Physics. — *Magnetic resolution and nuclear moment of Rhenium.* By P. ZEEMAN, J. H. GISOLF and T. L. DE BRUIN.

(Communicated at the meeting of January 30, 1932.)

Introduction.

The first details concerning the optical spectrum of Rhenium were published by MEGGERS in a preliminary note [1]). This note was followed by a complete description of the spectrum from 2500 Å to 8000 Å, while a beginning of the classification was made [2]). In that article MEGGERS gives an elaborate review of the literature concerning the discovery and preparation of Rhenium, and of the work done upon the Röntgen spectra.

The absorption spectrum of Rhenium was obtained by us, by means of an underwater sparc between a pair of Rhenium electrodes, photographed with a HILGER E_1 quartz spectrograph. It appears that the triplet: $\lambda\lambda$ 3452—3460—3465 gives strong absorption, and might therefore be considered as combinations with the ground level.

MEGGERS has now identified these three lines as combinations of a ${}^6P_{3/2,\,7/2,\,5/2}$ term with the groundterm $(d^5\,s^2)\,{}^6S_{5/2}$.

We have investigated the hyperfine structure and the magnetic resolution of these strong lines. The results of this investigation have been published already in a short note in "Nature" [3]).

A more complete description will be given now.

The hyperfine structure of the groundtriplet of Rhenium.

Experimental details. The photographs were made in the third order of a six inch grating with 15000 lines per inch and with a radius of curvature of 21 feet, in an Eagle mounting. The scale is 0.832 Å per millimeter.

The material used was powdered pure Rhenium, obtained from the "Chemische Werke, Leopoldshalle".

Some of this powder was brought upon the positive pole of a copper arc in vacuum. With a current of 5 ampères and 110 volts the Rhenium arc spectrum was extremely strong, so that exposures of about one minute were sufficient.

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[1]) MEGGERS, Phys. Rev. **37**, 219 (1931).

[2]) MEGGERS, Bureau of Standards Journal of Research **6**, 1027 (1931).

[3]) P. ZEEMAN, J. H. GISOLF, T. L. DE BRUIN, Nature **128**, 637 (1931).

Perutz Fliegerplatten were used for their very fine grain. By means of a ZEISS microphotometer which operates with a photocell, photograms were made from the photographs of the hyperfine structures.

The measurements were executed both on the original plates, and on the photograms. The results of these measurements differ very little. In the final dates the average is taken from the measurements on the plates and on the photograms.

Theory and results. The theory of hyperfine structure was first given by PAULI [1]) and has been described by several authors. A fairly complete review is given by PAULING and GOUDSMIT in their book "Structure of line spectra" chapter 11. It will therefore be sufficient to give a summing up of the facts which are necessary to give the interpretation of the patterns we have obtained.

To the nucleus is ascribed a spin moment $I \,.\, h/2\pi$, in which I is a new quantum number. This moment is composed with the mechanical moment J of the extranuclear electrons to a resulting total moment vector F. This vector will have the value $F \,.\, h/2\pi$, in which F is called the hyperfine structure quantum number.

An electron configuration with a mechanical moment J (an "electron state") will give rise to either $2I + 1$ hyperfine structure terms with hyperfine structure quantum numbers $F = J + I;\ J + I - 1;\ \ldots\ldots;\ J - I$, or to $2J + 1$ terms with quantum numbers $F = I + J;\ I + J - 1;\ \ldots\ldots;\ I - J$, according to wether I or J is the smaller of the two. Therefore it is possible to deduce the value of the nuclear moment from the number of hyperfine structure terms that belong to one electron state, provided that the J value of the considered electron state is known.

The energy difference between two hyperfine structure terms with quantum numbers F and $F-1$, belonging to one electron state, is given by the product of the quantum number F and a quantity A called the "interval constant", having the same value for all the hyperfine structure terms that belong to one electron state. (Interval rule.)

Thus the value of the quantum number F can be determined from the mutual position of the hyperfine structure terms and when the quantum number J is known, one may obtain the value of the nuclear spin I.

