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Ab initio study of germanium-hydride compounds under high pressure

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Motivated by the potential high temperature superconductivity in hydrogen rich materials and phase transitions, the germanium-hydride under high pressure was studied by a genetic algorithm. Enthalpy calculations suggest that the Ge and H compose Ge_3H, Ge_2H, GeH_3, and GeH_4 at about 32, 120, 280, and 280 GPa, respectively. These four germanium-hydride compounds are all stable up to at least 300 GPa. For Ge_3H, the most stable structure is P-3-Ge_3H at 32-220 GPa and $P6_3/m$-Ge_3H at 220-300 GPa. All the germanium-hydride compounds are metallic phases demonstrated by the band structure and density of states.

I. INTRODUCTION

In the past few decades, scientists have been trying best to seek and design high-temperature superconducting material [1-3]. And in high-pressure field, one of the most significant targets is to discover metallic hydrogen for high-temperature superconductor and the other one is to make production, transition and application of hydrogen. Theoretical works have been reported that hydrogen will metalize at about 440 GPa. However, it does not observe the experimental metallization till 342 GPa [4]. But it will lower the T_c because of chemical pre-compression [5]. Recently, it was suggested that dense hydrogen-dominated metallic alloys, in strongly compressed group IV hydrides, can be potential candidate materials for a high-temperature superconductor. Disilane has been studied by Jin *et al*.[6], and they had explored the crystal structures of disilane in a wide pressure range from 50 to 400 GPa, and three favored structures, P-1, Pm-3m, and $C2/c$. Remarkably, the large T_c of 80 K at 200 GPa for P-1 and 139 K at 275 GPa for Pm-3m are predicted by quantitative calculations. Germane has been forecasted by Gao *et al*.[7], and their calculated results suggested a remarkably wide decomposition pressure range of 0-196 GPa, above which a $C2/c$ structure is stable. Then GeH_4 [8] and $GeH_4(H_2)_2$ [9] were studied by Chao Zhang and Guohua Zhong *et al*. GeH_3 has been predicted to be a *Cccm* structure by Kazutaka Abe *et al*. [10], and the calculation of enthalpy indicates that *Cccm* GeH_3 can be formed at about 200 GPa.

In order to search out the real conditions of Ge_3H, Ge_2H and GeH_3, we extensively explored the structures of germanium-hydride compounds under high pressure using an *ab initio* evolutionary algorithm [11-12] for crystal structure prediction. We propose the compound of Ge_3H is more potential in the pressure range of 40 ~ 300 GPa. Enthalpy calculations suggest that *P*-3 structure is the most favorite one at 40~220 GPa and $P6_3/m$ structure is the most favorite one at 220~300 GPa. Calculations of DOS indicate that all of *Pnma* Ge_2H, *P*-3 Ge_3H, $P6_3/m$ Ge_3H and *Cccm* GeH_3 are metallic. For *Cccm* GeH_3, as an underlying candidate of high-temperature superconductor, the application of the Allen-Dynes modified McMillan equation [13] reveals high T_c of 80.3 K at 300 GPa for this structure. Our calculations have also revealed that there will be *P*-3 Ge_3H under high pressure which has been considered as that it will not form any compounds of Ge and H below about 32 GPa. We predict that Ge and H will compose GeH_3 above 280 GPa. At the same time, it is cleared that another metallic germanium-hydride structure *C2/c* GeH_4 [7] will not form before 280 GPa.

II.COMPUTATIONAL METHOD

Ab initio evolutionary algorithm [10-12], designed to search for the structure possessing the lowest free energy at given pressure conditions has been employed. The most significant feature of this method is the capacity of predicting the stable structure with only the knowledge of the chemical composition [5]. The details of the search algorithm and its first several applications have been described elsewhere. The underlying ab initio structure relaxations were performed using density functional theory within the Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) as performed in the Vienna *ab* initio simulation package VASP code to calculate projected density of states [14-15]. The PAW [16] potential with the valence states $1s^1$ for H and $4s^24p^2$ for Ge [17] has been employed with plane waves up to a cutoff energy of 720 eV, and the density of states has been calculated with a 8 x

8 x 9 k-point mesh created by the Monkhorst-Pack (MP) [18] method. Phonon dispersion and electron-phonon calculations were performed with density functional perturbation theory [19-20] using the program QUANTUM ESPRESSO [21]. Convergence tests gave the choice of kinetic energy cutoff 72 Ry and 8 x 8 x 9 Monkhorst Pack grids of *k*-points sampling for the electronic Brilliouin Zone integration. We calculated T_c using the Allen-Dynes equation. The q-point mesh in the first BZ of 4 x 4 x 4 for *Cccm* structure is used in the interpolation of the force constants for the phonon dispersion curve calculations. A denser k-point mesh 12 x 12 x 12 for *Cccm* structure is adopted to ensure k-point sampling convergence with a Gaussians width of 0.03Ry, which approximates the zero width limits in the calculation of EPC parameter λ. The hybrid functional calculations are implemented in the CASTEP code, together with norm-conserving pseudopotentials, and a cutoff energy of 600 eV. [22, 23]

