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GERMAN RESEARCH ON SEMI-CONDUCTORS, METAL RECTIFIERS, DETECTORS AND PHOTOCELLS

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German Research on Semi-Conductors, Metal Rectifiers, Detectors and Photocells.

Reported by

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Object of Trip

It was intended to follow up investigations, already started, on German Research on Semi-conductors, Metal Rectifiers, Detectors and Photo-cells (see B.I.O.S. Final Report 725 "German Research on Rectifiers and Semi-conductors") and also to pick up any new information on these and related subjects. Experimental results and theories advanced are reported here as given by the personnel interviewed and do not necessarily coincide with the the opinion of the author of this report.

A list of the individuals interviewed is given in the following table.

No	Name	Firm	Zone	Address	Subject of Interview	Date
1	Prof. R.W. Pohl	Göttingen University	British	First Physical Institute	Semi-conductors	25-3-47
2	Prof. R. Hilsch	Erlangen University	U.S.	Physical Institute	"	30-4-47
3	Dr. H. Sachse	Siemens-Halske	"	Haldweg 7. Mergelstätten	"	7.5.47
4	Prof. W. Schottky	Siemens-Halske	"	Pretzfeld - Erlangen	Rectifiers	29-4-47
5	Dr. K. Maier	Previously A.E.G. and S.A.F.	"	Stuttgarter Str. 9, Eislingen/Fils.	"	8-5-47
6	Prof. R. Brill	I.G. Farben & T.U. Darmstadt	"	Moltke Str. 8, Heidelberg	X-Ray Technique	21-4-47
7	Dr. H. Krebs	" " "	British	Malteser Str. 5, Bonn	" "	30-3-47
8	Dr. W. Koch	A.E.G. Rectifier Works	British	Belecke - Möhne	Se Rectifiers	31-3-47
9	Dr. M. Herbeck	Previously A.E.G. now A.V.A.	"	A.V.A. Göttingen	" "	24-3-47
10	Dr. C. Bosch	Previously A.E.G.	U.S.	Schlosshof, Heidelberg	" "	20-4-47
11	Dr. F. Waibel	Previously Siemens	British	Machandelweg 11, Berlin - Ch'burg.	Cu_2O "	7-4-47
12	Prof. P. Günther	Previously T.U. Breslau, now Siemens	U.S.	Heidenheim/Brenz	Detectors	7-5-47
13	Dr. H. König	Gottingen University	British	First Physical Institute	"	27-3-47
14	Prof. R. Frerichs	K.W.I. and T.U. Berlin	"	Königin Elizabeth Str. 6, Berlin - Ch'burg	Photocells	18/19-5-47
15	Dr. M. Treu	Previously Erlangen University	"	Arminius Str. 5, Nürnberg	"	1-5-47
16	Dr. W. Schaffernicht	A.E.G. Valve Works	"	Bauhof 7a Clausthal	"	20-5-47
17	Dr. J. Kaspar	Previously A.E.G.	U.S.	Idstein - Frankfurt a.M.	"	19-4-47
18	Dr. H. Pick	Göttingen University	British	First Physical Institute	"	26/27-3-47
19	Dr. H. Gaertner	Previously Heeres- Waffen-Amt	"	Simeon Kaserne, Block E, Minden	"	21-5-47
20	Prof. H. Kallmann	K.W.I. & T. U. Berlin	"	Jasmin weg 10, Berlin - Ch'burg	Neucleonics	17/19-5-47

Semi-conductors

(1) **Prof. R. W. Pohl.** Chief of the first Physical Institute at Göttingen University.

(1.1) Alkali-Halide Crystals. Prof. Pohl is at present working on photo-chemical processes, i.e. chemical changes produced in a compound when absorbing electro-magnetic radiation. Such a reaction would, e.g. be $ZnO + O + \nu h = ZnO_2$ where νh stands for the photon of light frequency ν.

For practical applications, such as radiation detectors, compounds with a short relaxation time are most useful, as they can follow rapid changes in radiation intensity; e.g. PbS cells will easily indicate variations in infra-red radiation intensity even at a rate exceeding 1,000 c/s. For fundamental research, however, photo-chemical changes, the products of which have a relatively long life, are much more suitable as they can be studied more leisurely and furthermore, the final equilibrium concentration of activated absorption centres is much higher and more amenable to quantitative investigation. Another reason why materials sensitive to infra-red (I.R.) radiation are not so suitable is that their absorption usually extends from the I.R. through the visible right into the U.V. region (see Fig. 1, curve a), i.e. they are opaque to visible light. There exist, however, certain ionic crystals, such as alkali-halides, whose main absorption bands lie in the U.V. region (curve b) and which are almost completely transparent to visible radiation. Any change in their absorption characteristic, such as the creation of a new absorption region F, is thus easily observable. It is mainly for these reasons that the Göttingen School has concentrated on alkali-halides and similar crystals.

(1.2) Colour Centres and Light Absorption. Alkali-halide crystals are grown from the purest melt (impurities less than $1:10^7$). A small crystal is put into the melt to form a nucleus on which further growth takes place. The temperature of the melt is kept constant to within 1°C. The top of the crystal is water cooled and the whole crystal is withdrawn very slowly and steadily as the growth proceeds. Perfect crystals of KCl and similar compounds have been grown up to a size of 5" diameter. This might take anything up to 48 hours. The whole furnace should be carefully shielded from any draught, and metal vapours must be prevented from reaching the melt when very clear transparent crystals are required.

The production of "colour centres" in these crystals may be achieved by any one of three different methods:

(1.2.1) By Diffusion of one of the constituent elements into the crystal.

A transparent KBr crystal, for instance, can be coloured by exposing it to the vapour of K or of Br (Fig. 2a). Into the narrow neck of a tube made of high-temperature resisting glass (Duran) place some metallic K. The transparent KBr crystal is put into the wider part of the tube which is then evacuated. With heater No. 1 bring the K to evaporation (a temperature of 500°C produces a K-vapour pressure of about 30 mm. Hg) and independently with heater No. 2 raise the crystal to a temperature slightly below its melting point, say to 700°C, so as to accelerate the rate of diffusion of the vapour into the crystal. This will introduce about 10^{18} K atoms into each cm.^{3} of the crystal, i.e. their concentration would be about $1:10^4$. These "colour centres" produce a deep blue colour; they are then "frozen" into the crystal by rapidly chilling it to room temperature. When using a lower K-vapour pressure, the concentration is correspondingly reduced and the depth of the colour is changed to a lighter hue but of same wavelength, about 5,000A°. The concentration of these colour centres can be determined fairly accurately from the value of the absorption co-efficient.

(1.2.2) By Direct Introduction of Electrons into the crystal (Fig. 2b).

A D.C. voltage of about 100 volts is applied to two opposite faces of the crystal which is heated to about 500°C. The + ve terminal makes contact with the crystal over a broad face, whilst the - ve terminal is connected to a gramophone needle stuck into the opposite face. Electrons pass from the needle into the crystal and produce a deep blue colour near the needle point, fading away toward the other electrode corresponding to the lower electron density there.

(1.2.3) By Exposure to X-Rays. When the transparent crystal is exposed to X-Rays, some of its constituent ions are further ionised (doubly charged) and provide electrons for the colour centres. This method, however, suffers from several disadvantages:

(a) On ionisation of a metal ion there is, for every electron provided for a colour centre, also a positive metallic ion produced right inside the crystal which is thus likely soon to pick up a free electron again, thereby killing the corresponding colour centre: the "life" of crystals coloured by X-Rays is much shorter, especially at elevated temperatures.

(b) Owing to the high energy of X-Ray photons, the efficiency of the process is rather low. For instance, a beam of 60 Kv X-Rays is completely absorbed in 6 mm of KCl; (if much thinner crystal plates were used most of the X-radiation would pass right through without producing any effect in the crystal). Each photon of this radiation produces, by secondary electron emission, on the average, 60 centres, i.e. about 100 eV are used up for the production of one centre whilst the energy stored in it only corresponds to about 2 eV, i.e. the quantum yield of the process is about 2%.

A recent practical application of such crystals is to the investigation of cosmic rays at high altitudes: coloured crystals are shot up into the atmosphere by rockets where they are exposed to cosmic radiation, and thereby discoloured to a certain degree. From the loss of colour, the intensity of the radiation can be deduced.

(1.3) Theory of Colour Centres.

(1.3.1) **F Centres.** The explanation of the colouration of ionic crystals, such as KBr, has been given by Pohl many years ago: in any such crystal there are certain "defect centres" ("Störstellen") where an ion of either type, K^+ or Br^-, is missing from the crystal lattice, leaving a "hole" of atomic dimensions there. The number of such holes, according to thermodynamic principles, rises sharply with temperature T, viz.,

$$N = N_0 \, \varepsilon^{-W/RT}.$$

Within each hole, the electric field differs from that in the main body of the crystal. Assume the missing ion to be Br^-. Then the hole is surrounded by six positively charged K^+ ions creating a strong electron affinity inside it. If now electrons are brought into the crystal by any one of the three methods described above, they are easily trapped in those holes, but will be free to oscillate inside them. Depending on the size of the hole, i.e. on the lattice constant of the crystal, the electrons could oscillate at a particular frequency ν_0. If then electro-magnetic radiation, i.e. visible light, of that same frequency falls on to the crystal, it is strongly absorbed by these electrons, i.e. the crystal appears coloured.

At that particular frequency the crystal will show a sharp absorption line. From the value of the absorption co-efficient, or, to be exact, from the area under the absorption curve (Fig. 3, curve b) the number of oscillators, i.e. filled holes, can be determined by the standard theory of scattering. It should be understood that these colour centres are due to absorption of <u>electrons</u> into the lattice and not, for instance, of ions or atoms. Therefore, the same colour is produced when, in the experiment described above (Section 1.2.1), an atmosphere of Na vapour is used instead of K. On arrival at the crystal surface the alkali atoms are ionised, and the electrons only diffuse into the crystal, leaving their alkali ions behind on the surface.

As mentioned above, the frequency ν_0 of the absorption line (Fig. 3, curve b) depends almost entirely on the lattice constant d. The relation found experimentally is $\nu_0 d$ = constant, i.e. the frequency becomes smaller for larger lattice spacings; KBr, for instance, absorbs radiation of longer wavelength than, say, NaCl. Similarly, at higher temperatures the crystal expands and the frequency is again reduced, i.e. the colour is shifted towards the red end. At the same time, however, the thermal vibrations of the adjacent metal ions surrounding the hole, partly interfere with the vibrating electron thus damping its oscillation. The absorption line is, at higher temperatures, correspondingly widened into a band of larger half-width and of lower intensity (Fig. 3, curves c,d).

(1.3.2) <u>F' Centres.</u> When radiation of frequency ν_0 falls on to the crystal, it is absorbed by the electrons which start oscillating themselves at the same frequency. By collision with neighbouring atoms they gradually lose their energy again. However, there is another mechanism by which they can lose the absorbed energy: the electron is ejected from its hole by the photon it absorbs and moves again along the lattice until it falls into another hole. On rarer occasions it might even fall into a hole which is already occupied, and thus form a double charge there (Fig. 4). This will alter the normal frequency and give rise to a new absorption band at a somewhat lower frequency (Fig. 5). These new centres are called F' centres. Prolonged exposure of a coloured crystal to radiation of its own characteristic frequency thus slowly destroys the number of original F centres, i.e. the depth of its colour, and produces new centres of a different colour - nearer the red end of the spectrum - instead. This process is reversible, but a certain amount of energy is lost thereby. As indicated in Fig. 5, the absorption band of F' -centres is much broader than that of F-centres, i.e., whereas the F-centres correspond to a sharply defined energy level, the F'-centres correspond to a band of much larger width (Fig. 6).

The transition from F- to F'-centres is helped considerably by heat motion, the quantum yield being very low at low temperatures but equal to 2 at high temperatures. It is, as first sight, perplexing to find a maximum yield of 2 and not of 1 as might be expected. This yield of 2, however, gave rise to the theory expounded above: One photon, by ejecting an electron from a hole, destroys thereby not only the corresponding F-centre, but also the other centre into which the ejected electron eventually falls, forming one F'-centre instead. On the other hand, the transition of F'-centres back to F-centres is easier at low temperatures (see Fig. 7). When exposed to "white" light, there is a continuous shift from F- to F'-centres and back, with the result that, owing to thermal collisions, the colour of the crystal is eventually destroyed altogether.

(1.4) Effect of Hydrogen.

When a coloured crystal is exposed to an atmosphere of hydrogen at high pressure, say 40 atmospheres, H_2 molecules, due to their small size, can easily diffuse into the crystal and find their way to electrons trapped in holes.

There, they form compounds of KH with the surrounding K^+ ions. The characteristic colour of the crystal is lost thereby, and a new absorption line appears instead in the near U.V. (Fig. 3, curve e, wavelength about 3,500A) corresponding to the absorption line of KH. When now irradiated with U.V. radiation of that same wavelength, the compound may be dissociated, $KH + h\nu \rightarrow K + H$, and the hydrogen can be driven off by heating the crystal when its original colour is restored. This is an example showing how alkali-halide crystals may be used for the study of photo-chemical processes.

(1.5) Absorption Bands due to Impurities.

When a small amount of, say, Ca is added to the melt during the growth of a KBr crystal, the Ca^{++} ions with their double charge, create new types of defect centres, so called "Z-centres". On exposure of such a crystal to K-vapour, as described above, the electrons trapped in defect centres have several different modes of transition open to them giving rise to several peaks in the absorption curve (Fig. 8). These few Ca^{++} ions do not fit very well into the $K^+ Br^-$ lattice and are much harder to shift. The Z-centres are thus more stable than F- or F'-centres. For instance, whereas F and F' colour centres are easily destroyed by exposure to X-Rays, the colour due to Z-centres is much more stable. It can, however, be rapidly removed by strong heating when the Ca^{++} ions become more mobile.

(1.6) Electrical Conductivity of Solids.

