

## Superconducting High Pressure Phase of Germane

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High-pressure structures of germane ( $\text{GeH}_4$ ) are explored through *ab initio* evolutionary methodology to reveal a metallic monoclinic structure of  $C2/c$  (4 molecules/cell). The  $C2/c$  structure consists of layerlike motifs containing novel “ $\text{H}_2$ ” units. Enthalpy calculations suggest a remarkably wide decomposition ( $\text{Ge} + \text{H}_2$ ) pressure range of 0–196 GPa, above which  $C2/c$  structure is stable. Perturbative linear-response calculations for  $C2/c$   $\text{GeH}_4$  at 220 GPa predict a large electron-phonon coupling parameter  $\lambda$  of 1.12 and the resulting superconducting critical temperature reaches 64 K.

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For decades, scientists have been going to great effort to design high-temperature superconducting material. Hydrogen, the lightest element, was predicted to become metallic under very strong compression and will probably become an extraordinary high-temperature superconductor [1–3], because of its low mass density and high elastic stiffness. However, hydrogen remains insulating up to extremely high pressures, at least up to  $\sim 342$  GPa [4]. It was recently predicted that group IV hydrides would also present a high superconducting critical temperature, while becoming metallic at lower pressures due to chemical precompression [5]. Towards this goal, extensive theoretical and experimental efforts [6–14] have attempted to uncover crystal structures and metallization of these hydrides. Two independent experimental works [10,11] have confirmed the metallization of  $\text{SiH}_4$  at rather low pressures of 50 or 60 GPa. Remarkably, superconductivity in  $\text{SiH}_4$  has been verified by Eremets *et al.* [11] with a transition temperature ( $T_c$ ) of 17 K at 96 and 120 GPa, respectively. Therefore, these very recent experiments have confirmed in the case of  $\text{SiH}_4$  Ashcroft’s theoretical prediction [5] that group IV hydrides could become superconductors under pressure, illustrating the beauty and predictive power of theory. However, studies on heavier  $\text{GeH}_4$  and  $\text{SnH}_4$  are scarce. Some estimates based on the polarizability of these molecules lead to a lower metallization pressure than that of  $\text{SiH}_4$  and, since the radii of Ge and Sn are larger than those in Si, the expected weaker Ge/Sn-H bonding might facilitate the complete dissociation of the Ge/Sn-H bond at lower pressure [14]. Indeed, the theoretical study on  $\text{SnH}_4$  has predicted a polymeric  $P6/mmm$  structure with two-dimensional Sn layers bridged by a pair of H atoms possessing an extremely high  $T_c$  of 80 K originated from a

higher Sn mass and strong vibrations of  $\text{H}_2$  units [14]. In view of the extremely high  $T_c$  in  $\text{SnH}_4$ , it is promising to explore the superconducting behavior in naturally existing  $\text{GeH}_4$ . Earlier theoretical studies on  $\text{GeH}_4$  by Li *et al.* [12] and us [13] simply borrowed the crystal structures of  $\text{SiH}_4$  proposed by Feng *et al.* [6] as educated guesses based on structures known for other materials. There is a possibility that hitherto unexpected structures are stable instead. Here, we have taken a new route using our newly developed approach [15–17] to explore the crystal structures of  $\text{GeH}_4$  in a wide pressure range (0–250 GPa). Two monoclinic ( $P2_1/m$  and  $C2/c$ ) structures are predicted here and found to be energetically much superior to earlier structures [12,13]. We have revealed a wide decomposition pressure range of 0–196 GPa, above which  $C2/c$  structure is stable. Remarkably, a large  $T_c$  of 64 K at 220 GPa is predicted for the  $C2/c$  structure.

