ELEMENTARY PHOTOGRAPHIC PROCESSES IN AN ELECTRIC FIELD

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CONTENTS

1. INTRODUCTION

ALL modern studies on the nature and mechanism of formation of the photographic latent image agree on one point, in spite of considerable divergences on many other points. The point of agreement is the idea that the origin and growth of the latent image consist in a repeated alternation of migrations of conduction electrons and interstitial Ag^+ ions to certain binding sites within the microcrystals of the photoemulsion. This concept, which was first incorporated into the theory of the photographic process by Gurney and Mott over twenty years ago, still retains its fundamental significance. Nevertheless, attempts have become widespread in recent years to modify or reject others of their concepts, especially the detailed mechanism for latent-image formation which they proposed at that time. Even Mitchell, who has diverged considerably further than the others from Gurney and Mott's initial conceptions and has developed quite a different detailed mechanism, has not disputed this point. Rather, he has raised this type of alternation of elementary electronic and ionic processes to the level of a special "Gurney-Mott principle," as he called it, now an essential part of any theory of the photographic process.

Since both elementary processes are phenomena involving charge migration, one may study both of them in detail with the aid of an electric field applied to the microcrystals of the emulsion. Experiments of this type should permit the settling of many controversial points in the theory, and of course, should be performed in preference to many other more indirect experiments. However, the short duration of both processes is a complicating factor, and hence, very brief pulsed fields are required. The technique of generating such fields has been developed primarily in the post-war years, and it has been possible to perform this type of experiment only within the last decade.

Without yet discussing the data thus obtained (to be taken up in the later sections), we shall merely state that the studies have shown the outstanding value of the electric field method, not only as a means of direct study of the processes leading to latent-image formation, but as a means of controlling them. Thus, it has been found possible to displace the latent image within the microcrystals in any direction, or in particular, to any surface. Apparently, it is also possible to change the size of the latent-image particles. Since the topography and disperseness of the latent-image centers within the individual microcrystals determine the developability of the latter, this action of the field must essentially imply the control of the sensitivity both of the individual microcrystals and of the photoemulsion as a whole. In fact, a report was recently published[1] of a method of "dramatically" increasing, as the author put it, the sensitivity of a photoemulsion to brief exposures by synchronized application of a pulsed field.

The importance of the control characteristics of an electric field in the further development of scientific and technical photography is worthy of more detailed discussion. As we know, among the numerous applications of photographic methods in recent years, we encounter more and more often the use of photoemulsions as recording media in various automatic devices. A particular example of this is given by the cosmic-ray emulsion cameras for ascents into the stratosphere and beyond. We can expect this type of application to become much more frequent in the immediate future in connection with the rapidly expanding space studies. Under these conditions, the ability of a photoemulsion to accumulate the effects of radiation becomes a serious defect, whereas it has previously been considered to be one of its great advantages as a recording medium. Thus, it is impossible to relate a given photographically-recorded event to a definite time interval. Also, one cannot prevent re-

cording of events of the same type before or after a given event, or even eliminate background phenomena. Hence, any way of controlling the recording ability of photoemulsions (or in other words, their sensitivity) in a definite time schedule, similar to "on-off" switching in electric circuits, is extremely important.

However, there have been up to now practically no ways of controlling the sensitivity of photoemulsions during exposure. Those suggestions which have been made and tested in the laboratory have concerned only the limiting, i.e., "turning off " the sensitivity from a certain moment of time on. In order to show the advantages of an electric field for this purpose, we shall briefly go over the possible "turning off" methods.[2] First, we can vary the temperature of the emulsion; this idea has been called the "heat shutter." In principle, we can also turn on an emulsion in this way, an advantage over the other methods given below. Nevertheless, its practical applicability is very limited, since, first, large temperature changes are hard to achieve (the effect of small temperature changes on the emulsion is not great enough). Second, the temperature change throughout the surface or volume of the emulsion does not take place simultaneously, and is not rapid enough. That is, the establishment of certain given conditions will take many seconds or even minutes. Another method, applicable only for turning off, is the action of chemicals. An example of this is the action of oxygen on photographic films containing dyes catalyzing the oxidation of the sensitivity centers, but not of the latent image.[3] We can combine chemical and temperature effects, as is done in the second stage of two-stage development of nuclear emulsions. Finally, we can turn off an emulsion simply by developing it during the experiment, as was done on the second Soviet space ship.[4] However, all these methods, just like the temperature method, are sluggish and cannot instantaneously and uniformly vary the properties of large volumes or areas of emulsion. Hence, they can only roughly establish the times of events, and the recording of the background can be stopped only after the event, not before.

In distinction to the methods enumerated above, the action of an electric field occurs simultaneously throughout the emulsion, and is macroscopically lag-free. Thus, it is much more effective in principle than the other modes of action. This alone should probably have been a sufficient cause for the recent interest in the whole set of problems involving the effect of fields on latent-image formation. Even more, the first practical results in the control of the sensitivity of emulsions have already been obtained. However, if we also take into account the value of such studies for the basis of photographic theory (as we have mentioned above), the heightened interest in the effect of electric fields seems quite natural. To a considerable extent, the published studies have thus far concerned just the theoretical side of the problem. Our knowledge of

the detailed mechanism of the processes in the emulsion crystals is still inadequate, and the quantitative approach to this subject has been based until recently upon data which are dubious at best. Somehow or other, the number of studies concerning the action of a field, either directly on photoemulsions, or on model systems (such as large single silver halide crystals or various polycrystalline systems) has grown continuously. Thus, a review at this time is quite appropriate.

The present review gives an account of the research along this particular line. The form and interpretation of many of the experiments discussed here cannot be understood without a knowledge of the existing views on the mechanism of latent-image formation and of the gist of the argument which has been carried on in this field. Hence, we have also found it necessary to include a section on this subject in the review preceding those directly relating to the action of an electric field.

2. MODERN NOTIONS OF THE ELECTRONIC AND IONIC STAGES IN THE PROCESS OF LATENT-IMAGE FORMATION

The various aspects of the nature and mechanism of latent-image formation have already been discussed to some degree in a number of reviews in this journal, both for the action of light.[5,6] and for the action of ionizing particles.[2,7,8] Hence, we shall limit ourselves here to a relatively brief presentation of these problems.

The first of the modern theories to appear is that of Gurney and Mott.[9] In order to explain the processes taking place in latent-image formation, this theory extrapolates two facts established for large silver halide crystals to the microcrystals of emulsions: 1) the existence of dark conductivity associated with thermal lattice defects, consisting solely in Frenkel cation defects (interstitial Ag^+ ions); and 2) the appearance of electronic photoconductivity upon illumination within the spectral range of the characteristic absorption of the crystals. An additional fact demonstrated directly on the microcrystals of emulsions was that the silver particles formed upon illumination always appear at discrete points in the crystals (at the points where a developer will subsequently begin to reduce the crystal). The Gurney-Mott theory interprets these facts upon a single basis as follows.

Upon illumination, one conduction electron appears in the microcrystals for each absorbed quantum. These are valence electrons of the halide ions raised into the conduction band by the energy of the quanta. As determined from experiments with large crystals, the mean free path of such electrons is comparable to the diameter of the emulsion crystals. Thus, we may assume that they will migrate throughout the crystal until they are caught by some type of "trap", i.e., a local level lying within the forbidden band. The capture will be effective, however, only when this level is situated far

enough below the bottom of the conduction band. As a rule, the traps are associated with various structural defects, such as always exist in real crystals. The traps distinguished by their depth are the sensitivity specks, or in other words, impurity centers intentionally created on the surfaces of the crystals by the so-called chemical sensitization. The capture of the electrons by the traps completes the first (electronic) stage of latent-image formation.

The positive holes, i.e., the halogen atoms remaining after transfer of the electrons into the conduction band, are not assigned any essential significance in the Gurney-Mott theory. They consider that, since the holes are not fixed in the lattice, they freely emerge at the surface of the crystals (possibly by a relay mechanism), where they react with the surrounding gelatin. The recombination of electrons and holes is practically excluded by the low mobility of the latter.

The second stage begins at the moment of capture of the electron by the trap. This stage involves the migration of the interstitial Ag^+ ions existing in the crystal to the negatively-charged sites, which are now the traps. The ionic stage is completed by the discharge of the ion at the trap by combination with the electron to form a silver particle. Since these particles function later to catalyze the reduction of the crystals by the developer, the most important particles will be those of sufficiently large dimensions, which lie on the surfaces of the crystals (and thus can contact the developer). These conditions will be satisfied especially by the particles formed at the most effective surface traps, which are the sensitivity specks. Hence, these are the sites where development will subsequently commence.

The electronic and ionic stages are quite different in duration, the latter lasting much longer than the former, even at room temperature. The difference becomes greater at lower temperatures. For the electronic stage, the change in duration with the temperature is generally small; within wide limits, it can be described by a $T^{-1/2}$ law resulting from the temperature-dependence of the thermal velocity of the conduction electrons. On the other hand, the ionic stage is highly temperature-dependent. Here the determining role is played by the dependence of the duration of the ionic stage on the ionic conductivity (σ) of the crystal, as follows from elementary considerations. The charge q which has been formed at the electron-capture center gives rise to a field of intensity $E = q/\epsilon r^2$. This brings about an ionic current $I = \sigma E \cdot 4\pi r^2$ $= 4\pi\sigma q/\epsilon$. Hence, the time required to neutralize the charge (i.e., the duration of the ionic stage) is $t_n = q/I$ $= \epsilon/4\pi\sigma$, or may be twice as large, if we assume that the transport numbers for ions and empty lattice sites are equal.[5] Of the quantities governing t_n, only σ is temperature-dependent, indeed, according to the law $\sigma = \sigma_0 \exp(-U/kT)$. Thus, we can directly derive a law of the type $\exp(U/kT)$ for the temperature-dependence

of t_n, where U is at least an order of magnitude larger than kT. For AgBr, $\epsilon = 13$, and $\sigma \sim 10^5$ CGS units at room temperature (see Sec. 4 for the origin and reliability of these values). Hence, $t_n \sim 10^{-5}$ sec. The decrease in σ with decreasing temperature is so rapid that at liquid-air temperature t_n is measured in hours, i.e., there is practically no ionic conduction. Hence, one of the obvious ways to test the Gurney-Mott theory experimentally is to study the temperature-dependence of the effect of light on a photoemulsion.

Among the many experiments performed to do this, the great majority being purely qualitative, some of the most convincing seem to be those of Webb and Evans.[10] They studied the Herschel effect (the bleaching of the latent image by a subsequent exposure to long-wavelength light) with various temperature schedules during the two exposures. These experiments demonstrated not only the existence of electronic and ionic stages which could be separated (which is all that the Gurney-Mott principle amounts to in Mitchell's interpretation), but also the fact that they occur in a quite definite sequence, the ionic stage following the electronic. These results were in precise agreement with the detailed mechanism of Mott and Gurney.

