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# First-principles calculation on phase stability and metallization in GeH<sub>4</sub> under pressure

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## Abstract

Using a first-principles calculation, we investigated some possible structures of GeH<sub>4</sub> similar to those of SiH<sub>4</sub> investigated by Feng et al. [J. Feng, W. Grochala, T. Jaron, R. Hoffmann, A. Bergara, N.W. Ashcroft, Phys. Rev. Lett. 96 (2006) 017006] and determined their metallization pressures. It is found that GeH<sub>4</sub> has different case with SiH<sub>4</sub> and has lower metallization pressure. Structure T<sub>2</sub> in germane emerges as an enthalpically competitive structure over the pressure range 55–62 GPa. The metallization pressure for GeH<sub>4</sub> with T<sub>3</sub> structure is about 50 GPa, which is much lower than that of 91 GPa assumed for the O<sub>3</sub> phase of SiH<sub>4</sub>, i.e. GeH<sub>4</sub> could be easier to be metallized than SiH<sub>4</sub>.  
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## 1. Introduction

In 1935, Wigner and Huntington proposed that solid hydrogen would become a quantum metal under sufficient compression [1]. Later, in 1968, Ashcroft suggested that metallic hydrogen would be a high-temperature superconductor [2] and its  $T_c$  could be calculated by the McMillan equation [3]. A high  $T_c$  of metallic hydrogen of the order of 10<sup>2</sup> K was further proposed by Papaconstantopoulos et al. [4], Min et al. [5] and Barbee et al. [6]. Since then, although the frontier of the maximum pressure available in a laboratory has been pushed increasingly forward, hydrogen is still hard to get metallized in laboratory [7, 8] even under 342 GPa. Therefore, a great deal of effort has been taken to seek an alternative route to hydrogen metallization. Recently, Ashcroft et al. suggested [9] that the group IV hydrides, methane (CH<sub>4</sub>), silane (SiH<sub>4</sub>), and germane (GeH<sub>4</sub>), might become metallic at pressures achievable in diamond anvil cells since the hydrogen in these materials is “chemically pre-compressed” by the presence of the group IV atoms in a crystal

lattice. Such materials may be feasible to be superconductors under external high pressure.

In a recent paper, Feng et al. show that silane (SiH<sub>4</sub>) is indeed much easier to get metallized than hydrogen [10]. In their paper, several possible structures under high pressure were calculated by the first-principles density-functional-theory (DFT) method. They predicted that a layered structure would be stable at pressures above 25 GPa and will become metallized at about 91 GPa, whereas CH<sub>4</sub> has so far not been metallized at pressures up to 301 GPa [11]. Since the atomic radius of Ge is larger than Si, we suppose that GeH<sub>4</sub> might be easier to become a metal than silane due to the fact that the lower row element of group IV usually takes the high pressure form of the upper row one. For example, Si crystallizes into the diamond structure at ambient condition, which is the high-pressure form of graphite. By replacing Si with Ge in the framework similar to Feng’s model, we studied the relative stability of these structures in GeH<sub>4</sub> by the density-functional-theory (DFT) method.

## 2. Details of method

The structure optimization, energy bands, and electronic density of states, as well as the enthalpies of the six

