

May 24, 1960

J. E. JACOBS
SEMI-CONDUCTOR

2,938,003

Filed Nov. 25, 1955

2 Sheets-Sheet 1

FIG. 1

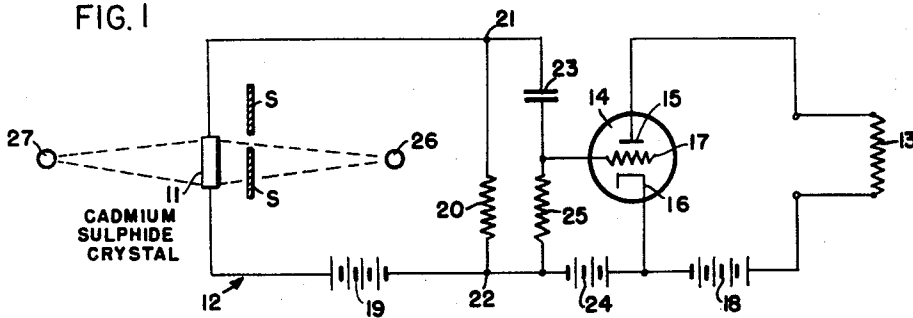


FIG. 2

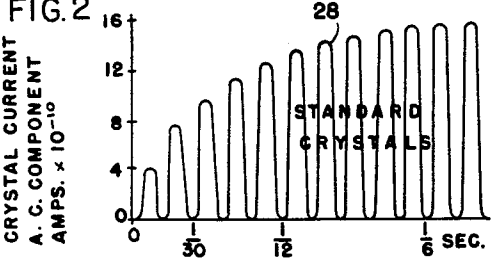


FIG. 3

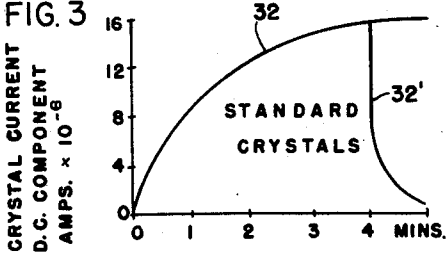


FIG. 4

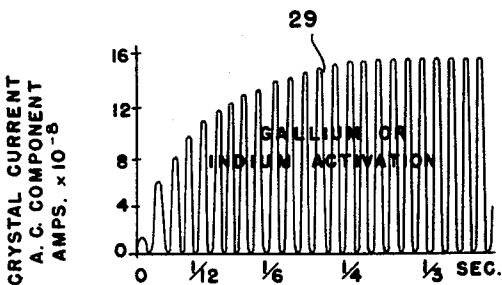
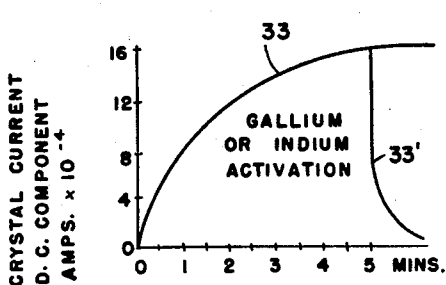


