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RESEARCH ARTICLE

Ab initio studies of copper hydrides under high pressure

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The crystal structure, electronic structure, and superconductivity of copper hydrides at high pressure have been studied by *ab initio* calculation. Consistent with experimental report, results show that the predicted stoichiometry Cu_2H with the P-3m1 space group is stable above 16.8 GPa. The stoichiometry of CuH with the Fm-3m space group is predicted to be synthesized above 30 GPa, but it is metastable and dynamical instable up to 120 GPa. The electronic band calculations reveal that Cu_2H is a good metal at a stable pressure range, whereas CuH is an insulator. Moreover, the other hydrogen-rich compounds CuH_2 and CuH_3 are thermodynamically and dynamically unstable, respectively. The calculated superconducting transition temperature (T_c) of Cu_2H at 40 GPa is 0.028 K by using the Allen-Dynes modified McMillan equation.

Keywords copper hydrides, superconductivity, density functional theory

1 Introduction

Although hydrogen has a high chemical activity, transition metals in group 6 to group 11, expect palladium (Pd), can barely react with hydrogen at normal temperature and pressure. Fortunately, high pressure conditions can help to discover new substances, new phenomena and new properties that are difficult to produce under normal conditions [1–6]. For hydrogen, high-pressure can improve its chemical potential, causing it to combine with transition metals to form the transition metal hydrides (such as PtH [7], WH_2 [8], RhH_2 [9], CoH_2 [10, 11], IrH_3 [12], FeH_3 [13], and even FeH_5 [14]). The synthesis of copper hydrides has been studied since 1844. In chemistry, it was first synthesized with Wurtz method [15] by reacting hypophosphorous acid with copper sulphate. Recently, Cu_2H was synthesized by diamond anvil cells under high pressure [16]. The results of synchrotron powder X-ray diffraction (XRD) show that a new stoichiometric composition of Cu_2H is confirmed at 18.6 GPa and remains stable up to 51 GPa. It is the first time in the experiment to report the synthesis of copper hydrides at the high pressure. The Cu_2H possesses P-3m1 space group and each unit contains one hydrogen atom and two copper atoms. CuH has been synthesized by the way of sonochemistry [17]. But there exists a lot of controversy about the stability of CuH. It is reported that CuH produced through a chemical method is unstable under ambient conditions. CuH decomposes at pressures below 8.4(6) GPa at room temperature conditions [18], although it can be stored permanently at low temperature [19]. In addition, a formation pressure of 30 GPa of CuH was predicted [18] by considering the Gibbs free energy calculations.

Hydrogen-rich materials are considered to be potential high temperature superconductors at low pressures due to "chemical pre-compression" proposed by Aschroft in 2004 [20]. For example, the new sulfur hydride H_3S [21, 22] has been predicted theoretically to possess a high T_c of 191–204 K at 200 GPa, and has been verified via the high-pressure experiment [23], indicating that room-temperature superconductivity can be achieved in compressed hydrogen-rich materials. For transition metal hydrides, YH_4, YH_6, and YH_{10} were predicted theoretically to be superconductors with high T_c of 84–95, 251–264 and 287–303 K at high pressure, respectively [24, 25]. The Fm-3m-LaH_{10} whose structure is the same as that of YH_{10}, is predicted theoretically to be 274–286 K at 210 GPa [26]. Subsequently, the Fm-3m-LaH_{10} is confirmed that its T_c is 260 K at 180–200 GPa [27]. Therefore, we wonder if hydrogen-rich CuH compounds are able to be synthesized at the high pressure and if they will be potential superconductors.

In this study, to understand the experimental synthesis of Cu_2H, solve the debate on CuH stability, and explore the superconductivity of H-rich CuH compounds, we focus our studies on crystal structure, electronic structure, dynamics and superconductivity of copper hydrides by combining *ab initio* density functional theory and evolutionary algorithm. The results show that Cu_2H is predicted to be synthesized above 16.8 GPa, which is in excellent agreement with experimental report. The stoichiometry of CuH

is dynamically instable below 120 GPa, which solves a long-time debate on CuH stability at high pressure. The electronic band calculations reveal that Cu_2H is a good metal in a stable pressure range, whereas CuH is an insulator. The other hydrogen-rich compounds CuH_2 and CuH_3 are thermodynamically unstable and dynamically unstable, respectively. The T_c of Cu_2H at 40 GPa is 0.028 K, which is much lower than YH_6. The low T_c of Cu_2H suggests that a large hydrogen fraction may be required to produce a high T_c for hydrogen-rich materials.

