IV. CONCLUSION

As a result of the calculation, a closed expression is given for the line shape for all values of the magnetic field. This suggests the experiment of following the fluorine resonance structure in LiF and CsF down in field to nearly zero field to corroborate the existence of the assumed cosine interaction. As for spins greater than one-half, the omission of a quadrupole coupling makes the calculation less useful. There still exist spectra, however, which have not yet been interpreted, particularly Cl^{35} and Cl^{37} in the alkali chlorides; and the possibility exists that large cosine coupling might explain the shape of the resonance.

The author expresses his gratitude to Professor R. Serber for several useful discussions.

PHYSICAL REVIEW VOLUME 82, NUMBER 6 JUNE 15, 1951

The Mobility of Electrons in Silver Chloride

J. R. Haynes and W. Shockley
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received February 20, 1951)

Techniques are described which utilize the "print out effect" to obtain both the direction and velocity of photoelectrons in silver chloride crystals in an electric field. Hall mobility of the electrons is calculated from their change in direction produced by crossed electric and magnetic fields. Drift mobility of the electrons is obtained by measurement of their velocity in known electric fields. The value obtained for the Hall mobility ($R\sigma$) multiplied by $8/3\pi$ is 51 cm^2/volt sec at 25°C. The values obtained for the drift mobility are shown to be a function of temperature. A value of 49.5 cm^2/volt sec was obtained at 25°C, which is within experimental error of $(8/3\pi)R\sigma$, indicating that acoustical scattering is the principal mechanism and that temporary trapping is unimportant. A summary of the behavior of conduction electrons in silver chloride, calculated from the results of these experiments, is included.

I. INTRODUCTION

THE measurements of the mobility of electrons in silver chloride described in this paper are a continuation of earlier experiments which were originally undertaken to furnish definite evidence of the role of electrons in certain photographic processes in this material. Not only were these early experiments successful in their primary objective, but they have also led to the development of new techniques for the study of the motion and trapping of electrons in silver halides.

The results of the early experiments, dealing largely with the trapping of electrons in silver chloride, were published by the authors in the Report of a Conference on the Strength of Solids.[1] The present paper presents later studies of mobility.

II. THEORY OF THE "PRINT OUT EFFECT"[2]

The original object of this investigation was to establish the mechanism of the "print out effect," which is very closely related to latent image formation (see Mott and Gurney[3] for a general discussion on this topic). It is observed that if a photographic emulsion is exposed to strong light for a long time, it becomes dark. Microscopic examination of the small (10^{-4}–10^{-5} cm in diameter) single crystals of the salt in the emulsion shows that the darkening is localized in the form of a number of small specks within the grain. Further research has shown that these specks are colloidal metallic silver[4] and that the total amount of metallic silver produced in the grain is approximately that which would be expected if every photon absorbed added one atom of silver to the colloidal specks.[5] Since the photons are absorbed in all parts of the grain, there must, therefore, be a transport mechanism by which the absorbed energy is made effective at the silver speck.

The transport mechanism proposed by Mott and Gurney involves the fact that silver chloride is an ionic conductor at room temperature and that its conductivity is due to the motion of silver ions. An illustration of how this conductivity occurs is shown in Fig. 1. Thermal agitation causes some silver ions to move from normal sites to interstitial positions B, thus leaving a vacant lattice point C in the normal lattice. A series of exhaustive experiments by Koch and Wagner[6] and by Tubandt and Eggert[7] has shown that both the vacant lattice points and positive interstitial silver ions are mobile and both contribute significantly to the conductivity, the negative chlorine ions making a negligible contribution.[7a]

---

[1] Conference on Strength of Solids, University of Bristol, July, 1947 (The Physical Society, London, England, 1948), pp. 151, 157.

[2] The following description of the "print out effect" is largely reproduced from the original article.

[3] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 122. For a recent review article see J. H. Webb, Phys. Today 3, No. 5, 8 (1950).

[4] R. Hilsch and R. W. Pohl, Z. Physik **77**, 421 (1932).

[5] J. Eggert and W. Noddack, Z. Physik **20**, 299 (1923); Handb. Wissenschaftlichen Angewandten Photographie **5**, 132 (1932).

[6] E. Koch and C. Wagner, Z. physik. Chem. **B38**, 295 (1937).

[7] C. Tubandt and S. Eggert, Z. anorg. Chem. **110**, 196 (1920).

[7a] It has been proposed by J. W. Mitchell that conduction by chlorine vacancies plays an important role in the photographic

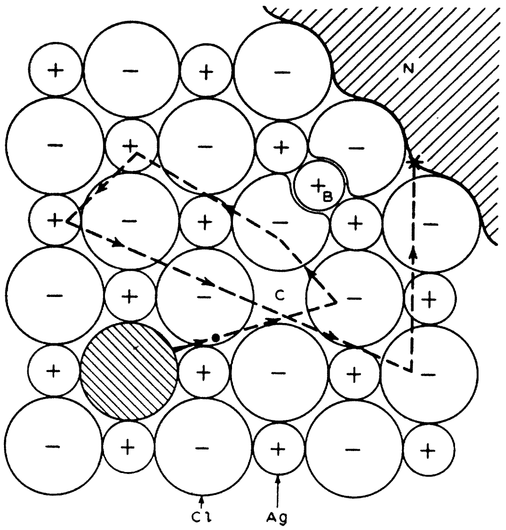

FIG. 1. Schematic representation of the Gurney and Mott theory of the print out effect.

The "print out effect" is supposed to occur as follows: A photon of light ejects an electron from a chlorine ion; this electron moves about in the crystal under the influence of thermal agitation, leaving the neutral chlorine behind. In the course of its wanderings it becomes trapped on a particle of metallic silver *N*. This produces a net negative charge on the metallic silver which is neutralized by silver ion conductivity. When the silver ion reaches the speck of silver, it can combine with it, neutralizing the negative charge and adding one atom of metal to the speck. Thus, the theory of Mott and Gurney supposes that thermally diffusing photoelectrons constitute the connecting link between the absorption of a photon at one point and the addition of a silver atom to a silver at another point.

