

HYPERFINE STRUCTURE IN SELENIUM, PALLADIUM AND GOLD.*

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Selenium (At. no. 34; At. wt. 79.2).

FOR purposes of classification of selenium spectra, the arc and spark lines of selenium have been mostly excited in tubes of various types with condensed or uncondensed electrical discharge through selenium vapour or between aluminium poles tipped with metallic selenium. A selenium arc either in vacuum or in an atmosphere of nitrogen has also been employed. Such sources however are not suited for hyperfine structure work, as the lines obtained are broad and diffuse. Moreover most of the prominent arc lines of selenium lie either in the near infra-red or in the extreme ultra-violet, thus rendering their analysis by high resolving power apparatus specially difficult. Some intense spark lines of selenium lie in the visible region; but under the conditions employed for their emission in discharge tubes, the broadening of the lines renders such sources unsuitable for hyperfine structure study. The apparatus used, the essential part of which is a water-cooled hollow cathode, is the same as that employed by Prof. Venkatesachar and the author in their investigation on the isotopic constitution of platinum.¹ The selenium powder took the place of the platinum foil in the tubular space of the cathode (Pl. XV, Fig. 1). For experimental details the above paper must be consulted.

Of the seventeen lines of selenium here examined, only two are arc lines and the remaining fifteen belong to the first spark spectrum of selenium.

Se I LINES.

λ in Å.U.	Classification
4739.03	5s(4S) 5S ₂ —6p(4S) 5P ₂
4730.79	5s(4S) 5S ₂ —6p(4S) 5P ₃

* An oral communication of the main results contained in this paper was made at the Meeting of the Academy on 19th June 1935.

¹ Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, 1, 955.

The spectral classification of the arc lines is taken from Meissner, Bartelt and Eckstein.²

The spark lines here analysed are listed below; they have been classified differently by Bartelt³ and Krishnamurthy and Rao⁴:

Se II LINES (λ in Å.U.).

5305.41	5143.15	4840.61
5253.69	5068.67	4763.66
5253.13	4992.88	4648.40
5227.53	4975.76	4618.75
5175.97	4844.98	4602.32

All the above Se I and Se II lines are sharp and single (Pl. XV, Fig. 2). Selenium, according to Aston, has the following isotopic constitution:

Mass number	74	76	77	78	80	82
Percentage abundance	0.9	9.5	8.3	24.0	48.0	9.3

The even isotopes of selenium amount to 91.7%; the single odd isotope Se 77 is present only to the extent of 8.3%. It is therefore difficult to observe the components arising from a splitting of the gross multiplet levels due to a nuclear spin in Se 77. In each of the lines examined the observed component is to be ascribed to the even isotopes whose total abundance is 91.7%. Even isotope displacement, if any, could have been detected because Se 80 (48%) is twice as abundant as Se 78 (24%), the other two Se 76 and Se 82 being nearly equally abundant (9.4%). The absence of structure revealed by the lines indicates that none of the levels here observed shows any even isotope displacement and that all the even isotopes of selenium have nuclear spins equal to 0. From an examination of two lines in the arc spectrum of selenium Rafalowski⁵ has come to the same conclusion. Though the absence of structure leads to the conclusion that the nuclear magnetic moment of Se 77 is small, there is however a faint component ($\sim +0.093 \text{ cm.}^{-1}$?) that accompanies 5227.53 Å, a fact which can be most simply explained by ascribing a nuclear spin of $\frac{1}{2} \frac{h}{2\pi}$ to the odd isotope 77.

² Meissner, etc., *Zeits. f. Physik*, 1934, 91, 432.

³ Bartelt, *Zeits. f. Physik*, 1934, 91, 450.

⁴ Krishnamurthy and Rao, *Proc. Roy. Soc.*, 1935, 149, 56.

⁵ Rafalowski, *Acta Physica Polonica*, 1933, 2, 119.

Palladium (At. no. 46 ; At. wt. 106.7).

Since the isotopic constitution of palladium by the mass-spectrograph method has not been found,† the hyperfine structure of the palladium lines is here studied with the object of determining, if possible, the isotopes of palladium. A thin palladium foil‡ is introduced into the hollow cathode, which is excited by a D. C. 1 kilowatt generator with a discharge current of 200 mA at 1700 v. The following arc lines were analysed; the classification of the lines is taken from Shenstone⁶:

Pd I LINES.

