Metallic and superconducting gallane under high pressure

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Using our newly developed particle swarm optimization algorithm on crystal structural prediction, we characterized the pressure-induced structural transition sequence of gallane (GaH₃). As has been observed in alane (AlH₃), enthalpy calculations reveal that the Pm₃n structure of GaH₃ becomes stable above 160 GPa, below which it is unstable with respect to elemental decomposition. Interestingly, the Pm₃n structure is metallic, and the application of the Allen-Dynes modified McMillan equation reveals a high superconducting transition temperature (Tc), which reaches 86 K at 160 GPa and increases with decreasing pressure (Tc = 102 K at 120 GPa). Our band structure calculations demonstrate that GaH₃ within the Pm₃n structure is a highly ionic solid, where the ionicity of H atoms plays an important role in the predicted high temperature superconductivity.

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I. INTRODUCTION

Long ago, Ashcroft predicted that metallic hydrogen might be a high-temperature superconductor; however, pressure-induced metallic transition of hydrogen is still an elusive goal of physics, even at pressures around 300 GPa. Recently, it has been proposed that hydrogen-rich compounds, such as group IVa hydrides (SiH₄, GeH₄, and SnH₄), might become metallic at lower pressures than hydrogen and might well be superconductors with high critical temperatures. Although the metallicity and superconductivity experimentally observed in SiH₄ under pressure were actually attributed to the formation of PH₃ and Si₅, its metallization pressure was predicted to be lower than in solid hydrogen. Our previous work also suggested that GeH₄ and SnH₄ might metallize and become good superconductors at experimentally accessible pressures. These results are sufficiently encouraging to prompt further studies of a wider range of hydrides.

Due to its potential application as a hydrogen storage material, alane (AlH₃) has recently been the subject of many theoretical and experimental investigations. Using a “random searching” technique, Pickard et al. predicted a metallic cubic phase (space group Pm₃n) for high-pressure AlH₃. Subsequently, Goncharenko et al. observed that AlH₃ becomes metallic at 100 GPa and confirmed the predicted structure. However, no superconducting transition was found down to 4 K, which disagrees with the theoretically estimated Tc of ~20 K. The origin for this disagreement between theory and experiment was explained by the high anharmonic renormalization of selected phonon modes inducing the superconducting transition, which considerably decreased the electron-phonon coupling parameter λ. Considering the larger polarizability of GaH₃ compared to AlH₃, according to the Goldhammer-Herzfeld criterion, GaH₃ should be a good candidate to metallize at even lower pressures. In this article, we apply our newly developed particle swarm optimization (PSO) technique on crystal structure prediction to extensively explore the crystal structures of GaH₃ under high pressure and characterize the electronic, dynamical, and superconducting properties of the predicted high-pressure structures.

II. COMPUTATIONAL DETAILS

The crystal structure prediction is based on a global minimization of free-energy surfaces merging ab initio total-energy calculations via PSO technique as implemented in the Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) code. This methodology has been successfully applied to many high-pressure structures on elemental, binary, and ternary compounds with metallic, ionic, and covalent bondings. The underlying ab initio structural relaxations were performed using density functional theory within the Perdew-Burke-Ernzerh (PBE) parameterization of the generalized gradient approximation (GGA) as implemented in the Vienna ab initio Simulation Package (VASP) code. The all-electron projector-augmented wave (PAW) method was adopted with the PAW potentials, where 1s and 3d4s4p electrons are treated as valence electrons for H and Ga atoms, respectively. A plane-wave basis set with an energy cutoff of 800 eV was used to get well-converged total energies. On the other hand, the plane-wave pseudopotential method within the PBE-GGA as implemented in the Quantum-ESPRESSO package was used to characterize the electronic properties, lattice dynamics, and electron-phonon coupling (EPC) for Pm₃n GaH₃. For these purposes, ultrasoft pseudopotentials for H and Ga were considered, and convergence tests concluded that suitable values would be a 100 Ry kinetic energy cutoff and a 12 × 12 × 12 Monkhorst-Pack (MP) k-point sampling mesh for the electronic Brillouin zone (BZ) integration. Phonon frequencies were calculated based on the density functional linear-response theory, and a 4 × 4 × 4 q-mesh in the first BZ was used in the interpolation of the force constants for the phonon dispersions. The EPC spectral function α²F(ω) can be expressed in terms of the phonon linewidth γqj, owing to electron-phonon scattering:

\[ α²F(ω) = \frac{1}{2πN_f} \sum_{qj} \frac{γqj}{ωqj} \delta(ℏω - ℏωqj), \]  

