



## Predicted Formation of Superconducting Platinum-Hydride Crystals under Pressure in the Presence of Molecular Hydrogen

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Noble metals adopt close-packed structures at ambient pressure and rarely undergo structural transformation at high pressures. Platinum (Pt) is normally considered to be unreactive and is therefore not expected to form hydrides under pressure. We predict that platinum hydride (PtH) has a lower enthalpy than its constituents solid Pt and molecular hydrogen at pressures above 21.5 GPa. PtH transforms to a hexagonal close-packed or face-centered cubic (fcc) structure between 70 and 80 GPa. Linear response calculations indicate that PtH is a superconductor at these pressures with a critical temperature of about 10–25 K. These findings help to shed light on recent observations of pressure-induced metallization and superconductivity in hydrogen-rich materials. We show that the formation of fcc noble metal hydrides under pressure is common and examine the possibility of superconductivity in these materials.

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Pt maintains the face-centered cubic crystal structure up to at least 304 GPa [1], which covers most of the range currently accessible in static diamond anvil cell (DAC) experiments, and makes it suitable for use as a pressure standard [2,3]. Pt is frequently used to form electrodes (which allow measurements of electrical resistance, the concentration of electrical carriers, and the Hall mobility) and as a heat coupler. As a noble metal, Pt is fairly unreactive at ambient conditions, and this has generally been assumed also to hold at high pressures. However, chemical reactions of Pt with other materials present in the sample chamber can lead to the unexpected formation of new compounds such as, for example, described by Gregoryanz *et al.* [4] who observed the formation of Pt nitride when heating nitrogen with a piece of platinum.

The hydrogen-dense material silane (SiH<sub>4</sub>) forms molecular crystals at low pressures. Two experimental studies of the metallization of SiH<sub>4</sub> under pressure have recently appeared [5,6]. The first study [6] provided optical evidence for metallization of SiH<sub>4</sub> above 60 GPa. Remarkably, the second study by Eremets *et al.* [5] reported superconductivity of SiH<sub>4</sub> in the pressure range 60–150 GPa with a superconducting transition temperature as high as 17 K. These experimental findings have motivated a number of theoretical investigations of compressed SiH<sub>4</sub> [7–9] suggesting that metallization and/or superconductivity can be achieved under pressure, but a clear explanation of the observations has not yet been achieved. While the above two experimental studies [5,6] reported metallization of SiH<sub>4</sub> above 60 GPa, some other experiments claimed decomposition, amorphization, and the

formation other metal-hydrogen alloys besides silane [10,11]. This complexity itself is associated with hydrogen as being extremely light and mobile, as well as extraordinarily reactive. The properties of hydrogen are becoming drastically enhanced under high pressure and temperature, and make the interpretation of experimental data for hydrides [12–14] rather inconclusive.

Degtyareva *et al.* [11] have speculated that the formation of PtH under high pressures might explain some of the observations reported in Ref. [5], and they provided indirect evidence to support the hypothesis of PtH formation. Moreover, it appears likely that the silane in the experiments of Eremets *et al.* [5] partially decomposed, leading to release of hydrogen. Indeed SiH<sub>4</sub> is a metastable compound at low pressures which is thermodynamically unstable to decomposition into H<sub>2</sub> and Si [11], so that the release of hydrogen might occur when the compression is sufficient to break bonds in the SiH<sub>4</sub> molecules. Released hydrogen may then have reacted with the Pt electrodes to form PtH as the pressure was further increased.

Confirming the formation of superconducting PtH at high pressures would change the interpretation of the data of Eremets *et al.* [5], but would in no way diminish the importance of the experiments. In the new interpretation these experiments will have led to the discoveries of superconducting PtH under pressure and a new insulating phase of SiH<sub>4</sub>, and to the understanding that compressed SiH<sub>4</sub> is prone to decomposition. Indeed, Degtyareva *et al.* [11] have suggested that hydrogen release from SiH<sub>4</sub> at high pressures could be useful in synthesizing metal hydrides.

