Ternary Gold Hydrides: Routes to Stable and Potentially Superconducting Compounds

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ABSTRACT: In a search for gold hydrides, an initial discouraging result of no theoretical stability in any binary AuH₂ at P < 300 GPa was overcome by introducing alkali atoms as reductants. A set of AAuH₂ compounds, A = Li, Na, K, Rb, and Cs, is examined; of these, certain K, Rb, and Cs compounds are predicted to be thermodynamically stable. All contain AuH₂⁺ molecular units and are semiconducting at P = 1 atm, and some form metallic and superconducting symmetrically bonded AuH₂⁺ sheets under compression. To induce metallicity by bringing the Au atoms closer together under ambient conditions, we examined alkaline earth ion substitution for two A, i.e., materials of composition AE(AuH₂)₂. For AE = Ba and Sr, the materials are already marginally metallic at P = 1 atm and the combination of high and low phonon frequencies and good electron–phonon coupling leads to reasonably high calculated superconducting transition temperatures for these materials.

INTRODUCTION

Our aim in this work is to pursue a realistic route to gold hydrides in the condensed state. The challenge we face is that gold is one of the least reactive metals. Gold, along with a few other noble metals, resists surface oxidation under ambient conditions. Whereas some gold alloys with alkali metals, transition metals, and compounds with main group elements, such as halides, exist, one way that gold’s inert nature is reflected is by the absence of stable hydrides in the condensed state. This is in sharp contrast to most other metals, which readily form binary alloys, or interstitial or molecular compounds with hydrogen. The passivity of gold can be expressed in still another way—almost every molecular anion will reduce gold ions (Au⁺ and Au³⁺) to pure gold. Or, alternatively, there are few gold compounds with negative formation energies.

An additional motivation for pursuing metal hydride systems in general, and gold hydrides in particular, is that the combination of high phonon frequencies associated with hydrogen and low ones for the heavy gold motions are two factors suggestive of potential high temperature superconductivity in compounds of these elements.¹⁻³

The literature reports attempts to fabricate gold hydrides, but high-pressure experiments attempting the synthesis of gold hydrides up to 113 GPa have so far failed.⁴ However, inelastic neutron scattering has provided evidence for the existence of surface gold hydride on nanostructured gold catalysts.⁵ Different theoretically plausible solid-state structures of AuH have also been discussed.⁶

While relatively scarce, both molecular and extended gold compounds, with negative heats of formation, do exist. Examples include gold halides (both molecular and extended), alkali gold binaries (which we will discuss later on), and alkali gold oxide ternaries.⁷⁻⁹ Metastable gold species, such as Au₂O₃, have also been made.¹⁰⁻¹² One of us participated in a study of AuO at various pressures that is relevant here.¹³ Gold hydrides have been detected as fleeting molecular gas-phase species,¹⁴ and as the products of laser-ablation in low temperature Ar and Ne matrices.¹⁵⁻¹⁶ Gold surfaces and variously sized gold clusters and complexes have, somewhat surprisingly, proven active as catalysts.¹⁷⁻¹⁹ The reasons behind the observed catalytic activity have been discussed at some length.²⁰ A variety of molecular gold-hydride complexes (Au–H containing molecules) have been made.²¹⁻²² Among these, we mention, by way of example, N-heterocyclic carbene stabilized gold(I) mono-hydride,²³ dinuclear gold(I) hydrides stabilized by chelating phosphorus-containing ligands,²⁴ and gold(III) monohydride stabilized by C–N–C pincer ligands.²⁵⁻²⁶ Gold’s interactions with hydrogen (within molecules) have been thoroughly reviewed.²⁷ One molecular example is shown in Figure 1.

RESULTS AND DISCUSSION

Are Binary Gold Hydrides Feasible? Whereas we will, as the title of this work suggests, provide what we believe to be a realistic route to gold hydrides at P = 1 atm, we first explored high-pressure conditions. The pressure variable can create new chemistries.²⁸⁻²⁹ Given the experimental evidence against the existence of gold hydride in the solid state both at 1 atm and under pressure up to 113 GPa,³ we first investigated whether the application of pressures beyond 100 GPa might change the situation. Unfortunately, particle-swarm optimization structure
How to Stabilize Gold Hydrides. The unfavorable formation of extended AuH (or other stoichiometries) might be traced to the similar electronegativity of hydrogen and gold (Au = 2.54, H = 2.2 on the Pauling scale, and Au = 1.92, H = 2.3 on the Allen scale), which mitigates against Au → H (or Au ↔ H) charge transfer necessary for ionic lattice stabilization. With the pressure option exhausted, we must perturb this balance in other ways, by the explicit introduction of additional electrons (or holes). Promising clues comes from gold’s neighbors in the periodic table, and from extended structures of group 10 and 12 compounds containing MH2 molecular units.

Consider, for instance, the transfer of one electron from an alkali metal atom to a gold atom. The electron affinity of gold is high. The resulting auride anion, Au−, is considerably less electronegative than Au, and will interact differently with hydrogen. Specifically, Au− will allow for Au → H charge transfer to occur. Au− has a d10s2 electronic configuration, and is, as such, iso-valence-electronic with Zn, Cd, and Hg, which form ZnH2, CdH2, and HgH2 as molecular metastable solids. In the latter, the H is formally hydridic and the metals take up a +2 oxidation state. The isoelectronic bonding analogy is with AuH−, a formally d9ML2 complex featuring Au(I) that is expected to be linear.