The combination of two hyperfine structure terms to a spectral line is subjected to the exclusion rules: $\triangle F = 0, \pm 1$ and $\triangle J = 0, \pm 1$, while the combinations $J = 0$ to $J = 0$ and $F = 0$ to $F = 0$ are forbidden.

The combinations of the hyperfine structure terms of two electron states form together a hypermultiplet. In such a hypermultiplet the strongest components will come from transitions by which $\triangle J$ and $\triangle F$ have the same sign and the intensity of these components will be ranged according to the F values of the initial terms.

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[1]) W. PAULI, Naturwiss. **12**, 741 (1924).

The value of the interval constant A may be very different for the various electron states of an atom.

The hypermultiplet that arises from the transition of one electron state to another, will have a very regular shape if one of the two electron states has an interval constant that is vanishing small. In this case the hypermultiplet consists of a number of lines of gradualy decreasing intensity and space for which the same interval rule holds as far the terms itself.

We found that in Rhenium the hypermultiplets λ 3452 $^6S_{5/2} - {}^6P_{3/2}$, λ 3460 $^6S_{5/2} - {}^6P_{7/2}$, λ 3465 $^6S_{5/2} - {}^6P_{5/2}$, are quite of this type and the measurements make it certain that it is the common electron state $d^5 s^2\, {}^6S_{5/2}$ that is practically simple.

The structures consist of respectively four, six and five components all three with the intensity and space decreasing to longer wavelength.

The measurements gave the following results:

λ 3452 $^6S_{5/2} - {}^6P_{3/2}$ (Fig. 4)

$$\Delta\lambda = 0 + 0.064 + 0.111 + 0.140 \ldots \text{Å}$$
$$\Delta\nu = 0 - 0.54 - 0.94 - 1.17 \ldots \text{c.m.}^{-1}$$

the accuracy for the first three components being about two units.

The interval ratios are: 4.0 : 2.9 : 1.8.

This gives for the hyperfine structure quantum numbers F the values 4, 3, 2 and 1.

It follows that $I = 5/2$.

The interval constant amounts to 0.134 cm^{-1} calculated from the first two intervals.

$\lambda = 3460\ {}^6S_{5/2} - {}^6P_{7/2}$ (Fig. 2)

$$\Delta\lambda = 0 + 0.070 + 0.127 + 0.170 + 0.201 + 0.224 \ldots \text{Å}.$$
$$\Delta\nu = 0 - 0.58 - 1.06 - 1.41 - 1.68 - 1.87 \ldots \text{c.m.}^{-1}$$

For the first two components the error in the measurements in less than one unit. For the following two it may be about two units.

The interval ratio is: 6.0 : 4.0 : 3.7 : 2.7 : 2.0. Thus the $^6P_{7/2}$ state has six hyperfine structure terms with quantum numbers: 6, 5, 4, 2, 1.

This gives again $I = 5/2$.

The interval constant calculated from the first two intervals is 0.096 c.m.^{-1}

$\lambda = 3465\ {}^6S_{5/2} - {}^6P_{5/2}$ (Fig. 3)

$$\Delta\lambda = 0 + 0.062 + 0.115 + 0.156 + 0.185 \ldots \text{Å}$$
$$\Delta\nu = 0 - 0.52 - 0.96 - 1.30 - 1.54 \ldots \text{c.m.}^{-1}$$

For the first three components the error in the measurements will not exceed two units.

The interval ratio is: 5.0 : 4.2 : 3.3 : 2.4.

