High Pressure Stabilization and Emergent Forms of PbH_4

Patryk Zaleski-Ejgierd,[1] Roald Hoffmann,[2] and N. W. Ashcroft[1]
[1]*Laboratory of Atomic and Solid State Physics and Cornell Center for Materials Research, Clark Hall, Cornell University, Ithaca, New York 14853-2501, USA*
[2]*Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301, USA*

(Received 17 October 2010; revised manuscript received 9 March 2011; published 11 July 2011; corrected 20 July 2011)

A wide decomposition pressure range of 132 GPa is predicted for PbH_4 above which it emerges in very different forms compared with its group-14 congeners. This triply Born-Oppenheimer system is a nonmolecular, three-dimensional, metallic alloy, despite a prominent layered structure. A significant number of enthalpically near-degenerate structures, with exceedingly small energy barriers for distortions, and characteristic instabilities in the phonon spectra suggest that even at very high pressures PbH_4 may exhibit both metallic and liquidlike properties and sublattice or even full melting.

DOI: 10.1103/PhysRevLett.107.037002 PACS numbers: 74.70.Ad, 74.62.Fj

Among group-14 hydrides, the lead-hydrogen system is special, for it clearly combines one of the heaviest (Pb) elements with the lightest (H). The attendant mass ratio (207:1) immediately implies a distinct separation of time scales for the ensuing dynamics, in very much the way that standard Born-Oppenheimer separation commonly applies to the electrons and both nuclei (Pb and H).

It has been suggested that group-14 hydrides, including methane (CH_4), silane (SiH_4), germane (GeH_4), and stannane (SnH_4), might become metallic under pressures lower than is projected for pure H_2 metallization [1]. Experimental attempts to metallize methane, the "lightest" of the hydrides, have so far failed. Silane passes through phases of increasing coordination but, despite initial findings of metallization, appears to remains nonmetallic to 150 GPa (see [2] and references therein). For germane [3,4] and stannane [5], metallization is predicted at a variety of accessible pressures; in both systems the high pressure phases interestingly contain paired H_2 units.

Chemically, PbH_4 still remains the most elusive of group-14 tetrahydrides. The first attempts to synthesize PbH_4, employing the classical methods used to synthesize GeH_4 or SnH_4, failed [6–9]. The pioneering theoretical work of Desclaux and Pyykkö utilized Dirac-Hartree-Fock relativistic calculations to predict the structure and stability of PbH_4 [10,11]. A predicted tetrahedral structure of an isolated molecule, with an equilibrium Pb-H distance of approximately 1.73 Å, was eventually confirmed by experiment [12,13]. Krivtsun, Kuritsyn, and Snegirev noted that the plumbane molecules are kinetically unstable and readily decompose to a metallic lead film and H_2 in approximately 10 s [9]. The high reactivity and short lifetime of PbH_4 have so far combined to prevent any crystallographic investigation of the species under normal conditions. We have therefore undertaken here a theoretical analysis of its structural, thermodynamic, and electronic properties, particularly at elevated densities.

As starting points and guides in a structure search, we used a number of geometries previously reported for group-14 tetrahydrides, EH_4, as well as other structures in which lead is two- to 16-fold coordinated by hydrogen, and with up to $Z = 4$ formula units per cell. We scanned 1000 randomly generated structures at the selected pressures, and these explorations were complemented by the use of the universal structure predictor evolutionary crystallography evolutionary algorithm [14,15] to seek the most stable of these. Finally, for the lowest enthalpy structures we also investigated the nuclear dynamics through calculated phonon spectra by using the PHON code [16], later pursuing any ensuing imaginary modes to more stable and secure minima. The methodology is detailed in Ref. [17].

