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Investigation of the vacancy-ordered phases in the Pd–H system

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Abstract

It has been shown that hydrogen–metal reactions operated at high pressures (3–5 GPa) may lead to hydrogen-induced lattice migration. The occurrence of fast diffusion processes that take place within the metal lattice has been established. Under these conditions, modifications of the diffusion kinetics and of the phases equilibria allow to produce vacancy-ordered phases with high vacancy concentrations (20%). An alternative route which leads to such phases that are stable at ambient pressure and temperature is presented. The structural properties of the Pd-(vacancy, H) system which have been studied by means of X-ray diffraction, scanning electron microscopy and transmission electron microscopy will be discussed. In the case of palladium, the vacancy-ordered state is characterized by the loss of superconductivity with respect to the Pd hydride. This spectacular modification of the physical properties will be presented and discussed in the light of band structure calculations that have been performed modeling different types of decorated vacancies with octahedral coordination. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen–metal reactions; Pd–H system; Vacancy-ordered phases

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1. Introduction

Hydrogen may be reversibly inserted at ambient pressure and temperature in many intermetallic compounds leading to interstitial compounds (hydrides) whose structural, chemical and physical properties are strongly modified upon hydrogen insertion. At higher hydrogen pressures, typically above 0.1 MPa, the heat of formation of a binary hydride, for example of a strongly electropositive element, may reach that required for the formation of a binary alloy. From a thermodynamic point of view, hydrogen insertion in a metallic lattice (gas–solid reaction), when operated under high pressure allows to modify the corresponding metal–hydrogen phase diagram. Then, at rather low temperatures some fast diffusion processes of metallic species, that usually take place at higher temperatures, may be activated giving way to the so-called hydrogen-induced lattice migration (HILM) [1,2]. The new crystal structures and/or the phase separation which are observed result from a new equilibrium state of the metal network. New phases may be thereby stabilized at temperatures close to room temperature with (or without) the need of hydrogen desorption. An interesting case is that of hydrogen-induced vacancy phases for which hydrogen desorption is accompanied by a reconstruction of the starting network. In this case, the metal diffusion kinetics being lower than that of hydrogen, vacancy coalescence favoured by defects (e.g. dislocations) gives way to stable nanometric or micrometric pores.

The joint use of hydrogen and very high pressures (>10 GPa) is a very suitable means to investigate transformations in intermetallic materials. Following the pioneering work of Fukai [3,4], an alternative and original route has been successfully developed [5] in order to synthesize vacancy-ordered phases in metallic systems such as Pd, TiNi, Ni. In the present work we report on the investigation of the Pd and Pd–H systems.

2. Experimental

Samples of pure palladium foils (99.95%) that had been cold-rolled down to a thickness of 0.12 mm and cut in disks 7 mm in diameter, were encapsulated together with an internal hydrogen source in a NaCl container (7 mm in diameter and 8 mm high) impervious to hydrogen. The high hydrogen pressure was applied using a CONAC-type cell developed at the I.H.P. at Troisk (Russia) and operated using a 1000 ton press. The pressure within the press reached 3.5 GPa. The process uses hydrogen under high pressure (4 GPa) that is issued from the decomposition of a hydrogen-rich precursor. Contrarily to reactive and air-

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unstable precursors such as $LiAlH_4$ that have been used so far, we have used solid hydrocarbons such as $C_{14}H_{10}$ or $C_{10}H_6$ which can be used in larger pressure cells and display higher chemical stability in air. The hydrogen provider was a pellet of $C_{14}H_{10}$; when heated it decomposes irreversibly above 400°C and supplies free H_2 that can react with the sample. The sample and $C_{14}H_{10}$ were separated by a BN disk 0.1 mm thick in order to avoid possible carbon diffusion. The resulting samples were characterized by routine X-ray diffraction procedures using a Siemens D5000 powder diffractometer operated with Cu Kα radiation. Scanning electron microscopy was performed using a JEOL 400T microscope.

3. Results

A cold-rolled foil of fcc palladium subjected to 3.5 GPa at 600°C, a temperature at which atomic diffusion is not likely, undergoes a monoclinic distortion that is not reversible [5]. This structural transformation results from an accommodation of dislocations by the lattice through a shear mechanism. The occurrence of slip bands revealed by scanning electron microscopy (see Fig. 1) bears witness to this shearing mechanism.

