

Formation of Superabundant Vacancies in Pd Hydride under High Hydrogen Pressures

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In situ x-ray diffraction on Pd hydride under 5 GPa of hydrogen pressure show that lattice contraction due to vacancy formation occurs in 2–3 h at 700–800 °C, and two-phase separation into PdH and a vacancy-ordered phase of Cu₃Au structure (Pd₃VacH₄) on subsequent cooling. After recovery to ambient conditions and removal of hydrogen, the vacancy concentration in Pd metal was determined by measuring density and lattice parameter changes to be 18 ± 3 at. %. This procedure provides a new method of introducing superabundant vacancies in metals.

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The Pd-H system is probably the most extensively investigated of all metal-hydrogen systems and yet some of its properties at high hydrogen concentrations still remain unexplained. The lattice parameter increases linearly at a normal rate only up to the hydrogen concentration of $x = [\text{H}]/[\text{Pd}] \approx 0.7$ and tends to level off thereafter [1]. Although the site occupancy in the lower-concentration region is known to be the O-site, near-surface hydrides formed by ion implantation have been reported to have hydrogen concentrations as high as $x = 1.3$ – 1.6 , well above the O-site capacity $x = 1.0$ [2]. Some of the anomalous effects in the Pd-D system at high D concentrations, reported under the name of “cold fusion,” may also be relevant. Hardly any structural information has been available, however, for Pd hydride in the high-concentration region.

A clue for understanding these anomalous properties at high concentrations was obtained in our recent high-pressure experiments [3]. We found that the lattice parameter of Pd and Ni hydride decreased in several hours when a specimen was held at high temperatures and high hydrogen pressures; by 0.79% for PdH at 700 °C at a hydrogen pressure of 5 GPa. The lattice contraction was conserved when the specimen was returned to ambient conditions and depleted of hydrogen by heating to 350 °C, but annealed out after heating to 800 °C. These observations were taken to be the evidence that a large number of metal-atom vacancies were formed in the hydride phase.

The purpose of this Letter is to report on the results of two different types of experiments performed to further characterize the hydrogen-induced vacancies in Pd.

The first type of experiment was to determine the concentration of hydrogen-induced vacancies by measuring the volume and lattice parameter changes on the same sample; the method developed by Simmons and Balluffi [4] to determine the equilibrium concentration of thermal vacancies in metals. In practice, we determined the volume change by measuring the density, and obtained the vacancy concentration x_v (in atomic fraction) from the

relation

$$x_v = -\Delta\rho/\rho_0 - 3\Delta a/a_0, \quad (1)$$

where $\Delta\rho$ and Δa are the changes in the density ρ and the lattice parameter a , respectively, from their original values ρ_0 and a_0 ; $\Delta\rho = \rho - \rho_0$ and $\Delta a = a - a_0$.

The samples were prepared by using a cubic-anvil press “Oz.FI” of our laboratory. A Pd sample of 2 mm diameter \times 0.2 mm in size, cut from 99.95% pure polycrystalline sheet supplied by Koch Chemicals Ltd., England, was encapsulated in a NaCl container (a hydrogen sealant) together with an internal hydrogen source LiAlH₄, which supplies hydrogen on thermal decomposition at ~ 300 °C. The sample and LiAlH₄ was separated by a BN disc 0.2 mm thick, which allowed only H₂ to reach the sample. (No reaction with Li or Al was detected in any recovered specimen.) The NaCl capsule was surrounded by a graphite tube heater, and was placed at the center of an 8 mm-cube pyrophyllite (a pressure transmitting medium). The cube was compressed from six sides by WC anvils of 6 mm \times 6 mm on the top face to produce nearly homogeneous pressure at the sample position.

The experimental procedure was the following: After compression to 5 GPa, the sample was heated to 700 °C for hydrogenation, maintained there for 3 h, quenched and returned to ambient pressure. (Our previous experiment [3] showed that saturation of hydrogen concentration, probably to $[\text{H}]/[\text{Pd}] = 1.0$, occurred in the course of heating to 700 °C, and its partial loss during and after the decompression in a few hours at room temperature.) Subsequently, the recovered specimen was heated to 350 °C *in vacuo* for 3 min for degassing hydrogen, and quenched. Three pieces of such specimens, weighing 13 mg in total, were prepared and their density was measured by the Archimedeian method, using water and an electronic balance (Mettler AE240) having the sensitivity of 10 μg .

