P-N LUMINESCENCE AND PHOTOVOLTAIC EFFECTS IN GaP **

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Summary

GaP crystals were prepared from the elements. Crystals made at low phosphorus pressure mainly showed n-conductivity with an activation energy of 0.07 eV. Crystals with p-conductivity were obtained by heating at high phosphorus pressure (activation energy 0.19 eV) or by doping with Zn. The non-doped crystals showed electroluminescence in bands at 6250 Å and 5650 Å. The electroluminescence is shown to be due to the recombination of charge carriers, within p-n junctions via levels within the forbidden gap. A level scheme for undoped GaP is proposed. The crystals showed point-contact rectification and photovoltaic effects. On measuring the photovoltage as a function of wavelength excitation bands were found at 4200 Å and 5600 Å in non-doped crystals and at 4200 Å and 6000 Å in Zn-doped crystals. The long-wave excitation peaks of the photovoltage are explained with a two-step mechanism, one optical and one thermal.

Resumé

Des cristaux de GaP ont été préparés à partir des éléments. Les cristaux préparés sous une pression de phosphore basse montrent une conductibilité du type n avec une énergie d'activation de 0,07 eV. Des échantillons ayant une conductibilité du type p ont été obtenus en chauffant sous une pression de phosphore élevée (énergie d'activation 0,19 eV) ou par l'introduction de Zn. Les cristaux non dopés sont électroluminescents avec bandes d'émission à 6250 Å et à 5650 Å. On montre que l'électroluminescence est causée par la recombinaison de porteurs de charge dans des jonctions p-n, par l'intermédiaire de niveaux dans la bande interdite. On propose une description des niveaux électroniques du GaP non dopé. Les échantillons montrent un effet de redressement pour des contacts par pointe et un effet photovoltaïque. Si l'on mesure la tension photovoltaïque en fonction de la longueur d'onde d'excitation, on trouve des bandes à 4200 Å et 5600 Å pour des cristaux non dopés et à 4200 Å et 6000 Å pour les cristaux dopés au Zn. On explique les maxima à grande longueur d'onde par un mécanisme d'excitation en deux étapes, l'une optique et l'autre thermique.

Zusammenfassung

GaP-Kristalle wurden aus den Elementen hergestellt. Kristalle, die bei niedrigem Phosphorbedauf hergestellt wurden, zeigten Elektronenleitung mit einer Aktivierungsenergie von 0,07 eV. Kristalle mit Löcherleitung erhielt man durch Erhitzen bei hohem Phosphorbedauf (Aktivierungsenergie 0,19 eV) oder durch Zinkdotierung. Undotierte Kristalle wiesen Elektrolumineszenz mit Maxima bei 6250 Å und 5650 Å auf. Es wird gezeigt, daß die Elektrolumineszenz durch Rekombination von Ladung-

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1. Introduction

The optical and electrical properties of GaP have recently been investigated by several authors. Folberth and Oswald 1) measured the refractive index and the band gap of GaP \( n = 3.37, E_g = 2.25 \text{ eV} \) at room temperature. Without giving further details these authors state that their crystals, which were generally p-conducting, showed point-contact rectification. Wolff, Hebert and Broder 2) 3) found that GaP shows electroluminescence. In non-activated GaP crystals they found an emission band extending from 5650 Å to the infrared. In Zn-doped GaP two emission bands were found, one at 5900 Å, the other between 6800 Å and 8900 Å. Since in most cases the light came from the vicinity of the cathode these authors suggest impact excitation to be the main mechanism of luminescence. In the (few) cases where the light did not appear at the cathode they considered p-n luminescence as a second possibility. Alfrey and Wiggins 4) found that the electroluminescence observed in their polycrystalline GaP samples came from grain boundaries. By use of a scanning electron-microscope they could show that there were p-n junctions at these grain boundaries. They consequently explained their emission as p-n luminescence. Loebner 5) found two emission bands in GaP, one at 6200 Å the other at 9000 Å, depending on the direction of the current. According to Loebner the band at 9000 Å is due to hole injection into n-type GaP followed by recombination via a Cu centre. In view of the partly controversial results of the authors quoted, we undertook a study of the optical and electrical properties of GaP, the first results of which are given in the present paper.

