

Philips Research

100 years of patents
and publications

PHILIPS

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100 years of patents
and publications



Content

Foreword _____ 5

100 years of patents and _____ 6
publications from Philips Research

- **Phase 1:** Start and diversification (1914 - 1945)
- **Phase 2:** Autonomous research (1945 - 1970)
- **Phase 3:** Connecting to the Product Divisions (1970 - 1990)
- **Phase 4:** Becoming a front-end innovation organization (1990 - 2013)
- Publishing
- Research and IP

Historical timeline _____ 12

1914 – 1923	14	1964 – 1973	36
Patents	14	Patents	36
Publications	16	Publications	38
1924 – 1933	18	1974 – 1983	40
Patents	18	Patents	40
Publications	20	Publications	42
1934 – 1943	22	1984 – 1993	46
Patents	22	Patents	46
Publications	24	Publications	48
1944 – 1953	26	1994 – 2003	50
Patents	26	Patents	50
Publications	28	Publications	52
1954 – 1963	32	2004 – 2013	54
Patents	32	Patents	54
Publications	34	Publications	56

Foreword

Innovation is absolutely core to what Philips is – it is part of our strategy, it is how we improve people's lives, how we make the world healthier and more sustainable. Innovation is how we create superior value for our customers and for our shareholders. We put people at the center of everything we do, responding to their aspirations, needs and desires.

Philips Research is a front-end of innovation organization that is a preferred co-creation partner for the Philips businesses and selected strategic relations. We work in multidisciplinary teams, and we are at the leading edge of core technologies that extend throughout the entire product portfolio of Philips, which allows the company to generate new businesses and real competitive advantage in the marketplace. We also have an extensive set of partnerships, because we don't have all necessary know-how in house.

Our approach has led to more than a century of breakthrough innovations. To be able to protect our ideas, we have been working closely together with Philips Intellectual Property & Standards (IP&S) to create intellectual property (IP). Over many years, IP&S has created a large IP portfolio with world-class IP solutions

to support the growth, competitiveness, and profitability of the Philips businesses.

Moreover, since our foundation by Gilles Holst in 1914, publishing papers about new developments in Research has been a means to position ourselves as an important player in the world of science and technology, and strengthen our reputation in innovation. By doing so, we are able to provide scientific underpinning for our commercial offerings, and at the same time attract talent and potential partners for innovation co-creation.

With this publication, we would like to give some insights in the most important and impactful patents and publications that have been created by Philips Research over the past 100 years. For each decade, we show the ten most-cited publications, as well as a few examples of patents that have contributed to value generation for Philips in the 100-years' existence of Philips Research. My special thanks go to Frank Toolenaar from Philips Research and Maaïke van Velzen from Philips Intellectual Property & Standards who compiled and edited the material brought together in this booklet.

This collection presents a fascinating insight in our rich history – I hope you will enjoy reading it.

Henk van Houten

General Manager Philips Research

January 2014





100 years of patents and publications from Philips Research

As a corporate Research organization, Philips Research has always been flexible in adapting to the demands of the time and to the strategy of Philips as can be seen in the several overviews that have been published on previous occasions^{1,2,3,4,5}. In 1994, Marc de Vries⁵ distinguished three distinct phases in the way Philips Research handled challenges in the then 80 years of its existence. We want to summarize his assessments and expand to 2013 with a fourth phase, with special attention to publications.

Phase 1: Start and diversification (1914 - 1945)

In the early 20th century, technological developments became more and more dependent on scientific knowledge⁶, especially in the fields of chemical technology and electricity, which led to the foundation of corporate scientific laboratories at companies such as General Electric (1900), Dupont (1902), Siemens (1905), AT&T (1910), Marconi (1912), and Philips (1914). Such laboratories typically were responsible for three types of tasks: (1) quality control for existing production processes, (2) knowledge acquisition for innovation and improvement of products or processes, based on existing science, and (3) acquisition of new knowledge that may result in new products.

Gerard Philips viewed research as a means of reducing costs in the production of incandescent lamps. On the other hand, Gilles Holst, the founder of the Research organization, aimed at understanding as well as controlling materials and processes. The main tasks at the *Natuurkundig Laboratorium* in its early years were

twofold: understanding the physics of the half-watt lamp, and experimenting with new light sources. Until 1923 there were really only two scientists (Holst and Oosterhuis), but that number grew fast when the lab began contributing to the diversification of Philips from light bulbs to other types of vacuum tubes.

Gas discharge lamps were the first products beyond incandescent light bulbs, followed closely by X-ray tubes such as the Metalix, a compact X-ray tube developed by Bouwers. This research can be considered as the basis of the later Medical Devices / Healthcare division. The development of radio tubes both for receiving and transmission purposes led to the fabrication of radios, which formed the basis of Consumer Electronics and various Professional Electronics divisions.

Research into magnetic ceramic ferrite materials started in in the 1920s, as an essential material in loudspeakers for radios. This led to applications in dynamos and in the first rotary shaver. Two basic material inventions were developed around WWII, (ferro-magnetic) Ferroxdure and (soft-magnetic) Ferroxcube, which after 1950 was to be applied widely in coil cores for various products. Other companies became very interested in using these materials and Philips was thus able to obtain Bell's transistor knowledge via a patent cross license.

Holst wanted to have researchers with excellent scientific reputations. To achieve this, he created a culture in which researchers felt free to do high-level scientific and technological research – with management ensuring appropriate

alignment with business priorities. He organized colloquia in which famous physicists (such as Ehrenfest, Einstein, and Pauli) shared their latest insights with the scientists of the lab. Holst also stimulated publications in academic journals as an independent and open forum for judging the lab's scientific output. Holst also hoped that a strong reputation as a serious scientific research institute would attract good scientific university graduates.

At the same time, Holst also stimulated that the outcomes of research were profitable for the company. Scientists were expected to submit ideas for patents (*white cards*), which were judged by Holst himself before submission to the Patent department. In 1936, Holst also created a special journal, the *Philips Technisch Tijdschrift* (with translations in English, French and German), to answer the increasing number of enquiries for data and particulars of Philips products and also to make contacts with the engineering world.

Phase 2: Autonomous research (1945 - 1970)

After the Second World War, Philips created separate product divisions with their own development laboratories, next to the corporate Research organization. Under Hendrik Casimir, one of the most visible successors of Holst, a trend developed to incorporate some of the forefronts of science into the research program of Philips Research, instead of just relying on contacts with academic institutions.

Casimir saw science and technology develop in a spiral in which technology uses scientific results, but with a time

lag, while science uses technology without such a time lag. He advocated that a research environment should exist within an industry to foster both science and technology. Researchers in such an environment should be given considerable freedom and be encouraged to communicate and share their findings in journals and at professional meetings. *Fundamental research* became a particular task as a cradle for creating future options for the company. Conversion into devices and systems was seen as the responsibility of the development labs at the Product Divisions (PDs). In such an environment, publishing was seen as important output and source of pride.

However, also during this period the *Natuurkundig Laboratorium* did make some very important contributions which created very profitable products for Philips. One example is the Plumbicon, a pickup tube for television cameras, which was an innovation that every company in the television broadcasting business had to use to remain compatible. Another success was LOCOS (LOCAL Oxidation of Silicon), a silicon process technology to create local silicon-dioxide areas on silicon to insulate the individual MOS transistors from each other. In the IC world of the 1980s, no company could ignore LOCOS. Both innovations generated significant value for Philips through use in products and licensing.

Phase 3: Connecting to the Product Divisions (1970 - 1990)

Around 1970 the post-war economic boom ended and the world began to face successive crises. This affected

companies by recurrent stagnation periods that forced them to reorganize to maintain efficiency, which for Philips coincided with strongly increasing competition from Japan. From the early 70s the notion grew that insights from the marketplace might be more important for industrial breakthroughs than basic research. Casimir's successor Pannenberg stated already in 1972² that attention should shift from *technology push* to *market pull* – Research should be oriented towards converting scientific developments into Philips products rather than in exploring new scientific fields. This resulted into a rapid termination of whole areas of research (Stirling motor, biology, futurology, solar cells, pollution) – and an increased focus on programs that were aligned with the business units' scope and strategies. The development of digital optical storage on disc during this period can be considered as one of the major breakthroughs in the consumer electronics area. On the basis of its broad research capabilities Philips – together with Sony – launched the compact disc in 1979. Due to the close co-operation with a partner like Sony and with the music industry, this success was extended to other formats.

The research on magnetic tape recording led to the highly successful Compact Cassette. The invention of the V2000 video-recording system lost against the competing VHS format, and a profitable business was created in the latter format. The core competency in mechanics and optics also led to the creation of a wafer stepper, laying the basis for ASML. Other leading work on electron microscopy (SEM, TEM) eventually led to the ground-breaking business position of FEI.

As Philips over time became a more focused business, global competitiveness increased, and because of the urgent need to cut costs and increase efficiency and effectiveness, it was realized that a next step was needed to ensure strong mutual commitment between Research and the Product Divisions.

Consequently in 1989 the Research budget was split into corporate (long-term) and contract-funded (with financing provided by the Product Divisions).

Phase 4: Becoming a front-end innovation organization (1990 – 2013)

In the mid-1990s Philips decided to concentrate on high-volume electronics, including semiconductors, displays, audio and TV, mobile phones, and data storage. However, towards 2000 it became clear that the company's position in many of these fields was not tenable, due to rapid price erosion, and the emerging fierce competition from Korean and Chinese industry. As a result, components and semiconductor divisions as well as the display, audio and television activities were divested. From that point onwards, there was increasing focus on healthcare, lighting and consumer products in the area of health and well-being – catering to unmet needs related to significant macro-economic and societal trends. In the Healthcare sector, a position was built in home healthcare next to the hospital franchise. In Lighting, focus was on the disruptive replacement of lamps by LEDs, and on the digitization of the industry, with LED lamps becoming part of the Internet of Things. In Consumer Lifestyle the focus shifted to domestic appliances, personal care, and well-being products.

For Research, this meant a massive reorientation on new fields of expertise – re-using as much as possible world-class competencies like signal and image processing, optics, and miniaturization. But new competencies needed to be added, from psychology to bio-molecular engineering and clinical sciences, data analytics, and service engineering.

In terms of ways of working, it was realized that it was not enough to have close contacts with the technical community in Philips' business sectors. The whole process from idea generation to production should be a close cooperation between R&D, strategy, business management, and marketing. Research needed to become a 'co-creation partner' of the businesses, with a focus on the front end of innovation, but extending into product development for the more disruptive types of innovation. This required a change in culture and competency profiles in the Research organization.

Open Innovation received much more attention as well. However, although this might seem paradoxical, it was

realized that this does not necessarily mean becoming more open – a clear strategy was needed on what type of widely available knowledge should be sourced from outside, what could be shared in joint research, and what should be kept fully controlled. Confidentiality therefore became much more explicit, which led to a decrease in focus on external publications.

Publishing

The policy on publishing has long been characterized by the 4th rule of Holst (as recorded by Casimir in 1969⁷): *Let them publish and take part in scientific activities*. In the regulations of Research it was stated explicitly that it was in the first place the responsibility of the researcher what, where, and how to publish. Over the years, authors were encouraged to submit manuscripts for external publication, after approval via an internal review round.

In this internal approval process, two ('peer') colleagues and the patent department evaluate the quality of and the absence or presence of patentable material in the manuscript. With this input the department head then makes the final decision about submission to a journal or conference. Recently, the policy has been reformulated from a more focused strategic perspective:

Publishing is a means to position ourselves as an important player in the world of science and technology, strengthen our reputation in innovation, attract talent, provide scientific underpinning for our commercial offerings, and support external cooperation and the innovative image of Philips.

Publishing is still seen as a quality benchmark when papers from Philips Research are accepted by top-rate journals and conferences, but:

External publishing is not a right of the employee, but it should be supporting the overall objectives of Philips Research in co-creating meaningful innovation.

In the end, industrial researchers simply must focus on helping bring new products onto the market, leading to profitable growth of the company.

Statistics on publications from Philips Research

Since the first paper by Lely and Hamburger in 1914⁸, publications have been meticulously recorded and collected in printed *Registers*, which contain the data of the publications, clustered on author's names and on subject. See Table 1 for the publication volume over the first 54 years.

Register	Years	Publications
1	1914-1935	1-1000
2	1935-1951	1001-2000; R1-R171
3	1951-1961	2001-3000; R175-R425
4	1961-1968	3001-4000; R426-R655

Table 1 Registers with data of publications from Philips Research Eindhoven between 1914 and 1968. The R-numbers refer to publications in Philips journals.

After 1968, the publications of the 'sister laboratories' in other countries were included, each with their own report types and numbering system. Between 1973 and 2012 around 18,000 publications are found – see Fig 1 for the numbers per year¹⁰.

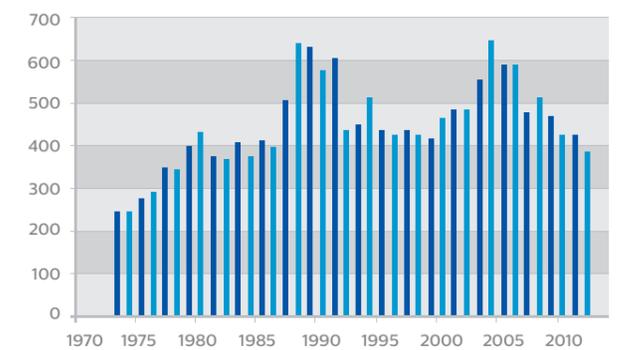


Figure 1 Publication totals from Philips Research⁹, data from Web of Science

If we compare the outputs of different corporate organizations (see Figure 2) – Philips is not that different from others – most show a gradual increase with a decline in recent years. The exception is Samsung that seems to be investing heavily in publishing.

It is difficult to determine the impact that publications from Philips (Research) have had on the business of

Philips. Unlike patents that impact is rarely if ever direct – although this may change in the future as publications underpinning professional (medical) claims will become more important. Of course, enhancing the image of Philips in the scientific community, and using that also as a means to attract top talent, is priceless.

We would like to give some insights in the most important and impactful publications in the 100-years existence of Philips Research. We have chosen citation data as objective criterion, but we are well aware that the citation behavior has rapidly changed over time. Therefore we have chosen to search for the top 10 most-cited publications per decade. From two of these papers we show the abstract or opening part and one or two characteristic figures.

This collection presents a fascinating insight in our rich history.

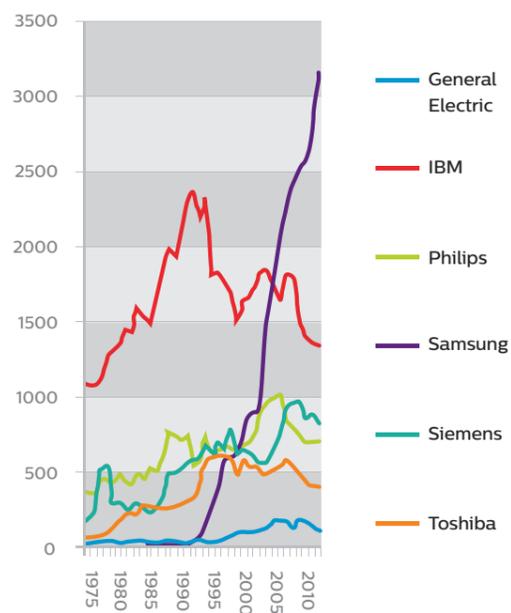


Figure 2 Publication output of several corporate organizations

Research and IP

Over many years, Philips Intellectual Property & Standards (IP&S) has worked closely with Research to create intellectual property (IP). IP&S has created a large IP portfolio with world-class IP solutions to support the

growth, competitiveness, and profitability of the Philips businesses.

Philips' IP portfolio currently comprises approximately 59,000 patent rights of which a significant part derives from activities in Research. In 2012, Philips registered approximately 1,500 patents, the majority of which relate to the growth sectors of healthcare and well-being. Through IP, the Philips businesses are enabled to grow, enter new markets, and increase competitive strength and profitability.

The IP portfolio has increased profitability of the Philips businesses in many of its activities ranging from television to healthcare. In addition to value created in the Philips businesses, the IP portfolio has been used to generate licensing income. In the early years of the 21st century, Philips started large licensing programs, e.g., on the audio cassette, LOCOS technology for semi-conductor industry, and optical recording/DVD and Blu-ray. These programs have made a significant contribution to Philips' profit over the years.

This collection gives examples of patents that are part of the portfolio that generated value for Philips. The patents in this collection originate from Philips Research. The full IP portfolio is composed of inventions generated in Research, the Philips businesses, and obtained by acquisition of IP or entire companies.

The list includes IP that covers products sold by the Philips businesses and IP that is part of larger licensing programs. Although a fully quantitative value determination for IP is difficult, we defined several components that contribute to value generation through IP. These components include direct revenue from licensing agreements and the contribution made by IP to the profit generated by the other Philips businesses.

Real value generation with IP usually starts several years after the filing of the patent applications and their publication 18 months later. Therefore, we also included a few patents of the most recent decade to show their potential for value generation.

The publications in this book are derived from the "Web of Science core collection" by Thomson Reuters and this book only includes a selection of peer-reviewed articles from 12,000 most renowned scientific journals and 150,000 conference proceedings. A publication was considered for inclusion if at least one of the authors has a Philips affiliation. Other publications created by Philips Research (such as scientific books and publications in newspapers, etc.) were

left out of the selection criteria. Nevertheless, it is important to stress that these publications were also crucial to the reputation of Philips Research as a thought leader. Here, we would like to give special mention to "Simulated Annealing and Boltzmann Machines", by E. Aarts and J. Korst (4,400 citations according to Google Scholar) and "The new everyday" by E. Aarts and S. Marzano (353 citations according to Google Scholar).

¹ Veertig jaren research; natuurkundig laboratorium der N.V. Philips' gloeilampenfabrieken, Philips Eindhoven 1955

² K. Boersma – Inventing structures for industrial research: a history of the Philips Nat.lab. 1914-1946, Aksant 2002

³ H.B.G. Casimir – An anthology of Philips research; (1891-1966), Philips 1966

⁴ Unsere Forschung in Deutschland I-IV, Philips Aachen 1964, 1972, 1980, 1988

⁵ Marc J. de Vries – 80 Years of research at the Philips Natuurkundig Laboratorium 1914-1994

⁶ A. Sarlemijn and P. Kroes – Between science and technology, North Holland, 1990

⁷ H.B.G. Casimir – Philips Res. Repts 24, 161-167 (1969)

⁸ D. Lely, L. Hamburger – Z. Anorg. Allgemeine Chemie 87, 209-228 (1914)

⁹ Searching for addresses containing "philips res*" or "philips forschung*" or "philips nat*" or limeil-brévannes or briarcliff.