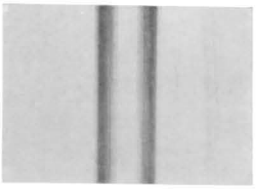

Fig. 1

Fig. 2

Fig. 3

Fig. 4

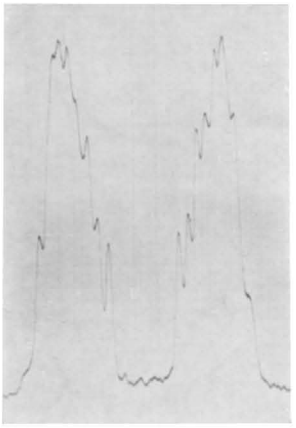

Fig. 5

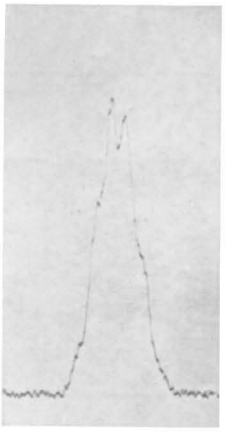

Fig. 6

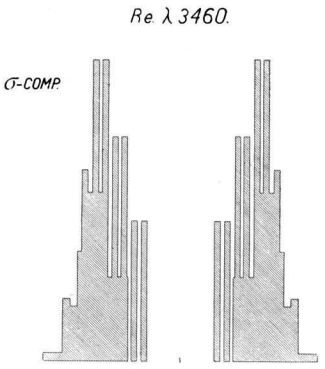

Fig. 5*a*

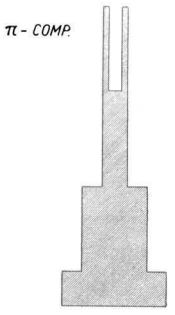

Fig. 6*a*

In this case a faint sixth component must be present, but it cannot be expected to be resolved.

Here too we get perfect agreement for a nuclear moment $I = {}^5/_2$.

The first two intervals give an A value of 0.107 c.m.$^{-1}$

So we can say that the nuclear moment has proved to be ${}^5/_2 \cdot h/2\pi$ as was suspected already by GREMMER and RITSCHL [1])

Meanwhile a short note has appeared of MEGGERS, KING and BACHER [2]), in which the same conclusion is expressed.

It must be noticed that Rhenium has two isotopes 185 and 187 in ratio 1.62 to 1. The structure of the multiplets makes it certain that both the isotopes have the same nuclear moment and that the difference of the interval constants, or the isotope displacement, if present, must be very small. In this time the same lines are under investigation with apparates of higher resolving power.

Magnetic resolution.

Experimental details. For this investigation is used the large WEISS electromagnet of this laboratory. A description can be found in an article by P. ZEEMAN and T. L. DE BRUIN [3]).

The endplanes of the conical polepieces have a diameter of one centimeter. With a distance of these planes of about 4 m.m. and a current of 100 A. the fieldstrength amounts to 38900 Gauss.

As a lightsource was used a vacuum trembler of BACK [4]). For this trembler it is necessary to have the material in the form of small bars, about two centimeters long, two millimeters broad and one millimeter thick. As the industry could not supply the Rhenium in the form of compact metal, we had to make our own electrodes.

The melting point of Rhenium being extremely high (3400°), this gave some trouble, but at least we succeeded in manufacturing bars of the desired dimensions, of quite pure and compact Rhenium, by melting the powder in the positive crater of a carbon arc.

The same bars were used as electrodes for the underwater spark in the investigation of the absorption spectrum that was mentioned at the beginning of this article.

The interrupted arc burned in air of 4 c.m. pressure with a current-strength of 2 Ampères and a tension of 110 Volts. Under these conditions the arc spectrum was very intense.

The optical arrangement was the same as in the experiments without magnetic field. The two states of polarisation were separated by means

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[1]) GREMMER and RITSCHL. Zeitschr. für Instrumentenkunde **51** 170 (1931).

[2]) MEGGERS, KING and BACHER. Phys. Review **38** 1259 (1931).

[3]) P. ZEEMAN and T. L. DE BRUIN. Handbuch der physikalische Optik Bd. II. Gehrcke pag. 602.

[4]) See BACK—LANDÉ „ZEEMAN-*effekt und Multiplettstruktur*" pag. 124.

of a calcspar rhomb. The time of exposure was varied from a half to three hours. The temperature of the grating was kept constant to 0.01° C. by using the principle: First regulate the room temperature to 0.1° and then regulate the grating temperature by a second step. This procedure first described in the article of ZEEMAN and DE BRUIN (Handbuch der phys. Optik, Gehrcke, Vol. 2, pag. 605, 1927) has been used with success by various physicists, with or without acknowledgment.

