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# THE PHOTOELECTRIC CONDUCTIVITY OF SULPHUR

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## Abstract

**Variation with electric field of the photoconductivity of sulphur.**—The primary current is proportional to the electric field from 20 to beyond 15,000 volts per cm. If there is a saturation voltage it is probably higher than 50,000 volts per cm. Light produces charges with and without the aid of the field. No evidences of secondary current were found.

**Variation with intensity of illumination.**—Current is proportional to intensity of illumination over the range investigated, about 100 to 1, and for all kinds of light.

**Variation with time of illumination.**—The variation of current with time is investigated in detail, and is explained quantitatively in terms of the charges remaining in the crystal. The positive part of the primary current flows without the help of infrared illumination, under the influence of the original illumination. Without illumination charges disappear very slowly.

**Variation with wave-length.**—The photocurrent referred to unit incident energy is measured from 420 to 650 m$\mu$; its maximum lies at 470 m$\mu$. The **optical absorption** is measured over the same range; it is large below 500m$\mu$, and complete in the violet. In the region between 500 and 650 m$\mu$ it has some unusual features. From the measured absorption values the photocurrents referred to unit absorbed energy are calculated. Formally at least, the quantum-equivalent law is not obeyed. A possible explanation is offered in terms of the peculiarities of the absorption curve. The absolute current yield based on a rough estimate is only about 0.005 times the theoretical value. This together with the absence of a saturation current differentiates sulphur from the other crystals of its class; in fact its behavior resembles that of crystals of the rock-salt type in many respects; but the resemblance is probably only formal.

**Variation with crystal orientation.**—Currents in different directions in the crystal are equal in absolute magnitude, but exhibit a curious unipolarity along one direction, that of the acute bisector of the optic axes, with components along other directions. The reverse currents exhibit parallel differences. The results suggest that sulphur has a polar axis due to atomic asymmetries, and should show the piezo- and pyro-electric effects.

## Introduction

SELENIUM is the most familiar example of a substance whose resistance decreases under the influence of light. The mechanism of this photoconductivity, in the case of selenium and many other substances, is very complicated because the resistance of these substances is comparatively low even in the absence of light. Little information concerning the mechanism of the effect was obtained until Gudden and Pohl, beginning in 1920, investigated crystals which were very good insulators in the dark. They soon found that photoconductivity in these crystals is due primarily to the liberation of electrons inside the crystal by absorbed light; secondary effects are caused by the positive charges, which are in general left behind in the crystal. They distinguished two kinds of crystals possessing photoconductivity, those in which the primary ionization takes place in the pure crystal material, and those in which the ionization is located in impurities or irregularities in the crystal structure. Examples of the second class are all the naturally and artificially colored quartzes and alkali halides; while to the first class belong selenium, cinnabar, zincblende, diamond, sulphur, and numerous others.

It was noticed by Gudden and Pohl that all crystals of the first class possessed a refractive index greater than two, and conversely, that all crystals with $n>2$ which they investigated had photoconductivity. Since the value 2 has no known theoretical significance, it became of interest to investigate sulphur, which has three indices, of which $n_\alpha>2$, while $n_\beta$ and $n_\gamma<2$, in order to see whether differences in the photoconductivity could be observed in specimens of different orientation.

The photoconductivity of sulphur has long been known[1,2,3]; but observations have hitherto been made on polycrystalline material, and have been purely qualitative. Several difficulties are involved in a quantitative investigation of single sulphur crystals. The currents are small, and the mechanical properties of the material are unfavorable. Rhombic sulphur has a hardness of only about 2; it is very brittle, and extremely sensitive to temperature changes; for example, it may crack when held in the fingers, or when laid, for polishing purposes, on a moist cloth cooled by evaporating water or alcohol. Furthermore, there are no good cleavage planes. On the other hand, sulphur offers certain advantages: large crystals are available, though not plentiful; the specific resistance in the dark is very high ($\rho_{20}>10^{18}$), and surface leakage is low. The smallness of the primary currents means that space charge complications are largely avoided; and hence the current-time relations can be studied in detail.

## II. Methods and Apparatus

The technique of the measurements was that developed by Gudden and Pohl. Currents were measured by observing the charging rate of a string electrometer. The electrodes were generally small cells filled with tap water and applied to the crystal with soft wax. The back face of these cells was of very thin glass. The insulation to ground was of amber or cast sulphur throughout, so that the leakage to ground was negligible. The light entered the crystal either parallel to the electric field, i.e., through the electrodes, or transversely. Monochromatic light was furnished by a two-prism constant-deviation monochromator. For some measurements the full radiation of an ordinary tungsten lamp or that of the mercury arc was used.

Between measurements, both electrodes were grounded and illuminated long enough to destroy the space charges left in the crystal during the measurement. In most cases the further precaution of keeping the crystal in the dark for several minutes before each measurement was adopted, cf. Section 1 of Results.

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[*] National Research Fellow.

[1] Monckman, Proc. Roy. Soc. **A46**, 143 (1889).

[2] A. Goldman & S. Kalandyk, Ann. d. Physik [4] **36**, 589 (1911).

[3] F. Kaempf, Phys. Zeits. **23**, 420 (1922).

## III. RESULTS

The following relations were investigated: the variations of the photocurrent (1) with the applied electric field; (2) with the intensity of illumination; (3) with the time of illumination; (4) with wave-length, (a) referred to incident energy, (b) referred to absorbed energy (the latter involving measurement of the optical absorption); and (5) with the orientation of the crystal specimen. The results of these measurements will be taken up in order.