The results are summarized in Table I. The vacancy concentration amounts to 18 at. %. This value is not

TABLE I. Vacancy concentration of Pd determined by density and lattice parameter measurements. The density ρ and the lattice parameter a of samples, degassed after recovery to ambient conditions from heat treatment under high hydrogen pressure, are compared with their original values ρ_0 and a_0 (ρ in 10^3 kg/m^3 and a in nm). The vacancy concentration x_v can be calculated from fractional changes of these values $\Delta\rho/\rho_0$ and $\Delta a/a_0$ by using Eq. (1).

ρ	ρ_0	$\Delta\rho/\rho_0$	a	a_0	$\Delta a/a_0$	x_v
9.87(13)	11.46(20)	-0.139(29)	0.3831(3)	0.3884(2)	-0.14(1)	0.18(3)

affected by the possible presence of residual hydrogen atoms in the lattice; their effect on volume and lattice parameter cancels with each other and their effect on the total weight is negligibly small. (The volume expansion due to interstitial hydrogen atoms is known to come solely through lattice parameter changes; see [5].) The relaxation volume of a vacancy (in units of atomic volume) can be obtained by dividing $3\Delta a/a$ by x_v . The value obtained, -0.29 ± 0.03 , is consistent with those reported on other fcc metals (-0.22 for Ni, -0.2 for Cu, -0.28 for Pt, and -0.15 for Au [6]).

The second type of experiment was to examine the structural properties of the vacancies by x-ray diffraction, anticipating that such a large number of vacancies should assume some ordered arrangement at lower temperatures. The x-ray diffraction was measured using a cubic-anvil press "MAX80" installed at the synchrotron radiation source of the Accumulation Ring of The National Institute of High Energy Physics (KEK). The sample assembly was nearly the same, except that the sample was 1 mm in diameter and amorphous boron-epoxy resin composite was used for the pressure-transmitting medium. The incident white x-rays were collimated to a beam of $0.1 \text{ mm} \times 0.2 \text{ mm}$, and diffracted x-rays were energy analyzed by a pure Ge solid state detector (SSD) placed at a fixed angle $2\theta = 4.0^\circ$ after passage through a pair of receiving slits. Owing to extremely small divergence of the beam, only the x-rays diffracted at the sample could be detected. (See Figs. 1 and 2.) Exposure time was 60–300 s for each measurement. Details of MAX80 system and the sample assembly are described in [7] and [8], respectively.

Variation of the lattice parameter with time, measured under a hydrogen pressure of 5 GPa, is shown in Fig. 1. The gradual lattice contraction, which occurred at 800°C , is believed to be caused by diffusion of vacancies from sample surface to the interior. The required length of time ($\sim 3 \text{ h}$) and sample thickness (0.2 mm) leads to the diffusivity of $10^{-12} \text{ m}^2/\text{s}$, which is quite reasonable. The asymptotic value of the lattice contraction, $\Delta a/a_0 = 0.0081 \pm 0.0010$ is close to the results of our previous experiment [3], indicating that the amounts of vacancies formed at 700 and 800°C are nearly the same.

Subsequently, the temperature was lowered to 500°C , and x-ray diffraction was measured. The observed diffraction pattern, shown in Fig. 2, exhibits two sets of peaks labeled A and B coming from two coexisting phases. The one labeled A comes from the fcc lattice with a lattice parameter $a = 0.4069(1) \text{ nm}$ and is assigned

to nearly stoichiometric PdH: Only this phase was observed in a separate run without a prolonged heating at high temperatures. The other set of peaks labeled B comes from the fcc phase with a slightly smaller lattice parameter $a = 0.4016(1) \text{ nm}$, and contains, in addition, superlattice reflections having simple-cubic indices (100), (110), (210), and (211). Four additional superlattice lines were observed when the diffraction angle was set at a higher value $2\theta = 6.0^\circ$ (see below). These superlattice lines were found to remain nearly as intense, when measured 40 h after decompression at room temperature.