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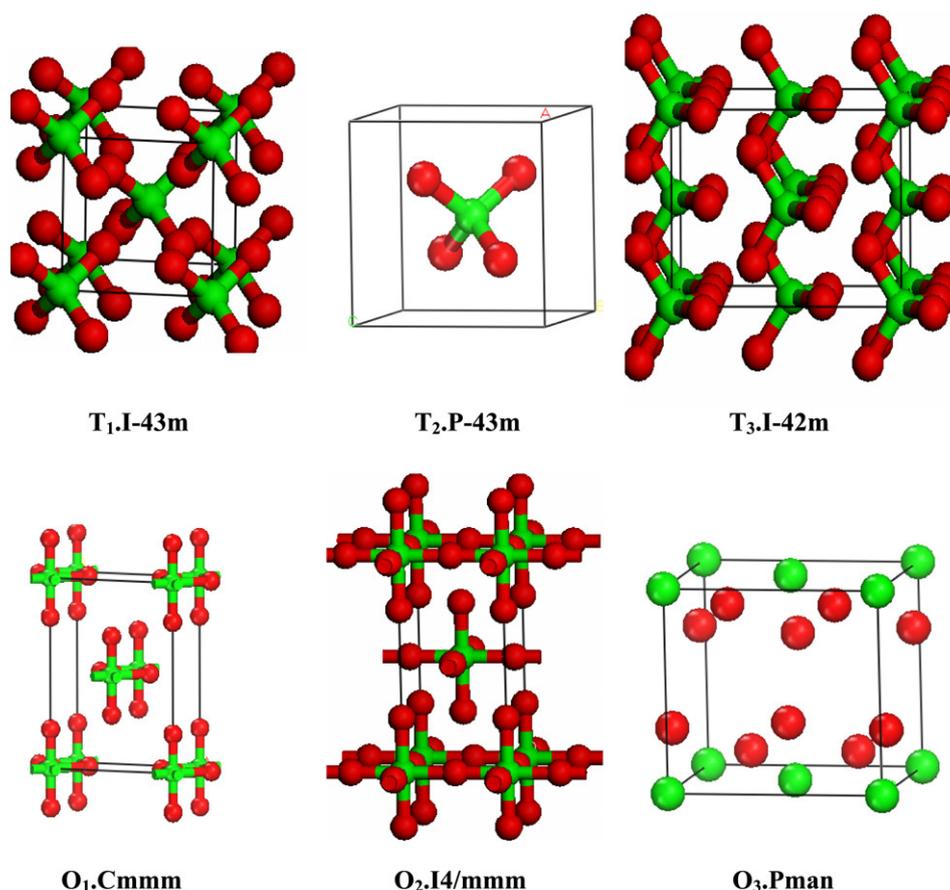


Fig. 1. The six candidate structures to be calculated (that are the most possible structures for  $\text{SiH}_4$  given by Feng et al. [10]). The green spheres are Ge atoms and red ones represent H atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

structures, were calculated using DFT with the Perdew–Wang generalized gradient approximation and ultrasoft Vanderbilt-type pseudopotentials for Ge and H. A  $16 \times 16 \times 16$  k-point grid for the Brillouin zone (BZ) sampling was generated via the Monk–Pack scheme in reciprocal space except for structure  $T_3$ . In structure  $T_3$ , a  $6 \times 9 \times 9$  k-point grid was used. Each structure was optimized with fixed pressure. We used a 450 eV cutoff for the kinetic energy of the plane waves and a self-consistent field tolerance of  $2 \times 10^{-6}$  eV/atom during the calculation.

### 3. Results and discussion

The six structures given by Feng et al. are presented in Fig. 1, with Si atoms substituted by Ge atoms. The number of nearest-neighbor H atoms increases from 4 to 8 from structure  $T_1$  to  $O_3$ . The structures  $T_1$ ,  $T_2$  and  $T_3$  all have tetrahedrally H-coordinated Ge atoms with bcc, sc, and fcc packings, respectively. Structure  $O_1$  is composed of one-dimensional chains of  $\text{GeH}_6$ , and structures  $O_2$ ,  $O_3$  consist of layers of  $\text{GeH}_6$ .

#### 3.1. The phase stability

A phase transition will happen at the point when two phases have equal Gibbs free energy. Since all our calculations are done at  $T = 0$  K, the Gibbs free energy becomes the enthalpy,

