

# GERMAN RESEARCH ON RECTIFIERS AND SEMI-CONDUCTORS

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BRITISH INTELLIGENCE OBJECTIVES

SUB-COMMITTEE

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GERMAN RESEARCH ON RECTIFIERS AND  
SEMI-CONDUCTORS

Reported by

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BIOS Trip No. 2015

BIOS Target Numbers:  
See Main Body of Report.

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INTERROGATING PERSONNEL

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## INTRODUCTION

The purpose of this Report is to give information on rectifiers and semi-conductors. Separate reports on other subjects investigated by Trip No. 2015 are concerned with:

- (1) ferric oxide and ferrites and their application to radar absorption (by Lt. G.B.Richardson, R.N.V.R. and A.C.Lynch)
- (2) (jointly with Trip No. 2011) relay contact materials (by N.E.Hyde and others).

A further Report is intended later (see below).

## OBJECT OF TRIP

Information was required on the state of technical development and research work on rectifiers and semi-conductors.

The type of information sought was:

theory of operation of rectifiers;  
range of materials known to give rectification;  
chemical and physical structure of blocking-layers;  
causes of ageing, and methods of life-testing of  
rectifiers;

and similar information on semi-conductors, and on related subjects such as that of photo-electricity.

Interrogation, in Britain, of Herr Weise suggested that his laboratories in Berlin and in Erlangen would be of interest.

A source of supply of germanium was also to be looked for.

## CHOICE OF TARGETS

Industrial production of rectifiers has already been reported on. Except for the A.E.G. evaporation process, there is little information new to British practice. Workers in universities and in industrial research laboratories, however, had not been adequately interrogated; this opinion was also shared by Col. Ranger, who, in his CIOS report, suggests further questioning of them.

A preliminary list of "targets", and a questionnaire in both English and German, was prepared at the Post Office Research Station by Dr. A.Fairweather in collaboration with Miss C.M.Lovett and Mr. J.F.P.Thomas, and <sup>with</sup> Mr. H.K.Henisch of R.A.E. The list of targets included the names of authors of selected papers published during the last twenty years, and of persons, already interrogated

by other investigators, who had shown interest in the subjects concerned.

Other targets were added as a result of examination of reports at RIAI headquarters and of suggestions by persons being interrogated.

#### METHOD OF INTERROGATION AND REPORTING

No examination of laboratories was attempted (in most cases this would have been useless, as the work had been discontinued and the apparatus dispersed). The selected individuals were questioned, and, whenever it appeared desirable, a questionnaire was left for written answers to be supplied later. Certain documents from commercial firms are also to be forwarded.

The present Report is prepared before most of these replies have been received; and a further Report, including material derived from them, and attempting to draw conclusions, is intended later.

The opinions given in this Report are those of the persons interrogated, unless otherwise stated. Comments by the interrogators have been inserted, where necessary, in square brackets.

Information obtained, but not relevant to the main purpose of this Report, has been collected into a separate section following the main body of the Report.

TABLE I

Report No.	PERSON INTERROGATED	ADDRESS	Ability to Speak English	DATE	INTERROGATION BY		
					J.E. Taylor	A.C. Lynch	K.O. Richards
1.1	Prof. Schotzky	Pretzfeld, near Ebermanstadt, near Erlangen	Fair	4.4	X		X
1.2	Prof. Hilsch	Phys. Inst., Erlangen Univ.	Very Good	5.4	X		X
2.1	Prof. Brill	Inst. fdr Cellulosechemie, Darmstadt (Private Address:- Moltkestrasse 8, Heidelberg)	Fair	1.4		X	X
2.2	Prof. Kossel	Phys. Inst., Heidelberg Univ.	Some	1.4		X	X
2.3	Prof. Kohlschutter, } Dr. Hummer }	Techn. Hochschule, Darmstadt	{ Good } { None }	23.3	X	X	X
2.4	Prof. Ott	Franz Schubertstrasse 3, Wurzburg	None	5.4	X		X
2.5	Dr. Joos	"Dustbin" (Kranzburg) (formerly of Zeiss, Jena)	Good	21.3		X	X
2.6	Dr. Rothe	Brunngartenstrasse 5, Dachau	Good	30.3	X		X
2.7	Prof. R.W.Pohl	Phys. Inst., Göttingen Univ	{ Will not } { speak English }	15.4	X	X	X
2.8	Dr. H.König			15.4	X	X	X
3.1	Prof. Kluvius	Kunigundenstrasse 41a, München	Very Good	28.3	X		X
3.2	Dr. H.Welker	Karlstrasse 10, Planegg, near München	Fair	28.3	X		X
3.3	Dr. Franke	Erbstadt, near Frankfurt	None	3.4		X	X
3.4	Osavi Mine Co.	Kurstrasse 16, Spandau, Berlin	None	12.4	X		X

TABLE I (continued)

Report No.	PERSON INTERROGATED	ADDRESS	Ability to speak English	DATE	INTERROGATION BY		
					J.E. Taylor	A.C. Lynch	K.O. Richards
3.5	Otavi Mine Co. (Herr Schröder)	Herzog Wilhelmstrasse 14, Bad Harzburg	Good	15.4	X	X	G.B.
4.11	} Dr. Baudisch	} Siemens-Schuckert, Stemensstadt, Berlin	{ Good	10.4/11.4	X		X
4.12				11.4	X		X
4.13	Dr. Irion	Selchowstrasse 12, Wilmersdorf, Berlin	None	12.4		X	X
4.14	Dr. A.Schmid	Rieppelstrasse 4, Siemensstadt, Berlin	Good	11.4		X	X
4.21	} Dr. Kipphan	} S.A.F., Turkengasse, Weissenberg	{ Poor	1.4	X		X
4.22					X		X
4.31	Dr. C.Bosch	Schloss Wolfbrunnensweg 33a, Heidelberg	Very Good	1.4		X	X
4.32	Dr. Herbeck	A.V.A., Göttingen	Good	16.4	X		
4.33	Dr. Koch	A.E.G., Belecke/Wöhne	Fair	17.4		X	X
4.34	Dr. Kalkner	A.E.G., Hohenzollerndamm 150, Berlin	Good	12.4		X	
4.41	} Dr. E.Friederich	} Marienburgerallee 52, Charlottenburg, Berlin	Good	12.4	X		X
5.1							
5.2	Dipl.-Ing. E.Weise	Rathsberg 16, Eriangen	Good	4.4	X		X
5.3	Dr. Klarmann	Siemens-Halske, Siemensstadt, Berlin	None	10.4	X		X
5.4	Dr. F.Rother	Lutz and Co., Lauf/Pegnitz	Good	3.4	X		X

TABLE II

Report No.	Person Interrogated	Source of Information on target *	Abstract of information obtained	Q	To be received Account of Interview	Report of Research
<u>1. THEORY</u>						
1.1	Schottky	Many publications	Worked on phosphorescence, selenium, rectifiers, thermo e.m.f.s., etc. since arriving at Pretzfeld			
1.2	Hilisch	CIOS XXXI-2; A.L. No. 45, sheet 22; B.H.F. 10444	Fundamental Physicist interested in semi-conductivity and low temperature physics.			
<u>2. CRYSTALLOGRAPHIC AND ALLIED STUDIES</u>						
2.1	Brill	Asst. Report H66A	Crystallographer; studied barrier layer in Se rectifiers by X-ray diffraction		X	
2.2	Kossel	Suggestion by Weise	Crystallographer; began work on orientation of cuprous oxide formed on copper		X	
2.3	Kohlschutter } Himmler }	Former associates of Prof. Wagner	Chemists. H. studied resistivity of silver sulphide containing traces of lead sulphide			
2.4	Ott	B.H.F. 10194, 10445	Physicist formerly working on silicon detectors			X
2.5	Joos	B.H.F. 10434 A.L. No. 10, sheet 16	Grew silicon crystals and made "model" rectifier using crystal and metal sphere			X
2.6	Rothe	suggestion by Knoll	Extensive study of electrical properties of detectors using purified silicon.			



- 7 -  
TABLE I (continued)

Report No.	Persons Interrogated	Address	Ability to Speak English	Date	INTERROGATION BY			
					J.E. Taylor	A.C. Lynch	K.O. Richards	G.B. Richardson
6.1	Graf von Schulenberg	c/o Military Government, Heidenheim	None	26.3	X	X	X	X
6.2	Dr. Randtner	Kaiser Wilhelm Inst., Krepelinstrasse 2, München	Good	28.3	X			X
6.3	Prof. Knoll	Böcklinstrasse 36, Nymphenburg, München	Good	30.3	X			X
7.1	Dr. Deutschmann	Rieppelstrasse 20, Siemensstadt, Berlin	Fair	11.4		X		X
7.2	Dr. Kluge	Schloss Pullach, Rosenheim, Bavaria	?	29.3	X			X
7.3	Dr. G. Wehner	Flugforschungsinstitut, Gauting bei München	Some	28.3	X			X
7.4	Dr. Schmiederemann	Siemens-Halske, München	Good	27.3	X			X
7.5	Dr. Telets (?)	Ceram Lamp Research Dept. Heidenheim	Very Good	26.3.		X		X

TABLE II (continued)

Report No.	Person Interrogated	Source of Information on target <b>x</b>	Abstract of information obtained	Q	To be received Account of Interview	Report of Research
2.7	Fohl	C108 XXX1 - 2	Studied thin layers of Germanium to find crystallographic conditions necessary for rectifying action			X
2.8	Konig	B.H.F. 10496				
<u>3. GERMANIUM DETECTORS AND SUPPLIES OF GERMANIUM</u>						
3.1	Kluvius	B.H.F. 10501	Chemist; suggested use of Germanium for detectors			X
3.2	Welker	suggestion by Kluvius	Developed a Germanium detector and worked on properties of Germanium			X
3.3	Franke	Suggestion by Kluvius	Thought there were no supplies of Germanium in Germany			
3.4	Oravi Co. Ltd.	"	20 tons of germanite are stored by the firm in Brunswick, Franke received supplies during the war.			
3.5	Schröder	Director of Oravi Mine Co.				
<u>4. COMMERCIAL RECTIFIERS</u>						
4.11	Baudisch	E.T.Z., 1934	Chief rectifier Engineer at Siemens; wide commercial knowledge			X
4.12	Nitsche	Suggestion by Baudisch	Worked with Waibel on capacitance in Cu <sub>2</sub> O rectifiers			X
4.13	Irion	E.T.Z., 1930	Engineer formerly working on Cu <sub>2</sub> O rectifiers.			X

TABLE II (continued)