The prevalence of DAC measurements and the steadily growing interest in high-pressure experimental studies of metal hydrides raises the possibility of decomposition and hydrogen release in such experiments. Inadvertent and undetected formation of noble metal hydrides could lead to erroneous pressure estimates and other effects which could substantially alter the interpretation of the data. A careful investigation of the possibility of pressure-induced reactions between hydrogen and noble metals such as Pt is therefore very important and timely.

We have used *ab initio* random structure searching (AIRSS) to predict crystal structures of PtH under pressure [15]. This approach has been used to predict the structures of materials such as hydrogen [16], metal hydrides [17], transition metals [18], and molecular crystals [19–21]. In this study we have used the simplest version of the AIRSS technique in which an ensemble of structures is prepared by generating unit cells of random shapes with reasonable volumes into which the atoms are placed at random positions. The cell shapes and atomic positions are then relaxed to an enthalpy minimum at fixed pressure. We studied simulation cells containing 1, 2, 4, 6, and 8 formula units of PtH. We found three particularly low-enthalpy metallic structures of PtH (the corresponding space groups are given in parentheses): fcc ( $Fm\bar{3}m$ ), hcp ( $P6_3/mmc$ ), and tetragonal ( $I4m2$ ).

We have assumed that PtH forms in the 1:1 stoichiometry. The fcc structure was used for Pt and an hcp molecular form for hydrogen [16], in which the  $H_2$  molecules are randomly oriented in space. The variation of the enthalpies  $H$  of the fcc, hcp, and tetragonal phases of PtH relative to that of  $Pt + \frac{1}{2}H_2$  is given in Fig. 1, which shows that PtH is more stable at pressures above approximately 20 GPa. We also calculated the dynamical stability of the PtH structures and evaluated their electron-phonon coupling (EPC)

strengths  $\lambda$  in order to study the possibility of phonon-mediated superconductivity in PtH. Since the zero-point motion of the hydrogen nuclei is substantial, we have included effects from the zero-point enthalpy (ZPE) calculated within the quasiharmonic approximation. For details of the computational methods we refer the reader to the Supplemental Material [22]. It should be noted that there are alternative ways of calculating the superconducting transition temperature  $T_c$ . In particular, there has recently been considerable progress within the framework of density functional theory in developing truly *ab initio* quantitative predictions of  $T_c$  in the absence of adjustable parameters, which combine electron-phonon coupling and Coulomb interactions [23–28].

Figure 1 shows that it is thermodynamically favorable for tetragonal PtH to form from elemental Pt and  $H_2$  above 18.7 GPa when the zero-point energy of the nuclei is neglected (above 21.5 GPa when the zero-point energy contribution is included; see the Supplemental Material [22]). Experimentally, tetragonal PtH was observed at room temperature, at 26 GPa on compression, and 20 GPa on decompression [29]. We find a transition from tetragonal to hcp or fcc PtH between 70 and 80 GPa (Fig. 1). The fcc and hcp structures differ only in the stacking of layers, making them virtually degenerate in energy (to within a few meV per formula unit). Under pressure, a previous calculation using a simple model suggested that the site occupied by hydrogen in *d*-metal monohydrides tends to change from the tetrahedral to the octahedral site and that the hydride transforms into the hcp or fcc structure [30], in good agreement with our findings. In the present context it is more likely for fcc PtH to form, since the Pt atoms as the heavier host material are arranged in that structure prior to exposure to hydrogen. Experimentally hcp PtH not fcc PtH was observed and we therefore speculate that kinetics might favor a sequence of structural transformation from tetragonal PtH to hcp PtH.

Having established the likely formation of PtH from Pt and  $H_2$  in the pressure range relevant for the experimental observations reported in Ref. [5], we evaluated the EPC strength in PtH to examine its potential for superconductivity, in a similar fashion to our studies of metal trihydrides [31,32], as summarized in the Supplemental Material [22]. This study is crucial because the formation of superconducting  $SiH_4$  was a central claim of Ref. [5], and perhaps superconducting PtH could provide an alternative explanation.

