Superconducting germanium hydride with A15 structure

N N Degtyarenko, K S Grishakov
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, 115409 Moscow, Russia

E-mail: NNDegtyarenko@mephi.ru

Abstract. The possibility of the formation of A15 germanium hydride is investigated theoretically by the density functional method. It is shown that A15 germanium hydride Ge$_2$H$_6$ is stable in a certain pressure range of about 125 GPa. The results of calculations of the structural, phonon and electronic properties, energy characteristics of the normal phase are presented. The critical temperature of the superconducting transition is estimated.

1. Introduction
At present, superconductivity in metallic hydrogen and various hydrides is being actively studied [1-8]. An urgent task is to search for new high-temperature superconducting materials (HTS) with a high hydrogen content, in which the transition to the superconducting state occurs under conditions close to ambient (normal pressure and room temperature). The solution of this problem is possible only by joint development of theoretical concepts, computer modeling and obtaining new experimental data. An obvious general trend is that all high-temperature hydrides (as well as conventional superconducting compounds with a structure such as A15 and HTS) have a high lattice symmetry. In this aspect, it would be interesting to compare the properties of high-pressure hydrides and conventional superconducting compounds with the same type of structure and symmetry, but different elemental compositions. A search was made for hydrides with the A15 structure. It was found that the Ge$_2$H$_6$ hydrides have a stable A15 structure in a certain pressure range about 125 GPa.

2. Calculation method
The search and calculation of the properties of hydrides was carried out within the framework of the density functional theory (DFT) in the plane wave basis, implemented in Quantum ESPRESSO 6.4.1 program [9,10], using exchange-correlation functional PBEsol with norm-conserving pseudopotentials and cut-off energy 90 Ry. In the inverse space, we used a grid with a distance between the points less than 0.025 Å$^{-1}$ for each coordinates.

3. Calculation results
3.1 Ge$_2$H$_6$ structure
Figure 1 shows the structure of Ge$_2$H$_6$ (at a pressure of 125 GPa). The hydrogen atoms are located on the faces of the unit cell, forming three mutually perpendicular equidistant chains with an interatomic distance of $d\approx1.6$ Å. There is also isosurface of the electron density distribution on the face of the unit
cell. From the picture of the electron density distribution (transparent areas of Fig. 1b), it follows that its value is approximately the same both inside and between the chains of H atoms.

\[ n_e \approx 0.4 \text{ [electron/Å}^3] \]

The gray surface is internal for a higher value of \( n_e \).

3.2 Pressure dependence of the Ge\(_2\)H\(_6\) enthalpy

In order to compare hydrides with different stoichiometry, relative enthalpy \( \Delta H(m,n) \) was determined as follows:

\[
\Delta H(m,n) = H(Ge_mH_n) - (m \cdot H(\text{Ge}) + n \cdot H(\text{H}_2)) / 2
\]

where \( H(Ge_mH_n) \) are calculated values of hydrides enthalpy; \( H(\text{Ge}), H(\text{H}_2) \) are calculated enthalpy values per atom for pure germanium and molecular hydrogen at the corresponding pressures; \( m \) and \( n \) are the numbers of Ge and H atoms in the unit cell of corresponding germanium hydride.

Optimization of the unit cell geometry and atom positions were carried out at different pressure values \( P \) for the following structures: pure Ge, molecular \( \text{H}_2 \), molecular dihermann \( \text{Ge}_2\text{H}_6 \), crystalline A15 \( \text{Ge}_2\text{H}_6 \), crystalline Ama2-Ge\(_2\)H\(_8\), as well as for the intermetallic A15 \( \text{Ge}_2\text{Nb}_6 \).

The relative enthalpies for germanium hydride structures (see Fig. 2a) are negative at pressures greater than 50 GPa, i.e., they are energetically stable with respect to decomposition into metallic Ge and molecular \( \text{H}_2 \). As seen from Fig.2a, for intermetallic compound \( \text{Ge}_2\text{Nb}_6 \), \( \Delta H < 0 \) at all pressures, including \( P = 0 \), which naturally corresponds to the stability of this compound under normal conditions. The plots of \( \Delta H(P) \) for the hydrides shown in Fig. 2a differ slightly. It can be noted, as the crystal structures of hydrides (\( \text{Ge}_2\text{H}_6, \text{Ge}_2\text{H}_8 \)) have larger negative values of relative enthalpy in comparison with the molecular digerman \( \text{Ge}_2\text{H}_6 \), so these structures are more preferable at high pressures.

