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Metallization of Magnesium Polyhydrides Under Pressure

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Evolutionary structure searches are used to predict stable phases with unique stoichiometries in the hydrogen–rich region of the magnesium/hydrogen phase diagram under pressure. MgH4, MgH12, and MgH14 are found to be thermodynamically stable with respect to decomposition into MgH2 and H2 near 100 GPa, and all lie on the convex hull by 200 GPa. MgH4 contains two H− anions and one H2 molecule per Mg2+ cation, whereas the hydrogenic sublattices of MgH12 and MgH14 are composed solely of H2− molecules. The high–hydrogen content stoichiometries have a large density of states at the Fermi level, and the $T_c$ of MgH12 at 140 GPa is calculated to be nearly three times greater than that of the classic hydride, MgH2, at 180 GPa.

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I. INTRODUCTION

In 1935, Wigner and Huntington predicted that hydrogen, which exists in the paired molecular state at ambient pressures and temperatures, would become an alkali–metal–like monoatomic solid when compressed to pressures exceeding 25 GPa.1 This turned out to be a bit of an underestimate. Structure searches based upon density functional theory calculations have identified a number of molecular ($P \leq 400$ GPa)2 and quasi–molecular or atomic ($P = 0.5 − 5$ TPa)3,4 structures in the cold phase diagram, and experiments in diamond anvil cells show that the insulating phase III with paired hydrogens is stable over a broad temperature range and up to at least 360 GPa.5 Recent experimental work at room temperature above 220 GPa, which showed a pronounced softening of one of the Raman active molecular vibrons upon compression6, and potential conductivity7 has generated much excitement.8 The newly discovered phase IV of hydrogen is thought to be a mixed structure composed of layers of molecular units, as well as weakly bonded graphene–like sheets9,10. Superconductivity at pressures of 450 GPa and temperatures up to 242 K has been predicted in the molecular phase11, whereas the superconducting transition temperature, $T_c$, may approach 764 K for monoatomic hydrogen near 2 TPa.12

What are the structural motifs that compressed hydrogen adopts when doped with an electropositive element? Theoretical work has predicted the presence of hydridic H− atoms, H2− molecules, H− ⋅ ⋅ ⋅ H2 motifs, symmetric H4− molecules, polymeric (H2)n∞ chains, and sodalite cage structures, with the nature of the hydrogenic sublattice depending upon the identity of the alkali or alkaline earth metal, and the pressure.13–20 The latter clathrate–like cage which encapsulated the calcium cation in CaH6 was shown to be susceptible to a Jahn–Teller distortion, giving rise to a remarkable electron–phonon coupling parameter of 2.69 at 150 GPa with a concomitant $T_c$ of $\sim 225$ K.20

Herein, evolutionary structure searches are used to seek out the stoichiometries and structures of magnesium polyhydrides, MgHn with $n > 2$, under pressure. MgH4 is predicted to become stable with respect to decomposition into MgH2 and H2 near 100 GPa, and it remains the most stable stoichiometry until at least 200 GPa. Cmcn–MgH4 contains two hydridic hydrogens and one hydrogen molecule per Mg2+ cation, and it becomes metallic as a result of pressure–induced band overlap. However, due to the low density of states at the Fermi level, the estimated $T_c$ at 100 GPa is only $\sim 10$ K higher than that of P63/mmc–MgH2 at 180 GPa. Two other stoichiometries, MgH12 and MgH14, are calculated as being thermodynamically stable at higher pressures. Because these hydrogen rich phases exhibit an “H3− belt” surrounding the Mg2+ cations, and do not contain any hydridic hydrogens, they have a high density of states at the Fermi level. Assuming typical values of the Coulomb pseudopotential, the $T_c$ of MgH12 is calculated as being between 47-60 K at 140 GPa. Phases with a greater ratio of H3− :H− tend to have a larger density of states at the Fermi level, and a higher $T_c$.

II. COMPUTATIONAL METHODS

The structural searches were performed using the open–source evolutionary algorithm (EA) XtalOpt release 8 along with the default parameter set.21 Evolutionary runs were carried out on the MgH2 stoichiometry at 0, 25, 50, 100, 150, 200 and 250 GPa with cells containing 2, 3, 4 and 8 formula units (FU). At 200 GPa additional searches on cells with 5 and 6 FU were performed. Only the known $\alpha$, $\delta$, and $\zeta$–phases were recovered, with the P63/mmc structure remaining the most stable up to the highest pressures considered. Exploratory searches at 200 GPa revealed that MgHn with $n = 2.5, 3, 3.5, 4.5, 5, ...$ were noticeably less stable than those with even $n$. Thus, a more refined search was carried out at 100 and 200 GPa which was restricted to even $n$ ranging from 4–16 with 2–4 FU for MgH4 and MgH6, 2–3 FU for MgH8, and 2 FU otherwise. Additional searches for $n = 4$ and $n = 6$ were carried out with 8 and 5 FU at 100 and 200 GPa, respectively. Duplicate structures were detected using the XtalComp22 algorithm. The spglib package23 was used to determine space–group symmetries.