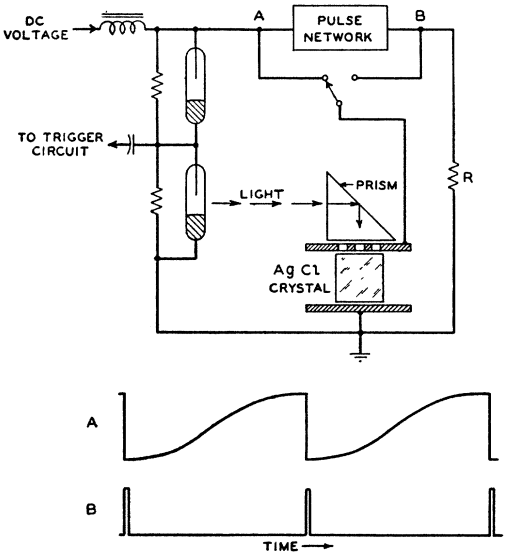

FIG. 2. Schematic diagram of equipment used to generate repetitive pulses of light and synchronized voltage waves.

A definite experimental prediction, which is a consequence of the above theory, is that it should be possible to displace the darkening in the "print out effect" by deflecting the photoelectrons with electric fields. The practical realization of this prediction, however, requires careful control of the experimental conditions.

III. EXPERIMENTAL CONDITIONS AND APPARATUS

It is impracticable to maintain a constant electric field of suitable magnitude in a silver halide crystal because the resulting steady ionic current would lead to decomposition. For this reason, the average current through the crystal must be zero, a result which can be ensured by applying all voltages through condensers which will not pass direct current.

The ionic conductivity imposes further conditions on the voltage wave form to be applied to the condenser plates. For the geometrical arrangement used it is found that the relaxation time for the field in silver chloride is 5×10^{-4} second. In other words, if a voltage were suddenly applied to the condenser, thus producing a field in the silver chloride, this field would drop to $1/e$ of its value in this time. Thus, it is necessary to set up conditions in which it suffices to have the field available for the order of only a few hundred microseconds.

Techniques suitable for operation in this time range have become generally available as a result of the development of radar. The apparatus used for these experiments was designed for testing fixed spark gap modulator tubes.[8] A schematic circuit diagram of this equipment is shown in Fig. 2. When the triggering voltage is applied, the pulse shaping network is discharged through the spark tubes and resistance load *R*. Networks designed to produce voltage pulses of 1 and 5 microseconds were used. The spark tubes consist simply of a mercury pool above which is suspended at a distance of 6 mm a perpendicular rod of molybdenum in an atmosphere of hydrogen at a pressure of 90 cm of mercury. During the time of discharge (network time) these tubes are an intense source of light ($>10^3$ candle power), which is largely that of excited mercury vapor.[9] This light is used to produce photoelectrons in a sample of silver chloride placed between condenser plates. The voltage wave forms at points *A* and *B* in the circuit are for convenience also shown below. Both of these waves have been applied to the condenser plates to create an electric field in the sample at the time of the light pulse and so move the photoelectrons.

---

process (Phil. Mag. **40**, 249 (1949)). Recent experiments by C. H. Berry (Phys. Rev. **82**, 422 (1951)) indicate that interstitial silver ions predominate over bromide vacancies in AgBr by a factor of at least 10.

[8] Goucher, Haynes, Depp, and Ryder, Bell System Tech. J. **25**, 563 (1946).

[9] J. R. Haynes, Phys. Rev. **73**, 891 (1948).

The experimental condenser arrangement used for simultaneously applying the light pulse and electric field to the silver chloride crystal is shown in Fig. 3. A large single crystal block[10] 5 mm×12 mm×15 mm was placed between the condenser plates with the field in the long direction. Between the condenser plates and the crystal were placed thin glass plates coated on the side in contact with the condenser electrodes with 25 percent transmission platinized film having a high conductance. The light entered through the upper film along an axis parallel to the field and illuminated three rectangles on the end of the crystal. In this way an equipotential surface was maintained across the crystal faces, and at the same time the relaxation time of the field was increased to several hundred microseconds through the introduction of the high capacitance produced across the glass plates.

When the voltage wave applied across the plates of the condenser arrangement was taken from the point A in the circuit, the electric field applied to the crystal was nearly constant during the time that the photoelectrons are free to move. When the voltage wave was taken from the point B, the field was on for a period less than this time.

Light pulses of one and five microseconds duration were used at repetition rates of 1000 and 500 per second. Under these conditions the charge of the trapped electron in a given pulse was neutralized by ionic conductivity before the next pulse of light was applied.[11] In order to avoid space charge effects in the individual pulse, the illumination intensity was reduced until 10^9 electrons/cm^2 per pulse were produced in the illuminated area of the crystal (as measured at liquid air temperature by the charge through a ballistic galvanometer). Under these conditions exposures of 16 hours or more were required to obtain satisfactory amounts of colloidal silver.

IV. SOME RESULTS OF EARLY EXPERIMENTS[12]

The early experiments showed at once that the darkening could be displaced from the illuminated region as if the connecting link were a negatively charged particle with a mobility of about 50 cm^2 per volt sec. This result may be regarded as an unambiguous confirmation of the basic assumption of the Gurney and Mott theory.

It was also found that the darkening could be reduced to negligible amounts by filtering the light through 10^{-3} cm of silver chloride, which shows that for practical purposes all of the photoelectrons in the experiments were produced within this distance of the surface.

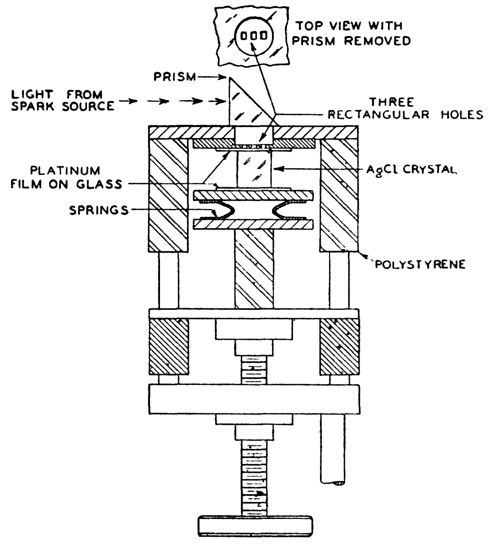

FIG. 3. Experimental condenser arrangement used for the simultaneous application of pulses of light and electric field to single crystals of silver chloride. [Pt. film on opposite side of glass from that in contact with AgCl.]

