Hyperfine Structure of Gold

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The spectrum of Au I and Au II has been examined for hyperfine structure in the region λ2300–6300A. Splitting has been observed in more than eight lines of the spectrum of Au I, whereas the hyperfine structure of Au II lines could not be resolved. From the four-component structure of the lines λ4437A and λ4607A it is shown that the mechanical moment of the gold nucleus is $(3/2)(h/2\pi)$. The effect of self-reversal in the resonance lines has been investigated and eliminated. The magnetic moment determined from the splitting of the unreversed resonance line λ2428A is found to be 0.195 proton-magneton. No other determination of the magnetic moment is at present possible because of the intermediate coupling shown to exist in the complex electronic configurations of Au I and the inadequacies of the present theory of hyperfine structure. The splitting of the $^2P_{1/2}$ level is estimated and found to be in approximate agreement with that calculated from the $^2S_{1/2}$ level. No indication of any abnormally large $^2P_{1/2}$ separation or of any isotope shift has been found.

INTRODUCTION

SINCE gold is of odd atomic number (79) and atomic weight 197.2, hyperfine structure is to be expected in its spectral lines. Frisch,[2] however, did not find any structure in the resonance line λ2676A with the use of a high resolving power grating. In a report on the spectrum of copper Ritschl[3] noted that the resonance lines of gold were both split into two components and had separations of 0.224 and 0.221 cm^{-1}, respectively. Sibaiya[4] found self-reversal in the above lines and estimated, on the assumption of a nuclear moment of 3/2 for gold, a nuclear magnetic moment of 0.20 nuclear magneton, which is slightly lower than that calculated from Ritschl's data. Preliminary work of the present writers,[5] including intensity measurements, indicated that this value was probably too large.

Although previous work on the atomic weight of gold leads one to believe that an isotope shift should be present, nevertheless, Dempster[6] concludes that if the isotope 199 exists, it is present to an extent of but 0.1 percent or less. One should expect this to be substantiated by a careful examination of the hyperfine structure.

[1] At present with The American Thermos Bottle Co., Norwich, Connecticut.
[2] W. Frisch, Zeits. f. Physik **71**, 92 (1931).
[3] R. Ritschl, Naturwiss. **19**, 690 (1931).
[4] L. Sibaiya, Proc. Indian Acad. Sciences **2**, 313 (1935).
[5] J. Wulff, Phys. Rev. **44**, 512L (1933).
[6] A. J. Dempster, Proc. Am. Phys. Soc. **75**, 8, 755 (1933).

EXPERIMENTAL

Excitation

A modified Schuler tube immersed in a mixture of carbon dioxide and acetone was used for excitation. The demountable design is shown in Fig. 1. The cathode is a spun cylinder of gold, closed at the lower end and fixed in a similar cylinder of aluminum, the latter to prevent the excitation of the copper and zinc of the tube in the event of rupture of the gold cylinder. Spectroscopically pure helium or argon supports the discharge and is continuously circulated through a charcoal trap immersed in liquid air (carbon dioxide and acetone in the case of argon) by a mercury diffusion pump. A 1000-volt generator in series with a stabilizing resistance is used for the power supply. Fig. 2 shows a characteristic curve for the discharge as ordinarily used. This curve is shown for a pressure of approximately two-tenths of a millimeter of mercury. Curves for other pressures do not differ materially from this one except at the point where the discharge changes to an arc. As the pressure decreases this point moves slowly to the left. The potential difference across the tube when arcing is about 130 volts at 0.8 ampere, depending upon the pressure and previous history of the tube. Since arcing is a serious problem in the operation of a tube of this design, the glass shield G was inserted to reduce the tendency to arc by lengthening the minimum anode-cathode distance.

