THE MAGNETIC MOMENT OF THE OXYGEN ATOM

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Abstract

The magnetic moment of the oxygen atom has been investigated by the atomic ray method of Stern and Gerlach. The atomic oxygen was formed by means of an electrodeless ring discharge and the ray was detected by its oxidizing action on freshly sublimed litharge. When the ray was passed through an inhomogeneous magnetic field the resulting image consisted of an undeviated central line and two broad lines displaced symmetrically, one on each side. Hydrogen was substituted for oxygen and the procedure was repeated. The separations obtained in the two cases provided the data necessary for the calculation of the effective magnetic moment of the oxygen atom. The experimental magneton values were zero and ± 1.67. The magneton numbers expected from the spectroscopic ground term of oxygen are 0, $\pm 3/2$, and ± 3. The effective magneton numbers which (due to overlapping of the images) would result from these values are zero and ± 1.71. The agreement is within the limits of experimental error.

Introduction

THE experimental method employed in this investigation is that developed by Stern and Gerlach.[2] Rays of atoms possessing a magnetic moment are deflected into separate rays when passed through an inhomogeneous magnetic field at right angles to the direction of the field. The deflection s_α experienced by those atoms in the ray having the most probable velocity is

$$s_\alpha = 1/4 \cdot M/RT \cdot \partial H/\partial s \cdot (L_1^2 + 2L_1L_2) \quad (1)$$

where M is the magnetic moment in gauss-cm per mol; L_1 is the length of the pole pieces of the magnet, or the distance the atoms must travel through the magnetic field; L_2 is the distance from the end of the field to the target; $\partial H/\partial s$ is the value of the inhomogeneity of the field in the path traversed by the atomic ray. In this equation $\partial H/\partial s$ is assumed constant throughout the path of the ray in the field. If the magnetic moment for one element is known, then the magnetic moment for another element can be calculated from the relative deflections obtained under identical conditions in the two cases. This method obviates the tedious mapping of the field necessary in the evaluation of $\partial H/\partial s$. The equation employed is

$$M_2 = M_1 \cdot s_{\alpha_2} T_2 / s_{\alpha_1} T_1 \quad (2)$$

where M_1 and M_2 may be expressed either in gauss-cm or in Bohr magnetons. In this investigation the hydrogen atom, assumed to have a magnetic mo-

[1] This communication is an abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Stern, Zeits. f. Physik **7**, 249 (1921); Gerlach and Stern, Zeits. f. Physik **8**, 110 (1922); **9**, 349, 353 (1922); Ann. d. Physik **74**, 673 (1924); **76**, 163 (1925).

ment of one Bohr magneton, is used as the reference substance in Eq. (2). Magneton values for the oxygen atom have been determined and compared with theoretical predictions.

Experimental

The electrodeless ring discharge. A long discharge tube of the R.W.Wood type with aluminum electrodes was used in the early attempts to prepare atomic oxygen. This method was found unsatisfactory since under optimum conditions for the discharge the aluminum electrodes were oxidized with a considerable evolution of heat, and a consequent decrease in the pressure due to the "clean-up" of the active species.

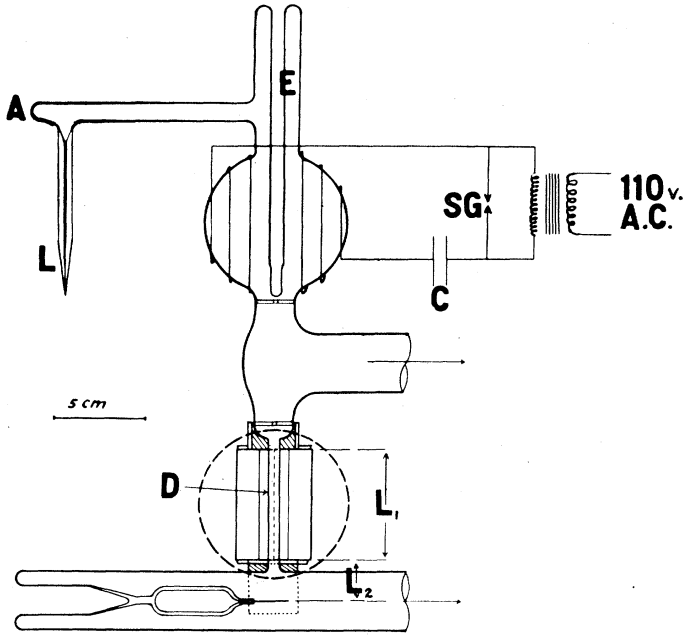

Fig. 1. Diagrammatic sketch of apparatus.