Pd2+ and Pt2+ are also iso-valence-electronic with Au−, and form linear PdH2− and PtH2− ions, readily stabilized in the solid state as persistent [A]2PdH2 and [A]2PtH2 salts (A = alkali metal). Several of these molecular solids show a surprising metallicity, which has been explained as arising from alkali metal s-states crossing the Fermi level. Pursued for possible hydrogen storage and high temperature applications, their design and synthesis is an active field of research.

Auride salts can be readily generated in the presence of strong reducing agents, such as alkali metals. Several different kinds of alkali metal gold binaries are known. They exhibit a range of properties, from, for instance, metallic KAu, to semiconducting RbAu and CsAu, with the latter having a band gap of ~2.6 eV. So, could such compounds be made to react with hydrogen, and is it possible then to stabilize AuH− salts in the solid state?

The AuH− Anion. The AuH− anion has been detected spectroscopically in matrix isolation experiments, using isotope labeling. We know, from high-level multiconfigurational calculations, that AuH− in isolation has a significant barrier to decomposition, a process which eventually proceeds through bond dissociation to Au− and H2. The large barrier, which amounts to 57 kcal/mol (2.5 eV) in vacuum, is likely reduced somewhat in an extended system, when the AuH− anion is surrounded by counterions that might facilitate Au− formation. However, it appears clear that, from a kinetic point of view, a AuH−-based salt might be persistent enough for room temperature handling. Whether such a material will be thermodynamically stable with respect to potential reagents and decomposition products is an entirely different question, however. And one we will attempt to settle.

### Ternary Alkali Metal Gold Hydride, [A]AuH2

Extensive structure searches using a particle swarm optimization algorithm (see the Methodology section) were performed on [A]AuH2 stoichiometries (here A = Li, Na, K, Rb, Cs), while allowing for 1–4 formula units in each unit cell. Different searches at 100 and 200 GPa on the binaries AuH2, AuH, and AuH, and subsequent pressure scans up to 300 GPa, showed no evidence for a pressure-induced negative heat of formation for any hydride (Figure 2). We limited our search to pressures below 300 GPa, because of a known phase transition in pure gold at ~290 GPa. So we cannot exclude the possibility that even higher pressures could lead to a AuH binary phase that is thermodynamically favorable relative to the elements.

Many of the low-energy binary AuH structures identified were of low symmetry, and most were close to degenerate in energy with other structures. This is likely a consequence of the search algorithms proceeding toward the enthalpically most favored state, which appears to be phase separation into elemental gold and hydrogen (this was implied by some of the optimized structures). Metastable structures without a clear route to synthesis, and with likely low barriers of activation to thermal decomposition, are of little practical interest. We have therefore not analyzed these binaries in detail, but selected structures are provided in the Supporting Information (SI). We now return to atmospheric conditions, and a different strategy for stabilizing gold hydrides.
dynamically stable phases were identified, some by the search algorithm directly, and some by following imaginary phonon modes out of some of the structures found by the search algorithm. The lowest energy phases of each alkali salt were then also recomputed for the other alkali metal counterions, to effectively increase the search space. Several phases were found close in energy, and all of these contain separate AuH$_2^-$ anions, as expected. The lowest energy structure identified for all alkali metals is of C2 symmetry (Figure 3).

**Figure 3.** Predicted C2 ground state of KAuH$_2$ (1 atm), and two dynamically stable higher energy phases. Relative energies are given in kcal/mol formula unit.

The [A]AuH$_2$ (C2) ground state can be understood in another way as a formal hydrogenation product of gold, forming AuH$_2^-$, inside of a CsCl-type AAu (Pn3m) sublattice (Figure 4). The linear AuH$_2^-$ anions can orient themselves in different ways in the AAu sublattice, generating several stable or metastable configurations close in energy over a range of pressures. Compare, for instance, the C2 and I4/mcm phases in Figure 3. The C2 ground state minimizes Au–Au and maximizes AuH–Au distances in a manner symmetric in all three dimensions, as shown in Figure 4.

**Figure 4.** Left: The predicted C2 ground state of [A]AuH$_2$ can be understood as a formal hydrogenation of [A]Au (A = alkali metal). Right: The AuH$_2^-$ anionic sublattice in [A]AuH$_2$ (C2) can be viewed as a 2D-plane that repeats also in the third dimension. Arrows indicate the twofold rotational symmetry of the lattice.

**Thermodynamic Stability.** To evaluate the thermodynamic stability of the target alkali metal gold hydrides one must, ideally, know the relative Gibbs energy of all possible decomposition products. The exploration of the complete isomer space of a ternary stoichiometry is a substantial challenge. It reduces to knowing all stable binary compositions, located on the edges of the triangle in Figure 5. Fortunately, our case is simplified by the absence of stable binary gold hydrides (Figure 1), and the prevalence of only one stable (ionic) A$_2$H$_2$ binary stoichiometry, at least under ambient conditions, which is our focus here. What remains to be determined is a knowledge of stable compositions of the gold alkali metal binaries. And there are several of these. For KAuH$_2$ we have considered 5 compositions, KAu$_8$, KAu$_2$, K$_2$Au$_3$, KAu, and K$_3$Au, experimentally known to be stable on the convex hulls of one (or another) alkali metal auride.