The same kind of treatment at 800°C with hydrogen leads to a simple cubic phase with a contracted lattice indicating a vacancy-containing phase. This structure has been maintained at ambient pressure and room temperature. The observed symmetry lowering (face centered cubic to simple cubic) corresponds to an ordering within the metal lattice since the X-ray scattering cross-section of hydrogen is negligible compared to that of palladium. The ordering is due to the presence of vacancies and is of Cu_3Au-type, thus leading to the formula $Pd_3(\Box H_x)$ [4]. The ordered vacancy phase is schematized in Fig. 2. The presence of vacancies is corroborated by a metallographic study using SEM and TEM that reveals the presence of pores which result from the coalescence of vacancies at the free surface of the sample. This phenomenon is well

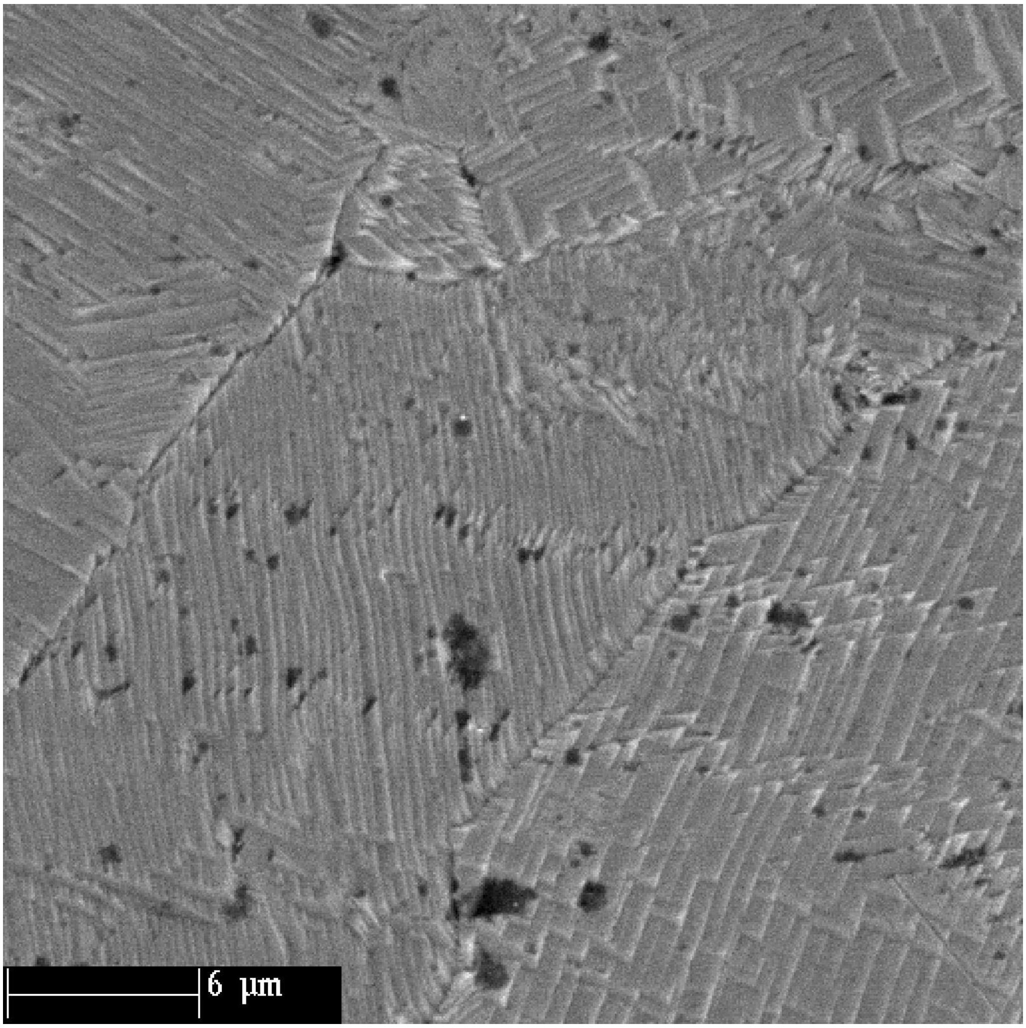

Fig. 1. SEM image of a high pressure-treated (3.5 GPa) Pd foil at 450°C.

