Chemical templates that assemble the metal superhydrides

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SUMMARY

The recent discoveries of metal superhydrides provide a new route to room-temperature superconductors. However, their structure trends and the chemical driving force needed to dissociate H_2 and form H covalent network cannot be explained by direct metal-hydrogen bonds. Here, we show that the understanding of superhydrides formation needs a perspective beyond the traditional chemical bonds. By analyzing high-throughput calculation results of metals across the periodic table and in various lattices, we show that, after removing H, the remaining metal lattices exhibit large electron occupations of the nonatomic interstitial orbitals, which matches excellently to H lattices and their wavefunctions like a template. Furthermore, H lattices consist of 3D aromatic building units that are greatly stabilized by chemical templates of metals near the *s*–*d* border. This theory can naturally explain the stability and structure trends of superhydrides and greatly enhance the efficiency of predicting new materials, such as two-metal superhydrides.

Keywords: Metal superhydrides, superconductivity, high pressure, interstitial quasi-atom orbitals, hydrogen 3D aromaticity, materials design

[1] Lead Contact

INTRODUCTION

Among many remarkable physical and chemical properties of hydrogen, its capability of achieving a superconducting state at or above room temperature has received intensive attention in condensed matter studies for many decades.[1–3] However, hydrogen is very resistive to metallization and polymerization which is an essential step toward superconductivity, and large driving forces are needed to overcome it. As predicted theoretically, a tremendous high pressure of 550 GPa is needed to drive the transformation of hydrogen to atomic phases.[1,4,5] Therefore, the idea of using chemical forces that can "pre-compress" the hydrogen became an attractive approach to superconductive hydrogen under moderate pressure[2] and has led to the predictions and syntheses of numerous hydrogen-rich compounds that brought us ever close to room temperature superconductivity.[6,7] These compounds can be categorized into metal hydrides and non-metal hydrides. Among the second type, H_3S showed a critical temperature (T_c) of 203 K near 150 GPa,[8,9] which is the first to break the 25-year T_c record of cuprates. Further improvements by mixing with other elements such as C are being pursued.[10–12] All H atoms in these compounds bond with *p*-block elements that are in hypervalent states.[13] In contrast, many metals near the *s*−*d* border such as Ca, Sc, Y, La, Ce, Nd, Ac, and Th incline to form superhydrides with exceedingly high H compositions in which all H atoms form extended lattices (Figure 1A–1C).[14–29] The H lattices in these compounds feature a strong covalent H−H network,[30] high electron density, and strong electron-phonon coupling, giving rise to superconductivity at very high temperatures.[31–33]

According to the traditional bond theory of solid-state, strong chemical interactions are the results of either the transfer or the sharing of electrons. Large electron transfer from metals to H is regarded as a driving force to dissociate H_2 molecules because the electrons will weaken the H−H bonds by occupying the antibonding states. However, the electron transfers also destabilize extended H lattices for the same reason, and the overall effect on H polymerization is insignificant (Figure 1D). The energy of the Cs−IV phase of metallic H actually goes up compared with the H_2 C_2/c phase while adding electrons (Figure 1D). Furthermore, the charge doping from metal to hydrogen in superhydrides decreases with increasing pressure, distinctly opposing the trend of internal energy. Besides electron transfer, the covalent bonding between metals and hydrogen seems to be another candidate for the driving force. However, both integrated Crystalline Orbital Hamiltonian Population (ICOHP)[34] (Figure 1E) and Electron Localization Function (ELF)[35] (Figure 1F) reveal that the M−H bond strengths are significantly weaker than H−H bonds and, therefore, can hardly cause the formation of extended H lattice. Especially, the very small ICOHP values between the 5*d*/4*f* orbitals of La and H 1*s* show that these orbitals do not play major roles in forming metal superhydrides. On the contrary, hydrogen forms an extensive covalent network that is the key to high T_c superconductivity, as revealed by a recent thorough ELF study of many superhydrides.[30] Besides, the volume effect also favors the formation of some superhydride but cannot provide a unified mechanism (see Figure S1 and the discussions thereafter).

In this work, we take a different approach that starts from the analysis of the electron states of the metal sublattices in the superhydrides. This approach is in alignment with

several earlier studies that view the solid-state compounds as the insertion of anions into the metal lattices[36–39]. These studies are based on an observation that the metal sublattices of many compounds often resemble a stable structure of metals under ambient or other conditions such as pressure. It has also been noticed that the interstitial sites of these metal lattices where the anions are inserted exhibit large electron densities and localizations. Similar observations have also been shown in recent studies of metal superhydrides[40,41], i.e. the electron localizations of the metal sublattices match well with the H sublattices in superhydrides. However, a true mechanism that shows the chemical driving force to form superhydrides is still unknown, and many phenomena, such as why metals near the *s*-*d* border are more promising to form superhydrides and why certain metal superhydrides prefer specific structures, have not been explained.

We will show that by invoking the point that the electron occupations of local quasi-atom orbitals at the interstitial sites of metal lattices are the essence of the electron localizations, the empirical anions-in-metal lattice approach of solid compounds could be fully developed into a chemical bond theory. This theory will allow us to show that instead of directly bonding with H, the presence of the metals significantly enhances the stability of the extended hydrogen lattices in superhydrides through a chemical template effect. By using the ELF as an indicator of electrons occupying quasi-atom orbitals, we are able to show that the metals near the *s*-*d* border tend to form superhydrides because of their stronger template effects. Furthermore, quantifying the template effects also enable us to search for new and complex superhydrides, especially those with higher H compositions and with mixed metals, on a massive scale and across the periodic table.

A new set of questions emerged after putting together all the recently predicted and synthesized metal superhydrides. Several different structures are often found for superhydrides with the same H compositions, and their energy order strongly depends on metals. Although the hydrogen lattices in these structures show intricate geometry, the metal atoms usually form simple lattices such as face-centered cubic (FCC), hexagonal close-packed (HCP), simple hexagonal (SH), *etc.*, or lattices slightly deformed from them. For example, most of the MH_9, except PrH_9 and PaH_9, adopt hexagonal structures in which the metal atoms form HCP or SH lattices. Also, the MH_{12} structure with the highest symmetry ($Fm\bar{3}m$) consists of FCC metal lattice and H cubo-octahedra located at the octahedral sites. However, BaH_{12} in this structure is significantly higher in energy than a distorted structure with $P2_1$ symmetry, although the Ba lattice in the latter structure forms a slightly distorted FCC lattice.[29] The stability trend of these structures is hard to be explained by the direct chemical interactions between metals and H, but can be explained by the template effect as will be shown in this paper.

RESULTS AND DISCUSSION

The interstitial electrons in metal lattices.

The first step toward understanding the formation of superhydrides is noticing that many metal lattices, despite whether they are stable structures or not, exhibit significant localized electrons at their interstitial sites, and the essence of this localization is the occupation of the non-atomic local orbitals (quasi-atom) centered at these sites. In extreme cases such as high-pressure electrides (HPE), the quasi-atom orbitals at the

interstitial sites, such as in *hP4* Na are completely occupied by electrons and play the role of anions in ionic compounds.[42,43] The electride concept and the corresponding quasi-atom view can be extrapolated to metal lattices under lower or zero pressure, in which electrons only partially occupy the quasi-atom orbitals. As a matter of fact, the La atoms in LaH_{10} at 300 GPa correspond to an FCC lattice at 12.4 GPa. It is slightly higher in enthalpy than the most stable structure of La in $R\bar{3}m$ symmetry at this pressure.[44] More importantly, its ELF exhibits maxima with considerable values of 0.62 and 0.45 at the centers of octahedral (E^O) and tetrahedral (E^T) sites (Figure 2A).