Since the colloidal silver is formed at points where electrons are trapped, a study of the distribution of darkening produced in an electric field reveals the location of these traps. This study shows that colloidal silver, crystal grain boundaries, and slip bands are all efficient electron traps. It was found, however, that the density of these traps could be greatly reduced by carefully annealing the crystals[13] so that the mean life of the photoelectrons could be increased in this way from 2 to 10 microseconds.

With this increased lifetime, the displacement of the electrons was sufficient to permit large numbers of them to pass completely through a crystal of silver chloride 15 mm long, using electric fields easily attained.

The experimental procedure was to connect the upper plate of the condenser arrangement, shown in Fig. 2, to the point A and to ground the lower plate. This resulted in the application of an electric field to the crystal which reversed at the time of the light pulse

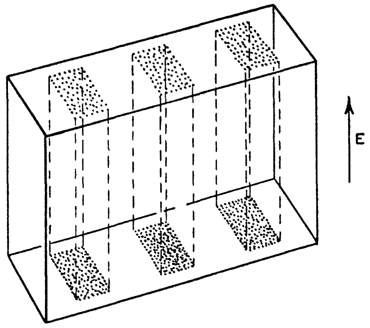

FIG. 4. Schematic diagram of displacement of photoelectrons by the electric field.

---

[10] The block was cut on a circular milling saw from cylinders of silver chloride about 3 in. in diameter and 2 in. long obtained from the Harshaw Chemical Company of Cleveland, Ohio.

[11] The time of neutralization of the charge of a trapped electron is $K/4\pi\sigma$ (esu), where σ is the conductivity of silver chloride and K is its dielectric constant (see reference 3, page 232).

[12] For a more complete description see reference 1.

[13] J. R. Haynes, Rev. Sci. Instr. **19**, 51 (1948).

and persisted in an upward direction in the figure for several hundred microseconds, which is long compared with the time that the electrons were free to move.

The displacement of the photoelectrons in the silver chloride crystal is shown schematically in Fig. 4. The light from the spark fell on the dotted area at the top and produced photoelectrons at, and very near, the top surface of the crystal. Since at this time the electric field in the crystal was directed upward, the electrons moved downward with a velocity equal to their mobility multiplied by the electric field intensity. With our experimental conditions, a large fraction of these electrons succeeded in completely crossing the crystal and were trapped at the lower surface. Since each trapped electron produced a silver atom, colloidal silver is formed in three rectangles on the lower surface as indicated in the figure by the densely dotted areas. With prolonged exposure visible amounts of colloidal silver were produced in these areas which, in a sense, are the electron images of the illuminated areas at the top surface of the crystal.

We will show how these techniques and experimental results may be utilized to provide new ways of measuring the mobility of conduction electrons in silver chloride.

V. DEFINITIONS OF MOBILITY

It has been pointed out[14] that the values of mobility determined in various ways will not necessarily agree. For the purposes of this paper, therefore, we need to clearly distinguish between three kinds of mobility as follows:

Microscopic mobility, μ_m; this is the mobility of a charge carrier in the conduction band of energies and is the conventional concept.

Drift mobility, μ_D; this is the velocity of drift of a charge carrier in unit electric field. The value of drift mobility will not agree with that of microscopic mobility if the carriers spend appreciable time in temporary traps. Thus, if the carriers spend half their time in traps and half in the conduction band, the result is that $\mu_D=\frac{1}{2}\mu_m$.

Hall mobility, μ_H; this is the experimentally determined value of the Hall coefficient multiplied by the conductivity of a sample. The relation between μ_H and either μ_m or μ_D is known only for certain simplifying assumptions which are considered in the next section.

VI. HALL MOBILITY

Most of our present day knowledge concerning the mobility of electrons in solids has been derived through the use of the Hall effect. The usual way of obtaining the Hall mobility is to measure the Hall constant and multiply by the conductivity of the sample. Alternately, the Hall mobility may be calculated from the Hall angle (angle between current and electric field) of a sample in a known magnetic field. In order for the significance of our results to be appreciated, the philosophy of the derivation of the Hall angle should be clearly in mind.[15] To that end we indicate the reasoning, neglecting the random motion of the electrons and considering that each electron after a collision starts its new path in the opposite direction to that of the applied electric field and suffers a collision after moving on the average for the relaxation time t'.

According to statistical theory, an electron has on the average been subject to the field for a time t' since its last collision and has therefore acquired a drift velocity equal to its acceleration Ee/m times t', or

$$\bar{v}=Eet'/m=\mu_m E.$$

Owing to the drift motion in the magnetic field, the electron has been subjected to a side thrust and has acquired a transverse velocity:

$$\theta\bar{v}=\omega t'\bar{v}=(eHt'/mc)\bar{v}=\mu_m H\bar{v}/c.$$

In this formula θ is the Hall angle and is equal to the circular frequency ω of an electron in a magnetic field times the mean free time t'. The Hall mobility $R\sigma$ defined above can also be expressed in terms of the Hall angle and reduces to

$$R\sigma\equiv\mu_H=\theta c/H=\mu_m.$$

For the idealized assumptions represented by the above equations, the relationship $\mu_H=\mu_m$ results.

It will be observed that the value assigned to the Hall mobility depends on the effects produced by crossed electric and magnetic fields on a *moving* charge carrier and will therefore be entirely unaffected by the time which the carrier may spend in shallow traps. In this sense, the Hall mobility should give a value in accord with the microscopic mobility μ_m but not necessarily with that of the drift mobility μ_D.