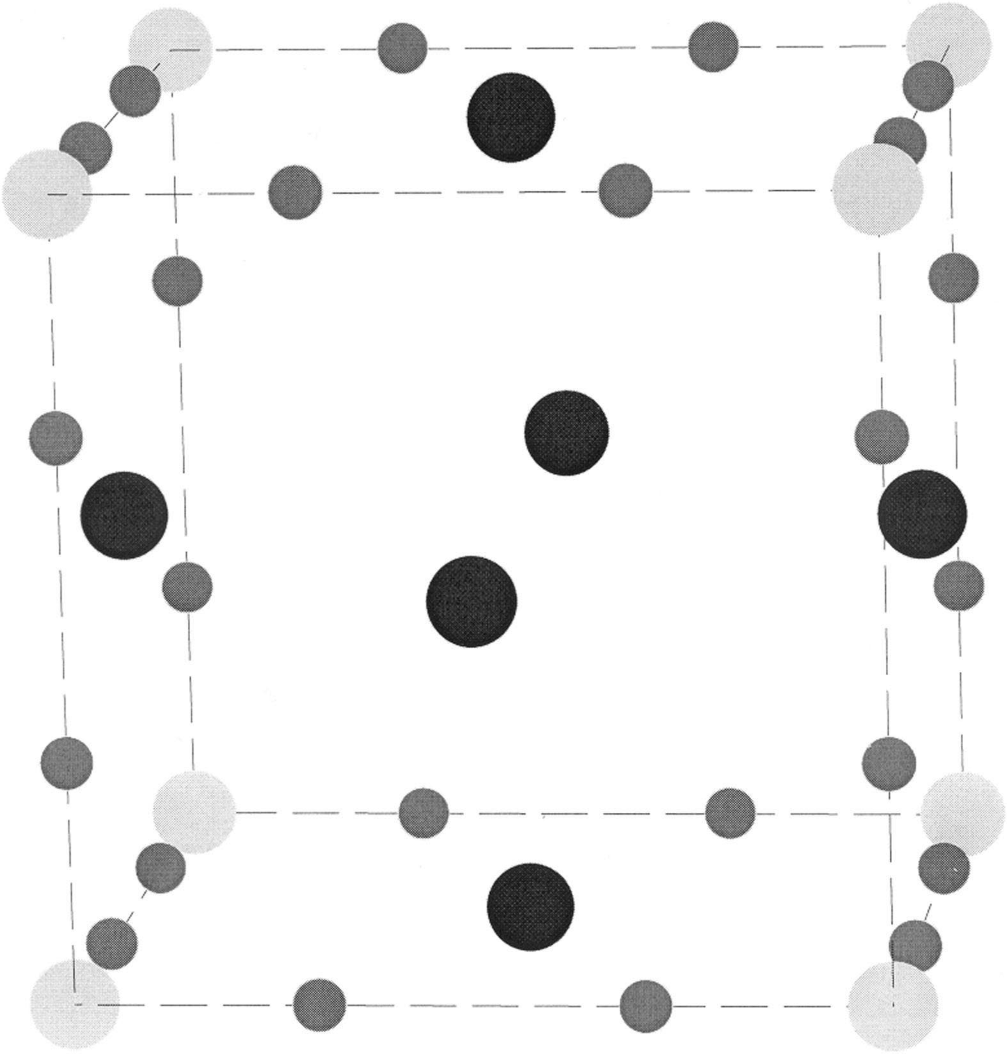

Fig. 2. Schematic representation of the $Pd_3(\square H_x)$ structure: in the cubic cell the large black spheres are for palladium atoms (0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0), the large white grey spheres are for the metal (Pd) vacancies (0,0,0), the small dark grey spheres are sites close to the vacancies that can be occupied by hydrogen atoms.

known in metallurgy and coalescence frequently occurs in dislocation-rich areas; they are from nano to micrometric sizes, those shown in Fig. 3. The vacancy concentration has been derived from the lattice parameter value and using the vacancy relaxation volume determined by Fukai [3], it reached more than 20%.

