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# THE OPTICAL SPECTRUM OF HAFNIUM

BY

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The present paper gives the detailed account of our measurements of the optical spectrum of hafnium which was announced in our preliminary note on this subject<sup>1</sup>. As well known, the element hafnium (Hf) of atomic number 72 was discovered in zirconium minerals by COSTER and HEVESY about a year ago<sup>2</sup>. Our investigations were started as early as possible during the progress of the work of COSTER and HEVESY on the concentration and isolation of hafnium. It was found that the spectrum of hafnium, in similarity with the spectra of the other elements in the same group of the periodic system of the elements, possesses a very great number of sharp lines in the visible and in the ultraviolet region. In our first letter to Nature it was moreover pointed out that this spectrum is quite different from the spectrum, ascribed in 1911 by URBAIN<sup>3</sup> to an element, celtium, having chemical properties very similar to those of the rare earth cassiopeium (or lutecium) with atomic number 71, and which was as-

<sup>1</sup> H. M. HANSEN and S. WERNER, Nature, March 10, 1923. In the meantime another preliminary list of some 20 strong lines in the region between 3500 and 4500 Å. U. has been presented on July 13 at the Gothenburg meeting of the Scandinavian naturalists (printed in Fysisk Tidskrift 21, p. 185, 1923) and later a fuller record of our measurements between 2500 and 3500 Å. U. has also been published (Nature, October 27, 1923).

<sup>2</sup> D. COSTER and G. v. HEVESY, Nature, January 20, February 24 and April 7, 1923, and G. v. HEVESY, Ber. d. d. chem. Ges., LVI, p. 1503, 1923.

<sup>3</sup> G. URBAIN, Comptes Rendus, 152, p. 141, 1911.

sumed by URBAIN and DAUVILLIER<sup>1</sup> to possess the atomic number 72. In a second letter to Nature<sup>2</sup> we have drawn attention to the fact that URBAIN's celtium lines are identical with certain lines in the spectrum of cassiopeium.

For the production of all our spectra we have used hafnium salts (hafnium oxide or hafnium ammonium double-fluoride) kindly prepared for us by Professor HEVESY and his assistants. As it is not difficult to separate hafnium from all other elements (including the rare earths) with the exception of zirconium, most of the preparations we have used contained zirconium as the only impurity; however, in some of them small traces of other elements, titanium, niobium, manganese and calcium were present. As the hafnium spectrum is much more difficult to excite than the zirconium spectrum, it is important to use very concentrated hafnium preparations to get the hafnium spectrum well developed. We have used therefore for the final exposures only preparations containing not more than from 1 to 4 per cent zirconium, according to X-ray analysis made by the method described by COSTER<sup>3</sup>.

The arc spectra were produced in an ordinary direct current carbon arc. In our first experiments, when we had only small amounts of hafnium salts at our disposal, we placed the salts on the cathode and, during the exposure, added potassium bifluoride. In this way we got rather intense spectra without wasting too much hafnium salt. In the later experiments we used exclusively hafnium oxide

<sup>1</sup> G. URBAIN, *Comptes Rendus* 174, p. 1349, 1922; A. DAUVILLIER, *C. R.* 174, p. 1347, 1922.

<sup>2</sup> H. M. HANSEN and S. WERNER, *Nature*, April 7, 1923. To this note we can add that already EXNER & HASCHER (1911) have found most of the celtium lines in the spectrum of element number 71.

<sup>3</sup> D. COSTER, *Z. f. Elektrochem.* 29, p. 344, 1923. *Chem. News*, August 3, 1923.

which was placed in the anode. In order to get intense hafnium spectra currents as high as 25 Ampères were used. The electrodes were commercial carbon electrodes, purified by repeated boiling in hydrofluoric and hydrochloric acid. The spark spectra were produced with a 40 cm induction coil, using a selfinduction coil of about 0.0005 Henry and a battery of Leyden-jars of a capacity of about 25000 cm. The spark electrodes were made of carbon, purified in the same way as the arc electrodes; before and during the exposure they were impregnated with a saturated solution of hafnium fluoride. Under these conditions the time of exposure with the grating for intense arc spectra was about 2 minutes, and for the red region 4 minutes; for spark spectra we had to expose from 1 to 1<sup>1</sup>/<sub>2</sub> hour. With the quartz spectrograph below 3500 Å. U. the arc was exposed about 15 seconds and the spark 3 minutes. A spectrum of pure zirconium which for the sake of comparison was always photographed on the same plate as the hafnium spectrum was produced in exactly the same way as the hafnium spectrum. It has been of great assistance to us, that HEVESY soon after the discovery of hafnium was able to supply us for this purpose with preparations of very pure zirconium, prepared from commercial zirconium by removing its hafnium content.

