V. CONCLUSIONS

The expansion of a spark discharge is accompanied by moving luminosity in a highly ionized gas which appears to increase in ion concentration as the luminosity advances. The ion concentration can be estimated by analysis of the Stark broadening of the Balmer lines in hydrogen. The relation between radiated intensity and ion concentration for the moving luminosity is that which would be expected of random electronic recombination.

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Plural Electron Scattering and Its Influence on Electron Diffraction Patterns*

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The peak ring intensity (I_R') and the background intensity (I_B') for the most intense rings in the electron diffraction patterns of aluminium and thallium chloride have been measured, as a function of film thickness and accelerating voltage.

It is shown that part of the discrepancy between the results and the theories of Bethe and Morse is due to plural electron scattering.

A semi-empirical theory that includes the effect of plural scattering has been developed to explain the variation of I_R' and I_B' with specimen thickness. The contrast in the patterns (I_R'/I_B') increases rapidly with accelerating voltage and falls rapidly with increase in film thickness. The maximum film thickness ($T_{\max}$) that will yield an observable pattern increases less rapidly than the accelerating voltage, between 50 and 150 kv, in agreement with the results of Möllenstedt.

INTRODUCTION

THE electron diffraction pattern obtained from a thin polycrystalline film of material consists of a number of rings seen against a continuous background. It has long been known that if the film thickness is increased, or the electron speed reduced, the intensity of the rings is reduced as compared with the background. In other words, the contrast in the pattern is reduced. Thomson[1] has attributed this to the attenuation of the diffracted beams by incoherent scattering in the film.

It has been difficult to treat this problem theoretically because of the complex character of electron scattering in the range of voltages and film thicknesses used. When electrons with energies of the order 10^5 electron volts pass through films with thicknesses between a few hundred and a few thousand Angstrom units (hereafter shown as A), they are, in general, scattered more than once, but not so many times that a mean angle of scattering can be calculated readily from a statistical consideration of the individual scattering processes. The phenomena is called plural scattering to distinguish it from multiple scattering in which the number of collisions is large enough to justify the use of statistical procedures. A general review of electron scattering has been given by Zworkin *et al.*,[2] who provide references to the earlier work.

The complexity of plural electron scattering also makes it difficult to interpret the results of scattering experiments. If the angular distribution of electrons scattered incoherently by a thin film is measured, there is no simple way of deducing the nature of the individual scattering processes from the results. On the other hand, the study of electron diffraction patterns permits the measurement of coherent and incoherent scattering in the same film and, hence, yields added information on the scattering process. As acknowledged below, the experimental realization of the method has been greatly facilitated by developments in other branches of experimental physics.

The electrons that enter the rings of a diffraction pattern must have been scattered in one of the following ways: (1) by an elastic coherent scattering process in one crystal; (2) by two or more elastic coherent scatterings in the same crystal. Such electrons have not made any incoherent or inelastic encounters. The electrons that enter the background have been scattered as follows: (3) by a single inelastic or incoherent scattering process; (4) by several successive encounters of type (3); (5) by a coherent scattering process of type (1) followed or preceded by scatterings of type (3) or (4); or (6) by successive elastic coherent scatterings in different crystals. In the type of pattern reported by Cowley, Rees, and Spink[3] such scatterings give rise to recognizable spots in the pattern. In the type of pattern discussed here, where the number of diffracting crystals is large, such spots would form part of the background; with many crystals none of the individual

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* Part of this paper was presented at the National Bureau of Standards Symposium on Electron Physics, Washington, D. C., November 5–7, 1951.

[1] G. P. Thomson, Proc. Roy. Soc. (London) **A125**, 352 (1929).

[2] Zworykin, Morton, Ramberg, Hillier, and Vance, *Electron Optics and the Electron Microscope* (John Wiley and Sons, Inc., New York, 1945).

[3] Cowley, Rees, and Spink, Proc. Phys. Soc. (London) **A64**, 609 (1951).

spots are resolved. In all but the thinnest films, scatterings of types (1), (4), and (5) seem to determine the contrast.

Thomson and Cochrane[4] in reviewing the studies of the background in electron diffraction patterns made prior to 1939 concluded that the results were anomalous, in that they did not agree with the theories of Bethe[5] and Morse,[6] based on single scattering.