2 Computation details

To explore the structures and stability of Cu-H system under high pressure, we employ the evolutionary algorithm USPEX (Universal Structure Predictor: Evolutionary Xtallography) [28–30] and AIRSS (*ab initio* random structure searching) method [31, 32]. They are very effective in predicting high-pressure crystal structures [33–36]. A plane-wave basis set cutoff of 300 eV and grid spacing of $2\pi \times 0.05$ Å^{-1} are sufficent to predict crystalline structures. The Perdew–Burke–Ernzerhof of the generalized gradient approximation (GGA) [37] and the all-electron projector-augmented wave method are used [38], implemented in the Vienna *ab initio* simulation package VASP code [39]. The $1s^1$ of H and the $3d^{10}4s^1$ of Cu are treated as valence electrons. Geometrical optimization is performed at high accuracy with the plane-wave basis set cutoff of 350 eV and a grid spacing of $2\pi \times 0.03$ Å^{-1}. The lattice dynamics and superconducting properties of Cu_2H are calculated by means of density functional perturbation theory [40], as implemented in the QUANTUM ESPRESSO code [41]. The norm-conserving pseudopotentials for H and Cu are used. Convergence tests give a kinetic energy cutoff of 80 Ry and Brillouin zone (BZ) sampling of $16 \times 16 \times 16$ Monkhorst-Pack [42]. A $4 \times 4 \times 4$ q-mesh in the first BZ is used to evaluate the phonon band structure. The phonon dispersion curves of CuH and CuH_3 are calculated by using a supercell approach, as implemented in the PHONON code [43]. The $4 \times 4 \times 4$ and $3 \times 4 \times 2$ supercells are suitable for CuH and CuH_3, respectively.

We evaluated the T_c by employing the Allen-Dynes modified McMillan equation, [44] which was derived on the basis of the strong coupling BCS theory:

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

$$\lambda = 2\int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} \mathrm{d}\omega , \quad (2)$$

where λ is the electron-phonon coupling constant, $\omega_{\log}$ is the logarithmic average frequency that can be directly obtained by calculating the phonon dispersion curves and μ^* is the Coulomb pseudopotential, where $\mu^* = 0.10$–0.13, which is suitable for hydrogen-rich materials. The Eliashberg spectral function $\alpha^2 F(\omega)$ is written as following:

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(\varepsilon_F)} \sum_{qv} \frac{\gamma_{qv}}{\omega_{qv}} \delta(\omega - \omega_{qv}) , \quad (3)$$

where $N(\varepsilon_F)$ is the electronic density of states at the Fermi level. The linewidth of a phonon mode arising from electron–phonon interaction is given by

$$\gamma_{qv} = 2\pi\omega_{qv} \sum_{mn} \sum_{k} |g_{k+q,k}^{qv,mn}|^2 \delta(\varepsilon_{k+q,m} - \varepsilon_F)\delta(\varepsilon_{k,n} - \varepsilon_F) , \quad (4)$$

where $|g_{k+q,k}^{qv,mn}|^2$ is square of the electron–phonon matrix element and the sum is over the BZ, and ε_k are the energies of bands according to the Fermi level at point k.

3 Results and discussion

We first predict the variable composition structure at 100 GPa by the AIRSS method and observe that Cu_2H and CuH are stable. We then predict the constant composition structure of Cu_2H and CuH_n (n = 1–3) at different pressures through the USPEX code. The calculated formation enthalpy (ΔHf) of the most favorable structures of the Cu–H system with respect to the elemental solids at 40, 100, 160, 200, and 300 GPa are provided in Fig. 1. Stoichiometries that are thermodynamically stable at the studied pressure can be deduced by constructing tie-lines. The convex hull is plotted in solid black and connects the thermodynamically stable compositions, which can be synthesized experimentally in principle. As shown in Fig. 1, at 40 GPa, Cu_2H is the first and only stable composition on the convex hull. It is also the global minimum stoichiometry untill 160 GPa. This stoichiometry is stable