All alkali metal gold hydrides exhibit negative energies of formation relative to the elements (Table 1). This, however, is not a guarantee of actual thermodynamic stability. LiAuH$_2$ is, for example, unstable with respect to the formation of LiH, Au$_2$Li, and H$_2$. NaAuH$_2$ is similarly unstable with respect to NaH, NaAu$_2$, and H$_2$. The lightest compound for which we can expect thermodynamic stability under ambient conditions appears to be KAuH$_2$. Phonon calculations have allowed extrapolation of thermal and entropic corrections to the electronic energy. Even considering the considerable entropic gain associated with gaseous H$_2$ formation, KAuH$_2$ is predicted to remain stable at room temperature. The margin of stability in Gibbs energy is small, however, only 0.7 kcal/mol, which is below the accuracy of our methodology. More certain appears the thermodynamic stability of RbAuH$_2$ and CsAuH$_2$ (Table 1), the latter being the best candidate for synthesis.

**Table 1** shows $\Delta E$ and selected $\Delta H$ and $\Delta G$ both at 300 K for some formation routes of AAuH$_2$. The table is complex to view, but then so is the thermodynamic richness of any ternary compound.

What structures are AAuH$_2$ (A = K, Rb, and Cs) likely to have? Structure searches did not always identify the C2 ground state as lowest in energy for those compounds, but when independently refined this structure was consistently lowest in energy. Whether it is in fact the true ground state structure, future experimental work and X-ray spectroscopy will hopefully reveal. Our main conclusion remains that the K$^+$, Rb$^+$, and Cs$^+$ salts of AuH$_2^-$ are thermodynamically accessible, and stable at P = 1 atm. If another lower energy crystal structure exists, it will only make this conclusion more certain.

To validate the relative accuracy of our electronic ground state ($T \to 0$ K) energies shown in Table 1, we performed PBE and HSE06 calculations on the least favorable formation reaction: $1/3\text{K}_2\text{Au}_3(s) + 1/3\text{KH}(s) + 5/6\text{H}_2(g) \rightarrow \text{KAuH}_2$. We here considered the $P2_12_12_1$ metastable phase of KAuH$_2$, which has a much smaller unit cell compared to the C2 ground state. The reaction energy calculates as $-7.4$ and $-9.0$ kcal/mol with PBE and HSE06, respectively. This agreement implies that PBE slightly underestimates the stability of the alkali gold metal hydrides, and suggests that our overall PBE-based stability estimates are conservative.
Table 1. Selection of Formation Routes to Alkali Metal (A= Li, Na, K, Rb, and Cs) Gold Hydrides\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E$</th>
<th>$\Delta E + ZPE$</th>
<th>$\Delta H_{298}$</th>
<th>$\Delta G_{298}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(s) + Au(s) + $1/2$H$_2$(g) $\rightarrow$ LiAuH$_2$</td>
<td>-16.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LiH(s) + Au(s) + $1/2$H$_2$(g) $\rightarrow$ LiAuH$_2$</td>
<td>+3.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1/3$Li$_2$Au(s) + $1/3$AuH(s) + $1/3$H$_2$(g) $\rightarrow$ LiAuH$_2$</td>
<td>+3.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$2/3$LiH(s) + $1/3$Au(s) + $2/3$H$_2$(g) $\rightarrow$ LiAuH$_2$</td>
<td>+8.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na(s) + Au(s) + $1/2$H$_2$(g) $\rightarrow$ NaAuH$_2$</td>
<td>-17.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1/3$Na$_2$Au$_3$(s) + $1/3$NaH(s) + $1/3$H$_2$(g) $\rightarrow$ NaAuH$_2$</td>
<td>+0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1/2$Na$_2$Au(s) + $1/2$Au + $1/2$H$_2$ $\rightarrow$ NaAuH$_2$</td>
<td>+7.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K(s) + Au(s) + $1/2$H$_2$(g) $\rightarrow$ KAuH$_2$</td>
<td>-22.9</td>
<td>-20.7</td>
<td>-22.2</td>
<td>-13.8</td>
</tr>
<tr>
<td>$1/3$K$_2$Au(s) + $1/3$Au + $1/3$H$_2$ $\rightarrow$ KAuH$_2$</td>
<td>-16.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Au(s) + KH(s) + $1/2$H$_2$(g) $\rightarrow$ KAuH$_2$</td>
<td>-14.9</td>
<td>-12.2</td>
<td>-12.9</td>
<td>-9.8</td>
</tr>
<tr>
<td>KAu(s) + $1/2$H$_2$(g) $\rightarrow$ KAuH$_2$</td>
<td>-10.6</td>
<td>-8.3</td>
<td>-9.9</td>
<td>-1.1</td>
</tr>
<tr>
<td>$1/3$K$_2$Au$_3$(s) + $1/3$KH + $1/3$H$_2$ $\rightarrow$ KAuH$_2$</td>
<td>-10.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1/3$K$_2$Au$_3$(s) + $1/3$KH + $1/3$H$_2$ $\rightarrow$ KAuH$_2$</td>
<td>-9.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1/3$K$_2$Au$_3$(s) + $1/3$KH + $1/3$H$_2$(g) $\rightarrow$ KAuH$_2$</td>
<td>-7.8</td>
<td>-5.6</td>
<td>-6.7</td>
<td>-0.7</td>
</tr>
<tr>
<td>Rb(s) + Au(s) + $1/2$H$_2$(g) $\rightarrow$ RbAuH$_2$</td>
<td>-23.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RbAu(s) + $1/2$H$_2$(g) $\rightarrow$ RbAuH$_2$</td>
<td>-10.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1/3$Rb$_2$Au$_3$(s) + $1/3$RbH(s) + $1/3$H$_2$(g) $\rightarrow$ RbAuH$_2$</td>
<td>-9.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cs(s) + Au(s) + $3/4$H$_2$(s) $\rightarrow$ CsAuH$_2$</td>
<td>-25.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1/3$Cs$_2$Au$_3$(s) + $1/3$CsH(s) + $1/3$H$_2$(g) $\rightarrow$ CsAuH$_2$</td>
<td>-12.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CsAu(s) + $3/4$H$_2$(s) $\rightarrow$ CsAuH$_2$</td>
<td>-10.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All possibilities are illustrated by the phase diagrams shown in Figure 5. The first lines provide corresponding calculated energies/heats of formation. Energies are given in kcal/mol for the reaction as written. Structures of alkali-gold binaries are taken from the Inorganic Crystal Structure Database (ICSD), unless otherwise specified.}
For this system, the application of pressure acts to raise the crystal symmetry. The $C_2$ phase quickly becomes less stable than a semiconducting $I_{4}/mcm$ phase at $\sim 2$ GPa. The $I_{4}/mcm$ phase becomes metallic at $\sim 30$ GPa, and transforms into the $P_{4}^{4}/mmm$ phase at $\sim 120$ GPa. The metastable $P_{2}^{1}2_{1}2_{1}$ phase is predicted to convert into the same $P_{4}^{4}/mmm$ phase at 60 GPa.

