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Studies on Silane to 70 GPa

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Abstract. Raman and x-ray diffraction studies were made on silane in the diamond anvil cell using three different gaskets, stainless steel, tungsten and rhenium. The structure existing between 10 and 27 GPa is well characterized by the monoclinic space group $P2_1c$ (#14). While the Gibbs free energy of formation of silane is positive at one atmosphere, it is calculated from the equation of state of silane and its reactants that this becomes negative near 4 GPa and remains negative until 13 GPa and then becomes positive again. At about 27 GPa, where quasi-quantum mechanical calculations suggest there should be a transformation from 4-fold to 6-fold (or even higher), the sample turns black. The Raman modes seize to exist beyond 30 GPa after showing softening above 25 GPa. At higher pressures it turns silvery. The gaskets play a different role as will be discussed. The sample brought back from 70 GPa contains amorphous Si (with attached hydrogen) as well as crystalline silicon. The lowest free energy system at high pressure is the decomposed reactants as observed.

1. Introduction

In 1935 Wigner and Huntington made a quasi-quantum mechanical calculation on hydrogen. This was the basis of their paper entitled "The Possibility of a Metallic Modification of Hydrogen," which had a possible metallization pressure of at least 25 GPa. The history of the progress of quasi-quantum mechanical calculations on hydrogen at high pressure is described elsewhere [2, 3]. It appears likely that a pressure of 600 GPa will be required for metallization. In as much as a static pressure of 560 GPa has been achieved in the diamond anvil cell [4], the metallization of hydrogen appeared to be a goal worthy of pursuit.

The field was greatly stimulated by a paper by Ashcroft [5] which concluded that metallic hydrogen was likely to be a high T_c superconductor, possibly even at room temperature. The following authors have successfully shown experimentally that hydrogen is not yet metallic at 210

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GPa [6], 320 GPa [7] and 340 GPa [2]. It was found that hydrogen diffuses into the diamond anvils of the high pressure cell and causes embrittlement and premature fracture [2]. This is not surprising considering the circumstances. At a distance from the diamond tip equal to about the diameter of the diamond anvil flat and along the axis of the anvil, the mean normal stress in the diamond is only 120 GPa when the hydrogen sample pressure on the diamond is 340 GPa [8]. The difference in the chemical potential of hydrogen at these two pressures is 4.7 eV.

The chemical potential of H_2 as function of pressure follows from the equation

$$\mu(P) = \int_{10^{-4}}^{P(GPa)} VdP \tag{1}$$

where V is the molar volume. A summary of V(P) data is given by Hemmes et. al. [9] and by Loubeyre et. al. from 5.5 GPa to 140 GPa [10]. The latter results were fit to the Vinet equation.

The fracture of the diamonds owing to hydrogen embrittlement has presently capped the available pressure attainable on hydrogen (unless a diffusion barrier can be created to prevent hydrogen from entering the diamond) [2].

After studies on the alkali hydrides [11], which from the phonon viewpoint have a reduced mass near one compared to 0.5 for hydrogen, it was decided [12] that CsH might be a good candidate for metallization [13] and high T_c superconductivity. This was given added stimulus by a later theoretical paper by Hama and Kawakami [14], who calculated that LiH shows band overlap at 226 GPa. While no calculations existed for CsH, it was thought that the metallization pressure of CsH would be lower [15]. The reflectivity did show a rapid rise in the infrared at 102 GPa and higher at 250 GPa. However, studies on CsD showed a strong isotope effect and that this rise was owing to phonon reflection [15]. The band gap had only decreased from 4.4 eV at zero pressure to 1.9 eV at 150 GPa. Assuming the curve can be extrapolated (no further phase transition) it was estimated that the transition pressure would be about 1 TPa. It should be noted that the high pressure form of CsH belongs to the Cmcm space group. There is the possibility that CsH pairs form, thus stabilizing the system against the metallic transition till much higher pressure.

We did not give up on attempting to make metallic hydrogen alloys. We studied CH_4 to 288 GPa [16]. Here an insulator to semiconductor transition was found but a sizeable gap (estimated at 1.4 eV) still existed. These studies were made with 35 μm tips and future studies with 20 and 10 μm tips which can achieve much larger pressures are planned.

Following the quasi-quantum mechanical calculations on SiH_4 which suggested metallization at 104 GPa [17], we attempted studies on silane. However we recently found that the sample had become contaminated in the glove box although the oxygen pressure reading was very low (falsely it turned out) [18], so these results were withdrawn [19]. We have repeated this experiment at truly low oxygen pressures as will be discussed later.

*1.1 Review of quasi-quantum mechanical calculations on Si*H$_4$

There are now three sets of calculations referred to as (Feng) [17], (Pickard) [20] and (Degtayareva) [21]. All three authors agree that at low pressure a bcc cubic phase has the lowest H, A and G. The SiH_4 molecule at the center has the H's of the Si-H bonds pointed toward four corners of the cube which are A-corners. All of the SiH_4 molecules have the same orientation as the center molecule. One Si-H bond at each A corners has the H of the Si-H bond pointed away from the center. For each of the four B-corners, the H of one Si-H bond is pointed toward the center. This is the T_1 structure of Feng. All assume static nuclei. This belongs to space group $I\bar{4}3m$.

