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High-Pressure Behavior of Nano-Pt in Hydrogen Environment *

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We choose nano-Pt in hydrogen environment to explore the size effect on the formation of metal hydrides. At 30 GPa, a phase transition in the metal lattice from the cubic to hexagonal phase is observed characterized by a drastically increased volume per metal atom, indicating the formation of PtH-$P6_3/mmc$. We find that nano-Pt could form PtH at a lower pressure than the bulk Pt due to its high specific surface and structure defects. The present work provides the possible route to new metal hydrides under mild conditions.

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High pressure can provide a different route to new material synthesis and manipulate novel physical properties. In the condensed and high-pressure environments, the atoms close together and bonding patterns change, resulting in new materials that cannot be synthesized under normal conditions.[1−4] By increasing the pressure, the chemical potential of hydrogen rises steeply and then hydrogen reacts with metals to form metal hydrides. Since Ashcroft proposed the idea of chemical precompression that doping metal atoms in the hydrogen sublattice may potentially reduce the pressure required to achieve the metallic hydrogen,[5] many density functional theory calculations have shown that pressure favors the stability of polyhydrides with high stoichiometry.[6,7] These polyhydrides present intriguing properties of superconducting T_c in calculation work such as H_3S with 203 K at 200 GPa,[8,9] CaH_6 with 235 K at 150 GPa,[10] LaH_{10} with 280 K at 210 GPa[11] and YH_{10} with 310 K at 250 GPa.[12] Among polyhydrides mentioned above, only the theoretical prediction of H_3S and LaH_{10} was confirmed.[13,14] Recently some H-rich polyhydrides were synthesized under high pressure and the H atoms exist in different forms in these polyhydrides: FeH_5 was synthesized above 130 GPa in a laser-heated diamond anvil cell, and it exhibits a layered structure with atomic hydrogen slabs, presenting a two-dimensional metallic character,[15] NaH_7 was synthesized above 40 GPa and 2000 K and it still presents nonmetallic properties due to H_3^- unit processing higher-frequency vibrations in Raman spectrum,[16] LaH_{10} was synthesized above 170 GPa and 1000 K and the structure matches the predicted cubic phase which has a clathrate structure of H_{32} cage.[11]

The novel noble metal hydrides synthesized by high pressure are considered as potential high temperature superconductors and have become one of the hot spots of scientific research. However, there are many unsolved controversy aspects such as synthesis conditions, formation mechanism, crystal structures and superconductivity. Using the high pressure diamond anvil cell technique and *in situ* high pressure experimental measurements, we aim to synthesize the hydrogen-rich noble metal hydrides from the typical noble metal elements Pt with hydrogen, explore the crystal structure, and chemical bonds under high pressure. The current research will provide new insight into metal hydrides.

Platinum nano-powder with particle size about 50 nm was purchased from Sigma-Aldrich Company. The symmetric diamond anvil cells (DAC) were used to generate pressure. The diamonds with culet 300 μm were coated with a 100-nm-thick layer of Al_2O_3 to prevent diamond failure by hydrogen diffusion. Tungsten gaskets were also coated with 100-nm-thick gold to prevent the diffusion of hydrogen. The hydrogen was compressed to 0.17 GPa, and the cells were unclamped to allow the hydrogen to flow into the chamber and were then resealed by gas-loading apparatus. The ruby R1 peak is used to calibrate the pressure.[17]

The x-ray diffraction (XRD) experiments were performed at the 4W2 beamline of Beijing Synchrotron Radiation Facility (BSRF) and 15U1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The incident wavelength of x-ray was 0.6199 Å. The MAR image plate detectors were used to collect the diffraction patterns and the two-dimensional XRD images were radially integrated using DIOPTAS software,[18] yielding intensity versus diffraction angle 2θ patterns. Prior to experimental measurement, a CeO_2 standard was used to calibrate the geometric parameters. All the experiments were carried out at room temperature. The reflex module in materials studio program was utilized to index and refine the XRD patterns.[19]

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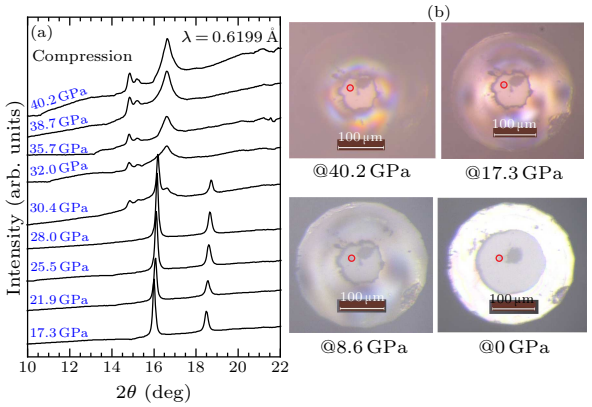

Fig. 1. (a) Typical XRD patterns of the sample at selected pressures upon compression up to 40.2 GPa. The incident wavelength is $\lambda = 0.6199$ Å. (b) The photomicrograph of the sample at different pressures.

