

## The Photo-Conductivity of "Incomplete Phosphors"

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Synthetic single crystals of CdS, CdSe, and CdTe have been produced by the reaction of cadmium vapor with  $H_2S$ ,  $H_2Se$ , and  $H_2Te$ , respectively. These "incomplete phosphors" show no phosphorescence but strongly developed photo-conductivity. Photo-cells made from these crystals are extremely sensitive in the whole region from the infra-red down to the ultraviolet, x-rays, and gamma-rays and for corpuscular rays, alpha- and beta-rays. Two different mechanisms of photo-conductivity occur. The normal photo-conductivity in the region of strong absorption from the blue to the ultraviolet, and the selective photo-conductivity in the region of weak absorption in the visible, x-rays, and corpuscular-rays region. The phenomena observed are in general accordance with the zonal theory of phosphorescence.

ONE of the most instructive examples of the zonal theory of solid structure is offered by the crystal phosphors. They combine the properties of isolators and electronic conductors, but unlike the metallic state, the number of conductive electrons in the crystal phosphor can be regulated by the process of light absorption and emission, and consequently a greater variety of conductive phenomena is to be expected in these substances.

The general idea of the coupling of motion of electrons with the optical properties of crystal phosphors has been already given in the early investigations of Lenard. Later, Gudden and Pohl, continuing and improving these researches, discovered the main laws and regularities of the electric conductivity connected with phosphorescence. Since these early researches, very little has been done in this particular field of research. Therefore, it might be worth while to give an account of some investigations of the author which deal in a rather extensive way with these hitherto neglected electric phenomena in crystal phosphors.<sup>1</sup> During the course of these investigations it has been found that it is quite possible to separate the electric and the optical properties of phosphors and to develop substances which show in a remarkable way the electric phenomena connected with phosphorescence but very little or no phosphorescence at

all. The name "incomplete phosphors" might be proposed for such substances.

Gudden and Pohl<sup>2</sup> accomplished their investigations with commercial zinc sulfide phosphors and with natural crystals of zinc blende, greenockite, and cinnabar. As these crystals are rare—especially greenockite—it seemed to the author to be important to resume this work with artificially prepared phosphor crystals.

### THE GROWING OF SINGLE CRYSTALS OF PHOSPHORS

Some preliminary experiments have been performed with a small condenser whose gap was filled with pulverized phosphors. In accordance with the results obtained by Gudden and Pohl, photo-conductivity could be easily measured at field strengths of some 10,000 volts/cm. The experiments carried on with different zinc-cadmium sulfides have shown that the photo-conductivity increases with increasing percentage of cadmium sulfide. By utilizing the best-known chemical methods of purifying, the late Dr. Schlegel in collaboration with the author succeeded in preparing very pure cadmium sulfide which showed remarkable photo-conductivity. As in the firing process involved, the phosphor easily dissociates; the cadmium sulfide was fired in thick-walled closed quartz tubes with the necessary sulfur added for producing a pressure of many atmospheres. But the difficulties of obtaining steady photo-currents with these phosphor powders were very large, as it was not

<sup>1</sup> The results of this investigation have been reported at the colloquium of the K. W. J. Dahlem of January 11, 1947. Dr. Rompe and Dr. Möglich, who have been engaged in the theoretical research on phosphorescence, some years ago in many discussions drew the attention of the author to this earlier work.

<sup>2</sup> B. Gudden and R. Pohl, *Zeits. f. Physik* 2, 181, 361 (1920).