In pure metals, electrons are free for conduction at all, even at the lowest temperatures. With increasing temperature T the metal ions start vibrating about their equilibrium positions in the lattice. The conduction electrons collide more frequently with them and have their "free path" correspondingly reduced, i.e. the conductivity drops with 1/T (Fig. 9, curve a).

In a typical electronic semi-conductor such as Si or Ge, there are no electrons free for conduction at low temperatures. Only as the temperature is increased are electrons freed from their atoms by thermal motion. The number of free electrons rises sharply with the temperature, i.e. the conductivity

$$\varkappa = \varkappa_0 \, \varepsilon^{-W/RT}$$

where W is the energy required to lift an electron into the "conduction band".

In pure ionic crystals also is conductivity at very low temperatures practically non-existent as all electrons are tied to the ions making up the crystal and the ions themselves are rigidly held in position. At higher temperatures some "holes" and other "defects" appear in the crystal, allowing a certain amount of freedom of movement to the ions which thus become available for the conduction of electricity. The number of holes and defects rises sharply with temperature, and the same type of law for the conductivity applies except that W here corresponds to the energy required for the production of a "hole", e.g. about 2 eV for AgCl. As the temperature is increased, more and more defect centres are created. Eventually, when all available ions have become free, the conductivity cannot rise any more and, at higher temperatures still, thermal collisions would only have the effect of impeding the drift of ions in the electrical field, i.e. the conductivity will drop just as in pure metals, (Fig. 9, curve b). In most ionic semi-conductors this "saturation" occurs at rather high temperatures T_o and the crystals usually start melting long before the maximum conductivity is reached. At very low temperatures, the intrinsic conductivity of both these types of semi-conductor, electronic as well as ionic, should, according to this theory, disappear. However, in practice it is found that there always remains some residual conductivity, even at very low temperatures. This residual conductivity ("Störleitung") can be attributed to foreign atoms or "impurities", always present in any real crystal. The "activation energy" of these impurities is usually much lower than W, say about 0.4 volts, and hence impurities become important for the conductivity at low temperatures, even if present in very small concentration (Fig. 10).

(1.7) Photo-chemical Effects.

Recently, Pohl has been able to demonstrate photo-chemical effects by conductivity measurements. $AgCl$ is a typical ionic conductor whose behaviour - in the dark - is adequately described by the previous paragraph (Fig. 11, range B C D). However, when exposed to light, a chemical change takes place and $Ag + Cl^-$ exhibits, apart from its typical ionic conduction, some pronounced electronic conduction. Photons impinging on the crystal produce, out of the $AgCl$, certain new chemical compounds with electronic conductivity. Their exact nature and amount depends mainly on the frequency and intensity of the radiation, but generally the chemical changes affect only a very small fraction of the bulk of the $AgCl$, owing to the limited number of quanta available and to the short life of the newly formed compounds. The additional electronic conductivity is, therefore, largely swamped by the much greater ionic one; but it is possible, by working at very low temperatures, to suppress the latter sufficiently so as clearly to bring out the electronic conductivity. This is shown in Fig. 11 from A' to B'. With increasing temperature, the new compounds formed by irradiation are excited by the higher thermal energy of the surrounding lattice to a larger and larger extent until at B' all such centres - still only a very small fraction of the whole bulk of the material - have been excited and are available for conduction. Further rise in temperature only increases the resistance (Fig. 11, B' C). At point C the intrinsic ionic conductivity of $AgCl$ sets in, and soon swamps the electronic conductivity of the photo-chemically excited constituents.

Literature:

H. Pick: Über die Farbzentren in KCl Kristallen mit kleinen Zusätzen von Erdalkali-Chloriden. Ann. d. Phys. 35 (1939) 73.
R. W. Pohl: Elektronenleitung und photochemische Reaktionen in Alkali-halogenid Kristallen. Phys. ZS. 39 (1938) 36.
E. Mollwo: Über die Farbzentren der Alkali-halogenid Kristalle. ZS. f. Phys. 85 (1933) 56.
R. W. Pohl: Elektrizitätslehre. Göttingen 1946.

(2) Prof. R. Hilsch, of the Physical Institute, Erlangen University, has worked with Pohl on colour centres in alkali-halide crystals until 1940.

(2.1) Semiconductors.

In any investigation of semi-conductors, purity of the material is of over-riding importance; impurities should not exceed 1:10^6. Nominally "pure" metals contain impurities of about 1:10^3 or 10^4: copper can, by special electrolytic refinement, be obtained up to 1:10^5 purity (some troubles in Cu_2O rectifiers have been traced to very small amounts of impurities). Metals, being opaque, cannot readily be checked for such degrees of purity, hence such transparent compounds as alkali or silver-halides are preferable for research on semi-conductors; they would soon get opaque if contaminated. For instance, AgCl loses its transparency when as little as 1:10^5 of Ag_2S is present. Generally, compounds formed by a strong chemical reaction such as highly polar salts, are likely to be of higher purity than metals: the chemical reaction is more likely to proceed between the pure components and tends to leave impurities of either constituent behind. For instance, very pure CuS can be prepared easily by evacuating a vessel containing purest copper wire and then admitting sulphur vapour. Cupric sulphide, CuS, is an electronic conductor with a very high conductivity, even higher then mercury, but cuprous sulphide, Cu_2S, is an almost perfect insulator.

(Miss) Dr. Eisenmann, in Prof. Hilsch's department, has studied the whole range of compounds from CuS to Cu_2S. Specimens were prepared by evaporating in vacuum a film of CuS, about 100 μ thick, on a thin mica plate, and then admitting sulphur vapour at varying pressures. The samples were weighed before and after admission of the vapour by means of a micro-balance and the increase in weight gave the excess sulphur present. As a result of conductivity measurements, E. found a smooth transition from the purely metallic conductivity of the CuS - conductivity inversely proportional to absolute temperature - to the characteristic semi-conductor behaviour of Cu_2S - log of conductivity proportional to 1/T (Fig. 12). For any given compound, the conductivity can be represented fairly accurately as the sum of that of the two components, CuS and Cu_2S according to their proportions, i.e. the two compounds behave as if they were connected electrically in parallel. Thus at very low temperatures, conductivity is mainly electronic due to the CuS, and at the higher temperatures mainly ionic due to the semi-conductor (see Fig. 13). Optical measurements have also been carried out on the samples from the near U.V. to the I.R. (0.4 to 3.0 μ). A 100 W lamp was used to irradiate the film and the amount of reflected and transmitted light was measured. From these values, both the refractive index and the absorption co-efficient could be determined (Fig. 14). The latter showed three distinct maxima, one in the U.V., one in the near I.R. (at about 2 μ) and one in the far I.R. These maxima are associated respectively with :-

(i) a transition from the highest filled electron band (Fig. 15) to the next (normally empty) band, requiring an energy of several electron-volts as in an insulator,

(ii) a transition from an intermediate "semi-conductor" level involving about 1 eV. Such intermediate energy levels are here produced by squeezing excess S atoms into interstitial places in the Cu_2S lattice (theory of Fröhlich and Mollwo). The position of this level can also be determined from the exponent in the expression for the semi-conducting conductivity.

(iii) a transition from the full to an over-lapping conduction band, requiring - as in any good metallic conductor - only a fraction of an eV.

(2.2) Super-Conductivity.

(2.2.1) Experiments.

Hilsch is greatly interested in this subject on which he has been working for the last seven years. He has built a simple but very efficient low-temperature plant with which he can reach liquid He temperatures within one hour from starting, and supply sufficient quantities of He to last for 13 hours' experimenting. With this plant he has investigated the critical temperature ("Sprungpunkt") of various pure metals, (i.e. that temperature at which super-conduction sets in), also the influence of a magnetic field (which has the effect of lowering the critical temperature) and the critical current ("Grenzstrom") which sets up a magnetic field of such magnitude as just to balance the external field. He also studied the very pronounced effects which some metals have on the critical temperature even if added in very small amounts only.

(2.2.2) Theory.

Defects in the lattice similar to those in an ionic crystal which are responsible for such effects as F-centres (see Section 1.3.1) might also account for super-conductivity; holes in the lattice might possibly present paths of easy flow to electrons giving rise to super-conductivity. Any foreign atoms present would tend to drift into these holes and thus a very small amount of impurity would be sufficient to block these paths and destroy the super-conductivity. If this picture is correct it would be interesting to produce a pure compound with a large number of holes - of atomic dimensions - in the crystal. This can be done either by raising the crystal almost to its melting point and chilling it rapidly, when a large number of defect centres, corresponding to the high temperature, is frozen into the crystal; or by forming a compound at a temperature much below the melting point of its metallic element. For instance, CuS is formed at 505°C whilst Cu melts at 1089°; similarly NbN is formed at a temperature far below the melting point of Nb. Both these compounds show pronounced super-conductivity.

Further evidence of the connection between atomic holes and super-conductivity has recently been obtained in the U.S.S.R. when Sn wire could be produced having a relatively high critical temperature (9° K) by putting it under excessively high strain.

Literature: Eisenmann: Elektrisches und Optisches Verhalten von Halbleitern. Ann. d. Phys. 38 (1940), 121.
R. Hilsch: Anlage für Verflüssigung von Wasserstoff. Ann. d. Phys. 42 (1942), 165.

(3) Dr. H. Sachse, physical chemist of Siemens & Halske. His early work concerned the systematic investigation of all

(3.1) Metallic Oxides, their preparation and properties. The most important result of this work is a rule referring to the electrical conductivity of metallic oxides. "Any metal which has all its valency electrons completely saturated by oxygen is a good insulator". Examples are:-

Uranium has six electrons in its two outermost incomplete shells, i.e. four in the 6d (P shell) and two in the 7s (Q shell).

In the compound UO_3 all these six electrons are saturated, its resistivity is $10^{10}\ \Omega$ cm.

In the compound UO_2 ("Urdox"), only four electrons are saturated, leaving two free for conduction; the resistivity is $1\ \Omega$ cm.

Indium has three electrons in the O shell (two in the 5s and one in the 5p sub-group).

In In_2O_3 they are all saturated; resistivity $10^3\ \Omega$ cm.

In In_2O only one is saturated, two are comparatively free; resistivity $1\ \Omega$ cm.

Copper has eighteen electrons in its last complete (M) shell and one in the N shell.

In Cu_2O this one 4s electron is completely saturated; resistivity about $10^{10}\ \Omega$ cm.

In CuO, another electron, from the M shell, is also required for bonding; the shell is then distorted and the compound becomes partly conducting; resistivity $10^4\ \Omega$ cm.

Silver. The electronic structure of its N and O shell is very similar to that of Cu in the M and N shell. Resistivity of Ag_2O is $10^6\ \Omega$ cm. and of Ag_2O_2, $10^2\ \Omega$ cm.

Most metal oxides are pronounced semi-conductors; their conductivity is greatly affected by a small excess or deficit of oxygen compared with the stoichiometric composition. For instance, pure NiO, with both valency electrons of the Ni saturated, is a good insulator ($10^{10}\ \Omega$ cm), but an excess of ½% of oxygen distorts the next complete electronic shell (M) somewhat, when conductivity is considerably increased, $10^4\ \Omega$ cm. Similarly, in CuI an excess of only 1% of iodine is sufficient to give very high conductivity.

Sachse has also investigated the magnetic properties of oxides. There is no connection between magnetic susceptibility and electrical conductivity. On the other hand, Heisenberg's theory implying a relation between ferromagnetism and co-ordination number on the one side, and exchange forces on the other, could be confirmed.

(3.2) Thermistors. ("Thernewid", German abbreviation for Thermal Negativer Widerstand).

The well-known "Urdox" type, UO_2 can only be used in vacuum or in a hydrogen atmosphere. It may be operated at temperatures up to 700 or 800°C where a small change in ambient temperature has comparatively little effect on the resistivity. Its useful temperature range is limited only by the stability of the contacts with the external connections.

Pure CuO, another typical semi-conductor, may be used in ordinary atmosphere. Its resistivity is $10\ \Omega$ cm. at 20°C and drops to $1\ \Omega$ cm. at 200°C.

These thermistors are used for compensation of instruments to correct for the positive temperature co-efficient of copper windings, for voltage stabilizers, etc. They are also used for surge protection, where they tend to reduce the voltage surge owing to their large conductivity when carrying higher currents. However, their large thermal inertia - they must become hot before their resistance drops - is rather a handicap in such an application.

(3.3) Resistances for Wireless Sets (Volume control, etc.).

Standard types of high-ohmic value resistors are made of carbon black, which is directly precipitated from the gas. This is sufficient for ohmic values up to, say, $10K\Omega$, when the wall thickness is about $20\ \mu$. For larger ohmic values still, the layer becomes so thin that perfect contact between individual carbon grains cannot be guaranteed, with the result of a certain amount of noise. The noise level due to this cause may be about 10 to 20 μV per volt D.C. applied across the terminals of the resistor. (Noise due to poor contact from the slider may reach a multiple of this value, say about 1 mV/V, if the mechanical construction is not very sound). A new method of manufacture was, therefore, developed: soot from an acetylene flame is mixed with a special lacquer dissolved in Xylol. This gives a more uniform layer that can be made as thin as a film of a few atoms thick and still give good contact between the grains. For values above 10KΩ, fine helical grooves were cut into the cylindrical wall of the resistor, and values beyond 30 MΩ can easily be obtained, the limit being about 1,000 MΩ in one unit. The grooves were usually cut with carborundum discs, but these had to be changed to fine diamond cutters with a bakelite binder when, for the largest ohmic values, the pitch had to be reduced to $\frac{1}{2}$ mm. ($\frac{1}{4}$ mm. conducting layer + $\frac{1}{4}$ mm. gap). Such resistors were usually very sensitive to moisture; for instance, with a change in relative humidity from 20 to 100%, the resistance used to change by about 5 to 10%. With the new coating described above, the corresponding change in resistance was reduced to about 1 - 3%.

