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Photo-conductivity

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Introduction

THE influence of light on the flow of current through certain solids had been observed for several decades, but without important results prior to the brilliant work of Gudden, Pohl, and their collaborators. These investigators made the important advance of passing from the study of polycrystalline semi-conductors having comparatively large conductivities, when not illuminated, over to single crystals of insulators. This enabled them to study the conductivity arising when the crystal is irradiated with light of suitable wave-length under simpler and more controllable conditions than had hitherto been obtainable. In many cases, they were able, by using feeble light and low voltages, to distinguish between phenomena which they called "primary" or "secondary." The distinction is fundamental and shall be treated at length in this article. We will begin with an account of the phenomenon designated by Gudden and Pohl as primary and sometimes classified under the name *internal photoelectric effect* to distinguish it from the so-called external photoelectric effect (i.e., ejection of electrons from substances into surrounding gas or vacuum by incident light). We then take up the secondary phenomena; first in cases where they coexist with primary, then in cases where they are observed alone. In the closing section, we discuss the cases in which electromotive forces are generated in solids by light.

There is an important classification of crystals due to Gudden and Pohl. Some are intrinsically photosensitive in their initial and pure condition; some owe their sensitiveness to commingled impurities, or acquire it through irradiation by x-rays or other agencies. The former are called "idiochromatic," the latter "allochromatic." The index of refraction (for light not strongly absorbed) is greater than 2 for the former and less than 2 for the latter. Typical idiochromatic crystals are diamond, zincblende, cinnabar and stibnite, sulphur and the red variety of selenium. The allochromatic crystals include the alkali, silver and thallium halides.

PHOTO-CONDUCTIVITY IN INSULATORS

Primary photoelectric currents in single idiochromatic crystals of insulators

The method of observing the photoelectric current obtained by irradiating the single crystal of an insulator with light of suitable wave-length can best be illustrated by Fig. 1, which schematically represents the experimental arrangement. The charge flowing through the crystal, when irradiated for a short period of time, can be measured by a galvanometer or any suitable measuring instrument connected in series with a source of potential and a crystal. According to Gudden and Pohl,[19] the fundamental equation of photoconductivity which determines the quantity of electricity observed is:

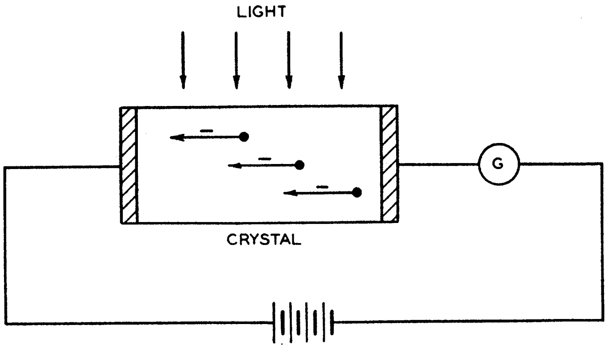

Fig. 1. Experimental arrangement. Arrows indicate motion of negative charges in crystal.

$$Q = Ne(X_- + X_+)/d \tag{1}$$

where N is the number of pairs of charges formed by the light, e the electronic charge, X_- and X_+ the distances the charges move, and d the thickness of the crystal or the distance between the electrodes. If all charges of each sign move to their respective electrodes, the above equation reduces to

$$Q_1 = Ne. \tag{2}$$

In this case, we would expect fulfilment of the quantum equivalent law. If we assume the charges of one sign remain fixed while the other one is free to move under the influence of the applied electric field to its respective electrode, then our original equation becomes,

$$Q_2 = Ne/2, \tag{3}$$

it being obvious that if charges are liberated uniformly throughout the body of the crystal the average distance moved by charges of one sign is $X = d/2$.

When a steady state is reached, in which case, both charges are free to move, original Eq. (1) takes the form

$$i = ne(X_+ + X_-)/d \tag{4}$$

where n is the number of pairs of charges formed per second, and X_+ and X_-, respectively, are the distances moved by the charges. In many crystals possessing sufficient purity and degree of physical perfection, currents were observed which obeyed the above equations.

These currents were found to conform to the following laws:

(a) The current is rigorously proportional to the incident light intensity, whatever the applied voltage.

(b) The curve of current *vs.* voltage rises from the origin, is sensibly linear at first, then concave downward and finally horizontal.

(c) The currents begin immediately on the beginning of illumination and end immediately on stopping of illumination.

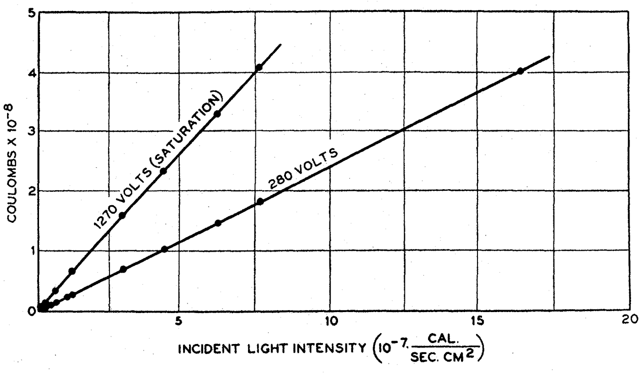

Fig. 2. Proportionality between incident light intensity and quantity of electricity separated for zincblende. Area of illuminated surface 25 mm^2, thickness of crystal 1.3 mm $\lambda = 4360$A.

Currents which conform to these laws are designated by Gudden and Pohl as "primary" currents.[9,10,15,19,22,63] Such currents were observed in diamond, zincblende and cinnabar, and to a lesser extent in sulphur, red-selenium, stibnite.

I now describe these laws in fuller detail.

(a) *Relation of photoelectric response and intensity of incident light.* The photelectric primary current was found to be rigorously proportional to the incident light intensity[22] for many of the materials investigated, provided the voltage was kept sufficiently low and small light intensities were used for short periods of illumination. In applying the methods used for testing this proportionality, one either measures the flow of charge for short periods of illumination with varying light intensity, as is shown in Fig. 2, or measures the total quantity of electricity which flows through the crystal with various periods of illumination by light of constant intensity,[63] as is exemplified by Fig. 3. In Fig. 2 are shown the results obtained on a thin single crystal of zincblende at two values of voltage, 1270 volts being above the saturation value, whereas 280 volts is much below it (see Fig. 4). This proportionality was also observed in materials in which saturation currents were not obtained, for example sulphur, red-selenium, stibnite. Slight deviations from proportionality were observed in stibnite for light which is strongly absorbed.

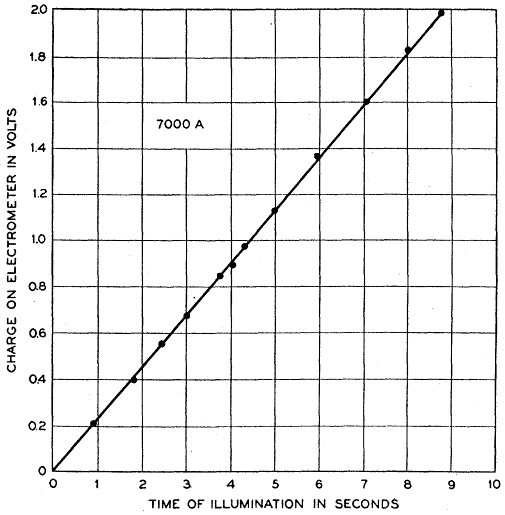

Fig. 3. Proportionality between time of illumination and quantity of electricity separated for stibnite.

(b) *Relations of current and voltage.* When a single crystal of zincblende is irradiated for short periods of time with monochromatic light of constant intensity, the current obtained varies with voltage in the manner shown in

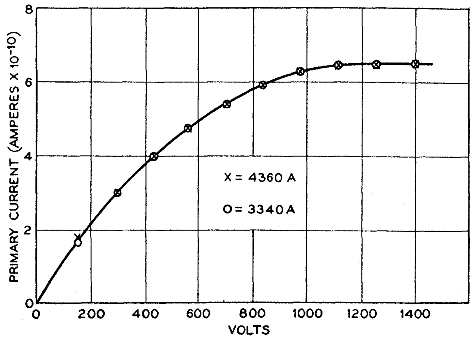

Fig. 4. Current-voltage characteristic for a zincblende crystal.

Fig. 4.[22] The initial values of current were plotted in order to avoid the disturbing effects of space charge. The absorption of the crystal for the two indicated wave-lengths of light were very different; the data thus suggest that the shape of the curve and the voltage at which saturation is obtained do not vary with the wave-length and intensity of the light.

On the other hand, results obtained by the writer in studying primary currents in single crystals of mercuric iodide indicate that this suggestion is not universally true; that instead, the saturation voltages and the general shape of the curves vary with both the wave-length and the intensity of the incident light.

Flechsig[59] has made special studies on the form of the voltage current curves for yellow rocksalt colored by irradiation with x-rays and was able to show that plots of quantity-of-charge *vs.* V/d^2 (V = voltage, d = thickness of crystal) give curves which showed pronounced saturation. Good saturation was obtained with crystals of zincblende, yellow rocksalt, whereas no indication was obtained for saturation with voltage of the primary photoelectric current for sulphur, red-selenium, stibnite. It is thought that saturation could be obtained for the three last named substances if sufficiently high potentials were used.

It was observed that the more nearly perfect the crystal was, the more nearly saturation could be obtained. This, together with other evidence to be presented later, led Gudden and Pohl to assume that ejected electrons do not move unhampered through the crystal lattice, but are impeded in the journey by lattice imperfections and submicroscopic cracks, or by foreign atoms embedded in the lattice. The distance moved by an electron before it is trapped by an imperfection of some kind is assumed to be proportional to the field strength. At low field strengths, the distance moved would, in many crystals, be small compared to the distance between the electrodes. On increasing the voltage, the average distance moved would be increased until finally all the electrons set free in the crystal reached the anode, at which point there would be saturation. Application of higher voltages would not further increase the current. In the foregoing argument, it is assumed that the flow of electricity is too small to affect materially the potential distribution.

A recent review by Gudden[67] gave unpublished results by K. Hecht obtained from studies with "light probes" on AgCl which further support this view. Very little evidence exists to sustain this standpoint for diamond and zincblende; whereas similar studies on single crystals of red-selenium and those to be reported in the next section on yellow rocksalt furnish strong evidence that electron "capture" occurs, the electrons being later released by heating or irradiation with infrared light. In view of this reasoning, it is not surprising to find that saturation currents were not obtained for the imperfect crystals of red-selenium and stibnite.

(c) *Instantaneity of the primary photoelectric current.* The time relations of the phenomena are probably important for theory. A commutator arrangement was improvised by Flechsig,[31] which impressed a "square-topped wave" of voltage across the crystal, a flash of light being directed against the crystal at some arbitrary moment of the cycle. The results showed that the negative component (hereafter to be defined) of the primary current begins in an interval of time smaller than 10^{-4} second after the beginning of the illumination. In view of the work of Lawrence and Beams, showing that in the external photoelectric effect the electrons begin to emerge in less than 10^{-9} second after the beginning of the illumination, it might be expected that the same is true for the internal effect.

