Superconductivity and unexpected chemistry of germanium hydrides under pressure

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Following the idea that hydrogen-rich compounds might be high-\(T_c\) superconductors at high pressures, and the very recent breakthrough in predicting and synthesizing hydrogen sulfide with record-high \(T_c = 203\) K, ab initio evolutionary algorithm for crystal structure prediction was employed to find stable germanium hydrides. In addition to the earlier structure of germane with space group \(Ama2\), we propose a new \(C2/m\) structure, which is energetically more favorable at pressures above 278 GPa (with inclusion of zero point energy). Our calculations indicate metallicity of the new \(C2/m\) phase of germane with \(T_c = 67\) K at 280 GPa. Germane is found to exhibit thermodynamic instability to decomposition to hydrogen and the new compound \(Ge_3H_{11}\) at pressures above 300 GPa. \(Ge_3H_{11}\) with space group \(I4m2\) is found to become stable at above 285 GPa with \(T_c = 43\) K. We find that the pressure-induced phase stability of germanium hydrides is distinct from its analogous isoelectronic systems, e.g., Si-hydrides and Sn-hydrides. Superconductivity stems from large electron-phonon coupling associated with the wagging, bending and stretching intermediate-frequency modes derived mainly from hydrogen.

High-throughput materials discovery using first-principles density functional theory (DFT) [1] has motivated many experimental studies. For years, scientists have been trying to find the best way to design high-temperature superconductors. It has been confirmed that high-\(T_c\) superconductivity can be found in systems with light elements. Hydrogen is the lightest element with rich structures and properties under high pressures. Within BCS (Bardeen-Cooper-Schrieffer) theory of superconductivity [2], high vibrational frequencies of hydrogen atoms and often high electron-phonon coupling make it possible to expect high-\(T_c\) in metallic hydrogen and hydrogen-rich hydrides.

However, metallic hydrogen seems to require very high pressure \(\sim 400\) GPa and proved elusive. Therefore, chemical precompensation by alloying with heavy element was proposed [3]. Many theoretical and experimental studies have been motivated by this idea to seek and design new high-\(T_c\) superconductors at high pressures [4–14].

In a recent breakthrough discovery, which was first predicted by the evolutionary algorithm USPEX coupled with DFT studies [15], high-temperature superconductivity with a transition temperature \((T_{c,0})\) of 203 K in hydrogen sulfide \(H_2S\) under pressure 200 GPa has been reported by Drozdov et al. [14]. This discovery not only set a record high-\(T_c\) for a conventional phonon-mediated mechanism, but also raised hopes of reaching room-temperature superconductivity in hydrogen-rich metallic alloys. This realization is the best argument to show the predictive power of DFT-based structure prediction and electron-phonon coupling calculations, and opens up avenues for discovering superconductors based on this approach.

Successful synthesis of hydrogen sulfides with superconducting properties was followed by a second high-\(T_c\) hydrogen-rich compound at high pressure \((PH_3)\) synthesized by Drozdov et al.[13]. Prior to \(H_2S\), the highest experimentally observed \(T_c\) in conventional superconductors, which obey the BCS theory was in \(MgB_2\), which opened avenues for searching for higher \(T_c\) superconductors. However, other magnesium borides \(MgB_x\) were shown to exhibit poor superconductivity with \(T_c < 3\) K. Besides these efforts, other superconductors have been predicted in hydrogen-rich compounds. In group-IV hydrides, \(SiH_4\) has been predicted to have \(T_c = 20-75\) K [16], while experiment got a lower value of 17 K [12]. Disilane \((SiH_6)\) has been predicted to favor \(Ccma\) structure with \(T_c\) of 98-107 K at 250 GPa [17]. Our work on tin hydrides showed rich chemistry of that system with high-\(T_c\) superconductivity. Tin hydrides have been predicted to form at high pressures, exhibiting high \(T_c\) of 81, 93, 97 K for \(SnH_8\), \(SnH_{12}\) and \(SnH_{14}\) at 220, 250 and 300 GPa, respectively [18]. In addition, novel linear and bent formation of \(H_3\) and \(H_4\) have been predicted to form in high-pressure phases of \(SnH_8\), \(SnH_{12}\) and \(SnH_{14}\) [18].