The resistors are rated to operate at temperatures up to 150°C without trouble. They may be used up to 220°C, but are then likely to drop slowly in ohmic value, probably owing to slow carbonisation of the binding lacquer.

A rather special design of volume control resistance, as shown in Fig. 16a, uses specially shaped sections of materials with different conductivities and gives a linear relationship of the logarithm of resistance with angle (Fig. 16b).

Literature: **H. Sachse:** Theory of Ferromagnetic Fe_2O_3 as a Model for the Heisenberg Theory of Ferromagnetism. ZS. f. Phys. Chem. 9 (1930), 83.

Temperaturabhängige Widerstände (Heissleiter) und ihre Anwendung in der Technik. Siemens ZS. 19 (1939), 214.

Rectifiers

(4) Prof. W. Schottky, consultant to Siemens Halske, is mainly interested in the development of the theory of contact rectifiers.

In 1942 he published a paper on contact rectification which he considers to be probably final in its essentials. He believes the barrier layer in the semi-conductor, adjacent to the metallic electrode to consist of a very thin insulating layer, about 100 A° thick. On that side of the barrier layer which is remote from the metal electrode "impurity centres" are ionised to a certain extent, thus producing a cloud of conduction electrons, the effective thickness of which cloud varies with the potential applied to the two electrodes. This theory is able to explain several characteristics of Se rectifiers, especially the observed change of capacitance with frequency. Quantitative values for the density of impurity centres at varying depths of the barrier layer can be derived from such capacitance measurements. The equivalent circuit of such a rectifier, Fig. 17, should consist of a capacitance C_1 of the barrier layer proper, in series with a resistance R of large ohmic value corresponding to the semi-conductor material. This resistance is shunted by a capacitance C_2 which comes into play especially at the higher frequencies, thus explaining the observed decrease of overall capacitance with increasing frequency.

Literature: W. Schottky: Theorie des Elektronen-rauschens in Mehrgitterröhren,
Ann. d. Phys. 32 (1932), 195.
Vereinfachte und erweiterte Theorie der Randschichtgleichrichter.
ZS. f. Phys. 118 (1942), 539.

(5) <u>Dr. K. Maier</u>, previously with A.E.G. and S.A.F., has been working on Se rectifiers. In the latest edition of his book "Die Trockengleichrichter", Maier discusses the following picture of the Se rectifier, (Fig. 18). The Ni plated base plate of Fe or Al carries the semi-conducting Se and on top of it a thin layer (about 1,000 A° thick) of SeO_2 to which the counter electrode (C.E.) is finally applied.

The electrical formation is a cataphorectic process: the application of an electrical potential difference across the thin layer of SeO_2 - about 10^{-5} cm - produces a very strong electric field there, 10^6 V/cm. Now, SeO_2, being a semi-conductor, has only comparatively few electrons in the conduction level, which are quickly removed by this process. The electrical formation thus produces a thin insulating film of amorphous red Se from the SeO_2 and this acts as the barrier layer. When, in operation, negative potential is applied to the C.E., electrons in large numbers are emitted from it into the insulating film and through the Se into the Fe plate. When, however, the C.E. is made positive it quickly pulls the few electrons available out of the Se. Thereafter, the layer acts as an insulator and no more current can flow in this, the "blocking direction". Iodine or chlorine, added to the Se in small quantities, are useful as supplying the impurity centres required for conduction. They lower the forward resistance by about 30%. Small additions of metals easily damage the rectifier by forming "bridges" right across the barrier layer; especially thallium, when present in the C.E. material even to the extent of 1:2000, will diffuse into the barrier and damage the rectifier. S.A.F. used to add metallic compounds, such as CeI to the Se in the proportion of $1:10^4$ to reduce the forward resistance of the cell, but this also reduced the blocking resistance to a certain extent. Maier also tested some Se rectifiers made by Siemens. Siemens purchased their Se, already chlorinated, from the Firm of Riedl. On the Se they evaporated a very thin layer of S to act as the barrier, and then applied the C.E. These rectifiers were as good as those made by S.A.F. except that, when switched on, they passed a very large reverse current for a short period (during which formation obviously took place).

S.A.F. found the Se as supplied by Riedl not pure enough, impurities of As, Ag and Cu always being present.

They, therefore, purified the Se themselves and were only satisfied when they had reduced impurities to below $1{:}10^6$, so that they would not swamp the effect of intentionally introduced admixtures (concentration $1{:}10^4$, see above).

Literature: K. Maier: Physik und Technik der Trockengleichrichter. A.f.E. 32 (1938), 799.

Ein Beitrag zur Theorie der Arbeitsweise von Sperrschicht - Trockengleichrichtern. A.E.G. Report, 1937.

(6) **Prof. R. Brill**, of I.G. Farben (Oppau nr. Ludwigshafen and T.H. Darmstadt), specialised in X-Ray work, and greatly improved techniques by producing a very fine beam of X-Rays by various collimating devices. Some of his outstanding research concerned:-

Electron Density distribution diagrams for various compounds to a higher degree of accuracy than hitherto available.

Valency: The minimum electron density along the line between two neighbouring atoms in a compound supplies information about the type of valency involved.

Catalysts of submicroscopic size: Their approximate size and shape could be obtained from the width of Debye - Scherrer rings. This work was of particular importance in the understanding of the action of catalysts, so far largely unexplained. One important application was, e.g. the activation process in the manufacture of NH_3 by I.G. Farben.

Soap Films on solid surfaces: Investigations by electron diffraction technique of a thin soap film gave a closely packed hexagonal pattern, i.e. one according to chains of cylindrical cross section, although the chains themselves were known to have a flat rectangular cross section. The conclusion reached was that these chains attach themselves to the surface but are free to rotate about an axis through the point of attachment and perpendicular to the surface.

Literature: R. Brill: X-Ray Analysis of Metallic Magnesium. Ann. d. Phys. 41 (1942), 37.

X-Ray Fourier Analysis of Quartz. Ann. d. Phys. 41 (1942), 233.

Journ. prakt, Chem. 161 (1942), 49.

Roentgen Untersuchungen an Se Gleichrichterschichten. Deutsches Luftfahrtministerium 1944.

Study of Chemical Linkages by Fourier Analysis, Naturwissenschaften 27 (1939), 676.

(7) Dr. H. Krebs, a chemist by training, with I.G. Farben.

(7.1) Crystal Structure of Se.

At the T.H. Darmstadt, Krebs developed, at Prof. Brill's suggestion, an X-Ray reflexion method to obtain photographs of high resolution and applied this to the investigation of the structure of Se. The results of this work can be stated as follows:-

Se, when grown on a plane surface, may exist in either of two structures,

(1) a closed chain of Se atoms in a plane parallel to the basal surface, or

(2) a long straight chain perpendicular to that surface.

(1) is the more stable form at lower and (2) at higher temperatures. The transition point between these two textures for purest available Se is somewhere between 80 and 90°C. There is some indication that texture (2) is responsible for weak spots in the barrier layer of Se rectifiers.

7.2) Heat Treatment of Se Rectifiers.

This has the effect of changing the Se from the amorphous (high resistivity) into the crystalline form. A further heat treatment (tempering) is required to reduce the number of defect centres to a certain optimal figure.

If this treatment is continued too long it tends to clean up those centres too far, i.e. the Se is transformed into an almost perfect crystal, which, owing to the lack of defect centres, has a very low conductivity, insufficient to carry the current in the forward direction.

(7.3) Addition of Impurities.

Addition of impurities into the Se changes the length of the Se chains, i.e. the degree of polymerisation and hence the rate of crystal formation, shorter chains being able to adjust themselves more readily into the crystal array than long ones. The polymerisation is strikingly demonstrated by the very great increase of the viscosity on addition of a comparatively small amount of impurities. The particular effect of each type of impurity depends largely on its electro-positive or -negative character as the case may be, the most definite changes being observed on the addition of alkali metals on the one hand, or of halogons on the other. Either of these, owing to their pronounced electro-valency can easily saturate one bond of a Se atom and thus break up the long chains. Chain length is gradually decreased as more of these impurities are added.

Literature: H. Krebs: Struktur Untersuchungen an Se-Gleichrichtern I. 1945.

(8)[+] Dr. W. Koch of A.E.G. Rectifier Works, Belecke.

The A.E.G. had developed Se rectifiers before the war, and had started large scale production by 1939. Troubles were soon experienced and research into the rectifiers had to be re-started. This was carried on in several different directions:-

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[+] Drs. Koch, Herbeck and Bosch were also interviewed independently by Mr. A. C. Lynch, whose notes were compared with those of the author and are included in Sections 8, 9 and 10.

(8.1) Measurement of Capacitance.

According to Schottky's theory (see Section 4), this furnished information on the distribution of impurity centres in the barrier layer. The effect of adding various chemicals, such as alkali or other metals (Tl, Hg, etc.), and of halogens, as well as the effect of various heat treatments could thus be directly observed. With increasing purification, the conductivity of the Se rose to a certain maximum, beyond which it dropped again owing to the lack of conductivity centres. Purification was always continued well beyond this point of maximum conductivity. Only after this was reached were certain elements added in controlled amounts. The A.E.G. concentrated on the addition of Br, S.A.F. on J, Siemens on Cl or on the addition of metal compounds. The amount of halogen added must not exceed a certain value, because then not only would the conductivity be decreased but electrolytic effects might also set in and produce excessive aging.

(8.2) Crystal Structure investigations by X-rays and by the electron microscope.

X-ray investigations were described in Section 7 above, and the Electron Microscope work was done by Drs. Mahl and Seeliger. The results demonstrated the influence of various forms of heat treatment on the crystal structure of the Se at its boundary with the base plate, though the external surface did not seem to change much.

(8.3) Chemical Analysis.

This had only been planned, but owing to the small amounts of impurities involved, the problem presented formidable difficulties and no practical results had yet been obtained.

(8.4) Counter Electrode (C.E.).

If the backing electrode is removed mechanically, and the Se then dissolved away in sodium sulphide or potassium cyanide, the C.E. is found to have on it a thin layer, believed to be a selenide. The thickness of the layer as shown by its colour, varies with duration and temperature of the forming treatment and affects the forward resistance of the rectifier. The layer may be either an excess or a defect conductor.

Dr. Koch thinks that the barrier layer exists in the Se and that it is in contact, not with the C.E., but with the selenide layer. The importance of the C.E. material is, therefore, in its chemical properties; and there must be sufficient, but not excessive, formation of compounds.

The type of material used for the C.E. is not very important, but there are some definite effects associated with each of them: Cd, e.g., seems to prevent aging.

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When the C.E. is evaporated on, the temperature of the Se is higher than when it is sprayed on, and the contact is intimate: the reaction therefore goes too far. A C.E. formed by the evaporating process seems to impede the electrical forming process. The blocking resistance with evaporated C.E. is initially (i.e. before forming) very high, but soon falls. A layer of SeO_2 applied before the C.E., helps to prevent excessive reaction. The electrical forming process normally results in considerably increasing the reverse voltage the cell might withstand: often the voltage could almost be doubled thereby. The critical parameter in forming is probably the voltage and not the total quantity of electricity, since only a part of the current is used in the forming process.

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"Forming" is the production of a double-layer at the interface; and the rectifications process involves both this and the Schottky space-charge effects. It is known from capacitance measurements that the number of "Störstellen" is increased by forming. Forming with alternating current shortens the time required since the temperature is raised during the forward half-cycles.

At the backing electrode, Bi is evaporated to prevent the formation there of a blocking layer between the Se and the base plate. A complete chemical reaction between the two has been confirmed by Brill, who identified the compound as Bi_2Se_3 (or NiSe). It has since been found useful to evaporate the selenide directly on to the base plate before applying the Se proper. Dr. Koch thinks that other manufacturers have used a layer of graphite for the same purpose.

Literature: W. Koch: Physikalische Probleme der Se Trockengleichrichter. Lecture at München, 14/5/1943
Über den Aufbau der Se Sperrschichten. Lecture at Prag, 11/1944.
Se - Gleichrichterfertigung. 7/1/1947.

(9) (Miss) Dr. M. Herbeck worked on the development of Se rectifiers in the A.E.G. under Dr. Koch.

(9.1) Time Constant.

Se rectifiers cannot generally be used for frequencies higher than a few kilo-cycles. One of the main purposes of Dr. Herbeck's investigations was to find means to reduce the time constant T of these rectifiers so that they could be used for higher frequencies, say up to 100 Kc/s.

As $T = RC$

where R = forward resistance (measured at two volts)

and C = capacitance (at zero voltage),

it was a question of reducing either of these quantities without increasing the other. For instance, with increasing thickness of the film, R increases and C decreases approximately in direct proportion, hence the time constant was found to be almost independent of the thickness unless the film was made very thin, i.e. a few atoms thick. (Film thickness was determined by direct weighing of the material before evaporation or by depositing it from a known volume of a dilute solution, the solvent being subsequently evaporated). Film thickness was varied from a few up to several hundred atomic diameters. In, Bi and Sb, when used as C.E., gave a lower time constant than any other metal. Very thin films of an insulating varnish of low permittivity were also tried. They increased the resistance considerably although they also reduced the capacitance somewhat, but, in effect, the time constant was found to have been reduced to about 1/3 to 1/4 of the normal figure.

(9.2) Counter Electrode.

Various pure metals, evaporated on, were used as counter-electrodes. A layer only a few atoms thick governed the properties of the rectifier, even if it were reinforced by a backing of some other metal. Bi, Sb, Te, Au, all reduced the threshold voltage V_o as defined in Fig. 19. Sn was especially good, but only Bi gave a really low forward resistance. Ge produced a high reverse resistance. These effects are perhaps due to a change of contact potential according to the density of defect electrons. The contact potential may be that due to certain compounds, for instance, selenides, which might be formed during the heat treatment. The resultant distribution of defect electrons, after Schottky's theory, was investigated by means of an audio-frequency bridge developed by Dr. Herbeck, and is shown in Fig. 20 for a normal rectifier, (curve a,) as well as for one with an intermediate insulating film, (curve b).