All three sets of calculations have plots of the data as $H_{structure} - H_{I\bar{4}3m}$. All assume that the most negative ΔH of these structures at a given pressure corresponds to equilibrium even at 300K. This is equivalent to the assumption that the entropy difference $\Delta S = S_{structure} - S_{I4\bar{3}M} = 0$ is always true.

Feng published results on seven structures: Four with hydrogens in tetrahedral coordination, one octahedral and one with eight nearest neighbors (Im3m, #217 called M_1 by Feng). The latter is simply a partial inwards collapse of the cubic reference structure as the cube is squeezed to eight-fold coordination. It might be expected that there would be only tiny activation energy for this process but Hennig calculated this to be around 0.5 eV [22]. A possible hypothesis is that a transition to an octahedral coordinated structure might have much higher activation energy so that it might be kinetically impossible to attain at room temperature even though it is thermodynamically favored.

Table 1 shows the structures and pressures ranges over which these structures are calculated to be stable by each research group.

Table 1. Comparison of lowest ΔH's by author on given pressure ranges.

Feng			Pickard			Degtyareva		
P(GPa) Lowest ΔH			P(GPa) Lowest ΔH			P(GPa) Lowest ΔH		
0-5	$I\bar{4}3m$	#217	0-15	$I4\bar{3}m$	#217	0-	$I4\bar{3}m$	#217
5-25	$I\bar{4}2m$	#121	15-50	P2/c	#13	0^+-27	27P2,1c	#14
25-	Pman	#53	50-255	$I4_1/a$	#88	27^+-	P2/c	#13*
			255^+-	C2/c	#15			
* Degtyareva also calculate Pman and find that its ΔH is only about .03 to .07 eV above P2/c; see this in their Figure 4. This is an insignificant difference; see Table 2.								

Table 2 shows structures whose ΔH(P) have been calculated by two or all three of the authors. These are a gentle reminder of the state of quasi-quantum mechanical calculations. Nonetheless, the calculations serve as a helpful guide to the experimentalist: Is the low pressure form cubic? Are tetragonal structures present? Are orthorhombic structures present? And if not…?

Table 2. Comparison of quasi-quantum mechanical calculations of ΔH(eV) @ 50 GPa.

Feng		Pickard		Degtayareva	
$14_1/a$	---	$14_1/a$	-0.90	$14_1/a$	-0.17
Pmna	-0.55	Pmna	-0.85	Pmna	-0.37
P2/c	---	P2/c	-0.90	P2/c	-0.45

2. Raman Results and Discussion

Figure 1 shows the Raman spectra of silane at various pressures in the solid phase. The region 2000 cm^{-1} to 2500 cm^{-1} is associated with the symmetric and asymmetric stretching (ν_1 and ν_3) modes of silane. At ambient conditions we observe only one mode at around 2206 cm^{-1}. The mode appears to be symmetric around 2206 cm^{-1}. At this pressure silane is a gas and compares well with the literature [23]. At 1.6 GPa silane undergoes a transition from gas to liquid at room temperature. The Raman spectra of the liquid phase was verified with the low temperature Raman spectra of SiH_4 [23]. At 3.1 GPa silane goes from liquid to phase I at 300 K, which is similar to the phase I observed at low temperatures and pressures from the Raman features [23]. In phase I the silane molecules can rotate freely, hence the difference in the Raman spectra of the liquid and phase I is a decrease in the linewidth.