A corroboration of this mechanism of differing character but also highly convincing is the following fact discovered by Berg[11] (which we shall take up again in Sec. 4). He found in a study of reciprocity-law failure for very brief exposures that the reciprocity law is strictly obeyed for all exposure times shorter than $\sim 10^{-5}$ sec, and only within this range. This limiting time value (turn-over point) agrees well with the estimate given above for the duration t_n of the ionic stage. It is pertinent here to recall that reciprocity-law failure is closely connected, in general, with the mechanism of latent-image formation (see, e.g., reference 12), and was first explained by precisely the Gurney-Mott theory. Hence, Berg considered the agreement in values which he found to be quite normal, as both time values are physically identical. As he proposed, what was manifest was merely the lag of the ionic process behind the electronic process. In fact, for exposures shorter than $\sim 10^{-5}$ sec, the completion of the ionic process unavoidably takes place only after the illumination stops. Hence, under these conditions the effect of any given exposure (for a given total exposure, of course) cannot depend on the duration of the exposure. A strong argument in favor of this explanation was the shift found in these same experiments of the limiting time value t_n when the temperature was changed. This shift followed the temperature-dependence of the conductivity σ, at least qualitatively. This fact was later confirmed by the author, who was able to vary t_n by varying σ, either as a function of the temperature,[13] or of the AgBr : AgCl ratio in the solid phase of the emulsion.[14] The data obtained showed not only a qualitative, but a quantitative agreement between the ionic

conductivity and the turn-over point.

Subsequently, this mechanism has been made considerably more precise. As we may easily show by calculation (see, e.g., reference 5), a trap which has been charged negatively by capture of an electron cannot accept the next electron until the first one has been neutralized by an arriving Ag^+ ion. Thus, the appearance of a latent-image center made of many Ag atoms does not take place simply as the successive occurrence of two events, the electronic and ionic stages, but as a repeated alternation of these events, accompanied by the growth of the center each time by only one atom. This fact is not essential in long exposures, in which the events of absorption of successive quanta and corresponding electron captures in the traps are so widely spaced in time that the neutralization of any one electron is always completed by the time the next one arrives. On the other hand, in exposures of short duration, this fact becomes highly important. Here, consequently, the formation of the latent image takes place simultaneously at many traps, with a corresponding decrease in the size of each of the centers formed. For exposures shorter than 10^{-5} sec, all of the centers must in general consist of one atom each. If, nevertheless, they later grow to dimensions sufficient to catalyze the development reaction, this can only be due to a supplementary process of latent-image redistribution. A discussion of the details of this process would extend beyond the limits of this review; we shall only state here that it is also based on an alternation of electronic and ionic processes.[12] Hence, even after these refinements, the Gurney-Mott mechanism amounts, as before, to a multiply repeated alternation of the faster electronic process, which is weakly temperature-dependent, and the slower ionic process, which is strongly temperature-dependent.

Since 1949, a number of authors have undertaken attempts to formulate other mechanisms. Of these, the first whom we should cite is Mitchell. His critique of the Gurney-Mott mechanism first[15] dealt principally with the ionic stage. Since he considered that the formation of particles within the emulsion crystals would involve the appearance of appreciable deformational stresses, he admitted the possibility of the ordinary Gurney-Mott mechanism only at surface centers. For internal centers, however, he suggested that the basic process in the second stage is the migration of vacant anion sites, or Schottky defects. Later, when the absence of any appreciable number of such defects in the crystals had been established quite firmly (at any rate, at room temperature and lower) Mitchell abandoned studies on this variant of the mechanism.

The author of one of the next attempts to abandon the Gurney-Mott mechanism was its creator, Mott[16] (Gurney had passed on by this time), whose position on the theory which he founded has never been distinguished by constancy. He proposed another theory on the basis of the existence of an effect in an emulsion film in which the photoconductivity continued to increase after cessation of the illumination (Miller and Hamm[17]). This theory involved an exciton (currentless) character of the first stage; discharge of the exciton resulted in the formation of an electron, or directly of an Ag atom. However, in subsequent experiments,[18] electric-field pulses were applied to the emulsion crystals with duration shorter than the time required for neutralization of the electrons by Ag^+ ions. These experiments definitely showed the presence of a photocurrent with negatively-charged carriers. It was later shown that the experiments of Miller and Hamm were generally erroneous,[19] and that the lag in photoconductivity which they observed was false, being due to transients in the input circuit of the amplifier.

A sequence of processes of charging and discharging of traps, opposite to that postulated by Gurney and Mott, was proposed by Matejec[20] on the basis of a study of the electronic and ionic conductivities of silver halide crystals. In his view, the first stage of latent-image formation is the capture of an interstitial Ag^+ ion at the surface (which may occur even prior to illumination). The second stage is the neutralization of this ion by a conduction electron. Such processes may be subsequently repeated again and again, leading to the formation of a particle. However, as Stasiw noted (see the report on the 1959 Liége colloquium[21]), this viewpoint gives no explanation for the various temperature experiments (e.g., that of Webb and Evans[10]), whereas the common Gurney-Mott mechanism explains them without difficulty.

The viewpoint of Matejec is also distinct from Mitchell's newest conception. The formulation of this conception was preceded by a large volume of experimental studies by Mitchell's group on photochemical phenomena in poly- and monocrystalline samples of silver halides considered as models of photoemulsions. The results which they obtained and the conclusions which they drew are presented with small variations in a series of review articles by Mitchell. The most thorough of these has already appeared in this journal.[6] The new mechanism of latent-image formation has been formulated most clearly in an article[22] of which Mott, who again changed his mind, was a co-author.

According to Mitchell, there is one false assumption at the basis of the Gurney-Mott mechanism, along with the correct ones. This is the assumption that the positive holes (atomic halogen) have low mobility, and concomitantly, show a low probability of recombination with electrons. While there have been no direct proofs of high mobility of holes in silver halides, Mitchell considers it to be no lower than that of electrons in any case. The fact that the mobility of the holes has not been observed experimentally is only an indication of their short lifetime, not of their low mobility, according to Mitchell. (Some data obtained subsequent to Mitchell's studies will be discussed in de-

tail in Sec. 5.) Hence, we can suppose that the holes emerge at the surfaces of the emulsion crystals earlier, or at least no later, than the conduction electrons, formed simultaneously with them. Then, the recombination of electrons and holes is not only probable, but unavoidable. Thus, in general, a latent image will not be formed on the surface unless special measures make possible a spatial separation of the capture sites for electrons and holes, and the latter become bound before recombination can take place.

Mitchell ascribes the role of the hole acceptor to the molecules of the chemical sensitizer, especially Ag_2S adsorbed on the surface of the crystal. Thus he views the essence of chemical sensitization as being the creation of such hole-acceptor centers. This treatment, we note, is highly different from that taken in the Gurney-Mott theory, where it was considered that the products of chemical sensitization, including Ag_2S, form impurity centers which serve as deep, and hence most effective electron traps. Upon being trapped by the acceptor, according to Mitchell, the hole is neutralized. That is, it transfers its charge to one of the nearest Ag atoms of the chemical sensitizer. The Ag^+ ion which appears diffuses into the lattice, and the acceptor site remains uncharged. Since all of this takes place before the electron arrives, there is no reason for it to be captured there. The trapping of electrons takes place near the so-called kink sites of the surface (see reference 6). If an Ag^+ ion occupies such a site, any Ag^+ ion absorbed next to it may serve as an electron-capture site but not as a hole-capture site, owing to its charge. The halide ions at the same sites are not traps for holes, and thus a spatial separation of electrons and holes becomes possible. Since the appearance of ions at the surface must precede the capture of electrons, the sequence of electronic and ionic processes in this mechanism is the opposite of that in the Gurney-Mott mechanism, just as in that of Matejec. The emergence of Ag^+ ions from the interior of the crystal consists in ordinary diffusion (as is the case for electrons in the Gurney-Mott theory). On the other hand, the migration of the electrons is due to the field of the bound Ag^+ ions.

While much in Mitchell's conceptions has seemed controversial and even dubious from the very beginning, they have been of undoubted value to the theory of the photographic process in that they have stimulated the performance of a large number of experimental studies. Among these, a significant role has been played by experiments in which the nature and duration of the elementary processes have been studied by application of an electric field. The individual results obtained will be presented in the following sections, while as a general conclusion we can state that most of the experimental data are not in favor of Mitchell's mechanism, certain data are simply incompatible with it. Among the latter, we must note especially two facts.

First, the positive holes, i.e., atomic halogen, not only are taken up by Ag_2S, but decompose it,[23,24] while substances which are more effective as halogen acceptors show no effect on the sensitivity of the emulsion crystals,[23] in contrast with Ag_2S. Hence, the fundamental role of Ag_2S in the process of latent-image formation does not consist in capture of holes, especially since a direct demonstration has been recently given that Ag_2S shows identical capture power for both electrons and holes.[24] Second, the mobility of holes is considerably less (by approximately two orders of magnitude) than that of electrons, and the lifetime of the former is considerably greater.[25,26] For this reason, the electron is neutralized by an Ag^+ ion, as a rule, before it can combine with a hole.[24,26] Thus we can speak only of the subsequent interaction of the atomic halogen with the atomic silver which has already been produced.

The objections to Mitchell's mechanism are not exhausted by the results enumerated here (see, e.g., references 27 and 28), and it cannot be retained in its present formulation. This does not at all nullify the value of the posing and successful solution by Mitchell of certain special problems, e.g., the possible role of dislocations in the crystals in creating sensitivity. We shall limit ourselves here to these remarks, since below we shall have to make repeated comparisons of Mitchell's conceptions as a working hypothesis with the experiments which have been set up to test them.

3. METHODS OF STUDY OF THE EFFECT OF AN ELECTRIC FIELD ON THE LATENT IMAGE AND THE PRINT-OUT PROCESS

The problem which the experimenter faces in studying the effect of a field essentially amounts to the direct observation of the latent image and its migration within an emulsion crystal. Since the latent image consists of a group of some tens or less of silver atoms, a direct solution of this problem requires exceedingly delicate methods by which the Ag centers can be enlarged to dimensions resolvable in the electron microscope without disturbing the form of the crystal or the distribution of the centers within it. Such a method is of interest in itself, and will be described in detail. However, we should first state that in cases in which the purposes and conditions of the experiments have permitted it, all the possible indirect methods have been taken. Let us mention some of them.

Many experiments with an electric field have been carried out on large mono- or polycrystalline samples, or on specially prepared emulsion crystals of flaky form with dimensions $\sim 10 - 100\mu$, i.e., on objects which can be easily studied in an optical microscope or even with the naked eye. In a number of cases, the action of light by itself or in combination with a field was sufficient (or more precisely, was made suffi-

FIG. 1. A coarse emulsion microcrystal showing a print-out effect displaced in an electric field.

FIG. 3. Envelope of an exposed emulsion microcrystal containing Ag-centers (after intensification) in the absence of a field.

cient) to carry the photolysis of the silver halide to the print-out stage, i.e., to the formation of visually resolvable silver particles, and the displacement of these particles by a field was observed directly (Fig. 1).[29,30] In other cases,[30] the visualization of the photolytic silver required a preliminary intensification by precipitation on it of additional silver or of another metal, e.g., gold. A quite suitable method for this purpose (Fig. 2) consists in weak physical development, i.e., development in a solution containing metal ions which can be reduced at the silver particles present. However, all of the enumerated methods either are inapplicable or require essential modifications when applied to the study of emulsion crystals of ordinary dimensions ($\sim 1\mu$). This entails a change from optical to electron microscopy.