The spectral region from 2250 to 3500 Å. U. was photographed with a HILGER quartz spectrograph of largest size (Model E 1); the region from 2500 to 3500 Å. U. could be taken in a single setting of the spectrograph with a very fine definition over the whole plate; in the region below 2500 Å. U. the definition was also very good. For the remaining part of the spectrum from 3500 to about 7200 Å. U. a small ROWLAND concave grating of 1,25 m radius of cur-

vature was used in a mounting, which permitted the photographing of the whole spectrum in the first order and up to 6450 Å. U. in the second order in a single exposure. Here Kodak Portrait Films (Par Speed) and Panchromatic Films were used, the errors which could arise from irregular curvature of the film being eliminated in the way described below.

For the final measurements all our hafnium lines are measured against zirconium lines as standards. As we do not claim a greater accuracy than about 0,05 Å. U. in this preliminary investigation, we think it justified to use this method, which for our work has proved very suitable. As well known, the position of a line especially in a grating spectrograph can shift slightly with varying illumination, when only a part of the grating is illuminated, especially if the grating is not a very perfect one and not very perfectly adjusted. Also in a quartz spectrograph such shifts can occur due to aberrations in the lens. When working with an arc, changes in the illumination during an exposure are unavoidable, which may cause shifts between the spectrum to be measured and the comparison spectrum. In our method errors due to such shifts are excluded, since we use the zirconium lines in the hafnium spectrum itself as reference lines, so that any change in the illumination will affect all lines in the same way. The zirconium spectrum is, even if only 1 per cent zirconium is present, strong enough to give numerous well defined reference lines, and the zirconium spectrum is very well known, since BACHEM<sup>1</sup>, in the institute of KAYSER, has measured it against iron normals with great accuracy. In fact he claims an accuracy of 0,01 Å. U. through the whole spectrum with the excep-

<sup>1</sup> A. BACHEM: Das Bogenspektrum des Zirkons. Dissertation Bonn 1910.

tion of the region of longest wave lengths, where perhaps errors up to 0,03 Å. U. are possible; all his wave lengths are given to 0,001 Å. U. in international Å. U.

The comparison spectrum of pure zirconium which, as mentioned, was always photographed besides the hafnium spectrum was never used for measuring purposes, but only to identify the zirconium lines and also the lines due to impurities in the carbon electrodes. Great care has of course been taken to exclude lines due to impurities in the hafnium preparation itself. Every line has been compared with the "codex" in KAYSERS: *Handbuch der Spektroskopie*, and with the two "codices" in EXNER and HASCHEK: *Die Spektren der Elemente bei normalem Druck*, and in every case, where a coincidence was possible, the whole spectrum of the element in question has been examined. If then none of the strongest lines of this element, especially none of the most persistent lines ("raies ultimes" of GRAMONT) were present, the coincidence has been taken as accidental, and the line given as a hafnium line<sup>1</sup>. In a few cases we have, in our table below, added to a line the symbol of an element, as for instance (Mn). This means that the line in question is exactly or nearly coincident with a line belonging to the spectrum of this element, traces of which we have mentioned as present in some of the preparations used, but that the line is so much stronger relatively to the other observed lines of that element that we think it most probable that the line really belongs to the hafnium spectrum<sup>2</sup>.

<sup>1</sup> In this part of the investigation the material of GRAMONT a. o. collected in the new book of F. TWYMAN: *Wavelength Tables for Spectrum Analysis*, Hilger 1923, has proved very useful.

<sup>2</sup> We do not think it necessary to go into detail in regard to the remarks to our letter in *Nature* of March 10, put forward by B. BRAUNER

All our spectra are measured with a measuring microscope from HILGER, using only the part of the sledge which had been found sufficiently perfect. For calculating the wave length from the measured position we have used for the spectrograph the dispersion formula of HARTMANN with 3 constants, and for the grating a formula of second degree, i. e. also with 3 constants. The remaining corrections were found in a graphical way, but for the grating they could amount only to a few tenths of an Å. U. except near some of the edges of the films. As every line always has been measured on several exposures, and the edges of the films never had the same positions in two exposures, errors arising from the distortion near the edges are avoided. In this way, due to the large number of well known reference lines, which allowed the drawing of the curve for the remaining small corrections with great certainty, all errors from local curvatures of the film, or similar causes were eliminated.