(1.1)
where \( N_f \) is the electronic density of states per atom and spin at the Fermi level. The linewidth of a phonon mode \( j \) at wave vector \( q \), \( \gamma_{qj} \), arising from electron-phonon interaction is given by

\[
\gamma_{qj} = 2\pi \omega_{qj} \sum_{k\text{m}} |g_{kn,k+qm}^j|^2 \delta(\epsilon_{kn}) \delta(\epsilon_{k+qm}),
\]

(1.2)

where the sum is over the BZ, and \( \epsilon_{kn} \) are the energies of bands measured with respect to the Fermi level at point \( k \), and \( g_{kn,k+qm}^j \) is the electron-phonon matrix element. The EPC parameter \( \lambda \) can be defined as the first reciprocal moment of the spectral function \( \alpha^2 F(\omega) \),

\[
\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega \approx \sum_q \omega_{qj} \omega(q),
\]

(1.3)

where \( \omega(q) \) is the weight of a \( q \) point in the first BZ. We substituted a Gaussian for the \( \delta \) function in Eq. (1.2). The superconducting transition temperature \( T_c \) has been estimated with the Allen-Dynes modified McMillan equation as

\[
T_c = \frac{\omega_{0\delta}^2}{\lambda} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],
\]

(1.4)

where \( \omega_{0\delta} \) is the logarithmic average frequency, and \( \mu^* \) is the Coulomb pseudopotential. An MP grid of \( 20 \times 20 \times 20 \) was used to ensure \( k \)-point sampling convergence with Gaussians of width 0.04 Ry, in order to approximate the zero-width limit in the calculations of the EPC parameter, \( \lambda \).

**III. RESULTS AND DISCUSSIONS**

Structural predictions were performed with the CALYPSO code, considering simulation sizes ranging from one to four GaH\(_3\) formula units (f.u.) at 5, 50, 100, 200, and 300 GPa. The predicted stable structures were then carefully optimized at a higher level of accuracy at other pressure points for enthalpy curve and electron-phonon coupling calculations. Before the structural searches converged to the most stable structures, we typically generated several hundred structures, we typically generated several hundred structures (e.g., at 300 GPa simulation, we need 100–400 structures to derive the most stable structure). Considering the low mass and the Ga-H distance of 1.73 Å. Moreover, H-H distances decrease very slowly with increasing pressure and become 1.458 Å at 300 GPa, showing that H atoms do not present any bonding trend.

The enthalpy curves of our predicted structures relative to \( R3\overline{c} \) as a function of pressure are presented in Fig. 2. It is clearly seen that below 182 GPa GaH\(_3\) is thermodynamically unstable with respect to decomposition of its elements. Actually, AlH\(_3\) is also thermodynamically unstable at standard temperature and pressure, and it releases H\(_2\) molecules under moderate heating.\(^{16,33}\) Above 182 GPa, the \( Pm\overline{3}n \) structure clearly becomes the most stable structure. Considering the low mass

![FIG. 1. (Color online) Predicted (a) Cc, (b) P2\(_{1}/m\), and (c) Pm\(_{3}n\) structures for GaH\(_3\). Gallium atoms are shown in pink, and hydrogen atoms are shown in green. The \( Pm\overline{3}n \) structure contains 2 f.u. for each cell, gallium atoms occupy the crystallographic 2\text{a} (0, 0, 0) site, and hydrogen atoms are located at the 6\( c\) (0.5, 0.25, 0) site.](image)

![FIG. 2. (Color online) The enthalpies per formula unit of various structures as a function of pressure with respect to \( R3\overline{c} \) structure. The decomposition (Ga + 3/H\(_2\)) enthalpies are calculated by adopting the C2/c structure for H\(_2\) and Cmca, I4/mmm, Fm\(_{3}m\), and \( R3\overline{c} \) structures for Ga.\(^{30}\) Respectively. Inset: Enthalpies for the \( Pm\overline{3}n \) structure relative to the decomposition (Fm\(_{3}m\)-Ga + C2/c-H\(_2\)) with the zero-point corrections.](image)
of H atoms, we applied the quasiharmonic approximation to estimate the zero-point (ZP) energies of GaH$_3$, Ga, and H$_2$ at 120, 160, and 200 GPa. Interestingly, the inclusion of ZP energies lowers the stabilization pressure of Pm$_3n$ to 160 GPa.