λ in Å.U.	Classification
3242.72	$5s\ ^3D_3-5p\ ^3D_3^{\circ}$
3251.66	$5s\ ^3D_1-5p\ ^1P_1^{\circ}$
3302.15	$5s\ ^3D_1-5p\ ^3D_1^{\circ}$
3404.60	$5s\ ^3D_3-5p\ ^3F_4^{\circ}$
3421.24	$5s\ ^3D_2-5p\ ^3D_2^{\circ}$
3433.44	$5s\ ^1D_2-5p\ ^1P_1^{\circ}$
3441.40	$5s\ ^1D_2-5p\ ^1D_2^{\circ}$
3460.76	$5s\ ^3D_3-5p\ ^3F_3^{\circ}$
3481.17	$5s\ ^3D_1-5p\ ^3F_2^{\circ}$
3489.79	$5s\ ^1D_2-5p\ ^3D_1^{\circ}$
3516.95	$5s\ ^3D_2-5p\ ^3P_1^{\circ}$
3553.10	$5s\ ^1D_2-5p\ ^1F_3^{\circ}$
3609.56	$5s\ ^3D_2-5p\ ^3F_3^{\circ}$
3634.70	$5s\ ^3D_3-5p\ ^3P_2^{\circ}$

Vide Pl. XVI, Fig. 3.

† After this paper was read before the Academy, Dempster (*Nature*, 1935, 136, 65) reports that his mass-spectrograph has revealed six isotopes for palladium with masses 102, 104, 105, 106, 108 and 110; the four middle isotopes are about equally abundant, while the less abundant Pd 110 is more abundant than Pd 102.

‡ Kindly lent by Sir C. V. Raman, Kt., F.R.S., N.L.

⁶ Shenstone, *Phys. Rev.*, 1930, 36, 669.

None of the lines above shows any isotope displacement of the even isotopes. It has therefore not been possible to determine the even isotopes of palladium or their relative abundance. A study of the known isotopes of elements in the neighbourhood of palladium shows that an odd isotope of mass number 105 should be expected to exist in palladium. Though most of the lines here examined are single, the existence of a close component ($\sim +0.100 \text{ cm.}^{-1}$) in a few lines renders it probable that the isotope Pd 105 with an abundance of the order of 15% has a nuclear spin $\frac{1}{2} \frac{h}{2\pi}$. The general absence of structure however indicates that the nuclear magnetic moment of Pd 105 is small. These observations in selenium and palladium support the conclusion that all nuclei with even atomic number and odd mass number have only small positive or negative magnetic moments.⁷

Gold (At. no. 79; At. wt. 197.2).

Frisch⁸ has concluded that the resonance line of gold $\lambda 2676 \text{ \AA}$ ($6^2S_{\frac{1}{2}} - 6^2P_{\frac{1}{2}}$) is single; Ritschl⁹ finds on the other hand that the two resonance lines $\lambda 2676 \text{ \AA}$ and 2428 \AA ($6^2S_{\frac{1}{2}} - 6^2P_{\frac{1}{2}, \frac{3}{2}}$) are each double. The satellites are observed at $+0.224 \text{ cm.}^{-1}$ and at $+0.221 \text{ cm.}^{-1}$ in the two lines respectively. The existence of this structure has been attributed by Ritschl to a nuclear spin of $\frac{3}{2} \frac{h}{2\pi}$. Since the two above lines are resonance lines, self-absorption in the source by normal gold atoms can produce a doubling of each of the resonance lines. The present work has been undertaken with the object of deciding between these conflicting results; it has been definitely shown that Ritschl's analysis of the resonance lines is correct. Wulff¹⁰ has reported that his results agree with those of Ritschl; but it has been remarked that a nuclear spin value of $\frac{5}{2}$ satisfies the interval rule better in a number of levels. In the present work the lines involving levels known to show isotope shift in the isoelectronic Hg II spectrum¹¹ are analysed, and it is concluded that gold consists of a single isotope of mass 197.

A hollow cathode made from a sheet of copper-gold alloy (containing about 0.5% gold) was first employed. $\lambda 2676 \text{ \AA}$ exhibited two components of nearly equal intensity; the possibility of this doubling arising out of self-reversal could not be ruled out. Hence the water-cooled hollow cathode previously described¹ was gold-plated on the inside; an examination of $\lambda 2676 \text{ \AA}$ revealed again the same two components. If the observed doublet

⁷ Grace, *Phys. Rev.*, 1933, 44, 362.

⁸ Frisch, *Zeits. f. Physik*, 1931, 71, 92.

