91. *Single-crystal Palladium Films and their Interaction with Gases.*

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The lattice constant of palladium leaf was referred by electron diffraction to $a = 2{\cdot}456$ A. for graphite, and found to be $3{\cdot}894 \pm 0{\cdot}005$ A. (by *X*-rays, $3{\cdot}882$ A.). Evaporation of palladium on to rocksalt cleavage surfaces between 350° and 450° gave specimens with the [100] axis of the palladium parallel to the [110] axis of the rocksalt, a second axis of orientation occurring simultaneously in most cases, resulting in " single-crystal " specimens. Above 450° the palladium oriented itself with its planes parallel to the similar planes of the substrate. A tentative explanation is advanced for these orientations.

Heat treatment in a vacuum at temperatures up to 800° caused no change in the diffraction patterns. Oxidation at 600° gave palladous oxide with its [210] axis parallel to the [110] axis of the metal, but specimens partly oxidised and then annealed had the (100) and (001) faces of the former parallel to the (110) and (001) faces respectively of the latter. The oxide was tetragonal with $a = 3{\cdot}05$ A. and $c = 5{\cdot}28$ A. Heat treatment of palladium or platinum in pure hydrogen or ammonia above 500° caused the 100 and 110 diffractions to appear; this is ascribed to the replacement of metal atoms by hydrogen ions at statistically distributed points of the lattice.

Electron diffraction is recognised as a powerful instrument in the study of interactions between solids and gases. In most investigations utilising it, the film or surface has been either amorphous or composed of a random arrangement of microcrystals, with the result that the diffraction patterns do not always afford a unique solution of the problems of relative orientation. This disadvantage, however, can largely be overcome by the use of highly oriented films or single-crystal specimens. Of the metals, possibly the most interesting is palladium on account of the considerable interest attached to the palladium–hydrogen system. The prepartion of " single-crystal " films of palladium by the method of Lassen (*Physikal. Z.*, 1934, **35**, 172) and Brück (*Ann. Physik*, 1936, **26**, 233) has been studied, and also the effects on the metal of heat treatment in vacuum, oxygen, and hydrogen.

EXPERIMENTAL.

The electron-diffraction experiments were carried out in two cameras of the Finch type (Finch and Wilman, *Ergebn. exakt. Naturwiss.*, 1937, **16**, 353) evacuated by oil-vapour diffusion pumps. Preliminary experiments showed that a rotary oil pump did not prevent all traces of oxidation during heating, so an electrically-heated silica-tube vacuum furnace was constructed, incorporating a mercury-vapour diffusion pump together with a tin-foil trap to minimise diffusion of mercury vapour to the specimen. A similar furnace, but without a diffusion pump, was employed for heating in oxygen, the gas being supplied from a cylinder. Heating experiments could also be carried out in a furnace attached to a port of one of the diffraction cameras. The specimens were supported in this furnace on a silica grid which could be drawn by fine platinum wires along two silica rails extending across the body of the diffraction camera and throughout the length of the silica-tube furnace. Specimens could be lifted from the silica grid, and adjusted with reference to the electron beam with the aid of a special specimen carrier attached to another port of the diffraction camera. The specimens could therefore be examined after heat treatment in vacuum or in a gas without being brought into contact with the atmosphere. Temperatures were measured by means of a platinum–platinum-rhodium thermocouple inside the silica tube. This furnace, in view of its large volume, was not used for the heat treatment of specimens in pure hydrogen. For this purpose separate apparatus was constructed without rubber connecting tubing, although a rubber bung connection to the silica furnace tube was necessary; this bung was cleaned in boiling 10% potassium hydroxide solution and washed with boiling water, and precautions were taken to keep it completely cold when the furnace was hot. Pure hydrogen, generated by electrolysis of dilute baryta solution, was cleansed and dried by passage over solid potassium hydroxide and phosphoric oxide. All stopcocks were lubricated with Apiezon "M" grease. Temperatures were measured with sufficient accuracy with platinum–platinum-rhodium thermocouples placed outside the silica furnace tubes.