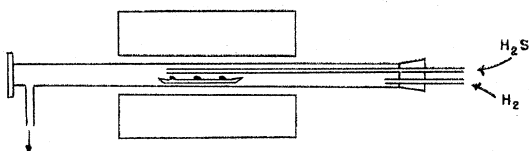


FIG. 1. Reaction tube for the production of CdS crystals.

possible to overcome the many troublesome contacts between the small particles. Later the author found a way of preparing rather large single crystals of these substances. Very little has been published up to now on the production and application of single crystal of phosphors.<sup>3</sup> According to Lorenz<sup>4</sup> artificial greenockite crystals of fairly large size are produced by the reaction of cadmium vapor and hydrogen sulfide. This method has been slightly modified (Fig. 1). Cadmium metal in a small porcelain boat was heated in a quartz tube to about 800 to 1000°C. The cadmium vapor was driven by a slow stream of hydrogen from the boat to the zone of the tube where it could react with a slow stream of hydrogen sulfide which passes there by a second quartz tube. By slowly cooling down, with the gases still flowing, crystals of very pure photoconductive cadmium sulfide are obtained. This method has two great advantages. As all impurities are separated by fractionate sublimation, it is not necessary to purify the cadmium; in fact ordinary technical cadmium yields as good results as the purest kind available. On the other hand, by cooling down in a steady stream of hydrogen sulfide, dissociation is entirely avoided. Crystals obtained by many hundred experiments show exactly the same photoelectric properties!<sup>5</sup>

The size of the crystals obtained depends on the size of the reaction tube, as the crystals grow like thick bushes across the interior of the tube. With tubes of about 100 mm in diameter, crystals up to 1–2 cm<sup>2</sup> have been obtained. They consist of rather thin yellow or slightly yellow

<sup>3</sup> Crystals of phosphorescent zinc sulfide which were accidentally obtained by N. Riehl have been mentioned by M. V. Ardenne as grainless screens for electron microscopes in his book on electron microscopy. Some methods of producing crystals of synthetic greenockite are mentioned in Gmelin, *Handbook of Inorganic Chemistry* (Verlag Chemie, Berlin, 1926), Vol. 33, "Cadmium."

<sup>4</sup> Lorenz, *Chem. Ber.* 24, 1509 (1891).

<sup>5</sup> This method of fractionate crystallization from the gaseous phase might be generally useful for the manufacturing of crystal phosphors.

green ribbons of the size of about 2 to 3 by 10 to 20 by 0.1 to 0.2 mm, which are flat and optically clear or of somewhat larger crystals with a rippled surface caused by irregularities in the speed of crystal growing. Very often the crystals are twinned with a fishbone structure. The color of larger and thicker crystals is yellow orange. The structure of these crystals is dihexagonal pyramidal hemimorph according to some Debye-Scherrer diagrams.<sup>6</sup> This structure seems to be essential because only hexagonal cadmium sulfide—the beta-form—shows photoconductivity. Cadmium sulfide obtained at room temperature by passing H<sub>2</sub>S through very pure cadmium sulfate solution, yielding the alpha-form of regular structure, shows no photoconductivity at all.

#### THE OPTICAL ABSORPTION OF CADMIUM SULFIDE

With such clear and flat ribbons, the optical absorption, whose measurement is rather difficult when crystallized phosphor powder is used, can be easily measured (Fig. 2). The crystals are transparent in the infra-red and red. Thin crystals show at room temperature, absorption beginning at about 6000Å. It rises slowly until it reaches a very steep absorption edge at 5200Å. From there toward shorter wave-lengths the crystals are entirely opaque; ribbons as thin as 0.005 mm show no transmission at all of the very strong blue and violet lines of the high pressure mercury arc. While the absorption coefficient above 5200Å amounts to 1 mm<sup>-1</sup>, below 5200Å it is some 10<sup>4</sup> to 10<sup>5</sup> times stronger. The absorption in this region is quite metallic, and the reflection

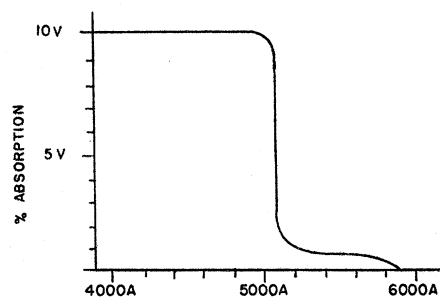


FIG. 2. Optical absorption of a CdS crystal 0.1 mm thick.