(9.3) Treatment.

The only effect of heat treatment is to produce the required crystalline form of Se. The electrical formation probably results in shifting defect electrons out of the barrier layer, thus increasing the reverse resistance. Forming with reverse D.C. is preferable to A.C. because of the reduced losses and heating. Unduly long forming periods increase the forward resistance. Breakdown voltage of the film may increase with forming from about 10 to approximately 20 volts, but not much further. With an intermediate insulating layer, forming is unnecessary and breakdown voltage may range from 40 to 60 volts, but this is associated with a higher forward resistance as well. Perfect contact between the Se and the C.E. is essential, hence the latter is normally sprayed on. The material used for the C.E. should have a low melting point to prevent over-heating of the already treated (crystalline) Se during the spraying process. However, the low melting point of the C.E. also limits the permissible operating temperature of the rectifier.

Literature: W. Schottky: Phys. ZS. 41 (1940), 570.

(10) Dr. C. Bosch of the A.E.G./F.I. (Research Institute), had been interested in growing single crystals of Se, and, subsequently, in the investigation of Se rectifiers.

Working with very pure Se which was obtained by repeated distillation, he found that the resistance of a rectifier in the forward (conducting) direction decreased with higher purity, but its permissible current loading was thereby decreased.

Working with Hg-diffusion pumps, Bosch encountered difficulties with Hg vapours: he found that they "poisoned" the Se crystals by forming an amalgam which seemed to attack the crystal edges first. The Hg also seemed to react with the Al base plate and to lead to the formation of hydroxides which seriously interfered with rectification.

At the interface between the Se and the counter electrode, Bosch noticed that diffusion took place, especially between Se and Cd, which seemed to form a number of different compounds such as CdSe, $CdSe_2$, etc., giving rise to some ionic conductivity. Such a diffusion of Cd or Cu into the Se can be observed under the microscope; at very high pressure, (10^4 atmospheres) it occurs within a few hours.

Cd is the most useful component in the alloys used for counter-electrodes, and its replacement by any other metal gave inferior rectifiers. When forming a counter-electrode by evaporation, the type of deposit obtained depends on the metal used and on the temperature of the rectifier disc. Rare metals such as Au, Ag, Pt, give good films, but base metals, such as Zn, Cd or Bi migrate over the surface if deposited at ordinary temperatures, and give uneven films. This effect was demonstrated by masking: Zn, Cd, Bi could migrate into positions under the mask. Better films were obtained by cooling the disc with liquid air. This involved enclosing the disc in a container of inert gas, cooling, and then pumping out while the rectifier remained cold; cooling by conduction and radiation only was insufficient.

If these precautions are taken there is little difference between the performance of evaporated and sprayed counter-electrodes, provided that satisfactory contact can be made. Contact to evaporated films of Cd, In or Tl was made by subsequent spraying with Woods' metal; this gave very good results.

Bosch has developed an electrical forming process of extremely short duration: he charges a large condenser, about 50 µF, up to 400 volts and discharges it in the "reverse" direction into the rectifier. This "burns out" weak spots; there is, however, some danger of also burning the thin film used as the C.E.

Bosch's work was later taken up by Dr. Herbeck, whilst he went over to photo-electric cells and image converters.

Literature: C. Bosch: Herstellung von Leuchtschirmen.
A.E.G. Report. 1/10/1944.

(11) Dr. F. Waibel, physicist with Siemens Halske, had studied various types of semi-conductors, mainly oxides and sulphides, for purely scientific reasons. In 1935, Siemens experienced difficulties in the manufacture of

(11.1) Cuprous-Oxide Rectifiers, when rejects of copper plate alone had risen to about 30%. Waibel traced the difficulties to two causes. (1) Fine surface cracks ("Querrisse") in the Cu ingots which got covered up in the rolling process but gave trouble when used for rectifiers, and (2) "Hydrogen illness" ("Wasserstoff Verkrankung") arising out of an unsatisfactory intermediate annealing process. These difficulties were overcome (1) by milling off the surface layer of the Cu ingots, and (2) by the development of a new etching technique. Rejects then dropped to about 5 - 10%, a figure more in line with other manufacturers' (e.g. Westinghouse) experience.

Subsequently, Waibel took charge of the manufacture of rectifiers. He laid down very definite instructions covering every detail in the manufacturing process, and these instructions had to be very strictly adhered to.

This particularly applied to cells to be used for metering instruments and for high frequency work.

(11.2) Aging.

Some trouble had been experienced from the aquadag which was used to stop the formation of a blocking layer at the "neutral" contact. This was overcome by using a silver coating instead. All rectifiers were subjected to a thermal aging process at the Works. From seven years' experience with these cells, further aging in operation was found to be less than 5%, i.e. the forward current at a given voltage did not drop to less than 95% within that period. Modulator cells were even kept within 3%. Operating temperature should preferably not exceed 50°C because of the danger of instability at higher temperatures. However, in some exceptional cases much higher temperatures, even up to 90°C, might be permitted. The temperature co-efficient is 1.2% per °C for forward and 5% for reverse resistance.

(11.3) Cu_2O vs Se Rectifiers.

Cu_2O rectifiers are preferable to Se types in the following fields:-

(1) For use in Instruments: Such cells are annealed to give highest conductivity. They are only lightly loaded, both with regard to forward current and reverse voltage (about 2 volts per cell). The leakage current is thus very low, especially when sealed into some ceramic tubing as protection from humidity in the atmosphere.

(2) For use in very Low Voltage circuits: Their forward drop is much lower than for Se rectifiers, and they are the only type that will give reasonable efficiency.

(3) For use with High Frequencies: These rectifiers have been used up to 100 Kc/s, but may be suitable even up to 1 Mc/s. They have been found to be stable even at these elevated frequencies. Se rectifiers have a much larger capacitance, and can thus be used only for lower frequencies (up to 3 Kc) beyond which they would become unstable.

Continuous loading with D.C. should be avoided for this as for all other types of contact rectifier. The conductivity in all these rectifiers is to some extent ionic; prolonged unidirectional current may lead to some chemical reaction which would tend to form a high-resistance layer, i.e. give rise to excessive aging.

(11.4) Theory.

Cu_2O when very pure is almost a perfect insulator, as most other pure ionic crystals. By the use of special high-vacuum techniques ensuring the removal of all excess oxygen, Waibel has actually produced Cu_2O films up to 0.3 mm thick and of resistivity as high as 10^{12} Ω cm. Due to the high mobility of the cuprous ions Cu^+ in the interior of the Cu_2O crystal, they can reach the surface easily. In an O_2 atmosphere they then combine with the oxygen on the surface, leaving behind, in the interior of the crystal, places deficient in Cu^+ (or with an excess of $O^=$). At these places, cupric oxide $Cu^{++}O^=$ is formed which is a conductor. It is these "impurity centres" of CuO that are responsible for the conductivity in the "barrier layer". This conductivity is almost entirely electronic, corresponding to positively charged electron - or "hole")conduction. Waibel has measured the distribution of these impurity centres as they penetrate into the Cu_2O, by etching off, step by step, thin slices (about 1/1000" thick) of the film at a time. He then found the reistivity to drop from 10^9 on the surface to about 10^6 Ω cm near the metallic Cu. Rectification ceases when the voltage applied to the barrier layer produces an electric field exceeding a certain critical value (about 10^5 V/cm, i.e. about 30 volts on a film of 3 μ thickness). Owing to the mobility of the Cu^+ ions, the conductivity thereafter rapidly increases and the barrier layer breaks down.

Literature: F. Waibel: Die elektrische Leitfähigkeit des Cu_2O in Abhängigkeit von der Wärmebehandlung. Wi. Ver. Siemens K. 10/4 (1931), 65.

Über den Aufbau der Sperrschicht beim Cu_2O Gleichrichter. Wi. Ver. Siemens K. 15/3. (1936), 75.

Die Bestimmung des O_2 Gehaltes von Cu. Wi. Ver. Siemens K. 15/3 (1936), 87.

(12) Prof. P. Gunther, physical chemist of Königsberg and Breslau University, now with Siemens.

A general survey of rectifiers and semi-conductors, started in Germany during the war, aimed at finding well defined crystals useful for rectification. Many naturally occurring sulphides have long been known to act as detectors, but their behaviour has always been erratic and it was, therefore, decided to synthesise them in the laboratory. The first experiments were made with the

(12.1) Synthesis of Pyrite Crystals. (FeS_2).

It is seen from the vapour-pressure curves of S and of FeS_2 (Fig. 21) that the vapour-pressure of S exceeds the disintegration pressure of FeS_2 at all temperatures below 770°C. Heating a mixture of Fe or FeS with S at lower temperatures will, therefore, always produce FeS_2. To accelerate the reaction a temperature of about 720°C is maintained in the process. As a result, polycrystalline FeS_2 is obtained from the reaction. For experiments in rectification, however, much larger single crystals were required, and it was eventually found that such crystals could be grown out of a melt of FeS_2 in $FeCl_2$ or in $FeBr_2$. Crystals obtained in that way could never be obtained as analytically pure FeS_2, but there was always a certain small amount of free S present which greatly influenced its electrical properties. The type of electrical conduction - excess or deficit conductivity - and the polarity of rectification seem to change sign when there is either an excess or deficit of S in the stoichiometric composition ("amphoteric conduction"). A maximum of rectification was, for instance, found with about 0.4% S, but it was almost impossible to determine quantitatively the amount of excess S to an accuracy better than, say, 0.2 or 0.3%. Generally the effect of free S on the electrical properties swamps all other effects such as intentionally added other impurities or materials used as C.E., etc., so that eventually it was concluded that pyrites were not, at present at least, a material suited for electrical investigations of a fundamental nature.

(12.2) Pure Silicon Crystals.

These were produced by the reduction of $SiCl_4$ by means of carbon in the presence of aluminium. This method has the advantage of working at temperatures far below the melting point of Si (1420°C). Small bits of pure Al were placed into a boat which was put near the closed end of a horizontal quartz tube. Adjacent to this boat, a large number of small carbon rods - 1.45 mm diameter, 8 mm long -are stacked, with their axis parallel to that of the tube. This quartz tube is open at one end and is placed into an outer quartz tube open at both ends, which is heated electrically by a winding arranged so as to concentrate its heat near the aluminium. One end of the outer tube is connected to a small bulb containing $SiCl_4$, the other to a vacuum pump. The whole system is first evacuated, with the $SiCl_4$ kept at a very low temperature; the oven then heats the Al to about 820°C and the temperature of the $SiCl_4$ is allowed to rise up to about - 10°C when its vapour-pressure is approximately 30 mmHg. A reaction then sets in between the Al vapour and the $SiCl_4$ vapour, reducing the chloride to pure Si which is given off in the atomic (quasi gaseous) state and sublimes on the small carbon rods producing a layer of a few thousandths of an inch in thickness. Rectification being a surface effect, this thickness is quite deep enough for detectors; these are made by simply breaking each carbon rod in two, one contact then being established on the broken carbon face and the other on the Si opposite.

There is always some Al left in the Si from the reaction; its amount has been determined by Ziegler at Breslau University from the absorption of light. Rectification was obtained only within a definite range of Al content; with an impurity of less than 0.1% the Si had a very high resistance in both directions, with more than 2% it acted as a good metallic conductor. Rectification was confined within these limits but the best results were obtained between 0.2 and 1.0% of Al. This rather contradicts Schottky's theory whereby an impurity amounting to $1:10^5$ should produce best rectification.

Typical values of the electrical resistance were approximately 100 ohms in the forward and 10,000 ohms in the reverse direction, breakdown voltage varied between 10 - 30 volts.

<u>Literature:</u> <u>P. Günther:</u> Künstliche Detektoren (Pyrit, Silicium). 1947.

(13) <u>Dr. H. König.</u> previously of T.H. Danzig, now at Göttingen University.

Before the war, he was working on thin films and their application to mirrors. At the start of the war, Herr Welker of Munich had obtained rectification with Si and Ge crystals when in contact with a thin W point. Owing to the scarcity of Ge, König tried to use thin films of Ge in place of the crystals. Purest available Ge was obtained from Messrs. Franke of Frankfurt a.M., and films of several hundred Ångstroms were evaporated on glass and molybdenum surfaces. Electron diffraction pictures showed a disorderly arrangement of small tetrahedral crystals which, on heating to 500°C, assumed a more regular pattern. No rectification was, however, obtained with these films; the only apparent difference from Welker's arrangement was the size of the crystals. Efforts to obtain larger crystals by the evaporation method failed. Eventually, it was found that by reducing $GeCl_4$, similarly as described in the previous section for $SiCl_4$, but using a stream of hydrogen as the reducing agent, the size of the crystals obtained could be varied from about 1/100 to 10 μ by varying the speed of the hydrogen stream. It was then found that with crystals larger than 1 μ, rectification could be obtained. A contact electrode of very thin tungsten wire was used, etched down to a few μ in diameter. König thinks that rectification with such crystals can only be obtained when the crystal size is of the same order of magnitude as the contact whisker, but he has no conclusive evidence for that opinion.

<u>Literature:</u> <u>H. Welker:</u> Über den Spitzendetektor end seine Anwendung zum Nachweis von cm Wellen. Jahrbuch 1941 d. deutschen Luftfahrtforschung S 11163/68.

Photocells

(14) Prof. R. Frerichs of the Kaiser Wilhelm Institute, Berlin-Dahlem and T.U. Berlin-Charlottenburg, has been working for the Osram Studiengesellschaft für elektrische Beleuchtung, on the development of new types of light sources and has taken a special interest in phosphors. When investigating mixed crystals of ZnS and CdS, he found the ZnS to be more sensitive to blue light - its maximum sensitivity lies at 4,200 A - whilst CdS was more sensitive in the long-wave (red-light) range, hence very useful in conjunction with incandescent filament lighting which always contains a large proportion of long-wave radiation. This investigation led to further work on CdS and its application to photocells. The work was speeded up during the war, when Frerichs joined the A.E.G. in 1941, with special applications for fire control of fighter planes, etc., in mind.

