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Velocity and Stability of Condensed Polymorphic SiH_4: A High-Temperature High-Pressure Brillouin Investigation *

Jiayu Wang(王佳钰), Qiang Zhou(周强), Siyang Guo(郭思洋), Yanping Huang(黄艳萍), Xiaoli Huang(黄晓丽), Lu Wang(王璐)**, Fangfei Li(李芳菲)**, Tian Cui(崔田)

State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China

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Silane (SiH_4) is a promising hydrogen-rich compound for pursing high temperature superconducting. Previous high pressure measurements of Raman, x-ray diffraction and theoretical studies on SiH_4 mainly focused on its polymorphic structures above 50 GPa, while the structure and the stability under lower pressure range are still unclear. Here we report an investigation of condensed SiH_4 by Brillouin scattering measurements at high temperature up to 407 K and high pressure up to 18 GPa. Brillouin scattering frequencies of fluid SiH_4 under compression are obtained under isothermal conditions of 300 K, 359 K and 407 K. The SiH_4 becomes unstable with increasing temperature and subsequently decomposes into silicon and H_2. We find that compression at room temperature induces two velocity anomalies corresponding to a fluid-solid state transition and a phase Ⅳ to phase V transition, respectively. Brillouin scattering spectra has been a powerful tool to investigate the fruitful phases and structure transitions in the hydrogen-rich compound under extreme conditions.

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Silane (SiH_4), a hydrogen-rich compound, has been extensively used for industrial productions of solar grade silicon, polysilicon in thin film photovoltaics, semiconductors and liquid-crystal displays.[1] Recently the condensed SiH_4 draws plenty of attention for possible high temperature superconducting.[1−8] Following the pioneering idea of metallic hydrogen and chemical precompression by Ashcroft, the metallization pressure of hydrogen-rich compounds is estimated to be much lower than that of pure hydrogen.[2,3] Several high-pressure structures of SiH_4 have been predicted,[2−5] in which metallization pressure are estimated to vary from 20 GPa to 380 GPa. Yao *et al.* predicted that SiH_4 transforms to a metallic phase with monoclinic $C2/c$ structure at about 60 GPa.[4] Feng *et al.* suggested the SiH_4 with an $O3$ structure should be metallic close to 91 GPa, and the superconducting transition temperature T_c would be 166 K at 202 GPa.[5] Pickard and Needs pointed out that the $C2/c$ structure of SiH_4 is probably a good metal with a high T_c.[6] Zhang *et al.* predicted that two metallic structures may be stable above 383 GPa, and their T_c may reach up to 29.65 K at 300 GPa and 31.57 K at 400 GPa.[7]

The stability of SiH_4 is a key issue for the experiments. Under ambient condition, spontaneous combustion occurs as soon as SiH_4 exposes to air.[8] Chen *et al.*[9] compressed the SiH_4 in a diamond anvil cell (DAC) and speculated an insulator-to-metal transition by the Raman and IR reflectivity measurements. Meanwhile, Eremets *et al.*[10] reported the observation of SiH_4 metallization based on electrical resistance measurement. However, it was found later that their measured resistance drop is caused by the decomposition of SiH_4 into Si and H_2 at pressures above 50 GPa. The conduction mostly arises from a chemical reaction between H_2 and environment materials like Pt or Re rather than from the SiH_4.[11,12] Hanfland *et al.*[13] showed that SiH_4 becomes amorphous above 60 GPa and recrystallizes above 90 GPa into a polymeric structures. Nevertheless, the structures and the stability of SiH_4 are still under debate, and in addition no superconducting phase has been confirmed yet.

Current investigations on SiH_4 are mainly focused on their polymorphic structures above 50 GPa by x-ray diffraction (XRD), Raman scattering, infrared reflectivity (IR) and theoretical calculations.[12−16] However, the structural stability under low pressure range before its decomposition is still unclear. Brillouin scattering spectra can provide velocity and elastic properties of materials, through which we can extract the structural stability under extreme conditions. They offer a good means to disclose the structure properties of compressed SiH_4.[17,18] In this Letter, we first report a high-temperature high-pressure (HTHP) Brillouin scattering measurements on condensed SiH_4 in a DAC up to the temperature of 407 K and the pressure of 18 GPa, the refractive indexes of fluid SiH_4 and the velocities of solid SiH_4 are presented and the elastic properties are unveiled.