Germanium (Ge) is in the same group-IV and is isovalent to Sn. One can expect germanium to exhibit similar chemistry as tin, but its smaller atomic radius and slightly higher electronegativity than Sn result in quite a different chemistry.

Germanene \((GeH_4)\) phases have been explored by Gao et al. [4] and their results show \(C2/c-GeH_4\) becomes stable at pressures above 196 GPa (including zero point energy (ZPE)) against decomposition into H and Ge. However, stability against decomposition into the elements is not a particularly stringent test, and stability against separation into other phases, e.g., \(GeH_4\) into \(Ge_2H_2\) and \(H_2\), which is important for understanding decomposition mechanism, should be taken into account. \(C2/c\) was predicted to be a superconductor with \(T_c = 64\) K at 220 GPa. In a recent theoretical study, a more energetically stable structure of germanene (with symmetry group \(Ama2\)) was predicted by Zhang et al. to have \(T_c\) of 47-57 K [19]. Now, with major progress of computational methods (enabling, for example, variable-composition searches), we can address all the outstanding issues.
We systematically explored the high-pressure phase diagram of Ge-H system with using evolutionary variable-composition search implemented in the USPEX code [20–23] from ambient pressure to 400 GPa. The effectiveness of this method has been shown by the prediction of high-pressure structures of various systems that were subsequently confirmed experimentally (e.g., [24–26]). In this method, we created initial generation of structures and compositions using the random symmetric algorithm [27]. Subsequent generations were obtained using heredity, transmutation, softmutation, and random symmetric generator [27]. Ge hydrides, in comparison with other hydrides of the same group, e.g., Si [16, 17], Sn [18] which often show simpler phase diagram, exhibit a unique and complex potential energy landscape. Unexpected stoichiometries Ge₄H, Ge₂H, GeH₃, GeH₄ and Ge₃H₁₁ emerge as stable at megabar pressures.

The underlying structure relaxations were carried out using VASP package [28] in the framework of density functional theory (DFT) and using PBE-GGA (Perdew-Burke-Ernzerhof generalized gradient approximation) [29]. The projector-augmented wave approach (PAW) [30] was used to describe the core electrons and their effects on valence orbitals. A plane wave kinetic energy cutoff of 1000 eV for hard PAW potentials and dense Monkhorst-Pack k-points grids with reciprocal space resolution 2π × 0.03 Å⁻¹ were employed [31] to sample the Brillouin zone.

 Phonon frequencies and superconducting properties were calculated using density functional perturbation theory as implemented in QUANTUM ESPRESSO package [32]. PBE-GGA functional is used for this part. A plane-wave basis set with a cutoff of 80 Ry gave a convergence in energy with a precision of 1 meV/atom. We used valence electron configurations of 3d¹⁰ 4s² 4p² and 1s¹ for germanium and hydrogen, respectively. Thermodynamic properties of germanium hydrides were calculated using the PHONOPY package with the implemented frozen-phonon approach [33].

The electron-phonon coupling (EPC) parameter λ was calculated using 5×5×2 and 4×4×4 q-point meshes for I₄m2-Ge₄H₁₁ and C2/m-GeH₄, respectively. Denser k-point meshes, 20×20×8 and 16×16×16 were used in the calculations of the electron-phonon interaction matrix elements. The superconducting T_c, was estimated using the Allen-Dynes modified McMillan equation [34].

The energetic stability of a variety of Ge₂H_y (x + y < 20) compounds was evaluated using the thermodynamic convex hull construction at different pressures (see Supplemental Material Fig. S1). To our surprise, in addition to reproducing various structures of Ge-H system [4, 9, 19, 35], Ge [36] and H₂ [37], previously unreported and unexpected composition of germanium hydrides Ge₃H₁₁ was found to be stable in wide pressure ranges.