¹⁰ As the publication data have never been converted into a practical database, it is unfortunately not possible to give yearly figures on output volumes before 1973. From Web of Science this is possible after 1973 when they began to add address data to their records. For the first 60 years between 1914 and 1973 we had to identify the most important authors from the Registers and then check these names for citations.

Historical timeline

1914 – 2013



G Holst



L Hamburger



GL Hertz



E Oosterhuis

1914 – 1923



G Blasse



A Slob



CM Hart



E Kooi



G Frens

1964 – 1973



K Posthumus



A Bouwers



B van der Pol



FM Penning

1924 – 1933



G van Gorkum



LF Feiner



AR Miedema



1974 – 1983



JL Snoek



A Horowitz



HC Hamaker



HJ Lemmens



C Bol

1934 – 1943

1984 – 1993



U Schiebel



F Vreeswijk



CWJ Beenakker



H van Houten

1994 – 2003



AJW Overbeek



BDH Tellegen



HBG Casimir



EJW Verwey

1944 – 1953



JN Huiberts



C Liednbaum



DM de Leeuw



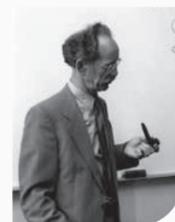
N Dimitrova



R Florent



K Compaan



G Bouwhuis



JA Haringx



EF de Haan

1954 – 1963

2004 – 2013



J Westerink



MWJ Prins



BHW Hendriks

Patents

Patents and IP have always been important in Philips. The first Philips Research patent dates back from June 11 1914, when Gilles Holst filed a patent on a new incandescent projection lamp. It was granted in 1918.

In 1921, Philips started its own IP department. In the next chapters you'll see examples of valuable patents and publications per decade.



G Holst

Aanvraag No. 4850 Ned. ingediend:	11 Juni 1914 te 2 uur 55 min. n.m.
Aanvraag openbaargemaakt:	15 Juni 1915.
Octrooischrift uitgegeven:	15 November 1918.
Dagteekening van het octrooi . . .:	25 September 1918.

NAAMLOOZE VENNOOTSCHAP PHILIPS' METAAL-GLOEILAMPENFABRIEK
en GILLES HOLST, beiden te Eindhoven.

Verbetering aan elektrische gloeilampen voor projectie-doeleinden.

Dese uitvinding heeft betrekking op een verbetering van de elektrische gloeilamp voor projectie- en andere doeleinden, waar het er om te doen is, in een bepaalde richting groote lichtintensiteiten te verkrijgen. Te dien einde wordt het gloeilichaam zoo in den ballon geplaatst, dat een spiegel (die eventueel op den ballon zelf kan worden aangebracht) een optische afbeelding van het gloeilichaam ontwerpt, die zoo goed mogelijk in het vlak van het gloeilichaam zelve valt. Teneinde het gloeilichaam op korten afstand van het condensersysteem te kunnen plaatsen, wordt een kleine, eventueel kunstmatig gekoelde ballon toegepast.

Het is wenschelijk, dat bij een lichtgevend systeem, dat voor projectie- en dergelijke doeleinden dienen moet, de gemiddelde vlaktheelderheid van den straler zoo hoog mogelijk gemaakt wordt. Bij gewone elektrische gloeilampen wordt aan deze gemiddelde oppervlaktehelderheid een bovenste grens gesteld door de eigenaardige constructieve moeilijkheden, die niet veroorlooven, de gloeidraden op een willekeurig kleinen afstand van elkaar te plaatsen. Teneinde nu toch een grootere gemiddelde vlaktheelderheid te verkrij-

gen, wordt volgens de uitvinding aan het gloeilichaam zoodanige vorm en plaats in den ballon gegeven, dat het door den spiegel gevormd optisch beeld van het gloeilichaam, in het vlak van het gloeilichaam zelf valt en wel zoodanig, dat deze afbeelding de, door het gloeilichaam zelf vrij gelaten ruimten zoo goed mogelijk aanvult. Hierdoor wordt een belangrijke verhooging van de gemiddelde oppervlakte helderheid verkregen.

Aan de hand van de bijbehorende teekening is de uitvinding nader toege-licht.

Fig. 1 geeft een voorstelling van het beeld, dat een dergelijk gloeilichaam op het oog maakt, terwijl

fig. 2 een doorsnede is door een gloeilamp volgens de uitvinding met bijbehorend lenzenstelsel.

In fig. 1 is het gloeilichaam zelf door de getrokken lijn voorgesteld, terwijl de gestippelde lijn het optische beeld van het gloeilichaam voorstelt.

Het verdient aanbeveling, het gloeilichaam klein te kiezen en ongeveer in het middelpunt van den spiegel te plaatsen, teneinde een zoo zuiver mogelijk optisch beeld van het gloeilichaam in het vlak

Exemplaren van dit Octrooischrift zijn tegen betaling van 60 cents per stuk verkrijgbaar bij het Bureau voor den Industrieelen Eigendom.

met meek uit een serie proefnemingen, dat als metaalspiegel met succes de verzilverde wand van een zorgvuldig uitgezochten glasballon genomen kon worden. Het is daarbij wenschelijk den ballon geheel met een metaalspiegel te bedekken en slechts dat gedeelte vrij te laten, waardoor de stralenbundel naar buiten moet treden. Hierdoor wordt o.a. bereikt, dat een groot gedeelte der warmtestralen na de reflectie den straler weder treffen, waardoor het nuttig effect van de lamp als bijkomstig voordeel vergroot wordt.

Teneinde een kleinen afstand tusschen gloeilichaam en condensor te verkrijgen, wordt het gloeilichaam in een kleinen ballon geplaatst, waarbij, om een overmatige verhitting van den ballon en den eventueel daarop aangebrachten metaalspiegel te verhinderen, een kunstmatige koeling aangebracht kan worden. Kiest men hiervoor bijvoorbeeld circuleerend water of een andere middenstof, die een grooten absorptiecoëfficiënt voor warmtestralen bezit, dan wordt bovendien het voordeel verkregen dat de, op het conden-

Bij daaromtrent uitgevoerde metingen bleek bij eenzelfde potentiaal verschil de lichtstroom der lamp binnen een openingshoek van 90° door het aanbrengen der bovenbeschreven constructie met 150 % te zijn toegenomen, terwijl het wattverbruik 5 % minder werd. Bij een zelfde temperatuur van het gloeilichaam was de vermeerdering der lichtsterkte ruim 120 %.

Conclusie. 50

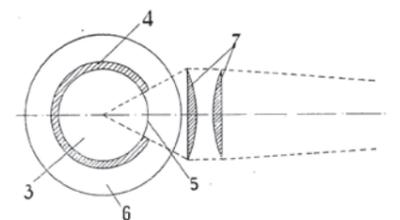
Verbetering aan elektrische gloeilampen voor projectie- en andere doeleinden, daarin bestaande, dat een spiegel, eventueel op den ballonwand van de lamp aangebracht is, die een optisch beeld van het kleine, ongeveer in het middelpunt van den spiegel geplaatste gloeilichaam ontwerpt in het vlak van het gloeilichaam zelf, en wel zoodanig, dat het optische beeld zoo goed mogelijk de door het gloeilichaam vrijgelaten ruimte aanvult. De lamp kan daarbij eventueel gekoeld worden.

Hierbij 1 blad teekeningen.

Fig. 1.



Fig. 2.



Octrooi No. 2660.



Publications

- 1 Über die Anregungs- und Ionisierungsspannungen von Neon und Argon und ihren Zusammenhang mit den Spektren dieser Gase

GL Hertz

ZEITSCHRIFT FÜR PHYSIK 18, 307-316 (1923)

Times Cited: 48

- 2 Over de elektrische geleiding in gassen

G Holst; E Oosterhuis

PHYSICA 1, 78-87 (1921)

Times Cited: 47

- 3 Über Trennung von Gasgemischen durch Diffusion in einem strömenden Gase

GL Hertz

ZEITSCHRIFT FÜR PHYSIK 19, 35-42 (1923)

Times Cited: 47

- 4 The sparking potential of gasses

G Holst; E Oosterhuis

PHILOSOPHICAL MAGAZINE 46, 1117-1122 (1923)

Times Cited: 38



GL Hertz

- 5 Ein neues Verfahren zur Trennung von Gasgemischen durch Diffusion

GL Hertz

PHYSIKALISCHE ZEITSCHRIFT 23, 433-434 (1922)

Times Cited: 37

- 6 Experimentelle Untersuchungen über die Wärmeleitfähigkeit der Gase. I

S Weber

ANNALEN DER PHYSIK 54, 325-356 (1917)

Times Cited: 34

- 7 Experimentelle Untersuchungen über die Wärmeleitfähigkeit der Gase. II

S Weber

ANNALEN DER PHYSIK 54, 437-462 (1917)

Times Cited: 32

- 8 Untersuchungen über das Gleichgewicht von Flüssigkeit und Dampf des Systems Argon-Stickstoff

G Holst; L Hamburger

ZEITSCHRIFT FÜR PHYSIKALISCHE CHEMIE 91, 513-547 (1916)

Times Cited: 31

- 9 Unikristallijn wolfram

AE van Arkel

PHYSICA 3, 76-87 (1923)

Times Cited: 26

- 10 Herstellung der Elemente Thorium, Uran, Zirkon und Titan

D Lely; L Hamburger

ZEITSCHRIFT FÜR ANORGANISCHE UND ALLGEMEINE CHEMIE 87, 209-228 (1914)

Times Cited: 22

Über die Anregungs- und Ionisierungsspannungen von Neon und Argon und ihren Zusammenhang mit den Spektren dieser Gase.

Von G. Hertz in Eindhoven (Holland).

Mit acht Abbildungen. (Eingegangen am 12. August 1923.)

Von den Edelgasen ist bisher das Helium das einzige, bei welchem die dem Atom durch Elektronenstoß zuzuführenden Energiequanten zuverlässig bekannt und in Beziehung zum Serienspektrum gesetzt sind. Für Neon und Argon liegt zwar auch eine ziemlich große Zahl von Messungen vor, welche aber zum Teil nur ungenau sind und deren Resultate sich insbesondere beim Neon in wesentlichen Punkten widersprechen¹⁾. Der Grund für die bei derartigen Messungen in diesen Gasen auftretenden Schwierigkeiten liegt zum Teil in der großen Empfindlichkeit dieser Gase gegen Spuren von Verunreinigungen. Vor allem scheint mir aber die hier im Vergleich zu anderen Gasen sehr viel kleinere Ausbeute der unelastischen Stöße unterhalb der Ionisierungsspannung eine Rolle zu spielen, welche bewirkt, daß die bei anderen Gasen, insbesondere bei Metaldämpfen sehr brauchbaren Methoden hier versagen. Um zu einwandfreien Resultaten zu kommen schien es mir daher nötig, die Methode zur Untersuchung der quantenhaften Energieübertragung zwischen Elektronen und Atomen zu verschärfen und durch ein einwandfreies, auch bei unelastischen Stößen von geringer Ausbeute anwendbares Verfahren zur Unterscheidung von Lichtemission und Ionisation als Folge der Zusammenstöße zu ergänzen.

Die bisherigen Methoden bestehen darin, daß die von einer bestimmten Geschwindigkeit der stoßenden Elektronen an auftretende Strahlung oder Ionisation, oder aber die Erscheinung, daß die Elektronen bei Zusammenstoßen Energie verlieren, als Merkmal für das Auftreten unelastischer Stöße benutzt wird. Man erhält hier stets Kurven, in denen sich die verschiedenen Energiestufen als Knickpunkte bemerkbar machen, deren genaue Auswertung besonders bei den höheren Energiestufen oft sehr schwierig ist. Es schien mir daher erwünscht, als Kriterium für die quantenhaften Energieübertragung ein Merkmal zu benutzen, welches unmittelbar nach dem Überschreiten der kritischen

¹⁾ F. Horton u. A. C. Davies, Proc. Roy. Soc. London (A) 97, 1, 1920 und 98, 124, 1920. G. Stead u. P. S. Gosling, Phil. Mag. 40, 413, 1920. H. C. Rentschler, Phys. Rev. 14, 503, 1919. G. Déjardin, C. R. 172, 1347, 1921. C. Found, Phys. Rev. 16, 41, 1921.
Zeitschrift für Physik. Bd. XVIII. 22

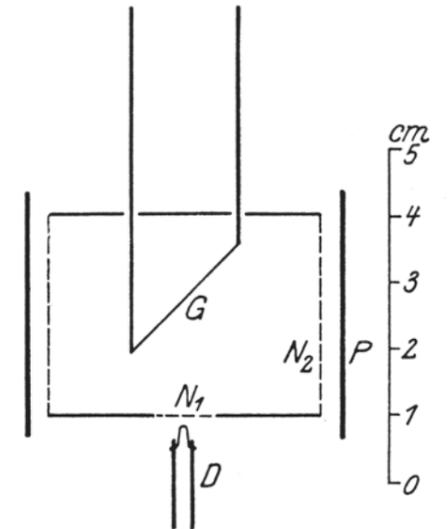


Fig. 5.

- 1 GL Hertz – Über die Anregungs- und Ionisierungsspannungen von Neon und Argon und ihren Zusammenhang mit den Spektren dieser Gase

D. Lely jr. u. L. Hamburger, Herstellung der Elemente Thorium usw. 209

Herstellung der Elemente Thorium, Uran, Zirkon und Titan.

Von

D. LELEY jr. und L. HAMBURGER.

Mit 5 Figuren im Text.

A. Allgemeine Gesichtspunkte.

Die Herstellung der obengenannten Metalle wird durch ihren hohen Schmelzpunkt und ihre große Affinität zu vielen anderen Elementen erschwert.

I. Im allgemeinen kann man wohl sagen, daß es sich bei der Bereitung dieser Metalle empfiehlt, nur solche Stoffe zu verwenden, von denen kein ungünstiger Einfluß auf das herzustellende Metall zu erwarten ist.¹ Als Regel ist dies aber gerade bei denjenigen Elementen, die so schwierig rein herzustellen sind, eine fast nicht zu erfüllende Bedingung. Dazu kommt noch die Einwirkung der Verunreinigungen, welche die Ausgangsmaterialien begleiten.

II. Es ist auch empfehlenswert, die Ausgangsstoffe so zu wählen, daß aus dem Reaktionsprodukt die nicht metallischen Teile bequem herausgewaschen werden können. Stoffe, die sich in Alkohol, Wasser oder verdünnten Säuren leicht auflösen, dürften zu diesem Zwecke brauchbar sein. Wir haben denn auch das Prinzip der alten Methode, die Metalle aus ihren Chloriden mit Hilfe von Natrium zu bereiten, angewendet.

Schon im Jahre 1882 ist von SETTERBERG² zur Herstellung eines so schwierig zu gewinnenden Metalles wie Vanadin, diese Methode mit ziemlich gutem Resultat befolgt worden.

III. Ein drittes Erfordernis für eine rationelle Herstellungsweise ist, daß man das Metall in einer Form erhält, in der es seine außerordentliche Angriffbarkeit verloren hat.

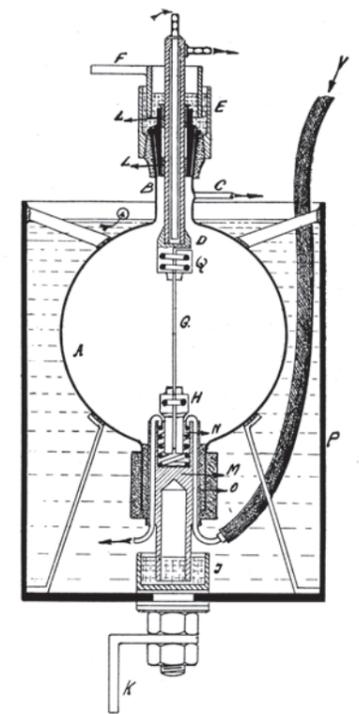
Dies wird der Fall sein, wenn man das gesuchte Element in nicht zu fein verteilter Form bekommt, wenn also das Metall zu größeren Teilchen zusammenschmolzen oder gesintert ist.

¹ So ist z. B. mit der Herstellung der Elemente aus ihren Oxyden mit Kohlenstoff die große Schwierigkeit der Verunreinigung des gesuchten Produktes mit dem Reduktionsmittel verbunden.

² Öfversigt K. Vet. Akad. Förhandl. 39, Nr. 10, 13-21.

Z. anorg. Chem. Bd. 87. 14

- 10 The first published paper from Philips Research: D Lely et al. – Herstellung der Elemente Thorium, Uran, Zirkon und Titan



Maßstab 1 : 5.7.
Fig. 3.

1924 – 1933

Patents

1 Pentode

G Holst; BDH Tellegen
US Patent 1.945.040 (1926)



A Bouwers



K Posthumus

2 X-ray tube

A Bouwers
US Patent 1.893.759 (1927)

3 Amplifier

K Posthumus
US Patent 1.996.830 (1928)

4 Strapper Magnetron

K Posthumus
US Patent 2.103.638 (1933)

Patented Jan. 10, 1933

1,893,759

UNITED STATES PATENT OFFICE

ALBERT BOUWERS, OF EINDHOVEN, NETHERLANDS, ASSIGNOR TO N. V. PHILIPS' GLOEILAMPENFABRIEKEN, OF EINDHOVEN, NETHERLANDS, A LIMITED LIABILITY COMPANY OF THE NETHERLANDS

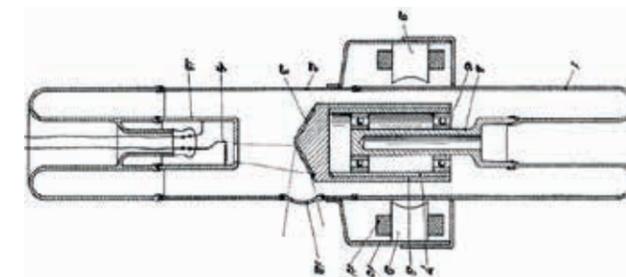
X-RAY TUBE

Application filed April 25, 1927, Serial No. 166,522, and in the Netherlands January 18, 1927.

The invention relates to X-ray tubes.

It is known that during the operation of an X-ray tube the anticathode becomes burnt in or is otherwise unfavorably affected when the load of the focal spot exceeds a definite value.

Theoretically it can also be proved that with a determined anticathode material a given amount of energy must cause per unit of time a determined rise of temperature. A greater allowable load is obtained by constituting the anticathode of good heat-conducting metal having a high melting point. Fundamentally, however, better results are obtained by mounting the anticathode so as to be movable.