The SiH_4 gas from the Alfa Aesar (99.999% purity) was stored in a compressed gas cylinder. We loaded the gaseous SiH_4 into the BX90 DAC (with

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**Corresponding author. Email: wanglu@jlu.edu.cn; lifangfei@jlu.edu.cn

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wide opening) chamber in a glove box purged with argon. The DAC was cooled down to a temperature below saline's boiling point when SiH_4 gas was puffed on, followed by an immediate sealing of the DAC as soon as the chamber was fully filled with liquid SiH_4. The diameter of the diamond anvil was 400 μm with a predrilled rhenium gasket as the sample chamber. The DAC could be heated by a resistance heater around the diamonds and the sample chamber, whose temperature was calibrated with a K-type thermocouple attached on the flank of the diamond. During measurements the temperature was controlled by a feedback power and the temperature error was normally controlled within 1 K. The pressure was also monitored by ruby fluorescence.[19] Taking into account of the temperature gradient around the sample chamber, the temperature dispersion between the anvil center and the side face of the diamond could not be ignored. In order to obtain a precise temperature on the sample, a ruby ball was placed in the sample chamber to measure the temperature dependence of the ruby fluorescence. The shifts of the luminescence at ambient pressure were recorded and compared with early publications.[20] The actual temperature in the center of sample chamber was thus calibrated for the following experiments.

In this study, the Brillouin scattering spectrum could be collected in both back (180°) and symmetric platelet (60°) scattering geometries.[21] A single-frequency green 532 nm laser was used as the incident excitation source. The laser was a solid-state diode-pumped frequency-doubled Nd:Vanadate laser from Coherent Company. The scattered signals were collected by 3+3 pass tandem Fabry–Pérot interferometer designed by Sandercock.[22]

For forward platelet scattering geometry measurements, the sound velocity of sample is calculated by[23]

$$V = \frac{\lambda_0 \Delta V}{2n \sin(\theta/2)}, \tag{1}$$

where V is the acoustic velocity, ΔV is the corresponding Brillouin frequency shift in gigahertz (GHz), λ_0 is the wavelength of the incident beam, n is the refractive index of sample, and θ is the angle between the incident and scattered beams. When a plate sample in DAC was studied, its sound velocity can be obtained to be independent of the sample's refractive index, which has been discussed elsewhere in detail.[24] To put it simply, in 60° platelet geometry, Eq. (1) can be expressed as

$$V_{60} = \Delta V_{60} \cdot \lambda_0, \tag{2}$$

It should be noticed that a complete dynamical theory of fluid sample is still absent, and has been approached by different levels of theory, including thermodynamic, hydrodynamic and more microscopic, detailed mechanism can be found elsewhere if interested.[25,26] The elementary excitation induced Brillouin shift in fluid is complicated and may not follow the linear dispersion relation, while we just calculate and use the velocity concept in later comparison and discussion for convenient. Then due to the isotropy in fluid, by collecting both 60° platelet and 180° back scattering signals, the refractive index of the sample can be estimated based on certain assumptions.[18] In the backscattering geometry Eq. (1) is rewritten as

$$V_{180} = \frac{\lambda_0 \Delta V_{180}}{2n}. \tag{3}$$

In this study, the liquid SiH_4 was heated up to a constant temperature, and then the pressure was increased manually until the sample finally solidifies. The temperature effect on liquid SiH_4 was compared between the isothermals. After solidification, only forward 60° scattering geometry measurements are performed as the velocity anisotropism appears. The solidification process was monitored either by a microscope or by analyzing the Brillouin scattering spectra.

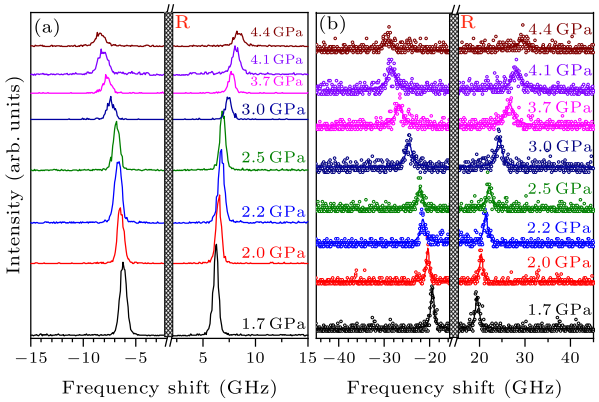

Fig. 1. High-pressure Brillouin spectra of liquid SiH_4 at 300 K (a) in the 60° forward platelet scattering geometry and (b) in the back scattering geometry. R refers to the Rayleigh peak.