Motivated by the search for metallic and high superconducting $T_c$ hydrogen-rich compounds within the reach of current experimental techniques, the electronic properties, lattice dynamics, and superconductivity of the Pm$_3n$ structure at 160 GPa were also analyzed. Figure 3 presents the calculated electronic band structure for Pm$_3n$ GaH$_3$ at 160 GPa. The overlap between the conduction and the valence bands under pressure makes Pm$_3n$ GaH$_3$ a metal. As can be seen in the $\Gamma R$ and $\Gamma M$ directions, two maxima in the band structure at $k$-points close to $\Gamma$ are located at the Fermi level, and they make GaH$_3$ have much larger density of states (DOS) at the Fermi energy ($3.1 \times 10^{-2}$ states/eV/Å$^3$) than our calculated data in AlH$_3$ ($1.1 \times 10^{-2}$ states/eV/Å$^3$ at 80 GPa).

In order to understand the role of H atoms in GaH$_3$, we also analyzed the band structure of a hypothetical system composed of only the hydrogen sublattice and a compensating background charge ("hydrogen subsystem"). As can be seen in Fig. 3, the band structures of GaH$_3$ and the hydrogen subsystem are qualitatively similar, which basically indicates that the introduction of Ga atoms does not strongly affect the band structure of the hydrogen sublattice. Therefore, the main role of Ga atoms in GaH$_3$ is to donate electrons that go to H-like bands, and Ga associated bands remain unoccupied. The charge transfer from Ga to H atoms indicates a strong ionic character of GaH$_3$, similar to those in AlH$_3$ and LiH$_n$. Compared with the behavior observed in AlH$_3$, near the Fermi energy, the presence of Ga atoms notably shifts the bands down at the $R$ point and slightly up at $M$. In the absence of Ga atoms, the electronic charge associated to states at $R$ piles up around gallium sites; however, when Ga atoms are present, the density profile is highly modified. As is shown in Fig. 4, electronic states at $R$ become highly localized around Ga atoms, and this lowers the energy associated with these states when compared to the hydrogen subsystem, which explains the previously mentioned energy shift in the band structure at $R$. The strong ionic character for H atoms in Pm$_3n$ GaH$_3$ is different from group IV hydrides (i.e., SiH$_4$, GeH$_4$, and SnH$_4$), where the H atoms are either bonded to the nearest H atoms to form semimolecular H$_2$, and/or they are covalently bonded to M (M = Si, Ge, or Sn) atoms to form M-H bonds. Interestingly, the high-pressure phase (Pm$_3m$) of Si$_2$H$_6$ also has H atoms with a strong ionic character, which has shown to favor the superconducting transition characterized by a predicted high

![Figure 3](image-url)  
**FIG. 3.** (Color online) Calculated electronic band structures (full black line) for Pm$_3n$ GaH$_3$ at 160 GPa compared with the hypothetical system composed of the hydrogen subsystem immersed in a jellium background (dashed red line).

![Figure 4](image-url)  
**FIG. 4.** (Color online) Electronic density contribution from states at the $R$ point close to the Fermi energy for Pm$_3n$ GaH$_3$ at 160 GPa, showing the density on the (100) plane for GaH$_3$ (a) and for the hydrogen system (b). Comparison of the densities in the [110] direction is also shown (c). The vertical lines indicate the positions of the Ga sites. Many periodic repetitions are shown for clarity.
The calculated phonon frequency logarithmic average \( \omega_{\ln} \), EPC parameter \( \lambda \), the electronic DOS at Fermi level \( N(E_f) \), and critical temperature \( T_c \) of \( \sim 130 \) K.\(^{37} \) Therefore, we expect that the same trend might also be observed in \( \text{Pm}\overline{3}n \text{GaH}_3 \). The absence of any imaginary frequency phonon modes [see Fig. 5(a)] proves the dynamical stability of the \( \text{Pm}\overline{3}n \) structure within the studied pressure range. As can be seen in Fig. 5(b), the low-energy phonon modes, with frequencies below 11 THz, are mainly associated with Ga atoms, as expected from their much higher atomic mass, while modes with higher frequencies correspond to H atoms.