<sup>6</sup> The author is indebted to Miss U. Martius for this structural analysis.

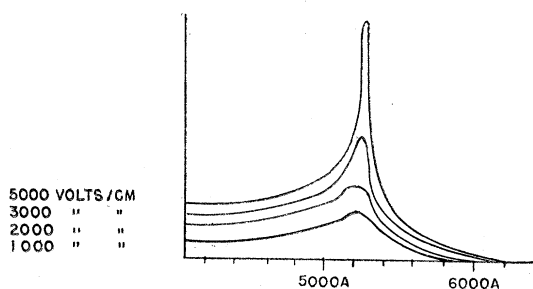


FIG. 3. Relative photo-conductivity of CdS crystals at different field strengths in arbitrary units.

power is accordingly high. Kroger<sup>7</sup> has observed that the absorption edge of the pulverized cadmium sulfide shifts rather strongly with changing temperature. The shift amounts to about  $1\text{Å}/^\circ\text{C}$  between  $90^\circ$  and  $298^\circ\text{K}$ . Using these data, Rompe and Möglich have developed a theory which links this shift with the thermal expansion of the crystal lattice.<sup>8</sup>

#### THE PHOTO-CONDUCTIVITY OF SYNTHETIC GREENOCKITE

Using natural crystals, Gudden and Pohl<sup>2</sup> have measured the photo-conductivity of ZnS, CdS, and HgS in the region 7000 to 2500Å. Their measurements cover a spectral region which contains the "selective" and the "normal" region of photo-conductivity. In the selective region the photo-conductivity depends very much on the field strength. Our measurements of the photo-conductivity of synthetic greenockite (Fig. 3) have been made with crystals on which two electrodes of aluminum, separated by a small gap of 0.2 to 0.3 mm, have been sputtered by evaporation in vacuum. The selective maximum is very sharp at field strengths of 5000 volts/cm, the width of the maximum being about 50Å. With decreasing temperature the maximum still increases and shifts to the violet, and with increasing temperature it diminishes and shifts to the red. The position of the selective maximum at different temperatures is given by the position of the absorption edge. The maximum is situated on the long wave-length side of the edge. At  $300^\circ\text{C}$  the photo-conductivity becomes very small and hardly perceptible.

<sup>7</sup>F. A. Kroger, *Physica* 7, 1 (1940).

<sup>8</sup>F. Möglich and R. Rompe, *Zeits. f. Physik* 119, 472 (1942).

The photo-conductivity in the region of shorter wave-lengths has been investigated by Gudden and Pohl and by the author down to 2500Å. Our measurements have been made with the lines of the high pressure mercury arc separated by a large Hilger-Müller double monochromator. The intensity of the spectral lines has been controlled by a thermocouple and the different lines have been reduced to one common intensity level by suitable platinum wedges sputtered on quartz plates. According to these measurements the photo-conductivity is constant over the whole region. As Gudden and Pohl<sup>2</sup> already pointed out, their measurements on HgS show some remarkable differences between these two effects. The photo-conductivity in the long wave region depends very much on the field strength and increases with it continuously until electric breakdown occurs. The photo-conductivity in the short wave region reaches saturation at higher field strengths and is on the whole much more stable and better defined than the former conductivity. The exact field strength at these measurements is not defined by the geometrical configuration of the electrodes. With strong illumination and high field strength the current slowly increases, indicating that probably conductive bridges are formed in the crystal. But, by suitable decreasing of the applied voltage, this effect can be entirely stopped and limited.

The currents obtained in these two effects are quite large. A photo-cell consisting of a crystal of the size  $3 \times 10 \times 0.1$  mm, with a sensitive area between the electrodes of  $0.2 \times 10$  mm, diminishes its resistance from more than  $10^8$  ohms to about  $10^4$  ohms, if the filament of a small incandescent lamp (10 watts) is projected by a lens 5 cm in diameter and 5-cm focal length on it. At an applied current of 10 volts, the current amounts to 1 ma. The energy effective on the small slit amounts in this case to  $0.3 \times 10^{-4}$  watt, and currents as high as 1 ma can be continuously passed through such crystals without destruction.

