III—The Structure and Physical Properties of Thin Films of Metal on Solid Surfaces

By E. N. DA C. ANDRADE, *F.R.S.*, *Quain Professor of Physics in the University of London*,
and J. G. MARTINDALE, *Ph.D.*

(Communicated by Sir WILLIAM BRAGG, O.M., F.R.S.—Received December 22, 1934—
Read February 2, 1935)

[PLATES 13–20]

INTRODUCTION

In spite of careful researches, extending over some fifty years,* investigations on the colour and other optical properties, and on the electrical resistance of thin films of metal deposited on solid surfaces, have frequently led to uncertain and even contradictory results. These have been generally set down as due to variations, of an unspecified nature, in the structure. Direct work on the structure was, however, scanty until the last few years, when Professor G. P. THOMSON and his school have obtained a number of valuable results, to which reference will be made later, by the application of the method of electron diffraction. This method tells us whether the film is amorphous or crystalline, and further gives information, if it is crystalline, as to the orientation of the axes and the spacing of the planes. The electron beam, however, examines an area of the order of a square millimetre, and the effect recorded is a statistical average for such a surface, and further the beam itself, with its inevitable heating effect, is liable to produce changes in the film. There is clearly room, then, for a detailed microscopic examination of the structure of sputtered films, which, as the following pages show, can furnish information as to local variations of structure which other methods cannot supply.

The work to be described deals with films of silver and of gold, of from 30 to 100 atoms thick, prepared on various surfaces by cathodic sputtering. In particular, the effect of deliberately heating the film under known conditions has been studied,

---

* One of the earliest studies is by KUNDT, ' Ann. Physik,' vol. 27, p. 59 (1886), in which year an investigation by DESSAU, " Ueber Metallschichten, welche durch Zerstäuben einer Kathode entstehen " also appeared. For early references, *see* V. KOHLSCHÜTTER, ' Jahrb. Radioaktivität,' vol. 9, p. 355 (1912) : for more recent work, WIEN–HARMS, ' Handb. der Exp.-Physik, vol. 13, Part 3, p. 400 *et seq.* (1929).

VOL. CCXXXV.—A 747 (Price 10*s.*) L [Published August 21, 1935

and it is shown that many of the irregularities of older results are due to uncontrolled heating of the film during preparation.

The choice of metals was dictated by many considerations. In the first place gold and silver give what has been called normal sputtering, as distinct from electrochemical sputtering, which takes place when the metal reacts with the residual gas, as, *e.g.*, with antimony and hydrogen, where a hydride is formed.* The films show the characteristic metallic lustre when prepared with air as the residual gas, which simplifies the technique, and experiments of BARTLETT's† go to show that the properties are unaffected by the presence of the gas. The simple face-centred cubic structure of crystals of gold and silver is a further advantage. Finally, much work has been done on the physical properties, such as colour and electrical conductivity of these metals, which provides material for comparison with our results.

The results fall into two classes. Firstly, series of changes in the heated film have been established which are quite independent of the nature of the non-metallic supporting surface, and involve the mobility and mode of crystallization of the metal. Secondly, alignments of the minute crystalline particles have been found which are highly characteristic of the supporting surface, and furnish evidence for the existence of submicroscopic surface cracks in certain types of amorphous and of crystalline substances.

A large number of results, many of which have hitherto presented puzzling features, can be explained in terms of the first class of results, while the second seem adapted to throw light on the question of crystal flaws, which are to-day invoked to account for the weakness of the natural, as distinct from the ideal, crystal lattice.

PREPARATION OF THE FILMS

It was desired in the first place to obtain uniform and reproducible films of any desired thickness. Previous workers have obtained very variable colours of sputtered films, without any very definite opinions as to what were the precise factors that determined the differences observed. WOOD‡ prepared gold films which were green, blue, violet or purple, the colour varying with the distance between the electrodes, the shape of the electrodes, and the degree of exhaustion. The more immediate cause of the differences of colour was not discussed. ROTHER and LAUCH§ found that their thin silver films were blue by transmitted light over most of the surface, but appeared red at the edges. Their gold films were always green, never blue. DREISCH and RÜTTEN,|| on the other hand, obtained gold films which were purple, blue and green-blue, and silver films which were red and reddish yellow. They drew attention to the dependence of the colour on the current passing, and

---

* *See e.g.*, WIEN–HARMS, *loc. cit.*

† 'Phil. Mag.,' vol. 5, p. 848 (1928).

‡ 'Phil. Mag.,' vol. 4, p. 425 (1902).

§ 'Phys. Z.,' vol. 24, p. 462 (1923).

|| 'Z. Physik,' vol. 60, p. 69 (1930), and RÜTTEN, 'Z. Physik,' vol. 60, p. 1 (1930).

attributed it to a temperature effect, without further discussion. These examples will serve, perhaps, to show the diversity of colours obtained. The different reactions to light have been attributed to a difference of particle size in the films, but no direct proof has been offered in support, neither has the fundamental factor which determines the colour of the freshly sputtered films been elucidated.

The preliminary experiments were carred out with two horizontal plane parallel electrodes in a vessel, actually a bell-jar, large enough for the field between them not to be disturbed by the glass walls of the enclosure. The film was deposited on a glass disc laid on the anode, and was examined visually for colour and uniformity. It would be both tedious and unnecessary to describe the various dispositions that were tried, but the results may be briefly mentioned. It was found that uniformity of thickness and colour was affected by the following conditions.

(*a*) The geometrical form of the two electrodes, which governs the distribution of the electric field. For instance, when the gold disc forming the cathode was held to an aluminium disc by two small lugs the density of the film varied markedly from point to point.

(*b*) The heating of the film during discharge, mainly by heat radiation from the hot cathode. This affects the colour, in particular. For instance, when the glass disc was laid on an anode consisting of an aluminium disc, supported at its centre by a stout aluminium rod, typical gold films were blue at the centre, and pink at the edge, with various transition purples in between. The thickness of the glass disc also influenced the colour of the film—the thicker the disc the redder the film. These effects, and others which were observed, are easily explained if the transition from blue to pink is due to heating, a supposition which was confirmed when the final apparatus, with cooled anode, was constructed.

(*c*) Traces of mercury vapour from the McLeod gauge. Even when the heating effects had been eliminated it was found that gold films often showed blotches of purple or pink of irregular shapes and sizes, which did not show the typical metallic reflection exhibited by the rest of the surface. These may be the " matte Stellen " mentioned by ROTHER and LAUCH, *loc. cit.* They were attributed by us to mercury vapour, and, as will be described, the use of effective traps ultimately eliminated this effect.

(*d*) The cleanliness of the surface. Any trace of grease, such as is left by the evaporation of ordinary water from a glass surface, produces irregularities of colour, and when the film is heated it tends to break up at the contaminated points, no doubt owing to evaporation of the impurity.

(*e*) The distance between the electrodes, particularly in relation to the size of the dark space. If the film was placed too close, say within a millimetre or two of the edge of the dark space, the colour and thickness were not uniform. The edges, for instance, were thicker, no doubt owing to space variations of the electric field, consequent on the fact that the limit of the dark space was not plane.

(*f*) The residual gases. Hydrocarbons have a pernicious effect. For instance, a silver film produced with a silver cathode when the residual air was contaminated with hydrocarbon vapours was brownish in colour, instead of purple, and behaved anomalously when heated.

All these effects are eliminated in the final form of apparatus used, which is represented in fig. 1. A bell-jar, 20 cm in diameter and 25 cm in height, was fitted at the top with a brass stopper, through which passed an aluminium rod A, the joints being made vacuum-tight with sealing-wax. This rod was provided with

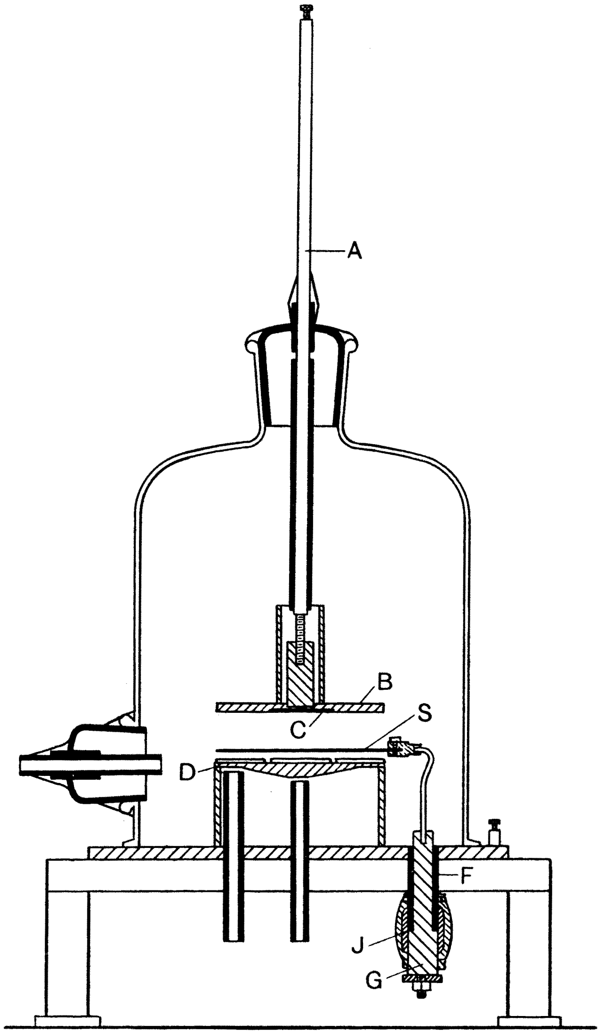


FIG. 1

a screw thread at its lower end, to which the cathode was adapted, as shown. This not only allowed a quick exchange of cathodes, but also enabled the distance between the electrodes to be easily varied. To secure uniformity of field over the area concerned in sputtering, the cathode consisted of a disc C of the metal, gold or silver, let into a larger aluminium disc so that the surfaces were flush. The aluminium does not sputter at all under the conditions of these experiments, and acts as a guard ring. When the metal was being sputtered on to glass, the glass disc, which lay on the anode, was likewise surrounded by a glass guard ring, cut from a similar sheet. The rod carrying the cathode was sheathed with glass tube inside the bell-jar, to restrict the cathode fall of potential to the inter-electrode space. The base plate was of brass, 25 cm square and 6 mm thick, suitably mounted on a stout wooden table.

The water-cooled anode D was a cylindrical brass box, 10 cm in diameter, closed at the top by a plate, of which the upper surface was plane, and the lower slightly conical, as shown. The water was introduced by a central tube, and carried away at the edge. The anode connection was made to the base plate.

It is advantageous to be able to protect the anode surface from deposition during the preliminary stages of the discharge. For this purpose a mica screen S was provided, which could be interposed at will by rotating the rod G. This rod fitted into a tube F carried by the base plate, the external joint J being protected by a brass sleeve over which a tight-fitting rubber tube was drawn. The screen was attached to G by an ebonite clamp and a glass rod, which did not disturb the interelectrode field. When everything was steady the shield was removed and the disc exposed for a given time.

For evacuation of the vessel a " hyvac " pump was used, which proved quite sufficient, as the pressure of the gas (air) used in all the experiments was about 0·1 mm of mercury. In the earlier experiments a special device was used to seal the bell-jar to the plate and allow easy removal. This need not be described, as subsequently the joint was made with " apiezon " sealing compound, smeared in a thick coating round the base of the jar from the outside. This proved perfectly satisfactory ; no hydrocarbon contamination was ever detected. The pressure was measured by a McLeod gauge. The potential difference was supplied by a battery of 450 two-volt Exide accumulators, and measured by a calibrated Ferranti electrostatic voltmeter. A 0–20,000 ohm variable resistance, in series with the discharge vessel, and a milliammeter, served to control the current.

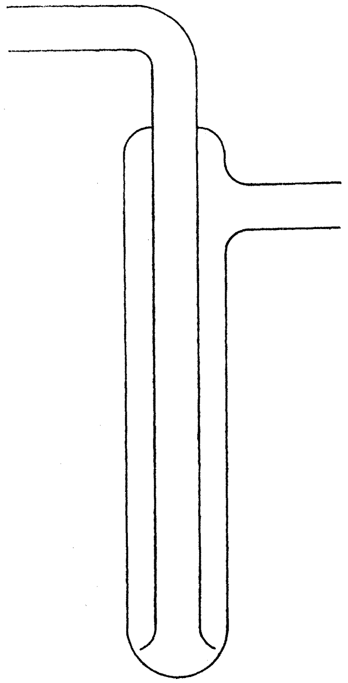


Fig. 2

It has been pointed out that the least trace of mercury vapour must be excluded from the sputtering vessel. A liquid air trap was therefore inserted. The first type of trap used was of ordinary design with the internal tube about 2 cm from the bottom of the outer vessel. Examination of the films, which revealed the type of contamination discussed later, proved this to be ineffective. A new type of trap was designed, in which the central tube is expanded and brought very near to the bottom, leaving an annular space not more than 1 mm wide, as shown in fig. 2. This is of the order of the mean free path for air at the pressure of the experiment, and tends to ensure that all mercury molecules shall strike the cooled walls in a restricted area, which facilitates condensation. A second similar trap was also inserted, containing gold leaf, which, after the apparatus had been opened once or twice with admission of air, was blown into the other trap as well, and adhered to the walls in both. With this system, not the slightest mercury contamination was ever detected on the films.

The materials on which the films were to be deposited were carefully cleaned with alcohol and nitric acid in the usual manner. When, in cases to be cited later, it was desired to take exceptional precautions the method was adopted which Hardy and Doubleday* showed to be effective in removing even mono-molecular films. The surface is washed with soap and water with the finger tips under a running tap. It is then rinsed with tap water, then with distilled water, and then boiled in chromic acid. Having been again washed with distilled water it was, in our case, heated in vacuo at 500° C for three hours and at once transferred to the sputtering apparatus.

The following are typical data for the deposition of a gold film :

Distance between the electrodes	3·0 cm
Length of dark space	1·5 ,,
Potential difference	710 volts
Current	23 milliamps
Pressure (mean)	0·1 mm of Hg
Time of sputtering	60 minutes
Mass of film on disc of 1·5 in diam.	0·30 mg
(Approximate thickness of film	= 35 atoms.)

The films obtained by this technique, on discs up to 38 mm in diameter, were absolutely uniform in colour and in thickness over the whole surface, so far as could be detected by careful ocular inspection. The gold films were a bluish-green and the silver films purple, and no variation of colour was ever obtained once the procedure had been standardized. The only effect of increased thickness was to deepen the tint, not to change it. Under the microscope, with all powers up to 1/12 inch oil immersion, and with all the varied conditions of lighting to be subsequently described, the field always appeared uniformly coloured : no structure was ever detected.

The variations of colour obtained by previous observers, cited in the introduction, are attributed by us to heating effects during sputtering,† which, when no deliberate cooling of the anode takes place, may depend upon the thickness of the glass disc, the pressure, the current, and other factors. These readily account for discrepancies;

---

* 'Proc. Roy. Soc.,' A, vol. 100, p. 550 (1921). The authors obtained coefficients of friction as high as 0·94 with surfaces cleansed in this way.

† The heating seems to be mainly due to radiation from the cathode, which gets very hot even with the moderate potentials and currents used in these experiments. No exact measurements of its temperature were made, but it was found to be well above 100° C when the discharge vessel was opened, and so some time after the cessation of a run.

but the various influences are seldom specified with enough precision to render detailed discussion of the recorded results profitable.

When the discs are large, the thickness can be found by direct weighing, assuming the density to be the same as that of the metal in bulk. On a Kuhlmann micro-analytical balance weighings can be made to within 0·001 mg, and the mass of a gold film 25 atoms thick on an area 38 mm in diameter is about 0·22 mg, and that of a silver film about 0·11 mg, the thicknesses being respectively 100 and 90 A. The films actually used for most of the experiments were deposited on discs only 13 mm in diameter, which makes the mass of film inconveniently small for direct weighing. The method of estimating the mass was to rely on the uniformity of conditions secured by the technique to give a uniform rate of deposition and a uniform film. Direct weighing of large films (38 mm in diameter) established a proportionality of weight to duration of sputtering, and gave the mass deposited per unit area per unit time. From this the mass of metal on a small disc, exposed for a given time under exactly similar conditions, was calculated.

The Effect of Heat on the Films

The films were heated in a quartz glass tube, surrounded by a small electric furnace, at various temperatures up to 600° C. A few preliminary experiments showed that, as might be expected, the silver films became oxidized at the higher temperatures, after which all films were heated in vacuo at a pressure of less than 0·01 mm of Hg. When not in use they were stored in a vacuum dessicator.

Various methods of illumination were used for the microscopic examination. All films were thin enough to be observed by transmitted light, which was always employed as one method. For dark ground illumination, which proved particularly useful in showing up the individual crystals, use was made of a Beck ring illuminator, which focusses parallel light from the plane sub-stage mirror down on to the specimen. The direct light from the sub-stage mirror is cut off by a stop. Intense oblique illumination, from above, was employed in looking for irregularities in the supporting surface, and was obtained by focussing a pencil of light, from a pointolite lamp, at an angle of about 15° with the surface. Lastly, polarized light was used.

All the photographs were taken with a box camera attachment, provided with a side tube for focussing, so that the image could be viewed up to the moment of beginning the exposure. Ilford soft gradation panchromatic plates were used, in conjunction with suitable light filters.

Effect of Heating—The Nature of the First Aggregates

Silver films, about 50 atoms thick, deposited on quartz glass, which had been maintained for about an hour at a temperature of 230° C, *in vacuo*, showed no change to the naked eye, retaining their original colour and metallic lustre. Under the microscope, however, small particles, which by their colour were markedly thicker than the rest of the film, appeared. By transmitted light, at a magnification of 1000 diameters, the particles, which were of the order of 1 μ across, appeared a golden brown colour, against a much lighter background. With dark ground illumination, produced by the ring illuminator, they appeared as bright spots, *see* fig. 16, Plate 16. The background was uniform right up to the particles, and did not show a region of clearance, as would be expected if the material of the particles was drawn from the immediate surroundings, a significant fact which is discussed later.

It is natural to suppose that these particles are the first stage of crystallization, and so they proved to be. Even with a 1/12 inch oil immersion objective, which on ordinary theory resolves two particles about 0·25 μ apart, it was impossible to detect any crystalline form, but this, perhaps, is not surprising even at this resolution, with particles 1 μ across. The particles were then examined in parallel plane polarized light between crossed Nicols, and found to give polarization figures. Each particle exhibits a black cross on a light ground, the arms being parallel to the polarizing planes of the two Nicols. The cross rotates as the Nicols are rotated, but remains stationary when the specimen is rotated. Fig. 5*a*, Plate 13, shows a portion of a silver film which is thickly covered with such particles, magnified 6000 times. This is an enlargement from the direct photograph, which was taken with a 1/12 inch oil immersion objective, at a magnification of 2000. The enlargement, of course, gives no extra resolution, but shows better in reproduction. At first sight the cross is reminiscent of the behaviour of a plate of uniaxial crystal cut perpendicular to the axis, but it is to be observed that for the uniaxial crystal the light must traverse the specimen in all directions, whereas the particles show this behaviour when the light passing through them is parallel.

There is a type of crystal aggregate, however, which has the properties of giving the cross figure, accompanied in favourable circumstances by rings, in parallel plane polarized light. These aggregates are the so-called spherulites, which are found in certain geological formations and can also be produced artificially by the slow growth of particles of certain compounds from colloidal solutions. In the paper of MORSE, WARREN, and DONNAY,* who have worked out fully the optics of spherulites, will be found many pictures of artificial spherulites, including one of particles of mercuric oxide, magnified by 1200, which is reproduced as fig. 5*b*, Plate 13, and shows the strongest resemblance to fig. 5*a*.

Spherulites consist of a mass of spicules or fibres of uniaxial crystal, radiating from a centre. Any fibre whose axis lies in the plane of polarization of either Nicol will clearly produce zero intensity in the image, which at once accounts for the black cross. In general, it can be shown* that concentric rings are also to be expected, just as in the familiar " rings and cross " of a plate of uniaxial crystal in convergent light, and when such rings can be observed it is easy to determine if the uniaxial

---

* ' Amer. J. Sci.,' vol. 23, p. 421 (1932).

crystal fibres are optically positive or negative. With particles of the size met with in the silver films, viz., of the order of 1 μ across, such rings cannot be resolved. There is, in fact, no evidence that the silver particles are complete spherulites ; an optical figure such as that observed would be produced by a conical section of a spherulite, having its apex on the glass surface, for instance, in a way recalling a single " set " in a smectic liquid-crystal layer ; or by a half of a complete sphere. It appears, however, that an arrangement of rod-like units radiating from a centre would account for our observations, these rods were birefringent. Suggestions as to how this may be possible with a substance normally arranged in a cubic lattice will be made when the results are discussed.

Particles showing this characteristic optical figure are of general occurrence as the first stage of crystallization, both in silver and in gold films. The possible suggestion that the birefringence is due to strain in the film, which has been freely invoked to account for the electrical properties, is clearly disproved by the fact that they appear in large numbers along any free edge of the film such as that bordering a scratch made by a needle-point through the film, *see* figs. 7, *a–f*, Plate 14 . Further, as will be shown later, they can be produced in densely packed masses by the heat-treatment of a mercury amalgam, where the film can have no mechanical strength. They are quite independent of the supporting surface, appearing in exactly the same way on optical glass, quartz glass, and the natural crystal faces of diamond and mica. Still more remarkable is the fact that when a comparatively large (111) face of a silver crystal has been formed by heating, as discussed later, and a second film of silver deposited on it by sputtering, then, on reheating, this second film gives rise to particles on the crystal face, which have the same appearance and properties as those on the surfaces just mentioned. Such particles on a silver crystal face are shown in figs. 14, 15, 29, 30, Plates 15 and 17.

Since this work was completed, Professor V. KOHLSCHÜTTER,* in whose presence we discussed the optical figure shown by the particles, has kindly sent us some photographs of mercury droplets 1-2μ in diameter, and of particles of galena of about the same size, taken under conditions of illumination and magnification similar to those adopted by us. The droplets gave a figure closely resembling that shown by the particles in fig. 5A, Plate 13, and fig. 7, Plate 14, which is no doubt due to symmetrical scattering and the accompanying polarization. It appears, therefore, that a spherical particle of the size in question may give a figure of the type under discussion. On the other hand, a small particle of cubic crystal will not be expected to give this figure unless it is symmetrically developed as regards external form, and so disposed that it has circular or four-fold symmetry about the axis of a microscope ; other conditions should give unequal illumination in the four quadrants. This is confirmed by Professor KOHLSCHÜTTER's photographs of three particles of galena, one of which shows no light in one quadrant while the other two quadrants are imperfect. Isolated particles on our metal films, however, always show the complete symmetrical figure.

---

* *See also* Faraday Society, 'Discussion on Structure of Metallic Coatings, Films, and Surfaces,' 1935, where *cf.* Tronstad.

It appears, then, that it cannot be claimed with confidence that the particles are spherulitic, although this is possible. In any case, however, they appear to exhibit a high degree of symmetry as regards the development of external faces, approximating to spherical form. We propose, therefore, to call the particles " spherulets," which leaves the question of birefringence open.

The Growth of the Aggregates on Heating

Films have been subjected, in the first place, to a series of heatings at one temperature, usually each an hour in duration, with examination between successive heatings; and in the second place to heatings at gradually increasing temperatures. The effects are, perhaps, best considered by discussing in detail a particular film for which the changes were studied at some length, and citing results obtained with other films in confirmation and extension of certain features.

The silver film denoted Ag 28 was about 50 atoms thick, on quartz glass. The first heating was for 3 hours at 280° C and produced a crop of small spherulets, such as are shown in figs. 7*a*, taken with crossed Nicols. In many parts of the film the number of spherulets per unit area was much greater. The light band running across is a needle-scratch which has removed the film. A second heating at 280° C for an hour produced new spherulets all over the film, and here, for example, an extensive crop along the edges of the scratch, as shown in fig. 7*b*. A third heating for an hour produced little change, except that the black centre became a little more pronounced in many particles, fig. 7*c*. The appearance of the film at this stage in ordinary transmitted light is shown in fig. 6*a*, Plate 13.

The film was then raised to a higher temperature, being heated for 2 hours at temperatures from 280° to 306° C. This produced a rapid growth in size of the particles, as shown in fig. 6*b* (ordinary transmitted light), accompanied by a great extension of the clear patches, which we call " windows," just appearing on 6*a*. The biggest windows are in the neighbourhood of large particles ; evidently the material from them has been drained into the growing crystal. Fig. 7*d* shows that the large particles, in particular the particle near the lower left-hand corner, appear mainly black between crossed Nicols at this stage. The edges, however, remain bright. A further series of heatings—1·5 hours at 290° C ; 1·5 hours at 312° C ; 1 hour at 325° C ; 1 hour at 325° to 340° C ; 1 hour at 340° to 350° C—causes the process to continue, fig. 7*e*. After a final heating for 1 hour at 345° C we have the state represented in figs. 7*f* and 6*c*, taken between crossed Nicols and in ordinary transmitted light respectively. The larger crystals show normal cubic properties, at any rate except at the bounding surfaces : for example, of the two in the lower left-hand corner (*see* fig. 6*b*) the upper one remains bright at the edges only, while the lower one, an exceptional one, is completely black between crossed Nicols. The particles which have not grown still show the fourfold optical figure. The windows have much increased. The particles which have grown into relatively large crystals have all developed mainly on a (111) face. Fig. 6*d* represents the film at the same stage as fig. 6*c*, but at a lower magnification.

From this film it would appear that prolonged heating in the region of 280° C produces a crop of spherulets which slowly increase in number to something like a constant value, while a rise of 60° C or so produces a rapid growth of the already existing particles and irregular windows, from which the material has flowed into the large particles. This type of behaviour was confirmed on about 30 other silver films.

These observations were extended by the detailed study of the behaviour of a silver film denoted Ag 9, likewise about 50 atoms thick, and on quartz glass. The glass was particularly carefully cleaned by the method of HARDY and DOUBLEDAY already quoted. Like all the other films, it was purple, and showed a bright metallic lustre in reflected light. Examined under the microscope when freshly prepared, it showed a feature never observed on any other film, silver or gold, namely well-formed and relatively large crystals, about 3 μ across, scattered over the surface.

Specimens of these crystals, photographed at a magnification of 1000 with a ring illuminator and a Beck 4 mm objective, are shown in fig. 8, Plate 15: owing to differences of size they are not all well in focus. They cannot be attributed to heating, as the conditions of preparation and the general appearance of the film were identical with those for all the other films. They differ, too, from the crystals produced by heating in that they are all sitting on a (100) face, while well-formed crystals grown by heat treatment were all, without exception, found to be on a (111) face, as typified in figs. 25 to 30, Plate 17. Further, which is very significant, they did not increase in size on heating. Apart from these large crystals, the film appeared perfectly homogeneous under the microscope, and on heating it showed just the same changes as did the other films. These crystals presenting a (100) face, which appear anomalously on what everything tends to show was a perfectly normal film, must therefore be attributed to some exceptional circumstance which did not interfere with the normal sputtering. It is suggested that they were broken off from the cathode ready made, owing to the chance disruption of a comparatively large crystalline patch on the surface, and were carried to the anode either by the discharge, or gravity, or by both. The cathode was examined microscopically to see if there were any traces of such an event, but the surface, which had merely been polished with fine emery, was much too rough for profitable investigation under a high power. These anomalous crystals do not interfere with the normal heat development of the film, and will not be further mentioned in its discussion.

The range of temperatures to which this film was subjected was wider than with Ag 28. The first heating was for 1·5 hours at 230° C, and sufficed to produce a crop of particles, shown in fig. 16, Plate 16, taken by ordinary light, with ring illuminator, at the same region as is represented in fig. 8.

Examination in polarized light, under higher magnification, showed the typical figure. The fact that many of these particles are arranged in a straight line is a characteristic which is discussed at length later. A second heating for 1·5 hours at 230° C produced little change. Heating for 1 hour at 300° C led to the appearance of further crystalline aggregates, and probably to some increase in size of those already formed, fig. 17, Plate 16. The next heating, for 1·5 hours at 380° C, produced a definite change, which is not nearly so marked by scattered light, fig. 18, Plate 16, as it is by transmitted light. The film constituting the general background to the crystallites was of a uniform purple colour before this heating, just as it was after the first preparation of the film. After the heating, however, each crystal was associated with a lighter (uncoloured) patch of irregular outline, as shown in fig. 19, Plate 16. Further heating for 1·5 hours at 415° C increased the area of these transparent windows, fig. 20, Plate 16. By this time many of the original spherulets had grown into well-developed crystals, from 5 μ to 15 μ across. Three such crystals, arbitrarily selected from many hundreds appearing on films, are shown in figs. 25, 26, and 27, Plate 17. It will be observed that they are all developed so as to present a (111) face.

The film was then further heated for periods of 1·5 hours and then of 2 hours at 405° C, which led to the further growth of the crystals and of the transparent areas surrounding them. (Fig. 21, Plate 16, by scattered light; fig. 22, Plate 16, by transmitted light.) It is to be noticed that in these later stages of heating no fresh crystallites are formed. A further heating at temperatures increasing from 420° to 505° C for 2 hours produced a remarkable effect. Figs. 23 and 24, Plate 16, show the same portion of the film, by scattered and by transmitted light, and it will be seen that a fresh crop of very small crystallites has appeared on the thin portion of the film.

This suggested that while, at a given temperature, a limit is reached for the number of crystallites formed from a comparatively (50 atoms) thick film, at a higher temperature crystal aggregates can be produced in the much thinner film which is left after material has been withdrawn to form the original crystallites. To confirm this point two films were prepared, one 55 atoms thick and the other, as estimated from the duration of sputtering, about 8 atoms thick. These were heated together in vacuo for 3 hours at 260°. Spherulets appeared on the thick film, but none of the methods of illumination showed any centres of aggregation in the thin film. Further heating for 2 hours at 340° C produced no essential change. A final heating for 1·5 hours at 420° C, however, produced in the thin film aggregates which showed the usual figure in parallel plane polarized light. This matter receives further comment in the general discussion of results.

One silver film 55 atoms thick, after a history of previous heatings which need not be detailed, was heated finally to a higher temperature than has hitherto been mentioned, namely up to 600° C. Under the microscope the surface appeared colourless, with a plentiful deposit of crystals in all stages of growth from small spherulets, probably formed as a second growth in the way just described, to large well-formed single crystals showing (111) faces. Fig. 13, Plate 15, shows this film at a magnification of 720. The colourless background was not, however, bare glass, but was covered with a very thin film of metal, as could be seen when the film was scratched with the point of a needle. The scratch showed light against a slightly darker ground.

We return to the light patches, such as are seen in fig. 19, Plate 16, which we have called windows. The method of the scratch shows that these are not bare areas but are covered with a layer which is much thinner than the original film : the windows scatter more light and transmit less light than the bare glass. A curious fact is illustrated by the comparison of fig. 21, Plate 16, taken by scattered light, and fig. 22, Plate 16, by transmitted light. The background of fig. 21 is mottled, to correspond to the light and dark patches in fig. 22 ; that is, light portions in the one correspond to light portions in the other, and dark to dark. This means that the windows scatter more light than the thicker parts of the film, a curious fact which leaves plenty of room for conjecture.

The temperature at which the windows make their first appearance has not been definitely fixed. With film Ag 9, for which the quartz glass was cleaned with particular care, the temperature of the first marked appearance was about 380°, but with other films of the same thickness the phenomenon has been detected at temperatures as low as 280° C, and was plainly visible at 300° C, *e.g.*, with Ag 28. With this latter film detailed observations were made on the increase of area of the windows. It appears that with heating at a given temperature a limit of area is reached after, *e.g.*, 5 hours, so that further heating at this, or at a lower temperature, causes no increase. Raising the temperature, *e.g.*, from 280° to 306° C, produces a great increase in area, even if the heating only lasts 0·5 hour, and after this each increase of temperature is accompanied by an increase in area, until at a temperature approaching 500° the film consists of a thin uniform window with crystals scattered on it. Briefly, the clear area formed at any temperature increases with time to a constant limit, after which the area can be increased by raising the temperature, until eventually all the original film is replaced by a much thinner film and crystalline particles. The second crystallization of such a film has already been described.

FURTHER OBSERVATIONS ON CRYSTAL GROWTH

The thickness of many large crystals, formed by prolonged heating, was measured by focussing with a high-power objective on the glass and on the top of the crystal, and found to lie between 0·5 μ and 1·5 μ : the crystal of fig. 25, Plate 17, for instance, which was 15 μ long, was only 0·5 μ thick. It is clear, then, that the crystals tend to grow by development of a (111) face, once begun. Heating for 3·5 hours at 410° C caused the crystal of fig. 25 to grow sideways, as shown in fig. 28, Plate 17 (same magnification, × 1000).

To see if the crystals could be made to grow by additions normal to the (111) face, the film Ag 9, which had been heated, as described, until there was a plentiful crop of well-developed crystals, was covered with a fresh deposit of sputtered silver about 55 atoms thick. Examined microscopically after sputtering, the crystals showed no change, while to the eye the film showed the usual bright metallic lustre of a freshly sputtered surface.