1. *Variation with electric field.* The current produced in sulphur by a given illumination, all other conditions being constant, is directly proportional to the applied field throughout the range investigated, or from 20 to 15,000 volts per cm. This is true for all light intensities. In Fig. 1 the current-voltage curves for diamond ($B$) and zincblende ($C$), taken from the papers of Gudden and Pohl,[4] are replotted to coincide in their initial portion with the sulphur curve ($A$). It will be seen that curves $B$ and $C$ depart from linearity at electric fields far below those required for saturation. Since no departures from linearity were found in sulphur, it is probable that the saturation value of the field strength, if there is one, is above 50,000 volts per cm. This is also found to be the case in the crystals of the rock salt group.

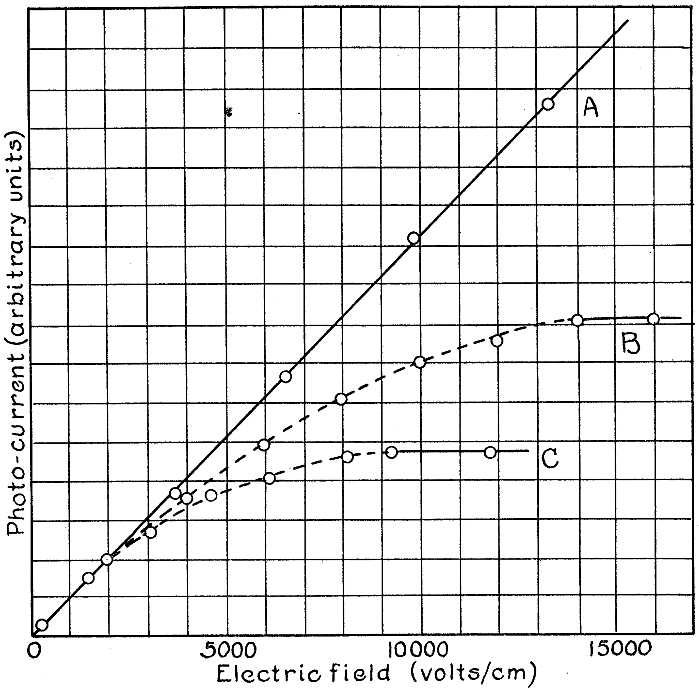

Fig. 1. Variation of photocurrent with electric field.

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[4] Gudden and Pohl, Zeits. f. Physik **17**, 331 (1923).

No evidences of secondary current[5] were ever found in sulphur, though a systematic search was made at high fields and light intensities.

It has long been doubtful whether the number of charges produced by light increases with the applied voltage, or whether the speed of migration alone increases. The question was answered, at least in part, by the observation[6] that illumination under zero field produces, in the case of rock salt, an excitation ("Erregung") in the crystal, which may last for hours in the dark and at room temperatures, but appears as a current when the crystal is subsequently heated or illuminated with strong infrared light. The original illumination produced charges without the help of the field, which were not free to move at room temperature. It was found that the amount of the excitation is the same whether it is produced with or without the field; furthermore, the excitation has a limiting value independent of the light intensity.

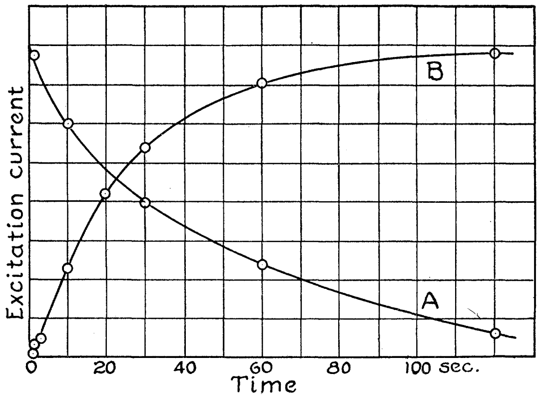

Fig. 2. Variation of excitation with time. (A) decay, (B) growth.

The same effect was found in sulphur, with the difference that here the charges are absolutely free to move. Thus a current flows in the dark as soon as a field is applied. This current will be called the excitation current. Fig. 2, *A* and *B*, records two series of excitation current measurements. In 2*A* the crystal is illuminated a very long time before each observation, with both electrodes grounded. Next follows a varying interval of darkness, after which the field is applied and the current flowing (still in the dark) is measured. This series shows the rate of decay of the excitation. In exactly similar manner the rate of growth of the excitation is recorded in 2*B*. The decay curve is approximately exponential; the growth curve is linear at first, and then approaches the maximum value asymptotically. The maximum value evidently represents equilibrium between the rate of formation and the rate of recombination. From the similarity of the growth and decay curves it follows that the rate of recombination is uninfluenced by the illumination, in spite of the fact that this was intense white light from a

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[5] Gudden and Pohl, reference 4, p. 333, and references given there.

[6] B. Gudden & R. Pohl, Zeits. f. Phys. **31,** 651 (1925).

100-watt tungsten lamp. Cutting off the wave-lengths above 500 m$\mu$ with a blue filter did not change the results.

Using the rate of formation given by the tangent to the formation curve at the origin, it was found that in sulphur also the charges are produced without the field at the same rate as in the field. The calculation involves the assumption that there has been no recombination in the primary current; but there are several justifications for this. The shape of the current-voltage curve for any crystal is independent of the light intensity even when there is a saturation current.[7] The recombination which takes place without the field doubtless takes place only between the original pairs of ions, for the average ion density in the excitation was only one pair in $10^{15}$ neutral atoms; such recombination is scarcely possible when the ions of each pair are being separated by the field as soon as they are formed.

The "ions" which constitute the excitation may, however, be nothing but atoms in a metastable excited state, from which they may return to the normal state after a thermal impact in zero field, or may be ionized by a thermal impact in the field. Hence the number of pairs of ions formed and measured may still be influenced by the field. In order to decide the question, the dependence of the excitation on the field used to measure it must be ascertained. This has not yet been done.