The electron occupations of the local quasi-atom orbitals are indicated by the ELF maxima at interstitials of metal lattices and can be more rigorously revealed by the wavefunctions. In another example, the ELF of atoms can show distinct shell structures originating from the atomic orbitals, whereas electron density cannot.[45] Indeed, the three highest occupied crystal orbitals (CO) at the Γ point are 2.33 (highest occupied crystal orbitals (HOCO)), 2.38 (HOCO−1), and 2.96 eV (HOCO−2) below the Fermi level show maxima at E^O sites, both E^O and E^T sites, and E^T sites, respectively (Figure 2B–2D), revealing the occupations of the quasi-atom orbitals on these sites. On the other hand, the occupations are only partial, and the charge distribution shows very small variations around E^O and E^T sites, rendering FCC La a metal instead of an HPE insulator. Similar interstitial occupations also happen to other metal lattices, for example, the Y body-center cubic (BCC) lattice in YH_6 (Figure 2E) and Y HCP lattice in YH_9 (Figure 2F).

The electron occupation in metal interstitials forming template is an intrinsic property of the metal and the lattice geometry. Especially, both the sites and the magnitudes of the occupation of quasi-atom orbitals evolve systematically with the size of the metal lattices. While the lattice constant reduces, the general trend of the electron occupation is from sites with fewer neighboring atoms to sites with more neighboring atoms (Figure 3A–3B). For example, while the unit length of a Ca FCC lattice reduces, the electron occupation shifts from bond centers (with 2 neighboring Ca) to E^T sites (with 4 neighboring Ca), and then to E^O sites (with 6 neighboring Ca) (Figure 3C–3D). For metals in the same period, the electron occupation at the interstitials decreases with increasing atomic number. They are the strongest for *s*-block metals and early transition metals and become much weaker for late transition and *p*-block metals such as Al (Figure 3E–3H). Interestingly, the electron occupations for early transition metals such as Y, La, Hf, *etc.* are strong on both E^O and E^T sites, an important feature that will stabilize MH_{10} superhydrides. It is important to notice the difference between electron occupation and electron distribution at the interstitial sites. Although metals like Al have very high electron densities at the interstitial sites, their electrons show little occupation of the quasi-atom orbitals. As will be shown, these metals cannot stabilize H lattice and form superhydrides.

The building units of H lattices.

The second key feature of superhydrides is that the H lattices consist of unique and intrinsic building units (Figure 4A) that are positioned right at the active regions of the metal templates. They can be identified by the geometry, symmetry, and crystal orbitals of H lattices (Figure 4B–4C). Some units are straightforward to identify by their appearance in the lattice, such as H_6 hexagons and H_4 squares in MH_6, and H_8 cubes and H_5 tetrahedrons in MH_{10}; whereas some others are quite unexpected. For example,

the H units in MH_9 are not H_5 and H_6 rings, but rather an H_6 corona and an H_8 bipyramid (Figure 4A). These two units share most of the symmetries of MH_9, and many occupied crystal states localize on them (Figure 4C). The ways that H lattices are divided into building units are also corroborated by their energies that are calculated using a He matrix model (see supplemental experimental procedures). Among the 6 building units in MH_6, MH_9, and MH_{10}, the H_6 hexagon, the H_8 cube, and the H_6 corona are significantly lower in energy. Also, their energies decrease by about 0.5 eV/atom while pressure increases from 100 GPa to 300 GPa (Figure 4D).

The remarkable stability of the H_6 hexagon, H_8 cube, and H_6 corona originates from an important feature of the H–H bond. Due to the quantum resonance, these bonds are conjugated and delocalized in the same way as the C–C 2*p* π bonds in organic molecules of which the stability is ruled by the aromaticity.[46,47] Because of the topology of the π bonds, the aromatic molecules need to assume a planar geometry and their electron counting needs to satisfy the 4*n*+2 rule, which ensures a gap between the fully occupied and unoccupied orbitals. However, in contrast to C π bonds, the conjugation of H–H bonds is not constrained inside the same plane. The corresponding three-dimensional aromaticity depends on the symmetry and the number of H in the cluster, and the above three H clusters are all aromatic. The energy levels of the H_6 hexagon resemble the energy levels of the benzene ring,[46] their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are doubly degenerate (Figure 4E). In contrast, the HOMO and LUMO of the H_8 cube are triply degenerate (Figure 4F). The HOMO–LUMO gaps of H_6 hexagon, H_8 cube, and H_6 corona are 8.50, 10.15, and 7.77 eV, respectively. Many other aromatic H clusters are also identified as building units in various superhydrides (Supplementary Section III).

The assembly of H covalent network on metal templates.

While the ELF and the COs of metal sublattices in superhydrides are overlaid on the corresponding H lattices, a striking feature of the superhydrides emerges. The H lattice matches excellently with the ELFs (Figure 5A–5C) and relative COs (Figure 5D) of the metal lattices that include no information of H atoms at all. The H_{10} lattice in LaH_{10} consists of two types of H, the H_8 cubes formed of H^1 atoms located at the E^O sites, and H^2 located at E^T sites. Although ELF provides a strong indication that electron states of metal lattices must play an important role in the formation of superhydrides, the strong chemical force that dissociates H_2 molecules and enforce the assembly of an H lattice relies on the matching of the COs of the metal sublattice and H sublattice. As a matter of fact, some COs of an H lattice, such as the lowest unoccupied CO of H_{10} at the Γ point (Figure 5E), consists of local orbitals at interstitial sites, E^O and E^T for LaH_{10}, matching well with the corresponding COs of the metal lattice. Therefore, while La and H_{10} lattices are interposed, the occupation of E^O and E^T orbitals in La valence bands will naturally dope H_{10} by occupying its conduction band states. As a result, the highest occupied state of LaH_{10} at the Γ point consists of local orbitals at E^O and E^T and matches well with both COs of H_{10} and La lattices (Figure 5F). Therefore, instead of a large charge transfer from La orbitals to H orbitals, electrons of La lattice already occupy the quasi-atom orbitals that match the H lattice and its wavefunctions, forming a chemical template awaiting and assisting the assembly of it.

The close match of the COs of the metal and the H lattices, as indicated by ELF, can be found for all metal superhydrides despite the large variety of structures and symmetries, such as MH_6 in $Im\bar{3}m$ structure (M= Sc, Ca, Y), MH_9 in $P6_3/mmc$ structure (M=Ce, Pr, *etc.*), MH_{10} in $Fm\bar{3}m$ structure (M=Y, La, *etc.*), MH_{12} in $Fm\bar{3}m$ structure (M= Ba) and MH_{16} in *P6/mmm* structure (M=La, *etc.*) and many others (Figure 5G–5I and Supplementary Section IV). The metals in these superhydrides may adopt many different structures, including FCC, HCP, SH, BCC, simple cubic (SC), or structures that are deformed along with high symmetry directions of them. These sub-lattices are not necessary the stable structures of metals. Especially, for non-cubic superhydrides, the stresses of the metal lattices might not be hydrostatic (Table S4). For example, the normal stresses of the Ce lattice in CeH_9 at 300 GPa are $\sigma_1=\sigma_2=1.1$ GPa, $\sigma_3=15.1$ GPa. Nevertheless, all-metal lattices show large electron occupations in the interstitial regions that match nicely with the locations and patterns of the H lattices in superhydrides, even if many superhydrides are in low symmetry structures, such as $R\bar{3}m$ SrH_6 and *Immm* Ti_2H_{13}. On the other hand, the strength of the template effect that can be estimated by the ELF values at the interstitial sites strongly depends on metals. While they are the strongest for metals at the *s*–*d* border, they decline quickly for metals away from that region and become insignificant for late transition metals (Figure 5G–5I and Figure S2). For example, in an Ir FCC lattice of a conceived IrH_{10} compounds, the maxima of ELF are no longer at the interstitial sites but in the regions between neighboring Ir atoms.