The photo-conductivity below 5200Å is somewhat smaller if the same amount of energy is applied. For these measurements the energy of different spectral lines of the high pressure mercury arc has been adjusted by monochromatic filters and variation of distance with the aid of a

thermocouple to the constant value of  $3.10^{-3}$  watt on the slit of the above-mentioned crystal. The resistance dropped to about  $3 \times 10^4$  ohms. These measurements with filters could be extended to the strong group of mercury lines at 3650A. With the above-mentioned monochromator the relative sensitivity of the cadmium sulfide crystals has been followed down to 2536A. Spectroscopic apparatus for the shorter region (vacuum spectrographs) was not at our disposal. It might be worth while to extend these measurements to shorter wave-lengths as it is to be expected that the photo-conductivity extends still farther down in the Schuman-region.

**THE PHOTO-CONDUCTIVITY BY X-RAYS AND CORPUSCULAR RAYS**

The general parallelism between phosphorescence and photo-conductivity of incomplete phosphors suggests that the sensitivity of these crystals extends farther down to the region of x-rays and corpuscular rays. The results of some measurements with different sources are collected in Table I. A few remarks have to be made on these measurements. The crystals used had an effective area of  $0.2 \times 10$  mm. The data on the energies are only approximate. There have been no calibrated ionization chambers for these measurements, which were made in the latter half of 1946, at the disposal of the author. Therefore, the data on distances, currents of tubes, and strengths of preparations have been given for additional information.

The measurements with x-rays were made with copper and iron tubes only. It is to be expected that cadmium sulfide will be still more effective in the region of the absorption edges of sulfur (5.00A) and cadmium (0.463A), respectively. The conductivities already obtained are very large. At a distance of 5 meters the photo-current in the above crystal amounted to about 1 micro-ampere. In the case of more penetrating radiation it might be useful to use the small face of the crystals. This would reduce the effective area to about  $0.2 \times 0.1$  mm, but, on the other hand, would increase the effective thickness to 10 mm. In the case of very hard radiation a number of such crystals might be lined up in the direction of the beam and connected either in parallel or in series. By connecting in series, the dark re-

TABLE I.

Radiation	Energy on crystal per second (effective area = 2 mm <sup>2</sup> )	Field strength	Current
x-rays: Fe-tube, 30 kv, 15 ma	$1 \times 10^8$ quanta	2500 volts/cm	$15 \times 10^{-6}$ amp.
gamma-rays: 10-mg Ra at a distance of 25 mm from the crystal	$2 \times 10^6$ quanta	2500 volts/cm	$2 \times 10^{-7}$ amp.
alpha-rays: Radium preparation emitting $10^2$ - $10^4$ alpha-particles per cm <sup>2</sup> per second	$10^3$ particles	2500 volts/cm	$7.5 \times 10^{-8}$ amp.
beta-rays: 10-mg Ra at a distance of 5 cm from the crystal	$10^4$ particles	2500 volts/cm	$1 \times 10^{-5}$ amp.

sistance, which is already very high and depends mainly on the mounting of these crystals, can be still further increased. Moreover, the density of cadmium sulfide compares very favorably with the absorption of air in ionization chambers.

In the case of alpha-particles, the preparation consisted of a thin layer of some radium compound on a metal plate of  $3 \times 4$  cm. The total number of alpha-rays emitted from this surface was known from some measurements of the ionization produced. The number of alpha-particles falling on the sensitive area of the crystal has been computed from the geometrical configuration.

The beta-radiation of a preparation of 10 mgs. of radium in a small, thin-walled glass tube has been computed.

The photo-conductivity of these crystals caused by irradiation with electrons of some 1000 volts had not previously been measured, but according to some unpublished results of Dr. E. Krautz obtained with plates sintered from cadmium sulfide powder, the incomplete phosphor shows a considerable amplification of the transverse current if it is irradiated by an electron beam of some thousand volts.