Palladium was used as leaf (at least 99·9%) or wire (99%), and precautions were taken to prevent contamination during the experiments. Trillat and Oketani (*Compt. rend.*, 1936, **203**, 1064) found that the support used affected the results obtained during the heat treatment of gold, and our preliminary experiments showed that palladium alloyed readily with nickel or platinum supports at temperatures exceeding 200° to give specimens yielding widely varying diffraction patterns which could not be correlated with the known structures of the bulk alloys. For this reason the palladium films were invariably supported on mica or rocksalt, or on palladium gauze, being earthed when necessary with a fine platinum wire.

Since mercury was present in the laboratory atmosphere, attempts were made to amalgamate palladium supported on mica, but no trace of amalgamation could be observed even after prolonged treatment either electrolytically or by exposure to mercury vapour. It was shown that the amalgamation previously reported (Aylmer, Finch, and Fordham, *Trans. Faraday Soc.*, 1936, **32**, 864) was a consequence of alloying with the nickel supports during exposure to the hot mercury vapour. Attempts to amalgamate palladium which had been heated in hydrogen or partly oxidised in oxygen also failed completely.

Palladium was also heated in atmospheres containing sulphur, and although the complicated diffraction patterns obtained could not be analysed satisfactorily, they sufficed to show that none of the results described below could be ascribed to the presence of sulphur fumes from grease or rubber in the apparatus.

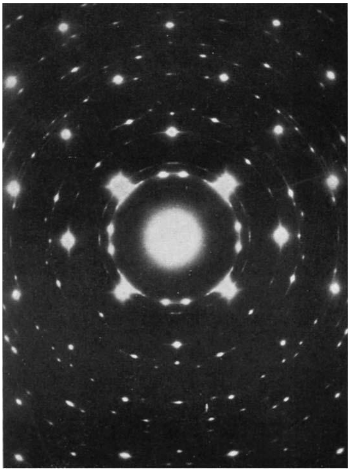
Preparation of Palladium Films.—The palladium films were prepared either from the leaf or by evaporation on to the cleavage face of rocksalt. In the former case dilute (50%) nitric acid was used for thinning, and the specimens gave normal face-centred cubic patterns composed of arcs, together with a faint band just inside the 111 diffraction. This band was attributed to oxygen from the nitric acid, since it could be removed by heating the thinned leaf in hydrogen, or avoided altogether by etching electrolytically on a chloride solution. The lattice constant of the palladium was determined with reference to gold with double shutter and superimposed patterns; on the assumption that *a* for graphite is 2·456 A. (Trzebiatowski, *Rocz. Chem.*, 1937, **17**, 73), that for palladium was 3·894 ± 0·005 A., compared with 3·882 A. obtained for the bulk metal by *X*-rays (Owen and Jones, *Proc. Physical Soc.*, 1937, **49**, 587). The origin of such discrepancies has been discussed by Finch and Fordham (*ibid.*, 1936, **48**, 85; see also Finch and Wilman, *loc. cit.*).

Transmission specimens which gave spot patterns due to palladium in cube-face orientation could be obtained by slow evaporation in a vacuum of metal from an electrically heated palladium-wire filament on to the freshly cleaved surface of a hot rocksalt crystal. The rocksalt was dissolved in water, and the metal film supported on rolled, fine-mesh wire gauze in such a manner that the directions in the palladium film parallel to the cube edges of the rocksalt were parallel to the edges of the photographic plate; thus the relative orientation of the metal and substrate could be determined. For the purpose of the present experiments these evaporated films are equivalent to single crystals and may conveniently be called such, although they are composed of a large number of small crystals in almost perfect alignment. Brück (*loc. cit.*) has stated that orientation of palladium on rocksalt occurs at temperatures exceeding 90°, but in our experiments below 350° orientation was confined to a preferential setting of the [111] axes of the crystals perpendicular to the rocksalt surface. Above 350°, spots appeared on the diffraction rings, indicating that the palladium was orienting itself with respect to the substrate lattice. Two types of orientation were observed, in both of which the (001) face of the metal was parallel to the (001) face of the rocksalt; they are referred to as types A and B, in which the [100] and the [110] axes, respectively, of the metal were parallel to the [110] axis of the rocksalt, the latter being the orientation usually observed during the evaporation of face-centred cubic metals on to heated rocksalt cleavage surfaces. At 450°, the palladium was almost entirely oriented according to type A, the resulting pattern (Fig. 1) consisting mainly of spots, the rings now being only faint. Above 450°, type B orientation began to displace type A, this displacement being complete at 550° (Fig. 2). Above 550°, the surface of the rocksalt crystals began to break up, and this effect was sufficiently marked even at lower temperatures to make it impossible to secure satisfactory reflection patterns of the evaporated palladium before solution of the substrate. It is significant that, in those specimens of type A in which the orientation was not perfect, the disorientation took the form of a rotation about the [100] axis of the palladium. Thus at 450° the primary tendency is for the metal [100] axis to lie parallel to the rocksalt [110] axis; similarly there must be a tendency for the [010] and [$\bar{1}$10] axes of the metal and rocksalt respectively to be parallel, and if both conditions are fulfilled simultaneously the observed cube-face orientation results. Such disorientation was not observed with specimens showing type B orientation.