Interferometer and spectroscopes

A Fabry-Perot interferometer following the general design of Hansen[7] sufficed for many of the photographs taken. For the long exposures required in the ultraviolet, the interferometer was arranged for evacuation so that the optical path difference could be kept constant.[8] Fused quartz etalons with evaporated films of silver, aluminum-silicon, and aluminum were used. Tolansky[9] has shown that a minor variation in film thickness can cause a severe change in the optical path difference because of the change in phase reversal which may occur with slightly varying film thicknesses. To produce, therefore, as uniform a film as possible, the plates were placed no less than twelve inches away from the evaporating source. The assembled etalons resulting showed no detectable sign of ring motion. The transmission of a single aluminum film used for the far ultraviolet was less than 0.1 percent at 4000A.

In the visible region the interferometer was used with a Zeiss three-prism constant deviation spectrograph with a one-meter focal length camera. In the ultraviolet a Hilger E2 quartz spectrograph was used. Since this is a Littrow-type instrument, the fringes were focused on the slit by means of a 50-cm quartz-fluorite doublet. The variation of focal length of this doublet was not determined, as in the case of the Zeiss instrument, by photographic trial and error method on the fringes themselves, since exposure would then be prohibitively long. Furthermore, a mercury arc was not used since the fringes obtained were too broad. A new method was devised for this work which we believe is not only extremely precise, but in addition, provides a rapid and convenient means of determining the chromatic aberration of any lens. The set-up employed is illustrated in Fig. 3. A mercury arc L was focused by the small lens P on the mirror M_1, thence reflected through the achromat A to the mirror M_2 and back through the achromat to the slit S of the spectrograph. The mirror M_1 is a piece of quartz $8\times2\times1$ millimeters on which one-mil wire had been wound and aluminum evaporated. When the wire was removed it left a series of fine intersecting rulings which formed an ideal object on which to focus. This mirror was placed as close as possible to the slit with its long edge parallel to the jaws. The mirror M_2 was a three-inch flat of good quality. A series of exposures (30 seconds) were made with the spectrograph and the achromat moved between successive ones. It is obvious from the diagram that M_1 and S are conjugate points only when both lie at the focal point of the achromat. A

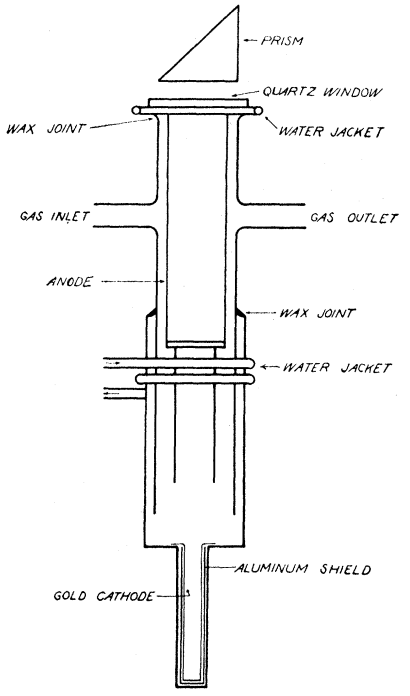

FIG. 1. Hollow cathode discharge tube.

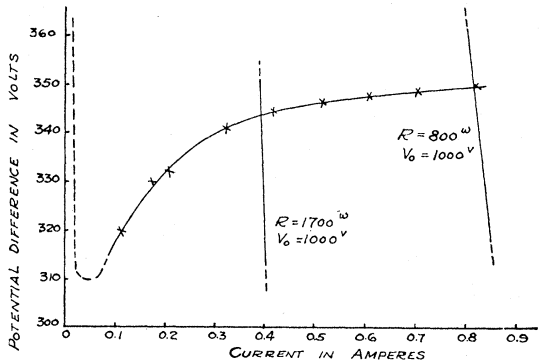

FIG. 2. Tube characteristic curve.

[7] G. Hansen, Naturwiss. **15**, 163 (1927); or Von Bayer, Physik. Zeits. **9**, 831 (1908).
[8] Details of the construction are to be published shortly.
[9] S. Tolansky, J. Sci. Inst. **13**, 8 (261).

