Chemistry. — *On the Allotropism of Rhodium and on Some Phenomena observed in the X-ray-Analysis of heated Metal-Wires.* By F. M. JAEGER and J. E. ZANSTRA.

(Communicated at the meeting of January 31, 1931).

§ 1. In a previous and the next paper [1]) it has been demonstrated, that the c_p—t-curves for *palladium* at about 1530° C. and for *rhodium* somewhere in the neighbourhood of 1200° C., doubtlessly show a *maximum,* which in the case of *rhodium* is even a very steep one. In connection with an apparent change of volume observed at temperatures exceeding 1200° C., in the crucible containing the *rhodium,* suspicion arose, that under these circumstances some structural change of the enclosed metal had taken place. The following experiments were, in both cases, executed with the purpose of elucidating these phenomena observed by means of an elaborated *X*-ray-analysis. In the course of these investigations, we met, however, with some particular phenomena, and, therefore, we extended our experiments, including also *platinum* within this series. In the present paper a review is given of the results obtained during these studies.

In the case of the metals mentioned it hitherto appeared impossible to state the occurrence of a transition-temperature ; all their physical properties in their dependance on the temperature rather seem to vary in a perfectly *continuous* way. Neither is there in literature, — for instance in the case of *rhodium,* — any indication to be found of an abrupt change in the behaviour of this metal: thus, HOLBORN and WIEN, WAIDNER and BURGESS, DAY and SOSMAN [2]) and many other investigators working with *rhodium* and its alloys, — they all found a *continuous* change of its physical properties with the temperature. We, in our previous paper, were able to state the same fact, although some peculiarities in the shape of the curves representing the change of the temperature-coefficient of the electrical resistance (turning-point between 1100° and 1200° C.) doubtlessly seem to indicate, that some change in the internal structure of the metal occurs. In the case of *palladium* and *platinum,* however, even these indications proved to be absent, and also *X*-ray-analysis failed to prove

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[1]) F. M. JAEGER and E. ROSENBOHM, Proceed. R. Acad. of Sciences Amsterdam, **33**, (1930), p. 457; **34**, (1931), p. 85.

[2]) L. HOLBORN and W. WIEN, Ann. d. Phys., **47**, (1892), 107; G. WAIDNER and K. BURGESS, Bull. Bur. of Standards, **3**, (1907), 200; A. L. DAY and R. B. SOSMAN, CARNEGIE-Publ. **157**, Washington, (1911), 120; A. L. DAY and L. HOLBORN, Ann. der Phys., **2**, (1900), 522; Amer. Journ. of Science, (4), **8**, (1899), 303.

the existence of other modifications of these metals. Notwithstanding this, on heating, they showed the same phenomena as those first stated in the case of *rhodium*.

§ 2. *Rhodium.*

If finely divided metallic *rhodium*, such as it may be obtained by the reduction of its salts in alkaline solution by means of hydrazine-hydrate, etc., is, without previous heating, examined by means of *X*-rays after DEBIJE-HULL's method, powderspectrograms are obtained, the diffraction-lines of which are very broad and hazy, reminding those of colloidal substances. At first sight they seem to be in agreement with the presence of a face-centred cubic lattice, the parameter a_0 of it having somewhat variable values, ranging from 3.77 Å. to 3.80 Å. Tentatives were made to obtain the metal in somewhat coarser grains, without heating it. With this purpose solutions of the chloride: $Na_3Rho\,Cl_6$, were electrolysed between a carbon-anode and a *rhodium*-cathode with a voltage of 2.5 Volts and a current-density of about 1.2 Amp. pro cm^2. The metal is slowly deposited in the form of darkly coloured clumps, which, under the microscope, have the appearance of cubes with rounded edges and curved facets, which are striated in three perpendicular directions; but no well developed crystals ever were obtained. The diffraction-lines of this product were no better than those mentioned before. A better product is obtained in the form of a greyish, brittle mass, if, instead of the chloride, the complex oxalate: $K_3\{Rho\ (C_2O_4)_3\} + 4\frac{1}{2}\ H_2O$ in very weakly acid solution, is subjected to electrolysis, with a current-density of about 3 Amp. pro cm^2. Even in this case, however, no good crystals were obtained. The finest powder obtained by grinding the product in a mortar, was used for *X*-ray-examination, and thus some better spectrograms, as well with copper-, as with iron-radiation were obtained, which, besides some stronger lines, showed a great number of much fainter ones. Later-on it was stated, that these spectrograms were identical with those obtained with the best product deposited from the chloride; also, that a heating at 1000° C. did not appreciably alter the character of the spectrograms. If, however, the powder, wrapped in platinium-foil, was heated for a long time at 1500° C. and then suddenly quenched, the obtained spectrogram was completely identical with that of the metal in wire-form, which afterwards will be described.

The results of the *X*-ray-analysis of the powder not previously heated, are collected in Table I; they were obtained by means of iron- and copper-radiation; the spectrograms produced by using a copper-target were practically identical with those obtained with iron-radiation; but occasionally they showed a greater number of faint lines than the latter ones.

Even, if the lines which practically coincide with those of the face-centred cubic form, are left apart, at least 39 lines remain, which cannot be accounted for in that lattice and which must be attributed to another modification, which is the stabler one at lower temperatures, and which

TABLE I.
Powder-Spectrograms of electrolytically deposited Rhodium.

N⁰. of line:	2l in mm.:	Int.:	λ:	θ:	sin² θ (observed):	sin² θ (calculated):	Σ:	Indices {h k l}:
1	× 32.92	1	α	10°37′	0.0339	0.0331	3	(111)
2	37.88	3	α	12 12	0.0477	0.0442	4	(200)
3	45.84	2	α	14 48	0.0652	0.0663	6	(211)
4	× 53.19	2	α	17 10	0.0871	0.0884	8	(220)
5	× 56.76	2	α	18 19	0.0988	0.0995	9	(221) ; (300)
6	× 59.95	2	α	19 20	0.1096	0.1105	10	(310)
7	62.15	2	β	20 3	0.1176	0.1178	13	(320)
8	65.81	3	α	21 14	0.1312	0.1326	12	(222)
9	68.66	4	α	22 9	0.1422	0.1436	13	(320)
						0.1618	←	β (111) of β-Modif.
10	74.39	2	β	24 0	0.1654	0.1658	(15)	—
11	77.62	1	α	25 3	0.1792	0.1768	16	(400)
						0.1954	←	α (111) of β-Modif.
12	81.86	5	α	26 25	0.1979	0.1989	18	(330) ; (411)
						0.2164	←	β (200) of β-Modif.
13	87.10	2	α	28 6	0.2219	0.2210	20	(420)
14	× 89.27	1	α	28 48	0.2321	0.2320	21	(421)
15	× 91.35	1	α	29 28	0.2419	0.2431	22	(332)
16	96.15	3	α	31 1	0.2655	0.2652	24	(422)
						0.2733	←	α (200) of β-Modif.
17	99.10	1	α	31 58	0.2803	0.2762	25	(430) ; (500)
18	×102.01	2	α	32 55	0.2953	0.2983	27	(333) ; (511)
19	×107.65	2	α	34 44	0.3246	0.3204	29	(432) ; (520)
20	108.92	3	α	35 8	0.3312	0.3315	30	(521)
21	113.57	3	α	36 38	0.3558	0.3536	32	(440)
22	119.27	1	α	38 29	0.3872	0.3867	35	(531)
23	121.10	2	α	39 4	0.3972	0.3978	36	(600)
24	×125.35	1	α	40 26	0.4206	0.4199	38	(532) ; (611)
						0.4310	←	β (200) of β-Modif.
25	127.49	3	β	41 8	0.4327	0.4310	(39)	—
26	×132.17	1	α	42 26	0.4554	0.4531	41	(540) ; (621)
27	×141.47	1	α	45 33	0.5095	0.5083	46	(631)
28	×143.05	4	α	46 9	0.5201	0.5190	(47)	—
						0.5232	←	α (220) of β-Modif.