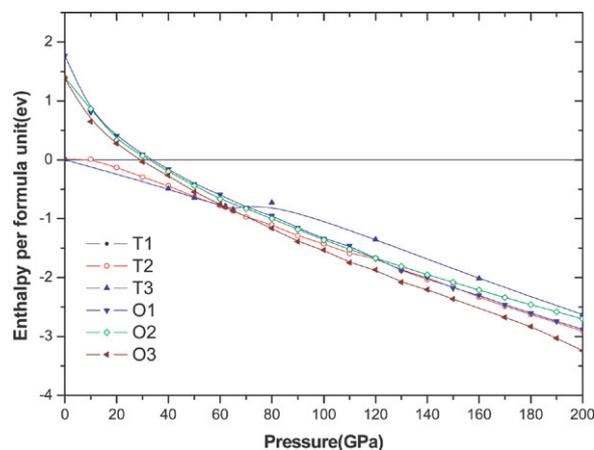
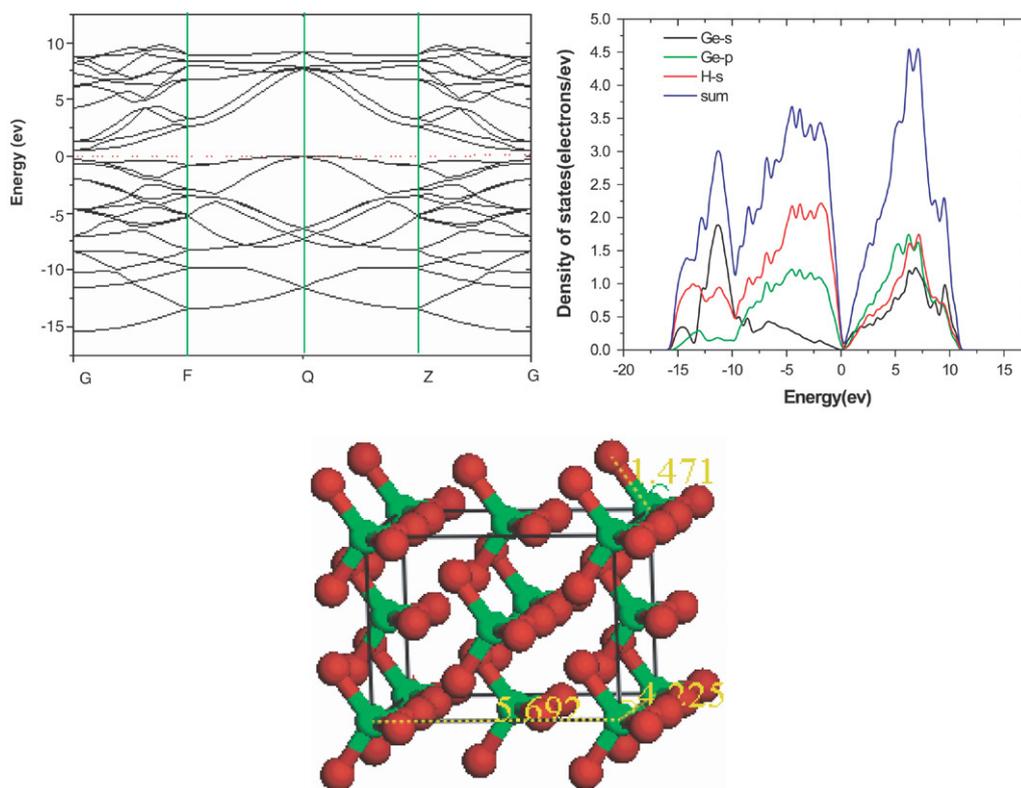
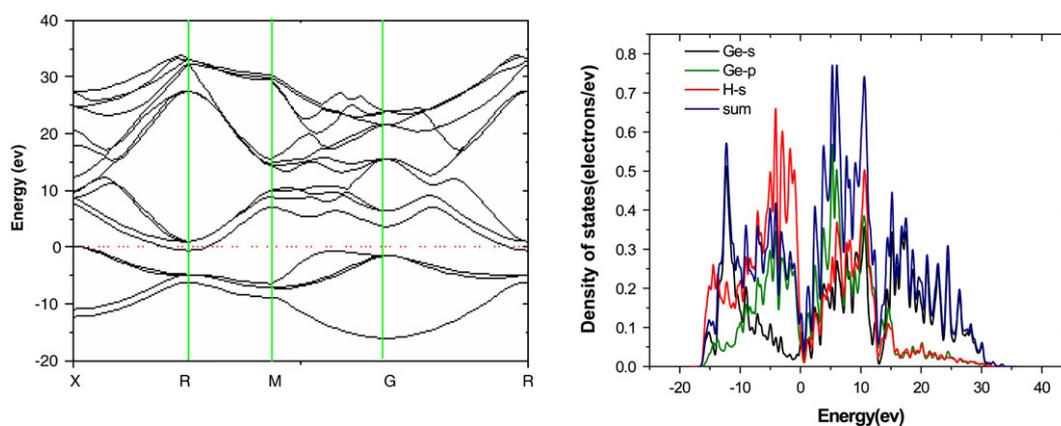


Fig. 2. Enthalpy per formula  $\text{GeH}_4$  unit under different pressure, referenced to the  $T_1$  phase.