The film was then heated for 2 hours at 300° C, and fig. 29, Plate 17, shows the result in the neighbourhood of the large crystal of fig. 28. The crystal has increased slightly in breadth and length, and a large number of new aggregates have formed both on the crystal face and on the general film. Fig. 30, Plate 17, shows the same crystal by transmitted light, at a slightly less magnification. This region was examined in polarized light in the usual way, and all the new aggregates showed the normal figure for spherulets, even those on top of the crystal, *see* figs. 14 and 15, Plate 15. In many other places on the film well-formed spherulets were detected on top of large crystals. The edges of the crystals remain bright between crossed Nicols, but do not show any spherulets. It would appear, then, that atoms on top of a (111) face are added with great difficulty to the regular crystal lattice, when compared with atoms at the edge of the face. It is to be noted that an edge parallel to the polarizing plane of either of the crossed Nicols appears dark. Fig. 15 shows the crystal of fig. 14 rotated through 60°, and it will be seen that the horizontal long sides are now dark, as against the short vertical sides in fig. 14. The planes of the Nicols were as shown.

THE INFLUENCE OF THE SUPPORTING SURFACE

Some experiments were carried out with silver films deposited on ordinary microscope cover glasses, the heating being carried out in stages, just as with silica glass. The range of temperature was, however, much smaller, the limit being 400° C, since it was found that at about 450° C a combination took place between the silver and the glass, giving a pale yellow colour, which could not be removed by washing with nitric acid. The formation of spherulets and subsequent crystallization took place exactly as with quartz glass. Films were also deposited on the natural faces of different diamond crystals, in connection with the work described in the second part of the paper, and on mica. Here again the same stages of crystallization were observed, so that it may be said that they are widely independent of the surface.

GOLD FILMS

The effects obtained with gold films were similar to those obtained with silver. In particular, two gold films, 25 atoms thick on silica glass, were subjected to successive heatings. These films were bluish-green by transmitted light, and before heating no structure could be detected with magnification up to × 1000 and the various types of illumination. Heating to 400° C for 2 hours produced spherulets, fig. 9, Plate 15. After heating to 470° C for 4 hours colourless windows, of long irregular shape, were seen in the green film, closely associated with crystalline particles, which might be supposed to have drained material from them, fig. 11, Plate 15, ordinary transmitted light. The parts of the film which had apparently retained their original thickness had changed to a pale green, less blue than the original colour. Viewed obliquely the film showed a reddish-orange lustre, instead of the original yellow-gold colour.

After heating to 600° C for 2 hours, the film was much clearer to the eye in transparent light, showing only a faint blue colour. Under the microscope no colour could be seen in the background ; the film was a dense mass of crystalline particles, as shown in fig. 12, Plate 15. This resembles the silver film heated at 600° C, shown in fig. 13, Plate 15. The chief difference between the gold and the silver films revealed by this examination is that with gold no crystals of the size of the larger silver crystals were seen, the biggest being about 2 μ in diameter. The heating, however, was not carried out so slowly, so that no particular significance is attached by us to this point.

Colloidal Gold Crystals

The nature of the first aggregates suggests that when crystallization is carried out very slowly, with a limited supply of material, the initial stage is the formation of a mass showing the symmetrical figure of four bright quadrants. It is well known that small gold crystals can be slowly grown in colloidal media, and it seemed worth while to investigate the nature of the particles so formed.

The growth of gold particles in silicic acid gel was, at the suggestion of Mr. E. Hatschek, carried out as follows. Concentrated hydrochloric acid was diluted with an equal volume of 0·5% gold chloride solution. Into 6 parts of this mixture were poured 7 parts of sodium silicate solution, with constant stirring. A glass plate was placed at the bottom of a small beaker, and about 10 cc of the mixture poured on it, and allowed to set, the beaker being maintained at 40° to 50° C. When the gel was firm, a few cc of either saturated oxalic acid or sodium sulphite solution were poured on. The reduction being complete the gel was washed with distilled water and then dissolved in KOH solution. The gold particles collected on the glass disc, the solution above was decanted, and the gold washed with several changes of distilled water. The remaining traces of water were removed with filter paper, and the residue, when dry, was examined between crossed Nicols in the usual way.

All the particles, which were of from 1 to 2 μ in diameter, appeared to be spherulets as shown in fig. 10. The particles naturally tended to bunch, owing to the surface tension of the water, so that the optical figures disturb one another, but good isolated specimens could be seen which showed a complete figure.

Reduction in aqueous solution was also tried, weak solutions (1/1000 to 1/10,000) of gold chloride being reduced by hydroquinone. The particles which collected were densely packed, and showed by reflected light an appearance not unlike that of a gold leaf with small holes in it. Between crossed Nicols the mass showed a bright pattern. In the case of the packed particles no detail could be distinguished, but some isolated particles were observed which showed the usual optical figure.

The Effect of Mercury on Silver Films

When films were prepared in the absence of special precautions to exclude the last trace of mercury vapour, they exhibited patches differing in appearance from the rest of the surface, and, if kept at atmospheric temperature, became more transparent in the course of time. When examined microscopically, such a silver film, newly removed from the sputtering vessel, was seen to be covered with small yellow spots, in general of a circular shape, on a background of the usual purple. These spots varied in diameter from about 1μ to 80μ. On one film, about $20 \mu\mu$ thick and $1 \cdot 3$ cm in diameter, as many as 800 spots of 10μ or more in diameter were counted. Spots which are small to begin with grow in course of time: fig. 31*a* shows a spot on a freshly prepared film, and fig. 31*b*, Plate 17, the same place three days later.

Various different types of spots were observed. In general there was a relatively large crystalline particle at the centre of a disc, as shown in figs. 32*a* and 32*b*, Plate 17 (same spot by transmitted and by scattered light), and fig. 33, Plate 17. In the first case a ring of small crystals occurs near the periphery, in the second the spot is tolerably uniform. Fig. 34, Plate 17, shows another type often observed, viz., concentric rings of small crystallites, reminiscent of LIESEGANG's rings. In all cases the appearance is consistent with a change starting at a centre, and extending out uniformly in all directions.

After three days, a film, originally of the usual purple colour, which was selected for study, had become definitely redder, and was covered with small spherulets similar to those which appear in the early stages of heating a film. This state appeared to be relatively stable, as no change was detected during the next few days, but in the course of some weeks the film gradually became paler in colour and more densely packed with spherulets, until eventually, five months later, no colour at all could be seen under the microscope by transmitted light, but the field was densely covered with spherulets. The general effect of the mercury, then, in the body of the film, was that of a prolonged heating at a moderate temperature. Within and around the spots, however, a different effect had taken place. Figs. 35 and 36, Plate 17, taken in parallel polarized light and by ordinary transmitted light respectively, show a typical distribution: the shape of the spot is clearly due to a spreading from two neighbouring centres. In the middle the crystallites have apparently developed the normal cubical form, since they show black between crossed Nicols. There are, then, several zones of spherulets* arranged in concentric circles, succeeded, as we go out, by a zone of large well-formed crystals, optically isotropic. Then comes the film which was originally purple, but is now densely packed with spherulets.

Various stages of heated films are, therefore, represented in the mercury-infected film. The only difference is the development of the well-formed crystals, which are not flat and do not present a (111) face. The resolution was not great enough to enable the outline to be carefully studied. The fact that the upper part of the crystals was never in focus at the same time as the lower part pointed to considerable thickness, and added to the difficulty of determining their habit and orientation.

Another way of investigating the effect of mercury contaminations is to heat the film before these spontaneous changes have taken place. A silver film, showing yellow spots, prepared in exactly the same circumstances as the one whose behaviour

---

* The optical figure is not clear in fig. 35, which is much reduced, but showed plainly in every particle in the original, which was × 1000.

has just been described, was heated *in vacuo* for 2·5 hours at 300° C shortly after its removal from the sputtering vessel. This treatment transformed the spots into densely crowded masses of particles. The appearance in ordinary transmitted light is shown in fig. 38, Plate 17, while the appearance in plane polarized light is shown in fig. 37, Plate 17. The surrounding film had become semi-transparent.

These mercury contaminations show a great variety of interesting minor phenomena, not described.

Discussion

The formation of the first aggregates, which are much thicker than the rest of the film, takes place at about 280° C or lower for silver, and at below 400° for gold. This shows that the atoms of the film must be freely mobile at temperatures very far removed from the melting point, which is 1062° C for gold and 960° C for silver. The fact that during the earlier stages there is little sign of any decrease of intensity of colour in the film, as seen by transmitted light, in the immediate neighbourhood of the aggregates, indicates that only the surface layers are concerned, and that atoms move in from distances which are many times the linear dimensions of the aggregates.

Many other observations point to a lesser mobility of the lower layers of the film. When, at a higher temperature, the windows form, they do not leave the glass bare, but a film a few atoms thick remains, from which crystalline particles can be formed at a definitely higher temperature, *e.g.*, about 420° C for silver. The silver film which was 8 atoms thick did not form any aggregates until heated to this temperature, whereas the film 50 atoms thick gave a copious crop at 260° C.

The mobility of very thin films, at temperatures far below the melting point of the metal, has been remarked by many previous workers, among whom VOLMER and ESTERMANN* (mercury at about − 50° C), ESTERMANN† (cadmium at − 120° C), and COCKCROFT‡ (cadmium at 15° C) may be cited. Recently DITCHBURN§ has also carried out experiments which have led him to conclude that sputtered films of cadmium are mobile at room temperature on glass and metal surfaces. The films of VOLMER and ESTERMANN were, from the method of experiment, of unknown thickness, but certainly not thicker than 100 atoms ; hexagonal crystalline flakes, some tenths of a millimetre across, were formed extremely rapidly on a glass surface. The conditions under which ESTERMANN and COCKCROFT observed the mobility were from the edge of a deposit some atoms thick on to a bare surface, which are clearly very favourable ; a similar case in our experiments was provided by the scratch seen in figs. 7*a* to *f*, which apparently became covered with a thin film on heating

---

[*] ' Z. Physik,' vol. 7, p. 13 (1921).

[†] ' Z. Physik,' vol. 33, p. 320 (1925).

[‡] ' Proc. Roy. Soc.,' A, vol. 119, p. 293 (1928).

[§] ' Proc. Camb. Phil. Soc.,' vol. 29, p. 131 (1933). *See also* general article by GERLACH, ' Ergebn. Exact. Naturw.,' vol. 3, p. 182 (1924).

to 280° C, as evidenced by the appearance of spherulets.* It is interesting to note that the minute spherulet visible in the middle of this scratch did not grow on heating, whereas the one on the scratch near the edge, figs. 7*e* and *f*, rapidly became larger.

The mobility, as is to be expected, seems to be dependent on the melting point of the metal, the lowest temperature for which it has been observed with mercury and cadmium being much lower than that found by us for silver and gold. With a given metal the mobility increases rapidly with the temperature ; VOLMER and ESTERMANN's mercury near the melting point was, for instance, extremely mobile, forming large crystals in a minute or so. The experimental conditions are, however, not yet precise enough for a quantitative discussion—*e.g.*, ESTERMANN's flow of a narrow streak of metal over the surrounding bare glass is scarcely comparable with our results, neither is there sufficient evidence as to the influence of the substrate. More exact control of the conditions may enable calculations along the lines of FRENKEL's theory† to be applied to the question.

The formation of windows is a consequence of the mobility of the atoms of the film, coupled with the cohesive (VAN DER WAALS) forces between them and the additional stability which is shown by these experiments to be possessed by a layer a few atoms thick in contact with the substrate. The cause of the characteristic irregular form of the channels left by the aggregating material, such as are shown in *e.g.*, figs. 6*d* and 11, is still obscure.

It has been shown that the polarization figure of the first aggregates is not a strain effect, firstly because no reasonable system of strain will give rise to the observed figure, and secondly because the jagged edge of a scratch, where there is unlikely to be strain in the film, is a particularly favourable place for the spherulets. The effect of mercury can also be cited (*see* pp. 77 and 84).

The process of crystallization can be supposed to take place somewhat in the following way. Atoms are moving about freely on the top layer of the film, which resembles a two-dimensional gas, the path between impacts being probably short, of the same order as the atomic diameter. By impact under favourable conditions, such as are discussed in theories of gaseous association,‡ an aggregate of first two atoms, and later of a small number of atoms, is formed. The arrangement will not be on a cubic lattice, since with a few tens, or a few hundreds of atoms the surface tension forces are likely to predominate and produce a roughly spherical aggregate. Later, as a result of the conflict between the forces tending to form a cubic lattice and the surface forces tending to a spherical aggregate, flat faces of limited extent will appear, so that the form is polyhedral, with purely local patches in which the

---

* A scratch shows up plainly in a film only a few atoms thick, and probably leaves the surface bare. There is a possibility, however, that a monomolecular layer remains, which sensitizes the surface. *Cf.* LANGMUIR, ' Proc. Nat. Acad. Sci.,' Wash., vol. 3, p. 141 (1917) ; COCKCROFT, *loc. cit.*, p. 309.

† ' Z. Physik,' vol. 26, p. 117 (1924).

‡ Such considerations as activation energy are involved. *See e.g.*, EUCKEN, " Lehrbuch der Chemischen Physik," p. 612 (1930).

atoms are ordered in an approximately square array. From these faces ordered columns grow out, which have an approximately cubic structure, but owing to the relatively small width of the columns, or fibres, compared with their length, the structure in them is tetragonal, with a small difference of axial ratio. This would seem to follow from LENNARD JONES'S* calculations of the different stable spacing in a plane lattice and in a cubic lattice, the tendency, for particles between which VAN DER WAALS forces prevail, being for a wider spacing in the former state. When the number of planes is relatively few and their dimensions are also restricted, as in planes parallel to the axis of a fibre, some tendency to the wider spacing should clearly persist. As the total width of the spherulitic particles is only a few thousand atoms, the single fibres may reasonably be supposed to be only a few tens of atoms across, and a few thousand atoms long.

On these lines the polarization figure can be explained as a birefringence phenomenon. However, Professor KOHLSCHÜTTER'S results show that we must consider scattering from an approximately spherical particle, without birefringence, as a possible cause. Such a particle of cubic lattice, developed externally as a polyhedron of high symmetry, can result from a conflict between surface tension and crystallization forces, as just indicated.

The electron diffraction results indicate that, in general, freshly prepared sputtered films consist of small crystalline aggregates with side lengths of a few unit cubes only. Since the films are inevitably heated to a certain extent during the process of examination, it is difficult to know if these very minute crystals are characteristic of the unheated metal film, but even if they should be, our picture does not need any essential modification. We have only to suppose that the aggregate is built up by an ordering of these very small blocks, instead of by the ordering of single atoms.

If the birefringent form, consisting of radial fibres with incompletely ordered atoms between them, really exists, it will clearly be metastable when it reaches a certain size, so that, if the atoms have a certain amplitude of vibration, the whole will gradually settle down to a cubic lattice form. The conversion will start at the centre, where the arrangement already approaches the close-packed state ; the atoms added subsequently to the original approximately spherical cluster will release the surface tension effect.

The next stage in growth confronts us with the following facts : (*a*) that the crystal develops preferentially on a (111) face, (*b*) that new metal sputtered on a (111) face of a well-grown crystal does not add itself to the crystal, but forms an amorphous layer, which on heating crystallizes into separate spherulets. A tentative explanation may be given in terms of ideas first put forward by KOSSEL,† who considered, however, only the simplest cubic structure. The atom of a face-centred cubic crystal has, in the body of the crystal, 12 nearest neighbours, distant $\sqrt{2}\,a$, if the side of the unit cube be taken as $2\,a$; 6 neighbours distant $2\,a$; 8 neighbours distant $\sqrt{6}\,a$. For an atom which has just been added to an incomplete

---

* 'Z. Kristallog.,' vol 75, p. 215 (1930).

† 'Nach. Ges. Wiss. Gött.,' p. 135 (1927) ; 'Phys. Z.,' vol. 29, p. 553 (1928).

row of an incomplete layer on a complete plane, *see* fig. 3*d*, the figures are just half these, namely, 6/3/4, the three figures indicating the number of neighbours of the three nearest classes, in order of distance.

Now we can consider an atom added to a crystal in three stages : first an atom added to a single row of atoms, fig. 3*a* ; secondly an atom added to a single layer so as to begin a fresh row, fig. 3*b* ; thirdly an atom added on top of a completed layer so as to start a fresh layer, fig. 3*c*. The sum of the energies involved in these three processes will give the total energy E involved in adding a new atom to a crystal in an incomplete plane, fig. 3*d*, and since the total energy for a large crystal is measured by NE, where N is the total number of atoms in the crystal, E must be the same however we consider the atom added, viz., to whatever face.

The Table I gives the number of neighbours of the three classes, indicated by their distances $\sqrt{2}\,a$, $2\,a$, and $\sqrt{6}\,a$, for building up step by step the elements of the three planes (100), (110), (111). Opposite I, II, and III are given respectively the numbers of neighbours when an atom is added to an isolated row, fig. 3*a* ; when an atom is added to start a fresh row in an isolated plane, fig. 3*b* ; when an atom is added to start a fresh plane on a completed plane, fig. 3*c*. The totals are, of course, the same whichever plane we consider. The energies pertaining to III, however, decide the relative ease with which a new plane is begun. For the (100) and (110) planes (which we call case A) the figures are the same ; to compare the (111) planes (case B) we have to consider the relative contributions of the different classes of neighbour to the gain in energy when an atom is added. If we take the energy to

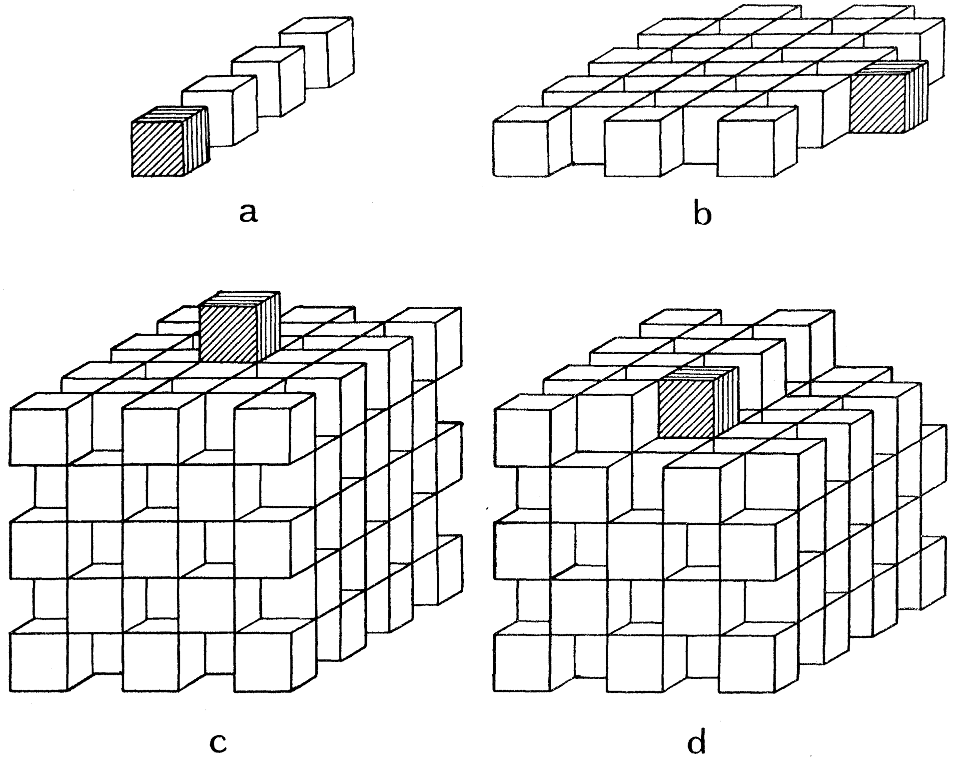


FIG. 3

TABLE I

	(100)			(110)			(111)		
	$\sqrt{2}\,a$	$2\,a$	$\sqrt{6}\,a$	$\sqrt{2}\,a$	$2\,a$	$\sqrt{6}\,a$	$\sqrt{2}\,a$	$2\,a$	$\sqrt{6}\,a$
I	0	1	0	1	0	0	1	0	0
II	2	1	0	1	2	0	2	0	2
III	4	1	4	4	1	4	3	3	2
Total . .	6	3	4	6	3	4	6	3	4

vary as r^n, we find that the gain is greater for case A than for case B, whatever the index n, the 1 extra $\sqrt{2}\,a$ neighbour and the 2 extra $\sqrt{6}\,a$ neighbours more than compensating for the 2 fewer $2\,a$ neighbours. If $n = 1$ the ratio of the gain of energy in case A to that in case B is 1·118 ; and the ratio increases as n increases, being, *e.g.*, 1·129, 1·149, 1·182 for $n = 2, 3, 4$, respectively. It is therefore clear that the crystal will tend to add atoms to the (100) and (110) faces rather than to the (111) face. The total figures, which represent the energy when an atom is added to continue the building of an incomplete plane on a complete face, fig. 3*d*, show that any incomplete crystal planes will grow tangentially, as first pointed out by KOSSEL.

As regards building up a first plane, the figures for continuing an incomplete row next to a completed row are 2/2/0 ; 2/2/0 ; 3/0/2, which are most favourable in the last, or (111), case. We can see in general, then, that a (111) face will first develop, but that the building of further (111) faces on top of it is unfavourable as compared with the sideways growth. The development of (100) and of (110) faces appears, from the table, to be, to the first approximation, equally favoured, but no definite experimental confirmation of this point is offered from the present work.

When a second film is sputtered on to well-developed crystals there are two factors to be taken into account, (*a*) the greater mobility of the upper layer of the new film and (*b*) the relative reluctance of a (111) surface to add atoms normally to itself. On these lines the formation of new spherulets on top of the old crystal can be understood.

The fact that the edges of the large crystals often show bright between crossed Nicols may possibly be interpreted to mean either that the first stage of the addition of atoms to the crystal is the ordering of neighbouring atoms into crystalline fibres normal to the surface, from which the tangential building up of the true cubic lattice then takes place, or that the whole surface planes have a spacing different from that of the planes in the bulk of the crystal. Alternatively, the phenomenon may be due to polarization effects connected with scattering or reflection at the edge.

GENERAL CONSIDERATION OF RESULTS

There are a large number of earlier results on these films which have an interesting bearing on the work described. These may be roughly grouped under the headings of electron diffraction, optical behaviour, and electrical resistance.

The work on electron diffraction has been mainly carried out by G. P. THOMSON and his school in England, and by RUPP[*] and KIRCHNER[†] in Germany. In his early experiments G. P. THOMSON used mostly etched foils, which do not compare with our films, but he records[‡] a result with a sputtered platinum film, prepared on glass and afterwards floated on to a thin celluloid backing. With a normal beam of electrons this gave no rings corresponding to a (111) face, a result which is natural if the platinum crystals (face-centred cubic, like gold and silver) were arranged with (111) faces parallel to the surface of the original glass. RUPP,[*] using the electron reflection method, which allows the use of thicker sheets than the transmission method, records that when films, deposited by evaporation on tungsten sheet, were " glowed in a high vacuum " a great part of the crystals so obtained had a (111) face parallel to the surface of the sheet. The films, which consisted of various face-centred cubic metals, of unmeasured thicknesses—estimated as of the order 10^{-4} cm—were exposed to further strong heating by the electron beam. We have never used such thick films, so that we cannot say why only a great part, and not all, of the crystals were so oriented. In another paper RUPP[§] records that with films of the order of 10^{-7} cm. thick it was not possible to obtain reproducible results, films which showed equal absorption to light giving electron diffraction rings of different degrees of perfection. This he attributes tentatively to thin places on the film, a supposition which is confirmed by our results.

G. P. THOMSON, STUART, and MURISON[||] have carried out a special investigation on sputtered films of platinum, using the method of electron reflection. They found in the first place that the majority of the rings indicated, by their width, reflection by crystals with about 20 unit cubes in the side, while a few indicated crystals with only about 6. This agrees with the order of size required by us for the cross-section of individual fibres of the possible spherulites. They further found frequent indication of preferential orientation of crystals ; they do not explicitly say that in these cases the lines were sharper, indicating larger crystals, but from the photographs given they appear to be so. Films showing the orientation with (111) parallel to the substrate were frequently found, but it appears that there were even more films showing the (100) as the preferred face. A single film showed one orientation, never a mixture of the two. We have recorded a case of the (100) face parallel to the face of the substrate, but have pointed out why we regard this as exceptional, viz., that the crystals were unchanged by heating. The films of G. P. THOMSON and his co-workers were heated during preparation and examination, but the heating effects were not sufficiently systematic to render any detailed examination in terms of our results possible.[¶]

---

[*] 'Ann. Physik,' vol. 1, p. 801 (1929).

[†] 'Z. Physik,' vol. 76, p. 576 (1932).

[‡] 'Proc. Roy. Soc.,' A, vol. 119, p. 651 (1928`

[§] 'Ann. Physik,' vol. 1, p. 773 (1929).

[||] 'Proc. Phys. Soc.,' Lond. vol. 45, p. 381 (1933).

[¶] I have constructed an electron diffraction apparatus on the lines of that of Professor G. P. THOMSON, to whom I am much indebted for friendly advice and the loan of drawings, and hope to solve this difficulty. (E. N. DA C. A.)

Dixit,* working in G. P. Thomson's laboratory, has investigated the orientation of the crystals formed by heating evaporated films deposited on various substrates. The silver films, on a polished molybdenum surface, varied in thickness from 10^{-4} to 10^{-6} cm. With both thick and thin films, heating at temperatures of 550° C produced crystals oriented with a (111) plane parallel to the substrate, but with thick films—10^{-4} cm—heating for two hours at 400° C failed to produce this effect. With thin films, of the order of thickness of ours, heating for ten minutes at 500° C failed to produce an orientation with both quartz and molybdenum as a substrate, but as we never tried such short heatings we cannot speak of agreement. At much higher temperatures (*e.g.*, 750° to 800° C) Dixit obtained evidence of orientation on both (200) faces and (111) faces, the two being about equally common. With aluminium he obtained first (111) orientation, and at higher temperatures (110) and (100).

Rama Swamy† has just published some results on sputtered gold films, in which heating produced crystals with (111) faces, parallel to the surface of deposition. The crystals started to grow rapidly at about 400° C, which agrees with our results.

Kirchner (*loc. cit.*) has carried out experiments with films deposited by evaporation on, in general, a celluloid or collodion surface. He used the method of electron diffraction, and observed a preferential orientation of the crystals, with a particular plane parallel to the substrate, which he gives as the (111) plane for bismuth (rhombohedral, nearly cubic), but does not specify for gold. His films were deposited by very rapid evaporation, *e.g.*, 10 to 30 seconds for gold films up to the order of 10^{-6} cm thick, so that the conditions are not precise enough to permit detailed considerations in terms of our results. There are on record interesting experiments on electron diffraction by thin films where the conditions are not sufficiently specific for the purpose of comparison.‡

As regards the optical property of the films, Rama Swamy§ carried out in this laboratory a quantitative investigation into the transmission of light by thin films of gold and silver at various temperatures, comparing the experimental results with Maxwell Garnett's theory.|| It was found that good agreement could be obtained by assuming that on heating the film breaks up with the formation of very thin windows, transmitting the light practically unchanged, and that the area of these windows is practically a linear function of the temperature. This is in excellent general agreement with what we have found, an agreement which can be extended into details.

Certain peculiar observations of Murmann¶ concerning the transmission of infra-red radiation by antimony and silver films are possibly explicable in terms of results described in this paper. He prepared his films by evaporation in vacuo, in

[*] 'Phil. Mag.,' vol. 16, p. 1049 (1933).

[†] 'Proc. Phys. Soc.,' Lond., vol. 46, p. 739 (1934).

[‡] *E.g.*, Taylor Jones, 'Phil. Mag.,' vol. 12, p. 641 (1931).

[§] 'Proc. Roy. Soc.,' A, vol. 131, p. 307 (1931).

[||] 'Phil. Trans.,' A, vol. 203, p. 385 (1904) ; and vol. 205, p. 237 (1905).

[¶] 'Z. Physik,' vol. 54, p. 741 (1929).

circumstances which leave a distinct possibility of contamination by mercury vapour. With antimony he found that small dark spots appeared on the surface which spread out as increasing discs until the whole film had been transformed, the process sometimes taking months and sometimes hours. The transparency of the two types of antimony film, original and transformed, for the infra-red was quite different, and he also obtained films of silver with either high or low transparency. He found that this varied, as did the electrical conductivity, from point to point of the film, and that the infra-red transmission would fall from nearly 100% to 30% or 40% in the course of some hours. All this pointed to a second modification of the silver, and MURMANN suggested that, as in his antimony films, the transformation commenced at certain centres and spread outwards until the film was transformed. All these results are easily explained as a result of mercury contamination, behaving in the way described by us. With antimony MURMANN observed with the microscope crystalline aggregates at the boundary of the two modifications, which agrees with what we observed with mercury-contaminated silver films, as shown, *e.g.*, in fig. 36, Plate 17. As regards the apparently special position of antimony, it may be pointed out that antimony and mercury are of the same crystal form, viz., rhombohedral.

As regards the electrical properties of thin films, it is well known that heating produces an irreversible change in the resistance, that is, a first heating to a given temperature modifies the resistance permanently, so that for subsequent heating and cooling within the range below that temperature the resistance is a function of the temperature only.* With films of the order of a few times 10^{-6} cm in thickness this irreversible change is a decrease up to a certain temperature where the resistance is a minimum, followed by an increase. For bismuth this temperature of minimum resistance is 150° C; for platinum it is 500° C; for gold 300° C, all temperatures being approximate. For gold the temperature is about that at which spherulets first appear, so that it is reasonable to assume that the irreversible increase of resistance is due to the thinning of the film which takes place when the upper layers move in to form the first aggregates, a thinning which rapidly increases as the temperature is raised, corresponding to the rapid increase of resistance, which finally becomes infinite, as would be expected from our results, *cf.* figs. 12 and 13. The cause of the permanent decrease of resistance which takes place in the early stages of heating is still obscure. Attempts have been made to explain it in terms of a postulated fine granular structure of the film† in which the rise of temperature produces a partial coalescence. The specific resistance of the newly prepared film is always much higher than that of the metal in bulk. Recently PERUCCA‡

---

[*] *See e.g.*, RICHTMYER and CURTIS, 'Phys. Rev.,' vol. 15, p. 465 (1920); KOLLER, *ibid.*, vol. 18, p. 221 (1921); CURTIS, *ibid.*, vol. 18, p. 255 (1921); BARTLETT, 'Phil. Mag.,' vol. 5, p. 848 (1928), and references given in these papers.

[†] *See e.g.*, KING, 'Phys. Rev.,' vol. 10, p. 291 (1917), and for very thin films ESTERMANN, 'Z. phys. Chem.,' vol. 106, p. 403 (1923).

[‡] 'Ann. Physik,' vol. 4, p. 252 (1930); 'Z. Physik,' vol. 91, p. 660 (1934). *See also* authors quoted in the latter paper.

has put forward an interesting hypothesis according to which the surface layer, of a thickness of a few atoms or more, has an anomalously high electrical resistance. A special surface property is in general accord with the special surface mobility which we have established for our films. If PERUCCA's hypothesis is correct it would appear that the depth of the anomalous layer can be irreversibly diminished by heating to temperatures up to 200° to 300° C with gold and silver.

For exceedingly thin films the effect of heat is, apparently, to produce an irreversible increase of resistance from the beginning.* Here again there is a lack of information as to the thickness of the films and other conditions : we cite the result as indicating a difference in the behaviour with thickness which may bear a relation to the difference in crystallization noted by us between the original film and the very thin film formed in the windows.

BARTLETT† suggests, to account for the regular results on ageing, that an unequal expansion in the film and the surface on which it is deposited opens or closes gaps as the temperature changes, and assumes a buckling of the film on heating. Microscopic examination has shown no sign of such effects of unequal expansion. On the other hand, the processes of crystallization and of the formation of windows described by us accounts naturally for the regular results observed. The windows observed by us bear no relation to BARTLETT's postulated gaps or tears, for they form on heating, and not on cooling.

The results on the electrical resistance of films exhibit a great variety, and reference has been made only to those which seem of wide generality. It would appear that the elimination of uncontrolled heating in the preparation of the films and systematic microscopic examination under high powers would do much to clear up the irregularities observed.

Finally, reference may be made to the results of INGERSOLL and his collaborators‡ on their nickel films of the order 10^{-5} cm thick. They found that cold-sputtered films were non-magnetic, but that heating to about 350° C to 450° C brought them to the magnetic state associated with nickel in bulk. Films sputtered with a hot cathode show the properties of aged films, and are magnetic. These results again point to the crystallization of the film into relatively large crystals, of the order of 1 μ across, at a certain temperature far below the melting point.

All the results discussed, then, indicate that, with films of the order 10^{-6} cm thick, the upper layers become mobile with the formation of crystalline aggregates, at a certain temperature, varying from 15° C for cadmium to 450° C with platinum, the critical temperature increasing with the melting point of the metal. It will clearly be of interest to try to fix, under more precise conditions, this critical temperature, above which the film cannot be treated as solid.

