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# Phase stability and superconductivity of lead hydrides at high pressure

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Density functional theory calculations and crystal structure predictions using the particle swarm optimization method have been combined to determine stable hydrides of lead under pressure. In contrast to other group-IVa hydrides, the stoichiometry  $\text{PbH}_6$  is the first hydride to become stable, at just under 1 Mbar. For two previously studied stoichiometries  $\text{PbH}_4$  and  $\text{PbH}_8$ , new energetically favorable phases were identified to become stable around 2 Mbar. In all structures, the hydrogenic sublattices comprises negatively charged  $\text{H}_2^-$  molecules. Competitive  $\text{PbH}_4$  and  $\text{PbH}_6$  structures are layered.  $\text{PbH}_6$  features  $\text{H}_2$  molecules intercalated between hexagonal close packed Pb-layers, the stable phase of dense pure lead, thus offering a potentially straightforward route towards synthesis. In  $\text{PbH}_8$ , the Pb lattice adapts a *beta*-Sn structure and hydrogen atoms form quasi-1D-chains. All structures were found to be metallic and to feature superconductivity in their respective stability range, with moderately high  $T_c$  in the range 60-100 K for  $\text{PbH}_4$  and  $\text{PbH}_6$ , and 161-178 K for  $\text{PbH}_8$ .

## I. INTRODUCTION

Compressed metallic hydrogen was proposed as potential high-temperature superconductor based on Bardeen-Cooper-Schrieffer (BCS) theory<sup>1</sup>, inspiring numerous searches for metallic hydrogen. Recently, conductivity measurements showed that hydrogen conducts above 360 GPa<sup>2</sup>; IR absorption measurements showed an abrupt drop in transmission at 420 GPa<sup>3</sup>, while optical measurements found a shiny phase at 495 GPa<sup>4</sup>. However, these pressures are very hard to reach, and detailed measurements are difficult. As a means of inducing metallicity in hydrogen at less extreme conditions, chemical pre-compression was suggested as a feasible pathway to produce metallic and superconducting hydrogen-rich compounds at lower pressure<sup>5</sup>. Along this line, a large number of stable hydride compounds with high transition temperature ( $T_c$ ) were successfully predicted at low pressure using crystal structural searches and electronic structure calculations, such as  $\text{SH}_3$ <sup>6</sup>,  $\text{CaH}_6$ <sup>7</sup>,  $\text{YH}_{10}$ <sup>8</sup>, and  $\text{LaH}_{10}$ <sup>8</sup>. Subsequent experimental results<sup>9,10</sup> demonstrated the ability of utilizing structural prediction and critical temperature calculation to discover potential hydrogen-rich compounds with high- $T_c$  superconductivity. This stimulated further work on phase diagrams and potential superconductivity of hydrogen-rich compounds under high pressure, to the extent that a neural network was trained on data of predicted  $T_c$  to find regions in the periodic table that hold the most promise for superconducting hydrides<sup>11</sup>. The latter, of course, depends on accurate screening of potential hydride compounds and their electronic properties.

The group IVa hydrides (Si,Ge,Sn) $\text{H}_4$  were at the forefront of studies of ‘chemically pre-compressed’ hydrogen. They have been extensively investigated in the past 15 years and exhibit metallization at lower pressure than pure hydrogen. So far, the metallization of methane has not been successfully achieved in experi-

ments, as it is likely to decompose before metallization would happen<sup>12,13</sup>. Eremets *et al.*<sup>14</sup> reported the transition of silane,  $\text{SiH}_4$ , from insulating molecule to metal at 50 GPa and subsequent superconductivity with  $T_c$  of 17 K at 96 and 120 GPa using Raman scattering and electrical resistance measurements, though the reported metallization and superconductivity of silane could not be reconciled with later theoretical<sup>15–17</sup> and experimental<sup>18–20</sup> works. As the atomic radius increases,  $\text{GeH}_4$ <sup>21,22</sup> and  $\text{SnH}_4$ <sup>23,24</sup> have been predicted to possess higher  $T_c$  of 70–84 K at 500 GPa and 80 K at 120 GPa, respectively. As for  $\text{PbH}_4$ , Zaleski-Ejgierd *et al.*<sup>25</sup> reported several layered structures above 132 GPa, which are different from other group IVa hydrides and all exhibit metallic behavior but they did not investigate potential superconductivity.