The $I_{4}/mcm \rightarrow P_{4}^{4}/mmm$ phase transformation, predicted just before 120 GPa, is geometrically interesting; it positions the hydrogens equidistant (1.73 Å) from their neighboring Au atoms. This equates to the formation of square planar sheets of hydrogen atoms, bonded with square planar sheets of gold. The sheets are then stacked with $K^+$ ions. One sees here a structural relationship to cuprate sheets in the superconducting cuprates, and to the $Im\bar{3}m$ $SH_3$ structure. However, the...
The latter case has hydrogen bonding the sheets (there SH$_2$) together in a still more symmetrical ReO$_3$-type lattice.

The bands we see at $P = 120$ GPa (Figure 9) are, of course, broader than those we have previously shown in Figure 6. The Au 5d peak in the DOS is prominent in the region of $-5$ to $-10$ eV. Interestingly, even K 3p, formally a core level included in our calculation, acquires some dispersion at this pressure, around 10 eV. The density of states at the Fermi level is predominantly made up of formal Au d > p > s orbital contributions with an admixture of H 1s. The Au 6s, normally high in energy, is stabilized by interactions with H 1s. The population of Au 6p at the Fermi level can similarly be inferred from the frontier $\sigma^u$ orbital of AuH$_2^-$ spreading out into a band (see SI for orbitals of AuH$_2^-$).

We have not performed the search for the ground state of each Au−K binary under elevated pressures, a procedure required to ascertain the absolute phase stability of the $P4/mmm$ with respect to decomposition. We nonetheless expect that the $P4/mmm$ phase should be accessible experimentally (be it stable or metastable) by applying pressure to a sample of KAuH$_2$ obtained at 1 atm. The reasons for this are as follows: C$_2$ is convertible into $I4/mcm$ by following low frequency ($\sim$9 Thz $\equiv$ 300 cm$^{-1}$) AuH$_2^-$ rotational modes (Figure 7). No structural rearrangement occurs in the $I4/mcm \rightarrow P4/mmm$ transformation (Figure 8), which implies that the process is barrierless. The AuH$_2^-$ anion is quite persistent in and of itself.

In looking for pressure-induced metallicity, we have focused on KAuH$_2$ over CsAuH$_2$. This is because of KAuH$_2$’s predicted smaller band gap, and because Cs is too large to allow the formation of a corresponding high-pressure $P4/mmm$ phase in which H is positioned equidistant between gold atoms. Next we show that a related strategy, of substituting alkali for alkaline earth metal ions, appears to provide a feasible route to metallic gold hydrides under ambient pressure conditions. The hunt for metallicity will lead us to tantalizing predictions of gold hydride-based superconductivity.