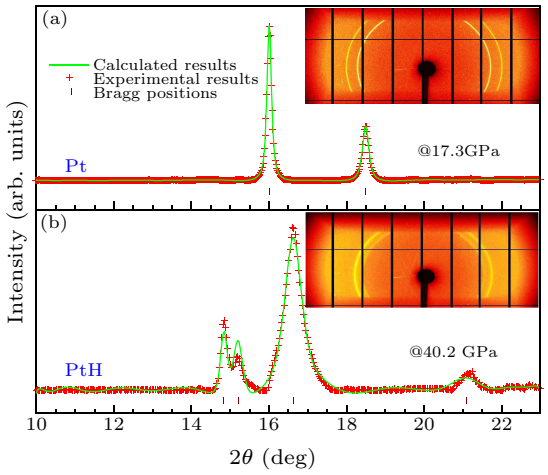

Fig. 2. The Rietveld refinements of XRD patterns for (a) Pt at 17.3 GPa and (b) PtH at 40.2 GPa, respectively. Inset: the corresponding raw diffraction rings.

During the compression process, we have collected the corresponding synchrotron XRD patterns and recorded the sample chamber, as shown in Fig. 1. After loading the Pt nano-powder and hydrogen into the DAC by gas-loading apparatus, we have sealed these two samples at about 8.6 GPa, and the original sample chamber has shrunk to half of the original size. Upon further compression, the sample did not show the obvious changes, from the pictures in Fig. 1. We have checked the XRD patterns carefully. At first, the diffraction pattern was undoubtedly determined to be cubic-Pt phase with space group $Fm-3m$, and the refined result is shown in Fig. 2(a). The obtained lattice parameters and volume of cubic-Pt phase are $a = 3.872(6)$ Å, and $V = 58.1(3)$ Å^3. Upon compression to 30.4 GPa, an additional phase appears in XRD patterns of Pt in Fig. 1(a). The new phase can easily be indexed in the $P6_3/mmc$ space group (hexagonal symmetry, see Fig. 2(b)). By Rietveld refinement, we have obtained the lattice parameter $a = 2.777(3)$ Å and $c = 4.736(4)$ Å, and volume $V = 31.6(2)$ Å^3 with Pt atoms in Wyckoff position $2a$ (0, 0, 0) and $6c$ (0.25, 0, 0.5) at 40.2 GPa. This indicates the formation of a new compound; i.e., a metal hydride instead of a phase transition in pure platinum. We have checked the previous work[20] on the synthesis of platinum hydrides by bulk platinum and hydrogen and found that the new patterns match the previous reported hexagonal PtH. Up to the highest pressure of 40 GPa, PtH remains stable and adopts the same structure throughout this pressure range. Upon decompression, hexagonal-PtH phase decomposed into the metal and hydrogen at 17 GPa.

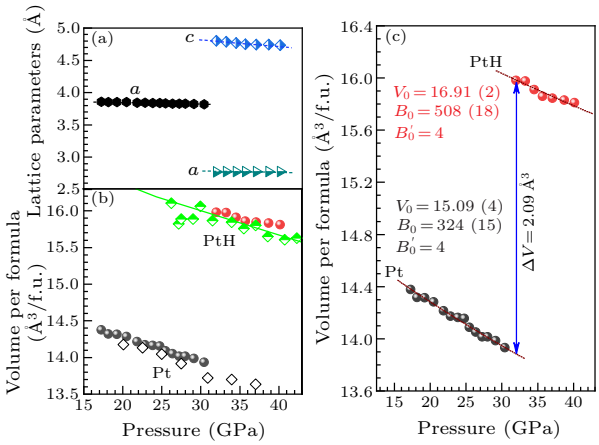

Fig. 3. (a) Lattice parameters and volume of the sample as a function of pressure. (b) The volume comparison between our work and previous results. The solid spheres represent the present experimental P–V data, while open diamonds and half-open diamonds represent the previous results.[20] (c) The volume per formula unit as a function of pressure. The dotted curves represent the Birch–Murnaghan equation fits of our experimental results.

Because of the weak x-ray scattering cross section of H atoms, we cannot obtain the positions and stoichiometry merely through XRD diffraction patterns. To further confirm the stoichiometry of the platinum hydride, we have obtained the lattice parameters and volume as a function of pressure, which can be seen from Fig. 3. The lattice parameters of the Pt sample changes very slowly with pressure, while the ones for the PtH sample move faster upon compression (Fig. 3(a)). We also compared our pressure-volume data with the previous data, and it is seen that the unit cell volume of our samples is larger than that of the bulk samples in Fig. 3(b), attributed to the quantum size effect.[21] The pressure-volume data are fitted by the third-order Birch–Murnaghan equation of state, as follows:

$$P = \frac{3B_0}{2}\left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}}\right] \cdot \left\{1 + \frac{3}{4}(B_0' - 4)\left[\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right]\right\},$$

where V_0 is the volume per formula unit at ambient pressure, V is the volume per formula unit at pressure P given in GPa, B is the isothermal bulk modulus, and B' is the first pressure derivative of the bulk modulus of many metals and alloys. For cubic-