For several group-IVa hydrides the predicted  $T_c$  values significantly increased after intercalating with additional  $\text{H}_2$ <sup>26,27</sup>. In early experimental works<sup>28–30</sup>,  $\text{SiH}_4(\text{H}_2)_2$  and  $\text{GeH}_4(\text{H}_2)_2$  were both observed with  $\text{SiH}_4$  and  $\text{GeH}_4$  molecules on *fcc* sites. The measured Raman and IR spectra for  $\text{SiH}_4(\text{H}_2)_2$ <sup>28</sup> and  $\text{GeH}_4(\text{H}_2)_2$ <sup>30</sup> revealed strong intermolecular interactions between  $\text{SiH}_4$  ( $\text{GeH}_4$ ) and  $\text{H}_2$  at low pressure, which are demonstrated as the main reason for the predicted high- $T_c$  superconductivity in *Ccca*- $\text{SiH}_4(\text{H}_2)_2$ <sup>26</sup>, while Zhong *et al.* mainly attributed the superconductivity in *P2<sub>1</sub>/c*- $\text{GeH}_4(\text{H}_2)_2$ <sup>27</sup> to the vibrations of  $\text{H}_2$  units. In the Pb-H system, Cheng *et al.*<sup>31</sup> combined extensive structural searches and electron-phonon coupling (EPC) calculations for  $\text{PbH}_4(\text{H}_2)_2$  and proposed three thermodynamically stable phases, where the *C2/m* phase has  $T_c$  of 107 K at 230 GPa. However, in contrast to all lighter group-IVa elements, lead does not form stable  $\text{XH}_4$  molecules, and its hydrides seem to contain  $\text{H}_2$  molecules only. There is therefore no reason to assume that  $\text{PbH}_4$  or  $\text{PbH}_8$ , the stoichiometries favourable for the lighter group-IVa hydrides, are also most relevant for lead, and a complete study of lead hydrides should include a wider range of compositions.

Here, we conduct a systematic computational study on the combination of the heaviest group IVa element Pb with H atoms aiming to systematically reveal the stable phases, their crystallographic structures, electronic properties, and examine potential superconducting properties. We find that a new hydride compound so far not present in the group-IVa hydrides,  $\text{PbH}_6$ , is in fact the first lead hydride to form under pressure, while we also uncover more stable structures for  $\text{PbH}_4$  and  $\text{PbH}_8$  that feature at higher pressures. All structures are metallic and exhibit moderately high  $T_c$  in the range 61-178 K in their respective stability range.

## II. COMPUTATIONAL METHODS

The CALYPSO code<sup>32,33</sup> based on the particle swarm optimization (PSO) method has been successfully applied to a variety of binary<sup>7,8,34</sup> and ternary<sup>34-36</sup> hydrides at high pressure. Herein, variable-cell crystalline structure predictions for  $\text{PbH}_4$ ,  $\text{PbH}_6$  and  $\text{PbH}_8$  containing 1 to 4 formula units per cell at 150 and 300 GPa were performed using the CALYPSO code. Generally, each search covered 50 generations and generated about 1500 trial structures. Structural relaxations, enthalpy and electronic structure calculations were conducted using the Vienna ab initio simulation (VASP) package<sup>37</sup> with the Perdew-Burke-Ernzerhof exchange-correlation functional<sup>38</sup> and projector-augmented wave (PAW) data sets<sup>39</sup> that employed the  $5d^{10}6s^26p^2$  and  $1s^1$  valence electrons for Pb and H, respectively. An energy cutoff of 800 eV and k-grid density of  $50/\text{\AA}^{-1}$  for Brillouin zone samplings were used in enthalpy calculations and geometries optimized below a force convergence threshold of 1 meV/ $\text{\AA}$ . Dynamical stability of the predicted structures was checked using the supercell approach as implemented in the Phonopy code<sup>40</sup>. Bader charge analyses were performed with the Critic2 program<sup>41,42</sup>. Elastic constants were calculated to check the mechanical stability for predicted phases. Phonon dispersions, EPC and superconductivities of predicted stable phase were calculated within linear-response theory as implemented in the Quantum-ESPRESSO package<sup>43</sup>. Ultrasoft pseudopotentials for Pb and H were adopted with a kinetic energy cutoff of 80 Ry. In EPC calculations, q-meshes (k-meshes) of  $4 \times 4 \times 6$  ( $24 \times 24 \times 36$ ) for  $P6mm$ - $\text{PbH}_4$ ,  $8 \times 4 \times 8$  ( $32 \times 16 \times 32$ ) for  $Pmnm$ - $\text{PbH}_4$ ,  $8 \times 8 \times 3$  ( $32 \times 32 \times 12$ ) for  $C222_1$ - $\text{PbH}_6$  and  $4 \times 4 \times 4$  ( $16 \times 16 \times 16$ ) for  $Fddd$ - $\text{PbH}_8$  were used.

## III. RESULTS AND DISCUSSIONS

We performed enthalpy calculations for the different Pb-H compounds across the full pressure range 0-400 GPa. Full enthalpy curves including possible decomposition reactions for  $\text{PbH}_4$ ,  $\text{PbH}_6$  and  $\text{PbH}_8$  as function of pressure are shown in Figure 1. The stable struc-

tures of Pb,  $\text{H}_2$ ,  $\text{PbH}$ , and  $\text{PbH}_2$  were taken from previously reported work<sup>31,44,45</sup>, in addition to the structures predicted in this work, previously reported stable structures of  $\text{PbH}_4$  (space groups  $Imma$ ,  $P2_1/m$  and  $Ibam$ , labelled VII, IIa, and VIII in<sup>25</sup>) and  $\text{PbH}_8$  ( $C2/m$ ,  $P\bar{1}$  and  $Pnmm$  in<sup>31</sup>) were also taken into consideration. We also constructed the convex hulls (see Figure 2a) by using formation enthalpies for the most favorable structure of each compound relative to elemental Pb and  $\text{H}_2$  to determine energetic stability. Combining the enthalpy curves and convex hull, the ground state phase diagram can be constructed and is depicted in Figure 2b. This differs substantially from the literature. Firstly,  $\text{PbH}_6$  emerges as the first lead hydride to become stable, at 96 GPa, and remain so, in a  $C222_1$  structure, up to 236 GPa. Previously suggested structures for  $\text{PbH}_4$  are superseded by

