EINDHOVEN
UNIVERSITY OF
TECHNOLOGY

Investigations on the preparation, photoconductivity and photoluminescence of doped gallium sulphide single crystals

Citation for published version (APA):
van der Leeden, G. A. (1973). *Investigations on the preparation, photoconductivity and photoluminescence of doped gallium sulphide single crystals*. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Applied Physics and Science Education]. Technische Hogeschool Eindhoven. https://doi.org/10.6100/IR79425

DOI:
10.6100/IR79425

Document status and date:
Published: 01/01/1973

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 17. Nov. 2023

INVESTIGATIONS ON THE PREPARATION, PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE OF DOPED GALLIUM SULPHIDE SINGLE CRYSTALS.

GERARD ANTON VAN DER LEEDEN

INVESTIGATIONS ON THE PREPARATION, PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE OF DOPED GALLIUM SULPHIDE SINGLE CRYSTALS.

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL TE EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF.Dr.Ir.G.VOSSERS, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VAN DEKANEN IN HET OPENBAAR TE VERDEDIGEN

OP DINSDAG 26 JUNI 1973 DES NAMIDDAGS TE 4 UUR

door

GERARD ANTON VAN DER LEEDEN

geboren te Delft

Dit proefschrift is goedgekeurd door de promotoren
Prof.Dr.M.J.Steenland en Prof.Dr.F. van der Maesen.

CONTENTS

	page
CHAPTER 1 INTRODUCTION	5
CHAPTER 2 THE PREPARATION AND ANALYSIS OF DOPED GALLIUM SULPHIDE SINGLE CRYSTALS	7
2.1 Introduction	7
2.2 The preparation of gallium sulphide	7
2.3 The growth of doped gallium sulphide single crystals	10
2.4 Spectrochemical analysis of gallium sulphide	14
2.5 Simple photoluminescence measurements	16
2.6 TSC and TSL measurements on cadmium doped gallium sulphide	17
2.7 Conclusion	19
CHAPTER 3 QUANTITATIVE SPECTROCHEMICAL ANALYSIS OF GALLIUM SULPHIDE AND GALLIUM SELENIDE	20
3.1 Introduction	20
3.2 A short introduction to emission spectrography	20
3.3 Apparatus	21
3.3.1 Excitation source	21
3.3.2 Electrode assembly	21
3.3.3 Spectrograph	22
3.3.4 Photographic processing	23
3.3.5 Densitoneter	23
3.4 Preparation of standards	23
3.5 Plate calibration	24
3.6 Racking plate spectra	25
3.7 Results	27
3.8 Conclusion	29
CHAPTER 4 A METAL CRYOSTAT AND SAMPLE HOLDER FOR PHOTO HALL-EFFECT STUDIES ON HIGH-OHMIC CRYSTALS IN THE 10-300 K TEMPERATURE RANGE	30
CHAPTER 5 PHOTOLUMINESCENCE MEASUREMENTS ON GALLIUM SULPHIDE	33
5.1 Introduction	33
5.2 Experimental arrangements	34
5.3 Results	38

5.4 Discussion 43
5.4.1 Crystals GaS(O) T60-3 and GaS(Na) T70-6 43
5.4.2 Crystals GaS(Cu) T52-1, GaS(O) T66-1, GaS(Na) T70-2 and GaS(Cd) T53-1 43
5.4.3 Crystals GaS(Cd) T51-1 and GaS(Cd) T68-1 45
5.4.4 The dependence of the luminescence intensity on the excitation light intensity 45
5.5 Conclusions 45

CHAPTER 6 PHOTOCONDUCTIVITY AND PHOTO HALL-EFFECT MEASUREMENTS 47
6.1 Introduction 47
6.2 Experimental arrangements 47
6.3 Results 51
6.4 The Klasens-Duboc model 58
6.5 Application of the Klasens-Duboc model 60
6.5.1 Crystal GaS(Na) T70-3 60
6.5.2 Crystal GaS(Na) T70-7 65
6.5.3 Crystal GaS(O) T54-1 65
6.6 The photo Hall-mobility 66
6.7 Conclusion 68

CHAPTER 7 CONCLUSIONS 70

Summary 72

Samenvatting 72

CHAPTER 1

INTRODUCTION

In 1964 a research program on chemical-, electrical transport- and optical properties of gallium sulphide was started in the Solid State Group at the Department of Physics of the Eindhoven University of Technology. In recent years a number of results of these investigations have been published by Lieth [1] and Kipperman [2]. In the course of these investigations photoconductivity measurements on a number of single crystals were carried out at roomtemperature. In some of the crystals the photoconductivity was found to depend superlinearly on the light intensity [3]. Vink [4] carried out temperature dependent photoconductivity measurements on one of these crystals and was able to give an explanation of the superlinearity involving three levels in the forbidden zone.
This superlinear behaviour was thought to be interesting enough to justify a more extensive investigation of the photoconductive properties of doped gallium sulphide single crystals. More specifically, the goal of these investigations is the preparation of intentionally and quantitatively doped single crystals which show a well defined photoconductive behaviour, such as a superlinear dependence on the light intensity. The results of these investigations are presented in this thesis.

The intensity- and temperature dependence of the photoconductivity in a semiconductor is mainly determined by trapping- and recombination centers [5,6] which often are caused by foreign impurities in the crystal lattice (dopes). Since doped gallium sulphide single crystals can not be obtained commercially the crystals had to be prepared by ourselves. The method of preparation is described in chapter 2. In this chapter some results of thermally stimulated current and luminescence measurements are also given.
The quantitative analysis of both trace impurities and dopes is necessary in semiconductor research. The results of spectrochemical analysis are given in chapter 3 together with a description of the method used in this case.
The temperature dependence of the photoconductivity has been investigated at temperatures between roomtemperature and 20 K. The variable temperature cryostat and crystal holder which has been used for this purpose is described in chapter 4. This description has been published previously [7].

Phenomena related to recombination- and trapping processes may yield parameter values which can support an explanation of photoconductivity results. TSC and TSL measurements have already been described in chapter 2; in chapter 5 the results of photoluminescence measurements are given.
Chapter 7 contains the results of photoconductivity and photo Hall-effect measurements on some doped gallium sulphide single crystals. The results are explained quantitatively in terms of the Klasens-Duboc model [5].
In each of the chapters a discussion of the results is included. In chapter 7 the relation between these results is discussed. Furthermore suggestions for further research are given in this chapter.

Gallium sulphide is a semiconductor with an indirect bandgap E_{gap} is 2.591 ± 0.002 eV at 77 K [8].

This thesis has been written in such a way that each chapter can be read separately. Literature is cited at the end of each chapter.

Literature

[1] Lieth, R.M.A., Thesis, Eindhoven University of Technology (1969).
[2] Kipperman, A.H.M., Thesis, Eindhoven University of Technology (1971).
[3] Kipperman, A.H.M. and Van der Leeden, G.A., Solid St.Comm., 6, 657 (1968).
[4] Vink, A.I., Il Nuovo Cimento, Serie x, 63B, 70 (1969).
[5] Bube, R.H., Photoconductivity of Solids, Wiley; New York (1960).
[6] Klasens, H.A., J. Phys. Chem. Solids, 7 176 (1958).
[7] Van der Leeden, G.A. and Queens, M.P.A., Cryogenics ,12, 51 (1972).
[8] Aulich, E., Brebner, J.L., and Mooser, E., Phys. Stat. Sol. 31, 129 (1969).

CHAPTER 2

THE PREPARATION AND ANALYSIS OF DOPED GALLIUM SULPHIDE SINGLE CRYSTALS

A method is described for the preparation of pure gallium sulphide, special attention is given to the preparation of stoichiometric material. It is possible to grow from this material quantitatively doped single crystals by a zone melting technique. A detailed description of the procedure is given.
The results of spectrochemical analysis of the gallium sulphide show that, if special care is taken, GaS can be prepared in which silicon and sodium impurities are detectable in quantities of approximately 5 ppm.
Thermally stimulated luminescense and current measurements indicate that cadmium introduces a trapping level in GaS.
Photoluminescence experiments give some evidence that Ga vacancies introduce recombination centers.

2.1 Introduction

A procedure is developed for the preparation of doped gallium sulphide single crystals for photoconduction and photoluminescense studies. Both the preparation of gallium sulphide from the elements and the preparation of the single crystals are described.
Spectrochemical analysis is used to determine the presence and quantity of the dopes and unwanted impurities to the lowest possible detection limit. Sometimes another method has a lower detection limit. In the case of cadmium dope, which introduces a trap in gallium sulphide, an appreciably lower detection limit can be reached by using thermally stimulated and / or current measurements.

2.2 The preparation of gallium sulphide

Although gallium sulphide prepared from very pure material is commercially available from Alusuisse [1], we had the following reasons to prepare it ourselves. First because, although the amount of impurities in both gallium and sulphur from which the commercially obtained gallium sulphide was prepared, was known to be low (not more than one or two ppm), the impurity concentration in the gallium sulphide was neither given nor guaranteed to be below a certain level. Second, the Alusiusse material was shown to contain silicon. Third, we wanted to be certain that the preparation of the material was always carried out under the same stringent conditions.

The preparation of our gallium sulphide is based on the method used by Lieth, Van der Heijden and Van Kessel [2] ; their method is a modification of the one described by Klemm and Von Vogel [3] .
In the preparation of gallium sulphide from the elements very pure (6 N) gallium pellets from Alusuisse [1] were employed.
These pellets were etched in an etch consisting one volume part HF (38 to 40% HF in water), three volume parts HNO_3 (65% HNO_3 in water) and four volume parts water. The etching has to be carried out at a temperature well below 20°C (we used ice water to cool the etch) otherwise the gallium pellets will melt by the heat generated in the etching process and flow together. The etching procedure is stopped as soon as the pellets, which had a dull grey color, get a bright blue metallic color which takes about three minutes. Afterwards, the pellets are rinsed in deionized water, dried in open air and weighed.
The sulphur initially used was from Johnson Matthey (catalogue number JM 775, purity 5N8) [4] . However, it turned out that gallium sulphide prepared from this sulphur had a black deposit on it. It was shown by Koningsberger [5] , who used the same sulphur in ESR experiments,that the sulphur contained a large amount of carbon and oxygen presumably bound to the sulphur. To separate the carbon and oxygen from the sulphur, the Von Wartenberg-method [6] was used, which consists of local heating of the melted sulphur to a temperature of approximately 700°C with a heater encapsulated in a silica tube. The carbon precipitates partly on the heater and can be scratched off.
SO_2, CS_4 and other volatile carbon-sulphur and carbon-oxygen compounds are removed by vacuum evaporation and the sulphur is then distilled into another silica container. Although no more ESR signal was found by Koningsberger after such a treatment, carbon could still be detected in our experiments. The following simple test was used to show this. Evaporation of one gram of sulphur from an open glass container left a residue on the glass wall. The amount of blackening is assumed to be a measure for the amount of carbon left in the sulphur. For purified material the blackening has decreased markedly as compared with the normal sulphur.
Gallium sulphide prepared with sulphur purified in this way has a high magnesium content. This may be due partly because more steps were used in the preparation process and partly to smoking in some of the rooms in which the weighing and other processes were carried out.
At present sulphur from M.C.P.Electronics, Middlesex, England is used. Judging from the blackening of the container from which this sulphur is evaporated the carbon content lies in between that of the normal and the purified Johnson-Matthey sulphur.

A silica container consisting of two ampoules connected by a tube (see fig.2.1) is used for the preparation of gallium sulphide. The container is made from Pursil 453 silica (Quartz and Silice, France).

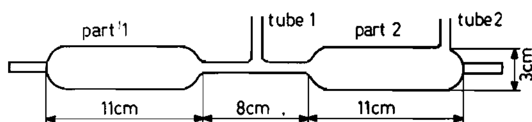


Fig.2.1 The silica container used for the preparation of gallium sulphide.

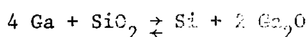
Prior to use the container (and other ampoules described later on) is degreased in chromic acid for at least 24 hours, rinsed with water and etched for 45 minutes in an etch consisting of one volume part HF (38 to 40% HF in water) and three volume parts HNO_3 (65% HNO_3 in water). Subsequently the ampoule is rinsed again with deionized water. Batches prepared in containers which had been cleaned in this way showed traces of calcium. However, calcium is no longer detectable when the containers are rinsed again with deionized water which has been recirculated through an ion exchanger and has a resistivity of approximately 22 Mohm cm.

The following procedure is used for filling the container. The gallium is put in part 1 of the container through tube 1. The container is then weighed on a balance with an accuracy of 0.1 mg. The amount of sulphur to be added is calculated using an atomic weight of 69.72 for gallium and 32.064 for sulphur; in the correction for the buoyancy in air, a density of 2.0 g/cm^3 for sulphur and 5.9 g/cm^3 for gallium is used. Weighing the sulphur is carried out with the container on the balance. Tube 2 is then sealed off and the container is evacuated (approximately 10^{-3} torr) through tube 1.

Approximately 40 grams of gallium and 20 grams of sulphur are used for each batch.

Two fifty centimeter long silica tubes are then welded to the ends of the container (see fig.2.1), which is thereafter situated in a furnace which provides a temperature gradient such that the gallium compartment is at a temperature of 960 to 980°C and the temperature at the sulphur side is less than 400°C.

Cochran and Foster [7] showed that gallium reacts with silica under the formation of gallium suboxide and silicon according to the following reaction



$$4\,Ga + SiO_2 \rightleftarrows Si + 2\,Ga_2O$$

and the silicon dissolves into the gallium. In gallium heated for 30 minutes at $1000^{o}C$ in a silica vessel Lieth et al [2] found $1.5.10^{4}$ ppm *) silicon. By rotating the container the reaction time could be considerably reduced; thus it was possible to obtain a complete reaction within 10 to 15 minutes.

Afterwards part 1 is sealed off from the rest of the container. In part 2 of the container dark rings are visible. If part 1 of the container remains connected to part 2 and part 2 is heated to a higher temperature (which occurs if the ampoule is shoved further into the oven) the black deposit disappears. It is assumed that the dark rings consist of a carbon deposit and that the disappearance is due to a chemical transport process in which sulphur is the carrier.

X-ray analysis shows that directly after the completion of the sulphur gallium reaction both gallium sulphide (GaS) and gallium sesquisulphide (Ga_2S_3) are present in part 1 of the container. To complete the reaction a procedure is followed in which the ampoule is kept for two hours at a temperature slightly above the melting point of gallium sulphide ($962^{o}C$) while being continuosly rotated.

Thereafter the ampoule is quickly cooled in deionized water.

This enhances the formation of small crystals which makes it possible to powder the batch afterwards. The ampoule is then put into the furnace again for another hour at $920^{o}C$. If this last step is not included , a green-gray layer is left on both the wall and the gallium sulphide. This layer is assumed to be a mixture of gallium and gallium sulphide (see reference [8]). The ampoule is cooled down slowly and opened.

Approximately 500 times less silicon is found in gallium sulphide prepared under such stringent conditions as compared to gallium sulphide prepared according to Lieth [8] .

2.3 The growth of doped gallium sulphide single crystals

As shown by Lieth [8] GaS single crystals can be grown by sublimation, iodine transport and from the melt. It takes 80 to 160 hours to prepare single crystals in these ways. Only in the melt growth technique, the Bridgman method, can the inclusion of foreign atoms be more or less forced. In growth from the vapour phase one can only hope that foreign atoms after being added to the bulk, will also sublimate or be transported to the lower temperature side. Even then quantitative control remains a problem.

Since the Bridgman method is a time consuming method and thus enhances the

*) Concentrations of impurities or dopes are given in gram atoms per Mole GaS in ppm.

possibility of contamination (with for example silicon) a zone melting [9] method was chosen.
The high resistivity, vapour pressure, and melting point of gallium sulphide (Lieth et al [10]) forced us to use a furnace and a resistance heater instead of an induction heater as in the case of germanium.
A Heraeus Rok 6.5/100 oven with an internal diameter of 6 cm and a length of 100 cm is used. The oven makes an angle of 2.5 degrees with the horizontal to compensate for density differences between fluid and solid GaS. One side of the oven is closed by means of a ceramic plate to prevent a chimney effect and to get a smaller temperature gradient. The oven temperature is regulated by means of a shielded chromel-alumel thermocouple which is connected to a West Gardian Q3X-PID controller. The temperature in the oven was found to remain constant (at the desired temperature of 910°C) within two degrees for six hours.

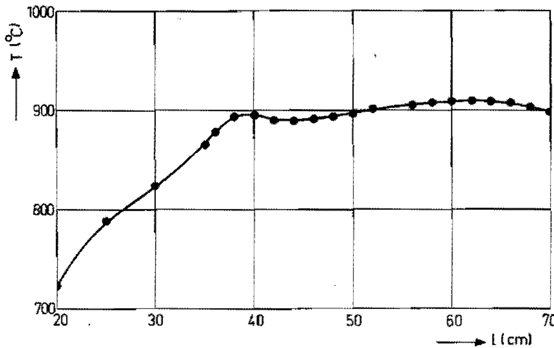


Fig. 2.2 The temperature measured along the oven axis.

In figure 2.2 the temperature is given measured along the oven axis. Measurements are made from the open side of the oven.

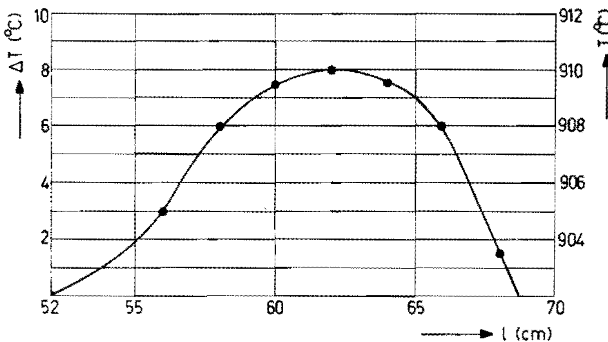


Fig. 2.3 The temperature in the maximum temperature region.

From figure 2.3 it can be seen that the temperature is constant within $5^{o}C$ over a 11 cm long region. The radial temperature gradient in this region is approximately $10^{o}C$ over 3 cm, measured from the oven axis to the oven wall.

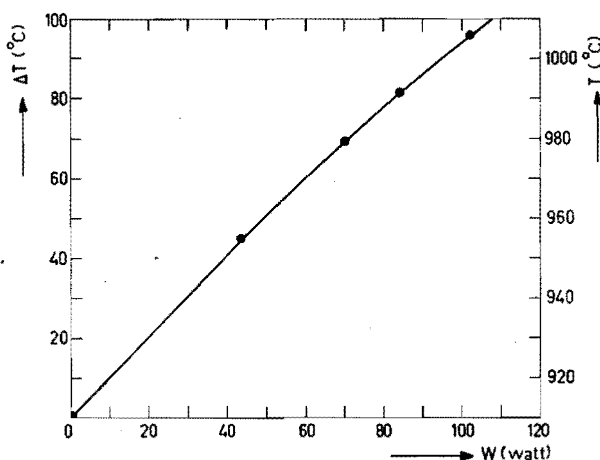


Fig. 2.4 Temperature rise in the center of the ringheater as a function of the dissipated power W in the ring.

Local heating is provided by a resistance heater consisting of a ring-shaped silica holder on which 45 cm of 0.6 mm thick Kanthal wire is wound (resistance 2.3 ohm). In figure 2.4 the temperature rise ΔT in the center of the ring as a function of the dissipated power W is given. It should be noted that the temperature is measured with a 2 mm thick thermocouple in the center of the ring.

A schematic drawing of the oven with ampoule, ring heater and moving mechanism is given in figure 2.5. The ampoule 1, consisting of a 10 cm long, 12 mm internal diameter silica tube is fastened to the silica support 2 and placed in the oven 3. The ring heater 4 can be moved along the ampoule by means of two silica tubes 5 and a support 6, this support can be moved by the motor-driven drum 7 which is connected with a thin metal ribbon 8 to the support 6.

The axis 9 along which support 6 moves is rotating, thus ensuring a low friction movement; it is driven by the motor 10.

The oven temperature is controlled with the thermocouple 11 as a sensing element and monitored by thermocouple 12. The thermocouple 11 is not influenced by the heat from the ring-heater since it is placed in a seperate ceramic tube close to the oven windings.

When the ring-heater is not activated thermocouple 11 indicates a 20°C higher temperature then thermocouple 12.

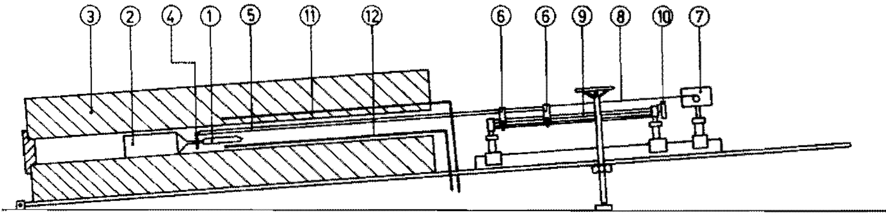


Fig. 2.5 Schematic drawing of the oven. For explanation of the numbers see the text.