Report No.	Person Interrogated	Source of Information on target x	Abstract of Information obtained	Q	Account of Interview	To be received Report of Research
4.24	Schmid	Mis-identified from F.I.A.T. files	Used copper-oxide rectifiers in ring-modulators			
4.21	Kipphan	Head of S.A.F. research	) Research on selenium rectifiers; noise, humidity, barrier parameters dependence on frequency etc.	X		
4.22	Lauckner	C.I.O.S. XVII - 38	)			
4.31	Bosch	C.I.O.S. XVII - 38	) Worked on commercial Se rectifiers; tried intermediate layers of varnishes etc.	( X		
4.32	Herbeck	Suggestion by Bosch	)	(		
4.33	Koch	Suggestion by Weise	) Research on selenium rectifiers; A.E.G. Manufacturing process	( X		
4.34	Kalkner	Head of Berlin Lab. A.E.G.	A.E.G. Research now moved to Belecke.		X	X
4.31 also 5.1	Friederich	Suggestion by Weise	Directed Osram research on commercial Cu <sub>2</sub> O rectifiers and non-ohmic resistors	X		
<u>5. NON-OHMIC RESISTORS</u>						
5.2	Weise	Arising from interrogation in U.K.	His records could not be traced; some probably destroyed in Berlin			
5.3	Klarman	Wiss. Veroff S.K. 1939	Research worker on non-linear resistors for Siemens.			
5.4	Rother	C.I.O.S. XXI - 22, XXIX - 48; Elect. Ins. Rep. 41/45; A.L. No. 15 Sheet 15.	A research worker in ceramics, with some experience of semi-conductivity			X

TABLE II (continued)

Report No.	Person Interrogated	Source of Information on target *	Abstract of information obtained	Q	To be received Account of Interview	Report of Research
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6. SECONDARY EMISSION

6.1	Schulenberg	Suggestion by Weise	Worked on secondary emission but not on semi-conduction			
6.2	Randtner	" " "	Tried to relate secondary emission from a semi-conductors surface with its suitability for use as a rectifier			
6.3	Kroll	" " "				

7. MISCELLANEOUS INTERVIEWS

7.1	Deutschmann	Phys. Zeits, 1929	No recent work on rectifiers.			
7.2	Kluge	A.L. No. 11, Sheet 1; No. 45, Sheet 45	Not interrogated personally			X
7.3	Wehner	A.L. No. 45, Sheet 17	No work on rectifiers.			
7.4	Schliedermann	Chance meeting	Gave addresses			
7.5	Telets	Suggestion by Schulenberg	interviewed to obtain addresses			

\* A.L. is Amendment List to SICESO 56; B.H.F. refers to A.L. No. 4;  
Elect. Int. Rep. is Electrical Intelligence Report.

1.

1.1 C1/842, C7/374, C9/941.

Professor Schottky came to Pretzfeld in February 1944 and until October of that year worked mainly on a theory of Phosphorescence. He had earlier been engaged on Luftwaffe research at Graz, Silesia. Papers on Phosphorescence were published in June and October 1944 in the Forschungs-führer der Luftwaffe. The earlier paper also dealt with colour centres in halides, and the movement of the boundary between the coloured and uncoloured positions of a crystal on the application of an electric field [Note that this is a continuation of Prof. Hilsch's pre-war work].

From June to July 1944 he worked on some electro-chemical problems including that of passive layers on iron.

From October to November 1944 he worked on selenium rectifiers, taking part in November in the meeting at Prague of German rectifier firms and their research workers [see Col. Ranger's report on this meeting for details of the discussion]. A large and complex fund of information was brought to light at that meeting and Schottky agreed that present theory was inadequate to interpret these observations fully.

His paper (on rectifiers) published in 1942 dealt with capacitance in rectifiers in some detail, but was only applicable at zero frequency. A new paper "Fundamentals of Rectifier Theory" [as yet unpublished] contains a recently edited chapter on capacitance which extends the theory so as to account for the observed variation of capacitance with frequency. The earlier theory had assumed a perfect barrier layer in which all the impurities were dissociated so that no change of space-charge could occur: the extended theory takes into account actual semi-conductors in which the above condition is not fully realised. The known variations of capacitance with temperature have also been the subject of theoretical study, and have been related to contact potential between the metal and semi conductor and also to the concentration and distribution of impurity centres.

Work is still in progress on the variation of the resistance of selenium with frequency, and Schottky said the results of experiments undertaken on this subject, carried out in Prague, were not satisfactory due to the shape of sample experimented upon. Prof. Gudden does not apparently believe wholly in Schottky's theory and that fact has, according to Schottky, reduced the value of the work carried out under his guidance [the Prague team under Prof. Gudden were working for S.A.F: note also that S.A.F. Weissenburg are continuing this work]. The resistance of a rod of selenium has been measured at frequencies from  $10^5$  to  $10^8$  c/s. The time constant of the barrier layer prevents contact effects obscuring changes in the resistance of the selenium itself, but Schottky pointed out that, with a rod-shaped specimen, electrostatic force lines would not remain within the selenium and that

(especially at the highest frequencies) a considerable radiation loss would be introduced.

Prof. Schottky has not done much work on selenium rectifiers since the 1944 meeting, but he plans to continue in Pretzfeld.

The decay of voltage across a rectifier disc when the impressed voltage is removed has been the subject of an investigation.

Schottky considered that physical imperfections in the contact between front electrode and selenium were the cause of the changes in resistance of discs when a pressure is applied, but he did not believe these irregularities to be essential to rectification. He believed rectifiers could be made with evaporated counter electrodes, but that this point should be looked into before conclusions were drawn.

Schottky does not consider that the composition of the counter electrode is of primary importance - the effect of Thallium is an exception. He believes the main factor to be the content, distribution and migration of non-metallic impurities in the semi-conductor.

Schottky thought there was no evidence for the suggestion [by S.A.F.] that a second barrier layer forms at the base electrode and contributes to the ageing of a rectifier.

He has recently done some theoretical work on the mechanism of conduction in a deficit semi-conductor, and also on the variation of the work function of a semi-conductor with the concentration of impurities. Theoretically, the concentration of atomic impurities should not affect the work function, but Schottky believes the impurities to be concentrated in groups of colloidal dimensions. He has analysed the performance of such a system, and succeeded in explaining the observed variation of work function with concentration. He was led to this theory by previous work on oxide-coated filaments. He has recently produced a theory of thermo-electric force.

Prof. Schottky was in poor health when visited, and said that after 6 months' work he usually had a collapse and a few months rest. He wished to be allowed to continue his work in Pretzfeld, but would like to come to England to meet scientists interested in his theories.

[Prof. Schottky has a large number of papers ready for publication, and since it was felt that these should be examined before he was questioned further, the interrogation was concluded].

1.2 C1/844, C7/376, C9/978.

Professor Hilsch has done some work on rectifiers with both ionic and electronic conductivity. Such rectifiers have very thick barrier layers, and it is possible to insert a controlling electrode in them. In 1940 he was told to develop such a rectifier for

military application, but this he believed to be impossible, and thought his experiments were of academic interest only.

He has not worked on commercial rectifiers, and did not offer opinions on the questions related to them. He has however had some contacts with Herr Weise, and mentioned his suggestion of a  $TiO_2$  rectifier. Hilsch believes work on selenium rectifiers must be unsatisfactory in view of the complexity of the problem. He prefers to carry on his fundamental researches with substances of no technical importance but which can be handled readily. Note that he expressed the same view in the subjects dealt with under Irrelevant Information7.

He considered that so many parameters were operative in a commercial rectifier, that physical imperfections in the contacts were almost certainly important and might be the essential feature. However he suggested that, mathematically, an irregular contact was less tractable than a space charge theory.

## 2. CRYSTALLOGRAPHIC AND ALLIED STUDIES

Professors Brill and Kossel are specialists in crystal structure, who were consulted in 1944 on rectifier construction.

### 2.1 C1/843, C7/375, C9/323.

Brill has X-ray apparatus intended for the study of thin layers of material. It produces a strong beam of monochromatic radiation by Johannson's method (the rays are focussed, by a concave quartz crystal, on a small aperture).

Brill studied samples supplied by A.E.G. and by S.A.F. They consisted of iron or aluminium plates carrying layers of bismuth (very thin, but visible) and, on the bismuth, selenium. The X-ray diffraction pattern showed that after the usual heat-treatment, though not before, there was present an additional substance. By comparison with a separate specimen, this substance was shown to be bismuth selenide,  $\text{Bi}_2\text{Se}_3$ .

It is known that amorphous selenium consists of long chain-like molecules. These probably exist also in liquid selenium, which therefore solidifies in the amorphous, not the crystalline, state. Subsequent heating breaks the chain structure; and then the selenium crystallises. The crystals are always hexagonal; if formed at  $200^\circ\text{C}$ . they are regular, if at  $120^\circ\text{C}$ . they are irregular.

The lattice constant of the crystals depends on the temperature and duration of the heat treatment. The diffraction pattern is broadened; the cause is lattice distortion (which gives a broadening proportional to  $\tan \delta$ , where  $\delta$  is the Bragg angle) and not irregular particle size (which would give broadening proportional to  $\sin \delta$ ).

The resistivity of the crystal depends on the regularity of the lattice. Brill did not investigate its dependence, if any, on the lattice constant.

For rectifying action there must be some distortion of the crystal lattice (otherwise the material would be of low resistivity and low breakdown voltage, but not too much (otherwise the resistivity would be high in both directions). This apparently assumes that metallic conduction occurs in pure selenium.

The function of halogens added to the selenium is to cause crystallisation. The selenium chains exist because the atoms have six valency electrons each, and form a group of eight electrons by sharing with a selenium atom on either side. A halogen atom, with seven valency electrons, enters the chain. Iodine is perhaps the most suitable because of the size of its atoms. Experiment shows that about 0.2 iodine is best, and this proportion causes crystallisation of the selenium at room temperature.



The bismuth layer on the base-plate probably behaves in much the same way as the counter-electrode; the difference is that the counter-electrode is not subjected to the heat-treatment.

This interrogation, in retrospect, was unsatisfactory. The bismuth selenide was detected in the absence of any counter-electrode; and it is not clear whether Brill thought that it constituted the material of the barrier-layer.

## 2.2 C1/846, C7/378, C9/979.

Kossel planned work on the orientation of the oxide lattice formed on a single crystal of copper. He thinks that, in a commercial rectifier, the random arrangement of crystals superposes a number of different electrical conditions and thus obscures the fundamental effects.

A spherical single crystal of copper was oxidised, and examined both optically and by X-rays. Both copper and cuprous oxide have copper atoms arranged on a face-centred cubic lattice, though with different lattice constants. On the spherical crystal there were regions of constant orientation of the oxide crystals, with discontinuous changes from one orientation to another.

No electrical tests were made.

Kossel considers the Schottky theory of rectification to be satisfactory. Impurities in a semi-conductor produce additional energy-levels; perhaps a pure material could not be a semi-conductor. There must be some broadening of the energy levels into bands (compare the effect on their natural frequencies of coupling together a number of pendulums).

But when a current is flowing, the conditions within the semi-conductor are not a "stationary state"; there is a moving electron-wave. Kossel has not considered what its velocity might be, but he sees no great difficulty in the idea.

Kossel agrees that the phenomena at the interface of a semi-conductor and a metal are analogous both to cold emission and to thermionic emission, but does not think it possible to choose either as the better analogy.

He did not study the effect of mechanical pressure on rectifiers, and has done no work on symmetrical non-linear materials.

2.3 # C1/847, C7/379, C9/980.