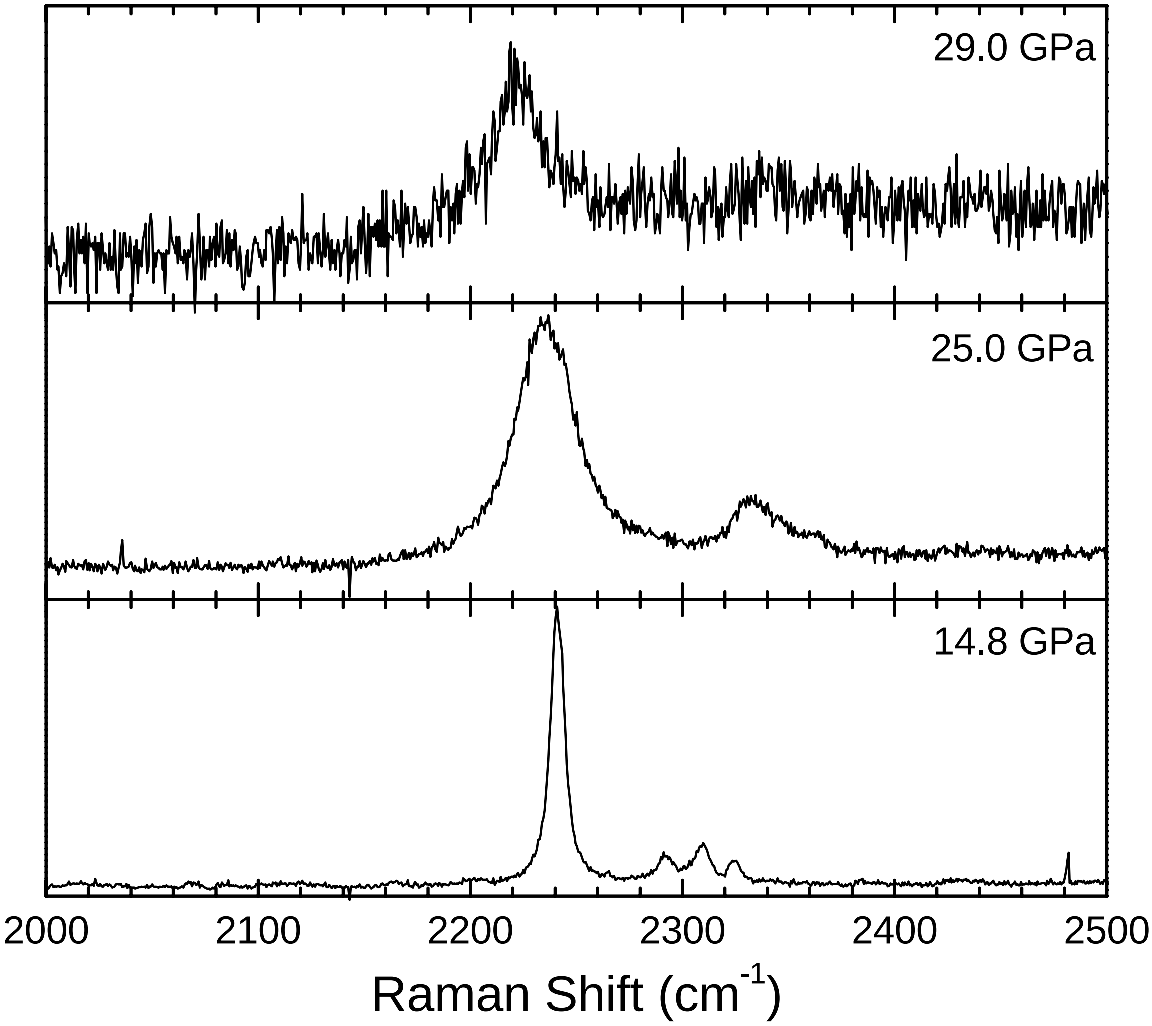

Figure 1. Raman spectra recorded at various pressures in the solid phase. This region of the Raman spectrum is dominated with the symmetric and asymmetric stretching modes of SiH_4.

Upon increasing the pressure, the rotational degree of freedom of the silane molecule is reduced leading to splitting of the ν_1 and ν_3 modes due to decrease in symmetry and the spectra recorded at 5 GPa matches well with reported temperature dependent Raman studies of SiH_4 [23] indicating the transition from phase I to phase II (orientational order-disorder transition). Structurally both these phases are similar, except for the decrease in the rotational degree of freedom of the silane molecule. When silane is observed under an optical microscope, the sample appears greyish in color. This is seen even in the phase II.

Above 10 GPa, we observe that the ν_1 and ν_3 modes are well separated and the ν_1 mode is symmetric and the ν_3 mode is split into three peaks (see Figure 1 bottom curve). Under an optical microscope the silane appears transparent at this pressure. In this phase we expect the silane to be 4-fold coordinated and could be probably a variant of the T3 structure [17,24]. Energy dispersive x-ray studies carried out at CHESS at 14.8 GPa shows the structure of Silane in this new phase (phase III) to be space group #14 as discussed later.

Above 23 GPa the Raman spectra changes accompanied with the change in color of the sample. The sample slowly converts to a black solid. The Raman spectra at 25 GPa is shown in Figure 1 (middle curve). At this pressure we find that the sample spontaneously turns to black solid, with appearance of slight silvery islands. Both the ν_1 and ν_3 modes broaden and the splitting in the ν_3 mode disappears. It is also interesting to note that the Raman modes soften (decreases in frequency). A possible scenario could be that with increasing pressure the Si-H bonds expand in order to transform from four-fold coordination to six-fold coordination. The increase in bond distances would imply a decrease in Raman frequency. The broadening of the Raman modes signifies disorder. At 29 GPa (see Figure 1 (top curve)) we observe that the Raman mode softens as well as the Raman intensity drops. The sample turns completely dark at 30 GPa and the Raman modes disappear. Based on the Raman spectra, we feel in the process of transforming from four-fold to six-fold coordination, the hydrogen atoms dissociate from the silicon, leading to the decomposition of silane. The black sample is amorphous silicon and the shiny sample observed as islands in the dark sample could be metallic silicon at high pressures.