Nine energetically competitive structures arise from this search (see Fig. S1 in Ref. [17]). They all show a surprisingly convergent evolution of the enthalpy, by which we mean that a number of quite different ground state structural possibilities, each corresponding to a metastable minimum, are enthalpically close to each other over a wide range of pressures (see Fig. 1). Below the calculated decomposition pressure (132 GPa), PbH_4 forms extended layered structures rather than crystalline forms with no vestige of distinct plumbane molecules. Were we to proceed to even larger unit cells (we are currently constrained to $Z = 2$ and $Z = 4$), we are confident that for $P <$ 132 GPa the layered structures we will find would segregate further towards the Pb + H_2 limit. The computed ΔH_f of a single gas-phase molecule is +2.74 eV, so this large decomposition pressure range comes as no surprise.

For $P >$ 132 GPa, at least seven distinct phases prove to be more stable than the separated elements. Per formula unit, all of them remain within approximately 0.1–0.2 eV of each other over the large pressure range, with the exception of phase I. The two most stable structures, phases VII (*Imma*) and VIII (*Ibam*), are representative and singled out for more detailed discussion. Figure 2 shows their

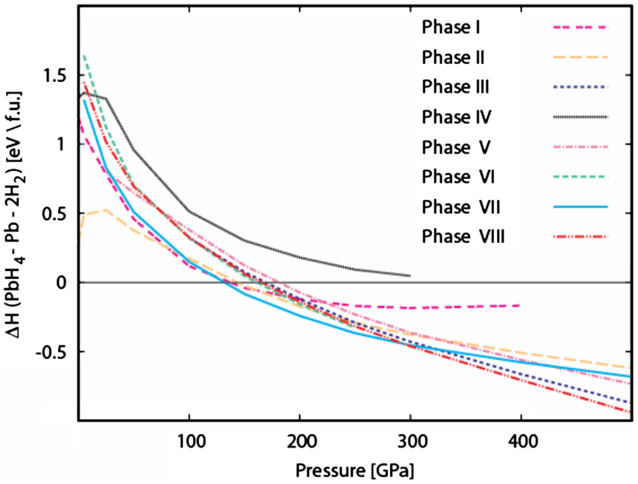
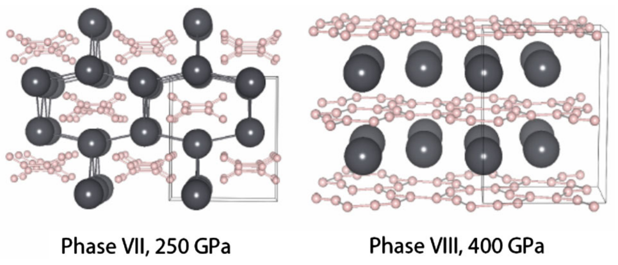


FIG. 1 (color online). Calculated enthalpy difference curves for PbH_4. The combined enthalpies of the elements in their most stable form [20,28] establish the reference (zero) line. Note both the smoothness and also the significant overlap of the curves over a wide range of pressures.

structure at 300 GPa, and Table I provides some salient structural parameters.

In phase VII, atoms of lead contribute to the binding of two neighboring layers with relatively short bonds of 2.64 Å at 300 GPa, these closely similar to the Pb-Pb bond distances within the lead layers (see Table I). The 3D lead framework has 1D-like infinite channels filled by H_2 units coupled in such a way that they form flat $(H_2)_2$ quartets. At even higher pressures, increasing coordination is developing; at 300 GPa, the shortest calculated intermolecular $H_2 - H_2$ separation, or contact, in the $(H_2)_2$ quartet is 1.07 Å, while the shortest distance between the parallel quartets is 1.36 Å.