# Prof. Kohlschutter was a colleague of Prof. Wagner, and Dr. Himmler was formerly Wagner's assistant. Wagner's interest had been in the mechanism of conduction in solids, rather than in semi-conductors as such. Himmler worked on the conductivity of silver sulphide with small admixtures of lead sulphide.

## C1/848, C7/380, C9/981.

## Himmler formed silver sulphide from silver foil (about 0.1 mm thick) mounted on platinum wire supports, by dipping it in sulphur maintained at 150°C. The resistance was measured by a low-voltage A.C. bridge, and the completion of the reaction was thus observable. No great accuracy was aimed at, as large changes were expected when lead was added to the silver. In practice, the presence of lead made little difference.

The resistivity of silver sulphide at this temperature is low - similar to that of an electrolyte in solution. Hence electronic conductivity is not detectable.

There is no evidence that surface or contact effects occur in these experiments. Non-linearity was not observed; neither was change of resistance with time, nor any large change with temperature. Himmler thought that the resistance might change with mechanical pressure, but he had not tested this.

2.4 C1/849, C7/381, C9/982.

Dr. Ott has worked on silicon detectors, but not on other types of rectifier.

Interrogation was almost impossible, owing to language difficulties, but he is to send a report on his work.

2.5 C1/845, C7/377, C9/752.

Dr. Joos worked with Zeiss, of Jena, on the production of artificial crystals. Dr. Ott had collaborated with him.

Joos tried to produce large crystals of silicon for use in silicon-carbon detectors for cm. waves. The method was deposition from a solution of silicon in molten aluminium. The crystals so obtained were spectroscopically pure [a surprising statement, but Joos was sure of it]. They were aggregations of thin plates. They were to replace an existing detector, which Joos never saw, but which he thought consisted of silicon evaporated on to compressed carbon. It was developed by the Phys-Tech. Reichsanstalt, Berlin. Joos thought that the size required was probably a few square mm.

He measured the D.C. characteristics of a model rectifier consisting of a metal sphere,  $1\frac{1}{2}$ mm. in diameter, pressed against the edge of a crystal. The pressure was of the order of 10 gm. weight, and a certain value of pressure could be found for which the current-voltage characteristic was the most sharply curved. The characteristic curves were satisfactorily reproducible.

Capacitance measurements were begun, but Joos did not know the results. He did not expect the capacitance to vary with voltage, and did not know of this effect in selenium rectifiers. The characteristics of these rectifiers did not change with time, and Joos had never heard of the "forming" of rectifiers.

In <sup>an</sup> alternative model rectifier, the metal sphere was pressed against a crystal face. This arrangement gave a less sharply curved characteristic.

Joos considers that the rectification process in this apparatus is the same as in the known carbon-silicon detector. There is perfect contact at a point which under load becomes a small area. There is no need to assume the presence of any impurities; though some, such as oxides, may be there. Joos did not try the effect of inert atmospheres.

Rectification by selenium or by copper-oxide is a different process, for which the Schottky theory is satisfactory. There is a layer in the copper-oxide in which the composition is graduated. Semi-conduction is always caused by impurities (Joos has discussed this with Prof. Pohl), which provide intermediate energy-levels. In selenium, there must be a broadening of the energy-levels into bands; but this effect is important only with very pure materials - i.e. in the laboratory - and not in commercial rectifiers. Joos learned in Wimbledon that the impurity in Urdox is titanium. He was not aware of the use of iodine in selenium rectifiers.

Thermal noise in semi-conductors is greater than in normal materials; perhaps through migration of electrons between regions in which the concentrations of impurity are different.

There is no fundamental reason for the use of any one particular metal for the counter-electrode of a commercial rectifier.

## 2.6 C1/850, C7/382, C9/983.

Dr. Rothe worked for Telefunken on detectors for cm. waves, but not on other types of rectifier. He found artificial silicon crystals the most satisfactory.

For H.F. work a point-contact rectifier is necessary, even apart from the question of capacitance. Only then is <sup>the</sup> resistance of the

barrier-layer high compared with that of the remainder of the crystal. The problem is then to reduce the forward resistance of the rectifier; a good value would be 100 ohms at zero voltage.

Rothe said that Dr. Gunther had shown the resistance of silicon to depend mainly on the crystal structure. Also, traces of silver or tungsten on the surface of the crystal resulted in decreased forward and increased reverse resistance. Gunther had made about 300,000 of these contaminated crystal surfaces; the results were not known to Rothe.

The dependence of resistivity of silicon on structure rather than on purity is analogous to the behaviour of germanium. "Evaporated" germanium, having very small crystals, can be made to rectify by gentle heating, which produces larger crystals. This excludes the possibility that impurities govern both the resistivity and the crystal size.

Rothe referred to Dr. König's work on polished silicon surfaces. Rothe (and Knoll, who was also present) thought that the skin produced during polishing might cause poor rectification; it would reduce the number of points of perfect contact required by Schottky's theory. Only the large crystals were suitable as rectifiers. Knoll said that the photo-electric effect in cadmium sulphide increases with purity and with crystal size.

The rectifying properties of a surface are destroyed by electron bombardment; this may be either a direct effect, or a result of heating of the crystal. Mechanical pressure causes permanent damage; the reason is unknown, but Knoll said that, similarly, mechanical pressure stops fluorescence.

The silicon is obtained by reaction of silicon fluoride and aluminium at 600 - 700°C. in a quartz tube which also contains carbon rods. The rods absorb the silicon vapour, and release it on subsequent heating. The silicon always contains traces of aluminium. If other metals are desired as impurities in the silicon, they are put in the tube with the carbon rods.

Attempts to select good spots on crystals before assembly into final form failed, possibly because of different conditions of mechanical pressure.

The contact to the silicon was made by a ring (not a needle) of tungsten. This was cathode tungsten; the effect of impurities was not tested. Molybdenum gave similar results. The properties sought for were strength, resistance to corrosion, and absence of reaction with silicon. Thermal conductivity had not been considered.

The test for satisfactory crystals was: forward resistance (to 50 c/s A.C.) less than 200 ohms, and reverse resistance greater than 100,000 ohms; also a specified D.C. output from a pulse input, 10 watts of 9 cm. wavelength.

Ratings were determined by experiment alone. For mixers, a wattage rating was set at  $\frac{1}{2}$  or  $\frac{1}{3}$  of that which would cause burn-out. For second detectors, a current rating was set. The increased rating possible under pulse conditions resulted from the absence of heating effects.

Noise in detectors was studied by Dr. Mataré before the war; the only paper published during the war was that by Dr. Welker. The noise was normally about twice that in a resistor, but in exceptional cases was as low as that of a resistor. No correlation had been found between the noise and the other characteristics of a detector. As the noise might be due partly to movements of the contact, a large pressure - about 400 gm. wt. - was used. This also resulted in low forward resistance, without affecting the back resistance. Experiments on the necessary pressure were unfinished.

The relation between pressure and curvature of the characteristic at the origin was studied.

The temperature coefficient was reproducible.

Other workers on rectifiers etc., included Dr. Hackenberg, formerly working at Göttingen on germanium and lead sulphide; and Prof. Schlege, formerly working in Berlin on fluorescence, and now in London.

## 2.7 C1/851, C7/384, C9/984.

Prof. Pohl confirmed that Dr. König had studied germanium and silicon rectifiers at Göttingen, without being able to explain the mechanism of rectification.

## 2.8 C1/852, C7/383, C9/985.

König had tried to find why rectification occurs in solid crystals, but not in thin films of germanium. Germanium was chosen for experiment because it rectifies even when nearly pure, and can be deposited from vapour. If rectifying thin films could have been made, they would have been of commercial use, because of the ease and economy of manufacture.

Electron diffraction photographs showed that the high-resistivity film first-deposited is nearly amorphous; heating to

500°C. produces a low-resistivity film, stable at room temperature, having a diamond-type structure. Both types of film give ohmic conduction. If the film is annealed in hydrogen at 700 - 800°C., its thickness may be up to 0.1  $\mu$ , but it still does not rectify well.

The high resistance of a mass of small crystals is caused by bad contacts, both crystal - to - crystal and crystal - to - graphite. [This was not borne out by a paper by Walkenhorst, of which König supplied a copy].

Films of 1 - 20  $\mu$  thickness can be deposited from germanium chloride vapour reduced in hydrogen at 800°C. The thinner ones give symmetrical non-linear conduction; the thicker ones rectify, but are of high resistance.

The best method of preparing germanium specimens is to cast rods in graphite moulds of a few mm diam. These rods are nearly single crystals.

Pure germanium, in batches of about 6 gm. was obtained from Dr. Franke of Frankfurt, accompanied by spectrographic analyses. The analyses showed freedom from arsenic and lead, and traces of the order of 1 in  $10^5$ , of copper, calcium, and aluminium. Other rectifier materials usually contain impurities: e.g., silicon carbide and iron in silicon, sulphur in lead sulphide.

In later tests, impurities were to have been added - e.g. copper and silver, which alloy with germanium. The addition of non-alloying materials would have been more difficult, as they would crystallise separately.

The radius of curvature of the needle must be small compared with the film thickness - this was proved by experiment with various film thicknesses. Tungsten, molybdenum, and platinum were satisfactory as needles; silver and copper were too soft. There were no systematic experiments on the choice of material.

There is no reason to think that the surface of the film is different from the main body.

König is interested in the condition of polished silicon surfaces (which may consist of a mass of small broken crystals) but he had not studied rectification in them.

### 3. GERMANIUM DETECTORS AND SUPPLIES OF GERMANIUM

#### 3.1 C1/853, C7/385, C9/986.

Professor Kluvius was consulted by Dr. Welker in 1942 for advice on H.F. detectors. It was Dr. Welker's job to evolve a detector with a higher resistance to burn-out than the pyrite one then in use.

Kluvius carried out some experiments and found that the discoloration rings, formed on the crystal around the point during burn-out, could be simulated by heat alone. In an attempt to provide a material resistant to high temperatures, he postulated the following necessary properties.

- 1) The substance must be oxidisable only at high temperatures
- 2) " " " not be decomposed " " "
- 3) To reduce local heating, the substance should have a high thermal conductivity.

Hence single crystals of a metal were needed, Germanium was suggested because of the ease with which it could be purified. The normal method of purification was used; germanium oxide is extracted from the ore by nitric acid and reduced with hydrogen. Arsenic remains, but is readily removed. The final impurity concentration was about 1 part in  $10^6$ .

When argyrodite (Ag, Ge, S) could no longer be obtained, the stocks of germanite held by the Otavi Mine Co. in Berlin were the only remaining source of germanium in Germany known to Prof. Kluvius. Dr. Franke of Opernplatz, Frankfurt/Main supplied germanium to Dr. Welker during the war, with certificates of his analysis.

Prof. Kluvius had no knowledge of impurities being added to the germanium before use, but some sub-oxide may remain undetected.

Prof. Kluvius was mainly concerned with this work in an advisory capacity, and has had no other experience of rectifier research.

[The postulation of a metal as a detector material is rather surprising, since rectification depends on a contact with a semiconductor. The relation between the electrical and thermal conductivities of germanium and its purity may be worth investigation.]