### TERNARY ALKALINE EARTH METAL GOLD HYDRIDES

What happens if we substitute two alkali metal counterions by a single alkaline earth ion? One reason for looking at such compounds is to see the effect of cation size on the lattice stabilization and electronic structure, while comparing to the alkali metal ternaries where larger cations increased stability while also increasing band gaps. By concentrating the positive charge, we supposed that AuH$_2^-$ subunits might be nudged closer, which should increase d-band dispersion and decrease band gaps. For the alkali metal ternaries we noticed that the radii$^\text{-}\text{c}^\text{+}$ of the alkali metal cations follow the energy of formation linearly, which argues for even larger counterions still (see the SI). There are also additional reasons, related to theories of superconductivity, which will be addressed toward the end of this paper.

We searched for alkaline earth metal analogues, i.e. [AE][AuH$_2$]$_2$ stoichiometries (AE = Sr, Ba), while allowing for 1−3 formula units in each unit cell. The predicted ground states of Sr(AuH$_2$)$_2$ and Ba(AuH$_2$)$_2$ are of $I4$ symmetry. The ground state assignment of Sr(AuH$_2$)$_2$ is less certain, as our structure searches did identify one $I4/mcm$ phase 1.5 kcal/mol lower than the $I4$ phase. However, the $I4/mcm$ structure is not dynamically stable, and our attempts at making it so by lowering the crystal symmetry and following imaginary modes failed. For thermodynamic reasons that will be discussed, we will, however, focus mostly on Ba(AuH$_2$)$_2$. Ba(AuH$_2$)$_2$ is of $I4$ symmetry, and its predicted unit cell and structure at 1 atm is shown in Figure 10.
Most of the ternary structures considered have nearest Au–Au separations far below the sum of the VdW distances (\(4.5–5\) Å, depending on the formal oxidation state of gold). In the \(C_2\) and \(P2_12_12_1\) phases of KAuH\(_2\), for example, the nearest Au–Au distances are 3.94 and 3.77 Å, respectively. Could there be an aurophilic interaction at work here? Since the phases of KAuH\(_2\) that have longer and fewer Au–Au contacts are lower in energy (Figure 3) aurophilic bonding appears unlikely. This is a contrast to Ba(AuH\(_2\))\(_2\) where our suggested ground state exhibits a Au–Au distance of only 3.03 Å along one direction of the crystalline lattice (Figure 10).

**Stability and Suggestions on Synthesis.** The energy of formation (relative to \(AE(s), Au(s),\) and \(H_2(g)\)) of Sr(AuH\(_2\))\(_2\) and Ba(AuH\(_2\))\(_2\) are computed as \(-46\) and \(-48\) kcal/mol, respectively. These values are larger than the stabilization energies of the previously considered alkali salts (Table 1), in part a consequence of the larger formula unit. At the PBE level these phases are only metastable with respect to decomposition into SrAu\(_2\) + 2H\(_2\) (\(-5.2\) kcal/mol) and BaAu\(_2\) + 2H\(_2\) (\(-4.0\) kcal/mol), respectively. A piece of the 3D convex hull of the Ba/H/Au system is illustrated in Figure 11. The Sr/H/Au convex hull is shown in the SI.

Figure 10. 4\(_4\) structure of metastable Ba(AuH\(_2\))\(_2\) at 1 atm. Note how the AuH\(_2^-\) subunits arrange in a manner similar to what we found for the alkali metal analogues, but how voids are unavoidably introduced by replacing two singly charged alkali metal cations with one doubly charged Ba\(^2\+) cation.

Figure 11. Calculated segment of the three-component phase diagram of Ba, Au, and H in the ground state (left). Blue lines between green circles connect stable phases. Unstable AuH\(_2\) binaries have been omitted. Ba(AuH\(_2\))\(_2\) is metastable (but just barely) with respect to decomposition into BaAu\(_2\) and H\(_2\). Its synthesis nevertheless appears possible from CsAuH\(_2\).

Ba(AuH\(_2\))\(_2\) and Sr(AuH\(_2\))\(_2\) should then be quite accessible via suitably chosen metathesis reactions, such as

\[2\text{CsAuH}_2 + \text{BaBr}_2 \rightarrow 2\text{CsBr} + \text{Ba(AuH}_2)_2,\]
\[\Delta E = -10\ \text{kcal/mol}\]  \(\text{(2)}\)

and

\[2\text{CsAuH}_2 + \text{SrBr}_2 \rightarrow 2\text{CsBr} + \text{Sr(AuH}_2)_2,\]
\[\Delta E = -13\ \text{kcal/mol}\]  \(\text{(3)}\)

**Electronic Structures of Sr(AuH\(_2\))\(_2\) and Ba(AuH\(_2\))\(_2\).** What about the electronic structures of Ba(AuH\(_2\))\(_2\) and Sr(AuH\(_2\))\(_2\)? The band structure and density of states with orbital contributions of Ba(AuH\(_2\))\(_2\) are shown in Figure 12. The corresponding data for Sr(AuH\(_2\))\(_2\) and phonon band structures for both compounds are reproduced in the SI. The smaller size of the Ba-counterion (Table S2), compared to two alkali metal ions, requires the gold atoms to move closer. This has significant implications for the electronic structure. Especially one d-band of gold achieves a remarkable dispersion (Figure 12), which crosses the Fermi level close to the zone center, then drops over 3 eV. A COHP analysis of the chemical bonding reveals largely concurrent Ba–H, Au–H, and Au–Au bonding below \(-2\) eV and a weak antibonding contribution near \(-1\) eV below the Fermi level.