In our preliminary note of March 10, we published 52 hafnium lines in the region between 2500 and 3500 Å. U. giving only the strongest of the lines, we had measured at that time (of intensity  $2\frac{1}{2}$  or more). All these lines (with one exception) are now confirmed, but the wave lengths of some of them must be slightly altered due to the greater material and more accurate measurements now available. In our letter to Nature we mentioned, that several of the

in "Chemistry and Industry Review", Sept. 14, 1923. He apparently believes that we have been ignorant as to the well known work of EXNER and HASCHER, and furthermore he ascribes a low accuracy to the measurements of BACHEM, which KAYSER in his "Handbuch" has given as by far the best zirconium measurements. He also has incorrect ideas as to the accuracy which can be reached with a "one prism spectrograph" and so in ascribing to our measurements a far too low accuracy, he can, of course, find casual coincidences between our hafnium lines and spectral lines of a number of other elements, etc.



strongest hafnium lines are present as weak lines in zirconium spectra measured by earlier investigators. This was to be expected, because all zirconium minerals and consequently all commercial zirconium preparations contain from one half to five per cent of hafnium. In fact, for the region of the zirconium spectrum where EXNER & HASCHEK's measurements are exhaustive we find almost all our stronger hafnium lines and also some of the weaker lines among their zirconium lines, especially among their spark lines, whereas BACHEM (l. c.) gives fewer of our lines; these latter are denoted in the table below with an asterisk. Until further investigations appear, these lines may be taken as the most persistent lines ("raies ultimes") of hafnium. Besides the marked lines, BACHEM in several places without giving any measurements mentions the presence of weak lines which probably are identical with others of our stronger hafnium lines.

A short time ago BARDET<sup>1</sup> has published a list of 82 lines belonging to the arc spectrum of hafnium in the region between 2300 and 3500 Å. U. He does not give any details concerning his method of producing the spectrum, or the concentration of his preparations. Nor does he state, and it cannot be inferred by comparing his and our wave lengths whether his lines are given in the international or in the Rowland scale. It is therefore sometimes difficult to decide whether a line in his table coincides with one of our lines or not. Some of his lines are given to 0,01 Å. U., others apparently only to 0,05 Å. U., but if we allow errors in his values up to several times 0,05 Å. U., it seems that nearly all his lines are present in our spectra. Yet of his two strongest lines, the only two which are denoted as

<sup>1</sup> J. BARDET, Comptes rendus, 176, p. 1711, 1923.

“forte”, we do not find the one, 2335,35 Å. U., in our plates, and this line can accordingly not be taken as a hafnium line. On the other hand he does not find all our stronger lines, not even all the strongest lines in our first table, and the relative intensities of his lines are rather different from ours. But as all his lines with the exception of 6 are stated as “moyenne”, “faible”, “extrêmement faible”, “à peine visible”, we think that his preparation has not been very concentrated, and it is not yet possible to conclude with certainty that the relative intensity of a line in the hafnium spectrum differs much according to the conditions of excitation, such as is the case with the zirconium spectrum<sup>1</sup>. Apparently no other investigations of the hafnium spectrum have as yet been published.

In the following table of the hafnium lines the wave lengths are given in international Å. U. in air. For each line its estimated intensity  $I$  is added, both in the arc and in the spark spectrum, using a scale of intensity from  $\frac{1}{2}$  to 6, 6 denoting very strong intensity, 5 strong, 4 rather strong, 3 not strong, 2 faint, 1 weak,  $\frac{1}{2}$  extremely weak,  $d$  diffuse. The difference between the arc and the spark spectrum is not very marked. Above 5100 Å. U. only the strongest lines in the spark spectrum have been observed, and the spark intensities given for these lines have only relative values and can be compared neither with the corresponding arc intensities nor with the spark intensities of shorter wave lengths. Above 6100 Å. U. only the arc spectrum could be observed. It must of course be borne in mind that due to the different sensibility of the photographic plates and films in different parts of the spectrum all statements of intensity have only a very limited value, and in-

<sup>1</sup> F. EXNER & E. HASCHKE, l. c., I. p. 4.

tensities for lines lying a greater distance apart cannot be compared at all.