#### 3.2 C1/857, C7/386., C9/990.

Dr. Welker developed a germanium detector to have a higher resistance to burn-out than the pyrite one. As part of this programme he carried out work on the electrical properties of germanium, the results of which are to be sent on.

The purest possible germanium was used for the

detectors, and was cast into rods, forming a single crystal, about 6" long: a graphite mould was used for this purpose and is still in Welker's possession.

The pressure normally applied by the whisker was between 10 and 20 gms. It was found that the forward conductance of the detector increased as the first power of whisker pressure, while the reverse conductance increased as the 2nd power. Welker thought the barrier layer would not be affected by pressure (unless the crystal structure was ruptured), and that the main effect was the crushing of the whisker point and consequent increase of the contact area; this effect was not observed directly. The effect of pressure on the selenium rectifier might be more marked than on the germanium detector since selenium is the softer material.

The detector property seems to depend on using a very fine point (of about 10  $\mu$  diameter) in contact with a crystal of at least 2 m.m. thickness. Crystal detector materials cannot be used in plate rectifiers, where a large contact area is associated with a small thickness of semi-conductor. The crystal detector has a barrier layer with a small resistance per square cm, but the arrangement of point against large crystals enables the barrier layer resistance to be made large compared with the spreading resistance from the point through the crystal.

Various whisker materials were tried, but both molybdenum and tungsten oxidised in time. Platinum was too expensive for use, but it was believed that American silver contacts were a considerable improvement.

No wax was used in the cartridges; pressure alone was relied upon for mechanical stability (it has been found that a filler produced an inadmissible deterioration in the detectors).

Dr. Günther was said to have worked with many types of detectors including Si, Ge and synthetic pyrite ones. He had also tried to use condensed Germanium films; such detectors had a large reverse current, which Welker believed to be partly due to small crystal size (annealing, allowing larger crystals to grow, improved these detectors). The many intercrystalline contacts were believed to introduce resistances which swamped the barrier layer effect.

Dr. Borgnis of the Technische Hochschule, Graz, was to have measured the conductivity of a rod of germanium by the damping it caused in a 12 cm resonant cavity; he has carried out such measurements on several other substances. Welker remarked that detector materials show a very high electron mobility.

This research was begun in 1942, in which year all the progress was made; since then, only laboratory scale production has been possible.



It may be noted that the germanium was used pure, and not doped, and that the characteristics obtained were similar to those of silicon detectors.

3.3 C1/854, C7/389, C9/987.

In the hope of tracing the source of German germanium, an attempt was made to find Dr. Franke in Opernplatz, Frankfurt, which was found to have been destroyed.

Dr. Franke was found in Erbstadt near Frankfurt: he has a well-equipped chemical laboratory. He said that he had worked 20 years ago on alloys of Ge with Al and Pb, but denied handling germanium during the war. As the ore came from S.W. Africa, he did not see how any could be in Germany.

On the basis of information then available, the interrogation could be carried no further. It was assumed at the time that this Dr. Franke, who had come from Frankfurt, was the person referred to by Kluvius. Subsequent information from the Otavi Mine Co., and from König (who gave Franke's address as Gärtnerweg, 41, Frankfurt), confirmed that a Dr. Franke of Frankfurt had analysed germanium during the war, but raised doubts as to whether the correct Franke had been found. Flitz (Frankfurt) were requested to re-interrogate Franke to ascertain if he was formerly of Opernplatz, 6, Frankfurt, and if he still has stocks of germanium.

3.4 C1/855, C7/388, C9/988.

Temporary offices of the Otavi Mine Co. in Berlin were visited for information about germanium ore and to check Franke's statement.

The firm imported germanite, purified it in their laboratories, and sold germanium to research laboratories in lots of about 5 gms. Welker and Kluvius were unknown to the firm; but Dr. Franke of Opernplatz, 6, Frankfurt/Main had bought germanium from the firm during the war; before the war he had purchased ore and carried out the purification himself. Siemens-Schuckert were also war-time customers.

The laboratories and offices of the firm in Berlin were destroyed during the war, and the temporary office is in the rooms of one of the employees. A sack containing approximately 40 kilos of 5% ore was found in the house. Director Schröder was mentioned as a source of further information.

On the basis of this interrogation, the request mentioned under Franke's interrogation was made.

3.5 C1/856, C7/387, C9/989.

Director Schröder of the Otavi Mine Co. was interrogated ~~and~~

in Bad Harzburg to obtain more information about germanium supplies.

This copper-mining firm had imported germanite from S.W. Africa about 20 years ago, and 20 tons of approximately 2 $\frac{1}{2}$ % ore is still stored in a Brunswick warehouse. Until recently, there was little demand for the ore. Dr. Franke of Opernplatz, Frankfurt, bought some before the war. When the demand increased, the firm decided to carry out the purification and supplied Franke with pure germanium during the war.

At the time the Berlin laboratories were destroyed, the apparatus was being moved to Bad Soxa, and has been moved again to Kellinghausen. Orders have been received from Siemens for small quantities, and the firm expects to be able to supply purified germanium in 2 to 3 months' time.

Another employee of the firm lives at Herzog Wilhelmstrasse, 27. Bad Harzburg.

It has been requested that the germanium stored in Berlin be brought to the U.K. This is thought to be worth while both because there is no source of supply of germanium in this country, and because the characteristics of German germanium detectors are fundamentally different from those of American ones.

#### 4. COMMERCIAL RECTIFIERS

##### 4.1 SIEMENS

##### 4.11 C1/858, C7/390, C9/635.

Dr. Baudisch is the technical manager of the Siemens-Schuckert rectifier plant, including the research laboratories. The Siemens research organisation was:

1. Fundamental research - Prof. Schottky
2. Experimental research - Dr. Waibel
3. Development and pre-production - Hr. Siebert

Other research workers included Dr. Spenke, Dr. Stenbeck and Dr. Wasserach. Research was carried on until 1944.

Siemens had worked on both copper-oxide and selenium rectifiers since 1930. They had also tried copper sulphide and titanium dioxide. The copper sulphide rectifier was abandoned 10 years ago because it had a very short life. Their titanium dioxide rectifier consisted of an iron plate, titanium dioxide and a silver counter-electrode. The barrier layer occurred at the iron-titanium dioxide surface. Fifty or sixty samples were made but the work was not continued as they found the rectifiers too expensive and they aged very badly.

Baudisch believed wholly in Schottky's theory, but thought much engineering research was needed before the theory could successfully be applied to the design of rectifiers (c.f. the gas-discharge theory and the mercury-arc rectifier). The theory was not yet far enough advanced to explain all rectifier problems. If any selenide compound was formed, it had no effect on the barrier layer; neither did the crystal structure of the selenium. He had made experiments to show that the crystal structure was continuous through the barrier layer of copper-oxide rectifiers and had remained so after 20,000 hours on load.

The barrier layer of a copper oxide rectifier was situated where the copper-oxide crystals grew from the copper plate, i.e., where the copper oxide was oxygen-free (no impurities). Very pure copper (1 part impurity in  $10^6$ ) would not make a good rectifier which led him to believe that impurities other than oxygen were important. Some non-ionised impurities were present in copper oxide but none in selenium. There were no chlorine impurities in the selenium barrier layer (c.f. no oxygen in copper-oxide barrier layer). However, there were a few metallic impurities even in the barrier layer, which were not removed by the electric field.

The capacitance of a rectifier depended upon the thickness of the space-charge which, in turn, depended upon the applied voltage. At higher frequencies the movement of ions and electrons was

restricted, changing the thickness of the space-charge and thus the capacitance. The effect of frequency only became pronounced above 1 Mc/s. Measurements on this had been made by Drs. Waibel and Mitsche.

Siemens only applied pressure to their rectifier discs in order to obtain good mechanical contact, e.g., 300 Kg. for 50 m.m. copper-oxide disc.

The curve for resistance against distance from copper plate for cuprous oxide would be inaccurate, due to the complications of the experiment - for example, a different surface for each measurement, small changes in temperature<sup>and</sup> humidity. Therefore no conclusions could be drawn from such an experiment. Baudisch had not made any similar experiments himself.

The ageing of copper oxide rectifiers was due to the continual formation of more oxide and hence the atmosphere in which a rectifier worked would affect its ageing. The A.E.G. selenium rectifier (with an evaporated counter-electrode) had the smallest ageing and the highest permissible voltage. With an evaporated electrode there was a greater contact area and a closer and more uniform contact. This made a small difference to the forward current but not as large as was expected. Ageing was caused by the counter-electrode peeling off the selenium and thus increasing the resistance. Copper oxide rectifiers aged less than selenium.

Baudisch was familiar with the effect of mercury vapour on selenium rectifiers but he could not explain it.

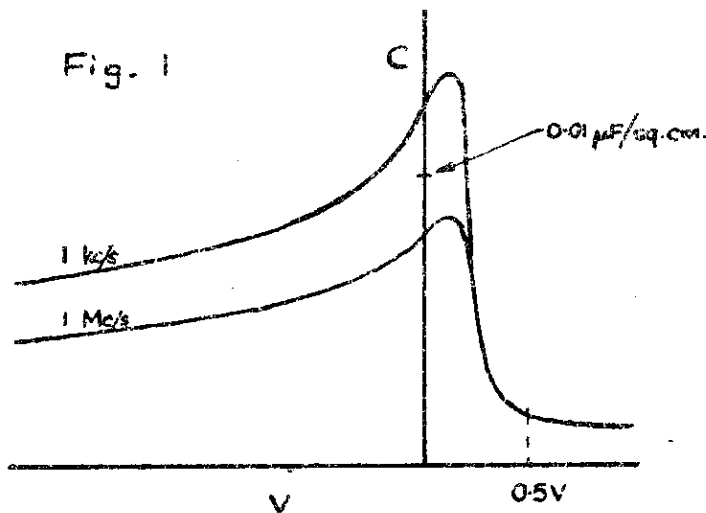
Siemens put the life of their copper-oxide rectifiers at 10 years' continuous running for battery charging work. Life tests were made with a battery-charging load. They had tested copper-oxide rectifiers for this period and selenium rectifiers from 3 to 5 years. The results obtained after 10,000 hours gave a good indication of the expected life. Their criterion of life was 10% drop in voltage in 12 months; 0.1% for instrument rectifiers. Tests on copper-oxide rectifiers with silver counter-electrodes on graphite showed that pronounced ageing occurred between 3000 and 5000 hours. This phenomenon began slightly earlier in an atmosphere of ozone.

Lead or a pure copper plate was used for the counter-electrode of copper-oxide rectifiers. Baudisch described two methods for producing high and low resistance copper-oxide discs. The low resistance discs were made by heating the copper discs in a furnace at 1020°C, cooling to 500°C and maintaining this temperature for 10 mins. and then quenching in an oil bath. The high-resistance discs were cooled to a temperature lower than 500°C, maintained at this for 20 minutes and then allowed to cool to room temperature. The former process made a thinner oxide layer with a different oxygen content to the high resistance discs. The low resistance

discs had a reverse voltage of 6 volts, the high resistance discs a reverse voltage of 10 to 12 volts. For manufacturing convenience Siemens used copper disc thicknesses of 0.1 and 0.75 m.m.