*Ab initio* evolutionary algorithm [15–17], designed to search for the structure possessing the lowest free energy at given  $P/T$  conditions, has been employed. The most significant feature of this methodology is the capability of predicting the stable structure with only the knowledge of the chemical composition. The details of the search algorithm and its first several applications have been described elsewhere [15–18]. The underlying *ab initio* structure relaxations were performed using density functional theory [19,20] within the Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) [21] as implemented in the Vienna *ab initio* simulation package VASP code [22]. The all-electron projector-augmented wave (PAW) method [23] was adopted with the PAW potentials taken from the VASP library [24] where  $1s^1$  and  $4s^2 4p^2$  are treated as valence electrons for H and

Ge atoms, respectively. A plane-wave basis set with an energy cutoff of 400 eV was used and gave well converged total energies. The plane-wave pseudopotential method within the PBE-GGA, through the Quantum-ESPRESSO package [25] was employed to study the electronic properties, lattice dynamics and electron-phonon coupling (EPC) for  $C2/c$   $\text{GeH}_4$ , where the converged structures from PAW calculation are fully reoptimized with a force convergence threshold,  $\sim 0.01$  eV/Å, to minimize the internal forces. The Troullier-Martins norm-conserving pseudopotentials for H and Ge are generated using the FHI98PP code [26] with  $1s^1$  and  $4s^2 4p^2$  as valence electrons, respectively. The pseudopotentials are then carefully tested by comparing the calculated electronic band structure for  $Cmca$ -Ge and the zero-point energy for  $C2/c$ -H2 with earlier results [27,28]. Convergence tests gave the choice of kinetic energy cutoffs of 60 Ry and  $8 \times 8 \times 8$  Monkhorst-Pack (MP) [29] grids of  $k$ -point sampling for the electronic Brillouin zone (BZ) integration. Phonon frequencies were calculated based on the density functional linear-response method [19,20]. A  $3 \times 3 \times 3$   $q$  mesh in the first BZ was used in the interpolation of the force constants for the phonon dispersion curve calculations. A MP grid of  $14 \times 14 \times 14$  was used to ensure  $k$ -point sampling convergence with Gaussians of width 0.04 Ry, which approximates the zero-width limits in the calculations of EPC parameter  $\lambda$ .

We performed variable-cell structure prediction simulations using the above evolutionary methodology for  $\text{GeH}_4$  containing one, two, three and four molecules in the simulation cell at 50, 100, 150, and 250 GPa, respectively. At 50 and 100 GPa, simulations predicted a  $P2_1/m$  structure (2 molecules/cell) as depicted in Fig. 1(a). This structure contains Ge zigzag chains bridged by “ $\text{H}_2$ ” molecules, somewhat resembling the  $P6/mmm$  structure proposed for  $\text{SnH}_4$  [14]. However, this structure is unstable to decomposition into the  $\text{Ge} + 2\text{H}_2$  mixture. Decomposition at low pressure for  $\text{GeH}_4$  is further confirmed by the subsequent enthalpy calculation (Fig. 2). At 150 and 250 GPa, a  $C2/c$  structure (4 molecules/cell) shown in Figs. 1(b) and 1(c) is found to be most stable. Within this structure, Ge atoms occupy the crystallographic  $4e$  sites and the two inequivalent H1 and H2 atoms sit on the  $8f$  sites. We note that the crystal structure of  $C2/c$   $\text{GeH}_4$  is substantially different from those for  $\text{SiH}_4$  proposed by Pickard *et al.* [7] and Yao *et al.* [8]. The primary difference is the formation of a  $\text{H}_2$ -unit from H1 site in our structure with a short H-H separation of 0.87 Å at 220 GPa—this is longer than the optimized distance in the free  $\text{H}_2$  molecule (0.76 Å). The different electronegativities and sizes of Ge and Si atoms might contribute to the distinct structures in  $\text{GeH}_4$  and  $\text{SiH}_4$ . Moreover,  $d$  orbitals in Ge are much shallower than those in Si and thus Ge-H bonds are expected to be less directional. Except for participating in the  $\text{H}_2$ -unit, the hydrogen atoms from H2 site form “bridges” between two Ge atoms. There are two such bridges between every pair

