THE MAGNETIC MOMENT OF THE HYDROGEN ATOM

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Abstract

The magnetic moment of the hydrogen atom has been investigated by the atomic ray method introduced by Stern and Gerlach. Atomic hydrogen formed in a discharge tube by the method of R. W. Wood was first used. The ray was formed in a special all-glass slit system of three slits sealed to the discharge tube. The ray was detected by the reduction resulting on contact with a target coated with molybdenum trioxide. A sharply defined blue line against a white background was the result. In the magnetic field the ray was separated into two branching rays. There was also evidence of a central undeviated ray which is believed to be due to hydrogen active chemically but probably not in the atomic state. From a measurement of the deflection the magnetic moment of the hydrogen atom was calculated to be one Bohr magneton within the limits of experimental error. This result is of interest because of the questions raised by the new quantum mechanics of Heisenberg, Born, and Jordan, and by the spinning electron theory of Uhlenbeck and Goudsmit. Atomic hydrogen formed by the hot filament method of Langmuir was next used. The increased velocity of the atoms in this case resulted in less separation of the ray, but a deflection was distinctly recorded. Finally, the product formed on exposing a mixture of mercury vapor and hydrogen to ultra-violet light was investigated. This is believed by Cario and Franck, Taylor, and others to be atomic hydrogen. Thus far attempts to form a ray which will reduce the target have been unsuccessful. The reasons for this are being investigated.

THE magnetic moment of the hydrogen atom is of great interest since the hydrogen atom is the basis for the calculation of the unit of magnetic moment in Bohr's theory of the atom. Moreover, the magnetic properties of the hydrogen atom have recently become of unusual interest because of the questions raised by the new quantum mechanics of Heisenberg,¹ Born and Jordan,² and by the new theory of Uhlenbeck and Goudsmit,³ which gives the "spinning electron" a magnetic moment of its own. Born,⁴ in quoting an unpublished work by Pauli on the theory of the hydrogen atom, has stated that Pauli's theory contemplates a non-magnetic atom. This however does not take into account the theory of Uhlenbeck and Goudsmit, which if accepted will make necessary an addition to Pauli's theory. This state of upheaval in the theories makes direct experiment very desirable.

- ² M. Born and P. Jordan, Zeits. f. Physik, 34, 858 (1925).
- M. Born, W. Heisenberg, and P. Jordan, Zeits. f. Physik, 35, 557 (1926).
- ³ Uhlenbeck and Goudsmit, Nature, **117**, 264 (1926).
- ⁴ M. Born, "Problems of Atomic Dynamics," M. I. T., Cambridge, Mass., '26.

¹ W. Heisenberg, Zeits. f. Physik, **33**, 879 (1925).

In this work the magnetic properties of the hydrogen atom have been investigated. The experimental method was that of atomic ray deflection introduced by Stern and Gerlach⁵ in their investigation of the magnetic moments of several of the metal atoms. Stern and Gerlach secured direct evidence of space quantization and orientation when their rays of atoms were divided into separate rays on passage through an inhomogeneous magnetic field. Silver, copper, and gold showed a magnetic separation which yielded a value of magnetic moment closely equal to the Bohr unit magneton. One of the authors⁶ verified the work of Stern and Gerlach on silver in a modified apparatus, and in addition found the alkali metals sodium and potassium to possess unit magnetic moments.

The equation relating the amount of deflection of the atomic ray to the magnetic moment of the atom is

$$\frac{1}{M} = \frac{1}{2s} \left(\frac{\partial H}{\partial s} \right)_0 \frac{l^2}{3.5RT} \left\{ 1 + \frac{l^2 M}{12 \times 3.5RT \times s} \left[\left(\frac{\partial H}{\partial s} \right)_l - \left(\frac{\partial H}{\partial s} \right)_0 \right] \right\}$$

Here s is the amount of deflection measured as shown later; M is the magnetic moment (gauss-cm per mol); l is the length of the pole pieces of the magnet, the distance the atomic ray must travel through the magnetic field; $(\partial H/\partial s)_0$ is the value of the inhomogeneity of the field at the point where the ray enters the field; $(\partial H/\partial s)_l$ is the corresponding inhomogeneity at the end of the field, after the deflection of the ray. This is not equal to $(\partial H/\partial s)_0$ since $(\partial H/\partial s)$ changes in value from point to point across the field between the pole pieces, being greatest next to the knife-edged pole piece. The values of $(\partial H/\partial s)$ are obtained for any distance of the ray from the knife edge by a preliminary mapping of the field. The 3.5 RT term comes from the expression which Stern⁷ found in his direct measure of the velocity of the silver atom. In the present work the hydrogen atom has been found to be magnetic and its magnetic moment has been calculated.