**THE ZONAL PICTURE OF INCOMPLETE PHOSPHORS**

During recent years the zonal theory of phosphorescence has been developed to a very elaborate description of the many processes involved. Therefore, one might expect that the phenomenon of photo-conductivity would fit

in the scheme of this theory, as incomplete phosphors are only a substantial part of ordinary phosphors.

Gudden and Pohl<sup>2</sup> investigated the photo-conductivity with zinc sulfide phosphors with different activators as well as with natural zinc blende which has to be considered as an incomplete phosphor. The observed phenomena of photo-conductivity are qualitatively identical in both cases. Quantitatively there are some slight differences depending on the activators used, but the general mechanism should be identical in both cases.

The zonal picture describes the phosphorescence by the assumptions shown in Fig. 4. Above the uppermost filled band *A* there is situated the normally empty conductive band *B*. In the intermediate space are located the trapping states *E* and the impurity states *C*. In some theories additional impurity states at *D* are assumed. The transition from the lower edge of the conductive band or—in the last mentioned theories—from the activator term *D* to the lower activator term *C* represents the light emission. The phosphorescence of longer duration is connected with electrons trapped in the states *E*. The trapped energy can be released either by thermal impacts or by infra-red irradiation. In both cases the electron is lifted up to the conductive band from which it might return to the above-mentioned transitions between the impurity states. This picture gives an adequate description of a great number of properties of crystal phosphorescence, and there are no essential objections to it. Considering this

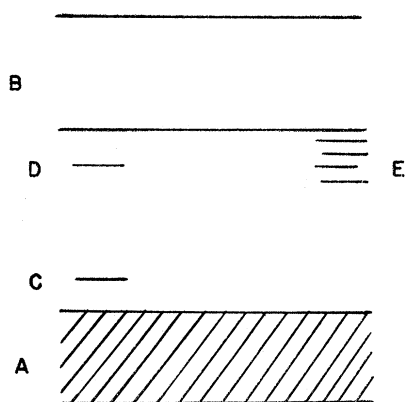


FIG. 4. The zonal picture of phosphorescence.

picture one has to attribute in the case of incomplete phosphors the absorption below 5200Å to the transition of the electrons from *A* to *B*. Consequently, the conductivity in this region is connected with electrons moving in the conductivity band under the influence of the electric field applied. The selective absorption above 5200Å corresponds to the transition *A*–*E*, and the selective conductivity should be attributed to the motion of electrons through the trapping states under the influence of the electric field applied. But, by assuming this picture it is difficult to understand why the conductivity at higher field strengths has such pronounced maximum at 5300Å. It might be worth while to investigate this maximum very thoroughly, using highly selective radiation and very strong electric field up to the breakdown potential. By suitable reduction of the intensity of illumination the electric load on the crystal could be kept constant at these measurements. In accordance with the theory of phosphorescence, where the electrons in the conductive band show a very short life, the inertia of the photo-conductivity in the short wave region is small, at least much smaller than the inertia of the conduction in the trapping states.

In the case of visible radiation less than or greater than 5200Å, the attribution of the conductivity to either of these two mechanisms follows directly from the wave-length of excitation. The decision in the region of x-rays or in the field of corpuscular rays affords some additional experiments. In ordinary phosphors the trapping states are connected with the lasting phosphorescence, and electrons can be trapped at these states, especially at low temperatures. If they are lifted up to the conductive band by thermal impact, they might return to the impurity states under emission of phosphorescence bands. As these states are metastable, the electrons can be lifted to the conductive band by suitable infra-red radiation. In the case of incomplete phosphors the mean life of the electrons in the trapping states is quite long, while the mean life in the conductive band is shorter by some orders of magnitude. Any electron lifted up to the conductive state by thermal impact or by absorption of long wave-lengths should therefore reduce the total conductivity. This effect is very large and