TABLE I (*Continued*).

Powder-Spectrograms of electrolytically deposited Rhodium.

N⁰. of line :	$2l$ in mm. :	Int. :	λ :	θ :	$\sin^2\theta$ (observed) :	$\sin^2\theta$ (calculated) :	Σ :	Indices $\{h\,k\,l\}$:
29	145.50	4	α	46°57′	0.5340	0.5304	48	(444)
30	148.90	2	α	48 3	0.5531	0.5525	50	(543) ; (505) ; (710)
31	152.72	2	α	49 16	0.5742	0.5746	52	(640)
						0.5920	←	β (311) of β-Modif.
32	158.34	2+	β	51 4	0.6053	0.6077	(55)	—
33	162.02	1	α	52 17	0.6257	0.6298	57	(544) ; (722)
34	×165.30	2	α	53 20	0.6434	0.6409	58	(730)
						0.6468	←	β (222) of β-Modif
35	167.79	2+	β	54 8	0.6568	0.6520	59	(731) ; (553)
36	173.0	1	α	55 49	0.6842	0.6851	62	(732)
37	177.0	3	α	57 6	0.7050	0.7072	64	(800)
38	×179.2	6	α	57 49	0.7163	0.7182	65	(740) ; (810)
						0.7191	←	α (311) of β-Modif.
39	×181.1	5	α	58 25	0.7257	0.7293	66	(554) ; (741) ; (811)
40	183.72	1	α	59 17	0.7391	0.7404	67	(732)
41	188.1	2	α	60 40	0.7600	0.7625	69	(742) ; (821)
42	190.54	3	α	61 28	0.7718	0.7735	70	(653)
						0.7818	←	α (222) of β-Modif.
43	193.10	4	α	62 18	0.7839	0.7955	72	(660) ; (822)
44	×198.69	1	α	64 6	0.8092	0.8067	73	(830)
45	×199.80	1	α	64 28	0.8140	0.8177	74	(743) ; (750) ; (831)
46	×202.63	1	α	65 22	0.8263	0.8288	75	(555) ; (751)
47	×204.50	1	α	65 58	0.8341	0.8398	76	(662)
48	208.61	2	α	67 18	0.8510	0.8508	77	(654) ; (832)
49	211.50	2	β	68 14	0.8625	0.8619	78	(752)
						0.8616	←	β (400) of β-Modif.
50	220.48	2	α	71 8	0.8954	0.8950	81	(744) ; (841)

The values of $2l$ are the *mean* values of *four* series of measurements with the comparator.

$R = 44{,}4$ mm. *Exposure*: 60—96 m. Amp. hours. *Iron*-anticathode.

Quadratic Equation: $\sin^2\theta = 0.01105 \,.\, (h^2 + k^2 + l^2)$. ($\alpha$-radiation).

$\sin^2\theta = 0.00906 \,.\, (h^2 + k^2 + l^2)$. ($\beta$ radiation).

Simple cubic lattice, with ; $a_0 = 9.211$ Å. ± 0.09.

occurs *besides* the ordinary form of the metal[1]) ; we will indicate it as the α-modification of the metal[2]). There is no doubt, however, that simultaneously also the ordinary β-form of the metal is present, and that, therefore, the product examined is a *mixture* of the two. This must be concluded from the fact, that in the spectrogram the lines N⁰. 10, 25, 28 and 32 correspond to a sum of squares of the indices equal to 15, 39, 47 and 55 respectively, — which cannot be accounted for in any other way, than by assuming that they belong to the β-modification itself. Also the other lines of this modification are met with exactly at or very nearly at the positions of the lines 12, 13, 17, 35, 38, 43 and 49, — from which they hardly can be separated, because they cause a broadening of the adjacent lines and an apparent increase of their intensities. From the rather weak intensities of these lines of the β-modification in comparison with those of the pure modification itself, it can be concluded that the amount of the β-modification in the mixture obtained by electrolysis, is only a rather moderate one[3]). The fact that all the lines mentioned practically coincide with those of the α-modification, also gives a rational explanation of the phenomenon of the hazy and broadned aspect of the lines of the spectrograms obtained from the *rhodium*-powder first studied in this way. Partially this hazy aspect is doubtlessly also caused by the semi-colloidal state of the particles : a rough estimation from the broadness of the lines taught us, that the particles must have a linear dimension of about 300 Å ; which means, that they consist of about 33 atoms arranged along each edge of the cubic particles. Also the phenomenon of the occasional occurrence of some multiple lines in the spectrograms at ordinary temperature is explained by this character of the preparations studied, as *mixtures* of the α- and β-modifications together.

The α-modification is, like the β-modification, cubic, but it has a simple cubic lattice with an edge of 9.211 Å. The number of atoms pro elementary cell can be estimated from the density of the preparation :

with 48 atoms in the cell, d must be 10.427 ;
with 32 atoms in the cell, d must be 6.951 ;
with 96 or 64 atoms in the cell, d must be twice the first or the second number respectively.

Bij four independant direct measurements with three different preparat-

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[1]) A spectrogram of a *rhodium-oxide*, presumably Rho_3O_4, which was prepared from the hydrate by heating it at 900° C., showed 27 lines, which as well with respect to their location as to their relative intensities, did *not* coincide with the lines here observed. An admixture of an oxide to the metal obtained by cathodical reduction being beforehand highly improbable, this control leaves no doubt as to the fact, that the lines observed are *not* produced by the presence of rhodium-oxide.

[2]) By comparison with the spectrogram of *α-iron*, we have, moreover, ascertained ourselves, that these lines *cannot* correspond to the presence of traces of iron, -the only imaginable impurity of the preparation.

[3]) About 12 %.

ions, we found the density to be: 10.68 at 20° C.; therefore. the number of atoms in the elementary cell of *α-rhodium* must be *fourty-eight*.

If to these 48 atoms in the cubic cell a fourty-eight-fold position (with 3 parameters x, y, z) shall be attributed, the α-modification only can belong to one of the four space-groups: O_h^1, O_h^2, O_h^3 or O_h^4. The uncertainty in the estimated relative intensities of the rather faint lines of the spectrograms does, at this moment, not allow us to decide, which of these four groups is the right one.

The α-modification seems to be stable besides the β-form, however, within a range of temperatures at least extending as high as 1000° C., always, however, diminishing in quantity, as the temperature increases.

§ 3. In contrast to this α-modification, the ordinary form of the metal is the face-centred cubic one, with a parameter a_0 having the value: 3.791 Å. The results obtained with a thin wire of the metal at room-temperature are collected in Table II, copper-radiation being used in these experiments. The occurrence of the lines 1, 6 and 20 proves, that somewhat of the other modification still is present, which also may be concluded from the fact, that the data for the specific weight of the compact metal, as given in literature, are rather variable. The lines 17 and 19 have the character of narrow doublets. The results obtained by means of iron radiation, as well in the case that the wire was rotated about its axis, as when it remained unmoved, were completely analogous to those mentioned. They are in agreement with the data previously published by other investigators ¹).

