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EXAMINATION OF ADDITIVELY COLORED ALKALI HALIDES FOR PHOTOELECTRIC HALL EFFECT

A THESIS

SUBMITTED TO THE FACULTY OF THE RICE INSTITUTE in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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Houston, Texas

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EXAMINATION OF ADDITIVELY COLORED ALKALI HALIDES
FOR PHOTOELECTRIC HALL EFFECT

A thesis

APPROVED FOR THE DEPARTMENT OF PHYSICS
OF THE RICE INSTITUTE

by ________________
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EXAMINATION OF ADDITIVELY COLORED ALKALI HALIDES FOR PHOTOELECTRIC HALL EFFECT

I. Introduction and General Survey

HISTORICAL

Perhaps the first known instance of photoconductivity in an insulating crystal was found by Joffe\textsuperscript{1}, who, in 1903, while studying the supposed dark conductivity of various x-radiated dielectrics, noticed that that of rock salt was diminished when clouds covered the sun. Colorless rock salt is not photo-sensitive, but, when exposed to x-rays, or even to ultra-violet light, turns a yellowish to brownish color, and is then photoconducting. Naturally-occurring colored rock salt (either yellow or blue) is likewise photoconducting.

It was immediately supposed that the light-excited conductivity increase of rock salt was due to electrons emitted within the crystal lattice, since, at room temperature, its dark conductivity (which Joffe\textsuperscript{1} presumed to be mainly or wholly electrolytic) is very small. This supposition was, apparently, confirmed in 1916 when Lukirsky\textsuperscript{2} reported that he had observed a Hall effect, of sign corresponding to the magnetic deflection of a stream of free electrons, for photoelectric currents in colored rock salt. The mean free path of the electrons, as calculated from these measurements
came out (according to Joffe\textsuperscript{1}) to be of the order of $10^{-5}$ or $10^{-6}$ cm.

Tartakowsky\textsuperscript{3} has described an apparatus by means of which he demonstrated, qualitatively, a "polarization" set up in a specimen of photoconducting rock salt by the magnetic deflection of the lines of current flow. He used a divided collecting electrode, the two parts of which were connected to opposite quadrant-pairs of an electrometer. Upon applying a magnetic field of about 30,000 gauss, the current to the two electrodes was redistributed, in a way consistent with the magnetic deflection of free electrons. Upon releasing the field still another (very temporary) redivision of current occurred, which was ascribed to a "polarization" of electrons built up by the Hall field.

The standard work on the Hall effect of photoelectric currents in insulating crystals, however, was performed by Lenz\textsuperscript{4}, not on colored rock salt, but on zincblende (sphalerite) and on diamond. He found relatively large Hall fields. For example in zincblende, with an applied electric field of 5300 volts/cm and a magnetic field of only 7000 gauss, he obtained a Hall E.M.F. of 70 volts/cm, or one part in 75 of the applied electric field. The effect in diamond was even larger, about one in 40. The Hall E.M.F. in both substances was linearly proportional to the applied magnetic field, and, up to a "saturated" value, to the electric field.
Stasiw attempted to measure the Hall effect for visible, moving clouds of electrons in thermally conducting KBr (Electrons when forced into a heated, transparent alkali halide crystal color it, and the motion of the electrons can be traced by the motion of the coloring.) The Hall E.M.F. as measured was 2 to 8 times as great as that calculated for the moving color centers from their observed visible mobility. This discrepancy Stasiw ascribed to an arising of "concentration changes" between the Hall electrodes by some action of the magnetic field, and thereafter abandoned further study of the induced transverse field.

These somewhat sparse results when taken in conjunction with other lines of evidence and the beautiful simplicity of the idea have caused it generally to be taken for granted that the primary component, at least, of the photoelectric current in solid dielectrics is electronic in nature.

SURVEY OF FACTS CONCERNING PHOTOCONDUCTIVITY

A survey of the experimental facts of photoconductivity will next be presented. According to Gudden and Pohl, photoconducting crystals belong to one or the other of two very different types. In the first, called by them "idochromatic", chemically pure and apparently structurally perfect crystals are photoconducting. Diamond and zincblende, the former with atomic, the latter with ionic, lattices, are among these.
Others are cinnabar, sulphur, stibnite, mercuric iodide, the red variety of selenium, and the silver halides.* It appears that crystals of this type suitable for study are rather scarce (since a substance must be a good insulator in the dark in order for its photoconductivity to stand out well). It is a curious fact that all idiochromatic crystals found thus far have refractive indices greater than 2.

In the second class, termed "allochromatic", the crystals have no detectable photoconductivity when in their pure and, usually, colorless state. They become photoconducting only when colored with "foreign" atoms not belonging to the regular lattice, or when subjected to certain physical agencies. The outstanding examples of this type are the alkali halides, others are fluorite and the thallium halides. These substances all have indices of refraction less than 2.

Knowledge of the processes underlying photoconductivity in both kinds of crystals was chaotic, despite the publishing of hundreds of papers (mostly on selenium), until Gudden and Pohl, by using short periods of low-intensity illumination, succeeded in separating the photoelectric current into "primary" and "secondary" components. The primary photoelectric current starts without appreciable time lag, i.e., in less than $10^{-4}$ seconds, and is, at least initially, proportional to the intensity of the illumination and to the strength of the applied

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*NiX$_6$ mistakenly refers to the silver halides as "allochromatic".
electric field. The secondary current (which is the main current in selenium but is almost non-existent in the alkali halides) is probably partly electrolytic, is more than proportional to the applied field and illumination, and persists after the light has been cut off. It is supposed to be induced by some action of the primary photoelectric current, rather than by direct action of the absorbed light itself.

The primary photoelectric current in turn has been shown to be composed of two parts, the electron primary current, which is the movement of photoelectrically-emitted electrons toward the anode, and the positive primary current, which is due to the motion of the positive charges created by the photo-emission of electrons toward the cathode. At very low (liquid air) temperatures, only the electron primary current is observed. The positive charges then appear to be fixed, or at least a large positive space charge, or polarization, builds up, which soon reduces the current to a very small value. The positive primary current however, is not, presumably, to be thought of as electrolytic, i.e., as consisting of the bodily motion of positive ions through the lattice, but rather as consisting of "hole conduction", in which the position of a positive charge moves toward the cathode by steps, each consisting of the capture of a (replacement) electron from a neutral neighbor situated between itself and the cathode (figure 1). The actual motion, then, at least on the classical picture of individual particles, is that of electrons coming in from the cathode to
Schematic process of hole conduction. The hole A consecutively occupies the positions 1, 2, 3, 4 and 5 by capture of an electron from a neighbor between itself and the cathode.
replace the photoelectrons collected by the anode.

Recombination plays a minor role--even with uniform illumination of the whole crystal, the photoelectrons themselves are not numerous enough to neutralize the positive charges left by other photoelectrons. At a sufficiently high temperature (room temperature in many instances) or if the illumination includes red or infra-red light, the electron and positive components of the primary photoelectric current flow together. Otherwise the positive component may persist after the light has been cut off, diminishing until the positive space charge has been removed.

The positive component, as measured by the residual current after a brief period of illumination, appears to have the same order of magnitude as the electron component--which is the experimental evidence that recombination, at least for small currents, is, indeed, slight. De Boer assumes that the two parts are exactly equal, and attempts an explanation, but he seems entirely to have overlooked the possibility of some recombination.

As a matter of fact, the sluggish component of the primary photoelectric current is not all composed of "replacement" current. The photoelectrons, after travelling a certain distance through the lattice toward the anode, do not generally lodge in electron vacancies waiting for them; more usually, they are trapped at certain lattice points to form excitation centers, from which they may be loosened simply by
thermal agitation. The process may be repeated; electrons detached from an excitation center diffuse in the electric field until again caught (either as another excitation center or by an electron hole) or until they reach the anode.

Light-excited currents in crystals follow laws similar to those of photoelectric currents emitted from metal plates into vacuum. Both the initial and the final steady magnitudes of the current are proportionally to the applied collecting field up to saturation values. Saturation is obtained in zincblende and other idiochromatic substances by field strengths of the order of a few thousand volts per centimeter. In colored rock salt saturation requires, however, a field of about 50,000 volts per centimeter. Colored KCl and KBr, on the other hand, yield saturated currents for considerably smaller fields than for rock salt, because of the so-called thermally increased range of the photoelectrons (instability of excitation centers at room temperature).

The first confirmation of the quantum equivalence law of photoelectricity was made by means of saturation photoconductive currents obtained in diamond and in zincblende by Gudden and Pohl. Near-quantum equivalence has also been obtained with colored rock salt. (Corresponding experiments with the external photoelectric effect give, generally, quantum yields which are several orders of magnitude less than the theoretically expected value of unity.) It has also been found that the yield of photoelectrons per unit of absorbed light energy at saturation fields is inversely proportional to the
frequency, i.e., directly proportional to the wave-length, of the absorbed radiation, in good agreement with Einstein's photoelectric equation. The slope of the curve photoelectrons-per-unit-absorbed-energy vs. wave-length can be used for a rough check on the value of Planck's constant.

Photoconductive currents are, as expected, also proportional to the intensity of illumination of a given wave-length, at least for weak light and short periods of illumination. For strong light or long illumination, increased polarization cuts down the current, which is therefore noticeably less than proportional to the amount of absorbed light energy of a given wave-length.

The flow of photoconductive currents depends on the temperature of the specimen in a complicated way, particularly in the alkali halides, which have been studied more than any other substances. The various components may be most fully separated at liquid air temperatures. In very cold rock salt, for example, if illuminated for ten or fifteen seconds with comparatively weak light of the wave-length corresponding to the F-band absorption maximum (4600 Å), the electron primary current flows with practically constant value and no time lag. Upon cutting off the light the dark conductivity is greater than before illumination and dies away exponentially; it is due to the flow of the primary replacement current. If the crystal is now illuminated with red or infra-red light, an additional current flows whose time integral (total charge) may be
several times greater than that of the initial electron flow. This additional current also dies away and is ascribed to the loosening of electrons bound at excitation centers.

At room temperature the primary electron current and the compensating replacement current flow more nearly simultaneously, although the latter still lags. At temperatures above about 200° C in the alkali halides, electrolytic conductivity is comparable in magnitude with the photoelectric conductivity; the excitation centers likewise are thermally unstable. The compensating current (of several components) then flows quickly and polarization is not appreciably built up, so that steady photoelectric currents many times greater than those at room temperature may be obtained. Also the photoelectric current may be considerably increased, even at room temperature, by simultaneously irradiating the conductor with red or infra-red light, thereby removing, partially at least, the excitation centers. Nevertheless, with strong illumination, polarization (at room temperature) inevitably builds up.

The initial electron component of the photoelectric current in diamond has been shown by Lenz\textsuperscript{10} to be independent of temperature down to about -250° C, if the narrowing of the absorption band at low temperatures is taken into account.

PRODUCTION OF COLOR CENTERS

The coloring associated with photoconductivity in the alkali halides may be produced in several ways which, even after close study, do not appear to bear any direct relation to
each other. The following sources of colored crystals have already been mentioned:

1. Natural crystals.
2. X-rayed crystals.
3. Crystals exposed to ultra-violet light.

Other methods of producing colored photoconducting specimens of alkali halides are the following:

4. Heating the crystal in the vapor of any of the alkali metals. In the case of such treatment the resulting color is a function of the substance of the crystal and not of the vapor in which it is heated, although presumably it must be that of some alkali metal.

5. Driving electrons off a pointed cathode into a heated crystal. To do this it is necessary that the temperature be such that the electrolytic conduction is easily measureable with a micro- or milliammeter. The necessary applied potential is of the order of 25 volts to several thousand volts, depending on the temperature and the substance. A visible cloud, whose color is a function of the substance, then grows out of the pointed cathode and spreads, within a few seconds to several minutes of time, over to the (plane) anode. As the cloud spreads the current generally increases, and, if the temperature and the applied voltage are not too high, reaches, after the crystal has been filled with color, a new steady value many times greater than its previous value. If the direction of the applied voltage be reversed, a clear space grows out of the
anode and the colored cloud all finally appears to vanish into the cathode.

6. Impregnating the crystal with "U-centers", as will be later explained, and then flooding it with ultra-violet light. The color then develops much more rapidly than if an untreated crystal is irradiated.

The coloring may be due either to colloidal metal particles or to atomically dispersed "F-centers" (Farbzentren) in the cases of additively colored crystals (electron impregnation or vapor diffusion). Rock salt, natural or artificial, containing colloidal sodium particles is blue. It is yellow or brown, however, if the stoichiometric excess of sodium is atomically distributed. KCl and KBr are blue with the atomic distribution, NaBr brown. Although the color centers have atomic dissemination at high temperatures (above about 500°C), the alkaline excess will coagulate into colloidal particles if the substance is allowed to cool slowly. It is necessary to "quench" the heated, colored crystal, i.e., cool it to room temperature within a few seconds, if the atomic dispersion is to be retained, even partially. (Some colloidal particles will always form.) Quenching, of course, subjects the specimen to severe mechanical strain, since all alkali halides have comparatively large coefficients of thermal expansion but are poor conductors of heat. Crystals with atomically scattered color centers are better for studies on photoconductivity because they pass much larger photoelectric currents for the same light intensity and collecting field
than will crystals of the same substance with colloidal coloring.

The number of color centers per unit volume may be determined optically or, in the case of electron impregnation, electrically. Where both methods (to be described) are applicable, fair agreement is obtained, and this is considered as evidence that the color centers are associated one-for-one with the penetration electrons. The electrical method, depending on the phenomenon of visible thermal conduction, is simple. It is assumed that, until the cloud of color has been driven clear across the crystal, each penetrating electron forces out, on the average, one halogen ion, and at the same time constitutes, effectively, one color center. The total current steadily increases during the coloring (as already mentioned), finally reaching a maximum steady value when the crystal is all colored, provided the applied voltage is not so great that thermal breakdown also follows. The initial background current is known to be entirely electrolytic; the increase is therefore ascribed to electrons. (Closer analysis by Mollwo and Roos\textsuperscript{11} shows that part of the original electrolytic current is also replaced by electron current during the actual process of coloring.) Then the number of penetrating electrons is the time integral of the increase in current during the coloring process, divided by the charge on one electron. The magnitude thus computed should be multiplied by 2, according to the correction of Mollwo and Roos' mentioned parenthetically above.
The numerical density of oscillators contributing to a given color absorption band has been shown on classical theory to be

\[ N_0 = 1.31 \times 10^{17} \frac{n_0}{(n_0^{2.5})^{\kappa}} K_{\text{max}} H \]

in which \( n_0 \) is the index of refraction of the crystal at the absorption band maximum frequency corresponding to \( K_{\text{max}} \), the absorption coefficient in \( \text{cm}^{-1} \) in the middle of the band, and \( H \) is the half-value width of the band in electron-volts (figure 2). The electrons forming F-centers may be regarded as oscillators, so that this formula gives their number per unit volume.

Crystals colored photochemically, i.e., by irradiation with x-rays or ultra-violet light, are not in exactly the same condition as those colored additively, i.e., by driving in electrons or heating in the metal vapor, although they have the same induced optical absorption band and the property of photo-sensitivity. Nothing material has been added in photochemically colored crystals. The theory is that the absorbed quanta split electrons off the negative halogens, leaving them neutral but invisible atoms; the electrons then travel a short distance (too short to be detected as a photoelectric current) and become lodged at, or near, a positive sodium ion, with a visible absorption spectrum. This, as a matter of fact, appears to be the ordinary process of light absorption by alkali halides,
Quantities entering into formula for optical computation of color center density.
all of which, although nearly perfectly transparent to visible light, have strong absorption bands in the far ultra-violet (see figure 3). If the place where the electron is caught is not also a "lattice defect", or a positive ion "adsorbed upon an internal surface", no permanent change results; the electron falls back almost immediately into its parent halogen ion, and its excitation energy is dissipated in thermal vibrations. But if it is caught at, or near, a lattice defect, it becomes a more or less permanent color center, which can be bleached, however, by absorption of visible light with or without passage of an accompanying photoelectric current.

The permanence of photochemical coloring varies from substance to substance. Bayley\textsuperscript{13} found that CsBr faded upon less than 10 seconds of exposure to daylight. KCl and KBr fade within an hour or less. Rock salt fades the most slowly of any alkali halide; Joffe\textsuperscript{14} says he has kept specimens in the dark and at room temperature for as long as 21 years with at least partial retention of their color.

The situation is quite different with additively-colored crystals which, in the first place, keep their coloring indefinitely at room temperature. It should be noted that the end result of driving in electrons or allowing metal ions to diffuse in, is apparently the same, namely, a stoichiometric excess of alkali metal atoms. When electrons are forced in by the high field intensity about a pointed cathode the large negative space charge which would be otherwise created is
FIGURE 3

compensated to a large extent by the forced withdrawal of halogen ions. These latter can actually be detected chemically at the anode. On the average a certain percentage of negative lattice points is, presumably, replaced by electrons. In an extreme case, that of fluorite \((\text{CaF}_2, \text{not an alkali halide})\) the number of the displaced ions may be made as great as one in ten, so that the resulting material has a measurably decreased density. In ordinary cases of alkali halides the number of displaced ions is about 1 in \(10^6\) or \(10^5\), but even with these low concentrations the alkaline excess may be detected chemically upon dissolving the crystal.

It is not certain just how the process of coloring a crystal by heating it in a metal vapor differs from the process of electron penetration. Rexer\(^{14}\) colored a crystal by allowing metal atoms to strike it from one side only, then removed the vapor while maintaining the crystal at the same constant high temperature. Then the coloring did not spread out homogeneously through the crystal, as might have been expected, but instead left by the same route as that by which it had entered. Evidently there was a space charge built up in the clear portion of the crystal which drove the coloring back. Alternative explanations are, either that neutral alkali atoms deposited on the crystal surface serve as "take-off" places for their electrons which, at the temperatures involved, are thermally ionizable, or, that the electrons serve as a vanguard or entering wedge for the alkali ions, which follow where the
electrons have first "shouldered" their way in. The final result is a stoichiometric alkali excess, but no one seems to have noticed whether, for example, the excess in NaCl heated in potassium vapor is potassium or sodium. Apparently, as will be shown below, an excess of either metal in NaCl would produce exactly the same color band, so a chemical means of distinguishing seems needed.

The stoichiometric metal excess in additively colored crystals can only be removed by electrolytic conduction, which at room temperature is vanishingly small. It is even doubtful if the small dark conductivity is mainly electrolytic.

OPTICAL PROPERTIES OF THE COLOR CENTERS

The energy relations between the characteristic ultra-violet absorption bands and the induced color bands are of interest. The ultra-violet bands, in which the alkali halides have a metallic opacity, appear to be determined, in position, by the halogen constituent, as shown by figure 3. Although the energy of the absorbed light is of the order of 7 or 8 electron-volts per quantum (7.7 e-v for the 1600 A° band of NaCl), this is not sufficient to throw electrons up to a conducting level, as shown by the absence of measureable photoelectric current during such absorption. But it is sufficient to create, under suitable conditions, color centers, from which electrons may be thrown up into a conduction level by absorption of visible light having energy of only 2 or 3 e-v per quantum (2.7 e-v for the F-band of NaCl which has its maximum at 4600 A°). Electrons
bound at color centers may thus be considered to be in energy levels considerably higher than those of ordinary electrons bound to halogen ions.

It might be supposed that the absorption spectrum of the color centers (figure 4) would be closely related to that of the free vapor of the corresponding alkali metal vapor, provided account were taken of the dielectric constant of the medium (it is a fact that NaCl and NaBr are colored yellow or yellowish brown, while KCl, KBr and KI are colored deep blue). And, in agreement with this idea, the absorption spectrum of fused alkali halide salts in the presence of their own or some other alkali metal vapor is found to be characteristic of the vapor, not the salt.

But Mollwo has shown that the maximum absorption frequency of all the colored alkali halides is a function only of the lattice distance $d$ according to the following simple empirical formula:

$$\sqrt{d^2} = \text{constant} = 50.2 \text{ cm}^2/\text{sec.}$$  \hspace{1cm} (1)

He further showed that the absorption maximum was shifted by the amount required by the formula when the lattice distance was increased by thermal expansion.

It is a remarkable fact, not only that the position of the $F$-band should be a function only of the lattice distance, when the color centers themselves number only about 1 to $10^6$ lattice points, but that the same constant should apply to all the alkali halides.
FIGURE 4

Energy of absorbed light in e-volts

Frohlich\textsuperscript{16} has offered an explanation which makes no use of the idea of lattice defects. As usual in applications of the quantum mechanics, he considers the positions of the permitted and forbidden energy zones in the lattice to be determined by the periodic potential field of the lattice, and chooses to use the sequence of alternating positive and negative ions in the 110 direction. Thereby he comes out with

$$\Delta \gamma = h \nu = \frac{\hbar^2}{16 \times dB}$$

(2)

for the difference in energy between the "first" and "second" permitted zones. Then

$$\nu d^2 = \frac{h}{16m} = 0.45 \text{ cm}^2/\text{sec.}$$

(3)

Since Möllwo's empirical relation contains the frequency of the maximum (center) of a given absorption band, Frohlich's result applies to transitions from about the middle of one zone to the middle of the next.

Frohlich's explanation, while in good numerical agreement with experiment, does not show why only color centers can supply electrons for the supposed transition. It has also been criticized by De Boer\textsuperscript{7} on the ground that the preferred direction of motion of free electrons in a rock salt crystal is not the cube-edge 100 direction, but the face-diagonal 110 direction, in which the distance between ions is greater by a factor $\sqrt{2}$. This has been experimentally demonstrated by Von Hippel in electrical breakdown experiments at high field strengths (these experiments will later be more fully described).
De Boer thus cuts down Frohlich’s apparent numerical agreement with experiment to one of order of magnitude only, and then proceeds to argue for his own hypothesis that the color centers consist of alkali atoms absorbed upon internal surfaces. The procedure of either Frohlich or De Boer, however, in arbitrarily picking out some direction of the crystal lattice and then considering a one-dimensional model consisting of the row of atoms found along that direction does not seem very satisfactory, in that apparently it leads to the result that electrons of one energy can travel in one direction, and electrons of some different energy can travel in some corresponding different direction.

Absorption of light in the induced F-band of a given alkali halide leads, temporarily, to the weakening of this absorption band and its partial replacement by a lower, broader band at longer wave-lengths, the so-called F’-band. This phenomenon is closely related to excitation, already referred to, in that excitation centers are considered to be responsible for this new absorption. The process is reversible. An F’-center by absorption of its characteristic frequency photon in the red or infra-red range may lose its electron, which then diffuses again in the electric field and may next be trapped either as an F-center or as an F’-center. In the alkali halides F’-centers and excitation centers are taken to be identical. Electrons may be thermally removed from F’-centers
much more easily than from F-centers. F'-centers are, for example, already unstable at room temperature in both KCl and KBr with an average life which is a very small fraction of a second.

De Boer seems quite certain that these F'-centers are formed at lattice disturbance points. Wolff\textsuperscript{17} also has identified them as such with some degree of positiveness by comparing the absorption spectrum shift ascribed to F'-centers with a similar shift which may be produced by simple mechanical straining of the crystal. That the F-centers themselves are connected in some way with lattice disturbance points has been shown by Pohl's students, who found that the maximum obtainable color center concentration in a given specimen of a substance depended upon its previous treatment.

U-CENTERS

The method of coloring crystals by filling them with "U-centers" and then sending ultra-violet light into them has been mentioned (page 11). Under certain conditions another absorption band, in addition to the F-band, may be produced in alkali halides. It is called the "U-band", and, by definition, "U-centers" are responsible for it (figure 5). Like F-centers, U-centers may be formed either during electron impregnation or during heating of a crystal in its metal vapor; likewise they are associated with a stoichiometric alkali excess. But they are not electrons, they are alkali hydride molecules, as Pohl and his students finally identified them (after several years of experimenting).
CHARACTERISTIC AND INDUCED COLOR BANDS IN NACl.

The substance-characteristic band at the extreme left is about 1,000,000 times as high as the F-band. The U-band is due to the presence of NaH molecules in the crystal.
The most direct method of producing "U-centers" is to heat a crystal already containing F-centers in an atmosphere of compressed hydrogen. If the pressure is raised to 100 atmospheres, hydrogen molecules (not protons, according to Pohl) diffuse inward at the rate of about 1 mm/sec., converting visible F-centers into invisible alkali hydride molecules with the characteristic bell-shaped U-absorption band at about 8000 Å in the ultra-violet.

With ordinary experimental precautions, hydrogen appears always to be present in such quantities that additive (visible) coloration by heating a crystal in its alkali vapor is accompanied by a slow inward diffusion of U-centers. This was the original method of producing them, before they had been identified; it requires much longer for the alkali hydride molecules to diffuse in than for the color centers. Also the process of electron impregnation appears, under ordinary experimental conditions, always to have U-center formation as a concomitant. If, for example, a crystal be filled with color by electrons from a sharp cathode, the electric field may be reversed and all the color apparently drawn back out by way of the pointed electrode. It is then found that only 40 to 60 percent of the penetrating electrons have been recovered; the rest, apparently, have been immobilized by incorporation in some manner into invisible U-centers.
Absorption of light in their frequency band by the U-centers does not produce photoelectrons, but visible color centers, which in turn by absorption of visible light give rise to photoconductivity. The process is reversible, but only in the absence of an electric field, which may, in fact, act effectively as a "developer". Absorption of light of the proper wave-length separates an NaH or KH molecule, as the case may be, into a color center and a hydrogen atom. Considerable energy is required to do so, e.g., 6.8 e-v in NaCl. If the color center next is separated into a "hole" and a photoelectron, it appears that the "hole" is likely to recombine with the hydrogen atom, restoring the U-center. But if the electron or the hole diffuses in an electric field, the constituents of the one-time U-center get too far separated ever to recombine.

An ultra-violet photograph might be taken with a KBr crystal filled with KH molecules somewhat as follows: an ultra-violet image focused on the crystal would give rise to a visible "latent image" of F-centers which (at sufficiently high temperature) could be drawn off by application of the "developing" field. Then upon flooding the crystal uniformly with visible light, only those parts would be colored which previously were not affected by the ultra-violet light and the original image would show up as a clear transparent region—corresponding to the developed negative plate.
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THERMAL CONDUCTION

The phenomenon of visible thermal conduction, already described in connection with the additive coloring of crystals by electrons, deserves additional discussion. The main point of interest is that the velocity of a cloud of electrons in the electric field may be visually observed. (An isolated cloud may be produced, as was done by Stasiw\textsuperscript{17} by replacing, at the right time, the pointed cathode with a plane one.) The mobility of such a cloud, however, is still conditioned by the sluggishness of the space-charge compensating current, which, in the clear portion of the crystal, is entirely electrolytic. Now below a certain critical temperature (680\textdegree{} C in KCl) the electrolytic conductivity is structure-sensitive, the so-called Storleitung of the German literature. The slope of the curve of electrolytic conductivity vs. temperature breaks sharply upward at this point. All of the ions of the crystal lattice become able, at this temperature, to participate in electrolytic conduction, which, therefore, above 680\textdegree{} in KCl, is structure-insensitive.

Stasiw, in observing the mobility of a small isolated cloud of color centers, found that below 680\textdegree{} C (in KCl) the boundaries of such a cloud rapidly became diffuse in an electric field, indicating a spread of mobilities. But above 680\textdegree{} C the cloud stayed together with rather sharp boundaries, suggesting a definite mobility for all of the participating centers. Stasiw took pictures of such clouds on a moving plate.
The mobility thus optically observed was found to increase exponentially with temperature according to the formula, of familiar Maxwellian form,

$$v_T = v_0 \exp \left( -\frac{\epsilon}{kT} \right),$$

(4)
in which $\epsilon$ is a binding energy, or thermal work function, of the order of 1 eV and the other symbols are obvious.

With increasing temperature the rest periods of the electrons between thermal ionizations become shorter and shorter, and, in the limiting case, are entirely eliminated. The mobility of the color centers has then reached its limiting value $v_0$, which comes out to be of the same order of magnitude as the same quantity for electrons in copper and other good conductors (for the same temperature).

In discussing this method of measuring mobilities, Pohl points out that low concentrations of F-centers must be used, otherwise the electrolytic conductivity will not be sufficient to neutralize the positive residual charges left by the electrons, and the measured mobility will be too small. Even with the fulfillment of this condition, it is still not clear how the electrons can move freely about unchecked by the sluggishness of the necessary compensating current—unless the crystal is completely filled with color centers, when electrons going out may be replaced by electrons going in. But in such a case—in which the crystal may be considered to be a "dilute metal"—nothing visible moves. Another alternative appears to be that above the critical temperature the electrolytic
mobility of the ions is greater than that of the electrons, but this seems unlikely.

When a heated crystal has been completely filled with color centers, electrolytic conduction, as mentioned, is no longer necessary to compensate for positive space charge left by the movement of thermally ionized electrons. Then the conduction of the crystal is mainly electronic, but there is still this difference in its behavior from that of an "ideal dilute metal"—there is a background of ion current.

The picture of a dilute metal holds only for visible thermal conduction. With photoelectric currents at room temperature the primary negative current is still electronic, but is no longer self-compensating, for the reason that many more photoelectrons are captured by excitation centers than by holes. Either the lattice points which may act as excitation centers are much more numerous than the holes—which is probably the case—or their mean absorbing cross-section per individual is much larger (which seems unlikely). Also at room temperature the anode seems unable to act as a source of free electrons without the helping process of hole conduction.

Some confusion may arise as to the possible migration of color centers, which in one sense are neutral metal atoms, in an electric field. But it is not neutral atoms or even alkali ions which move bodily; the motion rather is that of electrons racing from metal to metal ion. The coloring follows the electrons, because it is where they neutralize the positive
metal ions that F-centers exist. As a matter of fact the picture of an F-center as a single neutral atom is probably too simple. It is more likely that the electron is shared by many neighboring ions, this whole region then acting as an F-center. In the same way a "hole" should not be considered as a single particle lacking a normal electron but as a whole region, perhaps including 15 or 20 atoms, in which an electron is missing.

The thermal work-function, it may have been noticed, is about twice smaller than the energy per quantum of the long wave-length foot of the F-absorption band at room temperature. However with rising temperature the F-band is shifted considerably in the direction of longer wave-lengths, at the same time becoming broader and lower (figure 6). This partly removes the discrepancy, but not entirely. It is also possible that at high temperatures the allowed energy zones for electrons are pressed closer together, on account of the increase in lattice distance. In general it would seem that with increased lattice distance, electrons with longer wave-lengths, or lower energies, would "fit in", and therefore be free to travel.

It may also be noticed in figure 5 that, as there exemplified by KBr, the wave-length at which the absorption coefficient on the violet side is equal to one-half its value at the band maximum is constant for all temperatures. This peculiar behavior has been suggested by Pohl as ascribable to a transition between two "undisturbed" energy levels of the crystal.
FIGURE 6

SHIFTING OF THE F-ABSORPTION BAND WITH INCREASING TEMPERATURE. The horizontal lines marked \( H_1, H_2, H_3 \) and \( H_4 \) are the "half-value widths" of the band at the various temperatures. These lines all end on the violet side at the same wave-length, 5720 A°.
NATURE OF THE COLOR CENTERS

In attempting to arrive at a definite concept as to the nature of the color centers, their apparent sensitivity to structure must be taken into account. The dependence of obtainable concentrations of color centers in crystals as a function of their previous treatment has already been mentioned. De Boer states that the color concentrations obtainable by photochemical action likewise may be greatly increased in a given specimen by subjecting it to rough mechanical and thermal treatment. His idea, of course, is that light absorption in the characteristic ultra-violet absorption bands results in photochemical coloring only if the electrons detached from the halogen ions immediately hook on to alkali ions already "adsorbed" upon "internal surfaces", otherwise the process is one of excitation rather than of ionization.

Gurney\textsuperscript{18} has given a plausible explanation of the structure-sensitive formation of color centers, using a modification of the generally accepted reason as to why insulating crystals will not accept electron currents from metallic electrodes (despite the fact that, theoretically, a perfect lattice offers no resistance to the movement of electrons of the right energy, and apparently, on Fermi-Dirac statistics, a metal is full of electrons of any energy up to a rather large one). The explanation referred to concerning insulators is that at the boundary of a perfect crystal lattice localized electron energies occur which are in the disallowed zones of the interior. Electrons from a metal pressed against
the crystal will then fall into these surface zones, but get no farther. Such surface energy levels are known as "Tamm levels", in honor of their elucidator. Now, according to Gurney, there will also be localized Tamm levels at every sub-microscopic interior crack, having energies in the forbidden non-conducting zone. The formation of a color center photochemically then consists in the transfer of electrons to localized energy levels in the forbidden zone at internal surfaces. This explanation helps in the understanding of how F-centers, although creatable by the action of light of energy insufficient to throw electrons into a conducting level, nevertheless themselves are in a position to emit photoelectrons by absorption of light of much smaller energy still. In additive coloration, on this idea, color centers are formed by those electrons which happen to be attached to, or are in the close vicinity of, metal ions adsorbed on a lattice defect or internal surface. It will be noticed, however, that Gurney's theory gives no satisfaction at all concerning Mollwo's empirical result that the F-band absorption frequency depends on the lattice distance and on nothing else (that varies from alkali halide to alkali halide).

It appears, therefore, that both color centers and excitation centers are associated with structure defects. The distinction between them—aside from the obvious one of charge—becomes even more hazy in view of the fact, shown by Glaser and Lehfeldt, that the range of photoelectrically-emitted electrons
is inversely proportional to the color center concentration. This implies that F-centers act as electron traps, i.e., absorbers, as well as sources. It is possible to calculate the "average absorbing cross-section" of an F-center for a photoelectron; Pohl has done so and finds it to be about $4 \times 10^{-7}$ cm$^2$—which seems rather large.