$H = E_0 + PV$ , where  $E_0$  is the internal energy of the system. The enthalpies of the six structures under different pressures were obtained by our calculations, which are shown in Fig. 2. We can find the most stable structure under pressure by comparing the enthalpies of different structures under the same pressure. In silane ( $\text{SiH}_4$ ),  $O_3$  is the most stable structure over a large pressure range from about 25 to 160 GPa [9]. Among the six structures of germane ( $\text{GeH}_4$ ) similar to those of silane,  $T_2$ ,  $T_3$  and  $O_3$  are the most stable structures over the

Fig. 3. Energy band and density of states of structure  $T_3$  under 50 GPa.Fig. 4. Energy band and density of states of structure  $T_2$  under 55 GPa pressure.

pressure range 0–200 GPa. Structure  $T_3$  is more stable below about 55 GPa and  $O_3$  becomes the most stable phase above 62 GPa;  $T_2$  is the most stable structure over the pressure range 55–62 GPa and it could be a intermediate state between the  $T_3$  and  $O_3$  structures. It also could be concluded that the bonding H atoms to Ge tend to increase with phase transitions under increasing pressure. Every Ge atom has four-coordinated H atoms under low pressure and every Ge atom would have six-coordinated H atoms under pressure above 62 GPa.

### 3.2. Electronic structures

Since  $T_3$  is the most stable structure under pressure below 55 GPa, we will first describe its electronic structure. The crystal

lattice parameters of  $T_3$  are  $a = 5.69 \text{ \AA}$ ,  $b = c = 4.23 \text{ \AA}$  and the Ge–H bond length is  $1.47 \text{ \AA}$  under 50 GPa pressure. The energy band and electronic density of states of  $T_3$  under pressure 50 GPa are shown in Fig. 3. Structure  $T_2$  is the most stable one over the pressure range 55–62 GPa, and germane with this structure is a metal, as seen in Fig. 4. Both Ge and H atoms contribute to the metallic character of germane.

Over a pressure range from 62 GPa to 200 GPa,  $O_3$  becomes the most stable structure. Its crystal lattice parameters are  $a = 4.57 \text{ \AA}$ ,  $b = 3.17 \text{ \AA}$ ,  $c = 3.12 \text{ \AA}$  and it has two types of Ge–H bond with lengths  $1.51 \text{ \AA}$  and  $1.62 \text{ \AA}$  under 62 GPa pressure, as shown in Fig. 5(a). The energy band and electronic density of states under pressures of 62 GPa and 200 GPa for the  $O_3$  phase are shown in Fig. 5(b) and (c), respectively. Germane