(14.1) CdS Photo-Conducting Cell.

CdS crystals are prepared by the reaction of H_2S gas with Cd vapour. Clear yellow needles of the crystal are formed, about 10 x 2 x 2 mm^3 in size. Aluminium electrodes are soldered on to two opposite long faces of the crystal, leaving an area about 10 mm long by 2 mm distance between electrodes free for exposure. In the dark, such a crystal is a very good insulator, its resistance being about 10^8 to $10^9 \Omega$. When exposed to daylight, its resistance drops to a comparatively low value, about $10^4 \Omega$. The value of the photo-current is not uniquely determined by the amount of light falling on the cell, i.e. the photo-current does not reach a saturation value when the voltage across its terminals is increased, but rises proportionally with it until thermal effects begin to set in. In other words, it is a case of internal secondary photo-electric emission with a quantum yield much larger than 1, i.e. many electrons are liberated into the conduction band by each photon. CdS crystals may thus be used for very convenient and robust photocells by simply connecting a D.C. voltage of, say 20 volts across the crystal, with a simple milliammeter in series, no specially sensitive instrument or amplifier being required. The response of the cell extends far beyond the visible into the U.V. and even to X-Rays. It can, therefore, be used to build a very simple X-Ray dosimeter.

An application of the cell for military purposes, that did not, however, materialise owing to the "premature" end of the war, was as the detector element of an automatic fire control unit for fighter planes operating in daytime. The objective lens of a telescope throws light from the sky on to the photocell. Any sudden change in the illumination such as is produced by an approaching target, can be made to trigger off the fire control. With the characteristics of the CdS cell as described, such a device can be made very sensitive.

Some experiments were also made with CdSe and CdTe cells, the sensitivity of which extends to larger wavelengths, even into the IR. They are, however, much more difficult to manufacture and special precautions have to be taken owing to the poisonous nature of the reaction products.

(14.2) TlS Photo-Voltaic Cell.

I.R. detection methods can broadly be divided into two classes: the first method uses the heat radiation emitted from the target according to its surface temperature. This entails detecting radiation of fairly long wavelength. The exact intensity distribution of the radiation depends mainly on the surface temperature of the target: e.g. for a temperature of 500°C the intensity has its maximum at a wavelength of $3.73\,\mu$, for 250°C at 5.52 and for 0°C at $10.56\,\mu$. The best-known compounds exhibiting photo-conductivity under such radiation are those of lead, as for instance PbS, PbSe and PbTe.

The second method mentioned floods the target with I.R. radiation from a special source. This may be an ordinary incandescent lamp, the visible radiation of which is held back by a low-pass filter with a very sharp cut off somewhere near $0.7\,\mu$, the red end of the visibility limit of the human eye. In such cases the I.R. radiation used will have its maximum intensity in the near I.R. and photocells with maximum sensitivity in that region are required. TlS is such a substance, its photo-emission having a maximum response for radiation of about $0.9\,\mu$. In 1938, Nix in the U.S. described a TlS cell which, however, was rather difficult to produce. Tl is easily oxydised and Nix used complicated vacuum techniques to overcome that difficulty. Frerichs has developed another method by maintaining a continuous flow of hydrogen over the Tl until it is sulfided by a stream of H_2S. Such TlS cells were embodied in equipment "Flamingo" for use in U-boats. They consisted of an I.R. searchlight with a rotating mirror and a TlS detector and amplifier, the output of which was fed to a cathode ray display tube with circular time base. Targets could be detected at a range about 10 times bigger than that at which the U-boat itself could be seen by the red light which the filter would pass.

Literature: R. Frerichs: Über die Photoleitung des reinen CdS I.
A.E.G. Report, 1944. Messung von β und γ Strahlen durch innem Photoeffekt in Kristallphosphoren.
Natur Wi. 33 (1946), 251.
Über die optischen und elektrischen Eigenschaften des reinen CdS. Natur Wi. 33 (1946), 281.

(15) Dr. M. Treu was assistant to Prof. Gudden of Erlangen University, the pioneer in photo-electric research, who died in 1945. In 1935, Treu wrote his doctor's thesis on "Photo-Electric Properties of PbS" which was kept secret at the request of the O.K.W. (German High Command). In 1936, Gudden obtained a contract from the O.K.W. to start a special laboratory (called S-Labor) for the development of infra-red research, and Treu was detailed for this work which was transferred to Prague in 1939, after Czechoslovakia had been overrun.

(15.1) I.R. Photo-Conducting Cells.

He first developed a chemical process for the manufacture of PbS cells, based on the Swiss patent of Grutzmacher. This process was abandoned in 1938, and Treu went over to the evaporation process which was brought to completion during the war and was handed to Zeiss for manufacture of the cell. Thereafter, Treu turned to PbSe cells which have a sensitivity stretching farther into the infra-red, up to about 5 μ. He started off with an old U.S. patent, taken out by Case in 1914.

In the process as finally adopted, the purest available Pb and Se (pearls in the red formation) was used and brought to reaction in vacuum at a high temperature. The PbSe so obtained was heated again to drive off any excess Se. The pure PbSe was then evaporated on to a heated glass plate, oxygen being admitted in the process to produce the defect centres in the lattice necessary for photo-conductivity. (Oxygen can easily replace the Se to which it is closely related, in the PbSe lattice without introducing unduly large distortions). The supply of a very small amount of energy, as e.g. by photons of I.R. wavelength is sufficient to raise electrons in the immediate neighbourhood of such defect centres into the conduction band.

(15.2) Operation and Testing.

Small areas, about 2 mm square, of the photo-conducting film were used for testing. The resistance of such a film between two opposite edges was about 10^5 ohms. A D.C. supply voltage of about 10 V was connected across the cell with a load resistance of similar ohmic value in series. An amplifier of large band width was used to measure the voltage variation across the load. The "noise" of the cell, i.e. the amplifier output voltage, with the cell covered up to keep out any radiation, is plotted in Fig. 22 against the D.C. supply voltage (curve N). For low voltages the noise is fairly constant (part α) probably corresponding to Johnson noise; it is about 6 μV for an amplifier of band width 30–10,000 c/s. With higher supply voltages, the noise rises at a fairly constant rate (part β). This part of the noise is probably due to the semi-conducting nature of the cell. If the voltage is increased beyond point A, the electric field in the semi-conductor becomes sufficiently strong for ionisation by collision to set in which will create additional noise. When operated beyond this point, the cell is likely to be damaged. Measurements were, therefore, usually carried out in the range β where the ratio S/N is fairly constant (= 10 approximately).

Having now found the noise response, the cell was irradiated from a constant source of light, the beam of which was interrupted 300 times per second. The response of the cell to this "signal" (curve S) was again plotted against the supply voltage. This gave nearly a straight line up to the point A when the response started to flatten out.

This is due to a decrease in the number of defect centres available for carrying the signal, i.e. for photo-electric emission into the conducting band, as soon as ionisation by collision sets in. The intersection of curves N and S, (S/N = 1), corresponds to the practical limit of detection with these cells. It was found more convenient to adopt this method rather than to vary the intensity of the light beam until S/N = 1, as this would have entailed varying the distance between cell and source over a large range. Varying the <u>intensity</u> of the source might have affected its spectral distribution. With PbSe cells, a body of 300°C surface temperature could be detected directly by its heat radiation when two metres away, the radiation in this case giving a signal equal to noise. Much cooler bodies (even the heat from a human body!) could be detected at a distance of 20 metres by the use of a **mirror** of 60 cm diameter.

<u>Literature:</u> <u>M. Treu:</u> Elektrische u. lichtelektische Untersuchungen an Pbs. Thesis. Erlangen, 1935.

(16) <u>Dr. W. Schaffernicht</u> of A.E.G. Valve Works, Clausthal.

When working at Marburg University under Prof. Tomascheck, he became interested in photo-electric effects. In 1934 he joined the A.E.G. Research Institute, in charge of "Applied Electronics". During the war his main work was the development of image converters ("Bildwandler"), which reached a high degree of perfection. The I.C. has been described elsewhere, so only a short description will be given here.

(16.1) <u>Image Converters using Photo-emitting Cathodes.</u>

The I.C. consists of a photo-cathode, usually Cs_2O-Ag, on which an optical (I.R.) image of the target under observation is formed. Electrons emitted from the cathode are accelerated by a potential difference of 20 KV and pass through specially shaped electrostatic fields which act as an electron-optical lens system. All electrons emitted from any one spot of the photo-cathode are thus brought to focus on a fluorescent screen on which an image of the object is thereby made visible.

(a) The photo-cathode has its maximum sensitivity at 0.8 μ with a threshold at 1.3 μ, i.e. it is sensitive to the near infra-red. For maximum contrast of the image, emission from parts of the cathode which are not illuminated must be reduced to a minimum. This is done by preventing

(α) thermal emission, by cooling with solid CO_2 or, in special cases, with liquid air,

(β) electric field emission by keeping the electric field strength at the cathode surface very low, at about 100 V/cm.

(b) The acceleration of the electrons is done in two steps, i.e. with two anodes in series, the first bringing the speed of the electron up to about 2 KV and the second to full speed, about 20 KV. By such means the background intensity was reduced to 10^{-2} Apostilb at room temperature and to 10^{-6} when being cooled by liquid air. The latter figure coincides with the minimum amount of illumination visible to the eye, i.e. there is no point in reducing the background any further.

(c) The fluorescent screen is made of very fine grain - about 4 μ average size - of ZnS or CdS powder. The thickness of the layer is made such that the whole energy of the impinging electrons is absorbed in it, i.e. approximately 10 μ for an accelerating voltage of 20 KV. On top of the fluorescent layer, i.e. on the side facing the cathode, a transparent layer of Al, 0.1 μ thick, is evaporated. This prevents the screen from charging up, and also increases the intensity of the image by secondary emission. It also acts as a protection of the screen from Cs vapour given off by the cathode. Such vapours would greatly shorten the life of the I.C.

The resolution of such a screen is about 20 μ, or, with the finest available grain, about 10 μ.

(d) Sensitivity. With the I.C., targets could just be detected when they produced an image of radiation intensity of approximately 10^{-12} W/cm^2 at the cathode. A black body of 200°C surface temperature, e.g. gives off near infra-red radiation of sufficient intensity.

(e) Application. Image converters were used for

(1) signalling with I.R. light sources invisible to the enemy,

(2) observation of targets illuminated from an I.R. "searchlight",

(3) observation of targets by their own I.R. (heat) radiation.

(16.2) Image Converters using Photo-Conductors.

The response of photo-conductors stretches farther into the I.R. than that of photo-emitters, e.g. PbS has its threshold at about 3.5 μ against 1.3 μ for Cs_2O-Ag cathodes. For detection by heat radiation of targets with comparatively low surface temperatures - less than 200°C - I.C. using photo-conductors are obviously to be preferred. Such converters have, of course, to be designed on different principles. On the film of semi-conducting material the I.R. image of the target is formed, thereby lowering the resistivity of the illuminated portions of the surface. On to the other - reverse - side of the semi-conductor film a beam of electrons is directed from a hot filament or other convenient electron source. This beam charges the film according to its resistivity, and is then reflected on to a fluorescent screen on which the image can thus be observed directly or through a magnifying glass.

The development of such image converters was only in its initial stages in Germany at the end of the war.

Literature: W. Schaffernicht: Der Elektronenoptische Bildwandler. Z.S. f. tech. Phys. 17 (1936), 596.
Bildwandlerrohr Entwicklungen. 1944.
W. Veith: Bildwandler Entwicklungen. A.E.G. Report 1944.
C. Bosch: Herstellung von Leuchtschirmen. A.E.G. Report 1944.

(17) Dr. J. Kaspar, a physical chemist with the A.E.G., was mainly responsible for the chemical side of the development of I.R. photocells and image converters.

(17.1) Chemical Development of PbS Cell.

PbS cells only were used in practice, because the other cells available for I.R. detection (PbSe, PbTe, etc.) required complicated cooling systems. PbS cells were cooled fairly simply to -78°C by "dry ice" (solid CO_2).

Stoichiometrically pure PbS has a simple cubic crystal structure, and is a poor conductor. With an excess of either Pb or S, however, its conductivity increases amphoterically. On the substitution of a small number of its $S^{=}$ ions by $O^{=}$, it becomes photo-sensitive; the slight lattice distortion thus produced apparently creates additional conduction levels only slightly above the filled electronic levels in the crystal. The Firm of Kast & Ehinger of Stuttgart, who actually produced these cells, made X-Ray absorption measurements and found a concentration of $O^{=}$ ions of about $1:10^6$ sufficient for photo-conductivity.

Kaspar studied especially the formation of the PbO nuclei. A nucleus of very small dimensions will always dissolve as its vapour pressure is very large. Nuclei can thus only form if their size exceeds a certain critical value. The formation becomes a question of thermodynamic probability for a sufficient number of Pb^{++} and $O^{=}$ ions to be close together at any one moment to start the building up of a nucleus. It was found that the presence of a very few Cu^{+} ions could "poison" this formation, as they tend to form minute crystals of Cu_2S which, having a rather complex crystal structure, interfere with the building up of the simple structure of PbS and PbO at those rare moments when conditions, as described above, would be favourable.

When pure PbS cells were carefully evacuated and an atmosphere of nitrogen admitted, photo-conductivity was destroyed. In an atmosphere of oxygen, however, it was quickly restored. With carefully developed techniques a definite relationship could be established between the concentration of impurity centres, (i.e. partial pressure of oxygen) and the sensitivity. One main source of trouble in the past has been the difficulty of obtaining reproducible behaviour of PbS cells. This, according to Kaspar, is partly due to the long time required for many Pb - compounds to reach chemical equilibrium. Various plumbits (lead hydroxide) e.g. only reach equilibrium after several weeks.

