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DIFFRACTION OF HYDROGEN ATOMS

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Abstract

Diffraction patterns of a beam of hydrogen atoms reflected from LiF.—Improved technique in the photography of the diffraction patterns produced by the reflection of a beam of hydrogen atoms from a crystal of lithium fluoride has resulted in more complete patterns than those previously described by the author. The observed patterns are those expected on the assumptions (1) that the incident beam contains the distribution of wave-lengths derived from the Maxwellian velocity distribution by the use of the de Broglie relation between wave-length and velocity, and (2) that the surface of the crystal constitutes an impenetrable square array of scattering points with the arrangement and spacing of the ions of a single type as known from x-ray measurements.

Wave-length distribution.—The intensity distributions in the diffraction patterns were measured, and were found to have maxima at positions in good agreement with those expected on the basis of the above assumptions.

Interpretation of relative intensities in the different orders.—The relative intensities in the observed orders are discussed in relation to the scattering coefficients of the two types of ions, and in relation to the dependence of the scattering coefficient on azimuth.

Diffraction by the secondary structure of the crystal.—A secondary spectrum is described, arising from a lattice of wide spacing the lines of which are parallel to the 100 cleaved edges of the crystal face.

IT HAS been well established for some time that the quantum mechanics correctly describes the motion of a free or a bound electron. Its success in the interpretation of band spectra has also shown that the motions of atomic nuclei within the molecule could be included in the theory, and because of this, it appeared almost certain that the new mechanics would be found correct in its description of the free motion of atoms and molecules. The comparatively recent experiments of Estermann and Stern[1] and of the author[2] were not disappointing in this regard for they have demonstrated that atoms and molecules of low atomic weight behave as predicted, in that they exhibit the properties of a wave radiation of wave-length $\lambda = h/mv$ in the plane-grating diffraction phenomena which appear when these are reflected from the surface of a crystal. These experiments are of interest not only because of their confirmation of the predictions of quantum mechanics, but also because

[1] Estermann and Stern, Zeits. f. Physik **61**, 95 (1930). O. Stern, Die Naturwissenschaften **17**, 391 (1929).

[2] T. H. Johnson, Phys. Rev. **35**, 1299 (1930).

they introduce the possibility of applying atom diffraction to investigations of the atomic constitution of surfaces. A beam of atomic hydrogen, for example, with ordinary thermal velocities, has a range of wave-lengths of the right magnitude for this purpose, centering around 1A, and the complete absence of penetration of these waves will insure that the effects observed arise entirely from the outermost atomic layer.

The first experiments demonstrating the diffraction of hydrogen atoms when reflected from a crystal of lithium fluoride were described in some detail in the Journal of the Franklin Institute.[3] The diffraction patterns which were photographed in that earlier work were of low intensity and they showed only a part of the complete structure which should have been produced by the array of ions on the surface of the crystal. Because of the low intensity in these earlier patterns, satisfactory intensity measurements were impossible, and only a rough comparison could be made between the observed distribution of wave-lengths and that predicted from the Maxwellian velocity distribution and the de Broglie relation between velocity and wave-length.

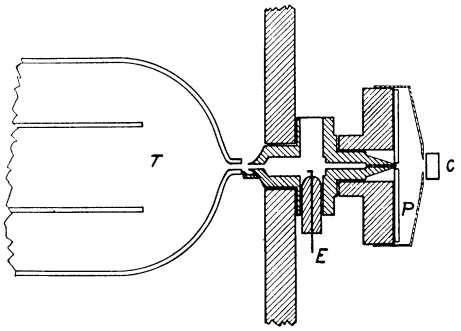

Fig. 1. Collimating system for normal incidence.

Recent improvements in the technique of obtaining photographic records of the diffraction patterns have overcome in large measure the deficiencies of the earlier work, and patterns of far greater intensity have been photographed which show all of the expected first-order branches. The intensity is now sufficient for the purposes of making photometric measurements of the wave-length distribution, and it has been possible to make some rough estimates of the relative intensities in the principle branches. In addition, some new features have been recorded which throw light upon the secondary structure of the crystal.

With the exception of a few modifications, the apparatus and the experimental procedure were the same as in the earlier work. A sharply defined beam of hydrogen atoms had its origin in a chamber T, Fig. 1, in which molecular hydrogen was dissociated by an electric discharge, and it was collimated by a series of tubes with suitable pumping systems for eliminating the excess gas. This beam was reflected from a freshly cleaved surface of a crystal (C) of lithium fluoride, and the reflected atoms were recorded on a plate (P)

[3] T. H. Johnson, Jour. Frank. Inst. **210**, 135 (1930).

coated with molybdenum oxide After an exposure the patterns recorded on the molybdenum oxide plate were made permanent by photographing in the usual way.

