Dynamical stability and superconductivity of (Ce,La)H$_9$ under high pressure

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Recent experiments have shown that CeH$_9$ and (Ce,La)H$_9$ can be synthesized under high pressure between 90-170GPa and become a superconductor with a high value of superconducting critical temperature ($T_c$) between 100-200K. In this work, we performed a theoretical study of a (Ce,La)H$_9$ compound where the Ce:La ratio is equal to 1. We used the density functional theory and the $ab$ initio molecular dynamics (AIMD) method. From the phonon dispersion, there exist some unstable modes around the K-point phonons. Then, we performed AIMD simulation at around 203K and found that the compound becomes stable. The superconducting spectral function can be calculated. We found that $\lambda$ is as high as 3.0 at 200GPa. By using Allen-Dynes-modified McMillan equation in the strong coupling regime, we found that $T_\text{c} \approx 87K$ at 200GPa.

INTRODUCTION

In 1968, Ashcroft suggested that metallic hydrogen can become a conventional superconductor with a high value of critical temperature [1]. He also pointed out that metal hydrides could become a superconductor [2,3]. Since then, the search for metallic hydrogen and hydride superconductors has been extensively explored by both theory and experiments [4-20]. Metal superhydrides have recently attracted much more of the scientific attention because they can be synthesized and characterized under high pressure. Furthermore, some of them have been found to be a superconductor with a close-to-room-temperature superconducting critical temperature ($T_c$). For instance, the $T_c$ of LaH$_{10}$ has been measured to be 250K under high pressure [21].

In 2019, cerium superhydride CeH$_9$ has been synthesized under high pressure between 80 and 100GPa by using the laser-heated diamond anvil cell combined with synchrotron X-ray diffraction [14]. It was found that CeH$_9$ is a hexagonal structure with a space group of P6$_3$/mmc. Its $T_c$ has been theoretically estimated to be 105 - 117K [14]. Recently, the (La,Ce)H$_x$ compounds have been successfully synthesized at pressure lower than 130GPa by Chen et al. [22]. They discovered that the compound resembles (La,Ce)H$_9$ with $T_c$ equal to 176K at 100GPa.

At the current stage, the trend has moved from searching for the superconductivity of a binary compound to searching for the superconductivity of a ternary hydride compound. This is because the mixing of different atomic species in the making of ternary compounds offers a slight and perhaps controllable modification to the electronic and dynamical properties of the hydride compounds, which sometimes tends to enhance $T_c$ [12, 17, 20, 23-26]. For example, Mg can be used as a substitution for Ca in the CaH$_6$ compound [17]. It is found that Mg$_{0.5}$Ca$_{0.5}$H$_6$ compound is stable at 200GPa and become a superconductor with $T_c \approx 288K$.

In this work, we performed the simulation of the Ce/La substituted of (Ce,La)H$_9$ at 200GPa, as both CeH$_9$ and LaH$_9$ share a common hexagonal structure with a space group of P6$_3$/mmc [14, 27, 28]. The hexagonal structure is also suggested by the experiment for the La-Ce-H compounds [22]. We calculated the electron-phonon interaction and evaluated the Eliashberg spectral function by the density functional theory (DFT). The $T_c$ can then be approximated. We also preformed the $ab$ initio molecular dynamics (AIMD) to examine the dynamical stability of (Ce,La)H$_9$.

COMPUTATIONAL DETAILS

In this work, we performed the DFT calculations with the generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA-PBE) functional [29] for the exchange-correlation functional, and the projector augmented wave (PAW) method [30], as implemented in the quantum espresso (QE) [31,32]. For the calculation of the electron-phonon interaction, a plane-wave energy cutoff of 60Ry was used. The electron-phonon coupling (EPC) matrix elements were computed in the first Brillouin-zone (BZ) on $4\times4\times2$ q-meshes using individual EPC matrices obtained with $24\times24\times16$ k-point meshes. The Allen-Dynes-modified McMillan equation [33] was used for the estimating $T_c$.

For the electronic structure, we used a plane-wave basis set with the cutoff energy of 600eV and the first BZ with $12\times12\times8$ k-point meshes. The pseudocore radii of Ce, La, and H are 2.57Bohr, 2.80Bohr, and 1.1Bohr, which are small enough to ensure that no core overlapping will occur at 200GPa. For $ab$ initio molecular dynamics (AIMD), the simulation was performed by using...
the \textit{NPT} ensemble with 160 atoms per supercell. The AIMD simulation was carried out at 203K and 200GPa. Both the electronic structure and AIMD were calculated by using the Vienna \textit{ab initio} simulation package (VASP) [34].

\section*{RESULTS AND DISCUSSION}

As both CeH$_9$ and LaH$_9$ share a common hexagonal structure with a space group of P6$_3$/mmc [14, 27, 28], as shown in Fig. 1(a). The unit cell of the P6$_3$/mmc structure contains two metal sites. We modelled the (Ce,La)H$_9$ compound by inserting an La atom into one of the metal site, and a Ce atom into the others. The Ce:La ratio is equal to 1. The symmetry is reduced from the space group of P6$_3$/mmc to P6m2, as shown in Fig. 1(b).

The electronic structures are shown in Fig. 2(a). Under high pressure, the (Ce,La)H$_9$ compound becomes metallic. The band dispersions exhibit the weaving of the up-running bands from below E$_F$ and down-running bands above E$_F$, similar to those of CeH$_9$ [14], CeH$_{10}$ [35], and LaH$_{10}$ [36]. The corresponding projected density of states (PDOS) of (Ce,La)H$_9$ is also shown in Fig. 2(a). There are several places near the Fermi level where the electronic structures exhibit flat dispersions, such as around the H-point and M-point. These flat dispersions lead to the so-called van Hove singularity (vHs). The vHs is marked by an arrow in Fig. 2(a). The Fermi surface topology (FST) is shown in Fig. 2(b). The FST exhibits a number of parallel surfaces, which should lead to Fermi surface nesting and enhance superconductivity.