A partial and tentative explanation of the two types of orientation is as follows. If a palladium film is evaporated on to cold rocksalt, and the substrate and film are then heated together to 550°, the resulting specimen shows no sign of orientation of either type A or B. It is clear, therefore, that the substrate can exert an orienting effect only on the nuclei or at the most on the very small crystals which later grow into the larger crystals of the final specimen. It is suggested that the smallest crystals are most stable in orientation A, whereas slightly larger but still extremely small crystals, relatively more mobile at higher temperatures, are more stable in orientation B. As may be seen from Fig. 3, a fair correspondence between the metal and substrate lattices may be found for small crystals in orientation A, whereas for orientation B no such correspondence is possible. Whatever their initial electronic state, the palladium atoms will tend to occupy above the unit cells of the rocksalt lattice those positions in which their potential energies are least; such positions must have a periodicity similar to that of the rocksalt surface, and therefore, by completion of the metal lattice, type A orientation is obtained. In particular, positively charged palladium ions will tend to form rows above the negative chloride ions of the rocksalt lattice; these rows will be parallel to the [110] axis of the rocksalt lattice and will have a unit translation corresponding to the [100] rows of the metal lattice. In this way crystals may form with only one direction of orientation. With type A orientation however, the ionic attractive and repulsive forces between a complete crystal and the substrate must approximately cancel, and the potential energy of such a crystal may be greater than that of a crystal in orientation B, for which, as shown in Fig. 3, positions may be found for small crystals in which the positively charged palladium ions occur more frequently near the negatively charged chloride ions than near the sodium ions. On this view type A orientation only occurs because below 450° there is not sufficient relative thermal agitation between crystal and substrate to permit displacement of the palladium atoms from their initial positions of least energy, probably above the chloride ions.

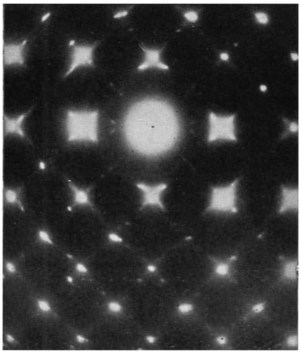
Comparison of the streaks and extra diffractions of Figs. 1 and 2 is interesting. Von Laue (*Ann. Physik*, **1936**, **26**, 55; **1937**, **29**, 211) has suggested an explanation of such effects in terms of the developed forms of the crystals, and if allowance is made for the distortion produced in the specimens on solution of the substrates, the theory explains many of the facts observed in our experiments. Nevertheless, according to the theory, the two patterns should be completely

FIG. 1.



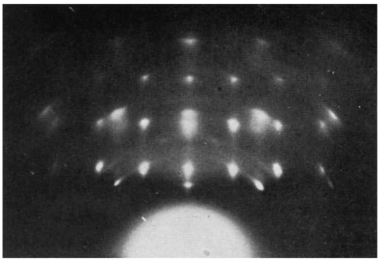
Pd *on* NaCl *at* 450°.

FIG. 2.