§ 4. After this we proceeded to the study of the influence which heating has on the structure of the metal. A drawn wire of purest *rhodium* ²), with a diameter of 0.3 mm and a length of 35 mm was fixed along the axis of a cylindrical camera, the latter one having a radius of 57.2 mm. The wire could be heated by means of an electric current of known intensity, its temperature at every moment being checked by means of a calibrated HOLBORN-KURLBAUM-pyrometer. The film was wrapped in black paper and applied to the outside of the camera; the increase of the radius by this sheet of paper was 0.15 mm. As *rhodium* above 600° C. is readily attacked by oxygen, the camera was surrounded by a cylindrical brass box, which during the experiments was continuously evacuated. The wire was heated at 750°, 1200° and 1400° C. successively and originally kept in an immovable position. Later-on the experiments were repeated with

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¹) A. W. HULL and W. P. DAVEY, Phys. Review, **17**, (1921), 571. Their value for a_0 was 3.820 Å. in the case of an electrolytically deposited rhodium. T. BARTH and G. LUNDE, Zeits. f. phys. Chem., **117**, (1925), 478, found $a_0 = 3.795$ Å. for the metal prepared by reduction of the oxide. A remarkable fact is, that for a wire previously heated, a_0 usually varies between 3.77 and 3.80 Å.

²) Before drawing the wire, the metal had previously been heated at 900°—1000° C

TABLE II.

Rhodium-Wire, drawn; diameter: **0.3** mm. At Ordinary Temperature.

N⁰. of Lines	2 l in mm.:	Int.:	λ:	θ:	$sin^2\,\theta$ (obs.):	$sin^2\,\theta$ (calc.):	Indices $\{h\,k\,l\}$:
1	68.34	1	α	17° 4′	0.0861	0.0825	(110)*
2	74.27	2	β	18 33	0.1012	0.1005	(111)
3	82.80	7	α	20 41	0.1247	0.1237	(111)
4	86.28	3	β	21 33	0.1349	0 1340	(200)
5	96 09	7	α	24 0	0.1654	0.1649	(200)
6	109.01	2	α	27 13	0.2093	0.2061	(210)*
7	125.12	3	β	31 15	0.2691	0.2679	(220)
8	140.65	9	α	35 8	0.3312	0.3298	(220)
9	150.30	3	β	37 52	0.3711	0.3684	(311)
10	159.23	1	β	39 46	0.4092	0.4019	(222)
11	169.92	9	α	42 26	0.4552	0.4535	(311)
12	179.29	4	α	44 47	0.4962	0.4948	(222)
13	187.46	1	β	46 49	0.5316	0.5358	(400)
14	212.60	2	β	53 6	0.6395	0.6363	(331)
15	217.61	3+	α	54 21	0.6603	0.6596	(400)
16	220.69	2	β	55 7	0.6729	0.6698	(420)
17	249.35 (△)	7	α	62 17	0.7831	0.7834	(331)
18	255.96	2	β	63 56	0.8069	0.8038	(422)
19	261.25 (△)	7	α	65 15	0.8247	0.8246	(420)
20	290.27	3	α	72 30	0.9095	0.9071	(332)*

Radius of Camera: 57.35 mm. Exposure: 20—40 m. Amp. hours.
Radiation: Copper-anticathode; $\lambda_\alpha = 1.540$ Å; $\lambda_\beta = 1.388$ Å.

The values here given are the mean values of three series of measurements; the distances 2 l were measured on the Comparator. △ are doublets.

Quadratic Equation: for the α-radiation: $sin^2\,\theta = 0.04123\,.\,(h^2 + k^2 + l^2)$.
for the β-radiation: $sin^2\,\theta = 0.03349\,.\,(h^2 + k^2 + l^2)$.

Face-centred cubic lattice [1]), with $a_0 = 3.791$ Å.; from the doublets △ another value: $a'_0 = 3.78$ Å. can be calculated. The values marked with an *, belong to the α-modification and correspond to: (222), α (521), etc. of its spectrogram.

a wire rotating about its axis with speeds varying from 60 to 5 times an hour; the apparatus used in the latter case is described below.

In the experiments with an immovable wire it was observed, that by heating, a process of recrystallisation sets in, the composing crystallites evidently being gradually enlarged: black spots appear, first in the diffraction-lines themselves [1]), which thus seem at last to have been broken up into spots of greater or smaller intensity; but soon an ever increasing number of irregularly shaped spots becomes visible, covering the whole extension of the film. When the temperature increases, the diffraction-lines gradually become fainter and fainter, the spots, however, more and more numerous. They are dispersed at random over the film; and above 1400° C. the lines at last vanish entirely, while only the spots remain.

Evidently, the large number of small crystallites in the wire, orientated in all possible directions in space, gradually are replaced by a considerably smaller number of much larger crystallites, which most probably simultaneously are orientated in some regular way with respect to the length-direction of the wire. According to POLANYI, this effect is produced because of the fact, that in the large crystallites, by their unfavorable orientation, the monochromatic radiation does not yield any longer the corresponding diffraction-lines, but the accompanying slight "white" radiation of the tube now produces a great number of superimposed LAUE-effects. By the rotation of the wire about its axis, the LAUE-effects are changed into a more or less continuous background on the film, on which the now again produced monochromatic diffraction-lines are clearly visible.

The most remarkable fact, however, is, that already at 750° C. and higher, first the outer lines, then also the other ones, are split into *two* lines, thus forming doublets which consist of an intensive line and a fainter satellite; the latter one will in the following be designed by *s*. With increasing temperature, the distance between the two components of each doublet increases, because the two components, as a consequence of the thermal dilatation of the lattice, both move towards the centre of the film, but the most intensive component apparently much more rapidly than the fainter satellite. In this way their mutual distance gradually increases. Both sets of lines exactly correspond to *two* face-centred cubic lattices which differ in their values of a_0 and apparently in their coefficients of thermal expansion. The dilatations of both lattices, as calculated from the values of a_0, are graphically represented in Fig. 1. The phenomenon makes the impression, as if already at ordinary temperature, the most intensive, diffraction-lines had been unresolvable doublets, the components of which are at increasing temperatures ever more separated. This behaviour manifests itself also in the case of *palladium* and platinum, where *no* allotropic modifications are found; the fact, therefore, appears not to be connected with an occasional presence of an allotropic modification as the one formerly described.

By controlling experiments we have convinced ourselves, that the

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[1]) The sharply limited spots may be expected where the crystallites already almost completely have reached their paratropic orientation; conf. A. E. VAN ARKEL, *Physica*, **3**, (1923), 84.

phenomenon described cannot be attributed to some disturbance caused by the experimental arrangement used. The divergency of the incident beam was determined to be 1°24′ (conical angle $2\varphi = 2°48'$). Its cross section on the wire (length 28 mm) was directly measured and found to be somewhat less than 5.4 mm. By pyrometrical measurements the length of the heated wire in the centre of the camera, which glowed at a practically *uniform* temperature, was found to be: at 800° C., 7 to 8 mm; at 1000° C., 14 mm; at 1200° C., 15 mm. At the top and at the bottom of the film, the temperature of the wire was about 20° lower than in the centre. From these data it can be concluded, that the pencil of incident X-rays covered the full middle part of the glowing wire over a length, which entirely was situated within the field of uniform temperature, its extension being, especially at the higher temperatures, considerably greater than the part intercepted by the weakly divergent beam. No source of error can, therefore, be produced by the colder extremities of the wire. In the experiments later to be described, we carefully have studied, what influence a possibly occurring stress in the wire might have produced, be it by incomplete thermal dilatation or by the pull of a small weight fixed at the lower end of the wire; or whether perhaps a torsion produced in the wire during its rotation, might be considered as the cause of the phenomenon described. It appeared, however, that the doublets are produced in the same way as before, if all these sources of possible disturbances are beforehand eliminated. Neither does heating with direct or with alternating current alter the phenomena described, safe for a little broadening of all lines.