The so-called "components" of the primary photoelectric current

Very little has been said hitherto concerning the components of the primary current. Gudden and Pohl[10,44] consider the primary process taking place on the absorption of light to consist in the ejection of an electron and its passage to the anode. The result of such a process would be the leaving behind of a residue of positive charges giving rise to a positive space charge, which, if allowed to accumulate, would materially distort the field in the crystal. From Eq. (4), it follows that the positive ions formed by the ejection of electrons must be neutralized by electrons coming from the cathode, if the charge recorded by the galvanometer is to be equal to the total charge (of either sign) set free in the form of ions by the light. In some cases, particularly that of diamond,[19] this effect was separately observed. It was found that when diamond is irradiated for a brief time with short wave light near the low-frequency side of the absorption band, a certain quantity of electricity flows through the galvanometer; if thereupon this irradiation is followed by illumination with red light (which does *not* give rise to photo-current in a crystal not previously illuminated with short wave light), an extra quantity of charge flows through the circuit, which, in limiting cases, is equal to the previous quantity observed at the time of irradiation by short wave light.

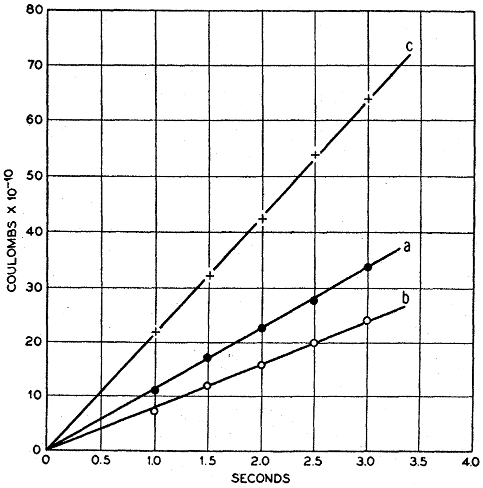

Fig. 5. Effect of "long-wave" light on the flow of the positive primary current in diamond. Thickness of crystal 1 mm, area of illuminated surface 3 mm², potential across crystal 1200 volts. (*a*) Irradiation with 3130A alone ($2.16 \cdot 10^{-6}$ cal./sec. cm²); (*b*) illumination with long wave light alone (5.10^{-2} cal./sec. cm²) *after* illumination with 3130A; (*c*) illumination with 3130A and long-wave light simultaneously.

The charge which flows through the galvanometer at the time of the irradiation with short wave light is called, by Gudden and Pohl, the "negative part of the primary current;" the charge which flows at the time of the subsequent illumination with red light is called "positive part of the primary current." These designations are somewhat misleading; while the earlier current flow is presumably due to the drawing of electrons out of the crystal into the anode, the latter current-flow is not to be similarly ascribed to motion of positive ions. Instead, we should think of electrons coming out of the cathode and dispersing themselves gradually throughout the crystal, neutralizing the positive charges which were left behind in the crystal when the original electrons departed into the anode.

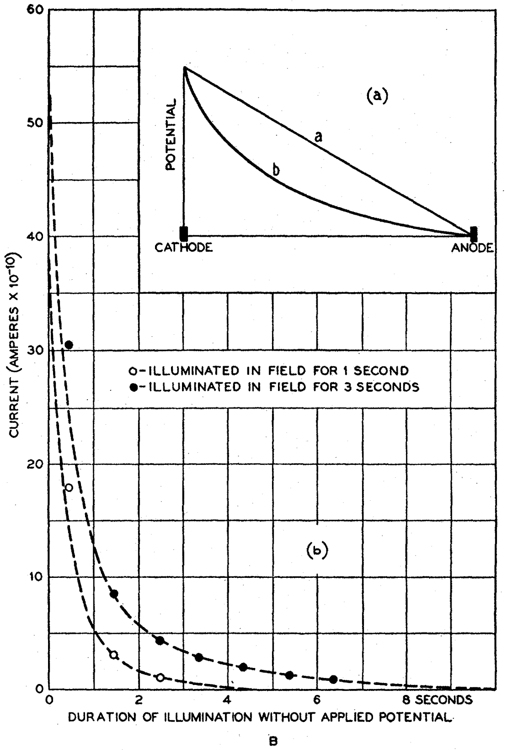

Fig. 6. (a) Potential distribution, *a*—before illumination, *b*—after illumination. (b) Reverse current in zincblende on illumination with 4360A (4.10^{-6} cal./sec. $\overline{\text{cm}^2}$) without applied potential. The crystal had been previously illuminated in a field with 4360A.

In some of the experiments by Gudden and Pohl, the separation of these two components was almost complete. Fig. 5 shows the results for diamond.[19] Curve *a* represents the charge which passed the galvanometer during irradiation with *short wave* light; *b* shows the total charge which passed on subsequent illumination with *long wave* light; *c* gives the total charge which passed when the crystal was illuminated simultaneously with both *short wave* and *long wave* light. Studies on zincblende showed that the two charges are unequal; it is to be inferred that part of the positive ions are neutralized during the first irradiation, or as Gudden and Pohl would put it, part of the positive current flows simultaneously with the negative current. In some cases, for example that of sulphur,[55] it has been impossible to separate the two components.

The positive component can best be elicited by use of long wave light or by heat (the same agencies as were used by Lenard in the restoration of his phosphors to their original condition). The light which is most effective is the long wave end of that region of the spectrum to which the crystal is sensitive in its initial or *unexcited* condition. In many of the earlier papers of Gudden and Pohl, they refer to it as *red light*; but in some cases, it had to be nearer the blue end of the spectrum.

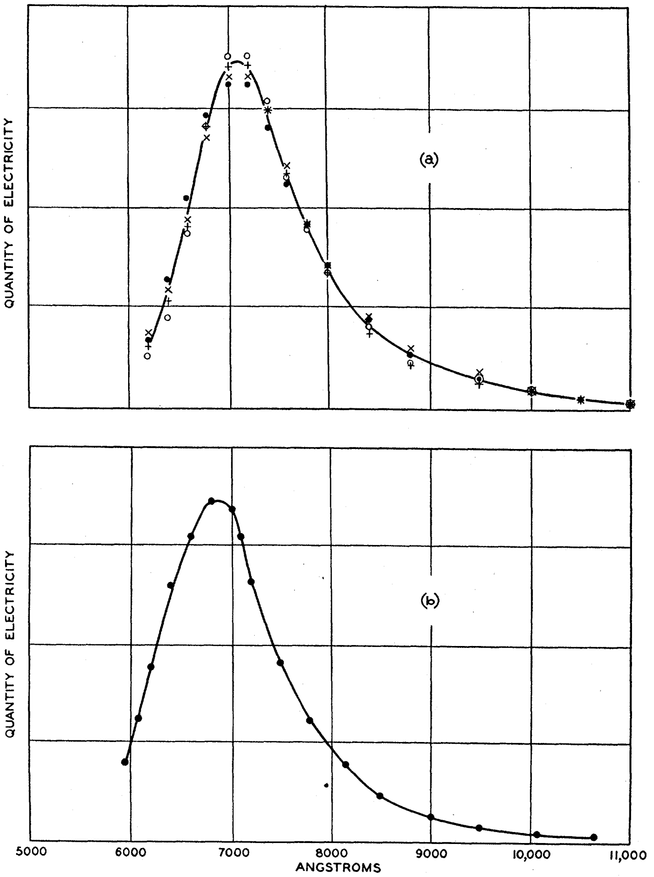

Fig. 7. Spectral distribution of the primary photoelectric current in a single crystal of red-selenium.

To obtain reproducible results with the crystals investigated, it was always necessary to irradiate with long wave light, to apply heat, or else to leave the crystal to itself, for a certain time, before repeating the measurements. Neglect of these precautions has been responsible for contradictory results in the case of studies on diamond.[17] With blue rocksalt, the irradiation with long wave light fails to restore the original condition; but this is perhaps not surprising in view of the extreme complexity of the absorption curve.[45,48]

On increasing the size of the photoelectric current, space charges of considerable magnitude could be observed.[10] Distortion of the potential distribution is due in large part to positive space charge; results of Tartakowsky[65] indicate some effect of a negative space charge in the case of yellow rocksalt. Fig. 6a depicts the potential distribution before and after illumination of the zincblende crystal. Further evidence for the existence of an opposing internal field[19] due to formation of space charges is given in Fig. 6b. This curve was obtained by permitting the current to flow for a time sufficiently long to form a large polarization, followed by the removal of the applied potential with subsequent illumination as before. The current decreases with time and continues to flow until the internal field disappears.

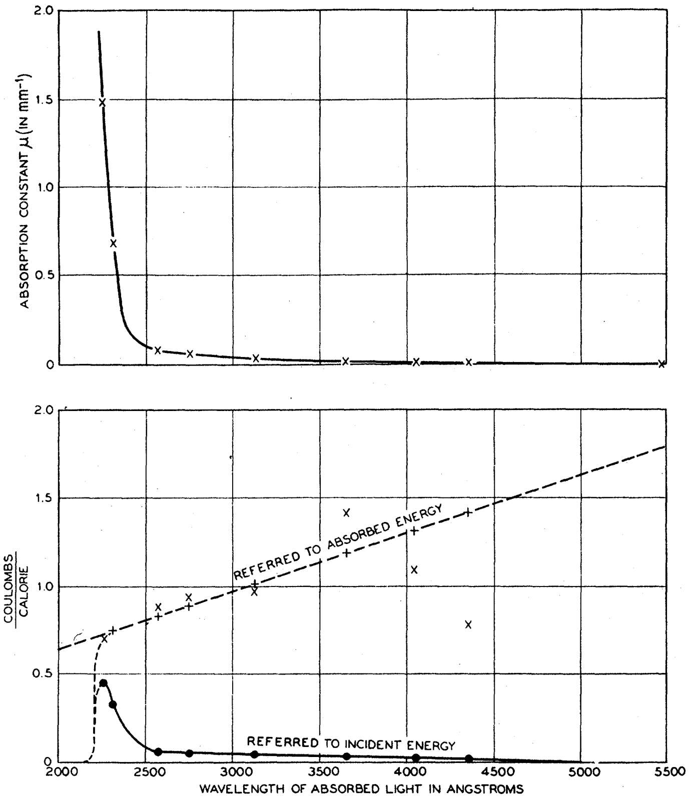

Fig. 8. Quantum equivalence in diamond.

Spectral sensitivity of idiochromatic crystals

Crystals belonging to this class are found to be photoelectrically sensitive to all absorbed light, with the exception of the far infrared. The shape of the spectral sensitivity curve is exemplified by the accompanying curve of Fig. 7a of red-selenium.[34] They are characterized by a maximum with a gradual slope on the long wave, a steep slope on the short wave side. The maximum is not located in the interior of the absorption band, but at the short wave edge of it (absorption measurements are lacking for red-selenium, but the fact is shown in Fig. 8 for a clear crystal of diamond). In many cases (for example, diamond, zincblende and cinnabar), the maximum occurs at a wave-length for which the absorption constant is *ca.* 1 mm^{-1}. The position of the short wave maximum in the spectral sensitivity curves of molybdenite (MoS_2) bears the same relation to the absorption band as with diamond and similar materials (molybdenite, as I will point out in the next section, is a semi-conductor in which the current is classified as secondary).

All explanations hitherto proposed to clarify this dropping off in the spectral sensitivity curve for regions of large optical absorption have been unsuccessful. The relationships hitherto described for the primary current are no longer valid when considerable amounts of impurities are present, apparently because of absorption of light in ways which do not give rise to photoelectrons. In the case of the red insulating variety of selenium displaying no detectable dark current, the position of the spectral sensitivity maximum depends on the orientation of the crystal relative to the incident light-beam. This dependence on the orientation is governed by the dichroic absorption of the crystal[34] (compare Figs. 7a and 7b).

For these primary currents, the shape and position of the spectral sensitivity curves are independent of the voltage and light intensity. They are also the same whether the light-beam is perpendicular to the lines of force of the electric field ("transversal" illumination) or parallel to them ("longitudinal").