Patented Jan. 30, 1934

1,945,040

UNITED STATES PATENT OFFICE

1,945,040

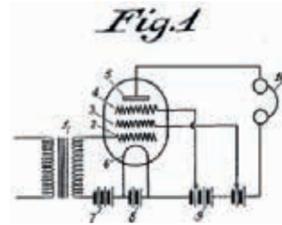
MEANS FOR AMPLIFYING ELECTRIC OSCILLATIONS

Gilles Holst and Bernardus Dominicus Hubertus Tellegen, Eindhoven, Netherlands, assignors to N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands, a limited-liability company of the Netherlands

Application November 25, 1927, Serial No. 235,504, and in the Netherlands December 14, 1926

26 Claims. (Cl. 250—27)

This invention has reference to the amplification of electric oscillations by means of thermionic devices. It is known that when these devices are to be used for amplifying purposes it is desirable that the slope of the grid voltage-anode current characteristic should be steep. With the customary triodes the steepness of the static characteristic decreases to an appreciable extent when oscillations are impressed on the control grid because these oscillations are transferred to the anode amplified, but in opposite phase, so that when the grid potential increases the anode current will on the one hand increase under the influence of the said increasing potential but the current will on the other hand decrease under the influence of the falling anode potential caused by the increased current flow so that the resulting increase of the anode current is diminished. In order to obviate this disadvantage with the final amplifier a so-called screening grid may be used between the control grid and the anode, said screening grid being maintained at a constant and fairly high positive potential, whereby the possibility remains of applying an appreciable negative grid bias to the control grid, which is very desirable in connection with the comparatively large output energy of the final amplifier.



1 G Holst; BDH Tellegen – Pentode

2 A Bouwers – X-ray tube

Publications

1 Der Niedervoltbogen

MJ Druyvesteyn

ZEITSCHRIFT FÜR PHYSIK **64**, 781-798 (1930)

Times Cited: **597**

2 Über die Stromung sehr verdünnter Gase durch Rohren von beliebiger Länge

P Clausing

ANNALEN DER PHYSIK **12**, 961-989 (1932)

Times Cited: **407**

3 On relaxation-oscillations. I

B van der Pol

PHILOSOPHICAL MAGAZINE **2**, 978-992 (1926)

Times Cited: **369**



FM Penning



B van der Pol

4 Forced oscillations in a circuit with non-linear resistance

B van der Pol

PHILOSOPHICAL MAGAZINE **3**, 65-80 (1927)

Times Cited: **362**

5 The heartbeat considered as a relaxation-oscillation and an electrical model of the heart

B van der Pol; J van der Mark

PHILOSOPHICAL MAGAZINE **6**, 763-775 (1928)

Times Cited: **318**

6 Über die Strahlformung bei der Molekularstromung

P Clausing

ZEITSCHRIFT FÜR PHYSIK **66**, 471-476 (1930)

Times Cited: **190**

7 Frequency demultiplication

B van der Pol; J van der Mark

NATURE **120**, 363-364 (1927)

Times Cited: **186**

8 Über den Zusammenhang zwischen Deformationsvorgang und Rekristallisationstextur bei Aluminium

WG Burgers; exper. PC Louwerse

ZEITSCHRIFT FÜR PHYSIK **67**, 605-678 (1931)

Times Cited: **160**

9 Über Ionisation durch metastabile Atome

FM Penning

NATURWISSENSCHAFTEN **15**, 818 (1927)

Times Cited: **147**

10 Darstellung von reinem Titanium-, Zirkonium-, Hafnium- und Thoriummetall

AE van Arkel; JH de Boer

ZEITSCHRIFT FÜR ANORGANISCHE UND ALLGEMEINE CHEMIE **148**, 345-350 (1925)

Times Cited: **146**

Der Niedervoltbogen.

Von M. J. Druyvesteyn in Eindhoven (Holland).

Mit 8 Abbildungen. (Eingegangen am 26. Juli 1930.)

Zwei Theorien des Niedervoltbogens werden besprochen, und zwar die Theorie von Holst und Oosterhuis und die von Compton und Eckart. Diese letztere wurde etwas erweitert und als die wahrscheinlichste Erklärung des Niedervoltbogens betrachtet. Die Erweiterung besteht in der Annahme einer Energieübertragung von schnellen auf langsame Elektronen; diese Wechselwirkung zwischen Elektronen wird bei großer Elektronenkonzentration (größer als 10^{17}) häufig auftreten müssen. Sodann wurde das Spektrum des Ar-Niedervoltbogens besprochen. An Ar- und Ne-Niedervoltbogen wurden Sondennmessungen vorgenommen, wobei ein Potentialmaximum von ungefähr 11,4 Volt (in bezug auf die Spannung der Kathode) bei Ar und 18,5 Volt bei Ne gefunden wurde, entsprechend der Anregungsspannung der 1s-Niveaus bei Ar (11,7 Volt) und der 2p-Niveaus bei Ne (18,5 Volt). Die höchste Elektronenkonzentration beträgt ungefähr $2 \cdot 10^{18}$ Elektronen/cm³. Die Sondentheorie von Langmuir und Motl-Smith wird erweitert. Mit der Formel (3) in § 5 kann man aus der Sondencharakteristik durch zweimaliges Differenzieren die Geschwindigkeitsverteilung der Elektronen finden.

§ 1. Einleitung. Ein Niedervoltbogen ist eine Gasentladung mit glühender Kathode, wobei die Spannung zwischen Kathode und Anode kleiner ist als die Anregungsspannung der Gasatome*. Holst und Oosterhuis** fanden 1924, daß die Spannung des Niedervoltbogens konstant sein kann, d. h. es kann ein nichtoszillierender Niedervoltbogen bestehen. In dieser Arbeit will ich mich auf den nichtoszillierenden Niedervoltbogen beschränken. Nach Holst und Oosterhuis ist der folgende Vorgang für das Bestehen des Niedervoltbogens wesentlich: Ein positives Ion rekombiniert sich mit einem Elektron, jedoch ohne Strahlungsemission, wobei die frei werdende Energie sich auf ein anderes Elektron überträgt. Dies Elektron kann nun ein Gasatom ionisieren. In § 2 werde ich die Theorie von Holst und Oosterhuis in eine Formel bringen. Daraus ergibt sich, daß die Zahl nichtstrahlender Rekombinationen zu gering ist, um das Bestehen des Niedervoltbogens genügend zu erklären.

1925 haben Compton und Eckart*** eine andere Erklärung für den Niedervoltbogen gegeben. Sie nehmen an, daß das Potential des Raumes zwischen den Elektroden nicht zwischen dem Potential der Anode und dem der Kathode liegt, sondern daß eine so starke positive Raumladung

* Andere Autoren nennen diese Entladung einen abnormen Niedervoltbogen.
** G. Holst und E. Oosterhuis, *Physica* **4**, 42, 1924.
*** K. T. Compton and C. Eckart, *Phys. Rev.* **25**, 139, 1925.

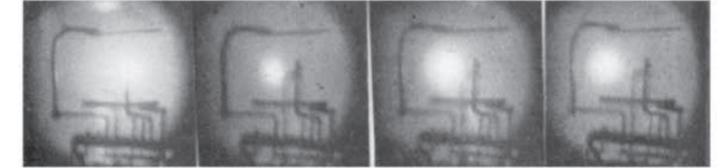


Fig. 2.

Niedervoltbogen in Neon; die zwei horizontalen Anoden sieht man auf der Seite, wie auch die indirekt geheizte Kathode. Von links nach rechts ist I, $i_g = 1,24 \text{ \AA}$, $i_b = 0,1 \text{ \AA}$, $V_b = 22 \text{ Volt}$. II, $i_g = 1,36 \text{ \AA}$, $i_b = 0,1 \text{ \AA}$, $V_b = 13 \text{ Volt}$. III, $i_g = 1,48 \text{ \AA}$, $i_b = 0,5 \text{ \AA}$, $V_b = 9 \text{ Volt}$. IV, $i_g = 1,69 \text{ \AA}$, $i_b = 0,5 \text{ \AA}$, $V_b = 9 \text{ Volt}$. i_g ist der Strom durch den Glühfaden der Kathode, i_b und V_b sind Bogenstrom und -spannung. Bei I ist das Licht um die Kathode konzentriert, bei III und IV sieht man ein freischwebendes Kugelchen.

1 MJ Druyvesteyn - Der Niedervoltbogen

From the PHILOSOPHICAL MAGAZINE, vol. VI, Suppl. November 1928.

The Heartbeat considered as a Relaxation Oscillation, and an Electrical Model of the Heart. By BALTH. VAN DER POL, D.Sc., and J. VAN DER MARK*.

[Plates X.-XII.]

1. Relaxation Oscillations.

THE equation $\ddot{v} - \alpha(1-v^2)\dot{v} + \omega^2 v = 0 \dots (1)$

is representative of an oscillatory system of which the resistance is a function of the elongation. When α is a positive quantity the system has a resistance which for a small amplitude is negative. Therefore, the position

$$v=0$$

is unstable. When, further,

$$\alpha^2 \gg \omega^2, \dots (2)$$

it is obvious that as long as

$$v^2 \ll 1,$$

the variable v will initially leave the value $v=0$ in an aperiodic way, but when later

$$v^2 > 1,$$

the resistance has changed its sign and has become positive and, therefore, v will have the tendency to go back again towards $v=0$. The possibility of (1) even with the condition (2) having still a purely periodic solution is made plausible by the above considerations, and a full description of the solutions of (1) was given by one of the present authors some years ago†.

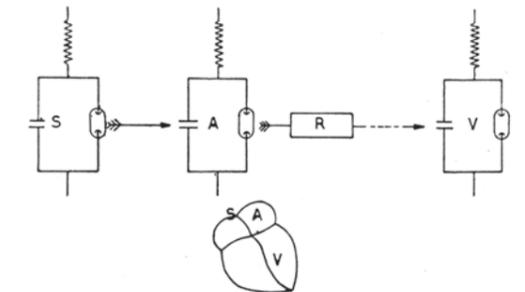
It followed from the research mentioned that the fundamental period T_{rel} of the solution of (1) with the condition (2) is

$$T_{rel} = 1.61 \frac{\alpha}{\omega^2}.$$

* A more detailed account of these considerations will appear in the next issue of *L'Onde Electrique*.

† Balth. van der Pol, *Phil. Mag.* ii, p. 978 (1926); *Jarhb. d. dr. Tel. (Zs. f. Hochfreq. Technik)* xxviii, p. 178 (1926), xxix, p. 114 (1927).

Fig. 3.



Schematic representation of the heart by three relaxation systems: S (=Sinus), A (=Auriculum), and V (=Ventriculum). R is a retardation system representing in the model the finite time necessary for a stimulus to be transmitted through the A-V bundle.

5 B van der Pol; J van der Mark - The heartbeat considered as a relaxation-oscillation and an electrical model of the heart

1934 – 1943

Patents

1 High pressure mercury vapour lamp

C Bol; W Ellenbaas; HJ Lemmens
US patent 2.094.694 (1934)

2 Rectifying device

FM Penning
US Patent 2.182.736 (1936)

3 Permanent Magnet

GB Jonas
US Patent 2.295.082 (1938)

4 Philishave rotary electric shaver

A Horowitz; A van Dam
US Patent 2.308.920 (1939)

5 Electron Discharge Device

JH de Boer
US Patent 2.159.946 (1939)

6 Ferroxcube

JL Snoek
US Patent 2.452.529 (1941)



C Bol



A Horowitz



HJ Lemmens

UNITED STATES PATENT OFFICE

2,094,694

VAPOR ELECTRIC DISCHARGE DEVICE AND METHOD OF OPERATION

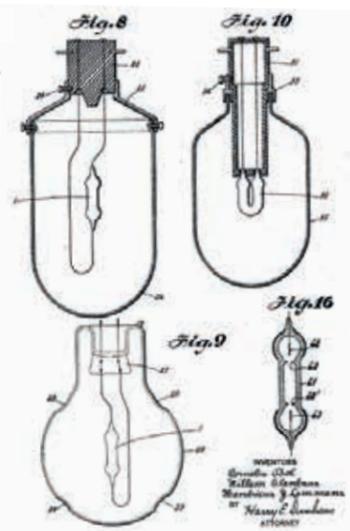
Cornelis Bol, and Willem Ellenbaas and Hendricus J. Lemmens, Eindhoven, Netherlands, assignors to General Electric Company, a corporation of New York

Application October 25, 1935, Serial No. 46,952
In Germany November 5, 1934

12 Claims. (Cl. 176-122)

Our invention relates to vapor electric discharge devices and includes improvements in both the apparatus and the method of operation.

Among the objects of our invention are to produce luminous vapor electric discharge devices of good color operating with a high degree of efficiency and with an extraordinarily high surface brightness or intrinsic brilliancy. Further objects are to provide constructions and methods of operation which enable extremely high vapor pressures to be used.



1 C Bol; W Ellenbaas; HJ Lemmens – High pressure mercury vapor lamp

Patented Jan. 19, 1943

2,308,920

UNITED STATES PATENT OFFICE

2,308,920

HAIR CUTTING DEVICE

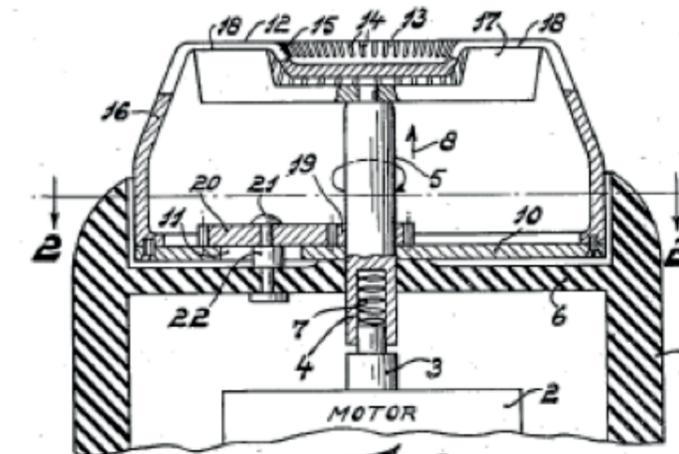
Alexandre Horowitz and Alexis van Dam, Eindhoven, Netherlands, assignors, by mesne assignments, to Hartford National Bank and Trust Company, Hartford, Conn., as trustee

Application February 23, 1940, Serial No. 320,484
In Germany February 23, 1939

4 Claims. (Cl. 30-43)

The present application, which is a continuation-in-part of our co-pending U. S. application S. N. 303,290, filed November 7, 1939, patented May 19, 1942, No. 2,283,834, relates to hair cutting or shaving devices having a shaving head consisting of an apertured, for instance slitted, cutting or shear plate and a rotary, preferably electrically-driven, cutter.

In our above-mentioned application we proposed to move the shear plate, for instance rotate the same, at a speed which is much less than that of the cutter in order that the hairs may be caught in the slits and cut in a better manner than in devices using a stationary cutting plate. However, we have found that when the plate is rotated continuously, it frequently happens that some hairs are not cut.



4 A Horowitz; A van Dam – Philishave rotary electric shaver

Publications

1 **The London - van der Waals attraction between spherical particles**

HC Hamaker

PHYSICA **4**, 1058-1072 (1937)

Times Cited: **1884**

2 **Electronic conduction of magnetite (Fe3O4) and its transition point at low temperatures**

EJW Verwey

NATURE **144**, 327-328 (1939)

Times Cited: **671**

3 **Electronic conductivity and transition point of magnetite (Fe3O4)**

EJW Verwey

Physica **8**, 979-987 (1941)

Times Cited: **616**

4 **Mechanism of electrical discharges in gases of low pressure**

MJ Druyvesteyn; FM Penning

REVIEWS OF MODERN PHYSICS **12**, 87-174 (1940)

Times Cited: **427**



HC Hamaker



JL Snoek

5 **Effect of small quantities of carbon and nitrogen on the elastic and plastic properties of iron**

JL Snoek

PHYSICA **8**, 711-733 (1941)

Times Cited: **425**

6 **Cation arrangement in a few oxides with crystal structures of the spinel type**

EJW Verwey; JH de Boer

RECUEIL DES TRAVAUX CHIMIQUES DES PAYS-BAS **55**,

531-540 (1936)

Times Cited: **268**

7 **The non-linear theory of electric oscillations**

B van der Pol.

PROCEEDINGS OF THE INSTITUTE OF RADIO

ENGINEERS **22**, 1051-1086 (1934)

Times Cited: **264**

8 **Die Glimmentladung bei niedrigem Druck zwischen koaxialen Zylindern in einem axialen Magnetfeld**

FM Penning

PHYSICA **3**, 873-894 (1936)

Times Cited: **248**

9 **Semi-conductors with partially and with completely filled 3d-lattice bands**

JH de Boer; EJW Verwey

PROCEEDINGS OF THE PHYSICAL SOCIETY **49**,

59-71 (1937)

Times Cited: **230**

10 **Heat dissipation of parallel plates by free convection**

W Elenbaas

PHYSICA **9**, 1-28 (1942)

Times Cited: **220**

11 **The propagation of radio waves over a finitely conducting spherical earth**

B van der Pol; H Bremmer

PHILOSOPHICAL MAGAZINE **171**, 817-834, (1938)

Times Cited: **27**

THE LONDON—VAN DER WAALS ATTRACTION BETWEEN SPHERICAL PARTICLES

by H. C. HAMAKER

Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken Eindhoven-Holland

Summary

Frequently we experience the existence of adhesive forces between small particles. It seems natural to ascribe this adhesion for a large part to London-van der Waals forces. To obtain general information concerning their order of magnitude the London-van der Waals interaction between two spherical particles is computed as a function of the diameters and the distance separating them. A table is calculated which enables numerical application of the formulae derived. Besides approximations are added, which may be used when the distance between the particles is small. In a separate section it is investigated how the results must be modified, when both particles are immersed in a liquid. Here we are led to the important conclusion that even in that case London-van der Waals forces generally cause an attraction.

§ 1. Introduction. Frequently we experience the existence of adhesive forces between small particles of any substance or between a particle and a surface. Of this the general occurrence of flocculation in colloidal systems is one of the most striking examples.

It seems natural, to date, to attribute this adhesion mainly to London-van der Waals forces and it may be of interest to possess formulae from which the magnitude and range of these forces can be estimated. It is the purpose of this paper to provide some data which may be used for such computations. To simplify the calculations we will consider spherical particles only; in practical problems the particles will mostly be of irregular shape; in such cases the formulae derived below must be applied with caution, a question that will be discussed more in detail in a subsequent paper¹⁾.