A. ATOMIC HYDROGEN FROM THE DISCHARGE TUBE

The discharge tube. Hydrogen was prepared by the electrolysis of barium hydroxide solution, dried when desired by passing through a liquid air trap, and admitted to the discharge tube through a regu-

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⁵ O. Stern, Zeits. f. Physik, 7, 249 (1921).

W. Gerlach and O. Stern, Ann. d. Physik, 74, 673 (1924).

W. Gerlach, Ann. d. Physik, 76, 163 (1925).

⁶ J. B. Taylor, Phys. Rev., 28, 576 (1926).

⁷ O. Stern, Zeits. f. Physik, 2, 49 (1920).

lated leak. In most of the work with the discharge tube, the hydrogen was not dried, in accordance with the procedure of R. W. Wood.⁸ The discharge tube was similar to that used by Wood, Bonhoeffer⁹ and Copaux.¹⁰ It was made of 18 mm Pyrex tubing and had a total length of 3.5 meters. The electrodes were cylinders made from aluminum sheet and crimped to tungsten lead-out wires. The electrode tubes were bent over as shown in Fig. 1, to prevent small particles dislodged from the electrode surface from falling into the central portion of the discharge tube. Such metallic particles were undesirable since they catalyze the recombination of atomic to molecular hydrogen, as was shown by the change in color of the discharge in the vicinity of such



Fig. 2. Method of preparing the glass slit system. Fig. 3. Completed slit system, showing preliminary target.

particles from deep pink to white. These particles were seen to glow intensely in the discharge on account of the heat liberated on their surface. The tube was operated on a 1 kw transformer at 25000 volts. The pressure of undried hydrogen was 0.12 mm. Under these conditions a pure spectrum consisting of intense lines of the Balmer series against a black background was observed by means of a Zeiss pocket spectroscope. When the tube was first put into operation the complex secondary spectrum sometimes appeared in the background, but with

- ⁹ K. F. Bonhoeffer, Zeits. f. Phys. Chem. 113, 199 (1924).
- ¹⁰ Copaux, Perperot, and Hocart, Bull. soc. chim. 37, 141 (1925).

⁸ R. W. Wood, Phil. Mag. 42, 729 (1921).

prolonged operation of the tube this disappeared and pure Balmer series remained. This phenomenon was first described by R. W. Wood.

The slit system. To form the atoms present into a ray, an all-glass slit system was sealed to the central portion or foot of the discharge tube as indicated in Figs. 1, 2, and 3. When a metal slit system was sealed to the midpoint of the discharge tube, the discharge for an inch or more to each side was distinctly white. For this reason glass as a material for the slit system was preferred to metal.

Each of the three slits used was 0.075 mm wide and 3 mm long. They were constructed by placing a steel ribbon of these dimensions through a glass apparatus (Fig. 2), which had been constricted at three points. This ribbon was suspended from one end as shown, stretched taut by a weight on the other end, and adjusted to hang perfectly straight through a guide which permitted no twist. Then beginning at the top each constriction was heated in turn and the glass pinched with knife-edged tweezers on to the ribbon. Each pinch was followed by careful heating and annealing to relieve all strain in the system. This procedure gave the three slits the perfect alignment necessary for the formation of a sharply defined ray of atoms. Finally, after the three pinches had been made, the whole tube carrying the slits was given a prolonged annealing in a large air-free gas flame. When cooled to approximately 100°C it was then immersed in a hot bath of hydrochloric acid to dissolve out the steel ribbon. The glass rod supports shown between the side tubes (Figs. 2 and 3) served to keep the slit system rigid during and after the pinching treatment and yielded support to the fragile slits. These supports were not heated during the annealing. The system was sealed off at c (Fig. 2) and later made part of the discharge tube as shown in Fig. 1, by sealing on at a and b.