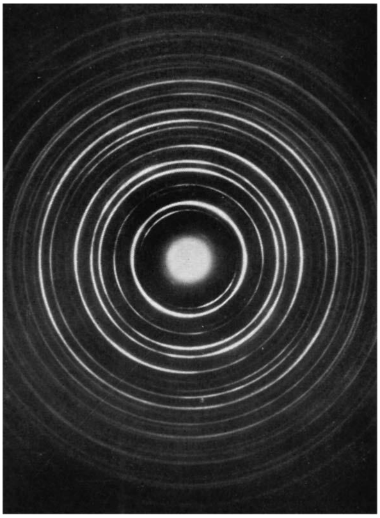
Pd *on* NaCl *at* 550°.

FIG. 4.



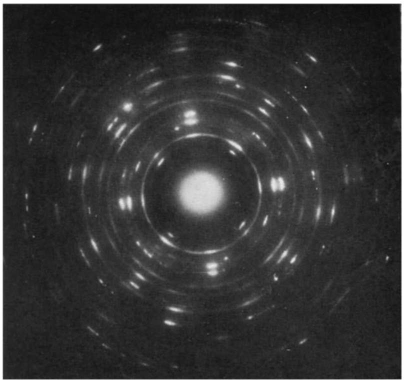
Pd *on* KBr.

FIG. 5.



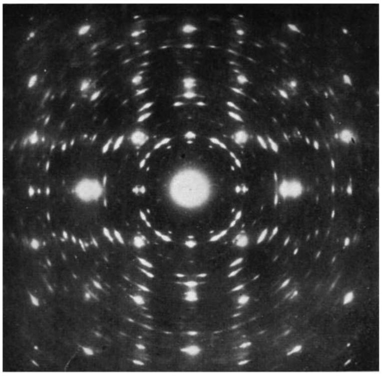
Palladous oxide.

FIG. 6.



Oxidised Pd *annealed.*

FIG. 7.



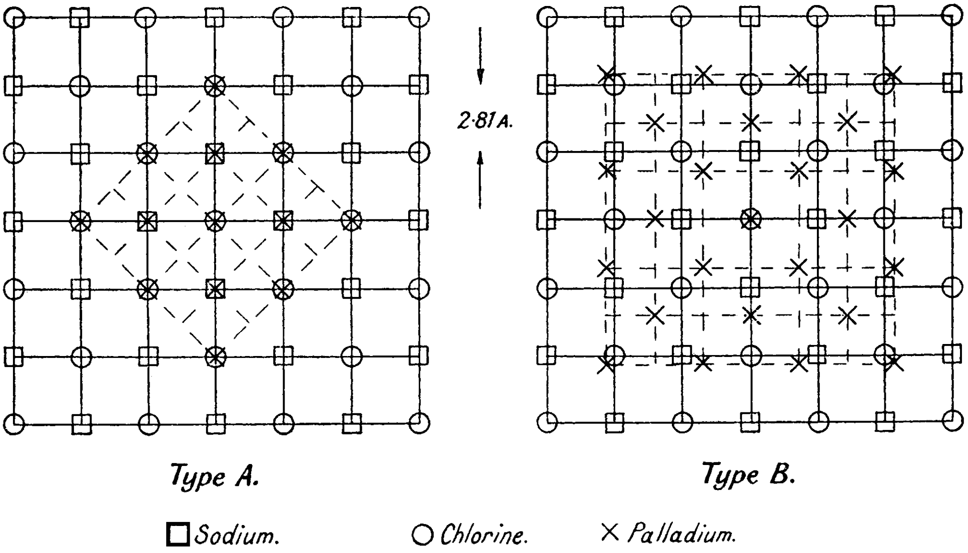
Oxidised Pd " *single crystal.*"

[*To face p.* 408.

equivalent, whereas in fact many slight but significant differences may be found between them. The most obvious difference lies in the streaks extending inwards from the 220 diffractions; in type B orientation the streak is a single radial line, but in the original negative of Fig. 1 (type A orientation) the streak is divided into two curved lines forming an arrowhead pointing outwards. It would seem that the streaks in these photographs cannot be explained entirely by the external shape of the metal crystals, which is probably similar in the two cases; nor does it seem possible to explain the differences in terms of crystal twinning which, as Cochrane (*Proc. Physical Soc.*, 1936, **47**, 723) and Menzer (*Z. Krist.*, 1938, **99**, 410) have shown, may lead to extra diffractions.