With the exception of the few lines of wave length greater than 6400 Å. U. which are only measured in first order spectra and therefore given to 0,1 Å. U. all lines in the table are given to 0,01 Å. U., but, as mentioned above, errors of about 0,05 Å. U. are possible. For the longest wave lengths in the region taken with the quartz spectrograph, viz. from 3000 to 3500 Å. U. the error may be still a little larger. This also is the case in the regions, where the cyanogene bands are very strong, and where we only were able to give the strongest lines.

As to the weakest lines, we have not measured the lines which both in the arc and the spark spectrum showed an intensity smaller than 1. Of the weakest measured lines of intensity 1 we have preferred to give all lines which seemed to belong to the hafnium spectrum, even if some of them may prove somewhat doubtful, since weak lines may be of interest for the purpose of finding series relations.

*B. H.* in the table denotes a head of a hafnium band, falling off towards longer wave lengths.

$\lambda$	I		$\lambda$	I		$\lambda$	I	
	arc	spark		arc	spark		arc	spark
7240,8	5		6906,4	1		6713,5	4	
37,1	5		6858,7	3		6691,0	2	
7131,8	6		50,0	1		59,5	2d	
19,5	2		36,5	1		56,7	2d	
7063,7	5		26,6	3		47,0	4	
30,3	2		19,0	6		44,7	6	
6980,9	4		03,0	1		31,5	1d	
79,6	2		6789,4	6		28,1	1d	
37,2	1		54,6	5		24,4	2	
35,2	1		47,6	3		6587,2	4	
11,4	3		34,8	2		84,6	1	

$\lambda$	I		$\lambda$	I		$\lambda$	I			
	arc	spark		arc	spark		arc	spark		
6567,5	2		5902,91	6	3	5590,73	2	1		
58,0	3		5890,48	4		75,85	4 <sup>1/2</sup>	2		
56,6	2		86,28	1		52,10	6	4		
41,2	1		83,66	3	1	50,58	6	4		
6486,5	2		47,74	2		41,93	1			
78,7	1		45,86	3		38,07	4d	1		
71,5	1		42,22	4 <sup>1/2</sup>	1	30,28	2			
57,0	2		38,87	2		24,90	1			
49,9	2		17,43	2	1	24,37	4	3		
31,8	2		11,24	1		10,40	3	2		
09,56	2		09,50	3		10,10	3			
*6386,36	5		08,37	1		03,16	1			
38,16	3		07,17	1		5497,24	3	1		
18,38	1		5799,70	1		63,31	6	3		
11,78	2		96,26	1		52,88	5 <sup>1/2</sup>	2		
6248,92	4		88,11	1		44,03	4	2		
* 38,51	3		67,16	3	2	38,76	4 <sup>1/2</sup>	2		
16,80	3		65,96	2		35,77	2			
11,94	1		65,31	2d	2d	23,98	3	1		
10,74	3		48,71	3	2	04,46	4	1		
09,47	2		42,62	1d	1	5398,70	1d			
02,80	1		34,59	3	1	91,32	2d	1		
6192,48	1		20,12	3		B. H.	89,39	4 <sup>1/2</sup>	1	
85,15	5		19,20	6	4		83,06	2		
35,15	1		13,26	4	2		73,88	6	3	
18,20	2	1	5698,08	4	2	B. H.	71,02	1d		
6098,67	4 <sup>1/2</sup>	2	73,58	1	1		68,55	1		
54,09	2d	1	62,95	1			61,41	1		
43,22	3d	1	62,06	2		(Ti)	58,34	2		
16,78	3	2	(Mn)	54,54	3	1		54,74	6	2
5992,98	2	1		50,72	3	1		48,44	3	1
86,48	1d	1d	(Ti)	44,50	1			46,30	3	2
78,66	4	2		28,18	2			24,28	4	2
74,30	4 <sup>1/2</sup>	3		13,96	3			11,54	6	4
33,72	4	3		13,28	5 <sup>1/2</sup>	3		09,66	4	1
26,50	2			00,79	2			07,82	3	

<sup>1</sup> The symbol (Zr) means that we have observed the corresponding line also in our comparison zirconium spectrum, but so weak that the line also must belong to the hafnium spectrum, whereas the lines denoted by an asterisk and which (compare p. 9) have been measured by BACHEM as weak zirconium lines never could be detected in our comparison spectrum of hafniumfree zirconium.

