IRIDIUM ISOTOPES AND THEIR NUCLEAR SPINS.

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Iridium is practically the only element whose isotopic constitution has not so far been revealed by the mass-spectrograph. The present authors have arrived at the isotopic constitution of platinum from a study of the hyperfine structure of its arc lines.[1] Almost simultaneously Dempster[2] has published the isotopic analysis of this element with the aid of his mass-spectrograph. He has more recently studied the isotopes of palladium and gold,[3] whose hyperfine structure data obtained by one of us is under publication. Of the four elements, *viz.*, Pd, Ir, Pt and Au, mentioned by Aston[4] as having withstood attempts to arrive at their isotopic constitution by the use of the mass-spectrograph, iridium alone remained without any information in this respect. A study of the hyperfine structure of the arc lines of iridium was undertaken with the view of determining its isotopes as well as their nuclear spins.

The hollow cathode used in this investigation is exactly similar to the one used previously ;[5] instead of the platinum foil, an iridium sheet (supplied by Messrs. Johnson Matthey & Co., Ltd., London) was inserted in the hollow cathode. A discharge current of about 200 mA. at 1000 v. brings up the iridium arc lines arising from transitions to the low-lying levels with enough intensity to enable a study of their hyperfine structure. The advantage of the particular type of hollow cathode employed here lies in the fact that only a few lines corresponding to transitions to ground and near low-lying levels are excited without any reversal. Fig. 1 shows that in platinum as well as in iridium the lines for which the hyperfine structure study has been possible are those arising from transitions to a few of the deepest levels only. It is a matter of great advantage in hyperfine structure work to obtain such significant lines of an element intensely without any complications of self-reversal.

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[1] Venkatesachar and Sibaiya, *Nature*, 1935, **136**, 65.
[2] Dempster, *Nature*, 1935, **135**, 993.
[3] Dempster, *Nature*, 1935, **136**, 65.
[4] Aston, *Proc. Roy. Soc.*, 1935, **149**, 404.
[5] Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, **1**, 955-960.

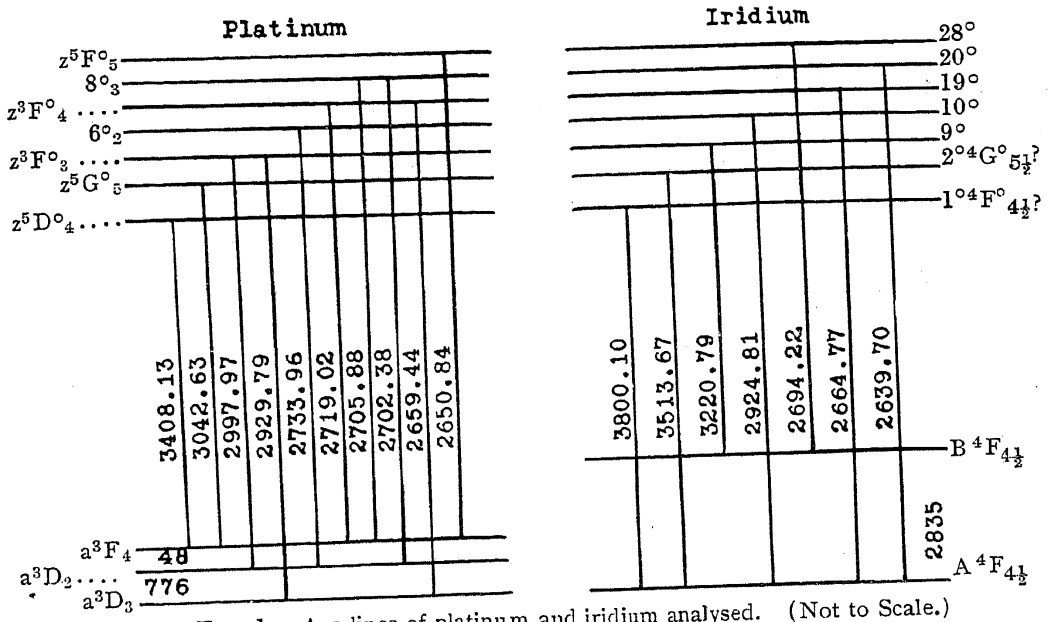


FIG. 1. Arc lines of platinum and iridium analysed. (Not to Scale.)