Geometry optimizations and electronic structure calculations were performed using density functional theory (DFT) as implemented in the Vienna ab–initio simulation.
package (VASP)\textsuperscript{24}. The exchange and correlation effects were treated using the Perdew-Burke-Ernzerhof (PBE) functional\textsuperscript{25} with plane–wave basis sets and a kinetic energy cutoff of 600 eV. The hydrogen 1s\textsuperscript{1} and magnesium 2p\textsuperscript{6}3s\textsuperscript{2} electrons were treated explicitly and the projector-augmented wave (PAW) method\textsuperscript{26} was used to treat the core states. The \( k \)-point grids were chosen using the \( \Gamma \)-centered Monkhorst–Pack scheme. The number of divisions along each reciprocal lattice vector was chosen such that the product of this number with the real lattice constant was 40 Å for the final geometry optimizations, as well as at least 50 Å for the electronic densities of states (DOS) and band structures.

In situations where band gap closure occurs as a result of pressure induced broadening, and eventual overlap of the valence and conduction bands, standard density functionals predict too low metallization pressures. For this reason we have calculated the DOS of select structures using the HSE06 screened hybrid functional, which has been shown to give good accuracy for band gaps\textsuperscript{27}. Due to the immense computational expense involved in hybrid calculations, the geometries employed have been optimized with PBE. Recently, it has been shown that inclusion of Hartree–Fock exchange in functionals such as HSE06 or PBE0 can have a significant impact upon the calculated transition pressures between different phases\textsuperscript{28,29}. Moreover, a study considering liquid nitrogen at pressures up to 200 GPa (and finite temperatures) has shown that the structural relaxations with a hybrid functional can lead to large Peierls distortions (which inevitably have an impact on the band gap)\textsuperscript{30}. It has been proposed that nontrivial exchange correlation effects can become quite important at extreme pressures, in particular when electron localization occurs (“electride” behavior\textsuperscript{31}), and/or when the semiconductor electrons interact\textsuperscript{32}. Since we do not observe significant broadening of the Mg 2p bands at the pressures considered here, it may be that structural relaxation with a hybrid functional will yield similar results as PBE. This will be considered in future studies. However, as expected, our calculations show that hybrid functionals increase the pressures at which band gap closure is predicted to occur.

Phonon calculations were performed using VASP combined with the phonopy package\textsuperscript{32} on supercells of 288 (MgH\textsubscript{2}), 160 (MgH\textsubscript{4}), 351 (MgH\textsubscript{12}) and 272 (MgH\textsubscript{16}) atoms. The electronic densities of states and phonon band structures obtained with VASP for MgH\textsubscript{2}, MgH\textsubscript{4} and MgH\textsubscript{12} at 180, 100 and 140 GPa showed good agreement to those computed using the Quantum Espresso (QE) program\textsuperscript{33}, and the computational settings described below.

In the QE calculations the H and Mg pseudopotentials, obtained from the QE pseudopotential library, were generated by the method of von Barth and Car with 1s\textsuperscript{1} and 3s\textsuperscript{2}3p\textsuperscript{0} valence configurations, along with the Perdew–Zunger local density approximation\textsuperscript{34}. We choose this particular Mg pseudopotential as it has been employed in numerous lattice dynamical studies of materials under pressure, see for example Ref.\textsuperscript{35}. Plane wave basis set cutoff energies, which gave an energy convergence to better than 0.3 mRy/atom were 55, 75 and 90 Ry for MgH\textsubscript{2}, MgH\textsubscript{4} and MgH\textsubscript{12}, respectively, and a \( 16 \times 16 \times 16 \) Brillouin–zone sampling scheme of Methfessel–Paxton\textsuperscript{36} with a smearing factor of 0.02 Ry was employed. Density functional perturbation theory, which is implemented in QE, was used for the phonon calculations. The electron–phonon coupling matrix elements were calculated using a \( 16 \times 16 \times 16 \) \( k \)-mesh and 4 \( \times 4 \times 4 \) \( q \)-mesh for MgH\textsubscript{2} and MgH\textsubscript{4}, along with a \( 12 \times 12 \times 12 \) \( k \)-mesh and \( 3 \times 3 \times 3 \) \( q \)-mesh for MgH\textsubscript{12}. The electron phonon coupling (EPC) parameter, \( \lambda \), was calculated using a set of Gaussian broadenings in steps of 0.005 Ry. The broadening for which \( \lambda \) was converged to within 0.005 was 0.035, 0.025 and 0.040 Ry for MgH\textsubscript{2}, MgH\textsubscript{4} and MgH\textsubscript{12}, respectively. The superconducting transition temperature, \( T_c \), has been estimated using the Allen–Dynes modified McMillan equation\textsuperscript{37} as:

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

where \( \omega_{\text{log}} \) is the logarithmic average frequency and \( \mu^* \) is the Coulomb pseudopotential, often assumed to be between \( \sim 0.1-0.13 \).