We conclude, from symmetry considerations, that the only possible structure for this second phase is such that one of the four simple-cubic sublattices constituting the fcc lattice is occupied by vacancies, i.e., the defect-ordered structure of Cu_3Au type ($L1_2$ structure), which can be written as Pd_3VacH_4 .

Although structure determination by more detailed analysis of diffraction patterns is hampered by strong energy dependence of the sensitivity of the SSD, and possible presence of preferred orientation of crystallites, the validity of the proposed structure is corroborated by the following two pieces of evidence.

First, the total number of vacancies estimated from the relative intensities of the two fundamental reflections (111) and (200) of the two phases based on the proposed defect-ordered structure is consistent with the result of density measurements. The ratio of the peak intensities I_B/I_A is 1.36 for the (111) and 1.19 for the (200) peak

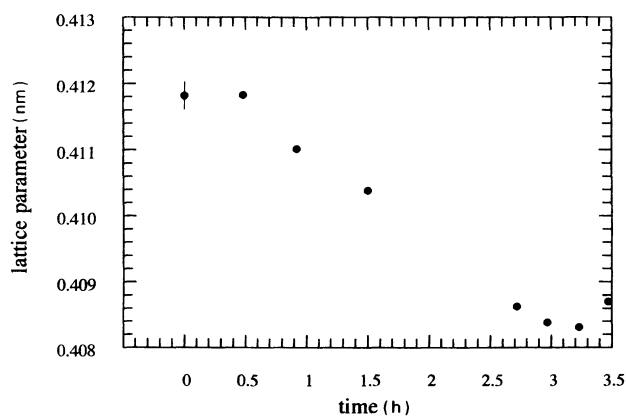


FIG. 1. Temporal variation of the lattice parameter of Pd hydride at 800°C and a hydrogen pressure of 5 GPa. A possible error in the least-squares fitting to six diffraction lines ($\sim 2 \times 10^{-4} \text{ nm}$) is inscribed.

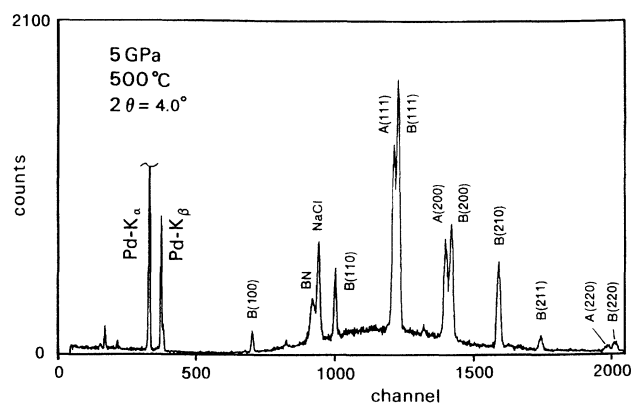


FIG. 2. X-ray diffraction pattern of Pd hydride at 500 °C and a hydrogen pressure of 5 GPa, after holding at 800 °C for 3.5 h. Diffraction angle was set at $2\theta = 4.0^\circ$. Separation into two phases, PdH (A) and a vacancy-ordered phase Pd_3VacH_4 (B), is clearly visible.

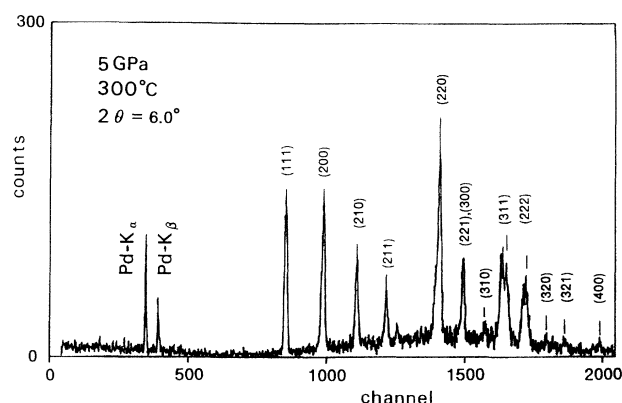


FIG. 3. X-ray diffraction pattern of Pd hydride at 300 °C and a hydrogen pressure of 5 GPa, after holding at 700 °C for 8.5 h. Diffraction angle was set at $2\theta = 6.0^\circ$. Many superlattice lines from the vacancy-ordered phase exist.