---

* HOULLEVIGUE, 'Ann. Chim. Phys.,' vol. 21, p. 197 (1910) ; WEBER and OOSTERHUIS, 'Proc. Akad. Sci. Amst.,' vol 19, p. 597 (1917).

† 'Phil. Mag.,' vol. 5, p. 848 (1928).

‡ INGERSOLL and DE VINNEY, 'Phys. Rev.,' vol. 26, p. 86 (1925) ; INGERSOLL and SORDAHL, *ibid.*, vol. 32, p. 649 (1928) ; INGERSOLL and HANAWALT, *ibid.*, vol. 34, p. 972 (1929).

THE INFLUENCE OF FAULTS IN THE SUBSTRATE

Fused Silica Glass

It was observed during the experiments described in Part I that the small crystalline particles formed by heating a silver film often showed a definite tendency to be arranged in lines, as shown, for example, in fig. 16, Plate 16. While the majority of the particles were scattered at random, this alignment is by no means uncommon, as many as 50 or 60 lines, varying in length from 0·05 mm to 2 mm, having been observed on a disc of silica glass 5 mm in radius. Figs. 39 and 40, Plate 18, show typical cases, the occurrence of close parallel lines being frequent.* Fig. 39 is a gold film, heated to 470° C, by scattered light, and shows well the preferential scattering by the thin windows, referred to in Part I ; fig. 40 is a silver film by transmitted light. Both are on quartz glass.

In order to decide whether the formation of lines was due to chance surface irregularities, to some property of the metal film, or to a permanent property of the surface, the film showing the easily distinguished quadrilateral pattern of fig. 41, Plate 18 (silver on quartz glass), was removed with nitric acid, and the disc washed with soap and water, rinsed and dried. Another silver film of the same thickness as the first was then deposited, and subsequently heated as before. The characteristic pattern was again obtained at the same spot as before, as shown in fig. 42. The film was again removed with acid, and this time the disc was drastically cleaned by the method of Hardy and Doubleday (*loc. cit.* in I) and afterwards heated *in vacuo* for 4 hours at 550° C, which should remove any water vapour. With subsequent sputtering and heating the pattern was once more repeated. The fact that drastic cleansing leaves a pattern of lines unaltered was observed at many different parts of the surface, with all three silver films, and was as definite in most, if not all, cases as in the one instance shown in the photographs. The feature of quartz glass surface which gives rise to the lines is therefore so permanent that the most thorough cleansing cannot remove it.

The surface of the disc was then mechanically polished by Messrs. Adam Hilger, who estimated that the thickness of the abraded layer was about 10^{-6} cm. When the process of sputtering and heating was repeated the characteristic pattern could no longer be found.

The first obvious suggestion is that the lines are due to scratches on the surface, the sharp edges of which might be supposed to offer convenient nuclei for crystallization, as a thread does in a salt solution. Such scratches are often formed during polishing by accidental specks of grit. A careful search was made for scratches, using various forms of illumination and different magnifications. They cannot, for instance, be seen either by transmitted light or by dark ground illumination at a magnification of × 1000. The most searching illumination in looking for such

---

* Taking the whole collection of lines on a given glass surface, however, no preferential orientation was evident.

scratches is grazing illumination of the surface by an intense beam of light, and by this method very fine polishing marks, invisible by other tests, were revealed on glass and metal surfaces. When, however, the silver films were examined in this way, no trace of any such scratch could be detected along the lines of crystalline particles. Fig. 43, Plate 18, was taken with an intense beam of light from a pointolite lamp, transverse to the lines, condensed by a lens on to the surface, the mean grazing angle being about 15°. The crystals appear as intense points of light, but there is no sign of any connecting scratch.

There are other features which are difficult to explain on a theory of chance surface scratches. In fig. 44, Plate 18, for instance, we have two lines meeting at right angles, but not running through one another, which is a very improbable event with two scratches. This behaviour of one line terminating on another, and not crossing it, has been frequently observed. The meeting at an angle of 90° has also been recorded more than once. The exactly parallel course, so often shown by neighbouring lines, also does not look like chance scratches.

To settle this point deliberate scratches were made on a silica glass surface, which was afterwards sputtered and heated. Polishing marks are due not to the polishing agent itself, which causes the surface of the glass to flow into an amorphous layer,* but to minute pieces of grit accidentally present. Three methods were used to produce scratches ; rubbing with very fine moist carborundum powder, polishing with finest optical rouge, with no precautions to avoid dust, and scratching with a needle-point. In the case of both powders the polishing was done, up and down, along one direction only. With carborundum, the film after heating sometimes showed lines of crystals which had formed on visible scratches on the surface, but, considering the vigorous treatment to which the surface had been subjected, the number of such lines was quite small, and the accompanying scratch was always easily visible under the microscope. In addition, these lines were very ragged when compared with those which appear on a normal glass surface ; there were frequent large gaps with no crystals along the scratch, unlike such lines as are shown in figs. 39 to 44, Plate 18 ; and the lines, instead of being sharp and straight, had many kinks and sudden small curves in them. Besides these lines on obvious scratches, others were found with the same characteristics as those seen on an unscratched glass surface, but these were arranged at random in all directions, and showed no influence of the fixed direction of the deliberate scratching treatment.

After polishing with rouge, which bore a more direct resemblance to the treatment glass might have gone through, many lines of crystals were formed on heating. Their directions were measured, and found to bear no relation to the direction in which the disc had been rouged. The needle scratch, fig. 45, Plate 19, was, as might be expected, very coarse, and resembled in no way the normal lines. There was some differential effect in the crystallization on the scratched and the unscratched surface, which has no interest for the point under discussion.

---

* Sir G. T. Beilby, "Aggregation and Flow of Solids," London, 1923 ; French, ' Proc. Roy. Soc.,' A, vol. 140, p. 637 (1933) ; Darbyshire and Dixit, ' Phil. Mag.,' vol. 16, p. 961 (1933).

There is strong evidence, then, that the origin of the lines of crystals is other than such fine scratches as might arise from polishing or from ordinary handling.

Films on Other Surfaces

The results on silica glass lead us to the belief that the lines of crystals must indicate the course of the extremely fine surface cracks, probably only a few atomic diameters across, which are assumed by Griffiths* and by Joffe† and others to be the cause of the abnormal weakness of all real solids. The fact that they withstand any cleansing, however drastic, but disappear after a very recent polishing which only removes about 10^{-6} cm, is in agreement with such a hypothesis, for modern work has confirmed Beilby's view that cracks are flowed over by a surface layer during polishing.

To confirm this, other surfaces were used. In the first place mica, which is known to have an unusually perfect cleavage surface, and to exhibit theoretical strength when loaded so as not to stress the edges,‡ was tried. Smooth cleavage surfaces were sputtered and heated to about 300° C. No lines of crystals were ever detected, which agrees with our hypothesis. It seemed natural to try rock salt, which has been so much used in researches on crystal structure. Fresh cleavage surfaces were sputtered and heated, and a variety of markings obtained, but the whole film became discoloured, probably due to the action of the chlorine ions on the metal of the film, and it did not seem safe to draw any conclusions. The observations were further complicated by the fact that there was a variety of faults which were visible under the microscope, each of which causes a local disturbance in the heated film.

A critical test case was furnished by the natural faces of diamond crystals. Robertson, Fox, and Martin,§ in their comprehensive study of the physical properties of diamonds, have clearly established the existence of two types. Crystals of what they call type 1 have usually perfect faces and are birefringent, while crystals of type 2 are largely isotropic. As a result of a large number of experiments they concluded that diamonds of type 1 are under strain, while in those of type 2 the strain has been released by slipping, on one or more systems of planes, occurring at some period in the formation, probably when the diamond was crystallizing from the plastic state. On this view a crystal of type 1 should be free from submicroscopic surface cracks, which, on the other hand, should be present in type 2.

Professor W. T. Gordon kindly lent us two crystals, one of each type, with well-developed natural (111) faces, being D 1 and D 2 of Robertson, Fox, and Martin's paper. The face of D 1, the diamond of type 1, was a perfect crystal face, pitted with shallow, equilateral triangular pits, such as are seen in figs. 46 and 47, Plate 19.

---

* 'Phil. Trans.,' A, vol. 221, p. 163 (1921) ; Inter. Congr. Appt. Mech. Delft, 1924, p. 61.

† *See e.g.*, "The Physics of Crystals," 1928, and Int. Congr. Phys., London, 1934, p. 72, where references are given.

‡ Orowan, 'Z. Physik,' vol. 82, p. 235 (1933).

§ 'Phil. Trans.,' A, vol. 232, p. 463 (1934).

The face of D 2, type 2, was a triangular cleavage face, crossed by a series of shallow steps, such as appear in fig. 48, Plate 19. Silver films were sputtered on these surfaces, and the diamonds heated *in vacuo* until a good crop of minute particles appeared.

With the diamond of type 1 the distribution of the particles was a random one ; in particular there was no tendency for the particles to align themselves along, or parallel to, the sides of the triangular pits which have just been mentioned. Figs. 46 and 47, Plate 19, are typical. The appearance with type 2 was in sharp contrast, for the surface was covered with lines of crystal particles. Some of these were along cracks or sharp edges that were visible with suitable illumination and high magnification, fig. 49, Plate 20, but the majority did not follow any visible crack or flaw, *e.g.*, fig. 50, Plate 20. Groups of strictly parallel lines were common, as in figs. 50 and 51, Plate 20. The lines are not always straight, but may show a gradual curvature, as in fig. 51. Another feature often observed is the radiation of two or more lines from a point, as seen at the top of fig. 48. Closely allied to this is the case where a natural line, probably a very shallow step, suddenly changes its direction to be parallel to a line of crystals, fig. 52.

Another interesting case is seen in fig. 48. The line of crystals running across the picture, from top to bottom, crosses two steps in the diamond, of which the one nearer the bottom of the photograph was $1 \cdot 8\ \mu$ high, the other being $1 \cdot 2\ \mu$ high. It is clear, then, that the crack is more than $3\ \mu$ deep, in which connection it may be worth recalling that GRIFFITHS calculated that the submicroscopic cracks which, on his theory, exist in quartz glass are about $2\ \mu$ deep or more. From the displacement of the line where it crosses the step it appears that the plane of the submicroscopic crack is inclined, and a very rough estimate of the angle which it makes with the surface can be made from the measurement of the displacement and the height of the step. It lies between 25° and 35°.

Many of these features—the parallel lines, the radiation of lines from a point, the slight curvature of some of the lines—are also found with the silica surfaces. The contrast between the two types of diamond, and the hardness of the diamond surface, finally puts out of court any suggestion that the alignment is due to chance scratches, in the ordinary sense. On the other hand, our hypothesis of submicroscopic cracks as a cause seems to agree very well with the experimental results, and we suggest that these results are the first direct proof of the existence of these surface flaws.

The ultramicroscopic method adopted by us in looking for visible cracks, *cf.* fig. 43, is capable of revealing particles only $5\ \mu\mu$ across, and several extremely minute specks are visible on the original photograph. A long crack is more easily visible than a single particle of the same width. It therefore seems probable that cracks which are invisible with strong oblique illumination and wide aperture are not likely to be more than 10 atoms across, and may well be much less.

It seemed of interest to inquire whether the cracks correspond to definite crystallographic planes, or run at random. The lines observed correspond to intersections with a (111) plane. The angle θ, which the intersection of a plane $(a\ b\ c)$ with a (111) face makes with a standard line was therefore worked out for various planes. If the intersection of a (100) face with the (111) face be taken as the standard line, then

$$\cos\theta = \frac{2a - b - c}{2\sqrt{\Sigma a^2 - \Sigma ab}}.$$

To simplify the problem no index higher than 2 was considered.

If we take the indices 2 1 0 $\bar{1}$ $\bar{2}$ three at a time we get 125 planes. Of these 222, 111, 000, $\bar{1}\bar{1}\bar{1}$, $\bar{2}\bar{2}\bar{2}$ are equivalent, being parallel to 111, and further the 3 planes obtained by permuting 110, and the 3 by permuting 100 are equivalent to the two sets of 3 obtained by substituting $\bar{1}$ for 1 everywhere, the two sets obtained by substituting 2 for 1, and the two sets obtained by substituting $\bar{2}$ for 1. Further, the three $1\bar{1}0$ planes are equivalent to the planes obtained by substituting 2 for 1, or $\bar{2}$ for 1. This means that there are 96 planes to be considered, but half of the number are simply obtained by changing the sign of all the indices, which give equivalent planes, so that there are 48 planes. Since there is complete trigonal symmetry about an axis perpendicular to the (111) plane, all the angles α made with a trigonal axis in the plane can be accounted for by considering $\frac{1}{3}$ of this number, *i.e.*, 16 planes. Calculation shows that the angles α, and the number of planes intersecting the (111) plane so as to make this angle, are as follows:

α	No. of planes
0	7
13·9°	2
19·1°	4
30°	3

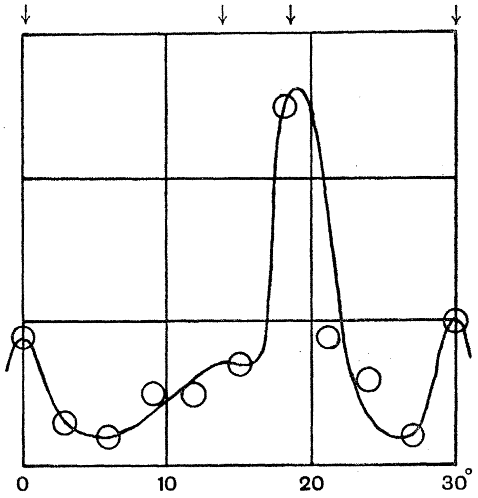


FIG. 4

The angular distribution of 85 lines of crystals on the (111) diamond surface was measured, and in fig. 4 is plotted the number of lines making an angle α with the nearest side of the equilateral triangular surface. It will be seen that there are pronounced maxima at 0, 19·1° and 30°. It is clear, then, that most of the lines of crystals correspond to the intersection of common crystallographic planes with the (111) face.

Of the planes making an angle of 19·1°, two, viz., $2\bar{1}0$ and $20\bar{1}$, are surfaces of the tetrakis hexahedron, and two, viz. $\bar{2}11$ and $21\bar{1}$, are surfaces of the icositetrahedron. The former are a family of 24 surfaces, four forming a square pyramid on each cube face, while the latter are surfaces forming a triangular pyramid on each octahedral face. It appears, then, that, in the diamond, submicroscopic cracks are likely to be established along one or both of these two families of planes.

Conclusions

The variations of colour and other properties which have been found by previous observers with films of gold and silver sputtered under apparently identical conditions are due to uncontrolled heating. By slow sputtering on a cooled surface films can be obtained which are perfectly uniform and reproducible. Films, some tens of atoms thick, which are so prepared, are amorphous to microscopic examination with the highest powers, and with various methods of illumination. They may possibly consist of crystals less than, probably much less than, 10^{-5} cm across, but the results obtained by other observers with electron diffraction cannot be applied to them with certainty, as the film may possibly be heated locally during examination by this method. Unless special precautions are taken the films are liable to contamination with mercury vapour, the nature of which contamination is described. Many of the effects produced by traces of mercury imitate those produced by heating the film.

When the films, some 50 atoms thick, are maintained at a temperature of about 230° for silver, and somewhat higher for gold, the first stage of crystallization takes place, which consists in the formation of small aggregates, which show a characteristic figure in polarized light. The phenomenon is independent of the nature of the (non-metallic) surface on which the film is supported.

The aggregates are formed by the motion of the upper layers of the film only, which therefore must move freely at a temperature some 700° C below the melting point. Prolonged heating at a temperature about 100° C above that of the first appearance of the approximated spherical aggregates leads to rapid growth, the particles developing into crystals with a well-defined outline, characteristic of the cubic lattice. The crystals so formed are all arranged with the (111) face parallel to the supporting surface ; growth normal to the (111) surface proceeds with difficulty. An explanation of this behaviour is given.

The growth of the crystals is accompanied by the formation of large, irregular, more transparent areas, from which the metal has retreated, leaving the surface not bare, but covered by a much thinner film. Raising the temperature leads to a crystallization in the regions of thinner film. It has been shown directly that it requires a much higher temperature to initiate crystallization in a film only a few atoms thick than in one a few tens of atoms thick. The upper layers of a thick film are more mobile than is a thin film on a rigid substrate. Heating silver films to 600° C leads to the formation of perfect cubic crystals on a background of very thin film.

Particles of gold formed very slowly by reduction of solutions of gold salts have been studied, as have also the small particles produced by the action of mercury vapour on gold and silver films.

Reasons are suggested for the optical figure shown by the aggregates found in the first stage of crystallization, and the relation of previous results, including those on the electrical resistance of metallic films, to the findings of this paper is discussed.

Arrangements of minute crystals in lines are observed when films on glass and quartz glass surfaces, but not on cleavage faces of mica, are heated. The same pattern of lines forms at a particular place, however rigorously the surface is cleansed between successive depositions and heatings of a metal film. The lines are attributed to submicroscopic surface cracks, of the type postulated to account for the weakness of the solid state. This attribution is strongly supported by results obtained with the two types of diamond recently discussed by ROBERTSON, FOX, and MARTIN. With one type no lines of crystallites are formed, while, with the other, lines of crystallites are formed, which fall mainly along the intersection of certain common crystallographic planes with the surface, although no surface cracks can, in general, be detected by microscopic examination.

We have much pleasure in expressing out thanks to Dr. R. E. GIBBS for much helpful discussion. We have had the advantage of a talk with Sir HERBERT JACKSON and Dr. HARRY MOORE on microscopic matters. Much of the optical apparatus was purchased from a grant made to one of us by the I.C.I. The other of us was in receipt of a grant from the D.S.I.R. while most of this work was being carried out. This help is gratefully acknowledged.

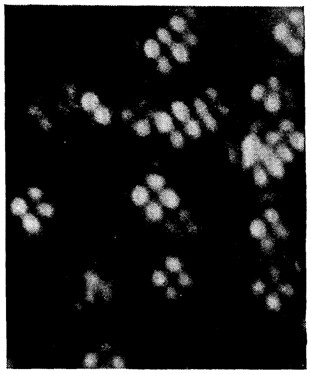


FIG. 5*a*. × 6000

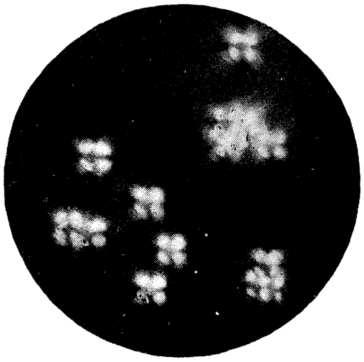


FIG. 5*b*. × 1200

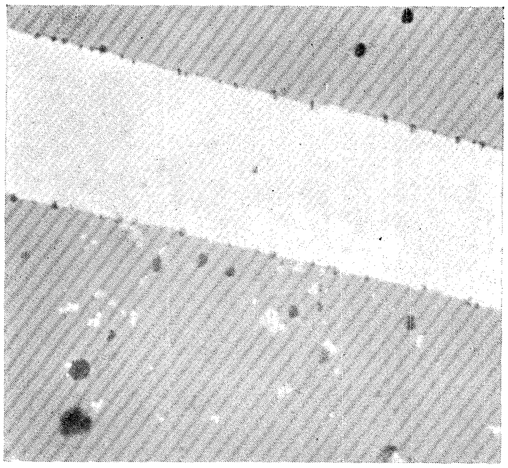


FIG. 6*a*. × 1000

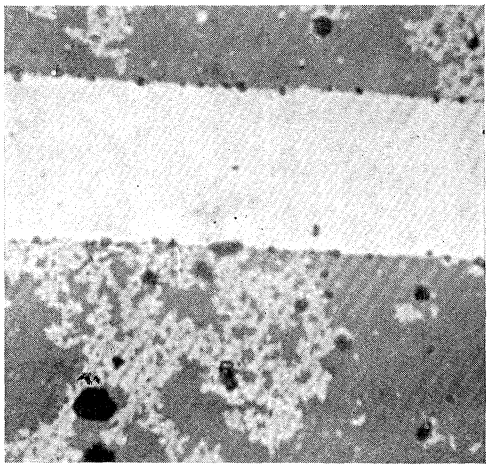


FIG. 6*c*. × 1000

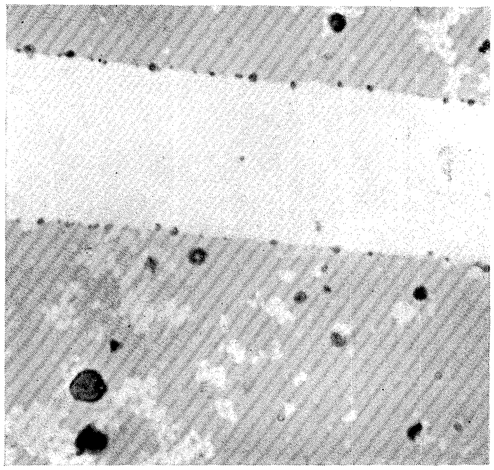


FIG. 6*b*. × 1000

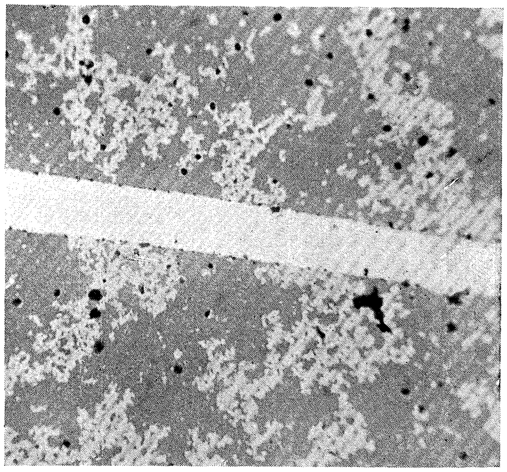
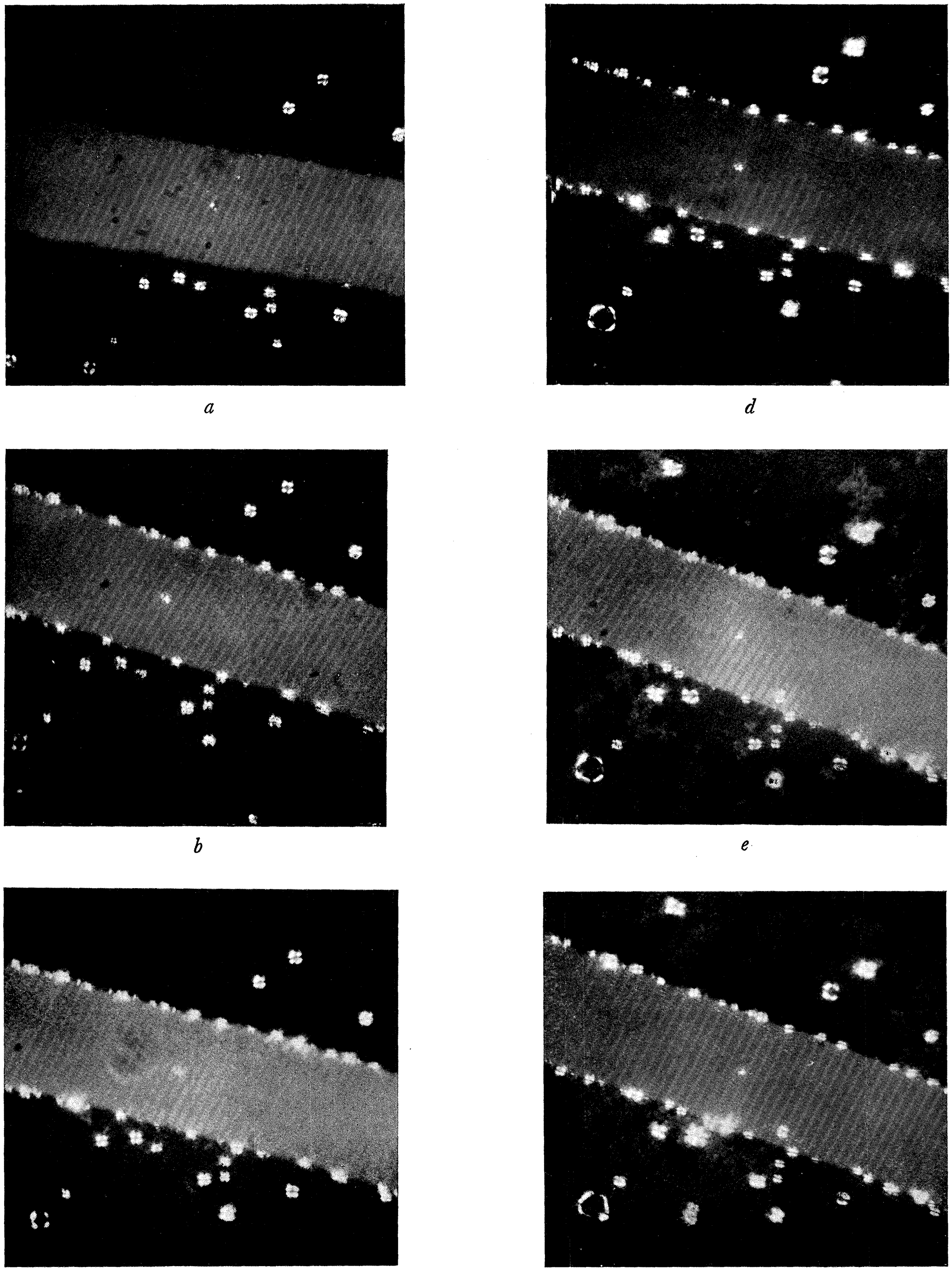


FIG. 6*d*. × 320



a *d*

b *e*

c *f*

Fig. 7

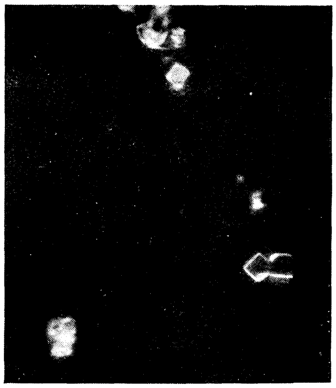


FIG. 8. × 1000

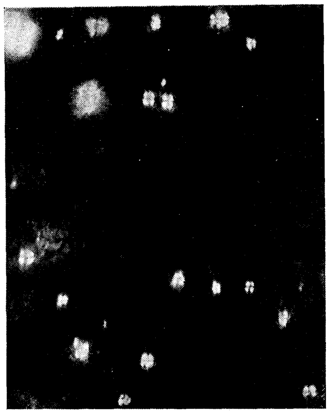


FIG. 9. × 2000

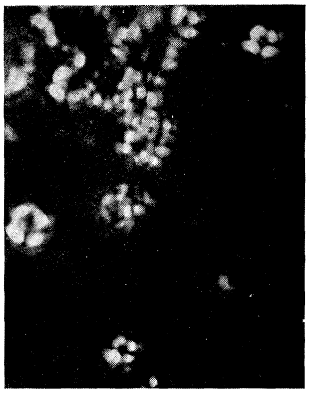


FIG. 10. × 2700

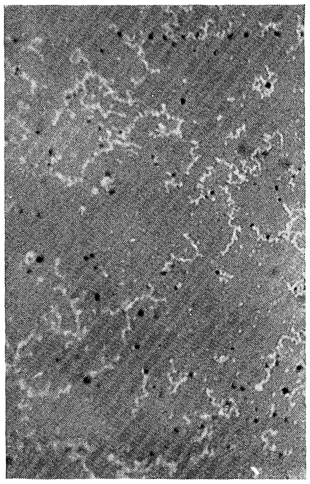


FIG. 11. × 320

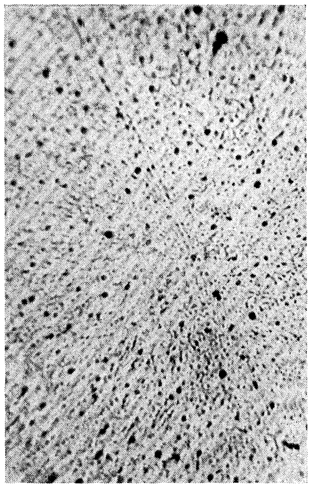


FIG. 12 × 720

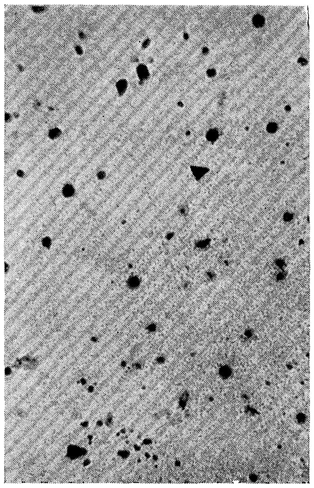


FIG. 13. × 720

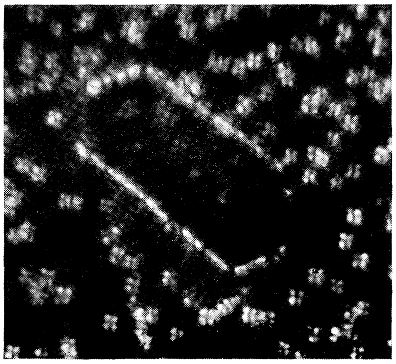
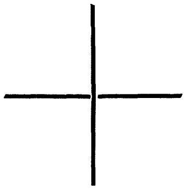


FIG. 14. × 2000



Planes of Nicols

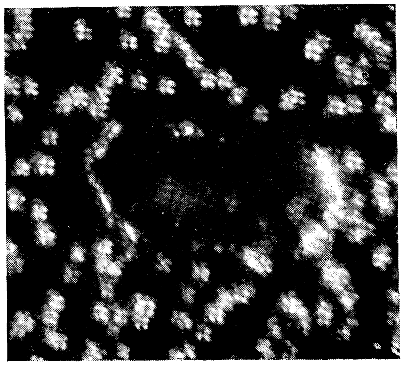


FIG. 15. × 2000

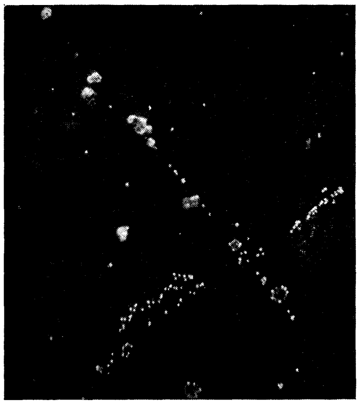


FIG. 16

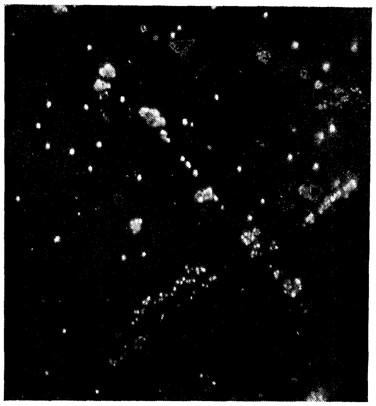


FIG. 17

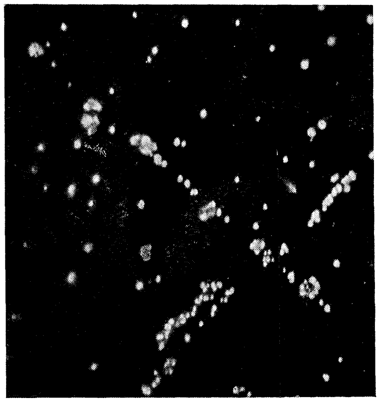


FIG. 18

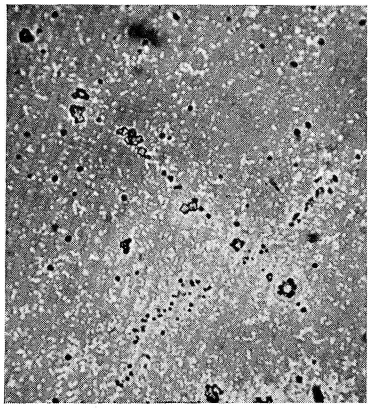


FIG. 19

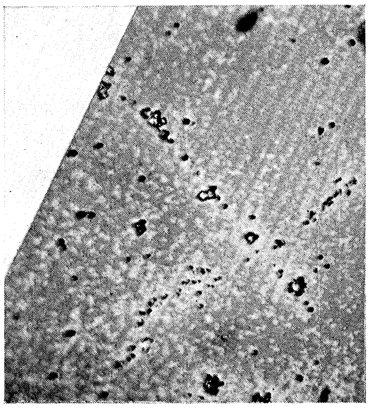


FIG. 20

FIG. 21

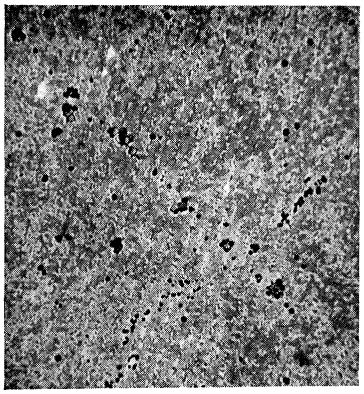


FIG. 22

FIG. 23

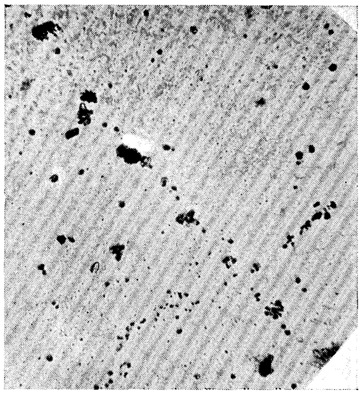


FIG 24

× 320

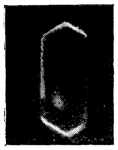


Fig. 25.
× 1000

Fig. 26.
× 1000

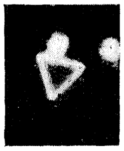


Fig. 27.
× 1000

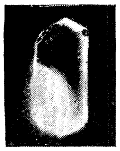


Fig. 28.
× 1000

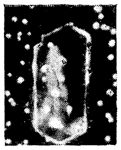


Fig. 29.
× 1000

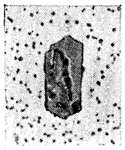
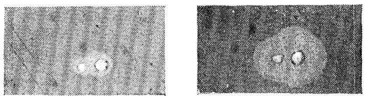
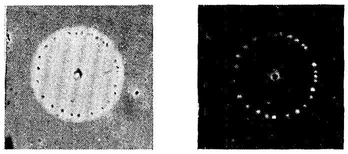