Again Perutz Fliegerplatten were used.

The measurements were made again both on the original plates and on the photograms.

Theory and results. The influence of the nuclear moment upon the magnetic resolution of the spectral lines was first found by BACK and GOUDSMIT [1]) for the Bismuth line λ 4722, and they could show that their very beautiful resolution patterns were in perfect agreement with PAULI's suggestion. For the theory of the ZEEMAN effect of the hyperfine structure we may refer to the book of PAULING and GOUDSMIT cited before. We will mention only the following facts.

In an external magnetic field, each electron state is split up in $2J+1$ "magnetic" states caracterised by magnetic quantum numbers m_j which are equal to $J, J-1, \ldots\ldots, -J$.

The energy differences between the successive magnetic states are equal, and are given by the product $g.o.H$. This is the ordinary magnetic resolution.

When there exists a nuclear moment, each of the $2J+1$ magnetic electron states gives rise to $2I+1$ equidistant magnetic hyperfine structure terms, with magnetic hyperfine structure quantum numbers $m_i = I, I-1, \ldots\ldots, -I$, provided the field is very strong.

The distance of the magnetic hyperfine structure terms that belong to one magnetic electron state with quantum number m_j, is given by the product of m_j and the interval constant A of that electron state.

At the transition of one electron state to another in such a very strong field, the magnetic quantum number m_i is not allowed to change. This makes that the nuclear moment causes a splitting up of each ordinary ZEEMAN component in $2I+1$ equidistant hyperfine structure components of equal intensity.

The distance between these hyperfine structure components which belong to the combination of two magnetic electron states with quantum number m_j and m'_j, and with interval constants A and A', is given by $m_j A - m'_j A'$.

We have seen that in the case of Rhenium, the common term $^6S_{5/2}$ of the triplet has an interval constant which is practically zero, and therefore in this case the distance of the $2I+1$ hyperfine structure components of

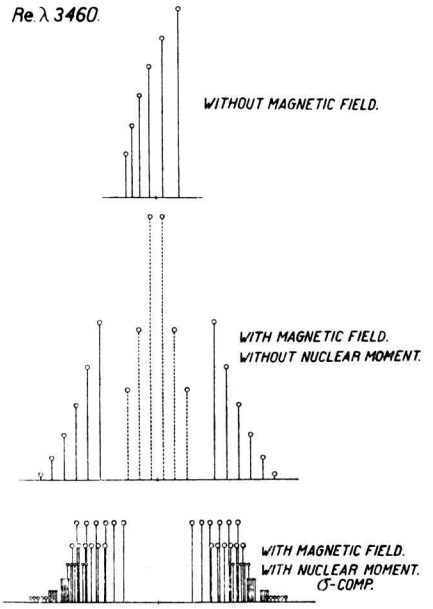
[1]) BACK and GOUDSMIT. Zeitschr. für Physik **47**, 174, (1928).

each ZEEMAN component is given by the product of the magnetic quantum number m_j and the interval constant A of the initial state.

The number of components in the magnetic resolution pattern may become extremely large when there is a nuclear moment, but most of these components wont be resolved in consequence of their very small mutual distance. Only for the ZEEMAN components which belong to the highest magnetic quantum numbers m_j it will be possible to resolve them each in their $2I + 1$ hyperfine structure components. The most favorable case is therefor found in the line $\lambda\,3460\ {}^6S_{5/2} - {}^6P_{7/2}$ for the transition $m_j = {}^7/_2$ to $m_j = {}^5/_2$:

$$\lambda\ 3460\ {}^6S_{5/2} - {}^6P_{7/2}\,.$$

In the following figure is given the magnetic resolution of this line without nuclear moment, and the resolution pattern for a nuclear moment ${}^5/_2\,.\,h/2\pi$ and an interval constant $A = 0.096$ c.m.$^{-1}$



In the photograph of the σ-components (fig. 1) the inner six components can be recognized immediately.