Since it is believed that atom diffraction may prove useful in studying the structure of surfaces a discussion of some of the technical features will be included for its interest to other investigators in this field.

Formation of the Beam

In designing a collimating system for the production of a molecular beam for use in diffraction experiments there are two requirements; the beam should be intense and it should be sufficiently sharp to resolve the effects sought. In the limit these demands are conflicting in that an increase in the sharpness of the beam results in a decrease in its intensity, and *vice versa.* Over the range of source chamber pressures which is of interest, the intensity of the beam, as regards its dependence on the configuration of the collimating system, is proportional to the area of the source aperture and inversely proportional to the square of the distance from the source to the point of detec-

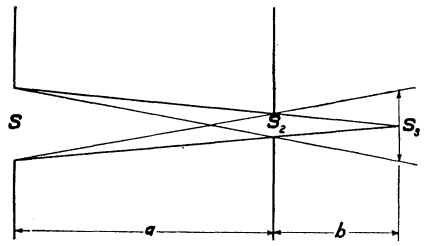

Fig. 2.

tion, and it is independent of the position and size of the collimating aperture as long as the point of detection is not occluded from any part of the source aperture. The sharpest beam, for a given intensity, may be obtained by making the collimating aperture a section of the cone of which the source aperture is the base, and the point of detection is the vertex. The linear dimensions (S_2, S_2') of the collimating aperture are therefore related to the corresponding dimensions (S_1, S_1') of the source aperture by

$$S_2 = S_1 b/(a + b), \tag{1}$$

where a and b are the distances indicated in Fig. 2. The corresponding dimensions of the cross-section of the beam at the point of detection are given by

$$S_3 = 2S_1 b/a. \tag{2}$$

Similar expressions also hold for the S' dimensions.

If a perfect reflector is placed a negligible distance behind the collimating aperture two reflected beams separated by an angle $\Delta\theta$ will be just resolved if their linear separation is equal to the beam width, i.e.

$$b\Delta\theta = 2S_1 b/a. \tag{3}$$

The resolving power of the collimating system, in the plane determined by S and the beam, defined as

$$R = 1/\Delta\theta = a/2S_1, \tag{4}$$

is independent of b and would remain unaffected by shortening this distance as much as permitted by convenience of construction.

The intensity I of the beam depends upon these dimensions of the collimating system in the manner

$$I \sim \frac{S_1 S_1'}{(a+b)^2} = \frac{aS_1'}{2R(a+b)^2} = \frac{a^2}{4RR'(a+b)^2}. \tag{5a, b}$$

From (5a) it is seen that, with fixed resolving power in one direction and fixed dimension S_1' normal to this direction, I has its greatest value, as regards its dependence on b when $b=0$, and, as regards its dependence on a, when $a=b$. If the resolving power is to be fixed in two dimensions, as, for example, would be the case with circular beams, (5b) shows that the intensity undergoes no variation with changes of the size of the collimating system, but it is inversely proportional to RR'.

Under the first of these conditions the greatest intensity is obtained with the collimating system as short as possible and the sizes of the apertures determined by (4) and (1) to yield the required resolving power.

The variation of beam-intensity with source-tube pressure is the next point to consider. The principles involved are not as clear in the case of atomic hydrogen beams as with other gases, for the degree of dissociation in the discharge tube depends, among other things, upon the pressure. With an incomplete understanding of discharge tube phenomena, considerations of this kind will be omitted and only the usual elements of the kinetic theory of gases will be taken into account.

On this basis the number of atoms leaving the source aperture in the direction of the beam is proportional to the pressure in the source chamber over the range of pressures for which "molecular flow" subsists. This number is diminished by collisions over the path a', between the source and the entrance to the collimating aperture, by the factor $e^{-a'/L}$ where L is the mean free path in this region. Since the speed of the diffusion pump which is used to eliminate the excess gas from the region between the first two apertures is approximately independent of the pressure, a constant ratio exists between the pressure within the source chamber (p) and that in the intermediate region, and L is inversely proportional to p. The intensity of the beam then varies with the pressure in the source chamber in the manner

$$I = Ape^{-p/p_0} \tag{6}$$

in which the constant p_0 is the pressure in the source chamber for which the intensity of the beam is a maximum. An expression of this form is in agreement with the observations on beam intensities in these experiments as well as with other published data, and with the apparatus used in these experi-

ments p_0 was found to be 0.3 mm. Corresponding to p_0, the intensity of the beam, from (6), is

$$I_0 = Ap_0/e. \tag{7}$$

From the above considerations it may be seen that p_0 is proportional to the resistance of the source aperture, to the speed of the pumping system operating between the source and first collimating aperture, and inversely proportional to the path a' of the beam in this region, while the constant A is proportional to the ratio of the number of atoms which have the direction of the beam to the total emission from the source, and inversely proportional to the resistance of the source aperture. To realize a large value of I_0, a high speed pump and large connecting tubes were used at the first stage, the path a' was made as short as possible by the use of an auxiliary collimating tube (Fig. 1), and the source aperture was tubular in shape to produce a favorable directional distribution of the emitted atoms.