Fig. 30.
× 720



a *b*

Fig. 31. × 320



a *b*

Fig. 32. × 320

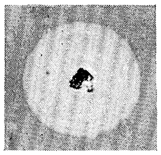


Fig. 33. × 320

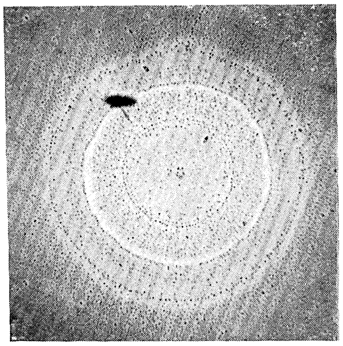


Fig. 34. × 320

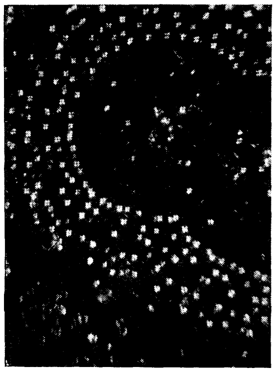


Fig. 35. × 720

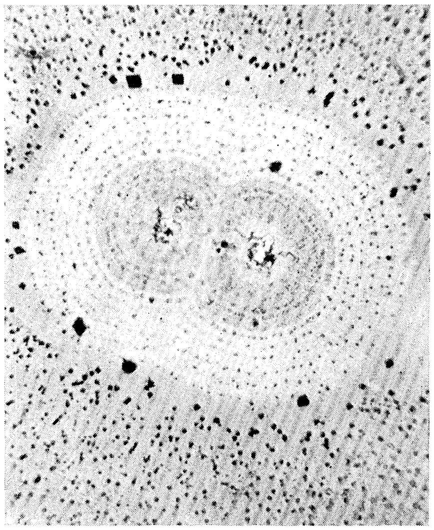


Fig. 36. × 720

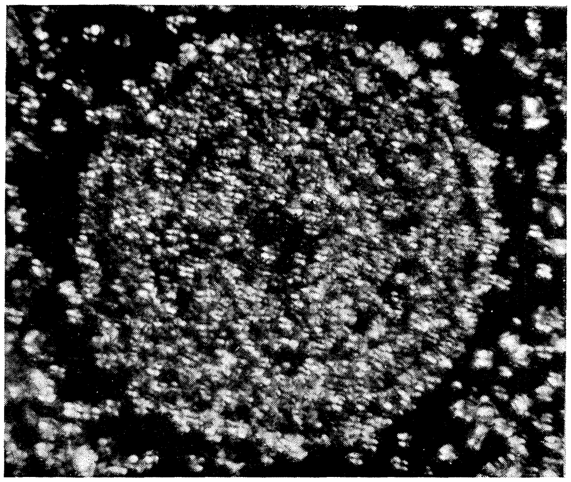


Fig. 37. × 2000

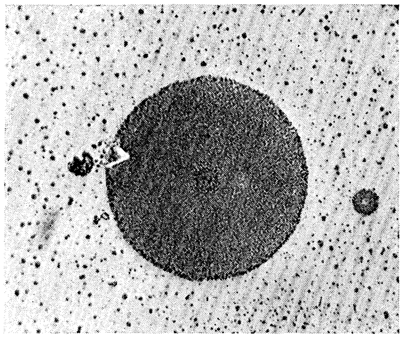


Fig. 38. × 320

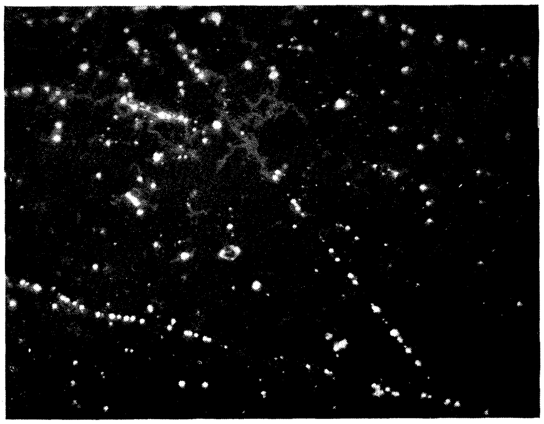


Fig. 39. × 320

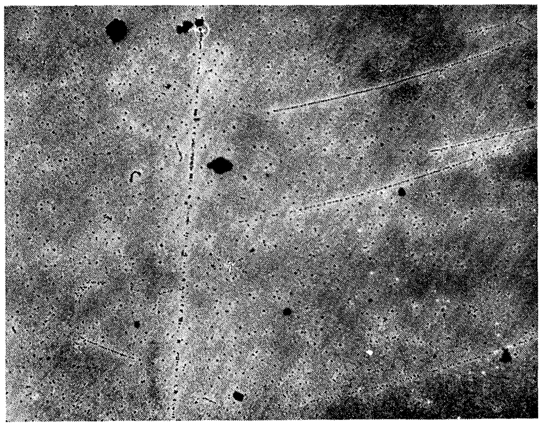


Fig. 40. × 320

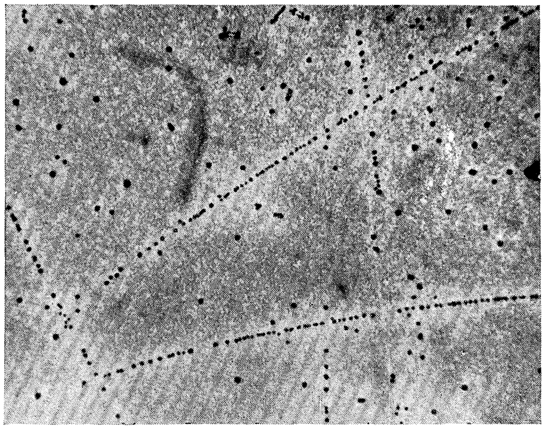


Fig. 41. × 320

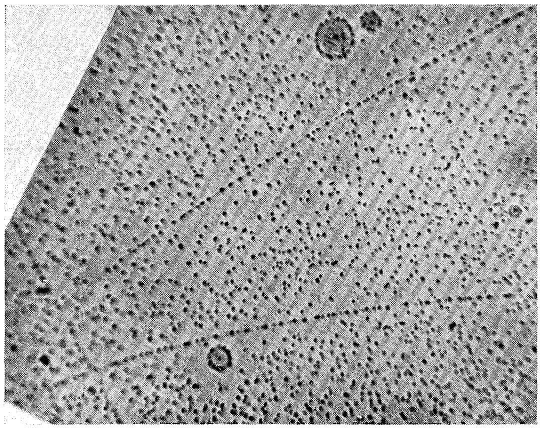


Fig. 42. × 320

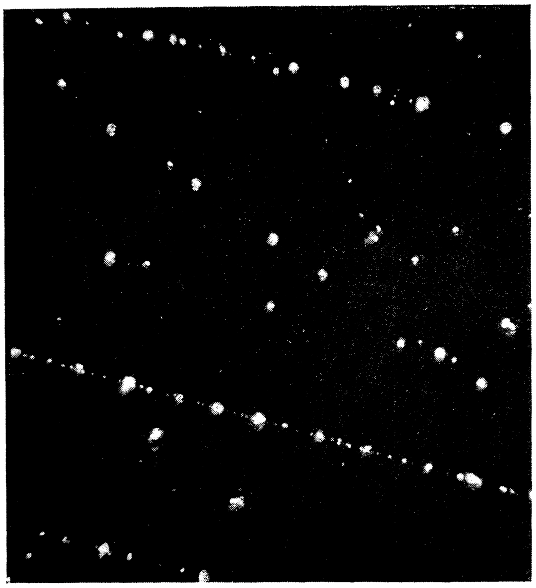


Fig. 43. × 1000

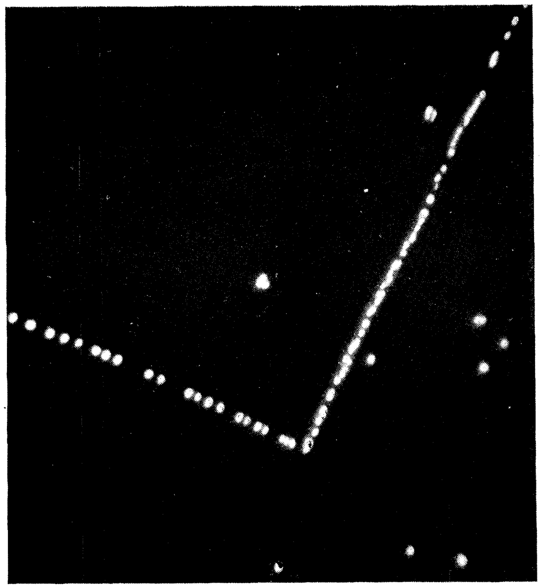


Fig. 44

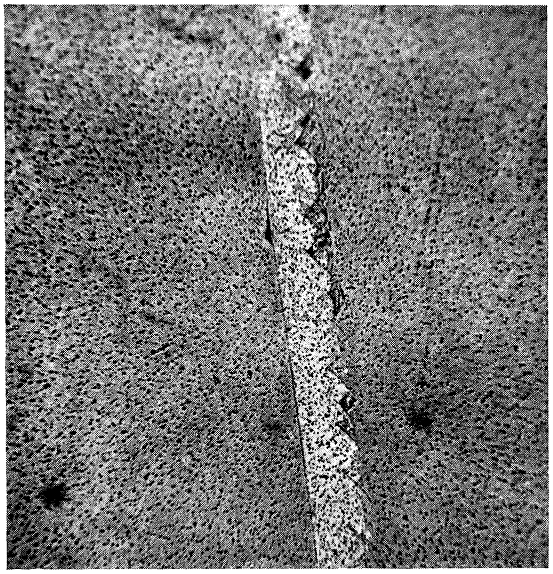


Fig. 45. × 320

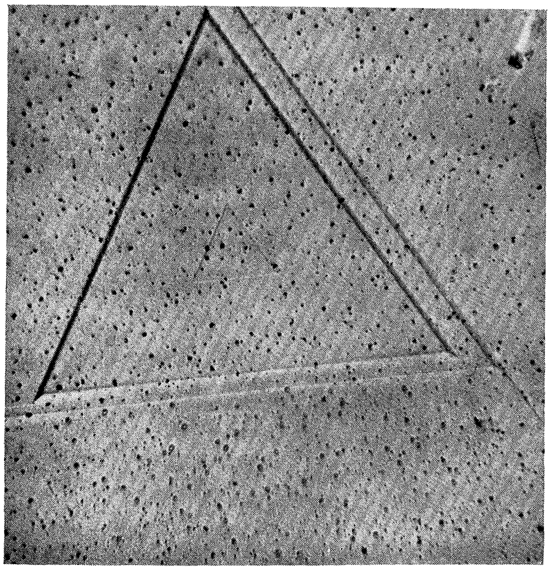


Fig. 46. × 320

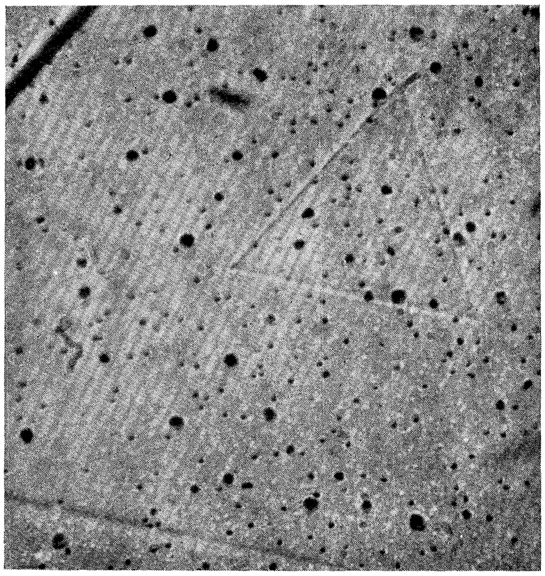


Fig. 47. × 1000