$\lambda$	I		$\lambda$	I		$\lambda$	I		
	arc	spark		arc	spark		arc	spark	
5304,17	2		5058,09	3	2	4858,43	3	4	
5299,85	2d		51,31	2	1	50,62	3	3	
98,04	6	3	47,43	5	4	48,48	2	3	
92,76	2d		45,28	1	1	43,98	3	3	
90,78	1		40,79	6	6	37,24	5	5	
89,93	1		37,32	2	1d	34,18	4 <sup>1/2</sup>	3	
86,09	3		25,80	2	2	18,86	4	4	
84,62	1		21,09	3	2	17,20	3	4 <sup>1/2</sup>	
75,05	4	1	18,14	6	4 <sup>1/2</sup>	13,86	1	2	
64,92	4 <sup>1/2</sup>	3	00,56	2	2	11,14	2	3	
60,41	4	2	4999,59	5	4	(Ti) 09,24	2	2	
58,75	2		92,26	3	2	07,14	2	3	
54,38	2d		84,66	2	2	00,51	6	6	
47,07	4	2	76,92	2	2	4795,98	2	2	
44,60	3		75,20	6	5	90,72	3	4 <sup>1/2</sup>	
43,97	5 <sup>1/2</sup>	2	69,26	2	1	82,77	4	5	
08,85	3		65,30	2	2	77,16	1	2d	
5194,56	2		47,34	2	1	74,90	3	3	
87,75	4	2	45,32	4	3	73,73	4	4	
81,92	6	3	34,34	4 <sup>1/2</sup>	4 <sup>1/2</sup>	66,51	4	4 <sup>1/2</sup>	
76,16	1		33,88	1)		65,80	2	3	
70,22	4 <sup>1/2</sup>	2	20,88	2	2	60,53	2	3	
53,15	3	1	15,24	4	3	57,60	3	3	
31,56	1d		10,05	2	2	38,61	3	3	
28,50	4	2d	07,20	2d	1	35,62	3	3d	
14,36	1		06,29	1d	1d	21,74	3	3	
11,28	1		04,44	3	4	08,85	3	3	
06,55	2		03,02	2d	3	4699,70	3	4	
01,64	2		4896,36	3	3	99,02	4	4 <sup>1/2</sup>	
00,68	2		89,78	2d	1d	70,93	—	2	
5098,20	1	B. H.?	78,14	3	3	(Ca) 69,24	2	2	
93,84	4	2	B. H. 77,59	4 <sup>1/2</sup>	5	64,13	5 <sup>1/2</sup>	5 <sup>1/2</sup>	
90,86	2		72,95	3	3	59,21	—	2	
79,57	3	3d	B. H.?	65,44	2	3	55,18	6	5
75,90	2	2	63,29	4	5	52,08	2d	3d	
74,71	3	3	B. H. 61,52	2	1	50,61	2	3d	
71,18	2	1	60,58	1	1	48,34	—	2d	
63,12	1	—	59,24	4 <sup>1/2</sup>	5 <sup>1/2</sup>	42,24	4	3	

<sup>1</sup> This line has been observed with very varying intensity (from 1 to 4) in different exposures, but cannot be identified as due to an impurity.