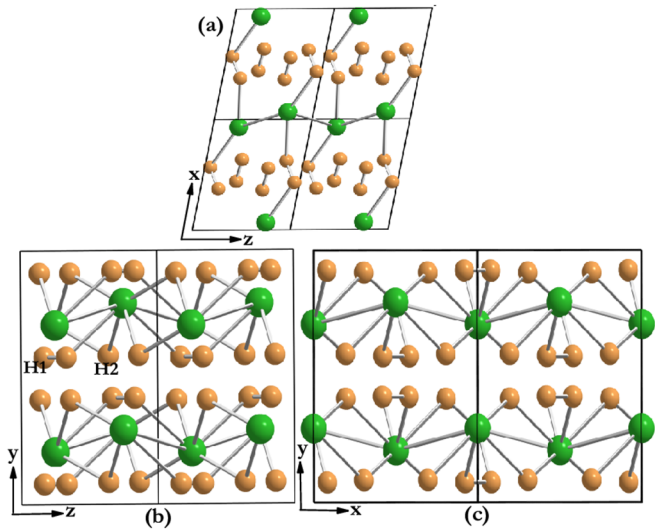


FIG. 1 (color online). (a) Top view of  $P2_1/m$  structure along  $y$ -axis. (b) and (c) Top view of  $C2/c$  phase along  $x$  and  $z$ -axis, respectively. The large and small spheres represent Ge and H atoms, respectively. For  $P2_1/m$  structure at 110 GPa, the lattice parameters are  $a = 3.997$  Å,  $b = 3.091$  Å,  $c = 3.324$  Å, and  $\beta = 78.799^\circ$  with atomic positions of Ge at  $2e$  (0.068, 0.25, 0.7353) and H atoms at  $2e$  (0.4299, 0.25, 0.946), (0.4416, 0.25, 0.3489), (0.6387, 0.25, 0.3654), and (0.3746, 0.75, 0.18). For  $C2/c$  structure at 220 GPa the lattice parameters are  $a = 4.025$  Å,  $b = 5.275$  Å,  $c = 3.018$ , and  $\beta = 96.49^\circ$  with atomic positions of Ge at  $4e$  (0, 0.2918, 0.25) and two inequivalent H1 and H2 atoms at  $8f$  (0.5831, 0.5788, 0.6697) and (0.8050, 0.4129, 0.6408), respectively.

of Ge atoms, forming a  $\text{Ge}_2\text{H}_2$  plane. The nearest neighboring Ge atoms are bonded to each other and each Ge atom is chemically bonded to 6 H atoms, which was confirmed by the analysis of the electron localization function. Therefore, this intriguing structure can be viewed as an intermediate packing between molecular and polymeric structures.

Figure 2 shows the enthalpy curves for  $C2/c$  structure, earlier structures ( $P2_1/c$ ,  $I-42m$ ,  $P-43m$ ,  $14/mmm$  and  $Pman$ ) [9,12,13] and the decomposition ( $\text{Ge} + 2\text{H}_2$ ) [27,30,31] with respect to our predicted  $P2_1/m$  structure. It is obvious that the currently proposed structures are much superior in enthalpy than earlier structures. However, a strikingly wide decomposition pressure range of 0–225 GPa is predicted, above which  $C2/c$  structure becomes stable. As it was suggested by Tse *et al.* [14] that the radii of Ge and Sn are larger than those in Si, the expected weaker Ge/Sn-H bonding might facilitate the complete dissociation of Ge/Sn-H bond at lower pressure. We have also considered the decomposition formula of  $\text{GeH}_4 = \text{GeH}_2 + \text{H}_2$ . Since the crystal structures of  $\text{GeH}_2$  are not known, the evolutionary variable-cell crystal structure predictions were performed at 50 and 100 GPa to explore its structures. It turns out that the resulting total enthalpy of  $\text{GeH}_2 + \text{H}_2$  is much higher than that of