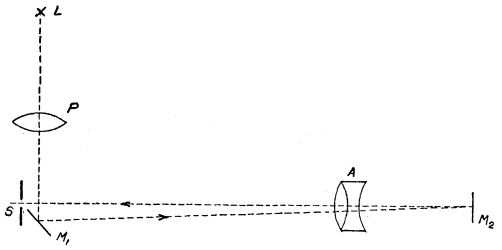

FIG. 3. Optical arrangement for focal length determination.

little consideration will also show that a displacement of the achromat results in a displacement of double the amount of the image of M_1. Moreover the focus of the achromat is determined with the spectrograph with which it is to be used and any deviations of the latter from perfect focus are automatically compensated.

RESULTS

Lines of Au I in which hyperfine structure has been observed are listed in Table I together with other broad but unresolved lines. The classifications and configurations are those of McLennan and McLay.[10] The classifications of Symons and Daley[11] are also given for the lines which they investigated in a study of the Zeeman effect. The latter classifications assume strict LS coupling.

In the following lines of Au I no splitting has been observed:

2701 $(5d^9{}_{5/2}\,6s^2{}_0)\ 1_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 3^0{}_{5/2}$
2848 $(5d^9{}_{5/2}\,6s^2{}_0)\ 1_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 2^0{}_{7/2}$
3123 $(5d^9{}_{5/2}\,6s^2{}_0)\ 1_{5/2}-(6p)\ {}^2P^0{}_{3/2}$
3308 $(5d^9{}_{5/2}\,6s^2{}_0)\ 2_{3/2}-(5d^9\ 6s\ 6p)\ 8^0{}_{5/2}$
3795 $(6p)\ {}^2P^0{}_{3/2}-(7d)\ {}^2D_{5/2}$
3898 $(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 1^0{}_{5/2}$
$-(5d^9{}_{5/2}\,6s_{1/2}\,7s_{1/2})\ 3_{7/2}$
3927 $(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 6^0{}_{3/2}$
$-(5d^9{}_{5/2}\,6s_{1/2}\,6d_{1/2})\ 7_{9/2}$
3915 $(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 6^0{}_{7/2}$
$-(5d^9{}_{5/2}\,6s_{1/2}\,6d)\ 8_{5/2}$
4040 $(5d^9{}_{3/2}-6s^2{}_0)\ 2_{3/2}-(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 3^0{}_{5/2}$
4065 $(6p)\ {}^2P^0{}_{1/2}-(6d)\ {}^2D_{3/2}$
6278 $(5d^9{}_{3/2}\,6s^2{}_0)\ 2_{3/2}-(6p)\ {}^2P^0{}_{1/2}$.

Four lines of Au II classified by McLennan and McLay[12] were investigated and no splitting was observed:

4053 $(6s)\ {}^3P_{3/2}-(6p)\ {}^3D_{3/2}$
3803 $(6s)\ {}^3P_{3/2}-(6p)\ {}^3D_{5/2}$
3123 $(6s)\ {}^3P_{3/2}-(6p)\ {}^3D_{5/2}$
2914 $(6s)\ {}^3F_{7/2}-(6p)\ {}^3D_{5/2}$.

The latter notation is that of McLennan and McLay; according to these authors, the lower terms involved in these lines, while not unambiguously assigned, probably belong to a system based on the d^8s ion of Au III. Two additional lines of Au II in which no splitting was observed are λ3874A and λ3581A. These are not listed by McLennan and McLay but are given by Symons and Daley.[11]

Figure 4 shows a series of microphotometer curves of the resonance line λ2676A as observed under different conditions of excitation. The reversal is quite evident in two curves, (a) and (b); but there is no indication of its presence in the bottom curve, (c). Inasmuch as measurements of the photographs which were taken with currents of 0.30 and 0.17 ampere agree to two percent, we

[10] J. C. McLennan and A. B. McLay, Proc. Roy. Soc. **A134**, 35 (1931).
[11] A. S. M. Symons and J. Daley, Proc. Phys. Soc., Lon. **41**, 431 (1929).
[12] J. C. McLennan and A. B. McLay, Trans. Roy. Soc. Can. **22**, 103 (1928).