2. Preparation

Crystals of GaP were made from the elements in sealed evacuated quartz tubes. One end of the tube contained Ga and was kept at a temperature of 1220 °C, the other end of the tube contained red phosphorus and was kept at 440 °C. The (lower) temperature of 440 °C corresponds to a phosphorus pressure of 2 atmospheres. The red phosphorus used was prepared from commercial red phosphorus by repeated sublimation *) and was spectrochemically pure. The Ga metal used was of commercial high-purity quality.

After 5 hours at the temperatures quoted the furnace was cooled down

*) The authors are indebted to Mr Schol for the purification of the phosphorus.
slowly to room temperature. The reaction product was a mixture of Ga metal and polycrystalline GaP plates. The excess Ga was dissolved in hot diluted HCl in Pt crucibles. The use of a vessel made of a metal nobler than Ga instead of glass greatly increases the speed of dissolution of the Ga metal. It appeared that, under the circumstances described, about 18 per cent of the Ga was converted into GaP. The GaP crystals obtained were found to have an orange colour and a specific resistance of the order of 10 Ω cm. The conductivity of the crystals was \( n \)-type as appeared from measurement of the thermo voltage (cf., however, section 3).

When GaP crystals are reheated at 1220 °C in a closed evacuated quartz tube part of the GaP decomposes into Ga and P. This decomposition proceeds until the equilibrium vapour pressure of GaP at 1220 °C is reached. From the amount of free Ga found after quickly cooling down the sample, the amount of phosphorus needed to build up this equilibrium pressure can be calculated. From this weight, from the volume of the quartz vessel and from the data about the molecular equilibria in the vapour of phosphorus, as published by Stock \(^8\), the (equilibrium) vapour pressure of GaP at 1220 °C was calculated and found to be 7 atmospheres. According to Folberth \(^7\) the equilibrium vapour pressure of GaP at its melting point (approximately 1350 °C) is at least 15 atmospheres. When \( n \)-conducting GaP crystals were reheated at 1220 °C at a phosphorus vapour pressure higher than 2 atm. a sharp decrease of the conductivity was found. This decrease extended over five orders of magnitude in the pressure range between 2 and 7 atmospheres. When fired at a phosphorus pressure of 8 atmospheres the crystals became weakly \( p \)-conducting, as shown by measurements of the thermo voltage (cf., however, section 3).

Crystals with high \( p \)-type conductivity could be made by doping with Zn. These crystals were prepared in the following way. First a mixture of Ga and GaP was prepared in the manner described. Then the part of the tube containing the phosphorus was cut off, and one atom per cent of Zn (calculated on the total amount of Ga present) was added to the end containing Ga + GaP. After resealing the whole tube was heated at 1220°C for one hour and afterwards cooled down slowly. The GaP first dissolves again into the excess of Ga at 1220 °C and then recrystallizes from a Zn-containing melt on cooling. The \( p \)-type crystals obtained after dissolution of the excess of Ga were dark-coloured. Spectrochemical analysis showed that they contained approximately \( 5.10^{-4} \) gram atoms of Zn per mole of GaP. If the Zn is added right at the start of the procedure described for making undoped crystals, no \( p \)-conducting crystals are obtained. The reason for this is that the Zn pressure in this case is determined by the low temperature of the tube end containing the phosphorus and apparently remains too low to make the crystals \( p \)-conducting. This complication may perhaps explain why Wolff, Hebert and Broder \(^2\) \(^3\) did not obtain \( p \)-type GaP on doping with Zn.
3. Point-contact rectification

On probing non-doped GaP crystals with a Mo point contact strong rectification effects were observed. In most cases the large-area contact was made with silver paint. No essential change was observed, however, when the crystals were merely pressed against a metal support by means of the metal point contact. It appeared that the direction of rectification was not the same in every region of the crystal surface. In some spots the charge transport was essentially carried by electrons, in others it was essentially carried by holes. Crystals prepared at low phosphorus pressure chiefly showed regions with n-type conductivity (cf. section 2). On the other hand, crystals prepared at phosphorus pressures exceeding 7 atmospheres (cf. section 2) mainly showed regions with p-type conductivity. Some typical rectification curves are given in fig. 1. The ratio of the currents in the forward and the reverse direction often amounted to $10^3$, in some cases even $10^5$.