4.12 C1/859, C7/391, C9/991.

Dr. Nitsche was a member of Siemens' development Laboratory but had been associated with Waibel on the capacitance of copper-oxide rectifiers. Measurements made were over the normal voltage range at frequencies from 1 to 1000 kc/s on discs from 2 to 20 m.m. in diameter. The effect of disc size was small but in order to eliminate edge-errors, he had plotted capacitance per unit area and not capacitance alone. Typical curves are shown in Fig.1



Nitsche had made no capacitance measurements on selenium rectifiers as Siemens did not intend to use them for H.F. and measurement work.

Nitsche had found that the counter-electrode<sup>composition</sup> of selenium rectifiers affected the rectifier resistance. The reverse resistance depended on the work function of the counter-electrode metals; e.g., with cadmium (large work-function), a high resistance, but with bismuth (a smaller work-function), a low resistance. But the electrical effect of varying the counter-electrode composition of manufactured rectifiers was smaller than expected. The A.E.G. counter-electrode was a eutectic mixture of tin, bismuth and cadmium (m.p. 105 - 110°C), the Siemens counter-electrode a mixture of tin and cadmium (m.p. 170°C).

Nitsche did not know what happened when a selenium rectifier was formed but he supposed it caused a change in the distribution of impurity centres. He also thought that this distribution was disturbed by impurities in the counter-electrode.

Waibel had made a copper oxide disc with a barrier layer

1/10 m.m. thick. He could thus decrease the thickness of the barrier layer by etching with nitric acid. A different forward/backward current ratio was obtained for each thickness. The experiment only showed that the oxygen content of copper-oxide had some effect on the rectifier characteristics. The whole of the semi-conductor was made into a blocking layer by removing excess oxygen. This was done by heating the disc in a quartz tube in vacuo at a temperature of 800 to 900°C.

Nitsche explained that Schottky used special rectifiers for work in connection with his theory. These rectifiers were not formed. One of Schottky's papers published in 1942 contained some work on the capacitance of rectifiers.

#### 4.13 CL/814, C7/392, C9/992.

Dr. Irion was with Siemens until the beginning of the war.

When visited at his home, Selchowstrasse, 12, Wilmersdorf, Berlin, he was too ill to be interrogated. However, a questionnaire was left with him, which he promised to complete and return.

#### 4.14 CL/860, C7/337, C9/993.

Dr. Schmid works for Siemens on carrier systems, and is concerned with rectifiers only as a user of copper-oxide rectifiers in ring-modulators. The old pattern, with contact made by graphite and lead washers, were not sufficiently uniform to be used without selection. The use of a sprayed counter-electrode of silver or gold, introduced about 1939 by Waibel, made selection unnecessary. Originally the rectifiers were clamped, by a screw acting on a spring washer, to a specified pressure. With a sprayed silver electrode this is unnecessary. The pressure is not kept off the active area.

The rectifiers were artificially aged by heat-treatment (probably for about 1 hour, but Schmid did not know the temperature used).

The capacitance was tolerable for use up to 1 Mc/s (at which 10-15 db loss occurred with a carrier level of 0.5V). Schmid was satisfied with this, and had not pressed for improvement.

Although copper-oxide rectifiers must be protected from humidity, they must have access to oxygen.

#### 4.2 S.A.F.

The firm of S.A.F. have only made selenium rectifiers and neither Kipphan or Lauckner had experience of any other types of rectifier.

\* CL/862, C7/394, C9/995. X CL/861, C7/395, C9/994

They believed the structure of the barrier layer to be more complex than the simple Schottky theory postulates. For rectifiers with intermediate varnish films, however, they agreed with Schottky that only the points where holes existed in the film, were of importance. They had measured the distribution of impurity centres ( $n$ ) for discs with and without varnish films, by Schottky's capacitance method.

They were of the opinion that imperfections in the contact between counter electrode and selenium could not be vital to the rectification effect since it was possible to make rectifiers with an evaporated counter electrode: imperfections would then be of molecular dimensions only. In view of moisture contamination etc. they considered such imperfections were only harmful to the rectifier.

The physical mechanism of rectification in the copper-oxide and selenium rectifiers is essentially the same, and the Schottky theory deals with the salient factors in each case. However, the theory is only applicable in the reverse direction for small voltages. An explanation of the decrease of reverse resistance at higher voltages was given in general terms - the barrier layer is not perfect, and contains a few "Störstellen"; the distance between them is large compared with the thickness of the barrier layer, but at high field strengths, the resistance of these weak spots becomes small, and large local currents flow. Thus the reverse characteristic can be split into two phenomena. a) The Schottky effect - the barrier layer increases in width and resistance with increase of reverse voltage.

b) The resistance of the weak spots falls under high field strengths, and causes the overall resistance of the barrier layer to fall.

The barrier layer in the copper oxide rectifier was believed to be oxygen-free oxide. They doubted the decrease of resistivity of the oxide as the barrier layer is approached, and could not explain such an effect: no work has been done on this subject.

Measurements have been carried out on the charge held on the selenium surface with a given current flowing. To do this, 3 electron beams were made to fall perpendicularly on the selenium surface of a rectifier disc that had no counter-electrode. The charge held on the surface was measured by the deflection of an electron beam that passed across the surface. When no current was being supplied to the disc, the measuring beam was parallel to the selenium surface; when a current was flowing, the beam became deflected upwards. [The significance of this experiment was not apparent. Some connection may exist between this work, the secondary emission experiments of Prof. Knoll]

The capacitance exhibited by a rectifier was said to be due to three things, 1) imperfections in the contact,  
2) the space charge barrier layer,  
3) imperfections in the selenium layer.

Of these, the second was assumed to be the most important since the Schottky theory gave the right order of capacitance. "Störstellen" distribution was, in fact, estimated by capacitance measurements.

Small pressures produce reversible changes in selenium rectifiers, large pressures destroy them. This was believed to be due to a destruction of the crystalline form of the selenium. Heavy pressure thus produces more imperfections in the selenium, lowers its resistance, and decreases the break-down voltage.

Ageing and creep are mainly due to migration of ions in the selenium. Formation of a second barrier layer, between the selenium and the back plate is thought to contribute to ageing. Differences between creep phenomena in selenium and copper oxide rectifiers had not been observed.

Experiment is in progress to reduce the noise in selenium rectifiers by means of varnish films.

Kipphan and Lauckner made three points about the effect of humidity on selenium rectifiers;

- a) Damage to rectifier discs by humidity was due to a surface film of water by-passing the barrier layer.
- b) Changes in the relative humidity of the air were believed to be the cause of seasonal variations in the quality of rectifier production. This problem is under investigation at the present time.
- c) Selenium dioxide, used for fuming the discs, attracts water vapour from the air if the humidity is greater than 65%.

The selenium is fumed with selenium dioxide vapour before the counter electrode is added to small discs to reduce the forming time. The method cannot be used for large discs since the increased forward resistance that results would cause over-heating of the discs in operation. It was suggested that a thin oxide film forms on the selenium surface even without fuming, but that a thicker one is produced by the above method. This is the first reference to such an oxide film and its effect on the rectifier resistance.

The effect of mercury vapour on selenium rectifiers was attributed to a film of mercury by-passing the selenium layer at its edges.

An alternating current was used for forming discs; the frequency had to be between 10 and 1000 c/s to be effective.

They had done a considerable amount of experimental work on the variation of rectifier resistance with frequency which they studied by means of the following equivalent circuit.



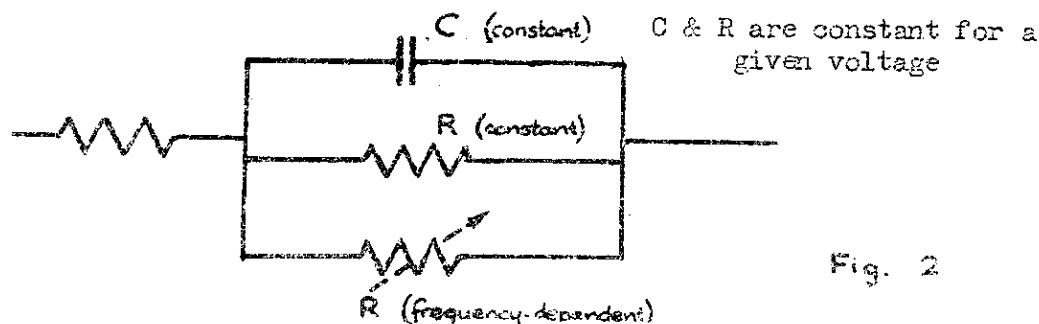


Fig. 2

[In retrospect, this interrogation was rather unsatisfactory mainly owing to language difficulties. However, answers to the questionnaire and details of their experimental work should be of interest- in particular, their work on the variation of resistance with frequency/.

4.5 A.E.G.

4.31 C1/659, C7/393, C9/723.

Dr. Bosch worked in Berlin on research and development. His notes and records were all lost there, and he spoke only from memory. He had often discussed rectifiers with Prof. Schottky. He thinks that a single theory cannot cover all types of rectifier.

The A.E.G. process was: on to an aluminium plate there were evaporated a thin layer of bismuth (to ensure adhesion of the selenium), and then a layer of selenium. The temperature and speed of deposition of the selenium were important; there was a risk of overheating by the latent heat of the condensing selenium. For the heat-treatment, wide limits of temperature were permissible. The counter-electrode was sprayed on after the rectifier had been exposed to selenium dioxide vapour. Bosch doubts whether the dioxide was desirable (particularly as it is hygroscopic) but this process was always included. For forming, a heavy current (e.g., 12A for a 0.3A rectifier) was passed for a short time (less than 1 minute).

The purity of the materials is important. Pure selenium is less useful than commercial selenium, or than selenium plus iodine.

No special heat-treatments were used to produce rectifiers for particular applications, probably there were no requests for such rectifiers.

A.E.G.'s life test was full-load conditions for 4 months, during which the efficiency was not to fall more than 10%. The Army (which took the entire output) did not encourage attempts to produce rectifiers with longer lives. No accelerated test had been devised; 30% over-voltage reduced the life greatly, but not in a known ratio.

The voltage rating was about 20 to 23V R.M.S. Excess voltage caused shorter life, or sometimes breakdown. Excess current melted the selenium.

Ageing was studied by A.E.G., not in Berlin, but at Belecke. Noise was not studied by A.E.G., but probably by Telefunken.

The effect of mechanical pressure was not considered, and in A.E.G. rectifiers the active area was under pressure.

Mercury vapour reaching either the selenium or the counter-electrode destroys a rectifier rapidly (e.g., in 2 days) and permanently; possibly by producing a closer contact between the selenium and the backing-plate. But on one occasion only, Bosch found that a selenium photo-cell had been temporarily sensitised to infra-red (as far as 11000<sup>o</sup>A); he cannot explain this.

Bosch had worked on the effects of various alloys in the counter-electrode and of intermediate layers between the counter-electrode and the selenium.