Field-free excitation has also been observed in diamond and zincblende[6]; but here it is said to be much smaller than the charges produced in the field.

2. *Variation with intensity of illumination.* In other crystals, strict proportionality between intensity of illumination and photocurrent has always been observed, provided that sufficient precaution was taken to avoid the effects of space charge. In sulphur, measurements over several different ranges of 10 to 1 confirmed the proportionality relation. The shapes of the current-voltage and current-wave-length curves are independent of the light intensities used. These observations are, in fact, the test for absence of secondary current.

3. *Variation with time of illumination.* When the crystal is brought to its normal state, the field applied, and the crystal illuminated, the current reaches its full value in less than the period of the electrometer string (1/10 to 1/100 sec.). This interval has actually been shown to be less than $10^{-4}$ sec. in the diamond and in other crystals,[8] and it is probably of the same order in sulphur. When the illumination ends, the current falls almost to zero immediately; a small current continues to flow, which is due to the motion of positive ions.

The initial value, as well as the subsequent shape, of the current-time curve depends on the previous history of the crystal. The various possibilities are shown in Table I. Each horizontal line represents one way of making the current measurement; the operations are performed in order from left to right; and the initial value of the current measured is given in the fifth column. The current is measured in the stage whose length is given as $t$.

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[7] B. Gudden, Ergebnisse der exakten Naturwissenschaften Vol. III, p. 151.

[8] W. Flechsig, Zeits. f. Physik **33**, 372 (1925).

The field and the light intensity were kept constant throughout these measurements.

$I_0$ is simply the leakage current over the crystal surfaces. $I_1$ is the excitation current, which has already been studied in detail. $I_2$ is the true photocurrent, taken by giving the crystal a long period of darkness just before the current measurement. $I_3$, in which this precaution was omitted, is the sum of $I_1$ and $I_2$. $I_4$ resembles $I_3$, except that the voltage was applied for a time while the crystal was still in the dark, so that the free charges are swept out; but in doing so a polarization is produced, so that the effective field is reduced; hence the initial value of the current is less than the true value. $I_5$ resembles $I_4$, except that now there are no more ions left to sweep out; so that the true current is observed. It is evident from these curves that in order to get comparable results a carefully defined procedure of measurements must be adopted.

TABLE I

*Various methods of making current measurements and the initial values of the currents in each case.*

| No field<br>Time of Illumination | No field<br>Time dark | Field on<br>Time dark | Field on<br>Time of Illumination | Value of current | Designation of current |
|---|---|---|---|---|---|
| ∞ | ∞ | *t* | | $0.3\times 4\times 10^{-14}$ | $I_0$ |
| ∞ | 0 | *t* | | 8 | $I_1$ |
| ∞ | ∞ | 0 | *t* | 20 | $I_2$ |
| ∞ | 0 | 0 | *t* | 28 | $I_3$ |
| ∞ | 0 | ∞ | *t* | 16 | $I_4$ |
| ∞ | ∞ | ∞ | *t* | 20 | $I_5$ |

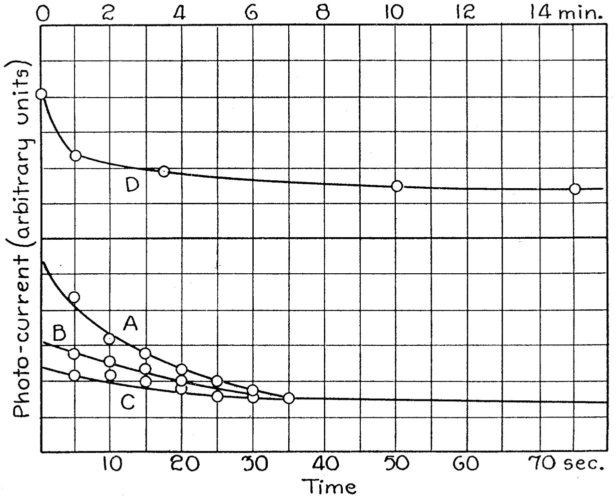

Fig. 3. Variation of photocurrent with time.

The differences between these various currents are due in one way or another to the excitation current. It should be said that the value obtained for the excitation current directly agrees well with that obtained by subtracting $I_2$ from $I_3$. As the excitation current decreases with time these differences grow less and less and finally disappear. The complete time-current curves are shown in Fig. 3, *A*, *B*, *C*, *D*, of which *B* and *D* show the true photocurrent.

As soon as the current flows, some of the positive ions begin to accumulate in the crystal, and these gradually reduce the effective field, so that the current decreases with time during the illumination. Fig. 3A, which represents the sum of the true photocurrent and the excitation current, has an abnormally steep initial drop due to the rapid decay of the excitation current; whereas Fig. 3C, which represents the true current already reduced by a certain amount of space charge, has a very flat initial portion—it has had a slight lead over the true current.

The question arises whether charges pass through the surface of the crystal. In general the answer is, they do. Continuous photocurrents can be made to pass for indefinite periods of time, and the total charge flowing through the crystal would, if retained within the crystal boundaries, produce an opposing electric field many times higher than the applied field. Gudden and Pohl,[9] have shown, however, that up to a certain limit charges remain inside a crystal, by measuring the charges flowing in the reverse current. This is the current due to the recombination of the charges, after the external field is removed and the crystal short-circuited. The charges flowing in the reverse current were found equal to those which had flowed in the direct current, up to a critical value of the charge which, if considered concentrated at the electrodes, would produce there a surface charge density of about $2\times 10^{-8}$ coulombs per sq. cm.