The work reported here began with a study of the influence of specimen thickness and accelerating voltage on contrast in the electron diffraction patterns from uniform thin films. If, in Fig. 1, Q_R = charge entering a given ring of the pattern, and Q_B = charge entering the background of the ring in the same time, then $C=Q_R/Q_B$ may be defined as the contrast in the pattern for this particular ring. It is convenient in practice to define the peak contrast as $C'=Q_R'/Q_B'$, where Q_R' = peak charge density in the ring, and Q_B' = charge density of the background at the peak density of the ring since this is more readily measured.

The maximum thicknesses of aluminum that will give observable patterns have been measured by Möllenstedt[7] for voltages up to 600 kv. Möllenstedt judged the visibility of the rings from observations made on a fluorescent screen. He states that when one ring could be seen on the screen, several could be observed in a photograph of the same pattern. It was considered desirable to repeat Möllenstedt's measurements in the range of voltages 50 to 150 kv (these being more widely available) determining at least C', as defined above, for a range of specimen thicknesses t. This would remove any ambiguity due to the characteristics of the fluorescent screen or photographic plate.

In the course of this work it was realized that measurements of the relation between Q_R' and t, and Q_B' and t separately would throw some light on the plural scattering process. Such measurements were subsequently made.

DESIGN OF THE EXPERIMENT

The study reported below has been greatly facilitated by recent advances in other fields of physics. Electron microscope studies of thin evaporated films have given us a better understanding of their morphology and, hence, permit us to choose films more nearly ideal for electron diffraction studies than the thinned or sputtered films that were previously in common use. Secondly, the development of the multiple beam interference techniques by Tolansky and particularly the method described by Scott, McLauchlan, and Sennett[8] provides a simple and dependable method of measuring the thickness of the films used in the experiments. Finally the more recent studies of the optics and faults of electron diffraction cameras by Hillier and Baker,[9] and Rymer and Butler[10] permit the experiments to be carried out so that the electron diffraction camera contributes negligible disturbances to the charge distribution in the diffraction pattern.

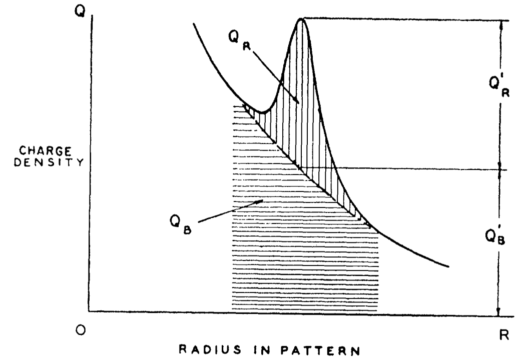

FIG. 1. An illustration of the method of defining the Q's.

The ideal scattering film for the type of experiment contemplated here would be a system of randomly oriented crystals forming a thin parallel faced slab. The film should be stable in air and under electron bombardment. The material should yield a sharp, well-defined, electron diffraction pattern, and one would prefer to be able to carry out the study on both metallic and nonmetallic films. One material chosen was thallium chloride, since Boswell[11] has shown that it yields very sharp electron diffraction patterns. Electron microscope studies of the thinner films of thallium chloride indicated that the particles had a very flat sessile form. In consequence, one would expect the effect of the inner potential to be small in the pattern. Evaporated thallium chloride films are not stable under the current densities of bombardment that are sometimes employed in the electron microscope but proved to be fairly, though not completely, stable under the current densities of bombardment used in the electron diffraction camera.[12] The thicker films appeared to be continuous so far as could be told from electron microscope observations and from the appearance of shadow images formed in the electron diffraction camera.

Evaporated films of aluminium were also used since this would provide a comparison with the work of Möllenstedt.[7] The aluminium films proved to be sufficiently stable for this work, and while the thinner films appeared to be irregular in thickness, the thicker ones were uniform enough for the present study.

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[4] G. P. Thomson and W. Cochrane, *Theory and Practice of Electron Diffraction* (Macmillan and Company, Ltd., London, 1939).

[5] G. Bethe, Ann. Physik **5**, 325 (1930).

[6] P. M. Morse, Physik. Z. **33**, 443 (1932).