A rigorous derivation shows that for spherical energy surfaces in the Brillouin zone and for degenerate statistics as in a metal, $\mu_m=\mu_H$. For the nondegenerate case, such as conduction electrons in silver chloride, it seems fair to assume a maxwellian distribution of velocities and a mean free path which is independent of direction and energy.[15a] The value of the constant relating the Hall mobility to the microscopic mobility then depends only on the shape assumed for the energy surfaces. If the customary assumption of spherical energy surfaces[16] is made, the velocities average to obtain the result,

$$\mu_m=(8/3\pi)\mu_H=(8/3\pi)(\theta c/H)\ \text{cm}^2/\text{esu volt sec},$$

---

[14] Pearson, Haynes, and Shockley, Phys. Rev. **78**, 295 (1950).

[15] A rigorous derivation along the lines discussed below is given in W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

[15a] If the mean free path is proportional to velocity, as indicated in reference 22 the factor $8/3\pi\doteq 0.85$ becomes unity. We shall return to this point in Sec. VIII, retaining the factor $8/3\pi$ in the meantime in order to stress the distinction between μ_m and μ_H.

[16] For a case where the energy surfaces are apparently not spherical, see reference 14.

or

$$\mu_m = (10^8)(8/3\pi)(\theta/H) \text{ cm}^2/\text{volt sec.}$$

for H measured in oersteds.

Since silver chloride is an ionic conductor, it would certainly be very difficult to measure the Hall mobility of electrons in this material using the usual procedure. However, by employment of new techniques a direct measure of the Hall angle of these carriers was obtained as follows:

A single crystal of silver chloride was inserted in the condenser arrangement which was then connected to apply an electric field of long duration, thereby moving a large fraction of the photoelectrons generated at the top surface all the way through the crystal as described in Sec. IV. In this experiment, however, two changes were made. The top surface was masked so that light was allowed to fall on only half of each of the rectangles at the top surface, and a magnetic field was applied in a direction perpendicular to the large surfaces of the crystal, as shown in Fig. 5a. The crystal was then exposed to one-microsecond light pulses and synchronized electric fields for 24 hours. During this time a large fraction of the photoelectrons produced by each light pulse in the illuminated areas at the top (dotted in the figure) was drawn through the crystal by the electric field before being trapped. In the absence of the magnetic field these electrons would have produced colloidal silver in the dotted areas at the lower surface. In the presence of the magnetic field, however, the paths of the electrons were turned through the Hall angle; and, in consequence of this, the rectangles of colloidal silver produced at the bottom surface were displaced to the left as indicated in Fig. 5a. The mask at the top was then moved so that the opposite half of the top of the crystal was illuminated, and the direction of the magnetic field was also reversed as shown in Fig. 5b. The crystal was then exposed for an additional 24 hours. During this second exposure the photoelectrons produced at the top surface were again deflected through the Hall angle but in the opposite direction. As a result the rectangles of colloidal silver formed at the lower surface were displaced toward the right and offset from the rectangles produced in the first exposure as indicated.

A photograph of a crystal exposed in this way is shown in Fig. 6. The offset in the rectangles of colloidal silver produced at the bottom surface is clearly visible. The distance of this offset divided by the length of the crystal gives a number which is very close to twice the Hall angle in radians.[17]

Six measurements of the distance of the offset were obtained with this single sample, the average value obtained being $(22\pm1)\times10^{-3}$ cm. Since the crystal was 1.48 cm long, the measured Hall angle $\theta = 7.5\times10^{-3}$ radian. The magnetic field used during the exposure had an intensity of 12.5×10^3 oersteds, so that the microscopic mobility of the photoelectrons as measured by the Hall angle on the above assumptions of spherical

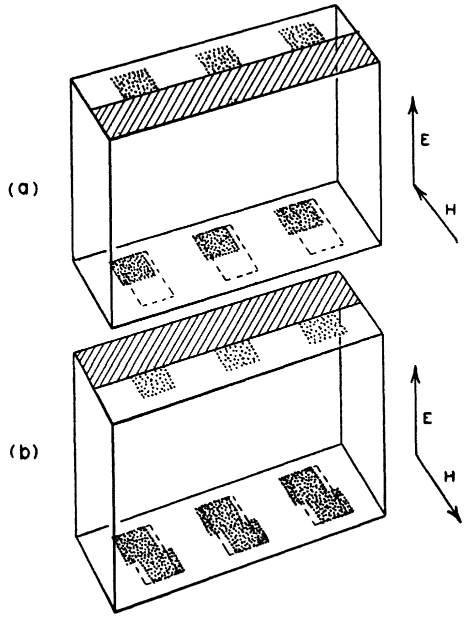

FIG. 5. Schematic diagram of procedure used for measuring the Hall angle of photoelectrons in silver chloride. (a) First exposure. (b) Second exposure.

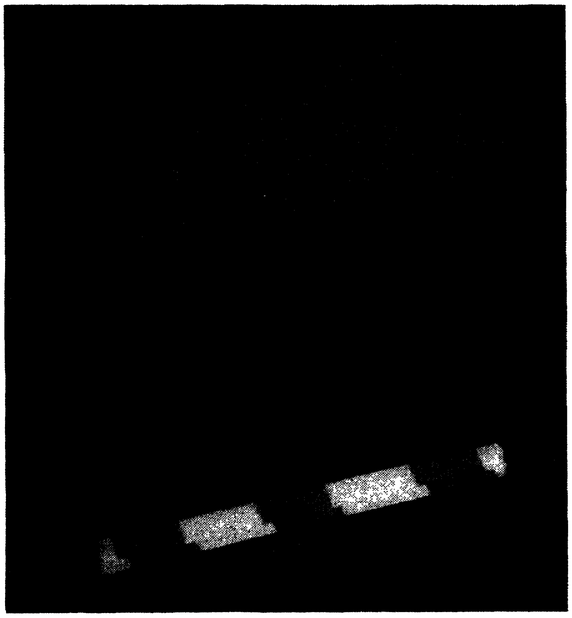

FIG. 6. Photograph of silver chloride crystal used to measure the Hall angle, showing displacement of colloidal silver (dark areas) by magnetic field. Bottom surface of crystal appears greatly compressed due to high index of refraction of crystal.

---

[17] It is worthwhile pointing out that in previous Hall angle determinations the change in direction of the electric field is measured, while the direction of the current remains fixed. Here the reverse is true because of the absence of space charge effects.