This result was obtained on a zincblende crystal. In sulphur the charge flowing in the reverse current was always considerably less than the charge which had previously flowed in the direct current. The smallest total charge which was observed in a reverse current, $8.5\times 10^{-12}$ coul., was only 30 percent of the charge in the corresponding direct current, so that if there is a critical density below which no charges leave the crystal, it is less than $4\times 10^{-12}$ coulombs per sq. cm, or over 4000 times smaller than in zincblende. Considering the high specific resistance and the other properties of sulphur, this is rather surprising. While the assumption made in this calculation concerning the distribution of charges is rather questionable, it is certain that the quantities measured are independent of the actual distribution of the charges in the crystal, and give the true value for the fraction of charge which has left the crystal, except for the small losses due to leakage. Nor does recombination affect the result; for, aside from the improbability of recombination, discussed above, the changes produced by its occurrence would be in exactly the same ratio in the direct and in the reverse currents.

Gudden and Pohl found, in the case of the diamond, that under illumination with short wave-lengths the positive-ion half of the primary current was not observed until after an illumination with longer wave-lengths. They were able to separate the positive and negative parts of the primary current

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[9] B. Gudden and R. Pohl, Zeits. f. Physik **16**, 176 (1923).

entirely and show that they are equal, thus proving that the positive charges are stationary until set free by long wave-lengths or heat motion. Attempts to separate the two halves of the primary current in sulphur failed; a subsequent illumination with long wave-lengths gave no current. Qualitative attempts to change the ratio of reverse to direct current by the use of filters, infrared radiation from an arc, etc., also gave negative results. A quantitative test with monochromatic light was impossible because of the smallness of the reverse currents. However, the full light of the mercury arc, passing through a water cell, produced exactly the same ratio of direct and reverse currents as the full light of the tungsten lamp. Since the migration of positive ions in the field alone is very slow, the conclusion is that the rate of migration* is increased by the same wave-lengths which produce the primary current. Similar behavior is observed in zincblende.

As time goes on, the current decreases more and more slowly (Fig. 3D), and finally becomes constant at about one-third of its initial value. If the light intensity was changed, the initial and steady values of the current were changed in the same proportion, as was also the initial value of the reverse current. These relations are immediately explained by the relation between the value of the direct current and the ratio of the total charges flowing in the direct and reverse currents. Table II gives the data. At the beginning, for about three minutes, the fraction of the charges which remains in the crystal is constant. During this time the direct current is decreasing, and the initial value of the reverse current is increasing. Thereafter the fraction of charge accumulating decreases more and more; the space charge builds up to its limit, and the direct and reverse currents reach a constant value. The action of the space charge is to reduce the effective field causing the direct current, and to build up a proportionate field for the reverse current.

TABLE II

| Time of flow of direct current (sec) | Mean value of direct current (amp) | Charge flowing in direct current, $Q_d$ (coulombs) | Charge flowing in reverse current, $Q_r$ (coulombs) | Ratio $Q_r/Q_d$ | Initial value of reverse current (amp) |
|---|---|---|---|---|---|
| 20 | $1.04\times10^{-12}$ | $22\times10^{-12}$ | $6.5\times10^{-12}$ | 0.30 | $.80\times10^{-12}$ |
| 40 | .96 | 40 | 12 | .30 | .92 |
| 80 | .86 | 73 | 22 | .30 | 1.08 |
| 180 | .76 | 142 | 38 | .27 | 1.32 |
| 710 | .54 | 418 | 77 | .19 | 1.52 |
| 26 min. | .44 (constant value) | 770 | 95 | .12 | 1.52 |

If the light intensity is changed, the initial and final values of the currents are changed in proportion, because the initial and final potential distributions in the crystal are the same as before; and for the same reason the initial value of the reverse current changes in proportion, the total charge remaining the same.

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* Migration is probably not an actual motion of the positively charged atom, but the process of handing an electron along from atom to atom in the opposite direction.

The initial value of the reverse current may, in fact, be higher than the initial value of the direct current. Since both are produced by the same illumination, the effective field of the residual charges must be higher than the applied external field. This seeming paradox is explained when we consider that while the external field is applied, the crystal, with its two electrodes, and two layers of charges inside, cannot be considered as a single condenser having the dimensions of the electrodes, but is equivalent to two condensers in series, each having much smaller plate separations. The capacity of this system is larger than that of the electrodes, since the distance between each electrode and its corresponding space charge layer inside the crystal is always less than one-half the electrode separation. On grounding both electrodes, however, the capacity is reduced to that of the single condenser, and the effective difference of potential rises accordingly.

A word should be said about the shape of the reverse current-time curves (not shown). The reverse current, of course, decreases with time. The curve corresponding to the lowest value (Table II) is accurately exponential; the other curves are increasingly bad approximations to exponentials, the decay being slower, especially after the first few seconds. This is reflected in the fact that the total charge flowing in the reverse current increases much more rapidly than the initial value (Table II, columns 4 and 6); and it means that as the total quantity of space charge left in the crystal increases, its geometrical distribution changes.

The experiments described in this section were performed for the most part on a very perfect crystal, having a volume of about 8 ccm and no less than eight pairs of parallel natural faces, among them four pairs of (111), two pairs of (011), and two pairs of (113) faces. Most of these were too small to work on. The measurements were made on a pair of (111) faces of area about one sq. cm, 27 mm apart. All the relations discussed have been found to hold for every other crystal examined. The electric field strength was for the most part about 100 volts per cm. Nothing is gained in using higher fields, because the leakage current increases in the same ratio as the photocurrent. The illumination was the full light of a tungsten 100-watt lamp (run on a battery at a considerable overload) at one meter.