As we know, a silver halide crystal is not transparent to an electron beam, as it is to a light beam. Hence, the silver particles which it contains cannot be distinguished. Besides, the rapid decomposition of the crystal under electron bombardment during the examination, being unavoidable even with low beam current density, completely distorts the picture. Hence, the silver halide must be removed before the examination. If the photolysis of the silver halide has proceeded to the print-out stage, we need only dissolve the silver halide, i.e., use ordinary photographic fixation. However, if the photolysis has proceeded only to the latent-image stage, we must also enlarge the formed centers to dimensions observable in the microscope.
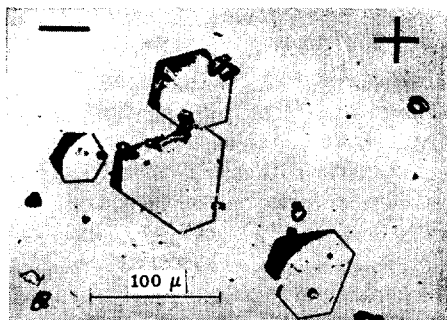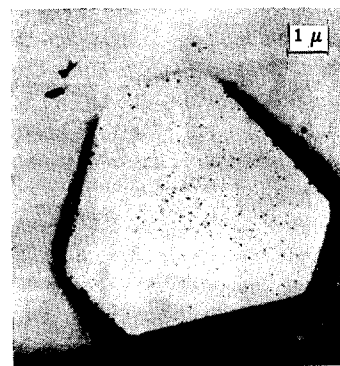
A suitable method is one of the variants of physical development, in which at first all of the crystal is dissolved but the silver particles, and then a metal is precipitated from solution on the remaining silver. However, precipitation prior to fixation is not excluded,[30,31] nor is weak chemical development (the reduction of cations from the crystal itself, rather than from solution) with subsequent fixation.[18,26]

The sites occupied by the individual microcrystals in the emulsion preparation remain visible after fixation, due to the presence of a coating around each crystal (denoted as the "envelope" in the American literature). The envelope consists of a thin film of gelatin adsorbed on the surface and bound in a gelatin-silver complex. It is permeable to solutions, and remains after the silver halide is removed. The mechanical strength of the envelope is low, and hence, it does not always reproduce the exact form of the crystal. In the early electron-microscope studies,[31,32] in which the problem was only that of determining the number and relative dimensions of the Ag centers, distortion of form played no great role. However, when it was necessary to determine the displacement of the photolytic silver, i.e., the asymmetry of its distribution in the crystal, it became exceedingly important to preserve the form of the crystal. The essential point in the successful solution of this problem is the elimination of excess strains on the envelope. This is best achieved by removing all or most of the gelatin not associated with the envelope. The necessary degree of removal of the gelatin cannot be attained by ordinary centrifugation and decantation, even if repeated several
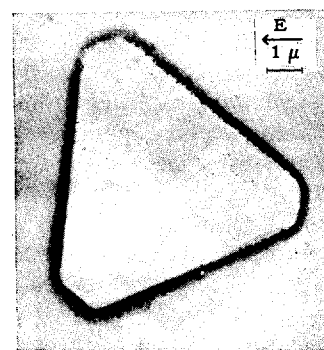

FIG. 4. The same as in Fig. 3, but with the application of an electric field during the exposure.

FIG. 2. Coarse emulsion microcrystals with a displaced latent image (photograph taken after physical development).

times.[32] Good results are obtained by digesting the gelatin outside the complex with enzymes,[31] but even under these conditions the forms of the envelopes of small or spherical crystals are not preserved well enough. Hence, the most reliable electron-microscope experiments[18,26,33] have been carried out exclusively on flaky, relatively large $(2-5\mu)$ crystals in special photoemulsions, in which it was possible to attain complete replication of the forms of the crystals by their envelopes. The possibilities of this method are presented in Figs. 3 and 4, which show photomicrographs of envelopes and Ag centers contained within them, as formed by light in the absence (Fig. 3) or the presence (Fig. 4) of a field.

Difficulties are also encountered in the electron-microscope method in the removal of the emulsion crystals or their envelopes from the support on which the emulsion preparation is placed during the exposure and chemical treatment, and in their transfer to the sample-holder (screen) of the electron microscope. Here it is necessary to preserve the orientation of the crystals with respect to the direction of the field applied during exposure. A successful choice of the substrate (formvar) coated on the glass before coating the emulsion[18] permitted stripping of the specimen as a whole from the glass and transfer to the screen. In another variant of the method, there is no substrate at all, and the emulsion layer is removed from the glass in warm water, the layer floating as a whole on the surface. However, in this method, a somewhat larger amount of gelatin must be retained in the specimen, with a loss in the resolution of details in the electron-microscope image.

Noddack and his associates[34] have proposed a more indirect method for observing the displacement of photolytic silver in an electric field, as a distinctive supplement to the methods described above. In particular, it is insensitive to the asymmetry of distribution of the silver on the surfaces of the crystals, which is so readily visible in the electron microscope, but it permits one to study the topography of the latent image, i.e., its distribution between the surface and the interior of the crystal. In microscopy, in which the study object is always a projection of the crystal on a plane, topographic observations are almost impossible.

The method, denoted as "peeling" by its authors, consists in the following. A series of coatings of the emulsion under study is prepared, all completely identical and exposed identically under an optical wedge. The subsequent chemical photographic treatment was different for each specimen. One specimen (the control) was developed immediately after exposure in the usual way, and the sensitivity of the emulsion determined from it. The next specimen was subjected before development to bleaching (treatment by a solution destroying silver on the surface of the emulsion crystals, but not silver halide). Then, a definite

amount of silver halide was dissolved (a layer of "peel" of controlled thickness was removed from each crystal). Then, only after this was the specimen developed in the same manner as for the first specimen. The difference in optical density or sensitivity between the first and second specimens was a measure of the relative amount of latent-image silver occurring in the superficial layer of the crystals which was removed. If we repeat such a "peeling" twice on the third specimen, we can then determine the amount of the latent image in the next sub-superficial layer of the crystal by comparison with the second specimen, etc. The thicknesses of the successively removed layers were found from the optical density before and after "peeling," since within rather wide limits, the optical density is proportional to the square of the mean diameter of the crystals. The authors of this method were able to repeat the removal of "peel" from one and the same set of crystals up to five times in their experiments. By a comparison of the results for the same emulsion with or without the application of a field, they were able to follow the redistribution of the latent image due to the action of the field. Their results are given in Sec. 6.

In speaking of the "peeling" method, we must note the following fact. This method basically follows a classical method of photographic research, in particular, sensitometry. Hence, it permits us directly to obtain a macroscopic expression of the microscopic changes which take place in the individual crystals, i.e., the change in the sensitivity of the emulsion as a whole. Such a combination of macro- and micro-methods is very convenient. On the other hand, in electron microscopy we must determine the characteristics of the individual crystals and the emulsion as a whole in independent experiments. If we add the fact that parallel sensitometric experiments have not been carried out in any of the electron-microscope studies, we would even now not be able to compare the phenomena observed in individual crystals and in the whole emulsion, unless we had at our disposal the results obtained by the "peeling" method.

4. IONIC CONDUCTIVITY OF SILVER HALIDE CRYSTALS AND IONIC PROCESSES IN AN ELECTRIC FIELD

The nature of the ionic current carriers in silver halides may be now considered to be finally established as a result of a prolonged discussion elicited by a paper by Mitchell.[15] Namely, at temperatures considerably below the melting points, the ionic conductivity of the silver halides is completely due to Frenkel defects, i.e., Ag^+ ions and corresponding vacancies. The fundamental interest in the study of the ionic stage of latent-image formation, whether within an electric field or not, is now concentrated on the measurement of two interconnected quantities: the ionic conductivity

of the crystals and the duration of the ionic stage. The importance of these measurements arises especially from the fact that there have been practically no data up to now on the dark conductivity of emulsion crystals at the usual temperatures of practical photography. Theoretical considerations on latent-image formation are still based on highly questionable values of σ. There are certain peculiarities in the temperature-dependence of σ in the silver halides, such that we cannot apply to the emulsion microcrystals results obtained from large single-crystal samples, just as we cannot extrapolate values of σ obtained at certain temperatures to another temperature range. Hence, we shall discuss the existing data on the ionic conductivity of the silver halides in somewhat greater detail.

Lehfeldt[35] was the first to show, with large single crystals of AgBr and AgCl, that the graph of $\ln \sigma = f(1/T)$ is not a straight line for the silver halides, as might be expected on the basis of the Boltzmann character of the relation of σ to T. Rather, the curve is broken, or in other words, consists of two linear portions differing in slope, i.e., in activation energy. The high-temperature portion of the curve (for AgBr, above 0° C) coincides for all samples, while the low-temperature portion depends considerably on the past history of the sample. At room temperature, σ equals $\sim 10^{-8}$ ohm^{-1}cm^{-1}, and this order of magnitude has later been confirmed repeatedly with large crystals of AgBr, independently of the principles or methods of the experiment. In all of the temperature experiments, the presence of a break in the curve has also been continually confirmed, and as the studies have been extended to lower temperatures, further breaks have been discovered. Thus, Matejec[20] went down to $-183°$ C, and found as many as five component parts of the curve of $\ln \sigma = f(1/T)$, each with a differing slope.

Shapiro and Kolthoff[36] have repeated the measurements of Lehfeldt on samples of a different texture, i.e., pressed and thermally-aged AgBr powders. Owing to their highly extended surfaces, such samples are much more like emulsion crystals than those studied by Lehfeldt. The latter authors also found two linear portions in the curve, with the essential difference that the low-temperature branch started at $50 - 100°$ C (Fig. 5). The slope of this branch was
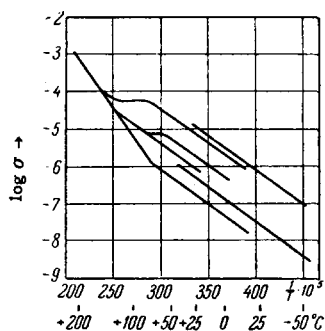
FIG. 5. The temperature-dependence of the ionic conductivity of pressed and thermally-aged AgBr powders (the various curves in the low-temperature range correspond to specimens with varying histories).

the same for all samples. That is, the activation energies, and thus also the physical nature of the low-temperature conductivity in them were identical. The authors associate the difference in values of σ for different samples with their differing surface areas, and suggest that surface conduction takes place within this temperature range. The extreme values within the entire series of samples differ by two orders of magnitude, and exceed the values obtained by Lehfeldt for this temperature range by one to three orders of magnitude. Thus, it is apparently impossible to apply a σ value found for larger crystals to emulsion crystals. This is all the more true, since in Lehfeldt's experiments $+20°$ C corresponded to the high-temperature branch.*

Until recently, the most direct determination of σ in emulsion crystals was that of Zimens.[38] He measured the rate of exchange of radioactive silver ions between a photographic film and a given solution. We have used the value which he obtained ($\sim 10^{-7}$ ohm^{-1} cm^{-1} or $\sim 10^{5}$ CGS units) in our calculations in Sec. 2, and have found good agreement of the duration of the ionic stage thus calculated with the turn-over point observed in the study of reciprocity-law failure. However, it was still not known on which branch of the σ-T curve this single experimental point lay, nor to what degree the value obtained depended on the peculiarities of the emulsion. In this regard, considerably more complete results have been obtained in experiments in which an electric field was applied, as outlined below.