(1.28 ± 0.08 on the average). Correcting for the ratio of scattering intensities per unit cell of the two phases, $9/16$, the number of unit cells in the two phases N_B/N_A becomes 2.27 ± 0.15 , and the average vacancy concentration can be estimated as $x_v = 0.25N_B/(N_A + N_B) = 0.174 \pm 0.003$. The value agrees excellently with the one obtained from the density measurement (0.18 ± 0.03).

Second, the temperature dependence of the intensity of superlattice reflections is very similar to the one reported for Cu_3Au [9]. Reexamination of our previous experiment [3] revealed that many superlattice lines existed in the spectra taken in the course of cooling after prolonged heating at 700 °C. The diffraction pattern observed at 300 °C is shown in Fig. 3. As the diffraction angle was set at a higher value ($2\theta = 6.0^\circ$), diffraction lines having higher indices were observed, including superlattice lines (210), (211), (221) and (300), (310), (320), and (321). The relative intensity of superlattice reflections was obtained, approximately, by dividing the sum of (210), (211), (221), and (300), intensities (evaluated by peak values) by the sum of (111), (200), and (222) intensities. The temperature dependence of the superlattice intensity is shown in Fig. 4. The superlattice intensity changes almost discontinuously at slightly above 873 K, indicating that the order-disorder transition is of first order. Comparison with the case of Cu_3Au [9] is facilitated by plotting the both sets of data on the common reduced scale T/T_c , with $T_c \approx 880$ K for the defect-Pd hydride and $T_c = 663$ K for Cu_3Au . The superlattice intensity of the defect-Pd hydride was normalized to its maximum value at $T/T_c \sim 0.8$ to derive approximately the long-range order parameter S . These two sets of data exhibit nearly the same temperature dependence, especially near T_c , which indicates that the order-disorder process in these two systems is the same. The gradual decrease of superlattice intensities at lower temperatures is believed to be due to gradual loss of supersaturated vacancies in the course of cooling.

We suggest that the superstoichiometric hydride formed by ion implantation at low temperatures [2] by be identified with this defect-hydride structure having the composition $[\text{H}]/[\text{Pd}] = 4/3$. Although structure determination of these superstoichiometric hydrides, including the position of hydrogen atoms, is difficult due to partial loss of hydrogen, in both cases, in bringing them to normal pressure and temperature, the presence of many vacancies in the ion-implanted region appears to make the formation of this defect-hydride structure very probable—much more probable than the other form of superstoichiometric hydride observed in a thin film [10].

Regarding the energetics of vacancy formation in the hydride phase, the following order-of-magnitude

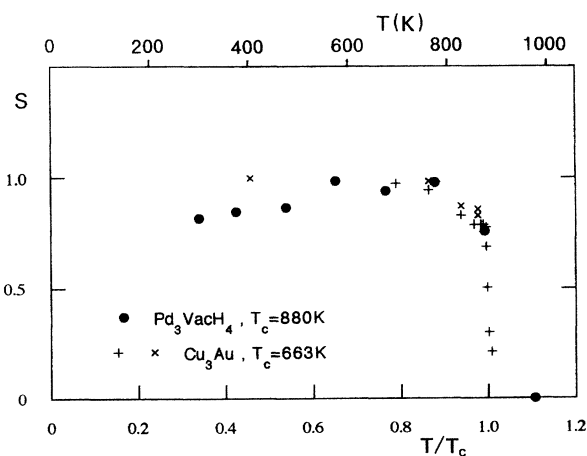


FIG. 4. Temperature dependence of the superlattice reflection intensity of the vacancy-ordered phase Pd_3VacH_4 (●) under 5 GPa of hydrogen pressure; temperature in K on the top scale and in reduced units ($T_c \approx 880$ K) on the bottom scale. The intensity is normalized at $T/T_c \sim 0.8$ to obtain the long-range order parameter S . For comparison, data reported for Cu_3Au , including those measured *in situ* (+) and after quench (×) [9], are inscribed on the reduced temperature scale ($T_c = 663$ K).