The electrodeless ring discharge was found to be a more satisfactory method. The electrical circuit is shown in Fig. 1. The secondary of a 1 k.w. 25000 volt transformer was connected with stranded leads of No. 8 B. & S. insulated copper wire through a condenser *C* of about 0.015 μf capacity, to six turns of copper tubing, about 0.3 cm in outer diameter, spaced equally around a Pyrex bulb of 200 cc capacity. The condenser consisted of 15 plates, each having an area of 500 cm^2. Two thicknesses of double-strength window glass between plates served as a dielectric, and the entire condenser was immersed in transformer oil. The spark gap *SG* consisted of two zinc electrodes, each having an area of 2 cm^2, placed about 1.5 cm apart.

In the preliminary experiments precautions were taken to insure the purity and dryness of the oxygen admitted to the discharge bulb. However,

ordinary commercial tank oxygen was found satisfactory and was used in all later experiments. The oxygen was admitted through a glass capillary, adjusted to give a suitable pressure in the discharge bulb.

The discharge was found to pass at any pressure between 0.007 and 0.45 mm. After experience had shown that the greatest chemical activity was found at a pressure of about 0.13 mm, this pressure was adopted in all later experiments. An intense line spectrum against a black background was observed under these conditions by means of a Zeiss pocket spectroscope. As seen by the eye in daylight, the discharge consisted of a general glow filling the bulb, with streamers of a different color following the directions of the coil. At low pressures the glow was a blue-gray while at high pressures a distinct pink color appeared in the blue. The streamers in both cases had a greenish blue appearance. Impurities such as mercury vapor and nitrogen were detected by their characteristic lines in the spectrum and by the changed appearance of the glow. Heating the walls of the bulb or running the discharge continuously for several hours had the effect of removing the impurities and intensifying the oxygen spectrum. The effect of water vapor as an impurity was unique and will be discussed at length in a later paragraph.

The detection of atomic oxygen. Freshly sublimed litharge was found to be an excellent detector at room temperature of atomic oxygen. The presence of water vapor, even in small traces, intensified the oxidizing conditions in the discharge. An extended investigation into the effect of varying amounts of water vapor upon the discharge led to the results summarized below.

Mixtures of oxygen and water vapor containing as much as 40 mol percent water vapor oxidized litharge in a few seconds to brown lead dioxide, when in direct contact with the discharge. Lead dioxide could be distinguished by chemical test from litharge and metallic lead, since it is very slightly soluble in 25 percent nitric acid, and gives a green color with an acetic acid solution of diphenylamine. If water vapor were in excess of about 40 mol percent the action was distinctly reducing, as in a hydrogen discharge; lead dioxide was reduced to litharge and litharge to metallic lead under these conditions. It was found that lead thus formed would be reoxidized directly to lead dioxide without the intermediate formation of litharge, when the conditions in the bulb became oxidizing.

The effect with dry hydrogen, with hydrogen saturated with water vapor at room temperature, or with water vapor alone in the discharge bulb was the stepwise reduction of lead dioxide to litharge, and of litharge to metallic lead, when these were in direct contact with the discharge. However, at a distance from the discharge, as under molecular ray conditions, lead dioxide was reduced to litharge but litharge was not reduced to metallic lead. This peculiar result has been noticed by another investigator.[3] Not only did the chemical effects indicate the presence of atomic hydrogen in all of these cases, but the Balmer series was observed to be very intense, and small particles on the walls of the discharge bulb glowed brightly. Both of these phenomena are characteristic of hydrogen atoms, and were never observed when dry

[3] DeHemptinne, Ann. Soc. Sci. Bruxelles **47B,** 143 (1927).

oxygen was admitted to a discharge bulb whose walls had been well outgassed. A very dry condition however, was not as conducive to intense oxidizing effects as was the presence of even a trace of water vapor. Hence in subsequent experiments the oxygen was saturated with water vapor at room temperatures before being introduced into the discharge bulb.

The detection of atomic oxygen with blue molybdenum oxide was also investigated. Since it was necessary to heat the oxide to a temperature of 200°C before oxidation by oxygen atoms occurred, it was considered less satisfactory than litharge.