The energy of interaction between two particles containing q atoms per cm^3 is given by:

$$E = - \int_{v_1}^{v_1 + \Delta v_1} \int_{v_2}^{v_2 + \Delta v_2} \frac{q^2 \lambda}{r^6} \quad (1)$$

$$- 1058 -$$

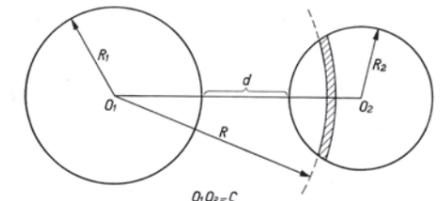


Fig. 2.

With respect to a second sphere of radius R_2 , the centres being a distance C apart, the same method may be applied and we obtain for the total energy of interaction (compare fig. 2):

$$E = \int_{C-R_2}^{C+R_2} E_p q \pi \frac{R}{C} \{R_2^2 - (C-R)^2\} dR =$$

$$= \frac{-\pi^2 q^2 \lambda}{C} \int_{C-R_2}^{C+R_2} \{R_2^2 - (C-R)^2\} dR \int_{R-R_1}^{R+R_1} \frac{\{R_1^2 - (R-r)^2\} dr}{r^5} \quad (6)$$

1 HC Hamaker – The London - van der Waals attraction between spherical particles

WITH COMPLIMENTS

from
Laboratoria der N. V. Philips' Gloeilampenfabrieken,
Eindhoven, Holland.

(Reprinted from NATURE, Vol. 144, page 327, August 19, 1939.)

Electronic Conduction of Magnetite (Fe₃O₄) and its Transition Point at Low Temperatures

We have measured the electronic conductivity, down to liquid nitrogen temperature, of a number of iron oxides of the homogeneous 'Fe₃O₄' phase, especially as a function of the exact stoichiometric composition of the material. This seemed of theoretical interest for several reasons:

(a) Fe₃O₄ is an abnormally good conductor among the semi-conductors with partially filled lattice bands¹.

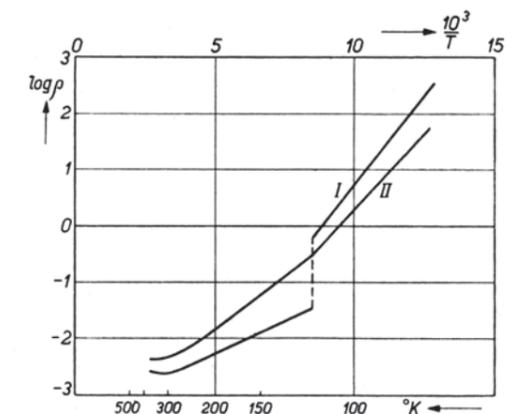
(b) Fe₃O₄ has a very remarkable crystal structure involving a probably statistical distribution of both Fe²⁺ and Fe³⁺ ions at equivalent lattice points².

(c) There are indications that Fe₃O₄ shows a transition point in the neighbourhood of 120° K. Anomalies in the magnetic behaviour³ at 120° K., in the specific heat⁴ and in the lattice constant⁴ at 114° K., have been found. The magnetic anomaly, however, depends on the mode of preparation⁵.

We thought it possible that the statistical distribution of Fe²⁺ and Fe³⁺, which is a statistical distribution of electrons about the double number of lattice points containing Fe²⁺, and which accounts for the rather high electronic conductivity of magnetite, would lead to some type of order at lower temperatures. A transition of this kind would probably offer an explanation of the anomalies at 120° K. One would expect such a transition to be very sensitive to the ratio Fe : O in the crystal, since an excess of oxygen (solid solutions of Fe₃O₄ and γ-Fe₂O₃) would imply: (a) vacant lattice points in the 16-fold position⁶ containing, in stoichiometrically pure Fe₃O₄, 8 Fe²⁺ + 8 Fe³⁺, and (b) an increase of the ratio Fe²⁺ : Fe³⁺ at this lattice position; both factors would be unfavourable with respect to order. For the irregularities found by Hilpert and Forrer this would supply an explanation more satisfactory than that put forward by these authors.

Furthermore, one would expect that such a transition, involving the conducting electrons, would be accompanied by very pronounced effects in the specific resistance at the transition temperature.

Actually we have found a strong discontinuity in the resistivity curves of some Fe₃O₄ samples, and a considerable influence of the ratio Fe : O.



The accompanying graph shows $\log \rho$ against $1/T$ for two bars: I with $\text{FeO} : \text{Fe}_2\text{O}_3 = 1 : 1.025$, and II with $\text{FeO} : \text{Fe}_2\text{O}_3 = 1 : 1.08$. All details of the curves are in full accordance with the picture proposed above for the nature of the transition and our concept of the cation arrangement in the Fe₃O₄ (and the γ-Fe₂O₃) lattice. In further support of our views, we found that sample I shows a distinct drop in the susceptibility for weak magnetic fields at about 117° K., whereas with sample II the corresponding effect is much weaker.

3 EJW Verwey – Electronic conduction of magnetite (Fe3O4) and its transition point at low temperatures

1944 – 1953

Patents

1 **Vorrichtung zur Verstaerkung kleiner Spannungen**

mit einer elektrischen Entladungsroehre

AJW Overbeek

DE 809220c1 (1944)

2 **Gyrator**

BDH Tellegen

US Patent 2.647.238 (1947)

3 **L-Cathode**

HJ Lemmens; MJ Jansen; R Loosjes

US Patent 2.543.728 (1947)

4 **Deltamodulation**

JF Schouten; F de Jager; JH Greefkes

US Patent 2.662.118 (1948)

5 **Ferroxdure**

JJ Went; GW van Oosterhout; EW Gorter

US Patent 2.762.777 (1950)

6 **X-ray image intensifier tube**

MC Teves; T Tol

US Patent 2.757.293 (1951)



BDH Tellegen

UNITED STATES PATENT OFFICE

2,647,238

PASSIVE FOUR TERMINAL NETWORK FOR GYRATING A CURRENT INTO A VOLTAGE

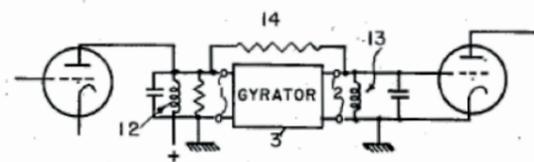
Bernardus Dominicus Hubertus Tellegen, Eindhoven, Netherlands, assignor to Hartford National Bank and Trust Company, Hartford, Conn., as trustee

Application March 6, 1948, Serial No. 13,506
In the Netherlands April 29, 1947

4 Claims. (Cl. 333—24)

For the impedance elements connected between the terminals of a passive electrical quadrupole or four terminal network use has hitherto been limited to inductances (L), resistances (R), capacities (C) and ideal transformers as the basic circuit elements. The first three elements are dipoles, the relation between the instantaneous values of the current i passing through and the voltage v set up across the elements being given by

$$v = L \frac{di}{dt}; v = iR \text{ and } v = \int \frac{i}{C} dt$$



2 BDH Tellegen – Gyrator

United States Patent Office

2,757,293
Patented July 31, 1956

2,757,293

LUMINOSCOPE

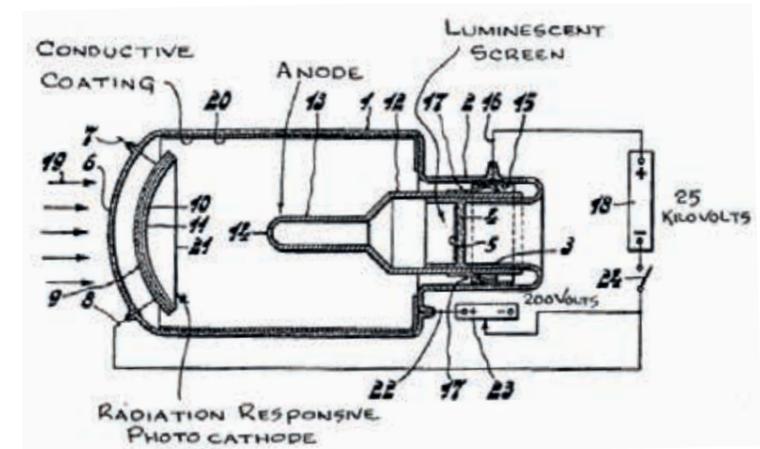
Marten Cornelis Teves and Taeke Tol, Eindhoven, Netherlands, assignors to Hartford National Bank and Trust Company, Hartford, Conn., as trustee

Application August 29, 1952, Serial No. 306,974

Claims priority, application Netherlands
September 26, 1951

3 Claims. (Cl. 250—213)

This invention relates to "luminoscopes," i. e., a device for converting an infra-red or X-ray image into a luminescent image having a different wavelength or a higher degree of brightness.



6 MC Teves; T Tol – X-ray image intensifier tube

Publications

1 **On the attraction between two perfectly conducting plates**

HBG Casimir

PROC KONINKLIJKE NEDERLANDSE AKADEMIE VAN WETENSCHAPPEN **51**, 793-795 (1948)

Times Cited: **1946**

2 **The influence of retardation on the London - van der Waals forces**

HBG Casimir; D Polder

PHYSICAL REVIEW **73**, 360-372 (1948)

Times Cited: **1554**

3 **Ferromagnetic compounds of manganese with perovskite structure**

GH Jonker; JH van Santen

PHYSICA **16**, 337-349 (1950)

Times Cited: **1350**



HBG Casimir



EJW Verwey

4 **On the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies**

CG Koops

PHYSICAL REVIEW **83**, 121-124 (1951)

Times Cited: **817**

5 **Physical properties and cation arrangement of oxides with spinel structures. I: Cation arrangement in spinels**

EJW Verwey; EL Heilmann

JOURNAL OF CHEMICAL PHYSICS **15**, 174-180 (1947)

Times Cited: **605**

6 **On Onsager's principle of microscopic reversibility**

HBG Casimir

REVIEWS OF MODERN PHYSICS **17**, 343-350 (1945)

Times Cited: **547**

7 **Physical properties and cation arrangement of oxides with spinel structures. II: Electronic conductivity**

EJW Verwey

JOURNAL OF CHEMICAL PHYSICS **15**, 181-187 (1947)

Times Cited: **494**

8 **Magnetic compounds with perovskite structure III: Ferromagnetic compounds of cobalt**

GH Jonker; JH van Santen

PHYSICA **19**, 120-130 (1953)

Times Cited: **420**

9 **Controlled-valency semiconductors**

EJW Verwey; PW Haaijman; FC Romeijn;

GW van Oosterhout

PHILIPS RESEARCH REPORTS **5**, 173-187 (1950)

Times Cited: **387**

10 **The effective permeability of mixtures of solids**

D Polder; JH van Santen

PHYSICA **12**, 257-271 (1946)

Times Cited: **330**

H. B. G. CASIMIR: *On the attraction between two perfectly conducting plates.*

(Communicated at the meeting of May 29, 1948.)

In a recent paper by POLDER and CASIMIR ¹⁾ it is shown that the interaction between a perfectly conducting plate and an atom or molecule with a static polarizability α is in the limit of large distances R given by

$$\delta E = -\frac{3}{8\pi} \hbar c \frac{\alpha}{R^4}$$

and that the interaction between two particles with static polarizabilities α_1 and α_2 is given in that limit by

$$\delta E = -\frac{23}{4\pi} \hbar c \frac{\alpha_1 \alpha_2}{R^7}.$$

$$\delta E/L^2 = -\hbar c \frac{\pi^2}{24 \times 30} \cdot \frac{1}{a^3}$$

1 HBG Casimir - On the attraction between two perfectly conducting plates

Physica XVI, no 3

Maart 1950

FERROMAGNETIC COMPOUNDS OF MANGANESE WITH PEROVSKITE STRUCTURE

by G. H. JONKER and J. H. VAN SANTEN

Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken
Eindhoven - Netherlands

Summary

Various manganites of the general formula $\text{La}^{3+}\text{Mn}^{3+}\text{O}_3^{2-} - \text{Me}^{2+}\text{Mn}^{4+}\text{O}_3^{2-}$ have been prepared in the form of polycrystalline products. Perovskite structures were found, i.a. for all mixed crystals $\text{LaMnO}_3 - \text{CaMnO}_3$, for $\text{LaMnO}_3 - \text{SrMnO}_3$ containing up to 70% SrMnO_3 , and for $\text{LaMnO}_3 - \text{BaMnO}_3$ containing less than 50% BaMnO_3 . The mixed crystals with perovskite structure are ferromagnetic. Curves for the Curie temperature versus composition and saturation versus composition are given for $\text{LaMnO}_3 - \text{CaMnO}_3$, $\text{LaMnO}_3 - \text{SrMnO}_3$, and $\text{LaMnO}_3 - \text{BaMnO}_3$. Both types of curves show maxima between 25 and 40% $\text{Me}^{2+}\text{Mn}^{4+}\text{O}_3^{2-}$; here all 3d electrons available contribute with their spins to the saturation magnetization. The ferromagnetic properties can be understood as the result of a strong positive $\text{Mn}^{3+} - \text{Mn}^{4+}$ exchange interaction combined with a weak $\text{Mn}^{3+} - \text{Mn}^{3+}$ interaction and a negative $\text{Mn}^{4+} - \text{Mn}^{4+}$ interaction. The $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ interaction, presumably of the indirect exchange type, is thought to be the first clear example of positive exchange interaction in oxidic substances.

1. *Introduction.* During our investigations ¹⁾ into the occurrence of the perovskite structure we prepared i.a. compounds of the general formula $A^{3+}B^{3+}O_3^{2-}$. One of these, LaMnO_3 , showed ferromagnetic properties at liquid-air temperature, whereas LaCrO_3 and LaFeO_3 did not. It appeared, however, that LaMnO_3 was ferromagnetic at this temperature only when it contained some manganese of a valency higher than three; by a suitable thermal treatment in an oxygen atmosphere, the substance took up more oxygen and Curie temperatures up to 210°K were found. A similar increase of valency of Mn was realized by preparing mixed crystals $\text{La}^{3+}\text{Mn}^{3+}\text{O}_3^{2-} - \text{Me}^{2+}\text{Mn}^{4+}\text{O}_3^{2-}$ ($\text{Me}^{2+} = \text{large divalent ion}$). An

— 337 —

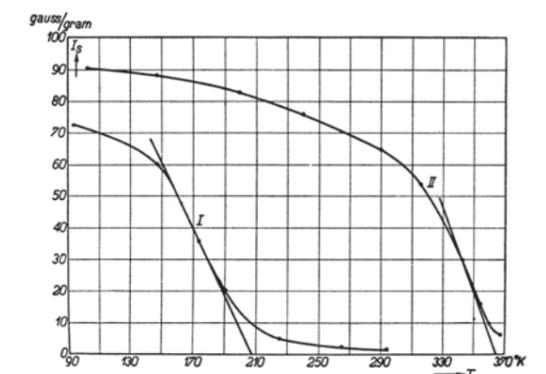


Fig. 3. Saturation magnetization I_s as a function of temperature T for mixed crystals $(\text{La}_{0.90}\text{Sr}_{0.10})\text{MnO}_3$ (I) and $(\text{La}_{0.70}\text{Sr}_{0.30})\text{MnO}_3$ (II).

8 GH Jonker et al. - Ferromagnetic compounds of manganese with perovskite structure



1923 Philips Natlab at Kastanjelaan Eindhoven

1954 – 1963

Patents

1 Gallium emitter

LJ Tummers; PW Haayman
US Patent 3.078.397 (1954)

2 Cathode-Ray Tube

J Haantjes; GJ Lubben
US Patent 2.866.125 (1954)



G Bouwhuis



EF de Haan



JA Haringx

3 Deplistor

OW Memelink
US Patent 3.081.404 (1958)

4 Spiral groove bearing

JA Haringx; EA Muijderman; H Rinia
US Patent 3.154.353 (1960)

5 Colour beam splitter

H de Lang; G Bouwhuis
US Patent 3.202.039 (1960)

6 Plumbicon

EF de Haan; PPM Schampers; JHN van Vucht
US Patent 3.372.056 (1963)

United States Patent Office 3,154,353
Patented Oct. 27, 1960

3,154,353
AXIAL THRUST BEARING FOR ROTARY SHAFT
Johannes Adrianus Haringx, Everhardus Albertus Muijderman, and Herre Rinia, all of Emmasingel, Eindhoven, Netherlands, assignors to North American Philips Company, Inc., New York, N.Y., a corporation of Delaware
Filed June 29, 1961, Ser. No. 120,779
Claims priority, application Netherlands July 23, 1960
8 Claims. (Cl. 308—9)

This invention relates to an axial thrust bearing for shaft rotating in a medium, comprising a fixed support member having a rotation-symmetrical cavity the generatrix of which is a curved line and the axis of rotation of which coincides with centre line of the shaft, when the shaft has a central thrust member co-acting with the supporting member during operation and the co-acting surfaces of the two members have the same shape. Su

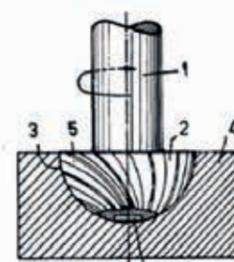


FIG. 1

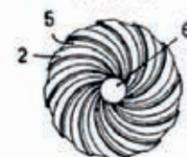


FIG. 2

4 JA Haringx; EA Muijderman; H Rinia – Spiral groove bearing

United States Patent Office

3,372,056
Patented Mar. 5, 1968

3,372,056
METHOD OF MANUFACTURING A PHOTORESPONSIVE DEVICE COMPRISING A PHOTORESPONSIVE PbO LAYER

Edward Fokko de Haan, Paulus Philippus Maria Schampers, and Johannes Hendrikus Nicolaas van Vucht, Emmasingel, Eindhoven, Netherlands, assignors to North American Philips Company, Inc., New York, N.Y., a corporation of Delaware

Filed Mar. 10, 1964, Ser. No. 350,713

Claims priority, application Netherlands, Mar. 12, 1963, 290,119

30 Claims. (Cl. 117—200)

ABSTRACT OF THE DISCLOSURE

A method of making a photoresponsive device, in particular a television camera tube, employing a layer of PbO in which the PbO is vapor-deposited and subjected to the action of oxygen in combination with water vapor, hydrogen sulfide, tellurated or seleniated hydrogen to render the layer of PbO photo-sensitive.