can be quite easily observed. Crystals illuminated with light  $> 5200\text{\AA}$  reduce their photo-conductivity if additional infra-red illumination is falling on the effective areas. The amount of reduction depends on the ratio of energies: visible light/infra-red light. The photo-conductivity due to weak visible radiation can be reduced to some 10 percent or less by a suitable amount of infra-red radiation. The exact shape of the coordinated absorption curve<sup>9</sup> has been measured with the double monochromator. At these measurements the crystals have been made conductive by weak illumination with green light filtered by a Schott-filter, and the reduction has been measured which takes place by additional illumination with a spectrum of constant energy.<sup>10</sup> The relative distribution is given by Fig. 5. The region of selective photo-conductivity extends very weakly but quite far in the red. At  $8750\text{\AA}$  additional illumination neither increases nor decreases the conductivity. Beyond this wave-length the curve shows two maxima at  $9300$  and  $11,400\text{\AA}$ . Above  $13,000\text{\AA}$  no extinguishing effect can be observed. According to our knowledge of ordinary phosphors, the extinguishing effect at shorter and at longer wave-lengths of this distribution should be different. Phosphors illuminated with rather long wave-lengths show a sudden increase of their luminosity ("flash") with following decrease. If they are illuminated with shorter wave-lengths, red or near infra-red, the luminosity decreases at once without this increase ("quenching"). The electric analog to the second effect can be observed by suitable periodical illumination of these crystals. A few words have to be said about the inertia of the conductivity by illuminating with modulated light. The general shape of the increase and decrease of photo-conductivity by illumination, with rectangular pulses of about 200/sec. registered with a small oscillograph, is identical with similar curves for selenium photo-resistances and with the brightness curves of phosphors illuminated with pulsed electron beams.<sup>11</sup> With

<sup>9</sup> In the nomenclature of Pohl,  $f'$ -center.

<sup>10</sup> The energy has been kept constant over the investigated region by previously measuring the necessary lamp current at different wave-lengths.

<sup>11</sup> For selenium see the book of G. P. Barnard, *The Selenium Photocell and Its Applications* (Constable, London, 1930).

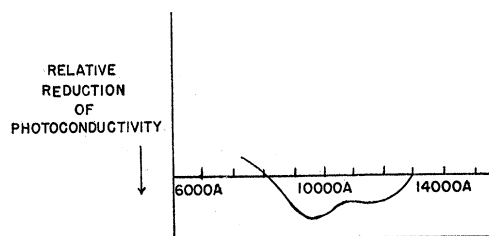


FIG. 5. The extinguishing of photo-conductivity of CdS crystals by additional illumination with infra-red radiation.

increasing intensity of illumination the curve becomes more and more rectangular (Fig. 6). On the other hand, if the crystals are illuminated with constant visible light and rectangular pulses of infra-red are superimposed, the general shape of these curves is given by Fig. 7.

If the crystal is excited by rectangular pulses of visible light and extinguished by short pulses of infra-red light, whose phase coincides with the "decreasing" part of the curve, curves of Fig. 8 are obtained. Such curves correspond to the "flash" of ordinary phosphors.

If one makes the assumption that the electrons are lifted up from the upper edge of the filled band to the trapping states, the state reached depends on the wave-length of the visible radiation. Therefore, one should expect that the conductivity in higher situated trapping states should be extinguished by correspondingly longer wave-lengths than the conductivity in lower states. By simultaneous variation of the exciting ( $V_1$ ) and the extinguishing ( $V_2$ ) wave-length by two monochromators, the exact state of the electron lifted up to the conductive band ( $V_1 + V_2$ ) can be measured. Such measurements should give valuable information on the return of the electrons from the different states of the conductive band to the lower band.

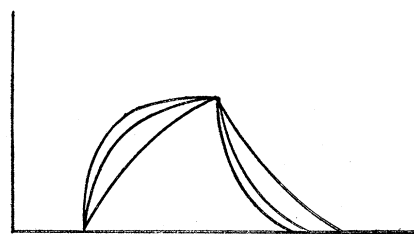


FIG. 6. General shape of the increasing and decreasing of photo-conductivity of CdS crystals by periodical illumination with pulses of 1/200-sec. duration. With higher intensity the current increases and decreases faster.