FIG. 5



INVENTOR:—
JOHN E. JACOBS
BY:—
Junius J. Cook, Jr.
ATT'Y

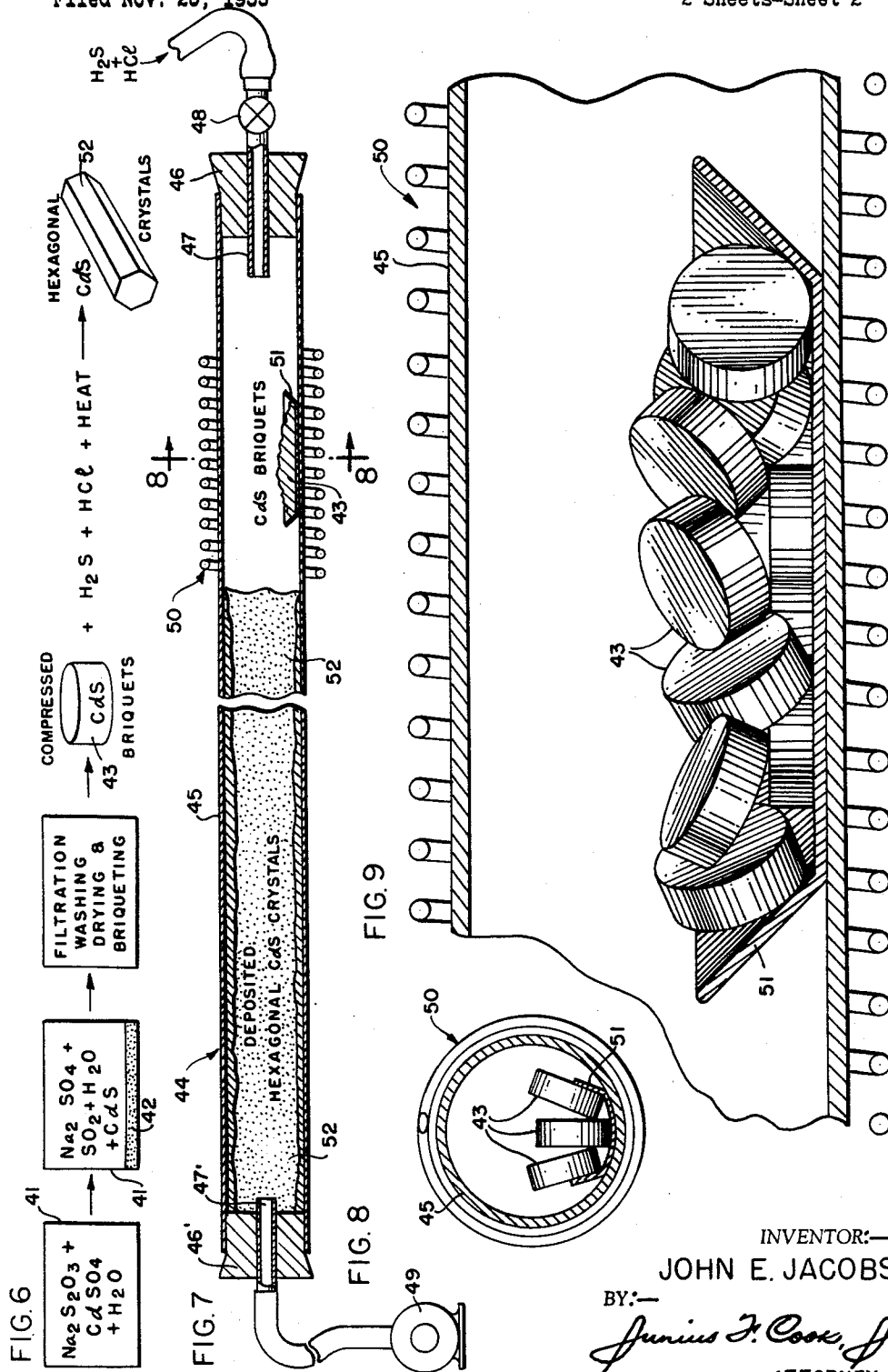
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2 Sheets-Sheet 2



INVENTOR:—
JOHN E. JACOBS
BY:—
Junius F. Cook, Jr.
ATTORNEY

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2,938,003

SEMI-CONDUCTOR

John E. Jacobs, Hales Corners, Wis., assignor to General Electric Company, a corporation of New York

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12 Claims. (Cl. 252—501)

The present invention relates in general to photosensitive semi-conductors, and has more particular reference to current amplifying semi-conductor materials of unusual photosensitivity particularly well suited for X-ray detection purposes, the present application comprising a continuation in part of copending applications for U.S. Letters Patent, Serial Numbers 228,333 and 269,276, respectively filed May 25, 1951, and January 31, 1952, both now abandoned, on the inventions of John E. Jacobs relating to semi-conductors.