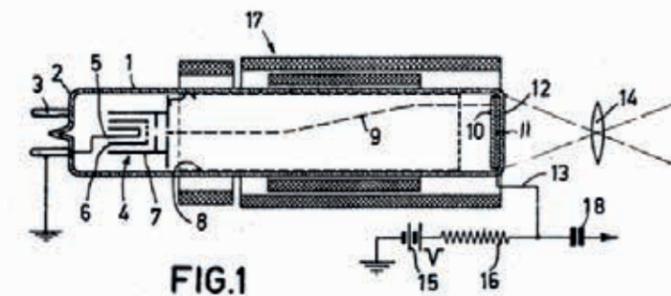


FIG. 1

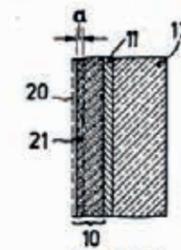


FIG. 2

6 EF de Haan; PPM Schampers; JHN van Vucht – Plumbicon

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1 Relations between the concentrations of imperfections in crystalline solids

FA Kröger; HJ Vink

SOLID STATE PHYSICS **3**, 307-435 (1956)

Times Cited: **1034**

2 Ferrites

J Smit; HPJ Wijn

PHILIPS TECHNICAL LIBRARY, 373 pages (1959)

Times Cited: **1032**

3 Topotactical reactions with ferrimagnetic oxides having hexagonal crystal structures. I

FK Lotgering

JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY **9**, 113-123 (1959)

Times Cited: **974**

4 Experimental and theoretical study of the domain configuration in thin layers of BaFe12O19

C Kooy; U Enz,

PHILIPS RESEARCH REPORTS **15** (1), 7-29 (1960)

Times Cited: **658**

5 Saturation magnetization and crystal chemistry of ferrimagnetic oxides

EW Gorter

PHILIPS RESEARCH REPORTS **9** (4), 295-320 (1954)

Times Cited: **453**

6 Magnetic compounds with perovskite structure. 4: Conducting and non-conducting compounds

GH Jonker

PHYSICA **22**, (8), 707-722 (1956)

Times Cited: **422**

7 Ferromagnetic resonance absorption in BaFe12O19, a highly anisotropic crystal

J Smit.; HG Beljers

PHILIPS RESEARCH REPORTS **10** (2), 113-130 (1955)

Times Cited: **419**

8 On the permeation of hydrogen and helium in single crystal silicon and germanium at elevated temperatures

A van Wieringen; N Warmoltz

PHYSICA **22** (10), 849-865 (1956)

Times Cited: **418**

9 Dislocations in the diamond lattice

J Hornstra

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS **5**, 129-141 (1958)

Times Cited: **410**

10 Correlation factors for diffusion in solids

K Compaan; Y Haven

TRANSACTIONS OF THE FARADAY SOCIETY **52** (6), 786-801 (1956)

Times Cited: **393**



K Compaan

Relations between the Concentrations of Imperfections in Crystalline Solids

F. A. KRÖGER AND H. J. VINK

Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven-Netherlands

I. Pure Stoichiometric Compounds.....	310
1. Atomic Disorder.....	310
2. Electronic Disorder.....	315
a. Electronic Disorder Not Involving Atomic Imperfections.....	315
b. Electronic Disorder Involving Atomic Imperfections.....	318
3. Complete Equilibrium Involving Both Electronic and Atomic Disorder.....	323
a. Equilibrium at High Temperatures.....	324
b. Processes Taking Place during Cooling.....	325
4. Migration of Atomic Imperfections; Ionic Conductivity.....	326
5. Electronic Conductivity Arising from Lattice Defects.....	328
II. Nonstoichiometric Compounds.....	329
6. Introduction.....	329
7. Reactions Involving Crystal and Vapor.....	329
8. Complete Equilibrium Crystal-Vapor for a Simple Case with Frenkel Disorder.....	333
9. A Method for Obtaining an Approximate Solution of Multi-Equation Relations Such as Those of Section 8.....	335
10. Complete Equilibrium between Crystal and Vapor for a Crystal Containing Completely Ionized Frenkel Defects.....	342
11. A More Complicated Case of Schottky-Wagner Disorder.....	344
12. Equilibrium between Crystal and Vapor for a Crystal MX with Antistructure Disorder.....	347
a. Pure Antistructure Disorder.....	347
b. Combination of Antistructure and Schottky-Wagner Disorder.....	349
13. Cooling; the State of the Crystals at Low Temperatures.....	352
14. The Deviation from the Simple Stoichiometric Ratio as a Function of the Atmosphere.....	357
15. The Position of the Fermi Level.....	360
16. Practical Limitations.....	362
17. Comparison with Experiment.....	363
18. The Effect of Heating in a Stream of Inert Gas.....	369
19. Equilibria Vapor-Liquid and Solid-Liquid.....	370
20. Surface Layers.....	372
III. Crystals Containing Foreign Atoms.....	373
21. Introduction.....	373

307

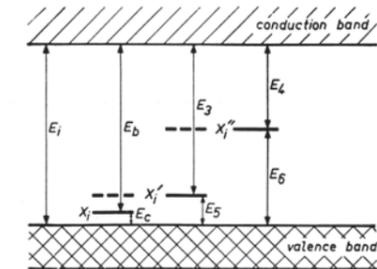


Fig. 3. A possible electronic energy level scheme of a crystal of composition MX containing interstitial X atoms.

1 FA Kröger et al. - Relations between the concentrations of imperfections in crystalline solids

R 248

Philips Res. Rep. 9, 295-320, 1954

SATURATION MAGNETIZATION AND CRYSTAL CHEMISTRY OF FERRIMAGNETIC OXIDES *)

by E. W. GORTER

621.317.421:548.3:548.736.453.2

Summary

Measurements of the saturation magnetization (σ) against temperature are carried out for a number of mixed crystal oxides with spinel structure. The results are in agreement with Néel's theory of ferrimagnetism: the resultant magnetic moment m is the difference of the moments of the tetrahedral (A) and octahedral (B) sublattices, either (a) with complete parallelism of the ionic moments inside each sublattice, or (b) with angles between the ionic moments inside one of the sublattices. The spinel structure is described in section 1.1, experimental and theoretical data from literature on cation distribution are summarized in section 1.2. Néel's theory is reviewed in section 2.2.1, with Yafet and Kittel's modification (section 2.2.2). When the moments of the two sublattices are approximately equal, Néel predicts a number of anomalous σ - T curves. All of these should occur in a series of mixed crystals of type (a) in which the resultant moment m changes sign. Our experimental methods are given in section 3. The measurements on the single ferrites $MgFe_2O_4$, with $M^{II} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}$ or $(0.5 Li^{2+} + 0.5 Fe^{2+})$ show that these belong to group (a); the mixed crystals $M_{1-a}Zn_aFe_2O_4$ with $a > \text{appr. } 0.4$ belong to group (b) (section 4). The moment of $Ca_{0.5}Zn_{0.5}Fe_2O_4$ is higher than that of any $MgZn$ ferrite, perhaps because the angle $A-O-B$ is increased by the presence of the greater part of the large Ca ions in the B sites, thus increasing the AB interaction; this behaviour would be in agreement with Anderson's theory (section 5.1; Anderson's theory is reviewed in section 2.3.2). The moments of ferrimagnetic oxides with other crystal structures may be predicted from the angles (metal ion)-(O²⁻ ion)-(metal ion); cf. $BaFe^{III}_4O_{10}$ and $KFe^{III}_4O_{12}$ (section 5.2). In a number of mixed-crystal series anomalous σ - T curves have been looked for: these are not found in the systems $Ni_{1-a}Fe^{III}_aTi_2O_4$ and $Ni_{1-a}Zn_aFe^{III}_aTi_2O_4$ because of the unexpected presence of Ti^{4+} ions in tetrahedral sites, proved for $Ni_{1-a}Fe^{III}_aTi_2O_4$ by measurements of the effective g -factor (section 6.1-2). In the system $Li_{1-a}Fe^{III}_aCr_2O_4$ ($0 < a < 2/3$) the distribution of the Li^{2+} and Fe^{2+} ions is anomalous as a result of short-range order. The resultant moment remains positive, and only one type of anomalous σ - T curve, viz. that for which the spontaneous magnetization changes sign with temperature, occurs in a wide range of compositions. For $a \leq 1/25$ the materials belong to group (a) (section 7). A change of sign of the resultant moment does occur in the system $NiFe^{III}_2Al_2O_4$. Anomalous σ - T curves are here found in a narrow range of compositions, but not all types predicted by Néel; the reasons are discussed (section 8). The presence of Mn^{2+} ions apparently promotes the formation of angles between the ionic moments in B sites; the complete system $MnFe^{III}_2Cr_2O_4$ belongs to group (b) (section 9), as well as $MnFe_2O_4$ prepared by other authors (section 4) and part of the system $Ni_{1-a}Mn_aFe^{III}_aTi_2O_4$ (section 6.3). In the first-named system m probably changes sign only as a result of these angles.

*) Thesis, University of Leyden, June 1954.

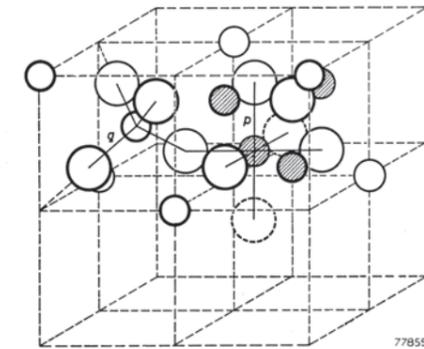


Fig. 1. Unit cell of spinel structure. The position of the ions in only two octants is shown. The dashed circles belong to other octants. The drawn lines indicate the fourfold and sixfold coordination of the respective metal-ion positions. $x = 0 - \frac{1}{2}$ $x = \frac{1}{2} - \frac{1}{2}$ $x = \frac{1}{2} - 1$. Large circles: oxygen ions; small hatched circles: metal ions at octahedral sites; small unhatched circles: metal ions at tetrahedral sites. The figure is drawn for $u = \frac{1}{2}$.

5 EW Gorter - Saturation magnetization and crystal chemistry of ferrimagnetic oxides

1964 – 1973

Patents

1 LOCOS

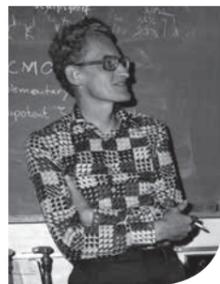
E Kooi
US Patent 3.970.486 (1976)

2 Charge transfer device

K Teer; FLJ Sangster
US Patent 3.621.283 (1968)



E Kooi



CM Hart



A Slob

3 Image sensor

LJM Esser; G Lock
US Patent 4.807.005 (1971)

4 Optical Recording

G Bouwhuis
US Patent 3.956.582 (1972)

5 Optical VLP record

P Kramer; K Compaan; RFK Forsthuber
US Patent 4.041.530 (1972)

6 Integrated injection logic (I2L)

CM Hart; A Slob
US Patent 4.056.810 (1972)

7 Fluorescent lamps

J Verstegen
US Patent 3.937.998 (1973)

United States Patent [19] [11] **3,970,486**
Kooi [45] **July 28, 1976**

[54] METHODS OF PRODUCING A SEMICONDUCTOR DEVICE AND A SEMICONDUCTOR DEVICE PRODUCED BY SAID METHOD

[75] Inventor: **Ela Kooi**, Eindhoven, Netherlands

[73] Assignee: **U.S. Philips Corporation**, New York, N.Y.

[22] Filed: **Feb. 14, 1975**

[21] Appl. No.: **549,526**

Related U.S. Application Data

[63] Continuation of Ser. No. 872,622, Oct. 3, 1967, abandoned.

Foreign Application Priority Data

Oct. 3, 1966 Netherlands..... 641,001A

[52] U.S. Cl. **148/187; 148/15; 257/50**

[51] Int. Cl.² **H01L 21/22**

[58] Field of Search **148/15, 175, 187, 188; 217/235, 357/50, 56**

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3,043,430	1/1965	Hughes	148/187
3,270,643	10/1966	Chambers et al.	148/188
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3,443,240	5/1969	Engelen	148/187
3,478,232	11/1969	Borgh et al.	148/15, 5

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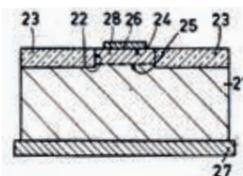
Silicon Nitride, A New Diffusion Mask, Doc. IEEE Transactions on Electron Devices, vol. 13, No. 7, pp. 561-563, July 1966.

Primary Examiner—L. Deweyne Rutledge.
Assistant Examiner—J. M. Davis.
Attorney, Agent, or Firm—Frank R. Trifari, Jack Osher

ABSTRACT

A method of making a semiconductor device is described in which a selected surface portion of a silicon wafer is masked against oxidation, and then the surface is oxidized to grow a thermal oxide which sinks into the silicon surface at the unmasked areas, with the result that the masked silicon remains as a mesa surrounded by the silicon oxide. Then semiconductor devices can be provided by various techniques in the silicon mesa. The advantages include the provision of flat junctions, as distinguished from disk junctions in the prior art, reduced capacitance resulting from the extension of the device interconnections over the silicon wafer, and a flatter surface on top of the wafer reducing the risk of damage to the deposited interconnections.

38 Claims, 13 Drawing Figures



1 E Kooi – LOCOS

United States Patent [19] [11] **3,956,582**
Bouwhuis [45] **May 11, 1976**

[54] **APPARATUS FOR READING A RECORD CARRIER ON WHICH INFORMATION IS RECORDED IN AT LEAST ONE TRACK**

[75] Inventor: **Gijsbertus Bouwhuis**, Eindhoven, Netherlands

[73] Assignee: **U.S. Philips Corporation**, New York, N.Y.

[22] Filed: **Dec. 24, 1974**

[21] Appl. No.: **536,161**

Related U.S. Application Data

[63] Continuation of Ser. No. 344,866, March 26, 1973, abandoned.

Foreign Application Priority Data

Sept. 5, 1972 Netherlands..... 7212044

[52] U.S. Cl. **178/6.6 R; 178/6.6 DD; 178/6.7 A; 179/100.3 V; 179/100.41 L**

[51] Int. Cl.² **H04N 5/76**

[58] Field of Search **179/100.3 V, 100.3 Z, 179/100.41 L, 100.3 N, 100.3 M, 100.3 G, 100.3 B, 100.3 D, 100.4 R; 178/6.6 R, 6.6 DD, 6.7 A; 340/173 LM**

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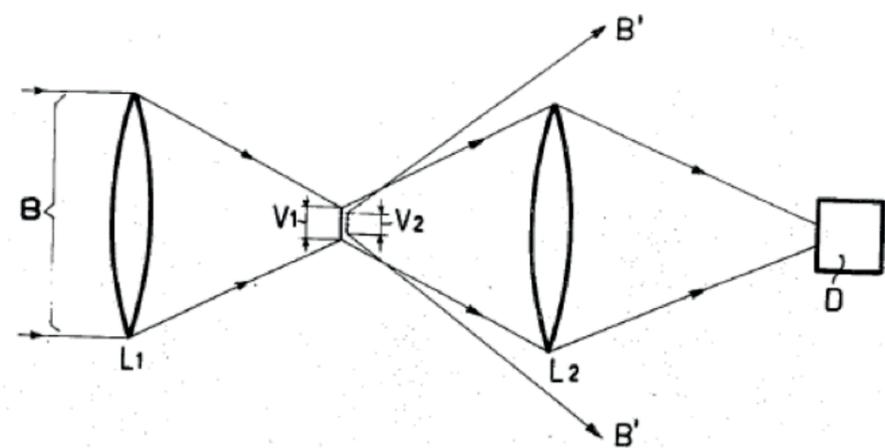
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Primary Examiner—Raymond F. Cardillo, Jr.
Attorney, Agent, or Firm—Frank R. Trifari; Simon L. Cohen

ABSTRACT

An apparatus for reading a record carrier on which information is recorded in at least one track is described. By illuminating the record carrier with a spot of light which is greater than the width of the track and by inserting in the path of the radiation from the record carrier to the detection system a limiting aperture such that at the wavelength of the radiation employed no details smaller than the width of the track are imaged on the detection system a simple and cheap arrangement may be used.

2 Claims, 3 Drawing Figures



4 G Bouwhuis – Optical Recording

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1 Controlled nucleation for regulation of particle-size in mono-disperse gold suspensions

G Frens

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G Blasse



G Frens

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AJ Bosman; HJ van Daal

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FC Eversteyn; PJW Severin; CHJV Brekel; HL Peek

JOURNAL OF THE ELECTROCHEMICAL SOCIETY 117 (1), 925–931 (1970)

Times Cited: 267

Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions

MANY properties of colloids and suspensions depend on the particle size. Series of monodisperse suspensions of the same chemical composition but of rather different particle sizes may be used to study particle size dependent phenomena, such as Brownian motion, light scattering, sedimentation and electrophoresis of small particles. We have used such series to demonstrate the increased tendency of metal suspensions to coagulate in the presence of electrolytes as the radius of the particles increases.

From Turkevich's data² we concluded that the reduction of gold chloride with sodium citrate in aqueous solution might be a promising procedure for the preparation of such a set of monodisperse gold suspensions with widely different particle diameters. We hoped by changing the relative amounts of reactants to bring about changes in the relative rates of the two independent processes of nucleation and growth of the metal particles. Whether the available gold is divided over more or fewer nuclei would make a considerable difference for the diameter of the resulting particles. Our expectations were borne out by the experiment.

Fig. 1 shows electron micrographs of six gold suspensions with particle diameters varying from 160 Å to 1500 Å. All

Table 1 Experimental Data on the Preparation of Mono-disperse Gold Sols

Sol	Amount of Solution II (ml.)	Diameter (Å)	Colour	t_{nuc} (s)	t_{red} (s)
A	1.00	160	Orange	25	145
B	0.75	245	Red	25	120
C	0.50	410	Red	25	70
D	0.30	715	dark red*	40	140
E	0.21	975	violet*	60	435
F	0.16	1470	violet*	80	850

* With a yellow Tyndall effect of the scattered light.

six suspensions were prepared by the same simple procedure, the only difference being in the concentration of sodium citrate during the nucleation of the particles.

A standard procedure for obtaining the monodisperse suspension C is as follows. Solutions are prepared of H₂AuCl₄ (10⁻³% by weight, solution I) and of Na₃-citrate (1% by weight, solution II). 50 ml. of solution I is heated to boiling, and 0.50 ml. of solution II is added. In about 25 s the boiling solution turns faintly blue (nucleation). After approximately 70 s the blue colour suddenly changes into a brilliant red, indicating the formation of monodisperse spherical particles. Reduction of gold chloride is practically complete after 5 min of boiling. Neither prolonged heating nor the addition of extra citrate produces any substantial change in the suspension after that period.