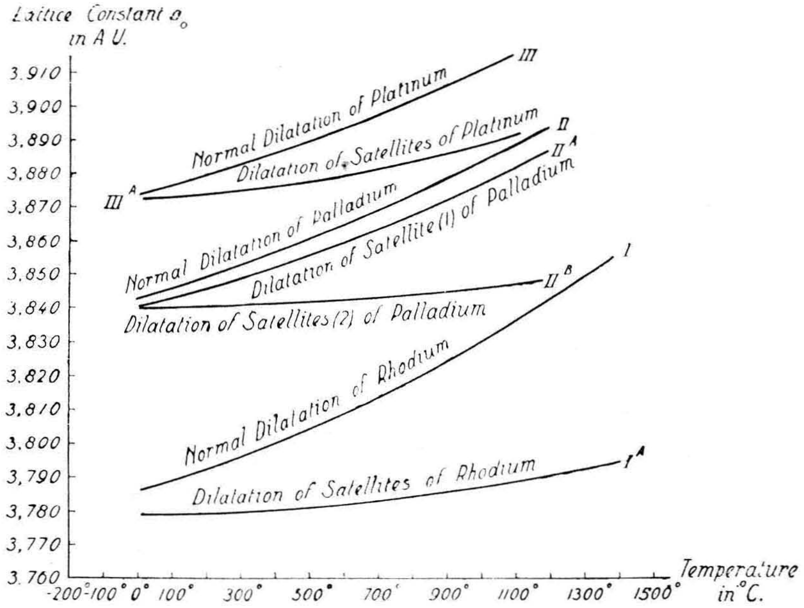

Fig. 1.

The phenomenon must therefore be considered as a *real* one, it being only dependant on the temperature of the wire.

§ 5. As we shall have much to do with these doublets, in the following, it is adviceable here already, to ask ourselves, whether this curious phenomenon of the splitting of the diffraction-lines in the spectrograms possibly has anything to do with absorption-phenomena occurring in the wire?

Now, there are three cases to be discerned [1]: either the absorption of the X-rays in the material investigated is complete; or there is no absorption at all; or the rays are partially absorbed, — which in practice is the most ordinary case.

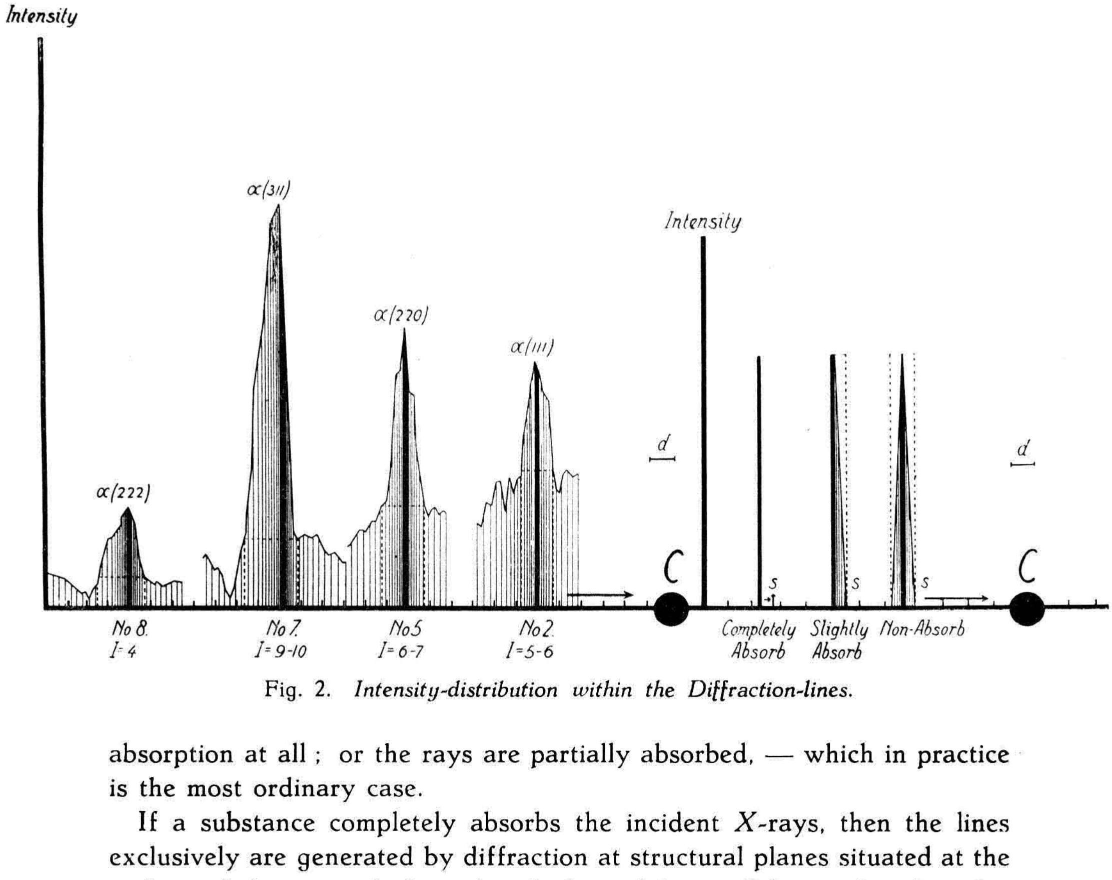

Fig. 2. *Intensity-distribution within the Diffraction-lines.*

If a substance completely absorbs the incident X-rays, then the lines exclusively are generated by diffraction at structural planes situated at the surface of the wire. A thin, sharply limited line will be produced in this case, the position of which will only be shifted through a little distance, depending on the diameter d of the exposed wire and on the glancing angle θ. If the substance only partially absorbs the incident rays, the line will have its maximum intensity at the side most distant from the centre of

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[1] A. HADDING, Centr. Blatt Miner., (1921), 631. See for the corrections to be applied also: P. DEBIJE, Phys. Zeits., **18**, (1817), 5; W. GERLACH and O. PAULI, Zeits. f. Phys., 7, (1921), 116; A. J. BIJL and N. H. KOLKMEIJER, Proceed. R. Acad. Amsterdam, **21**, (19), 496; F. G. FOOTE, F. C. BLAKE and W. G. FRANCE, Journ. of phys. Chem., **34**, (1930) 2236.

the film ; the intensity within the line itself gradually falling off towards the centre of the spectrogram ; while, if the substance does not at all absorb, the lines will be most intensive in the middle part of their extension, the intensity gradually diminishing in a symmetrical way towards the borders of the line.

We, therefore, have studied the intensity-distribution within the borders of the lines themselves, by means of photometrical measurements, using a thermopile and a sensitive galvanometer. The result was, that the lines near the centre of the film were almost symmetrically built ; which proved, that only little absorption in the thin wire takes place. The lines more distant from the centre, however, showed a distinctly *un*symmetrical distribution of their intensity ; but, here the most intensive part appeared always to be turned *towards the centre of the film*, i.e. exactly the reverse of what should be expected in the case of the absorption-phenomena mentioned above ; the intensity slowly falls off towards the outwardly placed satellite. There can, therefore, be no doubt as to the quite different character of the origin of the observed lines.