The spin separations even in the deepest levels of iridium are so small that many of the arc lines just appear widened and exhibit no structure. The three arc lines λλ 3800·10, 3513·67 and 2924·81 Å have a common lower level in the ground term $A\ ^4F_{4\frac{1}{2}}$ according to Albertson.[6] These three lines exhibit similar structure; but the components are so very close together that accurate measurements have been possible only in the intense line λ 3513·67 Å. The similarity in structure and the approximate equality of the component separations suggest that the structure in these lines must be attributed to a spin splitting of the ground term $A\ ^4F_{4\frac{1}{2}}$ with the upper levels unsplit. λ 3513·67 Å exhibits the following structure in cm.$^{-1}$ and the visual estimates of relative intensity are included in brackets:

IrI λ 3513·67 Å ($5d^86s\ ^4F_{4\frac{1}{2}} - 5d^86p\ ^4G^0_{5\frac{1}{2}}$)

$d\nu$ in cm.$^{-1}$ (Int.)	Remarks
+0·072 (7)	This component appears as a continuous patch between +0·072 and 0·000, indicating the presence of an expected satellite at +0·033 (9), *vide* Pl VIII.
0·000 (22)	Broad.
−0·073 (13)	
−0·145 (9)	

[6] Albertson, *Phys. Rev.*, 1932, **42**, 443.

Judging from the known isotopic constitution of elements with odd atomic numbers, iridium can have either *one* or *two* odd isotopes. If one assumes the existence of only one isotope, the chemical atomic weight 193·1 suggests that the isotope is Ir 193. No value of nuclear spin for Ir 193 even with the lower and upper levels both split can give the observed structure; this fact has been established by the method of Fisher and Goudsmit employed for explaining the structure of insufficiently resolved lines. Another alternative is that iridium should consist of two isotopes Ir 193 and Ir 195, because the chemical atomic weight is 193·1. Examining all the known odd isotopes of elements, it is found that 191 and 193 are the only two odd mass numbers missing in the neighbourhood of iridium; 195 has been previously shown to exist in platinum.[1,5] It appears further that the isotopes of an element with odd atomic number usually have no isobars in appreciable quantity. Since the isotope of mass 195 exists to an extent of about 30% in platinum,[7] the existence of Ir 195 in any quantity is very improbable. Remembering that no element with odd atomic number exhibits more than two odd isotopes, one need only consider 191 and 193 as the isotopes of iridium. Examining the data on the atomic weight determinations of iridium, it is found that there is great divergence in the values given by various investigators ranging from 192·59 to 193·40. In these circumstances much importance cannot be attached to the value of the atomic weight 193·1. In many cases where the mass-spectrograph has decided against the chemical atomic weight as in Tb, Tm, Au, Ta, etc., the chemical atomic weight has been in excess of the true value. The observed structure of the lines is accounted for uniquely by assuming the existence of the two isotopes 191 and 193 with the respective nuclear moments of $\frac{1}{2}\frac{h}{2\pi}$ and $\frac{3}{2}\frac{h}{2\pi}$. The

$\Delta i=0$			$\Delta i=\pm 1$					
		i			i			i
Cl	35, 37	$\frac{3}{2}$						
Cu	63, 65	$\frac{3}{2}$	Hg	199	$\frac{1}{2}$	Hg	201	$\frac{3}{2}$
Ga	69, 71	$\frac{3}{2}$						
Br	79, 81	$\frac{3}{2}$	Rb	87	$\frac{3}{2}$	Rb	85	$\frac{5}{2}$
Cd	111, 113	$\frac{1}{2}$						
Sn	117, 119	$\frac{1}{2}$	Sb	121	$\frac{5}{2}$	Sb	123	$\frac{7}{2}$?
Ba	135, 137	$\frac{3}{2}$						
Eu	151, 153	$\frac{5}{2}$	Xe	129	$\frac{1}{2}$	Xe	131	$\frac{3}{2}$
Re	185, 187	$\frac{5}{2}$						
Tl	203, 205	$\frac{1}{2}$	Ir	191	$\frac{1}{2}$	Ir	193	$\frac{3}{2}$