Pt phase, the fitted parameters are $V = 15.09(4)$ Å^3, $B = 324(15)$ GPa, and $B' = 4$, hexagonal-PtH phase with $V = 16.91(2)$ Å^3 and $B = 508(18)$ GPa with B' at 4. The bulk modulus of nano-PtH is larger than the reported bulk compound.[2] At 32 GPa, the sample exhibits a significantly larger volume per formula than pure platinum with the volume difference amounts to 2.09 Å^3 per metal atom, substantially equalling the interstitial metal hydrides (e.g., 2.1 Å^3 for V hydride[9]). Therefore, direct comparison with other metal hydrides suggests a ratio of 1:1 for platinum hydride (assuming full stoichiometry). However, such comparisons are not directly valid since estimating the hydrogen content by comparing unit-cell volumes is based on empirical findings in interstitial hydrides.

It is interesting to note that the diffusion of hydrogen sometimes appears to favor the formation of the fcc phase but the present nano-metal prefers the hexagonal phase. As shown in Fig. 4, a schematic diagram of the formation of platinum hydride. The volume per Pt atom increases by 2.09 Å^3 compared to pure Pt due to H atoms occupying the octahedral vacancies in the structure. This transition and associated volume change are in good agreement with previous observations of the formation of CoH and other transition metal monohydrides.[22,23] Meanwhile, the current work shows the hydride forming process with nano-powder platinum element at lower pressure, while bulk Pt exhibits two phases cubic-PtH and hexagonal-PtH at much higher pressure. These differences may arise from the nanoparticle Pt we used. This result can be explained as follows: nano-powder Pt has a large specific surface area, the increased surface area makes the diffusion of hydrogen atoms more efficient by offering a large number of dissociation sites and allowing hydrogen atoms permeation to reach saturation fast, without the intermediate cubic-PtH. The formation of hydrides between Pt nanocrystals and hydrogen can be explained by the hydrogen embrittlement effect.[24,25] The hydrogen embrittlement effect is manifested in the phenomenon that the metal itself breaks or becomes embrittlement due to the introduction of hydrogen atoms or the infiltration of hydrogen atoms into the metal materials during the production and preparation of metals. When Pt metal is subjected to pressure, the stress concentrates on the internal defects of the metal, and many cracks on the surface go deep into the structure, leading to the gradual destruction of the structure of the metal. In the presence of a crack, H_2 molecules first decompose on the crack surface, determined by the thermodynamic properties. When H atoms on the crack surface are adsorbed and saturated, H atoms are driven by the energy generated by the interaction between the high tensile stress field and the volume mismatch caused by the insertion of H atoms in the metal Pt lattice. The hydrogen atoms in the lattice gap interact with metal atoms, thus reducing the bonding ability between metal atoms and breaking the metal bonds in metal materials. In this process, high concentrations of hydrogen atoms react with surrounding Pt metal atoms forming metal hydride PtH. Although fcc-Pt is known to be stable up to 660 GPa,[26] the addition of hydrogen changes its lattice from fcc into hcp.

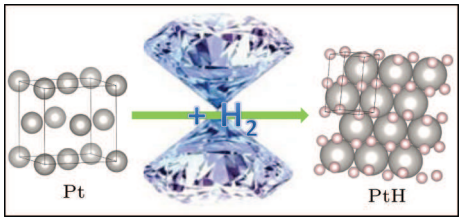

Fig. 4. A schematic diagram of the formation of platinum hydride.

It was recently suggested that in the dense group IVa hydrides, where hydrogen is a dominant constituent, metallic states and superconductivity could be reached by subjecting the hydrides to high compression.[5] The experimental confirmation quickly followed with the claim of the pressure induced metallization and superconductivity in silane (SiH_4) above 50 GPa.[27] It has been argued that at pressures above 50 GPa, silane partially decomposes, releasing hydrogen, which readily reacted with platinum electrodes used for the conductivity measurements.[28] The present work further confirms that the superconductivity and very low compressibility observed in Ref. [28] are much more likely to be due to the formation of the metallic platinum hydride rather than SiH_4.

In conclusion, we have reported the synthesis of platinum hydride in a diamond anvil cell, which has been confirmed by synchrotron x-ray diffraction. Above 30 GPa, we observe a known hexagonal-structure PtH-$P6_3/mmc$ space group, which is stable up to 40 GPa. The pressure-volume data of the discovered PtH are fitted by the third-order Birch–Murnaghan equation of state: $V = 16.91(2)$ Å^3 and $B = 508(18)$ GPa with B' at 4. The possibility of recovering the hydride to ambient pressure should be explored with further experiments at low temperatures.

The *in situ* angle dispersive XRD of this work was performed at 4W2 HP-Station, Beijing Synchrotron Radiation Facility (BSRF) and 15U1 beamline, Shanghai Synchrotron Radiation Facility (SSRF).

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