[7] G. Möllenstedt, Nachr. Akad. Wiss. Gottingen, Math.-physik. Kl. **1**, 83 (1946).

[8] Scott, McLauchlan, and Sennett, J. Appl. Phys. **21**, 843 (1950).

[9] J. Hillier and R. F. Baker, J. Appl. Phys. **17**, 12 (1946).

[10] T. B. Rymer and C. C. Butler, Phil. Mag. **36**, 515 (1945).

[11] F. W. C. Boswell, Phys. Rev. **80**, 91 (1950).

[12] The idea that evaporated films may be unstable receives support from other observations: recrystallization under electron bombardment in the electron microscope; the fact that even for continuous thin metal films the specific resistivity may be greater than that of the bulk metal; and the variation of the optical properties of thin films with time.

The diffraction camera was an experimental high voltage electron microscope that had previously been used for the study of contrast in electron microscopy. The lenses and specimen holder were rearranged to provide a camera of the sort that has been described by Hillier and Baker.[9] There was no lens between the specimen and the photographic plate so that the electron distribution in the diffraction pattern was not influenced by the chromatic aberration of the focusing lens. The distance from the specimen to the photographic plate was 47 cm and using magnesium oxide as a standard specimen the accelerating potentials were found from a measurement of ring diameters to be 51.5 kv, 99.5 kv, and 150 kv. The focal length of the first lens was made short enough that the width of the central spot was negligible compared with the minimum ring width in the diffraction patterns of thallium chloride or magnesium oxide. Most of the optical path was surrounded by three concentric cylinders of soft iron to provide magnetic shielding. There was, nevertheless, a small magnetic deflection in the final pattern, but care was taken to obtain the photometer traces along directions perpendicular to the direction of the magnetic shift which was small enough to introduce no error into the final results.

As shown by Hillier and Baker, electron scattering from the walls of the instrument and from a diaphragm in the first lens can give a background in the pattern which is not small compared with that produced by the specimen. Diaphragms were used in both lenses, and another was placed below the specimen so that the contribution of electrons scattered from the walls of the instrument was negligible in the pattern except for a very small region near the central spot which was not used in the final measurements. The illuminated area of the specimen was 16-mesh openings of a copper screen which had been etched until the individual openings were approximately 70-micron squares.

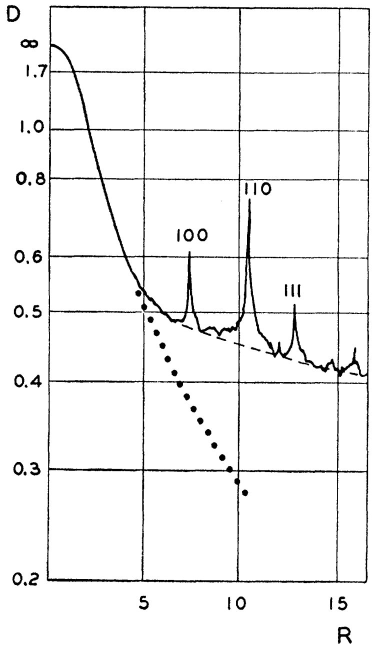

FIG. 2. Photodensitometer trace for one of the thicker thallium chloride films.

A focal series of exposures was taken with no specimen in the camera and with the photographic plate being rapidly traversed during the individual exposures. From these traces it was possible to estimate the residual value of the deflection due to stray magnetic field, the size of the central spot, and the exact current in the focusing lens at which the camera focused. These values were then used in the experiments described below.

EXPERIMENTAL PROCEDURE

The specimen materials, thallium chloride and aluminum, were evaporated onto collodion films supported on copper meshes which were themselves supported on clean glass microscope slides. Close to the meshes the microscope slides were covered by pieces of wire so that there would be a narrow strip on the slide not covered by the evaporated material. It was found that the spacial distribution of evaporated material was by no means uniform from the hair-pin filament used, but this did not influence the results since the thicknesses of the individual specimens were subsequently found by measuring the step height at the strip previously covered by the wire, using the variation of the Tolansky multiple beam interference technique described by Scott, McLauchlan, and Sennett. The collodion films used were found to have thicknesses between 80 and 120A.