4. *Variation with wave-length.* For these measurements, since the energy of the light was very low, high fields had to be used. The crystals, about $1\times4\times6$ mm, were cemented into an amber plate,[10] and water-cell electrodes were attached to the amber with soft wax. If this is done properly, the surface leakage over the crystal faces is eliminated, and the volume leakage through the cement substituted for it. The only cement found suitable for mounting the crystal was a mixture of thick canada balsam solution and pure paraffine, which melted at about 30°C. No other cement was found having a melting point sufficiently low to prevent cracking the crystal, and an electrical resistance sufficiently high to keep the dark current below $10^{-13}$ amperes and fairly constant. Even using this cement, only about one attempt in ten was successful.

[10] Gudden and Pohl, Reference 4.

Monochromatic light was obtained from the usual monochromator, in which only the central slit is moved to vary the wave-length. The spectral width of the light varied from 5 m$\mu$ at 430 m$\mu$ to 30 m$\mu$ at 700 m$\mu$ for the absorption measurements, and from 15 to 80 m$\mu$ between narrower limits for the current measurements. In each case the relative energies were measured with a thermopile and galvanometer. The spectral sensitivity curves of the photocells used in the absorption measurements were not steep enough to introduce an appreciable error into the absorptions with the slit-widths used. The large slit-widths used in the current measurements were necessary to secure measurable currents at the ends of the range; even so the maximum currents observed at 10,000 volts per cm were only of the order of $5 \times 10^{-12}$ amperes.

Fig. 4 shows the variation of current with wave-length, referred to unit incident energy. The curve has a maximum at 470 m$\mu$, and drops more slowly toward the red than toward the violet. The maximum is blunter than the corresponding curve for the diamond, even when the spectral slit-width is taken into account. The curve is based on measurements on two crystals, the set represented by the large circles being somewhat less accurate. Within the limits of error the curves for the two crystals coincide. The measurements were made at 8,000 and at 12,000 volts per cm.

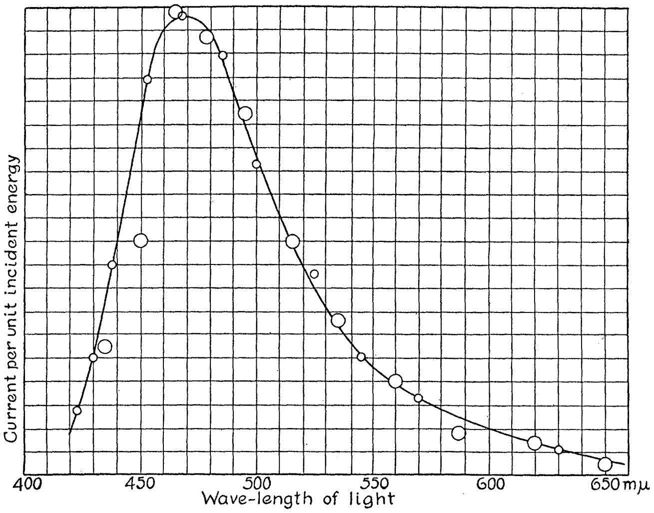

Fig. 4. Photocurrents at different wave-lengths, referred to incident energy.

The optical absorption was determined by measuring the ratio of incident to transmitted energies for a crystal of known thickness. Several different potassium hydride photoelectric cells were used to measure the energies, one in particular which was sufficiently sensitive out to 700 m$\mu$. The string electrometer again served to measure the currents.

Since it was found impossible to obtain perfect optical polish on the faces of the crystal, the corrections for reflection and scattering had to be determined in a lump sum, empirically. This was done by finding the transmission in a region where it was constant, i.e., the absorption presumably zero (in the extreme red at 700 mμ), and placing this equal to 100. The absorption coefficient for the other wave-lengths was then determined from the fractions transmitted at those wave-lengths. This procedure assumes that the fraction scattered and reflected is the same for all wave-lengths, which is true within the limit of the other errors involved.

It was found impossible to determine exactly the absorption of the same crystals upon which the electrical measurements were made, since the absorption coefficient is low in the region of greatest interest, and the thickness of those crystals was only about 1 mm. Measurements were made upon several crystals of thickness 9 to 12 mm, kindly furnished by Professor Bridgman, and the mean of three sets is given in Fig. 5*A*. The three large circles represent the average of many earlier measurements made on three 1 mm crystals; the agreement is very good.

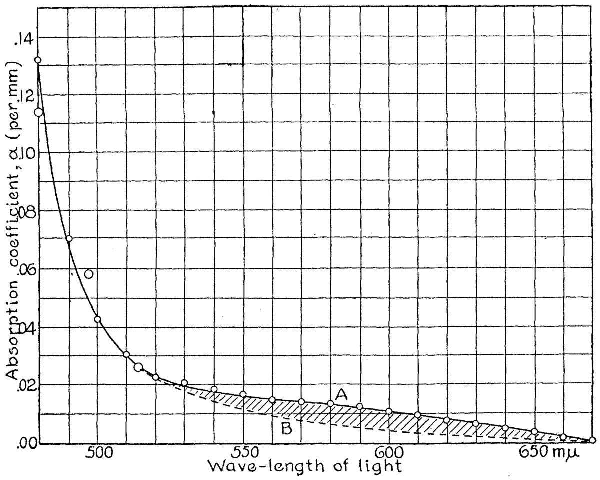

Fig. 5. Optical absorption.

Some of the smaller crystals were grown from $CS_2$ solution; the larger ones were all natural crystals from Sicily. The errors of the method of determining the scattering correction are rather large; and another cause of error is that sulphur is strongy doubly refracting. Nevertheless, the values of the absorption coefficient given in Fig. 5*A* are probably correct to 10 percent or better, while the ratio of the absorptions at any two not too distant wave-lengths is probably correct to 5 percent or better.

It will be noticed that in the yellow and red region the curve does not resemble the ordinary asymptotic absorption curve, but has a point of inflection near 570 mμ, and becomes concave downward until 650 mμ, where it becomes asymptotic. The curve looks as if a small flat maximum were superposed on the usual smooth absorption curve; and the individual sets of observations show this characteristic just as clearly.