Brillouin spectra of liquid SiH_4 under high pressures at 300 K were measured in both the 60° forward platelet scattering geometry and the back scattering geometry as shown in Fig. 1. The spectra are of good quality with a high signal-to-noise ratio. Both the longitudinal frequency shift peaks (V_{60}) and weak back scattering signal (V_{180}) can be observed in the platelet scattering geometry, but their intensity decreases dramatically with increasing pressure.

The velocities of liquid SiH_4 are calculated by Eq. (2) as the foregoing explanation, and their pressure dependence is represented in Fig. 2(a). The velocity increases smoothly and monotonously up to 4.5 GPa at 300 K. Since the velocity in an isotropic medium is independent of direction, its refractive index can be calculated from the ratio of the Brillouin scattering frequency shifts by Eqs. (2) and (3). As shown in Fig. 2(b), the refractive index for liquid SiH_4 also increases smoothly and monotonously with pressure.

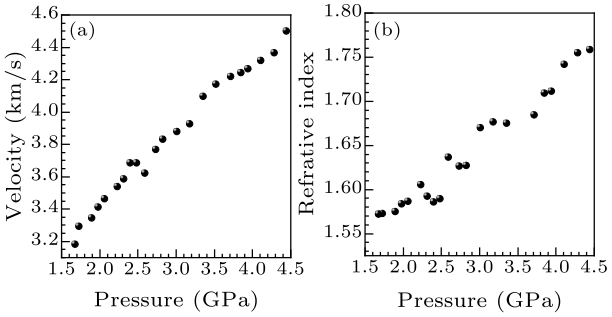

Fig. 2. Pressure dependence of the velocity (a) and the refractive index (b) for liquid SiH_4 at 300 K.

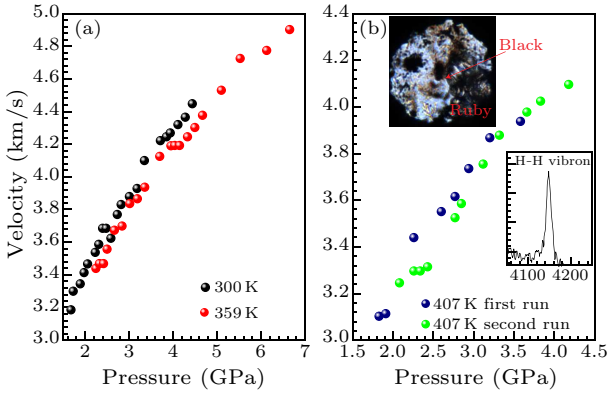

Fig. 3. Pressure evolutions of velocity along different isothermals. The upper inset in (b) presents the image showing a laser damage to the liquid SiH_4 at about 3.8 GPa and 407 K, and the lower inset gives the Raman spectrum of vibron of hydrogen detected in the sample chamber.

When the pressure is released at room temperature, the velocity decreases back to the original state, indicating stable molecular fluids within the measured pressure range. By resistance heating, the fluid SiH_4 in DAC was heated to higher temperatures, and pressure dependence of the velocities along 359 K and 407 K isothermals were collected. In Fig. 3(a) we can see that the variation of the velocity with temperature is smaller compared with its pressure dependence and just decreases slightly with increasing temperature at a similar constant pressure. The solidification pressure extends to a higher pressure of nearly 7 GPa at 359 K. However, when temperature increases up to 407 K, the transparent SiH_4 becomes opaque gradually at about 3.2 GPa, as shown in the photo in Fig. 3(b). Though the measured velocities along 407 K isothermal present monotonous increasing as usual, they most probably correspond to the SiH_4 decomposition.

As the opaque area appeared at the locations irradiated by the laser, it might be caused by heating effect of the focused laser. However, no changes were seen during 300 K and 359 K measurements, suggesting that the SiH_4 becomes unstable at higher temperatures. After the DAC was released to lower pressure, the opaque position did not disappear, implying a nonreversible process. If we heated the sample again up to 407 K and gradually increased pressure to measure the Brillouin frequencies on those transparent areas with ultralow laser power, a clear drop of the refractive index could be observed in this run, as presented in Fig. 4(b). Therefore, the SiH_4 is speculated to disintegrate in the first run that releases H_2 and silicon microcrystal. When a certain amount of silicon microcrystal appears, the chamber becomes opaque. The mixture of H_2 and undecomposed SiH_4 gives a decreased velocity and a drop of refractive index along the second 407 K isothermal run. To confirm this, the vibron of hydrogen was measured through Raman scattering measurements, as shown in the inset of Fig. 3(b).