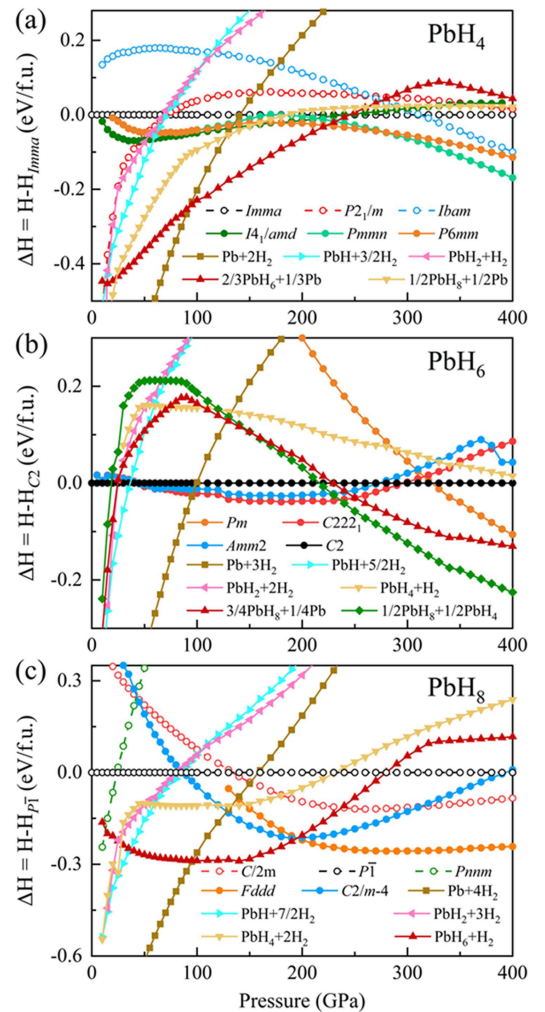


FIG. 1: The enthalpies per formula unit and decomposition enthalpies as a function of pressure for (a)  $\text{PbH}_4$ , (b)  $\text{PbH}_6$  and (c)  $\text{PbH}_8$ . The reported structures for Pb<sup>44</sup>,  $\text{H}_2$ <sup>45</sup>, and Pb-H<sup>25,31</sup> compounds are considered. Phases from the literature are drawn with empty symbols and dashed lines, new phases from this work in full symbols and solid lines.

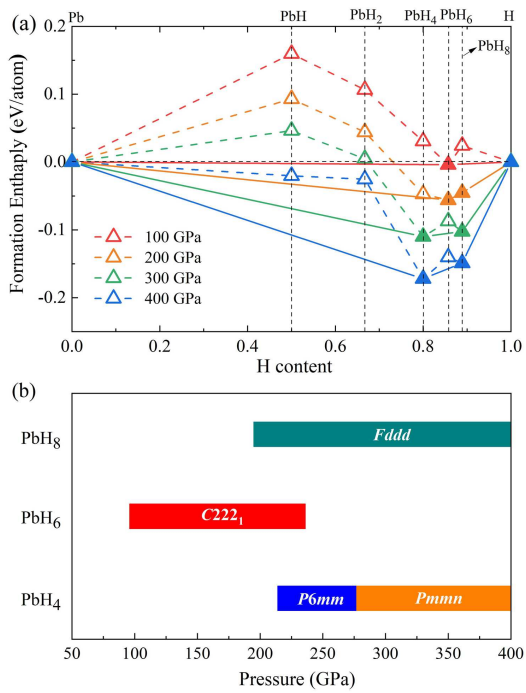


FIG. 2: Phase stabilities of lead hydrides. (a) Formation enthalpies of different Pb-H compounds at specific pressures. (b) Predicted ground state pressure-composition phase diagram of lead hydrides.

the presently predicted  $P6mm$  and  $Pmnm$  phases, see Figure 1a; the onset of stability for  $P6mm$ -PbH<sub>4</sub>, due to the presence of PbH<sub>6</sub>, is delayed to 214 GPa. At 277 GPa the  $Pmnm$  phase become more stable than  $P6mm$ . For PbH<sub>8</sub> (see Figure 1c), a newly predicted  $Fddd$  phase is more energetically favored than the  $C2/m$  phase (reported previously stable above 160 GPa<sup>31</sup>), and becomes stable above 195 GPa.