In contrast to all alkali metal gold hydride phases explored, our PBE calculations suggest that Ba(AuH\(_2\))\(_2\) is metallic under ambient conditions. The density of states at the Fermi level is small, however, and it is possible that a lower energy structure, not identified by our structure search, may open up a gap. The shape of the density of states around the Fermi level is vaguely reminiscent to the DOS of graphene. Two prominent van Hove singularities are seen at \(-1\) and \(-2.5\) eV. Optimization at the HSE06 level of theory does not change the geometry in any meaningful way. However, HSE06 band structure calculations on Ba(AuH\(_2\))\(_2\) lead to an indirect gap \((\Gamma \rightarrow M)\) of \(\sim 80\) meV. Such a minuscule gap should close with thermal excitation even at low temperatures, and disappear with very mild shrinkage of the unit cell under compression. We have not included any
correction for dispersion when obtaining the structures. This is because dispersion-uncorrected PBE provided unit cell volumes in better agreement with experimental reference data available for Li$_3$PdH$_2$ and Na$_2$PdH$_2$, which, however, arguably are subjected to thermal expansion (see the SI). With this in mind we are, if anything, overestimating the unit cell volumes. This sensitivity is important to keep in mind in later estimates of the electron-phonon coupling, carried out at the PBE level.

The corresponding I4 phase of Sr(AuH$_2$)$_2$ is metallic at both levels of theory. The main difference between the band structure of Sr(AuH$_2$)$_2$ (shown in the SI) and that of Ba(AuH$_2$)$_2$, shown in Figure 12, is that the band just above the Fermi level at the Z-point in Ba(AuH$_2$)$_2$ crosses the Fermi level in Sr(AuH$_2$)$_2$.

Though not unprecedented at low pressures, systems that are both ionic and metallic are not that common. Note the Ba 6p/5d–H 1s resonances in Figure 12. This is a sign of Ba–H bonding, not only Au–H. Such bonding needs to be considered for all compressed hydride structures. Ba–H bonding is also implied by the range of nearest-neighbor Ba–H bond distances of 3.17–2.87 Å, which are quite close to the 3.01–2.61 Å range in the Pnma ground state of BaH$_2$. A combined view, where the Ba–H sublattice is shown as prisms interlocked with AuH$_2$-bridges is shown in Figure 13.

THE MAKING OF A GOLD-HYDRIDE-BASED SUPERCONDUCTOR

One reason for looking into gold hydrides in the first place, aside from our academic interest in mitigating their nonexistence, is to search for novel superconducting materials. That hydrogen under high compression might form a phonon-mediated near room-temperature superconductor was proposed by one of us some time ago. The realization that compression of alloys of hydrogen may allow for superconductivity at more moderate compressions have since resulted in a flurry of theoretical and experimental work.

Gold is not a superconducting element in its natural state, but shows mK and μK superconductivity in alloys with Ga, Al, In, and Sn. Whereas there are a few examples to the contrary (such as $T_c = 1.5$ K in SrAuSi$_3$), superconductivity in gold compounds is rare. One proposed explanation is the avoidance of a +II oxidation state, and fluctuations around that as one sees in the cuprates. However, Au$^-$ is isoelectronic with Hg, which exhibits a critical superconducting temperature, $T_c$, of 4.2 K. If we limit our discussion to conventional superconductivity, then the most likely Cooper pairing mechanism (by popular consensus) is phonon-mediated. Au is, along with Cs and Ba, heavy, which
lowers the frequency of soft lattice phonons. Low frequency phonon modes are important for increasing the electron phonon coupling constant, $\lambda$,

$$\lambda = 2\int \frac{\alpha^2F(\omega)}{\omega}d\omega,$$

where $\alpha^2F$ is the Eliashberg spectral function, the phonon density of states weighted by an electron phonon coupling matrix element at each k-point and frequency. Whereas low phonon modes are important for raising $\lambda$, in turn crucial for a high $T_c$, they also decrease the average logarithmic frequency, $\omega_{\log}$

$$\omega_{\log} = \exp\left[\frac{2}{\lambda} \int \alpha^2F(\omega) \frac{\ln(\omega)}{\omega}d\omega\right].$$

A reasonably high average frequency is another prerequisite for enabling higher $T_c$. So a balance has to be struck in the “design” of superconductive materials. The introduction of strong Au–H bonding, forming AuH$_2$+, adds high frequency modes that increase $\omega_{\log}$ dramatically. Together, $\lambda$ and $\omega_{\log}$ are key factors to consider for rationalizing the occurrence of superconductivity. One way to do so is through the McMillan-Allen-Dynes approximation to the Eliashberg equations,$^{27,76}$

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

where $\mu^*$ is the electron-repulsion parameter, which typically is taken empirically to lie in the range of 0.10–0.15.