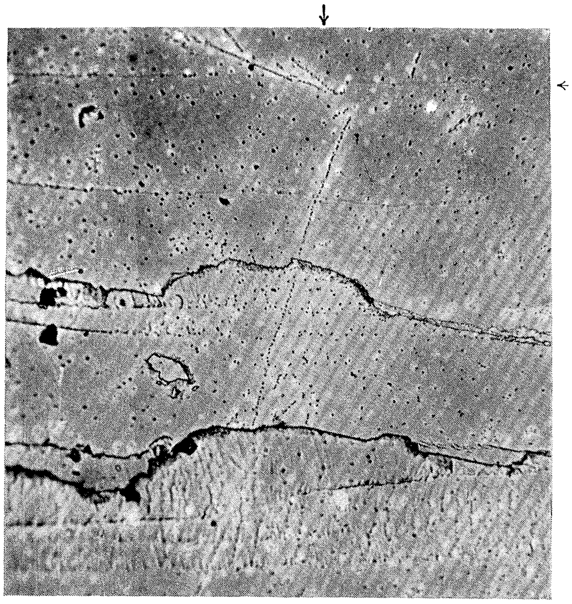


Fig. 48. × 320

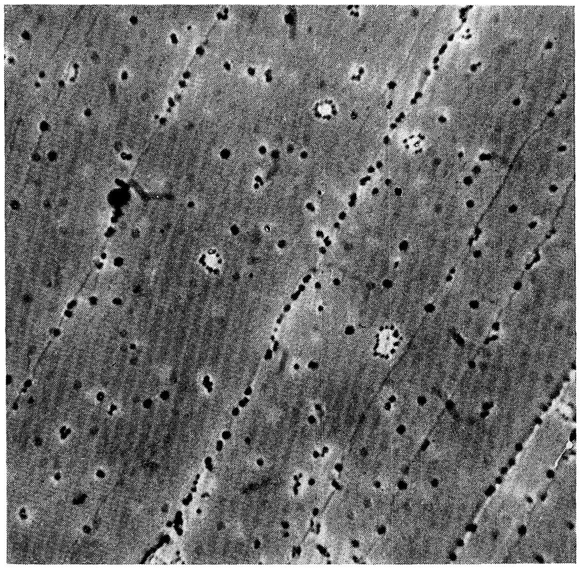


FIG. 49. × 1000

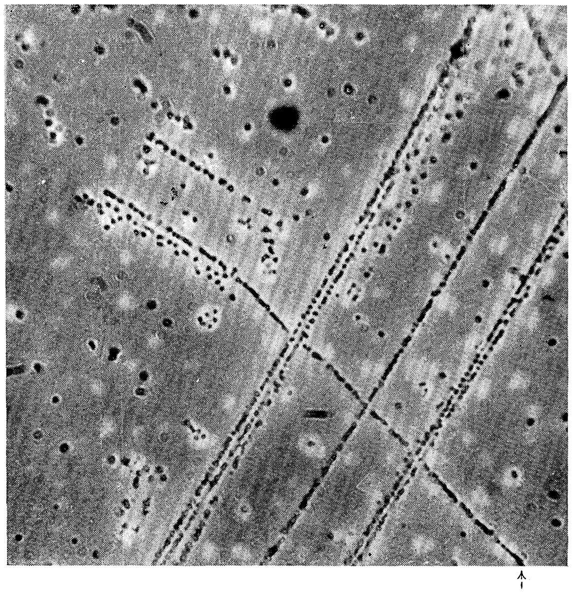


FIG. 50. × 1000

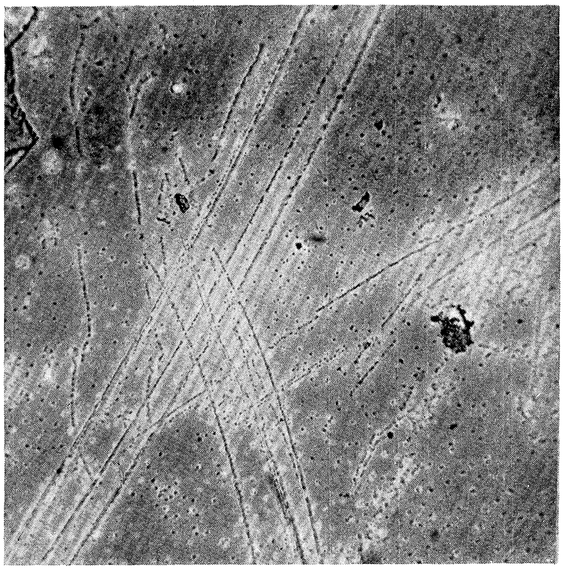


FIG. 51. × 320

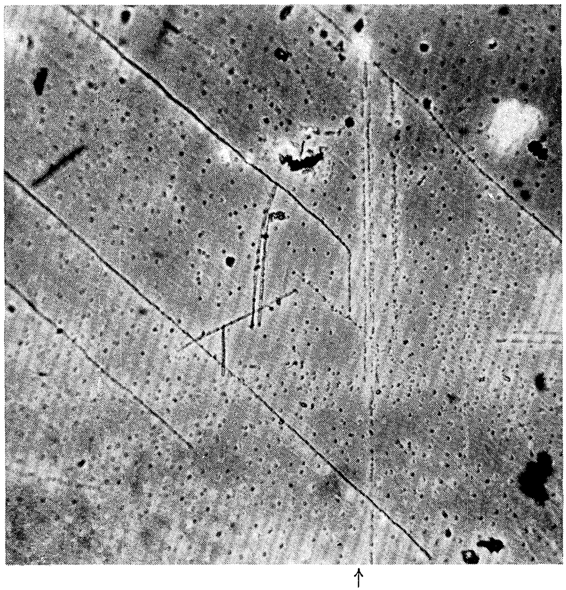


FIG. 52. × 320

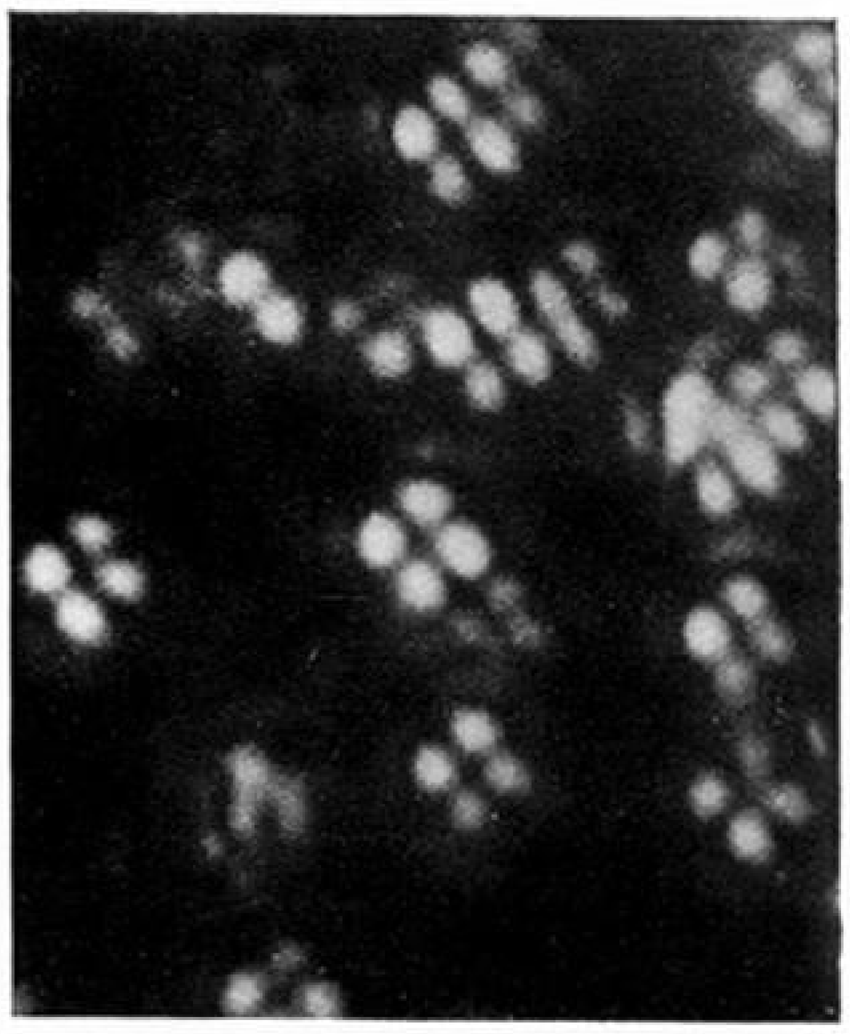


FIG. 5*a*. × 6000

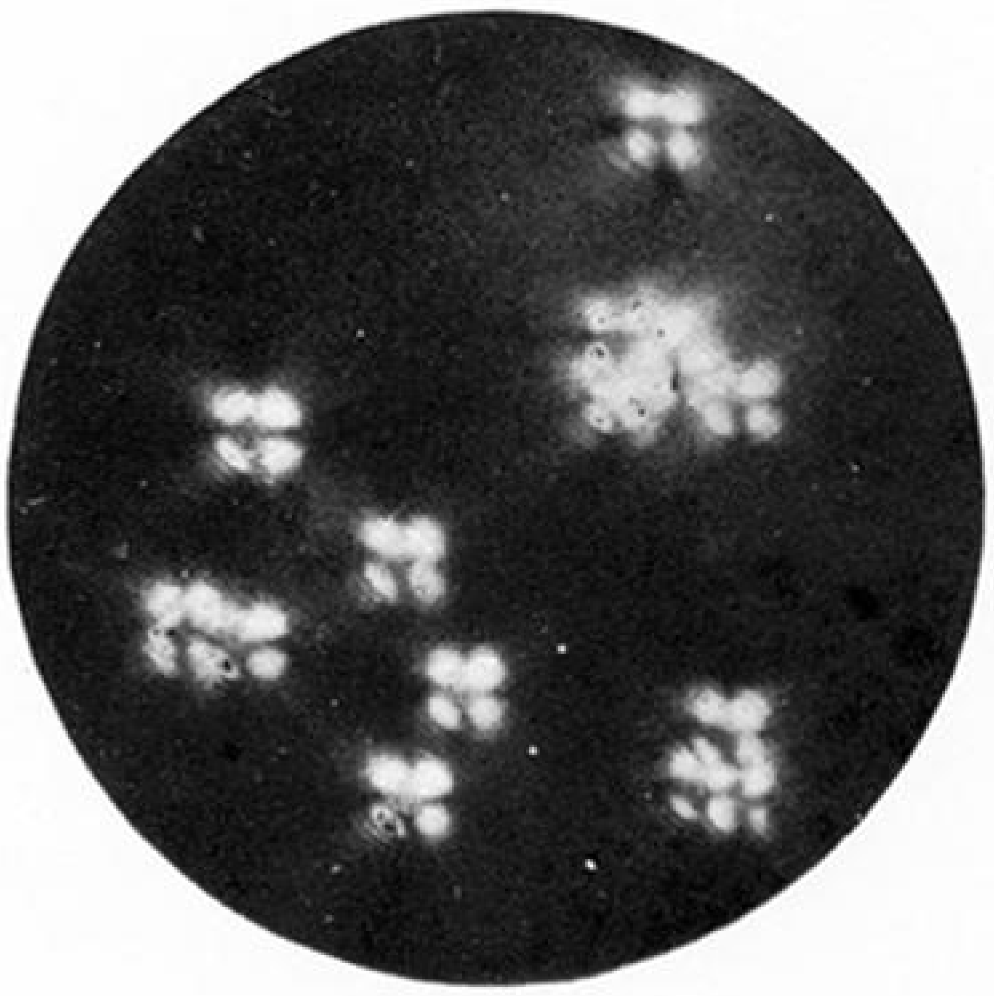


FIG. 5*b*. × 1200

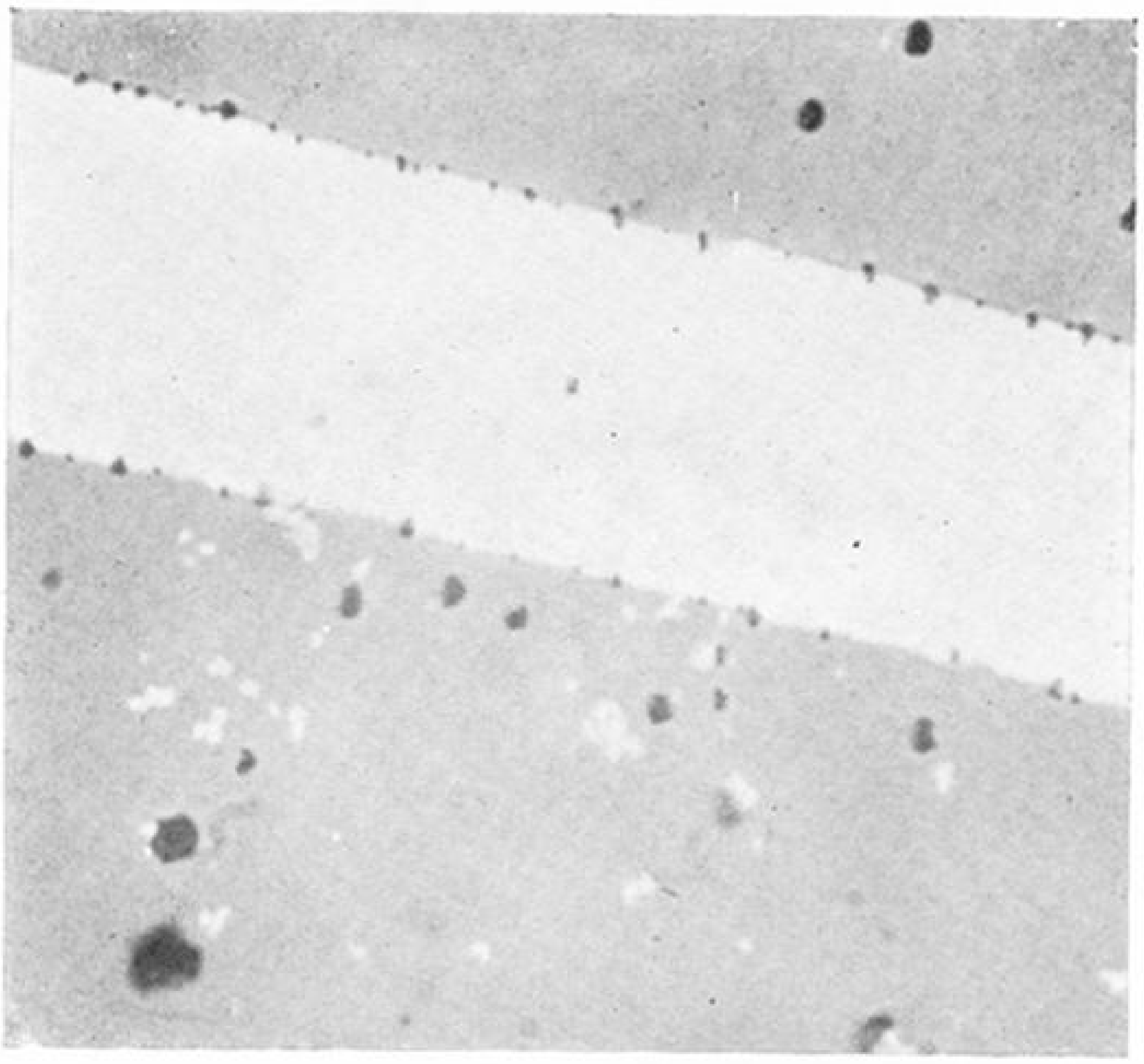


FIG. 6*a*. × 1000

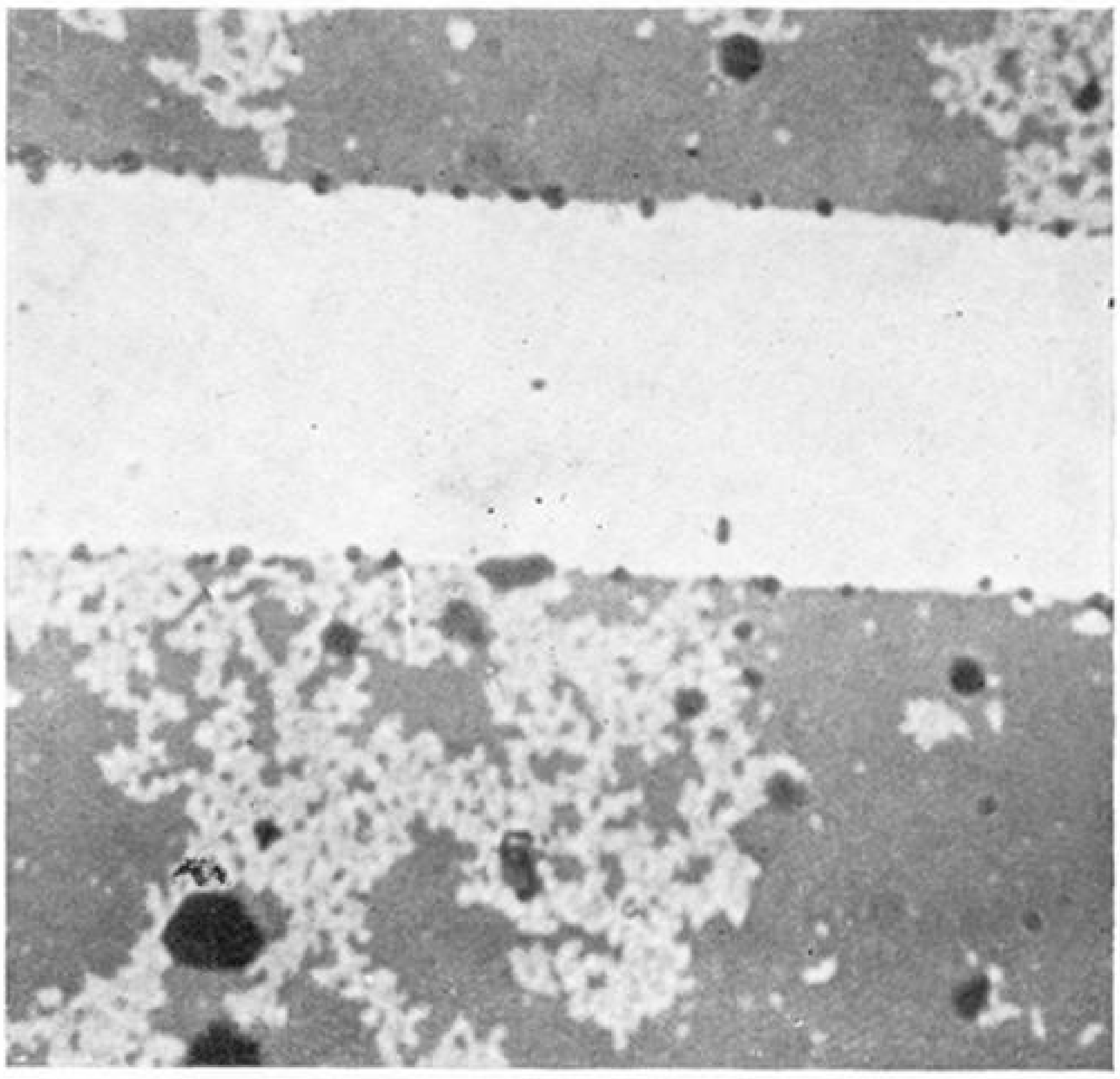


FIG. 6*c*. × 1000

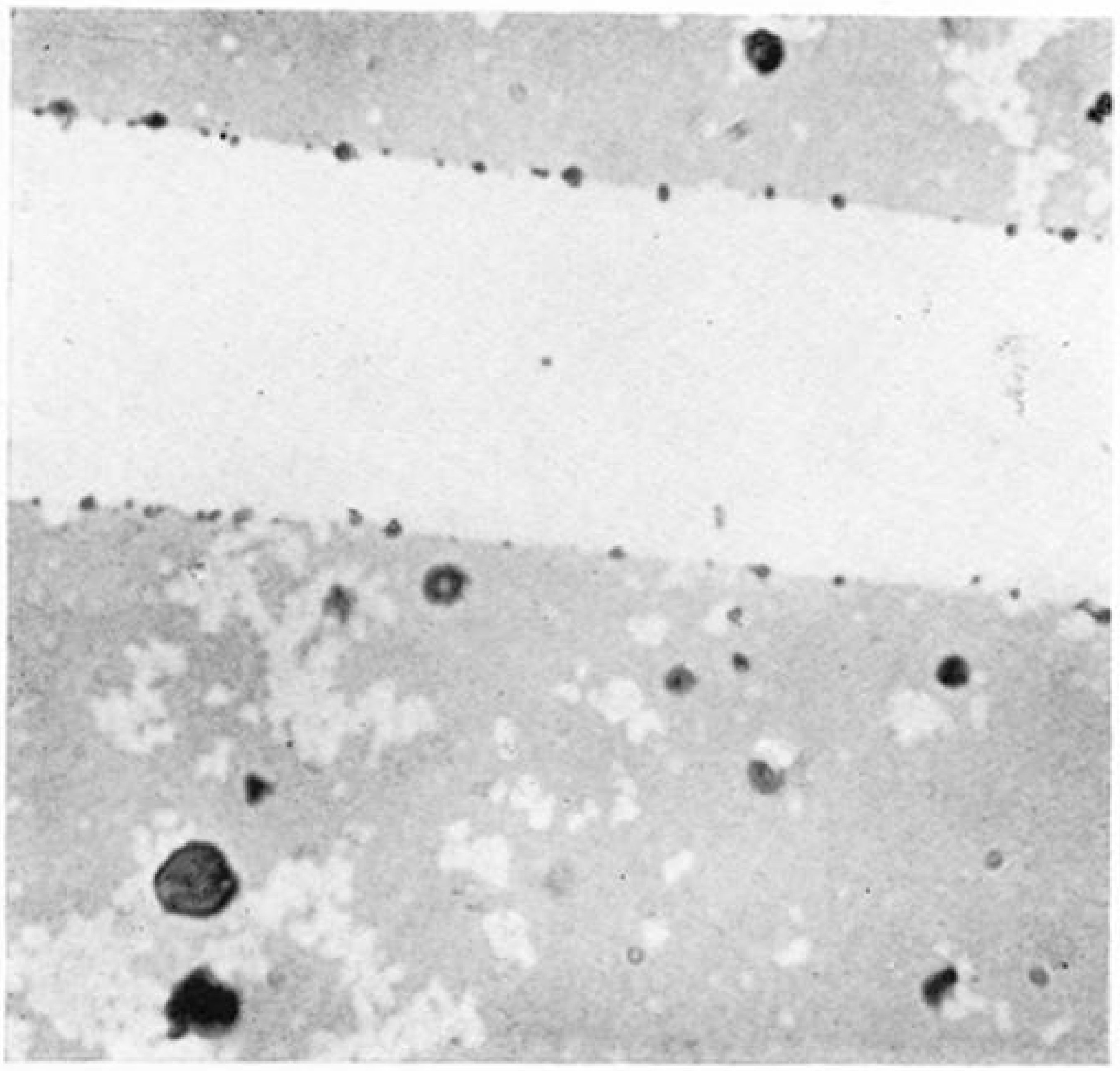


FIG. 6*b*. × 1000

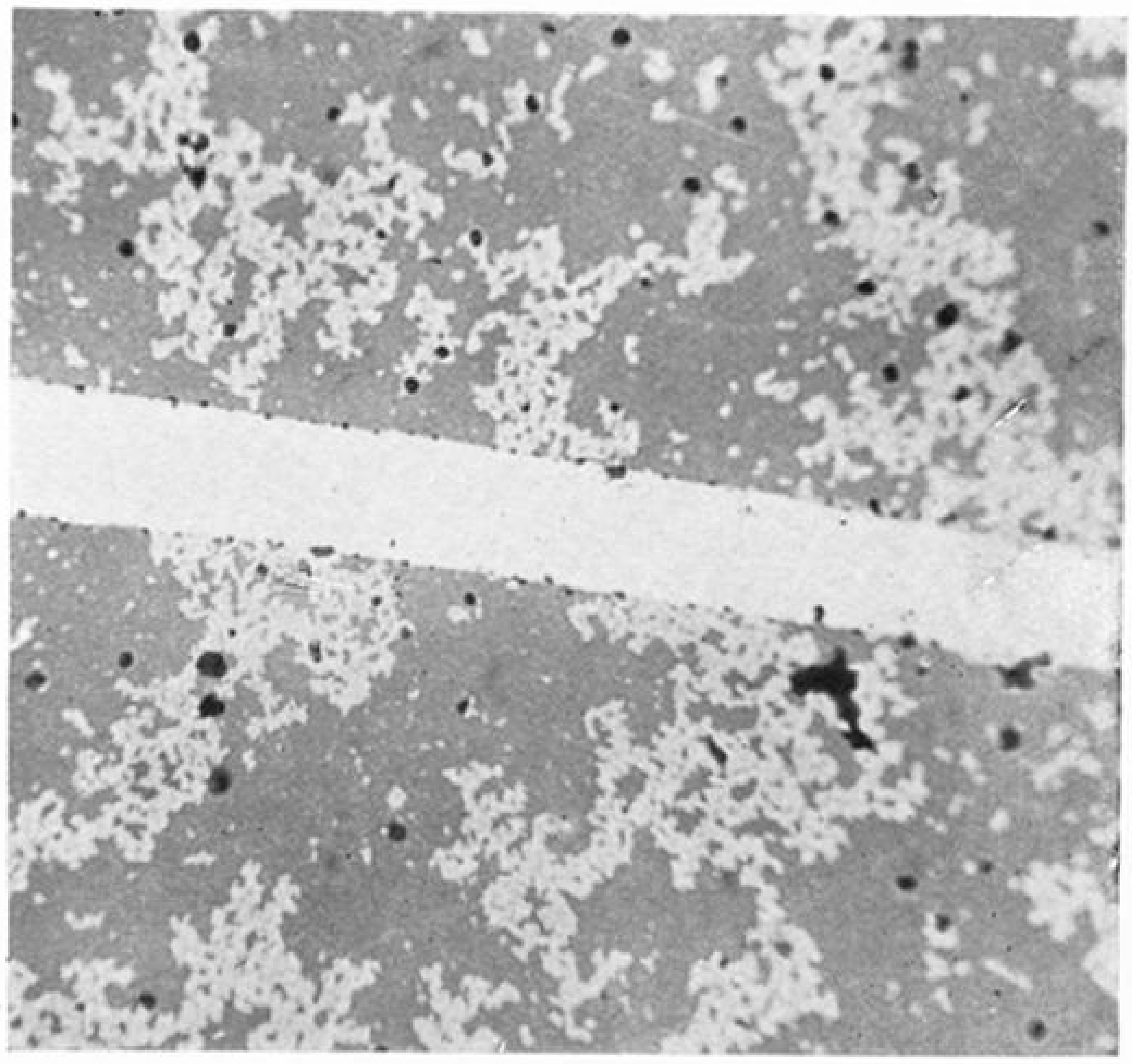


FIG. 6*d*. × 320

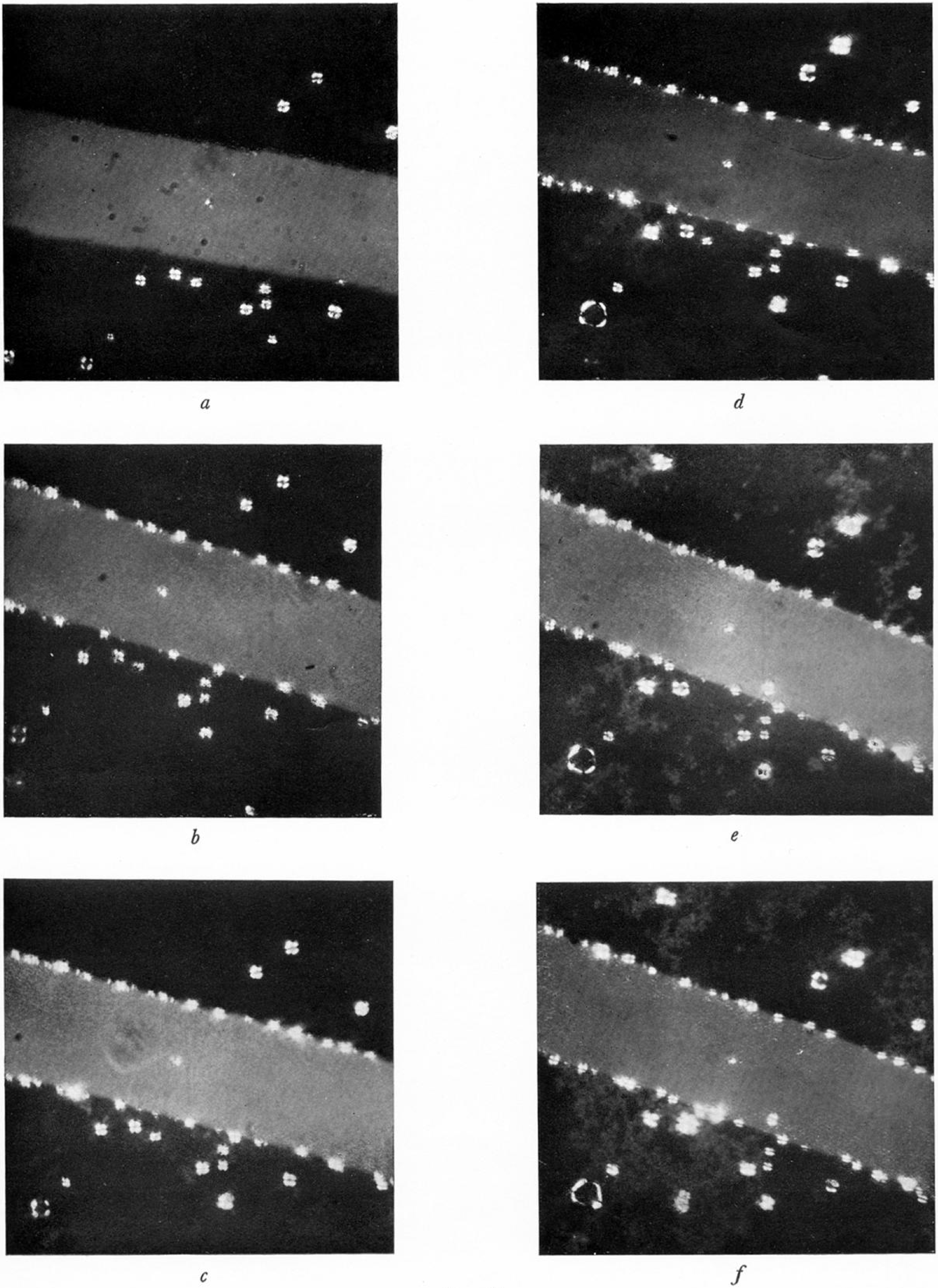

a d b e c f

FIG. 7

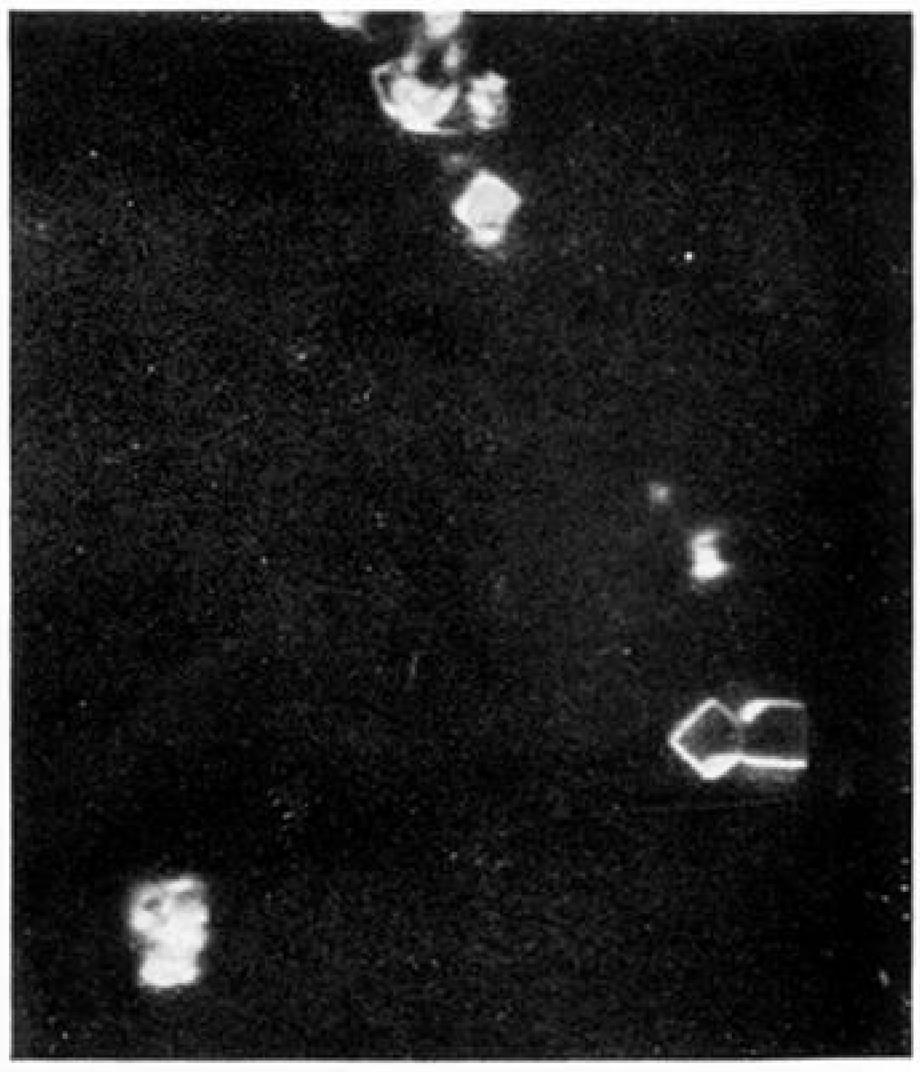


Fig. 8. × 1000

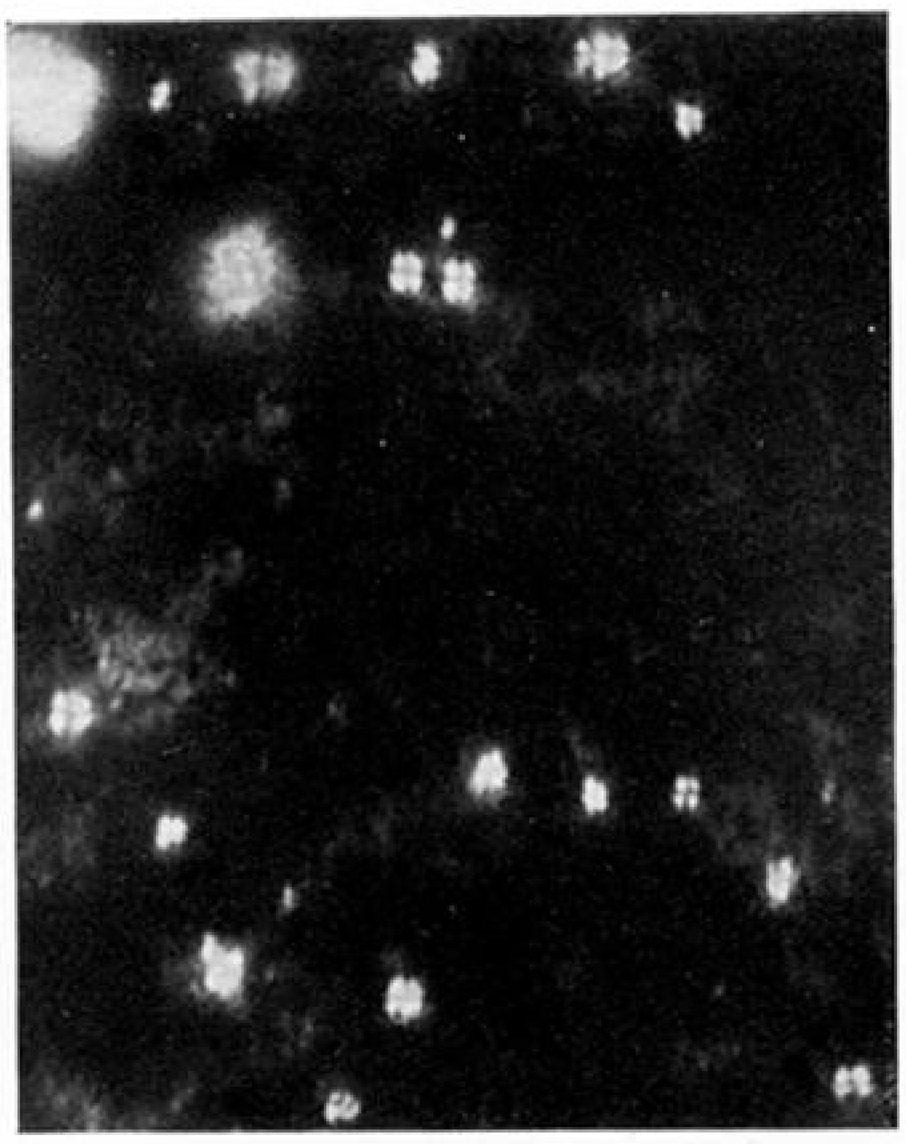


Fig. 9. × 2000

Fig. 10. × 2700

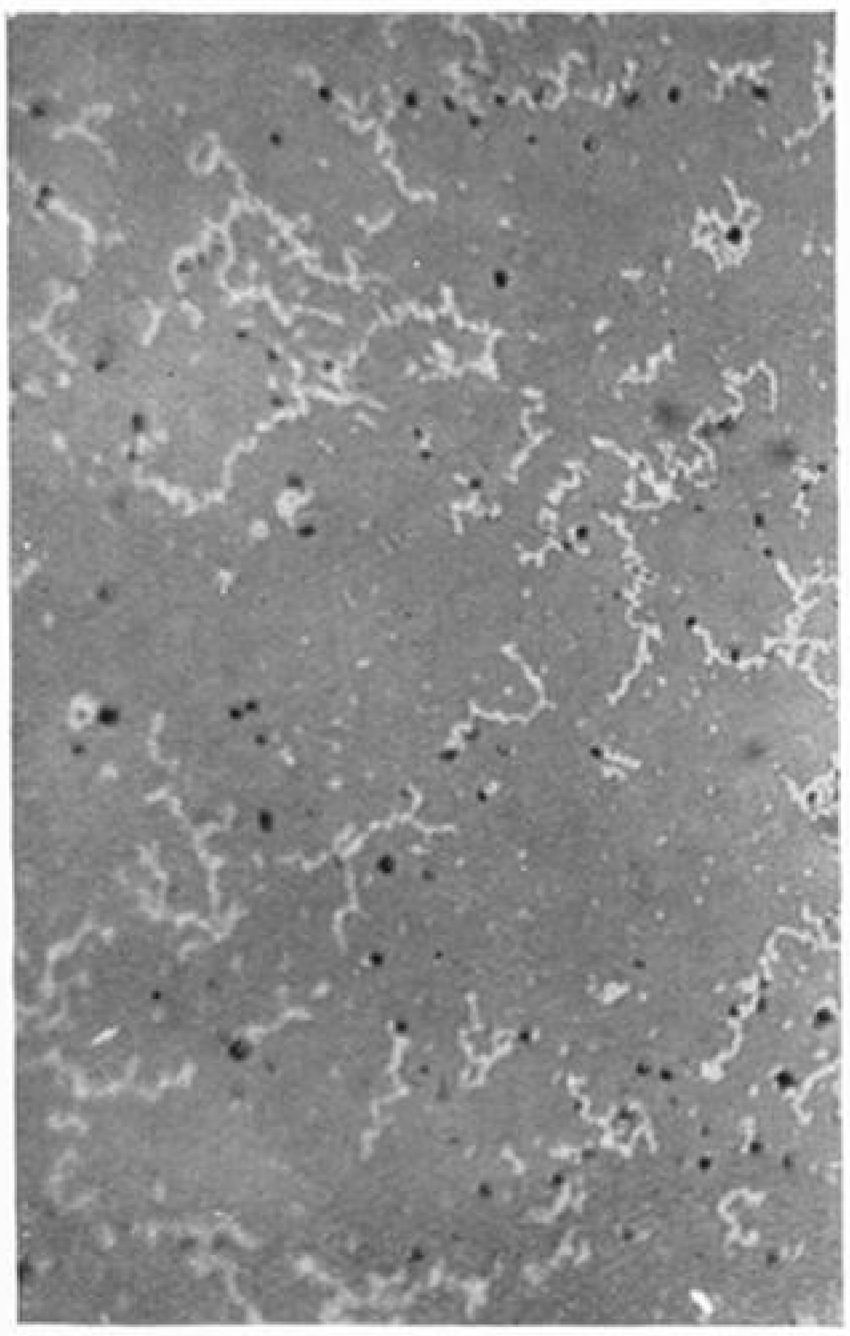


Fig. 11. × 320

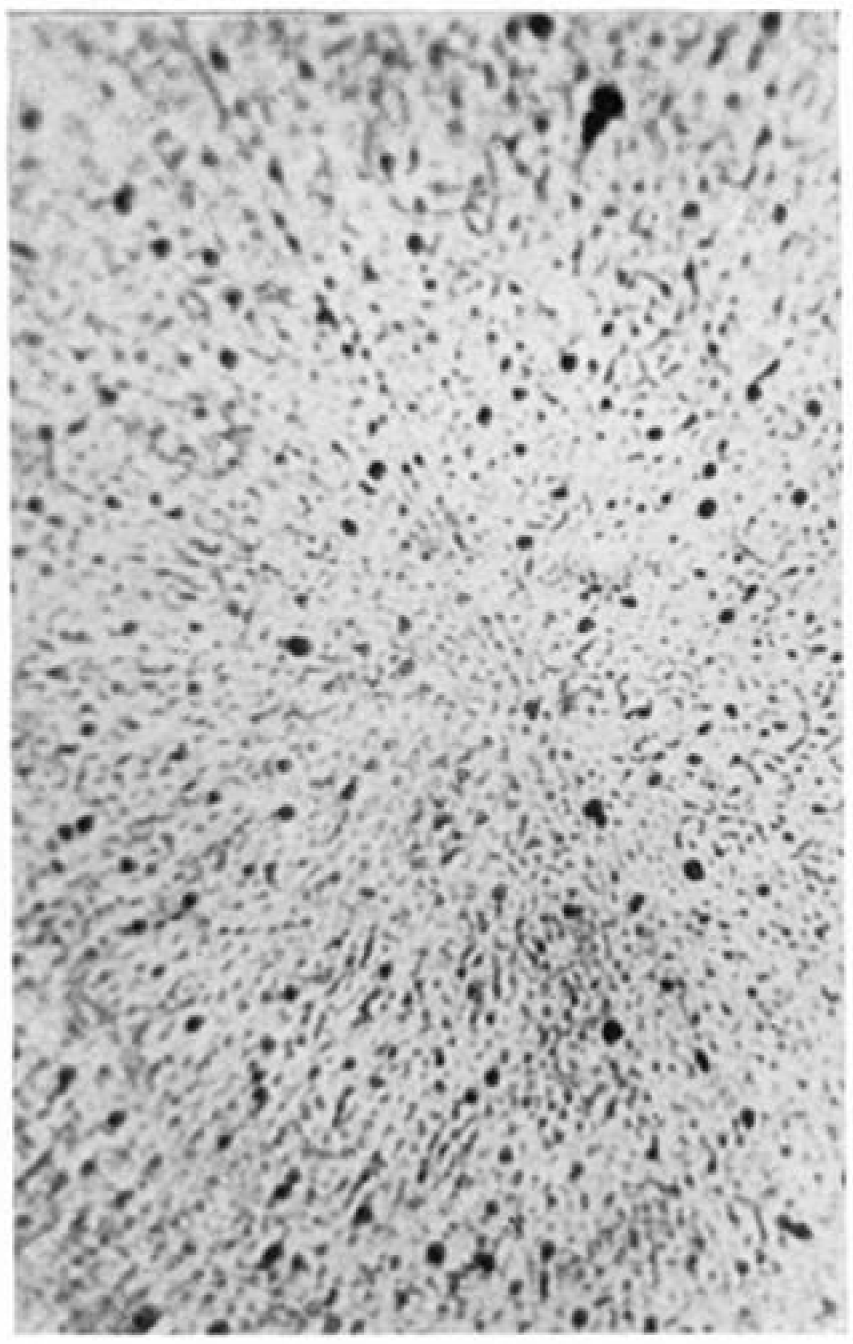


Fig. 12 × 720