Experiments with different velocities of the ring heater showed that with velocities higher then 6 cm/hour only very small crystals could be obtained. Velocities of 1 to 4 cm/hour resulted in crystals with large voids (up to 2 mm in diameter). However, these holes disappeared to a large extent when the ampoule was filled with nitrogen with a pressure of 40 cm Hg at room-temperature. In this way with velocities of 4 to 6 cm/hour usually 5 to 10 crystals were obtained with dimensions of approximately 3 x 3 x 0.2 mm^3. Since we did not need more or better crystals no experiments were carried out to enlarge either the single crystal yield or size.
Experiments of Prinsen [11] showed that crystal size and yield with a zone melting method using a vertical oven is approximately the same.
For growing doped single crystals the following procedure was used.
Metal impurities are added in the form of the metal sulphide to the GaS, iodine is incorporated by simply adding it as an element. The gallium sulphide thus obtained is used as starting material for single crystals with dopes of 100 ppm or higher. Lower concentrations could be obtained by diluting the starting material with undoped GaS.
For each run the silica ampoule is filled with approximately 10 grams of GaS, subsequently evacuated (approximately 10^{-3} torr) and filled with pure nitrogen at a room temperature pressure of 40 cm Hg. The ampoule is then placed into a furnace at a temperature of 980°C in which it is kept rotating about the oven axis, under an angle of 20 degrees with the axis for 30 minutes. Afterwards, the ampoule is halted in a horizontal position and cooled slowly. This gives the molten material a flat surface. Then ampoule 1 (see fig.2.5) is connected to the silica support 2 and placed into the oven 3.
The ring heater dissipation is 85 W, ensuring a maximum temperature rise of 80°C. Since the melting point of GaS is 962 ± 4°C [10] a molten zone is

created in the material in the ampoule. In each run the ring heater is drawn two or three times along the ampoule.
It should be noted that a lower oven temperature and a higher ring heater dissipation may result in a narrower molten zone but in that case sublimation from the molten zone to colder parts of the ampoule is considerable.

2.4 Spectrochemical analysis of gallium sulphide

Emission spectrography with a D.C.arc as excitation source was used for the analysis of the samples [13]. In table 2.1 the quantitative

Table 2.1 Quantitative detection limit for a number of elements in GaS in ppm

Element	Detection limit	Line (nm)
Zn	17	330.2
Cd	5	326.1
Ca	3	396.8
Cu	0.3	324.7
Mg	1	279.5
Na	3	588.9
Si	2	251.6

detection limits are given for a number of elements together with the wavelength of the line that was used, while in tables 2.2 and 2.3 the results of spectrochemical analysis of gallium sulphide are presented.

Table 2.2 The concentration in ppm of contaminating elements in bulk GaS

Batch Element	M37	M38	M43	M44	M48	M49	M50	M51	Alus*)
Ca	<3	<3	5-9	0-3	0-7	<3	5	n.d.	n.d.
Cu	0-5	3-5	2-3	2-4	.6-2.3	16-30	12	.6	.4-.6
Na	5-15	5-8	6-20	0-10	0-6	0-4	7-30	0-5	8-9
Si	4-9	4-13	14-60	6-12	7-10	0-16	12-22	4-6	18-30
Mg	1	1-4	1-2	1-5	7	7-19	7	1-2	n.d.

*) from Alusuisse

Table 2.3 The concentration of dopes and contaminating elements in zone melted GaS single crystal batches in ppm. Batch VE188 is grown by the Bridgman method (Lieth).

Batch	T10	T34	T35	T70	T69	T52	T50	T53	T49	T48	T51	T65	Ve 188
Dope added	Zn	Zn	Na	Na	J	Cu	-	Cd	Cd	Cd	Cd	Cd	-
Amount of dope (ppm)	100	100	100	100	1000	100	-	1	10	100	1000	100	-
Bulk batch	M18	M31	M34	M49	M49	M38	M37	M38	M37	M37	M37	M48	-
Element													
Ca	<3	<3	<3	<3	<3	<3	<3	<3	<3	0-5	<3	0-5	<3
Cu	0-.3	0-.4	0-.4	9-22	7-13	25-30	<.3	.8	0-.8	.4-.8	<.3	.4-1.5	.5-1.5
Na	n.a.	n.a.	20-90	9-110	n.a.	3-8	n.a.	0-13	n.a.	n.a.	4-6	7-18	0-11
Si	0-14	0-6	0-6	0-10	5-11	n.d.	0-6	0-8	0-6	0-40	n.d.	12-70	0-12
Mg	0-4	0-30	0-1.6	4-5	3-5	<1	0-18	1-1.2	0-30	0-2	<1	5-7	0-2
Zn	20-65	20-140	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7-18	60-100	7-80	n.d.

Table 2.2 gives the concentration of contaminating elements in a number of batches of bulk GaS together with an analysis of the GaS available from Alusuisse. Batches M37, M38 and M43 were prepared from normal Johnson Matthey sulphur, batches M44, M48, M49 and M50 were prepared from Johnson Matthey sulphur which had first been purified according to the Von Wartenberg-method. Batch M51 was prepared from M.C.P.Electronics sulphur (purity 5N5). Moreover, batch M51 was prepared in silica containers which had been cleaned with 22 Mohm cm water, while all preparations were carried out in a room where smoking was prohibited. The notation "n.d." in the tables means that the line in question could not be seen at all. The symbol "<" means that the line was still visible but no quantitative measurements were possible.

Table 2.2 shows the high magnesium content (6 ppm) in the batches prepared from purified Johnson Matthey sulphur (batch M48, M49 and M50). Magnesium, calcium and copper are not present in batch M51. The silicon content of this batch is about 10 times as low as that in the commercially available Alusuisse material.

Table 2.3 gives the concentration of dopes and contaminating elements in single crystals. Samples were taken from the middle part of the bulk material in an ampoule.

Sodium was not always analysed in the single crystal batches, since the analysis of sodium involved three separate exposures. This is noted by "n.a." in table 2.3.

It can be seen from table 2.3 that the dopant is incorporated into the single crystals, it is not very homogeneous. In the batches T48, T51 and T65 6 to 8% of the dope added is found in the single crystals. This is probably due to separation effects. In batches T50 and T49 a large amount of magnesium is found. This might have been caused by smoking.

In batch T49 and T52 a seperate analysis was carried out on GaS which had been in direct contact with the wall. The silicon content in these sample was found to be markedly higher: 25 and 600 ppm respectively.

2.5 Simple photoluminescence measurements

Batches doped with different elements did show some variation in luminescence if they were illuminated in liquid nitrogen by a blacklight i.e. by a high pressure mercury discharge lamp with a suitable filter to transmit only the 365 nm line. Since the differences in photoluminescence color of the single crystal batches were not large, the results are not given here. A marked difference in photoluminescence on the other hand was found between those bulk batches which had a green-gray substance on the surface of the GaS and the ampoule and those which did not. The green-gray layer,

assumed to consist of GaS and free gallium, did not show any luminescence while the bulk luminescence in this case was dark red. The batches which had been kept for one hour at 920°C showed a bright yellow orange luminescense while even green could be detected. Since the batches with the green-gray layer have too low a gallium content in their bulk, this might indicate that gallium vacancies give rise to a recombination center.
It should be mentioned that the Alusuisse material shows a red luminescense and thus might be gallium deficient.

2.6 TSC and TSL measurements on cadmium doped gallium sulphide

Thermally stimulated current (TSC) and thermally stimulated luminescense (TSL) measurements [14] can be applied as an analytical method to determine the amount of an impurity in a semiconductor if this impurity introduces a trapping level.
In fig.2.6 and 2.7 respectively, TSL and TSC curves measured on some of the

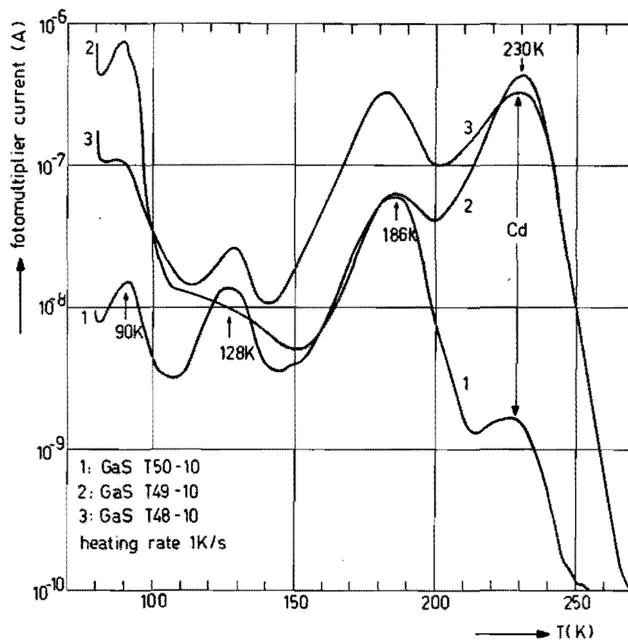


Fig.2.6 TSL measurements. Batch T50 is not doped, batch T49 is doped with 10 ppm cadmium, batch T48 is doped with 100 ppm cadmium.

GaS single crystals are given. The voltage over the evaporated gold contacts was 10 volt for the TSC measurements.

The TSL curves show four peaks, the TSC curves seven.
Apparently the peaks at 221 K in the TSC curves and at 230 K in the TSL curves are characteristic for cadmium. The absence of a difference in height between the 230 K TSL peaks in curve 2 and 3 (fig.2.6) is probably due to inhomogeneity of the cadmium. This is in accordance with the results of the analysis given in table 2.3, which show that a cadmium concentration overlap exists in some batches while the initial concentration calculated from the amount of dope added to the GaS differs by a factor 10. The 230 K peak from TSL curve 1 (fig.2.6) and the 221 K peak from crystal GaS-T69 are more than 100 times lower than the corresponding peaks in the cadmium doped samples. From this one can estimate that the cadmium concentration in batches which are not doped with cadmium is approximately 100 times lower than in those batches to which 10 or 100 ppm cadmium is added.

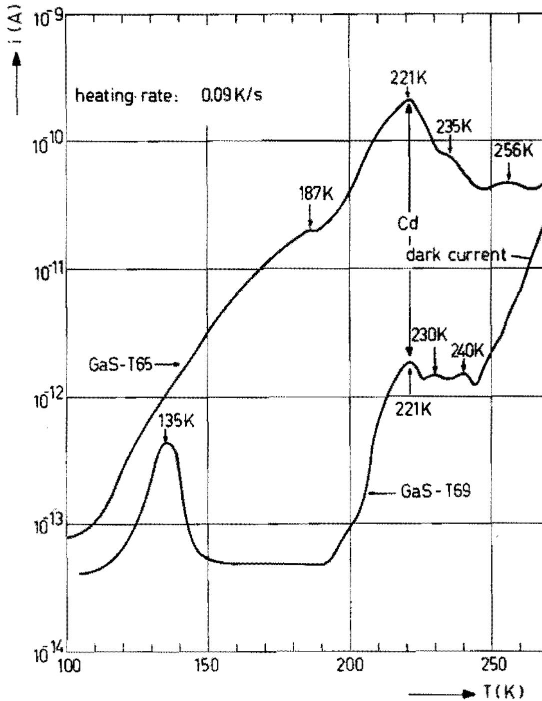


Fig.2.6 TSC measurements. Batch T65 is doped with 100 ppm cadmium, batch T69 with 100 ppm iodine.

From table 2.1 it can be seen that such a concentration, 0.1 to 1 ppm, is well below the spectrographical detection limit for cadmium.
The activation energy of the cadmium trap is found to be 0.43 ± 0.02 eV.
No research on the origin of the other peaks has yet been carried out.
However, it should be noted that the difference the heights of the 90 K

TSL-peaks is not caused by differences in concentration. The traps associated with these peaks are already emptying at the temperature at which the samples are irradiated (80 K).

2.7 Conclusion

It is shown that relatively pure GaS single crystals can be prepared by a zone melting technique. The crystal yield is not very high but it is possible that an improvement can be obtained by using considerably lower speeds of the molten zone and perhaps with a different atmosphere above the ingot. The purity which can be reached at present may be improved by better laboratory conditions. A more sensitive method of trace analysis will then be necessary.

The homogeneity of the dope in the single crystals is not very good. This is likely to be due to separation effects at the molten zone boundary. A careful study is necessary e.g., of separation effects, for improvements in this direction.

Cadmium is shown to cause a trapping level at 0.43 ± 0.02 eV which may provide an analytic tool for quantitative analysis of this material. A systematic study may show other impurities to give rise to trapping levels.

LITERATURE

[1] Alusuisse, Swiss Aluminium LTD, Buckerhauserstrasse 11, Zurich (Switzerland).

[2] Lieth, R.M.A.; Heijden, C.W.M. van der; Kessel, J.W.M. van, J.Crystal. Growth 5 (1969), 251.

[3] Klemm, W and Vogel, H.U. von, Z.Anorg.Allgem.Chemie 219 (1934), 45.

[4] Johnson, Matthey and Co. Ltd, 73 Hatton Garden, London (England).

[5] Koningsberger, D.C., Thesis, T.H. Eindhoven (1971).

[6] Wartenberg, H. von, Z.Anorg.Allgem.Chem., 286 (1956), 224.

[7] Cochran, C.N. and Foster, L.M., J.Electrochem.Soc. 109, (1962) 149.

[8] Lieth, R.M.A., Thesis, T.H. Eindhoven (1969).

[9] Pfann, W.G. Zone melting, Wiley, New York (1958).

[10] Lieth, R.M.A., Heijligers H.J.M. and Heijden C.W.M. van der, J.Electrochem.Soc.113 (1966) 798.

[11] Prinsen, L.M.L., Internal Report T.H.Eindhoven (1972) (in Dutch).

[12] Lieth, R.M.A., Heijligers H.J.M. and Heijden C.W.M. van der, Mater.Sci.Eng., 2 (1967), 193.

[13] to be published.

[14] Nicholas, K.H. and Woods J., Brit.J.Appl.Phys.15, (1964) 783.

CHAPTER 3

QUANTITATIVE SPECTROCHEMICAL ANALYSIS OF GALLIUM SULPHIDE AND GALLIUM SELENIDE

3.1. Introduction

When a research program on the photoconductive, photoluminescent,and electrical transport properties of gallium sulphide and gallium selenide was started, it soon became necessary to determine the presence and quantity of trace impurities in these materials. Emission spectrography was chosen since this method allows the detection of trace impurities in quantities between approximately one and one thousand ppm. Furthermore this way of analysis requires only small amounts (5 mg) of material.
A short introduction to emission spectrography is given together with a description of the apparatus, the preparation of standard samples and the establishment of working curves prepared by means of these standard samples. Detection limits resulting from these working curves are also given.

3.2 A short introduction to emission spectrography

Emission spectrography is based on the principle that excited atoms and ions emit light of well known discrete wavelengths. In order to analyse a solid spectrochemically the solid first has to be atomized. This can be done by evaporating it at high temperatures. At sufficiently high temperatures the atoms are excited or even ionized.
In the method described here a direct current arc between graphite electrodes is used as the excitation source. The lower electrode is loaded with a small amount (5 mg) of the substance to be analysed. When the arc is ignited this substance starts to evaporate and a hot plasma containing excited atoms and ions is formed between the electrodes. The plasma can reach temperatures of 5000 to 8000 K. The intensity of the spectral lines emitted from this plasma is dependent on the concentration of the atoms in the arc which in turn depends on the concentration of these atoms in the substance on the electrode. This intensity can be measured by using a spectrometer with photographic recording.
The blackening of the photographic plate after developing is a measure for the intensity to which the plate has been exposed. A graphic representation of the relationship between the relative intensity and the photographic response is called a calibration curve. A number of different representations of such a curve can be given two of which will be described.
A characteristic curve is obtained if the optical density D of the developed photographic plate is plotted as a function of the logarithm of

the light intensity I to which the undeveloped plate was exposed. If the relative transmission T of the partly blackened plate is defined as the ratio of the light intensity transmitted through the blackened part to the light intensity transmitted through a clear part of the plate, then D can be defined as

$$D = - {}^{10}\log T.$$

The relation between D and log I is linear over a small intensity range. The contrast of a photographic emulsion is given by γ

$$\gamma = \frac{dD}{d \log I} .$$

In another representation of a calibration curve the Seidel function S is used, defined by

$$S = \log(\frac{1}{T} - 1).$$

The relation between S and log I is linear over a larger intensity range than the relation between D and log I. For that reason it is easier to work with γ_s, given by

$$\gamma_s = \frac{dS}{d \log I} .$$

The relation between the concentration C of a certain element in the sample and the emitted light intensity can often be given by

$$C = K.I^n .$$

Both K and n are independent of the concentration, n has a value $\leqslant 1$.
A plot of the photographic response as a function of the concentration is called a working curve. If the Seidel function is plotted as a function of log C the working curve will be a straight line.
An extensive treatment of this method is given by Ahrens and Taylor [1] and Boumans [2] .

3.3. Apparatus

3.3.1. Excitation source

The excitation source is a continuous direct current arc, fed from a three phase, double sided rectifier. The primary voltage is 120 V, the operating current is 10 A.

3.3.2. Electrode assembly

The upper electrode is a 3.05 diameter flat top, graphite rod. The lower electrode, the anode, is a 4.6 mm outer diameter graphite rod with a 3.9 mm internal diameter, 3.2 mm deep crater. Both electrodes are obtained from

Le Carbon Lorraine, preform numbers 9110 and 9145, material grade 208.
The electrode gap is 4 mm.
The lower electrode holder is a Boumans' double-flow device [3] which is used for the suppression of CN-bands and to provide at the same time a stable burning arc. A schematic drawing of the device is given in figure 3.1.

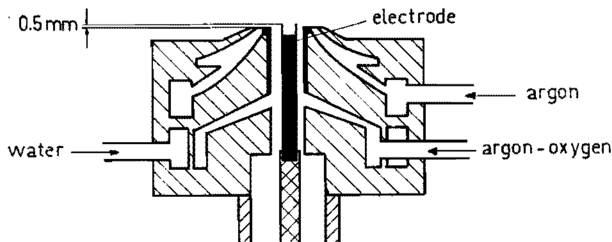


Fig. 3.1. Schematic drawing of the Boumans' double flow device. The device is machined from brass.

The principle of this device is that an inert gas, argon, flows along the lower electrode thus shielding the arc from the surrounding air; since the CN-bands are caused by the reaction of carbon from the electrodes with nitrogen from the air, the CN bands are suppressed by this shielding argon flow. However, the arc temperature which should be high to enhance emission from excited atoms is now lowered because part of the power dissipated in the arc arises from the reaction of carbon with oxygen from the surrounding air. Therefore an inner gasflow has to be provided containing oxygen. We used a 9:1 argon-oxygen mixture.
The gasflow rates for optimum operation of the device were determined by Boumans. Since in the experiments described here a different type and amount of material was used a separate determination of the gasflow rates was needed. It was found that the suppression of the CN-bands also depended strongly on the distance x from the top of the lower electrode to the top of the electrode holder. This fact was not mentioned by Boumans. The best operating conditions were found to exist for x = 0.5 mm and gasflow rates of 3.0 l/min for the argon flow and 8.0 l/min for the argon-oxygen mixture.

3.3.3. Spectrograph

A 2-meter PGS2 Aus Jena spectrograph is used. Two gratings with 651 rulings/mm provide a reciprocal linear dispersion of .72 nm/mm. One grating with a 275 nm blaze wavelength is used for the ultraviolet region (245-415 nm) in which all elements in which we were interested have at least one sensitive line, with the exception of sodium. The second grating, blazed for 590 nm, is used for the

analysis of sodium which has its most sensitive line at 589.592 nm. The slit-width is 9 μm for the ultraviolet region and 15 μm for the analysis of sodium. A six step neutral density filter, incorporated in the slit assembly, is used to extend the usable intensity range. The six filter steps which will be denoted by A, B, C, D, E and F, transmit 100% (filter step A) to approximately 5%(filter step F) of the incident light intensity.

3.3.4. Photographic processing

For the recording of spectral lines in the UV-range Agfa-Gevaert *34B50* plates are used, the sodium 589.592 nm line is recorded on Agfa IP 15 film. The *34B50* plates are developed in Agfa Metinol-U (6 minutes), the film is developed in Agfa Rodinal (1 + 25). Both plate and film are fixed in Agfa Acidofix. A solution consisting of 64 ml acetic acid (28%) and 45 gram desiccated sodium sulfate and an amount of water to make one liter is used as a stopbath. All processing is carried out at 20.0°C.

