

THE CRYSTAL STRUCTURES OF THE SYSTEM
PALLADIUM-HYDROGEN.

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ABSTRACT.

Crystal structures of the system palladium-hydrogen.—Palladium in the form of a fine wire, 1/4 mm diam., or of a narrow strip 1/20 mm thick, was more or less saturated with hydrogen and used to diffract x-rays of known wave-length as in the well-known powder method. Two crystal structures were present, both having a face-centered cubic arrangement of atoms. One, that of pure palladium, has a parameter 3.900×10^{-8} cm, while the other, that of hydrogen-saturated palladium, has a parameter varying between 4.000 and 4.039×10^{-8} cm, depending on the degree of saturation. A value near the upper limit, say 4.036×10^{-8} cm, probably corresponds to a *compound* Pd_2H , with a *density* of 10.76 gm/cm³. The arrangement of atoms may be as in Cu_2O , but there is no x-ray evidence for the positions of the hydrogen atoms. *Stability.* All the evidence so far obtained indicates that in the absence of sufficient free atomic hydrogen, the saturated state is unstable or metastable and that return to the hydrogen-free condition once initiated in any crystal proceeds rapidly to the end; also pure palladium is unstable in the presence of atomic hydrogen.

Occlusion of hydrogen by palladium.—A *necessary condition* is the presence of atomic hydrogen which may be supplied by electrolysis or by surface dissociation of hydrogen at high temperatures. The *penetration* into the wire was shown to be relatively slow; in the case of the strip it was somewhat irregular, probably depending on the orientation of the crystals. The crystal evidence provides an *explanation of the variations of electric resistance*. A *bibliography* of 66 titles, mostly 1900–1921, is appended.

THE effect of occluded hydrogen in increasing the electrical resistance of palladium has long been known to be, over a considerable range, a linear function of the amount of hydrogen taken up,¹ and in a study of the factors affecting electrical resistance it seemed of interest to find out, if possible, in what way the hydrogen entered and was held during the process. A direct and available method of attack was that of measuring the changes in crystal structure produced by the process of occlusion. The crystal structure of palladium was first determined by Hull² to be based on a face-centered cubic space-lattice. Metal of exceptional purity, samples of which had been analyzed by the same method in this laboratory,³ was available for the present research.

¹ W. E. McElfresh, Am. Acad., Proc., 30, 323–335 (1904).

² A. W. Hull, PHYS. REV. (2), 17, 571–588 (1917).

³ L. W. McKeehan, PHYS. REV. (2), 19, 537–538; 20, 424–432 (1922).

There appeared to be some confusion in the considerable literature of palladium-hydrogen systems,¹ as to the possible methods for obtaining high concentrations of hydrogen within the metal. The methods found effective in the present series of experiments furnish support to the theory of the process here advocated, and will therefore be discussed in connection therewith after description of the observed crystal structures.

The powder method of x-ray crystallography has been described so often that it will suffice to state here that the K-radiation of molybdenum, filtered through zirconium oxide,² was used, in which the two photographically important wave-lengths are 0.71212×10^{-8} cm and 0.70783×10^{-8} cm. The mean radius of the cylinder of photographic film was 20.36 cm. The palladium was either a wire 0.025 cm in diameter or a strip³ about 0.3 cm wide by 0.005 cm thick. The exposures used were of the order of 500 milliamperes-hours. In no case were the grains, even after prolonged annealing, large enough to give separately distinguishable diffraction spots,⁴ so that measurements were always made to the edges of smooth bands on the negative. Twenty or more such bands of the principal pattern present were almost always of sufficient intensity to permit their use in calculations, and the mean values of the parameters for the face-centered cubic space-lattices always observed are believed to be correct for each film to within one part in three hundred. Seventeen photographs were taken under various conditions.

There is a fairly well-defined limit in concentration of hydrogen below which the hydrogen is taken up with much greater facility, and the state reached at this limit may therefore with propriety be called the saturated state. If excess hydrogen be taken up the state can be described as supersaturated. With one exception, noted below, supersaturated states were probably not obtained. The method of examination, requiring as it does a relatively long time, is not well adapted to the study of conditions probably as transient as that of supersaturation at ordinary temperatures. Since the change in resistance follows a non-linear law above saturation, it was felt, also, that the lower range of concentration was of chief interest.