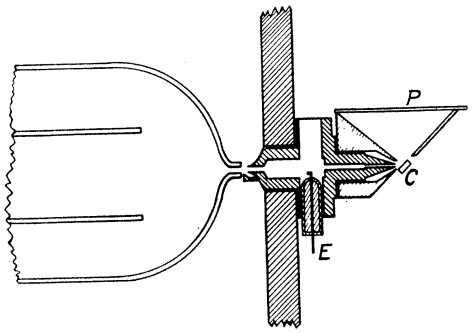

Fig. 3. Collimating system for 45° incidence.

Insofar as the directional distribution of the atoms emerging from the source aperture is unaffected by changes in its dimensions, the resolving power can be increased without affecting the intensity by diminishing the dimensions of the source aperture and simultaneously increasing the pressure in the source chamber so that the total number of atoms which emerge from the source aperture remains unchanged. A change of this character should leave the number of collisions in the intermediate chamber unaffected, for there the free path depends only on the rate at which gas is flowing in from the source chamber. This consideration therefore leads to the conclusion that the intensity can be increased, with fixed resolving power in *two* dimensions, by diminishing the size of the collimating system and simultaneously increasing the pressure in the source tube.

The collimating systems (Figs. 1 and 3) used in these experiments were constructed along the lines of these principles except that, in the arrangement for normal incidence, it was inconvenient to place the crystal directly in front of the last collimating aperture. The important dimensions are included in the following table.

Diameter of source tube	0.65 mm
Length of source tube	1.3 mm
Diameter of first collimating tube	0.67 mm
Diameter of second collimating tube	0.18 mm
Distance (a') from source tube to first collimating tube	1.0 mm
Distance (a) from source tube to far end of second collimating tube	24 mm
Distance (b) from end of second collimating tube to plate by way of specular reflection from the crystal at normal incidence	9 mm
Distance (b) for 45° incidence	10.5 mm

Elimination of High Energy Ions from the Atom Beam

One of the principal obstacles which stood in the way of the recording of intense patterns in the earlier work was the disintegration of the crystal surface by ion bombardment. Ions diffusing from the discharge chamber were

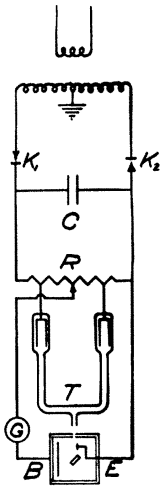

Fig. 4. Electrical connections.

subjected to a potential fall of the order of 5,000 volts between the center of the discharge and the observation chamber and some of these entered the beam and bombarded the crystal. The importance of their effect may be realized from the fact that, if unimpeded, the ion bombardment was sufficient to disintegrate the surface of the crystal in less than one minute to the extent of putting a stop to the regular reflection of atoms. The introduction of an electrode E (Figs. 4 & 1) to sweep the ions from the beam, materially improved the situation and exposures of three hours were feasible. There remained, however, a smaller number of neutral atoms of high energy in the beam which were formed in the first collimating tube by the neutralization of ions and these were not eliminated in this way. In the latest work, therefore, two additional precautions were taken. (1) The potential of the observation chamber was adjusted to be approximately the same as that of the center of

the discharge tube, so that ions diffusing from the source tube were accelerated as little as possible. (2) The remaining field between the center of the discharge and the entrance to the first collimating tube was made asymmetrical so that the ions were accelerated out of the line of the beam. The result of these precautions has been an almost complete elimination of the effects of bombardment with a resulting increase in the possible time of exposures to 24 hours or longer and a corresponding increase in the intensity of the patterns.