As small additions to the counter-electrode, he tried lead, cadmium, tin, thallium, indium and germanium. The work was incomplete. Indium gave a good sharply curved low-voltage characteristic.

As intermediate layers he tried phenol-formaldehyde resin, polystyrene, polyvinyl chloride (dissolved in tetra-hydro-furane), water-glass, sulphur and amorphous selenium. Of these, the last two had no useful effect. Of polystyrene and phenol-formaldehyde, one (Bosch forgets which) gave a good low-voltage characteristic, the other gave a reduced capacitance and a higher breakdown voltage. The effect of the phenol-formaldehyde was probably due partly to traces of water introduced by it. Hydrogen selenide would then be formed, and would attack the counter-electrode to produce metal selenides.

One object of using intermediate layers was to reduce the capacitance, which corresponds to that of a dielectric film of thickness about  $10^{-6}$  or  $10^{-5}$  m.m. (Bosch forgets the exact figure). The values of the components in the equivalent circuit were measured by using a range of frequencies; intermediate layers were found to reduce C and increase R.

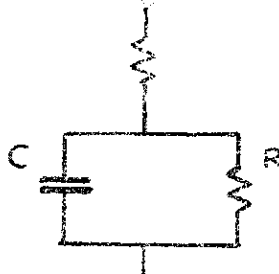


Fig. 3

4.32

Cl/863, C7/396, C9/1000.

Dr. Herbeck was formerly Bosch's assistant. All her records were lost in Berlin.

She had been particularly concerned with the use of intermediate layers between selenium and counter-electrode, working with styrene, polystyrene, phthalein, "resinol" and also (but unsuccessfully) sulphur. She did not use amorphous selenium. Layers of evaporated metals (bismuth, gold, etc.,) were also used. Dr. Herbeck spoke of these as if they were equivalent to the lacquer films.

If both an insulating and a metal layer were to be used, Dr. Herbeck found it better to place the insulating layer next to the selenium. The films were usually deposited from a 1% solution.

The object of the investigation was to reduce capacitance, increase breakdown voltage and (with the metal layers) to improve the low-voltage characteristic.

Small permittivity might have been the desirable property in the intermediate layer but paraffin wax was found to be no use. She thought the effect was both mechanical and chemical, the film completely separating the selenium surface from the counter-electrode.

The ageing of rectifiers during the first few days after manufacture suggests either chemical change or diffusion between the selenium and the counter-electrode. Ageing (after the first few days during which she made no tests) was less for rectifiers with intermediate layers, which may perhaps prevent chemical reaction or diffusion.

She believed her best products were comparable with Philips rectifiers which she thought made use of intermediate layers.

Dr. Herbeck thought that 10% change of characteristics during a 1000-hour life-test was reasonable for a normal rectifier. Owing to a bad war-time mains supply, A.E.G. could not conduct continuous tests; in any case, the continuous loading of small rectifiers was not considered worth observing, as it was not a practical condition of use.

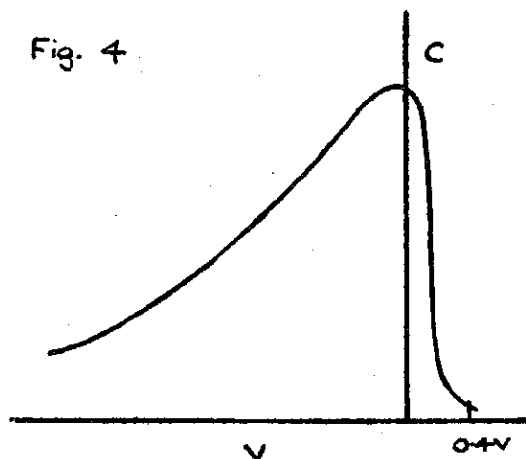
4.33 C1/864, C7/397, C9/999.

Dr. Koch said he understood only part of the mechanism of rectification. He thought that Schottky's theory was not exactly true as it discusses only part of the mechanism and cannot explain the blocking action at higher voltages. Koch believed that some other effect was superposed on Schottky's 'space charge' but he did not know whether it was a surface or body effect. He thought that both the body of the semi-conductor and the counter-electrode surface would be involved.

Koch said he was well acquainted with Schottky's work but not with Davydov's or Mott's. But he had obtained a V - I curve of the shape predicted by Davydov with selenium and a sprayed pure bismuth

counter-electrode.

The thickness of the barrier layer was a function of applied potential and the barrier layer defined the capacitance of a rectifier. The charge at the surface of the counter-electrode must equal the charge in the whole volume of the barrier layer. The current was a function of this space charge and the nature of the surfaces. Koch had made some capacitance measurements and had obtained curves as shown in



The curves showed that working with too high a voltage caused the space charge zone to break down and capacitance to fall off. In the forward direction a rectifier only has a capacitance at very small voltages. The variation of capacitance with frequency was only measured over the range 50 - 2500 cycles/sec. Koch thought the dependence of capacitance on frequency was due to an ionic effect. He had found that capacitance also varied with the composition of the counter-electrode. He likened the capacitance of a rectifier to the capacitance "sheets" around a probe electrode (Langmuir).

Koch believed that a greater number of impurity centres were present near the border of semi-conductor and counter-electrode but he did not know whether this was due to migration of impurity centres or the effect of the counter-electrode. Koch had found that the counter-electrode combined with the selenium and the chemical action was different for sprayed and evaporated electrodes. He dissolved away the selenium with sodium sulphide and studied the colours caused by the chemical action of the selenium on the counter-electrode surface. He found that these colours were a function of the time of contact of selenium with counter-electrode, i.e., a function of the age of the rectifier. He had used times ranging from a few minutes to several hours. This work was carried out in 1942 and described in a report - "Aufbau der Selen Sperrschicht" written by Koch and his collaborators. Koch only had a single copy and arrangements have been made with 'T' force for its duplication.

Ageing was due to the migration of impurity centres. With a large electrolytic component present, impurity centres would move out of the selenium towards the electrodes and the rectifier resistance would increase. Metal atoms of the counter-electrode would also diffuse into the selenium. Koch said the above report contained work on the distribution of impurity centres near a counter-electrode containing thallium. He had found that a good rectifier was obtained if the thallium content of the counter electrode was low. Thallium diffused very readily into the selenium. Mercury, however, diffused even more easily and destroyed the rectifier.

Creep was caused by the temporary migration of the more mobile impurity centres and was also a question of crystal structure.

Koch had found that mechanical pressure affected the selenium layer by destroying crystals at the selenium surface but he thought the effect neither important nor useful. The only condition should be that the applied pressure must not be too high.

The life of a rectifier was a question of impurities and crystal structure, e.g., a short life if too much bromine impurity.

The life of a rectifier also depended upon the forming process and was a function of the working temperature (a greater diffusion of counter-electrode particles at higher temperatures). The temperature of a rectifier determines its rating and should not exceed 65°C.

Koch explained that the reverse voltage of a rectifier could be increased by building in the impurities in a definite manner. To do this the temperature at which crystallisation takes place, the structure of the selenium and the pressure applied during manufacture of the plates, must be taken into account. Such a rectifier would have a reverse voltage of 30-40 volts and would not need forming. He had made a few of these units.

When questioned about A.E.G.'s evaporation process, Koch replied that the possibilities of this method were greater than any pressure process. Oven temperature and base-plate temperature had to be carefully controlled owing to the large latent heat of selenium. The base plate temperature was held to within 110 - 130°C., and the process carried out in vacuum.

A film of selenium dioxide was afterwards evaporated on to the selenium surface at room temperature. This increased the reverse voltage by 2 or 3 volts. The counter-electrode (a eutectic mixture of bismuth, cadmium and tin, m.p. 103 - 105°C.) was then sprayed on.

In the evaporation process there was an atomic building-in of impurities as opposed to a mechanical building-in in the pressure process. The evaporation process therefore gave a more stable product and was the only process which could be used for making rectifier discs for experimental work.

Koch had done some work on varnish inter-films during the war and this was included in "Aufbau der Selen Sperrschicht"; a varnish film lowered the number of impurity centres near the barrier layer. The electric force at the barrier layer was therefore lowered and hence the reverse current decreased. The main difficulty in the work was that the forward resistance of the rectifier was increased by the varnish layer. But Koch found there was a small range of thicknesses where this was not so, and he used this range for his test rectifiers.

4.34 CL/865, C7/398, C9/998.

Dr. Kalkner is head of the A.E.G. laboratory in Berlin. He is not a specialist in rectifiers. Work on rectifiers is now transferred to their factory at Belecke/Möhne; research there is directed by Dr. Koch and Dr. Brunke.

The A.E.G. manufacturing process is evaporation first of bismuth, then of selenium, on to large metal sheets. (This was done in tanks of mercury-vapour rectifier pattern). Other processes cannot be used for large sheets. These large sheets are then stamped into discs, the discs having closely similar properties.

There is no reason to fear damage in stamping; but any defects caused would be burnt out by the over-voltage which is applied as a test.

An artificial ageing process prevents subsequent changes and gives a more uniform product. Kalkner thinks this is in addition to the forming process, and that it includes the passage of a current.

A.E.G. rectifiers were intended for use at low frequencies, and capacitance was therefore unimportant. The life of the rectifiers had not yet been measured; but it is known to be shortened at temperatures over 50°C.

Mechanical pressure on the active surface produces no measurable difference in the characteristics.

4.4 OSRAM CL/787, C7/399, C9/997.

Dr. Friederich was in charge of Osram research on rectifiers and semi-conductors. Many of his records were destroyed or are now in Russian hands.

[Friederich's interrogation was unsatisfactory. Although he appeared to speak freely, he spoke of withholding information from previous investigators. His excursions into theory are very unconvincing.]

Osram formerly made cuprous-iodide rectifiers. They were

abandoned because of poor life; this was probably due to thickening of the barrier layer by continued chemical reaction with the lead counter-electrode. The ageing of these rectifiers was probably due to the same cause, and could be reduced by a film of lead sulphate on the lead. The life of the rectifiers was about 1000 hours, depending on the running temperature, which therefore fixed the current rating. Excess reverse voltage reduced the life. Parallel connection was not permissible. There was no known method of accelerating a-life test.

The conductivity of cuprous iodide depends on the presence of excess iodine (of the order of 0.1%). Cuprous iodide will absorb this iodine from the vapour phase, and in Osram's production process copper plates were left for 2 days in an atmosphere of iodine for the films to form. The purity of the copper and lead is unimportant, and commercial materials were adequate.

Cuprous iodide is an electronic conductor, though with few electrons; lead iodide, formed where it touched the counter-electrode, is an insulator. These conditions are sufficient to cause rectification; compare the action of a "concentration cell", in which a voltage is set up between two similar electrodes immersed in solutions of differing concentration separated by a porous barrier. Probably there will prove to be corresponding layers in a selenium rectifier.

For another example of the spontaneous formation of thin surface films, compare the films on boron crystals, which cause its resistivity to appear high in ordinary tests, although it is low if measured by eddy-current methods.

Schottky's theory may be right, but it is too mathematical to be directly useful, and its main use is for excluding experimental work in certain directions.

Friederich cannot explain the variation of capacitance with applied voltage.