The most widely known semi-conductors are those, such as selenium, which are particularly responsive to visible light, or rays of wave length adjacent that of visible light in the light spectrum. Such commonly known semi-conductors are not sufficiently responsive to X-rays to allow the useful application thereof to X-ray detecting purposes. The manner of applying cadmium sulphide for the effective detection of X-rays, is taught in U.S. Letters Patent Number 2,706,790, which issued April 19, 1955, on the invention of John E. Jacobs from an application for U.S. Letters Patent copending with the applications from which the subject matter hereof is derived. The impedance variation in response to X-ray irradiation exhibited by heretofore available crystals of the substances mentioned is not at all uniform. Considerable difficulty, therefore, has been encountered in attempting to apply crystals of the named material for X-ray detection purposes, since the response of each individual crystal to X-ray irradiation is apt to vary from that of other apparently identical crystals. It is thought that the irregularity of crystal response in the named X-ray sensitive semi-conductor material is due, in part at least, to lattice irregularities or distortions in the crystal structure, and to the occurrence in the crystals of varying quantities of contaminant foreign materials. It is, therefore, an important object of the present invention to provide semi-conductive crystals having substantially uniform response characteristics with respect to variations in the impedance of the material when excited by X-rays impinging thereon.

Another important object is to process cadmium sulphide to increase its semi-conductive photosensitivity not only to X-rays, but also to light rays within a wide wave length band, including visible light rays; a further object being to incorporate a sensitizing medium in the molecular lattice structure of the material.

Another important object is to apply indium or gallium as an activating medium, in the lattice structure of crystalline cadmium sulphide to thus greatly alter and improve its light responsive characteristics; a further object being to apply indium or gallium in trace quantities of the order of one part in one million, in the lattice structure of hexagonal cadmium sulphide crystals, to thus render the same semi-conductively photosensitive, especially to X-rays and similar rays of penetrating character.

Another important object is to provide cadmium sulphide as an activated, super-sensitive light responsive

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semi-conductor for any photoelectric control purpose, and especially for X-ray detection.

The foregoing and numerous other important objects, advantages, and inherent functions of the invention will become apparent as the same is more fully understood from the following description, which, taken in connection with the accompanying drawings, discloses a preferred embodiment of the invention.

Referring to the drawings:

Fig. 1 is a diagrammatic showing of apparatus embodying a semi-conductor for ray detecting purposes;

Figs. 2-5, inclusive, are graphical charts illustrating the performance of cadmium sulphide activated as a semi-conductor material in accordance with the present invention;

Fig. 6 is a diagrammatic representation of a process for making hexagonal cadmium sulphide crystals;

Fig. 7 is a sectional view taken through apparatus for producing crystalline material in accordance with the present invention;

Fig. 8 is a sectional view taken substantially along the line 8-8 in Fig. 7; and

Fig. 9 is an enlarged view of a portion of the structure shown in Fig. 7.

To illustrate the invention, the drawings show a semi-conductor element 11, interconnected in a suitable electrical translation system 12, designed to measure the impedance of the element 11 in terms of electrical power delivered to a load device 13 connected with the output side of the system. The load 13, of course, may comprise any suitable means for the performance of any desired operation in response to changes in the measured impedance of the element 11.

While any suitable or preferred translation system may be employed, the same, as shown in Fig. 1 of the drawings, preferably comprises an electronic amplifier including an amplifying tube 14 having an anode plate 15, a cathode 16, and a control grid 17, the plate 15 and cathode 16 being interconnected in an output circuit, including a suitable source of plate circuit power 18 and the operable device or load 13. The control grid 17 is interconnected in a control circuit in which the element 11 is also operatively connected, in order that the grid 17 may be electrically energized in accordance with the transitory impedance values of the element 11.

As shown, the control circuit may comprise the element 11, a preferably uni-directional power source 19, and a ballast or control resistor 20 interconnected in series, so that electrical potential corresponding with the impedance characteristics of the element 11 may be developed at the opposite ends 21 and 22 of the resistor 20. The control grid 17 may be connected with the control circuit at the connection point 21, preferably through a condenser 23, for filtering uni-directional voltage components and allowing the application only of fluctuating voltage components on the grid 17. If it be desired to apply uni-directional as well as fluctuating voltage components, on the control grid 17, the condenser 23 may be eliminated; and, if desired, means may be substituted for excluding fluctuating voltage components while passing only uni-directional voltage components to the grid, if it be desired to control the load device 13 in response to such uni-directional components.