Fig. 4 is a diagram of the electrical circuit which was used to operate the discharge. A d.c. source of potential was supplied by a transformer and two kenetrons connected for half-wave rectification. This method of connecting the kenetrons had the advantage that the potential of the observation box, when adjusted to equal that of the center of the discharge, was close to the ground potential, and no trouble was experienced with leakage currents although the design of the apparatus made it inconvenient to insulate the box to withstand high voltages. To reduce the fluctuation of potential which took place during the cycle of alterations of the primary e.m.f., a condenser (C) having a capacity of 0.08 mf was used. A water resistance (R) served as a convenient potential divider and ballast resistance for the discharge. This was constructed of a series of four interconnected glass U-tubes, each 1.5 meters in length and 5 mm in diameter through which tap water was continuously circulated. This resistance could be varied in any of its parts by the insertion of wires into the arms of the U's, and it was adjusted so that no current was registered through the galvanometer (G).

General Darkening of the Detecting Plate

In the recording of faint patterns requiring long exposures it was necessary to exercise care to avoid a general over-all darkening of the molybdenum oxide detecting plate. A darkening of this character might have been produced by any one of three causes. (A) Atomic hydrogen, dissociated in the source chamber, might have been diffusely emitted from the collimating tube after scattering from its walls, and these might have reached the detecting plate either directly or after other reflections in the observation chamber. (B) Atomic hydrogen might have been formed in the observation chamber itself by electrons which were emitted either photoelectrically from the walls of the observation chamber or thermionically from the crystal holder and its heating unit, and which attained high velocities in the fields which surrounded the electrode E and its lead wire. (C) The most important cause of over-all darkening was the reduction of the molybdenum oxide by molecular hydrogen. This reaction can take place only if the molybdenum oxide is heated, but unless precautions were taken, the radiant heat from the crystal holder at the temperature used for degassing the surface of the crystal was sufficient to cause trouble.

Unquestionably some trouble had been experienced from cause (A) but this was rendered negligible by plating the inside walls of the collimating tubes with platinum black so that scattered atomic hydrogen was adsorbed until recombination to molecular hydrogen took place. The effects of (B) and

(C) were almost eliminated by protecting the detecting plate with a metal shield which completely surrounded it except for a small opening close to the crystal through which the reflected atoms entered. (See Figs. 1 and 3.) The inside and outside walls of this shield as well as the interior walls of the observation chamber were cleaned and freshly plated with platinum black before each exposure. To facilitate the cleaning of the interior of the observation chamber a copper lining was constructed which was easily removed, cleaned and plated.

Photographic Technique

The detecting plate consisted of either a "black-nickel" plated brass plate or a blackened photographic plate upon which was deposited a thin coating of molybdenum oxide formed by the oxidation of metallic molybdenum in an oxygen-gas flame. Since the blue reduced molybdenum oxide faded slowly when exposed to the air, the detecting plate was photographed as soon as possible after it was removed from the apparatus. The camera was of special construction and gave a 2.86 to 1 enlarged image. The plate was illuminated from the front by two 100 watt lamps placed beside the camera lens. To prevent fading of the pattern by reoxidation when exposed to the heat from these lamps, water filters were introduced between the lamps and the plate. A Wratten Aero No. 1 color filter was used in front of the camera lens to increase the photographic contrast between the white background and the blue pattern. The best reproductions of the patterns were obtained on Eastman Process plates with their D-9 developer.

Preparation of the Crystal

The crystals of lithium fluoride were grown from a melt by the method of Kyropolus,[4] which proved to be extremely simple and satisfactory. These crystals are of the simple cubic lattice, and they are cleavable along the 100 planes. From the lens shaped crystals which were grown in this way rectangular blocks 2 mm $\times$ 2 mm $\times$ 4 mm were cut, the faces of which were parallel to the cleavage planes. During an exposure one of these crystal blocks rested in a grove in a copper holder of which two types were used to realize the desired orientations. These holders contained heating coils of tungsten wire wound on mica and imbedded in alundum cement. After all other adjustments had been made the crystal was cleaved and mounted, and as quickly as possible the apparatus was evacuated. Without further treatment the freshly cleaved surface at the start was generally found to give a weak specularly reflected beam of the order of 1 percent of the incident beam. An initial heating at 500°C for about 3 min. with a subsequent cooling to room temperature increased the reflecting power to something of the order of 10 percent of the incident beam, but this again fell off in the course of an hour to very nearly nothing. If the temperature of the crystal was maintained steadily at about 300°C its reflecting power was higher and it persisted for a much longer period of time, but it was still helpful to heat the crystal at 500°C for a few minutes

[4] Kyropolus, Zeits. f. anorg. allgemein. Chem. **154,** 308 (1926).

at four or five hour intervals. With this procedure it has been possible to maintain a high reflecting power during 24 hour exposures with no apparent diminution. During the major part of the exposure it has been found best to maintain the crystal at as low a temperature as is possible without seriously interfering with its reflecting power, for at the higher temperatures, in addition to difficulties introduced by the heating of the detecting plate, there was some troublesome diffuse reflection which might have arisen from either or both of two causes. (1) The roughening of the surface by thermal agitation may have produced a diffuse blurring of the regularly reflected and the diffraction beams. (2) Adsorbed hydrogen atoms may have been re-emitted from the hot crystal in the monatomic state, although at low temperatures these remained on the crystal surface until recombination to molecular hydrogen had taken place.