Zero-point (ZP) vibrational energy can play a crucial role in changing relative stabilities because of the pronounced nuclear quantum effects in hydrogen-rich compounds. To gauge their importance here, we recalculated the formation enthalpies of various Pb-H compounds, Pb and H<sub>2</sub> at 50, 100, 150, 200 and 300 GPa including ZP vibrational energy at the harmonic level, then reconstructed the convex hulls as displayed in Figure S1 in the Supplemental Material (SM)<sup>46</sup>. The phase diagram of stable phases remains qualitatively unchanged (see Figure S2): PbH<sub>6</sub> becomes the first stable hydride, at a slightly lower pressure of 91 GPa, followed by PbH<sub>8</sub> and PbH<sub>4</sub> around 150 GPa; the latter two remain stable up to at least 300 GPa. A monoclinic  $C2/m - 4$  phase of PbH<sub>8</sub> emerges as stable in a small pressure range. To further examine the dynamical stability of the predicted phases, we show the phonon dispersions for the different hydrides across their respective stability ranges in Figure S3; the absence of any imaginary modes confirms their dynamical stability. The  $C222_1$ -PbH<sub>6</sub> phase remains dy-

namically stable down to at least 50 GPa. The calculated elastic moduli are summarized in the Table S2, confirming that the predicted Pb-H phases are also mechanically stable, since they all meet the mechanical stability criteria<sup>47</sup>.

The predicted stable structures of PbH<sub>4</sub>, PbH<sub>6</sub>, and PbH<sub>8</sub> at specific pressure are displayed in Figure 3 and described below in more detail; their crystal structures are listed in Table S1. In general, all stable compounds comprise isolated Pb atoms in matrices of H<sub>2</sub> molecules; this is qualitatively similar to what has been found previously<sup>25,31</sup>. The two new structures for PbH<sub>4</sub>,  $P6mm$  and  $Pmnm$ , are shown in Figure 3(a) and Figure 3(b). In both structures, Pb atoms are 12-fold coordinated to surrounding H<sub>2</sub> molecules, and at the centers of distorted hexagonal prisms. In  $P6mm$ -PbH<sub>4</sub> at 250 GPa the nearest Pb-H separations are 1.958-1.987 Å [Figure 3(a)], and in  $Pmnm$ -PbH<sub>4</sub> at 300 GPa they are 1.871-1.998 Å [Figure 3(b)]. The Pb atoms form slightly distorted simple hexagonal lattices, with H<sub>2</sub> molecules placed in their trigonal prismatic holes; thus, both structures, in the form Pb(H<sub>2</sub>)<sub>2</sub>, approximate the CaHg<sub>2</sub> (or AlB<sub>2</sub>) structure type. The H<sub>2</sub> molecules in both structures have significantly elongated bond lengths - 0.809 Å in  $P6mm$ -PbH<sub>4</sub> and 0.831 Å in  $Pmnm$ -PbH<sub>4</sub>.

The  $C222_1$ -PbH<sub>6</sub> and  $Fddd$ -PbH<sub>8</sub> phases retain many of the same structural motifs, but the higher hydrogen content changes the Pb coordination environment and gives more variability to the hydrogenic sublattice, see Figure 3(c) and 3(d). The Pb lattice in  $C222_1$ -PbH<sub>6</sub> is hexagonal close packed but (due to H<sub>2</sub> intercalation) with

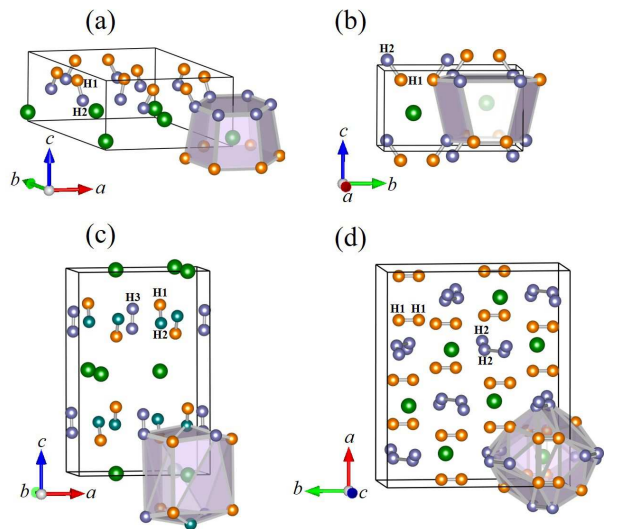


FIG. 3: Crystal structures of high-pressure lead hydrides. (a)  $P6mm$ -PbH<sub>4</sub> at 250 GPa, (b)  $Pmnm$ -PbH<sub>4</sub> at 300 GPa, (c)  $C222_1$  PbH<sub>6</sub> at 100 GPa, (d)  $Fddd$ -PbH<sub>8</sub> at 200 GPa. Green spheres represent Pb atoms, and yellow, light purple and dark cyan represent crystallographically distinct H atoms as labelled, respectively. Coordination polyhedra of Pb atoms are indicated in each structure.

TABLE I: H<sub>2</sub> molecular parameters: bond length, bond critical point charge density ( $\rho_{\text{BCP}}$ ) and Laplacian ( $\nabla^2\rho_{\text{BCP}}$ ). Bader-Yu-Trinkle (Y-T) charge analysis for all atoms, electron phonon coupling (EPC) parameters  $\lambda$ , electronic density of states at the fermi level  $N(E_f)$ , logarithmic average phonon frequency  $\omega_{\text{log}}$  and superconducting critical temperatures  $T_c$  of Pb-H structures, all at selected pressures.

