

Phase transitions in a hydrogen-rich compound: tetramethylsilane^{*}

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Abstract: High-pressure behavior of tetramethylsilane is investigated by synchrotron powder X-ray diffraction and Raman scattering at pressures up to 30 GPa and room temperature. Our results reveal the analogous phase transitions, though slight hysteresis for the certain phases. A new phase is found to appear at 4.2 GPa due to the disappeared Raman mode. These findings offer the possibility to understand the evolution of the H-H bonding with pressure in such hydrogen-rich compounds.

Key words: high-pressure, hydrogen-rich, phase transition

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1 Introduction

As an important challenge in modern physics, studies of hydrogen have long been a major driving force in high-pressure science and technology development [1], which originates from the possible superconductivity with high T_c (>200 K) under sufficiently strong compression [2, 3]. However, the experimental realization of metallic hydrogen in the condensed form has remained elusive. Excitingly, group IVa hydrides provide an alternative way to metallic hydrogen which was also predicted to be a superconductor with high transition temperature in monatomic and molecular phases. In group IVa hydrides, the hydrogen atoms probably have undertaken chemical precompression by the group IVa atoms within the unit [4], and thus the chemical pressure environments in these hydrides may greatly reduce the physical pressure necessary for metallic hydrogen. Many experimental and theoretical efforts are currently underway to investigate this prediction, such as SiH_4 [5–15], GeH_4 [16–20], SnH_4 [21–24], and PbH_4 [25]. However, very recently experiments show the possible decomposition of SiH_4 under irradiation from X-ray and lasers [26, 27]. This indicates that the metallization of SiH_4 may be realized at higher pressure than thought. The stability of group IVa hydrides at high pressures remains in debate. Searching new systems on the group IVa hydrides will be extremely urgent to achieve the metallic hydrogen at “low” pressures.

Tetramethylsilane (TMS), $\text{Si}(\text{CH}_3)_4$, has spurred a tremendous interest in the spectroscopy due to its highly symmetrical characters [28–33]. In the molecular struc-

ture of Fig. 1, the Si element is tetrahedrally coordinated by methyl groups ($-\text{CH}_3$), making the molecule with the T_d symmetry [31, 33]. In view of the feature that only one atom of each element is symmetry independent, and thus only one signal of each type is observed, TMS is usually used as an internal standard for calibrating chemical shifts in ^1H , ^{13}C and ^{29}Si NMR spectroscopy [34]. Studies on TMS at low temperature conditions suggested that the CH_3 groups play a central role in understanding the phase transitions and the CH_3 groups become non-equivalent and exhibit intermolecular interactions [35].

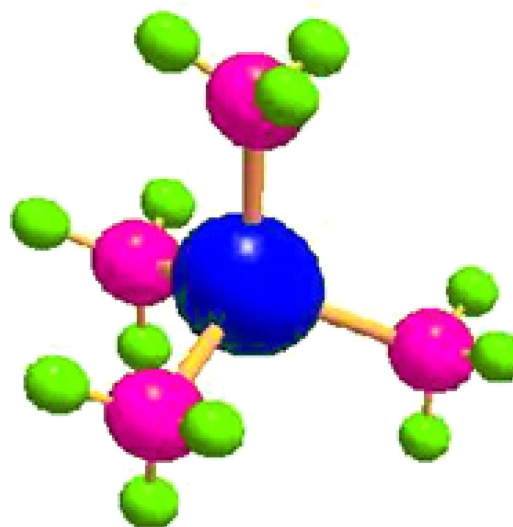


Fig. 1. The configurations of TMS with respect to ideally tetrahedral $T_d(-43\text{ m})$ symmetry.

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Additionally, applying pressure to TMS makes the CH_3 groups display different rotational angles at only 0.58 GPa [36]. Our recent work reveals that TMS shows no decomposition up to 142 GPa [37], although the metalization has not been reached yet.

In this paper we report high-pressure studies on TMS by combining synchrotron powder X-ray diffraction (XRD) and Raman scattering up to 30 GPa. A new phase at 4.2 GPa is identified by both Raman spectra and the XRD. We determine the possible crystal structure for the newly discovered phase. Our results provide the possibility of analyzing the pressure effects on the H-H bonding in such hydrogen-rich compounds.