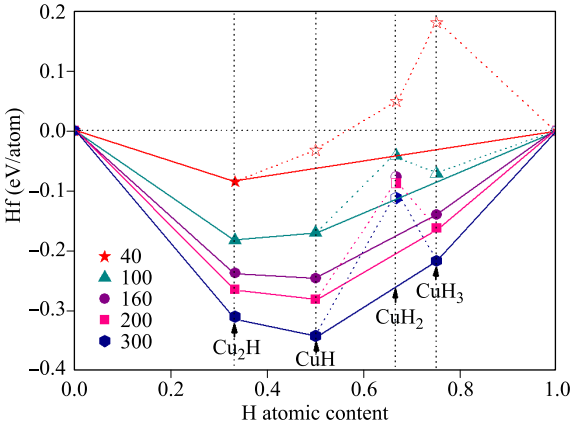

Fig. 1 Enthalpy of formation for the reaction $2Cu+1/2H_2=Cu_2H$ and $Cu+n/2H_2=CuH_n$ versus the element Cu (*Fm-3m*) and H ($P6_3/m$ at 0–100 GPa, $C2/c$ at 105–270 GPa and *Cmca* at 270-300 GPa) composition with varying pressure. The full filled symbols represent the structures that are on the tie-lines, and the half-filled symbols denote the structures that are not on the tie-lines.

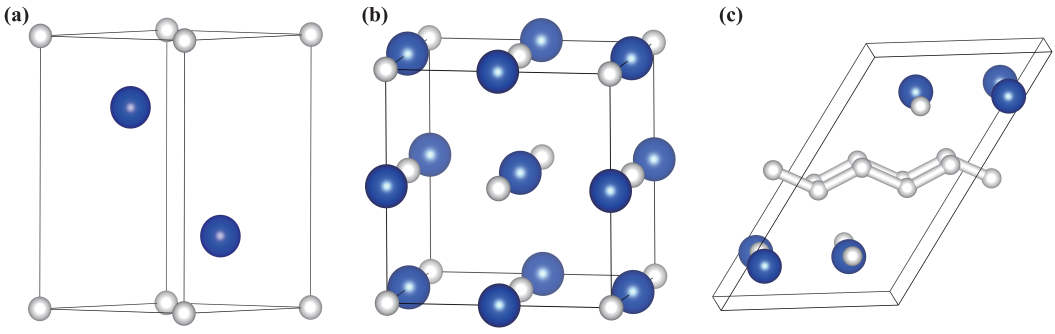

Fig. 2 **(a)** Cu_2H with P-3m1 space group. **(b)** CuH with Fm-3m space group. **(c)** CuH_3 with $C2/m$ space group. Blues spheres represent copper atoms while white small spheres represent hydrogen atoms.

with respect to solid H_2 and Cu at ∼16.8 GPa [Fig. 3(a)], indicating that it can be synthesized above this pressure, and this observation is in excellent agreement with the experimental results of 18.6 GPa [16]. When pressure is up to 100 GPa, CuH emerges on the convex hull, suggesting that it is energy stable above this pressure. When further compressed to 160 GPa, CuH_3 is located on the convex hull, and CuH becomes the most stable stoichiometry among all researched hydrides. CuH_2 is not located on the tie-lines in the whole pressure region indicating that it is thermodynamically unstable.

The crystal structures of the three stable compounds (Cu_2H, CuH, and CuH_3) are described in Fig. 2. Cu_2H takes on a hexagonal structure with P-3m1 space group, which agrees well with the experimental results [16]. In this structure, each unit contains one hydrogen atom and two copper atoms. Figure 3(a) shows that Cu_2H is stable with respect to solid H_2 and Cu at ∼16.8 GPa, indicating that it can be synthesized above this pressure, which is in excellent agreement with the experimental results of 18.6 GPa [16]. In the case of CuH, it has NaCl type structure with Fm-3m group space at 0–300 GPa, according with the character of noble metal monohydrides [45]. CuH can be synthesized with Cu and H_2 above 30 GPa depicted in Fig. 3, but it is metastability below 100 GPa. Moreover, it can be seen that CuH may decompose into Cu_2H and H_2. CuH_3 is predicted to possess a monoclinic $C2/m$ structure with H_2 units ranking with the "Z" chains. In this structure, Cu atoms and two kinds of nonequivalent H atoms occupy 4i, 4i, and 8j sites, respectively. The lattice parameters and atomic positions of Cu_2H at 40 GPa and CuH at 120 GPa are listed in Table 1.

Table 1 The lattice parameters and atomic positions of Cu_2H at 40 GPa and CuH at 120 GPa.