From each slit-chamber tubes led off through liquid air traps to separate high-speed mercury vapor pumps. This use of separate pumps maintained a progressively increasing vacuum in the system. In the discharge tube itself a pressure of 0.12 mm was produced through the leak valve from the hydrogen generator. The pump between the first and second slits then reduced this pressure to approximately 0.005 mm in the first chamber. On account of this reduced pressure, atoms leaving the discharge tube through the first slit and directed towards the second slit suffered only slight interference in their path. Then between the second and third slits another pump caused a reduction to less than 0.0001 mm. The increased free path in this chamber further favored the progress of the directed ray of atoms, and the third slit served to define the ray still more sharply. Stray hydrogen atoms may have been removed also by recombination on the glass walls. This would aid in the production of a well-defined ray.

The target. This unidirectional ray entered the chamber above the third slit where it was received on a target of molybdenum trioxide (Fig. 3). The target was a ground fire-polished surface of glass which was coated with a very fine-grained deposit of molybdenum trioxide. The deposit was formed by holding the cold target intermittently in the smoke produced by igniting a piece of molybdenum sheet in a hot oxygen-gas flame. Very fine smoke particles resulted from the ignition. A surface when prepared properly showed no grain under a magnification of $26 \times$ and was almost pure white, with a very slight yellow tinge. The image which the ray of atomic hydrogen formed on the target by reduction of the trioxide to a lower oxide, was a dark blue and was distinctly visible against the white background.

Assembly of the apparatus. In the preliminary tests without the magnetic field, the target was introduced as a re-entrant tube (Fig. 3, above the dotted line). The distance from the third slit to the target was 3 cm to reproduce the length of path required later in the magnetic measurement. With this preliminary apparatus the conditions for forming an image of the atomic ray were studied. When satisfactory conditions had been determined the upper portion was removed at d(Fig. 3) and the remaining slit system was cemented into the brass box (Fig. 4) containing the pole pieces.

This pole piece box had been used previously by one of the authors⁶ in the determination of the magnetic moments of the alkali metals, and it was modified only slightly to allow the replacement of the pair of metallic slits used in that investigation by the new glass slit system.

The slit system was held rigidly in a brass collar and plate with high melting de Khotinsky cement. Adjustment of the slit path to parallelism with the knife edge and to the desired distance from the knife edge was accomplished by motion of this plate, which was slotted about four screws set into the body of the box. When the slit path had been properly adjusted, the screws were tightened and all joints were made vacuum tight with a beeswax-rosin mixture. The pole-piece box with its slit attachment was then clamped between the broad faces of the electromagnet,¹¹ and sealed to the discharge tube at a and b (Fig. 1), and to the vacuum pumps at e, f, and g (Fig. 5). The target consisted of a re-entrant glass tube of the form shown in Fig. 4. The preparation of the molybdenum trioxide surface has been described above. The

¹¹ The same electromagnet used in the previous investigation already mentioned.

target was sealed into the annular channel at the top of the pole-piece box with beeswax-rosin mixture.

Fig. 5 shows the complete connections for a magnetic measurement with atomic hydrogen from the discharge tube. Pump No. 1 evacuated directly the first slit-chamber, and through stopcock S served to evacuate the discharge tube and connections to the hydrogen generator. Pump No. 2 evacuated the second slit-chamber and the pole-piece box. High range McLeod gauges were used to determine the vacuum conditions in the slit-chambers and pole-piece box.



Fig. 4. Pole-piece box with slits and target attached. Fig. 5. Diagrammatic sketch of complete connections. Dotted lines indicate position of electromagnet.

Procedure. With S open, a high vacuum of the order 10^{-6} mm or less was obtained in the entire system. S was then closed and the hydrogen leak regulated until an approximate pressure of 0.12 mm was obtained in the discharge tube, as recorded by McLeod Gauge No. 3. The discharge could not be maintained at pressures very much lower than this; while at higher pressures the ray became more diffuse, as was shown by a greater general reduction over the face of the target. For a run without magnetic field the discharge was then started. For a run with magnetic field the field was applied before the discharge was started. In the latter case, on account of the large heating effect caused by the magnetic field, it was found necessary to cool the foot of the discharge tube with running water. At the end of about twenty minutes a light line image caused by the ray could be seen distinctly by looking down on the target (as shown by the arrow in Fig. 4). It was rather surprising that the image could be seen from the reverse side in this manner. This very desirable result was due doubtless to the extreme thinness of the molybdenum trioxide deposit and to the penetrating power of the ray of atomic hydrogen. At the end of approximately four hours the image appeared to have reached its maximum density. The target was then removed, the image was examined under the microscope, and measured with a micrometer eyepiece. Photomicrographs were then made of the image and of a comparison scale (0.1 mm divisions), by which means the micrometer measurements were confirmed.