Papaconstantopoulos suggested that PtH could be superconducting under ambient conditions [33], but subsequent experiments found no evidence of PtH formation at low pressure [29,34]. Tetragonal PtH becomes more stable than  $Pt + \frac{1}{2}H_2$  above 20 GPa. We calculated the EPC of tetragonal PtH in the pressure range 20–60 GPa and found no significant coupling, so it is not likely that superconducting tetragonal PtH could exist. Figure 2 shows the variation of

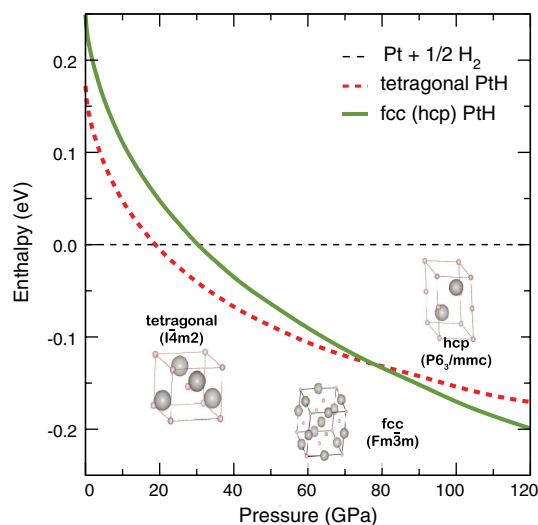


FIG. 1 (color online). Comparison of the enthalpies of  $Pt + \frac{1}{2}H_2$  and the tetragonal and fcc phases of PtH.

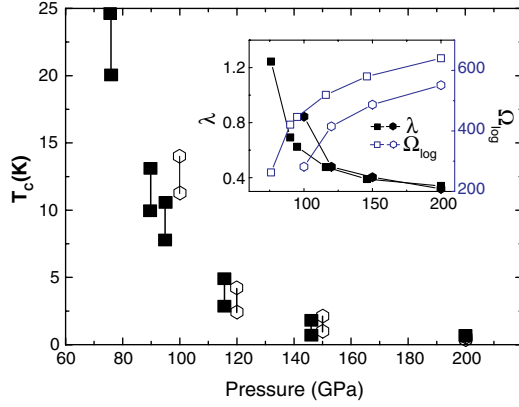


FIG. 2 (color online). Superconducting transition temperature  $T_c$  of PtH as a function of pressure. Filled squares and hollow hexagons show values of  $T_c$  for the fcc and hcp structures, respectively, with the higher  $T_c$  value at each pressure corresponding to the choice  $\mu^* = 0.10$  and the lower  $T_c$  value to the choice  $\mu^* = 0.13$ . The inset displays the evolution with pressure of the electron-phonon coupling parameter  $\lambda$  and the asymptotic phonon momentum  $\Omega_{\log}$  (see the Supplemental Material [22]). The fcc phase is dynamically unstable below 77 GPa and the hcp phase is dynamically unstable below 100 GPa.

the calculated superconducting transition temperature  $T_c$  of PtH with pressure. In the whole pressure interval of 80–200 GPa we used a fixed value for the effective Coulomb interaction parameter  $\mu^* = 0.13$ , as has been common procedure [35,36]. However, we also explored the effects on  $T_c$  of changing  $\mu^*$  to 0.10 [36,37]. With this, we have covered the two extreme choices of  $\mu^*$ , resulting in corresponding high- and low-estimates of  $T_c$  (Fig. 2). It is worth noting that the value of  $\mu^*$  may also be chosen to vary as a function of the electronic density of states at the Fermi level [38]. The highest value of  $T_c$  is found in the

vicinity of the onset of dynamical stability of the structures, as expected for phonon-mediated superconductivity [31,39,40]. The fcc structure is dynamically stable above 77 GPa where it possesses the highest  $T_c$  of around 25 K.  $T_c$  decreases monotonically and quite rapidly as the pressure rises, as shown in Fig. 2, and reaches essentially zero around 140 GPa. The hcp structure is dynamically stable above 100 GPa (and is almost degenerate in enthalpy with fcc PtH) and its maximum  $T_c$  of around 15 K occurs at 100 GPa.