Below 200 GPa, no hydrogen-rich composition is stable against decomposition into the elements. It is consistent with not having any solid H-rich Ge-hydrides at low pressures, although using in situ gas-condensation techniques, Maley et al. showed germane can form at ambient pressure [38]. Increasing pressure decreases formation enthalpies, implying a tendency for Ge-hydrides to be stabilized under further compression. Phases of elemental H and Ge for the convex hull construction were obtained from structure search, in good agreement with the ones reported in Ref [37] for hydrogen and for elemental Ge, we obtained a complex phase diagram with at least four phase transitions between 70 and 400 GPa, which are in good agreement with Ref [36].

At 250 GPa, the tetragonal Ge₃H₁₁ with space group I₄m2 is still metastable and lies just above the tie-line joining Amma-Ge₄H and Pnma-Ge₂H. At 300 GPa, we predict stable phases: Ge₂H (P6₃/m), Ge₃H (Pnma) and GeH₃ (Ccmm) in accord with previous predictions [9, 19]. In addition, we also found unexpected composition Ge₃H₁₁ that appears in the H-rich region, its structure featuring GeH₁₂ distorted icosahedra and GeH₁₆ Frank-Casper polyhedra. Moreover, germane transforms to a new monoclinic phase with space group C2/m with 3 f.u./cell at above 300 GPa (278 GPa with inclusion of ZPE), which is lower in enthalpy than all previously proposed structures [4, 9, 19] (see also Fig. 1(b)).

The stability fields of solids Ge₃H, Ge₂H, GeH₃, Ge₃H₁₁ and GeH₄ are illustrated in pressure-composition phase diagram of the Ge-H system, as shown in Fig. 1(a). Ge-rich compounds tend to stabilize at lower pressure (<200 GPa), while higher pressure (>200 GPa) is required for H-rich compounds to form. To the best of our knowledge, these unexpected, yet complex stoichiometries have not been reported in group-IV hydrides except MH₄ (M = Si, Sn, Pb). This rich chemistry makes Ge hydrides of special interests. It can be seen that the formation of Ge₃H₁₁ at 285 GPa lowers the convex hull and finally around 300 GPa causes GeH₄ to become thermodynamically metastable. The dynamical stability of structures shown in Fig. 1(a) were confirmed in their pressure ranges of stability via phonon calculations.

GeH₄ was predicted to become stable against decomposition into the elements at above 225 GPa (196 GPa with the inclusion of zero-point energy) [39], while our results reveal lower enthalpy of Ge₂H₄+H₂ indicating the need for somewhat higher pressure 244 GPa (216 GPa with ZPE inclusion) for GeH₄ to be stabilized (see Fig. 1(b)-inset). Upon increasing pressure, the Amma2 structure of GeH₄ transforms into the C2/m structure at 300 GPa. Structures predicted in the literature are also included for comparison. In the Amma2 → C2/m transition, the coordination number of Ge atoms increases from 10 to 12 and 16 with the formation of GeH₁₂ distorted icosahedra and GeH₁₆ Frank-Casper polyhedra at 300 GPa (Fig. 2(a)-inset). In addition, the average Ge-H bond lengths slightly increase from 1.698 Å to 1.704 Å in the Amma2 → C2/m transition.

GeH₄ is unstable against decomposition to H₂ (Cmca) and Ge₃H₁₁ (I₄m2) at pressures above 300 GPa, according to the convex hull (see Supplemental Material Fig. S1(b) and (c)). Similarly, GeH₃ decomposes to Ge₂H and Ge₃H₁₁.

Both in I₄m2-Ge₃H₁₁ and C2/m-GeH₄, each Ge atom is coordinated with 12 and 16 H atoms making distorted icosahedra and GeH₁₆ Frank-Casper polyhedra (see Fig. 2). The average
Ge-H bond lengths are 1.660 and 1.704 Å in $I\bar{m}2$-$Ge_3H_{11}$ and $C2/m$-$GeH_4$ at 300 GPa, respectively. Unlike other compressed hydrides [5, 18, 40, 41], there are no bonds between H atoms.