It was also possible to prepare single-crystal palladium specimens by evaporation on to the cleavage faces of heated sylvine; the orientation was always of type B, and the transmission patterns were similar to Fig. 2. Reflection patterns similar to Fig. 4 could be obtained in this case, and showed that (001) faces were developed on the outer surfaces of the metal crystals to give diffraction streaks perpendicular to the shadow edge on the photograph. The crystals therefore consisted of truncated pyramids with faces of the (100) and (111) forms.

FIG. 3.



Heat Treatment in Oxygen.—Etched leaf and evaporated palladium specimens could be heated in vacuum up to 800° without change in the electron-diffraction patterns; hence, all changes observed after heat treatment in gases must be ascribed to gas absorption or chemical combination.

Palladium leaf was heated in oxygen or air at 600° for 15 minutes, and the excess metal then dissolved in aqua regia. The resulting palladous oxide gave a pattern (Fig. 5), analysed in the table and agreeing with the tetragonal structure suggested by Levi and Fontana (*Gazzetta*,

Intensity.	Spacing, A.	Origin.	*X*-Ray intensity. L. & F.	Z.
m	5·36	001	—	—
vs	3·04	100	—	—
vvs	2·645	101 002	32·5	5
ms	2·165	110	13·5	1·25
s	2·01	102 111	—	—
vs	1·675	112	29	3
vs	1·535	200 103	24·2	4
f	1·475	201	—	—
fm	1·365	120 113	—	—
f	1·335	121	37·5	3·5
vs	1·32	004 202		
m	1·22	122 104	—	—
f	1·16	203	—	—
ms	1·135	114	14·0	0·75
s	1·08	220 123	24·0	2
s	1·005	204 222 105 301	30	3·5
m	0·96	310	15	1

1936, 56, 388) and by Zachariasen (*Z. physikal. Chem.*, **1927, 128,** 412), with $a = 2{\cdot}99$ and $c = 5{\cdot}20$ A. by *X*-rays, the mean lattice constants found by electron diffraction being $a = 3{\cdot}05$ and $c = 5{\cdot}28$ A., referred to palladium with $a = 3{\cdot}894$ A. The intensities of the *X*-ray diffractions in Debye–Scherrer photographs according to the above authors are reproduced in cols. 4 and 5, and it will be seen that there is but poor agreement between these and the electron-diffraction intensities. No explanation can be given for the presence in the electron-diffraction patterns of rings not observed with *X*-rays.

Etched palladium leaf was partly oxidised in oxygen at 500° and then annealed in vacuum at the same temperature. During annealing, considerable orientation took place, and the resulting pattern (Fig. 6) showed that the palladium and the palladous oxide each had their (001) planes parallel to the specimen plane, their (100) and (110) planes respectively also being parallel. This, however, probably represents the orientation of palladium on a palladous oxide support rather than the initial orientation of the oxide on the metal lattice.

A single-crystal palladium film, heated in a vacuum to 600° and oxidised at this temperature with air or oxygen, gave a pattern (Fig. 7) which showed that the palladous oxide was strongly oriented. The spots of this pattern are due partly to electrons diffracted by unoxidised excess palladium, partly to those diffracted by palladous oxide, and partly to those diffracted by each substance in turn; the origins of the diffractions may readily be deduced from the radial distances.

The spots of the palladous oxide pattern could be divided into two groups; in different patterns the relative intensities of the spots in each group remained substantially constant, but in one pattern one group almost entirely disappeared. The former group consisted of *hk*0 spots and indicated the existence of oxide in the orientation described above. The latter group consisted of many spots of (*hkl*) planes and could not be attributed to any single-crystal orientation. Moreover, when the specimen was tilted about the palladium [110] axis these spots lengthened into arcs and finally into rings; thus the oxide must have had an axis of orientation, not at right angles to the specimen plane, but probably parallel to the [110] axis of the palladium.