The Raman spectra of Silicon has two modes, a weak LO mode around 468 cm^{-1} and a very strong TO mode at 520 cm^{-1} at ambient conditions. In comparison, the Raman spectra of amorphous Silicon is a representation of the density of states of the phonons, since the selection rules break down due to lack of translational symmetry in the structure. Figure 2 shows the Raman spectra at ambient conditions after the samples had been loaded to 70 GPa. We have carried out the Raman spectroscopy of the recovered black solid and observe that the Raman spectra around 200 to 600 cm^{-1} is dominated by features resembling the density of states of the phonons [25]. The key feature is that the TO mode of Silicon is not symmetric and is shifted to the lower frequency characteristic of amorphous hydrogenated silicon. The peak at around 900 to 1000 is the second order Raman peak of silicon. It has been found that the sample is shiny when a stainless steel gasket is used. We believe this is due to the absorption of hydrogen liberated by the dissociation of silane by stainless steel gasket promoting crystalline silicon. This is reduced when a rhenium gasket or a tungsten gasket is used, proving the above assumption.

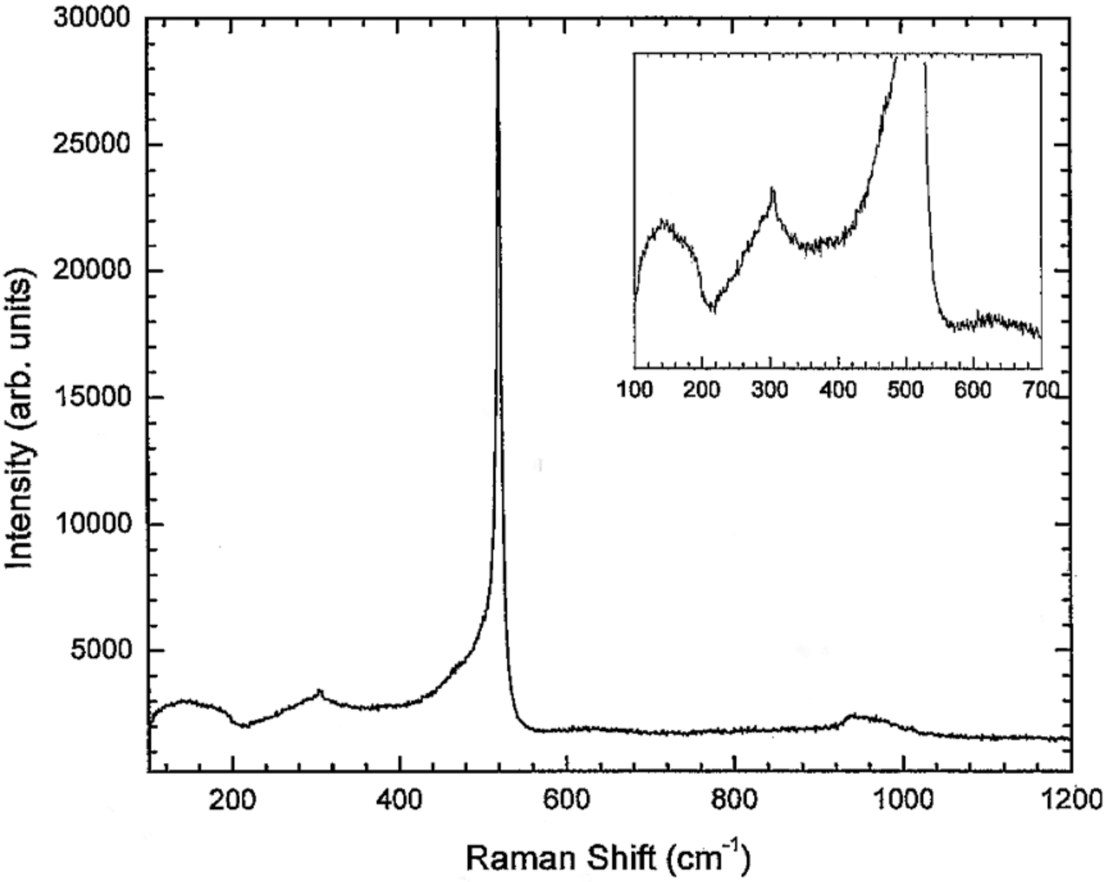

Figure 2. Raman spectra of the sample which has been recovered after the Silane high pressure run (black sample). The figure shows a strong 520 cm^{-1} silicon peak along with weak peaks in the range 100 to 700 cm^{-1} region (see inset). The peak around 900 to 1000 cm^{-1} is the second order Raman spectra of silicon. These clearly show that the sample has transformed into silicon as well as primarily to amorphous hydrogenated silicon.

3. EDX analysis of Silane for structure and EOS

Our experimental x-ray studies on silane ended on May 5, 2007. At that time there was a published set of experimental x-ray data on silane at the low temperature and atmospheric pressure by Sears and Morrison [26]. Two phases were noted, both possibly bct. The diffraction data for the higher temperature solid phase is shown in their Table 1. Their fit to a bct structure with thirty two atoms per cell is shown in their Figure 1. Here eight lines fit well to the bct structure while an additional eight that should be present for that structure were not observed. It appears that the structure is still to be determined. It is clearly not the bcc structure used as a reference by theorists as the low pressure form at room temperature. It is not necessary that it be so except that is the case for methane, which is fcc (four molecules per cell) in two studies [27,28].