2 Experimental details

TMS (m.p.178 K, b.p.299 K) as transparent liquid with 99.9% purity was purchased from Alfa-Aesar and used without further purification. The high-pressure experiments for TMS were carried out using Diamond anvil cell (DAC) with beveled anvils and the culets of 300 microns. A hole of ~ 100 microns in diameter drilled in a pre-indented tungsten gasket served as the sample chamber. To avoid volatilizing, the bottom of DAC was put into ice-water mixture half an hour before loading the sample. Liquid TMS was loaded into the chamber of DAC with a syringe. Because of a liquid sample, no pressure medium was used and ruby grains had been placed previously as pressure marker. Considering the volatilizing of samples, pressure was increased to 0.6 GPa after loading well the samples. Synchrotron radiation measurements were performed at the X17C beamline of the National Synchrotron Light Source at Brookhaven National Laboratory via angle-dispersive diffraction techniques using monochromatic radiation $\lambda=0.3989$ Å. The sample-to-detector distance and the image plate orientation angles were calibrated using CeO_2 standard. The two-dimensional diffraction images were converted to 2θ versus intensity data plots by the FIT2D software.

The same DAC was employed for the high-pressure Raman spectral experiment. Raman spectra were measured in a backscattering geometry with a spectrometer (with 1800 mm^{-1} grating) equipped with a di-monochromator and a charge-coupled device detector, giving a resolution of $\sim 1\text{--}2\text{ cm}^{-1}$. Radiation of 532 nm from a solid-state laser (0.5 W CW) was used for the excitation of the Raman spectra and all spectra were measured at ambient temperature.

3 Results and discussion

3.1 Analysis on phase transitions of the TMS under pressure based on the XRD

The pressure dependence of the scattering profile

provides evidence for several phase transitions. Fig. 2 shows the X-ray diffraction patterns of TMS at pressure up to 30.0 GPa. All the Bragg peaks shift to larger angles, showing the shrinkage of the TMS lattice. At 4.2 GPa, the X-ray diffraction pattern of TMS reveals a strong preferred orientation from the peak at $5.5^\circ\text{--}6.0^\circ$, which possibly results from the recrystallization of TMS. Until 9.9 GPa, all peaks become smooth accompanied by some peaks vanishing and new peaks appearing, suggesting a new phase transition. A similar case has been observed in recent work [37] that a new phase transition appeared at 9.0 GPa by the analysis on Raman spectra. For 6.5 GPa, we have difficulties in determining the structures for TMS. Upon further compression to 18.2 GPa, the intensities of most peaks change, indicating another phase transition. The new phase shows slight hysteresis compared with the recent experiments on the phase transition of TMS at 16.0 GPa [37]. Compressing the sample to 29.2 GPa, no change is observed from the XRD spectra. This observation coincides with the results detected by the Raman spectral experiments in our recent work [37]. All of the phase transitions can be clearly distinguished by the pressure dependence of the d-spacing, shown in Fig. 3.

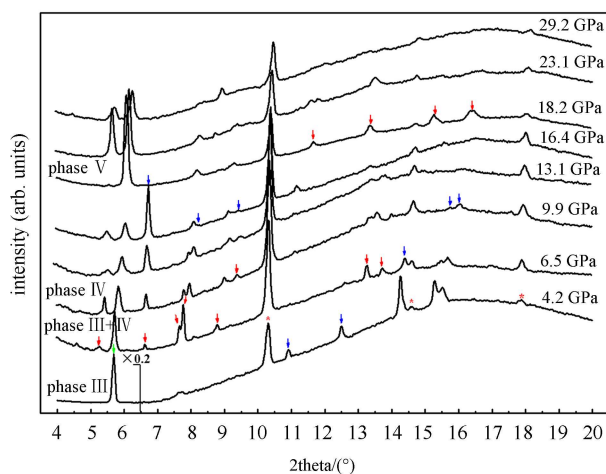


Fig. 2. (color online) Synchrotron radiation X-ray ($\lambda=0.3989$ Å) diffraction patterns of TMS during the pressurization from ambient conditions to 30.0 GPa. The red arrows indicate the appearance of new peaks and the blue arrows show the disappearance of the intrinsic peaks. Red asterisks illustrate the signals from the gasket material tungsten. The first peak was decreased at 4.2 GPa due to strong preferred orientation (green arrow).

For TMS, it is reported that TMS crystallizes into cubic structure with the space group Pa-3 [36], which is labeled as phase II via liquid phase (phase I), while compressed to only 0.58 GPa. It was found in recent