To test the template effects of metal lattices on stabilizing H lattices, we employ a He matrix model in which H_n clusters that are building units of H sublattices are inserted and their energies are compared with H_2 molecules, with no or different metals (see supplemental experimental procedures). This model allows comparing the energies of H clusters with H_2 molecules in the same chemical environment. The results show that the presence of the metal atoms can lower the energies of H units relative to H_2 by about 0.5 to 3 eV, including non-aromatic ones such as H_4 squares and H_5 tetrahedrons (Figure 5J and S3). Moreover, this template effect strongly depends on metals. The most profound changes happen to the elements around the *s*–*d* border and decline with increasing number of *d* electrons, which is consistent with the trend of ELF (Figure 5G–5I and S2). Among row 6 elements, those sitting at the *s*–*d* border such as Ba and La can lower the energies of all H units except H_5 below H_2 at 300 GPa; whereas late transition metals such as Pt and Au show a much weaker effect. Very few elements, including Ba, La, Th, *etc.*, could bring the energy of the H_8 cube below H_2.

Pressure is essential to the stability of the H lattice by directly lowering the energies of H units and influencing the effect of metal templates. The distances between metal atoms are larger under lower pressure, which usually reduces the electron density and localization in the interstitial region and weakens the chemical driving force from the templates. The expansion of the metal lattices, while more H atoms are packed into them, will reduce the template effect and therefore place a limit on H compositions of superhydrides.

The chemical template theory.

It is important to realize that the chemical template is a general effect that can present in numerous compounds containing metal sublattices. Compared with ordinary bonds such

as ionic or covalent bonds, it is a weaker interaction. However, in compounds like metal superhydrides, this effect becomes essential for their formation and stability.

The conventional theory of chemical bonds in molecules and solid compounds take free atoms as the initial states.[48] The charge transfer and the bond energies are obtained by referring to free atoms and their quantum orbitals. In contrast to this view, one can take the sublattices as the starting point. For example, a typical ionic compound such as KH can be split into K and H sublattices. In view of conventional bond theory, electrons transfer from K to H atoms, creating K^+ and H^- ions that form an ionic crystal (Figure S4). In view of the template theory or anion-in-metal approach, KH compound can be split into K and H sublattices (Figure S4). Correspondingly, the Hamiltonian of the compound consisting of metals and anions can be written as $H = H_M + H_A$, in which H_M an H_A are the Hamiltonians of the metal and the anion sublattices. We assume an electron state in a compound as ψ_0, e.g. the HOCO at Γ point, then $H\psi_0 = \varepsilon_0\psi_0$. The energy of this state consists of two parts, corresponding to the contributions from anion and metal lattices, respectively, i.e.

$$\varepsilon_0 = \langle\psi_0|H_M|\psi_0\rangle + \langle\psi_0|H_A|\psi_0\rangle. \quad (1)$$

For ionic and largely polarized compounds, ψ_0 mainly consists of orbitals located on anions, which minimizes the second term $\langle\psi_0|H_A|\psi_0\rangle$. The energy contribution of the metal sublattice is

$$\Delta\varepsilon = \langle\psi_0|H_M|\psi_0\rangle. \quad (1)$$

Assuming ψ_M^i are the crystal orbitals of the metal sublattice and *i* represents both *k* points and band numbers, H_M can be expressed as

$$H_M = \sum_i \varepsilon_M^i |\psi_M^i\rangle\langle\psi_M^i|, \quad (2)$$

and consequently,

$$\Delta\varepsilon = \sum_i \varepsilon_M^i \langle\psi_0|\psi_M^i\rangle^2. \quad (3)$$

Because $\varepsilon_M^i < 0$, the large overlap integral $S_{0M}^i = \langle\psi_0|\psi_M^i\rangle$ will lower $\Delta\varepsilon$ and the valence state energy, and therefore will stabilize the compound. If electrons in metal lattices occupy the quasi-atom orbitals at the interstitial sites that the anions locate, ψ_M^i largely overlap with ψ_0, S_{0M}^i will be maximized. Therefore, the presence of the chemical template could significantly stabilize the compounds because it optimizes the electron states for both anion and cation sublattices.

Neither the traditional bond theory nor the empirical anion-in-metals approach sets apart this template interaction from "direct" chemical interactions between metal and nonmetals. In ionic compounds such as KH or LaH_3, the electron states that are important for binding energy are more significantly determined by H_A, and $\Delta\varepsilon = \langle\psi_0|H_M|\psi_0\rangle$ is significantly smaller than $\langle\psi_0|H_A|\psi_0\rangle$. The major contribution to the energy and stability of these compounds is due to the charge transfer from metals to electronegative nonmetals. The template effect is a relatively weaker chemical interaction compared with conventional bonds and is not a determining factor for the formation of these compounds. In compounds such as superhydrides, H atoms form strong covalent lattices and lose their strong potential to acquire electrons. In such a case, the template effect becomes important and might determine the formation of the compounds.

The strong chemical interactions due to the template effect do not associate with large electron relocations, in contrast to both ionic and covalent bonds. The electron distributions in superhydrides are optimal not only for the whole compound but also for its consisting metal and H sub-lattices, which maximize the stability. Taking LaH_{10} as an example, the summation of the density distributions of the sub-lattices $\rho(La+H_{10}) = \rho[La$ lattice$] + \rho[H_{10}]$ resemble very nicely $\rho(LaH_{10})$ (Figure S5a), which can be seen more clearly by the fact that $\Delta\rho = \rho(LaH_{10}) - \rho(La+H_{10})$ is quite small. As a matter of fact, the integrated transferred charge calculated from $\Delta\rho$ is about -0.15*e* for La (Figure S5b), which is about 10% with respect to the Bader charge calculated from $\rho(LaH_{10})$ (Figure S5c). The negative value indicates an electron transfer to La, which can be misinterpreted as the presence of anionic La,[49] while it is actually the transfer of a small portion of charges around E^O and E^T sites in the lattice back to La atoms.

In the rest of the paper, we will apply this theory to the search for more complex superhydrides, including those with very high H compositions and those consisting of two metals (ternary superhydrides). In these cases, the structure search becomes significantly more challenging because of the greatly increased composition and structure space. The template theory will allow us to greatly reduce the structure search work via a two-step procedure and make it possible to search complex superhydrides formed by metals across the periodic table. In the first step, the metal lattices exhibiting a strong template effect will be identified by examining the ELF values at the interstitial sites; and in the second step, the H atoms will be inserted following the particle-swarm optimization (PSO) algorithm[50,51]. In the following two subsections, we will show how template theory can help us to explain the structure preferences of different superhydrides and to search for new binary and ternary superhydrides.

Chemical templates in single-metal superhydrides.