Figure 3 shows the spectral function  $\alpha^2F$  and the phonon density of states (PhDOS) at different pressures for both fcc and hcp PtH. At the lowest pressure at which the fcc phase is stable (77 GPa), the Pt and H atoms both contribute to the EPC [Fig. 3(a)]. With increasing pressure, the spectral function splits into high and low frequency bands as shown in the second and third panels of Fig. 3(a), and only hydrogen vibrations contribute to the EPC in the higher pressure band. The situation is similar in the hcp phase [Fig. 3(b)], in the sense that the respective contributions to the EPC parameter  $\lambda$  from Pt and H are nearly the same as at lower pressures. With increasing pressure, the integrated  $\lambda$  decreases as the phonon frequencies increase. This behavior can be understood from Eq. (3) of the Supplemental Material [22], where it can be seen that the spectral function  $\alpha^2F$  is divided by the phonon frequencies.

Interestingly, Eremets *et al.* reported an apparent divergence in  $T_c$  between 80 and 100 GPa [5] which coincides with our calculated transition pressure between fcc and hcp PtH. These structural transformations are accompanied by softening of the acoustic branch modes which is a precursor of structural transformation. High-pressure experiments on PtH have been reported earlier [29], but since they were performed at room temperature, no information regarding possible superconductivity could be

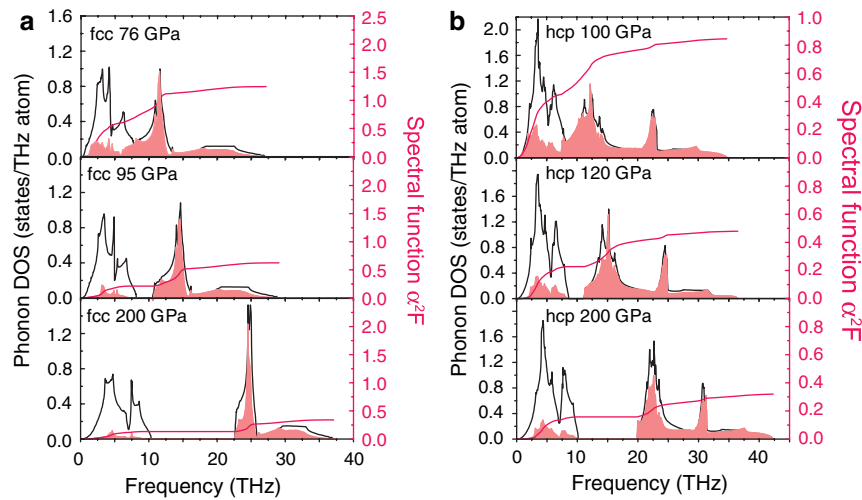


FIG. 3 (color online). Spectral function  $\alpha^2F$  (red shaded areas), the integral of the spectral function up to frequency  $\omega$  ( $\int_0^\omega \alpha^2F(\omega')/\omega' d\omega'$ ) (red line), and the phonon density of states (solid black line) as a function of frequency at selected pressures for (a) fcc PtH and (b) hcp PtH.

obtained. It would be very interesting to study compressed PtH at temperatures below 25 K to determine whether it is indeed superconducting.

At low pressures, fcc-Pt absorbs hydrogen and forms tetragonal PtH, which is a distortion of the fcc structure. At higher pressure the tetragonal PtH phase is restored to its original fcc structure or the similar close-packed hcp structure, which possess strong EPC and hence a high superconducting critical temperature. Such a structural transformation from a lower-symmetry phase to the fcc structure also applies to other hydrides formed by metals which are neighbors of Pt in the periodic table (referred to in the following as the Pt family of hydrides). We investigated the metals Rh, Pd, Ag, Ir, and Au, which all adopt the fcc structure at ambient pressure and have extremely small or zero superconducting  $T_c$ , and determined the onset pressure at which the corresponding fcc hydrides become dynamically stable. We find that fcc-RhH (lattice constant  $a = 4.02$  Å) and fcc-PdH ( $a = 4.08$  Å) are stable at almost ambient pressure, consistent with experimental observations [41–44]. Also, our calculations are in good agreement with the measured lattice constants which were reported to be 4.01 Å at 3.8 GPa (hydrogen gas pressure) for fcc-RhH [42,43] and 4.09 Å at ambient pressure for PdH [44]. The metal hydrides fcc-AgH ( $a = 4.00$  Å) and fcc-IrH ( $a = 3.88$  Å) are dynamically stable at 50 and 80 GPa, respectively. Dynamical stability of fcc-AuH ( $a = 3.80$  Å) is achieved only above 220 GPa. We emphasize that other hydride structures besides fcc might be stable at lower pressures.