At the highest analyzed pressures, phase VIII is most stable with quasihexagonal one-atom thick layers of lead intercalated by layers of hydrogen. All hydrogen atoms are coplanar, even though they are *not* constrained to be so during structural optimization. Within these planar hydrogen layers, the $(H_2)_2$ quartets remain distinctively present, as Fig. 2 shows. Once again, higher dimensionality for the hydrogen framework looms: At 300 GPa, the shortest $H_2 - H_2$ contact is 1.02 Å, while the next shortest contact is only 1.16 Å. The $(H_2)_2$ quartets can be viewed in such a way that they actually form 10-membered rings, as illustrated in Fig. 2. A somewhat similar layered structure has been observed by Martinez-Canales *et al.* for high pressure silane ($Pbcn$, $P > 220$ GPa). In it, slightly displaced square Si layers were intercalated by two-atom thick layers of hydrogen [18]. In contrast to PbH_4, the intra- and intermolecular H-H distances are far less equalized, at 0.74 and 1.35 A, respectively.


Phase VII, 250 GPa

Phase VIII, 400 GPa

FIG. 2 (color online). The two most stable high pressure structures of PbH_4. (Left) Phase VII at 250 GPa; the 3D lead framework is noteworthy. (Right) Phase VIII at 400 GPa; it is strikingly layered.

How shall we look at the unusual bonding in the H_2 layers in these PbH_4 structures? First, the initially (low P) unbound hydrogens appear to be closer to each other than in H_2 itself. At 300 GPa, the shortest *intermolecular* distances (Table I) are 1.07 (phase VII) and 1.02 Å (phase VIII). In the most stable H_2 structure at this pressure ($Cmca$-12), the corresponding distance is 1.10 Å [19]. Second, the *intramolecular* H_2 distance is notably longer in the PbH_4 structures—0.79 (phase VII) and 0.81 Å (phase VIII) vs 0.75–0.78 Å in H_2 ($Cmca$-12 at 300 GPa).

There may be two reasons behind this behavior: (a) The *effective* pressure on the hydrogen sublattice might be greater in PbH_4 than in H_2. Here the Pb's could well be thought of as now present in less compressible layers that reduce the effective volume (and concomitantly increase the effective pressure) on the H_2's. (b) There may be some "squeezing out" of electron density from the Pb layers at high pressures, impelling electrons into effective H_2 $\sigma_u{}^*$ levels (see also Ref. [5]).

A second important aspect of the hydrogen sublattice, one already noted, is that all of our proposed structures contain hydrogen units with a strongly expressed tendency for $H_2 - H_2$ pairing. That this is not just an imagined association may be seen in Fig. 3, where we show the electron localization function (ELF) [21] calculated for the phase VIII at 400 GPa. The small value of the ELF between two neighboring atoms in the direction perpendicular to lead layers supports the interpretation of the layered character of phase VIII. The enhanced value of the ELF between the H atoms of a single H_2 unit is expected, but note that the ELF also indicates significant bonding between *two* H_2 units, forming H_2 quartets, and a decrease of the ELF outside of the quartets.

Starting from 25 GPa, all phases behave almost identically upon compression, and hence the equation of state, which connects different phases as the pressure increases, is notably smooth (for the equation of state computed at $T = 0$ and for a static lattice, see Fig. S4 in Ref. [17]).

Over a wide range of pressures, a number of more-or-less layered structures, some structurally quite different, are actually quite close in enthalpy (Fig. 1). The zero point energy of each of the structures (not included in the curves displayed) is quite comparable to the difference in enthalpy of the various structures. This situation is suggestive of eventual hydrogen sublattice melting at elevated pressures or even of diffusive or liquidlike ground states. In fact, perhaps a way to think about these structures is as layers of lead effectively "lubricated" by highly mobile intercalated

TABLE I. Selected bond lengths (Å), number of Pb-H contacts[a], and r_s values calculated for selected phases of PbH_4 at 300 GPa.

