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Electronic and thermoelectric properties of some CuH crystals

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ABSTRACT

The first-principles calculations under the framework of density functional theory are applied to unveil electronic and thermoelectric properties of a few crystals of CuH. Lattice parameters of the B1, B2, B3 and B4 crystals are deduced. The B4 → B1, B3 → B1 pressure induced phase transitions are observed at 42.9 and 64.5 GPa respectively. Electronic bands structure calculations show that B3 and B4 crystals are semiconductors whereas B1 and B2 are metals. We report that the semi-conducting crystals B3, B4 have the indirect band gap. The E-**k** spectrum calculated from the first-principles method is interfaced with the Boltzmann transport equations to compute the thermoelectric properties. The Seebeck coefficient, electrical conductivity, power factor etc. are calculated. The electrical conductivity in the B4 structure is highly anisotropic. The calculated power factor $(2.0–2.7) \times 10^{-3}\ \mathrm{W/mK^2}$ of B4 is good enough for optimum usage in thermoelectric applications at very cold stations.

1. Introduction

Metal hydrides cover a fair section of the energy and functional materials [1–3]. These are a potential source of hydrogen in portable fuel cells [2–5]. Chemical processes offer to design fuel storage devices for operation with large cells in automobiles or where on-board power is needed [3–5]. For hydrogen storage, metal hydrides should have a high hydrogen-to-metal ratio. In addition, these should be sufficiently stable to release the hydrogen easily at moderate temperature. The reactions involved in hydrogen desorption or absorption must have rapid kinetics [1–6]. The BeH_2, MgH_2 etc. have high gravimetric hydrogen density [2–6]. Magnesium and magnesium-nickel hydrides contain a relatively high fraction of hydrogen by weight, but release the hydrogen at 250 or 300 °C [4,5]. Nickel-metal hydrides are in demand and require reversible hydrogen exchange for rechargeable batteries at room temperature. The metastable hydrides, such as AlH_3 and CuH may also be useful for small size portable power applications. Insertion of hydrogen altering pressure leads to formation of both stoichiometric and non-stoichiometric compounds together with a number of crystal structures. In many metals the absorption of hydrogen can lead to a premature failure under stress which is directly related to the bonding between atoms in crystal planes and stability of crystals [4,5].

Copper monohydride is an interesting compound for several reasons. No stable hydride is proposed in the Cu-H binary system [7,8]. Wurtz, synthesized it for the first time in aqueous media and reported hexagonal wurtzite (W)-type structure [9,10]. This is in contrast to the NiAs or NaCl type structures usually found in most of the transition metal (TM) hydrides wherein the metals form a close-packed host lattice and the interstitial sites are occupied by the hydrogen atoms [11]. Consequently, the presence of hydrogen atoms leads to a reasonable volume expansion [12]. Copper monohydride exhibits unusual bonding behavior and is unstable at atmospheric hydrogen pressure [11–14]. In fact, high pressure studies on the Cu-H system have found a number of CuH phases with different order and non-stoichiometries [15–19]. Unlike W-CuH, a few hydrides retain the *fcc* lattice of copper, and the hydrogen atoms occupy octahedral interstitial positions. The hydrogen content and ordering in other phases are unknown [11]. Applying pressure, experimentally, W-CuH could not be synthesized up to 51 GPa [17] whereas Gibbs free energy calculations proposed 30 GPa formation pressure [18]. These studies indicate that it is difficult to generate conducive thermodynamic environment to form CuH, despite being the easiest to synthesize under non-equilibrium conditions.

The interplay of thermodynamic potential of the metal and the chemical potential of the hydrogen play pivotal role in the formation and stability of Cu-H crystals. It is reported that accumulation of hydrogen in the copper forms gas-filled voids [20,21]. These cause stress which, in turn, has been proposed to be a reason of embrittlement in

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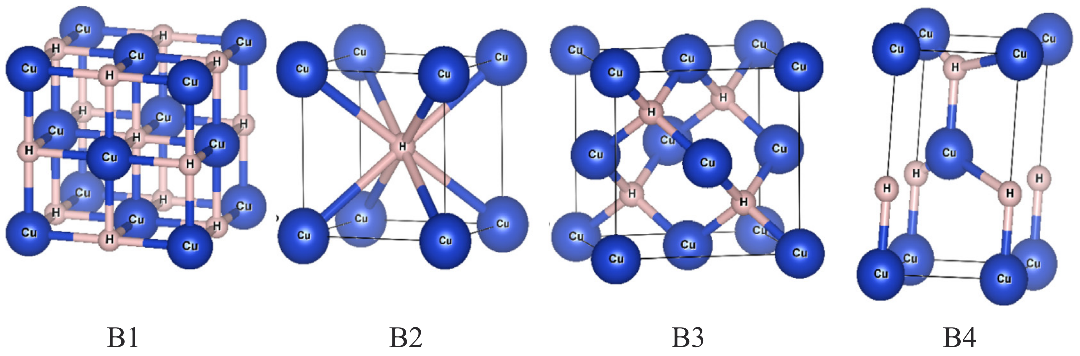

Fig. 1. Crystal structures of the B1, B2, B3 and B4 phases of the CuH.

metals [22]. It may be possible to have several modifications of the CuH as brittleness is directly related to the crystal structures and the nature of bonds. In particular, it was predicted that in metal hydrides, hydrogen may form a metallic sublattice at pressures achievable now-a-days at experimental facilities [23]. Moreover, under extreme conditions the Cu-H mixtures exhibit manifold distinct phases with remarkably different properties. The routes and conditions of synthesis indicate that the chemical reactions between TMs-H are very complex. In view of this, it is worthwhile to launch investigations of other modifications of CuH which can only be attained tuning the synthesis conditions.