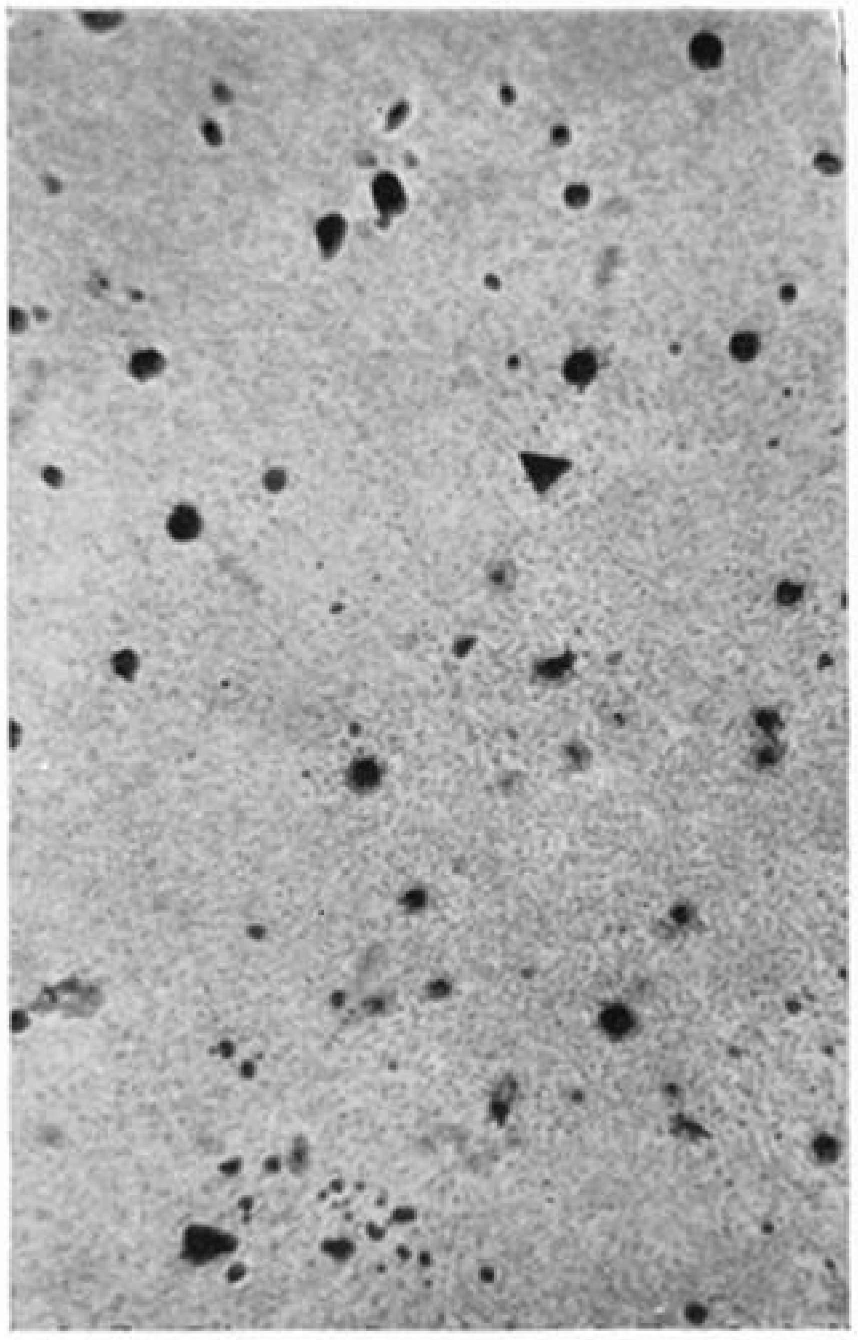


Fig. 13. × 720

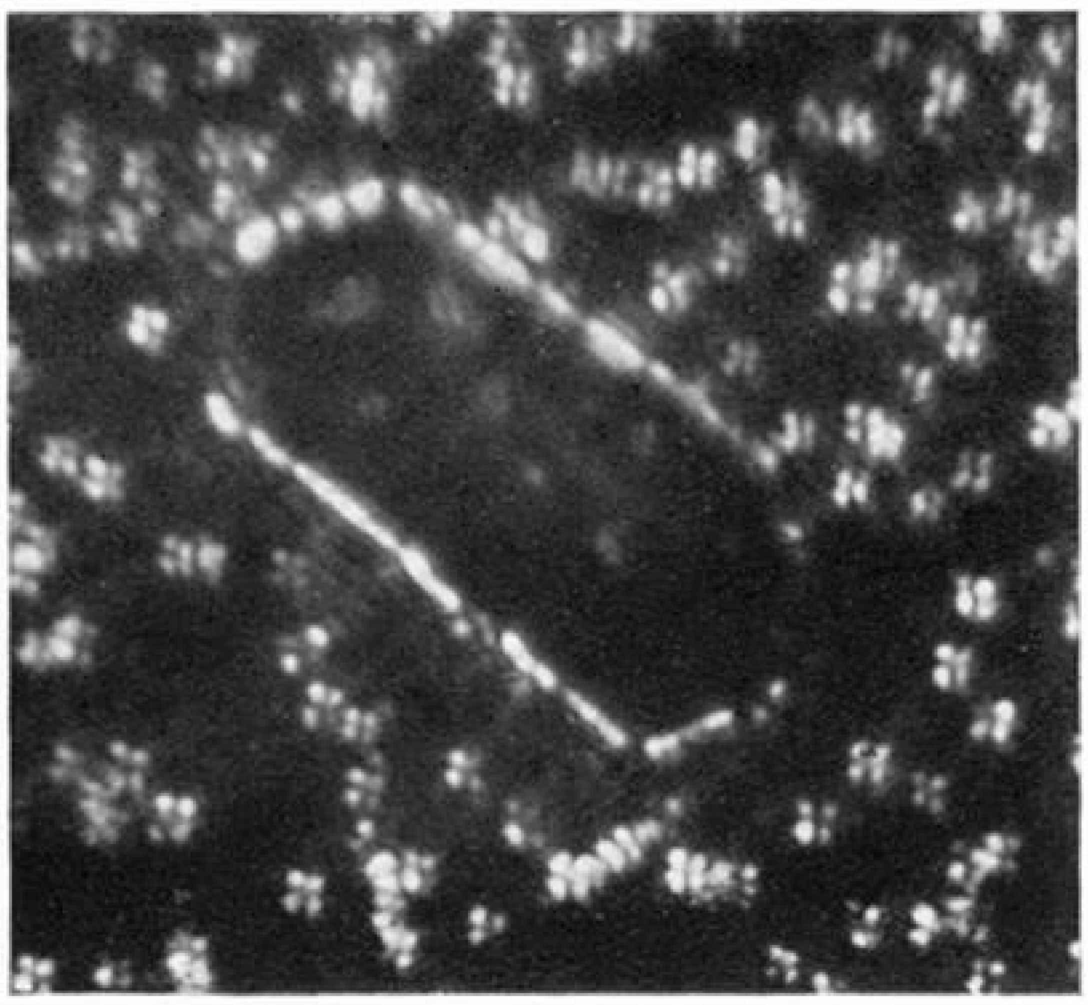


Fig. 14. × 2000

Planes of Nicols

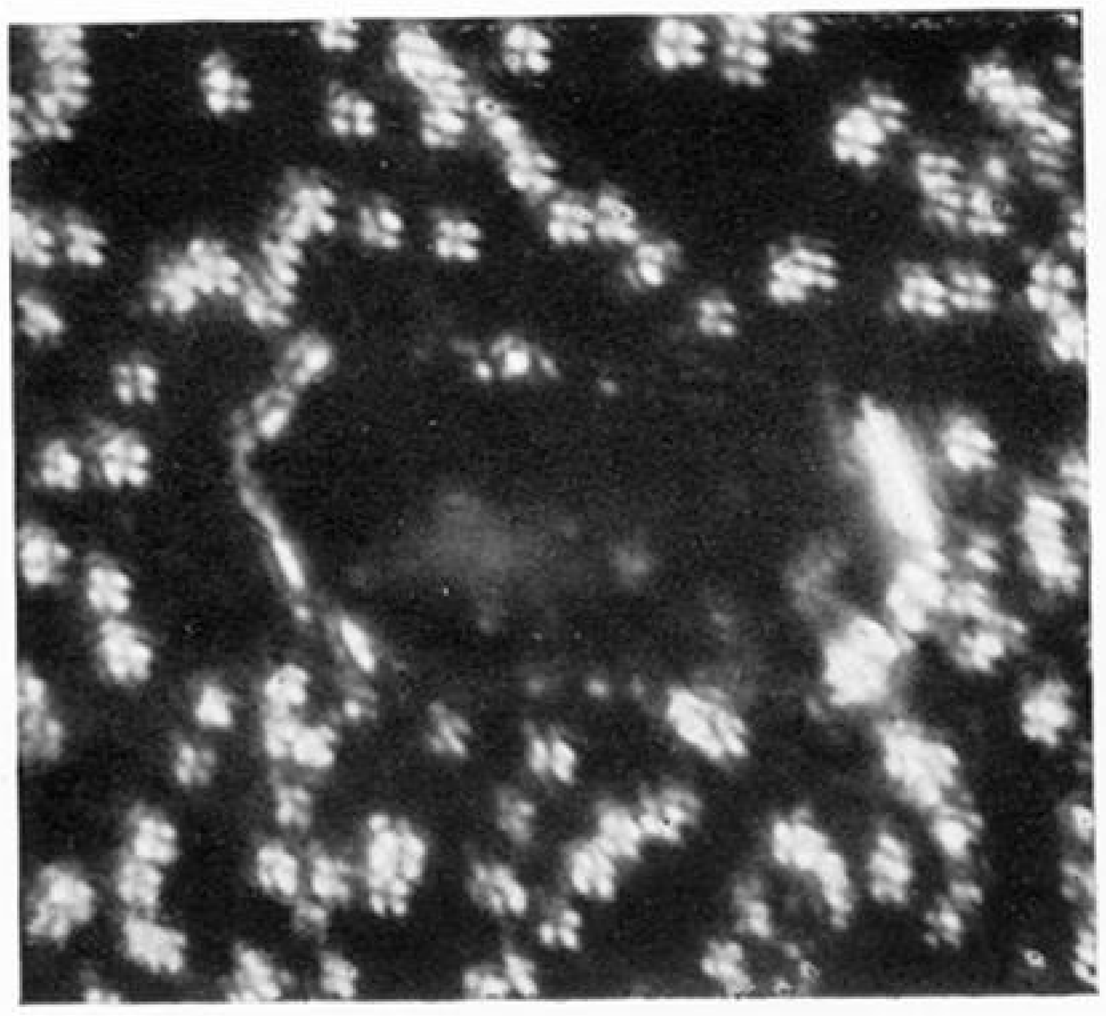


Fig. 15. × 2000

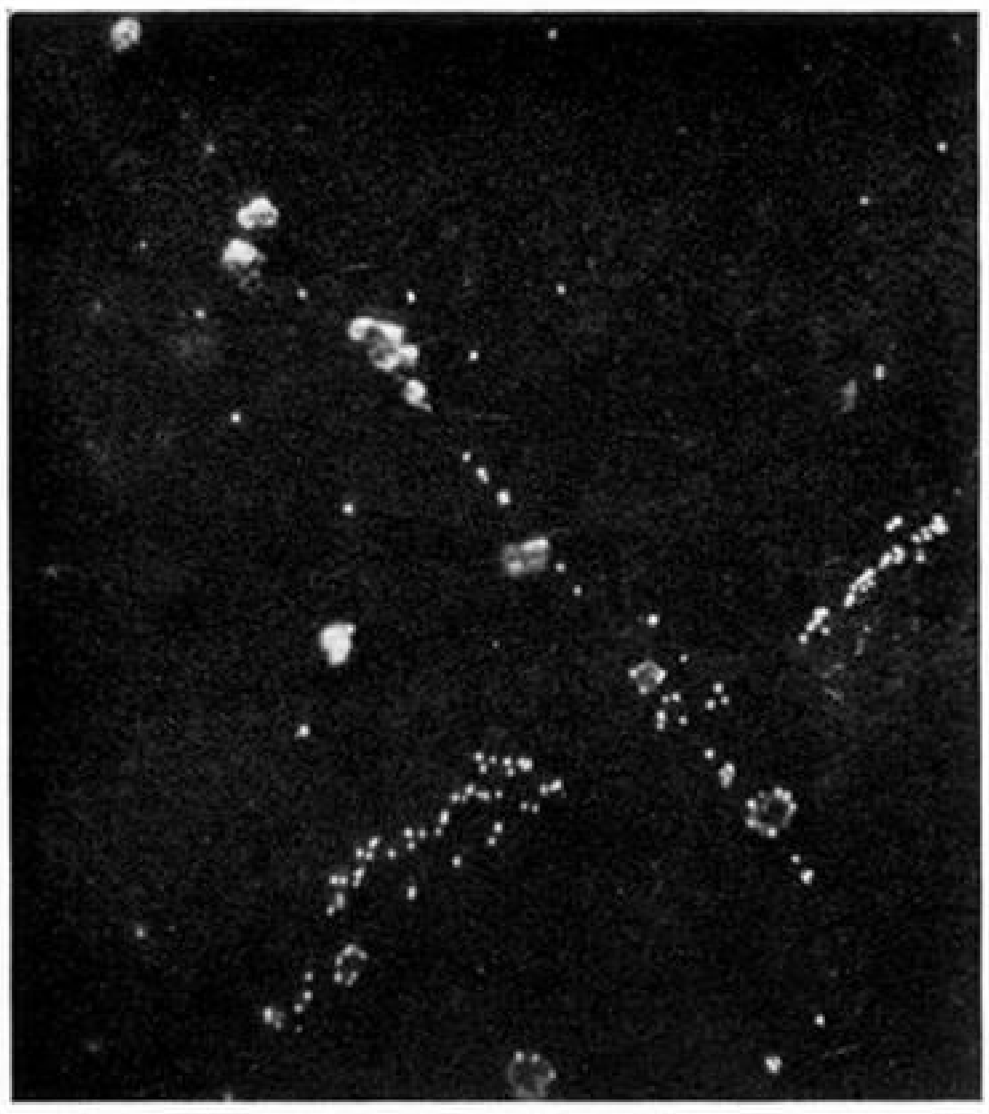


FIG. 16

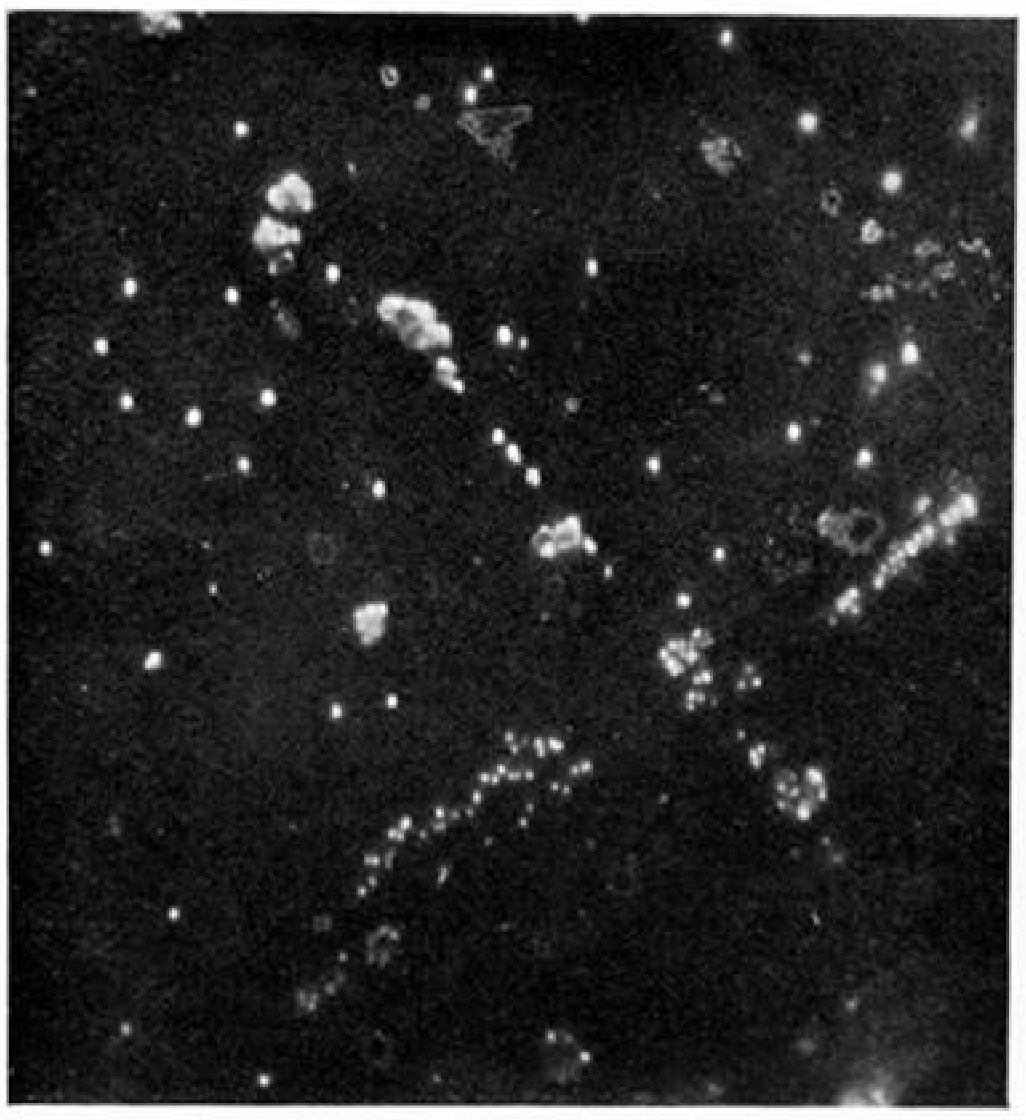


FIG. 17

FIG. 18

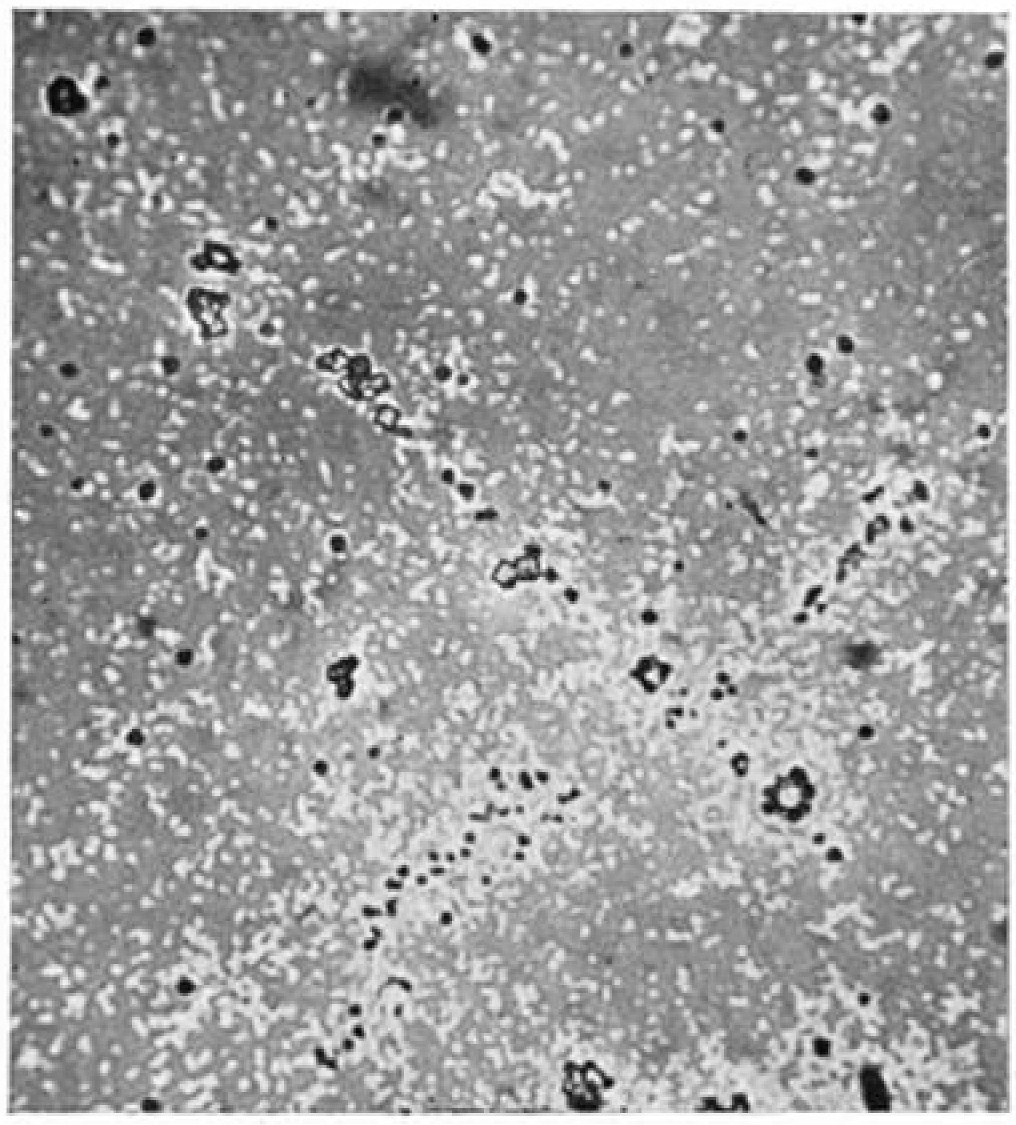


FIG. 19

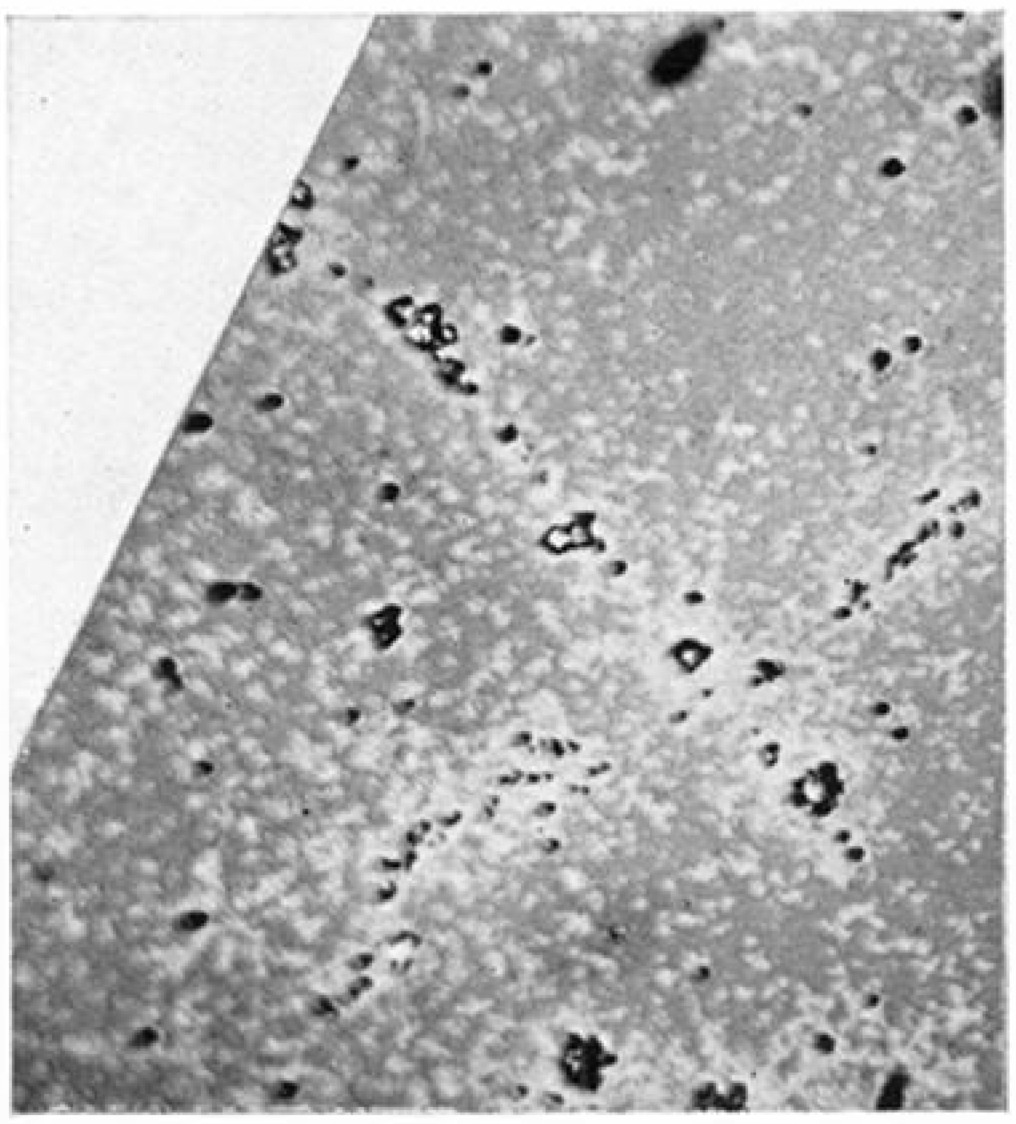


FIG. 20

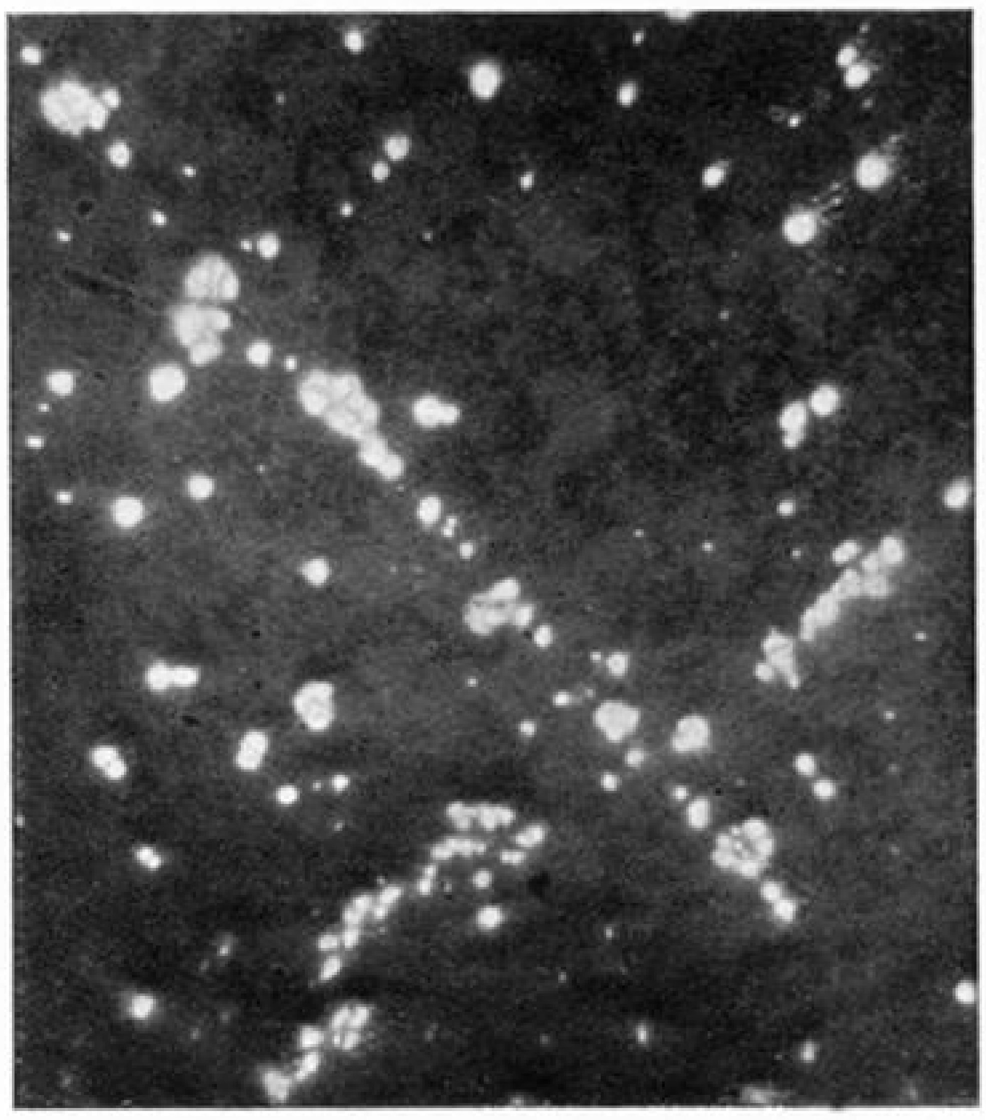


FIG. 21

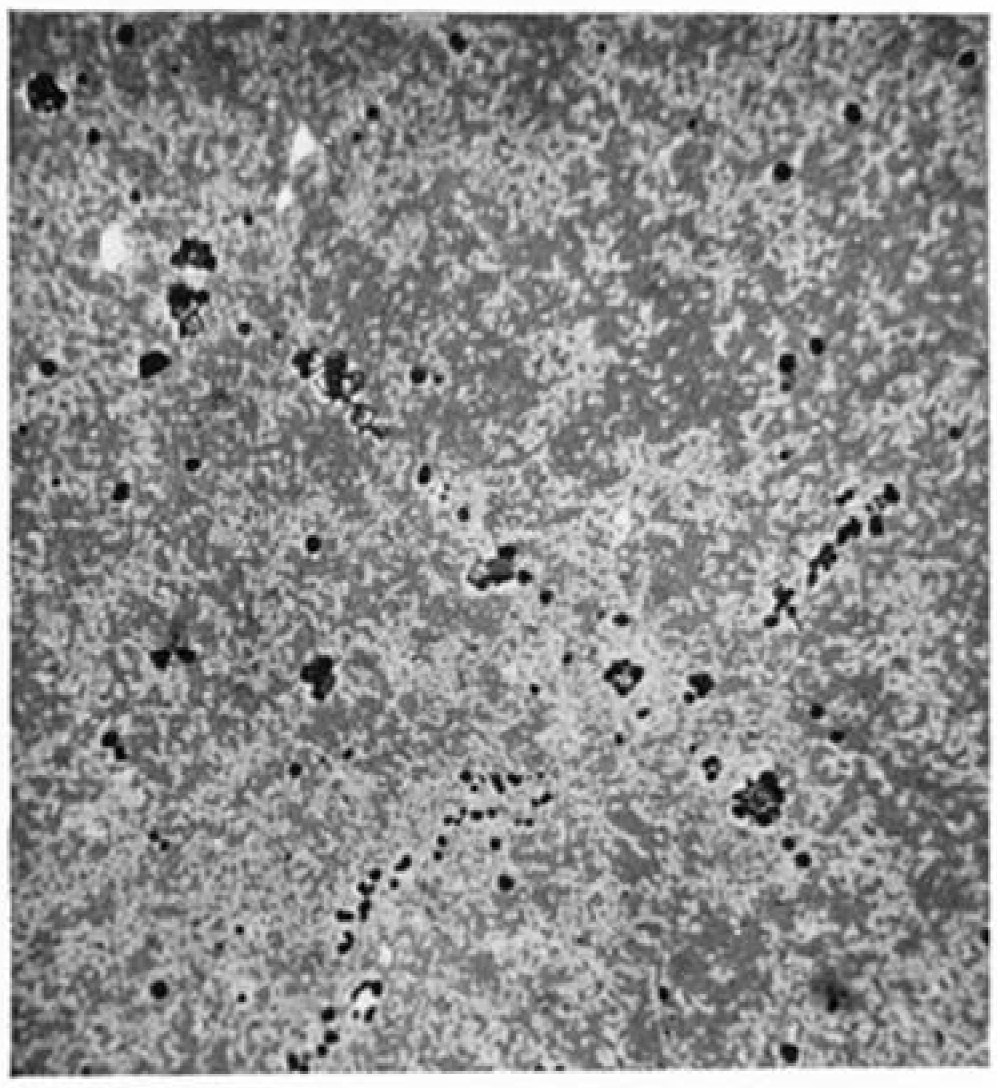


FIG. 22

FIG. 23

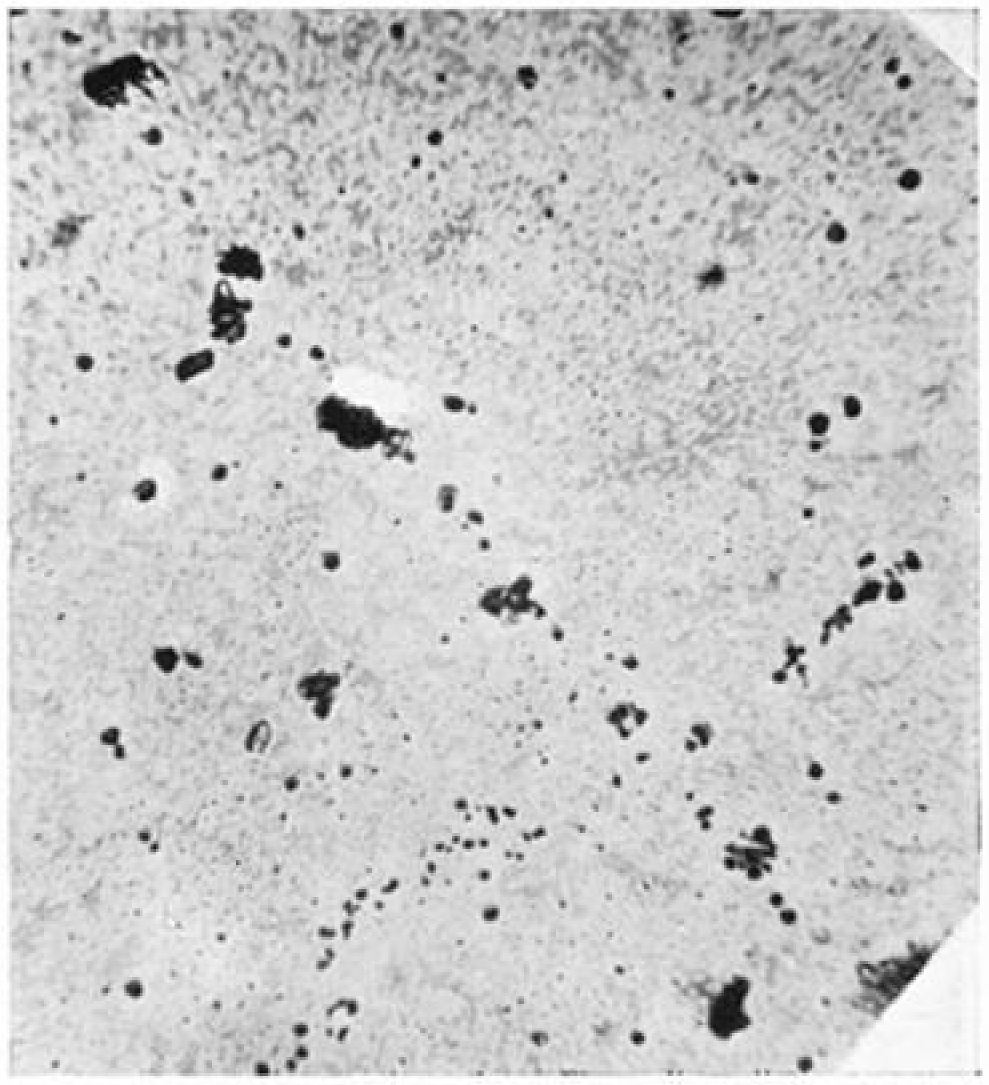


FIG 24

× 320

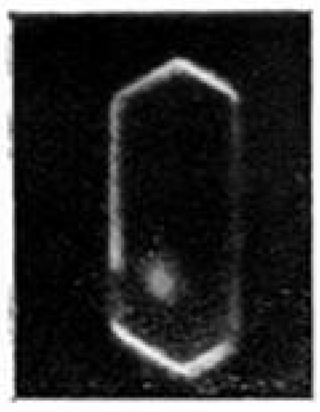


FIG. 25. × 1000

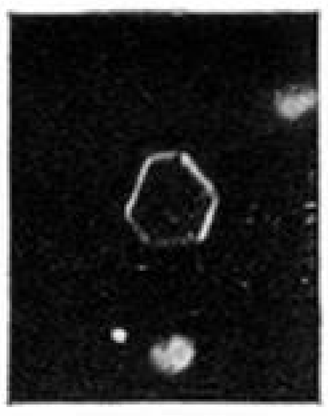


FIG. 26. × 1000

FIG. 27. × 1000

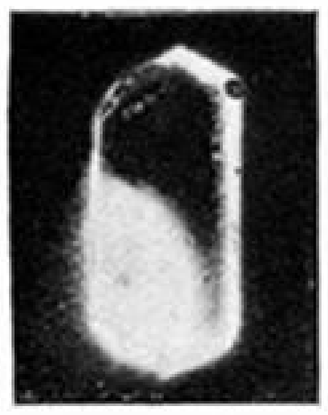


FIG. 28. × 1000

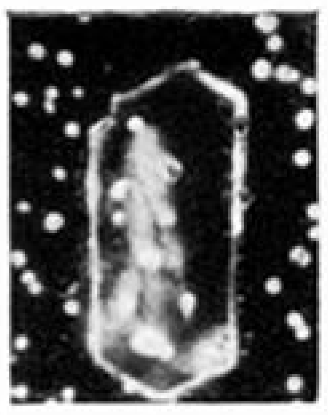


FIG. 29. × 1000

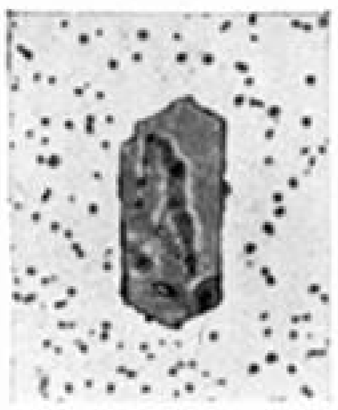
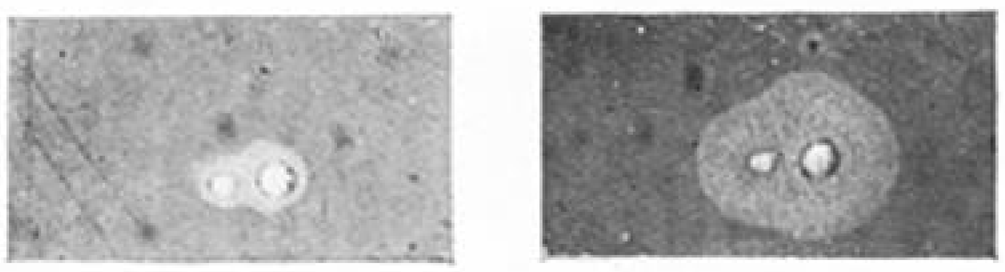
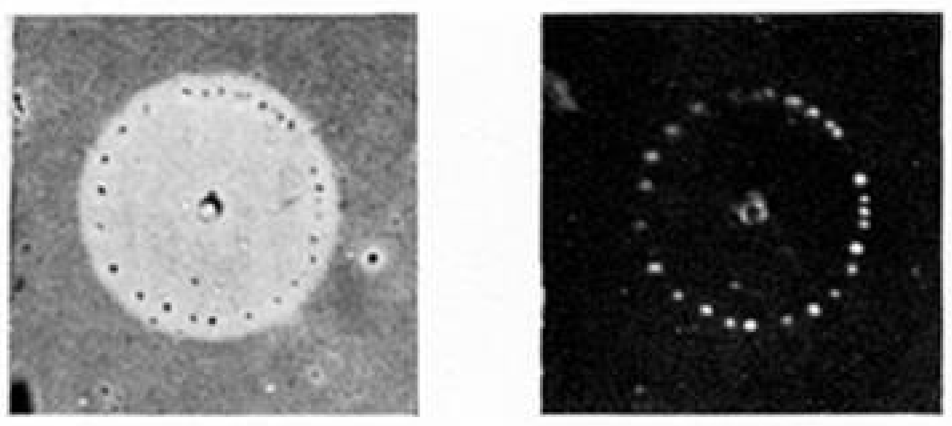