Here, as usual, a careful distinction must be made between F-centers and their debris, known as "holes", after emission of a photoelectron. Pohl's idea is that one light quantum releases one photoelectron from one F-center, leaving a positive hole to which is attributed no optical absorption at all. The photoelectron, at the end of a finite range $w$, is then captured by a positive metallic ion (not a hole) in the vicinity of another F-center. The positive ion and the assisting F-center are thereby converted into two optical F'-centers. On counting up it is seen that two F-centers have disappeared, one at the origin and the other at the destination of the photoelectron, and two F'-centers appeared in their place. The quantum equivalence of the reversible process F—F' has the limiting value 2, rather than unity—which, according to Pohl, is experimentally the case.

A tentative conclusion regarding the nature of color centers was reached by Pohl, N. F. Mott and others$^{20}$, at a conference on "The Conduction of Electricity in Solids" held in September, 1937, at Bristol. This conclusion was, in effect, that F-centers simply consist of electrons which have taken the place of halogen ions in the crystal lattice. This conclusion
was probably arrived at too hastily, in that it does not seem to include the case of photochemically colored crystals which have no alkali excess, it does not fully take into account the structure sensitivity of color centers, and it does not explain at all Mollwo's empirical $\sqrt{d^2}$=constant relation.

An interesting alternative viewpoint of the color centers has been offered by Von Hippel on the basis of his experiments on electrical breakdown. The excitation centers, and probably the color centers, are, according to his views, structure-insensitive. He remarks that the addition of an electron nearly doubles the effective radius of an alkali metal ion, so that it overlaps into the order regions normally claimed by its 12 alkali ion neighbors in the 110-, or face diagonal, directions. The electron being thus shared would be free to move on, except that, due to the non-rigidity of the ion lattice, the crowded positive ions are slightly rearranged, forming a potential cup in which the electron is trapped. That is, the electron has been caught in a sort of lattice defect of its own making. In support of this Von Hippel cites that color centers formed by copper atoms electrolyzed into a heated alkali halogen crystal are immobile; this fact follows, he says, because the copper ion, even after being transformed into an atom by capture of a passing electron, still has a rather small radius, so that it does not deform the lattice and hence is able to bind the electron tightly to itself.
The breakdown experiments already mentioned should perhaps be described a little more fully. The so-called preferential directions are shown, in these, by the visible breakdown paths remaining after the discharge has been cut off. If the breakdown field is applied along a cube-edge direction, the visible breakdown paths do not extend straight through the crystal parallel to a cube edge, but form zig-zag or staircase paths, each segment of which is parallel to a face diagonal direction. At high over-voltages the segments are parallel to room diagonals, i.e., the so-called second preferential direction is in the 111-direction.

Von Hippel's explanation of these facts is, that along a face diagonal the ions are all of one sign and farther apart than the ions (of alternating sign) along a cube-edge line; the potential hills, therefore, to be surmounted by an excursioning electron are lower and farther apart. At higher field strengths the greater distance between ions in the 111-directions more than compensates for the increased height of the potential hills, and so these become the preferred directions. It is assumed here that the condition for electric breakdown is that electrons can pick up more energy from the field along a free path than they will lose by inelastic collision with lattice ions at the end of such a path; the amount of energy usually exchanged in an inelastic collision between an electron and a lattice point is, according to Von Hippel, about 0.02 e-v.
Even so, it is not clear how the increase in free path gained by traveling along a face or room diagonal would give the electron any more energy along that path inasmuch as the field is applied in a cube-edge direction and the potential fall between two equi-potential planes is independent of the path traversed in moving an electron from one to the other (see figure 7). A fuller discussion of theories of electric breakdown will be given further along.

Von Hippel's ideas on electron-trapping have received some support by Gurney and Mott\textsuperscript{22}, who have applied the methods of wave mechanics to determine the time in which an electron may "linger" in the neighborhood of a single ion, and then compute the depth of the potential hole which the electron may thereby scoop out for itself. As a matter of fact they found that the average time an electron may stay near an ion is only about $1/1000$th that of the time required to excite a lattice vibration, so they postulate that "by accident" an electron remains on one positive ion for $10^{-12}$ second. Then the potential cup created by the electron comes out, in their calculations, to correspond to the observed energy required to release an electron photoelectrically from a color center.

CONDUCTION MECHANISM

The question of the conduction mechanism in photoconducting crystals has considerable interest, but will be discussed here particularly with reference to the colored alkali halides. The fact that Ohm's law is obeyed to a close
BREAKDOWN PATHS IN ROCK SALT. If the electric field is applied in the direction shown by X, the visible tracks remaining after electric breakdown have a staircase form, as shown by the jagged line. With the field as shown, the potential drop along a path such as AB is the same as that along AC.
approximation in photoconducting crystals may be reasonably explained upon either of two assumptions: (1) that the electric carriers (presumably electrons) have a definite mobility, i.e., their drift velocity is proportional to the electric field, or (2) that the carriers travel on the average a certain distance, also proportional to the applied field, before they are trapped. The former assumption was favored by early workers in photoconductivity, e.g., by Joffe' in his book, "The Physics of Crystals"; the latter has been generally preferred by later investigators, in particular by Pohl and his followers. Either assumption is quite sufficient to account for the phenomenon of saturation at high field strengths, when quantum equivalence is attained, but the second happens to fit in much better with the idea of excitation or F'-centers.

The average distance traveled by a photoelectron before being again trapped in the lattice, known as the range or thrust path, must be carefully distinguished from the idea of "mean free path". The range, presumably, consists of many "free paths", and this must be so because it is proportional to the electric field. Even in zincblende in which, according to the result of Hall effect measurements, electrons have a mean free path of about $10^{-6}$ cm, the range is many times greater still—about one millimeter, in fact, for fields of the order of a few hundred volts per centimeter.
In the case of NaCl the excitation centers are thermally stable at room temperature for a considerable time; red or infra-red light is necessary to loosen an electron from one of them. But in KCl and KBr the excitation centers are thermally unstable at room temperature, and what is known as the "thermally increased" range is of the order of 100 times as great as the initial range, or thrust-path proper. The fact that in these crystals a photoelectron, once emitted, ever comes to a complete permanent stop probably means that about every one-hundredth trapping is, in fact, a recombination with a hole.

The fact, previously mentioned, that the range, i.e., the average distance traveled between point of origin (F-center) and first stopping-place (F'-center), is inversely proportional to the color center concentration, really means that the photoelectric current obtainable with a given field and intensity of illumination is independent of the concentration of color centers. This holds especially well for rock salt at room temperature, which does not have the complication of thermally-increased range. The number of liberated photoelectrons is proportional to the number of color centers (for a thin plate) but the distance each travels is inversely proportional to the same quantity.

Why the range of a photoelectron should be proportional to the electric field in which it diffuses is a question which has not been completely answered. The
F-absorption band has an energy width of about 1 e-v; electrons emitted by light at the high frequency end of the band should therefore initially have about 1 e-v of kinetic energy. To gain a similar amount of energy in an electric field of the intensity used in ordinary photoelectric experiments (e.g., 600 volts/cm) an electron would have to travel a distance of $1/600$th cm-$=1.7 \times 10^{-3}$ cm—but this is seven times as far as the range given by Glaser for this field and a rather light coloration ($10^{16}$ centers per cubic centimeter). According to Von Hippel, an electron having a velocity corresponding to 0.02 e-v of energy or less is practically certain to be captured by the first positive ion which it attempts to crowd past. But, to gain this amount of energy in a field of 600 volts/cm, an electron would have to have a free path of $3.3 \times 10^{-5}$ cm, during which distance it would have to pass about 500 positive ions. If it be granted that an electron will evade capture until its energy, composed of its initial store plus that picked up by falling through the potential drop along its path, has been reduced, effectively, to $(3/2)kT$, it would seem that its path length would be so largely determined by its stock of initial energy that increasing the electric field would have comparatively little effect, in the case of fields far below breakdown strength.

As a matter of fact Frohlich\textsuperscript{23} has estimated that from $10^{2}$ to $10^{3}$ collisions with lattice points are needed to reduce an electron of 1 e-v initial energy to Maxwellian equilibrium
with the lattice. This number is the order of the number of lattice points along a thrust-path in NaCl with an ordinary field and an ordinary concentration of color centers. It would seem that experiments to measure the thrust-path as a function of the energy of the absorbed light are needed. An absolute measurement of thrust-path, it may be mentioned, requires that the number of absorbed light quanta be known.

The mean free path lengths of electrons in insulators are, generally speaking, not known with any accuracy. Even the order of magnitude, for most substances, is uncertain. Now in Sommerfeld's electron theory of conduction, the mean free path of an electron in a metal comes out to be of the order of $5 \times 10^{-6}$ cm. If Fermi-Dirac statistics be used to compute the average random velocity of the electrons, this value for the mean free path may be made to yield the order of mobility actually found for metallic conduction. There is no reason why the crystal lattice of an insulator should offer more resistance than that of a metal, except for this (as suggested by Von Hippel): in an ionic lattice there is more coupling between lattice points and any free electrons which may exist. Still, in zincblende, the mean free path is probably about $10^{-6}$ cm.

In rock salt, however, the mean free path, as calculated on quantum mechanical concepts by Frohlich$^{26}$, comes out to be of the order of one atomic distance; even so, the possible coupling between individual electrons and ions was neglected in making the calculation. It is interesting to
notice that if the classical expression for mean free path, namely, \( \lambda = 1/(\sqrt{2} \pi N d^2) \), be extrapolated to apply to "point electrons" in a solid (by setting \( d = r \) = radius of an ion), the free path comes out considerably less than an atomic distance—as it necessarily must since the cross-sections of the ions are larger than that of their interstices.

Bloch\(^2\)\(^4\), by an application of quantum mechanics, has shown that a perfect crystal lattice offers no resistance to the passage of a "permitted" electron (which, in a way, seems obvious). The resistance actually existing at ordinary temperatures is ascribed to distortion of the lattice by molecular thermal vibrations. Thus the long free paths found in metals, and the increase of resistance with rising temperature, are easily accounted for.

In connection with this discussion of the possible conduction mechanism in photo-sensitive crystals, the quantum mechanics explanation of the conducting or non-conducting property of a given substance should perhaps be more explicitly stated. It comes out in quantum mechanics that any crystal, conducting or insulating, may be looked upon as a kind of large molecule, possessing its electrons all in common. The quantum condition, that the energies of the electrons be such that their wave patterns fit into the periodic potential variation of the crystal lattice, when combined with the boundary condition, that the electrons be effectively
constrained within the volume of the crystal, determines a set, or several sets, called bands, of possible discrete energies, which within a set are very close together and equal, in number for a given band, to the number of atoms composing the crystal.\textsuperscript{25}

Each discrete energy level can accommodate two electrons of opposite spin. In metallic crystals, which have one valence electron per atom, the valence set of permitted energies has twice as many vacancies as there are electrons. Such electrons when accelerated in an electric field gain, along a possible free path, comparatively small amounts of energy, but there are always plenty of adjacent levels available, and conduction follows. It should be noted, however, that even in metals there is a wide gap, e.g., of about 60 e-v in Li, between the K-levels and the valence band—meaning that the K-electrons are immobile, they belong to particular atoms. Also only the electrons near the top of the energy distribution function can gain enough energy from the electric field to jump to the unoccupied levels, so that only a fraction of the valence electrons is actually available to carry the current.

The essential feature of an insulator, on the other hand, is that the number of electrons exactly fills all of the available levels in a certain number of allowed bands while the next vacant set of permitted levels is separated from these by a fairly wide gap—too large for an electron to cross by means of energy picked up in an ordinary electric field. In other words, an electron is prevented from absorbing energy from an
electric field because its resulting wave length would not fit into the potential topography of the crystal lattice.

ELECTRICAL VS. THERMAL BREAKDOWN

The mechanism of electric breakdown at high field strengths undoubtedly is related to that of photoconduction at ordinary fields. Von Hippel's experiments and their results have already been described in connection with his model of an F-center. His picture of the formation of an electron avalanche departs from the pure wave-mechanical treatment of an insulator, in that he considers the coupling between individual ions of the crystal lattice with electrons to be the decisive factor. Once past the critical velocity at which its gain from the field along a free path exceeds its loss during the ensuing collision, an electron, according to Von Hippel, will gain speed faster than ever, because its coupling with any particular ion will be reduced by reason of the small interaction time.

Frohlich\textsuperscript{36}, on the other hand, has attempted an explanation of Von Hippel's experimental results in a computation based on pure quantum mechanics. His general line of reasoning is the same, namely that if electrons having more than a certain critical kinetic energy (which must be less than the ionization energy) are still able to gain more energy from the field along a free path than they lose in the following inelastic collision, breakdown occurs. In particular, as a primary source
of electrons by which the breakdown process may be touched off, he assumes an initial temperature-dependent Bose-Einstein distribution of free electrons.

Seeger and Teller\textsuperscript{27}, however, in an argument supporting Von Hippel, say that Frohlich's proposed process is really not cumulative. The breakdown field thereby arrived at, in their opinion, is not great enough to accelerate the newly created-by-ionization electrons because a stronger field is required to give slow electrons a net gain of energy along a free path than the fast ones (by reason of the longer interaction time and consequent stronger coupling with the lattice).

Von Hippel's latest experiments\textsuperscript{28}, in which he applied fields of up to $10^6$ volts/cm to a KCl crystal, conducting either photoelectrically or in the dark, are interesting in that they seem to indicate that even the residual dark current at room temperature is not electrolytic—"its steep rise with voltage, its rapid fluctuations, and its noisiness point toward an electronic phenomenon". (When he connected the collecting electrode to a high-gain amplifier instead of to an electrometer tube, and used weak illumination, rattling noises were heard, apparently produced by single-electron produced avalanches, a kind of crystal photon counter.) The observed large increase in number of free electrons in dark conductivity at high field strengths, Von Hippel ascribes to the quantum "tunnel" effect.
Frenkel\textsuperscript{29} has offered his own theory of "augmented thermal ionization" to account for breakdown. According to him, the release of an appreciable number of electrons, even by "tunneling", requires a field five or ten times as great as that found for breakdown in practice. However, he says, the lowering of the potential barriers in a crystal lattice on one side accompanied by heightening on the other by an external (perturbing) field, together with the electron's energy of thermal agitation, is just enough to make the tunneling sufficient to account for the observed phenomena. He then derives "Poole's law" for the conductivity of an insulator before breakdown as a function of field strength, namely

$$\sigma = \sigma_0 \exp (\alpha E).$$ \hspace{1cm} (5)

This "law", however, Von Hippel found not to hold for photoconducting KCl at room temperature.

"Thermal" breakdown may also develop in an insulator if the Joule heating produced by the initial current is enough to lead to increased electrolytic conductivity, which in turn cumulatively leads to more Joule heating. For crystals at room temperature it would appear that the heating would have to be along local channels, as Von Hippel has found that the current just before breakdown (in KCl) is still too small to produce noticeable heating if distributed over the substance uniformly. Likewise Goldman and Wul\textsuperscript{50} showed that the breakdown strength of photo-sensitive rock salt was as great when illuminated as
when kept in the dark, provided allowance was made for the redistribution of field strength along its length caused by built-up space charge.

Walther and Inge\textsuperscript{31}, on the other hand, claim that the electrical process is never of importance as compared to the thermal one in breakdown. Their criterion to distinguish between electrical and thermal breakdown, the time lag involved, seems correct, but their sweeping assertion that the electrical process is never of importance is unjustified. It is only true for heated insulators, in which the breakdown field has a lower order of magnitude than that at room temperature, so that the electrical process is not even well started; or for pointed electrodes (with which Walther and Inge mainly worked), near which the lines of current flow are concentrated.

ELECTRIC CARRIERS IN COLORED ALKALI HALIDES

A summary of what has already been said concerning the motion of electric carriers in colored alkali halides will help in keeping the complete picture in mind. It will be recalled that the primary electron current flows immediately at the outset of illumination, followed by the "positive" primary, or replacement current, which is necessary to neutralize, wholly or in part, the positive space charge left behind by the migrating electrons. At room temperature some space charge is built up, however, and the total current, even with steady
illumination, gradually decreases to an equilibrium value. The time required to reach this equilibrium is a function of the kind of illumination (monochromatic or mixed) and its intensity, as well as of the particular substance of the crystal. The primary photoelectrons after diffusing on the average through a certain distance w are captured by other color centers (not holes left by emission of electrons from color centers) to form excitation, or F'-centers, which give rise to the new optical F'-absorption band in the red or near infra-red.

An F'-, or excitation center, is a point of excess negative charge, where an electron is caught; a hole is a region of excess positive charge which has been created by a photon operating on an F-center. An electron which has been re-emitted by an F'-center is associated with the original hole created when the electron was first liberated by photoelectric action in the sense that its motion is still retarded by the positive space charge contributed by that hole. The number of holes at an instant before any hole conductor has reached the cathode is equal to the sum of the photoelectrons in free flight plus those which have been collected by the anode plus the number of excitation centers—the latter each representing a photoelectron which did not reach the anode. Since the hole conductors are sluggish in action, their number in general exceeds that of the electrons still in the crystal, i.e., those in free flight plus those immobilized as F'-centers, so that a net positive space charge exists.
F'-centers and holes undoubtedly can exist as fairly close neighbors. When an F'-center and a hole actually coincide, recombination has occurred. However in a uniformly illuminated crystal most photoelectrons are captured at the end of their range by F-centers, not holes—otherwise the range would be inversely proportional to the density of holes, rather than to the density of color centers. A hole, if it travels at all, must do so by the process of pirating an electron from some particle, presumably a halogen ion, between itself and the cathode. If it takes the electron from a halogen ion it has transformed its very nature, from a set of alkali ions lacking an electron to a halogen atom—the last arising from the ruins of the halogen ion which lost its negative charge to the privateering hole. Whether the transformed hole is as ready to intercept migrating electrons as before is, of course, a moot question. At any rate the F-centers have a much greater numerical density than have the holes, although the latter must outnumber the F'-centers. The presumably small fraction of the photoelectrons captured by holes form new F-centers.

If the holes themselves were completely immobile, the accumulated space charge would soon be such that the applied electric field would be canceled over the length of the crystal. It might be thought that a small residual current, consisting of photoelectrons flitting from hole to hole would remain—but there would be no way for electrons to be supplied by the cathode (unless by the surface photoelectric effect)—the Tamm levels would shut them out.
For a steady residual photo-current to flow, therefore, as actually observed, it is certain that the holes must move—
not bodily as whole ions, but by the jumping in of electrons from the cathode in reverse order, the final jump being by an electron from the cathode to a hole which at last has moved up to it.

Nevertheless one cannot be certain as to the precise nature of the holes. According to the wave mechanics picture of an insulator, the photoelectrons, having been raised by the action of light to an ordinarily inaccessible but conducting level, have at the same time left a vacancy in the usually full level of the so-called valence electrons. There now being vacancies to which electrons accelerated by the field may go, this level, to some extent, has become conducting. On this idea, therefore, the holes consist of places where the valence electrons, usually bound, are perfectly free. Then their mobility should be the same as that of the free photoelectrons themselves. But it is not—instead the positive (electron replacement) component of the photoelectric current is very sluggish, and becomes increasingly so at low temperatures. Wilson's suggestion that the sluggishness is attributable to a "slowness" of the change of lattice form from a "non-conducting form" (neutral chlorine atoms embedded at random amongst negative chlorines) to a "conducting form" (all chlorines on the "same footing") seems arbitrary, and is hard to test by experiment.
In assuming that the holes left by photoelectrons ejected from F-centers are vacancies in a level usually non-conducting only because it is full, a serious oversight has been made—namely, of the fact that the F-centers themselves are different from ordinary ions of the normal lattice. Electrons existing as F-centers, or associated with F-centers, are already in an energy state considerably above that of the normal crystal band—the ordinary electrons cannot be thrown up into the conducting band by light of visible wave-length, nor even by ultra-violet light. This condition is explained, along lines previously mentioned, as due to the occurrence of "foreign", or Tamm levels, at crystal disturbance points. Thus it appears that the vacancies left by the departing photoelectrons are not in a normal permitted band at all but instead near the top of the forbidden zone. On this idea the holes would certainly move with difficulty, in fact it is hard to see how they could move at all.

Just as the color centers in a heated crystal move visibly under the force of an electric field, the process of hole conduction also may be made visibly evident under suitable circumstances. Mollwo found that a potassium iodide crystal could be colored with a stoichiometric excess of iodine by heating it in iodine vapor at 600° C under pressure of 10 atmospheres. The crystal, if quenched to room temperature, was then colored orange to brown, and its resulting absorption band in the visible region did not belong to free iodine. If
the crystal was next mounted between suitable electrodes, heated to a temperature of 400 to 600° C, and subjected to a potential difference of about 200 volts, the excess iodine could be seen visibly passing into the cathode.

The actual conduction mechanism, according to Pohl, consists of "electron replacement" in a crystal having an excess of halogen. (The phenomenon can also be shown with KBr.) The visible neutral halogen is changed back into an invisible negative ion by taking up a lacking electron. The concentration of excess halogen thus obtainable is always less than that of the vapor with which it is in equilibrium, corresponding formally to a negative binding energy—energy must be furnished to "dissolve" the halogen excess into the crystal. (The more easily obtained F-centers have a formal positive binding energy.)

The mobility of the electron-substitution current thus made visible is, in KI, four times smaller than the corresponding mobility of the F-centers, and 25 times smaller in KBr.

F-center-filled crystals are quite different in some respects according to the mode of their formation—photochemical or additive. Those colored photochemically and hence having no stoichiometric excess, fade rapidly upon absorption of light, with or without passage of a photoelectric current; the color centers reunite with their former partners, the halogens. Those colored additively can be faded only by a compensating
bodily movement of ions, an electrolytic conduction. But such electrolytic conduction is vanishingly small at room temperature for, probably, all of the alkali halides. For example in KCl, a comparatively soft substance, practically all of the dark conductivity, small as it is, comes from electrons, as has been shown by Von Hippel.

It appears then that even in a specimen uniformly filled with color centers and uniformly illuminated the simple picture of photoelectrons flitting from hole to hole, forming F-centers at each stopping place, actually is not realized. There is no source of photoelectrons at the cathode to replace those taken up at the anode; the Tamm levels act as a barrier. The positive charge left by the photoelectrons must therefore be drawn out by the process, probably, of hole conduction. The holes are not numerous enough to intercept many photoelectrons; recombination is not important. The F-centers themselves play a double role as emitters and absorbers. Hole conduction is probably by the mechanism of electron replacement, but the mobility of the holes is nevertheless less than that of free electrons.

OBJECT OF THIS INVESTIGATION

It will be seen that a final picture as to the mechanism of photoconductivity, particularly in the colored alkali halides, has not been completed. The length of the mean free path of the carriers in these substances is quite unknown; it is not even certain that the so-called thrust path corresponds to anything in reality. There is some doubt as to
the precise nature of the carriers of the various components of the photoelectric current, and the color centers themselves have not been finally identified. It was therefore considered that a study of the galvano-magnetic properties of the photoelectric currents in such crystals would be of value, especially since the Hall and Corbino effects are generally recognized as criteria for electronic conduction in solids.

The exact kind of information which the Hall or Corbino effects might give concerning the mechanism of photoconductivity will be discussed in the next section.

THEORY OF THE HALL AND CORBINO EFFECTS

The simplest possible "Hall effect" is found in the classical method of measuring the ratio e/m of cathode rays by balancing crossed electric and magnetic fields. The condition for no deflection of the beam,

$$Hev = Xe,$$  

(6)

shows that $hv$ acts essentially as a transverse electric field. Accordingly any theory of the Hall effect may be expected to give $Y$, the Hall field, in the form of the applied magnetic field multiplied by some velocity, averaged or otherwise.

The distinction between Hall and Corbino effects in a way seems trivial, but must be made in order to secure agreement with the usage of the terms in the literature. The Hall effect, properly speaking, is the potential difference set up between opposite sides of a long thin plate in which a current
is flowing longitudinally when a magnetic field is applied at right angles to the lines of current flow. No transverse current is supposed to flow; the measurement, therefore, must be either by means of an electrostatic instrument or a potentiometer. The Corbino effect, on the other hand, consists of the production of a circular current in a disk in which a radial current flows prior to the application of the magnetic field normally to the plane of the disk. This effect, in itself, is a rather specialized phenomenon, but it appears customary to refer to any current which flows by reason of a Hall potential difference as a Corbino current.

A simple deflection theory of the Corbino current is as follows: consider first an electron moving along a free path in the direction of the electric field, and being deflected at right angles to its motion by a magnetic field. The $x$-direction may be taken as that of the applied electric field. Then the amount the electron will be deflected in the $y$-direction while completing its free path will be approximately

$$y_o = \int_0^T v_y \, dt,$$

by neglecting the change in direction of the resultant velocity, to which the magnetic force acting on the electron is actually at right angles. This approximation is all right if the total sidewise deflection along a free path is very small compared to the length of that path. Then, again making a similar approximation,
\[ v_y = \int_0^t a_y \, dt \]
\[ = \int_0^t \frac{\text{H} \varepsilon}{m} \frac{dx}{dt} \, dt \]
\[ = \int_0^t \frac{\text{H} \varepsilon}{m} \frac{d}{dt} \left( \frac{3}{2} a_x t^2 \right) \, dt \]
\[ = \int_0^t \frac{\text{H} \varepsilon}{m} x_e t \, dt \]
\[ = \frac{1}{2} \text{H} \varepsilon t^2. \]  

Putting (9) in (7),
\[ y_0 = \frac{1}{3} \int_0^T \text{X}(e/m)^2 t^2 dt = \frac{1}{6} \text{H} \varepsilon t^2. \]  

\( T \), the mean free time, is related to the mean free path \( x_0 \) by
\[ x_0 = \frac{3}{2} a_x T^2 = \frac{1}{2} X(e/m) T^2, \]
so that
\[ T^2 = \frac{2x_0}{X(e/m)} \]

and
\[ y_0 = \frac{H}{3} \sqrt{2(e/m) x_0}. \]

Or
\[ y_0/x_0 = \frac{H}{3} \sqrt{2(e/m) x_0}. \]

This may be taken to be the ratio between the Hall field and the applied electric current provided it is assumed that (1) the flow of transverse current is due to, and is proportional to, a transverse E.M.F., (2) the resistivity is independent of the direction of current flow and of the
magnitude of the field producing that flow, and (3) the transverse drift velocity is to the longitudinal drift velocity as the transverse displacement per free path is to the free path (which has been taken in the direction of the electric field). That is,

$$\frac{Y}{X} = \frac{i_y}{i_x} = \frac{y_0}{x_0} = \frac{H}{2} \sqrt{\frac{2(e/m)X_0}{X}} = \frac{H}{2} \frac{e}{m} \text{T.}$$ (11)

This formula, despite the extreme simplications, bad approximations and free assumptions used in its derivation, is exactly the same as that obtained by Lenz by actually solving the classical equations of motion of an electron in crossed electric and magnetic fields, namely

$$\frac{d^2x}{dt^2} = eH \frac{dy}{dt} + eX$$ (12)

$$\frac{d^2y}{dt^2} = -eH \frac{dx}{dt} + eY.$$ (13)

These are appropriate to a solid conductor. The opposing Hall field y is built up by accumulation of charge on the Hall electrodes. Lenz solved (12) and (13) under the boundary conditions

$$x = y = \frac{dx}{dt} = \frac{dy}{dt} = 0 \text{ at } t=0,$$

which amount to assuming that the electron comes to rest at the end of each free path; it is therefore not surprising that he got the same result as that obtained by means of the "simpler" theory. Nevertheless by application of (11) to his experimental results Lenz ascribed free paths of the order of
10^{-6} \text{ cm to the photoelectrons in diamond and in zincblende.}
These are about the same lengths as the free paths of electrons
in metallic conductors according to the Sommerfeld theory.
Zincblende, in particular, differs from metals, not only in
being an insulator, but in having an ionic lattice.

Following Townsend's general method\textsuperscript{34}, the equations
of motion (12) and (13) have been solved by Heaps\textsuperscript{35} under
boundary conditions equivalent to assuming a drift velocity
superimposed by the electric field upon the random motions of
electrons along free paths between collisions, with the result

\[ \frac{Y}{X} = \frac{R_{\Theta T}}{m} = R_k \]

(14)

differing from Lenz's formula by a factor 3. (\(k_1\) is the
mobility of the electrons.) Lenz's neglect of the initial
velocities of the electrons along free paths appears to be a
poor approximation, even for "long" free paths of the order of
10^{-6} \text{ cm.} For a field of 5300 \text{ volts/cm} (the value of the field
used experimentally by Lenz in measuring Hall effects), the
kinetic energy picked up by an electron along a free path of
10^{-6} \text{ cm would be} 0.0053 e-v, as compared to the kinetic energy
of thermal agitation at room temperature of about 0.04 e-v.

Formula (14) could also be written

\[ Y = H(k_1 X) = H V \]

(15)
showing that on the simple classical theory, the Hall field is
equal to the product of the magnetic field and the drift
velocity.
Perhaps the most rigorous derivation of the expected magnitude of the Hall effect in electronic conductors based on classical mechanics was that by Gans. He considered the electrons in thermal agitation with velocities distributed according to the Maxwell distribution law, then calculated the change in the distribution function which would be produced by the application of crossed electric and magnetic fields. The new distribution function then enabled him to compute the resulting drift velocities $v_x$ and $v_y$ of the electrons in the direction of the electric field and at right angles to it respectively, and, finally, the Hall coefficient $R$, defined by

$$Y = R_l x H.$$  \hfill (16)

Gans found that $R$ should vary slowly as a function of the applied magnetic field according to the formula

$$R = R_0 \frac{\sigma_o}{\sigma} - B.$$  \hfill (17)

Here $R_o$ is the Hall coefficient for vanishingly small magnetic field, $\sigma_o$ is the corresponding conductivity, and $B$ is a function of the magnetic field, as well as of the fundamental constants of the conductor according to the following relations:

$$B(w) = \frac{1 - 2w^2 - 4e^w}{1 - w^2 + e^w} \frac{w^3}{w^4} \frac{\eta(-w)}{\eta(w)} = \frac{A(w)}{C(w)}.$$  \hfill (17)

$$w = \sqrt{\frac{3}{4mkT}} e^\lambda H = 2.28 \lambda H \text{ for } T = 500^\circ A;$$  \hfill (18)
\[ \Theta(x) = \int_x^\infty e^{-x^2} \, dx; \]
and
\[ \Theta(x) = \int_x^\infty \frac{e^{-x}}{x} \, dx. \]
Also
\[ \frac{\Theta}{\Theta_0} = C(w) + \frac{w^2}{4} A(-w) \cdot B(w). \]

For absolute values of \( w \) less than 0.1, \( B(w) \) is practically equal to unity, and so also is the ratio \( R/R_0 \).

Under usual experimental conditions, \( w \) is less than 0.1, as may be seen by substituting values for \( \lambda \) and \( H \) in (18).

For the "isothermal" Hall effect, Gans' ratio \( Y/X \) finally simplifies to
\[ \frac{Y}{X} = \frac{\sqrt{3} \pi (m/kT)^{\frac{1}{2}}}{4} \frac{e}{m} \lambda H. \tag{19} \]

For the sake of comparison the free time \( T \) in Eq. 15 may be taken as
\[ T = \frac{\lambda}{\nu}, \]
where
\[ \frac{1}{2} m \nu^2 = \frac{\lambda}{2} kT \quad \text{or} \quad \nu = (3kT/m)^{\frac{1}{2}}. \]
Then (15) may be written
\[ \frac{Y}{X} = \frac{\lambda}{\nu} \frac{eH}{m} = \frac{1}{2} \pi (m/kT)^{\frac{1}{2}} \frac{e}{m} \lambda H, \tag{15a} \]
which differs from Gans' only in the numerical factor.

Designating the numerical factors of (19) and (15a) by \( N_{19} \) and \( N_{15} \) respectively, it is seen that
\[ \frac{N_{19}}{N_{15}} = \frac{(\sqrt{3} \pi^{\frac{1}{2}}/4)}{3^{\frac{1}{2}}} = \frac{\sqrt{\pi}}{4} = 0.44. \]
QUANTUM MECHANICS EXPLANATION OF "ANOMALOUS" HALL EFFECTS

No classical theory of the Hall effect could account satisfactorily for its "anomalous" sign in many metals. (An ingenious attempt by Eldridge\textsuperscript{37} based on the "possibility" of electrons moving in random directions contributing differently to the sign of the Hall effect apparently was invalidated by an error in approximation, as pointed out by Page\textsuperscript{38}.) But in quantum mechanics "holes" in a zone of energy levels which is more than half full are shown to behave like electrons with positive charge, i.e., like positrons. Consequently a magnetic field should deflect them oppositely as compared to free electrons\textsuperscript{39, 40, 41, 42}. Such an opposite deflection comes out as a possibility because in quantum mechanics no account is taken of the orbits of individual particles—such orbits, in fact, have no meaning. Therefore if the position of a positive charge is found, at a time $t_2$, to have changed from its position at an earlier time $t_1$, it makes no difference by what (unobservable) mechanism the motion has taken place.