When the specimens had been placed in the diffraction camera, the focusing lens was turned off and the resulting shadow image of the specimen was examined on a small fluorescent screen with the aid of a low power light microscope. Care was taken to see that there were no holes in the region of the specimen that was used in the production of the diffraction pattern. This is important since if there had been thinner regions or holes in the specimen or if parts of the evaporated film had turned over and were parallel to the beam, an abnormally high contribution to the ring intensity might have been obtained with the thickest specimens in which the ring intensity normally falls to low values.

In most of the experiments one photographic plate recorded an exposure series in which the exposures were increased by a factor of two, the same specimen and the same accelerating voltage being used in all exposures. In some experiments the accelerating voltage and exposure time were maintained constant, and different specimen thicknesses were used for subsequent exposures. The plates used were Kodak Medium Lantern Slide. They were developed for three minutes in DK-71, diluted one to two, at 68°F.

The variation of photographic density with radial distance was recorded for all plates, using a Leeds and Northrup recording microphotometer. If the density D_P at the peak of the thallium chloride 110 ring is

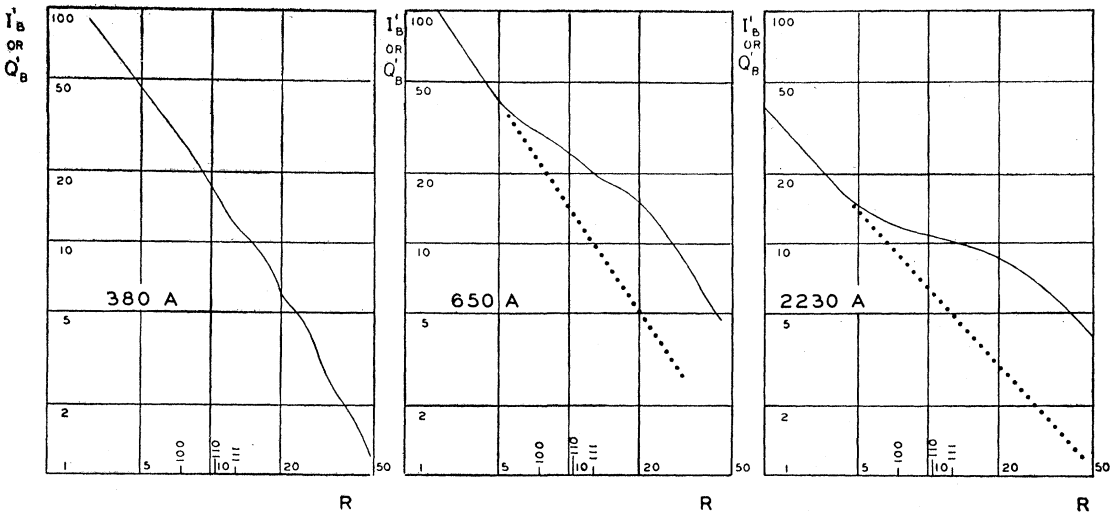

FIG. 3. Radial variation of background current density.

plotted against the log of the exposure (using the results from a single plate where the specimen and the accelerating voltage are identical in all exposures), one obtains a characteristic curve agreeing in shape with the curve published by Baker, Ramberg, and Hillier.[13] A curve of similar shape is obtained if one plots the densities from any other point in the pattern, or if one uses a different voltage, specimen, development time, or temperature. The only difference will be that the curves will be displaced along the log exposure scale. This feature of the characteristic curve has two important uses. All the results can be applied to establishing the shape of the characteristic curve. Any departure of the points of one exposure series from this characteristic curve indicates a change in the specimen during the production of the exposure series.

It was found in this way that the thallium chloride specimens became more crystalline under electron bombardment, eventually reaching a stable state. The results shown below are for the stabilized films.

In this work the characteristic of the photographic plate has been used to measure the ratio of charges. This can be done with acceptable accuracy if all the relevant measurements are made from one plate. It is less satisfactory to compare measurements of charge using plates which have been developed separately.