The absorption of light which leads to photoelectric current-flows causes a change in the optical properties of the crystal.[46,72] This manifests itself in an extension and increase in the absorption, both from optical and photoelectric measurement, on the long wave side of the absorption band. This cause for the change in the photosensitivity curve as well as in the absorption curve has been designated as "excitation" (it will be considered in detail in a later paragraph). The original condition can be restored by use of long wave light or by heating, or will restore itself after a certain length of time.

Quantum relations

The series of very fruitful investigations begun by Gudden and Pohl were initiated with hopes of verifying the "quantum equivalence law" of Einstein. If every absorbed photon were to release an electron, the "yield" would be given by the formula:

$$n = Q/h\nu = (Qc/h)\lambda$$

where n is the number of electrons ejected by the absorbed light energy Q of frequency ν, and h is Planck's constant. This expression is a linear function of λ, of positive slope.

In numerous investigations of the external photoelectric effect performed with like intention, the photoelectric yield had been found to be several orders of magnitude lower than the theoretical value, though recent work of Suhrmann on thin films of alkali metals disclosed yields amounting to as much as several percent of $Q/h\nu$. Worse yet, it appeared from these investigations that the yield decreases with increase of λ.

The first verification of the equivalent law for photoelectric effect was made on single crystals of zincblende and diamond, also qualitatively for cinnabar. (The photo-chemical studies of Warburg had previously shown that the quantum-equivalent yield is attained in the photo-chemical decomposition of hydrogen iodide and hydrogen bromide.)

Fig. 8 shows the results of studies on a clear crystal of diamond.[22] In obtaining the data, the voltage was made sufficient to produce saturation. The absolute value of incident light intensity was measured with a linear thermopile, the absorbed energy was deduced from it by the absorption measurements of Peters.[25] The plot of the coulombs per calorie of absorbed energy *vs.* the wave-length of the absorbed light, in the region of low light absorption, gave rigorous proportionality.

These results furnished the first quantitative evidence of a case in which the quantum equivalent law is valid. Each quantum of absorbed light separated a negative and a positive charge, amounting to $-e$ and $+e$; or in other words, for every quantum of light absorbed, one electron was sent around the circuit. As explained on page 728, both components of the primary current must be measured and added together in order to obtain the proper result.

An apparent violation of the equivalence law for both sulphur[55] and rocksalt[38] (which was previously rendered yellow by exposure to x-rays) was found. These measurements, however, were made at voltages far below saturation voltages, in which case it is not surprising to find the photoelectric current to be much below the theoretically expected amount because of the failure of some of the electrons to reach the electrodes. Subsequent current voltage measurements[59] on yellow rocksalt have shown that saturation could also be obtained when sufficiently high voltages are used, and it seems reasonable to suppose that if measurements were made at saturation voltages, the quantum equivalence law would be verified. The yield in yellow rocksalt increased with increasing wave-length, quite according to the requirements of the quantum equivalence law; however, the quantity of charge observed per photon of absorbed light was much below the required amount.[38]

Influence of temperature on the primary current

The effect of temperature on the primary photoelectric current in diamond, zincblende and yellow rocksalt has been measured over a range of temperatures down to those of liquid hydrogen. The early work of Lenz[39] (Fig. 9) indicated a marked temperature effect on the steady state current, which was erroneously interpreted as a decrease in the negative primary current. Gudden and Pohl[40] suggested an explanation based on the space charge effect of the positive ions, and it was later verified by Lenz.[57] This pronounced temperature effect is in reality due to the building up of a positive space charge caused by the increasing sluggishness of the positive part at these low temperatures. The space charge formed due to the sluggishness of the positive primary current attained such magnitudes at low temperatures as to virtually nullify the applied potential. The narrowing and shifting of the absorption band towards shorter wave-lengths was not duly considered by Lenz. In later work in Pohl's laboratory, Lenz[57] was able to show that when proper considerations were taken of the change in absorption and formation of disturbing space charges *"the initial negative part of the primary current is independent of temperature down to* $-250°C$."

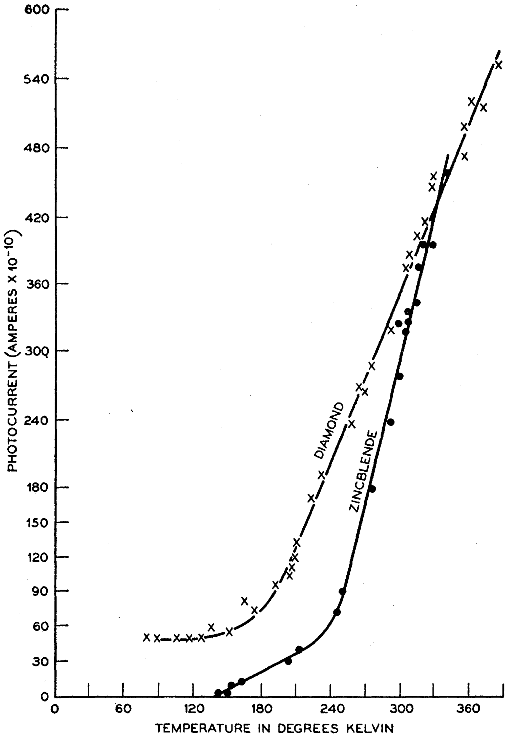

Fig. 9. The variation of the steady state photoelectric current with temperature.

It is not known whether or not the current voltage curves change with temperature. Spectral sensitivity measurements made on yellow rocksalt indicate that the photoelectric current changes only in accordance with the change in optical absorption. Lenz[39] observed that when electrons were shot into the crystal lattice with an electron-gun at various temperatures down to $-250°C$, the current was independent of temperature. Gudden[185] considers this to prove that the positive part of the primary current really consists in the displacements of the seats of positive charges.

Effect of magnetic field on the primary current

As early as 1916, Lukirsky[1] reported results obtained from Hall-effect measurements on yellow rocksalt, which indicated that the electric current resulting from irradiation with suitable light was electronic in nature. In more recent times, rather extensive experiments have been performed by Lenz[30] and to some extent by Arsenjeva,[41] on the effect of a magnetic field on the internal photoelectric effect. Lenz's measurements on zincblende and diamond indicated that the presence of a magnetic field would not influence the photoelectric effect. In the case of diamond, the Hall voltage was proportional to the magnetic field strength and increased proportionately to the electric field strength at low voltages, attaining a saturation value at 2500 volts per cm. The sign of the Hall voltage changed in a normal manner on reversal of the polarity of the magnetic field, giving the correct sign for negative carriers. The results on zincblende were not so consistent. However, normal behavior was observed when the trigonal axis was placed parallel to the lines of the electric field. In other crystallographic directions, the sign of the Hall voltage failed to change on reversal of the magnetic field. Hall-effect measurements made on currents obtained from placing electrons in the interior of the crystal lattice by means of an electron-gun gave results identical with those obtained from photoelectric currents. The Hall voltages were found to be independent of the temperature. As pointed out by Gudden,[185] these studies are of interest for the photoelectric phenomenon mainly because they furnish additional support for the contention that the primary current is electronic in nature.

Secondary currents

During the studies of Gudden and Pohl, it was found that the phenomena cease to conform to the laws above stated when voltage or intensity of light or duration of illumination exceed certain values. The effect ceases to be proportional to the light intensity (or time-of-illumination); spectral sensitivity curves are no longer independent of voltage; and saturation of photoelectric currents occurs with increase of voltage. Gudden and Pohl[9] ascribed these departures from the simple laws to the advent to what they called the "secondary current."

Taking in particular the relation of liberated charges Q to the time-of-illumination t, we may write in the most general case,

$$Q = at + bt^2 + ct^3 + \cdots.$$

If only the first term on the right is present ($Q \alpha t$), it is said that the current is "primary." If other terms are present, they are said to constitute the "secondary" currents.[9]

Fig. 10 shows, for a single crystal of ZnS and two wave-lengths of light, the effects of voltage on the curves of time-of-illumination *vs.* amount-of-electricity. For potentials up to *ca.* 1000 volts, the quantity of electricity was proportional to the time-of-illumination; for voltages above this value, it increased by higher powers of time. In Fig. 10b, an example is shown for a strongly absorbed wave-length; here a potential of 2000 volts produces a distinct deviation from proportionality of charge to time, though finally the two become proportional again with longer periods of illumination. Fig. 11b shows the variation of primary and secondary currents with light intensity.

The current values are obtained from results given in Fig. 11a. As explained in the preceding paragraph, primary current is given by the first term in the above equation, the secondary current by the second term.

The shape of the spectral sensitivity curves for the secondary currents depends upon the applied potentials (Figs. 12 and 13). For the cinnabar[23] single crystal of Fig. 12, potentials up to 100 volts gave currents which appear to be purely primary, with additional secondary components appearing as the voltage is increased; but with 200 volts, the current appears to be predominantly secondary. Fig. 13 gives the plot of the three spectral sensitivity curves, to the same scale, of current values *vs.* wave-length of incident light. These curves show quite clearly how the secondary current increases with increasing potential, finally predominating at higher voltages. In the case of polycrystalline ZnS phosphors, where secondary currents alone are observed, both time-of-illumination and voltage affect the spectral sensitivity curves. It follows from spectral measurements on materials in which secondary currents alone are observed that the spectral sensitivity curves cannot in any sense be considered as physical constants of the materials, whereas this appears to be the case where primary currents alone are observed.

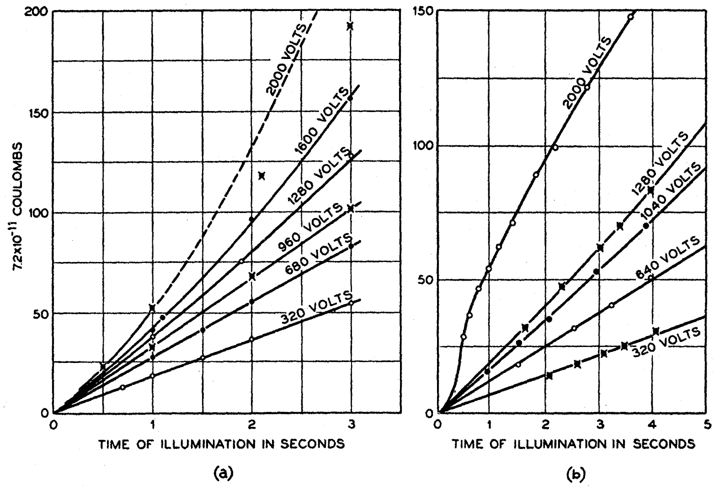

Fig. 10. Variation of quantity of charge with time-of-illumination. (a) Zincblende, crystal thickness 1 mm, illuminated area 1 $\overline{\text{cm}}^2$. Irradiated with 4050A of intensity $0.264 \cdot 10^{-7}$ cal/sec. $\overline{\text{cm}}^2$. (b) 3130A, light intensity $12.5 \cdot 10^{-7}$ cal/sec.$\overline{\text{cm}}^2$.

The photoelectric response for the primary currents was found to be proportional to the light intensity and time illumination, whereas for the secondary currents, as is to be seen from Figs. 14 and 15, the current increases initially approximately proportional-to-time, followed by a poor saturation with increasing time-of-illumination. The shapes of such photoelectric response *vs.* time illumination curves are a function of the previous history of the material. Fig. 14 shows such curves obtained from studies of secondary currents in greenockite.[2] The lower was obtained first, followed by subsequent measurements which gave the middle and upper curves respectively. One is struck by the extreme similarity between such curves and those obtained on commercial selenium and thalofide cells. We have also obtained similar curves for single crystals of metallic selenium. In Fig. 15, note how the current slowly increases with time, finally reaching a steady condition, then slowly decreases when the light is discontinued.[34]

The secondary current depends upon the mode of illumination, i.e., whether transversal or longitudinal, and also on the wave-length of the light used.[23] This is illustrated in Fig. 16. We would expect (because of great absorption in surface layers) the largest secondary currents to be observed in Figs. 16A and C, where 16A and B represent the condition for light strongly absorbed with the one type of illumination, and 16C and D that for light moderately absorbed.