$\lambda$	I			$\lambda$	I			$\lambda$	I	
	arc	spark			arc	spark			arc	spark
4622,70	4 <sup>1/2</sup>	5		4408,85	3	3		*4093,16	6	6
20,85	6	5		4385,46	1	2		83,33	4	4
19,46	2	2		79,18	2	2d		80,44	5	5
13,71	3d	3	?	67,91	4	5		67,81	2	3
08,10	4	4		65,37	3	3		66,20	4	4
05,76	3	4		56,32	5	6		64,78	2	2
4598,86	6	6		53,37	3	3d		62,85	4 <sup>1/2</sup>	5
97,94	3	3		52,59	3	3		57,45	3	2
86,24	—	3		50,52	4	6		50,90	3	3
73,78	4	4		49,77	3	3		50,62	3	3d
70,62	2	3		36,69	5	6		49,75	1	1
65,93	5	5		35,13	2	3		49,44	3	3
62,70	3	3d		34,63	3	4 <sup>1/2</sup>		47,97	3	4
47,76	—	2		30,30	4 <sup>1/2</sup>	4 <sup>1/2</sup>		44,38	3	3
46,96	2	2d		22,65	1	2		33,87	1	2d
44,00	3	4		20,65	4 <sup>1/2</sup>	5		32,28	4	4
43,00	2	2		18,15	4	4		29,18	3	3
41,73	1	1		03,59	3	3		20,26	3	3
41,28	1	3		4296,40	3	3		11,48	2	2d
40,88	4	4		72,82	4 <sup>1/2</sup>	5		08,44	2	3
35,32	2	3		69,66	4	4		07,34	2	3
33,15	5	5	(Ti)	63,40	4	4		03,76	2	2
24,66	—	3		62,70	3	3		3996,77	2	3
20,59	2	3		61,00	3	4		84,02	3	4
18,30	3	3		52,00	4	4	B. H.	79,34	3	4
4499,64	2	3		49,30	4 <sup>1/2</sup>	4 <sup>1/2</sup>		70,08	4	3
90,60	2	3		45,82	3	4		68,02	2	2
86,14	4 <sup>1/2</sup>	4 <sup>1/2</sup>		32,36	4 <sup>1/2</sup>	6		64,94	3	4
73,04	1	—		28,00	3	3		51,80	5	5
66,38	3	3		09,68	3	3		50,76	3	4
52,95	3	3		06,53	4 <sup>1/2</sup>	5 <sup>1/2</sup>		49,47	1	2
38,02	4	4	(Zr)	4177,47	3	4		45,31	2	2
32,94	1	2d		74,32	4 <sup>1/2</sup>	5		41,17	1	1
30,56	1	1		62,34	4	4		39,00	3	3
22,70	4	5		58,87	3	4		38,40	1d	2
22,24	2	2		45,75	3	4		35,67	3	3
17,85	3	4		36,36	2d	3d		31,78	2	2
17,34	4 <sup>1/2</sup>	6	(Ti)	27,75	4 <sup>1/2</sup>	5		31,33	3	4
16,14	2	2		13,53	4	4 <sup>1/2</sup>		27,57	2	4
15,05	—	2		04,24	2	3		26,40	3	3

B. H.

$\lambda$	I			$\lambda$	I			$\lambda$	I	
	arc	spark			arc	spark			arc	spark
3923,90	5	5		3698,32	2	2		3597,42	4 <sup>1/2</sup>	5
18,06	6	6		96,48	4	4		69,03	5 <sup>1/2</sup>	6
17,42	4	4		82,22	6	6		67,36	3	4
12,50	1d	1		81,35	3	3		64,28	3d	3d
09,18	3	3d		75,73	5	5		61,64	6	6
06,87	3	3		72,25	4	4		52,66	5	6
* 02,90	4d	4	(Fe)	66,72	2	3		48,79	3	3
3899,92	4	5		65,28	4 <sup>1/2</sup>	5		36,58	4	4
95,62	2	1		64,54	2	3		35,50	5	5
92,45	2	3		61,67	1	1		34,48	3	2
89,31	3	4		61,02	4	4 <sup>1/2</sup>		31,20	2	2
80,78	3	3		58,98	2	3		22,98	5	5
17,04	2	3	} Cyanogene band	54,20	3d	2d	B. H.?	21,56	2	2
00,39	4	4			51,78	4	4		18,72	3
3793,34	5	5	? }	50,47	3	3		13,26	3	3
85,39	5	5			49,06	4 <sup>1/2</sup>	4 <sup>1/2</sup>		11,74	1/2
77,73	5	5		48,31	3	3		06,82	3	3
47,50	3	3		45,78	1	1		* 05,20	6	6
46,80	4	4		44,29	6	6		03,57	3	3
44,97	3	3		37,58	3	3		3497,42	5	5
39,04	2	3		33,14	—	3		95,75	5	5
37,83	3	4		32,67	2	2		87,55	1/2d	3
33,80	4	4		30,83	4	4		79,20	6	6
26,48	3	3		27,79	3	2		72,38	5	5
19,28	6	6		22,42	2	3		67,59	3	2
17,80	5	5		19,98	3	3		62,66	4	4
08,85	2	2		17,68	3	3		41,85	3	2
05,38	4	4 <sup>1/2</sup>		16,86	5 <sup>1/2</sup>	6		28,38	5	5 <sup>1</sup>
01,12	5	6		3599,87	4 <sup>1/2</sup>	4	(Zr) *	19,18	5	4
3699,69	5	5		99,12	2	3		17,35	5	3

<sup>1</sup> The line 3438,25 given in our letter to Nature (October 27) has now been omitted. As this line is one of the strongest and ultimate zirconium lines the symbol (Zr) ought to have been added in the table in Nature, but was erroneously omitted in the final manuscript. The line was at that time considered also as a hafnium line, since this particular line in some exposures was somewhat stronger in the hafnium spectrum than in the zirconium comparison spectrum, whereas all other zirconium lines were much weaker in the hafnium spectrum. Yet we think, having now a larger material available, that this difference in behaviour is only accidental, and we think it best to omit this line.