3.3.5. Densitometer

The density measurements are carried out with an Aus Jena G II densitometer in which the internal galvanometer is replaced by a Fluke A 88 galvanometer amplifier. This makes it possible to record the lines on a Philips PM 9100 flat bed recorder.

3.4. Preparation of standards

For calibration purposes standards are necessary. These standards were prepared by adding metal sulphides to pure gallium sulphide to obtain dope concentrations of 100, 300 and 1000 ppm *); diluting these standards with the purest available GaS provided standard with concentrations of 30, 10 and 3 ppm.
The standards were homogeneized by keeping them for 30 minutes at 980°C in an evacuated silica ampoule. For some concentrations duplicate standards were prepared to check on systematic errors.
The choice of the elements (metals) to be incorporated in the standards was based on two criteria:

- the presence of the metal as an impurity element in gallium sulphide had been proved previously [4] ;
- the metal was expected to be an interesting potential dope.

According to these criteria the following elements were investigated: aluminium, cadmium, calcium, copper, germanium, iron, lead, magnesium, manganese,

*) Concentrations are given in gramatoms per Mole.

silicon , sodium, tin and zinc in gallium sulphide and copper, indium, silver, tin and zinc in gallium selenide.
It should be noted that elements such as the halogens, oxygen, nitrogen etc. do not have atom lines of sufficiently low energy (< 6 eV) and thus can not be detected spectrochemically.

3.5. Plate calibration

The *34B50* plates are calibrated by measuring the S values of the weakest available gallium line at 262.4 nm. The intensity of this line is such that if the six step filter is used (see section 3.3.3) the blackening of the plate can be measured for two of the steps. The values of S for the two filters will be denoted by S_E and S_F respectively. The values of S_E and $S_E - S_F$ measured for 90 different exposures are given in fig.3.2. The spread in the measured values of $S_E - S_F$ is much less than the spread in the measured values of S_E

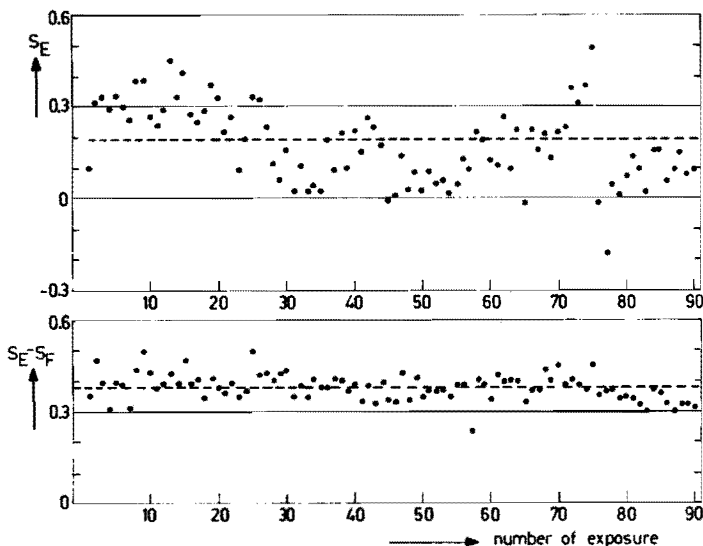


Fig.3.2. The values of S_E and S_E-S_F measured on the gallium 262.4 nm line for 90 different exposures. The mean value is denoted by a broken line.

because $S_E - S_F$ depends only on the properties of the photographic plate while S_E is also dependent on the arc conditions.
Those exposures showing values of S_E outside the range given by $0 < S_E < 0.4$ are not used for quantitative analysis. From figure 3.3 which gives the value

of S_E measured for different amounts of GaS in the lower electrode it can be estimated that in this way a relative error of less than about 40% is made.

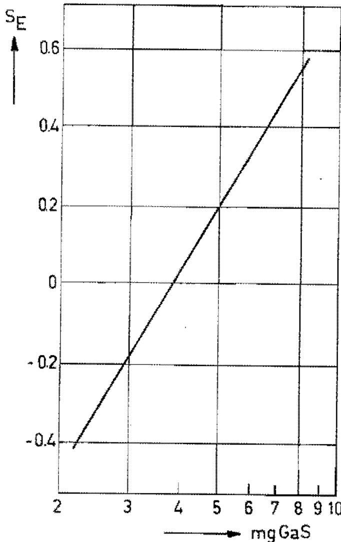


Fig. 3.3. The value of S_E measured for different amounts of gallium sulphide in the lower electrode.

3.6 Racking plate spectra

Racking plate spectra were taken to analyse the selective volatilisation of the different elements.
The following procedure is used. The slit height is adjusted to 0.9 mm.
At t = 0 the arc is ignited. After two seconds the shutter is opened and the plate is exposed during five seconds. The shutter is closed and in the next second the plate is moved up one mm. The shutter is opened again during five seconds, after which the plate is moved up one mm; this is repeated until the sample has completely disappeared from the electrode. The results are given in fig.3.4 and 3.5. From these figures it can be seen that the dope elements can evaporate before, simultaneously with and even after the gallium.
To understand the phenomena a description of the arcing is necessary. After approximately 35 to 40 seconds the crater wall of the lower electrode breaks down causing an effective increase in the electrode gap which takes a few seconds to correct. Then the intensity becomes markedly higher. At $t \approx 73$ seconds part of the residue on the electrode forms a globule which volatilizes in 5 to 7 seconds. Most of the iron, silicon, calcium, magnesium and aluminium evaporates at this time. After approximately 95 seconds no more evaporation takes place.

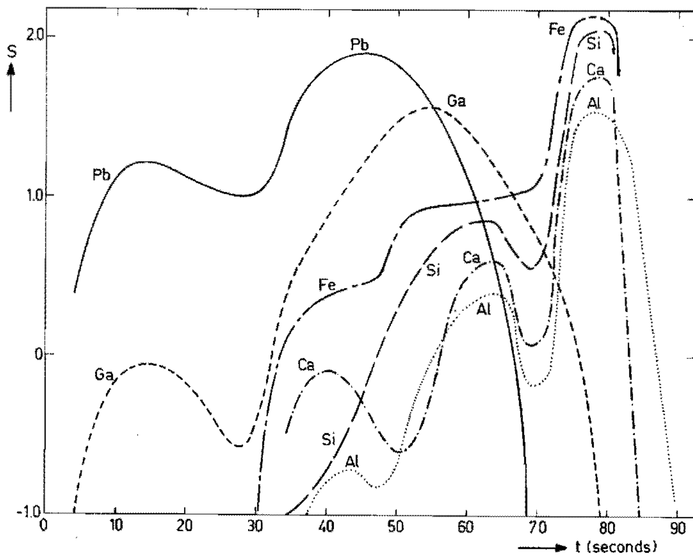


Fig. 3.4. Racking plate spectra for GaS with 1000 ppm silicon, iron, lead, aluminium, calcium and sodium.

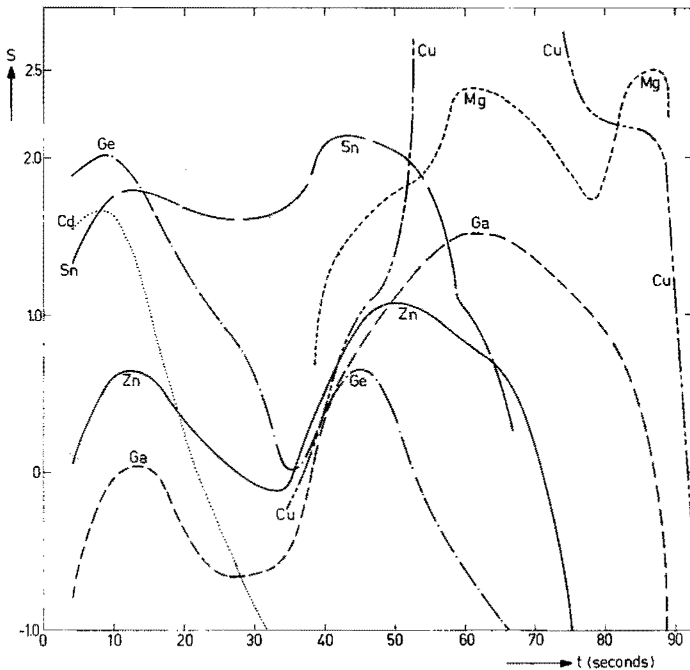


Fig. 3.5. Racking plate spectra for GaS with 1000 ppm magnesium, germanium, zinc, tin and copper.

It should be possible to lower some of the detection limits by exposing the plate only during the time at which the element under consideration volatilizes.

3.7 Results

The results of the trace impurity analysis are given in table 3.1 for gallium sulphide and in table 3.2 for gallium selenide. For most elements two lines were used as a check on systematic errors and to extend the concen-

Table 3.1. The detection limit and the value of n for some elements in gallium sulphide.

ELEMENT	LINE, nm	n	DETECTION LIMIT, ppm
Al	308.216	.9	16
Al	309.271	.9	9
Ca	317.933	1.0	9
Ca	396.847	1.0	3
Cd	326.106	1.0	5
Cd	346.620	1.0	25
Cu	327.396	.8	.6
Cu	324.754	.8	.3
Fe	259.837	1.0	5
Fe	259.940	1.0	1.5
Ge	265.118	1.0	2.5
Ge	303.906	1.0	4
Mg	279.553	.6	1
Mg	285.213	.6	2.5
Mn	279.482	.9	1
Mn	280.106	.9	2.5
Na	588.995	1.0	3
Na	589.592	1.0	6
Pb	280.199	1.0	3
Pb	283.306	1.0	2
Si	251.611	1.0	2
Si	252.851	1.0	6
Sn	283.999	.9	3.5
Sn	317.502	.9	3
Zn	334.502	1.0	17

Table 3.2. The detection limit and the value of n for some elements in gallium selenide.

ELEMENT	LINE, nm	n	DETECTION LIMIT, ppm
Ag	328.068	.9	.3
Ag	338.289	.9	.6
Cu	327.396	.8	.9
Cu	324.754	.8	.5
In	325.609	1.0	2
Sn	283.999	.9	8
Sn	317.502	.9	7
Zn	334.502	1.0	28

tration range; in fig.3.6 an example is given of two working curves as obtained for iron.

The value of n from the relation between the concentration C and intensity I

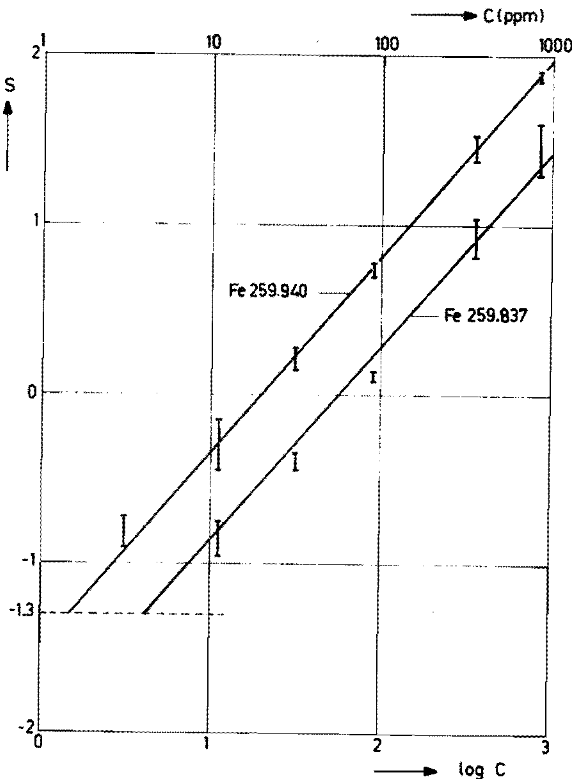


Fig. 3.6. Two working curves for iron.

(see section 3.2) is 1.0 for most elements. Lower values may be caused by self absorption.

The detection limit, found by extrapolation of the relation between S and C to a value of S = − 1.3, is lower than 10 ppm for all elements with the exception of zinc. It may be possible to reach a lower detection limit for zinc by using the Zn 213.856 line. In that case the use of a different type of plate is necessary since the Agfa Gevaert *34B50* plate is not sensitive at wavelengths below 220 nm.
For iron (see fig.3.6) one line with one filter can be used for the concentration range from 1.4 to 1000 ppm. If n is smaller than 1 and the wavelength is higher than 340 nm two lines or the use of more filter steps are necessary to cover this concentration range.

3.8 Conclusion

With the method described here a number of trace impurities in gallium sulphide and gallium selenide can be detected quantitatively with a detection limit which is lower than 10 ppm for most elements under consideration. The relative error in the impurity concentrations is less than 40%.

LITERATURE

[1] Ahrens, L.H. and Taylor, S.R., Spectrochemical Analysis, Addison Wesley publishing company, London (1961).

[2] Boumans, P.W.J.M., Theory of Spectrochemical Excitation, Hilger and Watts LTD, London (1966).

[3] Boumans, P.W.J.M., Spectrochimica Acta, 24B, 585 (1969).

[4] Lieth, R.M.A., Thesis, Eindhoven (1969).

CHAPTER 4 x)

A metal cryostat and sample holder for photo Hall-effect studies on high-ohmic crystals in the 10—300 K temperature range

G. A. van der Leeden and M. P. A. Queens

A number of cryostats for the temperature-range between 10 and 300 K have been reported in the literature.[1–4]

The cryostat described here was developed for measurements [5,6] of the photo Hall-effect and the light intensity dependance of the photo-conductivity on crystals with a high dark resistance. The cryostat and sample holder together have the following advantages:

temperatures between 10 and 100 K can be reached and kept constant to within a few millidegrees for a period of up to several hours;

four wires with a high resistance and a low capacitance to earth can be attached to the easily interchangeable sample;

due to the use of a sample holder filled with helium gas the temperature of the crystal changes less than 1 K (at 20 K) when the light intensity is changed from 0 to 10 W m^{-2} at the crystal site;

the sample holder can be detached from the cryostat and opened without loosening any of the soldered joints.

The authors are with the Physics Department, Low Temperatures Group, University of Technology, Insulindelaan 2, Eindhoven, The Netherlands. Received 29 June 1971.

Description of the cooling system and sample holder

The basic cryostat and the cooling system. The basic cryostat is a design of Severijns [7] (see Fig.1). It consists of a liquid helium reservoir, 8, surrounded by a gold-plated copper radiation shield, 7, which is attached to the copper bottom, 6, of the liquid nitrogen reservoir, 3, by means of six screws.

The helium and nitrogen reservoir are suspended from three tubes (5, 27) which are attached to the top flange, 1, with nuts, 28. Due to the special construction 29, of the suspension the rubber O-ring vacuum seals, 30, do not

x) This chapter was published as a " Technical and Research note " in Cryogenics, 12, 51 (1972).

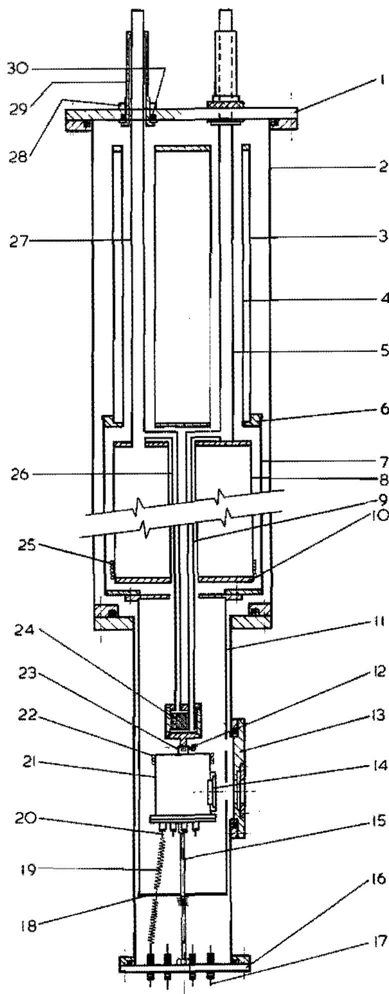


Fig.1 Schematic drawing of the cryostat

become cold. The suspension tubes of the helium reservoir pass through tubes, 4, soldered in the nitrogen reservoir. The cryostat can be completely dismounted without loosening any of the soldered or welded joints.

The cooling system is a modification of the one described by Brebner and Mooser.[3] The evaporating helium can be led either through the tubes, 26, 9, 5, or through the evaporation tube, 27; both sets of tubes can be closed outside the cryostat. In the first case the cold vapour passes through the copper heat exchanger, 24, to which the sample holder, 21, can be attached. The heat exchanger consists of a 20 mm long copper block in which approximately twenty holes of diameter 1 mm have been drilled. Lowering the temperature is accomplished by increasing the evaporation rate with the heater, 25. A higher temperature can be reached by using the heating coil, 22, on the sample holder. When the external valve in evaporation tube, 5, is closed, the sample holder is thermally isolated from the helium reservoir.

The sample holder. The sample holder (see Fig.1 and the upper part of Fig.2) consists of a base plate, 36, and a cylindrical copper box. They can be sealed with an indium O-ring. A removable quartz window 14 (diameter 25 mm, thickness 2 mm), also sealed with an indium O-ring, is mounted on the box. The heater, 22, is glued to the box with GE 7031 varnish.

A hollow cylinder, 23, (4 x 10 mm) is soldered on the top flange of the box. The lower part of heat exchanger, 24, consists of a 4 mm copper rod which fits hollow cylinder 23. After fitting the rod into the cylinder, the assembly can be thermally connected with the screw, 12.

The light used for the measurements passes through the quartz window, 14, and is then reflected onto the crystal by mirror 35.

Mounting the crystal

A crystal is mounted in the following way.

The crystal, 31, is pressed on the teflon crystal holder, 32, by four contact springs, 34. After crystal holder, 32, has been mounted on base plate, 36, the upper part of the sample holder (the cylindrical copper box) is sealed to the base plate. The sample holder is then filled with helium gas (1 cm Hg at room temperature) through a 3 mm copper tube (not shown), and mounted loosely on supporting tube, 15.

The assembly consisting of the sample holder, 21, supporting tube, 15, radiation shield base plate, 18, and

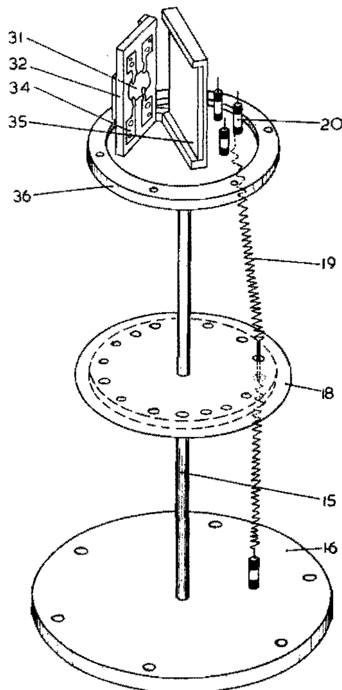


Fig.2 Schematic drawing of the (open) sample holder on the cryostat base plate

cryostat base plate, 16, can then be shoved into the cryostat tailpiece. The radiation shield base plate, 18, is pressed against the rest of the shield with a spring, after which the sample holder is fastened to the heat exchanger, 24, with the screw, 12. Mounting the flanges, 13 and 16, completes the operation.

Dimensions and materials

In Table 1 the dimensions of various cryostat parts have been given.

Table 1. Diameter *d*, height *h*, and wall thickness *w* of various cryostat parts

Part	*d*, mm	*h*, mm	*w*, mm
He, N_2 reservoir	100	230	0.5
Tubes 5 and 27	11.2	–	0.3
Tubes 4	25.4	–	0.5
Tubes 9 and 26	4.8	–	0.3
Radiation shield 8	115	300	1.0
Tailpiece radiation shield 11	60	220	1.0
Vacuum jacket 2	128	600	1.5
Tailpiece vacuum jacket	75	280	1.0

The cryostat is made mainly from stainless steel. The bottom flanges, 6 and 10, of the reservoirs, the radiation shields, 7 and 11, and the heat exchanger, 24, have been machined from copper. The sample holder is constructed from copper and brass. Joints have been either hard soldered or argon arc-welded.

Performance

After pouring liquid nitrogen into the nitrogen reservoir it takes approximately one hour before a stationary evaporation of 0.16 litres LN_2 per hour is reached. Precooling the sample holder is accomplished by pouring liquid nitrogen into the heat exchanger through tube, 5; after 40 minutes the temperature has dropped to 80 K.