The best explanation which can now be given of the continually diminishing reflecting power at low temperatures is that vapors from the picein wax, which sealed the many joints leading into the reflection chamber, gradually condensed on the crystal surface. To minimize this difficulty the concentration of this wax vapor was made as low as possible by the use of independently evacuated guard rings between the wax seals and the inside chamber. As further precautions against this vapor, a liquid-air-filled glass tube protruded into the observation chamber, and the inside walls were covered with an adsorbing layer of platinum black.

The Diffraction Patterns

For the purpose of demonstrating the principal features of the phenomenon of the diffraction of atoms, patterns were obtained by exposures with three different arrangements of the crystal and detecting plate. These will be referred to as (a) normal incidence (b) 45° incidence in the 110 azimuth and (c) 45° incidence in the 100 azimuth. In each case the patterns were those expected from the following two assumptions: (1) The distribution of wavelengths in the beam was that calculated from the Maxwellian velocity distribution by the use of the de Broglie relation, and (2) The diffraction grating was made up of scattering points arranged on the surface in a plane square array with a spacing d equal to the value 2.835A obtained by x-ray measurements for the distance between two adjacent ions of the same type. The principal axes of this array lie in the 110 azimuths and the angular positions (ϕ, θ) of the diffraction beams with respect to these axes can be correctly calculated from the plane cross-grating equations

$$\cos\theta_0 - \cos\theta = m\lambda/d \tag{8a}$$

$$\cos\phi_0 - \cos\phi = n\lambda/d \tag{8b}$$

in which m and n have the values $0, \pm 1$, etc.

Of the patterns which have been recorded, the most complete is that reproduced in Fig. 5 which was obtained with the crystal and the detecting plate arranged for normal incidence as is shown in Fig. 1. The specularly reflected

beam appears in the photograph at the center of the pattern superposed upon the hole drilled for the incident beam. The more intense dispersed branches of the pattern, which are reproduced in the vertical and horizontal directions, lie in the 110 azimuths of the crystal. These correspond to the four ways of assigning 0 and ± 1 to m and n in equations (8), and may be appropriately designated as (1, 0) beams. In addition to these, four other fainter beams are visible in the 100 azimuths corresponding to $n = \pm 1$, $m = \pm 1$. These will be designated as (1, 1) beams. The dispersion in these beams seems to be greater than that in the (1, 0) beams as would be expected since these may be considered as arising from a grating of the spacing $d/2^{1/2}$. The angular dimensions of the pattern may be judged from the fact that the distance from the crystal to the detecting plate, when increased in the ratio of the enlargement of the photograph, was 12.9 mm.

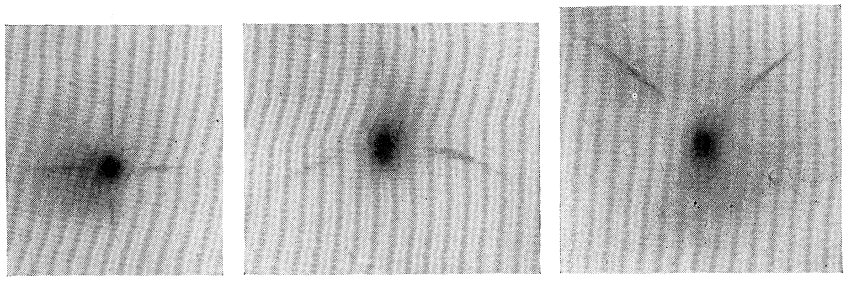

Fig. 5. Diffraction of hydrogen atoms reflected at normal incidence from an LiF crystal.
Fig. 6. Diffraction of hydrogen atoms reflected at 45° incidence in the 110 azimuth.
Fig. 7. Diffraction of hydrogen atoms reflected at 45° in the 100 azimuth.

