Some Recent Work on Isotopes and Hyperfine Structure of Spectral Lines.

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THE chemical and physical properties of an element are in the main determined by its atomic number. All elementary substances having the same atomic number but different mass numbers constitute a group of isotopes and occupy the same position in the Periodic Table. According to this definition of an isotope, H^2 (deuterium) and H^1 (ordinary hydrogen) are to be considered as two isotopes of hydrogen. Here, however, the difference in properties between the two isotopes is more marked than with other isotopes. This difference results from the pronounced inequality in the masses of H^2 and H^1.

The isotopic constitution of elements has been investigated mostly by Aston, Dempster and Bainbridge with the aid of mass spectrographs, each using an instrument of his own design. In all these instruments a mass ray containing charged atoms of the element has to be produced. For the production of such rays the existence of suitable volatile compounds frequently becomes a necessary preliminary condition. The search for such compounds has retarded the successful isotopic analysis of several elements. Of such elements palladium, iridium, platinum and gold stand prominent.

HYPERFINE STRUCTURE OF SPECTRAL LINES.

Spectral lines which appear single in spectroscopes of low resolving power often exhibit a structure when instruments of high resolving power are used, *i.e.*, in place of a single line a group of lines with small differences of wave-lengths is seen. Pauli was the first to make a fruitful suggestion to account for the hyperfine structure. In the light of subsequent theoretical development the suggestion of Pauli is equivalent to attributing a spin to an atomic nucleus: the interaction of the resulting nuclear magnet of comparatively small magnetic moment with the rest of the atom considered as a magnet would have the effect of splitting multiplet levels into bunches of close levels, the resulting transitions giving rise to the observed hyperfine structure. Taking I to represent the nuclear spin moment and J, the resultant mechanical moment of the rest of the atom, there will result $2I+1$ or $2J+1$ hyperfine levels according as $J>I$ or $I>J$. It is found that only isotopes with odd mass numbers have a nuclear spin, the even isotopes having zero spin moment. Though the spin of the even isotopes is zero they do not give rise always to coincident spectral levels. The separation of the levels in any case due to the even isotopes is called even isotopic displacement (Fig. 1). In the case of an odd isotope for purposes of evaluating isotopic displacement the centre of gravity