The evaporating helium vapour, which passed through the heat exchanger while the cryostat is being filled, brings the temperature (which is measured with a calibrated germanium thermometer) down to approximately 10 K. Cooling down and filling the two litre helium reservoir requires about 2.5 litres liquid helium. After the transfer has stopped an equilibrium temperature of 20 K is reached in half an hour. The steady state boil-off is 0.13 litres LHe per hour. Thus the cryostat can hold helium for about 15 hours. In Fig.3 the temperature of the crystal holder as a function of the evaporation rate is given. Although temperatures below 11 K can be reached, the helium consumption becomes relatively high in this case. In Fig.4 the extra cooling power as a function of the evaporation rate is given. The extra cooling power is defined as the power dissipated on the sample holder by using the heating coil, 22.

Once cold, a new temperature setting between 10 and 80 K is accomplished within 10 minutes. The temperature is kept constant within a few millidegrees without any difficulty. The temperature gradient over the sample holder was not measured accurately. A temperature difference of one degree over the sample holder is not unlikely. In a typical experiment a temperature change of approximately 0.9 K was measured when the germanium thermometer was mounted in place of the crystal and the light source was switched off.

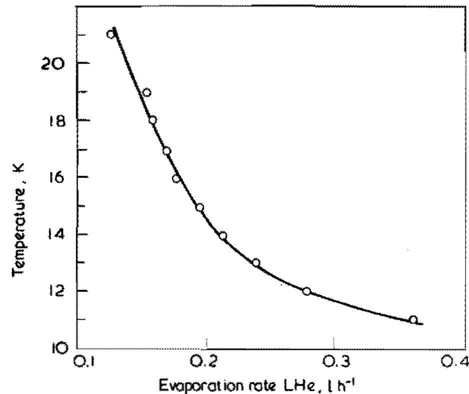


Fig.3 Temperature as a function of helium evaporation rate

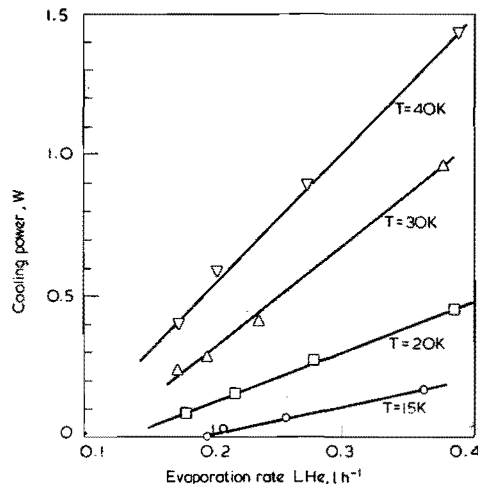


Fig.4 Extra cooling power versus helium evaporation rate for different temperatures

REFERENCES

1. SWENSON, C. A., and STAHL, R. H. *Rev Sci Instrum* 25, 608 (1954).
2. DANIL'CHENKO, V. E., KURTENOK, L. F., LUBYANOV, L. P., and STOLYAROV, V. M. *Cryogenics* 8, 51 (1968).
3. BREBNER, J. L., and MOOSER, E. *J Sci Instrum* 39, 69 (1962).
4. WHITE, G. K. Experimental Techniques in Low Temperature Physics, Ch 8 (Oxford University Press, 1968).
5. FISCHER, G., GREIG, D., and MOOSER, E. *Rev Sci Instrum* 32, 842 (1961).
6. KIPPERMAN, A. H. M., and VAN DER LEEDEN, G. A. *Sol St Comm* 6, 657 (1968).
7. SEVERIJNS, A. P. Philips Nat Lab Technical Note, No 144/67 (Internal Report Philips Research Laboratories, Eindhoven).

CHAPTER 5.

PHOTOLUMINESCENCE MEASUREMENTS ON GALLIUM SULPHIDE.

Photoluminescence spectra measured on not intentionally doped gallium sulphide single crystals and on crystals doped with copper, sodium and cadmium, are presented. Copper is shown to give rise to a broad luminescence band with a maximum at 2.00 eV and is probably also associated with a structured band at 2.4 eV. No specific band has been found for cadmium. In some crystals a structured peak at 2.58 eV, which may be caused by free exciton luminescence combined with phonon emission, is found.

5.1 Introduction.

Photoluminescence measurements on gallium sulphide single crystals have been reported by Springford [1], Akhundov et al [2], Karaman and Mushinskii [3] and Cingolani et al [4].
Springford published some measurements on a single crystal in the temperature range from 65 to 133 K. He found bands with maxima at 650 nm (1.92 eV), 750 nm (1.67 eV) and 870 nm (1.44 eV).
Akhundov et al [2] and Karaman and Mushinskii [3] measured the photoluminescence spectra of GaS_xSe_{1-x} crystals with $0 \leqslant x \leqslant 1$ at 77 K.
Akhundov et al reported in gallium sulphide a band starting at 450 nm (2.76 eV) and extending to 680 nm (1.82 eV), with peaks lying at 4.95 nm (2.50 eV) and 535 nm (2.32 eV). They assume that these bands are caused by transitions from the conduction band to an acceptor level.
For gallium sulphide Karaman and Mushinskii found luminescence bands at 2.55 eV, 2.17 eV and 1.62 eV which they ascribed to excitons, gallium vacancies and so called sulphur impurities respectively. These sulphur impurities are probably contaminations of the sulphur they used for the preparation of their gallium sulphide.
Cingolani et al [4] have found at 77 K a band at 2.15 eV which they assume to be caused by iodine. They furthermore report "edge emission" at 2.59 eV although their figures show that this emission band is centered at approximately 2.65 eV. It should be noted that, according to Aulich et al [5] the indirect band gap energy E_i is 2.591 $\pm$ 0.002 eV at 77 K; they found this value by combining steps which they measured in the absorption spectra with Raman band energies reported by Wright and Mooradian [6] and infrared absorption data reported by Kuroda et al [7]. This value indicates that the band found by Cingolani et al is associated with a direct band gap process. The direct band gap in gallium sulphide is 3.05 eV [8].
No work seems to have been done on intentionally doped gallium sulphide single crystals.

The purpose of the photoluminescence measurements described in this chapter is to identify recombination centers and to find support for models which can be deduced from the temperature- and intensity dependence of photoconductivity measurements on gallium sulphide.
A description is given of the experimental arrangements. The dependence of the photoluminescence intensity on photon energy and temperature are presented for crystals either doped or not intentionally doped.

5.2. *Experimental arrangements.*

The crystals are mounted in a metal cryostat of the type described in chapter 4. A different sample holder and cryostat tail piece are used (see figure 5.1). The sample holder 1 consists of a cylindrical copper block in which a hole is drilled with a diameter of 10 mm. The crystal 3 is mounted on a hollow cylinder 2 which fits the sample holder.

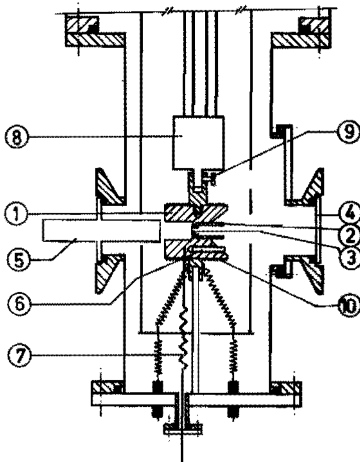


Fig.5.1. The cryostat tail piece and sample holder used for the photoluminescence measurements.

The excitation light reaches the crystal through the quartz window 4 and the hollow cylinder 2. On the opposite side of the cryostat tail piece a combined perspex window and light conductor 5 conducts the photoluminescence light. The perspex used for this purpose absorbs light with wavelengths below 375 nm, transmits light with wavelengths between 390 and 900 nm and does not show any luminescence in this wavelength region. The temperature is measured either with the germanium thermometer 6 or the thermocouple 7. The sampleholder is connected to the heat exchanger 8 with the screw 9. The temperature can be regulated with the heater coil 10.

The crystals are excited with light from a 150 W high pressure mercury discharge lamp. The 365 nm line is separated from the lamp spectrum with an UV interference filter combined with a 3 mm thick BG12 filter, a 2 mm thick UG2 filter and a KG3 infrared absorption filter. The UG2 filter is necessary to absorb a weak 600 nm luminescence band from the interference filter, while the BG12 filter is used to suppress the light transmitted by the interference filter at 730 nm. The maximum light intensity is 35 W/m^2 which corresponds to 6.10^{19} $photons/m^2$ s. The measurements of the luminescence light intensity as a function of the photon energy are carried out with an "Aus Jena" SPM2 monochromator equiped with a glass prism. A slitwidth of 0.5 mm is

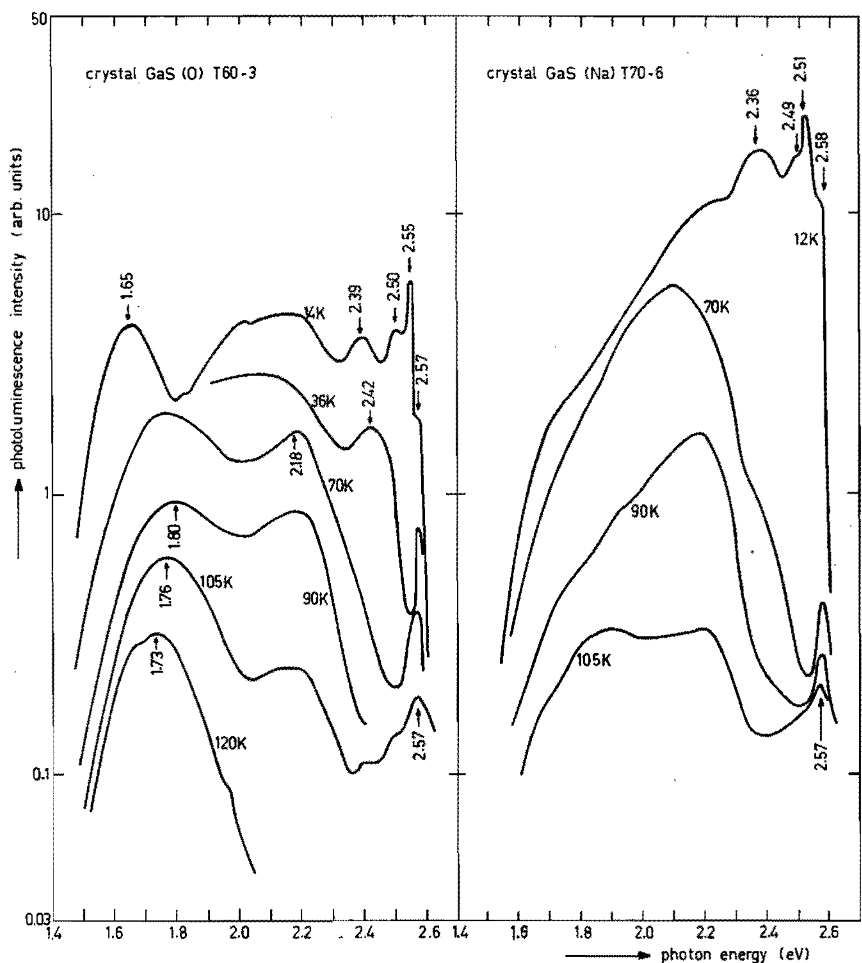


Fig.5.2. The photoluminescence spectra for crystals GaS(O) T60-3 and GaS(Na) T70-6.

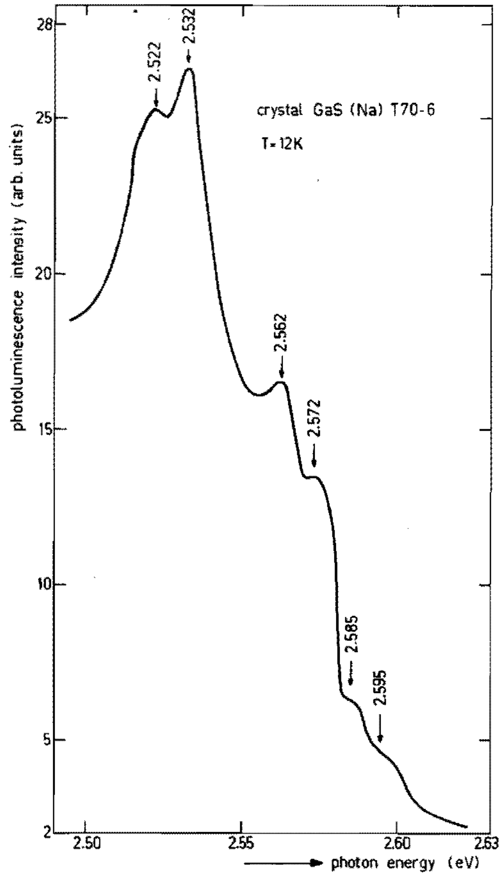


Fig. 5.3. The photoluminescence spectrum of the fine structure in crystal GaS(Na) T70-6. The measurements were carried out with a spectral resolution of 3 meV.

normally used resulting in a spectral resolution of 13 meV at 2.5 eV and 23 meV at 1.4 eV.
A cooled EMI 9558B photomultiplier is used as a detector. The photomultiplier is cooled with dry ice to -68°C in a Products for Research T-200 photomultiplier housing. The dark current of the photomultiplier of 4nA at roomtemperature is reduced to approximately 60 pA at -68°C.
The photomultiplier current is measured with a Keithley 602 electrometer and recorded on a Kipp BD 8 flat bed recorder. The photomultiplier noise is suppressed by connecting a capacitor parallel to the electrometer input resistance. This results in time constants of 1 to 12 seconds.Photoluminescence intensities are calculated by correcting the

photomultiplier current for the photomultiplier spectral response and the monochromator transmission and dispersion. The arbitrary units used here are proportional to the number of photons emitted per m^2, per second and per unit of photon energy. Intensities from different crystals can be compared to each other since the excitation energy and the irradiated crystal area were the same for all crystals.

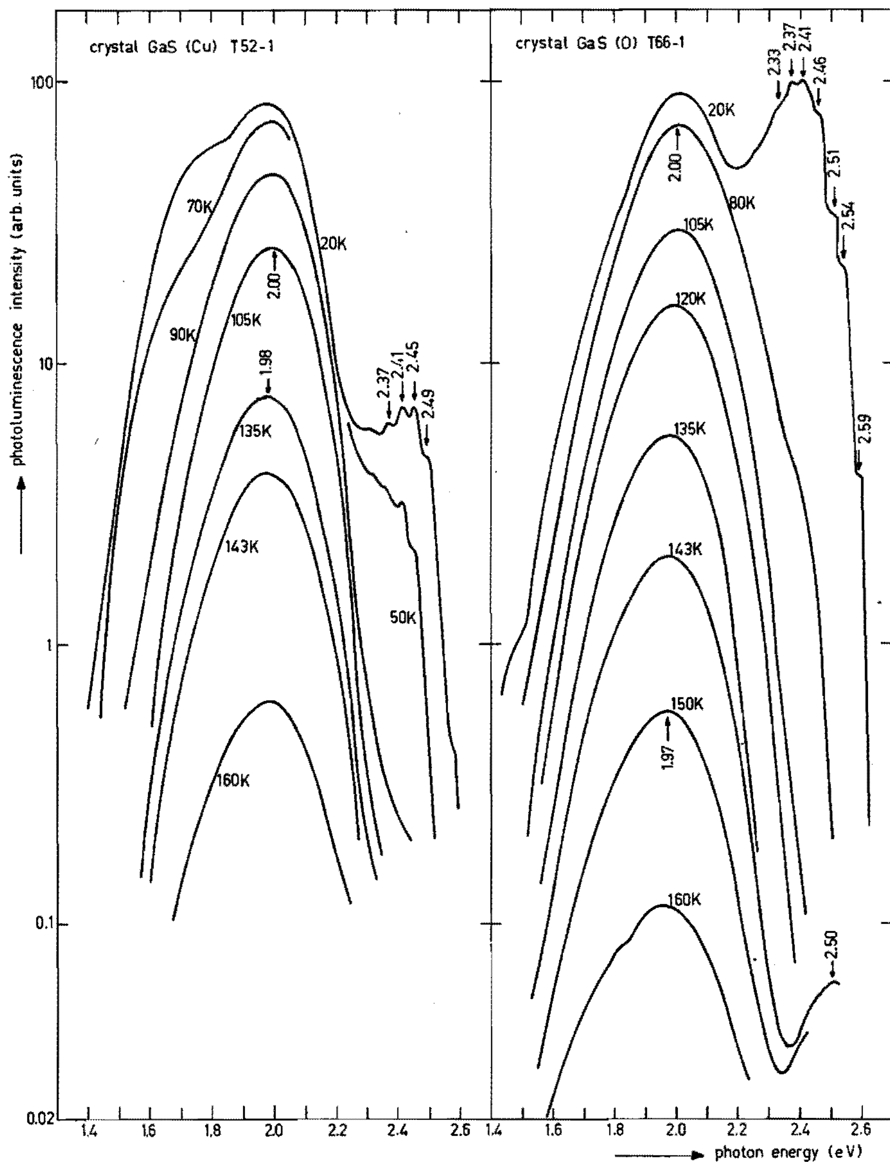


Fig. 5.4. The photoluminescence spectra for crystals GaS(Cu) T52-1 and GaS (O) T66-1.

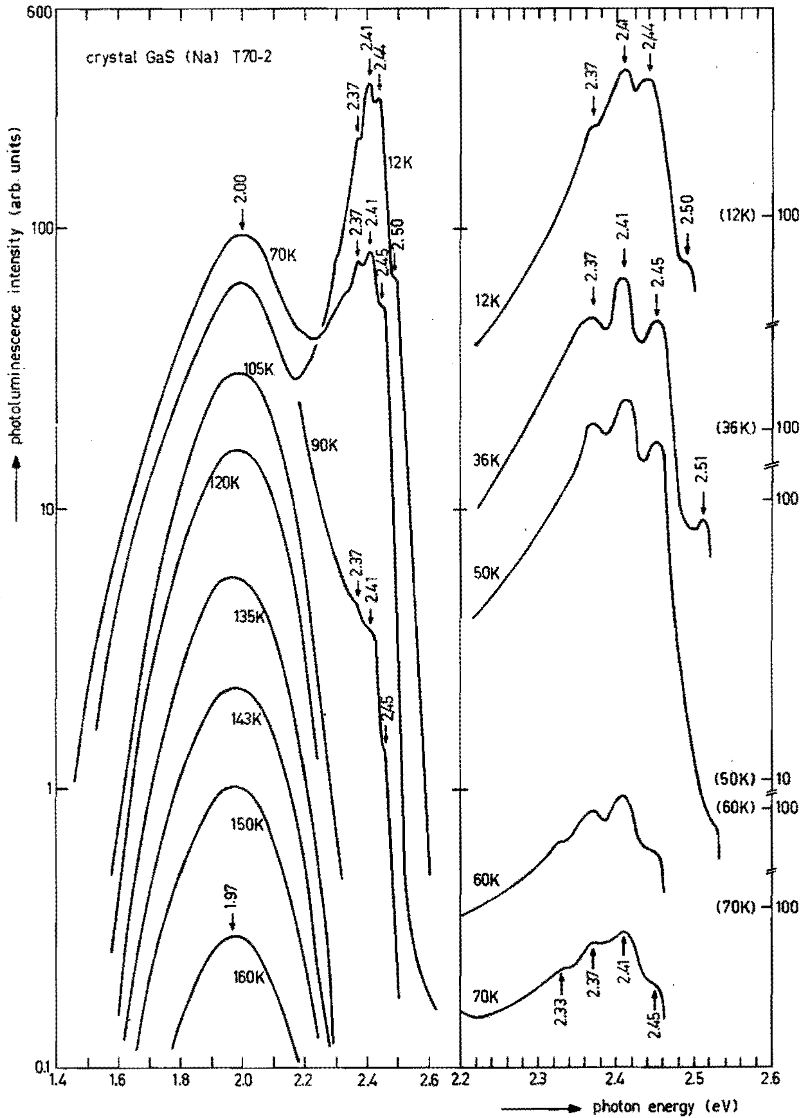


Fig. 5.5. The photoluminescence spectra for crystal GaS(Na) T70-2. The fine structure at 2.4 eV is given with an extended photon energy scale, the luminescence intensity scale is not the same for different temperatures.

5.3. Results

Measurements were carried out on not intentionally doped crystals and on crystals doped with copper, sodium and cadmium.