There are as yet only two studies concerning the action of a field on ionic current carriers in emulsion crystals. One of these (Klein and Matejec[30]) was purely qualitative, and in spite of its highly graphic character, only indicated the possibility of using a field to study the ionic process and its effect on the latter. The second study (Hamilton and Brady[33]) was quite quantitative and highly significant in volume of results obtained.

Klein and Matejec had the limited goal of directly demonstrating the participation of mobile interstitial Ag$^+$ ions in the formation of photolytic silver, in a way similar to that used to demonstrate this for the photoelectrons.[18,39] In their experiments, they used special very coarse-grained ($> 10 - 20\mu$) emulsions. A d.c. field of 10^4 volts/cm was applied to the crystals prior to the beginning of the exposure. The field caused the ionic defects in each crystal to migrate toward the cathode (interstitial Ag$^+$ ions) or to the anode (cation vacancies). Thus, a counter field was formed in each crystal opposing the external field and partially or completely (in the ideal case) compensating for it.

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*Neglect of this fact led Mitchell (see his private communication to Zharkov[37]) to an erroneous statement that the concentration of interstitial Ag$^+$ ions is so small that there are none within the volume of an ordinary emulsion crystal ($\sim 1\mu^3$) at room temperature.

Under these conditions, the photoelectrons which were formed during the subsequent exposure participated in forming Ag centers only on the cathode side of the crystals, even though the residual uncompensated external field initially displaced them toward the anode. As can be easily seen, the reason for this asymmetry was the absence of mobile Ag^+ ions at places other than the cathode side of the crystals. The other possible positive current carriers, electronic holes and anion vacancies, had no relation to the asymmetry of the formation of silver, the former in view of their known ability to destroy photolytic silver, and the latter because anion defects are absent in the silver halide structures up to fairly high temperatures.

The micrographs which the authors obtained make this quite obvious. Figure 2, which was introduced earlier in another connection, shows the distribution of the latent image in the experiments of Klein and Matejec. An analogous pattern has been observed also in the relatively longer exposures giving a print-out effect (Fig. 1). An interesting peculiarity in the latter case is the well-marked etching (solution) of the crystal on the anode side. This demonstrates the migration of a large number of Ag^+ ions from this part of the crystal. To judge from the way in which the side faces of the crystal have been preserved, the migration of ions took place through the interior, rather than on the surface of the crystal. We should state in this regard that the volume character of the migration of ions in the development process has been observed by the same authors by a very clever method.[40] They placed a drop of developer on the upper surface of a flat single-crystal plate of AgBr floating on water. After some time had elapsed, they made a replica and studied it in the electron microscope. They demonstrated surface etching in the region of the lower side opposite the drop of developer, without any changes in the remaining parts of the upper, lower, and lateral surfaces. That is, there was no noticeable surface conductivity. Since in both of the major competing theories (Mitchell and Gurney-Mott), development is considered to be a direct continuation of the photolytic process, the experiments outlined here also indicate the volume character of the ionic stage of photolysis.

In the second of the studies of interest to us on the action of a field (that of Hamilton and Brady), a rather coarse-grained $(2-5\mu)$ emulsion of the "primitive" type was used. The latter designation indicates that any factors capable of forming impurity centers were avoided as far as possible during preparation. The samples of this emulsion were subjected to a pulsed field in which the duration of each pulse was regulated within the limits $0.25-3$ μsec, and also to a pulsed illumination with duration 0.1 μsec. The frequency was 1000 pulses per second. Both the field and light pulses were square.

The illumination was retarded after the cut-off of the field by a certain given time interval which was varied from 0 to 16 μsec. After some thousands of repetitions of such pairs of pulses, latent-image centers appeared in an appreciable fraction of the crystals. These centers could be intensified by development (in these experiments chemical development was applied, rather than physical, as used by Klein and Matejec). The cycle of treatments of the samples described in Sec. 3 finally permitted them to see these centers in the electron microscope and measure the asymmetry of their distribution.

The quantity Δ, which was determined as follows, was taken as a measure of the asymmetry. Let N be the number of centers found in all the examined crystals, of which n_1 are displaced toward the edge in the direction of the field, n_2 are displaced toward the edge opposite the field direction, and n_3 are found outside the periphery. Then Δ is defined as the ratio of $n_1 - n_2$ to N. With the most complete displacement of the centers by the field, $n_1 = N$ and $\Delta = 1$; while in the absence of the field $n_1 = n_2$ (on the average) and $\Delta = 0$. Of course, it required considerable statistics to obtain reliable values of Δ, and in each case as many as 500 crystals or ~ 2000 centers were examined. Since Δ is a relative quantity, its physical meaning is not so important. In any case, it can serve as a measure of the internal field intensity. In specially designed experiments, a proportionality was established between Δ and the external field intensity up to $\sim 10^4$ v/cm, but saturation set in beyond this point. While the field intensity within the crystals is not precisely known, and differs from that of the external field, the existence of the direct proportionality between Δ and E compels us to assume a proportionality between the external and internal fields. Hence, Δ may characterize the relative internal field intensity. If we limit E to the range up to $\sim 10^4$ volts/cm, the decline in Δ with increasing lag of the illumination behind the field is completely equivalent to the decay of the polarization field in the crystal. Hence, we can always replace Δ by E/E_0 ($E = E_0$ when there is no lag), making use of the established relation between Δ and E.

Figure 6 gives the experimentally obtained relation of E/E_0 to the lag t_i of the exposure with respect to the field pulse (of duration 2 μsec) at three temperatures. (The temperature was controlled by a warmed or cooled air stream.) The time τ required for E/E_0 to decrease to $1/e$ amounted, respectively, to 0.33, 0.9, and 3.7 μsec. In its physical meaning, τ must be identical with the time constant of a circuit containing a capacitance and an ohmic resistance. In the first approximation, each flaky emulsion crystal may be considered to be a flat capacitor (for a detailed discussion of this assumption, see reference 18). Thus we have $C = \epsilon S/4\pi d$ and $R = (1/\sigma)(d/S)$. Hence, $\tau = RC = \epsilon/4\pi\sigma$. Thus, the value found for τ permits us immediately to determine σ and its temperature dependence. The former quantity at room temperature is 9×10^{-7} $ohm^{-1}cm^{-1}$ (8×10^5 CGS units), while the
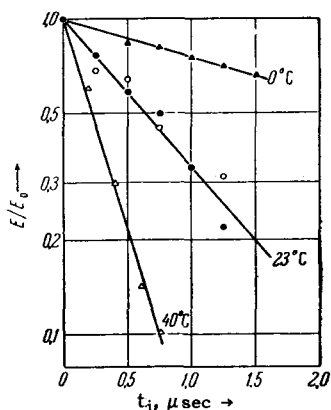
FIG. 6. The relaxation of the internal field in emulsion crystals as a function of the lag of the exposure behind the electric-field pulse.

latter is purely a Boltzmann function with an activation energy of 0.42 ev. Thus, the ionic conductivity of emulsion crystals in considerably higher than that of large single crystals.[35] Also, the temperature 23° C lies on the low-temperature branch of the conductivity curve, for which the activation energy is 0.36 ev, according to the literature data[20],[36] (see also reference 5). This highly important result loses none of its value from the erroneous interpretation made by its authors, which we shall discuss below.

An interesting result was obtained in this study by the action of "polarization" field pulses, in the terms of the authors. These were distinguished by rather long duration (up to 10^{-3} sec) and by a slower rate of change of the field. Thus, the migration of the Ag^+ ions was able to keep up with the changes in the internal field. The relaxation of the internal field after such pulses took place appreciably more slowly. Thus, at room temperature τ was now 3.6 μsec instead of 0.9 μsec, as for "instantaneous" pulses. This shows that no appreciable number of defects took part in the conductivity. Probably, this was because they were captured by the surfaces of the crystals and the surrounding gelatin. This fact may be essential if we apply the results obtained with "primitive" crystals to chemically sensitized crystals, whose surfaces contain plentiful traps. Even if the experimental conditions were varied, and the illumination was retarded with respect to the field by a period much greater than the relaxation time, the asymmetry of the latent image persisted partially, and τ was greater than for "instantaneous" pulses.

We shall now consider Hamilton and Brady's interpretation of the value of σ which they measured. Ascribing great significance to the difference between their data and those obtained for large single crystals, these authors correctly rejected Mitchell's conclusion that interstitial Ag^+ ions are absent in emulsion crystals at room temperature (see the last footnote). However, the other conclusions which these authors made on the basis of their experimental data seem at least to be debatable. For example, the authors persistently emphasize the difference between the values of σ and U obtained from purely photographic experiments

(from reciprocity-law failure) and from their experiments. From this difference, the authors draw the completely false conclusion, in our view, that Berg's experiments (described in Sec. 2) afford no proof in favor of the Gurney-Mott mechanism. In view of the great significance of this question in understanding the processes in emulsion crystals, we shall take up the question in more detail. Here we shall show that Hamilton and Brady's conclusions are due, to a considerable extent, to the use of certain unreliable data taken from the literature.

According to Hamilton and Brady, their new value of σ gives a poorer agreement by a whole order of magnitude than that previously found between the calculated duration of the ionic stage of latent-image formation and that measured experimentally by Berg. Here, Hamilton and Brady followed Berg in assuming that the experimental turn-over point for reciprocity-law failure is 4×10^{-5} sec at 20° C. The value of σ known theretofore from large-crystal experiments gave a calculated value $t_n = 2 \times 10^{-4}$ sec. The fivefold discrepancy was considered quite allowable. However, the value of t_n obtained by Hamilton and Brady (interpolated to 20° C) was 1.2×10^{-6} sec, so that the discrepancy became more than thirtyfold. However, in fact, Berg's data are quite unreliable, since the time range $\sim 10^{-5}$ sec was at the limit of measurement of his apparatus. Our data,[13],[41] obtained with more highly refined apparatus, show that the turn-over point for reciprocity-law failure is about 1×10^{-5} sec at room temperature. Thus, the discrepancy between calculated and experimental values becomes only eightfold, or about the same as it was before. We must also take into account the effect of the surface of the crystals on t_n, which was so clearly demonstrated in the cited experiments with "polarization" pulses. In particular, in Hamilton and Brady's "primitive" crystals, where this effect is much smaller, t_n must also be smaller than in the crystals in chemically sensitized emulsions, as were used in Berg's experiments and ours. Hence, the existing discrepancy provides no basis for definite conclusions counter to the generally-accepted conclusions from Berg's experiments.

If these considerations perhaps do not completely eliminate the discrepancy between theory and experiment, in any case, they do not favor Mitchell's theory. In fact, if the mechanism of the ionic stage of the photographic process is a diffusion process, rather than a Coulomb process, the rate of migration of the ions should be lower than would be expected from the calculation given in Sec. 2, and the duration of the ionic stage correspondingly longer. In fact, the converse is true, and hence, the migration of the ions is due to the attraction of the bound electrons, rather than to diffusion.