This very large vacancy concentration induced by high pressure hydrogen treatment can be understood by comparing the lattice relaxation energy with that required to form a vacancy in a palladium metal lattice that is 1.5 eV [6]. The H-□ (hydrogen-vacancy) bonding energy is approximately 0.2 eV, and the coordination number for a vacancy in the cubic host lattice may reach CN=6; then in the presence of hydrogen, the energy required to generate a vacancy can be lowered of up to 1.2 eV. We can thus qualitatively account for the superabundant vacancy concentrations observed in the $Pd_3(\square H_x)$ system. It is worth noting that we have been able to stabilize the superabundant vacancy phase $Pd_3(\square H_x)$ at room temperature and ambient pressure.

4. Physical study of the $Pd_3(\square H_x)$ system

Hydrogen insertion in a metallic lattice (e.g. d metal) gives way to a number of situations where the H atom exhibits both a donor character to the d metal states (proton model) or an anionic character (anion model) with the filling of new states at low energy and a lowering of the density of states (DOS) close to the Fermi level. Both models appear to be too simple and only represent the extreme limits of the actual case [7,8]. Considering the $Pd_3(\square H_x)$ system with a large fraction of vacancies and a new coordination for the metallic species, it is reasonable to expect a significant modification of the electronic

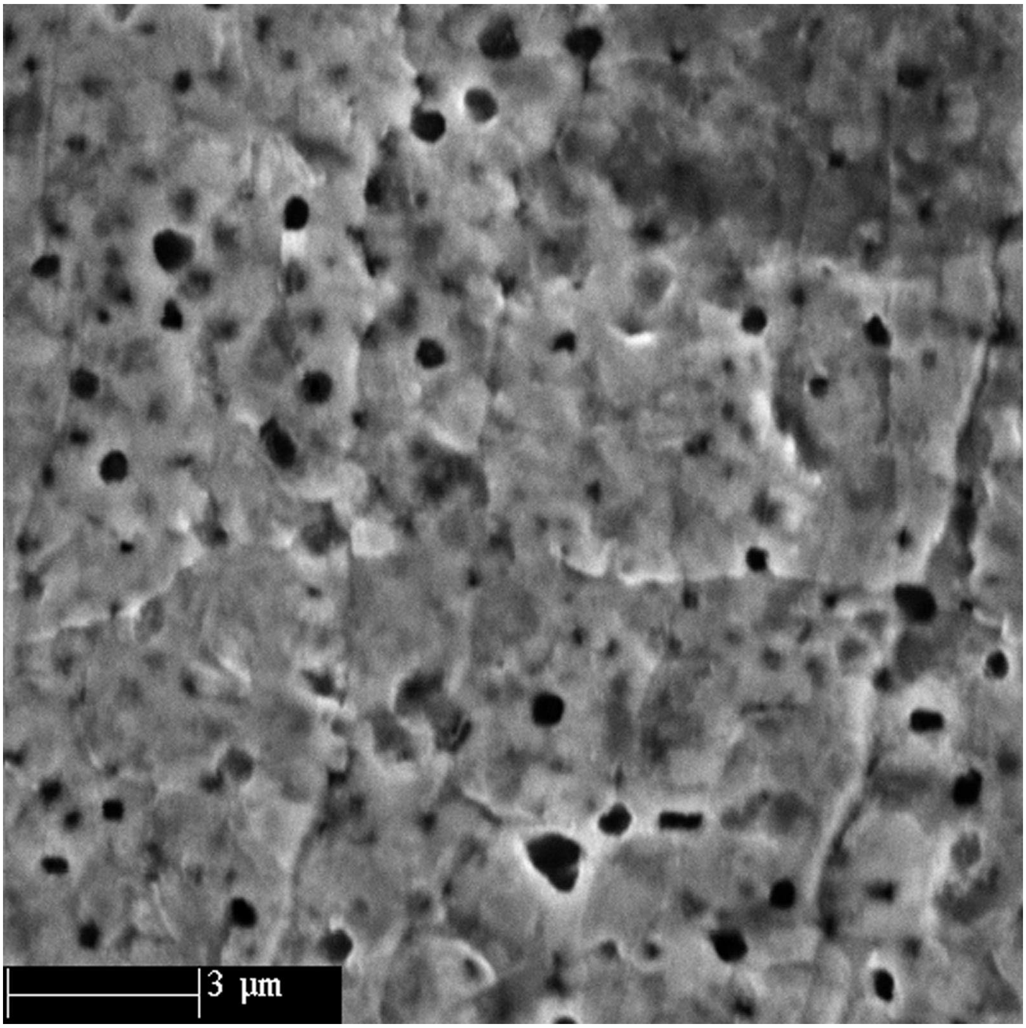

Fig. 3. SEM image of micrometric pores in $Pd_3(\square H_x)$.

structure with respect to that of the starting metal or the regular hydride.