In figure 5.2. the photoluminescence spectra are given of crystal GaS(O) T60-3[x)], which is not intentionally doped, and of crystal GaS (Na) T70-6, which has been kept in an evacuated silica ampoule for 40 hours at 840°C.
The fine structure in crystal GaS (Na) T70-6, measured with a spectral resolution of 3 meV,is given in figure 5.3.
In figures 5.4 and 5.5 the photoluminescence spectra of three single crystals containing approximately 20 ppm copper are presented. Crystal GaS (Cu) T52-1 is intentionally doped with copper while the crystals GaS (O) T66-1 and GaS (Na) T70-2 originate from single crystal batches prepared from starting material which contained approximately 10-20 ppm copper.
In figure 5.6 the fine structure in crystal GaS (Na) T70-2 measured with a spectral resolution of 3 meV is given.
The photoluminescence spectrum of crystal GaS (Cd) T53-1 is given in figure 5.7; batch T53 from which this crystal originates is prepared

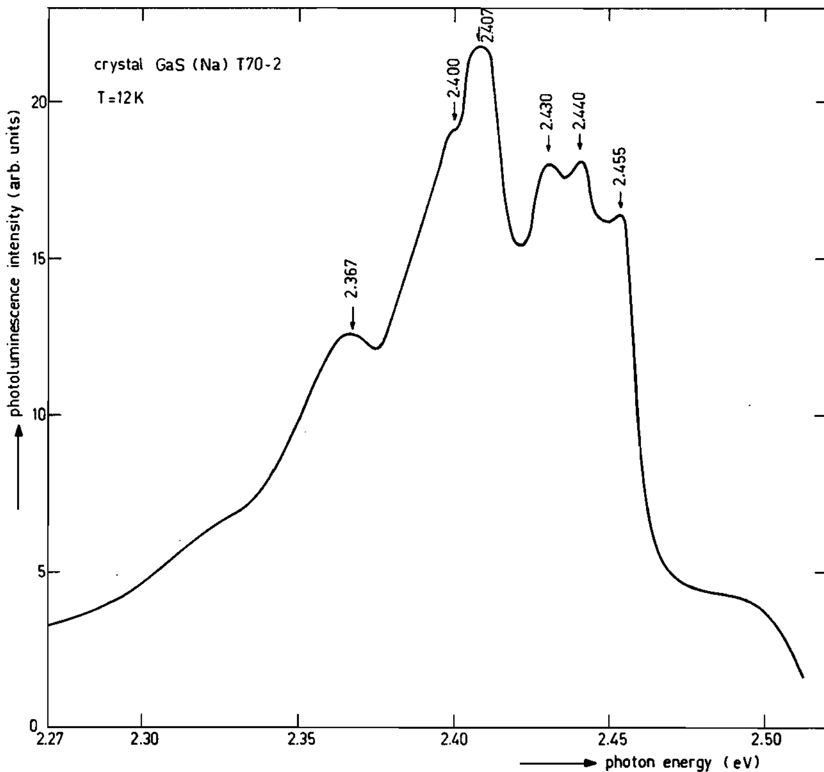


Fig.5.6. The photoluminescence spectrum of the fine structure in crystal GaS(Na) T70-2. The measurements were carried out with a spectral resolution of 3 meV.

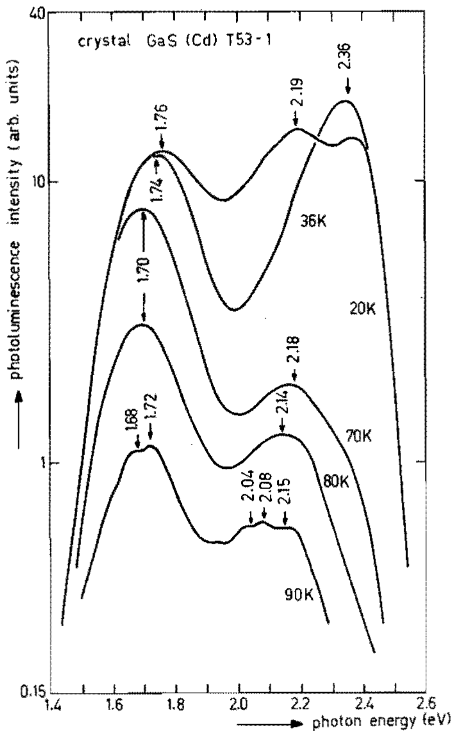


Fig.5.7. The photoluminescence spectra of crystal GaS(Cd) T53-1.

from the same starting material as batch T52. The influence of a copper dope can thus be seen by comparing the spectra from the crystals GaS (Cu) T52-1 and GaS (Cd) T53-1.

The photoluminescence spectra of the cadmium doped crystals GaS (Cd) T68-1 and GaS (Cd) T51-1 are presented in figure 5.8.

Figure 5.9 gives the photoluminescence light intensity of the 2.00 eV band in crystal GaS (Cu) T52-1 as a function of the excitation light intensity at various temperatures.

In table 5.1 the results of spectrochemical analysis are presented. From this table it can be seen that all single crystal batches prepared from starting material batch M49 contain 10 to 20 ppm copper which is due to the fact that this batch, M49, was contaminated with 16-30 ppm copper

x) The (0) sign indicates that a crystal is not intentionally doped.

as is indicated in table 2.2. Unfortunately the heat treated crystals from batch T70 were not etched before the analysis. The results of the analysis for this batch may therefore be due to surface contaminations.

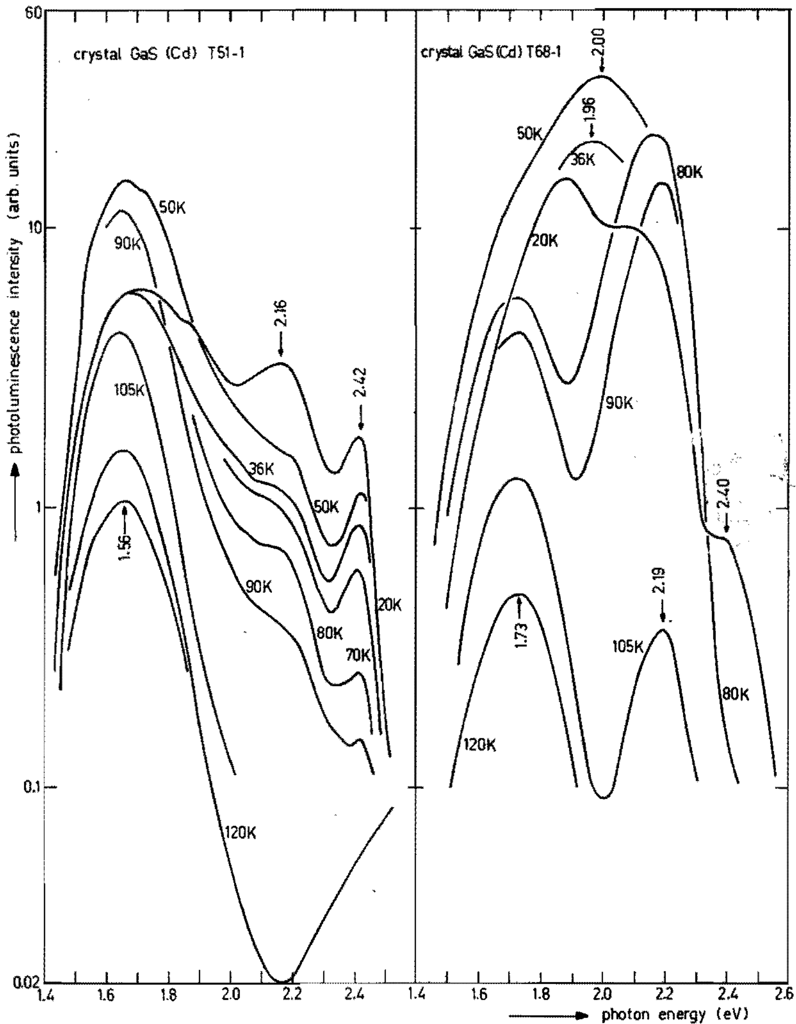


Fig. 5. 8. The photoluminescence spectra for the crystals GaS(Cd) T51-1 and GaS(Cd) T68-1.

Table 5.1. The concentration of dopes and contaminating elements in seven gallium sulphide single crystal batches.

Batch	T51	T52	T53	T60	T66	T68	T70	T70*)
Dope added	Cd	Cu	Cd	–	–	Cd	Na	Na
Amounts of dope (ppm)	100	100	1	–	–	114	100	100
Bulk batch	M37	M38	M38	M47	M49	M49	M49	M49
Element								
Cu	<0.3	24-32	0.8	1.3-2.5	15-22	4-14	9-22	34-50
Na	4-6	3-8	0-13	11	0-12	0-30	9-110	n.a.
Cd	60-100	n.d.	n.d.	n.d.	n.d.	10-24	n.d.	n.d.
Si	n.d.	n.d.	<2	15-90	0-12	0-20	0-10	45-60
Ca	<3	<3	<3	<3	<3	0-20	<3	0-5
Mg	<1	<1	1.2	5-6	2-2.4	1-6	4-5	3-11

*) After a heat treatment; traces of iron, lead, silver and indium were also found.

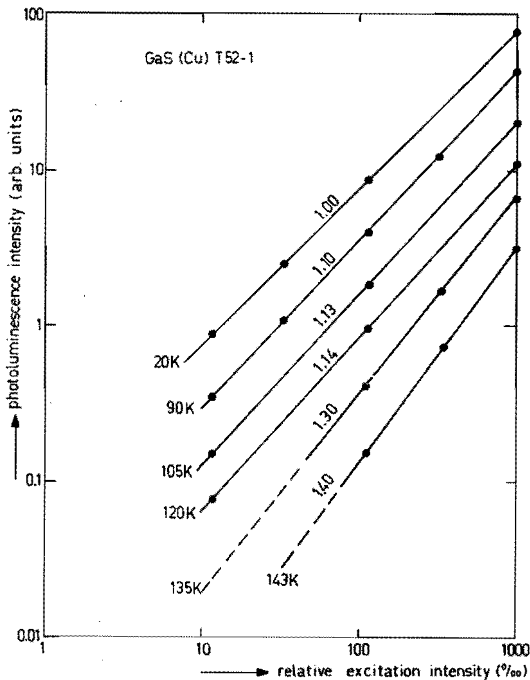


Fig.5.9. The photoluminescence intensity of the 2.00 eV peak in crystal GaS(Cu) T52-1 as a function of the excitation intensity at different temperatures. The slope is given for each curve.

5.4. *Discussion*

5.4.1. *Crystals GaS(O) T60-3 and GaS(Na) T70-6.*

Figure 5.2. shows that the luminescence spectrum for the crystals GaS(O) T60-3 and GaS(Na) T70-6 is rather complicated : at nearly every temperature new peaks appear while others disappear. The reason that the two crystal spectra are shown together is that they have one common feature : in both crystals a peak lying at approximately 2.58 eV is present. For crystal GaS(Na) T70-6 this "peak" was measured with a resolution of 3 meV (figure 5.3). The fine structure found here suggests a phonon process.

At 4.2K phonon energies of A_1 = 12 $\pm$ 2 meV, A_2 = 20 $\pm$ 2 meV, A_3 = 38 $\pm$ 2 meV and A_4 = 46 $\pm$ 2 meV are reported by Aulich et al [5] . Their values are found from absorption data and are in reasonable agreement with those from infrared absorption and Raman emission spectra [6,7] . The process with which the phonon emission is associated has an energy of 2.598 $\pm$ 0.003 eV. Let us assume that this process is either band-band or free exciton absorption.

The following tentative explanation can be given of the photoluminescence spectrum presented in fig.5.3. The step in the emission spectrum lying at approximately 2.595 eV is assumed to be free exciton or band-band emission x).The other steps and peaks in the spectrum could then be caused by phonon absorption. Table 5.2 gives a survey of the peaks and the associated phonon absorption.

5.4.2. *Crystals GaS(Cu) T52-1, GaS(O) T66-1, GaS(Na) T70-2 and GaS(Cd) T53-1.*

The crystals GaS(Cu) T52-1, GaS(O) T66-1 and GaS(Na) T70-2 all contain approximately 20 ppm copper (see table 5.1). The luminescence spectra of these crystals (see fig.5.4 and 5.5) show one broad luminescence band centered at 2.00 eV and one band at approximately 2.4 eV.

x) It should be noted that both processes are only possible if a phonon is emitted or absorbed at the same time, since the transition is indirect; in a crystal in which stresses are present it is possible that the zero-phonon processes are found.

Table 5.2. Luminescence peaks in crystal GaS(Na) T70-6 and the associated phonon(s).

Luminescence peak	Phonon(s) absorbed
2.595 eV	-
2.585 eV	$A_1 = 12$ meV
2.572 eV	$A_2 = 20$ meV
2.562 eV	$A_3 = 38$ meV
2.532 eV	$A_2 + A_3 = 58$ meV
2.522 eV	$A_2 + A_4 = 66$ meV

The 2.00 eV band is clearly caused by copper. Comparison of the spectra from crystal GaS(Cu) T52-1 and GaS(Cd) T53-1 shows that the 2.00 eV band is not found in the second crystal although both crystals have been prepared from the same starting material; the cadmium dope in crystal GaS(Cd) T53-1 is only 1 ppm.

The band at 2.4 eV is also present in the crystals containing copper, it is strongest in crystal GaS(Na) T70-2 which contains a relatively high sodium concentration. This may indicate that this band is caused by sodium or, since it is only found in crystals which contain copper, by a combination of copper and sodium. The fact that in crystal GaS(Cd) T53-1, which contains the same amount of sodium as crystal GaS(Cu) T52-1 but only a small amount of copper, the 2.4 eV band has not been found strongly indicates that this band is associated in some way with copper.

The fine structure in the 2.4 eV band is nearly the same for the three crystals; they show peaks at 2.33 eV, 2.37 eV, 2.41 eV, 2.45 eV and 2.49 eV. The fine structure in crystal GaS(Na) T70-2 measured at 12 K with a higher resolution of 3 meV is given in figure 5.6. From this figure it can be seen that actually more peaks are present. This spectrum seems to indicate a process with a relatively small half width, such as bound-exciton or donor-acceptor pair luminescence [9] combined with the emission of phonons. Free exciton luminescence is not possible since in other crystals (see section 5.4.1) emissions at higher phonon energies have been found. In the case of donor-acceptor pair luminescence the high energy shoulder at approximately 2.49 eV (see fig.5.6) would be pair emission in which the sharp lines are lost due to the low resolution of the spectrometer. If this is the case the "shoulder" should shift if

the excitation intensities are lowered. At 3% of the maximum excitation intensity no such effect could be detected within the experimental accuracy which means that the shift, if present, is less than approximately 6 meV. This does not exclude this type of emission.

5.4.3. Crystals GaS(Cd) T51-1 and GaS(Cd) T68-1.

The crystals GaS(Cd) T51-1 and GaS(Cd) T68-1 both contain cadmium while the latter crystal also contains copper since it has been prepared from starting material batch M49 (see table 5.1). The simultaneous incorporation of copper and cadmium in a gallium sulphide crystal appears to quench the 2.00 eV and the 2.4 eV band found in crystals containing copper (see section 5.4.2.).

The incorporation of cadmium does not seem to give rise to a specific luminescence band. A number of bands are present but they are different for the two crystals. Thus no conclusions can be drawn about the role of cadmium as a recombination center.

5.4.4. The dependence of the luminescence intensity on the excitation light intensity.

In fig.6.8 the luminescence intensity of the 2.00 eV band in crystal GaS(Cu) T52-1 is given as a function of the excitation intensity. From this figure it can be seen that at temperatures above 90 K the relation between photoluminescence- and excitation light intensity becomes gradually superlinear. Measurements should be carried out over a considerably larger intensity range to make an explanation in terms of for example the Klasens-Duboc model [10] possible.

For other crystals only a linear relation between photoluminescence- and excitation light intensity has been found.

5.5. Conclusions

A structured emission band found in the photoluminescence spectra of some gallium sulphide crystals is probably due to band-band or free exciton emission combined with phonon emission.

In gallium sulphide crystals doped with copper two photoluminescence bands have been found. One band, centered at 2.00 eV, is certainly caused by copper. The other band, lying at 2.4 eV, may be caused by either copper or by copper and sodium; to determine this photoluminescence measurements on crystals doped with different amounts of copper and sodium are necessary. The nature of this band, which shows a structured emission, can not be determined on basis of the present experimental evidence. A better resolution of the spectra is necessary to clarify the nature of this emission, while time resolved spectra and decay measurements will also provide useful information. Experiments at higher light intensities, e.g. with an argon laser, may also prove useful, but in that case a different type of cryostat is necessary since the cryostat used for the present investigation is not suitable for high excitation densities: the temperature of the crystal will become too high.

Photoluminescence measurements on cadmium doped gallium sulphide single crystals did not provide evidence that cadmium can act as a recombination center.

LITERATURE

[1] Springford, M., Proc. Phys. Soc., 82, 1020 (1963).

[2] Akhundov, G.A., Gasumov, G.M. and Ismailov, F.I., Opt. Spektrosk., 26, 642 (1969).

[3] Karaman, M.I. and Mushinskii, V.P., Sov. Phys. Semiconductors, 4 464,(1970).

[4] Cingolani, A., Minafra, A., Tantalo, P. and Paorici, C., Phys. Stat. Sol., A4, K 83 (1971).

[5] Aulich, E., Brebner, J.L. and Mooser, E.,Phys. Stat. Sol., 31, 129 (1969).

[6] Wright, G.B. and Mooradian, A., Bull. Amer. Phys. Soc. (II), 11, 812 (1969).

[7] Kuroda, N., Nishina, Y. and Fukuroi, T., J. Phys. Soc., Japan,24, 214 (1968).

[8] Brebner, J.L., J. Phys. Chem. Solids,25, 1127 (1964).

[9] See for example Pankove, J.I., Optical Processes in semiconductors, Prentice-Hall (1971).

[10] Klasens, H.A., J. Phys. Chem. Solids, 7, 175 (1958).

CHAPTER 6

PHOTOCONDUCTIVITY AND PHOTO HALL-EFFECT MEASUREMENTS.

Photoconductivity measurements have been made on three gallium sulphide single crystals as a function of light intensity and temperature. The results are explained in terms of the Klasens-Duboc model. At temperatures between 100 and 300 K a hole trap lying approximately 0.23 eV above the valence band is responsible for the temperature dependence of the photoconductivity which is p-type. At low temperatures this trap is filled and the conductivity becomes n-type.

6.1 Introduction

The behaviour of the photoconductivity as a function of light intensity and temperature depends in a semiconductor mainly on the recombination- and trapping mechanisms of electrons and holes. Thus it should be possible to study the behaviour of a dope which is a potential recombination or trapping center by incorporating it in the semiconductor and measuring the photoconductivity. By comparing results obtained from photoconductivity measurements with those obtained from thermally stimulated current-(TSC), thermally stimulated luminescence-(TSL) and photoluminescence measurements, recombination and trapping parameters may be established. This approach has been tried for gallium sulphide. Although a trapping center (cadmium, see chapter 2) and a recombination center (copper, see chapter 5) have been identified their influence on the photoconductivity could not be studied since the photoconductivity was mainly determined by other centers which could not be identified.
For three crystals measurements of the photoconductivity and photo Hall-effect as a function of temperature and intensity are presented. An explanation of some of the results in terms of the Klasens-Duboc [1,2] model is given.
A description of the experimental arrangements is included in this chapter.

6.2 Experimental arrangements

Both photoconductivity and photo Hall-mobility are measured according to the Van der Pauw-method [3]. This method is particularly suited to the flat thin samples of gallium sulphide that can easily be obtained by cleaving GaS, which has a layer structure [4].
Furthermore, by applying this method, only four contacts are needed as compared to at least five with other methods. In our case each contact consisted of two circular gold layers with a diameter of 0.5 mm at the

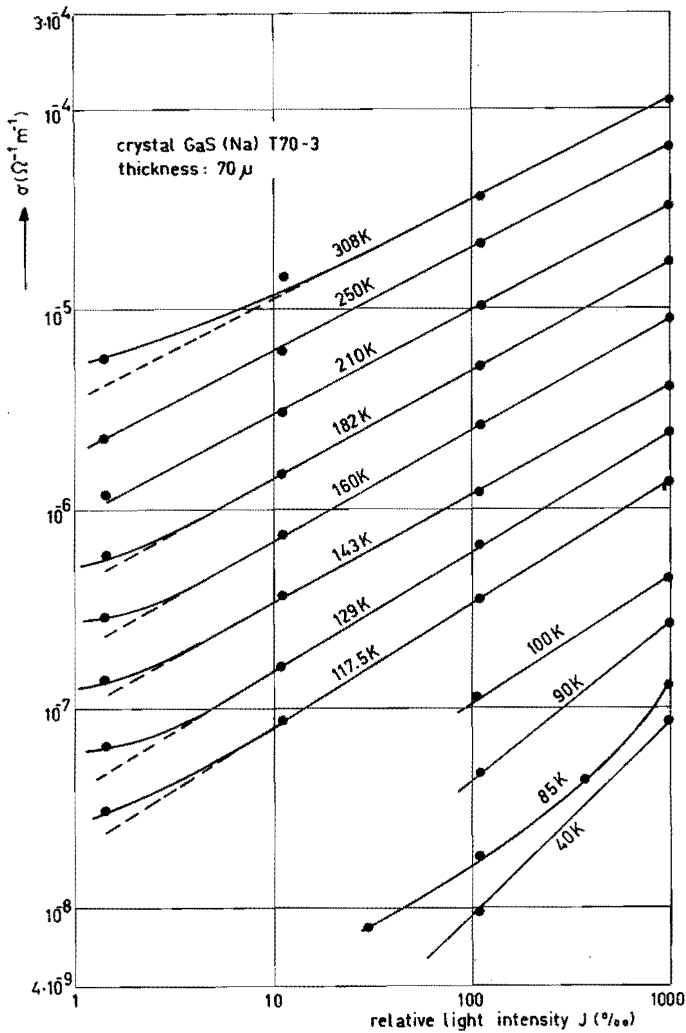


Fig. 6.1. The conductivity σ vs the relative light intensity J with the temperature as parameter for crystal GaS (Na) T70-3.

edge of the crystal and on opposite sides. Crystal dimensions varied from 3 x 3 to 5 x 5 mm^2, while the thickness of the crystals varied from 10 to 80 micron. The crystals are mounted in the cryostat described in chapter 4. The teflon sample holder with pressure contacts has been changed into a rectangular piece of silica on which four gold strips have been evaporated. To one end of these strips copper wires were soldered while to the other end the crystal contacts are fastened with a fluid indium-mercury mixture.