$\lambda$	I			$\lambda$	I			$\lambda$	I		
	arc	spark			arc	spark			arc	spark	
3413,77	5	3		3220,60	4	5		3080,75	6	6	
12,34	3	1		17,16	5	5		76,86	2	3d	
10,16	5	6	(Zr)	06,69	—	2		74,79	4	4	
07,77	4	4		06,17	5	4		74,09	3	3	
* 02,44	4	3	(Ti)	03,72	3	4		72,92	6	5	(Ti)
*3399,80	6	6		02,15	1	2		69,16	3	3	
97,50	4d	3d		00,01	4	5	(Ti)	67,37	6	5	
95,00	3	4		3195,62	2	2		57,02	5	5	
89,78	5	5		94,20	6	6		55,45	4	3	
86,10	4	4		93,50	5	5		54,48	4	3	
84,67	5	4		89,69	4	4		50,74	5	4	
84,17	1d	3d		81,02	4	4		46,03	4	4	
78,88	4	3		79,48	1	2d		34,54	2	1	
66,71	4	2		76,86	6	6		31,14	5	6	
60,07	4	3		74,92	1	1		25,32	—	4	
58,90	5	3		72,93	5	6		24,71	—	4	
52,01	6	6	(Ti)	62,58	5	6	(Ti)	22,04	—	2	
32,72	6	6		59,81	5	5		18,28	5	5	
28,16	5d	5		56,63	5	5		16,75	6	5	
24,16	1/2	2		51,64	4	3		12,87	6	6	
17,95	5	6	(Ti)	48,45	4	4		11,21	2	3	
17,19	1/2	1		45,32	5	6		01,83	1	2	
12,84	6	6		40,77	3	4		00,10	5	5	
10,90	1	3d		39,68	3	4		2991,99	—	1	
10,23	5	4		37,54	3	3		90,81	—	3	
09,24	4	3d		34,76	6	6		84,06	—	3	
3298,94	3	2		31,81	—	5		82,72	5	4	
94,57	—	1		* 28,74	3	3		* 80,82	5	5	
91,03	4	3		26,30	2d	3		79,24	5	4	
89,71	1	1		23,89	1	1		77,59	4	4	
83,40	5	3		19,96	4	4		75,89	5	6	
80,00	5	5		16,97	3	4		75,36	1	1	
67,12	5	3		14,85	—	1		74,09	2	3	(Nb)
62,53	3	3		09,12	6	6		73,40	—	3d	
55,28	5	6		02,45	—	1		68,85	6	5	
53,68	6	6		01,40	6	6		67,24	3d	4	(Ti)
49,50	4	3		00,75	—	1		* 64,84	5	5	
43,38	4	2		3096,75	5	4		61,80	4	4	
30,09	3	2		92,23	4	4		58,02	4	4	
26,96	2	3		91,73	1	2		54,22	5	5	