Peierls\textsuperscript{40} was first to explain anomalous Hall effects on the basis of opposite contributions from electrons and from hole conductors. He calculated the probability of an electron existing in a quantum state $(k, l, m)$ of a metallic crystal as a function of an applied (perturbing) electric field according to Dirac's ideas, i.e., the perturbing field was considered as effecting transitions from one quantum state to another, rather than as shifting the energy levels themselves, with the final
result

\[ R = \frac{Y}{H_1 x} = - \frac{2a^3}{ec \lambda} + \frac{2a^3}{ec(1 - \frac{n}{2\lambda})} \]  \hspace{1cm} (20)

in which \( a \)=lattice distance, \( e \)=electronic charge in e.m.u.'s, \( c \)=velocity of light, \( n \)=number of conduction electrons per atom, \( \lambda \)=number of quantum states per atom. If \( n=\lambda \), then the number of unoccupied energy levels is also equal to the number of conduction electrons, because each quantum state can accommodate two electrons (of opposite spin), and in this case (in which the number of holes would be equal to the number of electrons) the Hall coefficient is, by (20), zero. For \( n<\lambda \), hole conduction predominates and the Hall coefficient is positive.

Fowler has applied the same idea more particularly to the case of electronic semi-conductors and obtained for the Hall coefficient

\[ R = \frac{3}{8} \frac{\sigma_1 - \sigma_2}{e_1(n_1+n_2)} \]  \hspace{1cm} (21)

where

\[ \sigma_i = \frac{1}{3} \frac{e^2 \lambda n_i v}{kT}, \quad i=1 \text{ or } 2, \]

and \( \lambda \)=mean free path. \( \sigma_1, n_1 \) and \( \sigma_2, n_2 \) are conductivities and numbers-per-unit-volume of the electrons and the holes respectively.

Frenkel and Kontorowa, by an "elementary derivation" in which the magnetic deflection of electrons and holes is considered directly (instead of considering the effect on their
distribution functions by an applied magnetic field), obtain the formula

\[ R = \frac{1}{\text{ne}c} \frac{u_1 - u_2}{u_1 + u_2} \]  

(22)

in which \( R \) is expressed directly as a function of the mobilities of the electrons and holes respectively. Their result applies specifically to the case of an isotropic, divalent metal. The same formula had been previously derived by Blochinzew and Nordheim\(^{44}\) by computing the shift in the distribution function produced by application of a magnetic field.

It appears that no one has derived a quantum mechanics expression for \( R \) for the particular case of photoelectric conduction in an ionic crystal. Fowler's formula (21) might do, as an approximation, if the conductivities \( \sigma_1 \) and \( \sigma_2 \) were given in terms of more fundamental constants, and something were known about the magnitudes of \( n_1 \) and \( n_2 \). Formula (23) does give a value for the conductivities in terms of the electronic charge, the mean free path, the root-mean-square velocity, Boltzmann's constant, and the number-per-unit-volume of the carriers, but the concept of mean free path does not, properly speaking, fit in with the ideas of quantum mechanics. However, it appears that it may be replaced by the concept of "time of relaxation", or average time interval between successive collisions, and Frohlich\(^{26}\) has calculated such a time of relaxation for the specific case of NaCl. If Frohlich's time
of relaxation $\tau$ is combined with an assumed Maxwell
distribution of velocities of electrons (the free electrons
occurring in NaCl, even when photoconducting, are too few in
number to be considered as "degenerate") to compute a mean
free path $\lambda = v \tau$, the length of the mean free path comes out
to be very short, of the order of 0.5 to 0.9 of a lattice
cell—fitting in very nicely with the ideas of Von Hippel as to
the strong coupling between electrons and lattice points.

If in Gans' formula, Eq. 19, one puts $\lambda = 2 \times 10^{-8}$ cm,
$H = 12,000$ gauss, and the usual values for the other constants,
there is obtained

$$\frac{Y}{X} = 1/2200.$$  \hspace{1cm} (24)

According to Gans' work the Hall coefficient $R$ (for
the isothermal effect) comes out to be

$$R = \frac{3\tau}{8} \frac{1}{ne} ,$$
in terms of the number of electrons per unit volume $n$ and the
electronic charge $e$. In quantum mechanics the same quantity,
for free electrons, comes out to be simply*

$$R = \frac{1}{ne} .$$

In the absence of hole conduction, therefore, the classical
and the quantum mechanics predict Hall effects of the same
order of magnitude.

*See, for example, A. H. Wilson's book (reference 39), page 164.
---60---

In the usual method of expressing the result of measurements of the Hall effect in metals, the Hall coefficient is defined by the expression

$$E_H = R \cdot H \frac{i}{c},$$

(25)
in which $E_H$ is the potential difference produced between opposite sides of a strip of thickness $a$, and $i$ is the total current flowing longitudinally through the strip. This may be reduced to a ratio between the applied electric field and the Hall field by means of Ohm's law,

$$i = \frac{E_X}{r}, \quad \text{where} \quad r = \frac{\rho}{\Omega} \cdot \frac{a}{bc},$$

$a$, $b$, and $c$ being the length, breadth and thickness of the strip, respectively. Then

$$E_H = R \cdot H \cdot \frac{1}{c} \cdot \frac{E_X}{\rho \cdot \frac{a}{bc}} = R \cdot H \cdot \sigma \cdot \frac{E_X}{a},$$
or

$$\frac{E_H}{b} = \frac{E_X}{a} = \frac{Y}{X} = R \cdot H \cdot \sigma.$$ 

With respect to the possibility of detecting Hall fields in photoconductors, it is interesting to notice what some of the ratios $Y/X$ come out to be for metals subjected to a magnetic field of ordinary intensity.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Hall Coefficient</th>
<th>$Y/X$ for $H=7000$ gauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth</td>
<td>-4.95</td>
<td>1 to 3.45</td>
</tr>
<tr>
<td>Copper</td>
<td>-0.00052</td>
<td>1 to 480</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.0047</td>
<td>1 to 230</td>
</tr>
<tr>
<td>Iron</td>
<td>+0.0108</td>
<td>1 to 130</td>
</tr>
<tr>
<td>Cobalt</td>
<td>+0.24</td>
<td>1 to 5.6</td>
</tr>
<tr>
<td>Aluminum</td>
<td>-0.00038</td>
<td>1 to 1040</td>
</tr>
<tr>
<td>Antimony</td>
<td>+0.219</td>
<td>1 to 270</td>
</tr>
</tbody>
</table>

A Hall (or Corbino) effect too small to be detected could, therefore, taking into account the possible kinds of photoelectric carriers and the foregoing discussion, be interpreted in several ways.

1. The conduction is not electronic (improbable).
2. The positive carriers (hole conductors?) have a mobility such that their contribution nullifies that of the electrons.
3. The mean free path is very short.

The interpretation (2) suggests that, in principle at least, it might be possible to secure another experimental test as to the validity of the ideas of quantum mechanics. On the simple classical picture of the Hall effect, "hole conductors" should contribute to the transverse field additively with the photoelectrons in a photoconductor. On this model the movement of a hole actually entails only the movement of a replacement electron, which is in the same direction as that of the photoelectrons, namely, from the cathode toward the anode. For consider a hole A (figure 8) "undecided" whether to abstract an electron from a or b, which are halogen ions.
DEFLECTION OF A "HOLE" BY MAGNETIC FIELD NORMAL TO ELECTRIC FIELD. The hole $A$ has a better chance of moving in with "b" than with "a".
placed symmetrically between it and the cathode. In the absence of a magnetic field the predicaments of \(a\) and \(b\) are exactly equal. But if "assisted" by a magnetic field \(A\) has a slightly better chance of getting its electron from \(b\) than from \(a\), because an electron jumping toward the anode from \(b\) will be curved toward \(A\), whereas an electron starting from \(a\) will tend to curve above \(A\). The position of the positive charge is therefore more likely (other things being equal) to move toward its left, looking along its mobility vector, if electrons traveling in the opposite direction are deflected to their left. Positive space charge therefore builds up in the direction away from that in which negative space charge builds up, and the effects are additive.

**MAGNETO-RESISTANCE**

The classical galvano-magnetic theory of Gans\textsuperscript{36} indicates that the resistance of an electronic conductor should be slightly increased when a transverse magnetic field is applied to it, as given by the expression

\[
\frac{\Delta \rho}{\rho_0} = - \frac{\Delta \sigma}{\sigma_0} = \frac{9}{64} (4 - \pi) e^2 v^2 H^2
\]

\[
= 0.161 \frac{\Lambda^2 m(e)^2}{k T m} H^2, \tag{26}
\]

since \(v\), the mobility, has (on Gans' theory) the value

\[
v = (\frac{4}{3 \sqrt{m k T}})^{\frac{1}{2}} \lambda.
\]
According to (36) the sign of the change of resistance is independent of the sign of the charge \( e \) on a carrier, so that a change of resistance might occur even if the Hall effect, by reason of the opposite contributions from positive and negative carriers, was zero.

The reason, qualitatively, for expecting a magneto-resistance change, is that the paths of the carriers tend to be curled up under the influence of a transverse magnetic field—the component of the free path in the direction of the electric field is slightly decreased.

If in formula (36) there be substituted the values \( \lambda = 10^{-6} \) cm and \( H = 10^4 \) gauss, the fractional change of resistance comes out to be

\[
\frac{\Delta \rho}{\rho_0} = \frac{1}{10000}
\]

This agrees with the order of magnitude of the effect found in a few metals (gold, silver, copper, zinc) but in others the change is either much greater or much smaller. In the ferromagnetic metals there are even anomalies of sign in \( \Delta \rho \). The formula (36) might be expected to apply better to semi-conductors or photoconductors than to metals, however, because in its derivation a Maxwell distribution of velocities was assumed.

Granting that the mean free path of an electron in a photoconductor is of the order \( 10^{-6} \) cm, the possible 0.01%
change of resistance in a magnetic field of 10,000 gauss would still be very hard to detect. But if the mean free path were of the order $2 \times 10^{-8}$ cm, as seems likely to be the case for rock salt, then the expected change in resistance would be 2500 times smaller still. On this basis it would seem hopeless to look for such an effect.

Yet anomalous effects are sometimes produced in conductors by application of a magnetic field. The case of bismuth, among metals, is well-known; the resistance of a specimen of it at $18^\circ$ C is increased about 67% by placing it in a transverse magnetic field of 12,000 gauss. And, among photoconductors, there is the curious effect discovered by Kikoin and Noskov in cuprous oxide Cu$_2$O. They found that if a plate of cuprous oxide at liquid air temperature was placed in a magnetic field parallel to the plane of the plate but at right angles to its length, and then illuminated with normally-incident white or blue light, a potential difference of 3 to 5 volts could be produced between the ends of the plate. The sign of the potential reversed with the magnetic field and the effect decreased with rising temperature. In this phenomenon (as described by the discoverers) no electric field was initially applied to the specimen.
II. Apparatus

It was necessary to make the alkali halogen crystals from the fused salts, since natural crystals are uncertain in chemical constitution and physical properties. The method used was essentially that of Korth\textsuperscript{46} and Kyropoulos\textsuperscript{47}, namely, to raise a growing crystal slowly out of its melt by means of a cooling rod. The raising was done with a clockwork (following a suggestion by Walther\textsuperscript{48}) at the rate of 5 cm per hour. The apparatus is shown in figure 9. The lifter consisted of a platinum tube 8 mm in diameter and 10 cm long, the open end being silver-soldered to a Monel metal tube 1 cm in diameter and 33 cm long. Brass guides were arranged so that the whole tube had a smooth-sliding, vertical motion. The actual motivating power came from a counterweight, whose motion with that of the rod was regulated by an old alarm clock works. The wire running over and around various pulleys from the counterweight to the lifting rod also passed over a movable pulley which could be raised or lowered with a crank and axle, so that the rod could be moved independently of the clock.

Air was piped down the center of the cooling tube and sent against its rounded bottom (to which the growing crystals were attached) by a smaller inner copper tube. The fused salt was contained in an 80-cc platinum beaker, which sat on an iron stand in a small open electric furnace. About
FIGURE 9

APPARATUS FOR MAKING CRYSTALS

Legend: P=pulleys
MP=movable pulleys
Pt=platinum tube
W=weight
C=crank
S=slides
M=monel tube
1000 watts of power was consumed, but it was found necessary to wind nichrome coils of about 100% over-capacity in order for them to withstand temperatures up to 900°C without burning out within a few hours.

The procedure of making a crystal was as follows. The beaker-full of salt was melted, with the cover down on the oven. The time required for the melting was generally about an hour. Then the cover was replaced with a mica sheet which had a hole in its center to admit the lifting rod. The latter was then lowered slowly into the melt to a depth of four or five millimeters. The clock was next started and a small current of air sent through the lifter. Within a few minutes, if the temperature adjustment was right, a small, roughly hemispherical, transparent mass could be seen attached to the end of the rod. This was allowed to grow to a total diameter about twice that of the platinum tube, which in the meantime should have moved up a similar distance. The rod was then raised by hand (using the crank) until the initial mass of crystallites touched the melt in a circle of seven or eight millimeters diameter. This operation was necessary in order to reduce the number of crystallites in contact with the fused salt to a relatively small number, perhaps four or five. Then within the next centimeter or two of growth (if the operation was attended by good fortune) one of these crystallites would outstrip and dominate the others, so that the mass from then on would have a single set of cleavage planes, oriented, however, in a completely random direction.
This adjustment of the area of contact at the "bottle neck" required a good deal of care, since the contact was difficult to see clearly. After making this somewhat critical adjustment the clock and weight were allowed to proceed with the lifting, the air current was increased, and the temperature of the oven somewhat decreased (but if the oven current was cut down too much, the surface of the salt froze over by radiation to the top).

The size of the crystals grown in this way was limited by the amount of heat which could be conducted away through the "bottle neck" of the crystal mass. Still, with NaCl, onion-shaped bulbs about three or three and one-half centimeters long could be grown and from these sometimes could be split plates three-quarters of an inch long, a half inch wide and a quarter inch thick. Crystal plates half this size were big enough for the experiment, so that a larger, more elaborate crystal-growing outfit was unnecessary. It was found possible to grow crystals without a thermometer; a device to measure the temperature of the fused salt would have been helpful but, with practice, could be dispensed with. (It was desirable to keep the fused salt at as low a temperature as possible without it freezing over, in order to increase the size of the crystals.)

Crystals of the following substances were grown large enough in this apparatus for photoelectric experiments: NaCl, NaBr, KCl, KBr, and KI. NaCl and KCl were the easiest
to produce. As a matter of fact LiCl was the only substance tried out for which fair-sized single crystals could not be obtained with the apparatus just as described.

The crystals, once grown, had to be colored in some way in order to be photoconducting. (In a check experiment with clear rock salt, no photoelectric current whatsoever was detected by means of the sensitive direct-current amplifier, although the currents obtained with exactly the same conditions of field and illumination and colored crystals would have produced a galvanometer deflection of about 500 meters.)

There are several ways of coloring these crystals, as mentioned before; the one generally chosen was that of driving electron clouds off a pointed cathode into the heated specimen. A few crystals were colored photochemically with x-rays. The apparatus for forcing in electrons consisted of an asbestos-covered iron oven, about 12 inches long and 2½ inches inside diameter, mounted horizontally and with a small elevated table near the center on which the specimen was placed. The table served as one electrode while the other was a platinum needle clamped in a brass rod which was insulated from the oven by a quartz tube. The oven was closed with mica windows at each end, so that the coloring process could be watched. The oven was capable of maintaining a temperature of 750° C. The temperature was measured, for a while, by means of an iron-nickel thermocouple spot-welded on to the platinum plate upon which the crystal sat. The calibration of this
thermocouple, however, constantly shifted in the direction of less E.M.F. per degree difference of temperature. Next a platinum resistance thermometer was used with a bridge circuit sensitive to about a half degree change of temperature, which order of accuracy was sufficient.

A vertical pyrex oven was also sometimes used, but the temperature distribution within it was obviously very non-uniform, to the extent that the temperature of thermometer and crystal might differ by as much as 50° C—as shown by the apparently higher temperature required to start the coloring process in a given substance in this oven than in the other. Also with some crystals (in particular, NaCl) the 600° C upper safety limit for pyrex not subjected to pressure was still not a high enough temperature that the coloring (at that temperature) could be completed within a reasonably short time.

Specimens to be used in photoelectric experiments were, immediately after coloring, snatched from the oven by means of a long pair of forceps and quenched in a stream of air. It was found that quenching the crystals in a non-inflammable liquid, such as carbon disulphide, was too severe a treatment—it always caused the crystals to break up into pieces too small to be used in the experiments.

The borders of a colored piece, after quenching, were cleaved off, in order to have left a plate with uniform distribution of color centers clear out to its bounding surfaces.
The freshly-cleaved crystal was then placed under a bell-jar and sputtered with platinum. A good, conducting coating could be obtained in about 20 minutes. Since the sputtered film rubbed off rather easily, it was unnecessary to cover the faces which were not going to be used as electrodes; the film could be wiped off clean with a damp rag, after which the specimen would be rinsed in alcohol.

Electrodes made by smearing the crystal ends with graphite paint ("aquadag") were found unsatisfactory. The effective conductance of such electrodes was found to be increased many times by a trace of moisture in the crystal chamber. No such effect was noticed with the platinum films.

The Hall effect set-up will be described next. (See figure 10.) Details of the crystal holder are shown in figure 11. This crystal holder was held between the pole pieces of a Weiss electromagnet which could produce a field of about 12,000 gauss across an air gap of 16 mm between its pole pieces when a current of 14 amperes flowed through its coils (saturation was reached at about 10 amperes). B-batteries in series giving about 600 volts were the source of potential applied to the ends of the crystal. These batteries, which were connected to ground somewhere near their center, stood on a stand insulated by hard-rubber blocks coated with paraffin. Batteries and stand were encased in a copper-screen shielding box.
FIGURE 10

LEGEND

$P_S = 40,000 - 20,000 \, \Omega$

$P_P = 55,000 \, \Omega$

$PG =$ portable galv.

$LG =$ L&N. galv.

$S =$ switches

$AS =$ amber insulated switch

$H =$ Hall electr.

13.2 volts

$r_d =$ damping resistance

$R_G = 1.1 \times 10^{10}$

$R_L = 5000 \, \Omega$

$R_1 = 11.5 \, \Omega$

$R_2 = 38.5 \, \Omega$

3 volts

ELECTRICAL SET-UP FOR MEASURING CORBINO CURRENT,

including electrometer tube circuit.
FIGURE 11

LEGEND

HR = hard rubber block
R = brass rods
Q = quartz insulating tube
P = pyrex tube upon which guard ring is wound
S = brass springs
K = platinum blade
C = crystal
Sc = screw
Pi = pivot
O = opening to drying agent or vacuum system
E = electrode

CRYSTAL- HOLDER
A direct-current, electrometer-tube amplifier, with the circuit as given by Harnwell and Van Voorhis, was used for the measurement of small E.M.F.'s or currents. The essential feature of this circuit (which is a modification of one by DuBridge) is that small fluctuations in the filament emission of the tube are automatically and instantaneously balanced out by setting the currents collected by plate and by space charge grid against each other in a Wheatstone bridge arrangement, thereby practically eliminating the greatest single source of electrical instability found in the earlier electrometer-tube circuits. The method also gives greater absolute sensitivity (as pointed out by Harnwell and Van Voorhis) because the effect of a small change of grid potential on the two currents which are balanced is opposite.

The tube was a Western Electric D-96475. The circuit is shown in figure 10. The only change made from Harnwell and Van Voorhis' circuit was that a variable resistance (from 10,000 to 20,000 ohms in 1-ohm steps) was substituted for the fixed space-charge grid resistance. This change was made for greater convenience in keeping the galvanometer spot on the scale—the disadvantage of Harnwell and Van Voorhis' control method, that of changing the potential difference applied to the whole amplifier, is that, after making such a change, the filament emission requires several minutes to reach a new equilibrium value, during which time the galvanometer spot
continues to drift. The tube and all of the constant resistances were in an oil-sealed metal box containing a drying agent, \( \text{P}_{2}\text{O}_{5} \) powder.

Two galvanometers were alternatively available by means of tap switches, according to the magnitude of the current to be measured or the quickness of response desired. One, a small portable instrument with a current sensitivity of \( 5 \times 10^{-8} \) amp/div., was used for comparatively large currents, or for currents which changed rather rapidly with time. The other galvanometer was a standard Leeds and Northrup instrument with a period of 13.2 seconds and a current sensitivity (at one meter) of \( 1.0 \times 10^{-10} \) amp/mm. A large scale 3.3 meters long was set up at the distance 6.85 meters, however, and on this scale the sensitivity was \( 1.3 \times 10^{-10} \) amp/cm. When used with its critical damping resistance of 12,000 ohms the galvanometer was very steady; the focus of the moving mark on the scale was also good, so that deflections could be read to the nearest 0.5 mm. Electrical instability of the amplifier usually made such fine readings meaningless, but the large scale was still useful by reason of its good visibility from any part of the room.

Two additional ranges of voltage sensitivity for the sensitive galvanometer were also provided by connecting it in series with resistors of \( 1.25 \times 10^{5} \) and \( 1 \times 10^{6} \) ohms respectively, and tap switches. The over-all voltage sensitivity of the amplifier for each of the four ranges was as follows:
Portable galvanometer 450 div./volt
Sensitive galvanometer
  Full range  200,000
  First reduced range  23,000
  Second reduced range  3,100.

The maximum current sensitivity used in any measurement was
4.5 x 10^{-16} amp/div., obtained by using the full range of the
sensitive galvanometer and a grid resistance of 1.1 x 10^{10}
ohms. Usually this sensitivity was accompanied by fluctuations
of 10 to 25 scale divisions, however, so that the first
reduced range, giving a current sensitivity of 4 x 10^{-15}
amp/div. had to be used—but this still was a good sensitivity.

The sensitivity could also have been reduced by
inserting a smaller grid resistor, but it was more convenient
to change the sensitivity of the galvanometer.

The current sensitivity was found in a fairly direct
way, since the grid resistor resistance could be measured
directly (by connecting it in series with the sensitive
galvanometer and some B-batteries) and the voltage sensitivity
of the amplifier could likewise be calibrated directly (by
means of a Leeds and Northrup student potentiometer). However
the current sensitivity was also checked by applying the
current produced in a known high resistance (4.2 x 10^{10} ohms)
by a known small potential (1.5 volts) directly to the grid and
grid resistor. The deflection obtained with this "known"
current agreed within about 12% with the expected value
according to the calibration.
The amplifier calibrating device could be thrown on to the grid any time by a proper manipulation of switches (it was arranged so that the calibrating potential was applied through the regular amber-insulated grounding switch).

The fluctuations observed with the high range of sensitivity correlate with observations of Hafstad\textsuperscript{50} and MacDonald\textsuperscript{51} that electrometer tubes when not kept in a vacuum chamber are generally subject to voltage fluctuations of the order of $10^{-5}$, caused by random ionization of the air about the tube and the grid connections. The theoretical (and practical) limitation to stability set by shot and flicker effects in the residual thermionic current to the grid from the filament is considerably lower, so that in well-shielded, vacuum-encased systems, currents of $10^{-18}$ ampere have been detected and measured.

Because of the voltage instability the amplifier could be used in the conventional electrometer way (floating grid) only with the portable galvanometer or the second reduced range of the sensitive galvanometer. Even so, the voltage sensitivities of 450 and 3,100 divisions per volt (as already given), together with the small grid system capacity (about 30 $\mu$F) gave very high current sensitivities.

The set-up for measuring Hall or Corbino effects was peculiar in that only one cross-electrode was used. This arrangement was to eliminate the difficulty of mechanically or electrically adjusting two opposite cross-electrodes to the
same initial potential level, which adjustment would have necessarily been very close because of the high voltage sensitivity of the measuring device. Mechanical adjustment would have been difficult because the crystals were small and kept in a drying chamber. The size of the crystals was limited by the necessity of illuminating them completely, in order to obtain steady currents at field strengths far below saturation. The light came through a hole drilled in one of the pole pieces, which hole could not be made unduly large without distorting the magnetic field.

The sensitivity of the arrangement to Hall E.M.F.'s (or Corbino currents) was empirically calibrated by observing the change in current to the Hall electrode caused by a known small shift of the grounded point of the batteries. The way in which this worked may be shown by an application of Kirchoff's laws of current networks to the circuit consisting of the illuminated crystal, batteries grounded near center, Hall electrode, and grid resistor. This circuit is shown schematically in figure 12, in which \( R_1 \) represents the effective resistance between electrode \( A \) and the Hall electrode, \( R_2 \) is the corresponding resistance between \( B \) and the Hall electrode, and \( E_1 \) and \( -E_2 \) are the potentials of the end electrodes with respect to the grounded point \( G \). The condition for no resultant current through the Hall electrode, namely,

\[
i_H = i_1 - i_2 = 0
\]
APPLICATION OF KIRCHHOFF'S LAWS TO HALL NETWORK
may be written

\[
\frac{i_1-i_2}{E_1} = \frac{E_1}{R_1+R_g} = \frac{E_2}{R_2+R_g} = \frac{E_1}{R_1} = \frac{E_2}{R_2},
\]

since \( R_g \) (although large) was still, in general, much smaller than either \( R_0 \) or \( R_2 \), which were of the order of magnitude of \( 10^{13} \) or \( 10^{14} \) ohms even when the crystal was brightly illuminated.

The effect of shifting the grounded point by an amount \( \Delta E \) would be to increase the applied potential between \( A \) and the Hall electrode by an amount \( \Delta E \) (neglecting the comparatively small \( iR \) drop over \( R_g \), i.e., the small voltage actually applied to the electrometer tube), and to decrease that between \( B \) and the Hall electrode by the same amount. The change of current through the Hall electrode thereby resulting would be

\[
\Delta i_H = \Delta i_1 - \Delta i_2 = \frac{\Delta E}{R_1} - \frac{-\Delta E}{R_2} = \Delta E \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{\Delta E}{R_H}, \tag{27}
\]

where \( R_H \) is a somewhat fictitious quantity, a kind of total effective resistance between the Hall electrode and the two end electrodes. (It must be kept in mind that \( R_1 \) and \( R_2 \) have no direct relation to \( R_c \), the total resistance between the end electrodes. \( R_1 \) and \( R_2 \) may vary from about the same magnitude as \( R_c \) to a value 15 or 20 times greater. In the latter case \( R_c \) would act effectively as a short circuit to \( R_1 \) and \( R_2 \).)

Equation (27) could be written as a differential equation,
\[
\frac{d1H}{dE} = \frac{1}{R_h} = \frac{2}{R_1},
\]  

(28)

if \(R_1\) and \(R_2\) are nearly equal, giving the rate of change of current to the Hall electrode as a function of small changes in the grounded point. It was found experimentally that such changes were actually proportional to the voltage shifts producing them, as indicated by Eq. 28, provided these shifts were small. For larger shifts the effective resistances \(R_1\) and \(R_2\) of the Hall electrode are not constant.

In measurements on zincblende, it was found that it was immaterial whether the Hall electrode was "above" or "below" the crystal. (Reversing the direction of the electric field has the effect of reversing the relative position of the Hall electrode, as far as any physical changes are concerned which might proceed, in full or part, from the action of the field.) Therefore it seemed certain that if an exactly opposite cross-electrode had been pressed against the crystal and connected to a second amplifier \(A'\) (figure 13), it would have registered, during an induced Hall E.M.F., a current equal to, but opposite in direction to that registered by the "real" amplifier \(A\). In other words, the effect of an induced Hall E.M.F. of magnitude \(E_H\) across the width of the crystal would have been to change the potential of the Hall electrode with respect to any arbitrarily chosen point by the amount

\[
\Delta E = \frac{E_H}{2}.
\]  

(29)
It is seen from Eq. (29) that to produce the same change in current $\Delta i_H$ to the Hall electrode as would be produced by a given potential shift $\Delta E$ of the ground terminal, the Hall E.M.F. $E_H$ would have to be twice as great, or $2\Delta E$, across the total width of the crystal. In other words the sensitivity of the single electrode to Hall E.M.F.'s was only half as great as that of two electrodes, i.e., the Hall E.M.F. required to produce a noticeable deflection $\Delta D$ of the galvanometer would be twice as great as the ground shift necessary to produce $\Delta D$. This fact was taken account of in all calculations to set an upper limit to an undetected Hall effect.

The Hall electrode was protected against leakage currents across the ebonite frame of the crystal holder from the high potentials applied to the end electrodes by a grounded guard ring. Care was exercised in the design of this guard ring to keep its electrostatic capacity down.

The full light of a 32-candlepower, tungsten-filament lamp was used to illuminate the crystals. The absorption of long wave-length light is supposed to reduce "excitation" in a photoconducting crystal and thereby to increase the magnitude of the current. The motion of "excitation centers" is still limited by the "anchor" effect of the positive charges, however, and it is doubtful if the long wave-length light does much to increase the steady current—what it actually increases is the initial surge of electron current.
Since the light had to be sent through a long, small hole in one of the pole pieces of the magnet, a small intense source was needed. Nothing better for this was found than an ordinary automobile 6-8 volt headlight bulb, which could be run, if needed, at the over-voltage of 10, or even 12, but its life-time at 12 volts was rather short. A beam of light of fairly uniform intensity over its entire cross-section, where it passed into the crystal, was obtained by focusing the image of the collecting lens upon the crystal.

The back E.M.F. built up in the crystals by passage of a photoelectric current was found to be, to some extent, a function of the uniformity of illumination. For instance, the back E.M.F. built up in colored rock salt was only about half as great if the light source consisted of a Point-o-lite lamp, focused by a single short lens, instead of the arrangement actually used. The light source in a Point-o-lite is a round metal ball bombarded with ions and the Point-o-lite therefore emits according to Lambert's cosine law of intensity, producing a very uniform light spot. But direct current is required to operate this lamp, so that its intensity of illumination was found to vary slightly when the large magnetizing current was thrown on—both currents being necessarily from the same generator in the facilities available.

The magnetic field was determined by means of a Grassot fluxmeter connected to a test coil of known dimensions and number of turns. The same coil plus fluxmeter had been calibrated by Mr. F. T. Rogers, of the Rice physics
department, against an absolute Cotton balance, and found to
give correct results to within a few percent. The fluxmeter
separately had been recently checked against a line-turn meter
and another fluxmeter by Prof. C. W. Heaps, of Rice, and a
correction factor of 0.94 deduced for it, which factor was
used here.

Good shielding and insulation were primary
requirements, although the amplifier, when used to measure
small currents by the steady deflection method, did have the
advantage that the order of insulation necessary was
considerably less than that for electrometer rate-of-charge
measurements. The fact that the amplifier did not require a
high order of insulation was a direct result of its high
voltage sensitivity. For example, it was only necessary that
the leak resistance be about 100 times as great as that of
the grid resistor itself. The grid resistor used for most of
the measurements was 1.1 \times 10^{10} \text{ ohms}; 100 times this, or
about 10^{12} \text{ ohms}, is an insulation leak resistance which is not
hard to attain even in a fairly humid atmosphere.

To try out the experiment of Tartakowsky, a complete
new set-up had to be built (figure 14), including a new
\textit{(figure 15)}
crystal holder (all brass, with sulphur insulation), two
amber-insulated, \texttt{steel-needle-on-platinum-plate} electrometer
switches, an amber-insulated, variable air condenser, and a
shielding box for the electrometer, which also had to be set
up. The quartz suspension fiber was attached by the usual
FIGURE 14

TARTAKOWSKY'S SET-UP.

LEGEND

P=L. & N. student potentiometer
B=B-batteries
S=switches
AC=variable air condenser
AA
BB=quadrant-pairs of electrometer
FIGURE 15

LEGEND
C=crystal
E=electrodes
S=brass springs
P=sulphur plugs
G=glass plate
VS=tube to vacuum system

CRYSTAL-HOLDER FOR TARTAKOWSKY ARRANGEMENT
technique (shellac) to small brass hooks and then sputtered on both sides with platinum. The paper needle was found at first in a very wrinkled condition, from exposure to the damp climate, but was ironed out flat by pressing it between damp cloths and thin metal sheets with an ordinary electric flatiron. The aluminum paint on this needle was a very poor conductor, so that at first it appeared to charge up patchily, making adjustment of the electrometer difficult. This condition was remedied by sputtering both sides of the needle, too, with platinum.

The electrometer, when finally set up, was very stable in operation, with a sensitivity of 1070 divisions (mm) per volt at a scale distance of 2.2 meters. The calibration, made with a Leeds and Northrup student potentiometer and two fresh dry cells, was symmetrical for both directions of deflection, and for either pair of quadrants grounded. The zero point was inclined to shift a fraction of a centimeter or so from day to day. This may have been due to the fact that the plane of the needle was noticeably not parallel to that of the quadrants, or it may be that the level of the stone shelf on which the instrument stood shifted slightly.
III. Experimental Procedure and Results

INTRODUCTORY NOTE

The sensitivity obtained in the various attempts to observe galvanomagnetic effects in photoconducting alkali halides was limited principally by the phenomena of photoelectric polarization and by spontaneous fluctuations in the magnitude of the photoelectric currents.

Polarization resulted in the formation of comparatively large back E.M.F.'s which greatly reduced the magnitude of the obtainable steady currents. Furthermore it appeared impossible to obtain, at least within an ordinary length of time, a steady state of polarization at which no more polarization would be built up by continued flow of the photoelectric current. The building up of large back E.M.F.'s reduced the resultant electric field intensity in most parts of all the crystals studied, except rock salt, by a very large factor. The interpretation of results was thereby rendered uncertain, because a Hall field, if existent, would be expected, according to simple theory, to be a function of the longitudinal field.

Observed fluctuations in the photoelectric current in rock salt were about ten times greater than those which might have been expected to be produced by Brownian motion of electric carriers in the crystal (see page 160). Current fluctuations in KBr and KCl were still much larger. The
presence of these fluctuations increased the number of readings needed to establish a given upper limit to a possible small, unobserved Hall effect. Presumably the source of the fluctuations will have to be determined and eliminated before appreciably lower limits than those assigned during the course of the present investigation can be set.