The monodisperse suspensions with the smaller and with the larger particles are obtained by the same procedure, the only change being in the amount of citrate solution added (Table 1).

The smallest particles obtained in this way had a diameter of 120 Å. The average diameter in the coarsest suspensions was 1500 Å, obtained with 0.15 ml. of Solution II. At these low citrate levels the results are less reproducible, and boiling has to be continued for at least 30 min to complete the reaction. The citrate concentration in the standard procedure is such that overall formation of the particles proceeds as rapidly as possible. This concentration is about ten times smaller, and the reaction an order of magnitude faster than under the conditions² which are ordinarily used for the production of colloidal gold. That the resulting particle size in the suspensions is determined by the number of nuclei over which the available gold is divided and is not a result of the reduction of a different percentage of the available gold with different citrate concentrations was demonstrated in the following way. The average particle size and the size distribution of the suspensions can be determined with great accuracy from electron micrographs. Now assume that in each preparation all the available gold has been reduced—or at least that the gold has been reduced to the same degree in each preparation. This assumption, together with the average volume of a particle

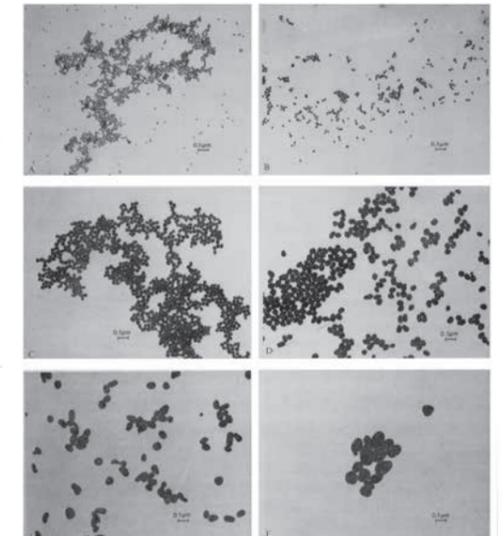


Fig. 1 Electron micrographs of the sols A-F described in Table 1.

1 G Frens – Controlled nucleation for regulation of particle-size in mono-disperse gold suspensions

R 722

Philips Res. Repts 25, 133-140, 1970

REVERSIBLE ROOM-TEMPERATURE ABSORPTION OF LARGE QUANTITIES OF HYDROGEN BY INTERMETALLIC COMPOUNDS

by J. H. N. van VUCHT, F. A. KUIJPERS and H. C. A. M. BRUNING

Abstract

Some hexagonal intermetallic compounds of the composition AB₅, where A represents a rare-earth metal and B nickel or cobalt, are reported to absorb and desorb easily large quantities of hydrogen gas under relatively small pressures at room temperature. For some selected compounds, viz. LaNi₅ and SmCo₅, absorption isotherms and X-ray data are given. Also data are given for the quasi-binary compounds La_{1-x}Ce_xNi₅. The compound LaNi₅ forms the hydride LaNi₅H₆₋₇ at room temperature under 2.5 atm of hydrogen pressure. Its unit cell expands 25 vol.%, and seems to retain its hexagonal symmetry. SmCo₅ forms the hydride SmCo₅H₃ at room temperature under 4.5 atm of hydrogen pressure, while its unit cell expands 10 vol.% and becomes orthorhombic. For both hydrides the heat of reaction is found to be about 7 kcal/mol H₂.

1. Introduction

Many metals and intermetallic compounds are known to form hydrides. A review was given recently by Westbrook¹. Some of these hydrides find application in the form of getters and as sources of pure hydrogen. Compared to these the family of intermetallic compounds described in this paper is exceptional in that they absorb hydrogen at room temperature quickly and reversibly, dependent only on hydrogen-gas pressure. This behaviour was recently discovered for the compound SmCo₅ by Zijlstra and Westendorp². The family may be described in general as having the formula AB₅ and being of the hexagonal CaCu₅ type of structure; A stands for a metal of the lanthanide series, calcium or thorium, and B represents nickel or cobalt.

2. Experimental

The intermetallic compounds were prepared by arc-melting under argon, using commercially pure components. After homogenizing, they were crushed in an agate mortar to grains with a mean size of 50 μm. Samples of about 1.5 grammes were enclosed in small brass containers, provided with a valve and a pressure gauge and connected to a hydrogen cylinder via a thin stainless-steel capillary tube. After exposing the metal powder to hydrogen gas at a certain pressure for some time the amount of absorbed hydrogen could be measured by disconnecting the tube from the cylinder and by allowing the hydrogen to flow out under water into a gas burette. Experiments not carried out at room

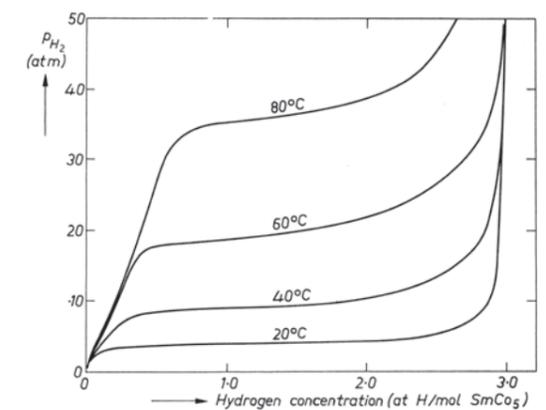


Fig. 3. Isotherms of hydrogen gas (pressure p atm) in equilibrium with absorbed hydrogen in SmCo₅ (concentration: H atoms/SmCo₅).

4 JH van Vucht et al. – Reversible room-temperature absorption of large quantities of hydrogen by intermetallic compounds

1974 – 1983

Patents

1 Fluorescent lamp with glasswool

J Hasker
US Patent 4.163.169 (1974)

2 Wafer stepper alignment system

G Bouwhuis; TF Lamboo
US Patent 4.251.160 (1976)

3 Data disc with pregroove

WJ Kleuters; GB Gerritsen; JJ Verboom
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4 Compact HG discharge lamp

GA Wesselink; H Roelofs; HM van Bommel
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5 Cold cathode

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6 MR

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7 Integrated FM-receiver

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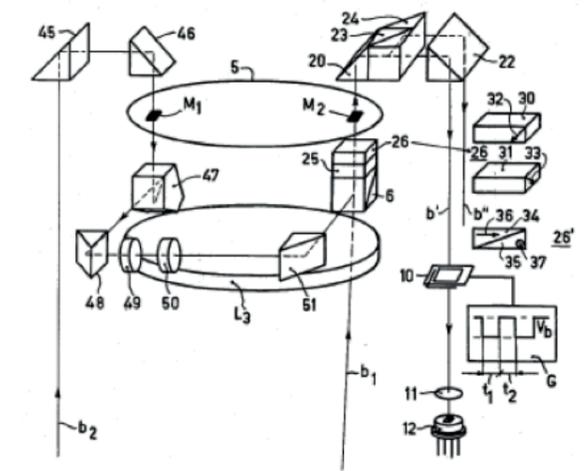
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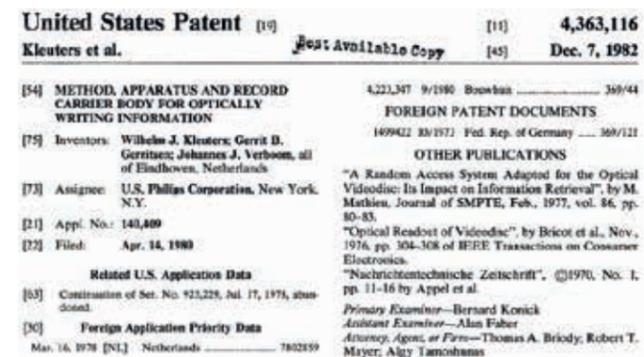
G van Gorkom



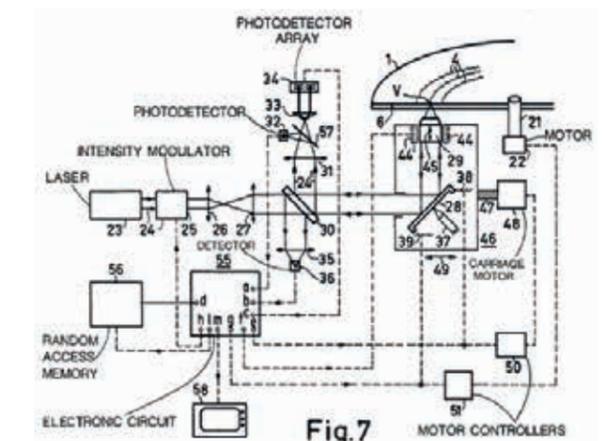
LF Feiner



2 G Bouwhuis; TF Lamboo - Wafer stepper alignment system



Disclosed is a method and apparatus for recording information on a disc-shaped record carrier body with a single beam of radiation. The record carrier body is provided with a servo track which preferably exhibits a phase structure and which contains a multitude of sector addresses each associated with a portion provided with a radiation sensitive layer. Before the information is recorded, the beam is switched to a low, read level and the desired address is located. Simultaneously, the radial position and tangential speed of the radiation spot and the focusing of the radiation beam are checked.



3 WJ Kleuters; GB Gerritsen; JJ Verboom - Data disc with pregroove

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- 1 New class of materials – Half-metallic Ferro magnets**
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AR Miedema; PF Dechatel; FR de Boer
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- 10 Heat of formation of solid alloys. II**
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AR Miedema

VOLUME 50, NUMBER 25 PHYSICAL REVIEW LETTERS 20 JUNE 1983

New Class of Materials: Half-Metallic Ferromagnets
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Research Institute for Materials, Faculty of Science, Torenboord 1, 6525 ED Nijmegen, The Netherlands
 and
 P. G. van Engen and K. H. J. Buschow
Philips Research Laboratories, 5600 ZA Eindhoven, The Netherlands
 (Received 21 March 1983)

The band structure of Mn-based Heusler alloys of the $C1_1$ crystal structure (MgAlAs type) has been calculated with the augmented-spherical-wave method. Some of these magnetic compounds show unusual electronic properties. The majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting.

PACS numbers: 71.10.+x, 71.35.Ff, 75.20.Eh

Magnetic materials based on the $L2_1$ and $C1_1$ crystallographic phases have been of interest to both theorists and experimentalists since they were first considered by Heusler.¹ His interest focused on the unusual result that some of these materials in these crystallographic phases were strongly ferromagnetic but were made by combining elements which at the time were considered to be nonmagnetic. Subsequently these materials have been used as both a testing ground for theoretical models and also for the development of new magnetic systems. In this Letter we will show that some of these $C1_1$ type compounds encompass a new class of materials. The members of the novel class share simultaneously the property of an energy gap between valence and conduction bands for electrons of one spin polarization and the property of continuous bands for the electrons of the other spin polarization. This asymmetric band character reflects the character of the $C1_1$ structure itself: The minority-spin electrons are semiconducting while the majority-spin electrons keep their normal metallic character. As a consequence we have the remarkable situation here that the conduction electrons at the Fermi level are 100% spin polarized. This property may exist for some of the conduction electrons in other ferromagnets, for example, for the d electrons of Ni or the V electrons of VPd_3 .² But in the present materials the unusual situation exists that the spin polarization entails all of the conduction electrons.

NiMnSb crystallizes in the $C1_1$ structure (MgAlAs type) which is face-centered cubic (fcc), space group $F43m$ (number 216 in the International Tables).³ This structure type is often observed for ternary transition-metal intermetallic compounds (XYZ) and is closely related to the ordinary $L2_1$ Heusler alloys (X_2YZ). Both structure types can be described by means of four interpenetrating fcc lattices. For the ordinary $L2_1$ Heusler alloys these fcc lattices can be characterized by the positions X_1 ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), X_2 ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), Y (0 0 0), and Z ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). The same holds for the $C1_1$ structure with the exception that the X_1 positions are empty. The nearest-neighbor coordination of the X_2 atoms is similar in the two types of Heusler alloys X_2YZ and XYZ . This coordination consists of two interpenetrating tetrahedrons, involving four Y atoms and four Z atoms, respectively. The coordination of the Mn atoms is distinct, though, in both types of materials. As a consequence of the X_1 sites being empty in XYZ , the point symmetry of the Mn sites has been modified from O_h in the $L2_1$ type to T_d in the $C1_1$ type. The importance of this broken inversion symmetry will be discussed below.

For the calculation we have used the augmented-spherical-wave method of Williams, Kibbler, and Gelatt.⁴ Scalar relativistic effects were included as described by Methfessel and Kibbler.⁵ The empty X_1 sites were treated as atoms with zero nuclear charge. The basis included s , p , and d functions for all sites. The secular matrix was complex of rank 36. The internal summations in the three-center contributions to the matrix element were carried out including $l=3$ contributions.⁶ The bands converged on a better than 1 mRy scale. The experimental lattice constants were used.⁷ Self-consistency was achieved in 12 iterations to a precision of $1 \cdot 10^{-3}$. Figures 1(a) and 1(b) show the band structure of NiMnSb in the majority- and minority-spin directions, respectively. A striking feature is that the minority band structure has a semiconducting gap straddling the Fermi level, whereas the majority band structure has metallic intersections. There are three main elements and their inter-

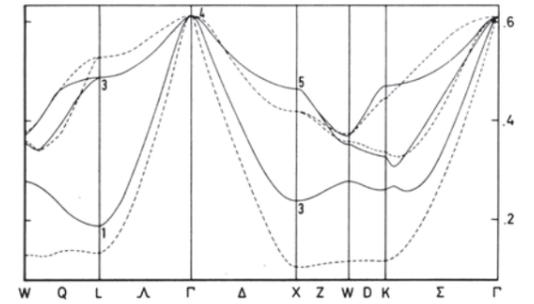


FIG. 2. Valence-band structure of minority-spin (semiconducting) NiMnSb ($C1_1$ structure) where the Ni- d states were deliberately removed from the Hamiltonian (full lines). For comparison the valence-band structure of GaSb (calculated with the same method) is shown (broken lines).

- 1 R de Groot et al. – New class of materials – Half-metallic Ferro magnets**

7336

Physica 100B (1980) 1–28
 © North-Holland Publishing Company

COHESION IN ALLOYS – FUNDAMENTALS OF A SEMI-EMPIRICAL MODEL
 A. R. MIEDEMA
Philips Research Laboratories, 5600 MD Eindhoven, The Netherlands
 and
 P. F. de CHÂTEL and F. R. de BOER
Natuurkundig Laboratorium, University of Amsterdam, 1018 XE Amsterdam, The Netherlands
 Received 7 December 1979

A semi-empirical model of alloy cohesion involving two material constants for each element is introduced by means of the physical ideas underlying the scheme. The resulting expressions for the heat of formation of binary alloys are presented and their applicability in various extreme situations is discussed. The model is shown to reproduce a vast amount of experimental information on the sign of heats of formation. Detailed comparison with experiment for particular classes of alloys will be presented in the sequel to this paper.

1. Introduction
1.1. Types of cohesion

In simple treatments of binding in crystals, one attempts to classify solids according to the type of interaction holding them together. In some cases, e.g. molecular crystals or ionic compounds, the classification is relatively straightforward and easy to apply. The fact that a variety of electronegativity scales has been introduced to assess the relative importance of ionic binding shows that the delineation of this type from metallic and covalent binding is not easy. In fact, a similar ambiguity exists in the classification of metals and semiconductors, where the terms 'covalent' and 'metallic' are often applied to compounds in a rather suggestive way, without giving much insight into the origin of the cohesive energy.

In molecular crystals, which include the solid noble gases, one describes cohesion in terms of the Van der Waals – London interaction between molecules. The interaction being due to the mutually induced dipole moments of the two molecules, the cohesive energy depends quadratically on the molecular polarizability. There is no need for an overlap between the charge densities of the interacting molecules for this attractive force to be effective. In fact, the overlap provides the repulsive force that keeps the solid from collapsing. In the case of solid noble gases, we find a simple relation between the fairly small electron density between atoms and the cohesive energy at $T = 0$ per unit molar surface area (fig. 1). This correlation implies that there is a proportionality between negative and positive contributions to the total energy at the equilibrium interatomic distance.

In ionic crystals, the cohesive energy can be accounted for by electrostatic interactions between distinct, oppositely charged ions of well-defined sizes and charges. In the case of fully ionic substances, i.e., compounds containing ions of integral charge units, the calculation of the binding energy is a relatively simple matter. However, fully ionic compounds represent a limiting case, never actually realized in nature. Even in the textbook examples of ionic crystals (alkali halides, oxides of metals with very low electronegativity) there must be some overlap between the oppositely charged ions which generates the necessary repulsive forces. Thus, one always deals with intermediate, partially ionic cases, where the electron density between ions is appreciable, and there is an ambiguity in the decomposition of the electronic charge distribution into positive and negative ions.