The trend of the final results will depend upon the division of the observed charges between the rings and the continuous background. The method employed therefore requires some justification, the more so since it may at first sight appear to be somewhat arbitrary. Figure 2 shows a typical photodensitometer trace for one of the thicker thallium chloride films. The background photographic density was estimated by drawing a smooth curve as shown by the dashed line. The corresponding charge densities Q_B' were deduced from the photographic characteristic and were plotted as a function of radial distance R in the photographic plate, Fig. 3. A comparison of the results for different film thicknesses is not justified since the graphs were obtained from different plates. The curves were smooth for thin films but for the thicker films showed an unexpected increase in background in the vicinity of the rings. This increase could be explained if it were supposed that diffraction in the part of the film nearer to the entrance side of the electrons caused fairly intense beams in the direction of the diffraction rings and that these beams were subsequently scattered through small angles to increase the background in the region of the rings when thick films were employed.

In the case of the thick films it will be noticed that $d(\log Q_B')/d(\log R)$ becomes the same outside the low order diffraction rings as at a smaller radius inside the rings. The dotted curve of Fig. 2 shows the values of photographic density corresponding to the dotted extrapolation of the $\log Q_B' : \log R$ curve of Fig. 3. The dashed curve of Fig. 2 is considered to be the proper estimate of the background since the shape of the lines for small film thickness will not justify using the dotted curve of Fig. 2 for the background. Secondly, in estimating the contrast it is the local background in the immediate vicinity of the diffraction rings that controls their visibility, and therefore, in any study of the variation of the visibility of these rings with specimen thickness and voltage it is the immediate background to the rings that must be measured.

RESULTS

In the range of film thicknesses (t) for which electron diffraction patterns can be obtained the distribution of background charge changes slowly with increase in film thickness. In a first approximation the charge density for the region inside the diffraction rings decreases with increasing film thickness, while the charge density in

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[13] Baker, Ramberg, and Hillier, J. Appl. Phys. **13**, 450 (1942).

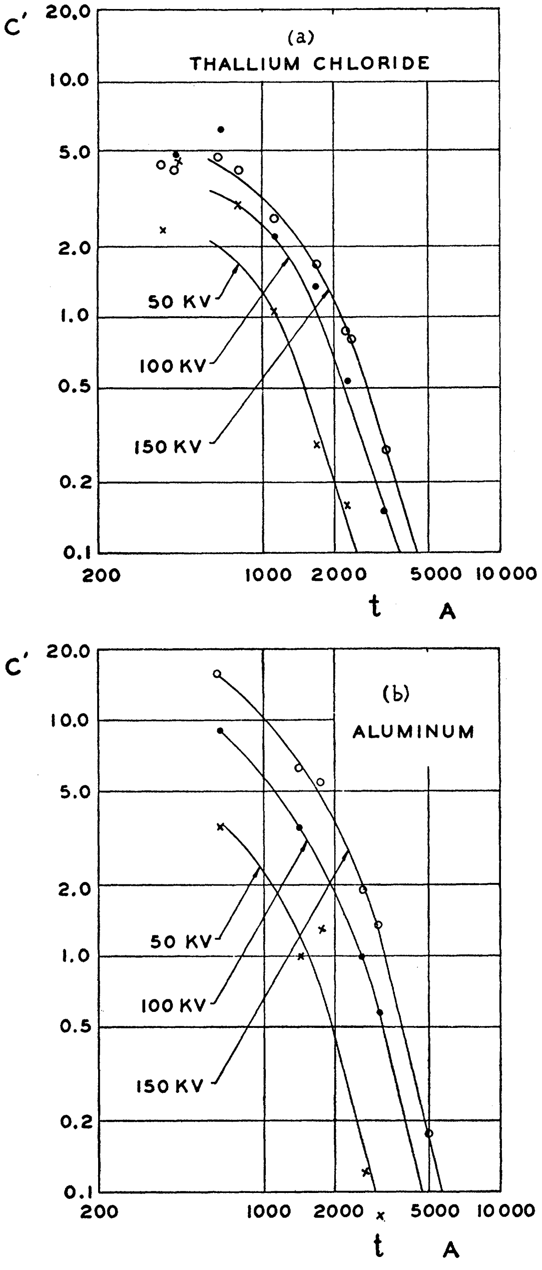

FIG. 4. Peak contrast as a function of film thickness (a) for thallium chloride (b) for aluminum.

the outer parts of the pattern increases with increasing film thickness. The charge density in the vicinity of the inner rings changes very little.