§ 6. For the purpose of a more detailed study of these phenomena, we have made use of a camera [1]) allowing the rotation of a heated wire within a perfect vacuum.

The camera consists of a cylindrical brass box *KK'*, with a diameter of

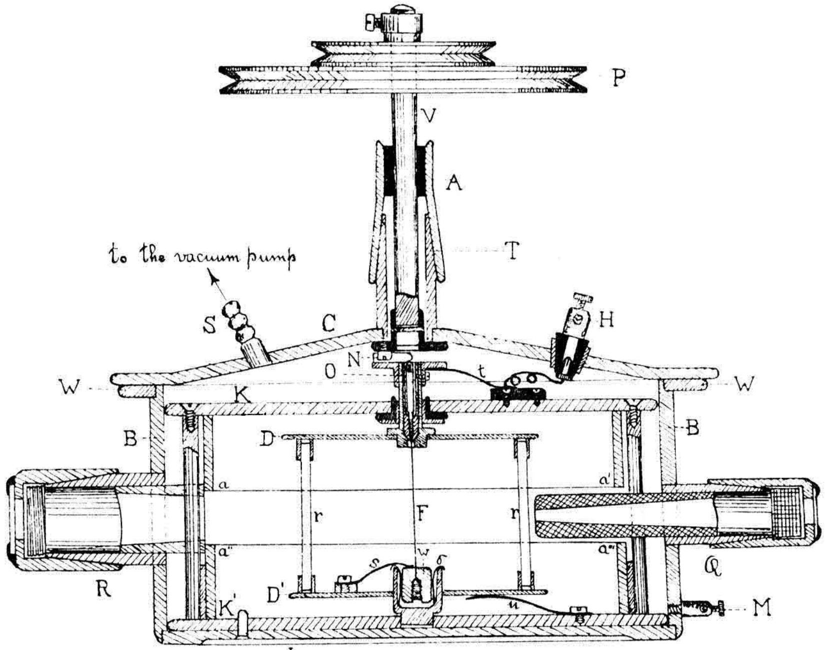

Fig. 3.

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[1]) This instrument was built in the shop of the laboratory by the mechanics A. VAN DER MEULEN and J. OLYSLAGERS.

114.4 mm. The central part of its vertical wall is cut, so that a horizontal slit is formed of about 2 cm broadness; the *X*-rays passing this opening *aa′ a″ a‴*, can reach the photographic film, which is fixed at the outside of the camera by means of two excentrical handles, which uniformly press it against the outer wall of the camera. *BLB′* is the wall of the vacuum chamber, equally made of brass and completely surrounding the camera *KK′*. Its lid *C*, provided with a broad, flattened and smoothly polished brim *W*, rests on the similar flat and carefully polished brim of the wall *BB′*, — the locking thus obtained being perfectly air-tight, if the brims are greased. The outlet *S* is connected with the vacuum-pump; on the other hand, *H* is the connection for the heating current (1—4 Amp.), while at the bottom of the chamber *M* represents the other electrode. The cover *C*, moreover, bears a removable projecting part, also made of brass, which has a conically shaped and carefully ground and polished surface at *T*, exactly fitting into an equally well polished conical tube *A*. This, in its turn, is immovably fixed to the axis of rotation *V*. This last one is moved by an electrical motor, which is provided with a transmission, consisting of an endless screw and cog-wheel, while its motion is transfered to the pulley *P*, by means of a string. During the rotation, the friction at the air-tight joint *T* is considerably reduced by thoroughly greasing the conical surfaces. The collimator *Q* fits in the wall of the vacuum-chamber, and is provided with the usual leaden screens and slits. The pencil of *X*-rays enters the chamber at *I* and leaves it at *E* through a very thin glass window, which simultaneously allows of observing the glowing wire and of controling its temperature at each moment by means of a calibrated optical pyrometer.

The axis of rotation *A*, at its lower end, bears a cog *N*, which, by the revolution of *A*, drags along the equally smoothly rotating part *O*, to which at the inside of the camera *KK′* the circular supports *D* and *D′* are fastened, joined together by three thin glass rods *r*. Within this light, movable framework *DrD′r*, the metallic and heated wire *F* to be studied is centrically fixed, its lower end bearing a small, carefully polished brass weight *W*. This last one is freely movable between the extremely flabby, very soft springs σ, which during its motion are perfectly gliding along it, steadily remaining in contact with it, but not causing any appreciable friction. These springs σ simultaneously are the contacts for the heating current, by which the wire *F* can be heated at different temperatures. Similarly, the springs *t*, *s* and *u* also are very soft and gliding contacts; they are necessary either as places of contact for the heating current or they are applied solely with the purpose of keeping the movable framework within the camera in the desired, perfectly central position.

The motion of *P* was in our experiments mostly regulated, in such a way that the number of rotations ordinarily remained within the limit of sixty each hour; it could, however, be diminished at five an hour. The black coloured parts in Fig. 3 all represent insulating materials (ebonite, piceine,

TABLE III.

Rhodium-Wire, drawn; diameter: 0.3 mm., at Different Temperatures.

N⁰. of Line:	VI. At ordinary Temperature, fixed or rotating about its axis.				III. At 750° C.; fixed.				IV. At 1000° C.; fixed.				V. At 1400° C.; fixed.				λ:	Indices $\{h\,k\,l\}$:
	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):		
1	—		—	—	84.64	1+	0.1301	0.1287	—		—	—	—		—	—	α	(110)*
2	95.00	2	0.1617	0.1615	94.79	2	0.1601	0.1582	94.03	1	0.1588	0.1569	—		—	—	β	(111)
3	—		—	—	104.89	4	0.1936	0.1930	104.15	4	0.1924	0.1914	102.32	—	0.1860	0.1877	α	(111)
3A	105.57	7	0.1972	0.1972	—		—	—	105.46 (*s*)	2	0.1967	0.1961	105.16 (*s*)	—	0.1956	0.1952	α	(111)
4	111.06	2	0.2165	0.2154	110.45	2	0.2133	0.2109	109.51	1	0.2111	0.2092	—		—	—	β	(200)
5	—		—	—	122.69	5	0.2585	0.2573	121.73	4	0.2558	0.2552	119.86	—	0.2490	0.2503	α	(200)
5A	123.45	6	0.2625	0.2629	—		—	—	123.36 (*s*)	2	0.2622	0.2614	122.60 (*s*)	—	0.2594	0.2603	α	(200)
6	—		—	—	162.84	1	0.4239	0.4218	161.91	1	0.4206	0.4184	—		—	—	β	(220)
6A	164.71	3	0.4330	0.4308	—		—	—	163.57 (*s*)	1	0.4310	0.4289	—		—	—	β	(220)
7	—		—	—	183.86	5	0.5163	0.5146	182.45	4	0.5100	0.5104	181.06	—	0.5038	0.5006	α	(220)
7A	185.80	7	0.5245	0.5258	185.59 (*s*)	2	0.5228	0.5235	185.22 (*s*)	2	0.5218	0.5228	184.92 (*s*)	—	0.5207	0.5206	α	(220)
8	—		—	—	199.25	2−	0.5821	0.5801	197.62	2	0.5765	0.5753	—		—	—	β	(311)
8A	201.68	2+	0.5931	0.5923	200.97 (*s*)	1	0.5891	0.5909	200.92 (*s*)	1	0.5897	0.5895	—		—	—	β	(311)
9	214.37	1	0.6467	0.6461	213.28	1	0.6422	0.6433	—		—	—	—		—	—	β	(222)
10	—		—	—	229.50	8	0.7091	0.7076	227.27	8	0.6993	0.7019	225.46	—	0.6922	0.6884	α	(311)
10A	232.50	9	0.7203	0.7229	232.24 (*s*)	4+	0.7185	0.7198	231.94 (*s*)	5	0.7179	0.7190	—		—	—	α	(311)
11	—		—	—	246.71	4+	0.7734	0.7720	243.62	5	0.7627	0.7657	241.04	—	0.7530	0.7510	α	(222)
11A	249.87	4	0.7854	0.7886	249.67 (*s*)	2	0.7840	0.7851	248.60 (*s*)	2	0.7808	0.7843	—		—	—	α	(222)
12	272.51	1	0.8603	0.8616	—		—	—	—		—	—	—		—	—	β	(400)