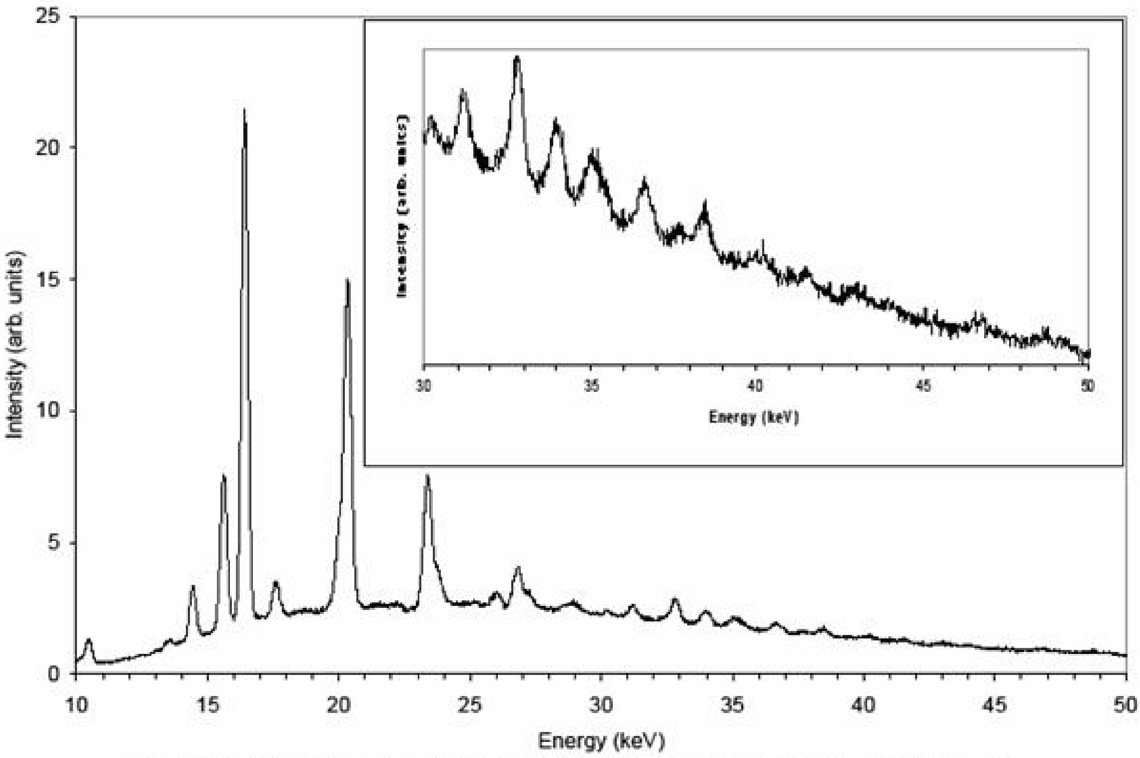

Figure 3. Energy dispersive x-ray diffraction spectrum of silane IV at 12.6 GPa

Room temperature DAC high pressure silane energy dispersive x-ray diffraction spectra from the B1 station of CHESS were analyzed with the program XRDA [29,30] using Ed = 47.369 ± 0.016 KeV-Å as determined with a gold foil. Pressure measurement was made using the shift [31] of the R1 fluorescence line of a small ruby chip placed in the DAC sample chamber. Figure 3 is a representative spectrum at a pressure of 12.6 GPa with 27 diffraction peaks. Figure 4 is the same spectrum with an inset showing the low energy escape peaks.