⁹ Ritschl, *Naturwiss.*, 1931, 19, 690.

¹⁰ Wulff, *Phys. Rev.*, 1933, 44, 512.

¹¹ Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, 1, 8.

structure is not caused by any reversal, it was argued that under suitable conditions of excitation each of these components would be reversed and four lines could be observed. A thin gold sheet was therefore introduced into the hollow cathode and a discharge current of 200 mA at 1000 v. from a D. C. 1 kilowatt generator was maintained. Pl. XVI, Fig. 4 shows the doubling of each of the two real components of λ 2676 Å due to self-reversal in the source. Thus it has been established that λ 2676 Å of gold consists of two components, *viz.*, 0.000 and +0.223 cm.⁻¹, with an intensity ratio of about 3 : 2. The satellite separation has been computed from all the above methods, including the one giving self-reversed components.¹²

The nuclear spin of gold has to be deduced from the intensity ratio of the components; it is however difficult from visual estimates of intensities to decide between the nuclear spin values $\frac{3}{2}$ and $\frac{5}{2}$, which demand the intensity ratios to be 1.67 and 1.40 respectively. The balance of evidence is in favour of the value $\frac{3}{2}$ because the following lines involving the metastable level $5d^9 6s^2 \ ^2D_{\frac{5}{2}}$ have the appearance of incompletely resolved flag patterns containing four components; nuclear spin values of $\frac{3}{2}$ and $\frac{5}{2}$ should yield four and six components respectively.

λ in Å.U.	Classification	Total width in cm. ⁻¹	Interval factor of $\ ^2D_{\frac{5}{2}}$
3029.22	$5d^9 6s^2 \ ^2D_{\frac{5}{2}} - 5d^9 6s6p \ ^2F_{\frac{7}{2}}$	0.163	0.018 cm. ⁻¹
2748.26	$5d^9 6s^2 \ ^2D_{\frac{5}{2}} - 5d^9 6s6p \ ^4F_{\frac{7}{2}}$	0.165	

The hyperfine levels in $\ ^2D_{\frac{5}{2}}$ are inverted.

One would expect that if gold should consist of two isotopes 197 and 199 as is suggested from its chemical atomic weight, the above lines should show the structure patterns due to the two isotopes separately. This is necessary because the $5d^9 6s^2 \ ^2D_{\frac{5}{2}}$ level in the isoelectronic spectrum of Hg II shows large isotopic displacement. The photographs of the hyperfine structure patterns of λ 3029 Å and 2748 Å are so well exposed that even if Au 199 should exist to the extent of about 5% its presence could not have escaped notice. It must be concluded that gold consists of a single isotope of mass 197 and that its accepted chemical atomic weight is too high. Further support to this conclusion is given by the fact that an odd isotope of an element with odd atomic number has no isobare in appreciable quantity;

¹² Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, 1, 321.

Au 199, if it should exist, would be an isobare with Hg 199 (16.45%). The following table gives the percentage abundance of isobares with odd mass numbers in the heavy elements.

At.No.	Element	Percentage abundance of odd isobares				
75	Re	187 (61.8%)				
76	Os	187 (0.6%)				
79	Au		197 (100%)			
80	Hg		197 (0.01%)	203 (0.006%)		
81	Tl			203 (29.4%)	205 (70.6%)	
82	Pb			203 (0.04%)	205 (0.03%)	209 (0.85%)
83	Bi					209 (100%)

Thus Au 199, if it does exist, must be present to an extent not exceeding 1% and probably it is entirely absent,* because whenever an element with odd atomic number contains two odd isotopes they will exist in comparable quantities.

The nuclear $g(I)$ factor can be computed from Goudsmit's formula for a penetrating s -electron¹³:

$$g(I) = \frac{3a}{8R\alpha^2} \times \frac{n_0^3}{Z_i Z_0^2} \times \frac{1838}{K(j, Z_i)}$$

For the normal $6s^2 S_{1/2}$ state of gold $a = 0.112 \text{ cm.}^{-1}$, $n_0 = 1.214$ and $K(j, Z_i) = 2.2$; and the $g(I)$ value becomes 0.136 while the magnetic moment of the nucleus is 0.20. White¹⁴ gives the nuclear magnetic moment as 1.8 after Fermi and Segre¹⁵; Schüler¹⁶ however obtains the value 0.15 for the $g(I)$ factor. My calculated value of 0.136 for the $g(I)$ factor agrees well with the theoretical value 0.133 of Lande.¹⁷ Using Goudsmit's formulæ for the

* More recently, Dempster (*Nature*, 1935, 136, 65) has obtained the same result with the aid of his mass-spectrograph.

