

## Hydride complex with ninefold H-coordination

Hydrogen, although being the simplest element, exhibits an exceptionally rich chemistry, forming various types of chemical bonds in materials. The chemical flexibility is a source of many interesting properties of hydrides, such as hydrogen storage, fast ionic conductivity, magnetism, and the metal–insulator transition [1]. In particular, the recent discovery of the superconductivity at 203 K in the sulfur hydride system [2] has spurred tremendous research activity toward the exploration of hydrogen-rich materials.

Complex transition-metal hydrides represent a class of hydrogen-rich materials, wherein a number of H atoms covalently bind to the transition metals to form a varied set of homoleptic transition-metal hydride complexes with a remarkably rich variety of H coordination modes. These complexes are stabilized by charge transfer from electropositive counterions, such as alkali and alkaline earth metals, to form insulating hydrides [1]. In general, the H-coordination number increases from right to left along a given period of the periodic table because of the trend of increasing atomic size, which allows more hydrogen binding. At the same time, despite research spanning the past several decades, the elements capable of forming hydride complexes had been thought to be limited to those in Groups 7–12 [3]. This limitation had precluded the further discovery of hydride complexes with higher H-coordination numbers; however, the recent high-pressure and high-temperature technique overcame this limitation, and we successfully synthesized the novel hydrogen-rich material  $Mg_3CrH_8$  as the first Group 6 hydride complex  $[CrH_7]^{5-}$  [4]. The results strongly indicate that there is no *a priori* reason for the limitation and pave the way for the discovery of hydride complexes with higher H-coordination comprising unexplored elements to the left of Group 7, as illustrated in Fig. 1.

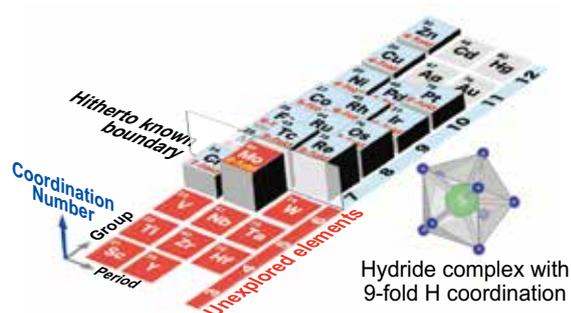


Fig. 1. Strategy for obtaining hydride complexes with high H-coordination.

On the basis of the above strategy, we examined the formation of novel transition-metal hydride complexes of the Group 6 element Mo [5]. Lithium was selected as a counterion because of its low electronegativity, which is expected to thermodynamically stabilize the complex hydride phases. Our density functional theory (DFT) calculations predicted that tricapped trigonal prismatic H-coordination (Fig. 1) allows the formation of strong  $\sigma$ -bonds between Mo and H, thus enabling the formation of the novel hydride complex  $[MoH_9]^{3-}$  with ninefold H-coordination in  $Li_5MoH_{11}$ . Subsequently, the optimized synthesis conditions were effectively determined by *in situ* synchrotron radiation X-ray diffraction measurements using a cubic-type multianvil press installed at SPring-8 BL14B1. The crystal structure of the synthesized sample was investigated using a combined experimental and *ab initio* approach.

Figures 2(a) and 2(b) illustrate the DFT ground-state structure of  $Li_5MoH_{11}$ . The nine H atoms (H1) form a tricapped trigonal prism around the Mo atoms located at the (0, 0, 0) and (0, 0, 1/2) coordinates of the hexagonal lattice, and two isolated H atoms (H2) are located at the approximate centers of the trigonal prisms formed by the six Mo atoms. The four Li atoms coordinate to the H2 atoms, forming a two-dimensional network of corner-sharing tetrahedra between the layers of  $MoH_9$  units.

Figure 2(c) shows the neutron diffraction (ND) profile of a sample obtained by the hydrogenation of a powder mixture of LiD and Mo at 5 GPa and 973 K for 48 h (open circles). We performed Rietveld refinement on the profile (black line in Fig. 2(d)) and obtained the  $P6cc$  structure (No. 184) of  $Li_5MoD_{11}$  with nine D atoms statistically distributed around the Mo atom, as depicted in Fig. 2(e). The statistical distribution is reasonably well reproduced by first-principles molecular dynamics (FPMD) calculations at 298 K, wherein the nine H1 atoms significantly rotate around the Mo atoms, generating a spherical shell-like distribution (Fig. 2(f)), as observed by the comparison of the simulated profile obtained from the FPMD trajectory (red line in Fig. 2(e)) with the Rietveld refinement fit. From these results, we concluded that the novel complex transition-metal hydride  $Li_5MoH_{11}$  containing the first reported ninefold H-coordination Group 6 hydride complex  $[MoH_9]^{3-}$  was successfully synthesized.