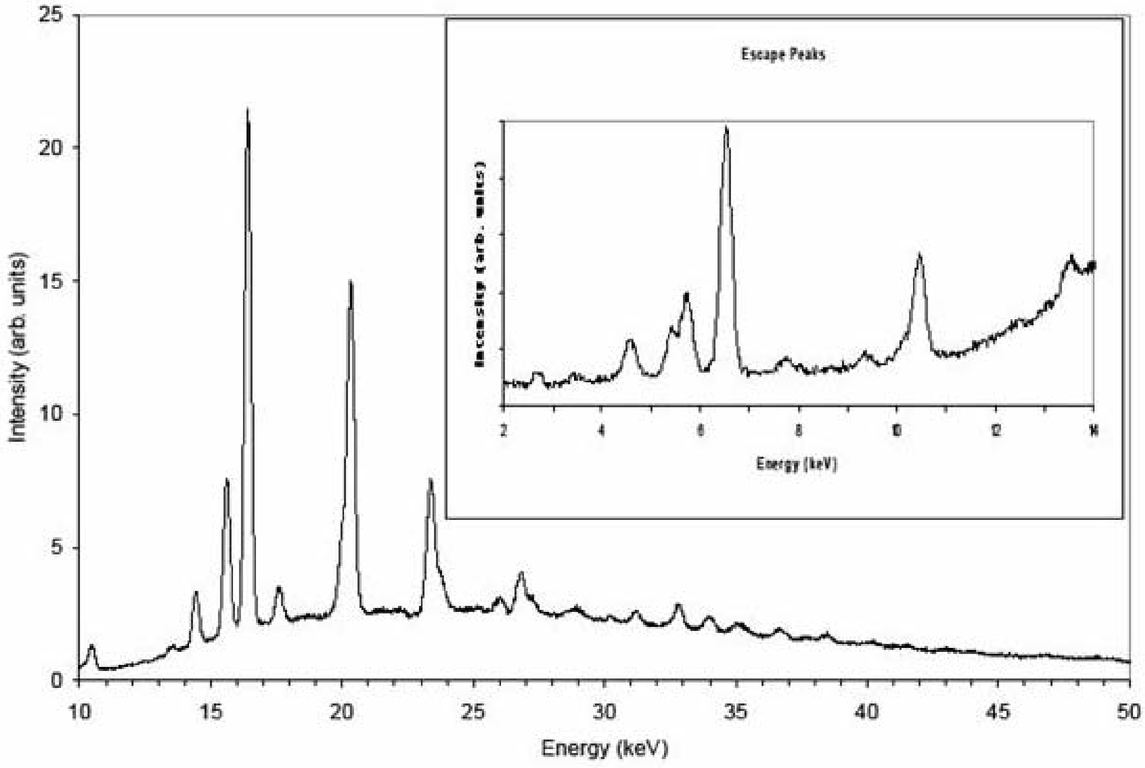

Figure 4. Energy dispersive x-ray diffraction spectrum of silane IV at 12.6 GPa showing low energy escape peaks

The structure was determined by the following procedure on the spectrum of Figure 3. First using the law of corresponding states with methane as a reference the SiH_4 molecular volume was estimated for a pressure of 12 GPa as discussed in another section of this paper. Trial and error attempts at indexing various simple Bravais lattices with cell volumes of up to eight formula units yielded a positive result for a monoclinic Bravais lattice with four formula units per cell and lattice parameters of a = 5.952 Å, b = 3.978 Å, c = 5.956 Å, and β = 104.1°. A trial indexing of this monoclinic cell with these lattice parameters using an fcc basis indexed nearly all of our diffraction lines.

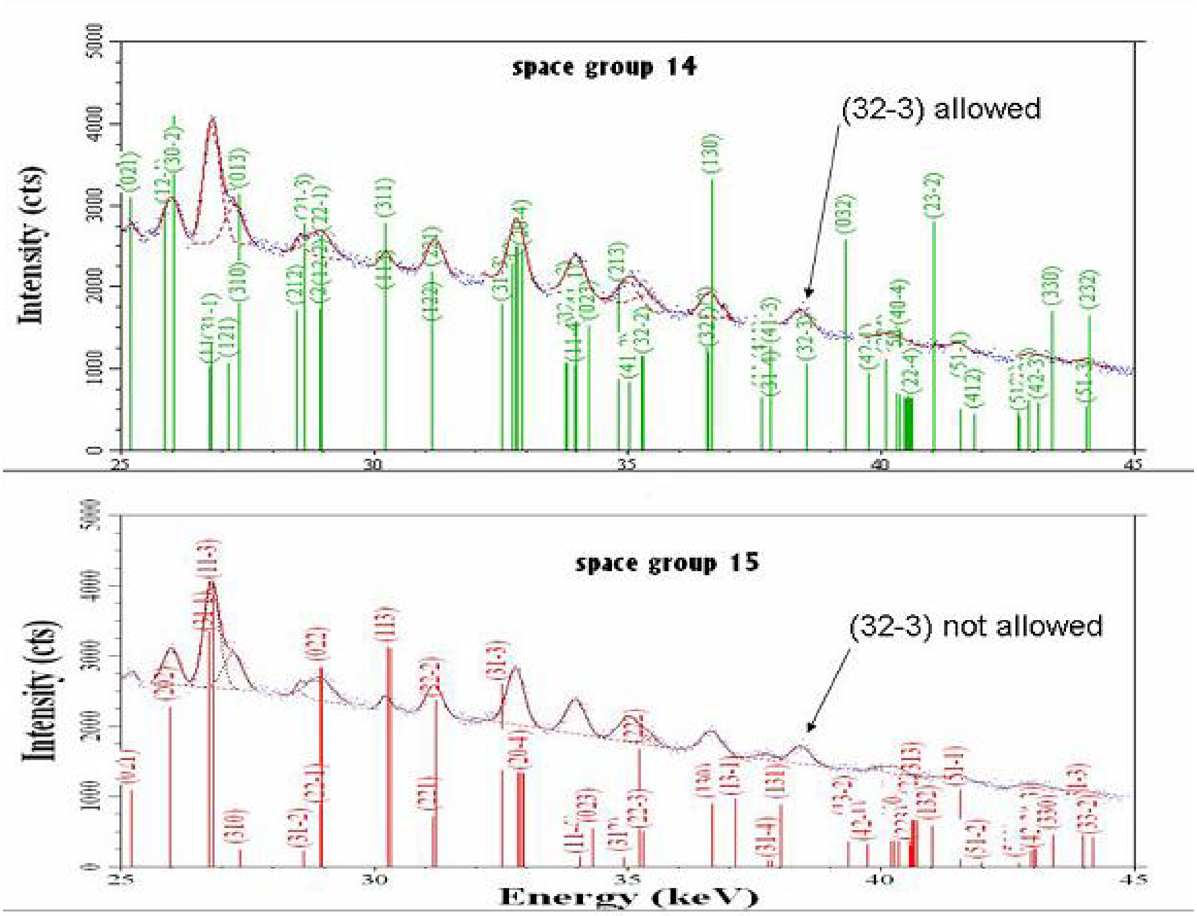

Figure 5. Energy dispersive x-ray diffraction spectra of silane IV at 12.6 GPa showing space group 14 vs. space group 15