III. RESULTS AND DISCUSSION

We performed variable-cell structure prediction simulations using the above evolutionary methodology for containing one, two, three, and four molecules in the simulation cell at 10, 30, 50, 100, 150, 200, 250 and 300 GPa, respectively. At 50 and 100 GPa, our simulations predicted a *P*-3 structure as depicted in Fig 1(a). The Ge and H atoms are depicted in violet and pink colors, respectively. Each H atom is in connection with three Ge atoms. Both of two kinds of atoms form the layered structure. Figure 2(b) shows the enthalpy curves for *P*-3 Ge_3H structure, and the decomposition of *Cmca* Ge and *c*2/*c* H_2 [24-26] with respect to our predicted *P*-3 structure. Obviously, the currently proposed structures are much superior in enthalpy than the other structures. At 200 and 250 GPa, our simulations predicted a $P6_3/m$ structure as depicted in Fig 1(b), and at 100 and 150 GPa, a *Pnma* structure as depicted in Fig 1(c). It is clear that *Cccm* GeH_3 [10] as depicted in Fig 1(d) will not be easily formed until 280 GPa and Ge and H will compose to *P*-3 Ge_3H at 32 GPa. Enthalpy calculations reveal that the *Cccm* structure is stable at 280 GPa up to at least 300 GPa, respectively, while *P*-3 Ge_3H and *Pnma* Ge_2H are the most stable two phases from 120 GPa to 220 GPa. From 220 GPa to 280 GPa, *Pnma* Ge_2H and $P6_3/m$ Ge_3H will coexist. No imaginary phonon frequencies were found in Brillouin Zones to confirm the *P*-3 Ge_3H structural stability of the new stable structure from 40 GPa to 220 GPa, $P6_3/m$ Ge_3H from 220 GPa to 300 GPa and *Pnma* Ge_2H from 50 GPa to 300 GPa. Due to the chemical precompression [5], the GeH_3 may be a good superconductor under high pressure. To explore the superconductivity of the *Cccm* GeH_3, the application of the Allen-Dynes modified McMillan equation [13] reveals high superconducting temperature of 80.3 K for the *Cccm* phase at 300 GPa and 100.8 K at 220 GPa. At the stability field of *P*-3, *Pnma* and $P6_3/m$, the electronic properties, lattice dynamics, and electron-phonon coupling of *P*-3, *Pnma* and $P6_3/m$ structure are explored. In accordance with our expectation, the superconduction transition temperatures of these three phases are very low as a result of the content of hydrogen is low. This result maybe approves that, to a great extent, superconduction transition temperature depends on the content of hydrogen in metal hydride.

To further confirm the dynamical stability of Ge_3H and Ge_2H, we calculate the phonon dispersion curves as shown in Fig. 3. No imaginary phonon frequencies were found in Brillouin Zones confirms the structural stability of the new structures. The calculated energy band structures and density of states of Ge_3H and Ge_2H are shown in Fig. 4 and Fig. 5, respectively. The overlap between the conduction and the valence bands suggests that Ge_3H and Ge_2H are metallic. The electronic band structure and density of electronic states (DOS) of *Cccm* GeH_3 are shown in Fig. 6, which shows significant overlap between the orbitals of *s* and *p* electrics. The band structure reveals metallic character with large dispersion bands crossing the Fermi level (E_F) and a flat band around E_F. The simultaneous occurrence of flat and steep bands near the Fermi level has been suggested as favorable conditions for strengthening electron and phonon coupling, which is essential to superconducting behavior [7]. Due to underestimation of band gaps of GGA functional, we also calculated the band structures of germanium-hydride compounds with hybrid functional HSE06 method. The band structures calculated by hybrid functional HSE06 method are the same as GGA results, suggesting that the structures at the pressures are all metallic phases.