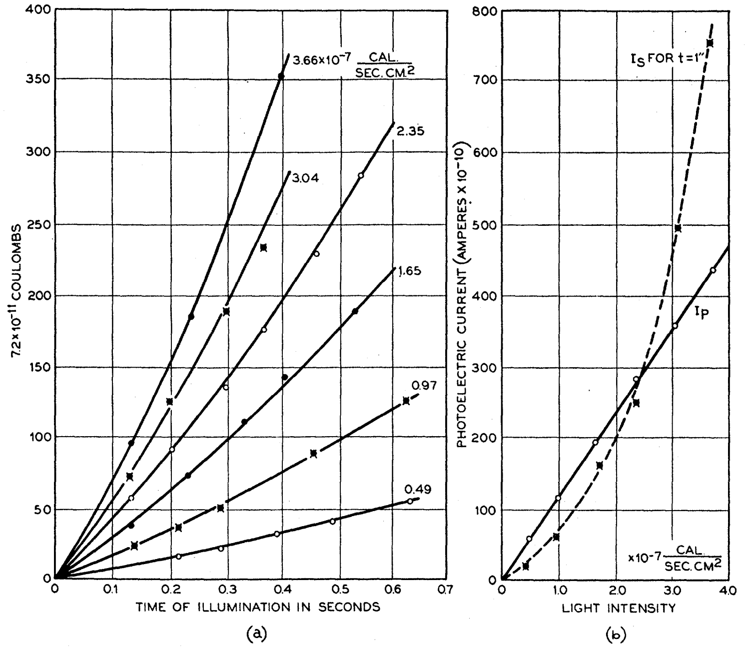

Fig. 11. Separation of the primary and secondary current in a zincblende crystal. In (a) is shown the variation of quantity of electricity with time-of-illumination for various light intensities; in (b) the primary current, I_P, and the secondary current, I_S, are plotted against light intensity.

This secondary current is thought to result from a primary process (that is, the reader will recall the ejection of an electron by the absorption of the photon giving rise to the negative part of the primary current followed by the flow of the positive component). It is often accompanied by a permanent decrease in the resistance of a crystal. In their earlier papers, Gudden and Pohl[9] were inclined to consider the secondary current to be electrolytic in nature. However, in later papers, they appear to have discarded this view.

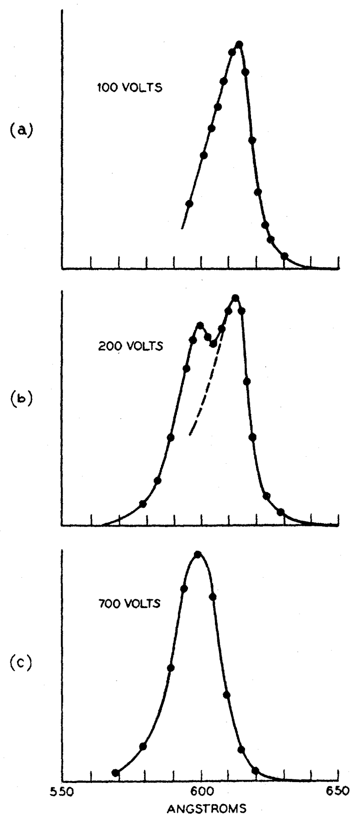

Fig. 12. Development of secondary current with increasing voltage in a cinnabar single crystal. The scale of ordinates is not the same for the curves *a*, *b* and *c*. Thickness of crystal, 1.35 mm.

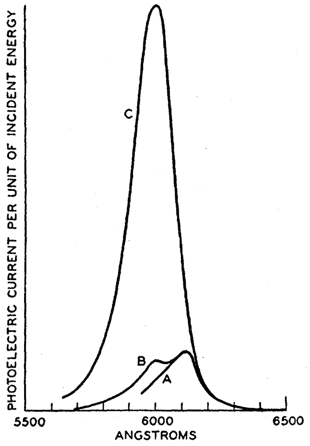

Fig. 13. Results given in Fig. 12 plotted to the same scale for the different voltages.

It is the opinion of the writer that the available evidence is not sufficient for developing a theory of this current component. It has often been, in the case of conduction of dielectrics, that actual transport and deposition of material must be observed before the current can be described as electrolytic in nature. Secondary current was observed in diamond, in which case it is rather difficult to imagine the existence of an ionic transport of material. Analogies have been suggested between the secondary current in photo-conduction and that part of the current in a self-sustaining glow-discharge which consists of ions formed in the gas itself.

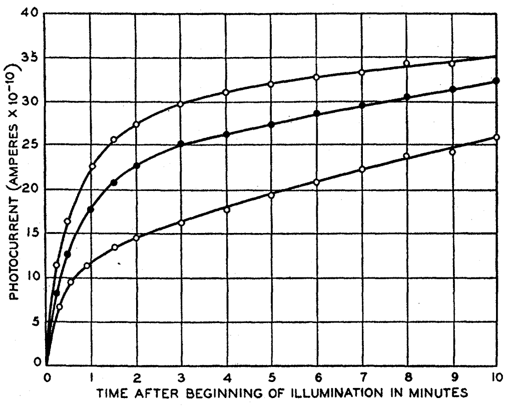

Fig. 14. Photoelectric current *vs.* time-of-illumination for greenockite.

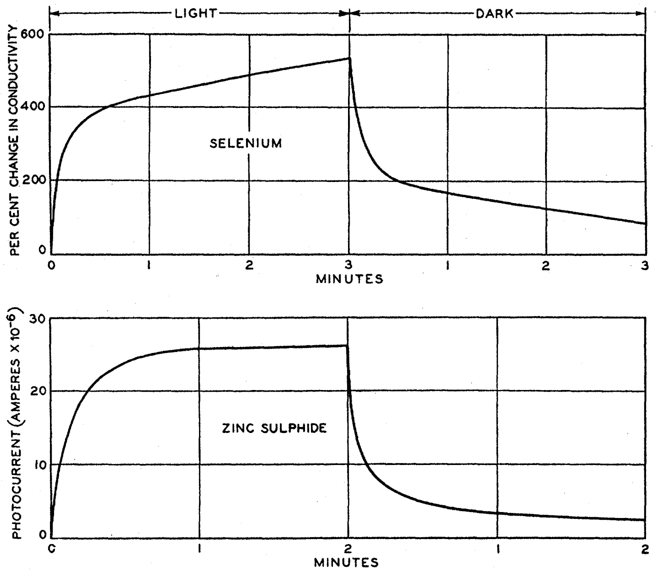

Fig. 15. Photoelectric response *vs.* time-of-illumination for selenium and polycrystalline zinc sulphide.

At any rate, it seems preferable to conceive the secondary currents as currents due not directly but indirectly to the absorbed light. From this picture, the terms observed in selenium, polycrystalline, ZnS, HgS, MoS_2, Ag_2S, CdS are actually secondary currents, the primary being masked by the former. Gudden and Pohl have often contended that intercrystalline boundaries act as hindrances to the passage of an electron current, but facilitate the passage of an electrolytic current (it is well known that they behave thus in ordinary electrolytic conductors). This, however, does not explain why primary currents are not observed in single crystals of grey metallic selenium. Currents in this variety of selenium have approximately the same properties for both mono- and polycrystalline states.

We shall discuss the semi-conductors in the next section and attempt to point out the various similarities between the currents which light produces in these, and the secondary currents of good insulators (in which also primary currents are the only ones observed). The resemblance is so pronounced as to lead one to believe that the currents hitherto observed in semi-conductors are in reality the secondary currents discussed in this section.

Photo-conductivity in allochromatic crystals

Joffé and Röntgen[13] observed that sunlight has a considerable effect on the influence of x-rays on the conductivity of rocksalt. It was then established that when various alkali halides, notably rocksalt and sylvin, had been irradiated with x-rays, and were then exposed to light of the visible spectrum, the light increased their conductivity greatly. This effect was correlated with another; a *coloring* of the crystals by x-rays and by other agents. The crystals assumed a yellow color on moderate exposures to x-rays at room temperature. This same coloration was also obtained by F. Giesel and by Siedentopf[49] by the impregnation of a clear rocksalt crystal with sodium vapor. This is accomplished by placing the crystal in a hot closed vessel containing sodium vapor. The diffusion of the vapor into the crystal lattice is accompanied by a coloration of the crystal. Goldstein observed a similar coloring of clear rocksalt crystals produced by ultraviolet radiation. It has since been found that *alkali halide crystals of any specific kind colored by any of the above processes*, i.e., by exposure to ultraviolet or x-radiation or to the vapors of the element which forms the cation of the salt in question, *are photosensitive and possess identical optical and photoelectric properties.*[47] Such crystals have been called (as I mentioned above) crystals of the second kind, or allochromatic crystals.

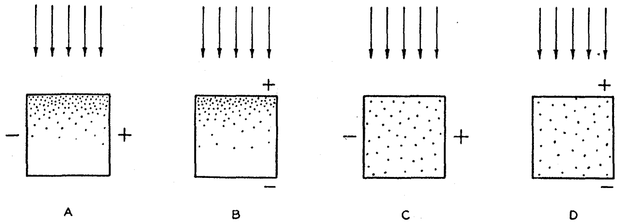

Fig. 16. Distribution of absorption centers. *A* and *B* strongly absorbed light; *C* and *D* weakly absorbed light.

This coloration is ascribed to so-called "centres" which the various agents call into being: It seems most probable that these centres are neutral metallic particles, which in the special case of yellow rocksalt may be individual atoms of sodium. The reason for assuming this degree of dispersion is the fact stated above—that the photoelectric and optical properties are the same, whatever the agent which brought about the coloration. Also, for the alkali halides, the energy corresponding to the first characteristic absorption band in the extreme ultraviolet region agrees well with the theoretical value for the energy of transfer of an electron from an anion to the cation.[82,71] The silver halides do not possess sufficiently sharp characteristic frequencies to make possible a similar computation.

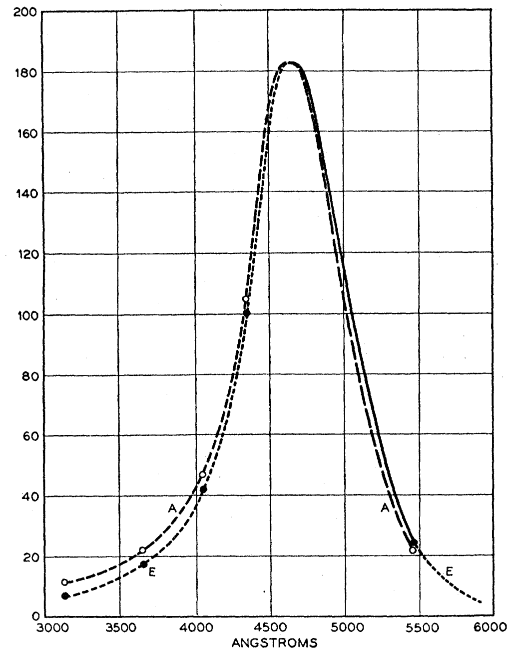

Fig. 17. Spectral distribution in yellow rocksalt. (*E*) photoelectric response, (*A*) absorption coefficient.