[7] Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, **2**, 101-103.

addition of two neutrons to the nucleus of the odd isotope of lower mass gives rise to an odd isotope of heavier mass with a change in nuclear spin of either 0 or ± 1; the change is 0 when the two added neutrons have opposite spin moments and is ± 1 when their spins have the same sign. Tamm and Altschuler[8] also consider that sometimes two neutrons do not form a closed shell with zero spin, but add up to give a spin of 1. The above table contains all the known cases where the nuclear spin change between two odd isotopes of an element is either 0 or ± 1.

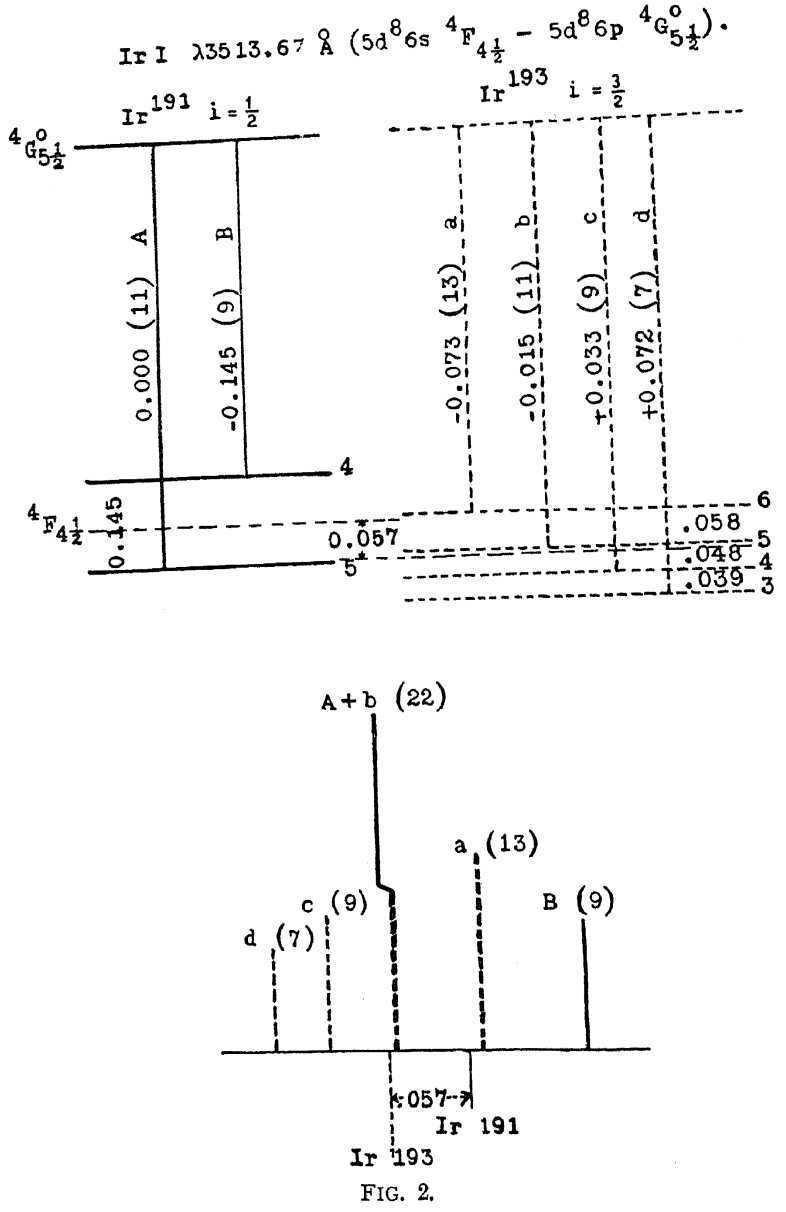
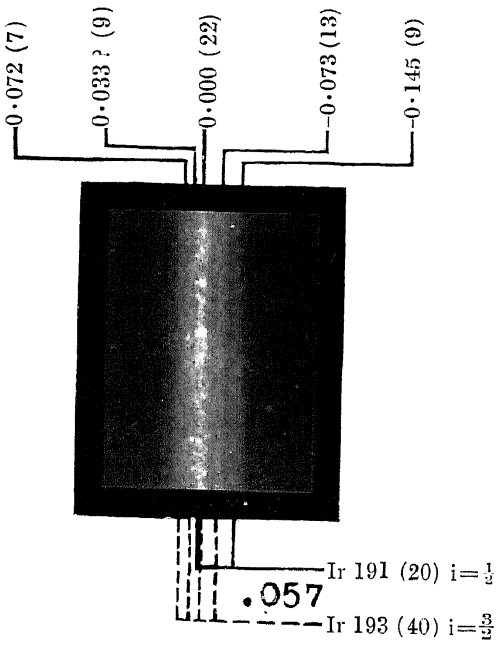