Structure # Space # Pressure	Parameters (Å, deg)	Atom	x	y	z
Cu_2H	$a = 2.48524$	H	0.000000	0.000000	0.000000
P-3m1	$c = 4.11495$	Cu	0.333333	0.666667	0.263189
40 GPa	$\gamma = 120$	Cu	0.666667	0.333333	0.736811
CuH		H	0.000000	0.000000	0.000000
Fm-3m	$a = 3.43020$	Cu	0.500000	−0.500000	−0.500000
120 GPa					

To explore the dynamic property of copper hydrides, we calculate their phonon band structure, as depicted in Fig. 4. For Cu_2H at 40 GPa and CuH at 120 GPa, no imaginary frequency given in the phonon dispersion curves implies that they are dynamically stable. For CuH, the imaginary frequency at Γ point emerges at 100 GPa, but it disappears when the pressure reaches 120 GPa. CuH can be synthesized thermodynamically above 30 GPa (Fig. 3),

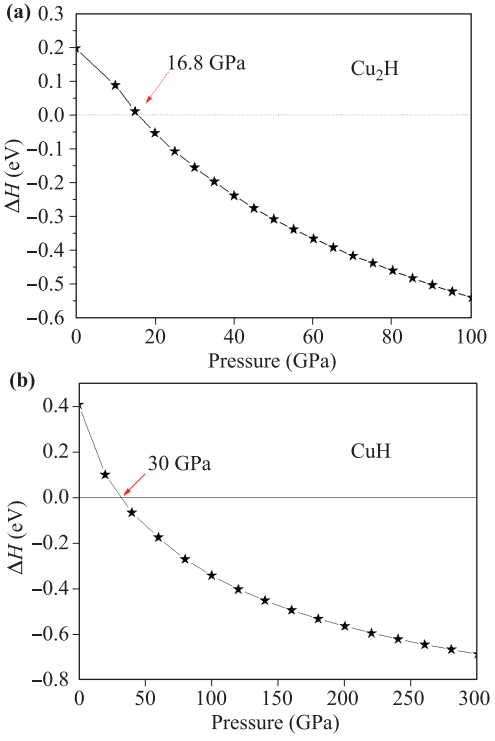

Fig. 3 The formation enthalpy of P-3m1-Cu_2H **(a)** and Fm-3m-CuH **(b)** with respect to Cu and H as a function of pressure.

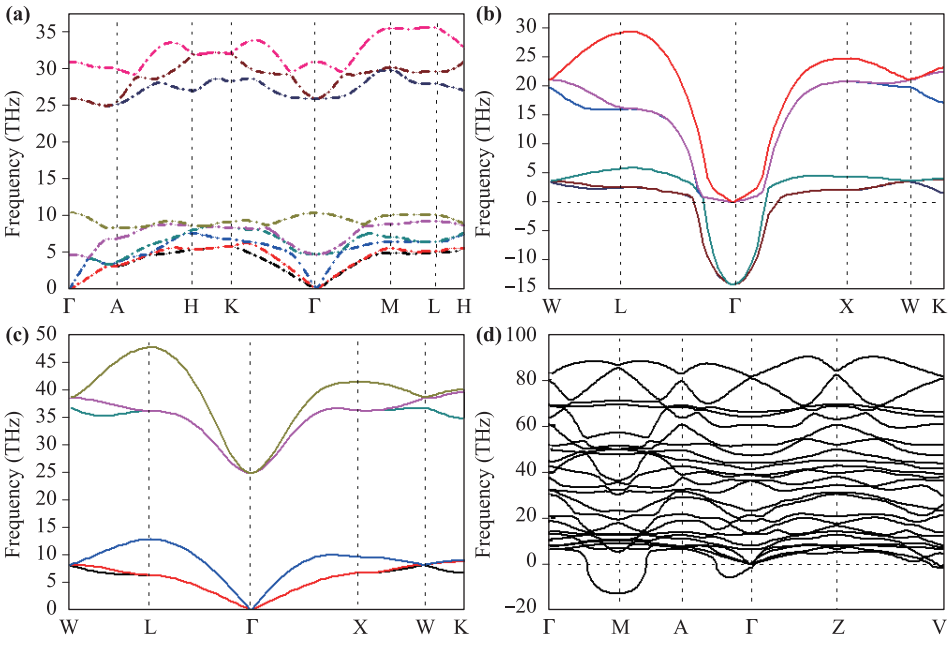

Fig. 4 The calculated phonon dispersion curves. **(a)** P-3m1-Cu_2H at 40 GPa, **(b)** Fm-3m-CuH at 100 GPa, **(c)** Fm-3m-CuH at 120 GPa, and **(d)** $C2/m$-CuH_3 at 300 GPa.

but it is not dynamically stable until 120 GPa. Regretfully, for the hydrogen-rich $C2/m$-CuH_3 stoichiometry, the imaginary frequency near M and Γ in the phonon band structure indicates that CuH_3 is not dynamically stable even up to 300 GPa, although it is thermodynamically stable above 160 GPa.