Since the diffraction pattern must be symmetrical about the projection of the axis of orientation on the plate, the latter must coincide with either the [100] or the [110] axis of the palladium. Moreover, the angle ϕ between this direction and the radius to the *hkl* diffraction on the plate is given, since the Bragg angle is small, by

$$\cos\phi = \frac{1}{\sin\beta}\cdot\frac{d_{hkl}(uh + vk + wl)}{\sqrt{\Sigma u^2a^2 + 2\Sigma uvab\cos\gamma}}$$

where [*uvw*] is the axis of orientation, which makes an angle β with the incident electron beam. This equation was solved for v/u, w/u, and β by measuring ϕ for the 100, 110, and 001 diffractions. Since it was not possible to distinguish between ϕ and $90° - \phi$, or between the 110 and $1\bar{1}0$ diffractions, four independent solutions were obtained, and for each of these the positions of the diffractions of the (111) form were calculated. The only solution affording values of ϕ agreeing with those observed was $v/u = 0{\cdot}509$, $w/u = 0$, $\beta = 87°$. This is equivalent, within the experimental error, to an orientation with the [210] axis of the palladous oxide parallel to the [110] axis of the palladium. The calculated and the observed values of ϕ for the innermost diffractions are given below :

Diffraction	100	010	001	110	$1\bar{1}0$	101	011	111	$1\bar{1}1$
ϕ, calc.	26·5°	63·5°	90°	18·5°	71·5°	39°	67°	28·5°	73°
ϕ, obs.	27	63	90	18	72	39·5	63·5	27	72·5

The palladium spots in these patterns showed that the metal was completely oriented according to type A; this could be checked by examination before oxidation, but this procedure led to a slight disorientation of the palladium, since several changes of support had to be made. The occurrence of only one axis of orientation in the palladous oxide could not be attributed to disorientation of the palladium, since the axis of orientation was parallel to the [110] and not to the [100] axis of the metal. Moreover, no explanation seems possible in terms of crystal twinning. By analogy with the orientation of palladium on rocksalt it would be expected that complete orientation should be observed at higher temperatures; at such temperatures, however, not only did the rocksalt supports decrepitate, but also palladous oxide itself became unstable.

It is difficult to account for the observed orientations on a basis of lattice distances. For instance, in the former type of orientation the lattice constants of the oxide, 3·05 and 5·28 A., bear no relation to the side of the unit cube of the palladium lattice, 3·894 A., or to its face diagonal, 2·754 A.; nor can a significant lattice relationship be found for the latter type of orientation. By analogy with type A orientation of palladium on sodium chloride, it would be anticipated that important rows of oxygen atoms would be parallel to the [210] axis of the palladous oxide lattice. It is not possible to confirm this, since the positions of the oxygen atoms in the palladous oxide lattice have not yet been determined.

No intermediate stages in the oxidation process could be detected apart from the band observed with specimens etched with nitric acid. Comparison with gold of the lattice constant of palladium heated in oxygen or hydrogen showed, as would be expected, that in neither case was sufficient gas held in solution after evacuation in the electron-diffraction camera to cause a detectable expansion (0·01 A.) of the metal lattice.

Heat Treatment in Hydrogen.—*X*-Ray work (Owen and Jones, *loc. cit.*) has shown that the palladium–hydrogen system consists of two face-centred cubic phases with parameters varying according to the hydrogen concentration. Electron diffraction cannot be used to study such reversible absorption, since the specimens must be examined in a vacuum, but it can be used to study the manner of retention of the hydrogen irreversibly absorbed even at very low pressures.