¹³ Goudsmit, *Phys. Rev.*, 1933, 43, 636.

¹⁴ White, *Introduction to Atomic Spectra*, 1934, p. 372.

¹⁵ Fermi and Segre, *Zeits. f. Physik*, 1933, 82, 729.

¹⁶ Schüler, *Zeits. f. Physik*, 1934, 88, 323.

¹⁷ Lande, *Phys. Rev.*, 1934, 46, 477.

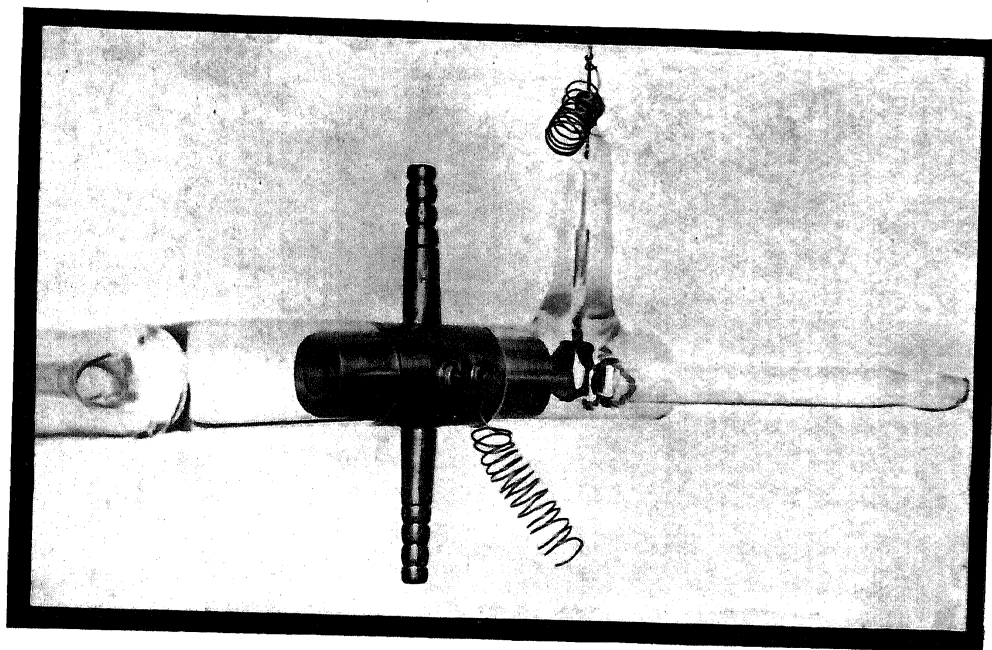


FIG. 1.