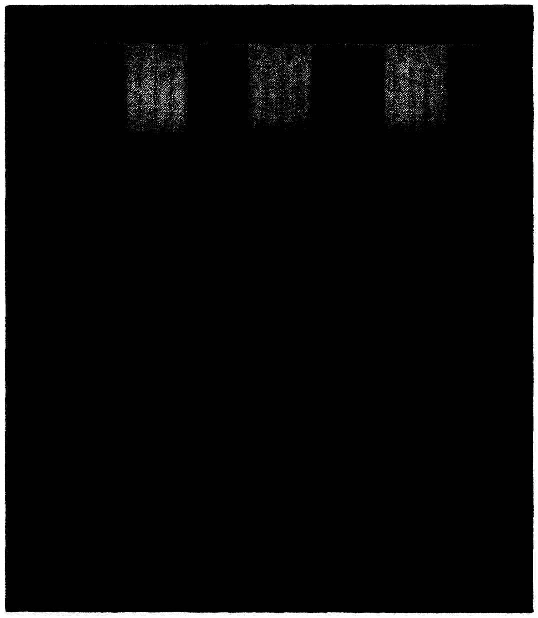

FIG. 7. Photograph of a crystal of silver chloride used to measure drift mobility of photoelectrons, showing columns of colloidal silver (light areas) produced by the electric field.

energy surfaces is

$$\mu_m = (8/3\pi)(7.5\times 10^{-3}/12.5\times 10^{3})(10^{8}) = 51\ \mathrm{cm}^2/\mathrm{volt\ sec.}$$

It will be shown that the electron mobility in silver chloride is a function of temperature. The temperature of the sample during this experiment was 25±3°C. Taking this uncertainty in sample temperature into account, as well as the uncertainty in the distance of offset, we have, finally, that the microscopic mobility of electrons in silver chloride at 25°C as determined by direct measurement of the Hall angle, is

$$\mu_m = (8/3\pi)\mu_H = 51\pm 3\ \mathrm{cm}^2/\mathrm{volt\ second.}$$

VII. DRIFT MOBILITY

The drift mobility of electrons in silver chloride has also been determined by means of the new techniques and the following experimental procedure: A well-annealed single crystal of silver chloride was placed in the condenser arrangement (Fig. 3) and the bottom plate was connected to ground as before. The top plate of the condenser was now connected to the point B in the circuit shown in Fig. 2. Under these conditions simultaneous pulses of light and an electric field were applied to the crystal. At the start of each light pulse an electric field was suddenly applied to the crystal and maintained nearly constant for a time approximately equal to the nominal pulse network time. The photoelectrons produced by the light at the top surface of the crystal in the three rectangles drift downward in the crystal with a velocity $\mu_D E$, where E is the electric field intensity in the crystal. At the end of the light and electric field pulse the electrons stop their systematic drift and are trapped locally, producing colloidal silver. Repeated pulses of light electric field results in the production of visible amounts of colloidal silver.

A photograph of a crystal exposed in this way for 16 hours is shown in Fig. 7. This photograph was taken in a direction perpendicular to the large surface of the crystal, with the illuminated areas in which the photoelectrons originated at the top of the photograph. In order to increase the contrast, the crystal was photographed against a dark background with a transverse beam of light so that regions containing colloidal silver are made visible by scattered light. In the photograph, therefore, the light regions are those containing colloidal silver. The colloidal silver is seen to extend in three columns from the top surface, corresponding to the illuminated areas, to a depth which is an appreciable fraction of the length of the crystal (1.4 mm). The colloidal silver produced at the maximum depth below the illuminated surface is due to electrons produced at the start of the light pulse, and therefore those that were able to move for the entire time that the electric field was applied. The colloidal silver lying nearer the surface is due in part to photoelectrons which had a range much less than the average, but it is chiefly due to photoelectrons produced at later times.

It will be observed that the density of the colloidal silver in each column decreases sharply at its lower boundary,[18] permitting the maximum displacement of the electrons from the surface to be measured with considerable accuracy. This is the expected result, since the diffusion distance of electrons is small compared with the distance which they are moved by the electric field.[19]

The distance of electron displacement is given by $l=\mu_D Et$, or $\mu_D = l/Et$. One can, therefore, make a good estimate of the drift mobility of the electrons by simply measuring the electric field and substituting for t the nominal pulse network time. Since, however, the voltage pulse applied to the crystal is a square wave pulse only

---

[18] When viewed with a microscope from a direction exactly perpendicular to the crystal surface, these boundaries appear even sharper.

[19] The relative effects of diffusion and electric field displacement may be deduced from the following considerations: The distance which an electron diffuses in the time which it is free to move, τ, is given by the usual diffusion formula,

$$d^2 = D\tau = kT\mu_D\tau/e,$$

where D is the diffusion constant of conduction electrons, k is Boltzmann's constant, T is the absolute temperature, and e is the electron charge. On the other hand, the electric field acting for a time t displaces the electron a distance $l=\mu_D Et$, so that $l^2=\mu Elt$. Therefore, the ratio of the distance which the electron diffuses to the distace which is translated to the electric field is $d/l=(kT\tau/eElt)^{\frac{1}{2}}$. At room temperature $kT/e=1/40$ ev. The mean life, τ, of a conduction electron in these crystals has been shown to be $\sim$10 microseconds (see reference 1). The electric field intensity used was $\doteq 8$ kv/cm. Thus, for an electric field applied for 1 microsecond $\doteq$ network time $\doteq t$, $l \doteq 0.2$ cm and the ratio of the diffusion distance to the electric field displacement is given by

$$d/l = 1\times 10^{-2}.$$

to a first approximation, appreciable errors are introduced. While these errors can be reduced by analysis of oscillograms of the voltage pulse as a function of time, a more accurate calculation of drift mobility can be made from other considerations in which this function enters only as a small correction factor.

The considerations which make it possible to neglect the voltage pulse time are easily understood with the aid of the equivalent circuit shown in Fig. 8. In this circuit the spark tubes are represented by a switch, the pulse network by its capacitance C, and the silver chloride crystal, mounted in the condenser arrangement, by three condensers and a resistance. The condensers C_1 have a value equal to the capacitance formed across the evaporated platinum films on the thin glass plates at either end of the crystal. The condenser C_2 has a value equal to that of a parallel plate condenser having an area equal to a cross section of the silver chloride crystal, a separation equal to its length, and a dielectric constant equal to the dielectric constant of silver chloride. The resistance R_1 is included to take account of the ionic conductivity of the silver chloride crystal.[20] The action of the spark tubes may be likened to the closing of the switch for a short period of time, long enough to permit discharge of the network capacitance C but not long enough to permit appreciable current to flow through the choke coil.