According to the McMillan formula [13], T_c is governed by three parameters: coupling-weighted phonon momentum, electron-phonon coupling, and conduction electrons near E_F. Conduction electrons near E_F are ruled out as the main contributor for the superconductivity behavior, since there is only a low density of Ge *s* electrons and even lower H *s* electrons. But the shape of the density of H *s* electrons is much like Ge *s* electrons, which is helpful to enhance the electron-phonon coupling. The change in coupling-weighted phonon momentum under pressure is seen to be in consistent with that of T_c. This leaves electron-phonon coupling as the dominant reason for affecting T_c. We thus explain the likeness between the respective behaviors of T_c and the hybridization function under pressure to be because of improvement enhancing electron-phonon coupling by the match of the energy level from Ge *p* electrons with the peak of H *p* electrons. The peak of Ge *p* electrons is found too high above E_F, and is found close to the E_F and can therefore contribute strongly to the electron-phonon coupling. The calculated electronic band structure and projected density of states (DOS) for *Cccm* GeH_3 at 280 GPa presented in Fig. 6 reveal that this structure is metallic. However, the less dispersed valence and conduction bands near the Fermi level represent a rather large electronic DOS at the Fermi level, which might favor the superconducting behavior. The calculated valence bandwidth is consistent with earlier predictions and recent theoretical results for dense hydrogen alloys [5]. The strong Ge-H hybridization can be got from the significant overlap of Ge-DOS and H-DOS. Phonon calculations performed at 280, and 300 GPa have proved the dynamical stability of *Cccm* structure by evidence of the absence of any imaginary frequency modes in the BZ. To explore the superconductivity of this phase we suggested, the EPC parameter λ, the logarithmic average phonon frequency ($\omega_{\log}$), and the Eliashberg phonon spectral function $\alpha^2F(\omega)$ [26] have been investigated at high pressures. The resulting λ for this phase at 220 and 300 GPa are 1.65, and 1.36, respectively, indicating that the EPC is fairly strong. The theoretical spectral function $\alpha^2F(\omega)$ [26] and the integrated $\lambda(\omega)$ as a function of frequency at selected pressures are shown in Fig. 7. The superconducting critical temperature can be estimated from the Allen–Dynes modified McMillan equation, which has been found to be highly accurate for many materials with $\lambda < 1.5$. The $\omega_{\log}$ is calculated directly from the phonon spectrum. The Coulomb pseudopotential μ is often taken as 0.1 for most metals; an appropriate one proposed by Ashcroft is 0.12 for hydrogen dominant metallic alloys that has been adopted in the works of GeH_4 and SnH_4. These current studies inevitably stimulate the future high-pressure experiments on the structural and conductivity measurements.

Extra phonon calculations show the stability range to be between 280 and at least 300 GPa [10]. Obviously, for low frequency area, Ge contributes a lot to phonon DOS, by contraries, for high frequency, all contribution come from the electrons of H atoms [27-28]. In general, the integrable function depends on the high frequency which is contributed by the electrons of H atoms.

IV. CONCLUSIONS

In summary, the structures of germanium-hydride are explored with the *ab initio* evolutionary method. The *P*-3 Ge_3H structure is the most stable one in a pressure range from 40 GPa to at least 220 GPa, the *Pnma* Ge_2H structure will coexist with *P*-3 in a pressure range from 120 GPa to at least 220 GPa and coexist with $P6_3/m$ Ge_3H from 220 GPa to 300 GPa. And the *ab initio* calculation of energy show Ge_3H and Ge_2H will be formed more easily than GeH_3 below 280 GPa. The calculated band structures of the all these four phases reveal a metallic character, specially, for *Cccm* GeH_3, with large dispersion bands crossing the Fermi level (E_F), which is necessary for superconductive behavior. Electron-phonon coupling calculations show that this phase is superconducting with a high T_c of 80.3 K at 300 GPa. The current study will inevitably stimulate the future high-pressure experiments on the structural and conductivity measurements.

Acknowledgements

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Figure Captions

Fig. 1 (a)Crystal structure of Ge_3H with the *P*-3 space group at 40 GPa.
(b)Crystal structure of Ge_3H with the *P*6_3*/m* space group at 220 GPa.
(c)Crystal structure of Ge_2H with the *Pnma* space group at 200 GPa.
(d)Crystal structure of GeH_3 with the *Cccm* space group at 300 GPa.

Fig. 2 Convex hull diagram for Ge-H system. At pressures of (a) 40 GPa, (c) 60 GPa, (d) 120 GPa, (e) (f) 220 GPa, (g) 280 GPa and (h) 300 GPa respectively. Enthalpy curves of *P*-3 Ge_3H (b).

Fig. 3 The phonon dispersion curves for the and the *P*-3 Ge_3H structure configuration at pressures of 40 GPa(a), 220 GPa(b), *Pnma* Ge_2H structure configuration at pressures of 50 GPa(c), 300 GPa(d) and the *P*6_3*/m* Ge_3H structure configuration at pressures of 220 GPa(e), 300 GPa(f).

Fig. 4 The electronic band structure of *P*-3 Ge_3H at 40 GPa(a), 220 GPa(b), *Pnma* Ge_2H at 150 GPa(c), 280 GPa(d) and *P*6_3*/m* Ge_3H at 220 GPa(e), 280 GPa(f).

Fig. 5 The density of electronic states (DOS) of *P*-3 Ge_3H at 40 GPa(a), 200 GPa(b), *Pnma* Ge_2H at 180 GPa(c), 240 GPa(d) and *P*6_3*/m* Ge_3H at 220 GPa(c), 280 GPa(d).

Fig. 6 The electronic band structure and density of electronic states(DOS) of *Cccm* GeH_3.

Fig.7 Eliashberg phonon spectral function $\alpha^2F(\omega)$ and the electron-phonon integral $\lambda(\omega)$ for phase *Cccm* of calculated at 300 GPa, respectively.

TABLE Ⅰ The parameters of *P*-3 structures correspond to 40 GPa, *Pnma* structures correspond to 200 GPa, *P*6_3*/m* structures correspond to 280 GPa.