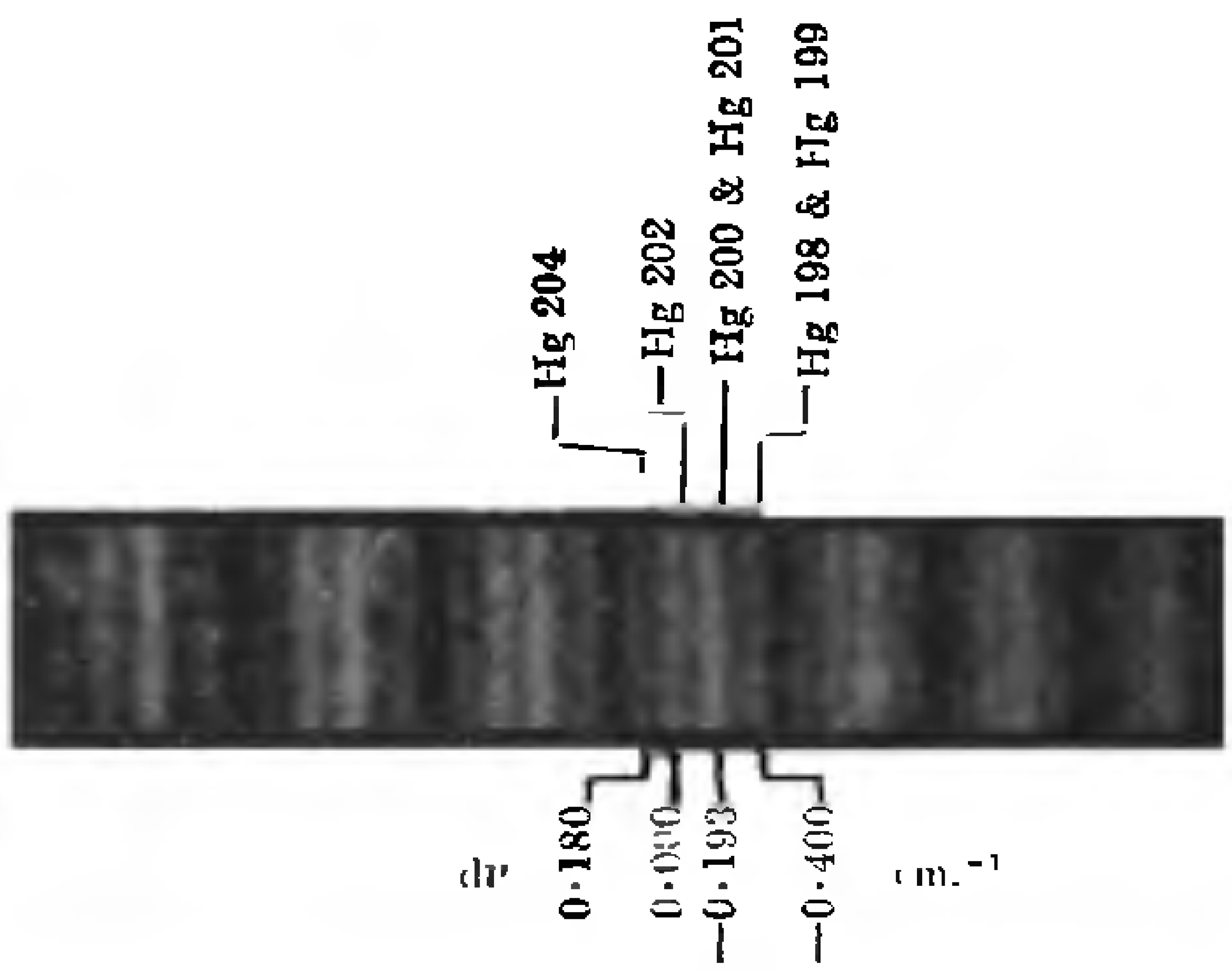

Fig. 1.
Structure pattern of Hg II 2262·33 Å ($5d^9\,6s^2\;{}^2D_{5/2}$ — $5d^9\,6s\,6p\;{}^2D_{5/2}$) showing isotope displacement.[1]

of the hyperfine levels is taken. This displacement of levels has an origin different from that due to a change in the mass of the nucleus in the expression for the Rydberg constant, the latter may be called a pure mass effect. It may be remarked that the doubling of the lines in the atomic spectrum of a mixture of H^2 and H^1 has its origin in the variation of the nuclear mass, in other words it is a pure mass effect.

In the laboratory of the author investigations on the hyperfine structure of the lines of the elements palladium, iridium, platinum and gold were undertaken with a view to determine their isotopic constitution and the nuclear spins of the odd isotopes. Sufficient theoretical and empirical information regarding the nature and origin of the hyperfine structure to enable one

[1] Venkatesachar and Sibaiya, "Hyperfine Structure of some Hg II lines," *Proc. Ind. Acad. Sci.*, 1934, **1**, 8.

to make such determination is available provided the structure patterns can be photographed without complications arising from self-reversal. Since the significant lines for this purpose arise from transition to the ground-level or levels very near it, avoidance of self-reversal becomes a matter of some difficulty. The following arrangement of apparatus has been evolved for the purpose as the result of a considerable amount of investigation.[2]

DESCRIPTION OF APPARATUS (Fig. 2).

The hollow cathode employed in this investigation is a double-walled copper cylinder hard-soldered at both ends with the inside hollow about 1 cm. in diameter and 6 cms. in length. Inlet and outlet tubes are provided so as to maintain a continuous flow of water in the space between the two cylinders during excitation. On to the shoulders cut in the outer copper cylinder are fitted pyrex glass tubings with a quartz window on one side and a ring anode on the other. The metal glass joint is rendered air-tight by Apiezon sealing wax and due to the continuous flow of water in the hollow cathode the joint continues to be air-tight under all conditions of discharge. The apparatus is set up *in situ* with a thin cylinder of the metal under investigation fitting tightly in the hollow cathode. The apparatus is next exhausted with a mercury diffusion pump backed by a Cenco Hyvac pump. The backing pump is then cut off and the activated charcoal is cooled by liquid air contained in a triple wall Dewar cylinder. Helium is now let in slowly, further purification being effected by its passage through the liquid air-cooled charcoal. When the required pressure of helium (about 1 or 2 mms. of mercury) is reached the supply is cut off. Requisite amount of helium is thus allowed to circulate continuously through the hollow cathode by the operation of the diffusion pump. The repeated passage of helium through the liquid air-cooled charcoal maintains its purity. A direct current dynamo of 1 kilowatt capacity is employed to send a discharge through the hollow cathode. For the excitation of the arc lines a discharge current of 150 mA at 1500 v. is found satisfactory. At this stage the hollow cathode glow is intense and is accompanied with little or no positive glow. The discharge conditions can be maintained steady for hours together by replenishing the liquid air from time to time.