With these considerations we now proceed to derive the required equation for μ_D using the notation:

Q = quantity of electricity (coulombs) stored in the pulse network,
V = voltage to which the network is charged at the time of closing the switch,
C = capacitance of the network,
R = load resistance in ohms,
i = current flowing through R when switch is closed,
V_1 = voltage across R,
t_1 = time of current flow (of the order of the network time),
E = electric field intensity in the AgCl crystal,
V_2 = voltage across the crystal,
L = length of the crystal,
l = distance that the photoelectrons are displaced by the electric field,
G = thickness of glass plates at either end of the crystal,
K_G = dielectric constant of glass plates,
K_C = dielectric constant of AgCl,
σ = conductivity of AgCl.

When the switch is closed, the electricity stored in the condenser flows around the circuit and through the load resistance, a negligible fraction flowing through the equivalent crystal network. Under these conditions,

$$Q=CV=\int_0^{t_1} idt.$$

Multiplying by R gives

$$RCV=\int_0^{t_1} Ridt=\int_0^{t_1} V_1dt.$$

During time T_1 the photoelectrons travel a distance l with a velocity $E=f(t)$, or

$$l=\mu_D\int_0^{t_1} Edt.$$

The electric field E is V_2/L; however, the voltage V_2 across the crystal will be less than V_1 because then condensers $C_1C_2C_1$ form a voltage divider of ratio

$$\alpha=C_1/(2C_2+C_1)=1/[1+(2GK_C/LK_G)]$$

and because of decay of the voltage across C_2 due to R_2; the reduction due to this factor, called β, is evaluated below. In terms of these correction factors we may write $E=\alpha\beta V_1/L$, so that,

$$l=(\alpha\beta\mu_D/L)\int_0^{t_1} V_1dt=\alpha\beta\mu_D RCV/L,$$

and

$$\mu_D=Ll/\alpha\beta RCV,$$

which is the required equation for drift mobility in which the pulse time does not appear. In order to use this equation, however, the small correction factors α and β must be evaluated.

The corection factor β is a constant only for a particular voltage pulse shape and time. Since, however, β introduces only a small correction to μ_D ($\sim$1 percent), very little error is introduced if the voltage pulses used of 1 and 5 microseconds are considered to be ideal square top voltage pulses persisting for exactly the nominal network time. With this assumption, $\beta=\bar{V}_e/\alpha V_1$, where $\bar{V}_2$ is the average value of V_2 over time t_1 and we can proceed to calculate β as follows:

Owing to the ionic conduction in the crystal the voltage V_2 decays exponentially with a time constant λ, so that

$$V_2=\alpha V_1 e^{-t/\lambda}.$$

The average value of V_2 during pulse time t_1 is,

$$\bar{V}_2=(\alpha/t_1)\int_0^{t_1} V_1 e^{-t/\lambda}dt,$$

or

$$\bar{V}_2=(\alpha V_1\lambda/t_1)(1-e^{-t/\lambda})=\alpha V_1\beta.$$

Therefore, we have

$$\beta=(\lambda/t_1)[1-\exp(-t_1/\lambda)],$$

or, since β is very close to unity, $\beta=1-(t_1/2\lambda)$.

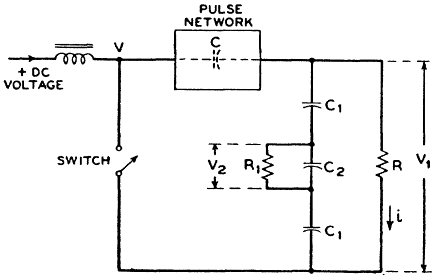

FIG. 8. Equivalent circuit used to derive equation for drift mobility.

---

[20] The conductivity produced by the photoelectrons is negligible compared with the ionic conductivity over the temperature range and light intensity used.

TABLE I. Drift mobility of electrons in silver chloride.[a]

Crystal length L (cm)	Electron displacement l (cm)	Pulse time t_1 (μs)	Network capacitance C (μf)	Correction factor $\alpha\beta$	Temperature in degrees centigrade	Drift mobility (cm²/volt sec)
1.45	0.874	5	0.0508	0.962	40	45.5
1.45	0.172	1	0.00980	0.971	38	45.6
1.42	0.195	1	0.00980	0.972	20	50.6
1.45	0.131	1	0.00980	0.960	100	35.1
1.45	0.128	1	0.00980	0.960	100	34.3
1.48	0.121	1	0.00980	0.960	113	33.1
1.44	0.252	1	0.00980	0.972	−25.5	66.4
1.45	0.253	1	0.00980	0.972	−26.5	66.9

[a] For all data: the network voltage $V=11.1$ kv, the load resistance $R=51.5$ ohms, the thickness of the glass plates $G=0.012$ cm, the dielectric constant of the glass plates $K_G=7.0$, and the dielectric constant of silver chloride $=12$.

The decay constant λ is equal to[21]

$$R_1(\tfrac{1}{2}C_1+C_2)$$
$$=[1/4\pi(9)(10^{11})](K_G/\sigma)[(K_C/K_G)+L/2G],$$

where σ is the conductivity of silver chloride in ohm^{-1} cm^{-1}.

The conductivity of these silver chloride crystals has been measured as a function of temperature. The results can be expressed to a high order of accuracy as

$$\sigma=0.038e^{-3960/T}\ \text{ohm}^{-1}\ \text{cm}^{-1}.$$

By means of this analysis the electron drift mobility can be accurately determined, since its value depends to a first order only on quantities which can easily be measured (l, L, R, C, and V), while G, K_C, K_G, σ, and t_1 enter only to provide a small correction term.