Figure 1

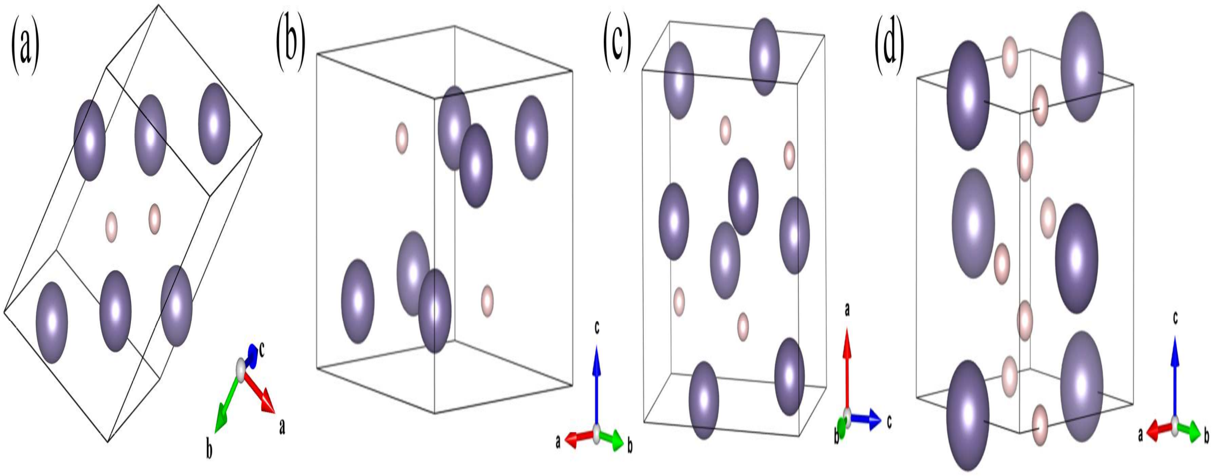

Figure 2

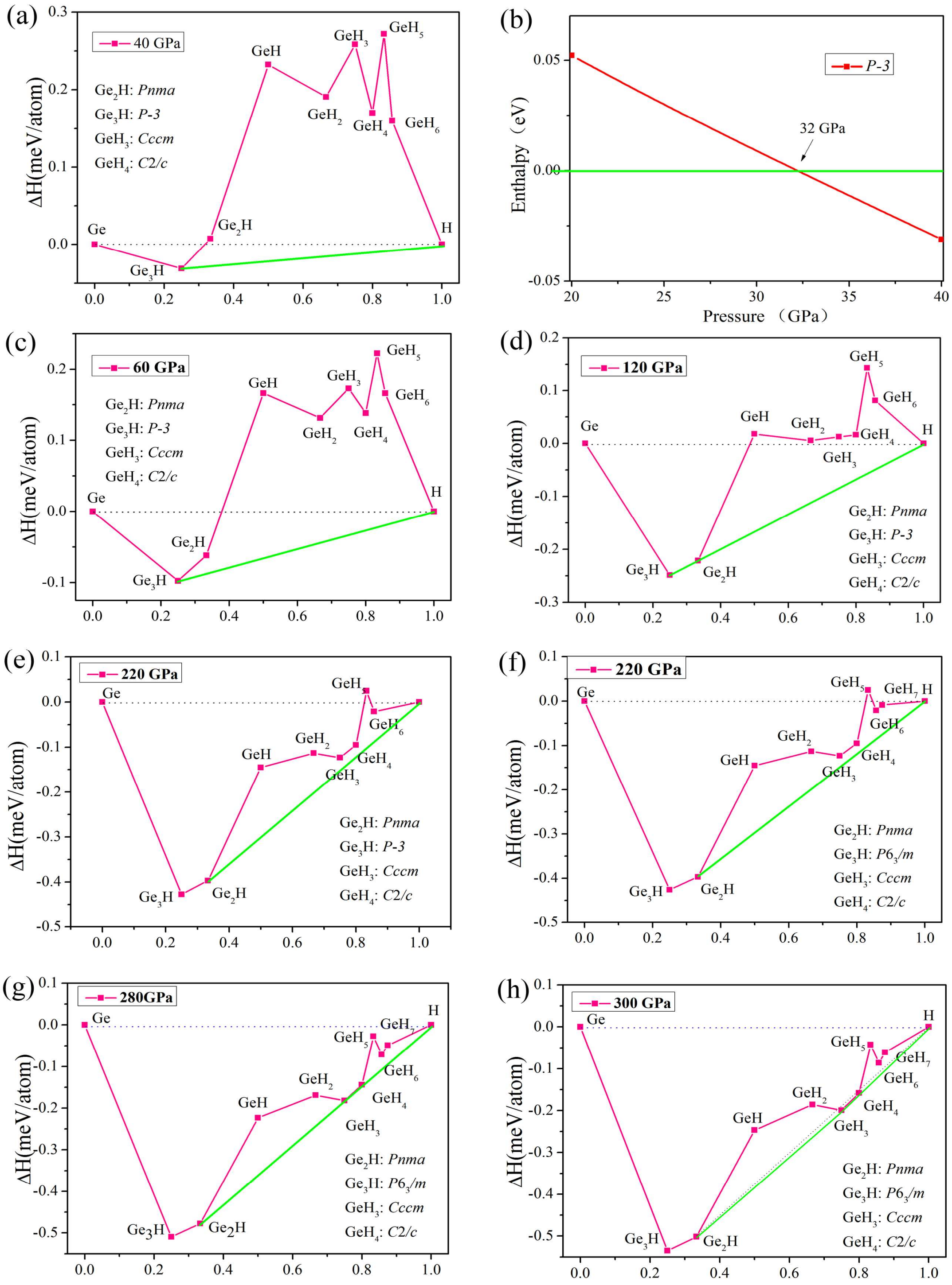
(a)
40 GPa
ΔH(meV/atom)
Ge₂H: Pnma
Ge₃H: P-3
GeH₃: Cccm
GeH₄: C2/c
Ge
Ge₃H
Ge₂H
GeH
GeH₂
GeH₃
GeH₄
GeH₅
GeH₆
H
(b)
P-3
32 GPa
Enthalpy (eV)
Pressure (GPa)
(c)
60 GPa
(d)
120 GPa
(e)
220 GPa
(f)
220 GPa
Ge₃H: P6₃/m
GeH₇
(g)
280GPa
(h)
300 GPa