The other arguments of Hamilton and Brady against the usual interpretation of Berg's experiments are based on the lack of agreement between the values of

U found in direct photographic experiments and those found by conductivity measurements. These arguments are even less convincing than those given above. The result taken for comparison with Hamilton and Brady's data was the value U = 0.69, which was obtained by Webb[42] from an analysis of reciprocity-law failure in the region of short exposure times at various temperatures. Actually, Webb's result is much closer to the value of U for high-temperature conductivity (~ 0.8 ev) than for low-temperature conductivity (0.36 ev). In any case, it is far from the value 0.42 ev found by the authors. However, Webb's result was due to a rather arbitrary and rough analysis of the reciprocity-law failure curves. In particular, the effect of temperature on the curves was for some reason reduced simply to a parallel shift. Such a rough approximation is not confirmed by any other experimental data,[11-13] and the value of U thus obtained can only provide an order of magnitude. Much more precisely, we may determine U from the same curves from the temperature shift of the reciprocity-law turn-over point. The corresponding values of U, according to our data,[13] are 0.41 ev for the temperature range from + 60° to − 20° C, and according to Berg's data,[11] ~ 0.4 ev for the range from + 20° to − 78° C, in very good agreement with Hamilton and Brady. Thus, the discrepancy in the values of U from photographic and electrical measurements, which had been made the basis for sweeping conclusions, actually does not exist.

The problem which remained least clear after all of these experiments was whether the conductivity in the emulsion crystals at room temperature was a surface or volume conductivity. The agreement of the U value from Hamilton and Brady's experiments with that obtained earlier by Shapiro and Kolthoff somehow implies a surface character of the conductivity. On the other hand, the experiments of Klein and Matejec (see above) indicate a volume character. However, we should note that Shapiro and Kolthoff did not present strict proofs of the surface character of the conductivity. Hence, the agreement between the U values only indicates that the processes in the emulsion crystals and in the pressed or heated powders are identical, but this is not enough to establish the nature of these processes. In any case, this problem requires more detailed study.

5. ELECTRON AND HOLE CONDUCTIVITY OF SILVER HALIDE CRYSTALS IN PULSED ELECTRIC FIELDS

In the study of the electronic stage in silver halide crystals, not only the measurements of the mobility, lifetime, and certain other characteristics of the current carriers are of interest, in contrast with the ionic stage, but also the establishment of the nature of the carriers taking part in this stage, in particular, the role of positive holes. Until recently, most of such

studies were performed on large single crystals. Although we have thus obtained much information on these problems, the data thus obtained can be applied to emulsion microcrystals to an even lesser extent than the data on the ionic stage. Data for macro- and microcrystals do not always agree even as to order of magnitude; this is due to the great influence on the results exerted by lattice defects, the surface of the crystals (including internal boundaries), presence of impurities (even in infinitesimal concentration), etc. The factors mentioned here create considerable experimental complications, far more than in the study of the ionic stage. Hence, many studies are still performed on large crystals with well-controlled degrees of lattice perfection and with precisely defined chemical composition. Nevertheless, as the experimental techniques have been perfected, studies performed directly on emulsion crystals have begun to appear. We shall discuss both types of studies here.

From the methodological standpoint, a characteristic peculiarity distinguishing the study of the electronic stage in an electric field is the fact that the illumination precedes the field instead of lagging, as in the study of the ionic stage. This mode of operation was chosen even in the first studies of Haynes and Shockley,[43,29] who were the first to study electronic processes in silver halides by means of pulsed fields. They have retained this method essentially without change in many later studies. Another peculiarity of the method of study of the electronic processes is the choice of a duration for the light pulse short enough that the ionic processes can exert no appreciable influence on the field within the crystals. Thus, it is no longer necessary to perform the experiments at low temperatures and thus to obtain data of doubtful value under ordinary photographic conditions.

In Haynes and Shockley's experiments, the material was AgCl, as in a number of other studies. This substance shows a number of advantages over AgBr, but is fully similar in its fundamental properties. The electrons were liberated in the surface layer of large rectangular single crystals by means of a periodic pulsed exposure. The duration of the pulses was 1 − 5 μsec, with a frequency of 500 − 1000 cps. The spectral composition of the light was such that the light was completely absorbed in a layer of thickness < 10^{-3} cm. Hence, electrons were initially present only in this layer. A synchronized pulsed field, also with pulses of duration 1 − 5 μsec, was applied. This field was able to displace the electrons within the crystal by macroscopically large distances, in some particular cases as far as 15 mm. With sufficiently great exposures, they could observe the appearance of columns of photolytic silver proceeding from the surface into the interior of the crystal in a direction opposite to the field (Fig. 7). If there were internal surfaces, dislocations, etc., within the crystals, the silver was deposited especially intensely on these features, thus
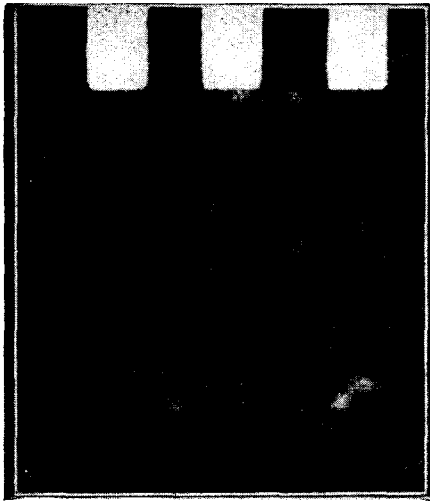
FIG. 7. Columns of photolytic silver in large single crystals of AgCl appearing at the depth to which the electric field has displaced the electrons (negative representation).

making the defects visible. In certain experiments, the Hall effect was studied on the same crystals; when the magnetic field was directed perpendicular to the electric field, curvature of the silver columns was observed. The sign, and thus the nature, of the current carriers was fully determined by the sign of the applied field. Thus, all of the measurements performed were characteristic of precisely the conduction electrons in the AgCl lattice.

The basic quantitative results of Haynes and Shockley are as follows. The drift mobility (μ_D) and the Hall mobility (μ_H) were the same within the experimental limits of error, being respectively, 49.5 and 51 cm^2/volt-sec at 25°C. In the opinion of the authors, this must indicate, first, that acoustic oscillations predominate in comparison with optical oscillations in the scattering of the electrons by the lattice, and second, that the electrons spend only a very small part of their lifetime τ trapped in shallow traps. In samples which had not been annealed to remove stresses, the lifetime amounted to 2 μsec, while annealing increased it to 10 μsec. The mean free path of the electrons was 33 A, while the total distance covered by an electron before it was finally captured was about 2×10^9 lattice constants.

Measurements of this type on large single crystals have been subsequently repeated a number of times. Süptitz[44] observed the distribution of photolytic silver in the interior of AgCl single crystals, under constant ultraviolet exposure in a pulsed field. The pulse frequency was 600 cps; the pulses were of duration 1 μsec and field intensity $4-6 \times 10^3$ v/cm. He found that μ_D = 52 cm^2/volt-sec at room temperature, in complete agreement with Haynes and Shockley. However, the τ value which Süptitz found for electrons was only ~0.1 μsec, when the specimens were of a high degree of purity. The value of τ increases to ~10 μsec, that obtained by Haynes and Shockley, under exposure to air and moisture. As Süptitz assumes, this is due to O^{--} ions and cation impurities adsorbed at the dislocations. Certain bivalent impurity ions (e.g., Ca^{++}),

when especially distributed along the dislocations, acted as traps and reduced μ_D to ~40. Brown[45] used an alternation of light and field pulses, and obtained a τ value in AgCl for electrons of $\lesssim 10^{-2}$ μsec if the crystals were annealed and free from traces of Ag or Ag$_2$O. In air or in the presence of moisture, τ was ~10 μsec. An attempt was made to measure the τ value for holes under the same conditions, with a negative result. This must mean that this τ is $< 4 \times 10^{-3}$ μsec, on the basis of the time resolution of the apparatus. However, as we shall see below, there is another way of interpreting this result. A value was obtained for μ_D close to the previous value, 46 cm^2/volt-sec.

In other studies, Brown's group has investigated the low-temperature behavior of AgCl crystals. Thus, Van Heyningen and Brown[46] observed a rapid decrease in the migration of electrons with decreasing temperature in the temperature range 6.5 − 178°K. This decrease was due to more frequent capture of the electrons by the traps. From these data, they could estimate the concentration and depth of the traps existing in the crystals. Two groups of traps were clearly manifested: a smaller group of deep traps (~0.5 ev) with a concentration of $\sim 10^{12} - 10^{15}$ cm^{-3}, and a group of shallow traps (< 0.1 ev) in much greater concentration than the deep traps. As we might expect, the shallow traps are not effective at room temperature. The mobility of the positive holes was not detected in these experiments. In a later study of the Hall effect in AgCl at very low temperatures (8°K), Kobayashi and Brown[47] also could detect no participation of holes in the conductivity. The measurement of μ_D for electrons did not give a definite result, due to the large (and rather unstable) role of repeated temporary capture of electrons by holes. In any case, the equality $\mu_D = \mu_H$ existing at room temperature was no longer obeyed.

Some data were also obtained by Brown and his associates for AgBr, which is more important in photography. However, no particular differences were found between AgBr and AgCl. At room temperature in air, the τ value for electrons was ~1 μsec.[48] That is, it was somewhat shorter than for AgCl under the same conditions. In vacuo, τ is of the same order of magnitude for AgCl and AgBr, namely ~5×10^{-3} μsec. In a study of the Hall effect at low temperatures,[49] a value was obtained for μ_H of the same order of magnitude as for AgCl. The temperature-dependence of μ_H expressed in the form ln μ_H = f(1/T) showed a strictly linear decrease for T > 40°K. This is characteristic of optical, rather than acoustic lattice oscillations. The same conclusion had been previously been drawn[46,47] for AgCl (incidentally, in contradiction to Haynes and Shockley). Hole conduction was not detected in AgBr, just as in AgCl.

The migration of current carriers in large crystals of the silver halides has also been studied with regard

to the use of these crystals as detectors for nuclear particles. The data obtained agree well, in general, with those of Brown's group. Thus, for AgBr at 77°K, μ_D was 210 cm²/volt-sec according to certain data,[50] and 240 cm²/volt-sec according to others.[51] The concentration of traps here was 3×10^{13} cm⁻³, and τ was 6.3 μsec. The values obtained for AgCl under the same conditions were:[51] $\mu_D = 60 - 70$ cm²/volt-sec (lower than Haynes and Shockley's value), $\tau = 1.2 - 3.6$ sec, and the concentration of traps was $(5 - 15) \times 10^{13}$ cm⁻³. With increasing temperature, μ_D decreased, becoming less than 100 cm²/volt-sec for AgBr at 200°K, while AgCl gave values of the order of those cited by Haynes and Shockley. The participation of holes in the conduction was not observed in a single instance.

The first account of hole mobility in the silver halides was a reference by Smith[52] to unpublished data of Moore. According to his data, the values of μ_D in AgCl at -100°C for electrons and holes were 70 and 41 cm²/volt-sec, respectively. Both current carriers showed the same value of τ, 1.5 μsec. These data have never since been confirmed, although they might well arouse interest in view of Mitchell's assumption that the mobility of holes is higher than that of electrons. Besides, if these data should be confirmed, and we take into account the ideas expressed by Mitchell and Mott[22] on the difference in the temperature-dependence of the mobilities of holes and electrons (the former increases while the latter decreases with increasing temperature), Mitchell's assumption is immediately convincingly confirmed. However, Mitchell did not pay proper attention to these data, and referred (see his review[6]) to the purely qualitative results on the resorption of photolytic silver or the change in conductivity of silver halide crystals in atmospheres of the halogens. However, it has been recently possible by such methods to obtain reliable quantitative data on hole mobility. These data have turned out to oppose Mitchell's assumption, and in all, to deprive Smith's results of any significance.