It is well known that a bleaching out of these coloration centres is accompanied by a disappearance of their absorption band. The absorption spectrum of a rocksalt crystal after it has been bleached is identical with that of the original colorless rocksalt, i.e., the crystal reverts to its original condition. This complete disappearance of the absorption band, resulting from the active centres on irradiation with light in the band was not observed for silver and thalium halides. We shall return to this in a later section.

The optical-absorption and photoelectric properties of the materials depend on the degree of coagulation of the neutral metallic atoms. This is illustrated by yellow rocksalt, containing individual sodium atoms dispersed throughout the crystal, and that of blue rocksalt, in which the particles are large clumps of sodium. The particles may range from individual atoms to clumps of colloidal dimensions. Hitherto, studies have been confined to the two extreme cases: That of crystals with individual metallic atoms scattered through their volume (e.g., yellow rocksalt) and that of crystals containing clumps of foreign matter, e.g., blue rocksalt. In the former case, simple relationships were found between the optical-absorption and the photoelectric properties; with blue rocksalt, no simple relationship was observed.[45] We shall return in a later section to a more detailed study of these centres and their relationships to the latent photographic image.

Fig. 17 depicts the absorption spectrum and photoelectric response for a rocksalt crystal after irradiation with x-rays.[38] The full drawn curve (E) represents the photoelectric response, the dashed curve (A) gives the variation of the absorption constant, plotted against wave-length.

Notice the striking difference between the relations of optical absorption and photoelectric spectral sensitivity in these allochromatic crystals and those for the idiochromatic crystals described in preceding pages. In idiochromatic crystals, each spectral-sensitivity curve has a maximum in the long wave edge of the absorption band and drops off to an immeasurably small value in the interior of the band; but these spectral-sensitivity curves for the allochromatic crystals follow those of the optical absorption. The curve shown in this figure for the spectral photoelectric sensitivity is slightly displaced from the other in the direction of larger waves, as is to be expected from quantum relations. (Arsenjeva,[41] on the other hand, found no such displacement, but reported an exact agreement between the absorption and photoelectric sensitivity curves. Gudden[185] believes this disagreement to be due to the failure of Arsenjeva to consider the ineffective light absorption of the colloidal particles.)

The yellow rocksalt gave a primary current when irradiated with suitable light, the initial values of which were proportional to the incident light intensity. The photo-current gradually decreased with time because of the building up of a positive space charge. When the complete crystal was illuminated, a steady state value of the primary current was reached; if only a part of the distance between the electrodes was illuminated, this current decreased to an immeasurably small value. The negative part of the primary current began, as in the case of the idiochromatic crystals, in less than 10^{-4} second after the onset of illumination (Flechsig[31]). The primary current increased initially proportional to the applied potential, followed by a gradual saturation just as was described for the idiochromatic crystals. The fields required to produce the saturation-current, in rocksalt treated by x-rays, were much higher than those required with zincblende, or diamond. Indeed it was not until as late as 1928 that saturation was obtained: In that year, Flechsig[59] achieved it by using extremely thin slabs of a cleaved rocksalt crystal (0.1 mm thickness).

Earlier tests of the quantum efficiency in rocksalt (Gyulai[38]) gave for the yield values *ca.* 1/3000 of the equivalence value; but since these measurements were made at voltages below saturation, it was not possible to decide definitely whether or not the electrons moved only 1/3000 (mean value) the thickness of the crystal or only a fraction of the absorbed light was effective in the ejection of electrons. The saturation voltage found by Flechsig agreed well with the value expected from Gyulai's measurements,* so that one can consider this to be another verification of the quantum equivalence law. This result permits all the processes hitherto studied to be unified under one general scheme, regardless of the nature of the active centres.

Experiments have been reported by Podaschewsky[62,64] showing that the photo-current decreases with increasing degree of plastic deformation. This is also accompanied by a shift in the position of the maximum and the long wave side of the spectral-sensitivity curve towards longer wave-lengths. If the deforming load is removed, the spectral sensitivity distribution gradually suffers a regression in a few days to its former state.

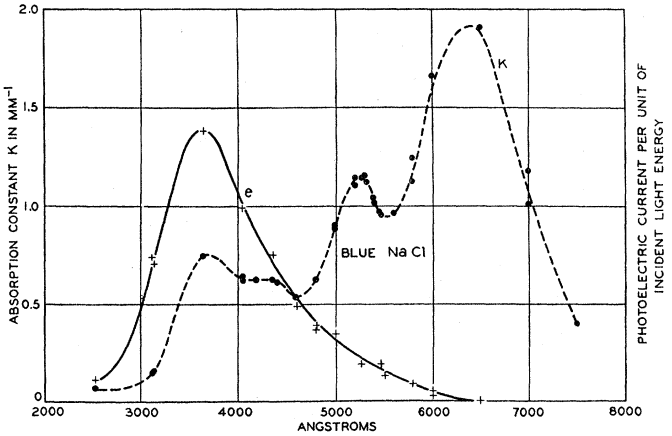

Fig. 18. Spectral distribution of photoelectric response (*e*) and absorption coefficient (*K*) for blue rocksalt.

With sodium particles of colloidal dimensions, the simple relationship between optical absorption and photosensitivity no longer exist. Fig. 18 shows the complex absorption curve for blue rocksalt (containing submicroscopic particles of sodium) and the curve of photoelectric sensitivity.[45] Gudden and Pohl consider that the absorption of light leads not only to the ejection of valence electrons, but also to heating of the crystal. This seems a plausible way to account for lack of close resemblance between the absorption spectrum and the photoelectric sensitivity curve. The similarity between the spectral sensitivity curves of the external photo-effect of massive sodium and the internal photo-effect of blue rocksalt is so striking as to lead one to suspect a close relationship between the two curves.[51] It was found that there was no additional flow of charge when the first illumination was followed by illumination with long wave light.

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* Gyulai estimated that the electrons moved on the average 1/3000 of the thickness of the crystal. The extrapolated voltage necessary to obtain saturation, that is, for all the electrons to reach the anode, agreed well with saturation voltage found by Flechsig.

The various steps in the flow of the primary currents in colored rocksalt crystals were very clearly illustrated by measurements made at different temperatures and light intensities as shown in Figs. 21 and 22.[35] These measurements were made with two different light intensities and at three temperatures.

Curve *bc* in Fig. 19a gives the sudden jump due to the onset of the negative part of the primary current on beginning of illumination, followed by a steady flow of current. The slight decrease in the current is attributed to a slow building up of an opposing potential, due to the formation of positive space charge. At the end of this illuminated period, the current dropped to a new value *f*. During this darkened interval, a current *fk* flows which is considered to be the positive primary current. On illumination with infrared light, the larger part of these seats of positive charges are displaced to the cathode. The obliquely shaded area illustrates a flow of this current which can be observed for a considerable time at this temperature. Fig. 20b shows similar measurements made at a higher temperature, 77°C. The current on beginning of the illumination obtained approximately the same value as in

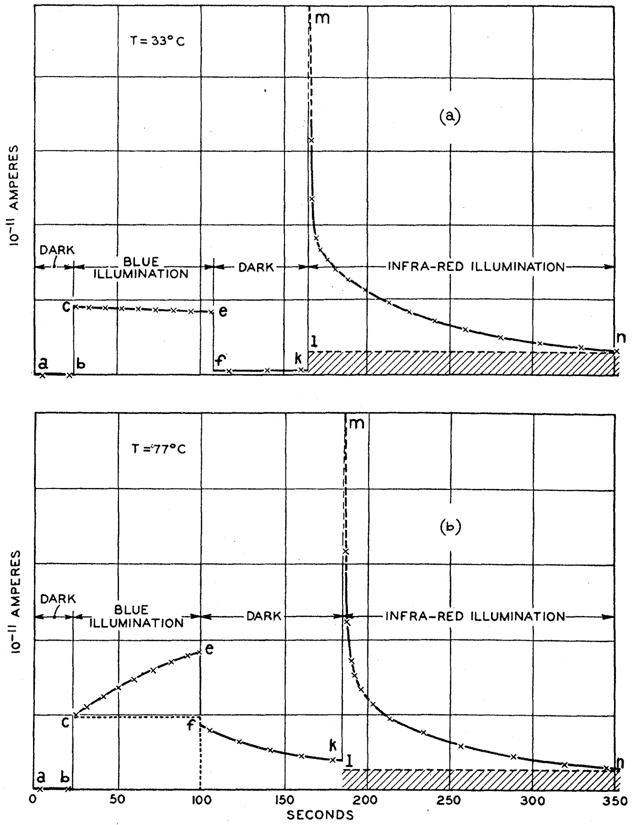

Fig. 19. Photoelectric currents in rocksalt at 33°C and 77°C. Light intensity weak.

the above described test (33°C); however, the current gradually increases because of the flow of trapped electrons and the greater ease of flow of the positive primary current. The behavior during subsequent periods of darkness and infrared illumination were much the same as for the 33°C experiment. Fig. 20a shows decidedly more complications. The curve *cde*, following the instantaneous flow of the negative primary current, represents the same general behavior as described for the 77°C experiment; of fundamental importance is the value *d* reached by the current. This exceeds the initial jump *bc* by more than twofold, indicating quite clearly that the trapped electrons are contributing considerably to the current. The small value of the current in the subsequent dark and "infrared illuminated" periods shows quite clearly that the larger part of the positive primary current flows simultaneously with the negative. The area, shaded with vertical lines, represents the electrolytic conduction of rocksalt at this elevated temperature. Fig. 20b corresponds to conditions like those of Fig. 19b except that the intensity of the light is much higher. The negative primary current decreases rapidly with increasing time-of-illumination (curve *ce*). These curves alone suffice to show that initial values only of the primary current may be used in the study of the primary photoelectric phenomena.

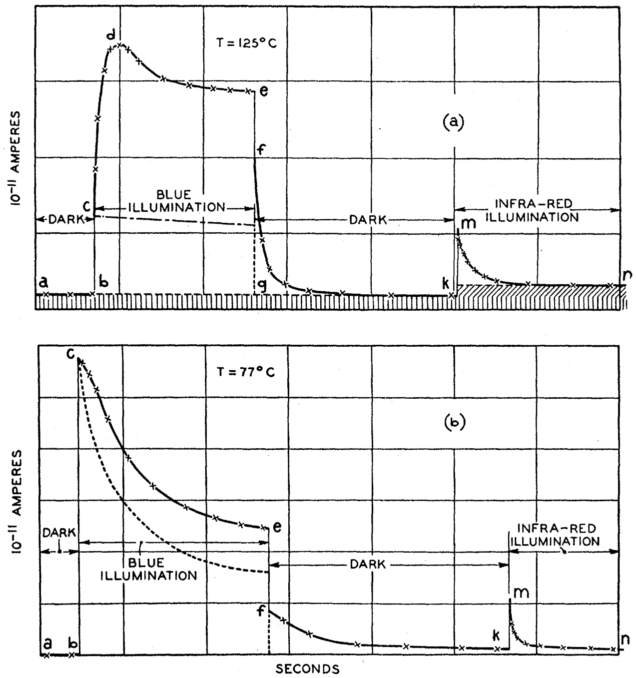

Fig. 20. Photoelectric currents in rocksalt. (a) at 125°C (weak light intensity), (b) at 77°C (strong light intensity).