For all pressures the plot of \( \Delta H(\text{Ge}_2\text{H}_6) \) is located slightly higher than that for \( \Delta H(\text{Ge}_2\text{H}_8) \) (the difference is less than 0.1 eV), i.e. the structure of \( \text{Ge}_2\text{H}_8 \) is less energetically favorable in comparison with \( \text{Ge}_2\text{H}_6 \). For clarity, Fig. 2b shows a graph of the difference between the relative enthalpies \( \Delta H(\text{Ge}_2\text{H}_6) \) and \( \Delta H(\text{Ge}_2\text{H}_8) \), \( \Delta H(\text{Ge}_2\text{H}_6) \) and the molecular digerman \( \Delta H(\text{Ge}_2\text{H}_6) \). The difference \( [\Delta H(\text{Ge}_2\text{H}_6,\text{mol}) - \Delta H(\text{Ge}_2\text{H}_6,A15)] \) is positive (Fig.2b, curve – 1) in the pressure range 80÷300 GPa, i.e., the structure of \( \text{Ge}_2\text{H}_6(A15) \) is stable with respect to the molecular phase of germanium dihydride. The difference \( [\Delta H(\text{Ge}_2\text{H}_6) - \Delta H(\text{Ge}_2\text{H}_6,A15)] \) is negative (Fig.2b, curve – 2), i.e., the structure of \( \text{Ge}_2\text{H}_6(A15) \) is metastable with respect to \( \text{Ge}_2\text{H}_6(Ama2) \) if only the electronic part of the enthalpy is taken into account.
3.3 Changes in the phonon spectra of Ge$_2$H$_6$ with pressure and the contribution of phonon oscillations to the Ge$_2$H$_6$ energy

Figure 3a shows phonon densities of state for Ge$_2$H$_6$ at two pressure values of 50 and 200 GPa. It can be seen that at a lower pressure, the maximum frequency of phonon oscillations is approximately 160 meV, and the frequency distribution is continuous. At a pressure of 200 GPa, two frequency intervals are detected: low frequency range (<50 meV) and high frequency range (75-225 meV). The low-frequency region corresponds to the vibrations of Ge atoms and the long-wave vibrations of hydrogen chains. The high-frequency region is mainly due to the vibrations of H atoms inside the chains. It is important that phonon spectra do not contain imaginary frequencies, i.e. this structure is dynamically stable in a given pressure range.

To correctly calculate the energetic stability of the Ge$_2$H$_6$ hydride, it is necessary to estimate the contribution of zero oscillations of hydrogen component, as well as the contribution of phonons to the Gibbs thermodynamic potential, i.e., to add the ZPE and TS values to the relative enthalpy $\Delta H$. ZPE is zero vibration energy per number of atoms in unit cell, TS is the product of temperature and phonon entropy. Figure 3b shows plots of $(ZPE+TS)$ as a function of temperature for different pressure values $P$. Similar calculations were performed for Am$_2$m-Ge$_2$H$_8$, for which the values of $(ZPE+TS)$ are higher, since the number of H atoms is larger. Thus, the value of Gibbs thermodynamic potential $G=E+PV+(ZPE+TS)$ is lower for Ge$_2$H$_6$ than for Ge$_2$H$_8$, i.e., A15 Ge$_2$H$_6$ becomes energetically more favorable when phonons are taken into account.