The slit system. To produce a ray of atoms, an all Pyrex slit system was sealed to the discharge bulb as shown in Fig. 1. This consisted of two slits, 0.12 cm long and 0.005 cm wide, aligned with each other at a distance of 6.6 cm.[4] The space between the slits was connected with tubing 3.0 cm in diameter through a liquid air trap to a high speed mercury vapor pump. The second slit was connected to the target chamber by means of the small tube *D*. The target chamber was connected through a liquid air trap to a second high speed mercury vapor pump.

The target. The target consisted of a microscope cover glass held in an all Pyrex clamp so designed that the cover glass could be easily removed and mounted, for convenience in handling and photographing, on a microscope slide. No sealing wax or cement was used in holding the target. Repeated failures to obtain images when sealing wax or de Khotinsky cement were present in the vacuum led finally to the conclusion that these substances had a desensitizing effect upon the litharge surface. (This effect was not noticed with molybdenum oxide surfaces exposed to rays of hydrogen atoms.) The litharge was active only when freshly prepared and kept in a vacuum. Even in a vacuum it became less sensitive if the walls of the target chamber were heated, for the purpose of outgassing.

The litharge was deposited upon the microscope cover glass by sublimation. An oxyhydrogen flame was directed against a surface of molten litharge, thus producing a dense cloud of very fine particles. In order to obtain a fine-grained surface the cover glass was held close to the molten litharge. Under the best conditions surfaces were produced which showed no grain under high magnification. A transparent pale yellow layer about 4×10^{-5} cm in thickness was produced in this manner.

The magnetic field. A large DuBois magnet, an exact replica of the magnet used in a previous investigation,[5] was used in this research. The pole pieces were similar to those employed by Leu[6] and in accordance with his observations the inhomogeneity of the field may be assumed to be uniform throughout the region traversed by the ray. A cross-sectional view of the pole pieces is shown in Fig. 2. These were 6 cm long and were placed 0.3 cm apart. The slot was 0.6 cm wide. The edge of the 60° wedge-shaped piece

[4] The method of constructing these slit systems was devised by one of the authors, and will be published later.

[5] Phipps and Taylor, Phys. Rev. **29**, 308 (1927).

[6] Leu, Zeits. f. Physik **41**, 551 (1927).

was 0.1 cm wide. The position of the small Pyrex tube D and the path of the ray between the pole pieces are shown in Fig. 2.

Procedure. The apparatus assembled for a run is shown in Fig. 1. The discharge bulb was placed above the magnet, since in this position the discharge suffered less disturbance from the magnetic field than in any other position. Even in this position the current in the magnet coils could not exceed 5 amperes without causing serious interference with the discharge. The leak L (Fig. 1) was adjusted to give a pressure of 0.13 mm with oxygen in the discharge bulb. The pressure was measured by means of a McLeod gauge attached through a liquid air trap to the system at the point A. Before passing the discharge it was necessary to seal off the McLeod gauge to avoid "clean-up" of the atomic oxygen by the mercury of the gauge.

A run was then made with oxygen. The current in the primary of the transformer was about 13 amperes and that in the magnet coils was about 3.5 amperes. The re-entrant tube E in the discharge chamber permitted the insertion of a thermometer or thermocouple into the discharge for measuring the temperature near the first slit. The temperature remained fairly steady

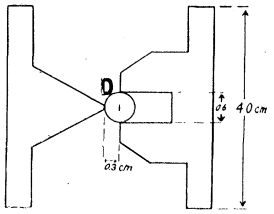

Fig. 2. Diagrammatic shetch of pole pieces (cross-section).

at about 340°C during the run. A thermometer was employed since a thermocouple was found unsatisfactory due to a disturbing effect of the discharge upon it.