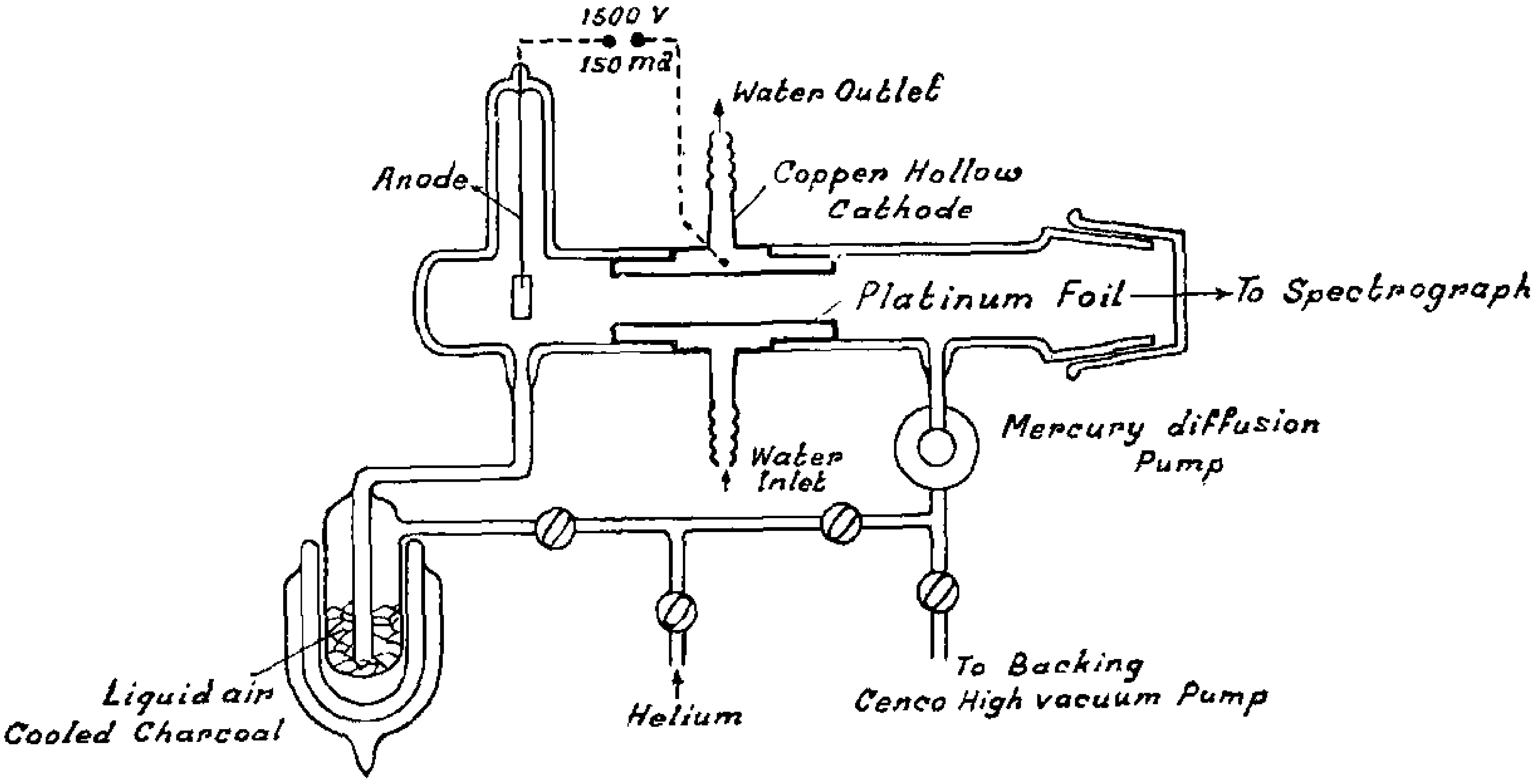

Fig. 2.
Hollow Cathode Source.[2]

The hollow cathode glow is concentrated on a Hilger Lummer Gehrcke plate of quartz (3·45 mms. thick and 20 cms. long) by means of a quartz lens carrying a double-image prism. One of the images is cut out and the light of the other, with its electric vector parallel to the plate, passes through. The pattern is focussed by a quartz achromatic lens on to the slit of a Hilger E1 spectrograph with a quartz train. The hyperfine structure patterns of the arc lines are

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[2] Venkatesachar and Sibaiya, "Platinum Isotopes and their Nuclear Spin," *Nature*, 1935, **136**, 65; *Proc. Ind. Acad. Sci.*, 1935, **1**, 955.