Discussion of images. Fig. 6, I and II are photomicrographs $7 \times$ of images secured without and with the magnetic field respectively. These photomicrographs were taken with light transmitted through the glass target and oxide coating. Separation into two lines is very distinct. A remarkable difference in the appearance of the image was noticed depending on whether it was viewed by transmitted or reflected light.



Fig. 6. I, II, III. Photomicrographs $(7 \times)$ of images secured with hydrogen discharge tube. I. Without field. II. With field, showing separation of ray. III. With field showing separation overshadowed by diffuse central ray.

IV, V. Images secured with atomic hydrogen from a hot filament. IV. Without field. V. With field, showing broadening secured with high velocity atoms.

VI. Diagrammatic sketch of II. s = 0.19 mm, c = 2.2 mm, D = 0.9 mm, A = 0.08 mm, B = 0.30 mm.

Fig. 6, II shows clearly the two lines which were always most prominent by transmitted light. Fig. 6, III shows the entirely different appearance by reflected light. Here a central undeviated line with diffuse edges overshadows the deviated branches to such an extent that a casual observer might fail to notice them.

The following tentative explanation of this phenomenon is offered. The two branches seen in Fig. 6, II (transmitted light) are due to atomic hydrogen. The undeviated central line of III (reflected light) is due to hydrogen active chemically toward molybde-num trioxide, but probably not in the atomic state. The dissociation of molecules into atoms in the discharge is far from complete. Bonhoeffer⁹ estimates that 20 percent

only is dissociated under conditions similar to those of this experiment. The ray then consists in large part of hydrogen molecules. It is conceivable that high speed hydrogen molecules or excited molecules produced in the discharge might be active chemically but show no appreciable deviation in the magnetic field, thus accounting for the central undeviated line.

If this explanation is received as plausible, it remains to explain why the two branches (Fig. 6, II) ascribed to atomic hydrogen should be indistinct by reflected but very plain by transmitted light; whereas the undeviated line (Fig. 6, III) ascribed to molecular hydrogen should be far more distinct by reflected than by transmitted light. If it be assumed that atomic hydrogen penetrates the molybdenum trioxide coating to a greater depth than does molecular hydrogen, it is apparent that there will be much greater depth to an image formed by atomic hydrogen than to one formed by molecular hydrogen, and this depth of image will best appear when it is viewed by transmitted light, under which condition one observes the accumulated effect of reduction in all the layers. On the other hand, reduction due to molecules would be more superficial in character, and such an image would appear strong by reflected light, but would show very little opacity by transmitted light.

To test the idea that the central line might have been caused by high velocity hydrogen molecules, the hydrogen entering the lowest slit was heated to 400° C in the absence of a discharge. (The temperature of the discharge had previously been shown to be about 400° C. See below.) After 17 hours no image was visible on the target. This result shows that normal hydrogen molecules at the temperature of the discharge probably could not have caused the central line. It seems not unlikely that this undeviated line may have been due to excited hydrogen molecules from the discharge. The peculiar character of the central line as described above, and our present conception of the hydrogen atom seem to preclude the possibility that it was caused by atomic hydrogen.

The flattened cusp at the center of the left branch (Fig. 6, II) marked "X" in Fig. 6, VI, shows the position of the knife-edged pole piece. At this point the ray has actually been drawn against the knife edge by the greater inhomogeneity of the field at the edge. For this reason the more uniformly deflected right hand branch was chosen for the measurement of s. Fig. 6, VI is a diagram of II with dimensions. The distance s is the quantity used in the calculation of M, the magnetic moment.