Radius of Camera: 57.35 mm. (corr.). All distances $2l$ are measured on the Comparator.

Radiation: Iron-anticathode; $\lambda_\alpha = 1.9366$ Å., $\lambda_\beta = 1.753$ Å.

Quadratic Equations: for α-radiation, $\sin^2\theta = A.(h^2+k^2+l^2)$.
for β-radiation, $\sin^2\theta = B.(h^2+k^2+l^2)$.
The coefficients A and B, and the corresponding parameters a_0, are given below for each case separately.

With (*s*) are indicated the satellites of the stronger lines of each doublet, generated on heating the fixed wire; with Int. the visually estimated intensities.

$A = 0.06572.$ $B = 0.05385.$ $a_0 = 3.777$ Å.	$A = 0.06433.$ $B = 0.05273.$ $a_0 = 3.817$ Å.	$A = 0.06381.$ $B = 0.05230.$ $a_0 = 3.832$ Å.	$A = 0.06258.$ $B = 0.05130.$ $a_0 = 3.870$ Å.
	$A'_s = 0.06548.$ $B'_s = 0.05367.$ $a'_0 = 3.784$ Å.	$A'_s = 0.06536.$ $B'_s = 0.05359.$ $a'_0 = 3.787$ Å.	$A'_s = 0.06502.$ $B'_s = 0.05330.$ $a'_0 = 3.796$ Å.
	In all three cases, the exposure was: 80 m.Amp. hours.		
Exposure: 60 m.Am. hours. The spectrograms of the fixed and of the rotated wire were identical, their lines corresponding in both cases to the satellites, developed on heating.	Moreover, the line indicated with * corresponds to the α-modification: α (222).		The other lines also seem to be doublets; but the spectrogram was too faint for allowing their measurement. For the same reason no estimation of the intensities were made in this case.

etc.). The apparatus has, up till now, completely answered its purpose, even at temperatures as high as 1600° C. By repeatedly heating in a vacuum at high temperatures, all gases occluded in the wire were finally driven out. Most experiments were made with a wire previously used in the measurements of the thermoelectric force, it thus being heated for a long time at temperatures as high as 1600° C. The surface of the wire appeared under the microscope to be rather smooth and it was *not* altered, even after repeatedly heating it. Occasional inegalities in this respect were, moreover, counterbalanced by rotating the wire during the experiments about its axis.

§ 7. By means of this arrangement it now is possible to study the heated wires as well, when they are immovable, as when they are rotated about their axis. The phenomena observed in both cases are the following.

A. If a wire is heated at 1500° C., finally all lines disappear and only innumeral spots remain visible, distributed at random over the film; when again cooled down to ordinary temperature, such a wire, if radiated through, only yields spots [1]). But if this cooled wire now be rotated about its axis, all lines on the film reappear at their exact places, *they all conciding this time with the positions of the former satellites s of each doublet.* As *rhodium* is a very plastic metal, possessing many gliding planes, evidently the crystallites, enlarged by recrystallisation, for the greater part gradually become arranged parallel to each other, — probably, as ETTISCH, POLANYI and WEISSENBERG [2]) have demonstrated, with [111] and [100] as paratropic directions, parallel to the length-direction of the wire. The significance of the spots and their vanishing on rotating the wire have already been explained in the above.

B. If the wire be heated at 900° C. and simultaneously rotated about its axis, a normal spectrogram of intensive lines appears; but this time *all lines coincide with the positions of the former intensive lines* of the doublets and *not* with those of the satellites; the latter ones, for the greater part, seem to have completely disappeared [3]). From the following data, this peculiar behaviour at once becomes evident:

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[1]) Such a wire was preserved during 9 weeks. After this lapse of time, the wire was, in an inmovable position, again studied with iron-radiation at 20° C. Now the beginnings of regular diffraction-lines really appeared in the spectrogram, but still amongst a great number of spots. Evidently during these 9 weeks the inner structure of the wire had already changed, the larger crystallites gradually either having crumbled down to smaller ones or partially having lost their paratropic orientation. These experiments will after some months once more be repeated.

[2]) M. ETTISCH, M. POLANYI and K. WEISSENBERG, Zeits. f. Physik, 7, (1921), 181.

[3]) This vanishing of the satellites must not be taken too literally, as it simply is a question of intensities. Indeed, in the case of *palladium* and *platinum* we occasionally obtained spectrograms, in which, — even after rotation; — a number of satellites remained visible. In judging the position of the lines, the small shift must of course be taken into account, which is a consequence of the thermal dilatation of the lattice at higher temperatures; but this fact does not lead to any confusion, if the comparison be carefully made.

I Rotating wire at 20° C. $2l$ in mM.:	II Immovable wire at 750° C. $2l$ in mM.:	III Rotating wire at 900° C. $2l$ in mM.:	IV Immovable wire at 1000° C. $2l$ in mM.:
95.0	94.79	94.24	94.03
105.57	104.89		$\underline{\Delta}$ 104.15 105.46 (S)
111.0	110.45	109.48	109.51
123.45	122.69	122.10	$\underline{\Delta}$ 121.73 123.36 (S)
164.7	162.84	162.12	$\underline{\Delta}$ 161.91 163.57 (S)
185.50	$\underline{\Delta}$ 183.86 185.59 (S)	182.97	$\underline{\Delta}$ 183.45 185.22 (S)
201.86	$\underline{\Delta}$ 199.25 200.97 (S)	198.44	$\underline{\Delta}$ 197.62 200.92 (S)
232.50	$\underline{\Delta}$ 229.50 232.24 (S)	228.0	$\underline{\Delta}$ 227.27 231.94 (S)
249.87	$\underline{\Delta}$ 246.71 249.67 (S)	244.40	$\underline{\Delta}$ 243.62 248.60 (S)

The phenomena observed at different temperatures may, moreover, be seen from Table III, in which the values of $2l$, of $\sin^2 \theta$ and the indices $\{hkl\}$ for *rhodium* under different conditions are collected, as well the coefficients A and B, as the parameters a_0 for each of the apparently occuring face-centred lattices being calculated in each case.

Four spectrograms were obtained at 800° C. with *the same* wire and the same camera, but the heating and exposure were consecutively extended during 6, 14, 21, and again 28 hours, alternately direct and alternating current being used in heating the wire. It appeared that *the ratio of the relative intensities of the components of each doublet was shifted towards an ever increasing intensity of the satellites in comparison with that of the other line, if the duration of the heating was augmented.* As the *time-factor*, therefore, appears to be of great influence, as far as the absolute intensities of the satellites be considered, there can be no doubt, that the effect observed must in some way directly be connected with the internal structure of the wire, the latter evidently being gradually changed, if the heating be continued during an ever longer interval of time.