Osram also tried sulphide rectifiers, but without success. Another Berlin firm had marketed a (? ferrous) sulphide rectifier for a time, but its life was short.

Cuprous bromide gives an irregular voltage-current curve, since it is an ionic conductor having a decomposition threshold voltage.

Carborundum would be the perfect rectifier material because of its permanence.

## 5. NON-OHMIC RESISTORS

### 5.1

Dr. Friederich said that Osram had found true non-ohmic resistors not consistent enough, and had done no serious work on them. Thyrite was the best of those available. The characteristic feature of their composition was the mixing of a conductor and a non-conductor (e.g. Silit contains 30%  $Al_2O_3$ ).

Urdox gives a temperature effect only. The name had been retained when uranium oxide was replaced by a mixture of oxides of magnesium and titanium. The notes on this interview refer, surprisingly, to  $Ti_2O_3$ . This requires confirmation. About 1% of the oxygen was removed and many alternatives to magnesium and titanium were tried.

The manufacturing process was to mix the oxides, together with a binder; to press and fire at  $1000^{\circ}C$ . in air; to cut to the required size; to dip the ends in a molybdenium-containing solution; to fire at from  $1400$  to  $1700^{\circ}C$ . in hydrogen in an alundum furnace; to fit molybdenum wires as end-connections; and to dip the ends in molten copper to metallise them and attach the wires. There was no difficulty over purity of materials, and no added impurities were required.

The resistances of 70% of the units so made were within commercial tolerances (say  $\pm 20\%$ ). The rejects could be heat-treated again to bring them within limits, as the temperature of the second firing governed the properties of the finished product. Variations of properties were probably due to bad temperature control, wrong porosity, or wrong grain size.

Thin, translucent, films were made by Weise (who was Friederich's assistant) using a cellulose binder. These films could be used as bolometers capable of detecting the heat of the human head at 10 metres. The size of reflector, if any, was not mentioned.

Meyer's work on non-ohmic resistors was published in Zeits. für Elektrochemie, 1944 (or 1945).

### 5.2 C1/866, C7/400, C9/627.

Herr Weise had been interrogated in U.K. and it was hoped to examine his records and apparatus with his assistance.

During Weise's stay in England his Lab. was dispersed. Some of his boxes remain in Rathsberg, but they contain no scientific documents or apparatus. It was believed that most of his documents



had been removed to Heidenheim, and the director of Osram's research laboratories, Dr. Theleis should have them.

It was suggested that Dr. Isensee (who works in Osram, S. Berlin) might help find Weise's documents in Berlin.

It has been requested that an attempt be made to trace Weise's laboratory reports and his experimental Jonsen Rahbek relays.

### 5.3 C1/867, C7/401, C9/98(a).

Klarmann was employed at Siemens-Halske. He worked on semi-conductors under Schottky between 1936 - 1938. Previously he had worked for a year on rectifiers. After 1938 he worked on aluminium oxide for electrolytic condensers.

Klarmann had worked on thin films of silica and varnish. He had found that it was not necessary for the varnish films to have holes. The conductivity of silica films depended on the applied voltage and Ohm's Law was only true at small voltages. This work had been done with de Boer and was published in the Siemens Journal for 1935.

Of the voltage-dependent type of non-linear resistor, he had worked with silicon carbide and boron carbide. Temperature-dependent types included cuprous oxide, titanium dioxide, zinc oxide, aluminium oxide, nickel oxide, cobalt oxide, zirconium oxide, vanadium pentoxide and yttrium oxide. The latter, in practice a mixture of rare earths, was not constant either in vacuum or air.

Klarmann had also tried mixtures of equal molecular parts of nickel and cobalt oxides, cadmium and zinc oxides, titanium dioxide and magnesium oxide. With the latter he claimed he had obtained a resistance range of 0 -  $10^{25}$  ohms by reduction to various extents. The titanium dioxide dissolved in the magnesium oxide. Osram had already done some work on this mixture and claimed that they had produced a resistor with a positive temperature coefficient but Klarmann was doubtful of this claim. With this mixture each resistance value had a different temperature coefficient (unlike cuprous oxide whose temperature coefficient is constant). The conductivity of the titanium dioxide-magnesium oxide mixture was less than that of pure titanium dioxide for the same temperature of reduction. Klarmann used reduction temperatures of 500°C in hydrogen atmosphere and 1200°C. in vacuum. The latter reduction temperature gave a temperature coefficient of zero. Klarmann thought the time of reduction was not important; he usually used a half hour period.

The smallest size of resistor made by Siemens was 0.2mm thick, the usual Osram size being 1 cm. Titanium dioxide resistors were first introduced as substitutes for uranium oxide. Osram then used it entirely, because of the bad ageing property of uranium oxide. Siemens however had a process which cured this bad ageing so that they continued to make uranium oxide resistors. Ageing was due to ionic conduction, caused by the presence of excess oxygen ( $UO_{2.3}$  instead of  $UO_2$ ). It was prevented by heating the resistors to  $600^{\circ}C$ . for two hours, passing a direct current whose direction was reversed every five minutes. After this treatment the D.C. resistance remained constant with time. Before treatment, although the A.C. resistance was constant, D.C. resistance decreased with time of application of the voltage.

Uranium oxide was reduced at  $1500^{\circ}C$  in a hydrogen atmosphere. The changes which took place were much more complicated than in the reduction of titanium dioxide. Klarmann pointed out that uranium oxide resistors were very sensitive to oxygen and traces of oxygen in the hydrogen reducing atmosphere caused the conductivity to drop. Uranium oxide was also liable to absorb oxygen when cool.

Of other materials, Klarmann had used, cuprous oxide had a conductivity of  $1000 \text{ ohm}^{-1} \text{ cm}^{-1}$ , at  $800^{\circ}C$ . If allowed to cool quickly to room temperature the conductivity fell to zero. If it cooled slowly for ten hours in an oxygen atmosphere, the conductivity fell only to 100.

The smallest time constant Siemens had ever obtained was  $\frac{1}{1000}$  second. This was obtained with a small crystal of semi-conductor embedded in Wood's metal so that it cooled down quickly when the current was switched off. The frequency used was above 1 kc/s.

Temperature dependent types of resistor were linear with voltage when the contact at the ends was well made. The best way of making the contact was to apply a paste of silver oxide. This was reduced to silver by heating at the time of reduction of the semi-conductor.

#### 5.4 C1/868, C7/402, C9/996.

In 1944 Dr. Rother observed that a ceramic with a blue discoloration had a low resistance (few ohm - cm). The ceramic contained cerium oxide, which, in the absence of an adequate oxygen supply (i.e. when the ceramic was in a reducing part of the furnace) partially reduced the  $TiO_2$ . A firing temperature of about  $1380^{\circ}C$ . was used [Note that Weise's semi-conducting material, which does not contain cerium oxide, is fired at a much higher temperature]. He has made up about 3000 semi-conducting samples; these contain a variety of rare earths, but they had not been tested electrically. To show

the effect of some ingredients, the following example was given. A mixture of 95% Rudiox and 5% lanthanum carbonate III gave a semi-conducting ceramic, but a mixture of 92% Rudiox and 8% lanthanum carbonate H showed no signs of reduction despite the fact that it was fired in the same part of the furnace and at the same time as the other mixture. This difference was believed to be due to the fact that lanthanum carbonate III is extremely pure, while lanthanum carbonate H contains 13%  $\text{Nd}_2\text{O}_3$  and 4%  $\text{Pr}_2\text{O}_3$  : one of these may have inhibited the reduction.

Rother believes that semi-conducting ceramics might be developed into economical rectifiers with advantage in view of Germany's present raw-material situation. He had not considered the fact that the ionic conductivity in his ceramics would be a disadvantage in a rectifier [nor did he seem to be aware of the work Osram have done on  $\text{TiO}_2$ .  $\text{MgO}$  semi conductors].

A rutile ceramic was exhibited which contained 7% barium carbonate and 5% zirconium oxide and whose surface turned blue while exposed to light. Apparently no further work has been done on light-sensitive ceramics.

Rother has worked on  $\text{Cu}_2\text{O}$  and Se photo-electric cells. He has also worked on magnetic ceramics [Lit. Richardson R.N.V.R. covered his work in this field], including some with additions of cuprous oxide.

To make a ceramic with a very high resistance (e.g. for use in his H.T. machine - for which see Col Ranger's report) he used  $\text{TiO}_2$  in place of  $\text{Ti}_2\text{O}_3$  - the possibility of reduction was<sup>thus</sup> eliminated.

Rother undertook to send results of his measurements on semi-conducting ceramics to the U.K. as soon as they were completed. He further expressed the desire to come to England to continue his researches since in Germany he was handicapped by a shortage of raw materials.

## 6. SECONDARY EMISSION

### 6.1 C1/869, C7/410, C9/1001.

Graf von Schulenberg was believed to have worked with Professor Knoll on an image converter tube for which one semi-conducting mosaic was supplied by Herr Weise: it was hoped to trace a model of this tube.

Schulenberg had worked on secondary emission from materials such as CdS and ZnS, but not from  $TiO_2$ . He had already given full details to an English commission.

Although secondary emission depends on the conductivity electrons, he did not expect any relation between it and semi-conduction.

Schulenberg has done no other fundamental work on rectifiers or semi-conductors.

### 6.2 C1/870, C7/409, C9/1002.

Dr. Randtner also worked under Prof. Knoll. He worked on television screens and long after-glow tubes and also tried to correlate the suitability as a detector of a point on the surface of a semi-conductor with its secondary emission. It had been hoped to use this property in the assembly of detectors. He also worked on ionoscopes, no models of which remain.

A film of lead sulphide, placed inside a cathode-ray tube, was scanned in 2 dimensions by an electron beam (see Fig. 5 ). Variations in secondary

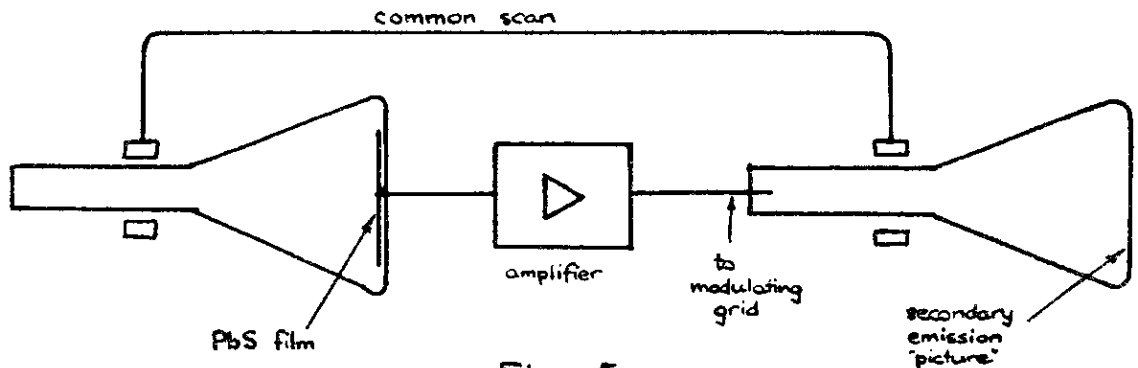


Fig. 5

emission current were used to modulate the brilliance of a second C.R.T. whose scan was synchronised with the first. The film was then removed from the C.R.T. and its surface was examined with a 0.1 mm point

at 1 mm intervals. The back to front ratio of observed resistance for a given voltage was taken as the measure of rectifying efficiency. The two sets of results obtained were found to be reproducible, but could not be correlated. It has been expected that points suitable for use as detectors would have a large secondary emission.