The molecular calculations on H\textsubscript{2} and MgH\textsubscript{12} were performed using the ADF software package\textsuperscript{38} and the revPBE gradient density functional. The band structures of select phases (see the Supporting Information, SI) were calculated using the tight–binding linear muffin–tin orbital (TB-LMTO) method\textsuperscript{39}, the VWN local exchange correlation potential along with the Perdew–Wang GGA.

III. RESULTS AND DISCUSSION

A. Squeezing MgH\textsubscript{2}

The potential for reversible hydrogen storage has resulted in much interest not only in crystalline MgH\textsubscript{2}, but also in nanoparticles based on the structure of the various phases of this soli\textsuperscript{40–44}. At 1 atm \( \alpha \)-MgH\textsubscript{2} assumes a TiO–rutile–type geometry and it undergoes a series of structural transitions, \( \alpha \) (\( P\text{a}2/m\text{mc} \)) \( \rightarrow \gamma \) (\( P\text{bnm} \)) \( \rightarrow \beta \) (\( P\text{a}3 \)) \( \rightarrow \delta \) (\( P\text{bcn} \)) \( \rightarrow \epsilon \) (\( P\text{nnma} \)), at 0.39, 3.84, 6.73 and 10.26 GPa\textsuperscript{45,46}. At around 165 GPa the \( P\text{nnma} \) phase slightly distorts to a higher symmetry \( P\text{63/mmc} \) Ni\textsubscript{2}In–type configuration, \( \zeta \)-MgH\textsubscript{2}, see Fig. 1, which was shown to be dynamically stable at 180 GPa. At lower pressures BaH\textsubscript{2}, CaH\textsubscript{2},\textsuperscript{47,48} and SrH\textsubscript{2}\textsuperscript{49} also adopt this structure. However, whereas the heavier alkaline earth dihydrides with \( P\text{63/mmc} \) symmetry are insulating, in MgH\textsubscript{2} metallization is predicted to occur by 170 GPa at the PBE–level of theory\textsuperscript{51}. Our evolutionary runs did not reveal any other phases of MgH\textsubscript{2} up to 300 GPa, a pressure at which the metallicity in \( \zeta \)-MgH\textsubscript{2} persists. Calculations using the HSE06 screened hybrid functional\textsuperscript{27} confirm the metallicity at \( \sim 180 \) GPa (see the SI).

\( \zeta \)-MgH\textsubscript{2} is metallic as a result of the closure of an indirect band gap. A flat band displaying H\textsuperscript{−} s–character rises above the Fermi level, \( E_F \), around \( \Gamma \) – \( A \), and a steep band that boasts primarily Mg s and a little bit of Mg p–character falls below \( E_F \) around the \( H \)–point, as illustrated in Fig. 1. However, whereas the heavier alkaline earth dihydrides with \( P\text{63/mmc} \) symmetry are insulating, in MgH\textsubscript{2} metallization is predicted to occur by 170 GPa at the PBE–level of theory\textsuperscript{51}. Our evolutionary runs did not reveal any other phases of MgH\textsubscript{2} up to 300 GPa, a pressure at which the metallicity in \( \zeta \)-MgH\textsubscript{2} persists. Calculations using the HSE06 screened hybrid functional confirm the metallicity at \( \sim 180 \) GPa (see the SI).

\( \zeta \)-MgH\textsubscript{2} contains half the number of valence electrons per formula unit as does MgB\textsubscript{2}, which becomes superconducting at
39 K\textsuperscript{52}. The B \( \sigma^- \) and H \( s^- \)-bands are comparable, in particular the “holes” at the top of the band spanning from \( \Gamma \) to \( A \). However, whereas MgB\textsubscript{2} consists of hexagonal boron sheets with Mg\textsuperscript{2+} intercalated in the hexagonal holes, the hexagonal network in \( \zeta \)-MgH\textsubscript{2} is made up of alternating Mg\textsuperscript{2+} and H\textsuperscript{−} ions, with the second set of hydrides located in the hexagonal holes. So the Fermi surfaces arising from the B \( \sigma^- \) and the H \( s^- \)-bands\textsuperscript{51} are not identical. We also noticed some similarities between \( \zeta \)-MgH\textsubscript{2} and the most stable CsH phase above 160 GPa\textsuperscript{54}. Whereas the former can be thought of as layers of graphitic sheets of alternating Mg\textsuperscript{2+} and H\textsuperscript{−} sandwiched in between the two layers, in CsH half of the H\textsuperscript{−} have been removed so that only layers of Cs\textsuperscript{+} and H\textsuperscript{−} are found.