Figure 3

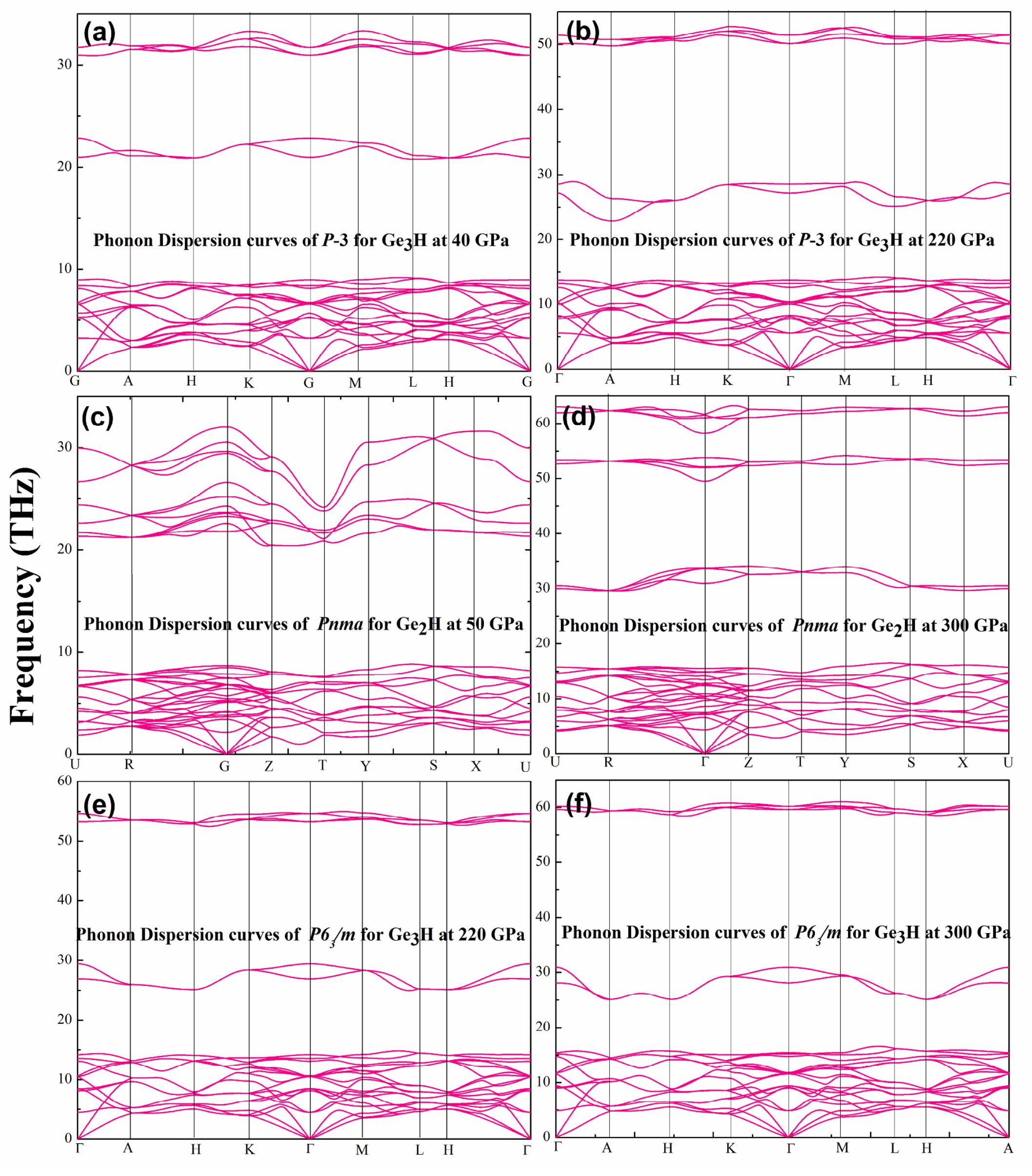
Frequency (THz)
(a)
Phonon Dispersion curves of P-3 for Ge3H at 40 GPa
G A H K G M L H G
(b)
Phonon Dispersion curves of P-3 for Ge3H at 220 GPa
Γ A H K Γ M L H Γ
(c)
Phonon Dispersion curves of Pnma for Ge2H at 50 GPa
U R G Z T Y S X U
(d)
Phonon Dispersion curves of Pnma for Ge2H at 300 GPa
U R Γ Z T Y S X U
(e)
Phonon Dispersion curves of P6/m for Ge3H at 220 GPa
Γ A H K Γ M L H Γ
(f)
Phonon Dispersion curves of P6/m for Ge3H at 300 GPa
Γ A H K Γ M L H A

