Origin of enhanced chemical precompression in cerium hydride CeH₉

Hyunsoo Jeon, Chongze Wang, Seho Yi & Jun-Hyung Cho

The rare-earth metal hydrides with clathrate structures have been highly attractive because of their promising high-\(T_c\) superconductivity at high pressure. Recently, cerium hydride CeH₉ composed of Ce-encapsulated clathrate H cages was synthesized at much lower pressures of 80–100 GPa, compared to other experimentally synthesized rare-earth hydrides such as LaH₁₀ and YH₆. Based on density-functional theory calculations, we find that the Ce 5\(p\) semicore and 4\(f\)/5\(d\) valence states strongly hybridize with the H 1\(s\) state, while a transfer of electrons occurs from Ce to H atoms. Further, we reveal that the delocalized nature of Ce 4\(f\) electrons plays an important role in the chemical precompression of clathrate H cages. Our findings not only suggest that the bonding nature between the Ce atoms and H cages is characterized as a mixture of ionic and covalent, but also have important implications for understanding the origin of enhanced chemical precompression that results in the lower pressures required for the synthesis of CeH₉.

In recent years, rare-earth metal hydrides have attracted much attention due to the possibility of their realization of room-temperature superconductivity (SC)\(^1\)–\(^8\). First-principles density-functional theory (DFT) calculations together with the Migdal–Eliashberg formalism have predicted that rare-earth metal hydrides such as yttrium, lanthanum, cerium hydrides host high-\(T_c\) SC at megabar pressures\(^9\),\(^10\), the origin of which is based on phonon-mediated electron pairing\(^11\). Subsequently, such a conventional SC of LaH₁₀ was experimentally observed with a superconducting transition temperature \(T_c\) of 250–260 K at a pressure of \(\sim\)170 GPa\(^3\),\(^4\). This \(T_c\) record of LaH₁₀ has been the highest temperature so far among experimentally available superconducting materials including cuprates\(^12\),\(^13\) and Fe-based superconductors\(^14\),\(^15\). Therefore, the experimental realization of room-temperature SC in LaH₁₀ has stimulated interests of the high-\(T_c\) community towards compressed metal hydrides under high pressure\(^16\)–\(^23\).

However, since the synthesis of LaH₁₀ was performed at \(\sim\)170 GPa\(^3\),\(^4\), it has been quite demanding to discover H-rich rare-earth hydrides synthesized at a moderate pressure below \(\sim\)100 GPa, which is easily and routinely achievable in the diamond anvil cell (DAC)\(^24\),\(^25\). Motivated by the first theoretical prediction of cerium hydride CeH₉ with a clathrate hydrogen cage structure, two experimental groups\(^5\),\(^6\) achieved its successful synthesis at a lower pressure of 80–100 GPa. X-ray diffraction measurements and DFT calculations\(^5\),\(^6\) confirmed the previously predicted\(^9\) crystal structure of CeH₉, which adopts a hexagonal clathrate structure with the space group P\(\bar{6}\)₃\(/\text{mmc}\). Here, each Ce atom is surrounded by the H\(_{29}\) cage consisting of 29 H atoms (see Fig. 1a). It is remarkable that the H–H bond lengths in CeH₉ are close to those of solid metallic hydrogen that can be produced at high pressure above 400 GPa\(^26\)–\(^29\). Therefore, the discovery of CeH₉ having clathrate hydrogen networks suggests that the metallic state of solid hydrogen can be attained at relatively lower pressures by using binary hydrides with \(f\)-electron metals. It is noteworthy that the sizable reduction of H–H bond lengths in CeH₉ reflects the presence of a larger chemical precompression\(^30\)–\(^32\) compared to other rare-earth metal hydrides such as LaH₁₀ and YH₆\(^9\),\(^10\),\(^33\)–\(^37\). However, the underlying mechanism of how the pressure required for the synthesis of CeH₉ is much reduced is yet to be identified.

In this paper, we investigate the electronic structure and bonding properties of CeH₉ at high pressure using first-principles DFT calculations with the inclusion of Hubbard on-site Coulomb interaction. The calculated band structure of CeH₉ shows a strong hybridization of the Ce 5\(p\) semicore and 4\(f\)/5\(d\) valence states with the H 1\(s\) state. We reveal that the delocalized nature of Ce 4\(f\) electrons contributes to yield a much larger chemical

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precompression of clathrate H$_{29}$ cages along the c axis than in the a–b plane. Despite a strong hybridization between the Ce- and H-derived electronic states, our Bader charge analysis shows a charge transfer from Ce to H atoms, thereby suggesting that the bonding nature between the Ce atoms and H$_{29}$ cages features the mixed ionic and covalent bonding. The present results provide new insight into understanding the underlying mechanism of the chemical precompression that requires relatively lower pressures for the synthesis of CeH$_9$\textsuperscript{5,6}, compared to other experimentally synthesized rare-earth hydrides LaH$_{10}$\textsuperscript{24} and YH$_6$\textsuperscript{24}.