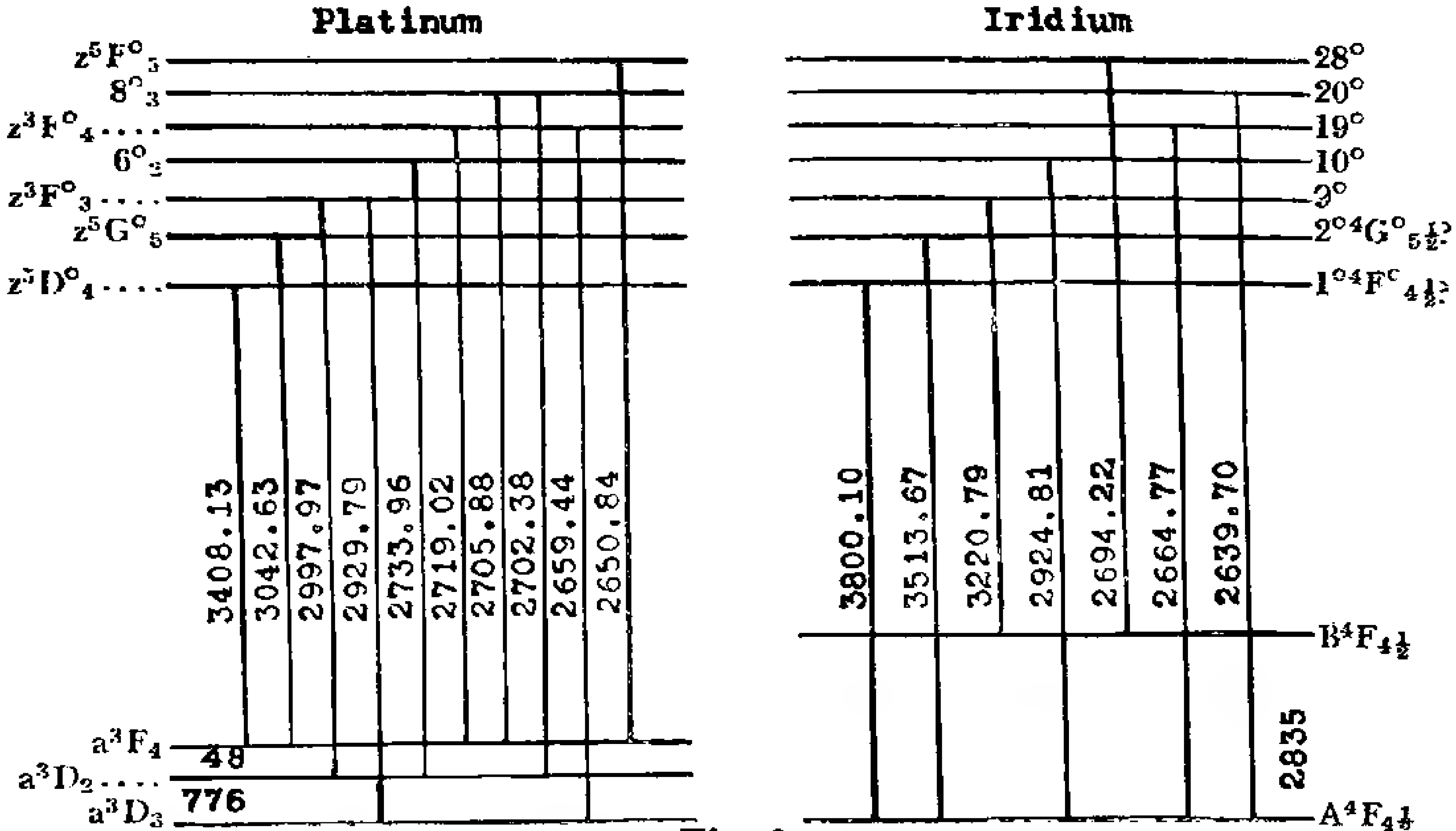

Fig. 3.