Apparently the basis for the monoclinic silane IV structure is somewhat degenerate to fcc. Space group #15 with Si at the Wyckoff letter ‘e’ positions is almost fcc and indexed all of our diffraction peaks with the exception of one at 38.5 keV. Allowing an additional reflection condition to index only this additional peak with indices (32-3) changes the space group to #14 with Si at the Wyckoff letter ‘e’ positions as shown in Figure 5 for our 12.6 GPa spectrum. This is our best structure for silane IV and sufficient for our needs to measure the equation of state. Figure 6 shows the fitting of this structure for our 12.6 GPa spectrum for the energy region not shown in Figure 5.

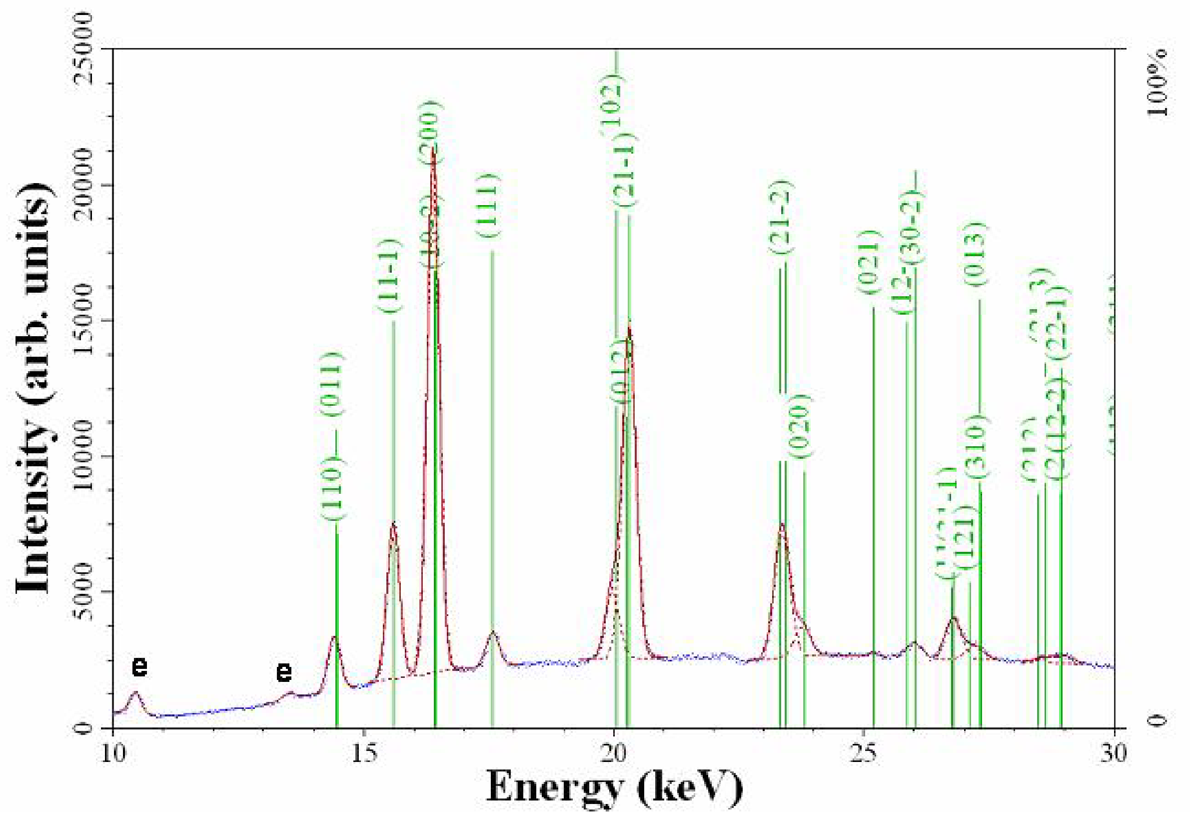

Figure 6. Energy dispersive x-ray diffraction spectrum of silane IV at 12.6 GPa showing fit to space group 14

It is important to recognize the limits of this type of structure determination for a complex Bravais lattice such as monoclinic with a many molecule basis using energy dispersive x-ray diffraction (these comments apply to a lesser but still significant extent to angle dispersive x-ray diffraction) on a quasi-hydrostatic DAC high pressure polycrystalline sample. The "International Tables for Crystallography [32]" give three cautions that apply to our situation. First, twinning for a monoclinic cell with $\beta \cong 90$ degrees such as ours cannot be ruled out and is a possible explanation of reflection conditions; i.e. either too many or too few conditions may be found. This is unlikely in our situation but we cannot positively exclude it. Finally, incorrect assignment of Laue symmetry may be caused by pseudo-symmetry by 'diffraction enhancement'. A further complication arises, in that based on reflection conditions alone, space group #9 and #15 cannot be distinguished. Our best judgement of the situation is that the space group is likely to be #9, #15 or #14. A strict interpretation of the data ignoring the subtleties of sample condition and structural determination would conclude the space group is #14.