In the first experiment a thin strip of metal was, after preliminary annealing, examined first in air and then in a stream of commercial hydrogen, at atmospheric pressure. By what must now be regarded as a happy accident, the strip took up enough hydrogen to saturate it. The parameter of the face-centered cubic lattice of hydrogen-free pal-

¹ See appended bibliography.

² W. P. Davey, *Optical Soc. America, J.*, 5, 479-493 (1921).

³ L. W. McKeehan, *Frank. Inst., J.*, 193, 231-242 (1922).

⁴ L. W. McKeehan, *Frank. Inst., J.*, 194, 87-92 (1922).

ladium is¹ 3,900. The pattern here obtained with hydrogen-saturated metal was similar to that of pure palladium, the parameter however being 4.038, or 3.5 per cent greater. This preliminary result has already been reported.²

In later experiments with the same strip it was found that after expulsion of the hydrogen by heating, the crystal structure became that of pure palladium again, but an attempt to repeat the cycle failed. This was traced to sulphidation of the surface, the hydrogen used being not quite free from H₂S. Other strips showed very little occlusion of carefully purified gaseous hydrogen at room temperature, whether treated immediately after rolling down or after annealing for a few hours at around 800° C. The electrolytic process, however, in which the palladium is made the anode in a weak solution of sulphuric acid, never failed to introduce any desired amount of hydrogen up to saturation. Another process³ found efficacious was to heat the palladium in a vacuum furnace to about 1100° C for an hour or more, turn off the heating current, and admit gaseous hydrogen when the temperature of the furnace had dropped to about 700° C. This had the disadvantage, however, as compared with the electrolytic method, of not permitting partial saturation. The anomalous result of the first test is now ascribed to the hydrogen sulphide present in the gas which furnished enough atomic hydrogen at the surface during the formation of palladium sulphide to saturate the thin layer of metal underneath.⁴ Subsequent attempts failed because of the protecting coating formed by this process.

Wires and strips partially saturated by the electrolytic method gave diffraction patterns in which each line was doubled. The clear space between the lines of each pair shows that crystals of two definite sorts are present, there being few if any crystals with intermediate dimensions. The ratio of intensities varied widely depending upon conditions. In the case of wires about 0.025 cm in diameter, no unsaturated metal lay near enough to the surface to contribute to the photograph if the increase in total resistance amounted to more than 30 per cent, the increase at saturation being nearly 70 per cent. When the saturated surface of partially saturated wires was removed by aqua regia the diffraction pattern due to unaffected metal was relatively intensified, confirming the conclusion that the penetration of hydrogen into the metal is progressive. With partially saturated strips 0.005 cm

¹ In Ångstrom units; to reduce to centimeters multiply by 10⁻⁸.

² L. W. McKeehan, *PHYS. REV.* (2), 20, 82 (1922).

³ R. M. Holmes, *Science*, 56, 201-202 (1922).

⁴ Cf. E. B. Maxted, *Chem. Soc., J.*, 115, 1050-1055 (1919); 117, 1280-1288 (1920); 119, 1280-1284 (1921).

thick the distribution of saturated crystals over the surface of the strip was irregular, as shown by imperfection in the resulting patterns. It is probable that differently oriented crystals become saturated with different facilities.

The smaller parameter obtained from the double patterns showed about the degree of variation usual in crystallography of a pure metal¹ and was apparently to be ascribed to pure palladium, the range of values being from 3.889 to 3.906. The larger parameter showed a greater variability, ranging from 4.000 to 4.039, which corresponds to a range of 0.24 cm in the position of the line due to reflection from the (531) planes of the lattice, the last lines visible in faint patterns. This range is considerably more than the probable error in measurement. The intensity of reflection was never considerable, however, unless these crystals had parameters in excess of 4.010, and the values for the parameter obtained from intense photographs cluster in the range between 4.023 and 4.039, indicating the existence of a true limiting value somewhere in this range; the value 4.036 is preferred.

An attempt was made to reduce the parameter of saturated crystals by heating them for a short time at 200° C, which treatment reduced the excess resistance in a particular case from 75 per cent, corresponding to slight supersaturation, to 30 per cent. Before heating, the single parameter apparently present was 4.038; after heating the two values 4.025 and 3.900 were obtained, the intensities being roughly the same for the two patterns. Judging by the greater breadth of the lines in the second experiment as compared with those usually observed, the crystals of both sorts were either very small or were badly strained.