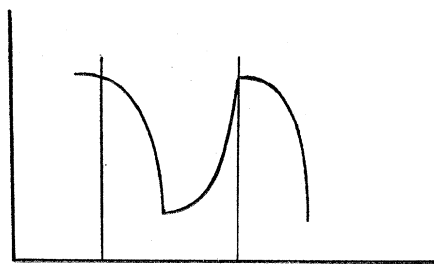


FIG. 7. General shape of the decreasing and increasing of photo-conductivity of CdS crystals by additional illumination with extinguishing infra-red light.

The conductivity excited by wave-lengths  $> 5200\text{\AA}$  cannot be extinguished by additional illumination. This is to be expected, since electrons cannot be transferred by strongly absorbed light to the trapping states which are sparsely distributed in the crystal lattice. The range of photo-conductivity due to the conductive band should extend over the whole ultraviolet down to the region of soft x-rays. On the other hand, in the region of x-rays, where the radiation penetrated deeper in the crystal, the selective photo-conductivity again prevails. The photo-conductivity caused by the  $K\alpha$  line of iron can be easily extinguished by infra-red illumination. The following mechanism might be proposed. The radiation produces "cascades" of secondary, tertiary, and higher order process electrons,<sup>12</sup> and the slowest of these are trapped in the states and thus produce, under the influence of the electric field, the conductivity. In the same way alpha-rays and beta-rays give rise to the selective photo-conductivity which can be reduced to a very small amount by infra-red illumination.

A complete theory of the photo-conductivity would have to deal with the presence of electrons in the stationary states and their motion under the influence of electric fields. On the other hand, the theory of ordinary phosphors deals with the transitions between these stationary states. By comparing complete and incomplete phosphors the cadmium sulfide crystals can be transformed into a complete phosphor by tempering in metal vapors. A very extensive theory of quantum phenomena in solid state should be obtained.

<sup>12</sup> F. M $\ddot{o}$ glich and R. Rompe, Zeits. f. tech. Physik 21, 304 (1940).

#### CADMIUM SELENIDE, CADMIUM TELLURIDE, AND MERCURY SULFIDE

The general regularities of similar incomplete phosphors can be deduced from the position of the elements involved in the periodical system. With increasing atomic number of the two components, the maximum of selective photo-conductivity and of the extinguishing curve shifts towards longer wave-lengths. Cadmium selenide has been prepared in rather small single crystals of 1–2 mm<sup>3</sup> by passing a stream of hydrogen at first over the heated selenium and then through the above-mentioned reaction tube. The absorption and the considerable photo-conductivity are shifted to the red. The maximum of the selective conductivity is situated at 6000 $\text{\AA}$ .<sup>13</sup> Cadmium telluride crystals are made in an analogous way. The small crystals show a further shift of the absorption and of the selective conductivity towards the red. The maximum which is much flatter than in the case of CdS and CdSe is situated at 6200 $\text{\AA}$ . In addition, for CdTe the extinguishing by additional infra-red illumination has been observed. This curve is shifted towards longer wave-lengths and has one wide maximum. Single crystals of the analogous zinc compound have not yet been produced. But as the general shape of the curves of natural and of synthetic greenockite are identical, the properties of ZnS might be taken from the measurements of Gudden and Pohl on natural zinc blende. The maximum of the selective effect which is much smaller, as in the case of cadmium sulfide, is situated at 4200 $\text{\AA}$ .<sup>14</sup> According to their measure-

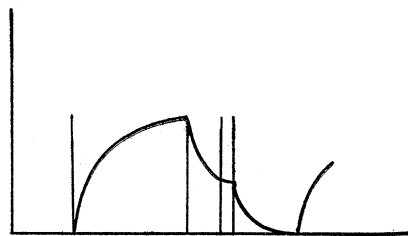


FIG. 8. General shape of the increasing and decreasing of photo-conductivity of CdS crystals by periodical illumination with long (1/200 sec.) pulses of exciting and short (1/2000) pulses of extinguishing light.