In particular, Hamm[25] has obtained the following results with large single crystals of AgBr sputtered on one side with a film of silver. Holes were injected on the side opposite the sputtered film by exposure to monochromatic ultraviolet light for 365 μsec. The depth at which this light was attenuated by a factor of 1/e was 1.5 μ. Under these conditions, he could observe a gradual bleaching of the silver film, provided that an electric field in the proper direction was applied to the crystals simultaneously. Without the field, no bleaching was observed. The values of μ_D and τ for holes were determined from the rate of bleaching; these were 0.5 cm²/volt-sec and 20 μsec, respectively. Hanson and Brown obtained a value of the same order of magnitude, but for μ_H, which is always as large as or greater than μ_D.[53] They found that μ_H was 1.7 cm²/volt-sec at 27°C in a study of the Hall effect in AgBr

specimens into which holes were injected from a bromine atmosphere. Thus, the mobility of holes was in all cases 1.5 − 2 orders of magnitude lower than that of electrons under comparable conditions.

The migration of electrons and holes in AgBr crystals was also observed in a study by West and Saunders.[24] They studied the distribution in depth of the photolytic silver as a function of the presence of impurities known in photoemulsion technology to be chemical sensitizers. Among the experiments which they carried out, the following are of especial interest. In these, a negative potential was applied to the surface of the crystal opposite the illumination, the light being completely absorbed within a distance considerably shorter than the distance between the surfaces. This led to a reduction of the blackening of this surface due to the migration of holes to it. We should note that certain other results were also obtained in the same study permitting a direct judgment on the role of holes in the photolysis of the silver halides. Thus, Mitchell's postulate that electrons and holes arriving at one and the same region of the surface will unavoidably recombine has not been confirmed. Rather, we might speak of the action of holes (i.e., atomic bromine) on silver atoms after the latter atoms have already been formed by combination of electrons with Ag⁺ ions. We shall also cite the fact discovered by West and Saunders that an intermediate Ag_2S layer in composite ("sandwich") crystals has the same acceptor power for electrons and holes, as has already been noted in Sec. 2.

In all of the studies described up to now, the exposures given were sufficient to produce a print-out effect. Smaller exposures generating silver in the form of a latent image are not suitable in experiments in which a field is applied to large single crystals. This is because it is impossible to intensify the silver within the crystals by development and thus render it visible. It was first possible to use exposures at the latent-image level only in experiments with specimens of a different type, namely, thin plane-parallel polycrystalline plates grown from silver halide melts between two glass plates. Such specimens, considered as models for a photographic emulsion, have been widely applied by Mitchell and his associates in various experiments, including some in which a field was applied. However, the latter type of experiment has played only an insignificant role in the studies of Mitchell's group, and has had only a qualitative character.

In one series of experiments by Mitchell,[54] the specimens were placed between the plates of a condenser and subjected to synchronized pulses (50 μsec) of light and of a weak field. In the specimens which had not been chemically sensitized, only an internal latent image was found, but not a superficial one. The authors assumed that this was due to recombination with bromine at the surface. Thus, in these experiments the field was not able to separate the electrons and holes spatially. They noted the liberation of silver on

the anode side in sensitized specimens, indicating a relation between the first stage of photolysis and the migration of electrons. (This is a conclusion which Mitchell later rejected.[6,22]) They also noted that the grain boundaries in polycrystalline specimens interfered with the diffusion of electrons. In another series of experiments,[55] pulses with a frequency of one cycle per second were applied, the light pulses being of 1 μsec duration, and the field pulses of 100 μsec, with a maximum potential of 10 kv applied to plates spaced ~ 7 mm apart. They noted again the absence of a superficial latent image in unsensitized specimens, and its presence in sensitized ones. A new result in these experiments was a distinct displacement of the latent image (only the superficial image, but not the interior image) from the illuminated portion of the crystal toward the anode side.

Mitchell's group was also the first to carry out studies on the effect of an electric field on photolysis in emulsion crystals themselves.[55] They used a coarse-grained (up to 8μ) emulsion having crystals of flaky form. The authors applied the same method which had permitted the displacement of the latent image in the polycrystalline specimens, but were unable to get an analogous result with the emulsion crystals. Whenever the latent image was found outside the illuminated portion of the crystal, it was distributed completely randomly about the periphery, regardless of the field polarity.

The first positive results with regard to the effect of a field on the crystals of a photoemulsion were obtained by Webb.[39] In his experiments, specimens of a very coarse-grained (up to 10μ) emulsion were repeatedly exposed to pulses of duration 3.33 μsec at frequencies up to 500 cycles. Each light pulse was followed by a field pulse of duration 20 μsec and intensity 11 kv/cm in the emulsion (i.e., the dielectric constants of the silver halide and the gelatin were taken into account). The chosen exposure level was sufficient to give a print-out effect. The lag of the field with respect to the light could be varied within the limits from 0 to 44 μsec. They observed a distinct displacement toward the anode of the photolytic silver formed in the crystals. This result definitely indicates the electronic character of the first stage of photolysis, in agreement with the Gurney-Mott mechanism. When the lag of the field with respect to the light was varied, the displacement remained at its maximum extent for times up to 10 μsec. Then it gradually declined, and vanished completely for lags of ~ 20 μsec. According to the initial interpretation, τ for electrons is thus ~ 15 μsec on the average, in good agreement with the data obtained from large single crystals. However, quite different, much smaller values of τ have been obtained in later experiments, and the value of 15 μsec has acquired a different interpretation.

Following Webb's study, another study from the same laboratory (Eastman Kodak) appeared (Hamilton, Hamm, and Brady[18]). This study was technically more refined and involved the latent image as well as the print-out effect. These authors used synchronized light pulses of 0.85 μsec duration (with a frequency of 750 or 60 cycles) and field pulses of 0.85 or 16 μsec duration (in the latter case only at 60 cycles) with a field intensity in the emulsion of ~ 1.5 × 10^4 v/cm.

In some cases, prolonged field pulses were applied, i.e., the so-called "polarization" pulses (which were discussed in Sec. 4). The illumination level within each individual pulse was chosen such that the number of photoelectrons formed during the pulse would be insufficient to create a space charge able to compensate for the external field. The major fraction of the experiments were performed, as usual, on a coarse-grained (> 5μ) "primitive" emulsion. However, emulsions having crystals of smaller dimensions (up to 1μ), some of which were chemically sensitized, were also used. The method of preparation and treatment of the specimens is described in Sec. 3.

A marked asymmetry was found in the distribution of the Ag centers in the crystals, both in the print-out effect (Fig. 8) and in the latent image (see Fig. 4). A displacement of the latent image was found at all exposure levels, beginning at the threshold level. The
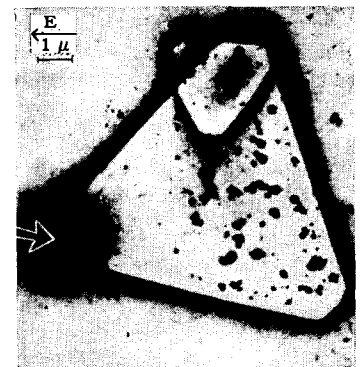

FIG. 8. Envelope of an exposed emulsion microcrystal with a displaced print-out effect and a bromine "cloud".

fraction of the total number of centers displaced by a given field in the crystals of a given emulsion did not depend on the intensity of the exposure. This constancy in the fraction of centers displaced was also found when the emulsions were subjected to identical exposures at different intensity levels, in spite of the fact that the size of the centers formed decreased regularly with increasing illumination intensity. (The reasons for this phenomenon are given in Sec. 2.) The direction of shift of the Ag centers definitely indicates the electronic nature of the first stage of photolysis at the latent-image level, as well as at the print-out level. The individual peculiarities of the emulsions used in this study had no effect on this fundamental result, in spite of all their differences. However, the phenome-

non was much more distinct with the "primitive" emulsions than with the sensitized ones.

Among the other results obtained by Hamilton's group, the "cloud" appearing at the cathode side of the crystal in the print-out effect (see Fig. 8) is of especial interest. In the absence of a field, the "cloud" is uniformly distributed about the perimeter of the crystal, while it is not observed at all at lower exposures which only produce a latent image. This explains its nature immediately: the cloud consists of bromine bound to the gelatin. Also, judging from its distribution, it must be due to the positive holes (atomic bromine) displaced by the field. An attempt to detect the displacement of holes at the latent-image level gave no definite result. The variations which could be observed in special experiments with a variable field direction during the exposure were within the limits of the variations found in control experiments without a field.

Another important result of this study is the fact that practically all the electrons displaced to the edge of the crystal were captured there within the duration of the briefest pulse (0.85 μsec). Hence, τ for electrons is $\lesssim 0.85$ μsec, although it is not clear how valid this value is in the absence of a field, since electron capture occurs near the crystal surface with its high concentration of traps. In any case, the value of τ was much smaller in the study of Hamilton et al. than in that of Webb under comparable conditions.

All that we have presented here has demonstrated that the Gurney-Mott mechanism is followed at every stage of the photolysis. The results still were somewhat indefinite, however, with regard to the role of holes in the emulsion crystals and the value of τ as well. Hence, the studies were continued. The results, which have been published rather recently,[33,26] have given very complete data on the behavior of all the carriers (electrons, holes, and cations), not only qualitatively, but also quantitatively. We have already discussed the portion of the data involving the ionic stage.

First, certain new facts were established with regard to the print-out effect. The bromine "cloud" (see Fig. 8) could be completely eliminated by washing the emulsion before the experiment with a $NaNO_2$ solution, which is known to be a bromine acceptor. The displacement of the photolytic silver in the crystals of such an emulsion disappeared when the field lagged behind the illumination by $\lesssim 1$ μsec. However, in emulsion crystals not treated with $NaNO_2$, the displacement of Ag and Br was observed even for lag times up to $10 - 15$ μsec, and disappeared at the same time for both Ag and Br. This means that the carriers which are the limiting factor for the displacement of the print-out image are holes, and the value of τ measured by Webb pertains particularly to them. The τ value for electrons is much smaller. Thus the lack of agreement between Webb's results and those of Hamilton's group has been resolved. Subsequent experi-

FIG. 9. The dependence of the asymmetry of the latent image on the lag of the electric-field pulse behind the exposure. 1 – "instantaneous" square field pulse, 2 – "polarization" field pulse.
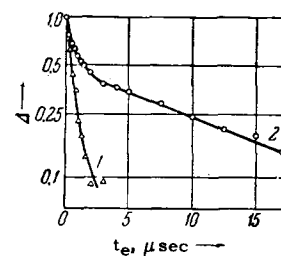
ments on the displacement of the latent image have fully confirmed this interpretation.