Results and discussion

We begin by optimizing the structure of CeH$_9$ using the PBE + U calculation. Figure 1a shows the optimized structure of CeH$_9$ at a pressure of 100 GPa, which is the same pressure employed in previous DAC experiments\textsuperscript{5,6}. Here, Ce atoms form a hcp lattice (see Fig. 1b) with the lattice constants $a = b = 3.717$ Å and $c = 5.666$ Å, in good agreement with the experimental\textsuperscript{5,6} data of $a = b = 3.66$ Å and $c = 5.58$ Å. Meanwhile, the H$_{29}$ cage surrounding a Ce atom is constituted by six tetragon rings, six pentagon rings, and six hexagon rings (see Fig. 1c).

Note that there are three species of H atoms [termed H–H and Ce–H bonds. The charge densities at the midpoints of the H$_1$–H$_2$ and H$_1$–H$_3$ bonds are close to those (0.98 and 1.21 Å) predicted from metallic hydrogen at ~500 GPa\textsuperscript{28}. It is thus likely that the synthesized CeH$_9$ binary compound CeH$_9$ with the clathrate H$_{29}$ cages is able to generate H networks comparable to metallic hydrogen even at a low pressure of 100 GPa.

Figure 2a shows the calculated total charge density $\rho_{\text{tot}}$ of CeH$_9$. It is seen that H atoms in the H$_{29}$ cage are bonded to each other with covalent-like bonding. Here, the charge densities of H–H and Ce–H bonds exhibit the saddle-point characters at their midpoints, similar to that of the C–C covalent bond in diamond\textsuperscript{38}. As shown in Fig. S1 in the Supplementary information, the calculated electron localization function also shows the covalent-like H–H and Ce–H bonds. The charge densities at the midpoints of the H$_1$–H$_2$, H$_1$–H$_3$, and H$_3$–H$_3$ bonds are 0.39, 0.56, and 0.85 e/Å\textsuperscript{3}, respectively. These values in CeH$_9$ are larger than the corresponding ones (0.32, 0.45, and 0.76 e/Å\textsuperscript{3} in Fig. 2b) obtained from the isolated H$_{29}$ cages whose structure is taken from the optimized structure of CeH$_9$.

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−9.47e (including the 5s^2 5p^6 semicore electrons), −1.34e, −1.31e, and −1.09e, respectively. Thus, we can say that Ce atoms lose electrons of 2.53e per atom, while H_1, H_2, and H_3 atoms gain electrons of 0.34e, 0.31e, 0.09e per atom, respectively.

In Fig. 3a, we display the calculated band structure of CeH_9 together with the local density of states (LDOS) for Ce and H atoms. The narrow bands located at ∼2 eV above E_F originate from Ce 4f electrons, while those located at around −20 eV below E_F are associated with Ce 5p semicore electrons. It is noticeable that the LDOS shape of Ce atoms is very similar to that of H atoms in the energy range between −15 eV and E_F, indicating a strong hybridization between Ce and H electronic states. In order to resolve the orbital characters of electronic states, we plot the partial density of states (PDOS) projected onto the Ce 5p-semicore and 4f/5d-valence states and the H 1s state in Fig. 3b. We find that the Ce 5p-semicore states are extended upward to reach up to E_F, while the 4f- and 5d-valence states are distributed downward to about −10 and −13 eV below E_F, respectively. Hence, these delocalized semicore and valence states hybridize well with the H 1s state. Such a strong hybridization between Ce and H electrons is likely associated with the Ce-encapsulated spherical H-cage structure of CeH_9. Consequently, the electron charges of Ce and H atoms show covalent characteristics between the Ce and H atoms, respectively.

Figure 2. Calculated total charge density ρ_tot of (a) CeH_9 and (b) isolated H_29 cages. The saddle points of charge densities between Ce and H_1/H_2/H_3 atoms are marked “×” in (a). The charges densities in (a) and (b) are plotted on the (110) plane with the contour spacings of 0.07 e/Å^3. The charge density difference ∆ρ (defined in the text) is displayed in (c), with the contour spacing of ±0.03 e/Å^3. The Bader basins of Ce and H atoms are displayed in (d).