Using the data of Figs. 4 and 5*A*, the photocurrents referred to unit absorbed energy were calculated, and are shown in Fig. 6*A*, while Fig. 6*B* shows the distribution which would be expected on the assumption that each absorbed quantum liberates a definite charge. The slope of the line 6*B* is so chosen that it passes through the maximum of the curve, and, of course, through the origin.

Experimentally it seems certain that the deviations from the quantum equivalent law are genuine. The values for the absorption and for the current referred to unit incident energy are each good to within 10 percent at least, while the deviations to be explained are as large as 100 percent and more. The wave-length scales are good to 1 mμ, and even if one of them were out by as much as 20 mμ in either direction, the shape of Fig. 6*A* would not be altered materially. It is true that the electrical measurements and the absorption measurements were not made on the same crystal. Still the various crystals examined gave identical results in all cases, so that individual peculiarities are probably not the cause of the deviations.

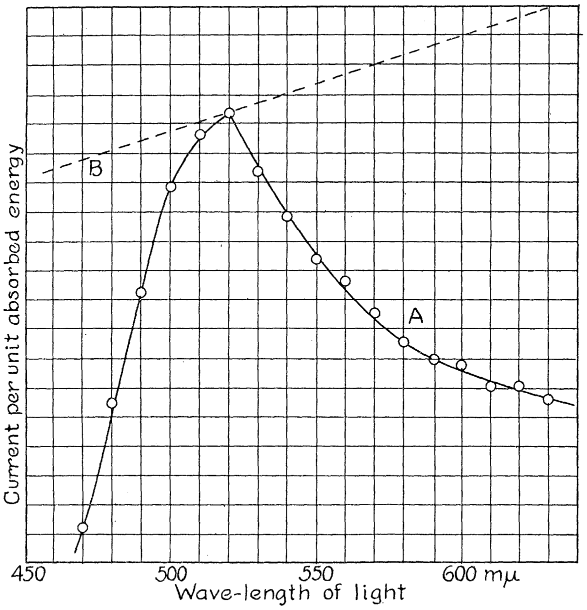

Fig. 6. Photocurrent at different wave-lengths, referred to absorbed energy.

The curve obtained may still be interpreted in two different ways. One is that the quantum equivalent law actually does not hold for sulphur, so that the yield is truly selective. This does not seem very probable, in the first place because of the similarity in behavior in all other respects between sulphur and the crystals for which the quantum equivalent law is known to hold; and in the second place because the curve obtained does not look like a genuine selective maximum, but more like a composite effect.

The alternate interpretation involves two considerations. The abnormal decrease in yield on the violet side of the maximum is found in the other crystals of the same class also.[4] The drop begins in all cases near the sharp upward bend of the absorption curve. There is as yet no satisfactory theoretical explanation of this drop; but it has been suggested that as the absorption processes increase in density in the crystal, they begin to interfere with each other in some way. On this simple theory, however, it is hard to understand the independence of the shape of the current curves and the light intensities (Section 2). The decrease in the yellow and red which remains to be accounted for is not found in any other crystal, and is entirely unexpected. It is possible that the explanation lies in the peculiar shape of the absorption curve, with its point of inflection at 570 m$\mu$. Fig. 5*B* shows the values of the absorption constant which would be necessary to give the quantum equivalent yield, assuming the values at 520 m$\mu$ to hold. While these calculated values are far outside the limit of the experimental values, they lie on a smooth curve which forms the normal continuation of the steeper part of the absorption curve. This gives additional probability to the existence of an electrically inactive absorption, represented by the shaded region in Fig. 5. Such absorption has been observed in other cases, though not superposed on active absorption. In particular, Coblentz[11] has found that sulphur has considerable absorption in the near infrared, down to 1$\mu$, which is doubtless inactive electrically.

Whether the above explanation is the true one or not, it is certain that formally at least the quantum equivalent law does not hold for sulphur. The absolute magnitude of the current yield was not determined accurately; but it is certainly smaller than in crystals where a saturation current is found. A rough estimate based on the spectral distribution curve of an incandescent lamp gives a yield of 0.002 to 0.01 electrons per absorbed quantum, at 15,000 volts per cm. A similar result has been found for rock salt. The explanation, in the case of rock salt, is that while each absorbed quantum produces a pair of ions, the charges move only a small fraction of the crystal thickness.[6] This is well confirmed by the measurements of Flechsig[8] on the time required for the reversal of the current when the applied field is reversed. To adopt this explanation for sulphur is impossible until confirmation by experiments similar to those of Flechsig is obtained; for difficulties are encountered in explaining the experimental facts that seventy percent of the charges flowing leave the crystal, that the positive-ion half of the current flows without the help of long-wave-length light, and that the charges produced in field-free excitation are free to move. Moreover, the differences between sulphur and the other crystals of its own class, namely, lack of saturation current and low current yield, can be understood when we remember the role of the refractive index. The value $n>2$ is the criterion of photoconductivity; and in sulphur $n$ is so much nearer the limiting value than in either the diamond or zincblende, that the saturation field strength ought to be much higher in sulphur than in either of these

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[11] W. W. Coblentz, Phys. Rev [1] **19,** 94 (1904).

crystals, for the rule is found to hold that the order of the saturation fields is the reverse of the order of the refractive indices.[12]