Means for applying a suitable bias between the cathode 16 and grid 17 may also be provided, the same preferably comprising a suitable source 24 of grid biasing power and a regulating resistor 25 interconnected in series with the power source 24 between the cathode and the grid, the connection point 22 of the control circuit being connected with the grid bias means, as at a connection point between the cathode 16 and the resistor 25.

The element 11 comprises crystalline cadmium sul-

phide activated by applying atomic traces of indium or gallium, in quantities of the order of one part in one million, in the molecular lattice structure of the material.

Activated hexagonal crystals of cadmium sulphide may be produced by vapor phase chemistry procedures, by mixing the activating substance in its vapor stage with the vaporized constituent component of cadmium sulphide, under controlled conditions, from which mingled vapor crystals of activated cadmium sulphide may be deposited. The mingled vapors may be created by heating cadmium sulphide together with an appropriate quantity of a salt of the activating metal, such as the chloride of indium or gallium, in a platinum boat, disposed in an end of a tubular glass retort, at a temperature of the order of 1000° C. The mingled vapors may then pass to a cooler zone, as at the other end of the retort, where crystals of the desired material may grow on the walls of the retort, at temperatures of the order of 600° C. and lower. The resulting crystals will have atomic particles of indium or gallium distributed, more or less at random, in the lattice structure thereof, which particles impart the desired photosensitive qualities in the material, such qualities being absent in material that is entirely free of lattice impurities.

For the production of hexagonal cadmium sulphide crystals the present invention contemplates the chemical reaction, as in a suitable container, tank or vat 41, of preferably pure sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) with preferably pure cadmium sulphate (CdSO_4), in the presence of water (H_2O) as a carrying medium. The chemical reaction of such substances results in the production of sodium sulphate (Na_2SO_4), sulphur dioxide (SO_2), water (H_2O), and cadmium sulphide (CdS). Sodium sulphate and sulphur dioxide, being soluble, become dissolved in the carrying medium, while cadmium sulphate, being insoluble in the carrying medium, is formed as a finely divided, powdery precipitate 42 in the vat 41.

The powdery, dust-like precipitate 42 probably comprises cadmium sulphide in its cubic crystalline form, and the same may be separated from the aqueous solution of sodium sulphate and sulphur dioxide by conventional filtration, after which the precipitate is preferably washed, as with pure water as a washing medium, and dried after separation of the washing medium from the precipitate, as by conventional filtration. The clean precipitate is then preferably formed into pellets or briquets 43 by compressing the chemically prepared cadmium sulphide precipitate, in a suitable press under a pressure of the order of 10,000 pounds per square inch. The resulting briquets preferably comprise cylindrical blocks having a diameter of the order of 1½ inches and a height of the order of ½ inch. A number of these blocks may then be evaporated in an atmosphere of hydrogen sulphide to produce cadmium sulphide vapor, from which hexagonal cadmium sulphide crystals may be condensed, in a manner hereinafter described.

The evaporation of the cadmium sulphide briquets 43, and subsequent condensation of hexagonal cadmium sulphide crystals from the resultant cadmium sulphide vapor, may be, and preferably is, accomplished in condenser apparatus 44 comprising an elongate sleeve-like housing 45. The housing 45 may comprise a tube of quartz glass having length of the order of 5 feet and internal diameter of the order of 3 inches. Suitable support means, of course, may be provided for mounting the tube in substantially horizontal operating position. The tube may be provided with suitable end closure means, such as corks or stoppers 46, 46', carrying inlet and outlet conduits 47, 47' sealed therein and opening therethrough. The inlet conduit 47 may be connected, as through a suitable control valve 48, with a source of hydrogen sulphide gas, such source preferably delivering hydrogen sulphide gas containing trace quantities of hydrochloric acid vapor. The conventional Kipp gen-

erator provides such a source. The discharge conduit 47' is preferably connected with an exhaust fan device 49 for continuously drawing vapors at a relatively slow, regulated rate longitudinally through the sleeve-like housing 45 from the inlet conduit 47 to the outlet conduit 47'.