If a well-oriented palladium specimen is heated to above 500° in 1 atm. of hydrogen, faint arcs appear, corresponding to the forbidden 100 and 110 diffractions of palladium, but these disappear if the specimen is heated to 600° in a vacuum. With single-crystal specimens this process also caused the streaks and extra diffractions to disappear, a fact which indicates that recrystallisation had taken place, presumably as a result of a temporary conversion into the α_2-phase. Owen and Jones (*loc. cit.*) have shown that palladium is left in a state of considerable strain after desorption of hydrogen, but the extra diffractions could not be attributed to this cause, since they were absent from patterns obtained after the hydrogenised specimens had been floated for a few minutes on a solution of hydrogen peroxide; nor could they have been due to repeated diffraction, since for palladium the reciprocal lattice bears the same aspect from all lattice points. They must therefore have been caused by absorbed hydrogen.

On account of its low atomic number, hydrogen as such can exert no appreciable influence on the diffraction patterns from palladium specimens, and the extra diffractions must indicate some change in the metal lattice itself. The most likely explanation is that palladium atoms are absent from statistically distributed points of the lattice and are replaced by ionised hydrogen, in a manner analogous to the formation, by electrons, of *F*-centres in alkali halide crystals; in this way faint 100 and 110 diffractions would be produced. The extent of the atom replacement cannot be deduced from the observed intensities, since these are affected by repeated diffraction. It is, however, not suggested that all the hydrogen retained by palladium at low pressures is held in this manner; its mobility suggests that much of it is held in solution between the atoms of the normal metal lattice, but such dissolved hydrogen could have no appreciable effect on the electron-diffraction patterns.

Similar results have been obtained with platinum, and also with palladium and platinum heated in gaseous ammonia; in the latter case the ammonia is doubtless catalytically decomposed by the metal. In these two metals, at least, it would seem to be possible for protons to replace metal ions in the lattice to some extent. It would be interesting to discover to what extent the process may occur with other metals.

DISCUSSION.

The causes of the mutual orientation of crystals at high temperatures are but imperfectly understood. Royer and others have shown that orientation at low temperatures during deposition from solution calls for agreement between the lattice parameters of the crystals involved to within 15%, and the results described above would seem to indicate that at high temperatures similar causes lead to parallelism between definite axes of the crystals. In general, however, orientation at high temperatures is not of this type. Preston and Bircumshaw (*Phil. Mag.*, 1936, **21**, 713) have suggested that at high temperatures oxides grow on metal surfaces with their most densely packed plane in contact with the metal, but such a rule seems to be of limited application. Finch (J., 1938, 1137) has suggested that equality in the angles between important lattice rows in the deposit and substrate, and not similarity in lattice dimensions, is the governing influence in orientation, and this rule seems to be obeyed when orientation is complete. For cubic lattices, however, it is possible to find many positions which agree with this rule, and it is not always clear which is to be preferred. Energy considerations, such as those discussed above, offer a means of approach to this problem, and are implicit in the arguments of Brück and of Menzer (*locc. cit.*) to explain the orientations of metals on rocksalt cleavage surfaces. Following the latter author, atomic radii may be used for estimating the forces between metal and substrate atoms, but in the actual calculation difficulty arises in the choice of suitable radii. For instance, for type B orientation of palladium on rocksalt, if the radii of the palladous and the chloride ions are taken as 0·50 and 1·80 A., respectively, the separation of the cube faces of the palladium and the rocksalt lattices may be assumed to be 2·30 A. Then, from Fig. 3, the nearest approach of palladium and sodium is 2·46 A., which is less than the interatomic distance to be expected in an alloy of these metals, where the sum of the radii of the atoms, 1·37 and 1·86 A. respectively, is 3·23 A. The objection to such an argument is that it is assumed that the palladium and sodium have definite electronic states which differ according to the nature of their nearest neighbours. Although mutual influence between atoms must occur, it is unlikely that it can be expressed adequately by choice of atomic radii as above. In fact, in view of the complicated nature of such surface interactions, it does not seem possible to form a quantitative estimate of the potential energies of metal crystals on rocksalt surfaces, and more experimental data are necessary before a satisfactory theory of orientation can be formed.

The authors wish to thank Prof. G. I. Finch for his interest and advice throughout this work. They are indebted to the Mond Nickel Co. Ltd. for the gift of exceptionally pure palladium leaf, and one of them (S. F.) to the Department of Scientific and Industrial Research for a grant which enabled him to carry out this work.

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[*Received, December 14th,* 1938.]