<sup>13</sup> The exact curves of CdSe and CdTe are at this time not at the disposal of the author.

<sup>14</sup> These crystals contain 1.6 percent Fe. The normal photo-conductivity below the absorption edge is about one order of magnitude less.

ments with ordinary phosphors with different activators, the maximum depends on the activator added. It shifts from 3700Å for a phosphor with an unknown activator to 4250Å for zinc sulfide with uranium activator.

According to Gudden and Pohl, natural cinnabar crystals show a very pronounced maximum of the selective conductivity at 6150Å. In this case the difference between the current-voltage curves in the normal and in the selective photo-conductivity is very pronounced. The normal photo-conductivity shows saturation. The selective photo-conductivity increases continuously with increasing voltage. Curves of the extinguishing effect have not been published by these authors, inasmuch as they already mention the diminishing of the photo-conductivity by red light, added *after* the excitation of the photo-conductivity by visible light.

#### THE USE OF INCOMPLETE PHOSPHORS AS PHOTO-CELLS

A few words might be said about the possibilities of using such incomplete phosphors, especially cadmium sulfide, as photoelectric cells. It is one advantage of these crystals that the current obtained with ordinary illumination (daylight) is very high as compared with alkali photo-cells. Resistances of about  $10^4$  ohms can easily be obtained with effective areas of some  $\text{mm}^2$ . In contradistinction to the selenium photo-resistance, the dark current is extremely small; in fact, with careful mounting on perfect insulating bases, it can be neglected for all practical uses. As Gudden and Pohl have already shown in the case of natural zinc blende, the resistance depends on the previous history. By periodical illumination it diminishes, and the current increases very much, but according to our observations these crystals can be used for some years if the load on the crystals does not exceed about one milliwatt/ $\text{mm}^2$  of the effective area between the electrodes. With frequencies up to 10,000 cycles the modulated part of the current decreases, but it is still much larger than in any other photo-cell known and can, therefore, be adjusted by suitable filters. The shape of the

current curve is somewhat detrimental to the reproducing of sound tracks. The decrease of inertia by using normal photo-conductivity with wave-lengths below 5200Å improves this curve considerably.

The possibilities offered by an effective photo-cell of such small dimensions in the region of x-rays hardly needs to be emphasized. From the great number of possible applications for registering x-ray spectrographs, registering structural analysis apparatus, dosimeters, and so on, one application might be mentioned which makes use of the possibility of reproducing x-ray pulses by such photo-resistances. The short wave-length shift of the continuous x-ray spectrum shifts periodically with the voltage curve of a half wave x-ray apparatus. A cadmium sulfide photo-resistance used with alternating current of the same frequency, but shifted in its phase  $90^\circ$  against the tube voltage, registers a nearly constant current on an oscillograph tube if it is irradiated by these pulsating x-rays. By inserting substances with selective absorption edges in the beam of x-rays, these edges are registered by small deflections in the oscillograms. Thus absorption spectroscopy can be performed without the use of a spectrograph.

In the x-ray region, as well as in the region of alpha-, beta-, and gamma-rays, the extinguishing effect might be used for intensity measurements.<sup>15</sup> If amplification is necessary, modulation of the photo-current can be obtained in two ways: first by modulation of the source by rotating sectors, and second by using the extinguishing effect of modulated infra-red radiation.

With symmetrical electrodes the photo-current is independent of the frequency of the current passing through the cell. Frequencies as high as  $3 \times 10^7$  pass through such cells and follow the variation of the irradiating light in the same way as direct currents.

Thus the incomplete phosphors might prove to be a simple and useful instrument for measuring the different radiations connected with the development of nuclear physics.

<sup>15</sup> The reaction of slow neutrons (Cd) on these crystals has not yet been investigated.