The same mixture is also used to connect the gold contacts on opposite sides of the crystal.
The measuring circuit for the conductivity and photo Hall-mobility measurements is essentially the same as the one described by Kipperman and Van der Leeden [5].

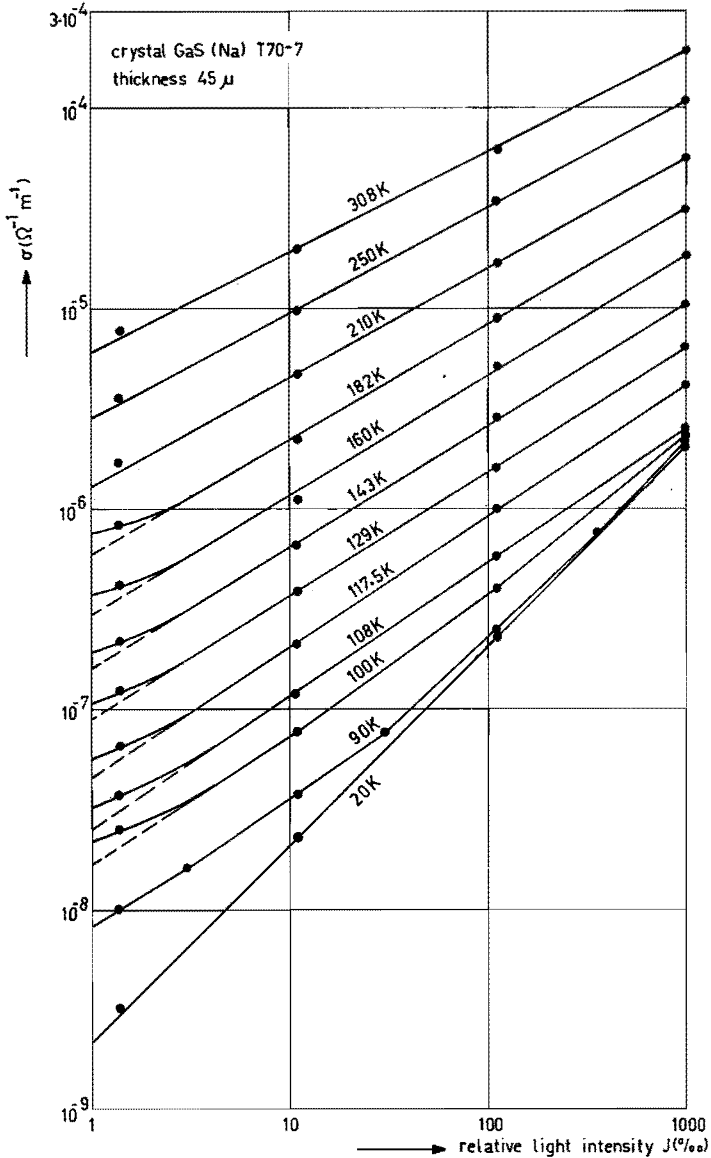


Fig. 6.2. The conductivity σ vs the relative light intensity J with the temperature as parameter for crystal GaS(Na) T70-7.

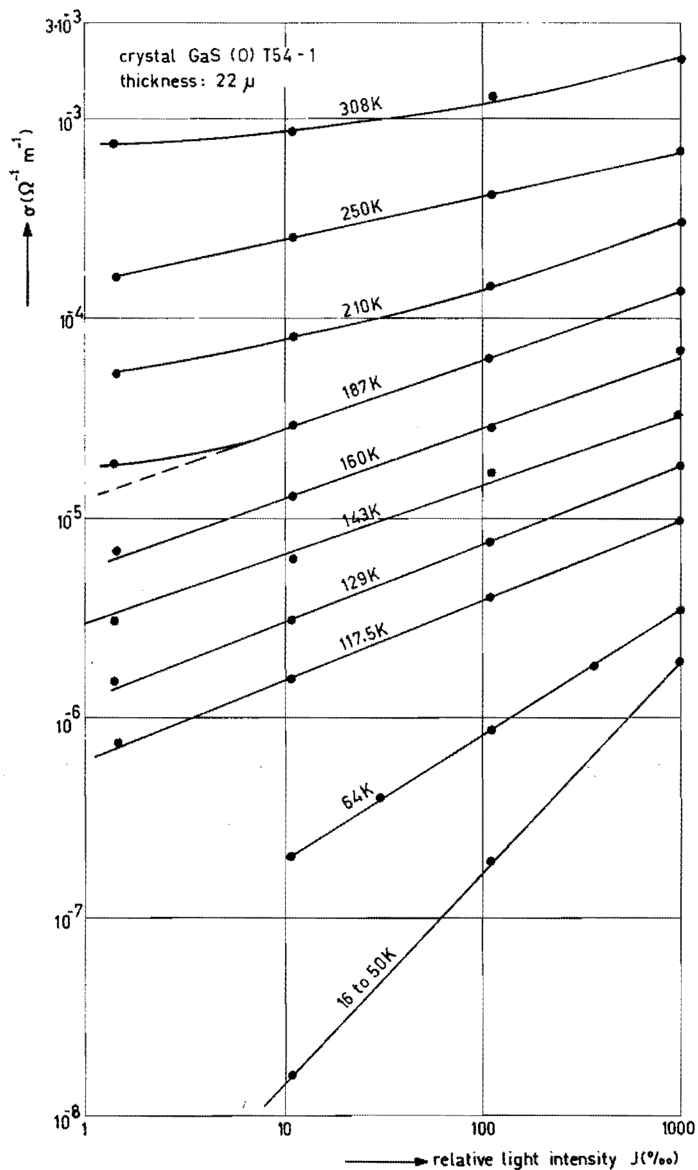


Fig. 6.3. The conductivity σ vs the relative light intensity J with the temperature as parameter for crystal GaS(o) T54-1.

A combination of a 150 W quartz halogen lamp, a Schott KG1 heat absorbing filter, a Balzers DT blue broad band metal interference filter and a set of Balzers neutral density filters are used as a light source with variable

intensity. The maximum light intensity on the place of the crystal is determined separately with a CdS light dependent resistor which has been calibrated against a Kipp CA1 thermopile. The maximum light intensity is 16 W/m^2, at a wavelength of 450 nm. This corresponds to approximately $3.5 \cdot 10^{19}$ $photons/m^2s$.
A Newport type E magnet is used for the photo Hall-effect measurements; this magnet gives a magnetic induction of 1 T with a current of 22 A.

6.3 Results

In this section the results are presented of measurements on three gallium sulphide single crystals.
Crystal GaS(0) T54-1 is a not intentionally doped crystal*, the crystals GaS(Na) T70-3 and GaS(Na) T70-7 come from batch T 70 which is doped with 100 ppm sodium but also contains approximately 10 ppm copper. Crystal GaS(Na) T70-7 has been kept for 40 hours at 840°C in an evacuated silica ampoule. The results of spectrochemical analysis of the batches T54 and T70 and of some of the crystals from batch T70 which underwent the heat treatment are given in table 6.1.

Table 6.1. The concentrations of dopes and contaminating elements in two GaS batches.

Batch	T54	T70	T70 **)
Dope added	-	Na	Na
Amount of dope (ppm)	-	100	100
Bulk batch	M45	M49	M49
Element			
Ca	<3	<3	0-5
Cu	0.7	9-22	34-50
Na	0-10	9-110	n.a.
Si	0-85	0-10	45-60
Mg	1-3.5	4-5	3-11

*) The index (0) indicates a not intentionally doped crystal.

**) After a heat treatment; traces of iron, lead, silver and indium were also found.

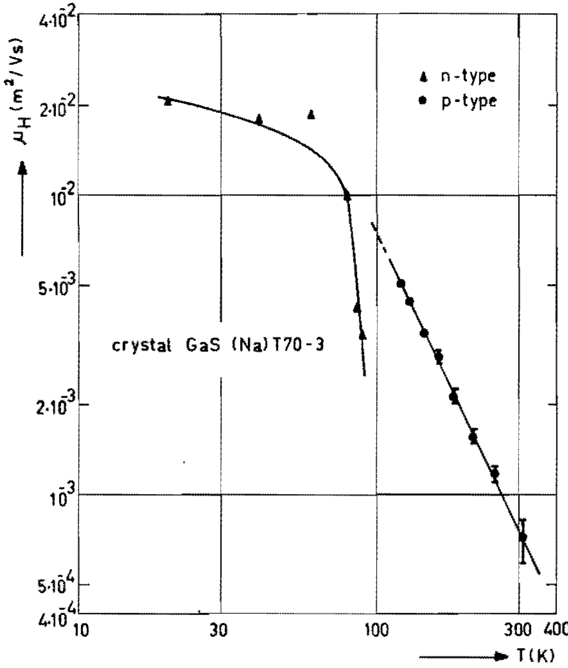


Fig. 6.4.
The photo Hall-mobility μ_H for crystal GaS(Na) T70-3 at maximum light intensity as a function of T. The mobility above 100 K can be expressed as $\mu_H = \mu_0 \left(\frac{T}{T_0}\right)^{-2.1}$.

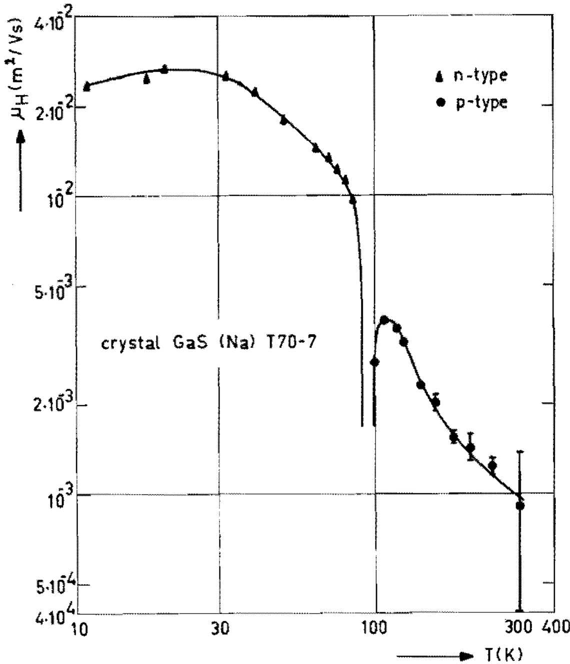


Fig. 6.5.
The photo Hall-mobility μ_H for crystal GaS(Na) T70-7 at maximum light intensity as a function of T.

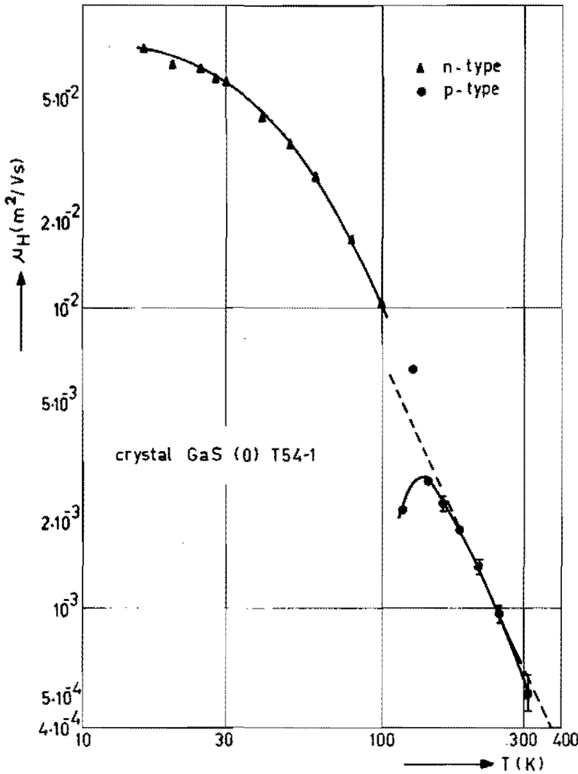


Fig. 6.6.
The photo Hall-mobility μ_H for crystal GaS(O) T54-1 at maximum light intensity as a function of T. The mobility above 100 K can be expressed as $\mu_H = \mu_0 \left(\frac{T}{T_0}\right)^{-2.1}$.

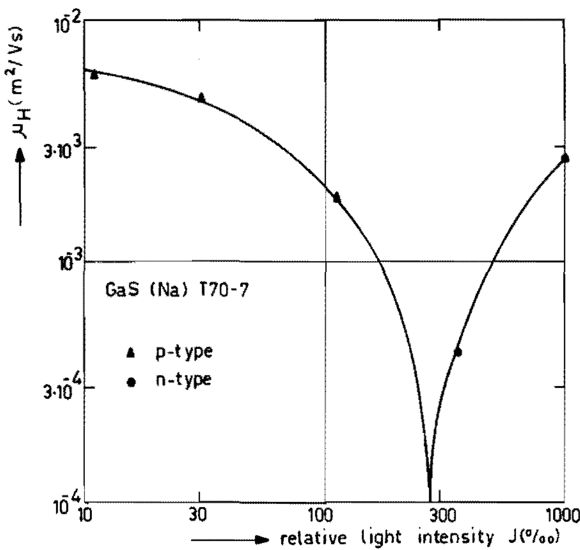


Fig. 6.7.
The photo Hall-mobility μ_H as a function of the relative light intensity J at T= 90 K for crystal GaS(Na) T70-7.

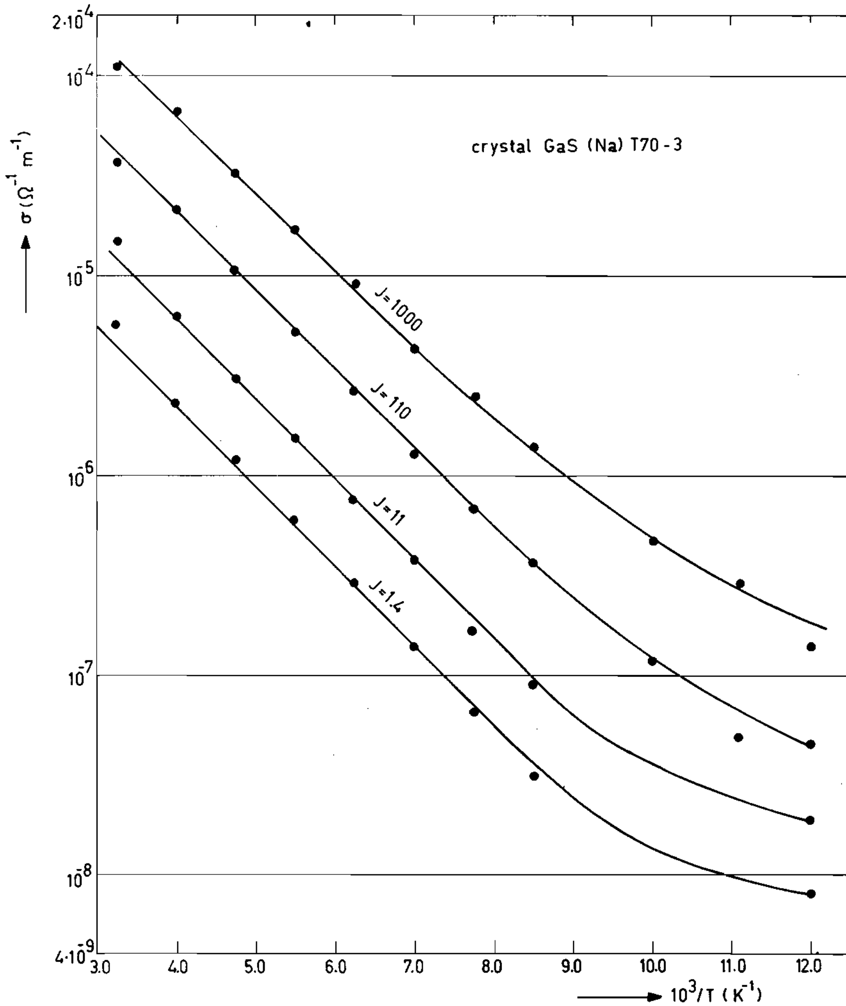


Fig. 6.8. The conductivity σ vs the reciprocal temperature with the relative light intensity J as parameter for crystal GaS(Na) T70-3.

The measurements on crystals GaS(Na)T70 and GaS(Na)T70-7 are representative for 23 crystals originating from 12 different batches which were either not doped or doped with cadmium, iodine and sodium.

In figures 6.1, 6.2 and 6.3 the conductivity σ is given as a function of the relative light intensity J with the temperature as parameter. The maximum light intensity corresponds to J = 1000 $^{o}/oo$. From these figures it can be seen that for the crystals GaS(Na)T70-3 and GaS(Na)T70-7 the value of $\frac{d \log \sigma}{d \log J}$ is 0.5 at temperatures above 100 K and J > 10$^{o}/oo$.
For temperatures below 70 K and J > 100$^{o}/oo$ the slope changes to 1.0.

For crystal GaS(O)T54-1 these values are 0.33 (below 200 K) and 1.0 respectively.
The figures 6.4, 6.5 and 6.6 in which for the same crystals the photo Hall-mobility μ_H at maximum light intensity is plotted as a function of the temperature, show that the conduction type changes from n-type at low

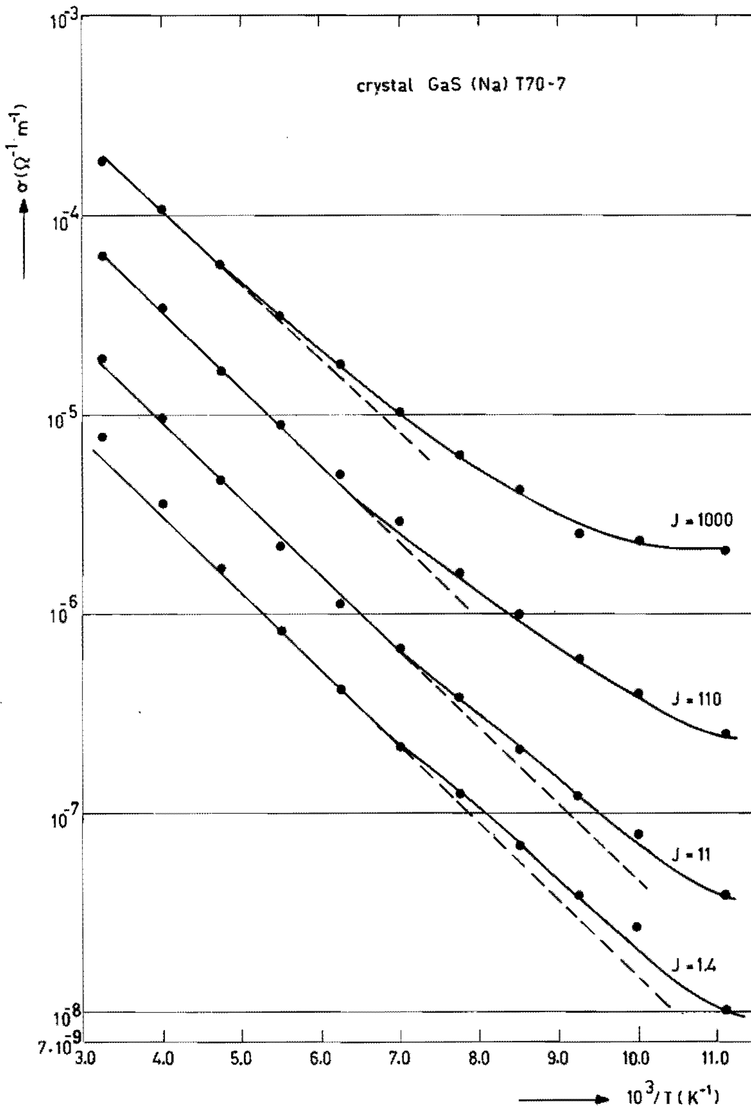


Fig. 6.9. The conductivity σ vs the reciprocal temperature with the relative light intensity J as parameter for crystal GaS(Na) T70-7.