Arc lines of platinum and iridium analysed. (Not to Scale.)[4]

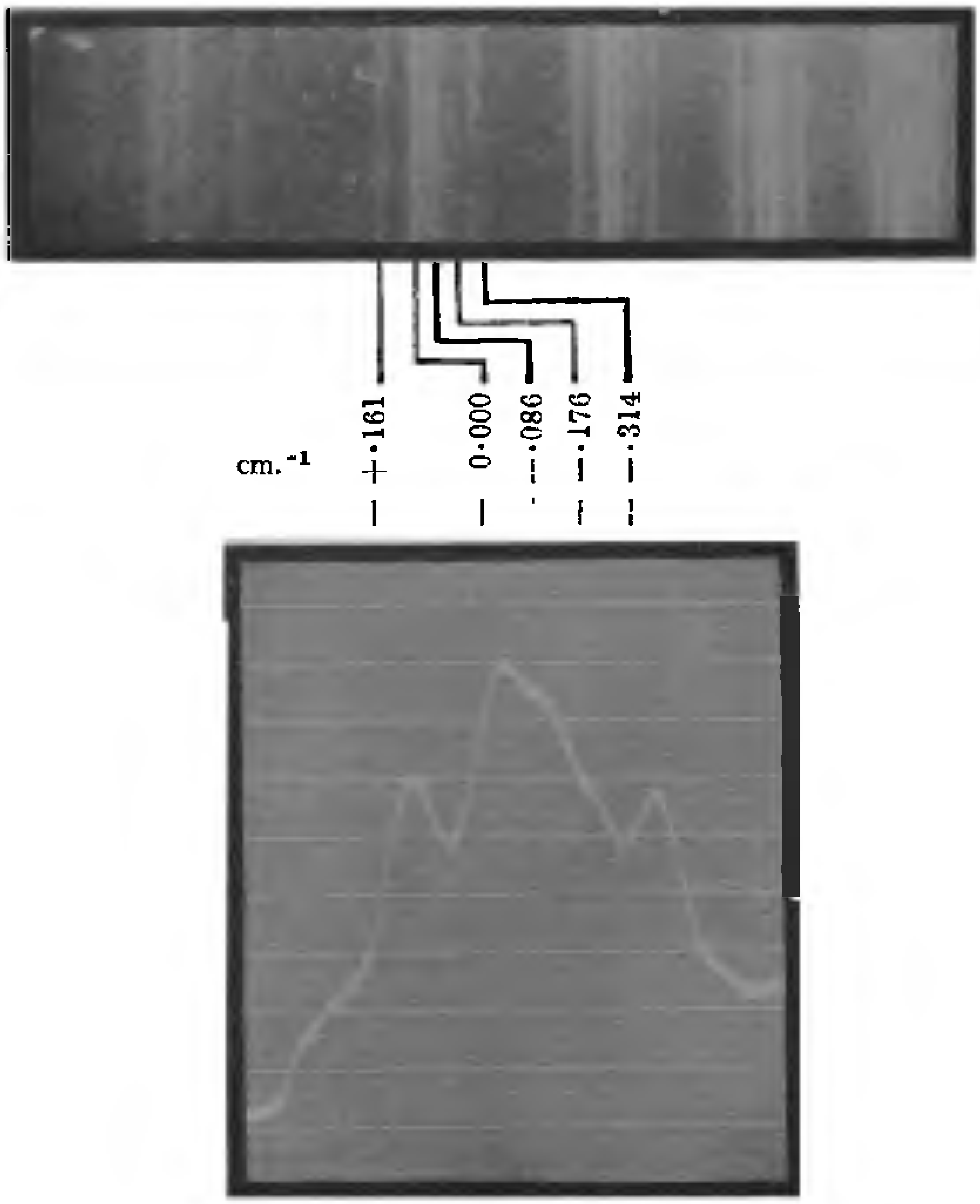

Fig. 4.

Structure Pattern of Pt I λ 3408·13 A with Microphotogram.[2,3]

photographed on hypersensitive panchromatic plates.

The advantage of the experimental arrangement used is that only the lines corresponding to transitions to the ground-level or to the levels close to it are excited without introducing complications arising from self-reversal. From the standpoint of hyperfine structure analysis these are generally the significant lines. For platinum and iridium the transitions giving rise to the lines excited are shown in the diagram above (Fig. 3).