The density of states at the Fermi level, \( g(E_F) \), of \( \zeta \)-MgH\textsubscript{2} is 0.01 eV\textsuperscript{−1}/electron at 170 GPa and by 300 GPa it decreases only slightly, see the SI. Despite the relatively low \( g(E_F) \) we were intrigued in the possibility of superconductivity in this system. Fig. 2 plots the phonon band structure and densities of states, phonon linewidths (\( \gamma(\omega) \)), Eliashberg spectral function (\( \alpha^2 F(\omega) \)), and \( \lambda(\omega) \) of \( \zeta \)-MgH\textsubscript{2} at 180 GPa. 38\% of the total EPC parameter, \( \lambda \), is a result of the low–frequency modes below \( \sim 700 \text{cm}^{-1} \) which are associated primarily with the motions of the heavier Mg ions, whereas the region between 750-2400 cm\textsuperscript{−1} is mostly due to motions of the H\textsuperscript{−} anions, contributes 62\% towards the total \( \lambda \) with the modes along \( \Gamma - K - M \) and \( H - L - A \) playing a dominant role. The modes above 2100 cm\textsuperscript{−1} are primarily caused by the set of H\textsuperscript{−} anions which are closer to the Mg\textsuperscript{2+} cations (the Mg–H distances at 180 GPa measure 1.58 and 1.81 Å). Despite the modest \( g(E_F) \) the total EPC parameter is calculated as being 0.58, and along with an \( \omega_{\log} \) of 1111 K gives rise to a \( T_c \) of 16–23 K for \( \mu^* \) ranging from 0.13 – 0.1, respectively, via the Allen–Dynes modified McMillan equation. For comparison, the EPC parameter and \( \omega_{\log} \) for BaH\textsubscript{2} in the simple hexagonal structure at 60 GPa have been calculated as being 0.22 and 780 K, respectively, giving rise to \( T_c \) on the order of only a few mK\textsuperscript{47}.

Given the recent interest in compressed hydrogen–rich solids as potential superconductors, we began to wonder if H\textsubscript{2} may mix with MgH\textsubscript{2} under pressure and what other metallic systems may be found. As will be shown in a moment, while the \( \zeta \) phase is preferred for MgH\textsubscript{2} above 165 GPa, it is not the most stable point on the hydrogen–rich Mg/H phase diagram at these pressures.

### B. Stabilization of the Polyhydrides

The first ionization–potential of magnesium is \( \sim 2 \text{eV} \) larger than that of lithium, suggesting that stabilization of the magnesium polyhydrides will occur at a somewhat higher pressure than the lithium polyhydrides (that is, above 100 GPa\textsuperscript{13}). The ionic radius of Mg\textsuperscript{2+} is about 30\% smaller than that of Ca\textsuperscript{2+}, and since CaH\textsubscript{2} was found to be the most stable stoichiometry at \( P = 50 - 150 \text{GPa} \) and CaH\textsubscript{8} at 200 GPa\textsuperscript{20}, we may expect that the most favorable MgH\textsubscript{n} combination has \( 2 < n < 6 \). How do these predictions — based upon chemical intuition that was developed by analyzing computational studies of compressed polyhydrides\textsuperscript{13–20} — compare with the results from our evolutionary structure searches?

The calculated enthalpies of formation, \( \Delta H_F \), of the important MgH\textsubscript{n} structures found in our searches are provided in Fig. 3 (see the SI for the plot of \( \Delta H_F \) vs. H\textsubscript{2} composition). At 100 GPa only MgH\textsubscript{4} is predicted to resist decomposition into MgH\textsubscript{2} and H\textsubscript{2}. In fact, MgH\textsubscript{4} persists as having the most negative \( \Delta H_F \) as the pressure is increased. By 200 GPa all stoichiometries except for MgH\textsubscript{2.5}, MgH\textsubscript{3} and MgH\textsubscript{3.5} have a negative \( \Delta H_F \). Because MgH\textsubscript{4}, MgH\textsubscript{12} and MgH\textsubscript{16} lie on the convex hull at 200 GPa, which is provided in the SI, they are thermodynamically stable with respect to

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**FIG. 1:** The electronic band structure of \( \zeta \)-MgH\textsubscript{2} at 180 GPa. The character of the bands which cross the Fermi level is highlighted. The Fermi energy is set to zero in all of the plots. A side and top view of \( \zeta \)-MgH\textsubscript{2} is shown on the right, with the Mg/H atoms colored in red/white.