STUDY OF ROCK SALT

The photoelectric back E.M.F. and the relative fluctuations were smaller in rock salt than in any other of the alkali halides studied. Measurements on rock salt, by use of the single electrode method and the amplifier indicated that the photoelectric Hall field, if present, was not greater than one part in 1000 of the applied longitudinal field, for a magnetic field of 12,000 gauss.

Although a knife-edge making good contact should, theoretically, be a very effective electrode (see appendix, page 187 of thesis), it was found in practice that such an electrode, when pressed against a photoconductor by a spring, collected a current ten or twenty times smaller than that expected. The reason, presumably, was that in the small region of intense field and concentrated current flow about a knife-edge, a large photoelectric space charge built up, greatly reducing the effective conductance of the knife-edge contact. It was found that use of a wider Hall electrode, consisting of a sputtered platinum strip, made it possible to
obtain considerably more sensitivity to the presence of possible galvano–magnetic effects.

The amplifier was used in two ways for the detection of small currents. The first, or "steady deflection" method, was simply to impress the $iR$ "drop" developed by a small current flowing through a high resistance $R_g$ upon the grid of the electrometer tube, and then to read the corresponding deflection of the galvanometer. Then

$$i = \frac{E_g}{R_g} = \frac{F_a d}{R_g}, \quad (30)$$

in which $F_a$ is the voltage sensitivity of the amplifier in volts per division, and $d$ is the deflection, in divisions, produced by the potential $E_g$, measured with respect to ground, impressed upon the grid.

The second was the "rate-of-charge" method, in which the grid was allowed to "float", and the current flowing into it determined by the time-rate at which its potential increased, according to the equation

$$\frac{dQ}{dt} = i - C \frac{dE_g}{dt} = CF_a \frac{\Delta d}{\Delta t}, \quad (31)$$

If a null result was obtained, i.e., no detectable change of grid potential occurred which could be ascribed to a possible Hall effect, then it could be deduced not only that no Hall current was flowing, but also that no detectable Hall E.M.F. was present.
In order to determine the current-sensitivity of the rate-of-charge method, the rate at which potential built up on the system Hall-electrode-plus-grid by means of a charging current $i_H$ as a function of the electrostatic capacity $C$ and the insulation leak resistance $R$ had to be computed. The insulation leak resistance $R$ was equivalent to a very large grid leak resistance $R_g$. For ordinary values of $R_g$, as used in the steady deflection method, the equilibrium voltage at which

$$\frac{E_q}{R_g} = i_g = i_H$$

built up within a few seconds, despite the finite capacity of the system and the smallness of $i_H$, because $E_q$ was also small. The insulation leak resistance, however, was about 1000 times greater than the $R_g$'s used in the steady deflection method, so that the corresponding equilibrium voltage for a given charging current $i_H$ was much greater and the time required to reach this equilibrium voltage correspondingly longer.

The rate of charging of a condenser by a small constant current $i_H$ working against a leak resistance $R$ is expressed by the equation

$$\frac{dQ}{dt} = \frac{dE}{dt} = i_H - \frac{E}{R}$$  \hspace{1cm} (32)$$
The solution of this equation for $E=0$ when $t=0$ is

$$t = -CR \log_e \left(1 - \frac{E}{E_H} \right) \quad (33)$$

$$= -CR \log_e \left(1 - \frac{E}{E_q} \right).$$

The effect of the built-up potential $E$ upon the incoming current $i_H$ has been neglected in Eq. 33. The current $i_H$, however, may be considered as produced by a (small) Hall E.M.F. $E_H$ acting upon an effective photoelectric resistance $r_c$, so that Eq. 32 should have been written

$$C \frac{dE}{dt} = i_H - i_R = \frac{E_H - E}{r_c} - \frac{E}{R} = \frac{H}{r_c} - \frac{E}{R} \left(\frac{1}{r_c} + \frac{1}{R} \right) \quad ,$$

i.e.,

$$\frac{dE}{dt} + \frac{1}{C} \left(\frac{1}{r_c} + \frac{1}{R} \right)E = \frac{H}{Cr_c} \quad .$$

This expression has the same form as (32) and its solution, for the same boundary conditions is, setting $1/r' = 1/r_c + 1/R$,

$$t = -Cr' \log_e \left(1 - \frac{r_c E}{r' E_H} \right)$$

$$= -Cr' \log_e \left(1 - \frac{E/r'}{E_H/r_c} \right) \quad (34)$$

As used above, $E_H$ is the part of the Hall E. M.F. actually impressed upon the Hall electrode and for the single electrode arrangement is only one-half of the total Hall E.M.F. across the crystal. $r_c$, the resistance across which
E_H may be considered to act, can be obtained only roughly by the calibration experiment. This resistance does not appear at all in formula (33), which, however, reduces to (34) only if \( R \ll r_c \), and this is not generally the case. But for \( E \) much smaller than \( i_H R \), and the latter in turn much smaller than \( E_H \), the following approximation may be used:

\[
\log_e(1-x) = -x + \frac{x^2}{2} - \frac{x^3}{3} + \frac{x^4}{4} - (\ldots) + \text{etc.}
\]

\[(-1 < x < 1)\]

\[= -x.\]

Applying this approximation, formulae (33) and (34) both reduce to

\[t = \frac{CE}{i_H},\]

which, of course, is the simple result which would have been obtained by considering \( R = \infty \) and \( i_H \)-constant.

Formula (33) is a better approximation than (35), however, and was generally used. Comparatively small Hall E.M.F.'s, of the order of 1 volt, are still very large compared to the smallest potential differences which could be detected by means of the amplifier, so that it was unnecessary to allow the "back E.M.F." built up on the Hall electrode to become comparable in magnitude with the expected \( E_H \).

The idea, then, was to adjust the apparatus so that the total deflection of the indicator during a certain time interval \( t \) while no magnetic field was applied was less than that expected, during an equal time interval, to be produced
by a Hall E.M.F. $E_H$, which then could be taken as the "upper limit" for an unobservable Hall E.M.F.

As a matter of fact it was quite impossible to locate a permanent "balance point" for the grounded position of the batteries, for the reason that photoelectric polarization continued slowly to build up in the crystal as long as the photoelectric current was allowed to flow (at least for time intervals up to 24 hours), thereby continually shifting the potential distribution along the length of the crystal. An adjustment was therefore made as closely as possible and the Hall electrode allowed to charge up to an approximate, small, equilibrium voltage, so that the residual rate of deflection of the galvanometer, while perceptible, at least was small and nearly constant over the interval of time required to take two consecutive readings.

With the best adjustment obtainable within an ordinary length of time, the galvanometer spot would still move 2 to 4 scale divisions in two minutes. But according to the result of the empirical calibration (to be given shortly) a Hall E.M.F. across the crystal of only 1/5th volt would have caused a rate of deflection appreciably greater.

After making the adjustment of the grounded point, the magnetic field was turned on and the resulting effect, if any, on the motion of the galvanometer spot was watched for.

As a matter of fact, the turning-on of the magnetizing current always did have some effect on the motion
of the spot. This effect, however, was obviously spurious, as shown by the following facts: (1) it was independent, both in direction and magnitude, of the direction of the magnetizing current, and (2) it was also present when the crystal was not illuminated. This spurious effect of the magnetizing current was due to a combination of mechanical and electrostatic disturbances produced when the magnetizing current was thrown on, as shown by the fact that it could be reduced by such devices as shielding the magnetizing coils, shunting the terminals of the magnetizing coils with a 50-watt lamp, grounding the magnetizing circuit at certain points, and additional electrostatic shielding of the Hall electrode. It was also found that the stray field of the magnet had an effect on the amplifier which "followed" the direction of the magnetizing current, but this effect was practically eliminated by moving the amplifier to a distance of about 1.5 meters from the magnet. The various spurious effects of the magnet were measured in separate experiments and corrections for them deduced.

The method as just outlined was used in one set of measurements according to which an upper limit of 1/150 was set for the ratio Y/X. However it was then found that more accuracy could be obtained by observing the change in rate of deflection of the galvanometer indicator caused by application of a magnetic field, rather than by waiting a certain time to see what distance the spot had moved. Individual readings
taken by this new procedure required less time, so that the polarization of the crystal was given less time in which to change. Besides, the somewhat risky approximation involved in the use of Eq. 33, namely that the effect of any built-up potential upon the magnitude of the charging current was negligible, was, by this method of taking readings, avoided to some extent. By means of a stopwatch the rate of deflection could be observed rather accurately.

The formula appropriate to the method of watching for changes in the rate of deflection produced by a possible Hall field may be obtained by differentiating Eq. 35 and then considering the differentials as increments.

\[ \frac{\text{d}t}{I_H} = \frac{C \text{d}E}{I_H} = \frac{CF \text{d}D}{I_H}, \]

or

\[ I_H = CFa \frac{\Delta D}{\Delta t}. \]

Here \( \Delta t \) is the time required for the indicator to move \( \Delta D \) scale divisions. Then the change in \( I_H \) (\( I_H \) now being taken simply as the total current through the Hall electrode) caused by a possible Hall field set up in the crystal by the applied magnetic field would be

\[ I_H = CFa \left( \frac{\Delta D}{(\Delta t)_1} - \frac{\Delta D}{(\Delta t)_2} \right), \]  

in which \( (\Delta t)_1 \) and \( (\Delta t)_2 \) are the time intervals required for the indicator to move the scale distance \( \Delta D \) with the magnetic field on and off respectively.
DATA ON ROCK SALT

The data by means of which a final upper limit was set to the possible Hall field in NaCl will be presently given in some detail. However the null results consistently obtained in the earlier attempts to detect a Hall effect lend support to the final conclusion and have, consequently, a certain amount of significance. They are presented below in Table I, in which the abbreviations are obvious.

<table>
<thead>
<tr>
<th>Kind of Electr.</th>
<th>Measur. Method</th>
<th>$\Delta i_H$ (10^{-15}Amp)</th>
<th>$E_H$ (volts)</th>
<th>$Y/X$</th>
<th>$H=12,000$g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kn. Edge</td>
<td>Elctrm. R. of Ch.</td>
<td>10</td>
<td>18</td>
<td>1 to 25</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>Amplfr. St. Defl.</td>
<td>10</td>
<td>8</td>
<td>1 to 50</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>R. of Ch.</td>
<td>10</td>
<td>8</td>
<td>1 to 50</td>
<td></td>
</tr>
<tr>
<td>Pt. Strip</td>
<td>R. of Ch.</td>
<td>5</td>
<td>3</td>
<td>1 to 150</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>St. Defl.</td>
<td>50</td>
<td>1</td>
<td>1 to 450</td>
<td></td>
</tr>
</tbody>
</table>

There was no direct relation between the upper limits to $\Delta i_H$ and $E_H$ because of variations in the experimental conditions. Sensitivity to possible small $E_H$'s depended more on the effective photoelectric conductance of the Hall electrode than on the current sensitivity of the measuring device. The upper limits to $E_H$ and $Y/X$ have all been assigned on the assumption that the single Hall electrode would have detected only half of any possible Hall E.M.F. existing across the width of the crystal.

Two "good" sets of measurements were finally obtained by use of the best technique developed, one by the steady
deflection method, the other by the rate-of-charge method. The latter will be described first.

Observations were made on the rate of deflection of the galvanometer as a function of the applied magnetic field, using the portable galvanometer because of its greater quickness of response (damped period 2.4 seconds.) Then the over-all voltage sensitivity was 450 divisions per volt. In order that the magnitude of the currents producing the observed rates of deflection should be known, the capacity of the system grid-plus-Hall-electrode had to be ascertained. This capacity was measured by observing the ballistic throws of the sensitive Leeds and Northrup galvanometer when the system was charged to 675 volts, being careful to subtract from the total capacity thereby obtained the capacity of the lead between galvanometer and grid system as found in the same way. The figure thus obtained for the capacity was compared with the geometrically-estimated capacity of the system, the largest single contribution to which was provided by the long shielded lead between the Hall electrode and the amplifier unit. The shield was a 4-inch copper pipe 145 cm long; the lead was made of No. 36 copper wire, diameter 0.01 cm. The total electrostatic capacity of the shielded lead was 11.5 µf. A capacity of 30 µf. was obtained for the whole system.

The value of the leak resistance $R$ also had to be known, in order to calculate whether a small Hall E.M.F. would produce an observable effect upon the amplifier unit.
despite the insulation leak. The rate of decrease of potential of the grid caused by leakage of a given initial charge could be observed, and $R$ obtained by substitution of observed quantities in the formula

$$i = \frac{dQ}{dt} = \frac{dE}{dt} = \frac{E}{R}, \quad \text{or} \quad R = \frac{E}{\frac{dE}{dt}}.$$

The leak resistance $R$ was found to be about $10^{13}$ ohms. The change of current to the Hall electrode resulting from a shift in the grounded point of the batteries of 1 volt (which, according to the theory of the calibration, would produce the same change as a Hall E.M.F. of 2 volts across the crystal) was empirically found to be about $6 \times 10^{-15}$ ampere, according to which the Hall electrode would charge up to only about 0.012 volts in 1 minute, corresponding to a deflection of about 5 scale divisions. The equilibrium voltage corresponding to a charging current of $6 \times 10^{-15}$ ampere and an insulation leak resistance of $10^{13}$ ohms is 0.06, which would not be approached until the lapse of several minutes.

The actual calibration for sensitivity was entirely empirical. The calibration data are given in the first column of the following table. The $\Delta V$'s are changes in rates of deflection obtained by observing, in succession, the rate of deflection for a given "balance", and the rate of deflection after conditions had been changed, either by shifting the grounded point by 1 volt, or by applying the magnetic field in a given direction.
TABLE II. Hall Effect Measurements on NaCl by Rate-of-Charge Method

<table>
<thead>
<tr>
<th>ΔV Produced by Shifting Gr. Pt. 1 V.</th>
<th>ΔV Produced by Magnetic Field &quot;West&quot;</th>
<th>ΔV Produced by Magnetic Field &quot;East&quot;</th>
<th>Max. Undetected Hall E.M.F.</th>
<th>Y/X for Across Crys. H=12,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.02</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.09</td>
<td>-0.10</td>
<td>-0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.79</td>
<td>-0.23</td>
<td>-0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.86</td>
<td>0.19</td>
<td>-0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.13</td>
<td>0.10</td>
<td>-0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.40</td>
<td>0.10</td>
<td>-0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.73</td>
<td>0.04</td>
<td>-0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.78</td>
<td>0.20</td>
<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.83</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.03</td>
<td>0.16</td>
<td>Avg. 0.04</td>
<td>Avg. -0.10</td>
<td>0.2 volt 1/1150.</td>
</tr>
<tr>
<td>1.13</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The data are displayed in order to show the order of reproducibility, the fluctuations, and the small regularities. Individual Δt's were generally of the order of 30 seconds. The changes produced by throwing on the magnetic field are seen to be of a fairly random nature, and certainly not greater, on the average, than 1/10th of that produced by shifting the grounded point 1 volt. The small systematic deviations were found to be still present with the light turned off. Granting, however, that they might have masked an effect of the same order as themselves, the Hall voltage across the width of the crystal must still have been less than 0.2 volt. The crystal was 0.4 cm wide, so that the maximum undetected Hall field was 0.5 volt/cm. The longitudinally applied average field was 690 volts/cm, or, subtracting the back E.M.F., 90 volts, from the applied E.M.F., 520 volts, and dividing by
the length of the crystal, 0.754 cm, the effective field must have been at least 570 volts/cm in the center of the crystal. Therefore the ratio of the maximum undetected Hall field to the longitudinal field was 1/1150.

It should be noticed that except for two readings the effect of applying the magnetic field "west" was to increase very slightly the flow of positive current into the Hall electrode, and conversely that the effect of applying the magnetic field "east", with two exceptions, was to decrease very slightly the flow of positive current into the Hall electrode. This small apparent regularity may have been entirely spurious or accidental, in view of the facts that a similar effect was present with the light turned off and the effect, if real, actually had the wrong sign for a "normal" Hall E.M.F. Nevertheless similar very small effects were later observed by means of a different experimental arrangement (see page 146). In any event the ratio of the Hall field to the longitudinal field was certainly less than 1 part in 1150.

A check run was then made by use of the steady deflection method. The current sensitivity of the amplifier unit was adjusted to be $4.0 \times 10^{-15}$ amperes/cm but, as before, the calibration was empirical. The applied magnetic field was the same as before, 12,200 gauss. In Table III, following, the $\Delta d$'s are galvanometer shifts produced by altering the conditions as stated:
**TABLE III. Steady Deflection Data on Rock Salt**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>6</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>12,000</td>
<td>0.76</td>
</tr>
<tr>
<td>1( \frac{1}{2} )</td>
<td>2</td>
<td>-1</td>
<td>-( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>-( \frac{1}{2} )</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>1( \frac{1}{2} )</td>
<td>1( \frac{1}{2} )</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>-( \frac{1}{2} )</td>
<td>-1</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>-1( \frac{1}{2} )</td>
<td>-1( \frac{1}{2} )</td>
<td>0.2</td>
<td>1/1150</td>
</tr>
</tbody>
</table>

23.076 Avg. 0.9

The effect of throwing on the magnet switch is seen, from the above, to have been quite random. Any persistent difference was certainly not greater than 0.76 cm, or the shift which would have been produced by changing the grounded point by 0.1 volt. Then the maximum Hall E.M.F. across the crystal was 0.2 volt. Or, as in the other set of measurements, the maximum Hall field was 0.5 volt/cm, and the ratio of the Hall field to the longitudinal field not greater than 1 part in 1150.

The steady deflection method had the advantage that it enabled the effect of throwing on the magnetizing current to be immediately apparent. Strictly speaking, of course, it would measure the Corbino current, rather than the Hall field, if one were present.

The deviations actually observed when the magnet switch was thrown were found to exist whether or not the light was shining, so that no effect whatsoever which might be interpreted
as produced by a Hall E.M.F. was found. However it was taken for granted, as before, that real effects of the order of the deviations might have been masked.

If the longitudinal field intensity at the center of the crystal was equal to the average field intensity between the end electrodes—and this might have been the case if the potential distribution across the crystal had been somewhat like that of figure 20 (page 144)—then these experiments indicated the ratio of the Hall field to the longitudinal field producing it was not greater than 1/1500.

Experiments by Von Hippel (page 31 of this thesis) on preferred directions of electron travel in rock salt suggested that perhaps the Hall effect also might have "preferred directions". Lenz, in fact, found the Hall effect in zincblende to depend upon the orientation of the specimen. A colored slab of rock salt, therefore, was cut so that the electric field could be applied in a face-diagonal (110) direction, and the Hall field, if any, measured in another face-diagonal direction (figure 16). According to Von Hippel's experiments, electrons diffusing in an electric field encounter less resistance in a 110-direction than in a 100-direction (parallel to a cube edge).

The slab was 7.34 x 4.14 x 2.57 mm in size. The Hall electrode was a sputtered platinum strip 0.25 mm wide. Its sensitivity to changes in the ground point was found to be 0.8 cm per volt. Data are given in Table IV, in which the
ORIENTATION OF CRYSTAL PLATE with sides and ends parallel to 110 directions. The form drawn with solid lines shows the position and orientation of the final cut crystal plate with respect to the original cleaved block from which it was cut (dashed lines).
d's are simply scale readings, taken at 1-minute intervals with the magnetic field as indicated.

**TABLE IV. Data on 110 Rock Salt Specimen**

<table>
<thead>
<tr>
<th>Magnetic Field Time</th>
<th>Off</th>
<th>&quot;West&quot;</th>
<th>&quot;East&quot;</th>
<th>Max. $E_H$ Max. $Y/X$ Undcld. for $H_z$ 12,000g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>18</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>26</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>26</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>26</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Averages</td>
<td>23</td>
<td>29.2</td>
<td>29.5</td>
<td>1 volt: 1/200</td>
</tr>
</tbody>
</table>

It may be seen that the magnet had a definite effect, which, however, was independent of the direction of its field. The difference in scale deflection produced by opposite directions of the field was negligible; moreover, the magnet was found, in a control experiment, to have the same effect upon the deflection whether or not the light was shining on the crystal. A Hall E.M.F. of 1 volt across the crystal would have produced an average deflection change of 0.4 cm, according
to the calibration experiment, or, for opposite directions of the magnetic field, a shift of 0.8 cm. The observed changes were certainly less than 0.8 cm. Fluctuations were of the order of 1 cm from the mean reading. Taking into account the specimen's dimensions, the Hall field must have been less than 3 volts/cm, or less than 1 part in 200 of the applied average field, 640 volts/cm, over the length of the crystal.

A similar set of readings taken with the direction of the electric field reversed gave a similar result. The apparent effect of the magnet was found to reverse with the direction of the photoelectric current, but was still independent of the direction of the magnetic field.

Although the possible Hall effect was not pushed down to as small an upper limit as in the more exhaustive experiments with the 100-directions, it was not deemed profitable to spend more time upon this part of the investigation.

HALL EFFECT MEASUREMENTS ON KCL

Hall effect measurements upon KCl by means of a cross-electrode were, by themselves, of doubtful significance, because separate experiments (see page 179) indicated that the main fall of potential in the specimen was concentrated near its ends, with a comparatively gentle potential gradient near where the Hall electrode was situated. Any induced Hall field at the center of the crystal presumably would have been proportional to the relatively weak electric field intensity. On the other hand, a comparatively small E.M.F. across the
width of the crystal near its center would have been initially unopposed by any back E.M.F. at the Hall electrode, and therefore would have produced a comparatively large initial Corbino current.

Using the steady deflection method, the average of six readings taken with the magnetic field "west" as compared with the average of six readings for the magnetic field reversed indicated that the effect of reversing the magnetic field was to change the scale deflection by not more than 0.1 cm, whereas changing the potential of the Hall electrode 1 volt with respect to the end electrodes produced, on the average, a change of 2 cm. Therefore, to take the maximum undetected Hall E.M.F. as 1 volt, because of the variations between individual readings, the generated Hall field was certainly less than 1 part in 350 of the average applied field.

The null result of these measurements, while, as previously mentioned, not in itself very conclusive, was fully confirmed and supported by an independent measurement, using a different set-up which will be described later (pages 136-143).

KCl, in common with KBr, KI, and NaBr, has the property of allowing a comparatively large surge of electron current to flow at the outset of illumination, followed by a rapid decrease of the current to a much smaller but still
slowly decreasing value. The absence of measurable Hall effect in the steady current conceivably could be due to equal and opposite contributions from the electron and the electron-replacement components of the current. In the initial surge of current, however, it seems probable that the electron-replacement component is only a small fraction of the total current, so that if a Hall effect existed at all, it might be "magnified" in this initial surge. Therefore the initial surge was examined for possible Hall effect by a ballistic method, by means of which the photoelectric charge passing into the Hall electrode during a short flash of illumination (controlled by a camera shutter) was measured as a function of the applied magnetic field.

In applying the ballistic method, it was found impossible to locate a balance point for which no deflection would be produced by a single flash of light. The initial current was comparatively large, of the order of $10^{-9}$ ampere, as compared to the final current of about $10^{-11}$ ampere, and built up photoelectric polarization, as well as back E.M.F., very rapidly, thereby changing the potential distribution materially along the length of the crystal. Therefore balance points could be found for which the current during the first part of the flash was into the Hall electrode, but during the last part of the flash was in the opposite direction, resulting in a double kick of the galvanometer. It was considered advisable to select a grounded point such that the
current into the Hall electrode had the same direction throughout the flash. About the smallest obtainable uni-directional ballistic throw of the galvanometer from a 1/10th second flash of light was of the order of 25 cm. Fluctuations of about 1 cm from the mean throw were commonly in evidence.

The significant data are displayed in Plate I. The crystal was grounded at each end and illuminated for $3\frac{1}{2}$ minutes after each flash of light, in order to discharge its accumulated photoelectric polarization. Switches were thrown on a regular time schedule, in order to reproduce conditions for each reading as nearly as possible. The $3\frac{1}{2}$-minute period of illumination of the grounded crystal was not sufficient to remove all of the polarization produced by one flash of light while the electric field was on (several hours would have been required for a "complete" discharge) but was long enough that at least 99% of the developed back E.M.F. was removed.

The average of 12 readings taken with the magnetic field "east" was a throw of 23.75 cm. The average of 12 readings taken with the magnetic field in the opposite direction was 23.83 cm. In the empirical calibration it was found that shifting the grounded point by 1 volt changed the corresponding ballistic throw by 2 cm (about twice as much as the average fluctuation). (Actually the grounded point was changed 3 volts and an average change of 6 cm observed in the resulting deflection.)
HALL EFFECT MEASUREMENTS UPON INITIAL ELECTRON SURGE OF PHOTOELECTRIC CURRENT IN KCL BY BALLISTIC USE OF AMPLIFIER.

○ = readings with magnetic field "east" (avg. = 23.75)
× = readings with magnetic field "west" (avg. = 23.33)
• = readings with grounded point shifted ±3 volts between consecutive readings.

N.G. = point discarded in taking average.
It appears certain that the effect of reversing the magnetic field was to change the ballistic throw by less than 1/2 cm. Such a result was indicated by the small variations between individual readings, as well as by the still smaller difference between the averages. But this assumed maximum change was produced by a reversal of the magnetic field, therefore the effect of the field for a single direction was less than 1/4th cm. But 1/4th cm was the change which might have been expected to be produced by a Hall E.M.F. of 1/8th volt across half the width of the crystal. A Hall E.M.F. of 1/4 volt across the entire width of the crystal would correspond to a Hall field of 0.71 volt/cm. The applied longitudinal field intensity was 660 volts/cm. Then the upper limit of the ratio Y/X was 1/850.

However the photoelectric back E.M.F. developed in 0.1 second in KCl was about one-half of the total applied E.M.F. Then the average (in time) of the resultant electric field near the Hall electrode during the flash was perhaps only 3/4th of the initial applied field, and likewise with the time average of a possible concomitant Hall field. Then

\[
\frac{(\Delta Q)_H}{(\Delta Q)_C} = \frac{(3/4)(E_H)_o}{\Delta E},
\]

or

\[
(E_H)_o = \frac{4}{3} \frac{\Delta E}{(\Delta Q)_C} (\Delta Q)_H.
\]

Here \( \Delta E \) is the potential shift of the grounded point in
the calibration experiment, \((\Delta Q)_c\) is the resulting change in the charge passing into the cross-electrode, \((\Delta Q)_H\) is the charge passing into the Hall electrode by reason of the Hall field, and \((E_H)_0\) is the initial value of the Hall field. Therefore the upper limit of the ratio \(Y/X\) has been set too small by a factor 3/4; a safer limit for the ratio \(Y/X\) in the initial electron surge of KCl is 1/640.

Even with the above correction, the Hall field, if any, developed in the initial surge of KCl was, relative to the applied electric field, at least ten times smaller than the Hall fields developed in diamond and zincblende by magnetic fields of comparable strength.

POTASSIUM BROMIDE

Photo-sensitive KBr, like KCl, has the property of allowing a large surge of electron current to flow at the beginning of illumination, followed by a rapid building-up of polarization and corresponding decrease of the current. The final "steady" current in the polarized crystal is further characterized by large fluctuations, many times too large to be accounted for by the Johnson or shot effects (see page 161 of thesis). The fluctuations to a side electrode placed near the center of the crystal, however, were found to be relatively much smaller than the fluctuations in the total photoelectric current through the crystal. That is, the potential distribution along the length of the crystal
remained fairly constant in time despite the fluctuations in longitudinal current. A comparatively small Hall E.M.F. across the middle of the crystal could have been detected, but, since the resultant electric field near the center was greatly reduced by photoelectric polarization, it is doubtful if a small value of the ratio \( Y/X \) could have been observed. As with KCl, the null result of apparently sensitive tests made with a side electrode had, by itself, little significance, and required confirmation by a different experimental arrangement, to be described later.

A lightly-colored specimen, size 7.20 x 4.48 x 0.80 mm, whose coloring was almost invisible to the eye, was chosen because experiments with rock salt had indicated that relatively less polarization was formed in lightly-colored crystals. Such was certainly not the case with KBr, however. The back E.M.F. built up by a steady photoelectric current in this lightly-colored KBr plate was nearly equal to that of the applied field (see page 170).

Data for KBr obtained by the single-electrode set-up are shown in Plate II. The usual calibration showed that a 1-volt shift of the Hall electrode potential with respect to the end electrodes produced a steady deflection of 6.4 cm. Therefore a Hall E.M.F. of 1 volt across the crystal should have produced a deflection of 3.2 cm. The average of 11 readings with the magnetic field "east" was a shift of 9 cm, which, as it happened, was in the direction which would have
PLATE II

DATA UPON POSSIBLE HALL EFFECT IN STEADY PHOTOELECTRIC CURRENT OF KBR CRYSTAL.

○ = readings with magnet "west".
× = readings with magnet "east".

The steady drift of the galvanometer was due to a continued building up of photoelectric polarization in the crystal. The zero position of the galvanometer is indicated by the dashed line. Variations between consecutive readings for reversed direction of the applied magnetic field appear to be entirely random.
been expected for the "normal" Hall effect. The average of 6 readings with the magnetic field reversed was a shift of 3.5 cm in the same direction. The difference, 5.5 cm, although probably spurious, might therefore have been attributed to an unsymmetrical Hall E.M.F. of about 1 volt across the crystal (for a single direction of the field), or, alternatively, a Hall effect of that magnitude masked by a superimposed throw of spurious origin. Then the Hall field would have been

\[
\frac{1 \text{ volt}}{0.45 \text{ cm}} = 2.3 \text{ volts/cm.}
\]

The applied voltage, 580, gave an average longitudinal field of 830 volts/cm. Therefore the Hall field was indicated by these measurements to be not greater than 1 part in 350 of the average applied field.

Ballistic measurements on the possible Hall effect in the initial electron surge were made with a faulty procedure, i.e., the crystal was illuminated with 1/50th second flashes of light at equally-spaced intervals of 5 minutes, but was not grounded and "discharged" between consecutive flashes. An equilibrium state was thus set up, in which the polarization built up by each flash was approximately equal to the polarization which had been lost in the preceding dark interval, but the residual back E.M.F. was such that the surges were only about 1/4th as great as if the crystal had been completely discharged after each illumination.
The sensitivity was 5 cm of ballistic throw per volt for potential shifts of the Hall electrode with respect to the end electrodes. The random fluctuations between consecutive throws were about two or three centimeters. The final null result, that the Hall field of the initial electron current was less than 1/350th of the average applied field, may be taken as preliminary. Its significance, if any, lies in its accord with the null result of the more properly performed, corresponding measurements upon KCl, whose photoelectric properties in other respects are similar to those of KBr.

CONFIRMATION BY MEASUREMENTS UPON A SUBSTANCE OF KNOWN GALVANO-MAGNETIC PROPERTIES

With so many null results the question naturally arose as to whether the experimental arrangement was actually capable of detecting the presence of a Hall E.M.F., or concomitant current, if one were present. Now diamond and zincblende appear to be the only substances in which accurate measurements of the photoelectric Hall effect have been made. The former substance is expensive and hard to obtain, so a sample of clear yellow sphalerite (zincblende) with perfect rhombic dodecahedral cleavage was secured. Following Lenz's suggestion, a plate (7.27 x 4.8 x 2.0 mm) was cut so that its longest dimension, along which the electric field was to be applied, was parallel to a direction symmetrical with respect to the three crystal axes.
The method of cutting was simply to find a suitable cleavage face, scratch out on it the outline of the plate, and then follow that outline as closely as possible. The resulting error in direction of orientation was probably about 5 or 6°. Lenz mentions that he had a good deal of trouble eliminating surface conduction. In the present case the plate was polished with rouge, then rinsed successively in strong acid and in alcohol, after which treatment the surface conductivity was found to be even less than that of freshly-cleaved rock salt kept in a drying chamber.

Since the photoelectric currents obtainable in zincblende are many times greater than the steady currents obtainable in the alkali halides, it was unnecessary to sputter a Hall electrode; a platinum knife-edge only was used. It was observed that the back E.M.F. set up by polarization in zincblende was somewhat less than that in rock salt, i.e., it was about 10% of the applied E.M.F. The photoelectric current in zincblende, however, did not decrease from a fairly large initial value to a much smaller steady value. Instead its initial value, as measured with the short-period galvanometer, was several percent less than its steady value, to which it built up within about 30 seconds. This increase of current was due, probably, to the formation of so-called secondary current by the action of the primary current, in disagreement with Lenz's assertion that secondary current in zincblende is not appreciable for field strengths less than 8000 volts/cm.
(It is possible that the amount of secondary current is a function of the particular specimen of zincblende, i.e., is structure-sensitive.) The dark resistance of the specimen here studied was approximately $2 \times 10^{15}$ ohms, corresponding to a resistivity of about $1.5 \times 10^{16}$ ohm/cm, about the same as that of rock salt.

Sets of readings on the Hall effect (as manifested by Corbino current) taken on three consecutive days were in excellent qualitative agreement. Readings taken the first day were scattered and unsystematic; they will not be given here.