Phase	Pb-Pb		H-H	H_2-H_2[b]	Pb-H	No. of contacts (Pb-H < 2.30 Å)	r_s
	Interlayer	Intralayer					
VII	2.64	2.55/2.67	0.79	1.07/1.36	1.90(x2), 1.95(x4), 2.10(x2) 2.12(x4), 2.15(x4)	16	1.56
VIII	3.06	2.62/2.71	0.81	1.02/1.16	1.88(x4), 2.03(x4), 2.17(x4) 2.18(x4)	16	1.55

[a] Selected shortest Pb-H distances.
[b] Shortest H-H separation.

layers of hydrogen molecules. The latter in turn begin to coalesce into quartets and an extended layer under pressure. How might we therefore probe a tendency towards liquid or partial liquid behavior, possibly even a liquid crystal in PbH_4? One direction is to examine the dynamics as revealed in phonon modes of these structures, in particular, as part of a search for low frequency transverse modes indicative of easy shearing.

In phonon calculations, within the pressure range of Fig. 1, all the structures exhibit only real frequencies at the Γ point. All show clearly separated hydrogen vibron modes located in the band 3500–4000 cm^{-1} for phases where the H_2 molecules are relatively unperturbed; they are $\sim$500 cm^{-1} lower when the H_2 molecules are elongated (phases VII and VIII). Nicely distinguishable low frequency modes are also associated with lead framework displacements.

Phase VIII is clearly interesting because of its pronounced layered character. In fact, we find it to be the most stable phase at pressures higher than 300 GPa. The full phonon dispersion spectrum and the corresponding phonon density of states per atom (and per cm^{-1}) calculated at 400 GPa is shown in Ref. [17]. Upon increase of the displacements (used to calculate the phonon modes), our calculations eventually yield imaginary frequencies. Attempts to follow these necessarily destabilizing modes result only in a restoration of the original structure. Analysis of the modes indicates that they correspond to transverse motions within the hydrogen sublattices, accompanied by negligible buckling of lead layers. Increase of pressure makes the imaginary modes less prominent. Deuterium also stabilizes the imaginary modes; using tritium enhances this mass effect further.

The fact that the layered phase VIII cannot support high-amplitude transverse phonons suggests that it has a very low shear modulus or that the hydrogen sublattices may even exhibit a 2D liquidlike character (sublattice melting or diffusion). Given this, we return to the point concerning the very significant differences in time scales between the lead and hydrogen subsystems. In the Born-Oppenheimer approximation, this suggests that, for temporarily fixed lead coordinates, the hydrogenic states may be integrated or traced out in favor of effective but purely Pb-Pb types of interactions. Since the hydrogens are appearing between Pb-Pb layers, this in turn suggests that (after averaging over the local phase space of hydrogen positions) the net interactions may be notably reduced (a form of "screening" is taking place).

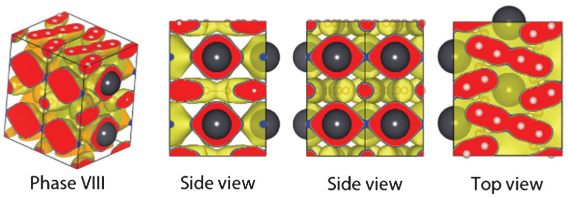


FIG. 3 (color). The phase VIII structure of PbH_4 with three superimposed ELF cross sections, calculated at 400 GPa. Note the high value of the ELF between four hydrogen atoms in $(H_2)_2$ quartets (see the text).

In this context we examine one of the standard measures (the "small parameter") associated with the adiabatic separation of time scales. For an electron-proton system, it is $(m_e/m_\mathrm{H})^{(1/4)}$ or $\sim$0.15 [22]. For the elements, the Born-Oppenheimer approximation is least well satisfied for hydrogen but is still generally adequate. For the hydrogen-lead system, it would be $(m_\mathrm{H}/m_\mathrm{Pb})^{(1/4)}$, which is just $(1/207)^{(1/4)}$ $\sim$0.26 yielding an interesting comparison with the electron-hydrogen case. Finally, for the electron-lead system, it will be $(m_e/m_\mathrm{Pb})^{(1/4)}$ $\sim$0.04 with the corresponding time scales then being exceedingly well separated, as is expected.