(17.2) Background Noise is due to four causes:

(a) Johnson Noise, due to thermal random movement of electrons, as occurs in any metal, is mainly dependent on temperature.

(b) Semi-Conductor Noise is due to the lifting of electrons into the conduction band and to their falling back again. The "lifetime" τ of an excited electron, i.e. the length of time for which it remains in the conduction level before falling back depends on the way the cells have been produced, and may vary from 1 to 10^{-4} seconds in PbS cells. (It is very much longer in the alkali-halide crystals described in Section (1)). Signals applied to a cell at intervals shorter than τ cannot be properly accepted by it, i.e. the upper frequency limit for devices using such cells is given by $\nu_o = 1/\tau$. On the other hand, the use of very low frequencies would entail large condensers and transformers in the amplifier. In practice, wave bands within a range of 400 to 4,000 c/s were used in conjunction with these cells.

Inherent in any semi-conductor is a relatively small number of free electrons present in the conduction band at any particular time. However, to provide reasonable sensitivity, i.e. a sufficient number of conducting electrons in spite of their short life-time - which is required for high signal frequency - electrons have to be raised very frequently to the conduction band. As every jump, up or down, creates a faint "click", the total noise is obviously large. The semi-conductor noise level is largely dependent on the magnitude of the electric field, and also on its polarity.

(c) Contact Noise ("Elektroden Rauschen"). At the boundary of a semi-conductor with a metal electrode, conditions similar to those in a contact rectifier arise which, according to Schottky's theory, lead to the establishment of a thin "barrier layer", i.e. a layer containing relatively few conduction electrons. Statistical changes in their number again give rise to large percentage changes and corresponding noise. This part of the noise is again dependent on field strength and polarity, and also on the nature of the electrode material.

(d) Grain Noise ("Korn Rauschen") is due to imperfect contact between individual grains in the film which are in contact at a few discrete points only. At these points the number of conduction electrons is rather small and conditions similar to those mentioned in the previous paragraph arise, except that this component of the noise is obviously independent of polarity.

(17.3) Performance and Application.

PbS cells, cooled by solid CO_2, have a sensitivity limit of approximately 0.2 μW at a signal frequency of 10 Kc/s, such a signal giving a ratio S/N = 1. This is sufficient to detect directly thermal radiation from a body of 350°C surface temperature. Using large mirrors to concentrate more radiation energy onto the cell, aeroplanes and ships a dozen or so miles away could be detected at night by their I.R. heat radiation. Similar devices were used for homing devices in rockets, proximity fuses, etc.

Literature: J. Kaspar: Infrarot - Fotohalbleiter. 1945.

(18) **Dr. H. Pick**, first assistant to Prof. Pohl at the first Physical Institute, Göttingen University, has been working on the development of PbS cells during the war. He has given a detailed description of this work in a report written in 1944.

PbS is a semi-conducting material. When exposed to infra-red light, its conductivity increases by as much as 100% under the brightest source available. In order to reduce the background noise level, measurements were not made under continuous illumination but with a beam of light interrupted at a frequency of 1,000 c/s. The main result of his investigation was that the quantum yield, i.e. the percentage change of conductivity for one quantum absorbed, was constant over the whole range of wavelengths from 0.25 μ (where the glass cover used in the cell became absorbent) right up to the threshold wavelength of 3μ.

Literature: **H. Pick:** 1946. PbS Zelle und innerer Photoeffekt.

(19) **Dr. H. Gaertner** now with the Bizonal Economic Department at Minden.

During the war he held a responsible position at the Heeres-Waffen-Amt, Berlin, in the Department for Optics and Measurement, where he had access to all work connected with I.R. research. He maintains to have handed over to allied personnel the following reports:-

1. Bedeutung der Ultraroten Strahlen für militärische Verwendungszwecke. Dr. H. Gaertner.

   Heft I : "Die Durchlässigkeit der getrübten Atmosphäre im Ultra-Rot Gebiet"

   Heft II: "Ultra-Rot Photographie"

2. Ultra-Rot empfindliche Phosphore und Wärme-Ortung - Dr. H. Gaertner.

3. Allgemeine Einführung in die Tarnung im U.R. - Dr. H. Gaertner.

4. Sichterweiterung durch Infra-Rot Moment-Photographie - Wilhelm Schlömer.

5. Leutschirme für Bildwandler-Röhren - Dr. Schaffernicht, A.E.G.

6. U.R. Feldstecher - Englisches Beutegerät - Dr. Kessler, C. Zeiss.

7. Beschreibung und Bedienungsanweisung des Gerätes "Mosel" - Siemens, A.E.G.

8. Beschreibung für Gerät "Donau 60", C. Zeiss.

9. Das Warmepeilgerät der Fa. C. Zeiss - H. Plesse.

10. Warmebildgerät Potsdam "II" - E. Leyboldts Nachf.

He, furthermore, supplied the following list of prominent workers engaged on I.R. research during the war :-

I. Image Converters.

   1. Dr. W. Schaffernicht
      A.E.G. Röhren - & Gleichrichterfabrik
      Glausthal-Zellerfeld I, Bauhofstr. 7a.

2. Dr. Veith
formerly A.E.G. Forschungsinstitut, Berlin-Reinickendorf,
now in Paris, working at Sorbonne.

3. Herr Schmalenberger
formerly best expert on tube making of A.E.G.,
now most probably engaged by the French.

4. Dr. Heimann
formerly Reichspost-Forschungsanstalt, Berlin-Kleinmachnow,
now Physikalisch-Technische Werkstätten, Wiesbaden, Langgasse.

5. Dr. Eckart
formerly physicist of A.E.G. Forschungs-Institut, Berlin-Reinickendorf,
now engaged by the Russians in Berlin.

6. Dr. Fenner
formerly Reichspost-Forschungsanstalt, Berlin-Kleinmachnow,
now engaged by the Russians in Berlin.

7. Dr. Allekotte
formerly physicist in Heereswaffenamt, Berlin-Charlottenburg,
now (22b) Idar-Oberstein 2, Postfach 49, French Z.

II. Infra-Red Phosphors.

Dr. Lotz, Berlin-Siemensstadt,
Forschungslabor von Siemens & Halske.

III. Bolometer-Receivers.

1. Dr. Plesse
formerly Zeiss, Jena,
now working with Zeiss Opton,
(14a) Königsbronn, Kreis Heidenheim, Herwart-stalt.

2. Prof. Dr. M. Czerny
Frankfurt a. Main, Physikalisches Institut der Universität, Robert Mayerstr. 2.

IV. Photo-Cells.

1. Dr. Kutzscher
   formerly Elektroakustik,
   Kiel, Weddigenring.

2. Dr. Treu
   formerly assistant of the late Prof. Gudden,
   Prag.

3. Dr. Casper
   formerly A.E.G. Forschungs-Institut,
   Berlin-Reinickendorf,
   now perhaps in Konstanz, Bodensee.

4. Dr. Guillery
   Siemens-Schuckert,
   Nürnberg, Landgrabenstr. 100.

V. Infra-Red Filters.

Dr. Rein
formerly I.G. Farben, Werk Mainkur
Frankfurt-Fechenheim.

(20) Prof. H. Kallmann of the Kaiser Wilhelms Institut, Berlin-Dahlem, and Prof. of Theoretical Physics at T.U. Berlin-Charlottenburg, is largely interested in atomic theory. In 1933 he started working on neutrons and in 1935 he joined the I.G. Farben to develop a method of

(20.1) Photography by Neutrons similar in principle to X-Ray photography: Bodies opaque to ordinary light are irradiated by a beam of neutrons which are absorbed according to their speed and to the nature of the target. The transmitted beam is made to produce one of several possible reactions which eventually produces a chemical reaction on the photographic plate, and thus the image. Neutron reactions which have been tested include the following:-

(1) Slow neutrons falling on Li or B and producing H_3^1 or He_4^2.

(2) Neutrons captured by Gd with subsequent electron (β-ray) emission.

(3) Absorption of slow neutrons by Cd with subsequent γ-ray emission.

The first pictures were obtained by Kallmann and Kuhn in 1938.

Neutron photography might find a practical application in the examination of very heavy targets which are opaque even to the most energetic γ - radiation.

(20.2) α - Particle Recorder.

Kallman has recently developed a scheme that will record the energy of individual α- particles: α-particles from a radium source impinge on a fluorescent screen of activated ZnS which is placed over the window of an electron multiplier tube, the output of which is fed through an amplifier to a C.R. display tube. Whenever a particle strikes the fluorescent screen, a scintillation occurs which releases about a thousand electrons from the photo-cathode of the multiplier. These electrons are amplified about 100,000 times in number in the tube, and thus pass a signal of about 10 to 100 mV into the amplifier. The amplitude of the signal is directly proportional to the energy of the α - particle. The multiplier is cooled by solid CO_2 to reduce its background noise to a level sufficiently below the signal. To reduce pick-up of heat radiation and thus the noise level, the photocell should have its maximum sensitivity at the same colour as the scintillation and should be fairly insensitive to noises and to longwave - I.R. - radiation. The thickness of the fluorescent layer is fairly critical: if the layer is too thin the α - particles pass across it without giving up their whole energy; if too thick, the light of the scintillation is absorbed before it can leave the screen.

Various materials have been investigated for the fluorescent screen. ZnS is most suitable for the detection of α- particles, and $CaWO_4$ for β- particles.

<u>Literature:</u> <u>H. Kallmann:</u> Durchleuchtung und Photographie mittels Neutronen. Naturwissenschaften 1947.

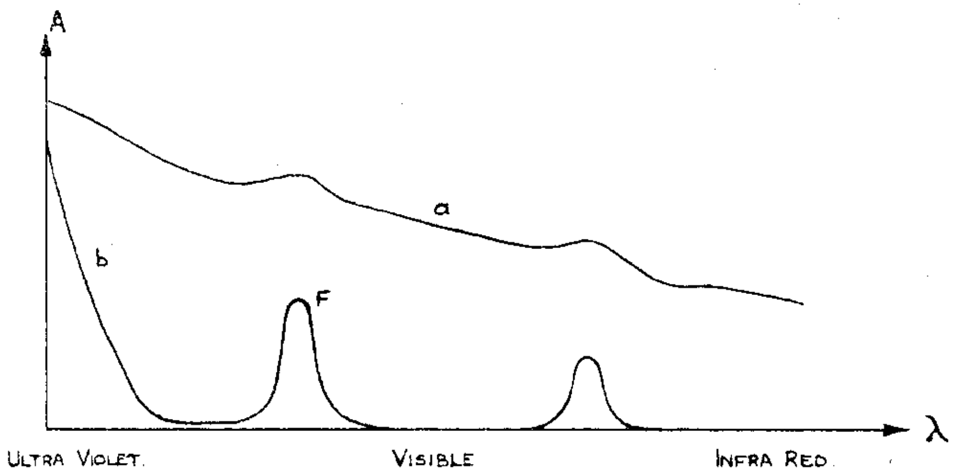
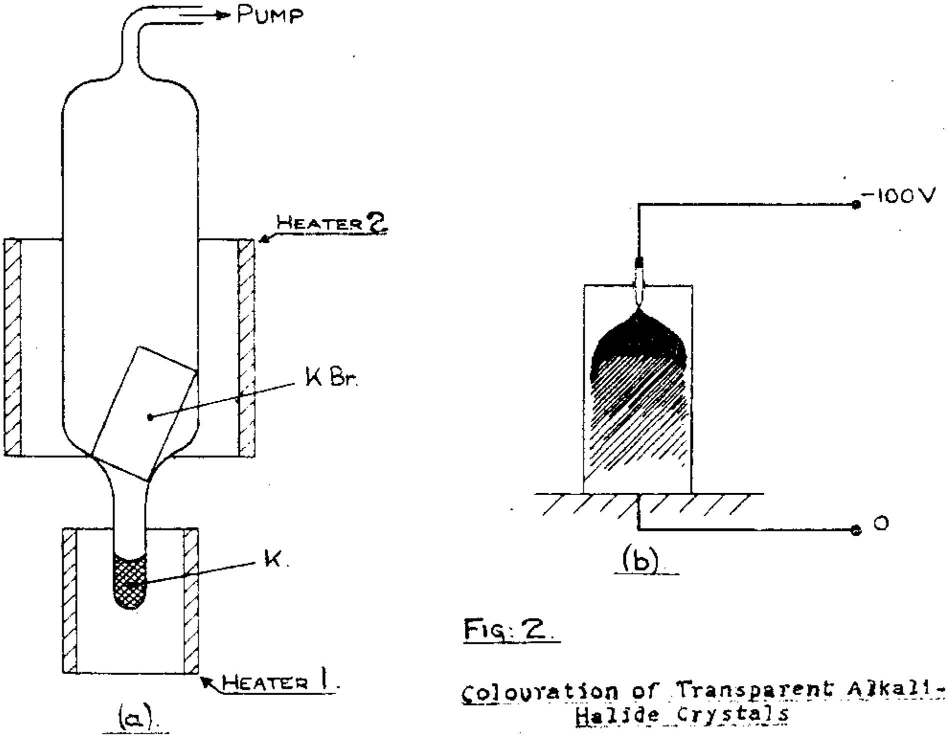


Fig. 1.

Absorption Curves

(a) PbS
(b) KBr



(a).

(b).

Fig: 2.

Colouration of Transparent Alkali-Halide Crystals

(a) by vapour (b) by electrons directly.