An undeviated central line appeared after about two hours as a brown streak of lead dioxide on a pale yellow litharge background. After about nine hours faint lines on each side of the central line appeared. The run was continued for twenty hours,[7] after which the target was removed and attached to a microscope slide. In order to facilitate measurements of the image, photomicrographs of the image (7X) were taken (Fig. 3). It was found that blue transmitted light gave the best photograph of the oxygen image. Cramer's Super-contrast plates were employed. A density study of the re-

[7] In a preliminary run without the magnet, with 20 amperes in the primary circuit, images were visible in the vacuum within fifteen minutes. In the run with the magnet described above it was necessary to use a smaller current for a longer time due to the low capacity of the transformer. It was at first a source of surprise that twenty hours of running should be necessary to bring out the side lines to an intensity which made photographing possible. This is probably due (1) to the fact that the magnet current reduces the intensity of the discharge considerably, (2) to the fact that the magnetic field broadens the deflected ray and thus reduces its intensity, and (3) to the inadequacy of the transformer for continuous duty with large primary currents. Beyond this, however, it is probable that some unknown condition was unfavorable in this particular run.

sulting photographic negative was then made with a Moll Recording Microphotometer (Fig. 5a). A microphotometer study of the original image was unsuccessful, probably due to the slight difference in transmission coefficients of litharge and lead dioxide for the longer wave-lengths.

Fig. 3. Photomicrograph of oxygen image (7X).

Fig. 4. Photomicrograph of hydrogen image (7X).

The method employed in this investigation involves a comparison under identical conditions of the relative deflections of rays of oxygen and hydrogen atoms. The next step then was the substitution of hydrogen for oxygen

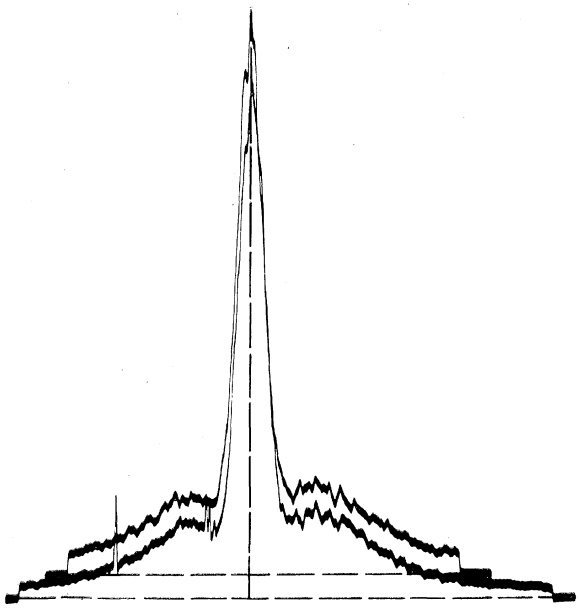

Fig. 5a. Microphotometer record of negative of oxygen photomicrograph.

in the discharge bulb. Molybdenum trioxide was used as a detector. The current in the primary of the transformer was 16 and that in the magnet coils was 3.5 amperes. The temperature of the discharge as recorded by the

thermometer near the first slit was 328°C. After fifty minutes the double-line splitting characteristic of the hydrogen atom appeared. The run was continued for three hours, after which the target was removed from the vacuum and photographed (Fig. 4).

Appearance of the images. Fig. 3 shows the photomicrograph of the oxygen image taken by transmitted blue light. From the image it can be seen that the inner edge of the deflected ray is relatively sharp compared with the

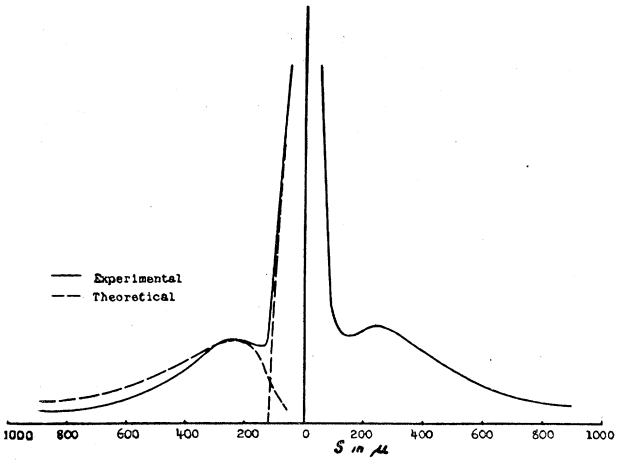

Fig. 5b. Smooth curve constructed from Fig. 5a.

outer edge, where the density falls off very gradually. This condition is unfavorable to the direct determination of points of equal density in the deflected ray, a procedure necessary to the calculation of the results. For this reason the microphotometer record (Fig. 5a) was made from the negative. Measurements were then made from Fig. 5b, which is a smooth curve constructed from Fig. 5a. The unsymmetrical appearance of the microphotometer curve for the two side lines in Fig. 5 is due to the fact that the

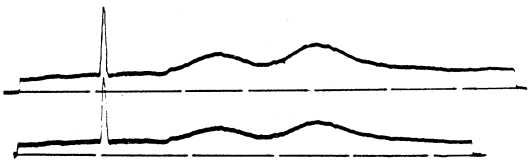

Fig. 6a. Microphotometer record of negative of hydrogen photomicrograph.

value of $\partial H/\partial s$ is not constant over the entire region traversed by the ray. served by means of light scattered along the X axis.