5. *Variation with crystal orientation.* The variation of current with orientation in the crystal was one of the principal points of interest when the research was undertaken. Sulphur is an orthorhombic crystal, with the axial ratios $a:b:c=0.813:1:1.900$, and the refractive indices (for the red $K$-line 768 m$\mu$) $n_\alpha=1.93$, $n_\beta=2.00$, and $n_\gamma=2.19$. The plane of the optic axes is that of the $a$ and $c$-axes, the $a$-axis being the acute bisector. Most of the crystals examined were very one-sidedly developed; but one, a natural crystal from Sicily, had two large natural faces perpendicular to the $c$-axis, and was about a centimeter thick. It had been used for the absorption measurements. It is shown in plan view in Fig. 7, in two-thirds natural size, the dotted lines indicating the size of the lower face, the heavy lines natural edges. The diagonal dotted line indicates the direction of the bisector of the optic axes. The illumination was the full light of a tungsten lamp, or that of the mercury arc, at various distances. The electrodes were small water-cells placed on the upper (horizontal) surface of the crystal with soft wax, and numbered as shown. The lines connecting the electrodes lay along previously determined directions in the crystal. With each pair of electrodes pairs of current readings were taken, the conditions being the same for each reading of any pair except that the direction of the current was reversed. The value of the reverse current was also observed with each pair of primary current readings. The results are shown in Table III, where the readings for parallel directions are grouped together. The various currents are all for the same light intensity, assuming the illumination to be homogeneous over the whole surface.

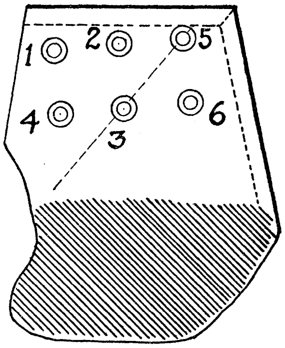

Fig. 7. Crystal used to measure variation of photocurrent with orientation.

Comparing the values up and down the columns, i.e., between different pairs of electrodes, we see that the currents are of the same order of magnitude in all directions; beyond this the readings are not comparable; nor are the differences in any way systematic. This is to be expected, because the various electrodes were not strictly equidistant, having been spaced only by eye; and because some of them are situated over the overhanging edge

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[12] B. Gudden, Reference 7, p. 147.

TABLE III

| Electrodes | | Direct Current | | Reverse Current | | Angle with Plane of Opt. Axes | Difference in Direct Currents (percent) |
|---|---|---|---|---|---|---|---|
| 1st | 2nd | First Elect. neg. | Second Elect. neg. | First Elect. neg. | Second Elect. neg. | | |
| 1 | 3 | 1.54 | 1.54 | 0.11 | 0.10 | 90° | 0 |
| 2 | 6 | 1.47 | 1.52 | .01 (?) | .06 | " | 3 |
| 2 | 4 | 1.59 | 1.25 | .23 | .03 | 0° | 25 |
| 5 | 3 | 1.30 | 1.07 | .15 | .02 | " | 19 |
| 1 | 2 | 1.36 | 1.47 | .10 | .12 | 45° | 8 |
| 4 | 3 | 2.04 | 2.23 | .08 | .16 | " | 9 |
| 2 | 5 | 1.56 | 1.73 | .06 | .14 | " | 10 |
| 3 | 6 | 1.88 | 2.02 | .05 | .18 | " | 7 |
| 1 | 4 | 1.66 | 1.51 | .21 | .11 | 45° | 9 |
| 2 | 3 | 2.01 | 1.86 | .12 | .05 | " | 8 |
| 5 | 6 | 1.75 | 1.68 | .08 | .06 | " | 5 |

of the crystal (the lower face being smaller), some electrode pairs draw charges from a larger volume of crystal than others. If these things are taken into account, the absolute values of the various currents are as closely equal as could be expected.

The two values in each horizontal row are much more comparable, for they were taken under identical conditions except for the reversal of the applied field. Here the differences become perfectly systematic. In directions perpendicular to the plane of the optic axes, i.e., parallel to the *b*-axis, the two currents are the same within experimental error. Along the *a*-axis, the bisector of the optic axes, the two readings of each set differ by 20 to 25 percent of their mean value. Along any intermediate direction, say at 45° to the *a*- and *b*-axes, an intermediate difference of 8 to 10 percent is observed. Furthermore, the differences in the intermediate directions always have the same sense that they would have as components of the vector representing the largest difference in direction and amount. Thus the current $2-4$ is larger than the current $4-2$ by 25 percent, and we find that the currents $2-1$ and $2-3$ are larger than $1-2$ or $3-2$ by 8 percent each; but $2-5$ is smaller than $5-2$, showing that the sense and amount of the difference are functions not of the particular electrodes, but of the crystal directions. The initial values of the reverse currents show a similar consistency, considering their greater inaccuracy, except that the percentage differences are much larger; in fact in one direction, that of the bisector, one of the reverse currents is practically zero. Just why the reverse current should be larger where the direct current is larger is not at all obvious, especially as the percentage differences are out of all proportion. The total charges flowing in the various reverse currents have not yet been investigated, but it is quite possible that they are more nearly proportional to the corresponding direct currents.

These effects are so novel that it is worth discussing the possibility of their being caused by unsuspected experimental errors. Local impurities and cracks in the crystal may be eliminated as causes, because the differences were found to be distributed in the same fashion all over the crystal. There is no reason to suppose that such impurities existed, the crystal being clear and flawless except for a few small cracks in the lower face of the crystal, and except for the large portion shaded in Fig. 7, where no measurements were made. Invisible cracks, even if oriented along the optic axes or perpendicular to them, should produce currents of different magnitudes but without unipolarity; whereas the reverse is actually found. The order in which the measurements were taken was found not to influence the result; and besides the crystal was restored to its normal condition after each reading by a carefully defined procedure which included darkening the crystal to eliminate the excitation current. The differences were reproducible from day to day. The electrodes used were all of the same material (water), and of the same size. The fact that the electric field was inhomogeneous is harmless, because the inhomogeneity is the same for all the measurements.