Chemical template theory can be applied to explain the energy order of different structures and guide the search for new superhydrides (Figure 6A–6B). In the past several years, many metal superhydrides MH_n with very different structures have been predicted and/or synthesized. The key to understanding the intricate structure preference is, again, the metal sublattices in superhydride structures and the corresponding electron occupations at the interstitial sites. Even for the same metal, different superhydrides structures exhibit different electron occupations, which strongly depends on the size of the metal lattice that is tuned by pressure. If the geometry and the size of the metal lattice yield strong chemical template effects on all the interstitial sites where the hydrogen atoms are located in the superhydrides, the corresponding structure is favored; otherwise, it is not. For example, between the two MH_9 structures,[16,21,52] $P6_3/mmc$ (CeH_9) and $F\bar{4}3m$ (PrH_9), most metals prefer the former except PrH_9 and PaH_9 prefer $F\bar{4}3m$ structure (Figure 6A). Cs and Ba superhydrides are not stable in $F\bar{4}3m$ structure because their metal lattices show no significant electron occupations at E^O sites. On the other hand, Y and La exhibit strong localizations bridging E^T–E^T pairs (Figure 6C) in the HCP lattice, which can lower the energy of superhydrides in $P6_3/mmc$ structure by relaxation in (111) direction. In contrast to the above cases, Pr and Pa superhydrides show no mechanism

to favor $P6_3/mmc$ structure, whereas the large electron occupations at E^O sites of FCC metal lattice stabilize the $F\bar{4}3m$ structure of the superhydrides.

The chemical template theory can guide us to discover more superhydrides. Instead of large-scale crystal structure searches of various compositions, we can now focus on the metal lattices that show a strong template effect and only create the compatible superhydride structures in the search. The chemical space of binary superhydrides has been extensively explored. Instead of repeating many earlier results, we focus on searching for superhydrides built on SC and SH metal lattices. Most notable superhydrides such as CaH_6, LaH_{10}, and CeH_9 are built on close-packed lattices such as BCC, FCC, and HCP. In contrast, SC and SH have larger interstitial regions and potentially can incorporate more H atoms. However, not many metals can maintain a strong template effect (high ELF values) in these lattices.

For SC metal lattices, strong electron localizations are found at their body center in alkali metals and Ba, suggesting possible superhydrides in the LaB_6 structure. As a matter of fact, the MH_6 superhydrides of most alkali metals and Ba are more stable in LaB_6 structure than CaH_6 structure. However, in most of the cases except NaH_6, their energies are slightly higher than BaH_6 *Imm2* structure[53]. Among all the known structures, NaH_6 is the most stable in the LaB_6 structure (Figure 6D). While constructing the convex hull of Na–H binary compounds, NaH_6 is found to be only 22 meV above the convex hull at 200 GPa.

For SH metal lattices, a promising compound LaH_{16} in *P6/mmm* structure has been predicted. In this structure, La forms an SH lattice, and its ELF shows large electron localization at the prism interstitial sites (Figure 6E). However, the ELFs of many other metal SH lattices are distinctly different from La. Especially, there is a lack of electron localization near the hexagonal metal planes that are necessary to stabilize the LaH_{16} structure. Even if these metals can form MH_{16}, their structures will be very different from LaH_{16}. We, therefore, performed a crystal structure search using PSO algorithm by inserting 16 H atoms into one unit cell of SH lattices of selected metals that show strong template effects, including Sr, Ba, Hf, *etc.* Two MH_{16} structures are found, including a new *Pbam* structure built on the SH metal lattice (Figure 6F), and a $P\bar{4}m2$ structure built on a slightly deformed SC metal lattice. The latter structure has been found in a structure prediction study of AcH_n compounds under high pressure.[25] By adding these structures to the convex hull, we found that SrH_{16} in the *Pbam* structure is stable at pressures above 186 GPa (Figure 6G). HfH_{16} is also stable, but only at pressures below 110 GPa. Although the *Pbam* structure is the lowest in energy for BaH_{16}, it is slightly above the convex hull at pressures below 300 GPa, mainly due to the exceedingly stable BaH_{12} compound.[54] After calculating the phonon frequencies and electron-phonon coupling using DFT method, we obtain a T_c of 138 K for SrH_{16} using the McMillan-Allen-Dynes formula (see supplemental experimental procedures). To test the efficacy of templates, we compare the energy evolutions of searching SrH_{16} structures with and without the Sr metal template using PSO. As shown in Figure 6H, the PSO structure search found the lowest energy *Pbam* structure at the 2nd generation while the Sr SH template was used, whereas the structure search without the template could not find the lowest energy structure up to 30 generations.

Chemical templates in two-metal superhydrides.

While almost all possible binary superhydrides have been tried out, one way of achieving higher T_c at lower pressure is the search for novel ternary superhydrides composed of two different metals or one metal and one nonmetal.[22,55–64] Constructing a complete phase diagram of ternary superhydrides based on full-scale DFT calculations is extremely difficult, and the search for optimal compounds across the entire periodic table as we have done for binary superhydrides is a very difficult task. In the past two years, a number of ternary superhydrides have been studied, including the predictions of Li_2MgH_{16} (T_c=473K at 250 GPa)[55], $LaBeH_8$ (T_c =185 K at 20 GPa)[62], $LaBH_8$ (T_c =120 K at 50 GPa, and T_c =170 K at 77 GPa while considering quantum anharmonicity)[59,63] and the syntheses of cubic hexahydride (La, Y)H_6 and decahydrides (La, Y)H_{10} (T_c =253 K at 183 GPa)[64]. In most of these studies, the thermochemistry calculations focus on a small region of the phase diagram with carefully chosen sample points. In contrast to the conventional crystal structure predictions used in these studies, the template theory allows us to assess the formation of ternary superhydrides by examining and screening the metal lattices first. Based on this theory, we conducted high-throughput calculations for combinations of most metals on the periodic table, including all transition metals and selected rare earth metals. The results show a strong correlation between the enhancements of the template strength while mixing metals and the energy of the formation of two-metal superhydrides.

High-throughput calculations based on the chemical template theory reveal two mechanisms of yielding stable two-metal superhydrides. In the first case, the combination of the two "template-active" metals might strengthen the effect. The ELF of two-metal lattices adapted from metal structures in MH_6, MH_{10}, and MH_9 at 100 GPa by partially replacing metal atoms (Figure 7A–7E and S6) show the mixture with later transition metals greatly lowers the ELF values at the interstitial sites. In contrast, if both metals are close to the *s–d* border such as Sr, Y, and Zr (Figure 7B–7D), the resulting electron localization might be enhanced, which can be measured by $\Delta\mathrm{ELF} = \mathrm{ELF}^{1/2,1/2,0}_{\mathrm{MM'H_{12}}} + \mathrm{ELF}^{1/2,0,0}_{\mathrm{MM'H_{12}}} - \mathrm{ELF}_{\mathrm{MH_6}} - \mathrm{ELF}_{\mathrm{M'H_6}}$ (Figure 7F). More importantly, $\Delta\mathrm{ELF}$ shows a strong correlation with the stability of the ternary superhydrides that is calculated as the reaction enthalpies $\Delta H = [H(\mathrm{MM'H_{12}}) - H(\mathrm{MH_6}) - H(\mathrm{M'H_6})]/14$ (Figure 7G). For example, while mixing Sr and Y, the average ELF increases (Figure 7B) and the $SrYH_{12}$ is stable against the decomposition into SrH_6 and YH_6 (Figure 7G). In contrast, the mixture of Y and Zr leads to a lower average ELF (Figure 7C) and correspondingly $YZrH_{12}$ is not stable (Figure 7G). A similar trend can be found for MH_9 and MH_{10} related two-metal superhydrides (Figure S7). By applying a recently proposed method[30] that distinctly connect the T_c of a superhydride with its bond strength (also indicated by its ELF), H composition and the H fraction of DOS at the Fermi level, we estimated the T_c of these ternary superhydrides. The results suggest that the mixing of metals in superhydrides of the same type can potentially improve T_c (Figure S8). We also calculated the T_c of $CaYH_{12}$ by DFT method and found it to be 170 K which compares well with the value of 190 K estimated by the above method.