In addition to these arguments arising from traditional phonon-mediated superconductivity theory, there are other proposed Cooper pair formation mechanisms to consider. Purely electronic coupling via polaron and bipolarons$^{79}$ and polarization waves arising in a localized core–electron framework$^{80}$ are two such suggestions. Even as they are difficult to implement in current electronic structure codes, the latter two suggest an importance of polarizability. Heavy elements are more polarizable, and few more so than Cs and Ba.$^{81}$

The arguments for superconductivity in ternary gold hydrides are enticing. However, a prerequisite is a metallic ground state. We have discussed two gold-hydride compounds in more detail, KAuH$_2$ under high compression, and Ba(AuH$_2$)$_2$ at 1 atm. How do they fare with respect to superconductivity?

The high-pressure $P4/mmm$ phase of KAuH$_2$ is predicted to be a superconductor, albeit with a quite meager $T_c$ of 0.3 K at 120 GPa. The electron–phonon coupling constant $\lambda$ calculates as 0.3, which places this material within the weak-coupling limit where the McMillan–Allen–Dynes approximation works well. The $T_c$ of 0.3 K was calculated using a Coulomb pseudopotential parameter $\mu^*$ set to 0.11. We single out this value of $\mu^*$ as it also reproduces the $T_c$ obtained after iteratively solving the Eliashberg equations (Figure 14).

The electron–phonon coupling $\lambda$ is, in the limit of homogeneously coupled k-space, proportional to the density of states at the Fermi level, $N(\varepsilon_F)$, which in the case of KAuH$_2$ at 120 GPa is dominated by Au-d states. From the flat density of states on both sides of the Fermi level (Figure 9) we can infer that no additional bands can be made to contribute to $N(\varepsilon_F)$, and that little can be gained, in terms of $\lambda$, from further compression of KAuH$_2$ beyond 120 GPa.

Turning then to Ba(AuH$_2$)$_2$ at 1 atm, our calculations predict a $T_c$ of ~30 K. This analysis hinges on its poor metallicity, a property, as we described, of which we cannot be completely certain. The Fermi surface is limited, with pockets of holes only close to the $\Gamma$-point, and of electrons near M in the Brillouin zone. Sensitivity of the electronic structure with respect to lattice distortion (phonon motion and the unit cell volume) is close to the $\Gamma$-point, and of electrons near M in the Brillouin zone. Sensitivity of the electronic structure with respect to lattice distortion (phonon motion and the unit cell volume) is suggested both by the band structure near $\Gamma$ and when comparing the $M$ and $Z$ points, where the latter shows an unfilled conduction band very close to the Fermi level. At our level of theory, the electron phonon coupling comes out as $\lambda = 2.0$. This is unusually large and comparable to DFT estimates of $\lambda = 1.5–2.5$ in high-pressure H$_2$S.$^{82–85}$ the phase believed responsible for $T_c = 203$ K superconductivity in compressed H$_2$S.$^{86}$

The strong coupling predicted for Ba(AuH$_2$)$_2$ limits the reliability of the McMillan–Allen–Dynes approximation (eq 6). Nevertheless, when $\mu^* = 0.12$ is chosen, eq 6 provides a $T_c$ in good agreement with the numerical solution to the Eliashberg equations, which predict superconducting gap closure at ~30 K (Figure 14). In comparison, the $I4$ phase of Sr(AuH$_2$)$_2$ has a smaller calculated electron phonon coupling constant $\lambda$ of 0.9, and is predicted to turn superconducting below 10 K.
CONCLUSIONS

This work begins by computationally showing the infeasibility of preparing simple binary gold hydrides at any pressure below 300 GPa. This is not a reason for giving up in a quest for stable hydrides of Au. Turning to ternary compounds, we consider the kinetically stable AuH$_2^-$ anion and predict that it can be stabilized in the condensed phase under ambient conditions ($P = 1$ atm, $T = 298$ K) by the introduction of both alkali ($M_a \geq K$) and alkaline earth (Ba and Sr) counterions.

Exploration of ternary phase diagrams is never easy, but a careful analysis indicates that the AuH$_2$ salts of K, Rb and Cs are all thermodynamically stable. It should be possible to synthesize them from the elements under an excess of H$_2$. CsAuH$_2$ is the most stable ternary and, in turn, the most promising intermediate for the formation of metastable Ba(AuH$_2$)$_2$ and Sr(AuH$_2$)$_2$ via suitably chosen metathesis reactions. The thermodynamics discussed, and the inherent stability of AuH$_2^-$ in isolation, makes us optimistic as to the possibility of high barriers to decomposition of [A]AuH$_2$ and [AE](AuH$_2$)$_2$ and the possibility of room temperature handling.

The alkali salts are semiconducting, with band gaps in the range of 2–3 eV. In looking for ways to attain metallicity in such compounds, we have done a more detailed analysis of the smallest band gap semiconductor that is predicted stable, namely, KAuH$_2$. The computed ionic ground state is made up of well-separated AuH$_2^-$ molecular subunits; the predominant molecular character is clear from the limited phonon dispersion, which mirrors closely the vibrational frequencies of the isolated molecular anion. Upon compression, KAuH$_2$ is predicted to metallize at $\sim 30$ GPa, and at $\sim 120$ GPa, to lose all molecular character and transform into a Au–H–Au equidistant network, square sheets sandwiching a K$^+$ layer. The high pressure KAuH$_2$ structure is predicted to have a superconducting critical temperature of 0.3 K.