In the case of the hydrogen image also it was found advantageous to make the measurements from a microphotometer record of the negative. The density curve and the smooth curve constructed from it are given in Figs. 6a and 6b.

Since the value of $\partial H/\partial s$ is more constant on the side of the ray toward the slotted pole piece, all measurements were made from the corresponding side (left side) of the microphotometer curves.

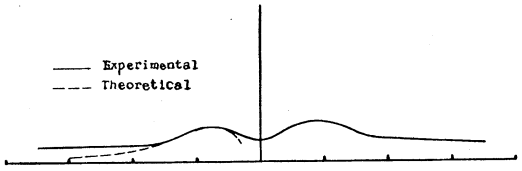

Fig. 6b. Smooth curve constructed from Fig. 6a.

Results and Calculation of Magneton Values

In order to calculate the relative magnetic moment of the oxygen atom from Eq. (1) it is necessary to know the value of s_α for both hydrogen and oxygen. This value however cannot be measured directly from the microphotographs of the images but must be calculated by means of an equation derived by Stern[8] from a consideration of the width of the undeflected ray and the Maxwellian distribution of velocities of the atoms in the ray. This equation is

$$s_\alpha = 3s_1s_2/(s_2-s_1)\left[\ln(s_2/s_1)+a^2/s_1^2\left\{2-4s_\alpha/3s_1+s_\alpha^2/6s_1^2\right\}\right] \qquad (3)$$

where s_1 and s_2 are points on the inner and outer edge, respectively, of the deflected streak, which have the same intensity; a is one-half of the width of the undeflected ray. Values of s_1 and s_2 for oxygen were obtained from

Table I
Dimensions of Apparatus

Distance between the slits	6.6 cm
Distance from the second slit to the target	9.6 cm
Length of the pole pieces, L_1	6.0 cm
Distance from the end of the field to the target, L_2	2.3 cm
Width of the first slit	0.0045 cm
Width of the second slit	0.005 cm
Length of the slits	0.12 cm
One-half the width of the undeflected line, a	0.0060 cm

Measurements from Microphotometer Records

Substance	T °K		s_1 μ	s_2 μ	s_α μ	M Bohr magnetons
Hydrogen	601		100	214	383	
			129	179	405	
				Avg.	394	1
Oxygen	613	Experimental	171	300	636	
			186	286	649	
				Avg.	642	1.67
		Theoretical	175	310	658	
			190	290	666	
				Avg.	662	1.71

[8] Stern, Zeits. f. Physik **41**, 563 (1927).

measurements upon Fig. 5b, and for hydrogen were obtained from Fig. 6b. These values are given in Table I.

From these values of s_1 and s_2 corresponding values of s_α for oxygen and hydrogen were calculated by means of Eq. (3). These values were then substituted in Eq. (2) to obtain the average value of ± 1.67 Bohr magnetons for the relative effective magnetic moment of the oxygen atom,—besides the value of zero.

Discussion of errors. The maximum probable error of s_α for oxygen is about three percent, and for hydrogen about four percent, and for each of the values of T about one percent. The value of $\partial H/\partial s$ is sufficiently uniform throughout the region traversed by the ray so that any error introduced by the use of Eq. (1) instead of a more exact equation is negligible.

Theoretical prediction of the magnetic moment. The ground term of the oxygen atom has been calculated by Hund[9] from a consideration of atomic structure to be a ^3P triplet state. This prediction has been confirmed by spectroscopic data.[10] The atom has one stable state, the $^3P_2$ state, and two metastable states, the $^3P_1$ and $^3P_0$ states. Since the term values for the triplet level are known, the relative probability of each state can be calculated from the equation

$$W=(2j+1)e^{-E/kT}=(2j+1)e^{-h\Delta\nu c/kT}. \tag{4}$$

The values of the probability W calculated for each state appear in column 4, Table II. The magneton values in column 5 have been calculated according to the usual method[9] for each of the P terms.