As shown in the Fig. 2., liberating one hydrogen atom from a 3 f.u. cell turns a GeH$_{16}$ polyhedra to a less coordinated germanium atom and leads to the formation of a distorted icosahedron, i.e., GeH$_4$ consists of two GeH$_{16}$ polyhedra and a GeH$_{12}$ icosahedron, however, Ge$_3H_{11}$ turns out to have one GeH$_{16}$ polyhedron and two distorted icosahedra. The detailed crystallographic data are listed in Table I.

Because of high concentration of hydrogen in GeH$_4$, contribution of zero-point energy (ZPE) would be important in determining the relative stability of hydrogen-rich phases [6, 18, 39, 42, 43]. However, our results show that ZPE does not change the topology of the phase diagram of GeH$_4$, and quantitative effects are just moderate shifts in transition pressures. For example, the inclusion of ZPE lowers the formation enthalpies of Ama$_2$ and $C2/m$ structures and shifts the transition pressure $Ama_2 \rightarrow C2/m$ from 300 to 278 GPa indicating enhanced stability of $C2/m$ phase owing to ZPE (see Fig. 1(b)-inset).

Analyzing the electronic band structures of GeH$_4$ ($C2/m$ and $Ge_3H_{11}$ ($I\bar{m}2$) (see Supplemental Material Fig. S2(a) and (b)) indicates indirect band overlap which results in metallic behavior, with highly dispersive bands crossing the Fermi level, these bands being basically due to germanium states with $p$-character and marginally due to hydrogen states with $s$-character. These H-derived states near Fermi level resemble those of solid metallic hydrogen. The $C2/m$ structure is a metal with parabolic dispersive bands crossing the Fermi level along the $\Gamma$-$Z$ symmetric line with several electron and hole pockets at the Fermi level. In the energy region near $E_F$, the DOS of Ge is about two times that of H, which indicates the dominance of Ge atoms contribution in the bands near the Fermi level. The total DOS at $E_F$, N($E_F$), is 0.27 states/eV/f.u. for the $C2/m$-GeH$_4$ structure at 300 GPa, while we see higher N($E_F$) = 0.31 for Ama$_2$ phase at 300 GPa. The Fermi levels of GeH$_4$ and $Ge_3H_{11}$ fall on a shoulder of the density of states, while the record $T_c$ in H$_2$S is explained to be due to van Hove singularity close to the Fermi level [44, 45], therefore, doping can be expected to raise N($E_F$) and $T_c$ values. These values of DOS at the Fermi level N($E_F$) are lower than those in H$_2$S (0.54 states/eV/f.u.).

To probe the possible superconducting behavior, electron-phonon coupling (EPC) calculations were performed for $C2/m$-GeH$_4$ and $I\bar{m}2$-$Ge_3H_{11}$ structures at 280, 300 and 320 GPa. Phonon dispersions, phonon density of states, the corresponding Eliashberg spectral function $\alpha^2 F(\omega)$ and the EPC parameter $\lambda$ as a function of frequency are calculated and shown in Fig. 3(a) and (b) for $C2/m$-GeH$_4$ and $I\bar{m}2$-$Ge_3H_{11}$ at 300 GPa, respectively.

The low frequency bands below 430 cm$^{-1}$ are mainly from the strongly coupled vibrations between Ge and H that contribute about 26% (25%) of the total $\lambda$, while higher-frequency phonons, predominantly wagging, bending and stretching modes between 550-2300 cm$^{-1}$ are mostly related to the H atoms bonded to Ge and contribute 74% (75%) of $\lambda$ of $C2/m$-GeH$_4$ ($I\bar{m}2$-$Ge_3H_{11}$) phase.

The resulting integral $\lambda$ and logarithmic average phonon frequencies ($\omega_{\text{log}}$) are calculated using the Eliashberg formalism and then $T_c$ values are estimated using Allen-Dynes modified McMillan equation with using Coulomb pseudopotential parameters $\mu^*$ = 0.1 and 0.13 as commonly accepted values. Table II summarizes data for the total EPC parameters $\lambda$, logarithmic phonon average frequencies and corresponding $T_c$ values at given pressures.