TABLE I. *Lines of* Au I *in which hyperfine structure has been observed.*

WAVE-LENGTH	CLASSIFICATION McLENNAN AND McLAY	CLASSIFICATION SYMONS AND DALEY	INTENSITY AND SEPARATION
2428	$(6s)\ {}^2S_{1/2}-(6p)\ {}^2P^0{}_{3/2}$		(10) 0 (6) 0.214 cm^{-1}
2641	$(5d^9{}_{5/2}\,6s^2{}_0)\ 1_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 4^0{}_{7/2}$		(10) 0 (3) 0.10 Not completely resolved
2676	$(6s)\ {}^2S_{1/2}-(6p)\ {}^2P^0{}_{1/2}$		(10) 0 (6) 0.218 cm^{-1}
2748	$(5d^9{}_{5/2}\,6s^2{}_0)\ 1_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 2^0{}_{7/2}$		Broad but not resolved
3029	$(5d^9{}_{5/2}\,6s^2{}_0)\ 1_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 1^0{}_{5/2}$	$6s''\ {}^2D_{5/2}-a$	(4) 0 (10) 0.11 Not completely resolved
4437	$(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 3^0{}_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,7s_{1/2})\ 4_{5/2}$	$6p''\ {}^4F_{5/2}-6d''\ {}^4D_{5/2}$	(2) 0 (6) 0.066 (7) 0.161 (10) 0.285 cm^{-1}
4607	$(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 4^0{}_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,7s_{1/2})\ 4_{5/2}$	$6p''\ {}^4P_{3/2}-6d''\ {}^4D_{5/2}$	(2) 0 (6) 0.065 (8) 0.147 (10) 0.244 cm^{-1}
4792	$(6p)\ {}^2P^0{}_{3/2}-(6d)\ {}^2D_{5/2}$	$6p\ {}^2P_{3/2}-6d\ {}^2D_{5/2}$	Width less than 0.05 cm^{-1}
4811	$(6p)\ {}^2P^0{}_{3/2}-6d\ {}^2D_{3/2}$	$6p\ {}^2P_{3/2}-6d\ {}^2D_{5/2}$	Width less than 0.04 cm^{-1}
5065	$(5d^9{}_{5/2}\,6s^2{}_0)\ 2_{3/2}-(6p)\ {}^2P^0{}_{3/2}$	$6s''\ {}^2D_{3/2}-6p\ {}^2P_{3/2}$	Width less than 0.05 cm^{-1}
5147	$(5d^9{}_{5/2}\,6s_{1/2}\,6p_{1/2})\ 7^0{}_{3/2}-(5d^9{}_{5/2}\,6s_{1/2}\,7s_{1/2})\ 5_{3/2}$	$6p''\ {}^2P_{3/2}-6d''\ {}^4D_{3/2}$	(8) 0 (10) +0.088 cm^{-1}
5262	$(5d^9\ 6s\ 6p)\ 8^0{}_{5/2}-(5d^9{}_{5/2}\,6s_{1/2}\,7s_{1/2})\ 5_{3/2}$	$6p''\ {}^2D_{5/2}-6d''\ {}^4D_{3/2}$	(10) 0 (7) 0.114 (6) 0.176 cm^{-1}
5837	$(6p)\ {}^2P^0{}_{1/2}-(7s)\ {}^2S_{1/2}$		Width less than 0.4 cm^{-1}

feel sure that reversal is absent at these low currents. The small currents required to obtain the resonance lines free from reversal, together with the fact that the fused quartz etalons begin to absorb at about λ2500A, necessitated exposures of over sixteen hours, even with the most sensitive photographic plates. The accuracy of measurements may be judged from the fact that four separate measurements of the line λ2676A agree to less than two percent. The typical "flag" pattern of the line λ4437A is quite evident from the microphotometer curve of Fig. 5.