The drift mobility of electrons in silver chloride has been measured in this way over a temperature range of from −26 to 113°C. Temperatures above room temperature were achieved by placing the sample in a thermostatically controlled electric oven provided with a glass window. Temperatures below room temperature were obtained by placing the sample in a transparent Dewar flask cooled by thermostatically controlled air flow through a copper coil immersed in a toluene and dry ice mixture.

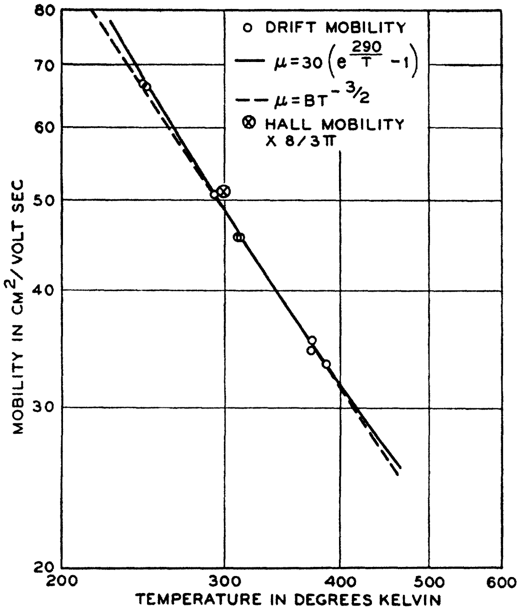

FIG. 9. Mobility of conduction electrons in silver chloride as a function of temperature.

The results are shown in Table I. It may be observed that the electron displacement due to the applied electric field, l, varies from a little over a millimeter (1 microsecond pulse network at 113°C) to nearly a centimeter (5 microsecond pulse network at 40°C) and that the correction factor $\alpha\beta$ is near unity in all cases.

The sample used to obtain the data tabulated in the last line of Table I was cut from an ingot of silver chloride produced by the Harshaw Chemical Company more than six months after the ingots from which the rest of the samples were produced, and it was visibly clearer. No significant difference, however, is observed in the measured mobility. This result is interpreted as evidence that impurity scattering and trapping play a negligible roll in these crystals at temperatures at least as low as −26°C.

The values of mobility of Table I plotted as a function of temperature are shown in Fig. 9. The data can be fitted within experimental error by the theory of Fröhlich and Mott[22] in which it is assumed that the conduction electrons are scattered by optical vibrations of the ions. The mobility expressed in practical units, based on the mean free time (Eq. (6.10) of the second paper) is[23]

$$\mu_m=(1/300)3(2k\theta m^*)^{-\frac{1}{2}}ea_0(e^{\theta/T}-1)KK_0/(K-K_0)$$

where $\theta=(hc/\lambda k)(K/K_0)^{\frac{1}{2}}=290°$K is the characteristic temperature for longitudinal polarization waves, λ being the wavelength for infrared absorption $=87$ microns for AgCl[24], c the speed of light, k Boltzmann's constant, $K=12.3$ and $K_0=4.01$ the low and high frequency dielectric constants,[25] m^* the effective mass, and $a_0=\hbar^2/m^*e^2$. Substituting these values and assuming $m^*=0.70$ m, where m is the mass of the free electrons, gives

$$\mu_m=30(e^{290/T}-1).$$

This function is plotted in Fig. 9 (solid line).

An equally good fit of the data, however, may be obtained using a theoretical equation first derived by

---

[21] See E. Frank, *Pulsed Linear Networks* (McGraw-Hill Book Company, Inc., New York, 1940), p. 141.

[22] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **171A**, 496 (1939). Some corrections to the original theory have been presented by Fröhlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950).

[23] This formula may be too large by a factor of 2, see footnote at the end of the second paper of reference 22. According to C. Herring, on the other hand, this factor should be 3 but is partially counterbalanced by a factor of 2 in the other direction due to numerical error.

[24] H. Rubens, Preuss. Akad., Wiss. Physik. Math. Klass., p. 513 (1913), as quoted by R. Hofstadter, Nucleonics 4, No. 5, 29 (1949).

[25] The values of dielectric constant of silver chloride are taken from Mott and Gurney's book (see reference 3).

Wilson[26] on the assumption that the conduction electrons are scattered by acoustic vibrations,

$$\mu_m = BT^{-\frac{3}{2}}.$$

This equation, with $B = 2.54\times 10^5$, is also plotted in Fig. 9 (dotted line).

It is therefore impossible to determine from the data alone whether the scattering is due principally to the acoustic or to the optical vibration of the crystal. From theoretical considerations, however, it appears likely that the optical vibrations should be largely responsible for the electron scattering, and that the close fit of the data to $T^{-\frac{3}{2}}$ is pure coincidence. It should be noted, however, that the mobility values obtained by Hofstadter[27] fit the acoustic scattering equation at low temperatures much better than the optical scattering equation. Hofstadter's values for the mobility of electrons in silver chloride at 77°K range from 114 to 400 cm²/volt second. The acoustic scattering equation gives a value of mobility of 376 cm²/volt second at this temperature, while the optical scattering equation yields a value of 1230 cm²/volt second.

VIII. COMPARISON OF HALL MOBILITY AND DRIFT MOBILITY

If we assume that the conduction electrons are scattered principally by acoustical modes, the mean free path is independent of velocity and $\mu_m = (8/3\pi)\mu_H$, as indicated in Sec. IV. The value of the microscopic mobility calculated on this assumption from the experimentally measured value of the Hall angle is plotted in Fig. 9. It is seen to lie within experimental error of the drift mobility values. This result may be interpreted in two ways:

(1) $\mu_D = (8/3\pi)\mu_H < \mu_m$. If the conduction electrons spend part of their time in temporary traps, $\mu_D < (8/3\pi)\mu_H$. On the other hand,[14] if the energy surfaces in the Brillouin zone are re-entrant, $\mu_m > \mu_H$. The possibility therefore exists that although the energy surfaces are re-entrant, the amount of temporary trapping was, in this case, just sufficient to compensate, so that although $\mu_D = (8/3\pi)\mu_H$, both are less than μ_m.

(2) $\mu_D = (8/3\pi)\mu_H = \mu_m$. This is the expected result if the energy surfaces are spherical and if the electrons spend a small fraction of their mean free time in temporary traps.