Figure 4

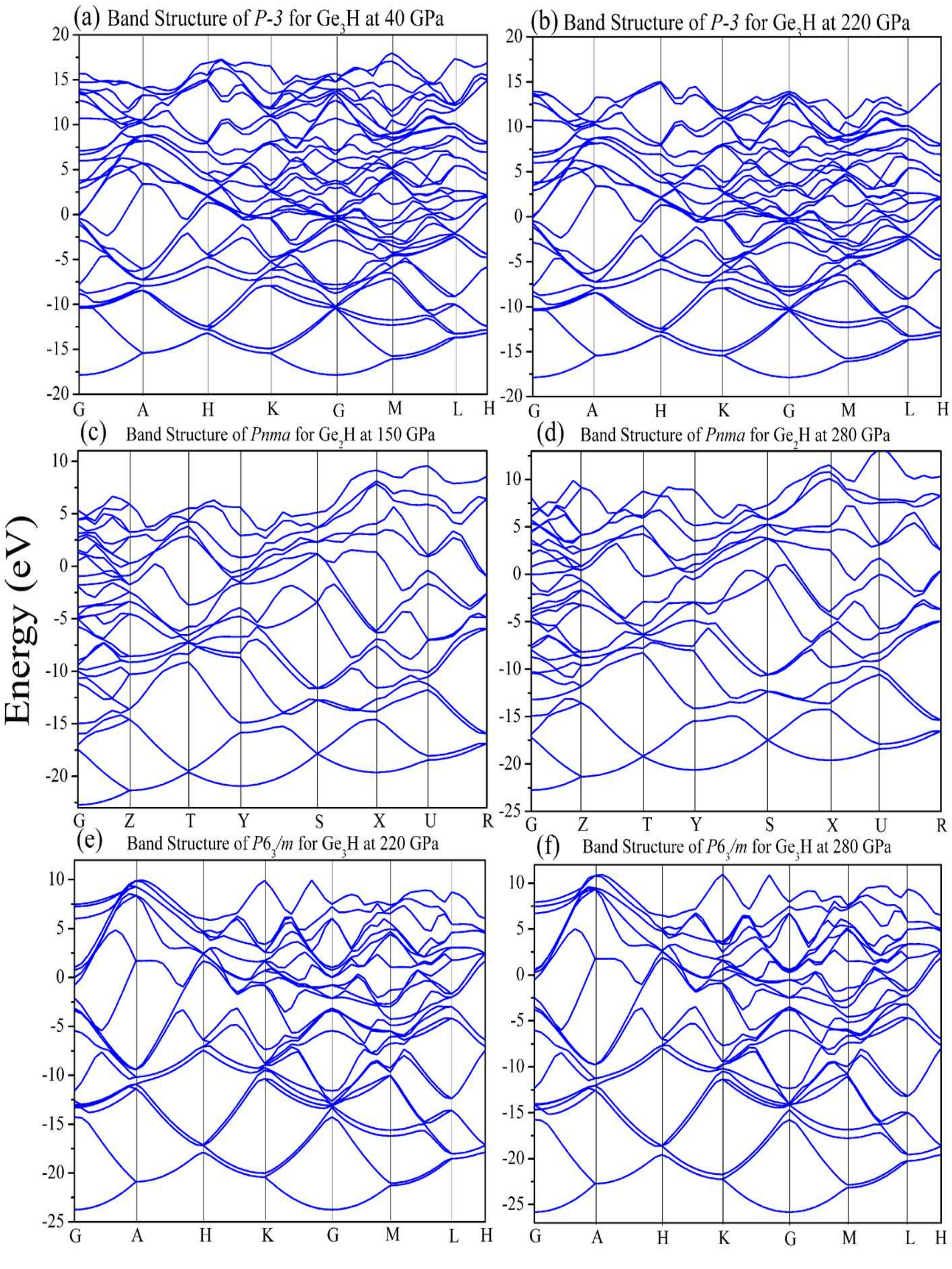
(a) Band Structure of *P-3* for Ge$_3$H at 40 GPa
(b) Band Structure of *P-3* for Ge$_3$H at 220 GPa
(c) Band Structure of *Pnma* for Ge$_2$H at 150 GPa
(d) Band Structure of *Pnma* for Ge$_2$H at 280 GPa
(e) Band Structure of *P6$_3$/m* for Ge$_3$H at 220 GPa
(f) Band Structure of *P6$_3$/m* for Ge$_3$H at 280 GPa
Energy (eV)
20
15
10
5
0
-5
-10
-15
-20
-25
G A H K G M L H
G Z T Y S X U R