A pattern produced by reflecting the beam at 45° incidence in the 110 azimuth is reproduced in Fig. 6. In this instance the arrangement of the crystal and detecting plate was that represented in Fig. 3. The (0, 0) specularly reflected beam again appears at the center of the pattern and the (1, 0) beams are now a straight line in the plane of incidence and a parabola symmetrically placed with respect to this line and intersecting it in the specularly reflected beam. If θ designates the angles measured from the rows of ions which are parallel to the plane of incidence, and ϕ those measured from the perpendicular rows, then the beam which is dispersed in the plane of incidence is represented by $m = +1$, $n = 0$ in equations (8). The two branches of the parabola, on the other hand correspond to $m = 0$ $n = \pm 1$. The straight branch in the plane of incidence on the lower side of the specular beam corresponding to $m = -1$, $n = 0$ might have been expected to appear but the dispersion was such that the most probable wave-length fell below the plane of the crystal, and, on account of the greater dispersion in this branch and the paucity of the wave distribution in the region of short wave-lengths, this branch was too faint to appear in the photograph.

The (1, 1) beams in this case take the form of two hyperbolae intersecting in the specular beam but these were perhaps too faint to be distinctly visible

in the reproduction. Unquestionably they could be brought out more intensely if a special effort were made.

The pattern at 45° incidence in the 100 azimuth (Fig. 7) was obtained with the same arrangement of Fig. 3, except that the crystal was rotated in its own plane 45° from its former position. The plane of incidence was in this case parallel and perpendicular to the cleaved edges of the crystal so that the principal axes of the surface lattice intersected the plane of incidence at angles of 45°. The (1, 0) branches of the pattern now appear as the two hyperbolic intercepts with the plane of the detecting plate of the two cones, $\theta = 60°$, and $\phi = 60°$. The branches which lie above the specular beam are intense but those lying between the specular beam and the plane of the crystal, although visible, are weak for the same reasons as were given in regard to the $n = 0$, $m = -1$ beam of Fig. 6. The (1, 1) beams in Fig. 7 should have the form of the (1, 0) beams of Fig. 6 except for greater dispersion but these were too faint to appear.

The Distribution of Wave-Lengths

Assuming the Maxwellian law for the distribution of velocities of the atoms per unit volume in the beam, the distribution in wave-lengths of the intensity of the atom waves falling on the crystal as predicted by the de Broglie relation is given by

$$dI/d\lambda = Ae^{-\lambda_0^2/\lambda^2}/\lambda^5 \tag{9}$$

in which λ_0 has the value $h/(2mkT)^{1/2}$. The expected distribution of intensity along the path s of a branch of the diffraction pattern is calculable from (9) by the relation

$$\frac{dI}{ds} = \frac{dI}{d\lambda}\frac{d\lambda}{d\theta}\frac{d\theta}{ds} \tag{10}$$

$d\lambda/d\theta$ may be obtained by differentiation of the grating equations (8) and $d\theta/ds$ is calculable from the geometry of the arrangement.

Since the intensity measurements were to be made with a densitometer the straight line patterns at normal incidence seemed at first sight to be the easiest to manipulate. A comparison of these patterns with those obtained at 45° incidence however showed that the latter were less obscured by diffuse radiation and for this reason were less subject to errors. To combine this advantage with ease of measurement it was decided to use a pattern obtained with the crystal oriented for 45° incidence in the 110 azimuth and a slightly different arrangement of the detecting plate as shown in Fig. 8. With this arrangement branches dispersed along the periphery of the 45° cone appeared on the detecting plate as a circle (Fig. 9) and this form of pattern was easily measured with a Koch and Goos densitometer by the use of a simple attachment constructed to give rotary motion. Besides its adaptation to measurement this pattern had two other great advantages. (1) All points of the circle were equally distant from the surface of the crystal and for this reason the general

darkening of the plate was distributed somewhat evenly. (2) The calculations were extremely simple and involved only the measurements of the angular positions ψ on the plate.

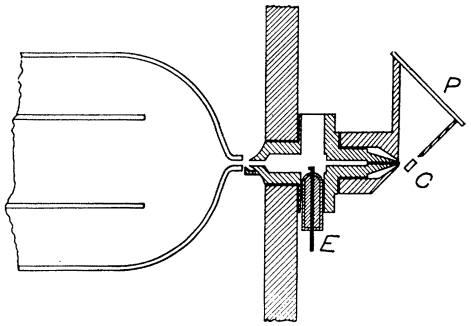

Fig. 8. Arrangement of plate holder for circular patterns.

The grating equation (8b) in this instance reduces to

$$\cos\phi = n\lambda/d \tag{11}$$

and the measured angle ψ of the circular pattern is related to ϕ by

$$\cos\phi = \sin\psi \sin 45°, \tag{12}$$

from which

$$dI/d\psi = A'e^{-2\lambda_0^2/d^2\sin^2\psi} \cos\psi/\sin^5\psi. \tag{13}$$

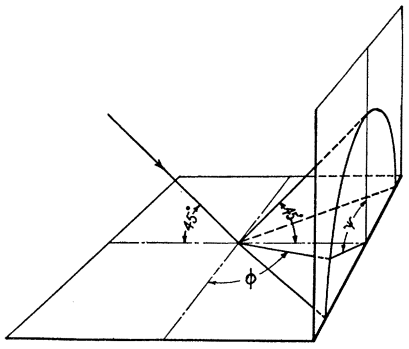

Fig. 9.