Temporary traps could be produced either by lattice imperfections or by impurities. In either case the density of these traps should have varied widely in the samples used in the drift mobility experiments.[28] It is observed, however, that all of the drift mobility values obtained fall on a smooth curve so that temperature appears to be the only variable. We therefore conclude that temporary trapping is an unimportant process and that $\mu_D = (8/3\pi)\mu_H = \mu_m$ if the electrons are scattered largely by acoustical vibrations of the ions.

If, on the other hand, we assume that the electrons are scattered principally by optical modes we are led to a mean free time independent of velocity resulting in $\mu_m/\mu_H = 1$ instead of $8/3\pi$. The microscopic mobility calculated from our experimentally determined Hall angle would then have the value of 60±3 cm²/volt second and consequently be definitely outside of the experimental error of the drift mobility.[29]

This discrepancy cannot easily be explained since we have shown experimentally that temporary trapping is unimportant. Complex energy bands can, of course, change the value of μ_m/μ_H; in general, however, deviations from a spherical form appear to produce ratios greater than unity and thus increase the disagreement. On the theoretical grounds also one would expect the conduction band to arise from 5*s* wave functions on silver and hence to be a simple nondegenerate band with a single effective mass.

It appears probable that, over the temperature range considered, both the acoustical and optical modes play some role in scattering the conduction electrons so that $1 > \mu_m/\mu_H > 8/3\pi$ and $m^*/m < 0.7$. However, in order to make the drift mobility values agree with either the Hall mobility results or Hofstadter's low temperature mobility values it appears necessary to assume that acoustical scattering predominates.

IX. SUMMARY OF BEHAVIOR OF ELECTRONS IN SILVER CHLORIDE

In the early experiments reported at the Conference on Strength of Solids[1] the mean range ($\mu_D E\tau$) of photoelectrons in these annealed crystals was found to be approximately 1.5 cm with a field of 3.2×10^3 volts/cm at room temperature. Combining this information with the measured mobility values, one can calculate the following concerning the behavior of conduction electrons in silver chloride at room temperature (298°K):

drift mobility, $\mu_D = 49.5$ cm²/volt sec,
mobility from Hall effect, $(8/3\pi)\mu_H = 51\pm 3$ cm²/volt sec,
relaxation time, $\mu_m m/e = 2.8\times 10^{-14}$ sec,
mean free path, $\mu_m mv/e = 33$A,
mean free lifetime, $\tau = W/\mu_D E \approx 10$ microseconds,
total uncoiled length of path $= \tau v = 110$ cm,
number of lattice constants traversed before final trapping $= \tau v/a = 2\times 10^9$,

where *e* is the charge of the electron, *m* is its mass, *W* is its mean range, *v* is its average thermal velocity, and *a* is the lattice constant of silver chloride.

It is a pleasure to acknowledge the advice and assistance of many persons in this organization, particularly J. Bardeen, F. S. Goucher, W. L. Bond, and R. A. Chegwidden.

---

[26] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1934), p. 211.

[27] R. Hofstadter, Nucleonics 4, No. 5, 29 (1949).

[28] The samples used were cut from a variety of crystals obtained from two different melts. These melts certainly contained different amounts of impurities (see Sec. VII). Also, some of the samples used had acquired considerable strain subsequent to annealing, so that the permanent trap density was greatly increased locally as judged by the change in density of colloidal silver.

[29] It is very difficult to see how the drift mobility measurements can be in error by more than a few percent.

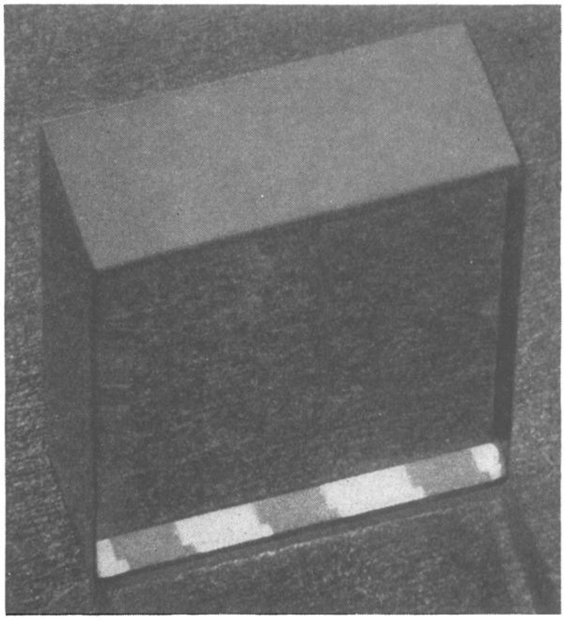

FIG. 6. Photograph of silver chloride crystal used to measure the Hall angle, showing displacement of colloidal silver (dark areas) by magnetic field. Bottom surface of crystal appears greatly compressed due to high index of refraction of crystal.

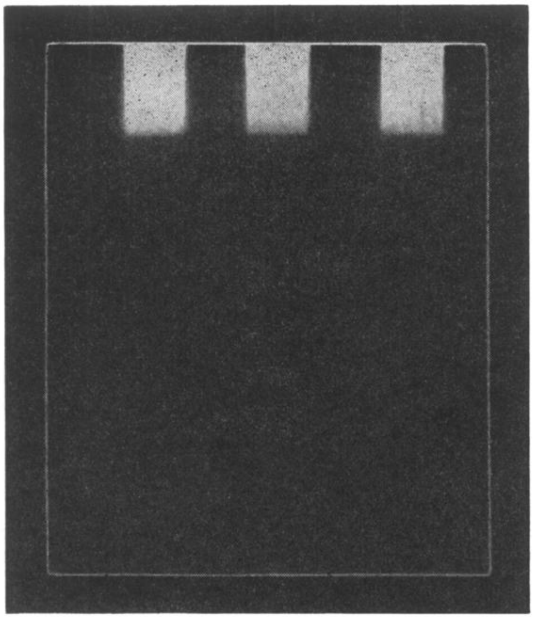

FIG. 7. Photograph of a crystal of silver chloride used to measure drift mobility of photoelectrons, showing columns of colloidal silver (light areas) produced by the electric field.