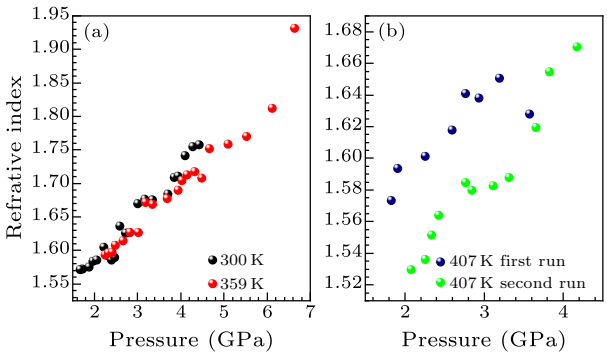

Fig. 4. Pressure dependence of refractive index n in fluid SiH_4 along different isothermals.

At room temperature the liquid state of SiH_4 exists to about 4.5 GPa, then it turns into solid state with the transverse mode velocity appearing, as shown in Fig. 5. The longitudinal (V_L) mode has a strong intensity than the transverse (V_T) mode, and their intensities both decrease remarkably with increasing pressure. After crystallization, the SiH_4 has different sound velocities in planar 180° rotational measurements. The Brillouin scattering frequencies of solid SiH_4 increase monotonically in all directions, at one of which the frequencies is compared under compression and presented in Fig. 5.

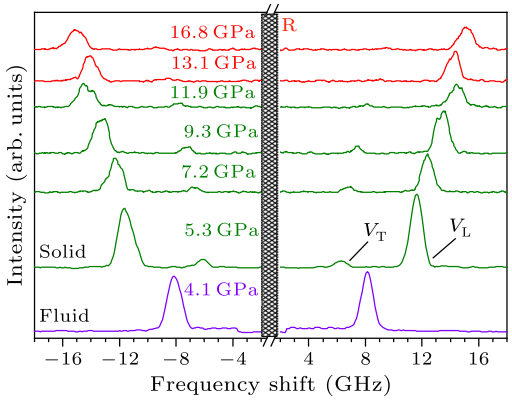

Fig. 5. Brillouin scattering spectra of SiH_4 at different pressures. R refers to the Rayleigh scattering, V_L is the longitudinal mode and V_T is the transverse mode.

Upon compression, a continuing increase of lon-

gitudinal frequency could be seen. However, above 13 GPa a sudden drop was observed followed by a monotonic increase of the Brillouin frequency. To better understand these behaviors, the direction dependence of sound velocities at different pressures and the pressure dependence of the velocities within the whole pressure range are plotted in Fig. 6. After crystallization, the rollercoaster of the velocity anisotropy is clearly seen along each direction, while the curvatures of velocity variations keep constant under pressure up to 11.9 GPa. Then the anisotropy becomes dramatically larger than before. The maximal difference of the velocities between different direction is about 1.1 km/s, while it was only 0.5 km/s below 13 GPa. Thus there may be a phase transition above 13 GPa.

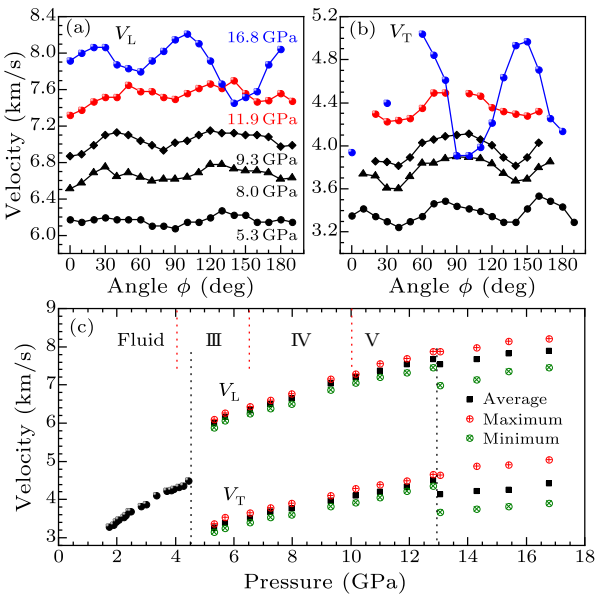

Fig. 6. Direction dependence of velocities for SiH_4 at different pressures and room temperature. Longitudinal and transverse velocities are denoted by V_L (a) and V_T (b), respectively. (c) Pressure dependence of velocities of the SiH_4. The maximum (red circles), minimum (green circles) and averaged (black square) velocities are shown by different symbols for clearness. The upper red dotted lines show a series of phase separations from Chen's document in Ref. [9].