		<i>P6mm</i> -PbH <sub>4</sub>	<i>Pmnm</i> -PbH <sub>4</sub>	<i>C222</i> <sub>1</sub> -PbH <sub>6</sub>	<i>Fddd</i> -PbH <sub>8</sub>		
		250 GPa	300 GPa	100 GPa	200 GPa		
H <sub>2</sub> bonds	Distance (Å)	0.809	0.831	0.770	0.769	0.777	0.817
	$\rho_{\text{BCP}}$	0.239	0.228	0.261	0.260	0.262	0.232
	$\nabla^2\rho_{\text{BCP}}$	-0.819	-0.570	-1.288	-1.193	-1.147	-0.749
Y-T Charge integrals	H AVG charge	1.165	1.177	1.077	1.075	1.074	1.137
	Pb AVG charge	13.336	13.292	13.548		13.159	
EPC	$\omega_{\text{log}}$ (K)	771.14	843.00	566.11		1000.93	
	$\lambda$	1.21	1.24	2.03		1.99	
	$N(E_f)$	9.59	6.53	9.29		9.94	
	$T_c$ (K), $\mu^*=0.10$	69.68	78.69	102.94		178.04	
	$T_c$ (K), $\mu^*=0.13$	61.88	70.15	93.33		161.59	

an extremely large  $c/a$  ratio of 2.67. Note that the Pb lattice in PbH<sub>6</sub> is the same as the high-pressure elemental form of Pb. The formation of PbH<sub>6</sub> could therefore progress against relatively low reaction barriers, involving only the intercalation of H<sub>2</sub> molecules between the layers of high-pressure *hcp*-Pb. The Pb lattice in *Fddd*-PbH<sub>8</sub> has the *beta*-Sn structure. While in *C222*<sub>1</sub>-PbH<sub>6</sub> the two types of H<sub>2</sub> molecules have very similar H-H distances of 0.769 Å (H1-H2) and 0.770 Å (H3-H3), the *Fddd*-PbH<sub>8</sub> structure features two very different types of H<sub>2</sub> molecules, with separations of 0.777 Å and 0.817 Å. The first type H1-H1 (0.777 Å) are along the  $b$  axis [Figure 3(d)]. The second type H2-H2 (0.817 Å) are roughly along the  $c$  axis, and form quasi-1D chains along that axis.

To understand the drivers of formation of these hydrides better, we analyzed their chemical bonding both in real and reciprocal space. Real space analyses are based on Bader's Quantum Theory of Atoms in Molecules<sup>48</sup>,

where a topological analysis of the charge density identifies critical points, lines and surfaces. Critical points are associated with ions or center points of bonds which appear as maxima or saddle points in the charge density. For ionic critical points, integrating the charge within the charge basin volume gives an effective charge. For bond critical points (BCP), the value ( $\rho$ ) and the curvature ( $\nabla^2\rho$ ) of the charge density at the BCP help to characterise the bonding type and strength with ionic bonds having positive curvature and lower charge densities at the BCP. These regions can be calculated and visualized using gradient path analysis with gradient paths seeded from the critical points as seen in Figure 6 and S4. We find that the extended H<sub>2</sub> bond lengths are due to partial negative charge acquired from the Pb atoms. From the Bader-Yu-Trinkle charge analysis listed in Table 1, each H<sub>2</sub> unit in *P6mm*-PbH<sub>4</sub>, *Pmnm*-PbH<sub>4</sub>, *C222*<sub>1</sub>-PbH<sub>6</sub> and *Fddd*-PbH<sub>8</sub> accepts approximately 0.330 e, 0.354 e, 0.154/0.150 e and 0.148/0.274 e from Pb atoms, respectively. These electrons partially occupy the antibonding orbital of the H<sub>2</sub> molecules, and the bond lengths in the H<sub>2</sub> units increase roughly linearly with the number of electrons transferred from Pb to H. The charge transfer from the Pb atom to each H<sub>2</sub> unit increases with pressure (in *C222*<sub>1</sub>-PbH<sub>6</sub> at 200 GPa it is 0.158 e) and, at comparable pressures, increases with hydrogen content. The topological structure of the charge density for the four structures are shown in Figure 6 and S4, and properties of the resulting BCPs and charge basins are also listed in Table 1. This data confirms a strong correlation between H<sub>2</sub> bond length increase and reduction in covalent bond strength (as measured through BCP charge density  $\rho_{\text{BCP}}$  and Laplacian  $\nabla^2\rho_{\text{BCP}}$ ).