Temperature of the discharge. Before a calculation of magnetic moment could be made, it was necessary to measure the temperature in the discharge tube. This temperature appears to be very uncertain on account of the violent electrical conditions existing in the discharge. To get an approximation of the temperature a glass-sheathed thermocouple (chromel-alumel, B. & S. No. 28) was sealed into the discharge tube and made to extend centrally down the entire length of the foot of the discharge tube (Fig. 1), a length of about 25 cm. The junction was not more than 3 cm distant from the point at which the slit system was sealed. A glass sheath was used in order to avoid to a large degree the false temperature effect which would have been observed with a bare thermocouple on account of recombination of atomic hydrogen on its surface. The temperature recorded was about 390°C at the pressure (0.12 mm) used in the magnetic experiments.

Calculation of the magnetic moment. The data for the calculation of M, the magnetic moment of the hydrogen atom, are as follows. l, the pole piece length, 3 cm; the distance from the middle of the slits (i.e. of the ray) to the knife edge, 0.29 mm, corresponding to the value $(\partial H/\partial s)_0 = 140,600$ gauss/cm; s = 0.19 mm; $(\partial H/\partial s)_l = 107,800$ gauss/cm; T the absolute temperature, 663° K. Upon substitution of these values into the equation given above, there results M = 6050 gauss-cm. This is 8 percent higher than 5600 gauss-cm, the magneton value calculated on the basis of Bohr's theory.

Errors. Should a high precision determination of the moment of the hydrogen atom be made, the following errors must be eliminated. (a) Errors in $(\partial H/\partial s)_0$ and $(\partial H/\partial s)_1$ may amount to 2 percent. (b) Three independent measurements of s by different observers from the same photomicrograph agreed within 2 percent. s cannot be measured with extreme accuracy at present since the deflected ray is slightly diffuse at its edges and is broader than the original ray. This "spreading" is a consequence of the Maxwellian distribution of velocities, i.e. the s for individual atoms is spread over a range of values. This can be remedied by producing a ray of single (or narrow-range) velocity atoms. Narrower slits would also reduce the uncertainty in the measurement of s by decreasing the width of the image of the deflected ray relative to the total splitting. The detection of the ray on targets of molybdenum trioxide was very satisfactory. The images formed were easily visible and permanent. (c) The temperature (velocity) error. There is an uncertainty of perhaps as much as 25° (approximately 4 percent) in the above value of the temperature of the discharge from the following causes. Slight fluctuations in pressure were unavoidable; and it was found that the temperature varied inversely as the pressure. Another uncertainty was the unknown extent to which the glass sheathing of the thermocouple catalyzed the recombination of the hydrogen atoms. This operated no doubt to make the observed temperature higher than the true temperature of the discharge. Since this factor was though to be a very important one, 390°C probably represents a maximum value for the temperature of the discharge. Losses by conduction away from the thermocouple junction were minimized by leading the thermocouple wires through a considerable length of the discharge tube. For obvious reasons a metal radiation shield could not be introduced into the discharge, and consequently radiation losses were uncertain and perhaps large. On account of the uncertainty of measuring the temperature of the discharge, a direct determination of the velocity of the atoms leaving the discharge tube (by a method similar to that used by Stern⁷ with silver atoms) will probably be the best way in the future of eliminating the temperature error.

The summation of errors in the above determination of the magnetic moment of the hydrogen atom may amount to 10 percent. Within experimental error then the hydrogen atom has been shown to have a magnetic moment equal to one Bohr magneton. This experimental result appears to be in harmony with Bohr's conclusions as to the magnetic properties of the hydrogen atom, and provides a condition that must be met by the newer quantum theories.

B. Atomic Hydrogen from a Hot Filament

Following the tests on atomic hydrogen made in a discharge tube, atomic hydrogen formed by the hot filament method of Langmuir¹² was investigated. The discharge tube was replaced by a simple glass chamber containing a tungsten filament spot-welded through nickel intermediate supports to tungsten lead-in wires (B. & S. No. 18). The filament consisted of 15 turns of 7 mil wire closely wound on a core of approximately 1 mm diameter. The filament was heated by a current of 2.5 amperes to a temperature estimated at 2800°C. It was placed within less than 1 mm of the first slit. Hydrogen was admitted as described for the discharge tube and the same pressure was used. To prevent possible poisoning and deterioration of the filament the hydrogen was first dried by passing it through a liquid air trap. The chamber was water-jacketed.