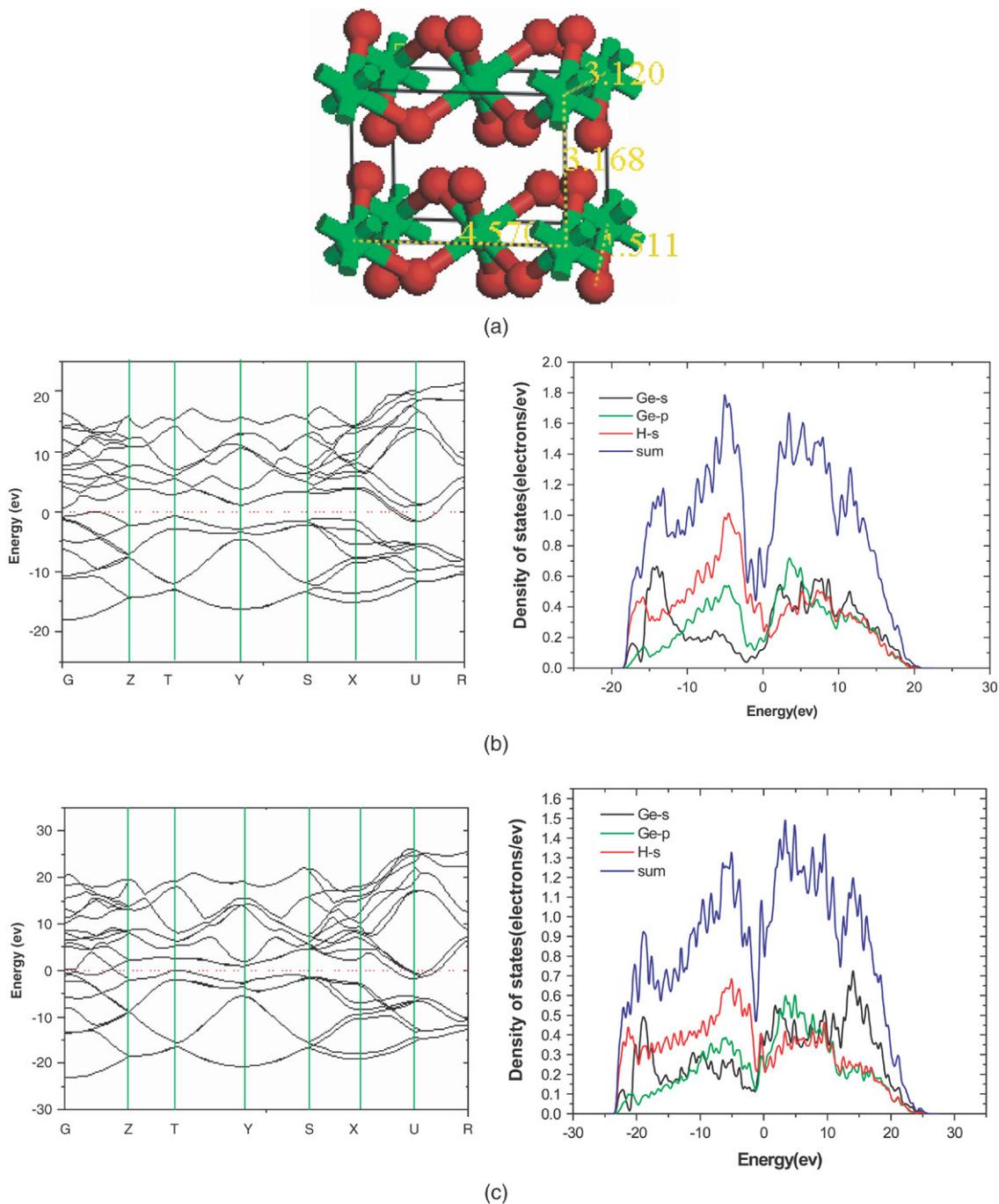


Fig. 5. (a) Crystal lattice parameters of O<sub>3</sub> structure under 62 GPa pressure. Energy band and density of states of (b) O<sub>3</sub> under 62 GPa pressure and (c) O<sub>3</sub> under 200 GPa.

with structure O<sub>3</sub> under pressure 62 GPa is a metal since the energy bands cross over the Fermi energy around the U point. The energy bands broaden slightly, but the electronic density of states at the Fermi energy does not show much difference with increasing pressure.

### 3.3. Metallization pressure

We found in our calculation that germane with structure T<sub>3</sub> could be metallized under about 50 GPa (as shown in Fig. 3), which is much lower than the metallization pressure (91 GPa)

of silane with the O<sub>3</sub> structure [10], but germane with the O<sub>3</sub> structure can only exist under a pressure above 62 GPa. As the energy gaps tend to be underestimated because of the well-known shortcomings of GGA method, the metallization pressure of GeH<sub>4</sub> with T<sub>3</sub> structure is likely to be higher than 50 GPa. If the actual metallization pressure of T<sub>3</sub> structure is higher than 55 GPa, the insulator to metal phase transition would occur under a pressure of 55 GPa driven by a structural phase transition from T<sub>3</sub> to T<sub>2</sub>. But we can confirm that germane indeed needs a lower pressure to be metallized than silane by our calculation. A comparison of the relative stability