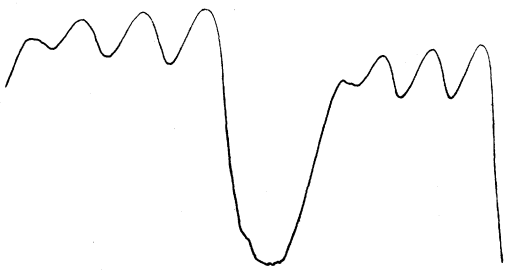

FIG. 5. Photometer curve (retouched) λ4437A, Mag. 30×, separator 1.04 cm.

DISCUSSION AND CONCLUSIONS

The observations on the resonance lines λ2676A and λ2428A permit a determination of the splitting of the $^2S_{1/2}$ and $^2P_{1/2}$ states. The term diagrams are shown in Fig. 6. The theory of Goudsmit shows that the ratio of the splitting in the $^2S_{1/2}$ and $^2P_{3/2}$ states should be over a hundred to one, so that the splitting of the line λ2428A should give directly the separation of the $^2S_{1/2}$ level. The separation of the $^2P_{1/2}$ level can then be determined from the $^2S_{1/2}$ separation and the measurement on λ2676A. The value found is 0.006 cm^{-1}. From the $^2S_{1/2}$ separation the theoretical separation in the absence of perturbation for the $^2P_{1/2}$ level may be calculated. This value is 0.011 cm^{-1}. These values may be considered as in essential agreement when one remembers that the experimental value is determined from the difference of two large quantities. There is no indication, however, of an abnormally large $^2P_{1/2}$ separation. This conclusion is supported by the observations on the lines λ5837A and λ4065A, both of which involve the $^2P_{1/2}$ level and neither of which is split. Because of the high resolving power of the interferometer in this region one would expect to observe such an abnormal splitting if present.

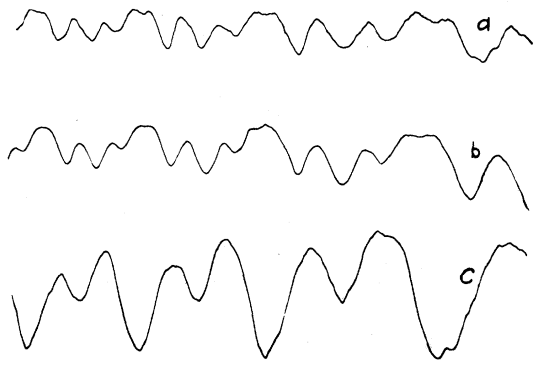

FIG. 4. Photometer traces (retouched) of λ2676A—Mag. 30×. (*a*) Current 0.9 amp.; separator 1.04 cm. (*b*) Current 0.8 amp.; separator 1.04 cm. (*c*) Current 0.17 amp.; separator 1.00 cm.

The evidence for a spin of 3/2 lies in the lines λ4437A and λ4607A. These lines involve the same upper level $(5d^9_{5/2}\,6s_{1/2}\,7s_{1/2})\,4_{5/2}$ according to both McLennan and McLay and Symons and Daley. The major portion of the splitting occurring in the two lines originates in the common level involving two *s* electrons.

If the nuclear spin is 3/2 the interval factor calculated from the observed four components in λ4437A, assuming no splitting of the lower level, is 0.032. If the nuclear spin is 5/2, we should have six components, the spacing between the last three being 0.048 cm^{-1} and 0.024 cm^{-1}. Certainly, two components with this spacing could not have escaped notice with the resolving power available at this wave-length. The failure to observe six components and the fact that the interval rule is obeyed more closely for the value 3/2 than 5/2 is indicative of a spin of 3/2.