The electronic band structure of Cu_2H and CuH is calculated to explore their electronic properties, as depicted in Fig. 5. For Cu_2H, the overlap valence bands and conduction bands at 40 GPa reveals that it takes on the characteristics of metal, and its superconductivity should be further studied. In CuH, a small band gap occurs in the electronic band structure even at 300 GPa. As is well known, GGA usually underestimates band gap [46–48]. In other words, the real band gap is wider than our calculated results. Therefore, CuH is an insulator below 300 GPa.

To explore the superconductivity of Cu_2H, the phonon frequency logarithmic average ($\omega_{\log}$), electronic density of states DOS at Fermi level $N(E_f)$ and EPC parameter (λ) at 40 GPa are calculated. Our calculations show that $\omega_{\log}$ is 857.03 K, $N(E_f)$ is 3.02 states/Ry/unit cell, and λ is 0.24 at 40 GPa, yielding T_c of 0.028 K calculated by using the Allen-Dynes modified McMillan equation with μ^* of 0.10. The low T_c suggests a crucial rule that a large hydrogen fraction may be an essential condition to produce the high T_c for hydrogen-rich materials. As a function of the frequency of P-3m1-Cu_2H at 40 GPa, the Eliashberg spectral function $\alpha^2F(\omega)$ and the integrated λ are presented in Fig. 6. Cu atomic vibrations in the frequency region below 11 THz contribute approximately 35% to the total λ, whereas high-frequency modes between 25 and 35 THz contribute 65% of λ.

4 Conclusions

In conclusion, we have systematically studied the crystal structures, electronic structures, dynamics and superconductivity properties of the copper-hydrogen system. The results show that Cu_2H is predicted to be synthesized above 16.8 GPa, which is in excellent agreement with ex-

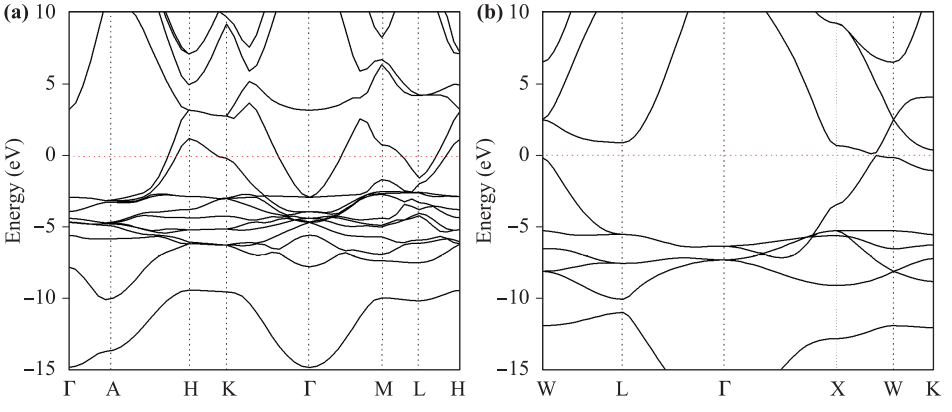

Fig. 5 The electronic band structure **(a)** Cu_2H at 40 GPa and **(b)** CuH at 300 GPa, respectively. The red dotted line represents the Fermi level.

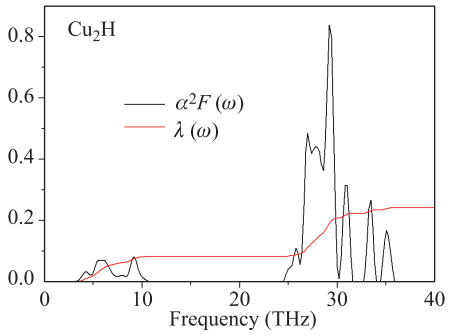

Fig. 6 The Eliashberg phonon spectral function α^2F (ω) and the partial electron-phonon integral λ (ω) for Cu_2H with P-3m1 symmetry at 40 GPa.

perimental report. The predicted stoichiometry CuH with the Fm-3m space group can be synthesized above 30 GPa, but it is metastable and dynamically instable up to 120 GPa. This finding solves a long-time debate on CuH stability at high pressure. Cu_2H is a good metal and CuH is an insulator. Furthermore, electron-phonon calculations show that the estimated T_c of Cu_2H is 0.028 K. The low T_c in Cu_2H indicates that a large hydrogen fraction may be required to produce the high T_c for hydrogen-rich materials.

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