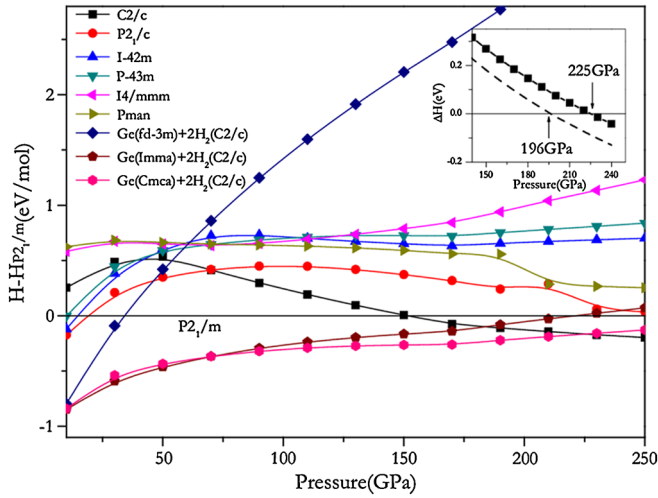


FIG. 2 (color online). The enthalpies per formula unit of various structures as a function of pressure with respect to our predicted  $P2_1/m$  structure.  $P2_1/c$  is the experimental structure for  $\text{SiH}_4$  (Ref. [9]). The decomposition ( $\text{Ge} + 2\text{H}_2$ ) enthalpies are calculated by adopting the  $C2/c$  structure (Ref. [28]) for  $\text{H}_2$  and  $Fd-3m$ ,  $Imma$ , and  $Cmca$  structures for Ge (Ref. [27,30,31]), respectively. Inset: Enthalpies for  $C2/c$  structure relative to the decomposition ( $Cmca\text{-Ge} + C2/c - \text{H}_2$ ) with (dashed line) and without (solid line and symbols) the zero-point corrections.

$\text{Ge} + 2\text{H}_2$  at the studied pressures, which rules out the decomposition into  $\text{GeH}_2 + \text{H}_2$ .

It is known that quantum effects related to hydrogen atoms can be very important. In particular, due to the low mass of the hydrogen atom, the zero-point (ZP) energy is

expected to be large and might significantly alter the structural stability. We thus have estimated the ZP vibrational energies for  $C2/c \text{H}_2$  [28],  $Cmca \text{Ge}$  [27] and  $C2/c \text{GeH}_4$  at 220 GPa using the quasiharmonic model. The resultant ZP energy of  $Cmca \text{Ge} + 2C2/c\text{H}_2$  is about 1.244 eV, higher than that (1.156 eV) of  $C2/c \text{GeH}_4$ . As a first-order, the enthalpy difference of 0.088 eV has been assumed constant and considered in the decomposition curve as plotted in the inset of Fig. 2. This lowers the decomposition  $\rightarrow C2/c$  transition pressure to 196 GPa. At the current *ab initio* technique, the full inclusion of quantum effects beyond zero-point motion is not allowed and out of our scope. In view of the stability field ( $>196$  GPa) of  $C2/c$ , the electronic properties, lattice dynamics, and electron-phonon coupling of  $C2/c$  structure at 220 GPa are explored.

The calculated electronic band structure and projected density of states (DOS) for  $C2/c \text{GeH}_4$  at 220 GPa, presented in Figs. 3(a) and 3(b), reveal that this structure is metallic. Moreover, the less dispersed valence and conduction bands near the Fermi level signify a relatively large electronic DOS at the Fermi level (4.82 states/spin/Ry/Unit cell), which might favor the superconducting behavior. The calculated valence bandwidth of 23.5 eV is consistent with earlier predictions [5] and recent theoretical results [8,14] for dense hydrogen alloys. The strong Ge-H hybridization can be derived from the significant overlap of Ge- and H-DOS [Fig. 3(b)]. Phonon calculations performed at 160, 180, 220, and 300 GPa have established the dynamical stability of  $C2/c$  structure by evidence of the absence of any imaginary frequency modes in the BZ. The phonon band struc-