In the second case, an active metal such as Li, Na, Mg, *etc.* is mixed with metal at the *s–d* border and enhances their template effect by doping electrons. For example, Sc_3Mg

in $P6_3/mmc$ structure shows strong enhancement of the Sc template by adding Mg. The ELFs of the metal lattice with and without Mg show the same topology, but the values are significantly higher while adding Mg (Figure 7H), which is caused by the electron transfer from Mg to Sc crystal orbitals. We thus conducted a structure search by adding H atoms into the Sc_3Mg metal lattice, which leads to the discovery of a superhydride Sc_3MgH_{24} also in $P6_3/mmc$ space group (Figure 7I). This compound is stable against the decomposition into ScH_6, MgH_4, and H_2, with −0.54 meV/atom reaction enthalpy at 200 GPa. It shows considerable DOS at the Fermi level and its T_c is calculated to be 40 K which is close to the value of 47 K estimated by the model proposed by Belli *et. al*.[30] The results show that a large-scale study of the two-metal lattices adapted from known intermetallic compounds and the change of their ELF is a promising and affordable approach to predicting two-metal superhydrides on a massive scale. The two-metal lattices adapted from MH_6, MH_{10}, and MH_9 in this work are also structures of known intermetallic compounds. Furthermore, the Li-Mg lattice in Li_2MgH_{16} is isostructural to Laves phase $MgCu_{12}$.[55] We also tested the efficacy of two-metal templates for searching ternary superhydrides. Figure 7J shows the energy evolutions of sampled Sc_3MgH_{24} structures as functions of PSO generations with and without Sc_3Mg template. The new $P6_3/mmc$ structure was found by PSO search with Sc_3Mg template at 9th generation, whereas without the template, this structure was not found up to 30th generation.

CONCLUSIONS

By studying the mechanism of metal superhydrides formation, we revealed a significant driving force for solid compound formation that is not known before, *i.e.* the chemical template effect. The proposed theory is in good alignment with a long-standing approach that also view solid-state compounds as insertion of anions into the metal lattices. Despite of this common starting point, our theory is based on the new concept that the essence of the electron localization at the interstitial sites of metal lattices is the occupation of the local quasi-atom orbitals. This allows us to develop the empirical anion-in-metals approach into a chemical bond theory that can describe this secondary interaction between the sublattices and separate it from the stronger direct chemical interactions between metals and nonmetals. This is essential for understanding the formation of compounds like superhydrides in which the direct interactions are greatly reduced by the nonmetal bonds and template effects become the determining factor.

By analyzing the results of large-scale calculations of isolated metal lattices and He matrix model with metals across the periodic table, we explained that the strong template effect of metals near the *s*–*d* border can assist the dissociation of H_2 molecules and stabilize the aromatic building units of H sublattices. Furthermore, the chemical template theory explains the large structural variations and their energy orders for superhydrides with the same H composition but different metals. The potential of the chemical template mechanism in searching for novel superhydrides, especially with higher H compositions and two-metal is demonstrated. High-throughput calculations revealed a strong correlation between the strength of the chemical templates and the stability of the two-metal superhydrides, indicating it can be used for a large-scale search of ternary and quaternary superhydrides. It will greatly enhance the efficiency of searching for superhydride materials that might become superconducting at higher temperatures and lower pressures.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Maosheng Miao (mmiao@csun.edu).

Materials availability

All materials generated in this study are available from the lead contact.

Data and code availability

All the data supporting the findings of this study are available within the paper and the Supplementary Information, and also from the Lead contact upon reasonable request.

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AUTHOR CONTRIBUTIONS

Conceptualization, M.M.; Methodology, M.M. and Y.S.; Software, Y.S.; Formal Analysis, Y.S. and M.M.; Investigation, Y.S.; Writing – Original Draft, M.M.; Writing – Review & Editing, M.M. and Y.S.; Funding Acquisition, M.M.; Resources, M.M.; Supervision, M.M.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at www.cell.com.

REFERENCES

1. Ashcroft, N.W. (1968). Metallic hydrogen: A high-temperature superconductor? Phys. Rev. Lett. *21*, 1748–1749. 10.1103/PhysRevLett.21.1748.

2. Ashcroft, N.W. (2004). Hydrogen dominant metallic alloys: High temperature superconductors? Phys. Rev. Lett. *92*, 187002. 10.1103/PhysRevLett.92.187002.

3. R. J., H., M., A., H., L., and M., S. in Proceedings of the International Symposium - Superconductivity and Pressure: A Fruitful Relationship on the Road to Room Temperature Superconductivity (in Proceedings of the International Symposium - Superconductivity and Pressure: A Fruitful Relationship on the Road to Room Temperature Superconductivity(ed. Alario-Franco, M. A.) 199–213 (Fundación Ramón Areces, 2019).).

4. Mao, H., and Hemley, R.J. (1994). Ultrahigh-pressure transitions in solid hydrogen. Rev. Mod. Phys. *66*, 671–692. 10.1103/RevModPhys.66.671.

5. Gregoryanz, E., Ji, C., Dalladay-Simpson, P., Li, B., Howie, R.T., and Mao, H.-K. (2020). Everything you always wanted to know about metallic hydrogen but were afraid to ask. Matter Radiat. Extrem. *5*, 038101. 10.1063/5.0002104.

6. Bi, T., Zarifi, N., Terpstra, T., and Zurek, E. (2019). The Search for Superconductivity in High Pressure Hydrides. In Reference Module in Chemistry, Molecular Sciences and Chemical Engineering (Elsevier).

7. Zurek, E., and Bi, T. (2019). High-temperature superconductivity in alkaline and rare earth polyhydrides at high pressure: A theoretical perspective. J. Chem. Phys. *150*, 050901. 10.1063/1.5079225.

8. Errea, I., Calandra, M., Pickard, C.J., Nelson, J.R., Needs, R.J., Li, Y., Liu, H., Zhang, Y., Ma, Y., and Mauri, F. (2016). Quantum hydrogen-bond symmetrization in the superconducting hydrogen sulfide system. Nature *532*, 81–84. 10.1038/nature17175.

9. Drozdov, A.P., Eremets, M.I., Troyan, I.A., Ksenofontov, V., and Shylin, S.I. (2015). Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system. Nature *525*, 73–76. 10.1038/nature14964.

10. Smith, G.A., Collings, I.E., Snider, E., Smith, D., Petitgirard, S., Smith, J.S., White, M., Jones, E., Ellison, P., Lawler, K.V., et al. (2022). Carbon content drives high temperature superconductivity in a carbonaceous sulfur hydride below 100 GPa. Chem. Commun. *58*, 9064–9067. 10.1039/D2CC03170A.

11. Sun, Y., Tian, Y., Jiang, B., Li, X., Li, H., Iitaka, T., Zhong, X., and Xie, Y. (2020). Computational discovery of a dynamically stable cubic SH_3-like high-temperature superconductor at 100 GPa via CH_4 intercalation. Phys. Rev. B *101*, 174102. 10.1103/PhysRevB.101.174102.

12. Wang, X., Bi, T., Hilleke, K.P., Lamichhane, A., Hemley, R.J., and Zurek, E. (2022). Dilute carbon in H_3S under pressure. Npj Comput. Mater. *8*, 87. 10.1038/s41524-022-00769-9.

13. Miao, M., Sun, Y., Zurek, E., and Lin, H. (2020). Chemistry under high pressure. Nat. Rev. Chem. *4*, 508–527. 10.1038/s41570-020-0213-0.

14. Peng, F., Sun, Y., Pickard, C.J., Needs, R.J., Wu, Q., and Ma, Y. (2017). Hydrogen clathrate structures in rare earth hydrides at high pressures: Possible route to room-temperature superconductivity. Phys. Rev. Lett. *119*, 107001. 10.1103/PhysRevLett.119.107001.