Platinum.—The photograph of the structure pattern of the line Pt I 3408·13 Å ($a\,^3F_4 - z\,^5D^\circ_4$) has five components. In interpreting this pattern, the structures of other lines of platinum have been taken into account.[2] The result of the examination is that the extreme components on either side are due to the odd isotope of mass number 195 with a nuclear spin of ½ and the three inner components are due to the even isotopes of mass numbers 196, 194 and 192. The relative abundance as deduced from measurements on a microphotogram (Fig. 4) is as follows[3]:—

Mass number ..	196	195	194	192
Relative abundance	16	13	10	2

Dempster has recently published* the isotopic constitution of platinum obtained by using a spark discharge between platinum electrodes and a new type of mass-spectrograph. He finds five isotopes; according to him the isotopes 194, 195 and 196 are nearly equal in abundance, isotope 198 is distinctly less in abundance and isotope 192 occurs in very small amounts. One would infer from this that the component ascribed to 192 may be due to the isotope 198 recognised by Dempster. This, however, would give a negative isotope shift instead of a positive one. The centre of gravity of the lines due to an odd isotope lies usually nearer the line due to the lighter even isotope. This rule would be violated if the faint component in the pattern of 3408 Å is attributed to isotope 198. The isotopes 194 and 196 are however markedly unequal in abundance and cannot be said to be nearly equal as would appear from the communication of Dempster to *Nature*.

Iridium[4].—The structure pattern of the line Ir I 3513·67 Å ($5d^8 6s\,^4F_{4\frac{1}{2}} - 5d^8 6p\,^4G^\circ_{5\frac{1}{2}}$) is shown in the photogram (Fig. 5). The relative intensities and number of the hyperfine components in the patterns of the lines