4. Conductivity measurements

In order to determine the activation energies for the n-type and p-type conductivity observed, the conductivity of GaP was measured as a function of temperature. In these measurements the GaP crystals were mounted on a copper support which could be cooled with liquid air. The crystal was electrically insulated from the copper support by a thin layer, on which the crystal was fixed.
Fig. 1b. Rectification characteristic of a $p$-type region in undoped GaP.

Fig. 1c. Rectification characteristic of an $n$-type region in undoped GaP.
by conducting silver paint. A point contact served as a second electrode. The whole set-up was put in a vessel which could be evacuated and which had a quartz window opposite the crystal. In these measurements the point contact was always biased in the forward direction. Figure 2 shows the results for a p-type region of a crystal fired at high phosphorus pressure and for an n-type region of a crystal fired at low phosphorus pressure. The activation energies for electron and hole conductivity found in this way were 0.07 eV and 0.19 eV respectively.

Fig. 2. Temperature dependence of the conductivity; curve 1: p-type region in undoped GaP, curve 2: n-type region in undoped GaP.

In principle one could expect a modulation of the carrier concentration due to injection of charge carriers from the point contact. Because the applied forward voltage was always large as compared to the band gap and because in numerous experiments we did not find any dependence on the geometry and nature of the point contact we think that injection from the point contact does not play an important role in these experiments.

5. Electroluminescence

When a voltage was applied to (non-doped) GaP crystals they showed electroluminescence as previously found by other authors. The luminescence occurs both with point contacts and with large-area contacts similar to SiC. The spots where the light is emitted differ under various circumstances. In some cases it seems that practically the whole crystal emits light, in other cases the light originates in the vicinity of the point contact, of the large-area electrode
or from any other spot inside the crystal. In determining the spectral distribution of the light a Leiss monochromator was used in conjunction with an RCA-photomultiplier tube IP 28 or IP 21 and a narrow-band phase-sensitive amplifier. The mounting of the crystals was the same as used for the conductivity measurements described in section 4. During measurements the crystals were cooled, but because the electric power needed to make the light output sufficiently large to measure the spectral distribution was rather high (up to 4 watts), the crystals certainly were at a higher temperature than the liquid-air cooled support. Figure 3 shows the spectral distribution of the light emitted by a

![Fig. 3. Spectral distribution of the p-n luminescence in undoped GaP; curve 1: point contact negative, curve 2: point contact positive.](image)

![Fig. 4. Spectral distribution of the p-n luminescence in undoped GaP showing separation of the emission peaks.](image)
crystal contacted at an n-type region with a tungsten point. Curve 1 of fig. 3 was obtained when the point contact was biased in the forward direction and curve 2 was found in reverse direction.

In both directions the maximum is at about 6250 Å, but in the reverse direction the band is broader and shows a hump on the short-wave side, indicating a second band at about 5650 Å. In some cases, mostly with high power input, the short-wave band (5650 Å) was resolved (fig. 4).

Our strongly Zn-doped crystals, which were of a dark colour and which showed homogeneous p-conductivity, did not show any electroluminescence. In weakly Zn-doped crystals, which still showed the same orange-red colour of pure GaP and were mainly n-conducting, no differences in spectral distribution were found when compared with undoped crystals.

When GaP powder, prepared by grinding the crystals in dry air, was excited with long-wave u.v. at low temperature, a deep red luminescence was observed. The spectral distribution of this red luminescence is shown in fig. 5. At room temperature the powder did not show any luminescence on excitation with u.v.

![Fig. 5. Spectral distribution of the photoluminescence in undoped GaP, excitation 3650 Å.](image)