**FIG. 2:** Phonon band structure, phonon density of states and the Eliashberg spectral function, \( \alpha^2 F(\omega) \), of \( \zeta \)-MgH\textsubscript{2} at 180 GPa. Circles indicate the phonon linewidth with a radius proportional to the strength. At this pressure \( \lambda = 0.58 \), \( \omega_{\log} = 1111 \text{K} \), and \( T_c = 16 - 23 \text{K} \) assuming \( \mu^* = 0.13 - 0.1 \).
decomposition into other phases and MgH₂/H₂. Fig. 3 illustrates that whereas the ΔHₚ of MgH₄ starts to become negative near 92 GPa, for MgH₁₂ and MgH₁₆ this occurs at 122 and 117 GPa, respectively. Comparison of these findings with the predictions based upon our newly developed chemical intuition under pressure illustrates that we did reasonably well in predicting the stabilization pressures and most stable stoichiometry without performing any computations. Now, let us begin our exploration of the structural peculiarities and electronic structures of the magnesium polyhydrides falling on the convex–hull.

### C. MgH₄: H₂ molecules and hydridic atoms

The phase with the most negative enthalpy of formation throughout the pressure range studied, 𝐂𝐦𝐜𝐦–MgH₄, forms a distorted CsCl bcc lattice with H²⁻ atoms taking up the vertex positions of the underlying cube–like cages. The body–centered positions are occupied by a 1:1 mix of Mg²⁺ cations and H₂ molecules with slightly elongated bonds, as highlighted by the red and blue polyhedra in Fig. 4(a). The size mismatch between the two results in the hydrides forming different sized cages around them. The same 𝐂𝐦𝐜𝐦–MgH₄ structure was discovered in evolutionary runs carried out at 100 and 200 GPa, and phonon calculations at 100 GPa showed it was dynamically stable.

Interestingly, the lowest enthalpy I₄/mmm–symmetry CaH₄ structure found using the particle–swarm optimization technique in a recent study can be described the same way as 𝐂𝐦𝐜𝐦–MgH₄. The difference between the two is the manner in which the cations and the H₂ molecules are distributed: in CaH₄ they are dispersed homogeneously, but in MgH₄ they are arranged into interwoven zig–zag chains. Additionally, the hydride cages are more distorted in the MgH₄ structure with the smallest face which surrounds an Mg²⁺ being the one which links one magnesium cation to another. Actually, the structure can also be viewed as sheets of MgH₂ with H₂ molecules trapped in the larger gaps between the sheets, one such sheet is shown at the right of Fig. 4(a).

Within PBE the total density of states of 𝐂𝐦𝐜𝐦–MgH₄ at 100 GPa is quite small; in fact it is lower than that of the I₄/mmm analogue. The former is 42 meV/atom more stable than the latter at this pressure, but the volume of I₄/mmm–MgH₄ is 0.04 Å³ per atom smaller than that of 𝐂𝐦𝐜𝐦–MgH₄. The formation of the zig–zag like chains illustrated in Fig. 4(a) must therefore have a substantial impact on the electronic contribution to the enthalpy.

As the pressure increases from 100 to 300 GPa, the shortest distance between the metal cations decreases from 2.56 Å to 2.32 Å, and the Mg 2p core bands broaden from 0.19 to 0.58 eV due to core overlap. The shortest Mg–H₂ distance decreases from 1.74 Å to 1.55 Å, as does the Mg–H₂ separation (1.92 Å/1.68 Å). The molecular H₂ bonds lengthen somewhat from 0.78 Å to 0.79 Å. This is slightly longer than the intramolecular distance in pure compressed H₂ at these pressures, 0.73 Å and 0.75 Å, respectively.
Since MgH$_4$ contains H$^-$ units, it becomes metallic as a result of pressure induced band broadening and eventual overlap, like LiH$_2$ and NaH$_2$. Metallization occurs within PBE already by 20 GPa, even though Cmcm– MgH$_4$ is not stable with respect to decomposition into H$_2$ and MgH$_2$ at this pressure. A band displaying H$^-$ s-character rises above $E_F$ at the Y–point, whereas bands exhibiting predominantly Mg $sp$ and a little bit of H$_2$ $\sigma^*$–character fall below it at the Z and $T$–points (see Fig. 4(b), and the “fat bands” in the SI). Calculations using the HSE06 functional increase the metallization pressure to $\sim$150 GPa (see the SI).

D. MgH$_{12}$ and MgH$_{16}$: the H$_2$修身 belt

The absence of H$^-$ anions in the other structures lying on the convex hull at 200 GPa, MgH$_{12}$ and MgH$_{16}$, has important consequences for their electronic structure. The hydrogenic sublattices of these phases are composed solely of H$_2^-$ molecules with slightly stretched bonds, just like the CaH$_{12}$ structure predicted in a previous study.