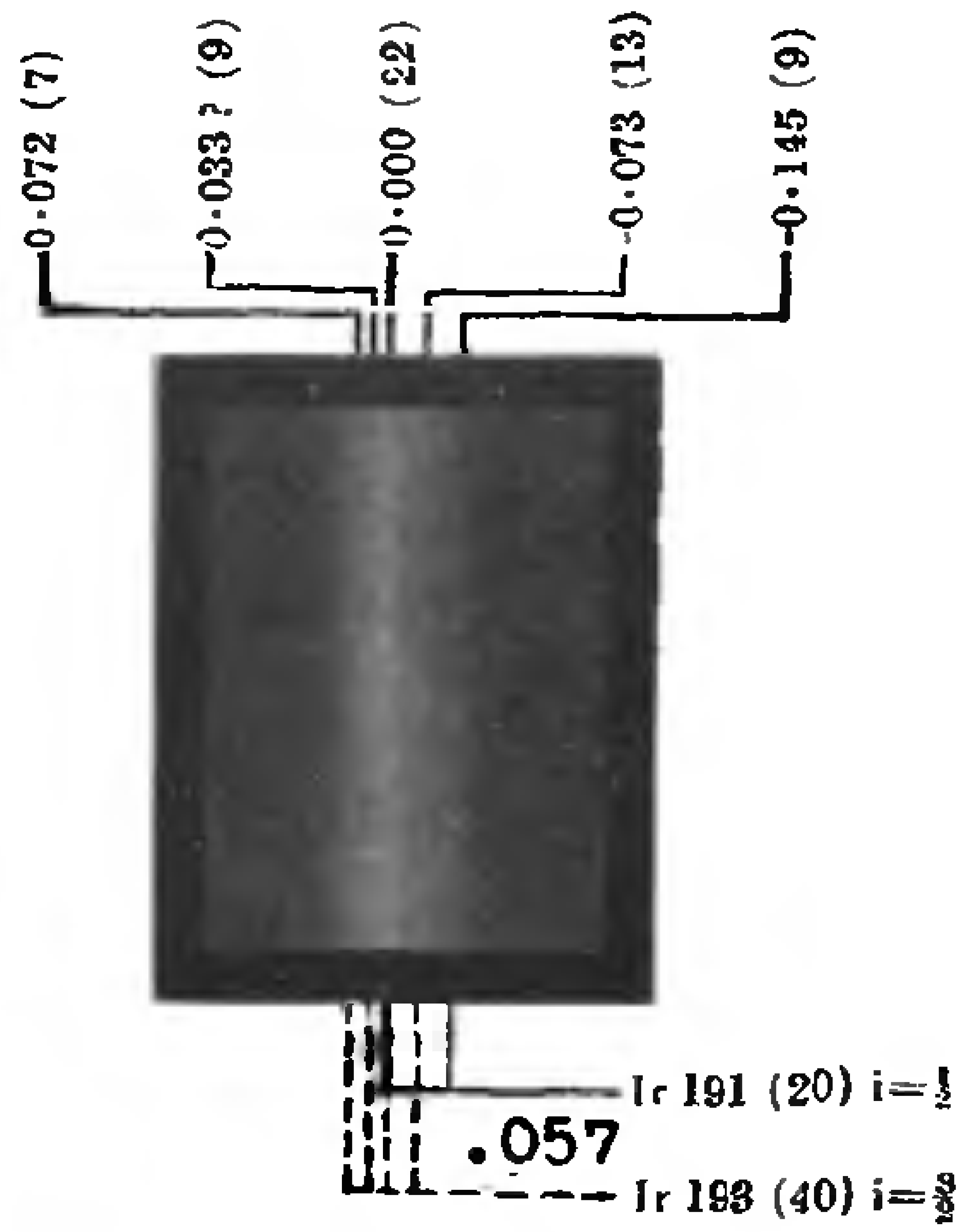

Fig. 5.
Structure pattern of Ir I λ 3513·67 Å.[4]

examined and the fact that iridium is an element of odd atomic number with its atomic weight in the neighbourhood of 193 leads to the unique interpretation that iridium consists of two isotopes 191 and 193 with a relative abundance of nearly 1 : 2. The nuclear spin of the isotope 191 is ½ and of 193, 3/2. Isotope 193 gives rise to the four dotted components *a*, *b*, *c* and *d* shown in the figure and isotope 191 gives rise to the two "full" lines A and B in the case of λ 3513·67 Å (Fig. 6).

Palladium.—Using the apparatus above described, Sibaiya who has collaborated with the author in this work has examined the hyperfine structure of the arc lines of palladium and gold.[5] Analysis of fourteen arc lines of palladium belonging to the transitions $5s\,^{1,3}D - 5p\,^{1,3}(P, D, F)$ has revealed an absence of structure in the lines leading to the inference that none of the levels concerned shows any even isotope displacement. An examination of known isotopes in the neighbourhood of palladium indicates that an odd isotope of mass 105 should exist in palladium. The hyperfine structure data show that the percentage abundance of this isotope exceeds 10%, and that its nuclear magnetic moment is small. The nuclear spin of Pd 105 cannot be fixed with certainty but the value ½ is probable. The absence of even isotope displacement in

[3] Venkatesachar and Sibaiya, "Isotope Abundance in Platinum," *Proc. Ind. Acad. Sci.*, 1935, **2**, 101.

* *Nature*, 1935, **135**, 903.

[4] Venkatesachar and Sibaiya, "Iridium Isotopes and heir Nuclear Spins," *Proc. Ind. Acad. Sci.*, 1935, **2**, 203.

[5] Sibaiya, "Hyperfine Structure in Selenium, Palladium and Gold," *Proc. Ind. Acad. Sci.*, 1935, **2**, 313.