Fitting of the cell volume of this structure vs. pressure data of eight spectrum with pressures from 12.6 to 23.5 GPa to the Birch-Murnaghan equation of state [33] with $K_0' = 4$ yielded $V_0 = 250 \pm 0.5$ Å^3 and $K_0 = 7.3 \pm 0.1$ GPa. It should be noted that our P(V) results are the same for all three space groups (within the errors noted). After this paper was presented at the conference, another paper on x-ray diffraction of this phase was published [34]. The results and conclusion agree.

4. Calculation of $\Delta G(P, 298.15k)$ of formation of silane

For the reaction

$$Si + 2H_2 = SiH_2, \quad \Delta G° = 56{,}900 \text{ Joules/mole [35].} \tag{2}$$

If the pressure increases to a pressure P,

$$\Delta G(P, 298.15K) = \Delta G + \text{integral } (VSiH_4 - 2V_{H_2} - V_{Si})dP \qquad (3)$$

where the volumes are molar volumes.

Silicon has a number of phase transitions. The volume of silicon as a function of pressure is known to P = 250GPa [35-38]. For the volume vs. pressure of hydrogen to the freezing point at 298.15K the compilation of Hemmes, et al was used [39]. Above the freezing point the data of Loubeyre, et al, [40] was used.

For silane the equation of state from the present paper was used above the freezing point at 1.8 GPa. Below the freezing point of silane the law of corresponding states [41] was used to calculate P(V) at 298.15K from the equation of state given by a function to 2 GPa by Saltzman and Wagner [42].

The predictability of this procedure was checked by calculating the equation of state of CF_4 to 1 GPa [43]. The critical parameters are from the following: CH_4 [42], SiH_4 [44], CF_4 [43]. The resultant curve for ΔG (P, 298.15K) is shown in Figure 7. This reference is used with the results of Figure 8, to obtain Figure 9 which shows a region of stability in the pressure range of 3-15 GPa. However, above 15 GPa SiH_4 is again thermodynamically unstable. Note that the quasi-quantum mechanical calculations show the P2/c structure more stable than the $SnBr_4$ structure (Space group #14) above 28 GPa and the Pmna structure more stable than the $SnBr_4$ structure above about 30 GPa. It should be noted that in the $SnBr_4$ atom has four nearest hydrogen neighbors, while in the P2/c structure the carbon atom has ten hydrogen neighbors and the Pmna structure has eight. We have already noted that quasi-quantum mechanical calculations give an activation energy of 0.5 eV for the very simple $I\bar{4}3m$ structure with a carbon atom with four nearest neighbors (head-to-base) to the $I\bar{4}3m$ structure with a carbon atom with eight nearest neighbors [M_1(Feng)] where one would not be surprised to find an activation energy to near zero. The transitions from $SnBr_4$ to P2/c and Pmna are likely to have large activation barriers and therefore it is unlikely that they will form as metastable compounds if the path to decomposition is easier. It should be noted that decomposition could involve products other than the Si, such as Si_2H_2, S_2H_4, etc. with SiH_2 being a possible precursor for polysilene as C_2H_2 is for polyacetylene, etc. The stainless steel gasket (and possibly the rhenium gasket) absorbs H_2 at pressure while W does not, even at 40 GPa, for one month at 298.15K. Thus the steel gasket probably both catalyze decomposition in Equation 2 but also makes decomposition more thermodynamically stable absorbing H_2.

Conclusions

Silane at pressures between 10 and 27 GPa was found from energy dispersive x-ray diffraction studies to have a monoclinic crystal structure with space group $P2_1c$ (#14), the fit being shown in Figure 5. All the Raman spectra below 23 GPa gave a good indication of the presence of the SiH_4 molecular unit. Around this pressure the different samples began to turn black and the Raman modes began to broaden and soften, indicating the weakening of the Si-H bonds. The Raman spectra disappeared around 30 GPa. The samples became increasingly silvery as the pressure increases and appeared to be metallic at 40 GPa. At 70 GPa there was no sign of an x-ray pattern from the sample. When the sample was unloaded it was non-crystalline and showed a Raman spectrum corresponding to that of a hydrogenated-amorphous silicon alloy, or Si:H. Quasi-quantum mechanical calculations had shown that above 27 GPa, a 6-fold structure, such as Pmna, is thermodynamically more stable than the 4-fold $P2_1c$ structure. Using the equations of state of SiH_4, Si and H_2 the authors calculate that above 13 GPa, $Si + 2H_2$ is thermodynamically more stable than SiH_4.

We suspect that there is a sizeable activation barrier for the 4-fold to 6-fold transition and for the 4-fold decomposition products and instead the crystalline $P2_1c$ structure transforms to the amorphous metallic alloy, ∂ Si-H.

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