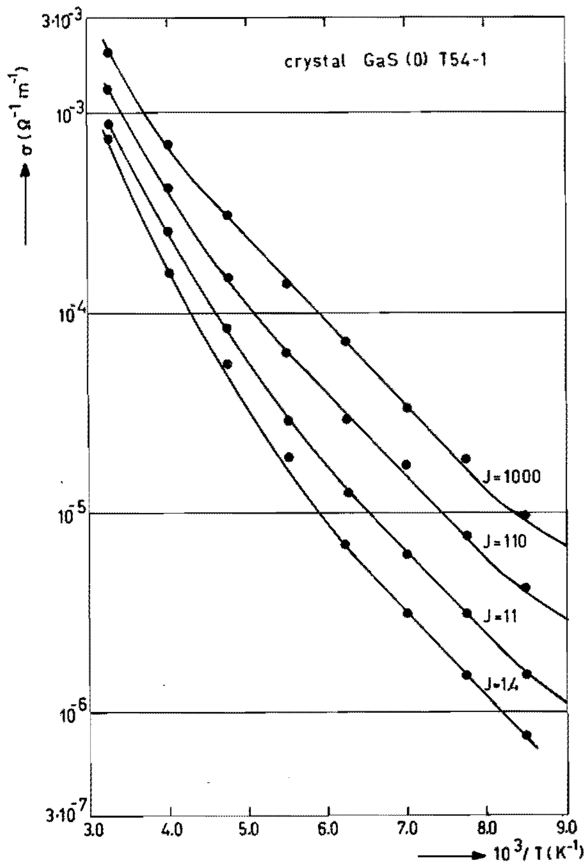


Fig. 6.10.
The conductivity σ vs the reciprocal temperature with the relative light intensity J as parameter for crystal GaS(O) T54-1.

temperatures to p-type at high temperatures. This change of conduction type is also dependent on the light intensity as can be seen in figure 6.7. In this figure the photo Hall-mobility μ_H is given as a function of relative light intensity at T = 90 K for crystal GaS(Na)T70-7.
The temperature dependence of the conductivity can be obtained from figures 6.8, 6.9, 6.10 and 6.11 in which the conductivity σ is plotted as a function of the reciprocal temperature. These figures show that at temperatures above approximately 100 K the conductivity increases with increasing temperature while at lower temperatures it reaches a constant value. Activation energies for σ are approximately 0.08 eV. From current measurements it could be seen that at high temperatures the dark current in crystal GaS(O)T54-1 is nearly as high as the photo current at the maximum light intensity. This explains the aberrations from the 0.33 slope in conductivity vs light intensity characteristic (see fig. 6.3) and the seemingly higher activation energies (see fig. 6.10) at high temperatures for this crystal.

To enable comparison of the results for the three crystals in fig. 6.11, σ is plotted as a function of the reciprocal temperature for the maximum light intensity.

It should be noted that in all crystals a conductivity of $10^{-8}\ \Omega^{-1}m^{-1}$ corresponds to a contact-to-contact resistance of approximately $10^{12}\ \Omega$.

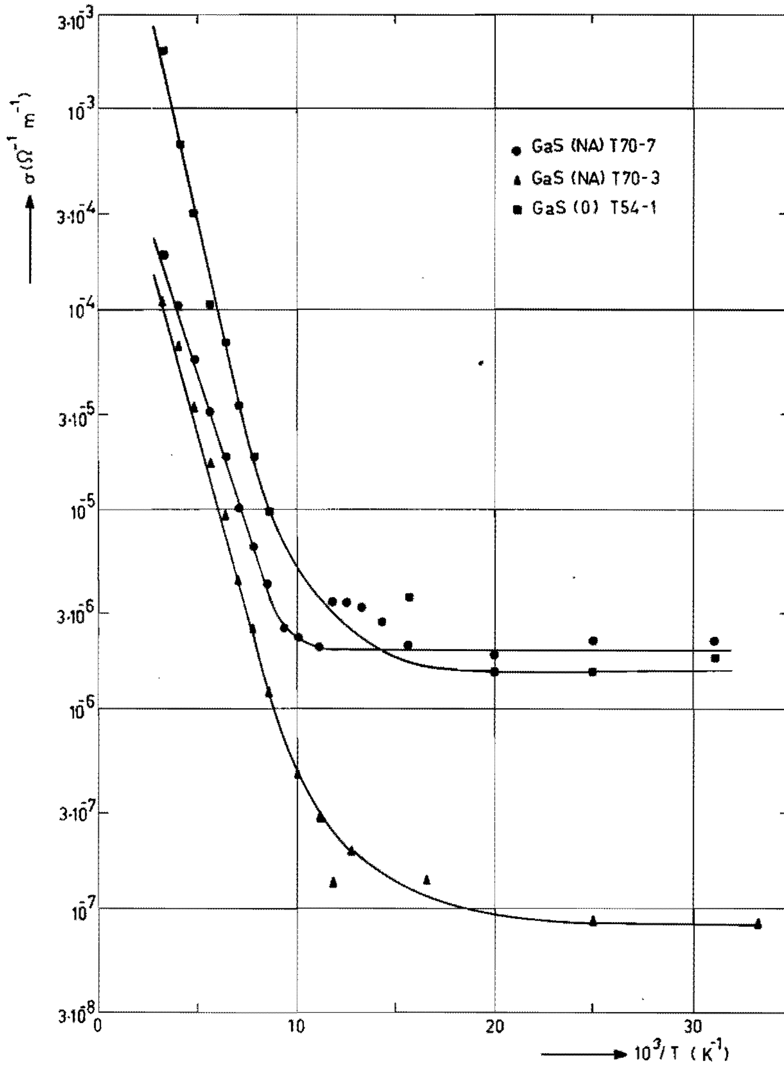


Fig. 6.11. The conductivity σ vs the reciprocal temperature at maximum light intensity for three GaS crystals.

In figure 6.12 the results of a TSC measurement after illumination at 20 K is given for crystal GaS(Na)T70-7. The 88 K peak was found in all crystals on which TSC measurements were made after low temperature illumination. According to Haake [6] this peak is not high enough to

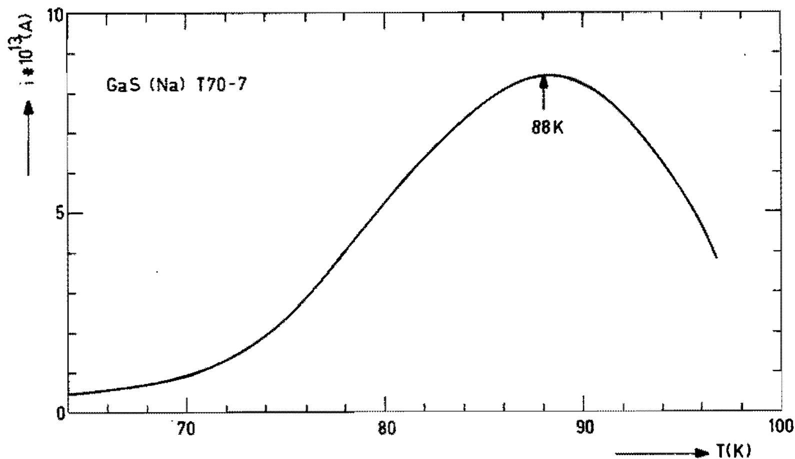


Fig. 6.12. A TSC curve for crystal GaS(Na) T70-7.

apply the method of Garlick and Gibson [7] for the determination of the trap depth E. However, an estimation can be obtained from Randall and Wilkins' [8] rule of thumb $E = 25$ to $30\ kT_{max}$ yielding a value of approximately 0.2 eV for the trapdepth.

6.4 The Klasens-Duboc model

Klasens [1] has introduced a model for the light intensity and temperature dependence of stationary state photoconductivity in semiconductors. Instead of giving an explanation for one special case he imposed a number of well chosen restrictions on a general model and stated the eight equations describing the stationary state for his model. By systematically simplifying these equations it was possible to find 128 different situations which can be solved easily. This approach was first used by Duboc [2]. A summary of Klasens' method will be given here. His notation will be used throughout this chapter.
The model used by Klasens consisted of a band model with two centers introducing discrete energy states in the forbidden zone. The Fermi-energy level in the dark is assumed to lie between these two states. Transitions of electrons and holes between the bands and the centers are assumed to be

possible with the exception of transitions between the centers. Band-band recombinations are being neglected since their probabilities are assumed to be small compared to those of the recombinations over one of the two states. With these restrictions Klasens reached a scheme of transitions which is given in fig. 6.13.

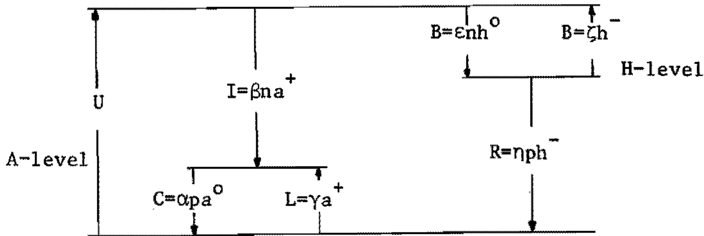


Fig.6.13. Schematic drawing indicating the transitions in the model proposed by Klasens.

The symbols n and p denote the concentrations of free electrons and holes, while the density of empty and occupied H and A levels is given by the symbols h^o, h^-, a^o and a^+ respectively. The different transition rates between the two states and the bands are denoted by I, C, E, R, L and B. The transition rates follow from the Guldberg-Waage law.
According to this model Klasens formulates the following six independent relations:

$$a = a^o + a^+ \quad (1)$$
$$h = h^o + h^- \quad (2)$$
$$a^+ + p = h^- + n \quad (3)$$
$$U = I + R \quad (4)$$
$$C = L + I \quad (5)$$
$$E = B + R \quad (6)$$

The aforementioned simplification of these equations consists of the assumption that in each of these equations two of the concentrations or rates are large compared to the third (and fourth). Thus 128 simplified situations are generated which can all be easily solved yielding simple expressions for the variable concentrations and rates as a function of the excitation rate U and containing the process constants α, β, γ, ε, ζ and η and the level concentrations a and h. $\frac{\gamma}{\alpha}$ and $\frac{\zeta}{\varepsilon}$ can be written as

$$\frac{\gamma}{\alpha} = N_v \exp\ (- E_A/KT)$$

and

$$\frac{\zeta}{\varepsilon} = N_c \exp\ (- E_H/kT)$$

in which N_v and N_c are the effective densities of states of the valence

and the conduction band while E_A and E_H are the energy differences between a free and a trapped hole resp. electron.
Instead of numbering the 128 situations from 1 to 128 Klasens assigns to each situation a code number consisting of 6 digits from which the approximations used in this situation can be seen directly. In table 6.2 this system is presented. From this table it can be seen that for example the code number 111212 is assigned to the situation in which $a = a^o$, $h = h^o$, $a^+ = h^-$, U = R, C = L and E = R or in other words both the A and H levels are nearly completely empty ($a = a^o$ and $h = h^o$). The concentration of free carriers is small compared to that of the trapped carriers ($a^+ = h^-$), the A-level is in quasi-thermal equilibrium with the valence band (C = L) and recombination occurs at the H-centers (U = R) from which the thermal release rate B is small (E = R).

Table 6.2. The composition of the code number relating to one of the simplified situations in the Klasens-Duboc model.

value digit	1	2	3	4
first	$a=a^o$	$a=a^+$		
second	$h=h^o$	$h=h^-$		
third	$a^+=h^-$	$a^+=n$	$p=h^-$	$p=n$
fourth	U=I	U=R		
fifth	C=L	C=I		
sixth	E=B	E=R		

The solutions for a number of the more important possible situations have been given in detail by Klasens.
Each situation can only be valid in a finite temperature and excitation range. The changeover from one situation to another can usually be detected from a change in the slope of the log conductivity - log intensity characteristic of a crystal.
For more details of this method one is referred to Klasens' original paper from which only a small part has been summarized here.

6.5 Application of the Klasens-Duboc model

6.5.1 Crystal GaS(Na) T70-3

The temperature region above 100 K, where the conduction is p-type, will be considered first. From the temperature dependence of the conductivity (see fig. 6.8) it can be seen that the concentration of free holes is

temperature dependent which indicates that the A-level is a hole trap. The maximum number of holes p_{max} for this crystal is found at T = 308 K and J = 1000°/oo. Using the values $\sigma = 1.2 \cdot 10^{-4}$ ohm^{-1} m^{-1} and $\mu_H = 6.10^{-4}$ m^2/Vs (see fig. 6.1 and 6.4) p_{max} can be calculated from

$$p = \frac{\sigma}{e\mu_H}$$

which yields $p_{max} = 1.2 \cdot 10^{18}$ holes/m^3. Now let us assume that $p >> a^+$. In that case two possibilities can be distinguished: $a = a^+$ and $a = a^o$. If $a = a^+$ the number of A levels would be smaller than $10^{19}/m^3$ which seems rather small. If $a = a^o$ this would mean that the number of free holes could not increase appreciably with increasing temperature which is in conflict with experimental evidence. Thus p must be smaller than a^+ and the third digit in the code number must be 1. This reduces the number of possible situations from 128 to 42. The slope of the log σ - log J characteristics provides the next possibility of reducing the number of possible situations. The value of $\frac{d \log \sigma}{d \log J}$ is 0.5. Only three situations *) are now possible characterized by the code numbers 111111, 111211 and 111212. The expressions for p and n in these situations are given in table 6.3.

Table 6.3. Expressions for n and p for the cases indicated by code numbers 111111, 111211 and 111212.
E_{ACT} is the activation energy for p-type conductivity.

E_{ACT}	Codenumber	n	p	$\frac{p}{n}$
$E_A - \frac{1}{2}E_H$	111111	$\left(\frac{\zeta U}{\beta\ \varepsilon\ h}\right)^{\frac{1}{2}}$	$\left(\frac{\gamma^2 \varepsilon\ h\ U}{\alpha^2 \beta\ \zeta\ a^2}\right)^{\frac{1}{2}}$	$\left(\frac{\gamma}{\alpha a}\right)\left(\frac{\varepsilon h}{\zeta}\right)$
$\frac{1}{2}E_A$	111211	$\left(\frac{\alpha\zeta^2\ a\ U}{\gamma\varepsilon^2\eta h^2}\right)^{\frac{1}{2}}$	$\left(\frac{\gamma U}{\alpha\eta a}\right)^{\frac{1}{2}}$	$\left(\frac{\gamma}{\alpha a}\right)\ \left(\frac{\varepsilon h}{\zeta}\right)$
$\frac{1}{2}E_A$	111212	$\frac{U}{\varepsilon h}$	$\left(\frac{\gamma U}{\alpha\eta a}\right)^{\frac{1}{2}}$	$\left(\frac{\gamma\varepsilon h}{\alpha\eta a}\right)^{\frac{1}{2}} U^{-\frac{1}{2}}$

The three expressions for p given in table 6.3 all satisfy the experimental conditions. Only in the case of codenumber 111111 it is

*) According to the tables in Klasens original paper a fourth situation is possible with code number 221112. However, his calculation in this case is not correct. The calculations for the situations with code numbers whose first three digits are 221 are partly wrong.

necessary to assume that $E_H < 2\,E_A$ to explain the temperature behaviour. And if we assume that $a = h$ and $N_v = N_c$ the value of p/n is only higher than 1 if $\gamma/\alpha \gg \zeta/\varepsilon$ or $E_H - E_A \gg 0$.

To make a further choice possible the low temperature behaviour will be considered. At low temperatures the A centers will be filled with holes. The temperature at which this occurs can be estimated from Randall and Wilkins' rule of thumb for maxima in TSC curves:

$$E_{trap} = 25 \text{ to } 30\ kT_{max}.$$

In figure 6.14 σ/μ, which is a measure for p, is given for J = 1000 ^{o}/oo as a function of the reciprocal temperature yielding an activation energy E_{ACT} of 0.115 eV. Now for code numbers 111211 and 111212 the energy E_A is twice the activation energy or E_A = 0.23 eV. Thus the trap should be filled at approximately 90-105 K which is in good agreement with the experimental evidence. For code number 111111 the activation energy

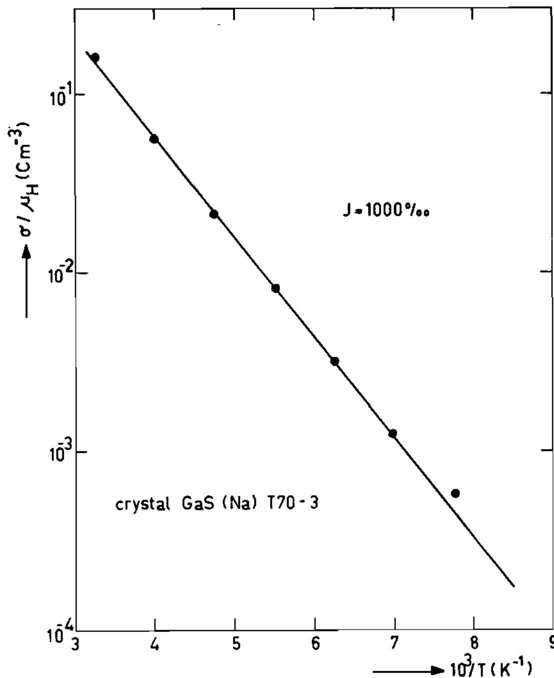


Fig. 6.14. σ/μ_H as a function of the reciprocal temperature for crystal GaS(Na) T70-3. The slope corresponds to an activation energy of 0.115 eV.

would be equal to $E_A - \frac{1}{2} E_H$. Since E_H and E_A must satisfy the conditions that $E_H < 2 E_A$ and $E_H - E_A >> 0$ the activation energy corresponds to a value considerably lower than $\frac{1}{2} E_A$. In this case the temperature at which the trap would be filled should be considerably lower than 100 K which rules out the situation characterized by code number 111111.
If the trap A becomes occupied with holes the code number changes since this means that $a = a^+$. The code number thus changes from 111211 in 211211 or from 111212 in 211212. In table 6.4 the expressions for p and n are given in these cases.

Table 6.4. Expressions for n and p for cases indicated by the code numbers 211211 and 211212.

Codenumber	n	p
211211	$\frac{\zeta a}{\varepsilon h}$	$\frac{U}{\eta a}$
211212	$\frac{U}{\varepsilon h}$	$\frac{U}{\eta a}$

Since the low temperature photoconductivity is temperature independent, proportional to the excitation rate and n-type, the code number must be 211212.
The photoconductivity of crystal GaS(Na)T70-3 can now be explained as follows. At low temperatures most of the holes are trapped in a level lying 0.23 eV above the valence band. The conductivity is then determined by temperature independent recombination processes. At high temperatures the hole trap can reach a quasi thermal equilibrium with the valence band and the conduction becomes p-type. The number of free electrons can be written as $n = \frac{U}{\varepsilon h}$ while for high temperatures $p = (\frac{\gamma U}{\alpha \eta a})^{\frac{1}{2}}$.
Some numerical values for various parameters will now be calculated.
Assuming that each photon generates one hole-electron pair the maximum excitation rate U_{max} at maximum light intensity J_{max} follows from

$$U_{max} = \frac{J_{max}}{d}$$

in which d is the crystal thickness.

With $J_{max} = 3.5 \cdot 10^{19}$ photons/m^2s and $d = 70\ \mu$ we find

$$U_{max} = 5 . 10^{23}\ m^{-3}\ s^{-1}.$$

The hole concentration at 308 K and $U = U_{max}$ was already calculated in the first part of this section and was found to be $p = 1.2 \cdot 10^{18}\ m^{-3}$.