Palladium absorbs hydrogen to form the superconducting hydride $PdH_{x<1}$. The local DOS at the Fermi level (mainly of d character) is strongly reduced upon bonding with hydrogen as an interstitial element. By analysing the various contributions to the chemical potential upon hydrogenation through hybridization, the differential character of d and s electrons could be distinguished in the Pd–H system.

We have performed band structure calculations in order to determine the electronic structures of Pd, PdH and $Pd_3(\square H_x)$. These calculations were carried out using the WIEN code in which the energy, the wave functions and the potential are evaluated self consistently using the full potential linearized augmented plane wave method (FLAPW) [9]. In these calculations, the space is divided into interstitial regions and non overlapping muffin-tin spheres centered at Pd and H sites where their radii are set to 2.0 and 1.32 a.u., respectively. Inside the atomic spheres a linear combination of radial functions times spherical harmonics is used, whereas the plane waves are used in the remaining space. This method is free of shape approximations to the charge density or the potential. Self consistency is assumed to be reached when the total energy difference between subsequent iteration steps is less than 0.1 mRy.

For palladium and its corresponding hydride, the electronic density profiles that have been previously determined by Papaconstantopoulos et al. [10] were reproduced. In addition the lowering of the DOS at the Fermi level (mainly due to the lowering of the d states) due to s–d hybridization was evidenced in PdH. A careful analysis of the charge transfers shows that the band charge of s character at the H site is strongly modified (0.6 electron), whereas that of the d band remains almost unchanged.

Calculation of the electronic density of the new vacancy phase $Pd_3(\square H_x)$ shows a recovery of the DOS at the Fermi level. This increase results mainly from a strong d contribution as shown in Fig. 4. The projected charges at

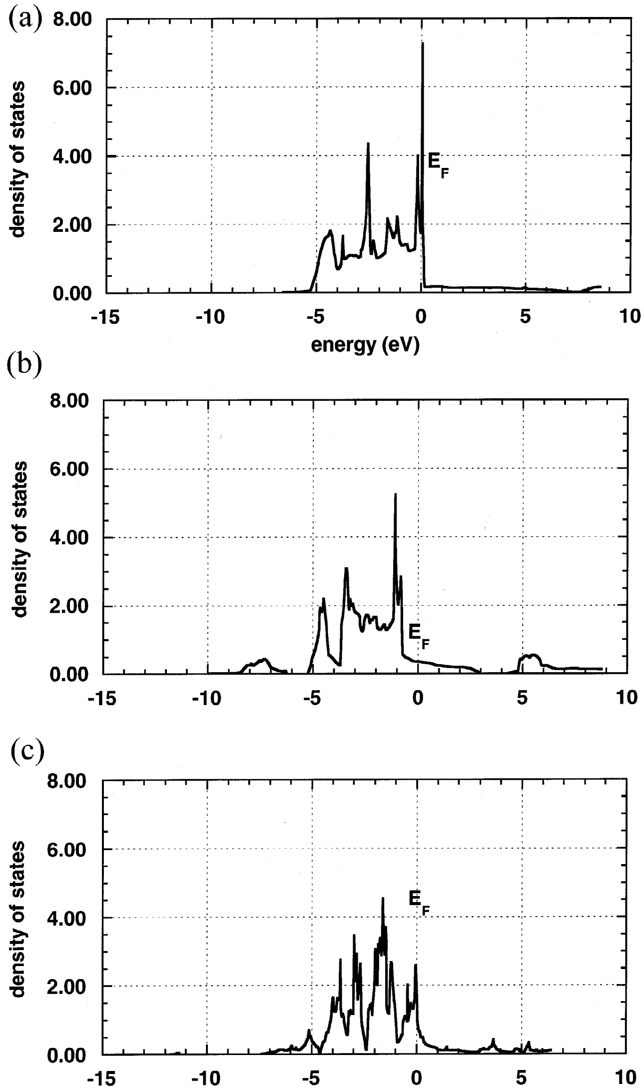

Fig. 4. Calculated total DOS of (a) Pd, (b) PdH and (c) $Pd_3(\square H_x)$ from top to bottom, respectively.