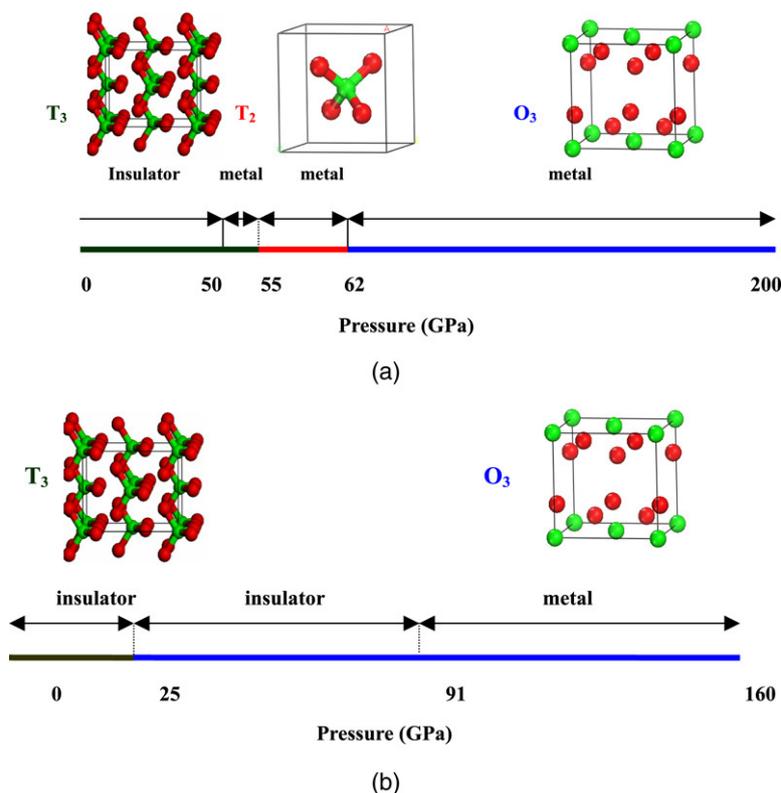


Fig. 6. (a) Phase diagram of germane and (b) phase diagram of silane at  $T = 0$  K.

of the structures of germane and silane is shown in Fig. 6. The phase diagram of germane is shown in Fig. 6(a) and the phase diagram of silane is shown in Fig. 6(b). T<sub>3</sub> structure is the most stable structure of germane under low pressure, and the T<sub>3</sub> to T<sub>2</sub> phase transition occurs under 55 GPa pressure; then the T<sub>2</sub> to O<sub>3</sub> phase transition occurs under a pressure about 62 GPa. The metallization pressure of germane is about 50 GPa. Compared with our calculation, the most stable structure of silane under low pressure is T<sub>3</sub>, and O<sub>3</sub> is the most stable structure over a wide pressure range 25–160 GPa. The metallization pressure of silane with the O<sub>3</sub> structure is about 91 GPa, which is much higher than the metallization pressure of germane.

#### 4. Summary

Using the DFT method, we calculated the electronic properties and metallization pressures of some possible crystal structures of GeH<sub>4</sub> under high pressures. The candidate structures are similar to those proposed for SiH<sub>4</sub> in Ref. [10]. We find that T<sub>3</sub> is the most stable structure at low pressure and that the T<sub>3</sub> to T<sub>2</sub> phase transition in germane may take place at about 55 GPa; then a T<sub>2</sub> to O<sub>3</sub> phase transition occurs under a pressure of about 62 GPa. The bonding H atoms to Ge tend to increase with increasing pressure. Germane with structures of T<sub>2</sub> and O<sub>3</sub> is metallic under pressure. The metallization onset pressure of GeH<sub>4</sub> with structure T<sub>3</sub> is about 50 GPa. It

is concluded from our calculations that germane is easier to be metallized than silane, and GeH<sub>4</sub> might offer an attractive possibility for a hydrogen-rich high- $T_c$  superconductor.

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