The angle ψ_0 of maximum intensity is found by equating to zero the derivative of the right hand member of (13) and it is given by

$$\cos^2\psi = -(2\lambda_0^2/d^2 - 3)/8 + [(2\lambda_0^2/d^2 - 3)^2/64 + \tfrac{1}{4}]^{1/2} \tag{14}$$

If it is assumed that the temperature of the source of the atom beam was

that of the water which circulated in a jacket surrounding the discharge tube[5] then

$$T = 300° K \qquad d = 2.835A$$
$$\lambda_0^2 = 3.13 \times (10)^{-16}\ \text{cm}^2 \qquad \psi_0 = 32.7°.$$

Intensity measurements were made from the photographic negatives. As regards the position of maximum intensity this method of measurement would have been independent of the plate calibration were it not for the fact that the pattern was superposed upon a background of variable intensity in spite of the advantages of the arrangement for overcoming this trouble. In order to correct the measurements for this background intensity the plate was also measured along the circumference of a circle of slightly different diameter from that of the diffraction pattern itself, and this set of measurements was applied to the first set as corrections. A calibration of the densitometer deflection in terms of the intensity of an atom beam was obtained by exposing a separate plate in various places to the primary beam for successively increasing times so that a series of dark spots was formed which covered the intensity range of the patterns. This plate was photographed and developed under exactly the same conditions as pertained in the case of the plates which contained the patterns. Densitometer measurements then showed that the difference of the deflection produced by the center of one of the spots and that produced by the unexposed portions of the plate was very nearly proportional to the time of exposure of the spot. This fortunate coincidence led to the simple rule that the deflections of the densitometer could represent atom beam intensities if corrected by subtracting the deflection at an adjacent point of the background. Although this method of making intensity measurements cannot be regarded as possessing a high degree of reliability, as will be recognized by those familiar with the precautions necessary in ordinary photographic photometry, yet it led to surprisingly consistent results in good agreement with what was expected for the angle of maximum intensity. Eight corrected sets of measurements from plates made from three different molybdenum oxide originals gave a weighted mean value of $\psi_0 = 31.6°$ with a probable error of 2.2° as compared with the calculated value of 32.7°. This accuracy probably speaks more for the uniformity of the background than for the method of calibration and correction, and it is felt that a more reliable calibration must be devised before the photographic method can be used satisfactorily for precise intensity measurements.

Relative Intensities of the (1, 0) and (1, 1) Beams

Measurements of the relative intensities in different orders of x-ray spectra have been applied[6] to a determination of the relative scattering powers of the different atom species in the crystal. It is of interest to attempt the same thing using the different orders in the atomic diffraction patterns.

[5] From the work of J. B. Taylor, Phys. Rev. **29**, 309 (1927) this seems to be a reasonable assumption.

[6] W. H. Bragg and W. L. Bragg, X-rays and crystal structure, page 187, et seq.

Because of the overlapping of the 1, 0 and 2, 0 orders these beams are not well adapted to this purpose until more homogeneous velocities can be used, but it is interesting to compare the intensities in the 1, 0 and 1, 1 branches. In terms of the scattering powers U of the two ion types in the two directions, the ratio of the intensity of a (1, 1) beam of a particular wave-length to that of a (1, 0) beam of the same wave-length may be expressed, by the use of the principle of the superposition of amplitudes, as

$$I_{11}/I_{10} = (U_{11\mathrm{F}} + U_{11\mathrm{Li}})^2/(U_{10\mathrm{F}} - U_{10\mathrm{Li}})^2. \tag{15}$$

If the U's are assumed to be spherically symmetrical functions of space, i.e., $U_{11} = U_{10}$, the ratio $U_{\mathrm{F}}/U_{\mathrm{Li}}$ can be determined from the measured ratio of intensities I_{11}/I_{10}.

In making the intensity measurements one must take account of the fact that the beams are not homogeneous in wave length but they contain a distribution (9) which is more highly dispersed in the (1, 1) than in the (1, 0) branches. The maximum of intensity on the plate in the (1,0) branches of the normal incidence patterns should fall, according to these considerations, at a distance S from the central spot equal to 0.408 l, where l is the distance between the crystal and the plate. The calculated position of maximum intensity in the (1, 1) branches is at $S = 0.589\ l$.