While the ring width at any one voltage is approximately independent of film thickness, the current into the ring decreases rapidly with increasing film thickness so that eventually the ring becomes invisible against the continuous background. Since the ring diameter is proportional to $V^{-\frac{1}{2}}$ (V is the accelerating potential applied to the electron gun) and the contribution of the inner potential to the ring width is proportional to V_i/V (V_i is the inner potential), increasing the voltage on the camera produces a smaller but also sharper pattern.

It will be seen from Fig. 3, that the background charge densities Q_B' are not simply related to the radius R. The slopes $d(\log Q_B')/d(\log R)$ are shown in Table I.

The quantity Q_B' is proportional to the function $f(r)$ discussed by Thomson and Cochrane.[14] From the above results one would judge that the films used by White[15] and Kirchner[16] were thick enough to give considerable plural scattering. For the thinner films above, $f(r)$ approaches the form r^{-2}, though even in these cases the films are not thin enough for single scattering to predominate. It cannot be concluded that the results of Table I are in disagreement with the theoretical work of Bethe[5] and Morse.[6]

With all specimens an increase in electron speed produces an increase in contrast (C'), and this is often very marked (Fig. 4). For example with a 2000A film of thallium chloride the contrast increases from 0.2 to 0.65 to 1.2 on increasing the voltage from 50 to 100 to 150 kv. If, on the other hand, $T_{\max}$ denotes the greatest film thickness that will yield an observable pattern (the value of t for which $C'=0.1$ was taken as $T_{\max}$ in this study), it is found that $T_{\max}$ increases only as $V^{\frac{1}{2}}$ for V less than 150 kv. This trend is in agreement with the results of Möllenstedt,[7] though his values for $T_{\max}$ correspond more nearly to those for $C'=0.8$. Möllenstedt, on the other hand, finds that at higher voltages $T_{\max}$ increases more nearly as V^2.

The variation of contrast with specimen thickness could not be reconciled with the theoretical treatment due to Thomson.[1] To clarify the situation, measurements of the current entering the ring (I_R) and the current entering the background (I_B), for a given current (I_0) entering the specimen, were made for different specimen thicknesses. If τ is the exposure time for a given pattern,

$$Q_R = I_R\tau, \quad Q_B = I_B\tau.$$

It is convenient to define I_R' and I_B' by

$$Q_R' = I_R'\tau, \quad Q_B' = I_B'\tau.$$

At any one voltage the line profile does not change with specimen thickness; therefore, the functional form

TABLE I. Variation of background charge distribution with specimen thickness.

Specimen	Thickness, A	Voltage, kv	$d(\log Q_B')/d(\log R)$	$\mathrm{Sin}\theta/\lambda$
Thallium chloride	380	150	-1.7	0.9×10^8
	380	150	-1.4	0.07×10^8
	2230	150	-1.1	0.07×10^8
Aluminium	650	150	-1.6	0.2×10^8
	5157	150	-1.0	0.2×10^8

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[14] Reference 4, p. 103, ff.

[15] P. White, Phil. Mag. 9, 641 (1930).

[16] F. Kirchner, Ann. Phys. 13, 38 (1932).

of the relation between I_R' and t is similar to that between I_R and t. Since the absolute value I_0 of the current incident on the specimen is unknown, the absolute values of I_R and I_B are of no interest. It then simplifies the measurements to make them in terms of Q_R' and Q_B', which are in turn proportional to I_R' and I_B'. The significance of the measurements will be more apparent if they are considered in the light of the theory outlined below.

THEORY

We shall calculate the total current entering one diffraction ring I_R and the total current entering the background at the ring I_B. Figure 5 shows the significance of the symbols used.

Consider a current I_0, proceeding in the Ox direction and entering a film of thickness t. The film is considered to be polycrystalline. Of this current, a residue I remains unscattered when it reaches the lamina AB of thickness dx.

Let it be supposed that (1) a fraction Ik_1dx is coherently scattered into the solid angle defined by 2θ and $2\theta+d\theta$; (2) a fraction Ik_2dx is incoherently scattered into the same solid angle; (3) a fraction Ik_3dx is scattered in directions other than the solid angle defined above.