With all other conditions identical with those of Section A, an image on the molybdenum trioxide target was visible in about 40 minutes. However, as indicated in Plate 5, a splitting of the image did not appear. Because of the greatly increased velocity of the atoms formed on the glowing filament, the deflection of the ray in the magnetic field appeared only as a slight broadening. On account of the presence in the ray of extremely high velocity molecules, probably capable of reducing molybdenum trioxide, a heavy undeviated central line helps to overshadow the separation. Plate 4 shows the image in the absence of a magnetic field. With narrower slits the broadening might be resolved into a separation which would allow a calculation of the magnetic moment.

¹² I. Langmuir, J. Am. Chem. Soc., 38, 2221 (1916).

C. ACTIVE HYDROGEN BY THE MERCURY VAPOR, HYDROGEN, ULTRA-VIOLET LIGHT METHOD

Recently Cario and Franck,¹³ Taylor and Marshall,¹⁴ Bonhoeffer,¹⁵ and others have investigated the chemical reactions of the product formed on exposing a mixture of hydrogen and mercury vapor to ultraviolet light. The nature of the reactions obtained indicated the presence of atomic hydrogen. To conclude the present investigation, it was thought desirable to test the magnetic properties of active hydrogen produced by this method. The chamber containing the tungsten filament was replaced by a shorter chamber with a quartz end-plate and a reservoir of mercury. This chamber was heated to 45°C (the temperature employed in Cario and Franck's experiment), and exposed to the ultra-violet light from a water-cooled mercury arc. The quartz window of the arc was placed in contact with the quartz end-plate of the slit system. A pressure of hydrogen from 0.1 to 0.2 mm was maintained. The slit system and the rest of the apparatus were the same as in Sections A and B.

Preliminary trials in which re-entrant rods coated with molybdenum trioxide were sealed into the lower chamber resulted in almost instantaneous reduction of the white trioxide to the blue lower oxide. The test rods were then removed. After several runs with a slit system and target, one of which lasted for 43 hours, no trace of an image was secured on the target. This unexpected result led to a short investigation of the reasons for the failure to obtain a ray of the active product. A bare thermocouple (platinum, platinum-rhodium, B. & S. No. 36) was sealed into the reaction chamber in order to note any rise of temperature due to recombination of hydrogen atoms on its surface. No rise was noted. The same thermocouple sealed into a side tube leading from the discharge tube (Section A) and at 10 cm distance from the discharge showed a rise of temperature of more than 600°C. Furthermore a small amount of molybdenum trioxide introduced into the ultra-violet reaction chamber showed only slightly more than a surface reduction after an eight hour period of exposure. Boats of the trioxide similarly placed in side arms of the discharge tube showed reduction to a depth of a millimeter in a few minutes time.

The conclusion which may be drawn from the behavior of thermocouples, and from the chemical activity in the discharge tube and

¹³ Cario and Franck, Zeits. f. Physik 11, 161 (1922).

¹⁴ H. S. Taylor and A. L. Marshall, J. Phys. Chem. 29, 1140 (1925); J. Phys. Chem. 30, 34 (1926).

¹⁵ K. F. Bonhoeffer, Zeits. f. Phys. Chem. 119, 474 (1926).

the ultra-violet chamber respectively, is that atomic hydrogen if present in the latter case can be there in small amounts only. This may explain the failure to secure a detectable ray of atomic hydrogen in a reasonable length of time from the ultra-violet chamber. However, since our preliminary experiments with oxide coated rods showed that appreciable amounts of molybdenum trioxide were reduced by *some* active substance in the ultra-violet chamber, the failure to produce a beam may also be explained by the assumption that the active substance consisted not of atomic hydrogen but of short-lived excited hydrogen molecules¹⁶ or of mercury hydride.¹⁷ Either of these products might be expected to possess sufficient chemical activity to reduce molybdenum trioxide when first formed in the lower chamber, but might have too short a life to form a ray. This question is receiving further investigation.

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¹⁶ E. K. Rideal and Hirst, Nature, 117, 449 (1926).

¹⁷ K. T. Compton, Phil. Mag., 48, 360 (1924).

K. F. Bonhoeffer, Zeits. f. Phys. Chem., 116, 391 (1925).



Fig. 6. I, II, III. Photomicrographs $(7 \times)$ of images secured with hydrogen discharge tube. I. Without field. II. With field, showing separation of ray. III. With field showing separation overshadowed by diffuse central ray.

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