Figure 3. (a) Calculated band structure of CeH_9 together with the LDOS for Ce and H atoms. The energy zero represents E_F. The PDOS of CeH_9 is also given in (b).
We find that in the pressure range between 100 and 160 GPa, both the lower synthesis pressure of larger values of the f-core and (iii) the delocalized nature of Ce 4f electrons. The occupation of f electrons. Here, we note that Ce atom with the electron configuration [Xe]4f15d6s2 has one 4f electron, while La atom with [Xe]5d6s2 represents no occupation of f orbitals. It is thus expected that the lower synthesis pressure of CeH9 would be caused by the presence of the delocalized Ce 4f states (see Fig. 3b). To confirm how the delocalized nature of Ce 4f electrons contributes to the chemical precompression of H32 cages, we optimize the structure of CeH9 as a function of pressure using the f-core scheme, where Ce 4f electrons are considered as core electrons. Therefore, the interactions of 4f electrons with valence electrons are completely removed to simulate the localized nature of 4f electrons. The band structure and PDOS of CeH9 calculated using the f-core scheme are displayed in Fig. S2. We find that the band dispersions of the Ce 5d and H 1s states change largely around EF because their hybridizations with the Ce 4f states are avoided in the f-core scheme. In Fig. 4a, the lattice parameters computed using the f-core scheme are compared with those of the f-valence scheme as well as the experimental data. We find that in the pressure range between 100 and 160 GPa, both the f-core and f-valence schemes predict similar values for a and b, close to the experimental values2. However, the f-core scheme predicts larger c values than the f-valence scheme and experiment3 by ~6% in the same pressure range. As a result, in contrast to both the f-valence scheme and experiment1, the f-core scheme gives relatively larger values of the c/a ratio between 100 and 160 GPa (see Fig. 4b). These results indicate that the delocalized nature of Ce 4f electrons plays an important role in determining the chemical precompression along the c axis, while it hardly affects the chemical precompression in the a–b plane.

In order to check whether the localized/delocalized nature of Ce 4f electrons influences the dynamical stability of CeH9, we calculate the phonon spectrum at 100 GPa using both the f-core and f-valence schemes. The calculated phonon spectrum of the f-core scheme exhibits imaginary frequencies in the whole Brillouin zone [see Fig. S3(a) in the Supplementary information], indicating that CeH9 is dynamically unstable. On the other hand, the f-valence scheme shows that CeH9 is dynamically stable without any imaginary-frequency phonon mode [see Fig. S3(b)]. Therefore, we can say that the delocalized nature of Ce 4f electrons is necessary for stabilizing the clathrate structure of CeH9.

Conclusion

Our first-principles DFT + U calculations for CeH9 have shown that (i) the Ce 5p semicore and 4f/5d valence states strongly hybridize with the H 1s state, (ii) the charge transfer occurs mostly from Ce to H1 and H2 atoms, and (iii) the delocalized nature of Ce 4f electrons is an essential ingredient in the chemical precompression of clathrate H32 cages. The present results not only suggest that the bonding nature between the Ce atoms and H cages is characterized as a mixture of ionic and covalent, but also provide an explanation for the enhanced chemical precompression in CeH9. We thus proposed that the large chemical precompression of H-rich clathrate structures can be attained in rare-earth hydrides with delocalized 4f electrons. It is noteworthy that, according to DFT calculations, PrH6 with clathrate H cages begins to destabilize at a pressure below about ~100 GPa, which is relatively lower than that (226 GPa) of YH10. These different destabilization pressures of PrH6 and YH10 are likely to reflect the variation of chemical precompression, due to the influence of delocalized f electrons. Indeed, PrH6 was experimentally synthesized at a pressure of ~100 GPa. We also note that YH6 containing no f electrons begins to destabilize at a pressure below ~72 GPa, which is much lower than that (~226 GPa) of YH10. Here, the different stabilization pressures of YH6 and YH10 were explained20 in terms of the size of Y atom: i.e., YH10 having denser, larger hydrogen cages with shorter H–H distances requires a higher stabilization pressure.

Methods

Our DFT calculations were performed using the Vienna ab initio simulation package with the projector-augmented wave method14–16. For the exchange-correlation energy, we employed the generalized-gradient approximation functional of Perdew–Burke–Ernzerhof (PBE)17. The 5s5p5 semicore electrons of Ce atom were included.
in the electronic-structure calculations. For Ce 4f electrons, we considered the effective on-site Coulomb interaction of $U_{eff}(U-U_J) = 4$ eV, where the Hubbard parameter $U$ is 4.5 eV and the exchange interaction parameter $J$ is 0.5 eV. A plane-wave basis was used with a kinetic energy cutoff of 1000 eV. The k-space integration was done with 12$\times$12$\times$8 k-points for the structure optimization and 24$\times$24$\times$16 k-points for the DOS calculation. All atoms were allowed to relax along the calculated forces until all the residual force components were less than 0.005 eV/Å. Phonon calculations were performed by a finite displacement method with the PHONOPY code.  

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Author contributions
H.J., C.W., and S.Y. contributed equally to this work. J.H.C. designed the research; H.J. and C.W. performed the theoretical calculations; all the authors analyzed the data and wrote the paper.

Competing interests
The authors declare no competing interests.

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