For reciprocal space analysis of the bonding in these hydrides, we show in Figure 4 the electronic band structures and densities of states (DOS), both projected onto atomic H- $s$  and Pb- $s/p/d$  orbitals. Firstly, the data indicates good metallic character, without noticeable pseudogaps, for all lead hydrides. The DOS's at the Fermi level mainly originate from the Pb atoms, with substan-

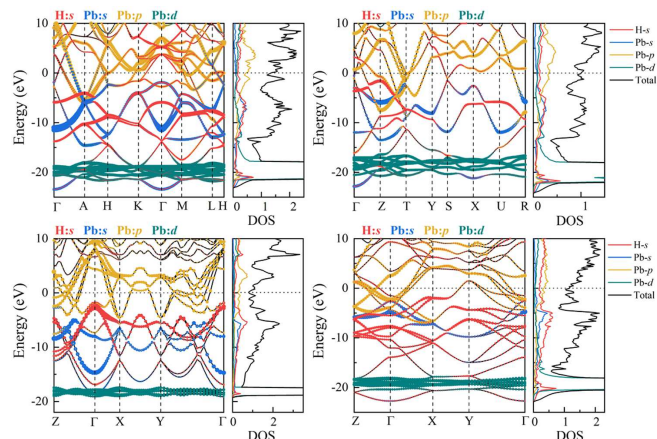


FIG. 4: The calculated electronic band structure and projected DOS for (a) *P6mm*-PbH<sub>4</sub> at 250 GPa, (b) *Pmnm*-PbH<sub>4</sub> at 300 GPa, (c) *C222*<sub>1</sub>-PbH<sub>6</sub> at 100 GPa, (d) *Fddd*-PbH<sub>8</sub> at 200 GPa.

TABLE II: Integrated COHP (ICOHP) up to the Fermi level for different atom pairs in Pb-H compounds: Pb-H, averaged over all first coordination shell Pb-H contacts; H-H, intramolecular covalent contacts; and H $\cdots$ H, closest intermolecular contacts.

Compounds	Pb-H	ICOHP (eV/atom pair)		
		H-H	H $\cdots$ H	H $\cdots$ H
<i>P6mm</i> -PbH <sub>4</sub> (250 GPa)	-1.03	H1-H2: -4.23	H1 $\cdots$ H1: -0.52	
<i>Pmnm</i> -PbH <sub>4</sub> (300 GPa)	-1.02	H1-H2: -3.87	H1 $\cdots$ H1: -1.22	
<i>C222<sub>1</sub></i> -PbH <sub>6</sub> (100 GPa)	-0.88	H1-H2: -5.34	H3-H3: -5.65	H1 $\cdots$ H2: -0.18
<i>Fddd</i> -PbH <sub>8</sub> (200 GPa)	-0.69	H1-H1: -5.33	H2-H2: -4.66	H2 $\cdots$ H2: -0.79

tial contributions from H-derived states. Some bands that cross the Fermi levels show signature of mixed character, and therefore hybridization of Pb- and H-states (for example along  $\Gamma$ -A in *P6mm*-PbH<sub>4</sub>, or along  $\Gamma$ -Z in *Pmnm*-PbH<sub>4</sub>), but the majority of bands is dominated by clear Pb-*p* or H-*s* character. An alternative to quantify interatomic interactions is the Crystal Orbital Hamilton Population (COHP) analysis<sup>49,50</sup>. In Figure 5 we show the COHP projected onto individual atom pairs: averaging the first coordination shell Pb-H contacts; the intramolecular H-H covalent bonds; and intermolecular H $\cdots$ H contacts. In plotting the negative projected COHP (-pCOHP), positive/negative values refer to bonding/anti-bonding interactions. Table II gives the integrated COHP (ICOHP) up to the Fermi level, a measure of total atom pair interaction strength. Firstly, we note that intramolecular H-H bonds all have antibonding character at the Fermi level, corroborating the partial charge analysis above; the H-H ICOHP also correlates with charge transfer: the larger the H partial charge, the lower the covalent H-H bond strength. Secondly, we note that Pb-H interactions are noticeable as measured by ICOHP, but are dominated by interactions of H-*s* with Pb-*d* states about 20 eV below the Fermi energy. The Pb-H interactions around the Fermi level are very weak, and Pb-H hybridization should not be a major factor for properties that depend on the states near the Fermi energy (such as electron-phonon coupling, see next paragraph). Thirdly, intermolecular H $\cdots$ H interactions are weak but increase with pressure; the *Fddd*-PbH<sub>8</sub> phase is an outlier with comparatively strong H2 $\cdots$ H2 interactions.

Metallic hydrides have previously been shown to be potential superconductors at high pressure. Thus, we conducted EPC calculations for the four metallic Pb-H compounds identified above. Relevant properties, including  $T_c$  at relevant pressures are listed in Table 1.  $T_c$  values were estimated from the modified McMillan-Allen-Dynes equation<sup>51</sup>:  $T_c = \frac{\omega_{log}}{1.2} \exp[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}]$ , where