As T$_c$ can be related to the number of electronic states at the Fermi surface, it is useful to consider the local density of states (LDOS) [37,38], which is defined as

\begin{equation}
N(E, r) = \sum_n \int \frac{d^3 k}{(2\pi)^3} \delta(E - \epsilon_{nk}) |\psi_{nk}(r)|^2,
\end{equation}

where $\psi_{nk}(r)$ and $\epsilon_{nk}$ are the Kohn-Sham eigenfunctions and eigenvalues of the system. The LDOS allows us to evaluate the number of the electronic states at the Fermi level, which can be related to electron pairings in the superconducting state. The LDOS indicates that the Fermi surface of the (Ce,La)H$_9$ compound contains 0.91 states/eV.

Next, we calculated the isotropic Eliashberg spectral function, which is written as

\begin{equation}
\alpha^2 F(\omega) = \frac{1}{N_F} \sum_{\nu, k, k'} |g^\nu_{kk'}|^2 \delta(\epsilon_k) \delta(\epsilon'_{k'}) \delta(\omega - \omega_{\nu k}),
\end{equation}

where $N_F$ is the density of states at the Fermi level, $k$ and $k'$ are the electronic states, and $\nu$ are the phonon modes. $N_{\nu k}$ ($N_{\nu q}$) is the total number of $k$ ($q$) points in the simulation cell, $\epsilon_k$ is the energy eigenvalue of the Kohn-Sham state with respect to the Fermi level, and $g^\nu_{kk'}$ is the electron-phonon matrix elements for the scattering between the electronic states $k$ and $k'$ via a phonon with wave vector $q = k' - k$, and $\omega_{\nu k}$ are the frequencies of phonon modes $\nu$ and phonon band $\nu$. The calculated Eliashberg spectral function $\alpha^2 F(\omega)$ is shown in the right panel of Fig. 3.

The corresponding phonon dispersions are also shown in the left panel of Fig. 3. It is obvious that the acoustic modes are well-seperated from the optical modes. The optical modes are in the frequency range between 360cm$^{-1}$ and 1814cm$^{-1}$. The acoustic modes are in the frequency range between 0-281cm$^{-1}$, and contain several imaginary frequencies around the K-point phonon modes, as shown in the left panel of Fig. 3. These modes indicate that the (Ce,La)H$_9$ compound with the hexagonal structure would indeed be an unstable structure. We will reexamine this point in more detail later.

From $\alpha^2 F(\omega)$, we can evaluate the average coupling strength $\lambda$ as a function of $\omega$ by

\begin{equation}
\lambda(\omega) = 2 \int_0^\omega d\omega' \frac{\alpha^2 F(\omega')}{\omega'},
\end{equation}

This is the so-called accumulated $\lambda(\omega)$. The result of $\lambda(\omega)$ is also shown in the right panel of Fig. 3. The total $\lambda$ can be obtained by integrating over all available frequencies. We found that for (Ce,La)H$_9$, $\lambda$ is as high as
3.0. Thus, the electron-phonon interaction in (Ce,La)H$_9$ enters the strong coupling regime. As a consequence, we chose the Allen-Dynes-modified McMillan equation with strong coupling correction for describing the superconducting critical temperature, as follows:

$$T_c = f_1 f_2 \frac{\omega_{\text{log}}}{1.2} \exp \left[ - \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],$$

(4)

We chose $\mu^* = 0.1$. We found that $f_1$ and $f_2$ are 1.22 and 1.20, respectively. The $\omega_{\text{log}}$ is 327K. We found that $T_c$ is 87K. Despite of the large value of $\lambda$ and $N(E_F)$, the $\omega_{\text{log}}$ is very low. This is because the bandwidth of $\alpha^2 F(\omega)$ is very large [15]. As a result, $T_c$ becomes not as high as we might expect.

At this stage, we discuss the structure stability. From the phonon dispersion in the left panel of Fig. 3, there exist some unstable phonon modes at 0K. In order to take the effects of temperature into account, we performed the AIMD simulation, with the NPT ensemble. The simulation cell was construct from a $2 \times 2 \times 2$ hexagonal supercell with 160 atoms. We chose temperature of 203K and pressure of 200GPa. The energy as a function of time is shown in Fig. 4 (a). The time step is 1 fs. We performed the AIMD integration to 1,000 time step. After the simulation is in equilibrium, we took several snapshots, as shown in Fig. 4 (b)-(e). The hexagonal structure remains stable during the simulation time. The AIMD simulation suggests that the effects of temperature would help stabilize the hexagonal structure of the (Ce,La)H$_9$ compound.

CONCLUSION

We studied the dynamical stability and superconductivity of the (Ce,La)H$_9$ compound. The symmetry is reduced from the space group of P6$_3$/mmc, as of CeH$_9$ and LaH$_9$, to P6$m2$. The phonon dispersions showed some unstable phonon modes around the K-point phonons. However, the Eliashberg spectral function can still be evaluated. We found that $\lambda$ is as high as 3.0 and $N(E_F)$ is as large as 0.91 states/eV. Despite of high values of these favorable parameters, the $\omega_{\text{log}}$ appears to be very low. This results in a low $T_c = 87K$.

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