The major portions of the housing 45 may be exposed to normal atmospheric temperature. Suitable heating means, such as an electrical heating coil 50, may be provided to heat a portion of the housing 45 in order to constitute a hot zone in the housing, adjacent the inlet end thereof, at a temperature in excess of the vaporizing temperature of cadmium sulphide. The surrounding atmosphere will cool the housing 45 on opposite sides of such hot zone. The heater 50 is preferably spaced from the inlet end of the housing a distance of the order of 12 inches, such that circumambient air will maintain the inlet end of the housing at a temperature sufficiently low to avoid causing deterioration of the closure means 46. It will be noted, also, that the wall temperature of the housing 45, due to the cooling effect of circumambient air, will decrease progressively from the hot zone toward the discharge end of the housing, the housing being of such length that, when the equipment is in operation, its end portions at and adjacent the discharge end of the housing will be substantially at atmospheric temperature.

A supply of briquets 43 may be loaded in a porcelain boat 51 and introduced into the sleeve-like housing 45 through the inlet end thereof, as by removal of the closure means 46, the boat 51 containing its charge of briquets 43 being placed in the housing 45 within the hot zone thereof. After the boat 51 and its contents has been placed in the housing, the closure means 46 may be replaced in sealed condition on the end of the housing. The valve 48 may be opened to deliver hydrogen sulphide carrying traces of hydrochloric acid vapor into the housing at the inlet end thereof, and the fan device 49 may be set in operation to progress the hydrogen sulphide and hydrochloric acid gases, together with the cadmium sulphide vapor evolved from the briquets 43, through the housing at a relatively low rate of speed which may be determined by controlling the speed of operation of the fan device 49.

The apparatus may be maintained in operation over an extended period of the order of 5 days, more or less, during which period hexagonal cadmium sulphide crystals 52 will become deposited and grow upon the inner wall surfaces of the housing 45 between the hot zone and the discharge end of the housing. After the inner walls of the housing shall have thus become coated with crystals 52, the housing may be cooled by disabling the heater 50 and allowing the cooling to be accomplished slowly by action of the circumambient atmosphere for a period of the order of 24 hours, after which the crystals may be removed, as by scraping the same, from the inner walls of the housing 45, by removing the closure means 46' to allow access to the housing 45.

In order to introduce an activator substance, such as indium or gallium, into the crystal material thus deposited by condensation upon the inner walls of the housing 45, measured quantities of a suitable salt of the activating substance may be uniformly mixed with the cadmium sulphide precipitate 42 after filtration, washing and drying thereof, and before the formation of the same into briquets 43. To this end, the chlorides of gallium or indium may be uniformly mixed with the powdery cadmium sulphide precipitate 42 in precisely measured quantities, whereby to obtain a desired atomic dispersion of the selected metallic activator substance or substances in the resulting crystals 52.

The foregoing procedure results in the production of crystals having substantially uniform X-ray responsive impedance variation characteristics. The procedure is not at all critical and is not affected by variations in atmospheric conditions from day to day, as has been

found to be the case with other attempted methods for the synthesis of X-ray sensitive semi-conductors.

Crystals of cadmium sulphide activated in accordance with the teachings of the present invention show particularly uniform semi-conductive characteristics, such uniformity being accomplished by controlling the amount of activating substance in the lattice structure of the resulting crystals. The desired crystals may thus be produced by introducing a desired proportion of activating substance, in its vapor stage, with the mingled vapors from which the resulting crystals are produced. Such activated crystals are thought to contain atoms of the activating substance, more or less uniformly distributed throughout the lattice structure of the crystalline material, thereby forming electron donor centers which serve to constitute the crystal as a photosensitive semi-conductor, having current amplifying characteristics.