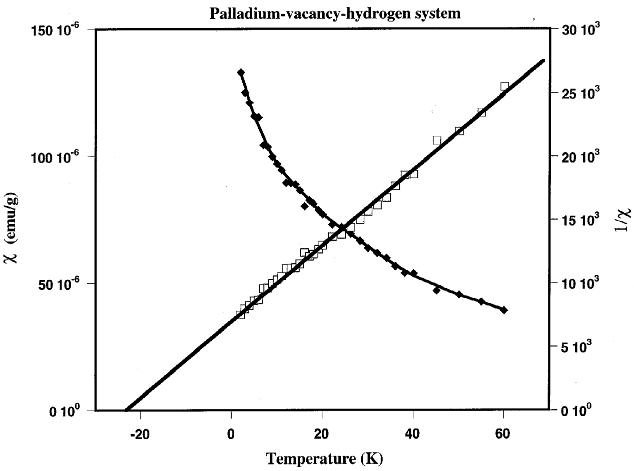

Fig. 5. Measured susceptibility of $Pd_3(\square H_x)$ and its reverse.

the various sites are comparable to those of the starting metal. Under these drastic changes the hydrogen-vacancy phase is no longer superconducting. This was confirmed by a susceptibility measurement in the temperature range between 1.6 and 60 K. It can be seen from Fig. 5 that the sample is no longer diamagnetic (i.e. superconducting), the inverse susceptibility of $Pd_3(\square H_x)$ is of Curie–Weiss type. A negative paramagnetic Curie temperature ($T_C = -22.5$ K) has been interpolated and from the slope of the inverse susceptibility curve we have derived the effective moment $\mu_{\mathrm{eff}} = 1.7\ \mu_B$/Pd atom.

It is worth noting that this new metallic arrangement behaves like a normal paramagnet. The bump-like susceptibility anomaly of palladium which was ascribed to exchange enhancement and accounted for by the spin fluctuation theory has vanished. The Pauli paramagnetic susceptibility for a metal is usually proportional to the DOS at the Fermi level; in addition it is generally temperature independent provided that the DOS is almost constant near the Fermi level in a small range of width kT. This is expressed in the formula:

$$X(T) = 2\bar{\mu}^{2} n(E_{\mathrm{F}})$$

where $\bar{\mu}$ is the effective moment. It has been deduced from the susceptibility curves of Pd [11] and $Pd_3(\square H_x)$, the values are 0.11 μ_B for Pd and 1.67 μ_B for $Pd_3(\square H_x)$. The values of susceptibility at low temperatures are $X(\mathrm{Pd}) = 10^{-6}$ emu g^{-1} and $X(Pd_3(\square H_x)) = 100 \times 10^{-6}$ emu g^{-1}. Note that for palladium, the susceptibility has been renormalized and the enhanced-exchange correction [12] has been removed. Then, the DOS at Fermi level for both compounds can be calculated and the ratio $[n_{\mathrm{Pd}}(E_{\mathrm{F}})]/[n_{\mathrm{Pd_3\Xi H_x}}(E_{\mathrm{F}})]$ can be estimated, it is found to be close to 2 and it is in excellent agreement with that computed from our band structure calculations.

5. Conclusion

High pressure hydrogen treatment of metals allows to modify the equilibrium phase diagrams and to stabilize new vacancy ordered phases whose physical properties are totally new compared to those of the starting metal or hydride. We have reported on the Pd–H system and shown that the new phase behaves like a Pauli paramagnet, which intermediate between the almost ferromagnetic (strongly exchange-enhanced paramagnet) starting metal Pd and the superconducting (diamagnetic) hydride PdH. The rough structural features of the vacancy ordered phase are understood, however the formation mechanism of the vacancies as well as their ordering process (local coordination) needs to be further investigated. In this respect in situ X-ray diffraction experiments under high pressure are planned.

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