Surface irregularities in the newly cut crystal caused complications in the secondary emission picture, while if these were removed by polishing no rectification was observed. No explanation of this effect could be given.

Similar experiments to the above were carried out on selenium discs. Discs consisting of back plate and selenium deposit were cut in half. Part was made into a rectifier by the addition of a counter electrode and the total secondary emission was measured for the other part. Again no correlation was found between the "goodness" of a rectifier and the magnitude of the secondary emission from the surface of its semi conductor [perhaps the secondary emission could have been correlated with some one feature of the rectifier's properties rather than with the back to front ratio; again the voltage used in the rectifier part of the experiment may be important].

Some details were then given of the iconoscope designed to use the titanium dioxide film screen prepared by Weise. It was found that the smallest rise in temperature of the screen which could be detected varied between 0.01 and 0.1°C. The former value was thought satisfactory, but all models could not be made so sensitive. Randtner claimed the iconoscope to be sensitive to longer wavelengths than one using a CdS mosaic.

Thinner films were not thought to offer a possible improvement since they became transparent to electrons and of too small a resistance. (Weise made films 20 u thick). A further limit was set to the sensitivity by the fact that the scanning beam ionised the film and so varied its resistance.

No apparatus remains, but a full description was published in Zeits. für Physik 122, 137, 1944.

### 6.3 C1/719, C7/408, C9/809.

Professor Knoll had no further information to offer about his work with Randtner; he had been engaged on it from 1942 to 1944. Some of his remarks at his joint interrogation with Rothe are reported in under 2.6, others are included in the miscellaneous information.

7. MISCELLANEOUS INTERVIEWS

C1/806, C7/407, C9/1003.

7.1 Dr. Deutschmann worked on rectifiers under Prof. Schottky before 1930, but not since that time. He was therefore not interrogated further.

C1/714, C7/406, C9/811.

7.2 It was not possible to interrogate Professor Kluge, but a questionnaire was left for him.

C1/871, C7/405, C9/1004.

7.3 Dr. Wehner has done no work on rectifiers or semi-conductors.

C1/872, C7/404, C9/1005.

7.4 Dr. Schniederma was encountered by chance and provided some information about the addresses of his Siemens colleagues. Since he had been interrogated on rectifiers while in England, he was not questioned further.

C1/873, C7/403, C9/1006.

7.5 The Director of Osram Research Laboratory at Heidenheim (Dr. Teleis?) was concerned only with lamps. No research on rectifiers or semi-conductors was in progress, but would soon be started in Erlangen. He gave information on the present location of certain former research workers.

## 8. IRRELEVANT INFORMATION OBTAINED INCIDENTALLY

Prof. Brill studied films of caesium and caesium-oxide, as used in photo-electric cells. He measured the variation of work-function of caesium when it was illuminated by monochromatic light of various wavelengths, both for pure caesium and after the introduction of km small amounts of oxygen. The graph of work-function against wavelength is a curve whose peak is shifted towards longer wavelengths by the admission of oxygen. There are many compounds of caesium and oxygen; one, probably Cs<sub>7</sub>O, has a minimum work-function which is therefore the apparent work-function of the caesium-oxygen system.

Prof. Kossel studied oxide layers used as protection for aluminium mirrors. These films are amorphous when formed, but crystallise if heated to 700°C.

Dr. Himmeler is now working on the speed of corrosion of metals, and on the use of a glass electrode for pH measurements.

Dr. Schaefer, of Frankfurt University, works on oscillators of all types.

During the war, Siemens introduced a range of synchronous driven switch rectifiers which Baudisch thought would eventually replace metal rectifiers for heavy current work. A typical rectifier was rated for 10,000 amps, 400 volts; weight 800 Kg, efficiency 97%. A copper oxide rectifier of the same rating would weigh ten times as much. Other models were made for heavy currents and low voltages (9 volts). A big advantage of these rectifiers was their close regulation obtained by the use of saturated cores. Such regulation was not possible with metal rectifiers. Details of these rectifiers had previously been obtained by Mr. Thomson of G.E.C. and Mr. Wool of English Electric. [They are thought to be similar to those developed by F.Koppelman: see B.I.O.S. Final Report No. 8, Item No. 21, pp.6, 16 and 17 and the report of B.I.O.S. Party No. 1875]

Dr. Welker has been engaged on a theory of super-conductivity [a paper on this subject will be published in the second report].

Dr. Wehner has worked on "Plasma" oscillations [see Japrbuch 1942 der deutschen Luftfahrtforschung S III 24/32].

Dr. Bombe of Herrsching has worked on crystal oscillators.

Prof. Schleder of the Technisches Hochschule, Bln, has worked on fluorescence.

Prof. Hilsch has been engaged on light absorption by films of Cu<sub>2</sub>S containing excess sulphur. The effect of temperature has been found and the experiments were extended to liquid helium temperatures.

For this purpose a modified Simon Diquéfier was used with quartz windows, and external controls to enable the sample to be removed from or replaced at the cold spot. This work is almost ready for publication.

Prof. Hilsch has also worked on super-conductivity, which he believes also depends on impurities. Justi of the Technisches Physicalisches labs. Bln., produced NbN with a transition point of 15°K and later attained a value of 22°K. Mixtures of NbN (metal) and Nb<sub>2</sub>N (insulator) have been made with transition points as high as 100°K. These mixtures were prepared at 1200°C. in an electric light bulb. Interesting as these abnormally high values are, Hilsch believes they have little value from a theoretical viewpoint because of the complexity of the systems used. He prefers to work with Cu<sub>2</sub>S, CuS mixtures [see his experiments on light absorption].

It has been shown by Shalikov that the transition points for pure metals are fixed quantities; for tin for example, the value is 3.7°K. Hilsch has shown however, that if a tin deposit be found on a quartz plate at a few°K, the transition point is raised by at least 1°K. Warming the deposit destroys the effect irreversibly. It was also noted that, contrary to expectation, the sharpness of the transition point decreases with crystal size.

Prof. Hilsch has a very well laid out low temperature laboratory and uses an air liquifier of his own design. Air at 10 atmospheres pressure is blown into a tube at right angles to its axis. The jet is offset laterally so that the air stream enters the tube tangentially. The tube is approximately 1 cm in diameter and 30 cms long. The inlet is about 10 cms from one end and an orifice is fitted inside the tube adjacent to the inlet and between it and the nearer end of the tube. Hot air emerges from the remote end of the tube and cold air from the near end (this air having passed through the orifice). A tap near the open end of the hot half of the tube controls the ratio in which the air stream is divided between the two halves, and so controls the temperatures of the two streams; when this tap is correctly set, the cold air is at a temperature of about -45°C. The size of the jet and of the orifice were stated not to be critical, but an insert has been fitted to the tube opposite the jet and this has the effect of giving the spiralling air stream an inward velocity.

[It is felt that Hilsch's apparatus should be worth closer study and it has been requested that working drawings of and details of experiments concerned with the design of his air liquifier be obtained from him].

This tube is mounted in a cylindrical steel case about 40 cms long and 10 to 15 cms in diameter. Details of the remainder of its contents are not know, but they are believed to consist in heat interchangers only. Liquid air can be drawn off from this apparatus by means of a tap at the bottom of the cylinder, 10 minutes after the compressed air has been turned on.



INFORMATION OBTAINED DURING INTERROGATIONS ON LOCATION OF OTHER TECHNICAL WORKERS.

TABLE III

Person	Location or other information	Source of information
* Dr. Krebs	Malteserstrasse 5, Bonn	Prof. Kohlschutter
Dr. Hammer	became farmer before 1939	"
Dr. Hauffe	entered industry before 1939; probably Degussa, Frankfurt	"
Dr. Gundermann	deceased	"
Dr. R.Bauer	Siemens-Halske, Berlin (Wernerwerke I.)	Siemens-Halske
* Dr. Brunke	A.E.G., Belecke/Möhne	A.E.G., Berlin
Dr. Spenke	Inst für Virusforschung, Sielbeck Mutin/Halstein	Prof. Schottky
* Dr. Waibel	Machandelweg 11b, Charlottenburg 9, Berlin	"
Dr. Rompe	Wilhelmstrasse 68, Berlin W.8	"
Dr. W.Hartmann	Deceased	Dr. Schniedermann
* Dr. K.Maier	Stuttgarterstrasse 9, Eislingen/Fils	-
Dr. H.Neldel	Te Ka De, Nürnberg	Dr. Schniedermann
Dr.H.Schweickert	Augustenstrasse 2, Nürnberg	S.A.F., Nürnberg
Dr. Klein	Bismarckstrasse 15, Nurnberg.	"
* Dr. Justi	Marburg (but may take post in Techn. Hochschule, Hannover)	Dr. Friederich

Person	Location of other information	Source of Information
* Dr. Krauz	Marburg	
* Dr. Lämmchen	Hildesheim	FIAT Forward
Dr. Hackenberg	Berlin (possible working for Telefunken)	Göttingen University.

\* If opportunity arises, these persons should be interrogated; so also should Dr. Noldge, Inst. für Angewandte Physik der Hanseatischen Univ., Hamburg, who was not visited by the present party.

Now in U.S.A.:

Prof. C. Wagner, Dr. Mass,

Now in Russia:

Dr. Stenbeck

Believed to be in Russian zone:

Dr. F.H. Müller, Dr. W. Meyer, Dr. Scheibe (and all staff of Phys. Techn. Reichsanstalt), Dr. A. Schmitt (working for Telefunken).

TENTATIVE CONCLUSIONS

[these are liable to modification when reports of researches are to hand].

It is generally felt that there **have** been few war time developments of note in Germany concerned with rectifiers and non-linear resistors and that this is due to three main reasons:

- (1) Concentration of effort on production of standard articles to meet an overwhelming demand.
- (2) Disruption of experimental work by air raids and the continual necessity of evacuating laboratories to new sites.
- (3) Drafting of research workers to other subjects or into the armed forces.

Several interesting points were however unearthed and it is hoped that some of these may be followed up either in this country or in peace-time Germany. In the latter case, facilities should be provided for the results of German research to be made available in this country. At the moment, the facilities for the publication of scientific work in Germany and especially in the American Zones, are far from adequate. Many workers such as Prof. Schottky have several papers ready for publication, but with no prospect of their getting into print for some time to come. It is felt that it would be an assistance to workers in this country if publication were made easier in Germany and if it were possible for German scientists to publish their works in English journals.

In general no difficulty was experienced due to lack of co-operation on the part of scientists interrogated, but in ~~some~~ cases it was felt that the standard of research work was not very high - due no doubt, in fact to the reasons mentioned at the beginning of these conclusions.

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