Qualitatively, the electronic structures of complex transition-metal hydrides can be viewed as consisting of low-lying H 1s- and high-lying transition-metal ( $T$ ) *spd*-derived states (Fig. 3). The ligand field induced

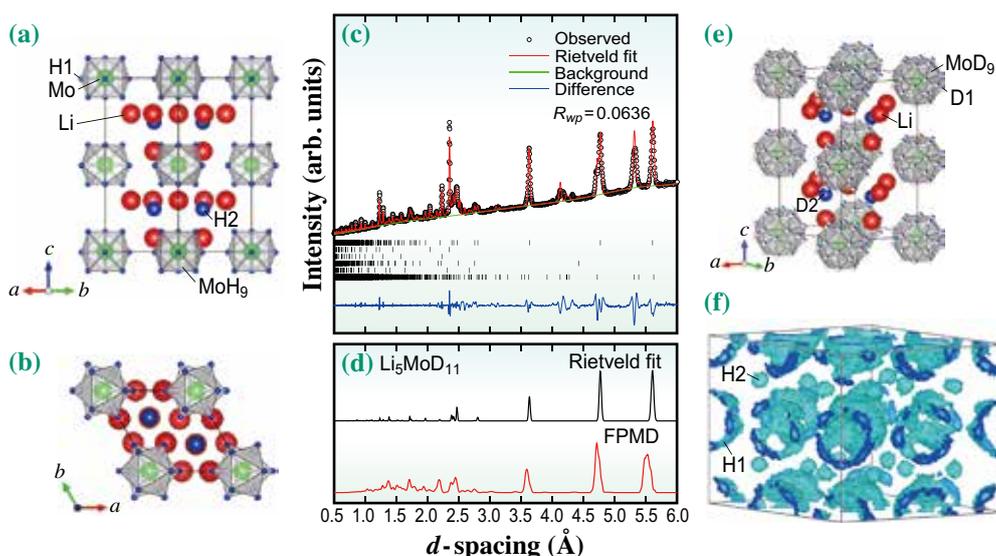


Fig. 2. DFT ground-state structure of (a)  $\text{Li}_5\text{MoH}_{11}/\text{Li}_5\text{WH}_{11}$  and (b)  $\text{Li}_6\text{NbH}_{11}/\text{Li}_6\text{TaH}_{11}$ . (c) Experimental ND profile of  $\text{Li}_5\text{MoD}_{11}$  measured at room temperature. The positions of Bragg reflections (tick marks) are shown for  $\text{Li}_5\text{MoD}_{11}$  (top),  $\text{LiD}$  (second),  $\text{Mo}$  (third),  $\text{LiOD}$  (third from bottom),  $\text{Li}_2\text{O}$  (second from bottom), and the unknown phase (bottom). (d) Rietveld fit of experimental profile (black line) and simulated profile obtained from FPMD trajectory at 298 K (red line). (e) Crystal structure of  $\text{Li}_5\text{MoD}_{11}$  determined by Rietveld analysis. (f) Time-averaged atomic-density profile obtained from the FPMD trajectory of H atoms at 298 K.

by the H-coordination divides the  $T$   $spd$  states into nonbonding and antibonding states, and  $E_F$  normally falls in the ligand-field gap in order to accommodate the so-called 18-electron rule. The most striking point here is that the contribution from the H 1s-derived states in the valence bands increases with an increasing H-coordination number, reaching  $E_F$  at ninefold coordination. Such hydrogen-rich materials are very rare among solid-state hydrides containing transition metals and might be of interest in terms of high- $T_c$  superconductivity if the band gaps close under compression.

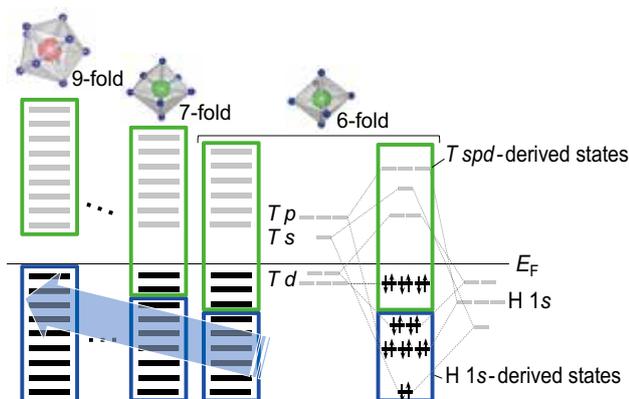


Fig. 3. Strategy for obtaining complex transition-metal hydrides with H 1s-derived states reaching the Fermi level ( $E_F$ ). The electronic structures roughly comprise low-lying H 1s- and high-lying  $T$   $spd$ -derived states. The contribution from H 1s-derived states to the valence bands increases with increasing H-coordination number and reaches  $E_F$  at ninefold H-coordination.

In addition to the above electronic feature,  $\text{Li}_5\text{MoH}_{11}$  has a characteristic phonon property such that the ninefold hydride complexes exhibit significant rotational motion even at room temperature, as demonstrated by our FPMD calculations. This type of motion has never been observed in complex transition-metal hydrides, but has often been discussed in relation to the occurrence of fast ion conduction in alkali metal *closo*-polyborane salts. Although we observed no obvious translational diffusion of  $\text{Li}^+$  ions in our FPMD calculations because of the limited simulation time (12 ps) and the unit cell size (136 atoms), the significant rotational motion of  $[\text{MoH}_9]^{3-}$  ions, as observed in Fig. 2(f), suggests the potential for fast lithium ion conduction even at room temperature.

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### References

- [1] S. Takagi and S. Orimo: Scripta Mater. **109** (2015) 1.
- [2] A.P. Drozdov *et al.*: Nature **525** (2015) 73.
- [3] K. Yvon: Chimia **52** (1998) 613.
- [4] S. Takagi *et al.*: Angew. Chem. Int. Ed. **54** (2015) 5650.
- [5] S. Takagi, Y. Iijima, T. Sato, H. Saitoh, K. Ikeda, T. Otomo, K. Miwa, T. Ikeshoji and S. Orimo: Sci. Rep. **7** (2017) 44253.