Satisfactory or optimum results are obtained when indium or gallium is present, in the vapor mixture from which the activated crystals are grown, in amounts not exceeding 0.01% by weight of cadmium vapor in the mixture produced. Such a result may be attained by evaporating a mixture of cadmium sulphide and indium chloride in the proportions of 10,000 to 1.5, by weight. Where the activating metal is gallium, optimum results may be attained by evaporating cadmium sulphide mixed in the proportions of 10,000 to 2 by weight. By reducing the amount of activating metal salt in the evaporable mixture, the resistivity of the semi-conductor may be correspondingly increased to any desired extent. In crystals produced from vapor containing indium or gallium in quantities appreciably exceeding 0.01% by weight of the cadmium component, the dark current, that is, the current which flows through the semi-conductor in the absence of irradiation, is unduly large, and the ability of the crystal to distinguish sharply between variations in light intensity is correspondingly impaired. This impairment of discriminating sensitivity, of course, is the result of reduction of the inherent electrical resistivity of the crystal due to the presence of excess quantities of the activating metal in the crystal.

When a crystal 11 of cadmium sulphide, activated with indium or gallium as herein disclosed, is exposed to X-rays emanating as from a ray source 26, the impedance of the crystal changes substantially in proportion to the intensity of impinging X-rays. Where the applied rays are of pulsating character, the impedance change in the crystal precisely follows the pulsations of the impinging rays and consequently establishes a corresponding pulsating voltage across the resistor 20, which, being applied to the control grid 17, produces corresponding power pulsations for application to the load device 13.

X-rays produced by operation of the usual X-ray generating tubes, electrically excited by alternating current power at 60 cycles, comprise X-ray energy pulsations at a frequency corresponding with that of the energizing power applied for the operation of the ray generator, X-rays of uniform, non-pulsating character may, of course, be produced and applied upon the crystal 11, in which case the voltage developed across the resistor 20 will be of uni-directional character. Consequently, the translation system 12 should be designed to measure the magnitude either of the uni-directional impedance of the crystal or the fluctuating impedance thereof, depending upon the uni-directional or fluctuating character of the impinging rays.

Semi-conductors of the character herein contemplated exhibit impedance changes when exposed to visible light rays, as from a light source 27, and the extent of such visible light induced impedance change is in proportion to the intensity of rays impinging on the crystal from the source 27. Accordingly, when a crystal is exposed to rays to which it is sensitive, from a source other than the X-ray source 26, the voltage available at the connec-

tion points 21 and 22 may contain components which correspond with the impedance value of the crystal, determined by the light rays from such other source as well as components corresponding with the rays emanating from the X-ray source 26. If the rays impinging on the crystal from the source 27 are of uniform intensity, the corresponding voltage component across the resistor 20 will be uniform. Where the impinging X-rays are of fluctuating character, the same may be applied through the condenser 23 for the control of the amplifier 14, while the uniform voltage component established by illumination of the crystal from the source 27, at uniform intensity, as well as the uni-directional X-ray induced voltage component, will be excluded from the amplifier system by the action of the condenser 23.

The present invention, of course, is not necessarily limited to the excitation of the crystal 11 by visible light or other rays from a source 27 and by pulsating X-rays from the source 26, but, in its broadest aspects, the invention applies to the excitation of the crystal 11 by means of visible light or by means of X-rays or both, and whether or not the light rays or the X-rays pulsate, there being many possible advantageous applications involving the excitation of the crystal either by X-rays or by other light rays including visible light, where either the light rays or X-rays are of uniform or of pulsating intensity character.