15. Liu, H., Naumov, I.I., Hoffmann, R., Ashcroft, N.W., and Hemley, R.J. (2017). Potential high-T_c superconducting lanthanum and yttrium hydrides at high pressure. Proc. Natl. Acad. Sci. *114*, 6990. 10.1073/pnas.1704505114.

16. Li, X., Huang, X., Duan, D., Pickard, C.J., Zhou, D., Xie, H., Zhuang, Q., Huang, Y., Zhou, Q., Liu, B., et al. (2019). Polyhydride CeH_9 with an atomic-like hydrogen clathrate structure. Nat. Commun. *10*, 3461. 10.1038/s41467-019-11330-6.

17. Wang, H., Tse, J.S., Tanaka, K., Iitaka, T., and Ma, Y. (2012). Superconductive sodalite-like clathrate calcium hydride at high pressures. Proc. Natl. Acad. Sci. *109*, 6463–6466. 10.1073/pnas.1118168109.

18. Ye, X., Zarifi, N., Zurek, E., Hoffmann, R., and Ashcroft, N.W. (2018). High hydrides of scandium under pressure: Potential superconductors. J. Phys. Chem. C *122*, 6298–6309. 10.1021/acs.jpcc.7b12124.

19. Semenok, D.V., Kvashnin, A.G., Ivanova, A.G., Svitlyk, V., Fominski, V.Yu., Sadakov, A.V., Sobolevskiy, O.A., Pudalov, V.M., Troyan, I.A., and Oganov, A.R. (2020). Superconductivity at 161 K

in thorium hydride ThH_{10}: Synthesis and properties. Mater. Today *33*, 36–44. 10.1016/j.mattod.2019.10.005.

20. Kruglov, I.A., Kvashnin, A.G., Goncharov, A.F., Oganov, A.R., Lobanov, S.S., Holtgrewe, N., Jiang, S., Prakapenka, V.B., Greenberg, E., and Yanilkin, A.V. (2018). Uranium polyhydrides at moderate pressures: Prediction, synthesis, and expected superconductivity. Sci. Adv. *4*, eaat9776. 10.1126/sciadv.aat9776.

21. Zhou, D., Semenok, D.V., Duan, D., Xie, H., Chen, W., Huang, X., Li, X., Liu, B., Oganov, A.R., and Cui, T. (2020). Superconducting praseodymium superhydrides. Sci. Adv. *6*, eaax6849. 10.1126/sciadv.aax6849.

22. Liang, X., Bergara, A., Wang, L., Wen, B., Zhao, Z., Zhou, X.-F., He, J., Gao, G., and Tian, Y. (2019). Potential high-T_c superconductivity in $CaYH_{12}$ under pressure. Phys. Rev. B *99*, 100505. 10.1103/PhysRevB.99.100505.

23. Zhou, D., Semenok, D.V., Xie, H., Huang, X., Duan, D., Aperis, A., Oppeneer, P.M., Galasso, M., Kartsev, A.I., Kvashnin, A.G., et al. (2020). High-pressure synthesis of magnetic neodymium polyhydrides. J. Am. Chem. Soc. 10.1021/jacs.9b10439.

24. Semenok, D.V., Kruglov, I.A., Savkin, I.A., Kvashnin, A.G., and Oganov, A.R. (2020). On distribution of superconductivity in metal hydrides. Curr. Opin. Solid State Mater. Sci. *24*, 100808. 10.1016/j.cossms.2020.100808.

25. Semenok, D.V., Kvashnin, A.G., Kruglov, I.A., and Oganov, A.R. (2018). Actinium hydrides AcH_{10}, AcH_{12}, and AcH_{16} as high-temperature conventional superconductors. J. Phys. Chem. Lett. *9*, 1920–1926. 10.1021/acs.jpclett.8b00615.

26. Li, Z., He, X., Zhang, C., Wang, X., Zhang, S., Jia, Y., Feng, S., Lu, K., Zhao, J., Zhang, J., et al. (2022). Superconductivity above 200 K discovered in superhydrides of calcium. Nat. Commun. *13*, 2863. 10.1038/s41467-022-30454-w.

27. Ma, L., Wang, K., Xie, Y., Yang, X., Wang, Y., Zhou, M., Liu, H., Yu, X., Zhao, Y., Wang, H., et al. (2022). High-temperature superconducting phase in clathrate calcium hydride CaH_6 up to 215 K at a pressure of 172 GPa. Phys. Rev. Lett. *128*, 167001. 10.1103/PhysRevLett.128.167001.

28. Drozdov, A.P., Kong, P.P., Minkov, V.S., Besedin, S.P., Kuzovnikov, M.A., Mozaffari, S., Balicas, L., Balakirev, F.F., Graf, D.E., Prakapenka, V.B., et al. (2019). Superconductivity at 250 K in lanthanum hydride under high pressures. Nature *569*, 528–531. 10.1038/s41586-019-1201-8.

29. Zhong, X., Sun, Y., Iitaka, T., Xu, M., Liu, H., Hemley, R.J., Chen, C., and Ma, Y. (2022). Prediction of above-room-temperature superconductivity in lanthanide/actinide extreme superhydrides. J. Am. Chem. Soc. *144*, 13394–13400. 10.1021/jacs.2c05834.

30. Belli, F., Novoa, T., Contreras-García, J., and Errea, I. (2021). Strong correlation between electronic bonding network and critical temperature in hydrogen-based superconductors. Nat. Commun. *12*, 5381. 10.1038/s41467-021-25687-0.

31. Flores-Livas, J.A., Sanna, A., and Gross, E.K.U. (2016). High temperature superconductivity in sulfur and selenium hydrides at high pressure. Eur. Phys. J. B *89*, 63. 10.1140/epjb/e2016-70020-0.

32. Pickard, C.J., Errea, I., and Eremets, M.I. (2020). Superconducting hydrides under pressure. Annu. Rev. Condens. Matter Phys. *11*, 57–76. 10.1146/annurev-conmatphys-031218-013413.

33. Errea, I., Belli, F., Monacelli, L., Sanna, A., Koretsune, T., Tadano, T., Bianco, R., Calandra, M., Arita, R., Mauri, F., et al. (2020). Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride. Nature *578*, 66–69. 10.1038/s41586-020-1955-z.

34. Dronskowski, R., and Blöchl, P.E. (1993). Crystal orbital Hamilton populations (COHP): energy-resolved visualization of chemical bonding in solids based on density-functional calculations. J. Phys. Chem. *97*, 8617–8624. 10.1021/j100135a014.

35. Silvi, B., and Savin, A. (1994). Classification of chemical bonds based on topological analysis of electron localization functions. Nature *371*, 683–686. 10.1038/371683a0.

36. Brese, N.E., and O'Keeffe, M. (1992). Crystal chemistry of inorganic nitrides. In Complexes, Clusters and Crystal Chemistry Structure and Bonding. (Springer), pp. 307–378. 10.1007/BFb0036504.

37. O'Keeffe, M. (1977). On the arrangements of ions in crystals. Acta Crystallogr. A *33*, 924–927. 10.1107/S056773947700223X.

38. Vegas, A. (2000). Cations in Inorganic Solids. Crystallogr. Rev. *7*, 189–283. 10.1080/08893110008044245.

39. Molina, Á.V., and Vegas, Á. (2018). Structural Models of Inorganic Crystals: From the Elements to the Compounds (Editorial Universitat Politècnica de València).

40. Yi, S., Wang, C., Jeon, H., and Cho, J.-H. (2021). Stability and bonding nature of clathrate H cages in a near-room-temperature superconductor LaH_{10}. Phys. Rev. Mater. *5*, 024801. 10.1103/PhysRevMaterials.5.024801.