The assumption that the upper level of λ4437A is not split can be justified. Most important is that no splitting is observed in the case of the lines λ2701A and λ4040A which should involve this level according to McLennan and McLay. The interval factor for this level $(5d^9_{5/2}\,6s_{1/2}6p_{1/2})\,3^0_{5/2}$ calculated on the basis of pure *LS* coupling and using the splitting factor of 0.107 for the 6*s* electron determined from the resonance line is only 0.001; on the basis of *j–j* coupling it is either 0.021 or 0.015, depending upon the *j* value of the ion formed by removing

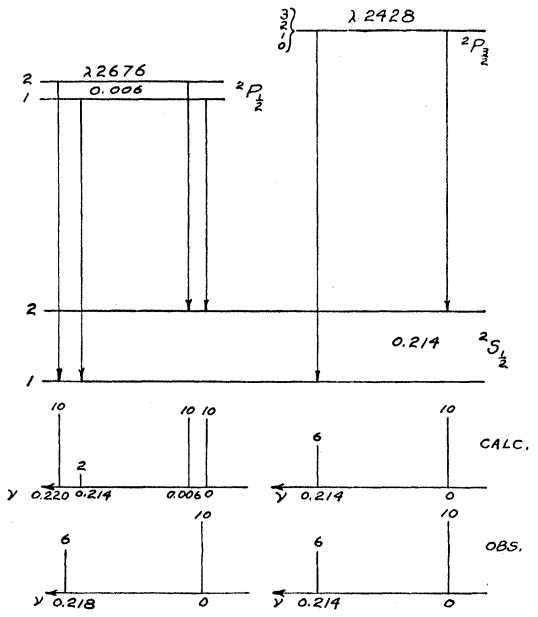

FIG. 6. Energy level diagrams for the resonance lines of Au.

the s electron. Experimental evidence discussed below indicates that the coupling in the complex electronic configuration is probably intermediate, so that the interval factor for the $3^0_{5/2}$ level should be small. The fact that the line λ4437A does follow the interval rule closely is further proof that the lower level is not split.

From the observations on λ4607A the splitting of the lower level $4^0_{3/2}$ can be estimated. Since the pattern is not completely resolved the graphical method of Fisher and Goudsmit[13] may be used. The graph for the line λ4607A is shown in Fig. 7. The short vertical dashes represent the observed positions of components and the best fit is obtained for a percentage ratio of +22. This corresponds to an interval factor of 0.008 cm^{-1} for the $4^0_{3/2}$ level.

From the splitting factor for the $6s$ electron calculated from the resonance line, the theoretical factor on the assumption of pure LS coupling for the $4^0_{3/2}$ level is 0.026 cm^{-1}, according to the work of Goudsmit and Bacher.[14] For pure jj coupling it is −0.021. From this we conclude that the coupling must be intermediate, a conclusion in accord with the point of view of McLennan and McLay.

The splitting factor of the $7s$ electron in the $4_{5/2}$ configuration of both λ4607A and λ4437A cannot be obtained from measurements on these lines since this type of configuration (three electrons of which two are s electrons) has not as yet been treated theoretically for any type of coupling.

The two lines λ5147A and λ5260A, both of which show splitting, again involve a common upper level to which McLennan and McLay assign a configuration containing two s electrons. The patterns in this case, however, are incompletely resolved and it is not possible to determine the splitting of the lower levels involved. An approximate value of the A factor for the $5_{3/2}$ state may, however, be calculated from the splitting of λ5262A if one assumes that the lower level is not split. This value is 0.035 cm^{-1}.

Because of the exceedingly small value of the magnetic moment of gold, certain lines corresponding to those which prove so valuable in the hyperfine structure analysis of copper[15] show no splitting in the case of gold.

From the observed value of 3/2 for the spin of the gold nucleus and the splitting of the resonance line λ2428A, the magnetic moment of gold may be deduced.

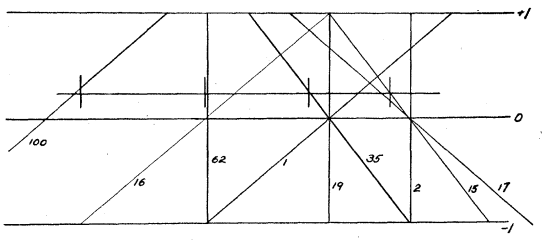

FIG. 7. Graphical analysis for λ4607A.