The ratio γ/α can be written as

$$\frac{\gamma}{\alpha} = N_v \exp\left(\frac{-E_A}{kT}\right).$$

With $N_v = 10^{26}\ m^{-3}$ and $E_A = 0.23$ eV we find from the expression for p at high temperatures $p = \left(\frac{\gamma U}{\alpha \eta a}\right)^{\frac{1}{2}}$

$$\eta a = 6.10^{9}\ s^{-1}.$$

Assuming a to be $3.10^{23}\ m^{-3}$ (1 : 10^5 levels/mol GaS) becomes

$$\eta = 2.10^{-14}\ m^3/s.$$

If η is written as the product of the thermal velocity v for holes and the capture cross section S_T of the H center for holes

$$\eta = v\ S_T,$$

this capture cross section becomes with $v = 10^5$ m/s

$$S_T = 2.10^{-19}\ m^2$$

which should be compared to values of 10^{-17} to $10^{-19}\ m^2$ used by Klasens. For εh the relation

$$\varepsilon h = \frac{U}{n}$$

is valid and at low temperatures we may assume that

$$\sigma = ne\ \mu_H$$

yielding

$$\varepsilon h = \frac{U \mu_H e}{\sigma}\ .$$

At maximum light intensity and T = 40 K the values for σ and μ_H become $\sigma = 9.10^{-8} \Omega^{-1} m^{-1}$ and $\mu_H = 1.8.10^{-2}\ m^2/Vs$ (see fig.6.1. and 6.4) so that εh becomes

$$\varepsilon h = 1.6 \cdot 10^{10}\ s^{-1}$$

It should be noted that the values for εh and ηa are consistent with the

model. As can be seen from table 6.4 the ratio of free electrons and free holes is

$$\frac{n}{p} = \frac{\eta a}{\varepsilon h} .$$

Inserting the values for ηa and εh yields $\frac{n}{p} = 5$ which is in agreement with the experiment since the crystal is n type.

6.5.2. Crystal Ga S(Na)T70-7

The interpretation of the photoconductivity is the same for crystal GaS(Na) T70-7 as for GaS(Na)T70-3. The higher conductivity in the n-type region may be explained by assuming a lower concentration of recombination centers h.

6.5.3. Crystal Ga S(o)T54-1

The main difference between the conductivity of crystal GaS(o)T54-1 and the other two crystals is the difference in the value of $\frac{d \log \sigma}{d \log J}$ which is 0.33 for this crystal instead of 0.5 (see fig. 6.3).
Two situations with code numbers 113112 and 111112 are applicable.
The expressions for p and n are given in table 6.5.
In both situations the A-level is both a hole trap and the main recombination center. The number of free holes is somewhat small to accept situation 113112. In this situation the number of free holes should be large as compared to the number of trapped holes (see section 6.5.1.) Moreover, assuming the A-level to be the same as for crystal GaS(Na)T70-3, the slope of the log σ - 1/T characteristic should be steeper for the case with code number 111112. From fig.6.11 it can be seen that this indeed is the case. The numerical data are not sufficient to calculate values for the 6 independent parameters in the expression for p (see table 6.5).

Table 6.5. Expressions for n and p for cases indicated by the code numbers 111112 and 113112. E_{ACT} is the activation energy for p-type conductivity.

E_{ACT}	Codenumber	n	p
$\frac{2}{3}E_A$	111112	$\left(\frac{\gamma \eta U^2}{\alpha \beta^2 \varepsilon h a}\right)^{1/3}$	$\left(\frac{\gamma^2 \varepsilon h U}{\alpha^2 \beta \eta a^2}\right)^{1/3}$
$\frac{1}{3}E_A$	113112	$\left(\frac{\gamma^2 \eta U^2}{\alpha^2 \beta^2 \varepsilon a^2 h}\right)^{1/3}$	$\left(\frac{\gamma \varepsilon h U}{\alpha \beta \eta a}\right)^{1/3}$

Assuming that at low temperatures the A-level will become filled with holes the code number changes to 211112. The expressions for n and p in this case are $n = \frac{U}{\beta a}$ and $p = \frac{\varepsilon h U}{\beta \eta a^2}$. The conduction will become n type if $n/p \gg 1$ or $\frac{\eta a}{\varepsilon h} \gg 1$.
This is the same condition as in the case of crystal GaS(Na)T 70-3 at low temperatures. For that crystal $\frac{\eta a}{\varepsilon h} = 5$. Now here the H level is not the important recombination center anymore. This indicates that the number of levels h must be smaller or the recombination parameter η must be larger as compared to the crystal GaS(Na) T70-3.
In that case the value of $\frac{\eta a}{\varepsilon h}$ would be considerably higher than the value found for crystal GaS(Na) T70-3. Thus the ratio n/p is probably higher than 5 and n-type conductivity at low temperatures is satisfactorily explained.

6.6. The photo Hall-mobility

Kipperman and Vermij [9] found for the photo Hall-mobility of p-type gallium sulphide in the temperature range from 100 to 300 K

$$\mu_H = \mu_o \left(\frac{T}{T_o}\right)^{-2.4}$$

with T_o = 300 K and $\mu_o = 7$ to 12.10^{-4} m^2/Vs. In the experiments described here the relation

$$\mu_H = \mu_o \left(\frac{T}{T_o}\right)^{-2.1}$$

is found (see fig. 6.4 and 6.6) with T_o = 300 K and $\mu_o = 5$ to $7 \cdot 10^{-4} m^2/Vs$. The lower value of the exponent may be caused by the mixed Hall effect at temperatures around approximately 100 K which would lower the value of μ_H and thus decrease the slope of the log μ_H - log T characteristic. The intensity dependence of the Hall-mobility as given in fig. 6.7 can be understood on the basis of the proposed model. At 90 K electrons and holes are equally present causing a mixed Hall-effect. At high light intensities there are more electrons than holes, at low intensities the number of holes becomes higher than the number of electrons. From the formula for mixed Hall-effect

$$\mu_H = \frac{-n\mu_n^2 + p\mu_p^2}{n\mu_n + p\mu_p}$$

it can be seen that the mobility should become zero in the intermediate range which is in agreement with the results presented in figure 6.7.

In figure 6.15 and 6.16 the results of a calculation of μ_H and σ as a function of the relative light intensity J are given. The values of the various parameters have been chosen in such a way that the Hall-mobility is zero at J = 280 ^{o}/oo and 1.9 . 10^{-3} m^2/Vs at J = 110 ^{o}/oo, and are in accordance with values measured for crystal GaS(Na)T70-7 at 90 K. The concentrations of free holes and free electrons are assumed to be proportional to $J^{\frac{1}{2}}$ and J respectively.

The following values of the parameters have been used:

- the Hall-mobility is 64.10^{-4} m^2/Vs for holes and 125.10^{-4} m^2/Vs for electrons;
- at maximum light intensity the concentration of free holes is $5.10^{14} m^{-3}$ and the concentration of free electrons 2.5 . $10^{14} m^{-3}$.

The experimental points given in fig.6.15 and 6.16 are for crystal GaS(Na)T70-7 at 90 K (see also fig.6.2 and 6.7). From these figures it can be seen that with the aforementioned assumptions the calculated values are in reasonable agreement with the measured values.

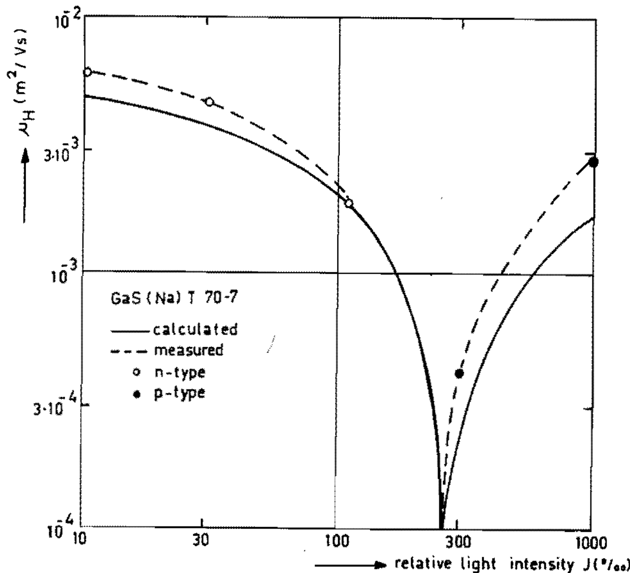


Fig. 6.15 Calculated and measured values for the Hall-mobility in crystal GaS(Na)T70-7 as a function of the relative light-intensity J. The values of the parameters used in the calculation are given in the text.

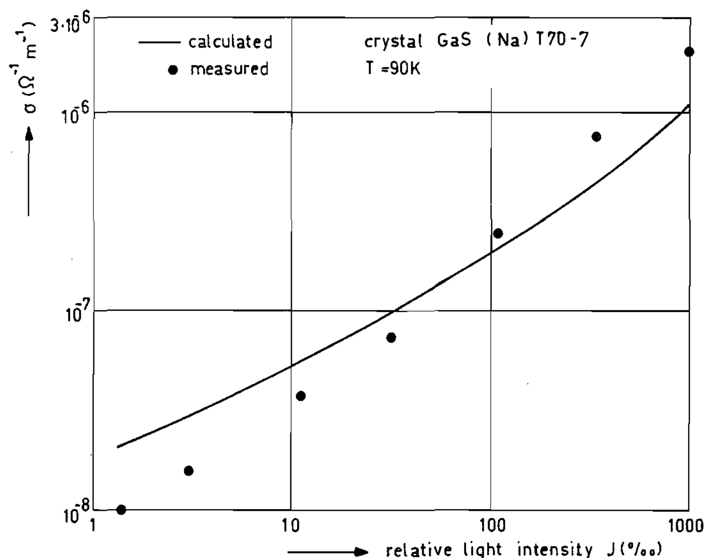


Fig. 6.16 Calculated and measured values for the conductivity of crystal GaS(Na)T70-7 as a function of the relative light-intensity J. The values of the parameters used in the calculation are given in the text.

6.7 Conclusion

The results of the photoconductivity measurements on some gallium sulphide single crystals can be explained quantitatively with the Klasens-Duboc model [1,2]. A hole trap, lying 0.23 eV above the valence band, is responsible for the high temperature (100-300 K) photoconductivity. This trap is probably the same as a trap found in TSC measurements with T_{max} = 88 K.
Temperature dependent photo Hall-mobility measurements agree roughly with values found by Kipperman and Vermij [9]. The difference may be due to a mixed Hall-effect.

LITERATURE

[1] Klasens, H.A., J. Phys. Chem. Solids, 7, 175 (1958).

[2] Duboc, C.A., Brit. J. Appl. Phys. Suppl. No. 4, 107 (1955).

[3] Van der Pauw, L.J., Philips Res. Repts., 13, 1 (1958).

[4] Hahn, H. and Frank G., Z. anorg. u. allgem. Chemie, 278, 340 (1955).

[5] Kipperman, A.H.M. and Van der Leeden, G.A., Sol. Stat. Comm. 6, 657 (1968).

[6] Haake, C.H., J. Opt. Soc. Amer. 47, 650 (1957).

[7] Garlick, G.F.J. and Gibson, A.P., Proc. Phys. Soc., 60, 574 (1948).

[8] Randall, J.T. and Wilkins, M.F.H., Proc. Roy. Soc. A, 184, 366 (1945).

[9] Kipperman, A.H.M. and Vermij, C.J., Il Nuovo Cimento, 63B, 29 (1969).

CHAPTER 7

CONCLUSIONS

One of the goals set forward at the start of the work resulting in this thesis was the preparation of "pure" gallium sulphide and of doped gallium sulphide single crystals. To a certain degree this goal has been reached. The impurity content of bulk gallium sulphide prepared according to the method described in chapter 2 is lower than that of commercially available gallium sulphide, only the impurity magnesium forms an exception. A number of elements have been incorporated in gallium sulphide single crystals and two of these elements clearly influence the properties of these crystals: cadmium gives rise to a trap center and copper to a recombination center. On the other hand the main purpose of doping gallium sulphide was to influence the photoconductivity behaviour as a function of light intensity in such a way that a specific response could be obtained. This goal has not been reached, which must be mainly attributed to the occurance of a hole trap. The nature of this trap has not been clarified. Application of the Klasens-Duboc model yields a value of 0.23 eV for the trap depth.
The spectrographic analysis of the batches, described in chapter 3, was found very useful. The attribution of the 2.00 eV luminescence band to copper was only possible because in a number of batches showing a characteristic red luminescence copper impurities were spectrographically detected. Furthermore the practically instantaneous availability of analysis results for the bulk batches made it possible to prepare very pure gallium sulphide.
A secondary goal was the application of other methods capable of yielding independent information on trapping- and recombination parameters in order to find supporting evidence for the explanation of photoconductivity measurements. Photoluminescence-, thermally stimulated luminescence- and thermally stimulated current measurements were used for this purpose. In two cases some evidence has been found:

1) a peak in the TSC spectrum lying at 88 K is probably caused by the hole trap lying 0.23 eV above the valence band derived from the photoconductivity experiments;
2) crystals taken directly from batch GaS(Na)T70 show strong photoluminescence with two characteristic bands and have a low photoconductivity at low temperatures. Crystals from the same batch which underwent a heat treatment have a low photoluminescence intensity with different bands and a high photoconductivity at low temperatures (see fig.5.2, 5.4, 6.1 and 6.2). This behaviour is in agreement with the explanation given for the photocondcutivity measurements.

Further research could be directed along several lines.
The clarification of nature of the 0.23 eV hole trap seems most important.
For this reason experiments with GaS single crystals prepared with excess gallium or sulphur may prove useful. Another approach would be to assume that either magnesium or silicon causes this trap since these are the only impurities present in detectable quantities.
An interesting phenomenon is the 2.4 eV luminescence band in copper doped crystals. The assumption that copper plays a role in the origin of this band seems justified since it has only been found in crystals containing copper.
On the other hand sodium seems to enhance the intensity of this band so that simultaneous doping with copper and sodium may be the best approach in an effort to trace the origin of this band. The use of higher light intensities as for example can be provided by an argon-ion laser may prove useful if more research on the fine structure of the 2.4 eV luminescence band is to be carried out.
A more extensive research program in which systematic doping with other elements must play a mayor role seems necessary to reach the original goal of preparing a gallium sulphide photoconducting device with well defined properties.

Summary

In this thesis the results of photoconductivity-, photoluminescence and photo Hall-effect measurements on doped gallium sulphide single crystals are described. The measured dependence of the photoconductivity on temperature and light intensity is explained in terms of the Klasens-Duboc model. At temperatures between 100 and 300 K the photoconductance of most crystals is determined by a hole trap lying 0.23 eV above the valence band. The origin of this trap has not been clarified.
Copper is shown to give rise to a recombination center resulting in a red photoluminescence band centered at 2.00 eV. From thermally stimulated current- and thermally stimulated luminescence meaurements it can be concluded that cadmium gives rise to a trapping level lying 0.43 ± 0.02 eV from one of the bands.
A detailed description is given of the preparation of pure gallium sulphide. The preparation of doped gallium sulphide single crystals with a zone melting method is also described. Results of spectrographical analysis are given.

Samenvatting

In dit proefschrift worden de resultaten beschreven van fotogeleidings- en fotoluminescentiemetingen aan gedoseerd verontreinigde gallium sulphide eenkristallen. De gevonden afhankelijkheid van het fotogeleidingsvermogen van temperatuur en lichtintensiteit wordt verklaard met behulp van het Klasens-Duboc model. Bij temperaturen liggend tussen 100 en 300 K wordt het fotogeleidingsvermogen voornamelijk bepaald door een gatentrap die 0.23 eV boven de valentieband ligt. Het is niet gelukt vast te stellen waardoor deze trap wordt veroorzaakt.
Koper blijkt een recombinatiecentrum te veroorzaken waardoor een rode luminescentie-band ontstaat met een maximum bij 2.000 eV. Uit thermisch gestimuleerde stroom- en luminescentiemetingen blijkt verder dat cadmium een trap veroorzaakt, met een energieniveau in de verboden zône dat 0.43 ± 0.02 eV van de geleidings- of valentieband afligt.
Een gedetailleerde beschrijving wordt gegeven van de methode volgens welke zo zuiver mogelijk gallium sulfide gemaakt wordt. Verder wordt beschreven hoe met behulp van een zône smelt methode gedoseerd verontreinigde gallium sulphide eenkristallen kunnen worden gemaakt. Resultaten van spectrografische analyses worden gegeven.

Aan het tostandkomen van dit proefschrift hebben velen meegewerkt. Hen allen wil ik graag hiervoor bedanken en in het bijzonder:

- Ronald Lieth voor de vele "chemische" discussies en voor het kritisch doorlezen van een gedeelte van dit proefschrift;
- Peter Kivits en dipl. ing. J.Pachaly voor de TSL metingen die in Berlijn in het IIe Physikalische Institut der Technische Universität Berlin door hun zijn gedaan;
- dr.P.W.J.M.Boumansvan het Philips Natuurkundig Laboratorium voor het beschikbaar stellen van de werktekeningen van de electrodehouder;
- A.P.Severijns van het Philips Nat. Lab. voor zijn adviezen betreffende de constructie van de cryostaat;
- Ad Vink, eveneens van het Philips Nat. Lab. voor zijn kritiek op en suggesties bij de interpretatie van de photoluminescentie-metingen;
- Ronald van Zolingen en Gert van Overbruggen voor het verrichten van een groot deel van de photoluminescentie-metingen;
- Daniël Spitzer, Frans Gouverneur, Fons Rutten en de vele andere studenten, die tijdens hun stages veel van de langdurige fotogeleidinsmetingen hebben gedaan;
- mevr.R.Schaafsma-van Noort, Elly Nagelkerke, Ank Wennink-Latour en Marilou Hoffman, die dit proefschrift hebben getypt;
- Ruth Gruyters voor het maken van de vele tekeningen in dit prentenboek;
- de heren van de werkplaatsvoor de vele apparaten die zij voor mij hebben gemaakt;
- Peter van Tuyl en Willem van Vleuten voor hun technische assistentie;
- Jos van Amelsvoort vloeibare hulp;
- Wim de Jonge en mijn Marja voor het in elkaar plakken van dit proefschrift.
- Les Polgar voor hetcorrigeren van mijn "engels".

Zonder de technische assistentie van Rinus Queens zou dit proefschrift òf niet òf pas in de verre toekomst tot stand zijn gekomen. Aan hem ben ik zeer veel dank verschuldigd.

Mijn ouders die mij in staat stelden te studeren wat ik wilde, waar ik wilde, maar niet hoelang ik wilde ben ik daarvoor nog steeds dankbaar.

LEVENSLOOP

30-11-1939	*Geboren in Delft*
juni 1958	*Eindexamen HBS-B*
dec.1958-juni 1960	*dpl.sld.,dpl.sld.I, dpl.kpl. bij de verbindingstroepen.*
juni 1960-sept.1960	*bordenwasser op de "Statendam".*
sept.1960-maart 1967	*studie voor natuurkundig ingenieur*
april 1967-apr.1968	*wetenschappelijk assistent aan de THE.*
vanaf april 1968	*wetenschappelijk medewerker in tijdelijke dienst aan de THE.*

Stellingen behorende bij het proefschrift van G.A. van der Leeden.

1) Zo er in de natuur regels bestaan die altijd en overal geldig zijn, is het in ieder geval niet bekend welke regels dit zijn; in verband hiermee verdient het aanbeveling om in natuurkunde boeken het betrekkelijke karakter van zogenaamde wetten aan te geven.

2) Het is wenselijk het aantal studenten dat zich kan inschrijven voor de studierichting natuurkunde te beperken tot een zodanig aantal dat in de maatschappelijke behoefte aan natuurkundigen, zoals deze kan worden vastgesteld op basis van prognoses, wordt voorzien. Een dergelijke maatregel heeft slechts zin indien gelijktijdig het aantal studenten dat zich in kan schrijven voor andere studierichtingen wordt beperkt

   Ned.T. v. Natuurk.,39, 106 (1973)
   Ned.T. v. Natuurk.,39, achterblad (1973).

3) Het verdient aanbeveling om het gebruik van de door de Consumentenbond opgestelde "Consumentenvoorwaarden" wettelijk verplicht te stellen bij aankopen door of opdrachten van particulieren, indien de met dergelijke aankopen of opdrachten gepaard gaande kosten een bepaald bedrag te boven gaan.

   Consumentengids ,21, 187 (1973).

4) Het is mogelijk om de temperatuur, waarbij de door Bongaarts et al gevonden verandering in de kristalstructuur van $NiCl_2.2H_2O$ plaatsvindt, nauwkeuriger te bepalen uit het verloop van de optische absorptie met de temperatuur.

   Bongaarts, A.L.M., Van Laar, B., Botterman,A.C. and De Jonge, W.J.M.,Phys.Letters, 41A, 411(1972).

5) Het verdient aanbeveling om, zowel voor een studieprogramma in zijn geheel als voor ieder onderdeel ervan, het formuleren van een doelstelling verplicht te stellen.

6) Het is gewenst dat de mogelijkheid wordt geopend om in een proefschrift in plaats van de verplichte zes stellingen een hoofdstuk op te nemen dat de resultaten bevat van een onderzoek over een maatschappelijk relevant onderwerp buiten het eigen vakgebied.

   Academisch Statuut, art 222, lid 1.

26 juni 1973.