41. Yao, S., Wang, C., Liu, S., Jeon, H., and Cho, J.-H. (2021). Formation mechanism of chemically precompressed hydrogen clathrates in metal superhydrides. Inorg. Chem. *60*, 12934–12940. 10.1021/acs.inorgchem.1c01340.

42. Miao, M.-S., and Hoffmann, R. (2014). High pressure electrides: A predictive chemical and physical theory. Acc. Chem. Res. *47*, 1311–1317. 10.1021/ar4002922.

43. Miao, M., and Hoffmann, R. (2015). High-pressure electrides: The chemical nature of interstitial quasiatoms. J. Am. Chem. Soc. *137*, 3631–3637. 10.1021/jacs.5b00242.

44. Chen, W., Semenok, D.V., Troyan, I.A., Ivanova, A.G., Huang, X., Oganov, A.R., and Cui, T. (2020). Superconductivity and equation of state of lanthanum at megabar pressures. Phys. Rev. B *102*, 134510. 10.1103/PhysRevB.102.134510.

45. Becke, A.D., and Edgecombe, K.E. (1990). A simple measure of electron localization in atomic and molecular systems. J. Chem. Phys. *92*, 5397–5403. 10.1063/1.458517.

46. Naumov, I.I., and Hemley, R.J. (2014). Aromaticity, closed-shell effects, and metallization of hydrogen. Acc. Chem. Res. *47*, 3551–3559. 10.1021/ar5002654.

47. Carey, F.A., and Sundberg, R.J. (2008). Advanced Organic Chemistry, Part A: Structure and Mechanisms 5th Edition. (Springer).

48. Pauling, L. (1960). The Nature of the Chemical Bond Third Edition. (Cornell University Press).

49. Liu, L., Wang, C., Yi, S., Kim, K.W., Kim, J., and Cho, J.-H. (2019). Microscopic mechanism of room-temperature superconductivity in compressed LaH_{10}. Phys. Rev. B *99*, 140501. 10.1103/PhysRevB.99.140501.

50. Wang, Y., Lv, J., Zhu, L., and Ma, Y. (2010). Crystal structure prediction via particle-swarm optimization. Phys. Rev. B *82*, 094116. 10.1103/PhysRevB.82.094116.

51. Wang, Y., Lv, J., Zhu, L., and Ma, Y. (2012). CALYPSO: A method for crystal structure prediction. Comput. Phys. Commun. *183*, 2063–2070. 10.1016/j.cpc.2012.05.008.

52. Salke, N.P., Davari Esfahani, M.M., Zhang, Y., Kruglov, I.A., Zhou, J., Wang, Y., Greenberg, E., Prakapenka, V.B., Liu, J., Oganov, A.R., et al. (2019). Synthesis of clathrate cerium superhydride CeH_9 at 80-100 GPa with atomic hydrogen sublattice. Nat. Commun. *10*, 4453. 10.1038/s41467-019-12326-y.

53. Hooper, J., Altintas, B., Shamp, A., and Zurek, E. (2013). Polyhydrides of the alkaline earth metals: A look at the extremes under pressure. J. Phys. Chem. C *117*, 2982–2992. 10.1021/jp311571n.

54. Chen, W., Semenok, D.V., Kvashnin, A.G., Huang, X., Kruglov, I.A., Galasso, M., Song, H., Duan, D., Goncharov, A.F., Prakapenka, V.B., et al. (2021). Synthesis of molecular metallic barium superhydride: pseudocubic BaH12. Nat. Commun. *12*, 273. 10.1038/s41467-020-20103-5.

55. Sun, Y., Lv, J., Xie, Y., Liu, H., and Ma, Y. (2019). Route to a superconducting phase above room Temperature in electron-doped hydride compounds under high pressure. Phys. Rev. Lett. *123*, 097001. 10.1103/PhysRevLett.123.097001.

56. Wei, Y.K., Jia, L.Q., Fang, Y.Y., Wang, L.J., Qian, Z.X., Yuan, J.N., Selvaraj, G., Ji, G.F., and Wei, D.Q. (2021). Formation and superconducting properties of predicted ternary hydride $ScYH_6$ under pressures. Int. J. Quantum Chem. *121*, e26459. 10.1002/qua.26459.

57. Muramatsu, T., Wanene, W.K., Somayazulu, M., Vinitsky, E., Chandra, D., Strobel, T.A., Struzhkin, V.V., and Hemley, R.J. (2015). Metallization and superconductivity in the hydrogen-rich ionic salt $BaReH_9$. J. Phys. Chem. C *119*, 18007–18013. 10.1021/acs.jpcc.5b03709.

58. Shi, L.-T., Wei, Y.-K., Liang, A.-K., Turnbull, R., Cheng, C., Chen, X.-R., and Ji, G.-F. (2021). Prediction of pressure-induced superconductivity in the novel ternary system $ScCaH_{2n}$ (i = 1–6). J. Mater. Chem. C *9*, 7284–7291. 10.1039/D1TC00634G.

59. Di Cataldo, S., Heil, C., von der Linden, W., and Boeri, L. (2021). $LaBH_8$: Towards high-T_c low-pressure superconductivity in ternary superhydrides. Phys. Rev. B *104*, L020511. 10.1103/PhysRevB.104.L020511.

60. Liang, X., Bergara, A., Wei, X., Song, X., Wang, L., Sun, R., Liu, H., Hemley, R.J., Wang, L., Gao, G., et al. (2021). Prediction of high-T_c superconductivity in ternary lanthanum borohydrides. Phys. Rev. B *104*, 134501. 10.1103/PhysRevB.104.134501.

61. Semenok, D.V., Troyan, I.A., Sadakov, A.V., Zhou, D., Galasso, M., Kvashnin, A.G., Kruglov, I.A., Bykov, A.A., Terent'ev, K.Y., Cherepahin, A.V., et al. Effect of magnetic impurities on superconductivity in LaH_{10}. Adv. Mater. *n/a*, 2204038. 10.1002/adma.202204038.

62. Zhang, Z., Cui, T., Hutcheon, M.J., Shipley, A.M., Song, H., Du, M., Kresin, V.Z., Duan, D., Pickard, C.J., and Yao, Y. (2022). Design principles for high-temperature superconductors with a hydrogen-based alloy Backbone at moderate pressure. Phys. Rev. Lett. *128*, 047001. 10.1103/PhysRevLett.128.047001.

63. Belli, F., and Errea, I. (2022). Impact of ionic quantum fluctuations on the thermodynamic stability and superconductivity of $LaBH_8$. 10.48550/arXiv.2206.07439.

64. Semenok, D.V., Troyan, I.A., Ivanova, A.G., Kvashnin, A.G., Kruglov, I.A., Hanfland, M., Sadakov, A.V., Sobolevskiy, O.A., Pervakov, K.S., Lyubutin, I.S., et al. (2021). Superconductivity at 253 K in lanthanum–yttrium ternary hydrides. Mater. Today *48*, 18–28. 10.1016/j.mattod.2021.03.025.

Figure 1. Structure, stability, and bonding features of metal superhydrides (A – C) The sodalite structures of three major types of metal superhydrides, including CaH_6 in $Im\bar{3}m$ structure, LaH_{10} in $Fm\bar{3}m$ structure, and CeH_9 in $P6_3/mmc$ structure. The large blue, green, and yellow balls represent the Ca, La, and Ce atoms; and the small white balls represent the H atoms. (D) The internal energies of hydrogen lattices (after removing metal atoms from superhydrides) in YH_6, LaH_{10}, and CeH_9 and of metallic hydrogen in Cs–IV structure relative to molecular hydrogen phase as functions of added charges. (E) The ICOHP of La–H^1, La 5*d* – H^1 1*s*, La 4*f* – H^1 1*s*, H^1 – H^1, and H^1 – H^2 as functions of pressure. (F) The ELF (isosurface = 0.1) of YH_6 at 300 GPa, viewed from (111) direction. A [111] cutoff plane is placed at a distance of 4.40 Å from the origin.