TABLE II. *Probabilities of the normal states.*

state	term values[10]	$\Delta\nu$	W	magneton values
$^3P_2$	109833 cm^{-1}	0	5	± 3, $\pm 3/2$, 0
$^3P_1$	109674	159	2.07	$\pm 3/2$, 0
$^3P_0$	109607	226	0.59	0

By summing up the probabilities for the magneton values in the separate states the total probability for each of the values is obtained. These are given in Table III. They are used later in calculating the resultant effective magnetic moment of the oxygen atom.

TABLE III. *Probabilities of the magneton values.*

magneton values	W
$+3$ or -3	0.438
$+3/2$ or $-3/2$	0.741
0	1

The theoretical intensity distribution curve for hydrogen is presented in Fig. 7, based upon the value of s given in Table I. The equation of Stern[8]

$$J/J_0=\tfrac{1}{2}\left[e^{-y}(y+1)\right]_{s\alpha/s-a}^{s\alpha/s+a} \tag{5}$$

[9] Hund, "Linienspektren" (1928).

[10] Hopfield, Nature **112,** 437 (1923); Phys. Rev. **21,** 710 (1923); Astrophys. J. **59,** 114 (1924).

was employed, in which J is the intensity of the deflected ray at a distance s from the center of the undeflected ray; s_α and a are the same quantities which appear in Eq. (3); and J_0 is the average intensity of the undeflected ray.

From the value of s_α for the hydrogen atom ($M=1$, $T=601°$K) were calculated values of s_α for the oxygen atom ($M=\pm 3/2$ and ± 3, $T=613°$K). Similar intensity distribution curves were plotted for these values (curves B and C in Fig. 7). Curves B and C are intensity distribution curves respectively for $M=3/2$, and $M=3$ with the proper statistical weights given to the values of J/J_0, shown in Table III. Curve D which is a summation curve from curves B and C represents the intensity distribution which should

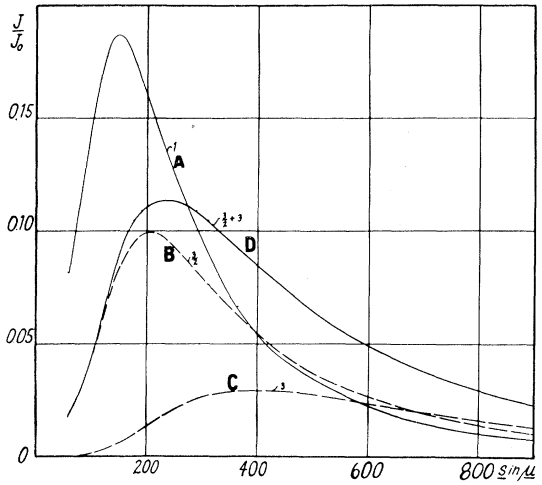

Fig. 7. Intensity distribution curves calculated as follows
A for $M=1$, $s=394\mu$. B for $M=3/2$, $s=580\mu$.
C for $M=3$, $s=1160\mu$. D is a summation of B and C.

obtain for the oxygen image. This curve appears also in Fig. 5b, for convenience in comparing it with the experimental intensity distribution curve. The theoretical curve is not expected to coincide with the experimental density distribution curve since the latter may be distorted in the direction of the intensity axis. However values of s_α and hence of M calculated from corresponding values of s_1 and s_2 taken from the two curves should agree. The extent of the agreement can be seen from a comparison of s_α (exp.) with s_α (theoret.) for comparable values of s_1 or s_2, as given in Table I, or from a comparison of the two curves in Fig. 5b. The experimental values of the effective magnetic moment of the oxygen atom, zero and ± 1.67 agree within the limits of experimental error with the theoretical values zero and ± 1.71 Bohr magnetons.

In conclusion the writers wish to thank Professors A. P. Carman and E. H. Williams of the Department of Physics for their kindness in allowing the use of the large Dubois magnet, and Mr. H. N. Swenson of the Department of Physics for his aid in making the microphotometer records.

Fig. 3. Photomicrograph of oxygen image (7X).

Fig. 4. Photomicrograph of hydrogen image (7X).