Despite the complexities involved in formation and stoichiometries of the Cu-H binary system, the W-CuH is technologically important. While it is unstable in the ambient environment, it can be stored permanently at temperatures below −5°C [24]. To work on stable CuH less than −60 °C is required [15,19]. So in the low temperature region its electronic and thermoelectric properties may be useful. The chemical applications include usage as a reagent for reduction reactions in organic synthesis [25,26] and to get reactive catalyst [24,27]. It is pyrophoric and not water reactive so may be safely kept in water between −5 and −60 °C [28].

From the above discussion it is obvious that, in the Cu-H binary system, stoichiometric compounds CuH_2, Cu_2H and CuH can be synthesized. The hydrogen can occupy the tetrahedral or the octahedral positions in the *fcc* arrangement of the copper atoms. So it can have some modifications. For instance, the formation of tetrahedrally coordinated i.e. ZnS-type and the octahedrally coordinated NaCl-type structures. These structures may also energetically compete with the intermediate CsCl-type modification. Not only the routes and conditions of chemical synthesis of TMs-H are very complex, the non-stoichiometry, disorder and instability of the Cu with H pose experimental difficulties and it is claimed that at room temperature CuH should act as an explosive [11,15,16,19]. In such cases, the first-principles computation can be deployed to first model and then explore properties of all these modifications of CuH. Moreover, in the low temperature range, a few crystals are stable so it is worthwhile to unveil the electronic and thermoelectric properties in that range. The central objective of this paper is to eloquently present the electronic and thermoelectric properties of copper monohydride (CuH) in the B1, B2, B3 and B4 structures. Using modern first-principles energy computations, the equations of states are obtained and the crystal parameters are deduced. Possibilities of the pressure-induced structural phase transitions are examined. To predict electronic properties the bands dispersion curves are calculated. As W-CuH is stable up to −5 °C, the thermoelectric (TE) properties may be very useful for technological applications under difficult survival conditions and planetary activities. Therefore, this work also investigates, for the first time, the thermoelectric properties of the four CuH crystals by interfacing the first-principles computations with the Boltzmann transport equations.

2. Computational methods

2.1. Crystal structures and the DFT-LCAO method

Since the middle of the 19th century Copper hydride, CuH, is known. It was prepared by Wurtz from an aqueous solution [9,10,29]. The synthesis of good samples, purification and characterization of CuH has remained a challenging task. The material is stable against moisture and air, metastable at ambient conditions, and stable against vacuum for a longer time [13–17]. It starts decomposing into constituents during synthesis which completes within 24 h [13–17]. So one must operate below −60 °C to work on the stable compound [15,19,24]. Mueller and Bradley reported hexagonal packing of copper atoms with cell parameter $a = 2.89$ Å and $c/a = 1.59$–1.60 using X-ray diffraction [9]. Using neutron diffraction Goedkoop and Andresen assigned the wurtzite structure [10] but could not; specify the position of hydrogen atoms, and refine the crystal structure. The existence of a cubic copper hydride from the elements under high pressure is also reported [16]. All these observations have reached, unequivocally, to a consensus that irrespective of the method of preparation, the CuH product is the same having the hexagonal lattice identified in all earlier relevant studies for structure determination [27].

Burtovyy et al. [15,16] and several other workers [17–19,27] have observed the hexagonal wurtzite type structure of CuH belonging to the space group (SG) $P6_3mc$. In this structure, belonging to the SG#186, both Cu an H atoms occupy the *2b* Wyckoff positions. The zincblende structure has hydrogen at the tetrahedral sites. It belongs to the SG $F\bar{4}3m$. The structure has the SG#216 wherein the Cu and H atoms, in order, occupy the *4a* and *4c* Wyckoff positions. We have also considered the NaCl or rocksalt type structure with hydrogen at the octahedral interstitial positions in CuH. It belongs to the SG $Fm\bar{3}m$ having SG#225. The Cu and H atoms occupy the *4a* and *4b* Wyckoff positions respectively. Lastly, the CsCl type structure belonging to the SG $Pm\bar{3}m$ is also considered. This structure has the SG#221 wherein the *1a* and *1b* Wyckoff positions are occupied by the Cu and H atoms. The unit cell contains one formula unit giving a total of 30 electrons. For the sake of discussion we will use the B1, B2, B3 and B4 symbols to refer the NaCl type, CsCl-type, Zb-type and W-type crystals of CuH. All these crystal structures are shown in Fig. 1.

Calculations are performed following the first-principles periodic Linear Combination of Atomic Orbitals (LCAO) method within the framework of Density Functional Theory (DFT) by implementing the CRYSTAL14 code [30–32]. In this non-cellular method, local functions are expressed as linear combination of a certain number of normalized Gaussian functions. Available basis sets of Cu and H are taken [33,34]. The Perdew–Burke–Ernzerhof (PBE) *ansatz* based on the generalized gradient approximation (GGA) is applied to treat exchange and correlation (XC) part of the Kohn-Sham (KS) Hamiltonian [35]. The charge and energy self-consistent calculations were performed taking sufficient tolerances and considering Monkhorst-Pack net of 16 × 16 × 16 size