§ 8. *Palladium.*

The phenomena observed in the case of *palladium*, — which does not

TABLE IV.

Palladium-Wire, drawn; diameter: 0.3 mm., at Different Temperatures.

	I.A At Ordinary Temperature. (Wire immovable).				I.B At Ordinary Temperature. (Wire rotated).				II.A At 800° C. (Wire immovable).				II.B At 800° C. (Wire rotated).				III. At 1200° C. (Wire immovable).				λ:	Indices $\{h\,k\,l\}$:
N⁰. of Line	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):	$2l$ in mm.;	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):	$2l$ in mm.:	Int.:	$\sin^2\theta$ (obs.):	$\sin^2\theta$ (calc.):		
1	93.70	3	0.1577	0.1563	93.33	2	0.1558	0.1556	93.12	2	0.1566	0.1535	92.51	3	0.1539	0.1528	92.23	2	0.1529	0.1527	β	(111)
2	103.82	7	0.1913	0.1907	103.71	6	0.1908	0.1899	103.51	5	0.1901	0.1873	102.61	7	0.1869	0.1864	102.73	5	0.1874	0.1863	α	(111)
3	109.29	2	0.2103	0.2084	108.80	3	0.2085	0.2075	108.46	2	0.2073	0.2047	108.05	3	0.2056	0.2037	107.61	2	0.2043	0.2036	β	(200)
4	121.37	5	0.2548	0.2543	121.11	5	0.2538	0.2532	120.68	6	0.2520	0.2498	120.11	7	0.2500	0.2485	119.92	4	0.2492	0.2484	α	(200)
4A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	121.51 (s)	1	0.2553	0.2532	α	(200)
5	161.19	3	0.4177	0.4169	160.68	3	0.4155	0.4150	159.74	2	0.4112	0.4094	159.23	3	0.4092	0.4074	158.62	1	0.4066	0.4072	β	(220)
5A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	161.71 (s)	1	0.4198	0.4153	β	(220)
6B	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	176.81 (s′)	2	0.4852	0.4854	α	(220)
6	181.68	9	0.5067	0.5086	181.16	9	0.5041	0.5064	180.21	6+	0.5000	0.4995	179.31	8	0.4962	0.4970	178.64	5	0.4933	0.4968	α	(220)
6A	—	—	—	—	—	—	—	—	182.53 (s)	1	0.5102	0.5065	181.12 (s)	2	0.5041	0.5074	182.01 (s)	1	0.5078	0.5065	α	(220)
7	—	—	—	—	—	—	—	—	194.95	2	0.5641	0.5629	193.84	3	0.5592	0.5601	193.62	1+	0.5583	0.5599	β	(311)
7A	196.46	2	0.5708	0.5732	196.32	3	0.5702	0.5706	—	—	—	—	197.41 (s)	1	0.5748	0.5720	196.51 (s)	1	0.5710	0.5708	β	(311)
8	—	—	—	—	208.57	1	0.6224	0.6224	206.35	1	0.6127	0.6140	205.64	2	0.6099	0.6110	—	—	—	—	β	(222)
9B	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	219.31 (s)	3	0.6675	0.6674	α	(311)
9	225.58	10	0.6927	0.6993	225.29	10	0.6916	0.6962	223.33	8	0.6835	0.6868	221.92	10	0.6778	0.6834	222.14	5	0.6787	0.6832	α	(311)
9A	—	—	—	—	—	—	—	—	226.61 (s)	2	0.6967	0.6964	225.21 (s)	2	0.6914	0.6977	225.11 (s)	1	0.6911	0.6964	α	(311)
10	241.70	4	0.7555	0.7628	241.30	4	0.7540	0.7595	238.11	3	0.7419	0.7492	237.43	5	0.7393	0.7456	236.42	2	0.7353	0.7453	α	(222)
10A	—	—	—	—	—	—	—	—	242.21 (s)	1	0.7573	0.7597	242.21 (s)	1	0.7576	0.7652	239.62 (s)	1	0.7477	0.7597	α	(222)
11	—	—	—	—	260.73	1	0.8230	0.8299	257.22 (s)	1	0.8111	0.8187	256.81	3	0.8097	0.8147	—	—	—	—	β	(400)
12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	262.73	1+	0.8295	0.8145	β	(400)
12A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	263.81 (s)	1	0.8333	0.8302	β	(400)
13	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	303.24	2	0.9393	0.9447	β	(331)
13A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	309.26	2	0.9512	0.9671	β	(331)
14B	—	—	—	—	—	—	—	—	—	—	—	—	321.42	3	0.9715	0.9675	—	—	—	—	β	(331)
14	324.6	2	0.9767	0.9900	—	—		—	324.94	2	0.9766	0.9722	322.65	2	0.9767	0.9880	322.04	2	0.9724	0.9859	β	(331)
14A	—	—	—	—	—	—	—	—	329.13 (s)	2	0.9815	0.9859	—	—	—	—	—	—	—	—	β	(331)
15	—	—	—	—	—	—	—	—	347.52	5	0.9966	0.9989	347.63	5	0.9964	0.9941	—	—	—	—	α	(400)

Radius of Camera: 57.35 mm. All distances $2l$ were measured on the Comparator.

Radiation: Iron-anticathode: $\lambda_\alpha = 1.9366$ Å.; $\lambda_\beta = 1.753$ Å. **Exposure**: 60—96 m. Amp. hours.

With (s) and (s′) the components of the doublets and triplets are indicated, developed on heating. Int. are the visually estimated intensities.

The lines 13—15 only can approximately be measured, because they are situated at the very borders of the film and thus appear much distorted.

$A = 0.06343$. $B = 0.05199$. $a_0 = 3.844$ Å.	$A = 0.06343$. $B = 0.05199$. $a_0 = 3.844$ Å.	$A = 0.06243$. $B = 0.05117$. $a_0 = 3.875$ Å. $A' = 0.06331$. $B' = 0.05189$. $a'_0 = 3.848$ Å.	$A = 0.06213$. $B = 0.05092$. $a_0 = 3.885$ Å. $A' = 0.06343$. $B' = 0.05200$. $a'_0 = 3.845$ Å.	$A = 0.06211$. $B = 0.05090$. $a_0 = 3.885$ Å. $A' = 0.06331$. $B' = 0.05189$. $a'_0 = 3.848$ Å.	$A'' = 0.06067$. $B'' = 0.04972$. $a''_0 = 3.93$ Å.

show any allotropic modifications and whose curve of the electrical resistance in its dependance on the temperature is a quite normal one, — are actually the same as those observed in the case of *rhodium*. But here the further complication occurs, that in the spectrogram at 1200° C. not only doublets, but also a number of *triplets* occur, the components here being indicated by s' and s; the central lines of the triplets are always the most intensive ones of the three. The data obtained are collected in Table IV. It must be remarked that in the case of the triplets, the coincidence of the lines produced in the case of rotation of the wire, be it with the satellites or with the other ones, is not in all cases as perfect, as it is in the case of *rhodium*; in most cases all three lines remain visible.

§ 9. *Platinum.*

Also *platinum*-wires show similar phenomena, when heated in a vacuum. Some results obtained at ordinary temperature and at 800° C. are reproduced in Table V. No triplets were observed here.