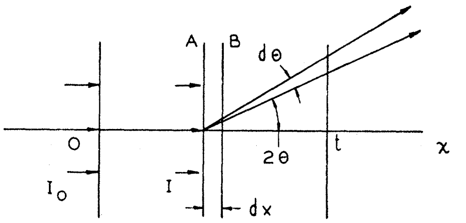

FIG. 5. Geometrical arrangement.

Let $K=k_1+k_2+k_3$. Then

$$I=I_0e^{-Kx}. \tag{1}$$

Of the current Ik_1dx a fraction $e^{-K(t-x)}$ remains unscattered between AB and the exit side of the film.

$$I_R=\int_0^t I_0k_1e^{-Kx}\cdot e^{-K(t-x)}dx$$

$$=I_0k_1e^{-Kt}t. \tag{2}$$

The ring intensity is therefore a maximum for

$$t=1/K, \tag{3}$$

and falls off rapidly with increasing film thickness.

In Fig. 6 $\log(I_R'/t)$ is plotted against t for aluminum at 150 kv.

It might be thought that, employing a similar argument, the background current is

$$I_B=I_0k_2e^{-Kt}t. \tag{4}$$

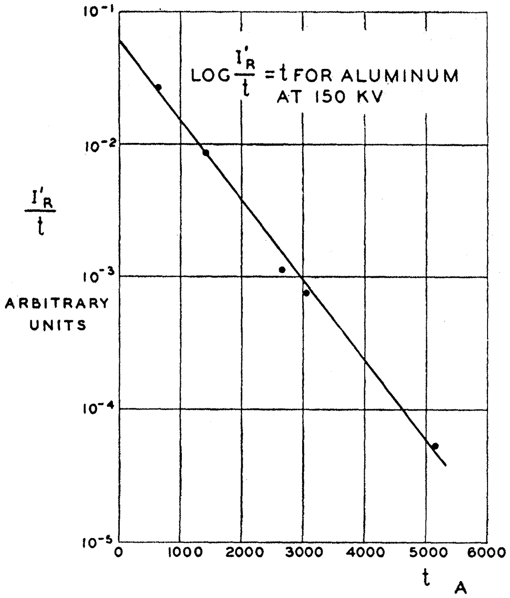

FIG. 6. Variation of ring intensity with specimen thickness.

This is shown in Fig. 7 by the dotted curve. It is evident that electrons are entering the lamina AB in other than the Ox direction and are being scattered into the background at the ring. The effective value of I is, therefore, larger than I_0e^{-Kx}. If one writes

$$I=I_0, \tag{5}$$

then

$$I_B=I_0(k_2/K)(1-e^{-Kt}). \tag{6}$$

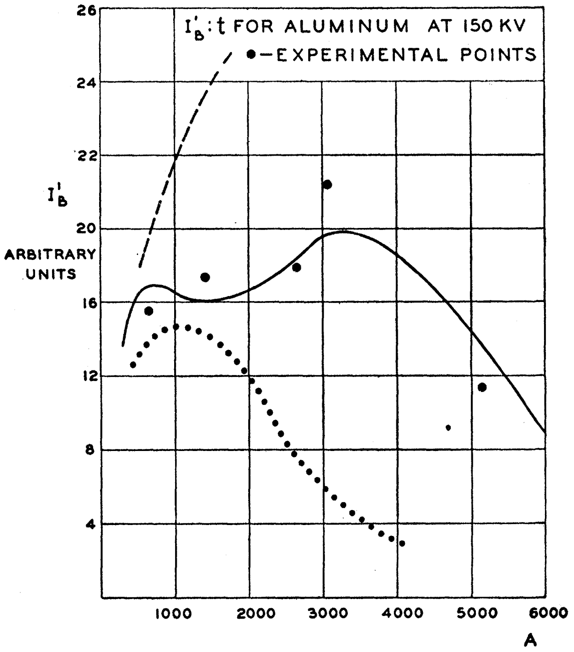

FIG. 7. Variation of background intensity with specimen thickness. The line ······ is a plot of $I_0k_2e^{-Kt}\cdot t$, and the line ------- a plot of $I_0(k_2/K)(1-e^{-Kt})$.

TABLE II. Scattering parameters for evaporated aluminum films.