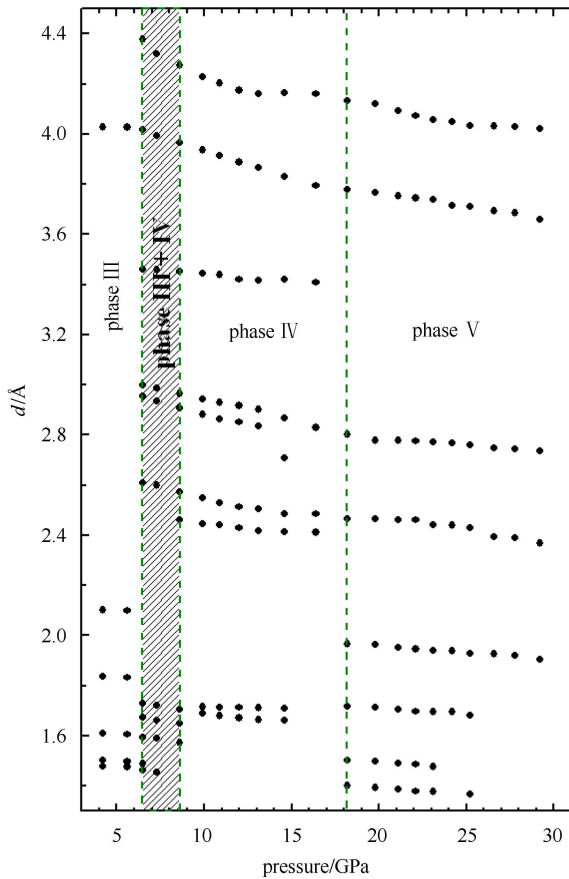


Fig. 3. The pressure dependence of d-spacing from the XRD.

Raman experiments that no new phase transition appeared until 9.0 GPa, therefore, cubic structure at least should be kept with compression to 6.5 GPa. However, fitting the XRD pattern at 4.2 GPa using the space group Pa-3 with lattice parameters of $a=10.7328$ Å failed. Gratifyingly, indexing yields a reasonable solution, which leads to an orthorhombic cell (space group Pnma) at this pressure. Additionally, a study on possible crystal structures of TMS was performed by global lattice-energy minimization using force-field methods. The results indicated that the Pnma space group is the second low-energy structure for TMS [35]. The phase was fitted with the space group of Pnma using Le Bail method with GSAS software [38] and the measured and fitted data are shown in Fig. 4. As can be seen, the positions and intensities of the diffraction peaks of TMS at 4.2 GPa are fitted well within the indexed structure for phase III. Up to now, phase transitions of TMS under pressure should be liquid state (phase I), 0.6–4.2 GPa (phase II), 4.2–6.5 GPa (phase III), 6.5–9.9 GPa (phase III+IV), 9.9–18.2 GPa (phase IV) and 18.2–29.2 GPa (phase V).

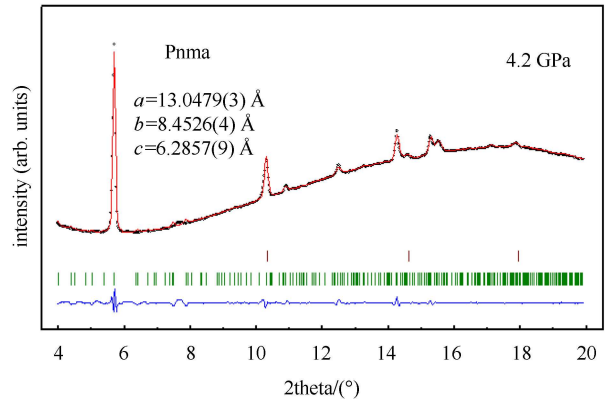


Fig. 4. (color online) X-ray powder diffraction patterns of liquid TMS at pressures of 4.2 GPa. The refined lattice parameters for the space groups are given. The symbols represent the measured intensities and the red lines the results of profile refinements by the best Le Bail-fit with the space group. The positions of the Bragg reflections are marked by vertical lines and the difference profiles are shown at the bottom (blue lines). The R values are $R_p=0.2\%$, $R_{wp}=0.4\%$ for the fitting at 4.2 GPa.

3.2 Raman spectra of TMS under pressure

Vibrational spectroscopy is crucial for characterizing high-pressure phase transition of low- Z molecular materials. On the basis of group theory, the irreducible representation (of all the normal vibrational modes) is $\Gamma=3A_1+A_2+4E+4F_1+7F_2$. According to the selection rule, the A_1 , E and F_2 vibrations are Raman active. In recent work, the modes have been assigned well to all kinds of types of vibration in view of the doubly degenerate modes [37]. To further determine the changes in phase transitions, other high-pressure Raman spectral experiments are performed in detail upon compression to 29.9 GPa. With increasing pressure, nearly all of our measured peaks except for 1420 cm^{-1} which is influenced by the strong peak of diamond at 1332 cm^{-1} , shift to higher frequencies. All spectra become weak and some of them nearly vanish. These rich Raman features reveal the pressure-induced structural revolutions. For convenience eight modes are labeled as ν_1 to ν_8 sequentially in the bottom of Fig. 5. Compressed to 0.6 GPa, two new modes appear in the frequency of $\sim 850\text{ cm}^{-1}$ and $\sim 1240\text{ cm}^{-1}$, which are due to the splitting of the intrinsic modes ν_5 and ν_6 . The intensities of ν_1 and ν_2 modes in the lowest frequency region change differently. This provides evidence for both modes to exchange the symmetry assignment of these two modes as a result of Fermi resonance [39], definitely suggesting to undergo the phase transition from liquid phase to phase II.