It is of some considerable interest that all of the reported structures are computed to be metallic, and strongly so, as determined by the band structures and densities of states. The metallic character is found over the whole studied pressure range, and, in fact, at high pressures PbH_4 exhibits properties of a nearly free-electron metal. By way of example we present in Fig. 4 the electronic density of states (DOS) calculated for phases VII and VIII at 300 GPa (the corresponding band structures are in Ref. [17]). We emphasize that the overall DOS is very much free-electron-like in a three-dimensional context; in the DOS, there is no sign of the gap (as in the case of CH_4) or pseudogap found in calculations on other EH_4 systems (E = Si, Ge, Sn) [4,16,23–27].

Detailed analysis shows that hydrogen states contribute to the DOS throughout this band (see Ref. [17]). These observations indicate, therefore, that at high pressure PbH_4 might reasonably be viewed as an alloy of metallic lead and metallic hydrogen. Note also that there is no sign in the total DOS of any rectangular onsets, the hallmark of two-dimensionality at low energy. While for phase VIII the structure appears geometrically layered, it is *decidedly* three-dimensional in electronic terms.

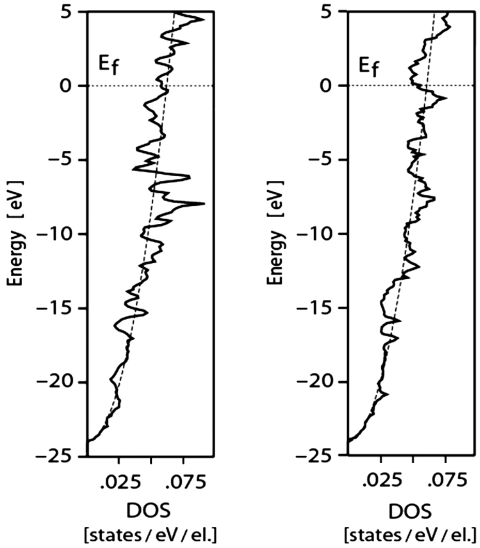


FIG. 4. The total DOS calculated at 300 GPa for phases VII (left) and VIII (right). The dashed curves depict the densities of states for noninteracting electrons, in a three-dimensional environment.

For PbH_4, the heaviest group-14 tetrahydride, decomposition into the elements over a wide pressure range ($0 < P < 132$ GPa) is indeed first predicted. A solid containing the molecular plumbane form PbH_4, analogous to CH_4, is *never* stable thermodynamically. But above the decomposition pressure we find a large number of energetically almost indistinguishable local minima. One of these is phase VII (*Imma*), and in it a three-dimensional lead framework is packed with one-dimensional hydrogen chains composed of characteristic $(H_2)_2$ dimers. Above 296 GPa, phase VIII (*Ibam*) is found to be the most stable; in it layers of lead are intercalated by parallel layers of hydrogen, but the ensuing electronic structure is notably three-dimensional.

From the standpoint of possible experiments, it also may be important to note that both phases are metallic at *any* of the studied pressures and the density of states at the Fermi level is close to the free-electron value. Also, the H-H distances in these structures are more equalized than those in pure H_2. It appears that the effective pressure for the hydrogens is greater than the nominal one, but despite the layerlike geometry of phase VIII (the most stable) we have for this hypothetical phase a three-dimensionally delocalized alloylike electronic structure.

Thus, the present study shows that external pressure can notably stabilize PbH_4, one of the heaviest elements now combined with the lightest. A significant number of enthalpically near-degenerate structures, with small energy barriers for distortions and characteristic instabilities in the phonon spectra, also suggest that even at very high pressures PbH_4 may exhibit not only metallic but also diffusive or liquidlike properties.

We thank the National Science Foundation (DMR-0907425) for financial support. Part of this research was carried out in conjunction with EFree, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DESC0001057.

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