To explore the superconducting properties, we calculated the electron-phonon coupling (EPC) parameter, \( \lambda \), the logarithmic average phonon frequency, \( \omega_{\ln} \), and the electronic DOS at the Fermi level, \( N(E_f) \), at several pressures (Table I).

According to our calculations, at 160 GPa, \( \lambda \) reaches 0.98, and \( \omega_{\ln} \) is 1271 K, so that the estimated \( T_c \) becomes 76–83 K, considering typical Coulomb pseudopotential parameters, \( \mu^* \), of 0.13 and 0.1, respectively. The large \( T_c \) in the \( \text{Pm}\overline{3}n \) structure is mainly attributed to the strong electron-phonon coupling, \( \lambda \), and the high \( \omega_{\ln} \). In order to understand the origin of this strong \( \lambda \), we also calculated the Eliashberg phonon spectral function, \( \alpha^2 F(\omega)/\omega \), and the partial electron-phonon integral, \( \lambda(\omega) \). As can be seen in Fig. 5(c), although compressed AlH\(_3\) and GaH\(_3\) share the same structure, the resulting Eliashberg phonon spectral functions are quite different. Contrary to AlH\(_3\),\(^{15,17} \) the main contribution to \( \lambda \) in GaH\(_3\) is not associated with phonons around just two modes at the \( X \) point. Similar to the group IVa hydrides,\(^{12–14} \) in GaH\(_3\) there is an overall contribution of different modes to \( \lambda \), and the contribution associated with the previously mentioned two modes around \( X \) becomes negligible [Fig. 5(c)]. Therefore, we also expect that the predicted anharmonic renormalization for AlH\(_3\),\(^{17} \) of these two modes at \( X \) will not affect the calculated \( T_c \) in GaH\(_3\). Note that the low-frequency vibrations provide a contribution of 25\% of the total EPC parameter, while the phonon frequencies between 30–40 THz account for nearly 50\% of \( \lambda \). To further explore the contribution associated with different phonon modes, solid circles with the radius proportional to the electron-phonon coupling are also plotted in Fig. 5(a). Interestingly, phonon modes between 30 and 36 THz along \( M-R \) are primarily responsible for the main peak in the Eliashberg phonon spectral function, \( \alpha^2 F(\omega)/\omega \), and give an important contribution to \( \lambda \). Moreover, these phonon modes are mainly associated with the vibrations of ionic H. Under pressure, all the phonon modes and the spectral function shift to higher energy, and the major contribution of the intermediate phonon modes to \( \lambda \) remains.

With increasing pressure, the calculated \( \lambda \) and the resulting \( T_c \) decrease down to 60 K at 240 GPa. However, \( \lambda \) is predicted to increase up to 1.19 when pressure decreases to 120 GPa, which is the same value as in the \( \text{Cmca} \) structure for solid hydrogen at 428 GPa.\(^{38} \) As is shown in Table I, although the calculated \( \omega_{\ln} \) lowers with decreasing pressure, reaching 1158 K at 120 GPa, the resulting \( T_c \) is predicted to increase up to 102 K, and becomes higher than group IV hydrogen-rich compounds.

In summary, theoretical calculations reveal that a metallic cubic structure for GaH\(_3\) is stable at high pressures

\[ T_c \text{ (K)} \text{ with } \mu^* \text{ = 0.1, 0.13} \]

\begin{align*}
| \text{P(GPa)} | \text{Lambda (}\lambda\text{)} | \omega_{\ln} \text{ (K)} | N(E_f) \text{ states/Spin/Ry/cell} | T_c \text{ (K)} \\
120 & 1.19 & 1158 & 6.65 & 102 \quad 91 \\
160 & 0.98 & 1271 & 6.13 & 86 \quad 73 \\
200 & 0.85 & 1349 & 5.70 & 72 \quad 59 \\
240 & 0.76 & 1407 & 5.33 & 60 \quad 48 \\
\end{align*}
show that the \( \text{Pn}3\text{\textgamma} \) phase of \( \text{GaH}_3 \) is superconducting with a high \( T_c \) of 73–86 K at 160 GPa, and even a much higher \( T_c \) of 102 K might be expected at 120 GPa. Our results demonstrate that hydrogen-rich compounds with H atoms of ionic character might have a higher \( T_c \) than those with H bonded to metal atoms and/or those forming semimolecular \( \text{H}_2 \), supporting the conjecture that hydrogen-rich compounds provide a way to achieve a metallic and superconducting phase at accessible experimental pressures.

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