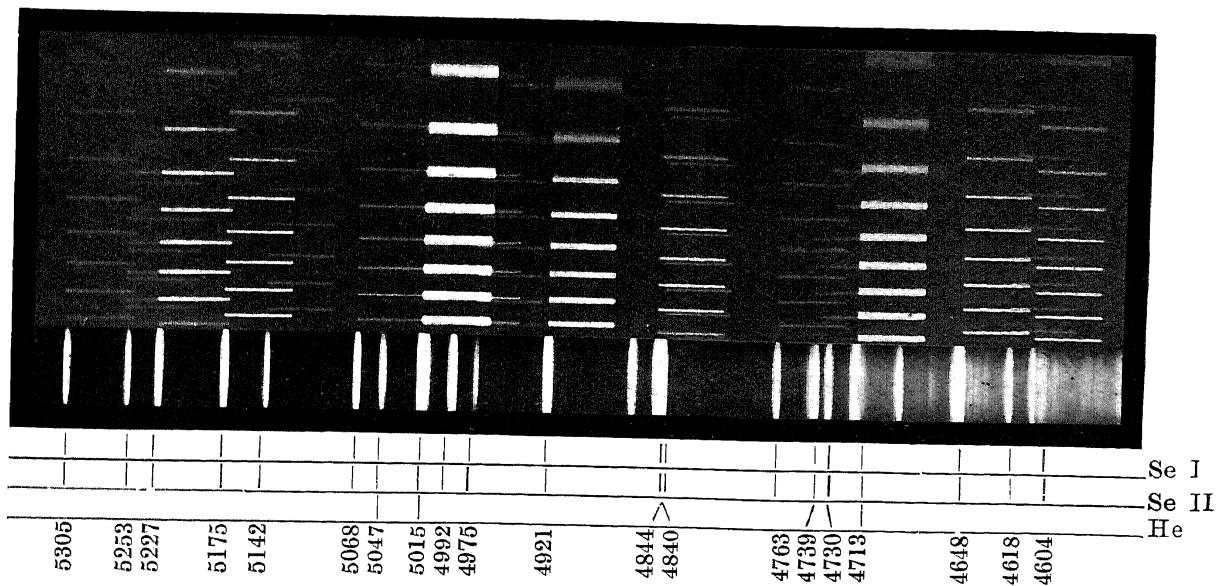


FIG. 2.

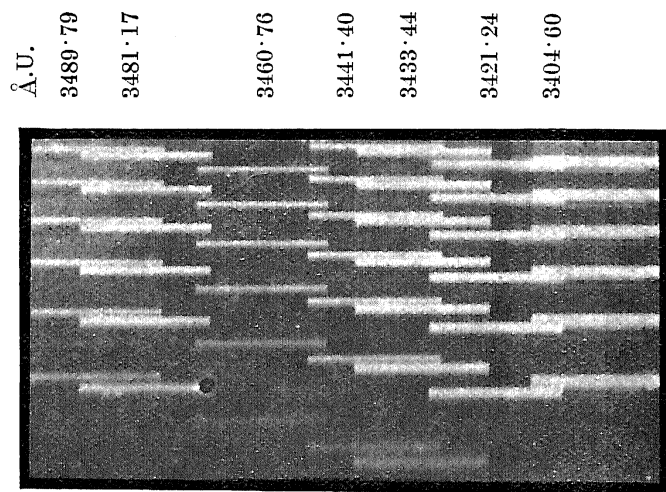


FIG. 3. Structure Pattern of Palladium Arc Lines.

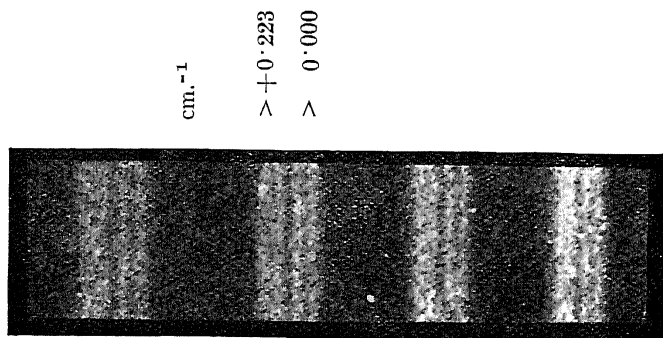


FIG. 4. Structure Pattern of Au I 2676Å ($6^2S_{1/2} - 6^2P_{1/2}$) with each of the two components doubled by self-absorption in the source.

p-electrons it is found that the levels $5d^{10} 6p^2 P_{\frac{1}{2}, \frac{3}{2}}$ have total separations amounting to 0.024 cm.^{-1} and 0.008 cm.^{-1} respectively. These separations are too small to be resolved in the lines involving these levels. The larger separation ($\sim 0.164 \text{ cm.}^{-1}$) with an interval factor of 0.018 cm.^{-1} in $5d^9 6s^2 {}^2D_{\frac{5}{2}}$ is consistent with theoretical expectations.

In conclusion I wish to thank Prof. B. Venkatesachar for his helpful guidance.

Summary.

Hyperfine structure analysis of some selenium and palladium lines shows that none of the levels examined reveal any even isotope displacement. The nuclei of Se 77 and Pd 105 have very small magnetic moments and their spin moment is probably $\frac{1}{2} \frac{h}{2\pi}$.

The doublet structure ($\Delta \nu = 0.224 \text{ cm.}^{-1}$) observed by Ritschl in the resonance lines of gold has been confirmed by the redoubling of each component due to self-reversal in the source; this test proves that the originally observed doublet structure does not arise from self-reversal as the earlier results of Frisch would suggest. While in the isoelectronic spectrum of Hg II the $5d^9 6s^2 {}^2D_{\frac{5}{2}}$ level exhibits isotope displacement, arc lines of gold involving this level point definitely to the existence of a single isotope of mass 197; the accepted chemical atomic weight is therefore considered to be too high. The nuclear spin moment of gold is $\frac{3}{2} \frac{h}{2\pi}$ and the $g(I)$ factor comes out as 0.136 agreeing with Lande's theoretical value.