Voltage, kv	50	150
K, cm^{-1}	2.22×10^5	1.37×10^5
α, cm^{-4}	4.46×10^{19}	6.45×10^{18}
k_1'/k_2'	2.9	8.4
K^{-1} (A)	450	730

This is shown by the dashed curve of Fig. 7. A closer analysis of the scattering in successive laminae suggests that I_B has the form

$$I_B=I_0k_2e^{-Kt}\cdot t(1+a_1t+a_2t^2+a_3t^3+\cdots), \tag{7}$$

and that empirically it may be possible to approximate I_B by

$$I_B=I_0k_2e^{-Kt}(t+\alpha t^n). \tag{8}$$

The contrast for a uniform film of material would then be

$$C=I_R/I_B \tag{9}$$

$$=k_1/[k_2(1+\alpha t^{n-1})]. \tag{10}$$

From the slope of the $\log C'$:$\log t$ curves at large t, one obtains $n=5$ for aluminium at 150 kv, taking the nearest integral value. In a graph of C':$C't^4$ the intercept on the C' axis is k_1'/k_2' and the slope is $-\alpha$. The dashes again refer to peak values. The graph of $\log I_R'/t$:t gives K (Fig. 6).

The values of K, and α deduced in this way have been substituted in Eq. (8), and the value of I_0k_2 has been adjusted to give the best fit. The result is shown by the full line of Fig. 7.

Table II lists some values of the parameters that have been determined for aluminium.

CONCLUSIONS

These results clearly indicate the important role played by plural scattering in limiting the visibility of electron diffraction rings. In this connection it is of interest to observe the reduction of the background obtained by Boersch[17] through the use of a filter which removed from the scattered beam electrons that had lost more than a few electron-volts of energy.

It can also be seen that plural scattering affects the radial distribution of background current density, making it more uniform as the specimen thickness is increased. It follows that if one fails to obtain diffraction rings but the radial variation of background current is large, i.e.,

$$d(\log Q_B')/d(\log R)>-1.6,$$

then the specimen is lacking in crystallinity. On the other hand, if the background current shows a more uniform distribution a possible cause of failure to obtain diffraction rings may be excessive specimen thickness.

The simple theory given above further indicates that for very thin unsupported films the peak contrast should approach k_1'/k_2'. The experimental points in this region were scattered, perhaps owing to orientation and the presence of a supporting membrane. Mukherjee and Row[18] have suggested that there is an optimum thickness for an evaporated aluminium film which will give a pattern of maximum contrast. This seems probable since with very thin films the lines may be broadened owing to a decreased crystal size, and furthermore, a given amount of amorphous contaminant will produce a proportionately greater background with a thin film specimen. It is not believed that the results of Mukherjee and Row invalidate the theoretical considerations outlined above.

The scheme of analysis shown above permits the construction of a semi-empirical theory of electron scattering for substances that can be obtained in thin crystalline films. In some studies it is important to work as near as possible to the region of single scattering. This is the case when studying the characteristic energy losses of electrons in passing through solids. It can be seen that for single scattering to predominate, we require $t<K^{-1}$ for the particular electron speed being used.

While it appears likely that equations of the form of Eqs. (2), (8), and (10) will hold for other materials and other angles of scattering, it is not possible to make these equations more general in a quantitative sense. One reason for this is that the parameters k_1 and k_1' depend both on the degree of crystallinity of the diffracting material, and the extent to which it may show specific orientation with respect to the incident electron beam. A specimen with a completely random orientation of crystals is perhaps more rare in electron diffraction studies than is generally recognized.

A surprising feature of the results is the rather slow increase of $T_{\max}$ with V in the range of voltage used here. $T_{\max}$ is the greatest film thickness that will yield observable rings. This implies that the usefulness of an electron diffraction camera may increase less rapidly than the accelerating voltage, but the result, as stated, holds only for the study of uniform thin films. Equations (2) and (8) can be used for the calculation of the contrast when the specimen has other morphologies. This will be the subject of a subsequent paper.

I wish to acknowledge the help given by Dr. E. G. Ramberg and Dr. James Hillier of this laboratory in several discussions of the experimental results. Dr. Ramberg derived the expansion of Eq. (7).

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[17] H. Boersch, Optik **5**, 436 (1949).

[18] N. R. Mukherjee and O. Row, J. Appl. Phys. **22**, 681 (1951).