The detection characteristics of the crystals do not alter upon exposure thereof to X-rays and other light rays. In this connection, the performance of cadmium sulphide crystals of the so-called beta or hexagonal form, including standard crystals containing usual lattice impurities, and crystals activated with indium in accordance with the present invention, has been investigated, using X-rays, having wave length of 1.54 Angstroms, for crystal excitation. The X-ray beam thus applied to the examined crystals was of pulsating character at a frequency of 60 cycles. To determine its impedance response characteristics, a suitable uni-directional electromotive force, of the sort supplied by the source 19 in Fig. 1, may be applied to the crystal and the resultant current flow there-through accurately measured. The resulting crystal current obtained in response to pulsating X-ray irradiation of the crystal was found to contain an alternating as well as a uni-directional component. The uni-directional component was found to vary substantially linearly with the intensity of incident X-rays, the alternating component substantially as the square of incident X-ray intensity. This phenomenon is explainable upon the theory that the alternating component is proportional to the rate of recombination of electrons in the effective conduction band or zone of the irradiated crystal.

The magnitude of the uni-directional component of crystal current was found to be approximately 10,000 times that of the alternating component at intensities of approximately 10^5 quanta/second, in standard cadmium sulphide crystals containing "natural" impurities as activating media in the crystal structure, as well as in crystals activated with indium or gallium in accordance with the present invention. The ratio was found to be somewhat variable, each crystal having its own characteristic ratio. At higher incident intensities the ratio diminishes, and it is supposed that the ratio approaches unity in response to progressively increasing ray intensity.

In standard cadmium sulphide crystals, the time lag before crystal current reaches a maximum value following initial application of the X-ray beam is of the order of several minutes so far as the uni-directional crystal current component is concerned, but is of the order of $\frac{1}{6}$ of a second for the alternating component, in the same crystal. Cadmium sulphide crystals activated with indium or gallium exhibit time lag characteristics of the order of 5 minutes and $\frac{1}{3}$ second, respectively, for the uni-directional and fluctuating components of crystal current.

Crystal sensitivity, which may be shown as the ratio of

measured output current to incident X-ray intensity, varies from one crystal to the next in accordance with the nature and extent of activating foreign matter in the lattice structure of the crystals. Under comparable test conditions, the magnitude of the X-ray induced current flow, both fluctuating and uni-directional, in standard cadmium sulphide crystals, as compared with current flow in crystals activated with indium or gallium, is as one is to one hundred. These characteristics are illustrated in the graphs comprising Figs. 2-5. The curves shown in Figs. 2 and 4 illustrate crystal response data obtained, under like test conditions, by photographing, as on an electron oscilloscope, the fluctuating component of crystal current immediately following the application of X-rays to the crystals. The curve 28 in Fig. 2 shows the approximate response obtained from a standard CdS crystal. The curve 29 in Fig. 4 shows the corresponding response obtained for crystals activated with indium or gallium. The curves 32 and 33 in Figs. 3 and 5 respectively illustrate the values of uni-directional crystal current immediately following X-ray application to a standard crystal and to a crystal activated with indium or gallium. The curves 32' and 33' illustrate the decline of uni-directional crystal current component from the maximum value following discontinuation of X-ray application to the crystals. Upon termination of X-ray irradiation on the crystals, flow of fluctuating crystal current ceases immediately at the conclusion of the cycle of crystal current flow then in being.

It will be noted that in standard as well as in crystals activated with indium or gallium the time lag required for the uni-directional current component to reach a maximum value is many times that within which the fluctuating current component of the crystal reaches its maximum value. This phenomenon may be explained upon the theory that the fluctuating component is a measure of the change in the number of electrons present in the conduction band of the crystal, as a function of time. Accordingly, employment of the fluctuating component of crystal current, to the exclusion of the uni-directional component, will permit the almost instantaneous measurement of crystal current for the determination of X-ray intensity, thus avoiding the more extended delay necessary to achieve a stable condition in using the uni-directional current component. Measurement of the fluctuating current component only permits the advantageous use of high gain fluctuating current amplifiers in the translation system, in the interests of effective instrumentation.

In this connection, it will be noted that crystals activated with indium or gallium have time lag response characteristics comparable to standard crystals, the time lag response of indium activated cadmium sulphide being substantially slower than that of the same material when activated with other metals, such as copper, silver and manganese. As a consequence, indium activated cadmium sulphide crystals are less desirable for ultra high speed detecting purposes, than crystals activated with copper, silver or manganese, but, because of the relatively much larger values of crystal current obtainable in indium or gallium activated crystals, they are very much more sensitive than crystals activated with other materials, and may be employed to advantage wherever speed of response is a negligible factor. Indium or gallium activated crystals, because of extreme sensitivity, are especially suitable for use in visible light ray detection.