We shall now summarize the fundamental results relating to latent-image formation. For the details of the characteristics of the light and field pulses and the way in which the asymmetry of the distribution of the Ag centers is expressed, we refer the reader to Sec. 4, where this part of the work has been discussed. The most important relations are shown in Fig. 9, in which the asymmetry Δ of the latent image has been plotted on a semi-logarithmic scale as a function of the lag time t_e of the field with respect to the exposure for two types of field pulses. These types were: an "instantaneous" square pulse of duration 3 μsec, and a prolonged "polarization" pulse. Before discussing these curves, we note two facts which facilitate their interpretation. First, as a special analysis performed by these authors showed, when it is the photoelectrons (rather than the ions, as in Sec. 4) which are displaced by the field, Δ has an exact physical meaning: it directly expresses the ratio of the number (n_1) of electrons displaced toward the anode side to the total number N of photoelectrons formed in the crystal. Second, the character of the field relaxation in the crystal depends on the type of pulse. Thus, the effect of a pulse of duration 3 μsec is manifest in the displacement of only those carriers which have been captured in traps before the pulse ceases. The abruptly marked phenomenon in which the field reverses at the instant of pulse cut-off leads to the consequence that all the carriers of greater lifetime will hardly be displaced. This is the result of almost identical displacements in the forward and reverse directions. On the other hand, with a "polarization" pulse, relaxation occurs in an undistored way, and thus one may study the kinetics of capture for carriers having any value of τ.

Let us refer again to Fig. 9. If the linear portion of curve 2 is extrapolated to its intersection with the vertical axis, the difference between extrapolated and actual values of Δ may be plotted as a curve similar in form and in calculated values to curve 1 in the same diagram. Thus, the total curve for the field relaxation over a broad range of variation of t_e can clearly be resolved into two components, which obviously characterize two groups of carriers with widely differing values of τ. The simplest way to determine the identity of these groups was to repeat the same experiments on emulsion preparations treated with $NaNO_2$ solution,

as mentioned above. No change was brought about in the short-lived component in this way, but the long-lived component was shifted vertically on the graph in a parallel fashion. Hence, the latter component must pertain to holes. The shift which it undergoes is associated with the fact that the action of the bromine at the cathode side is reduced because of the added acceptor action. Then, the number of centers (n_2) formed there is increased correspondingly, with a decrease in the asymmetry (Δ) of the silver distribution. The behavior of the short-lived component when $NaNO_2$ is introduced into the emulsion undoubtedly indicates its electronic nature, just as does its lifetime (which is in complete agreement with previous results[18]). Thus, from one experiment it is possible to find the regularities of behavior of both types of carriers participating in the electronic stage. The interpretation presented here for the curves $\Delta = f(t_e)$ is of great importance in testing Mitchell's assertion that the value of τ for holes is small in comparison with that for electrons. As we see, the curves obtained refute this assertion. Hence, another assertion of Mitchell also fails: that hole conduction cannot be observed in many experiments (including those discussed above) because of the short τ of holes.

The quantitative regularities of electron and hole conduction may easily be found from an analysis of the curves in Fig. 9. Thus, if we plot the short-lived component in the form of a graph $\Delta_0/\Delta = f(t_e)$ (where $\Delta = \Delta_0$ when $t_e = 0$), it will be a linearly-increasing function. If we take into account the fact that for the electrons $\Delta = n_1/N$, and replace Δ_0/Δ by N_e/N_0 (where N_e is the number of free electrons in the crystal at time t_e after the exposure), we may derive a hyperbolic law for the decay of the electronic conductivity: $N_e = N_0/(1 + \alpha t)$. An analogous relation has been established by Meiklyar[56] for the relaxation of the photoconductivity in large mono- and polycrystalline samples of AgBr and AgCl, although with a fractional exponent in the hyperbolic relation. From the slope of the line $\Delta_0/\Delta = f(t_e)$, α is equal to 3.7 μsec^{-1}. That is, the half-life of the electronic conductivity is 0.27 μsec. The analysis of the long-lived component is even simpler: the linearity of the semilogarithmic plot shows directly that the number of free holes decreases exponentially: $N_h = N_0 e^{-t/\tau}$. Here, $\tau_h \sim 15$ μsec at room temperature, as it is in the print-out effect.

The hyperbolic decay law of the electronic conductivity does not, however, prove it to have a bimolecular (recombination) mechanism, since as experiments have shown, there is no necessary relation in such a case between the decay and the illumination intensity. However, the electrons do not remain in the conduction levels all the time, since this would lead to an exponential law. If an electron is assumed to have the mobility shown in large crystals, it should be able to spend some time in the vicinity of every ion

in the emulsion crystal within a period of the order of tenths of a microsecond, and it would be captured by the growing Ag centers. The number and dimensions of these centers increase with the illumination intensity and with the exposure. Nevertheless, neither factor has an effect on the decay of the conductivity, as has been shown by experiment. We may consider the most probable mechanism to be short-term capture of the electrons by adhesion levels with subsequent thermal ejection into the conduction band, repeated capture, etc. It is to this type of capture that we should ascribe the measured value of τ. The mobility μ_D of electrons estimated from the displacement of the Ag-centers in microcrystals is only ~ 0.2 $cm^2/volt$-sec, two orders of magnitude smaller than μ_D in large single crystals or μ_H (since in the latter, $\mu_D = \mu_H$). From the ratio of μ_D to μ_H we may estimate the ratio of times which the electron spends in the conduction band and in the traps. This ratio turns out to be ~ 1: 100. If we ascribe the observed difference in the values of μ_D in large crystals and in emulsion crystals to the large role of traps in the latter, we must also assume that these traps are mainly distributed on the surface, which plays a much greater role in emulsion crystals than in large crystals. We may suppose that the depth of these traps, at least in "primitive" microcrystals is small ($\sim kT$), and that the traps themselves are locally distributed.

The determination of the mobility of holes is less reliable because of the difficulties of measuring their migration. In any case, μ_D for them is $\sim 10^{-3}$ $cm^2/volt$-sec, two orders of magnitude smaller than for electrons, as is true also in large crystals.[25,53] A value of μ_D for holes close to that obtained in this study was recently measured[57] in experiments on the photolysis of fused films of AgBr in bromine vapor. Thus, the small mobility of holes is the reason that their participation in the conduction remained unnoticed in many experiments (see above). Thus, the postulate upon which Mitchell based his critique of the Gurney-Mott mechanism loses all its foundation.

The value of the results obtained with regard to the mechanism of latent-image formation is not at all exhausted with the refutation of Mitchell's postulate. Let us just recall some more important conclusions from Hamilton and Brady's study. First of all, if we compare the durations which they measured for electronic, ionic, and hole processes at room temperature (< 0.3, ~ 1, and ~ 15 μsec, respectively), it becomes obvious that the holes compete poorly with the Ag^+ ions in neutralizing the charge of the bound electrons. The role of recombination of electrons and holes in latent-image formation by the action of light must be judged to be insignificant. We may consider only the subsequent rebromination of silver. The same conclusion on the role of recombination may be drawn from other recent experiments, in particular, the measurement of the photoconductivity of emulsion layers.[58]

The repeated transitions found by Hamilton and Brady of electrons from one trap to another until they are finally bound must be of great significance in latent-image formation. This is obvious from the following considerations. We have noted in Sec. 2 that certain purely photographic phenomena, e.g., the effect of very brief exposures, cannot be explained without assuming the existence of another stage, the redistribution of the latent image, completing the process of its formation. [12,59] The same is true of the action of particles on a photoemulsion.[8] The detailed mechanism of the redistribution, as formulated on the basis of the study of the photographic action of high-frequency intermittent exposure,[59] has incorporated precisely these repeated electronic transitions as a very important constituent part. However, there were no direct proofs for the existence of such transitions at that time. Thus, data obtained[56] in a study of the relaxation of photoconductivity in large silver halide crystals were adduced to create a basis for the mechanism. However, direct confirmation has now been found for the fact that such transitions take place in emulsion crystals as well.

In concluding this section, we shall give a graphic picture of the process of latent-image formation (Fig. 10) as given by Hamilton[60] on the basis of the data of the cited study. There is no need for a special explanation after all of the preceding discussion.

6. THE SENSITIVITY OF A PHOTOGRAPHIC EMULSION IN AN ELECTRIC FIELD

If we omit the intrinsic action of an electric field on a photoemulsion layer, i.e., the formation of a
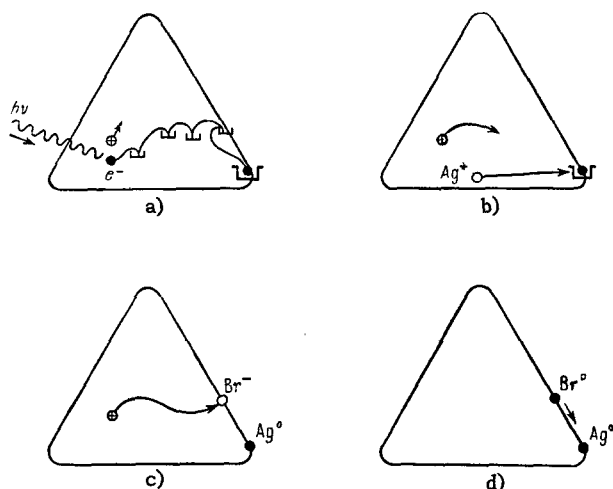

FIG. 10. Diagram of the mechanism of latent-image formation according to Hamilton. a) Absorption of a light quantum, formation of an electron and a positive hole, multiple transitions of the electron from one shallow trap to another, capture of the electron in a deep surface trap; b) competition between an Ag^+ ion and a positive hole in the neutralization of the charge of the bound electron, and the neutralization of the electron by the Ag^+ ion, with formation of a silver atom; c) emergence of the positive hole at the surface of the microcrystal at the site of one of the Br^- ions; d) formation of a bromine atom and (the possible) reaction of it with the previously-formed silver atom.

latent or visible image by the application of a field without exposure to light, the number of studies concerning the action of field together with exposure is still very small.

Noddack, Schaller, and Hecker[34] have studied the effect of an electric field on the sensitivity of an emulsion and the volume distribution of the latent image in microcrystals with the aid of the "peeling" method which they developed (see Sec. 3). The exposed emulsion (they used "Agfa-Laue" film) was placed between two glass plates which were half-silvered for electrical contact. The gap between them was 0.57 mm. The plates imparted a constant potential difference up to 4 kv, corresponding to a field intensity up to 7×10^4 v/cm. Typical results for exposure to white light are given in Fig. 11. Such a pattern has also been observed in exposure to x-rays, although the original distribution of silver was somewhat different in this case (in particular, the fraction of the latent image found in the interior was greater than with light).
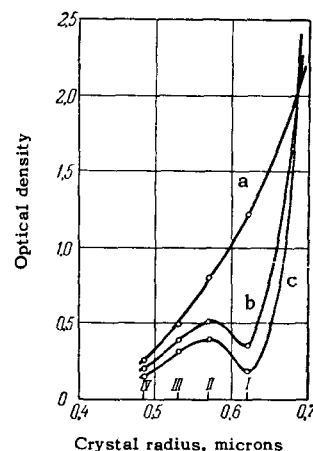

FIG. 11. The dependence of the developed optical density of "Agfa-Laue" film exposed to white light on the extent of dissolution of the microcrystals (the number of "peeling" operations for each experimental point is indicated by the Roman numeral at the corresponding radius of the remaining crystals). a) — in the absence of a field; b) — field of 17,000 v/cm; c) — field of 70,000 v/cm.