Figure 2. Electron occupation of local interstitial orbitals (quasi-atoms) in metal lattices. (A) The ELF (isosurface = 0.25) of La sublattice in LaH_{10} at 300 GPa. (B – D) Crystal orbitals HOCO (isosurface = 5×10^{-3}), HOCO–1(isosurface = 3.5×10^{-3}), and HOCO–2 (isosurface = 5×10^{-3}) at the Γ point of La sublattice in LaH_{10}. (E) The ELF (isosurface = 0.35) of Y BCC lattice in YH_6 at 100 GPa. (F) The ELF (isosurface = 0.35) of Y HCP lattice in YH_9 at 300 GPa.

Figure 3. The evolutions of quasi-atom occupations in metal lattices. (A) ELF values at interstitial sites in Ca FCC as functions of unit length. The shaded area shows the unit lengths of Ca lattice in a conceived CaH_{10} at pressures from 100 to 300 GPa. (B) ELF values at interstitial sites in BCC Ca as functions of unit length. The shaded area shows the unit lengths of Ca lattice in CaH_6 at pressures from 100 to 300 GPa. (C) ELF (isosurface = 0.5) of Ca FCC lattice with a unit length of 6.5 Å. At this length, FCC Ca show large electron localization at E^T sites. (D) ELF (isosurface = 0.4) of Ca FCC lattice with a unit length of 4.7 Å. This length corresponds to Ca FCC lattice in a conceived CaH_{10} under 300 GPa. (E) ELF values at interstitial sites in FCC Al as functions of unit length. The shaded area shows the unit lengths of Al lattice in a conceived AlH_{10} at pressures from 100 to 300 GPa. (F) ELF values at interstitial sites in BCC Al as functions of unit length. The shaded area shows the unit lengths of Al lattice in a conceived AlH_6 at pressures from 100 to 300 GPa. (G) ELF (isosurface = 0.4) of Al FCC lattice under ambient pressure. (H) ELF (isosurface = 0.42) of Al BCC lattice under ambient pressure. Both ELFs show that electrons in Al lattices localize mainly around Al atoms due to the occupation of Al orbitals.

Figure 4. The building units of H lattices in superhydrides. (A) The six building units of the H lattices in MH_6, MH_{10}, and MH_9 superhydrides, including the H_6 hexagon, the H_4 square, the H_8 cube, the H_5 tetrahedron, the H_6 corona, and the H_8 bipyramid. (B) The H_8 cube, a building unit of H_{10} lattice in LaH_{10}. (C) The H_6 corona, a building unit of H_9 lattice in CeH_9. (D) The energies of the H units relative to H_2 molecules as functions of pressure. The calculations are performed by use of the He matrix model. (E) The symmetries and the calculated energy levels of an H_6 hexagon. (F) The symmetries and the calculated energy levels of an H_8 cube.

Figure 5. Assemble H lattices in metal templates. (A) The ELF (isosurface = 0.35) of a Y BCC lattice overlaid on the H_6 lattice. (B) The ELF (isosurface = 0.25) of La lattice in LaH_{10} at 300 GPa, overlaid on the H_{10} lattice. (C) The ELF (isosurface = 0.35) of Ce lattice in CeH_9 at 300 GPa, overlaid on the H_9 lattice**.** (D) The density distribution of state HOCO−1 (isosurface = 3.5×10^{-3}) at Γ point of La lattice in LaH_{10} at 300 GPa. (E) The density distribution of the LUCO (isosurface = 5×10^{-3}) at Γ point of the H_{10} lattice (after removing La atoms) in LaH_{10} at 300 GPa. (F) The density distribution of the HOCO (isosurface = 3.5×10^{-3}) of LaH_{10} at the Γ point at 300 GPa. (G) The ELF values at E^T sites of 6th-row metal BCC lattices with a unit length correspond to MH_6 at 100 GPa. The dashed line corresponds to the value at the E^T site of the Ca BCC lattice in CaH_6. (H) The ELF values at E^O and E^T sites of the 6th-row metal FCC lattice with a unit length corresponding to MH_{10} at 100 GPa. The dashed lines correspond to the values at E^O and E^T sites of the La FCC lattice in LaH_{10}. (I) The ELF values at E^O and E^T sites of 6th-row metal HCP lattice with a unit length corresponding to MH_9 at 100 GPa. The dashed lines correspond to the values at E^O and E^T sites of Ce HCP lattice in CeH_9. (J) The energies of the H units relative to H_2 with the presence of metals in the 6th row of the periodic table, calculated by use of the He matrix at 100 GPa.

Figure 6. The chemical templates and the structures of single-metal superhydrides. (A) Structure preferences of MH_9 for selected metals. Two major structures, $P6_3/mmc$ and $F\bar{4}3m$ are compared. (B) Structure preferences of MH_6 of selected metals. (C) The ELF (isosurface = 0.45) of Y sublattice in YH_9 in the $P6_3/mmc$ structure. (D) The ELF (isosurface = 0.5) of Na sublattice in NaH_6 in the $Pm\bar{3}m$ structure (LaB_6). (E) The ELF (isosurface = 0.25) of La sublattice in LaH_{16} in the $P6/mmm$ structure. (F) The ELF (isosurface = 0.25) of Sr sublattice in SrH_{16} in the $Pbam$ structure. (G) Partial convex hull of Sr−H superhydrides. SrH_6 is assumed to be stable throughout the pressure range. (H) The evolution of the sampled structure energies over generations during the search of SrH_{16} structures. The red and the blue circles represent structure searches with and without metal templates.

Figure 7. The chemical template effects in two-metal superhydrides. (A) The ELF values of $MM'H_{12}$ two-metal superhydrides at the interstitial points, including (1/2, 1/2, 0) and (1/2, 0, 0). M is Sr, Y, and Zr, and M' is a 5th row metal element. (B–E**)** The ELF (isosurface = 0.2) of $SrYH_{12}$, $SrZrH_{12}$, $YZrH_{12}$ and $SrAgH_{12}$. (F) The average ELF of M M' H_{12} superhydrides at 100 GPa, $\Delta\mathrm{ELF} = \mathrm{ELF}^{1/2,1/2,0}_{\mathrm{MM'H_{12}}} + \mathrm{ELF}^{1/2,0,0}_{\mathrm{MM'H_{12}}} - \mathrm{ELF}_{\mathrm{MH_6}} - \mathrm{ELF}_{\mathrm{M'H_6}}$, in which M and M' are Ca, Sc, Sr, Y, Zr, La, Ce, Pr, Hf, and Th. (G) The reaction enthalpy of forming $MM'H_{12}$, $\Delta H = (H(\mathrm{MM'_H{}_{12}}) - H(\mathrm{MH_6}) - H(\mathrm{M'H_6}))/14$, at 100 GPa. In both (F) and (G) the squats filled with green and orange colors show MH_6 superhydrides that are predicted by DFT calculations and synthesized by DAC experiments, respectively. (H) ELF (isosurface = 0.4) of Sc_3Mg sublattice in Sc_3MgH_{24} superhydrides. (I) Top view of the ELF (isosurface = 0.4) of Sc_3Mg lattice overlayed with H_{24} lattice in Sc_3MgH_{24}. (J) The evolution of the sampled structure energies over generations during the search of Sc_3MgH_{24} structures. The red and the blue circles represent structure searches with and without metal templates.