Readings taken the second day were with the electric field "north". (Frequent reversals of electric field were impractical, because of the considerable length of time required for equilibrium to be reached; also upon each reversal a new "balance" had to be found.) In taking data not only was the steady deflection of the galvanometer produced by the Corbino current in evidence, but also an initial "throw" was noted, whose magnitude was about three times greater than that of the steady deflection (see page 134). This throw was attributed to the lack of polarization about the Hall electrode initially opposing the Hall field, which polarization, however, built up within a few seconds, reducing the Corbino current to its steady value. The data is displayed in Table V. All numbers, except the times, are simply scale readings.
TABLE V. Corbino Effect in Zincblende

<table>
<thead>
<tr>
<th>Time</th>
<th>Mag. Off</th>
<th>Magnet &quot;West&quot;</th>
<th>Time</th>
<th>Mag. Off</th>
<th>Magnet &quot;East&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Init.</td>
<td>Stdy.</td>
<td></td>
<td>Init.</td>
<td>Stdy.</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>56</td>
<td>0</td>
<td>65</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>66</td>
<td>67</td>
<td>3</td>
<td>65</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>66</td>
<td>59</td>
<td>5</td>
<td>64</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>59</td>
<td>56</td>
<td>7</td>
<td>66</td>
<td>81</td>
</tr>
<tr>
<td>8</td>
<td>66</td>
<td>60</td>
<td>9</td>
<td>66</td>
<td>74</td>
</tr>
<tr>
<td>10</td>
<td>69</td>
<td>57</td>
<td>11</td>
<td>69</td>
<td>80</td>
</tr>
<tr>
<td>12</td>
<td>65</td>
<td>60</td>
<td>13</td>
<td>74</td>
<td>83</td>
</tr>
<tr>
<td>14</td>
<td>69</td>
<td>61</td>
<td>15</td>
<td>69</td>
<td>82</td>
</tr>
<tr>
<td>16</td>
<td>70</td>
<td>62</td>
<td>17</td>
<td>70</td>
<td>83</td>
</tr>
<tr>
<td>18</td>
<td>68</td>
<td>60</td>
<td>19</td>
<td>65</td>
<td>70</td>
</tr>
<tr>
<td>20</td>
<td>65</td>
<td>58</td>
<td>65</td>
<td>65</td>
<td>70.5</td>
</tr>
</tbody>
</table>

There is clearly apparent a lack of symmetry between the effects of magnetic field "west" and "east". The asymmetry, however, was shown in control measurements with the light turned off (see table VI following) to be due at least partly to a spurious uni-directional effect of the magnet, which cancelled or more than cancelled the Corbino steady deflection for "magnet west" but added to the Corbino deflection for the opposite direction of field. Nevertheless the initial throws of the Corbino current overbalanced in every case the spurious throw. According to the foregoing set of readings, the average difference in the final steady position of the indicator caused by reversal of the magnetic field was only 2.7 cm, in the correct direction for a normal Corbino effect. Part of the effect was still masked by a spurious action of the magnet, however, as shown by control readings taken with the illumination cut off, now to be given as Table VI.
TABLE VI. Effect of Magnet

<table>
<thead>
<tr>
<th>Time</th>
<th>Mag. Off</th>
<th>Magnet &quot;West&quot;</th>
<th>Time</th>
<th>Mag. Off</th>
<th>Magnet &quot;East&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Init.</td>
<td>Stdy.</td>
<td></td>
<td>Init.</td>
</tr>
<tr>
<td>0</td>
<td>12</td>
<td>15</td>
<td>1</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>5</td>
<td>10</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>9</td>
<td>13</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>7</td>
<td>14</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>11</td>
<td>10</td>
<td>12</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td></td>
<td>9.4</td>
</tr>
<tr>
<td>Avgs.</td>
<td>9.8</td>
<td>8.4</td>
<td>13.0</td>
<td></td>
<td>9.6</td>
</tr>
</tbody>
</table>

It is to be noticed, in the above, that the final steady deflection for magnet "west" was, for some peculiar reason, abnormally large. Its difference from the average steady deflection for the opposite direction of the field was opposed to the effect of the Hall field, so that this difference, 3.4 cm, should be added to the uncorrected result. Making this correction, the total effect of opposite Hall fields was to produce an average shift of 6.2 cm. It was reassuring to notice that the initial spurious throw of the magnet was several times smaller than the initial throw caused by the first action of the Hall field.

In the empirical calibration it was found that the steady deflection was 1.8 cm per volt change of the Hall electrode with respect to the ends of the crystal. The sensitivity to induced Hall E.M.F., therefore, was one-half this amount, or 0.9 cm per volt. For one direction of the field the average Hall deflection was $\frac{1}{2} \times 6.2$ cm = 3.1 cm. Then the Hall E.M.F. across the crystal at its middle was 3.5 volts, giving a Hall field of 7.3 volts/cm. The assumption
has been made, of course, that the Hall field was proportional to the Corbino current which was actually measured. The average applied field was 645 volts + 7.27 cm=890 volts/cm. Therefore the ratio of the inferred Hall field to the average applied electric field was 1 to 130.

For an applied field of 5300 volts/cm, Lenz obtained a Hall field of about 70 volts/cm as the average of the two directions of the magnetic field. His value for Y/X was thus 1/75, somewhat greater than the value for the same ratio here found. Moreover Lenz used a field of only 7,000 gauss, as compared to 12,200 gauss used here. Still the results agree as to order of magnitude, and the apparent discrepancy might easily be due to one or several of the following reasons:

1. Structural or chemical differences in the samples of zincblende.

2. Non-validity of the assumption made here, that the Hall field was proportional to the Corbino current.

3. A large difference in the current densities used by Lenz, and in the measurements here described. Lenz's current densities were about 200 times greater per unit of applied voltage. Lenz has verified that the ratio Y/X is independent of current density over a "wide range", but the smallest total current density in the table which he submits as proof is still 130 times as great as that in the measurements here performed.

A still closer agreement with Lenz's results was obtained upon increasing the intensity of illumination so that
the current density per unit of applied field was "only" 40 times smaller than in Lenz's measurements. Thereby the sensitivity of the experiment was also increased to the point that deflections, both initial and permanent, caused by action of the induced Hall field were several times as great as those produced by spurious actions of the magnet.

The data is displayed in Table VII, on the following page. For this set of measurements the direction of the electric field was reversed from that of Table V, and, as should have been the case, the deflections ascribed to the Hall E.M.F. were reversed in direction.

The difference in steady deflection caused by opposite induced transverse fields was, on the average, 42 cm. From this had to be subtracted the corresponding difference when no light was shining on the crystal, namely 2 cm. (The direction of the spurious effect of the magnet had "followed" that of the electric field.) The change in deflection per unit shift of ground point was 17 cm/5 volts=5.7 cm/volt. One volt of Hall E.M.F. would have produced half this amount of shift, or 2.8 cm. The measured deflection difference 40 cm was produced by opposite Hall fields, hence the potential difference developed across the crystal by the Hall field was 40 x 5.7=7 volts. This value corresponds to a field of 15.5 volts/cm, whose ratio to the applied field is 1 to 60--about the same ratio as that obtained by Lenz with a magnetic field not much more than one-half as strong.
### TABLE VII. Hall Effect in Zinblende

<table>
<thead>
<tr>
<th>Time</th>
<th>Magnet &quot;West&quot;</th>
<th></th>
<th>Magnet &quot;East&quot;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78</td>
<td>128</td>
<td>87</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>85</td>
<td>133</td>
<td>96</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>89</td>
<td>130</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>93</td>
<td>141</td>
<td>62</td>
<td>64</td>
</tr>
<tr>
<td>12</td>
<td>96</td>
<td>143</td>
<td>101</td>
<td>64</td>
</tr>
<tr>
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<td>97</td>
<td>143</td>
<td>106</td>
<td>64</td>
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<td>94</td>
<td>142</td>
<td>110</td>
<td>65</td>
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<td>94</td>
<td>141</td>
<td>109</td>
<td>64</td>
</tr>
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<td>22</td>
<td>97</td>
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<td>108</td>
<td>66</td>
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<td>110</td>
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<td>26</td>
<td>96</td>
<td>142</td>
<td>113</td>
<td>69</td>
</tr>
<tr>
<td>28</td>
<td>92</td>
<td>142</td>
<td>109</td>
<td>65</td>
</tr>
<tr>
<td>30</td>
<td>95</td>
<td>142</td>
<td>111</td>
<td>66</td>
</tr>
<tr>
<td>32</td>
<td>96</td>
<td>142</td>
<td>115</td>
<td>70</td>
</tr>
<tr>
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<td>142</td>
<td>111</td>
<td>66</td>
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<td>95</td>
<td>140</td>
<td>112</td>
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<td>96</td>
<td>142</td>
<td>110</td>
<td>65</td>
</tr>
<tr>
<td>40</td>
<td>94</td>
<td>143</td>
<td>109</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>93</td>
<td>141</td>
<td>107</td>
<td>63</td>
</tr>
</tbody>
</table>

**Averages:** 93.7

The above table shows the initial throw, steady deflection, and reverse throw for both the "West" and "East" magnets. The numbers are given in volts.

### CALIBRATION

<table>
<thead>
<tr>
<th>Change in Grounded Pt. (Volts)</th>
<th>Initial Throw</th>
<th>Steady Deflc.</th>
<th>Reverse Throw</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>117</td>
<td>20</td>
<td>-139</td>
</tr>
<tr>
<td>3</td>
<td>117</td>
<td>20</td>
<td>-138</td>
</tr>
<tr>
<td>3</td>
<td>116</td>
<td>16</td>
<td>-135</td>
</tr>
</tbody>
</table>
The agreement, however, was twice as good as for the other set of data, perhaps because the current density was nearer to that used by Lenz.

The galvanometer deflections here ascribed to Corbino currents produced by a Hall field were very positive and unmistakable, and at least five or six times as great as the spurious effects and fluctuations combined. As a further check, however, a Dolezalek electrometer with a voltage sensitivity of 1070 divisions per volt was substituted for the amplifier as a measuring instrument; nothing else was changed.

No disturbance at all of the electrometer needle could be seen when the magnetic field was applied with the crystal in the dark. Then, after illuminating the crystal, the grounded point was adjusted until the rate of deflection of the electrometer was less than 0.083 divisions (mm) per second. Then a positive effect was produced by throwing on the magnetic field. The indicator started moving to left or right, according to the direction of the field, at a rate easily perceptible. Stopwatch readings were made of the deflection rate. Because of the comparatively high Hall E.M.F., a final steady deflection could not be obtained except by laborious readjustment of the grounded point of the batteries. The principal interest was in the order of magnitude, so only a few readings were taken. The average of these is given in Table VIII, in which the V's are rates of deflection of the indicator in mm/second.
TABLE VIII. Check on Zinblende With Electrometer

<table>
<thead>
<tr>
<th>V—Magnet Off</th>
<th>V—Magnet &quot;West&quot;</th>
<th>V—Magnet &quot;East&quot;</th>
<th>V Produced by Shifting Gr. Pt. 1 v.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.077</td>
<td>-0.70</td>
<td>0.32</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The difference in rate of deflection according to whether the magnetic field was in one direction or the other, 1.02 mm/second, therefore corresponded to a Hall E.M.F. of 5.7 volts across the crystal, or a field of 12.5 volts/cm. The ratio of this to the applied field of 675 volts/cm was 1/55, in fair agreement with the ratio 1/60 obtained by use of the amplifier in the same experiment.

As when using the amplifier, indications were obtained that the initial Corbino current was several times as large as the steady Corbino current. The steady value of the Corbino current was reached within about 30 seconds of first applying the magnetic field.

CHECKS BY THE METHOD OF TARTAKOWSKY

Thus with check experiments making use of the known galvano-magnetic photoelectric properties of zinblende the null result of previous attempts to detect a Hall effect in rock salt and other alkali halides was confirmed. The fact remained that Lukirsky had reported a Hall effect in photoconducting rock salt of the same order of magnitude as that found in zinblende (as shown by the computed mean free paths ascribed to the electrons, assuming similar methods of computation), and Tartakowsky had reported a deflection
of the photoelectric current through a rock salt crystal by a magnetic field in the direction corresponding to bending of free electrons. Their experiments were done with photochemically colored, i.e., x-rayed crystals, however, whereas additively colored crystals had been, thus far, exclusively used in the present investigation. Still it appeared necessary to repeat the experiment of Tartakowsky as exactly as possible. (An exact description of Lükirsky's experiment was unavailable.)

It appeared likely that the difference in results was due to the difference in mode of preparation of the crystals, since the condition of photochemically and additively colored crystals is quite different. Hence both kinds were used in the attempted duplication of Tartakowsky's work.

The method of Tartakowsky consists in the use of a divided electrode, the two approximately equal parts of which are connected differentially to the two pairs of quadrants of an electrometer (see figure 14, following p. 80). A balance in the rate of charging of the quadrant pairs, so that no net deflection occurs, is obtained by connecting one pair of quadrants (that pair which by trial is found to charge up more rapidly) to one side of a variable air condenser. Then any change in the differential rate of charging caused by application of a magnetic field to the crystal can be observed. In practice it was found almost impossible to secure a perfect adjustment, but this difficulty
was got around by observing the residual slow rate of deflection with a stopwatch.

The procedure was as follows. A photoelectric current was allowed to flow through the specimen for several minutes, during which time both pairs of quadrants were grounded, until a fairly steady state was reached. Then both switches were opened "simultaneously"—which with practice could be done so that no noticeable throw of the needle would occur—and the adjustment made with the variable condenser. The magnetizing current was next turned on, in one direction or the other, and the quadrants again simultaneously isolated from ground. After an initial wait of 30 seconds, to allow things "to settle down", the spot was timed over 5 scale divisions. The procedure was then repeated for the other direction of the magnetic field. In this way the initial conditions were duplicated to a fair degree of approximation, and it was certain that the electrometer was charged up to only a few volts, the total current to either pair of quadrants being about $10 \times 10^{-12}$ ampere. Also the accumulated voltage was nearly the same for consecutive trials.

The calibration was by comparing the total change in the rate of deflection with the rate of deflection of either quadrant when the other was grounded. For example, if the rate of deflection $V_A$ due to quadrants $AA$ was increased by $\Delta V_A$, it could be assumed that the average potential difference between electrodes $A_1$ and $C$ had been fractionally increased
by $\Delta V_A/V_A$. If at the same time the rate of deflection $V_B$ due to quadrants BB was decreased by $\Delta V_B$, it could likewise be assumed that the average potential between electrodes $B_1$ and $C$ had been fractionally reduced by $\Delta V_B/V_B$. That is, it has been assumed that

$$\frac{\Delta V_A}{V_A} = \frac{\Delta i_A}{i_A}, \quad \text{and} \quad \frac{\Delta V_B}{V_B} = -\frac{\Delta i_B}{i_B}.$$ 

If the initial applied potential before application of the magnetic field was $E_0$, then by symmetry the potential between $C$ and the mid-point of the opposite end of the crystal would still be $E_0$ after formation of the Hall field $Y$. Then the average change of potential over the contact between electrode $A_1$ and the crystal caused by the Hall field is (figure 17)

$$E_A = aY,$$

$a$ being the distance from the mid-point of the end of the crystal to the mid-point of $A_1$. Likewise

$$E_B = -bY.$$ 

Also

$$\Delta i_A = \frac{\Delta E_A}{R_A} = \frac{ay}{R_A}, \quad \text{and} \quad \Delta i_B = \frac{\Delta E_B}{R_B} = \frac{-by}{R_B},$$

where $R_A$ and $R_B$ are the effective resistances between electrode $C$ and electrodes $A_1$ and $B_1$ respectively.
FIGURE 17

CALIBRATION OF TARTAKOWSKY'S METHOD
The total change in the rate of deflection of the electrometer would be

\[ \Delta V = \Delta V_A - \Delta V_B = V_A \frac{\Delta i_A}{i_A} + V_B \frac{\Delta i_B}{i_B} = \frac{V_A a Y}{E_o R_A} + \frac{V_B a Y}{E_o R_B} = \frac{Y}{E_o} (V_A + V_B). \]

Or, if \( V_A \) is approximately equal to \( V_B \),

\[ \frac{\Delta V}{V_A} = \frac{2Y(a + b)}{E_o} = \frac{E_H}{E_o}, \]

assuming that the gap between the nearly equal electrodes is small.

The change in rate of deflection observed with the differential electrometer might therefore be expected to be proportional to the whole Hall E.M.F. across the width of the crystal. A factor \( \frac{1}{2} \) due to the average change of potential over one electrode with respect to the other electrode has been compensated by a factor 2 due to the differential action of the instrument.

Experiments with zincblende concerning the validity of the assumptions made in obtaining Eq. 34 will be described on page 125.

It must be noticed that the ratio \( Y/X \) still does not bear any definite relation to the ratio of the generated Hall E.M.F. to the total potential drop over the length of the crystal, because in general the electric field in the layer next to the divided electrodes will be either greater or smaller than the average applied field. If the crystal has a resultant positive charge everywhere (which is the case for zincblende but probably not for the alkali halides) the
electric field strength next to the divided electrode will be
greater than \( E_0/L \) if it is the cathode, smaller if it is the
anode (see figure 20, page 144).

A number of practice readings on NaCl agreed in
giving no indication of any galvano-magnetic effect. The
following "good" set of readings is given in Table IX as
representative of the data. The \( \Delta t \)'s are the times, in
seconds, required for the indicator to move 1 cm, corresponding
to 0.01 volt, across the electrometer scale.

**TABLE IX. Tartakowsky Check on Rock Salt**

<table>
<thead>
<tr>
<th>( \Delta t ) (Mag. &quot;West&quot;)</th>
<th>( \Delta t ) (Mag. &quot;East&quot;)</th>
<th>( V_w - V_e )</th>
<th>( (V_w - V_e)/V_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.4</td>
<td>17.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.3</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.0</td>
<td>18.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avgs. 18.2</td>
<td>17.6</td>
<td>0.0018</td>
<td>1/950</td>
</tr>
</tbody>
</table>

\( V_t \) above is the rate of deflection produced by charging of
one pair of quadrants alone. Its value for this set of
readings was 1.75 cm/second. The quantity \( (V_w - V_e)/V_t \), is,
according to Eq. 34, equal to the ratio \( E_H/E_0 \), where \( E_H \)
is the Hall E.M.F. generated across the entire width of the
crystal's end.

**CHECK WITH ZINCBLENDE**

Since a null result had once more been obtained,
even with Tartakowsky's arrangement, it was deemed desirable
to check the working of the apparatus again with the substance of known properties, zinblende. With it in the apparatus the following set of readings was taken. In Table X the letters R and L placed in front of a $\Delta t$ indicate which way the indicator was moving along the scale; other symbols are the same as before.

**TABLE X. Zinblende by Tartakowsky Set-up**

<table>
<thead>
<tr>
<th>$\Delta t$ (Mag, &quot;W&quot;)</th>
<th>$V_w$ (cm/sec)</th>
<th>$\Delta t$ (Mag, &quot;E&quot;)</th>
<th>$V_e$ (cm/sec)</th>
<th>$V_w-V_e$</th>
<th>$E_H/E_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R 8.6</td>
<td>0.116</td>
<td>$\infty$</td>
<td>0.000</td>
<td>0.116</td>
<td></td>
</tr>
<tr>
<td>R 9.6</td>
<td>0.104</td>
<td>$\infty$</td>
<td>0.000</td>
<td>0.104</td>
<td></td>
</tr>
<tr>
<td>R 8.2</td>
<td>0.122</td>
<td>$\infty$</td>
<td>0.000</td>
<td>0.122</td>
<td></td>
</tr>
<tr>
<td>R 13.0</td>
<td>0.077</td>
<td>L 19</td>
<td>-0.053</td>
<td>0.130</td>
<td></td>
</tr>
<tr>
<td>R 24</td>
<td>0.043</td>
<td>L 12.6</td>
<td>-0.080</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>L 8.2</td>
<td>-0.122</td>
<td>L 4.8</td>
<td>-0.208</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td>L 8.0</td>
<td>-0.125</td>
<td>L 4.5</td>
<td>-0.222</td>
<td>0.087</td>
<td></td>
</tr>
<tr>
<td>Avg.</td>
<td>0.111</td>
<td></td>
<td>1/78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The total rate of charging of one pair of quadrants was such that $V_t = 4.3$ cm/sec. Since the fractional change $(V_w-V_e)/V_t$ was due to a reversal of the magnetic field,

$$\frac{E_H}{E_o} = \frac{1}{2} \frac{(V_w-V_e)}{V_t},$$

according to which formula the value for $E_H/E_o$ given in Table X was computed.

Taking into account the dimensions of the specimen, 7.27 x 4.8 mm, and assuming $X$ to be uniform over the specimen's length, the ratio $Y/X$ computed for
ZnS from Table X was 1/52, somewhat larger than the corresponding value 1/60 deduced for the same specimen by the single-electrode method.

The agreement appears excellent, particularly in view of the fact that the divided electrode in the Tartakowsky set-up was made the cathode, in the vicinity of which, in ZnS, the electric field strength is greater than $E_0/L$. For the data given in Table X, however, the applied potential was only 45 volts, the total photoelectric current was only $9 \times 10^{-12}$ ampere, and the photoelectric current density was considerably less than for that set of data, taken with the single electrode arrangement, for which the ratio $Y/X$ came out to be only 1/120 (Table V). And, as a matter of fact, another set of data obtained with the current density increased by a factor of 3, gave a considerably larger value, 1/40, for the ratio $Y/X$. Finally, when the current density was made 10 times greater than that for Table X, the ratio $Y/X$ came out to be 1/25.

DISCUSSION OF TARTAKOWSKY'S METHOD

The rather large discrepancy in results obtained by Tartakowsky's method as compared to those by the single-electrode method indicated two things:

1. The Tartakowsky arrangement, for some reason, was very sensitive to galvano-magnetic effects.

2. Something was wrong with the theory of the calibration.
With respect to point (1), not only did the arrangement appear to "magnify" the Corbino effect in zincblende, it also gave a larger effect (12 to 30%) for divided electrode as cathode than as anode. These facts suggested that the Tartakowsky method would be suitable for testing substances such as the potassium salts in which the photoelectrically-developed back E.M.F. created comparatively large potential gradients near the ends of the specimens.

As to which method—Tartakowsky's or the cross-electrode—involved the worse assumptions in the theory of the calibration, it was impossible to decide by a simple comparison of results with those of Lenz. The ratios \( Y/X \) obtained by the Tartakowsky method were, after reduction to the same magnetic field, were generally about 50% greater than Lenz's value, and the corresponding ratios obtained by the single-electrode method, about 50% smaller than Lenz's value. In this connection it should be remembered that if it had been assumed that the single electrode was capable of detecting all of the induced Hall E.M.F. across the crystal, rather than \( \frac{1}{2} \) as was actually assumed, the computed Hall field would have been two times smaller. Clearly the use of this factor \( \frac{1}{2} \) was justified. In the case of tests made upon the alkali halides, it led to a more conservative estimate of the magnitude of the largest undetected Hall effect. In NaCl, for example, neglect of the factor \( \frac{1}{2} \) would have led to assigning the value 1/2300 as the maximum for the ratio \( Y/X \), rather than 1/1150 as actually assigned.
HALL EFFECT AS A FUNCTION OF SIZE OF SPECIMEN

To learn something about the factors involved in the calibration, as well as to try to gain some idea as to the reason for the sensitivity of the Tartakowsky arrangement to galvano-magnetic effects, measurements were made upon zincblende specimens of different shapes and sizes.

The method of measurement was slightly modified for these tests. Instead of balancing the rate of deflection of the differential electrometer by means of a variable condenser, as previously, each pair of quadrants was connected to ground through a high resistance, of the order of $4 \times 10^{10}$ ohms.

Then if currents $i_a$ and $i_b$ flowed respectively through the resistors $r_a$ and $r_b$ connecting the quadrant-pairs AA and BB to ground, the potential difference between AA and BB was

$$V_a - V_b = i_a r_a - i_b r_b,$$

and the resulting deflection of the differential electrometer was

$$d = (i_a r_a - i_b r_b) / F_e.$$

$F_e$ is the sensitivity in volts per division of the electrometer. If the currents $i_a$ and $i_b$ were constant, a steady deflection was obtained. These currents generally differed from each other by about 10 to 25%, but the high resistances $r_a$ and $r_b$ likewise were unequal. In
practice it was found possible to secure comparatively small
deflections of the differential electrometer by connecting the
electrode with the higher equivalent conductance to that of the
quadrants which was grounded by the smaller of the two resistors.

To try out this steady deflection use of the differential electrometer, as just described, the Corbino effect in
the original zincblende specimen was first measured. With an
applied potential of 460 volts and a "moderate" intensity of
illumination, the deflection of the electrometer in either
direction (with one pair of quadrants directly grounded) was
160 cm. This deflection corresponded to a photoelectric
current of about 40 x 10^{-12} ampere. The "total" deflection
of the differential electrometer was therefore 320 cm. With
both pairs of quadrants grounded only through the resistors,
it was found that reversing the direction of the applied magnetic
field produced a steady change in position of the indicator of
about 8 cm. The effect was unmistakable. The shift was
completed within about 30 seconds, so that the motion of the
indicator was easily perceptible. The drift of the indicator,
when no magnetic field was acting, was negligible, while random
fluctuations were of the order of 2 mm. The effect of reversing
the magnetic field was therefore about 40 times greater than
the random fluctuations, which apparently were due to
fluctuations in the magnitude of the photoelectric current
itself.
The steady deflection use of the differential electrometer in connection with Tartakowsky's arrangement afforded the most positive test of any yet tried for the detection of small galvano-magnetic effects. The principal limitation to sensitivity was, that it required comparatively large longitudinal photoelectric currents, for the resistors here used. Commercial resistors about ten times as large as those used may be obtained, but might not help much because of the fluctuations.

The zincblende plate was next turned sideways in the apparatus (after sputtering one of the long sides), so that its former "length" became its "breadth" and its former "breadth" its new "length". In making this change, a large corner of the plate was accidentally chipped off, but the resulting deformity should not have materially affected the qualitative result of the experiment, which was as follows: the effect of reversing the applied magnetic field was to bring about a shift in the indicator position amounting to 1/60th of the "total" deflection (sum of the deflections produced by separate charging of the quadrant-pairs). This result is to be compared with a corresponding effect of 1 part in 40 found for the plate when oriented the "long" way.

The plate was next cut down so that it had approximately the same shape as originally, only with its "length" in the direction of its original "breadth". The dimensions of the reduced plate were 4.8 x 2.6 mm, i.e., it had the same
length as in the preceding measurements, but was about three
times as narrow. It was then found that the relative effect
of reversing the magnetic field was smaller still, i.e.,
about 1 part in 110.

These scattered measurements upon variously sized
and sna ped zincblende plates, therefore, appeared to indicate
that the relative amount of shifting of current from one part
of the divided electrode to the other caused by reversing the
direction of the applied magnetic field could be increased
either by increasing the breadth of the plate or its length,
or both. The relative amount of current shift did not appear
to depend on the shape of the plate, in contrast to the case
of Hall effects in metallic conductors. Proof as to the
non-dependence of the effect upon the shape of the plate,
however, was not conclusive, since, in the small plate, the
orientation of the applied electric field with respect to the
crystal axes was different than in the case of the large
plate of similar shape, and it has been found by Lenz that the
Hall effect in zincblende is a function of the orientation.

The experiments showed fairly well, however, that
decreasing the width of the specimen while maintaining its
length constant decreased the relative amount of current shift,
and this result was in qualitative agreement with the theory
of the calibration. More experiments upon the magnitude of
the Hall and Corbino effects in zincblende as a function of
the size and shape of the specimen are needed.
PHOTOCHEMICALLY COLORED ROCK SALT

It remained to test the photoelectric Hall effect in photochemically colored rock salt, the substance used by both Lukirsky and Tartakowsky. Here a difficulty was immediately encountered which had not been suspected from a reading of the literature—namely, that the photochemically colored crystals faded so fast under the fairly bright illumination needed to yield "steady" currents of sufficient magnitude for sensitive tests, that it was difficult to make the adjustment of the equalizing condenser before all of the photo-sensitivity had vanished. It was, furthermore, impossible to obtain a steady state of photoelectric polarization of the specimen before its photo-sensitivity had been used up; and the superior steady deflection method, in which the potential drops of the photoelectric currents through high resistances are applied to the differential electrometer, could not be used at all with the resistors on hand.

A fairly dense coloring would not last longer than about three or four minutes under the illumination employed. It would be interesting to measure the rate of decrease of the photoelectric current as a function of time of illumination; this has not yet been done, but would be relatively easy.

Stopwatch measurements showed that the changes in rate of deflection of the differential electrometer over intervals of the order of ten seconds were smaller than the changes which might be expected to be caused by rather small
Hall fields, if present. This fact suggested the procedure of taking rate-of-deflection readings for fairly poor adjustments. After a pair of readings—one for each direction of the magnetic field—a change in the adjustment was made in the proper direction. By this procedure no photoelectric sensitivity of the specimen was "wasted", and the adjustment gradually got better from pair to pair of readings.

A strong field, 650 volts/cm, was applied in order to get a comparatively "large" current, $3 \times 10^{-12}$ ampere, with comparatively "weak" illumination. It was necessary to take a reading of the total rate of deflection caused by charging one pair of quadrants separately after each pair of readings. Even so, the crystal had to be resensitized several times before sufficient data could be accumulated. For the process of resensitization the crystal was left in its holder, and the latter taken out of the apparatus and put under the x-ray tube.

About an hour's exposure of the specimen to 50 KV tungsten x-rays, with a current of 3 or 4 milliamperes, would produce a coloration whose density was of the order of 1/10th or 1/20th of the maximum obtainable by the methods of additive coloring.

The data is shown in Table XI. $V_T$ is the sum of the separate total rates of deflection produced by the opposing quadrant-pairs, so that $\frac{1}{2}(V_W-V_E)/V_T$ is the fractional change of current to either electrode produced by applying the magnetic field in one direction. (The
assumption is made that the observed effect was due to a Hall field symmetrical with respect to the direction of the magnetic field.) A minus sign in front of \( \frac{1}{2}(V_w-V_e)/V_T \) indicates that the apparent shift caused by the application of the magnetic field was in the proper direction for a normal Hall effect; positive values indicate the apparent shift was in the direction for an anomalous Hall effect. The rate of deflection was taken as positive if toward the right. Individual "times" are not given but were generally of the order of 10 to 25 seconds; distances varied from 0.25 to 1.0 cm along the scale.

### TABLE XI. Test of Photochemically Colored NaCl

<table>
<thead>
<tr>
<th></th>
<th>( V_w ) (cm/sec)</th>
<th>( V_e )</th>
<th>( V_T )</th>
<th>( \frac{1}{2}(V_w-V_e)/V_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Set</td>
<td>0.173</td>
<td>0.177</td>
<td>1.40</td>
<td>1/700</td>
</tr>
<tr>
<td></td>
<td>0.139</td>
<td>0.133</td>
<td>1.00</td>
<td>-1/350</td>
</tr>
<tr>
<td></td>
<td>0.119</td>
<td>0.104</td>
<td>0.90</td>
<td>-1/180</td>
</tr>
<tr>
<td>2nd Set</td>
<td>0.0863</td>
<td>0.0286</td>
<td>0.55</td>
<td>1/480</td>
</tr>
<tr>
<td></td>
<td>0.0333</td>
<td>0.0278</td>
<td>0.64</td>
<td>-1/240</td>
</tr>
<tr>
<td></td>
<td>0.0338</td>
<td>0.0362</td>
<td>0.60</td>
<td>-1/240</td>
</tr>
<tr>
<td>3rd Set</td>
<td>0.029</td>
<td>0.000</td>
<td>4.8</td>
<td>-1/145</td>
</tr>
<tr>
<td></td>
<td>0.088</td>
<td>0.087</td>
<td>5.3</td>
<td>1/8000</td>
</tr>
<tr>
<td></td>
<td>0.085</td>
<td>0.083</td>
<td>7.5</td>
<td>-1/2400</td>
</tr>
<tr>
<td></td>
<td>0.088</td>
<td>0.088</td>
<td>9.2</td>
<td>1/9000</td>
</tr>
<tr>
<td></td>
<td>0.106</td>
<td>0.094</td>
<td>4.8</td>
<td>-1/640</td>
</tr>
<tr>
<td>4th Set</td>
<td>-0.093</td>
<td>-0.076</td>
<td>2.94</td>
<td>1/350</td>
</tr>
<tr>
<td></td>
<td>-0.106</td>
<td>-0.094</td>
<td>2.90</td>
<td>1/480</td>
</tr>
<tr>
<td></td>
<td>-0.125</td>
<td>-0.111</td>
<td>2.64</td>
<td>1/380</td>
</tr>
<tr>
<td></td>
<td>-0.122</td>
<td>-0.118</td>
<td>2.32</td>
<td>1/1200</td>
</tr>
<tr>
<td></td>
<td>-0.109</td>
<td>-0.115</td>
<td>1.66</td>
<td>-1/520</td>
</tr>
<tr>
<td></td>
<td>-0.294</td>
<td>-0.270</td>
<td>3.2</td>
<td>1/280</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>-0.009</td>
<td>2.8</td>
<td>-1/400</td>
</tr>
<tr>
<td></td>
<td>-0.018</td>
<td>-0.017</td>
<td>1.54</td>
<td>1/1600</td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>-0.006</td>
<td>1.86</td>
<td>-1/600</td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>-0.007</td>
<td>1.10</td>
<td>-1/320.</td>
</tr>
</tbody>
</table>
The individual $V_T$'s, in Table XI, do not uniformly decrease during a "set" of readings because the illumination intensity was increased from time to time.

It may be seen that the difference $(V_w - V_e)$ for any pair of readings was apparently due to random fluctuations. For some pairs of readings the fluctuations were small and the effect of reversing the magnetic field obviously negligible.

The size of the crystal was $7.48 \times 5.03 \times 1.76$ mm. No attempt was made to calculate an upper limit to the ratio $Y/X$ set by these measurements, in view of the doubtful validity of the assumptions in the calibration. However a direct comparison with the result of the corresponding measurements upon zincblende seemed permissible. For zincblende, with a specimen of approximately the same size, the quantity $\frac{1}{2}(V_w - V_e)V_T$ was about $-1/80$. But, according to Table XI, the effect in photochemically colored NaCl of reversing the magnetic field was not greater than 10% of the corresponding effect in zincblende.