§ 10. The question now arises: how to explain these facts? Neither exhausting the camera, nor filling it with a gas, like air; nor any other modification in the way of experimenting, so as to avoid any possible stress in the wire, — appeared to alter the results mentioned before to any appreciable degree.

If from the best data available in literature about the thermal dilatation of these metals (HOLBORN and DAY for *platinum* and *palladium*; FIZEAU, VALENTINER and WALLOT for *rhodium*), we calculate the values for a_0 in the case of these metals, we find the following results:

Pt at 800° C.: $a_0 = 3.908$ Å; *Pd* at 800° C.: $a_0 = 3.885$ Å; at 1000° C.: 3.895 Å; at 1200° C.: 3.910 Å; *Rho* at 750° C.: $a_0 = 3.81$ Å; at 1000° C.: 3.83 Å; at 1400° C.: 3.85 Å.

In comparing these values with those calculated from our direct experiments, there can be no doubt about the fact, that in each case studied the *inner* component of each doublet or triplet corresponds to that value of a_0, which results from the *normal* thermal dilatation of the lattice; the outer satellite, on the other hand, corresponds to the original value of a_0 at room-temperature or a slightly higher one. In the case of the triplets, the central most intensive component corresponds to the dilatation at a temperature, somewhere between those of the two other components. These facts stamp the phenomenon observed as one of a very particular kind of "thermal hysteresis", which doubtlessly must intimately be connected as well with the process of recrystallisation going on at higher temperatures, as with the paratropic orientation of those enlarged crystallites with respect to the length-direction of the wire. There must be some reason, why a minor part of the crystallites present are impeded in their normal thermal dilatation by

TABLE V.

Platinum-Wire, drawn: diameter: 0.3 mm.

	At Ordinary Temperature.				At 800° C. (rotating wire).					
N⁰. of line:	2*l* in mm.:	Int.:	$sin^2 \theta$ (obs.):	$sin^2 \theta$ (calc.):	2l in mm.:	Int.:	$sin^2 \theta$ (obs.):	$sin^2 \theta$ (calc.):	λ:	Indices $\{h\,k\,l\}$:
1	92.73	3	0.1547	0.1536	92.03	1	0.1524	0.1501	β	(111)
2	103.11	6	0.1888	0.1874	101.82	3	0.1844	0.1840	α	(111)
3	108.25	3	0.2067	0.2048	107.19	4	0.2029	0.2001	β	(200)
4	120.45	6+	0.2513	0.2499	119.19	8	0.2465	0.2454	α	(200)
5	159.75	4	0.4117	0.4096	157.96	4	0.4073	0.4002	β	(220)
6	180.18	9	0.5004	0.4998	177.72	8	0.4894	0.4908	α	(220)
6A	—	—	—	—	180.70	2+	0.5023	0.4976	α	(220)
7	195.10	6	0.5649	0.5633	192.32	3	0.5529	0.5503	β	(311)
8	207.52	2	0.6181	0.6145	—		—	—	β	(222)
9	223.44	10	0.6842	0.6873	220.06	8	0.6704	0.6748	α	(311)
9A	—	—	—	—	223.20	1	0.6832	0.6841	α	(311)
10	238.89	7	0.7449	0.7498	235.28	2	0.7311	0.7362	α	(222)
10A	—	—	—	—	238.35	2	0.7429	0.7464	α	(222)
11	258.65	2	0.8162	0.8194	254.05	4	0.8002	0.8005	β	(400)

Radius of Camera: 57.35 mm. *Exposure:* 80 m.Amp. hours.
Iron-radiation: $\lambda_\alpha = 1.9366$ Å; $\lambda_\beta = 1{,}753$ Å. The lines are all measured on the Comparator.
The satellites also remain visible on rotating the wire.

$A = 0.06248.$
$B = 0.05121.$
$a_0 = 3.874$ Å.

Two lines more were visible at the very ends of the film; but they were not suited for accurate measurements.

$A = 0.06135.$ $A' = 0.06219.$
$B = 0.05003.$ $B' = 0.05097.$
$a_0 = 3.909$ Å. $a'_0 = 3.883$ Å.

Here the change in the relative intensities of some lines, e.g. of 2 and 3; 4 and 6; 7, 9 and 10; 10 and 11, is remarkable. The same occurs at 1000° C.; line 3 is about twice as intensive as 5 at this temperature.

the presence of the major part of the surrounding and parallelly orientated individuals, — which, in their turn, either freely can expand (doublets), or partly can do so, while others also remain behind (triplets) at some intermediate temperature. It is a remarkable fact, that the appearance of triplets at a given temperature seems to be limited to some lines, like (220), (311), (331), while the other lines at that same temperature only are transformed into doublets. Most remarkable, however, is, that in the spectrograms *no broad, smeared-out bands* are found, as beforehand would be expected, but *quite sharp lines,* forming doublets or triplets, although the heating of the wire in all cases has gone on during no less than 8 or 10 hours consecutively. If the duration of the heating is prolongated, the relative intensities of the satellites with respect to the other components are increased, in stead of being diminished, as one perhaps beforehand would expect.

The fact, that a wire after being kept at a temperature high enough to yield only irregularly distributed spots in the spectrogram, and after having been preserved for some months, again begins to show lines, — directly proves, that such a wire has reached a state, which at lower temperatures is an unstable one; it gradually, although extremely slowly, goes back to its original internal structure, which for a good deal consists of small crystallites arbitrarily orientated in space. The larger crystallites generated by the process of recrystallisation at higher temperatures, evidently at room-temperature partially crumble down into smaller individuals or loose their paratropic orientation. Also the other phenomenon: that such a heated wire again yields a normal spectrogram, as soon as it be rotated about its axis, — is an indication of the fact, that a more thoroughly regular orientation of the enlarged crystallites with respect to the length-direction of the wire really accompanies the process of recrystallisation at higher temperatures; which orientation, — in contrast to what has been stated by some other investigators, — evidently also partially and gradually gets lost at lower temperatures, if the wire only be preserved during a sufficiently long time. As to the orientation with respect to the length-direction of the wire, — this doubtlessly is, also in these cases, connected with the presence of gliding planes in the crystallites: *rhodium* and *palladium,* for instance, are so plastic, that even at ordinary temperature they cannot be ground in a mortar without being flattened out into thin layers. Most probably [111] and [100] are the principal paratropic directions in such wires, if drawn out at somewhat higher temperatures. The paratropic orientation of the crystallites composing the wire can, however, be no complete one, neither at ordinary, nor at higher temperatures; because on rotating the wire, constantly the lines (111), (311) and (331) occur and they belong to the most intensive ones: these diffraction-lines belong 1), however, neither to the zone [111], nor to the zone [100]. It must, therefore, be assumed that in such a drawn wire, at least a certain number of the composing crystallites preserve their arbitrary orientation in space besides the other

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1) The triplets: (110), (220), (221), (331), (332) belong to a zone with the zonal axis $[\bar{1}10]$; (111), (200), (300), (311), (222), (400), (422) to a zone with the axis $[01\bar{1}]$; triplets like: (110), (220). (200), (300), (400), (310), (420), also to a zone with the axis [001]; etc. etc.

ones. Perhaps this contrast between the two groups may something have to do with the retardation in the thermal dilatation observed.

Momentaneously no final explanation of the curious phenomena observed can yet be given. The investigations are, therefore, continued, especially with the purpose of elucidating the apparently *discontinuous* character of the effect.

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