Figure 5

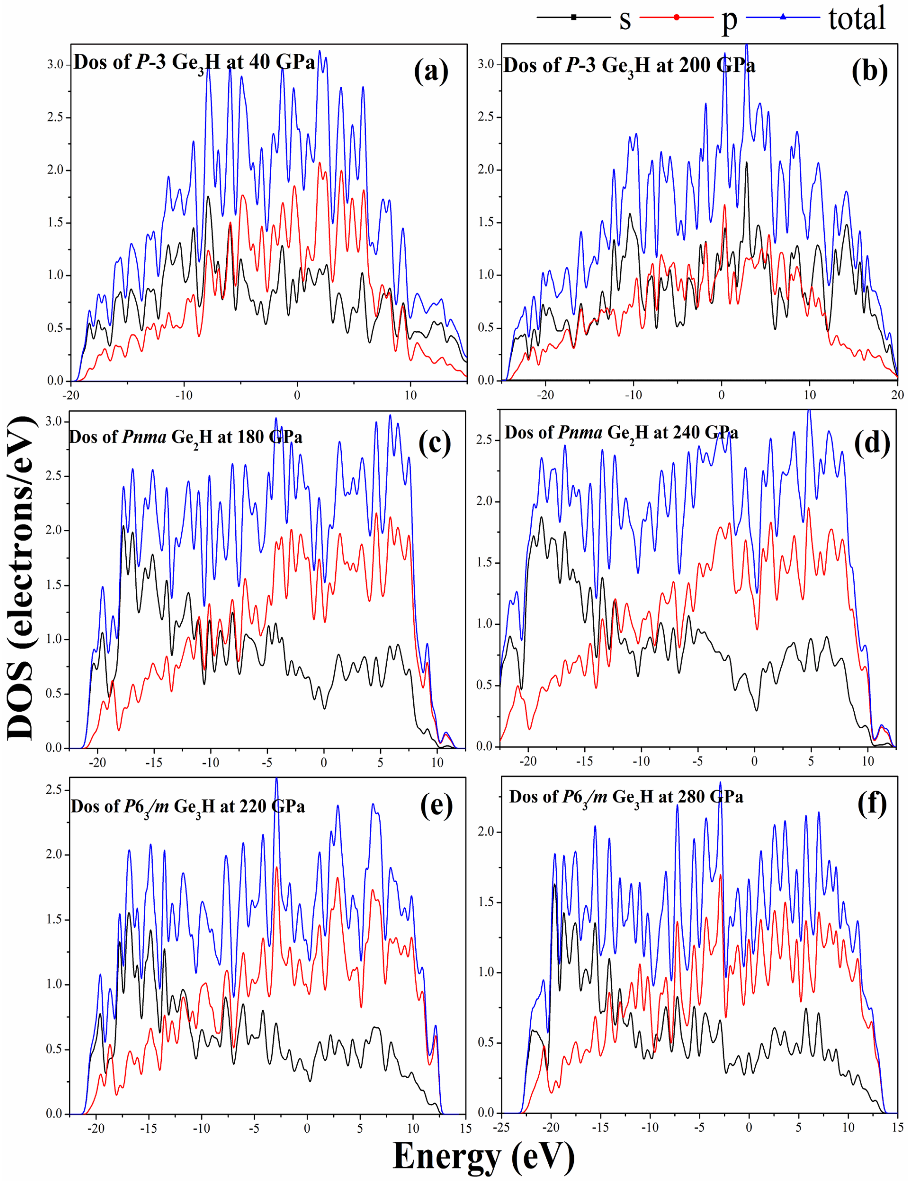
s
p
total
Dos of P-3 Ge$_3$H at 40 GPa
(a)
Dos of P-3 Ge$_3$H at 200 GPa
(b)
Dos of Pnma Ge$_2$H at 180 GPa
(c)
Dos of Pnma Ge$_2$H at 240 GPa
(d)
Dos of P6$_3$/m Ge$_3$H at 220 GPa
(e)
Dos of P6$_3$/m Ge$_3$H at 280 GPa
(f)
DOS (electrons/eV)
Energy (eV)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
-25
-20
-15
-10
-5
0
5
10
15
20