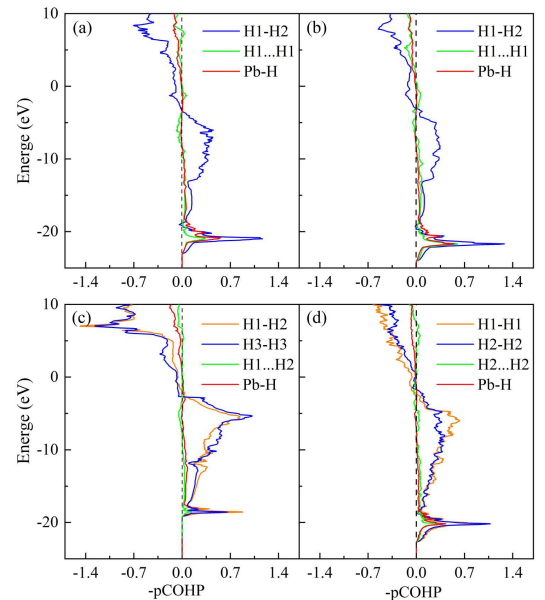


FIG. 5: -pCOHP for pairs of Pb-H, H-H and H $\cdots$ H in (a) *P6mm*-PbH<sub>4</sub> at 250 GPa, (b) *Pmnm*-PbH<sub>4</sub> at 300 GPa, (c) *C222<sub>1</sub>*-PbH<sub>6</sub> at 100 GPa, (d) *Fddd*-PbH<sub>8</sub> at 200 GPa. Energies are normalized to the respective Fermi level.

the screened Coulomb potential parameter  $\mu^*$  was set to 0.1-0.13 as previously suggested for metal hydrides<sup>5</sup>. For  $\lambda$  larger than 1.6, strong-coupling and shape correction multipliers ( $f_1$  and  $f_2$ ) are considered in the  $T_c$  equation:  $T_c = f_1 f_2 \frac{\omega_{log}}{1.2} \exp[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}]$ . All four structures have moderately high  $T_c$ . The *Fddd*-PbH<sub>8</sub> phase's  $T_c = 161.59$  K and averaged EPC coupling  $\lambda = 1.99$  are significantly higher than the previously reported  $T_c = 107$  K and  $\lambda = 1.296$  in *C2/m*-PbH<sub>4</sub>(H<sub>2</sub>)<sub>2</sub><sup>31</sup>, while superconductivity of PbH<sub>4</sub> or PbH<sub>6</sub> has not been reported previously. We find a gradual increase in  $T_c$  with increasing hydrogen content; the pressure dependence of  $T_c$  (see Table S3) is relatively weak.

We analyse the *Fddd*-PbH<sub>8</sub> phase in more detail, while the EPC results for other three structures are shown in Figure S4 and discussed in the SM. The electronic charge contour lines and gradient paths, the phonon dispersion curves overlaid with phonon linewidth  $\gamma(\omega)$ , phonon DOS, EPC parameter  $\lambda$  and Eliashberg spectral function  $\alpha^2F(\omega)$  of *Fddd*-PbH<sub>8</sub> at 200 GPa are compiled in Figure 6. The H<sub>2</sub> molecules in *Fddd*-PbH<sub>8</sub> (see Figure 5d, 6a and Tables 1 and 2) are clearly distinct; the H1-H1 set are weakly negatively charged (partial charge  $\delta_H = -0.074$ ) and strongly bound ( $\nabla^2\rho_{BCP} = -1.147$ , ICOHP = -5.33eV), the H2-H2 set have larger partial charge ( $\delta_H = -0.137$ ), weaker covalent bonding ( $\nabla^2\rho_{BCP} = -0.749$ , ICOHP = -4.66eV) and comparatively stronger intermolecular interaction ( $\nabla^2\rho_{CP} = 0.065$ , ICOHP = -0.79eV), resulting in quasi-1D chains along the *c* axis. These can be seen from the three planes plotted in Figure 6a that link two symmetrically equivalent H2-H2 molecules. Coupling between H<sub>2</sub> molecules was reported

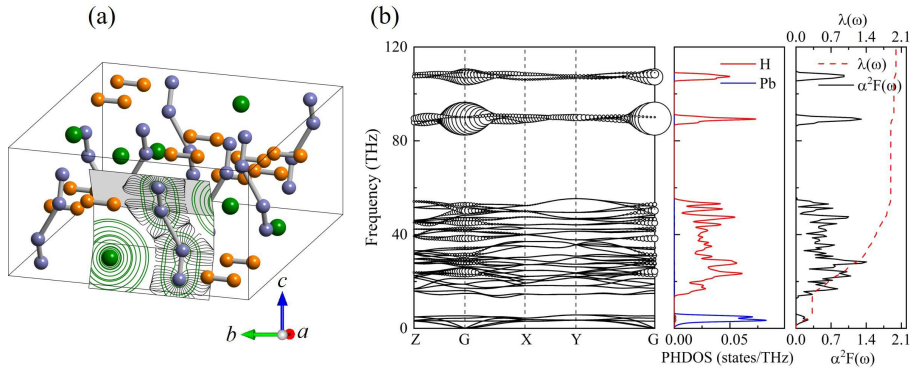


FIG. 6: (a) Charge density topology analysis of  $Fddd$ - $PbH_8$  with cross sections that show charge density contours (green lines) and gradients (black lines). (b) Calculated phonon dispersion (radius of black circle is proportional to the phonon line-width), projected phonon density of states, Eliashberg phonon spectral function  $\alpha^2F(\omega)$  and integrated electron-phonon coupling  $\lambda(\omega)$  for  $Fddd$ - $PbH_8$  at 200 GPa.

qualitatively for  $PbH_8$  structures<sup>31</sup>, while the formation of  $(H_2)_2$  tetramers was identified in  $PbH_4$ <sup>25</sup>.