A metallic state is facilitated by Au-d level overlap. To enable this under ambient conditions we replace alkali metal counterions with barium and strontium, which necessitates AuH$_2^-$ units moving closer together. The molecular, ionic, barely metallic solid Ba(AuH$_2$)$_2$ has a small Fermi surface, which makes electron–phonon coupling calculations sensitive to the level of theory, meriting caution and further study. With that disclaimer, we predict Ba(AuH$_2$)$_2$ to be a superconductor below 30 K at $P = 1$ atm. The analogous phase of Sr(AuH$_2$)$_2$ is calculated to be a superconductor below 10 K.

More importantly than the final predicted $T_c$ is the route we took there, which sets out some design principles. Starting with light and heavy atoms (suggested by a phonon mediated BCS view of superconductivity) we overcame an electronic hindrance to phase stability by moving from a binary to a ternary, incorporating alkali metal ions. This is a chemical maneuver rooted in electronegativity considerations. A second instance of chemical reasoning, essentially ionic or ion size considerations, led us from KAuH$_2$ semiconducting (at $P = 1$ atm) to borderline metallic and computed as superconducting Ba(AuH$_2$)$_2$ and Sr(AuH$_2$)$_2$. Throughout we paid attention to realistic prospects of synthesis. We believe we have opened up new “search spaces” for superconductivity, and have made good use of chemical ideas in devising strategies for attaining new superconductors.

METHODOLOGY

Geometry Optimization. Initial calculations relied on periodic DFT calculations performed using VASP, version 5.3.5.78,79 The Predew–Burke–Ernzerhof (PBE)80 generalized gradient approximation (GGA) functional was used to generate electronic wave functions that were expanded in a plane-wave basis set with a kinetic energy cutoff of 800 eV. Projected augmented wave (PAW) potentials82,83 were used to treat core electrons and incorporate the associated relativistic effects of gold. The number of explicitly treated electrons were $n(e) \approx 1$ for alkali and alkaline earth metal atoms, 18 for H, and 6s5d for Au. Brillouin zone sampling was performed on $k$-meshes with a reciprocal space resolution of at least $2\pi \times 0.03$ Å$^{-1}$. Energies and their gradients were converged to $<1$ meV per atom. This approach provided geometries in excellent agreement with experimental X-ray structures for the related Li$_2$PdH$_2$ and Na$_2$PdH$_2$ salts (see the SI), and this level of theory was therefore used throughout. Dispersion correction (DFT-D3) caused an underestimation (<10%) of the unit cell volumes, and for this reason this correction was not used. We stress that this is not necessarily a fault of the DFT-D3 correction, but at least partly a consequence of us omitting the effects of thermal expansion in the materials when comparing to experimental data obtained at $T > 0$.

Electronic Structure. In addition to using PBE throughout, selected relative energies and densities of states were refined using the Heyd–Scuseria–Ernzerhof (HSE06)91,92 screened-hybrid functional, using either a 400 or 600 eV kinetic energy cutoff. HSE06 has a reported mean absolute error of 0.2 eV for band gaps.93 Compared to the more accurate HSE06 method, PBE was consistently found to underestimate the relative energy of discussed ternary systems, i.e., offer a more conservative estimate to their stability. The reasonably small differences (<4.5 kcal/mol) between HSE06 and PBE are of little consequence to our conclusions.

Structure Prediction. Searches for the global minima on the potential energy surface were performed using a particle swarm optimization algorithm94 implemented in the CALYPSO code.95 Typically two or more structure searches, each allowing for 1–4 units of a given stoichiometry, were performed. The reliability of the approach was validated on a related ternary system; the algorithm correctly identified the experimentally known $I4/mmm$ ground state of Li$_2$PdH$_2$ and Na$_2$PdH$_2$.

Dynamic Stability. Thermal corrections to the energies were calculated from force constants obtained through the direct method, i.e., from Hellmann–Feynman forces induced by small displacements introduced to a supercell, using the PHONOPY 1.9.7 code.96 For the phonon calculations a kinetic energy cutoff of 400 eV was used.

Superconductivity. The Full Potential Linear Augmented Plane Wave (FP-LAPW) method implemented in the ELK code97 was used for calculating $T_c$ using both eq 6, and by iteratively solving the Eliashberg equations. Initial muffin tin radii used were B$_{latm}$ = 2.4, Sr$_{latm}$ = 2.6, K$_{120GPa}$ = 2.0, Au$_{latm}$ = 2.1, Au$_{120GPa}$ = 1.8, H$_{latm}$ = 1.1, and H$_{120GPa}$ = 1.2 bohr. Phonons were calculated using a supercell approach similar to what is described above, where for KAuH$_2$ and [Ba/Sr](AuH$_2$)$_2$ we used a $3 \times 3 \times 3$ and $2 \times 2 \times 2$ supercell, respectively.

Electron–phonon coupling for the latter compounds was evaluated using $32 \times 32 \times 32$ $k$-meshes. Convergence of the phonon density of states and Gibbs energy with respect to supercell size was made with VASP (see the SI). The inclusion
of spin–orbit coupling had very minor influences on the Fermi surface of compressed KAuH2, and no effect on the Fermi surface of Ba(AuH2)2 (see the SI).

This work relied on the Atomic Simulation Environment (ASE)99 and AFLOW.100

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