It should be emphasized that the sensitivity of the electrometer used here was almost exactly the same as that of Tartakowsky's instrument, 1070 divisions/volt as compared to 1000 divisions/volt. On the other hand Tartakowsky used a magnetic field of about 30,000 gauss, or two and one-half times stronger than that used here. Possibly use of this stronger field enabled him to detect an effect which was not detectable here.
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In his paper Tartakowsky gives only one curve (reproduced as figure 18) and puts down no units, not even arbitrary ones. The smoothness of his curve indicates that he had no trouble with random fluctuations of the photoelectric current, nor with irregular polarization.

A photoelectric Hall polarization, similar to that depicted by the reverse throw of Tartakowsky's electrometer upon release of the magnetic field, has been actually observed, during the course of the present investigation, for zincblende. However the effect was more in evidence in experiments by use of the cross-electrode than by use of the Tartakowsky arrangement.

The phenomenon in zincblende was as follows. Upon applying the magnetic field, an initial deflection occurred which was about 2½ times as great as the following steady deflection of the indicator from its zero position. About ten seconds was required for this initial deflection to reach its maximum value (galvanometer period 13.2 seconds). Thirty seconds after turning on the magnet the deflection, by then reduced, had become practically steady. Then upon releasing the magnetic field, a comparatively large throw of the galvanometer in the other direction occurred; this reverse deflection, again within about 30 seconds, decayed to near-zero. Upon applying the magnetic field in the direction opposite to that at first, the corresponding deflections were similar, but opposite in direction.
TARTAKOWSKY'S "HALL EFFECT" (Zeits. f. Phys. 66, 830, 1930). Ordinates are proportional to deflection of the differential electrometer but no units or scale are given. The time from points B to C is "5 or 7 minutes", that from C to D "of the order of one minute".
These phenomena are clearly shown in figure 19, in which the plotted points are the averages of a set of 20 complete series of readings (the same as given in detail in Table VII, page 114). The points have been corrected for the effect of throwing on the magnetizing current with the crystal unlighted.

The filled-in curve gives the approximate time-course of the galvanometer deflection between the recorded points as reproduced from memory; no actual readings were taken between the points plotted. But the nature of the phenomenon appeared sufficiently plain. The comparatively large initial Corbino current built up a back E.M.F. against itself, and as soon as the Hall field was removed, the developed "back Hall E.M.F." caused a "Corbino current" to flow temporarily in the opposite direction.

These deflections were observed when the electrometer was used as the measuring instrument, instead of the amplifier, with the single-electrode set-up. Attempts to observe a similar effect in zincblende, using the Tartakowsky arrangement, were not conclusive.

No permanent deflection of the differential electrometer by the magnetic field was claimed by Tartakowsky. The deflection, as shown by figure 18, had returned to zero by the time the magnetic field was taken off.
FIGURE 19

PHOTOELECTRIC HALL POLARIZATION IN ZINCBLENDE
MORE MEASUREMENTS WITH THE DIFFERENTIAL ELECTROMETER

The arrangement of Tartakowsky had been found particularly adopted to the testing of photoelectrically polarized crystals for the following reasons (some of which have already been given):

1. The differential electrometer was comparatively insensitive to spurious effects of the magnet.

2. In conjunction with the rate-of-charge method, the arrangement could be used for very small photoelectric currents, of the order of $1 \text{ or } 2 \times 10^{-12}$ ampere, and still have a fair degree of sensitivity.

3. The arrangement appeared suited for "catching" a possible concentration of Hall effect near the end of a photoelectrically polarized crystal, in which most of the potential drop was concentrated near the electrodes.

4. The arrangement could be modified to produce a steady deflection by connecting the quadrant-pairs through high resistances to ground. High sensitivity by such a circuit, however, required comparatively large photoelectric currents. Data could be obtained rapidly by this steady deflection method, as only a few individual readings were required.

5. The results obtained could be compared empirically with the properties of zincblende as measured by means of the same set-up.
Check measurements, therefore, were also undertaken for KCl and KBr by Tartakowsky's method, as well as measurements upon KI and NaBr, the last two substances not having been previously studied by the cross-electrode apparatus.

In addition, the Tartakowsky arrangement could be used to measure the effect, if any, of a magnetic field on the initial electron current, although the attainable sensitivity was less than for the corresponding ballistic measurements made with the amplifier and cross-electrode. The use of the electrometer as a ballistic instrument is simple. The throw produced by "instantaneously" putting a charge \( Q = CV \) upon one pair of its quadrants is given by

\[
d = d_0 (\lambda + 1) = \frac{V}{F_e} (\lambda + 1) = \frac{Q}{F_e C} (\lambda + 1).
\]

\( d_0 \) is the steady deflection produced by placing the charge \( Q \) upon the electrometer quadrants of capacity \( C \); \( F_e \) is the voltage sensitivity of the electrometer in volts per division, and \( 1/\lambda \) is the ratio between successive swings to left and right of the electrometer needle.

In no single measurement upon an alkali halide was any positive indication of the existence of a Hall E.M.F. or Corbino current found. Since these measurements lend substantial support to the general result that the photoelectric Hall and Corbino effects, if present at all in the alkali halides, are very small, they will be summarized in Table XII, and Table XIII.
### TABLE XII. Tests on Steady P.E. Currents in Four Substances by Tartakowsky's Arrangement

<table>
<thead>
<tr>
<th>Substance</th>
<th>NaF</th>
<th>KCl</th>
<th>KBr</th>
<th>KI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen size (mm)</td>
<td>4.4x3.8</td>
<td>5.5x4.0</td>
<td>3.7x3.5</td>
<td></td>
</tr>
<tr>
<td>Applied voltage</td>
<td>90</td>
<td>225</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>Approx. P.E. cur. (10^{-12})</td>
<td>14</td>
<td>3</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

#### PART I. DIVIDED ELECTRODE CATHODE

| $V_m$ (cm/sec) | 3 | 16 |
| N°. rdgs. (pairs) | 5 | 4 |
| Av. defl. rate $W$ $V_m$ | 0.064 | 0.082 |
| " " $E$ $V_m$ | 0.061 | 0.081 |
| $\frac{1}{2}(W_W-E_e)/V_m$ (Av. indivl. prs) | ±1/700 | ±1/6000 |
| Effect of mag. (ZnS-1) | ±1/8 | ? |
| Av. Fluc. (fractnl.) | ±1/400 | ±1/1500 |

#### PART II. DIVIDED ELECTRODE ANODE

| $V_m$ (cm/sec) | 14 | 5 | 15 |
| N°. rdgs. (prs.) | 3 | 6 | 4 |
| Av. defl. rate $W$ $V_m$ | 0.100 | 0.095 | 0.035 |
| " " $E$ $V_m$ | 0.097 | 0.094 | -0.009 |
| $\frac{1}{2}(W_W-E_e)/V_m$ (Av. indivl. prs) | ±1/2300 | ±1/1700 | ±1/4000 |
| Effect of mag. (ZnS-1) | ±1/20 | ? |
| Av. fluc. (fractnl.) | ±1/1200 | ±1/400 | ±1/2500 |

### STEADY DEFORMATION MEASUREMENTS

| Specimen size (mm) | 4x3 | 5.8x4.5 | 7.5x4.5 |
| Applied voltage | 290 | 460 | 135 |
| Approx. P.E. cur. (10^{-12}) | 20 | 100 | 100 |

#### PART I. DIVIDED ELECTRODE CATHODE

| $d_T$ (cm) | 75 | 300 | 400 |
| N°. rdgs. (prs.) | 9 | 9 | 5 |
| Av. defl. mag. $W$ $d_T$ | 11.74 | 26.55 | 1.55 |
| " " $E$ $d_T$ | 11.78 | 26.59 | 1.42 |
| $\frac{1}{2}(W_W-E_e)/d_T$ | -1/4000 | -1/15000 | -1/4000 |
| Effect of mag. (ZnS-1) | 1/20 | 1/50 | 1/50 |
| Av. fluc. (fractnl.) | ±1/1500 | ±1/6000 | ±1/1000 |

#### PART II. DIVIDED ELECTRODE ANODE

| $d_T$ (cm) | 40 | 300 | 200 |
| N°. rdgs. (prs.) | 11 | 8 | 7 |
| Av. defl. mag. $W$ $d_T$ | 7.92 | 39.0 | 5.52 |
| " " $E$ $d_T$ | 7.92 | 39.4 | 5.67 |
| $\frac{1}{2}(W_W-E_e)/d_T$ | 1/8000 | -1/3000 | -1/2500 |
| Effect of mag. (ZnS-1) | 1/40 | 1/15 | 1/20 |
| Av. fluc. (fractnl.) | ±1/1500 | ±1/6000 | ±1/1200 |
TABLE XIII. Ballistic Measurements on Initial P.E. Current by Tartakowsky's Arrangement

<table>
<thead>
<tr>
<th>Substance</th>
<th>KCl</th>
<th>KBR</th>
<th>KI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen size (mm)</td>
<td>8.5x4.0</td>
<td>7.5x4.5</td>
<td>3.7x3.5</td>
</tr>
<tr>
<td>Applied voltage</td>
<td>530</td>
<td>270</td>
<td>550</td>
</tr>
<tr>
<td>Time of flash (sec.)</td>
<td>0.2</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>Disch.time betw. rdgs.(min)</td>
<td>2</td>
<td>5(dark)</td>
<td>1</td>
</tr>
<tr>
<td>Avg.cur. dur. flash(10-12amp)</td>
<td>800</td>
<td>1000</td>
<td>320</td>
</tr>
</tbody>
</table>

**PART I. DIVIDED ELECTRODE CATHODE**

| Total throw $T_T$ (cm) | 200  | 47   | 80   |
| No. rdgs. (pr3.) | 10   | 3    | 10   |
| Av. throw mag. $W$ $T_{W}$ (cm) | 29.9 | 46.8* | 4.53 |
| $E$ $T_{E}$ | 30.4 | 46.8* | 4.73 |
| $1/2(T_{W} - T_{E})/T_T$ | 1/800 | -1/225 | -1/630 |
| Av. fluc. (fractnl.) | ±1/100 | ±1/60 | ±1/200 |

**PART II. DIVIDED ELECTRODE ANODE**

| Total throw $T_T$ | 200  | 80   |
| No. rdgs. (pr3.) | 10   | 10   |
| Av. throw mag. $W$ $T_{W}$ | 3.41 | 3.11 |
| $E$ $T_{E}$ | 3.33 | 3.33 |
| $1/2(T_{W} - T_{E})/T_T$ | 1/500 | -1/740 |
| Av. fluc. (fractnl.) | ±1/100 | ±1/300 |

*One pair of quadrants grounded.

EXPLANATION OF TABLES XII AND XIII

The "total" deflection rates $V_T$ and "total" deflections $d_T$, etc., were obtained by adding the absolute values of the deflection rates and deflections, respectively, etc., to left and right when one or the other quadrant-pairs of the differential electrometer was directly grounded. Then the quantities $1/2(V_W - V_E)/V_T$ and $1/2(d_W - d_E)/d_T$ are the fractional changes in current to either part of the divided (produced by one direction of the magnetic field) electrode, since for a genuine magnetic deflection of current flow from one segment to the other, half of the quantities $(V_W - V_E)$, etc., would be due to increase of current to one segment, and the other half would be due to decrease of
current to the other segment (assuming $i_{ar} = i_{br}$).

A minus sign placed before the values of $\frac{1}{2}(V_w - V_e)/V_T$, etc., indicates that the effect was in the right direction for a normal Hall effect. A plus-or-minus sign indicates that the sign fluctuated at random from pair to pair of readings. The comparisons with the magnitude of the corresponding effect in zincblende are strictly empirical and made wherever possible with the effect obtained in a zincblende plate of approximately the same dimensions as those of the specimen being compared. In cases where the size of the specimen differed considerably from that of any measured zincblende specimen, the relative effect is designated with a question mark or entirely omitted.

The average fluctuation for a given set of measurements was computed either by taking the average deviation of the individual readings from their mean value, or by taking the average of the deviations of each reading from the mean of the readings immediately before and after it. This latter method was employed in cases where the magnitude of the total deflection continually decreased during the measurements because of continually-increasing polarization. The total deflections, or rates of deflection, as given, were taken at the conclusion of a set of measurements. The corresponding quantities at the beginning of a set of readings were sometimes several times as great; likewise, in about the same proportion, the fluctuations.
The fractional fluctuations, therefore, as given in the foregoing tables are generally too large, since they are the ratios of the average absolute fluctuation of a given series of readings to the final value of the total deflection or rate of deflection.

EXPERIMENTAL DETAILS

Readings were generally taken after the magnetic field had been on for 30 seconds, the natural period of the electrometer being about 20 seconds. In taking the balanced rate-of-charge measurements, care was taken not to let the electrometer quadrants ever to be charged to more than about 10 volts; the general method of procedure was to isolate the quadrant-pairs from ground simultaneously, allow the photoelectric current to flow into them for 30 seconds, and then time the indicator as it moved across 1 cm.

Total deflections by the steady deflection method which were far off the scale were measured by substituting a smaller resistance $R_o$ for the usual resistance $r_a$, the ratio of the deflections $d_o/d_a$ caused by impressing the same current over the resistors $R_o$ and $r_a$ being empirically determined.

The lightly-colored specimen of KBr which had been used in the measurements with the electrometer tube amplifier did not yield large enough steady photoelectric currents to be used in the Tartakowsky arrangement. On the other hand, densely-colored specimens of KBr which did have a large
photo-sensitivity, appeared also to give comparatively large dark currents, even before passage of any photoelectric current, of the order of 1/5th of the magnitude of the steady photoelectric current. (The initial photoelectric current was about 100 times greater still.) Repeated cleaning of the surfaces of such dark-conducting KBr crystals failed to reduce the effect, but in a control experiment with a clear crystal, no such current could be detected at all. That this dark conductivity was a volume effect was also indicated by the fact that it was greatly reduced by the building-up of photoelectric back E.M.F.

The balanced rate-of-charge method was very unsuitable for testing such dark-conducting KBr crystals for photoelectric Hall effect, because it was almost impossible, by it, to separate the photoelectric from the dark component of the current. Presumably the dark component was of the same nature as the primary replacement, or hole conduction current. This dark current was separately tested for Hall effect by the steady deflection method. A steady shift of the indicator, slightly greater than the average fluctuation, and in the direction corresponding to an anomalous Hall effect, was actually obtained upon reversing the direction of the applied magnetic field. The effect of a single direction of the magnetic field upon the current into either electrode was approximately 1/1500. There is a remote chance that this shift was due to a bona fide Hall effect, of the correct sign for positive carriers.
In Table XII the total deflection given for KBr was that ascribed to photoelectric action alone. With the steady deflection method the fraction of the current at a given instant caused by photoelectric action could be approximately determined by shutting off the light and observing the residual deflection remaining after 30 seconds, or when the deflection had become nearly steady again. Within 30 seconds the loss of photoelectric back E.M.F. in unlighted KBr was comparatively small, as shown by an independent experiment.

CONCLUSIONS FROM TABLES XII AND XIII

The result of the measurements made with the single cross-electrode, that the Hall or Corbino effects if existent at all in KCl and KBr, must be very small, are fully confirmed by the data obtained using the Tartakowsky arrangement. In most cases the effect of reversing the direction of the applied magnetic field was even smaller (as shown by taking the average of a number of readings) than the random fractional fluctuations of current. In several instances the sign of the indicated effect fluctuated in a random fashion from pair to pair of readings. In other instances, notably the steady deflection measurements on KCl and KBr, a small persistent effect, of sign corresponding to the normal Hall effect, but of the same order of magnitude as the fluctuations, was shown. Even in such cases, a direct empirical comparison showed that the effect, if "real", was not larger than about 1/20th of that found in zincblende, using the same apparatus.
The relative effect, if any, of the magnetic field upon the current flow, was smallest, among the substances studied, in KI. Only one KI specimen was tried, however, and it had very small dimensions; it is intended to repeat the measurements upon this substance, using a larger specimen. The fact that the random fluctuations among individual readings were considerably smaller for KI than for readings taken on specimens of any other substance gives the obtained null result some significance, however.

No indication whatsoever of a Hall effect was found in NaBr, but, as in the case of KI, the only specimen examined was small. It is somewhat difficult to obtain good photoelectric contacts on NaBr by sputtering because the surface of the crystal hydrolyzes very rapidly upon exposure to damp air, forming a white frost. The procedure was to cleave off fresh surfaces of a specimen, being careful not to breathe on it while so doing, and then to insert it as quickly as possible under a bell jar, and pump out. A heavily-sputtered platinum coat thus obtained would not immediately hydrolyze upon renewed exposure to the air, but again in placing the specimen in the crystal-holder, it was necessary to cleave off fresh faces for all sides of the specimen not used as electrodes, and then to set it in place as quickly as possible. A quick way of obtaining a fairly-vacuum tight seal between the brass block which formed the vacuum chamber and the glass plate covering it (see figure 15) was to apply melted Cenco "Tackli-wax" to the edges of the plate.
EFFECT OF SPACE CHARGE

If the transverse Hall field generated at a point in a crystal is proportional to the resultant electric field intensity existing at that point, and if a thin slice, bounded by equi-potential planes (chosen before application of the magnetic field) of the crystal is taken, then the total Hall E.M.F. generated across the width of the crystal in that slice by an applied magnetic field should be proportional to the average electric field intensity in that slice. Then for crystals in which the potential gradient is concentrated near the ends by reason of the formation of photoelectric space charge and photoelectric back E.M.F., the Hall field and total E.M.F. might be expected to be small near the center, but comparatively large near one or the other or both ends. If the volume space charge has the same sign at all points of the crystal, the field will be diminished at one end of the crystal and increased at the other, according to Poisson's equation. Specifically, for the case of uniform positive space charge, the electric field will be larger near the cathode and smaller near the anode (see figure 20).

In a test upon zincblende, the change in current to the respective parts of the divided electrode produced by a Hall field was found to be about 12% greater when the divided electrode was negative than when it was positive. This test was made by means of the reliable steady deflection method. The actual difference in the observed shifts was about 0.9 cm, several times larger than the random fluctuations.
POTENTIAL FALL ALONG ZINCBLENDE CRYSTAL AS OBSERVED BY LENZ. The curves were obtained by means of a movable test electrode connected to an electrometer. The solid straight line was for the crystal unlighted, the curved line for the crystal when illuminated. It may be seen that the electric field intensity (given by the slope of the tangent) is about twice as great near the cathode as its average value, but only about half as great as its average value when near the anode. The average applied electric field intensity was 5300 volts/cm.
Consecutive readings with alternating direction of the applied electric field were taken within about one minute of each other. It was ascertained that the specimen had no rectifying effect upon the photoelectric current, i.e., the total steady photoelectric current was the same to within 1% for both directions of current flow.

The potential distribution along the length of a photoelectrically polarized KBR crystal, in which the developed photoelectric back E.M.F. was about 99% of the applied voltage, was tested by means of a movable probe. The probe, consisting of a platinum knife-edge, could only be moved by taking the crystal-holder clear out of the apparatus, since the knife-edge "dug into" the crystal. Readings were taken for five separate positions of the probe. The method was to adjust the grounded point of the applied batteries until, in the steady state of polarization, no current flowed into the probe, which was connected to the grid of the vacuum tube amplifier, and to ground through the grid resistor. Then the difference of potential between the grounded point and the end of the crystal was equal to the P.D. between the probe and the same end of the crystal.

The result, shown in figure 21, clearly indicates that most of the potential drop did occur near one end of the crystal, i.e., near the cathode; a somewhat smaller potential drop was indicated near the anode. For each position of the probe, a balance was obtained for both directions of the
applied field. If the crystal had been electrically homogeneous, the two curves thus obtained would have been mirror images of each other with respect to an ordinate drawn at the center of the crystal. The large irregularities in the positions of individual points are simply due to irreproducibility of experimental conditions from reading to reading, a result of the procedure of entirely removing the crystal holder from the apparatus between readings.

A consideration of the facts just presented, namely, the dependence of the magnitude of the current shift in zincblende upon the electric polarity of the collecting electrode, and the proved existence of large longitudinal potential gradients near the ends of a KBr crystal (actually the same one as used in the Hall effect measurements), suggests that the null result of the measurements upon KBr (as well as upon KCl and KI) by means of the Tartakowsky arrangement is indicative of an even smaller upper limit to the undetected Hall (or Corbino) effect than has here been assigned.

SMALL ANOMALY IN ROCK SALT

It remains to describe a small galvano-magnetic anomaly in the behavior of rock salt which, although not yet demonstrated to be of photoelectric origin, might possibly be a manifestation of a small, bona fide, but probably unsymmetrical Hall effect. The data so far collected on this anomaly, all by the steady deflection use of the Tartakowsky arrangement, are summarized in Table XIV.
Potential distribution along photoelectrically polarized KBR crystal as determined by probe.
<table>
<thead>
<tr>
<th>Specimen Number &amp; Size</th>
<th>Appl. Volts</th>
<th>Total Defl. d_T(cm)</th>
<th>Avg. d_w(cm)</th>
<th>Avg. d_e(cm)</th>
<th>[\frac{d_w-d_e}{d_T}]</th>
<th>Effect of Mag. ZnS=1</th>
<th>Avg. Fluc. (Frttl.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 6.7x4.6</td>
<td>-460</td>
<td>135</td>
<td>8.24</td>
<td>7.86</td>
<td>-1/650</td>
<td>1/15</td>
<td>±1/1500</td>
</tr>
<tr>
<td>II 3.3x6.2</td>
<td>460</td>
<td>175</td>
<td>6.94</td>
<td>6.87</td>
<td>1/5000</td>
<td>-1/80</td>
<td>±1/1200</td>
</tr>
<tr>
<td>I (redneck) 460</td>
<td>460</td>
<td>205</td>
<td>6.51</td>
<td>6.43</td>
<td>1/5000</td>
<td>-1/80</td>
<td>±1/600</td>
</tr>
<tr>
<td>II turned thru. 90°</td>
<td>480</td>
<td>135</td>
<td>37.0</td>
<td>37.1</td>
<td>1/2700</td>
<td>-1/60</td>
<td>±1/450</td>
</tr>
<tr>
<td>III 6.7x4.2</td>
<td>460</td>
<td>110</td>
<td>10.12</td>
<td>9.85</td>
<td>-1/800</td>
<td>1/20</td>
<td>±1/1100</td>
</tr>
<tr>
<td>IV 6.6x5.8</td>
<td>-460</td>
<td>170</td>
<td>35.24</td>
<td>35.61</td>
<td>-1/900</td>
<td>1/22</td>
<td>±1/850</td>
</tr>
<tr>
<td>V 6.2x3.2</td>
<td>460</td>
<td>100</td>
<td>6.18</td>
<td>5.85</td>
<td>-1/600</td>
<td>1/15</td>
<td>±1/400</td>
</tr>
<tr>
<td>VI (No. V cut to 6.2 x 3.0)</td>
<td>-460</td>
<td>48</td>
<td>10.12</td>
<td>9.78</td>
<td>1/300</td>
<td>-1/7</td>
<td>±1/150</td>
</tr>
<tr>
<td>VII 6.6x3.0</td>
<td>460</td>
<td>120</td>
<td>35.2</td>
<td>35.3</td>
<td>1/2400</td>
<td>-1/40</td>
<td>±1/200</td>
</tr>
</tbody>
</table>

The average "d's" given are in most cases for 10 pairs of readings.

As in Tables XII and XIII, a minus sign has been given to the quantity \((d_w-d_e)/d_T\) where the apparent effect of the magnetic field was in the direction corresponding to a normal Hall field. In four different specimens, Nos. I, III, IV, and VI, an effect of roughly the same order of magnitude, namely, about 1/20th of the corresponding effect
in a zincblende specimen of approximately the same size, and of the correct sign for a normal Hall effect, was found.

The effect obtained by reversing the magnetic field was about $1\frac{1}{2}$ or 2 times as great as the average random fluctuations; the corresponding movement of the indicator could plainly perceived when the reversing switch in the magnetizing circuit was thrown. No. I crystal was reinserted in the apparatus and measured again, with good agreement as to the size and sign of the anomaly. No. II, in which no anomaly could be observed either when its short or its long dimension was used as the direction of the electric field, was not uniformly colored; the other specimens were very uniformly colored. The sign of the effect in crystal No. V apparently reversed when the width of the crystal was reduced, but the fluctuations in the measurements showing this reversal were unusually large. In general the effect seemed to be smaller in the narrower specimens.

The principal reason for not recognizing the anomaly as a bona fide Hall effect was the following: in most cases application of the magnetic field "east" had practically no effect, or even a small effect in the same direction as application of the magnetic field "west"; the main part of the shift was due to the magnetic field applied "west". Still, an unsymmetrical Hall effect has been proved for zincblende by Lenz, the degree of asymmetry being a function of the crystal orientation with respect to the applied
electric field. It is also possible that a superimposed small, spurious, uni-directional effect caused by the magnetization of the magnet pole pieces (or by something else) might add up with the effect of one direction of the Hall field, and tend to cancel out with the other. A small spurious effect of nearly the right order needed was, in fact, sometimes observed in tests with the crystal unlighted, but it had the wrong direction to fit in with such an explanation of the anomaly. The existence of such an additional (dark) anomaly, as a matter of fact, suggested that the apparently light-dependent anomaly under discussion was also of some spurious origin.

The following should be a conclusive test as to whether the anomaly was in part or whole a bona fide Hall effect: to measure the photoelectric current to the segments of the divided electrode separately while the magnetic field is applied in first one direction and then the other. If the current to one segment could be shown actually to increase at the expense of current into the other segment for one direction of the magnetic field, and the reverse to occur for the other direction of the magnetic field, then there could not be much doubt but what a real Hall deflection of current had taken place. Such an experiment has been tried with the differential electrometer as the measuring instrument, but with an inconclusive result; the effect upon one quadrant or the other separately was too small to be detected with
certainty. The experiment will be repeated soon, using the amplifier as a measuring instrument.

The conclusion so far reached concerning the anomaly is as follows: if a Hall deflection of current does occur in rock salt, the effect is at least 20 times smaller than the corresponding one in zincblende.

PHOTOELECTRIC MAGNETO-RESISTANCE

The order of the change of resistance in most metals produced by a strong magnetic field is only about 0.005%, whereas changes of resistance smaller than about 0.2% usually could not be detected with certainty in measurements on photoelectric magneto-resistance changes attempted during this investigation. The limitation to sensitivity apparently was the fundamental one imposed by the magnitude of the fluctuations in the photoelectric current itself. For this reason the results are considered to have little significance, and the experiments will be only briefly described.

The best measurement of possible magneto-resistance changes in photoconducting rock salt, among several attempted, happened to be upon the plate cut with its length and breadth in the 110-directions. The total deflection of the galvanometer caused by the photoelectric current was approximately 330 cm; the spot had to be brought back on the scale by adjustment of the resistance $R_g$ (figure 10).
In eight trials (see Plate III) the average position of the spot while the magnetic field was applied was less than 0.1 cm different from that with the magnet off. The applied field was 12,200 gauss. The indicated upper limit to the change in resistance, if 0.5 cm be arbitrarily assigned as the smallest persistent deflection which would have remained unobserved, is 1 part in 650. Or, if it be assumed that no persistent effect greater than the average effect of applying the magnetic field would have gone undetected, the indicated upper limit to the magneto-resistance change was 1/3000.

The fluctuations in the total steady photoelectric current in KBr and KCl were relatively much larger than in rock salt. In these substances an upper limit to the magneto-resistance change could only be assigned as 1 part in 300 and 1 part in 400, respectively. The percentage fluctuations were found to increase with applied voltage. With an average applied field of 820 volts/cm in KBr, for example, the fluctuations had increased to 40 or 50% of the total current.

Better measurements upon photoelectric magneto-resistance were secured upon zincblende than upon any of the alkali halides, for the reason that the photoelectric current through it was not subject to as large fluctuations. Computations as to the magneto-resistance change to be expected in photoconducting zincblende, based upon the length of mean free path of the photoelectrons as shown by
PLATE III

EXAMINATION OF NAACL FOR POSSIBLE PHOTOELECTRIC MAGNETO RESISTANCE CHANGES (Magnetic field=12,000 gauss).

\( \times \) = galv. defl. for magnetic field off.

\( \circ \) = galv. defl. for magnetic field on.

The fluctuations in the galvanometer readings appear to be entirely random.
Hall effect measurements, indicated that an effect of the order of 0.05% might exist. However the upper limit set by these measurements (the data of which are exhibited in Plate IV) to a possible magneto-resistance change in zincblende was only 1 part in 700, or 0.14%, so again the result had little significance.

The only conclusion warranted from the results of this part of the investigation, therefore, was that no anomalously large photoelectric magneto-resistance changes, of the kind found, for example, in bismuth, among metals, exist in any of the substances studied.

VALIDITY OF NULL RESULTS

Arguments for the validity of the consistently null result of all attempts to detect a Hall E.M.F. or Corbino current in the alkali halides may be summarized as follows:

1. NaCl, KBr and KCl all were tested in two quite different experimental arrangements, namely that of the single cross-electrode and that of Tartakowsky. Small current changes to the cross-electrode were detected with a direct current amplifier, which was alternatively used as a rate-of-charge and as a steady-deflection indicator. In the Tartakowsky arrangement, the differential electrometer was also used in the two ways. The steady-deflection use of the differential electrometer, using very large resistors, was particularly satisfactory.
PLATE IV

EXAMINATION OF ZINCBLEND FOR POSSIBLE PHOTOELECTRIC MAGNETO-RESISTANCE CHANGES

\( \times \) = readings with magnet off (avg. 698.85 cm).
\( \circ \) = readings with magnet on  (avg. 698.90 cm).

The fluctuations were reduced to less than \( \pm 0.5 \) cm when the light was taken off the crystal.

Galv. Defl. (cm)

Time—minutes
2. With both set-ups, ballistic measurements were made upon the effect of a magnetic field upon the initial surge of electron current, in which a relatively larger Hall effect might be expected, but no effect was found in any of the substances studied.

3. Five different alkali halide substances have been examined with consistently null results for all.

4. Photoelectric contacts were by platinum-sputtered films on fresh surfaces and undoubtedly were very good.

5. Both experimental arrangements were tested by means of a substance of known galvano-magnetic properties and found capable, not only of giving an easily observable response to the presence of a photoelectric Hall or Corbino effect, but also to give quantitative results of the correct order of magnitude. Experiments with zincblende indicated that the response of either of the experimental arrangements to the presence of a Hall field did not critically depend upon such details as accurate alignment of the Hall electrode, the shape of the specimen, or a fine adjustment of the electrical balance.

6. The calibration of sensitivity for the single-electrode method was empirical, consisting of observing the effect of a small arbitrary shift of the potential of the Hall electrode with respect to the end electrodes upon the photoelectric current passing into the Hall electrode. The calibration of sensitivity for the Tartakowsky arrangement was by direct comparison with the effect produced in zincblende when put in the same apparatus.
6. Upper limits to possible unobserved Hall fields have been conservatively assigned. More weight has been given to the individual fluctuations between consecutive readings of the instruments than to the still smaller differences between the averages of several readings.

Measurements upon NaBr and KI were with the differential electrometer only, and upon rather small specimens, so they should perhaps be considered as preliminary.

It is hard to account for the positive Hall effects reported in photochemically colored rock salt by Lukirsky and by Tartakowsky. Lukirsky's results are not directly available, but, according to Joffe' (in whose laboratory Lukirsky worked), they indicated a mean free path of the order \(10^{-5}\) or \(10^{-6}\) cm for the photoelectrons. Such a length for the mean free path is about the same as that calculated for zincblende upon the basis of the Hall effect in it. Therefore the Hall effect in photochemically colored rock salt should be of about the same relative magnitude (with respect to the electric field) as the Hall effect in zincblende. But photochemically colored rock salt was also used in one part of this investigation, and no effect whatsoever could be observed in it.

The electrometer throws observed by Tartakowsky (see figure 18, following page 133) and ascribed by him to the deflection of electron currents by a magnetic field would appear, from the single experimental curve which he displays,
to have been of an easily observable magnitude (although he
gives no scale). But Tartakowsky's experiment has been
duplicated as exactly as possible during the course of this
work, using an electrometer of the same sensitivity as that
used by him. Both additively and photochemically colored
rock salt were studied by means of this, Tartakowsky's,
arrangement, and no galvano-magnetic effect found (beyond
a small, presumably spurious effect whose magnitude lay
upon the border-line of the observational limit set by
fluctuations in the photoelectric current).

Photochemically colored crystals, which were the
kind used by Tartakowsky and Lukirsky, bleach out rather
rapidly upon exposure to light. It is therefore difficult
to get them into a steady state of polarization before their
photo-sensitivity has been used up, and in other ways to
reproduce conditions exactly for consecutive readings of the
measuring instrument.

In the experiments conducted here a potential
of about 500 volts was applied to the photochemically colored
rock salt crystal, in order to obtain a photoelectric current
of sufficient magnitude without the use of intense light.
Tartakowsky's effect was obtained with an applied potential
of only 100 volts.

It was observed, however, that even with good
electrostatic shielding and no magnetic materials of any kind
in the photoelectric circuit or in the crystal supports, some very small effects were sometimes produced on the electrometer deflection when a strong magnetic field was thrown on. These effects were too small to be detected at all with the original arrangement of Tartakowsky, but could be detected when that arrangement had been modified by connecting the differential electrometer to ground through high resistances.