An attempt has been made to find places for the hydrogen atoms in the saturated crystals which would at the same time satisfy the observed cubic symmetry and the formula Pd₂H proposed by earlier investigators for a supposed hydride. The process of occlusion would on this basis be analogous to the volume oxidation of calcium crystals, where the introduction of the oxygen atoms actually pulls the metal atoms closer together,² and where the process stops definitely at the composition CaO. The low atomic weight of hydrogen makes any such hypothesis regarding its arrangement purely speculative since the proposed structure cannot be checked by intensity measurements. The arrangement already familiar in Cu₂O and Ag₂O is suitable, and, nothing being known about the crystallographic properties of the hypothetical Pd₂H except the facts here recorded, cannot be contradicted. This would place the hydrogen atoms on a body-centered cubic lattice with the same parameter as that

¹ L. W. McKeehan, *PHYS. REV.* (2), 19, 537-538; 20, 424-432 (1922).

² A. W. Hull, *PHYS. REV.* (2), 17, 42-44 (1921).

here found for the face-centered cubic lattice of palladium atoms, the points of the former lying symmetrically on the trigonal axes (cube body-diagonals) of the latter. This is expressed more formally by stating that palladium atoms occupy the points $(0, 0, 0)$, $(0, a/2, a/2)$, $(a/2, 0, a/2)$, $(a/2, a/2, 0)$ and hydrogen atoms the points $(a/4, a/4, a/4)$, $(3a/4, 3a/4, 3a/4)$, where $a = 4.036$ is the parameter of a simple cubic lattice. The density of the compound Pd_2H would then be 10.76 gm/cm^3 , that of Pd being¹ 11.87 gm/cm^3 . Another possibility is to put both of the two hydrogen atoms absorbed by each face-centered cube of palladium atoms at the centers of opposite faces of one of the eight smaller cubes into which it can be divided. This preserves the identity of the hydrogen molecule as the other arrangement does not, but is less symmetrical, requiring a unit of structure containing 108 palladium atoms and 54 hydrogen atoms to attain cubic symmetry, and is therefore improbable. The variability in the parameter of saturated crystals is against the idea of a definite compound being formed in every case. It is probably only the limit which is approached more or less closely, depending upon the temperature and other factors determining the equilibrium condition.

CONCLUSION.

The phenomena here observed seem consistent with the following physical assumptions, some of which have been previously made by others:²

1. Palladium and hydrogen are not miscible in all proportions at ordinary temperatures and pressures. Two crystalline phases can coexist, one being practically pure palladium, the other a saturated solution of hydrogen in palladium.
2. The amount of hydrogen in a saturated crystal of palladium, and the distention of the crystal space-lattice thereby, decrease with increase in temperature and with reduction in pressure of dissociated hydrogen in the neighboring space.
3. Unsaturated crystals in conditions favorable to saturation become saturated very rapidly because the introduction of any hydrogen atoms into the interatomic spaces so strains the space-lattice that the entrance of additional hydrogen atoms is facilitated.
4. Saturated crystals are in unstable or metastable equilibrium in air and lose hydrogen by diffusion at a rate which is accelerated by heating. Desaturation once started in any crystal proceeds rapidly to the end because of the intense local strains set up by the removal of a few hydrogen atoms.

¹L. W. McKeehan, *PHYS. REV.* (2), 19, 537-538; 20, 424-432 (1922).

²See appended bibliography.

5. An unsaturated crystal lying too deeply below a surface exposed to atomic hydrogen at ordinary temperatures is unaffected until a considerable part of its bounding surface is covered by saturated crystals, because hydrogen can reach it through neighboring crystals or through intercrystalline amorphous metal by slow diffusion only, and it therefore becomes exposed to hydrogen in quantity only by the opening of pores by expansion of the overlying crystals.

6. The linear resistance-change throughout the greater part of the range of occlusion is due to the varying proportions of the two sorts of crystals which, in consequence of (3) and (4), are the principal constituents of the system. This type of resistance-change is, in fact, a criterion for alloys which are mechanical mixtures of two phases.

7. The small initial rise in resistance and the final slow approach to a limiting value are due to changes in the resistance of intercrystalline material or to defects in intercrystalline contact, or to both.

8. The temporary change in resistance observed when the process of saturation is interrupted¹ is due to the transient presence of partially saturated crystals, the whole mixture simulating the condition of a uniformly dispersed solid solution.

9. Occlusion requires the presence of atomic hydrogen, which may be supplied either by electrolysis at ordinary temperatures or by surface dissociation of gaseous hydrogen at high temperatures.

The appended bibliography may be of service in coördinating the experimental studies in this field in the light of the new crystallographic data.

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