Superconducting TaH$_5$ at high pressure

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**Abstract**

Recently, the significant development, in the field of high-temperature superconductivity among the compressed elements hydrides (such as LaH$_{10}$), opens up a door in pursuing room-temperature superconductors. Therefore, the investigations of excellent superconductivity in hydrogen-rich materials have become a hot topic of considerable interest. Herein, we explore the stabilities of compressed tantalum polyhydrides TaH$_n$ ($n = 1–6$) and the superconductivity by using a particle swarm optimization structure prediction methodology in combination with the first-principles electronic structure framework. As a result of structure searches, we identified a stable TaH$_5$ compound under high pressure, which consists edge shared TaH$_{12}$ polyhedra. Remarkably, within Allen–Dynes modified McMillan equation, our predicted TaH$_5$ is a superconductor with superconducting critical temperature ($T_c$) of 18–23 K at 100 GPa.

**Introduction**

Bardeen–Cooper–Schrieffer (BCS) theory [1], developed by Bardeen, Cooper and Schrieffer in 1957, is the first microscopic theory that could successfully interpret electron–phonon coupling (EPC) superconductors [2–7]. The BCS theory suggested electron cooper pairs mediated by phonons can transport without any resistance in metal. In this theory, high phonon frequencies and large electronic density of states at the Fermi level are necessary for improving the superconducting transition temperature ($T_c$). As we well known that high pressure may offer a unique degree of freedom to discovery new materials [8–10]. Therefore, hydrogen, as the lightest element in the periodic table, is intuitively considered as a promising candidate for high-temperature superconductor owing to its large vibration frequency, once solid hydrogen becomes a metallic phase at sufficiently high pressure. A large number of theoretical calculations have predicted metallic hydrogen possess high $T_c$ values ranging from 100 to 760 K [11], depending on which crystal structure of solid hydrogen is adopted. To date, the metallization of solid hydrogen, however, has not been indeed verified in many different high-pressure experiments.

In 2004, Ashcroft scientifically suggested that hydrogen dominant metallic alloys have the potential for becoming an alternate way to approach high-temperature superconductor [12], since ‘chemical pre-compression’ mechanism could significantly lower the metallization pressure of hydrogen-rich materials. As early as 1970, 8 K superconductivity was first observed in the hydrogen-rich compound Th$_3$H$_{12}$ at ambient pressure [13]. Much theoretical effort has devoted to the investigation of the superconductivity in the compressed hydrides, however, not many of the predicted phases were confirmed by the later experiments (for example, NaH$_3$ and NaH$_2$ [14], LiH$_2$ and LiH$_6$ [15], FeH$_3$ [16], NbH$_{1.5}$ and NbH$_3$ [17], Ni$_2$H$_3$ [18], TaH$_3$ [19] and CoH$_3$ [18]). Recently, the astonishing discoveries of superconductivity with $T_c$ above 200 K in compressed H$_2$S [20, 21] and LaH$_{10}$ [6, 22–23], both initiated by previous theoretical works, suggested the feasibility of searching for high $T_c$ in hydrogen-rich materials at high pressures. These observations have generated a flurry
of searching for new hydrogen-dominating superconductors under pressures. It has been found that some dense hydrides with hydrogen clathrate frameworks are possible to become potential high-temperature superconductors (e.g. MgH$_2$ [3], CaH$_6$ [4] and YH$_6$ [5]: $T_c >$ 200 K). These theoretical and experimental results indicate hydrogen-rich materials may hold a key to a deep understanding of high-temperature superconducting property.

Among the various H-rich compounds [3–5, 15, 20], metal hydrides as the potential superconductors have attracted attention owing to large density of states at the Fermi level, high phonon frequencies, strong electron–phonon coupling, and lower synthesis pressures. Our recent work indicates Ta could react with hydrogen to form trihydrides at high pressure [19], but no detailed theoretical information on the Ta–H system with hydrogen content larger than 3. In this work, therefore, we have performed extensive structure searches on the Ta–H system at 100 GPa via the first-principles swarm-intelligence structure search. Besides the confirmed Ta–H compounds, we found a hitherto unknown TaH$_5$ phase in the moderate region of pressure, which was not reported in a previous study [24]. Moreover, we systematically studied the structural stability, electronic properties and superconductivity of the TaH$_3$ compound at 100 GPa via first-principle calculations.

Computational details

The structure prediction of the TaH$_n$ ($n = 1–6$) system at 100 GPa was performed by globally minimizing the potential energy surface at varied stoichiometries via an in-house developed crystal structure analysis by particle swarm optimization (CALYPSO) methodology [25, 26] and its same-name code in combination with ab initio density functional theory total-energy calculations. Our CALYPSO method unbiased by any known structural information has been benchmarked on various known systems with various chemical bondings and several successful high temperature superconductor (H$_2$S$_2$, LaH$_{10}$) predictions. The underlying energetic calculations were performed using the plane-wave pseudopotential method within the generalized gradient approximation through the Perdew–Burke–Ernzerhof exchange–correlation functional [27], as implemented in the Vienna Ab Initio Simulation Package code [28]. The electron–ion interaction was described by the projected-augmented-wave potentials with 1$s^2$ and 5$p^6d^56s^2$ as valence electrons for H and Ta, respectively. The kinetic cutoff energy of 600 eV and the Monkhorst–Pack scheme with a k-point grid of $2\pi \times 0.025 \text{ Å}^{-1}$ were chosen to ensure that the total energy well-converged. The phonon calculation for evaluating the lattice dynamic stability was carried out by using a supercell approach through the PHONOPY code [29]. The EPC was calculated within the framework of the linear–response theory as carried out in the Quantum ESPRESSO package [30].