The presence of hydridic hydrogens in systems with a small mole fraction of hydrogen, and their absence in phases with a high hydrogen content was rationalized by Wang and co–workers by considering the formal number of ‘effectively added electrons’ (EAE) which are donated from the alkaline earth metal valence bands into the H$_2$ $\sigma^*$–bands for various CaH$_n$ stoichiometries. If the EAE is small, the dihydrogen bond simply stretches as a result of the population of H$_2$ $\sigma^*$, and hydridic hydrogens are not formed. If the EAE is large enough, the molecule dissociates into two H$^-$ units.

The most stable MgH$_{12}$ structure found in our evolutionary searches had R$3$–symmetry and was shown to be dynamically stable at 140 GPa. The hexagonal building block for this phase consists of an Mg$^{2+}$ cation surrounded by six H$_2^{1/3}$ molecules, as illustrated in Fig. 5(a). The dihydrogen molecules in these hexagons appear to arrange in a ‘belt’ around the metal cation in a side–on fashion. The hexagons are tiled in parallel sheets forming an ABCABC… close–packed structure. This description is, however, somewhat misleading as the distance between Mg$^{2+}$ and a hydrogen atom within the MgH$_{12}$ building block is comparable to the shortest distance between the metal ion and a hydrogen atom in a different building block. For example, the intra– and inter–building block Mg–H measurements are 1.76 and 1.81 Å, respectively, at 140 GPa. The dihydrogen bonds in MgH$_{12}$ are substantially elongated to 0.82 and 0.81 Å at 140 and 300 GPa, when compared with the typical bond lengths of pure H$_2$ at these pressures (0.74/0.75 Å). A gas phase geometry optimization on a H$_2^{1/3}$ molecule at 1 atm showed that the bond stretched from 0.75 to 0.79 Å. So the expansion of the H–H bond observed in MgH$_{12}$ is consistent with the partial filling of the H$_2$ $\sigma^*$–bands.

The lowest enthalpy MgH$_{16}$ configuration we found, which exhibited $P – 1$ symmetry and was dynamically stable at 130 GPa, could be thought of as being made up of similar MgH$_{12}$ units with excess H$_2^-$ molecules stuffed between the hexagons, as illustrated in Fig. 5(b). These ‘interstitial’ dihydrogens lie on top of the Mg$^{2+}$ cations in the MgH$_{12}$ building blocks. The intramolecular distance in H$_2^{1/4}$ at 1 atm was calculated as being 0.78 Å, whereas the bond lengths of the dihydrogens in MgH$_{16}$ range from 0.76 to 0.85 Å at 130 GPa, with the interstitial hydrogen molecules being shorter (0.76–0.78 Å) than those in the belt (0.79–0.85 Å). The unequal bond lengths in the H$_2$ $\sigma^*$ units may be a result of different charge states, or be due to their local bonding environments, or both.

As the pressure increases, the intramolecular H–H bond lengths decrease, with the interstitial and belt hydrogens measuring 0.74–0.76 Å and 0.78–0.84 Å, respectively, at 300 GPa.

Since MgH$_{12}$ and MgH$_{16}$ are metallic as a result of the partial filling of the H$_2$ $\sigma^*$–bands like LiH$_6$, they have a high density of states at $E_F$, see Fig. 6. Both phases remain good metals upon compression up to at least 300 GPa, and the Mg $2p$ bands broaden only slightly to $\sim$0.15–0.2 eV at 300 GPa as a result of core overlap. A comparison of the DOS of MgH$_{12}$ at 140 GPa calculated with PBE and the HSE06 screened hybrid functional showed that latter valence DOS was slightly broader (as expected for metallic systems) and the core Mg $2p$ bands shifted to lower energies. However, the $g(E_F)$ computed with the two functionals was essentially the same (see the SI). This is in–line with our previous results which showed that $g(E_F)$ is relatively insensitive to the choice of the functional in sodium polyhydrides that did not contain hydridic hydrogens.$^{14}$ The nearly free–electron like valence bands of MgH$_{12}$ and MgH$_{16}$ exhibit primarily H s–character, with a little bit of Mg $sp$ spanning throughout (see the fat bands in the SI). Nonetheless, the computed DOS of these structures match quite well with a hypothetical system where the metal cations have been removed, the (H$_{12}$)$_2^{2-}$ and (H$_{16}$)$_2^{2-}$ lattices (see the SI), suggestive of almost full ionization of the Mg valence 3s electrons into the H$_2$ $\sigma^*$–bands.
A number of MH\textsubscript{12} clusters, where M is a transition metal atom, have been predicted as being stable in the gas phase by quantum chemical calculations\textsuperscript{60}. Moreover WH\textsubscript{4} (H\textsubscript{2})\textsubscript{4}, which contains four hydridic hydrogens and four dihydrogen s bonded to the metal center in a side–on fashion, has been made in a neon matrix\textsuperscript{61}. Unsurprisingly, molecular calculations on both the optimized MgH\textsubscript{12} building blocks as well as (MgH\textsubscript{12})\textsuperscript{2+} with \textit{D\textsubscript{6h}} symmetry revealed numerous imaginary frequencies, so these clusters will not be stable at 1 atm. Nonetheless, it is instructive to compare the electronic structure of the MgH\textsubscript{12} building block with the DOS computed for \textit{R3}–MgH\textsubscript{12} at various pressures.