Hard phonons in H-rich materials are described to play an important role in high-$T_c$ superconductivity [46], but because such hard phonons do not always produce large coupling constant, high-$T_c$ superconductivity is still elusive. In the $C2/m$-GeH$_4$ structure, high-frequency vibrations that contribute the most to EPC parameter, produce a larger coupling constant i.e., 25% higher than similar frequency modes in $I\bar{m}2$-$Ge_3H_{11}$. Additional flat bands in the high frequency region of $C2/m$-GeH$_4$ phonon modes, can be ascribed to the higher coupling constant and eventually result in getting higher $T_c$ value for $C2/m$-GeH$_4$.

We investigated the pressure dependence of the critical transition temperature. The results show that the calculated $T_c$ decreases monotonically with pressure with approximate rates of -0.19 and -0.20 K/GPa for $C2/m$-GeH$_4$ and $I\bar{m}2$-$Ge_3H_{11}$ in the pressure range 280-320 GPa. Higher $T_c$ of the $C2/m$ phase, compared to the previously reported phase Ama$_2$-GeH$_4$, can be related to the considerably higher average phonon frequency, which also can be explained through a BCS mechanism.

In summary, we explored high-pressure phase diagram of the Ge-H binary system by exploring its compositional and configurational space with an evolutionary crystal structure prediction method. Based on analysis of current and prior theoretical studies on Ge-hydrides, we have established thermodynamically stable phases, superconducting properties, structural features and new decomposition lines in the pressure range 0-400 GPa.

At 250 GPa, all the stoichiometries Ge$_2$H, Ge$_3$H and GeH$_4$ are energetically stable against any decomposition into the elements or any other compounds. At 300 GPa, GeH$_3$ and Ge$_3$H$_{11}$ become stable, while GeH$_4$ becomes unstable.

A unique metallic phase of germane with $C2/m$ space group is found to be energetically more favorable than all previously proposed structures at pressures above 278 GPa (if zero-point energy is included). Our results reveal that germane decomposes to hydrogen and the newly found compound Ge$_3$H$_{11}$ at the pressures above 300 GPa. According to electron-phonon coupling calculations, $C2/m$-GeH$_4$ and $I\bar{m}2$-$Ge_3H_{11}$ are excellent superconductors with high-$T_c$ of 67 K and 43 K for $C2/m$-GeH$_4$ at 280 GPa and $I\bar{m}2$-$Ge_3H_{11}$ at 285 GPa, respectively.
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### TABLE I: Predicted crystal structures of Ge$_3$H$_{11}$ and GeH$_4$ at 300 GPa.

| Phase       | Lattice parameters | Atom   | x    | y    | z    |
|-------------|--------------------|--------|------|------|------|
| I$\bar{4}m$-Ge$_3$H$_{11}$ | a=2.891 Å, c=9.845 Å | Ge$_1$(4e) | 0.0000 | 0.0000 | 0.1750 |
|             |                    | Ge$_2$(2b) | 0.0000 | 0.0000 | 0.5000 |
|             |                    | H$_1$(8i)  | 0.2248 | 0.0000 | 0.3320 |
|             |                    | H$_2$(8i)  | 0.7377 | 0.0000 | 0.0351 |
|             |                    | H$_3$(4f)  | 0.0000 | 0.5000 | 0.1031 |
|             |                    | H$_4$(2c)  | 0.0000 | 0.5000 | 0.2500 |
| C2$/m$-GeH$_4$ | a=10.226 Å, b=2.967 Å, c=2.922 Å, $\beta$=74.46° | Ge$_1$(2b) | 0.0000 | 0.5000 | 0.0000 |
|             |                    | Ge$_2$(4i) | 0.8483 | 0.0000 | 0.6037 |
|             |                    | H$_1$(8j)  | 0.3501 | 0.2383 | 0.1187 |
|             |                    | H$_2$(4i)  | 0.2822 | 0.0000 | 0.9765 |
|             |                    | H$_3$(4i)  | 0.2806 | 0.0000 | 0.6187 |
|             |                    | H$_4$(4i)  | 0.4274 | 0.0000 | 0.5731 |
|             |                    | H$_5$(4i)  | 0.9953 | 0.0000 | 0.7488 |