Results and discussion

The variable-composition structure searches were performed at a variety of Ta–H stoichiometries containing up to 4 formula units per simulation cell at 100 GPa. We focused our structure search on the H-rich compounds, which might be potential superconductors. It is well known that the zero-point energy plays an important role in stabilizing these hydrogen-rich materials under high pressure. The energetic stabilities of a series of TaH$_n$ ($n = 1–6$) compounds were evaluated through their formation enthalpies ($\Delta H$) relative to the products of dissociation into constituent elements or compounds at 100 GPa, as depicted in figure 1(a). The H-rich TaH$_5$ is unstable against the dissociation into elemental TaH$_3$ and H$_2$. However, besides the TaH, TaH$_2$, ThH$_3$, and TaH$_4$ phases, a new TaH$_5$ phase becomes energetically favorable over the elemental dissociation and emerges on the convex hull.

The energetically favored structure of TaH$_5$ was predicted to crystallize in a monoclinic structure (space group P2$_1$/c). The lattice parameters are $a = 2.94$ Å, $b = 3.12$ Å, $c = 10.59$ Å, and $\beta = 104.09^\circ$, with atomic positions of Ta at 4e (0.628, 0.027, 0.375) and H atoms at 4e (0.694, 0.537, 0.290), (0.922, 0.311, 0.205), (0.847, 0.646, 0.625), (0.216, 0.708, 0.959) and (0.271, 0.032, 0.043). It consists of 12 coordinated Ta atoms with the formation of edge shared TaH$_{12}$ polyhedra (figure 2(a)). Furthermore, we performed the electron localization function to understand chemical bonding feature of this predicted structure at high pressure. The results clearly show typical ionic bonding feature in this structure, as shown in figure 2(b). The calculated enthalpy curve of our predicted structure is presented relative to elemental decomposition for TaH$_3$ and H as a function of pressure in figure 1(b). It is found that TaH$_5$ hydride becomes thermodynamically stable with respect to decomposition of its competitive phase above 35 GPa. In order to check the lattice dynamic stability of TaH$_5$, we have simulated the phonon spectrum as shown in figure 3(a). The absence of any imaginary frequency in the whole Brillouin zone (BZ) clearly indicates the dynamical stability of this predicted phase.

Motivated by the search for metallic and high superconducting $T_c$, hydrogen-rich compounds within the reach of current experimental techniques, we analyzed the electronic properties and superconductivity of the
stable TaH₅ structure. From the calculated electronic band structure and projected density of state for the predicted TaH₅ phase, as illustrated in figure 3(b), it was found that the new phase exhibits good metallic feature. In this compound, the Ta₉ and H₈ electrons mainly contribute the valence band, and the most of the electronic states above the Fermi level are from Ta₉ electrons. To explore its superconducting property, we estimated the superconducting temperature of our predicted structure using the Allen–Dynes modified McMillan equation based on the BCS theory. We derived Tc from the spectral function, α²F(ω), within a typical Coulomb pseudopotential of μ* = 0.1–0.13.
Here, $\lambda$ is described as below:

$$\lambda = 2 \int_0^{\infty} \frac{\alpha^2 F(\omega)}{\omega} d\omega \approx \sum_q \gamma_q \omega(q),$$

where $\omega(q)$ is the weight of a $q$ point in the first BZ, and the EPC spectral function, $\alpha^2 F(\omega)$, is expressed in terms of the phonon line width, $\gamma_q$, arising from EPC

$$\alpha^2 F(\omega) = \frac{1}{2\pi N_f} \sum_q \gamma_q \delta(\omega - \omega_q) \omega(q).$$

Here, $N_f$ can be understood as the electronic density of electron state at the Fermi level of predicted structure. The linewidth, $\gamma_q$, of phonon mode $j$ at wave vector $q$ arising from EPC is

$$\gamma_q = 2\pi \omega_q \sum_{nm} \int_{\Omega_{BZ}} \frac{d^3k}{\Omega_{BZ}} |g^{\dagger}_{n,k,q}\rangle |g_{m,k+q,m}\rangle^2 \times \delta(\xi_{kn} - \xi_{k}) \times \delta(\xi_{k+q,m} - \xi_{k}).$$

According to our EPC simulations, $\lambda$ reaches 0.69 and $\omega$ is 642 K at 100 GPa. As a result, the $T_c$ of TaH$_5$ is estimated to be 23–18 K, considering typical Coulomb pseudopotential parameter of $\mu^* = 0.1–0.13$. 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 figure 4. Within the phonon DOS, the phonon
density of states divided the vibrational modes into two subsets and the contribution from the Ta–H framework is minor, comparing with the H–H bond stretching. We decompose the total λ into individual contributions and found that the H–H stretching modes give the notable contribution (70%) to the EPC parameter, making a decisive contribution to improve superconducting critical temperature.

Conclusion

In summary, we have performed a systematic simulation on the Ta–H system at high pressure. Our theoretical calculations reveal that a metallic monoclinic structure for TaH₅ is stable at moderate pressure region. Our more results demonstrate that compressed TaH₅ is ionic hydride with superconductivity. EPC calculation shows that the transition temperature of our predicted TaH₅ phase is approximately 18–23 K at 100 GPa. Our current results provide a new superconducting candidate of metal hydrides and a possible synthesis at accessible experimental pressures.

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