IV. **Conclusion and Discussion of Results**

It has been established that the Hall field in a photoconducting rock salt crystal subjected to a magnetic field of 12,000 gauss, if it exists at all, is less than $1/1000$th of the applied electric field. Or, alternatively, the magnetic deflection of photoelectric current in a crystal arranged with a divided electrode is less than $1/20$th of the corresponding effect in zincblende. The Hall effects in KCl and KBr are likewise very small, not greater than the upper limit which has been assigned for rock salt. Also the Hall effect in the large initial surge of electron current found in KBr and KCl is small—not greater than 1 part in 640 of the applied electric field in the case of KCl. Presumably, also, the Hall fields in NaBr and KI are very small, although the tests so far made on these last two substances are not as extensive and reliable as for the others.
In view of the consistently null results which have been obtained for the five substances studied, it seems unlikely that any measureable photoelectric Hall effect exists in any others of the alkali halide family.

If, to take the particular case of rock salt, the null result were to be interpreted as meaning that the free paths of the photoelectrons in the crystal lattice are comparatively short, the equation of Gans,

$$\frac{Y}{X} = \frac{\sqrt{2}}{4} \frac{\pi (m_e^*)}{kT} \frac{e}{m} \lambda H,$$  \hspace{1cm} (20)

for the isothermal Hall effect, could be used to determine the order of magnitude of the maximum mean free path corresponding to the experimentally determined upper limit of the Hall effect. Putting $Y/X=1/1000$ and $H=12,000$ gauss in Eq. 20, it is found that

$$\lambda = 4.5 \times 10^{-8} \text{ cm}.$$  

This length is not much greater than the dimensions of a lattice cell. The result for the mean free path is in agreement with Von Hippel's ideas as to the length of electron free paths in rock salt.

An alternative interpretation of the null result would be that in NaCl (as well as in the other colored alkali halides) the contribution of the photoelectrons to the Hall field is nearly or exactly cancelled by the contribution of the positively-charged carriers. Such a cancellation, conceivably, could occur in either of two ways:
1. The positive carriers are ions which move bodily with a mobility equal to that of the negative carriers.

2. The positive carriers move by the process of electron-replacement, or hole conduction, and are, to all effects, positrons.

Neither of these two alternatives seems to fit in very well with other experimental facts. The first would be realized if the negative carriers were predominantly ions, instead of electrons, but that does not appear likely. On the other hand there is a possibility that positive ions have a mobility through the crystal lattice equal to that of the electrons, but the evidence seems to be that even the dark current of the alkali halides at room temperature is mainly electronic.

The second alternative is interesting by reason of the novel concept involved, but, aside from its obvious incompatibility with classical ideas, does not fit in well with the observed sluggishness of the "positive" component of the primary photoelectric current. This sluggishness of the positive component of the current (shown by its failure to remove the positive charges created by the photoelectric action of the light as rapidly as the negative charges are drawn out) indicates that the mobility of the carriers of the positive component of current, whatever their nature, is markedly less than that of the photoelectrons.
It has been mentioned (page 61) that replacement-electrons, according to classical ideas, should contribute to a Hall field additively with the photoelectrons which they, effectively, are replacing. A positron current would, of course, even on classical notions, contribute oppositely to the Hall field. On quantum mechanics theory the hole conductors, if in fact they transport positive charge toward the cathode with a mobility equal to that of free electrons, are almost the same thing as positrons, since their behavior (up to this point) is the same as that of positrons. Their behavior would exactly coincide with that of positrons if it could be shown that their contribution to the Hall effect was opposite to that of electrons. Then, for all practical purposes, they would be positrons.

If, by an independent determination, the mean free path of the electrons could be shown large enough that their contribution to the Hall effect, in the absence of carriers of the opposite sign, ought to be measureable, then a distinction might be made between classical and wave-mechanical concepts as to the nature of the hole conductors. Such an independent determination has, in effect, been made by Von Hippel in his experiments upon electrical breakdown. The result, which depends upon a certain theory of the process of electrical breakdown, was that the mean free path was somewhat less than the distance across a lattice cell. If this result is correct, so that there is some reason for
believing that the mean free of photoelectrons in rock salt is about $2 \times 10^{-8}$ cm, then, by Cans' formula, Eq. 20,

$$Y/X = 1/2250.$$ 

Detection of a Hall effect of such a small relative magnitude was slightly past the limit of sensitivity of the present investigation, but should not be impossible to attain. It is probable that the sensitivity of the single-electrode method could be exactly doubled by going to the additional trouble of using two electrodes. For the rest, the limit to attainable sensitivity is probably set by the shot effect, or fluctuations in the numbers of photoelectrons passing into the Hall electrodes, and by the Johnson effect, or fluctuating E.M.F. set up by the thermal agitation of conduction electrons.

The mean square variation in the magnitude of an electron current, or stream, assuming that the motion of each electron is independent of that of each of the others, is, from simple statistical theory,

$$\overline{\Delta i^2} = i_0(e/t),$$

in which $i_0$ is the average current, $e$ is the charge on one carrier, and $t$ is the time over which the variation occurs. If $i_0$ be taken as $10^{-11}$ ampere, the order of the currents used in the present investigation, and the time be taken as one second, then

$$\Delta i = 1.2 \times 10^{-15} \text{ ampere.}$$
Such a fluctuation, if extending over one second, would have given, according to the formula for the ballistic use of the amplifier, Eq. 39, page 175, a galvanometer throw (for the set-up used here) of 0.2 cm. The fluctuations observed were actually about ten times as great, so it would seem that the upper limit to sensitivity set by shot effect had not been reached.

Regarding the Johnson effect, Hafstad\textsuperscript{50} has shown that for a direct current amplifier, the mean square fluctuation of E.M.F. impressed upon its grid by a resistance is

$$\overline{E^2} = \frac{kT}{C}.$$  

According to this expression, the magnitude of the fluctuating E.M.F. is independent of the magnitude of the resistance, and can be made smaller by increasing the capacity $C$ of the grid-plus-connections, at the expense, of course, of the quickness of response of the instrument. (The quickness of response of the sensitive amplifier unit to small voltages was set by the period of the galvanometer rather than by the time required for a small current to charge up the grid.)

Substituting in the above equation $C=50 \times 10^{-12}$ farad $=30 \times 10^{-12} \times 10^{-9}$ e.m.u., and $T=300^\circ$, there is obtained for the fluctuating E.M.F.

$$E=1.2 \times 10^3 \text{ e.m.u.}=1.2 \times 10^{-5} \text{ volts}.$$

The fluctuations observed, while making measurements
upon NaCl with the amplifier, were actually five to ten times as great, so again it appears that the natural limit to sensitivity set by Brownian motion of electrons had not been reached by a considerable factor.

It therefore seems possible to extend the sensitivity of the experiment to the point where Hall E.M.F.'s arising from electron motion along free paths of the minute order of $2 \times 10^{-8}$ cm could be detected and measured. If the sensitivity were thus to be increased and still no Hall effect showed up, it might then be assumed that the hole conductors had indeed cancelled out the electron contribution, i.e., that the hole conductors were in fact exactly equivalent to positrons.

The fact that no Hall effect has been detected even in the large initial currents in KCl, KBr and KI presumably consisting almost entirely of electron flow points to the conclusion that, regardless of the sign of the contributions of the various components of photoelectric current to the Hall field in the steady flow, the electronic mean free path in the alkali halides is small. Such an interpretation, as already mentioned, is supported by, and in turn supports, the experimental results of Von Hippel.

If a magneto-resistance change could be detected in a photoconductor which had no measurable Hall effect (which situation, for any given photoconductor, does not appear very likely), it might be assumed that the contributions of the positive and negative components of the photoelectric current to the Hall field had indeed cancelled out. Contributions to magneto-resistance are supposed to be independent,
in sign, of the kind of carrier. However in the case of metals, magneto-resistance changes appear to bear no close relation to the sign or magnitude of the Hall effect, and from the complex phenomena observed, no very good conclusions have been drawn. In the same way magneto-resistance anomalies, if found in photoconductors, might be interesting but probably would not help greatly to clear up the situation.

SUGGESTIONS FOR FURTHER EXPERIMENTS

With respect to the colored alkali halides, the main interest would appear to lie in the possibility of setting a still lower limit to the maximum unobserved Hall effect, or, alternatively, to measure its magnitude if a small Hall effect, near the limit of observation, does exist.

It has already been indicated that the natural limit to sensitivity set by Brownian motion of electrons was probably not reached in the course of the present work. Still there were undoubtedly fluctuations in the photoelectric currents studied, particularly in KBr and KCl. Under some conditions the fluctuations amounted to as much as 50 percent of the total current (see appendix, page 180). The source of these fluctuations has not been finally determined; to attempt to do so would make an interesting study in itself. It appears that the magnitude of these fluctuations must either be reduced, presumably after first ascertaining their cause, or that the photoelectric currents themselves must
be increased in some way which does not increase the fluctuations in proportion.

It may be mentioned that measurements by the conventional cross-electrode arrangement appeared less subject to these fluctuations than those by the longitudinal arrangement of Tartakowsky. Even with the latter, however, fluctuations of the indicator position of the differential electrometer when connected to the two parts of the divided electrode were considerably less than the fluctuations when one pair of quadrants was connected to both parts of the divided electrode. In other words, it appeared that the fluctuations in current to the two parts of the divided electrode cancelled out to a large extent in their effect upon the deflection of the electrometer. It would seem, from this, that current fluctuations to the two parts of the electrode were, for any given instant, of the same sign.

In measurements made upon NaCl with the amplifier and cross-electrode, the observed fluctuations were due in part at least to the instability of the amplifier. As mentioned on page 74, an electrometer tube amplifier operated with the tube in air is subject to voltage fluctuations of an order 10 to 100 times as great as the Brownian fluctuations which still remain when the tube is kept in vacuum. In making further refinements upon Hall effect measurements in NaCl, using the amplifier, a necessary first step would be to put the electrometer tube and all of the grid connections in vacuum.
At higher temperatures (up to about 200° C, above which the color centers are thermally unstable) the obtainable steady photoelectric current in alkali halides is greater than at room temperature by several orders of magnitude. Using such comparatively large currents, a relatively very small Hall effect might be detected. Thermal fluctuations would probably also be increased. Going in the other direction, to liquid air temperatures, steady obtainable P.E. currents would be close to zero. Ballistic measurements upon the initial electron surge could still be made, but even this initial current, at least for the potassium salts, would be much smaller than at room temperature, because the large initial current in them is due to "thermally increased range" of the photoelectrons.

An interesting possible method for detecting a very small Hall effect would be to use a rapidly alternating electric field upon a specimen, thereby, presumably, entirely eliminating the phenomena of photoelectric polarization and back E.M.F. Naumann\textsuperscript{55}, as a matter of fact, succeeded in obtaining alternating photoelectric currents in KBr approximately 1000 times as great as the obtainable steady current. He used frequencies up to 100,000 cycles. Such rapidly oscillating photoelectric currents would probably consist mostly of electrons, and therefore should be particularly liable to galvano-magnetic effects. A complication would lie in separating the pure photoelectric
current from the dielectric polarization charging component, which is large in KBr. Naumann does not mention meeting with such a difficulty, however. Furthermore it has been stated by Wenderowitsch and Drisina\textsuperscript{54} that the back E.M.F. of dielectric polarization in NaCl can be greatly reduced by careful annealing of the crystal after manufacture. The same thing should apply to the back E.M.F. of dielectric polarization in the other alkali halides.

An alternating Hall E.M.F. could be measured either with a suitable amplifying unit or with an electrometer connected "idiostatically". Wood\textsuperscript{55} has recorded that the Hall E.M.F. in tellurium is probably less than 4° out of phase with the longitudinal current when the latter is oscillating at the rate of 25,000 cycles per second.

Crystals of KBr and KI have been colored at Göttingen with a stoichiometric excess of halogen. It would be interesting to try for the Hall effect in such materials.

The thrust–path, or range, of a photoelectron in NaCl, KBr and KCl apparently is a function of the electric field intensity and the concentration of color centers only. It would seem that it should also be a function of its initial energy, i.e., of the wave-length of the absorbed light, and also that it should be a function of the density of positive space charge. The effect of density of positive space charge, i.e., of recombination, upon the thrust path would be easier to measure than the effect of the wave-length
of the absorbed light, since the latter measurement would involve bolometric or similar determinations of the quantity of absorbed light.

The inverse proportionality of thrust path to color center concentration was established by Glaser and Lehfeldt for additively colored crystals only. It would be interesting to see if such a relation also holds for photochemically colored rock salt, whose fast fading under bright illumination has already been mentioned.

Other miscellaneous experiments which suggest themselves are:

To attempt to bleach an additively colored crystal by passing a large photoelectric current through it for a long time.

To measure the possible "swelling" of a crystal when filled with color centers. (A positive ion which captures an electron to become an atom requires considerably more space than before, according to Von Hippel.)

Some additional possible studies on space charge effects in alkali halides will be discussed in the appendix, Part I.

The small anomaly found in rock salt should be further studied, and a final decision reached as to whether it is really a Hall effect on the borderline of observational limit.
It is also remotely possible that a Hall effect of the correct sign for a stream of positive carriers was observed, during the course of the present investigation, in the dark current of densely-colored KBr. This matter could be looked into more closely.

The only substances in which a photoelectric Hall effect appears to have been conclusively demonstrated are diamond and zincblende. Both of these belong to the "idiochromatic" class of photo-conductors, having intrinsic photoconductivity in their pure state. It has been shown here that several typical "allochromatic" substances, have, at the most, very small Hall effects. The index of refraction of a substance would not seem to have much to do with whether it possessed intrinsic photoconductivity or not, yet all known allochromatic crystals have indices of refraction less than 2, and all idiochromatic crystals have indices greater than 2. It is possible that the Hall effect is another such distinguishing property between the two classes of crystal, i.e., that other idiochromatic crystals, such as sulphur, the silver halides, stibnite and cinnabar all have Hall effects; and that other allochromatic crystals (the rest of the alkali halides, also fluorite, calcite and the thallium halides) do not, any of them, have photoelectric Hall effects of measurable magnitude.

RANDOM REMARK

If zincblende, with an ionic lattice, has a Hall—
Appendix

PART I. POLARIZATION

The formation of space charge, or polarization, inevitably accompanies the passage of photoelectric current in colored alkali halides at room temperature and often leads to erratic electrical behavior of the specimen which may be perplexing in the extreme. The phenomena of polarization, in fact, compose the greatest single obstacle to the investigation of any problem in photoconductivity. It therefore seems worthwhile to describe some of the polarization phenomena, which although presumably encountered by every worker in the field, do not usually appear in print.

With respect to polarization, NaCl was the "best behaved" of any substance studied, but it was still subject to rather complicated polarization effects. The back E.M.F. developed in NaCl was not as great as that in KBr, KCl and others, but it took a great deal longer for it to "subside".

The back E.M.F. of polarization was measured in a rough way by switching suddenly the applied voltage from its initial value, at which the polarization had been built up, to some smaller value, and observing the resulting direction and magnitude of the current. In doing this it appeared best to remove the illumination before the switch was thrown, otherwise the surge of current caused by the release of dielectric polarization partly masked the current produced by photoelectric polarization. If the smaller voltage thus
applied to the crystal was less than that of the photoelectric back E.M.F., the current, upon re-illumination of the crystal, would flow in the opposite direction for some time, diminishing rather gradually. Then might follow a considerable length of time in which the applied voltage and the back E.M.F. (developed by the photoelectric current of the former higher voltage) almost exactly balanced. If the smaller voltage was almost, but not quite, equal to the back E.M.F., a small reverse current would initially flow, followed by a slow growth of current in the former direction—in this case it appeared that the applied voltage could finally overcome the back E.M.F. If the applied voltage was almost exactly equal to the back E.M.F.—or at least this was the interpretation put on the matter—the current grew slowly to the steady value appropriate to that voltage.

In this way the following values of the back E.M.F. were obtained for the substances and initial voltages stated:

<table>
<thead>
<tr>
<th>Substance</th>
<th>NaCl</th>
<th>NaBr</th>
<th>KCl</th>
<th>KBr</th>
<th>KI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Voltage</td>
<td>500</td>
<td>90</td>
<td>590</td>
<td>590</td>
<td>550</td>
</tr>
<tr>
<td>Back E.M.F.</td>
<td>90</td>
<td>67</td>
<td>545</td>
<td>581</td>
<td>290</td>
</tr>
</tbody>
</table>

If the voltage were entirely removed after the full back E.M.F. had been developed and the crystal grounded, then a large initial current, gradually decreasing with time, flowed in the direction opposite to that of the original "charging" current. The initial magnitude of this current appeared to be equal, approximately, to the difference between the value of the initial current for the applied voltage and its final
steady value; also its rate of decay seemed closely to parallel that of the original current as it decreased to its steady limiting value (see plate V).

For example, in NaCl, on one occasion, the initial current produced a deflection of 89 scale divisions of the short-period galvanometer (period 2.4 seconds), while the final steady current gave 66 scale divisions. (For convenience an arbitrary unit of current, the "scale division", will be adopted in this discussion; 1 scale division = 0.2 \times 10^{-12} ampere.) Upon releasing the applied field, a current of 27 scale divisions flowed initially in the other direction. This illustrates what was always the case, that the sum of steady and "residual" currents was slightly greater than the initial current—which might have been due to the finite time of action of the galvanometer.

It was found that the photoelectric polarization built up in rock salt, as well as in other substances, could be retained for a surprisingly long time. For example, in the individual experiment on NaCl mentioned above, in which it was found that the back E.M.F. would produce an initial current of about 27 scale divisions (consecutive readings were very closely reproducible), the back E.M.F. was then allowed to build up as before, but the crystal thereafter kept in the dark for 20 hours with no external potential applied to it. Then upon turning on the same light and with the crystal still grounded, a current of 17 scale divisions immediately
PLATE V

CURRENT TIME CURVES FOR KBR.

Curve I shows the photoelectric current in a KBr crystal under an applied potential of 100 volts as a function of time. Readings were taken with the direct current amplifier unit, using a galvanometer of 2.4-second period. Units are "scale divisions" = 2 x 10^-13 amp. The first point on Curve I corresponds to a current of 20 x 10^-12 ampere, but the "initial" current, as shown by ballistic measurements, was about 50 times greater still.

Curve II shows the photoelectric current in a grounded KBr crystal produced by the back E.M.F. previously developed by illumination under an applied potential of 315 volts. As for curve I, the initial deflection of the galvanometer was far off the scale. Ballistic measurements showed that the initial magnitude of this "discharge current" was nearly as great as that of the initial surge of current when the crystal was "charged up".
flowed, decreasing at about the same rate as if it had been illuminated immediately after "charging". It was found that somewhat smaller back E.M.F.'s could be "stored up" for several days in NaCl, and "released" at will by illumination. Sodium bromide was found capable of retaining a photoelectrically produced polarization about as well as rock salt. The potassium salts likewise could retain measurable photoelectric back E.M.F.'s for periods of the order of one to three days.

An almost exactly parallel phenomenon has been reported for photoconducting sulphur crystals by Nadjakoff. The decrease of the photoelectric current produced by back E.M.F., although at first rapid, soon became very slow. In one rock salt crystal, for example (plate VI) it decreased to 1 scale division in 15 minutes, but was still considerably more than $\frac{1}{3}$ scale division at the end of 30 minutes. Whether the shape and extent of this long foot of the depolarization current-time curve was a function of the original time of "charging" is a question which would bear more detailed investigation. Scattered observations indicated such a dependence.

The initial photoelectric currents produced in NaBr, KCl, KBr and KI were much larger than in rock salt, large enough, in fact, to produce deflections of the sensitive galvanometer if the latter was connected directly in series with the illuminated crystal and the batteries. But since these large
PLATE VI

DISCHARGE CURRENT IN GROUNDED NACL CRYSTAL, which previously has been subjected to intense illumination and an applied potential of 500 volts.

The time integral of this discharge current was graphically estimated as about $1100 \times 10^{-12}$ coulomb. The estimate was uncertain by a factor of perhaps 10, because of the unknown extension of the foot of the curve. But, accepting the figure as given, the number of elementary charges per unit volume of the "charged" crystal was computed to be $10^{11}$.

Goldman and Wul^30 found the space charge of photoelectrically polarized NaCl crystals subjected to an electric field of breakdown strength to be about $10^{15}$ elementary charges per unit volume, or 10,000 times as great as the value found here. Their field, however, was 1400 times as great. It is possible that the area under the curve given here was underestimated by a factor 10. Also it was assumed that the space charge was uniformly distributed throughout the volume of the crystal, whereas it may have been concentrated near the ends of the specimen. The crystals of Goldman and Wul also were prepared in a different way, i.e., their crystals were photo-sensitized by impregnation with "U-centers," followed by irradiation with ultra-violet light.
initial currents decreased to a fraction of their magnitude within considerably less than a second of time (because of the rapid building up of polarization), a ballistic method of measurement was generally resorted to, using the amplifier as a ballistic instrument.

A formula for the ballistic use of the amplifier was found as follows: the total charge passed through the measuring galvanometer is, by the standard formula

$$Q_G = \frac{T_G F_G}{2\pi} \int_0^\Delta t i_G \, dt,$$

(35)
in which $F_G$ is the figure-of-merit of the galvanometer, $T_G$ its period, and $i_G$ the current which flows through it. But $i_G$, by the calibration of the amplifier, had been found to be proportional to $v_g$, the applied voltage on the grid, that is,

$$i_G = K v_g = F_G d = \frac{F_G}{F_a} v_g$$

because

$$v_g F_a = d,$$

the galvanometer deflection. $F_a$ is the voltage sensitivity of the amplifier. Then (35) reduces to

$$\frac{T_G d}{2\pi} = \frac{1}{F_a} \int_0^\Delta t v_g \, dt.$$

(36)

$v_g$, the voltage on the grid, does not instantly leap to its final value; the finite capacity of the grid (plus Hall electrode and connections) must be taken into account. This has already been done in connection with the rate-of-charge method as applied to a leaky electrometer. Equation (31), namely
\[ t = -CR \log_e (1 - \frac{V}{I_R H}) \]

when put in exponential form and the subscripts changed so as to be appropriate to the situation under discussion becomes

\[ v_g = i_0 R_g (1 - \exp (-t/R_g C)) \]

\( R_g \) is the value of the grid resistor and \( i_0 \) is the current flowing on to the grid and its connections from the crystal. Equation 36 then becomes

\[ \frac{T_{gd}}{2 \pi} = \frac{i_0 R_g}{F_a} \int_0^{\Delta t} (1 - \exp (-t/R_g C)) dt, \]

which, integrated, is

\[ \frac{T_{gd}}{2 \pi} = \frac{i_0 R_g}{F_a} \left\{ t - R_g C e^{-t/R_g C} \right\}_0^{\Delta t} \]

\[ = \frac{i_0 R_g}{F_a} \left\{ \Delta t - R_g C (e^{-\Delta t/R_g C} - 1) \right\}. \quad (37) \]

This expression may be simplified by the relation

\[ 1 - e^{-x} = x - \frac{x^2}{2} + \frac{x^3}{2 \cdot 3} - ( ) + \cdots \]

for small \( x \). Then (37) becomes

\[ \frac{T_{gd}}{2 \pi} = \frac{i_0 R_g}{F_a} \left\{ \Delta t - R_g C \frac{\Delta t}{R_g C} (1 - \frac{\Delta t}{2R_g C}) \right\} \]

\[ = \frac{i_0 R_g \Delta t^2}{F_a 2R_g C} = \frac{i_0 \Delta t^2}{2C} \]
or

\[ i_0 = \frac{T_g F_a C d}{\pi \Delta t^2} \]  \hspace{1cm} (38)

It is a little surprising to find \( R_g \) gone. Formula (38) may be made a little more accurate by including the damping factor of the galvanometer, i.e., by writing

\[ i_0 = \frac{T_g F_a C}{\pi \Delta t^2} (1 + \frac{\Delta}{2}) d \]  \hspace{1cm} (39)

where \( \lambda \) is the natural logarithm of the ratio of successive swings of the galvanometer to left and to right, past the zero point.

Using flashes of light of approximately 0.01 second duration and the voltage sensitivity range of the amplifier \( F_a = 3.2 \times 10^{-4} \) volts/cm, it was found that the initial currents in both KBr and KCl were of the order of \( 5 \times 10^{-9} \) ampere. In the case of KBr this value was about 100 times as great as that for the final steady current.

There is a possibility that the effective resistance of a polarized crystal is greater than its initial effective resistance to an applied E.M.F., i.e., that \( R_p \), defined by

\[ R_p = \frac{(\text{Applied E.M.F.}) - (\text{back E.M.F.})}{\text{steady P.E. current}} \]
is greater than \( R_0 \), defined by

\[
R_0 = \frac{\text{Applied E.M.F.}}{\text{initial current}}
\]

In other words it appeared (according to somewhat hasty and rough measurements) that the current per unit of "effective" E.M.F. was greater for the initial surge of photoelectric current than for its limiting steady flow after the back E.M.F. had built up to its equilibrium value. If such were actually the case, the most likely explanation would be that the increased effective resistance of the polarized crystal was the result of increased recombination between positive and negative carriers.

(The possibility of \( i_0 \), the ballistically-measured initial current, not remaining constant even during the short flashes of 0.01 second was considered. It was found, however, that the galvanometer throws due to the first three or four flashes were practically the same (even for intervals between flashes of only 5 seconds, during which very little polarization could have been "lost"), but that they thereafter became smaller rather rapidly, until an equilibrium was reached at which the polarization built up during one flash was "lost" during the dark interval to the next. (See plate VII.)

The reverse current caused to flow by back E.M.F. was, as might have been expected, proportional to the steady current which previously had flowed, i.e., was increased by increasing the intensity of illumination. But in KBr and KCl
FORMATION OF SPACE CHARGE IN KBR CRYSTAL BY 0.01-SECOND FLASHES OF LIGHT AT 1/5-SECOND INTERVALS. The ballistically measured charge produced by each flash of light was approximately constant for the first two or three flashes, but thereafter decreased to an approximate "equilibrium value" which was about 1/4th as great as the initial value.
the final steady current could not be greatly increased by multiplying the intensity of illumination—it appeared that the additional polarization thereby built up nearly cancelled the effect of the additional liberation of photoelectrons.

With NaCl it was always possible to increase the steady photoelectric current very markedly by increasing the intensity of illumination up to the maximum intensity available. But it was observed that the back E.M.F. built up by passage of photoelectric current at a comparatively small intensity of illumination would prevent the passage of the direct photoelectric current due to an applied potential slightly less than the back E.M.F. just developed, but under considerably greater intensity of illumination. That is, an E.M.F. built up by a small current could prevent the passage of a current which, in the absence of the previously-formed back E.M.F., would have been much larger.

KCl was like KBr, in that a comparatively very large initial current diminished with time to a final smaller steady value. But the initial rate of decrease of current was much smaller, although the final steady value was about the same, and about the same time was required to reach it. Thus, in KCl, the large initial current lasted long enough that a "steady" (but diminishing) deflection of the sensitive galvanometer (period 13.2 seconds) when hooked directly in series with the crystal could be obtained, indicating an
"initial" current of about $8 \times 10^{-10}$ ampere. Ballistic measurements had shown that the first surge of electron current must have really been about ten times this great, however.

The polarization built up in KBr and KCl, while more effective in forming back E.M.F., was not as hard to remove as that formed in NaCl. Five minutes of illumination of an "excited" KBr or KCl crystal was enough to reduce its back E.M.F. to one or two volts (but much longer was required to remove it completely). Several hours of the "depolarizing treatment" on NaCl had about the same effect as five minutes of such treatment of the potassium salts—several volts of back E.M.F. would still remain. These facts might be interpreted as indicating that most of the photoelectric polarization in KBr and KCl was in the layers next to the end electrodes, although part of it was "deeper", i.e., more uniformly distributed throughout the volume, whereas in rock salt the "deep-seated" polarization was 

\begin{verbatim}
relatively
greater, but the "shallow" polarization much less.
\end{verbatim}

Another measurement which possibly indicated that the back E.M.F. built up in a KCl crystal was mostly localized in the end layers was the following: with the grounded point adjusted so that the steady current into the Hall electrode was practically zero, then a shift of that grounded point produced a relatively small change in the Hall electrode current, but with larger shifts the change-in-current-per-volt
became much larger, as shown in the following table (in which the $\Delta v$'s are measured from the original "balanced" grounded point):

<table>
<thead>
<tr>
<th>$\Delta v$</th>
<th>$\Delta I$ (skt)</th>
<th>$\Delta v$</th>
<th>$\Delta I$ (skt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22$\frac{3}{4}$</td>
<td>-1.3</td>
<td>-22</td>
<td>0.5</td>
</tr>
<tr>
<td>45</td>
<td>2.5</td>
<td>-44</td>
<td>2.5</td>
</tr>
<tr>
<td>66$\frac{1}{2}$</td>
<td>-5.5</td>
<td>-66</td>
<td>9.0</td>
</tr>
<tr>
<td>88</td>
<td>-21.0</td>
<td>-38</td>
<td>14.0</td>
</tr>
<tr>
<td>109$\frac{1}{2}$</td>
<td>-50</td>
<td>-110</td>
<td>24</td>
</tr>
<tr>
<td>131</td>
<td>-84</td>
<td>-132</td>
<td>37</td>
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<td>153</td>
<td>-119</td>
<td>-154</td>
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<tr>
<td>175</td>
<td>-161</td>
<td>-220</td>
<td>88</td>
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<tr>
<td></td>
<td>-242</td>
<td>95</td>
<td></td>
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<tr>
<td></td>
<td>-286</td>
<td>135</td>
<td></td>
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</tbody>
</table>

The proportionately larger changes in Hall electrode current produced by large potential shifts might, by reference to figure 22, be interpreted to mean that the equipotential lines were distributed through the crystal somewhat as there shown—far apart in the center, but crowded together near the ends.

Now Pohl and his students have found that the range of photoelectrons in KBr and KCl is "thermally extended" (at room temperature) to several hundred times its value at liquid air temperatures, and this fact probably accounts for the large initial surges of photoelectric current observed in these substances. But it also appears that the "thermally extended" range of the photoelectrons does not greatly, if at all, increase the magnitude of the final steady current. It is probable that "thermally extended" range does not release the electrons from the anchoring effect of the residual positive charges; it only allows them to proceed further on the first jump.
FIGURE 22

PROBABLE DISTRIBUTION OF EQUI-POTENTIAL PLANES IN PHOTOELECTRICALLY POLARIZED KCL CRYSTAL
The steady current of KBr (and KCl too, to a lesser extent) is rather peculiar, in that, although small, it is subject to violent fluctuations, of the order of 50% of its own magnitude. With an applied voltage of only 590 (to a crystal 7.2 mm long) violent kicks of the short-period galvanometer were observed at 2- or 3-second intervals. These were not due to short-circuiting around the crystal, because they stopped the instant the light was turned off. The applied average field was of the order of 1,000 times smaller than the breakdown field (according to Von Hippel's measurements); also it was at least 30 times smaller than the saturation field. But the possibility remains that the field was of near-breakdown magnitude over some short lengths in the crystal, probably near the ends, where the space charge density was large.

Thus the thermally-extended range of a photoelectron in lightly-colored KBr at 25°C may be computed, from data given by Glaser and Lehfeldt, to be about one-third of a millimeter for a field of 820 volts/cm, as used here. But if the potential drop, and therefore also the field, were mainly concentrated over one-tenth or less of the length of the crystal, the range of the photoelectrons therein would be 0.3 cm or more, a "very" macroscopic distance. But such an intensified field, in a crystal 7.2 mm long, could not extend over a length of more than about 0.07 cm, so that saturation and more-than-saturation would be attained. Then, to make use
of crude figure-of-speech, the situation would be similar to that of timber floating down a spring freshet when it "clogs up" in a mill pond. The gentle potential fall over the main part of the crystal would not carry many photoelectrons across, but those that did cross might complete their trip in a hurry—by jerks. At least there seems to be no doubt about the existence of the fluctuations.

In concluding this discussion of photoelectric polarization in colored halides, it may be mentioned that even a Hall E.M.F. should be sufficient to produce it. Such polarization by the Hall E.M.F. was, during the course of this investigation, unmistakably observed in zincblende. (See figure 19). Moreover, in the halides, it appeared that any small change in applied potential was sufficient to rearrange, slightly, the space charge. For example, the effect of changing the grounded point, in the Hall arrangement, by one or two volts was always to produce an initial shift of the galvanometer several times larger than the final steady change—and for this initial, comparatively large shift to be produced, the light had to be shining on the crystal. This observation indicates that the instantaneous introduction of any small E.M.F. is not initially opposed by any back E.M.F., although back E.M.F. exists in opposition to previously applied potentials. In KBr, for example, a suddenly induced Hall E.M.F. might be expected to produce a Corbino current one or two hundred times greater than its final steady magnitude.
The sensitivity to a small Hall E.M.F. which might thus be obtained, however, would be limited by the fact that presumably a back E.M.F. would be developed very quickly in opposition to the Hall E.M.F., so that the time-integral of the accompanying Corbino current might still be rather small. As a matter of fact, Hall effect observations were taken on KCl with the galvanometer connected while the magnet was thrown on. The galvanometer throws thus produced, however, were small and, also, spurious—since they did not change direction with reversal of the direction of the magnetizing current.

A search through the literature of photoconductivity for data on the actual distribution of potential along an "excited" KBr or KCl crystal has, so far, turned up nothing.

Appendix--Part II

GENERAL PROPERTIES OF THE PHOTO-SENSITIVE ALKALI HALIDES.
MISCELLANEOUS OBSERVATIONS

Mention of the general photoelectric properties of the crystals here worked with seems justified in order to show that the standard of technique employed was not too far below that of other (more practiced) workers in the field.

The currents used here were generally of the same order of magnitude, under similar conditions, as the currents used by Pohl's students at Gottingen. This order of magnitude is such that the unit $10^{-12}$ ampere was generally very convenient for their measurement. In all specimens examined for Hall effects, current-voltage readings were made upon the
longitudinal current through the crystal, and it always came out that the magnitude of the steady current was proportional to the applied voltage. The initial current was likewise proportional to voltage (it was measured with the amplifier for NaCl, and with the electrometer for NaBr, KBr, KCl and KI).