Similarly to PtH, the dynamical stability of other fcc-structure hydrides can be regarded as precursors for superconductivity, while lower symmetric structures might form at much lower pressures [45]. Figure 4 shows the calculated  $T_c$  at the onset of dynamical stability of the fcc

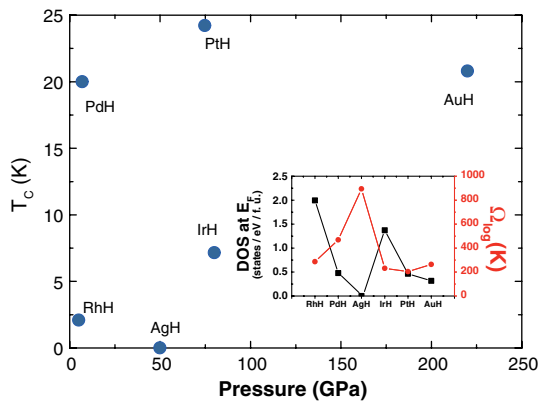


FIG. 4 (color online). Maximum  $T_c$  (calculated at the onset of dynamical stability of the fcc phase) for the metal hydrides RhH, PdH, AgH, IrH, PtH, and AuH. Note that the corresponding elemental metals in their fcc form all possess either extremely small  $T_c$  (Rh and Ir) or are not superconducting at all (Pd, Ag, Pt, and Au).

structure in the Pt family of hydrides. PdH is calculated to possess a  $T_c$  of 20 K, which is compatible with experiments on nonstoichiometric PdH<sub>x</sub> which reported a  $T_c$  of 9 K [44], although we note that our results do not reproduce the observed isotope dependence of  $T_c$  in PdH/PdD [46]. We predict IrH to have a  $T_c$  of 7 K at 80 GPa. Remarkably, the  $T_c$  of fcc-AuH is estimated to be 21 K; however, it takes a very high pressure of 220 GPa to reach this superconducting state. As the pressure is increased, the  $T_c$  of all these fcc hydrides will decrease, analogously to the case of PtH. We predict that AgH is not a superconductor, because the electronic density of states exhibits a small band gap at the Fermi level. AgH does, however, possess the highest  $\Omega_{\text{log}}$ , and therefore, if electrons were to be donated in a complex alloy, this could lead to a good superconducting material, such as (PdAg)H<sub>x</sub>, possessing a  $T_c$  of about 16 K [47]. RhH has a small  $T_c$  and it is worthwhile to note that no superconductivity of RhH has been detected at  $T > 0.3$  K [48].

In conclusion, we have shown from first principles that formation of PtH from Pt and H<sub>2</sub> can occur under pressure. Based on the empirical Allen-Dynes equation (see Supplemental Material), the resulting product is predicted to be a superconductor. Throughout the studied pressure interval of 80–200 GPa, we used the effective Coulomb interaction parameter  $\mu^* = 0.13$ , a value which has often been used [35]. We did, however, consider the effect of changing  $\mu^*$  to 0.10 on the predicted  $T_c$ . If our prediction concerning the formation of superconducting PtH at high pressures would be experimentally confirmed then this might lead to new interpretation of the data of Eremets *et al.* [5]. That work would mark the discovery of superconducting PtH under pressure and a new insulating phase of SiH<sub>4</sub>, and to the understanding that compressed SiH<sub>4</sub> is prone to decomposition. We expect these findings to be relevant to recent observations of pressure-induced metallization and superconductivity in hydrogen-rich materials. Indeed, our calculations show that the formation of superconducting fcc metal hydrides under pressure may be a common phenomenon among noble metal hydrides. The pressure-induced formation of PtH and of other noble metal hydrides, along with their associated superconductivity, represents an important aspect which should be considered in the interpretation of diamond anvil cell experiments whenever the corresponding metals and hydrogen are present, with the latter introduced either directly or entering via decomposition of hydrides.

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*Note added in proof.*—Recently, X.-F. Zhou *et al.* submitted a study on a superconducting high-pressure phase of PtH which appeared in Phys. Rev. B [49].

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