6. Photovoltaic effect

By using a point contact a photovoltage could be observed on GaP crystals when they were irradiated with white light. Because the impedance of the crystals was relatively low (about $10^4$ to $10^5$ Ω), the photovoltage could easily be measured with a high-ohmic voltmeter. Figure 6 gives the open-circuit voltage $V_0$ as a function of wavelength for non-doped and for Zn-doped crystals. In these measurements a tungsten-band lamp was used, the light being passed through a Leiss monochromator. The curves of fig. 6 show the photovoltage without correction for the energy distribution of the band lamp. When the curves
are plotted for constant photon density (taking dispersion of the monochromator into account), only small changes in the position of the maxima occur (fig. 7). There are always two distinct maxima, viz. at 4200 Å and 5600 Å in non-doped crystals and at 4200 Å and 6000 Å in Zn-doped crystals. Further, the open-circuit voltage and the short-circuit current $i_s$ were measured as a function of the intensity of monochromatic light. Figure 8 shows that the open-circuit voltage increases linearly at low light intensities and exponentially at
high light intensities. The short-circuit current is directly proportional to the light intensity (fig. 9). When crystals were put into direct sunlight an open-circuit voltage of about 0.8 V was observed. With more-intense light sources the photovoltage could rise up to 1.3 V. The short-circuit current density \( J_s \) was estimated to be about 3-4 mA/cm\(^2\) with sunlight. In the estimation of
current density $J_s$ the whole crystal surface was supposed to be optically active. In fact, the estimate of $J_s$ given will be on the low side because part of the surface is undoubtedly inactive.

7. Discussion

The experiments described in this paper strongly suggest that the electroluminescence observed in undoped polycrystalline GaP is due to recombination of injected minority carriers from $p-n$ junctions, via levels within the forbidden gap.

The arguments supporting this conclusion may be summarized as follows. We could show that irregularly distributed $n$- and $p$-regions were present. The light is emitted from various regions inside the crystals. The spot of the light essentially depended on the switching direction, but the occurrence of electroluminescence as such was independent of the switching direction. Alfrey and Wiggins 4) showed that the place where the light was emitted in their crystals coincided with grain boundaries where the conductivity changes its type; this probably also applies in our polycrystalline samples. Finally, the observations of photovoltaic effects (cf. second part of this discussion) also points to the presence of effective $p-n$ junctions. In line with this picture, crystals made homogeneously $p$-type by doping with Zn did not show electroluminescence and photovoltaic effects.

Wolff, Hebert and Broder 2) 3), working with point contacts, generally found emission at the cathode. These authors proposed impact excitation in these cases. Considering the fact that they essentially worked with single crystals, which therefore probably did not contain $p-n$ junctions (no grain boundaries), the mechanism of impact excitation might apply in their case.

From the fact that the samples switch from $n$-type conductivity to $p$-type conductivity when the phosphorus pressure at which they are prepared is increased (cf. section 2), it may be concluded that the acceptors and donors in our non-intentionally doped samples are connected with Ga vacancies $V_{Ga}$ and P vacancies $V_{P}$, respectively. Furthermore, all undoped crystals showed the same activation energies for $n$-type and $p$-type conductivity. The donor level $V_{P}$ was found to be at 0-07 eV from the conduction band, the acceptor level $V_{Ga}$ at 0-19 eV from the valence band (cf. section 4). Both levels may act as recombination centres for free carriers. Disregarding Franck-Condon shifts, which are probably small in substances like GaP, one can estimate the wavelength of the emissions caused by recombination by subtracting the activation energies of 0-07 eV and 0-19 eV from the band gap of 2-25 eV. This gives 5700 Å and 6050 Å respectively, which corresponds fairly well to the actually found emission bands at 5650 Å and 6200 Å for electroluminescence and at 6300 Å for photoluminescence. On this basis the level scheme depicted in fig. 10 is proposed for (undoped) GaP.
In order to establish whether the source of the photovoltage is at the point contact or somewhere inside the crystals, the point contact (diameter < 0.1 mm) was screened from the exciting light with a cylindrical sleeve of 1.5 mm diameter as is shown in fig. 11. The photovoltages measured under these circumstances dropped by a factor of 2 to 10; the screening, however, reduces both the peak at 4200 Å and the peak at 5600 Å (cf. section 6) by about the same extent. If the source of the photovoltage were at the metal-semiconductor contact, the light, with screened contacts, could only reach the contact area via internal reflections at grain boundaries. Consequently, photovoltages raised by 4200-Å radiation, which is completely absorbed in a thin surface layer, should decrease much more than those raised by irradiation at the long-wave side of the absorption edge (5600-Å band). Furthermore, if the photovoltage were generated at the barrier between metal and semiconductor, the excitation spectrum of the photovoltage should depend on the nature of the metal used as a point contact. Experiments, however, showed that the excitation spectrum remained
the same, irrespective of whether Fe or Mo points were used for contacting the GaP samples. We therefore conclude that the photovoltages observed are the reciprocal effect of the electroluminescence, and are generated at the p-n junctions.