discussion can be made. From the observed vacancy concentration $x_v = 0.18$ at $T = 973$ K, the formation enthalpy h_f can be roughly estimated using the relation

$$x_v/(1 - x_v) = e^{s_f/k} e^{-h_f/kT} \simeq 10e^{-h_f/kT}, \quad (2)$$

with $s_f = (2-3)k$ known to hold for the formation entropy of a vacancy in many metals [6]. The value obtained is $h_f = 0.32$ eV. This is a drastic reduction in comparison to the corresponding value in metallic Pd of $h_f = e_f + pv_f = 1.99$ eV. [An estimate $e_f = 1.68$ eV was derived from the empirical formula $e_f \approx 9.3kT_m$ [11] with $T_m = 2100$ K at 5 GPa, and $pv_f = 0.31$ eV from the formation volume of a vacancy derived above, $v_f = (1 - 0.29) \times 0.388^3/4 = 0.010$ nm³.] This reduction of h_f can be explained, at least qualitatively by considering the energy change of hydrogen atoms adjacent to a vacancy. From channeling experiments, a single vacancy in Pd is known to trap up to six hydrogen atoms, the first two with a binding energy of 0.23 eV and the remaining four with 0.15 eV [12]. Thus, the energy of a vacancy in Pd is lowered, effectively, by the sum of binding energies, $0.23 \times 2 + 0.15 \times 4 = 1.06$ eV. This value is comparable with the observed reduction of h_f . If one prefers to compare PdH with its electronic analog Ag having $e_f = 1.1-1.2$ eV [6], the conclusion remains essentially the same. More detailed discussions on the formation of the defect hydride structure can be made only after full-scale electronic energy calculations.

Since reported values of the vacancy-hydrogen binding energy are invariably large [13], the lowering of e_f always occurs in the presence of interstitial hydrogen atoms. Thus, as long as interstitial hydrogen exists in the lattice at temperatures where metal-atom vacancies can migrate over a sample size, vacancy concentrations well above the thermal equilibrium value in pure metallic state can be attained in any case. In fact, we have observed such vacancy formation in Mn, Ni, Pt, Au, and some Pd alloys, and vacancy ordering in some of them (Ni, Pd-Rh, and Pd-Pt alloys). These results will be reported in due course.

This technique of generating vacancies in a hydride phase and subsequent degassing provides a method to introduce hitherto unattainable amount of vacancies in metals. Metals and metal hydrides containing superabundant vacancies constitute a new group of materials, of which various novel properties can be expected.

One such property is the melting-point reduction due to vacancies. In his attempt to draw a universal melting diagram of metals and alloys by considering the relative stability of crystalline, amorphous, and liquid states as a function of vacancy concentration, Fecht [14] showed that there was a maximum possible concentration of vacancies in solids; $x_v = 0.077$ in his model calculation. The concomitant lowering of the melting point was substantial: T_m of pure metals was reduced to $0.35T_m$ at the critical vacancy concentration. In contrast to these predictions, we observed that Pd hydride containing

18 at.% vacancies does exist in a crystalline state, and that the T_m of Pd hydride was lowered only slightly, if at all, by the introduction of 18 at.% vacancies. [Pd hydride without the vacancy generation treatment melted slightly above 800 °C (800–850 °C) at 5 GPa, but remained crystalline at 800 °C even after the vacancy generation.] Admitting that a detailed comparison of the present experiments with Fecht theory is hindered by the presence of interstitial hydrogen, we still suggest that these gross discrepancies require serious reconsideration of the validity of the theory. On the experimental side, closer examination of the melting of defective metals containing controlled amount of vacancies has become feasible by the sample preparation technique developed here, and is believed to be worthy of further pursuit.

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