Whereas in an optimized MgH\textsubscript{12} cluster the Mg–H and intramolecular H–H distances were calculated as being 2.20 and 0.79 Å, these values measure 2.34–2.58/1.76–1.78 Å and 0.79/0.82 Å in \textit{R3}–MgH\textsubscript{12} at 5/140 GPa. So the gas phase cluster is actually a little bit more ‘compressed’ than the building block within the solid at 5 GPa. The energy level diagrams and canonical molecular orbitals (MOs) of these clusters are illustrated in Fig. 7(a). The six MOs lowest in energy resemble the canonical MOs of benzene, except that they do not contain a node which bisects the dihydrogen molecules. A large gap is found between the highest occupied molecular orbital (HOMO) and HOMO-1 of the optimized cluster, but a small gap separates the HOMO and lowest unoccupied molecular orbital (LUMO). The HOMO–HOMO-1 gap decreases as the cluster is compressed, as do the analogous sets of bands in the extended system, as illustrated in Fig. 7(b).

The frontier orbitals of the 1 atm cluster contain substantial character arising from H, and the HOMO also has an important contribution from the Mg 3\textit{p} and the LUMO from the Mg 3\textit{s} orbitals. Our fragment orbital analysis\textsuperscript{62} shows that the LUMO+1 contains primarily H–character with less than 4% of Mg 3\textit{d} states mixed in. In the ‘less–compressed’ cluster extracted from the solid at 5 GPa the frontier orbitals swap positions so that the HOMO displays Mg 3\textit{s} and the LUMO Mg 3\textit{p}–character. This is in–line with the projected densities of states which illustrate that the predominant contribution around the Fermi level is due to Mg \textit{s} at 5 GPa. At 140 GPa the gap between the hydrogenic and the metallic bands between -6 to -3 eV closes in the solid, and the HOMO and HOMO-1 orbitals in the cluster come closer together in energy. Moreover, as a result of the pressure induced \textit{s} \rightarrow \textit{p} transition in Mg, the states around the Fermi level contain about an equal amount of Mg \textit{s} and \textit{p}–character. In the cluster the energy ordering of the molecular orbitals also changes, so that the HOMO is more Mg \textit{p}–like, and the LUMO displays primarily H \textit{s} character. So the gas phase clusters are able to mimic some of the essential features of the projected DOS of the solid at different pressures.
FIG. 8: Phonon band structure, phonon density of states and the Eliashberg spectral function, $\alpha^2 F(\omega)$, of MgH$_4$ at 100 GPa. Circles indicate the phonon linewidth with a radius proportional to the strength. At this pressure $\lambda = 0.74$, $\omega_{\text{log}} = 941$ K, and $T_c = 29 - 37$ K assuming $\mu^* = 0.13 - 0.1$.

F. Superconductivity in the polyhydrides

Our computations have estimated the $T_c$ of the classic alkaline earth hydride, $P6_3/mmc$–MgH$_2$, as being $\sim 20$ K at 180 GPa. We wondered what the $T_c$ of the aforementioned hydrogen–rich phases would be in comparison, and if $T_c$ would be influenced by the hydrogenic sublattice of the polyhydride. Computations have been carried out on $Cmcm$–MgH$_4$ and $R3$–MgH$_{12}$ at 100 and 140 GPa, respectively, since these are pressures slightly larger than when $\Delta H_F$ was computed as becoming negative, and since both systems were found to be metallic within PBE at these pressures.

Within PBE the density of states at the Fermi level of $Cmcm$–MgH$_4$ at 100 GPa is comparable to the one calculated for $\zeta$-MgH$_2$ at 180 GPa. The total EPC parameter is nearly 28% larger, however. In both phases the low–frequency modes which are mostly due to the vibrations of the Mg atoms contribute $\sim 0.2$ to the total $\lambda$; compare Fig. 8 and Fig. 2. The main reason why the overall EPC parameter is larger for the polyhydride than the classic hydride is a result of the total coupling provided by the modes between $\sim 500$-2500 cm$^{-1}$, which are primarily due to the motions of the hydrogen atoms. Whereas the classic hydride contains only hydridic hydrogens, there is an equal number of H$_2$ and H$^-$ hydrogens in MgH$_4$. The H$_2$ vibron, located around 3500 cm$^{-1}$ contributes only 1.5% to the total coupling strength in the polyhydride. This is not surprising, since the bands crossing the Fermi level displayed only a small amount of H$_2$ s–character. Despite the higher $\lambda$ that MgH$_4$ has as compared to MgH$_2$, the prefactor in the modified McMillan equation, $\omega_{\text{log}}$, is calculated as being 15% smaller so the total $T_c$ of MgH$_4$ is estimated as being $\sim 14$ K higher than that of the classic alkaline earth hydride.