FIG. 30. × 720



a *b*

FIG. 31. × 320



a *b*

FIG. 32. × 320

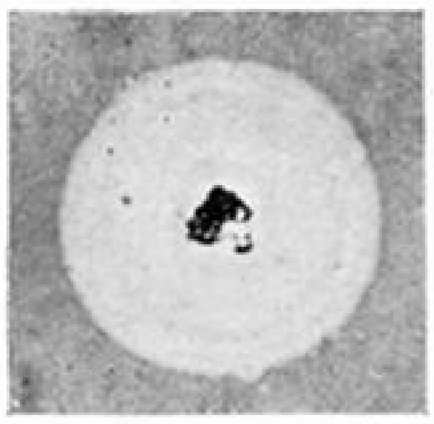


FIG. 33. × 320

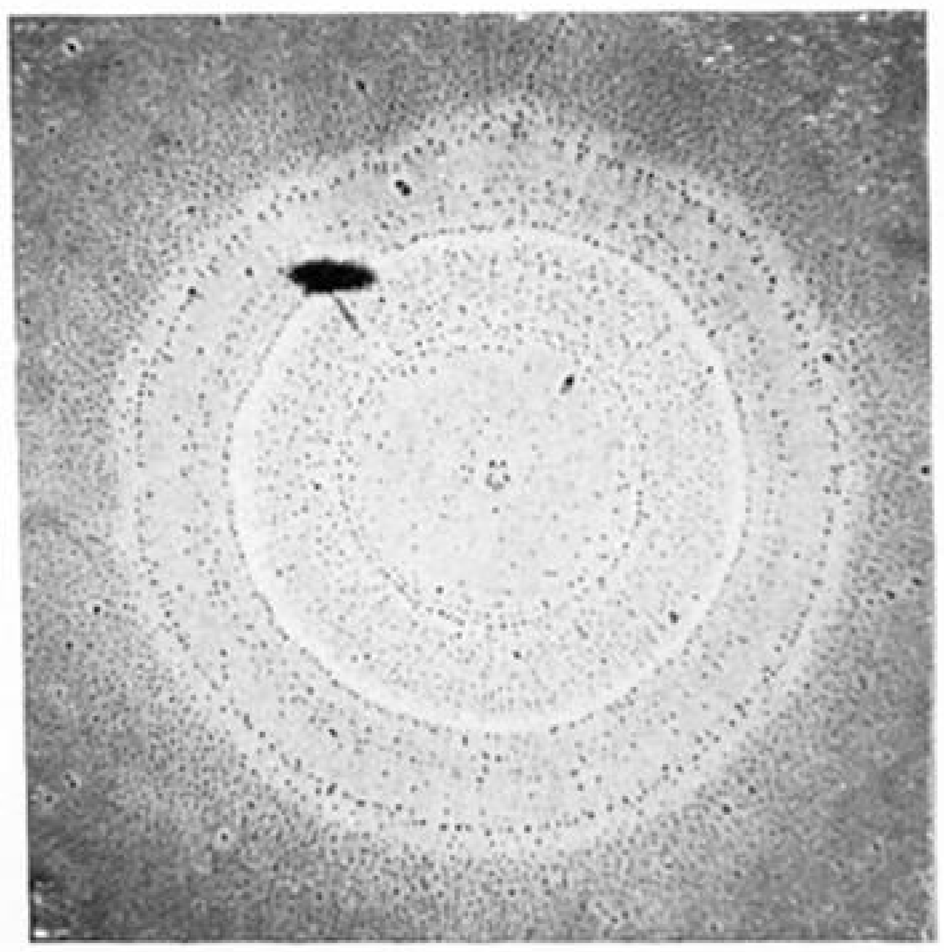


FIG. 34. × 320

FIG. 35. × 720

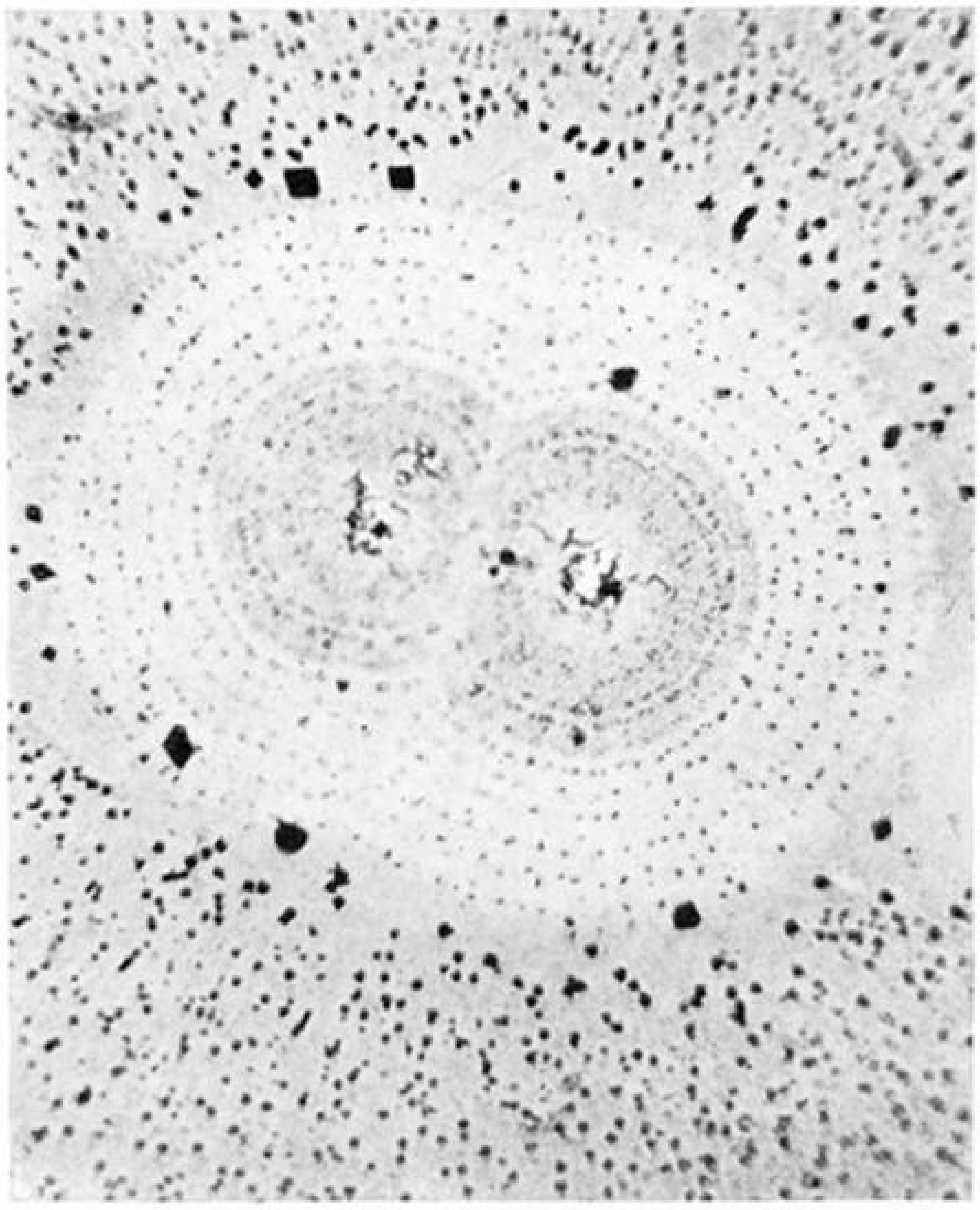


FIG. 36. × 720

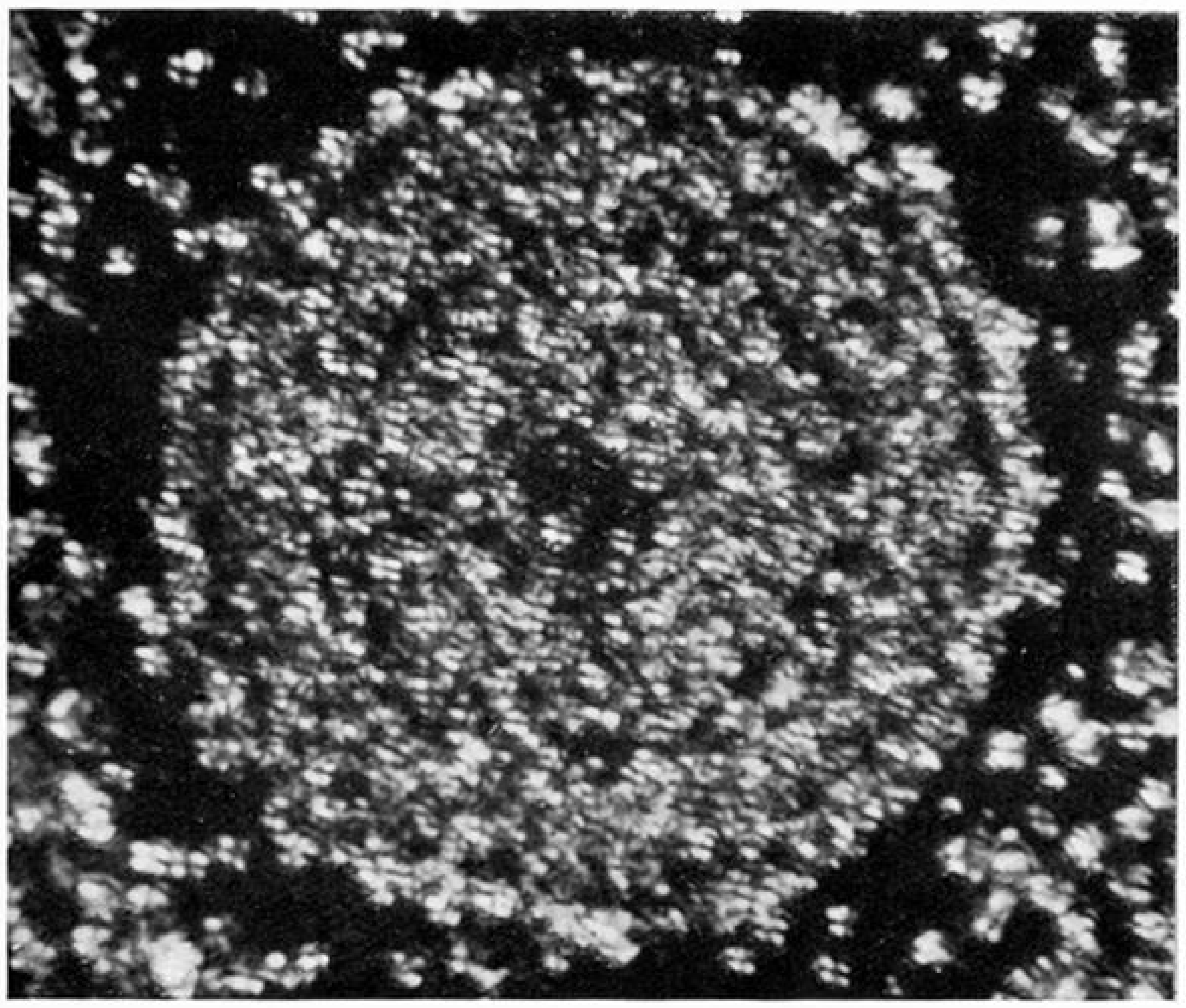


FIG. 37. × 2000

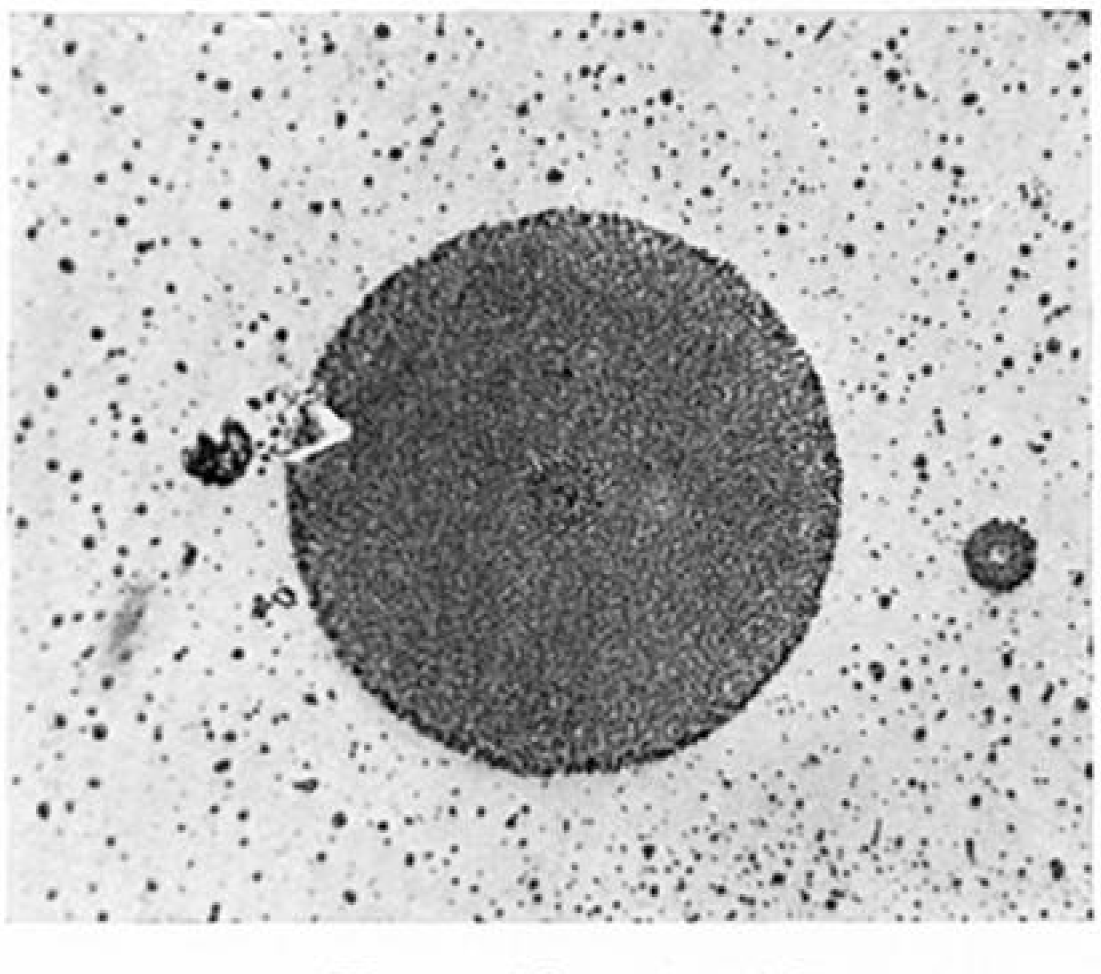


FIG. 38. × 320

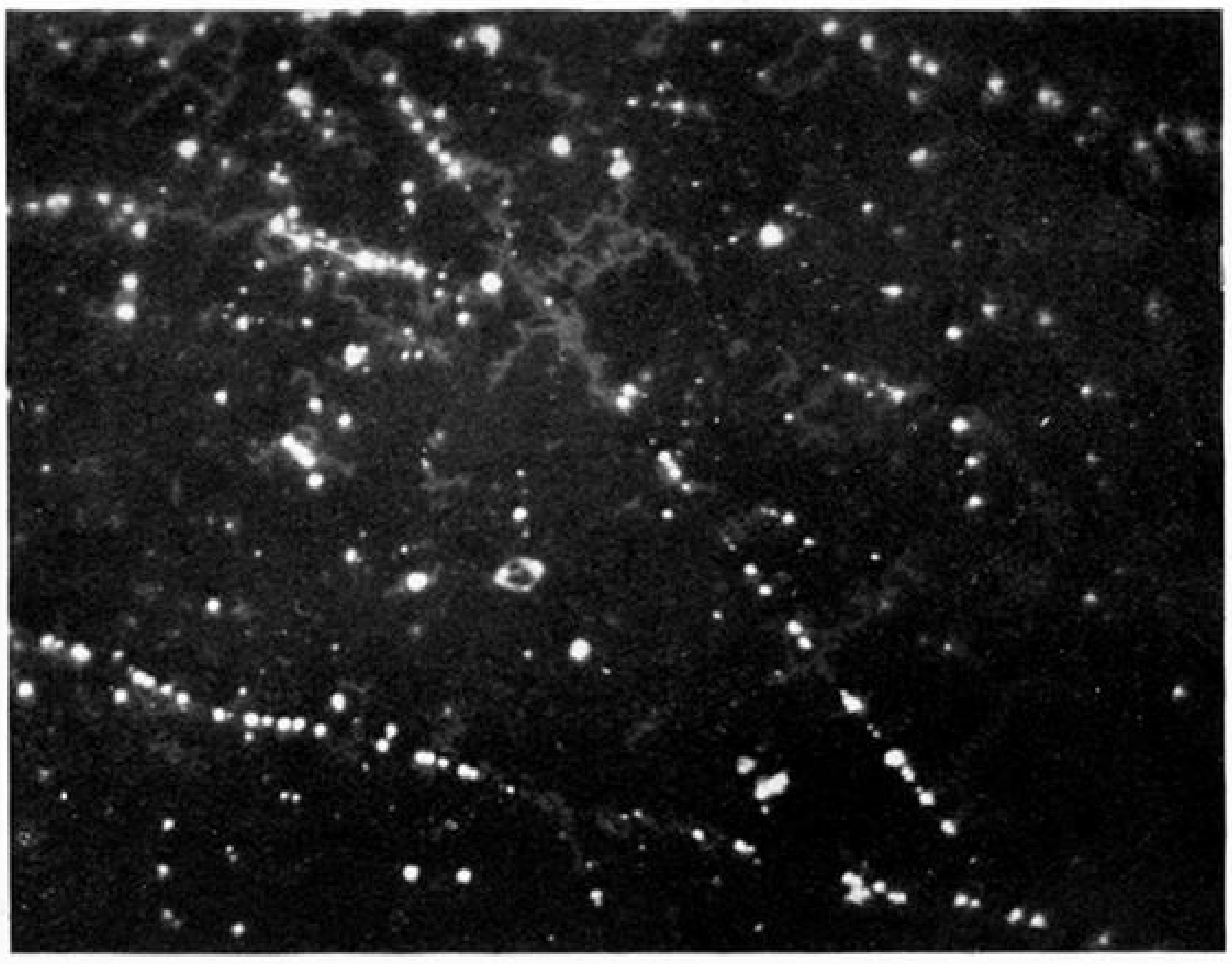


FIG. 39. × 320

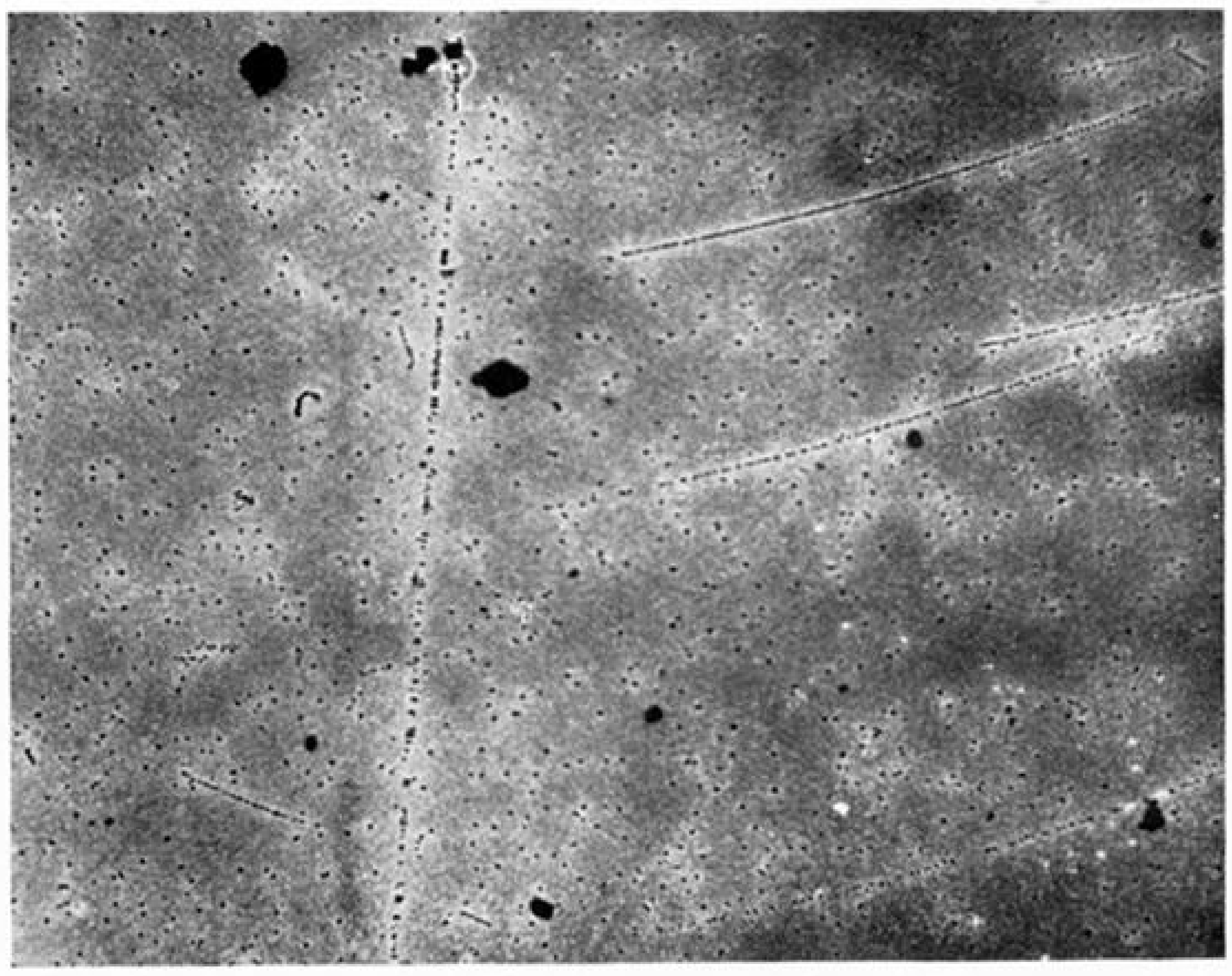


FIG. 40. × 320

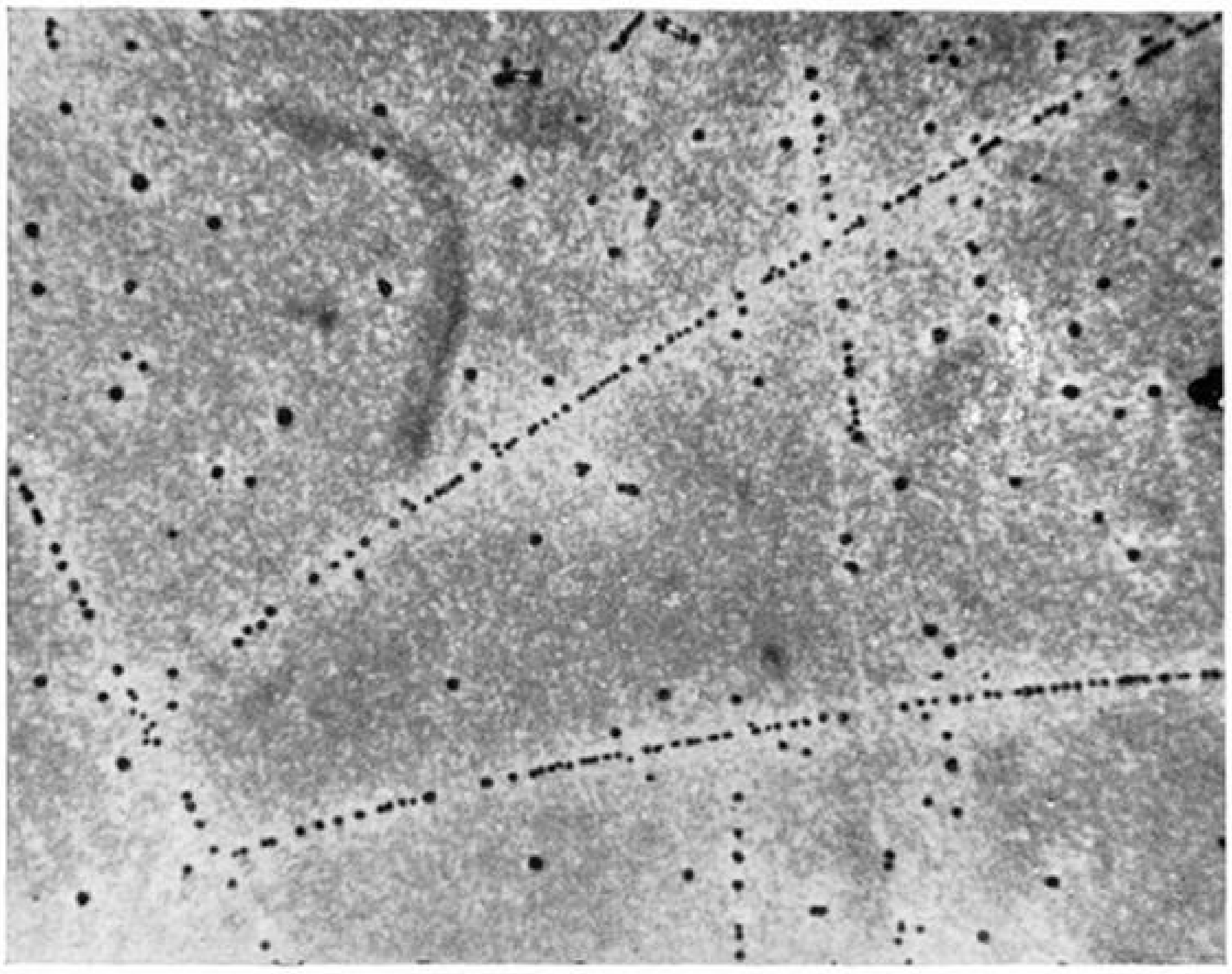


FIG. 41. × 320

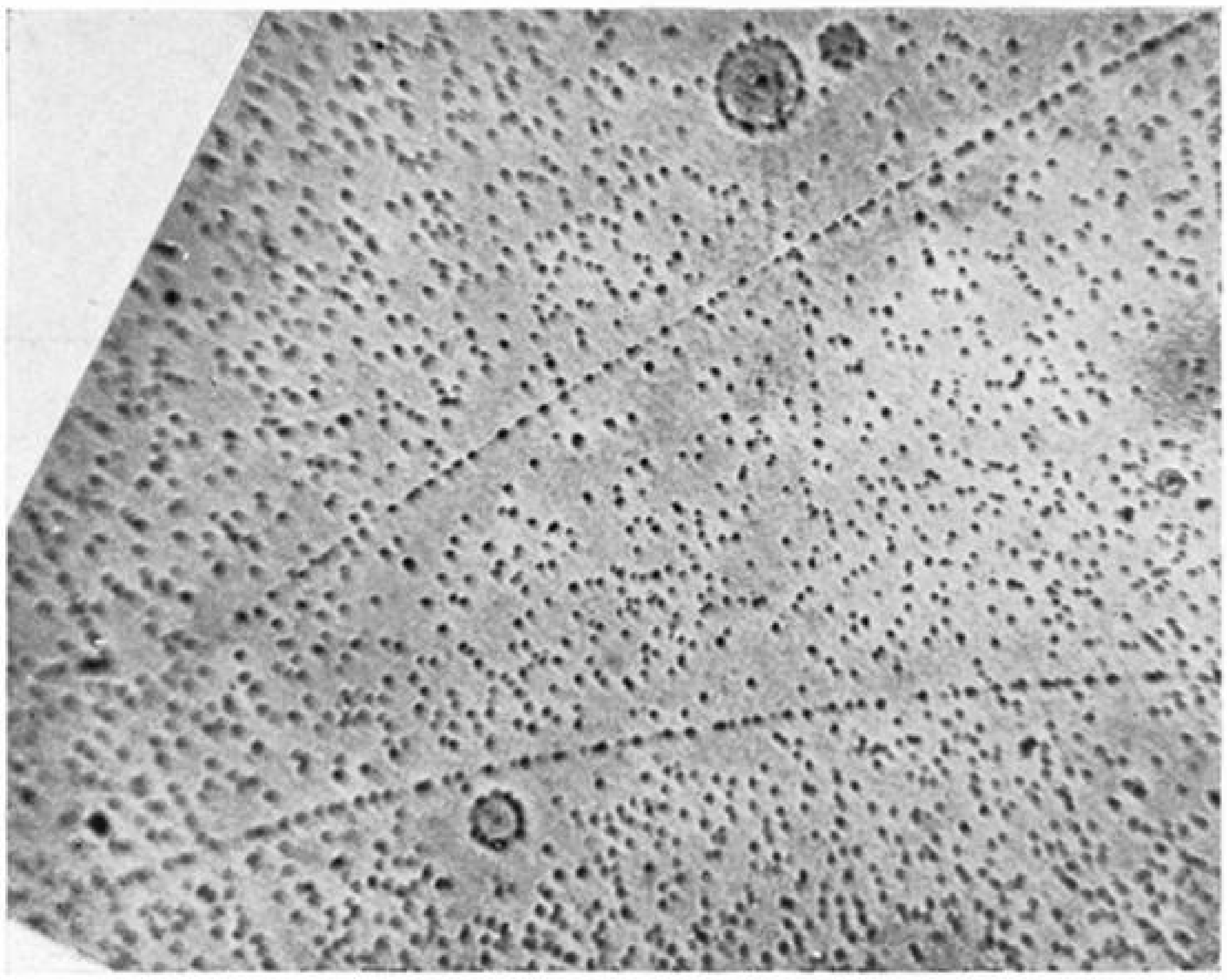