For the mean distance of these components is measured the value 0.334 c.m.$^{-1}$ This distance must be ${}^7/_2\ A$. So we find for A the value 0.095 c.m.$^{-1}$, while the value of A found from the hyperfine structure without magnetic field is 0.096 c.m.$^{-1}$. The center of the group of six hyperfine structure components gives the place of the first ZEEMAN component when no nuclear moment is present.

From the place of this centre, we calculate for the LANDÉ splitting factor g, of the ${}^6P_{7/2}$ state the value 1.76, while the LANDÉ formula gives the

value 1.714. However, from the structure of the ^6P state it is obvious that the coupling deviates strongly from the RUSSELL—SAUNDERS type and so one need not wonder that a slight anomalous g-value is found. We have assumed that the $^6S_{5/2}$ state has its normal g-value: $g = 2.000$, this being probable in connection with the g-sum rule. The observed positions of the six subcomponents of the strongest σ-components and the positions calculated with $g = 1.76$ and $A = 0.096$ $c.m.^{-1}$ are given below.

Obs:	+2,91	+2,62	+2,24	+1,95	+1,60	+1,25	... c.m.$^{-1}$
Calc.:	+2,94	+2,60	+2,26	+1,93	+1,59	+1,26	... c.m.$^{-1}$
Obs:	−2,90	−2,60	−2,28	−1,93	−1,61	−1,24	... c.m.$^{-1}$
Calc.:	−2,94	−2,60	−2,26	−1,93	−1,59	−1,26	... c.m.$^{-1}$

The small deviations may be sufficiently explained by the overlapping of the non resolved groups of hyperfine structure components of the other components, as is seen in the preceding figure.

None of the other ZEEMAN components can be resolved in their subcomponents. Representing groups of non resolved components by rectangles, we have constructed the intensity distribution as predicted by the theory (fig. 5*a* and 6*a*). Comparing with the photograms (fig. 5 and 6) the agreement is excellent. The two pikes at the outer side of each of the σ-groups originate from the magnetic quantum numbers $m_j = {}^1/_2$ and $m_j = -{}^1/_2$.

$$\lambda\ 3465\ {}^6S_{5/2} - {}^6P_{5/2}.$$

This line is much less suitable for the observation of the magnetic resolution of the hyperfine structure, because of the smaller m_j values and because of the smaller difference between the g-values of the two electron states. At the inner side of the σ-group and at the outer side of the π-group traces of hyperfine structure components can be seen.

Comparing the photogram of the resolution pattern (fig. 7 and 8) with the type calculated with the normal g-value and the A of the hyperfine structure without field (fig. 7*a* and 8*a*) the agreement is very satisfactory, though the g-value is probably not quite normal.

$$\lambda\ 3452\ {}^6S_{5/2} - {}^6P_{3/2}.$$

The calculated intensity distribution (fig. 9*a* and 10*a*) agrees with the observed type (fig. 9 and 10). In consequence of the small m_j values we cannot expect to resolve any of the hyperfine structure components.

In connection with a small asymmetry of the intensities as is seen from the photograms one is forced to consider whether the magnetic field can be called "very strong".

GOUDSMIT and BACHER [1]) have adapted the calculations of DARWIN [2])

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1) GOUDSMIT and BACHER, Zeitschr. für Physik **66**, 13 (1930).

2) C. G. DARWIN. Proc. Roy. Soc. (A) **115**, 1 (1927).