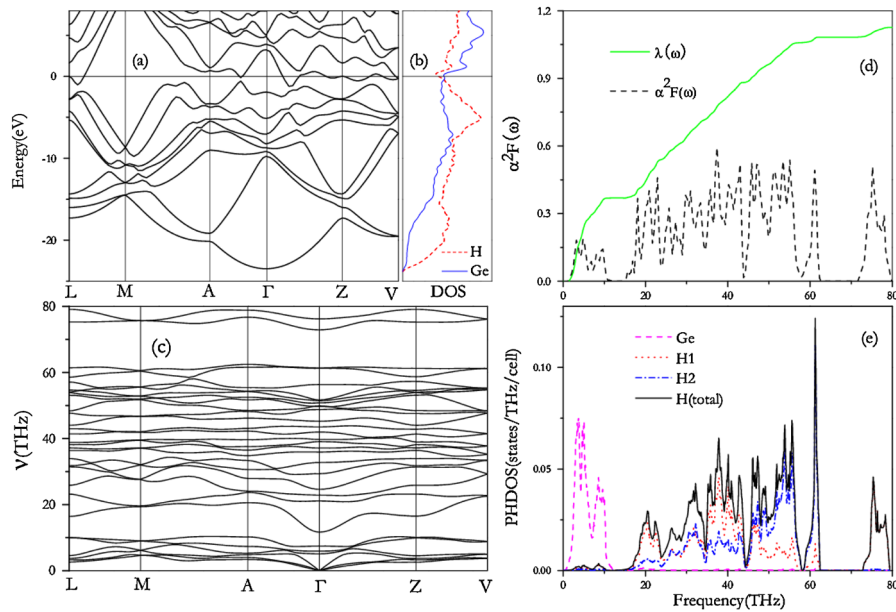


FIG. 3 (color online). (a) and (b) The calculated electronic band structure and projected electronic DOS on Ge and H atoms for  $C2/c \text{GeH}_4$  at 220 GPa. (c) The calculated phonon band structure for  $C2/c \text{GeH}_4$  at 220 GPa. The Eliashberg phonon spectral function  $\alpha^2F(\omega)$  and the electron-phonon integral  $\lambda(\omega)$  in (d) are compared to the phonon DOS projected on Ge, H (total), H1, and H2 atoms in (e).

ture and projected phonon DOS at 220 GPa are shown in Figs. 3(c) and 3(e). Low-energy phonon modes located at 2–14 THz are mainly associated to Ge atoms as expected from its much higher atomic mass. The intermediate frequencies in the range of 14–70 THz correspond to H atoms, while above 70 THz, intramolecular H<sub>2</sub> vibrations dominate.

To explore the superconductivity, the EPC parameter  $\lambda$ , the logarithmic average phonon frequency ( $\omega_{\log}$ ), and the Eliashberg phonon spectral function  $\alpha^2F(\omega)$  [32] have been investigated at 220 GPa. The resulting  $\lambda$  is 1.12, indicating that the EPC is fairly strong. The theoretical spectral function  $\alpha^2F(\omega)$  and the integrated  $\lambda(\omega)$  as a function of frequency are shown in Fig. 3(d). It is found that the low-frequency Ge translational vibrations (<14 THz), the intermediate-frequency modes (14–70 THz), and the intramolecular vibrational modes (>70 THz) contribute 33%, 63%, and 4% to the EPC  $\lambda$ , respectively. Interestingly, the vibrations of H1 atoms are mainly responsible for the phonon DOS from 15 to 48 THz and above 70 THz, while H2 atoms are essentially responsible for those between 48 and 70 THz, as can be seen from Fig. 3(e). Therefore, it is suggested that H1 atoms (H<sub>2</sub> unit) play a significant role in the superconductivity of GeH<sub>4</sub>. The  $T_c$  can be estimated from the Allen-Dynes modified McMillan equation [33]  $T_c = \frac{\omega_{\log}}{1.2} \exp[\frac{1.04(1+\lambda)}{\lambda - \mu^*(1-0.62\lambda)}]$ . This equation has been found to be highly accurate for materials with  $\lambda < 1.5$ . The Coulomb pseudopotential  $\mu^*$  is taken as 0.13, an appropriate value proposed by Ashcroft [5]. With the calculated  $\omega_{\log}$  of 897 K, the estimated  $T_c$  reaches a very high value, 64 K. Particular care was also taken to consider the influence of DFT functionals on  $T_c$ . Our results suggest a negligible change.

In conclusion, theoretical calculations have revealed that a novel C2/c monoclinic structure with layered molecular-like stacks containing novel “H<sub>2</sub>” units is stable at high pressures (> 196 GPa) against the remarkably wide decomposition. Electron-phonon coupling calculations show that this phase is superconducting with a high  $T_c$  of 64 K at 220 GPa. The “H<sub>2</sub>” unit has been suggested to be mainly responsible for the large  $T_c$  in contrast to the smaller value ( $\sim 17$  K) in SiH<sub>4</sub> possessing the completely molecular structural nature. The current study will inevitably stimulate the future high-pressure experiments on the structural and conductivity measurements.

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