Crystal excitation and the positive primary photoelectric current

Röntgen and Joffé[13] in their early investigations found that the spectral sensitivity curves of yellow rocksalt colored by irradiation with x-rays are influenced by the order in which the measurements are made. When measurements are made with successively greater wave-lengths, the maximum of the curve is lower and extends further toward the red than when they are made with successively smaller wave-lengths. This peculiar phenomenon can be explained from results of Gudden and Pohl's extensive investigations. Curves plotted from absorption measurements on yellow rocksalt were found to vary in much the same manner as the spectral sensitivity curves of Röntgen and Joffé.

Curve 1 of Fig. 21a is the absorption curve for a crystal obtained by a series of measurements at the various indicated wave-lengths, with a period of illumination by infrared light interpolated between each pair of measurements.[37] It is supposed that the infrared light restores the crystal to the so-called normal state. When, however, measurements are made at the indicated wave-lengths, with a period of illumination by light of frequency near the high-frequency side of the induced absorption band, interpolated between each pair of measurements, curve 2 of the aforesaid figure was obtained. Curves 1 and 2 of Fig. 21b, relating to photoelectric effect instead of absorption coefficient, were obtained in a similar manner. The alteration of the state

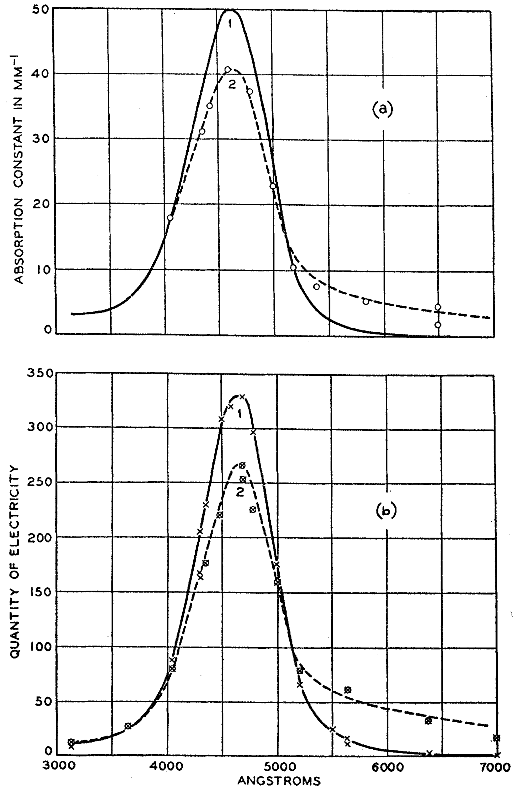

Fig. 21. Spectral distribution of photoelectric response and absorption in rocksalt.

of the crystal, produced by visible or ultraviolet light and revealing itself in altered absorbing power and photoelectric response, is called *excitation*; the crystal is said to have been excited.

Crystal imperfections and heating of the crystals affect the absorption in much the same manner as excitation. Flechsig[43] found that synthetic rocksalt crystals possessed a much broader and flatter absorption band than the natural mineral. As the temperature is lowered, the band becomes narrower, with a shift in the maximum towards shorter wave-lengths. The magnitude of the excitation, as measured by the difference in the absorption coefficients of curves 1 and 2 in Fig. 21a, is also a function of the temperature—the lower the temperature, the greater excitation attainable.

Excitation has been observed with a large number of the alkali halides; not, however, with the halides of silver and thallium.[75]

The investigation of the effect of excitation on the absorption in idiochromatic crystals has been limited to a few measurements on diamond on the long wave side of the absorption band. The absorption in this spectral region increased on excitation, in much the same manner as was described for the alkali halides. Experimental difficulties prevented measurements in the interior of the band. In the red insulating variety of selenium, excitation caused the photoelectric sensitivity to be increased (Fig. 22) on the long wave side of the spectral sensitivity maximum in much the same manner as was shown for yellow rocksalt; however, no detectable change was observed in the remainder of the spectral sensitive region.[34] The crystals were too small for measurements of absorption; nevertheless, it can be fairly safely assumed that the absorption would be affected in much the same way. The results of these investigations might possibly be interpreted as showing the difference between the excitation for the two crystal classes.

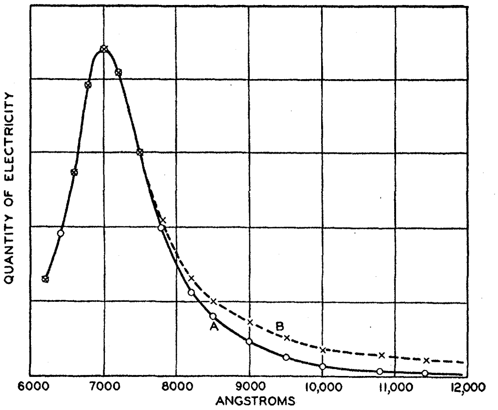

Fig. 22. Photoelectric spectral distribution in the red insulating variety of selenium. (*A*) Normal state; (*B*) "excited" state.

In the numerous publications from Pohl's laboratory in late years, the view has consistently been taken that preferred centres in the crystals themselves, rather than the normal atoms or ions of the lattice, are to be considered as the seats of the photoelectric processes. It is my opinion that very little direct evidence exists in support of this view; however, some observations indicate that such is the case. It is rather difficult to understand why no well-defined threshold exists for the onset of electron ejection by light in the interior of the crystal, if the normal atoms or ions of the space lattice are considered to be the seats, at which the processes occur. The differences in the shape of the absorption band observed with crystals of varying degrees of imperfection indicate that the centres are directly affected by the physical state of the crystal. This view of Pohl and his collaborators is closely akin to a theory propounded by Smekal to account for the electrolytic conductivity in salts, in which, he ascribes a large part of the conduction at low temperatures to *Lockerionen*, situated at fault places in the lattice. Zwicky has postulated the existence of a mosaic structure in crystals, supposing regions of constant density arranged in block formation and separated by others of different density. Further considerations of such theories would lead us too far afield.

Excitation is thought to arise from disturbances caused by ejection of electrons by the absorbed light.[44] When light ejects an electron from an active centre, it moves through the crystal lattice under the influence of an applied electric field if one is present; if there is no field, the electron probably moves some distance from the active centre by virtue of the energy received from the absorbed photon. When the crystal is sufficiently free from imperfections, a saturation current is finally reached at high voltages, as was described in a foregoing section; the electrons quit the crystal. The centres are then positively charged. The absorption band should then move towards shorter wave-lengths if the centre is to be thought of as remaining positively charged. In view of the fact that the absorption domain does not shift in this expected direction, it is supposed that the centres lose their positive charge, thereby reverting, more or less, to their former state. Gudden and Pohl consider the loss of the positive charge by the centre to consist in the capture of an electron from a neighboring ion or atom. These processes then continue until the centre finds itself strongly influenced by the positive charges in its immediate vicinity, and is thus capable of absorbing light of longer wave-length than was hitherto possible. This would account for the extension and increase of the absorption on the long wave side of the absorption band. As the process of electron ejection and subsequent capture by the centre from one of its neighbors continues, the area from which the capture of the electrons occurred suffers a kind of change similar to recrystallization, in that these positive ions themselves receive electrons from another group nearer the cathode, thereby becoming neutral again. This process is thought to continue until all the unbalanced positive charge left behind in the crystal by the ejected electrons has once more been balanced by electrons coming ultimately from the anode—the process which manifests itself in the flow of the positive primary current. This process can be accelerated, as was previously discussed in foregoing sections, by means of long wave-length light or by heating. The lower the temperature, the slower it is. There remains much work to be done in the clarification of the rôle played by the long wave light.

The induced absorption centres in allochromatic crystals and the photographic latent image

The allochromatic crystals can be rendered photosensitive by the several processes discussed in the section dealing with the general photoelectric properties of such crystals. Of these various processes (irradiation with x-rays or ultraviolet light and exposure to the vapors of the metal which forms the cation of the crystal), the irradiation with ultraviolet light is the most suitable for making quantitative measurements on the production of such centres. Any absorbed light, with the exception of the residual rays and infrared, gives rise to these centres, the properties of which are independent of the wave-length of the light used. The alkali halides in general possess characteristic absorption bands lying in the deep ultraviolet, whereas the induced centres absorb light in the visible region of the spectrum, their so-called induced absorption bands having simple bell-like forms. The centres disappear when the crystal is exposed to light of frequency which they absorb: They are said to be bleached out, with disappearance of the induced absorption band. The absorption of the bleached crystal is limited to the original characteristic absorption in the ultraviolet.

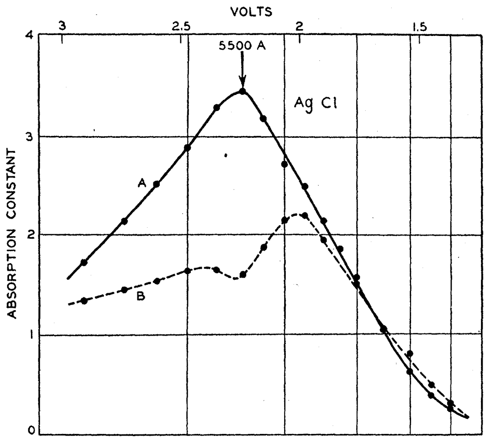

Fig. 23. Absorption spectrum of the induced centres in AgCl. (*A*) normal absorption curve; (*B*) absorption after irradiation with intense 5500A light.

The bleaching process is *irreversible*, in contrast to the *reversible* excitation. Both processes often occur together, the relative prominence of the two being a function of the temperature. With the alkali halides, light of any frequency included in the induced absorption band is capable of bleaching all the centres; but with silver halides, light of any particular frequency bleaches only a fraction of the centres. This is best represented by Fig. 23. The full drawn line (*A*) represents the absorption of the induced centres.[75] After exposure to an intense beam of 5500A light, the absorption for AgBr changes considerably in the vicinity of this wave-length, but not appreciably in other parts of the band. This is illustrated by the dashed curve (*B*). The bleaching out of the induced centres in some silver halides is rendered very difficult because of the overlapping of the characteristic absorption regions of the uncolored crystal with those of the induced centres, so that the same light simultaneously bleaches and colors the substance. Fig. 24 illustrates such an overlapping of the two absorption regions for silver chloride.[75] Silver halides, in contrast to the alkali halides, do not possess pronounced characteristic absorption maxima.

The formation of the centres by light is considered to consist in an electron transfer from a negative to a positive ion of the crystal lattice. This is represented by

$$M^+ + H^- \rightarrow M + H.$$

This theory was advanced by Fajans, and independently by Sheppard and Trivelli, to account for the formation of the photographic latent image. The latent image, in the case of AgBr emulsions, is considered to consist of free silver and bromine; the silver forming the nucleus, on which additional silver is deposited during the chemical reaction in the developing process. Pohl and Hilsch[75,79] succeeded in producing concentrations of induced centres in single crystals of AgBr comparable to those of the ordinary photographic latent image. From optical measurements, this concentration was found to be *ca.* $3.6 \cdot 10^{15}$ or one centre for every $6.2 \cdot 10^6$ molecules. It was found that the quantum equivalence law was fulfilled for small concentrations of induced centres in AgBr single crystals, i.e., one centre was formed for every quantum of light absorbed. Eggert and Noddack found that approximately one silver atom was liberated for each quantum of absorbed light in a thin layer of AgBr emulsion. This striking similarity between the results obtained in AgBr single crystals and AgBr emulsions led Pohl and Hilsch to identify the induced centres with the photographic latent image; in which case, we could speak of the absorption band of the induced centres as that of the latent

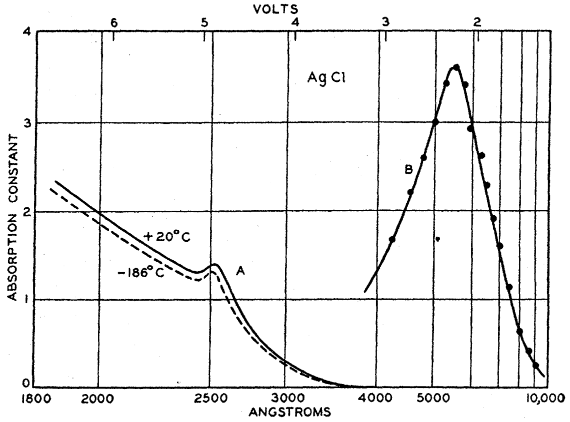

Fig. 24. Absorption spectra of AgCl. (*A*) Characteristic absorption band. The absorption constants are of the order of 10^5 mm^{-1}. (*B*) Induced absorption band. The maximum absorption constant is of the order of 0.1 mm^{-1}.

image. It is also of interest to note that the more imperfect a crystal is, the greater the concentration of centres attainable.