Using Goudsmit's formula, we first determine the g factor:

$$g=\frac{1838\ 3n_e^3a}{8\ R\alpha^2Z_iZ_0^2K}.$$

The value of n_e for the $^2S_{1/2}$ state can be determined from the relation

$$T=RZ_0^2/n_e^2.$$

[13] R. A. Fisher and S. Goudsmit, Phys. Rev. **37**, 1057 (1931).

[14] S. Goudsmit and R. F. Bacher, Phys. Rev. **34**, 1501 (1929).

[15] R. Ritschl, Zeits. f. Physik **79**, 1 (1932).

The term value of the $^2S_{1/2}$ state is given as 74461 cm^{-1} by McLennan and McLay. This corresponds to a value of n_e of 1.21. The value of Z_0 is unity for Au I, and the value of a is 0.214/2 or 0.107 cm^{-1}. The relativity correction K can be calculated from the results of Racah.[16] For $Z_i=79$, $j=\frac{1}{2}$, the value is 2.19. The value for g thus determined is 0.130, which for a spin of 3/2 results in a nuclear moment of 0.195 proton magnetons.

Because of the intermediate coupling present in the complex electronic configurations, no determination of the magnetic moment can at present be made from the splitting observed in the levels corresponding to these configurations.

The 7s electron of the $^2S_{1/2}$ state of λ5837A must possess a small interval factor since no splitting has been observed in this line. This is not surprising in view of the rapidity with which the a factor decreases with increasing total quantum number. In the case of Tl II, the ratio of the a factor for the 6s and 7s electrons is over eight to one; and in Bi I, over thirteen to one. The ratio in the case of Au I is probably at least five to one—how much greater we cannot say.

In conclusion, the present work shows that the nuclear spin of gold is 3/2 and the magnetic moment 0.195 proton-magneton within an experimental error of two percent, disregarding inadequacies in the theory. No indications of an abnormally large $^2P_{1/2}$ separation or of an isotope shift have been found. Electron configurations of McLennan and McLay have been confirmed for several states.

[16] G. Racah, Nuovo Cimento 8, 178 (1931); and Zeits. f. Physik 71, 431 (1931).

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The Fine Structure of the Line λ4686 of Ionized Helium

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The fine structure of the line λ4686 of ionized helium emitted from a discharge tube with hollow cathode cooled by liquid air was measured with a Fabry-Perot interferometer. The formula for the pattern obtained with this instrument expressed in Fourier series was applied in the analysis. Of the eight components predicted by theory, four were definitely observed, while the remaining weak ones were inferred from the pattern to be present. Relative intensities and positions of the eight components were found to be in general agreement with theory. The separation between the two strongest components was 0.0095±0.0024 IA or 0.4529 ±0.0109 cm^{-1}. The Rydberg constant for helium was calculated to be 109,722.430±0.030.

ALTHOUGH the fine structure of the lines of ionized helium is of equal interest with that of hydrogen and deuterium, there has been relatively little study made of it. This paper is the report of the use of a Fabry-Perot interferometer, instead of the customary diffraction grating, for this purpose. The difficulty, of course, lies in the overlapping of the orders, but by using a variety of plate separations, the errors caused by this can be minimized.

EXPERIMENTAL ARRANGEMENT

The light came from a hollow cathode glow, excited by direct current. The cathode, made of a copper cylinder 3.4 cm in diameter and eight cm in length, formed the bottom of the discharge tube. Its inside was aluminized by evaporation in order to avoid the emission of ionized copper lines, one of which has a wave-length 4682 so close to the line 4686 that it could not be separated by the prism. The cathode was immersed in liquid air whose level was kept a little lower than the junction where the tapering top of the cathode was sealed to the glass tube. The anode was an aluminum ring just above the cathode and was of such a size that it would not intercept the light from the cathode to the window of the tube. The distance between the anode and