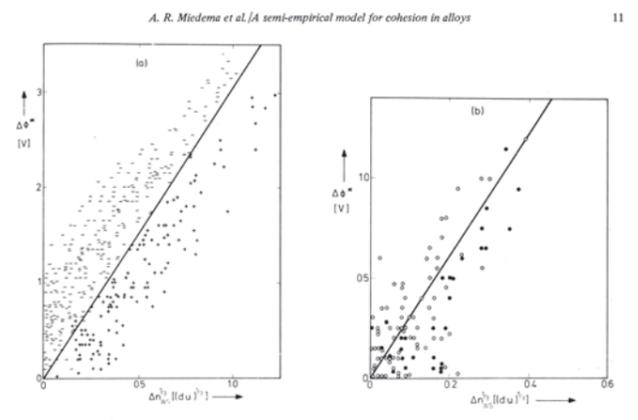
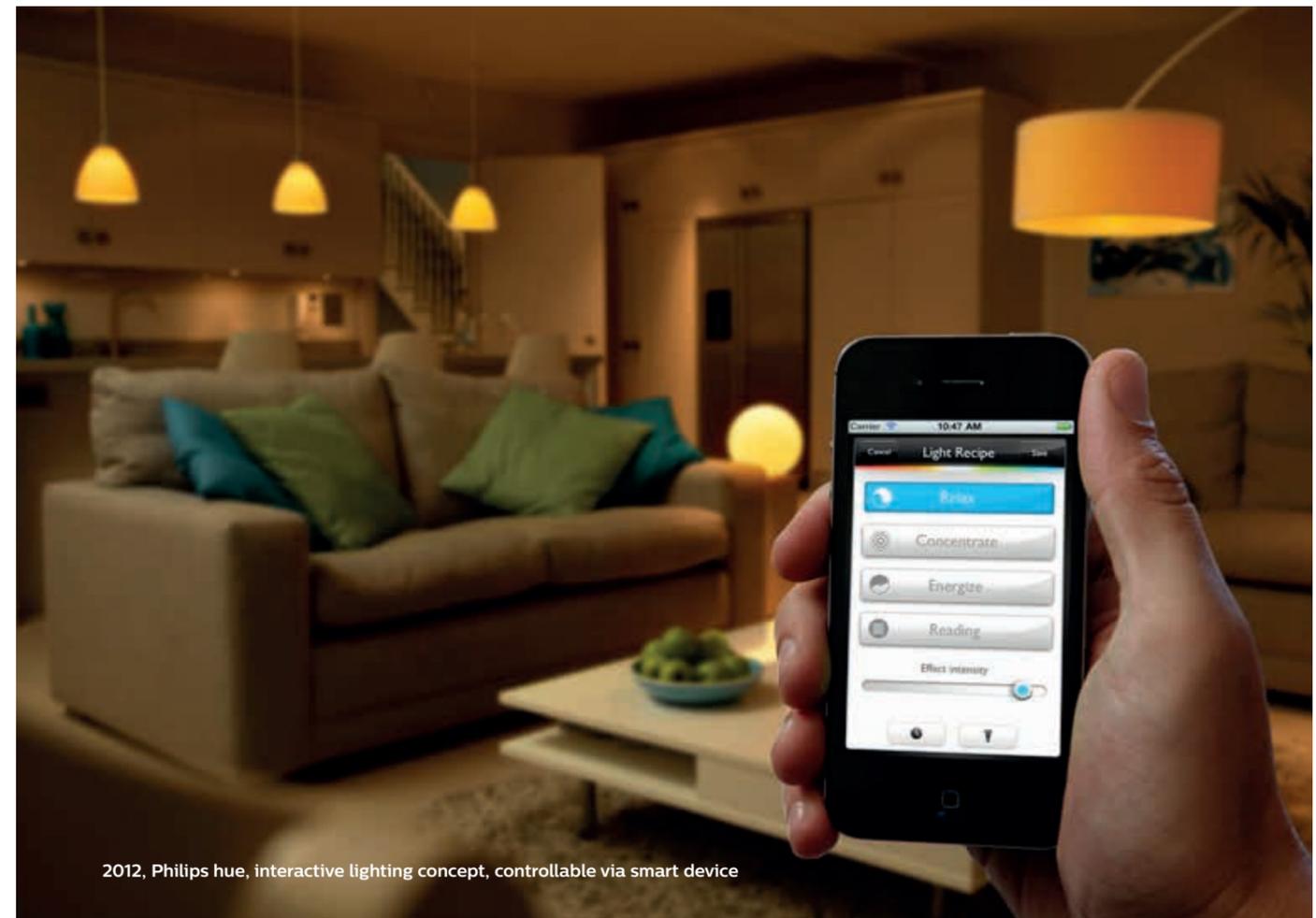


Fig. 8. Demonstration of the validity of eq. (7) for solid binary alloys consisting of a transition metal and a transition, noble, alkali or alkaline earth metal.
 (a) – In the binary system one or more compounds exist, which are stable at low temperatures (indicating that ΔH is negative); + There are no compounds in the system and both solid solubilities are smaller than 10 at.% (indicating that ΔH is positive).
 (b) – There are no compounds or ordered phases in the system, but at least one of the solubilities in the solid state is larger than 10%. It can be postulated that ΔH will not differ much from zero. This figure does indeed show that open circles mainly occur in the neighbourhood of the origin, which in the quadratic eq. (7) means that ΔH is small; ● As for the open circles, but now the solubility drops to low values at low temperatures or there is only incomplete miscibility in the solid state, although both metals have the same crystal structure. The quantity ΔH is expected to have a small but positive value.

- 2 AR Miedema et al. – Cohesion in alloys – Fundamentals of a semi-empirical model**



1914, Philips NatLab on 4th floor at Emmasingel, Eindhoven



2012, Philips hue, interactive lighting concept, controllable via smart device



1964, Philips launches its first color TV

1984 – 1993

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1 NMR with permanent magnet

H Zijlstra

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3 IC, Audio transmission

RJ Sluyter et al.

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4 HD-MAC

F Vreeswijk; J van der Meer; H Begas; TI Trew

US Patent 5.043.810 (1988)

5 MR

D Kunz; KG Bomsdorf; JS Wieland

US Patent 4.924.183 (1988)

6 Audio/video coding. AC3, MPEG. Copy code on information carrier

G Lohhoff; R Roth; W Raaymakers

US Patent 5.060.219 (1988)

7 UHP Lamp

HE Fischer; H Hörster

US Patent 5.109.181 (1988)

8 Method of determining spectral distribution of nuclear magnetization in a limited volume, and device for performing the method

KGH Bomsdorf; D Kunz; JS Wieland

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9 Electrochemical cell

PHL Notten

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US Patent 5.184.018 (1990)

11 Video Coding

W de Haan; J van der Meer

US Patent 5.740.310 (1990)

12 Video coding; variable length coding as used in JPEG and MPEG

P Vogel

German Patent 4.336.101 (1993)

13 Display

D Broer; J Lub

US Patent 5.506.704 (1993)



F Vreeswijk



U Siebel

United States Patent [19] Patent Number: 5,043,810 Vreeswijk et al. [45] Date of Patent: Aug. 27, 1991

[54] METHOD AND APPARATUS FOR TEMPORALLY AND SPATIALLY PROCESSING A VIDEO SIGNAL

[75] Inventors: Franciscus W. P. Vreeswijk; Jan Van Der Meer; Henk W. A. Begas, all of Eindhoven, Netherlands; Timothy I. P. Trew, Horley, England

[73] Assignee: U.S. Philips Corporation, New York, N.Y.

[21] Appl. No.: 288,058

[22] Filed: Dec. 20, 1988

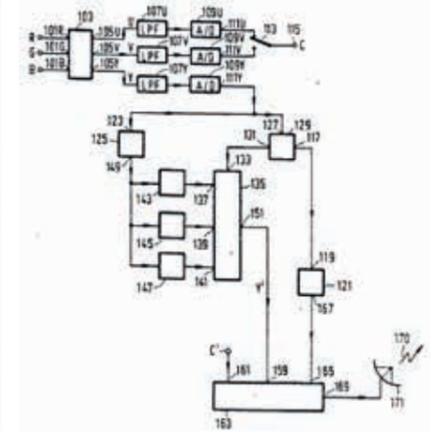
Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 281,294, Dec. 7, 1988, Pat. No. 4,965,687.

Foreign Application Priority Data

Dec. 22, 1987 [GB] United Kingdom 8729878
Feb. 23, 1988 [NL] Netherlands 8800449

[57] **ABSTRACT**
A transmitting section of the system according to the invention has transmitting section signal paths for at least three classes of motion, each with a preprocessing circuit (143, 145 and 147) which are provided with means for individually sampling. These sampling means sample in accordance with separate sampling patterns so that each preprocessing circuit (143, 145 or 147) supplies a video signal which is suitable for a display with an optimum distribution of temporal and/or spatial resolution for the associated class of motion. Dependent on the class of motion determined, one of the preprocessing circuits (143, 145 or 147) is coupled to a channel (170). The video signal to be supplied to the channel (170) is therefore a video signal suitable for a display with an optimum distribution of temporal and/or spatial resolution for the given class of motion (FIG. 1A). A



4 FWP Vreeswijk; J van der Meer; HW Begas; TI Trew - HD-MAC

United States Patent [19] Patent Number: 4,924,183 Kunz et al. [45] Date of Patent: May 8, 1990

[54] METHOD OF DETERMINING THE SPECTRAL DISTRIBUTION OF THE NUCLEAR MAGNETIZATION IN A LIMITED VOLUME, AND DEVICE FOR PERFORMING THE METHOD

[75] Inventors: Dietmar Kunz, Quickborn; Karl Georg H. Bomsdorf, Hamburg; Jürgen S. Wieland, Pinneberg, all of Fed. Rep. of Germany

[73] Assignee: U.S. Philips Corporation, New York, N.Y.

[21] Appl. No.: 309,465

[22] Filed: Feb. 10, 1989

[30] Foreign Application Priority Data
Feb. 17, 1988 [DE] Fed. Rep. of Germany 3804924

[51] Int. Cl. G01R 33/20
[52] U.S. Cl. 324/309
[58] Field of Search 324/307, 309, 311, 312

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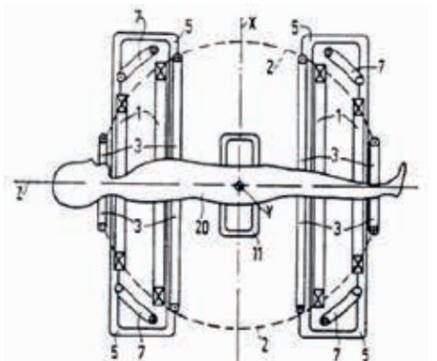
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Primary Examiner—Hezron E. Williams
Assistant Examiner—Kevin D. O'Shea
Attorney, Agent, or Firm—Jack D. Slobod; Thomas A. Briody; Jack E. Haken

[57] **ABSTRACT**
A method of a device for determining the spectral distribution of a nuclear magnetization in a limited volume, wherein each sequence of r.f. and gradient excitation comprises a sub-sequence which dephases the nuclear magnetization everywhere outside a defined layer. This sub-sequence is followed by three r.f. pulses, the first two of which are layer-selective. These three r.f. pulses excite the nuclear magnetization in an area of intersection between said layer and two layers which extend perpendicularly to one another and to said layer. In order to suppress undesirable FID signals and to enhance the spectrum, phase cycling is performed.

20 Claims, 3 Drawing Sheets



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Quantized Conductance of Point Contacts in a Two-Dimensional Electron Gas

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 (Received 31 December 1987)

Ballistic point contacts, defined in the two-dimensional electron gas of a GaAs-AlGaAs heterostructure, have been studied in zero magnetic field. The conductance changes in quantized steps of e^2/h when the width, controlled by a gate on top of the heterojunction, is varied. Up to sixteen steps are observed when the point contact is widened from 0 to 360 nm. An explanation is proposed, which assumes quantized transverse momentum in the point-contact region.

PACS numbers: 72.20.Jr, 73.40.Cg, 73.40.Lq

As a result of the high mobility attainable in the two-dimensional electron gas (2DEG) in GaAs-AlGaAs heterostructures it is now becoming feasible to study ballistic transport in small devices.¹⁻³ In metal leads tools for such studies are constrictions having a width W and length L , much smaller than the mean free path l_e . These are known as Sharvin point contacts.⁴ Because of the ballistic transport through these constrictions, the resistance is determined by the point-contact geometry only. Point contacts have been used extensively for the study of elastic and inelastic electron scattering. With use of biased point contacts, electrons can be injected into metals at energies above the Fermi level. This allows the study of the energy dependence of the scattering mechanisms.⁵ With the use of a geometry containing two point contacts, with separation smaller than l_e , electrons injected by a point contact can be focused into the other contact, by the application of a magnetic field. This technique (transverse electron focusing) has been applied to the detailed study of Fermi surfaces.⁶

In this Letter we report the first experimental study of the resistance of ballistic point contacts in the 2DEG of high-mobility GaAs-AlGaAs heterostructures. The single-point contacts discussed in this paper are part of a double-point-contact device. The results of transverse electron focusing in these devices will be published elsewhere.⁷ The point contacts are defined by electrostatic depletion of the 2DEG underneath a gate. This method, which has been used by several authors for the study of 1D conduction,^{8,9} offers the possibility to control the width of the point contact by the gate voltage. Control of the width is not feasible in metal point contacts.

The classical expression for the conductance of a point contact in two dimensions (see below) is

$$G = (e^2/h) k_F W/L \quad (1)$$

in which k_F is the Fermi wave vector and W is the width of the contact. This expression is valid if $l_e \gg W$ and the Fermi wavelength $\lambda_F \ll W$. The first condition is satisfied in our devices, which have a maximum width $W_{max} \approx 250$ nm and $l_e \approx 8.5 \mu\text{m}$. The second condition should also hold when the devices have the maximum width. We expect quantum effects to become important when the width becomes comparable to λ_F , which is 42 nm in our devices. In this way we are able to study the transition from classical to quantum ballistic transport through the point contact.

The point contacts are made on high-mobility molecular-beam-epitaxy-grown GaAs-AlGaAs heterostructures. The electron density of the material is $3.5 \times 10^{11} \text{ cm}^{-2}$ and the mobility $85 \text{ m}^2/\text{Vs}$ at 0.6 K. These values are obtained from the devices containing the studied point contacts. A standard Hall bar geometry is defined by wet etching. Using electron-beam lithography, a metal gate is made on top of the heterostructure, with an opening 250 nm wide (inset in Fig. 1). The point contacts are defined by the application of a negative voltage to the gate. At $V_g = -0.6$ V the electron gas underneath the gate is depleted, the conduction taking place through the point contact only. At this voltage the point contacts have their maximum width W_{max} , about equal to the opening between the gates. By a further decrease of the gate voltage, the width of the point contacts can gradually be reduced, until they are fully

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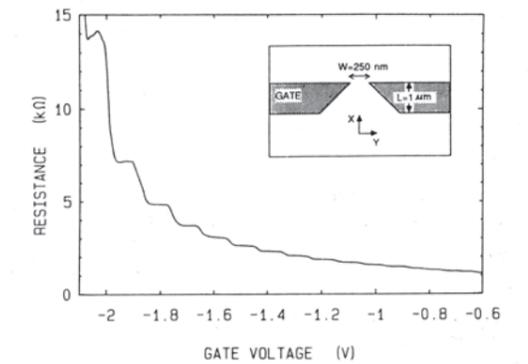


FIG. 1. Point-contact resistance as a function of gate voltage at 0.6 K. Inset: Point-contact layout.

1 BJ van Wees et al. - Quantized conductance of point contacts in a two-dimensional electron-gas

Matching Properties of MOS Transistors

MARCEL J. M. PELGROM, MEMBER, IEEE, AAD C. J. DUINMAIJER, AND ANTON P. G. WELBERS

Abstract—The matching properties of the threshold voltage, substrate factor, and current factor of MOS transistors have been analyzed and measured. Improvements to the existing theory are given, as well as extensions for long-distance matching and rotation of devices. Matching parameters of several processes are compared. The matching results have been verified by measurements and calculations on several basic circuits.

I. INTRODUCTION

MISMATCH IS THE process that causes time-independent random variations in physical quantities of identically designed devices. Mismatching is a limiting factor in general-purpose analog signal processing, but especially in multiplexed analog systems [1], digital-to-analog converters [2], reference sources, etc. In digital circuits matching can also be important, e.g., in the read and write circuits of digital memories and even in the voltage margins of static RAM cells. The impact of (mismatching) MOS transistors becomes more important because the dimensions of the devices are reduced and the available signal swing decreases.

Despite the widely recognized importance of matching, there are only a limited number of specialized open literature contributions in this field. Shyu *et al.* [3], [4] has analyzed the variation in capacitors and current sources in terms of local and global variations. Local variations are characterized by a short correlation distance: the concept of local variations is also part of the analysis of this paper. The effect of the global variations is a constant term in Shyu's mismatch description. In the following sections a more detailed description will be used, thereby introducing spacing dependence. The analysis of current mismatch in [4] is based on four physical causes: edge effects, implantation and surface-state charges, oxide effects, and mobility effects. The resulting measurements confirm the global trend in current matching, but matching is not further specified in parameter terms.

Lakshminarayanan *et al.* [5] described MOS-transistor matching by means of threshold-voltage and current-factor standard deviations. The starting points were again the possible physical causes. Their analysis of the contributions to the current factor mismatch is not supported by

the experiments in this paper. The limited variation in W/L ratios in his experiments cannot distinguish between alternative hypotheses.

This paper is a contribution to the discussion on matching and will include an analysis and measurements of the mismatch in threshold voltage, the current factor, and the substrate factor of the MOS transistor as a function of area, distance, and orientation. The starting point is not the wide range of possible mismatch causes, but a mathematical treatment of classes of mismatch behavior which occur during every fabrication phase of the devices. Then the measurements are used to verify the theory and to derive the unknown constants in the theory. The origins of mismatch in several MOS parameters have been studied by means of additional experiments. The applicability of the results is demonstrated on several basic circuits.

II. ANALYSIS

Mismatch that can be observed between the parameters of a group of equally designed devices (MOS transistors in this paper) is the result of several random processes which occur during every fabrication phase of the devices. This definition excludes batch-to-batch or wafer-to-wafer variations of the absolute value of parameters and unwanted offsets caused by electrical, lithographic, or timing differences.

In general the value of a parameter P is composed of a fixed part and a randomly varying part, resulting in differing values of P at different coordinate pairs (x, y) on the wafer. If the variations are small, the average value of the parameter over any area is given by the integral of $P(x, y)$ over this area. The actual mismatch in parameter P between two identical areas at coordinates (x_1, y_1) and (x_2, y_2) is

$$\Delta P(x_{12}, y_{12}) = \frac{1}{\text{area}} \left(\iint_{\text{area}(x_1, y_1)} P(x', y') dx' dy' - \iint_{\text{area}(x_2, y_2)} P(x', y') dx' dy' \right) \quad (1)$$

This integral can be interpreted as the convolution of double box functions formed by the integral boundaries with the "mismatch source" function $P(x, y)$. By means of a two-dimensional Fourier transformation the geomet-

Manuscript received December 5, 1988; revised May 5, 1989. The authors are with the Philips Research Laboratories, 5600 JA, Eindhoven, The Netherlands. IEEE Log Number 890108.

2 MJM Pelgrom et al. - Matching properties of MOS transistors

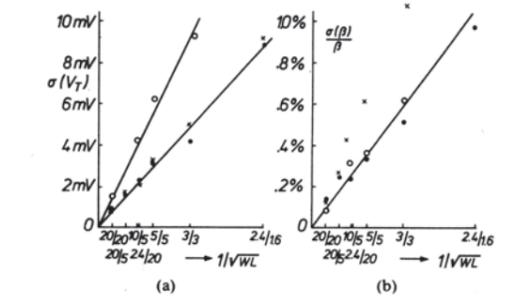


Fig. 6. Standard deviation of (a) V_T and (b) β versus the square root of the inverse area of an NMOS transistor pair for a 25-nm gate-oxide process (dots) and a 50-nm gate-oxide process (circles). Crosses are measurements on devices processed in a 25-nm process with direct wafer writing. The cross for the 2.4/1.6 device is at 2.2 percent.