It was also verified that, in NaCl, the photoelectric current-density per unit applied field and the same illumination was practically independent of the color-center concentration. No systematic observations were made, and, as a matter of fact, only three individual specimens were exhaustively studied, but these three specimens were purposely chosen with a wide range of color density. One was very dense, so that it looked like a piece of chocolate candy, another was colored so lightly that it was nearly transparent, while the third was in between. The lightly colored specimen allowed a somewhat greater steady current-density to pass, under identical conditions of applied voltage and illumination, because in it comparatively less polarization appeared to be built up. At least the back E.M.F. developed for a given applied field was less.

It has been shown (by other workers) that the photoconductivity of the colored alkali halides is due to absorption of light within a definite range of frequency, namely the F-band, which for NaCl extends from about 3800 to 6000 Å with maximum absorption at 4600 Å. Now in experiments with filtered light, it was found that light which had passed through a No. 70 Wratten filter, which presumably has a
cut-off at about 6400 Å, was nevertheless capable of producing a steady photoelectric current in rock salt, at least for 12 hours of continuous illumination. It seems certain that any F'–centers would have been used up long before the end of such a period of illumination. However the explanation must have been that the cut-off of shorter wave-lengths was not as sharp as supposed. It was, however, found that the current due to light filtered by No. 70 (red) could be substantially increased by first illuminating the crystal with white light, or light filtered by Wratten No. 44 (blue, with red cut out); and that with No. 70 in place, the difference between initial and steady currents was considerably greater than for white or blue light. The specimen, therefore, was considered to have passed the test. (See plate VIII.)

A few points were also observed in regard to visible thermal conduction that have not been seen in he literature. For example, it was found impossible, in the limited number of times it was attempted, to get a satisfactory measurement of the quantity \( \int \frac{i}{e} dt \), in the case of NaCl. (This quantity was needed for an electrical determination of the color–density produced by electron impregnation.) The difficulty appeared to proceed from an obvious source, it was a matter again of polarization. For example, when it was tried to color rock salt by electron penetration at a temperature of 550°C (in order to secure a lightly–colored specimen) the color went in all right, although slowly, for several minutes. The current,
PLATE VIII

CURRENT-TIME CURVES FOR ROCK SALT AS A FUNCTION OF KIND OF ILLUMINATION. The current scale is different for the three curves, being so chosen for each that the first points coincide.

#44 = curve for illumination through Wratten filter No. 44 (blue).

#70 = curve for illumination through Wratten filter No. 70 (red).

1 2 3 minutes
however, as measured with a milliammeter, was seen to be decreasing (instead of increasing as had been expected), and after about 30 minutes the color, by that time advanced halfway to the anode, appeared to be "stuck", and never did get any farther, even the voltage applied was finally doubled (to 700 volts) in an effort to dislodge the "sticking" of the color.

At the temperature of 650° C an electron cloud would advance through an NaCl crystal very steadily, requiring only a few minutes to reach the anode. But for this temperature the background of electrolytic current was so great as to mask the component connected with the electron penetration. The current did actually increase several times in magnitude, but most of the increase was due to heating action of the current, as shown by the fact that a current sent through the crystal in the opposite direction, although it would not produce coloring, would grow almost as fast (see plate IX).

With KCl and KBr, both softer crystals, it was easier to get electrical stability during the coloring process. In these, as it should have, the current increased steadily (but with fluctuations) up to a magnitude several times its initial value, and then remained steady (this steady value was sometimes somewhat less than the maximum value of current attained during the coloring process, i.e., at the moment the coloring first reached the anode).
PLATE IX

COLORING ALKALI HALIDE CRYSTALS BY DRIVING ELECTRONS INTO HEATED SPECIMENS.

The "long" time scale is for NaCl at 550°C.
It was also noticed, in NaCl, that the process of drawing the color centers in and out of the crystal could not be repeated indefinitely. After drawing them out once, the second cloud was much fainter than the first, and the third fainter still. This progressive decrease of the color concentration obtainable with successive penetrations and withdrawals of electron clouds may have been due to trapping of many of the electrons as invisible U–centers, or, alternatively, to the loss of free chlorine at the anode--this loss would tend to make the process irreversible.

The rapidity with which photochemically-colored crystals faded was rather surprising. A deep blue color in KBr would not last more than a day or two, even in the dark, while KCl would bleach out in indoor light within a half-hour. Rock salt kept its color longer than KBr or KCl but, as has been mentioned elsewhere, was faded within a minute or two, with accompanying total loss of its photosensitivity, when exposed to the focused beam of an automobile headlight bulb.

It was also found that x–raying rock salt left it in a decidedly "excited" condition, so that it would act as a battery for about 24 hours. The current thus given off was apparently independent of any illumination. It was of the same order as the photoelectric current which could be simultaneously obtained, but lasted long after the latter had been reduced to near–zero by fading of the crystal.
Appendix—Part III

EFFECTIVE RESISTANCE OF A SIDE ELECTRODE

Moulton\textsuperscript{53} has shown how to calculate the effective resistance between two electrodes of arbitrary length and arbitrarily placed against the sides of a 2-dimensional rectangular conductor by means of Schwarz's transformation. By the transformation chosen (actually consisting of two successive transformations), the family of curved equipotential lines in the original plate, taken in the complex \( z \)-plane, becomes a set of parallel straight lines in the complex \( w \)-plane, parallel, in fact, to the transformed electrodes, which in the transformation become the ends of a rectangle in the \( w \)-plane. Details of the transformation will not be given here; the idea of the transformation is shown qualitatively by figure 23 (in which current lines, rather than equi-potential lines are drawn).

The result comes out in terms of elliptic functions and is most simply expressed as the ratio of the resistance between the two arbitrarily chosen electrodes to that between electrodes covering the ends of the plate.

\[
\frac{\text{Resistance between electrodes } OP \text{ and } OR}{\text{Resistance between ends of plate}} = \frac{L' / L}{K / K'}, \quad (40)
\]

in which \( K / K' \) is the ratio of length to width of the original plate, and \( L' / L \) is the ratio of length to width of the "transformed" plate. \( L \) is the complete elliptic integral, to be found in tables, corresponding to the elliptic modulus \( \lambda \), which, in terms of the coordinates of the ends of the
FIGURE 23

$z$-plane

$w$-plane

SCHWARZ'S TRANSFORMATION
electrodes on the original plate (see figure 23), is given by

\[ \lambda^2 = \frac{(\text{sn}^2 z_4 - \text{sn}^2 z_3)(\text{sn}^2 z_1 - \text{sn}^2 z_2)}{(\text{sn}^2 z_1 - \text{sn}^2 z_3)(\text{sn}^2 z_4 - \text{sn}^2 z_2)} \]  \hspace{1cm} (41)

L' is the complete elliptic integral corresponding to the complementary modulus \( \lambda' \), where

\[ \lambda^2 + \lambda'^2 = 1. \]  \hspace{1cm} (42)

One corner of the plate may be chosen as origin, but some of the \( z \)'s will still be complex numbers. Their elliptic sines, however, may be worked out by the following formulae (Nos. 715 and 732 respectively in Pierce's Integral Tables):

\[ \text{sn} (u \pm v) = \frac{\text{sn} u \cdot \text{cn} v \cdot \text{dn} v \pm \text{cn} u \cdot \text{sn} v \cdot \text{dn} u}{1 - k'^2 \text{sn}^2 u \cdot \text{sn}^2 v} \]

\[ \text{sn} (iu, k) = \frac{i \text{sn} (u, k')}{\text{cn} (u, k')} \]

where

\[ k'^2 + k'^2 = 1. \]

By means of these formulae the resistance between a small electrode placed at the center of one side of a plate and an electrode covering one of the ends of the plate was calculated for various widths of the side electrode. The calculation was made for a plate the ratio of whose length to its width was 1.54. (This ratio simplified the computation and also represented a plate whose shape was fairly typical of those used in the present investigation.)
The results of the computation are shown in Plate X, in which effective conductances, rather than resistances, between a side electrode and an end electrode are plotted as a function of the length of the side electrode, the latter expressed as a fraction of the assumed total length $a$ of the plate.

Although the resistance from one end to an infinitely narrow side electrode (point electrode in the 2-dimensional case) is infinite, the resistance to an electrode only $1/40,000$th as long as the length of the plate still comes out to be only $3.31$ times as great as that between the opposite ends of the plate.
EFFECTIVE CONDUCTANCE BETWEEN A SIDE ELECTRODE AND AN END ELECTRODE AS A FUNCTION OF THE LENGTH OF THE SIDE ELECTRODE.

Length of Side Electrode in terms of Crystal Length.
ACKNOWLEDGMENTS

The writer wishes to acknowledge his indebtedness to Prof. C. W. Heaps for suggestion of the problem, as well as for taking part in many long and helpful discussions concerning the progress of the work and the concepts involved in the interpretation of the phenomena of photoconductivity.

He also desires to thank Prof. H. A. Wilson for his continued interest in the investigation, valuable advice in the design of apparatus, suggestions for further experiments, and cooperation in obtaining equipment.
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   For synopsis of result, see Joffe's book, p. 129.


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Examination of Colored Alkali Halides for Photoelectric Hall Effect

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Five additively colored alkali halides have been examined for photoelectric Hall effect by means of two different arrangements, a single cross-electrode set-up and Tartakowsky's divided electrode method. The consistently null results obtained were checked by using zincblende, a substance of known photoelectric galvanomagnetic properties, in both arrangements. From the upper limit assigned to the Hall effect, it was computed that the mean free path of photoelectrons in rocksalt is not much greater than the dimensions of a lattice cell—in agreement with Von Hippel's result for the electronic mean free path on the basis of electrical breakdown experiments. This interpretation of the null result was supported by the fact that the large initial surge of electron current in KCl and KBr at the outset of illumination also showed no Hall effect. The magnetic deflection of photoelectric current reported in rocksalt by Tartakowsky was not found, either for additively or photochemically colored specimens.

POHL\textsuperscript{1} and his collaborators have made exhaustive studies upon the photoelectric properties of additively colored alkali halide crystals, but so far have not reached a definite decision as to the nature of the color centers or of the complete conduction mechanism of the photoelectric current. Lukirsky\textsuperscript{2} has reported a Hall effect in photochemically colored rocksalt such that the mean free path of the photoelectrons was calculated (according to Joffé\textsuperscript{3}) to be "of the order of $10^{-8}$ or $10^{-6}$ cm." Tartakowsky\textsuperscript{4} has described an apparatus by means of which he demonstrated an "electron polarization" set up in photochemically colored rocksalt by the magnetic deflection of the lines of current flow to a divided collecting electrode. Von Hippel,\textsuperscript{5} however, on the basis of experiments upon electrical breakdown in rocksalt, has concluded that the mean free path of electrons therein is of the order of the dimensions of one lattice cell. His conclusion was supported by a theoretical calculation of the "relaxation time" of electrons in rocksalt made by Fröhlich.\textsuperscript{6} In view of the discrepancy between Lukirsky's and Von Hippel's results when applied to the determination of electron mean free paths in rocksalt, and also because of the sparseness of available data on photoelectric Hall effects in general, it was considered desirable to examine several colored alkali halides in detail for the photoelectric Hall effect.

APPARATUS

First measurements on NaCl, KCl and KBr were by means of a single cross-electrode arrangement, shown schematically in Fig. 1. The cross electrode was connected directly to the grid $A$ of a sensitive direct-current amplifier, with circuit as given by Harnwell and Van Voorhis.\textsuperscript{7} A current sensitivity of $4 \times 10^{-18}$ amp. = 1 scale division was used. B-batteries connected in series to the amount of about 300 volts were applied to the ends of the crystals. These batteries were

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_1.png}
\caption{Schematic showing single cross-electrode method for testing Hall effect in crystal. The rotation of equipotential lines by the Hall field is also shown.}
\end{figure}

\textsuperscript{4} P. Tartakowsky, Zeits. f. Physik 66, 830 (1930).
\textsuperscript{5} A. von Hippel, J. App. Phys. 8, 815 (1937).
\textsuperscript{7} G. P. Harnwell and S. N. Van Voorhis, Rev. Sci. Inst. 5, 244 (1934).
grounded near their center, the grounded point $G$ being varied by steps of $1\frac{1}{2}$ volts until no current flowed into $H$ when the crystal was steadily illuminated. Batteries and leads were electrostatically shielded.

Measurements on NaCl, KCl and KBr were repeated by means of Tartakovsky’s divided electrode arrangement (Fig. 2). KI and NaBr were also measured with this latter apparatus.

Single crystals of the substances studied were manufactured from chemically-pure, fused salts with an apparatus similar to that described by Walther.\(^8\) Photoelectric contacts with the crystals were made by sputtering mirror-like, platinum coats on to freshly cleaved faces. The small side electrodes were made by scraping away all of the sputtered coat on one side of a specimen except that covered by a clamped safety razor blade (thickness 0.24 mm). Crystals were additively colored by electron impregnation at high temperature (500 to 700°C) and then “quenched” in an air stream to secure atomic dispersion of color centers.

The crystals were gripped between brass electrodes by the steady pressure of spiral brass springs, the electrodes being mounted in a hard rubber block frame. The frame, with glass plates, also served as a low vacuum chamber. The Hall electrode was protected from leakage currents by a guard ring. Crystals were illuminated over their complete length by the full light from the tungsten filament of a 6–8-volt, 50-cp automobile headlight bulb, the focused light beam being sent through a long hole in one pole piece of the Weiss electromagnet which produced the magnetic field.

\(^8\) H. Walther, Rev. Sci. Inst. 8, 406 (1937).

**Procedure and Results**

The procedure was to adjust the position of the grounded point of the applied batteries until with the light shining on the specimen, no photoelectric current flowed into the cross-electrode. Then a magnetic field was applied normal to the principal plane of the specimen, and any resulting effect upon the current into the Hall electrode observed.

The arrangement was empirically tested for its sensitivity to small e.m.f.’s by shifting the grounded point of the batteries by a small amount and noting the corresponding effect on the steady deflection of the indicating instrument. Such a shift had the effect of increasing the potential difference between the Hall electrode and the respective ends of the crystal by an amount $\pm \Delta E$.

It was assumed, from considerations of symmetry, that a transverse Hall e.m.f. $E_H$ across the crystal would rotate the equipotential lines of the electric field about their points of intersection with the longitudinal center of the crystal, i.e. (Fig. 1), that the potential difference between the Hall electrode and the ends of the crystal would be changed by $\pm \frac{1}{4}E_H$, respectively. This assumption was made plausible by an experiment upon zineblende, which from Lenz\(^9\) work is known to have an easily detectable photoelectric Hall effect. With zineblende in the apparatus it was found that the direction of the Hall current into the single cross-electrode could be reversed by reversing the direction of the applied electric field, indicating that if a second cross-electrode $H'$ (Fig. 1) had been connected to a second amplifier $A'$, the latter, during application of a magnetic field, would have recorded a Hall current equal and opposite to that recorded by $A$. Hence it was assumed that the Hall e.m.f. $E_H$ across the width of a given alkali halide crystal could not be greater than the smallest voltage shift $\Delta E$ of the grounded point which would produce a positive effect.

No positive indication of a Hall e.m.f. or associated Hall current was found for the steady photoelectric current in additively colored NaCl, KBr or KCl. In one set of readings upon rocksalt it was found that the steady change in the

PHOTOELECTRIC HALL EFFECT

reading of the indicating instrument for small shifts of the grounded point was 7.5 cm/volt, whereas turning on the magnetic field (of 12,200 gauss) produced random shifts of about 1.5 cm. The variations apparently caused by application of the magnetic field were found to be present with or without the light shining on the crystal. The average of 8 readings taken with the magnetic field in one direction differed by less than 0.3 cm from the average of 8 readings with the magnetic field reversed. Therefore, assuming that for the very small currents involved any Hall e.m.f. present would be proportional to the transverse photoelectric current produced by it, it was concluded that the effect of reversing the magnetic field was less than that produced by shifting the grounded point of the batteries by 0.1 volt. With the calibrating factor of $\frac{1}{2}$, the Hall e.m.f. was less than 0.2 volt across the crystal (dimensions $7.5 \times 4.0 \times 1.2$ mm), or, the Hall field $V$ was less than 0.5 volt/cm.

The steady photoelectric current under the applied voltage, 520, was found to build up a photoelectric "back e.m.f." of 90 volts, as determined by the applied potential which would just prevent the built-up back photoelectric e.m.f. from sending a current in the opposite direction. Then the total "effective" potential difference over the length of the crystal was 430 volts, and the average resultant field 570 volts/cm. Therefore the ratio $V/X$ of the Hall field to the electric field near the center of the crystal was less than $1/1150$.

The measurements just described were taken with a very lightly colored specimen, color density estimated at about $5 \times 10^{16}$ centers/cm$^2$. According to Glaser and Lehelde$^{19}$ the so-called "thrust paths" of the photoelectrons in rocksalt are inversely proportional to the color center density. A thrust-path, however, presumably consists of many free paths.

The measurements were checked and confirmed by using the amplifier in a slightly different manner, namely, by allowing the grid to "float" ($R_g$ = insulation leak resistance = about $10^{13}$ ohms) and noting its rate of increase of potential, if any, caused by application of a magnetic field to the illuminated crystal.

Lenz$^2$ found the photoelectric Hall effect in zincblende to depend in sign and magnitude upon the orientation of the specimen, while Von Hippel$^8$ found preferred directions of electron movement in rocksalt. It therefore appeared likely that the Hall effect in rocksalt might be a function of the orientation of the specimen. A plate was cut and sputtered so that the electric field could be applied in a 110-direction, and the possible Hall field measured in another 110-direction. No effect was found, the upper limit to the ratio $V/X$ for a magnetic field of 12,200 gauss being set at $1/200$.

It seemed possible that the small value of the Hall effect indicated for the steady photoelectric current was due to opposite and canceling contributions by the equal components of electron and "hole conduction" current, since, according to an application of quantum mechanics by Fowler,$^{11}$ the Hall coefficient for an electronic semi-conductor is

$$R = \frac{kV}{HX} = \frac{3}{8} \frac{e(n_1 - n_2)}{\varepsilon(n_1 + n_2)}$$

where $k$ = constant, $H$ = magnetic field, $\varepsilon$ = charge on a carrier, $n_1$ and $n_2$ are the numerical concentrations of the negative and positive carriers, respectively, and $\varepsilon_1$ and $\varepsilon_2$ are the corresponding conductivities. Now the colored potassium salts are characterized by a comparatively large initial surge of photoelectric current$^{14}$ at the outset of illumination, followed by a rapid decrease to a final "steady" (but still decreasing) value about 100 times smaller than the initial current. The rapid decrease of current is attributed to the formation of space charge, resulting from the failure of the positive component of photoelectric current to remove positive charge as rapidly as the negative charge is drawn out. The initial photoelectric surge therefore consists mostly of electrons, and consequently in it the canceling contribution of the positive carriers to the Hall effect should be small. Therefore measurements were taken of the effect of an applied magnetic field upon the photoelectric current flowing during a 1/10 second flash of light in KCl and KBr, with the amplifier, still connected to the cross-electrode, as a ballistic instrument.


Fig. 3. Upper curve, "photoelectric Hall back e.m.f." effect in ZnS by single cross-electrode set-up. The initial large throw of the indicating instrument upon application of a magnetic field was ascribed to a lack of photoelectric back e.m.f. initially opposing the Hall current; the decrease to a nearly steady value within 30 seconds was ascribed to the formation of a photoelectric back "Hall" e.m.f., whose presence then caused the reverse throw upon release of the magnetic field. Inset lower curve, Tartałkowski's curve for rocosalt, showing a similar "polarization" by means of the divided electrode arrangement.

With the KCl specimen (7.0×3.5×1.0 mm) and intense illumination, the smallest obtainable unidirectional throw of the indicating galvanometer (for 0.1-second flashes) was about 25 cm. (Space charge built up rapidly during the flash, changing the potential distribution along the length of the crystal, so that for some positions of the grounded battery point the direction of the photoelectric current into the Hall electrode reversed during the flash.) Changing the grounded point by 3 volts changed the ballistic throw, on the average, 6 cm, or 2 cm/volt, whereas, for 12 pairs of readings, the average for the magnetic field in one direction did not differ by more than 0.1 cm from the average with the magnetic field reversed. Random fluctuations between consecutive readings were of the order of 1 cm but a persistent effect of ½ cm would have been easily detected. The assumed maximum unobserved effect of ½ cm was due to reversing the magnetic field, so that the effect of applying the magnetic field in one direction must have been less than ½ cm, the effect which according to the calibration would have been produced by a Hall e.m.f. of ½ volt, or a Hall field of 0.7 volt/cm. The upper limit to the ratio Y/X then came out to be 1/850 for H=12,200 gauss.

However, the photoelectric back e.m.f. developed during the flash was about one-half of the total applied e.m.f., or the resultant time average of the longitudinal electric field near the Hall electrode during the flash was about three-fourths of the initial applied field; likewise with the time average of a possible accompanying Hall field. Making this correction, the limit for ratio Y/X for the initial electron surge of current was taken as 4/3×1/850=1/640.

The crystal was grounded and illuminated for 3½ minutes between consecutive flashes, or long enough to remove at least 99 percent of the developed photoelectric back e.m.f. and to restore the crystal to approximately the same condition for each reading.

In similar measurements upon KBr, in which the photoelectric polarization built up by successive flashes was not completely discharged between consecutive trials, the upper limit to Y/X was 1/225.

To test whether the experimental arrangement was capable of detecting the presence of a small Hall current or e.m.f., a specimen of clear yellow zinccblende (sphalerite), 7.27×4.8×2.0 mm, cut with its length parallel to a direction symmetrical with respect to the crystal axes (following a suggestion by Lenz), was substituted in the apparatus. A Hall current, whose direction reversed both with reversal of the electric and the magnetic fields, was found to flow upon application of the magnetic field. Data (averages of 20 trials for both directions of the magnetic field) are shown in Fig. 3 for one direction of the electric field.

The change in steady deflection per unit shift of grounded point was 5.7 cm/volt, while the change produced by reversing the magnetic field was 40 cm. From these data, and using the calibration factor of 2, it was found that the Hall field was 14.5 volts/cm, the average applied electric field being 890 volts/cm. According to Lenz the electric field near the middle of a photoelectrically polarized zinccblende plate is equal, approximately, to the average applied field. Therefore the value, 1/60, found for the ratio Y/X in zinccblende subjected to 12,200 gauss, agreed well, at least in order of magnitude, with Lenz' value for the same ratio, 1/44, extrapolated to the same value of magnetic field. (Lenz showed that the Hall field in zinccblende is linearly proportional to the strength of the magnetic field.) The difference could be due to structural differences between the specimens of the zinccblende, to the assumption made
here that the Hall e.m.f. was proportional to the Hall current, or to the fact that Lenz’ current densities were about 40 times greater than those used here. In any event it appeared that the single-electrode method was capable of detecting a photoelectric Hall effect.

An effect ascribed to “photoelectric Hall back e.m.f.” is shown in the graphical display of the data on zincblende. Upon turning on the magnetic field the galvanometer deflection was about 2½ times greater than its steady deflection. If the magnetic field was then removed, an opposite initial deflection occurred, of the same order of magnitude as the original initial deflection. The original large initial deflection was ascribed to a lack of photoelectric back e.m.f. at the Hall electrode initially opposing the Hall current. The decrease of Hall current was ascribed to the building up of a photoelectric back “Hall” e.m.f., and the reverse current to the action of this built-up e.m.f. after removal of the original Hall field.

A similar effect, obtained by using a divided electrode and a differential electrometer, has been described for x-rayed rocksalt by Tartakowsky. His curve is reproduced as an insert in Fig. 3 for the purpose of comparison. An attempt to duplicate Tartakowsky’s curve for rocksalt by means of his set-up was unsuccessful.

The photoelectric back e.m.f. developed by a steady current in KCl was found to be about 90 percent of the total applied e.m.f., and about 99 percent in KBr. Potential measurements made with a movable side electrode showed that the developed back e.m.f. was mostly due to charges collected near the ends of a crystal. The potential distribution along a photoelectrically “excited” KBr crystal is shown in Fig. 4. The irregularity of individual points is a result of the procedure of taking the crystal-holder out of the apparatus between readings in order to move the probe.

The potential distribution resembles closely that found in a gaseous discharge tube. The electric field intensity is greatest close to the electrodes and comparatively small near the middle of the specimen. It might therefore be expected that the Hall field generated by a magnetic field would also be greater near the ends of such a crystal, so that a method for detecting such a possible concentration of Hall field near the electrodes was needed.

According to Lenz the potential distribution along a photoelectrically polarized zincblende crystal is such as to indicate a resultant positive space charge throughout. The electric field intensity, in accordance with Poisson’s equation, is increased near the cathode and diminished near the anode. In the present investigation, zincblende was placed in the divided electrode arrangement of Tartakowsky. It was then found that the magnetic deflection of current from one part of the divided electrode to the other was approximately 12 percent greater when the divided electrode was used as cathode than when used as anode. The difference was about ten times greater than the average random fluctuation between consecutive readings. It therefore appeared that the Tartakowsky arrangement (first set up for the purpose of checking Tartakowsky’s experiment with colored rocksalt) should be suitable for the detection of small Hall fields concentrated near the ends of a specimen. (It was ascertained that the zincblende specimen as a whole had no rectifying effect upon the photoelectric current.)

Check measurements upon NaCl, KCl and KBr were made with the divided electrode arrangement, as well as measurements upon NaBr and KI. No conclusive evidence of a Hall deflection of current was found in any of these substances. Upper limits to the possible Hall fields in the various substances were assigned by direct comparison with the behavior

![Fig. 4. Potential distribution along photoelectrically polarized KBr crystals, as determined by a movable probe.](image-url)
of zincblende in the same apparatus. In Table I, $i$ is the total (average) current to one segment of the divided electrode, $\Delta \gamma$ is the change of current to that segment (average of 10 readings) caused by the magnetic field, and $\Delta \phi$ is the average fluctuation in the current for a single observation from its average value. In the last column, $R$ is the effect of the magnetic field upon the current flow in a given alkali halide as compared to its effect upon zincblende. This ratio has been assigned the positive sign if the apparent (very small) current deflection indicated by the average of 10 readings was in the same direction as for zincblende.

There is probably no significance to the fact that the very small magnetic deflection (if any) in KCl, KBr, and NaBr had the correct sign for a normal Hall deflection of current, because for these the average fractional change of current to one part of the divided electrode after application of the magnetic field was several times smaller than the average fractional fluctuation of current between consecutive readings. In rocksalt, however, a small "anomaly," slightly larger than the average fluctuations, and of the correct sign for a normal Hall current, was found. The anomaly was not recognized as an indication of a bona fide Hall effect for the following reasons:

1. In 6 specimens tested, the anomaly had the "wrong" sign in one, and did not exist in another (which happened to be a plate with non-uniform coloring).

2. Most of the effect was found to be produced by application of the magnetic field in one direction; the other direction of field had no effect, or even a small effect in the "wrong" direction.

3. Similar effects, but several times smaller, were sometimes observed with the crystal unilluminated.

A possibility remains, however, that this anomaly was an indication of a small Hall effect on the borderline of observational limit, superimposed upon a small, spurious, unidirectional effect of the magnet or magnetizing circuit. The effect was too small to be observed with the original "balanced-rate-of-charge" method of Tartakowsky; it was only observed with the steady deflection method, using high resistors to impress potential differences upon the differential electrometer (Fig. 2).

The differential electrometer could also be used to measure the difference in charge collected by the two parts of the divided electrode as a function of the applied magnetic field during a short flash of light. It was found that the charge collected by one electrode-part was changed by less than 1 part in 800 for KCl, 1 in 225 for KBr, and 1 in 600 for KI, by application of a magnetic field of 12,200 gauss, lending further confirmation to the previous null results.

Null results thus far described were obtained with additively colored specimens, having a stoichiometric excess of alkali atoms. Lukirskey's and Tartakowsky's reported positive results had been with photochemically colored rocksalt. It seemed possible that the discrepancy was due to the difference in the method of preparation of the specimens. Rocksalt colored by exposure to 50-kv tungsten x-rays was therefore tested in the Tartakowsky set up, using the balanced rate-of-change method.

An unsuspected difficulty was immediately encountered—namely, that the x-rayed crystals faded so fast under the fairly bright illumination needed to give "steady" currents of sufficient magnitude that it was hard to make the adjustment of the equalizing condenser before all the photo-sensitivity had disappeared; also it was impossible to obtain a steady state of photoelectric polarization. A fairly dense coloring would last only about five minutes. However by resensitizing the crystal several times, and by making small adjustments between consecutive pairs of readings (one reading for each direction of the magnetic field) so that little photoelectric sensitivity of a specimen was "wasted" and the adjustment constantly improved, sufficient data was finally accumulated. The conclusion was that no persistent effect

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specimen Size (mm)</th>
<th>$\Delta \gamma$</th>
<th>$\Delta \phi$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>6.7 x 4.6</td>
<td>1/880</td>
<td>±1/1000</td>
<td>1/22</td>
</tr>
<tr>
<td>NaBr</td>
<td>4.4 x 3.6</td>
<td>1/4000</td>
<td>±1/1300</td>
<td>1/20</td>
</tr>
<tr>
<td>KCl</td>
<td>5.5 x 4.5</td>
<td>1/1700</td>
<td>±1/600</td>
<td>1/50</td>
</tr>
<tr>
<td>KBr</td>
<td>7.5 x 4.5</td>
<td>1/2300</td>
<td>±1/1000</td>
<td>1/50</td>
</tr>
<tr>
<td>KI</td>
<td>3.7 x 3.5</td>
<td>±1/5000</td>
<td>±1/2000</td>
<td>±1/40</td>
</tr>
</tbody>
</table>
greater than 1/10 of the corresponding effect observed in zincblende under the same conditions existed in rocksalt colored by x-rays. The electrometer used had almost exactly the same sensitivity as that of Tartakowsky’s instrument. The working of the arrangement was tested with zincblende. The discrepancy is hard to explain. Tartakowsky, however, used a magnetic field of 30,000 gauss, compared to 12,200 gauss used here.

Besides being tested for possible photoelectric Hall effect, NaCl, KBr, and KCl, and also zincblende were examined for possible changes in photoelectric resistance caused by a magnetic field. Fluctuations in the longitudinal photoelectric current itself were found to limit the sensitivity to the extent that the null result uniformly found indicated only that large magneto-resistance anomalies do not exist in the photo-conductors studied. Upper limits to the magneto-resistance change caused by a field of 12,200 gauss were set as follows: NaCl, 0.15 percent; KCl, 0.3 percent; KBr, 0.25 percent; ZnS, 0.14 percent. The maximum expected effect in ZnS, according to calculations based upon the photoelectron mean free path as deduced from Lenz’ Hall effect measurements, was only 0.05 percent.

The fluctuations of photoelectric current were five to ten times greater than those which would be expected from shot and Johnson effects. The fluctuations apparently were due to some phenomenon in the crystals. They were observed, not only with the direct-current amplifier, but also with the differential electrometer, which, when electrically shielded, is less sensitive to random ionization of the air about it than the amplifier. The ratio of the fluctuations in current to the entire current increased with increasing applied voltage. In KBr, for example, the fluctuations were about 50 percent of the total current when 600 volts were applied to a crystal 7.2 mm long.

CONCLUSION AND DISCUSSION

It has been established, by means of two different experimental arrangements, both checked with a substance of known properties, that the photoelectric Hall field in additively colored rocksalt, if it exists at all, is less than 1/1000 of the applied electric field (for $H=12,200$). Similar upper limits have been obtained for four other colored alkali halides. If, to take the particularly important case of rocksalt, the null result is interpreted as meaning that the free paths of the photoelectrons in the crystal lattice are comparatively short, the equation of Gans,\textsuperscript{14}

$$\frac{Y}{X} = \frac{3}{4}\left(\frac{3\pi m}{kT}\right)^{1/4} \frac{e}{\lambda II},$$

for the isothermal Hall effect in an electronic conductor could be used to determine the order of magnitude of the maximum mean free path ($\lambda$) consistent with the experimentally determined upper limit of the ratio $Y/X$. Putting $Y/X = 1/1000$ and $H = 12,200$ gauss in the foregoing equation, it is found that

$$\lambda = 4.5 \times 10^{-4} \text{cm}.$$

Such a length is not much greater than the dimensions of a lattice cell. Von Hippel, from his experiments on electrical breakdown in rocksalt, concluded that the electronic mean free path was of the order $2 \times 10^{-4}$ cm. Such a mean free path, by Gans’ formula, would give a Hall field, for 12,000 gauss, of

$$Y/X = 1/2250.$$

Detection of a Hall effect of such a magnitude was slightly beyond the sensitivity of the measurements which have been described.

An alternative interpretation, that the contribution of the photoelectrons to the Hall field in colored alkali halides is nearly or entirely canceled by the contribution of the positively-charged carriers, might be made, but appears unnecessary in the view of the fact that no Hall effect was found even in the comparatively large initial surge of photoelectric current in KCl, KBr, and KI, this initial surge being, in all probability, almost entirely composed of electrons.

The writer wishes to acknowledge his indebtedness to Professor C. W. Heaps for suggestion of the problem, as well as for many helpful discussions concerning it; and to Professor H. A. Wilson for his continued interest in the investigation and valuable advice in the design of apparatus.

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\textsuperscript{13} L. R. Hafstad, Phys. Rev. 44, 201 (1933).
\textsuperscript{14} R. Gans, Ann. d. Physik 20, 293 (1906).