$\lambda$	I		$\lambda$	I		$\lambda$	I	
	arc	spark		arc	spark		arc	spark
*2950,70	5	5	2850,11	3	3	2718,54	5	5
47,14	3	4	49,18	5	5	13,84	4	3
44,71	4	4	45,79	5	5	13,46	$\frac{1}{2}$	1
* 40,78	5	5	34,14	4	3	06,68	6	5
40,23	1	2	33,30	5	4	05,60	6	5
29,91	4	4	29,32	3	4	03,13	1	2
* 29,62	6	5	22,69	6	6	2697,05	2	2
26,42	1	3	* 20,22	6	6	(Ti) 88,33	2	1
24,62	3	3	(Zr) 19,75	4	3	85,17	3	4
19,57	6	6	18,94	4d	3d	83,37	5	6
18,61	5	4	17,70	5	3	78,34	1	2
* 16,51	6	5	16,09	1	2	77,55	2	3
13,15	$\frac{1}{2}$	1	14,79	3	3	76,56	2	3
12,75	1	1	14,46	4	4	71,18	3	4
09,87	5	5	(Ti) 13,86	4	4	68,98	5	4
* 04,80	5	5	12,31	2	2	68,26	4	3
* 04,40	5	5	09,59	1	1	65,94	5	5
*2898,75	5	4	08,00	5	5	61,85	5	5
* 98,27	6	5	2786,31	3	4	57,82	5	5
94,84	1	1	84,48	$\frac{1}{2}$	1	57,47	4	4
94,00	—	1	79,36	5	5	52,75	3	2
92,55	4	3	75,25	4	3	52,31	1	2
89,62	5	5	(Mn) * 74,04	5	4	49,09	3	4
87,53	4	3	(Ti) * 73,39	6	6	* 47,27	6	6
87,13	4	4	72,98	3	3	42,70	5	3
85,49	3	4	72,33	3	4	* 41,39	6	6
79,11	4	4	70,44	4	4	* 38,68	6	6
76,34	5	5	66,95	4	3	36,96	4	3
73,63	3	2	64,53	$\frac{1}{2}$	1	35,77	3	4
67,77	1	2	62,69	4	3	26,92	3	4
* 66,36	6	6	61,65	5	4	22,72	6	6
* 63,37	3	2	56,92	3	4	20,91	1	2
* 61,70	6	6	51,84	5	5	16,60	4	3
* 61,04	5	6	(Nb) 43,61	4	3	14,27	1d	2
60,57	3	3	* 38,74	5	6	13,59	4	5
60,32	1d	3	* 37,81	3	2	12,56	3	2
58,69	1	2	(Mn) 35,06	—	1	09,97	3	2
57,65	4	4	31,10	1d	2	08,42	3	3
51,22	5	4	(Ti) 29,08	4	3	07,27	2d	2
50,92	4	3	27,42	3	2	* 07,02	5	5

$\lambda$	I		$\lambda$	I		$\lambda$	I		
	arc	spark		arc	spark		arc	spark	
2606,38	5	5	2510,41	—	2	2400,77	4	4	?
02,86	3	3	02,65	4	3	*2393,78	4	5	
02,66	3	3	00,73	3	4	93,33	4	5	
2599,14	1	2	2497,01	5	5	93,16	2	3	
95,57	1d	2	95,12	1	3	83,53	1	1	
91,29	5	5	94,35	—	2	81,00	2	3	
82,48	5	5	* 81,38	2	3	80,30	4	5	
78,15	5	5	73,87	4	5	77,58	—	1	
76,81	5	5	69,15	4 <sup>1/2</sup>	6	65,97	2	2	
74,89	1	2	65,01	3	3	51,19	5	6	
73,90	5	5	64,18	5	5 <sup>1/2</sup>	47,42	5	5	
72,93	1	2	63,86	—	3	43,29	4	4	
71,68	5	6	60,45	6	6	37,30	3	4	
70,69	2	3	59,41	—	2	36,41	—	2	
63,61	4	5	(Mn) 55,16	1	2	32,92	2	3	
59,23	4	5	53,97	1	2	24,85	3	4	
51,37	5	6	53,31	3	4 <sup>1/2</sup>	23,22	3	4	
49,11	—	2	52,26	2	3	* 22,43	4	5	
48,97	—	1	49,40	4	4 <sup>1/2</sup>	21,12	3	4 <sup>1/2</sup>	
48,51	1	2	47,22	5	6	18,45	—	1	
48,17	4	4	41,02	1	2	13,42	—	1	
37,31	5	5	34,73	1	3	2298,32	—	2	
32,94	4	4	33,50	3	5	91,62	1	2	
32,11	—	1	28,94	3	5	84,54	1	2	
31,16	5	5	25,93	4	4 <sup>1/2</sup>	* 77,12	3	5	
21,47	3	4	(Nb) 17,64	5	6	73,10	2	3	
17,85	1	2	10,10	5	6	66,78	2	4	
* 16,86	6	6	06,40	3	4	66,49	1	3	
15,48	4	4	* 05,40	4 <sup>1/2</sup>	5 <sup>1/2</sup>	55,08	1	3	
13,00	6	5	04,54	2	3	53,95	2	4	
12,69	6	5	03,58	1	2				

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