduct showing strong dependence of \( T_c \) on the hydrogen content [28]. In any case, the idea that PtH might be superconducting is very interesting in itself and certainly deserves further experimental attention.

In our own experiments on silane, we observe the SnBr\(_4\) phase (Ref. [20]) up to 50 GPa at room temperature. Above this pressure, we detect a decomposition of silane into pure Si and H\(_2\). This is documented by the observation of the diffraction signal from hcp Si (Fig. 3b). The strongest peak (101) of the hcp Si is observed with a d-spacing that agrees with the reported Si lattice parameters and equation of state [29]. Hydrogen, released during the decomposition of silane, reacts with the Re gasket and participates in the formation of Re hydride, as discussed below. Earlier theoretical calculations [14] reported that silane is unstable to decomposition into hydrogen and silicon at pressures up to approx. 50 GPa, which supports our observations. We note that the very complex and kinetically driven behavior of silane between 50-75 GPa includes partial decomposition, pressure induced amorphization and a subsequent re-crystallization. These and other results will be described in detail in a separate paper [30, 31].

Above 50 GPa at room temperature, we obtain a diffraction pattern that contains an hcp phase from rhenium metal (used as a gasket material in our diamond anvil cell setup) with an atomic volume of 13.02(1) Å\(^3\) at 65 GPa
and another hcp phase similar to Re but with a larger atomic volume of 13.84(1) Å³ (Fig. 3a). The ”expanded Re” phase can be identified as a Re hydride if one takes into account the fact that hydrogen is known to increase the volume of a metal by approx. 2.1 Å³ per hydrogen atom (as discussed above). The atomic volume difference between the pure and ”expanded” Re phases of 0.82 Å³ gives a composition of ReH₀.₃₉. This corresponds within error to the known composition (ReH₀.₃₈) of the saturated Re hydride obtained above 8.6 GPa in which Re atoms form an hcp structure with a c/a ratio of 1.58 [32, 33], very close to c/a=1.57 of the hcp phase of ”expanded” Re obtained in our data. We observe that the expansion of Re gasket due to the hydride formation (volume increase of about 6.3%) happens inward the sample chamber, meaning that Re hydride forms inside the sample chamber (inset in Fig. 3c). We note that this would make the reflectivity measurements of silane at these pressures very difficult.

The obtained Re hydride is found to be stable up to 108 GPa, the maximum pressure reached in this study (Fig. 3c), in accord with previous studies on Re hydride to 120 GPa [35]. Our data show that the compressibility of Re hydride is very similar to that of Re. This agrees with previous studies to 20 GPa that showed an apparent incompressibility of the interstitial hydrogen, such that the difference in volume between rhenium metal and rhenium hydride remained nearly constant. The Pt hydride PtH with hcp structure remains stable up to at least 192 GPa, as can be deduced from the stability of the ”metallic hcp phase of silane” from Ref. [12] that we have identified here as PtH, showing compressibility very similar to that of pure Pt. For comparison, the platinum carbide PtC, that is also synthesized under pressure, is reported to remain stable in its fcc structure up to at least 120 GPa [36].

In our experiments at low temperatures of 100 K, the decomposition of silane is observed at higher pressure of 60 GPa in comparison with the decomposition pressure of 50 GPa at room temperature. The decomposition of silane and the formation of metal hydrides are strongly dependent on temperature as well as on time, which points to a kinetic origin of the process. We also note that we have not observed the claimed ”metallic hcp phase of silane” [12] in any of our experiments.
4. Conclusions

Present high-pressure experiments on silane demonstrate the importance of taking into account possible decomposition and chemical reaction of the sample and surrounding materials when analyzing the data from high-pressure measurements. Silane (SiH$_4$) is shown to partially decompose releasing hydrogen which reacts with the Re gasket that contains the sample inside the diamond anvil cell, forming Re hydride. The "metallic hcp phase of silane" from Ref. [12] is identified here as PtH [19] that forms upon the decomposition of silane and reaction of released hydrogen with platinum metal that is present in the sample chamber. A formation of tungsten hydride is reported in the studies of silane and hydrogen mixture under pressure using a tungsten gasket [37]. In view of these observations, the reported metallization of silane at pressures 50-60 GPa [12, 13] should be critically reconsidered. Our present measurements suggest that silane might not metallise until much higher pressures [30], in agreement with theoretical predictions that pressures as high as 220-250 GPa might be required to obtain metallic silane [14, 18].

On the other hand, silane turns out to be useful for the high-pressure synthesis of metal hydrides. At pressures above 50 GPa, silane decomposes releasing pure hydrogen which readily reacts with the surrounding metals forming metal hydrides. The fact that silane is pyrophoric at normal conditions makes it difficult to load. However, silane has a certain advantage in comparison to other hydrogen-containing materials used as internal hydrogen sources [1, 6], as its decomposition on compression does not require heating. This property may prove to be useful for measurements of superconductivity of metal hydrides synthesized under pressure, where heating above room temperature is undesirable.

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Figure 1: Fig. 1. Powder diffraction spectra of (a) the claimed "hcp phase of metallic silane" \cite{12} and (b) hcp phase of PtH synthesised at high pressure \cite{19}. The tick marks in (b) show peak positions calculated from the reported lattice parameters for PtH in its hcp phase: $a = 2.730(1)\ \text{Å}$, and $c = 4.288(1)\ \text{Å}$.
Figure 2: Eq. 2. Equation of state for silane shown in comparison with PtH and Pt. Filled squares are from measurements on SnBr$_4$ phase of silane from Ref. [20], filled circles show measured data on the I$_{4}$_1/a phase of silane from Ref. [12], and stars show the predicted points for I$4_2$d and I$_{4}$_1/a phases [14]. The observed range of amorphous silane and region of its partial decomposition are indicated by the vertical lines. The thick line denoted as PtH shows the volume of the hcp phase of PtH from Ref. [19]. The open circles are for the "hcp phase of silane" from Ref. [12]. The solid line shows the equations of state for pure Pt from Ref. [24].
Figure 3: X-ray diffraction spectra on Re hydride obtained in the present work. (a) The spectrum at 65 GPa contains hcp phase of Re (used as gasket material) shown with upper tick marks, and Re hydride shown with the lower tick marks. The two most intense diffraction peaks are marked with their hkl indices for both phases. (b) The spectrum at 71 GPa contains the Re hydride shown with tick marks, as well as the hcp phase of Si (most intense peak is indicated). The arrow points to a weak diffuse signal from amorphous silane with more information on it given elsewhere [30]. "+" indicates the two strongest peaks from a small amount of the hcp phase of Re. Other weak peaks in (c) originate from the re-crystallized silane sample. Inset in (c) shows the micro-photograph of the (recrystallized) silane sample and Re hydride that has formed inside the sample chamber around the edges of the gasket hole. The dimension of the figure is about 100 μm.