The pressure dependence of the velocity variations in Fig. 6(c) can be divided it into three areas: one fluid phase and two crystallized phases. The liquid-to-solid phase transition is confirmed by the appearance of transversal velocity, and the enhancement of the velocity anisotropy of solid-to-solid phase transition is at about 13 GPa. In the figure, the maximum and minimum velocities propagating along different directions are shown with red and green symbols separately, and the averaged velocity is given by solid black circles. All velocities increase smoothly with pressure without any changes of the anisotropy. However, above 13 GPa, the minimum V_L decreases about 6.4% and the minimum V_T decreases about 15.8%. The velocity anisotropic increases more than double across the boundary.

The structural transition of SiH_4 within the low pressure range is complicated and unclear till now. Chen *et al.* reported the Raman and IR spectra of SiH_4 and showed that there are three phase transitions below 20 GPa,[9] including the fluid state to phase Ⅲ, phase Ⅲ to phase Ⅳ and finally to phase V. Their phase separations are plotted in Fig. 6(c) for a direct comparison. The fluid-to-solid phase transition around 4.5 GPa observed in this work is consistent with Chen's report. Based on Raman measurements, they observed a discontinuity in the V_1, V_2, and V_3 Raman-active modes at 6.5 GPa, which indicates the transition from phase Ⅲ to Ⅳ. The transition from phase Ⅲ to phase Ⅳ however cannot be identified from this velocity measurement. This suggests that the transition between phase Ⅲ and phase Ⅳ may be an isostructural transition where no enormous change occurs. The transition at about 13 GPa we found in this study may correspond to the phase Ⅳ to V transition presented by Chen *et al.*, though there appeared a little difference between these two transition pressures.

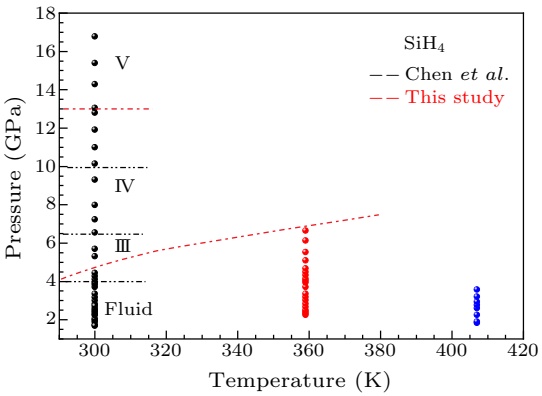

Fig. 7. Pressure–temperature phase diagram of SiH_4. The measured pressure points of three isotherms are labeled by circles are given in the figure.

In addition, a previous structural investigation on SiH_4 suggested the $P2_1/c$ symmetry between 10 GPa and 25 GPa,[27] corresponding to the phase V existing between 10 GPa and 27 GPa.[9] Then, there is no other structural information available for the complex phase transitions of SiH_4. The lack of the space group information becomes a main constraint on elastic constants analysis. However, we can still provide probable stability estimations based on the velocity variations. The Brillouin scattering spectra can be used as a novel method to investigate the phase transitions and stability under extreme conditions. The high pressure Brillouin scattering spectra of SiH_4 are collected along three isotherm experiments at 300, 359, and 407 K. The measured data points from this work are shown in Fig. 7 together with previous literature data.[9] The phase diagram of SiH_4 is extended up to 407 K.

In summary, by the high-pressure high-temperature Brillouin scattering measurements, the Brillouin frequency shifts, velocities, refractive index n and their respective pressure dependencies are all calculated and presented here. The velocities and refractive indexes of fluid SiH_4 along 300 K, 359 K and 407 K isothermal experiments are obtained and compared under pressure, both of which increase monotonously and smoothly with increasing pressure but decrease slightly with the increasing temperature at a similar pressure. High temperature weakens the stability of SiH_4 molecules, leading to partial decomposition, into silicon and H_2. The pressure partly enhances the interactions in solid SiH_4. The velocity variations prove the transitions from fluid to solid and finally to phase V, consistent with early Raman reports. The transition from phase Ⅲ to phase Ⅳ may be an isostructural process so that no obvious velocity jumps or curvature change occurs.

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