Figure 3. a) The partial density of phonon states for Ge$_2$H$_6$ (A15) at pressures $P=50$ and 200 GPa. b) The dependence $(ZPE+TS)$ on the temperature for different pressure values $P$, ZPE – the zero oscillations energy, TS – the product of temperature $T$ by the phonon entropy $S$. 
3.4 Electronic properties of A15 Ge₂H₆
In the weak coupling approximation of Bardeen – Cooper – Schrieffer theory of superconductivity (BCS) [11] the electron-phonon interaction constant \( \lambda \) significantly depends on the electron density of the states at the Fermi level \( N(E_F) \). In the BCS model, this relationship is very simple: \( \lambda = N(E_F)V \), where \( V \) is electron-phonon coupling potential. For transition metal compounds \( \lambda \geq 1 \) (i.e. for superconductors with a strong bond) a consistent description of the superconductivity phenomenon requires solving the Eliashberg equations [11, 12]. Therefore it is important to calculate the density of electronic states near the Fermi level \( E_F \).

Fig. 4a shows the partial density of electronic states \( g(\varepsilon) = \text{PDOS}(\varepsilon) \) for A15 Ge₂H₆.

For Ge₂H₆, the Fermi level falls on the narrow peaks of s- and p- electron density of states. The latter is due to the high symmetry of this compound and the presence of linear chains of hydrogen atoms (Van Hove singularities). Similar calculations of \( g(\varepsilon) = \text{PDOS}(\varepsilon) \) for Ge₂Nb₆ intermetallic compound at \( P=0 \) GPa show that the narrow peak, consisting mainly of the d- states, takes a place at the Fermi level, and its amplitude is about 2 times greater than that for Ge₂H₆ at \( P=175 \) GPa (Fig. 4b).

![Figure 4. Electronic density of states \( g(\varepsilon) = \text{PDOS}(\varepsilon) \) for (a) A15 Ge₂H₆, (b) A15 Ge₂Nb₆.](image)

3.5 Critical temperature of the superconducting transition
The spectral function \( \alpha^2 F(\omega) \) preserves the presented features of the partial densities of phonon states PDOS (Fig. 3). The main peaks in Fig.3 correspond to vibrations of hydrogen atoms. Calculations of the electron-phonon interaction constants \( \lambda \) and the critical temperature of superconducting transition \( T_c \) in Ge₂H₆ gave the following results, caused by the above features of the phonon and electron spectra:

\[
\begin{align*}
\text{Ge}_2\text{H}_6 & \ P=150 \ \text{GPa} \quad \lambda \approx 4.9, \mu^* \approx 0.1, \ T_c \approx 46 \ \text{K}; \\
\text{Ge}_2\text{H}_6 & \ P=200 \ \text{GPa} \quad \lambda \approx 4.0, \mu^* \approx 0.1, \ T_c \approx 50 \ \text{K}.
\end{align*}
\]

For comparison, the critical temperature for intermetals with the A15 structure is \( T_c \approx 18 \) K, and the electron-phonon interaction constant is \( \lambda \approx 1 \div 1.5 \) [13]. Note that the ratio of the characteristic oscillation frequencies of the H and Nb atoms is proportional to \( \omega(\text{H})/\omega(\text{Nb}) \approx [m(\text{Nb})/m(\text{H})]^{1/2} \approx 10 \), i.e., the replacement of heavy Nb atoms with light H atoms increases the oscillation frequency by an order of magnitude, but \( T_c \) increases only 2-3 times.

4. Conclusions
Based on calculations of the electronic part of the enthalpy and the energy of zero phonon oscillations (ZPE), comparison of molecular digermain and Ge₂H₆ (structure with Am2m symmetry) with germanium hydride GeH₆ with the structure A15 has revealed the energy preference of the latter phase in the pressure range of 75 ÷ 200 GPa. The dynamic stability of germanium hydride Ge₂H₆ with the A15 structure in a certain pressure range about 125 GPa was established. The calculated value of the critical
temperature $T_c$ of the superconducting transition in this phase is 2-3 times higher than that for the transition metal intermetallicides A15. This comparative increase in $T_c$ is due to the high value of the electron-phonon coupling constant $\lambda$, which is associated with the vibrational, bending, and stretching modes of the chains of light hydrogen atoms. However, the amplitude of the peak density of the $s$- and $p$-electron states near the Fermi level is somewhat smaller than that for the $s$, $p$, and $d$-states, for example in the Ge$_2$Nb$_6$ intermetallic compound with the same structure. This is probably prevents an increase in the $T_c$ value.

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