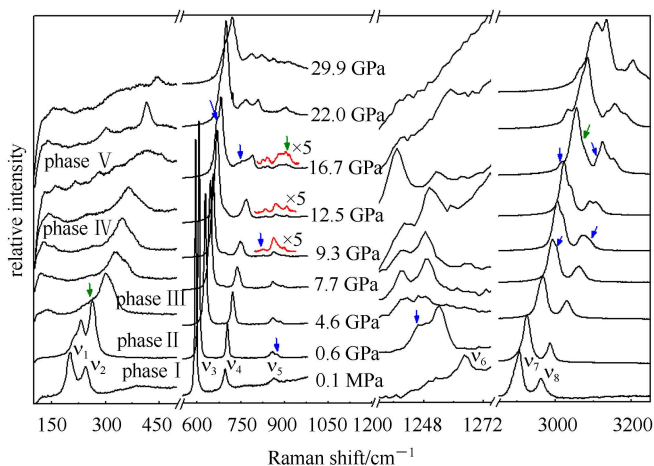


Fig. 5. (color online) Representative Raman spectra of TMS in the full spectral regions at ambient conditions upon compression to 30 GPa. The blue arrows are to make the appearance of part Raman modes clear to observe and green arrows show the disappearance of the Raman modes. All observed modes in liquid TMS were marked as ν_1 to ν_8 sequentially in the bottom of the figure.

The homologous phase transitions were characterized by the appearance of the new modes in the lower frequency of mode ν_5 and in the higher frequency of mode ν_8 at 9.3 GPa for phase IV, the splitting of several modes, and the disappearance of some modes at 16.7 GPa for phase V respectively. It shows slight hysteresis for phase IV and phase V compared with recent work although the result proves again possible high-pressure phases of TMS [37]. Unexpectedly, mode ν_1 becomes extremely weak so that it is difficult to resolve from the spectrum, whereas the mode existed in the compressed process, only weakening in the recent high-pressure Raman experiment. This temporarily provides evidence for phase III from the Raman spectroscopy. Additionally, mode ν_7 has split at 7.7 GPa suggesting that phase IV has appeared before compression to 9.3 GPa, which suitably illustrates reasonableness for the transient state.

Structural transformation at different temperatures and pressures has been a critical issue in exploring the feasibility of the hydrides with regard to their metallization. For cubic system of TMS at 0.6 GPa, no rotational mode in intrinsic spherically shaped molecules of TMS

at ambient conditions is assigned, yet it exhibits softening vibration for mode ν_6 related to the rotation of CH_3 group(s) [40–42], which is different from the softening behaviors in hydrogen-rich complexes such as $\text{SiH}_4\text{-H}_2$ [43–47] and $\text{GeH}_4\text{-H}_2$ [48, 49]. The Raman bands of the new compound remarkably decrease in frequency starting at pressure as low as 7 GPa. Until phase IV appeared at 9.9 GPa, softening vanishes as a result of the external pressure to lock in the positions and to restrict the mobility of the hydrogen atoms inside CH_3 groups, which might suggest that C-H bonds in solid $\text{Si}(\text{CH}_3)_4$ are not isolated with further increase of intra- and intermolecular interactions. It is uncertain whether all hydrogen atoms are built up in a network structure by means of the closest packing [4, 9, 13], which has significant implications for metallic hydrogen at high pressures. Upon compression above 16.7 GPa, drastic spectral changes, especially the observation of abundant new internal modes, strongly suggest enhanced intermolecular interaction with covalent nature.

4 Conclusions

We have performed high-pressure powder X-ray diffraction and Raman scattering measurements on TMS up to 30 GPa. Our results revealed the homogeneous process of phase transitions for TMS with compression to 29.9 GPa, compared to the aforementioned work on Raman spectroscopy investigations on liquid TMS. A new phase at 4.2 GPa was identified by the XRD patterns and Raman spectra with pressure up to 30 GPa. Before undergoing phase transition of phase IV, a transient state would exist. These transitions were suggested to result from the changes in the inter- and intra-molecular bonding of this material. Additionally, Pnma would be a possible space group for phase III. Our studies revealed the bonding changes with pressure in a hydrogen-bearing system.

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