Figure 6

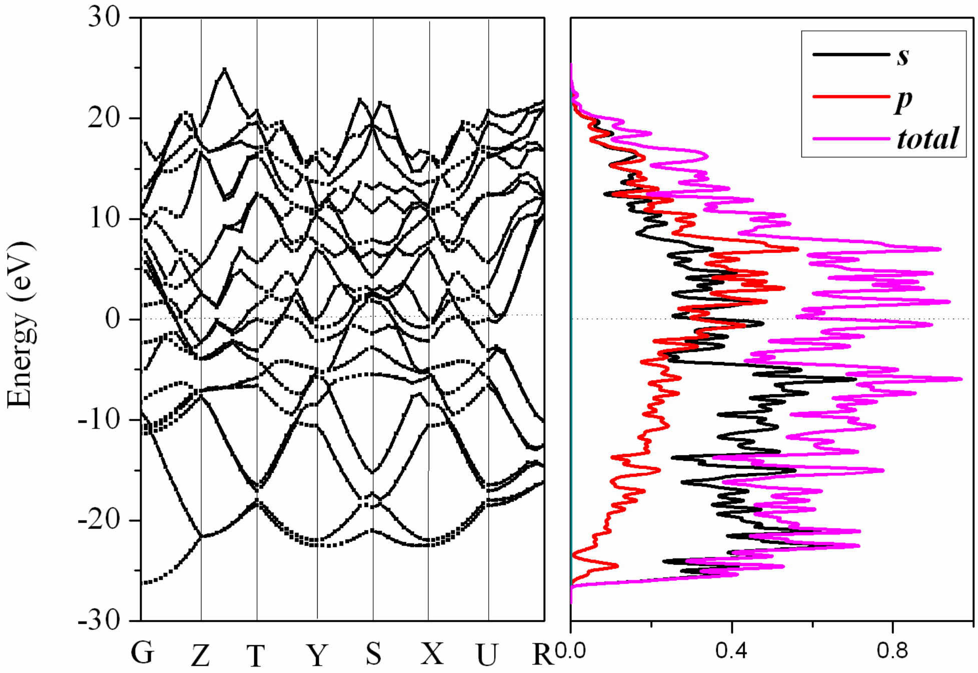

Figure 7

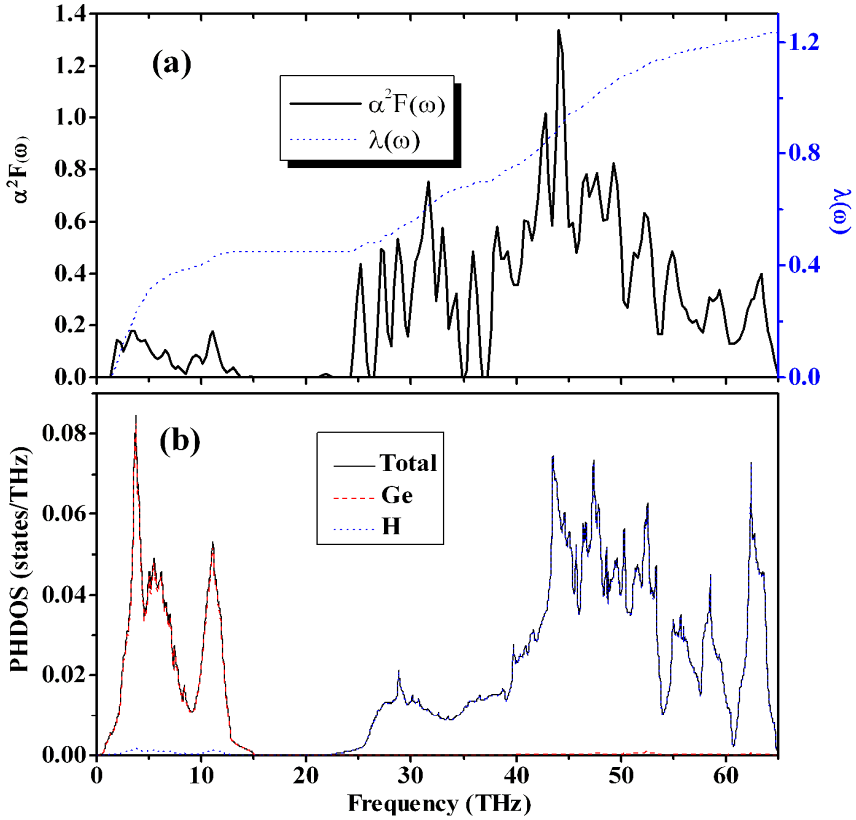
(a)
$\alpha^2F(\omega)$
$\lambda(\omega)$
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1.2
0.8
0.4
0.0
(b)
Total
Ge
H
PHDOS (states/THz)
0.08
0.06
0.04
0.02
0.00
0
10
20
30
40
50
60
Frequency (THz)

TABLE Ⅰ

pressure (GPa)	**space group**	**lattice parameter (Å)**	**atomic coordinates**			
40	*p-3*	a= b= 4.97724 c= 4.114922 α= β= 90° γ=120°	Ge1 H1	0.65731 0.66667	0.70024 0.33333	0.24985 0.25031
200	*Pnma*	a= 4.559771 b= 3.534107 c= 5.306068 α= β=γ= 90°	Ge1 Ge2 H	0.12917 1.04057 0.25837	0.75000 0.75000 0.75000	-0.10391 -0.65622 -0.40183
220	*P*6_3*/m*	a= b= 4.403848 c= 3.716815 α= β= 90° γ= 120°	Ge H	-0.04740 0.33333	-0.70651 -0.33333	0.25000 0.25000