Despite the increased hydrogen content and higher density of states at the Fermi level, the total EPC parameter of $R3$–MgH$_{12}$ at 140 GPa is almost the same as of $Cmcm$–MgH$_4$ at 100 GPa. However, a comparison of the $\lambda(\omega)$ in Fig. 9 and Fig. 8 shows that the relative contributions to the overall $\lambda$ are quite different in the two polyhydrides. MgH$_{12}$ does not contain any hydridic hydrogens, and is metallic because of the partial filling of the H$_2$ $\sigma^*$–bands. In contrast to what was found for MgH$_4$, the H$_2$ vibron contributes about 11.1% to the total $\lambda$. This corresponds quite well to the 11.3% calculated for a compressed KH$_6$ phase$^{19}$ whose hydrogenic sublattice only contained H$^-$ motifs. The EPC associated with the low–frequency modes below 400 cm$^{-1}$, which are dominated by the motions of the heavier metal atoms, is about a third of the amount calculated for the phases containing H$^-$ units. The main contribution to $\lambda$, 79%, arises from the intermediate frequency regime, which is primarily due to the H$_2$ motions. The reason why the $T_c$ of MgH$_{12}$ is estimated as being $\sim 20$ K higher than that of MgH$_4$ is due to the larger $\omega_{\text{log}}$. Unfortunately, the computational expense precluded us from calculating the EPC parameter of compressed $P = 1$–MgH$_{16}$, or from exploring the pressure dependence of $T_c$.

The values we calculate for the total EPC parameter and the $T_c$ of the magnesium polyhydrides falls within the range of 0.5-1.6 and 10-139 K, respectively, computed for a number of hydrogen–rich systems$^{20}$. We show that comparable $\lambda$ values may be obtained for polyhydrides with very different hydrogenic sublattices, but their $\omega_{\text{log}}$, and therefore $T_c$, may differ. The magnesium polyhydrides are predicted to have a larger $T_c$ than MgH$_2$ under pressure, and phases with a larger mole percent ratio will likely have a higher $T_c$.

IV. CONCLUSIONS

Evolutionary structure searches coupled with density functional theory calculations are used to predict the most stable structures and stoichiometries of the magnesium polyhydrides, MgH$_n$ with $n \geq 2$, under pressure. The thermodynamically stable structures found in this study have a hydrogenic
sublattice containing H\(^-\) anions and H\(_2\) units (MgH\(_4\)), or H\(_2\) molecules which are less strongly bonded than those found in pure molecular hydrogen at 1 atm (MgH\(_{12}\) and MgH\(_{16}\)).

Metallization in \(P6_3/mmc\)–MgH\(_2\) occurs as a result of an H\(^-\) s–band rising above, and a Mg sp band falling below the Fermi level. \(T_c\) is estimated as being between 16-23 K at 180 GPa, with a sizable contribution to the total electron phonon coupling parameter arising from vibrations related to both the hydrogen and magnesium atoms.

MgH\(_4\), which starts to become thermodynamically stable with respect to decomposition into MgH\(_2\) and H\(_2\) near 100 GPa is found to contain one H\(_2\) molecule and two hydridic hydrogens per Mg\(^{2+}\) cation. Metallization occurs as a result of pressure–induced band gap closure, but the density of states at the Fermi level is quite low. Around 120 GPa other stoichiometries, whose hydrogenic sublattices contain only H\(_2\)\(^-\) molecules with slightly stretched bonds, emerge as being thermodynamically stable. MgH\(_{12}\) and MgH\(_{16}\) are metallic in part as a result of the partial filling of the H\(_2\) \(\sigma^*\)–bands and have a high density of states at the Fermi level. Their electronic structure at various pressures can be traced back to the molecular orbital diagram of their building block, the MgH\(_{12}\) cluster. Despite the very different hydrogenic sublattices, both MgH\(_4\) and MgH\(_{12}\) are found to have similar electron phonon coupling parameters. The main reason why the \(T_c\) of MgH\(_{12}\) at 140 GPa is calculated as being larger than that of MgH\(_4\) at 100 GPa, 47-60 K vs. 29-37 K assuming typical values of \(\mu^*\), is because of the larger average logarithmic frequency computed for MgH\(_{12}\).

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