In the phonon dispersion (see the left panel of Figure 6b), largest phonon linewidths are present in the H<sub>2</sub>-H<sub>2</sub> vibron modes, however EPC is mostly contributed from the mid-frequency range 12-55 THz, where phonon branches are related to intermolecular vibrations of H<sub>2</sub> molecules (78.7% in  $\lambda$ ). Even though absolute bond strength in the hydrogen sublattice is small (as measured via intermolecular ICOHP( $H \cdots H$ )), its linear response to perturbations in the electronic structure (as quantified in the EPC) is considerable. This agrees with the previous report on  $C2/m$ - $PbH_4(H_2)_2$ <sup>31</sup>, where coupling between H<sub>2</sub>-H<sub>2</sub> were argued as the primary cause of  $T_c$ , and is also found in the other three Pb-H structures (see SM). This sets lead hydrides apart from the early experimental observations in  $SiH_4(H_2)_2$  and  $GeH_4(H_2)_2$ <sup>28,30</sup>, where strong intermolecular interactions between the  $SiH_4$  ( $GeH_4$ ) and H<sub>2</sub> molecules at low pressure were found as the main reason for their superconductivity.

Significant electron-phonon coupling related to the intermolecular vibrations of the H<sub>2</sub> sublattices results in promising superconductivity in all compounds. There is a clear separation in  $T_c$  achievable in  $PbH_4$  and  $PbH_6$  (around 60-100 K) *vs*  $PbH_8$  (around twice as high). The former structures are essentially layered, at least structurally (the electronic DOS's in Figure 4 do not show square onsets typical for 2D systems but are also entwined with the Pb 5*d* manifold of states). While this does not systematically affect their metallicity (as measured by  $N(E_f)$ , see Table 1), it leads to weakened EPC  $\lambda$  or  $\omega_{log}$ , thus limiting  $T_c$ . The  $PbH_8$  structure is more three-dimensional in character (as seen through the Pb sublattice) and features stronger intermolecular H<sub>2</sub>-H<sub>2</sub> interactions (as seen through COHP, once pressure differences are accounted for).

Its predicted  $T_c$  value of 161-178 K at 200 GPa places lead hydrides amongst the most promising *p*-block metal

hydrides - where other candidates involve  $BiH_5$ ,  $SbH_4$ ,  $AsH_8$ ,  $AlH_3(H_2)$  (all predicted  $T_c=118$ -151K at 150-450 GPa<sup>52-55</sup>), as well as  $GaH_3$ ,  $InH_3$ ,  $SnH_4$  and  $PoH_4$  (all  $T_c < 100$ K<sup>23,56-58</sup>). Some of these compounds feature atomic hydrogen ( $SbH_4$ ,  $GaH_3$ ) or H<sub>3</sub> units ( $BiH_5$ ,  $InH_3$ ), while others, like the lead hydrides, contain metal cations and negatively charged sublattices of H<sub>2</sub> molecules. The ‘chemical precompression’ of hydrogen in the latter type achieves the equivalent of a metallic *molecular* phase of pure hydrogen, clearly at much lower pressures than in pure hydrogen itself. However, it has been argued that superconducting  $T_c$ 's in these types of structures are ultimately limited by relatively low electron-phonon coupling, as the electronic structure is not heavily influenced by motion of negatively charged H<sub>2</sub> molecule<sup>59,60</sup>. While  $\lambda=1.99$  as found here for  $PbH_8$  is clearly a respectable value, other hydrides - most prominently the rare earth hydrides with atomic hydrogen cages<sup>61</sup> - that resemble the equivalent of metallic *atomic* hydrogen phases, again at much lower pressures than in pure hydrogen, seem to be able to overcome that limitation.

#### IV. CONCLUSIONS

In summary, we have systematically investigated hydrogen-rich Pb-H compounds under pressure using crystal structure prediction and electronic structure calculations. We suggest that  $PbH_6$  should be the first lead hydride to form under pressure, below 100 GPa. Its structure, with H<sub>2</sub> molecules intercalated in a *hcp*-Pb lattice, should make it accessible in experimental synthesis, and it could be quenched back to lower pressures: we find the  $C222_1$ - $PbH_6$  phase dynamically stable down to at least 50 GPa. For previously investigated compositions  $PbH_4$  and  $PbH_8$ , we report more stable structures. In particular,  $Fddd$ - $PbH_8$  was identified more energetically stable than previously predicted  $C2/m$ - $PbH_4(H_2)_2$ , and features quasi-1D H<sub>2</sub> chains along *c*-axis. In all stable

phases, hydrogen appears in molecular form surrounding Pb cations, and charge transfer from Pb to H<sub>2</sub> results in elongated H<sub>2</sub> molecules and metallic character in all hydrides. Despite being more stable than previous reports, the structures discussed here show more promise for high- $T_c$  superconductivity, which we predict to surpass 160 K in PbH<sub>8</sub>.

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