The practical increase in sensitivity in the experiments of Noddack's group is not large. Nevertheless, the field intensity here was several times larger than that which Hamilton's group found sufficient to displace the latent image completely to the surface in crystals of considerably larger dimensions. The reason for this difference, we may suppose, consists in the chemical sensitization, which was absent in the crystals of the "primitive" emulsions used by the American authors. As has been noted in Sec. 5, sensitized emulsions never gave such a clear pattern of displacement of the Ag centers as did "primitive" emulsions. The impurity centers created by the sensitization greatly decrease the mean free path of the photoelectrons in the emulsion crystals, as is implied, e.g., by the decrease in the photoconductivity of emul-

sions during the chemical sensitization.[58] Hence, the
electric field is able to extract to the surface of these
crystals not all of the electrons which are formed, but
only those concentrated in a certain sub-surface layer.
In fact, the curves in Fig. 11 demonstrate quite dis-
tinctly the appreciable depletion of photolytic silver
in the zone of the crystals lying nearest the surface,
whereas the amount of silver in the interior of the
crystals remains constant. It is a characteristic fact
that such a redistribution of the silver takes place in
approximately the same way in exposure to any type
of radiation (light of various long wavelengths, x-rays).
We also note that the limitation of the mean free path
of the electrons in emulsion crystals had already been
indirectly established previously[61] on the basis of a
study of the action of soft x-rays on emulsions having
crystals of different dimensions. The estimate made
in these experiments of the depth of the sub-surface
zone from which electrons can emerge to the surface
($\sim 0.08\mu$) agrees well with the data of Fig. 11.

The basic practical conclusion which we can draw
from the experiments of Noddack's group is that in
working with actual factory-made emulsions, a much
higher electric field intensity is required than in ex-
periments with "primitive" and other special labora-
tory emulsions. Rothstein,[1] who has performed the
most successful experiments of this type, was success-
ful only with fields of intensity two orders of magni-
tude larger. The high field intensities in Rothstein's
experiments were attained by a considerable decrease
in the width of the gap between the plates. Indeed, the
probability of dielectric breakdown was considerably
increased here, and the requirements on the insulating
properties of the emulsion and the components of the
apparatus were heightened.

An emulsion layer 5μ thick was placed between two
transparent electrodes (glass with an SnO_2 film) to
which potential differences of $1 - 2$ kv were applied.
Thus, the field intensity amounted to $2 \times 10^6 - 4 \times 10^6$
v/cm. The exposure was carried out with a special
sensitometer having a pulsed light source with a nom-
inal flash duration $\sim 10^2 \mu sec$. It was assumed that the
field pulse, synchronized with the exposure, would have
the same duration. However, in fact it was never pos-
sible to apply the field throughout the exposure, owing
to the rapid appearance of breakdown, and thus the
duration of the field pulse was ordinarily kept down
to 50 or even 12 μsec.

Figure 12 gives the results of some parallel experi-
ments of Rothstein on Kodalith emulsions. As we see,
the optical density in the presence of the field is al-
ways considerably higher than in its absence, espe-
cially in the high-density region. Control experiments
showed that a field has no action without the exposure.
Hence, the observed increase in the optical density
must be ascribed only to the intensification of the ac-
tion of the light by the field. The increase in the sen-
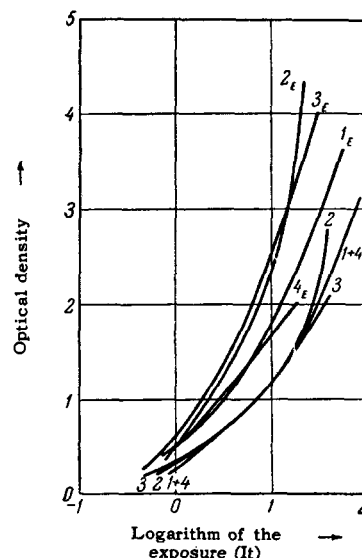sitivity was measured, as usual, by the decrease in

FIG. 12. Characteristic curves for "Kodalith" film for four
parallel experiments in which a field was applied (curves in-
dicated with a subscript), and in the absence of a field (curves
without a subscript); the curves with the same numbers refer to
the same experiment.

the exposure necessary to give a certain optical den-
sity. This increase was in any case at least twofold,
and at the higher optical densities, about fivefold. Be-
sides, as the author reported, the character of the
time variation in brilliance of the pulsed light source
was such that only $\frac{1}{17}$ of the light energy falling on the
film during the overall exposure time was utilized
within the time between application and cut-off of the
field. Hence, Rothstein considered that the actual in-
crease in sensitivity was 17 times greater than that
observed, and might amount to two orders of magni-
tude.

This result, if it can be attained reproducibly, must
be considered quite sufficient for the solution of the
problem of programmed control of the sensitivity of
an emulsion. However, we may assume that the actual
increase in sensitivity is smaller than Rothstein's es-
timate. As we may conclude from the many studies
cited above, in particular that of Hamilton and Brady,
the polarization appearing in the emulsion crystals as
a result of the external field must reduce the field
within the crystals to zero within a time of an order
no greater than tens of microseconds. Thus, the cut-
off of the field before the end of the exposure (which
was necessary to avoid breakdown) may not have
caused any substantial changes in the action of the
light, since the internal field might have already re-
laxed to an appreciable extent by this time. The co-
efficient of "under-utilization" of the field, which
was 17 in Rothstein's estimate, may actually be hardly
different from unity, and the gain in sensitivity would
then amount to one order of magnitude, rather than two.
Nevertheless, even such an increase in sensitivity is
of great significance for practical purposes.

There are as yet no definite data on which to base

the mechanism of the increase in sensitivity in fields of the order of 10^6 v/cm. For example, we can assume that the field brings about a redistribution of the latent image within the volume of the crystal. This redistribution would be of the same type as was observed by Noddack et al. in weaker fields, but merely involving a correspondingly greater depth. Rothstein holds a different viewpoint, assuming either a spatial separation of the electrons and the holes in the crystal by the field, so that recombination is prevented, or the appearance of avalanche discharges due to acceleration of the electrons by the field. He considers the first assumption less probable; in view of the series of papers[24,26,58] which we have discussed above (see Sec. 5), we may generally disregard recombination in the formation of the latent image by light. The second assumption, which is quite new in the theory of the photographic process and specific for strong fields, must be considered in more detail.

An avalanche can arise in an emulsion crystal, provided that the electron collides with a valence electron within a path length no longer than its mean free path, and excites the valence electron into the conduction band. Thus, it performs a function which would require another light quantum in the absence of a field. In other words, the quantum yield becomes appreciably greater than unity. Hence, an estimate of the field necessary to bring about avalanche formation may be given by the ratio of the width of the forbidden energy band to the mean free path. The latter has been measured only for large crystals, namely of AgCl (Haynes and Shockley[29]), but it is also valid on a rough approximation for AgBr. The required field intensity corresponds to several electron-volts per tens of Angström units, i.e., $\sim 10^7$ v/cm.

If we take into account the local levels in the forbidden band due to the structural defects in real crystals, we can make the estimate an order of magnitude smaller, in good agreement with the field intensity at which Rothstein was able to get positive results. Nevertheless, we must treat such an agreement with caution. First, the data on the mean free path and the depth of the traps are so approximate that they cannot guarantee even getting the correct order of magnitude of the field sufficient for avalanche formation. The fact is even more important that we have as yet no other proofs of avalanche formation in silver halide crystals, nor did Rothstein present any. We must also deal cautiously with Rothstein's assumption that under his experimental conditions, an avalanche could propagate from one emulsion crystal to others in its vicinity. The energy of the electrons in the avalanche does not exceed (or rather, does not reach) $1-2$ kev, on the basis of the applied potential difference. This corresponds to a path of the electron in the silver halide of no more than $10^{-2}\mu$. Hence, the probability of emergence of the avalanche electrons even from the superficial layer of the crystal is quite small. Thus, the

problem of the role of electron avalanches in latent-image formation has not at all been clarified as yet.

7. CONCLUSION

To summarize what has been discussed, we should note first that the existing studies on the effect of an electric field on latent-image formation have established considerable clarity on the fundamental problem of photographic theory. A certain indefiniteness in the interpretation of many experimental data has appeared in recent years in connection with the emergence of Mitchell's theory, but no longer exists. It has become obvious that the rejection of most of the established conceptions in favor of some poorly grounded hypotheses is in no way justified at the present state of our knowledge. Also, our knowledge of the details of the processes occurring in silver halide crystals has expanded greatly as a result of these studies. Above all, this expansion has been due largely to the use of data obtained directly from emulsion microcrystals, rather than objects substituted for them to simplify the experiment.

A result no less important is the practical attainment of a considerable increase in the sensitivity of photoemulsions by the application of an electric field during exposure. The introduction to this review has already discussed the potential significance of this method. It is also important that, as a result of the theoretical studies discussed here, we now possess sufficient information for practical purposes on the time course of the individual elementary processes and on the characteristics of the current carriers taking part in them. That is, we have the initial data for a theoretical, rather than an empirical choice of the controlling field.

However, a number of problems still remain unsolved, both theoretical and practical. As it seems to us, the basic gap in the theoretical field must be considered to be the lack of a sufficient connection between the physical and photographic experiments. On the one hand, the effect of a field on each of the elementary processes comprising the total mechanism of latent-image formation has been observed. On the other hand, an increase in the optical density after development has been observed, due to the action of a field during exposure. We see from the latter fact that an increase in the number, and probably of the dimensions, of the Ag centers on the surfaces of the emulsion crystals has taken place. However, we cannot see which of the elementary processes was involved therein, since all of these processes are sensitive to the action of a field. Until we have determined this, the choice of the parameters of the controlling field will remain fundamentally "blind," since the characteristics (in particular, the duration) of all the constituent processes are different. Although these characteristics are known for each of the proc-

esses, it is still not clear which of them will govern.

Among the practical problems to solve, those of selection of the emulsion and avoidance of dielectric breakdown are very important and interconnected, as well. As we suggested above, a considerable increase in the field intensity is necessary in experiments with ordinary emulsions, as compared with "primitive" emulsions. This is because the mean free path of electrons is much shorter in the former than in the latter, due to the chemical sensitization.

If this is true, it is reasonable to study the recording properties of "primitive" emulsions, especially since a 100-fold or even a 10-fold increase in their sensitivity at the moment of application of a field makes these emulsions comparable with many factory-made emulsions. However, if the use of "primitive" emulsions turns out to be inexpedient, or the concepts expressed above are not confirmed, the application of fields of $\sim 10^6 - 10^7$ v/cm is unavoidable. Then it will become of primary significance to eliminate dielectric breakdown, which is not a factor with lower fields. This problem is especially important in going to emulsion films of greater thickness than in Rothstein's experiments, since the maintenance of a given field intensity is associated with a proportional increase in the applied potential difference. Besides, much here also depends on the properties of the emulsion layer, the part of the circuit which most frequently undergoes breakdown. In particular, we may expect an improvement in the electrical properties of the emulsion due to replacement of the gelatin by polymers. As it happens, this problem of photographic technology is being intensively developed at present, although not in connection with the application of an electric field.

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