Employment of the alternating component of crystal current, for X-ray detection purposes, permits the application of secondary illumination as a light bias to the crystal for increasing the X-ray sensitivity thereof. When such a light bias is directed on a crystal, sensitive to the bias irradiation, while simultaneously irradiated with pulsating X-rays, both the uni-directional and fluctuating components of X-ray induced crystal current are increased by a factor of the order of 10, as compared

with such X-ray induced components in the absence of the light bias. Each different kind of crystal may have a corresponding optimum light bias wave length producing maximum response, the response being reduced by variation of the light bias wave length above or below the optimum wave length value characteristic of the crystal. For cadmium sulphide crystals, however, regardless of the manner of activation, the optimum sensitizing effect is obtained in response to light bias having a wave length of the order of 5200 Angstroms.

It is thought that the invention and its numerous attendant advantages will be fully understood from the foregoing description, and it is obvious that numerous changes may be made in the form, construction and arrangement of the several parts without departing from the spirit or scope of the invention, or sacrificing any of its attendant advantages, the form herein disclosed being a preferred embodiment for the purpose of illustrating the invention.

The invention is hereby claimed as follows:

1. A photoconductive semiconductor consisting essentially of cadmium sulphide activated with a metal of the class consisting of indium and gallium.

2. A photoconductive semiconductor consisting essentially of cadmium sulphide in its hexagonal crystalline form and activated with indium.

3. A photoconductive semiconductor consisting essentially of cadmium sulphide in its hexagonal crystalline form and activated with gallium.

4. A photosensitive semi-conductor, consisting essentially of a crystal of cadmium sulphide having atomic particles of a metal of the class consisting of indium and gallium dispersed in the lattice structure of the crystal to form electron donor centers therein.

5. A photosensitive semi-conductor, consisting essentially of a crystal of cadmium sulphide having atomic particles of a metal of the class consisting of indium and gallium dispersed in the lattice structure of the crystal, in trace quantities of the order of one part in one million, to form electron donor centers therein.

6. A photoconductive semiconductor consisting essentially of cadmium sulphide condensed in its hexagonal crystalline form from a vapor produced by the evaporation of the constituents of cadmium sulphide and a salt of an activating metal of the class consisting of indium and gallium in proportions producing cadmium and the activating metal in the vapor in the relative proportions of 10,000 to 1 by weight.

7. A photoconductive semiconductor consisting essentially of cadmium sulphide condensed in its hexagonal crystalline form from vapor containing its constituent elements together with traces of an activating metal selected from the class consisting of indium and gallium in quantities of the order of 0.01% by weight.

8. A photoconductive semiconductor consisting essentially of cadmium sulphide in its hexagonal crystalline form containing atomic particles of gallium dispersed in the molecular lattice structure of the crystal to form electron donor centers therein.

9. A photoconductive semiconductor consisting essentially of cadmium sulphide in its hexagonal crystalline form containing atomic particles of gallium dispersed in the molecular lattice structure of the crystal in quantity of the order of one part gallium to one million parts cadmium sulphide.

10. A photoconductive semiconductor consisting essentially of cadmium sulphide condensed in its hexagonal crystalline form from vapor containing its constituent elements together with traces of gallium in quantities of the order of 0.01 percent by weight of the cadmium constituent.

11. A photoconductive semiconductor consisting essentially of cadmium sulphide condensed in its hexagonal crystalline form from a vapor produced by the evaporation of the constituents of cadmium sulphide and a salt

of gallium in proportions producing cadmium and gallium in the vapor in the relative proportion of 10,000 to 1 by weight.

12. A photosensitive semi-conductor consisting essentially of gallium activated cadmium sulphide condensed from vapors containing not more than one part of gallium to 10,000 parts of cadmium by weight.

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