The reality of the differences is further confirmed by the observation that each of the direct currents recorded in the table is directly proportional to the field between 20 and 200 volts per cm.

The currents along the *c*-axis show no differences when the voltage is reversed. It is, therefore, not the plane of the optic axes, but the direction of their bisector that is unique.

No explanation of these curious partial unipolarities is offered at this time. The results strongly suggest, however, that sulphur has a polar axis, if not crystallographically, then at least due to atomic asymmetries. If this is so, then sulphur might show the piezo- and pyroelectric effects. While searching for the latter effect, an interesting electrostatic demonstration of the photoconductivity was noticed. A small, thin rod-like fragment of sulphur and a similar rod of glass were suspended side by side, from single fibers of silk, in an electric field of several hundred volts per cm. When the field was applied, both rods set themselves along the lines of force. With a strong light in the room, if the direction of the field was reversed after ten seconds, the sulphur rod turned through 180° as if its ends were permanently charged, the glass rod remaining stationary, though its natural conductivity was higher. If the light in the room was weak, the sulphur would not turn through 180° until the field had been on at least fifty seconds. Evidently the light had caused charges to flow in the crystal; they could be destroyed by illumination after the field was removed.

## IV. SUMMARY

As the phenomena of photoconductivity are unfamiliar to a large number of readers, an attempt will be made, in summarizing, to state briefly the present conceptions of the nature of photoelectric conduction.

This type of conductivity is found only in certain crystals. A crystal has photoconductivity if it is a pure crystal of refractive index $n>2$, or, regardless of its refractive index, if it has dispersed throughout its volume certain types of impurities such as metallic colloids. The light produces in the crystal equal numbers of positive and negative charges; the seat of the ionization is, in the first case, the material of the crystal lattice, in the second, the particles of the impurities.

The crystal may or may not be a good insulator in the absence of light. In either case the primary mechanism of photoconductivity is the same; but if the crystal in question is already a poor insulator, secondary processes affect the currents, and the relation between the current and the other variables of the system becomes very complicated. The complications may be traced to a general loosening of the crystal structure due to the accumulation of charges inside the crystal.

If the crystal is a good insulator, certain simple relations may be expected. These have been comfirmed experimentally whenever precautions were taken to avoid the secondary phenomena due to the accumulation of charges. The photocurrents observed depend on three main factors, the light, the crystal, and the field. We shall consider these factors in order.

The current is strictly proportional to the intensity of the incident light. Different wave-lengths are active in different degree, only because they are absorbed differently by the crystal. Every quantum of light absorbed results in an ionization process. Where apparent exceptions to this rule are found, an explanation is always possible in terms of one of the other factors: thus in colored rock-salt, the charges produced move through only a small fraction of the crystal thickness, hence the number of charges observed appears too small. In sulphur both the actual current yield and the wave-length distribution of the yield depart from the rule; the one departure may be explained by the absence of a saturation voltage, the other by the existence of peculiarities in the absorption of the crystal. Both explanations, however, require further confirmation.

The charges produced by light are of two kinds, electrons, and positive ions. The former are free to move in the field through the whole thickness of the crystal. They are not materially impeded by the atoms of the space-lattice, but are caught or slowed down by all kinds of cracks, irregularities, or impurities. In fact, if these are sufficiently numerous the photocurrent may disappear altogether. Positive ions have a much lower mobility, which varies with the specific resistance of the crystal. Under the influence of light, however, the positive charges may also "move" with large velocities. In this case, the "motion" consists of a handing along of electrons toward the cathode. Such currents may occur simultaneously with the electron current under the influence of the original illumination, (sulphur, zinc-blende), or they may occur subsequently, under the influence of light of longer wave-lengths (diamond, rock-salt), or of thermal agitation even at room temperatures (cinnabar). The electronic part of the current flows within $10^{-4}$ sec. of the beginning of illumination, and ceases in a corresponding interval. The positive part of the current may flow almost as rapidly, or it may require any longer interval up to several hours, depending on the conditions.

When charges flow, they do not always leave the crystal. In order that they be observed as a current, it is sufficient that they move through a part or the whole of the potential difference applied to the crystal. Those that are left inside the crystal produce distortion of the homogeneous field, and cause a diminution of the current. When the external field is removed they produce a field in the opposite direction, and a reverse current if there is illumination. The total charge flowing in the reverse current measures the charge left in the crystal during the flow of the primary current. The relations between the time of flow and the values of the primary and reverse currents may be followed quantitatively in terms of the total charge left behind.

The field enables the charges produced by the light to flow and be measured. The number of charges observed varies with the field; for low fields it is proportional to the voltage; but for high fields, in most cases, it becomes independent of the voltage. The current and field for which this condition is first reached are called the saturation current and field respectively. The saturation current is determined by the light intensity. The increase of current with field at the lower values may be due either to an increase in the number of charges, or to an increase in their mobility, or to both causes. Currents may be observed when the illumination precedes the application of the field, of the same amount as when the two factors appear simultaneously. This observation offers a means of deciding what part the field plays in the production and motion of charges. This is one of the fundamental questions connected with the phenomenon. Another fundamental question is that of the resistance of the crystal material to the motion of electrons, and the conditions under which an electron may cross the boundary. Why may electrons once liberated inside the crystal cross the boundary freely, whereas electrons cannot penetrate from the outside under any ordinary experimental conditions? In this connection the observation of unipolar photocurrents, in sulphur, with definite orientations in the crystal, promises to be of importance.

This investigation was suggested by Professors Pohl and Gudden; it was begun in their laboratory at the University of Göttingen, and later continued at Harvard University. I wish to thank Professors Pohl and Lyman, who placed the resources of their respective laboratories at my disposal, as well as Professor Bridgman, who furnished the large sulphur crystals and took a constant interest in the work.

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June, 1927.