Fig. 25 shows, in contrast to the relations for the characteristic and latent image absorption regions in AgCl, an apparently wide separation between the locations of the two regions for KBr.[82] This, however, is generally characteristic of the alkali halides. The surprising results given in Fig. 26 were obtained on illumination of a previously "colored" KBr crystal, with light of wave-length in the latent image absorption band. Curve *OAB* shows the ballistically measured flow of electricity with time-of-illumination for a freshly colored KBr crystal. Measurements obtained on subsequent illumination with the same light are given by curve *OC*. The branch *OA* of curve *OAB* is interpreted as due to the breaking down of the centres previously produced by irradiation with ultraviolet light, the section *AB* and curve *OC* as due to the simultaneous building up and breaking down of centres. This interpretation necessitates the overlapping of the characteristic and latent

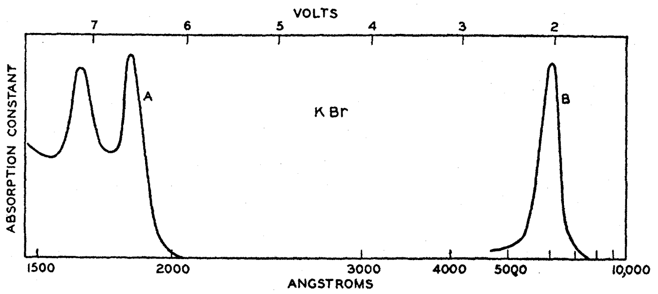

Fig. 25. Absorption spectra of KBr. (*A*) Characteristic absorption; (*B*) induced absorption band.

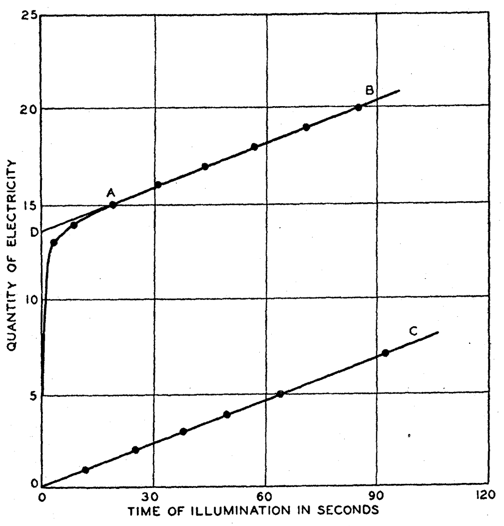

Fig. 26. Photoelectric response *vs.* time-of-illumination for KBr.

image absorption bands. The existence of such overlapping of the absorption regions furnishes a powerful method of following the long wave side of the characteristic absorption band out to much longer wave-lengths than is possible by ordinary photometric means. This method depends on the fact, that no flow of charge is observed in a crystal to which a potential is applied while the induced centres are being formed; whereas, the irradiation of the latent image with suitable light is accompanied by a flow of electrons under such conditions. This permits one to irradiate a clear crystal with light on the long wave side of the characteristic absorption band and thereafter to ascertain whether or not absorption occurred. If absorption has occurred, we will find that if we illuminate with light on the long wave side of the induced absorption region, a flow of electric charges will result. By this means, Hilsch and Pohl were able to follow the tail of the long wave side of the first characteristic absorption band out to 3650A.

This implies a simultaneous formation and breaking down of the latent image which has led Pohl[82] to suspect that perhaps the largest source of the photoelectrically active centres might be sought in these induced centres.

PHOTO-CONDUCTION IN SEMI-CONDUCTORS

In the years from 1900 to 1917, a large number of inorganic and organic solid materials were discovered to possess photosensitivity, having characteristics similar to their forerunner, selenium. Amongst the more or less simple inorganic compounds are to be named stibnite (Sb_2S_3), mercuric iodide (HgI_2), molybdenite (MoS_2), cuprous oxide (Cu_2O), bismuthinite (Bi_2S_3), argentite (Ag_2S), silver and thallium halides, and iodine; in addition, many complex metallic sulphides, carbonates, and also a rival of the commercial selenium cell, thalofide. All of the investigations were performed on polycrystalline materials; the primary current discussed in the foregoing sections was not observed, presumably because of lack of purity and uniformity in the materials. The very large number of investigations on the grey metallic variety of selenium (about 2000 in number) produced no understanding of the underlying processes. It remained for Gudden and Pohl,[34] who discovered the red insulating variety of selenium to be photosensitive, to show quite clearly that this variety possessed photoelectric properties which permitted it to be classed among the group of insulators comprising diamond, zincblende, cinnabar, etc. However, this does not justify a recent assertion by Joffé,*[1] that photo-conduction in the *grey metallic variety* has been appreciably clarified.

These studies of semi-conductors possess interest for this article largely because of the pronounced similarity of their photoelectric characteristics to the secondary currents discussed in the foregoing section. This is best seen in the extensive studies made by Coblentz and his collaborators in the United

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* "It is especially satisfactory that Pohl and Gudden succeeded in clearing up the problem of the photoelectric conductivity of selenium which, because of its practical importance was repeatedly studied and created quite an extensive and inconsistent literature." That this statement is inaccurate and misleading will become more obvious in the following pages.

States Bureau of Standards. Fig. 27a shows the results obtained from studies on the mineral molybdenite (MoS$_2$[108,106,107]). The photoelectric current increases slowly as one passes from the deep infrared to shorter wave-lengths of light. The short wave maximum in the photoelectric sensitivity curve occurs at the long wave edge of the absorption band. This, it will be recalled was the behavior of the primary currents observed with idiochromatic crystals of insulators. The optical absorption extending out into the infrared is attributed to the electronic dark conductivity of this material. Fig. 27b illustrates the variation in the photoelectric response with light intensity for two wave-lengths. It is of interest to note that the longer the wave-length of the incident light, the more nearly is proportionality attained between photoelectric response and light intensity.

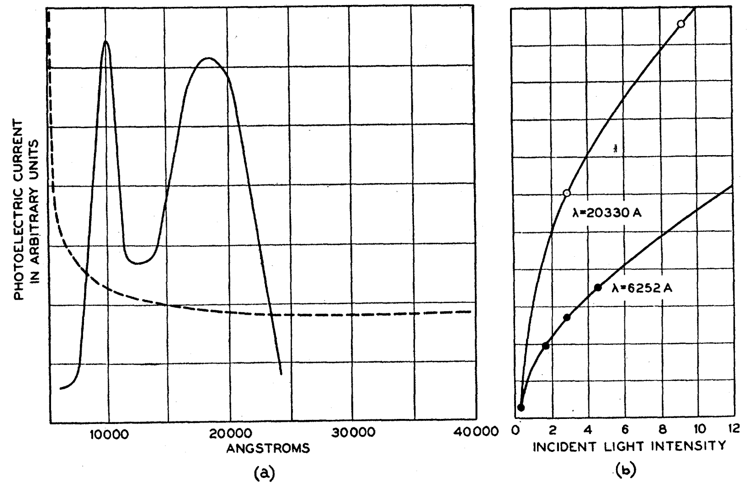


Fig. 27. Spectral photoelectric response and absorption for the mineral molybdenite. (a) —Photoelectric response;--absorption. (b) Photoelectric response *vs.* light intensity.

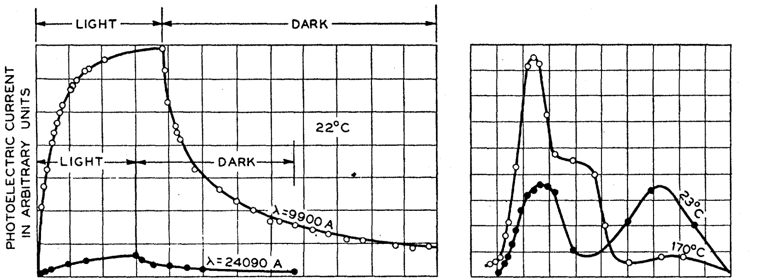
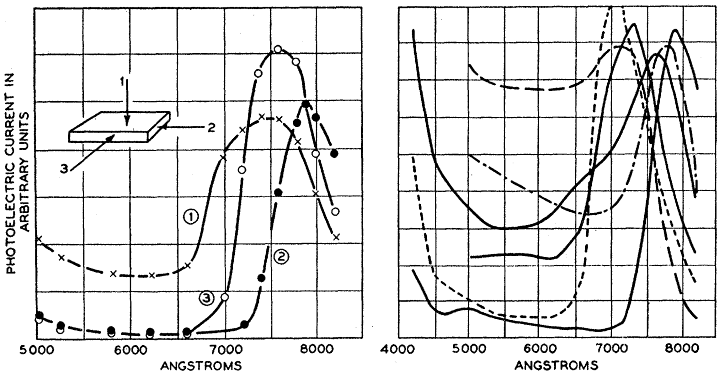


Fig. 28. Molybdenite. (a) Photoelectric response *vs.* time-of-illumination. (b) Photoelectric spectral distribution at 23°C and 170°C.

Fig. 28a depicts the variation in photoelectric current with time-of-illumination for several wave-lengths in MoS$_2$. The resemblance is most pronounced between these curves and those given for grey metallic selenium and polycrystalline ZnS. Fig. 28b shows the effect of temperature and applied voltage on the spectral sensitivity curves of MoS_2 crystals. In many of these investigations, considerable dark conductivity was encountered. The voltages at different temperatures were varied in order to obtain dark currents of equal magnitudes. This procedure, of course, masks somewhat the effect of temperature on the spectral sensitivity curves. The curves show quite clearly the arbitrariness involved in the selection of current values. They resemble the curves given in the section treating secondary currents in insulators: The electric currents resulting from irradiation of the materials discussed in his section are believed by Gudden and Pohl to be identical with the secondary currents. The photoelectric response curve is not to be considered as a physical constant of the material, since it is a function of the past history thereof, as well as the light intensity, temperature and applied voltage.



(a) (b)

Fig. 29. Spectral photoelectric response for single crystal of metallic selenium. (a) Effect of illuminating a single crystal in different directions. (b) Spectral sensitivity curves for a number of single crystals.

Earlier measurements on cuprous oxide, by Pfund,[95] and also by Coblentz,[115] indicated that this material should be classed among the semi-conductors, yielding only secondary photoelectric currents. Recently, however, Gudden[67] has reported measurements from the Erlangen laboratory which show that the photoelectric currents obtained under some conditions possess the characteristics defining primary currents.

Published photoelectric current measurements on mercuric iodide[96,113,119,130] possess characteristics which indicate that secondary currents alone were observed. However, recent results of the writer on single crystals of HgI_2 indicate that primary currents are observed when care is taken to eliminate disturbing surface conduction.