### TABLE II: The calculated EPC parameter ($\lambda$), logarithmic average phonon frequency ($\omega_{\log}$) and critical temperature ($T_c$) (with $\mu^*$ = 0.10 and 0.13) for C2$/m$-GeH$_4$ and I$\bar{4}m$2-Ge$_3$H$_{11}$ at given pressures.

| Structure | Pressure (GPa) | $\lambda$ | $\omega_{\log}$ (K) | $T_c$ (K) |
|-----------|---------------|-----------|---------------------|----------|
| C2$/m$-GeH$_4$ | 280 | 0.895 | 1162 | 67 ($\mu^*$=0.10) |
|            | 300 | 0.867 | 1154 | 63 ($\mu^*$=0.10) |
|            | 285 | 0.721 | 1155 | 43 ($\mu^*$=0.10) |
|            | 300 | 0.690 | 1140 | 38 ($\mu^*$=0.10) |
|            | 320 | 0.668 | 1127 | 35 ($\mu^*$=0.10) |
| I$\bar{4}m$2-Ge$_3$H$_{11}$ | 300 | 0.690 | 1140 | 38 ($\mu^*$=0.10) |
|            | 320 | 0.668 | 1127 | 35 ($\mu^*$=0.10) |
FIG. 1: (a) Predicted pressure-composition phase diagram of the Ge-H system. The dashed areas represent thermodynamically metastable structures. (b) The enthalpies per formula unit of various structures of germane as a function of pressure with respect to the previously reported Ama2 structure [19]. Decomposition (GeH$_4$) enthalpies are calculated by adopting the C2/c structure for H$_2$ (Ref. [37]) and Ge$_2$H in the Pnma structure. The elemental decomposition enthalpies are also added for comparison. Inset: Enthalpies for C2/m structure relative to Ama2 structure with the zero-point corrections. The superscript "∗" and "∗∗" represent the structures predicted by Gao et al. [4] and Zhang et al. [19], respectively.

FIG. 2: Predicted structures of Ge-H compounds at high pressures: (a) GeH$_4$ in the C2/m structure, (b) Ge$_3$H$_{11}$ in the I4m2 structure. Small and large spheres represent H and Ge atoms, respectively. Different color of germanium atoms represent different type of polyhedra, i.e., black spheres represent GeH$_{16}$ polyhedra and purple spheres show GeH$_{12}$ icosahedra.
FIG. 3: Calculated phonon dispersion curves, phonon density of states (PHDOS), Eliashberg EPC spectral functions $\alpha^2 F(\omega)$ and electron-phonon integral $\lambda(\omega)$ of (a) GeH$_4$ [C2/m] at 300 GPa, (b) Ge$_3$H$_{11}$ [I4m2] at 300 GPa.
Superconductivity and unexpected chemistry of germanium hydrides under pressure

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FIG. S1: Predicted formation enthalpy of Ge$_{1-x}$H$_x$ as a function of H concentration at given pressures. Open circles above the convex hull show unstable compounds with respect to decomposition into the two adjacent phases on the convex hull, while solid circles show thermodynamically stable compounds. Pure Ge structures are consistent with Ref. [1], and pure H phases are taken from Ref. [2].

[1] F. J. Ribeiro and M. L. Cohen, Phys. Rev. B 62, 11388 (2000).
[2] C. J. Pickard and R. J. Needs, Nature Phys. 3, 473 (2007).
FIG. S2: Electronic band structure along with the projected electronic DOS of: (a) GeH$_4$ in the \textit{C2/m} structure at 300 GPa, (b) Ge$_3$H$_{11}$ in the \textit{I\bar{4}m2} structure at 300 GPa.