FIG. 2.

[8] Tamm and Altschuler, "*Ac*", *U.R.S.S.*, 1934, **1**, 455.


0·072 (7)
0·033 ? (9)
0·000 (22)
0·073 (13)
0·145 (9)
Ir 191 (20) i=½
·057
Ir 193 (40) i=3/2

The observed structure of λ 3513·67 Å is explained on the basis of two isotopes 191 and 193 with nuclear spins of $\frac{1}{2}$ and $\frac{3}{2}$ respectively in Fig. 2. The eye-estimates of the intensities of the components is consistent with theoretical expectations and give for the relative abundance of the isotopes 191 and 193 a ratio approximately equal to 1 : 2. The correct ratio however must await a microphotometric study of the structure pattern. The above estimate gives an atomic weight of 192·4, which is perhaps a little too low. There is no doubt however that the accepted chemical atomic weight is too high, and that the correct atomic weight of iridium must lie between 192 and 193. An accurate estimate of the relative abundance of the isotopes is further impeded by the uncertainty of the J-value of the ground term; Meggers and Laporte give it as $2\frac{1}{2}$ while Albertson gives it as $4\frac{1}{2}$. The ground term exhibits an isotope displacement of 0·057 cm.$^{-1}$ with the heavier isotope lying deeper as in the cases of copper and thallium.[9] The existence of this isotope shift favours the suggestion that the ground term of iridium is a $^4F_{4\frac{1}{2}}$ term as suggested by Albertson arising from an electronic configuration $5s^25p^65d^86s$ in preference to a $^2D_{5/2}$ term from $5s^25p^65d^9$ as given by Meggers and Laporte[10]. It is for this reason that the J-value of the ground term has been here assumed as $4\frac{1}{2}$ in calculations of intensity, intervals and isotope shift. The incompletely resolved patterns of a few other IrI lines 3220·79, 2694·22, 2664·77 and 2639·70 support the conclusions obtained above regarding the isotopes of iridium and their nuclear spin. The fine structure levels in $B^4F_{4\frac{1}{2}}$ of Albertson are regular in Ir 191 and inverted in Ir 193, while in $A^4F_{4\frac{1}{2}}$ the reverse is the case. The ratio of the nuclear magnetic moments of the two isotopes is therefore about −1·0.

Summary.

The hyperfine structure patterns of some of the significant arc lines of iridium have been photographed using as source a hollow cathode tube already described in a paper by the authors on the isotopic constitution of platinum. An examination of the hyperfine structure data of the iridium lines leads to the result that it consists of two isotopes with nuclear spins $\frac{1}{2}\frac{h}{2\pi}$ and $\frac{3}{2}\frac{h}{2\pi}$. A consideration of known facts regarding the occurrence of isotopes of different mass numbers in the various elements has led to the inference that the mass numbers of the two iridium isotopes are 191 and 193 with a relative abundance of nearly 1 : 2, the isotope with the higher mass number having the higher nuclear spin.

[9] Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, **1**, 13.

[10] Meggers and Laporte, *Phys. Rev.*, 1926, **28**, 660.