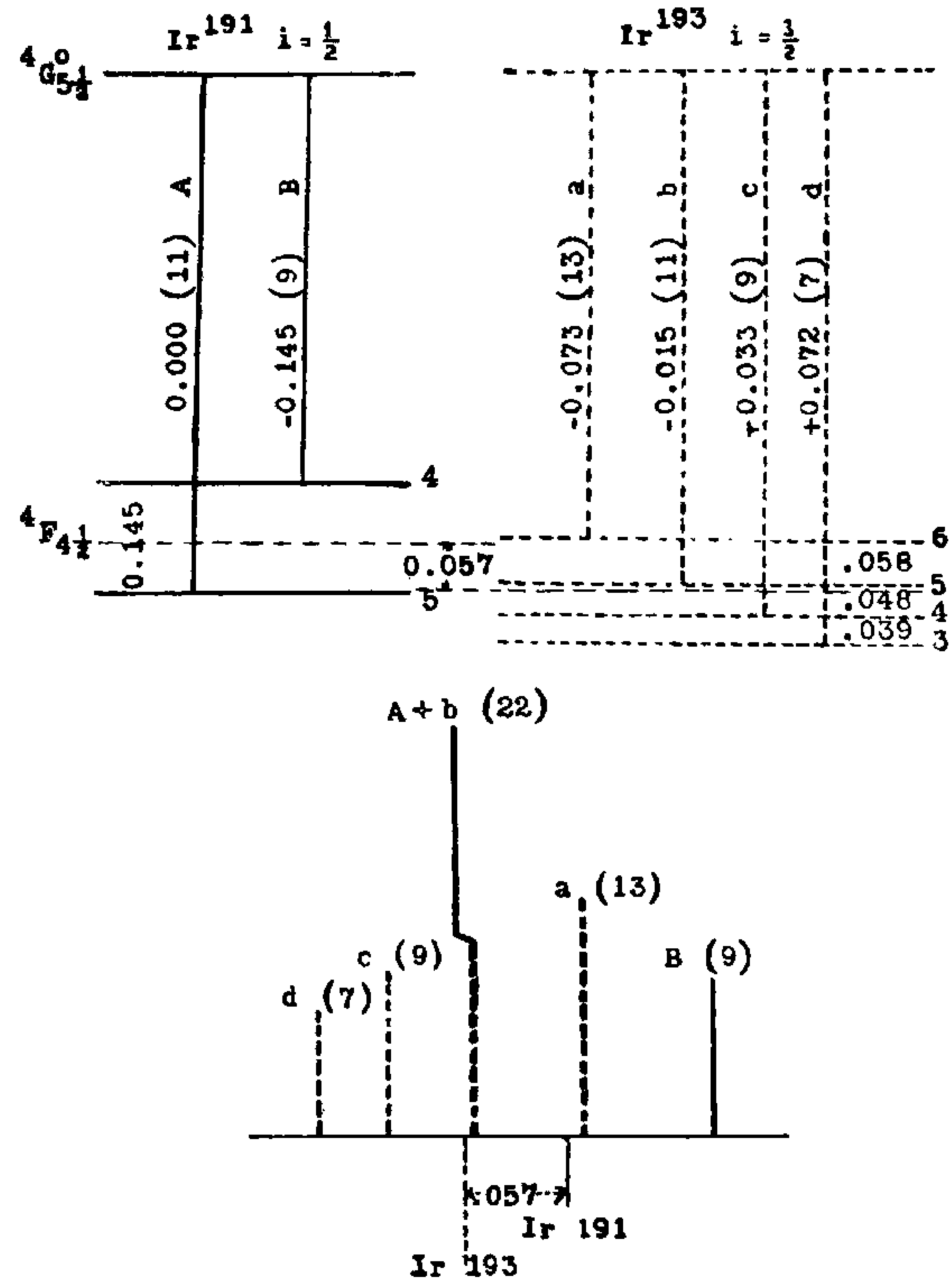

Fig. 6.

Ir I λ3513.67 Å ($5d^8 6s\ ^4F_{4\frac{1}{2}} - 5d^8 6p\ ^4G^o_{5\frac{1}{2}}$)[4]

palladium has rendered the determination of its isotopic constitution from a study of the hyperfine structure of its arc lines alone not possible. Recently Dempster has reported† six isotopes for palladium with masses 102, 104, 105, 106, 108 and 110. The four middle isotopes are nearly equal in abundance, while Pd 110 is markedly less abundant and Pd 102 is the least abundant in the group.

Gold.—Arc lines of gold involving the level $5d^9 6s^2\ ^2D_{5/2}$, which shows large isotope displacements in the isoelectronic spectrum of Hg II, have been analysed. The results show definitely that gold consists of a single isotope of mass 197 with a nuclear spin of $\frac{3}{2}$ and a nuclear magnetic moment of 0·20. The accepted chemical atomic weight of gold suggests however that gold must have another isotope of mass 199; known facts regarding the occurrence of odd isobares, along with the hyperfine structure data, point to the conclusion that Au 199 is entirely absent. Thus it follows that the chemical atomic weight of gold is too high. The more recent mass-spectrographic results of Dempster corroborate the above conclusions. The experimental value of the nuclear g(I) factor, *viz.*, 0·136, is in good agreement with Landé's theoretical value, 0·133.

In conclusion one may remark that platinum, iridium and gold are perhaps the only elements, whose isotopic constitution has been first revealed by a study of the hyperfine structure of the spectral lines.

† *Nature*, 1935, **136**, 65.