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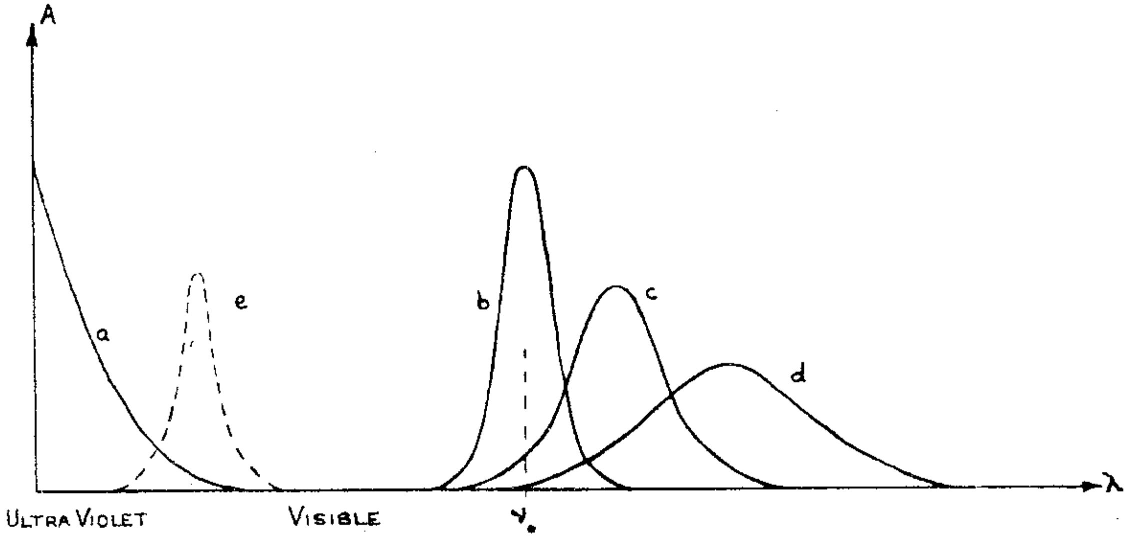
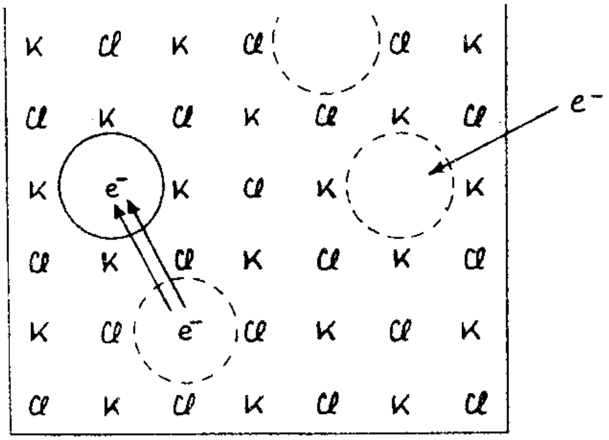


FIG. 3.

Absorption Curves of an Alkali-Halide Crystal

(a) transparent (absorption in U.V. region only)
(b) with colour-centres at low temperature
(c,d) with colour-centres at higher temperature
(e) after absorption of hydrogen



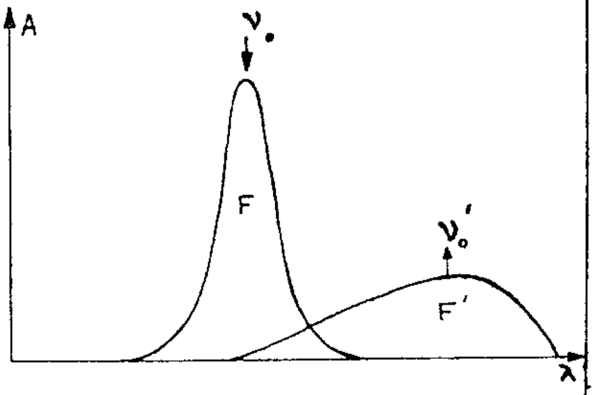


FIG. 4.

Colour-Centres:

F centres (e) and F' centres (2e)

FIG. 5.

Absorption due to F and F' Centres

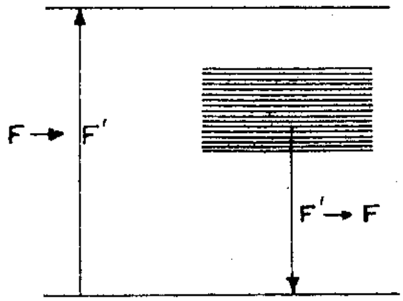


Fig. 6.

Energy levels corresponding to Transition between F and F' Centres

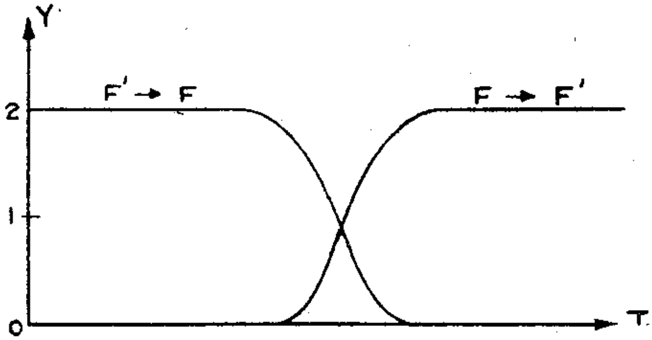


Fig. 7.

Quantum Yield of Transition between Colour-Centres

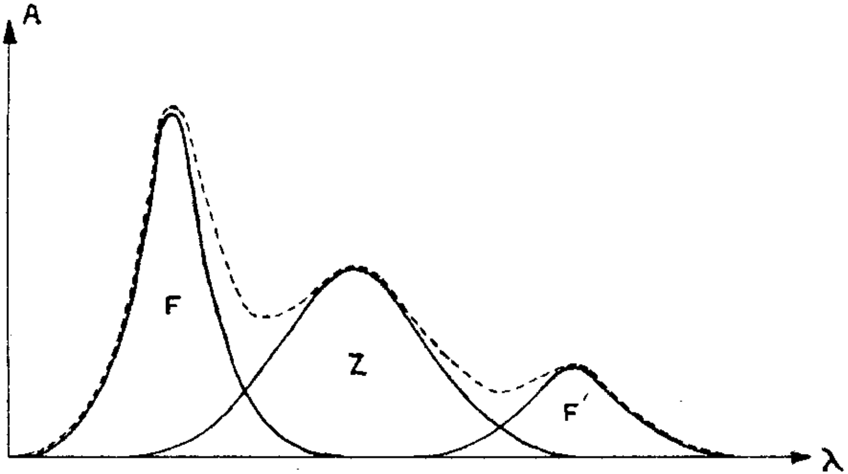


Fig. 8.

Absorption of Crystal

with several different types of colour-centres (F,F',Z)
-------- resultant absorption

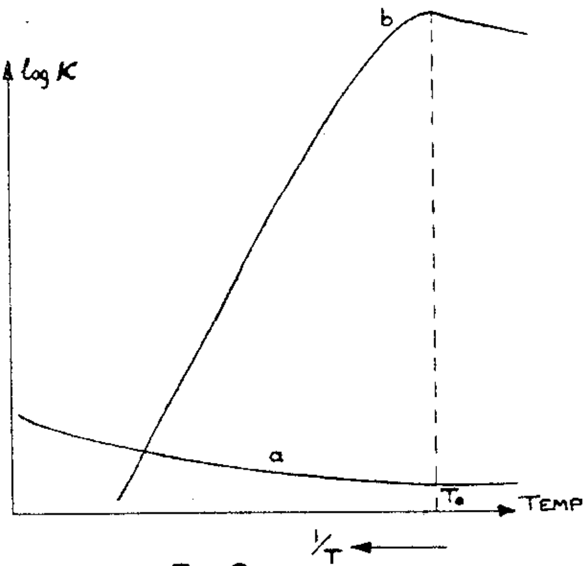


FIG: 9.

Electrical Conductivity of a

(a) metal
(b) pure semi-conductor

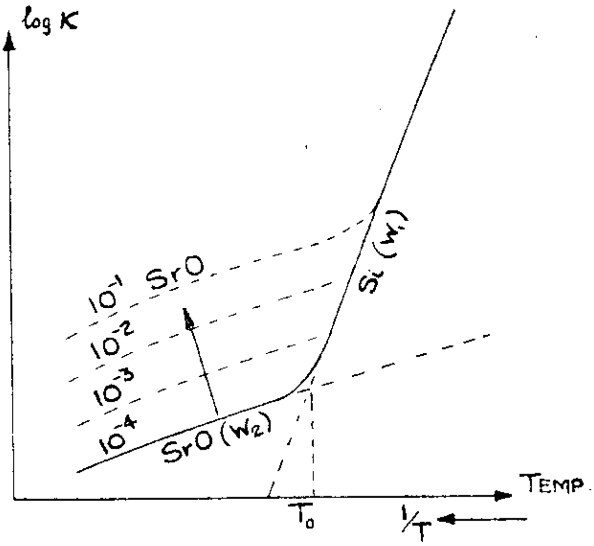


FIG: 10.

Electrical Conductivity of Semi-Conductor

(e.g. Si, activation energy W_1), with various amounts of added impurity (e.g. SrO, activation energy W_2).

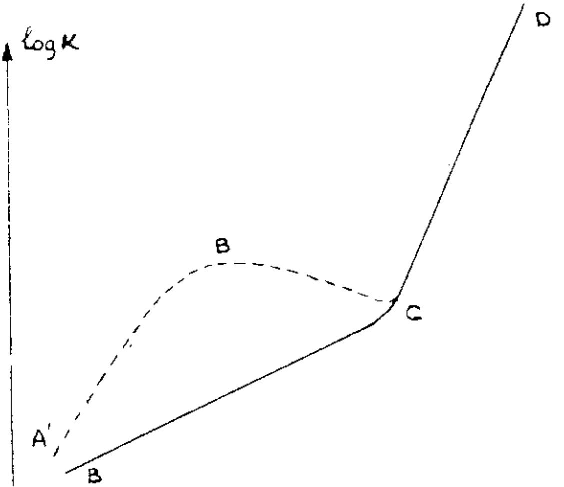


FIG. 11.

Conductivity of AgCl

——— in the dark
------ after illumination

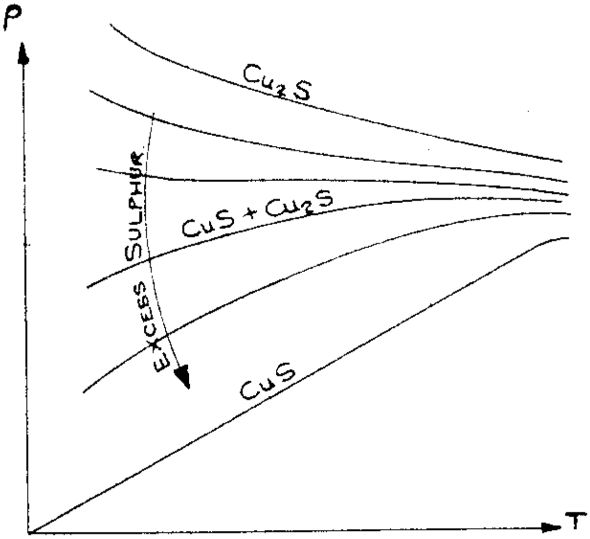


FIG: 12.

Resistivity of Compounds

ranging from cupric to cupreous sulphide

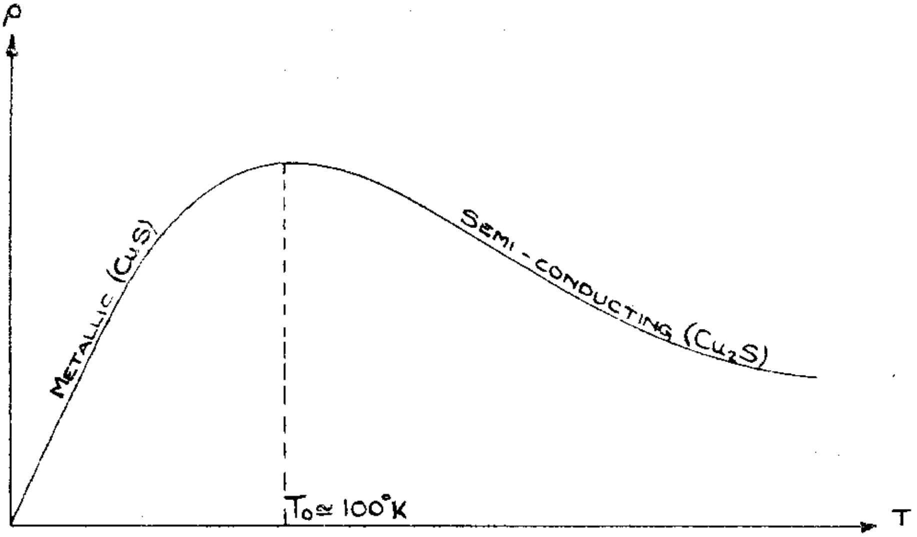


Fig: 13.

Resistivity of CuS with 20% excess S

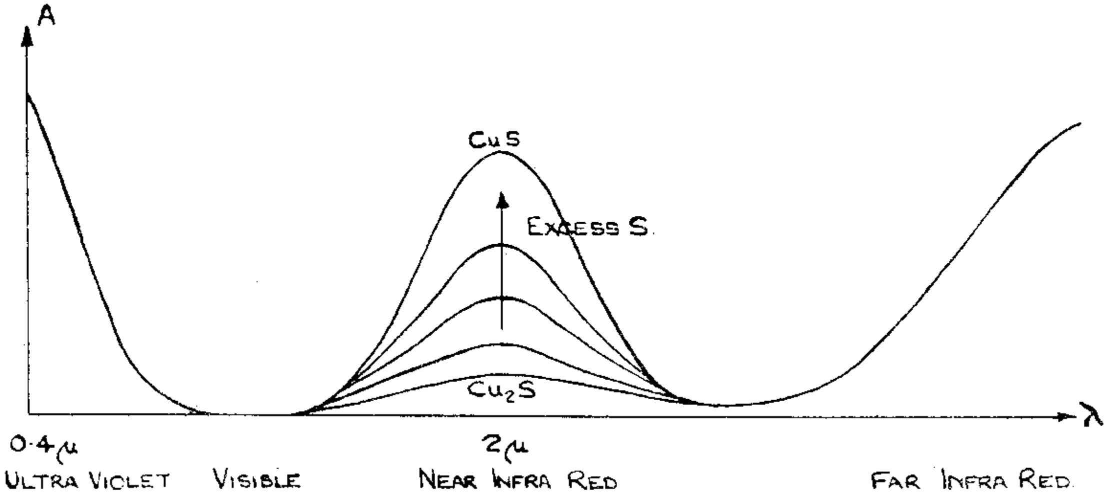


Fig: 14.