Selenium (metallic variety)

The investigations on metallic selenium prior to about 1913 were made exclusively on polycrystalline material. These materials were rendered photosensitive by annealing previously deposited amorphous selenium at *ca.* 150°C thereby transforming it into the light-sensitive metallic variety. The first essential step towards clarification of the problem was made by Brown[84,87,88] and his collaborators when they produced single crystals of photosensitive selenium from the vapor phase. Photoelectric measurements on these crystals yielded spectral sensitivity curves which were functions of the crystal orientation. Fig. 29a shows this variation in the photoelectric spectral curves with the position of the incident light beam on the crystal. Transversal illumination was used exclusively. Fig. 29b depicts a series of spectral sensitivity measurements on a number of single crystals. These curves (Fig. 29b) resemble the spectral sensitivity curves for a number of commercial selenium cells made by various processes. The change in current on illumination of selenium is not proportional to the light intensity, but varies roughly as the square root thereof. This is true both for single crystals and for polycrystalline selenium.

Transmitted effect

It was observed by Brown[86,90] that when a single crystal of selenium was placed between electrodes and allowed to extend beyond them, using the usual series connection of battery and galvanometer, a change in conductivity was observed when the portion of the crystal outside the electrodes was illuminated with light. The photoelectric characteristics of this so-called transmitted effect were found to be identical with those of the normal change in conductivity on illumination of the selenium between the electrodes. Extensive searching has failed to find this mysterious effect in other photosensitive materials. This led Gudden[185] to question its existence. I have repeated and confirmed Brown's experiments on hexagonal single crystals of selenium of about 2 cm in length. General radiation from a tungsten lamp was allowed to fall on a small portion of the crystal some 10 mm distant from the outer edge of the electrodes. Photoelectric response *vs.* light intensity measurements on many crystals showed the photoelectric current to be proportional to the light intensity, whereas with other crystals it turned out to be proportional to the square root of the incident light intensity. I was unable to find a cause for these contradictory results.

PRODUCTION OF ELECTROMOTIVE FORCE IN SEMI-CONDUCTORS BY LIGHT

The occurrence of an electromotive force excited by light, in photosensitive semi-conductors which undergo changes in resistance when illuminated, has been observed in many substances in the past several decades. Adams and Day[137] noticed that electric current flowed on illumination of contacts between pieces of platinum and a piece of selenium, the circuit being closed through a galvanometer without a battery. Similar effects have been observed in various commercial selenium cells, as well as single crystals of the metallic variety of selenium. Other materials showing a similar phenomenon are molybdenite (MoS_2), argenite (Ag_2S), acanthite (Ag_2S), Cu_2S, Cu_2O, PbS, diamond.

Grondahl and Geiger[147,148] appear to have been the first to observe that an electromotive force is produced in a cuprous oxide rectifier by irradiation of the oxide surface. Illumination provokes the flow of an electric current when the copper base is connected in series with a low-resistance galvanometer and an auxiliary electrode on the Cu_2O surface without an external source of potential; Fig. 30 shows schematically the rectifier with circuit and illustrates the effect. The production of an electromotive force in Cu_2O rectifiers has been extensively investigated by Schottky,[150,151,154,161] Auwers,[149,173] Kerschbaum[149,152,173] and their collaborators, and to some extent by Lange,[153,159] Perucca, Deaglio,[163,172] Teichmann[158] and others.

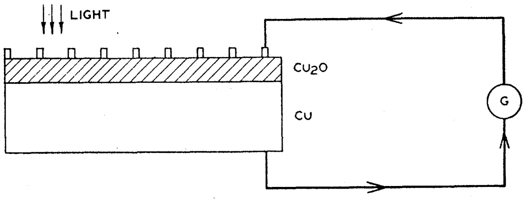


Fig. 30. Cu-Cu_2O photo-e.m.f. cell. A wire grid, indicated in the diagram by small rectangles, forms the auxiliary electrode on the Cu_2O surface. Arrows indicate the direction of flow of electrons in the external circuit.

The cells are made by oxidizing the surfaces of small copper plates. The oxidation process in most cases produces Cu_2O, with an outer layer of CuO. The cupric oxide is then removed from the surface by dissolving in some suitable solution, leaving behind a clear layer of red Cu_2O on the copper base. The electrode on the cuprous oxide surface usually consists of a thin transparent metallic film, or a wire spiral or net. The currents obtained on illumination vary from 10^{-4} to 10^{-5} amp./lumen.

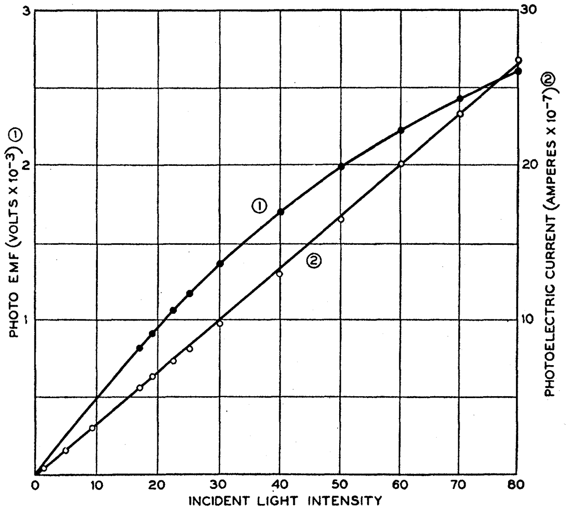


Fig. 31. Dependence of photo-e.m.f. and current on light intensity for a Cu-Cu_2O "back-wall" cell.

Schottky[150,151,149] and his collaborators concluded from extensive studies of photo-e.m.f. and rectification, that an extremely thin layer exists at the boundary between the copper base with the Cu_2O, and is really the seat of the photo-e.m.f. and rectification effects. This "blocking layer" (*Sperrschicht*) hinders the electrons from passing from the cuprous oxide to the copper, but it permits them to flow with comparative ease in the reverse direction. The difference in apparent resistance of the blocking layer for the two directions of electron flow gives rise to a rectification of electric current. Experiments yielded the surprising result that the flow of electrons in the case of illumination with light, without an external potential source, is opposite to the favored direction of electron flow when the cell is used as a rectifier. On the illumination of the Cu_2O surface, (the Cu_2O stratum being thin enough to permit the light to reach the blocking layer) electrons flow from the cuprous oxide into the copper. The resulting photoelectric current is directly proportional to the light intensity: When the two electrodes are not connected through an external circuit, the electromotive force which is formed is not proportional to the incident light intensity.

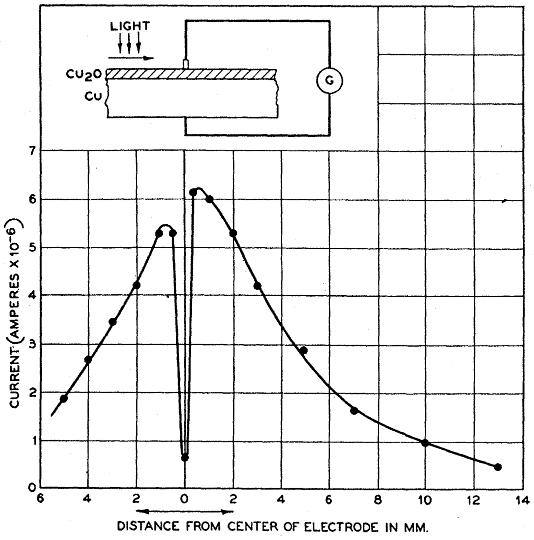


Fig. 32. Dependence of photoelectric current on the position of the incident light beam realtive to the auxiliary electrode.

This is illustrated in Fig. 31* where the variation of the photoelectric current (without external battery) and open-circuit e.m.f. with light intensity is plotted for the so-called back-wall Cu_2O-Cu cell (to be defined later). An explanation of this phenomenon is given by Auwers and Kerschbaum,[149] who show that if the cell is regarded as equivalent to a *current-source circuit*, as

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* Perucca and Deaglio, on the other hand, found both photo-current and e.m.f. to be proportional to the incident light intensity. Auwers and Kerschbaum explained this as due to the use of a nonlinear resistance in the external circuit.

distinguished from a *potential-source circuit*, the observed characteristics are explained.

Fig. 32 shows the variation in the photoelectric current when the light beam is moved across the Cu_2O surface.[151] The current increases as the beam approaches the small gold electrode on the Cu_2O surface. This variation in the photo-current as a function of the distance of the illuminated region from the electrode was attributed to the leaking back of the electrons into the Cu_2O layer. The shape of the curve in Fig. 32 has been interpreted by Auwers and Kerschbaum as evidence of attenuation of the photo-current as it flows through the Cu_2O layer to the electrode, the attenuation constant being proportional to the square root of the product of the series resistance of the Cu_2O layer and the leakage conductance of the blocking layer.

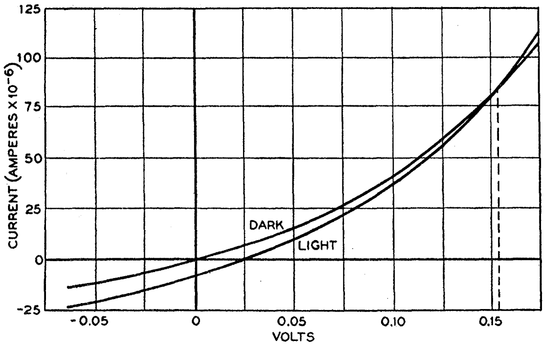

Fig. 33. Voltage-current characteristics of a Cu-Cu_2O cell.

The voltage-current characteristics of a Cu_2O-Cu cell in darkness and under illumination are shown in Fig. 33. The difference between the values of the electron current in the two cases becomes smaller as the electrode on the Cu_2O is made more positive.[149] This is thought to be due to an increase of the change in conductivity of Cu_2O produced by light; the photo-e.m.f. predominates so long as the applied voltage is small, but as this latter is increased, the effect of the conductivity-change becomes relatively as well as absolutely greater, and finally overwhelms the other.

The cells discussed hitherto in this article are the so-called back-wall cells. In these cells, the effect is supposed to arise at the boundary of Cu_2O-Cu, the hypothetical blocking layer. Duhme and Schottky found that irradiation of Cu_2O surfaces, which were covered with a transparent metallic film, resulted in an electron current flow from the Cu_2O into this surface film, i.e., in the opposite direction to electron flow in the back-wall cells. The photo-currents obtained per unit light energy were found to be larger in cases where the Cu_2O surfaces were etched with some suitable agent, before the application of the metallic coating. The seat of this photoelectric process is assumed to occur at the transition layer between the Cu_2O and the metallic film. Cells in which this effect is observed are called front-wall cells.[154] In a selenium cell recently reported by Bergmann,[164] the front-wall effect occurs alone. These cells were made by spraying selenium on a small iron disk, and then coating it with sputtered gold or silver; the selenium must be of the photosensitive metallic variety. The electrons flow from the selenium into the sputtered metallic film. The photo-e.m.f. and current-*vs.*-light intensity curves are found to be qualitatively the same as for the Cu_2O cell.

Dember[166,169] has recently reported measurements on large single crystals of the mineral cuprite (Cu_2O) which seem to indicate that the direction of the incident light beam relative to the electrode determines the polarity of the e.m.f. Bergmann[179,181] has since reported measurements on a number of photosensitive semi-conductors in which similar effects appear. Dember[188] considers the results to indicate that the e.m.f. cannot be fully explained by the postulated blocking layer, and other causes must be sought.

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