FIG. 42. × 320

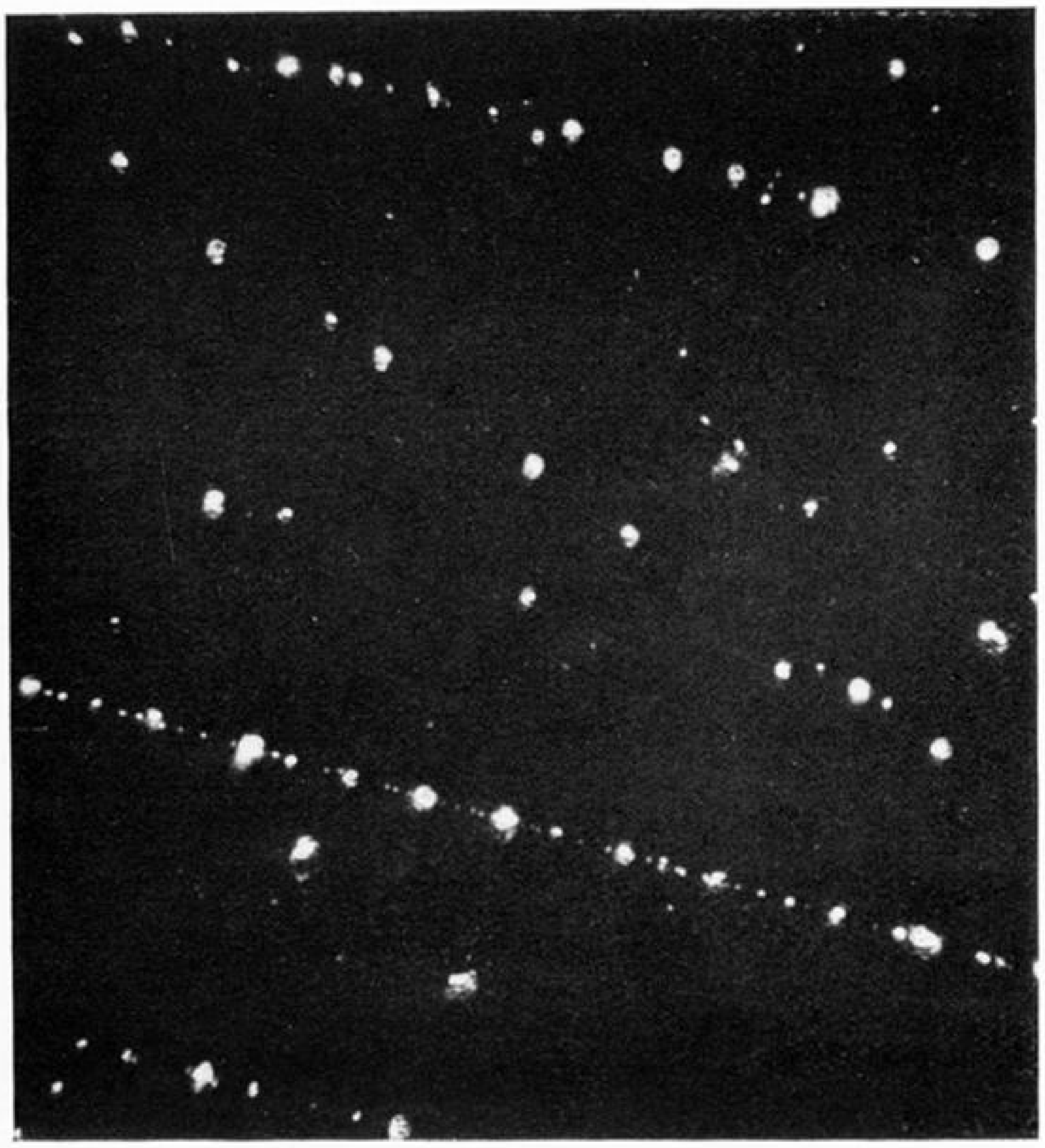


FIG. 43. × 1000

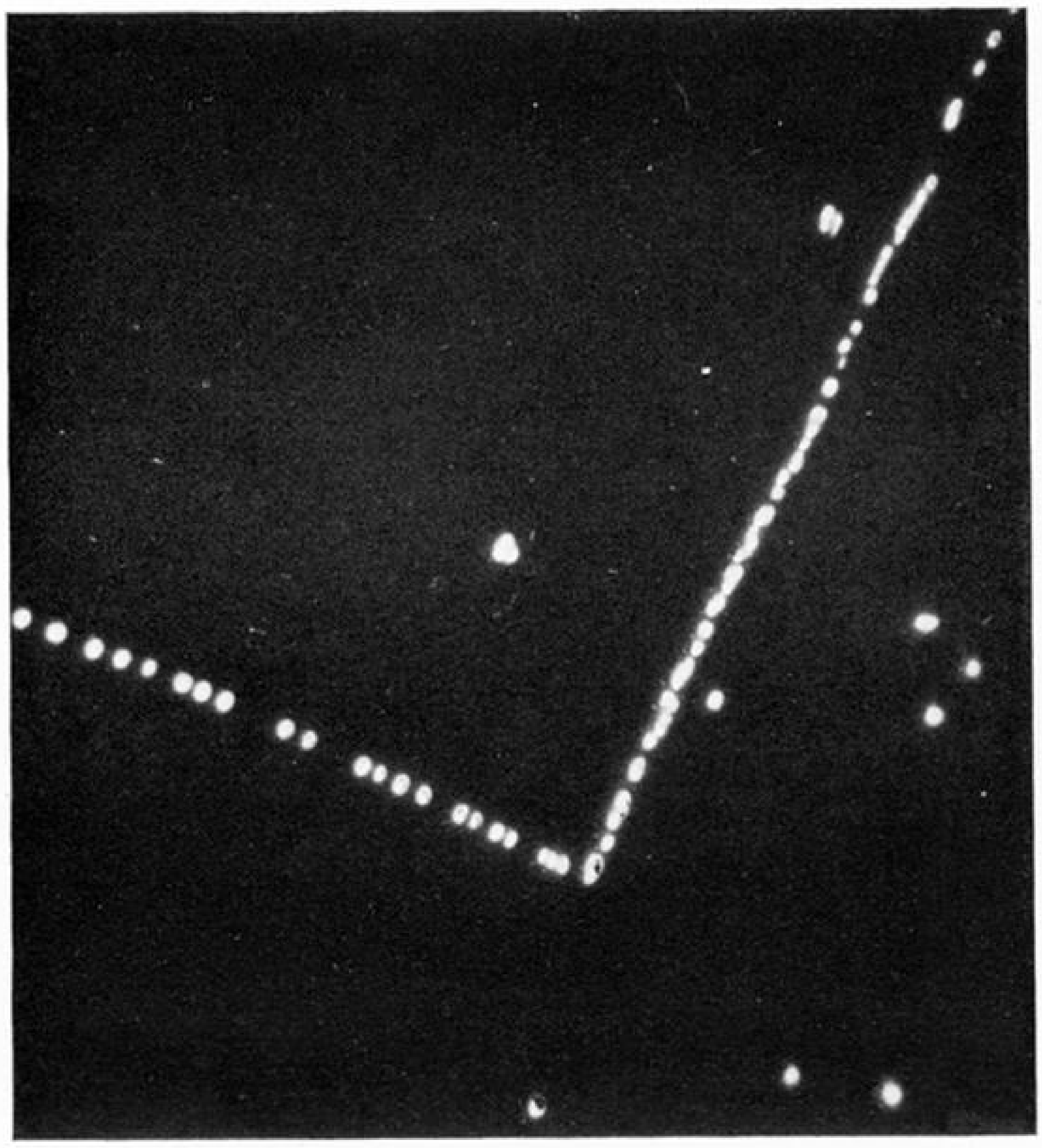


FIG. 44

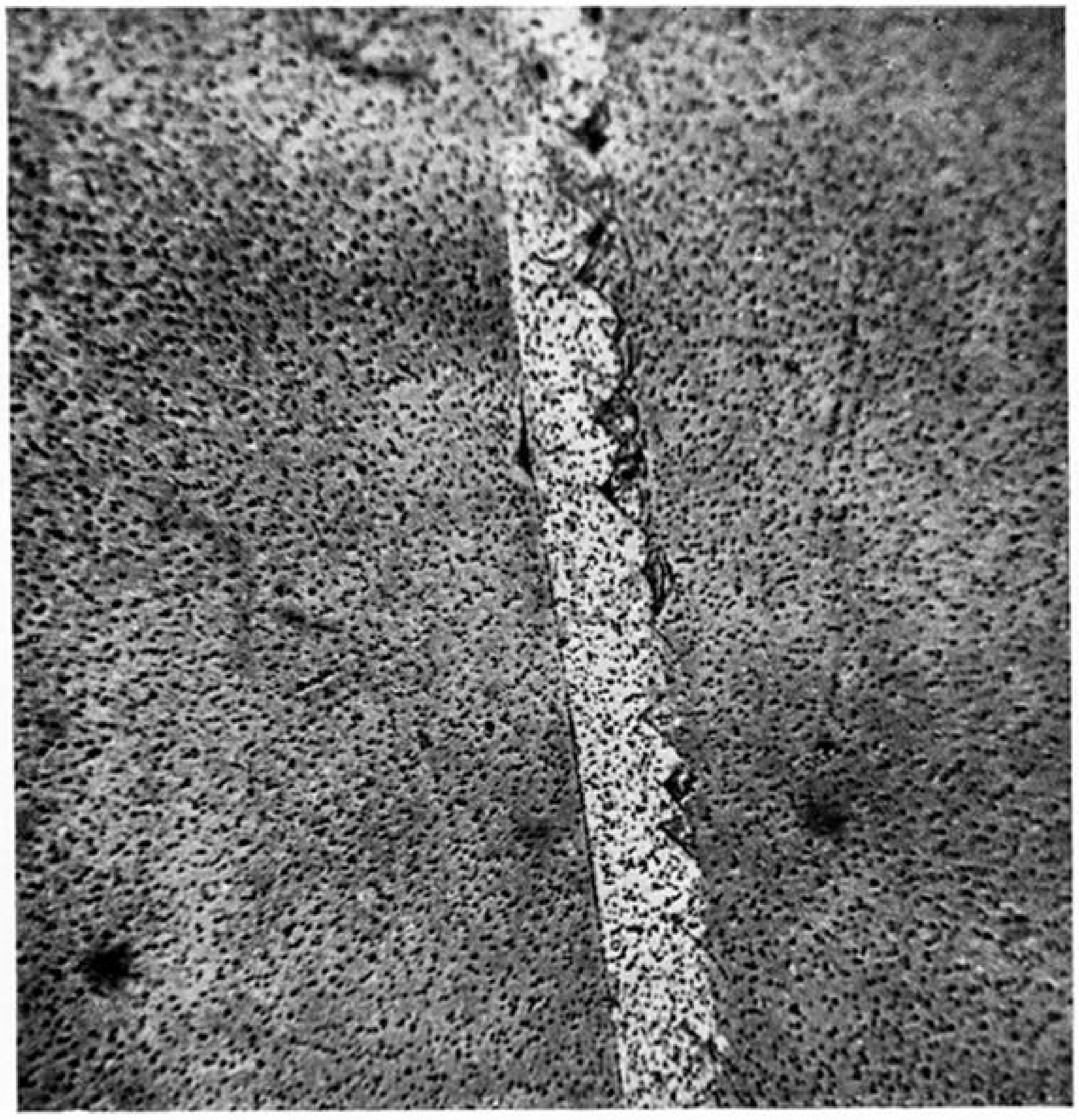


Fig. 45. × 320

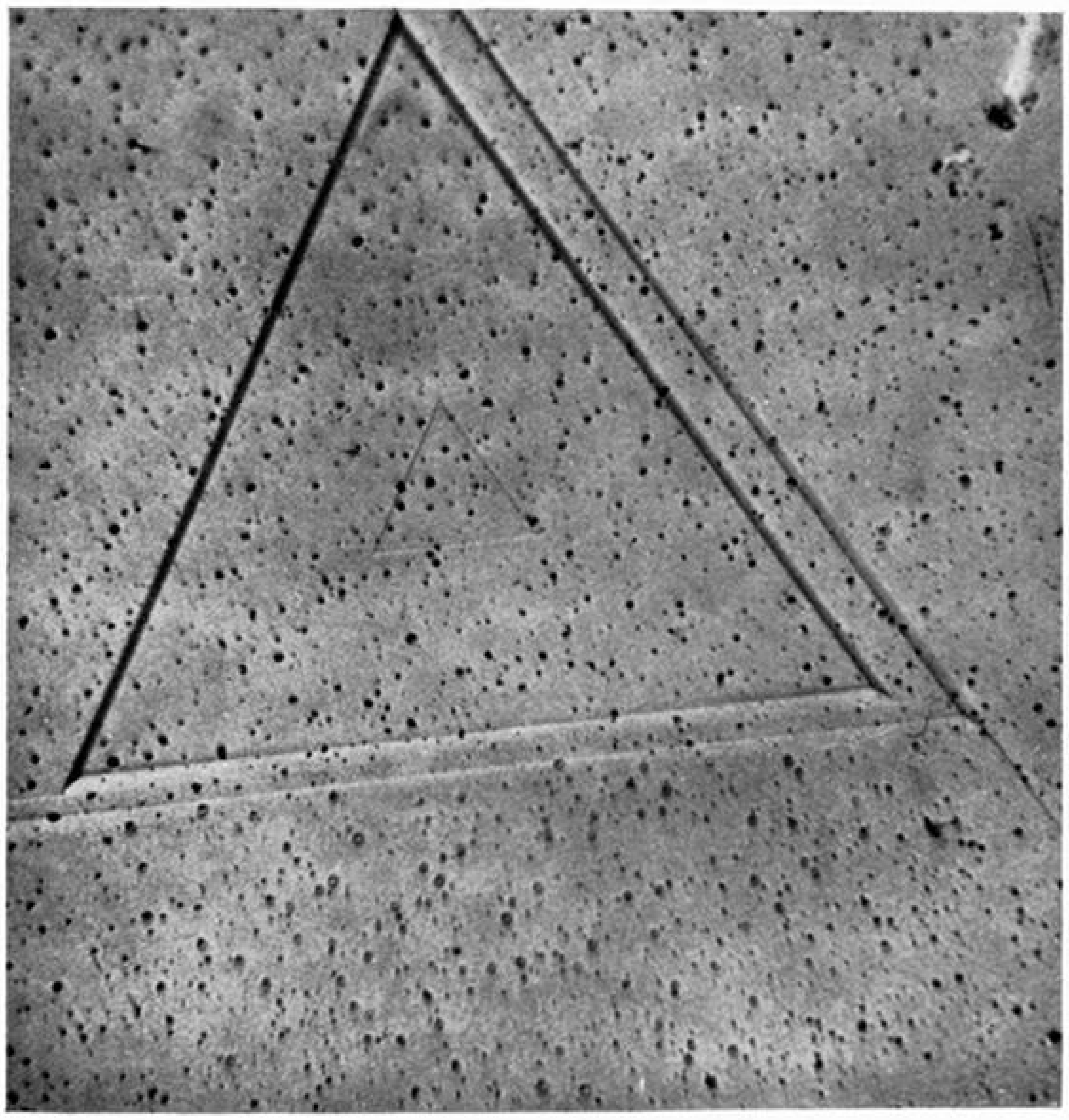


Fig. 46. × 320

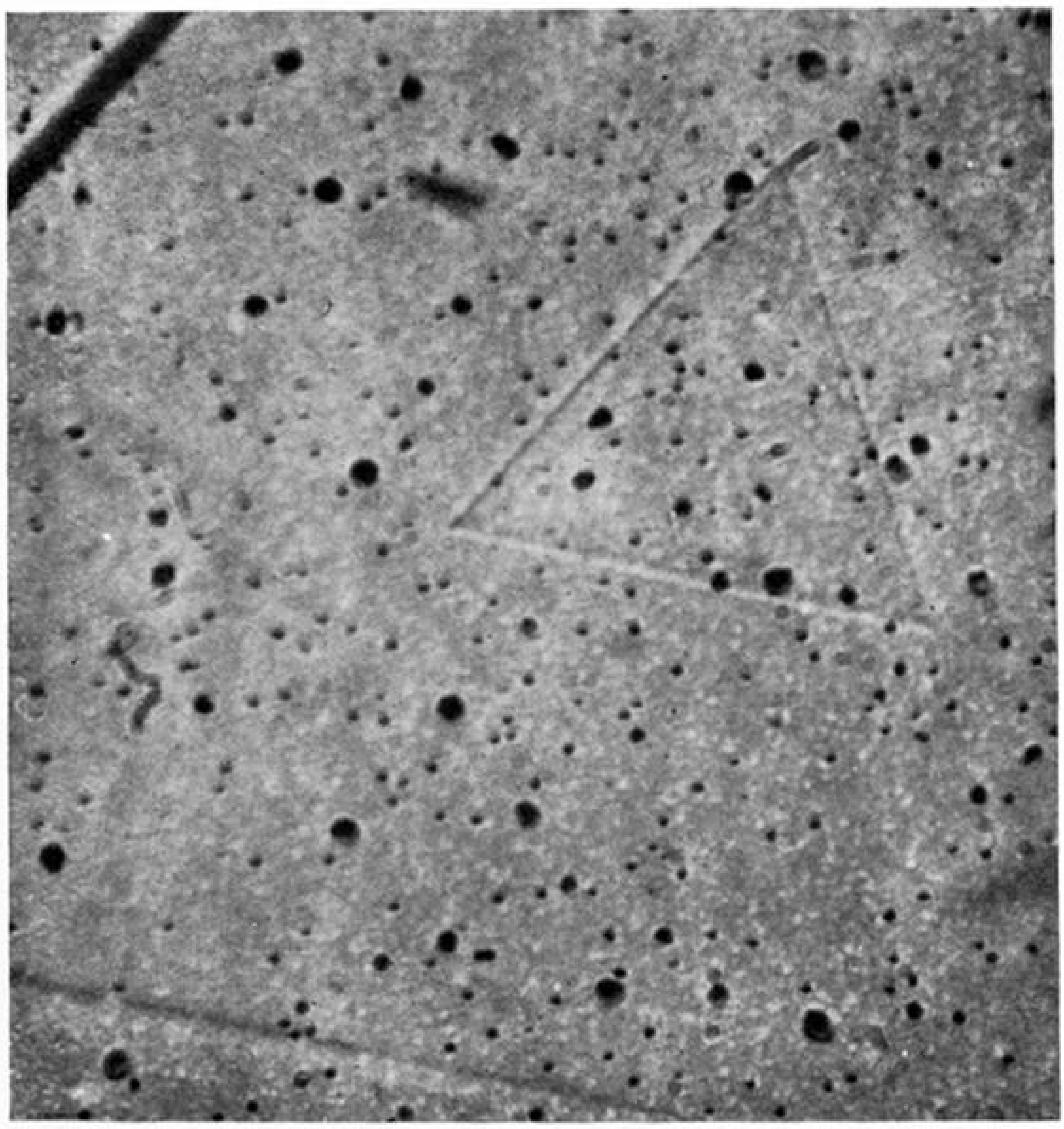


Fig. 47. × 1000

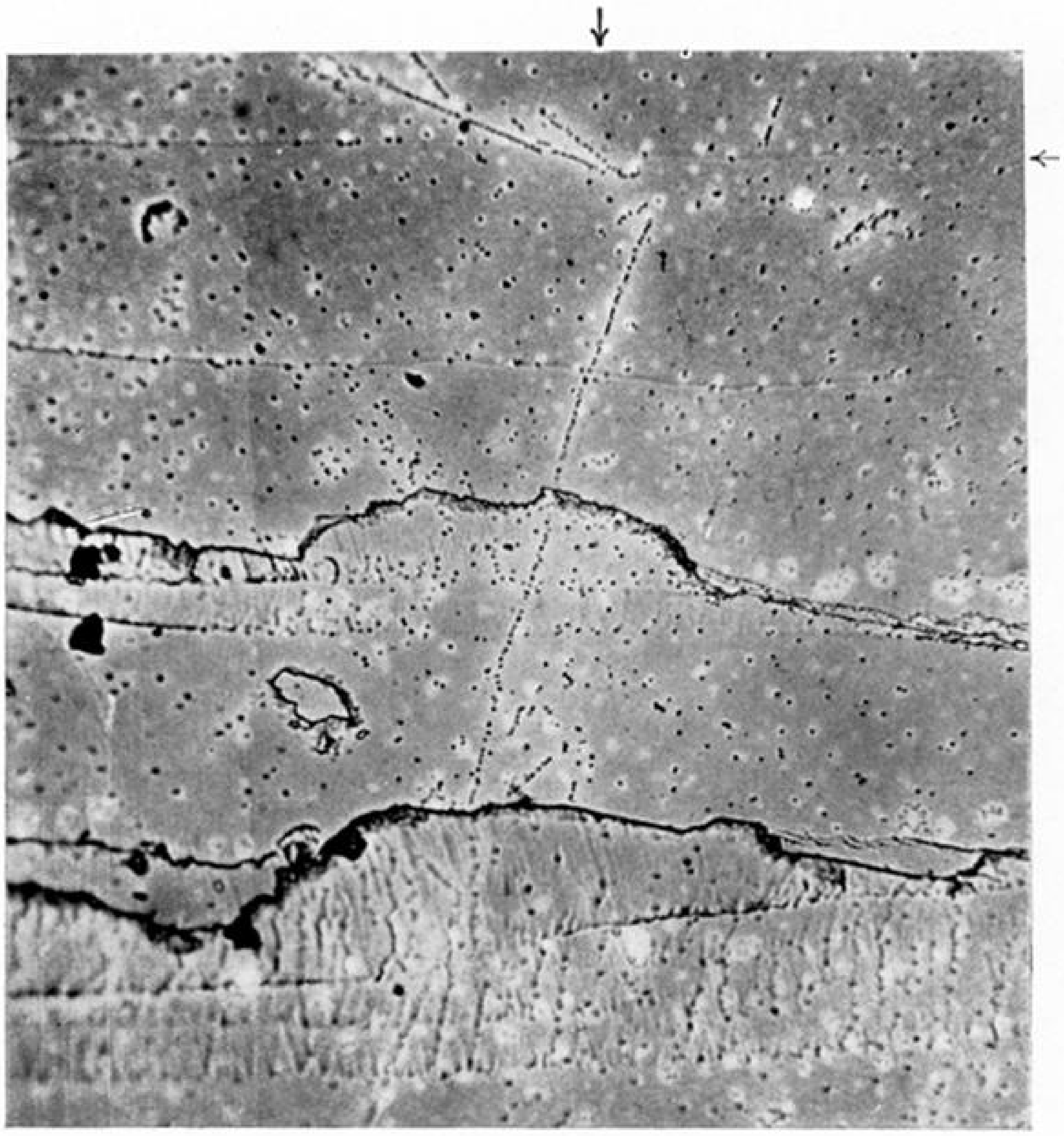


Fig. 48. × 320

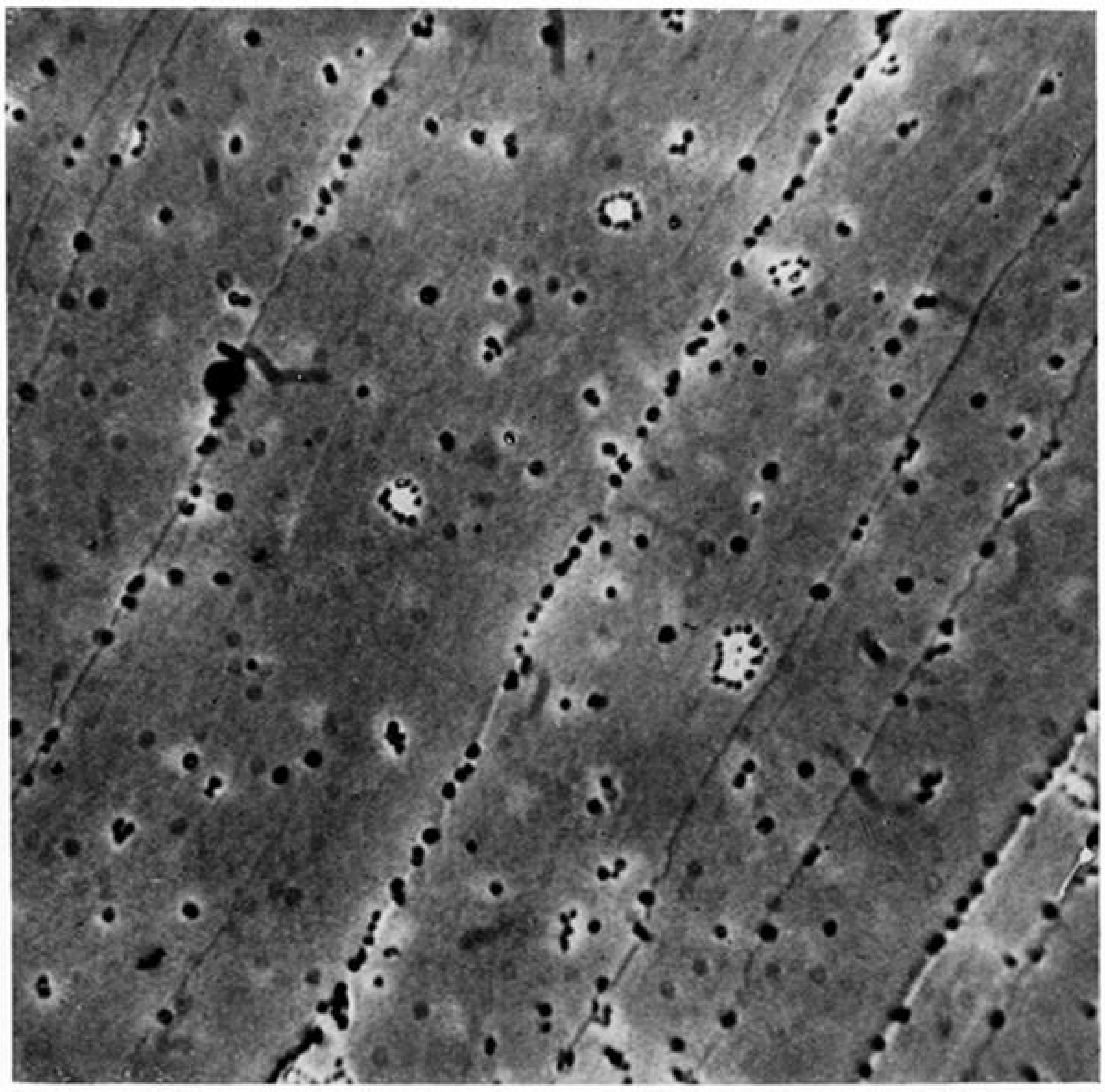


FIG. 49. × 1000

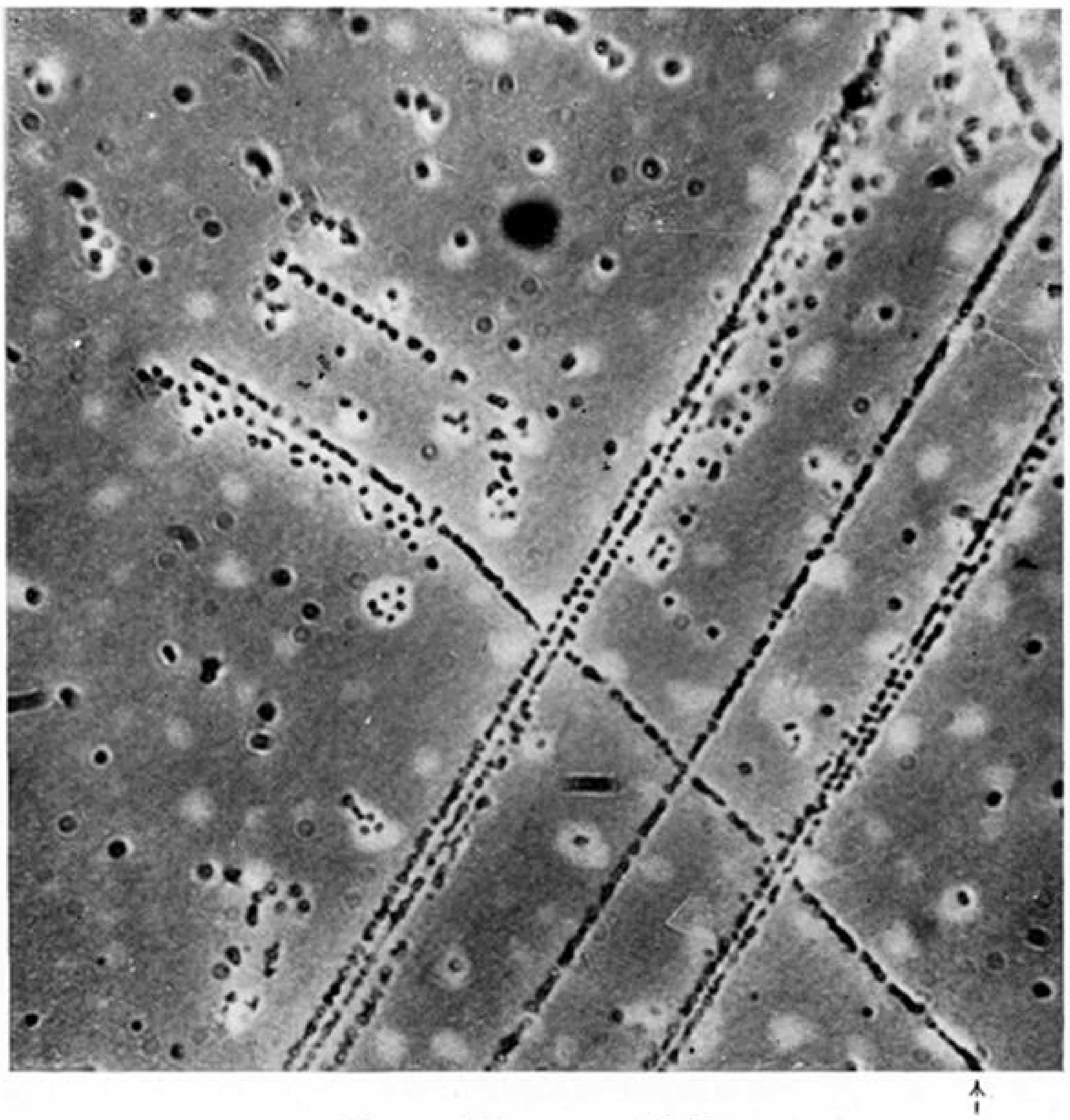


FIG. 50. × 1000

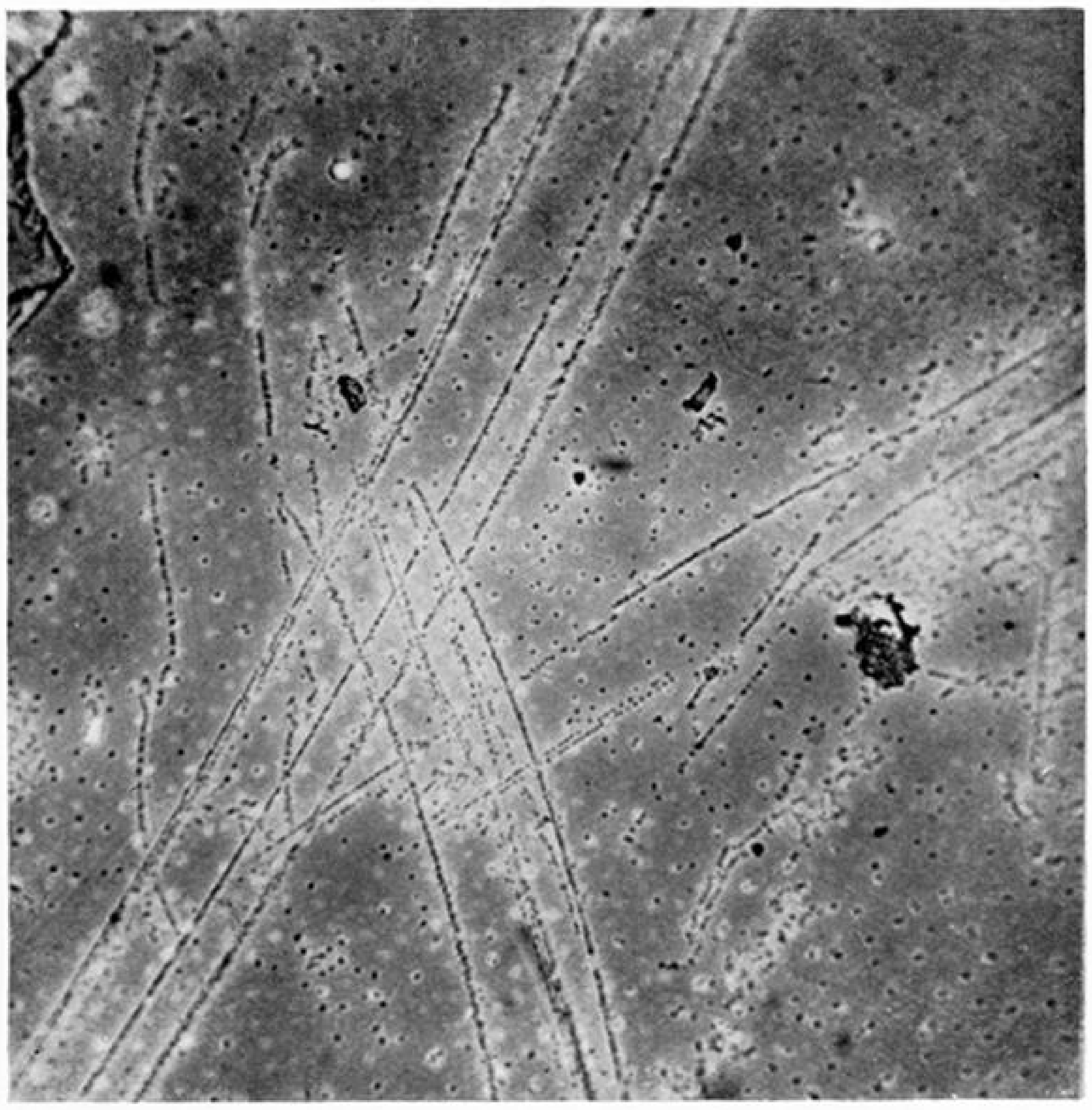


FIG. 51. × 320

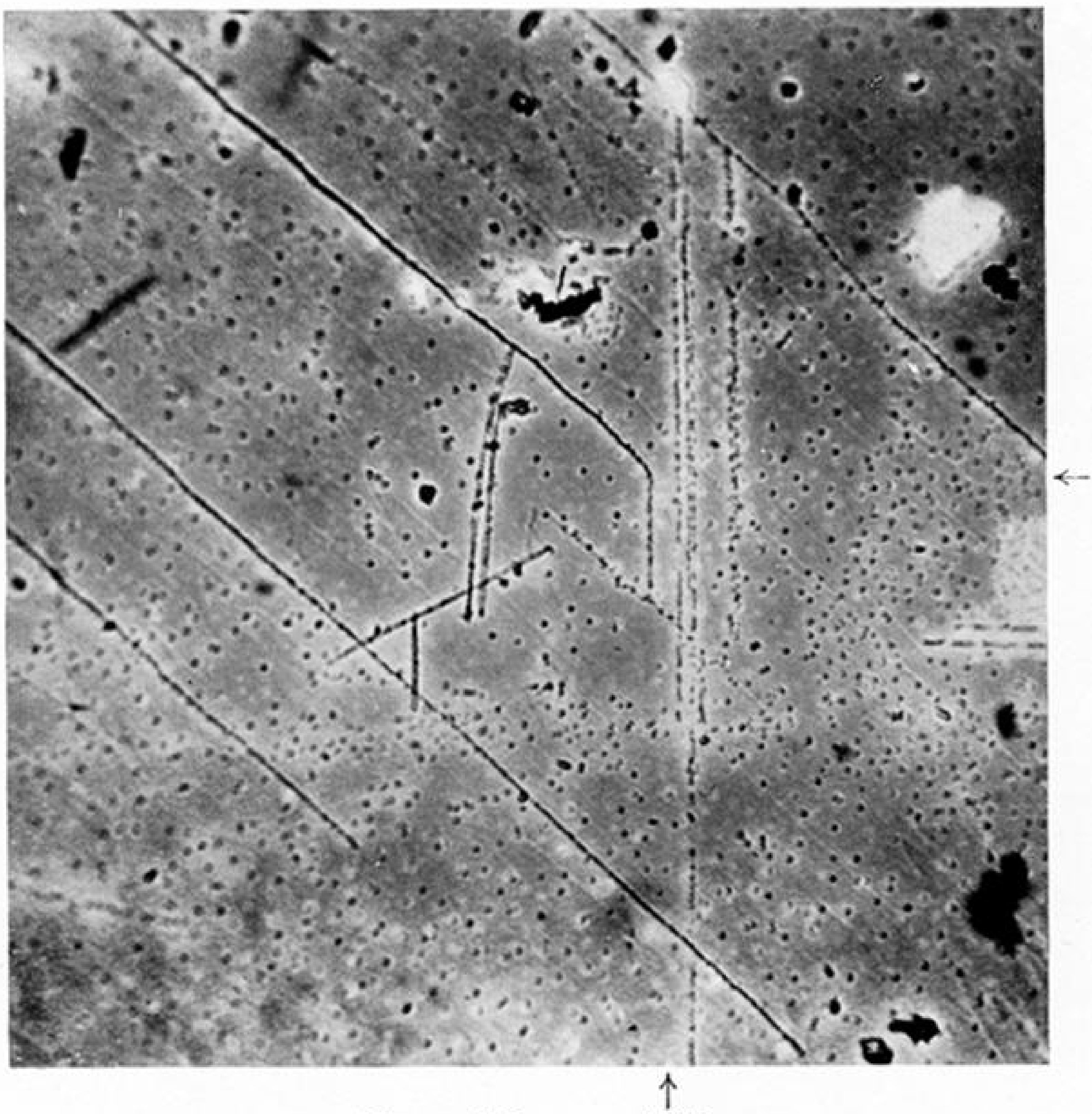


FIG. 52. × 320