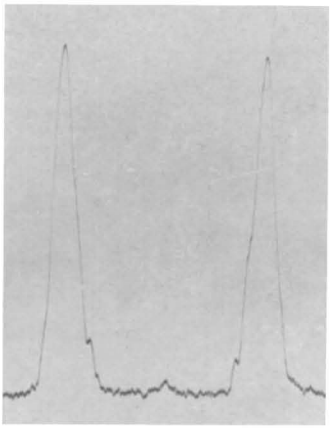

Fig. 7

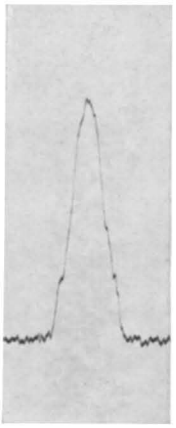

Fig. 8

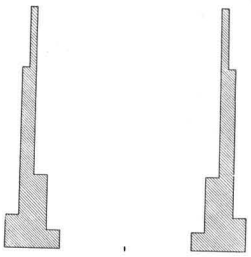

Fig. 7*a*

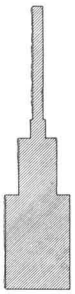

Fig. 8*a*

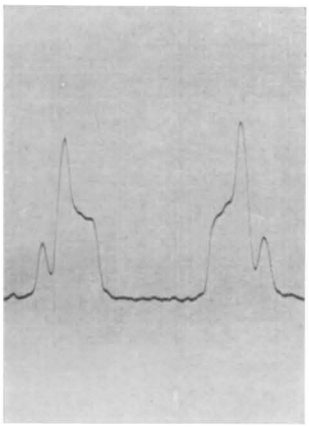

Fig. 9

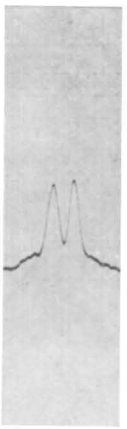

Fig. 10

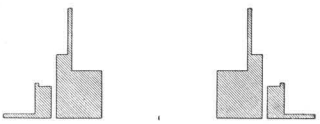

Fig. 9*a*

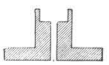

Fig. 10*a*

for the ordinary PASCHEN—BACK effect to the magnetic resolution of the hyperfine structure.

As a second order aproximation the energy of a magnetic hyperfine structure state with quantum number m_i, which belongs to a magnetic electron state with quantum number m_j is given by:

$$E(m_i, m_j) = m_j g(j) oH + Am_i m_j + \\ + \frac{A}{2g(j) oH} [m_j \{I(I+1) - m_i^2\} - m_j \{J(J+1) - m_j^2\}]$$

In the preceding pages we have considered only the first two terms of the energy. When the third term is so small that it can be neglected, the field will be "very strong".

We have calculated the influence of this third term for the different transitions. These corrections are however smaller than the displacements of the intensity maxima due to the overlapping of several components and so we have not further considered them.

Resuming we can say that both the natural hyperfine structure and the magnetic resolution give independently for the nuclear moment of both the Rhenium isotopes the value $I = {}^5/_2$.

Laboratory "Physica" Amsterdam.

DESCRIPTION OF THE PLATES

Fig. 1. Resolution pattern of Rhenium λ 3460 (σ-components). Enlargement 8 times. At each side of the centre the six subcomponents belonging to the strongest ZEEMAN components can be seen. The distance between these hyperfine structure components is 0,04 Å.

Fig. 2. Zeiss photogram of the same line λ 3460 without magnetic field. The total breadth is 0.224 Å.

Fig. 3. λ 3465 without magnetic field. Total breadth 0,185 Å.

Fig. 4. λ 3452 without magnetic field. Total breadth 0,140 Å.

Fig. 5. This is a photogram of the same magnetic resolution pattern of which an enlargement is shown in fig. 1. The inner six components at each side of the centre are the hyperfine structure components belonging to $m_j = {}^7/_2$. The outer two components at each side are non resolved groups belonging to $m_j = +{}^1/_2$ and to $m_j = -{}^1/_2$.

Fig. 5*a*. In this figure we have constructed the intensity distribution, representing non resolved groups by rectangles.

Fig. 6 and Fig. 6*a*. Observed and calculated photogram of the π-components of the same line λ 3460. Non of the groups of hyperfine structure components are resolved.

Fig. 7 and Fig. 8. λ 3465 σ- and π-components.

Fig. 7*a* and Fig. 8*a*. Calculated types for λ 3465 σ- respectively π-components.

Fig. 9 and 10. λ 3452 σ- and π-components.

Fig. 9*a* and Fig. 10*a*. Calculated types for λ 3452 σ- respectively π-components.

The figures 7*a* to 10*a* are calculated with normal g-values. The g-values however may be a little anomalous, but they could not be deduced from the resolution patterns with sufficient accuracy.