1994 – 2003

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N Dimitrova

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[73] **Assignee: U.S. Philips Corporation, New York, N.Y.** Primary Examiner—Vu Le
 Assistant Examiner—Luzanne P. Din
 Attorney, Agent, or Firm—John C. Fox

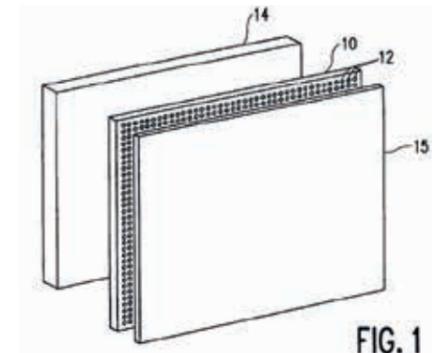
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 [22] **Filed: Feb. 12, 1997**

[30] **Foreign Application Priority Data**
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[51] **Int. Cl.⁷ H04N 13/00**
 [52] **U.S. Cl. 348/31, 348/42**
 [58] **Field of Search 348/42, 51, 59, 350/330, 167; 345/32; H04N 13/00**

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20 Claims, 5 Drawing Sheets



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Huiberts et al. (45) **Date of Patent: *Jun. 5, 2007**

(54) **ORGANIC ELECTROLUMINESCENT DEVICE** (56) **References Cited**
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(75) **Inventors: Johannes N. Huiberts, Eindhoven (NL); Loïc C. A. Mourier, Eindhoven (NL); Peter Van De Weijer, Eindhoven (NL); Coen T. H. F. Liedenbaum, Eindhoven (NL); Martinus H. W. M. Van Delden, Eindhoven (NL)**
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(73) **Assignee: Koninklijke Philips Electronics N.V., Eindhoven (NL)**

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 11 days.

This patent is subject to a terminal disclaimer.

(21) **Appl. No.: 11/080,883**
 (22) **Filed: Mar. 15, 2005**

(65) **Prior Publication Data**
 US 2005/0162072 A1 Jul. 28, 2005

Related U.S. Application Data

(63) **Continuation of application No. 10/284,503, filed on Oct. 30, 2002, now Pat. No. 6,888,317, which is a continuation of application No. 09/666,888, filed on Sep. 22, 2000, now Pat. No. 6,525,484.**

(30) **Foreign Application Priority Data**
 Sep. 22, 1999 (EP) 99203103

(51) **Int. Cl. G09G 3/10 (2006.01)**
 (52) **U.S. Cl. 315/169.3; 313/506**
 (58) **Field of Classification Search 315/169.3, 315/169.1; 313/504-506; 345/76, 77**
 See application file for complete search history.

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 11 days.

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(21) **Appl. No.: 11/080,883**
 (22) **Filed: Mar. 15, 2005**

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 US 2005/0162072 A1 Jul. 28, 2005

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(63) **Continuation of application No. 10/284,503, filed on Oct. 30, 2002, now Pat. No. 6,888,317, which is a continuation of application No. 09/666,888, filed on Sep. 22, 2000, now Pat. No. 6,525,484.**

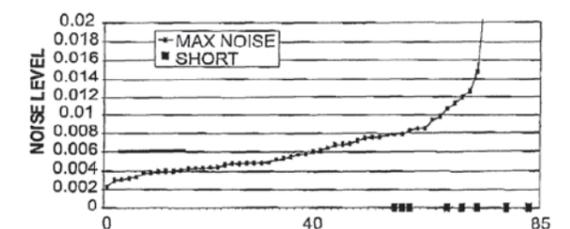
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 See application file for complete search history.

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 Primary Examiner—Triuh Dinh
 Assistant Examiner—Ephrem Alemu
 (74) **Attorney, Agent, or Firm—Aaron Waxler, Paul Im**

(57) **ABSTRACT**
 The invention provides a tool to select reliable organic LED devices, where the risk for failure before the end of its lifetime is low. This tool comprises the steps of:
 i) subjecting the device to a high electric field over the electroluminescent layer. This leads to a division of the devices into two, clearly separated, populations, namely one population with a low leakage current (current through the electroluminescent layer in reverse voltage operation) and one population with a high leakage current. In this step, the first population is selected in accordance with a current criterion.
 ii) detecting instabilities in the leakage current, referred to as noise. It has been established that these instabilities arise in particular at reverse driving voltages between 1 and 10 Volts. These instabilities are a measure of the occurrence of early failures during operation. In this step, the devices are selected in accordance with a noise criterion.

16 Claims, 5 Drawing Sheets



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H Siringhaus; PJ Brown; RH Friend; MM Nielsen; K Bechgaard; BMW Langeveld-Voss; AJH Spiering; RAJ Janssen; EW Meijer; P Herwig; DM de Leeuw
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DM de Leeuw

Two-dimensional charge transport in self-organized, high-mobility conjugated polymers

H. Siringhaus*, P. J. Brown*, R. H. Friend*, M. M. Nielsen†, K. Bechgaard†, B. M. W. Langeveld-Voss†, A. J. H. Spiering†, R. A. J. Janssen†, E. W. Meijer†, P. Herwig‡ & D. M. de Leeuw§

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Self-organization in many solution-processed, semiconducting conjugated polymers results in complex microstructures, in which ordered microcrystalline domains are embedded in an amorphous matrix¹. This has important consequences for electrical properties of these materials: charge transport is usually limited by the most difficult hopping processes and is therefore dominated by the disordered matrix, resulting in low charge-carrier mobilities² ($\approx 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Here we use thin-film, field-effect transistor structures to probe the transport properties of the ordered microcrystalline domains in the conjugated polymer poly(3-hexylthiophene), P3HT. Self-organization in P3HT results in a lamella structure with two-dimensional conjugated

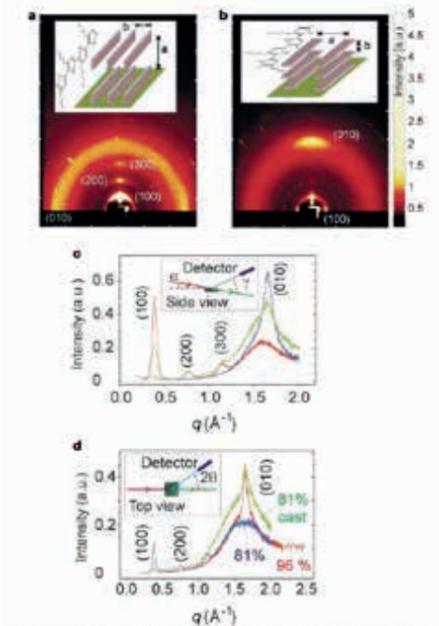


Figure 1 Two different orientations of ordered P3HT domains with respect to the FET substrate. **a, b**, The wide-angle X-ray scattering images are a colour representation of the two-dimensional distribution of scattered Cu K α X-ray intensity from spin-coated, 70–100 nm thick P3HT films with regioregularity of 96% (**a**) and 81% (**b**) on SiO₂/Si substrates. The vertical (horizontal) axes correspond to scattering normal (parallel) to the plane of the film. The insets show schematically the different orientations of the microcrystalline grains with respect to the substrate. **c, d**, The change of orientation is confirmed by high-resolution synchrotron X-ray diffraction measurements for constant, grazing-incidence angle with out-of-plane (**c**) and in-plane (**d**) scattering geometry. Red, 96%, spin coated; blue, 81%, spin coated; green, 81%, solution-cast. The intensities plotted versus the total scattering vector are corrected for polarization and geometric factors¹⁰.

- 1 H Siringhaus - Two-dimensional charge transport in self-organized, high-mobility conjugated polymers

Optical Properties of Manganese-Doped Nanocrystals of ZnS

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X. Hong and A. Nurmikko

Division of Engineering and Department of Physics, Brown University, Providence, Rhode Island 02910 (Received 3 August 1993)

We report for the first time that doped nanocrystals of semiconductor can yield both high luminescent efficiencies and lifetime shortening at the same time. Nanocrystals of Mn-doped ZnS with sizes varying from 3.5 to 7.5 nm were prepared by a room temperature chemical process yielding an external photoluminescent quantum efficiency 18% and a luminescent decay at least 5 orders of magnitude faster than the corresponding Mn²⁺ transition in the bulk crystals. The quantum efficiency increases with decreasing size of the particles. These results suggest that doped nanocrystals are indeed a new class of materials heretofore unknown.

PACS numbers: 78.55.Cr, 61.46.+w, 61.72.Nv, 79.60.Jv

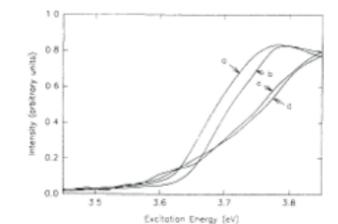


FIG. 3. Magnetic field shifts of the PLE spectra (band edge 590 nm) of ZnS:Mn at 1.6 K. (a) is bulk with $H=4.5$ T, (b) is bulk with $H=0$, (c) is nanocrystalline with $H=4.5$ T, and (d) is nanocrystalline with $H=0$.

- 2 RN Bhargava - Optical-properties of manganese-doped nanocrystals of ZnS

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Gottenbos et al. (43) Pub. Date: **Jan. 15, 2009**

(54) **DROPLET JET SYSTEM FOR CLEANSING** (86) PCT No.: **PCT/IB2005/05244**
(75) Inventors: **Bart Gottenbos, Huidel (NL); Jozef Johannes Maria Janssen, Eindhoven (NL); Marinus Karel Johannes De Jager, Eindhoven (NL); Adriaan Willem Cense, Eindhoven (NL); Paulus Cornelis Duineveld, Beetssterzwaag (NL); Jon W. Hayenga, Redmond, WA (US); William E. Bryant, North Bend, WA (US); Martijn Jeroen Dekker, Groningen (NL)** (86) § 371 (c)(1), (2), (4) Date: **Aug. 6, 2008**

Related U.S. Application Data
(60) Provisional application No. 60/537,690, filed on Jan. 20, 2004.

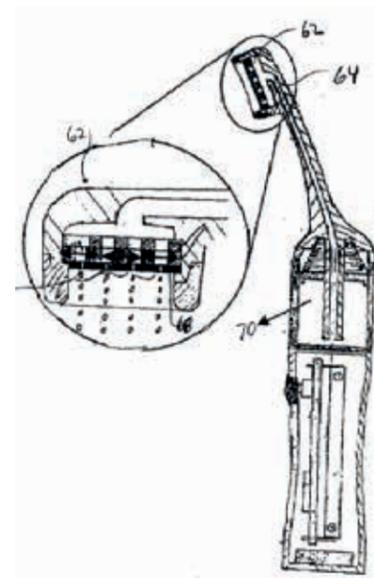
Publication Classification
(51) Int. Cl. **A61C 17/16** (2006.01)
(52) U.S. Cl. **433/216; 433/89**

ABSTRACT
(57) The system includes a reservoir for fluid; a droplet generator for creating a stream of fluid droplets from the fluid wherein the velocity of the stream of droplets is within a range of 20 meters per second to 200 meters per second and the size of the droplets is within a range of 5 microns to 200 microns. A nozzle or nozzles direct the stream of droplets to safely clean a selected tooth or teeth surface area. The specific momentum of effective fluid droplets within the stream of fluid droplets is important in safe and effective cleaning.

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(21) Appl. No.: **11/814,060**
(22) PCT Filed: **Jan. 20, 2005**



1 B Gottenbos; JJM Janssen; MKJ de Jager; A Cense; PC Duineveld etc. - Airfloss

(12) **United States Patent** (10) Patent No.: **US 8,237,434 B2**
Van Lankveld et al. (45) Date of Patent: **Aug. 7, 2012**

(54) **ELECTROMAGNETIC SYSTEM FOR BIOSENSORS** (52) U.S. Cl. **324/239; 324/204; 324/240; 324/244**
(58) **Field of Classification Search** **324/239; 324/204, 240, 244.1; 335/219**
See application file for complete search history.

(75) Inventors: **Petrus Johannes Wilhelmus Van Lankveld, Boekel (NL); Menno Willem Jose Prins, Rosmalen (NL); Albert Hendrik Jan Immink, Eindhoven (NL)** (56) **References Cited**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 416 days.

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§ 371 (c)(1), (2), (4) Date: **Aug. 27, 2009**
(87) PCT Pub. No.: **WO2008/107827**
PCT Pub. Date: **Sep. 12, 2008**

(65) **Prior Publication Data**
US 2010/0117772 A1 May 13, 2010

(30) **Foreign Application Priority Data**
Mar. 6, 2007 (EP) 07103629

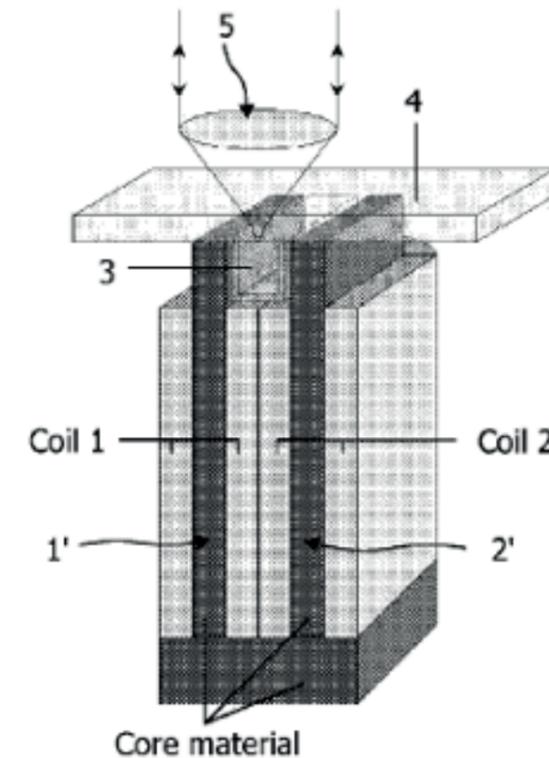
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(57) **ABSTRACT**
An electromagnetic system for biosensors including two independent electromagnetic units separated in the region of pole shoes of the electromagnetic units positioned under a gap, a cartridge positioned in the gap providing a sample volume and a biosensor having a sensor surface located at one or more inner surfaces of the cartridge proximate to the pole shoes.



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1 Flexible active-matrix displays and shift registers based on solution-processed organic transistors

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S Kuiper; BHW Hendriks
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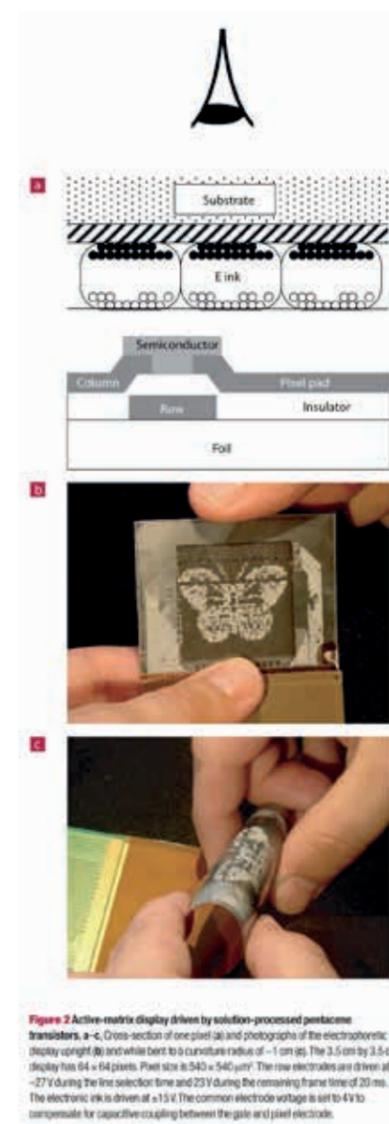


Figure 2 Active-matrix display driven by solution-processed pentacene transistors. a-c, Cross-section of one pixel (a) and photographs of the electrochromic display upright (b) and while bent to a curvature radius of -1 cm (c). The 3.5 cm by 3.5 cm display has 64×64 pixels. Pixel size is $540 \times 540 \mu\text{m}^2$. The row electrodes are driven at -27 V during the line selection time and 23 V during the remaining frame time of 20 ms. The electronic ink is driven at $+15$ V. The common electrode voltage is set to 4 V to compensate for capacitive coupling between the gate and pixel electrode.

LETTERS

Flexible active-matrix displays and shift registers based on solution-processed organic transistors

GERWIN H. GELINCK*, H. EDZER A. HUITEMA, ERIK VAN VEENENDAAL, EUGENIO CANTATORE, LAURENS SCHRIJNEMAKERS, JAN B. P. H. VAN DER PUTTEN, TOM C. T. GEUNS, MONIQUE BEENHAKKERS, JACOBUS B. GIESBERS, BART-HENDRIK HUISMAN, EDUARD J. MELJER, ESTRELLA MENA BENITO, FRED J. TOUWSLAGER, ALBERT W. MARSMAN, BAS J. E. VAN RENS AND DAGO M. DE LEEUW
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APPLIED PHYSICS LETTERS

VOLUME 85, NUMBER 7

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Variable-focus liquid lens for miniature cameras

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 (Received 1 March 2004; accepted 2 June 2004)

The meniscus between two immiscible liquids can be used as an optical lens. A change in curvature of this meniscus by electrowetting leads to a change in focal distance. It is demonstrated that two liquids in a tube form a self-centered lens with a high optical quality. The motion of the lens during a focusing action was studied by observation through the transparent tube wall. Finally, a miniature achromatic camera module was designed and constructed based on this adjustable lens, showing that it is excellently suited for use in portable applications. © 2004 American Institute of Physics.
 [DOI: 10.1063/1.1779954]

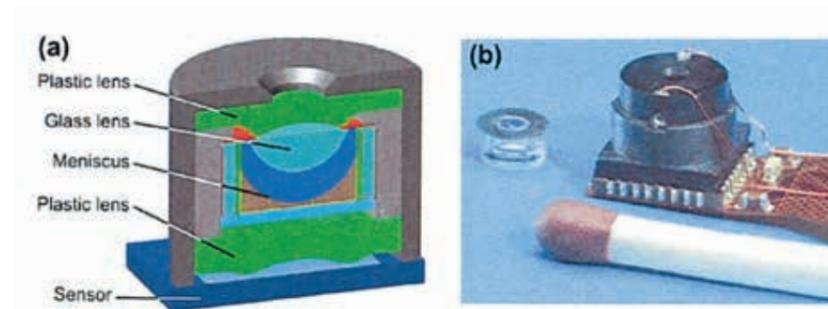


FIG. 3. (Color) (a) Optical design of the camera module containing a liquid lens; (b) the assembled camera module and the liquid lens.

1 GH Gelinck et al. - Flexible active-matrix displays and shift registers based on solution-processed organic transistors



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