The ratio of intensities at these two points of maximum intensity is found from (9), (10) and (15) to be

$$\left(\frac{dI}{ds}\right)_{11} \Big/ \left(\frac{dI}{ds}\right)_{10} = (U_{\mathrm{Li}} + U_{\mathrm{F}})^2/6.3(U_{\mathrm{Li}} - U_{\mathrm{F}})^2. \tag{16}$$

The actual measurements carried out by means of the photometric technique described in the previous paragraph give a value of this ratio of about 1/6 with the possibility of an error of 100 percent or more arising not only in the unreliability of the method of calibration but also from the faintness of the 1, 1 branches. Although this inaccuracy of measurement renders a quantitative determination of $U_{\mathrm{Li}}/U_{\mathrm{F}}$ impossible, the assumption of spherical symmetry of the U's leads to a small value of this ratio. The same conclusion results from a consideration of the great intensity in the 1, 0 orders where the contributions to the amplitude from the two ion types is 180° out of phase. From these measurements it is not necessary to conclude that the scattering power of an ion is definitely less in the 1,1 direction than in the 1,0 direction as Estermann and Stern found from the extremely small intensity which they observed in the (1,1) beams, although this conclusion would be necessary if a more accurate determination of the ratio (16) leads to a value greater than 1/6.

Diffraction by a Secondary Lattice of Wide Spacing

In addition to the spectra which have been described, arising from the surface array of ions, another type of spectrum of very low dispersion appeared on the plates. This type of spectrum was first noticed on a plate exposed at

45° incidence in the 100 azimuth where it appeared as a slight smearing of the specular beam in the plane of incidence. Later the same phenomenon was noticed on the plates exposed at 45° incidence in the 110 azimuth and in this case the spectra took the form of a blurred X extending out from the specular beam. These features may perhaps be distinguished in Figs. 6 and 7. An exposure at grazing incidence in the 100 azimuth increased the dispersion in this spectrum as shown in Fig. 10 but failed to separate the maximum of the

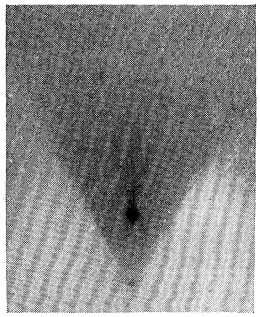

Fig. 10. Secondary structure spectrum at grazing incidence.

wave length distribution from the specular beam. It has been pointed out[7] that this spectrum indicates the existence of a secondary periodicity on the crystal surface parallel to the 100 planes in agreement with the theory of Zwicky.[8] Work is now under way to increase the resolving power in this spectrum with the hope of measuring the constant of the secondary lattice.

The writer wishes to take this opportunity to acknowledge his indebtedness to Mr. C. K. Boyer and Mr. M. A. Roesch, both of the Drexel Institute, who have assisted in this work.

[7] T. H. Johnson, Phys. Rev. **37,** 87 (1931).
[8] Zwicky, Helvetica Physica Acta III, 269 (1930).

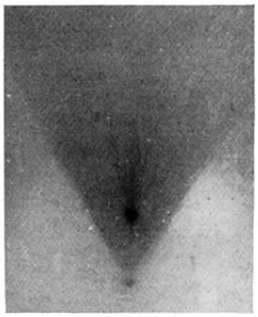

Fig. 10. Secondary structure spectrum at grazing incidence.

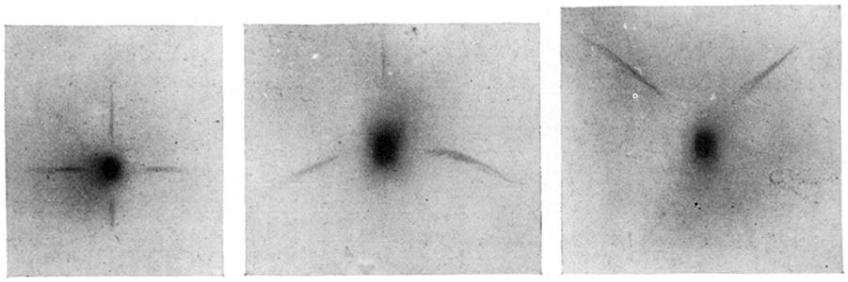

Fig. 5. Diffraction of hydrogen atoms reflected at normal incidence from an LiF crystal.
Fig. 6. Diffraction of hydrogen atoms reflected at 45° incidence in the 110 azimuth.
Fig. 7. Diffraction of hydrogen atoms reflected at 45° in the 100 azimuth.