Absorption of Cu_2S with excess S

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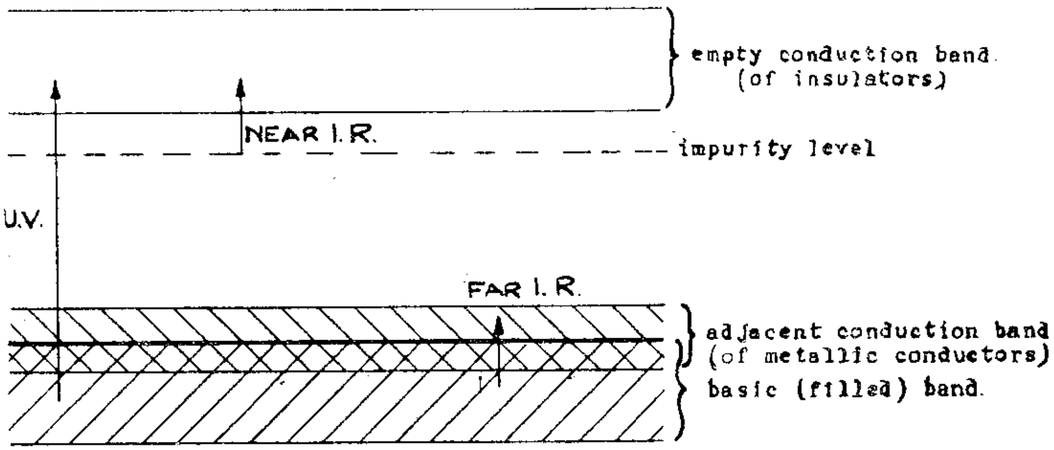
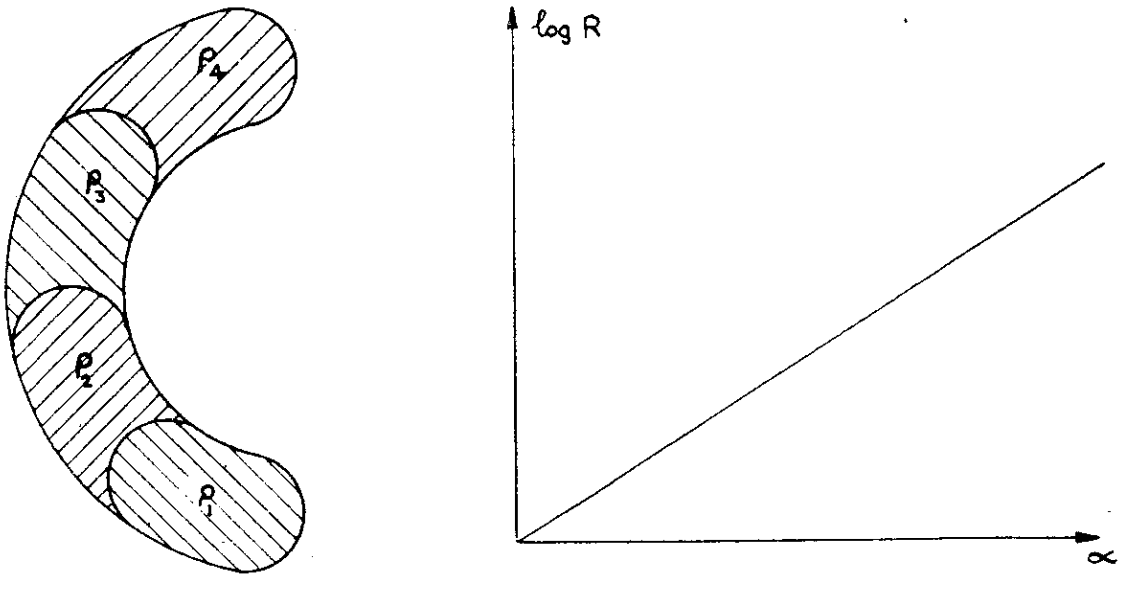


FIG: 15.

Energy Levels and Bands in Various Types of Solid Conductors with corresponding Absorption of Radiation



(a)

(b)

FIG. 16.

Volume Control Resistor

(a) containing parts of different resistivity ρ_1, ρ_2, ρ_3, ρ_4.
(b) linear characteristic of log R vs angle α

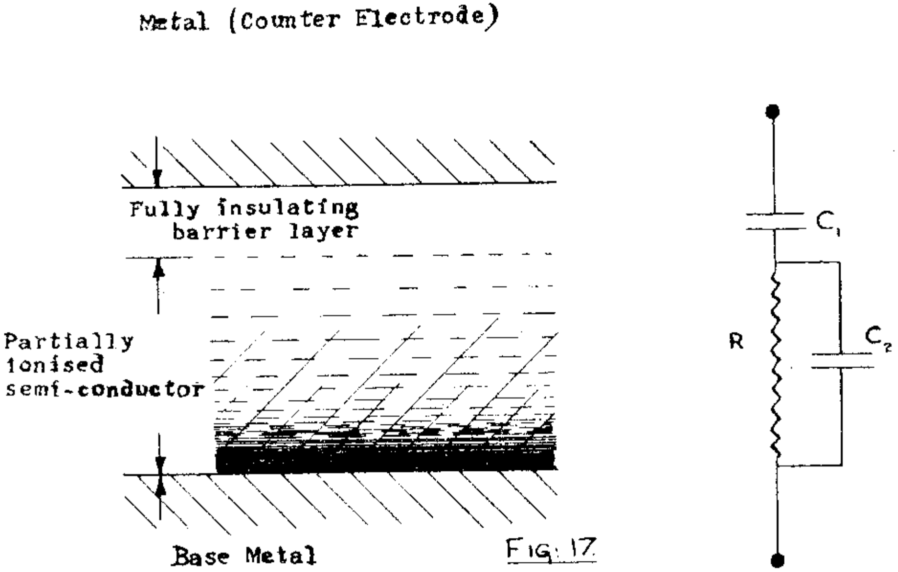


FIG. 17

Arrangement and Equivalent Circuit of Contact Rectifier

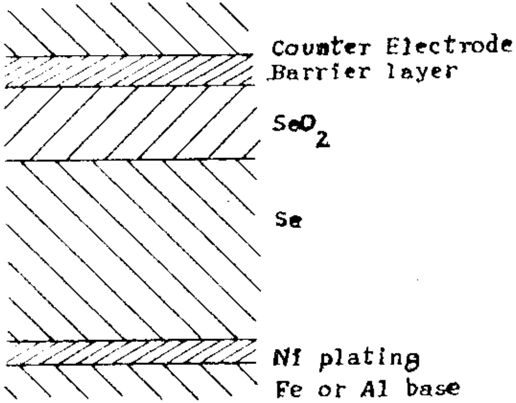


FIG. 18.

Se Rectifier

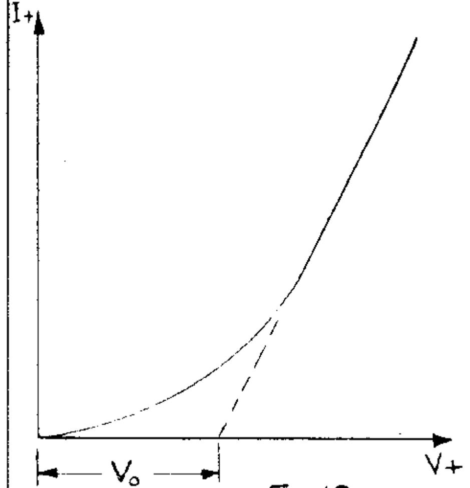


FIG: 19.

Definition of Threshold Voltage

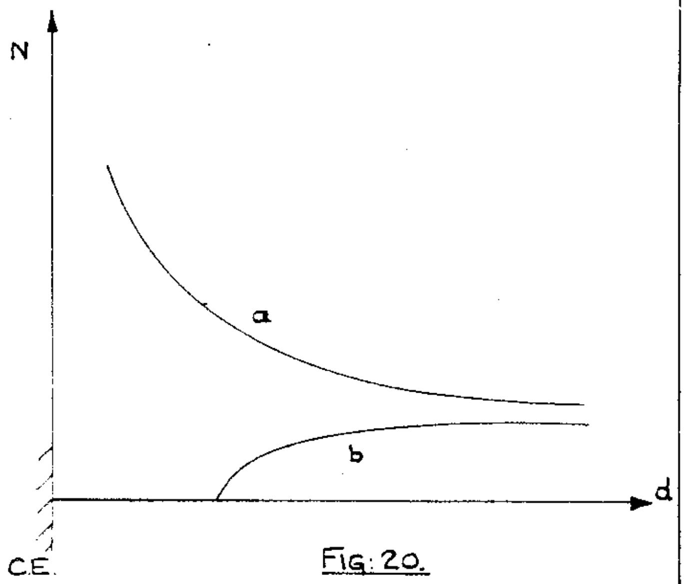


FIG: 20.

Distribution of Conduction Electrons

(a) in standard Se rectifier
(b) with insulating film

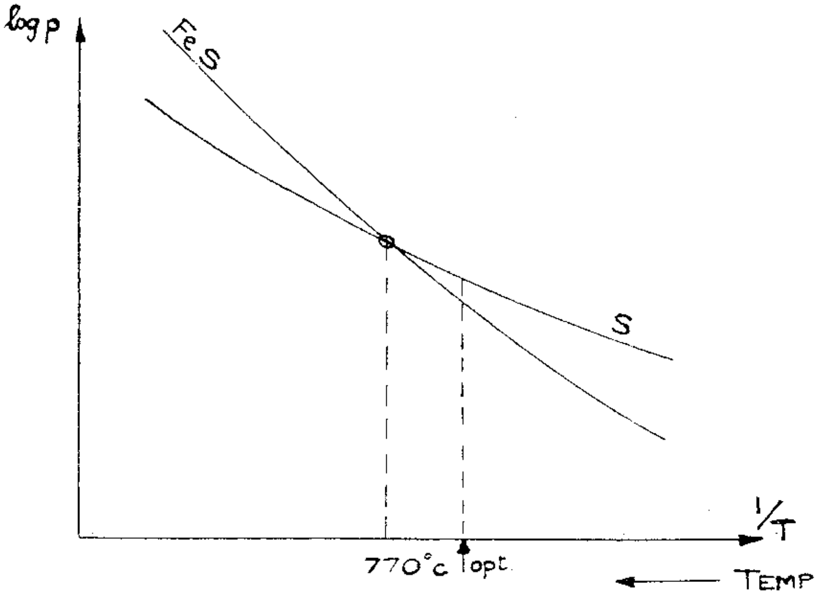


FIG. 21.

Vapour Pressure of S and Disintegration Pressure of FeS_2

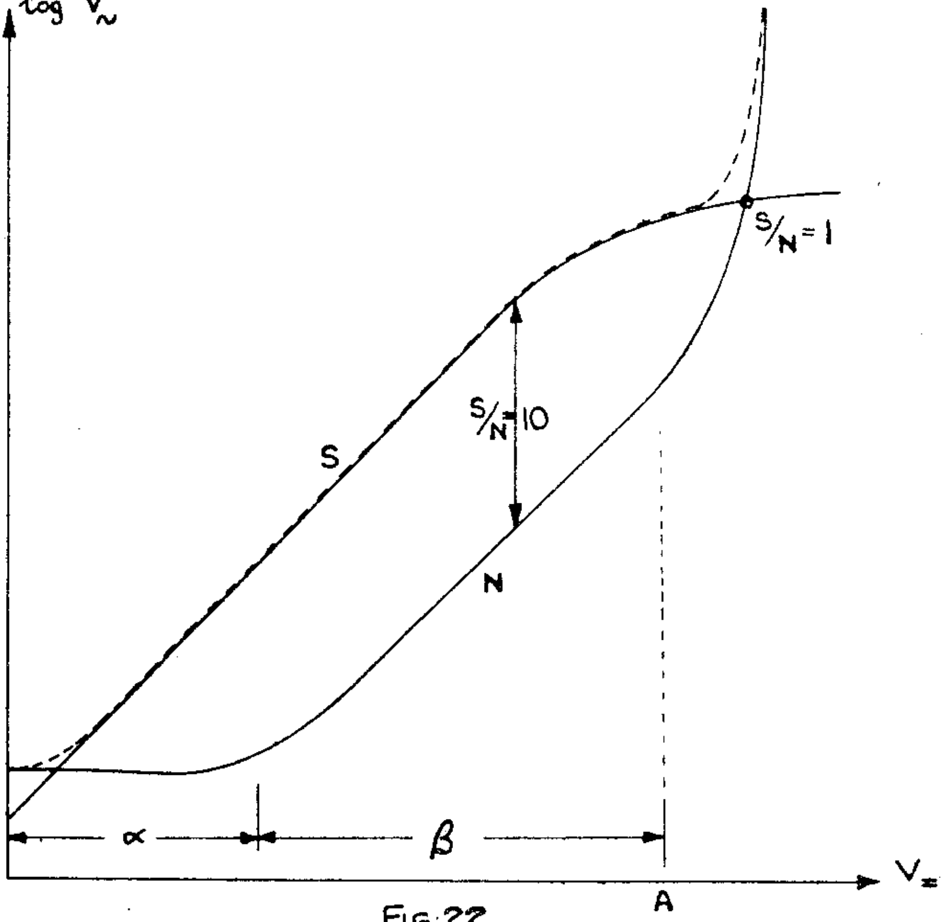


Fig. 22.

Response of PbS cell with varying D.C. voltage applied across it

S = Response to signal, N = Noise. ------ = Resultant

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