According to the theory of p-n photocells \(^8\), the total external current \(i\) can be described by the following equations

\[
i = i_r \left[ \exp \left( \frac{Ve}{kT} \right) - 1 \right] - i_t \tag{1}
\]

\[
i_t = FeRg \tag{2}
\]

with

\[
g = I/p(\lambda) \tag{3}
\]

where

- \(g\) is the rate of generation immediately beneath the surface,
- \(F\) is the area,
- \(i_r\) is the saturation current in the reverse direction in a non-irradiated p-n junction,
- \(V\) is the extra voltage at the p-n junction,
- \(e\) is the charge of an electron,
- \(R\) is a factor which does not depend on intensity \(^8\),
- \(I\) is the incident number of photons per cm\(^2\) per second,
- \(p(\lambda)\) is the wavelength-dependent penetration depth of the light.

For \(V = 0\), the only term contributing becomes \(i_t = i_s\), the short-circuit current

\[
i_s = -\frac{FeR}{p(\lambda)} I = aI \tag{4}
\]

Because \(a\), at a given wavelength, is a constant, \(i_s\) is directly proportional to the intensity of the incident (monochromatic) light. As fig. 9 shows, this relation holds both for the undoped and the (weakly) Zn-doped GaP crystals. Combination of eqs (1) and (2) for \(i = 0\) gives for the open-circuit voltage, when

\[Ve \gg kT, \text{ i.e. } I \text{ is large}\]

\[
V_0 = \frac{kT}{e} \ln I + \beta, \tag{5}
\]

where \(\beta = (kT/e) \ln (a/i_s)\) is a constant for monochromatic excitation.

For low excitation densities \((Ve \ll kT)\) the exponent in eq. (1) can be expanded, giving

\[
V_0 = \frac{kT}{e i_r} I = \gamma I, \tag{6}
\]

where \(\gamma\) is a constant for monochromatic excitation.
According to theory, the open-circuit voltage $V_0$ should vary exponentially with light intensity at high irradiation levels (eq. 5) and linearly at low irradiation levels (eq. 6). As follows from the diagrams in fig. 8 these requirements are fulfilled in our GaP samples. The slopes of the straight lines in fig. 8 are approximately 0.09, which is steeper than the theoretical slope of $2.3 \frac{kT}{e} = 0.06$ following from eq. 5. At present, we are unable to give an explanation of these deviating slopes. Similar deviations were found by Gremmelmaier in GaAs.

It is clear that stationary photovoltages and internal currents can be generated only when the exciting radiation creates both mobile holes and electrons. Actually, stationary photovoltaic effects have hitherto only been observed with exciting radiation of an energy larger than the band gap. Schottky raised the question under which circumstances stationary photovoltages and photocurrents could be generated by excitation of impurity centres. According to Schottky this can only be achieved by a two-step optical excitation via levels located roughly halfway between the valence and the conduction band. In undoped GaP and (slightly) Zn-doped GaP we found excitation peaks of the photovoltage on the long-wave side of the absorption cut-off (cf. figs 6 and 7). As the long-wave excitation peaks are rather close to the absorption cut-off, a two-step excitation mechanism is proposed in which one step is optical and the other thermal.

The optical step might be the transfer of an electron from a filled level near the valence band to the conduction band, or the transfer of an electron from the valence band to an empty level close to the conduction band. If the lifetime of these excited states is long enough, the holes or electrons might escape to the valence or conduction band. In this way a stationary photovoltage and photocurrent may be generated with radiation of an energy slightly less than the band gap. The long-wave excitation peak of the photovoltage was found at 5600 Å in undoped GaP, i.e. at about the same wavelength as the short-wave emission peak found in electroluminescence. For this reason we are inclined to attribute the optical step in the long-wave excitation of photovoltages in undoped GaP to the transfer of an electron from the valence band to an empty $V_P$ level (cf. fig. 10) and the thermal step to the release of this electron to the conduction band. In the case of the long-wave excitation peak at 6000 Å in (weakly) Zn-doped GaP a similar interpretation might apply with a Zn level close to the valence band. The reason why the excitation of photovoltages on the short-wave side of the absorption cut-off is restricted to a rather narrow region around 4200 Å (cf. fig. 7) is still obscure. It is hoped that measurements on well-defined $p-n$ junctions will help to clarify this point.
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